PRESSURE BROADENING OF INFRARED

ABSORPTION LINES AT MODERATE DENSITIES

by

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ABSTRACT

The pressure broadening of several infrared vibration-rotation lines of HF and HCl by 15 to 140 atm of argon has been studied using a tunable optical parametric oscillator spectrometer. To campare with these experiments, estimates have been made of a formal theory for the density expansion of the pressure broadened lineshape.

Comparison is made in second order in density, between the theory, the experiments described in this work, and other experiments on the absorption coefficient and on the diffusion coefficient. Also, comment is made on the difficulty of finding third order (logarithmic) density terms, especially with regard to preliminary experiments with a tunable diode laser.

Thesis Supervisors: Jeffrey I. Steinfeld and Irwin Oppenheim

Titles: Associate Professor of Chemistry and Professor of

       Chemistry

To the reader, if there ever
is one, in whose honor it is written
in the first person plural.

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

LIST OF FIGURES

8

LIST OF TABLES

I   OPTICAL PARAMETRIC OSCILLATOR EXPERIMENTS

A. Introduction

This thesis contains both experimental and theoretical results on the shapes of infrared absorption lines broadened by moderate densities of foreign gas. Part I of the thesis reports on the broadening of HCl and HF vibration-rotation lines by 15 to 140 atmospheres of argon, studied with a tunable laser spectrometer. The second part attempts the numerical estimation of a formal theory of the density dependence of transport coefficients. It also discusses the agreement of these estimates with experiment, especially with the line broadening data of Part I.

Line broadening has been studied for a number of reasons, most often to gain information on intermolecular potentials through the application of scattering theory to the effective cross sections obtained from linewidths. But here we wish chiefly to compare observations at moderate densities with a statistical mechanical theory approximated in such a fashion that cross sections are not calculated but taken from low density measurements.

The original reason for undertaking this study was to investigate the theoretical prediction of a logarithmic term in the density expansions of transport coefficients. The physical origin of this term, and the considerable theoretical speculation and several experimental searches it has

12

occasioned are discussed in Section II A. These previous studies of viscosity and thermal conductivity experiments have been inconclusive as to the existence of a logarithmic term because the relevant properties are difficult to measure and the data exhibits considerable random scatter. Yet the statistical mechanical calculation of the absorption coefficient is similar to that of these more familiar transport coefficients, and it has been predicted that at the zero density resonance frequency, its density expansion should also contain a logarithmic term. It was hoped that spectroscopic measurements could be made with greater precision. Such is indeed often the case, but here the spectrometer, based on a tunable optical parametric oscillator, was only able to measure linewidths with the precision on the order of that of the best transport coefficient measurements.

Since the logarithmic term is to appear in third order in density, it seemed unlikely that parametric oscillator experiments would ever attain the required precision to find it. But effects of second order in the density have long been seen in transport coefficient experiments. It is this study of second density effects on the linewidth that occupies the bulk of this thesis. Their size and theoretical estimates of what is expected could be used to predict the size of possible logarithmic terms. This will not be attempted here, but since, as

13

we will find in Section II D, the observed second density effects if they exist at all are almost within the noise level of the data, we can conclude that effects on the linewidth of higher order in the density, such as logarithmic terms, could not be found with the present parametric oscillator spectrometer. (As discussed in Section II A the logarithmic term may also manifest itself in the shape of the line, but again the parametric oscillator data has too much noise for there to be any chance of finding it. Although no experiments were done using a tunable diode laser, the possibility that its different properties might make it more appropriate for such studies is discussed in Appendix E.)

In addition to the interest in agreement between theory and experiment, there are other, practical reasons for this research. The design of high pressure gas lasers requires knowledge of the pressure broadened linewidth, and some laser systems operate at pressures where higher density effects might be expected to show up. However, the conclusion to be drawn from this work is that as an engineering approximation linewidths vary linearly with density up to the range of 100 atmospheres.

Another reason for this project is that since absorption profile measurements require accurate knowledge of both relative intensity and frequency, they make an excellent first test of a new tunable laser system. Indeed the

development of the parametric oscillator as a spectrometer together with the assumption that higher density effects are small make it a useful system for measuring low density linewidths, as we shall see in Sections I D and I E.

B. General Description of Experiment

Absorption measurements were made using the tunable infrared radiation from a Chromatix optical parametric oscillator, in the wavelength region of 2.55 to 2.65 microns for the HF P branch and from 3.3 to 3.4 microns for the R branches of HCl and DF. A block diagram of the apparatus is presented in Figure 1.

The parametric oscillator is pumped by the .532 micron green line of a Chromatix Q-switched frequency-doubled Nd:YAG laser. The laser is externally pulsed at 30 Hz using a General Radio model 1217-A pulse generator. Operation and maintainance of the Chromatix system are discussed in Appendix A.

The infrared beam passes through a quartz lens, which makes it less divergent, to a germanium beamsplitter. The beamsplitter has one side anti-reflection coated and has a (Valpey) coating on the other side such that 90 per cent of the infrared in reflected through the sample cell to an infrared detector, and 10 per cent is transmitted to a reference detector. (However, germanium with only the anti-reflection coating could also be used, giving about half transmitted and half reflected, by compensating with detector amplification.) The design of the monel high pressure sample cell, as well as the details of the vacuum and high pressure system and pressure measurement may be found in Appendix B.

16

Figure 1: Tunable laser absorption

spectrometer block diagram.

Pulse
Generator

Gate Trigger Pulses from Laser Power Supply

Q-Switched
Frequency
Doubled
Nd:YAG Laser

Optical
Parametric
Oscillator

Reference
Detector

Graphics
Display

Paper
Tape
Punch

Sample
Cell

HCl or HF
and
1-100 atm
Argon

C-Cor
4376P
Preamps

Gated
Op-Amp
Integrator

A/D Converter
and
PDP/8-L
Computer

D/A Converter

Chart
Recorder
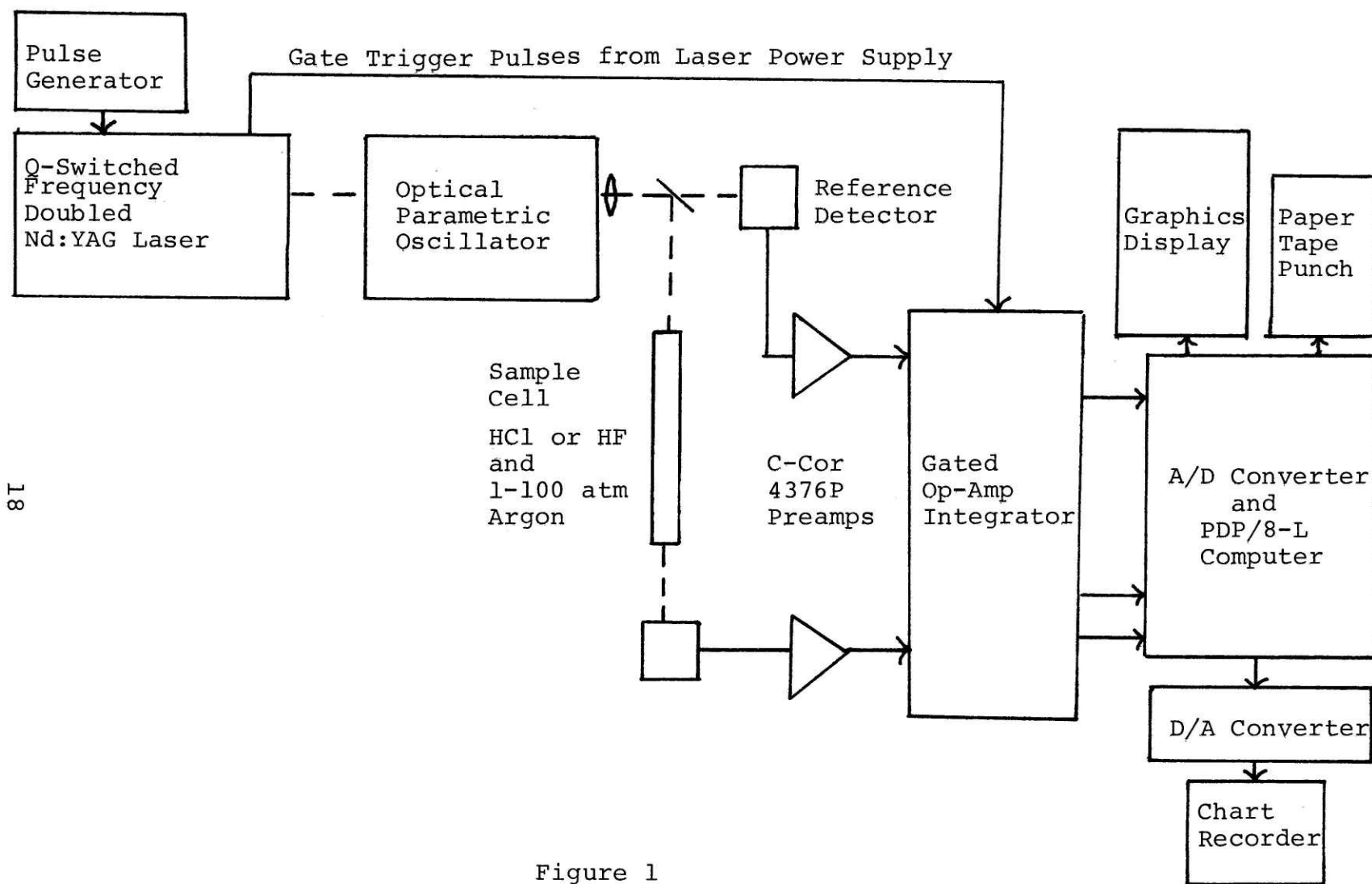
Figure 1

Appendix C includes the biasing circuit for the infrared detectors. They were photoconductive, usually Mullard RPY77 InSb detectors operated at room temperature with the laser focused directly onto the face of the detector by a two inch focal length, quartz, anti-reflection coated lens. Some data was also taken using laser light scattered onto Ge:Au liquid nitrogen cooled detectors, in an attempt to alleviate the intensity measurement problems discussed in Section I C. However, the quality of the data turned out to be the same for both sets of detectors.

The voltage pulses from the detectors are less than 200 nsec in width. They are attenuated using a selection of terminators ranging from 50 to 1000 ohms, and then amplified by C-Cor 4376P pulse amplifiers. The preamplifiers are operated with a nominal gain of ten, although the actual gain factor is a little over twenty. Terminators are selected so that the amplifier output has about one volt peak height, since the amplifiers saturate for pulses much above this value.

The voltage pulses from the cell and reference detectors are integrated by an operational-amplifier integrator circuit, a block diagram of which is shown in Figure 2. Because the laser pulse is immediately preceded by a large amount of electrical noise, a FET switch controlled by trigger pulses from the laser power supply is used to gate the input so that only the laser pulse is integrated. Integration produces

19

Figure 2: Gated operational-amplifier integrator block diagram, showing input and output waveforms as they appear in oscilloscope traces.

Integrating Integrating
Window Window
Position Width

Laser Power Supply

Lamp Sync Out

74121

74121

74121 Monostable

Q-Switch Sync Out

74107 Flip-flop

74121

74121

CD4016 Switch

CD4016 Switch

40J Op Amp

Input

5 mV to 1 V

0.1 μsec

Output

to A/D

0.1 to 5 V

300 μsec
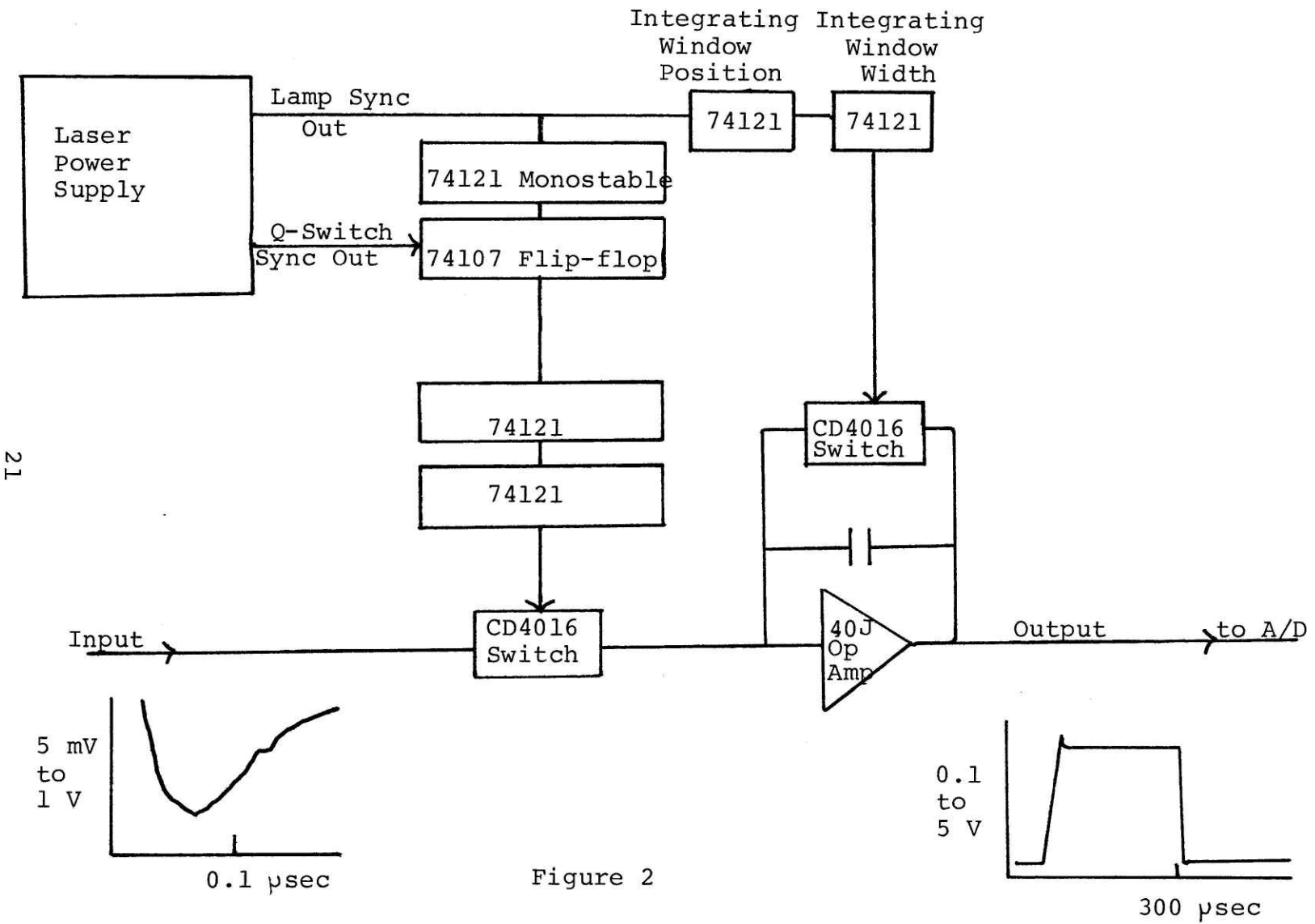
Figure 2

essentially a DC level which is read by the analog to digital converter interfaced to the PDP-8/L minicomputer, after which the integrator level is returned to its initial value by a second switch. The parametric oscillator pulses from the infrared detectors with peak values of 1 to 2 volts produce integrated levels of 5 to 10 volts. More detailed schematics, specifications, and operating instructions for the gated op-amp integrator are contained in Appendix C.

The computer averages the ratio of reference to cell pulse areas and outputs this at intervals onto a Heath strip chart recorder, and onto punched tape, so that several scans may be later averaged. Since the laser is externally pulsed, a certain number of pulses has a fixed relation to a certain amount of parametric oscillator scanning time, and therefore to a frequency increment.

The computer can also output the value for single pulses from the reference and cell detectors as the x and y coordinates of a point on the ARDS graphics display terminal, as discussed in Section I C to look at random errors in intensity measurement. The machine language programs used in acquiring the data are listed and commented on in Appendix D. In addition, FOCAL programs used in reading the punched tapes of absorption data, processing and plotting out absorption curves, and generating Lorentzian fits to experimental data are given in Appendix D. An example of the treatment of a set of tapes to produce an averaged lineshape and a fit to a sum of

22

Lorentzians is given is Section I C.

C. Precision of Frequency and Amplitude Measurements

Absorption lineshape measurements are among the most difficult that can be attempted using laser spectroscopy, since one needs accurate measurement of both relative intensity and frequency. In particular, an optical parametric oscillator (OPO) is difficult to work with since it has a finite frequency bandwidth of around 0.4 cm^{-1} and instability in pulse amplitude over all time scales. Parametric oscillation involves the generation of infrared and red light amplified out of quantum noise by the action of the green Nd:YAG laser light on a crystal possessing a nonlinear optical susceptibility. (The theory of the optical parametric oscillator is discussed further in References 1-6.)

The fact that these nonlinear susceptibilities are small means that when the pump laser is operated at maximum available power its 30 and 40 per cent variations are reflected in the output of the parametric oscillator, while at any lower power the same fluctuations in laser power are translated into OPO pulses which range from a maximum amplitude all the way to zero. Figure 3 shows oscilloscope displays of the laser and OPO pulses.

Another property of parametric oscillation is that generation can occur anywhere under a gain envelope of about 1 cm^{-1} in width, an instability which is magnified when the frequency is being scanned. This and other aspects of

Figure 3a:Oscilloscope traces of Nd:YAG
laser and optical parametric oscillator
pulses. In the upper trace, the green laser
light scattered off a white screen is detected
by a PIN photodiode with 100Ω termination.
The laser was operating at 380 V lamp voltage
and 30 Hz repetition rate, and gave an average
power of 19 mW. In the lower trace is shown
the OPO infrared pulse from an InSb detector
with a 330Ω terminator and 10x amplification.
The laser if focused directly onto the face of
the detector, and the OPO is operating at
415°C with Pl mirrors. For all traces the
horizontal scale is 100 nsec/cm, and the
vertical scale is 1.0 V/cm.

Figure 3b: Same as 3a except at higher laser
power, so that now fluctuations in OPO output
are those of the Nd:YAG laser, rather than
going all the way to zero.

25

Figure 3a

Figure 3b

26

the frequency and amplitude characteristics of the OPO
will be discussed in this section, as well as an example
of the treatment of experimental data.

The frequency characteristics of the OPO introduce
both a systematic and random error into the measurement
of linewidths, which we discuss in turn. The finite laser
linewidth produces additional broadening of the observed
absorption line, like the instrumental broadening due to
the finite slit width of conventional spectrometers. In
that case, the observed lineshape is a convolution of the
true lineshape and the instrument function, defined as

$$\int_{-\infty}^{\infty} d\omega' g(\omega-\omega') f(\omega')$$ where $g(\omega-\omega')$ is the true lineshape

and $f(\omega')$ is the instrument function.

A number of schemes have been devised to deconvolute
observed absorption profiles to obtain true lineshapes.
A classic iterative method first convolutes the observed
data with an assumed instrument function, and then uses the
difference between the original shape and the deconvolution
to obtain a first approximation to a deconvolution.[7] Here
we use a method which uses the ratio instead of the difference
as a correction, giving the procedure better mathematical
properties as described in Reference 8. The deconvolution
program is listed in Appendix D. It was originally designed
to address the analogous problem of deconvoluting out the
effect of velocity selector "shutter function" on molecular

beam scattering results, although Reference 8 cites work in which the ratio method has been applied to incompletely resolved spectra.

Our instrument function, the optical parametric oscillator lineshape, is found by making absorption scans using only a few torr of HF, so that on the scale of the laser linewidth the absorption line is infinitely narrow. One set of eight measurements on around 5 torr of HF was used to obtain the laser line information used to deconvolute the data. The lineshape, shown in Figure 4a, was obtained after averaging the traces and then averaging around the line center to produce a symmetric shape. This last was done because the deconvolution program only took symmetric instrument functions, and seemed to fail for asymmetric lineshapes. Besides, there was no evidence that the OPO lineshape was not on the average symmetric.

This laser lineshape was used to deconvolute a number of sample Lorentzians. An example of the two initial line profiles and the resulting deconvoluted lineshape is given in Figure 5. These samples are used to construct a plot of the amount by which the linewidth is reduced as a function of the initial linewidth, which appears in Figure 6. Its form can be understood by considering that while an infinitely narrow line is broadened by the full amount, an infinitely broad line would not be instrumentally broadened at all.

This procedure of deconvoluting computer generated

Figure 4: Averaged optical parametric oscillator lineshapes, from absorption scans of low pressure HF lines. An average of eight measurements on around 5 torr of HF is shown in (a), while (b), taken a year later but having almost the same width, is an average of 13 traces of about 8 torr of HF.

30

0.5 cm^{-1}
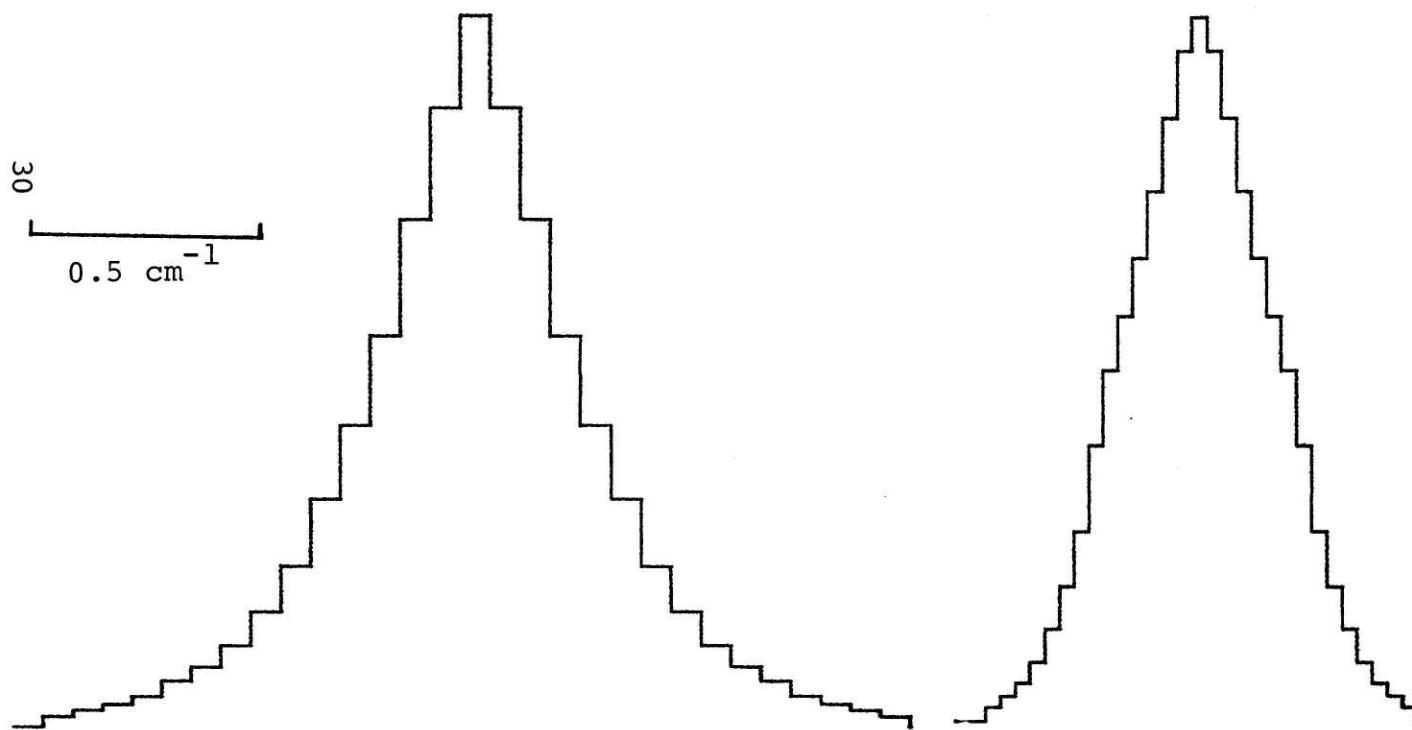
·Figure 4a   ·Figure 4b

Figure 5: Initial (a) and deconvoluted (b) lineshapes, and parametric oscillator instrument function (c). The Lorentzian initially had a halfwidth of 1.44 cm^{-1} and went to 1.28 cm^{-1} after deconvolution. The instrument function is the same as that in Figure 4a, but averaged into larger boxes. Note that even choosing the initial line to be slightly off center introduces asymmetry into the deconvoluted lineshape.

Figure 6: Deconvolution correction plot.

1.0 cm^{-1}

(a)

(b)

(c)

Figure 5

Deconvolution Correction, cm^{-1} vs. Initial Halfwidth, cm^{-1}
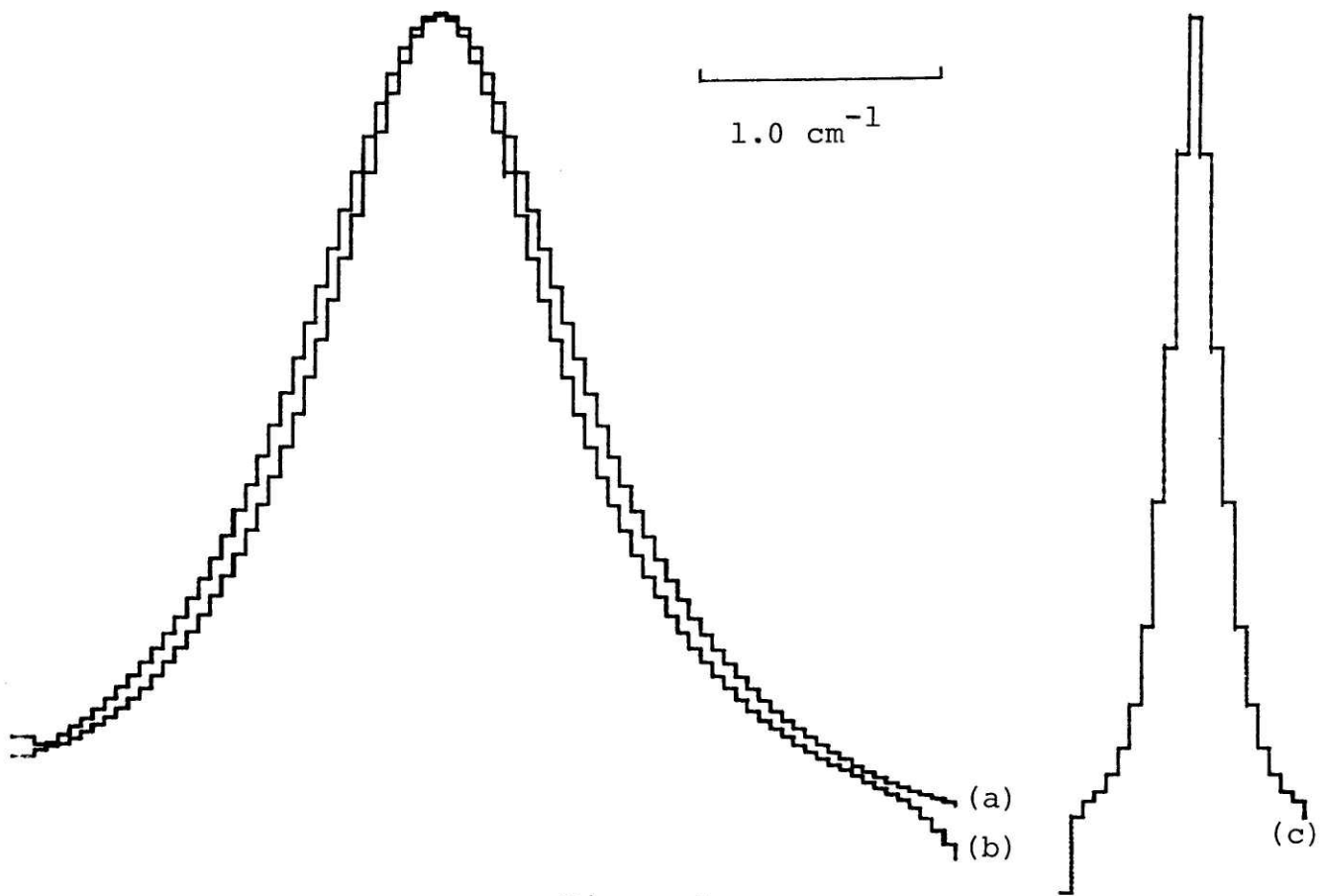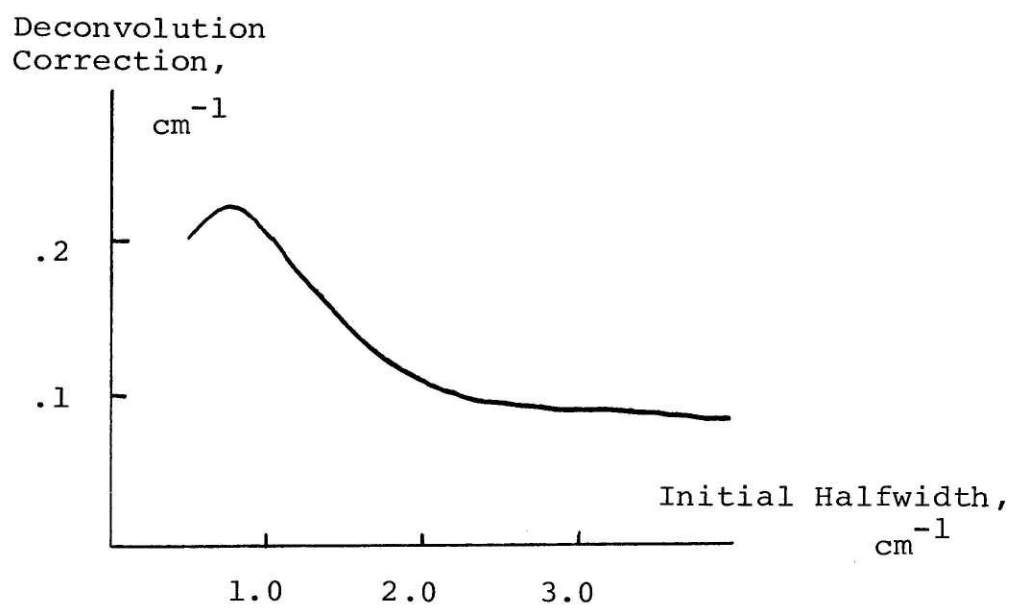
Figure 6

Lorentzian functions was used rather than individual
deconvolution of each experimental profile for two reasons.
First, deconvolution is time-consuming, and more importantly,
the procedure, or at least the method used here, seems to
magnify any irregularity or asymmetry in the initial lineshape.
Since the amount to be subtracted is small and random
fluctuations in linewidth and lineshape are large, it was
felt that no more sophisticated procedure was justified.

One could also least squares fit to each lineshape, using
a simple Lorentzian or a Lorentzian convoluted with an assumed
instrument function,[9] but again it was felt that the accuracy
of the data did not warrant such care.

A year after the first laser lineshape study was done a
second set of measurements were made on around 8 torr of HF,
the result of which appears in Figure 4b. The laser linewidth
here is less than 10 per cent smaller than the earlier line.
Figure 7 shows the individual lines before averaging and
symmetrizing gave the resulting OPO profile. This figure
brings us to the other effect of fluctuating laser linewidth
and position, that of generating random errors in absorption
and so linewidth during scanning.

This effect should be more noticeable for narrower lines,
since the steeper slopes give a larger change in absorption
for a given frequency, reaching a maximum for these essentially
delta-function low density absorption lines. For the lines in
Figure 7, the root-mean-square deviation around the average

Figure 7: Individual low pressure absorption
traces before averaging into the instrument
function of Figure 4b, shown in the two traces
at bottom right. The line under each trace
in the leftmost column denotes the position of
the baseline for that row.

Figure 7

1.0 cm^{-1}
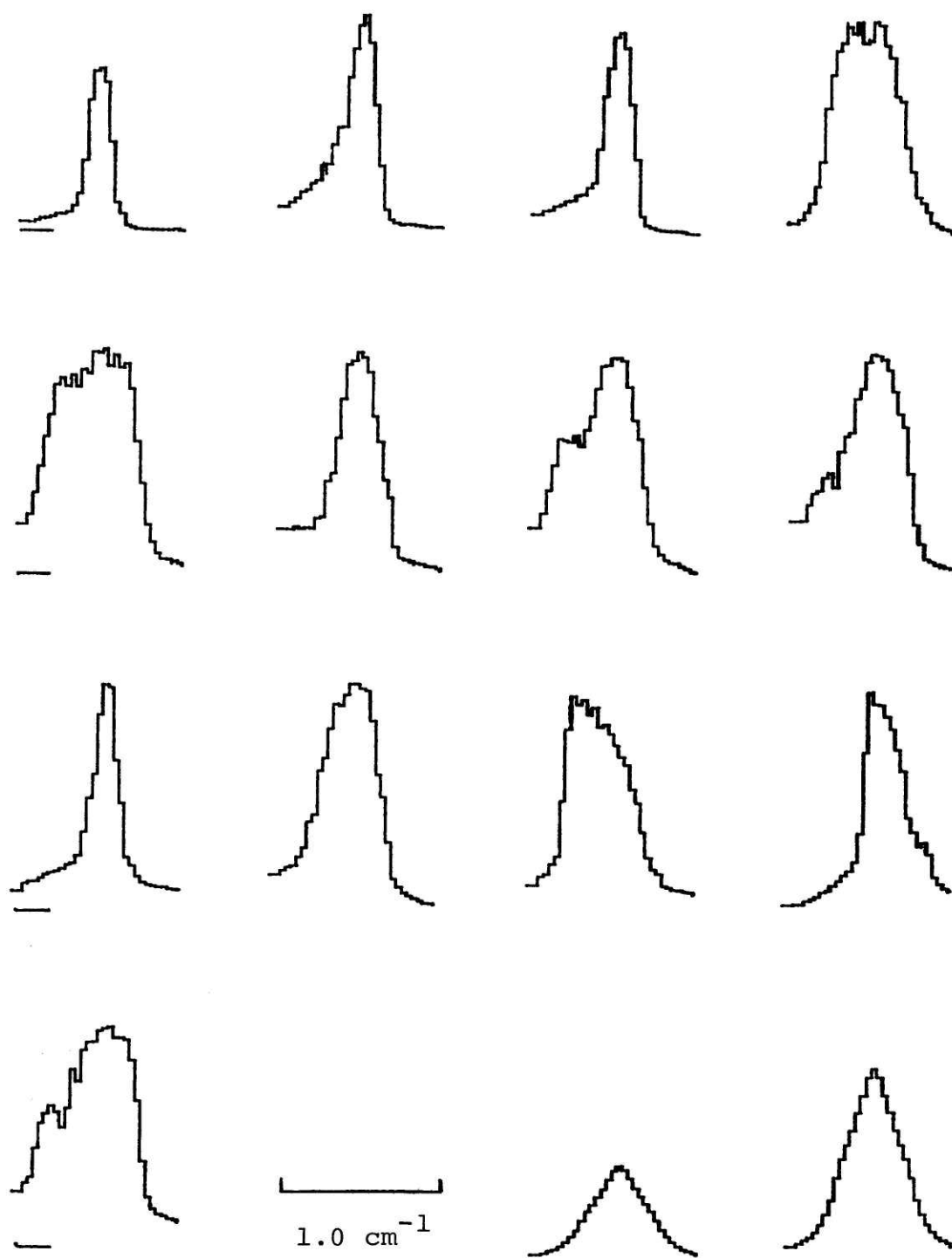
width of 0.33 cm^{-1} is 0.13 cm^{-1}. In general we find that
variations of several tenths of a wavenumber in widths in
scans of the same absorption line are common. Since averaged
lineshapes never include more than ten experimental traces,
and sometimes in early work as few as three or four, we can
expect this random error to remain to the extent of 0.1 to
0.2 cm^{-1}.

We can also see another source of systematic error, in
that the width of the averaged OPO line, 0.4 cm^{-1}, is larger
than the average of the individual widths. This sort of
broadening due to errors in superimposing lines during
averaging will also occur to roughly the same extent for the
experimental lineshapes. Thus it is proper that it be
included in the instrument function and be deconvoluted out.

There is another problem which contributes to random
noise in the lineshape scans, whose cause is unknown and
which has gone unsolved. It is that the ratio of the integrated
energy of single pulses seen by the cell and reference detectors
fluctuates randomly from pulse to pulse. This can be shown
clearly by a modification of the data acquisition program
described in Appendix D which plots a point on the ARDS
graphics display terminal whose x and y coordinates are the
integrated outputs of the two detectors. A perfect detection
system would produce a straight line plot passing through zero,
indicating a constant ratio between the two detectors, while
a scattered plot indicates random variations in the ratio.

37

Figure 8: (a) Two Ge:Au detectors receiving

scattered infrared give the x and y

coordinates of the points. Cell

detector has 200Ω termination, reference

has 100Ω , and both have 10x amplification.

(b) Upper scatter plot is infrared

straight on to a Ge:Au detector versus

red light scattered onto a PIN photodiode.

Lower plot of two PIN diodes looking at

red OPO light. In both photographs the

x and y scales are 8 volts maximum.
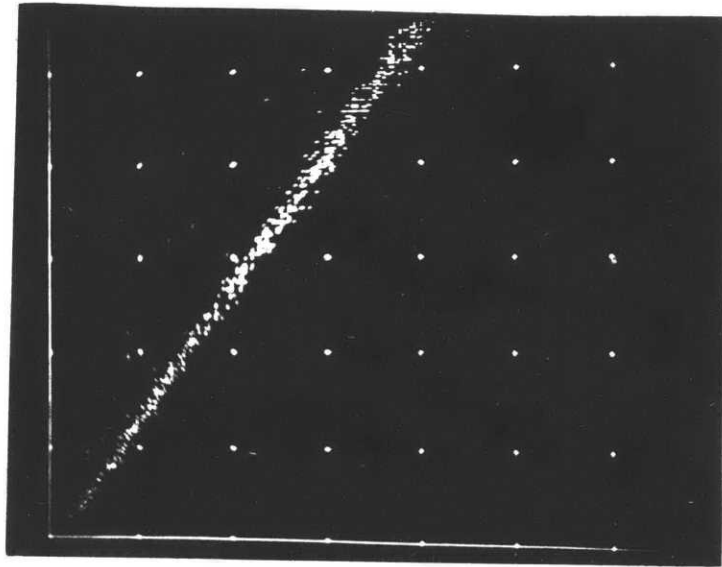
Figure 8a

Figure 8b

Figure 9: (a)   Two separate PIN photodiodes
looking at scattered green Nd:YAG
laser light.

(b)   Two separate PIN photodiodes
looking at scattered red OPO light.
The OPO was at 370°C and the scales
were 8 volts maximum.

Figure 10: Infrared pulse from reference InSb
detector put into both integrators-
so absence of scatter is not
surprising.
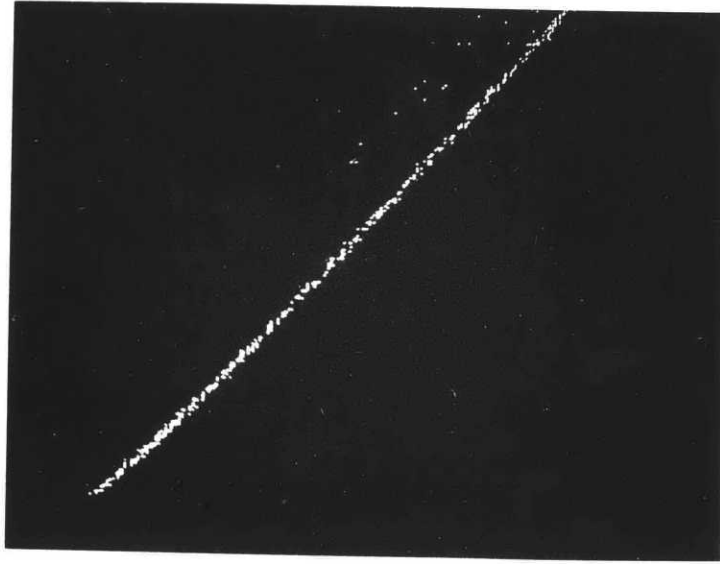
Figure 9a
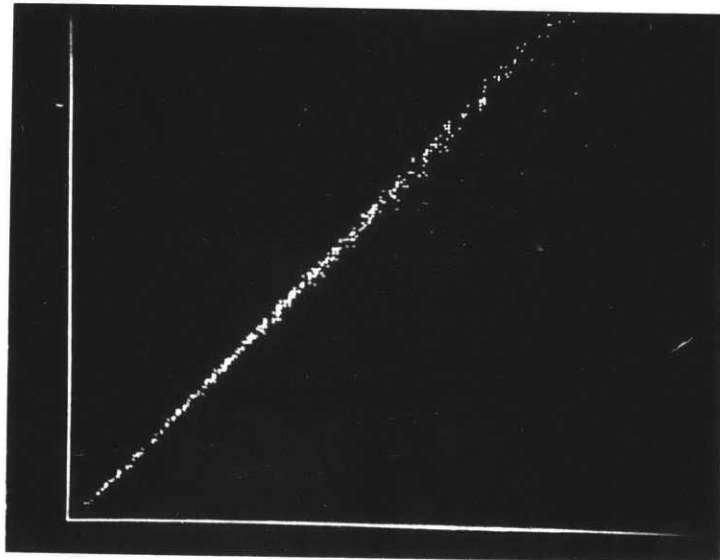
Figure 9b
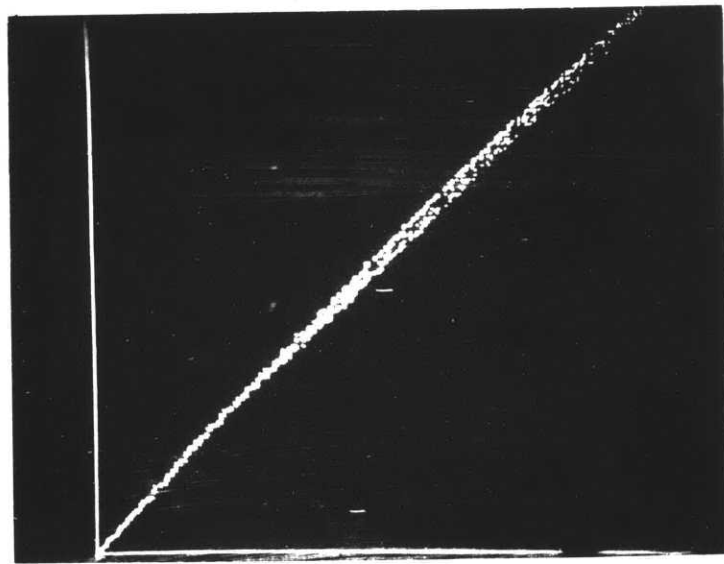
Figure 10

Figure 11: (a) Upper plot is infrared scattered
onto a Ge:Au detector (100Ω terminator,
10x amplification) versus red light
scattered onto a PIN photodiode (100Ω,
10x). Lower plot is infrared directed
onto a Ge:Au detector (connected directly
to integrator) using a mirror, versus red
light scattered onto a PIN diode (200Ω,10x).
(b) Infrared pulses from two InSb
detectors. Spots focused through
collimating lens (and for cell detector,
through a 2 inch focal length lens at
about 2.5 inches from detector). Cell
detector has 200Ω termination, reference
100Ω, and both have 10x amplification.
Plots are 8 volts full scale.
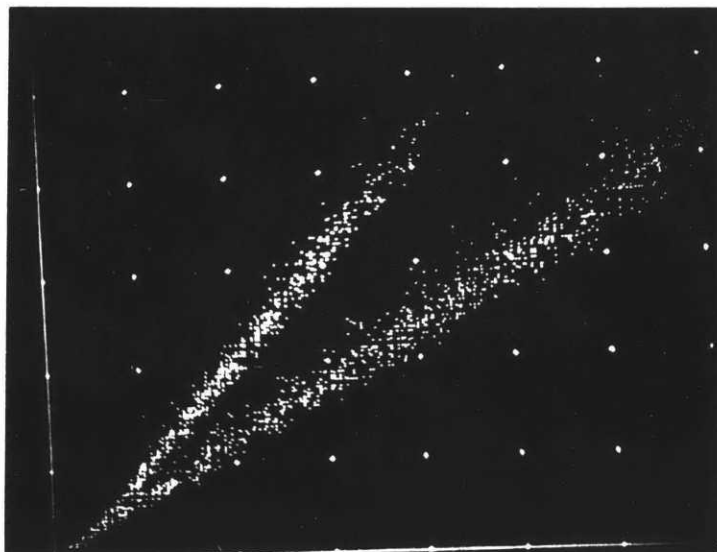
Figure 11a
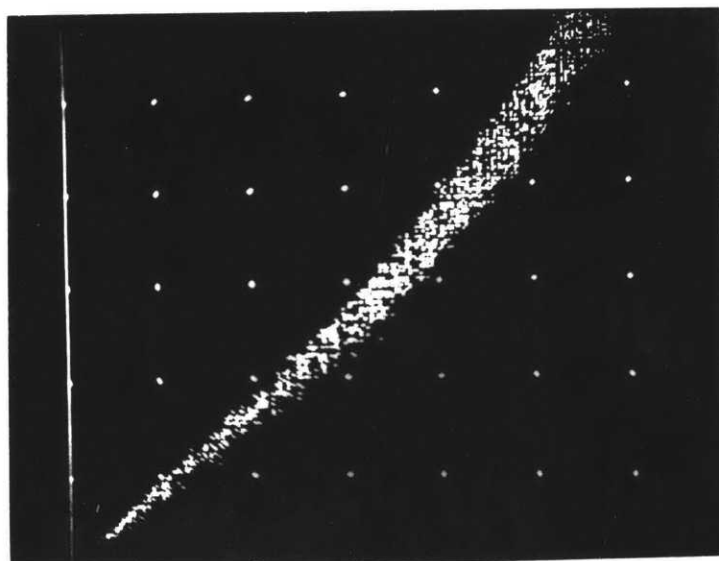
Figure 11b

Examples of this sort of this sort of random variation are shown in Figure 8.

That the fault seems not to be with the integrator or any of the electronics after the detectors can be seen in Figure 9 in which the outputs of two separate PIN photodiodes looking at scattered green laser or red OPO light pulses give a linear plot. But infrared pulses plotted as a function of the corresponding red pulses show both a random scatter and often a systematic dropping off of infrared amplitude for large pulses, as shown in Figure 8b. And it is not a property of the infrared pulse alone, as shown by Figure 10 of the same infrared detector pulse put into both integrator channels.

It was thought that the problem might be caused by the laser pulse falling off the surface of one detector more than the other, depending on the intensity and direction of the OPO beam. Therefore much of the experimental data and Figure 8a were taken by scattering the infrared from a white card onto liquid nitrogen cooled Ge:Au detectors (chosen since they were more responsive). However, Figure 11a compares scattered and direct methods of detection and shows little difference. So most data was taken by the simpler method of focusing a partially collimated OPO beam directly onto the face of room temperature InSb detectors. One example of the scatter plot resulting from this is given in Figure 11b. But with all methods of detection the amount of scatter seems to be

somehow dependent on the exact physical adjustment of the detectors or some other unknown parameter, so that at times the pulse to pulse fluctuations in ratio can be small, as in Figure 12.

Although this problem contributes to the short term fluctuations, noise on the scale of one data point (0.03 cm^{-1}), the frequency fluctuations mentioned above, on the scale of 0.1 to 0.2 cm^{-1} are a considerably larger problem. (But when attempts were made to use the internal etalon to select out one OPO cavity mode, this intensity measurement problem was aggravated by the lower power and larger fluctuations of the OPO output. Indeed with the etalons available to us, in the 3.5 micron wavelength region where the OPO operation is poor anyway, it was impossible to tell when we were on an absorption line and when we were not.)

Before we can obtain Lorentzian linewidths from experimental data we must know the tuning rate of the OPO in cm^{-1}/min, and the baseline, or ratio of reference to cell intensity when the cell is evacuated. An estimate of both quantities can be obtained from absorption traces like the one in Figure 13, of about 6 torr of HF. The upper trace is the region from P(2) to P(3) and the lower from P(3) to P(4). Measuring the distance between lines P(3) and P(4) on the chart paper and converting by the recorder speed we find that the lines are separated by 42.25 minutes of scanning time. Then taking the line spacing[10] as 45.47 cm^{-1} we get a tuning

46

Figure 12: A particularly felicitous scatter plot due to infrared pulses from two InSb detectors. The cell detector had 200Ω termination, the reference detector had 100Ω, and both had 10x amplification. Full scale on this plot is 9 volts, and the minimum voltage read was 0.4 volts.

Figure 12
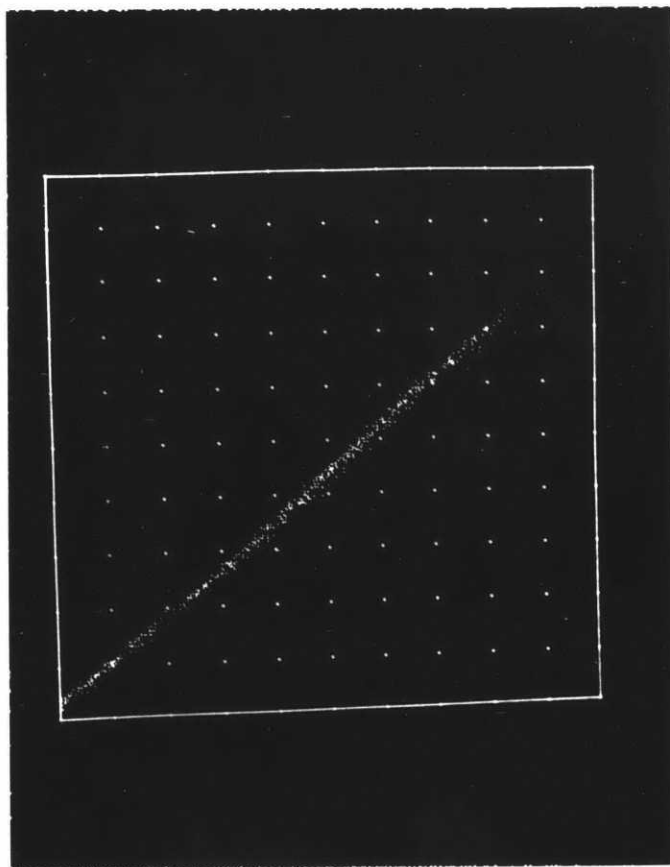
Figure 13: An absorption scan of about 6 torr

of HF only, useful in choosing baselines

for high pressure absorption traces and in

calculating the frequency scan rate from

the distances between lines. Upper trace

is the region between P(2) and P(3), and the

lower trace is the region between P(3) and P(4).

Figure 13

10 cm^{-1}

50
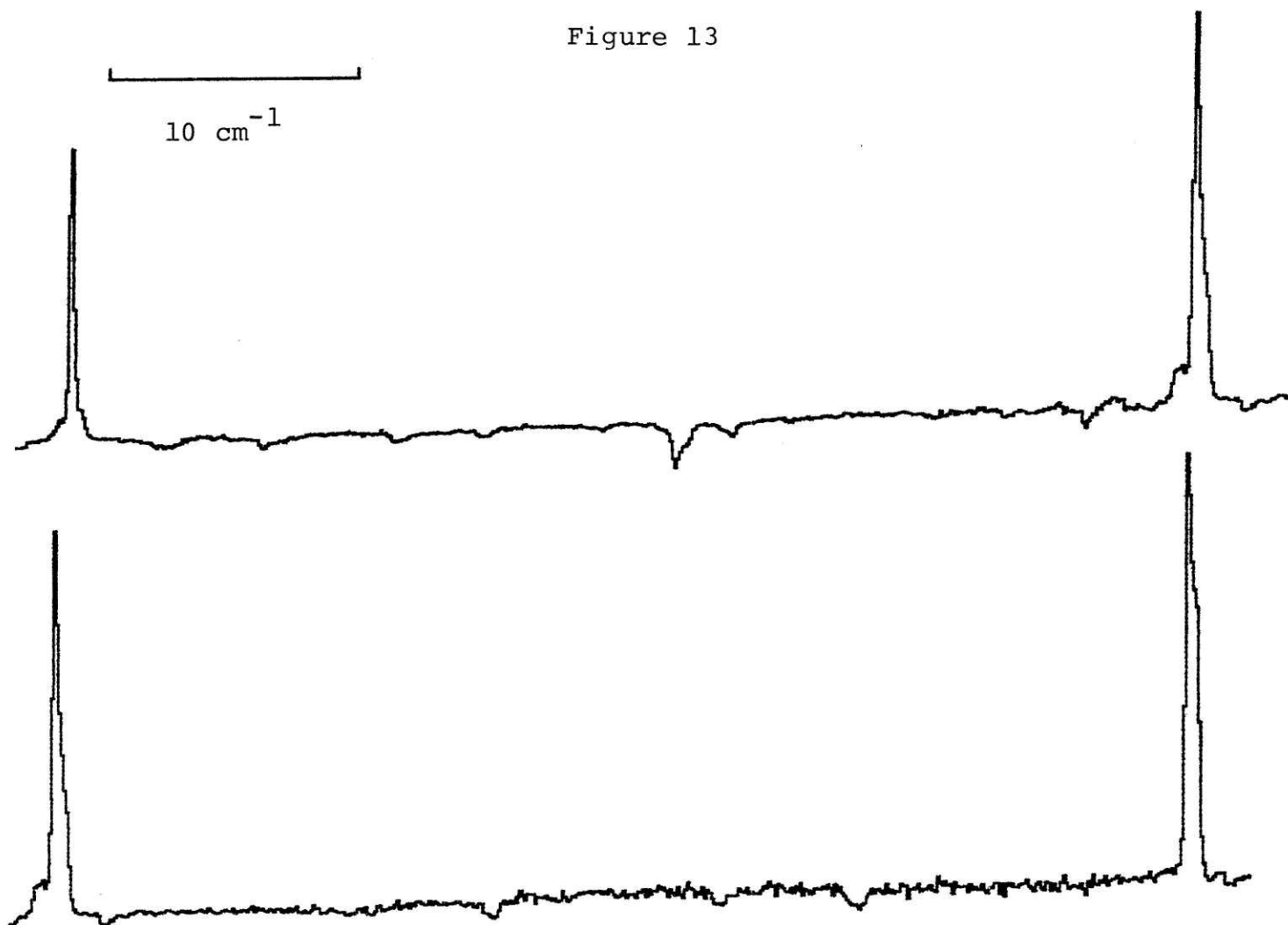
rate of 1.07 cm^{-1}/min. (Reference 11 gives line frequency distances up to 0.2 cm^{-1} different than those of Reference 10 even though both measure to 0.01 cm^{-1}.) Another scan taken just before the one shown in Figure 13 gave 1.08 cm^{-1}/min, while one taken the day before gave 1.07 cm^{-1}/min, which was used to process the data which we will discuss below.

The P(2)-P(3) distance in Figure 13 gives 1.05 cm^{-1}/min, the trace immediately before it gave 1.06 cm^{-1}/min, while the trace from the day before gave 1.03 cm^{-1}. One can also use frequency differences obtained from pressure broadened lines. Although pressure shifts are large at high densities, they are all very close to the same size.[12,13,19,24] So for example the distance between the first P(4) line in Figure 14 and the P(3) line on the same tape, both broadened by 130.5 atm of argon, gives a factor of 1.07 cm^{-1}/min.

The two or three per cent fluctuations in tuning rate in different measurements are common and another source of error. However, the differences in tuning rate as a function of frequency are consistently observed. Tuning rates at the longest wavelength, 3.5 microns, are as large as 1.20 cm^{-1}/min, obtained using the HCl line spacings of Reference 14. This trend can be understood if we assume there is a direct relationship between temperature and scanning time, and note that in Figure 37 in Appendix A that the slope of the wavelength versus temperature graph increases with higher temperature.

The small-scale noise in the baseline portion of Figure 13

51

is due to the intensity detection problem discussed above. We see this especially near P(4) , toward the end of the OPO mirror tuning range and where the OPO output is more erratic. The larger dips, though, are associated with a large drop in intensity of both cell and reference signals. These are presumably due to absorption by atmospheric water vapor and a slight difference in path lengths to cell and reference detectors. However, attempts to assign water vapor lines using literature spectra[15] were unsuccessful.

The average value of the reference to cell ratio for a small region between the P(3) and P(4) lines in Figure 13 is 1.07. In the trace immediately preceding it, however, it was 1.11 for the same region. These sorts of fluctuations are also commonly observed, so for most of the data baselines were actually chosen by the best fit to a Lorentzian. For the P(4) line measured just before the vacuum trace in Figure 13, the best fit baseline was indeed 1.07.

Figure 13 also shows that this baseline ratio is not constant, although its variation is slow enough over the range of interest to be approximated by a line. This slope is also chosen by the best fit to a Lorentzian. Of course, the double-beam experimental setup was designed to eliminate both short and long term variations in ratio when all other conditions remain unchanged. It is possible, but not proven, that this slow variation has the same origin as the pulse to pulse fluctuations.

As an example of the treatment of experimental data, and of the sort of experimental errors encountered, we present the treatment of data taken on the same day as the low pressure scan of Figure 13. We consider the measurements of the HF P(4) line broadened by 130.5 atmospheres of argon, recorded on tapes 450 through 453 and on the end of tape 443. These five traces are shown in Figure 14.

To average them, the original traces on chart paper are superimposed, and the amount of each scan to be discarded so that all scans will line up is measured off the chart, then converted into the number of data points. With the present choice of pulse rate (30 Hz) and number of pulses which are averaged to give one data point (48), there are 33 data points output per minute. Then the tapes are added by computer, (using programs in Appendix D), and the initial and final values of the ratio in the wings are sampled, to get an estimate of the initial baseline and its slope. The averaged initial ratio was 1.15, although individual values at the same point were 1.18,1.12,1.14,1.17, and 1.16. The baseline found to best fit a Lorentzian was 1.07 and its slope was a positive .00023 ratio per data point.

The fits are made visually, by generating Lorentzian lineshapes and superimposing them on the experimental traces. Sometimes several iterations of the process of choosing baselines and slopes and generating Lorentzians are needed to obtain a good fit. The final averaged line plotted on an

53

Figure 14: Five individual absorption traces of HF P(4) broadened by 130.5 atmospheres of argon. Their average is shown in Figure 16.
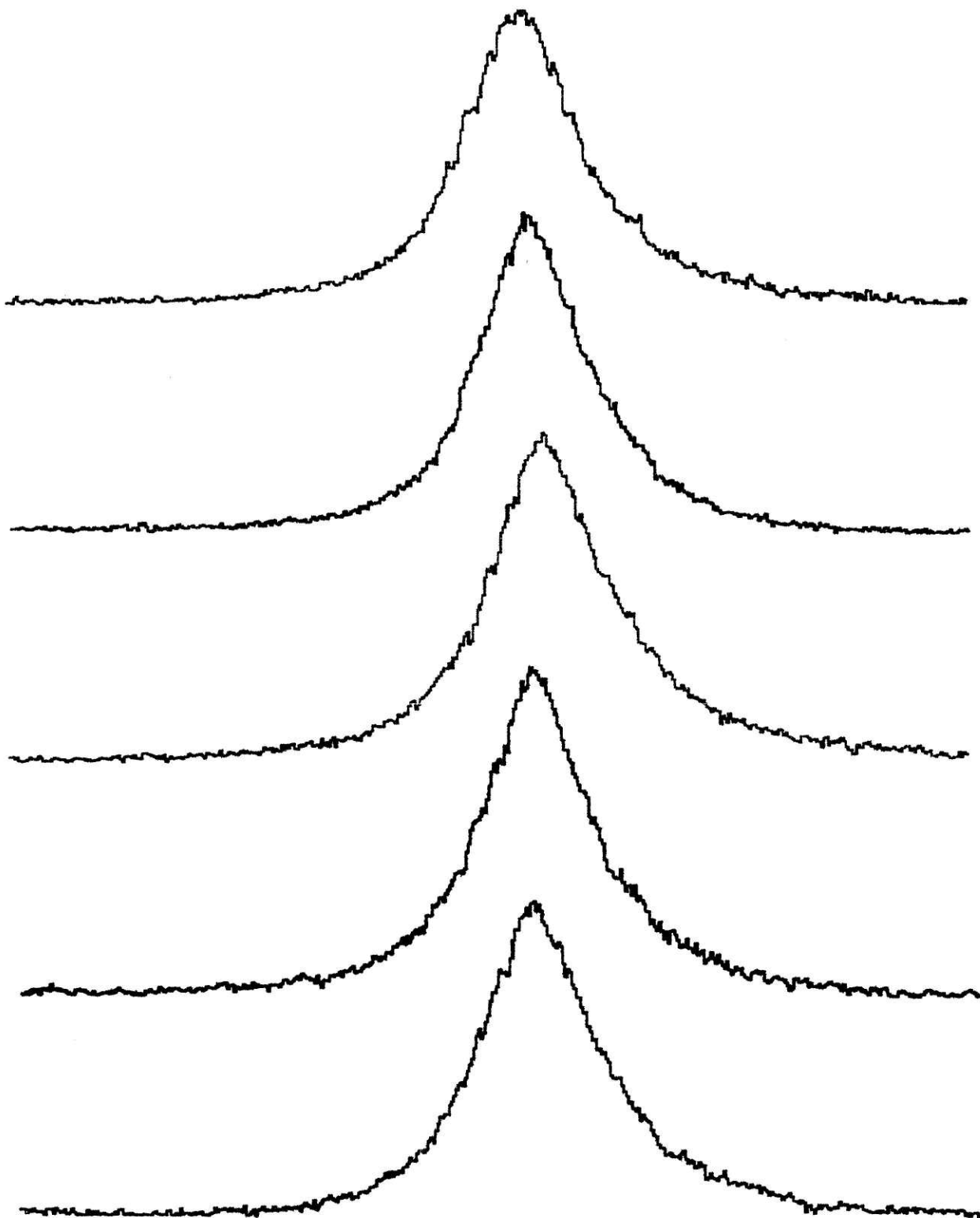
Figure 14

x-y recorder and the Lorentzian fit are shown in Figure 16 in Section I D. The halfwidths of the five individual lines were 2.68, 2.78, 2.88, 2.72 and 2.92 cm^{-1}, giving an average halfwidth of 2.78 cm^{-1} with a root-mean-square deviation of 0.1 cm^{-1}. The width of the averaged line before deconvolution was 2.82 cm^{-1}, so here 0.04 cm^{-1} was added by averaging.

To fit a Lorentzian to the experimental trace using the program in Appendix D, we must calculate the scaling factor SC in cm^{-1} per x-y recorder point. In this case this is given by SC= 3/6.4 data points/ x point times 1/33 minutes per data point times 1.07 cm^{-1}/min, or .0152 cm^{-1}/x point. These factors can be used to estimate values for the width and center point of the experimental curve. Then these parameters and the peak height and initial value and slope of the baseline are varied to obtain the best visual fit. When several lines are used in the Lorentzian fit, the relative intensities are taken from the peak absorption values for HF in Reference 16, or from the line strengths for HCl of Reference 17. The ratios of the low density widths of neighboring lines to that of the line being fit are used to pick linewidths for the fit. But the effect of these neighboring lines on the linewidth is usually small, except for the case of the HCl isotopic doublet.

D. <u>HF Low Density Linewidth Results</u>

In this section we present the measurements of widths
of HF vibration-rotation lines broadened by argon. We will
also fit the lower density data to obtain a linewidth linear
in density which may be compared with previous measurements
of the pressure broadening coefficient done at low pressures.
Discussion of possible second order density dependence will
be left to Section II E.

The HF lines studied were P(2), P(3), and P(4), measured
at room temperature and over an argon pressure range of 10
to 140 atmospheres. The linewidths were obtained by fitting
a Lorentzian (or at the very highest densities a sum of
Lorentzians) to the experimental trace, as detailed in the
previous section. From Figures 15 and 16 we can see that the
lineshape is indeed a Lorentzian function out to many
halfwidths from line center, to within the accuracy of the
experimental trace. In Figure 16 we also see that HF lines
overlap very little even at the highest densities. This makes
them easier to fit than HCl, discussed in the next section,
whose lines overlap even at low densities.

Figures 17 through 19 are plots of the half width at half
maximum after deconvolution as a function of the density of
the perturbing argon. The deconvolution procedure has been
described in Section I C. It assumes a laser full width of
less than 0.5 cm^{-1}, so that the corrections are around 0.2 cm^{-1}
or less. The densities are expressed in amagats, units of the

Figure 15: Sample trace of HF P(2) broadened
by 51.5 atmospheres of argon. The experimental
trace is the average of five data tapes. The
Lorentzian fit has a halfwidth of 1.45 cm^{-1}.

Figure 16: Sample trace of HF P(4) broadened
by 130.5 atmospheres of argon. The experimental
trace is the average of five data tapes. The
Lorentzian fit is composed of a central peak
with a halfwidth of 2.75 cm^{-1} and two
neighboring lines (off each side of the figure)
with appropriately scaled widths.

Figure 15

Absorbance, (arbitrary units)

Experiment

Fit

Frequency, (1 cm^{-1} per division)

Figure 16

Absorption, (arbitrary units)

Frequency, (5 cm^{-1} per division)

60
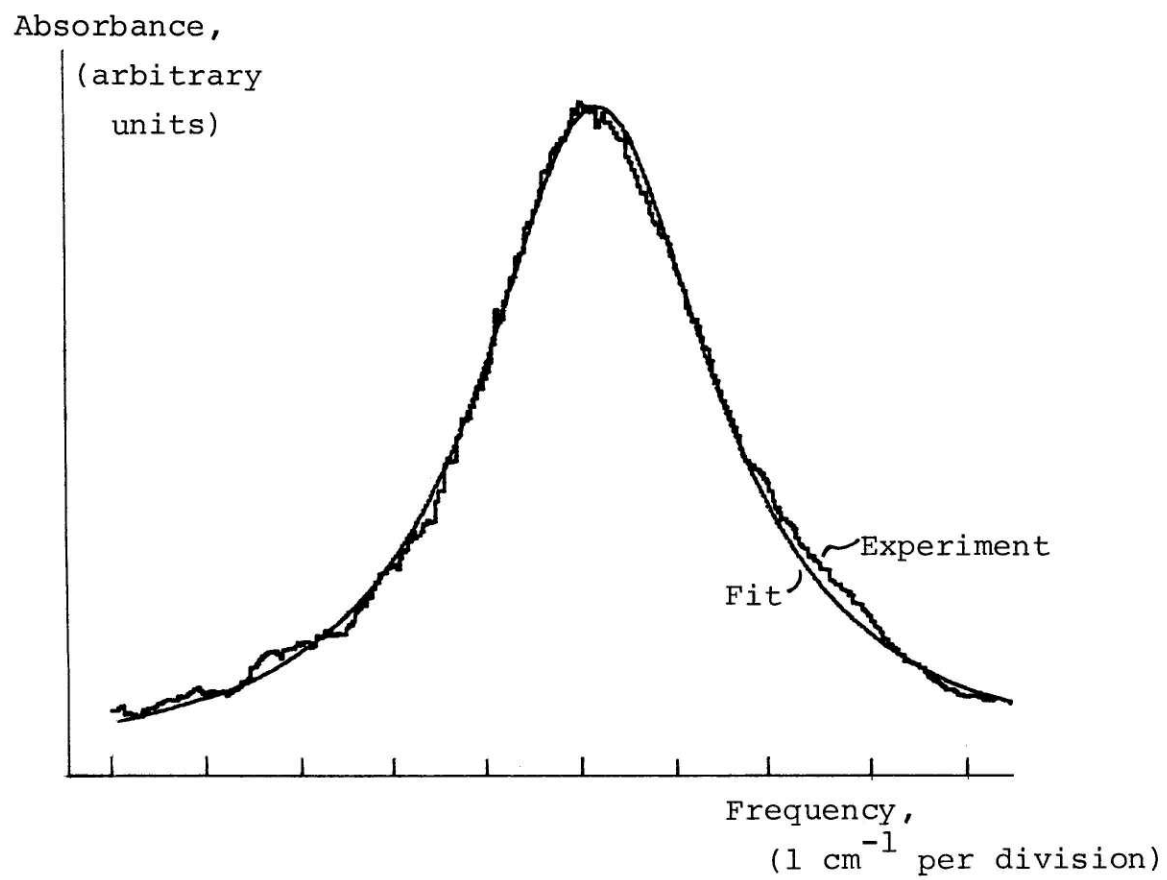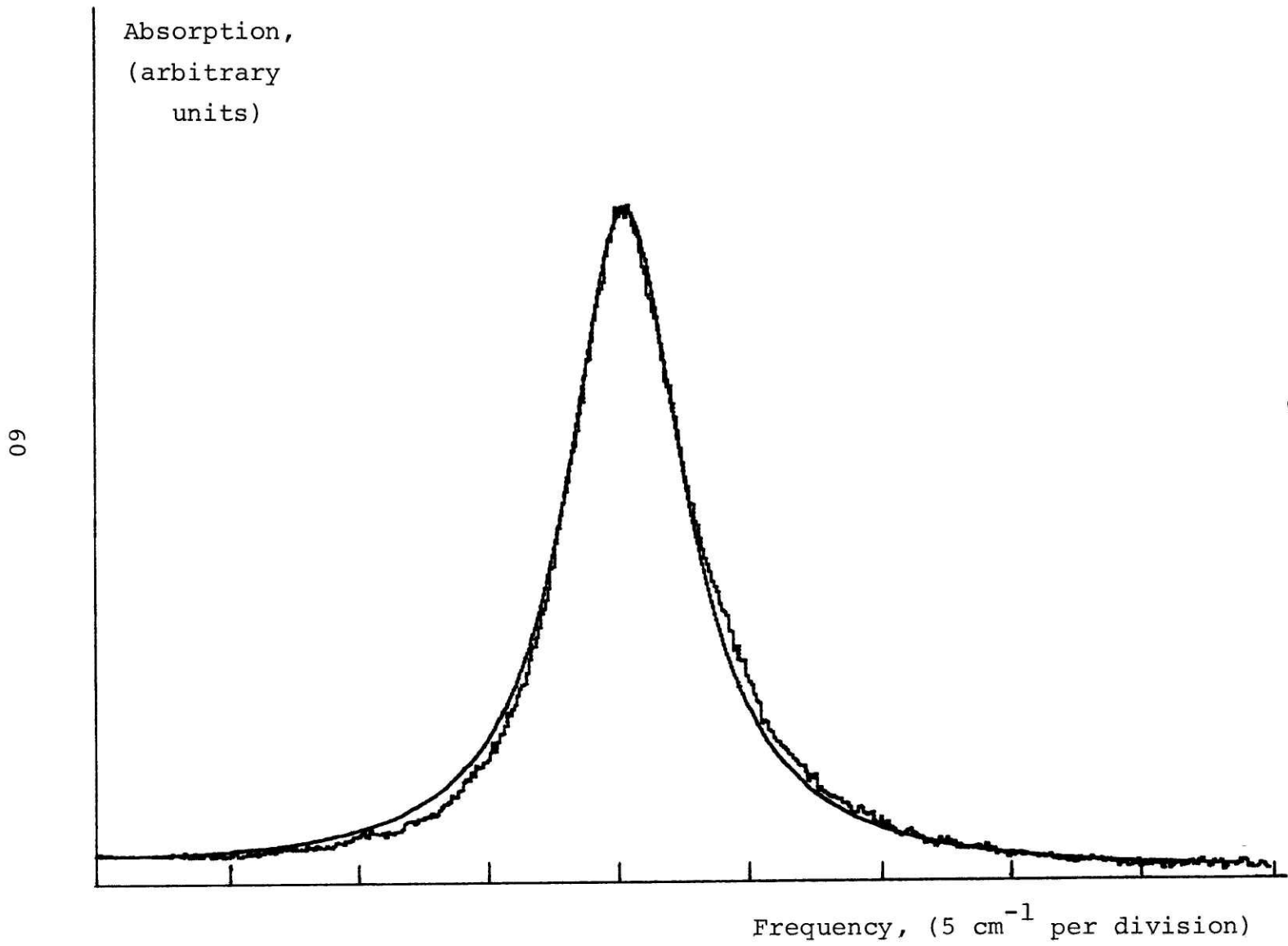
of a perfect gas at 0° C, and are obtained assuming a
second virial coefficient of -16 cm^3/mole for argon at
298° K.[18] (Throughout most of the density range studied
here, the effects of the nonideality of the gas and
conversion to standard temperature partially cancel.
For low densities only the substantial temperature factor
remains. In Section I E we will see that one must be
careful on this account when comparing literature values.)
Also plotted in Figures 17 through 19 are the linear
extrapolations of the low density measurements of Wiggins
and coworkers,[19] and the least squares line fit through
the experimental points and constrained to pass through
zero. (Of course, as the density goes to zero, there
remains a contribution to the linewidth due to Doppler
broadening. However is this spectral region the Doppler
width is less than 0.01 cm^{-1} and can be neglected.)

Table 1 gives linear pressure broadening coefficients
determined by fitting the experimental points up to 100
amagats. (Somewhat lower densities can also be used for
upper limits without changing the values obtained.) Also
listed is the standard deviation in the slope calculated
from the least squares fit. This is not necessarily a
good measure of the error, since the average deviation per
point for the fit is considerably smaller than the
experimental error estimate, discussed in Section I C.
Also listed are the values of Wiggins and coworkers[19] and

61

Table 1 : Linear Pressure Broadening Coefficients for HF

Line	This Work	Reference 19
P(2)	$.029 \pm .001$ cm^{-1}/am	$.036 \pm .001$ cm^{-1}/am
P(3)	$.023 \pm .001$	$.031 \pm .001$
P(4)	$.020 \pm .001$	$.024_5 \pm .001$

Figure 17: Plot of half width at half
maximum of the P(2) line of HF as a
function of the perturbing argon density.
In this and the following two figures,
the squares are experimental points, the
solid line is the least squares fit through
them constrained to pass through the origin,
and the dashed line is the linear
extrapolation of the low density results
of Reference 19.

Figure 18: Plot of linewidth of HF P(3)
versus argon density.

Figure 19: Plot of linewidth of HF P(4)
versus argon density.

Figure 17

64

Half Width at Half Maximum, cm^{-1} vs. Argon Density, Amagats

Figure 18

65

Figure 19

66
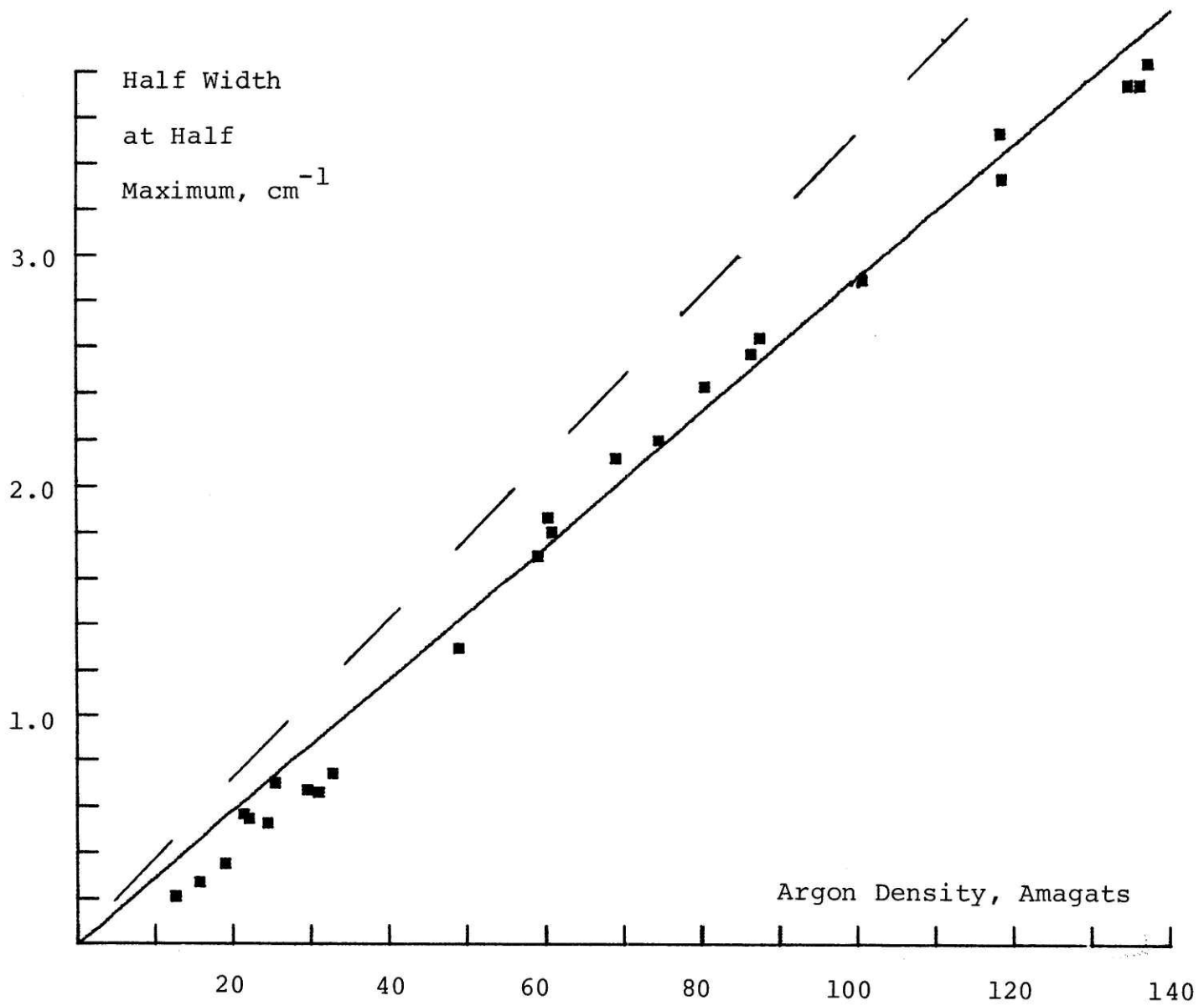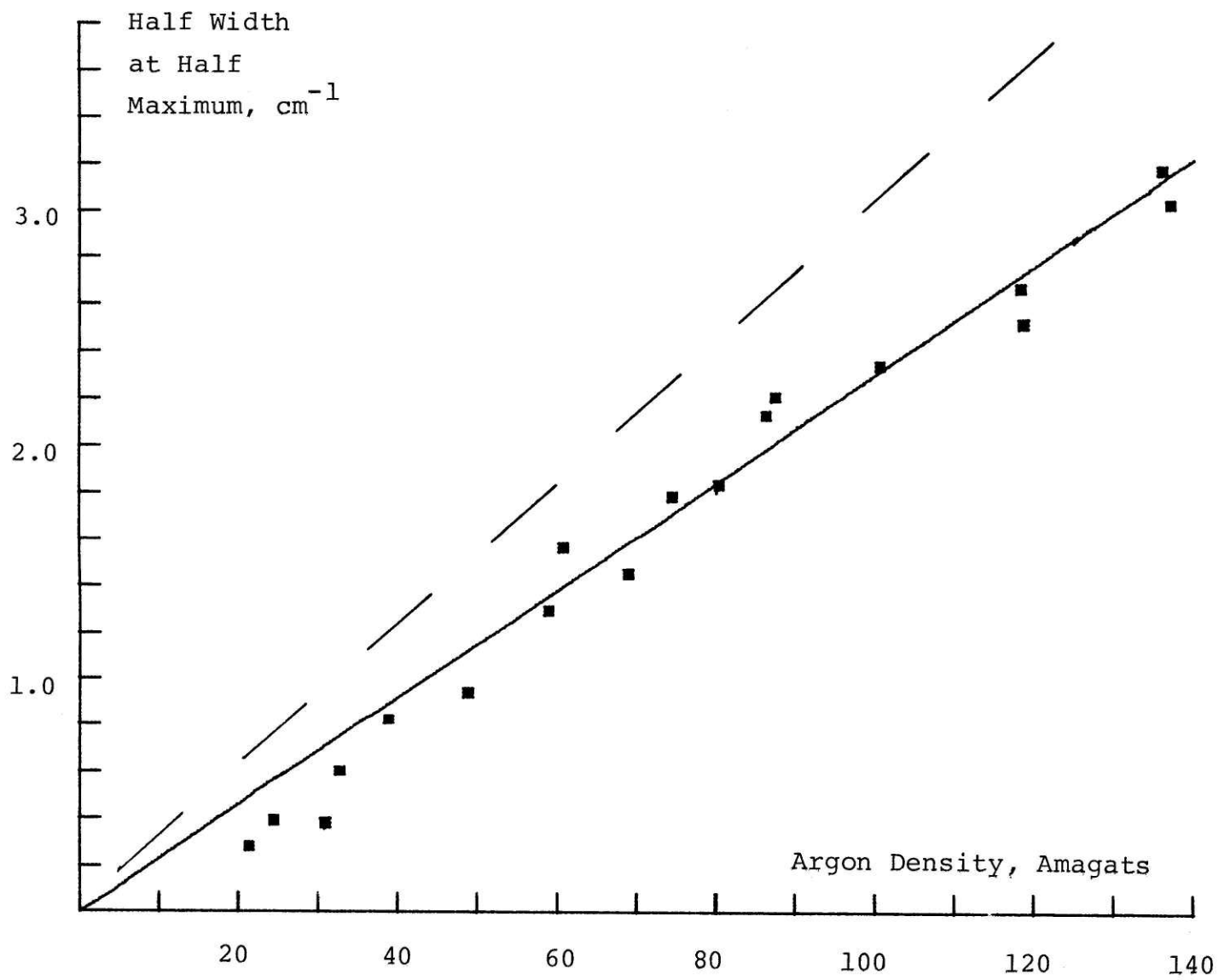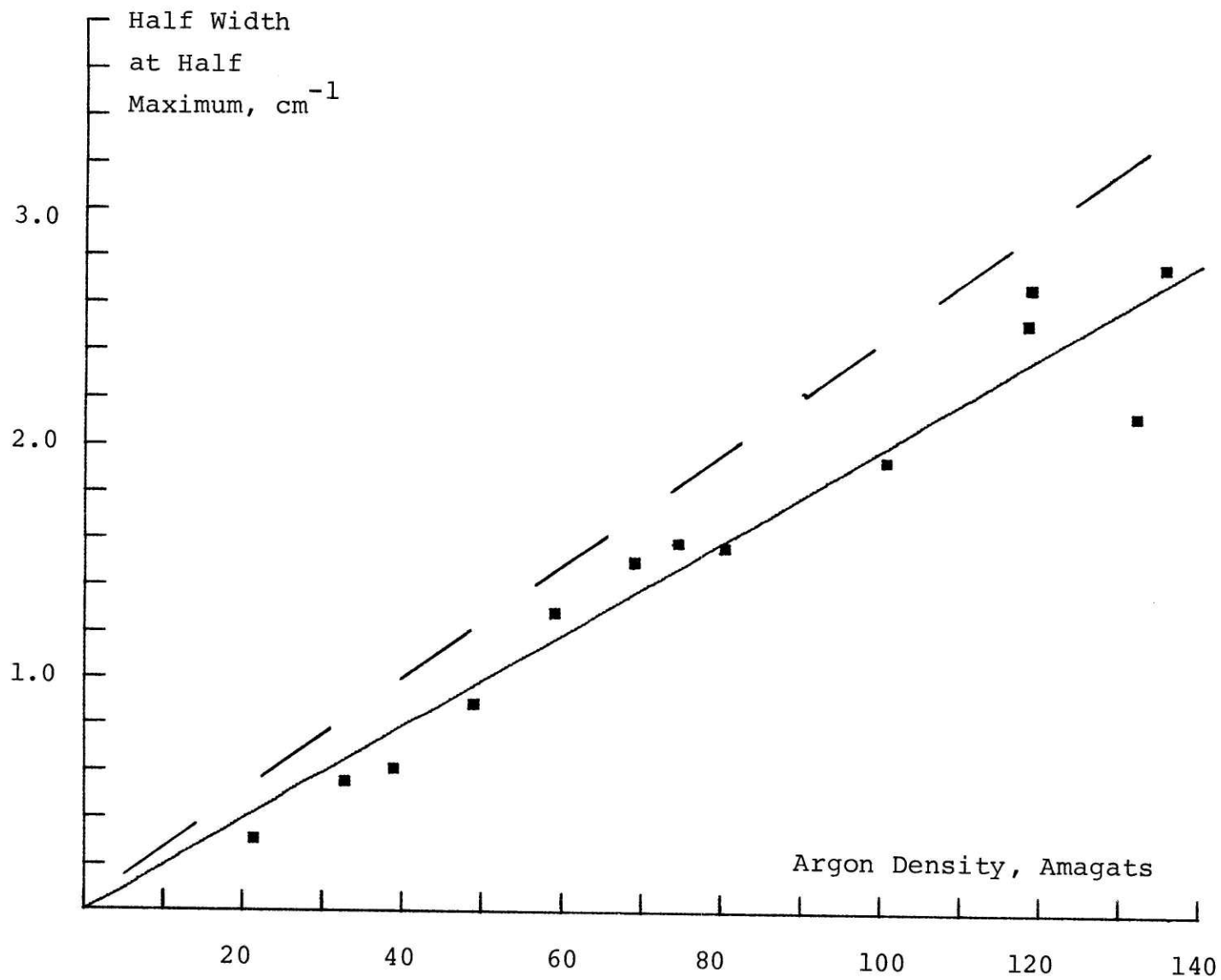
their error estimate. We note that the linewidths reported by Wiggins and coworkers are significantly larger than ours. This will be discussed further in Section I E, where we will find that the HCl linewidths measured by Rank and Wiggins and coworkers are systematically larger than those obtained in later work on the same system.[25,26]

The decrease of linewidth with increasing J is commonly observed, and can be explained by simple models. For instance, one can argue that rotational energy levels are spaced farther apart at high J so that inelastic collisions become less probable.[20,27] Or, in another way of thinking, fast rotation tends to average out angle dependent forces which give rise to reorientation contributions to line broadening.[28]

In Table 2 we present some theoretical calculations of the broadening by argon of the three HF lines studied here. The recent calculation by Jarecki and Herman[20] uses a form of the theory of Baranger, in which isotropic effects represented by a phase shift are included to all orders in the interaction potential, and inelastic contributions are calculated to second order. Bachet[21] uses standard Anderson theory, to calculate pure rotational linewidths.

We also include results of several different experiments, the pure rotation widths measured by Bachet,[21] the R branch values of Oksengorn,[22] and the first overtone measurements of Atwood and Vu.[23] These values should all be somewhat different, but they are at least interesting for comparison.

<u>Table</u> <u>2</u> : Comparison with Theory and Related Experiments on HF Linewidths

　　　In the first column we repeat the results of the present work. We

identify the succeeding columns by the number of the reference, as discussed

in the text. All values are in cm^{-1}/amagat. The values from Reference 22

are actually for the lines R(1) through R(3), and those of Reference 21 marked

Pure Rot. are for the pure rotational lines J $1 \rightarrow 2$, $2 \rightarrow 3$, and $3 \rightarrow 4$. See

Table 1 for comparison with experiments on the same lines.

| | This | Theory | | Ref. 22 | Ref. 21 | |
Line	Work	Ref. 20	Ref. 21	R-Branch	Pure Rot.	Ref. 23
P(2)	.029	.034	.0339	.051	.037	$.063_5$
P(3)	.023	.019	.0269	.043	.025	.038
P(4)	.020	.015	.0236	.037	.015	

Reference 20 contains a discussion of the vibrational dependence of linewidths. The general trend is that pure rotation lines are somewhat narrower than fundamental vibration-rotation lines, while first overtone lines are broader. It also discusses differences in width for corresponding lines in the P and R branches, concluding that these are due to the differing effects of inelastic collisions. Again, in the HF-argon system these effects are relatively small.

E.   HCl Low Density Linewidth Results

This section contains the same discussion for HCl lines broadened by argon as the preceding one did for HF. For HCl the lines studied were R(1) through R(6) at room temperature broadened by up to 100 atmospheres of argon. Figures 20 through 22 show some sample experimental traces. Figure 20 shows that even at low densities the two lines due to the 35 and 37 isotopes of chlorine are broadened into each other, while Figures 21 and 22 show that at high densities the gaps between rotational lines begin to fill in. Figure 22 also includes a trace of just a few torr of HCl.

The plots of linewidth versus density appear in Figures 23 through 28, and the linewidths obtained by a linear least squares fit to all the experimental points are presented in Table 3. Again, the errors quoted are the standard deviations from the least squares fit, and our estimates of experimental error are larger. Also as before the least squares fits were made giving equal weight to each experimental point, since as for the HF data, fits weighted by the quality of the lineshape gave identical results.

In the case of HCl there are three low density measurements of the same lines, one by Rank and Wiggins and coworkers[24] and two more recent sets of data by workers in France.[25,26] The agreement between our data and the last two references strengthens their assumption that (at least for the higher rotational lines) the linewidth values measured by Rank and

70

Figure 20: Sample trace of the HCl R(4)
isotopic doublet broadened by 29.5 atm
of argon. The experimental trace is an
average of three data tapes. The
Lorentzian fit is composed of six lines,
the central isotopic doublet with 0.9 cm^{-1}
halfwidths and two neighboring doublets
with appropriately scaled widths.

71

Figure 20

72

Absorbance, (arbitrary units)

Fit to Sum
Experiment of Lorentzians

Frequency, (1 cm^{-1}/division)
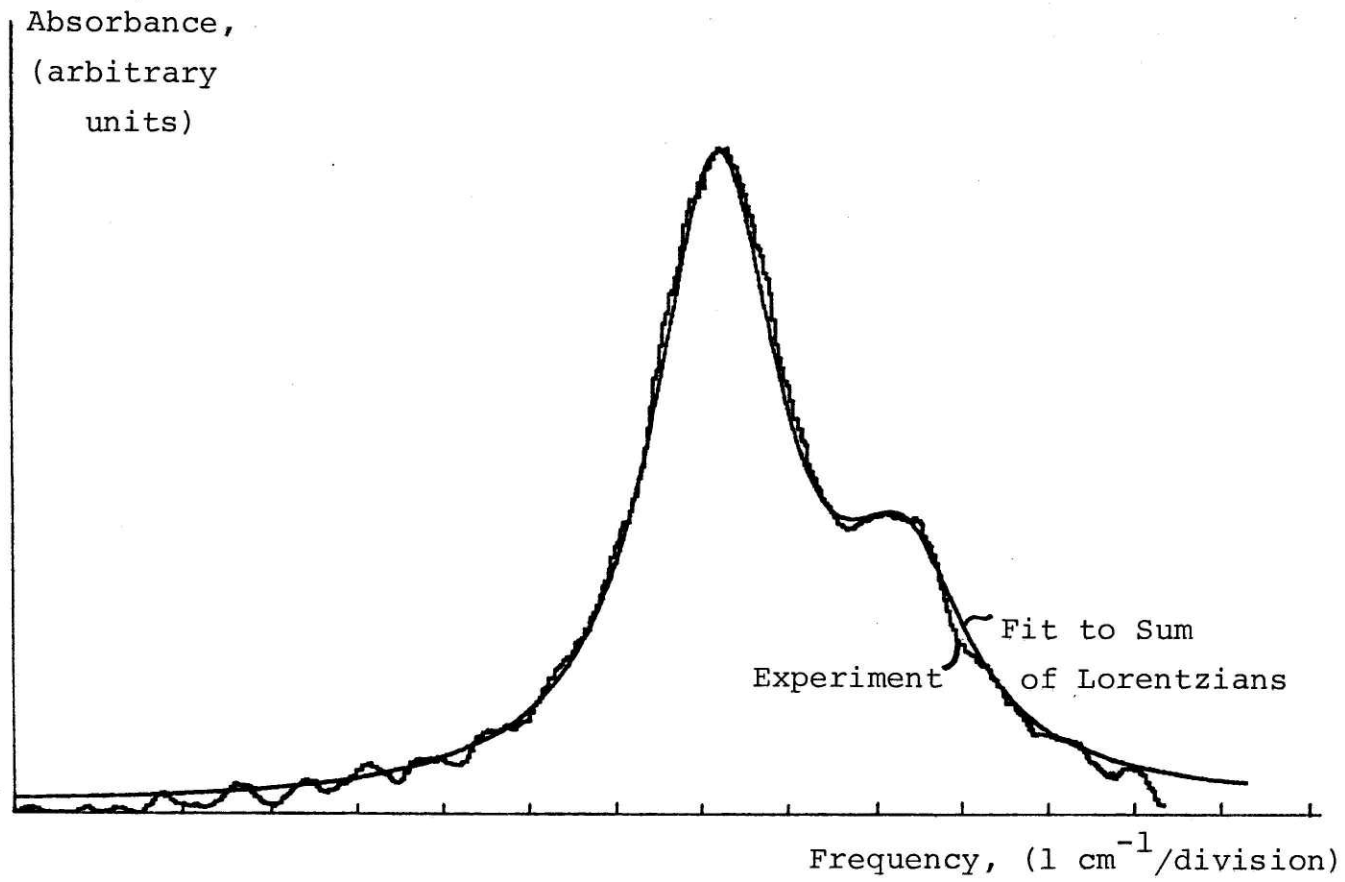
Figure 21: Sample trace of two sets of
HCl lines, R(3) and R(4), broadened by
102 atmospheres of argon so that the
isotopic splitting entirely disappears.
This trace is the average of 7 experimental
scans, and like the rest of the earliest
HCl data was produced by measuring points
off each chart recorder trace, averaging
them, and replotting.

Figure 21

Absorption, (arbitrary units)
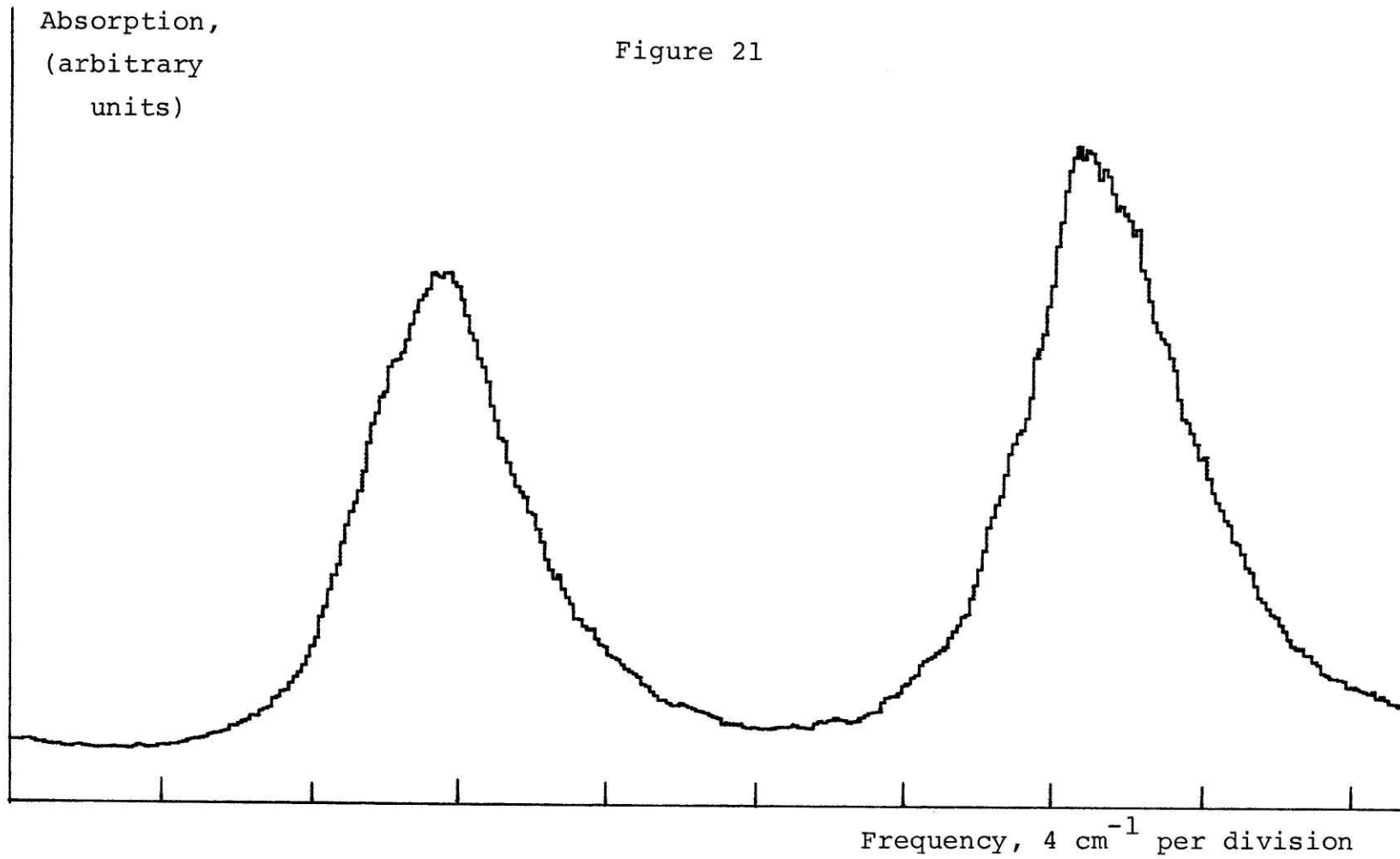
Frequency, 4 cm^{-1} per division

74

Figure 22: Sample trace of HCl R(4) through
R(1) broadened by 91 atmospheres of argon,
showing that the gaps between the lines are
filling in considerably at high pressures.
Also shown is a trace of just a few torr of
HCl, using the same baseline used for the
high pressure scan.

R(4)

R(3)

HCl R(4)−R(1) Lines Broadened by 91 atm Argon

R(2)

R(1)

Absorbance

76

HCl, with no argon

0

10 cm⁻¹ per division
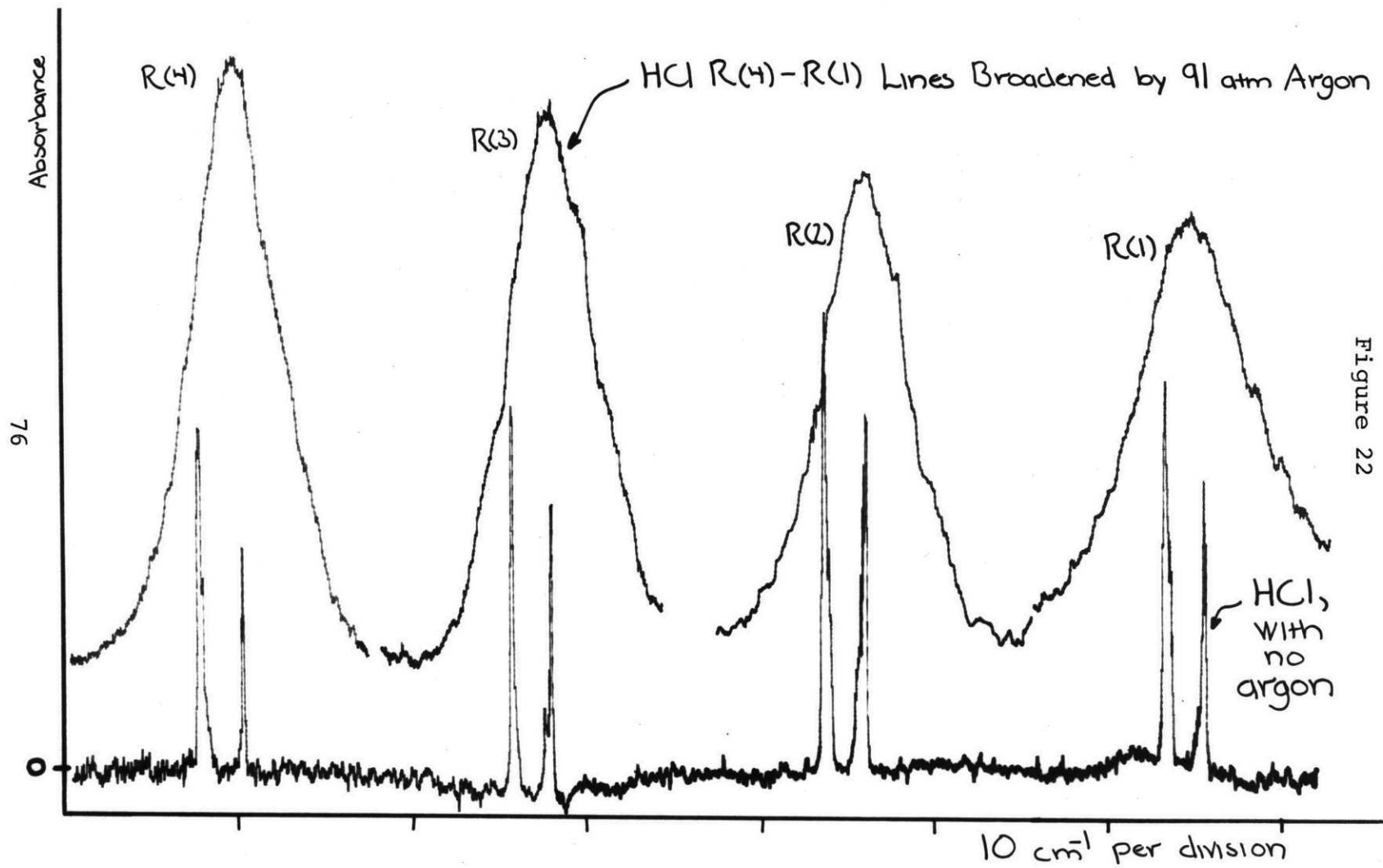
Figure 22

Table $\underline{3}$: Linear Pressure Broadening Coefficients for HCl

Line	This Work		Ref. 24	Ref. 25	Ref. 26
R(1)	$.042 \pm .001$	cm^{-1}/am	$.042_5$	.0387	.0421
R(2)	$.034_5 \pm .001$		$.044_5$	.0336	.035
R(3)	$.032 \pm .001$		.039	.0315	.0306
R(4)	$.028 \pm .001$		.028	.0274	.0268
R(5)	$.021_5 \pm .001$		$.024_5$	.0226	.0236
R(6)	$.016 \pm .001$		.020	.018	

Figure 23: Plot of the half width at half

maximum of the HCl R(1) line as a function of

perturbing argon density. In this and the

following 5 figures, the squares are experimental

points, and the solid line is a least squares

fit through them constrained to pass through the

origin. The long dashed line is the linear

extrapolation of the low density results of

Reference 24, the medium dashed line the same for

Reference 25, and the short dashed line for

Reference 26. (Because some of the linear linewidth

values are very close to each other, not all lines

may be plotted on any one graph. Consult Table 3

for the values omitted.)

Figure 24: Plot of the linewidth of HCl R(2)

versus argon density.
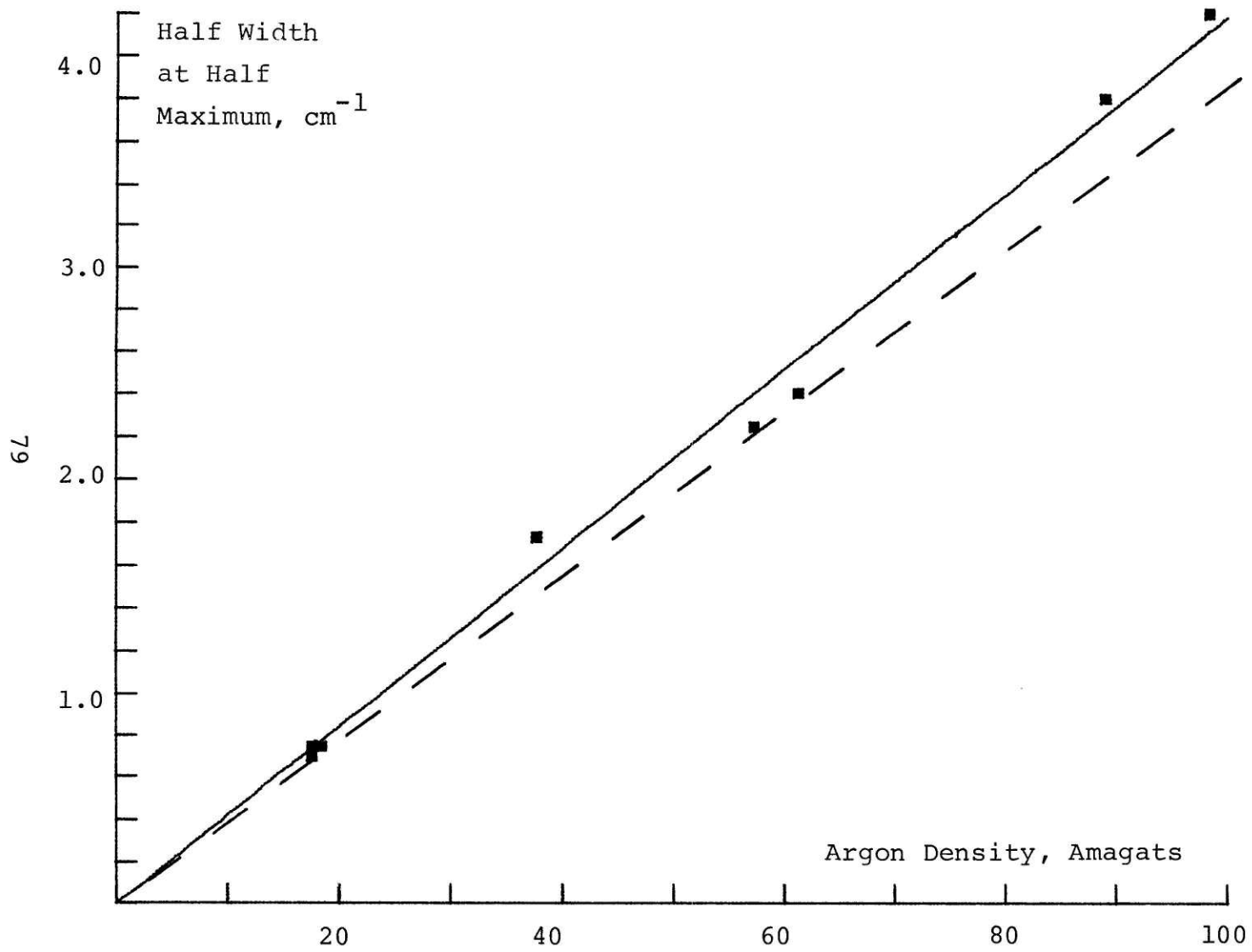
Figure 23
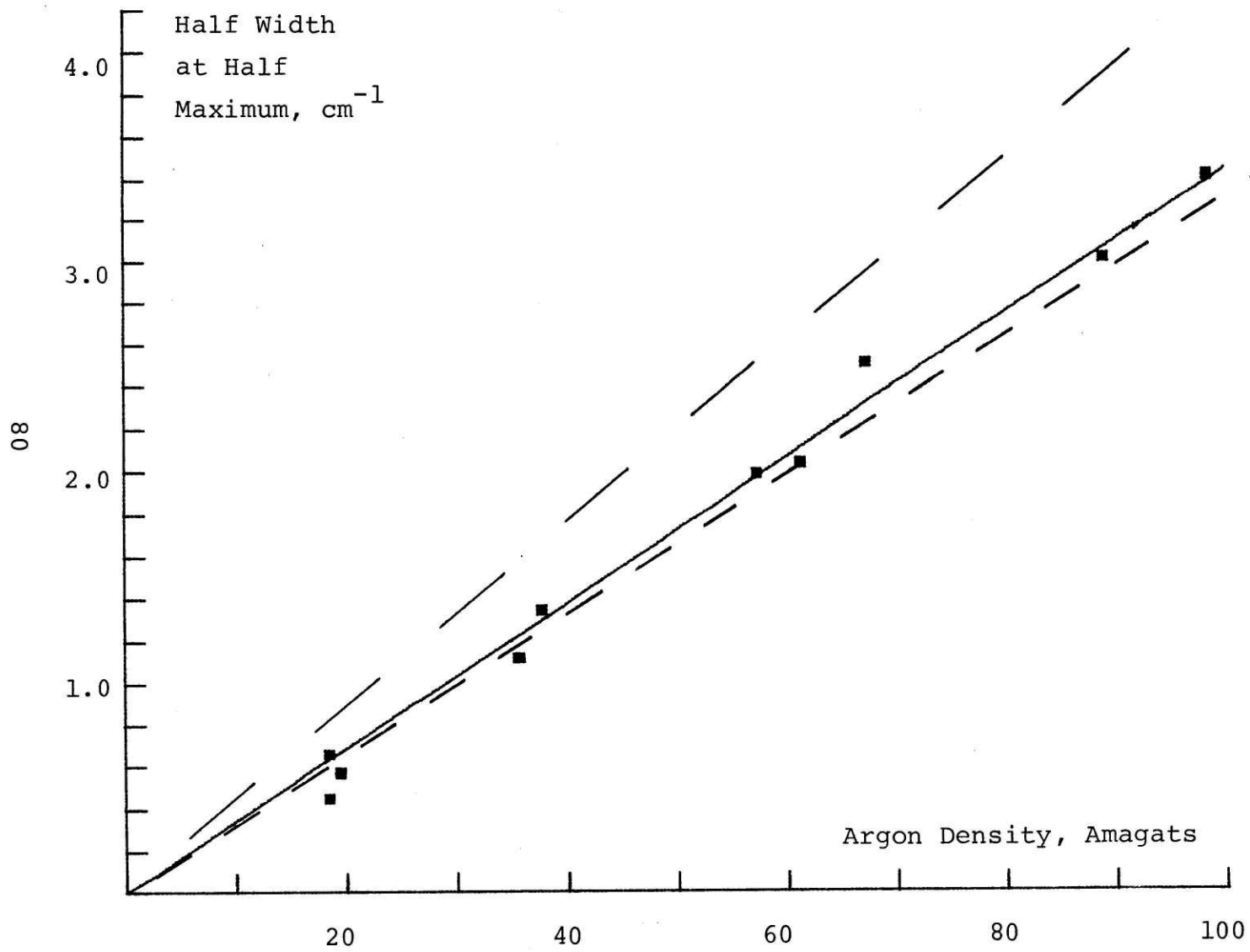
Figure 24

Figure 25: Plot of the linewidth of HCl R(3) versus argon density.

Figure 26: Plot of the linewidth of HCl R(4) versus argon density.

Figure 27: Plot of the linewidth of HCl R(5) versus argon density.

Figure 28: Plot of the linewidth of HCl R(6) versus argon density.

Figure 25

82
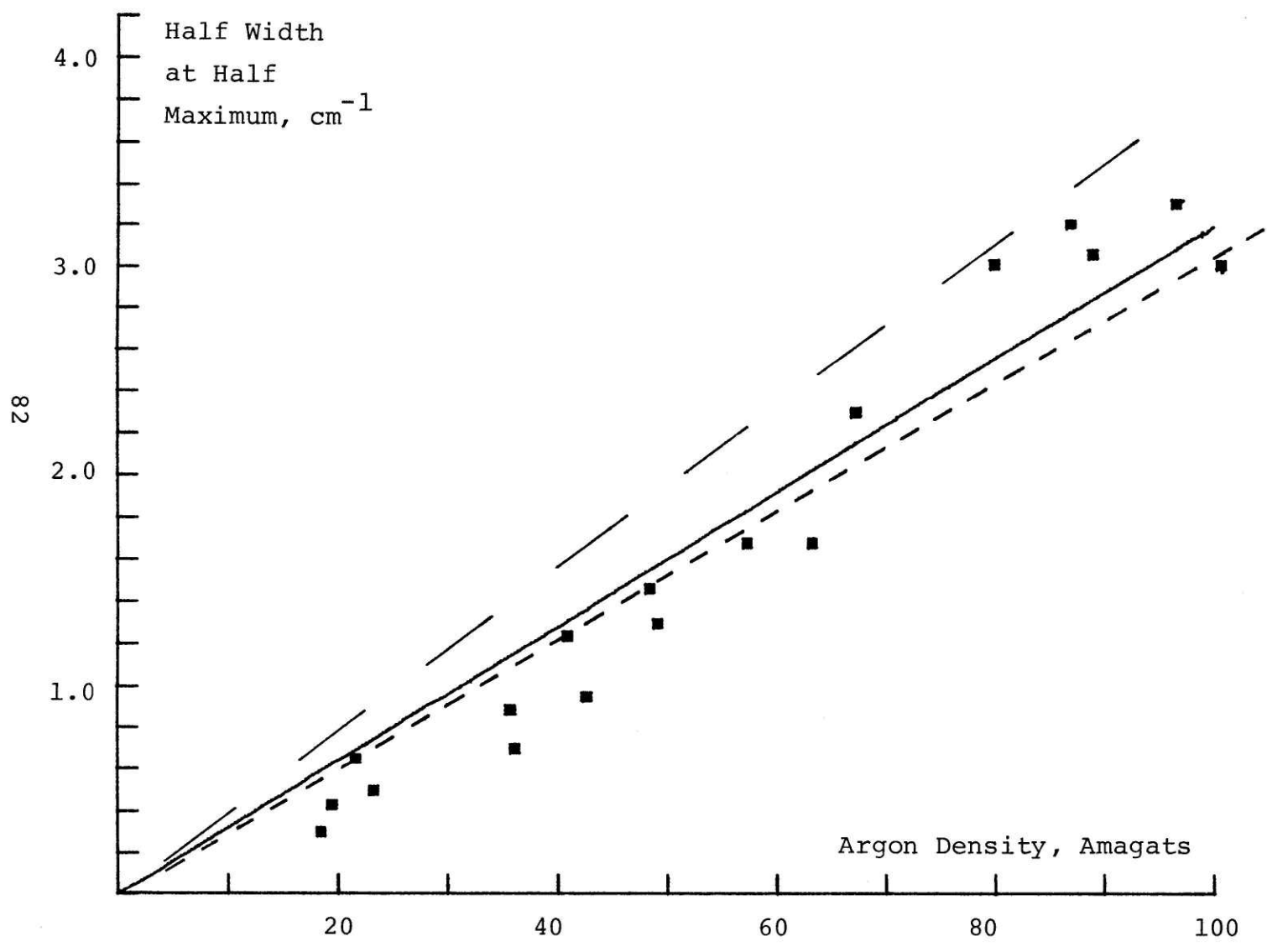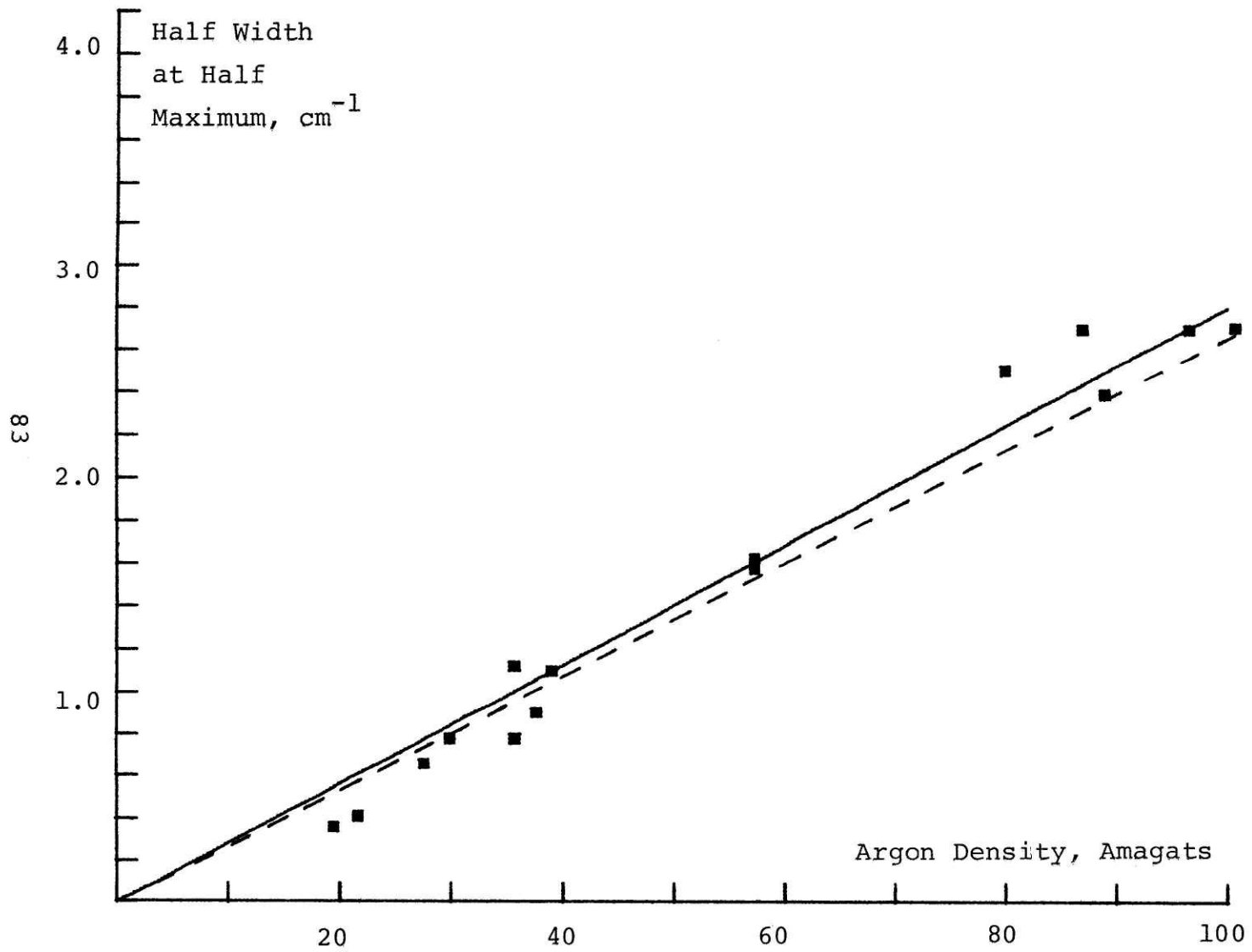
Figure 26

Figure 27

84
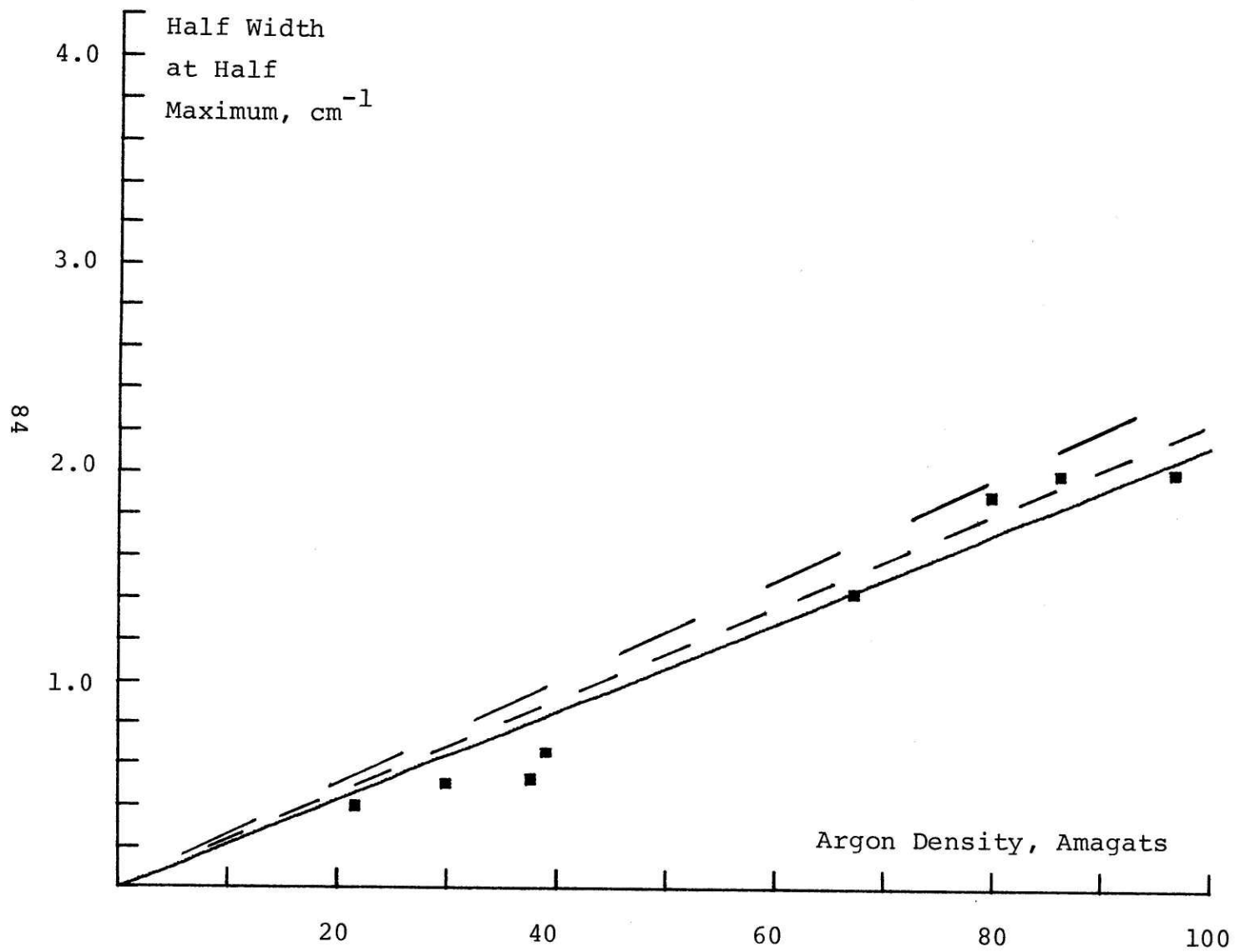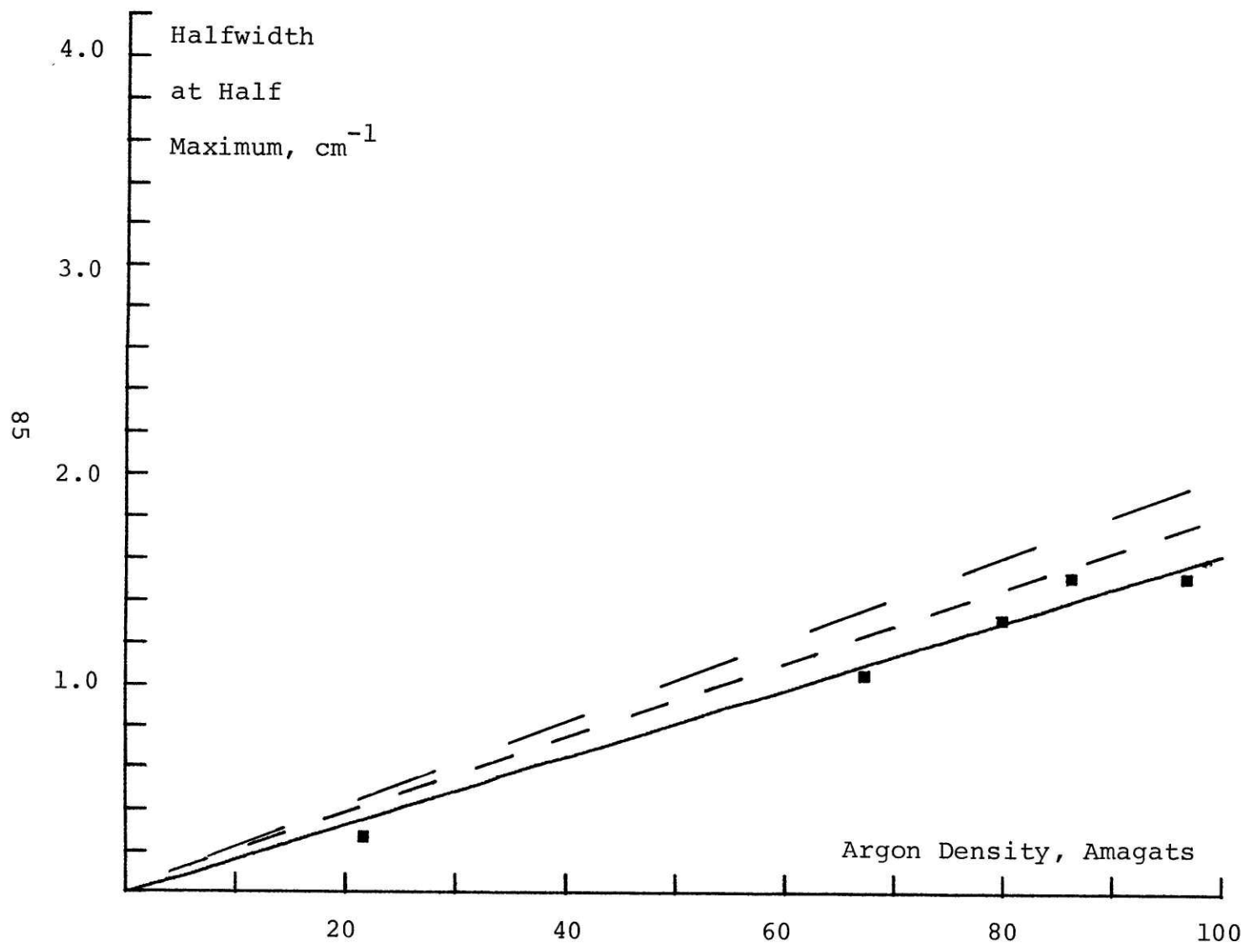
Figure 28

Wiggins are too high, and lends weight to the argument in Section I D that the HF linewidths measured by Wiggins are also too large. This conclusion is further supported by considering that our tunable laser spectrometer, with its finite linewidth and necessity for averaging by super-imposing several traces, possesses systematic errors which only tend to produce observed linewidths which are too large. Yet for HF our line broadening coefficients before any deconvolution are still smaller than those of Wiggins. (We anticipate the discussion of Section II E on second order density effects to note that if it is indeed the practice of the French workers to measure linewidths at pressures of 5 to 10 atmospheres in order to reduce their instrumental error, then my estimates would say that they might actually be making a systematic error in causing their linewidths to be a few per cent too small.)

However, looking over Table 3 we conclude that the agreement between the sets of data is not too bad. Indeed, it is better than either of the French groups claims, for the following reason. Levy and coworkers[25] report their results in mk/bar. (A millikayser, abbreviated mk, is 0.001 cm^{-1}.) The bar is a unit of pressure equal to .9861 atm. Then since argon at 1 atmosphere is essentially a perfect gas, we need only convert to standard temperature by the rather substantial factor of $298^{\circ}K/273.15^{\circ}K$. In Reference 26 Houdeau and coworkers also made this conversion of the results of Reference 25, but further in their comparison

86

with Rank and Wiggins and coworkers [24] they assumed that

units of cm^{-1}/standard atmosphere meant cm^{-1}/atm. Yet

Rank clearly states that his standard atmosphere is pressure

at $0^{O}C$, and for HF Wiggins simply quotes cm^{-1}/amagat. So

Reference 26 is in error in converting and making the values

of Rank look even larger, while Reference 25 is wrong in not

converting their measurements in mk/bar before comparing

with Rank.

In Table 4 we again give comparisons with theory and

with pure rotation measurements. The calculation of Tipping

and Herman[29] uses the formal expression of Baranger for the

linewidth, expanded to second order in the interaction

potential. Although this is the same order as Anderson

theory, this procedure results in some modifications.

Houdeau[26] uses standard Anderson theory with the potential

used by Tipping and Herman. Boulet, Isnard and Levy[30] use

a modification of Anderson theory[31] and a potential due to

Buckingham, which they compare with the potential of Tipping

and Herman.

The calculation of Marcus and Fitz[32] uses semiclassical

S-matrix theory, while that of Neilsen and Gordon[33] uses

a classical path method for translation but solves the

coupled equations for the quantum mechanical scattering matrix

for rotational states. Gordon offers a wide variety of

potentials, and here we choose the one compared by Marcus.

Both calculations give no difference between corresponding

87

Table <u>4</u> : Comparison with Theory and Related Experiments on HCl Linewidths

In the first column we repeat the results of the present work. We identify the succeeding columns by the number of the reference, as discussed in the text. All values are in cm^{-1}/amagat. The values from References 32 and 34 are theoretical and experimental results for the pure rotation transition J 4 5, and the results of Reference 33 are also best compared with pure rotation experiments.

Line	This Work	Ref. 33	Ref. 32	Ref. 29	Ref. 26	Ref. 30	Ref. 34	Ref. 35
R(1)	.042	.0438		$.048_5$	.0388	.038		.0406
R(2)	$.034_5$	.035		.046	.0351	.033		.0337
R(3)	.032	.0285		.037	.033	.032		.0237
R(4)	.028	.023	.0237	.022	.031	$.027_5$	.022	.0217
R(5)	$.021_5$	.019		$.015_5$	.0293	$.022_5$		.0216
R(6)	.016			$.011_5$		.0187		

88

R and P branch lines, and are best compared with pure
rotation measurements. Also the results of both calculations
are expressed in terms of cross sections. In comparison,
conversion from linewidths to cross sections requires some
care, since it is essentially an arbitrary definition. Here
we will define the cross section σ in cm^2 by[31]

$$\Delta \nu_{1/2} = \tilde{N}/\tilde{V} \; \bar{v}_{12} \; \sigma/2\pi c$$

where $\tilde{N}$ is the Avogadro number, $\tilde{V}$ is the molar volume, $\bar{v}_{12}$
is the thermal average relative velocity, and $\Delta \nu_{1/2}$ is the
linewidth in cm^{-1}/am. (For HCl at 298°K this means multiplying
the linewidth in cm^{-1}/am by 1.22 gives the cross section in $\overset{\circ}{A}^2$.)
By checking their conversion of the data of Rank, Gordon seems
to use this factor, while Marcus uses a larger factor (which
might be due to his again assuming that the values of Rank
are expressed in cm^{-1}/atm instead of cm^{-1}/amagat).

In addition Table 4 presents two measurements of pure
rotation lines,[34,35] which are in general expected to be
smaller than the corresponding vibration-rotation linewidths.
Reference 29 has a discussion of the vibrational dependence
of linewidths. Also Gordon[33] quotes some unpublished pure
rotational widths due to Scott and Sanderson of Ohio State.

After the studies of HCl and HF, some preliminary
measurements were maded on DF broadened by argon. DF is a
molecule which has been little studied, but which has lately
become quite interesting.[36] All that can be said presently
is that the lines are quite narrow, at least as narrow as the

corresponding HF lines. This means that although they have roughly the same rotational spacing as HCl (and are in the same spectral region) they do not have the serious problem of overlapping rotational lines at high densities.

II   THEORY, AND DISCUSSION OF EXPERIMENTS

A. Summary of Formal Theory

In this section we will present a reprise of the formal theory of Albers and Oppenheim[37-39] for the density expansion of the lineshape, in order to reach our own forms of the triple collision contributions. We will also include a short discussion of the physical origin of the logarithmic divergence and density dependence, although in three dimensions this occurs in third order in the density and we shall be most interested in second order density corrections. Additional discussion of the theory in its classical mechanical form is contained in References 40 through 44.

Since we will begin our density expansion with the correlation function expression for the absorption coefficient, we should give some explanation of that form. While it can be derived from perturbation theory,[39,45-47] there are some assumptions which have their best justification in linear response theory,[48] and we shall use that here.

To begin, we consider a total Hamiltonian $H_T(t)=H+H_1(t)$, where H describes the motion and interaction of an N particle system including an absorbing particle, and $H_1(t)$, the coupling to the outside world, will eventually be $\vec{E}(t)\cdot\vec{p}$, where $\vec{p}$ is the dipole moment and $\vec{E}(t)$ the electric field of the light. So for foreign gas broadening we want the nonequilibrium average of a single dipole moment $\vec{p}$, which in quantum mechanics is $\overline{\vec{p}(t)} = \sum_n \rho_n \langle n t|\vec{p}|n t\rangle$. Instead of

91

time dependent energy states, $|n\,t\rangle$, we use the equation

(1) $i\hbar\,\partial/\partial t\,|n\,t\rangle = H_T(t)\,|n\,t\rangle$

with $|n\,-\infty\rangle$ being $|n\rangle$ to introduce time development operators,

$U(t)\,|n\rangle = |n\,t\rangle$.   Then

(2) $\overline{\vec{p}(t)} = \text{Tr}\,(\rho_{eq}\,U^\dagger(t)\,\vec{p}\,U(t))$

where $\rho_{eq} = e^{-\beta H}/\text{Tr}\,e^{-\beta H} = e^{-\beta H}/Z$ and Tr denotes

a sum over diagonal matrix elements. In order that $U(-\infty)=1$

(if $\vec{E}(t)$ is like $\vec{E}_o \cos\omega t$) we will have to write $H_1(t)$ as

$\lim\limits_{\epsilon\to 0_+} e^{\epsilon t}\,\vec{E}(t)\cdot\vec{p}$ to show that the disturbance was

adiabatically turned on at $t = -\infty$.

By trace invariance to order of operations, Equation (2)

becomes

(3) $\overline{\vec{p}(t)} = \text{Tr}\,(\rho(t)\,\vec{p}\,)$

with $\rho(t)$ given by

(4) $\rho(t) = U(t)\,\rho_{eq}\,U^\dagger(t)$,

whose equation of motion is

(5) $\dot{\rho}(t) = -\tfrac{i}{\hbar}\,[H_T,\rho(t)]$

Now we make the linear response assumption, by saying the

solution of Equation (5) is $\rho(t) = \rho_{eq} + \rho_1(t)$ If we

substitute and keep only linear terms, we find

(6) $\dot{\rho}_1(t) = -\tfrac{i}{\hbar}\,[H,\rho_1(t)] - \tfrac{i}{\hbar}\,[H_1(t),\rho_{eq}]$

or rewriting,

(7) $\tfrac{d}{dt}\left(e^{iHt/\hbar}\,\rho_1(t)\,e^{-iHt/\hbar}\right) = -\tfrac{i}{\hbar}\,e^{iHt/\hbar}\,[H_1(t),\rho_{eq}]\,e^{-iHt/\hbar}$

Integrating,

(8) $\rho_1(t) = -\tfrac{i}{\hbar}\,\int_{-\infty}^{t} d\tau\; e^{-iH(t-\tau)/\hbar}\,[H_1(\tau),\rho_{eq}]\,e^{iH(t-\tau)/\hbar}$

or with $H_1(t) = \vec{E}(t)\cdot\vec{p}$,

92

(9) $\rho_1(t) = \frac{-i}{\hbar} \int_{-\infty}^{t} d\tau \, e^{-iH(t-\tau)/\hbar} [\vec{p}, \rho_{eq}] e^{iH(t-\tau)/\hbar} \cdot \vec{E}(\tau)$

In equilibrium, $\vec{p}(t) = e^{iHt/\hbar} \vec{p} \, e^{-iHt/\hbar}$ so that

(10) $\rho_1(t) = \frac{-i}{\hbar} \int_{-\infty}^{t} d\tau \, [\vec{p}(\tau-t), \rho_{eq}] \cdot \vec{E}(\tau)$

Now we can write

(11) $\overline{\vec{p}(t)} - \langle \vec{p} \rangle = \int_{-\infty}^{t} \overleftrightarrow{f}_{pp}(t-\tau) \cdot \vec{E}(\tau)$

where the tensor

(12) $\overleftrightarrow{f}_{pp}(t) = \frac{-i}{\hbar} Tr(\vec{p}(t) [\vec{p}, \rho_{eq}])$

is the response function. The brackets $\langle \rangle$ denote a trace over ρ_{eq}, and here $\langle \vec{p} \rangle$, the equilibrium value of $\vec{p}$, is zero.

Now we assume that

(13) $\vec{E}(t) = \lim_{\epsilon \to 0_+} \vec{E}_0 \cos \omega t \, e^{-\epsilon t}$

so that Equation (11) becomes

(14) $\overline{\vec{p}(t)} = \lim_{\epsilon \to 0_+} Re \int_{-\infty}^{t} \overleftrightarrow{f}_{pp}(t-\tau) e^{-\epsilon \tau} e^{i\omega \tau} d\tau \cdot \vec{E}_0$

or with $s = t - \tau$,

(15) $\overline{\vec{p}(t)} = \lim_{\epsilon \to 0_+} Re \int_{0}^{\infty} \overleftrightarrow{f}_{pp}(s) e^{i\omega s} e^{-\epsilon s} \cdot \vec{E}_0 e^{i\omega t} \equiv Re \, \overleftrightarrow{\chi}(\omega) \cdot \vec{E}_0 e^{i\omega t}$

or writing the susceptibility $\overleftrightarrow{\chi}$ as $\overleftrightarrow{\chi}' + i\overleftrightarrow{\chi}''$,

(16) $\overline{\vec{p}(t)} = \overleftrightarrow{\chi}'(\omega) \cdot \vec{E}_0 \cos \omega t - \overleftrightarrow{\chi}''(\omega) \cdot \vec{E}_0 \sin \omega t$

For one dipole the power absorbed, dU/dt, is $\overline{\vec{p}(t)} \cdot d\vec{E}/dt$. So since $d\vec{E}/dt = -\omega \vec{E}_0 \sin \omega t$, (taking the ϵ limit here),

(17) $dU/dt = \frac{1}{3}(-\omega \chi'(\omega) \cos \omega t \sin \omega t \, E_0^2 + \omega \chi''(\omega) \sin^2 \omega t \, E_0^2)$

where the 1/3 comes from averaging over polarizations to take $\vec{E}_0 \cdot \overleftrightarrow{\chi} \cdot \vec{E}_0$ to χE_0^2. Now we average over one period to get the power absorbed per unit time,

(18) $\frac{1}{3} \omega E_0^2 \chi''(\omega) \frac{\omega}{2\pi} \int_{0}^{2\pi/\omega} \sin^2 \omega t \, dt = \frac{1}{3} \frac{\omega}{2} E_0^2 \chi''(\omega)$

$\qquad = \frac{1}{3} \frac{\omega}{2} E_0^2 \lim_{\epsilon \to 0_+} Im \int_{0}^{\infty} e^{-\epsilon t} e^{-i\omega t} \frac{i}{\hbar} Tr(\vec{p}(t) [\vec{p}, \rho_{eq}]) dt$

Then $A(\omega)$, the power absorbed per unit distance, is simply

93

Equation (18) divided by the speed of light c and $E_0^2/2\pi$. Now,

writing the trace as a sum of diagonal matrix elements, and

using $\vec{p}(t) = e^{iHt/\hbar}\,\vec{p}\,e^{-iHt/\hbar}$,

(19) $A(\omega) = \frac{1}{3\hbar c}\pi\omega \lim_{\epsilon \to 0_+} \mathrm{Im}\, i \int_0^\infty e^{-\epsilon t} e^{i\omega t} \sum_{mn} \langle m|e^{iE_m t/\hbar}\vec{p}\,e^{-iE_n t/\hbar}|n\rangle \langle n|[\mu, \rho_{eq}]|m\rangle$

Now we use the definition of the δ function, and

$\langle n|[\mu, \rho_{eq}]|m\rangle = \langle n|\mu\rho_{eq}|m\rangle - \langle n|\rho_{eq}\mu|m\rangle = e^{-\beta E_m}(1-e^{-\beta(E_n-E_m)})\mu_{nm}/Z$

We have in $A(\omega)$

(20) $\mathrm{Im}\, i \sum_{nm} 2\pi\delta(\omega-\omega_{mn})e^{-\beta E_m}(1-e^{-\beta\hbar\omega_{nm}})$ or $\mathrm{Re} \sum_{nm} 2\pi\delta(\omega-\omega_{mn})e^{-\beta E_m}(1-e^{-\beta\hbar\omega})$

Reversing,

(21) $A(\omega) = \frac{\pi\omega}{3\hbar c}(1-e^{-\beta\hbar\omega}) \lim_{\epsilon\to 0_+} \mathrm{Re} \int e^{i\omega t} e^{-\epsilon t} \mathrm{Tr}\,(\mu\, e^{iHt/\hbar}\rho_N\mu\, e^{-iHt/\hbar})$

Following Albers, we introduce the tetradic operator L by

$e^{-iLt}\rho_N\mu = e^{iHt/\hbar}\rho_N\mu\, e^{iHt/\hbar}$.   We can now perform the time

integration, and , if we define

(22) $\int_0^\infty dt\ e^{-\epsilon t} e^{-i\omega t} e^{iLt} = (\epsilon + i\omega + iL)^{-1} \equiv G$,

then

(23) $A(\omega) = \frac{\pi\omega}{3\hbar c}(1-e^{-\beta\hbar\omega}) \lim_{\epsilon\to 0_+} \mathrm{Re}\langle \mu, G\mu\rangle$

The brackets $\langle\rangle$ denote an equilibrium average which in classical

mechanics is an integration over all coordinates and momenta

of N-1 structureless particles and on absorber, weighted by the

classical distribution function. In quantum mechanics, they

become a trace (Tr) over all states weighted by the correspond-

ing quantum mechanical density matrix, $\rho_N = \exp(-\beta H)/\mathrm{Tr}(\exp(-\beta H))$,

where the Hamiltonian H describes the translational motion of

all N particles, the internal motion of the absorber, particle 1,

and pair interactions between all N particles,

(24) $H = H_0 + H_{int}(1) + V = \sum_i^N H_0(i) + H_{int}(1) + \sum_{i<j}^N V_{ij}$

94

giving corresponding $L_o(i)$, $L_{int}(l)$ and L'_{ij} operators. We can divide the trace into Tr_1 over the translational states of particle 1, TR_1 over the internal states of 1, and Tr_{N-1} over the translational states of N-1 structureless perturbers, so that

(25) $A(\omega) = {}^{\pi\omega}/_{3\hbar c} (1 - e^{-\beta\hbar\omega}) \lim_{\epsilon \to 0^+} Re\, Tr_1 TR_1 \mu_1 Tr_{N-1} G \rho_N \mu_1$

Now we want to expand in two particle operators, by isolating the effect of a binary collision in an operator T_{12} defined by

(26) $G_{12} = G_o - G_o T_{12} G_o$ or $T_{12} = -G_o^{-1}(G_{12} - G_o)G_o^{-1}$

where $G_o = (\epsilon + i\omega + iL_o + iL_{int}(l))^{-1}$, $G_{12} = (\epsilon + i\omega + iL_o + iL_{int}(l) + iL'_{12})^{-1}$

This operator is also discussed in Appendix F. By the identity $\frac{1}{A+B} = \frac{1}{A} - \frac{1}{A} B \frac{1}{A+B}$, we have

(27) $G_{12} = G_o - G_{12} iL'_{12} G_o$ so that $G_o T_\alpha = G_{12} iL'_{12}$

Also by the identity, (with α being all pairs of molecules)

(28) $G = G_o - \sum_\alpha G_o iL'_\alpha G$

and

(29) $G = G_{12} - \sum_{\beta \,nor\, 12} G_{12} iL'_\beta G = G_{12} - \sum_{\alpha \,nor\, 12} G_o T_\alpha G_\alpha$

Using Equation (29) to iterate Equation (28), we obtain the binary collision expansion (BCE),

(30) $G = G_o - \sum_\alpha G_o T_\alpha G_o + \sum_{\alpha \,nor\, \beta} G_o T_\alpha G_o T_\beta G_o + \dots$

As in Albers this expansion may be generalized to include triple collisions, by defining an operator which takes into account all processes that three particles can perform other than the first two binary collision processes,

(31) $T(ijk) = -G_o^{-1} G_{ijk} G_o^{-1} - \sum_\alpha T_\alpha + \sum_{\alpha \,nor\, \beta} T_\alpha G_o T_\beta$

95

where $G_{ijk}^0 = (\epsilon + i\omega + i(L_o(i) + L_o(j) + L_o(k) + L'_{ij} + L'_{ik} + L'_{jk}))^{-1}$

So we will use

(32) $G = G_o + \sum_\alpha G_o T_\alpha G_o - \sum_{\alpha \text{ not } \beta} G_o T_\alpha G_o T_\beta G_o - \sum_{i<j<k} G_o T_{(ijk)} G_o$

By restoring the time integration and explicitly writing out the trace as the sum of diagonal matrix elements, it is easy to obtain[37]

(33) $Tr_1 \; G_o(1) \tilde{\rho}(1)$

for the first term, where $G_o(1)$ is $(\epsilon + i\omega + iL_o(1) + iL_{int}(1))^{-1}$ and $\tilde{\rho}(1)$ is $Tr_{N-1} \rho_N$.

Since collisions not involving particle 1 do not affect its motion, only terms in $Tr_{N-1} \sum_\alpha G_o T_\alpha G_o$ in which α is $1j$ are nonzero. (This can be shown using the invariance of the trace to representation.) Since the N-1 other particles are identical, and $(N-1)/V \simeq N/V = \rho$, the sum over α becomes

(34) $\rho \, Tr_{N-1} G_o V T_{12} G_o \rho_N = \rho \, G_o Tr_2 V T_{12} G_o \tilde{\rho}(12)$

Similarly, from the last two terms, Tr_{N-1} gives

(35) $\rho^2 G_o(1) Tr_{2,3} V T_{12} G_o(123)(VT_{13} + VT_{23}) G_o(123) \tilde{\rho}(123)$

$- \rho^2 G_o(1) Tr_{2,3} V^2 T(123) G_o(123) \tilde{\rho}(123)$

By explicitly writing out the trace over particle 1, using the diagonality of $H_o(1)$ and H_{int} in momentum and internal energy states respectively, and the tranlational invariance of $\tilde{\rho}$ to reduce the matrix elements, and then restoring to trace and operator form, one finds that (again as in Reference 37)

(36) $Tr_1 TR_1 \mu_1 G_o(1) \tilde{\rho}(1) \mu_1 = Tr_1 TR_1 \mu_1 R(1) \tilde{\rho}(1) \mu_1,$

where the internal resolvent R(1) is $(\epsilon + i\omega + iL_{int}(1))^{-1}$ and $\tilde{\rho}(1)$ is in the internal and translational space of particle 1.

96

For the second term, $TR_1 Tr_1 \mu_1 \rho G_0 Tr_2 V T_{12} G_0 \tilde{\rho}(12)$, we

can write[37] the reduced density matrix as a sum of correlated

and uncorrelated parts,

(37) $\tilde{\rho}(12) = \tilde{\rho}(1)\tilde{\rho}(2) + \tilde{\chi}(12)$

Examination of matrix elements using momentum conservation

gives the resulting two terms as

(38) $TR_1 Tr_1 \mu_1 R(1) Tr_2 V T_{12} \tilde{\rho}(2) R(1) \tilde{\rho}(1) \mu_1 + TR_1 Tr_1 \mu_1 R(1) Tr_2 V T_{12} G_0(12) \tilde{\chi}(12)$

Similarly it can be shown that to second order in the density,

the trace of the last two terms is

$$TR_1 Tr_1 \mu_1 \left(\rho^2 R(1) Tr_{23} V T_{12} R(1) V T_{13} R(1) \tilde{\rho}(1) \tilde{\rho}(2) \tilde{\rho}(3) \right.$$

(39) $$+ \rho^2 R(1) Tr_{23} V T_{12} R(1) V T_{13} G_0(13) \tilde{\rho}(2) \tilde{\chi}(13)$$

$$\left. + \rho^2 R(1) Tr_{23} V^2 \tau(123) R(1) \tilde{\rho}(1) \tilde{\rho}(2) \tilde{\rho}(3) \right) \mu_1$$

where terms involving the trace over particles 2 and 3 of T_{23}

can be shown (in Appendix A of Reference 37) to vanish because

of the form of T_{23} and the fact that the translational density

matrix vanishes for large momentum.

Now defining

$$\mathcal{L}(1) = Tr_2 V T_{12} \tilde{\rho}(2)$$

$$\tau_1(1) = Tr_2 V T_{12} G_0(12) \tilde{\chi}(12)$$

and $\tau^{v}(1) = Tr_{23} V^2 \tau(123) \tilde{\rho}(2) \tilde{\rho}(3)$

the six lowest order terms can be collected and written as

$$TR_1 Tr_1 \mu_1 \left(R(1)(1 - (\rho \mathcal{L}(1) - \rho^2 \mathcal{L}(1) R(1) \mathcal{L}(1) + \rho^2 \tau^v(1)) R(1)) \tilde{\rho}(1) \right.$$

(40) $$\left. - R(1)(1 - \rho \mathcal{L}(1) R(1)) \rho \tau_1(1) \right) \mu_1$$

Looking at the density expansion Equation (40) we see

there is an obvious problem. The ab tetradic element of $R(1) =$

$(\epsilon + i\omega + i L_{int}(1))^{-1}$, $(\epsilon + i\omega + i/\hbar(E_a - E_b))^{-1} = (\epsilon + i(\omega - \omega_{ba}))^{-1}$

behaves like ϵ^{-1} on resonance. So in the limit of $\epsilon \to 0$ the expansion Equation (40) diverges. What we want, (as pointed out by Zwanzig, Reference 49), is a series in $R(1)^{-1}$.

If the operators in the above equation were classical, or if the full density matrix $\tilde{\rho}$ factored into single particle distribution functions, we could write a density expansion for the inverse of Equation (40), multiply the two series together and solve for the coefficients of the inverse series, which would involve only $R(1)^{-1}$, and then take the $\epsilon \to 0$ limit and reinvert. (Later, I will actually do only this.) But because $t_1(1)$ satisfies a different algebra than $\mathcal{L}(1)$, we should treat these two independently, as follows.

As is suggested by the first three terms from the binary collision expansion,

$$\left(R(1) - \rho R(1)\mathcal{L}(1)R(1) + \rho^2 R(1)\mathcal{L}(1)R(1)\mathcal{L}(1)R(1) \right) \tilde{\rho}(1)$$

one can easily show that there is a general term $R(1)(-\rho\mathcal{L}(1)R(1))^n \tilde{\rho}(1)$ where n is 0 to ∞, resulting from the term in the BCE

$$\rho^n \, Tr_{n-1} \, G_0 V T_{12} \, G_0 V T_{13} \ldots G_0 V T_{1n} \, \tilde{\rho}(1)\tilde{\rho}(2) \ldots \tilde{\rho}(n)$$

There are also general terms of the form $R(1)(-\rho^2 \tau^r(1)R(1))^n \tilde{\rho}(1)$, and indeed $R(1)\left(\frac{m!}{n!(m-n)!}\right)(-\rho^2 \tau^r(1)R(1))^n(-\rho\mathcal{L}(1)R(1))^{m-n}$ from the m-n permutations of the term from the binary collision expansion

$$\rho^{m+2n} \, Tr_{m+2n-1} \, G_0 V^2 \tau(123) G_0 V^2 \tau(145) \ldots G_0 V^2 \tau(1\,2n-1\,2n) G_0 V T_{1\,2n+1}$$

$$\times \ldots G_0 V T_{1\,2n+m} \, \tilde{\rho}(1) \ldots \tilde{\rho}(2n+m)$$

and finally a general term $R(1)(-\rho\mathcal{L}(1)R(1))^n \rho \, \tau_1(1)$ One can also show that all other terms are of higher order in the density for that particular process, or vanish.

Then from the identity $\sum_{0}^{\infty}(-x)^n = \frac{1}{(1+x)}$, where x is

$R(1)(\rho \mathcal{L}(1) + \rho^2 t^r(1))$ for the series ending with $\tilde{\rho}(1)$, and

$R(1)\rho\mathcal{L}(1)$ for the $t_1(1)$ terms, we can see that $Tr_{N-1} G \tilde{\rho}_N$

becomes

$$(R(1)^{-1} + \rho \mathcal{L}(1) + \rho^2 t^r(1))^{-1} \tilde{\rho}(1) - (R(1)^{-1} + \rho \mathcal{L}(1))^{-1} \rho t_1(1)$$

So if we send ϵ to zero from the positive side and denote

operators in that limit by $(\quad)_+$, we get

$$A(\omega) = \pi \omega / 3 \hbar c (1 - e^{-\beta \hbar \omega}) Re Tr_1 TR_1 \mu_1 ((9(\omega + L_{int}(1)) + \rho \mathcal{L}(1) + \rho^2 t^r(1))_+^{-1} \tilde{\rho}(1)$$
$$- (9(\omega + L_{int}(1)) + \rho \mathcal{L}(1))_+^{-1} t_1(1)_+) \mu_1$$

(41)

which is Equation (3.28) of Albers.[37]

One can also resum by using the same identity in reverse,

$(1-x) = \frac{1}{\sum (x)^n}$, and taking only terms in the sum which are

to the same order in density as x. Thus using the identity in

either direction there is an assumption of ordering in terms

of density.

To compare with observed linewidths, we really want to

put all terms in one denominator. We will discuss this in

Section II D.

On resonance, however, there is one more problem, coming

from $t^r(1) = Tr_{2,3} V^2 t(123) \tilde{\rho}(2) \tilde{\rho}(3)$ where $t(123)$ is

$-\sum_{\alpha \beta \gamma} T_\alpha G_0 T_\beta G_0 T_\gamma$ plus terms involving more T operators,

where the indices involve only particles 1, 2, and 3. It is

most easily drawn and explained in two dimensions.

Specifically, the problem comes from terms like

$T_{12} G_0 T_{13} G_0 T_{12}$ (in two dimensions) whose matrix elements can,

99

in either quantum mechanical or classical formulations,

eventually be written to include the integral

$$(42) \quad \int d\vec{K}\, d\vec{v}_{12}\, d\vec{v}_{12}'\; T_{12} (\epsilon + i\vec{K}\cdot\vec{v}_{12})^{-1}\, T_{13} (\epsilon + i\vec{K}\cdot\vec{v}_{12}')^{-1}\, T_{12}$$

so that (in two dimensions) the sum over fourier components

of the G_O operators diverges (logarithmically) for small $\vec{k}$,

or large distances, or values of the scattering angle Θ_k'

which are close to π . Figure 29 is a schematic representation

of this recollision event.

Physically, we have, through an admittedly unlikely set

of initial momenta and impact parameters, the possibility that

after particle 1 collides with 2 it travels a large distance,

before being hit by particle 3 in just such a fashion that it

returns to recollide with 2. But even though as the excursion

of particle 1 between collisions with 2 becomes larger the

probability of the right set of collision parameters to

complete the ring decreases, still if one tries to count up all

such processes, which allow particle 1 to go even as far as

infinity, make a head-on collision, and return, their

contribution increases slightly faster. This gives rise to

a logarithmically infinite contribution, the weakest divergence,

but still a serious problem.

Of course it is obvious that such events would not take

place if the other particles in the system were taken into

account, and introducing a cutoff k of order of an inverse

mean free path would be a good guess. Since the mean free

path depends on the density (approximately as $1/\rho$), this

Figure 29: A schematic drawing of a
three body recollision event, showing
the momenta posessed by the particles
at various stages. In two dimensions,
processes of this sort in which particle 1
travels a large distance before encountering
particle 3, and in which the angle θ_{12}''
is close to π, give rise to the logarithmic
divergence.
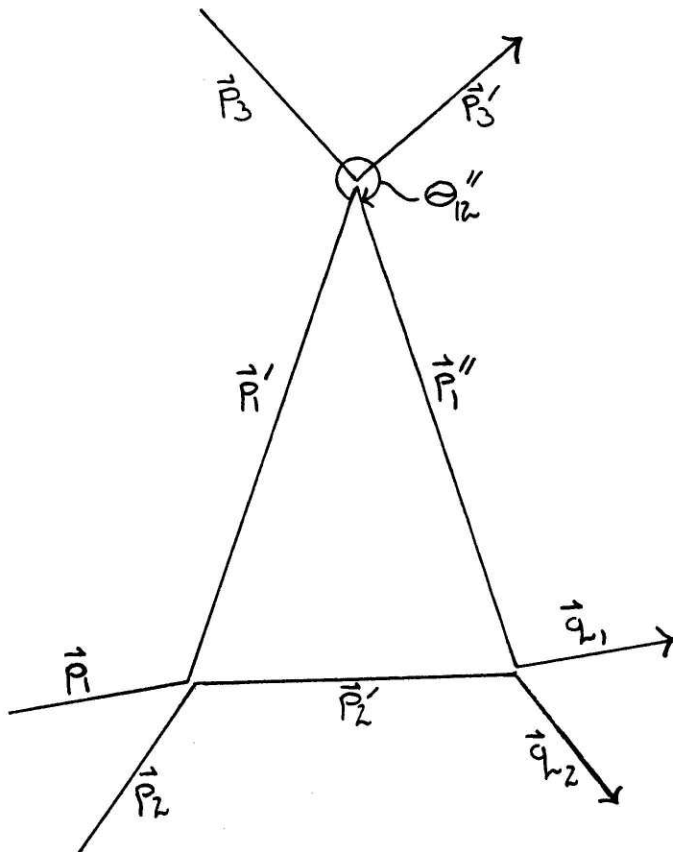
would give a logarithmic density dependence.

In fact, one can take into account the effect of the other particles by resumming the most likely (most divergent) terms.[41] This replaces T_{13} and the intermediate G_o by $\rho \ell$ and by a propagator which is damped by a factor $\rho \ell$, so that the contribution to the triple collision term is

$$\text{Tr}_2 \, V T_{12} \, (\epsilon + i\omega + iL_o(12) + iL_{int}(1) + \rho\ell(12))^{-1} \, \rho\ell(12) \, G_o T_{12} \, \tilde{\rho}(12)$$

which permits an integration over $\vec{k}$ which does not diverge but gives the expected logarithmic density factor.

For the case of the absorption coefficient, when we are off the resonance frequency, the singularity is damped anyway. So we might expect[38] that terms would become anomalously large only around 0.1 cm^{-1} from line center.

This logarithmic term has been heavily discussed.[50,51] Its existence has been questioned,[52] its size has been estimated,[53] and the density dependence of transport coefficients has been studied to find experimental evidence for it.[51] Even the work here on second density effects has implications for finding logarithmic terms, which appear in three dimensions in third order in density. In three dimensions the same sort of trouble arises from certain four body collisions.[53] Although we cannot hope to see these directly, one might be able to infer something about their size from the size of the second order density effects discussed in this work.

We will conclude this section by giving the explicit

tetradic element espressions for the three contributions from
three body collision processes, (dynamical correlations in
second order in the density), $T_{12}G_oT_{13}G_oT_{12}$, $T_{12}G_oT_{23}G_oT_{12}$,
and $T_{12}G_oT_{23}G_oT_{13}$.

First we look at $\frac{V}{\hbar^3}\text{Tr}\left(V^2 T_{12}G_oT_{13}G_oT_{12}\,\tilde{\rho}(2)\,\tilde{\rho}(3)\right)$, which
becomes (by the rules of tetradic algebra, given in References
37 and 39),

$$\begin{aligned}
\frac{V}{\hbar^3}\sum_{\substack{\vec{p}_1\,\vec{p}_1'\,\vec{p}_1'' \\ \vec{p}_2\,\vec{p}_2'\,\vec{p}_2'' \\ \vec{p}_3\,\vec{p}_3'\,\vec{q}_2 \\ \vec{q}_1\,\vec{q}_1'\,\vec{q}_1''}} V^2\, T_{12}(a\vec{p}_1\vec{p}_2\,b\vec{p}_1\vec{p}_2\,a\vec{p}_1'\vec{p}_2'\,b\vec{p}_1''\vec{p}_2'')\; G_o(a\vec{p}_1'\vec{p}_2'\,b\vec{p}_1''\vec{p}_2'') \\
\times\, T_{13}(a\vec{p}_1'\vec{p}_3\,b\vec{p}_1''\vec{p}_3\,a\vec{q}_1'\vec{p}_3\,b\vec{q}_1''\vec{p}_3')\; G_o(a\vec{q}_1'\vec{p}_2'\,b\vec{q}_1''\vec{p}_2'') \\
\times\, T_{12}(a\vec{q}_1'\vec{q}_2'\,b\vec{q}_1''\vec{p}_2''\,a\vec{q}_1\vec{q}_2\,b\vec{q}_1\vec{q}_2)\;\tilde{\rho}_{q_2}\,\tilde{\rho}_{p_3'}
\end{aligned} \tag{43}$$

By translational invariance (see Equation (B.4) of Reference
37) the T operators contain momentum conservation conditions.
From the first T_{12} we have $\vec{p}_1 + \vec{p}_2 = \vec{p}_1' + \vec{p}_2'$ and $\vec{p}_1 + \vec{p}_2 = \vec{p}_1'' + \vec{p}_2''$,
or $\vec{p}_2'' = \vec{p}_2' + (\vec{p}_1' - \vec{p}_1'')$. And from $\vec{p}_1' + \vec{p}_3 = \vec{q}_1' + \vec{p}_3$ and
$\vec{p}_1'' + \vec{p}_3 = \vec{q}_1'' + \vec{p}_3'$, by subtracting we find $\vec{p}_1' - \vec{p}_1'' = \vec{q}_1' - \vec{q}_1''$.
It is useful to define $\hbar\vec{k} = \vec{p}_1' - \vec{p}_1''$, so that when we sum over the
two delta functions in $\vec{p}_2'$ and $\vec{q}_1''$ we get

$$\begin{aligned}
\frac{V}{\hbar^3}\sum_{\substack{\vec{k}\,\vec{p}_1\,\vec{p}_1' \\ \vec{q}_1\,\vec{q}_1'\,\vec{q}_2 \\ \vec{p}_2\,\vec{p}_2' \\ \vec{p}_3\,\vec{p}_3'}} V^2\, T_{12}(a\vec{p}_1\vec{p}_2\,b\vec{p}_1\vec{p}_2\,a\vec{p}_1'\vec{p}_2'\,b\vec{p}_1'-\hbar\vec{k}\,\vec{p}_2'+\hbar\vec{k})\; G_o(a\vec{p}_1'\vec{p}_2'\,b\vec{p}_1'-\hbar\vec{k}\,\vec{p}_2'+\hbar\vec{k}) \\
\times\, T_{13}(a\vec{p}_1'\vec{p}_3\,b\vec{p}_1'-\hbar\vec{k}\,\vec{p}_3\,a\vec{q}_1'\vec{p}_3\,b\vec{q}_1'-\hbar\vec{k}\,\vec{p}_3')\; G_o(a\vec{q}_1'\vec{p}_2'\,b\vec{q}_1'-\hbar\vec{k}\,\vec{p}_2'+\hbar\vec{k}) \\
\times\, T_{12}(a\vec{q}_1'\vec{p}_2'\,b\vec{q}_1'-\hbar\vec{k}\,\vec{p}_2'+\hbar\vec{k}\,a\vec{q}_1\vec{q}_2\,b\vec{q}_1\vec{q}_2)\;\tilde{\rho}_{q_2}\,\tilde{\rho}_{p_3'}
\end{aligned} \tag{44}$$

From Equation (3.13) of Reference 37, to first order in $\vec{k}$,
we have that

$$G_o(a\vec{p}_1'\vec{p}_2'\,b\vec{p}_1'-\hbar\vec{k}\,\vec{p}_2'+\hbar\vec{k}) = \tag{45}$$
$$\left(\epsilon + \hbar\omega + \frac{V}{\hbar}\left(E_a - E_b + E(\vec{p}_1'\vec{p}_2') - E(\vec{p}_1'-\hbar\vec{k}\,\vec{p}_2'+\hbar\vec{k})\right)\right)^{-1}$$
is $\left(\epsilon + \hbar(\omega - \omega_{bo}) + \frac{\hbar\vec{k}\cdot\vec{p}_{1k}'}{m}\right)^{-1}$

104

For $T_{12}G_oT_{23}G_oT_{12}$ we have[39]

$$
V_{/\hbar^3}V^2 \sum_{\substack{\vec{P_1}\vec{P_1}' \\ \vec{P_2}\vec{P_3}\vec{P_2}'\vec{P_3}' \\ \vec{q_1}\vec{q_2}\vec{q_1}'}} T_{12}(a\vec{P_1}\vec{P_2}\, b\vec{P_1}\vec{P_2}\, a\vec{q_1},\vec{q_2}\, b\vec{q_1}'(\vec{q_2}-\vec{q_1}+\vec{q_1}'))\, G_o(a\vec{q_1},\vec{q_2}\, b\vec{q_1}'(\vec{q_2}-\vec{q_1}+\vec{q_1}))
$$

$$
(46) \qquad \times T_{23}(q_2 P_3(q_2-q_1'+q_1)P_3\, q_2'P_3'(q_1+q_2'-q_1')P_3')\, G_o(a\vec{q_1}\vec{q_2}\, b\vec{q_1}'(\vec{q_2}-\vec{q_1}+\vec{q_1}))
$$

$$
\times T_{12}(a\vec{q_1},\vec{q_2}'\, b\vec{q_1}'(\vec{q_2}-\vec{q_1}'+\vec{q_1})\, a\vec{P_1}'\vec{P_2}'\, b\vec{P_1}'\vec{P_2}')\, \tilde{\rho}_{P_2'}\, \tilde{\rho}_{P_3'}
$$

which becomes

$$
V_{/\hbar^3}V^2 \sum_{\substack{\vec{P_1}\vec{P_1}' \\ \vec{P_2}\vec{P_3}\vec{P_2}'\vec{P_3}' \\ \vec{q_1}\vec{q_2}\vec{q_1}'\vec{K}}} T_{12}(a\vec{P_1}\vec{P_2}\, b\vec{P_1}\vec{P_2}\, a\vec{q_1},\vec{q_2}\, b\vec{q_1}-\hbar\vec{K}\,\vec{q_2}+\hbar\vec{K})(\epsilon+i(\omega-\omega_{ba})+i\vec{K}\cdot\vec{P_{12}}_{/m})^{-1}
$$

$$
(47) \qquad \times T_{23}(\vec{q_2}\vec{P_3}\,\vec{q_2}+\hbar\vec{K}\,\vec{q_3}\,\vec{q_2}'\vec{P_3}'\,\vec{q_2}'+\hbar\vec{K}\,\vec{P_3}')(\epsilon+i(\omega-\omega_{ba})+i\vec{K}\cdot\vec{P_{12}}_{/m})^{-1}
$$

$$
\times T_{12}(aq_1,q_2'\, bq_1-\hbar K\, q_2+\hbar K\, a\vec{P_1}'\vec{P_2}'\, b\vec{P_1}'\vec{P_2}')\, \tilde{\rho}_{P_2'}\, \tilde{\rho}_{P_3'}
$$

with $\hbar\vec{K}=\vec{q_1}-\vec{q_1}'$, $\vec{P_{12}}_{/m}=\vec{q_1}_{/m_1}-\vec{q_2}_{/m_2}$, $\vec{P_{12}}'_{/m}=\vec{q_1}_{/m_1}-\vec{q_2}'_{/m_2}$

And for $T_{12}G_oT_{23}G_oT_{13}$ we have[39]

$$
V_{/\hbar^3}V^2 \sum_{\substack{\vec{P_1}\vec{P_1}' \\ \vec{P_2}\vec{P_3}\vec{P_3}'\vec{q_3} \\ \vec{q_1}\vec{q_2}\vec{q_1}'\vec{q_2}' \\ \vec{q_2}\vec{P_2}'}} T_{12}(a\vec{P_1}\vec{P_2}\, b\vec{P_1}\vec{P_2}\, a\vec{q_1}\vec{q_2}\, b\vec{q_1}'\vec{q_2}')\, G_o(a\vec{q_1},\vec{q_2}\, b\vec{q_1}'\vec{q_2}')
$$

$$
(48) \qquad \times T_{23}(\vec{q_2}\vec{P_3}\,\vec{q_2}'\vec{P_3}\,\vec{P_2}'\vec{q_3}\,\vec{P_2}'\vec{q_3}')\, G_o(a\vec{q_1}\vec{q_3}\, b\vec{q_1}'\vec{q_3}')
$$

$$
\times T_{13}(aq_1 q_3\, bq_1'q_3'\, a\vec{P_1}'\vec{P_3}'\, b\vec{P_1}'\vec{P_3}')\, \tilde{\rho}_{P_2'}\, \tilde{\rho}_{P_3'}
$$

which with $\vec{q_1}-\vec{q_1}'=\vec{K}$ so that $\vec{q_2}'=\vec{q_2}+\vec{K}$ and $\vec{q_3}'=\vec{q_3}+K$ becomes

$$
V_{/\hbar^3}V^2 \sum_{\substack{\vec{P_1}\vec{P_1}' \\ \vec{P_2}\vec{P_3}\vec{q_1}\vec{q_2} \\ \vec{K}\vec{q_3}\vec{P_1}'\vec{P_3}'}} T_{12}(a\vec{P_1}\vec{P_2}\, b\vec{P_1}\vec{P_2}\, a\vec{q_1}\vec{q_2}\, b\vec{q_1}-\hbar\vec{K}\,\vec{q_2}+\hbar\vec{K})(\epsilon+i(\omega-\omega_{ba})+i\vec{K}\cdot\vec{q_{12}}_{/m})^{-1}
$$

$$
(49) \qquad \times T_{23}(q_2 P_3\, q_2+\hbar K\, P_3\, P_2'q_3\, P_2'q_3+\hbar K)(\epsilon+i(\omega-\omega_{ba})+i\vec{K}\cdot\vec{q_{13}}_{/m})^{-1}
$$

$$
\times T_{13}(a\vec{q_1}\vec{q_3}\, b\vec{q_1}-\hbar\vec{K}\,\vec{q_3}+\hbar\vec{K}\,a\vec{P_1}'\vec{P_3}'\,b\vec{P_1}'\vec{P_3}')\, \tilde{\rho}_{P_2'}\, \tilde{\rho}_{P_3'}
$$

In Section II C, the results of Equations (44) and (45) will be obtained again from expressions in Reference 38, and will serve as a basis for the estimation of three body recollision corrections to the linewidth. With the approximations made there, the contibutions of Equations (47) and (49) can then be estimated by analogy, without additional detailed calculations.

105

B. The Low Density Limit

The Lorentzian function,

$$(50) \quad \alpha(\omega) \propto \frac{\gamma/}{((\omega-\omega_{ba})^2 + \gamma^2)}$$

is often used to represent lineshapes at low densities. The linewidth γ is a number often written as $\rho\bar{v}\sigma^{pb}/2\pi c$ in frequency units, where ρ is the density, $\bar{v}$ an average velocity, and σ^{pb} a pressure broadening cross section.[31]

In this section, we want to detail the approximations necessary to obtain the simple Lorentzian from the form for the absorption coefficient derived in Section A or taken from Reference 37, Equation (3.28), to lowest order in the density, so considering only binary collisions.

This is

$$(51) \quad \mathrm{Tr}_1 \left(\mu_1 (\epsilon + i\omega + iL_{int}(1) + \rho\mathcal{L}(1))^{-1} \mu_1 \, \tilde{\rho}(1) \right)$$

Writing out in matrix and tetradic elements, the trace is defined as

$$(52) \quad \sum_{\substack{aba'b'c \\ P_1'P_1}} \mu_{ba} (\epsilon + i\omega + iL_{int}(1) + \rho\mathcal{L}(1))^{-1} \langle a_R b_R a'_{P_1'} b'_{P_1'} \rangle \tilde{\rho}^{(1)} \langle a'_{P_1'} c_{P_1} \rangle \mu_{cb}$$

The distribution function $\tilde{\rho}^{(1)}$ should also be taken to lowest order in the density, and since we know that matrix elements of

$$\tilde{\rho}^{(0)}(1) = \frac{e^{-\beta(H_0 + H_{int}(1))}}{\sum \bar{e}^{\beta(H_0^a H_{int}(1))}}$$

will just lead to factors of $e^{-\beta P_1^2/2m}$ and $e^{-\beta E_{a'}}$, $\tilde{\rho}(1)$ is diagonal in internal state indices.

We now write the operator identity

$$(53) \quad \frac{1}{(\rho\omega + \rho_{int} + \rho\mathcal{L})} = \frac{1}{(\rho\omega + \rho_{int})} \left(1 + \rho\mathcal{L} \sum_{0}^{\infty} \left(\frac{1}{(\rho\omega + \rho_{int})} \rho\mathcal{L} \right)^n \frac{1}{(\rho\omega + \rho_{int})} \right)$$

and first take internal state tetradic elements,

$$(54) \quad (i\omega + iL_{int} + \rho\mathcal{L})^{-1}_{abcd} = \left(\frac{1}{i(\omega - \omega_{ba})} \Delta_{ab}\Delta_{cd} + \frac{1}{i(\omega-\omega_{ba})} \rho\mathcal{L}_{abcd} \frac{1}{i(\omega-\omega_{dc})} \right.$$
$$\left. + \sum_{mn} \frac{1}{i(\omega - \omega_{ba})} \rho\mathcal{L}_{abmn} \frac{1}{i(\omega-\omega_{mn})} \rho\mathcal{L}_{mncd} \frac{1}{i(\omega-\omega_{dc})} + \cdots \right)$$

106

Now if we are looking at isolated lines, which is true except at the highest desities for HCl and perhaps HF, the frequency denominators will eliminate all ω_{mn} except the ω_{ba} near the ω we observe with, because $(\omega-\omega_{mn}) \gg \mathcal{L}_{abmn}$ for all mn but ab. (For a discussion of the case of overlapping lines, see Reference 54 or 55.) So we have $\mathcal{L}_{abab}$, which can now appear in the denominator.

We have more difficulty in treating the momentum tetradic elements in such a fashion that Equation (52) may be replaced by an expression with a momentum dependent tetradic element of $\mathcal{L}$ in the denominator. If we look at

$$\sum_{\vec{P}_1\vec{P}_1'} (\tilde{I}(\omega-\omega_{ba}+\rho\mathcal{L}(1))^{-1}(\vec{P}_1\vec{P}_1\vec{P}_1'\vec{P}_1')\phi(\vec{P}_1') = \sum_{\vec{P}_1\vec{P}_1'} \left(\frac{1}{\tilde{I}(\omega-\omega_{ba})} \Delta\vec{P}_1\vec{P}_1' \Delta\vec{P}_1\vec{P}_1' \right.$$

(55)

$$\left. + \frac{1}{\tilde{I}(\omega-\omega_{ba})} \rho\mathcal{L}(\vec{P}_1\vec{P}_1\vec{P}_1'\vec{P}_1)\frac{1}{\tilde{I}(\omega-\omega_{ba})} + \sum_{\vec{P}_1''} \frac{1}{\tilde{I}(\omega-\omega_{ba})} \rho\mathcal{L}(\vec{P}_1\vec{P}_1\vec{P}_1''\vec{P}_1'')\frac{1}{\tilde{I}(\omega-\omega_{ba})} \rho\mathcal{L}(\vec{P}_1'\vec{P}_1'\vec{P}_1'\vec{P}_1')\frac{1}{\tilde{I}(\omega-\omega_{ba})} + \dots \right)\phi(\vec{P}_1')$$

one approximation we can make is to assume a constant change of momentum (on the average) so that $\vec{p}_1 - \vec{p}_1'' = \vec{p}_1'' - \vec{p}_1'$ and so on, and we may have $\rho\mathcal{L}(\vec{p}_1\vec{p}_1\vec{p}_1'\vec{p}_1')$ in the denominator.

A more drastic approximation is to assume that initial and final momenta are the same, so that $\mathcal{L}(\vec{p}_1\vec{p}_1\vec{p}_1\vec{p}_1)$ may immediately appear in the denominator. This straight-line path approximation is actually useful in pressure broadening theory, because collisions which change, for instance, the orientation or speed of rotation of a diatomic molecule can involve long range forces which have little effect on the momenta.[29, 61-64] The approximation that the momentum change of particle 1 in a collision is negligible is certainly good in the limit of

107

a Brownian particle, of much greater mass than the perturbers.[64]

If as an extension of these series expansions in powers of $\rho\mathcal{L}$ one assumes that $\rho\mathcal{L}$, though an operator describing momentum changes during collisions, operates on its momentum eigenfunctions to give a number, not a function of momentum, one obtains the analog of the Chapman-Enskog approximation.[57-60]

There is yet another way of approaching this problem, variations of which have been used in treating the problem of combined Doppler and collision broadening.[65-67] (We will discuss Doppler broadening at the end of this section.) As discussed in Appendix F and Section II C, the binary collision operator (and therefore $\mathcal{L} = \langle V T_{12} \rangle_2$) is composed of two parts, a noninteracting part $\mathcal{L}^{non}$ which is diagonal in momentum and an interacting part $\mathcal{L}^{int}$ which is not. So instead of the expansion in Equation (55) we may have

$$
\begin{aligned}
\sum_{\vec{p_1}\vec{p_1}'} &\Big(\frac{1}{(i(\omega-\omega_{ba})+\rho\mathcal{L}^{non}_{(p_1)})} \Delta_{\vec{p_1}\vec{p_1}'}\Delta_{\vec{p_1}\vec{p_1}'}\,\phi_{(p_1')} \\
(56) \qquad &+ \frac{1}{(i(\omega-\omega_{ba})+\rho\mathcal{L}^{non}_{(p_1)})}\,\rho\mathcal{L}^{int}_{(\vec{p_1}\vec{p_1}'\vec{p_1}')}\,\frac{1}{(i(\omega-\omega_{ba})+\rho\mathcal{L}^{non}_{(p_1')})}\phi_{(p_1')} \\
&+ \sum_{\vec{p_1}''} \frac{1}{(i(\omega-\omega_{ba})+\rho\mathcal{L}^{non}_{(p_1)})}\,\rho\mathcal{L}^{int}_{(\vec{p_1}\vec{p_1}\vec{p_1}''\vec{p_1}'')}\,\frac{1}{(i(\omega-\omega_{ba})+\rho\mathcal{L}^{non}_{(p_1'')})}\,\rho\mathcal{L}^{int}_{(\vec{p_1}''\vec{p_1}''\vec{p_1}'\vec{p_1}')}\,\frac{1}{(i(\omega-\omega_{ba})+\rho\mathcal{L}^{non}_{(p_1')})}\phi_{(p_1')} + \ldots \Big)
\end{aligned}
$$

There are two complementary limits which may be taken in order to sum this expansion. In one, we imagine that the value of $\mathcal{L}^{int}$ depends only on the last indices, the momentum after collision, and that each contains a Maxwellian distribution function for this last momentum, so that each term factors into powers of

$$
\int \frac{\phi_{(p)}dp\;\rho\mathcal{L}^{int}_{(p)}}{(i(\omega-\omega_{ba})+\rho\mathcal{L}^{non}_{(p)})}
$$

and the spectrum is proportional to

$$\int \phi(p)\,dp\ \left(\wp(\omega - \omega_{ba}) + \rho \mathcal{L}_{(p)}^{non}\right)^{-1}$$

(57)
$$\left(1 - \int \frac{\overline{\phi(p)\,dp}\ \rho \mathcal{L}_{(p)}^{int}}{\left(\wp(\omega - \omega_{ba}) + \rho \mathcal{L}_{(p)}^{non}\right)}\right)$$

This is the hard collision approximation, so called because each collision is violent enough to destroy all memory of the previous momenta. It is discussed in References 68 through 71.

The alternate soft collision limit of small momentum changes with a Gaussian distribution centered around zero is based on the same assumptions that allow on to obtain the Fokker-Planck equation form the Boltzmann equation.[72-78]

Moving on to other approximations, the full expression for T_{12} and thus $\mathcal{L}(1)$, given in References 38 and 79, depends on ω. The assumption that the frequency difference $\omega - \omega_{ba}$ in the range of interest, of the order of $\rho \mathcal{L}_{ab}$, is negligible compared with the energies found in the definition of the t matrices, or alternatively (in fourier transform space) that the time between collisions which change the energy by no more than a specified amount is much greater than the time of a collision, is the basis of the impact approximation.[31,80-87]

Next, $\mathcal{L}(1)$ still depends on p_1, and so in general an integration over the Maxwellian and this momentum dependent denominator has a effect on the lineshape, but it is small.[88-89] Therefore the usual approximation made[31] is to say that the integration over the Maxwell distribution has the effect of

109

replacing the momenta in $\mathcal{L}(p_i)$ by their thermal averages.

Then with the integration over the momentum part of $\tilde{\rho}(1)$, the internal part, $e^{-\beta E_a}$, is just the statistical weight for the initial state, and $\rho\mathcal{L}$ is just a number which we can call γ , so indeed we have obtained the Lorentzian lineshape, Equation (50), by taking the real part of the denominator.

There is, however, yet one more approximation which we must discuss, involving the contribution of Doppler broadening. In Equations (51) and (52) we had actually made the dipole approximation[91], which says that since the wavelength of light λ (or the reciprocal of the wave vector k, k = $^{4\pi}/\lambda$) is much larger than a molecular size, we can ignore the fact that Equation (51) should actually be

$$(58)\quad \text{Tr}_1\, \mu_1\, e^{i\vec{K}\cdot\vec{r}_1}(\epsilon + i\omega + iL_{int}(1) + iL_\delta(1) + \rho\mathcal{L}(1))^{-1}\,\tilde{\rho}(1)\, e^{-i\vec{K}\cdot\vec{r}_1}\,\mu_1$$

so that Equation (52) becomes

$$(59)\quad \sum_{\substack{a b a' b' c \\ \vec{q}_1 \vec{q}_1' \vec{q}_1''}} \mu_{ba}\langle\vec{p}_1|e^{i\vec{K}\cdot\vec{r}_1}|\vec{q}_1\rangle(\epsilon + i\omega + iL_{int}(1) + iL_\delta(1) + \rho\mathcal{L}(1))^{-1}(\circ\, \vec{q}_1\, b\, \vec{p}_1, a'\vec{p}_1'\, b'\vec{q}_1'')$$
$$\times\tilde{\rho}^{(1)}(a'\vec{p}_1'\, c\, \vec{q}_1'')\langle\vec{q}_1''|e^{i\vec{K}\cdot\vec{r}_1}|\vec{q}_1'\rangle\mu_{cb'}$$

or, quickly making some of the same approximations,

$$(60)\quad \sum_{\substack{a b \\ \vec{p}_1, \vec{p}_1'}} \mu_{ba}(\epsilon + i\omega + iL_{int}(1) + iL_\delta(1) + \rho\mathcal{L}(1))^{-1}(\circ\vec{p}_1 + \hbar\vec{K}\, b\vec{p}_1, \circ\vec{p}_1'\, b\vec{p}_1' + \hbar\vec{K})\tilde{\rho}^{(1)}_{a\vec{p}_1}, \mu_{ab}$$

In the expansion analogous to Equation (65), the tetradic element of G_o is

$$(\epsilon + i\omega + iL_{int}(1) + iL_\delta(1))^{-1}(a\vec{p}_1, -\hbar\vec{K}\, b\vec{p}_1, a\vec{p}_1'\, b\vec{p}_1' + \hbar\vec{K}) = \langle\epsilon + i(\omega - \omega_{ba} - \frac{i\vec{K}\cdot\vec{p}_1}{m})^{-1}$$

where $\vec{k}$ is still the wave vector of light. When $\frac{\vec{K}\cdot\vec{p}_1}{m}$ is large compared to $\rho\mathcal{L}_{ab}$, we need only retain the first term (G_o) in the expansion. Then integration of the denominator and the Maxwellian distribution of momenta produces a Gaussian frequency distribution, the Doppler lineshape.

110

We will perform this integration in two different ways, since each method has some instructive features. First, we proceed straightforwardly from Equation (60) and its following definition. If we take the $\vec{k}$ vector to be in the p_z direction, and ignore the normalization of the Maxwell distribution and all other prefactors, we have

$$\text{Re} \quad i \int_{-\infty}^{\infty} e^{-\beta p_{1z}^2/2m} \left(i\epsilon - (\omega - \omega_{ba}) + K p_{1z}/m \right)^{-1} dp_{1z}$$

which is

$$\text{Re} \quad -\pi \, \text{Res} \left(i\epsilon - (\omega - \omega_{ba}) + K p_{1z}/m \right)^{-1} e^{-\beta p_{1z}^2/2m}$$

evaluated at the pole $p_{1z} = \frac{m}{K}((\omega - \omega_{bo}) - i\epsilon)$. (The pole only contributes πi because as ϵ goes to zero, the pole is on the real axis and the integration path is only indented around an angle π.) So letting ϵ go to zero, taking the real part, and again ignoring constants we have the Gaussian frequency distribution of the Doppler lineshape,

$$e^{-\beta/2m \left(\frac{(\omega - \omega_{ba})m}{K} \right)^2} = e^{-\beta m/2 \left(\frac{(\omega - \omega_{ba})}{K} \right)^2}$$

In an alternative method we rewrite the denominator as an integration over a variable t which has the units of time, which means effectively returning to the time representation of Equation (21).

$$\int_0^{\infty} e^{-\left(\epsilon + i(\omega - \omega_{ba}) - iK p_{1z}/m \right)^{-1}} dt$$

We then integrate over momentum and the Maxwell distribution, now writing the normalization simply as N.

$$N \int_{-\infty}^{\infty} e^{-\beta p_{1z}^2/2m} e^{-iK p_{1z} t/m} dp_{1z}$$

$$= N \, e^{-K^2 t^2/2m\beta} \left(\int_{-\infty}^{\infty} e^{-\beta/2m(p_{1z} + iKt/\beta)^2} d(p_{1z} + iKt/\beta) \right) = e^{-K^2 t^2/2m\beta}$$

Having obtained this Gaussian in time, the Doppler time
correlation function, we can let ϵ go to zero and do the time
integration, again by completing the square in the exponent,
so that

$$\int_0^\infty e^{i(\omega - \omega_{ba})\tau} \, e^{-K^2 \tau^2/2m\beta} \, d\tau$$

$$= e^{-K^2/2m\beta (m\beta/K (\omega - \omega_{ba}))^2} \int_0^\infty e^{-K^2/2m\beta (\tau + im\beta/K^2 (\omega - \omega_{ba}')^2} \, d\tau$$

$$\propto e^{-m\beta/2K^2 (\omega - \omega_{ba})^2}$$

The one-dimensional root-mean-square velocity, which we
denote by $\bar{v}_z$, is $\langle 1/\beta m \rangle^{1/2}$. The half width at half maximum of
a Gaussian e^{-x^2/a^2} is reached when x/a is $\sqrt{\ln 2}$. So the Doppler
halfwidth is given by the simple formula $\sqrt{2\ln 2} \, K \bar{v}_z$.

In the case when neither pressure broadening nor Doppler
broadening is negliglible, if we use one of the approximations
discussed above to put the linewidth operator into the
denominator, we must still integrate over a speed dependent
width along with a Doppler shift. Again, the effect is small.[90]
So if we ignore it we obtain a function intermediate between
a Gaussian and a Lorentzian and traditionally used to describe
combined Doppler and pressure broadening, the Voigt profile
(61)

$$\alpha(\omega) \propto \int (i(\omega - \omega_{ba}) - i\vec{K} \cdot \vec{P}_1/m + \rho \mathcal{L}_{ab})^{-1} \phi(P_1) \, d\vec{P}_1$$

And, of course, if $\vec{K} \cdot \vec{P}_1/m$ is much smaller than $\rho \mathcal{L}_{ab}$, we may
ignore it and again obtain a Lorentzian. This approximation
is obviously good at high densities, and will be used in all
that follows.

112

To summarize, we list approximations we found to be needed to arrive at a Lorentzian lineshape.

1. To obtain a linewidth which is linearly proportional to the density we assumed only binary collisions occur. This was done by resumming the binary collision expansion only in lowest order in the density. We also ignored correlations in the density matrices for different particles.

2. We assumed isolated lines, thus ignoring interference terms which can lead to a non-Lorentzian shape.

3. We had to adopt some approximation in regard to the momentum change in order to obtain a momentum dependent collision operator in the denominator of the linewidth expression. In pressure broadening theory this is most often the straight-line path assumption.

4. We made the impact approximation, which can be expressed as ignoring the ω dependence of the t matrices.

5. After Approximation 3, we then assumed a momentum-independent width.

6. We ignored the Doppler shift.

In Appendix F and Section II C we justify the use of the simple Anderson[31] formula for the linewidth in terms of a cross section, $\frac{\rho \bar{v} \sigma \rho_b}{2\pi c}$. For more accurate, fully quantum-mechanical calculations one may use the formulas of Baranger[80-82] in terms of scattering amplitudes. Semiclassical approximations may be used on the quantum formulas we began with, for instance to obtain the classical Fourier integral[92,93] or Anderson theory[94].

113

C. The Triple Collision Contribution to the Linewidth

We begin our discussion of of the triple collision contributions with the $T_{12}G_oT_{13}G_oT_{12}$ term, whose tetradic element representation was given in Section II A. However, we will start here with a version of Equation (2.24) of Reference 38,

$$
\begin{aligned}
(62) \quad &\sum_{\substack{\vec{k}\vec{P_2}\vec{P_2'}\\ \vec{P_1}\vec{P_3}\vec{P_3'}\\ \vec{q_1}\vec{q_2}\\ \vec{q_1''}\vec{P_1'}}} \tfrac{1}{\hbar^3}V^2\, T_{12}(a\vec{P_1}\vec{P_2}\,b\vec{P_1}\vec{P_2}\,a\vec{q_1}\vec{q_2}\,b\vec{q_1}{-}\hbar\vec{k}\vec{q_2}{+}\hbar\vec{k})(\epsilon+i(\omega-\omega_{ba})+i\vec{k}\cdot\vec{v}_{12})^{-1}\\
&\qquad \times T_{13}(a\vec{q_1}\vec{P_3}\,b\vec{q_1}{-}\hbar\vec{k}\,\vec{P_3}\,a\vec{q_1''}\vec{P_3'}\,b\vec{q_1''}{-}\hbar\vec{k}\,\vec{P_3'})(\epsilon+i(\omega-\omega_{ba})+i\vec{k}\cdot\vec{v}_{12}')^{-1}\\
&\qquad \times T_{12}(a\vec{q_1''}\vec{q_2}\,b\vec{q_1''}{-}\hbar\vec{k}\,\vec{q_2}{+}\hbar\vec{k}\,a\vec{P_1'}\vec{P_2'}\,b\vec{P_1}\vec{P_2})\,\tilde{\rho}_{P_2'}\tilde{\rho}_{P_3'}
\end{aligned}
$$

This expression differs from Equation (2.24) of Reference 38 in that all momenta involved in the trace have been summed over, and the sums over intermediate internal states have been omitted since (as discussed in Section II B) vibration-rotation lines are spaced widely enough that only one G_o denominator (here the ab element) contributes for a given frequency. (The wave vector $\vec{k}$ is $(\vec{q_1}-\vec{q_1'})/\hbar$ and was generated by momentum conservation conditions in the T operators, as discussed in Section II A and Reference 38. Since terms of order $\vec{k}^2$ are unimportant in the G_o denominators, we can ignore the $\vec{k}$ dependence of $\vec{v}_{12}$ and $\vec{v}_{12}'$ and find from Equations (2.28) and (2.29) of Reference 38 that $\vec{v}_{12}$ is $\vec{q_1}/m_1 - \vec{q_2}/m_2$ and v_{12}' is $\vec{q_1''}/m_1 - \vec{q_2}/m_2$.

With approximations discussed in Appendix F, as an example the first T_{12} tetradic when expressed in terms of t matrix elements becomes (writing the volume normalization explicitly)

114

$$\rho \left(t_{\frac{1}{v^2}a\vec{p}_1\vec{p}_2\,a\vec{q}_1\vec{q}_2\Delta\,\vec{p}_1\vec{q}_1,-\hbar\vec{k}\,\Delta\vec{p}_2\vec{q}_2+\hbar\vec{k}} - t^*_{\frac{1}{v^2}b\vec{p}_1\vec{p}_2\,b\vec{q}_1,-\hbar\vec{k}\,\vec{q}_2+\hbar\vec{k}\,\Delta\vec{p}_1\vec{q}_1\,\Delta\vec{p}_2\vec{q}_2}$$

$$(63) \qquad + 2\pi i\,\delta(E(a\vec{p}_1\vec{p}_2) - E(b\vec{q}_1\vec{q}_2))\,t_{a\vec{p}_1\vec{p}_2\,a\vec{q}_1\vec{q}_2}\,t^*_{b\vec{p}_1\vec{p}_2\,b\vec{q}_1,-\hbar\vec{k}\,\vec{q}_2+\hbar\vec{k}} \;)$$

The first two and last terms are referred to as noninteracting,
or forward scattering, and interacting terms respectively.

From Equation 63 it can be seen that both T_{12} terms
contain a matrix element of the form $t_{\vec{p}_{12}\,\vec{p}_{12}+\hbar\vec{k}}$, while T_{13}
will give no low order $\vec{k}$ dependence. In the classical path
version of this $\vec{k}$ vector formalism,[95] it is from these two
T_{12} operators that one obtains a factor $e^{i\vec{k}\cdot\vec{\rho}}$, where $\vec{\rho}$ is a
function of the parameters of the first and second 1-2
collisions. This factor seems to be necessary to show that
the part of the $T_{12}G_oT_{13}G_oT_{12}$ term which contains the
noninteracting part of the T_{13} operator is zero. Of course
it is easy to see physically why that part should give no
contribution, since two successive collisions between two
particles cannot occur without some change in the intermediate
path of at least one particle.[95-97]

(The fact that in the first order term, $\langle\gamma T_{12}\rangle_{\frac{1}{2}}$, the
contribution from the noninteracting part of T_{12} is larger
and of opposite sign than that from the interacting part, while
in one of the three T operators in the triple collision
expression the noninteracting part gives zero will mean that
the contribution from these triple collisions will be negative
with respect to the first order linewidth. We will give more
discussion on this point when we transform into cross sections.)

115

In the quantum mechanical formulation t matrix elements from the two T_{12} tetradics contain a similar factor $e^{i\vec{K}\cdot\vec{r}_{12}}$ along with some function of the (finite range) intermolecular potential $V(\vec{r}_{12})$. This will also make the contribution to the $\vec{k}$ integral from large values of $\vec{k}$ finite, effectively cutting off the region of integration at some upper limit k_o. Estimates of the size of k_o using step and square well potentials and the first Born approximation are made in Appendix G.

So with these comments we may ignore the $\vec{k}$ dependence of the T operators, but we must retain $\vec{k}$ in the G_o denominators. We can write (relabeling momenta)

$$
(64) \quad \frac{V}{\hbar^3}\frac{V}{\hbar^2} \sum_{\substack{\vec{k},\vec{R},\vec{R}_2 \\ \vec{R}',\vec{R}_2',\vec{R}_3 \\ \vec{R}_1'',\vec{q}_1,\vec{q}_2}} T_{12}(a\vec{R}\vec{P}_2\, b\vec{R}\vec{P}_2\, a\vec{P}_1'\vec{P}_2'\, b\vec{R}'\vec{P}_2')(\epsilon + i(\omega-\omega_{bb}) + i\vec{K}\cdot(\frac{\vec{P}}{m_1}-\frac{\vec{P}_2'}{m_2}))^{-1}
$$
$$
\times T_{13}(a\vec{P}_1'\vec{P}_3\, b\vec{P}_1'\vec{P}_3\, a\vec{P}_1''\vec{P}_3'\, b\vec{P}_1''\vec{P}_3')(\epsilon + i(\omega-\omega_{bb} + i\vec{K}\cdot(\frac{\vec{P}_1''}{m_1}-\frac{\vec{P}_2'}{m_2}))^{-1}
$$
$$
\times T_{12}(a\vec{P}_1''\vec{P}_2'\, b\vec{R}''\vec{P}_2'\, a\vec{q}_1\vec{q}_2\, b\vec{q}_1\vec{q}_2)\,\tilde{\rho}_{q_2}\,\tilde{\rho}_{P_3'}
$$

where $\frac{\vec{P}_1'}{m}$ and $\frac{\vec{P}_1''}{m} = \frac{\vec{P}_1''}{m_1} - \frac{\vec{P}_2'}{m_2}$ are relative velocities before and after the 1-3 collision, m being the reduced mass. We keep in mind that the sum over $\vec{k}$ now has an upper limit.

Next we go from the matrix elements of t operators to elastic and total scattering cross sections. By Equation (19.37) of Reference 98 the scattering amplitude f is related to t by

$$(65) \quad t = \frac{-2\pi\hbar^2}{m} f$$

so that

$$(66) \quad \frac{\partial\sigma^{el}}{\partial\Omega} = |f|^2 = \frac{m^2}{(2\pi)^2\hbar^4} t\, t^* \simeq \frac{2\pi m^2}{\hbar} \frac{t_{aa}\, t_{bb}^*}{(2\pi\hbar)^3}$$

in three dimensions, while in two dimensions,

$$(67) \quad \frac{2\pi m}{\hbar}\frac{t\,t^*}{(2\pi\hbar)^2} = v\,|f(x)|^2 = v\,\frac{\partial\sigma}{\partial x}$$

where 6 has units of length. And by the optical theorem,

for instance Equation (19.74) of Reference 98,

(68) $v6^{tot} = -2t''/\hbar \simeq i(t_{aa} - t_{bb}^{*})/\hbar$

where in Equations (66) and (68) the approximations follow

since the intermolecular potential for the initial and final

states involved in infrared transitions are not very different.

We can transform momenta to center of mass and relative

variables, for instance by

$$\vec{P}_2 \to \vec{P}_{12} \quad \vec{P}_3 \to \vec{P}_{13}' = \vec{P}_1'/m_1 - \vec{P}_3/m_3 \quad \vec{P}_1' \to \vec{P}_{12}' \quad \vec{P}_2' \to \vec{P}_{12}'$$

$$\vec{P}_1'' \to \vec{P}_{13}'' \quad \vec{P}_3' \to \vec{P}_{13}'' \quad \vec{q}_1 \to \vec{q}_{12} \quad \vec{q}_2 \to \vec{Q}_{12}$$

With $\vec{k}$, and $\vec{p}_1$ whose integration over $\tilde{\rho}_1$ remains outside the

lineshape expression, this accounts for all 10 momenta summed

over in Equation (64). Evidently the 1-2 relative velocity

after the 1-3 collision, $\vec{v}_{12}'' = \frac{\vec{P}_1''}{m_1} - \frac{\vec{P}_2'}{m_2}$, is not an independent

variable, but a function of $\vec{p}_{12}'$, $\vec{p}_{13}'$, and $\vec{p}_{13}''$. Yet we will

want to integrate over $\hat{v}_{12}''$ in the second denominator, and so

we introduce a Jacobian $J = \frac{\partial \Omega_{13}''}{\partial \Omega_{12}''}$. In three dimensions Ω_{13}''

represents the two angles Θ_{13}'' and ϕ_{13}'', while in two it is Θ_{13}''.

Integration over this Ω_{13}'' would ordinarily change $\frac{\partial 6^{el}}{\partial \Omega}$ into

6^{el} , so to avoid complication we must assume that the

scattering amplitude is independent of angle, and simply $\frac{6^{el}}{4\pi}$

in three dimensions or $\frac{6^{el}}{2\pi}$ in two dimensions.

By Equation (63) we write schematically

$$\frac{T}{\hbar} \to \left(\frac{-2t''}{\hbar} \frac{\Delta\Delta}{v^2} - 2\pi\delta(E-E') \frac{t t^*}{v^4 \hbar} \right) \to \left(\frac{v6^{tot}}{v^2} \langle P|P'\rangle \Delta\Delta - \frac{(2\pi\hbar)^3}{m^2} \frac{6^{el}}{4\pi} \frac{\delta(E-E')}{v^4} \langle P_{12}|P_{12}'\rangle \langle P_{12}|P_{12}'\rangle \right)$$

where in the center of mass matrix elements we are still using

the normalization $\langle P_{12}|P_{12}\rangle = V$. So again schematically, after

117

changing to an integration over momentum the interacting parts

of both T_{12} operators will become

$$\int d\vec{p}\,' \ (2\pi\hbar)^3 \ \frac{\sigma^{el}}{m^2} \ _{4\pi} \ \delta(E-E')$$

this is (69)

(69)

$$\to \int v'\, d(\tfrac{1}{2}mv'^2)\, \delta(E-E')\, \sigma^{el}\, (2\pi\hbar)^3 = (2\pi\hbar)^3\, v\, \sigma^{el}$$

Now we go to the continuous momentum limit, using

$$\sum_p \to \left(\frac{V}{(2\pi\hbar)^d}\right)\int d\vec{p} \quad \text{and} \quad \tilde{\rho} \to \left(\frac{(2\pi\hbar)^d}{V}\right)\phi$$

in d dimensions, where ϕ is the Maxwellian momentum

distribution function. So we get factors of $\left(\frac{V}{(2\pi\hbar)^3}\right)^q$ in three

dimensions from the momentum integration, since the sum over

p_1 remains outside, and $\left(\frac{(2\pi\hbar)^3}{V}\right)^2$ from $\tilde{\rho}_2\tilde{\rho}_3$ going to $\phi_2\phi_3$. Now,

for the interacting parts of the T operators we get factors of

v^2 and $\left(\frac{(2\pi\hbar)^3}{V}\right)$ from the two center of mass Δ functions. That is,

$$\left(\frac{V}{(2\pi\hbar)^3}\right)\int dP'_{12} \ \frac{t_{P_{12}P'_{12}}}{V^2}\frac{t^*_{P_{12}P'_{12}}}{V^2} \to \left(\frac{V}{(2\pi\hbar)^3}\right)\int dP'_{12} \ \frac{t_{P_{12}P'_{12}}}{V}\frac{t^*_{P_{12}P'_{12}}}{V}\frac{\langle P_{12}|P'_{12}\rangle}{V}\frac{\langle P_{12}|P'_{12}\rangle}{V}$$

$$\to \frac{t_{P_{12}P'_{12}}\, t^*_{P_{12}P'_{12}}}{V^2}$$

because $\frac{V}{(2\pi\hbar)^3}\int dP'_{12}\, \frac{(2\pi\hbar)^3}{V}\, \delta(P'_{12}-P_{12})\, \frac{\langle P_{12}|P'_{12}\rangle}{V} = 1$

since $\langle P_{12}|P_{12}\rangle = \int \frac{d\vec{r}_{12}}{V} = 1$.

So, including $(2\pi\hbar)^3$ from Equation 69, the fact that

$$\frac{1}{V^{12}}\left(\frac{V}{(2\pi\hbar)^3}\right)^q V^6\left(\frac{(2\pi\hbar)^3}{V}\right)^3\left((2\pi\hbar)^3\right)^3\left(\frac{(2\pi\hbar)^3}{V}\right)^2 = \frac{1}{(2\pi\hbar)^3}$$

means that looking at the real collision parts of all three

T operators we have shown that all volume dependence disappears,

as it must.

For the noninteracting parts, $(t - t^*)$, the $V^2\left(\frac{(2\pi\hbar)^3}{V}\right)(2\pi\hbar)^3$

from each tt^* is instead obtained from $\left(\frac{(2\pi\hbar)^3}{V}\right)^2$ from $\Delta_{P_1P_1'}\, \Delta_{P_2P_2'}$

going to $\delta(P_1-P_1')\delta(P_2-P_2')$, a factor of $\langle P_{12}|P_{12}\rangle = V$, and the absence of

$1/V^2$ normalization for a second t matrix element. So again, we

are left only with a factor of $\frac{1}{(2\pi\hbar^3)}$, which we associate with

118

the integration over the momentum $\hbar\vec{k}$.

Therefore, collecting the results of the above discussion, Equation (64) has become, in three dimensions,

$$(70) \quad -\int \frac{d\vec{K}}{(2\pi)^3} d\vec{P}_{12}\,\phi_2\, d\vec{P}_{13}\,\phi_3\, d\hat{P}_{12}'\, d\hat{P}_{12}''\, J\, v_{12}\, \frac{\langle \sigma^{tot} - \sigma^{el}\rangle}{4\pi}\, v_{13}'\, \frac{\sigma^{el}}{4\pi}\, v_{12}''\, (\sigma^{tot} - \sigma^{el})}{(\epsilon + \hbar(\omega - \omega_{b_0}) + \hbar\vec{K}\cdot\vec{v}_{12}')(\epsilon + \hbar(\omega - \omega_{b_0}) + \hbar\vec{K}\cdot\vec{v}_{12}'')}$$

So here $T_{\vec{P}_{12}\vec{P}_{12}}$ denotes an operator which becomes

$$\hbar v_{12}\, \sigma^{pb} = \hbar v_{12}\, (\sigma^{tot} - \sigma^{el})$$

with σ^{pb} being the pressure-broadening cross section. Also, it is the fact that T_{13} has become only $-\sigma^{el}$ that has reversed the sign of the entire term in Equation (70). In the spirit of using average values of momenta, in Equation (70) we have ignored the dependence of $\vec{v}_{12}''$ on $\vec{P}_{13}''$, and have simply integrated over $\delta(E_{13}' - E_{13})$. We have also changed $\phi_{P_2'}$ and $\phi_{P_3'}$ to ϕ_{P_2} and ϕ_{P_3}.

In proceeding further, with integrations over momenta, it is instructive to look at the two dimensional case first. It is shown in Appendix H that in two dimensions the Jacobian J, $\partial\Theta_{13}''/\partial\Theta_{12}''$, is $\left(\frac{m_1}{m}\right)\vec{P}_{12}''\cdot\vec{P}_{13}''/P_{13}''^2$. So we simply consider

$$(71) \quad \int \frac{d\vec{K}}{(2\pi)^2} d\vec{P}_{12}\,\phi_2\, d\vec{P}_{13}\,\phi_3\, d\hat{P}_{12}'\, d\hat{P}_{12}''\, \left(\frac{m_1}{m}\right) \frac{\hat{P}_{12}''\cdot\hat{P}_{13}''}{P_{13}''^2} \left(-v_{12}'\, \frac{\sigma^{pb}_{12}}{2\pi}\, v_{13}'\, \frac{\sigma^{el}_{13}}{2\pi}\, v_{12}''\, \sigma^{pb}_{12}\right)}{(\epsilon + \hbar(\omega - \omega_{b_0}) + \hbar\vec{K}\cdot\vec{v}_{12}')(\epsilon + \hbar(\omega - \omega_{b_0}) + \hbar\vec{K}\cdot\vec{v}_{12}'')}$$

We have shown in Appendix H that by momentum conservation

$$\vec{P}_{13}'' = \vec{P}_{13}' - \left(\frac{m_1}{m}\right)(\vec{P}_{12}' - \vec{P}_{12}'')$$

So in terms of Θ_{13}' and Θ_{12}'', the angles of $\vec{p}_{13}'$ and $\vec{p}_{12}''$ with respect to $\vec{p}_{12}''$, $\left(\frac{m_1}{m}\right)\left(\vec{P}_{13}''\cdot\vec{P}_{12}''/P_{13}''^2\right) =$

$$(72) \quad \frac{\left(\frac{m_1}{m}\right)\left(\left(\frac{m_1}{m}\right)\left(P_{12}''^2 + P_{12}''P_{12}'\cos\Theta_{12}''\right) + P_{13}'P_{12}''\cos(\Theta_{12}'' - \Theta_{13})\right)}{\left(\frac{m_1}{m}\right)^2(P_{12}'^2 + P_{12}''^2) + P_{13}'^2 + 2\left(\frac{m_1}{m}\right)^2 P_{12}'P_{12}''\cos\Theta_{12}'' - 2\left(\frac{m_1}{m}\right)P_{13}'P_{12}'\cos\Theta_{13} + 2\left(\frac{m_1}{m}\right)P_{13}'P_{12}''\cos(\Theta_{12}'' - \Theta_{13})}$$

The angle Θ_{12}'' is the χ of Reference 41, where it is shown that integration over χ and Θ_{12}', the angle of $\vec{p}_{12}'$ with respect to $\vec{k}$, gives the result that $\Theta_{12}'' \rightarrow \pi$. (After integration over angles, we would obtain a k integral similar to that in Equation (13) of Reference 41.) If we take this $\Theta_{12}'' \rightarrow \pi$ limit in the Jacobian, we obtain

(73)
$$\frac{\left(\frac{m_1}{m}\right)^2 p_{12}'' \left(p_{12}' + p_{12}''\right) - \left(\frac{m_1}{m}\right) p_{12}'' p_{13}' \cos\Theta_{13}'}{p_{13}'^2 + \left(\frac{m_1}{m}\right)^2 \left(p_{12}'' + p_{12}'\right) - 2\left(\frac{m_1}{m}\right) p_{13}' \left(p_{12}'' + p_{12}'\right) \cos\Theta_{13}'}$$

Now the energy delta function from T_{13} said $\frac{p_1'^2}{m_1} + \frac{p_3^2}{m_3} = \frac{p_1''^2}{m_1} + \frac{p_3'^2}{m_3}$ and using $\vec{p}_1' + \vec{p}_3 = \vec{p}_1'' + \vec{p}_3'$ this means $p_{13}' = p_{13}''$. But this means that in the denominator of J,

(74) $\quad 2 p_{13}' \cos\Theta_{13}' - \left(\frac{m_1}{m}\right)\left(p_{12}' + p_{12}''\right) = 0$

This equation agrees with the discussion in Reference 95, where for the case that $m_1 = m_2 = m_3$ so that $\frac{m}{2} = m$, and taking $\hat{p}_{12}'$ to define the direction of the x coordinate, it is shown that $p_{12x}'' = p_{13}' \cos\Theta_{13}' - p_{12}'$ and $p_{12y}'' \simeq 0$. These relations follow from Equation (74) when we realize that it is for the case $\Theta_{12}'' \rightarrow \pi$, describing a long narrow triangle between collisions. It is important to note that the integration of J over momenta should give a contribution which is less than one because p_{12x}'' is the difference of two quantities which are on the average almost equal. This should be especially true in Reference 95 where for the case of viscosity the factor of p_{12}'' enters raised to the third power.

But where Reference 95 is discussing terms in a density expansion and so can average each term over $\vec{p}_1$, we wish to look

120

at the effect of thermal averaging on the linewidth while
leaving the integral over $\vec{p}_1$ outside the lineshape. So we
choose to integrate our modified J over Θ_{13}',

$$(75) \quad \int_0^{2\pi} d\Theta_{13}' \left(\frac{m_1}{m}\right) \frac{P_{13}' \cos\Theta_{13}' (P_{13}' \cos\Theta_{13}' - P_{12}')}{P_{13}'^2} = 2\pi$$

Equation (75) means that if we had despaired of integrating
J and decided to choose a number with which to replace it,
that number might as well have been 1. With this and with
the results of the integrations over Θ_{12}' and Θ_{12}'' as in
Equation (13) of Reference 41, as well as a 2π from the free
angle of $\vec{k}$, Equation (71) has become

$$(76) \quad -\int_0^{k_0} \frac{2\pi \, k \, dk}{(2\pi)^2} \int d\vec{P}_{12} \phi_2 \, d\vec{P}_{13} \phi_3 \, 2\pi \, \frac{v_{12}' G_{12}^{pb}}{2\pi} \frac{v_{13}' G_{13}^{el}}{2\pi} \frac{v_{12}'' G_{12}^{pb} (2\pi)^2}{v_{12}' v_{12}''}$$
$$\frac{}{\left(k^2 + \left(\frac{\epsilon + i(\omega - \omega_{ba}')}{\gamma_{12}'} + 1/\Lambda\right)^2\right)^{1/2} \left(k^2 + \left(\frac{\epsilon + i(\omega - \omega_{ba}')}{\gamma_{12}''}\right)^2\right)^{1/2}}$$

The k dependent integrand differs from that in Reference
41 in that one denominator contains a cutoff $1/\Lambda$, where Λ is
of the order of a mean free path, necessary because in two
dimensions the $\vec{k}$ integral is also divergent at the lower limit.
The derivation and physical interpretation of this cutoff is
discussed extensively in References 38, 41, and 44, and has been
touched on in Section II A. The k integral can be done as in
Reference (41) to obtain

$$\ln\left(\left(k^2 + \left(\frac{(\epsilon + i(\omega - \omega_{ba}))}{\gamma_{12}'} + 1/\Lambda\right)^2\right)^{1/2} * \left(k^2 + \left(\frac{(\epsilon + i(\omega - \omega_{ba}))}{\gamma_{12}''}\right)^{1/2}\right)\right)$$

Evaluating at k_0 and zero, and finally taking the limit $\epsilon \to 0$,
this becomes (after some algebra)

$$(77) \quad \ln \frac{2k_0/}{\left(2\left(\frac{\omega - \omega_{ba}}{\gamma}\right)^4 + k_1^4\right)^{1/4}}$$

Being of the order of an inverse mean free path, k_1 increases

with increasing density, so that at the sort of densities at which the triple collision term becomes important, the term $\frac{(\omega - \omega_{bo})}{\bar{v}}$ with $\bar{v}$ the average velocity, is the same size or smaller for any frequency difference of interest. So we will simply use ln (k_o/k_1) as an estimate of the logarithmic term.

We know that the cross sections do not have an important dependence on momentum.[88-90] So if we carry to new depths an approximation often used in line broadening theory, and assume that the cross sections have no velocity dependence and imagine that the Maxwellians, originally ϕ_2' and ϕ_3' have become ϕ_{12} and ϕ_{13}, or alternatively if we just replace all momenta by their thermal averages, $\bar{v}$, we obtain for Equation (76) the estimate in two dimensions,

(78) $$\bar{v} \, \sigma^{pb} \, \sigma^{el} \, \sigma^{pb} \, \ln \, k_o/k_1$$

In three dimensions, we find, again from Appendix H, that J or $\frac{\partial \Omega_{13}''}{\partial \Omega_{12}''}$ is $\left(\frac{m_1}{m}\right)^2 \frac{p_{12}''^2}{p_{13}''^2} \frac{\vec{p}_{12}'' \cdot \vec{p}_{13}''}{p_{12}'' p_{13}''}$. This is difficult to integrate accurately, so although it may mean an error of up to an order of magnitude, at the present state of caluculation we perhaps do best by replacing J by one. (In Appendix H we attempt an integration which says that J might be worth 4 rather than 1, for the case that $(m_1/m)^2 = 4$. However, on physical grounds and to agree with experiment one wants J to be less than one, so we compromise.)

With this approximation, we can use $\lim_{\epsilon \to 0} (\epsilon + ix)^{-1} = \pi \delta(x) - iP\frac{1}{x}$ and $P \int_{-1}^{1} \frac{d\upsilon}{\upsilon - \upsilon_o} = 0$ to evaluate the integrals over the angles of $\vec{p}_{12}'$ and $\vec{p}_{12}''$ in Equation (70),(angles measured with respect to $\vec{k}$),

122

so that
$$\int \frac{\sin\Theta_{12}'\,d\Theta_{12}'\,\sin\Theta_{12}''\,d\Theta_{12}''}{(\epsilon+i(\omega-\omega_{ba})+iKv_{12}'\cos\Theta_{12}')(\epsilon+i(\omega-\omega_{ba})+iKv_{12}''\cos\Theta_{12}'')}$$

just contributes $\dfrac{\pi^2}{K^2 v_{12}' v_{12}''}$. We also have factors of 2π from

integrations over ϕ_{12}' and ϕ_{12}'', and a factor of k_0 since $1/k^2$

from the denominators leaves simply $4\pi\int_0^{K_0} dK$. Then using

integration over the Maxwellians only to replace momenta by

their averages, we approximate (70) by

$$(79) \qquad -K_0/8 \;\; \bar{v}\, G^{pb}\, G^{el}\, G^{pb}$$

The first order linewidth coefficient $\Delta\nu_{1/2}$ in cm^{-1}/atm is

$\dfrac{\bar{v}G^{pb}}{2\pi c}$, so to convert one G^{pb} to sec^{-1}/atm, we multiply by

$2\pi c$. The term $T_{12}G_0 T_{23}G_0 T_{12}$ ought to behave precisely as

$T_{12}G_0 T_{13}G_0 T_{12}$ except for the small difference between the 13

and 23 cross sections. However, the third term, $T_{12}G_0 T_{23}G_0 T_{13}$,

also has a contribution from the noninteracting part of the

T_{23} operator, which is of opposite sign (and of the same sign

as $\Delta\nu_{1/2}$), and which for this estimate may be taken to be about

double the interacting part. In other words, for an estimate

of triple collision contributions in three dimensions it suffices

to take

$$(80) \qquad \frac{-2\pi c}{\bar{v}}\, G^{el}\, K_0/8\, (\Delta\nu_{1/2}\text{ in } cm^{-1}/\text{atm})^2 \quad \text{or} \quad \simeq -3/4\, \frac{c}{\bar{v}}\, G/r_0\, (\Delta\nu_{1/2})^2$$

If we perform a quick numerical estimate, with $r_0 = 1/k_0$

being estimated in Appendix G, we find (with values roughly suited

to the HF-Ar system)

$$-3/4\; \frac{3\times10^{10}\,cm/sec}{6\times10^4\,cm/sec}\; \frac{30\times10^{-16}\,cm^2}{3\times10^{-8}\,cm}\; (.03\,cm^{-1}/\text{atm})^2 \simeq -.000035\;\frac{cm^{-1}}{\text{atm}^2}$$

or around $-.35$ cm^{-1} at 100 atm out of 3 cm^{-1}, an observable effect,

by itself. More estimates for various systems will be given in

Section II E.

D. The Statistical Contribution to the Linewidth

We wish to treat the statistical corrections in second order in the density _as if_ they appeared in the denominator of the lineshape expression and thus contributed directly to the linewidth. We begin with Equation (5.15) of Reference 40 and construct a density expansion from it by equating terms of the same order in the density ρ ,

$$(81) \quad (G_o^{-1} + \rho \mathcal{L} + \rho^2 \Gamma)^{-1} (1 + \rho a_1 + \rho^2 a_2) A = (W^o + \rho W^1 + \rho^2 W^2) A$$

where A is an arbitrary function. The first term in the density expansion is obtained by solving $G_o^{-1} W^o A = A$ so that $W^o = G_o$. Similarly, $\rho a_1 A = G_o^{-1} \rho W^1 A + \rho \mathcal{L} W^o A$ means

$$W^1 = G_o a_1 - G_o \mathcal{L} G_o.$$ Finally

$$\rho^2 a_2 A = G_o^{-1} \rho^2 W^2 A + \rho \mathcal{L} \rho W^1 A + \rho^2 \Gamma W^o A$$

$$= G_o^{-1} \rho^2 W^2 A + \rho \mathcal{L} \rho (G_o a_1 - G_o \mathcal{L} G_o) A + \rho^2 \Gamma G_o A$$

which gives $W^2 = G_o a_2 - G_o \mathcal{L} G_o a_1 + G_o \mathcal{L} G_o \mathcal{L} G_o - G_o \Gamma G_o$.

Then to put everything into a denominator we solve

$$(G_o^{-1} + \rho \mathcal{L} + \rho^2 \Gamma + \rho a_1 b_1' + \rho^2 a_2 b_1^2 + \rho^2 a_1 b_2')^{-1} A = WA$$

Again equating powers of ρ , $\rho \mathcal{L} W^o A + G_o^{-1} \rho W^1 A + \rho a_1 b_1' W_A^o = 0$ says that $b_1' = - G_o^{-1}$. Then

$$G_o^{-1} \rho^2 W^2 A + \rho \mathcal{L} \rho W^1 A + \rho^2 \Gamma W^o A + \rho^2 a_2 b_1^2 W^o A + \rho^2 a_1 b_2' W^o A - \rho^2 a_1 G_o^{-1} W^1 A = 0$$

or

$$a_2 - \mathcal{L} G_o a_1 + \mathcal{L} G_o \mathcal{L} G_o - \Gamma G_o + \mathcal{L} G_o a_1 - \mathcal{L} G_o \mathcal{L} G_o + \Gamma G_o - a_1^2 + a_1 G_o \mathcal{L} + a_2 b_1^2 G_o + a_1 b_2' G_o = 0$$

so $b_1^2 = - G_o^{-1}$ and $b_2' = a_1 G_o^{-1} - \mathcal{L}$. So the second order statistical term in the denominator is

$$(82) \quad - G_o^{-1} a_2 + G_o^{-1} a_1^2 - \mathcal{L} a_1$$

Here we use the definitions that the two particle distribution function $\tilde{\rho}(12) = g(12) \tilde{\rho}(1) \tilde{\rho}(2)$ (or $g_{12} \tilde{\rho}_1 \tilde{\rho}_2$), and f_{12} is not $\tilde{\rho}(12) - \tilde{\rho}(1) \tilde{\rho}(2)$ as in

124

Reference 37, but $f_{12} = g_{12} - 1$. Also we use brackets $\langle \rangle$ to indicate the average over one particle distribution functions. The using the definitions, $G_o^{-1} a_2$ is $\langle -VT_{12} g_{12}^{(o)} f_{12} f_{23} \rangle_{23}$, which we shall show is the second order contribution from the Enskog theory of dense gases, plus other terms,

$$\langle V^2 T_{12} G_o T_{13} g_{13}^{(o)} (f_{12} + f_{23} + f_{12} f_{23}) \rangle_{23} + \langle V^2 T_{12} G_o T_{23} g_{23}^{(o)} (f_{12} + f_{13} + f_{12} f_{13}) \rangle_{23}$$

The term $G_o^{-1} a_1^2$ could be written as $\langle -V^2 T_{12} G_o T_{13} f_{12} f_{13} f_{23} \rangle_{23}$ while $-\mathcal{L} a_1$ is $\langle -VT_{12} G_o T_{13} f_{13} f_{23} \rangle_{23}$. We note that there are many more terms than the first Enskog correction.

We now comment on some previous methods for approximating the statistical corrections. If one expands Equations (5.15) and (5.16) of Reference 40 ignoring ϵ,

$$\tfrac{1}{\rho \mathcal{L}} (1 + {}^{\rho \Gamma}\!/_{\mathcal{L}})^{-1} (1 - \rho a_1) = {}^{V}\!/_{\rho \mathcal{L}} (1 + {}^{\rho \Gamma}\!/_{\mathcal{L}} - \rho a_1),$$

they are indeed equivalent to order ρ^2. However, if one includes ϵ, which in our case contains the factor $f(\omega - \omega_{ba})$, the expansion of Equation (5.15) is

$$\tfrac{1}{\epsilon} (1 - {}^{\rho \mathcal{L}}\!/_{\epsilon} + \rho a_1 + {}^{\rho^2 \Gamma}\!/_{\epsilon} + {}^{\rho^2 \mathcal{L}^2}\!/_{\epsilon} + {}^{\rho^2 \mathcal{L} a_1}\!/_{\epsilon})$$

which is not equal to

$$\tfrac{1}{\epsilon} (1 - {}^{\rho \mathcal{L}}\!/_{\epsilon} - {}^{\rho^2 \Gamma}\!/_{\epsilon} + {}^{\rho^2 \mathcal{L} a_1}\!/_{\epsilon} + {}^{\rho^2 \mathcal{L}^2}\!/_{\epsilon})$$

obtained from (5.16)

So if one went directly from an ϵ series or from the correctly summed Equation (5.15), and used the definition of the second virial coefficient $B(T) = -\tfrac{1}{2} \int f_{12} \, d\vec{r}_{12}$, one would not want to approximate the first density correction as $(1 - 2 \rho B)$ multiplied times a linewidth or cross section, as Equation (5.16) might suggest, but rather to include a factor $(1 - 2B)$ in lowest order

125

in the density. As discussed in Reference 56, the reduced
volume factor $(1-2\rho B)$ is only one of two contributions, the
other being due to shielding by a third particle to reduce
the probability of collisions. The entire statistical
correction factor in Enskog theory comes from averaging the
density expansion of the pair correlation function $g(12) = 1 + f(12)$
Its density expansion to second order is $\bar{e}^{\beta V_{12}} (1 + \rho \int f_{13} f_{23} d\vec{r}_3 + \dots)$
If $V_{12}(r_{12})$ is a hard sphere potential, the integration over
$\vec{r}_3$ can be done[99] to obtain the original Enskog result,

$$1 + \rho \, ^5/_{12} \pi d^3 \, , \text{d the hard sphere diameter.}$$

Given that the third virial coefficient $C(T)$ is

$$C(T) = -1/_{3V} \int f_{12} f_{23} f_{13} \, d\vec{r}_1 \, d\vec{r}_2 \, d\vec{r}_3 \, ,$$

one might then want to approximate the first order statistical
correction to the linewidth as $\rho^C/_B$ times the linewidth.[100]
However, there are better approximations to the Enskog term
which have been traditionally used. We will discuss one in the
next section, but first we must satisfy ourselves that this term
is the most important.

To gain an idea of the relative magnitudes of the
statistical terms, we will write out the traces over tetradic
and matrix elements. We want to look first at the Enskog term,
$\langle V T_{12} \langle g_{(12)}^{(0)} f_{13} f_{23} \rangle_3 \rangle_2$, in which we shall denote the operator
averaged over the coordinates and momenta of particle 3 as E_{12}.
The derivation which follows would work as well for a term
$\langle V T_{12} g_{12} \rangle_2$, or $\langle V T_{12} f_{12} \rangle_2$. (The latter object, as if a_1 were
$V f_{12}$, might indeed result from an evaluation of the term $\mathcal{L} a_1$,

126

as we shall see in the next section.)

We begin with

(83) $$\sum_{\vec{P}_2\vec{P}_1'\vec{P}_2'\vec{P}_1''\vec{P}_2''} V^2 \, T_{\frac{1}{\hbar}\vec{P}_1\vec{P}_2 \, \vec{P}_1\vec{P}_2 \, \vec{P}_1'\vec{P}_2' \, \vec{P}_1''\vec{P}_2''} \, E_{\vec{P}_1'\vec{P}_2'\vec{P}_1''\vec{P}_2''} \, \tilde{\rho}_{\vec{P}_2''}$$

Summation over $\vec{p}_{12}''$ and the momentum conservation conditions in

T_{12} such that $\vec{p}_1' + \vec{p}_2' = \vec{p}_1'' + \vec{p}_2''$ generate a momentum $\vec{k} = \vec{p}_1' - \vec{p}_1''$

just as in Section II C, and give factors of $T_{\vec{P}_{12}\vec{P}_{12} \, \vec{P}_{12}\vec{P}_{12}'-\vec{k}}$

and $Y_{\vec{P}_{12}'\vec{P}_{12}'-\vec{k}}$. We change the remaining three momenta, $\vec{p}_2 \, \vec{p}_1'$

and $\vec{p}_2'$ to center of mass variables $\vec{p}_{12} \, \vec{p}_{12}'$ and $\vec{P}_{12}$. Going to

continuous momenta, center of mass delta functions give us a

factor of V from E_{12} and cause $T_{\frac{1}{\hbar}}$ to go to

$$\frac{V_{12} G^{tot}}{V^2} \, V \left(\frac{(2\pi\hbar)^3}{V}\right)^2 \, \delta_{\vec{P}_{12}\vec{P}_{12}'} \, \delta_{\vec{P}_{12}\vec{P}_{12}'} - \frac{(2\pi\hbar)^3}{m^2} \, \delta(E-E') \, \frac{S^{el}}{V^4} \, V^2 \left(\frac{(2\pi\hbar)^3}{V}\right)$$

which we call

$$\frac{1}{V} \, V_{12} \frac{G^{pb}}{4\pi} \, \delta_{\vec{P}_{12}\vec{P}_{12}'} \, \delta_{\vec{P}_{12}\vec{P}_{12}'} \left(\frac{(2\pi\hbar)^3}{V}\right)^2$$

With explicit volume normalization, we have

(84) $$\left(\frac{V}{(2\pi\hbar)^3}\right)^4 \int d\vec{p}_{12} d\vec{p}_{12}' d\vec{P}_{12}' d\vec{k} \, V^2 \frac{1}{V} \, V_{12} \frac{G^{pb}}{4\pi} \, \delta_{\vec{P}_{12}\vec{P}_{12}'} \, \delta_{\vec{P}_{12}\vec{P}_{12}'} \left(\frac{(2\pi\hbar)^3}{V}\right)^2 \frac{1}{V^2} E_{12 \, \vec{P}_{12}'\vec{P}_{12}'-\vec{k}} \frac{V}{(2\pi\hbar)^3} \, \phi_{\vec{P}_2-\vec{k}} \frac{(2\pi\hbar)^3}{V}$$

The last factor of $\frac{(2\pi\hbar)^3}{V}$ comes about because one can argue

that $E_{\vec{P}_{12}'\vec{P}_{12}'-\vec{k}}$, being approximately $\int d\vec{r}_{12} E_{12} e^{i\vec{k}\cdot\vec{r}_{12}/\hbar}$, should be

$$\int d\vec{r}_{12} E_{12}(\vec{P}_{12}) \frac{(2\pi\hbar)^3}{V} \, \delta(\vec{k}) \quad \text{since} \quad \int d\vec{r}_{12} e^{i\vec{k}\cdot\vec{r}_{12}/\hbar} = V \frac{(2\pi\hbar)^3}{V} \delta(\vec{k}) = \int d\vec{r}_{12} E_{12}(\vec{P}_{12}) \frac{(2\pi\hbar)^3}{V} \delta(\vec{k})$$

(Similarly, f_{12} can be approximated by $\beta \frac{(2\pi\hbar)^3}{V} \delta(\vec{k})$) Actually

E_{12} (and f_{12}), being of finite range in $\vec{r}_{12}$, can be approximated

by a square well, and will lead to a cutoff k_0 as discussed in

Appendix G. But this k_0 is much less than a thermal average

momentum, and, in contrast to the denominators discussed in Section

II C, here appears only added to the relative momentum.

127

If we use the average over the Maxwellian to simply substitute in average momenta, Equation (84) simplifies to $\bar{V} G^{Pb} E$ (where from above E for hard spheres was $\frac{5}{12}\pi d^3$).

Next we look at $\langle V^2 T_{12} G_0 T_{13} g_{13}^{(0)} f_{13} \rangle_{23}$, from $\mathcal{L}_{a_1}$. We begin with

(85)
$$\sum_{\substack{\vec{P}_{12}\vec{P}_1'\vec{P}_2'\vec{P}_3' \\ \vec{q}_1\vec{k}\vec{q}_3\vec{k}'}} T_{12}(\vec{P}_{12}\vec{P}_{12}\vec{P}_{12}'\vec{P}_{12}-\vec{k}) \; T_{13}(\vec{P}_{13}'\vec{P}_3'\vec{q}_{13}'\vec{q}_{13}-\vec{k}')$$
$$\times \; G_0(\vec{q}_{13}\vec{q}_{13}\vec{k}') (g_{13}^{(0)} f_{13})(\vec{q}_{13}\vec{q}_{13}\vec{k}') \vec{P}_2 \vec{P}_3$$

Actually, the second $\vec{p}_1'$ in T_{13} is $\vec{p}_1' - \vec{k}$, and the $\vec{q}_{13}' - \vec{k}$ index is really composed of $\vec{q}_1' = \vec{q}_1 - \vec{k}'$ and $\vec{q}_3' = \vec{q}_3 + \vec{k}' - \vec{k}$. But this $\vec{k}$ momentum index is really zero because there are no more particle 2 operators in the expression, and therefore with this definition of $\vec{k}$ and $\vec{k}'$ we have not only $\vec{q}_1+\vec{q}_3 = \vec{q}_1'+\vec{q}_3'-\vec{k}$ from T_{13} but also $\vec{q}_1 + \vec{q}_3 = \vec{q}_1' + \vec{q}_3'$ from the momentum conservation condition in f_{13}.

Changing to integrations over center of mass momenta, we obtain

(86)
$$\left(\frac{V}{(2\pi\hbar)^3}\right)^8 \int d\vec{P}_{12} d\vec{P}_{12}' d\vec{P}_{12}' d\vec{P}_{13} d\vec{q}_{13} d\vec{k} d\vec{Q}_{13} d\vec{k}' \, V^2 \frac{1}{V} \frac{V_{12} G^{Pb}}{4\pi} \delta_{P_{12}P_{12}'} \delta_{\vec{P}_{12}\vec{P}_{12}'} \left(\frac{(2\pi\hbar)^3}{V}\right)^2 G_0(\vec{k}')$$
$$\times \frac{1}{V} \frac{V_{13} G^{Pb}}{4\pi} \delta_{P_{13}'q_{13}} \delta_{Q_{13}Q_{13}'} \left(\frac{(2\pi\hbar)^3}{V}\right)^2 \frac{g_{13}^{(0)} f_{13}}{V^2} (2\pi\hbar)^3 \delta(\vec{k}) \phi_2 \phi_3 \left(\frac{(2\pi\hbar)^3}{V}\right)^2$$

We can simplify Equation (86) by again using $\lim_{\epsilon\to 0}(\epsilon+\text{P}x)^{-1} = \pi\delta(x) - i\text{P}\frac{1}{x}$ on G_0 to do the integration over the angles of $\vec{k}'$. Cancellation leaves one factor of $\frac{1}{(2\pi\hbar)^3}$, which we incorporate into $\vec{k}'$ to make it a wave vector. Then we include a cutoff wave vector k_0' as an upper limit (which can be determined by the estimation methods in Appendix G, perhaps using $\int_0^\infty V(\vec{k}) k' dk' = \frac{k_0'^2}{2} \int V_{12}(0) r_{12}^2 dr_{12}$). We argue that the result of the radial integration, $\pi^2 k_0'^2 / \bar{v}_{13}$, approximately cancels the $\bar{v}_{13} G_{13}$ resulting from T_{13}, since we

128

choose k'_0 to be of the order of a molecular diameter. Then substituting in average momenta, and taking $g_{13}^{(0)}$ to be one, we can approximate Equation (86) by $-2B\, \frac{V_6}{(2\pi)^3}$, since neglecting $\vec{k}$ in the matrix element of f_{13} it is approximately $\int f_{13}\, d\vec{r}_{13} = -2B$.

Terms like $\langle V^2 T_{12} G_0 T_{13} g_{13}^{(0)} f_{12} \rangle_{23}$ go in much the same fashion, so we look at only one more, $\langle V^2 T_{12} G_0 T_{13} g_{13}^{(0)} f_{12} f_{13} \rangle_{23}$, which if we immediately take $g_{13}^{(0)}$ as one becomes

$$\left(\frac{V}{(2\pi\hbar)^3}\right)^8 \int d\vec{p}_2\, d\vec{p}_1'\, d\vec{p}_2'\, d\vec{k}\, d\vec{p}_3\, d\vec{q}_1\, d\vec{q}_{23}\, d\vec{k}'$$

$$(87) \qquad \times\, V^2 \left(\frac{1}{V}\, \frac{V_{12}\, 6^{Pb}}{4\pi}\, \delta_{P_2 P_2'}\, \delta_{\vec{P}_{12} \vec{P}_{12}'}\, \left(\frac{(2\pi\hbar)^3}{V}\right)^2 (i\epsilon - \vec{k}\cdot\vec{q}_{12} - \vec{k}'\cdot\vec{q}_{13})^{-1}\right.$$

$$\times\, \left(\frac{1}{V}\, \frac{V_{13}\, 6^{Pb}}{4\pi}\, \delta_{P_{13} P_{13}'}\, \delta_{P_{13} P_{13}'}\, \left(\frac{(2\pi\hbar)^3}{V}\right)^2 \frac{f_{12}}{V^2}\, V\delta(\vec{k})\, \frac{f_{23}}{V^2}\, V\delta(\vec{k}')\, \phi_2 \phi_3\, \left(\frac{(2\pi\hbar)^3}{V}\right)^2\right.$$

Here two factors of $\frac{1}{(2\pi\hbar)^3}$ survive and are incorporated into integrals over $\vec{k}$ and $\vec{k}'$. So again cancelling $T_{13}G_0$ as above and breaking averages over momenta Equation (87) could be crudely approximated by $\frac{V_6}{(2\pi)^6}\, 4B^2\, \frac{4\pi K_0^3}{3}$. We will find ourselves in desparate need of this factor of $\frac{V}{(2\pi)^6}$ when we estimate the relative sizes of the statistical terms, which we now proceed to do.

If we first, only for an order of magnitude estimate, use the hard sphere Enskog expression, we find $\frac{5}{12}\pi d^3$ to be 1.2×10^{-3}/atm for d, the hard sphere diameter, taken as 3.2 A. Interestingly, B for an attractive potential like that for argon-argon is around -16 $\frac{cm^3}{mole}$[18] so that $-2B$ is 1.4×10^{-3}/atm. Therefore from our estimate of Equation (86), terms like $\langle V^2 T_{12} G_0 T_{13} g_{13}^{(0)} f_{13} \rangle_{23}$ might be of the same size as the Enskog term, were it not for the factor of $\frac{1}{(2\pi)^3}$, left over from a k integration which the

129

Enskog term did not have. Similarly, if we estimate (87) by
again cancelling the integration over $G_o(k)$ with T_{13}, and
approximating $\langle \gamma_{13} \gamma_{25} \gamma_{23} \rangle$ by $4B^2$, we find multiplying times $4\pi K_o^3/3$
gives about 8 times the 2B found in the above f_{13} correction.
But fortunately, $1/(2\pi)^6$ is 1/61529 so this contribution is also
negligible.

So we need consider only the Enskog type term out of all
the statistical corrections in second order in the density.
For further discussion of this term see References 100-106.
We will actually not use the hard sphere Enskog theory, but
will discuss in the next section a commonly used method of
approximating the Enskog term for real potentials.

E. Discussion of Theory and Experiment

We begin this section comparing theory and experiment
by exhibiting the results of a number of other workers
on the density dependence of the diffusion coefficient.
We do this because the diffusion coefficient and the
effective cross section derived from it are in closest
analogy of all transport coefficients to the absorption
coefficient and the cross section obtained from the
linewidth.

This is so because the higher density contributions
to both the absorption and diffusion coefficients arise
only from the increased local density around the particle
of interest described by the statistical terms of Section
II D and from the triple collision events of Section II C.
In the case of other transport processes, like viscosity
and thermal conductivity which involve transfer of
momentum or kinetic energy over a given boundary, the
transport can occur due to collisions at the imaginary
boundary, in addition to transport due to crossing the
boundary. In the hard sphere Enskog theory for dense gases[56]
this effect is shown to be larger than the statistical,
collision frequency correction from the radial distribution
function, χ in the Enskog theory. Diffusion and absorption
of radiation involve properties, the mass of the molecule
and the dipole moment, which cannot be transferred by
collision, so the Enskog relation for the diffusion constant

131

D in terms of its low density limit D_o is just $D=D_o/\chi$.

For purposes of comparison, all diffusion coefficients were reduced to density dependent effective cross sections σ using the relation from simple kinetic theory,[107]

(88) $$D= \tfrac{3}{8} \left(\tfrac{KT}{\pi m} \right)^{\frac{1}{2}} \tfrac{1}{\rho \sigma}$$

This cross section would be constant if diffusion involved only binary collisions. A linear least squares fit of the effective cross section as a function of density gives a low density limiting value for the cross section as an intercept and a second density correction as a slope. These parameters for a number of systems are presented in Table 5.

In Figures 30 through 33 we give some examples of this sort of cross section plot. The general trend of all the data, as shown in the least squares fits, is for the effective cross section to decrease with increasing pressure, as is the effective collision frequency were increasing at a less than linear rate. The plots are useful to show that while there are some excellent measurements in which the second density effect is clearly visible, many sets of data contain such random error as to cast doubt on the exact size if not the existence of this effect. It is the well known difficulty in making transport coefficient measurements precisely which led us to look for density effects in lineshapes. When the linewidth data of the present work is put into the same format of a plot of effective cross section against density, we will find that the scatter in the data compares favorably with much

132

Table 5 : Density Dependent Effective Cross Sections from Diffusion Coefficients

This table gives the low density cross section (σ) and first density correction in A^2/amagat (in the column marked Slope) obtained from a linear least squares fit to diffusion coefficient data. The first three columns give the system studied, the temperature for the measurements (seen to have a noticeable effect on σ), and the literature reference. The column labeled MET is the estimate of the modified Enskog theory for the first density correction in A^2/am, and the column labeled Eq. (79) is the estimate of the contribution to the same property from recollisions. To compute this last, we need the average relative velocity $\bar{v}$, here listed in units of 10^4 cm/sec, and a cutoff radius r_o, here in A. Also listed is the linewidth equivalent of the diffusion cross section, $\bar{v}\sigma/2\pi c$,given in cm^{-1}.

System	Temp.	Ref.	σ	Slope	MET	$\bar{v}$	r_o	$\bar{v}\sigma/2\pi c$	Eq. 79
Kr-He	35°C	109	25.1 A^2	-.016	0	13.0	2.5	.046	-.018
Ar-Ar	49.4	108	39.1	-.01	-.007	5.6	3	.033	-.06
CO_2-H_2	35	114	41.2	-.004	-.002	18.5	3.2	.11	-.007
	100		44.3	-.0095	-.01	20.4		.13	-.009
Kr-Ar	35	109	41.9	-.032	-.007	4.9	3.3	.03	-.076
	-25		43.0	-.027	-.011	4.4		.03	-.09

Table 5 : (continued)

System	Temp.	Ref.	σ	Slope	MET	$\bar{v}$	r_o	$\bar{v}\sigma/2\pi c$	Eq. 79
Kr-N$_2$	35	109	42.8	-.024	-.022	5.6	3.3	.03	-.057
	-25		43.4	-.027	-.027	5.0			-.073
CO$_2$-Ar	75	113	43.1	-.014	-.012	5.9	3.3	.03	-.052
	50		44.2	-.016	-.006	5.7		.03	-.055
	25		44.0	-.018	-.005	5.5		.03	-.060
Kr-Kr	35	109	47.7	-.026	-.009	3.9	3.4	.027	-.10
	0	111,	51.1	-.043	-.0003	3.7	3.6	.027	-.]2
	-53	112	57.3	-.042	-.004	3.3	3.8	.027	-.15
Kr-CO$_2$	35	109	49.3	-.070	-.005	4.75	3.5	.033	-.10
CO$_2$-CO$_2$	100	115	51.3	-.017	-.013	6.0	3.6	.044	-.12
	75	116	52.0	-.038	-.008	5.8	3.6	.043	-.12
	50	116	53.2	-.026	-.003	5.6	3.6	.042	-.13
	45	110	57.2	-.060	-.003	5.55	3.8	.045	-.20
	35	115	56.5	-.013	-.002	5.45	3.8	.044	-.15
	25	116	54.8	-.019	-.0026	5.35	3.7	.042	-.14
	25	110,117	59.7	-.078	-.0029	5.35	3.9	.046	-.17
	20	118	59.6	-.027	-.004	5.3	3.9	.045	-.17

Figure 30: A plot of effective cross section
for Kr-Ar derived from diffusion coefficient
data using Equation (88), as a function of Ar
density. Data taken from Reference 109.

Figure 31: Effective cross section plot for
Kr diffusing through Kr (squares) and N_2
(triangles). Data from Reference 109.

Figure 30

136
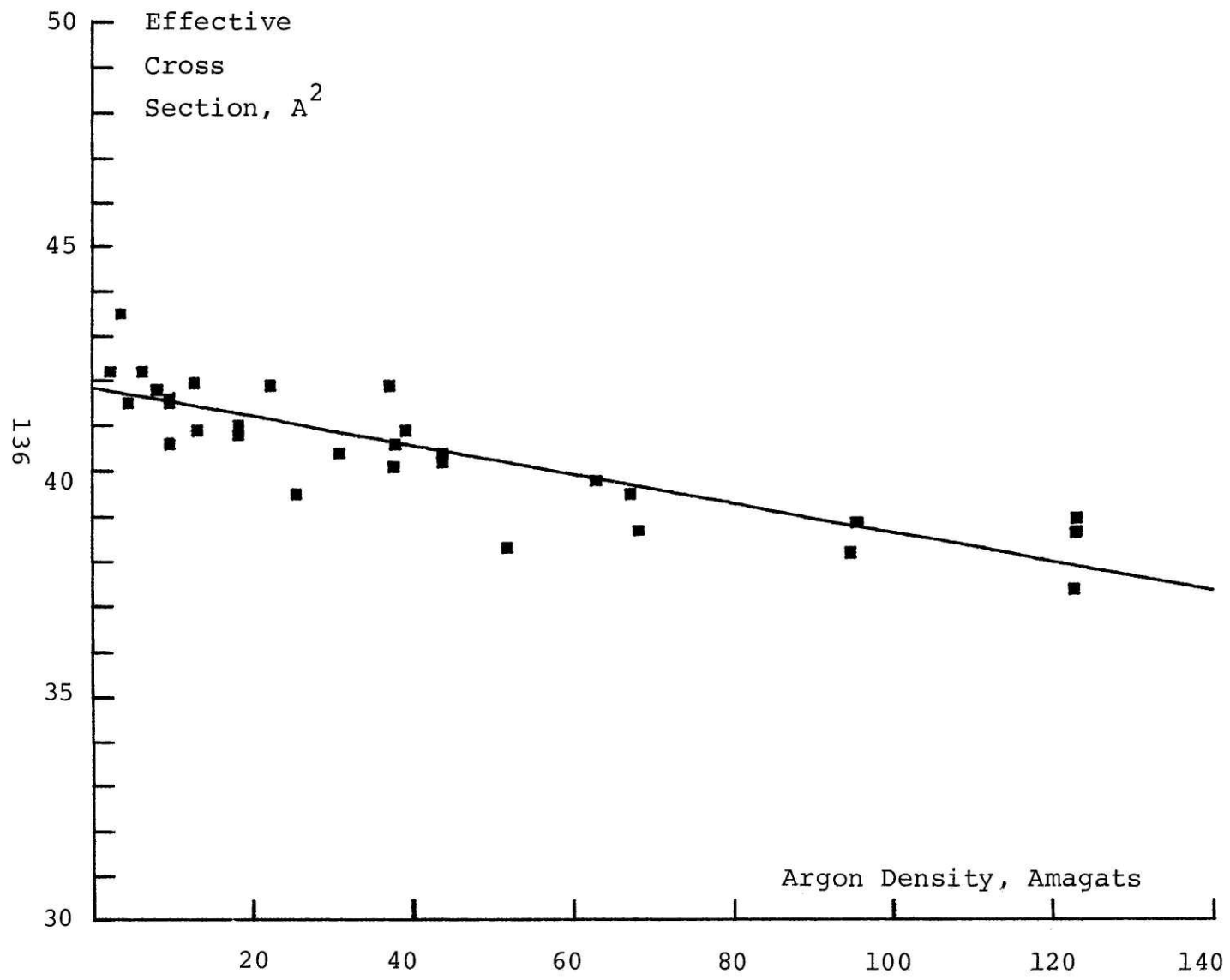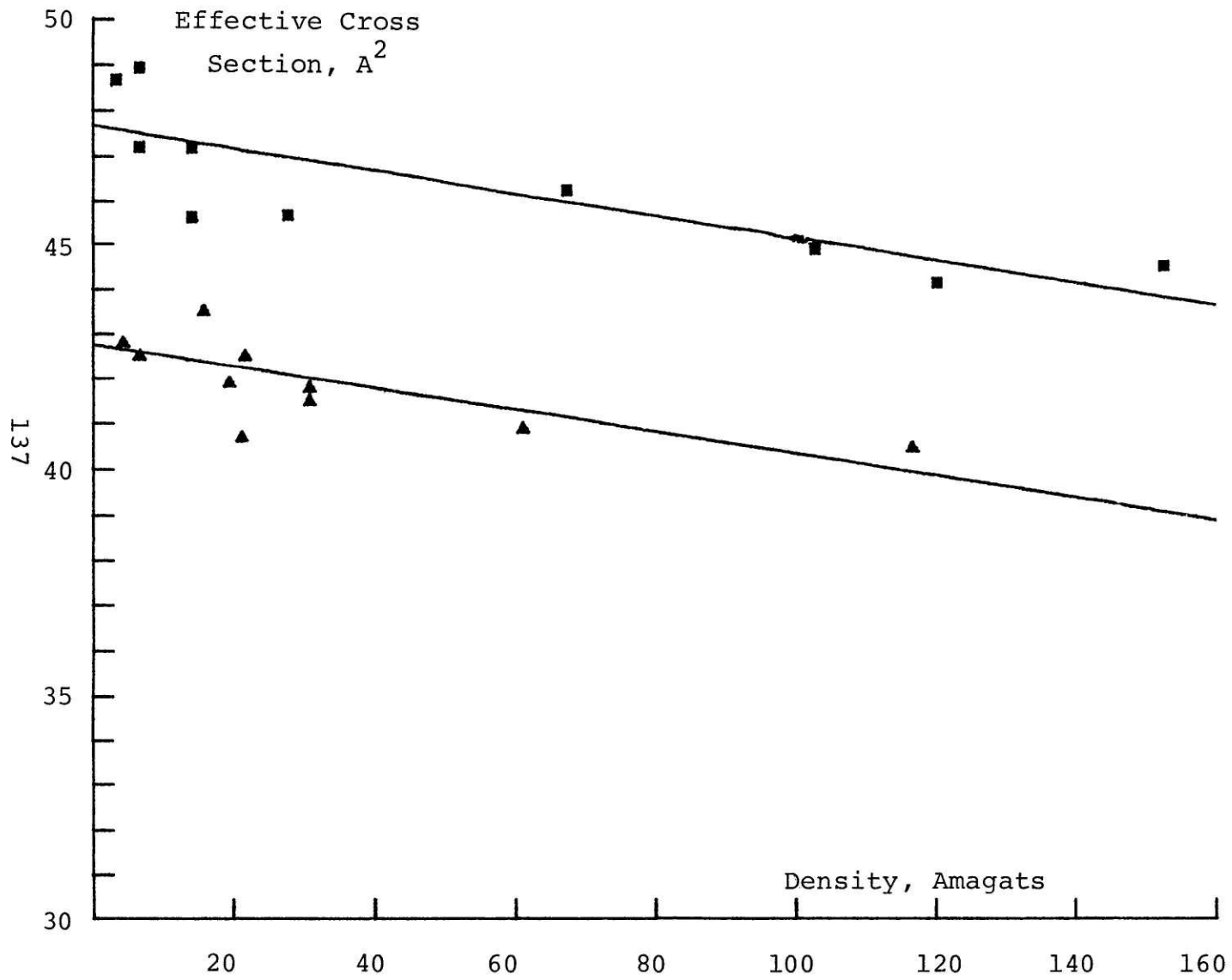
Figure 31

Figure 32: A plot of effective cross section derived from Ar self diffusion as a function of Ar density. Data from Reference 108.

Figure 33: A plot of effective cross section derived from CO_2 self diffusion as a function of CO_2 density. References 110 and 117 gave the data.
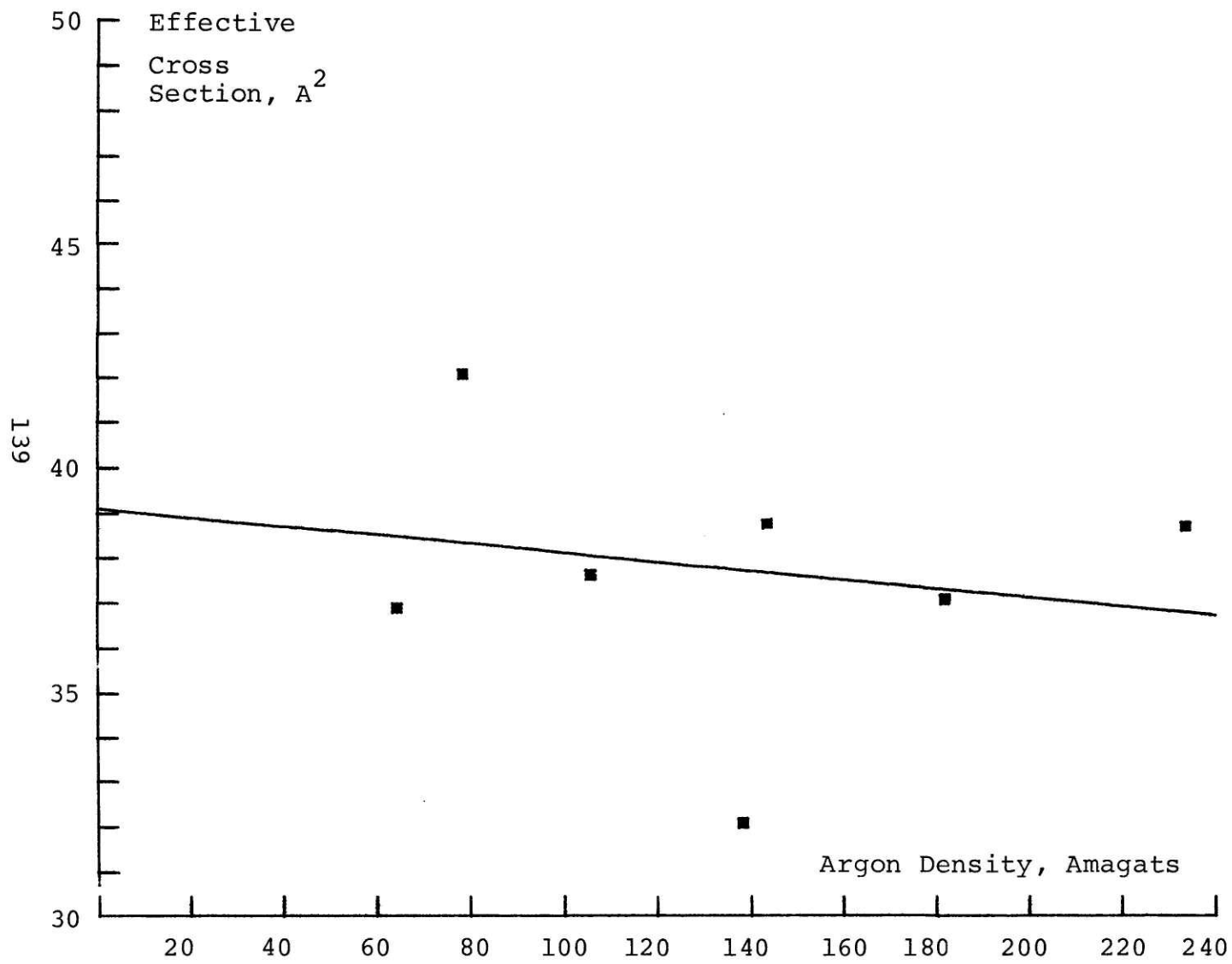
Figure 32

Figure 33

140
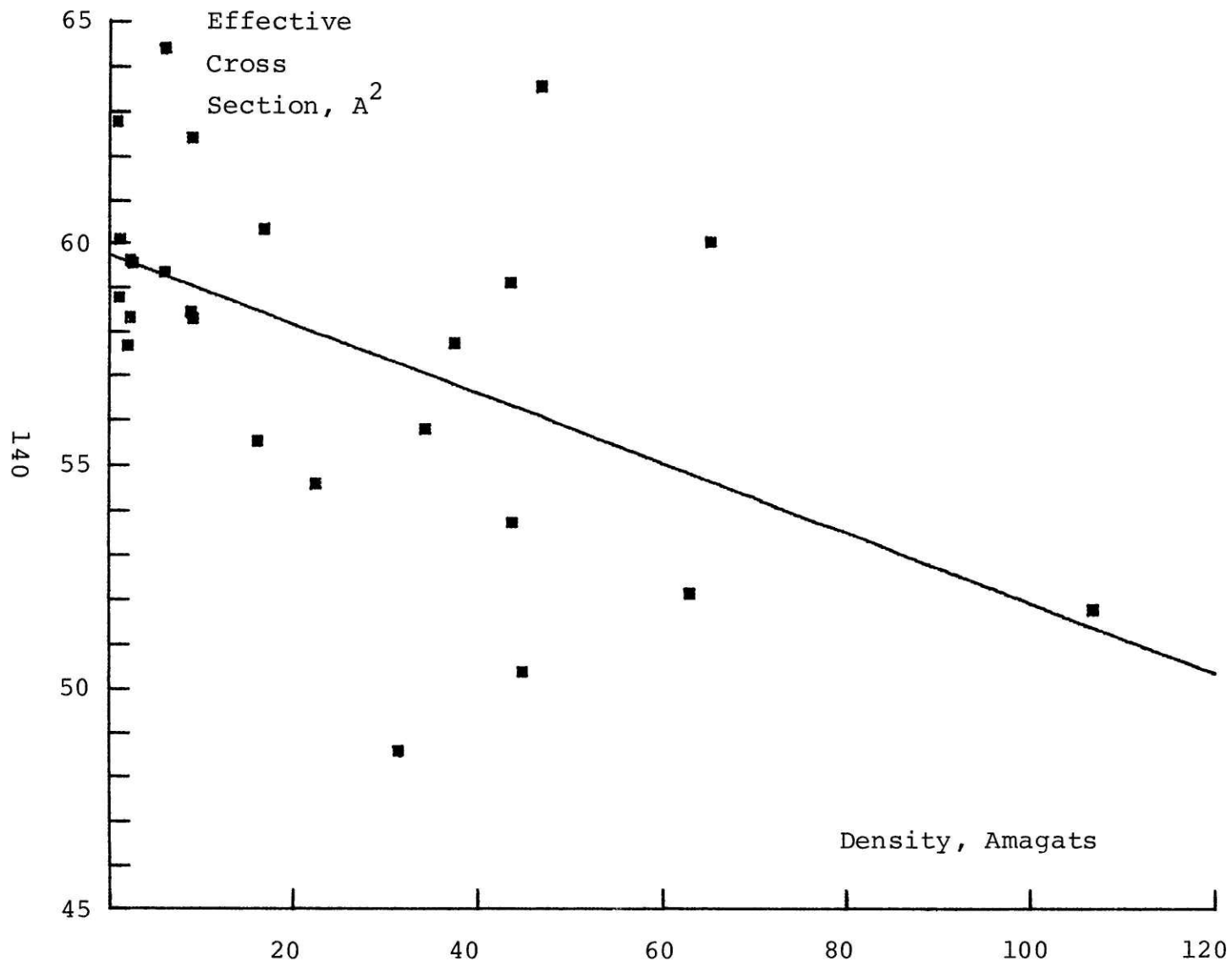
of the diffusion coefficient data, at least at high enough
densities that the absorption linewidth is considerably
larger than the laser linewidth.

Before we can compare estimates of triple collision
contributions to experiment, we must find a reliable way
of estimating the statistical correction discussed in Section
II D. We will use a method first suggested by Enskog, of
incorporating experimental compressibility data (and therefore
properties of real gases), now known as modified Enskog
theory (MET).[106] The pair correlation function appearing
in our formulation of the staistical term becomes for the
case of hard spheres the expression found in the Enskog
equation of state,

(89) $$PV/RT = 1 + b\rho\chi$$

where $\chi = (1 + \frac{5}{8} b\rho + \ldots)$ and $b = \frac{2}{3}\pi d^3$ with d being
the hard sphere diameter. In other words, we have an
effective $\frac{1}{b\rho}$ (PV/RT - 1) in the denominator multiplying the
low density cross section.

It was the suggestion of Enskog that, first, the pressure
P be replaced by the "thermal pressure" $T\left(\frac{\partial P}{\partial T}\right)_V$.[106] (Or as
in Reference 56, since P becomes $P + a\rho^2$ in the Van der Waals
equation of state, we should have P go to $T\left(\frac{\partial P}{\partial T}\right)_V$. Then,
one can use experimental compressibility data in the form
of a virial expansion, (PV/RT = 1 + Bρ + Cρ^2 + ...), to obtain

$$b\rho\chi = \frac{1}{R}\left(\frac{\partial PV}{\partial T}\right)_V - 1 = T\frac{\partial}{\partial T}(PV/RT)_V + PV/RT - 1$$

Then we substitute in the virial expansion, and insist that

141

$\chi \to 1$ as $\rho \to 0$ so that we identify $b = B + T\,dB/dT$, we have

(90) $\qquad \chi = 1 + \rho \dfrac{(C + T\,dC/dT)}{(B + T\,dB/dT)} + \cdots$

in $D = D_o/\chi$.

So, to compute second order density corrections to the effective cross section or collision frequency we need not only the second virial coefficient but the third, as well as their temperature dependences.

For purposes of this estimation, we will take our virial coefficient data from the compilation given in Reference 119. Of course, virial data are not known perfectly, and in particular the third virial coefficient and its temperature derivative may be more inaccurate than even the second order density dependence we wish to compare them to. However, all the estimates display the properties of the following example, for Kr-Ar.

At 35°C, virial coefficient data from Reference 119 is given in Table 6. The third row of the table is calculated by assuming that the virial coefficients are functions of hard sphere diameters, and that these diameters obey the addition rule. In other words, we take $B_{12} = \frac{1}{2}(B_1^{1/2} + B_2^{1/2})^2$ and $C_{12} = \frac{1}{2}(C_1^{1/4} + C_2^{1/4})^4$. Note that the temperature derivatives in both cases are larger than and of opposite sign to the virial coefficients. So with both signs reversed, the ratio remains negative, thus giving a decrease in effective cross section with increasing density. However, the difference $C + T\,dC/dT$ is

142

Table 6 :   Example of Virial Coefficient Data

System	B	$T\,dB/dT$	C	$T\,dC/dT$
Ar	-14.2 cm^3/mole	59 cm^3/mole	1130 $(\frac{cm^3}{mole})^2$	-1330 $(\frac{cm^3}{mole})^2$
Kr	-48	114	2420	-2640
Ar-Kr	-28.6	84	1685	-1900

now smaller than C alone. So continuing our example we have

-215/55 = -3.9 cm^3/mole. Dividing by 22414 cm^3atm/mole gives

a fractional contribution of -1.7×10^{-4} / am, and multiplying

by the cross section, 41.9 A^2, our estimate of the second

density contribution is -.007 A^2/am, while the observed value

was -.032 A^2/amagat.

And indeed, looking down the column labeled MET in Table

5, where we list the first density corrections obtained by

Equation (90), we conclude that by this method of estimation

the Enskog term seems too small to explain the observations

for the diffusion coefficients by itself.

Using the simple expression for the linewidth,

and the conversion from density in mole/cm^3 to amagats,

3.72×10^{-20} atm cm^3, we can also convert our observed line

broadening coefficients to effective cross sections, and

produce the same sort of plots we used to show second density

dependence in the diffusion coefficient. (An amusing

coincidence is that for HF-Ar the factor $\bar{v}/_{2\pi c}(3.72 \times 10^{-20})$

is precisely 0.001×10^{16} at 310°K, so that anywhere around

room temperature cross sections in A^2 and linewidths in

thousandths of wavenumbers (millikaysers) per amagat are

numerically equal.)

Only our data for HF broadened by argon is sufficiently

reliable and goes to high enough densities that there is any

hope of finding believable second density affects. Also, the

data at low densities, where the linewidth is of the same size

144

as the width of the laser line, is too unruly to include in
any fit. Therefore, the plots of effective cross section
versus density in Figures 34 through 36 and the results of
the least squares fit given in Table 7 are based on data above
50 amagats. (Choosing other nearby points at which to begin
the fit will change these numbers by around 20 per cent. And
certainly for the smaller lines the magnitude of the effect
is very much in doubt. But it seems clear that at high
densities there is a second order density effect, very similar
to that seen in the diffusion coefficient.)

Table 8 presents the observed second density terms for
the HF-Ar system, together with the calculation of my estimate
of the triple collision contribution derived in Section II C,
Equation 80,

$$-3/4 \; c/\bar{v} \; 6/r_o \; (\Delta \nu_{1/2})^2$$

where v is the average velocity, 6 is the elastic cross section,
$1/r_o$ is a cutoff wave vector, and $\Delta \nu_{1/2}$ is the observed line
broadening coefficient. This is at best an order of magnitude
estimate, and the close agreement is fortuitous. Also in the
table we present these estimates for the HCl-Ar and DF-Ar
systems, although the quality of the data does not allow
obtaining experimental values. (We note however that the total
second density terms for the low J HCl lines cannot possibly
be as large as my triple collision estimate, since otherwise
they would be seen.)

Table 9 reports the results of some linewidth measurements

145

Figure 34: A plot of effective cross sections derived from HF P(2) linewidths by assuming the linewidth is given by $\rho \bar{v} \sigma^{pb}/4\pi c$, plotted as a function of argon density.

Figure 35: A plot of effective cross sections from HF P(3) linewidths.

Figure 36: A plot of effective cross sections from HF P(4) linewidths.

Figure 34

147
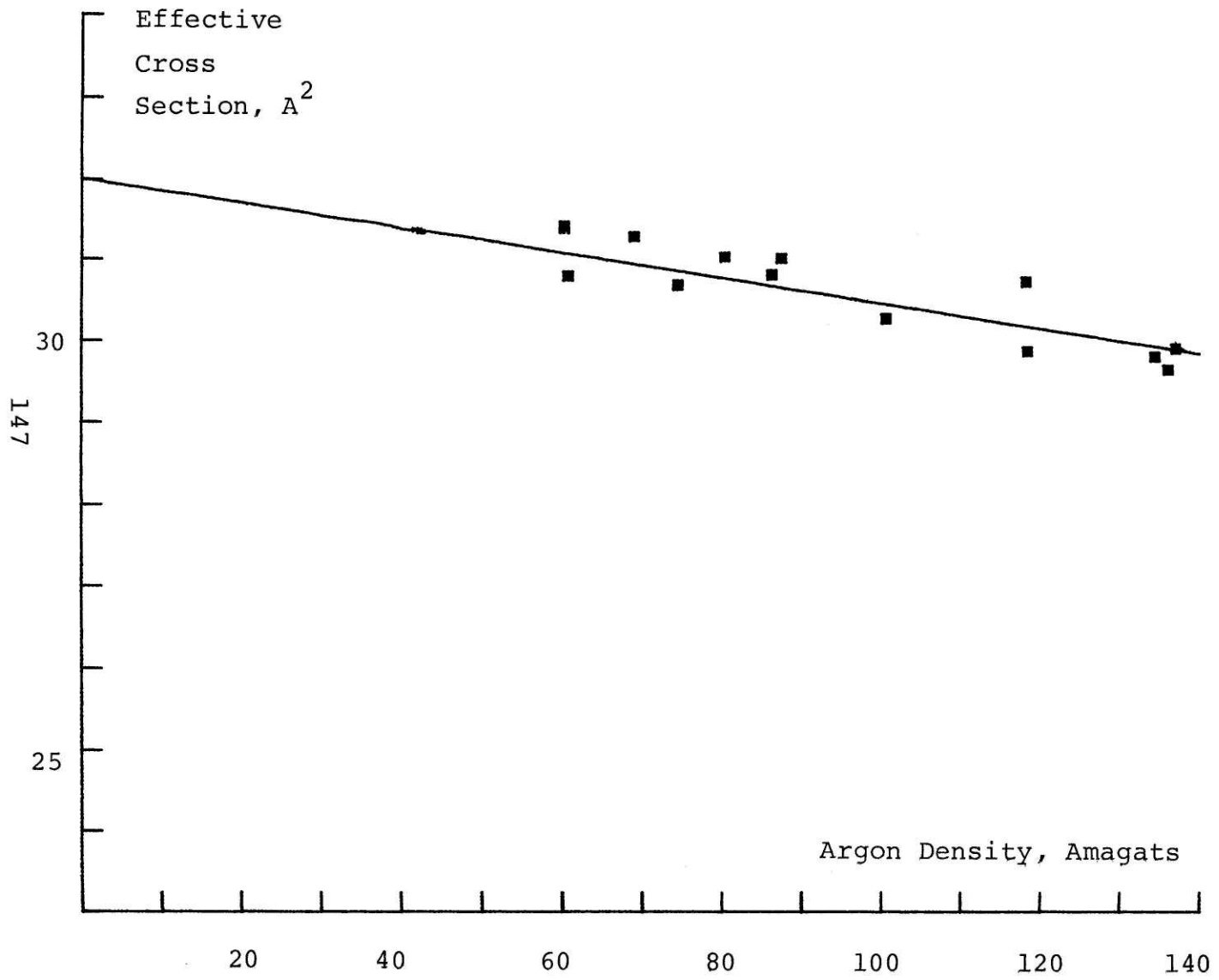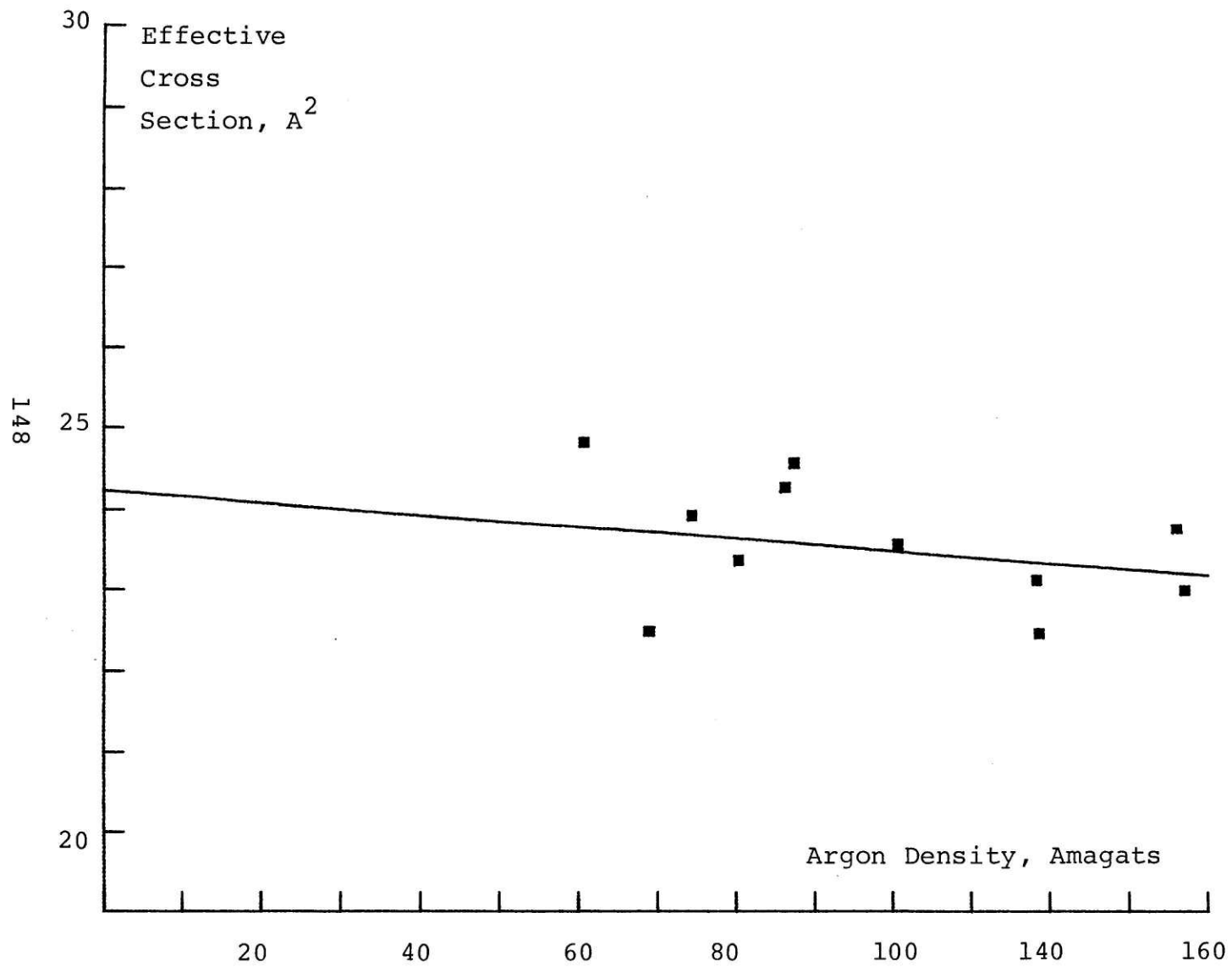
Figure 35

Figure 36

149
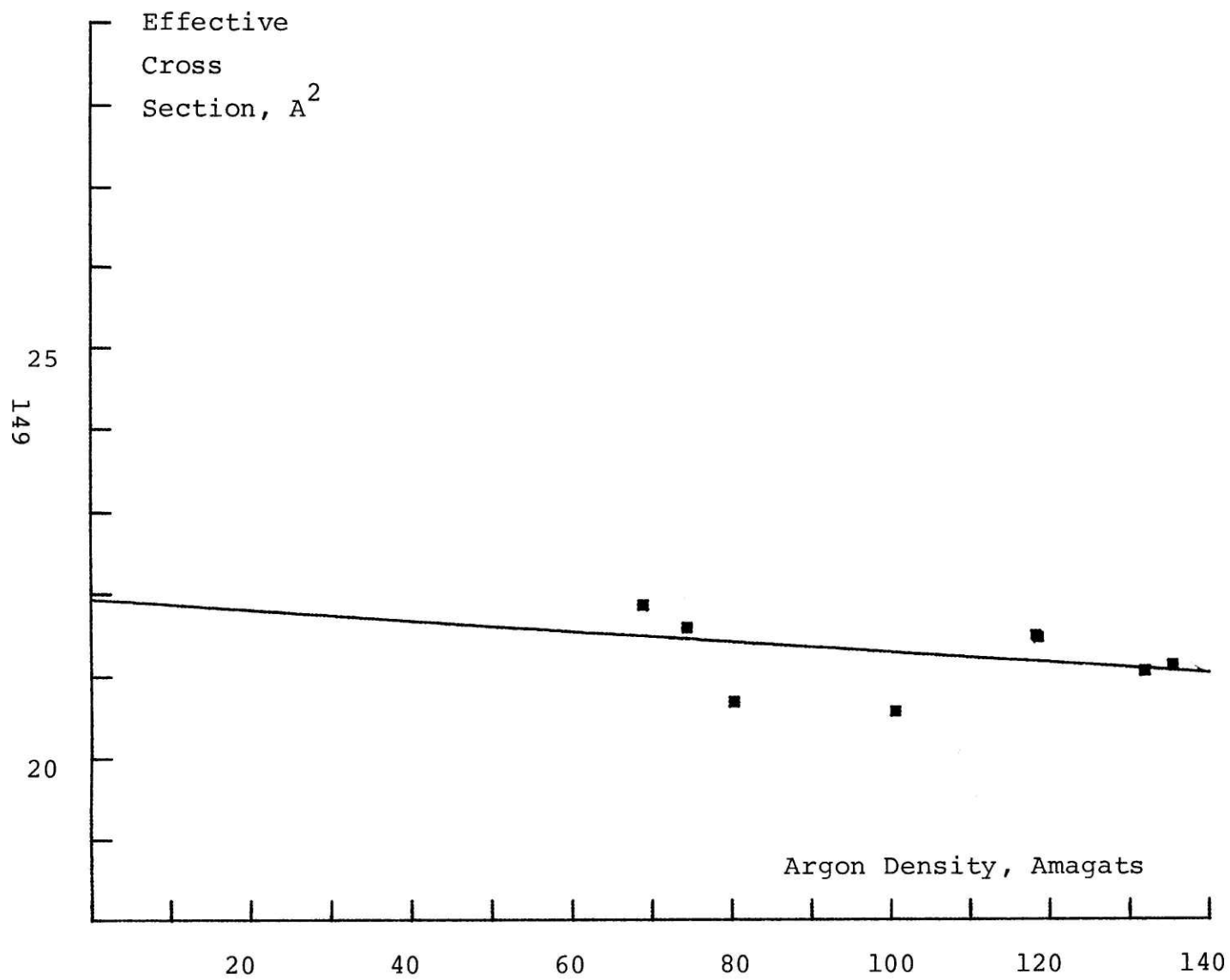
Table 7 : HF Linewidth Second Order Density Effects

This table reports the results of a linear least squares fit to a plot of effective cross section derived from HF linewidths as a function of density. The column marked Intercept gives the low density limit of the effective cross section, and that labeled Slope gives the second density correction. Both values are listed with the standard deviations obtained from the fit.

Line	Intercept	Slope
P(2)	$32.0 \pm .6$ A^2	$-.031 \pm .006$ A^2/am
P(3)	24.5 ± 1.5	$-.015 \pm .015$
P(4)	21.8 ± 1.0	$-.012 \pm .01$

Table <u>8</u> : Estimates of Triple Collision Contributions to Linewidths

    For use in estimating triple collision terms, this table includes columns of the average velocity $\bar{v}$ listed in units of 10^4 cm/sec, the cutoff r_o in A, the elastic cross section σ (obtained from rare gas values) in A^2, and the line broadening coefficient $\Delta\nu_{v_L}$ from this work in cm^{-1}/am. The last two columns give the observed second density term and its estimate using Equation (80).

System		$\bar{v}$	r_o	σ	$\Delta\nu_{v_L}$	Observed	Equation (80)
HF-Ar	P(2)	6.9	3	31	.029	$-.000031 \; \dfrac{cm^{-1}}{am^2}$	$-.000028 \; \dfrac{cm^{-1}}{am^2}$
	P(3)				.023	-.000015	-.000018
	P(4)				.020	-.000013	-.000012
HCl-Ar	R(1)	5.8	3.25	36.3	.042		-.000076
	R(2)				$.034_5$		-.00005
	R(3)				.032		-.000044
	R(4)				.028		-.000034
	R(5)				$.021_5$		-.00002
	R(6)				.016		-.000011
DF-Ar	R(2)				(.023)		-.000018
	R(4)				(.016)		-.000009

Table 9 : Estimates of Triple Collision Contributions to Other Linewidths

The numbers listed in the first few columns of this table are explained in Table 8. The line broadening coefficients were taken from the same reference as the density dependence. In contrast to the previous table, the last two columns give the observed deviation from the linear linewidth at the highest pressure studied.

System		$\overline{v}$	r_o	6	$\Delta\nu_{\frac{1}{2}}$	Observed	Equation (80)
HCl-Ar 0-2,	P(1)	5.8	3.5	35	.063	$-.11$ cm^{-1} at	$-.015$ cm^{-1} at
Ref. 120	P(3)				.047	$-.065$ 10 atm	$-.008$ 10 atm
	R(5)				.033	$-.047$	$-.004$
HCl-HCl 0-2,	R(8)	6	3.5	34	.115	$-.039$ cm^{-1} at	$-.012$ cm^{-1} at
Ref. 121	R(5)				.178	$-.056$ 5 atm	$-.029$ 5 atm
	R(4)				.208	$-.05$	$-.039$
	P(3)				.23	$-.074$	$-.048$
HCl-Xe 0-2,	P(1)	4.3	3.6	52	.077	0 at 9 atm	$-.01$
Ref. 25	R(6)				.054	0	$-.005$

Table 9: (continued)

System		$\bar{v}$	r_o	$\subseteq$	$\Delta\nu_{v_2}$	Observed	Equation (80)
HF-HF 0-1,	R(6)	8	2.5	26	.158	$-.03$ cm^{-1} at	$-.018$ cm^{-1} at
Ref. 10	R(5)				.238	$-.06$ 5 atm	$-.06$ 5 atm
	R(4)				.354	$-.24$	$-.09$
	R(3)				.446	$-.31$	$-.14$
	R(2)				.537	$-.715$	$-.20$
	R(1)				.496	$-.615$	$-.17$
	R(0)				.453	$-.405$	$-.14$
	P(4)				.453	$-.465$	$-.14$
	P(5)				.295	0	$-.06$
	P(6)				.174	$+.35$	$-.02$
HCl-Ar	J 0-1	5.8	3.5	35	.06	0 at 15 atm	$-.03$
Pure Rot.	1-2				.037	0	$-.01$
Ref 34	2-3				.026	0	$-.006$
	3-4				.025	0	$-.006$

from the literature in which second order density effects on the linewidth had at least some chance of being observed. Of course there is no guarantee that deviations from a linear behavior for the linewidth are not due to some other trouble with the experiment. Indeed, for some experiments, both those which show an effect and those which see nothing, the experimental data consists of only two points.

In Table 5 we present a column (marked Eq. 79) of my estimates of the triple collision contribution to the diffusion coefficient. This simply assumes that the collision frequency correction Equation (79) ($-k_0/_8 \, \bar{\sigma}^3$) in $\sec^{-1} am^{-2}$ is the average velocity $\bar{v}$ times a cross section correction in cm^2/am.

These estimates are obviously too large. But this is not surprising considering our discussion in Section II C showing that transport coefficients, in which the collision operator operates on functions of momentum, have reduced triple collision terms due to constraints on the angles of the relative momenta. Exactly what factor should be used to reduce the estimates is a matter for detailed calculation which will not be attempted here.

In order to finish our discussion of the second density effects on the linewidth, we should compute estimates for their Enskog contribution. We might like to simply conclude that the contributions will have the same characteristics as the MET estimates for systems studied by diffusion, that is, having the same sign and order of magnitude but not being

154

large enough to explain the observed effect by themselves.

If we wish to do better, however, repeating the MET calculations for systems like HF-Ar and HCl-Ar is difficult. There exist some compressibility data for HCl[122,123] and HF[124], and even some indication that the third virial coefficients are of the same order of magnitude as those previously encountered[122] and decrease with increasing temperature[123]. But even if the data for the individual virial coefficients were trustworthy, which is not, the procedure of using combining rules to obtain virial coefficients for an HCl-Ar mixture is probably not justified.

Another possible approach is to use the expressions for B and C and their temperature derivatives for a Lennard-Jones 6-12 potential from Reference 125. For instance, for the isotropic HCl-Ar potential used by Gordon[33] (originally from Reference 126) the r_o is 3.39 A and the well depth is $205°$K so that $T^* = kT/\epsilon$ is 1.45. From Reference 125, with $B^* = B/b_o$, $C^* = C/b_o^2$, and $b_o = \frac{2}{3}\pi \tilde{N} \sigma^3$, at $T^* = 1.45$ we have $C^* = .556$, $TdC^*/dT = -.364$, $B^* = -1.28$, and $TdB^*/dT = 2.53$. With b_o being 46.9 cm^3/mole, this means a MET second density contribution of $+ 7.2$ cm^3/mole is obtained, which is larger and of opposite sign to those from experimental virial coefficients.

So perhaps we indeed do best by assuming that the statistical corrections are of the order of the MET estimates made for the diffusion constant, and that therefore recollision

155

terms the size of those obtained in Section II C may be needed for agreement with experiment.

Further it seems a fair conclusion that the experiments do support the existence of a second order in density correction to the linewidth, but this term is small, almost within the experimental uncertainty. Therefore, any third order terms, logarithmic in density or not, would be very small at moderate densities, and very difficult to measure.

III APPENDICES

Appendix A : The Chromatix Laser and Parametric Oscillator

This appendix contains a discussion of the routine operation and maintainance of the Chromatix Nd:YAG laser and optical parametric oscillator (OPO), the frequency and power characteristics of the parametric oscillator and some comments on its operation with an intracavity etalon. Much of the information given here is also contained in the Chromatix manuals for the laser, parametric oscillator, and crystal oven, but like all manuals they benefit from the addition of personal experience.

We begin with the normal operation of the Nd:YAG laser as it is used to produce green pump light for the parametric oscillator. First, the power for the laser is normally kept turned off at the laboratory circuit breaker (number 8). Second, cooling water for the refrigerator heat exchanger must be flowing through the garden hose at an adequate rate or the laser refrigeration system circuit breaker will open. Assuming operation in the green region, the laser may be run without refrigeration, and indeed it seems one may obtain slightly higher power without it. On some occasions, however, the laser seems to have had better long term stability with the refrigeration on. In any case, going from one to the other changes the laser cavity and necessitates readjustment.

Only when the power and water have been turned on can the laser be turned on at the power supply. However, the flashlamp

should still not be turned on until it is verified that either the pulse rate knob is on, or the laser is being triggered externally. For these experiments, the laser was triggered by a pulse generator (General Radio model]2]7-A) through the Lamp Trigger In connection, as specified in Section 1.4 of the Chromatix laser manual. When the laser is triggered externally, the pulse rate knob is set to zero, which turns on a red warning light beside the laser power knob. Turning on the power when the laser is totally untriggered will charge the capacitors well above a safe level, causing at worst a component failure and at best an unpleasant time when the flashlamp is required to discharge the overload.

Operation of the parametric oscillator requires that the Nd:YAG laser be Q-switched, and also demands close to its maximum safe power. There are four adjustments commonly used to peak the laser output. The first two, the back mirror knobs, will need readjustment almost every time the laser is turned on. The back mirror is on a triangle mount, and the knob closest to the operator (corresponding to vertical tilt if the cavity were not bent) is quite sensitive, while the far knob, with a gear arrangement, is less so. It is this knob, however, which controls the laser frequency. (If this knob is too far out of adjustment, the laser can operate on a green line at 531 nm, instead of the considerably stronger 532 nm line.) Only the back mirror should be adjusted, with the front mirror kept fixed.   158

Next the frequency doubler will often need alignment, but this should only be done with great care. When its green output is not maximized, the doubler crystal absorbs the infrared radiation and can be thermally damaged. Furthermore, this adjustment has an extremely narrow maximum. This maximum lies between two secondary maxima, so at times a quick check should be made to see that the knob is at the central peak. (The maximum height of the pulse from the visible monitor, an internal PIN photodiode, appears to occur at the two intermediate minima around the central laser power peak. Therefore all adjustments should be made using the power meter, a Scientech model 36-0001 1 inch Disc Calorimeter, and a sensitive voltmeter.) Often a change in the doubler angle will necessitate a change in the back mirror alignment, and one should go back and forth between the two adjustments to make sure the output has been optimized.

Finally, an adjustment which can sometimes have a sizable effect on the output is the Q-switch vernier control. This positions the window in the radio frequency field applied to the acousto-optic Q-switch over the maximum in the flashlamp pulse. For this experiment, any adjustment of the Q-switch vernier will necessitate repositioning of the integrator switch window (described in Appendix C) over the laser pulse before it can be detected. It is possible that this Q-switch vernier adjustment may contribute to the pulse to pulse stability of the laser.

Another source of instability is competition between transverse modes of the laser. The laser should operate only in the TEM_{00} mode. This can be checked by expanding the beam using a lens and projecting it onto a wall, looking for any sign of TEM_{01} or TEM_{10} modes. These can then be eliminated by closing down the diaphragm in the laser cavity.

In the best of times, a clean, well adjusted laser should produce around 16 mW average power at 370 volts across the flashlamp and 30 Hz pulse repetition rate, and 20 mW at 390 volts. However, the laser is dirty enough that these power levels are only attained at 10 or 20 volts higher lamp voltage.

If the preceding routine adjustments do not result in the desired power level, there are several items which may be checked. First, the laser water and coolant systems should be flushed every month, or every few weeks if the laser is being operated every day. The laser may show up to a five or ten per cent increase in power after a flush. Additional cleaning may be achieved by flushing with a solution of around one per cent of EDTA (in coolant system only) and Liquinox soap. However, the laser will inevitably become dirtier, and even frequent flushes can only slow this trend. The flashlamp water jacket can be swabbed out during lamp changes using a mild HCl solution and a Q-tip, which can be checked for any brown deposits. The top of the reflector cavity can even be removed to check for deposits on the laser rod. However,

160

removing and cleaning the rod itself is a major and difficult operation, which has only been attempted once. Preventive maintainance is advised to forestall this unpleasant task.

A second source of power loss may be a deteriorating flashlamp. Their output may show some falloff after 3 or 4 million pulses. This possibility is easy to check, using the simple lamp replacement procedure given in the laser manual.

Two other components which may be adjusted occasionally for maximum pulse stability and amplitude during Q-switched operation are the RF switch and RF oscillator. The RF switch is located in the laser head and has an impedance-matching network which can be optimized with two screwdriver adjustments. There is a BNC tee on the switch which allows observation of the Q-switch RF during these adjustments using an oscilloscope probe. The RF oscillator is a large vacuum tube located in the laser power supply next to the circuit boards. It should be optimized first. It has two very sensitive knobs, of which the upper one should be adjusted first. The object of both these adjustments is to maximize the peak-to-peak value of the Q-switch RF, but also more importantly to maximize the laser power and stability.

Now we discuss the normal operation of the optical parametric oscillator. When the parametric oscillator is already producing red and infrared light, it is customary to vary the alignment of one or both mirrors and perhaps the crystal oven and visually maximize the red output. The true

161

maximum in output cannot be located by more systematic methods, but "walking" the cavity is a dangerous practice and may result in straying far away from best alignment. When this happens, or when mirrors are changed so there is no output at all, it is necessary to follow the alignment procedure discussed below.

First, before the oven temperature controller is turned on, the pressure from the ultrapure oxygen cylinder should be raised to ten pounds from slightly above zero, where it is always left to keep dust away from the crystal. Second, the OPO crystal has four quadrants, with different coatings which make some difference in operation in various spectral regions. The crystal is installed so that quadrant 1 is at the top and closest to the operator. Two adjustment knobs on the oven allow the various quadrants to be moved onto the laser spot, which can be seen to become more diffuse when moving through a boundary. Quadrant 1 is used with the P1 mirrors, while quadrant 2 is used with P2 and P3 mirrors. (See Figure 37 for ranges of operation of these sets of mirrors.)

When aligning the OPO the Nd:YAG laser should not be Q-switched and should be operated near threshold lamp voltage and with the green attenuator. Also, no light should be put onto a cold crystal. The oven should be set somewhere in the wavelength region for the mirrors being aligned (near the center, if there is no output to start with).

Several measurements have been made on the power of the red light at around 6710 to 6680 A wavelength or 335 to 340°C

162

Figure 37: A plot of wavelength of optical parametric oscillator output as a function of crystal oven temperature. The bars mark the regions of operation of the various mirror sets, P1 mirrors being used in the longest wavelength regions and then P2 and P3. The P2 and P3 regions overlap, while there is a small wavelength region which is not easily obtained using either P1 or P2 mirrors.
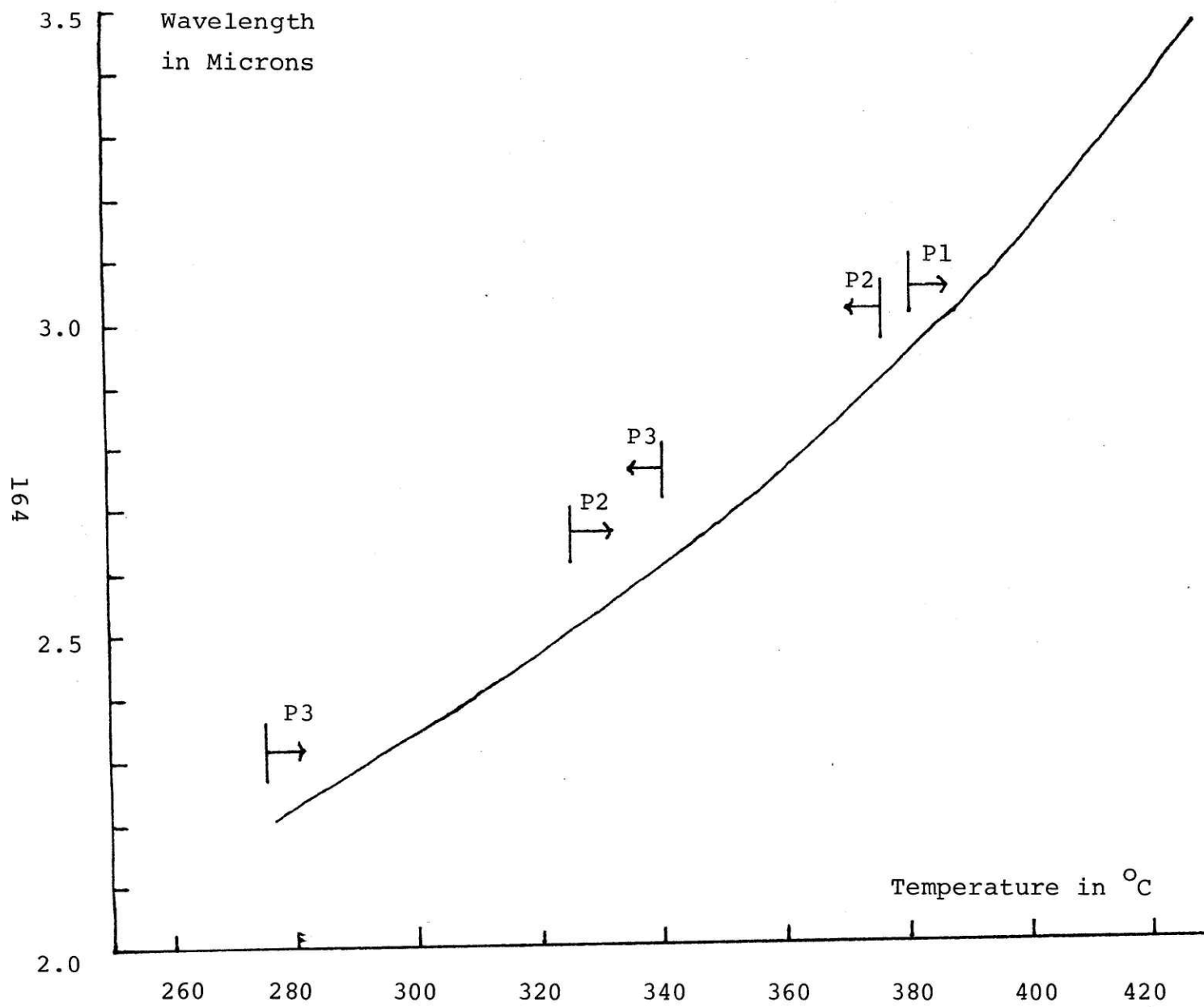
Figure 37

oven temperature. (The infrared power is too weak to be measured directly.) The results are that with a 30 Hz pulse rate, an average green pump power of 16 to 18 mW produced 2.1 to 2.3 mW red power. Assuming a pulse width of 100 nsec this translates into a peak red power of 800 watts. The corresponding infrared power levels would be about 0.5 mW average power at 30 Hz, and 200 watts peak power. These figures vary with wavelength, and would be smaller in the 3.5 micron region, at the end of the OPO gain curve.

The parametric oscillator crystal can be damaged by too high peak pump laser power. A good safe maximum is 0.75 mJ per pulse. Since this translates into about 8 kW peak power, or 22 mW average power at 30 Hz, it is also close to a safe maximum for the pump laser. The actual damage threshold may be much above these figures, according to people who have enough money to find out.

For a well adjusted parametric oscillator, 14 mW average pump laser power should be enough to produce red light in almost any spectral region, and 16 mW should be enough to give stable operation.

Although no experimental measurements were taken with the intracavity etalon and external spectrum analyzer, a good deal of time was spent in characterizing them. Here we shall simply state the progress made in finding the properties of the etalon and spectrum analyzer, and then describe their alignment procedures.

165

We have three intracavity Fabry-Perot etalons, numbered EY 45, 46, and 57, with finesses (free spectral range divided by bandwidth) of 4, 7, and 11 respectively. They are solid, temperature tuned etalons, all with a bandwidth of about 0.6 cm^{-1} and coated for the region of 2.7 to 3.3 microns. The etalon temperature controller also has a knob which allows matching the OPO modes to the peak of the etalon window. This is done by changing the cavity length by means of a piezoelectric transducer on the output mirror. The number of cavity modes passed by the etalon can be checked using an external etalon, or spectrum analyzer (Spectra-Physics model 422). This is also scanned by a piezoelectric transducer, controlled by a Lambda model 4 power supply.

Briefly, the following characteristics have been observed. The spectrum analyzer indicates that single mode operation can be obtained using the two highest finesse etalons, with the finesse of 4 etalon passing between 1 and 3 modes. Single mode operation can be stable in frequency for periods of 5 to 15 minutes. Using the etalon temperature control one can move from one OPO cavity mode to the next. This mode spacing is 10 to 20 etalon temperature units. This spacing, around 0.04 cm^{-1}, is also around 35 to 40 volts for the spectrum analyzer. It is also consistently about 300 volts on the OPO cavity piezoelectric control, although this shows some unpredictable behavior in between transmission peaks. The free spectral range of the etalon is on the order of 100 temperature units

on the etalon oven control, and that of the spectrum analyzer is 200 to 220 volts.

Finally, we discuss the alignment of the etalon and spectrum analyzer. In aligning the etalon, one should take the same precautions in regard to temperature and laser power as were described for mirror alignment. Three very faint spots will be seen on a scatter screen placed behind the output mirror. The two that move toward each other as the etalon is tilted are the ones to superimpose. (An equivalent procedure is to superimpose the two spots that can be seen between the OPO lens and the input mirror.)

The spectrum analyzer is aligned using a Spectra-Physics model 132 helium-neon laser, an iris to prevent reflections from interfering with the laser output, a photodiode, and the 90 volt sawtooth wave generated by an oscilloscope at a time base setting of around 10 msec/cm, used to drive the piezo-electric transducer. Alignment begins by centering the He-Ne laser spot on the input lens of the spectrum analyzer and tilting and translating until the laser comes through. Roughly align by watching the reflections off the spectrum analyzer onto the iris. When the system is well aligned, four spots are seen, one small bright spot, one small rather weak spot, one medium-sized very dim spot, and one large bright spot. The best alignment is when the second and fourth spots, and probably the third, are superimposed.

Final adjustments on the spectrum analyzer are made by

changing the mirror separation while looking at the pattern
on the oscilloscope due to the transmitted light detected by
the photodiode with changing ramp voltage. As shown in
Figure 38, the pattern consists of repeated scans of the
He-Ne laser output. The object in alignment is to maximize
the sharpness of the peaks.

To allow changing mirror separation, one of the spectrum
analyzer mirrors is on a screw thread mount, adjusted with a
special tool. When starting from the beginning, turn the screw
all the way in and slowly back it out, about two revolutions.
Each time the separation is changed the tilt has to be adjusted.
If the scope pattern moves to the right as the tilt is adjusted
then the separation screw should be turned in, and vice versa.
Alignment is achieved when the resolution of the laser peaks
is maximized and when they decrease in amplitude without moving
either to the right or to the left when the spectrum analyzer
is tilted.

Figure 38a: Oscilloscope trace of He-Ne
laser output detected through the spectrum
analyzer driven by the 90 volt ramp from
the scope. The x scale is 10 msec/cm and
the y scale is 0.2 volts/cm. The spectrum
analyzer was using the number 18 mirrors.

Figure 38b: The same, but using number 7
mirrors. These mirrors give much sharper
peaks, and were used during the studies
of the internal etalon in the 3.5 micron
region of the infrared.
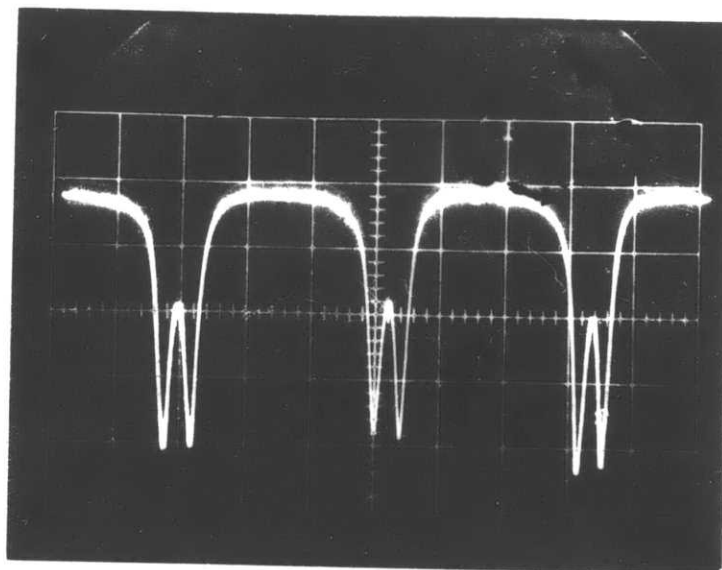
Figure 38a

Figure 38b

170
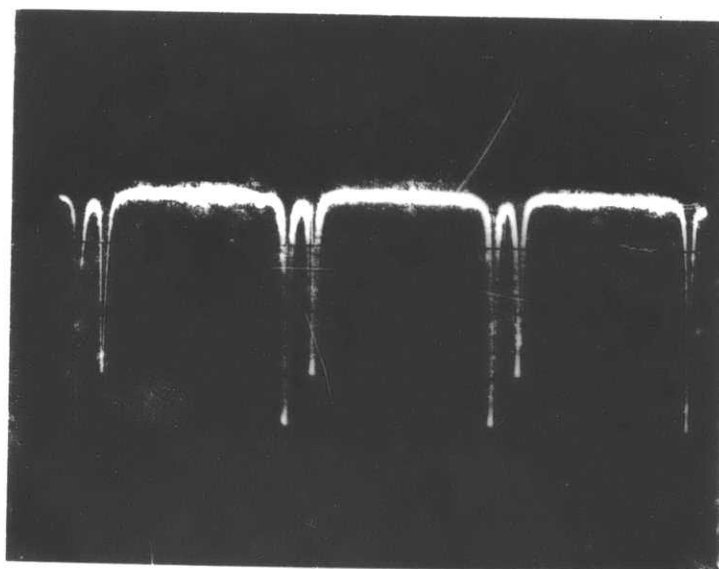
Appendix B : Sample Cell and High Pressure System

This appendix details the construction and components
of the high pressure and vacuum system. A rough sketch of
the window mounting of the monel sample cell is given in
Figure 39. This design has the advantage that the high
pressure is held in by the large outer bolts, and can only
seat the sapphire window more firmly onto its O-ring. The
plate and small screws need only hold the window against the
one atmosphere pressure encountered when the cell is
evacuated. (Both inner and outer screws should be tightened
using a torque screwdriver for even compression of the
O-rings and to avoid cracking a window.)

Figure 40 is a schematic diagram of the metal part of
the high pressure and vacuum system. High pressures, up to
2000 pounds per square inch of argon, are measured by a
Heise stainless steel Bourdon gauge with 5 psi divisions,
calibrated to within 2 psi. The sample pressures (typically
a few torr) are measured with a U-tube manometer with one
monel arm and one glass arm. It is filled with 13-21
Halocarbon oil (specific gravity 1.9).

In filling the cell, one normally takes the sample gas
trapped between the two valves on the lecture bottle and
expands it into the rest of the system. After measuring the
pressure with the oil manometer, the valve to the cell is
closed and the rest of the system is evacuated through a
liquid nitrogen trap in the glass system. (Alternatively,

171

after the cell valve is closed most of the remaining sample gas can be frozen out into the stainless steel trap marked N in Figure 40, for reuse.) The high pressure argon is first put into the system up to the cell valve. Then the valve is opened, causing argon to fill the cell to the desired pressure on the gauge, without allowing the sample gas to escape.

Figure 39: A sketch of the window
assembly of the monel sample cell.
A parts list is given in Table 10.

Figure 40: A block diagram of the
high pressure system. A parts list
is given in table 11.

174

A

C

B

D

E

F
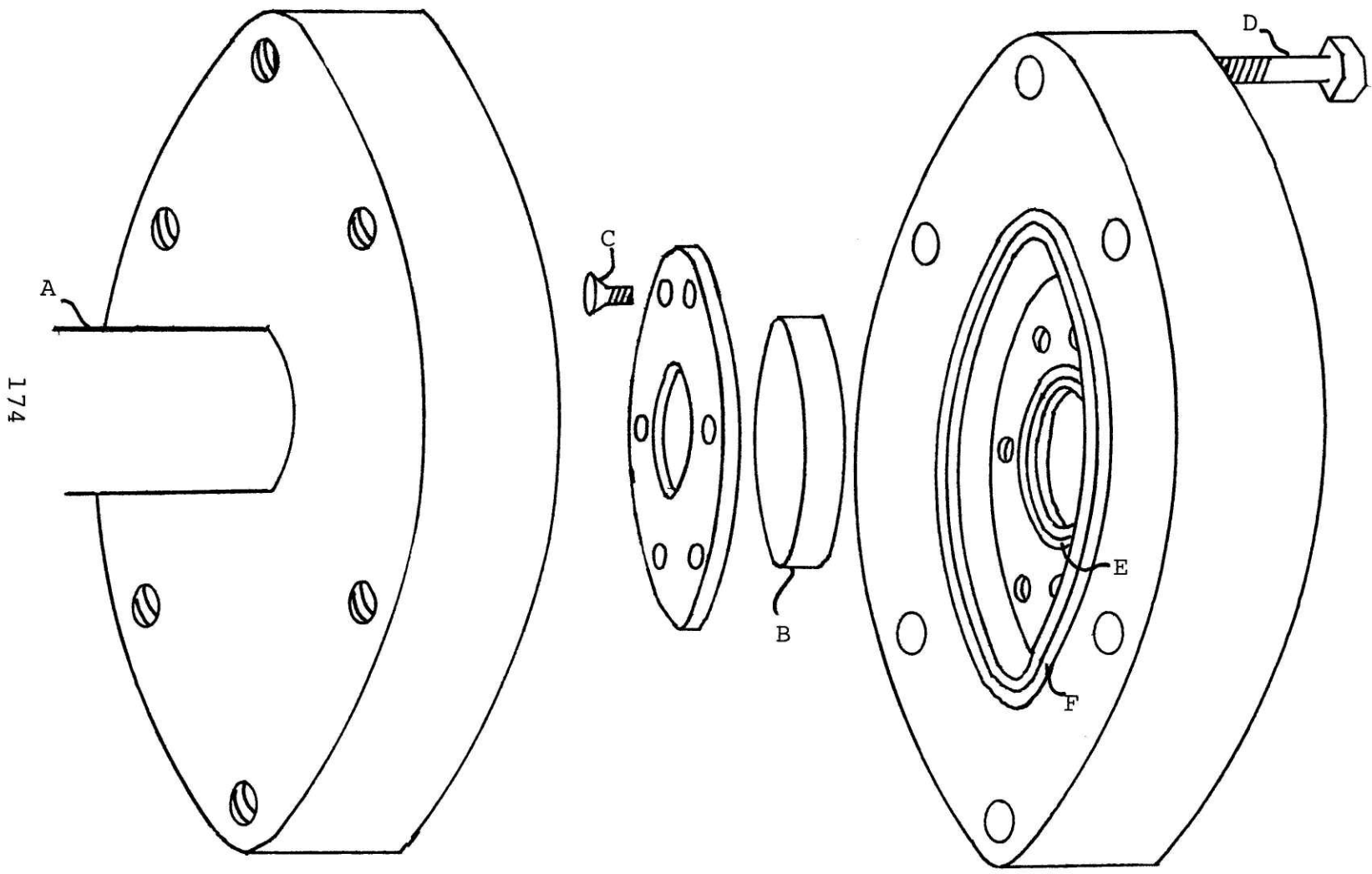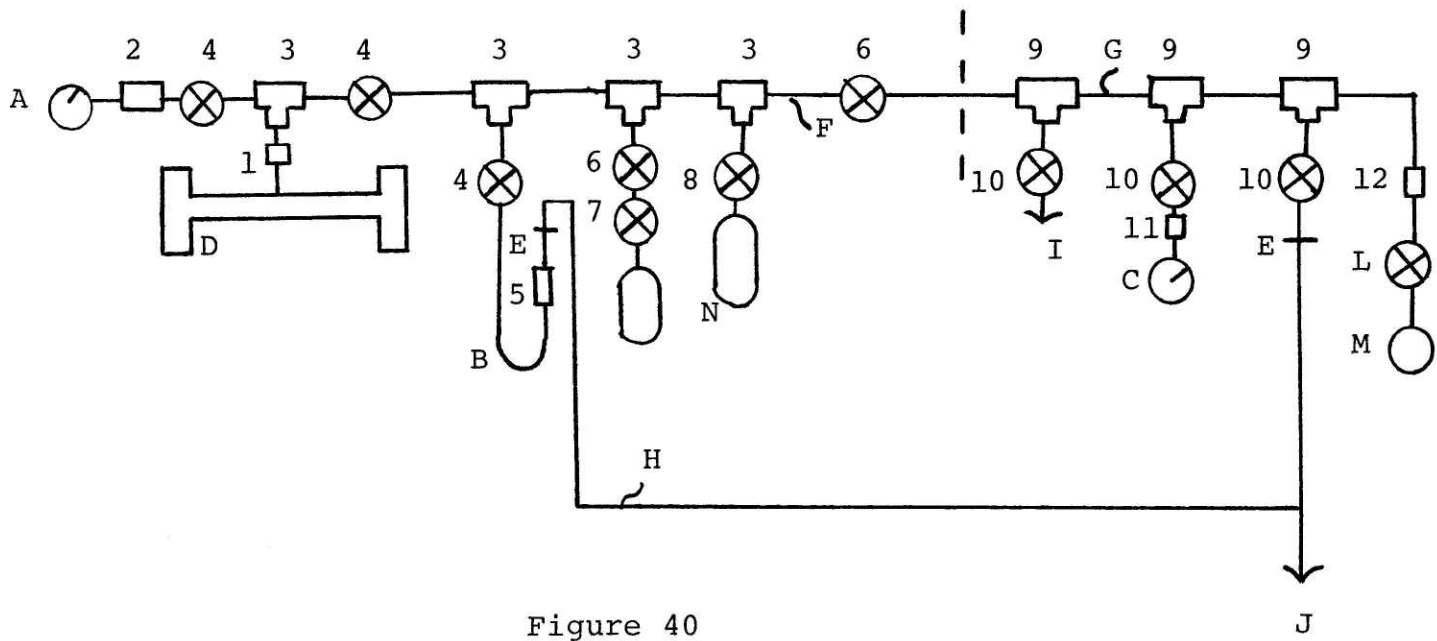
Figure 39

Figure 40

Table 10: Parts List for Figure 39, Monel Sample Cell

A. 20" by 1/2" schedule 40 monel pipe

B. 1" diameter, 1/4" thick sapphire windows (Adolf Meller)

C. 6-32 3/8" flat head monel screws

D. 1/4-20 1 1/2" hex head steel bolts

E. Teflon 018 O-ring, 3/4" i.d., 1/16" width

F. Teflon 226 O-ring, 2" i.d., 1/8" width

Table 11: Parts List for Figure 40, High Pressure System

1. M-400-6 Swagelock monel union

2. 400-1-4-316 Swagelock stainless steel 1/4" male

    pipe thread connector

3. M-400-3 Swagelock monel union tee joint

4. 1VS4-M Whitey monel valve

5. 400-6-316 Swagelock stainless steel union

6. 1RS4-M Whitey monel regulating valve

7. Matheson 60L monel valve

8. 1VS4-M4-A-316 Whitey stainless steel angle valve

9. 400-3-316 Swagelock stainless steel union tee joint

10. 1VS4-316 Whitey stainless steel valve

11. 810-6-4-316 Swagelock stainless steel reducing union

12. B-400-1-4 Swagelock brass 1/4" male pipe thread connector

Table 11: (continued)

A. Heise 8 1/2" Bourdon gauge with 1/4" female pipe thread
    fitting

B. Oil manometer with 1/4" o.d. monel and 3/16" o.d. glass
    tubing

C. Consolidated Electrodynamics GP-140 vacuum gauge with
    GP-001 Pirani tube

D. Monel sample cell

E. Glass to metal seal

F. 1/4" o.d. by .049" wall monel tubing

G. 1/4" o.d. stainless steel tubing

H. 5/16" o.d. glass tubing

I. Tygon tubing leading to hood

J. Glass vacuum manifold and mechanical pump

K. Sample lecture bottle

L. Matheson 4-580 high pressure regulator

M. Argon cylinder

N. Trap, Matheson 6-635-2520 500 ml stainless steel sampling
cylinder with 1/4" female pipe thread fitting

Appendix C : <u>Integrator Description and Operation</u>

In order to do absorption spectroscopy using a pulsed laser it is necessary to transform the size of a voltage pulse on the order of 100 nsec in width into a form whose amplitude can be measured, in our case by the analog to digital converter of the PDP-8/L computer. This could be done by integration using a simple RC circuit. Indeed, this was originally attempted, but there was found to be a complication. Just before the laser pulse there occurs a large pulse of electrical noise, which when integrated contributes the larger part of the total signal.

In order to reject this noise, a switch is placed in front on the integrator, here a very fast FET switch which can be opened just long enough to admit the laser pulse. This type of switch means that the integration must be done by an operational amplifier integrator circuit, a block diagram of which was given in Figure 2. In this circuit, with its extremely long decay time, integration results in a nearly constant voltage on the integrating capacitor. This voltage is read by the computer and then returned to zero by a second switch across the capacitor.

This appendix describes the operation of the op-amp integrator, referring to the schematic drawing of the front and back panels in Fig 41. The detailed integrator circuitry is shown in Figure 42, the triggering circuitry in Figure 43, and the physical placement of the components in Figure 44.

179

A list of the potentiometers and capacitors involved in the adjustments on the front and back panels is given in Table 12.

The laser power supply produces two types of trigger pulses, one associated with the discharging of the flashlamp and one synchronized with the windows in the Q-switch RF. However, the actual laser pulse occurs at varying times after the lamp trigger. And the Q-switch is free-running with a reset before each lamp flash, meaning that there are many Q-switch windows, only one of which contains the laser pulse.

The problem of positioning the input switch window in time so that it falls directly on the laser pulse is solved by using an integrated circuit known as a 74107 JK flip-flop. Briefly, this is an integrated circuit whose output voltage will change state upon receiving a certain sequence of pulses. Here, the lamp trigger pulse from the laser power supply (connected from Lamp Sync Out on the laser power supply to the lamp trigger input on the integrator box) gives rise to a longer voltage pulse referred to as the stretched lamp pulse. The length of this pulse can be adjusted so that it drops to zero just before the chosen Q-switch pulse, the one before that containing the laser pulse. (This lamp trigger stretch adjustment, monitored by the stretched lamp trigger output, can be useful in maximizing the stability of the triggering circuitry, which is touchy and not well understood.) At the trailing edge of this pulse the output voltage of the JK flip-flop (monitored at the Q-switch trigger output on the

180

Figure 41: Location of adjustment
potentiometers and BNC connectors on
integrator box panels.

Figure 42: Operational amplifier
integrator and post-amplifier
circuit diagram.

Figure 43: Input and integrator
switch trigger circuit.

Front Panel

Input Switch Out

Channel Zero In
Channel Zero Out
Channel One In
Channel One Out

Trigger Out
Test Out

Input Window Position
Input Window Width

Channel Zero Tilt
Channel Zero Level

Channel One Tilt
Channel One Level

Idiot Light
Power Switch

182

Back Panel

Integ Switch Out
Lamp Trigger In
Str Lamp Trigger Out
Q-Switch Trigger In
Flip-Flop Out

+5 V
-10 V
+10 V
Ground

Integ Switch Position
Integ Switch Width
Lamp Trigger Stretch
Trigger-Test Position
Test Width
Test Voltage Divider

Fuse
Power

Figure 41

Figure 42

Figure 43

184

Figure 44: In this drawing, components of
the operational amplifier integrator are
represented by boxes of the appropriate size
and shape rather than by conventional circuit
diagram symbols. In addition, resistors are
denoted by —▯▯▯▭⊢ , and zener diodes by ⊣▯▭⊢ .
The notation "Wiper" on one resistor in the
biasing network on the front side of the input
switch indicates that it is attached to the
center post of the bias potentiometer on the
front panel, while the other two resistors are
attached to each side. The two boxes labeled
"Transistor" actually include a number of resistors,
as shown in the circuit diagram Figure 43. Also,
the resistors and capacitors associated with the
trigger integrated circuits are omitted. The
wiring is color coded, with the signal represented
by red (- - - in the drawing) as much as possible.
The logic connections are gray wire, ground is green,
and the +5 V power supply for the logic is blue.
The plus and minus 10 V from the dual power supplies
are purple and black, and the plus and minus 5 V
obtained through the zener network are yellow and
white, respectively.

185

Figure 44

186
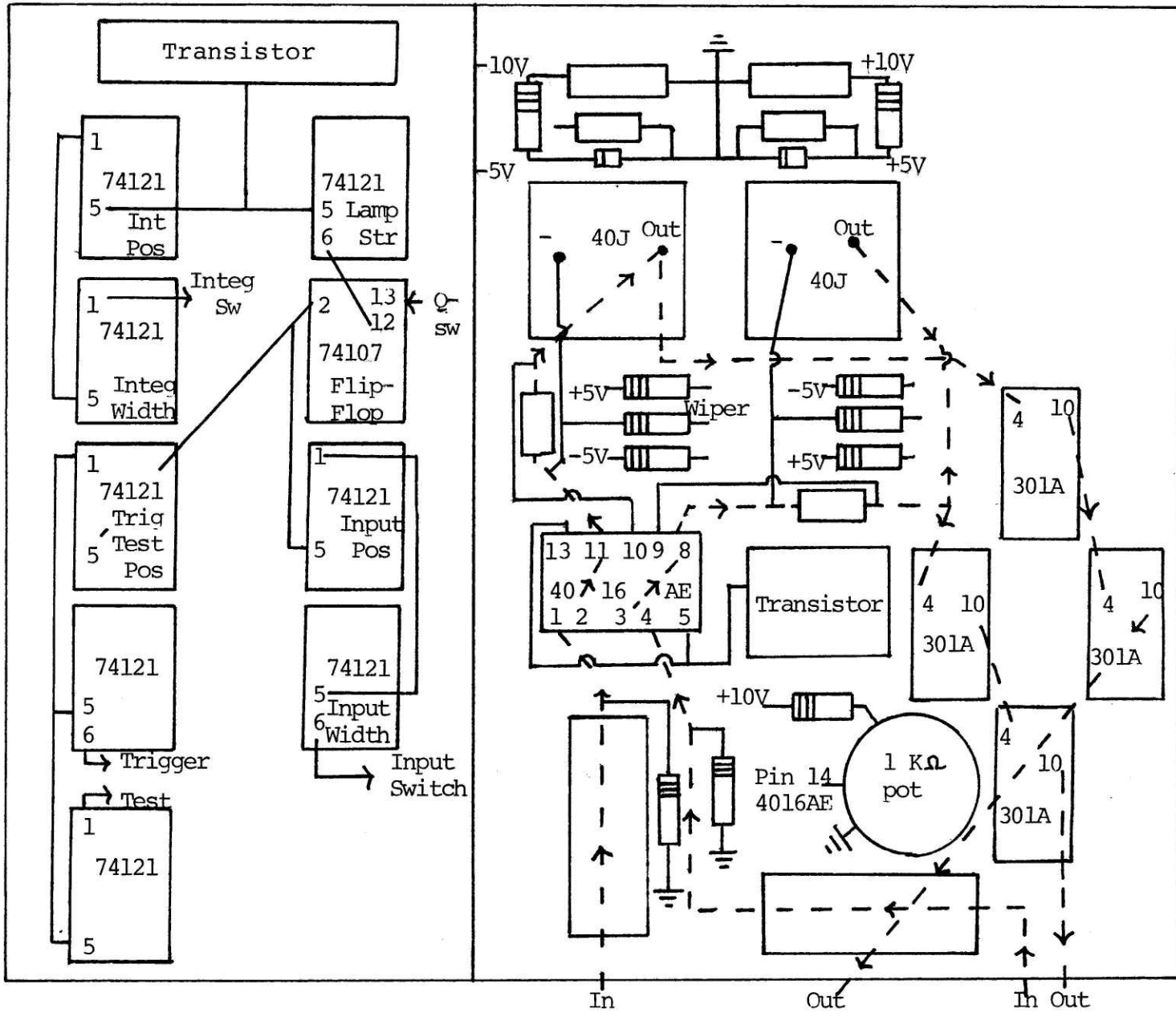
Figure 45: Bias circuit used for Mullard
RPY77 InSb infrared detector. A somewhat
different circuit was used for the Ge:Au
detectors (nominal resistance 70 KΩ at
liquid nitrogen temperature). The detector
and a 100 KΩ bias resistor are connected
from the two posts of a 22.5 V battery in
parallel to ground. The oscilloscope monitors
the voltage across the bias resistor.

Figure 46: (a) Wiring diagram for power supplies.
(b) Zener diode circuit. The zener
diodes are 5 V, 1N 4733.

Figure 45

Detector Battery Box

45 V

2 KΩ

Output
BNC

Input to
Integrator

Detector
BNC

Nominal
Resistance
800

Detector

Fuse

AC

MD-10D

Switch

AC

MM-5H-OV

Light

Ground

Ground
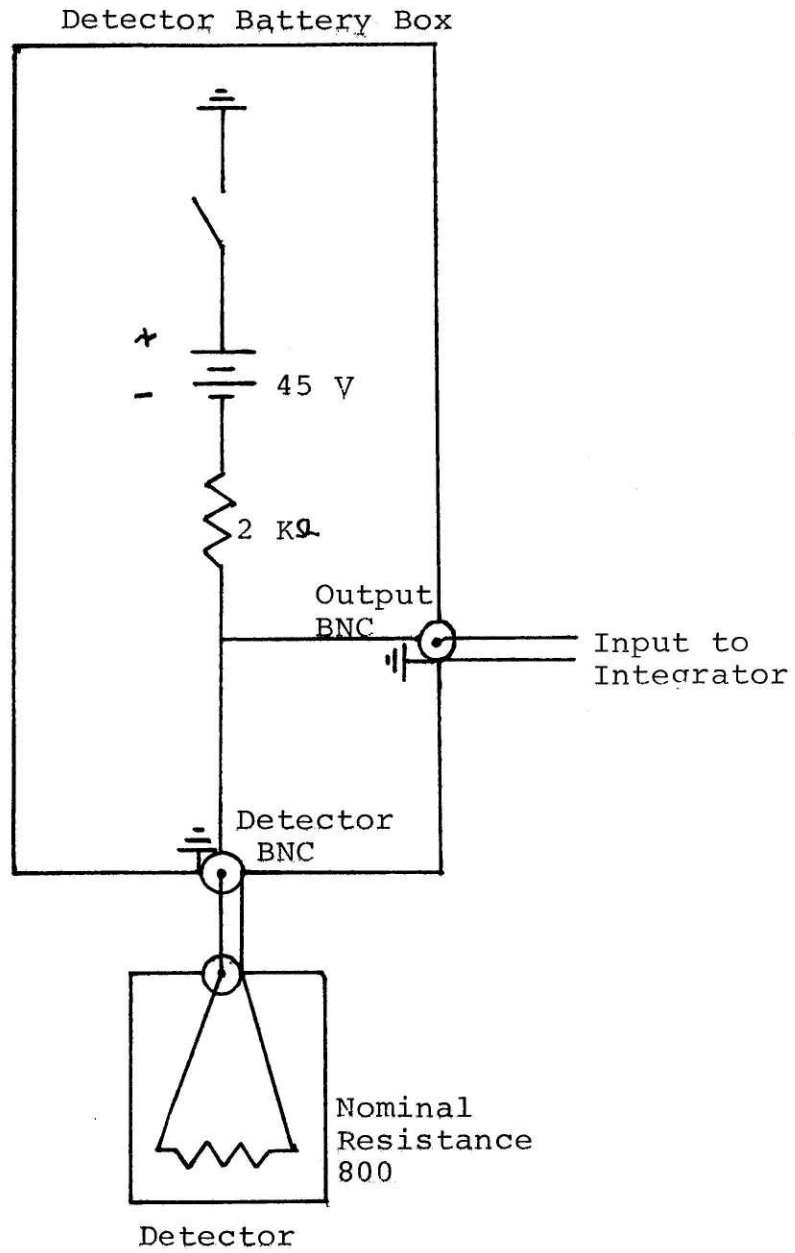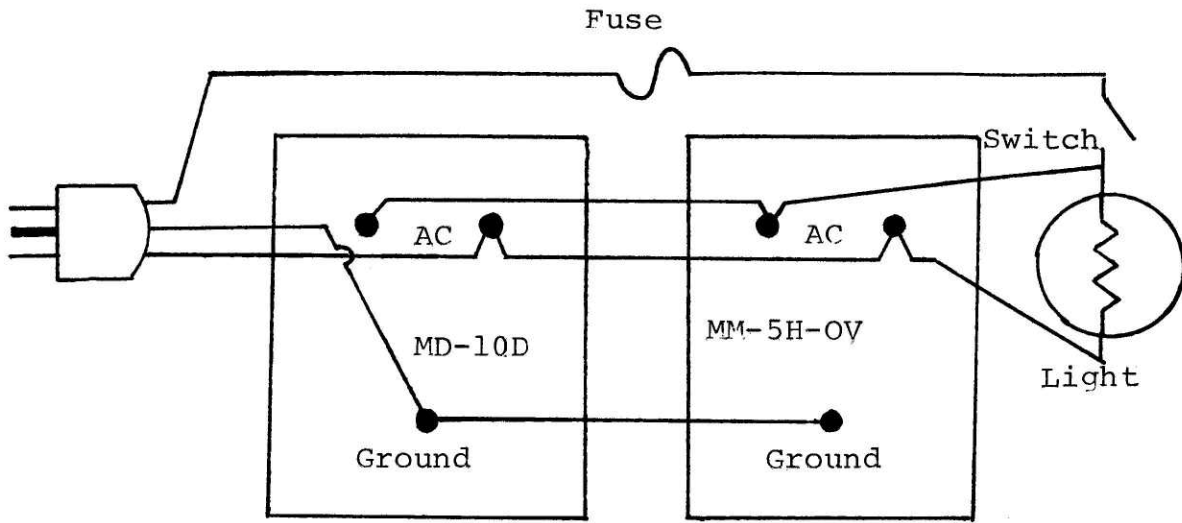
Power Supplies

Figure 46a

+5 V

240 Ω

-5 V

240 Ω

+10 V

-10 V

+

+

10 μF

56 μF

56 μF

10 μF

+

+

Figure   46b

189
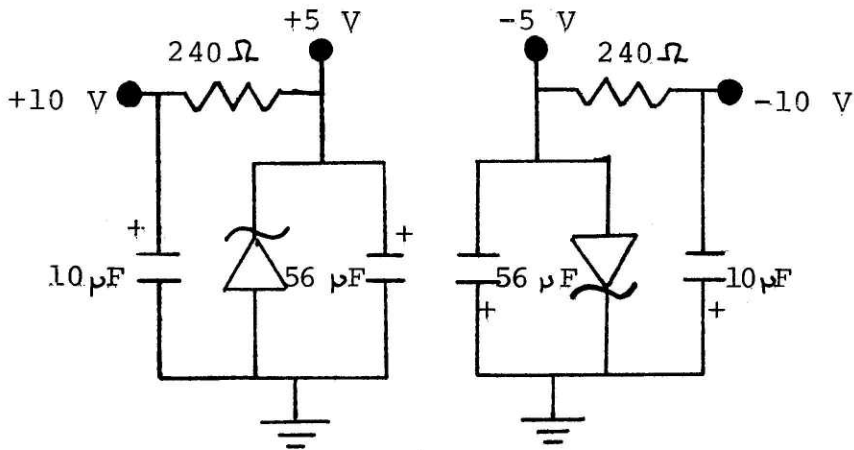
Table 12: Trigger Circuit Potentiometers and Capacitors

Adjustment	Potentiometer	Capacitor	Nominal Time	Nominal Resistance	Maximum Time
Integrator Position	50 K	.047 F	60 sec	2 K	1400 sec
Integrator Width	50	.022	500	35	600
Lamp Stretch	25	.047	150	4.5	900
Trig Test Position	20	.033	250	10	500
Test Width	20	.001	-	0.8	0.2 to 10
Input Width	20	.0022	2	1.3	0.2 to 40
Input Position	20	.033	250	11	500
Trigger Width	-	.001	3	5.1	3

back of the integrator box) becomes negative. It is returned
to zero by the trailing edge of the Q-switch pulse preceding
that containing the laser. (The connection for Q-switch trigger
pulses is from Q-switch Sync Out on the laser power supply to
the Q-switch input on the integrator box.) Thus the trailing
edge of this pulse is synchronized with the Q-switch pulses,
and therefore with the laser pulse (to within some tens of nsec)
and is used to trigger the position of the input switch window.

The laser pulse and the input switch output can be
superimposed using a dual beam scope and the input window
position adjustment. The width can then be adjusted to
eliminate as much noise as possible without cutting out the
laser pulse. There are similar position and width adjustments
for the integrator switch, but they are less critical, since
it only need be opened before the laser pulse and closed after
the computer has read the voltage.

Before the computer can read the voltage levels, the A/D
converter must receive a positive trigger pulse, which can be
obtained from the trigger output on the front of the box. Its
position can be adjusted so that the A/D reads at some time
while the integrator switch is open. (The reading process can
be seen as a small disturbance on the oscilloscope trace of the
of the integrator output.)

The trigger positioning logic also controls a negative
test voltage pulse which can be used to model the laser pulse.
Its width can be adjusted, as can its height through a voltage

divider also located on the back of the box.

When a detector, such as that diagrammed in Figure 45, or its output through an amplifier is plugged into the input of either integrator channel, it has an effect on the integrated voltage level, whether the detector is receiving the laser or not. There are two adjustments which allow normalization with the laser blocked. The tilt adjustment can change the voltage level at the input side of the integrating capacitor so that with the input switch closed it will not integrate a DC voltage level and produce a ramp form. The level adjustment is a trim potentiometer on the integrating operational amplifier. In normal operation, it is used to set the integrator level with the laser blocked to several tenths of a volt, (while using the tilt to produce a horizontal level.) This is done so that small fluctuations in the level do not carry it negative, where it cannot be read by the A/D converter.

The power supplies are a Power-Mate MM-5H-OV supplying a positive 5 volts to the logic board, and a Power-Mate MD-10D giving plus and minus 10 volts. (These outputs and ground can be accessed at banana plugs on the back of the box.) The plus 10 volts is cut down to around 7.7 volts using a voltage divider before powering the FET switch, to prevent leakage of current into the integrating capacitor. The plus and minus 10 volts are also reduced to plus and minus 5 volts by a zener diode network, in order to power the bias adjustment on the integrating operational amplifier. Figure 46 shows the power

192

supply wiring and the zener diode circuit.

Appendix D : Computer Programs

In the following pages we reproduce a listing of the machine language program Ratio Averager which reads the integrated outputs of the cell and reference detectors through the analog to digital converter, then ratios and stores them. We also list modifications which periodically output the ratio into the digital to analog converter and a chart recorder, or onto punched tape. The original program was written and commented by Paul Houston. Here we present additional remarks on the functions of the various subroutines, after which we will demonstrate its operation by example. A flow chart is given in Figure 47.

The subroutine COMP compares two binary numbers. It is used to see if the integrated voltages are within the upper and lower acceptable limits. If QB is greater than QS it exits with 1 in the accumulator, while if QB is less than QS it exits with zero. CALIB is a subroutine to set up the calibrate mode, which sets MODE to 1, SLOPE0 and SLOPE1 to 1, and INT1 and INT0 to zero. The initialization subroutine INIT gets and stores the run number, slopes, intercepts, and minimum and maximum voltages, then sets MODE equal to zero. INTEG is a subroutine to convert a floating point number in the floating point accumulator (FLAC) into a binary number in the AC. It is used to convert maximum and minimum voltages into numbers that can be compared with the reading of the A/D converter.

AVRG does the averaging upon receiving an interrupt by the

Figure 47 : Ratio Averager program
flow chart.

Figure 47

196
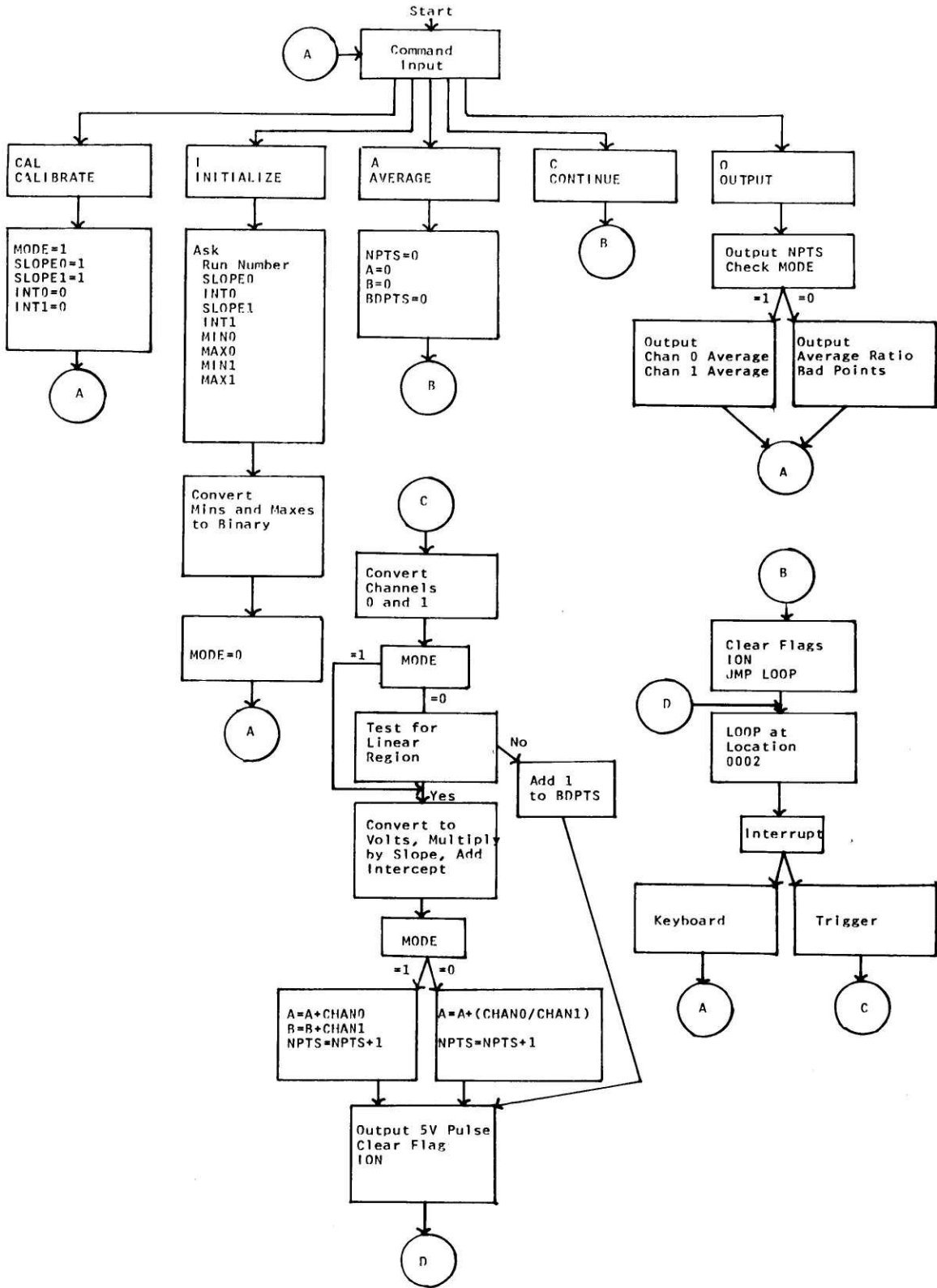
(Text resumes on page 220.)

```
                   ORIGINAL RATIØ AVERAGER   TAPE 1
                           *0000
    0000   0000   0
    0001   5531             JMP I SSERV
    0002   5002   LØØP,     JMP .
                           *0007
    0007   5600             5600      /PØINTER TØ FP PKG 3
                           *0044
    0044   0000   FLAC,     0
    0045   0000             0
    0046   0000             0
                           *0055
    0055   0001             0001      /FØR CR AFTER ØUTPUT
    0056   7777             7777      /FØR LF AFTDR ØUTPUT
    0057   0000             0
    0060   0000             0
    0061   0000             0
                           *70
    0070   0000   AC,       0
    0071   0000   L,        0
    0072   0000   BUFF,     0
    0073   0200   TRUN,     200
    0074   4000   TEXT,     4000
    0075   0240   TSLØP0,   240
    0076   0300   TINT0,    300
    0077   0340   TSLØP1,   340
    0100   0400   TINT1,    400
    0101   0000   RUN,      0
    0102   0000             0
    0103   0000             0
    0104   0000   SLØP0,    0
    0105   0000             0
    0106   0000             0
    0107   0000   INT0,     0
    0110   0000             0
    0111   0000             0
    0112   0000   SLØP1,    0
    0113   0000             0
    0114   0000             0
    0115   0000   INT1,     0
    0116   0000             0
    0117   0000             0
    0120   0000   NPTS,     0
    0121   0000             0
    0122   0000             0
    0123   0000   A,        0
    0124   0000             0
    0125   0000             0
    0126   3400   SCØMP,    CØMP
    0127   1000   SØUT,     ØUT
    0130   3000   SINIT,    INIT
    0131   1200   SSERV,    SERV
    0132   1400   SINPT,    INPT
    0133   3600   SAVRG,    AVRG
    0134   1022   SCRLF,    CRLF
    0135   1300   SSTRT,    STRT
    0136   2400   SFINI,    FINI
    0137   1030   STYPE,    TYPE
    0140   2200   SCLEAR,   CLEAR
    0141   2600   SCALIB,   CALIB
    0142   0000   MINO,     0
    0143   0000   MIN1,     0
    0144   0000   MAXO,     0
    0145   0000   MAX1,     0
```

197

```
0146    3200    SINTEG,   INTEG
0147    0000    QB,       0
0150    0000    QS,       0
0151    0440    TMIN0,    440
0152    0600    TMIN1,    600
0153    0640    TMAX0,    640
0154    0700    TMAX1,    700
0155    0740    TCH0,     740
0156    1000    TCH1,     1000
0157    1040    TBDPT,    1040
0160    0000    BDPTS,    0
0161    0000              0
0162    0000              0
0163    0540    TAV,      540
0164    0500    TPTS,     500
0165    0000    MØDE,     0
0166    0001    ØNE,      0001
0167    2000              2000
0170    0000              0000
0171    0000    B,        0
0172    0000              0
0173    0000              0
0174    0000    ZERØ,     0
0175    0000              0
0176    0000              0
                *200
0200    7300              CLA CLL      /PRØGRAM STARTS HERE
0201    6046              TLS          /T3 SET PRINTER FLAG
0202    5603              JMP I SCF
0203    1604    SCF,      INPT+204
```

```
                    *OUT
1000    0000    OUT,    0               /SUBROUTINE TO OUTPUT TEXT
1001    7300            CLA CLL
1002    7000            NOP
1003    1072            TAD BUFF
1004    3236            DCA BUFFPT
1005    4222            JMS CRLF
1006    1636    CHRTYP, TAD I BUFFPT
1007    1241            TAD MDOLAR
1010    7450            SNA
1011    5217            JMP .+6
1012    7300            CLA CLL
1013    1636            TAD I BUFFPT    /GET A NON-$ CHAR
1014    4230            JMS TYPE        /TYPE IT
1015    2236            ISZ BUFFPT
1016    5206            JMP CHRTYP      /GET ANOTHER CHAR
1017    7300            CLA CLL         /HERE IF $
1020    7300            CLA CLL
1021    5600            JMP I OUT
1022    0000    CRLF,   0
1023    1237            TAD K215
1024    4230            JMS TYPE
1025    1240            TAD K212
1026    4230            JMS TYPE
1027    5622            JMP I CRLF
1030    0000    TYPE,   0
1031    6041            TSF
1032    5231            JMP .-1
1033    6046            TLS
1034    7200            CLA
1035    5630            JMP I TYPE
1036    0000    BUFFPT, 0
1037    0215    K215,   215
1040    0212    K212,   212
1041    7534    MDOLAR, 7534
                    *SERV
1200    3070    SERV,   DCA AC          /SERVICE SUBROUTINE
1201    7004            RAL
1202    3071            DCA L
1203    6031            KSF             /KEYBOARD?
1204    7410            SKP             /NO
1205    4532            JMS I SINPT     /YES
1206    6301            SLTF            /TRIGGER
1207    7410            SKP             /NO
1210    4533            JMS I SAVRG     /YES
1211    7410            SKP
1212    7777    K7777,  7777
1213    1212            TAD K7777       /A HALT SHOWING 7777
1214    6041            TSF             /INDICATES ILLEGAL INTERUPT
1215    7410            SKP
1216    7402            HLT
1217    6021            PSF
1220    7410            SKP
1221    7402            HLT
1222    6011            RSF
1223    7410            SKP
```

```
1224    7402            HLT
1225    6531            ADSF
1226    7410            SKP
1227    7402            HLT
1230    7402            HLT             /ROOM FOR OTHER FLAG TESTS BELOW
                *STRT
1300    0000    STRT,   0
1301    7300            CLA CLL
1302    4407            FENT
1303    5174            FGET ZERO
1304    6120            FPUT NPTS
1305    6123            FPUT A
1306    6171            FPUT B
1307    6160            FPUT BDPTS
1310    0000            FEXT
1311    5700            JMP I STRT
                *INPT
1400    0000    INPT,   0               /SERVICES INTERUPT BY KEYBOARD
1401    7300            CLA CLL
1402    6046            TLS             /TO SET PRINT FLAG
1403    1074            TAD TEXT
1404    3222            DCA TXTPT
1405    6211            CDF +10
1406    6031    CRLA,   KSF
1407    5206            JMP .-1
1410    6036            KRB
1411    6046            TLS
1412    3622            DCA I TXTPT     /READS CHARACTER PRINTS IT
1413    1622            TAD I TXTPT     /AND STORES IT
1414    1221            TAD MCR         /TEST FOR CR
1415    7450            SNA
1416    5223            JMP .+5
1417    2222            ISZ TXTPT       /GET MORE
1420    5206            JMP CRLA
1421    7563    MCR,    7563
1422    0000    TXTPT,  0
1423    4534            JMS I SCRLF     /INPUT TERMINATED
1424    7300            CLA CLL
1425    1222            TAD TXTPT
1426    3245            DCA TXTEND
1427    1074            TAD TEXT
1430    3222            DCA TXTPT
1431    3246            DCA COMND
1432    1622            TAD I TXTPT
1433    1246            TAD COMND
1434    3246            DCA COMND       /EVALUATING COMMAND
1435    1245            TAD TXTEND
1436    7041            CIA
1437    2222            ISZ TXTPT
1440    1222            TAD TXTPT
1441    7450            SNA
1442    5247            JMP .+5
1443    7300            CLA CLL
1444    5232            JMP .-12        /GET MORE OF COMMAND
1445    0000    TXTEND, 0
1446    0000    COMND,  0
1447    7300            CLA CLL         /EXECUTE COMMAND
1450    6201            CDF +00
1451    1246            TAD COMND       /INITIALIZE ?
1452    7041            CIA
1453    1347            TAD CINIT
1454    7440            SZA
1455    5260            JMP .+3
1456    4530            JMS I SINIT
```

200

```
1457    5760            JMP I SCMT
1460    7300            CLA CLL
1461    1246            TAD CØMND
1462    7041            CIA
1463    1350            TAD CI
1464    7440            SZA
1465    5270            JMP .+3
1466    4530            JMS I SINIT
1467    5760            JMP I SCMT
1470    7300            CLA CLL          /AVERAGE ?
1471    1246            TAD CØMND
1472    7041            CIA
1473    1352            TAD CA
1474    7440            SZA
1475    5300            JMP .+3
1476    4535            JMS I SSTRT
1477    5361            JMP BACK
1500    7300            CLA CLL
1501    1246            TAD CØMND
1502    7041            CIA
1503    1351            TAD CAVER
1504    7440            SZA
1505    5310            JMP .+3
1506    4535            JMS I SSTRT
1507    5361            JMP BACK
1510    7300            CLA CLL          /ØUTPUT ?
1511    1246            TAD CØMND
1512    7041            CIA
1513    1354            TAD CØ
1514    7440            SZA
1515    5320            JMP .+3
1516    4536            JMS I SFINI
1517    5760            JMP I SCMT
1520    7300            CLA CLL
1521    1246            TAD CØMND
1522    7041            CIA
1523    1353            TAD CØUT
1524    7440            SZA
1525    5330            JMP .+3
1526    4536            JMS I SFINI
1527    5760            JMP I SCMT
1530    7300            CLA CLL          /CØNTINUE ?
1531    1246            TAD CØMND
1532    7041            CIA
1533    1356            TAD CC
1534    7440            SZA
1535    5337            JMP .+2
1536    5361            JMP BACK
1537    7300            CLA CLL
1540    1246            TAD CØMND
1541    7041            CIA
1542    1355            TAD CCØNT
1543    7440            SZA
1544    5346            JMP .+2
1545    5361            JMP BACK
1546    5757            JMP I CPGE       /NØ MØRE CØMMANDS, GET ØN NEXT PAGE
1547    3762    CINIT,  3762             /SUM ØF LETTERS IN INITIALIZE
1550    0311    CI,     311
1551    2573    CAVER,  2573
1552    0301    CA,     301
1553    2361    CØUT,   2361
1554    0317    CØ,     317
1555    3145    CCØNT,  3145
1556    0303    CC,     303
1557    1600    CPGE,   1600
```

201

```
1560    1604    SCMT,   SCMX
1561    7300    BACK,   CLA CLL
1562    6041            TSF                 /HAVE TO MAKE SURE PRINTER WAS
1563    5362            JMP .-1             /BEFORE WE TRY TO CLEAR ITS FLAG
1564    4540            JMS I SCLEAR
1565    6001            ION
1566    5002            JMP LOOP
                *INPT+200
1600    5215            JMP BELO            /FOR MORE COMMANDS
1601    7300    XT,     CLA CLL
1602    1211            TAD CQ
1603    4537            JMS I STYPE
1604    7300    SCMX,   CLA CLL
1605    1212            TAD CC0
1606    4537            JMS I STYPE
1607    5610            JMP I CRD
1610    1403    CRD,    INPT+3
1611    0277    CQ,     277
1612    0272    CC0,    272
1613    1120    CAL,    1120
1614    3407    CCAL,   3407
1615    7300    BELO,   CLA CLL
1616    1636            TAD I CMND
1617    7041            CIA
1620    1213            TAD CAL
1621    7440            SZA
1622    5225            JMP .+3
1623    4541            JMS I SCALIB
1624    5204            JMP SCMX
1625    7300            CLA CLL
1626    1636            TAD I CMND
1627    7041            CIA
1630    1214            TAD CCAL
1631    7440            SZA
1632    5235            JMP .+3
1633    4541            JMS I SCALIB
1634    5204            JMP SCMX
1635    5201            JMP XT
1636    1446    CMND,   COMND
```

```
                  *CLEAR
2200   0000    CLEAR,   0
2201   6022             PCF      /HSP
2202   6032             KCC      /TTY
2203   6302             CLTF     /TRIGGER
2204   6534             ADRB     /AD CONV
2205   6042             TCF      /TTY
2206   6012             RRB      /HSR
2207   7300             CLA CLL
2210   5600             JMP I CLEAR
                  *FINI
2400   0000    FINI,    0                        /SUBROUTINE TO OUTPUT ANSWERS
2401   7300             CLA CLL
2402   6046             TLS                       /TO SET PRINTER FLAG
2403   1164             TAD TPTS
2404   3072             DCA BUFF
2405   6211             CDF +10
2406   4527             JMS I SOUT
2407   6201             CDF +00
2410   4407             FENT
2411   5120             FGET NPTS
2412   0014             OUTPUT
2413   0000             FEXT
2414   7300             CLA CLL
2415   1165             TAD MODE             /CHECK FOR MODE
2416   7650             SNA CLA              /CALIBRATE?
2417   5221             JMP .+2              /NO
2420   5251             JMP X1               /YES
2421   1163             TAD TAV
2422   3072             DCA BUFF
2423   6211             CDF +10
2424   4527             JMS I SOUT
2425   6201             CDF +00
2426   4407             FENT
2427   5123             FGET A
2430   4120             FDIV NPTS
2431   7000             FNOR
2432   0014             OUTPUT
2433   0000             FEXT
2434   7300             CLA CLL
2435   1157             TAD TBDPT
2436   3072             DCA BUFF
2437   6211             CDF +10
2440   4527             JMS I SOUT
2441   6201             CDF +00
2442   4407             FENT
2443   5160             FGET BDPTS
2444   7000             FNOR
2445   0014             OUTPUT
2446   0000             FEXT
2447   7300             CLA CLL
2450   5600             JMP I FINI           /DONE
2451   7300    X1,      CLA CLL              /HERE IF CALIBRATE MODE
2452   1155             TAD TCHO
2453   3072             DCA BUFF
2454   6211             CDF +10
2455   4527             JMS I SOUT
2456   6201             CDF +00
2457   4407             FENT
```

203

```
2460    5123        FGET A
2461    4120        FDIV NPTS
2462    7000        FNOR
2463    0014        OUTPUT
2464    0000        FEXT
2465    7300        CLA CLL
2466    1156        TAD TCH1
2467    3072        DCA BUFF
2470    6211        CDF +10
2471    4527        JMS I SOUT
2472    6201        CDF +00
2473    4407        FENT
2474    5171        FGET B
2475    4120        FDIV NPTS
2476    7000        FNOR
2477    0014        OUTPUT
2500    0000        FEXT
2501    7300        CLA CLL
2502    5600        JMP I FINI      /DONE
```

```
                    *CALIB
2600    0000    CALIB,    0              /HANDLES CALIBRATE COMMAND
2601    7300              CLA CLL
2602    7001              IAC
2603    3165              DCA MODE        /SET MODE=1 INDICATING CALIBRATE MODE
2604    4407              FENT
2605    5166              FGET ONE
2606    6104              FPUT SLOP0
2607    6112              FPUT SLOP1
2610    5174              FGET ZERO
2611    6107              FPUT INT0
2612    6115              FPUT INT1
2613    0000              FEXT
2614    5600              JMP I CALIB
                    *INIT
3000    0000    INIT,     0              /INITIALIZATION SUBROUTINE
3001    7300              CLA CLL         /TO GET RUN NUMBER SLOPES
3002    6046              TLS             /AND INTERCEPTS
3003    1073              TAD TRUN        /TLS SETS TTY FLAG
3004    3072              DCA BUFF
3005    6211              CDF +10         /TEXT IS IN UPPER 4K
3006    4527              JMS I SOUT      /ASK FOR RUN NUMBER
3007    6201              CDF +00
3010    4407              FENT
3011    0013              INPUT           /GET RUN NUM AND STORE
3012    7000              FNOR
3013    6101              FPUT RUN
3014    0000              FEXT
3015    7300              CLA CLL
3016    1075              TAD TSLOP0              /GET SLOP0
3017    3072              DCA BUFF
3020    6211              CDF +10
3021    4527              JMS I SOUT
3022    6201              CDF +00
3023    4407              FENT
3024    0013              INPUT
3025    7000              FNOR
3026    6104              FPUT SLOP0
3027    0000              FEXT
3030    7300              CLA CLL         /GET INT0
3031    1076              TAD TINT0
3032    3072              DCA BUFF
3033    6211              CDF +10
3034    4527              JMS I SOUT
3035    6201              CDF +00
3036    4407              FENT
3037    0013              INPUT
3040    7000              FNOR
3041    6107              FPUT INT0
3042    0000              FEXT
3043    7300              CLA CLL         /GET SLOP1
3044    1077              TAD TSLOP1
3045    3072              DCA BUFF
3046    6211              CDF +10
3047    4527              JMS I SOUT
3050    6201              CDF +00
3051    4407              FENT
3052    0013              INPUT
```

205

```
3053    7000        FNØR
3054    6112        FPUT SLØP1
3055    0000        FEXT
3056    7300        CLA CLL              /GET INT1
3057    1100        TAD TINT1
3060    3072        DCA BUFF
3061    6211        CDF +10
3062    4527        JMS I SØUT
3063    6201        CDF +00
3064    4407        FENT
3065    0013        INPUT
3066    7000        FNØR
3067    6115        FPUT INT1
3070    0000        FEXT
3071    7300        CLA CLL              /CET MINS AND MAXS
3072    1151        TAD TMIN0
3073    3072        DCA BUFF
3074    6211        CDF +10
3075    4527        JMS I SØUT
3076    6201        CDF +00
3077    4407        FENT
3100    0013        INPUT
3101    7000        FNØR
3102    3364        FMPY F4095
3103    4367        FDIV FTEN
3104    7000        FNØR
3105    0000        FEXT
3106    4546        JMS I SINTEG
3107    3142        DCA MIN0
3110    1153        TAD TMAX0
3111    3072        DCA BUFF
3112    6211        CDF +10
3113    4527        JMS I SØUT
3114    6201        CDF +00
3115    4407        FENT
3116    0013        INPUT
3117    7000        FNØR
3120    3364        FMPY F4095
3121    4367        FDIV FTEN
3122    7000        FNØR
3123    0000        FEXT
3124    4546        JMS I SINTEG
3125    3144        DCA MAX0
3126    1152        TAD TMIN1
3127    3072        DCA BUFF
3130    6211        CDF +10
3131    4527        JMS I SØUT
3132    6201        CDF +00
3133    4407        FENT
3134    0013        INPUT
3135    7000        FNØR
3136    3364        FMPY F4095
3137    4367        FDIV FTEN
3140    7000        FNØR .
3141    0000        FEXT
3142    4546        JMS I SINTEG
3143    3143        DCA MIN1
3144    1154        TAD TMAX1
3145    3072        DCA BUFF
3146    6211        CDF +10
3147    4527        JMS I SØUT
3150    6201        CDF +00
3151    4407        FENT
```

```
3152  0013           INPUT
3153  7000           FNOR
3154  3364           FMPY F4095
3155  4367           FDIV FTEN
3156  7000           FNOR
3157  0000           FEXT
3160  4546           JMS I SINTEG
3161  3145           DCA MAX1
3162  3165           DCA MODE          /FOR REGULAR MODE
3163  5600           JMP I INIT        /DONE
3164  0012  F4095,   0012
3165  3777           3777
3166  4000           4000
3167  0004  FTEN,    0004
3170  2400           2400
3171  0000           0000
             *INTEG
3200  0000  INTEG,   0                 /CONVERTS NUMBER IN FLAC TO
3201  7300           CLA CLL           /AN INTEGER IN THE AC
3202  1044           TAD FLAC
3203  7510           SPA
3204  5242           JMP NEG           /THE FL PT EXPONENT IS NEG
3205  7300           CLA CLL
3206  1046           TAD FLAC+2
3207  0244           AND K4000         /GET LEFT BIT
3210  7450           SNA
3211  5213           JMP .+2
3212  7020           CML
3213  1045           TAD FLAC+1
3214  7004           RAL
3215  7100           CLL
3216  3246           DCA INT
3217  1044           TAD FLAC
3220  1250           TAD M12
3221  7540           SMA SZA
3222  5237           JMP XY            /LARGER THAN 2**12
3223  7500           SMA
3224  5234           JMP XX            /=0
3225  3247           DCA SHFT
3226  1246           TAD INT
3227  7100           CLL
3230  7010           RAR
3231  2247           ISZ SHFT
3232  5227           JMP .-3
3233  5600           JMP I INTEG
3234  7300  XX,      CLA CLL
3235  1246           TAD INT
3236  5600           JMP I INTEG
3237  7300  XY,      CLA CLL
3240  1245           TAD K7777
3241  5600           JMP I INTEG
3242  7300  NEG,     CLA CLL
3243  5600           JMP I INTEG
3244  4000  K4000,   4000
3245  7777  K7777,   7777
3246  0000  INT,     0
3247  0000  SHFT,    0
3250  7766  M12,     7766
             *COMP
3400  0000  COMP,    0
3401  7300           CLA CLL           /DOES ABSOLUTE COMPARISON,
3402  1147           TAD QB            /IE: 4000>3777
3403  7700           SMA CLA
3404  5210           JMP .+4
3405  7240           CLA CMA           /QB IS MINUS
```

207

```
3671    7012            RTR
3672    3045            DCA 45
3673    3046            DCA 46
3674    1342            TAD C13
3675    3044            DCA 44
3676    4407            FENT
3677    7000            FNØR
3700    3335            FMPY TØVØLTS
3701    3104            FMPY SLØP0
3702    1107            FADD INT0
3703    7000            FNØR
3704    6327            FPUT CHAN0
3705    0000            FEXT
3706    7300            CLA CLL
3707    1343            TAD STR1        /THIS CHANGES DIGITAL
3710    7012            RTR             /INFORMATION TØ ACTUAL
3711    3045            DCA 45          /VØLTS. SAME AS ABØVE
3712    3046            DCA 46          /IT ALSØ MULTIPLIES BY
3713    1342            TAD C13         /SLØPE AND ADDS INT.
3714    3044            DCA 44
3715    4407            FENT
3716    7000            FNØR
3717    3335            FMPY TØVØLTS
3720    3112            FMPY SLØP1
3721    1115            FADD INT1
3722    7000            FNØR
3723    6332            FPUT CHAN1
3724    0000            FEXT
3725    7300            CLA CLL
3726    5747            JMP I XY
3727    0000    CHAN0,  0
3730    0000            0
3731    0000            0
3732    0000    CHAN1,  0
3733    0000            0
3734    0000            0
3735    7772    TØVØLTS,7772
3736    2401            2401
3737    2005            2005
3740    7772            7772
3741    2401            2401
3742    0013    C13,    0013
3743    0000    STR1,   0
3744    0000    STR0,   0
3745    0001    K0001,  0001
3746    4042    ØØT,    ØIT
3747    4000    XY,     XZ
                *AVRG+200
4000    7300    XZ,     CLA CLL
4001    1165            TAD MØDE        /CHECK MØDE
4002    7650            SNA CLA
4003    5205            JMP RAT         /NØRMAL MØDE; GET RATIØ
4004    5222            JMP CBRAT
4005    7300    RAT,    CLA CLL
4006    4407            FENT
4007    5120            FGET NPTS
4010    1166            FADD ØNE
4011    7000            FNØR
4012    6120            FPUT NPTS
4013    5652            FGET I CH0
4014    4653            FDIV I CH1
4015    1123            FADD A
4016    7000            FNØR
4017    6123            FPUT A
4020    0000            FEXT
4021    5242            JMP ØIT
```

208

```
3406    3244            DCA SB
3407    5212            JMP .+3
3410    7201            CLA IAC         /QB IS POS OR ZERO
3411    3244            DCA SB
3412    1150            TAD QS
3413    7700            SMA CLA
3414    5226            JMP .+12
3415    1244            TAD SB   /QS IS MINUS
3416    7700            SMA CLA
3417    5242            JMP NO
3420    1150            TAD QS
3421    7041            CIA
3422    1147            TAD QB
3423    7700            SMA CLA
3424    5240            JMP YES
3425    5242            JMP NO
3426    1244            TAD SB          /QS IS PLUS OR ZERO
3427    7700            SMA CLA
3430    5232            JMP .+2
3431    5240            JMP YES
3432    1150            TAD QS
3433    7041            CIA
3434    1147            TAD QB
3435    7700            SMA CLA
3436    5240            JMP YES
3437    5242            JMP NO
3440    7201    YES,    CLA IAC         /QB>QS AC=1
3441    5600            JMP I COMP
3442    7300    NO,     CLA CLL         /QB<QS AC=0
3443    5600            JMP I COMP
3444    0000    SB,     0
```

```
                    *AVRG
3600   0000   AVRG,    0
3601   7300            CLA CLL         /HERE IN 29.3 MICROSEC
3602   6542            ADSC            /SELECT CHANNEL 0
3603   7300            CLA CLL         /AND CONVERT
3604   6531            ADSF            /SKIP WHEN DONE
3605   5204            JMP .-1
3606   6534            ADRB            /READ INTO AC
3607   3344            DCA STR0
3610   1345            TAD K0001
3611   6542            ADSC            /SELECT CHANNEL 1
3612   7300            CLA CLL
3613   6531            ADSF
3614   5213            JMP .-1
3615   6534            ADRB
3616   3343            DCA STR1        /VOLTAGES ARE STORED
3617   1165            TAD MODE        /CHECK MODE
3620   7650            SNA CLA         /CALIBRATE?
3621   5223            JMP .+2
3622   5267            JMP CON         /YES
3623   1344            TAD STR0        /NO
3624   3150            DCA QS
3625   1144            TAD MAX0        /CHAN0<MAX0?
3626   3147            DCA QB
3627   4526            JMS I SCOMP
3630   7650            SNA CLA
3631   5260            JMP BAD         /NO
3632   1344            TAD STR0        /YES; CHAN0>MIN0?
3633   3147            DCA QB
3634   1142            TAD MIN0
3635   3150            DCA QS
3636   4526            JMS I SCOMP
3637   7650            SNA CLA
3640   5260            JMP BAD         /NO
3641   1343            TAD STR1        /YES; CHAN1<MAX1?
3642   3150            DCA QS
3643   1145            TAD MAX1
3644   3147            DCA QB
3645   4526            JMS I SCOMP
3646   7650            SNA CLA
3647   5260            JMP BAD         /NO
3650   1343            TAD STR1        /YES; CHAN1>MIN1?
3651   3147            DCA QB
3652   1143            TAD MIN1
3653   3150            DCA QS
3654   4526            JMS I SCOMP
3655   7650            SNA CLA
3656   5260            JMP BAD         /NO
3657   5267            JMP CON
3660   7300   BAD,     CLA CLL         /HERE IF NOT ON LINEAR REGION
3661   4407            FENT            /OF VOLTAGE CURVE
3662   5160            FGET BDPTS      /INCREMENT BDPTS
3663   1166            FADD ONE
3664   6160            FPUT BDPTS
3665   0000            FEXT
3666   5746            JMP I OOT
3667   7300   CON,     CLA CLL
3670   1344            TAD STR0
```

210

```
3671    7012            RTR
3672    3045            DCA 45
3673    3046            DCA 46
3674    1342            TAD C13
3675    3044            DCA 44
3676    4407            FENT
3677    7000            FNØR
3700    3335            FMPY TØVØLTS
3701    3104            FMPY SLØP0
3702    1107            FADD INTO
3703    7000            FNØR
3704    6327            FPUT CHANO
3705    0000            FEXT
3706    7300            CLA CLL
3707    1343            TAD STR1
3710    7012            RTR           /THIS CHANGES DIGITAL
3711    3045            DCA 45        /INFØRMATIØN TØ ACTUAL
3712    3046            DCA 46        /VØLTS. SAME AS ABØVE
3713    1342            TAD C13       /IT ALSØ MULTIPLIES BY
3714    3044            DCA 44        /SLØPE AND ADDS INT.
3715    4407            FENT
3716    7000            FNØR
3717    3335            FMPY TØVØLTS
3720    3112            FMPY SLØP1
3721    1115            FADD INT1
3722    7000            FNØR
3723    6332            FPUT CHAN1
3724    0000            FEXT
3725    7300            CLA CLL
3726    5747            JMP I XY
3727    0000    CHANO,  0
3730    0000            0
3731    0000            0
3732    0000    CHAN1,  0
3733    0000            0
3734    0000            0
3735    7772    TØVØLTS,7772
3736    2401            2401
3737    2005            2005
3740    7772            7772
3741    2401            2401
3742    0013    C13,    0013
3743    0000    STR1,   0
3744    0000    STRO,   0
3745    0001    K0001,  0001
3746    4042    ØØT,    ØIT
3747    4000    XY,     XZ
                *AVRG+200
4000    7300    XZ,     CLA CLL
4001    1165            TAD MØDE      /CHECK MØDE
4002    7650            SNA CLA
4003    5205            JMP RAT       /NØRMAL MØDE; GET RATIØ
4004    5222            JMP CBRAT
4005    7300    RAT,    CLA CLL
4006    4407            FENT
4007    5120            FGET NPTS
4010    1166            FADD ØNE
4011    7000            FNØR
4012    6120            FPUT NPTS
4013    5652            FGET I CHO
4014    4653            FDIV I CH1
4015    1123            FADD A
4016    7000            FNØR
4017    6123            FPUT A
4020    0000            FEXT
4021    5242            JMP ØIT
```

211

```
4022   7300   CBRAT,   CLA CLL           /CALIBRATE MØDE
4023   4407            FENT
4024   5120            FGET NPTS
4025   1166            FADD ØNE
4026   7000            FNØR
4027   6120            FPUT NPTS
4030   5652            FGET I CH0
4031   1123            FADD A
4032   7000            FNØR
4033   6123            FPUT A
4034   5653            FGET I CH1
4035   1171            FADD B
4036   7000            FNØR
4037   6171            FPUT B
4040   0000            FEXT
4041   5242            JMP ØIT
4042   7300   ØIT,     CLA CLL
4043   6551            6551              /ØUTPUT +5 VØLTS TØ CHAN1
4044   1254            TAD K4000
4045   6551            6551              /ØUTPUT 0 VØLTS
4046   7300            CLA CLL
4047   6302            CLTF              /NEED ØNLY CLEAR FLAG CAUSING INTRPT
4050   6001            IØN
4051   5002            JMP LØØP
4052   3727   CH0,     CHANO
4053   3732   CH1,     CHAN1
4054   4000   K4000,   4000
```

212

FIELD=1
*200

0200	0322	322	/R
0201	0325	325	/U
0202	0316	316	/N
0203	0240	240	/
0204	0316	316	/N
0205	0325	325	/U
0206	0315	315	/M
0207	0302	302	/B
0210	0305	305	/E
0211	0322	322	/R
0212	0272	272	/:
0213	0244	244	/$

*240

0240	0323	323	/S
0241	0314	314	/L
0242	0317	317	/O
0243	0320	320	/P
0244	0305	305	/E
0245	0260	260	/0
0246	0272	272	/:
0247	0244	244	/$

*300

0300	0311	311	/I
0301	0316	316	/N
0302	0324	324	/T
0303	0305	305	/E
0304	0322	322	/R
0305	0303	303	/C
0306	0305	305	/E
0307	0320	320	/P
0310	0324	324	/T
0311	0260	260	/0
0312	0272	272	/:
0313	0244	244	/$

*340

0340	0323	323	/S
0341	0314	314	/L
0342	0317	317	/O
0343	0320	320	/P
0344	0305	305	/E
0345	0261	261	/1
0346	0272	272	/:
0347	0244	244	/$

*400

0400	0311	311	/I
0401	0316	316	/N
0402	0324	324	/T
0403	0305	305	/E
0404	0322	322	/R
0405	0303	303	/C
0406	0305	305	/E
0407	0320	320	/P
0410	0324	324	/T
0411	0261	261	/1
0412	0272	272	/:
0413	0244	244	/$

213

```
                    *500
0500    0316          316       /N
0501    0325          325       /U
0502    0315          315       /M
0503    0302          302       /B
0504    0305          305       /E
0505    0322          322       /R
0506    0240          240       /
0507    0317          317       /O
0510    0306          306       /F
0511    0240          240       /
0512    0320          320       /P
0513    0317          317       /O
0514    0311          311       /I
0515    0316          316       /N
0516    0324          324       /T
0517    0323          323       /S
0520    0275          275       /=
0521    0244          244       /$
                    *540
0540    0301          301       /A
0541    0326          326       /V
0542    0305          305       /E
0543    0322          322       /R
0544    0301          301       /A
0545    0307          307       /G
0546    0305          305       /E
0547    0240          240       /
0550    0322          322       /R
0551    0301          301       /A
0552    0324          324       /T
0553    0311          311       /I
0554    0317          317       /O
0555    0275          275       /=
0556    0244          244       /$
                    *440
0440    0303          303       /C
0441    0310          310       /H
0442    0301          301       /A
0443    0316          316       /N
0444    0316          316       /N
0445    0305          305       /E
0446    0314          314       /L
0447    0240          240       /
0450    0260          260       /0
0451    0240          240       /
0452    0315          315       /M
0453    0311          311       /I
0454    0316          316       /N
0455    0272          272       /:
0456    0244          244       /$
                    *600
0600    0303          303       /C
0601    0310          310       /H
0602    0301          301       /A
0603    0316          316       /N
0604    0316          316       /N
0605    0305          305       /E
0606    0314          314       /L
0607    0240          240       /
0610    0261          261       /1
0611    0240          240       /
0612    0315          315       /M
0613    0311          311       /I
0614    0316          316       /N
0615    0272          272       /:
```

214

0616	0244	244	/$
		*640	
0640	0303	303	/C
0641	0310	310	/H
0642	0301	301	/A
0643	0316	316	/N
0644	0316	316	/N
0645	0305	305	/E
0646	0314	314	/L
0647	0240	240	/
0650	0260	260	/0
0651	0240	240	/
0652	0315	315	/M
0653	0301	301	/A
0654	0330	330	/X
0655	0272	272	/:
0656	0244	244	/$
		*700	
0700	0303	303	/C
0701	0310	310	/H
0702	0301	301	/A
0703	0316	316	/N
0704	0316	316	/N
0705	0305	305	/E
0706	0314	314	/L
0707	0240	240	/
0710	0261	261	/1
0711	0240	240	/
0712	0315	315	/M
0713	0301	301	/A
0714	0330	330	/X
0715	0272	272	/:
0716	0244	244	/$
		*740	
0740	0301	301	/A
0741	0326	326	/V
0742	0305	305	/E
0743	0322	322	/R
0744	0301	301	/A
0745	0307	307	/G
0746	0305	305	/E
0747	0240	240	/
0750	0317	317	/Ø
0751	0306	306	/F
0752	0240	240	/
0753	0303	303	/C
0754	0310	310	/H
0755	0301	301	/A
0756	0316	316	/N
0757	0316	316	/N
0760	0305	305	/E
0761	0314	314	/L
0762	0240	240	/
0763	0260	260	/0
0764	0240	240	/
0765	0275	275	/=
0766	0244	244	/$
		*1000	
1000	0301	301	/A
1001	0326	326	/V
1002	0305	305	/E
1003	0322	322	/R
1004	0301	301	/A
1005	0307	307	/G
1006	0305	305	/E
1007	0240	240	/

215

1010	0317	317	/Ø
1011	0306	306	/F
1012	0240	240	/
1013	0303	303	/C
1014	0310	310	/H
1015	0301	301	/A
1016	0316	316	/N
1017	0316	316	/N
1020	0305	305	/E
1021	0314	314	/L
1022	0240	240	/
1023	0261	261	/1
1024	0240	240	/
1025	0275	275	/=
1026	0244	244	/$

*1040

1040	0316	316	/N
1041	0325	325	/U
1042	0315	315	/M
1043	0302	302	/B
1044	0305	305	/E
1045	0322	322	/R
1046	0240	240	/
1047	0317	317	/Ø
1050	0306	306	/F
1051	0240	240	/
1052	0302	302	/B
1053	0301	301	/A
1054	0304	304	/D
1055	0240	240	/
1056	0320	320	/P
1057	0317	317	/Ø
1060	0311	311	/I
1061	0316	316	/N
1062	0324	324	/T
1063	0323	323	/S
1064	0275	275	/=
1065	0244	244	/$

```
                 *AVRG
3600    0000     AVRG,    0
3601    7300              CLA CLL        /HERE IN 29.3 MICROSEC
3602    6542              ADSC           /SELECT CHANNEL 0
3603    7300              CLA CLL        /AND CONVERT
3604    6531              ADSF           /SKIP WHEN DONE
3605    5204              JMP .-1
3606    6534              ADRB           /READ INTO AC
3607    3344              DCA STRO
3610    1345              TAD K0001
3611    6542              ADSC           /SELECT CHANNEL 1
3612    7300              CLA CLL
3613    6531              ADSF
3614    5213              JMP .-1
3615    6534              ADRB
3616    3343              DCA STR1        /VOLTAGES ARE STORED
3617    1165              TAD MODE        /CHECK MODE
3620    7650              SNA CLA         /CALIBRATE?
3621    5223              JMP .+2
3622    5267              JMP CON         /YES
3623    1344              TAD STRO        /NO
3624    3150              DCA QS
3625    1144              TAD MAXO        /CHANO<MAXO?
3626    3147              DCA QB
3627    4526              JMS I SCOMP
3630    7650              SNA CLA
3631    5260              JMP BAD         /NO
3632    1344              TAD STRO        /YES; CHANO>MINO?
3633    3147              DCA QB
3634    1142              TAD MINO
3635    3150              DCA QS
3636    4526              JMS I SCOMP
3637    7650              SNA CLA
3640    5260              JMP BAD         /NO
3641    1343              TAD STR1        /YES; CHAN1<MAX1?
3642    3150              DCA QS
3643    1145              TAD MAX1
3644    3147              DCA QB
3645    4526              JMS I SCOMP
3646    7650              SNA CLA
3647    5260              JMP BAD         /NO
3650    1343              TAD STR1        /YES; CHAN1>MIN1?
3651    3147              DCA QB
3652    1143              TAD MIN1
3653    3150              DCA QS
3654    4526              JMS I SCOMP
3655    7650              SNA CLA
3656    5260              JMP BAD         /NO
3657    5267              JMP CON
3660    7300     BAD,     CLA CLL        /HERE IF NOT ON LINEAR REGION
3661    4407              FENT           /OF VOLTAGE CURVE
3662    5160              FGET BDPTS     /INCREMENT BDPTS
3663    1166              FADD ONE
3664    6160              FPUT BDPTS
3665    0000              FEXT
3666    5746              JMP I OOT
3667    7300     CON,     CLA CLL
3670    1344              TAD STRO
3671    7012              RTR
3672    3045              DCA 45
```

217

```
3673   3046            DCA 46
3674   1342            TAD C13
3675   3044            DCA 44
3676   4407            FENT
3677   7000            FNOR
3700   3335            FMPY TOVOLTS
3701   3104            FMPY SLOPO
3702   1107            FADD INTO
3703   7000            FNOR
3704   6327            FPUT CHANO
3705   0000            FEXT
3706   7300            CLA CLL
3707   1343            TAD STR1
3710   7012            RTR             /THIS CHANGES DIGITAL
3711   3045            DCA 45          /INFORMATION TO ACTUAL
3712   3046            DCA 46          /VOLTS. SAME AS ABOVE
3713   1342            TAD C13         /IT ALSO MULTIPLIES BY
3714   3044            DCA 44          /SLOPE AND ADDS INT.
3715   4407            FENT
3716   7000            FNOR
3717   3335            FMPY TOVOLTS
3720   3112            FMPY SLOP1
3721   1115            FADD INT1
3722   7000            FNOR
3723   6332            FPUT CHAN1
3724   0000            FEXT
3725   7300            CLA CLL
3726   5747            JMP I XY
3727   0000   CHANO,   0
3730   0000            0
3731   0000            0
3732   0000   CHAN1,   0
3733   0000            0
3734   0000            0
3735   7772   TOVOLTS,7772
3736   2401            2401
3737   2005            2005
3740   7772            7772
3741   2401            2401
3742   0013   C13,     0013
3743   0000   STR1,    0
3744   0000   STR0,    0
3745   0001   K0001,   0001
3746   4063   OOT,     OIT
3747   4000   XY,      XZ
               *AVRG+200
4000   7300   XZ,      CLA CLL
4001   1165            TAD MODE        /CHECK MODE
4002   7650            SNA CLA
4003   5205            JMP RAT         /NORMAL MODE; GET RATIO
4004   5243            JMP CBRAT
4005   7300   RAT,     CLA CLL
4006   4407            FENT
4007   5120            FGET NPTS
4010   1166            FADD ONE
4011   7000            FNOR
4012   6120            FPUT NPTS
4013   5672            FGET I CHO
4014   4673            FDIV I CH1
4015   1123            FADD A
4016   7000            FNOR
4017   6123            FPUT A
4020   0000            FEXT
4021   2274            ISZ NBPTS
4022   5263            JMP OIT
4023   4407            FENT
```

218

```
4024    5123            FGET  A
4025    3267            FMPY  FK40
4026    0000            FEXT
4027    4546            JMS  I  SINTEG
4030    1276            TAD  K4000
4031    6551            6551
4032    7300            CLA  CLL
4033    1275            TAD  NCPTS
4034    3274            DCA  NBPTS
4035    4407            FENT
4036    5174            FGET  ZERO
4037    6123            FPUT  A
4040    6120            FPUT  NPTS
4041    0000            FEXT
4042    5263            JMP  OIT
4043    7300    CBRAT,  CLA  CLL          /CALIBRATE  MODE
4044    4407            FENT
4045    5120            FGET  NPTS
4046    1166            FADD  ONE
4047    7000            FNOR
4050    6120            FPUT  NPTS
4051    5672            FGET  I  CH0
4052    1123            FADD  A
4053    7000            FNOR
4054    6123            FPUT  A
4055    5673            FGET  I  CH1
4056    1171            FADD  B
4057    7000            FNOR
4060    6171            FPUT  B
4061    0000            FEXT
4062    5263            JMP  OIT
4063    7300    OIT,    CLA  CLL
4064    6302            CLTF
4065    6001            ION
4066    5002            JMP  LOOP
4067    0003    FK40,   0003
4070    2000            2000
4071    0000            0000
4072    3727    CH0,    CHAN0
4073    3732    CH1,    CHAN1
4074    7720    NBPTS,  7720
4075    7720    NCPTS,  7720
4076    4000    K4000,  4000
```

219

trigger flag. First it converts channels 0 and 1 to digital values. If in calibrate mode it adds CHAN0 to A, CHAN1 to B, and 1 to NPTS. If in normal mode, it checks that voltages read are within the specified region, and if so adds CHAN0/CHAN1 to A and 1 to NPTS. If not it simply adds 1 to BDPTS. In any case, it then clears the trigger flag and turns the interrupt facility on, and jumps back into the waiting loop, line 0002.

The subroutine STRT gets ready for averaging by setting NPTS, A, B, and BDPTS equal to zero. CLEAR clears all flags, FINI outputs information, and INPT interprets and directs commands. SERV services an interrupt and determines where an interrupt came from. TYPE types a character, CRLF types a carriage return and a line feed, and OUT outputs text starting at the location given in BUFF and ending when a $ is encountered.

We now discuss the operation of the Ratio Averager programs with the help of the flow chart in Figure 47 and the sample dialog in Figure 48. To begin, one normally types CAL and then A, to read the voltage levels on channels 0 and 1. These are adjusted on the integrator while the laser is running but blocked from the detectors, commonly to around 0.4 volts so that fluctuations in the integrator level do not carry it negative. Then during the initialization step the negative of these levels are input as the intercepts for each channel. The minimum voltages are chosen around 0.15 volt larger, again so that fluctuations in the integrator levels do not cause a value which is actually zero to be read. The slope values can be used to

220

Figure 48: Sample Ratio Averager initializing dialog. Since the laser was fluctuating when the example was taken, the average ratio calculated from the voltage levels taken after returning to CAL mode is .66 as compared with .64 taken during ratio averaging, when pulses below the minimum level were being rejected.

```
 CAL
:A

Ɔ

NUMBER ØF PØINTS=+0.1635000E+04

AVERAGE ØF CHANNEL 0 =+0.6334226E+00

AVERAGE ØF CHANNEL 1 =+0.4445503E+00
:I

RUN NUMBER:1

SLØPE0:1.

INTERCEPT0:-.63

SLØPE1:1.

INTERCEPT1:-.44

CHANNEL 0 MIN:.78

CHANNEL 0 MAX:9.

CHANNEL 1 MIN:.59

CHANNEL 1 MAX:9.

ARDS PLØT MAX:8.
:A

Ɔ

NUMBER ØF PØINTS=+0.4800000E+03

AVERAGE RATIØ=+0.6396517E+00

NUMBER ØF BAD PØINTS=+0.2000000E+01
:CAL
:A
Ɔ

NUMBER ØF PØINTS=+0.6559998E+03

AVERAGE ØF CHANNEL 0 =+0.4304985E+01

AVERAGE ØF CHANNEL 1 =+0.6009995E+01
:
```

Figure 48

compensate for differences in amplification, but they are normally set to 1. The maximum voltage levels are set 1 or 2 volts below 10 volts, which is the limit of the A/D converter and also the point where the integrator amplifiers saturate.

In the original program, typing O causes the average ratio, the number of points contributing, and the number of points outside the voltage limits to be typed out. In the chart modification, the average of every 48 points (a number specified by the NBPTS counter) is output though channel 1 of the D/A converter through the command 6551. The amplitude scale of the shart trace is set by the variable FK40, usually adjusted by changing line 4070 (or 4104 in the modification with the punch) using the switch register.

To operate the Ratio Averager modification which periodically outputs the ratio through the high speed punch as well as onto a chart recorder is more difficult, because changes must be made in the floating point package so that output is punched rather than typed. (All versions of the Ratio Averager program contain the Floating Point Package 3, which is not listed here but in its own DEC manual.) Here the problem of changing over to the punch is handled rather inelegantly, as follows. The original program is loaded and initialized using the teletype. Then the computer is stopped, the punch is turned on, and the modified tape 5 is loaded. The modification to punched output is made by changing line 7345 to 6021 and line 7347 to 6026. Also, to speed up output only three significant

RATIO AVERAGER WITH PUNCH   TAPE 5

```
                    *AVRG
3600    0000    AVRG,    0
3601    7300             CLA CLL          /HERE IN 29.3 MICROSEC
3602    6542             ADSC             /SELECT CHANNEL 0
3603    7300             CLA CLL          /AND CONVERT
3604    6531             ADSF             /SKIP WHEN DONE
3605    5204             JMP .-1
3606    6534             ADRB             /READ INTO AC
3607    3344             DCA STRO
3610    1345             TAD K0001
3611    6542             ADSC             /SELECT CHANNEL 1
3612    7300             CLA CLL
3613    6531             ADSF
3614    5213             JMP .-1
3615    6534             ADRB
3616    3343             DCA STR1         /VOLTAGES ARE STORED
3617    1165             TAD MODE         /CHECK MODE
3620    7650             SNA CLA          /CALIBRATE?
3621    5223             JMP .+2
3622    5267             JMP CON          /YES
3623    1344             TAD STRO         /NO
3624    3150             DCA QS
3625    1144             TAD MAXO         /CHANO<MAXO?
3626    3147             DCA QB
3627    4526             JMS I SCOMP
3630    7650             SNA CLA
3631    5260             JMP BAD          /NO
3632    1344             TAD STRO         /YES; CHANO>MINO?
3633    3147             DCA QB
3634    1142             TAD MINO
3635    3150             DCA QS
3636    4526             JMS I SCOMP
3637    7650             SNA CLA
3640    5260             JMP BAD          /NO
3641    1343             TAD STR1         /YES; CHAN1<MAX1?
3642    3150             DCA QS
3643    1145             TAD MAX1
3644    3147             DCA QB
3645    4526             JMS I SCOMP
3646    7650             SNA CLA
3647    5260             JMP BAD          /NO
3650    1343             TAD STR1         /YES; CHAN1>MIN1?
3651    3147             DCA QB
3652    1143             TAD MIN1
3653    3150             DCA QS
3654    4526             JMS I SCOMP
3655    7650             SNA CLA
3656    5260             JMP BAD          /NO
3657    5267             JMP CON
3660    7300    BAD,     CLA CLL          /HERE IF NOT ON LINEAR REGION
3661    4407             FENT             /OF VOLTAGE CURVE
3662    5160             FGET BDPTS       /INCREMENT BDPTS
3663    1166             FADD ONE
3664    6160             FPUT BDPTS
3665    0000             FEXT
3666    5746             JMP I OOT
3667    7300    CON,     CLA CLL
3670    1344             TAD STRO
3671    7012             RTR
3672    3045             DCA 45
```

224

```
3673    3046            DCA 46
3674    1342            TAD C13
3675    3044            DCA 44
3676    4407            FENT
3677    7000            FNOR
3700    3335            FMPY TOVOLTS
3701    3104            FMPY SLOPO
3702    1107            FADD INTO
3703    7000            FNOR
3704    6327            FPUT CHANO
3705    0000            FEXT
3706    7300            CLA CLL
3707    1343            TAD STRI
3710    7012            RTR             /THIS CHANGES DIGITAL
3711    3045            DCA 45          /INFORMATION TO ACTUAL
3712    3046            DCA 46          /VOLTS. SAME AS ABOVE
3713    1342            TAD C13         /IT ALSO MULTIPLIES BY
3714    3044            DCA 44          /SLOPE AND ADDS INT.
3715    4407            FENT
3716    7000            FNOR
3717    3335            FMPY TOVOLTS
3720    3112            FMPY SLOP1
3721    1115            FADD INT1
3722    7000            FNOR
3723    6332            FPUT CHAN1
3724    0000            FEXT
3725    7300            CLA CLL
3726    5747            JMP I XY
3727    0000    CHANO,  0
3730    0000            0
3731    0000            0
3732    0000    CHAN1,  0
3733    0000            0
3734    0000            0
3735    7772    TOVOLTS,7772
3736    2401            2401
3737    2005            2005
3740    7772            7772
3741    2401            2401
3742    0013    C13,    0013
3743    0000    STRI,   0
3744    0000    STRO,   0
3745    0001    K0001,  0001
3746    4042    OOT,    OIT
3747    4000    XY,     XZ
                *AVRG+200
4000    7300    XZ,     CLA CLL
4001    1165            TAD MODE        /CHECK MODE
4002    7650            SNA CLA
4003    5205            JMP RAT         /NORMAL MODE; GET RATIO
4004    5222            JMP CBRAT
4005    7300    RAT,    CLA CLL
4006    4407            FENT
4007    5120            FGET NPTS
4010    1166            FADD ONE
4011    7000            FNOR
4012    6120            FPUT NPTS
4013    5706            FGET I CHO
4014    4707            FDIV I CH1
4015    1123            FADD A
4016    7000            FNOR
4017    6123            FPUT A
4020    0000            FEXT
4021    5242            JMP OIT
4022    7300    CBRAT,  CLA CLL         /CALIBRATE MODE
4023    4407            FENT
```

225

```
4024   5120           FGET  NPTS
4025   1166           FADD  ØNE
4026   7000           FNØR
4027   6120           FPUT  NPTS
4030   5706           FGET  I CHO
4031   1123           FADD  A
4032   7000           FNØR
4033   6123           FPUT  A
4034   5707           FGET  I CH1
4035   1171           FADD  B
4036   7000           FNØR
4037   6171           FPUT  B
4040   0000           FEXT
4041   5242           JMP   ØIT
4042   7300    ØIT,   CLA CLL
4043   6302           CLTF
4044   2310           ISZ NBPTS
4045   6001           IØN
4046   1310           TAD NBPTS
4047   7440           SZA
4050   5002           JMP LØØP
4051   7300           CLA CLL
4052   6026           6026
4053   4407           FENT
4054   5123           FGET  A
4055   4120           FDIV  NPTS
4056   7000           FNØR
4057   0014           ØUTPUT
4060   5123           FGET  A
4061   3303           FMPY  FK40
4062   0000           FEXT
4063   4546           JMS I SINTEG
4064   1312           TAD K4000
4065   6551           6551
4066   6022           6022
4067   7300           CLA CLL
4070   1311           TAD NCPTS
4071   3310           DCA NBPTS
4072   4407           FENT
4073   5174           FGET  ZERØ
4074   6123           FPUT  A
4075   6120           FPUT  NPTS
4076   0000           FEXT
4077   7300           CLA CLL
4100   6302           CLTF
4101   6001           IØN
4102   5002           JMP LØØP
4103   0003    FK40,  0003
4104   2000           2000
4105   0000           0000
4106   3727    CHO,   CHANO
4107   3732    CH1,   CHAN1
4110   7720    NBPTS, 7720
4111   7720    NCPTS, 7720
4112   4000    K4000, 4000
```

figures are retained, by changing memory location 7325 to 7776. Then to run the program, load address 3601 and start.

Finally, we make some explanatory comments on the Ratio Averager modification which plots points on the ARDS graphics display terminal whose x and y coordinates are the integrated outputs of the two detectors. This modification was originally carried out by Bruce Garetz. We refer to the listings on following pages.

In tape 1, there are some additional floating point memory locations. AMAX is the maximum value of the ARDS plot, typed in during the initial dialogue. SCALE is the number of ARDS display points along the entire x or y axis, while SHIFT is half that and is used to move the zero of the plot from the center of the screen to the lower left corner. SPLOT is an added subroutine reference, and the definition of TAMAX gives the address of the text for the plot maximum question on tape 6.

The only change in tape 4 is to draw the axes after the initial dialogue. In line 3162 we go to the subroutine AXES, on tape 4.5. The subroutine takes through line 2633 to ask for the maximum of the ARDS scale. Then the instruction 6312 clears the ARDS flag. The character KERASE, which is zero, is read by the ARDS on the command 6314. There is a loop which checks to see if the ARDS is done reading, including the command 6311 to skip the following statement if done. Lines 2643 through 2646 are a delay to give the ARDS time to erase. Lines 2651 through 2655 put the ARDS into set point

RATIØ AVERAGER WITH ARDS   TAPE 1

```
                    *0000
0000    0000        0
0001    5531                JMP I SSERV
0002    5002        LØØP,   JMP .
                    *0007
0007    5600                5600        /PØINTER TØ FP PKG 3
                    *0015
0015    0000        AMAX,   0000
0016    0000                0000
0017    0000                0000
                    *0023
0023    0012        SHIFT,  0012
0024    2070                2070
0025    0000                0000
0026    0013        SCALE,  0013
0027    2070                2070
0030    0000                0000
0031    2730        SPLØT,  PLØT
0032    1100        TAMAX,  1100
                    *0044
0044    0000        FLAC,   0
0045    0000                0
0046    0000                0
                    *0055
0055    0001                0001        /FØR CR AFTER ØUTPUT
0056    7777                7777        /FØR LF AFTDR ØUTPUT
0057    0000                0
0060    0000                0
0061    0000                0
                    *70
0070    0000        AC,     0
0071    0000        L,      0
0072    0000        BUFF,   0
0073    0200        TRUN,   200
0074    4000        TEXT,   4000
0075    0240        TSLØP0, 240
0076    0300        TINTO,  300
0077    0340        TSLØP1, 340
0100    0400        TINT1,  400
0101    0000        RUN,    0
0102    0000                0
0103    0000                0
0104    0000        SLØP0,  0
0105    0000                0
0106    0000                0
0107    0000        INTO,   0
0110    0000                0
0111    0000                0
0112    0000        SLØP1,  0
0113    0000                0
0114    0000                0
0115    0000        INT1,   0
0116    0000                0
0117    0000                0
0120    0000        NPTS,   0
0121    0000                0
0122    0000                0
0123    0000        A,      0
0124    0000                0
0125    0000                0
0126    3400        SCØMP,  CØMP
```

228

```
0127   1000   SØUT,    ØUT
0130   3000   SINIT,   INIT
0131   1200   SSERV,   SERV
0132   1400   SINPT,   INPT
0133   3600   SAVRG,   AVRG
0134   1022   SCRLF,   CRLF
0135   1300   SSTRT,   STRT
0136   2400   SFINI,   FINI
0137   1030   STYPE,   TYPE
0140   2200   SCLEAR,  CLEAR
0141   2600   SCALIB,  CALIB
0142   0000   MINO,    0
0143   0000   MIN1,    0
0144   0000   MAXO,    0
0145   0000   MAX1,    0
0146   3200   SINTEG,  INTEG
0147   0000   QB,      0
0150   0000   QS,      0
0151   0440   TMINO,   440
0152   0600   TMIN1,   600
0153   0640   TMAXO,   640
0154   0700   TMAX1,   700
0155   0740   TCHO,    740
0156   1000   TCH1,    1000
0157   1040   TBDPT,   1040
0160   0000   BDPTS,   0
0161   0000            0
0162   0000            0
0163   0540   TAV,     540
0164   0500   TPTS,    500
0165   0000   MØDE,    0
0166   0001   ØNE,     0001
0167   2000            2000
0170   0000            0000
0171   0000   B,       0
0172   0000            0
0173   0000            0
0174   0000   ZERØ,    0
0175   0000            0
0176   0000            0
              *200
0200   7300            CLA CLL      /PRØGRAM STARTS HERE
0201   6046            TLS          /TØ SET PRINTER FLAG
0202   5603            JMP I SCF
0203   1604   SCF,     INPT+204
```

229

```
                   *CALIB
2600    0000    CALIB,    0            /HANDLES CALIBRATE COMMAND
2601    7300              CLA CLL
2602    7001              IAC
2603    3165              DCA MODE          /SET MODE=1 INDICATING CALIBRATE MODE
2604    4407              FENT
2605    5166              FGET ONE
2606    6104              FPUT SLOPO
2607    6112              FPUT SLOP1
2610    5174              FGET ZERO
2611    6107              FPUT INTO
2612    6115              FPUT INT1
2613    0000              FEXT
2614    5600              JMP I CALIB
                   *INIT
3000    0000    INIT,     0                /INITIALIZATION SUBROUTINE
3001    7300              CLA CLL          /TO GET RUN NUMBER SLOPES
3002    6046              TLS              /AND INTERCEPTS
3003    1073              TAD TRUN         /TLS SETS TTY FLAG
3004    3072              DCA BUFF
3005    6211              CDF +10          /TEXT IS IN UPPER 4K
3006    4527              JMS I SOUT       /ASK FOR RUN NUMBER
3007    6201              CDF +00
3010    4407              FENT
3011    0013              INPUT            /GET RUN NUM AND STORE
3012    7000              FNOR
3013    6101              FPUT RUN
3014    0000              FEXT
3015    7300              CLA CLL
3016    1075              TAD TSLOPO               /GET SLOPO
3017    3072              DCA BUFF
3020    6211              CDF +10
3021    4527              JMS I SOUT
3022    6201              CDF +00
3023    4407              FENT
3024    0013              INPUT
3025    7000              FNOR
3026    6104              FPUT SLOPO
3027    0000              FEXT
3030    7300              CLA CLL          /GET INTO
3031    1076              TAD TINTO
3032    3072              DCA BUFF
3033    6211              CDF +10
3034    4527              JMS I SOUT
3035    6201              CDF +00
3036    4407              FENT
3037    0013              INPUT
3040    7000              FNOR
3041    6107              FPUT INTO
3042    0000              FEXT
3043    7300              CLA CLL          /GET SLOP1
3044    1077              TAD TSLOP1
3045    3072              DCA BUFF
3046    6211              CDF +10
3047    4527              JMS I SOUT
3050    6201              CDF +00
3051    4407              FENT
3052    0013              INPUT
3053    7000              FNOR
```

230

```
3054    6112        FPUT SLØP1
3055    0000        FEXT
3056    7300        CLA CLL          /GET INT1
3057    1100        TAD TINT1
3060    3072        DCA BUFF
3061    6211        CDF +10
3062    4527        JMS I SØUT
3063    6201        CDF +00
3064    4407        FENT
3065    0013        INPUT
3066    7000        FNØR
3067    6115        FPUT INT1
3070    0000        FEXT
3071    7300        CLA CLL          /CET MINS AND MAXS
3072    1151        TAD TMINO
3073    3072        DCA BUFF
3074    6211        CDF +10
3075    4527        JMS I SØUT
3076    6201        CDF +00
3077    4407        FENT
3100    0013        INPUT
3101    7000        FNØR
3102    3366        FMPY F4095
3103    4371        FDIV FTEN
3104    7000        FNØR
3105    0000        FEXT
3106    4546        JMS I SINTEG
3107    3142        DCA MINO
3110    1153        TAD TMAXO
3111    3072        DCA BUFF
3112    6211        CDF +10
3113    4527        JMS I SØUT
3114    6201        CDF +00
3115    4407        FENT
3116    0013        INPUT
3117    7000        FNØR
3120    3366        FMPY F4095
3121    4371        FDIV FTEN
3122    7000        FNØR
3123    0000        FEXT
3124    4546        JMS I SINTEG
3125    3144        DCA MAXO
3126    1152        TAD TMIN1
3127    3072        DCA BUFF
3130    6211        CDF +10
3131    4527        JMS I SØUT
3132    6201        CDF +00
3133    4407        FENT
3134    0013        INPUT
3135    7000        FNØR
3136    3366        FMPY F4095
3137    4371        FDIV FTEN
3140    7000        FNØR
3141    0000        FEXT
3142    4546        JMS I SINTEG
3143    3143        DCA MIN1
3144    1154        TAD TMAX1
3145    3072        DCA BUFF
3146    6211        CDF +10
3147    4527        JMS I SØUT
3150    6201        CDF +00
3151    4407        FENT
3152    0013        INPUT
3153    7000        FNØR
3154    3366        FMPY F4095
3155    4371        FDIV FTEN
```

```
3156   7000          FNØR
3157   0000          FEXT
3160   4546          JMS I SINTEG
3161   3145          DCA MAX1
3162   4774          JMS I SAXES
3163   7300          CLA CLL
3164   3165          DCA MØDE          /FØR REGULAR MØDE
3165   5600          JMP I INIT       /DØNE
3166   0012   F4095,  0012
3167   3777          3777
3170   4000          4000
3171   0004   FTEN,   0004
3172   2400          2400
3173   0000          0000
3174   2620   SAXES,  AXES
              *INTEG
3200   0000   INTEG,  0                /CØNVERTS NUMBER IN FLAC TØ
3201   7300          CLA CLL          /AN INTEGER IN THE AC
3202   1044          TAD FLAC
3203   7510          SPA
3204   5242          JMP NEG          /THE FL PT EXPØNENT IS NEG
3205   7300          CLA CLL
3206   1046          TAD FLAC+2
3207   0244          AND K4000        /GET LEFT BIT
3210   7450          SNA
3211   5213          JMP .+2
3212   7020          CML
3213   1045          TAD FLAC+1
3214   7004          RAL
3215   7100          CLL
3216   3246          DCA INT
3217   1044          TAD FLAC
3220   1250          TAD M12
3221   7540          SMA SZA
3222   5237          JMP XY           /LARGER THAN 2**12
3223   7500          SMA
3224   5234          JMP XX           /=0
3225   3247          DCA SHFT
3226   1246          TAD INT
3227   7100          CLL
3230   7010          RAR
3231   2247          ISZ SHFT
3232   5227          JMP .-3
3233   5600          JMP I INTEG
3234   7300   XX,     CLA CLL
3235   1246          TAD INT
3236   5600          JMP I INTEG
3237   7300   XY,     CLA CLL
3240   1245          TAD K7777
3241   5600          JMP I INTEG
3242   7300   NEG,    CLA CLL
3243   5600          JMP I INTEG
3244   4000   K4000,  4000
3245   7777   K7777,  7777
3246   0000   INT,    0
3247   0000   SHFT,   0
3250   7766   M12,    7766
              *CØMP
3400   0000   CØMP,   0                /DØES ABSØLUTE CØMPARISØN,
3401   7300          CLA CLL          /IÈ: 4000>3777
3402   1377          TAD Q
3403   7700          SMA CLA
3404   5210          JMP .+4
3405   7240          CLA CMA          /QB IS MINUS
3406   3244          DCA SB
3407   5212          JMP .+3
```

232

```
3410   7201          CLA IAC        /QB IS PØS ØR ZERØ
3411   3244          DCA SB
3412   1150          TAD QS
3413   7700          SMA CLA
3414   5226          JMP .+12
3415   1244          TAD SB   /QS IS MINUS
3416   7700          SMA CLA
3417   5242          JMP NØ
3420   1150          TAD QS
3421   7041          CIA
3422   1147          TAD QB
3423   7700          SMA CLA
3424   5240          JMP YES
3425   5242          JMP NØ
3426   1244          TAD SB         /QS IS PLUS ØR ZERØ
3427   7700          SMA CLA
3430   5232          JMP .+2
3431   5240          JMP YES
3432   1150          TAD QS
3433   7041          CIA
3434   1147          TAD QB
3435   7700          SMA CLA
3436   5240          JMP YES
3437   5242          JMP NØ
3440   7201   YES,   CLA IAC        /QB>QS AC=1
3441   5600          JMP I CØMP
3442   7300   NØ,    CLA CLL        /QB<QS AC=0
3443   5600          JMP I CØMP
3444   0000   SB,    0
```

233

```
                    *AXES
2620    0000    AXES,   0
2621    7300            CLA CLL
2622    1032            TAD TAMAX
2623    3072            DCA BUFF
2624    6211            CDF +10
2625    4527            JMS I SOUT
2626    6201            CDF +00
2627    4407            FENT
2630    0013            INPUT
2631    7000            FNOR
2632    6015            FPUT AMAX
2633    0000            FEXT
2634    7300            CLA CLL
2635    6312            6312
2636    1321            TAD KERASE
2637    6314            6314
2640    6311            6311
2641    5240            JMP.-1
2642    7300            CLA CLL
2643    1312            TAD K4000
2644    7001            IAC
2645    7510            SPA
2646    5244            JMP.-2
2647    6312            6312
2650    7300            CLA CLL
2651    1320            TAD GSS
2652    6314            6314
2653    6311            6311
2654    5253            JMP.-1
2655    6312            6312
2656    7300            CLA CLL
2657    1313            TAD M540
2660    4431            JMS I SPLOT
2661    1314            TAD K480
2662    4431            JMS I SPLOT
2663    1311            TAD RSS
2664    6314            6314
2665    6311            6311
2666    5265            JMP.-1
2667    6312            6312
2670    7300            CLA CLL
2671    1317            TAD K0
2672    4431            JMS I SPLOT
2673    1316            TAD M1020
2674    4431            JMS I SPLOT
2675    1315            TAD K1020
2676    4431            JMS I SPLOT
2677    1317            TAD K0
2700    4431            JMS I SPLOT
2701    7300            CLA CLL
2702    1320            TAD GSS
2703    6314            6314
2704    6311            6311
2705    5304            JMP.-1
2706    6312            6312
2707    7300            CLA CLL
2710    5620            JMP I AXES
2711    0036    RSS,    0036
```

234

```
2712   4000   K4000,    4000
2713   6744   M540,     6744
2714   0740   K480,     0740
2715   1774   K1020,    1774
2716   6004   M1020,    6004
2717   0000   K0,       0000
2720   0035   GSS,      0035
2721   0000   KERASE,   0000
2722   3300   SFLØT,    FLØT
               *PLØT
2730   0000   PLØT,     0
2731   7500             SMA
2732   5335             JMP.+3
2733   7040             CMA
2734   1360             TAD K4001
2735   3357             DCA  TEMP
2736   1357             TAD  TEMP
2737   7004             RAL
2740   7200             CLA
2741   1357             TAD  TEMP
2742   0356             AND  MASK37
2743   7004             RAL
2744   1361             TAD  K1000
2745   4762             JMS  I  SØAT
2746   1357             TAD  TEMP
2747   7012             RTR
2750   7012             RTR
2751   7010             RAR
2752   0356             AND  MASK37
2753   1361             TAD  K1000
2754   4762             JMS  I  SØAT
2755   5730             JMP  I  PLØT
2756   0037   MASK37,   0037
2757   0000   TEMP,     0000
2760   4001   K4001,    4001
2761   0100   K1000,    0100
2762   2770   SØAT,     ØAT
               *ØAT
2770   0000   ØAT,      0
2771   6314             6314
2772   6311             6311
2773   5372             JMP.-1
2774   6312             6312
2775   7300             CLA CLL
2776   5770             JMP  I  ØAT
```

235

```
                    *FLØT
3300    0000    FLØT,       0
3301    3045                DCA 45
3302    3046                DCA 46
3303    1311                TAD C13
3304    3044                DCA 44
3305    4407                FENT
3306    7000                FNØR
3307    0000                FEXT
3310    5700                JMP I FLØT
3311    0013    C13,        0013
                    *FFIX
3320    0000    FFIX,       0
3321    7200                CLA
3322    1044                TAD 44
3323    7540                SZA SMA
3324    5327                JMP.+3
3325    7200                CLA
3326    5344                JMP DØNE+1
3327    1345                TAD M13
3330    7450                SNA
3331    5343                JMP DØNE
3332    3044                DCA 44
3333    7100    GØ,         CLL
3334    1045                TAD 45
3335    7510                SPA
3336    7020                CML
3337    7010                RAR
3340    3045                DCA 45
3341    2044                ISZ 44
3342    5333                JMP GØ
3343    1045    DØNE,       TAD 45
3344    5720                JMP I FFIX
3345    7765    M13,        -13
```

```
                     *AVRG
3600    0000    AVRG,    0
3601    7300             CLA CLL          /HERE IN 29.3 MICRØSEC
3602    6542             ADSC             /SELECT CHANNEL 0
3603    7300             CLA CLL          /AND CØNVERT
3604    6531             ADSF             /SKIP WHEN DØNE
3605    5204             JMP .-1
3606    6534             ADRB             /READ INTØ AC
3607    3344             DCA STRO
3610    1345             TAD K0001
3611    6542             ADSC             /SELECT CHANNEL 1
3612    7300             CLA CLL
3613    6531             ADSF
3614    5213             JMP .-1
3615    6534             ADRB
3616    3343             DCA STR1         /VØLTAGES ARE STØRED
3617    1165             TAD MØDE         /CHECK MØDE
3620    7650             SNA CLA          /CALIBRATE?
3621    5223             JMP .+2
3622    5267             JMP CØN          /YES
3623    1344             TAD STRO         /NØ
3624    3150             DCA QS
3625    1144             TAD MAXO         /CHANO<MAXO?
3626    3147             DCA QB
3627    4526             JMS I SCØMP
3630    7650             SNA CLA
3631    5260             JMP BAD          /NØ
3632    1344             TAD STRO         /YES; CHANO>MINO?
3633    3147             DCA QB
3634    1142             TAD MINO
3635    3150             DCA QS
3636    4526             JMS I SCØMP
3637    7650             SNA CLA
3640    5260             JMP BAD          /NØ
3641    1343             TAD STR1         /YES; CHAN1<MAX1?
3642    3150             DCA QS
3643    1145             TAD MAX1
3644    3147             DCA QB
3645    4526             JMS I SCØMP
3646    7650             SNA CLA
3647    5260             JMP BAD          /NØ
3650    1343             TAD STR1         /YES; CHAN1>MIN1?
3651    3147             DCA QB
3652    1143             TAD MIN1
3653    3150             DCA QS
3654    4526             JMS I SCØMP
3655    7650             SNA CLA
3656    5260             JMP BAD          /NØ
3657    5267             JMP CØN
3660    7300    BAD,     CLA CLL          /HERE IF NØT ØN LINEAR REGIØN
3661    4407             FENT             /ØF VØLTAGE CURVE
3662    5160             FGET BDPTS       /INCREMENT BDPTS
3663    1166             FADD ØNE
3664    6160             FPUT BDPTS
3665    0000             FEXT
3666    5746             JMP I ØØT
3667    7300    CØN,     CLA CLL
3670    1344             TAD STRO
3671    7012             RTR
```

237

```
3672   3045          DCA 45
3673   3046          DCA 46
3674   1342          TAD C13
3675   3044          DCA 44
3676   4407          FENT
3677   7000          FNØR
3700   3335          FMPY TØVØLTS
3701   3104          FMPY SLØPO
3702   1107          FADD INTO
3703   7000          FNØR
3704   6327          FPUT CHANO
3705   0000          FEXT
3706   7300          CLA CLL
3707   1343          TAD STR1
3710   7012          RTR          /THIS CHANGES DIGITAL
3711   3045          DCA 45       /INFØRMATIØN TØ ACTUAL
3712   3046          DCA 46       /VØLTS. SAME AS ABØVE
3713   1342          TAD C13      /IT ALSØ MULTIPLIES BY
3714   3044          DCA 44       /SLØPE AND ADDS INT.
3715   4407          FENT
3716   7000          FNØR
3717   3335          FMPY TØVØLTS
3720   3112          FMPY SLØP1
3721   1115          FADD INT1
3722   7000          FNØR
3723   6332          FPUT CHAN1
3724   0000          FEXT
3725   7300          CLA CLL
3726   5747          JMP I XY
3727   0000   CHANO,  0
3730   0000          0
3731   0000          0
3732   0000   CHAN1,  0
3733   0000          0
3734   0000          0
3735   7772   TØVØLTS,7772
3736   2401          2401
3737   2005          2005
3740   7772          7772
3741   2401          2401
3742   0013   C13,    0013
3743   0000   STR1,   0
3744   0000   STR0,   0
3745   0001   K0001,  0001
3746   4072   ØØT,    ØIT
3747   4000   XY,     XZ
              *AVRG+200
4000   7300   XZ,     CLA CLL
4001   1165          TAD MØDE     /CHECK MØDE
4002   7650          SNA CLA
4003   5205          JMP RAT      /NØRMAL MØDE; GET RATIØ
4004   5252          JMP CBRAT
4005   7300   RAT,    CLA CLL
4006   4407          FENT
4007   5120          FGET NPTS
4010   1166          FADD ØNE
4011   7000          FNØR
4012   6120          FPUT NPTS
4013   5702          FGET I CHO
4014   4703          FDIV I CH1
4015   1123          FADD A
4016   7000          FNØR
4017   6123          FPUT A
4020   5702          FGET I CHO
4021   3026          FMPY SCALE
4022   4015          FDIV AMAX
```

238

```
4023    2023            FSUB  SHIFT
4024    7000            FNØR
4025    0000            FEXT
4026    4705            JMS  I  SFFIX
4027    3702            DCA  I  CHO
4030    4407            FENT
4031    5703            FGET  I  CH1
4032    3026            FMPY  SCALE
4033    4015            FDIV  AMAX
4034    2023            FSUB  SHIFT
4035    7000            FNØR
4036    0000            FEXT
4037    4705            JMS  I  SFFIX
4040    3703            DCA  I  CH1
4041    7300            CLA  CLL
4042    1702            TAD  I  CHO
4043    4431            JMS  I  SPLØT
4044    7300            CLA  CLL
4045    1703            TAD  I  CH1
4046    4431            JMS  I  SPLØT
4047    4320            JMS  DRAW
4050    7300            CLA  CLL
4051    5272            JMP  ØIT
4052    7300    CBRAT,  CLA  CLL         /CALIBRATE MØDE
4053    4407            FENT
4054    5120            FGET  NPTS
4055    1166            FADD  ØNE
4056    7000            FNØR
4057    6120            FPUT  NPTS
4060    5702            FGET  I  CHO
4061    1123            FADD  A
4062    7000            FNØR
4063    6123            FPUT  A
4064    5703            FGET  I  CH1
4065    1171            FADD  B
4066    7000            FNØR
4067    6171            FPUT  B
4070    0000            FEXT
4071    5272            JMP  ØIT
4072    7300    ØIT,    CLA  CLL
4073    6551            6551            /ØUTPUT +5 VØLTS TØ CHAN1
4074    1304            TAD  K4000
4075    6551            6551            /ØUTPUT 0 VØLTS
4076    7300            CLA  CLL
4077    6302            CLTF            /NEED ØNLY CLEAR FLAG CAUSING INTRPT
4100    6001            IØN
4101    5002            JMP  LØØP
4102    3727    CHO,    CHANO
4103    3732    CHI,    CHAN1
4104    4000    K4000,  4000
4105    3320    SFFIX,  FFIX
                *DRAW
4120    0000    DRAW,   0
4121    7300            CLA  CLL
4122    1343            TAD  RSK
4123    6314            6314
4124    6311            6311
4125    5324            JMP.-1
4126    6312            6312
4127    7300            CLA  CLL
4130    1345            TAD  K1
4131    4431            JMS  I  SPLØT
4132    1345            TAD  K1
4133    4431            JMS  I  SPLØT
4134    1344            TAD  GSK
4135    6314            6314
```

```
4136   6311           6311
4137   5336           JMP.-1
4140   6312           6312
4141   7300           CLA CLL
4142   5720           JMP I DRAW
4143   0036   RSK,    0036
4144   0035   GSK,    0035
4145   0001   K1,     0001

BAD      3660
CBRAT    4052
CHAN0    3727
CHAN1    3732
CH0      4102
CH1      4103
CØN      3667
C13      3742
GSK      4144
K0001    3745
K1       4145
K4000    4104
JIT      4072
JJT      3746
RAT      4005
RSK      4143
SFFIX    4105
STR0     3744
STR1     3743
TJVJLT   3735
XY       3747
XZ       4000
```

240

```
                        *AXES
2620    0000    AXES,   0
2621    7300            CLA CLL
2622    1032            TAD TAMAX
2623    3072            DCA BUFF
2624    6211            CDF +10
2625    4527            JMS I SØUT
2626    6201            CDF +00
2627    4407            FENT
2630    0013            INPUT
2631    7000            FNØR
2632    6015            FPUT AMAX
2633    0000            FEXT
2634    7300            CLA CLL
2635    1324            TAD GSS
2636    6314            6314
2637    6311            6311
2640    5237            JMP.-1
2641    6312            6312
2642    7300            CLA CLL
2643    1322            TAD M540
2644    4431            JMS I SPLØT
2645    1320            TAD K540
2646    4431            JMS I SPLØT
2647    1321            TAD RSS
2650    6314            6314
2651    6311            6311
2652    5251            JMP.-1
2653    6312            6312
2654    7300            CLA CLL
2655    1323            TAD K0
2656    4431            JMS I SPLØT
2657    1322            TAD M540
2660    4431            JMS I SPLØT
2661    1323            TAD K0
2662    4431            JMS I SPLØT
2663    1322            TAD M540
2664    4431            JMS I SPLØT
2665    1320            TAD K540
2666    4431            JMS I SPLØT
2667    1323            TAD K0
2670    4431            JMS I SPLØT
2671    1320            TAD K540
2672    4431            JMS I SPLØT
2673    1323            TAD K0
2674    4431            JMS I SPLØT
2675    1323            TAD K0
2676    4431            JMS I SPLØT
2677    1320            TAD K540
2700    4431            JMS I SPLØT
2701    1323            TAD K0
2702    4431            JMS I SPLØT
2703    1320            TAD K540
2704    4431            JMS I SPLØT
2705    1322            TAD M540
2706    4431            JMS I SPLØT
2707    1323            TAD K0
2710    4431            JMS I SPLØT
2711    1322            TAD M540
```

241

```
2712    4431            JMS I SPLØT
2713    1323            TAD KO
2714    4431            JMS I SPLØT
2715    4717            JMS I SGRID
2716    5620            JMP I AXES
2717    3450    SGRID,  GRID
2720    1034    K540,   1034
2721    0036    RSS,    0036
2722    6744    M540,   6744
2723    0000    KO,     0000
2724    0035    GSS,    0035
                *PLØT
2730    0000    PLØT,   0
2731    7500            SMA
2732    5335            JMP.+3
2733    7040            CMA
2734    1360            TAD K4001
2735    3357            DCA TEMP
2736    1357            TAD TEMP
2737    7004            RAL
2740    7200            CLA
2741    1357            TAD TEMP
2742    0356            AND MASK37
2743    7004            RAL
2744    1361            TAD K1000
2745    4762            JMS I SØAT
2746    1357            TAD TEMP
2747    7012            RTR
2750    7012            RTR
2751    7010            RAR
2752    0356            AND MASK37
2753    1361            TAD K1000
2754    4762            JMS I SØAT
2755    5730            JMP I PLØT
2756    0037    MASK37, 0037
2757    0000    TEMP,   0000
2760    4001    K4001,  4001
2761    0100    K1000,  0100
2762    2770    SØAT,   ØAT
                *ØAT
2770    0000    ØAT,    0
2771    6314            6314
2772    6311            6311
2773    5372            JMP.-1
2774    6312            6312
2775    7300            CLA CLL
2776    5770            JMP I ØAT
```

```
                    *FLØT
3300    0000    FLØT,    0
3301    3045             DCA  45
3302    3046             DCA  46
3303    1311             TAD  C13
3304    3044             DCA  44
3305    4407             FENT
3306    7000             FNØR
3307    0000             FEXT
3310    5700             JMP I FLØT
3311    0013    C13,     0013
                    *FFIX
3320    0000    FFIX,    0
3321    7200             CLA
3322    1044             TAD  44
3323    7540             SZA  SMA
3324    5327             JMP.+3
3325    7200             CLA
3326    5344             JMP  DØNE+1
3327    1345             TAD  M13
3330    7450             SNA
3331    5343             JMP  DØNE
3332    3044             DCA  44
3333    7100    GØ,      CLL
3334    1045             TAD  45
3335    7510             SPA
3336    7020             CML
3337    7010             RAR
3340    3045             DCA  45
3341    2044             ISZ  44
3342    5333             JMP  GØ
3343    1045    DØNE,    TAD  45
3344    5720             JMP I FFIX
3345    7765    M13,     -13
                    *GRID
3450    0000    GRID,    0
3451    7300             CLA  CLL
3452    1357             TAD  M648
3453    3365             DCA  X
3454    1357             TAD  M648
3455    3366             DCA  Y
3456    1364             TAD  M11
3457    3367             DCA  M
3460    7300    BEG1,    CLA  CLL
3461    1365             TAD  X
3462    1360             TAD  K108
3463    3365             DCA  X
3464    1364             TAD  M11
3465    3370             DCA  N
3466    7300    BEG2,    CLA  CLL
3467    1366             TAD  Y
3470    1360             TAD  K108
3471    3366             DCA  Y
3472    1355             TAD  GSS
3473    6314             6314
3474    6311             6311
3475    5274             JMP.-1
3476    6312             6312
3477    7300             CLA  CLL
3500    1365             TAD  X
```

243

```
3501   4431              JMS  I  SPLØT
3502   1366              TAD  Y
3503   4431              JMS  I  SPLØT
3504   1356              TAD  RSS
3505   6314              6314
3506   6311              6311
3507   5306              JMP.-1
3510   6312              6312
3511   7300              CLA  CLL
3512   1362              TAD  K2
3513   4431              JMS  I  SPLØT
3514   1361              TAD  KO
3515   4431              JMS  I  SPLØT
3516   1363              TAD  M4
3517   4431              JMS  I  SPLØT
3520   1361              TAD  KO
3521   4431              JMS  I  SPLØT
3522   1362              TAD  K2
3523   4431              JMS  I  SPLØT
3524   1361              TAD  KO
3525   4431              JMS  I  SPLØT
3526   1361              TAD  KO
3527   4431              JMS  I  SPLØT
3530   1362              TAD  K2
3531   4431              JMS  I  SPLØT
3532   1361              TAD  KO
3533   4431              JMS  I  SPLØT
3534   1363              TAD  M4
3535   4431              JMS  I  SPLØT
3536   2370              ISZ  N
3537   5266              JMP  BEG2
3540   7300              CLA  CLL
3541   1357              TAD  M648
3542   3366              DCA  Y
3543   2367              ISZ  M
3544   5260              JMP  BEG1
3545   7300              CLA  CLL
3546   1355              TAD  GSS
3547   6314              6314
3550   6311              6311
3551   5350              JMP.-1
3552   6312              6312
3553   7300              CLA  CLL
3554   5650              JMP  I  GRID
3555   0035   GSS,       0035
3556   0036   RSS,       0036
3557   6570   M648,      6570
3560   0154   K108,      0154
3561   0000   KO,        0000
3562   0002   K2,        0002
3563   7774   M4,        7774
3564   7765   M11,       7765
3565   0000   X,         0
3566   0000   Y,         0
3567   0000   M,         0
3570   0000   N,         0
```

mode. Then putting up first M540 and then K480 and going to the PLOT subroutine (discussed below) sets the ARDS beam at the upper left corner of the screen. Lines 2663 through 2667 put the ARDS into long vector mode. The ARDS is given the projections of the vector on the x and y axes and draws a line of that length from the point previously set. So giving it 0 and M1020 and then K1020 and 0 means it draws first a y and then an x axis.

The program arrives at the subroutine PLOT with an argument character (coordinate) in the accumulator. This is then operated on to recast it in the form accepted by the ARDS, as described in the ARDS operating manual, page 4-10. Here we take as an example the coordinate M540 which sets a point at the extreme left of the screen. Line 2731 checks for a negative argument. M540, which is 6744 in octal or 110 111 100 100 in binary, is negative. So it is complemented, producing 001 000 011 100, the last ten bits of which (bits 10 through 1) add up to 540. Then adding 4001 puts the negative sign in bit 12, and ensures that the complement of 7777 is 1 tather than 0. The sum is stored in TEMP. The left rotation i line 2737 puts the sign bit in the link. Then retrieving the argument from TEMP, using the AND command with MASK37 leaves the last five bits (bits 1-5, the least significant). Another left rotation puts the sign in bit 1, and adding 0100 puts a 1 in bit 7, signifying that this is an argument character. At this point this first argument character

245

is in correct form to be given to the ARDS for plotting through the subroutine OAT. Taking the argument out of TEMP again, five right rotations and the use of MASK37 give the other five digits. After adding 0100 again this too is output through OAT.

In tape 4.7, the subroutines FFIX and FLOT are analagous to the decimal-binary conversion routines of the Floating Point Package, DECON and DECONV.

In tape 5, the subroutine DRAW plots the data points by the method already discussed. It operates in long vector mode, where a point is the shortest possible vector of length 1,1. Also reproduced here are modifications of tapes 4.5 and 4,7 which draw a grid along with the axes.

Having discussed the machine language programs which produce lineshape data, we now turn to the FOCAL programs used in processing that data. An example of the treatment of data tapes to produce an averaged absorption lineshape is given in Section I C. In following pages we give a listing of the FOCAL program Alpha Reader used to do that, and begin this portion of the appendix with some comments on the functions of various sections.

Sections 2, 3, and 4 form a loop which adds in tapes, storing the data points in the array SUM. In section 7 these ratios are operated on (in line 7.21) to obtain absorbances. The initial baseline and its slope are estimated from values in the wings of the line or from recent vacuum baselines, and

```
01.10 ERASE
01.90 A "HOW MANY POINTS ARE YOU CONSIDERING ?",MAX,!

02.05 A "DO YOU WISH TO ADD ANOTHER TAPE ?",AN,!
02.10 IF (AN-OYES)7.01,3.01,7.01

03.01 SET N = N+1
03.05 A "HOW MANY POINTS DO YOU WISH TO THROW AWAY ?",TA,!
03.06 IF (TA)3.50,3.7,3.5
03.50 FOR I=1,TA; DO 3.6
03.51 GT 3.7
03.60 *; ASK X;*
03.70 FOR I=1,MAX; DO 4.05
03.71 GT 2.05

04.05 *;A X;A Y;*;S SUM(I)=SUM(I)+(X+Y)/2

05.05 F I=1,MAX; IF (SUM(I))5.10,5.10,5.20
05.10 SET SUM(I)=0
05.20

07.01 A !, "BASELINE ?   ",M,!!
07.02 A "SLOPE?   ",SL,!!
07.03 A "END LINE?   ",EL,!!
07.05 T "    I   ALPHA",!!
07.10 F I=1,EL,MAX; D 7.20; T !
07.12 A !!!!"WANT A * PLOT?   ",ANS,!
07.13 IF (ANS-OYES)7.14,8.01,7.14
07.14 A !!!!!"WANT AN XY PLOT?   ",ANT,!
07.15 IF (ANT-OYES)12.01,9.05,12.01
07.20 F J=1,EL; D 7.21; D 7.22;
07.21 S SUM(I+J-1)=1.8519*FLOG(SUM(I+J-1)/N*M); S M=M+SL
07.22 T %4.0 I+J-1, %5.03 SUM(I+J-1)

08.01 A "POINTS PER * ?   ",SP,!
08.02 A "PEAK VALUE?   ",PV,!
08.03 A "MAXIMUM SPACES? ",MS,!!
08.04 S SMX=SP*PV/MS
08.10 F I=1,SP,MAX; S XX=0; T "*",!; D 8.11; D 8.12
08.11 F K=1,SP; SET XX=XX+SUM(I+K-1)
08.12 FOR J=0,XX/SMX; T " "
08.30 GT 7.14

09.05 A "XF?   ",XF,!
09.06 A "YF?   ",YF,!
09.07 A "INX?   ",INX,!
09.08 A "IMY?   ",IMY,!
09.09 F I=2,MAX; D 9.11; D 9.13
09.10 GT 9.20
09.11 F IX=0,INX; D 9.12
09.12 S Z=FDIS(XF*(I-1+(IX/INX)),YF*SUM(I-1));
09.13 F IY=0,SG/(FABS(SUM(I-1)-SUM(I))+.01),IMY;D 9.14
09.14 S Z=FDIS(XF*I,YF*(SUM(I-1)+IY*((SUM(I)-SUM(I-1))/IMY)))
09.16 A "ANOTHER XY?   ",RAT,!
09.18 IF (RAT-OYES)9.20,9.05,9.20
09.20 A "WANT A LORENTZIAN FIT?   ",ANR,!
09.21 IF (ANR-OYES)9.22,12.02,9.22
09.22 QUIT
09.30 SET Z=FDIS(0,0)
```

247

```
10.10  S  Z=FDIS(0,YF*SUM(1))
10.20  F  I=1,1000;C
10.30  G  9.09

12.02  A  "YF?   ",YF,!
12.04  A  "H0W MANY PKS?   ",L,!
12.05  A  "NUMBER 0F DIVISI0NS?   ",MX,!
12.06  A  "SC?   ",SC
12.20  F  K=1,L; D0 12.3
12.21  GT 12.5
12.30  T  %1, !"F0R PEAK   ",K; G0T0 12.32
12.32  A  !"L0CATI0N  ",W(K),"   ABS0RBANCE  ",R(K),"   WIDTH  ",P(K)
12.50  T  !  "GIVE THE INITIAL AND FINAL P0INTS, AND INCREMENT Y0U"  !
12.60  A  "WISH EVALUATED.   ",M,N,J
12.90  T  !!!"   H        W        100*A"!!

13.10  F  H=1,MX; D 13.20; D 13.25
13.15  GT 13.30
13.20  F  W=M+(H-1)*(N-M)/MX,J,M+H*(N-M)/MX; D 14
13.25  T  %3,H+1,"   ", %6.03,(W-W(1))*SC,"   ", %5.03, 100*T,!
13.30  QUIT

14.10  S  T=0
14.20  F  K=1,L; D 15
14.30  S  Z=FDIS(W,YF*T*100)

15.10  SET  S=R(K)/(((<W-W(K)>*SC/P(K))↑2+1)
15.20  SET  T=T+S;R

16.30  S  SUM(I)=1.8519*FL0G(FEXP(SUM(I)/1.8519)*MI/MT)
16.40  S  MI=MI+SL
16.50  S  MT=MT+ST

29.10  S  Z=FNEW(2);T SUM(I);S Z=FNEW(3,1);S Z=FNEW(1)

31.10  S  Z=FNEW(2);S Z=FNEW(3,300)
31.20  W  A
31.30  S  Z=FNEW(3,300); S Z=FNEW(1)
*
```

```
03.10  F  I=1,MAX;  IF  (SUM(I))3.30,3.30,3.50
03.30  S  SUM(I)=0
03.50

04.05  F  I=1,MAX;*;A  X;A  Y;*;S  SUM(I)=SUM(I)+(X+Y)/2

07.10  F  I=1,EL,MAX;D  7.20;T  !
07.20  F  J=1,EL;D  7.21;D  7.22
07.21  S  SUM(I+J-1)=1.8519*FLOG(SUM(I+J-1)/N*M);S  M=M+SL
07.22  T  %4.0  I+J-1,%5.03  SUM(I+J-1)

09.09  F  I=2,MAX;D  9.11;D  9.13
09.11  F  IX=0,INX;D  9.12
09.12  S  Z=FDIS(XF*(I-1+(IX/INX)),YF*SUM(I+SH-1))
09.13  F  IY=0,IMY;D  9.14
09.14  S  Z=FDIS(XF*I,YF*(SUM(I+SH-1)+IY*((SUM(I+SH)-SUM(I+SH-1))/IMY)))

16.30  S  SUM(I)=1.8519*FLOG(FEXP(SUM(I)/1.8519)*MI/MT)
16.40  S  MI=MI+SL
16.50  S  MT=MT+ST

30.10  S  Z=FNEW(2);T  SUM(I);S  Z=FNEW(3,1);S  Z=FNEW(1)

31.10  S  Z=FNEW(2)
31.20  W  A
31.30  S  Z=FNEW(1)
*
```

249

then adjusted to best fit a Lorentzian. This section also prints out each point as it is calculated, and the value given the "END LINE?" question specifies how many points will be printed on a line before a carriage return- usually 5. This printing out is useful in finding reader errors before plotting, in finding the peak value for scaling, and in checking for negative values in the wings. These last are unavoidable when fitting a baseline through a noisy zero absorption trace. Yet they cannot be plotted, since the x-y recorder only accepts positive values. Once the final baseline is chosen, section 5 is used to set these small negative values to zero.

Section 8 is a simple plotting routine for the teletype, helpful in superimposing tapes with no original chart trace since the data points are easy to count.

Section 9 plots the lineshape on the x-y recorder, given the scaling factors XF and YF which convert data point number and absorbance amplitude into x-y recorder points. The granularities INX and IMY are the number of divisions in traveling from one point to the next, used to reduce pen overshoot. In this particular version, the y plotting loop 9.14 contains an automatically varying step size, where SG should be set to between .01 and .02. Section 10 positions the pen before x-y plotting begins.

Sections 12 through 15 calculate Lorentzian lineshapes and plot them on the x-y recorder for comparison with experiment. The number of divisions, MX, determines how many

points on the Lorentzian are typed out. The calculation of the scaling factor SC is discussed in Section I C. The location of the Kth line W(K) is measured in chart recorder points, as are the initial and final points and increment to be evaluated, M,N, and J. The half width at half maximum P(K) is measured in cm^{-1}. The peak absorbance R(K) is input in true absorbance units, cm^{-1}, although in section 7 the amplitudes calculated and output are 100 times larger.

Section 16 allows changes in baseline and slope for a set of data already operated on. Section 29 outputs an averaged line onto punched tape.

An elaborate program such as that described above allows room for only a little over 500 data points. To process longer scans, a short version of the Alpha Reader program is used, in which the variables must be defined by equations. This is listed following the longer program.

We also give a listing of the deconvolution program, a modification of one used by J. Logan and C. Mims. Its dialog has been written out in detail so that its operation should be self-explanatory.

```
01.04 S C0=0
01.05 A "NUMBER OF ITERATIONS?   ",CN,!!
01.06 A "SCALING FACTOR?   ",SB,!
01.20 A  "MAXIMUM POINTS (BINS) OF CONV  ",TC
01.22 F I=1,TC; D 1.24
01.23 G 1.25
01.24 S H(I)=0;   S M(I)=0;   S N(I)=0
01.25 T !
01.26 A "DATA ON TAPE?   ",C,!
01.28 I (C-0YES) 1.30,5.0,1.30
01.30 A "LORENTZIAN?   ",D,!
01.31 I (D-0YES) 1.40,1.36,1.40
01.32 F I=1,TC; D 5.0
01.34 G 1.49
01.36 F I=1,TC; D 7.0
01.38 G 1.49
01.40 F I=1,TC; D 1.48
01.44 G 1.49
01.48 T    "H(",%3.00,I,")= ";A H(I)
01.49 T %6.02 !," I   NORM CONV",!!
01.50 F I=1,TC;D 1.58
01.54 G 1.59
01.58 T %3.0,I, %6.03 H(I),!; S M(I)=H(I)
01.59 T !
01.60 A "INSTRUMENT FUNCTION WIDTH (BINS)  ",NS,!
01.64 F I=-(NS-1)/2,1,(NS+1)/2-1; D 1.70
01.66 G 1.80
01.70 *; A SH(I); *;
01.80 S Z=FNEW(1)
01.82 IF (C0-CN+2) 1.90,1.84,1.84
01.84 T !!,"BIN    FREQ    DECONV   RECONV",!
01.90 F I=1,TC; D 2.0
01.94 G 4.04

02.10 S X=0; F J=-(NS-1)/2,1,(NS+1)/2-1; D 3
02.20 S N(I)=M(I)*H(I)/X
02.25 IF (C0-CN+2) 2.35,2.30,2.30
02.30 T !,%2.00,I,%6.03,(I-W(1))*SC,N(I),X
02.35

03.10 S K=I+J;    I (K) 3.2,3.2,3.25
03.20 S K=K+TC;   G 3.30
03.25 I (K-TC) 3.3,3.30,3.28
03.28 S K=K-TC
03.30 S X=X+M(K)*SH(J)

04.04 S C0=C0+1
04.05 IF (C0-CN)4.20,4.10,4.10
04.10 A !!,"MORE ITERATIONS?   ",CM,!
04.12 IF (CM-0N0) 4.14,4.30,4.14
04.14 S CN=CN+CM; GT 4.20
04.20 F A=1,TC; D 4.26
04.22 G 1.82
04.26 S M(A)=N(A); S N(A)=0
04.30 A !!,"PLOT ORIG CONVOL?   ",Q; I (Q-0YES)9.16,9.05,9.16
04.40 T !
04.41 Q
04.50 S Z=FNEW(2); F I=1,TC; T N(I),!,0,!
04.55 S Z=FNEW(1)
04.60 Q
```

```
05.10  *; A H(I),E; *; I (H(I))5.3
05.20  S SB=SB+H(I); R
05.30  S H(I)=0

06.01  F I=1,40; T !,%2.00,I,%6.02,H(I)

07.04  A "HØW MANY PKS?   ",L,!
07.06  A "SC?   ",SC
07.20  F K=1,L; D 7.3
07.21  G 7.6
07.30  T %1, !"FØR PEAK  ",K; G 7.32
07.32  A !"LØCATIØN ",W(K)," ABSØRBANCE ",R(K),"   WIDTH  ",P(K)
07.60  F I=1,TC; D 7.64
07.62  R
07.64  F K=1,L; D 7.66
07.66  S H(I)=H(I)+R(K)/((((I-W(K))*SC/P(K))↑2+1)

09.05  A "XF?  ",XF,!,"YF?  ",YF,!
09.06  A "INX?  ",INX,!,"IMY?  ",IMY,!
09.08  F J=1,200; S Z=FDIS(0,YF*H(1))
09.09  F I=2,TC; D 9.11; D 9.13
09.10  G 9.16
09.11  F IX=0,INX; D 9.12
09.12  S Z=FDIS(XF*(I-1+(IX/INX)),YF*H(I-1));
09.13  F IY=0,IMY; D 9.14
09.14  S Z=FDIS(XF*I,YF*(H(I-1)+IY*((H(I)-H(I-1))/IMY)))
09.16  A !,"PLØT DECØNV?  ",RT; I (RT-0YES)9.50,9.18,9.50
09.18  A !,"PEAK RATIØ?  ",RA;  S YF=YF/RA
09.19  F J=1,200; S Z=FDIS(0,YF*N(1))
09.20  F I=2,TC; D 9.24; D 9.26
09.22  G 9.50
09.24  F IX=0,INX; D 9.25
09.25  S Z=FDIS(XF*(I-1+(IX/INX)),YF*N(I-1));
09.26  F IY=0,IMY; D 9.27
09.27  S Z=FDIS(XF*I,YF*(N(I-1)+IY*((N(I)-N(I-1))/IMY)))
09.50  A !,"PLØT INST FUNCT?  ",TR; I (TR-0YES)9.8,9.51,9.8
09.51  A !,"PEAK RATIØ?  ",RB; S YF=YF/RB
09.52  F J=1,200; S Z=FDIS(0,SH(1))
09.53  F I=-(NS-1)/2,1,(NS+1)/2-1; D 9.56; D 9.58
09.54  G 9.8
09.56  F IX=0,INX; D 9.57;
09.57  S Z=FDIS(XF*(I+(NS-1)/2+(IX/INX)),YF*SH(I-1))
09.58  F IY=0,IMY; D 9.59;
09.59  S Z=FDIS(XF*(I+(NS+1)/2),YF*(SH(I-1)+IY*((SH(I)-SH(I-1))/IMY)))
09.80  Q

31.10  S Z=FNEW(2);S Z=FNEW(3,300)
31.20  W A
31.30  S Z=FNEW(3,300); S Z=FNEW(1)
*
```

Appendix E : The Tunable Diode Laser

This appendix on the tunable diode laser has two objectives. One is to show by example that though the diode laser has its own very different characteristics as a spectroscopic tool compared with those of the parametric oscillator discussed in Section I C, it also has possibly serious problems in the measurement of its frequency and amplitude. The other object is to present, as measures of performance, some very preliminary lineshape data for ammonia lines, both for Doppler broadening and pressure broadening by ammonia and air. These indicate that with more measurements and some improvement in technique, interesting experiments can be done.

The theory and operation of the Arthur D. Little diode laser used in these studies has already been described in detail in Reference 127. Additional general information on diode lasers can be found in References 128-130. We will simply repeat here that the laser output, in the 4.6 and 10.6 micron regions, is very weak, extremely narrow in frequency, and is easily and continuously tunable by changing the current passing through the diode.

However, a major problem is the existence of several laser modes at one current, as shown in Figures 49 through 52. Figures 49-51 show the diode output at several current settings as a function of monochromator setting and so frequency. Data from these measurements and from line overlaps went into making

254

Figure 49: Scanning monochromator at constant
diode laser current for the 4.6 micron diode.
(Since the monochromator is scanned manually the
frequency scale is actually irregular.) One can
follow the progress of individual modes toward
higher frequency with increasing current. One can
also compare this set of scans with one taken an
hour later, shown in Figures 50 and 51. Comparison
at -1.55 A or -1.575 A shows similar mode structure
but different intensities.

Figure 50: More diode laser monochromator scans,
taken soon after Figure 49.

Figure 51: More diode laser monochromator scans-
a continuation of Figure 50.

Figure 49

256

Figure 50

-1.575 A

-1.55 A

-1.525 A

2195   2197   2199   2201 cm^{-1}

257

Figure 51

-1.725 A

-1.7 A

-1.675 A

-1.65 A

-1.625 A

-1.6A

2200   2202   2204   2206 cm⁻¹

258
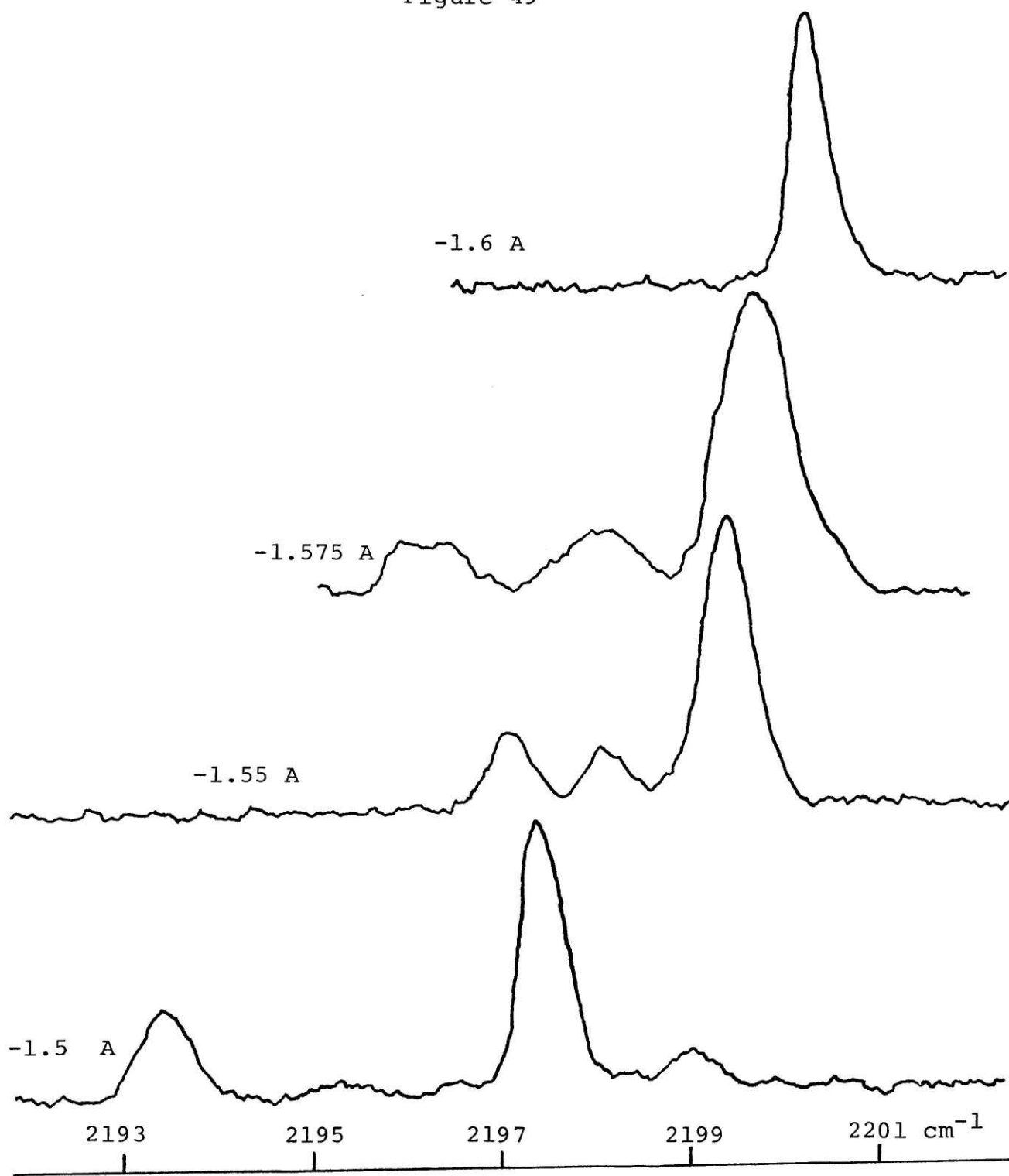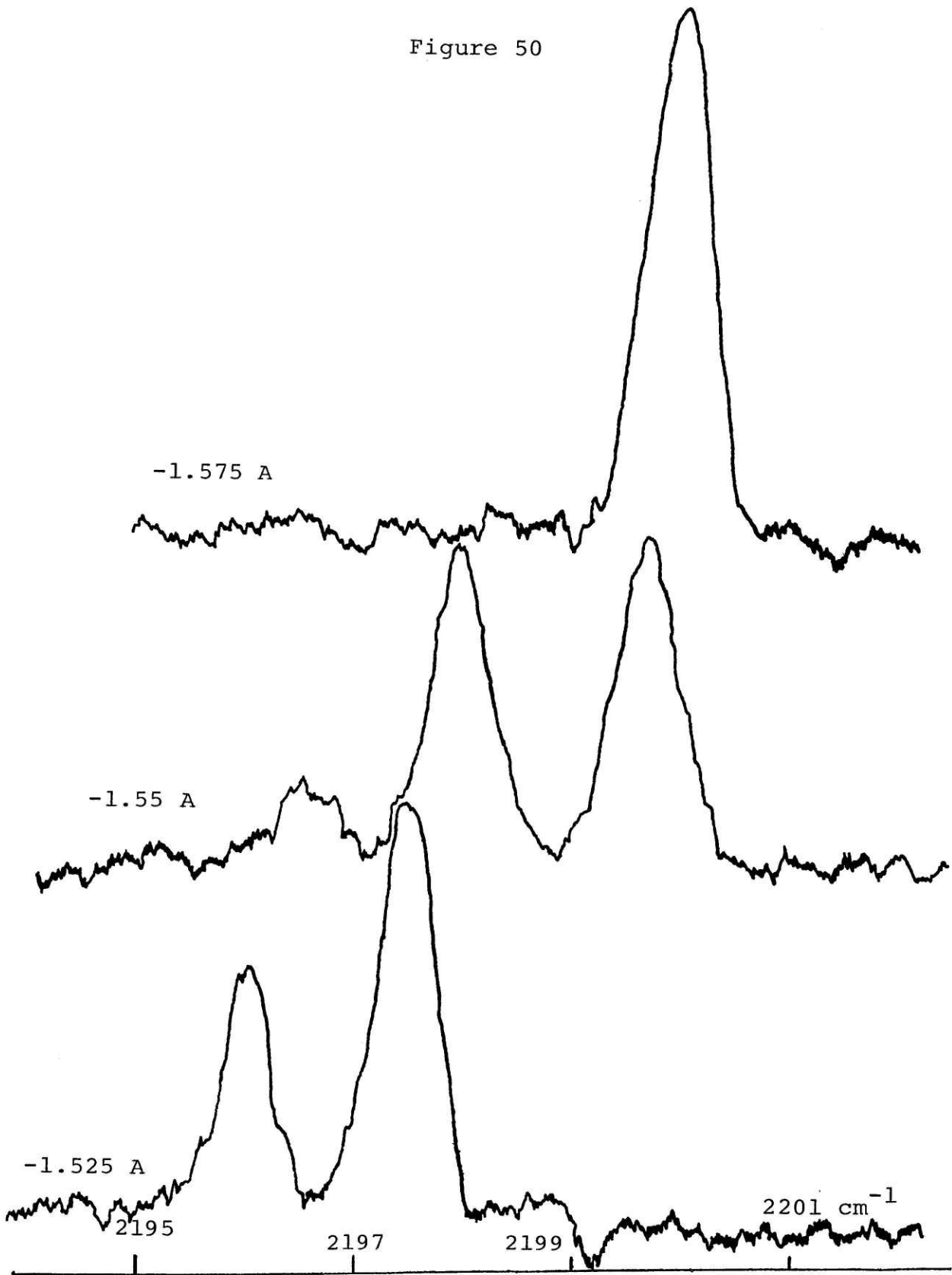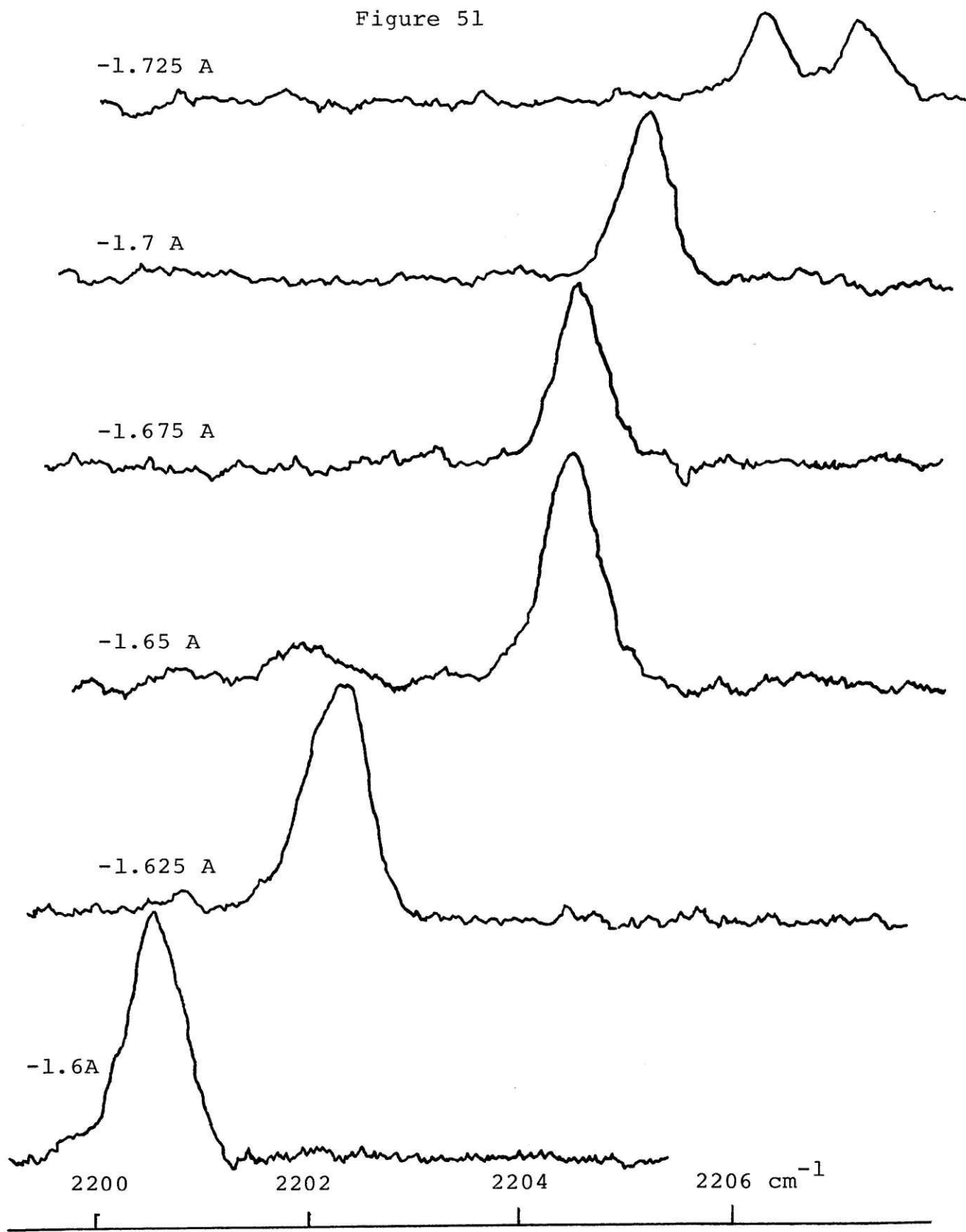
Figure 52: Graph of frequency of output of the 4.6 micron diode laser as a function of diode current. (Since diode characteristics change over time, the graph is no longer accurate.) The dots are diode laser output observed a fixed frequency by scanning the monochromator. The diagonal lines represent an attempt to organize the points into modes. The solid horizontal lines show positions of CO absorption lines, the long and short dashed lines the positions of DCl^{35} and DCl^{37} lines, and the two dot-dash lines are HI lines. Most overlaps of the diode laser modes with absorption lines predicted by this graph were actually observed. The modes marked A, B, and C are discussed in the caption to Figure 53.

Figure 52

260
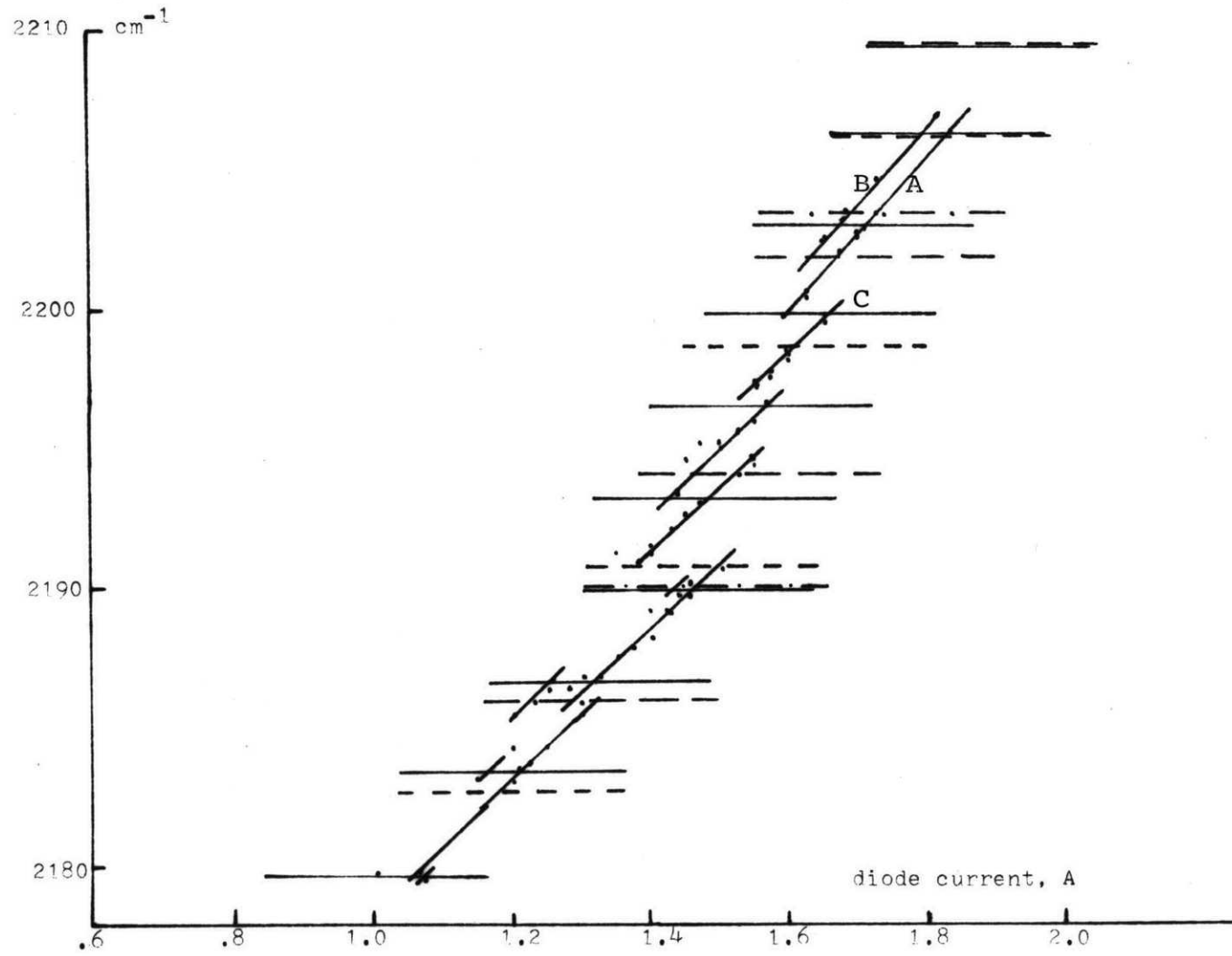
Figure 52, showing output in the 4.6 micron region as a function of current and making an attempt to sort it into modes. Also Figure 53 gives an example of overlaps with absorption lines, in which some lines appear more than once because of parallel modes.

Next we exhibit some results to show that the diode laser can give plausible results for low density linewidths. For ammonia at room temperature, the Doppler width is 42 MHz.[131] Figure 54 shows a number of lines at ammonia pressures of 100 to 560 mtorr, most of which are around 47 MHz wide, while the narrowest is 41 MHz.

From references 132 and 133, common self-broadened microwave linewidths are between 20 and 25 MHz/torr. Dividing the increase in ammonia pressure into the increase in linewidth for the lines in Figure 55 gives values from 15 to 21 MHz/torr. (Figure 56 shows two of those lines and an etalon scan, which must always be used to set the frequency scale.)

Finally, References 132-134 give nitrogen broadened microwave linewidths of 3.1 to 5.1 MHz/torr for the 1,1 to 12,12 inversions, while oxygen broadened lines are smaller. Figure 57 shows one of a set of traces taken with around 1 torr NH_3 and one of several with 10.9 torr of added air. The difference between the averages gives 2.7 MHz/torr. (Another line studied gave 1.8 MHz/torr.)

These linewidths are measured without converting to absorbance, and with only an estimate of where the true base-

Figure 53: A series of diode laser traces showing overlaps with absorption lines of CO, HI, and DCl. The monochromator was at 934 drum setting, corresponding to 2204 cm^{-1}, and had 1 mm entrance and exit slits. The lock-in amplifier was set at 1 mV sensitivity and 1 second time constant. The diode current scan rate was .0005 A/sec. In the lowest trace, involving CO lines and the germanium etalon, the etalon was deliberately misaligned so the fringes would not obscure the lines. Referring to Figure 52, a possible interpretation is that the overlaps are first mode C with the CO line at 2200 cm^{-1}, then mode B with the 2203 cm^{-1} CO line, mode A with the 2202 cm^{-1} DCl line, mode B with th HI line, mode A with the 2203 cm^{-1} CO line and then the HI line, and finally mode B with the CO line around 2206 cm^{-1}. This interpretation assumes that mode B had a somewhat steeper tuning rate than that drawn (so that the last CO overlap will appear close to that of mode A with HI) and that mode B did not extend down far enough on that day to overlap the 2202 cm^{-1} DCl line.
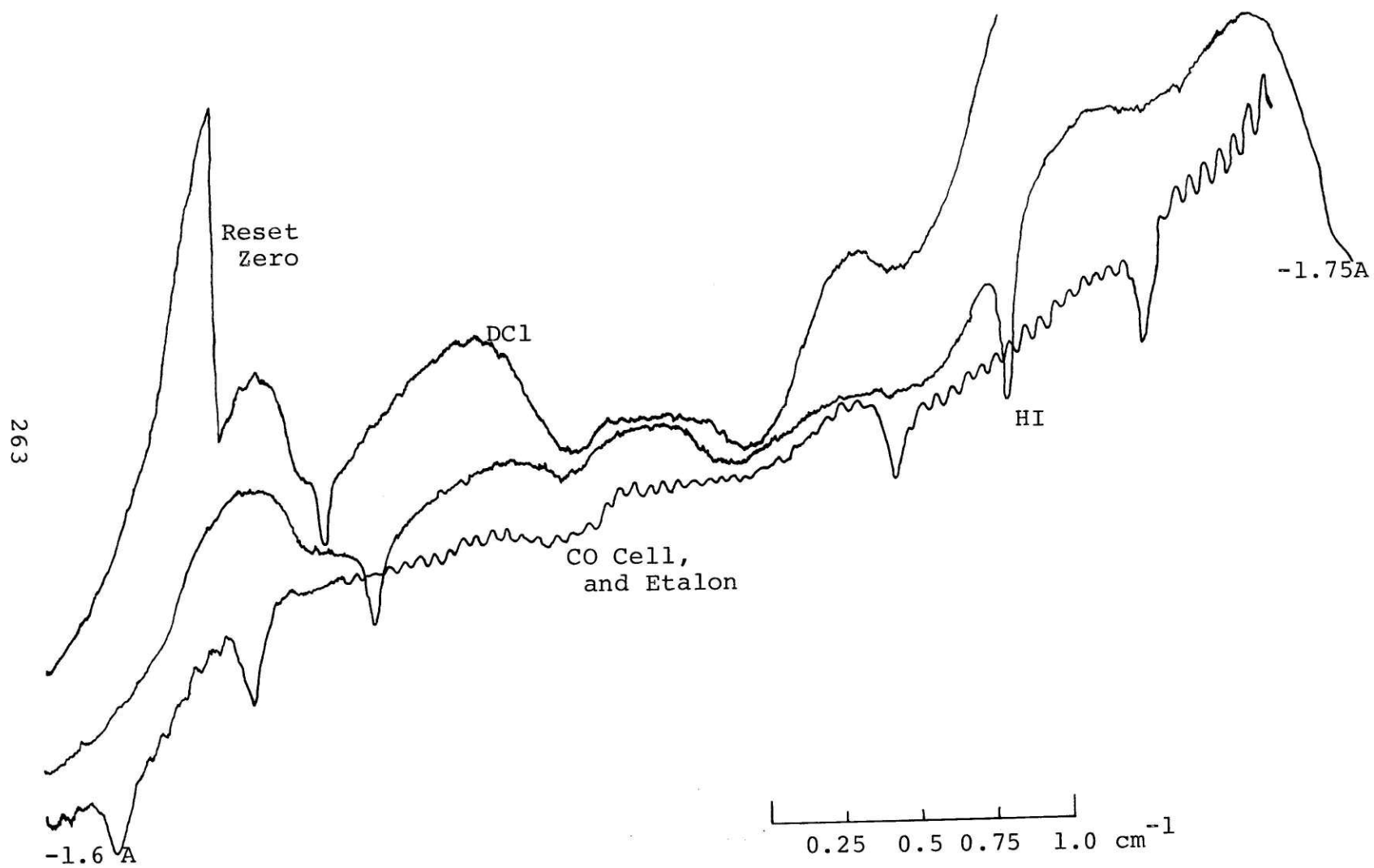
Figure 53

Figure 54:   From top to bottom, traces are of an absorption line due to 107, 195, 288, 400, and 560 mtorr of ammonia, showing the Doppler limit.

Figure 55:   From top to bottom, traces are of an absorption line due to 2.3, 4.6, 5.8, 7.9, 9.2, and 11.5 torr of pure ammonia, illustrating self broadening.

Figure 56:   The same ammonia lines at 2.3 and 4.6 torr as shown in Figure 55, and a trace due to the germanium etalon, which must always be used to set the frequency scale.   The distance between etalon peaks is 0.05 cm^{-1}.

0.01 cm^{-1}
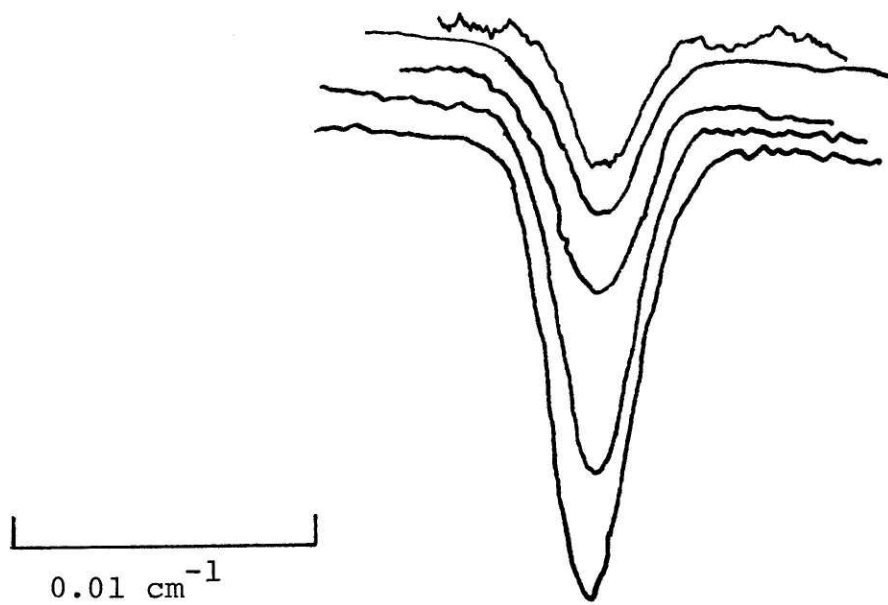
Figure 54

Figure 55

0.01 cm^{-1}
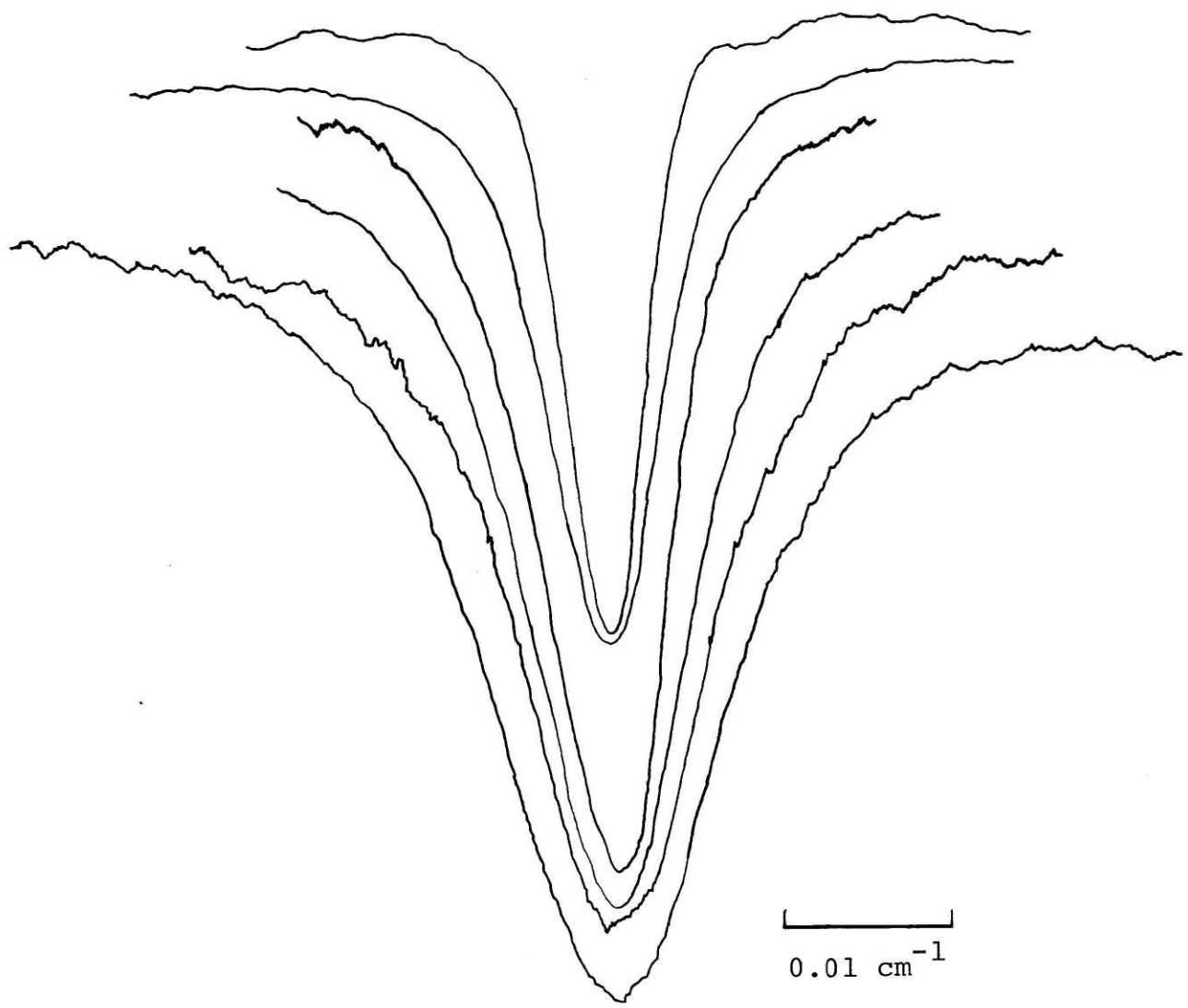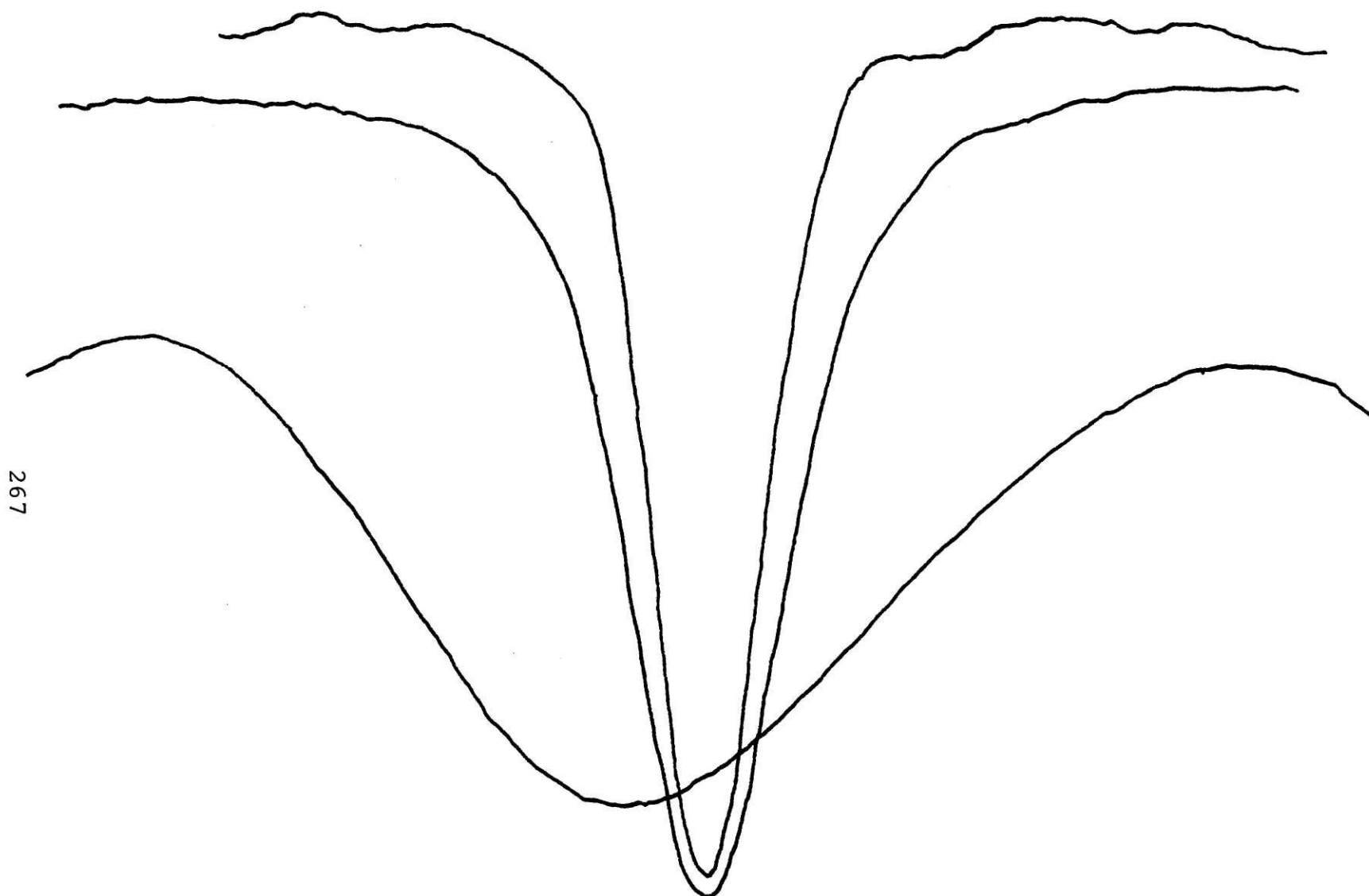
Figure 56

Figure 57: The upper trace is an absorption line due to around 1 torr of ammonia only, while the lower is the same line broadened by 10.9 torr of added air. The upper trace was taken with the Cu:Ge detector, the lower with the HgCdTe detector, which here was much noisier. The difference was not always so striking, and the fact that the HgCdTe detector operates at liquid nitrogen temperature rather than liquid helium makes it more attractive to operate.

Figure 57

269
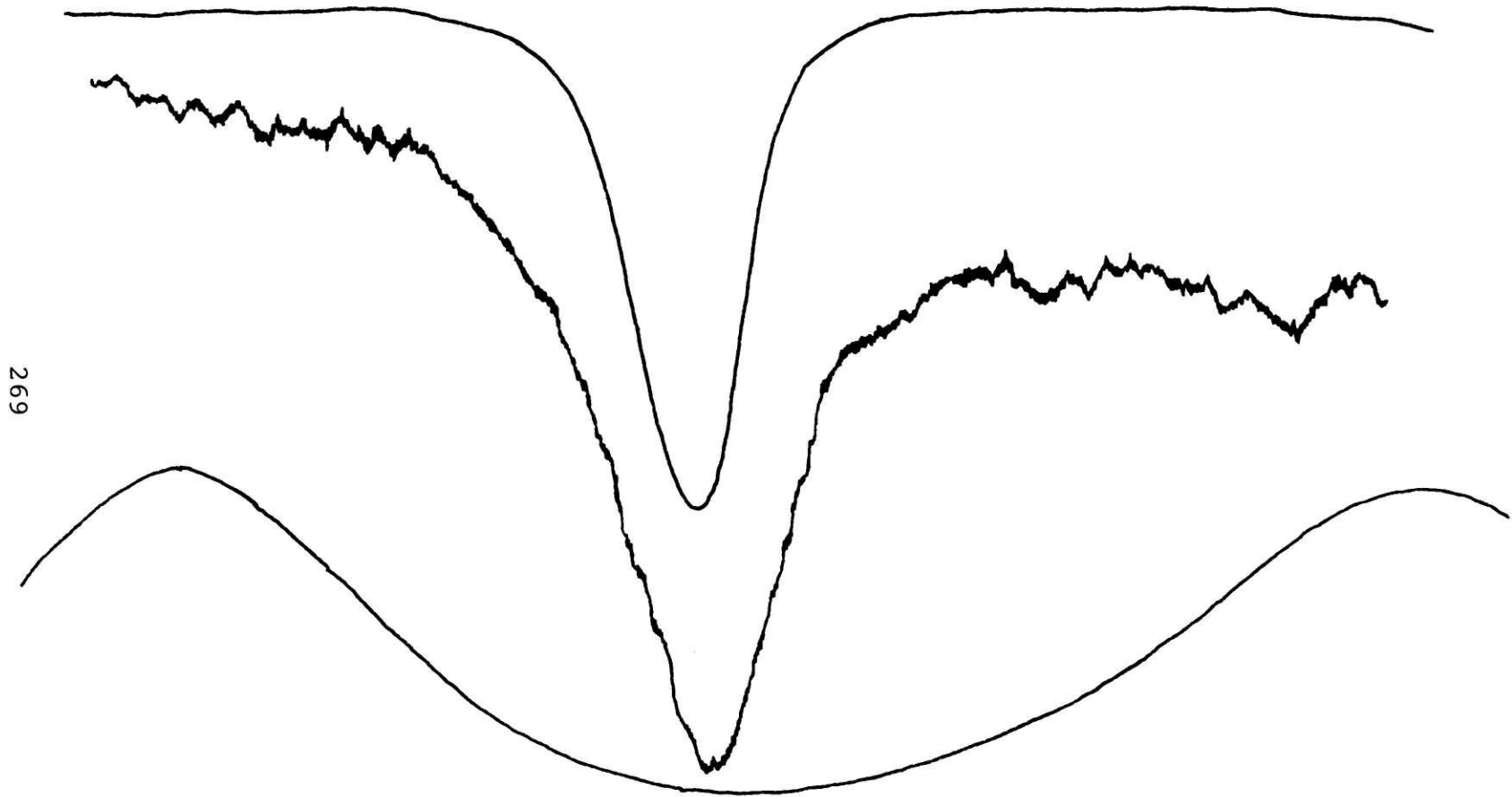
line is, so the 10 to 20 per cent scatter in repeated line-width measurements is not unexpected. Uncertainties in pressure measurement could contribute to twenty per cent differences observed in measuring identical samples on different days. But there are other disturbing observations. One is shown in Figure 58. The broader trace is one of five measurements on 150 mtorr of NH_3 alone, all giving 62 MHz to within a few per cent. The lower trace is one of five more taken with .77 torr of added air, giving an average width of only 51 MHz. These experiments were done in order to find just such an effect, which could be due to Dicke narrowing of the Doppler linewidth.[135-136] But this seems to be the wrong pressure regime for Dicke narrowing, and subsequent attempts under similar conditions could never uncover any more clear evidence for the effect.

Even if the tuning rate stability and spectral purity of the tunable diode laser were satisfactory, there are problems with amplitude measurement. Since the tuning range of the diode laser will obviously not allow choosing a baseline by looking at the absorption far in the wings of the lines, intensity measurement must also be accurate and reproducible. In practice, this means a double beam setup must be used, because although over short periods of time the amplitude may be fairly reproducible, over the time needed to record absorption traces and evacuate the cell the single beam intensity can change by 20 and 30 per cent. Yet considering

Figure 58: The lower trace was taken with 150 mtorr
of ammonia only, while the upper (and narrower) trace
had .77 torr added air.

Figure 59: Two successive scans of the same 100 mtorr
pure ammonia line, showing irreproducibility found
when using the diode laser in a single beam configuration.

Figure 58

Figure 59

273
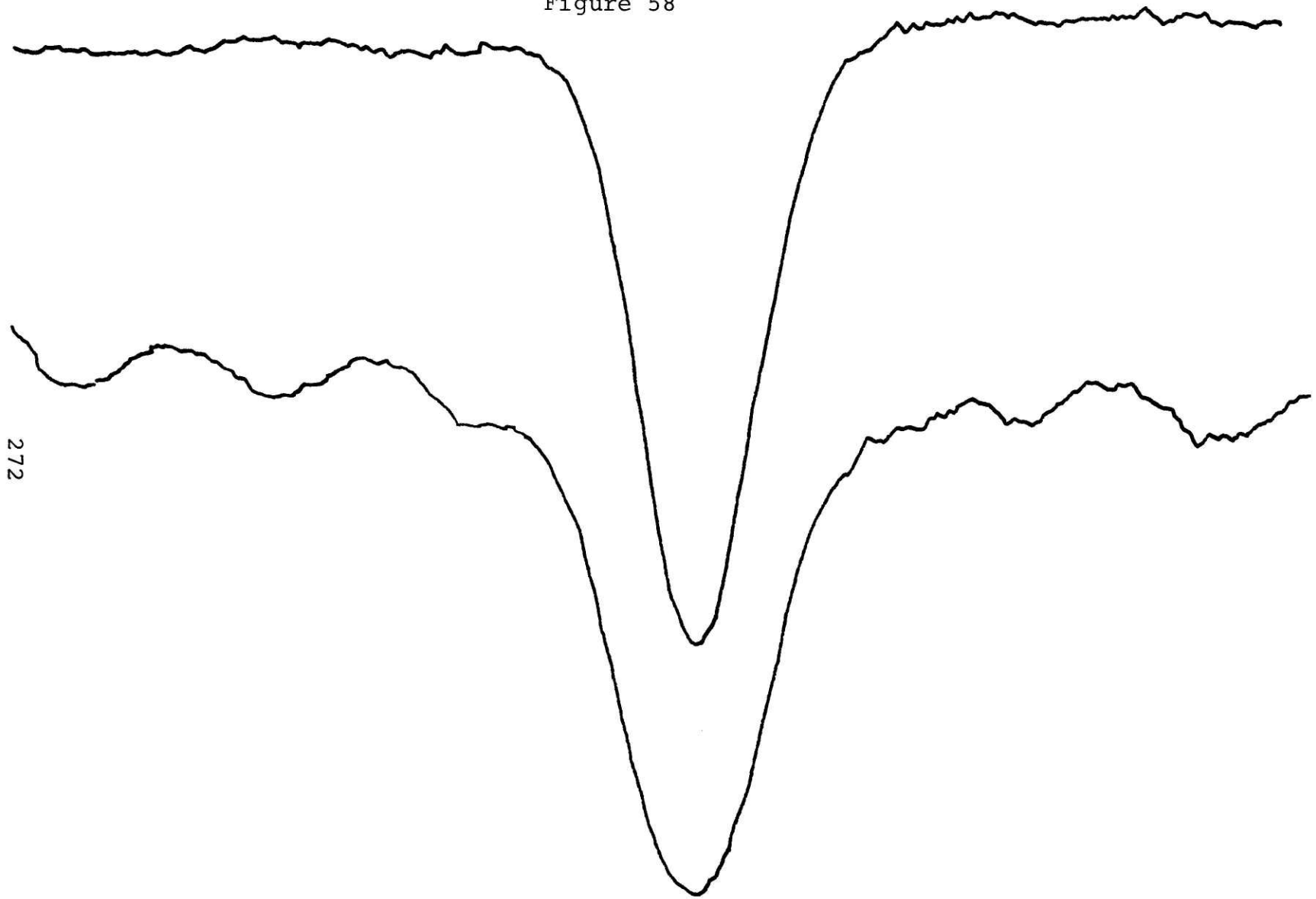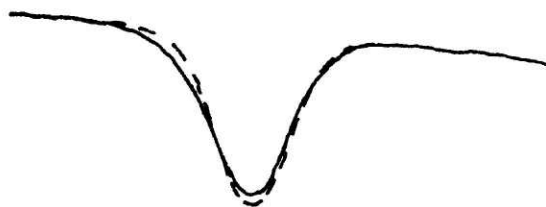
the low output power of the diode laser, a double beam setup would be very difficult to achieve. So even if one diode laser mode could be tuned without interference over several wavenumbers, obtaining lineshapes and linewidths at high pressures would be a difficult task. (Figure 59 is another example of non-reproducibility.)

Yet there is a type of higher order density effect which could be studied using the diode laser, with its high signal-to-noise ratio and narrow bandwidth over short tuning ranges. Indeed, perhaps this proposed experiment could be done in a single beam arrangement, making it easier to set up. As mentioned in Section II A, the logarithmic density dependence of the lineshape is expected to occur only close to the zero density resonance frequency, causing some sort of irregularity on the order of 0.1 cm^{-1} wide. Since the line shifts with pressure, the above point would be rather far out on one wing. So one would look for some lump or dip in the high pressure absorption scan of one wing which did not appear in the other. The diode laser, with its sensitivity to small spectral features might still prove useful in setting an upper limit on possible logarithmic terms.

Appendix F : Relation of the Binary Collision Operator to

Widths and Shifts

In the following we discuss the scattering tetradic T as we define it here in relation to the T operators used by Fano[137], T_F, and Albers[37], T_A. Then we will give examples of how the T operator is related to Lorentzian widths and shifts.

The following discussion is given in order to arrive at a definition for the width and shift operator $\mathcal{L}(1) = T_{r_2} T_{12} \tilde{\rho}(2)$ such that in the denominator of the lineshape expression it appears with a positive sign with respect to $i\omega$. As a preliminary we note that Equation (3) of Fano for the absorption coefficient is

$$Re \int_0^\infty e^{i\omega t} Tr(\mu \mu(t) \rho)\, dt$$

while Equations (3.1) and (3.2) of Albers give

$$Re \int_0^\infty Tr \mu e^{-i\omega t} e^{-iLt} \rho\mu \, dt$$

so the ω of Fano is $-\omega$ in Albers. Therefore Equation (40) of Fano becomes

$$(91) \quad T_F = L' + L' \frac{1}{-\omega - L_0} T_F = L' - L' \frac{1}{\omega + L_0} T_F$$

To get appropriate definitions of the width and shift we will want $T = iT_F$. But if we substitute this ($T = iT_F$) into Equation (91) we obtain not Equation (2.18) of Albers[37],

$$T_A = -iL' + iL' G_0 T_A$$

but rather $-iT = L' + iL' \frac{1}{i\omega + iL_0} iT = L' - L' G_0 T$ or

$$(92) \quad T = iL' - iL' G_0 T$$

which we take as our definition.

We now quickly run through the binary collision
expansion and resummation process to show that Equation (92)
gives the desired result. With α denoting a pair of
particles, $T_\alpha = iL'_\alpha - iL'_\alpha G_0 T_\alpha$ says

$$T_\alpha G_0 = \frac{iL'_\alpha G_0}{(1 + iL'_\alpha G_0)} = iL'_\alpha G_\alpha \,,$$

and by $\frac{1}{A+B} = \frac{1}{A} - \frac{1}{A} B \frac{1}{A+B}$,

$$(iL_0 + iL'_\alpha)^{-1} = \frac{1}{iL_0} - \frac{1}{iL_0} iL'_\alpha \frac{1}{iL_0 + iL_\alpha}$$

$$= G_0 - G_0 iL'_\alpha G_\alpha = G_0 + G_0 T_\alpha G_0$$

So we can write $G = G_0 - \sum_\alpha G_0 iL'_\alpha G_\alpha$ and

$$G = G_{12} - \sum_{\beta \, not \, 12} G_{12} iL'_\beta G_\beta = G_{12} - \sum_{\beta \, not \, 12} G_0 T_\beta G_0$$

and use the second equation to iterate the first, obtaining

$$G = G_0 - \sum_\alpha G_0 T_\alpha G_0 + \sum_{\alpha \, not \, \beta} G_0 T_\alpha G_0 T_\beta G_0 + \dots$$

So eventually after averaging we get

$$Tr \; \rho \left(R(1) - R(1) \rho \pounds(1) R(1) + R(1) \rho \pounds(1) R(1) \pounds(1) R(1) - \dots \right) \tilde{\rho}(1) \rho$$

where $R(1) = (\epsilon + i\omega + iL_{int}(1))^{-1}$ and resumming gives us

$$(93) \quad Tr \; \rho \left(i\omega + iL_{int}(1) + \rho \pounds(1) \right)^{-1} \tilde{\rho} \rho$$

where the linewidth operator $\rho \pounds(1)$ does indeed appear with a
positive sign.

If we use Equation (55) of Fano for the scattering
tetradic we can obtain the analog of Equation (A.8) of Albers,[38]
or of Equation (D.18) of Reference 39, (writing the volume
normalization of the t matrices explicitly),

$$T_{abcd} \Rightarrow i(t_{ac} \underset{V^2}{(E_b - \omega)} \Delta_{bd} - t^*_{bd} \underset{V^2}{(E_c + \omega)}$$

$$(94) \qquad + i\pi \delta(E_a + \hbar\omega - E_c) t_{ac}(E_a) \underset{V^4}{t^*_{bd}(E_d)} + i\pi \delta(E_b - \hbar\omega - E_d) t_{ac}(E_c) \underset{V^4}{t^*_{bd}(E_b)})$$

There are more terms in the expression for the T operator

given by Fano. In the discussion following his Equation (55)
he explains that they describe transient, or duration of
collision effects, and can be ignored in the impact
approximation. Also in Appendix D of Reference 39 it is
shown that this ignoring of terms not in Equation (94)
corresponds to the $\vec{k} \to 0$ limit of $T_{12}(\vec{p_1}\vec{p_2}\ \vec{p_1}\vec{p_2}\ \vec{p_1'}\vec{p_2'}\ \vec{p_1''}\vec{p_2'})$
where $\vec{k} = \vec{p_1'} - \vec{p_1''}$.

If we look at T_{abab}, and make the approximation $\omega = \omega_{ba}$
Equation (94) becomes

$$(95) \quad i\left(\underset{\gamma^2}{T_{aa}^0} - \underset{\gamma^2}{T_{bb}^*} + 2\pi i\, \delta(E_b - E_a)\underset{\gamma^4}{T_{aa}T_{bb}^*} \right)$$

We now want to look at the consequences of our definition
of T on its relation to line widths and shifts. First the
presence of the weighting factor $\tilde{\rho}_a$ or $e^{\beta E_a}/\sum_i e^{\beta E_i}$ in the
lineshape expression tells us that in $\mathcal{L}(abab)$ or $\mathcal{L}_{ab}$ a is the
initial state, and so in absorption it is the lower state. We
want $\omega_{ba} = \frac{\epsilon_b - \epsilon_a}{\hbar}$ to be greater than zero, and if ϵ_a and ϵ_b are
negative, we want $|\epsilon_a| > |\epsilon_b|$, or ϵ_a should indeed be the ground
state energy. (In Anderson theory[31] the frequency is also ω_{fi}.)

The Anderson theory lineshift appearing in the Lorentzian
(for instance in Equation (78) of Reference 138), $n v S_i^0$, is
proportional to $V_i - V_f$, or $V_a - V_b$, and $\Delta\nu$, the experimentally
observed shift is $-n v S_i^0 \propto V_b - V_a$. So looking at the first Born
approximation to Equation (94), $\text{Im}\,\mathcal{L} \propto \text{Im}(i(V_{aa} - V_{bb})) = V_a - V_b \propto S_i^0$
To check against Fano, since his ω is $-\omega$ of Albers, his
Equation (1) has a perturbed frequency of $i\omega_{ba} - id_{ba} - w_{ba}$ so

277

that his shift $d \propto \delta\rho$ (and his Equation (57)) is $d \propto V_a - V_b$. Fano says that in $(\omega_F - \omega_{ab} - \langle M_c \rangle_{abab})^{-1}$ the shift $d = Re\langle M_c \rangle$ So by $-i\mathcal{L} = \langle M_c \rangle$, $d = Im\mathcal{L}$, so again $Im\mathcal{L} \propto \delta\rho$.

In absorption, most shifts of HCl and HF lines due to collisions with rare gas atoms are experimentally observed to be negative (red), meaning that $\delta\rho$ is positive.[12,13,19,24] Now $\delta\rho \propto Im\mathcal{L}_{ab} \propto V_{aa} - V_{bb}$, and since $\delta\rho > 0$, $V_{aa} > V_{bb}$. But V_{aa} and V_{bb} are negative if attractive, so $|V_{aa}| < |V_{bb}|$, when averaged over those collisions which contribute to shifts. This is plausible if we ascribe shifts primarily to long range collisions where forces are attractive. One might indeed expect the upper state to be more attractive because of its greater average size due to vibrational excitation and therefore its greater polarizability. Thus with the upper state shifted down more by this weighted average than the lower state, a red shift results. (There are also rotational effects which for low J can increase the importance of the repulsive part of the potential, which one would expect to be higher at a given intermolecular distance for the larger upper state, and even lead to a blue shift.

Fano[137] says that in $(\omega - \mathcal{L}_0 - \langle M_c \rangle)^{-1}$ the Lorentzian width w corresponding to the Anderson theory[31] width $n\nu\delta_\gamma$ is $-Im\langle M_c \rangle$, which is $Re\mathcal{L}$ by $-i\mathcal{L} \propto \langle M_c \rangle$. (Also in Cattani,[63] his $\bar{H}$ is our $\mathcal{L}$, and his shift term $s \propto -Im\bar{H}$ is the experimentally reported shift.) And indeed from Equation (93) we see that $Re\,\rho\mathcal{L}_{ab}$ is the theoretical quantity corresponding to the observed half

width $\Delta \nu_{1/2}$.

That $\rho \mathcal{L}_{ab}$ is itself positive can be seen using a version
of the optical theorem,[139] for instance as in Equation (19.74)
of Reference 98,

$$i(\tau_{aa} - \tau_{aa}^{*}) = -2 \mathrm{Im}\, \tau_{aa} = 2\pi \sum_{c} \delta(E_c - E_a) \tau_{ca}^{*} \tau_{ca}$$

Then the first two terms of Equation (95) become

$$(96) \quad \pi \sum_{c} \left(|\tau_{ac}|^2 \delta(E_c - E_a) + |\tau_{bc}|^2 \delta(E_c - E_b) \right)$$

an expression which is manifestly positive. Especially in the
limit that V_b is very much like V_a, one can just as easily see
that the third term of Equation (95) is negative. However in
this limit it is related to the elastic cross section, while
Equation (96) is related in the same way to the larger total
scattering cross section, so that the difference is positive.

So in summary in the approximations of Anderson theory $\mathcal{L}$
will become $v(\delta_r + i \delta_i)$, and from Equation (21) of Fano,
$-(i\omega_F - i\omega_{ab} - i\langle M_c \rangle)^{-1}$ with $-\omega_F = \omega$ and $\langle M_c \rangle \Rightarrow -i \rho \mathcal{L}$ we obtain $(i(\omega - \omega_{ba}) + \rho \mathcal{L})^{-1}$
in our lineshape expression.

A final word of caution is in order. When our $\mathcal{L}$ is
reduced to a number, in the Lorentzian function $\gamma/((\omega - \omega_{ba})^2 + \gamma^2)$
when the distance from line center squared, $(\omega - \omega_d)^2$ equals γ^2,
the value of the function is 1/2. So theoretically we are
computing the half width at half maximum (HWHM). The full
width at half maximum (FWHM) is twice that, and either may be
reported in experimental papers.

279

Appendix G : <u>Determination of Cutoff k_o for a Square Well</u>

In this appendix we wish to gain an estimate of the upper limit cutoff wave vector k_o by approximating the $\hat{k}$ dependence of the T operators in the simplest possible way. We use the first Born approximation and simply look at $V(-K,0) = \int d\vec{r}\, e^{i\vec{K}\cdot\vec{r}_{12}} V(r_{12})$. We first take a step function for our potential, $V(r_{12}) = \epsilon_w$ for $0 \leqslant r_{12} \leqslant r_w$ and 0 for $r_{12} > r_w$. Then by $\int_{-1}^{1} du\, e^{iKru} = 2\frac{\sin Kr}{Kr}$ and $\int x \sin ax\, dx = \frac{1}{a^2}\sin ax - \frac{x}{a}\cos ax$,

$$V(-K,0) = \frac{4\pi}{K}\left(\frac{\epsilon_w}{K^2}\sin Kr_w - \frac{\epsilon_w}{K}r_w \cos Kr_w\right),$$

while $V(0,0) = 4\pi\epsilon_w \frac{r_w^3}{3}$.

To determine the effective k_o due to two k dependent T_{12} factors, we solve

$$(97)\quad \int_0^\infty dK\left(\frac{\sin Kr_w}{K^3} - \frac{r_w}{K^2}\cos Kr_w\right)^2 = \int_0^{K_o} dK\left(\frac{r_w^3}{3}\right)^2 = K_o\left(\frac{r_w^3}{3}\right)^2$$

or, changing to a dimensionless K by $R_w = \bar{p}_{12}r_w/\hbar$, Equation (97) becomes

$$(98)\quad \frac{\hbar^5}{\bar{p}_{12}^5}\int_0^\infty dK\left(\frac{\sin KR_w}{K^3} - \frac{R_w}{K^2}\cos KR_w\right)^2 = K_o\left(\frac{\hbar}{\bar{p}_{12}}\right)^6\left(\frac{R_w^3}{3}\right)^2$$

For $\bar{p}_{12}$ being the thermal average momentum and r_w on the order of 3 A, R_w is 100. We can note that since $J_1(z) = \frac{\sin z}{z^2} - \frac{\cos z}{z}$ and $J_1(KR_w) = \left(\frac{\pi}{2KR_w}\right)^{1/2}J_{3/2}(KR_w)$ the integral in Equation (98) is

$$(99)\quad R_w^4\int_0^\infty dK\, \frac{1}{K^2}\left(\frac{\sin KR_w}{(KR_w)^2} - \frac{\cos KR_w}{(KR_w)}\right)^2 = R_w^4\,\frac{\pi}{2}\int_0^\infty \frac{dK}{R_w K^3}\left(J_{3/2}(KR_w)\right)^2$$

On page 331 of Volume 1 of Reference 140 we find that Mellin transform (33) is $\int_0^\infty J_\mu(ax)J_\nu(ax)x^{s-1}dx$, $a > 0$

$$= 2^{s-1}a^{-s}\frac{B(1-s, \frac{1}{2}\mu + \frac{1}{2}\nu + \frac{1}{2}s)}{\Gamma(\frac{1}{2}\nu - \frac{1}{2}\mu - \frac{1}{2}s + 1)\,\Gamma(\frac{1}{2}\mu - \frac{1}{2}\nu - \frac{1}{2}s + 1)}\quad \text{for}\ -Re(\mu+\nu) < Re(s) < 1$$

where the beta function $B(x,y) = \frac{\Gamma(x)\Gamma(y)}{\Gamma(x+y)}$, $\Gamma(n-1) = \frac{\Gamma(n)}{(n-1)}$, and $\Gamma(n) = (n-1)!$

So Equation (99) becomes $\frac{\pi}{15}R_w^5$. (The same result is also

obtained using the Hankel transform 8.11 (4) on page 4 of

Volume 2 of Reference 140.) This means that k_o is $\frac{9\pi}{16 r_w}$

or approximately 1/1.7A for r_w around 3 A.

We can also investigate more complicated step function

potentials, such as one for which $V(r_{12})$ is ϵ_b for $0 \leqslant r_{12} \leqslant r_b$,

ϵ_a for $r_b \leqslant r_{12} \leqslant r_a$, and 0 for $r_{12} > r_a$. For this, k_0 is

defined by $\int_0^\infty ((\epsilon_b - \epsilon_a) R_b^{3/2} J_{3/2}(KR_b) + \epsilon_a R_a^{3/2} J_{3/2}(KR_a))^2 \, dK/K^3$

$= (\epsilon_b - \epsilon_a)^2 \frac{\pi}{15} R_b^5 + 2(\epsilon_b - \epsilon_a)\epsilon_a \frac{\pi}{12} \frac{R_a^3 R_b^3}{(R_a^2 R_b)} {}_2F_1 (\frac{1}{2}, 2, 4, \frac{4 R_a R_b}{(R_a + R_b)^2}) + \epsilon_a^2 \frac{\pi}{15} R_a^5$

$\equiv K_o ((\epsilon_b - \epsilon_a)(\frac{R_b^3}{3}) + \epsilon_a (\frac{R_a^3}{3}))^2$

But the hypergeometric function ${}_2F_1$ is difficult to evaluate,

so numerical integration was used for several examples. For

this potential the results depend on the relative sizes of ϵ_a

and ϵ_b , where in the simplest case the value of k_o was

independent of ϵ_w. So for instance for the choices $\epsilon_b = 4$,

$\epsilon_a = -1$, $r_b = 3$ A, and $r_a = 6$ A, k_o is around 1/2.1 A, while

for $\epsilon_b = 4$, $\epsilon_a = 1$, $r_b = 3$ A and $r_a = 6$ A, k_o is around 1/3A.

In the estimates made in Section II we will take r_o, the

reciprocal of k_o, to be 3 A, but this is obviously only an

order of magnitude guess.

Appendix H : <u>The Jacobian between $\hat{p}''_{13}$ and $\hat{p}''_{12}$</u>

From T_{13} we have an integration over the angles of $\vec{p}''_{13}$, the momentum after the 1-3 collision, but we would rather integrate over the angles of $\vec{p}''_{12}$, which appears in the G_o denominator. So in two dimensions we need the Jacobian

$J = \partial\Theta''_{13}/\partial\Theta''_{12}$.

By momentum conservation, $\vec{p}'_1 + \vec{p}_3 = \vec{p}''_1 + \vec{p}'_3$, or $\vec{p}'_1 - \vec{p}''_1 = \vec{p}'_3 - \vec{p}_3$, so that $\vec{p}'_{12}/m - \vec{p}''_{12}/m = \vec{p}'_1/m_1 - \vec{p}''_1/m_1$ is

$m/m_1 (\vec{p}'_1/m_1 + \vec{p}_1/m_3 - \vec{p}''_1/m_1 - \vec{p}''_1/m_3) = m/m_1 (\vec{p}'_1/m_1 - \vec{p}_3/m_3 - \vec{p}''_1/m_1 + \vec{p}'_3/m_3)$

$= m/m_1 (\vec{p}'_{13}/m - \vec{p}''_{13}/m)$

Therefore,

(100) $\quad p''_{13x} = p'_{13} \cos\Theta'_{13} - (\tfrac{m_1}{m})(p'_{12}\cos\Theta'_{12} - p''_{12}\cos\Theta''_{12})$

and

(101) $\quad p''_{13y} = p'_{13} \sin\Theta'_{13} - (\tfrac{m_1}{m})(p'_{12}\sin\Theta'_{12} - p''_{12}\sin\Theta''_{12})$

so that

(102) $\quad \partial p''_{13y}/\partial\Theta''_{12} = (\tfrac{m_1}{m}) p''_{12}\cos\Theta''_{12} = (\tfrac{m_1}{m}) p''_{12x}$

and so on. So with $\Theta''_{13} = \tan^{-1} p''_{13y}/p''_{13x}$,

(103)
$$\frac{\partial\Theta''_{13}}{\partial\Theta''_{12}} = \frac{1}{(1 + (\frac{p''_{13y}}{p''_{13x}})^2)} \left((\tfrac{m_1}{m}) \frac{p''_{12x}}{p''_{13x}} + p''_{13y}\times(\tfrac{m_1}{m})\frac{p''_{12y}}{p''^2_{13x}}\right)$$
$$(\tfrac{m_1}{m}) \frac{(p''_{12x}p''_{13x} + p''_{12y}p''_{13y})}{(p''_{13x})^2 + (p''_{13y})^2} = (\tfrac{m_1}{m}) \frac{\vec{p}''_{12}\cdot\vec{p}''_{13}}{p''^2_{13}}$$

In three dimensions, we can shorten our path to the Jacobian by first transforming dp''_{13} into $(\tfrac{m_1}{m})^3 dp''_{12x}dp''_{12y}dp''_{12z}$ and into $(\tfrac{m_1}{m})^3 p''^2_{12} dp''_{13} \partial p''_{12}/\partial p''_{13} \sin\Theta''_{12} d\Theta''_{12} d\phi''_{12}$ Then $\vec{p}''_{12} = (\tfrac{m}{m_1})(\vec{p}''_{13} - \vec{p}'_{13}) + \vec{p}'_{12}$ means that $p''_{12} = ((\tfrac{m}{m_1})^2|\vec{p}'_{13} - \vec{p}''_{13}|^2 + p'^2_{12} + 2(\tfrac{m}{m_1})\vec{p}'_{12}\cdot(\vec{p}''_{13} - \vec{p}'_{13}))^{1/2}$. So using $\partial p''_{13z}/\partial p''_{13} = p''_{13z}/p''_{13}$ and so on, we find

(104) $\quad \partial p''_{12}/\partial p''_{13} = \tfrac{1}{p''_{12}}((\tfrac{m}{m_1})^2(\vec{p}'_{13} - \vec{p}''_{13})\cdot\tfrac{\vec{p}''_{13}}{p''_{13}} + (\tfrac{m}{m_1})\tfrac{\vec{p}'_{12}\cdot\vec{p}''_{13}}{p''_{13}}) = \tfrac{1}{p''_{12}}(\tfrac{m}{m_1})\tfrac{\vec{p}''_{12}\cdot\vec{p}''_{13}}{p''_{13}}$

so that

(105) $\quad J = \partial(\cos\theta_{13}''\,\phi_{13}'')/\partial(\cos\theta_{12}''\,\phi_{12}'') = \left(\frac{m_1}{m}\right) P_{12}''^2 /_{P_{13}''^2}\ \vec{P}_{12}''\cdot\vec{P}_{13}''/_{P_{12}''P_{13}''}$

Since this is an important result, it is worth while to also obtain it straightforwardly. We use

$$P_{13}''x = P_{13}'\sin\theta_{13}'\cos\phi_{13}' - \left(\frac{m_1}{m}\right)\left(P_{12}'\sin\theta_{12}'\cos\phi_{12}' - P_{12}''\sin\theta_{12}''\cos\phi_{12}''\right)$$

(106) $\quad P_{13}''y = P_{13}'\sin\theta_{13}'\sin\phi_{13}' - \left(\frac{m_1}{m}\right)\left(P_{12}'\sin\theta_{12}'\sin\phi_{12}' - P_{12}''\sin\theta_{12}''\sin\phi_{12}''\right)$

$$P_{13}''z = P_{13}'\cos\theta_{13}' - \left(\frac{m_1}{m}\right)\left(P_{12}'\cos\theta_{12}' - P_{12}''\cos\theta_{12}''\right)$$

with $\theta_{13}'' = \tan^{-1}\left((P_{13}''x^2 + P_{13}''y^2)^{1/2}/_{P_{13}''z}\right)$, $\phi_{13}'' = \tan^{-1}P_{13}''y/_{P_{13}''x}$, $\cos\theta_{13}'' = P_{13}''z/_{P_{13}''}$,

and $\partial\sin\theta/\partial\cos\theta = -\cos\theta/_{\sin\theta}$.

We will want[141] the difference of

$$\partial\cos\theta_{13}''/\partial\cos\theta_{12}'' = \left[\frac{\left(\frac{m_1}{m}\right)P_{12}''}{P_{13}''} - \frac{P_{13}''z}{P_{13}''^3}\frac{1}{2}\left(2P_{13}''z\left(\frac{m_1}{m}\right)P_{12}''\right)\right]$$

(107)

$$\qquad -\left[\frac{P_{13}''z}{P_{13}''^3}\left(2P_{13}''x\left(-\left(\frac{m_1}{m}\right)P_{12}''\frac{\cos\theta_{12}''}{\sin\theta_{12}''}\cos\phi_{12}''\right) + 2P_{13}''y\left(-\left(\frac{m_1}{m}\right)P_{12}''\frac{\cos\theta_{12}''}{\sin\theta_{12}''}\sin\phi_{12}''\right)\right)\right]$$

times

(108) $\quad \partial\phi_{13}''/\partial\phi_{12}'' = \dfrac{P_{13}''x^2}{(P_{13}''x^2 + P_{13}''y^2)}\left(\dfrac{P_{13}''x\,P_{12}''y\left(\frac{m_1}{m}\right)}{(P_{13}''x)^2} + \dfrac{\left(\frac{m_1}{m}\right)P_{12}''x\,P_{13}''x}{(P_{13}''x)^2}\right)$

and

(109) $\quad \partial\cos\theta_{13}''/\partial\phi_{12}'' = \dfrac{-\frac{1}{2}P_{13}''z}{P_{13}''^3}\left(-2P_{13}''x\left(\frac{m_1}{m}\right)P_{12}''y + 2P_{13}''y\left(\frac{m_1}{m}\right)P_{12}''x\right)$

times

(110) $\quad \partial\phi_{13}''/\partial\cos\theta_{12}'' = \dfrac{P_{13}''x^2}{(P_{13}''x^2 + P_{13}''y^2)}\left(\dfrac{-P_{13}''y}{(P_{13}''x)^2}\left(\left(\frac{m_1}{m}\right)P_{12}''\frac{\cos\theta_{12}''}{\sin\theta_{12}''}\cos\phi_{12}'' - \left(\frac{m_1}{m}\right)\frac{P_{12}''}{P_{13}''x}\frac{\cos\theta_{12}''}{\sin\theta_{12}''}\sin\phi_{12}''\right)\right)$

We denote the two terms in square brackets in Equation (107) as A and B, and first look at $B\,\partial\phi_{13}''/\partial\phi_{12}'' - \partial\cos\theta_{13}''/\partial\phi_{12}''\ \partial\phi_{13}''/\partial\cos\theta_{12}''$

$$= \frac{1}{2}\frac{P_{13}''z}{P_{13}''^3}\frac{P_{13}''x^2}{(P_{13}''x^2 + P_{13}''y^2)}\frac{P_{12}''}{(P_{13}''x)^2}\left(\frac{m}{m_1}\right)\frac{\cos\theta_{12}''}{\sin\theta_{12}''}\left(\frac{m_1}{m}\right)$$

(111) $\quad \times\Big[2P_{13}''x\cos\phi_{12}''\left(P_{13}''y\,P_{12}''y + P_{12}''x\,P_{13}''x\right) + 2P_{13}''y\cos\phi_{12}''\left(2P_{13}''x\,P_{12}''y - 2P_{13}''y\,P_{12}''x\right)$

$\qquad + 2P_{13}''y\sin\phi_{12}''\left(P_{13}''y\,P_{12}''y + P_{12}''x\,P_{13}''x\right) + 2P_{13}''x\sin\phi_{12}''\left(2P_{13}''x\,P_{12}''y - 2P_{13}''y\,P_{12}''x\right)\Big]$

283

The terms in the square bracket in Equation (111) reduce to

$$2 P_{12}'' \sin \Theta_{12}'' (P_{13}''^2_x + P_{13}''^2_y),$$

so that the entire contribution is

$$\left(\frac{m_1}{m}\right)^2 P_{12}''/P_{13}'' \; P_{13z}'' P_{12z}'' / P_{13}''^2 .$$

Then $A \, \partial\phi_{13}''/\partial\phi_{12}''$ is

$$\frac{1}{(P_{13x}''^2 + P_{13y}''^2)} \left(\frac{m_1}{m}\right)(P_{13y}'' P_{12y}'' + P_{12x}'' P_{13y}'')\left(\frac{m_1}{m}\right)\frac{P_{12}''}{P_{13}''}\frac{1}{P_{13}''^2}(P_{13}''^2 - P_{13z}''^2) = \left(\frac{m_1}{m}\right)^2 \frac{P_{12}''}{P_{13}''}\frac{(P_{13y}'' P_{12y}'' + P_{12x}'' P_{13x}'')}{P_{13}''^2}$$

So J is indeed $\left(\frac{m_1}{m}\right)^2 P_{12}''/P_{13}'' \; \vec{P}_{13}'' \cdot \vec{P}_{12}'' / P_{13}''^2$

It is interesting to compare the result, $2(2\pi)^3 \pi^2$, of integrating $\int \sin\Theta_{13}' d\Theta_{13}' d\phi_{13}' \sin\Theta_{12}' d\Theta_{12}' d\phi_{12}' \sin\Theta_{12}'' d\Theta_{12}'' d\phi_{12}''$ over two "delta plus" functions, $\left(\pi \delta(\upsilon - \upsilon_0) - \mathcal{P}(\frac{1}{\upsilon - \upsilon_0})\right)$, with u being $\cos\Theta_{12}'$ and $\cos\Theta_{12}''$, with that obtained by including $\left(\frac{m_1}{m}\right)^2 \vec{P}_{13}'' \cdot \vec{P}_{12}'' / P_{13}'' P_{12}''$ in the integration.

First we do the ϕ integrals, using Equations (106) and

$$\int_0^{2\pi} \sin\phi \, d\phi = 0 = \int_0^{2\pi} \cos\phi \, d\phi \, , \quad \int_0^{2\pi} \sin^2\phi \, d\phi = \pi = \int_0^{2\pi} \cos^2\phi \, d\phi .$$

We obtain

(112) $\frac{1}{P_{13}''} (2\pi)^2 \left(\frac{m_1}{m}\right)^2 \left(2\pi \sin^2\Theta_{12}'' \left(\frac{m_1}{m}\right) + 2\pi \cos\Theta_{12}'' (P_{13}'' - \left(\frac{m_1}{m}\right)(P_{12}'\cos\Theta_{12}' - P_{12}''\cos\Theta_{12}''))\right)$

The delta functions say that $\sin\Theta_{12}''$ in the first term goes to 1, while $\cos\Theta_{12}''$ goes to zero. But the second term has a contribution from

$$\mathcal{P} \int \frac{\cos\Theta_{12}'' \sin\Theta_{12}'' d\Theta_{12}''}{((\omega - \omega_{b0}) + K v_{12}'' \cos\Theta_{12}'')} \to \int_{-1}^{1} \frac{\upsilon d\upsilon}{(\upsilon - \upsilon_0)} = 2$$

and from the same integration over Θ_{12}' . So with a factor of two from the Θ_{13}' integration, we obtain $2(2\pi)^3 \left(\frac{m_1}{m}\right)^3 (\pi^2 - P_{12}'/P_{13}''^4)$

If we say p_{12}'/p_{13}'' averages to around one, and choose the case of equal masses, so $(m_1/m) = 2$, then this is about $80(2\pi)^3$, so comparing with around $20(2\pi)^3$ without integrating over J, we might conclude that J is worth about 4. But there are enough

284

considerations which have been left out of the calculation
that we are as well justified in simply ignoring J, that
is, taking it to be 1, as we are in assuming some other
effective value.

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