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ANALYTICAL LINES FOR LONG-PATH INFRARED ABSORPTION
SPECTROMETRY OF AIR POLLUTANTS USING DIODE LASERS

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Analytical lines for long-path
infrared absorption spectrometry
of air pollutants using diode lasers

by

Bruce M. Golden

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ABSTRACT¹

A scheme for selecting resonant frequencies for the analysis of gaseous air pollutants using long-path absorption of narrow-band infrared sources is presented. A computer search is conducted using existing spectrometric data to determine lines with minimum interference and maximum sensitivity. Results are given for the pollutants O_3 , N_2O , CO , CH_4 , and the non-polluting species, H_2O and CO_2 . In addition, accurate absorption line half-widths (HWHM) of NO were determined using a conventional high resolution infrared spectrometer and modern data-taking procedures.

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INTRODUCTION

With the advent of diode lasers and other narrow-band infrared radiation sources, ultra-high resolution spectrometry promises to become an increasingly important analytical tool. Of particular interest is the area of atmospheric monitoring, where high resolution spectrometry could be used in the determination of a number of common gaseous pollutants. In order to obtain the highest degree of sensitivity and selectivity, the choice of resonant frequency has to be made with care so that the pollutant of interest has minimal interferences from other atmospheric constituents.

This thesis presents a generalized scheme for selecting resonant frequencies for the analysis of gaseous air pollutants using long-path absorption of narrow-band sources. A computer search is conducted using existing spectrometric data to determine the optimum frequencies and magnitudes of interferences for the analysis of several gaseous pollutants. This study had been limited to the pollutants O_3 , N_2O , CO , and CH_4 , and the non-pollutant interferences H_2O and CO_2 , for which reliable spectrometric data were available.

In addition, accurate absorption line half-widths (half of the absorption line's width at half of its maximum intensity) of the pollutant NO were obtained using conventional infrared equipment and modern data-taking procedures, so that

NO can eventually become incorporated into the above scheme.

This thesis describes in detail both the computational methods used in deriving the optimum frequencies for pollution analysis and the experimental and computational procedures used in determining accurate half-widths of NO.

REVIEW

Monitoring of the atmosphere is basic to any air pollution study. Most classical methods of analyzing air pollutants are wet chemical analyses and, while reliable, suffer from a number of drawbacks (3,20). In particular, a specific procedure is usually required for each pollutant in question, and the procedures are usually tedious so that rapid data acquisition systems are not feasible. The time required for analysis also impedes the study of atmospheric systems in the dynamic rather than the equilibrium regime. Optical techniques, by comparison, are essentially instantaneous, can be used for remote sensing, and have the potential of making multi-component analyses.

Long-path laser absorption techniques, as applied to pollution monitoring, have recently been under investigation by a number of researchers (5-10,14-16,18,19), resulting from the high resolution affordable with these laser systems. Most of the work has been in the information-rich infrared portion of the spectrum, where practically all gaseous pollutants have at least one absorption band. In a system developed by L. R. Snowman as cited by Maugh (16), several carbon dioxide laser emission lines from the many available are used for the detection of several pollutant gases. Laser emission lines are chosen whose frequencies overlap absorption lines of the

pollutants in question. Emitted radiation is returned to the system's detector by means of a remote retroreflector. This system has a reported detection limit of 14 ppb of ethylene and 19 ppb of ammonia over a 6100 m path.

Although fixed frequency lasers have been used for pollution monitoring, as in the example above, they suffer from the distinct disadvantage that they depend on the fortuitous match of laser emission line and pollutant absorption line. The match may be far from perfect and may suffer from many interferences. Tunable lasers appear to have a much brighter future in pollution analysis resulting from their ability to scan into exact coincidence with a pollutant absorption line. Kreuzer et al. (14) have used a "spin flip" Raman laser in the detection of nitric oxide at the 10 ppb level. The laser works by focusing a carbon monoxide laser onto a sample of InSb in a variable magnetic field. This laser has output at infrared frequencies which can be varied by changing the magnetic field. This approach, however, requires the use of heavy, complex, and expensive equipment, thereby limiting its use in routine pollution monitoring.

By far, the most promising area for pollution monitoring is the semiconductor diode laser (9,10,16,18). A semiconductor diode laser is a single crystal of semiconductor material grown in such a way as to have a p-n junction. When current is passed through this crystal at cryogenic temperatures,

lasing occurs at the p-n junction. The output frequency depends upon the composition of the laser crystal. Hinkley et al. (10) have reported that lead-tin-telluride ($\text{Pb}_{1-x}\text{Sn}_x\text{Te}$) diodes can be fabricated to emit radiation between 6.5 and 32 μ depending on the stoichiometric parameter x . In addition the laser can be tuned quasi-continuously over a limited range by varying the current through the laser, varying an applied magnetic field, or by changing the pressure or temperature of the laser crystal. Typically, a semiconductor diode laser can be magnetically tuned over a 20 cm^{-1} range with an emission profile of less than 10^{-3} cm^{-1} . At atmospheric pressure or lower, the half-widths of typical vibrational-rotational absorption lines of gases are on the order of 0.01 to 0.1 cm^{-1} . The laser can thus be seen to have the ability for extremely high resolution spectrometry, especially when compared with conventional high resolution infrared spectrometers, whose best resolution is about 0.1 cm^{-1} . By the proper choice of absorption frequency, determination of a given pollutant should thus be accomplished with high sensitivity and selectivity.

Until now, however, no attempt has been made to determine absorption frequencies which are the most suitable for the analysis of gaseous pollutants, i.e., those frequencies where the contribution to the total absorbance of the pollutant of interest is high and all other contributions are low.

Consequently, it has been common to rely on accidental coincidences of gaseous absorption lines with fixed frequency lasers (7,14,19) or on the assumption that only lines in the "atmospheric windows" are useful (7,8). To avoid such a hit and miss approach, and to establish the best spectral lines for infrared absorption spectrometry for the common air pollutants, a scheme was devised which allows a systematic search of all reasonably strong absorption lines of a given gas and determines which lines are the most suitable for use as analytical lines (AL's).

As will be seen in the next section of this thesis, synthetic spectra of all species of interest are computer-generated using existing high resolution spectrometric parameters. A complete infrared spectrum of any molecule can be generated if, for each vibrational-rotational transition, the resonant frequency, the half-width, and the line strength are known. The resonant frequency, or line center, is the frequency of highest absorption for a given transition. The line strength is a measure of how intense the transition is and the half-width determines the distribution of intensity with respect to frequency, or how "spread out" an absorption line is. In order to generate an accurate spectrum, all of these parameters, in turn, must be accurately known. Unfortunately, accurate spectrometric data exists for only a handful of the common pollutants.

In the case of nitric oxide, accurate line centers (13) and line strengths (25) were known, but half-widths were known only to moderate accuracy. In order that NO might become incorporated into the scheme for determining AL's, a study was initiated which determined accurate half-widths of a number of NO transitions, which, in turn, could provide enough information to determine all NO half-widths from theoretical considerations.

COMPUTATIONAL PROCEDURE

This study will be limited to the infrared spectral region from 4 to 20 μm , where practically all gaseous pollutants have vibrational-rotational resonances and where diode lasers and gas lasers are known to work well. Of special interest in this region are H_2O and CO_2 , the non-polluting atmospheric constituents, whose strong absorptions in certain parts of this region make them a major source of interference in determining pollutant concentrations. In this spectral region, reliable spectral information is available (4,17) for each of the six molecules H_2O , CO_2 , O_3 , N_2O , CO , and CH_4 , and the calculations are based on this. The calculations can readily be extended to include other pollutants, e.g., NO , NO_2 , SO_2 , H_2S , H_2CO , HNO_3 , once the appropriate spectral information becomes available. The entire infrared spectrum of each species is computed from 4 to 20 μm using an IBM 360/65 computer. The only reason for computing the entire spectrum of each molecule is that after the initial calculation of the individual spectra, "backgrounds" for any set of concentrations are easily constructed and are available for all frequencies within the spectral region. Calculation of the degree of interference at an arbitrary frequency is thus facilitated. This is important because the frequencies of the AL's of a given pollutant are not known in

general.

Actual computation of a molecule's spectrum involves knowing (1) the resonant frequency of each transition of that molecule, (2) the half-widths, (3) the line strengths, and (4) the energies of the lower states involved. Such spectral data has been obtained through a recent compilation by R. A. McClatchey et al. (17) and revised by K. Fox (4). Instead of the assumption of a Lorentz line shape, a "super-Lorentzian" line shape (24) was chosen on the basis that the latter is probably a slightly better approximation, and has a tendency to overestimate rather than underestimate absorbances at far wings. (The mathematical forms of both Lorentzian and super-Lorentzian line shapes are given in Appendix A.) The "worst case" for the interferences can thus be determined. The spectrum is generated over the entire spectral range at 0.01 cm^{-1} increments, a resolution easily attained with diode lasers and one that will adequately define pressure broadened infrared absorptions. A temperature of 25°C and a pressure of 1 atm are assumed throughout. To facilitate computation, contributions to the spectrum are neglected if they fall below $2.7 \times 10^{-14} \text{ ppm}^{-1} \text{ m}^{-1}$ in magnitude, or, for line-wing contributions, if they fall below 10^{-6} of the absorbance at line center. In the former case they cannot significantly contribute to any long-path measurements and in the latter case the super-Lorentzian assumption cannot be expected to

hold. (A listing of the computer programs needed to generate spectra is given in Appendix B.)

Upon completion of the individual spectra, a "background" is constructed for each pollutant. This is simply the sum of spectra of interfering constituents, taking into account all atmospheric species except the species of interest. A different background is generated for each pollutant. The concentrations used for background spectra generation are typical of ambient concentrations (17) and are shown in Table 1. Figures 1 and 2 show the calculated spectrum of methane, and its associated background, respectively, for the region from 1250 to 1290 cm^{-1} .

For a given pollutant, the values of its absorbance at all resonant frequencies are then compared to the corresponding background absorbance values. For a ratio of absorbance-of-pollutant to absorbance-of-background of unity, the interfering species accounts for half of the absorbance. This was chosen to be the threshold value. Any resonant absorption having an absorbance-to-background ratio greater than unity is considered to be a preliminary analytical line for that molecule. Figure 3 shows the methane absorbance-to-background ratio over the same frequency region used in Figures 1 and 2. Note the presence of many lines that have ratios greater than 1. Figure 4 shows the difference of methane absorbance and methane background for the

Table 1. Ambient Concentrations of Atmospheric Constituents

Molecule	Concentration (ppm)
H ₂ O	10,000*
CO ₂	330
O ₃	0.48**
N ₂ O	0.28
CO	0.075
CH ₄	1.6

*Corresponds to about 30% relative humidity at 25°C.

**Typical maximum concentration is used here to determine effects in the worst case. Ambient ozone levels can be as low as 0.02 ppm.

Figure 1. Computer-generated absorption spectrum of methane.

Figure 2. Computer-generated background spectrum for methane.
All constituents have the concentrations listed in
Table 1. Path length = 1 m.

Figure 3. Ratio of methane spectrum to methane background.

Figure 4. Difference of methane spectrum and methane background. If, for any point, the background exceeds the absorbance of methane, the difference is set to zero.

same region. The difference spectrum is also important because estimates of absolute sensitivities can be made from it.

The concentrations of H_2O and CO_2 are so high relative to typical pollutant concentrations that contributions to the absorbance at frequencies which are at considerable distances from band centers are non-negligible. This necessitates a refined calculation of absorptivities of the two molecules at the preliminary AL frequencies for the other molecules, taking into account such contributions. The absorptivities for all other molecules are retrieved from the original calculated spectra. These values are then used to make a quantitative estimate of the amount of interference from each species for the AL's, along with a measure of the sensitivities for the AL's.

EQUIPMENT AND EXPERIMENTAL PROCEDURE

Nitric oxide is an important pollutant which could be incorporated into the analytical line scheme, given adequate spectrometric information. In a complementary study by Tejwani, Golden, and Yeung (23), high resolution spectrometric information has been generated for NO. For this undertaking to be complete, however, a few accurate experimental determinations of NO absorption line half-widths were needed. To this end, a high resolution study of the $5.4\text{ }\mu\text{m}$ NO fundamental band was initiated using a conventional high resolution spectrometer.

It is a well-known fact that absorption bands of molecules are broadened by intermolecular collisions (2,21,22,24). In fact, the amount of broadening of a given absorption line is a function of the number of collisions experienced by the molecular species in question, i.e., a function of the pressure. At low pressures, the amount of broadening is too small to be resolved by conventional infrared spectrometers, but if the total pressure of the gas is increased, the line broadens to the extent that resolution is now possible. It is this phenomena that has been exploited in the measurement of NO absorption line half-widths.

A schematic diagram of the experimental arrangement is shown in Figure 5. The monochromator employed is a Perkin-

Figure 5. Schematic diagram of equipment used to determine
NO half-widths.

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Elmer E1 monochromator used in the double pass mode with a diffraction grating having 144 lines/mm. The infrared glower was replaced by a Nernst glower, Beckman model 28649, because of higher intensity levels produced by the Nernst glower, which are needed for high resolution work. Radiation was detected with a PIRE HgCdTe semiconductor detector and was modulated with a tuning fork chopper, model L-40, supplied by the Bulova Company, whose fundamental frequency is 1 kHz. The sample cell was specially designed for high total pressures. It was made from a cylinder of aluminum having an outer diameter of 4.4 cm, a bore of 1.9 cm, and a path length of 4.2 cm. The windows used are sodium chloride disks 1.0 cm thick and 2.5 cm in diameter. The windows were fitted to the cell with rubber O rings and secured with aluminum flanges. Gas entered the cell via a Hoke valve.

The slits of the monochromator were set to a value corresponding to the maximum theoretical resolution ($\sim 0.1 \text{ cm}^{-1}$) capable for the monochromator. Under these conditions, the amount of infrared radiation passing through the monochromator to the detector is extremely small, thus the output signal is quite low. For this reason modern signal processing techniques were employed to attain the highest possible signal-to-noise ratios.

The signal, as received by the detector, was amplified by a preamplifier supplied with the detector. The preampli-

fier output was amplified further by a conventional operational amplifier circuit with an approximate gain of 10^3 . The output of this circuit was then used as input to a Princeton Applied Research model HR-8 lock-in amplifier. The lock-in amplifier is a phase sensitive amplifier which was synchronized to the period of the tuning-fork chopper. With this amplifier, signals of precisely the same frequency and phase of the chopper are preferentially amplified while others are rejected. The lock-in amplifier then converts the amplified r.m.s. a.c. signal into a proportional d.c. voltage. This signal is then fed into a chart recorder and to a computer controlled analog to digital converter (ADC). The chart recorder used is a Houston Instruments Omniscribe chart recorder. The ADC is a Datel System 256, 64 analog channel multiplexer, analog to digital convertor, which was interfaced to a Digital Equipment Corp. PDP 8/E minicomputer. Under the control of the minicomputer, the ADC sampled the output of lock-in amplifier at predetermined intervals. (Appendix B gives a listing of the assembler code used to access the ADC.) The digitized signals were then punched onto paper tape for future processing.

Commercial grade NO was purified by passing it through a column of silica gel at dry ice/acetone temperature and was stored condensed at liquid nitrogen temperature (11). All measurements were made at a NO partial pressure of 400 torr.

All pressure-broadened measurements were made at a total pressure of 4.8 atm, with dry nitrogen used as the broadening gas. For calibration purposes and slit function determination, measurements were made with pure NO in the pressure cell.

A general scan of the NO absorption envelope from 1800 to 1950 cm^{-1} was made at moderate resolution ($.4 \text{ cm}^{-1}$) to determine which absorption lines would be most suitable for half-width determination. An identical scan was made with the cell evacuated. Although the monochromator was being purged with dry nitrogen, a significant number of atmospheric absorptions from water vapor were present in the spectrum. Interference was especially pronounced in the P branch of the spectrum and this region was therefore not considered for further investigation. Q branch lines were too closely spaced with respect to frequency and resolution at elevated pressures was thus impossible. The R branch lines had the least amount of interference and were therefore chosen for further investigation. In particular, the R(1/2) singlet and the partially resolved doublets of the R(29/2) through R(39/2) lines were chosen because interference was minimal and these lines could provide the needed information.

To determine the half-widths, each line was scanned at a rate of $0.036 \text{ cm}^{-1}/\text{min}$ with the monochromator slits being set at $75 \mu\text{m}$. The output of the lock-in amplifier was digitized

once every 16.7 sec corresponding to a frequency increment of 0.01 cm^{-1} while the recorder chart drive was set at 0.1 in/min. Low pressure scans (400 torr NO) were made for frequency and 100% transmittance calibration purposes, and in the case of the $\text{E}(1/2)$ line, for determination of the slit function. Pressure broadened (400 torr NO, 4.8 atm total pressure) spectra were taken over the same frequency ranges as low pressure spectra. Zero percent measurements were taken with the slits completely closed. In all cases, appropriate measures were taken to minimize the effects of slit and wavelength drive backlash. In addition, multiple scans were made of each line so an estimate of precision could be made.

EVALUATION OF DATA

The profile of an absorption line as measured by a spectrometer differs from the true line profile resulting from various instrumental effects, such as finite slit width, diffraction and imperfections in the optical system. The effect of the measuring system on the true spectrum is characterized by the instrument function, or, more commonly, the slit function. If the true line profile is represented by the function $f(x)$, the slit function by $h(x)$, and the recorded spectrum by $g(x)$, where x is the frequency, $g(x)$ can be described by Equation 1.

$$g(x) = \int_{-\infty}^{\infty} f(y) h(x-y) dy \quad (1)$$

This well known function as applied to spectrometry is treated in numerous texts and articles (12,21,22) and will not be dealt with further here. The point to make here is that the convolution integral can be approximated by numerical methods if the slit function and line spectrum are known and in digital form. The numerical approximation to Equation 1 is given in Equation 2,

$$g(i) = \sum_l f(l)h(i-l) \quad (2)$$

where the indices i and l replace the frequency variables x and y , respectively, and the summation replaces the integral.

The slit function of the spectrometer is obtained from a low pressure scan of the $R(1/2)$ absorption line of NO. At low pressures, absorption lines are very narrow and the spectrum observed approximates the slit function. The slit function obtained in this manner is then refined by a method given by Jansson (12).

A series of theoretical NO spectra are then generated, each spectrum corresponding to a given half-width, using the accurate line position data given by Keck (13) and line intensity data calculated by Yeung (25), assuming a Lorentzian line profile. These spectra are then numerically convolved with the slit function according to Equation 2 to yield approximations to the observed spectra. For each synthetic spectrum, a point-by-point comparison is made with the observed spectrum. Specifically, the point-by-point deviation is squared and summed over all points. The sum of the squared deviation as a function of half-width yields a smooth curve with a distinct minimum. (Appendix B gives a listing of this computer program.) The half-width corresponding to this minimum is taken as the measured half-width, whose value is easily determined to ± 1 percent of the total half-width,

which was small in comparison to the variance in the half-widths determined by successive scans of the same absorption lines, which showed an average standard deviation corresponding to approximately 6 percent of the total half-width. The reported half-widths are the averages of the half-widths determined in the individual scans.

RESULTS AND DISCUSSION

The results of the NO half-width determinations are shown in Table 2, along with associated standard deviations. The half-width values given by Abels and Shaw (1) are in reasonable agreement with the values reported here. However, the method employed in this study provided a superior determination of NO half-widths than the "curve of growth" method used by Abels and Shaw, which essentially relies on the determination of peak absorptance (a single point on the measured spectrum), whereas this study relies on an overall fit to the measured spectrum using well-known NO spectrometric data as a starting point. The standard deviations indicate good agreement among the several scans taken for each of the absorption lines. A typical "best fit" of the theoretical spectrum to the experimental spectrum for the R(31/2) doublet is shown in Figure 6. Visual inspection of this graph shows the theoretical curve to be in very good agreement with the observed spectrum.

Table 3 is a listing of the absorptivities for all of the molecules of this investigation at the selected AL frequencies. This is the most valuable information of the AL portion of this study in that it gives the frequencies that are most suitable for analytical determination of the four molecules O_3 , N_2O , CO , and CH_4 and permits calculation of the

Table 2. NO half-widths

Line identi- fication	Line Center (cm^{-1})		Half-Width ($\text{cm}^{-1}/\text{atm}$)	Std. Dev. ($\text{cm}^{-1}/\text{atm}$)
	$\pi_{1/2}$	$\pi_{3/2}$		
R (1/2)	1881.04	-	0.075	0.001
R (29/2)	1923.52	1924.46	0.055	0.004
R (31/2)	1926.29	1927.27	0.048	0.002
R (33/2)	1929.03	1930.06	0.050	0.002
R (35/2)	1931.73	1932.79	0.047	0.002
R (37/2)	1934.39	1935.49	0.047	0.003
B (39/2)	1937.02	1930.16	0.044	0.003

Figure 6. Transmittance spectrum of the R(31/2) NO doublet.

Table 3. Analytical Lines and Interferences*

	Frequency	H ₂ O	CO ₂	O ₃	N ₂ O	CO	CH ₄
O ₃	1025.08	6.3x10 ⁻¹²	4.6x10 ⁻¹¹	3.1x10 ⁻⁴	3.3x10 ⁻⁹	0.0	0.0
	1026.52	6.7x10 ⁻¹²	4.6x10 ⁻¹¹	3.4x10 ⁻⁴	3.3x10 ⁻⁹	0.0	0.0
	1031.00	8.1x10 ⁻¹²	4.5x10 ⁻¹¹	4.7x10 ⁻⁴	5.8x10 ⁻⁹	0.0	0.0
	1034.84	6.9x10 ⁻¹²	4.5x10 ⁻¹¹	4.3x10 ⁻⁴	8.0x10 ⁻⁹	0.0	0.0
	1038.53	7.2x10 ⁻¹²	4.6x10 ⁻¹¹	3.9x10 ⁻⁴	1.2x10 ⁻⁸	0.0	0.0
	1047.61	7.7x10 ⁻¹²	5.3x10 ⁻¹¹	4.8x10 ⁻⁴	2.2x10 ⁻⁸	0.0	0.0
N ₂ O	1278.11	1.3x10 ⁻⁸	2.8x10 ⁻¹⁴	4.8x10 ⁻⁸	9.0x10 ⁻⁴	0.0	6.1x10 ⁻⁶
	1292.29	1.5x10 ⁻⁸	2.5x10 ⁻¹⁴	4.1x10 ⁻⁸	1.0x10 ⁻³	0.0	3.6x10 ⁻⁶
	1293.89	1.6x10 ⁻⁸	2.5x10 ⁻¹⁴	3.9x10 ⁻⁸	1.1x10 ⁻³	0.0	9.0x10 ⁻⁶
	1295.48	1.7x10 ⁻⁸	2.5x10 ⁻¹⁴	3.8x10 ⁻⁸	1.1x10 ⁻³	0.0	9.1x10 ⁻⁶
	1297.05	1.7x10 ⁻⁸	2.4x10 ⁻¹⁴	3.6x10 ⁻⁸	1.1x10 ⁻³	0.0	6.6x10 ⁻⁶
CO	2111.55	6.3x10 ⁻¹⁰	1.0x10 ⁻⁶	5.7x10 ⁻⁷	8.0x10 ⁻⁷	2.0x10 ⁻³	0.0
	2115.63	6.3x10 ⁻¹⁰	1.1x10 ⁻⁶	2.7x10 ⁻⁵	8.6x10 ⁻⁷	2.3x10 ⁻³	0.0
	2119.68	6.2x10 ⁻¹⁰	1.1x10 ⁻⁶	4.3x10 ⁻⁵	9.2x10 ⁻⁷	2.5x10 ⁻³	0.0
	2123.70	8.0x10 ⁻¹⁰	1.1x10 ⁻⁶	3.7x10 ⁻⁵	9.9x10 ⁻⁷	2.5x10 ⁻³	0.0
	2127.69	5.9x10 ⁻¹⁰	1.2x10 ⁻⁶	1.8x10 ⁻⁵	1.1x10 ⁻⁶	2.3x10 ⁻³	0.0
	2154.60	4.6x10 ⁻¹⁰	1.4x10 ⁻⁶	1.0x10 ⁻⁷	3.8x10 ⁻⁶	2.2x10 ⁻³	0.0
CH ₄	1283.45	1.8x10 ⁻⁸	2.4x10 ⁻¹⁴	4.6x10 ⁻⁸	7.7x10 ⁻⁵	0.0	3.8x10 ⁻⁴
	1303.71	1.8x10 ⁻⁸	2.1x10 ⁻¹⁴	2.9x10 ⁻⁸	9.6x10 ⁻⁵	0.0	5.5x10 ⁻⁴
	1306.11	2.6x10 ⁻⁸	2.1x10 ⁻¹⁴	2.6x10 ⁻⁸	1.6x10 ⁻⁴	0.0	7.1x10 ⁻⁴
	1327.06	2.5x10 ⁻⁸	1.8x10 ⁻¹⁴	4.0x10 ⁻⁹	9.9x10 ⁻⁷	0.0	7.0x10 ⁻⁴
	1332.71	3.1x10 ⁻⁸	1.8x10 ⁻¹⁴	1.2x10 ⁻⁹	7.3x10 ⁻⁷	0.0	6.8x10 ⁻⁴

*Units: ppm⁻¹meter⁻¹; absorptivities are set to zero when less than 2x10⁻¹⁴.

amount of interference expected from any arbitrary set of concentrations for the major air constituents. Calculations can also be made to determine the sensitivities of the various AL's. Note that Table 3 is only a partial listing of the analytical lines obtained from this study. The ones listed are the best in terms of the amount of interference predicted when all species are assumed to have the ambient concentrations listed in Table 1. A complete listing of all AL's for each of the molecules studied is contained on a magnetic tape, which is described in Appendix C.

Table 4 shows the amount of interference predicted for each of the AL's in Table 3 on the basis of percent contribution to the total absorbance by each molecule. Ideally, 100 percent of the absorbance should be due to the molecule to be determined, indicating no contributions from other species. It is seen that at the ozone AL frequencies a nearly ideal situation exists. This is also true for over 100 other resonant frequencies in the frequency region from 1010 to 1050 cm^{-1} . In this case selection of practically any ozone resonant frequency will give satisfactory results.

For the remaining three pollutants the case is far from ideal. Nitrous oxide and methane are seen to have AL's in the region centered around 1300 cm^{-1} , N_2O having AL's generally below this frequency and CH_4 having AL's generally above. For both of these species there are non-negligible

Table 4. Percent Contribution to Total Absorbance at AL Frequencies

	AL Freq (cm ⁻¹)	H ₂ O	CO ₂	O ₃	N ₂ O	CO	CH ₄
O ₃	1025.08	0.0	0.0	99.9	0.0	0.0	0.0
	1026.52	0.0	0.0	99.9	0.0	0.0	0.0
	1031.00	0.0	0.0	100.0	0.0	0.0	0.0
	1034.84	0.0	0.0	100.0	0.0	0.0	0.0
	1038.53	0.0	0.0	100.0	0.0	0.0	0.0
	1047.61	0.0	0.0	100.0	0.0	0.0	0.0
N ₂ O	1278.11	33.6	0.0	0.0	63.9	0.0	2.5
	1292.29	33.2	0.0	0.0	65.6	0.0	1.3
	1293.89	32.9	0.0	0.0	64.1	0.0	3.0
	1295.48	34.4	0.0	0.0	62.7	0.0	3.0
	1297.05	35.3	0.0	0.0	62.4	0.0	2.2
CO	2111.55	1.3	68.9	0.6	0.0	29.2	0.0
	2115.63	1.2	65.2	2.4	0.0	31.2	0.0
	2119.68	1.1	63.4	3.6	0.0	31.9	0.0
	2123.70	1.4	63.7	3.0	0.0	31.8	0.0
	2127.69	1.0	67.2	1.5	0.1	30.2	0.0
	2154.60	0.7	74.1	0.0	0.2	25.1	0.0
CH ₄	1283.45	22.2	0.0	0.0	2.7	0.0	75.1
	1303.71	16.9	0.0	0.0	2.5	0.0	80.6
	1306.11	18.3	0.0	0.0	3.0	0.0	78.7
	1327.06	18.6	0.0	0.0	0.0	0.0	81.4
	1332.71	22.1	0.0	0.0	0.0	0.0	77.9

contributions to the total absorbance at their AL frequencies from water vapor. The average amount of interference is about 34 percent for N_2O and approximately 20 percent for CH_4 . An important point to note is that the calculation of interference is based on the background concentrations listed in Table 1. For H_2O , the concentration listed is 10^4 ppm, a figure representing a relative humidity of about 30 percent. Thus, the contribution to the total absorbance at AL frequencies from water vapor, as shown in Table 4, will be higher for higher ambient H_2O concentrations. Table 4 also shows that N_2O and CH_4 also interfere with each other, but in this case the amount of interference is relatively small, and would be of little consequence in an experimental situation. Another point worthy of mention is the proximity of N_2O and CH_4 AL's. Diode lasers generally have limited output frequency ranges. By choosing AL's whose frequencies are closely spaced, analysis of more than one pollutant may be accomplished using one diode laser, as may be the case with the N_2O line at 1278.11 cm^{-1} and the CH_4 line at 1283.45 cm^{-1} .

Of the four pollutants studied carbon monoxide had the most severe interferences. In this case CO_2 is the major source of interference, amounting to over 60 percent for the best CO AL's. Minor interferences can also be expected from water and ozone.

It can be seen, however, that as the concentration of any one pollutant increases from its typical ambient concentration, the amount of relative interference for that pollutant decreases. This point is shown graphically in Figure 7 for increasing methane concentrations. For the AL at 1303.71 cm^{-1} the background interference amounts to approximately 20 percent when all species are at ambient concentrations. As the methane concentration is doubled, the relative interference drops to 11 percent and drops further to 7 percent at 6.4 ppm. Thus, as the concentration of the pollutant of interest increases, interference naturally becomes less of a problem.

Because of the relatively large amounts of interference expected in monitoring certain pollutants, it may be necessary to do a multicomponent analysis to determine the concentrations of pollutants whose AL's have major interferences, especially at concentration levels close to ambient. For this reason, AL's for H_2O and CO_2 are also needed. Listed in Table 5 are a number of AL's and their associated absorptivities for water and carbon dioxide. These AL's are determined at line centers, as are all AL's, and have essentially no interferences. Thus, absorptivities of other molecules are not listed. The concentrations of H_2O and CO_2 determined from these lines could then be used to correct for interferences present in AL's for the pollutants.

Figure 7. Absorption of methane in air at various concentrations.

Table 5. Analytical Lines for H₂O and CO₂

Molecule	Frequency (cm ⁻¹)	Absorptivity (ppm ⁻¹ m ⁻¹)
H ₂ O	1690.13	4.1 x 10 ⁻⁵
	1714.80	1.4 x 10 ⁻⁵
	1710.96	2.6 x 10 ⁻⁶
	1721.56	1.8 x 10 ⁻⁶
CO ₂	650.41	4.4 x 10 ⁻⁴
	690.37	2.1 x 10 ⁻⁴
	649.54	3.6 x 10 ⁻⁵
	710.00	1.8 x 10 ⁻⁶
	2359.39	1.6 x 10 ⁻³
	2375.79	3.6 x 10 ⁻⁴
	2297.19	2.1 x 10 ⁻⁴

The AL's for H_2O and CO_2 were chosen not only on the basis of minimal interference, but also on the basis of absorptivity. Lines were chosen that had a range of absorptivities (thus sensitivities) because the strongest line is not always the most desirable for analysis. An AL which is less sensitive may be needed if the transmittance from the strong line is too low to measure accurately in the same path as for the determination of the pollutants.

As an alternative to a multicomponent analysis, instrumentation may be able to electronically subtract out background interferences. This type of scheme is feasible for AL's which are imposed on a slowly or constantly changing background with respect to frequency. The average background about a given transition is subtracted from the rapidly changing resonant peak. In Figure 7, the methane transition centered at 1303.71 cm^{-1} is imposed on a background which is relatively constant from 1303.50 cm^{-1} to 1303.75 cm^{-1} . At higher frequencies the background is seen to have an absorbance due to a resonance line centered at 1303.91 cm^{-1} . If an average background measurement was made that included the interfering resonance line, an erroneous value of CH_4 concentration could result. Thus, this CH_4 AL is not well suited to this particular type of analysis. A derivative technique, however, such as described by Hinkley et al. (10), might be useful in the determination of CH_4 by the 1303.71 cm^{-1} AL

since the background is constant over most of the line. In addition, Ku et al. (15) have recently shown that a derivative technique can also be used to minimize the effects of atmospheric turbulence on long-path absorption measurements. The information generated by this study can therefore be used to determine whether a given scheme of analysis is feasible using a given AL, by a simple examination of the background in proximity to the AL.

The sensitivities of the AL's can be determined from the information compiled in this study. A common measure of sensitivity of a given transition is expressed as the concentration required for an absorbance of 0.01 for a specified path length. Table 6 shows the sensitivities of the various pollutant AL's for a path length of 1 m. The actual detection limit for a given line is obviously determined by the detection system used. Assuming a 1 percent change in the transmittance as the detection limit, a path length of about 25 m would be needed to detect CO and O₃ at their ambient concentrations. Methane and nitrous oxide could be detected at ambient concentrations using a shorter path length because the absorbance per unit path length is more favorable than for carbon monoxide and ozone. Fortunately, the differences in absorbances per unit path length are not great so that all four species can conveniently be measured over the same path length.

Table 6. Sensitivities* of AL's

Molecule	Frequency (cm^{-1})	Sensitivity (ppm)
O ₃	1025.08	33.0
	1026.52	29.0
	1031.00	21.0
	1034.84	23.0
	1038.53	25.0
	1047.61	21.0
N ₂ O	1278.11	11.0
	1292.29	10.0
	1293.89	8.9
	1295.48	9.1
	1297.05	9.4
CO	2111.55	5.1
	2115.63	4.4
	2119.68	4.0
	2123.70	4.0
	2127.69	4.3
	2154.60	4.6
CH ₄	1283.45	27.0
	1303.71	18.0
	1306.11	14.0
	1327.06	14.0
	1332.71	15.0

*Concentration that produces 0.01 absorbance for a 1 m path, neglecting the effects of interferences.

The scheme described here, however, is not without its limitations. The accuracy of AL frequencies and associated absorptivities is dependent on the spectroscopic data used to generate the spectra, and on the validity of the super-Lorentzian line shape approximation. Interferences from other atmospheric pollutants to AL's have been unaccounted for, but in most cases the interference would probably be small, as with N_2O and CH_4 interfering with each other. Thus, as more accurate spectral data on line positions, line strengths, line shapes and half-widths become available, these calculations can be refined. Such data should become accessible with current laser spectroscopic studies and other high resolution spectrometric studies, such as the one described here for the determination of NO half-widths.

It must be emphasized that these results are only a first approximation in determining the best frequencies for analysis. Actual analytical lines and their associated absorptivities must be measured experimentally. This will eliminate the need for assumptions such as the super-Lorentzian line shape.

CONCLUSION

The measured half-widths of NO will be of immediate use in calculating a number of high resolution spectrometric parameters so that NO will be able to be incorporated into the AL scheme.

The AL scheme as it stands is capable of providing information on the amount of interference that can be expected at any frequency and the associated sensitivities for any molecule, provided the proper spectroscopic data are available. As witnessed from this test case, it is not always possible to find lines where interference effects are negligible. However, one can determine the optimum frequencies, where interference is minimal and sensitivity is the highest, and can obtain a quantitative estimate of both. These results should be immediately useful since it is not expected that further refinement of spectroscopic data would appreciably alter the choice of AL's. Refinements are needed only to define precisely the degree of interference of the other atmospheric constituents on a particular AL. Finally, it is noted that it is in fact possible to have AL's not in the "atmospheric window" regions (e.g., N_2O and CH_4), as long as one can determine the magnitudes of the interferences.

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BIBLIOGRAPHY

1. L. L. Abels and J. H. Shaw, J. Mol. Spec. 20, 11 (1966).
2. W. S. Benedict, R. Herman, G. E. Moore and S. Silverman, Can. J. Phys. 34, 830 (1956).
3. F. L. Cross, Handbook on Air Pollution Control (Technomic Publishing Co., Westport, Conn. 1973).
4. K. Fox, Technical Report No. AFCRL-TR-73-0738, 1974 (unpublished).
5. H. J. Gerritsen, in Physics of Quantum Electronics, edited by P. L. Kelly et al. (McGraw-Hill, New York, 1966), p. 581.
6. B. D. Green, and J. I. Steinfeld, in New Concepts in Air Pollution Research, edited by J. Willums (Birkhauser-Verlag, Basel and Stuttgart, 1974).
7. P. L. Hanst, Appl. Spectry. 24, 161 (1970).
8. E. D. Hinkley, Development and Application of Tunable Diode Lasers to the Detection and Quantitative Evaluation of Pollutant Gases, MIT Lincoln Lab. Report, 1972 (unpublished).
9. E. D. Hinkley, Ed., Laser Monitoring of the Atmosphere (Springer-Verlag, Heidelberg) (to be published).
10. E. D. Hinkley, K. W. Nill, and F. A. Blum, in Laser Spectroscopy of Atoms and Molecules, edited by H. Walther (Springer-Verlag, Heidelberg) (to be published).
11. E. E. Hughes, J. Chem. Phys. 35, 1531 (1961).
12. P. A. Jansson, J. Opt. Soc. Amer. 60, 184 (1969).
13. D. B. Keck, Ph.D. Thesis, Michigan State University, 1967 (unpublished).

14. L. B. Kreuzer, N. D. Kenyon, and C. K. N. Patel, *Science* 177, 347 (1972).
15. R. T. Ku, E. D. Hinkley, and J. O. Sample, *Appl. Opt.* 14, 854 (1975).
16. T. H. Maugh, *Science* 177, 1090 (1972).
17. R. A. McClatchey, W. S. Benedict, S. A. Clough, D. E. Burch, R. F. Calfee, K. Fox, L. S. Rothman, and J. S. Garing, Environmental Research Paper No. 434, AFCRL-TR-73-0096, 1973.
18. I. Melngailis, *IEEE Trans. Geosci. Electron.* 10, 7 (1972).
19. R. T. Menzies, *Appl. Opt.* 10, 1532 (1971).
20. G. B. Morgan, G. Ozolins, and E. C. Tabor, *Science* 170, 289 (1970).
21. K. S. Seshadri and R. N. Jones, *Spectrochim. Acta* 19, 1013 (1963).
22. J. S. Stewart, *Infrared Spectroscopy* (Marcel Dekker, Inc., New York, 1970).
23. G. D. T. Tejwani, B. M. Golden, and E. S. Yeung (to be published).
24. P. Varanasi, S. K. Sarangi, and G. D. T. Tejwani, *J. Quant. Spectry. Radiat. Transfer* 12, 857 (1972).
25. E. S. Yeung (unpublished).

APPENDIX A: MATHEMATICAL FORM OF LINE SHAPES

It has been assumed throughout this study that absorption lines at pressures above a few torr predominantly take their shapes from pressure-related phenomena. The most common line shape in the pressure-broadened regime is the so-called Lorentzian line shape given in the expression

$$k(\nu) = (S/\pi\gamma) [\{ (\nu - \nu_0)/\gamma \}^2 + 1]^{-1} \quad (\text{A-1})$$

where $k(\nu)$ is the absorptivity at frequency ν , γ is the half-width which is proportional to the pressure for a given temperature, $S = \int_{-\infty}^{\infty} k(\nu) d\nu$ is the line strength, and ν_0 is the frequency of the line center.

A similar expression is given for the super-Lorentzian line shape

$$k(\nu) = (S/\pi\gamma) \{ (\eta/2) \sin(\pi/\eta) \} [\{ |\nu - \nu_0|/\gamma \}^\eta + 1]^{-1} \quad (\text{A-2})$$

where all symbols have the same meanings and η is a constant dependent on the type of interactions the molecule has with its surroundings. In this study, η was assumed to have a value of 1.75 for H_2O , O_3 , N_2O , and CO , and a value of 1.60

for CO_2 and CH_4 .

For a further discussion of the merits of these line shapes, see reference (24).

APPENDIX B: COMPUTER PROGRAM LISTINGS

Program LINESHAPE

The program LINESHAPE, written in H level FORTRAN, calculates the super-Lorentzian line shape at 0.01 cm^{-1} increments from the line center to an arbitrary frequency away from line center and places the information on magnetic tape. It does this for a range of half-widths at half-width increments of 0.001 cm^{-1} . In this study, the amount of information needed for a single line shape exceeds the installation's maximum record length. Therefore line shapes were stored in multiple records, and a set of indices that points to the records that begin new line shapes were calculated and punched. This information is then used in the program SPECTRUM.

C***** LINESHAPE *****

C
C
C
C
C
C

THIS PROGRAM CALCULATES A SERIES OF SUPER-LORENZIAN
LINE SHAPES AND PLACES THEM ON MAGNETIC TAPE.

```

INTEGER KCAL(115)
INTEGER JJ(115), INDEX(115)
REAL KNU(27000)/27000*0.0/
MTRXEL(DELTA)=(DELTA/0.01)+1.0
READ(5,9) GAMINT,GAMFIN,FRAC,ETA,KMAX
WRITE(6,29) GAMINT,GAMFIN,FRAC,ETA,KMAX
PI=3.14159265
K1Q=KMAX/4
K2Q=2*K1Q
K3Q=3*K1Q
K1Q1=K1Q+1
K2Q1=K2Q+1
K3Q1=K3Q+1
INDEX(1)=1
A=(ETA*SIN(PI/ETA)/(PI*2))
GAMMA=GAMINT-0.001
CUTOFF=10.0** (ALOG10(150.0)/ETA)
CALCUT=10.0** (ALOG10(FRAC)/ETA)
KGAMAX=(GAMFIN-GAMINT+0.00105)/0.001)
DELTA=0.0
DO 10 I=1, KGAMAX
  GAMMA=GAMMA+0.001
  B=A/GAMMA
  DELCUT=GAMMA*CUTOFF
  KCUT=MTRXEL(DELCUT)
  DELCAL=GAMMA*CALCUT
  KCAL(I)=MTRXEL(DELCAL)
  IF(KCAL(I).GT.KMAX) KCAL(I)=KMAX
  DO 20 K=1, KCUT
    KNU(K)=B/((DELTA/GAMMA)**ETA+1.0)
    DELTA=DELTA+0.01
20  CONTINUE
    KCUT=KCUR+1
    KCAL1=KCAL(I)
    DO 30 K=KCUR,KCAL1
      KNU(K)=B*((DELTA/GAMMA)**(-ETA))
      DELTA=DELTA+0.01
30  CONTINUE
    J=1
    WRITE(9) (KNU(K), K=1, K1Q)
    IF(KCAL1.LE.K1Q) GO TO 1
    J=2
    WRITE(9) (KNU(K), K=K1Q1, K2Q)

```



```

IF(KCAL1.LE.K2Q) GO TO 1
J=3
WRITE(9) (KNU(K),K=K2Q1,K3Q)
IF(KCAL1.LE.K3Q) GO TO 1
J=4
WRITE(9) (KNU(K),K=K3Q1,KMAX)
1 II=I+1
INDEX(II)=INDEX(I)+J
JJ(I)=J
DELTA=0.0
10 CONTINUE
WRITE(6,49)
WRITE(7,59) (KCAL(I),I=1,KGAMAX)
WRITE(7,69) (INDEX(I),I=1,KGAMAX)
DO 40 K=1,KGAMAX
WRITE(6,89) K, INDEX(K), JJ(K), KCAL(K)
40 CONTINUE
9 FORMAT(2F5.4,E10.3,F5.3,I5)
29 FORMAT(1X,F6.4,2X,F6.4,2X,E10.3,2X,F6.4,2X,I5)
49 FORMAT('1')
59 FORMAT(10I5)
69 FORMAT(10I3)
89 FORMAT(1X,I3,3X,I3,3X,I1,3X,I5)
STOP
END

```

Program SPECTRUM

The program SPECTRUM, written in H level FORTRAN, calculates the spectrum of a given molecule on a line-by-line basis using the spectrometric information supplied by references (4,17). The function of each section of code is contained in comment statements within the program.

C***** SPECTRUM *****

C
C
C
C
C
C
C

THIS PROGRAM COMPUTES THE SPECTRUM OF ANY MOLECULE GIVEN
LINE CENTERS, HALF-WIDTHS, LINE INTENSITIES, AND
ENERGY ABOVE GROUND STATE (BOLTZMAN FACTOR)

REAL KNU(59010), NUFLAG, KNU1(6750), NUINT, NUSTRT, NUSTOP,
& NUBOT
REAL NU(40), S(40), ALPHA(40), EDP(40)
REAL NUINCR
REAL KNUMIN
REAL NUDUM, SDUM, EDPDUM, ALPDUM
INTEGER AFTAPE/10/, MOT(40)
INTEGER INDEX(115), KSTOP(115)
COMMON KNU, KNU1, NUINT, NUSTRT, NUSTOP, NUBOT, NUFLAG, KTOP,
& KSTOP
COMMON INDEX, KGAMAX, NUINCR
COMMON C2, ETA
COMMON NUDUM, SDUM, EDPDUM, ALPDUM
DEFINE FILE 20(290, 6750, U, INT)

C
C

NUDUM=0.0
SDUM=0.0
EDPDUM=0.0
ALPDUM=0.0
PI=3.14159
READ(5, 79) ETA, KNUMIN
WRITE(6, 89) ETA, KNUMIN
C1=(ETA/(2.0*PI))*SIN(PI/ETA)
C2=KNUMIN/C1

C
C

READ(5, 99) KGAMAX, NUMREC, NARRAY, (INDEX(K), K=1, KGAMAX)
WRITE(6, 109) KGAMAX, NUMREC, NARRAY
READ(5, 39) (KSTOP(K), K=1, KGAMAX)
DO 30 N=1, KGAMAX
WRITE(6, 119) N, INDEX(N), KSTOP(N)
30 CONTINUE

C
C

DO 40 K=1, NARRAY
KNU(K)=0.0
40 CONTINUE

C
C
C

KTOP IS 1/4 OF THE NUMBER OF LOCATIONS NEEDED TO STORE THE
VALUES OF THE SUPER LORENTZIAN LINE-SHAPE PARAMETERS FOR A

```

C      GIVEN HALF-WIDTH
C
C
C      READ(5,49) KTOP,NUINCR
C      WRITE (6,69) KTOP,NUINCR
C
C      READ THE TAPE PRODUCED IN LINESHAPE AND PLACE ON DISK
C
C
C      DO 10 I=1,NUMREC
C      READ (9) KNU1
C      WRITE (20,I) KNU1
10 CONTINUE
C      REWIND9
C
C
C      NUSTRT & NUSTOP ARE THE LOWER & UPPER LIMITS FOR
C      SPECTRUM GENERATION.  MOLID IS THE I.D. NUMBER OF
C      THE MOLECULE WHOSE SPECTRUM IS BEING COMPUTED
C
C
C      READ(5,9) NUSTRT,NUSTOP,MOLID
C      WRITE (6,59) NUSTRT,NUSTOP,MOLID
C
C
C      NUINT IS THE LOWEST FREQUENCY USED IN SPECTRUM
C      GENERATION.  NUBOT IS A REFERENCE FREQUENCY FOR
C      ASSIGNING ARRAY LOCATIONS.
C
C
C      NUINT=NUSTRT-KTOP*0.04
C      NUBOT=NUSTRT
C      NUFLAG=NUSTRT+KTOP*0.04+NUINCR
C
C
C      THE AFCRL COMPILATION OF MOLECULAR DATA IS READ.  THESE
C      VALUES ARE PASSED TO SUBROUTINE NUPICK FOR FURTHER
C      PROCESSING.
C
C
C      DO 20 I=1,5000
2  READ(AFTAPE,19,END=1) J,NU(1)
C      IF (NU(1).GE.NUINT) GO TO 3
C      GO TO 20
1  REWIND AFTAPE
C      AFTAPE=AFTAPE+1
C      GO TO 2
20 CONTINUE
3  BACKSPACE AFTAPE
C      BACKSPACE AFTAPE

```

```

6 READ (AFTAPE,29,END=5) K, (NU(J), S(J), ALPHA(J), EDP(J),
&   BB1, BB2, BB3, BB4, BB5, BB6, BB7, IDAT, ISOT, MOL(J), J=1, 40)
  CALL NUPICK (NU, ALPHA, S, EDP, MOL, &4, MOLID)
  GO TO 6
5 REWIND AFTAPE
  AFTAPE=AFTAPE+1
  GO TO 6
4 STOP
9 FORMAT(2F10.3,I1)
19 FORMAT(I10,F10.3)
29 FORMAT(I10,40(F10.3,E10.3,F5.3,F10.3,7A5,I3,I4,I3))
39 FORMAT(10I5)
49 FORMAT(I5,F10.3)
59 FORMAT(1X,'NUSTRT=',F10.3,'NUSTOP=',F10.3,3X,'MOL I.D.=',
&   I1)
69 FORMAT(1X,'KTOP=',I5,3X,'NUINCR=',F10.3)
79 FORMAT(F5.3,5X,E10.3)
89 FORMAT(1X,'ETA=',F5.3,5X,'KNUMIN=',E10.3)
99 FORMAT(I3,2X,I3,5X,I5,/, (10I3))
109 FORMAT(1X,'KGAMAX=',I3,3X,'NUMREC=',I3,3X,'NARRAY=',I5)
119 FORMAT(1X,I3,3X,I3,3X,I5)
  END

```

```

SUBROUTINE NUPICK (NU, ALPHA, S, EDP, MOL, *, MOLID)
INTEGER INDEX (115), KSTOP (115)
INTEGER MOL (40)
REAL NU (40), ALPHA (40), S (40), EDP (40), NUZERO
REAL KNU (59010), NUFLAG, KNU1 (6750), NUINT, NUSTRT, NUSTOP,
&  NUBOT
REAL NUINCR
REAL NUDUM, SDUM, EDPDUM, ALFDUM
COMMON KNU, KNU1, NUINT, NUSTRT, NUSTOP, NUBOT, NUFLAG, KTOP,
&  KSTOP
COMMON INDEX, KGAMAX, NUINCR
COMMON C2, ETA
COMMON NUDUM, SDUM, EDPDUM, ALFDUM

```

C
C
C
C
C
C
C

NUPICK SELECTS LINE INFORMATION HAVING THE PROPER I. D.
NUMBER AND BEING WITHIN THE PROPER FREQUENCY RANGE.
THIS DATA IS THEN PASSED TO KNUCAL FOR FURTHER
PROCESSING.

```

DO 10 I=1, 40
IF (NU (I) .LE. NUINT) GO TO 10
IF (MOL (I) .NE. MOLID) GO TO 10
IF (NU (I) .GT. NUFLAG) CALL KNUOUT (&3)
IF (NU (I) .EQ. NUDUM) GO TO 2
4  NUDUM=NU (I)
   SDUM=S (I)
   EDPDUM=EDP (I)
   ALFDUM=ALPHA (I)
   CALL KNUCAL (NU (I), S (I), ALPHA (I), EDP (I))
   GO TO 10
2  IF (EDP (I) .NE. EDPDUM) GO TO 4
   IF (S (I) .NE. SDUM) GO TO 4
   IF (ALPHA (I) .NE. ALFDUM) GO TO 4
10 CONTINUE
   RETURN
3  RETURN 1
   END

```

C

SUBROUTINE KNUOUT(*)

THIS SUBROUTINE IS USED TO DUMP A BLOCK OF DATA
ON MAGNETIC TAPE AND DECIDES WHETHER OR NOT TO CONTINUE
PROCESSING. IF PROCESSING IS CONTINUED, THE INDICES
OF THE WORKING ARRAY ARE SHIFTED TO COMPUTE A NEW
BLOCK OF DATA.

INTEGER INDEX(115),KSTOP(115)
REAL KNU(59010),NUFLAG,KNU1(6750),NUINT,NUSTRT,NUSTOP,
& NUBOT
REAL NUINCR
REAL NUDUM,SDUM,EDPDUM,ALFDUM
COMMON KNU,KNU1,NUINT,NUSTRT,NUSTOP,NUBOT,NUFLAG,KTOP,
& KSTOP
COMMON INDEX,KGAMAX,NUINCR
COMMON C2,ETA
COMMON NUDUM,SDUM,EDPDUM,ALFDUM
TOP=NUBOT+NUINCR
WRITE(6,19)NUBOT,TOP

WRITE(15) NUBOT,(KNU(K),K=1,5000)

TEST=NUSTOP-NUBOT-10.0
IF(TEST.LE.NUINCR) RETURN 1
NUFLAG=NUFLAG+NUINCR
NUBOT=NUBOT+NUINCR
KMAX=8*KTOP
KINCR=(NUINCR/0.01)+5.0E-2
DO 10 K=1,KMAX
K50=K+KINCR
KNU(K)=KNU(K50)
10 CONTINUE
KMIN=KMAX+1
KMAX=KMAX+KINCR
DO 20 K=KMIN,KMAX
20 KNU(K)=0.0
19 FORMAT(' ',20X,'SPECTRUM FROM ',F10.3,' TO ',F10.3,
& ' WAVENUMBERS AT 0.01 WAVENUMBER INCREMENTS',/)
RETURN
END

SUBROUTINE KNUCAL (NU,S,GAMMA,EDP)

C
C
C
C
C

THIS IS THE WORKHORSE ROUTINE OF SPECTRUM. IT READS THE
PROPER LINE SHAPE FROM DISK, CALCULATES CONTRIBUTION
TO THE SPECTRUM AND DOES A LOT OF FREQUENCY BOOKKEEPING

REAL NUINCR

REAL KNU (59010), NUFLAG, KNU1 (6750), NUINT, NUSTRT, NUSTOP,

6 NUBOT

REAL NU, NU1, SAFETY/5.0E-2/

REAL NUDUM, SDUM, EDPDUM, ALFDUM

INTEGER KMAX1 (115), INDEX (115)

COMMON KNU, KNU1, NUINT, NUSTRT, NUSTOP, NUBOT, NUFLAG, KTOP,

6 KMAX1

COMMON INDEX, KGAMAX, NUINCR

COMMON C2, ETA

COMMON NUDUM, SDUM, EDPDUM, ALFDUM

NAMelist/UNDER/NU1, GAMMA1, S1, EDP1

NAMelist/OVER/NU1, GAMMA1, S1, EDP1

MTRXEL (NUBOT, FREQ) = ((FREQ - NUBOT + 0.01) / 0.01) + SAFETY

MNU = NU / 0.01 + SAFETY

RNU = NU - MNU * 0.01

IF (RNU.GE.0.005) MNU = MNU + 1

NU = MNU * 0.01

NU1 = NU

S1 = S

GAMMA1 = GAMMA

EDP1 = EDP

GAMMA = GAMMA / 0.001 + SAFETY

IG = GAMMA

DIG = GAMMA - IG

IF (DIG.GE.0.5) IG = IG + 1

IF (IG.LT.1) GO TO 101

IF (IG.GT.KGAMAX) GO TO 102

GO TO 103

101 WRITE (6, UNDER)

IG = 1

GO TO 103

102 WRITE (6, OVER)

IG = KGAMAX

103 I = INDEX (IG)

FIND (20'I)

S = S * EXP (-EDP / (0.695004 * 296.0))

C

DELTA = GAMMA1 * ((C2 * GAMMA1 / S) ** (-1.0 / ETA))

KMAX4 = (DELTA / 0.01) + 1.0 + SAFETY

C
C

IFLAG = 1

DNSTRT = NU - NUBOT


```

DNSTOP=NUSTOP-NU
IF (DNSTRT) 3,3,4
4 IF (DNSTOP) 5,5,6

C
C
3 KMIN1=-(DNSTRT/0.01)+1.0+SAFETY
  JMIN=KMIN1/KTOP
  KMIN2=KMIN1-JMIN*KTOP
  IF (KMIN2.EQ.0) GO TO 51
52 CONTINUE
  I=I+JMIN
  FIND (20'I)
  M=1
  JMIN=JMIN+1
  KMAXB=(DNSTOP/0.01)+1.0+SAFETY
  KMAX3=KMAX1(TG)
  KMAX3=MIN0(KMAX3,KMAXB)
  KMAX3=MIN0(KMAX3,KMAX4)
  IF (KMIN1.GE.KMAX3) GO TO 7
  JMAX=KMAX3/KTOP
  KMAX2=KMAX3-JMAX*KTOP
  IF (KMAX2.EQ.0) GO TO 53
54 CONTINUE
  JMAX=JMAX+1
  IF (JMAX-JMIN) 7,8,11
51 KMIN2=KTOP
  JMIN=JMIN-1
  GO TO 52
53 KMAX2=KTOP
  JMAX=JMAX-1
  GO TO 54
7 RETURN
8 IF (KMAX2-KMIN2) 7,7,11
11 I=I-1
17 DO 10 J=JMIN,JMAX
  IF (IPLAG.EQ.0) GO TO 16
  I=I+1
  READ(20'I) KNU1
16 IPLAG=1
  IF (J.EQ.JMIN) GO TO 12
  KMIN=1
  GO TO 13
12 KMIN=KMIN2
13 IF (J.EQ.JMAX) GO TO 14
  KMAX=KTOP
  GO TO 15
14 KMAX=KMAX2
15 DO 10 K2=KMIN,KMAX
  KNU(M)=KNU(M)+S*KNU1(K2)
  M=M+1

```

10 CONTINUE
GO TO 7

C
C

```

5  M=MTRXEL (NUBOT,NUSTOP)
   KMIN1=- (DNSTOP/0.01) +1.0+SAFETY
   JMIN=KMIN1/KTOP
   KMIN2=KMIN1-JMIN*KTOP
   IF(KMIN2.EQ.0) GO TO 61
62 CONTINUE
   I=I+JMIN
   FIND (20'I)
   JMIN=JMIN+1
   KMAXR=(DNSTRT/0.01) +1.0+SAFETY
   KMAX3=KMAX1(IG)
   KMAX3=MIN0 (KMAX3,KMAXR)
   KMAX3=MIN0 (KMAX3,KMAX4)
   JMAX=KMAX3/KTOP
   KMAX2=KMAX3-JMAX*KTOP
   IF(KMAX2.EQ.0) GO TO 63
64 CONTINUE
   JMAX=JMAX+1
   IF (JMAX-JMIN) 7,18,21
18  IF (KMAX2-KMIN2) 7,7,21
61  KMIN2=KTOP
   JMIN=JMIN-1
   GO TO 62
63  KMAX2=KTOP
   JMAX=JMAX-1
   GO TO 64
21  I=I-1
27  DO 20 J=JMIN,JMAX
   IF (IFLAG.EQ.0) GO TO 26
   I=I+1
   READ (20'I) KNU1
26  IFLAG=1
   IF (J.EQ.JMIN) GO TO 22
   KMIN=1
   GO TO 23
22  KMIN=KMIN2
23  IF (J.EQ.JMAX) GO TO 24
   KMAX=KTOP
   GO TO 25
24  KMAX=KMAX2
25  DO 20 K2=KMIN,KMAX
   KNU (M)=KNU (M)+S*KNU1 (K2)
   M=M-1
20 CONTINUE
   GO TO 7

```

C

C

```

6  MZERO=MTRXEL (NUBOT, NU)
   READ (20'I) KNU1
   IFLAG=0
   KNU (MZERO)=KNU (MZERO) +S*KNU1 (1)
   MR=MZERO
   MB=MZERO
   KMAXR=(DNSTRT/0.01)+1.0+SAFETY
   KMAXB=(DNSTOP/0.01)+1.0+SAFETY
   KMAXR=MINO (KMAXR, KMAX1 (IG))
   KMAXR=MINO (KMAXR, KMAX4)
   KMAXB=MINO (KMAXB, KMAX1 (IG))
   KMAXB=MINO (KMAXB, KMAX4)
   KKMAX=MINO (KMAXB, KMAXR)
   JJMAX=KKMAX/KTOP
   KKMAX1=KKMAX-JJMAX*KTOP
   IF (KKMAX1.EQ.0) GO TO 71
72  CONTINUE
   JJMAX=JJMAX+1
   KDMAX=KMAXR-KMAXB
   IF (KDMAX.EQ.0) GO TO 31
   KMIN2=KKMAX1+1
   IF (KMIN2.GT.KTOP) GO TO 32
   JMIN=JJMAX
   IFLAG=0
   GO TO 33
71  KKMAX1=KTOP
   JJMAX=JJMAX-1
   GO TO 72
32  KMIN2=1
   JMIN=JJMAX+1
   IFLAG=1
33  KMAX0=MAX0 (KMAXB, KMAXR)
   JMAX=KMAX0/KTOP
   KMAX2=KMAX0-JMAX*KTOP
   IF (KMAX2.EQ.0) GO TO 73
74  CONTINUE
   JMAX=JMAX+1
   IF (KDMAX) 34,31,35
34  ISIG=2
   GO TO 36
35  ISIG=3
   GO TO 36
73  KMAX2=KTOP
   JMAX=JMAX-1
   GO TO 74
31  ISIG=1
36  JFLAG=0
   DO 30 J=1, JJMAX
   IF (JFLAG.EQ.0) GO TO 41

```

```
I=I+1
READ(20'I) KNU1
41 JFLAG=1
   KKMIN=1
   IF (J.EQ.1) KKMIN=2
   IF (J.EQ.JJMAX) GO TO 37
   KKMAX=KTOP
   GO TO 38
37 KKMAX=KKMAX1
38 DO 30 K2=KKMIN, KKMAX
   MR=MR-1
   KNU (MR)=KNU (MR)+S*KNU1(K2)
   MB=MB+1
   KNU (MB)=KNU (MB)+S*KNU1(K2)
30 CONTINUE
   GO TO (7,117,127), ISIG
117 M=MB+1
   GO TO 17
127 M=MR-1
   GO TO 27
END
```

Subroutine for ADC Control

The following subroutine, run on the PDP 8/E minicomputer and written in the PAL III assembly language, is used to control the Datel ADC. Program comments define the function of each instruction, but a few added comments are in order. The octal instructions 6524, 6525, and 6526 are special purpose instructions which communicate with the ADC. The 6525 and 6526 instructions are used to control the input lines of the ADC. They are the selective set and selective clear instructions, respectively, and are used to give conversion commands and analog channel address information to the ADC. The 6524 instruction loads the result of the conversion from the ADC's output to the computer's accumulator. Special consideration was given to the timing needed to achieve a valid analog to digital conversion. This is reflected in the use of the NOP instruction at address 7506 and the delay loop starting at address 7511.

This subroutine is called by a program written in 4K FORTRAN which controls all other input / output functions and controls the time between analog to digital conversions.

ADDR	INSTR	MNEMONIC	/COMMENTS
		*7500	
7500	00C0	CHNO,0	/SUBROUTINE FOR A TO D CONVERSION
7501	7240	STA	/SET THE ACCUMULATOR 7777
7502	6525	6525	/CLEARS INPUT LINE TO SYSTEM 256
7503	7200	CLA	/CLEAR THE AC (SET TO 0000)
7504	1320	TAD CONV	/LOAD CONVERSION CMND INTO AC
7505	6526	6526	/GIVE A TO D CONVERT CMND TO SYS 256
7506	70C0	NOP	/WAIT FOR 1.2 MMSEC
7507	6525	6525	/SELECTIVE CLEAR, REMOVE CONVERT CMND
7510	7200	CLA	/CLEAR THE AC
7511	1322	TAD DEL	/LOAD DELAY PARAMETER INTO THE AC
7512	3323	DCA D1	/PUT DELAY PARM INTO D1
7513	2323	ISZ D1	/INCREMENT D1, IS D1 ZERO?
7514	5313	JMP .-1	/NO: WAIT A LITTLE LONGER, TRY AGAIN
7515	6524	6524	/YES: LOAD RESULTS OF CONVERSION IN AC
7516	3721	DCA I OUT	/DEPOSIT CONVERTED NUMBER IN ADDR 7576
7517	57C0	JMP I CHNO	/GO BACK TO CALLING PROGRAM
7520	10C0	CONV,1000	/CONVERT CMND, CHANNEL ZERO ADDRESS
7521	7576	OUT,7576	/LOCATION WHERE CONVERSION IS STORED
7522	7760	DEL,7760	/DELAY PARM, ALLOWS TIME FOR CONVERSION
7523	00C0	D1,0	/DUMMY DELAY PARM FOR CONVERSION

Program NOSIM

The program NOSIM simulates the spectrum of nitric oxide. Written in F level PL/1, it calculates the "infinite resolution" spectrum of NO for a range of half-widths and convolves these spectra with the slit function. Appropriate measures are taken to assure the frequency calibration of the theoretical spectrum is in coincidence with the measured spectrum. Program comments clarify the functions of various sections of code.

/****** NOSIM *****/

/*DEFINITIONS:

SLIT (NSLIT) - SLIT FUNCTION ARRAY HAVING NSLIT MEMBERS

NSLMAX - POSITION OF MAX SLIT VALUE

EXSPEC (NEXSPEC) - EXPERIMENTAL SPECTRUM ARRAY HAVING NEXSPEC MEMBERS

PREX_ZERO - STARTING FREQUENCY OF EXPERIMENTAL SPECTRUM

FREX_INCR - FREQUENCY INCREMENT OF EXP DATA POINTS

SPEC (NSPEC) THEORETICAL SPECTRUM HAVING NSPEC MEMBERS

FREQ0 - STARTING FREQUENCY OF THEORETICAL SPECTRUM

SHIFT_RANGE - UNCERTAINTY IN FREQUENCY CALIBRATION

NSR (=SHIFT_RANGE/FREX_INCR) - FREQ INCREMENTS IN SHIFT_RANGE

RELATIONSHIPS:

FREQ0=PREX_ZERO - ((NSR + NSLIT + 1)/2)*FREX_INCR

POSITION:

1 START OF DATA IN INFINITE RESOLUTION SPECTRUM

NSPEC END OF DATA IN INFINITE RESOLUTION SPECTRUM

NSLMAX START OF DATA IN THEO CONVOLVED SPECTRUM

NSPEC1 END OF DATA IN THEO CONVOLVED SPECTRUM

(=NEXSPEC+NSR+NSLMAX-1)

*/

MATCH: PROC OPTICNS (MAIN);

DCL SLIT(*) CTL FLOAT DEC,

SPEC(*) CTL FLOAT DEC,

EXSPEC(*) CTL FLOAT DEC,

WORK(*) CTL FLOAT DEC,

FREQ(*) CTL FLOAT DEC;

DCL (NLOW,NHIGH) FIXED BIN;

DCL (FREQ_LOW,FREQ_HIGH) FLOAT DEC;

DCL 1 A1,

2 NEXTOT FIXED BIN,

2 IDN FIXED BIN,

2 FINC FLOAT DEC,

2 F0 FLOAT DEC;

DCL FILE_NAME CHAR (4);

DCL (PREX_ZERO,FREX_INCR,

FREQ0,SHIFT_RANGE,

HW, HW_LOW,HW_HIGH,HW_INCR) FLOAT DEC;

DCL (NSLIT,NSPEC,NEXSPEC,

NSLMAX,NSPEC1,NSR) FIXED BIN;

DCL (AREA1,AREA2,SUM1) FLOAT DEC;


```

DCL 1 LINE_DATA BASED (PT1) ,
    2 LINE_CTR FLOAT DEC,
    2 S FLOAT DEC,
    2 UPPER_ENERGY FLOAT DEC,
    2 PT2 PTR;

```

```

DCL (PT3,PT4) PTR;

```

```

DCL (J,JJ) FIXED BIN;

```

```

DCL GRAPH_ENTRY (FIXED BIN, (*) FLOAT, (*) FLOAT, FIXED BIN,
    FIXED BIN, FLOAT, FLOAT, FLOAT, FLOAT, FLOAT, CHAR(20),
    CHAR(20), CHAR(20), CHAR(20));

```

```

DCL GRAPHS_ENTRY (FIXED BIN, (*) FLOAT, (*) FLOAT, FIXED BIN,
    FIXED BIN, CHAR(20));

```

```

DCL GLAB CHAR(20);

```

```

DCL GRAPH_BIT BIT(1) INIT ('0'B);

```

```

DCL (WAVE_NO, WAVE_ZERO) FLOAT DEC;

```

```

DCL (IGRAPH, M, MJ) FIXED BIN;

```

```

/* GET EXPERIMENTAL BAND INFO, ALLOCATE SPACE */

```

```

    GET LIST (FREX_INCR);
    PUT SKIP LIST (FREX_INCR);
    GET LIST (FREQ_LOW, FREQ_HIGH, FILE_NAME);
    PUT SKIP DATA (FREQ_LOW, FREQ_HIGH, FILE_NAME);
    OPEN FILE (DISK) TITLE (FILE_NAME) RECORD INPUT;
    READ FILE (DISK) INTO (A1);
    PUT DATA (A1);
    GET LIST (A1);
    PUT DATA (A1);
    NLOW = ((FREQ_LOW - F0)/FREX_INCR + 1.5);
    NHIGH = ((FREQ_HIGH - F0)/FREX_INCR + 1.5);
    NEXSPEC = NHIGH - NLOW + 1;
    ALLOCATE WORK (NEXTOT);
    READ FILE (DISK) INTO (WORK);
    CLOSE FILE (DISK);
    ALLOCATE EXSPEC (NEXSPEC);
    II = 1;
    DO I = NLOW TO NHIGH;
        EXSPEC (II) = WORK (I);
        II = II + 1;
    END;
    FREE WORK;
    FREX_ZERO = FREQ_LOW;
    GET LIST (SHIFT_RANGE);
    PUT SKIP DATA (SHIFT_RANGE);

```

```

/* GET SLIT, ALLOCATE SPACE, FIND POSITION OF MAX SLIT VALUE */
    GET LIST (NSLIT);

```

```

ALLOCATE SLIT (NSLIT);
GET LIST (SLIT);
  PUT SKIP(2) DATA (NSLIT);
  SLIT = 1. - SLIT;
  PUT SKIP EDIT (SLIT) (R(FOR1));
AREA1 = SUM(SLIT); SLIT = SLIT/AREA1;
CALL MAXPOS (SLIT, NSLMAX);

AREA1 = SUM(-LOG(EXSPEC)); /* CT(E) -> S(CA(E)) */
  PUT PAGE DATA (NEXSPEC);
  PUT SKIP EDIT (EXSPEC) (R(FOR1));
  PUT SKIP DATA (AREA1);

/* GET HALF WIDTH INFO */
GET LIST (HW_LOW, HW_HIGH, HW_INCR);
  PUT SKIP(2) EDIT ('HALF WIDTH WILL BE INCREMENTED FROM ',
    HW_LOW, ' TO ', HW_HIGH, ' BY ', HW_INCR)
    (A, F(5, 3), A, F(5, 3), A, F(5, 3));
/* GET ALL LINE INFO */
  PUT PAGE EDIT ('ABSORPTION LINE INFORMATION:',
    'LINE CENTER      INTENSITY      BOLTZMAN ') (A, SKIP, A, SKIP);
GET LIST (GRAPH_BIT, IGRAPH);
ON ENDFILE (SYSIN) GO TO MASTER;

DO I = 1 TO 100;
  ALLOCATE LINE_DATA SET (PT1);
  GET LIST (LINE_CTR, S);
  UPPER_ENERGY = 0.0;
  PUT SKIP ;
  PUT EDIT (LINE_CTR, S, UPPER_ENERGY)
    (X(1), F(8, 3), X(6), E(10, 3), X(6), E(10, 3));
  S = S * 2.21; /**** PATH=4.2 CM, PRESSURE=400 TORR ***/
  IF I = 1 THEN PT4 = PT1;
    ELSE PT3 -> PT2 = PT1;
  PT3 = PT1;
END;
MASTER: PT3 -> PT2 = NULL;
FREE PT1 -> LINE_DATA;

/* MAKE DEFINITIONS, ALLOCATE SPACE FOR THEORETICAL
   SPECTRUM AND WORK SPACE */

NSR = ABS (SHIFT_RANGE / FREX_INCR);
NSPEC = NEXSPEC + NSR + (NSLIT - 1);
NSPEC1 = NEXSPEC + NSR + NSLMAX - 1;
FREQ0 = FREX_ZERO - ((NSR + NSLIT + 1) / 2) * FREX_INCR;
FREQ_INCR = FREX_INCR;
PUT SKIP DATA (NSR, NSPEC, NSPEC1, FREQ0);
ALLOCATE SPEC (NSPEC);
ALLOCATE WORK (NSPEC);

```

```

IF GRAPH_BIT THEN DO;
  ALLOCATE FREQ (NEXSPEC);
  WAVE_NO = FREX_ZERO;
  DO M = 1 TO NEXSPEC;
    FREQ (M) = WAVE_NO;
    WAVE_NO = WAVE_NO + FREQ_INCR;
  END;
  WAVE_ZERO = WAVE_NO - FREQ_INCR;
  CALL GRAPH (NEXSPEC, FREQ, EXSPEC, 3, 7, 10.0, 10.0, 0.3333333,
    WAVE_ZERO, 0.10, 0.0, 'WAVENUMBERS;', 'TRANSMITTANCE;',
    'OBSERVED SPECTRUM;', ' ');
END;
PUT PAGE;

/* THE MEAT OF THE PROGRAM FOLLOWS */

DO HW = HW_LOW TO HW_HIGH BY HW_INCR;

  SPEC = 0.0; /* INITIALIZE SPECTRUM */

  /* CALCULATE INFINITE RESOLUTION SPECTRUM */
  PT1 = PT4;
  DO I = 1 TO 100 WHILE (PT1 /= NULL);
    CALL LORNTZ (SPEC, HW, S, LINE_CTR, UPPER_ENERGY, FREQ0,
      FREX_INCR, NSPEC);
    PT1 = PT2;
  END;

  SPEC = EXP(-SPEC); /* A(G) -> T(G) */
  /* CONVOLVE SPECTRUM WITH THE SLIT FUNCTION */
  /* T(G) -> CT(G) */
  CALL SMOOTH (SPEC, SLIT);

  /* NORMALIZE AREA OF SPEC TO AREA OF EXSEC */
  SPEC = -LOG(SPEC); /* CT(G) -> CA(G) */
  /* CA(G) -> S(CA(G)) */
  PUT SKIP(2);

  /* SHIFT THE THEORETICAL SPECTRUM AND FIND THE INTEGRATED
    DIFFERENCE BETWEEN EXPERIMENTAL AND THEORETICAL SPECTRA */
  DO I = 1 TO NSR;
    AREA2 = 0.0;
    JJ = NSLMAX + I - 1;
    DO J = JJ TO JJ + NEXSPEC - 1;
      AREA2 = AREA2 + SPEC(J);
    END;
    RATIO = AREA1/AREA2;
    IF (GRAPH_BIT & (IGRAPH = I)) THEN DO;
      MJ = JJ;

```

```

DO M = 1 TO NEXSPEC;
  WORK (M) = EXP (-RATIO * SPEC (MJ));
  MJ = MJ + 1;
END;
PUT STRING (GLAB) EDIT ('HALF WIDTH = ',HW,':')
  (A(13),F(5,3),A(1));
CALL GRAPH (NEXSPEC,FREQ,WORK,3,4,10.0,10.0,0.33333333,
  WAVE_ZERO,0.10,0.0,'WAVENUMBERS;','TRANSMITTANCE;',
  'SIMULATED SPECTRUM;',GLAB);
END;
SUM1 = 0.0;
DO J = 1 TO NEXSPEC;
  SUM1 = SUM1 + (EXSPEC(J) - EXP (-RATIO*SPEC (JJ)))**2;
  JJ =JJ +1;
END;
PUT LIST (SUM1);
END;
PUT SKIP DATA (RATIO);
PUT SKIP DATA (HW);
END;

FOR1: FORMAT ( SKIP, 10 (E(10,3),X(2)));

MAXPOS: PROC (X,MAXPOS1);
/* THIS ROUTINE RETURNS THE ELEMENT OF AN ARRAY
   CORRESPONDING TO ITS MAXIMUM VALUE */

DCL X(*) FLOAT DEC;
DCL XX FLOAT DEC;
DCL (I,M,MAXPOS1) FIXED BIN;

M = DIM (X,1);
XX = X(1);
MAXPOS1 = 1;
DO I =2 TO M;
  IF X(I) > XX THEN DO;
    XX = X(I);  MAXPOS1 = I;
  END;
END;
END MAXPOS;

SMOOTH: PROC (X,SMCOEF);
/* THIS ROUTINE CONVOLVES 2 ARRAYS */

DCL X(*) FLOAT DEC;
DCL SMCOEF (*) FLOAT DEC;

```

```

DCL NSMOOTH FIXED BIN;
DCL XX FLOAT DEC;
DCL (I,J,JJ) FIXED BIN;

```

```

  WORK = X;
  NSMOOTH = DIM (SMCOEF,1);
  DO I = NSLMAX TO NSPEC1;
    XX = 0.0;
    JJ = I - NSLMAX + 1;
    DO J = 1 TO NSMOOTH;
      XX = XX + SMCOEF(J) * X(JJ);
      JJ = JJ + 1;
    END;
    WORK (I) = XX;
  END;
  X = WORK;
END SMOOTH;

```

```

LORNTZ: PROC (K,HW,S,LINE_CTR,UPPER_ENERGY,FREQ0,FREQ_INCR,
  NSPEC);

```

```

/* THIS SUBROUTINE COMPUTES THE INFINITE RESOLUTION
   SPECTRUM OF A MOLECULE, ONE LINE PER CALL */

```

```

DCL KT FLOAT INITIAL(204.);
DCL PI FLOAT INITIAL (3.14159);

```

```

DCL (HW,S,LINE_CTR,UPPER_ENERGY) FLOAT DEC;
DCL (FREQ0,FREQ_INCR,FREQUENCY) FLOAT DEC;
DCL (I,NSPEC) FIXED BIN;

```

```

DCL K(*) FLOAT DEC;

```

```

  CONSTANT=HW*S/PI;
  FREQUENCY = FREQ0;

```

```

  DO I = 1 TO NSPEC;
    K(I) = K(I) + CONSTANT/((FREQUENCY-LINE_CTR)**2 + HW*HW);
    FREQUENCY = FREQUENCY + FREQ_INCR;
  END;

```

```

  RETURN;
END LORNTZ;
END MATCH;

```

APPENDIX C: DESCRIPTION OF MAGNETIC TAPE

Much of the information produced in this thesis has been compiled on an unlabelled, 9 track magnetic tape. A separate file is used for each of the spectra and their backgrounds. Each file contains a number of records, each record containing 5001 floating point numbers. The first element of the record is the starting frequency for the 50 cm^{-1} block of the spectrum which follows in the next 5000 entries. The records were written in unformatted WRITE statements for efficient use of space and computer time. Table A-1 lists the first 13 data sets with pertinent information.

The 14th file contains the frequencies whose spectrum-to-background ratios are greater than two for the molecules studied. The frequencies are listed in order of decreasing ratio. Each record has the following format:

ID- (INTEGER*4) ,

N- (INTEGER*4) ,

FREQ(N) - (REAL*4)

where ID is the molecular identification number (see Table A-1) , and N is the number of frequency values in FREQ to follow, but can be no greater than 100. When N is less than 100, 100 frequency values are still written, with only the first N values being valid. H_2O , CO_2 , and O_3 each have mul-

tiple records assigned to them. As before, this information was written on tape by unformatted WRITE statements.

Table A-1: File Description of Magnetic Tape

File	Data Set Name	Description of Data Set
1	H2O	H ₂ O spectrum, absorptivities*
2	CO2	CO ₂ spectrum, absorptivities
3	O3	O ₃ spectrum, absorptivities
4	N2O	N ₂ O spectrum, absorptivities
5	CO	CO spectrum, absorptivities
6	CH4	CH ₄ spectrum, absorptivities
7	BKGD0	total background**
8	BKGD1	background for H ₂ O
9	BKGD2	background for CO ₂
10	BKGD3	background for O ₃
11	BKGD4	background for N ₂ O
12	BKGD5	background for CO
13	BKGD6	background for CH ₄
14	RSORT	AL frequencies

*Units of absorptivities are cm²/molecule.

**Background constituents have concentrations listed in Table 1. Path = 1 cm.