

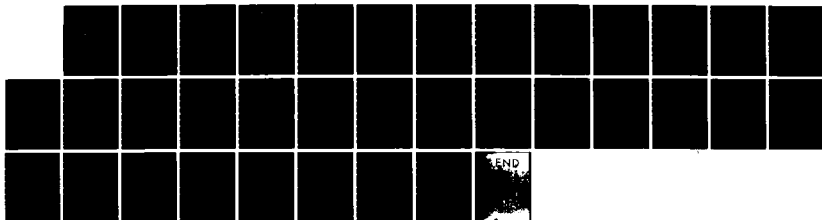
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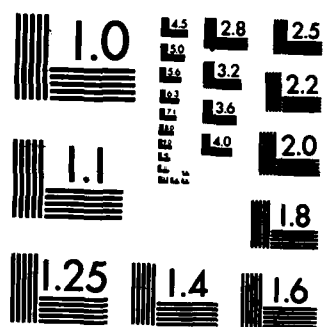
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CONTINUUM ABSORPTION BY H₂O IN THE 700-1200 cm⁻¹ AND
2400-2800 cm⁻¹ WINDOWS

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May 1984

Scientific Report No. 1

Approved for public release; distribution unlimited

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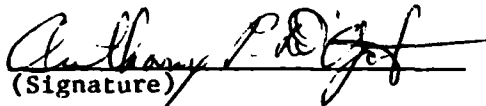
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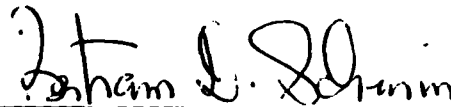
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20. ABSTRACT

temperatures. Coefficients for N₂ broadening have been measured in both windows, and the results compared with previous work. The results have been compared with the data base for the well-known transmission computer code LOWTRAN 6.

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SECTION 1

INTRODUCTION

BACKGROUND

The H₂O continuum is a major contributor to the infrared absorption by the lower atmosphere in the important windows from 700 to 1200 cm⁻¹ and from 2400 to 2800 cm⁻¹. This continuum has been the subject of several experimental and theoretical studies¹ in these and in other spectral regions from the near-infrared to the millimeter waves. In spite of the extensive work that has been done, the continuum absorption is still not well understood.

Absorption by the extreme wings of H₂O lines is almost certainly a major contributor to the continuum. Dimers (H₂O:H₂O) and more complex molecules may also contribute in some of the windows, but the amount is very much in doubt and is still the subject of much controversy. Since the molecular mechanisms involved in the absorption are not understood, it is impossible to calculate reliably the amount of absorption that takes place in the atmosphere under conditions that cannot be simulated in the laboratory.

Although the absorbing mechanism is poorly understood, it has been known for several years that continuum absorption in the 700-1200 cm⁻¹ and 2400-2800 cm⁻¹ windows has the following 3 important general characteristics:

1. The amount of absorption in a given optical path length increases very rapidly with increasing H₂O density. At high densities, the absorption is approximately proportional to the square of the density.
2. The dependence on N₂ broadening (due to interactions of the absorbing H₂O molecules with N₂ in the atmosphere) is much weaker than in most of the spectral windows.
3. The absorption cross section per H₂O molecule increases rapidly with decreasing temperature.

The present laboratory study of these two windows was undertaken with the following 4 main objectives in mind:

1. Determine coefficients for self broadening that are more accurate than those previously available.
2. Obtain data on self broadening at various temperatures near room temperature and below to improve the understanding of the temperature dependence and permit more reliable extrapolations to lower temperatures.

¹D. E. Burch, AFGL-TR-81-0300, Final Report, AFGL Contract No. F19628-79-0041 (1982).

3. Measure the coefficients for N_2 broadening, or as a minimum, determine maximum values if the coefficients are too small to measure reliably.
4. Investigate the absorption by samples with the H_2O concentration at or near saturation to determine if any anomalous absorption takes place.

All of these objectives have been met, but with different degrees of success. Improved experimental techniques have enabled us to obtain data on self broadening, near room temperature and below, that we believe are more accurate than those reported previously. Because of the very low values of the N_2 -broadening coefficients, we have been unable to measure them with good precision, but we have established reliable upper limits. Absorption coefficients based on samples at or near saturation show no anomalous differences from those derived from samples at moderate relative humidity. This result is inconsistent with hypotheses that H_2O dimers or clusters of more complex molecules form near saturation and cause great increases in the absorption.

This report is limited mostly to the new data and to comparisons with our previous results¹⁻⁴ and the widely used LOWTRAN 6⁵ computer code. Comparisons with results of other workers would be informative, but they are beyond the scope of this present study.

DEFINITIONS AND SYMBOLS

ν ,	wavenumber (cm^{-1})
T ,	transmittance
$-\ln T$,	optical depth
L ,	geometrical path length (cm)
ρ ,	density of H_2O (molecules/ cm^3)
u ,	absorber thickness = ρL (molecules/ cm^2)

²D. A. Gryvnak, D. E. Burch, R. L. Alt, and D. K. Zgonc, AFGL-TR-76-0246, ADA039380, Final Report, Contract F19628-76-C-0067 (1976).

³D. E. Burch, Semi-Annual Tech. Report, AFCRL Contract No. F19628-69-C-0263. U.S. Air Force (31 January 1970).

⁴D. E. Burch, D. A. Gryvnak, and J. D. Pembroke, AFCRL-71-0124, AD882876, Contract No. F19628-69-C-0263, U.S. Air Force (1971).

⁵F. X. Kneizys, E. P. Shettle, W. O. Gallery, J. H. Chetwynd, Jr., L. W. Abreu, J. E. A. Selby, S. A. Clough, and R. W. Fenn, AFGL-TR-83-0187, ADA137786, Environmental Research Papers, No. 846, Air Force Geophysics Laboratory, Atmospheric Transmittance/Radiance: Computer Code LOWTRAN 6 (1983).

- p , partial pressure of H_2O (atm)
 p_N partial pressure of N_2 , or dry air (atm)
 P , total pressure of gas sample (atm)
 θ , temperature of gas sample ($^{\circ}K$)
 C_s^0 , self-broadening coefficient for H_2O continuum absorption
 (molecules $^{-1}$ cm 2 atm $^{-1}$)
 C_N^0 , nitrogen broadening coefficient for H_2O continuum absorption
 (molecules $^{-1}$ cm 2 atm $^{-1}$)

For continuum absorption at a given wavenumber over a uniform path of length L ,

$$-\ln T = u C_s^0 p + u C_N^0 p_N, \text{ or} \quad (1)$$

$$-\frac{\ln T}{L} = C_s^0 p^2 + C_N^0 p_N p (7.34 \times 10^{21}/\theta) \quad (2)$$

C_s^0 and C_N^0 are functions of both temperature and wavenumber.

The optical depth, $-\ln T$, for a non-uniform path is equal to the sum of the optical depths of the layers that make up the entire path. In making computations, each layer is made thin enough that the densities and temperature can be considered constant throughout the layer.

LOWTRAN 6 and previous versions of LOWTRAN employ a similar but somewhat different set of symbols and notation. Data on continuum absorption appearing below in this report may be compared to data in LOWTRAN 6 by using the following to relate quantities that are defined and used differently in the two reports.

Temperature is symbolized by T in LOWTRAN 6, and by θ in the present work. The geometrical path length s in LOWTRAN 6 is equivalent to L in this report.

The subscript s denotes self-broadening in both reports; the subscript f used in LOWTRAN 6 for foreign broadening corresponds to the subscript N in this report.

LOWTRAN 6 defines the continuum absorption coefficients in terms of optical depth and molecular density, whereas this report uses a combination of molecular density and pressure to be consistent with previous reports from our

laboratory. For example, the optical depth due to the continuum for a uniform sample at temperature T is expressed in LOWTRAN 6 as

$$\int k_c dS = C_s (\nu, T) S \left(\frac{\rho_s}{\rho_0} \right) \rho_s + C_f (\nu, T) S \left(\frac{\rho_f}{\rho_0} \right) \rho_s. \quad (3)$$

The quantity ρ_0 is the molecular density at 1013 mb (1 atm) and 296K. It follows that C_s and C_f in LOWTRAN 6 have different units ($\text{molecules}^{-1} \text{cm}^2$) than those of the corresponding quantities ($\text{molecules}^{-1} \text{cm}^2 \text{atm}^{-1}$) in this report. For the special case of $\theta = 296 \text{ K}$, the quantities C_s and C_f in LOWTRAN are numerically equivalent to C_s^0 and C_N^0 , respectively, in this report. These simple relationships do not hold at other temperatures because one set of parameters is defined in terms of pressure and the other in terms of density.

The data base in LOWTRAN 6 employs another pair of quantities, $\tilde{C}_s$ at 296 K and 260 K, and C_f at 296K. These quantities, which have important physical significance when relating the continuum absorption to the shapes of the extreme wings of absorption lines, are related to the above-defined quantities by:

$$C_f (\nu, 296) = \nu \tanh \frac{h c \nu}{2 k 296} \tilde{C}_f, \text{ and} \quad (4)$$

$$C_s (\nu, 296) = \nu \tanh \frac{h c \nu}{2 k 296} \tilde{C}_s. \quad (5)$$

A similar expression is given for C_s at 260 K. The quantity $hc/k = 1.43879 \text{ }^\circ\text{K/cm}^{-1}$; h , c , and k are Planck's constant, the speed of light, and Boltzmann's constant, respectively.

The values of C_s^0 and C_N^0 listed in the following pages for the present data include all of the contributions to the absorption except for local lines centered within approximately 1 cm^{-1} of the wavenumbers where the measurements are made. These wavenumbers were chosen where any lines centered within 1 cm^{-1} are extremely weak and can be accounted for with little error. Thus, all of the lines contributing to the continuum defined in this way are sufficiently far from the measurement point that the contribution of each line is proportional to its width, and thus proportional to the sample pressure. The absorption lines centered in the two window regions covered in this report are very weak. Consequently, very little of the continuum absorption is due to lines centered between 1 cm^{-1} and 25 cm^{-1} from the wavenumbers where the measurements were made. Thus, the values listed may also be treated as due to the wings of distant lines and therefore closely correspond to the continuum coefficients as defined and used in LOWTRAN 6. Experimental values of the coefficients obtained by the present method would not, in general, represent values in LOWTRAN 6 because a significant portion of the continuum for most spectral regions is due to lines centered at distances between approximately 1 cm^{-1} and 25 cm^{-1} .

SECTION 2

EXPERIMENTAL

The experimental methods are similar to those we have used for several investigations of absorption by H_2O and other atmospheric gases. Gas samples are contained in a large multiple-pass absorption cell that provides optical paths long enough to produce measurable absorption in spectral windows where the absorption is very weak. We have recently added the capability to cool the absorption cell and have incorporated a few changes in our techniques to improve the measurement accuracy.

TRANSMISSION MEASUREMENTS

Infrared radiation from a Nernst glower is chopped and directed through a window into the multiple-pass absorption cell that contains the sample to be studied. After the beam of energy has passed back and forth the desired number of times in the cell, it is directed out through an exit window to a grating spectrometer.

The spectrometer is used either to scan a portion of the spectrum of interest or to remain set so it will pass only a narrow spectral interval at one of the wavenumbers where the continuum absorption is being measured. These narrow intervals are chosen between H_2O absorption lines where the line absorption does not interfere with the continuum measurement.

The transmittance of pure H_2O samples is determined by comparing the level of the infrared signal measured with the sample in the cell with that measured when the cell is evacuated. A similar procedure is followed when studying N_2 broadening except that the two signal levels compared are those measured with the H_2O+N_2 sample and those with the same amount of H_2O in a pure H_2O sample.

Most of the measurements have been made by the following procedure to reduce errors due to variations in source brightness and detector responsivity. The spectrometer is adjusted to a desired wavenumber, and the signal levels V_4^* and V_{28}^* are measured with the sample cell evacuated and the multiple-pass optics adjusted to 4 passes and 28 passes, respectively. These two measurements are made within a few minutes during which the brightness and detector responsivity are nearly constant. This procedure may be repeated at other wavenumbers. The gas sample is then introduced into the cell and all of the measurements of V_4 and V_{28} are repeated at 4 passes and 28 passes.

The effective transmittance at a given wavenumber is given by

$$T = \frac{V_{28}}{V_4} \frac{V_4^*}{V_{28}^*}, \quad (6)$$

and the effective path length L is 707 meters, the increase in optical path length in going from 4 passes to 28 passes. By reducing the data in this manner, we greatly decrease the effects of slow changes in source brightness and detector responsivity, as well as any possible changes in transmittance of the cell windows due to absorbed water on the window surfaces.

When changing the number of passes of the sample cell, we make use of an alignment aid built into the cell to repeat accurately the vertical position of the source image on the entrance slit of the spectrometer. This position is set by an external adjustment of the tilt of one of the multiple-pass mirrors. An external azimuthal adjustment of the same mirror changes the number of passes and places the image in the correct horizontal position on the slit to produce maximum detector signal.

SAMPLING

All of the new data reported here were obtained with samples of either pure H_2O vapor or of $H_2O + N_2$ in a multiple-pass absorption cell with a 29-meter base length. The typical sampling procedures are as follows:

The cell is evacuated to less than 0.1 torr immediately before H_2O vapor is added. Distilled liquid water is contained in a small "boiler" attached to the sample cell by a short piece of tubing with a valve. The tubing is connected to the liquid container above the liquid level so that only the vapor can pass through the tubing to the cell. After the valve is opened to allow H_2O vapor to enter the cell, the liquid is heated to speed up the evaporation and the transfer of vapor from the container to the sample cell. Approximately 10-15 minutes is normally required to add H_2O to a pressure of 15 torr (approximately 0.02atm). The pressure is allowed to stabilize before spectral measurements are made.

Another tubing with a valve connects the upper portion of the liquid container to a vacuum pump that removes any air from the container before the valve is opened in the tubing to the sample cell. The tubings to the pump and sample cell are electrically heated to avoid condensation in them.

Sample pressures below approximately 0.1 atm are measured with an oil manometer; higher pressures are measured with a mercury manometer. The manometers are at room temperature, making it necessary to use extra care to avoid condensation in them while studying samples at pressures above the H_2O vapor pressure at room temperature. Normally, the manometer and the tubing connecting it to the sample cell are filled with dry N_2 to a pressure slightly higher than that of the gas in the cell. The valve is then opened to connect the manometer to the cell and allow a small amount of N_2 to flow into the cell until the pressure comes to equilibrium. Because of the very large volume of the sample cell, the small amount of dry N_2 entering from the manometer line makes a trivial change in the sample pressure.

Samples of $H_2O + N_2$ are made by first adding the H_2O to the evacuated cell and allowing the pressure to come to equilibrium. If the H_2O is added and allowed to remain, the pressure decreases by 20-30% during the

first 24 hours and may continue to decrease slowly for another 1 or 2 days because of the slow adsorption of H_2O on the walls of the cell. The H_2O pressure is normally brought to near equilibrium much more quickly by first adding H_2O to a pressure 10-20% higher than the desired equilibrium pressure. The gas is allowed to remain for several minutes, then part of it is pumped out until the pressure is approximately equal to the desired equilibrium pressure. If this sample is allowed to remain, the pressure does not normally change more than a few percent during the next several hours.

The effect on the continuum absorption of adding N_2 is determined by comparing the transmitted radiation through the pure H_2O with that transmitted through the $H_2O + N_2$ mixture containing the same partial pressure of H_2O . Therefore, the transmission measurements are made through the equilibrated H_2O sample just prior to adding the N_2 .

Dry N_2 from commercial cylinders is slowly added to the H_2O in the sample cell through 4 different ports distributed evenly along the length of the cell. While the N_2 is entering the cell, mixing fans inside the cell are turned on periodically to ensure good mixing. Immediately before the spectral data for the $H_2O + N_2$ sample are obtained, the H_2O partial pressure is measured with a dewpoint meter inside the sample cell. The results are compared with two H_2O pressure measurements made before adding the N_2 : one with the dewpoint meter and one with the manometer. Any small changes in the H_2O partial pressure that occur between the two sets of transmission measurements can be accounted for during the data reduction.

Samples above laboratory temperature are produced by electrically heating the entire sample cell, which is thermally insulated to reduce temperature gradients and improve stability. The cell temperature is regulated by manually controlling the electrical current through the heating wires. This method of controlling the temperature leads to much better stability in the optical alignment than can be obtained with an automatic controller that varies the heating current. The 284 K samples are obtained by maintaining the laboratory at approximately 290 K and circulating cold air through an insulated enclosure that surrounds the sample cell. The circulating air is cooled by 2 commercial air conditioners.

Several thermocouples located at key locations in the sample cell make it possible to determine the uniformity and stability of the cell temperature. Essentially all of the gas in the optical path is within $\pm 1^\circ K$ of the mean temperature when the cell is either heated or cooled.

Possible errors in transmission measurements due to adsorption of water on the optical surfaces in the cell are greatly reduced by heating the windows and the internal mirrors to approximately $3^\circ K$ above the gas temperature. Transmission measurements made with pure non-absorbing N_2 indicate that there is negligible effect due to any turbulence or temperature nonuniformities caused by the heated optical components.

SECTION 3

RESULTS IN 700-1100 cm^{-1} REGION

Most of the lower atmospheric absorption by H_2O vapor in this well-known window is due to the continuum, although the window also contains many very weak absorption lines. All of the absorption measurements reported herein were obtained at wavenumbers between the weak absorption lines where essentially none of the absorption is due to lines centered within 25 cm^{-1} . Therefore, all of the data applies to continuum absorption only.

SELF BROADENING

The data points and lower curve of Figure 1 show the results of our recent continuum measurements for self broadening in examples at 296K. Also shown for comparison is a curve based on data we² reported in 1976 and repeated in another report¹ in 1982. All of the data in this and other figures on self-broadening are from measurements on samples of pure H_2O vapor in the sample cell. We note that most values from the curve representing the recent data are 15-20% less than the corresponding values from the earlier data. The decrease is probably due to the minor changes in experimental techniques employed in the recent work.

As explained previously¹ the decrease in the self broadening coefficient with increasing wavenumbers is probably due to increasing distance from the centers of the very strong rotational H_2O lines centered at smaller wavenumbers. The recent work has been limited to approximately the 700-1000 cm^{-1} region where the H_2O continuum absorption is great enough to measure with reasonable accuracy, and varies significantly from one end of the region to the other. As the results presented below in this section indicate, the H_2O continuum in this portion of the window also contains a contribution by N_2 broadening. The H_2O continuum coefficients in the data base of LOWTRAN 6³ are based largely on the earlier data represented by the broken curve in Figure 1.

Figure 2 shows results of measurements made with samples at 284K and at H_2O pressures up to approximately 0.012atm (9 torr). Comparison of the curve representing these data with the curves for 296K repeated from Figure 1 reveals the strong dependence of the coefficients on gas temperature. This strong negative temperature dependence is consistent with results we¹ have reported for other spectral regions where much of the continuum is due to the extreme wings of strong absorption lines.

¹D. E. Bruch, AFGL-TR-81-0300, Final Report, AFGL Contract No. F19628-79-0041 (1982).

²D. A. Gryvnak, D. E. Burch, R. L. Alt, and D. K. Zgonc, AFGL-TR-76-0246, ADA039380, Final Report, Contract F19628-76-C-0067 (1976).

³F. X. Kneizys, E. P. Shettle, W. O. Gallery, J. H. Chetwynd, Jr., L. W. Abreu, J. E. A. Selby, S. A. Clough, and R. W. Fenn, AFGL-TR-83-0187, Environmental Research Papers, No. 846, Air Force Geophysics Laboratory, Atmospheric Transmittance/Radiance: Computer Code LOWTRAN 6 (1983).

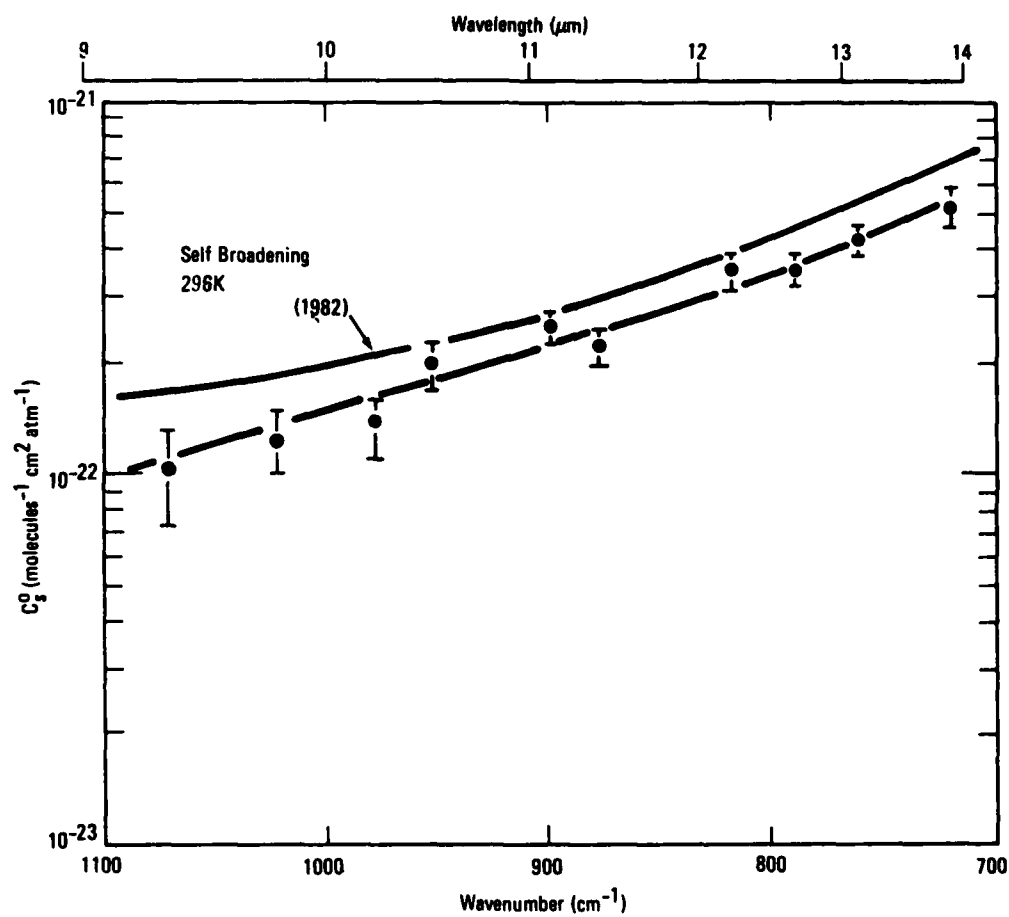


Figure 1. Self-broadening coefficient from 700 cm⁻¹ to 1100 cm⁻¹ at 296 K. The upper curve represents our previous results. See Ref. 1 and 2.

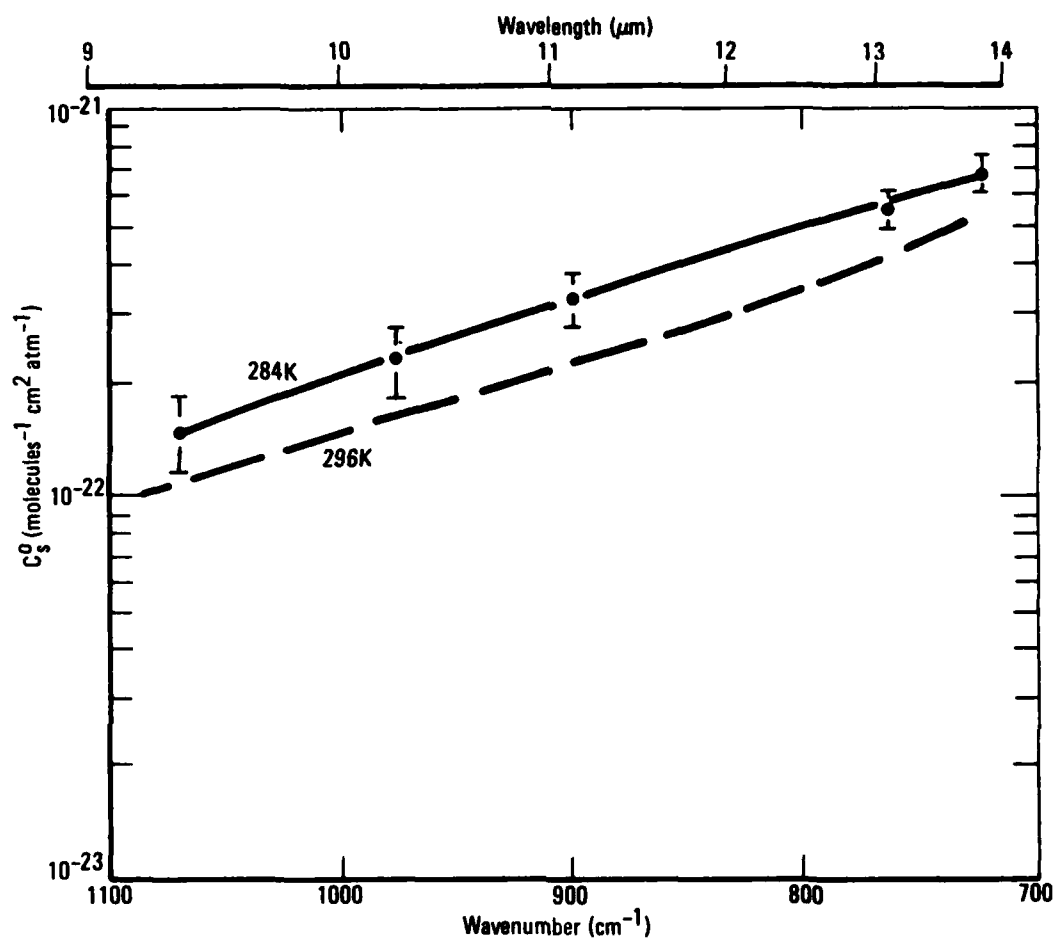


Figure 2. Self-broadening coefficient from 700 cm^{-1} to 1100 cm^{-1} at 284 K. The curve for 296 K from Figure 1 is repeated for comparison. Values of $10^{24} C_s^0$ from the smooth curves (in $\text{molecules}^{-1} \text{cm}^2 \text{atm}^{-1}$) are:

(cm^{-1})	284 K	296 K	(cm^{-1})	284 K	296 K
700	775	620	900	319	219
720	710	550	920	292	199
740	650	485	940	268	183
760	600	435	960	246	168
780	550	390	980	224	157
800	500	345	1000	205	145
820	460	312	1020	187	133
840	420	284	1040	170	122
860	385	260	1060	153	112
880	355	240			

The temperature dependence of the self-broadening coefficients at two different wavenumbers is illustrated in Figure 3 over a wide temperature range. Data points in the figure have been obtained from curves relating the self-broadening coefficients to wavenumbers at the temperatures indicated. The data for samples at 392K and 430K are from our previous work², whereas the non-circled points for 296 and 284K are from Figure 2.

Absorption coefficients with a strong negative temperature dependence frequently can be related to temperature θ by an equation of the following form:

$$C(\theta) = C(\theta_0) \exp (B/\theta), \text{ or} \quad (7)$$

$$\ln [C(\theta)/C(\theta_0)] = B/\theta.$$

A temperature dependence given by Equation (7) would yield a straight line in Figure 3 where the ordinate is proportional to the logarithm of the attenuation coefficient and the abscissa is linear in the reciprocal of temperature. The data points at 284 K occur, within experimental uncertainty, on the straight lines drawn between the points representing high temperatures and those representing 296 K. However, the two temperatures, 296K and 284K, are not separated enough to justify concluding that the simple relationship given by Equation (7) is valid at much lower temperatures. The straight lines in Figure 3 are extrapolated to 260K to illustrate the values of the coefficients if Equation (7) is valid at temperatures this low.

The encircled points in Figure 3 represent values of C_0^0 derived from the tables of $\tilde{C}_s$ in the data base of LOWTRAN 6. As is also apparent from Figure 1, the coefficients for 296K on which values in LOWTRAN 6 are based are larger than the corresponding coefficients from the present work. The rate of increase with decreasing temperature is also slightly greater for the LOWTRAN 6 data base than for the present work.

N₂ BROADENING

Figure 4 summarizes the results of the measurements of the N₂-broadening coefficients for the H₂O continuum. These coefficients are very small and difficult to measure precisely, as is indicated by the large uncertainty associated with each data point. In a typical measurement, a sample of pure H₂O vapor is introduced into the sample cell and allowed to stabilize; the level of the infrared signal at a particular wavenumber transmitted through the sample is then measured. Nitrogen is then added to the sample until the total pressure is approximately 1 atm, and the transmitted signal is measured. The coefficient C_N^0 is based on a small difference in the two transmitted signals, one with H₂O vapor only and one with the H₂O vapor and the N₂. Accurate measurement of C_N^0 depends strongly on good stability of the instrument and the gas sample during the time between the measurements.

²D. A. Gryvnak, D. E. Burch, R. L. Alt, and D. K. Zgonc, AFGL-TR-76-0246, ADA039380, Final Report, Contract F19628-76-C-0067 (1976).

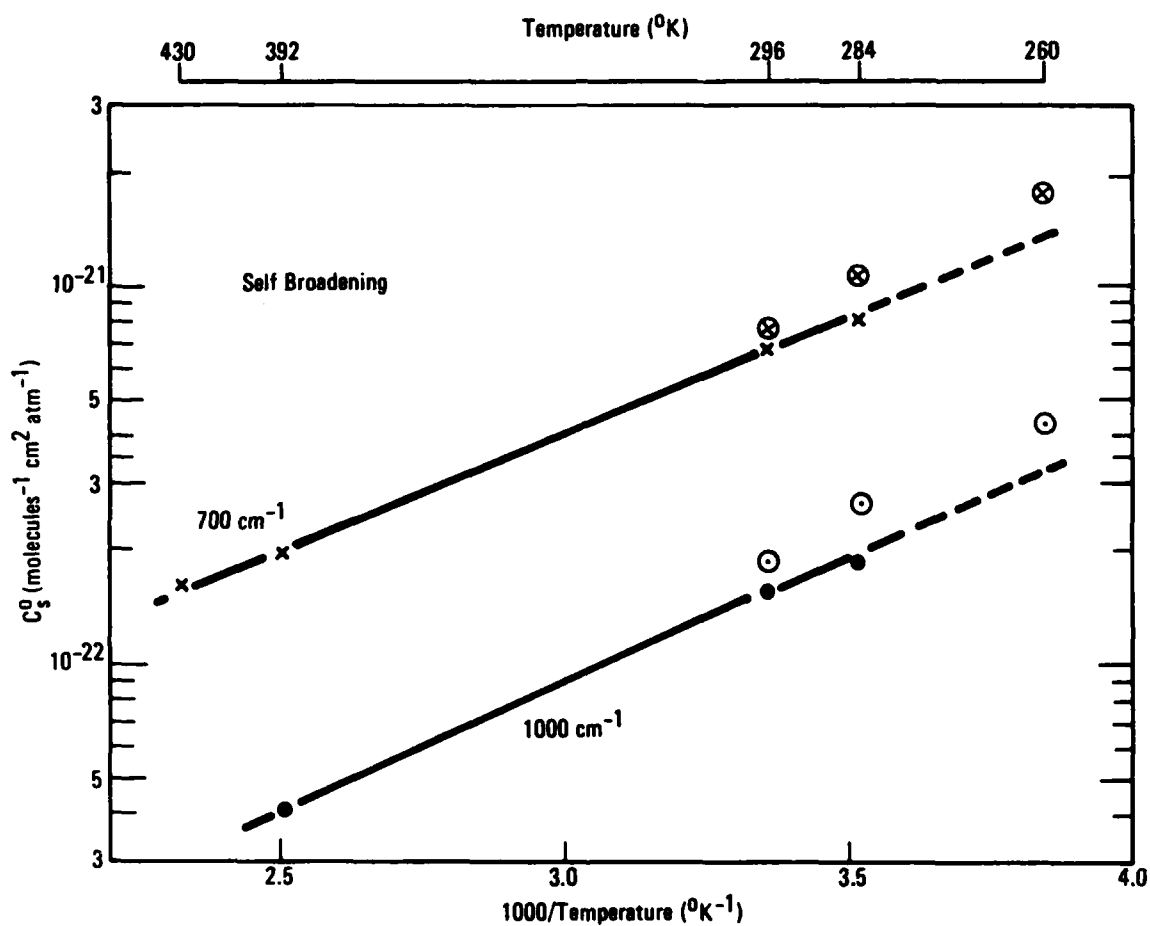


Figure 3. Plots of the self-broadening coefficients at 700 cm^{-1} and 1000 cm^{-1} versus the reciprocal of temperature.

- x this work, 700 cm^{-1}
- ⊗ LOWTRAN 6, 700 cm^{-1}
- this work, 1000 cm^{-1}
- ⊙ LOWTRAN 6, 1000 cm^{-1}

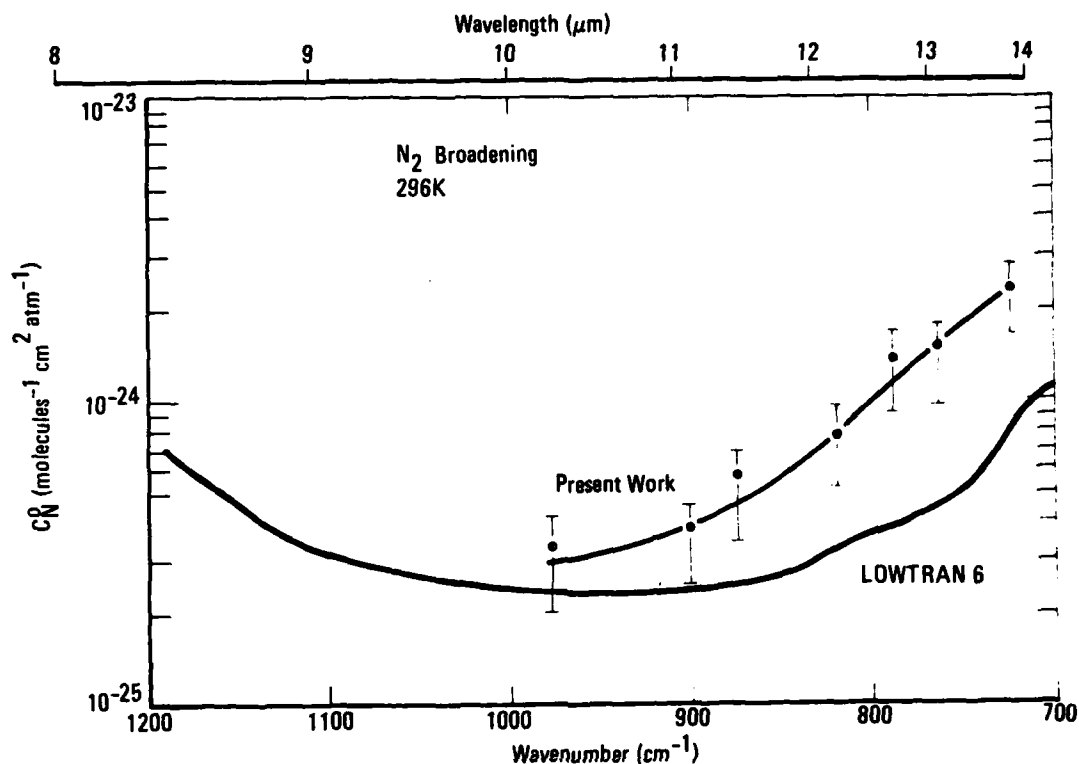


Figure 4. N₂ broadening coefficient from 700 cm⁻¹ to 1200 cm⁻¹ at 296 K. Values of 10²⁶ C_N⁰ from the smooth curves (in molecules⁻¹ cm² atm⁻¹) are:

(cm ⁻¹)	Present	LOWTRAN 6	(cm ⁻¹)	LOWTRAN 6
700	285	111	1020	25.5
720	242	90.4	1040	26.5
740	200	58.4	1060	27.5
760	162	46.1	1080	29.7
780	127	40.9	1100	32.2
800	100	36.7	1120	36.4
820	79	32.7	1140	41.5
840	63	27.7	1160	51.3
860	51	25.9	1180	62.0
880	43	25.1	1200	83.7
900	38	24.2		
920	33	23.9		
940	32	24.0		
960	30	24.1		
980	29	24.4		
1000	28	24.9		

In our early work³ on continuum absorption, we attempted to measure N_2 -broadening coefficients between 800 cm^{-1} and 1200 cm^{-1} , but we were unable to obtain results that we felt were accurate enough for reliable calculations of atmospheric transmission. The results indicated that the ratio C_N^O/C_S^O was very low in this spectral region, possibly less than 0.001. McCoy et al⁶, using a CO_2 laser as a radiation source, and samples in a laboratory cell, subsequently determined this ratio to be approximately 0.005. However, Roberts et al⁷ examined the data from a series of long path measurements and concluded that the ratio 0.001 was more nearly correct than 0.005. Thus, the contribution to the continuum by N_2 broadening has been quite uncertain although many different types of measurements of the continuum have been made during the past 15 years. The amount of continuum absorption cannot be calculated reliably on a strictly theoretical basis because of the lack of knowledge about the shapes of the extreme wings of absorption lines, and about the characteristics and numbers of H_2O dimers and other molecular complexes.

The measurement of C_N^O has been included in the present study in another attempt to determine values that could be used reliably in calculations of atmospheric transmission. All of the improved experimental techniques described in Section 2 have been employed in making these measurements. Although the uncertainty in the data represented in Figure 4 is greater than we had hoped for, these data provide a reasonably reliable basis for atmospheric calculations. If the measured values are in error by more than the approximately $\pm 30\%$ indicated by the error bars, the true values are probably lower than the measured values. We believe this to be true because most sources of systematic error in the measurements would cause the attenuation to appear greater than it really is. Thus, the curve can probably be considered to represent maximum values for C_N^O .

In compiling 8, 9 tables of $\tilde{C}_f$, which is related by equation (4) to our C_N^O , the authors⁸, of LOWTRAN 6 combined newly developed theories about line shapes with continuum data in these windows as well as in other spectral regions. Unfortunately, no reliable data on N_2 broadening existed in this spectral region for the LOWTRAN 6 authors to test the validity of the values they derived by the combined theoretical/empirical method. Values of C_N^O based on the LOWTRAN 6 listings are represented in Figure 4 by the lower curve.

Figure 5 compares spectral plots of the ratio C_N^O/C_S^O based on the present data with those from the data base of LOWTRAN 6. In previous work,

⁶J. H. McCoy, D. B. Rensch, and R. K. Long, Appl. Opt. 8, 1471 (1969).

⁷R. E. Roberts, J. E. A. Selby, and L. M. Biberman, Appl. Opt. 15, 2086 (1976).

⁸S. A. Clough, F. X. Kneizys, L. S. Rothman, and W. O. Gallery, SPIE Proceedings 277 (1981).

⁹S. A. Clough, F. X. Kneizys, R. Davis, R. Gamache, and R. H. Tipping. (1980). Theoretical line shape for H_2O vapor; Application to the continuum, Atmospheric Water Vapor, A. Deepak, T. D. Wilkerson, and L. H. Ruhnke, Eds., Academic Press, New York.

we¹ have found that spectral plots of this ratio reveal important information about the relative shapes of N₂-broadened and self-broadened H₂O absorption lines. The ratio approaches a maximum value of approximately 0.2 at wavenumbers where most of the continuum absorption is due to the wings of lines centered within a few cm⁻¹. As the distance from the centers of the contributing lines increases, the ratio decreases. This result which we found true in several spectral regions, appears true in Figure 5. This dependence of the ratio C_N^O/C_S^O on distance from the major contributing absorption lines implies a difference between the shapes of self-broadened lines and those of N₂-broadened lines. The coefficient due to the extreme wing of each N₂-broadened line apparently decreases faster with increasing distance from the line center than does the corresponding coefficient for a self-broadened line. Most of the continuum absorption between 700 cm⁻¹ and 950⁻¹ is due to very strong, rotational absorption lines centered below 700 cm⁻¹. The 950-1200 cm⁻¹ portion of the LOWTRAN 6 curve in Figure 5 is based on the assumption that most of the continuum absorption is due to the wings of the very strong vibrational-rotational lines centered between 1250 and 1600 cm⁻¹.

As is seen from Figure 1, the spectral curves of C_S^O for the present data and the LOWTRAN 6 data are quite similar, with values for a given wavenumber differing by only 15-20% between the two curves. Thus, the large difference between the two curves in Figure 5 is due mainly to differences between the values of C_N^O .

TOTAL CONTINUUM ABSORPTION

Although the curves in Figure 5 differ by a very large factor, calculations of the total continuum absorption based on LOWTRAN 6 do not differ greatly from those based on the present data. This result is illustrated in Table 1, which compares calculated values for a 296K atmospheric path in which the H₂O pressure is 0.0188 atm (14.3 torr). (This H₂O content corresponds to the mid-latitude summer atmospheric model). The second and third columns contain calculated values of the optical depth of a 1-kilometer path. The fourth and fifth columns show the percentages of the calculated optical depths due to the N₂-broadening represented by the second term of Equation (1). Note that these percentages are quite small, particularly those based on LOWTRAN 6, indicating that most of the absorption is due to self-broadening. Thus, the large differences in values of C_N^O do not lead to large differences in the calculated optical depths. It follows that accurate values of C_N^O cannot be determined from long-path atmospheric measurements of the total continuum absorption, particularly in humid atmospheres, because the self-broadening contribution is quite large and must be accounted for.

¹D. E. Burch, AFGL-TR-81-0300, Final Report, AFGL Contract No. F19628-79-0041 (1982).

Optical depths appearing in columns 2 and 3 of Table 1 agree quite well for the model atmosphere represented. Values of C_S^0 derived from the LOWTRAN 6 data base are significantly larger than the corresponding values from the present work, but these differences are approximately balanced out by the smaller values of C_N^0 from LOWTRAN 6. The agreement would be less for some atmospheric models in which the H_2O pressure is different. The percentage of attenuation due to N_2 broadening is approximately proportional to the reciprocal of H_2O pressure. Thus, for very dry atmospheres, the large uncertainty in values of C_N^0 may lead to larger percentage errors in the calculated optical depths.

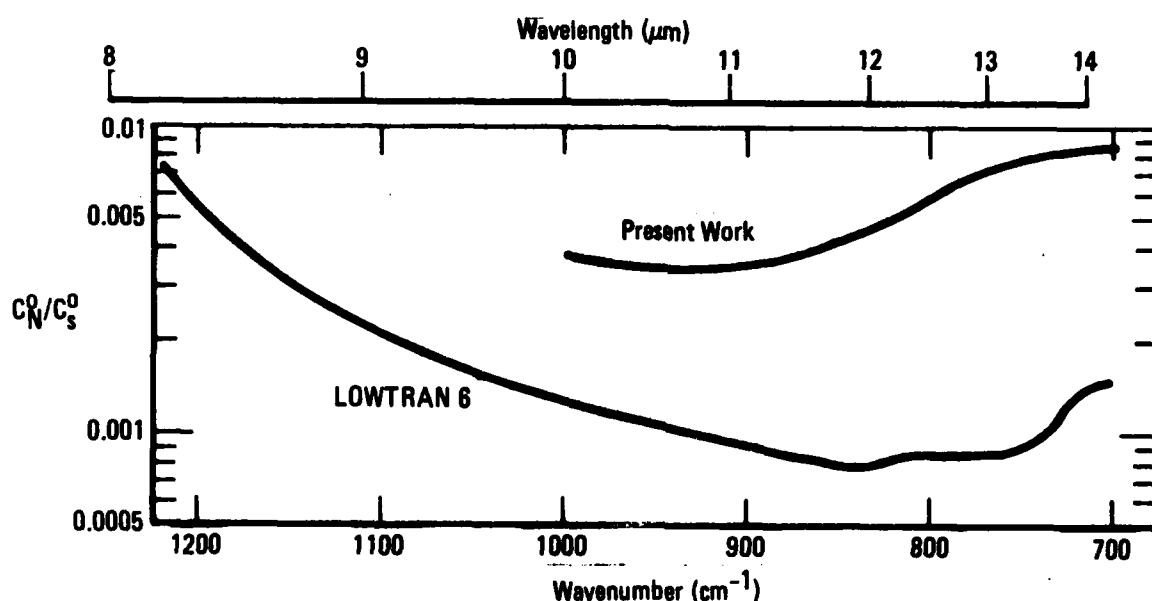


Figure 5. Comparison of ratios of C_N^0/C_S^0 between 700 cm^{-1} and 1200 cm^{-1} from the present work and from LOWTRAN 6. Temperature is 296K. The percentages of uncertainty in the experimental values of C_N^0 are much greater than those in the corresponding values of C_S^0 . Therefore, the percentages of uncertainty in the values of the ratio C_N^0/C_S^0 for the present work are approximately the same as those indicated for C_N^0 in Figure 4.

TABLE 1. COMPARISON OF MEASURED CONTINUUM ABSORPTION WITH
CALCULATED VALUES BASED ON LOWTRAN 6*

Wavenumber (cm ⁻¹)	Optical Depth* per Kilometer		Percent of Continuum Absorption Coefficient Due to N ₂ Broadening	
	Present Data	LOWTRAN 6	Present Data	LOWTRAN 6
700	0.675	0.722	19.3	7.05
720	0.594	0.636	18.7	6.52
740	0.517	0.553	17.7	4.83
760	0.456	0.490	16.3	4.31
780	0.401	0.438	14.5	4.28
800	0.349	0.393	13.1	4.27
820	0.310	0.354	11.7	4.22
840	0.278	0.320	10.4	3.96
860	0.252	0.292	9.28	4.07
880	0.230	0.267	8.55	4.30
900	0.210	0.246	8.30	4.51
920	0.190	0.228	7.96	4.80
940	0.175	0.213	8.34	5.16
960	0.161	0.199	8.52	5.54
980	0.151	0.187	8.79	5.97
1000	0.140	0.177	9.15	6.44
1020		0.169		6.91
1040		0.161		7.52
1060		0.155		8.11
1080		0.151		9.00
1100		0.148		10.0
1120		0.146		11.4
1140		0.147		12.9
1160		0.151		15.5
1180		0.158		18.0
1200		0.172		22.3

*Values are based on 0.0188 atm (14.3 torr) partial pressure of H₂O, total pressure of 1 atm and temperature of 296 K.

SECTION 4

RESULTS IN THE 2400-2800 cm^{-1} REGION

This atmospheric window contains several very weak lines of H_2O and HDO , but like the 700-1200 cm^{-1} window, the continuum produces most of the H_2O absorption over typical lower-atmospheric paths. The H_2O continuum absorption in the 2400-2800 cm^{-1} window is very weak, making it difficult to make laboratory samples near room temperature that produce enough absorption to be measured accurately. Impurities in the sample cell absorb between 2600 and 2800 cm^{-1} , and make it difficult to obtain accurate data on H_2O absorption in this region. Some data obtained in this region have enabled us to set upper limits on the H_2O continuum coefficients.

SELF BROADENING

Figure 6 summarizes data obtained as part of the present work on samples of pure H_2O at 296K and 328K. At 328K, samples of pure H_2O at pressures up to approximately 0.13 atm (100 torr) have been studied without condensation occurring in the cell. These samples produce enough absorption that it can be measured with a precision of approximately $\pm 5\%$. However, at 296K, the 0.028 atm vapor pressure of water limits the maximum sample pressure, and thus the maximum amount of absorption. This, in turn, leads to larger percentage errors.

Figure 7 compares the results of the present work with data we first reported in 1971. The curves corresponding to the three highest temperatures, 338K, 384K, and 428K are based on laboratory data obtained at these temperatures. Because of the difficulties in measuring the absorption near room temperature we did not obtain any data on 296K samples at that time. We cross-plotted the data for higher temperatures and extrapolated to 296K to provide data for atmospheric transmission calculations until better data became available. The curve made up of short dashes in Figure 7 represents the extrapolated data. The two solid curves representing data from the present work at 296K and 328K are repeated from the previous figure. A large discrepancy is apparent between the extrapolated curve for 296K and the present data for the same temperature, indicating that the assumptions made in the extrapolation did not adequately account for the rapid increase in the absorption coefficients with decreasing temperature.

Cross plots based on the curves of Figure 7 are shown in Figure 8 for three different wavenumbers. As in Figure 3 discussed in Section 3, values of C_0 from the smooth curves of Figure 7 are plotted versus the reciprocal of temperature in Figure 8. The points corresponding to 428K, 384K and 338K are from the 1971 work, whereas those corresponding to 328K and 296K are from the present work. We used this same type of plot in the 1971 work to determine the extrapolated values for 296K by assuming that the points would fall on a straight line.

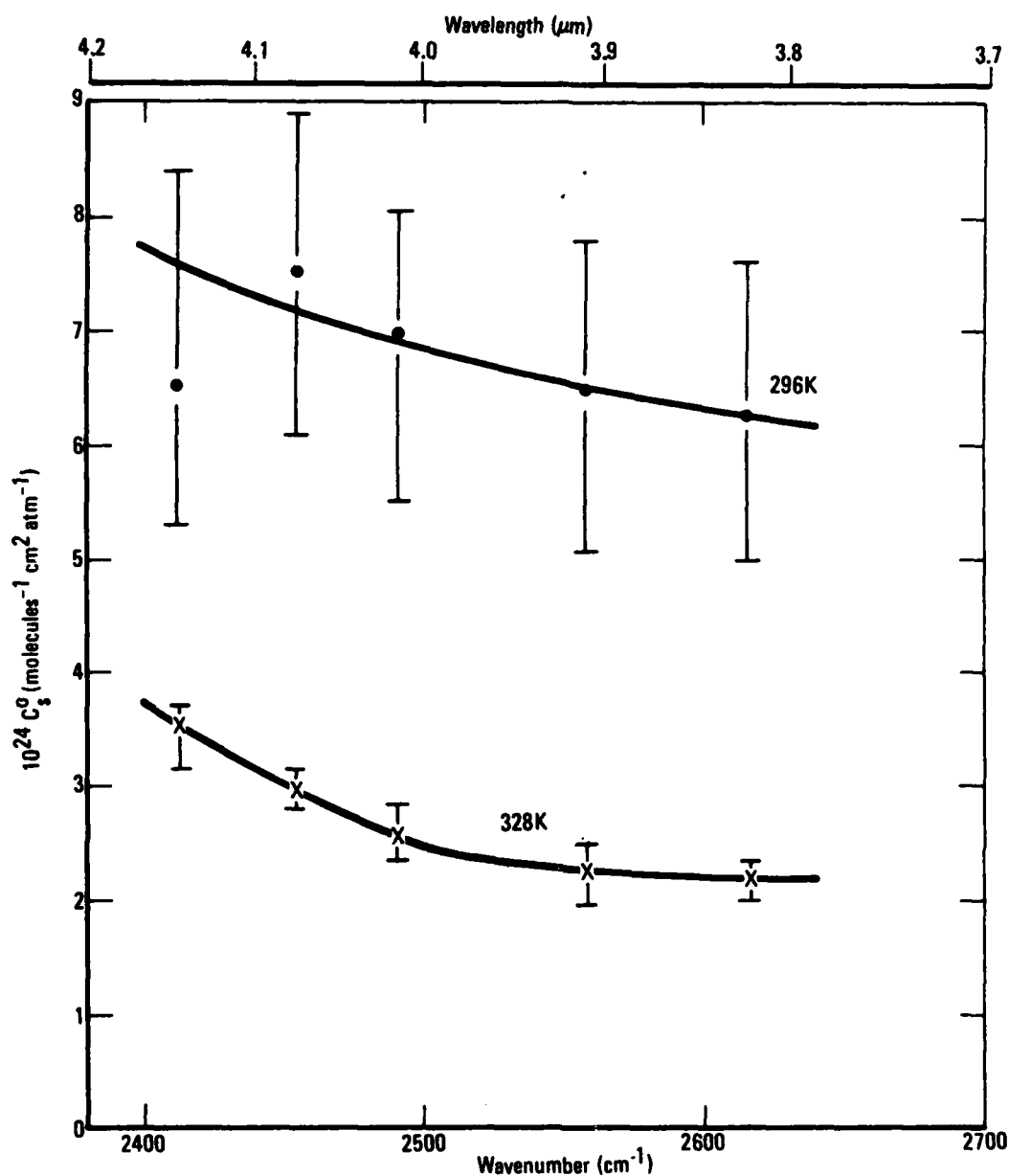


Figure 6. Self-broadening coefficients between 2400 and 2640 cm^{-1} for 296 K and 328 K. Values of $10^{24} C_s^0$ from the smooth curves (in $\text{molecules}^{-1} \text{cm}^2 \text{atm}^{-1}$) are:

(cm^{-1})	296 K	328 K	(cm^{-1})	296 K	328 K
2400	7.71	3.76	2540	6.59	2.30
2420	7.51	3.43	2560	6.49	2.26
2440	7.32	3.15	2580	6.39	2.23
2460	7.14	2.89	2600	6.31	2.21
2480	6.97	2.66	2620	6.24	2.19
2500	6.82	2.47	2640	6.19	2.18
2520	6.70	2.37			

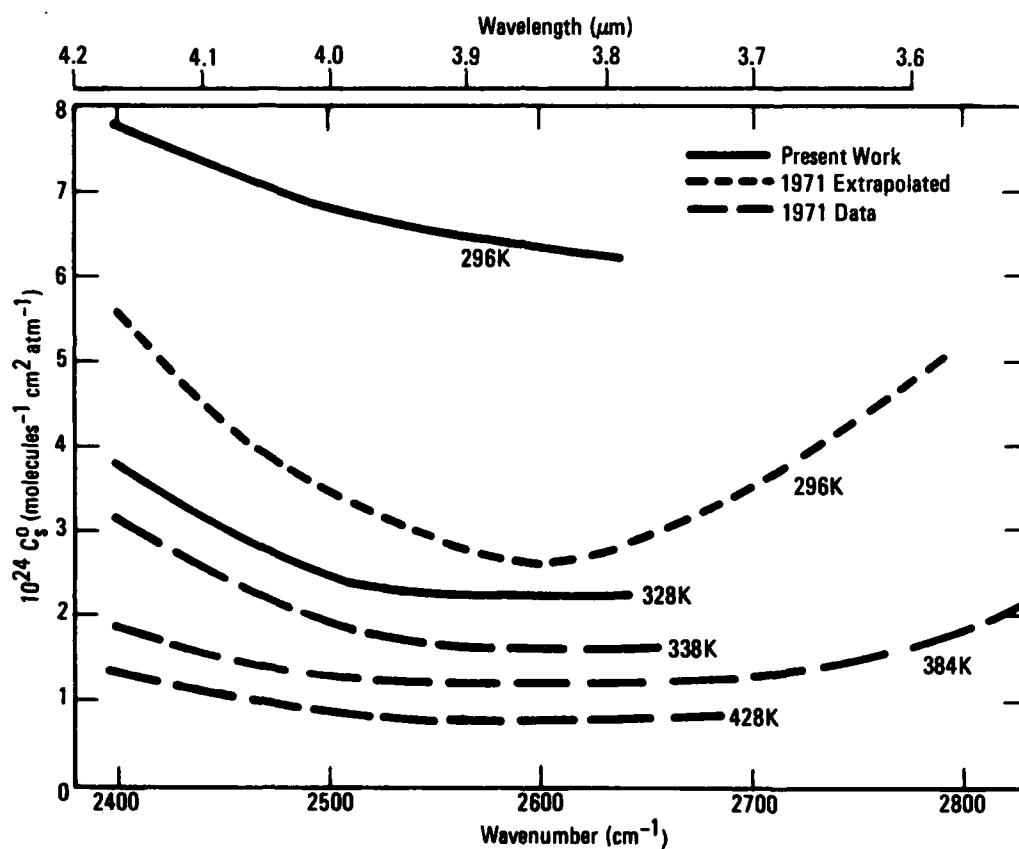


Figure 7. Self-broadening coefficients between 2400 and 2800 cm⁻¹ at various temperatures. The solid curves represent the present work; the broken curves are from our 1971 report⁴.

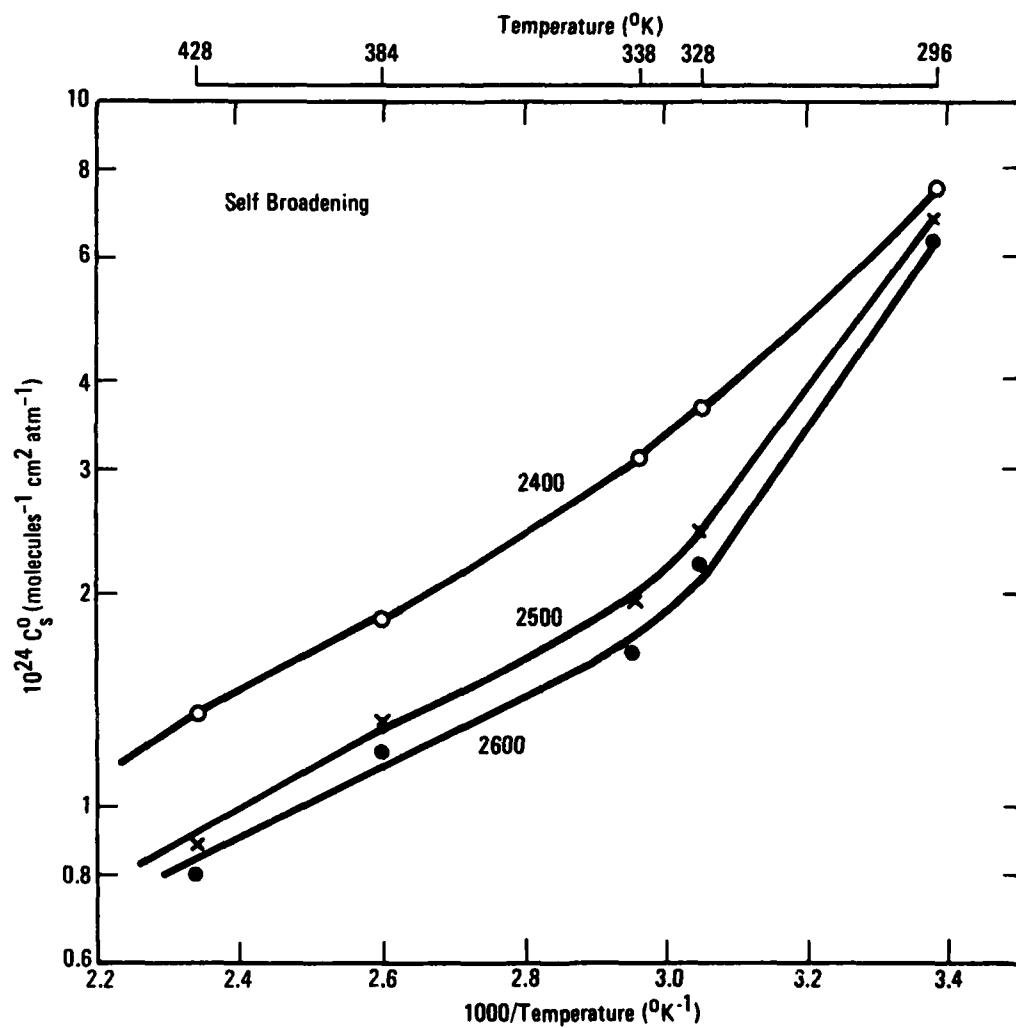


Figure 8. Plots of the self-broadening coefficients at 2400 cm^{-1} , 2500 cm^{-1} and 2600 cm^{-1} versus the reciprocal of temperature.

The rapid increase in the absorption coefficients with decreasing temperature leads to the important practical question of how large these coefficients are at even lower temperatures where accurate laboratory data cannot be obtained. Knowing the continuum coefficients at reduced temperature would be useful in understanding the molecular mechanism that produces the attenuation, but it is less important than it may seem for practical problems related to radiative transfer through the atmosphere. Although the coefficients increase rapidly, the maximum H₂O vapor pressure probably decreases even more rapidly with decreasing temperature. Thus, the maximum amount of continuum absorption in a given path length decreases with decreasing temperature, and a larger fraction of the total attenuation is due to other mechanisms such as H₂O and HDO line absorption, pressure-induced absorption by N₂, CO₂ absorption, and attenuation by haze. It follows that, at low atmospheric temperature, the uncertainties in these other attenuating mechanisms may be much greater than the uncertainty in the attenuation by the H₂O continuum.

Figure 9 compares the present data for 296K with the corresponding curves based on LOWTRAN 6 and on our extrapolated laboratory data of 1971 shown in Figure 7. The 1971 data served as the basis for some of the earlier transmission models, but changes led to the curve of LOWTRAN 6 to bring about better agreement with subsequent measurements over long atmospheric paths. Values for LOWTRAN 6, not shown in the figure, reach a minimum near 2900 cm⁻¹ and increase at higher wavenumbers because of the wings of the strong lines centered between 3000 and 4000 cm⁻¹. The present data agree reasonably well with the LOWTRAN 6 curve near 2400 cm⁻¹, but the discrepancy near 2600 cm⁻¹ is larger than the expected experimental uncertainty.

N₂ BROADENING

The coefficients for N₂ broadening are extremely small and even more difficult to measure accurately than the self-broadening coefficients. In addition to the normal sources of errors, this spectral region contains absorption by a pressure-induced band of N₂ that must be accounted for between approximately 2400 and 2650 cm⁻¹. In the lower wavenumber portion of this region, between approximately 2400 and 2500 cm⁻¹, the pressure-induced absorption by N₂ in the atmosphere is larger than the increases in H₂O absorption due to the presence of N₂.

In a typical measurement, we start with 0.018 atm (approximately 14 torr) of pure H₂O vapor in the absorption cell with a 707 m path difference between the two paths used. Adding N₂ to 1 atm total pressure increases the attenuation by only approximately 0.006 in the regions free of pressure-induced absorption. Thus, it is apparent that small fluctuations in the instruments could lead to a large percentage error in the measured coefficients.

The combined results of several measurements indicate values of C_N^0 (in molecules⁻¹ cm² atm⁻¹) of $2.1 (+/-1.0) \times 10^{-25}$ at 2559.6 cm⁻¹ and $1.7 (+/-1.0) \times 10^{-25}$ at 2616.0 cm⁻¹. The uncertainties indicate the mean deviation in the values obtained for repeated measurements made under similar conditions.

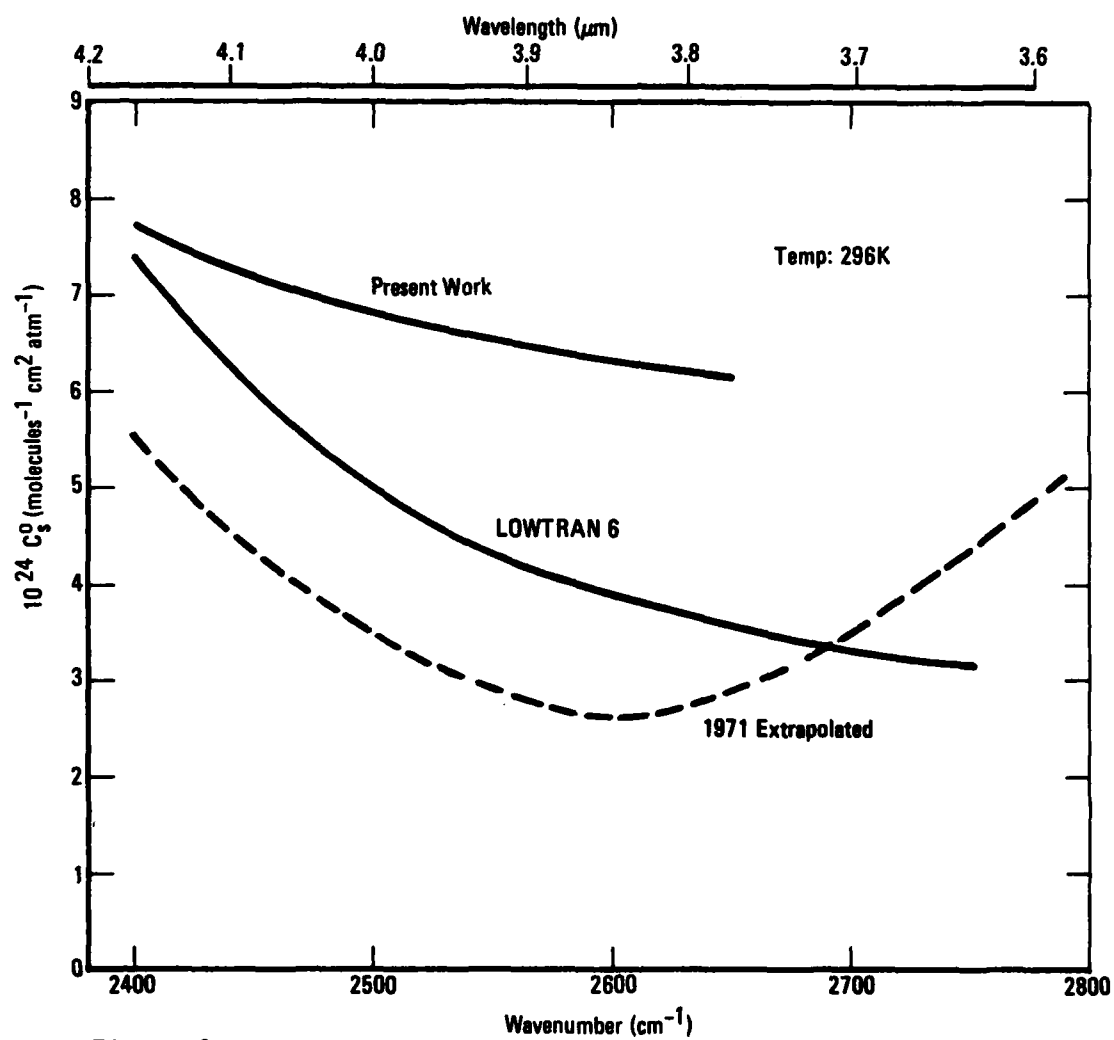


Figure 9. Comparison of self-broadening coefficients between 2400 cm $^{-1}$ and 2800 cm $^{-1}$.

In spite of our efforts to eliminate any sources of significant systematic errors, such errors may still exist and cause the average values measured to be consistently high or low. Turbulence, impurities, improper mixing, and adsorption of water on the optical surfaces in the sample cell are examples of such possible sources of systematic errors. Any systematic errors due to these sources are more likely to cause the measured absorption to be too large than too small. Therefore, it is very unlikely that the true values exceed our measure values by more than 50 percent, but they may be less than the measured values by a bigger percentage.

We have also investigated the continuum due to N_2 broadening at different wavenumbers between 2400 and 2559.6 cm^{-1} . In this region the absorption to be measured is much less than that due to the pressure-induced band of N_2 . Thus, the accuracy of the measurements is severely limited by uncertainty in accounting for the pressure-induced absorption. Although the accuracy of the data is limited, we can conclude that the contribution of the H_2O continuum between 2400 and 2560 cm^{-1} is not greatly different from that measured at 2559.6 cm^{-1} and at 2616 cm^{-1} .

We also made some measurements near 2775 cm^{-1} , where we know the accuracy is limited by impurities in the absorption cell. We estimated the impurity absorption in the samples near 2775 cm^{-1} by comparing the observed absorption with that at nearby wavenumbers where the impurity absorption is known from other measurements to be greater. From the resulting estimates of impurity absorption, we determined that 4×10^{-25} molecules $^{-1} cm^2 atm^{-1}$ represents a maximum value of C_N^O near 2775 cm^{-1} .

Table 2 compares our measured values of C_N^O for 3 different wavenumbers with several values derived from the tabulated values of C_f in LOWTRAN 6. The values from the present data are only about half as large as those from LOWTRAN 6, which are based on a combination of theoretical and experimental results. The best understood line shapes predict much less continuum absorption due to N_2 broadening of the H_2O lines than appears to take place over very long atmospheric paths. Therefore, the authors of LOWTRAN 6 have added an empirical continuum to bring about reasonable agreement with field data.

All of the above discussion about the increase in H_2O continuum absorption due to interactions of the H_2O molecules with the N_2 molecules has been based on the assumption that the increase is due to broadening of the H_2O absorption lines. The data accumulated over the past several years tend to confirm this assumption for most spectral regions. However, other sources of N_2 -produced continuum absorption may be strong enough to be significant in regions such as the 2400-2800 cm^{-1} window where wing absorption is very weak. Tipping⁹ has suggested that molecular complexes that include N_2 molecules temporarily attached to H_2O molecules may be such a source of weak absorption. This absorption, like the N_2 -broadened portion of the H_2O continuum, would increase with the addition of either N_2 or H_2O , making it difficult to distinguish between the two types of absorption.

¹⁰R. Tipping, Oral paper presented at Annual Review Conference on Atmospheric Transmission Models (May 1983).

TABLE 2. COMPARISON OF N₂-BROADENING
RESULTS WITH LOWTRAN 6

Wavenumber (cm ⁻¹)	10 ²⁶ C _N ^O (molecules ⁻¹ cm ² atm ⁻¹)	
	LOWTRAN 6	Present Work
2400	39.3	
2450	39.5	
2500	39.8	
2560	40.9	21 ± 10
2600	42.8	
2616	43.3	17 ± 10
2650	45.2	
2700	46.3	
2750	46.4	
2775	46.7	<40
2800	47.1	

SECTION 5

SUMMARY AND CONCLUSIONS

Improved experimental techniques have been used to obtain new data on the attenuation by the H_2O continuum in the important atmospheric windows from 2400 to 2800 cm^{-1} and from 700 to 1100 cm^{-1} . The data in each window cover self broadening at two temperatures, including room temperature, and N_2 broadening at room temperature. The results are expected to be useful in developing models and computer codes for calculations of atmospheric transmission over a wide variety of atmospheric conditions. Information from the spectral curves of the attenuation coefficients may also add to the understanding of the shapes of the extreme wings of H_2O absorption lines.

The accuracy of the data, particularly those for N_2 broadening, is not as good as we had originally hoped for nor as good as may be desired for modeling. However, the data do make it possible to set reliable upper limits on the amount of attenuation due to the H_2O continuum. In the 2400-2800 cm^{-1} window, and to some extent in the 700-1200 cm^{-1} window, the uncertainty in calculated continuum absorption is probably less than the uncertainty in the attenuation due to aerosols and minor atmospheric constituents.

The low-temperature data indicate that the absorption coefficients continue to increase with decreasing temperature at about the rate that would be expected from previous data on samples at elevated temperatures. This result is particularly important because some scientists have suspected that the coefficients increase at a much more rapid rate with decreasing temperature.

Absorption in each of the 2 windows by pure H_2O has been found to increase with increasing pressure, within experimental uncertainty, as predicted by Equation (1). No significant deviation from this relationship has been observed as the pressure increased to saturation of the H_2O vapor. This result is contrary to previous suggestions by some scientists that H_2O complexes form near saturation and greatly increase the amount of continuum absorption. In previous work we have found that the attenuation in a multiple-pass sample cell did increase more rapidly than expected near saturation when the mirrors in the cell were not clean and were at the same temperature as the gas. We attributed the "extra" attenuation to a coating of adsorbed water on the reflecting surfaces. We suspect that this phenomenon contributed to the extra attenuation observed by others. This effect was greatly reduced, if not completely eliminated, in the present work by using freshly coated mirrors and maintaining them 2 or 3°C above the gas temperature. The absence of any extra attenuation near saturation in the dust-free interior of the sample cell does not rule out the possibility of clusters being formed on small particles in the atmosphere.

The main use of the new data presented in this report will probably be in revising models and computer codes such as LOWTRAN 6 for calculating atmospheric attenuation. We recommend that these data be combined with accurate field data on the attenuation by a variety of long atmospheric paths. It is essential that the atmospheric conditions such as temperature, relative humidity and aerosol content be measured while the field data are being obtained. Neither the laboratory data nor any one set of field data are accurate enough to serve as the sole basis for revised models. The best models can undoubtedly be determined from a combination of laboratory and field data.

SECTION 6

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