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SEMI-ANNUAL TECHNICAL REPORT
INVESTIGATION OF THE ABSORPTION OF INFRARED RADIATION BY ATMOSPHERIC GASES

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Publication U-4784

Amount of Contract: $148,145
Effective Date: 15 May 1969
Expiration Date: 14 July 1970
Program Element: 62301 D

31 January 1970

SEMI-ANNUAL TECHNICAL REPORT
INVESTIGATION OF THE ABSORPTION OF INFRARED RADIATION BY ATMOSPHERIC GASES

Principal Investigator and Project Scientist: Darrell E. Burch
(714) 833-1611 Ext. 2832

Approved: Paul M. Sutton
Paul M. Sutton, Manager
Physics and Chemistry Laboratory

Sponsored by: Advanced Research Projects Agency
ARPA Order 1366 Amendment 1

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This research was supported by the Advanced Research Projects Agency of the Department of Defense and was monitored by Air Force Cambridge Research Laboratories under Contract No. F19628-69-C-0263

ABSTRACT

The continuum absorption by H_2O between 800 and 1250 cm^{-1} and by CO_2 from 780 to 900 cm^{-1} has been measured. The continuum results from the extreme wings of very strong absorption lines centered outside the 800-1250 cm^{-1} interval. Experimental results are compared with calculated values based on various line shapes. The extreme wings of N_2-broadened H_2O lines produce less than 0.005 as much continuum absorption as self-broadened H_2O lines at the same pressure. Self-broadened H_2O lines absorb more than Lorentz-shaped lines, but the wings of self-broadened CO_2 lines absorb only approximately 0.01 as much in the 780-900 cm^{-1} region as if they had the Lorentz shape. The shapes of the wings of the CO_2 lines which produce the continuum between 780 and 900 cm^{-1} are similar to those near 2400 cm^{-1} for both self broadening and N_2 broadening. Suggestions on methods for using the results for atmospheric transmission calculations are given.

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SECTION 1

INTRODUCTION AND SUMMARY

The 8-14 μ (1250-700 cm^{-1}) window is bounded on the low wavenumber side by the very strong ν_2 CO_2 band centered near 667 cm^{-1}. Between 900 and 1100 cm^{-1} are two bands, $00^01 \leftarrow 10^00$ and $00^01 \leftarrow 02^00$, which have received much attention the past few years because they are involved in the CO_2 laser. Absorption in the intermediate region, from approximately 700 to 900 cm^{-1}, results from several, weak bands and the continuum which is due to extreme wings of lines of the ν_2 band. Section 2 of this report presents the results of an experimental investigation of the CO_2 continuum between 780 and 900 cm^{-1}. The continuum absorbs only about 1 percent as much as it would if all the lines in the ν_2 band had the Lorentz shape. At 296K the extreme wings of these lines are apparently similar in shape to the lines of the ν_3 band near 2400 cm^{-1}. Measurements at 240K indicate that the continuum increases with decreasing temperature at a faster rate than is predicted by simple theories on line broadening. Results are presented for both self broadening and N_2 broadening. Since the earth's atmosphere is approximately 80 percent similar to that by N_2, it is probably safe to assume that N_2 broadening applies to the atmosphere.

Until recently the upper atmosphere where the H_2O concentration is low was believed to be very transparent near 865 cm^{-1} where the CO_2 absorption is minimum. However, Murcray et al,[1] using a balloon-borne spectrometer, have found that HNO_3 occurs in the stratosphere and absorbs in this region. Carbon dioxide is the primary absorber on the low wavenumber side of the HNO_3 band while CO_2 and O_3 absorb on the high wavenumber side between 900 and 1100 cm^{-1}.

Between 900 and 1800 cm^{-1}, the absorption by CO_2 is very weak and probably negligible in comparison to absorption by CH_4, N_2O, and H_2O in the same

region. The CO_2 absorption is due primarily to two pressure-induced bands of the $C^{12}O_2^{16}$ molecule and to two very weak bands of $C^{12}O^{16}O^{18}$. Results of an experimental study of this region will be reported within the next few weeks.

Although the absorption by H_2O is relatively weak in the 700-1250 cm^{-1} window, many weak absorption lines occur throughout this region. For most atmospheric paths, particularly in the lower atmosphere, the absorption by these weak lines is less than the continuum absorption due to the extreme wings of very strong H_2O lines centered on both sides of the window. Section 3 of this report gives results of an experimental investigation of the continuum absorption by pure H_2O. The absorption is not predictable by theory based on line shapes ordinarily used. As in the case of CO_2, the temperature dependence of the continuum is also not predictable by theory.

SECTION 2

CONTINUUM ABSORPTION BY CO_2 BETWEEN 780 AND 900 cm^{-1}

Samples of pure CO_2 and $CO_2 + N_2$ were contained in either of two multiple-pass absorption cells. The longer cell was operated at room temperature, 296K, with path lengths from 123 m to 1185 m and at pressures up to 1.5 atm. The shorter cell provided path lengths between 4.2 and 32.9 m at pressures as high as 14.6 atm. Temperatures in the short cell varied between 296K and 240K. Refrigeration was provided by liquid nitrogen flowing in tubing coiled through a mixture of water and ethylene glycol in which the absorption cell was submerged. The absorption cells joined a grating spectrometer built into a vacuum tank to avoid absorption by atmospheric gases. Reference 2 describes the apparatus and experimental techniques in more detail.

Representative spectral curves for two samples are shown in Fig. 2-1. The continuum absorption due to the extreme wings of very strong lines whose centers occur below 760 cm^{-1} is indicated by the broken curves. The samples represented in Fig. 2-1 are essentially opaque between approximately 600 cm^{-1} and 800 cm^{-1} as a result of the very strong lines in that interval. The continuum absorption for a single sample cannot be determined from its spectral curve alone, but it can be determined from samples covering a wide range of pressures.

The transmittance $T(\nu)$ at wavenumber ν is given by

$$T(\nu) = \exp\left[-u\kappa(\nu)\right], \qquad \text{or} \qquad -\ln T(\nu) = u\kappa(\nu). \tag{2-1}$$

The absorber thickness u is expressed in molecules cm^{-2} and is proportional to the product of path length and CO_2 pressure, p, with a slight correction

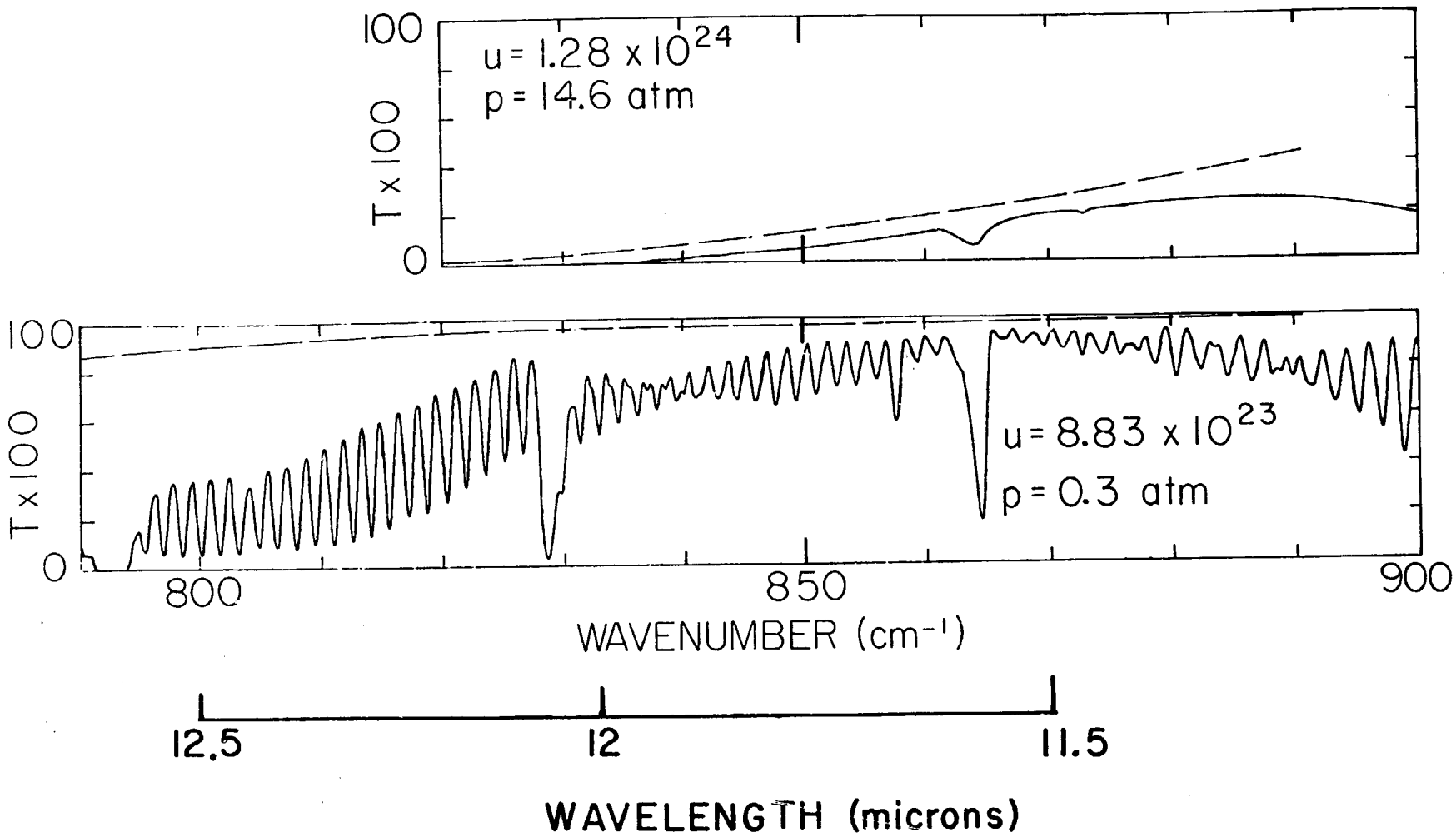

FIG. 2-1. Representative spectral curves of two samples of pure CO_2. Values of u are in molecules cm^{-2}. The broken curves represent the transmittance of the continuum due to lines centered below 760 cm^{-1}. Beyond 900 cm^{-1} the transmittance of the local lines decreases because of the $00^01 \leftarrow 10^00$ band centered near 961 cm^{-1}.

factor $(1 + 0.005p)$ to account for the non-linear relationship between CO_2 pressure and density. It follows that the units for the absorption coefficient $\kappa(\nu)$ are $mol^{-1}\ cm^2$.

In the spectral region of interest, where there is absorption by the continuum and by the nearby, or local, lines,

$$\kappa = -(1/u)\ln T = \kappa(\text{local}) + C. \qquad (2\text{-}2)$$

The portion of the absorption coefficient due to the local absorption lines is denoted by $\kappa(\text{local})$, and C is the continuum absorption coefficient. It is understood the T, κ, and C are functions of ν; however, for simplicity $T(\nu)$ is written as T, $\kappa(\nu)$ as κ, etc. The remainder of this section deals with the continuum portion of the absorption coefficient, although $\kappa(\text{local})$ was determined at several wavenumbers in order to solve for C in Eq. (2-2) after substituting values for the observed transmittance.

The absorption coefficient of the wing of a collision-broadened line is known to be proportional to pressure; therefore, we expect the continuum coefficient for a mixture of p atm of CO_2 and p_N atm of N_2 to be given by

$$C = C_S^o\, p + C_N^o\, p_N. \qquad (2\text{-}3)$$

The self-broadening and N_2-broadening coefficients normalized to 1 atm are denoted by C_S^o and C_N^o, respectively.

Before C can be found from a spectral curve, we must determine $\kappa(\text{local})$, which, for sample pressures less than a few atm, varies rapidly with wavenumber because of the line structure. Since the spectral slitwidth of the spectrometer was greater than the line widths at the low pressures, $\kappa(\text{local})$ could not be measured directly at a given point. It is known from line-broadening theory that the average of $\kappa(\text{local})$ over an interval containing one or more lines is essentially independent of pressure if the interval contains all the lines contributing to the absorption. Therefore, the average transmittances $\bar{T}$ of intervals approximately 3-5 cm^{-1} wide were used instead of transmittances read from points on the spectral curves. If we consider only the transmittance of the local lines, $(-1/u)\ln \bar{T}(\text{local})$ is equivalent to $\kappa(\text{local})$. However, we do not read $\overline{\ln T}$ from a spectral curve, but a slightly different quantity, $\ln \bar{T}$. The difference between these two quantities decreases with wider lines, and thus with increasing pressure; it also decreases with increasing average transmittance by the lines. We first assumed $\ln \bar{T} = \ln \bar{T}(\text{local}) + \ln \bar{T}(\text{continuum})$, and that $(-1/u)\ln \bar{T}(\text{local}) = \bar{\kappa}(\text{local})$ to calculate C and an approximate value for $\kappa(\text{local})$ by the method described below. The positions and approximate widths of the lines are known, so that by applying simple, band-model theory, we were able to calculate a corrected $\bar{\kappa}(\text{local})$ and to adjust the values of $\bar{T}$ which were then used to determine C. The correction was

usually small since the continuum was determined at wavenumbers of minimum absorption by the local lines. At 14.6 atm, the maximum pressure used, C was usually from 3 to 10 times as great as κ(local), so that errors in κ(local) did not introduce large errors in C.

For self broadening, we typically used two samples of pure CO_2, one at less than 5 atm and one at more than 10 atm. At each narrow interval where the continuum was measured, the contribution of κ(local) was the same for both samples, with a small correction made for the line structure as discussed above. If we indicate the parameters of the two samples by subscripts 1 and 2, and use T to denote the average transmittance over the narrow intervals,

$$C_S^o = \frac{1}{p_2 - p_1}\left[\frac{1}{u_1}\ln T_1 - \frac{1}{u_2}\ln T_2\right]. \tag{2-4}$$

After solving for C_S^o, κ(local) could be found from Eqs. (2-2) and (2-3). Several pairs of samples were used to determine C_S^o at each of the narrow intervals. Because of the wide variation in absorption across the interval investigated, each pair of samples usually provided reliable data at only two or three different intervals. The path lengths were typically adjusted so that the transmittance was between 0.2 and 0.8 in order to minimize the uncertainty in ($-\ln T$) due to errors in reading the spectral curves and in placing the 100 percent transmittance curve.

Values of C_N^o were determined by comparing the transmittance, T_1, of a pure CO_2 sample with T_2, the transmittance of the sample after N_2 had been added to it. It follows from Eqs. (2-2) and (2-3) that

$$C_N^o = \left(\frac{1}{u\ p_N}\right)\left(\ln T_1 - \ln T_2\right). \tag{2-5}$$

Most of the local lines between 780 and 900 cm^{-1} arise from transitions from excited vibrational states. Consequently, the line strengths decrease rapidly with decreasing temperature, and the correction for the local lines was less severe at 240K than at 296K. At temperatures significantly above 296K, the contribution of the local lines would dominate, making the continuum difficult to measure accurately.

The experimental results for self broadening are summarized in Fig. 2-2 for the two temperatures where measurements were made. The points are at the centers of the narrow intervals where the continuum was computed from the spectral curves. Some of the plotted points represent averages of several measurements. The most careful measurements were made near 873 cm^{-1} where the local lines absorb the least. Large samples were used to determine κ(local), C_S^o and C_N^o at this point. These values were then used to adjust the position of the 100 percent transmittance curves for the smaller samples.

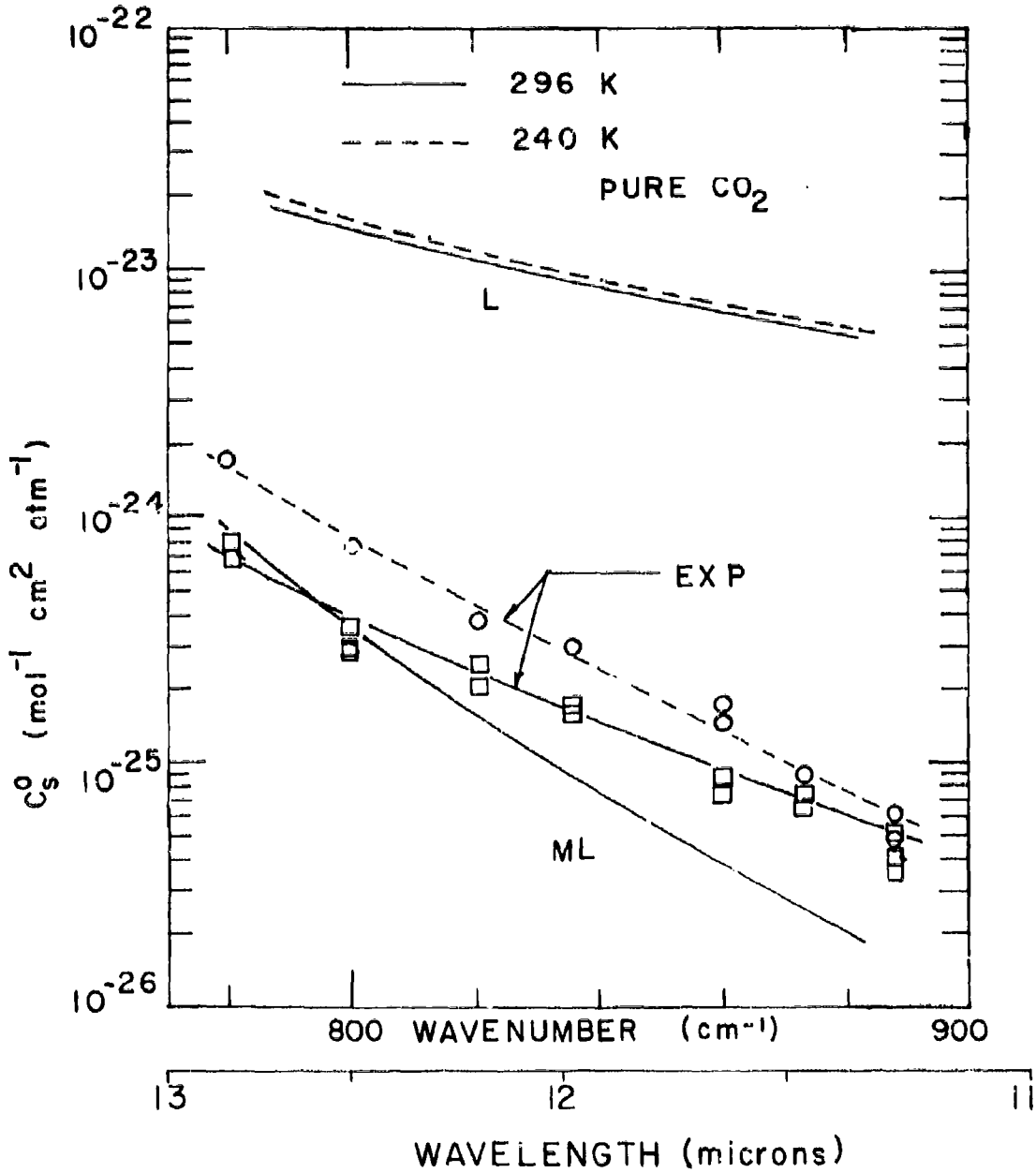

FIG. 2-2 Normalized absorption coefficient for the continuum due to self-broadened CO_2 lines. The experimental results for samples at 296K and 240K are indicated. The calculated continuum based on the Lorentz line shape is indicated by the curves labelled L; ML denotes the calculated continuum based on the modified Lorentz shape used in Ref. 2 to describe the shapes of self-broadened CO_2 lines near 2400 cm^{-1}. The modified Lorentz curves for both temperatures are essentially coincident.

In order to ensure that the continuum curve we obtained represented only the contribution due to lines centered below 760 cm^{-1}, we used tabulated strengths of the lines within the 760-900 cm^{-1} interval to estimate their contributions to the observed results (See Reference 3). Line shapes based on previous work[4] in our laboratory were used for the wings of the lines. Except for the Q-branches, the contributions of lines more than 5 cm^{-1} from the points of measurement were negligible. The distances from the Q-branches to the points of observation are several times the half-widths of the lines; therefore, the contribution of the Q-branches to the absorption coefficient is proportional to pressure, and cannot be distinguished from the continuum due to very distant lines. The calculated contributions of the Q-branches were subtracted from the observed results so that the experimental curves represent only the continuum due to lines centered below 760 cm^{-1}. The correction varied with temperature and position; it was usually less than 10 percent and never more than 25 percent of the observed results.

A few reduced-temperature measurements were made when the samples varied by a few degrees Kelvin from 240K. These results were adjusted to 240K in accordance with the temperature dependence discussed below and are included as 240K data.

Figure 2-2 also includes three curves of the calculated continuum absorption coefficient. The curves labelled with an L represent values calculated by assuming that all of the strong lines between 500 and 760 cm^{-1} have the Lorentz shape. The strengths and widths of these lines are reasonably well known, so that the large deviation between the calculated and experimental values can be attributed to deviations from the Lorentz line shape. It is quite significent that the observed continuum near 890 cm^{-1} is nearly two orders of magnitude less than the calculated value based on the Lorentz shape.

Also shown in Fig. 2-2 is a curve based on a modified-Lorentz line shape derived from measurements of the CO_2 continuum near 2400 cm^{-1} due to the extreme wings of strong lines in the ν_3 band.[4] The modified-Lorentz shape from Reference 4 corresponds to 296K. No modified shape has been determined for the 2400 cm^{-1} region at reduced temperatures, so the same shape was used for calculations at both temperatures. The experimental curve for 296K agrees well with the modified-Lorentz curve from approximately 780 to 820 cm^{-1}, but at higher wavenumbers, the experimental curve lies well above the calculated one. The modified-Lorentz curve near 900 cm^{-1} is strongly dependent on the assumed shapes of lines more than 200 cm^{-1} from their centers. The uncertainty in the modified shape at such large distances is great; therefore, the factor of 2 between the experimental and calculated continuum is not necessarily surprising.

Figure 2-3 shows corresponding curves for N_2 broadening. As for self broadening, the experimental values are approximately 2 orders of magnitude

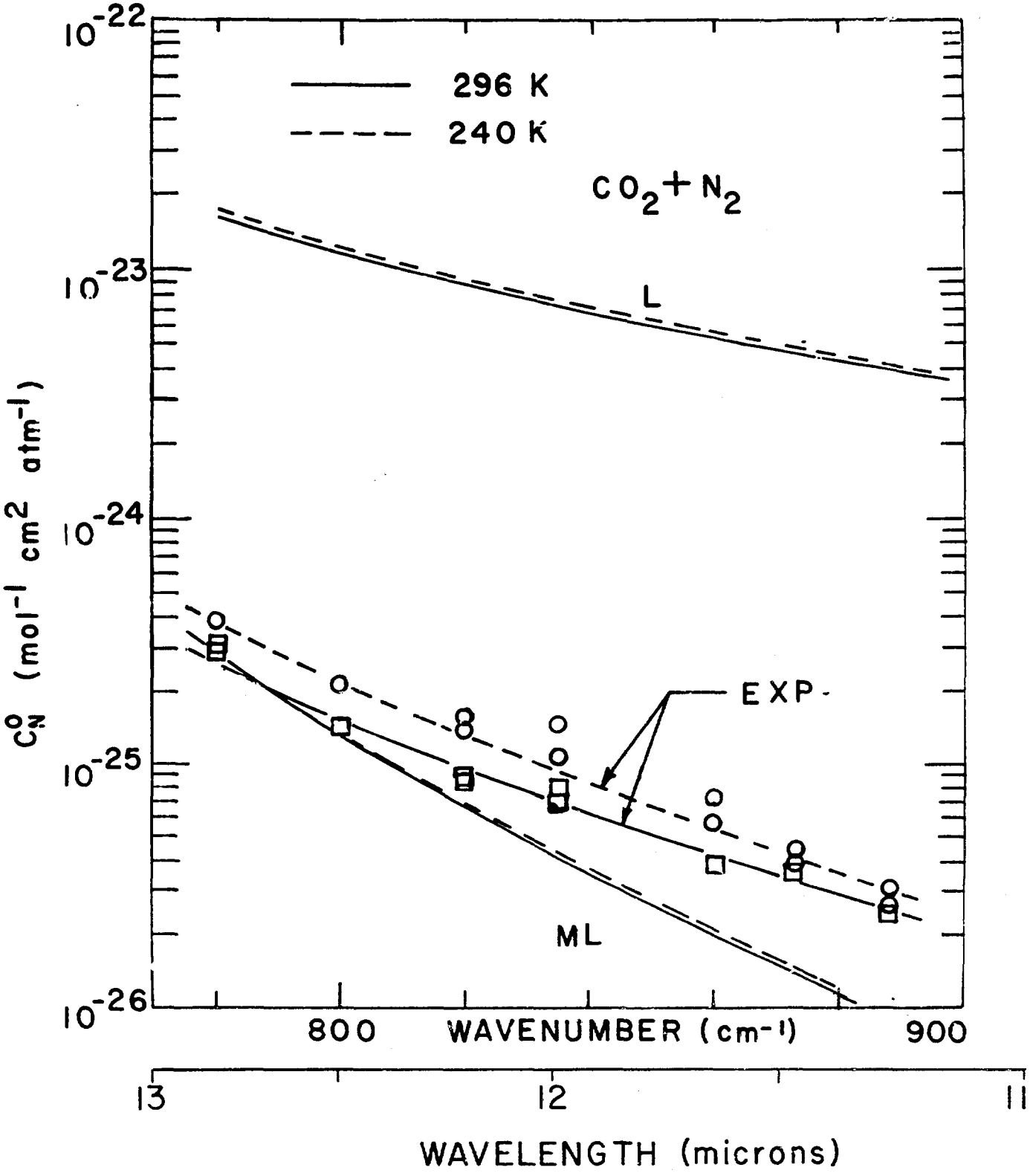

FIG. 2-3. Normalized absorption coefficient for the continuum due to N_2-broadened CO_2 lines. The experimental results for samples at 296K and 240K are indicated. The calculated continuum based on the Lorentz line shape is indicated by the curves labelled L; ML denotes the calculated continuum based on the modified Lorentz shape used in Ref. 2 to describe the shapes of N_2-broadened CO_2 lines near 2400 cm^{-1}.

below those calculated on the basis of the Lorentz line shape. The experimental points also agree well with the modified-Lorentz prediction between approximately 780 and 820 cm^{-1}, and, as for the self-broadening curves, the experimental curve lies above the calculated curve at higher wavenumbers.

The sum of the strengths of all of the lines used to calculate the continuum is 90.6×10^{-19} mol^{-1} cm^2 cm^{-1}. The half-widths of the lines normalized to one atm pressure were assumed to be 0.09 cm^{-1} for self broadening and 0.07 cm^{-1} for N_2 broadening at 296K. Changes in the strengths and widths of the lines with temperature were accounted for in the calculations. The strengths are based on data from Kyle[3] and the half-widths normalized to 1 atm were assumed to vary inversely as the square-root of temperature, θ.

Values from the smooth, experimental curves in Figs. 2-2 and 2-3 are listed in Table 2-1. The estimated uncertainty in the tabulated values is 10 to 15 percent. The major sources of error are in locating the proper 100 percent transmittance curve and in accounting for the local lines. At 240K, the measurements were somewhat less reproducible than at 296K because the optics were less stable; but on the other hand, the correction for the local lines was less at the reduced temperature.

The continuum absorption is seen to increase significantly as the temperature decreases, although the calculated continuum shows only a slight temperature dependence. This experimental result is consistent with the findings in the previous study[4] of the continuum near 7000 cm^{-1}. The temperature dependence on the continuum is greater at the lower wavenumber end of the interval than at the higher wavenumbers. We have derived a simple, empirical equation which is shown as a footnote of Table 2-1 to relate the continuum to temperature. The constant, τ, which is a function of ν, was found by substituting the values from the smooth curves for experimental points at 296K and 240K into the empirical equation. Although no physical significance can be attached to τ_S or τ_N, the empirical equation is probably valid for temperatures between approximately 220K and 320K, which covers nearly any situation encountered in the earth's atmosphere. A limited number of data points obtained near 273K agree with the empirical equation within experimental error.

Application to Atmospheric Transmission Calculations

It is probably safe to assume that C_N^o, the normalized N_2-broadening coefficient is appropriate for air which consists of approximately 80% N_2 with only 0.03% CO_2. According to Eqs. (2-2) and (2-3) the transmittance of the continuum for an atmospheric path at constant temperature and pressure can be found from

$$-\ln T = u\, C_N^o\, p_{air}, \quad \text{(continuum)}$$

where C_N^o is determined from Table 2-1 for the appropriate temperature, and u is the CO_2 absorber thickness. Slant paths, or any path of non-uniform temperature or pressure, can be divided into layers, each of which can be considered uniform. The value of $-\ln T$ for the continuum for the entire path is the sum of the corresponding quantities for each layer.

The transmittance at any wavenumber is the product of the transmittances of the continuum and the local lines. The continuum as given in Table 2-1 accounts for all the lines centered outside the 789-900 cm^{-1} interval. Calculating the transmittance of the local lines can be done by several methods, including the use of band models, or line-by-line techniques or combinations of these. The line-by-line method involves summing the contributions of all the lines at points chosen sufficiently close together that the line structure is retained. Since previous work[4] in our laboratory showed that N_2-broadened CO_2 lines deviate from the Lorentz shape within less than 1 cm^{-1} from the line centers, the Lorentz shape is not appropriate for the wings of the lines and should not be used. In accordance with the previous work, the values of χ listed in Table 2-2 should be substituted into the following equation to determine the absorption coefficient k for each line at a distance $|\nu-\nu_o|$ from ν_o, the line center. Values of χ for $|\nu-\nu_o|$ between the values listed can be found by interpolation.

$k = k_L \chi$, where k_L is the Lorentz coefficient,

$$k_L = \frac{S}{\pi} \frac{\alpha}{(\nu-\nu_o)^2 + \alpha^2}.$$

The absorption coefficient for all the local lines is found by summing the values of k for each line.

The strength of the lines is denoted by S, and the half-width by α. The line parameters S and α for most of the lines between 780 and 900 cm^{-1} have been calculated by Drayson and compiled by Kyle.[3] Preliminary comparisons of the calculated values with some experimental results obtained recently in our laboratory show fair agreement. We plan to adjust the strengths of many of the lines to be consistent with the experimental results and publish the revised values within the next few months.

Considerable computer time can be saved in a line-by-line method without introducing significant error by excluding the contribution of the extreme wings of the local lines. Because of the high concentration of lines in the Q-branches, these lines produce a significant portion of the absorption at points further from their centers than do the other local lines. The absorption coefficient at any point can be approximated by including the calculated contribution by the continuum, the three Q-branches near

793, 828, and 864 cm^{-1}, and the local lines centered within 5 cm^{-1} of the wavenumber of interest. The other local lines may be excluded.

The criteria for truncating the contribution of each line is only approximate but is based on maintaining the error due to truncation less than 3 or 4 percent of the total absorption coefficient. It is clear that lines could be truncated closer in some regions than in others, and that the distance depends on temperature since the local lines and the continuum vary quite differently with temperature. More complicated criteria could be developed to save even more computer time; however, the ones given above are simple to apply and probably adequate.

TABLE 2-1

CONTINUUM ABSORPTION COEFFICIENTS

ν cm^{-1}	$C_S^o \times 10^{26}$ (at 296K)	$C_S^o \times 10^{26}$ (at 240K)	τ_S	$C_N^o \times 10^{26}$ (at 296K)	$C_N^o \times 10^{26}$ (at 240K)	τ_N
780	78	161	3.5	26	37.1	1.7
790	55.9	112	3.4	20	28.8	1.8
800	40.7	80	3.3	15.5	22.3	1.8
810	30.4	58	3.1	12.4	17.5	1.7
820	23.4	42.5	2.9	10	13.7	1.6
830	18.2	31.3	2.6	8.1	10.8	1.4
840	14.3	23.1	2.3	6.7	8.6	1.2
850	11.3	17.4	2.1	5.5	6.9	1.1
860	9.0	12.8	1.7	4.52	5.5	0.92
870	7.1	9.7	1.5	3.75	4.37	0.76
880	5.7	7.3	1.2	3.0	3.49	0.59
890	4.52	5.5	0.96	2.59	2.0	0.37

Values of C_S^o and C_N^o are in mol^{-1} cm^2 atm^{-1}; τ_S and τ_N are dimensionless. From the data at two different temperatures, we have derived values for τ_S so that C_S^o can be calculated at other temperatures by use of the following equation:

$$C_S^o(\theta) = C_S^o(296K) \left[\theta/296\right]^{-\tau_S}.$$

Corresponding values of τ_N are also given for N_2 broadening. No physical significance is attached to τ_S and τ_N. The empirical equation is probably adequate for temperatures encountered in the earth's atmosphere, but is not recommended for more extreme temperatures.

TABLE 2-2

MODIFICATION FACTOR FOR ATMOSPHERIC CO_2 LINES

$\lvert\nu-\nu_o\rvert$ (cm^{-1})	χ
0.	1.00
0.5	1.00
0.6	0.96
0.7	0.89
0.8	0.82
0.9	0.77
1.0	0.70
1.2	0.60
1.5	0.50
2.0	0.41
2.5	0.36
3.0	0.31
5.0	0.29
8.0	0.23
10.0	0.19

SECTION 3

CONTINUUM ABSORPTION BY H_2O BETWEEN 800 AND 1250 cm^{-1}

Figure 3-1 shows a representative spectrum of H_2O in the 800-1250 cm^{-1} region. The H_2O absorption in this region is different than in most regions since a significant portion of it is due to the extreme wings of much stronger lines whose centers occur outside the region. These extreme wings give rise to the continuum absorption which can be approximated by drawing a smooth envelope curve through the points of maximum transmittance. Within the region there are several narrow intervals at which the influence of lines closer than a few cm^{-1} is much less than the continuum absorption. The continuum has been investigated by making measurements at these small window regions.

Calfee and Benedict[5] have calculated the strengths and widths of all the H_2O lines in a wide range of wavelengths, including the 8-12 μ interval. These calculations are based in part on atmospheric spectra obtained with the sun as a radiation source. Although the calculated strengths and widths of many of these lines may require adjusting as better experimental results become available, they are generally known well enough that reliable absorption calculations can be made. The remainder of this section deals with the continuum absorption, which has received most of the attention in the H_2O study since least was known about it.

As discussed in Section 2, the transmittance of the continuum for an $H_2O + N_2$ mixture is related to the absorber thickness u and the normalized absorption coefficients by

$$(-1/u)\ln T = C = C_S^o\, p + C_N^o\, p_N. \qquad (3\text{-}1)$$

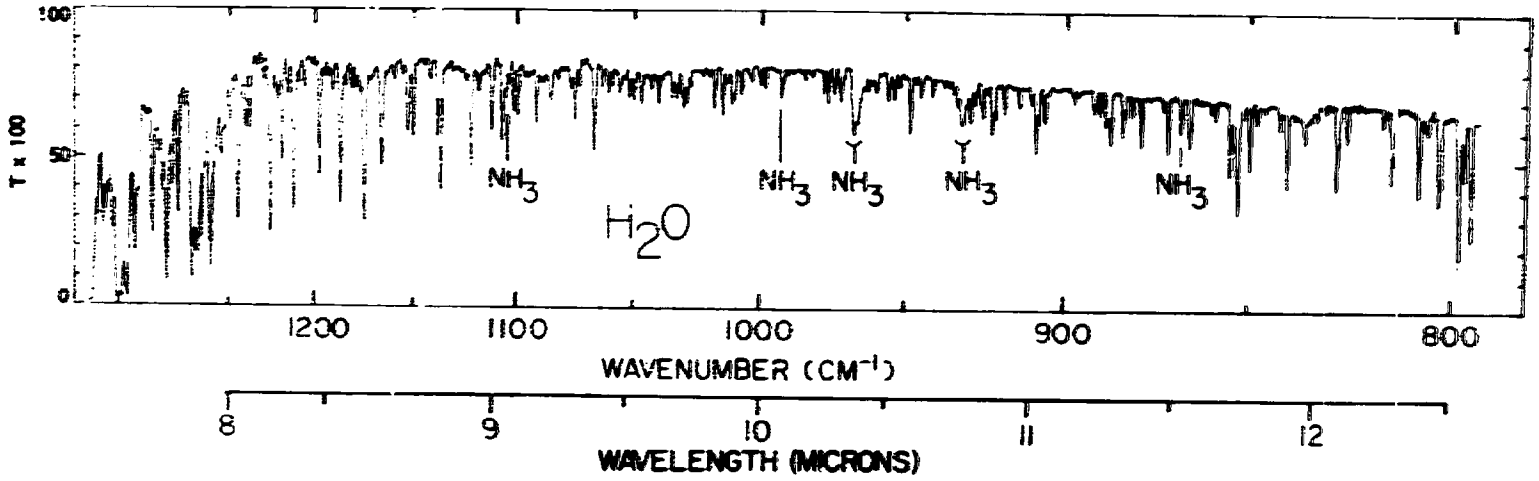

FIG. 3-1. Representative spectrum of H_2O between 800 and 1250 cm^{-1}. The sample is pure H_2O at 14.2 torr; path length is 1185 meters; $\bar{u}$ - 5.48 x 10^{22} molecules/cm^2; temperature is 296K. The spectrum contains a few lines due to a trace of ammonia in the sample; some of the stronger lines are indicated. The ammonia lines can be accounted for by comparing the spectrum with one of pure ammonia.

The H_2O and N_2 partial pressures in atmospheres are denoted by p and p_N, respectively, and the absorber thickness u is in molecules cm^{-2}. The coefficients C_S^o, C_N^o, and the transmittance T are slowly varying functions of ν for the continuum.

Figure 3-2 shows a typical plot of the observed absorption coefficient versus pressure of a pure H_2O sample at one of the narrow windows. In accordance with Eq. (3-1), the absorption coefficient is proportional to pressure, thus confirming the assumption that the absorption is due to the continuum rather than to unresolved lines.

We have found that $C_N^o \ll C_S^o$ for H_2O continuum absorption between 800 and 1250 cm^{-1}. In fact, C_N^o is so small we have not been able to measure it reliably. Further attempts to measure this quantity are planned for the near future. The remainder of this section deals with self broadening only.

From the calculated values[5] of strengths and widths of the very strong H_2O lines centered outside the 700-1250 cm^{-1} interval, we have calculated the continuum expected within the interval. In accordance with previous work[6] in our laboratory, we assumed that at a given pressure self-broadened H_2O lines are five times as wide as N_2-broadened lines, for which the values of Calfee and Benedict apply. The calculations were made for the three different line shapes shown below which have been proposed for collision-broadened lines.

$$k \quad \frac{S}{\pi} \frac{\alpha}{(\nu-\nu_o)^2 + \alpha^2}. \qquad \text{(Simple Lorentz)} \quad (3\text{-}2)$$

$$k \quad \frac{S}{\pi} \frac{\nu}{\nu_o} \left[\frac{\alpha}{(\nu-\nu_o)^2 + \alpha^2} - \frac{\alpha}{(\nu+\nu_o)^2 + \alpha^2} \right]. \qquad \text{(Full Lorentz, Ref. 7)} \quad (3\text{-}3)$$

$$k \quad \frac{S}{\pi} \left(\frac{\nu}{\nu_o}\right)^2 \left[\frac{\alpha}{(\nu-\nu_o)^2 + \alpha^2} + \frac{\alpha}{(\nu+\nu_o)^2 + \alpha^2} \right]. \qquad \text{(Van Vleck-Weisskopf, Ref. 7)} \quad (3\text{-}4)$$

In most cases of interest in the infrared, $|\nu-\nu_o| \ll \nu_o$; so that all three of the above equations are equivalent and the simple Lorentz equation is used. The centers of many of the lines contributing to the H_2O continuum lie below 300 cm^{-1} so that $|\nu-\nu_o|$ may exceed ν_o. Consequently, calculated values based on the various shapes are quite different.

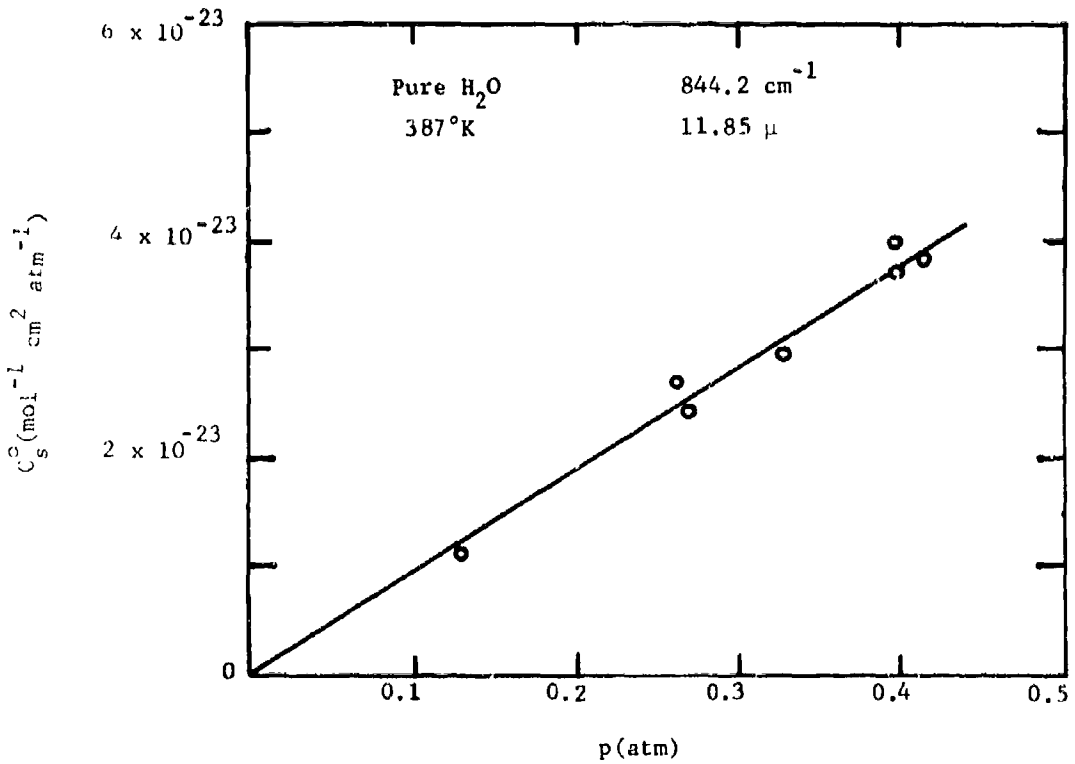

FIG. 3-2. Plot of absorption coefficient at 844.2 cm^{-1} versus pressure of a pure H_2O sample. The sample is at 387K and the path length is 933 meters.

Curves of the calculated continuum coefficient are shown in Fig. 3-3, along with points representing our experimental results. From the results we conclude that the extreme wings of self-broadened H_2O lines absorb more than Lorentz shape lines. By contrast, we recall from Section 2 that the extreme wings of self-broadened CO_2 lines are much less absorbing than Lorentz lines. Although we have been unable to measure C_N^o, the normalized absorption coefficient for the N_2-broadened H_2O continuum, we believe that it is less than 0.005 C_N^o. Therefore, we conclude that the extreme wings of N_2-broadened H_2O lines also are weaker than Lorentz lines.

A normal atmosphere contains less than 4 percent H_2O. Thus, if C_N^o and C_S^o were approximately equal, N_2 broadening would dominate and $-\ln T$ would vary linearly with p, the H_2O partial pressure. ($-\ln T$ is equivalent to absorptance A for $A \ll 1$.) However, since $C_N^o \ll C_S^o$, self broadening dominates, at least in a moderately humid to humid atmosphere. Consequently, $-\ln T$ for the continuum may vary as p^2. This strong dependence on p may be the reason for the unusually large increase in atmospheric absorption with increasing humidity observed in long, horizontal paths by Taylor and Yates[8] and by Streete[9] and in slant paths by Bignell et al[10] who used the sun as a radiation source.

McCoy, Rensch, and Long[11] have used an absorption cell similar to ours to make H_2O absorption measurements with a CO_2 laser source operating at the line P20. This laser line is known to be isolated from any significant H_2O absorption line, so that the absorption by water vapor is due to the continuum. Their results for pure water vapor compare favorably with ours at the same wavelength.

Figure 3-4 compares experimental results for H_2O at three different temperatures. The absorption coefficient decreases rapidly with increasing temperature throughout the region, a result which is contrary to theory if we assume that the line shapes remain the same. Varanasi, Chou, and Penner[12] have measured the absorption by a 2 cm long sample of H_2O at 10 atm pressure and approximately 500°K. We have obtained a value at 1000 cm^{-1} from one of their curves and calculated the absorption coefficient. The value of their curve is too small to be read with better than 25% accuracy, but it is approximately 2.7×10^{-23} mol^{-1} cm^2 at 1 atm. Therefore, we conclude that the absorption coefficient continues to decrease with increasing temperature.

Varanasi, Chou, and Penner have suggested that the continuum absorption in this region results from the association of water molecules due to hydrogen bonding, rather than to the extreme wings of the rotational and vibration-rotational lines. The absorption coefficient by the mechanism they propose, like the absorption due to the extreme wings of lines, is expected to increase linearly with pressure. The mechanism proposed by Varanasi et al is based, at least in part, on the strong

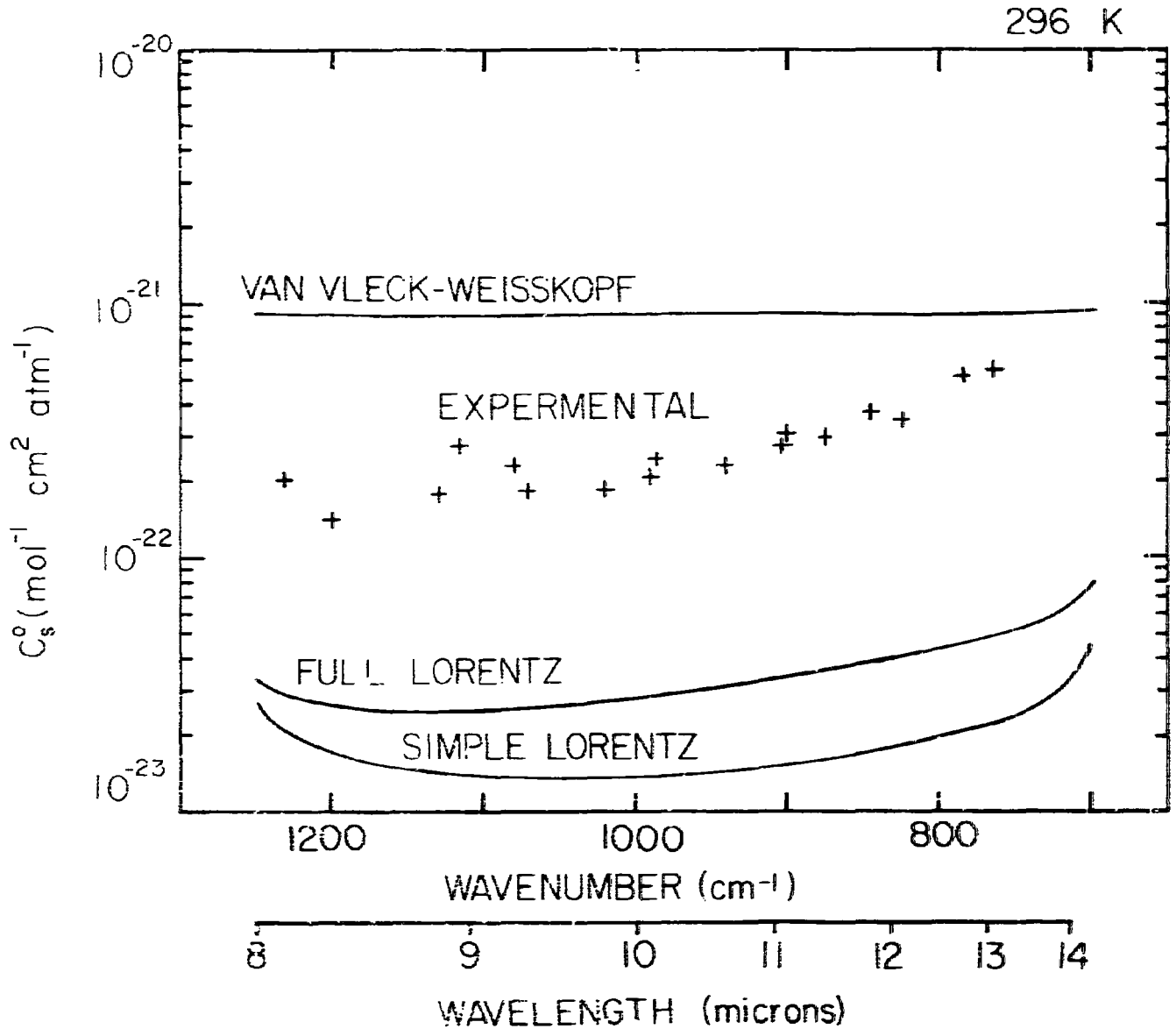

FIG. 3-3. Comparison of experimental and calculated continuum absorption coefficients for H_2O between 700 and 1250 cm^{-1}. The calculated curves are based on the corresponding line shapes given by Eqs. (3-2), (3-3), and (3-4).

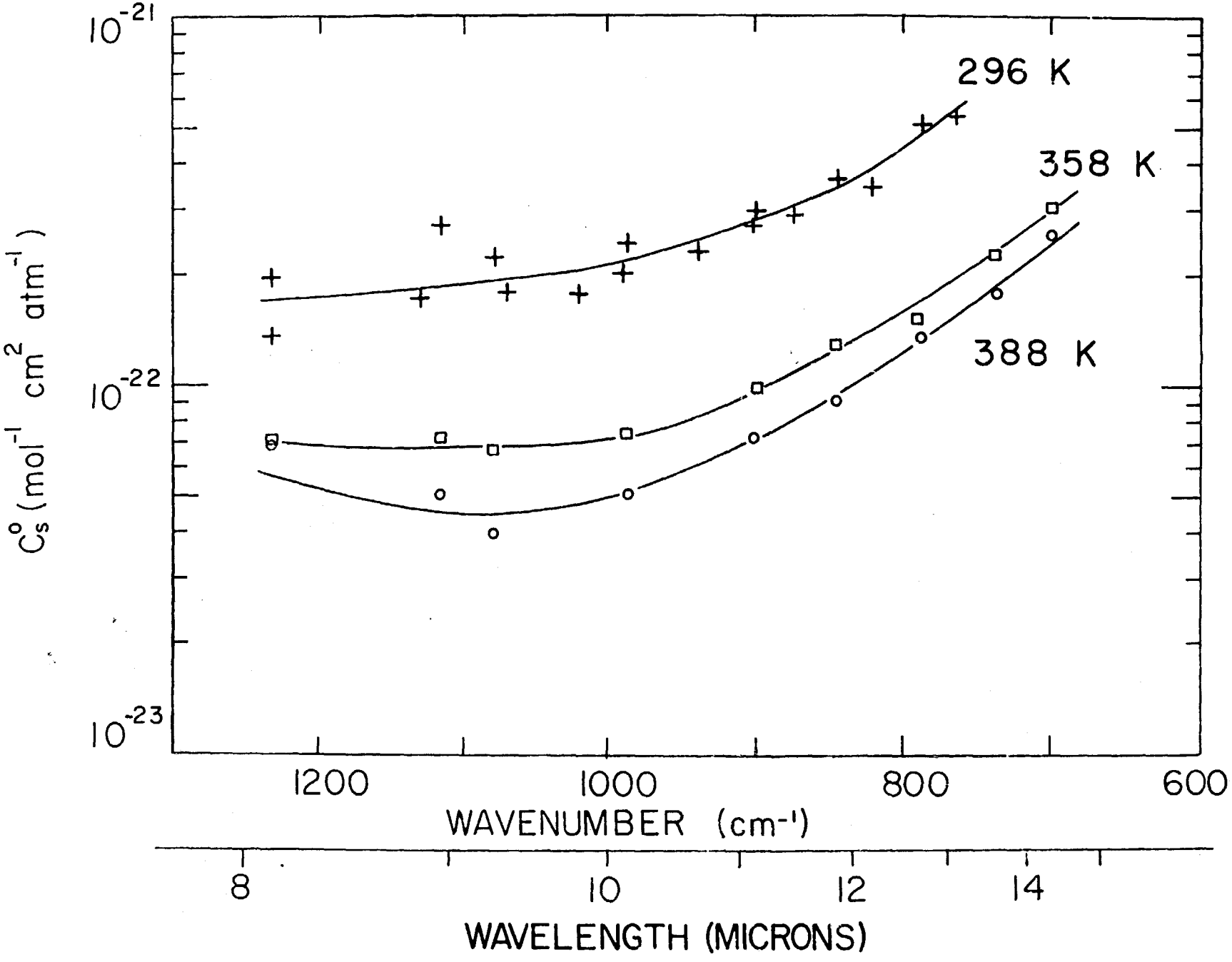

FIG. 3-4. Comparison of the continuum absorption coefficient at three temperatures.

temperature dependence of the absorption. The temperature dependence that we have observed is not in contradiction with the assumptions on binding energy suggested by these workers. However, since so little is known about the behavior of the extreme wings of lines, absorption by them cannot be ruled out.

Application to Atmospheric Transmission Calculations

The H_2O transmittance at any point in the window region is the product of the transmittances of the local lines and the continuum. The strengths and widths of the local lines have been calculated and tabulated by Calfee and Benedict[5] so that their contribution can be determined. We plan to compare the calculated values with values based on some experimental results and to make adjustments where necessary. Preliminary comparisons indicate that only minor adjustments will be required.

At any point between approximately 850 and 1150 cm^{-1}, the contribution by all the local lines more than 5 cm^{-1} away can be ignored since it is much less than that due to the lines within 5 cm^{-1} and to the continuum due to lines centered outside the 700-1250 cm^{-1} region. From 1150 to 1250 cm^{-1} and from 700 to 850 cm^{-1}, several lines occur which are much stronger than any between 850 and 1150 cm^{-1}. Because of these stronger lines, the influence of all lines within 10 cm^{-1} of a point of calculation should be considered in the 700-850 cm^{-1} and 1150-1250 cm^{-1} regions.

The continuum absorption due to self broadening can be calculated by

$$-\ln T = u\, C_S^o\, p, \quad \text{(continuum)}$$

where p is the H_2O pressure. Values of C_S^o can be obtained from Fig. 3-4. Since there is quite a strong temperature dependence, and no data are provided for temperatures below 296K, extrapolation to lower temperatures may be required. Although there is little physical justification for the type of empirical equation given with Table 2-1, this equation is probably adequate for extrapolation to lower temperatures encountered in the atmosphere. Values of τ for the equation can be determined from the curves in Fig. 3-4. Extrapolation to very low temperatures may introduce sizeable errors in the continuum coefficient; however, at these temperatures the H_2O pressures are so low that the H_2O continuum absorption is slight.

As discussed above, C_N^o is very small and difficult to measure. At present we have not been able to obtain reliable values for this quantity. Until other data are available, we suggest that $C_N^o = 0.005\, C_S^o$ be used to determine the continuum due to N_2 and O_2 broadening of the H_2O lines. This relationship between C_N^o and C_S^o is based on data of McCoy, Rensch, and Long.[11] Our results indicate that the constant (0.005) should be even smaller; therefore, values calculated by use of this constant will probably represent a maximum contribution by the N_2 and O_2 broadening.

We plan to continue investigating the H_2O absorption in this region in order to obtain reliable values for C_N^o and to determine the temperature dependence of C_N^o and C_S^o. Publication of a scientific report containing the improved data is expected within a few months.

SECTION 4

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UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Advanced Development Operation Aeronutronic Division Philco-Ford Corporation	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP

3. REPORT TITLE

Investigation of the Absorption of Infrared Radiation by Atmospheric Gases

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Semi-Annual Technical Report (31 July 1969 - 31 January 1970)

5. AUTHOR(S) (First name, middle initial, last name)

Darrell E. Burch

6. REPORT DATE 31 January 1970	7a. TOTAL NO. OF PAGES 26	7b. NO. OF REFS 12
8a. CONTRACT OR GRANT NO. F19628-69-C-0263 b. PROJECT NO. c. d.	9a. ORIGINATOR'S REPORT NUMBER(S) U-4784 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	

10. DISTRIBUTION STATEMENT

Distribution of this document is unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY

13. ABSTRACT

The continuum absorption by H_2O between 800 and 1250 cm^{-1} and by CO_2 from 780 to 900 cm^{-1} has been measured. The continuum results from the extreme wings of very strong absorption lines centered outside the 800-1250 cm^{-1} interval. Experimental results are compared with calculated values based on various line shapes. The extreme wings of N_2-broadened H_2O lines produce less than 0.005 as much continuum absorption as self-broadened H_2O lines at the same pressure. Self-broadened H_2O lines absorb more than Lorentz-shaped lines, but the wings of self-broadened CO_2 lines absorb only approximately 0.01 as much in the 780-900 cm^{-1} region as if they had the Lorentz shape. The shapes of the wings of the CO_2 lines which produce the continuum between 780 and 900 cm^{-1} are similar to those near 2400 cm^{-1} for both self broadening and N_2 broadening. Suggestions on methods for using the results for atmospheric transmission calculations are given.

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Security Classification

14 KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
H_2O						
CO_2						
Continuum						
Line Shape						
Atmospheric Transmission						
Absorption						