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DEPARTMENT OF PHYSICS
SCHOOL OF SCIENCES AND HEALTH PROFESSIONS
OLD DOMINION UNIVERSITY
NORFOLK, VIRGINIA

Technical Report PTR-81-6

HIGH-RESOLUTION LASER ABSORPTION SPECTROSCOPY
OF OZONE NEAR 1129.4 cm⁻¹

By
Lawrence N. Majorana

Principal Investigator: Gary E. Copeland

Final Report
For the period October 25, 1979 - October 24, 1981

Prepared for the
National Aeronautics and Space Administration
Langley Research Center
Hampton, Virginia

Under
Research Grant NAG1-1
James M. Hoell, Technical Monitor
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Submitted by the
Old Dominion University Research Foundation  
P.O. Box 6369  
Norfolk, Virginia 23508

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ABSTRACT

HIGH-RESOLUTION LASER ABSORPTION SPECTROSCOPY OF OZONE NEAR 1129.4 CM⁻¹

Lawrence N. Majorana
Old Dominion University, 1980
Director: Dr. Gary Copeland

A Beer's Law experiment was performed with a tunable diode laser to determine self broadened line shape parameters of one infrared absorption ozone line in the ν₁ band for ten pressures from 0.26 to 6.29 Torr at 285K. SO₂ line positions were used for wavelength calibration. Line shapes were iteratively fitted to the Voigt function at a Doppler width of 29.54 MHz (HWHM) resulting in values for the integrated line strength, (S), of \((0.144 +/- 0.007) \times 10^{-20} \text{ cm}^{-1} \text{ molecule cm}^{-2}\), line center frequency, \(ν₀\), of 1129.426 cm⁻¹ and the Lorentzian contributions to halfwidth, \(q_L\). A linear least squares fit of \(q_L\) as a function of pressure yielded a zero intercept of 15.27 +/- 0.29 MHz (rho = 0.99) and a broadening parameter, \(a_0\), of 5.71 +/- 0.29 MHz/Torr. This results in a line width (FWHM) of 0.144 +/- .007 cm⁻¹ at 760 Torr and 285K.
ACKNOWLEDGEMENTS

This research was carried out under NASA grant NAGl-1. I would like to thank the personnel of NASA LaRC Laser and Spectroscopy Branch, IRD, for their support of this work and the members of my thesis committee: Dr. Forest P. Clay, Dr. James L. Cox Jr., Dr. Charles N. Harward and Dr. Mark D. Havey for their time and useful suggestions.

Also I extend personal thanks to the physics graduate students at Old Dominion for their fellowship, Alison Demarest for her support, and Dr. John Sipe for our interesting discussions.

I would especially like to convey my most sincere gratitude to Dr. Gary E. Copeland, my thesis advisor, for his many hours of tireless instruction, guidance and inspiration, without whom this work would not have been possible.
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I. INTRODUCTION

PURPOSE

With the advent of semi-conductor lasers and their recent application to spectroscopy [2,16,17,22], there has been a revolution in the study of infrared spectra. Use of the tunable diode laser (TDL) has permitted ultra high resolution (<0.0001 cm⁻¹) studies to be performed for several atmospheric constituent molecules of high current interest (ClO, HNO₃, SO₂, CF₂Cl₂, etc.) [2,17,37]. This study is concerned with the experimental determination of pressure broadening characteristics of a single ozone absorption line near 1129.4 cm⁻¹, utilizing a TDL as a radiation source.

The shape of any spectral line contains information which is indicative of the conditions existing in the vicinity where the absorption or emission of radiation takes place. Consequently, spectral analysis of the factors which contribute to the finite width, strength, and position of an observed line leads to a determination of temperatures, pressure, concentrations, and species of the source molecules, even while existing in extraordinarily small
amounts or at extreme distances. Remote sensing techniques such as heterodyne radiometry and differential lidar have been developed [16,22] in the application of calculating atmospheric transmittance. These systems are designed to retrieve high resolution spectral line profiles, from which by means of analytical inversion methods, it is possible to infer concentration and temperature profiles of atmospheric constituents. Most of these techniques operate in spectral regions where the molecular species of interest exhibits a strong absorption coefficient and absorption by interfering species is minimal. In order to produce accurate results, a precise knowledge of spectral line parameters is required.

A high resolution ground observation infrared Fourier Transform spectrogram of solar spectra around 8.85 microns by Goldman et.al. [12] is shown in figure 1. An indicator marks the ozone vibration rotational transition (v1,v2,v3,J,KA,KC) (1,0,0,31,1,31 ← 0,0,0,32,0,32) centered at 1129.426 cm⁻¹ (8.85406 microns). This line is a good candidate for use in the remote sensing of ozone since it meets the criteria with respect to windows, strength and favorable ground state.
Figure 1. High resolution solar spectra at high and low sun.
The subject of this thesis is an experimental investigation of this line which results in a determination of the absorption coefficients from which "independent" values of line strength, Lorentz self pressure broadened halfwidth, Doppler width, and ozone-ozone collision cross section are found. In addition we will explore some of the physical phenomena that contribute to spectral line broadening and the experimental method used to measure spectral line parameters.

REVIEW OF RESEARCH

A survey of relevant ozone line parameters available to date (mid 1980) is presented in Table 1. [15]. Column 1 of the table lists the author; column 2 the spectral range; column 3 whether band model parameter or single line parameter; columns 5, 6, 7, and 8 list values for half-width at half absorption maximum, $\alpha$, for ozone-ozone, ozone-oxygen, ozone-nitrogen and ozone-air broadening, respectively. Column 9 indicates whether it was an experimental (e) or theoretical (t) determination.
### TABLE ONE

SUMMARY AND COMPARISON OF OZONE HALF-WIDTH DETERMINATIONS

<table>
<thead>
<tr>
<th>Authors</th>
<th>Date</th>
<th>Reference</th>
<th>Spectral Region</th>
<th>Band Model</th>
<th>Temperature Kelvin</th>
<th>Ozone Half-widths (cm-atm)</th>
<th>Type t/e</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tejwani</td>
<td>(1975)</td>
<td>[41]</td>
<td>MW(GHz)</td>
<td>n</td>
<td>300.</td>
<td>0.113 0.0411 0.0752 0.068</td>
<td>t</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>?</td>
<td>n</td>
<td>300.</td>
<td>0.110 0.0362 0.0640 0.058</td>
<td>t</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>?</td>
<td>n</td>
<td>200.</td>
<td>-- 0.0538 0.0591 0.0986 0.078</td>
<td>t</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>?</td>
<td>n</td>
<td>200.</td>
<td>-- 0.0474 0.0861 0.0780 0.078</td>
<td>t</td>
</tr>
<tr>
<td>Walshaw</td>
<td>(1975)</td>
<td>[45]</td>
<td>IR(cm⁻¹)</td>
<td>y</td>
<td>293.</td>
<td>-- -- -- 0.078</td>
<td>e</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1000-1060</td>
<td>y</td>
<td>293.</td>
<td>-- -- -- 0.078</td>
<td>e</td>
</tr>
<tr>
<td>Goldman</td>
<td>(1970)</td>
<td>[11]</td>
<td>IR(cm⁻¹)</td>
<td>y</td>
<td>235.</td>
<td>-- -- -- 0.085</td>
<td>e</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>955-1180</td>
<td>y</td>
<td>235.</td>
<td>-- -- -- 0.085</td>
<td>e</td>
</tr>
<tr>
<td>Lichtenstein</td>
<td>(1971)</td>
<td>[29]</td>
<td>MW(GHz)</td>
<td>n</td>
<td>293.</td>
<td>0.117 -- -- --</td>
<td>e</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>110-118</td>
<td>n</td>
<td>293.</td>
<td>0.117 -- -- --</td>
<td>e</td>
</tr>
</tbody>
</table>
TABLE ONE
(Continued)

<table>
<thead>
<tr>
<th>Authors</th>
<th>Date</th>
<th>Spectral Region</th>
<th>Band Model</th>
<th>Temperature Kelvin</th>
<th>Ozone Half-widths (cm-atm)^(-1)</th>
<th>Type t/e</th>
</tr>
</thead>
<tbody>
<tr>
<td>McAfee</td>
<td>1975</td>
<td>IR(cm^-1)</td>
<td>y</td>
<td>298.</td>
<td>0.070</td>
<td>e</td>
</tr>
<tr>
<td>[31]</td>
<td></td>
<td>1054</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aida</td>
<td>1975</td>
<td>IR(cm^-1)</td>
<td>n</td>
<td>293.</td>
<td>0.082</td>
<td>t</td>
</tr>
<tr>
<td>[1]</td>
<td></td>
<td>1050</td>
<td>n</td>
<td>250.</td>
<td>0.093</td>
<td>t</td>
</tr>
<tr>
<td>Menzies</td>
<td>1976</td>
<td>IR(cm^-1)</td>
<td>n</td>
<td>298.</td>
<td>0.0935</td>
<td>e</td>
</tr>
<tr>
<td>[34]</td>
<td></td>
<td>1054</td>
<td>n</td>
<td>298.</td>
<td>0.105</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1049</td>
<td>n</td>
<td>298.</td>
<td>0.121</td>
<td>e</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1043</td>
<td>n</td>
<td>298.</td>
<td>0.10</td>
<td>e</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1043</td>
<td>n</td>
<td>298.</td>
<td>0.12</td>
<td>e</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1043</td>
<td>n</td>
<td>298.</td>
<td>0.10</td>
<td>e</td>
</tr>
<tr>
<td>Monnanteuil</td>
<td>1980</td>
<td>MW(GHz)</td>
<td>n</td>
<td>292.</td>
<td>0.124</td>
<td>e</td>
</tr>
<tr>
<td>[35]</td>
<td></td>
<td>76.533</td>
<td>n</td>
<td>292.</td>
<td>0.119</td>
<td>e</td>
</tr>
<tr>
<td></td>
<td></td>
<td>77.602</td>
<td>n</td>
<td>292.</td>
<td>0.127</td>
<td>e</td>
</tr>
<tr>
<td></td>
<td></td>
<td>93.955</td>
<td>n</td>
<td>292.</td>
<td>0.127</td>
<td>e</td>
</tr>
<tr>
<td></td>
<td></td>
<td>96.228</td>
<td>n</td>
<td>292.</td>
<td>0.111</td>
<td>e</td>
</tr>
<tr>
<td></td>
<td></td>
<td>96.228</td>
<td>n</td>
<td>245.</td>
<td>0.139</td>
<td>e</td>
</tr>
</tbody>
</table>
From an examination of table 1, it is apparent that:

1.) Only 2 experimental determinations of O₃-O₃ broadening, have been reported, both at microwave wavelengths.
2.) No O₃-N₂ measurements have been reported in any spectral region.
3.) No direct measurements in the infrared have been made.

The early low resolution study by Walshaw 1954 [45] estimated average air broadened linewidths in the v₃ fundamental band to be 0.078 cm⁻¹atm⁻¹ (HWHM) at 20°C. This "independent" value has been used as a standard, implicitly or explicitly, by many later workers.

The millimeter wave spectrum of ozone has since been observed by Lichtenstein et. al. 1971 [29] and produced the only experimental measurements of individual linewidths until this year (1980). They reported self-broadened linewidths for two transitions at 118.4 GHz (J,Ka,Kc) = (1,1,1 ← 0,0,0) and 110.8 GHz (6,1,5 ← 6,0,6) yielding an average halfwidth of 4.63 +/- 0.24 MHz/Torr (0.17 cm⁻¹/atm⁻¹) (HWHM). The exact experimental situation is unclear from their paper, however, and thus leaves some question as to the purity and pressure of the ozone in their work.

Tejwani and Yeung 1975 [41] present a theoretical calculation of O₃-O₃, O₃-O₂, O₃-N₂ and O₃-air linewidths based on Tsao-Curnutte-Anderson theory for both A and B type bands. The average self broadened HWHM value for type A and
B bands was found to be $0.1128 \text{ cm}^{-1} \text{ atm}^{-1}$ and $0.1104 \text{ cm}^{-1} \text{ atm}^{-1}$ respectively. From their tabulation it is seen that "a $O_3-O_3$ show quite appreciable variation with respect to quantum numbers." The broadening parameter value obtained by this calculation depends in part on the quadrupole moment adopted for $O_3$ which is not well known. Their method was to use a value which gave the closest fit to the experimental data of Lichtenstein et. al. [29]. Not surprisingly therefore, the data agrees well with Lichtenstein's and so the result is not independent. It is the Tejwani-Yeung average halfwidth value that is currently listed on the AFCRL line parameters compilation [32].

Recently, Monnanteuil 1980 [35] has reported privately unpublished values for $O_3O_3$ of 5 microwave transitions listed in table 1. Details of the study, however, are not available at this time.
II. THEORETICAL FORMULATION

The theory and application of direct absorption spectroscopy is discussed in many references [6,14,18,42,43] to which the reader is referred for detailed development. However, in order to introduce and define some important concepts used here, the spectroscopic procedure and theory are briefly outlined below.

1. Transmittance

Basically, as radiation of intensity $I_0(\nu)$, incident on a transparent cell containing a gaseous sample of the molecule of interest is "tuned" in frequency, absorption of the radiation will occur at discrete frequencies which give rise to the molecular spectrum. At these frequencies the portion of the radiation absorbed is governed by the strength of the particular line. The ratio of incident intensity, $I_0(\nu)$, to the intensity that passed through the cell, $I(\nu)$, is defined as the transmittance ($T$). A typical plot of the transmission function over a single line may
appear as in our result (figure 11). The line center \((v_0)\) is the point in frequency where the transmittance is least (maximum absorption).

2. Absorption Coefficient

The transmittance is proportional to the concentration of molecules in the cell and is given by Beers' law (sometimes referred to as the Lambert - Bouguer law) given by:

\[
T(v) = \frac{I(v)}{I_0(v)} = \exp(-k(v)lp)
\]

where \(l\) is the path length of absorption, \(p\) is the partial pressure, of the absorbing gas, and \(k(v)\) is the absorption coefficient evaluated at the frequency, \(a\). Figure 12 is a plot of the absorption coefficient which gives rise to the transmittance shown in figure 11. Commonly, a parameter used to quantify this profile is the full width at half maximum intensity (FWHM) designated by \(a\). This parameter has special significance with respect to the lifetime of the excited state. Another parameter used to describe the profile is the integrated line strength and is defined as the integral of the absorption coefficient with respect to frequency.
3. Units

As a matter of reference, frequency or wavelength is customarily given in units that are contingent on the spectral region of interest. In the infrared, spectroscopists often use the wavenumber (ν'), rather than wavelengths. Wavenumber is the number of waves per unit length, i.e. the reciprocal of wavelength. The units are expressed in reciprocal centimeters (cm⁻¹), while wavelengths are in units of microns (µ) where 1µ = 1 x 10⁻²⁰ cm = 10,000 cm⁻¹. Another name for the cm⁻¹ is the Kayser, the relation being, 1 millikayser (mk) = 1 x 10⁻³ cm⁻¹ = 30 MHz.

THE OZONE MOLECULE

Ozone is a minor constituent of the earth's atmosphere existing in concentrations on the order of a few ppm in a tenuous layer 5 to 10 km thick at an altitude of about 30 Km in the stratosphere. It plays an extremely important role in radiative transfer and in the photo-chemical cycles of the atmosphere. The molecule has several absorption bands in the ultraviolet (λ<300nm) that are responsible for filtering approximately 99% of the radiation that would otherwise reach the earth's surface. Most of this is due to the Hartley absorption band which consists of a strong
continuum between 300 and 220 nm with a very high and almost symmetrical peak near 255 nm [19].

This triatomic, non-linear molecule is a slight asymmetric top (Ia\#Ib\#Ic) with \( C_2v \) symmetry and an apex angle of 116.8° [44]. Its symmetry and three fundamental vibrational modes are illustrated in figure 2.

![Normal vibrational modes of the ozone molecule.](image)

The resulting spectra of ozone as any asymmetric molecule is fairly complex. Ozone is a slight to weak dipole having a dipole moment of 0.53 debye (0.53 \( \times 10^{-18} \) esu) [44]. From microwave studies [36] fundamental rotational constants are determined to be:

\[
\begin{align*}
A &= 106,534.74 \text{ MHz} \\
B &= 13,348.95 \text{ MHz} \\
C &= 11,834.30 \text{ MHz}
\end{align*}
\]

The rotational constants are defined as \( A=\hbar/8\pi^2I_a \),
B = h/8π²I_b, C = h/8π²I_c, where h is Planck's constant and I_a, I_b, I_c, are the inertial moments about the corresponding axes. From these constants, vibrational rotational band centers have been designated by Kaplan et al. [28] as:

v_1 = 1110 cm⁻¹
v_2 = 705 cm⁻¹
v_3 = 1042.2 cm⁻¹

These moments of inertia yield a value of -0.97 for Ray's asymmetry parameter (K), defined as:

\[ K = \frac{(2B - A - C)}{A - C} \]

Thus, for the ground state, this molecule is very nearly a prolate symmetric top.

The small binding energy (Dissociation energy of 1.04 eV [19]) accounts for the extreme reactivity so characteristic of this most oxidizing of all molecules. This fact has hindered extensive study of high pressure ozone due to the imposing problems of purification and explosive hazard.
THEORY OF LINewidths AND SHAPES

The spectral profile of figure 11 is fundamental to our study. It is actually a convolution of several separate broadening processes. They are the natural, Doppler, and collisional lineshapes that are observed together and are referred to as the Voigt shape. Each is briefly considered below.

1. Natural Lineshape

The natural or radiative lineshape is a direct consequence of the finite lifetime of an atomic or molecular energy state. It can be viewed either in a classical sense or quantum mechanically, both yielding the same result.

Classically, we can picture the system as a bound harmonic oscillator damped by virtue of its own radiation [6,27]. A good approximation of the equation of motion for the oscillating electron is given by:

$$\ddot{x} + \gamma \dot{x} + \omega_0^2 x = 0$$  \hspace{1cm} (2)

where:

$$\gamma = \frac{e^2 \omega_0^2}{6\pi\varepsilon_0 c^3 m}$$
is the classical decay rate and $\omega_0$ is resonant angular frequency.

For $\gamma \ll \omega_0$, Equation (2) has solution:

$$x = x_0 \exp(-\gamma t/2) \exp(-i\omega_0 t)$$

which has the form of a damped oscillation. The electric field can be determined through Maxwell's equations to be:

$$E(t) = E(0) \exp\left(-i(\omega_0 - \frac{1}{2} \gamma)t\right) \quad t \geq 0$$

$$E(t) = 0 \quad t \leq 0$$

which are similarly time dependent. Since the wave train is not infinite, it is not truly monochromatic and can therefore be resolved into its component frequencies by taking the Fourier transform:

$$E(\omega) = \left(\frac{1}{2\pi}\right) \int_{-\infty}^{\infty} E(t) \exp(i\omega t) dt$$

The intensity or power distribution, $I(\omega)$, is proportional to $E(\omega)^2$ and so is found to be:

$$I(\omega) = I_o \frac{\gamma/2\pi}{(\omega-\omega_0)^2 + \gamma^2/4}$$
or in terms of frequency:

\[ I(v) = I_0 \frac{(\gamma/4\pi)^2}{(v - v_0)^2 + (\gamma/4)^2} \]  

(7)

where \( I_0 \) is the maximum intensity at the line center frequency \( \omega_0 \), or \( v_0 \), and

\[ \gamma = \frac{1}{t_{\text{classical}}} = \frac{1}{\text{classical lifetime}} \]  

(8)

This important functional form, (6) or (7), is called a Lorentzian distribution and is the natural lineshape. It is illustrated in figure 3. The linewidth FWHM is given by,

\[ \alpha = \gamma = 1/T_{\text{classical}} = 2\pi\Delta v \]  

(9)

Quantum mechanically the same result can be obtained in a simple manner by an application of the uncertainty principle:

\[ \Delta E \Delta t \geq \hbar \]  

(10)

\( \Delta t \) is the time uncertainty that an atom will spend in an excited state and is measured by the mean lifetime of the state. \( \Delta E \) is the corresponding energy uncertainty of the level, which is,
Figure 3. Lorentzian line profile. The half width is given by $\Delta = \gamma / 2 = 1 / 2 \pi \tau_{\text{class}}$. 
So the frequency spread of a particular state, say $j$, can thus be written:

$$\Delta \nu_j = \frac{1}{2\pi \tau_j}$$

which compares to equation (9). Actually one should use an uncertainty of $\nu = \nu + \nu$, but is negligible for the ground or metastable state since $\tau \to \infty$.

The lifetime of an excited state is related to the transition probabilities by,

$$\tau = \frac{1}{1/\tau A_{ji}}$$

if more than one transition is possible. It can be shown [42] (in MKS units) that $A_{ji}$ is proportional to $\nu^3$ by:

$$A_{ji} = \frac{4\pi^3}{3} \frac{\nu^3}{\varepsilon_0 c^3} \frac{P_{ox}^2}{\hbar}$$

where $P_{ox}^2$ is the dipole moment matrix element. Consequently natural line width decreases rapidly in the infrared. A comparison of the magnitude of natural widths in the infrared to optical frequencies can be gained using
(11), (12), and (13), i.e.

$$\Delta \nu = \nu^3$$  \hspace{1cm} (14)

Halfwidth of a transition at ten microns compared to one at say .5 microns is approximately four orders of magnitude smaller. Natural width in the infrared will normally be several orders of magnitude less than Doppler or collision broadened width.

2. Doppler Broadening

In the regime of low gas pressure the observed linewidth is due primarily to the Doppler shifting of emitted or absorbed frequencies due to thermal motion of the molecules. Molecules moving with a component of velocity away from the observer give rise to a red shift and conversely those moving towards, shift blue. Since the shift varies from one molecule to another the effect is not the same for all molecules and therefore classified as an inhomogeneous broadening mechanism.

The observed shifted angular frequency is given by,

$$\omega' = \omega (1 - v^2/c)$$  \hspace{1cm} (15)
where \( \hat{P} \) is a unit vector in a direction from the observer to the molecule and \( \omega_0 \) is the emitted or absorbed frequency of the stationary atom.

Statistically the probability of an atom having a velocity between \( v \) and \( v + dv \) in a one dimensional coordinate system is given by the Maxwellian distribution,

\[
P(v) dv = \left( \frac{M}{2\pi kT} \right)^{\frac{3}{2}} \exp \left( -\frac{Mv^2}{2kT} \right) dv \tag{16}
\]

where,

- \( M \) = mass of the atom
- \( T \) = absolute temperature
- \( k \) = Boltzmann's constant

Let the line width parameter, \( \Delta \), be defined by

\[
\Delta = 2 \frac{\omega_0}{c} \left( \frac{2kT}{M} \right)^{\frac{1}{2}} \tag{17}
\]

then from (15), (16), and (17) the probability of absorbed or emitted radiation having an angular frequency between \( \omega_0' \) and \( \omega_0' + d\omega_0' \) is given by,

\[
P(\omega_0') d\omega_0' = \frac{2}{\Delta} \frac{1}{\pi^{\frac{3}{2}}} \exp \left\{ -\frac{4(\omega_0' - \omega_0)^2}{\Delta^2} \right\} d\omega_0' \tag{18}
\]

This form of the profile is a Gaussian distribution (due to the Maxwellian velocity distribution), about the central
frequency $\omega_0$, whose width (FWHM) is given by,

$$\alpha_0 = \Delta (\ln 2)^{\frac{1}{2}} = 2 \frac{\omega_0}{c} \left( \frac{2kT}{M} \ln 2 \right)^{\frac{1}{2}} = 7.16 \times 10^{-7} \omega_0 \left( \frac{T}{A} \right)^{\frac{1}{2}} \tag{19}$$

Compared to the Lorentzian function, the Gaussian drops off rapidly on either side of its center, (see figure 5). In fact, 99.994% of the area under the curve is contained within the bounds of +/- four linewidths. The Doppler width in terms of wavelength is given by

$$\alpha_0 = 7.16 \times 10^{-7} \lambda \sqrt{\frac{T}{A}} \tag{20}$$

It is apparent that $\alpha_0$ varies linearly with wavelength. For the ozone molecule, ($A = 48$), at a temperature $T = 300K$, one finds in the ultraviolet ($10nm$), the Doppler width is approximately $1.8 \times 10^{-5}$ nm which is on the order of the natural width. In the infrared ($\approx 10\mu$) the Doppler width of ozone is approximately 60 MHz, two orders of magnitude greater than the natural width. Observed spectra in this experiment is Doppler limited.
3. Collision Broadening

In all real physical situations of interest a molecule is not alone in the universe, and so will consequently be subjected to interactions by neighboring atoms, ions, or electrons, which in turn perturb the molecular energy levels. For a large collection of such events averaged over many molecules, broadening of its spectral lines is observed.

The first successful qualitative collision theory was formulated by Lorentz [30] in seeking explanations of absorption experiments by Angstrom and Hallo. He envisioned the excited electron oscillating with a subsequent field \( f(t) \) and assumed that the perturbation due to the interaction of a colliding molecule quenched the radiating wave train abruptly. Disregarding the relatively small radiation damping, a Fourier analysis of \( f(t) \) similar to that for the natural broadened line yields the power distribution illustrated in figure 4b. For many collisions, averaging over all possible values of \( t \), produces the Lorentzian profile:

\[
I(\omega) = I_0 \frac{(1/\tau)^2}{(\omega - \omega_0)^2 + (1/\tau)^2} \tag{21}
\]

shown in figure 4c, where \( \tau \) is the mean time between collisions and the FWHM \( a_L = 2/\tau \).
Figure 4. Effect of abrupt cut-off of radiation. (a) shows the rectangular cut-off function of duration $t_u$. (b) shows the frequency spread resulting from the cut-off of width $2\pi/t_u$. (c) shows the Lorentzian distribution obtained by averaging (b) over all possible values of $t_u$. $\tau$ is the mean value of $t_u$. 
This method of calculation is termed the impact approximation and assumes that the duration of a collision is small compared to the time between collisions. This result is used in many cases to describe line broadening below 100 Torr. Collision theory has since been extended to include other effects: phase changes on impact [46,47]; density of perturbers; long and short range forces, and other mechanisms of interaction.

Compared to the Doppler profile, the Lorentzian distributes more energy away from the spectral center. Consequently, pressure effects are dominant in the wings of the line.

The mean time between collisions, $T_C$, in terms of the mean free path is found from kinetic gas theory to be,

$$T_C = \lambda/V \quad (22)$$

The mean relative velocity, $\bar{v}$, is given for a Boltzman distribution of like collision partners as:

$$\bar{v} = 4 \sqrt{\frac{kT}{\pi m}} \quad (23)$$

Thus, the linewidth, $\alpha_L$, is given by

$$\alpha_L = \frac{2}{T_C} = 2N\sigma\bar{v} \quad (24)$$
where $N$ is the number density and $\sigma$ is the collision cross section.

4. The Voigt Profile

In almost any absorption experiment, the observed lineshape will not be a simple Lorentzian or Guassian, but a convolution of the two called the Voigt profile. It is derived by averaging the Lorentz function (equation 21) over the thermal distribution of equation 16, resulting in the probability distribution $P(x,y)$, (normalized to unity over $v-v_0$), given by Armstrong[3]:

$$P(x,y) = \frac{1}{a_0} \sqrt{\frac{\ln 2}{\pi}} \cdot K(x,y)$$

(25)

where $K(x,y)$ is given by:

$$K(x,y) = \frac{k_v}{k_0} = \frac{y}{\pi} \int_{-\infty}^{\infty} \frac{\exp(-t^2)}{y^2 + (x-t^2)} \, dt$$

(26)

and is known as the Voigt function. $K(x,y)$ is a reduced absorption coefficient, where:

$$k_0 = \frac{S}{a_0} \sqrt{\frac{\ln 2}{\pi}}$$

(27)

equals the dimensional constant of the reduced absorption
coefficient. \( S \), is the integrated line strength given by:

\[
S = \int_{-\infty}^{\infty} k_{\nu} \, d\nu
\]  

(28)

It is commonly expressed in units per absorbing molecule (cm\(^{-1}\)/molecule cm\(^{-2}\)).

\[
\alpha_0 = v \left( \frac{2kT \ln 2}{\text{Mc}^2} \right)^{\frac{1}{2}} \quad \text{(Doppler half width HWHM)}
\]  

(30)

where \( v_0 \) is the wave number at line center and \( v \) is the wave number at which \( K_{\nu} \) is to be evaluated.

The shape of this profile is determined by the ratio of Lorentz to Doppler widths, designated here as \( y \), where

\[
y = \frac{\alpha_L}{\alpha_0} \left( \ln 2 \right)^{\frac{1}{2}}
\]  

(31)

It is this parameter that will be evaluated from the experimental data. Unfortunately, the Voigt profile cannot be expressed in a concise analytic form, but it can be evaluated numerically. It has been tabulated by several authors [7,10,25,8] whose results have been utilized by others to fit the observed profiles.
Figure 5 illustrates the contribution of the Doppler and Lorentz profiles to the Voigt for the case of $a_L/a_0 = (\ln 2)^{1/2}$. A change in the ratio quantifies the dominance of one case over the other. Physically "pure" cases are not observed. In the limits of the ratio however, it should be noted that the shape reduces to the independent broadening formula; i.e. for the "pure" Doppler regime, as $a_L \to 0$, $K(x,0) = \exp(-x^2)$; similarly for "pure" Lorentz as $a_0 \to 0$,

$$P(x=\infty, y=\infty)_{x/y} \approx \frac{(v - v_0)}{a_L} = \frac{1}{\pi} \frac{a_L}{(v - v_0)^2 + a_L}$$
Figure 5. Comparison of the shapes of the Lorentzian distribution, the Gaussian distribution, and the Voigt line profile. $a_L/a_D = (\ln 2)^{1/2}$ and profiles are normalized to the same peak intensity and halfwidth.
TUNABLE DIODE LASERS

The radiation source used in this experiment was a PbSnSe diode laser manufactured by Laser Analytics, Inc. graciously made available by the Laser Spectroscopy Branch, NASA Langley Research Center. Extensive use of tunable diode lasers (TDL) for this type of application has been made since the first publication in 1970 of Doppler limited spectra within the 10.6 micron band of SF$_6$ [20]. An excellent review of these devices is presented by Butler [5].

The semiconductor laser is mounted on an oxygen-free copper cold head which is cooled by a closed cycle Helium refrigerator, manufactured by CTI - Cryogenics Helix, Waltham, Ma. A forward bias applied to the diode produces emission at a wavelength determined by the energy gap of the semiconductor. Total output power is typically about one milliwatt continuous wave.
There are two main aspects which make the application of this type of device to spectroscopy advantageous. First, their unprecedented narrow line width (<10 MHz) is orders of magnitude narrower than conventional prism instruments. The high resolution virtually eliminates instrumental width limitations [40] permitting essentially undistorted measurements of individual line profiles so that pressure broadening studies can be carried out by direct linewidth measurements. Secondly, they are tunable in a piecewise fashion through most of the infrared (three microns to thirty microns). Tuning can be accomplished in several ways: varying the diode temperature, applying a magnetic field, applying external pressure, or sweeping the current through the semiconductor. A practical arrangement used here, was to stabilize the diode temperature at approximately 370 K and vary the current linearly with time (at a sweep rate of 2.0x10^-4 Amp/sec) from 1.0630 to 1.0839 Amps (±20 ma change) with a corresponding frequency sweep of approximately .12 cm^-1 (3.6 GHz).

EXPERIMENTAL ARRANGEMENT

A schematic of the TDL spectroscopy apparatus is shown in figure 6. The laser's output radiation was collected by a germanium f/1.5 lens, chopped, and passed through a
Figure 6. Optical setup for simultaneous measurement of reference gas spectrum, test gas spectrum and etalon tuning curve.
Czerny-Turner double pass monochromator to isolate one of several longitudinal modes normally emitted by these lasers. The output from the monochromator is divided by a beam splitter which directs 40% through a solid 5.08 cm germanium etalon and is focused on a LN$_2$ cooled HgCdTe detector [26]. The transmission signal through the etalon provides a calibration scale to convert the laser current scale into relative wavenumbers, providing the free spectral range (FSR) is some small fraction of the tuning range of the mode. In this case the FSR is 0.02445 cm$^{-1}$. In addition, this signal may be used to monitor the laser tuning characteristics which are often complicated by effects such as mode hopping, multimode output, and non-linearities [16]. The remaining 60% is directed to another beam splitter which directs a portion of the beam through a reference cell on to another detector. This cell contains SO$_2$ at a pressure of one Torr as a reference gas, whose spectrum in this region is precisely known [21,39]. An accurate determination of wavelength can be made by measuring its separation from any of the reference lines. The remaining radiation passes through the 50 cm O$_3$ single pass absorption cell to a third detector.

Windows of the absorption cell were made of KCl 50 mm in diameter and 6.5 mm thick. Ozone pressure is measured by a 0-100 Torr Datametrics Barocell pressure sensor and electronic manometer.
This particular arrangement permitted simultaneous measurement of the ozone spectra, the reference gas spectra, and the etalon curve with the same laser sweep.

Figure 7 illustrates the signal processing path through a block diagram of the electronics. Output signals from the three detectors are passed through appropriate electronic filters, phase sensitive amplifiers, and then digitized using a 16 channel 12 bit ADC coupled to a PDP-8 minicomputer which records the data on 7-track tape for future processing. Simultaneously the data is monitored by an oscilloscope and a 2 channel Hewlett Packard chart recorder.

PROCEDURE

Ozone was generated from pure dry oxygen using the silent electrical discharge method [13], in a sealed glass system. The gas was condensed in a trap by liquid nitrogen (77K) and concentrated by pumping off excess oxygen. The cell was previously conditioned with ozone to minimize the effect of reactions with the cell walls, thus reducing impurities, and explosion potential.

Prior to producing ozone, a series of laser mode scans was performed to locate a strong, stable operational mode of the diode at the desired wavelength. The laser control
Figure 7. Electronics block diagram and signal processing path.
system is designed to automatically tune the laser over a predetermined frequency range once initiated.

The first scan was made with the laser's output blocked to determine an optical zero. The second scan is made through the evacuated absorption cell in order to record an unattenuated power curve (Io) by which the following transmission curves are normalized. Ozone was then introduced into the cell at a pressure of 6.3 Torr and the first pressure scan is performed. Ozone is pumped from the cell for each successive scan reducing the pressure by approximately one Torr for each scan. This procedure was repeated for ten scans.

Throughout a scan, the amplified detector outputs, the TDL current, and the SO₂ and O₃ pressures were fed to the A/D converter and transferred to tape by the PDP-8. However, due to inconsistencies in the data tapes, (poor A/D performance) they were not used in the final data analysis. Instead the X-Y recording was digitized using a Numonics digitizer and recorded on magnetic tapes which were read into and stored on a Dec-system 10 for later analysis.
IV. DATA ANALYSIS

A series of Fortran programs were developed to efficiently reduce the spectroscopic data collected through the procedure described in the previous section and are included in Appendices A and B. The flow chart of figure 8 illustrates their sequence and purpose. The programs QUICK and VFIT perform the body of data analysis. They are interactive programs written for use on the DEC system-10 with Tektronics graphics routines. Their important functions and organization are briefly described below.

PROGRAM QUICK

Program QUICK provides frequency calibration for the laser current array, and generates from the raw data an array of absorption coefficients from which the line parameters will later be determined.

The raw digitized data is organized into separate files consisting of the independent and dependent variables for each type of scan as illustrated in each curve of figure 9.
Figure 8. Data processing flow diagram illustrating sequence of analysis.
Figure 9. Uncalibrated raw data as collected by the PDP/8 minicomputer and recorded on seven track tape. The upper trace is the SO2 reference spectrum. The middle traces represent the unattenuated power spectrum (I₀), and the 1129.426 cm⁻¹ ozone absorption line (I), at 2.03 Torr. The bottom trace is the etalon tuning curve.
The independent variable is always the laser current, CUR, in arbitrary units. The dependent variables are the detector signals. The detector signal through the empty cell is called EMPTY. The detector signal recorded with an optical path through the etalon is stored in the array ETALON. The signal corresponding to the optical zero is called ZERO, and the absorption cell or the reference cell signals are stored in the array GAS (the difference designated in the data file header record). Program QUICK is designed to perform all the calibration functions with the reference gas array first, then loop back and read in the absorption gas array (ozone) in its place to complete the analysis and thus the reason the GAS file will contain either the reference or the ozone gas data.

Immediately after reading each data file, subroutine CURFIT is called to "dress" the data before analysis. Here a cut off level is determined to eliminate portions of data with low S/N, as well as smoothing and alignment of the data arrays. Within this routine another subroutine, LINFIT, is called which by means of a linear least squares fit calculates and stores the slope and intercept of the current versus the location in the array. This provides a check on the linearity of laser current over time as well as an efficient way to store and manipulate the current array by reducing storage requirements from an entire array to only two numbers. Normalization is accomplished by dividing the
GAS curve by the EMPTY curve by use of the subroutine NORMAL.

Subroutine CNTFND is called to locate line centers (center minimums for absorption gas data and maximums for ETALON used later). This is done by numerically differentiating the entire gas curve and then determining where the derivative array passes through zero from positive to negative sense. Greater accuracy in location of line centers is gained by interpolation between the adjacent crossing points. An array of line center locations is passed back to the main program.

At this point a plot of the normalized reference data with marked centers can be produced, a sample of which is shown in figure 10 for SO₂ as the reference gas. This facilitates selection of a reference line for frequency calibration. The user is now asked to input the absolute frequency of the reference line.

In preparation for conversion of the current array to frequency the etalon trace is considered by subroutine ETPREP. After first smoothing the etalon trace the maximum intensity positions are determined by CNTFND. The change of current between peaks is calculated and stored in an array from which the average and standard deviation are derived. A plot of the etalon transmissions with marked maxima and a histogram of the fringe widths vs. their frequency of
Figure 10. Normalized reference spectra (SO₂), over the frequency range of TDL scan, plotted by program QUICK. Marked are the line centers and center frequency of the selected reference line at 1129.418 cm⁻¹ used for calibration (21,39).
occurance may be generated from this subroutine. This process is important to detect subtle laser mode shifts and nonlinearities that can occur during operation of TDLs.

Conversion of the current array into absolute frequency is initiated by first transforming current to relative frequency (subroutine RELFREQ). A conversion factor is found by the ratio of the free spectral range of the etalon (.02445 cm\(^{-1}\) for our case) to the average fringe width previously calculated. Both the current and line center arrays are converted by multiplying each data value by the conversion factor. Transformation of this array to absolute values (ABFREQ) is determined by the difference between the absolute frequency value of the reference line and its value in the relative array just calculated.

A loop to the beginning of QUICK reads in the first ozone absorption curve as GAS which is then similarly chopped, smoothed, aligned and normalized. Since the current array is identical the calibration sections of the program are bypassed.

A normalized, calibrated plot of the ozone transmission function is generated, an example is shown in figure 11. An array of absorption coefficients is calculated using the Beer-Lambert law (equation one) and optionally appended to a data file for later processing by VFIT. Transmittances may also be appended to a separate data file. Data files
Figure 11. Transmittance of the ozone absorption line at 2.03 Torr and 285K after processing by program Quick.
remaining for different pressures may be successively opened by QUICK and processed using the same calibration data.

PROGRAM VFIT

Program VFIT iteratively fits the Voigt function, $K(x,y)$ (equation 26), to the absorption coefficients $k(v)$ calculated in QUICK and produces estimators for the background signal, the center frequency of the absorption line, Lorentz and Doppler widths (HWHM), and the integrated line strength.

It utilizes the data files generated by QUICK. The spectral line center is determined by the maximum functional value of a parabolic fit to the line peak. This center frequency is removed from all data and the Doppler width (HWHM) is calculated (equation 30) for ozone at 285K. Next the program estimates from the data a first guess at the spectral line width and numerically integrates the absorption coefficient to obtain an estimator of the line strength. The data transformation is performed that converts the absorption coefficient versus frequency value to the reduced absorption coefficient (equation 26) as a function of frequency in Doppler units ($x$).
This observed profile is to be fitted to the function $K(x,y)$ - the Voigt profile with a fixed Doppler width. The function $K(x,y)$ is generated for given $x,y$ values using the code described by Armstrong [3]. At line center ($x=0$), the value of the reduced absorption coefficient $K(0,y)$ is observed. That value is compared with a table of values of $K(0,y)$ generated by the function subprogram named $K_1$. A linear interpolation is performed in the table of values of $K(0,y)$ to find the closest first guess for the value $y$ (equation 31).

The value of $y$, as determined above, is increased by 25% and the reduced chi squared statistic is calculated for the data. This statistic is calculated for decreasing values of the parameter $y$ in an iterative scheme until it is minimized. At this point the value of $y$, i.e. the ratio of the Lorentz to Doppler width is determined. A plotting routine is then called for displaying the data and the "best" fit (see figure 13).

Line strength is calculated over a symmetric interval about line center, determined by the number of data points above the 10% level of the peak. Wider lines are integrated over a proportionately wider data interval.

Minor functions of the program include data weighting options and background corrections.
V. RESULTS AND CONCLUSIONS

PRELIMINARY DATA SCREENING

The transmittance of the O₃ absorption line taken at 2.03 Torr and 285K is shown as figure 11 which is typical of the ten transmission curves after normalization and calibration. The 1129.418 cm⁻¹ line of SO₂ (v₁,v₂,v₃,j,κα,κc) [1,0,0,33,3,31←0,0,0,34,2,32] was selected as the standard reference line because of its proximity to the O₃ line under study and the recent heterodyne confirmation [39] of its position at 1129.41835 cm⁻¹. Using the selected SO₂ reference data, the O₃ line center occurs at 1129.4260 ± 0.0003 cm⁻¹. The absorption coefficient k(ν) for all pressures were derived in QUICK and a typical example is shown in figure 12 for the same experimental conditions as in figure 11.

ANALYSIS

The line shape factors are derived by fitting a Voigt function to the absorption coefficient as described above. An example of the best (lowest reduced chi squared) fit for
the same experimental conditions as in figure 11 are shown as figure 13. The Doppler width (HWHM) at 285 K is calculated to be 29.54 MHz. This value was used as the fixed Gaussian portion in the Voigt profile from which the Lorentzian (HWHM) contributions ($a_L$) were determined as a function of pressure. These are tabulated in Table 2 along with the integrated line strengths. The singular behavior of the 1.49 Torr data warranted its elimination in the final analysis.

A linear least squares fit of the halfwidth data as a function of O$_3$ pressure shown in figure 14 yields a zero pressure intercept of 15.27 +/- 0.29 MHz and a slope ($a_0$) of 5.71 +/- 0.29 Mhz/Torr ($\rho=0.99$). This results in a calculated (FWHM) line width at 760 Torr and 296 K of 0.1445 +/- 0.007 cm$^{-1}$ including the Doppler contribution. The zero pressure intercept value cannot be interpreted as the natural line width, since it implies an upper state lifetime of 5.2 nanoseconds, i.e. too fast. Instead this Lorentzian contribution is interpreted as the convolution of the upper and lower state widths, the laser's width (estimated to be 5-10 MHz) and, possibly, a small contribution from power broadening.

The integrated line strengths (Table 2) are found to be independent of pressure and equal to 0.144 +/- 0.007 x10$^{-20}$ cm$^{-1}$/molecule-cm$^{-2}$ at 285 K.
Figure 13. Absorption coefficient profile with best fit Voigt function at 2.03 Torr as determined in program VFIT.
### TABLE 2
HALF WIDTHS HWHM AND STRENGTHS VS PRESSURE AT 285 K

<table>
<thead>
<tr>
<th>Pressure (Torr)</th>
<th>Half Widths (mA)</th>
<th>Strengths (cm⁻²Torr⁻¹)</th>
<th>Units (cm⁻¹/molecule cm⁻² x 10⁻²¹)</th>
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</thead>
<tbody>
<tr>
<td>0.26</td>
<td>.2942</td>
<td>8.819</td>
<td>.5457</td>
</tr>
<tr>
<td>0.50</td>
<td>.3012</td>
<td>9.060</td>
<td>.5345</td>
</tr>
<tr>
<td>1.00</td>
<td>.3485</td>
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<td>.5198</td>
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<td>2.03</td>
<td>.4616</td>
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<td>.5167</td>
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<td>2.47</td>
<td>.4384</td>
<td>13.14</td>
<td>.4888</td>
</tr>
<tr>
<td>3.01</td>
<td>.5467</td>
<td>16.39</td>
<td>.5126</td>
</tr>
<tr>
<td>3.90</td>
<td>.6167</td>
<td>18.49</td>
<td>.4674</td>
</tr>
<tr>
<td>4.98</td>
<td>.7728</td>
<td>23.17</td>
<td>.4906</td>
</tr>
<tr>
<td>6.29</td>
<td>.8366</td>
<td>25.08</td>
<td>.4978</td>
</tr>
</tbody>
</table>

Units = (cm⁻¹/molecule cm⁻²) x 10⁻²¹
Figure 14. Lorentz FWHM contribution as determined by Voigt fit versus pressure. $Y = 0.1905 \times X + 0.5086$ (mk).
The observed values of $K(0,y)$ as a function of the parameter $y$ (see equation 31) are plotted in figure 15 together with the calculated values. Generally, there is good agreement with the expected broadening function. At the lowest pressures the observed values are somewhat lower than expected, this may be due to the spectral characteristics of the diode laser. Notice here that the value of the ratio $a_L/a_0$ is approximately one, indicating the range of data to be comfortably within the Voigt region.

The Voigt function $K(x,y)$, evaluated at line center, $(x=0)$, should be inversely proportional with pressure, see equation 26. Indeed this is the case and is shown in figure 16. A linear least squares fit yields:

$$K(0,y) = 0.7697 - 0.0351 \times P(\text{torr}) \text{ with } \rho = -0.977.$$  

Ozone - ozone collision cross section for this transition and these conditions is calculated utilizing equations (23), (24), and (25) with with our halfwidth value of 4.32 GHz (0.144 cm-latm-l) and a number density, $N$, at atmospheric pressure of $2.6 \times 10^{19}$/cm$^3$. The resulting value of the cross section, $\sigma$, is $1.66 \times 10^{15}$ cm$^2$. 
Figure 15. The Voigt reduced absorption coefficient (solid line) and the observed values (circles) plotted as a function of the ratio of Lorentz to Doppler halfwidths (y).
Figure 16. Observed values of the Voigt reduced absorption coefficient, $K(x,y)$ evaluated at line center ($x = 0$) versus ozone pressure.
SUMMARY AND COMPARISONS

The line parameters derived in this experiment are summarized in Table 3 along with the limited work of others.

This short list of available comparisons reveals slight discrepancies especially in the broadening parameter, $a_0$, but generally there is reasonable overall agreement.

Line center, $v_0$, is in slight disagreement with the value of 1129.442 cm$^{-1}$ listed on the AFCRL Line Parameters Compilation (1979). The compilation, however, has recently been revised to our value to appear on the 1980 version [38].

CONCLUSIONS

The independent values for self broadened halfwidth and line strength, summarized in table two, have been determined for the 1129.426 cm$^{-1}$ absorption line of ozone in a direct absorption experiment. With this information physical constants may be determined. A workable scheme has been outlined for collection of spectroscopic data as well as software for data reduction and interpretation have been presented.
### Table 3

**Comparison of Experimentally Determined Line Parameters**

<table>
<thead>
<tr>
<th>Investigator</th>
<th>$\nu_0$ (cm$^{-1}$)</th>
<th>$\alpha$ (cm-atm)$^{-1}$</th>
<th>$\alpha_0$ (MHz/Torr)</th>
<th>Units</th>
</tr>
</thead>
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<td>1129.426</td>
<td>.144</td>
<td>5.71</td>
<td>.144</td>
</tr>
<tr>
<td>Lichtenstein [29]</td>
<td>-</td>
<td>.117</td>
<td>4.63</td>
<td>-</td>
</tr>
<tr>
<td>Monnanteuil [35]</td>
<td>-</td>
<td>.124</td>
<td>-</td>
<td>-</td>
</tr>
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<td>AFCRL Tape [32]</td>
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<td>-</td>
<td>.167</td>
</tr>
</tbody>
</table>

Units = (cm$^{-1}$/molecule cm$^{-2}$) x10$^{-20}$
The results are in reasonable agreement with previous investigators' microwave data and theoretical calculations in the development of Armstrong, but there is a lack of existing infrared data available for comparison.

This ultra-high resolution measurement will reduce uncertainty in interpretations of retrieved ozone data when applied in remote sensing applications discussed, if used.
REFERENCES


[17] Harward C.N., Copeland G.E., Ultrahigh resolution infrared absorption spectra of CCl2F2 from 1150 to 1173 cm⁻¹ and temperature dependence of the V6 fundamental at 1161 cm⁻¹, Old Dominion University Research Foundation, Technical Report PTR-80-6 (1980).


[38] Rothman L. - Private Communication


APPENDIX A

PROGRAM QUICK

This program is designed to perform the main data processing tasks as described in detail in the section DATA ANALYSIS. This program is written in Fortran-10 and runs on a DecSystem-10 time shared computer under the Tops10 operating system. Extensive use is made of the Tektronix PLOT10 graphics package, as well as, data handling routines selected from those of Bevington [4] and the International Mathematics and Statistical Library Version 8.0.

PROGRAM QUICK
C ANALYSIS PROGRAM FOR SPECTRAL ABSORPTION DATA
C G.E.COPeland, L.N.MAJORANA
C OLD DOMINION UNIVERSITY
C NORFOLK, VA
C
C C.H.BAIR
C NASA LANGLEY RESEARCH CENTER
C HAMPTON, VA
C
DIMENSION CUR(501), EMPTY(501), GAS(501), ETALON(501)
1, ZERO(600), IMAX(4), CSI(3,2), CENTER(2,501), DDS(501)
2, ETCUR(501)
COMMON/A/CUR, EMPTY, GAS, ETALON, ZERO
COMMON/B/CSI, ETCUR, IMAX, CENTER
DOUBLE PRECISION FILEN
C
C INPUT THE NAME OF THE DATA FILE
C
43 TYPE 44
44 FORMAT(/,1X, 'INPUT THE NAME OF THE DATA FILE?',$) ACCEPT 45, FILEN
45 FORMAT(A10)
C
OPEN(UNIT=21,ACCESS='SEQIN',FILE=FILEN)
5 CALL DATA.:N(N,KK,K2,K3,K4,K10,P3)
C
ALL ARGUMENTS ARE CHANGED IN SUBROUTINE
C
USE CURFIT TO CHOP AND ALIGN DATA FOR EACH SCAN.
GOTO( 10, 20, 30,40), KK
10 CONTINUE
I-1
CASE WHERE WE CALL EMPTY
    CALL CURFIT(KK,N,CUR,EMPTY,IMAX,CSI,SIGMA,STORE,L)
    GOTO 5
20 CONTINUE
CASE WHERE I-2 GAS
    CALL CURFIT(KK,N,CUR,GAS,IMAX,CSI,SIGMA,STORE,L)
    IF(K10 .EQ. 3) GOTO 55
    GOTO 5
30 CONTINUE
CASE I-3 ETALON
    CALL CURFIT(KK,N,CUR,ETALON,IMAX,CSI,SIGMA,STORE,L)
    GOTO 5
40 CONTINUE
CASE I-4 ZERO (NO CURFIT)
    IMAX(4)=N
50 CONTINUE
CALL ZEROUT(EMPTY,GAS,ETALON,ZERO,IMAX)
      move above line over to do the plot
CPAUSE
55 CALL NORMAL(EMPTY,GAS,ETALON,IMAX)
C THE FOLLOWING SUBROUTINE DIFFERENTIATES THE GAS CURVE
C AND FINDS THE ABSORPTION LINE CENTERS.
    CALL CNTFND(CUR,GAS,IMAX(2),DDS,IPTS,i)
    IF(K10.EQ.3) GO TO 60
C K10 = 0 IS NOTHING
C K10 = 1 IS SO2
C K10 = 2 IS FREON
C K10 = 3 IS OZONE
TYPE 433
433 FORMAT(1X,'WOULD YOU LIKE A PLOT OF NORMALIZED RAW DATA? ',$)
    ACCEPT 431,TOPLT
431 FORMAT(A5)
    IF (TOPLT.EQ.'NO') GO TO 434
    CALL NPLOT(DDS,GAS,ETALON,IMAX,IPTS)
434 NT=0
    CALL ABFREQ(DAVE,NT,IPTS,ABCAL,IABS)
    CALL ETPREP(ETALON,DAVE,DDS)
437 CALL ABFREQ(DAVE,NT,IPTS,ABCAL,IABS)
C NOW READ IN OZONE DATA
    IF(K10.EQ.0) CLOSE(UNIT=21)
    IF(K10.EQ.0) GO TO 43
60 CALL EPLOT(GAS,IPTS,2)
    CALL TAU(P3,IPTS,K2,K3,K4)
    CALL TRANS(P3,IPTS,K2,K3,K4)
TYPE 69
69 FORMAT(1X,'IS THERE ANOTHER GAS CURVE? ',$)
    ACCEPT 79,ANS
79 FORMAT(A5)
    IF(ANS.EQ.'YES') GO TO 43
CLOSE(UNIT=21)
STOP
END

SUBROUTINE DATAIN(N,KK,K2,K3,K4,K5,K6,K7,K8,K9,K10,K11,P3)

DIMENSION CUR(501),EMPTY(501),GAS(501),ETALON(501),ZERO(600)

COMMON/A/CUR,EMPTY,GAS,ETALON,ZERO

C READ AND TYPE HEADER DATA
C
10 READ(21,211)KK,N,K2,K3,K4,K10,TAPENO,P3
211 FORMAT(1X,I2,1X,I4,3('2,1X),I1"1X,A5,1X,F)
C10
READ(21,*)KK,N,K2,K3,K4,K5,K6,K7,K8,K9,K10,K11,TAPENO
C
1, PRES,TOTAV,P3
IF(K10.EQ.3) GO TO 599
IF(KK.GT.1) GO TO 910

599 TYPE 900
900 FORMAT(/,2X,'READING IN DATA:',//,13X,'KK',5X,'OF DATA PTS',7X,'DATE'/)
910 TYPE 100,KK,N,K2,K3,K4
IF(N .GT. 501) TYPE 998
IF(N .GT. 501) STOP
998 FORMAT(' SORRY CHARLIE----TOO MANY DATA POINTS!')
C THE HEADER DATA IS AS FOLLOWS:
C
C KK = TYPE OF SCAN; KK-1 IS AN EMPTY CELL
C KK-2 GAS IN CELL
C KK-3 ETALON SCAN
C KK-4 OPTICAL ZERO
C KK-5 USED TO INDICATE END OF PDP TAPE
C N = TOTAL NUMBER OF POINTS
C K2 = MONTH
C K3 = DAY
C K4 = YEAR
C K5 = RUN
C K6 = ESTIMATED FREON PRESSURE IN MICRONS...EXCEPT...FOR PDP TAPES 69667,RTT20,12119,11800, AND 222 FOR WHICH IT IS GIVEN IN TORR.
C K7 = ESTIMATED FREQUENCY (IN MORE OR LESS ARBITRARY UNITS)
C K8 = STARTING CURRENT
C K9 = DIODE TEMPERATURE
C K10 = 1 FOR SO2 (REF GAS), 2 FOR FREON, 3 FOR OZONE
C K11 = ESTIMATED CELL TEMPERATURE FOR ALL PDP TAPES BEFORE 69667
C = THERMOCOUPLE READING FOR ALL PDP TAPES AFTER 69667
(INC)
C TAPENO = PDP-8 TAPE NUMBER
C PRES = ESTIMATED TOTAL PRESSURE
C TOTAV = TEMPERATURE AVERAGED OVER 5 CHANNELS
C P3 = TOTAL PRESSURE (TORR)
C
TYPE *,N
GO TO(20,30,40,50,60),KK
C
C20 READ(21,*)( (CUR(J),EMPTY(J),J=I,I+4),I=1,N,5)
C
C 20 CALL READDT(CUR,EMPTY,N)
C
DO 25 J=1,N
C25 TYPE 90, CUR(J),EMPTY(J)
GO TO 60
C
C30 READ(21,*)((CUR(J),GAS(J),J=I,I+4),I=1,N,5)
C
C 30 CALL READDT(CUR,GAS,N)
C
GO TO 60
C
C40 READ(21,*)((CUR(J),ETALON(J),J=I,I+4),I=1,N,5)
C
C 40 CALL READDT(CUR,ETALON,N)
C
GO TO 60
C
READ NO MORE THAN 600 ZERO DATA POINTS.
50 IF(KK.EQ.4.AND.N.GT.600) N=600
C51 READ(21,*)((ZCUR(J),ZERO(J),J=I,I+4),I=1,N,5)
C
C 51 CALL READDT(ZCUR,ZERO,N)
C
60 CONTINUE
90 FORMAT(F,F)
100 FORMAT(10X,I5,8X,I5,7X,3I4)
1 'J FORMAT(1X,'THE DATA HAS BEEN READ IN')
C999 FORMAT(10(1X,F7.4))
999 FORMAT(10(F/.4,1X))
C
CHANGED ON JULY 11 FORM 999 FORMAT(10F8.0) TO READ THE
C DIGITAL TABLET RESULTS
C
C RETURN
END
C---------------------------------------------------------
SUBROUTINE CURFIT(KK,N,Y,X,IMAX,C,SIGMA,STORE,L)
DIMENSION B(2),IMAX(3),SIGMA(3),X(1),Y(1),C(3,2)
CHOPS AND ALIGNS THE DATA
IF(KK .NE. 1) GO TO 110
C SMOOTH EMPTY CELL DATA ONLY
50 CALL SMOOTH(X,N)
   XMAX=X(1)
C FIND THE ACTUAL MAXIMUM DETECTOR SIGNAL, X(KMEAN)
   DO 60 I=2,N
      IF(X(I) .LT. XMAX) GO TO 60
      XMAX=X(I) ; KMEAN=I
60 CONTINUE
CUTOFF IS THE DETECTOR LEVEL BELOW WHICH THE LOWER 10%
C IS DIREGARDED TO ELIMINATE THE PORTIONS OF DATA
C WITH LOW S/N RATIO.
   CUTOFF=0.1*XMAX
C FIND THE FIRST POINT ABOVE CUTOFF (KMIN).
   KMIN=1
   DO 70 I=1,N
      IF(X(I) .LT. CUTOFF) GO TO 70
      KMIN=I ; GO TO 80
70 CONTINUE
80 CONTINUE
C FIND THE LAST POINT ABOVE CUTOFF (KMAX).
   KMAX=N
   DO 90 I=1,N
      K=N+1-I
      IF(X(K) .LT. CUTOFF) GO TO 90
      KMAX=K ; GO TO 100
90 CONTINUE
100 CONTINUE
CHECK THAT KMEAN IS NOT AT THE END OF THE CURRENT SCAN
C (WITHIN 2 POINTS OF END). IF IT IS, SET IT IN THE
C MIDDLE.
   IF(KMEAN .GT. (N-2)) KMEAN=(KMAX+KMIN)/2
C SMOOTH CURVES FOR ETALON AND GAS DATA
110 CONTINUE
   IF(KK .EQ. 3) CALL SMOOTH(X,N)
   IF(KK .EQ. 2) CALL SMOOTH(X,N)
C DEFINE KT2, THE NUMBER OF POINTS BETWEEN KMIN and KMAX +
C 1.
   KT2=KMAX-KMIN+1
   XKMIN=KMIN
   CALL LINFIT(XKMIN,Y(KMIN),KT2,B,SIGMA(KK),2)
C STORE SLOPE AND INTERCEPT OF CURRENT VS LOCATION IN
C ARRAY CALCULATED IN LINFIT.
   DO 190 I=1,2
      C(KK,I) = INTERCEPT
      C(KK,2) =SLOPE
190 C(KK,I)=B(I)
C COUNT (KOUNT) THE NUMBER OF POINTS GREATER THAN 3SIGMA AWAY
FROM
C THE CALCULATED STRAIGHT LINE. (HOPEFULLY THERE ARE
NONE)
PRINT THIS VALUE AT END OF ROUTINE.

SIG3=3.0*SIGMA(KK)
KOUNT=0
DO 200 I=1,N
AMP=C(KK,1)+C(KK,2)*I
DIF=ABS(AMP-Y(I))
IF(DIF .GT. SIG3) KOUNT=KOUNT+1
200 CONTINUE

CALCULATE WHAT THE CURRENT IS FROM THE STRAIGHT LINE FIT
C (EMPTY CELL ONLY)
IF(KK .GT. 1) GO TO 210
C Y = MX + B
C CURRENT = SLOPE * X ORIGINATE + INTERCEPT
YMIN = C(KK,2)*KMIN + C(KK,1)
YMEAN = C(KK,2)*KMEAN + C(KK,1)
YMAX = C(KK,2)*KMAX + C(KK,1)
210 CONTINUE
C RECALCULATE KMIN and KMAX FOR ALL SCANS FROM
C SLOPE AND INTERCEPT STRAIGHT LINE FIT FOUND IN LINFIT.
C X = Y - B / M = KMIN
KMIN=(YMIN-C(KK,1))/C(KK,2)
KMAX=(YMAX-C(KK,1))/C(KK,2)
CHECK THAT KMIN IS NOT ZERO
IF(KMIN .LE. 0) KMIN=1
CHECK KMAX IS AT LEAST 2 POINTS FROM THE END DATA POINT IF IT
C HAPPENS TO APPEAR THERE
IF(KMAX .GT. (N-2))KMAX=N-2
KMEAN=(YMEAN-C(KK,1))/C(KK,2)
C SHIFT AND ALIGN THE ARRAYS!
K=0
DO 220 I=KMIN,KMAX
K=K+1
IF(I.EQ.KMEAN) STORE=K+.5
220 X(K)=X(I)
IMAX(KK)=K
C IMAX IS THE ARRAY POSITION OF THE MAX CURRENT USED.
C TYPE 230,KK,N,K,KMIN,KMAX,KOUNT,STORE,
C I C(KK,1),C(KK,2),SIGMA(KK)
RETURN
230 FORMAT(6I5,F7.1,1PE12.3,2E12.3)
END

SUBROUTINE SMOOTH
C PURPOSE:
C SMOOTH A SET OF DATA POINTS BY AVERAGING ADJACENT CHANNELS
C USAGE:
C CALL SMOOTH(Y,NPTS)
DESCRIPTION OF PARAMETERS:

Y-ARRAY OF DATA POINTS
NPTS-NUMBER OF DATA POINTS

SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED:

NONE

SUBROUTINE SMOOTH(Y,NPTS)
DIMENSION Y(1)
IMAX=NPTS-1
YI=Y(1)
DO 24 I=1,IMAX
    YNEW=(YI+2.*Y(I)+Y(I+1))/4.
    YI=Y(I)
24    Y(I)=YNEW
    Y(NPTS)=(YI+3.*Y(NPTS))/4.
RETURN
END

SUBROUTINE LINFIT(XI,Y,N,B,SIGMA,NTIMES)
DIMENSION Y(1),B(2)

THIS ROUTINE CHECKS THAT THE CURRENT IS RECORDED
AT A CONSTANT RATE; THAT IS, CHECKS CURRENT VS TIME
OR POSITION IN ARRAY, BY A LEAST SQUARES FIT.
GIVES THE SLOPE AND INTERCEPT AS OUTPUT RESULTS (B).
SIGMA=1.0E+08

M=0
SX=0.0; SY=0.0; SXX=0.0; SXY=0.0
DO 30 I=1,N
    IF(SIGMA .GT. 1.0E+07) GO TO 20
    F=B(1)+B(2)*XI+I
    DIF=ABS(F-Y(I))
    IF(DIF .GT. SIG3) GO TO 30
20    X=XI+I
    SX=SX+X
    SY=SY+Y(I)
    SXX=SXX+X*X
    SXY=SXY+X*Y(I)
    M=M+1
30    CONTINUE
    B(2)=(M*SXY-SX*SY)/(M*SXX-SX*SX)
    B(1)=(SY-B(2)*SX)/M
    SUM=0.0
    IF(SIGMA .GT. 1.0E+07) GO TO 50
    DO 40 I=1,M
        F=B1+B2*(XI+I)
        DIF=ABS(F-Y(I))
        IF(DIF .GT. SIG3) GO TO 40
        F=B(1)+B(2)*XI+I
        SUM=SUM+(F-Y(I))*F-Y(I))
50    RETURN
CONTINUE
SIGMA=SQR(SUM/M)
ICOUNT=N-M
GO TO 70
DO 60 I=1,N
F=B(1)+B(2)*(XI-1+I)
60 SUM=SUM+(F-Y(I))*(F-Y(I))
SIGMA=SQR(SUM/N)
SIG3=3.0*SIGMA
B1=B(1); B2=B(2)
IF(SIGMA.GT.1.0E+07) SIGMA=1.0E+06
IF(NTIMES.EQ.1) GO TO 70
GO TO 10
RETURN
END

SUBROUTINE NORMAL(EMPTY,GAS,ETALON,IMAX)
C PURPOSE:
C TO NORMALIZE GAS AND ETALON DATA
C FOR PLOTTING NORMALIZED TRANSMITTANCE PLOTS.
DIMENSION EMPTY(1),GAS(1),ETALON(1),IMAX(1)
IF(IMAX(2).NE.IMAX(3)) TYPE 300
300 FORMAT(' IN NORMAL IMAX(2) .NE. IMAX(3)')
C CHECK TO SEE IMAX(1)=IMAX(2)=IMAX(3)
C IF NOT FORCE THEM TO BE EQUAL TO THE SMALLEST OF THEM
IM=MIND(IMAX(1),IMAX(2),IMAX(3))
C FORCE ALL TO BE IM
IMAX(1)=IM
IMAX(2)=IM
IMAX(3)=IM
C
DO 10 I=1,IMAX(2)
10 GAS(I)=GAS(I)/EMPTY(I)
DO 20 I=1,IMAX(3)
20 ETALON(I)=ETALON(I)/EMPTY(I)
CONTINUE
PAUSE
RETURN
END

SUBROUTINE CNTFND(CUR,GAS,NP,DDS,IPTS,KT)
DIMENSION
DS(501),CENTER(2,501),BPAR(4),C(501,3),
1DDS(501), GAS(1), CUR(1), ETCUR(501), CSI(3,2), IMAX(4)
COMMON/B/CSI, ETCUR, IMAX, CENTER
C PURPOSE: TO FIND LINE CENTERS OF GAS DATA
C PASSED TO ROUTINE:
C DS - ARRAY OF POINTS 1ST DERIVATIVE SPECTRUM
C NPTS - LENGTH OF THE ARRAY
C KT - TYPE OF SCAN IDENTIFIER. IF KT=2 THIS ROUTINE
C WILL FIND CENTER MAXIMUMS. KT=ANYTHING ELSE IT
C FINDS MINIMUMS.
C
C PASSED BACK TO CALLING PROGRAM:
C
CENTER - ARRAY OF LINE POSITIONS OF THE LINE
CENTERS
C (1,501) = GAS CENTERS DATA
C (2,501) = ETALON PEAKS DATA
C IPTS = NUMBER OF LINES = NUMBER OF ENTRIES IN
CENTER
C (REQUIRED FOR SUPRESSION OF 2ND DIFF. CALCULATION)
IC=501
C
CSave THE ORIF NGONAL ARRAY AND USE DDS AS A NEW CURRNET
ARRAY
C
TYPE FIRST 10 ENTRIES OF CUR GOING INTO FILL
C DO 76 I2=1,10
C76 TYPE 78,(I2,CUR(I2))
CALL FILL(NPTS,CUR,DDS)
C TYPE FIRST 10 ENTRIES OF NEW ARRAY DDS COMING FROM
FILL
C DO 77 I1=1,10
C77 TYPE 78 ,(I1,DDS(I1))
78 FORMAT(1X,I4,F)
DO 601 IK=1,4
601 BPAR(IK)=0.0
C
SMOOTH THE DATA 1ST
NSMOOT=5
DO 330 IK=1,NSMOOT
330 CALL SMOOTH(GAS,NPTS)
CALL ICSICU(DDS,GAS,NPTS,BPAR,C,IC,IER)
CALL DCSEVU(DDS,GAS,NPTS,C,IC,DDS,DS,NPTS,DDS,0,IER)
C THIS LOOP FINDS WHERE LINE CENTERS OCCUR BY CHECKING
C WHERE THE FIRST DERIVATIVE( FOUND IN DCSEVU) PASSES
C THROUGH ZERO FROM +TO -.
DO 332 IK=1,NSMOOT
332 CALL SMOOTH(DS,NPTS)
IPTS=0
DO 60 NPT=1,NPTS-1
PT1 = DS(NPT)
PT2 = DS(NPT+1)
    IF(KT.EQ.2)GO TO 10

C MIN FINDING LOOP
C DETERMINES WHERE THE DIFFERENTIATED ARRAY (DS)
C PASSES THROUGH ZERO FROM + TO -.
    IF(PT1-PT2)40,40,60
40    IF(PT1.LT.0.0 .AND.PT2.GT.0.0) GOTO 50
    GO TO 60

C MAX FINDING LOOP
C DETERMINES WHERE THE DIFFERENTIATED ARRAY (DS)
C PASSES THROUGH ZERO FROM + TO -.
    CONTINUE
10    IF(PT1-PT2)60,45,45
45    IF(PT1.GT.0.0 .AND.PT2.LT.0.0) GOTO 50
    GOTO 60

CHECK THE 2ND DERIVATIVE TO SEE IF <0.0 THEN A MINIMUM FOR SURE
C50    IF( DDS(NPT+1) .GE. 0.0) GOTO 60
50    CONTINUE
C
C IPTS=IPTS+1
C INTEPOLATE
C
CENTER(KT,IPTS)=DDS(NPT)-(PT1/(PT2-PT1))*(DDS(NPT+1)-DDS(NPT))
C CENTER(KT,IPTS)=CUR(NPT)-(PT1/(PT2-PT1))*(CUR(NPT+1)-CUR(NPT))

60    CONTINUE
    TYPE 62,IPTS,CENTER(KT,IPTS)
62    FORMAT(1X,' ',I4,' CENTERS LAST LINE IS ',F,/) IF( IPTS .EQ. 0) TYPE 8883
8883    FORMAT('	 NO LINE CENTERS FOUND-----CONTINUUM')
    RETURN

C-------------------------------------------------------------
SUBROUTINE NPLOT(CUR,GAS,ETALON,IMAX,IPTS)
DIMENSION CUR(1),CAS(1),ETALON(1),IMAX(3),ISTRIN(15)
1,IVERT(13),CENTER(2,1),IXLABI(7)
DATA
ISTRIN/78,79,82,77,65,76,73,90,69,68,32,80,76,79,84/ DATA IVERT/84,82,65,78,83,77,73,84,84,65,78,67,69/ DATA IXLAB1/67,85,82,82,69,78,84/ C PLOTS NORMALIZED DATA
    CALL INITT(120)
    AMIN=1000.
    AMAX=-100000.
    CALL BINITT
    CALL NPTS(IMAX(2))
CALL MNMX(GAS,AMIN,AMAX)
CALL DLIMY(0.,AMAX)
CALL XFRM(2)
CALL YFRM(2)
CALL CHECK(CUR,GAS)
CALL DDISPLAY(CUR,GAS)
IF( IPTS .GE.1)CALL ARROW(IPTS,1)
CALL ARROW ONLY IF THERE ARE REALLY SEPERATE LINES
CALL NPTS(IMAX(3))
CALL LINE(2)
CALL CDISPLAY(CUR,GAS)
CALL MOVAABS(650,730)
CALL HLABEL(15,ISTRIN)
CALL MOVAABS(400,50)
CALL HLABEL(7,IXLAB1)
CALL MOVAABS(25,500)
CALL VLABEL(13,IVERT)
CALL BELL
CALL TINPUT(ANS)
RETURN
END

C-------------------------------------------------------

SUBROUTINE ARROW(IPTS,KT)
DIMENSION CSI(3,2),CENTER(2,501),IMAX(4),ETCUR(501)
COMMON/B/CSI,ETCUR,IMAX,CENTER

C	 PLOT A LINE AT THE POINTS WHERE WE HAVE FOUND A
C	 SPECTRAL LINE BY LOOKING AT THE 1ST DERIVATIVE

CALL NPTS(IPTS)
YMAX=.10
YMIN=.05
DO 10 I=1,IPTS
CALL MOVEA(CENTER(KT,I),YMAX)
CALL DRAWA(CENTER(KT,I),YMIN)
10 CONTINUE
RETURN
END

C-------------------------------------------------------

SUBROUTINE FILL(NPTS,X,XNEW)
DIMENSION X(1),XNEW(1)

C	 PURPOSE: TAKE AN ARRAY (X) THAT HAS REPEATING
SEQUENCES
C	 OF NUMBERS AND CHANGE IT SUCH THAT IT IS
MONOTONICALLY
C	 ASCENDING IN VALUE
C
RETURNED ARRAY IS XNEW
SAVE THE OLD ARRAY

DO 300 I=1,NPTS
   XNEW(I)=X(I)
   FS=XNEW(I)
   NSAME=0
   DO 20 I=2,NPTS
      IF( XNEW(I)-FS ) 7,8,10
      NSAME=NSAME+1
   7      IF( I .EQ. NPTS) GOTO 14
   GOTO 20
   FS=XNEW(I)
   IF( NSAME .GT. 1 .AND. I .LT. NPTS) GOTO 11
   IF( NSAME .EQ. 0) GOTO 20

C JUST 2 NUMBERS ARE THE SAME
XNEWCH=XNEW(I)-XNEW(I-1)
XNEW(I-1)=XNEW(I-1)+XNEWCH/2.
NSAME=0
GOTO 20
11      CONTINUE
NT=0
DO 13 J=I-NSAME,I-1
   NT=NT+1
   XNEW(J)=XNEW(J)+NT*(XNEW(I)-XNEW(I-NSAME-1))/FLOAT(NSAME+1)
13      CONTINUE
   NSAME=0
   GOTO 20
8      WRITE(5,100)
100     FORMAT( ' ARRAY IS DECREASING IN VALUE**********' )
20      CONTINUE
RETURN
C MAKE SURE LAST ONE IS DIFFERENT THAN NEXT TO LAST ONE
14      NT=0
   DO 16 J=NPTS-NSAME+1,NPTS
      NT=NT+1
16      XNEW(J)=XNEW(NPTS-NSAME)+NT*(XNEW(NPTS)-XNEW(I))/FLOAT(NPTS)
RETURN

C-----------------------------------------
SUBROUTINE ETPREP(ETALON,DAVE,DDS)
DIMENSION
DDS(1),CENTER(2,501),D(100),FREQ(100),WTH(100)
COMMON/B/CSI,ETCUR,IMAX,CENTER
C THIS ROUTINE CONSIDERS THE ETALON TRACE ALONE, PREPARING IT FOR LATER CONVERSION TO RELATIVE AND ABSOLUTE FREQUENCY. ETALON PEAKS AND THE CHANGE OF CURRENT BETWEEN THEM IS FOUND THEN A SHORT STATISTICAL ANALYSIS IS PERFORMED. A HISTOGRAM PLOT IS OUTPUT, USEFUL TO DETERMINE MODE SHIFTS. RECALCULATE ETALON CURRENT ARRAY FROM SLOPE AND INTERCEPT.

NPTS = IMAX(3)
DO 5 NE=1,NPTS
5 ETCUR(NE) = ((CSI(3,2))*FLOAT(NE))+CSI(3,1)
C DO 73 I=1,10
C TYPE 6,I,ETCUR(I)
73 CONTINUE
C SHIFT ARRAYS IF NECESSARY, SO CURRENT BEGINS AT ZERO.
IF(ETCUR(1).LT.0.0)GO TO 41
GO TO 51
41 SHIFT = ETCUR(1)
DO 51 I=1,NPTS
ETCUR(I) = ETCUR(I)-SHIFT
51 CONTINUE
C DO 9 I=1,10
C TYPE 8,I,ETCUR(I)
9 CONTINUE
C SMOOTH THE DATA
NSMOOT = 10
DO 330 IK=1,NSMOOT
330 CALL SMOUTH(ETALON,NPTS)
C DO 9 I=1,10
C TYPE 8,I,ETALON(I)
9 CONTINUE
C FIND CENTERS OF ETALON PEAKS.
CALL CNTFND(ETCUR,ETALON,NPTS,DDS,IEPTS,2)
C FIND CHANGE OF CURRENT BETWEEN PEAKS, STORE IN ARRAY D().
    NUM=IEPTS-1
    DO 10 N=1,NUM
10    D(N) = CENTER(2,N+1)-CENTER(2,N)
C FIND AVERAGE CHANGE OF CURRENT BETWEEN PEAKS (DAVE).
    DTOT = 0.
    DO 20 M=1,NUM
20    DTOT=DTOT+D(M)
    DAVE=DTOT/FLOAT(NUM)
TYPE 435

FORMAT(1X,'WOULD YOU LIKE A SHORT STATISTICAL
PLOT
1 OF THE ETALON TRACE?')$)

ACCEPT 436,STAT

436 FORMAT(A5)
IF (STAT.EQ.'NO') GO TO 437
C PLOT ETALON TRACE AND CENTERS FOUND
CALL EPLT(ETALON,IEPTS,1)
DO 14 N=1,NUM
TYPE 15,N,D(N)
15 FORMAT(1X,'D(',I2,') = ',F)
14 CONTINUE
C CONTINUE
C
TYPE 25, DAVE
FORMAT(1X,'DAVE = ',F)
C FIND STANDARD DEVIATION, (SIG)
SUM=0.
DO 30 I=1,NUM
SUM=SUM+(D(I)-DAVE)**2
30 CONTINUE
SIG=SQRT(SUM/(FLOAT(NUM)-1.) )
C CONTINUE
C
TYPE 40, SIG
40 FORMAT(1X,'STANDARD DEVIATION IS',F)
PAUSE
C AT THIS POINT WIDTHS OF ETALON PEAKS WILL BE
C COMPARED IN ORDER TO DETECT SUBTLE MODE SHIFTS
C THAT MAY HAVE BEEN PREVIOUSLY OVERLOOKED. THE
C WIDTHS WILL BE SORTED AND PLOTED VS THEIR
C FREQUENCY OF OCCURANCE, (HISTOGRAM).
C THE DISTRIBUTION SHOULD BE GAUSSIAN!
C FIND MIN AND MAX ETALON PEAK WIDTHS,(DMIN and
DMIN=D(1)
DO 50 K=2,NUM
50 IF(D(K).LT.DMIN)DMIN=D(K)
DMAX=D(1)
DO 60 L=2,NUM
60 IF(D(L).GT.DMAX) DMAX=D(L)
C WHAT IS THE RANGE IN VALUES OF D?
RANGE = DMAX-DMIN
C BUILD ARRAY OF SLOTS.
XINC = RANGE / FLOAT(NUM-1)
WTH(1)=DMIN
DO 70 N=2,NUM
70 WTH(N) = WTH(N-1)+XINC
C SORT ETALON WIDTHS AND FIND THEIR FREQUENCY OF
OCCURANCE, FREQ(I).
DO 90 M=1,NUM
I=1
85 IF(D(M).LE.WTH(I)) GO TO 87
I = I+1
GO TO 85
87 \ FREQ(I) = FREQ(I) + 1.
90 \ CONTINUE
C CALL PLOT ROUTINE TO PLOT HISTOGRAM.
CALL HISPLT(WTH, FREQ, NUM)
437 \ RETURN
END
C----------------------------------------------------
SUBROUTINE HISPLT(WTH, FREQ, NUM)
DIMENSION FREQ(1), WTH(1), IYLAB(17), IXLAB(12)
DATA IXLAB/69, 84, 65, 76, 79, 78, 32, 87, 73, 68, 84, 72/
TYPE 10, NUM
10 \ FORMAT(' FREQ WIDTH NUM=', I)
DO 20 I = 1, NUM
20 \ TYPE 21, (FREQ(I), WTH(I))
21 \ FORMAT(1X, F, 1X, F)
C \ PAUSE
C \ PLOT THE HISTOGRAM
CALL INITT(120)
CALL BINITT
CALL NPTS(NUM)
CALL VBAST(8, 0, 0)
CALL XFRM(1)
CALL YMFRM(1)
CALL CHECK(WTH, FREQ)
CALL DSPLAY(WTH, FREQ)
CALL MOVABS(400, 20)
CALL HLABEL(12, IXLAB)
CALL MOVABS(25, 575)
CALL VLABEL(17, IYLAB)
CALL BELL
CALL TINPUT(ANS)
RETURN
END
C----------------------------------------------------
SUBROUTINE EPL0T(ETALON, IEPTS, ITYFG)
DIMENSION ETCUR(501), ETALON(1), ISTRIN(15), CSI(3, 2)
1, IVERT(13), CENTER(2, 501), IMAX(4)
DIMENSION IVERT3(15), IEITSTR(23)
DIMENSION IXLAB1(7), IXLAB3(13)
COMMON/B/CSI, ETCUR, IMAX, CENTER
DATA ISTRIN/78, 79, 82, 77, 65, 76, 73, 90, 69, 68, 32, 80, 76, 79, 84/
DATA IVERT/84, 82, 65, 78, 83, 77, 73, 84, 84, 65, 78, 67, 69/
DATA IVERT3/65, 66, 83, 32, 67, 79, 69, 70, 32,
1 66, 65, 83, 69, 32, 69/
DATA IXLAB1/67, 85, 82, 82, 69, 78, 84/
DATA IXLAB3/65, 66, 83, 32, 70, 82, 69, 81, 85, 69, 78, 67, 89/
DATA
C PLOTS NORMALIZED GAS DATA
IVALUE = IMAX(3)
CALL INITT(120)
CALL BINITT
CALL NPTS(IVALUE)
CALL XFRM(2)
CALL YFRM(2)
CALL CHECK(ETCUR,ETALON)
CALL DSPLAY(ETCUR,ETALON)
IF(IEPTS .GE.1)CALL ARROW(IEPTS,2)
CALL ARROW ONLY IF THERE ARE REALLY SEPERATE LINES
CALL MOVABS(600,730)
IF(ITYFG.EQ.1)CALL HLABEL(23,IETSTR)
IF(ITYFG.EQ.1.OR.ITYFG.EQ.3)GO TO 10
CALL HLABEL(15,ISTRIN)
10 CALL MOVABS(25,500)
IF(ITYFG.EQ.1.OR.ITYFG.EQ.2)CALL VLABEL(13,IVERT)
CALL MOVABS(25,600)
IF(ITYFG.EQ.3)CALL VLABEL(15,IVERT3)
C NOW PUT IN THE X LABELS
C
CALL MOVABS(425,25)
IF(ITYFG.EQ.1)CALL HLABEL(7,IXLAB1)
IF(ITYFG.EQ.3.OR.ITYFG.EQ.2)CALL HLABEL(13,IXLAB3)
C
CALL BELL
CALL TINPUT(ANS)
ITYFG=0
RETURN
END
C---------------------------------------------------------------
SUBROUTINE RLFFREQ(DAVE,IPTS)
DIMENSION CENTER(2,501),ETCUR(501),CSI(3,2),IMAX(4)
COMMON/B/CSI,ETCUR,IMAX,CENTER
C THIS ROUTINE CONVERTS THE CURRENT ARRAY TO RELATIVE FREQUENCY
NPTS = IMAX(3)
C THERE ARE .02445 CM-1 BETWEEN PEAKS.
C FIND A CONVERSION FACTOR (CONF)
CONF = .02445/DAVE
C CONVERT CURRENT TO RELATIVE FREQUENCIES
DO 10 J=1,NPTS
10 ETCUR(J) = IRR(J)*CONF
C
DO 30 I=1,1000
C
C TYPE 20,1,ETCUR(I)
20 FORMAT(1X,'ETCUR(',I2,') = ',F)
CONVERT GAS CENTER ARRAY TO REL FREQS.
DO 40 K=1, IPTS
   CENTER(1,K) = (CENTER(1,K))*CONF
40  CONTINUE
RETURN
END

SUBROUTINE ABFREQ(DAVE, NT, IPTS, ABCAL, IABS)
DIMENSION CSI(3,2), ETCUR(501), IMAX(4), CENTER(2,501)
COMMON/B/CSI, ETCUR, IMAX, CENTER
ABFREQ CONVERTS THE CURRENT ARRAY FIRST TO RELATIVE FREQUENCIES (C: LING RELFREQ), THEN TO ABSOLUTE FREQUENCIES. IT ASKS WHICH LINE OF THE REFERENCE SPECTRUM IS TO BE USED FOR FREQUENCY CALIBRATION AND ITS KNOWN CENTER FREQ.

IF(NT.EQ.1)GOTO 55
TYPE 9
   FORMAT(/,3X,'CENTER ',6X,'CURRENT POSITION',/) 
   DO 20 I=1, IPTS
      TYPE 10, I, CENTER(1,I)
      10   FORMAT(1X,'CENTER(',I3,') = ',F)
   20  CONTINUE
   C	 INPUT ABSOLUTE LINE FOR CALIBRATION.
   TYPE 30
      FORMAT(/,1X,'INPUT WHICH CENTER IS TO BE USED FOR ABSOLUTE FREQ. CALIBRATION?'$)
      ACCEPT *, IABS
      TYPE 35
      FORMAT(/,1X,'WHAT IS ITS ABSOLUTE FREQUENCY ?'$)
      ACCEPT *, ABCAL
      NT=1
RETURN

CHANGE CURRENT ARRAY TO RELATIVE FREQUENCY.
55  CONTINUE
   CALL RLFREQ(DAVE, IPTS)
   DIFF = ABCAL - CENTER(1,IABS)
CHANGE RELATIVE ARRAY TO ABSOLUTE FREQUENCIES
   DO 60 L=1, IMAX(3)
      ETCUR(L)=ETCUR(L)+DIFF
   60  CONTINUE
   C	 DO 70 I=1, 10
   C	 TYPE 75, I, ETCUR(I)
   75  FORMAT(1X,'ETCUR(',I2,') = ',F)
   70  CONTINUE
RETURN
END

C----------------------------------------------
SUBROUTINE TAU(P3,IPTS,K2,K3,K4)
DIMENSION COF(501),CUR(501),EMPTY(501),GAS(501)
DIMENSION CSI(3,2),ETCUR(501),IMAX(4)
COMMON/A/CUR,EMPTY,GAS
COMMON/B/CSI,ETCUR,IMAX
DOUBLE PRECISION FILEA

C PURPOSE:
C TAU CALCULATES AN ARRAY OF ABSORPTION COEFFICIENTS
C USING THE BEER-LAMBERT LAW:
C TRANSMITTANCE=EXP(-COF)(XL)(P3)
C THEN APPENDS THIS DATA TO A FILE (OPTIONAL).
C MAJOR VARIABLES:
C XL = CELL LENGTH ('M)
C COF = ABSORPTION COEFFICIENT
C EMPTY(K)/GAS(K) = TRANSMITTANCE
C P3 = GAS PRESSURE IN CELL
C IMAX(2) = OF DATA PTS IN GAS CURVE. (FROM CURFIT)
CELL LENGTH IS SET HERE
XL= 50.0
CALCULATE ABSORPTION COEFFICIENTS.
DO 10 K=1,IMAX(2)
   COF(K)=(-ALOG(GAS(K))/(P3*XL))
10 CONTINUE
CALL EPL0T(COF,IPTS,3)
C APPENDING ROUTINE.
TYPE 61
61 FORMAT(1X,'DO YOU WANT ABS COFS APPENDED TO A DATA
FILE?'$)
   ACCEPT 62,ANS
62 FORMAT(A5)
   IF(ANS.EQ.'NR') GO TO 75
   TYPE 63
63 FORMAT(1X,'FILE NAME?'$)
   ACCEPT 622,FILEA
622 FORMAT(A10)
   OPEN(UNIT=21,ACCESS='APPEND',FILE=FILEA)
C
C ONLY WRITE OUT MULTIPLES OF 5 DATA PAIRS
C
ITES=IMAX(2)/5
IT=5*ITES
C
WRITE(21,*)IT,K2,K3,K4,P3
C APPEND TRANSMITENCES TO DATA FILE
C
WRITE(21,999)( (ETCUR(I),COF(I),I=J,J+4),J=1,IT,5)
999 FORMAT(5(1X,F,1X,F))
75 CONTINUE
RETURN
END
SUBROUTINE READDT(X,Y,N)
DIMENSION X(1),Y(1)
READ(21,END=22,334)((X(I),Y(I),I=J,J+4),J=1,N,5)
334 FORMAT(F7.4,1X)
WRITE(5,*)( (X(I),Y(I),I=J,J+4),J=1,N,5)
RETURN
22 CONTINUE
TYPE 33
FORMAT(' RAN OUT OF DATA IN READDT---RECAP FOLLOWS')
TYPE 34,N
FORMAT(' NUMBER OF DATA POINTS =',I)
WRITE(5,*)( (X(I),Y(I),I=J,J+4),J=1,N,5)
RETURN
END

SUBROUTINE TRANS(P3,IPTS,K2,K3,K4)
DIMENSION CUR(501),EMPTY(501),GAS(501),TRA(501)
DIMENSION CSI(3,2),ETCUR(501),IMAX(4)
COMMON/A/CUR,EMPTY,GAS
COMMON/B/CSI,ETCUR,IMAX
DOUBLE PRECISION FILEA
C PURPOSE:
C APPENDS TRANSMITTANCE DATA TO A FILE (OPTIONAL).
C MAJOR VARIABLES:
C TRANSMITTANCE (TRA) = GAS(K)/EMPTY(K) (CALCULATED IN NORMAL)
C IMAX(2) = OF DATA PTS IN GAS CURVE. (FROM CURFIT)
C TYPE *,IMAX
C DO 10 K=1,IMAX(2)
C TRA(K) = GAS(K)/EMPTY(K)
10 CONTINUE
C APPENDING ROUTINE.
C TYPE 61
61 FORMAT(1X,' WANT TRANSMITTANCES APPENDED TO A DATA FILE?')
ACCEPT 62,ANS
62 FORMAT(A5)
IF(ANS.EQ.'NO') GO TO 75
TYPE 63
63 FORMAT(1X,'FILE NAME?')
ACCEPT 622,FILEA
622 FORMAT(A10)
OPEN(UNIT=21,ACCESS='APPEND',FILE=FILEA)
C ONLY WRITE OUT MULTIPLES OF 5 DATA PAIRS
C ITES=IMAX(2)/5
IT = 5 * ITES
C TYPE *, IMAX(2), ITES, IT
WRITE(21, *) IT, K2, K3, K4, P3
C APPEND TRANSMITENCES TO DATA FILE
C
WRITE(21, 999)( (ETCUR(I), GAS(I), I = J, J+4), J = 1, IT, 5)
999 FORMAT(5(1X, F, 1X, F))
75 CONTINUE
RETURN
END
APPENDIX B

PROGRAM VFIT

Program VFIT is listed in this appendix as discussed in the section Data Analysis. It is written to run in an interactive mode and uses plotting routines from the Tektronix PLOT10 graphics package and from Bevington [4]. The program is coded in Fortran-10 and is designed to run on a 36 bit DecSystem-10 time shared computer under the Tops10 monitor Version 6.03A. Some of the Format statements use the Fortran-10 free field characteristics (F instead of Fw.d) and a few DO loops have indices that are non-integer. Otherwise, this code conforms to the ANSI standard.

PROGRAM VFIT
DIMENSION KV(500),V(500),KABS(500)
DIMENSION X(500),Y(500),SIGMAY(500),A(5)
DIMENSION YFIT(300)
DIMENSION ZVAL(300),ZIND(300)
DIMENSION RES(20),YGUESS(20)
REAL KV,KABS,LN2,MASS,KBOLTZ,K0,KMAX
REAL K1,K2,K3
DOUBLE PRECISION XFILE

C
C
C THIS PROGRAM IS DESIGNED TO READ IN ABSORPTION
C COEFFICIENT DATA FOR A SINGLE LINE AND FIT
C A VOIGT FUNCTION TO IT.

C
C VOIGT FUNCTION IS GENERATED BY THE FUNCTIONS
C K,K1,K2,K3 AS DESCRIBED BY B.H. ARMSTRONG

C
C THESE ARE ASSEMBLED IN THE FILE ARM.FOR

C
C WRITTEN BY DR. G.E. COPELAND AND L.N. MAJORANA
C DEPT OF PHYSICS
C OLD DOMINION UNIVERSITY
C NORFOLK, VA 23508

C
C DATA ARE IN FILE COF?.DAT
INPUT DATA LOOKS LIKE THIS

360, 12, 3, 79, 0.2600000
1129.3619 -0.0000081 1129.3623 -0.000016 1129.3626 -0.0000303 1129.3629 -0.0000414 1129.3632 -0.0000426

FREQUENCY IN CM⁻¹ FOLLOWED BY ABS COEFFICIENT BASE

5 DATA PAIRS PER LINE

OPEN THE DATA FILE

OPEN(UNIT=21,ACCESS='SEQIN',FILE=XFILE)
READ(21,*)NPTS,MON,NDAY,NYEAR,PRES

DO 10 I=1,NPTS,5
READ(21,*)V(J),KABS(J),J=I,I+4
10 CONTINUE

YMAX IS THE MAX OF THE ABS COEFFICIENT

DO 22 I=1,NPTS
V(I)=V(I)-1129.
22

YMAX IS THE MAX OF THE ABS COEFFICIENT

JJ IS POINT IN DATA IT OCCURS

REMOVE 1129 CM⁻¹

DO 22 I=1,NPTS
V(I)=V(I)-1129.
22

Y= A(1)+ A(2)*X+ A(3)*X*X
THEN THE POSITION OF THE MAX OF POLYNOMINAL
WILL BE THE CENTER LINE FOR ALL FUTURE CALCULATIONS

GENERATE THE X AND Y ARRAYS FOR FITTING

NST=JJ-3
NFIN=JJ+3
NK=0
DO 30 I=NST,NFIN
NK=NK+1
X(NK)=V(I)
Y(NK)=KABS(I)
30

TYPE *,X,Y
PAUSE

GENERATE THE MEAN AND ESTIMATED ERRORS FOR A SET OF
DATA
CALL XFIT(Y,SIGMAY,NK,MODE,YMEAN,SIGMAM,SIGM:*)
DO 833 I=1,NK
833 SIGMAY(I)=SQRT(( Y(I)-YMEAN)**2/(FLOA** & -1.))

BEVINGTON P76

NOW CALL POLFIT BEVINGTON P140
CALL POLFIT(X,Y,SIGMAY,NK,3,MODE,A,CHISQR)
DO 49 I=1,NK
ZVAL(I)=A(1)+A(2)*X(I)+A(3)*X(I)**2
1+A(4)*X(I)**3! +A(5)*X(I)**4
49 CONTINUE

TYPE *,X,Y,ZVAL
PAUSE

CALL PLOT(X,Y,NK,X,ZVAL,2,PRES,XFILE)

PAUSE

TYPE *,CHISQR,A

CENTER OF THE LINE IS AT -A(2)/(2.*A(3))
VCEN=-A(2)/(2.*A(3))
FMAX=A(1)+A(2)*VCEN+A(3)*VCEN**2
TYPE 33,VCEN
33 FORMAT(' CENTER FREQUENCY =',F)

STRIP OUT THE LINE CENTERS
DO 50 I=1,NPTS
50 V(I)=V(I)-VCEN

CALCULATE THE DOPPLER WIDTH
PI=3.141592654
SQPI=SQRAT(PI)

MASS=3.*15.9994
C = 2.99/9250E10
C SPEED OF LIGHT IN CM/S
KBOLTZ = 1.380622E-16
C BOLTZMAN CONSTANT ERG/K
T = 285.
C TEMP IN KELVIN
AMU = 1.660531E-24
C 1AMU IN GRAMS
LN2 = ALOG(2.)
SRLN2 = SQRT(LN2)
C
AD = SQRT( 2.*KBOLTZ*T*LN2/(MASS*AMU))/C
AD = AD*(1129.+VCEN)
AD1 = AD*1000.
AD2 = AD1*C/1.E+9
CTYPE *, AD2
TYPE 331, AD1, AD2
331 FORMAT(' DOPPLER WIDTH<FWM> = '1PE'
MILLIKAYSERS'<0P8.3'MHZ'
C
CALCULATE THE 1ST APPROXIMATION TO THE LINE STRENGTH S
C
C NEED TO GET A DIFFERENT PIECE THAN WE DID FOR THE
LINE CENTER
C DETERMINATION.......THE NARROWER THE LINE THE LESS
WE NEED
C THE WIDER THE LINE THE MORE WE NEED.
C THIS IS DETERMINED BY PRESSURE
C WE COULD LOOK AT THE PRESSURE BUT INSTEAD LETS
C COUNT THE NUMBER OF POINTS ABOVE
C THE 10% LEVEL OF THE PEAK
C IF THIS IS GREATER THAN 12 WE WILL GET
C ONLY +/- 25 POINTS
C
C REPORT THE CUTOFF CRITERIAN-----CUTOFF VALUE
C
C
C IF THIS IS LARGER WE WILL GET MORE POINTS FOR A
BETTER
C WING FIT
CUTOFF = 0.1*YMAX
TYPE 44 , CUTOFF
44 FORMAT( ' CUTOFF IS 10 PERCENT OF YMAX ',F)
ICUT = C
DO 469 I=1,NPTS
IF( KABS(I).GT.CUTOFF) ICUT=ICUT+1
469 CONTINUE
TYPE *, ICUT
PAUSE
IEXTRA = 30
IF( ICUT.GE. 16) IEXTRA=40
NST=JJ+IEXTRA
NFIN=JJ+IEXTRA
NK=0
DO 303 I=NST,NFIN
NK=NK+1
X(NK)=V(I)
303
Y(NK)=KABS(I)

S=AREA(X,Y,NK,3)
TYPE *,S

GENERATE KO

KO=(S/AD)*SRLN2/SQPI
TYPE 990,KO

FORMAT(' DIMENSIONAL CONSTANT OF THE REDUCED ABSORPTION 1 COEFFICIENT = ',1PE)

GENERATE THE VARIABLE X

CUT OFF POINTS ON FAR WINGS
JL=JJ+IEXTRA
JR=JJ+IEXTRA
NP=0
DO 88 I=JL,JR
NP=NP+1
88
X(NP)=V(I)*SRLN2/AD
C

TYPE *,V

TYPE 451,NP
451 FORMAT(' TOTAL NUMBER OF DATA PAIRS USED IN ANALYSIS = ',I4)

GENERATE THE KABS DATA IN NORMAL FORM KABS/KO
NP=0
DO 89 I=JL,JR
NP=NP+1
89
KV(NP)=KABS(I)/KO

CALL A PLOTTING ROUTINE
CALL PLOT(X,KV,NP,X,KV,O,PRES,XFILE)

GUESS WHAT THE INITIAL VALUE OF Y =AL*SQLN2/AN IS???
USE THE FUNCTIONS K(X,Y) WITH X=0.0 TO GUESS THE START UP OF Y
C

KMAX= VALUE OF THE K FUN
KMAX=-10.
DO 41 I=1,NP
IF(KMAX .LT. KV(I) ) KMAX = KV(I)
41
CONTINUE
TYPE 991,KMAX
991
FORMAT(' MAX VALUE OF KABS/KO(AT LINE CENTER)
= ',F)
NZ=0
DO 66 Z=0.0,3.0,0.025
NZ=NZ+1
ZIND(NZ)=Z
66
ZVAL(NZ)=ARM(0.0,Z)
C
TYPE *,ZVAL
CALL A ROUTINE TO INTERPOLATE TO GET CLOSER TO THE REAL Y VALUE
C
CALL INTERP(ZVAL,ZIND,NZ,3,KMAX,YOUT)
TYPE 992,YOUT
992
FORMAT(' INTERPOLATED VALUE OF Y = ',F)
DO 661 I=1,NP
661
ZVAL(I)=ARM(ABS(X(I)),YOUT)
C
TYPE *,ZVAL
PAUSE
CALL PLOT(X,KV,NP,X,ZVAL,2,PRES,XFILE)
C
NOW WE HAVE A GOOD GUESS FOR THE VOIGT PROFILE
C
WILL CHANGE THE Y VALUE OVER 10 VALUES OR SO AND CALCULATE
THE CHI SQUARE TO THE DATA AND FIND MINIMUM Y FOR THOSE AND DO
UNTIL CHI SQUARE IS MINIMUM
C
X ARRAY HAS THE INDEPENDENT VARIABLES IN REDUCED FORM.
C
KV ARRAY IS THE REDUCED DATA
C
ZVAL IS THE FITTED DATA
C
NP IS NUMBER OF DATA POINTS
C
1ST START UP THE CHI SQR CALCULATION USING YOUT AS THE
1ST VALUE OF THE K(X,Y)---THEORY FIT ABOVE
DO 551 I=1,NP
551
SIGMAY(I)=0.0
C
CALL XFIT(KV,SIGMAY,NP,MODE,YMEAN,SIGMAM,SIGMA)
C
CALCULATE THE SIGMAY'S
DO 561 I=1,NP
   SIGMAY(I)=SQRT( ( KV(I)-YMEAN)**2/(FLOAT(NP)-1.))
   NFREE=NP-2
   REST=FCHISQ(KV,SIGMAY,NP,NFREE,MODE,ZVAL)
   C
   REST IS THE REDUCED CHI SQUARE FOR THE GUESS
   YST=YOUT-YOUT/10.
   YEND=YOUT+YOUT/10.
   YSTEP=YOUT/100.
   95  
   I=0
   DO 552 YS=YST,YEND,YSTEP
   I=I+1
   552  
   YGUESS(I)=YS
   ITOTAL =I
   I=0
   C
   CALL THE FCHISQ ROUTINE
   TYPE 441,I,REST,YOUT
   DO 553 I=1,ITOTAL
   C
   CALCULATE THE ZVAL'S FOR THIS YGUESS
   DO 554 J=1,NP
   554  
   ZVAL(J)=ARM( ABS(X(J)) ,YGUESS(I) )
   C
   C
   GENERATE THE SIGMAY'S
   DO 5551 IK=1,NP
   5551  
   SIGMAY(IK)=0.0
   DO 5661 IH=1,NP
   5661  
   SIGMAY(IH)=SQRT( ( KV(IH)-YMEAN)**2/(FLOAT(NP)-1.))
   CALL XFIT(KV,SIGMAY,NP,MODE,YMEAN,SIGMAM,SIGMA)
   RES(I)=FCHISQ(KV,SIGMAY,NP,NFREE,MODE,ZVAL)
   TYPE 441,I,RES(I),YGUESS(I)
   441  
   FORMAT(' TRY ',I2,' REDUCED CHISR=','1PE','Y =','1PE)
   C
   C
   SKIP OUT IF REDUCED CHISQ DOES NOT CHANGE BY 0.005
   IF( I.EQ.1) GOTO 553
   C
   C
   IF(ABS( ( RES(I)-RES(I-1) )/RES(I) ) .LT. 0.005) IKEEP=I
   553  
   CONTINUE
   68  
   CONTINUE
   YMIN=10.
   DO 69 I=1 ITOTAL
   IF( RES(I) .LT. YMIN) IKEEP=I
   IF( RES(I) .LT. YMIN) YMIN=RES(I)
CONTINUE
IF( IKEEP.EQ. ITOTAL) TYPE 510
510 FORMAT( 'OOPS! STILL DECREASING AT EDGE OF SEARCH. I WILL CONTINUE....')
IF( IKEEP.EQ. ITOTAL) YST=YEND
IF( IKEEP.EQ. ITOTAL) YEND=YST+YOUT/10.
IF( IKEEP.EQ. ITOTAL) GOTO 95
6812 TYPE 690, YGUESS(IKEEP)
690 FORMAT( 'RATIO OF LORENTZ TO DOPPLER WIDTH = ', 1PE)
AL=YGUESS(IKEEP)*AD/SRLN2
AL1=AL*1000.
AL2=AL1*C/1.E+9
TYPE 691, AL1, AL2
691 FORMAT( 'LORENTZ WIDTH ', 1PF, ' MILLIKAYSERS - '0PF8.3, ' MHZ')
C PAUSE
CPREPARE A RICHER ARRAY FOR PLOTTING MAKE IT 3*NP LONG
C DO 46 I=1, NPTS
46 KABS(I)=0.0
DO 461 I=1, NPTS
461 V(I)=0.0
IL=1
DO 47 J=1, NP
V(IL)=X(J)
V(IL+1)=X(J)
V(IL+2)=X(J)
KABS(IL)=KV(J)
KABS(IL+1)=KV(J)
KABS(IL+2)=KV(J)
IL=IL+3
47 CONTINUE
C TYPE *, V, KABS
C CALCULATE A RICH NEW X ARRAY FOR INDEPENDENT VARIABLE
C FOR THE SECOND GRAPH OF FITTED VS. X
C XMIN=V(1)
XMAX=V(NP3)
C STOKE NEW INDEPENDENT VARIABLE IN Y
C
XINC=2.*XMAX/FLOAT(NP3)
IC=0
DO 201 XO=XMIN,XMAX,XINC
IC=IC+1
20;
   Y(IC)=XO
C   TYPE *,IC,NP3
C   PAUSE
C
CALL ROUTINE TO GET THE NEW DEPENDENT VARIABLE AT THE SPACING
C   DESIRED....XINC
C
STORE IN ZVAL
DO 345 I=1,NP3
345   ZIND(I)=ARM( ABS(Y(I)),YGUESS(IKEEP))
C   PAUSE
C
CALL PLOT(V,KABS,NP3,Y,ZIND,2,PRES,XFILE)
END
C
C----------------------------------------------------------
C
SUBROUTINE PLOT(X,Y,NP,X1,Y1,IPLT,P,XFILE)
DIMENSION X(1),Y(1)
DIMENSION X1(1),Y1(1)
DIMENSION YLABEL(18),IYLAB(18)
DIMENSION TR(4)
DIMENSION XLABEL(48),IXLAB(48)
DIMENSION TITLE(22),ITIT(22)
DIMENSION TITLE2(28),ITIT2(28)
DOUBLE PRECISION XFILE
C
C   DATA FOR THE TITLES FOR THE GRAPHS
C
DATA TITLE/'V','O','I','T','A',
   'F','U','N','C'T',
   'I','O','N',
   'F','I','T','O','N',
   'F','O','R','M',
   'K','E','E','P','I',
   '2','W','I','T','H','O','F','F','S','M','K','2'
C22   CHARACTERS
DATA TR,'T','O','R','R',
C   4 CHARACTERS
DATA
XLABEL/ W','A','V','E','N','U','M','B','E','R',
   'S','C','A','L','E','D',
   2'W','I','D','T','H','E','9','S','M','K','2'
C48   CHARACTERS
DATA YLABEL/ REDUCE,C
   1'C','O','F','F','E','C','F','E','C'
C18   CHARACTERS
DATA TITLE2/'O', '3', 'L', 'I', 'N', 'E', 'A', 'T', '1, 1', '2', '9', '4', '3', 'C', 'M', '-', '1', 'F', 'R', 'O', 'M'
C28 CHARACTERS
CALL INIT(240)
CALL BINIT
CALL NPTS(NP)
CALL XFRM(2)
CALL YFRM(2)
IF(IPLT .NE.0) CALL SYMBL(1)
IF(IPLT .NE.0) CALL LINE(-1)
CALL CHECK(X,Y)
CALL DSPLAY(X,Y)
IF(IPLT .EQ.2) CALL SYMBL(0)
IF(IPLT .EQ.2) CALL LINE(0)
IF(IPLT .EQ.2) CALL CPLOT(X1,Y1)
C MOVE AND PUT ON LABELS
C
CALL MOVABS(20,600)
CALL KAS12AS(18,YLABEL,ILYLAB)
CALL VLABEL(18,ILYLAB)
CALL KAS12AS(48,XLABEL,IXLAB)
CALL NOTATE(325,20,48,IXLAB)
CONTINUE
CALL KAS12AS(28,TITLE2,ITIT2)
CALL MOVABS(200,750)
CALL HLABEL(28,ITIT2)
CALL ANMODE
TYPE 10,XFILE
  FORMAT(1X,A10)
CALL KAS12AS(22,TITLE,ITIT)
CALL MOVABS(200,725)
CALL HLABEL(22,ITIT)
CALL ANMODE
TYPE 11,P
  FORMAT(1X,F8.2)
CALL BELL
CALL TINPUT(IEND)
CALL ERASE
RETURN
END
C-- -------------------------------------------------------
CODE TO CALCULATE THE VOIGT PROFILE
C
TAKEN FROM
SPECTRUM LINE PROFILES: THE VOIGT FUNCTION
BY B.H. ARMSTRONG
JQSRT 7, PP61-88, (1967)
FUNCTION ARM(X,Y)
C THIS FUNCTION IS THE REAL PART OF THE COMPLEX PROBILITY FUNCTION
C OR THE VOIGT SPECTRUM LINE PROFILE
REAL K1,K2,K3
COMMON W(10),T(10),Y2
DATA W/4.62243670E-1,2.86675505E-1,1.9817206E-1,
1 2.48105209E-2,3.24377334E-3,2.28338656E-4,
2 7.80255648E-6,1.08606937E-7,4.39934099E-10,2.22939365E-13/
DATA T/0.245340708,0.737473729,1.23407622,1.73853771,2.25497400,
2 3.880606,3.34795457,3.94476404,4.60368245,5.38748089/
Y2=Y*Y
C C TESTS
C IF(Y.LT.1.0.AND.X.LT.4.0.OR.Y.LT.1.8/(X+1.0)) GOTO 300
IF(Y.LT.2.5.AND.X.LT.4.0) GOTO 200
100 ARM=K3(X,Y)
RETURN
200 ARM=K2(X,Y)
RETURN
300 ARM=K1(X,Y)
RETURN
END
C------------------------------------------------------------
C FUNCTION K1(X,Y)
REAL K1
DOUBLE PRECISION C(34),COEF,BNO1,BNO2,BN,X1,F
F3(T)=EXP(T**2-X**2)
C FROM HERE TO STATEMENT 30 WE CALCULATE DAWSONS FUNCTION
C ENTER HUMMERS CHEBYSHEV COEFFICIENTS C(I)
DATA C/ .1999999999972224,-.18400000029998,
1 .155839999965025,-.1216640000043988,.0877081599940391,
2 -.0585147248086907,.0362157301623914,-.0208497654398036,
3 .0111960116346270,-.56231896167109D-2,.26487634172265D-2,
4 -.11732670757704D-2,.48995199/8088D-3,-.1933630801528D-3,
5 .72287/446789D-4,-.2565512444979D-4,.86620/36841D-5,
6 .27876379719D-5,.8566873627D-6,-.251843784D-6,
!C7!709360221D-/,...191732257D-7,...49801256D-8,...1244734D-8,
 8.2997//D=9,...696450D-10,...156262D-10,...3389/D-11,...7166D-12,
 9...1447D-12,...285D-13,...55D-14,...10D-14,...2D-15/
Y2=Y*Y
IF((X**2-Y2).GT.70.0)GO TO 2
U1=EXP(-X**2+Y2)*COS(2.*X*Y)
GO TO 5
2U1=0.0
5IF(X.GT.5.0)GO TO 1000
C
CLENSHAWS ALGORITHM AS GIVEN BY HUMMER
BN01=0.0D0
BN02=0.0D0
X1=X/5.0D0
COEF=4.0D0*X1**2-2.0D0
DO 20 I=1,34
 1I=35-I
BN=COEF*BN01-BN02+C(I)
BN02=BN01
20BN01=BN
30F=X1*(BN-BN02)
40DN01=1.0-2.0*X*SNGL(F)
1100DN02=SNGL(F)
GO TO 1200
1000
DN01=(.5/X**2+.75/X**4+1.875/X**6+6.5625/X**8+29.53125/X**10 +
 1 162.4218/X**12+1055.7421/X**14)
DN02=(1.-DN01)/(2.*X)
1200
FUNCT=Y*DN01
IF(Y.LE.1.0E-8)GO TO 2500
Q=1.0
YN=Y
DO 2000 I=2,50
DN=(X*DN01+DN02)*(-2.)/FLOAT(I)
DN02=DN01
DN01=DN
IF (MOD(I,2))2000,2000,1500
1500Q=-Q
YN=YN*Y2
G=DN*YN
FUNCT=FUNCT+Q*G
IF (ABS(G/FUNCT).LE.1.00E-08)GO TO 2500
2000CONTINUE
2500K1=U1-.12837917*FUNCT
RETURN
END
C
C-----------------------------------------------------
C
FUNCTION K2(X,Y)
REAL K2
COMMON W(10), T(10), Y2
G=0.0
DO 100 I=1,10
R=T(I)-X
S=T(I)+X
100
G=G+(4.*T(I)**2-2.)*(R*ATAN(R/Y)+S*ATAN(S/Y)-.5*Y*(ALOG(Y2+R**2)*2)
1 +ALOG(Y2+S**2))*W(I)
K2=0.318309886*G
RETURN
END

C---------------------------------------------------------
FUNCTION K3(X,Y)
REAL K3
COMMON W(10), T(10), Y2
G=0.0
DO 100 I=1,10
100
G=G+(1.0E0/((X-T(I))**2+Y2)+1.0E0/((X+T(I))**2+Y2))*W(I)
K3=0.318309886*Y*G
RETURN
END