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

Technical Report PTR-82-5

SCIENCE AND SOFTWARE SUPPORT FOR SPACECRAFT
SOLAR OCCULTATION EXPERIMENTS

By

Ghiassi-Hessameddin

and

Jacob Becher, Principal Investigator

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For the period ending September 1979

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

Under
Research Contract NSG-1341
Michael P. McCormick, Technical Monitor
Instrument Research Division
Langley Research Center

June 1982



OLD DOMINION UNIVERSITY RESEARCH FOUNDATION

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P.O. Box 6369
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By

Ghiassi-Hessameddin*

ABSTRACT

The temperature dependence of absorption coefficients of ozone was studied between 7567 Å and 4630 Å. When the gas was cooled from room temperature to -108°C , an overall increase in the absorption coefficients was noticed. The maximum increase of 5% occurred at $\lambda = 6020 \text{ Å}$. In general, the absorption is linearly dependent on temperature.

INTRODUCTION

Ozone is one of the simplest triatomic molecules. Its importance in atmospheric chemistry has been the main reason for the sustained interest in its spectrum and molecular structure. A uniform and consistent set of ozone absorption coefficients is highly desirable since such data are important in atmospheric monitoring and quantitative ozone technology (such as rocket propulsion, water purification, disinfection, sterilization of containers for food, and sterilization of sewage). A number of basic research projects during the last decade have supplied new data and expanded the knowledge of the absorption spectrum.

Ozone has absorption bands extending from the infrared and visible to the ultraviolet (UV). The infrared regions' bands, which have been extensively studied, start at $3.3 \mu\text{m}$ and extend to $14.3 \mu\text{m}$, with the strongest at $9.6 \mu\text{m}$. The UV absorption spectrum consists of three bands: Chalonge

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Lefebvre band (3400 Å to 3650 Å); Huggins band (3050 Å to 3400 Å); and Hartley band (2200 Å to 3000 Å). The strongest and most featureless absorption in UV is the Hartley band with a maximum at 2550 Å, filtering most of the incoming radiation to the atmosphere that would otherwise reach the earth's surface. The Huggins band is a weak band with well-defined features that are further enhanced by lowering the gas temperature. The weakest is the Chalonge Lefebvre band with known features, similar to Huggins bands, that increase in prominence by decreasing the temperature. The only band in the visible is the Chappuis band--a very weak band with a maximum of 6020 Å with few apparent features. This band is used for monitoring concentrations of atmospheric ozone, even though the absorption coefficients in UV are better known. Other visible atmospheric absorption measurements for ozone are preferred because of the simplicity in experimental design and operation of the apparatus. Of the five studies (refs. 1-5) of absorption of coefficients in the visible region, only two agree substantially (refs. 3 and 4). The others reported that the magnitude of the absorption coefficients differed by about 10%. The major disagreement surrounds the conclusion reported on the temperature dependence of the absorption coefficient. This controversy was the motivation for doing this research.

The weakness of the absorption in the visible region requires spectroscopic measurements to be made with a cell containing a high concentration of the gas. The technique to obtain highly concentrated ozone has made it necessary to produce pure liquid ozone and then boil the liquid for transferring the ozone into the absorption cell. This is particularly dangerous since the slightest vibration could cause an exothermic reaction that could result in a serious explosion. This potential hazard may account for the fact that many important physical properties of this substance are not accurately known. The usual techniques for determining physical properties can rarely be applied; contact with materials usually used in experimental work must be avoided. Experience has shown that the most satisfactory materials for construction of the vacuum system are glass and teflon, which have been used in this work.

REVIEW OF PREVIOUS RESEARCH

Absorption Coefficients

The absorption coefficients of ozone in the visible region have been the subject of numerous studies (refs. 1-5). Early experiments used ozonized oxygen whereas those performed later by Inn and Tanaka (ref. 4) and Griggs (ref. 5) used pure ozone. The measurements performed with ozonized oxygen relied on a separate measurement of the composition; thus, the early measurements of absorption were limited by the effectiveness of determining the compositions of the two measurements. These compositions would vary over the time of the experiment, since a small amount of impurities and concentration of O_3 are the determining factor of O_3 -decomposition rate. In view of the weakness of the Chappuis absorption, high concentrations of the gas are required in the optical path to set a detectable signal. Thus, the researcher who used a mixture of ozone and oxygen had to use a long path to compensate for the oxygen in the tube. The concentration in the cell was determined either chemically or by observing the UV spectrum. The pressure measurements in the absorption tube were determined using a H_2SO_4 manometer. This type of manometer has a vapor pressure which introduces impurities into the gas sample, affecting the decomposition rate of O_3 . Pure ozone absorption measurements of the Chappuis band by Inn and Tanaka were the results of an interpolation dependent on O_3 decomposition. The spectrum they measured was corrected by observing the decay of ozone which was monitored at a fixed wavelength using a gas cell at the same temperature and pressure. They reported a decay of about 12% in a five- to ten-minute interval. Later, Griggs purified ozone to 100% and was unable to detect any decay, yet he confirmed the findings of Inn and Tanaka in UV. However, in the visible region his measurements seem to agree better with the previous work by Vigroux (ref. 3).

Temperature Dependence of Absorption Coefficients

In 1882 Chappuis, who two years earlier discovered the band that now bears his name, was the first to report the influence of temperature on the

temperature on the absorption coefficient (ref. 6). The mixture he used to perform measurements in the range from room temperature to -50°C contained 5% ozone. In 1935 Lefebvre (ref. 7) found the absorption spectrum in this region to be exactly the same at -80°C and room temperature using a mixture containing 6% ozone. Later, the variation in absorption coefficients was reported by Vassy (ref. 8), who had used a more concentrated mixture of ozonized oxygen containing 60-70% ozone. His values for absorption were about 20% higher than those reported earlier. He found a variation of nearly 30% for the temperature range of 18°C to -105°C . In 1947, Humphrey and Badger (ref. 9), used a mixture of 6% ozone and found no significant change in the absorption coefficients from room to dry ice temperatures. Later in 1948, Vassy and Vassy (ref. 2) investigated their previous findings, and corrected the error in the wavelengths they reported but confirmed the temperature dependence. Finally in 1953 Vigroux (ref. 3) measured the absorption coefficients and temperature effects for all three ranges (infrared, visible, and UV). He established new values for the absorption coefficient in the visible region with peak of absorption of 0.059 cm^{-1} (base 10) at $\lambda = 6020\text{ \AA}$ using an ozone concentration of approximately 30%. He employed a cross-shaped absorption tube, one arm of which was always used to determine the concentration of ozone by monitoring the UV band. Consequently, he was able to obtain the reduced thickness. Concerning temperature dependence, Vigroux supported the results of Humphrey and Badger. It should be noted that the determination of impurities and spectral data were not performed simultaneously. Inn and Tanaka (ref. 4) conjectured that a systematic error existed in Vassy's method of measuring the reduced thickness of ozone, and that the error could account for the large discrepancies between Vassy's findings and those of later researchers.

All the temperature effect measurements were performed photographically. The researchers had to cope with the problem of thermal equilibrium in the absorption cell at low temperatures. To avoid condensation of moisture on cell windows, pure air was blown on both ends of the cell. This moving dry air caused some heat exchange through the windows between the ozone molecules.

CHARACTERISTICS OF OZONE

Appropriate handling of ozone requires some knowledge of its physical and chemical properties. This knowledge is particularly important in the processes of purification and variation of temperature.

Physical Properties of Ozone

The following physical properties of ozone were important for our experiment and its spectral analysis:

A. Ozone is a blue gas with a characteristic odor (ref. 10). The boiling and melting points of pure ozone are -111.9°C (ref. 11) and -192.5°C (ref. 12) respectively. The binding energy for ozone is 1.04 eV (ref. 13). This small value is indicative of the reactivity and oxidizing characteristics of this molecule.

B. The ozone molecule O_3 is an isosceles triangle belonging to symmetry group C_{2v} (i.e., a two-fold symmetry axis and two planes of symmetry containing this axis). In this point group there are four types of electronic states which, according to Herzberg (ref. 13), are classified as A_1 , A_2 , B_1 , B_2 (Table 1). Taking into account the electron spins and the rotational motion of the molecule (which produce a magnetic field), the four electronic states are split into eight components (four singlets and four triplets).

Table 1. Character table of the symmetry group C_{2v} .

C_{2v}	I	$C_2(z)$	$\sigma(yz)$	$\sigma(xz)$
		2	v	v
A_1	+1	+1	+1	+1
A_2	+1	+1	-1	-1
B_1	+1	-1	+1	-1
B_2	+1	-1	-1	+1

The description of electronic states in polyatomic molecules such as ozone depends largely on the method of calculation. Among the variety of approaches (such as MO, HF, LCAO-SCF, VB, SCVMO, and GVB) used to provide a description and calculation of electronic states, the method of generalized valence bond (GVB) leads to a firm conceptual model for understanding the nature of ozone's molecular states. In addition, the GVB method is based on rigorous quantum mechanical considerations using high-speed digital computers for calculation of the electronic wave functions. The emphasis here is to introduce concepts that make it easier to visualize electron configurations without doing specific calculations. The GVB model assigns an orbital for each electron (each pair consists of two highly overlapping orbitals). The orbitals are often localized onto centers different from their atomic origins. The description of molecules in the GVB approach requires an understanding of chemical bonding principles which, briefly stated, are as follows: In order to obtain a strong covalent bond between atoms it is essential that (1) a singly occupied orbital on each atom be such that it overlaps significantly when the atoms are brought together, and (2) the orbitals of the bond must be nearly orthogonal to the other orbitals of the molecule not involved in the bond.

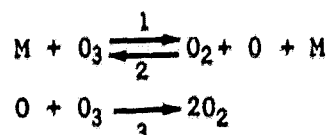
In order to apply the GVB approach for O_3 (ref. 14) we first examined the atomic orbitals of O , O_2 , and, finally, O_3 . The usual orbitals for oxygen are $(1s)^2$, $(2s)^2$, $(2p)^4$ with doubly occupied $1s$, $2s$, $2p(p_x)$ and two singly occupied $2p(p_y)$, $2p(p_z)$ orbitals. Taking two oxygen atoms, there are two ways to couple the p orbitals. (Molecular orbitals that arise from p atomic orbitals are often called π orbitals.) Case A (Figure 1) shows a doubly occupied p_x orbital belonging to the right atom combined with a singly occupied p_x of the left atom and a singly occupied orbital (p_y) on the right atom with a doubly occupied orbital (p_y) on the left atom. In p_x orbital combination, the energy of the singly occupied p_x orbital of the left oxygen atom increases as the interatomic distance R decreases (antibonding character) leading to the orthogonalization between the double- and single-occupied orbitals. Furthermore, the double-occupied p_x orbital diminishes its electron-electron interaction by delocalizing onto the left oxygen atom decreasing the shielding of the left nucleus. The interaction produced by these three electrons

leads to a binding energy of about 30 kcal. The same situation exists for the p_y orbitals leading to the same energy. Thus, total bonding for O_2 would be about 60 kcal. In case B, the two singly occupied p_x of each oxygen are combined to form a doubly occupied, high overlapping orbital. This brings the p_y orbitals together, acquiring antibonding character in order to be orthogonal to each other. The increased antibonding in case B compared to case A makes it reasonable to expect case A to be more stable (ground state). Similar to cases A and B, the third oxygen atom can be combined in two ways to one of the O in O_2 . (These configurations are classified by the numbers of electrons in π orbitals.) One can easily conclude that π^4 configuration is more stable than π^5 ; therefore, it is the ground state (O_3). The manifold of electronic states of ozone can be obtained from π^4 (ground state) by exciting an electron in a doubly occupied p orbital (in the plane) of O to a singly occupied orbital (perpendicular to the plane of the molecule). This results in a π^5 electronic state with two equivalent configurations (Figure 1). This in turn leads to two singlet and two triplet states. Again, by exciting an electron from the doubly occupied p orbital (in the plane) of O to the singly occupied (perpendicular to the plane), π^6 configuration appears with two states ($2^1A_1, 3^1B_2$). In the 2^1A_1 state the singly occupied orbitals (in the plane with spins of $-1/2$ and $+1/2$) can bond together yielding to an energy of about 1.5 eV above the ground state. Other states of ozone can be obtained by taking the most loosely bound electrons to various higher orbitals. Figure 2 shows the energies of different configurations of ozone based on theoretical calculations.

All of these predicted states have bond angles (ref. 15) ranging from 100 degrees to 120 degrees (Figure 3) with the exception of state 2^1A_1 which has an angle of 60 degrees (ring ozone). Transitions between states of ozone have been identified (refs. 16-19) as $3^1B_2 \leftarrow 1^1A_1$ for infrared, $1^1B_2 \leftarrow 1^1A_1$ for Hartley band, and as a blend of transitions for Chappuis region, ($1^1B_1 \leftarrow 1^1A_1$ and $1^1A_2 \leftarrow 1^1A_1$). There is no consensus for Huggins band though it has been suggested (refs. 20 and 21) that it could belong to the same transition as Hartley band.

Chemical Properties of Ozone

The decomposition of ozone is extremely complex and difficult to study. Although the decomposition of the gaseous phase has been the subject of extensive research, no satisfactory mechanism has ever been suggested to explain either the thermal or photochemical decompositions. Most of the known results indicate that the thermal decomposition is a result of the following mechanism:



Reaction 2 is much faster than reaction 3 where M may be an inert molecule (such as O₂, N₂, CO₂, He). The relative efficiencies depend on the particular gas M in activating O₃ (compared to O₃ itself). The effectiveness of the reactions 1 and 2 are: O₂ = 0.44, N₂ = 0.41, CO₂ = 1.06, and He = 0.34 compared to O₃ = 1.00. The rate constants for reactions 1 through 3 are as follows (ref. 22):

$$k_1 = 4.61 \times 10^{12} \exp(-24000/RT) \text{ liter}/(\text{mole} \times \text{sec.}) \quad (1)$$

$$k_2 = 6.00 \times 10^7 \exp(+600/RT) \text{ liter}^2/(\text{mole}^2 \times \text{sec.}) \quad (2)$$

$$k_3 = 2.96 \times 10^{10} \exp(-6000/RT) \text{ liter}/(\text{mole} \times \text{sec.}) \quad (3)$$

where R is universal gas constant in cal/moles. The specific rate constants of equations 1-3 are k₁, k₂, k₃. The atomic oxygen reaction rates for the mechanism 1-3 are:

$$+\left(\frac{d[O]}{dt}\right)_1 = k_1 [M] [O_3] \quad (4)$$

$$-\left(\frac{d[O]}{dt}\right)_2 = k_2 [O_2] [O] [M] \quad (5)$$

$$-\left(\frac{d[O]}{dt}\right)_3 = k_3 [O] [O_3] \quad (6)$$

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Assuming a stationary state for atomic oxygen, it follows that:

$$+\left(\frac{d[O]}{dt}\right)_1 - \left(\frac{d[O]}{dt}\right)_2 - \left(\frac{d[O]}{dt}\right)_3$$

Substituting equations 4, 5, and 6 into equation 7 we obtain:

$$k_1[O_3][M] = k_2[O_2][M][O]_{ss} + k_3[O]_{ss}[O_3] \quad (7)$$

solving the above equation for $[O]_{ss}$ we get equation 8:

$$[O]_{ss} = \frac{k_1[O_3][M]}{k_2[O_2][M] + k_3[O_3]} \quad (8)$$

In order to obtain the reaction rates for O_3 while atomic oxygen is in equilibrium, we can write from mechanisms 1, 2, and 3 the following rate equations:

$$-\left(\frac{d[O_3]}{dt}\right)_1 = k_1[M][O_3] \quad (9)$$

$$+\left(\frac{d[O_3]}{dt}\right)_2 = k_2[O_2][O]_{ss}[M] \quad (10)$$

$$-\left(\frac{d[O_3]}{dt}\right)_3 = k_3[O]_{ss}[O_3] \quad (11)$$

Thus

$$-\left(\frac{d[O_3]}{dt}\right)_{total} = k_1[M][O_3] - k_2[O_2][O]_{ss}[M] + k_3[O]_{ss}[O_3] \quad (12)$$

Using equations (8) and (12) we obtain for the decomposition rate of ozone:

$$-\left(\frac{d[O_3]}{dt}\right)_{\text{total}} = 2k_3[O_3][O]_{ss} \quad (13)$$

Combining equations (8) and (13), which describe ozone's decomposition dependence on O_2 concentration, yields:

$$-\left(\frac{d[O_3]}{dt}\right)_{\text{total}} = 2k_3[O_3] \frac{k_1[O_3][M]}{k_2[O_2][M] + k_3[O_3]} \quad (14)$$

Two special cases at standard temperature pressure (STP) will be examined:

Case A. High ozone concentration limit where $[O_3] \gg [M]$ and $[O_2] = [M]$. Taking a typical O_3 concentration of 98% and a 2% O_2 yields:

$$-\left(\frac{d[O_3]}{dt}\right) = (9.29)10^{-9} \text{ mole}/(\text{liter} \times \text{sec})$$

Thus the percent decomposition rate of O_3 would be $R_1 = (2)10^{-5}$ in percent per sec.

Case B. Low ozone concentration limit where $[O_3] \ll [M]$. Assuming a 5% ozone concentration and 95% oxygen, the ozone percent decomposition rate would be: $R_2 = (1.6)10^{-7}$ in percent per sec.

Comparison of R_1 with R_2 shows that the percent decomposition rate of O_3 at high ozone concentration is about 125 times faster than the percent decomposition rate of O_3 at low ozone concentration. Therefore the initial presence of O_2 is a major factor determining the ozone decomposition. Not only oxygen, but small amounts of hydrocarbonic impurities (such as H_2 and Br_2) found in the vacuum system are efficient catalysts and can sensitize rapid ozone decomposition leading to explosions. In addition, many solid substances such as coal and metal (Fe, Pt group)--especially silver--are very active catalysts (ref. 23). It is therefore important to recognize that decomposition of ozone depends on the particular strongly vacuum system that has been used.

Pure ozone is photochemically decomposed when exposed to visible or UV light. Visible light is proposed to decompose O_3 into O_2 , the mechanism being $O_3 + h\nu \longrightarrow O_2 + O(^3P)$. The O atom (at the ground state 3P) will react with another ozone molecule, $O + O_3 \longrightarrow O_2 + O_2$. Thus, in spectroscopic studies of ozone's thermal decomposition, unnecessary exposure to light should be minimized.

Safety and Precaution

Ozone is second to fluorine in its oxidation potential. This means that ozone will react with most materials, which will lead to the destruction of ozone and impurities from the oxidized materials. Therefore, only glass and teflon could be used in the apparatus because they are resistant to oxidation and ensure the cleanliness of the system; this limited the quantities of impurities that could affect the ozone concentration. The use of these inert materials was also important for safety because the decomposition can be very rapid when there is a high concentration of ozone, resulting in explosions. Care was taken to limit the impurities, minimize vibrations, and ensure that there would be no sudden pressure or temperature variations--all of which could lead to the rapid decomposition of ozone. In addition, the use of silica gel was helpful because it safely stores quantities of ozone. Also, nonhydrocarbon vacuum pump oil was used because it does not react with oxygen and ozone as regular hydrocarbon oils do. As an added precaution, goggles and face shields were used and a shield of plexiglass was erected in front of the apparatus to protect the operator from flying glass caused by an explosion. Inhalation of ozone should be avoided; a threshold limit value of 0.1 ppm of ozone in the air has been established by the American Conference of Government Industrial Hygienists. For this reason an exhaust fan was installed in the lab.

EXPERIMENTAL APPARATUS

Experimental Setup

The experimental apparatus included an ozonizer pump for initial evacuation and purification of ozone, pressure gauges, cell and coolant

system, and spectrophotometer with recording system. A diagram of an ozone generating system is shown in Figure 4. All valves are teflon or stainless steel. The glass trap containing silica gel was joined to the stainless steel portion of the system using a kovar seal. In Figure 4 the high vacuum portion of the system, which was stainless steel, is represented by thick solid lines; the teflon valves, 0.63 cm inside diameter, are marked by



; and the stainless steel valves are designated by



Ozonizer

The ozonizer is a sealed box which contains six glass tubes 65 cm in length and 5 cm in diameter. The glass tubes cover stainless steel foils which are connected in a series to serve as an electrode (Figure 5). The production of ozone was initiated by the introduction of O_2 into the ozonizer which generated ozone by the silent electrical discharge method. This method is considered to be the most practical way to quickly produce a large quantity of ozone for laboratory purposes. This electrode was connected to a potential difference capable of generating 15 kv-AC while passing a current of about 3 amps. The operation of the ozonizer required a steady current of water to keep it cool. Under these conditions the ozonizer generated about 2% ozone for an oxygen flow of 4 liters per minute. For an experimental run the ozonizer was operated anywhere from 15 to 30 minutes while the generated ozone was trapped in the silica gel.

Pumps

Three different types of pumps were used to prepare the system and to purify the created ozone.

1. A mechanical roughing pump contained silicon base oil in order to minimize interaction with ozone. The pump was connected to the system with a Linde molecular sieve type 13X which is a good catalyst to decompose ozone, thus limiting any ozone getting into the roughing pump. This pump provided a vacuum as low as 50 microns during the cleanup of the ozonizer. After the silica gel was saturated by gaseous ozone the pump was used to remove residual oxygen and other impurities.

2. A Varian vac-sorb roughing pump operating at 70 microns to 10^{-4} torr and containing absorbent material was employed to provide the base pressure for starting the vac-ion pump. This pump was not used during the purification process.

3. A Varian vac-ion pump of 20 liters per second was initially used to obtain a high vacuum in the cell and then to pump on the liquid ozone. The operating pressure range is 10^{-3} to 10^{-7} torr for a non-baked system.

Pressure Gauges

The cell pressure was measured by a 222HS-A-1000 series of MKS Baratron electronic manometer. This is a stainless steel manometer which operates on the variable capacitance principle with response time of 5 msec and an accuracy of 1.5%. The input voltages are ± 15 DC which are maintained by two independent power supplies. The output is displayed on a digital voltmeter. The Baratron measurements were calibrated before the experiment against a mercury manometer at room temperature, noting that no compensation for temperature is needed in the operating range from 0° to 100° C. Pressures during purification and evacuation of the system between 1000 and 10 microns were read on a Hasting vacuum gauge type DV-6M and lower pressures were measured using the vac-ion pump.

The Absorption Cell

The absorption cell (Figure 6) has a triple quartz wall with double supersill windows. The cell was used to confine a purified sample of gaseous ozone through a teflon valve and then to study the dependence of absorption coefficients on temperature. Low temperatures were achieved by passing cooled, vaporized N_2 through the space between the inner and middle walls. A stable temperature for the gas sample was achieved by wrapping the cell and the teflon valve with 10 layers of glass wool-insulating material. This temperature was measured with a type K (chromel-alumel) thermocouple with reference junction at 0° C, inserted between the inner and middle walls of this cell. This temperature was monitored on a digital electrometer (Keithle 616 electrometer). Condensation of water vapor on the windows of

the cell was avoided by the evacuation of the space between the middle and outermost walls. In addition, thermal exchange was minimized by coating the outside surface of the outermost cell with silver. The following are the detailed specifications of the cell.

1. Innermost cell: 8 cm in length, 2 cm in diameter with an inlet from outside (5 cm) which had an 0.37-cm inside diameter; the windows were glass-to-glass sealed.
2. Inner cell: enclosed with a glass cover and sealed off before the windows, thus designating the middle cell.
3. Outermost cell: total length, 13 cm; diameter, 38 mm, concentric with the inner cell having glass-to-glass sealed windows.
4. Space between middle and outermost walls was initially evacuated to 10^{-6} torr.
5. Space between innermost and middle walls was accessible by two glass tubes 0.635 cm in diameter for passing coolant to obtain temperature control.
6. Distance between innermost and middle walls was 4 mm.

Cooling Technique

Temperature was controlled by forcing N_2 from a pressurized tank, which was passed through liquid nitrogen, into a 50-liter stainless steel dewar. The inlet tube was made of copper and was immersed in liquid nitrogen. Passing of N_2 through the copper tube caused the liquid to vaporize, creating a positive pressure inside the dewar. An insulated teflon tube above the liquid level then transported the cold nitrogen vapor around the cell. By adjusting the rate of the flowing N_2 into the dewar the required temperature was obtained. With this technique temperatures as low as $-150^\circ C$ were produced. The time required to reach such a temperature was five to ten minutes depending on the flow rate of N_2 into the container and the level of liquid nitrogen in the dewar. In order to raise the

temperature, the outlet of the dewar from the cell had to be disconnected and the inlet side of the cell had to be attached directly to the dry N₂ valve of the laboratory by means of another copper tube. Then, by heating the copper tube, temperatures up to 80° C could be obtained (Figure 7).

Spectrophotometer

The absorption coefficients were measured by a Perkin-Elmer Model 200 dual-beam spectrophotometer with a variable spectral band pass from 0.2 to 4.0 nm. The accuracy of the band pass was confirmed by using iodine gas. In this experiment the band pass was set to 0.3 nm so that high resolution was sufficient throughout. The light sources were a tungsten lamp for the visible and a D2 source for the UV. These light sources together with the electronics require a warm-up time of approximately 45 minutes to achieve stable operation. To maintain long-time variation a calibration was done before each experiment by taking the absorption spectrum of the empty cell for the required spectral range.

The spectrophotometer is designed to compare the light intensity passing through the sample with the light intensity passing through the reference cell (Figure 8). Because of the space requirement for the sample cell insulation, the reference cell was removed, leaving a space in the optical path instead of the reference cell. The absorption coefficient, which is constant throughout the gas, can be calculated from Beer's Law:

$$I = I_0 e^{-\alpha x} \quad (15)$$

where I_0 is the intensity of the light entering the gas and I is the intensity exiting the gas cell with the thickness x . To correct for the cell windows' absorptions, the absorption of the empty cell was recorded. Thus:

$$I(\lambda)_{\text{empty}} = I_0 A_{\text{cell}}(\lambda) \quad (16)$$

And for the gas-filled cell:

$$I(\lambda)_{\text{gas}} = I_0(\lambda)A_{\text{cell}}(\lambda)e^{-\alpha x} \quad (17)$$

Dividing equation (17) by equation (16) we obtain:

$$\frac{I_{\text{gas}}(\lambda)}{I_{\text{empty}}(\lambda)} = e^{-\alpha x} \quad (18)$$

Solving for α we obtain:

$$\alpha = \frac{1}{x} \log \frac{I_{\text{gas}}}{I_{\text{empty}}} \quad (19)$$

Then the absorption coefficient at standard temperature and pressure would be $\alpha_{\text{stp}} = \frac{(76)T}{273P} \alpha$ (temperature is in degrees kelvin and the pressure is in cm of Hg).

Analog-To-Digital Converter

The output signal from the spectrometer takes on values from 0 to 1 volt, which corresponds to 0% and 100% of absorption. These signals were fed directly into the North-Star Horizon microcomputer. The signals had to be first amplified by a factor of 10, then converted by an ANALOG-TO-DIGITAL MODULE that interpreted the 0- to 10-volt signal to an integer data from 0 to 1023; the accuracy of determining the percent absorption was then 100/1023.

XY Recorder

The variation of the absorption with temperature for a fixed wavelength was monitored on the Y-axis and X-axis of a Gould Brush 500 XY recorder. The X-axis input was connected to the spectrometer and the Y-axis to the thermocouple. The recorder was calibrated to known voltages (voltage calibrator, DCV 8500) prior to the experiment.

EXPERIMENTAL PROCEDURE

The experimental procedure is divided into four parts: purification and pacification of the system; creation of ozonized oxygen, purification of ozone; and measurement of absorption coefficients of ozone in the absorption cell. Descriptions of each part follow.

Part I. The complete system with the exception of the ozonizer and silica gel cold trap was helium-leak tested; then, using the roughing pump, the complete system was evacuated. The silica gel, used to absorb small quantities of ozone safely, can easily absorb moisture which was removed by baking the silica gel while pumping with the vac-sorb pump. This procedure made it possible to attain a pressure as low as 8 microns. In the next step the glass, teflon valve and fittings of the vacuum system, and the MKS baratron were exposed to ozonized oxygen for two days in order to pacify the system. This is a normal procedure used to reduce the impurities during the process of making ozone. Once the system was pacified, all valves except the venting valve (#2) and oxygen inlet valve (#1) were opened. Then a roughing pump was used to obtain a vacuum down to 50 microns. A high vacuum was then obtained in the cell, isolating it from the rest of the system by closing valves #12 (pumping main valve), #6 (valve separating the final cold trap from double trap), and #5 (pressure gauge valve). At this point the vac-sorb pump was cooled with LN₂ to reduce the pressure so that the vac-ion pump could be started. Once the pressure was reduced to 10 μ the system was isolated from the vac-sorb pump by closing valve #13 (vac-sorb valve). Thus evacuation of the cell continued until 10⁻⁶ torr was reached. While the vac-ion pump was working on the cell, ozone was created.

Part II. The dewar under the silica gel cold trap was filled with a mixture containing dry ice and alcohol. This produced a stable temperature of -78° C in the silica gel. The water circulated around the ozonizer was turned on to remove the dissipated energy from the ozonizer. This was accomplished by a constant current of water (about 14 gal/hour). The next step in the procedure was to close valve #14 (roughing valve) and to fill the system with pure oxygen. This was accomplished by opening valve #1 (inlet oxygen valve) and monitoring the pressure until a slight over-pres-

sure was detected. Then valve #2 (venting valve) was opened and oxygen was allowed to pass through the system to remove the trapped impurities. This was necessary to allow the electric discharge to occur in pure oxygen. Then the ozonizer was turned on with a 75-volt reading on the input transformer--noting a current of 3 amps. This procedure produced ozonized oxygen with 2% ozone concentration. The positive oxygen pressure forced the ozonized oxygen to pass over a bed of silica gel that selectively absorbed the ozone, allowing the oxygen to pass out of the system. After 10 minutes the silica gel turned blue and the ozonizer was turned off, followed by the closure of valves #2 (venting valve) and #1 (inlet oxygen valve). At this point the created ozone in the silica gel was isolated from the ozonizer by closing valve #3 (inlet ozonized oxygen valve).

Part III. Ozone was purified by the following steps: (1) Valve #14 (roughing valve) was opened slowly which allowed the remaining oxygen in the silica gel cold trap to be pumped out. After pumping on the silica gel for 45 minutes, the pressure reduced to 120 microns. At this point pumping had to be stopped to remove ozone. (2) The ozone was further purified when passed through the double trap to the single cold trap. In order to do so the dewar under the double trap was filled with dry ice and alcohol while valves #11 and #7 were closed (valve #11 connects the glass section to the stainless steel portion and valve #7 connects the single trap to the teflon tube). In the next step, valves #6 and #5 were opened (valve #6 separates the final cold trap from the double trap and valve #5, between the cold trap and the MKS pressure gauge). Subsequently the dewar of liquid nitrogen (77 K) was put under the single trap. The process of transferring ozone into the single cold trap was started by increasing the temperature of the silica gel. Thus, only impurities that do not freeze below -78°C were allowed to pass through the double cold trap, while the ozone accumulated in the single cold trap. (3) Purification of liquid ozone proceeded by closing valve #6. Thus the pump was allowed to operate on the cold trap until a pressure of 50 microns was reached. Since the vapor pressure of oxygen is about 130 mm Hg at LN_2 temperature and the vapor pressure of ozone is only about 0.1 mm Hg, the pump was used to remove oxygen from the trap, leaving the ozone. (4)

Further purification was performed after the ozone was distilled into the double trap. In order to do so, first the double cold trap had to be cleaned by increasing its temperature and evacuating it (valve #11 was opened until a pressure of 50 microns was obtained). Subsequently, valves #5 and #10 (separating silica gel from the double cold trap) were closed and LN₂ was placed under double cold trap. In order to transfer the ozone from the single trap to the double trap, valve #6 (located between the single and double cold trap) was opened and the single cold trap was heated. At this point pumping on the double trap was initiated by opening valve #5 (pressure gauge valve). The pressure was again reduced to about 50 microns. Valve #6 was closed and liquid ozone was vaporized by removing the LN₂ dewar. This provided a fairly purified gaseous ozone. To further absorb impurities that freeze below -78° C, the double cold trap was enclosed by a mixture of dry ice and alcohol. Thus the gaseous ozone in the double cold trap served as a reservoir for the remainder of the experiment. (5) Small amounts of ozone were transferred into the single cold trap for final purification. This was done by closing valve #5 and opening valve #6 for a short period of time. Then LN₂ was placed under the single cold trap and valve #7 was slowly opened so that pumping by vac-ion pump could proceed until a pressure of 10⁻⁶ torr was achieved. (6) To free any trapped impure molecules mixed with liquid ozone, valve #7 was closed allowing the liquid ozone to slowly vaporize by removing the LN₂ under the trap. This process allowed the adhered impurities together with the ozone to be brought into gaseous state. At this point the LN₂ was re-introduced under the trap, liquifying the ozone while releasing some of the adhered impurities. These residual impurities were removed by opening valve #7 and pumping until a pressure of 10⁻⁶ torr was reached. The fact that oxygen at LN₂ temperature has a vapor pressure of 130 mm of Hg indicates that at a pressure of 10⁻⁶ torr the liquid should be 100% pure ozone. It is worth noting that the vaporization of this liquid, which took 10 minutes, was not accompanied by decomposition. (This is discussed later in this report.) The gas that was produced was used to fill the cell for measuring the temperature dependence of the absorption coefficients.

Part IV. The followings steps were taken to measure the absorption coefficients: (1) During the 10 minutes when the vaporization of ozone in

the single cold trap occurred, the reference spectrum of the evacuated empty cell was recorded. The spectral region between 7567 Å and 4630 Å was scanned, taking about 10 minutes. This produced a spectrum which was used for background correction. (2) The next step was to fill the cell with ozone which was isolated from the vac-ion pump by closing valve #7. To measure the pressure in the cell, valve #4 was closed and valve #5 was opened long enough to read the pressure. This avoided any decomposition of ozone on the surface of the stainless steel in the MKS pressure gauge. Then valve #9 (valve to the cell) was closed until the end of the experiment. (3) Several scans were taken with the filled cell in the optical path of the spectrophotometer. At the end of each scan the wavelength was automatically set to the same starting point. The low temperature spectrum was obtained by cooling the cell for approximately 20 minutes--enough time for the confined molecules to reach equilibrium. To raise the temperature, dry N₂ gas was circulated around the cell, requiring about 20 minutes to stabilize. In addition to the above procedure for measuring, the variation of absorption coefficients on temperature was monitored by selecting a fixed wavelength while changing the temperature. These results were recorded on an XY recorder.

RESULTS AND CONCLUSION

Several sets of absorption coefficients in the visible region were obtained by changing the temperature of the purified confined gas sample. These measurements were performed using a spectrophotometer with an 8-cm quartz absorption cell. The technique for determining temperature dependence was different from those used by previous investigators (for example, photoelectric detectors, pure ozone, and a capacitance pressure gauge were used instead of photographic detectors, ozonized oxygen, and a sulfuric acid manometer). The absorptions recorded at room temperature in the visible region can be compared with those previously reported.

The absorption spectrum obtained in this work together with those of Inn's and Tanaka's, Vigroux's and Griggs' are shown in Figure 9. The general spectral features found in the present work agree closely with Inn and

Tanaka except that in the present work the difference in absorption coefficients between the two peaks was the same as that reported by Vigroux; Inn and Tanaka reported a smaller difference. Our measurements could differ from Inn's and Tanaka's because their values for the absorption coefficients were reached using interpolated decomposition values. They reported 10 to 12% thermal decomposition of O_3 over a period of 5 to 10 minutes. On the other hand we vaporized and liquified our ozone ten times in the sealed cold trap during a period of 90 minutes, showing only 0.3% decomposition.

The temperature effect was examined in this study by measuring the absorption coefficients for the Chappuis band in a sealed-off, gas-filled cell raised to different temperatures. The study consisted of three runs. In the first two runs there were several continuous spectral scans at different temperatures; in the third run, variations of absorption were recorded for specific wavelengths as a function of temperature. In each run the evacuated cell (10^{-6} torr) was filled with pure ozone at room temperature. The pressures for the first, second, and third runs were 24, 37, and 45 cm Hg respectively.

During the first run three scans were taken, each scan starting at 4630 Å and stopping at 7567 Å. The first scan was obtained at room temperature of 303 K and pressure of 24 cm Hg. The absorption coefficients are exhibited in Figure 10. The second scan was performed thirty minutes later at a temperature of -108° C (thirty minutes were needed to cool the cell from room temperature). Having completed the second scan, the cell was brought back to room temperature and the third scan was obtained about 30 minutes later. The absorption coefficients of the second and third scans are shown in Figures 11 and 12 respectively. Using computer program ozone (Appendix B), the difference between the first and the last scan is illustrated in Figure 13, showing a shift of 0.0008 cm^{-1} (base 10) in the background. Figures 14 and 15 show the differences between the first and the last two scans. These figures signify an overall increase in absorption coefficients with a maximum of 6% at $\lambda = 6020 \text{ Å}$ in going from room temperature to -108° C. In addition to the overall increase of absorption coefficients, there seemed to be local maximums and minimums (Figure 15)--between 6000 Å and 4630 Å--but because the wavelength reproducibility was 10 Å we were unable to determine the wavelength associated with these various regions.

In the second run which lasted 44 hours, seven scans (Figures 16-22) of absorption coefficients were performed starting at 4630 Å and stopping at 7567 Å. The first four of these spectrums were taken successively, each 25 minutes from the previous one. In order to evaluate the quantitative decomposition of ozone in the absorption cell, the last two scans were performed 43 and 44 hours after filling the cell (Figures 21 and 22). The fill temperature and pressure of the ozone in the absorption cell for the second run was 303 K and 37 cm Hg. Using the fill condition, a spectral scan was performed (Figure 16). The next scan was performed at 198 K, noting that the maximum increase (4.5%) occurred at $\lambda = 6020 \text{ \AA}$ (Figure 17). The third scan was obtained at 30° C (Figure 18). We reproduced the conditions of scans 2 and 3 for scans 4 and 5 except that the low temperature for the fourth scan (Figure 19) was -108° C. The fifth scan (Figure 20) was taken 1.5 hours after the fourth one. At this point we examined the difference between low- and high-temperature spectra. The differences between the first and second scans and the third and second scans are exhibited in Figures 23 and 24. The difference between the third and fourth scans is associated with the largest temperature differential, and showed a 6% increase at $\lambda = 6020 \text{ \AA}$ (Figure 25). The difference of absorptions between scans 3, 5, and 7 from the first scan are shown in Figures 26, 27, and 28 respectively. These figures, in particular Figure 28, were used to evaluate the decomposition rate which was found to be approximately 0.3% per hour.

The fill pressure in the third run was 45 cm Hg at room temperature. Selecting wavelengths on the spectrophotometer, we monitored on an XY recorder the absorption while the ozone was liquified (at $T = -111.9^\circ \text{ C}$) and then vaporized and finally brought to room temperature. Each process of cooling and heating took 15-20 minutes. In Figure 29 the Y axis represents the absorption of 0% to 100% and the X axis represents the temperature in C. On each graph cooling and heating is designated by C or D respectively. Analyzing these graphs reveals that for the fixed wavelength chosen at several peaks and valleys the variation of absorption coefficients as a function of temperature is linear (shown in Table 2).

Table 2. Slopes of the variations of absorption coefficients as a function of temperature for fixed wavelengths.

Wavelength (Å)	5200	5698	5858	6020	6500
Slope (mV.c ⁻¹).10	5	8	7	11	4

It is worth to mention that there was a temperature difference between the cell and its inlet tube, introducing some errors. Examining this effect the calculations were carried out with the result that a 100° C temperature difference would introduce only 0.8% in ozone absorption.

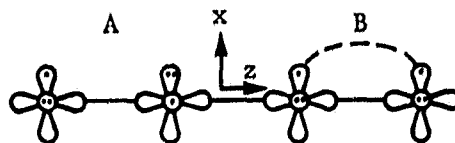
The spectrums in the first two runs lead to the firm conclusion that this band is temperature dependent with maximum change in absorption of 5% at $\lambda = 6020 \text{ Å}$ for a difference temperature of -108° C to 30° C, whereas the reported values were 1% to 2%.

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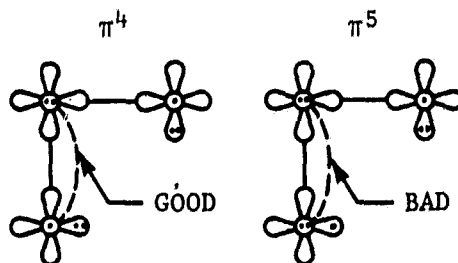
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(a) GVB CONFIGURATIONS OF O₂



(b) GVB CONFIGURATIONS OF O₃



(c) THE π^4 CONFIGURATION OF O₃

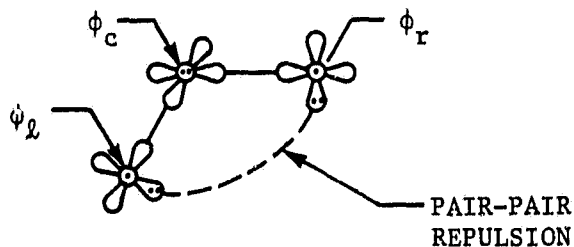


Figure 1. A schematic representation of the GVB orbitals. The Orbitals are represented by a normal two-lobed shape, if in the plane and a circle if perpendicular to the plane. (a) The bonding GVB configurations O₂. The bonding GVB configurations of O₃. The upper two O atoms represent the original O₂ molecule to which the lower O atom is added, resulting in the two configurations shown. (c) The π^4 configuration of ozone.

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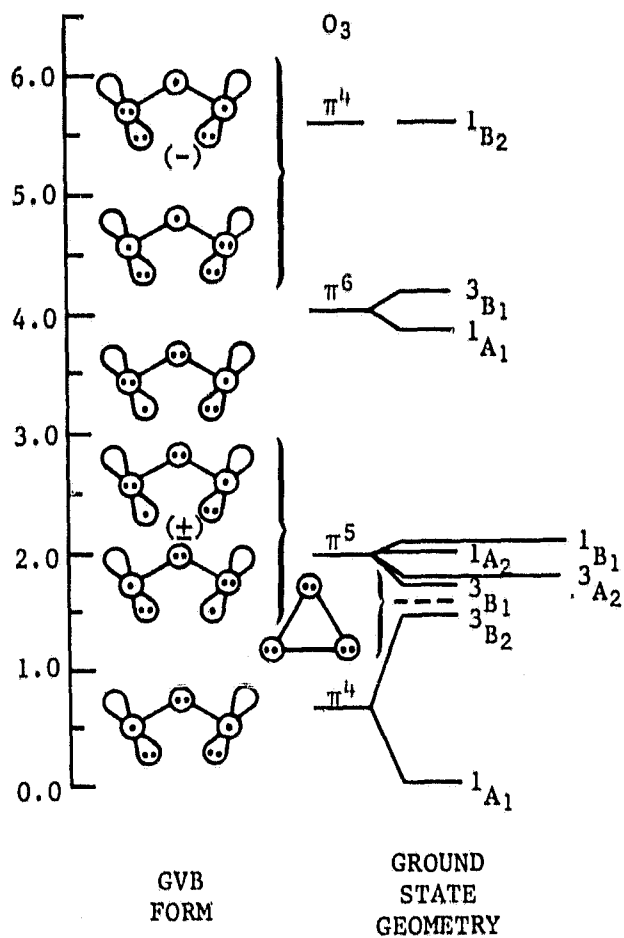


Figure 2. The energy levels of O_3 shown based upon the theoretical calculations.

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O₃ (R = 2.415)

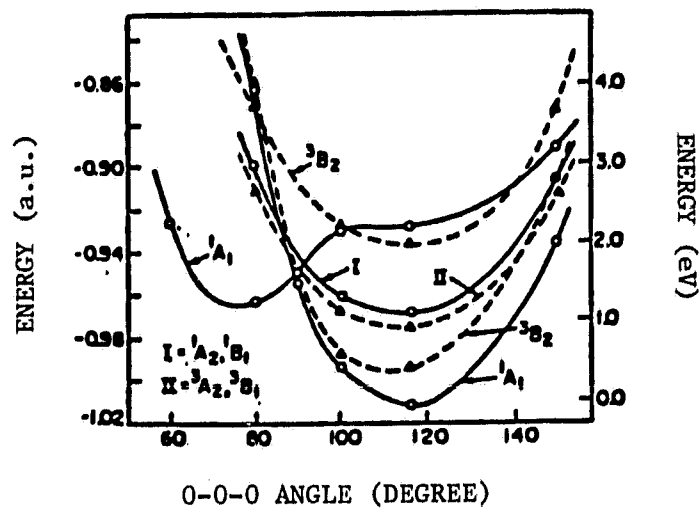


Figure 3. The energy curves (GVB) for the excited states of ozone. In these calculations the O-O bond length was kept fixed and only the angle varied.

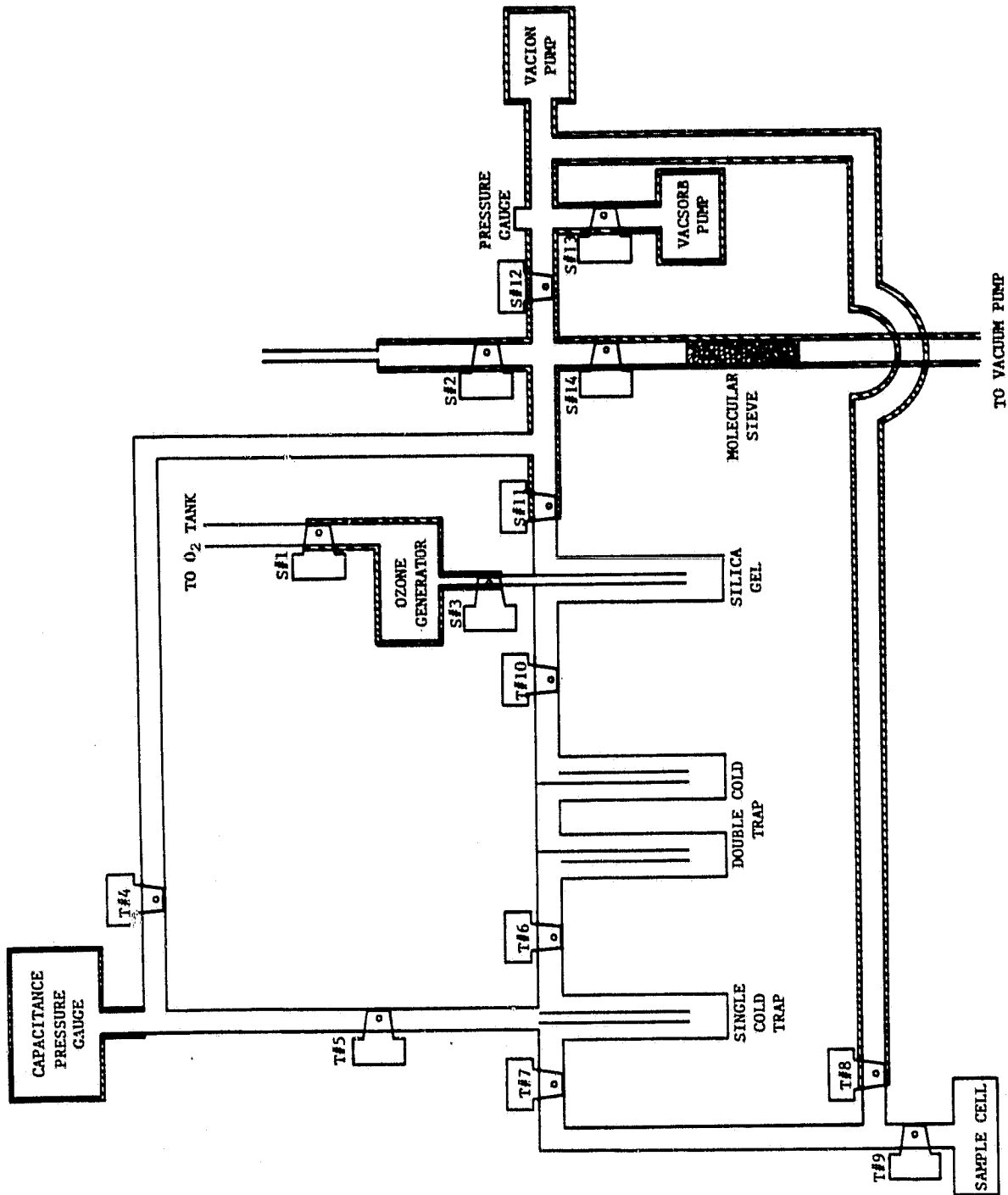


Figure 4. Diagram of ozone generating system.

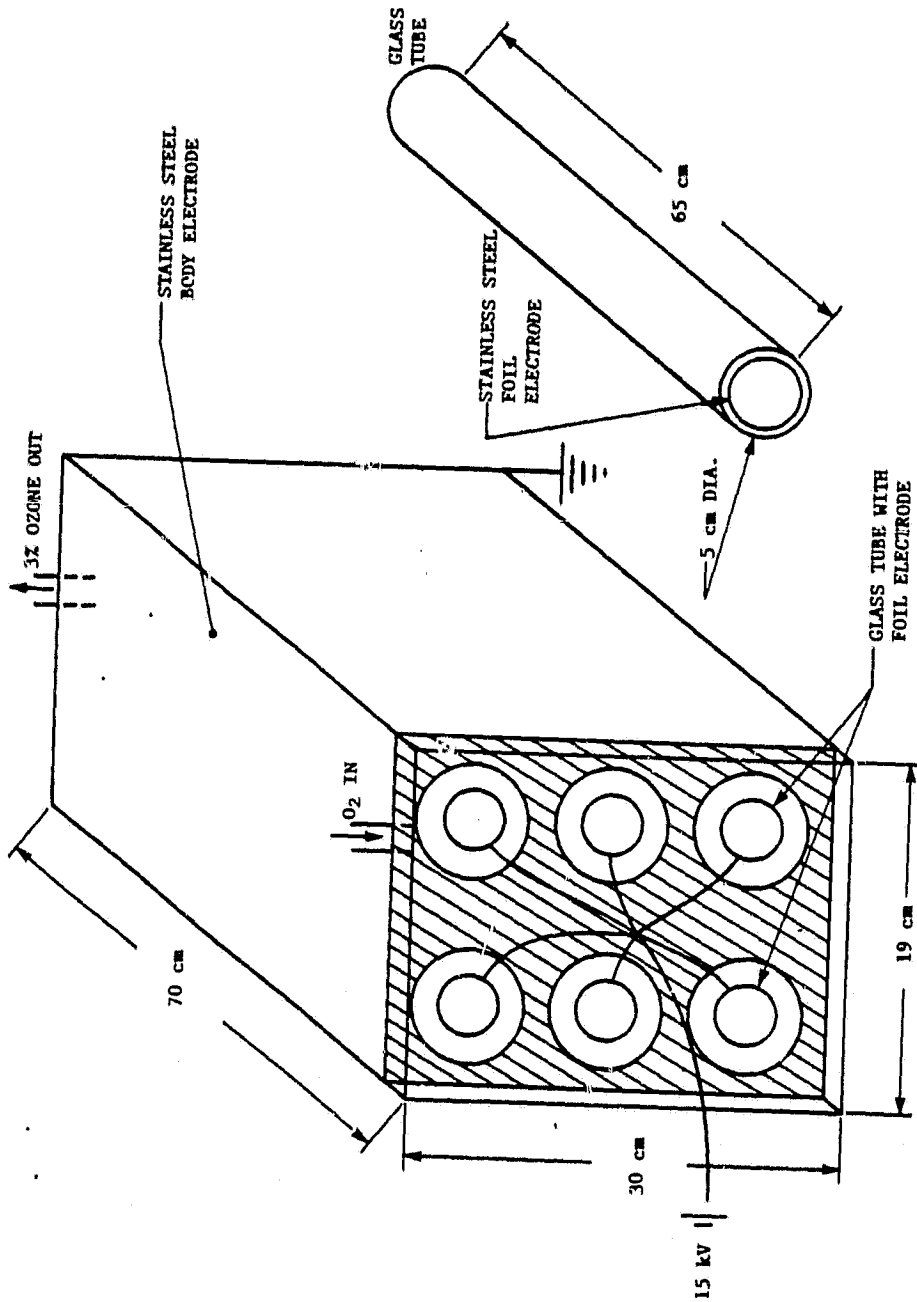


Figure 5. Schematic diagram of ozone generator.

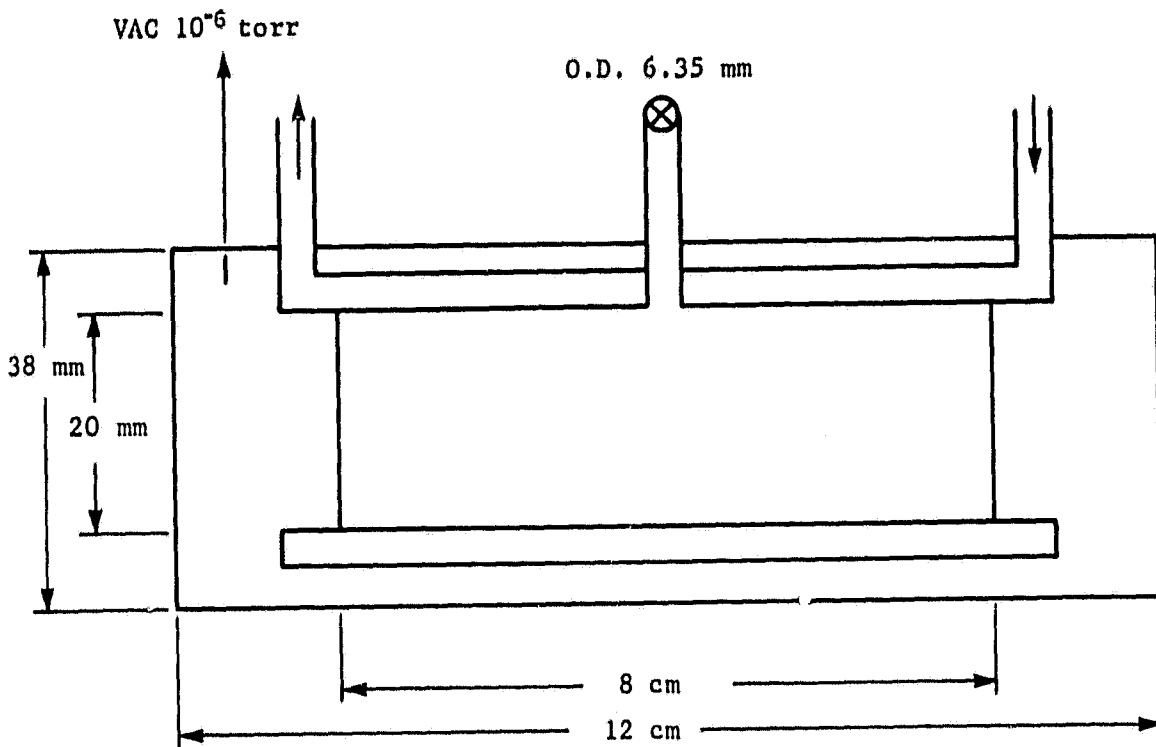


Figure 6. Schematic of the absorption cell.

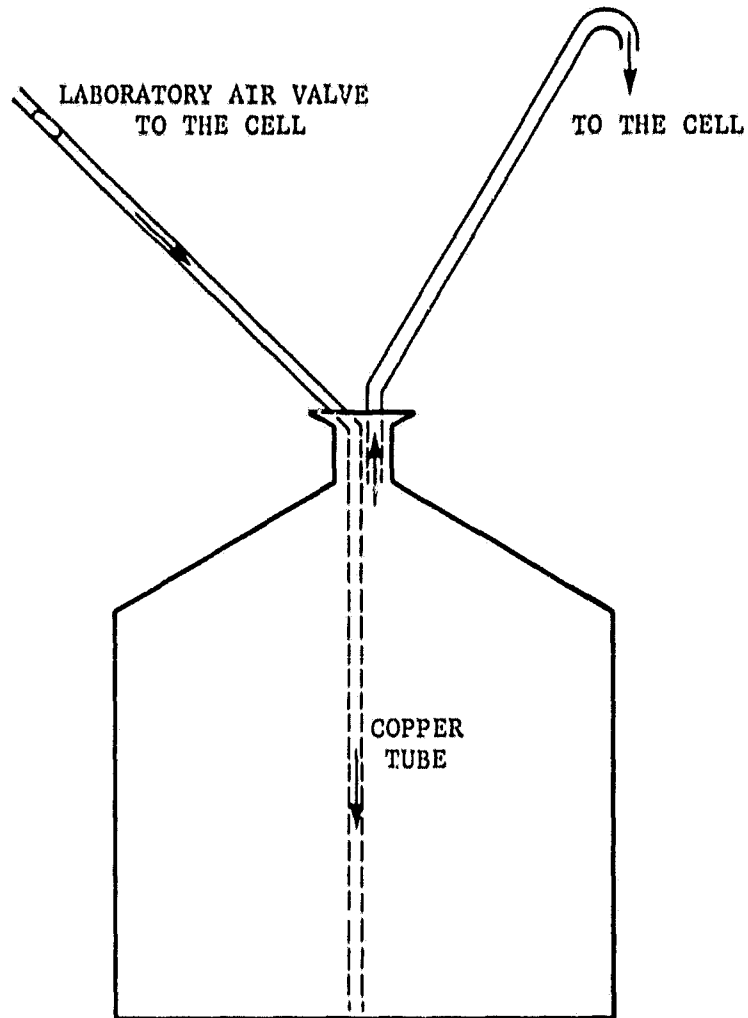


Figure 7. Schematic of the stainless steel container.

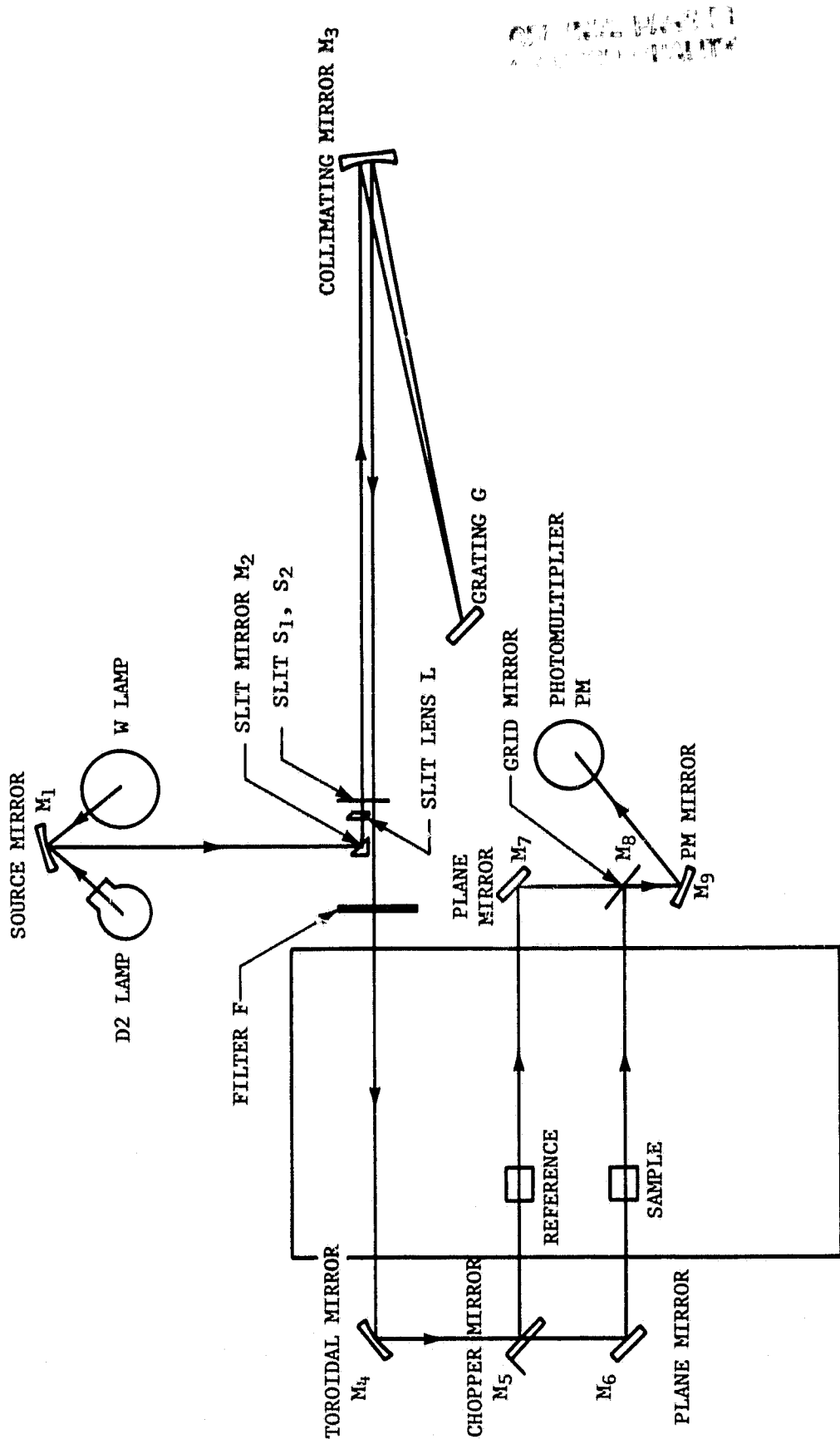


Figure 8. Optical schematic, Model 200 Spectrophotometer.

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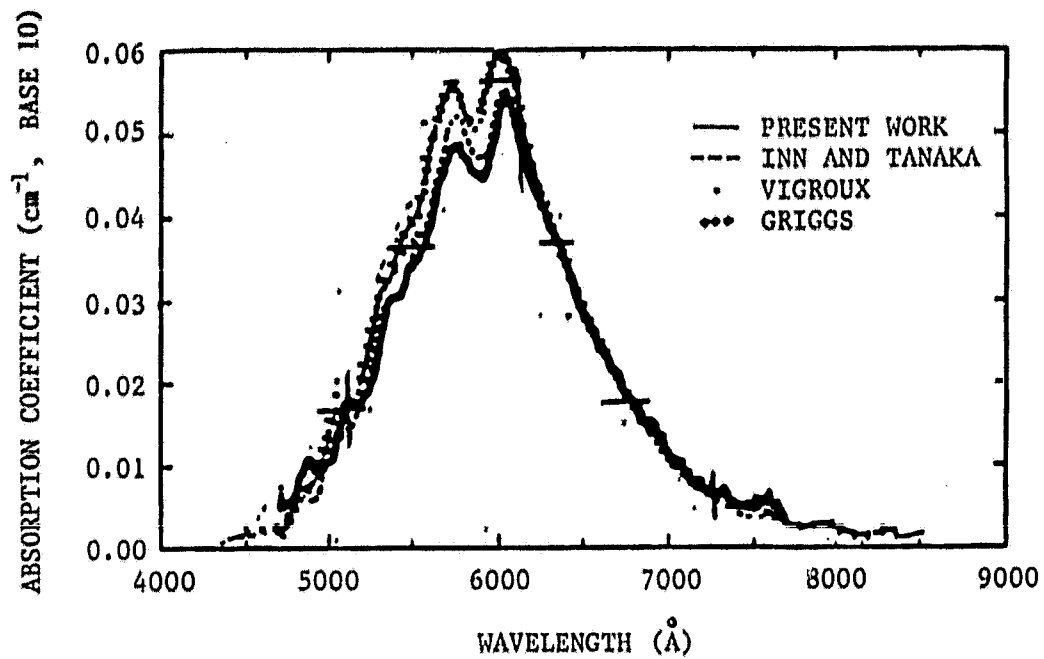


Figure 9. Chappuis band (4400-8500 Å) absorption coefficients.

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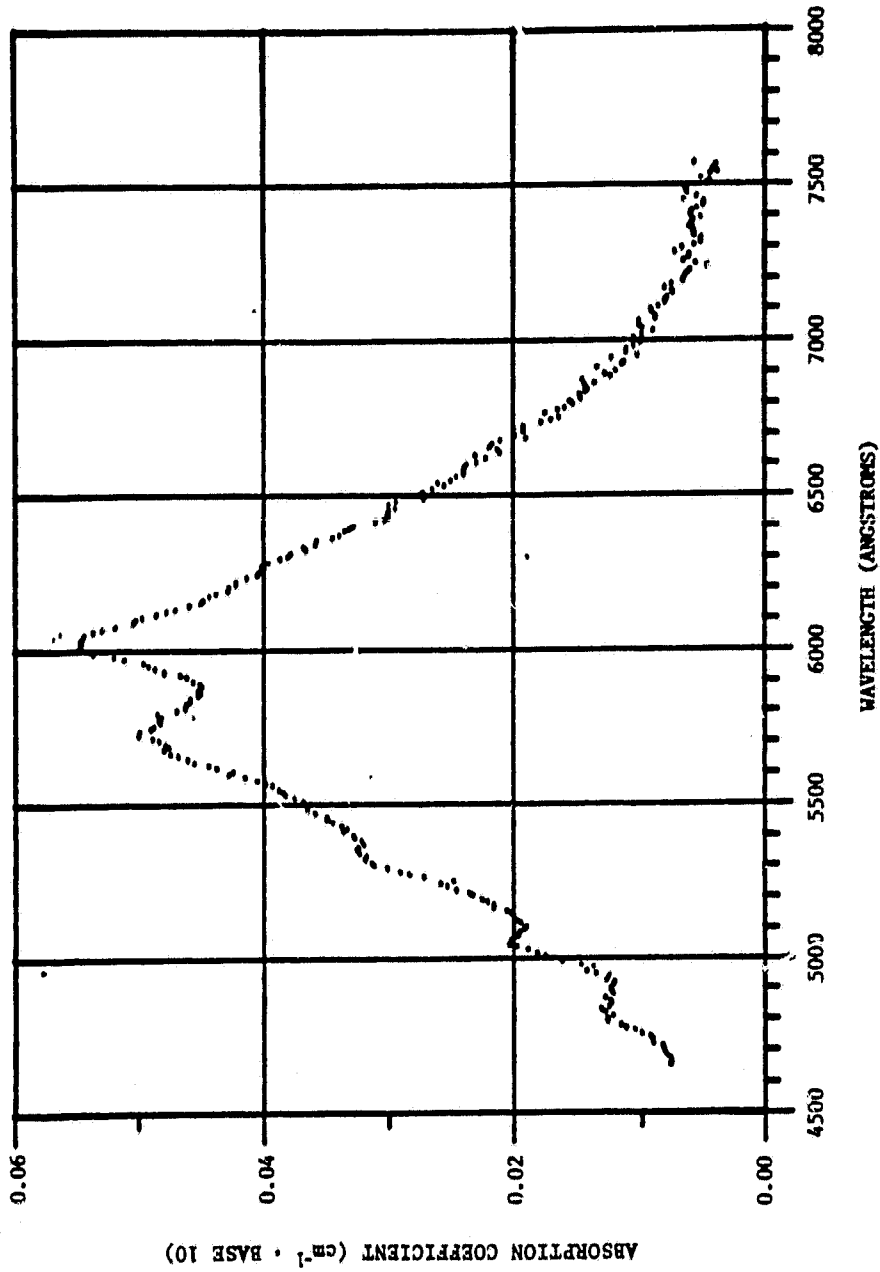


Figure 10. Calculated absorption coefficients of ozone at STP, using a gas sample at T = 303 K and P = 24 cm Hg (fill 1).

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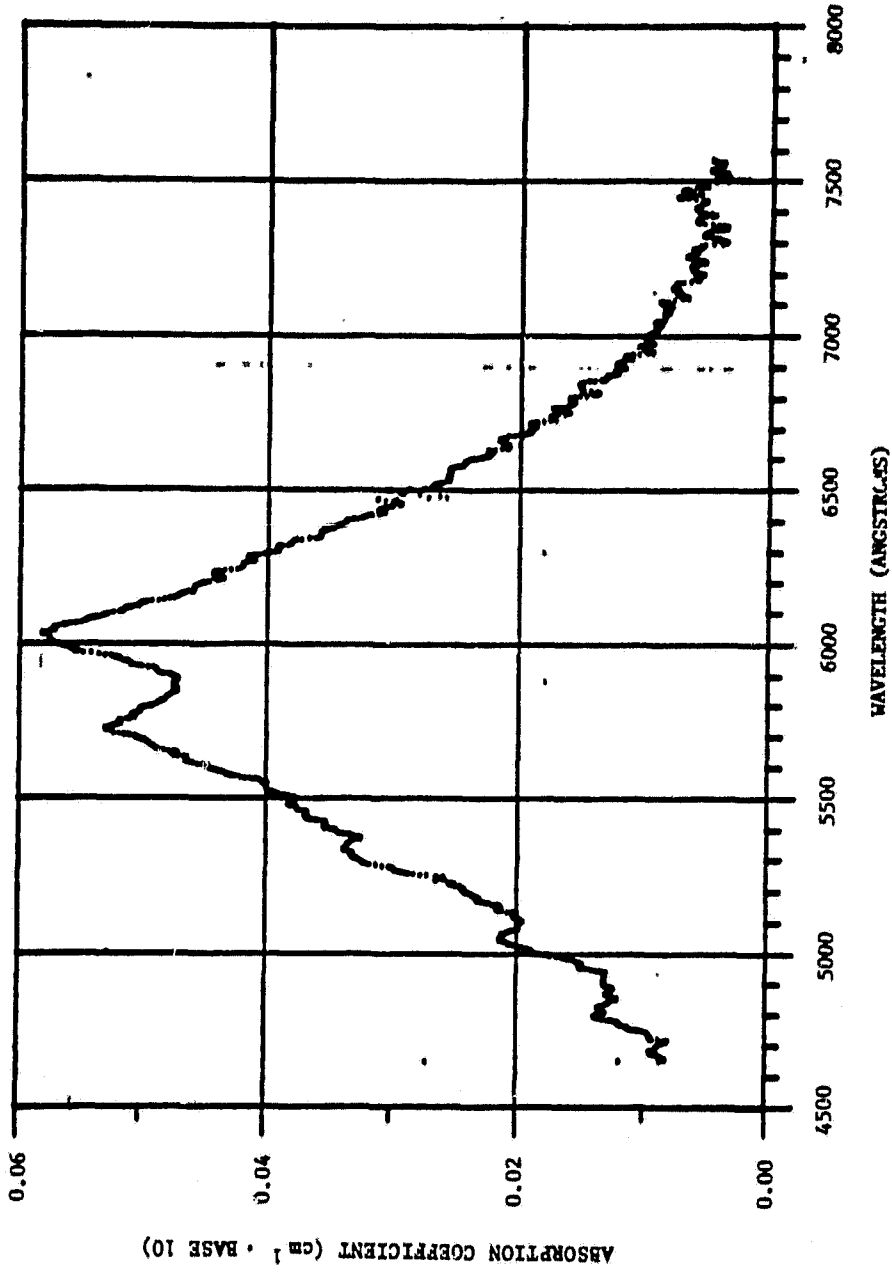


Figure 11. Calculated absorption coefficients of ozone at STP when temperature of the gas was decreased from 303 K to 165 K (50 minutes after filling) at P = 24 cm Hg (fill 1).

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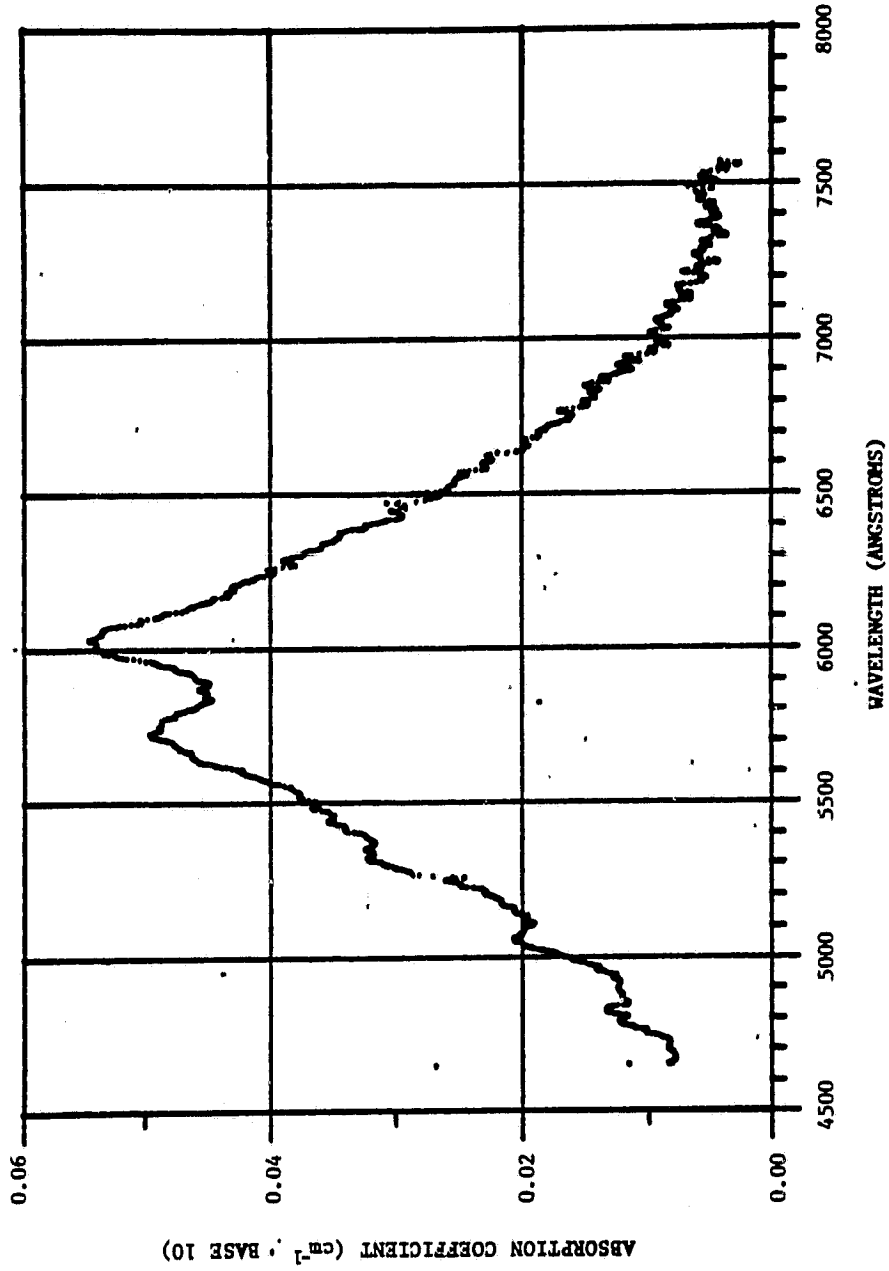


Figure 12. Calculated absorption coefficients of ozone at STP (90 minutes after filling) at T = 303 K (fill 1).

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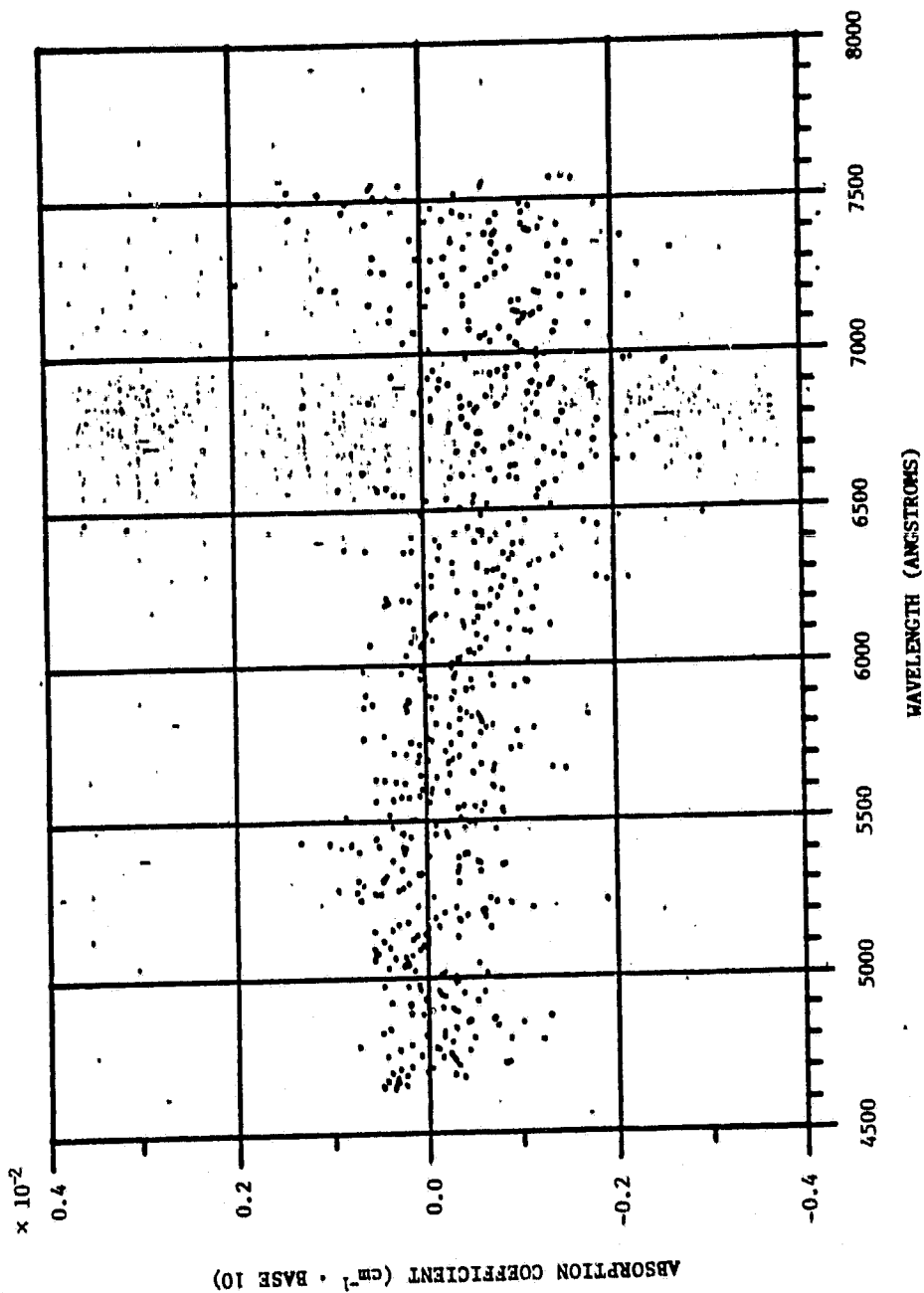


Figure 13. Difference of absorption spectrum at T = 303 K (time interval between these two spectrums was 90 minutes, fill 1).

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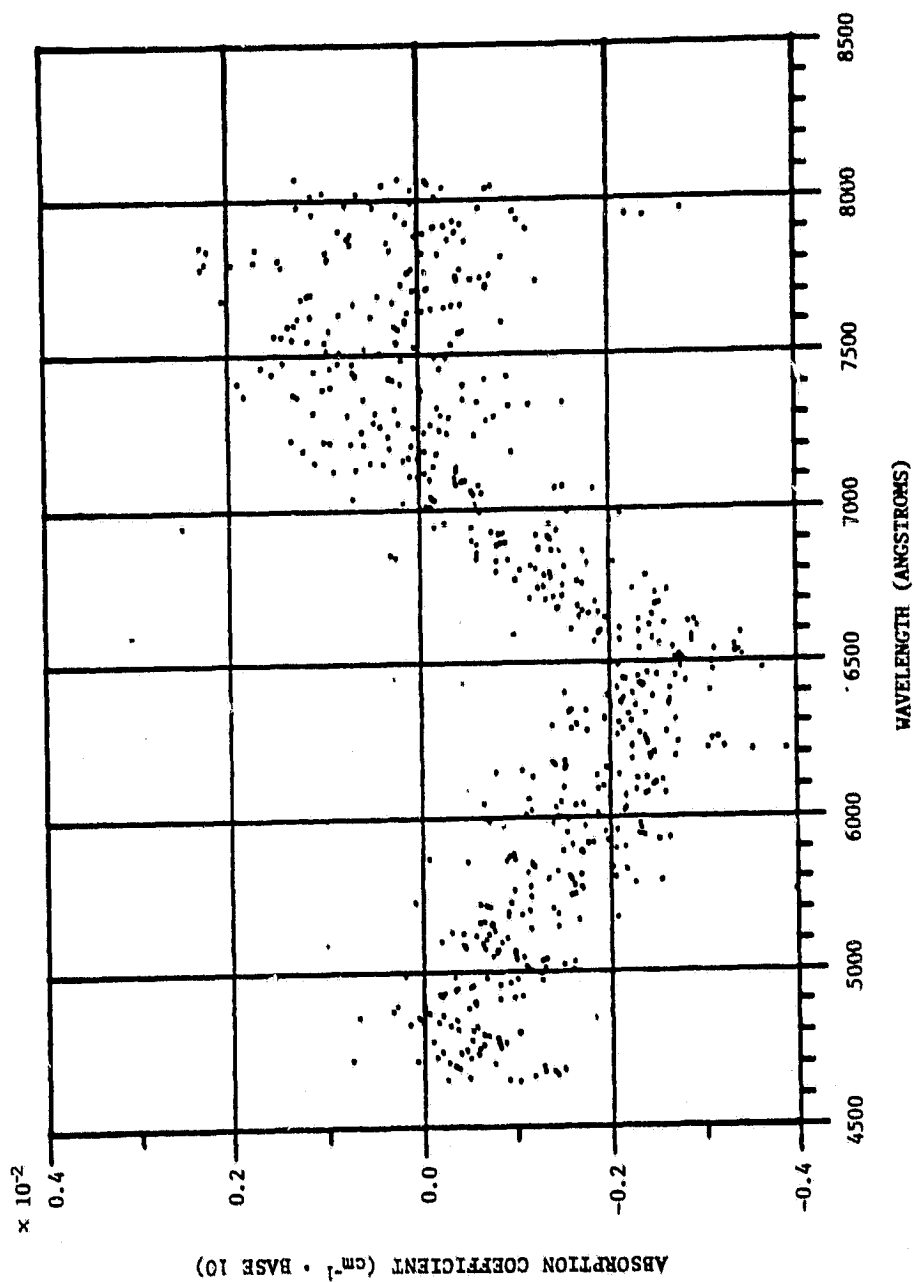


Figure 14. Difference of absorption spectrum when temperature was decreased from 303 K to 165 K (fill 1).

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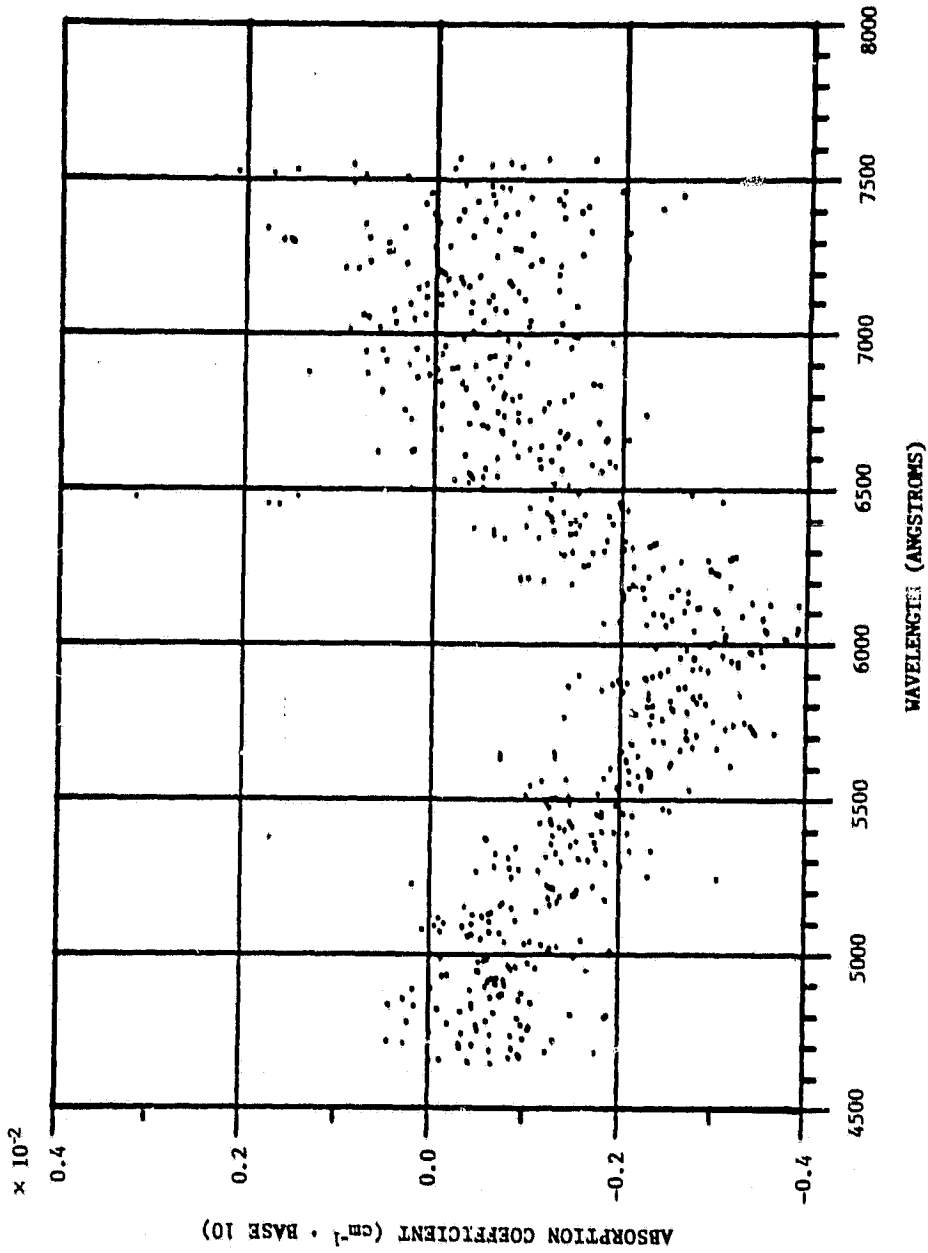


Figure 15. Difference of absorption spectrum when temperature was increased from 165 K to 303 K (fill 1).

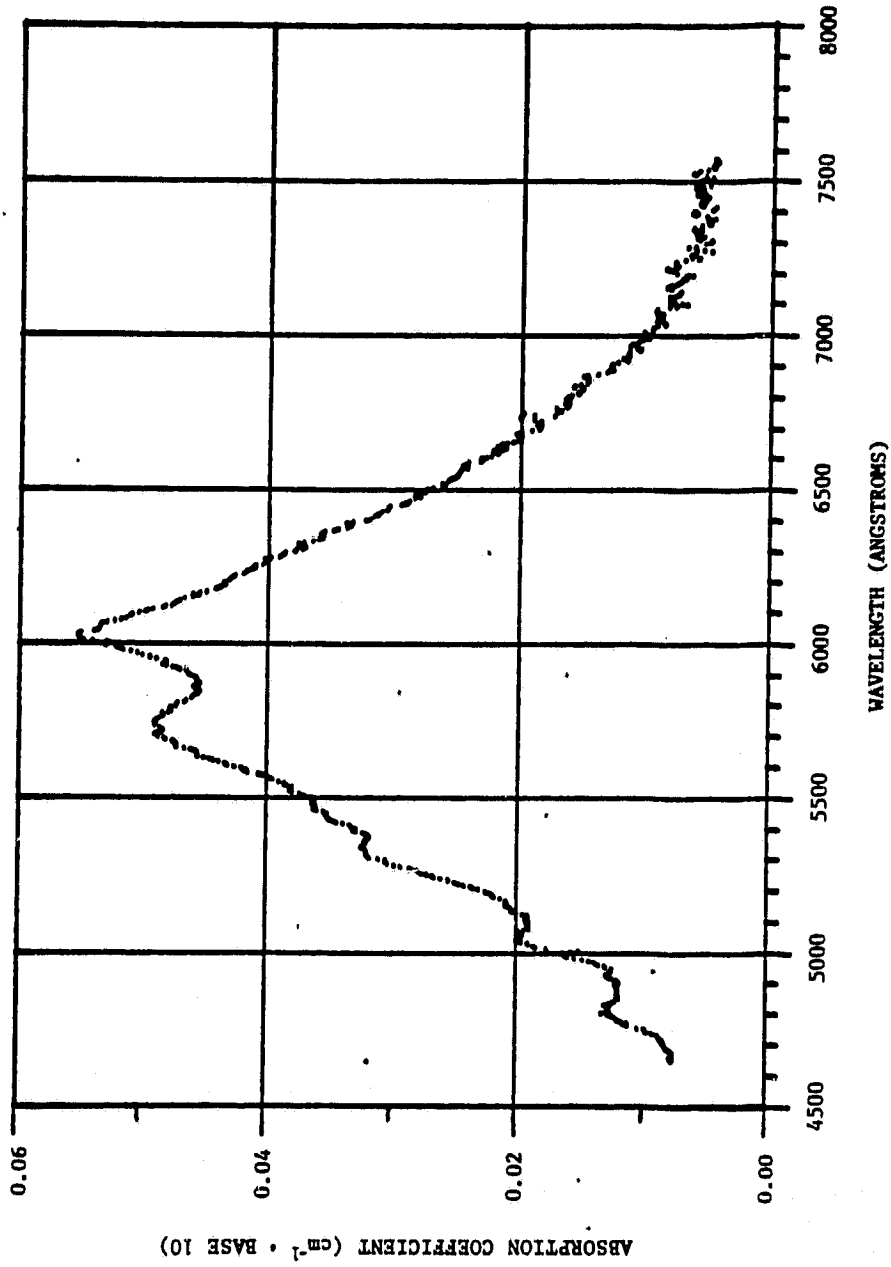


Figure 16. Calculated absorption spectrum of ozone at STP using a gas sample which was at $T = 303 \text{ K}$ and $P = 37 \text{ cm Hg}$ (fill 2).

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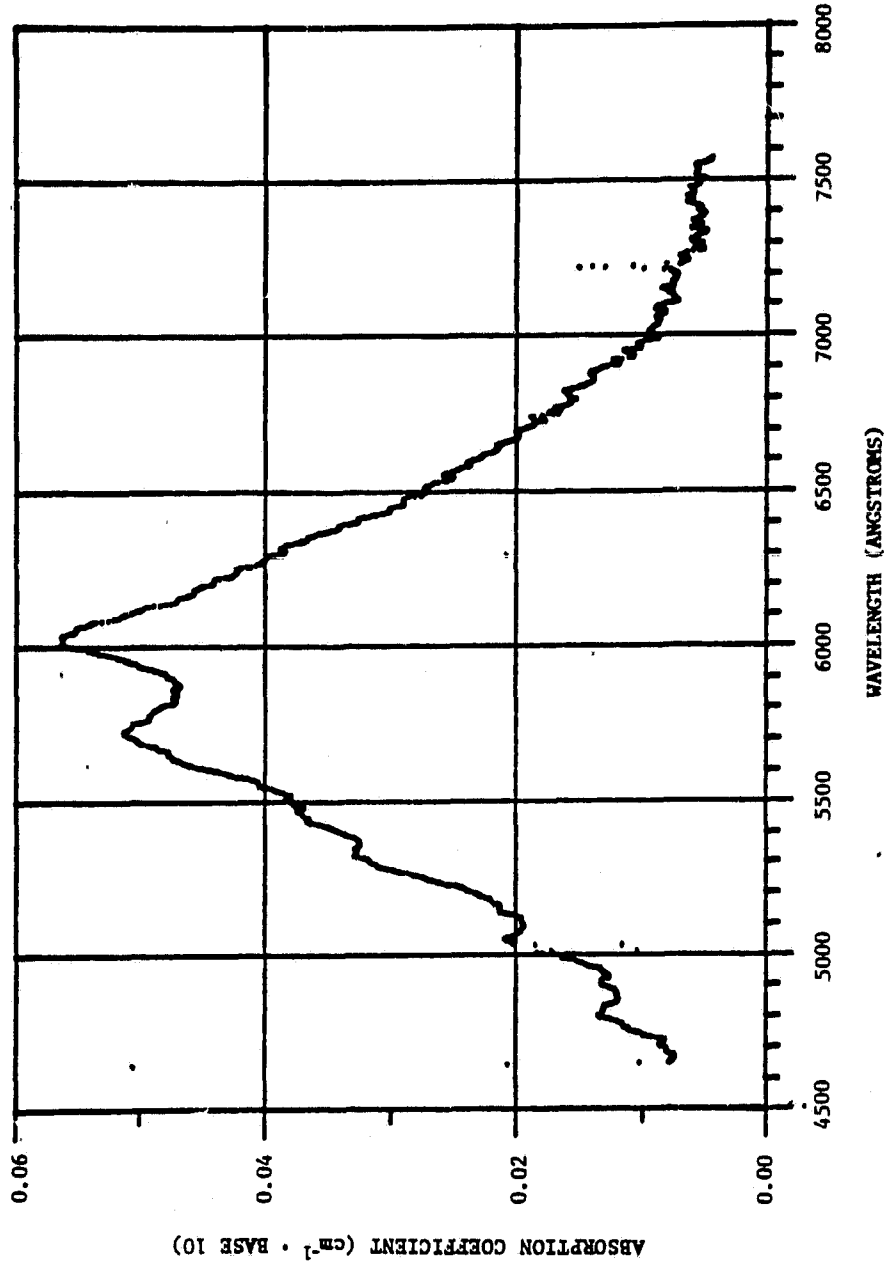


Figure 17. Calculated absorption spectrum at STP (40 minutes after filling) at $T = 198$ K (fill 2).

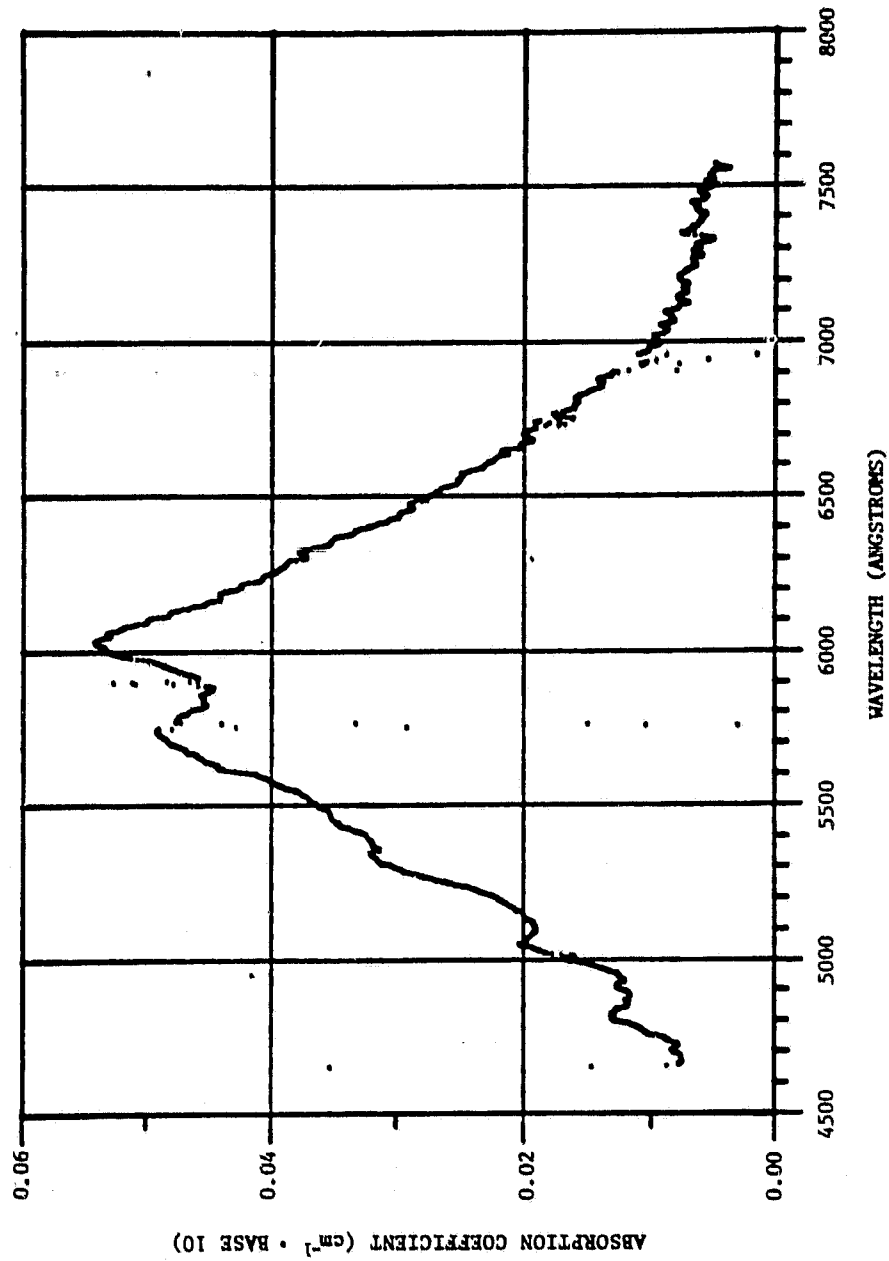


Figure 18. Calculated absorption spectrum at STP (60 minutes after filling) at T = 303 K (fill 2).

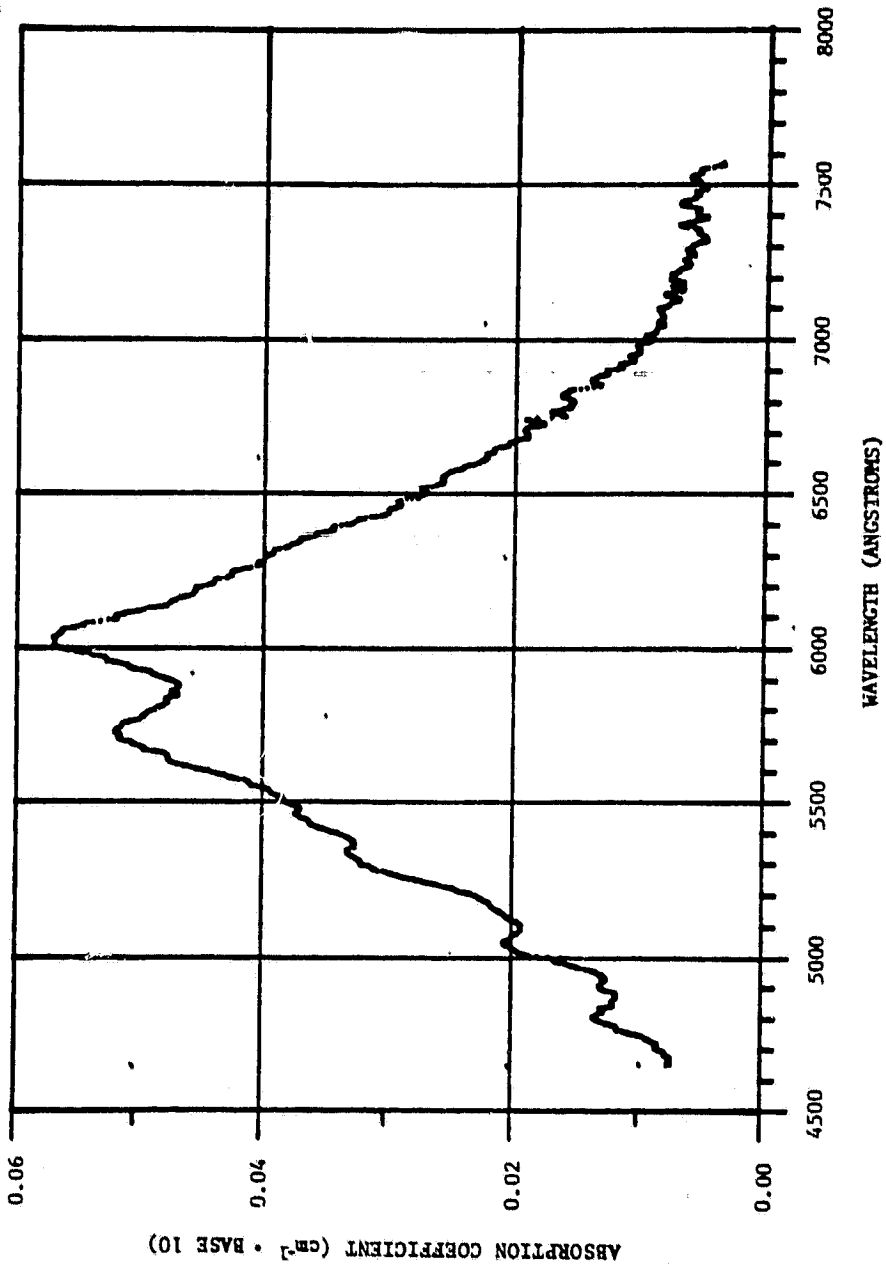


Figure 19. Calculated absorption spectrum at STP (2 hours after filling) at T = 165 K (fill 2).

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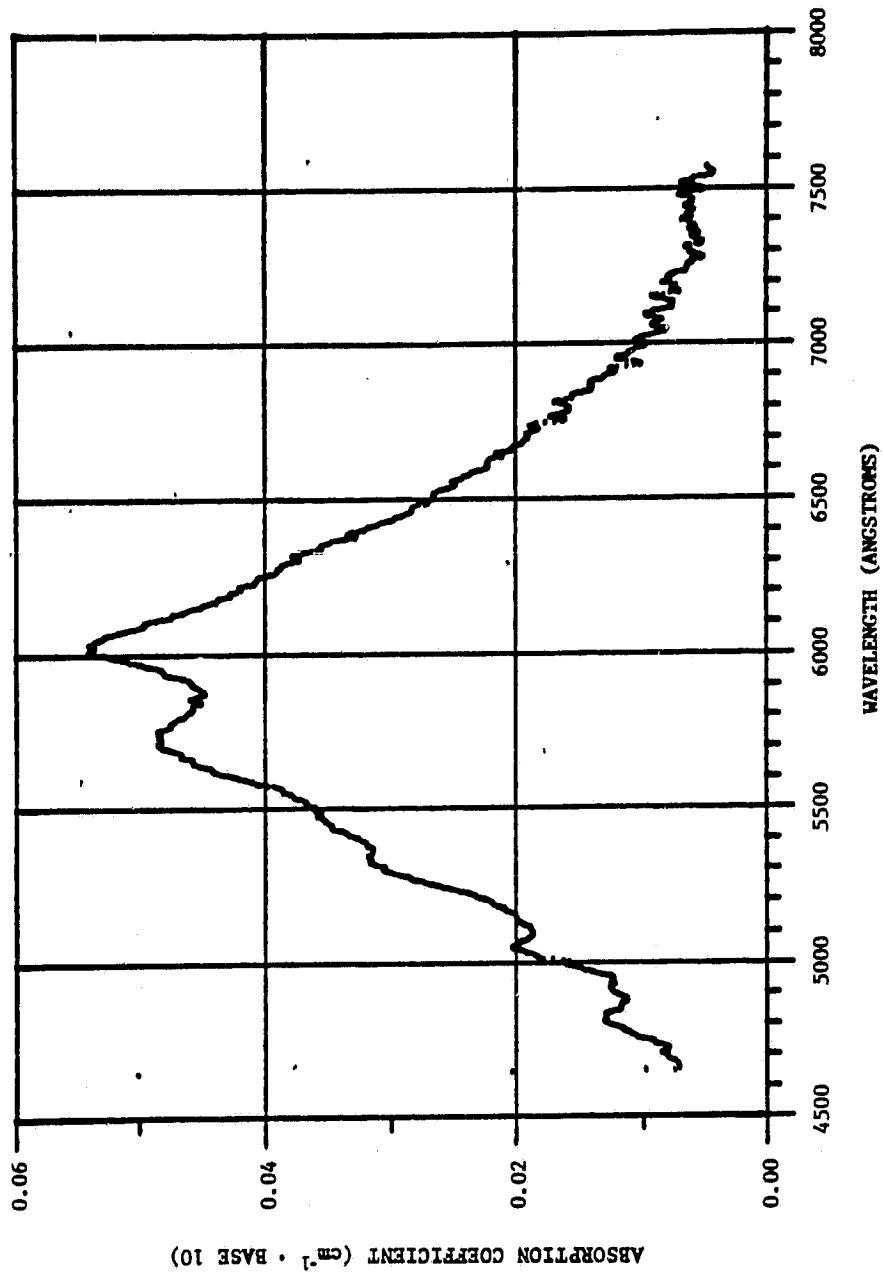


Figure 20. Calculated absorption spectrum at STP (about 3 hours after filling) at 303 K (fill 2).

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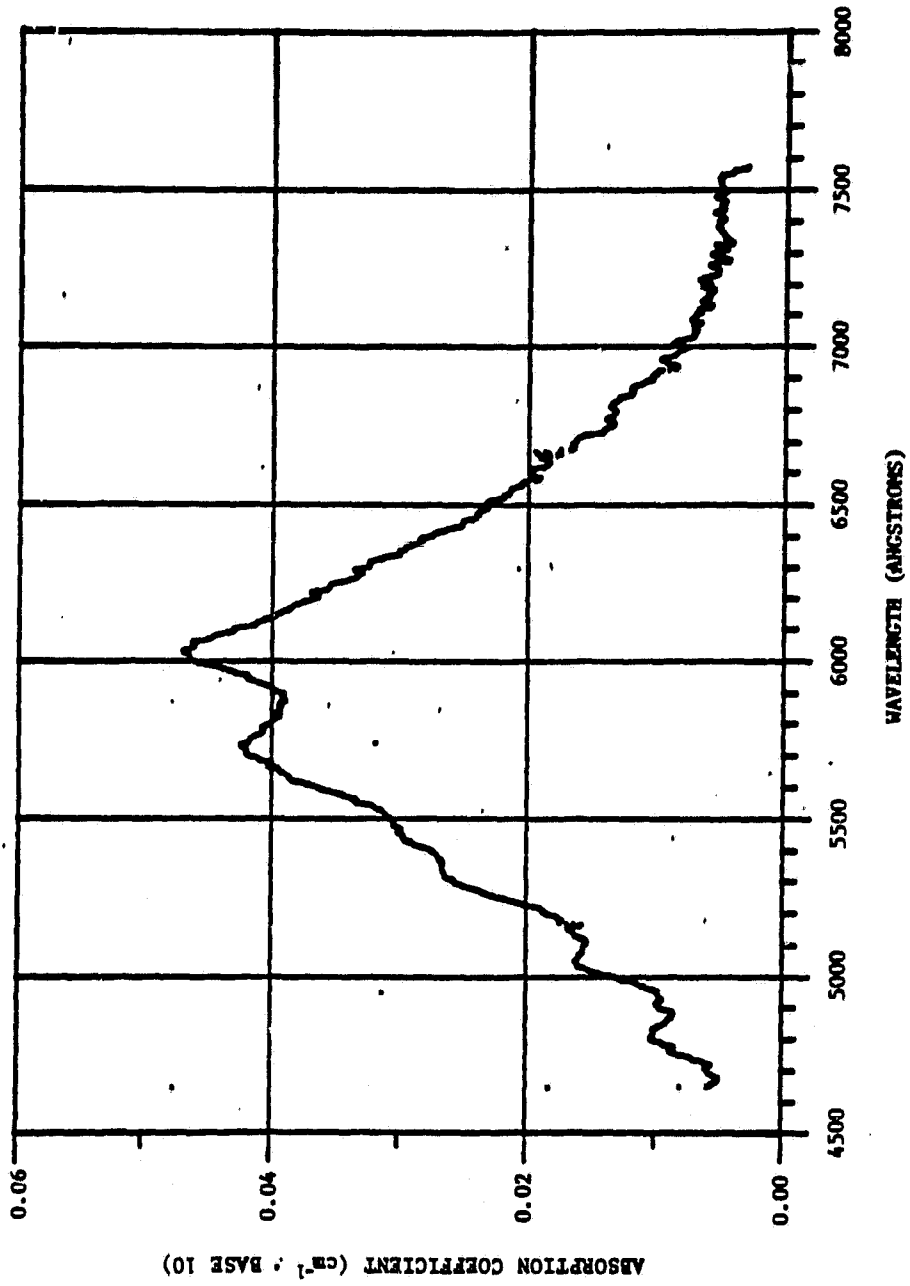


Figure 21. Calculated absorption spectrum at STP (about 43 hours after filling) at T = 303 K (fill 2).

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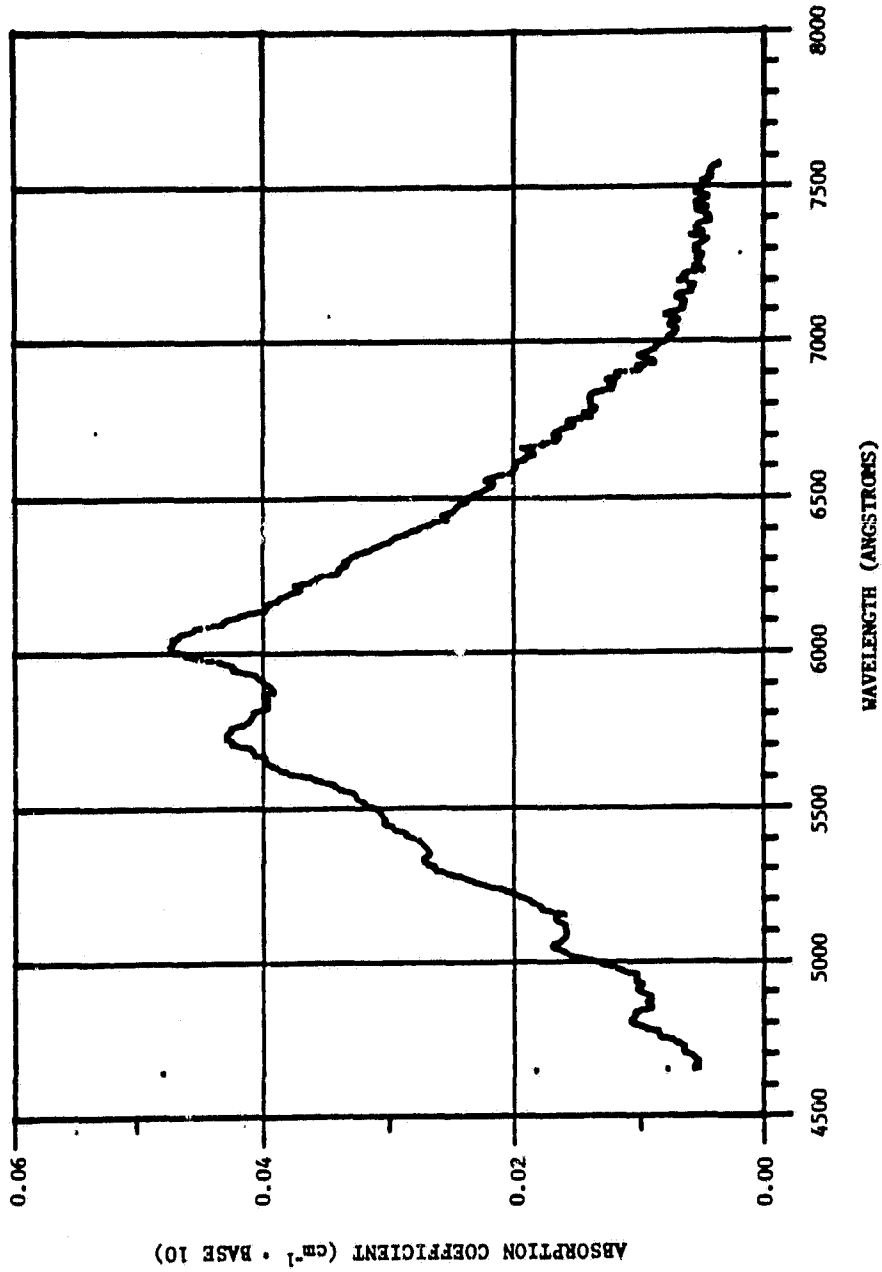


Figure 22. Calculated absorption spectrum at STP (44 hours after filling) at T = 303 K (fill 2).

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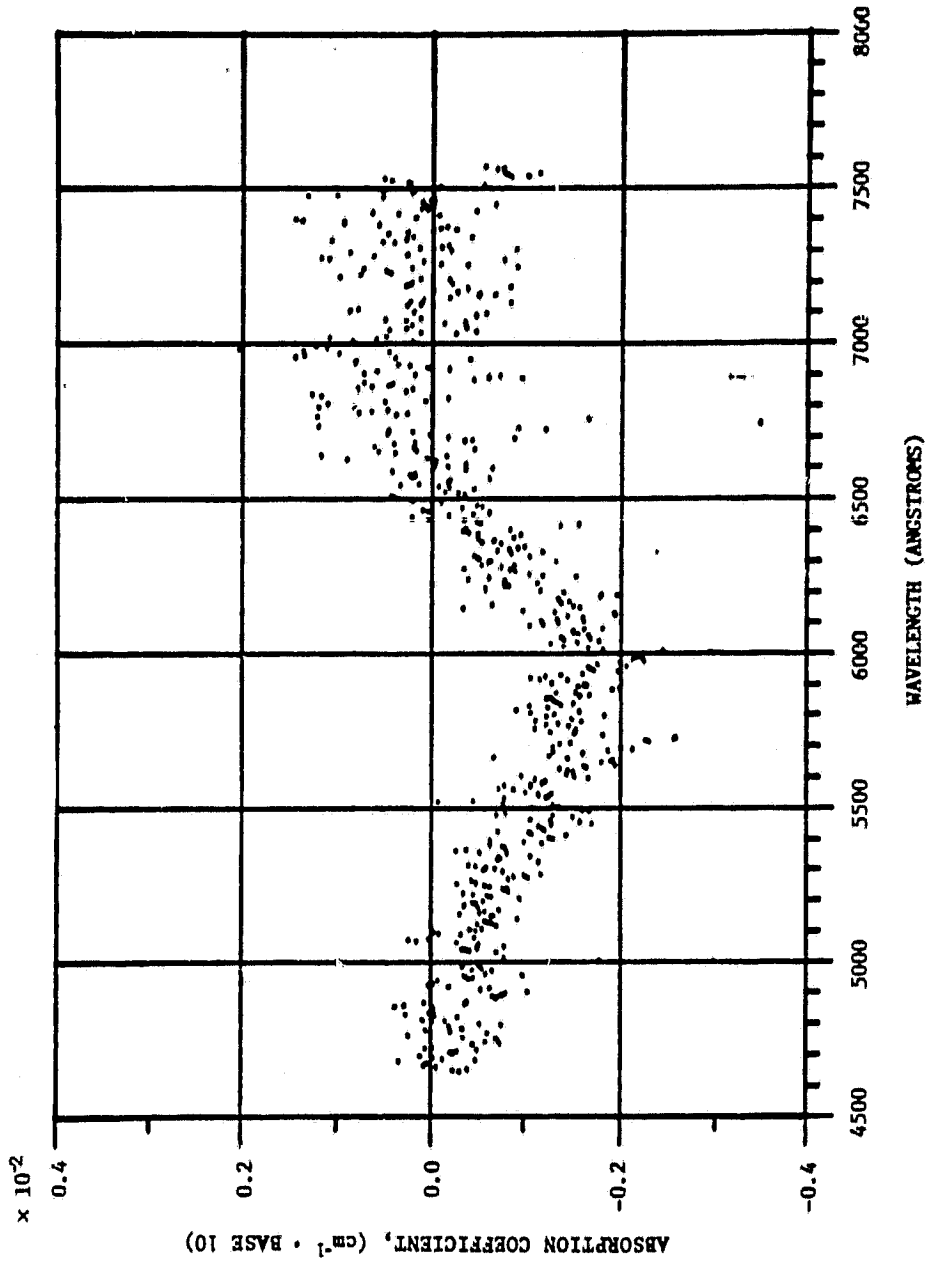


Figure 23. Difference of absorption coefficients when temperature was reduced from 303 K to 298 K (time interval between these two spectrums was about 35 minutes, fill 2).

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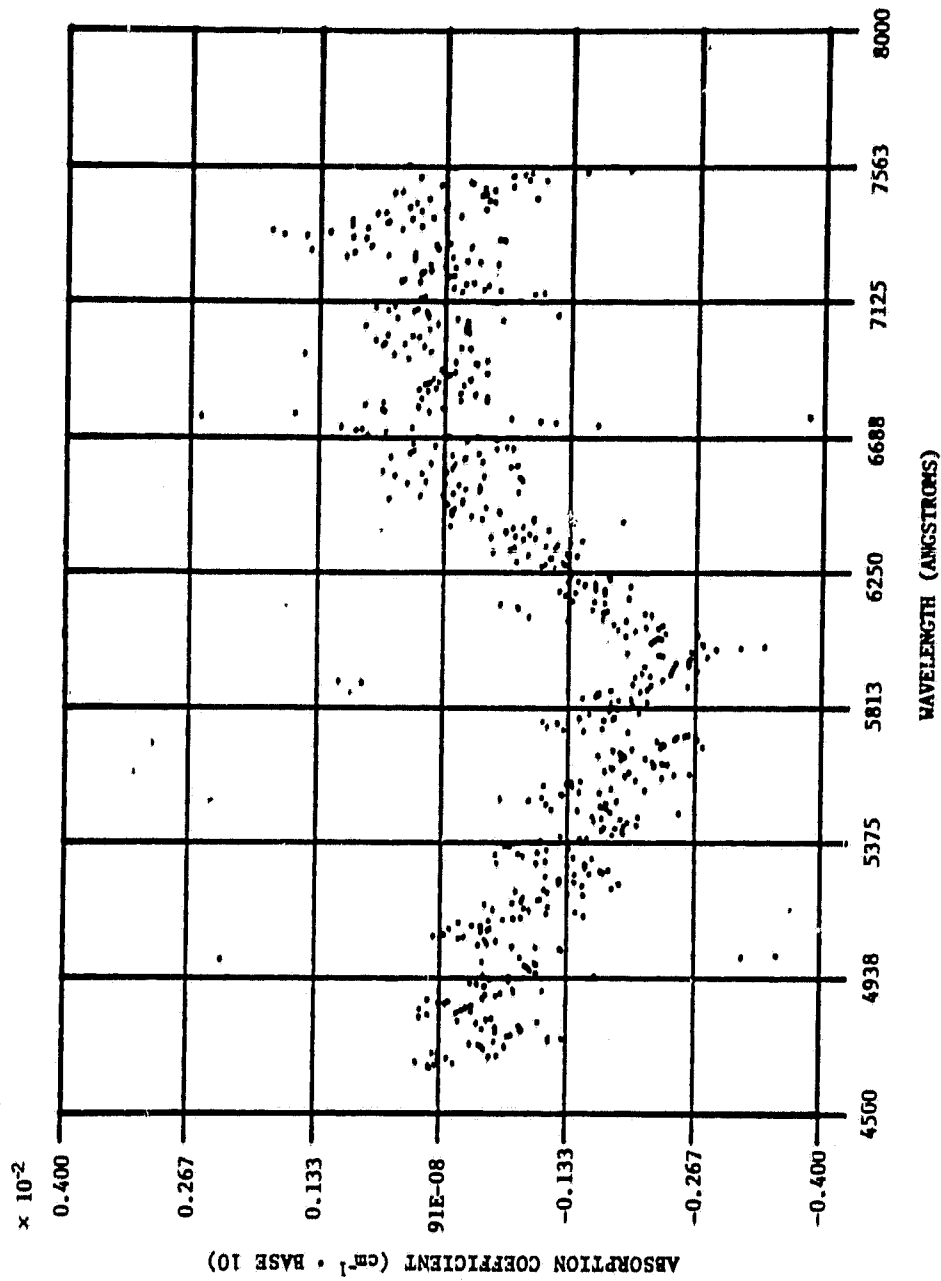


Figure 24. Difference of absorption spectrum when temperature was increased from 198 K to 303 K (time interval between these two spectrums was about 20 minutes, fill 2).

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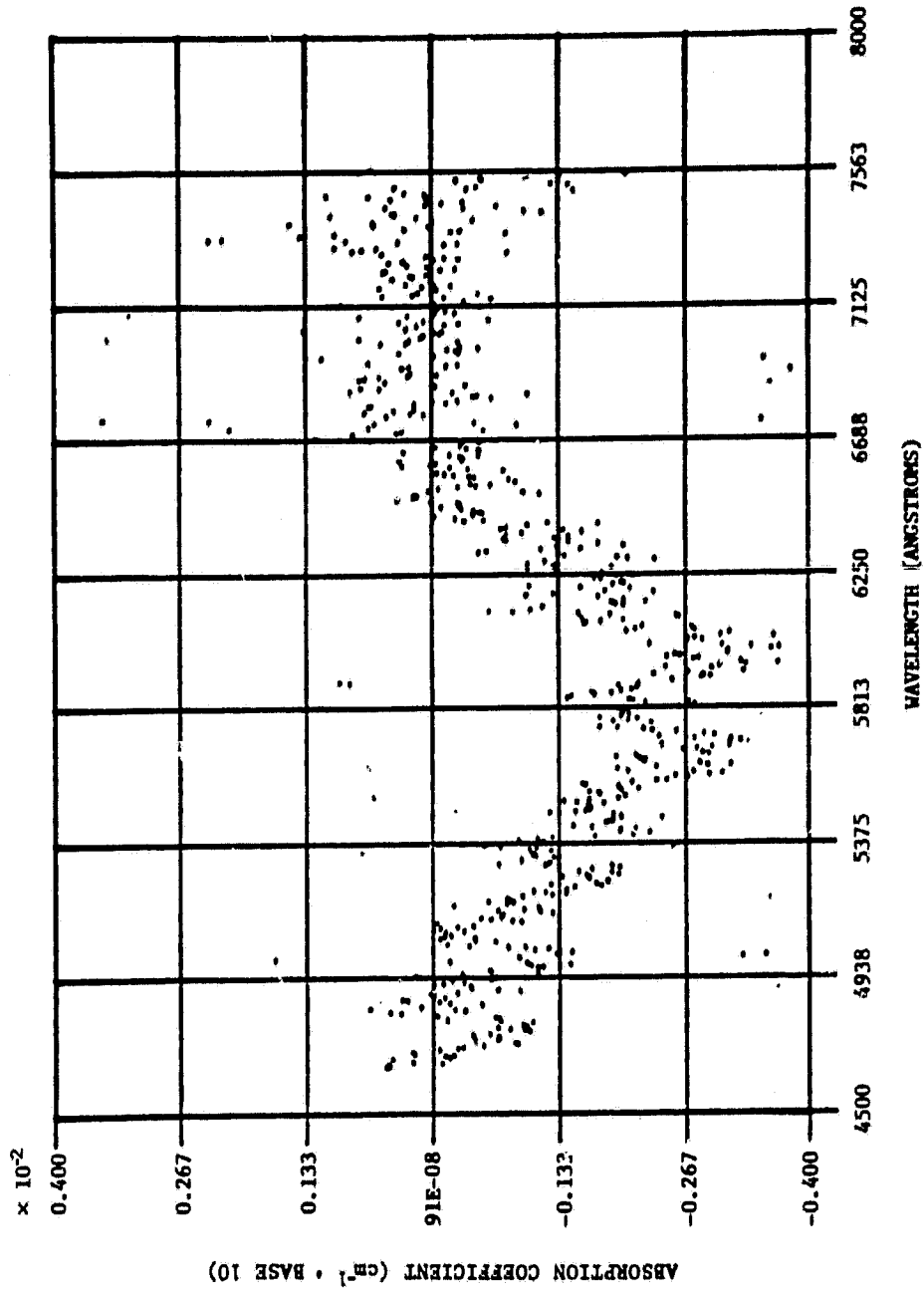


Figure 25. Difference of absorption spectrum when temperature was decreased from 303 K to 165 K (time interval between these two spectrums was about 60 minutes, fill 2).

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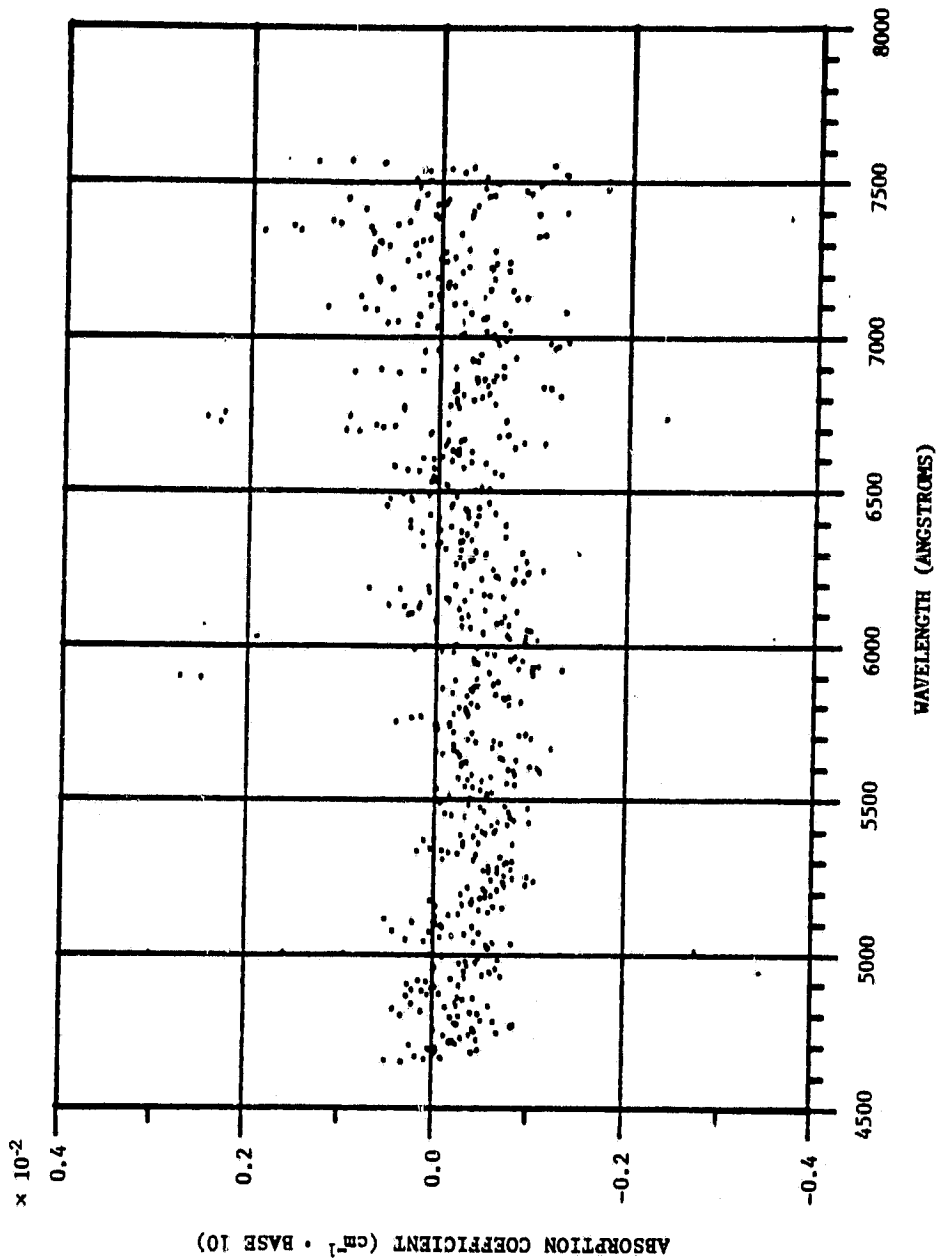


Figure 26. Difference in absorption coefficients after one temperature cycle at 303 K (time interval between these two spectrums was 60 minutes, fill 2).

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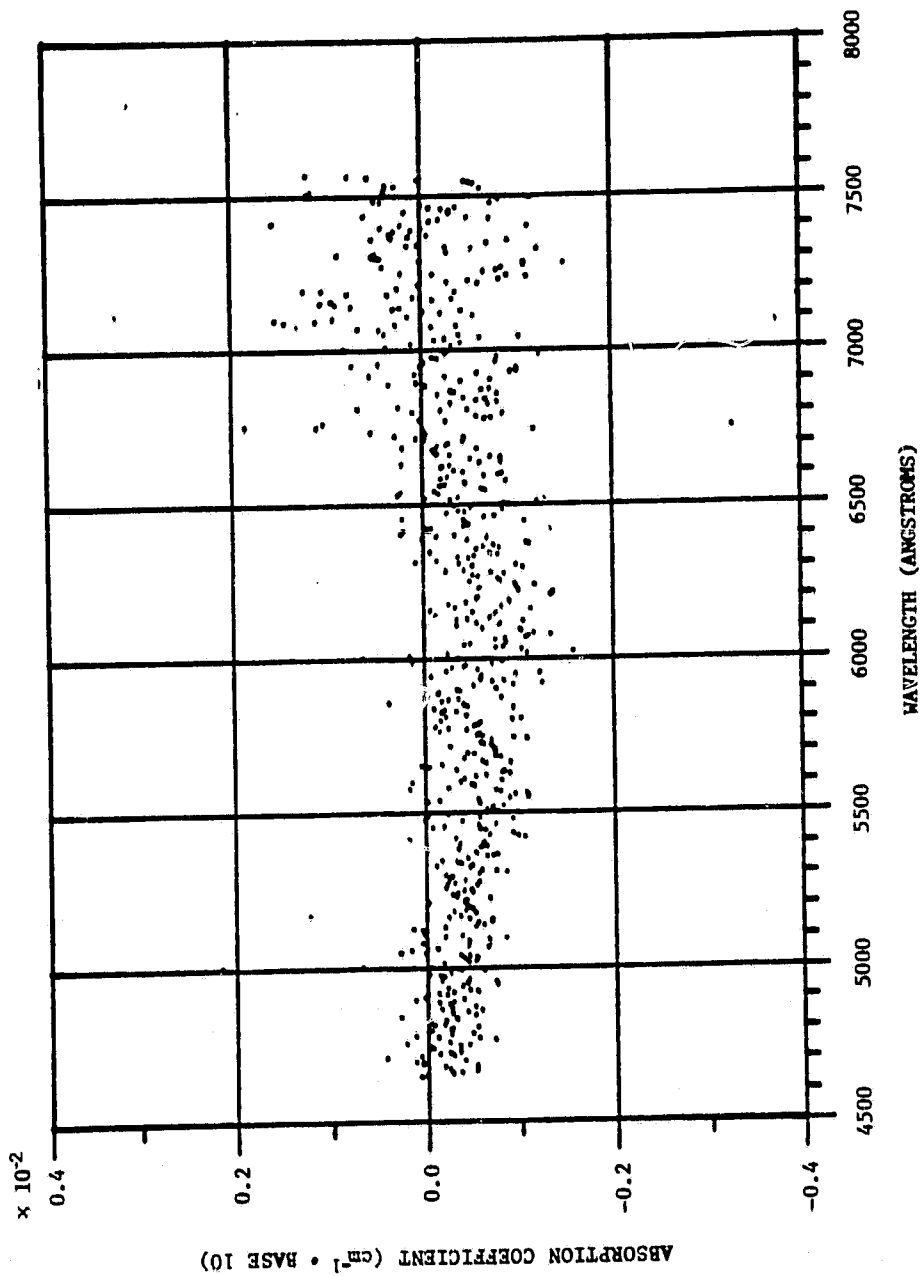


Figure 27. Difference in absorption coefficients after two temperature cycles at $T = 303 \text{ K}$ (time interval between these two spectrums was about 3 hours, fill 2).

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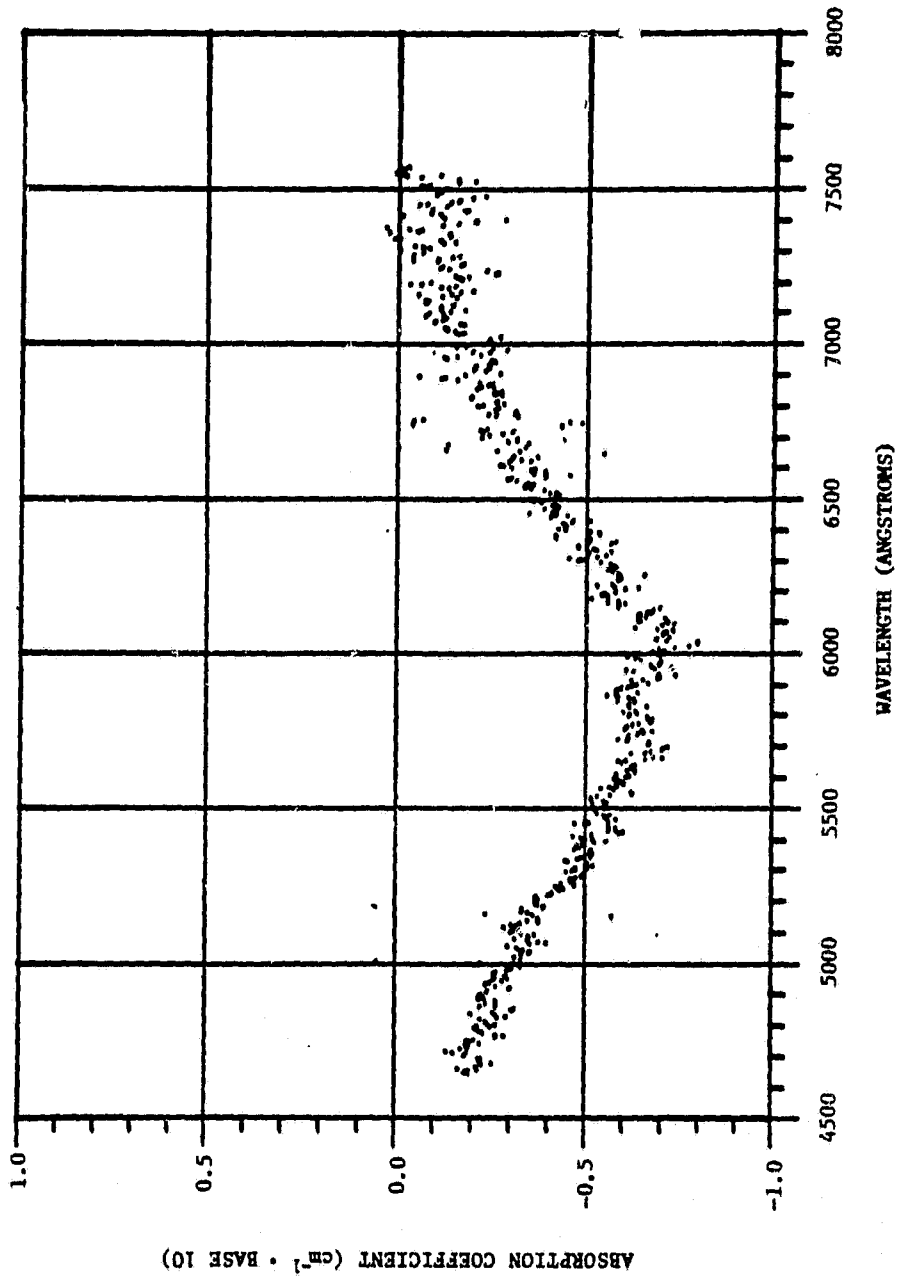


Figure 28. Difference in absorption coefficients after two temperature cycles at $T = 303$ K (time interval between these two spectrums was 44 hours, fill 2).

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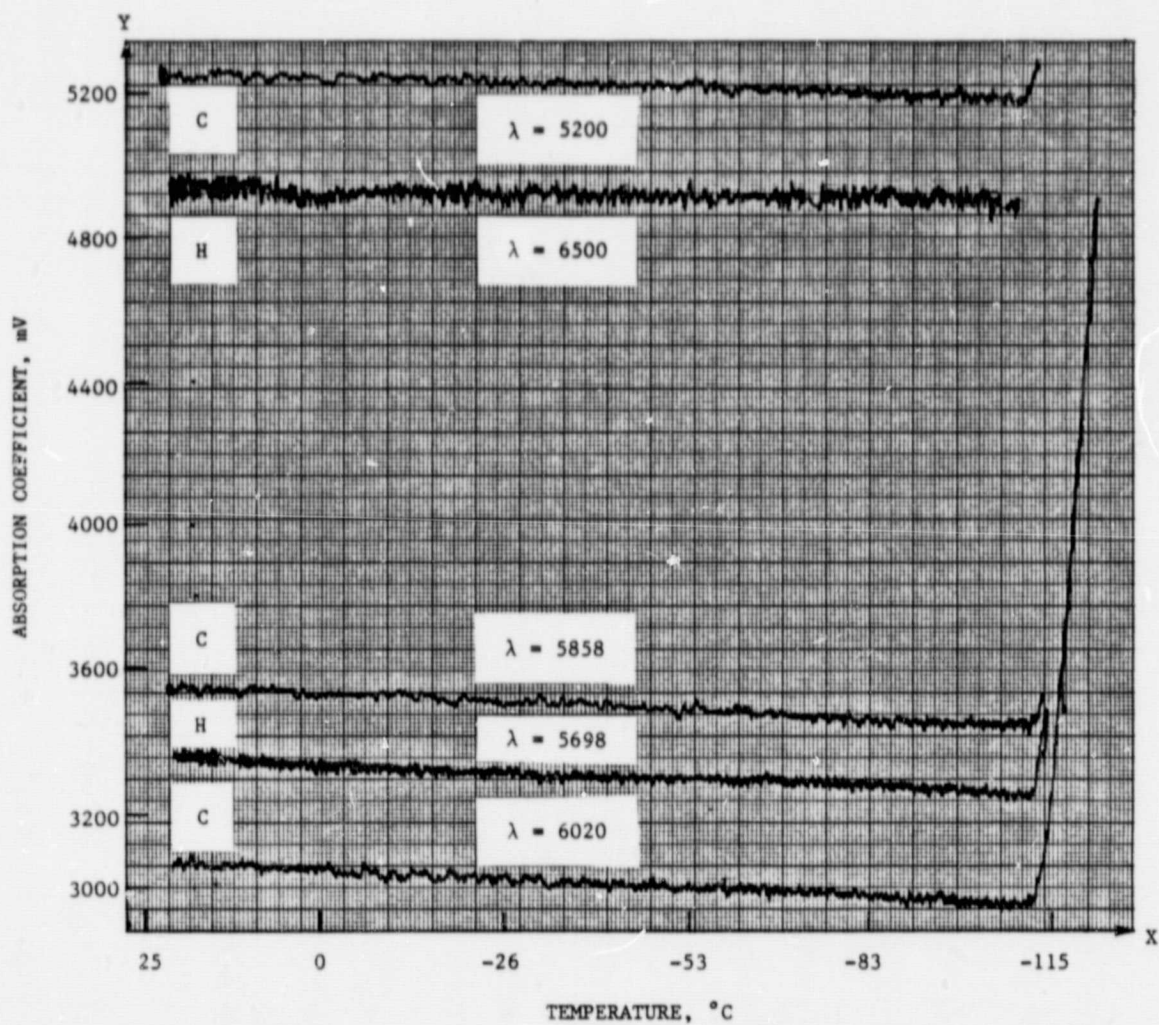


Figure 29. Variation of absorption coefficients for fixed wavelengths as a function of temperature. C and H designate cooling and heating of the gas sample during the experiment.

APPENDIX A

APPENDIX A

PROGRAM ADC

This program accepts analog input originating from Perkin-Elmer Model 200 and creates a disk file on drive B:. The data contains 6000 blocks with one sample per block. These files were transferred to Dec-10 time shared computer, where the data was converted into decimal numbers.

```

;
;
BEGIN:  MVI      A,2H
        STA      FCB          ; DISK B AS DATA DISK
        CALL     INIT        ; INIT MEMORY LOCN'S
        CALL     PROMT
        CALL     CHECK       ; SEE IF FILE IS THERE
MAIN:   CALL     INLINE      ; TEXT LINE AT START
        CALL     CALIB
        CALL     DATIME     ; GET THE TIME
        CALL     INPT
        CALL     SETSZ      ; COMPUTE FILE SIZES
        CALL     FILE
        CALL     MORE
        JRZ      MAIN
        JMP      NUL        ; RETURN TO CPM
;
;      *** PROMPT THE USERS ***
;
PROMT:  LXI      D,MSG        ; "# OF CHANNELS"
        CALL     OUTSTR
        CALL     ECHO
        SBI      30H
        CPI      1H
        JM       PROMT
        CPI      3H
        JP       PROMT
        STA      CNT
        STA      NUM
        CALL     ECHO
        CPI      CR
        JRNZ    PROMT
        XRA      A
        STA      SEE
PRMA:   LXI      D,MSGO       ; SAMPLES / BLOCK(CH 0)
        CALL     OUTSTR
        CALL     INUM
        JM       PRMA
        LXI      D,SIZE
        XCHG

```

```

PRMB:  CALL SAVEN2
        LXI D,MSG1 ; # OF BLOCKS
        CALL OUTSTR
        CALL INUM
        JM PRMB
        LXI D,NUMBLK
        XCHG

PRMC:  CALL SAVEN2
        LXI D,MSG3 ; # STEPS PER BLOCKS ??
        CALL OUTSTR
        CALL INUM
        JM PRMC
        CALL SETSTP ; CALCULATE PULSES/STEP
        LXI H,STEPS
        CALL SAVEN2

PRM1:  LXI D,MSG2 ; SAMPLES PER CHAN(1)
        CALL OUTSTR
        CALL INUM
        JM PRM1
        CALL SETIM
        LXI H,CSTO
        CALL SAVEN2
        LDA CNT
        CPI 1 ; ONLY ONE ?
        JRZ PRM3
        LXI D,MSGE ; SAMP..SEC..(25 MAX).
        CALL OUTSTR
        CALL INUM
        JM PRM2
        CALL SETIM ; COMPUTE
        LXI H,CST1
        CALL SAVEN2

PRM3:  XRA A
        STA SLOW
        STA SEE
        LXI D,MSG5 ; FAST/SLOW MONITOR ??
        CALL OUTSTR
        CALL ECHO
        CPI 'S'
        CZ SETSLO ; MUST BE SLOW MON
        CALL ECHO
        CPI CR
        JRNZ PRM3
        LXI D,MSGT
        CALL OUTSTR ; WANT TO WATCH ?
        CALL ECHO
        CPI 'Y'
        CZ SETSEE
        CALL ECHO
        CPI CR
        JRNZ PRM4
        LXI D,MSGA ;TYPE 'B' TO BACKUP
        ;..OR 'F' FORWARD...
        ; .. <RETURN> TO EXIT

        CALL OUTSTR
        CALL ZERO
        RET

SETSLO: STA SLOW
        RET
SETSEE: STA SEE

```

RET

**** SAVE THE RESULT IN MEM ****

```
SAVEN2: CALL    SAVEN
SAVEN:  MOV     M,E           ; LOW ORDER BYTE FIRST
        INX    H
        MOV    M,D
        INX    H
        RET
```

**** CHECK FOR MORE FILES ****

```
MORE:   LXI    D,MSGR           ; "MORE ? "
        CALL  OUTSTR
        CALL  ECHO
        CPI   'N'             ; NOPE ??
        JRZ  MCHEC
        CPI   'Y'
        JRNZ MORE
        CALL  ECHO
        CPI   CR
        JRNZ MORE
        LDA  NUM
        STA  CNT
        LXI  D,MSGB           ; RETURN LOCN OR NEW ?
        CALL  OUTSTR
        CALL  ECHO
        CPI   CR
        CNZ  ZERO             ; ??
        CZ   RTURN
        LHLD NUMBLK+2
        SHLD NUMBLK           ; RESTORE FILESIZE
        CALL  INIT
        CALL  INFLO           ; GET NEW FILENAME
        XRA  A
        RET
MCHEC:  CALL  ECHO
        CPI   CR
        JRNZ MORE
        DCR  A
        RET                   ; NON ZERO
```

**** CALIBRATE THE A TO D CONVERTER ****

```
CALIB:  MVI    A,NUL
        STA  UNI
        LXI  D,MSG4           ; "UNIPOLAR OR BIPOLAR"
        CALL  OUTSTR
        CALL  ECHO
        CPI   'B'
        CZ   SETUNI           ; -1 = BIPOLAR
        CPI   'U'
        JRNZ CALIB
        CALL  INCH
        CPI   CR
        JRNZ CALIB
```



```

LDA    UNI
ORA    A
JM     ETC           ; BIPOLAR
LXI    D,MSG5       ; SWITCH TO THE LEFT
MVI    B,7H
CALL   CALP
LXI    D,MSG7       ; LEFT POT TO '01FF'
MVI    B,6H
JMPR   CALP
ETC:   LXI    D,MSG8       ; SWITCH TO THE RIGHT
MVI    B,7H
CALL   CALP
LXI    D,MSG10      ; LEFT POT TO '03FF'
MVI    B,6H
JMPR   CALP

;
;
SETUNI: CMA
STA
MVI    A,'U'       ; SET TO -1
RET           ; FAKE OUT REST

;
;
CALP:  CALL   OUST
CALL   LOOP
IN     DAT
RET

;
;
LPT1:  IN     STAT
ANI    2H

LOOP:  MVI    A,CR           ; CALL W/ CHAN # IN 'B'
CALL   OUCH
MOV    A,B
OUT    DSTAT
NOP

LP1:   IN     DSTAT
RRC
JRC    LP1
NOP
IN     DDAT
MOV    C,A
NOP
IN     DDAT
ANI    03H
CALL   CNVERT
MOV    A,C
CALL   CNVERT
LDA    SLOW
ORA    A
JRZ   LPT1
MVI    A,LF
CALL   OUCH
CALL   INCH
CPI    CR
RZ
JMPR   LOOP

```

```

CNVERT:  PUSH      PSW
          RRC
          RRC
          RRC
          RRC
          CALL     VERT
          POP      PSW
VERT:    ANI       0FH
          ADI      30H
          CPI      3AH
          CP       ABIAS
          CALL     OUCH
          RET
ABIAS:   ADI      7H
          RET

```

```

;
;
; **** INSERTING TEXT AT THE BEGINNING ****
;

```

```

INLINE:  LXI      H, TXTBUF
          LXI      D, MSGL
          CALL     OUST
          MVI      C, 0      ; POSITION COUNTER
TXTLP:   CALL     ECHO
          CPI      7FH      ; <RUBOUT>
          JRZ     BACUP
          CPI      08H      ; <OH>
          JRZ     BACON
          CPI      18H      ; <ESC>
          JRZ     INLINE
          MOV      M, A
          INX     H
          INR     C
          CPI      CR
          JRNZ   TXTLP
          MVI     A, LF
          CALL     OUCH
          MOV      M, A
          INX     H
          MVI     M, 26     ; <Z>
          INR     C
          INR     C
          MVI     H, 0
          MOV     L, C
          SHLD   TXTSZ
          SHLD   TXTSZ2
          RET

```

```

;
;
BACON:   DCR      C
          JM      INLINE
          DCX     H
          JMPR   TXTLP
BACUP:   DCR      C
          JM      INLINE
          DCX     H
          MOV     A, M
          CALL   OUCH
          JMPR   TXTLP
;

```

**** CREATING THE DISK FILE ****

```

;
;
;
FILE:  CALL    SETUP
      LXI     D,STARTO
      LHLD   SHLO
      CALL   RITE
      RZ
      CALL   SETUP
      LXI     D,START1      ; START OF FILE BLOCK 1
      LHLD   SHL1          ; FILE 1 SIZE
      JMP    RITE

```

**** CHECKING FOR A FILE ALREADY THERE ****

```

;
;
;
CHECK: LDA    FCBFN          ; LOOK AT FILENAME
      CPI    ' '
      JRZ    INFLO          ; GET ONE
      CALL   DFIND
      CALL   CLRFN
      INR    A
      RZ
      CALL   CRLF
      LXI     D,MSGF        ; RENAME NEW FILE ??
      CALL   OUTSTR
      CALL   ECHO
      CPI    59H           ; 'Y'
      JRZ    INFILE
      CALL   CRLF
      LXI     D,MSGW        ; WARN THE SUCKER
      CALL   OUTSTR
      CALL   ECHO
      CPI    59H           ; HES SURE ??
      JRNZ   INFILE        ; NOPE
      CALL   INCH          ; GET <CR>
      CPI    CR
      JRNZ   INFILE        ; MUST NOT BE SURE
      CALL   DERASE        ; ELSE ERASE IT
      CALL   CLRFN
      RET

```

```

;
;
INFILE: CALL   INCH
      CPI    CR
      JRNZ   CHECK
INFLO:  LXI     H,FCB+1
      MVI    B,12
      CALL   SETBLK
      CALL   CLRFN
      CALL   CRLF
      LXI     H,FCB+1
      LXI     D,MSGQ        ; NEW FILENAME :
      CALL   OUTSTR
INFL1: CALL   ECHO
      CPI    7FH           ; RUBOUT ??
      JRZ    INFLO
      CPI    2EH          ; '.'
      JRZ    INFL2

```

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```

CPI      CR
JRZ      CHECK
MOV      M,A
INX      H
JMPR     INFL1
INFL2:  LXI      H,FCB+9
MVI      B,3
INFL3:  CALL     ECHO
CPI      7FH
JRZ      INFLO
CPI      CR
JRZ      CHECK
MOV      M,A
INX      H
DCR      B
JRNZ     INFL3
CALL     INCH
CPI      CR
JRNZ     INFLO
JMP      CHECK

```

```

;
;
;      **** CLEAR THE GARBAGE AT END OF FCB ****
;

```

```
CLRFN:  PUSH     PSW
MVI     B,21
LXI     H,FCB+12
CALL    CLRBLK
POP     PSW
RET

```

```

;
;
;      **** SETTING FILE SIZES ****
;

```

```
SETS:   LXI     D,MSGP
CALL    OUST
LXI     D,SIZO+1
LXI     H,SHLO+1
MOV     A,M
SBI     OFFO
CALL    CALCSZ
SBI     OFF1
CALCSZ: MOV     M,A
MOV     B,A
XRA     A
MOV     A,B
RAR                      ; DIV BY 2 HI BYTE
STAX    D
DCX H
DCX D
MOV     A,M
RAR                      ; LO BYTE
STAX    D
INX H
INX H
INX H
INX D
INX D
INX D
MOV     A,M

```

RET

```

;
;
; **** SET UP FOR DISK WRITES ****
;
SETUP: CALL    DMAKE          ; CREATE THE FILE
        INR      A
        JZ       CRERR
        CALL    DOPEN        ; OPEN IT
        INR      A
        JZ       FLERR
        RET

```

```

;
;
; **** WRITING TO THE DISK ****
;
RITE:   CALL    HEADER
        JMPR   RITE2
RITE1:  LXI     H,BUFF
        MOV    A,L
        STA   BLKSZ          ; SIZE OF BLOCK
RITE2:  CALL    BLK           ; TRANSFER THE BLOCK
        JRC   DONE
        PUSH  B
        PUSH  D
        CALL  DWGIT
        ORA   A
        JNZ   WRER
        POP   D
        POP   B
        JMPR RITE1
DONE:   XRA    A
        SUB   L
        MOV   B,A
        CALL CLRBLK
        CALL DWGIT
        CALL DCLOS
        CALL UPFILE          ; UPDATE FILENAME
        CALL CLRFN
        LDA   CNT
        DCR   A
        STA   CNT
        RET

```

```

;
;
; *** UPDATING THE FILENAME ***
;
UPFILE: LDA    FCB+6      ; *****?.***
        INR    A
        CPI    ':'        ; OVERFLOW ?
        CZ    UPFL1
        STA    FCB+6
        RET
UPFL1:  LDA    FCB+5      ; *****?.***
        INR    A
        CPI    ':'        ;
        CZ    UPFL2
        STA    FCB+5
        MVI    A,'0'
        RET

```

```

UPFL2: LDA    FCB+4 ; ***?**,***
      INR    A
      CPI    '!'
      JZ     CRERR ; TOO MANY !!
      STA    FCB+4
      MVI    A, '0'
      RET

```

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```

;
;
;
; **** DISK FILE TRANSFER ****
; ... SOURCE <DE> ... DESTINATION <HL> ...
; .. LENGTH "BLKSZ" ... FILE SIZE <BC> ...
;

```

```

BLK:  LDA    BLKSZ
      DCR    A
      STA    BLKSZ
      JM     BLKQ
      LDAX  D
      MOV   M,A
      INX  H
      INX  D
      DCR  C
      JRZ  HIBLK
      MOV  A,C
      CPI  OFFH
      JRNZ BLK
      DCR  B
      JMPR BLK
HIBLK: MOV  A,B
      ORA  A
      JRNZ BLK
      STC
      RET
BLKQ:  XRA  A
      RET

```

```

;
;
; **** INSERT HEADER INFO ****
;
HEADER: PUSH  H
      PUSH  D ; SAVE THE SOURCES
      LXI  H,BUFF ; SET UP DEST ADDRS
      LXI  D,FCBFN ; NAME + EXT
      MVI  B,11
      CALL BLT
      MVI  B,3
      CALL SETBLK
      CALL TIMEX ; DATE & TIME
      CALL OFFSET
      RAL ; X 2
      LXI  D,SIZO
      CALL FILNUM ; # OF SAMPLES
      MVI  B,27
      LXI  D,SMPSC ; SAMPLES. SAMPLE PER.
      CALL BLT
      LDA ; OFFSET
      RAL
      RAL ; X 4
      LXI  D,CSTO ; CSTO+OFFSET = # CLOCKS/SAMPLE

```

```
CALL FILNUM  
LXI D,CLKDT ; 3.3280 MS/CLOCK  
MVI B,20  
CALL BLT  
XRA A ; NO OFFSET  
LXI D,SIZE ; SAMPLES/BLOCK  
CALL FILNUM  
LXI D,DMSG  
MVI B,15  
CALL BLT  
XRA A  
LXI D,NUMBLK+2 ; BLOKS/RUN  
CALL FILNUM  
MOV A,L  
CMA  
INR A  
STA BLKSZ  
LXI D,DM2  
LXI B,13  
CALL BLK  
PUSH H  
LHLD TXTSZ  
MOV B,H  
MOV C,L ; BC - SIZE OF TEXTFILE  
POP D  
LXI H,TXTBUF ; DE>DEST ... HL>SOURCE  
XCHG  
CALL BLK  
CNC TRITE  
POP D  
POP B  
RET  
OFFSET: LDA CNT  
MOV B,A  
LDA NUM  
SUB B  
STA OFST  
RET
```

```
; ;  
; ***** TEXT WRITING TO DISK *****  
;
```

```
TRITE: PUSH B  
PUSH D  
CALL DWRIT  
ORA A  
JNZ WRER  
POP D  
POP B  
LXI H,BUFF  
MOV A,L  
STA BLKSZ  
CALL BLK  
RC  
JMPR TRITE
```

```
; ;  
; ***** TRANSFERRING A NUMBER TO FILE *****  
;
```

```

FILNUM: ADD      E
        MOV      E,A          ; CORRECT OFFSET
        XCHG
        MOV      C,M          ; DE-BUFF HL-SRC OF #
        INX      H
        MOV      H,M
        MOV      L,C          ; DE-BUFF HL-#
        LXI      B,M10000
        CALL     FINUL
        LXI      B,10000
        DAD      B
        LXI      B,M1000
        CALL     FINUL
        LXI      B,1000
        DAD      B
        LXI      B,M100
        CALL     FINUL
        LXI      B,100
        DAD      B
        LXI      B,M10
        CALL     FINUL
        MOV      A,L
        ADI      3AH          ; CORRECTION+ASCII '0'
        STAX     D
        INX      D
        XCHG
        RET
FINUL:  PUSH     D
        MVI      D,'0'
        DAD      B
        MOV      A,H
        ORA      A
        JM       FINUL2
        INR      D
        JMPR     FINUL+3
FINUL2: MOV      A,D
        POP      D
        STAX     D
        INX      D
        RET

```

```

;
;
; **** INSERTING DATE & TIME IN FILE ****
;

```

```

DATIME: CALL     GET
        XRA      A
        STA      HH
        STA      MM
        STA      SS
        LXI      B,TT
        LXI      H,C8600
        CALL     SUBT
        LDA      H2
        ANI      80H
        JRNZ     NODAY
NEWDAY: LXI      H,DD
        INR      M
        CALL     SETHW
        JMPR     SUBHR
NODAY:  LXI      B,TT

```



```

LXI      H,C8600
CALL    ADDT
SUBHR:  LXI      R,TT
        LXI      H,C3600
        CALL    SUBT
        LDA     H2
        ANI    80H
        JRNZ   SUBPR
        LXI    H,HH
        INR    M
        JMPR   SUBHR
SUBPR:  LXI      B,TT
        LXI      H,C3600
        CALL    ADDT
SUBMI:  LXI      B,TT
        LXI      H,C60
        CALL    SUBT
        LDA     H2
        ANI    80H
        JRNZ   SUBSC
        LXI    H,MM
        INR    M
        JMPR   SUBMI
SUBSC:  LXI      B,TT
        LXI      H,C60
        CALL    ADDT
        LDA     TT
        STA     SS
        RET

;
;      ** MOVE TIME TO BUFFER **
;
TIMEX:  LXI      D,DD
        CALL    BINAS
        CALL    MONTH
        LXI    D,HH
        CALL    BINAS
        MVI    M,':'
        INX    H
        LXI    D,MM
        CALL    BINAS
        MVI    M,':'
        INX    H
        LXI    D,SS
        CALL    BINAS
        MVI    M,CR
        INX    H
        MVI    M,LF
        INX    H
        RET

;
;
ADDT:   MVI      E,3
        XRA     A      ; CLEAR CARRY
LOOPA:  LDAX    B
        ADC     M
        STAX   B
        DCR    E
        RZ
        INX    H

```

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```
INX      B
JMPR     LOOPA

;
;
SUBT:    MVI      E,3
         XRA      A
LOOPS:   LDAX     B
         SBB     M
         STAX    B
         DCR     E
         RZ
         INX     H
         INX     B
         JMPR    LOOPS

;
;
GET:     IN       TO
         STA      HO
         IN       T1
         STA      H1
         IN       T2
         STA      H2
         ANI      8H
         JRNZ     GET      ; NOT READY
         LDA      H2
         ANI      1H
         STA      H2
         RET

;
;
BINAS:   LDAX     D      ; GET TIME
         MVI     C,HUND
         MVI     D,0
         CALL    TCON
         INR     D
BA1:     MOV      A,E
         MVI     C,TEN
         CALL    TCON
         CPI     '0'
         JRNZ    BA2
         DCR     D
         JRNZ    BA3
BA2:     MOV      M,B
         INX     H
BA3:     MOV      A,E
         ADI     '0'
         MOV     M,A
         INX     H
         RET

TCON:    MVI     B,2FH
         INR     B
         SUB     C
         JRNC   TCON+2
         ADD     C
         MOV     E,A
         MOV     A,B
         RET

;
;
SETHW:   LDA      HO
```

```

OUT      TO
LDA      H1
OUT      T1
LDA      H2
OUT      T2
RET

;
;
MONTH:   LDA      MON
        MVI      D,0
        MOV      E,A
        LXI      B,MONT
        XCHG
        DAD      B
        XCHG
        MVI      B,17
        JMPR     BLT      ; RETURN FROM THERE

;
;
;      ***** BLOCK TRANSFER *****
;
;.....SOURCE: <DE> .....DEST: <HL> .....LENGTH: <B> .....
;
BLT:     LDAX     D          ; GET CHAR
        MOV      M,A        ; MOVE IT
        INX      H          ;
        INX      D
        DCR      B
        JRNZ     BLT
        RET

;
;
;      ***** CLEARING A BLOCK OF MEMORY *****
;      ***** OR SETTING A BLOCK TO ' ' *****
;
SETBLK:  MVI      A,20H
        JMPR     CLRBLK
CLRBLK:  MVI      A,NUL
CLRBLK:  MOV      M,A
        INX      H
        DCR      B
        JRNZ     CLRBLK
        RET

;
;
;      ***** OUTPUTTING A STRING *****
;
OUTSTR:  LDAX     D          ; GET CHARACTER
        CPI      '$'
        RZ
        CALL     OUCH
        INX      D
        JMPR     OUTSTR

;
;
;      *** OUTPUTTING STRING + <CR><LF> ***
;
OUST:   CALL     OUTSTR
        JMPR     CRLF

```

*** OUTPUTTING A NUMBER FROM PROMPT ****

```
NUMBER: LDA     SEE
        INR     A
        STA     SEE
        ADI     2FH      ; LET OUCH DO THE REST
```

**** OUTPUTTING A CHARACTER ****

```
OUCH:  PUSH    PSW
        IN      STAT
        ANI    1
        JRZ   OUCH+1
        POP    PSW
        OUT    DAT
        RET
```

**** INPUTTING A CHARACTER ****

```
INCH:  IN      STAT
        ANI    2H
        JRZ   INCH
        IN     DAT
        ANI    7FH
        CPI    STAT      ; @C
        RNZ
        JMP    NUL      ; REBOOT
```

**** INPUT OUTPUT W/ECHO ****

```
ECHO:  CALL    INCH
        JMPR   OUCH
```

**** <CR><LF> ****

```
CRLF:  MVI     A,CR
        CALL   OUCH
        MVI   A,LF
        JMPR  OUCH
```

**** INPUTTING A NUMBER STRING ****

*** N<=64K ***

**** RESULT LEFT IN HL PAIR ****

```
INUM:  LXI     H,NUL
INLP:  CALL    ECHO
        CPI    CR
        RZ
        SBI    30H
        RM
        CPI    0AH      ; WON'T WORK IF < '0'
        JM     INLP2    ; N > 9 ???
        XRA    A        ; NOPE..IT'S GOOD
        XRA    A        ; CLEAR IT
```

```

DCR      A          ; SET NEGATIVE
RET
INLP2:   LXI      D,NUL
DAD      H
XCHG
DAD      D
DAD      H
DAD      H
XCHG
DAD      D
MVI      D,NUL
MOV      E,A
DAD      D
JMPR     INLP

;
;
;
;
;
;
INPT:    LXI      D,MSG12      ; <CR> WHEN READY
CALL     OUST
CALL     ECHO
CPI      STAT      ; 0C ??
JZ       NUL       ; JUMP TO CPM
CPI      CR
JRNZ     INPT
LXI      H,RAN1    ; TWO CHANNELS
LDA      CNT
DCR      A
JRNZ     INSKP    ; MUST BE TWO
INSKP:   LXI      H,RANO
SHLD     JMPVCT
CALL     INCHEK
MVI      A,BELL    ; DING DONG
CALL     OUCH
RADM:    CALL     TICK      ; PAUSE ONE CLOCK TICK
CALL     INSTEP     ; CHECK FOR ABORT
LHLD     JMPVCT
PCHL     ; JMP FROM HERE
RAN1:    LXI      H,CST1
CALL     TIME
JRNC     RANO
LHLD     SHL1
MVI      A,1
CALL     ADAV
SHLD     SHL1
RANO:    LXI      H,CSTO
CALL     TIME
JRNC     RADM
LHLD     SHLO
MVI      A,0
CALL     ADAV
SHLD     SHLO
LDA      SEE
ORA      A
CNZ     MONIT
LDA      SIZE
DCR      A
STA      SIZE

```

```
JRZ      HISIZ
CPI      OFFH
JRNZ     RADM
LDA      SIZE+1
DCR      A
STA      SIZE+1
JMPR     RADM
HISIZ:   LDA      SIZE+1
        ORA      A
        JRNZ     RADM
        CALL     STEP      ; ADVANCE
        LHLD    SIZES    ; RESET BLOCK SIZE
        SHLD    SIZE
        LDA     NUMBLK
        DCR     A
        STA     NUMBLK
        JRZ     HISTP
        CPI     OFFH
        JRNZ     RADM
        LDA     NUMBLK+1
        DCR     A
        STA     NUMBLK+1
        JMPR    RADM
HISTP:   LDA     NUMBLK+1
        ORA     A
        RZ
        JMPR    RADM
```

```
;
;
;
;
;
;
**** STEPPING MOTOR AHEAD ****
```

```
STEP:   LHLD    STEPS    ; GET # STEPS
        XCHG
STLP:   CALL    STP
        DCX    D
        MOV    A,E
        ORA    D
```

JRNZ STLP
RET

*** LEAP BACKWARD ***

LPBACK: LXI D,1000H ; 400 NUMBERS
SBLP: CALL BSTP
DCX D
MOV A,E
ORA D
JRNZ SBLP
RET

**** STEP MOTOR ONE STEP BACKWARD ****

BSTP: PUSH B
MVI B,2
STPLPB: MVI A,0
CALL POUT
MVI A,2
CALL POUT
MVI A,0
CALL POUT
DCR B
JRNZ STPLPB
POP B
RET

POUT: OUT 0 ; MOTOR LOC'N
WAIT: PUSH B ; SAVE IT
LXI B,02H
WTLP: DCR B
JRNZ WTLP
DCR C
JRNZ WTLP
POP B
RET

**** STEPPING FORWARD ****

STP: PUSH B
MVI B,2
STPLPF: MVI A,4H
CALL POUT
MVI A,6H
CALL POUT
MVI A,4H
CALL POUT
DCR B
JRNZ STPLPF
POP B
RET

```

;
;
; **** ZERO-ING START LOCATION ****
ZERO:  CALL    INCH          ; GET CMD
        CPI     'B'         ; BACK OPE STEP
        JRZ    ZBACK
        CPI     'L'         ; LEAP BACK
        JRZ    ZLEAP
        CPI     'F'         ; ONE STEP FORWARD
        JRZ    ZFORW
        CPI     'J'         ; JUMP FORWARD
        JRZ    ZJUMP
        CPI     CR
        JRZ    ZEND
        MVI    A,BELL
        CALL   OUCH
        JMPR   ZERO
ZBACK:  CALL   BSTP
        JMPR   ZERO
ZLEAP:  CALL   LPBACK
        JMPR   ZERO
ZFORW:  CALL   STP
        JMPR   ZERO
ZJUMP:  LXI    D,1000H
        CALL   STLP
        JMPR   ZERO
ZEND:   DCR    A           ; NON-ZERO RETURN
        RET

```

```

;
;
; **** RETURN TO ORIGINAL START ****
RTURN:  LHLD   NUMBLK+2
        INX    H           ; CORRECT IT
TRTLP:  XCHG
        LHLD   STEPS
        XCHG
        CALL   SBLP
        DCX    H
        MOV    A,L
        ORA    H
        JRNZ  TRTLP
        LXI    D,500H
        CALL   SBLP
        LXI    D,500H
        JMP    STLP

```

```

;
;
; **** CHECKING FOR INPUT ****
INCHEK: CALL   INSTEP
        XRA    A
        CALL   ADDRIV
        XRA    A           ; SET TO 0
        ADD    E           ; ANYTHING ??
        RNZ
        ADD    D           ; OR HERE ??
        JRZ    INCHEK     ; NOPE
        RET

```



```

;
; **** OC ABORT CHECK ****
;
INSTEP: IN      STAT
        ANI     DAT
        RZ
        IN      DAT
        ANI     7FH
        CPI     03H      ; OC
        RNZ
        JMP     NUL      ; ABORT TO CPM
;
;
; **** COMPUTING STEPS PER 'TIC' ****
;
SETSTP: XRA     A        ; CLEAR CARRY
        MOV     A,H      ;
        RLC     ; LEFT INTO CARRY
        MOV     D,A      ; RESULT TO DE
        MOV     A,L
        RLC
        MOV     E,A
        RET
;
;
; **** COMPUTING SAMPLE INTERVAL TIMES ****
;
SETIM:  MOV     A,H      ; COMPLIMENT TO BC PAIR
        CMA
        MOV     B,A
        MOV     A,L
        CMA
        MOV     C,A
        INX     B        ; ..DONE COMPLIMENTING
        LXI     H,MAX    ; 300/SEC
        LXI     D,NUL    ; CLEAR BC PAIR
SETLP:  DAD     B
        MOV     A,H
        ORA     A
        RM      ; RESULT LEFT IN <DE>
        INX     D
        JMPR   SETLP
;
;
; **** COMPUTES ELAPSED TIME ****
;
TICK:   IN      6
        ANI     4H
        JRZ     TICK
        MVI     A,50H
        OUT     6
        RET
;
;
;
TIME:   MOV     A,M
        DCR     A
        MOV     M,A
        JRZ     HITIM
        CPI     OFFH    ; UNDERFLOW ??
        JRNZ   GOODT   ; NO CARRY..NO ZERO

```

```

INX      H
MOV      A,M
DCR      M
RET
HITIM:  INX      H
        MOV      A,M
        ORA      A
        RNZ          ; ZERO..NO CARRY
        PUSH     D
        MOV      E,L
        MOV      D,H
        INX      H
        INX      H          ; LOOK AT SAVED COPY
        MOV      A,M
        STAX     D
        DCX      H
        DCX      D
        MOV      A,M
        STAX     D
        POP      D
        STC          ; SET CARRY
        RET
GOODT:  XRA      A          ; CLEAR EVERYTING
        RET
;
;
;
;
MONIT:  MVI      A,20H    ; SPACE
        CALL     OUCH
        CALL     OUCH
        CALL     OUCH
        MOV      A,D
        CALL     CNVERT
        MOV      A,E
        CALL     CNVERT
        MVI      A,CR
        JMP      OUCH
;
;
;
;
ADAV:   PUSH     H
        LXI     H,NUL
        MVI     B,20H    ; = 32
ADLP2:  PUSH     PSW      ; COLLECT 32 SAMPLES
        CALL     ADDRIV
        POP      PSW
        DAD     D
        DCR     F
        JRNZ    ADLP2    ; END OF SAMPLES
        MVI     B,5H     ; 2**5 = 32
ADLP3:  XRA      A          ; DIVIDING BY 32
        MOV      A,H
        RAR
        MOV      H,A
        MOV      A,L
        RAR
        MOV      L,A
        DCR     B

```

```

JRNZ ADLP3 ; END OF DIVISION
XCHG
POP H ; SAVE RESULT
MOV M,D
INX H
MOV M,E
INX H
RET

```

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```

;
;
; ***** A TO D DRIVER *****
;

```

```

ADDRIV: OUT DSTAT
NOP
ADLP1: IN DSTAT
RRC
JRC ADLP1
IN DDAT
MOV E,A
IN DDAT
ANI 03H
MOV D,A
RET

```

```

;
;
; *** SAVE THE FILENAME ***
;

```

```

SAVEFN: LXI H,SAVFIL ; DESTINATION
LXI D,FCB ; SOURCE
MVI B,11 ; FILENAME + EXT
JMP BLT ; TRANSFER & RET
RESTFN: LXI D,SAVFIL ; SOURCE
LXI H,FCB ; DESTINATION
MVI B,11
JMP BLT

```

```

;
;
; ***** BDOS DRIVERS *****
;

```

```

DMAKE: LXI D,FCB
MVI C,CREATE
CALL BDOS
RET

```

```

;
;
DOPEN: LXI D,FCB
MVI C,OPEN
CALL BDOS
RET

```

```

;
;
DWRIT: LXI D,FCB
MVI C,WRITE
CALL BDOS
RET
;

```

```
;  
DCLOS: LXI    D,FCB  
        MVI    C,CLOSE  
        CALL   BDOS  
        RET  
  
;  
;  
DFIND: XRA    A  
        STA    TEMP    ; CLEAR TEMP  
        LDA    CNT  
        STA    TEMP2   ; GET # OF CHANNELS  
        CALL   SAVEFN  ; SAVE THE FILENAME  
DFLP:  LXI    D,FCB  
        MVI    C,FIND  
        CALL   BDOS  
        INR    A  
        CNZ    SETEMP  ; NONZERO = FILE FOUND  
        CALL   UPFILE  ; UPDATE FILENAME  
        LDA    TEMP2   ; GET COUNT  
        DCR    A  
        STA    TEMP2  
        JRNZ   DFLP    ; STILL MORE TO CHECK  
        CALL   RESTFN  ; RESTORE FILENAME  
        LDA    TEMP    ; FOUND STATUS...0= NONE FOUND  
        DCR    A      ; -1 = NON FOUND  
        RET  
  
;  
;  
SETEMP: MVI    A,DAT   ; NON ZERO  
        STA    TEMP    ; SET IT  
        RET  
  
;  
;  
DERASE: CALL   SAVEFN  
        LDA    CNT  
        STA    TEMP2  
RASLP:  CALL   CLRFN   ; START FRESH  
        LXI    D,FCB  
        MVI    C,ERASE  
        CALL   BDOS  
        CALL   UPFILE  
        LDA    TEMP2  
        DCR    A  
        STA    TEMP2  
        JRNZ   RASLP   ; ERASE THE NEXT ONE  
        CALL   RESTFN  ; RESTORE THE FILENAME  
        RET  
  
;  
;  
; **** INIT MEM LOC'S ****  
;  
INIT:  XRA    A  
        OUT    0      ; TURN OFF MOTOR  
        LXI    H,SHLO  
        LXI    D,START0  
        CALL   SAVEN  
        LXI    D,START1  
        JMP    SAVEN
```

```
;  
; ***** ERROR EXITS AND MSG CALLS *****  
;  
CRERR: LXI D,ERRM1  
JMPR ERRQ  
FLERR: LXI D,ERRM2  
JMPR ERRQ  
WRER: LXI D,ERRM3  
JMPR ERRQ  
MSCER: LXI D,ERRM4  
ERRQ: CALL OUST  
MVI A,BELL ; DINGALING  
CALL OUCH  
JMP NUL
```

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```
;  
;  
;  
;  
;  
UNI: .BYTE 0  
CNT: .BYTE 0  
NUM: .BYTE 0  
SEE: .BYTE 0  
SLOW: .BYTE 0  
OFST: .BYTE 0  
BLKSZ: .BYTE 0  
H0: .BYTE 0  
H1: .BYTE 0  
H2: .BYTE 0  
HH: .BYTE 0  
MM: .BYTE 0  
SS: .BYTE 0  
TEMP: .BYTE 0  
TEMP2: .BYTE 0  
JMPVCT: .WORD 0  
TXTSZ: .WORD 0  
TXTSZ2: .WORD 0  
CST0: .WORD 0  
CSTS0: .WORD 0  
CST1: .WORD 0  
CSTS1: .WORD 0  
SIZE: .WORD 0 ; SAMPLES/BLOCK  
SIZES: .WORD 0  
NUMBLK: .WORD 0,0 ; #BLOCKS/RUN  
STEPS: .WORD 0,0 ; STEPS BETWEEN BLOCKS  
SHL0: .WORD 0  
SHL1: .WORD 0  
SIZ0: .WORD 0  
SIZ1: .WORD 0  
C8600: .BYTE 128,81,1  
C3600: .BYTE 16,14,0  
C60: .BYTE 60,0,0  
C1: .BYTE 1,0,0  
SAVFIL: .BLKB 12  
MON: .BYTE 85  
MONT: .ASCII @ JANUARY 1982 @ ; 0  
MON2: .ASCII @ FEBRUARY 1982 @ ; 17  
MON3: .ASCII @ MARCH 1982 @ ; 34  
MON4: .ASCII @ APRIL 1982 @ ; 51  
MON5: .ASCII @ MAY 1982 @ ; 68
```

MON6: .ASCII * JUNE 1981 * ; 85
MON7: .ASCII * JULY 1981 * ; 102
MON8: .ASCII * AUGUST 1981 * ; 119
MON9: .ASCII * SEPTEMBER 1981 * ; 136
MON10: .ASCII * OCTOBER 1981 * ; 153
MON11: .ASCII * NOVEMBER 1981 * ; 170
MON12: .ASCII * DECEMBER 1981 * ; 187
SMPSC: .ASCII * SAMPLES. SAMPLE PERIOD = *
CLKDT: .ASCII * TIMES 3.3280 MSEC

*
DMSG: .ASCII * SAMPLES/BLK ; *
DM2: .ASCII * BLKS/RUN
*
MSGA: .ASCII *
REVERSE FORWARD

STEP: 'B' 'F'
JUMP: 'L' 'J'

...TO EXIT : <CR> : ? \$*
MSGB: .ASCII *
TO RESET START POINT...<CR>
ELSE ...<SPACE> : ? \$*
MSG4: .ASCII *
UNI- OR BI-POLAR ? (U OR B) : \$*
MSG5: .ASCII *
SET SWITCH TO LEFT (U)*
MSG6: .ASCII *
ADJUST RIGHT POT FOR "0000" (END W/<CR>)*\$*
MSG7: .ASCII *
ADJUST LEFT POT FOR "01FF"*\$*
MSG8: .ASCII *
SET SWITCH TO THE RIGHT (B)*
MSG9: .ASCII *
ADJUST CENTER POT FOR "0200" (END W/<CR>)*\$*
MSG10: .ASCII *
ADJUST LEFT POT FOR "03FF"*\$*
MSGF: .ASCII *
FILE(S) ALREADY ON DISK....RENAME NEW FILE ? \$*
MSGQ: .ASCII *
NEW FILENAME(.EXT) : \$*
MSGW: .ASCII *
OLD FILE(S) WILL BE DESTROYED...ARE YOU SURE ? \$*
MSGs: .ASCII *
FAST OR SLOW MONITOR ?? (F=9600,S=300) : \$*
ERRM1: .ASCII *
CANNOT CREATE FILE....
*
ERRM2: .ASCII *
FILE ERROR.....
\$*
ERRM3: .ASCII *
WRITE ERROR ON DISK \$*
ERRM4: .ASCII *
?????*\$*
MSG12: .ASCII *
TYPE A <CR> WHEN READY.*
MSG14: .ASCII *
ABORT BY TYPING A <C> \$*
MSGR: .ASCII *

```

WANT TO TAKE MORE DATA (Y OR N) : $*
MSGT: .ASCII *
WANT TO MONITOR INPUT ? (Y OR N) : $*
MSGP: .ASCII *
COLLECTION COMPLETE..PLEASE WAIT$*
MSGL: .ASCII *
ONE LINE FOR INPUT >>>* [BELL]
MSGL2: .ASCII *
<CR> ENDS ... <ESC> RESETS ... <RUBOUT> DELETES $*
MSG: .ASCII *
# OF CHANNELS (1-2): $*
MSG0: .ASCII *
SAMPLES PER BLOCK (CHAN 0) : $*
MSG1: .ASCII *
BLOCKS PER RUN : $*
MSG2: .ASCII *
SAMPLES PER SECOND ? (100 MAX) CHAN(#0) :$*
MSGE: .ASCII *
SAMPLES PER SECOND ? (100 MAX) CHAN(#1) :$*
MSG3: .ASCII *
STEPS BETWEEN BLOCKS : $*
TX'BUF: .BLKB 80H ; TEXT BUFFER
;
;
NUL == 00H
DAT == 2H
STAT == 3H
BELL == 07H
CR == 0DH
LF == 0AH
DSTAT == 41H
DDAT == 40H
MAX == 012CH
TO == 0FCH
T1 == T0+1
T2 == T0+2
TT == H()
DD == 0FFFH
M10000 == 0D8F0H
TTHOU == 10000
M1000 == 0FC18H
THOU == 1000
M100 == 0FF9CH
HUND == 100
M10 == 0FFF6H
TEN == 10
START0 == 1000H
OFF0 == 10H
START1 == 90C0H
OFF1 == 90H
;
;
;
;
;
**** BDOS EQUATES ****
;
BDOS == 05H
OPEN == 15 ; -1 IF NOT FOUND
WRITE == 21 ; 0=SUCCESS
; 1=ERROR IN EXTENDING
; 2=NO MORE ROOM

```


APPENDIX B

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APPENDIX B

C
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OZONE.FOR

THIS PROGRAM ACCEPTS Z-80 GENERATED ADC FILES
ORIGINATING FROM DATA TAKEN ON A PERKIN-ELMER
DOUBLE BEAM SPECTROPHOTOMETER AND PLOTS EITHER
TRANSMISSION OR
ABSORPTION COEFFICIENTS VRS. WAVELENGTH OR ENERGY

COMMON/PARAM/NPTS, T, NMBLKS, NSPB, START, STOP
COMMON/PLOT/NPS, XMIN, XMAX, YMIN, YMAX, XGPN, , YGPN,
1XGPOX, YGPOX, NUPAGE, NUGRAF, LNTYP, ISTP, ISYM, IXSCL,
LIYSCL, IT

DIMENSION Y(6500), TIT1(59), TIT2(59), YB(6500)

DIMENSION XA(6500), XDAT(6500), YDAT(6500)

DIMENSION TIT3(59), TIT4(59), TIT5(59)

EQUIVALENCE (YDAT, YB)

DOUBLE PRECISION FNAME, BNAME

DATA TIT1/'E', 'N', 'E', 'R', 'G', 'Y', ' ', ' ('
1, 'E', 'V', ')', 48* ' ' /

DATA TIT2/'A', 'B', 'S', 'O', 'R', 'P', 'T', 'I', 'O', 'N'
1, 49* ' ' /

DATA TIT3/'T', 'R', 'A', 'N', 'S', 'M', 'I', 'S', 'S'
1, 'I', 'O', 'N', 47* ' ' /

DATA TIT4/'W', 'A', 'V', 'E', 'L', 'E', 'N', 'G', 'T', 'H'
1, ' ', '(', 'A', 'N', 'G', 'S', 'T', 'R', 'O', 'M', 'S', ')'
1, 37* ' ' /

DATA TIT5/'W', 'A', 'V', 'E', 'N', 'U', 'M', 'B', 'E',
1'R', ' ', '(', 'C', 'M', '-', '1', ')', 42* ' ' /

C
C
C

TYPE 78

FORMAT(1X/1X'PLOT TRANSMISSIONS(1) ABSORP. COEF.

1(2) INDUCED ABSORB.(3) DIFFERENCE(4)?:'\$)

ACCEPT *, PLOT

NORM=0

IF(PLOT.EQ.1.OR.PLOT.EQ.2.OR.PLOT.EQ.4) GO TO 1000

TYPE 15

15 FORMAT (1X, /1X, 'TYPE IN PRE-IRRAD. FILE NAME:'\$)

ACCEPT 6, BNAME

CALL READ(YB, BNAME)

1000 TYPE 5

5 FORMAT (' TYPE IN FILE NAME:'\$)

ACCEPT 6, FNAME

6 FORMAT (A10)

CALL READ(Y, FNAME)

```

IF(PLOT.EQ.4) TYPE 5
IF(PLOT.EQ.4) ACCEPT 6, FNAME
IF(PLOT.EQ.4) GO TO 664
TYPE 18
18  FORMAT(1X/1X'NORMALIZE ? FILENAME?')
ACCEPT *, NORM
IF(NORM.EQ.1) ACCEPT 6, BNAME
664  IF(NORM.EQ.1) CALL READ(YB,BNAME)
IF(PLOT.EQ.4) CALL READ(YB,FNAME)
IF(NORM.NE.1) GO TO 82
DO 66 IJ=1,NPTS
IF(YB(IJ).LE.0.80) YB(IJ)=YB(IJ-1)
66  Y(IJ)=Y(IJ)/YB(IJ)
82  IF(PLOT.EQ.4) CALL DIFF(Y,YB)
IF(PLOT.EQ.1.OR.PLOT.EQ.4) GO TO 2000
IF(PLOT.EQ.2) GO TO 1001
CALL INDABS(Y,YB)
GO TO 3
1001 CALL ABSORP(Y)
3  CONTINUE
2000 TYPE 300
300  FORMAT(1X/1X'SMOOTH DATA N TIMES..ENTER N')
ACCEPT *, NSMOOT
IF(NSMOOT.EQ.0) GO TO 301
DO 17 I=1,NSMOOT
17  CALL SMOOTH(Y,NPTS)
301  NUPAGE='YES'
NUGRAF='YES'
IXSCL=1
IYSCL=1
224  XGPON=1.
YGPON=1.
XGPOX=7.5
YGPOX=5.5
XHLPOS=2.75
YHLPOS=.25
XVLPOS=0.
YVLPOS=5.0
IT=5
911  TYPE 173
173  FORMAT(1X/1X'YMIN,YMAX ?')
ACCEPT *, YMIN,YMAX
TYPE 177
177  FORMAT(1X/1X'X-AXIS: ENERGY(EV) (1), WAVELENGTH
(2),
1WAVENUMBER (3) ?:'$)
ACCEPT *, NIX
CALL XCALIB(XA,NIX)
TYPE 189
189  FORMAT(1X/1X'ENTER XMIN XMAX')
ACCEPT *, XMIN,XMAX
178  LNTYP=-4
ISTP=1
ISYM=0
L1=1

```

```

TYPE 70
70  FORMAT(1X/1X'TAKE EVERY --TH POINT')
    ACCEPT *, NSKIP
    DO 62 K=1,NPTS,NSKIP
    XDAT(L1)=XA(K)
    YDAT(L1)=Y(K)
62  L1=L1+1
    NPS=L1-1
188  CALL PLTGEN(XDAT,YDAT)
    IF(NIX.EQ.2) CALL LABL(XHLPOS,YHLPOS,'H',TIT4,0.)
    IF(PLOT.EQ.1) CALL LABL(XVLPOS,YVLPOS,'V',TIT3,0.)
    IF(NIX.EQ.1) CALL LABL(XHLPOS,YHLPOS,'H',TIT1,0.)
    IF(PLOT.EQ.2) CALL LABL(XVLPOS,YVLPOS,'V',TIT2,0.)
    IF(NIX.EQ.3) CALL LABL(XHLPOS,YHLPOS,'H',TIT5,0.)
    NUPAGE='NO'
    NUGRAF='NO'
67  CONTINUE
    CALL MOVABS(600,710)
    CALL ANMODE
    TYPE 1234, FNAME
1234 FORMAT(1XA10)
    CALL TINPUT(KL)
    CALL ERASE
    NUPAGE='YES'
    NUGRAF='YES'
    TYPE 142
142  FORMAT(1X/1X'GRAPH AGAIN ?')
    ACCEPT *, GRAG
    IF(GRAG.EQ.1) GO TO 911
    TYPE 63
63  FORMAT (1X/' CHOOSE ANOTHER FILE? YES(1) NO(0)'/)
    ACCEPT 2, IANS
2    FORMAT(I5)
    IF (IANS.EQ.1) GO TO 68
    CALL EXIT
    END

```

C
C
C

```

SUBROUTINE INDABS(Y,YB)
COMMON/PARAM/NPTS,T,NMBLKS,NSPB,START,STOP
DIMENSION Y(1),YB(1)
TYPE 16
16  FORMAT (1X/1X,'THICKNESS OF SAMPLE (IN CM)'/)
    ACCEPT *, T
    T=1/T
44  DO 4 K=1,NPTS
11  XX=1/Y(K)
    TD2=XX**2
    Y(K)=ALOG(XX)
    Y(K)=T*Y(K)
    XX1=1/YB(L)
    TB2=XX1**2
    XX2=ALOG(XX1)
    XX2=T*XX2

```

```

Y(K)=Y(K)-XX2
4 CONTINUE
RETURN
END

```

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```

SUBROUTINE READ(Y,FNAME)
COMMON/PARAM/NPTS,T,NMBLKS,NSPB,START,STOP
DIMENSION Y(1),N(6500)
DOUBLE PRECISION FNAME
TYPE 100
100 FORMAT(1X/1X'SUBROUTINE READ')
OPEN(UNIT=23,FILE=FNAME)
READ(23,*) NMBLKS,NSPB,NPTS,START,STOP
READ(23,200) (N(K),K=1,NPTS)
200 FORMAT(8(I4,1X))
DO 10 I=1,NPTS
Y(I)=N(I)/1023.
10 CONTINUE
CLOSE(UNIT=23,FILE=FNAME)
RETURN
END

```

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```

SUBROUTINE XCALIB(X,NIX)
COMMON/PARAM/NPTS,T,NMBLKS,NSPB,START,STOP
DIMENSION X(1)
TYPE 500
500 FORMAT(1X/1X'SUBROUTINE XCALIB')
DO 4 K=1,NPTS
ZIP=START-FLOAT(K)*(START-STOP)/NPTS
XX3=ZIP*1.0E-8
IF(NIX.EQ.1)X(K)=((2.9979E10/XX3)*6.6256E-27)/1.6E-12
IF(NIX.EQ.2) X(K)=ZIP
IF(NIX.EQ.3) X(K)=1./XX3
4 CONTINUE
RETURN
END

```

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```

SUBROUTINE ABSORP(Y)
COMMON/PARAM/NPTS,T,NMBLKS,NSPB,START,STOP
DIMENSION Y(1)
TYPE 77
77 FORMAT(1X/1X'BASE 10(1) OR BASE E(2) ?:$')
ACCEPT *,BASE
TYPE 16
16 FORMAT(1X/1X,'OPTICAL PATH LENGTH (IN CM):$')
ACCEPT *,T
T=1/T
TYPE 22

```

```

22  FORMAT(1X/1X'ENTER TEMP(KELVIN) AND
PRESSURE(CM):'$)
    ACCEPT *, TEMP ,SP
    STP=76*TEMP/(SP*273)
44  DO 4 K=1,NPTS
    IF(Y(K).LE.0.0) Y(K)=Y(K-1)
11  XX=1/Y(K)
    IF(BASE.EQ.1) GO TO 66
    Y(K)=STP*T*ALCG(XX)
    GO TO 4
66  Y(K)=STP*T*ALOG10(XX)
    4 CONTINUE
    RETURN
    END

```

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```

SUBROUTINE DIFF(Y,YB)
COMMON/PARAM/NPTS,T,NMBLKS,NSPB,START,STOP
DIMENSION Y(1),YB(1)
FRAC=76./273.
TYPE 10
10  FORMAT(1X/1X'SUBROUTINE DIFF')
TYPE 20
20  FORMAT(1X/1X'ENTER P1,T1 AND P2,T2:$)
    ACCEPT *, P1,T1,P2,T2
TYPE 60
60  FORMAT(1X/1X'ENTER OPTICAL PATH LENGTH (CM):'$)
    ACCEPT *, T
    T=1./T
    DO 11 I=1,NPTS
    ARG=(YB(I)**(T2/P2) / Y(I)**(T1/P1))
    Y(I)=ALOG10(ARG)*T*FRAC
11  CONTINUE
    RETURN
    END

```