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A Critical Review of Measurements of Water Vapor Absorption in the 840 to 1100 cm^{-1} Spectral Region

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Table of Contents

Tables

Figures

Abstract

A set of eleven measurements of the water vapor continuum absorption in the 840 to 1100 cm^{-1} spectral region is reviewed and compared with spectral models maintained by the Air Force Geophysics Laboratory. The measurements were made in four different ways: spectrometer with a White cell, CO_2 laser with a White cell, CO_2 laser with a spectrophone, and broadband radiation source over a long atmospheric path. Where possible, the data were selected at a water vapor partial pressure of ten torr buffered to 760 torr with N_2 or synthetic air and a temperature of between 296 and 300K.

The intercomparison of the data leads to several observations and conclusions. First, there are four sets of laboratory data taken with nitrogen as the buffer gas which generally agree well mutually and with AFGL's HITRAN code. Second, there is one set of laboratory data that shows that using air as the buffer gas gives a few percent decrease in the water vapor continuum compared with using nitrogen as the buffer gas. Third, the atmospheric long-path measurements for water vapor partial pressures below about 12 torr are roughly grouped within 20% of the HITRAN value. For higher water vapor partial pressures, there is an apparent decrease in the water vapor absorption coefficient compared to the models. This is attributed here to aerosol effects at high relative humidities. Fourth, there are three sets of spectrophone data for water vapor in synthetic air which are significantly higher than any of the other measurements. This discrepancy is attributed here to the effects of impurity gases in the cell, possibly from the water sample or leached or desorbed from the cell materials by the presence of the water vapor, making it difficult to monitor. However, errors from other sources, or the possibility that the measurements are essentially correct, cannot be ruled out. It is suggested that such experiments be repeated and compared with similar measurements made with nitrogen as the buffer gas, for which a more justifiable data set exists. Fifth, measurements of the absorption coefficients of strong water vapor lines at CO_2 laser frequencies indicate that there are sizable errors in the synthetic water vapor line parameters for about half the cases investigated which should be corrected with actual measurements in this spectral region.

I. Introduction

A knowledge of the pressure, temperature, and spectral dependences of the water vapor continuum absorption is very important for a number of applications including radiative transfer considerations and remote sensing applications. Unfortunately, a survey of the literature on the nature of the water vapor continuum absorption and its various dependences in the 840 to 1100 cm^{-1} spectral region reveals considerable variation in the reported values over the past twelve years. The purpose of this technical report is to present the laboratory data in one fashion and in one place to critically analyze that data, to recommend an interpretation of that body of data, and to suggest what further research and analyses might be undertaken in order to help resolve the issues present.

II. Water Vapor Continuum Absorption Theory

The theory for the water vapor continuum has been presented in a number of places (see, e.g., Suck et al., 1979, Clough et al., 1980, Suck et al., 1982, Loper et al., 1983, Thomas and Nordstrom, 1985, Clough et al., 1986a, and Hinderling et al., 1987). The more recent work suggests that collisional broadening affecting the wings of distant water vapor lines, rather than the existence of dimers, accounts for the water vapor continuum. However, definition of the continuum is not fully agreed upon. For example, Burch and Alt, 1984, consider the continuum to be the minimum absorption envelope in a broad spectral region from lines greater than 1 cm^{-1} distant from the "windows" where the minimum absorptions are measured. Clough et al., 1986a, on the other hand, define the continuum as that portion of the water vapor absorption occurring from lines greater than 25 cm^{-1} from the frequency under consideration. Since both definitions allow for some contributions from the wings of distant lines, there are problems associated with obtaining unique determinations of both the experimental and theoretical values for the continuum absorption. However, the uncertainties due to the different definitions are small compared with the measurement uncertainties.

III. Measurements

There are at least eleven measurements of water vapor continuum absorption coefficients that have been reported (see Table 1 for a summary of the measurement parameters). This section presents and discusses the results.

A. Spectrometer with White Cell

The foremost among the measurements using a grating spectrometer with a White cell are those by Burch and Alt, 1984. A 29.5-m White cell was used, with 4 passes used for the reference measurement and 28 passes used for the water vapor measurement, for a total differential path of 707 m. Measurements were made with water vapor, nitrogen, or water vapor plus nitrogen, in order to determine both the self-broadening coefficients and the N_2-broadening coefficients. The mirrors in the cell were heated a few degrees above the cell temperature in order to prevent water vapor from condensing on them as had been the case in earlier measurements (Burch, 1982), which resulted in a ~20% reduction in the measured coefficients compared with previous results (Burch, 1982). Two temperatures were used: 286 and 296 K. A spectrometer with 0.3-cm^{-1} resolution was used in the measurements, and "window" regions between water vapor lines were used to determine values for the continuum. The earlier work formed the basis for the values in LOWTRAN 6 (Kneizys et al., 1984) while the more recent results form the basis for the values in HITRAN (Rothman et al., 1987) and FASCOD2 (Clough et al., 1986b).

Figure 1a shows the values reported by Burch and Alt, 1984, while Figure 1b shows their values including the nitrogen-broadening contribution replotted in terms of extinction coefficient, rather than self-broadening coefficient, along with the values on HITRAN (Rothman et al., 1987), which are based on the data of Burch and Alt, 1984, over the spectral region from 700 to 1100 cm^{-1}, as supplied by Clough, 1987. Since the data were fit over the wide region, the fit from 870 to 1080 cm^{-1} is not the best for this region. In fact, as will be shown in the work by Peterson et al., 1979, and Hinderling et al., 1987, there is evidence for a rapid decrease in the continuum absorption in going from 940 to 960 cm^{-1}.

B. Laser with White Cell

Measurements by the group at Ohio State (Nordstrom et al., 1978 and Peterson et al., 1979) are the foremost measurements of this category. A 15-m-long White cell was used, with 100 passes, resulting in a path length of 1.5 km. A CO_2 laser was tuned to a number of laser lines. In Peterson et al., 1979, measurements were made at 297.5 K with nitrogen as the buffer gas. The mirrors were not heated above the cell temperature.

The results for those CO_2 laser lines which are not thought to be significantly affected by nearby water vapor lines are shown in Figure 2. (See Table 2 for a list of CO_2 laser lines considered to not be affected by water vapor line or ammonia absorption.) Data are included for more CO_2 laser lines than for some of the subsequent data sets because there was no apparent increase in absorption strength for such data. Such data is indicated by parentheses. It should be noted that these results agree very well with those of Burch and Alt, 1984, shown in Figure 1. This agreement helps give a high degree of confidence for the measurements from both laboratories.

C. Laser with Spectrophone

The laser photoacoustic or optoacoustic technique, developed in 1972 (Kreuzer et al., 1972), is a very sensitive technique for measuring absorption coefficients. (A list of reviews of the technique can be found in Tam, 1987.) In this approach, a laser beam is directed into a sample cell which contains the gas of interest and a microphone (the combination is called a spectrophone). Usually, a cw laser is used and it is chopped so that phase-sensitive detection can be employed. Absorptions as weak as 10^{-6} can be measured using this approach. Advantages of this approach include the facts that a small path length (10-20 cm) can be used, and that the temperature can be varied over a much larger range than is easy for long White cells.

A number of measurements have been made on water vapor using the photoacoustic technique: Shumate et al., 1976, Peterson et al., 1979, Ryan et al., 1983, Loper et al., 1983, and Hinderling et al., 1987. Those by Shumate et al., Ryan et al. and Loper et al. were with synthetic air as the buffer gas (without CO_2 due to problems with "laser kinetic cooling" (Shumate et al., 1976)), while those by Peterson et al. and Hinderling et al. used nitrogen as the buffer gas. Most measurements were made with the $^{12}C^{16}O_2$ laser (925-1088 cm^{-1}), but Ryan et al. extended the range to 840 cm^{-1} by using $^{13}C^{16}O_2$ and $^{14}C^{16}O_2$ isotopic species. Table 3 provides details of the spectrophone measurement parameters.

One problem with understanding these photoacoustic measurements is the fact that the photoacoustic technique gives relative rather than absolute measurements. Thus, the apparatus has to be calibrated with a reference gas or water vapor line. Most researchers have used ethylene as the reference gas, usually using the 10P(14) CO_2 laser line where ethylene has a strong absorption line. Unfortunately, the accepted value for this absorption coefficient has varied from a low of 29.1 atm^{-1} cm^{-1} to 35.0 atm^{-1} cm^{-1}. Thus, the photoacoustic measurements of water vapor were reported with different values for reference gas. An analysis of eight reported measurements of the ethylene absorption coefficient for the 10P(14) CO_2 laser line yielded a value of 35.0 $\pm$2.2 atm^{-1} cm^{-1} (Grant et al., 1987). When the reported measurements for CO_2 laser lines near strong water vapor line absorptions were adjusted to this value, good agreement was achieved for many of the lines (see Table 4, which has been revised from the version in Grant et al., 1987, to account for apparent impurities in the spectrophones by shifting the data downward to remove the "anomalous" continuum absorption). Note that only measurements made using synthetic air were used in the comparison. Eng et al., 1974, had pointed out that air is about 90% effective as N_2 in broadening water vapor lines. Thus, air-broadened absorption coefficients will be higher near the absorption line center than for nitrogen-broadened absorption coefficients, and lower in the wings.

Note that there is poor agreement between half of the photoacoustic measurements of the strong water vapor lines and the values at those frequencies on the AFGL HITRAN code (Rothman et al., 1987), Table 5. The significant H_2O line absorptions in this spectral region are mainly pure rotational or ν_2 vibrational band transitions with large values of ΔK_a. The positions and strengths for these, according to Rothman et al., 1987, have been computed using molecular parameters determined from measurements of lines outside this spectral region. Rothman estimates the accuracy of the calculated line strengths to be 20% and the line positions to be about 0.002%. The disagreement between the measurements and the AFGL predictions seems too large, in many cases, to be accounted for with this level of uncertainty. The major cause of the discrepancy is probably that the water vapor spectral line data on the AFGL tape was determined using theoretical calculations with a sparse amount of experimental data from spectral regions outside the 9-11 μm region. In any case, it seems clear that accurate spectroscopic measurements of the H_2O line absorptions in this spectral region are needed.

Buoyed by the good mutual agreement for the spectrophone measurements for the strong water vapor lines, I decided to see whether a similar result could be obtained for the water vapor continuum. A preliminary analysis was performed for CO_2 laser lines for which at least three measurements were reported near 300 K and 10 torr in air or nitrogen, and for which nearby water vapor lines were not thought to contribute more than 1 or 2% to the absorption coefficient, checked using AFGL's HITRAN (Clough, 1987) (see also Table 2). The results indicated that the photoacoustic values were significantly higher than the AFGL values based on the measurements by Burch and Alt, 1984 (Grant et al., 1987).

One set of data not considered in Grant et al., 1987, is that by Peterson et al., 1979 (Figure 2). They used a non-resonant differential spectrophone, designed to eliminate the effects of window absorption on the measurement. The spectrophone data were normalized in this case using the strong water vapor absorption line at the 10R(20) CO_2 laser line. Although the spectrophone data appear to be a few percent higher on average than the White cell data, the agreement between the two data sets and Burch and Alt's, 1984, data is quite good.

This realization that spectrophone and White cell water-vapor continuum data could agree if the same buffer gas and sufficient experimental care were used prompted a further look at the effects of oxygen and nitrogen on the continuum absorption coefficients. (Note that this was not a "blind comparison" as is the case for most of the rest of the data reported here.) In a 1978 paper, Nordstrom et al. compared White cell water vapor data for five CO_2 laser lines for 100% N_2, 80% N_2:20% O_2 and 60% N_2:40% O_2. For the two CO_2 laser lines which are thought to overlap primarily with water vapor continuum and not the wings of water vapor lines (10P(28) and 10R(28)), the measured absorption for the 80:20 mixture was a few percent lower than for the pure N_2 mixture at 10 torr of water vapor. While the authors found it difficult to fully analyze the results, partly because it was difficult to unambiguously separate absorption line wings from the continuum, this result suggests that the effect of oxygen on the continuum absorption has to be considered.

The next data set to consider is that of Hinderling et al., 1987. It, too, was measured in pure N_2 buffer gas (10 torr in 760 torr total pressure, 296 K). Values where water vapor lines are not expected to contribute significantly (greater than 1 or 2%) to the measurements are shown in Figure 3. In the 925 to 985 cm^{-1} spectral region, these data agree well with the data in Figures 1 and 2, although the spread in the data is larger than in those figures. However, in the 1030 to 1090 cm^{-1} region, the data are 40 to 70% higher. The authors admit that trace contaminants did produce a perceptible background in this region, so these data are not as reliable as those in the 925 to 985 cm^{-1} region. Thus, with the exception of the higher energy values by Hinderling et al., 1987, the N_2-buffered data at 10-torr water vapor partial pressure at 296 K agree quite well.

Now let us turn to the synthetic-air buffered water vapor data, considering data for 10 torr of water vapor in a total pressure of 760 torr at a temperature of 296 or 300 K. (According to the data of Burch and Alt, 1984, the values at 300 K should be about 8% lower than those at 296 K.)

The first set of such data are those of Shumate et al., 1976, taken using a resonant spectrophone shown in Figure 4 at 300K. They had cleaned their glassware with ammonia, and could not seem to entirely rid the chamber of residual ammonia, so had to correct some of the data for ammonia absorption (data points denoted by X's). In the 930 to 980 cm^{-1} region, their values, corrected for the ethylene absorption coefficient value (they used 29.1 $atm^{-1}cm^{-1}$), are roughly 30 to 70% higher than the AFGL HITRAN values, while in the 1040 to 1090 cm^{-1} region, their values are 75 to 100% higher. The reported measurement statistical uncertainty of 5% and actual data spread of no more than about 10% are relatively small compared with the differences. The relatively flat dependence of the continuum absorption with frequency is similar to that reported by Hinderling et al., 1987.

Loper et al., 1983, reported data under the same conditions as Shumate et al., 1976, but only in the 930 to 985 cm^{-1} spectral region, using a non-resonant cell. Values tend to be about 10% higher than those of Shumate et al., and the data appear to have a smaller spread (Figure 5). Not shown are additional data taken at a variety of partial pressures and temperatures down to 263 K.

Finally, there are the data of Ryan et al., 1983, taken at 296 K for 10-torr partial pressure of water vapor in synthetic air. They used three isotopic species of CO_2: $^{12}C^{16}O_2$, $^{13}C^{16}O_2$, and $^{14}C^{16}O_2$, enabling them to cover the region from 840 to 1090 cm^{-1}. Their data for continuum absorption are shown in Figure 6. (Note that their originally published data was in error because the flow tube used to measure water vapor concentration was not calibrated for water vapor, and they used a value of 30 atm^{-1} cm^{-1} for the ethylene absorption coefficient at the 10P(14) CO_2 laser line.) Data from Ryan et al. were included only if the data at one laser frequency measured at two water vapor partial pressures seemed to exhibit a quadratic dependence with pressure. While the spread in the data is larger than for the other measurements, there are still some interesting points to make about the data. First, the data agree reasonably well with the data of Loper et al., 1983; the values are roughly 70% higher than the AFGL HITRAN values. Second, the data over the entire spectral region show a decrease with increasing frequency.

It is difficult to satisfactorily sort out the effects of using air rather than nitrogen as the buffer gas for the spectrophone measurements. In the only set of measurements where the continuum absorption was compared for the two buffer gases (Nordstrom et al., 1978), a decrease of a few percent was found for air as opposed to nitrogen. However, since these authors subsequently obtained measurements of the water vapor continuum absorption in nitrogen that agreed with and predated the results of Burch and Alt, 1984, these data should be considered to be reliable.

Sample and cell purity seems to be a major problem with spectrophone measurements. Perhaps water can cause adsorbed gases to desorb from the cell walls (Ryan, 1987), an effect that would not be detected even while dual chamber measurements were being made, as by Loper et al., 1983. Also, the water used was known to have impurities in at least one case with ammonia detected, and methanol and formaldehyde suspected (Hinderling et al., 1987).

For an absorption coefficient of 10 atm^{-1} cm^{-1}, the impurity gases would only have to be present in the 20-40 ppb range to account for the "excess" water vapor absorption. Note that this is a plausibility argument, rather than a definitive one. Other sources of measurement error cannot be ruled out, nor can the possibility that the values determined using spectrophones are substantially correct.

D. Broadband Source with Long Atmospheric Path

There have been at least three sets of data reported using a broadband spectral source over a long (2 to 44 km) path in the atmosphere for the measurement of the water vapor continuum absorption coefficients (Kneizys et al., 1984, Cutten, 1985, and Ben-Shalom et al., 1985).

The Kneizys et al. data sets were compared with LOWTRAN 5 and found to be in good agreement except for water vapor content greater than 14 gm/m^3, where the data yielded lower values than expected. (LOWTRAN 5 values are about the same as for LOWTRAN 6, and are about 20% higher than the FASCOD2 or HITRAN values presently adopted.)

Cutten, 1985, found that his atmospheric measurements for water vapor contents of less than 13 gm/m^3 yielded water vapor continuum transmittances about 20% greater than for LOWTRAN 6, while for higher water vapor contents, the deviations were much higher.

Ben-Shalom et al., 1985, measured water vapor continuum over a 5 to 44 km path at more than fifty wavelength regions on the 8 to 13 µm region. The measurement error at each wavelength was about $\pm$10 to $\pm$15%. They found that the water vapor continuum absorption was weaker than in LOWTRAN 5 by about 20%, which would make it nearly consistent with the more recent FASCOD2, although their data plotted in Clough et al., 1986b, indicates that the values are somewhat higher than for FASCOD2.

It is possible that changes in the aerosol scattering could account for the discrepancy at the higher partial pressures (see, e.g., Cutten, 1985, Bohren and Koh, 1985, Smith and Carswell, 1986 and Isaacs et al., 1987). As the relative humidity rises above 85%, aerosols grow rapidly as they take on more water, and become more nearly spherical. Forward scattering can be changed, as can total extinction, possibly leading to the observed effects of high R.H.

While the atmospheric long-path data are difficult to analyze due to interferences from CO_2, ozone, aerosols, atmospheric turbulence, possible inaccuracies in measuring the temperature and water vapor distribution along the path, calibrating the instrument, and properly accounting for strong water vapor lines, the three sets of data are fairly mutually consistent and indicate that for water vapor content of less than 13 gm/m^3 the water vapor continuum absorption probably lies above the value for HITRAN. For higher water vapor content for which lower absorption coefficients were measured, aerosol effects are probably more important. However, atmospheric long path measurements are considered more to bound the continuum absorption coefficients, rather than provide a direct measure of them, due to the inherent difficulties in monitoring the atmosphere along the path or cell.

E. Comparison of Experimental Features of the Various Measurement Techniques

As should be evident by now, the various approaches for measuring the water vapor continuum absorption coefficients each have their problems, as well as advantages and disadvantages when compared with the other approaches. In spite of the experimental difficulties, skilled researchers seem to have coaxed acceptable values from their laboratory measurement apparatus, while those making atmospheric long-path measurements seem not to have due to the complex nature of the real atmosphere and the difficulty in simultaneously monitoring enough of the parameters to enable a reliable value for the water vapor contribution to be extracted. Nonetheless, the atmospheric measurements do serve to support the lower value laboratory measurements.

In Table 6, the three techniques, spectrophone, White cell, and atmospheric long-path, are compared by listing the problems faced in using the approach, as well as some of the advantages of the approach. A number of the items listed as problems have been overcome and are now handled routinely, but are included so that newcomers to the field are made aware of them, and so that they can be kept in mind when examining earlier data sets. It is probably fair to say that a skilled experimenter can obtain reliable data using any one of the three approaches, as long as sufficient care is taken in sample preparation, equipment calibration, and sample monitoring.

IV. Summary

Based on the foregoing critical review, I draw the following conclusions:

1. While there is a considerable amount of disparity among the different water vapor continuum data sets, there appears to be substantial agreement for the data taken by Peterson et al., 1979, Burch and Alt, 1984, and the 10-micron data by Hinderling et al., 1987. These data also represent the lowest values for the continuum absorption among comparable data sets. I consider these data sets to be the "accepted values" at this time, although the degree of certainty in accepting these values is not as high as it should be.

2. When the effects of oxygen on the water vapor continuum absorption spectrum are included, the absorption coefficients should be reduced by a few percent to represent values in air, rather than nitrogen.

3. The AFGL HITRAN code is in reasonable agreement with the data measured by Burch and Alt, 1984, and Peterson et al., 1979 for the continuum, although the effects of oxygen and the possible existence of broad structure on the continuum have not been included.

4. The AFGL HITRAN code appears to have errors associated with its values for absorption by strong water vapor lines in the 9 to 11 micron region.

5. Some of the spectrophone work may have been affected by the presence of impurities in the cell, or other experimental difficulties, leading to anomalously high values for the continuum absorption.

6. The atmospheric long-path measurements may be affected by absorption by other molecular species, absorption by strong water vapor lines, scattering by aerosols, atmospheric turbulence, and water vapor content inhomogeneities along the measurement path, and so are deemed to be unreliable.

V. Recommendations

Based on the above summary, there are a number of measurements and other investigations that can be performed to resolve some of the issues and extend the knowledge base.

1. A uniform definition of "continuum absorption" should be adapted.

2. Measurements should be made of the strong water vapor absorption lines in the 9-11 micron region at various temperatures and pressures in synthetic air so that the data base can be improved. Tunable diode lasers may be useful in this effort, especially for water vapor lines near CO_2 laser lines, since this would aid further measurements using CO_2 lasers. FTIR spectrometers could also be used.

3. Spectrophone measurements should be repeated and extended in temperature and pressure with synthetic air as the buffer gas, taking advantage of what has been learned in the past and, perhaps, making some improvements. Possible sources of the (anomalously) high values reported by some researchers could be investigated. A large volume-to-surface ratio seems to be important in reducing the effects of impurities on the measurements, with the exception of the impurities brought in with the gasses themselves in each fill. This implies use of a resonant cell, with a moderate Q, and some technique to stabilize or monitor the resonant frequency during the measurements. The technique for calibrating the spectrophone should be extended to the 9 micron region and include more than just the ethylene absorption at the 10P(14) CO_2 laser line. Perhaps water vapor lines could be used, if they are known well. Perhaps an inert gas, such as a freon, could be used, as long as the absorption coefficients can be well characterized as a function of temperature and, perhaps, pressure. The flowing gas approach demonstrated by Ryan et al., 1983, might be employed in an attempt to control the water vapor partial pressure well.

4. White cell measurements could also be extended. It would be worthwhile considering the use of a CO_2 laser or a spectrometer with resolution greater than 0.3 cm^{-1}.

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Table 1. Summary of Water Vapor Continuum Absorption Measurement Parameters

Source	Cell	Path length (m)	Spectral region (cm^{-1})	Water vapor partial pressure (torr)	Buffer Gas	Temperature (K)	Reference
Spectrometer	White	707	700-100 2400-2800	14.3	N_2	284,296,328	Burch and Alt, 1984
CO_2 laser	White	1500	944-980	6-14	N_2 $80\%N_2:20\%O_2$ $60\%N_2:40\%O_2$	296	Nordstrom et al., 1978
CO_2 laser	White	1500	935-1082	4-15	N_2	297.5	Peterson et al., 1979
CO_2 laser	Spectrophone	0.20	933-1086	5,10,15	Air	300	Shumate et al., 1976
CO_2 laser	Spectrophone	0.23	935-1082	4-15	N_2	297.5	Peterson et al., 1979
CO_2 laser	Spectrophone	0.32	935-983	17-10	Air	263-300	Loper et al., 1983
CO_2 laser (isotopes)	Spectrophone	0.30	840-1090	3.5-11	Air	296	Ryan et al., 1983
CO_2 laser	Spectrophone	0.28	925-1088	10	N_2	286,296,325	Hinderling et al., 1987
Carbon arc/ filter	Atmosphere	2250 8000	800-1250 2000-3300	5-20	Air	280-300	Kneizys et al., 1984
Carbon arc/ filter	Atmosphere	5000 7000 9000	850-1220	5-25	Air	291-305	Cutten 1985
Carbon arc/ filter	Atmosphere	5000 to 44000	800-1280 1800-2300	15-20	Air	298-299	Ben-Shalom et al., 1985

Table 2. $^{12}C^{16}O_2$ Laser Lines Thought Not to Be Affected Significantly by Water Vapor Line or Ammonia Absorption[a]

Designation	Frequency[b] (cm^{-1})	Designation	Frequency[b] (cm^{-1})
10P (38)	927.0083	9P (36)	1031.4774
34	931.0014	34	1033.4880
32	932.9604	26	1041.2791
30	934.8945	24	1043.1632
28	936.8037	22	1045.0217
26	938.6883	20	1046.8542
22	942.3833	18	1048.6608
18	945.9802	14	1052.1955
12	951.1923	12	1053.9235
8	954.5451	8	1057.3002
6	956.1850		
		9R (6)	1069.0141
10R (24)	978.4723	8	1070.4623
26	979.7054	20	1078.5906
28	980.9132	22	1079.8523
32	983.2522	26	1082.2962
36	985.4883	28	1083.4788
38	986.5674	34	1086.8698
		38	1089.0011

[a]To the 1-2% level for water vapor line absorption.
[b]Bradley et al., 1986.

Table 3. Spectrophone Measurement Parameters

Parameter	Peterson	Hinderling	Shumate	Ryan	Loper
Mechanical					
Cell length	29.5 cm	16 cm	20 cm	30 cm	14.9 cm
Cell Volume	30 cm^3	1810 cm^3	3530 cm^3	11.5 cm^3	11.5 cm^3
Cell Volume/Surface Ratio	0.3 cm	2.18 cm	3.16 cm	0.17 cm	0.24 cm
Cell Wall Material	Stainless Steel	Copper	Pyrex	Glass	Stainless Steel
Number of Compartments	2	3	1	1	2
Resonant Frequency	NA	3460 Hz	2750 Hz	695 Hz	NA
Q	NA	340	200	17	NA
Window Effects Reduction	Dual cell, laser beam alignment	3 cells			Dual cell
Experimental					
H_2O Partial Pressure	4-15 torr	10 torr	5,10, 15 torr	3-11 torr	3-10 torr
Source of Water	Triple Distilled				
Flowing gas or static?	Static	Static	Static	Flowing	Static
Calibration					
Original Value Used for Ethylene Absorption	NA	34.76 atm^{-1} cm^{-1}	29.1 atm^{-1} cm^{-1}	33 atm^{-1} cm^{-1}	34.76 atm^{-1} cm^{-1}
Correction Factor for Ethylene	NA	1.007	1.20	1.06	1.002

Table 4. Spectrophone Measurements of Strong Water Vapor Line Absorption Coefficients at 300 K, 10-Torr Partial Pressure, in Synthetic Air, and (α) C_2H_4 = 34.76 atm^{-1} cm^{-1}, for Selected CO_2 Laser Lines

CO_2 laser line	Shumate ($10^{-6}cm^{-1}$)	Nordstrom ($10^{-6}cm^{-1}$)	Ryan ($10^{-6}cm^{-1}$)	Loper ($10^{-6}cm^{-1}$)	Average ($10^{-6}cm^{-1}$)	Relative uncertainty (%)
10P(40)			12.4		12.4	
10P(20)	1.02	1.09	0.69	0.92	0.93 ± 0.15	16
10P(16)[a]	1.09		0.98	1.08	1.05 ± 0.05	5
10R(12)[a]	2.07		2.19	2.07	2.11 ± 0.06	3
10R(14)[a]	1.70	1.8		1.66	1.72 ± 0.06	3
10R(16)	1.60		1.24	1.26	1.37 ± 0.17	12
10R(18)	1.07		0.89	0.88	0.95 ± 0.08	8
10R(20)	12.68	10.7	11.38	9.09	11.30 ± 1.3	12
10R(22)	1.59	1.32	1.20	1.28	1.35 ± 0.15	11
9P(28)	2.76		3.10		2.93 ± 0.17	6
9P(10)	2.86	3.4	2.65		2.97 ± 0.32	11
9R(12)	0.82		1.14		0.98 ± 0.16	16
9R(14)	3.62		3.49		3.56 ± 0.07	2
9R(16)[a]	0.93		0.84		0.89 ± 0.05	5
9R(30)[a]			2.78		2.78	
9R(32)	0.97		1.13		1.05 ± 0.08	8

[a]Ammonia interference possible for this CO_2 laser line.

Table 5. Comparison of Spectrophone Measurements of Strong Water Vapor Line Absorption Coefficients using CO_2 Lasers with the Values using HITRAN for 10-Torr Partial Pressure, 300 K, $(\alpha)\ C_2H_4 = 35.0\ atm^{-1}\ cm^{-1}$

CO_2 laser line designation	CO_2 laser line frequency[a] (cm^{-1})	CO_2 laser value[b] ($10^{-6}\ cm^{-1}$)	AFGL value[c] ($10^{-6}\ cm^{-1}$)	H_2O Center Frequency (cm^{-1})
10P(40)	924.9740	12.40 ± 1.5	20.5 ± 4.1	924.9882
10P(20)	944.1940	0.93 ± 0.16	0.88 ± 0.10	944.4210
10P(16)	947.7420	1.05 ± 0.08	1.05 ± 0.11	948.2635
10R(12)	970.5472	2.11 ± 0.15	2.03 ± 0.25	970.5705
10R(14)	971.9303	1.72 ± 0.12	0.88 ± 0.10	971.6561
10R(16)	973.2885	1.37 ± 0.19	1.08 ± 0.12	973.2528
10R(18)	974.6219	0.95 ± 0.10	0.79 ± 0.08	973.9833
10R(20)	975.9304	11.30 ± 1.5	10.4 ± 2.1	975.9436
10R(22)	977.2139	1.35 ± 0.17	1.04 ± 0.11	977.4314
9P(28)	1039.3693	2.93 ± 0.25	1.63 ± 0.18	1039.5441
9P(10)	1055.6251	2.97 ± 0.38	2.28 ± 0.29	1055.5177
9R(12)	1073.2785	0.98 ± 0.17	1.57 ± 0.18	1073.2807
9R(14)	1074.6465	3.56 ± 0.23	1.87 ± 0.21	1074.4071
9R(16)	1075.9878	0.89 ± 0.07	1.00 ± 0.10	1075.3781
9R(30)	1084.6351	2.78 ± 0.28	0.62 ± 0.06	1084.8271
9R(32)	1085.7654	1.05 ± 0.11	0.75 ± 0.08	1085.5502

[a] Bradley et al., 1986

[b] Includes 6.24% uncertainty due to the uncertainty in determining the value of the ethylene absorption coefficient for the 10P(14) CO_2 laser line.

[c] JPL and AFGL (Clough, 1987) determinations, with the line strengths thought to be accurate to ±20%, and the continuum to ±10%.

Table 6. Comparison of Problems and Advantages for Three Approaches for Measuring Water Vapor Continuum Absorption Coefficients

Problems	Advantages
Spectrophone	
Sample and cell purity	Small cell size
Non-tunability of source	Temperature can be easily varied
Volume-to-surface ratio	
Calibration	Uniform gas mixture
Maintaining resonant frequency	Easy to calibrate
Window effects	
Laser beam alignment	
Water vapor concentration	
Laser kenetic cooling of CO_2	
Knowledge of water vapor line absorption	
Adsorption and desorption of water vapor to walls	
White cell	
Low spectral resolution with spectrometer	Large volume-to-surface ratio
Non-tunability of CO_2 laser	
Knowledge of water vapor line absorption	Impurities less of a problem
Definition of continuum	
Coating of mirror surfaces	Continuous tunability
Calibration	
Adsorption of water vapor to walls	
Water vapor concentration uniformity	
Sample purity	
Atmospheric long-path	
Aerosols	
Water vapor inhomogeneity	No window effects
Other absorbing gases	
Water vapor line absorption	No wall adsorption
Calibration	
Low resolution	
Lack of control of temperature and pressure	

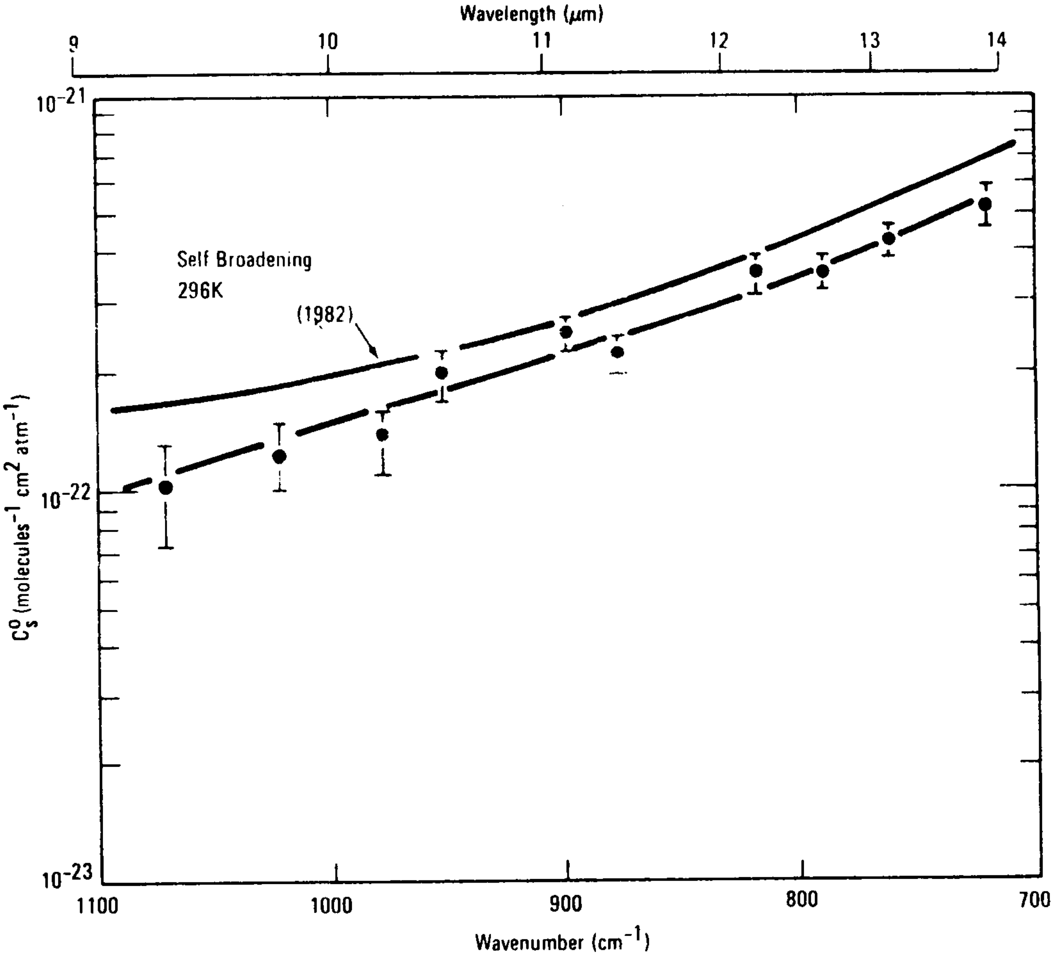

Figure 1a. Experimental data for the water vapor continuum self-broadening coefficient from Burch and Alt, 1984, measured using a spectrometer with 0.3 cm^{-1} resolution, and a White cell.

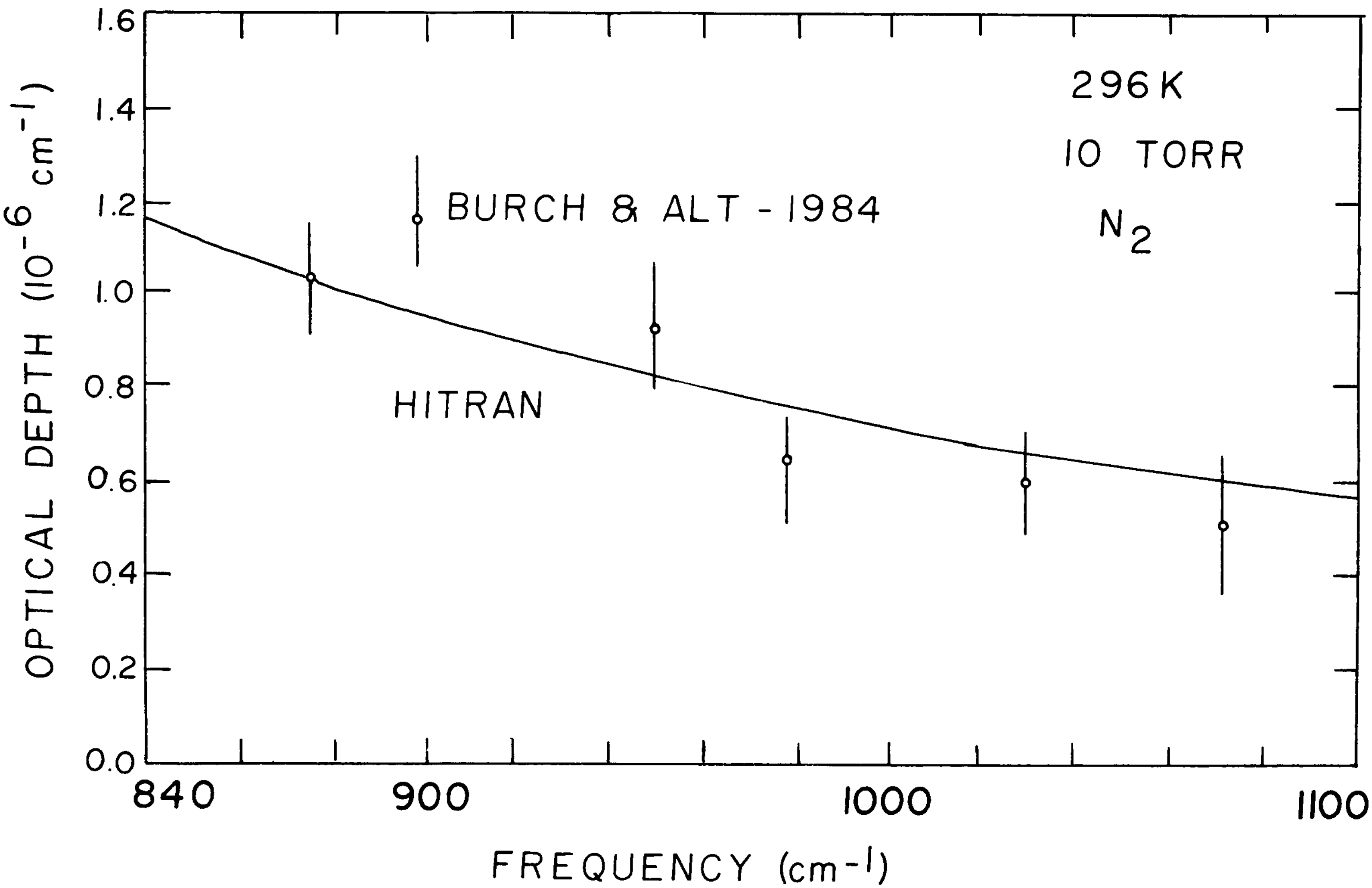

Figure 1b. Values of water vapor continuum absorption coefficient at 14.3 torr water vapor in nitrogen for a total pressure of 760 torr at 296 K were converted to values at 10 torr using Table 1 of Burch and Alt. Also shown are the AFGL values on HITRAN (Rothman et al., 1987), courtesy of Clough, 1987. Note that 1 torr = 1.058 g/m^3.

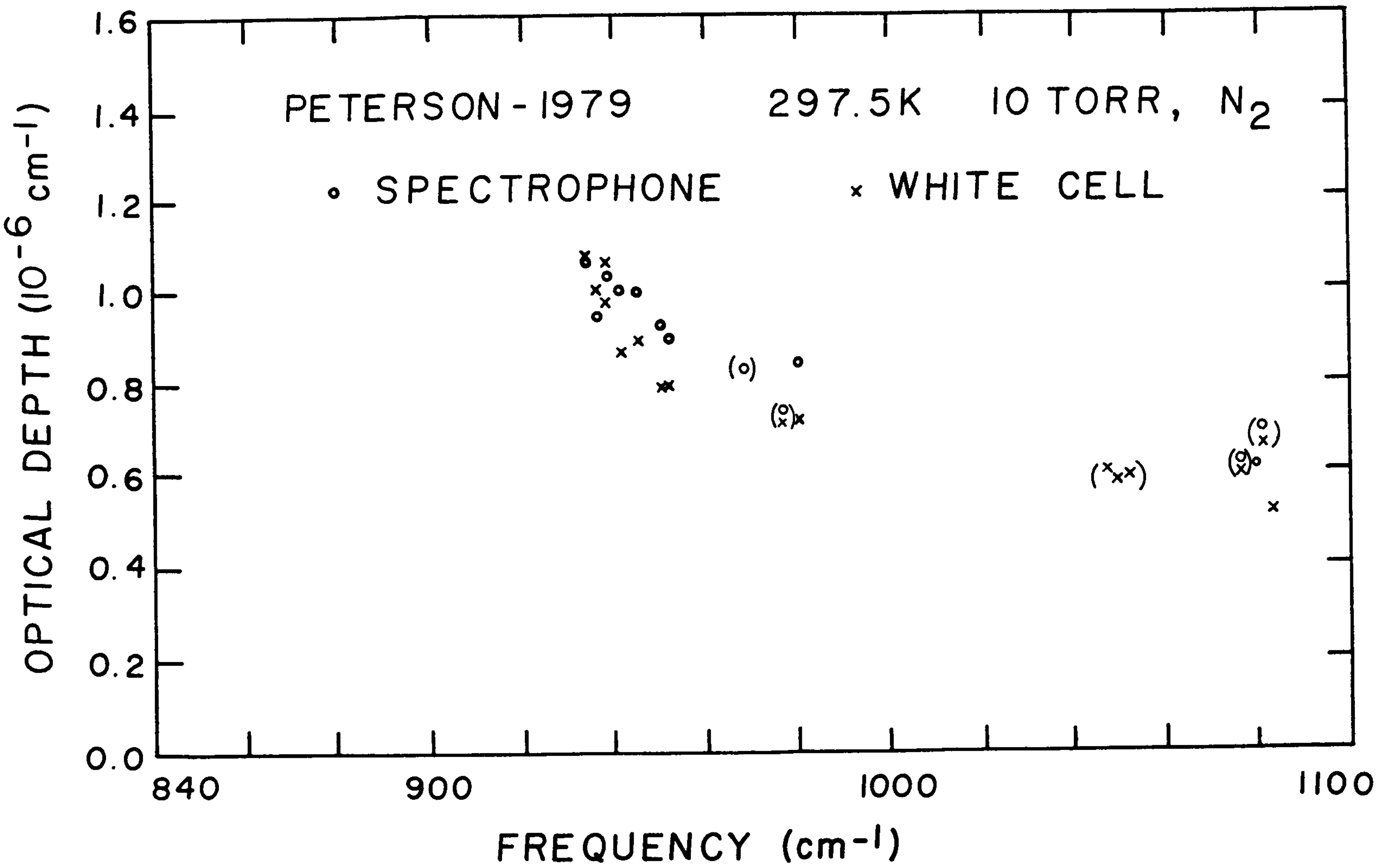

Figure 2. Experimental values for water vapor continuum from Peterson et al., 1979, for 10 torr of water vapor in nitrogen at a total pressure of 760 torr at 297.5 K. A CO_2 laser was used to make the measurements. The dots indicate values for spectrophone measurements, while Xs indicate values measured in a White cell. Those values which could be affected by nearby water vapor lines or ammonia are enclosed in parentheses. The values were calculated from the data in their Table I, with reference to the data in their Figures 3 to 5.

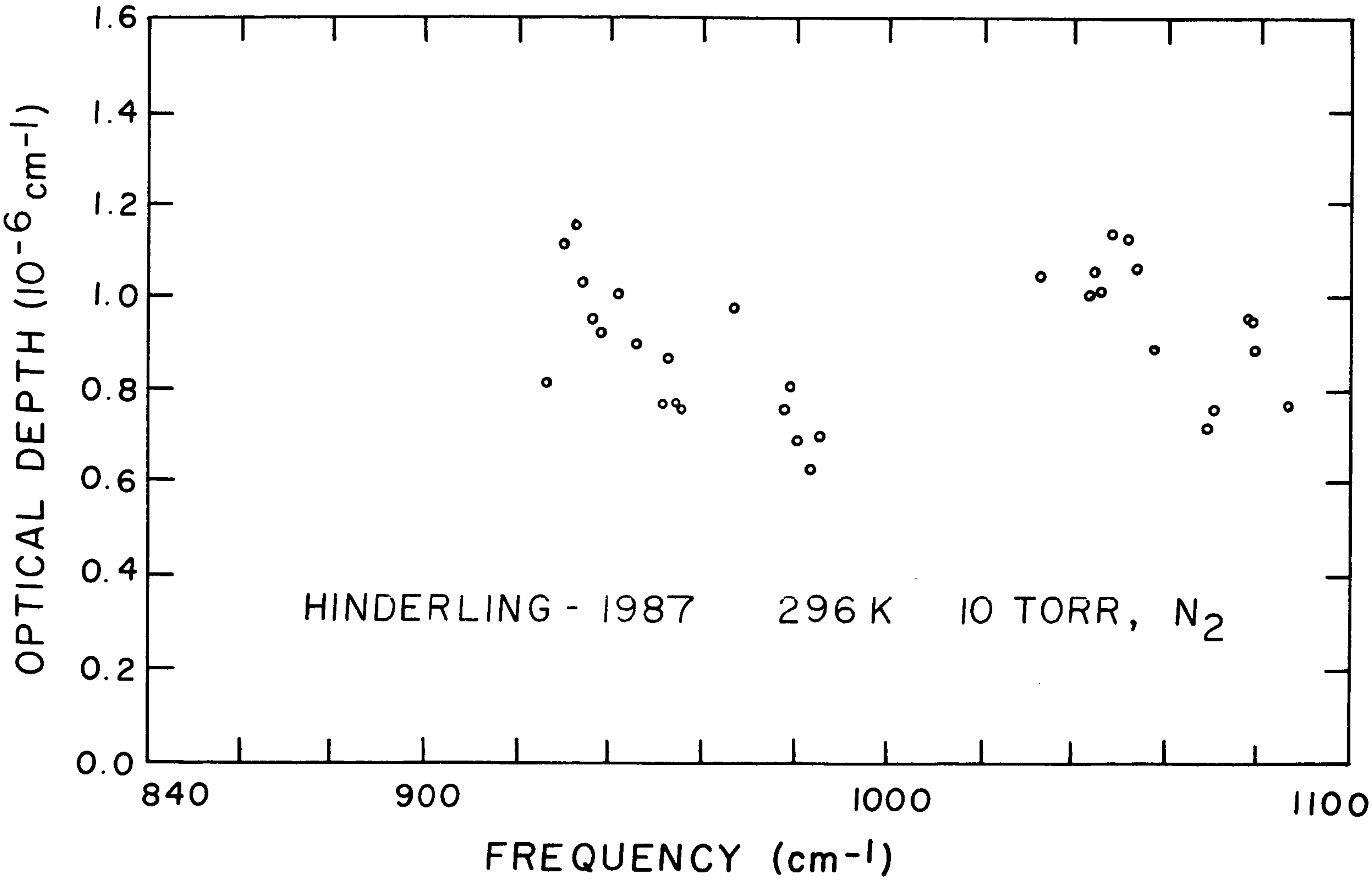

Figure 3. Experimental values for water vapor continuum absorption measured by Hinderling et al., 1987, using a spectrophone for 10 torr of water vapor in nitrogen for a total pressure of 760 torr at 296 K. The values in the 1030 to 1090 cm^{-1} spectral region may have been affected by trace contaminants in the cell.

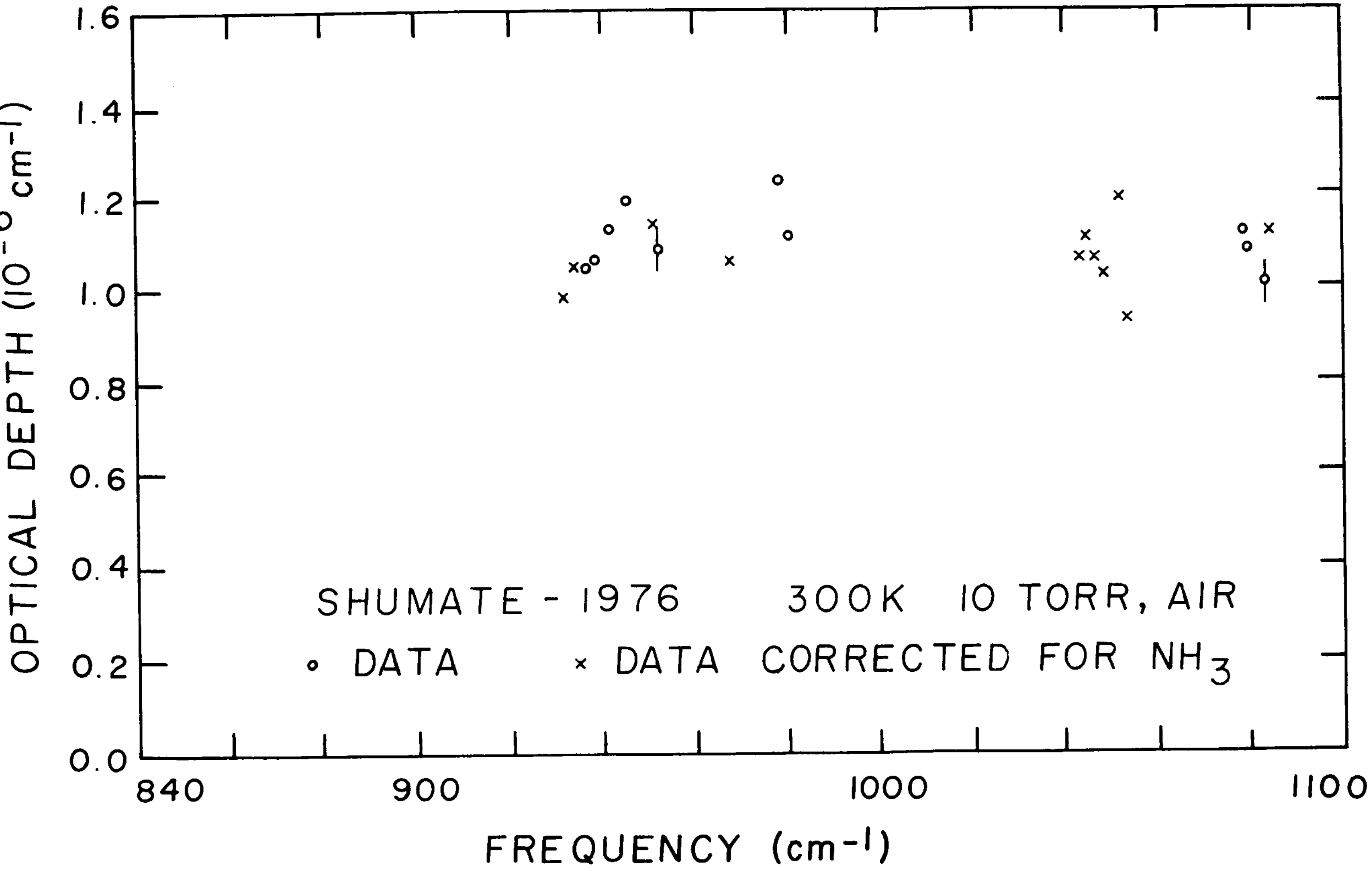

Figure 4. Experimental values for water vapor continuum absorption measured by Shumate et al., 1976, using a spectrophone at 10 torr in synthetic air at a total pressure of 760 torr and 300 K. The values reported have been increased by 21% to account for the difference in the ethylene absorption coefficient used by them (29.1 atm^{-1} cm^{-1}) and the current best value (35.0 ± 2.2 atm^{-1} cm^{-1}). The dots represent normal data; the Xs represent data which they corrected for the presence of ammonia in the spectrophone.

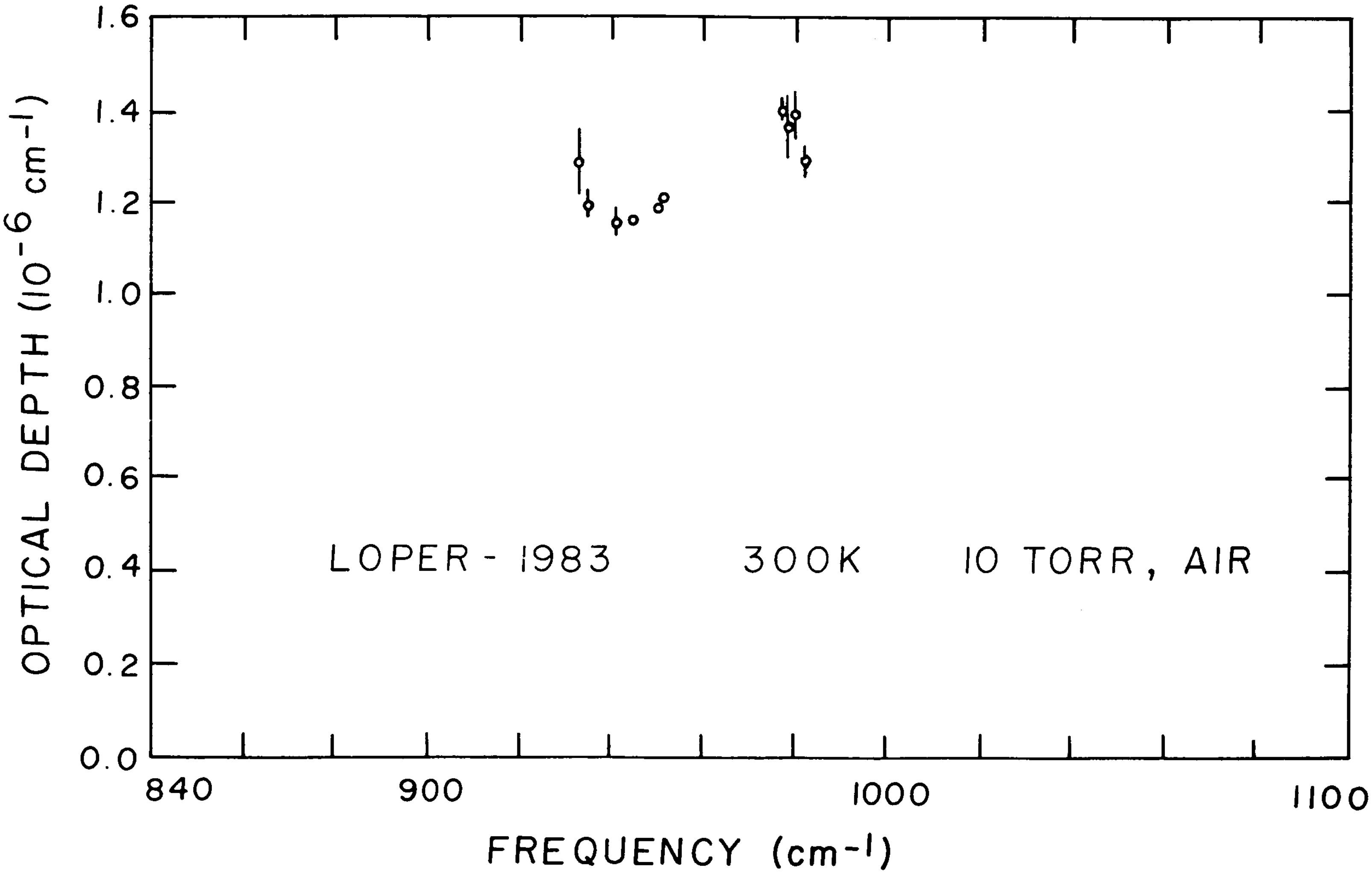

Figure 5. Experimental values for water vapor continuum absorption measured by Loper et al., 1983, using a spectrophone, at 10 torr in synthetic air at a total pressure of 760 torr and 300 K.

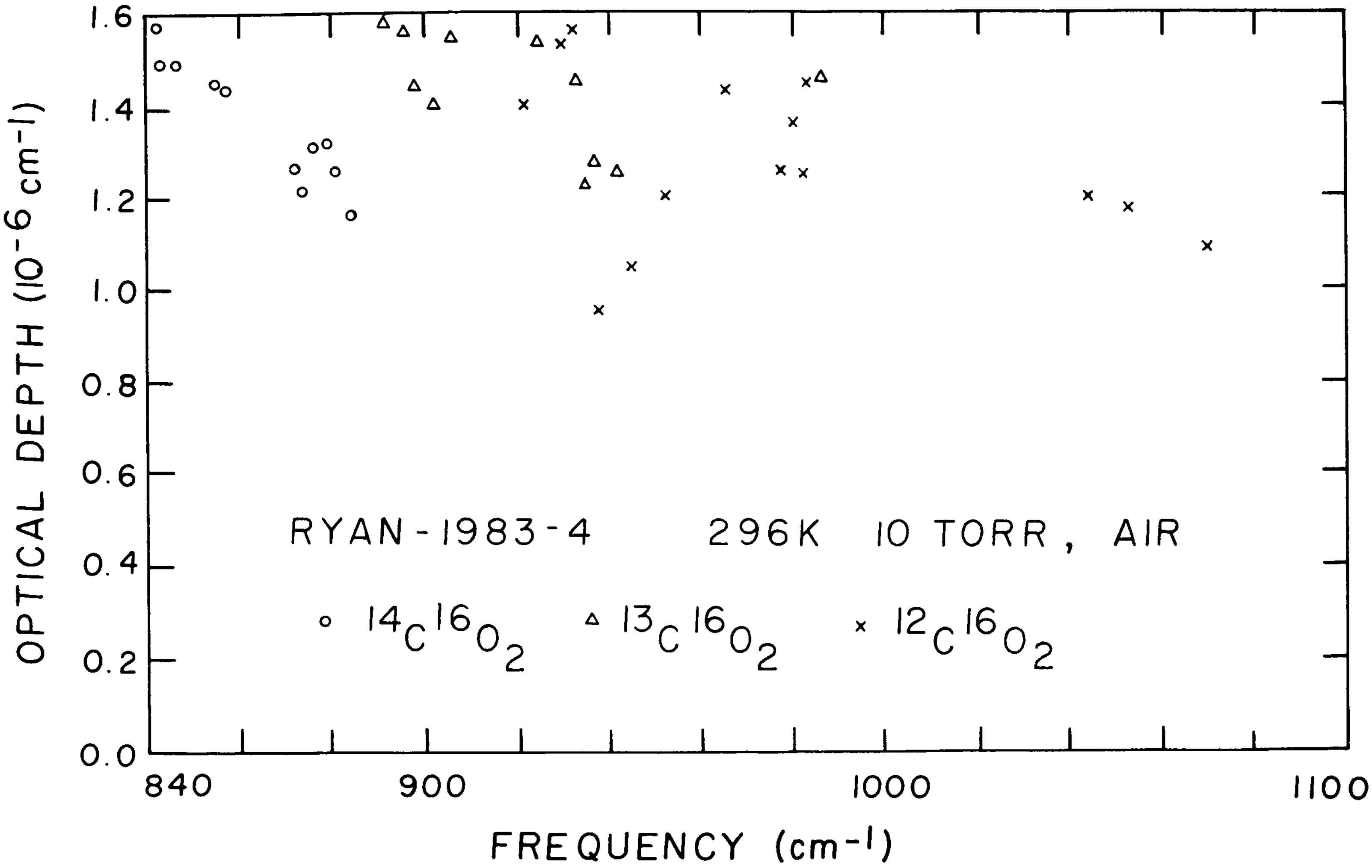

Figure 6. Experimental values for water vapor continuum absorption measured by Ryan et al., 1983, using a spectrophone, at 10 torr in synthetic air at a total pressure of 760 torr and 296 K. The Xs represent data obtained using a $^{12}C^{16}O_2$ laser at 8.4 and 10 torr. The Δs represent data obtained using a $^{13}C^{16}O_2$ laser at 8.4 and 10.7 torr and the o's represent data obtained using a $^{14}C^{16}O_2$ laser at 8.6 and 11 torr both adjusted to 10 torr assuming a pressure-squared dependence of the absorption.

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16. Abstract

A set of eleven measurements of the water vapor continuum absorption in the 840 to 1100 cm^{-1} spectral region is reviewed and compared with spectral models maintained by the Air Force Geophysics Laboratory. The measurements were made in four different ways: spectrometer with a White cell, CO_2 laser with a White cell, CO_2 laser with a spectrophone, and broadband radiation source over a long atmospheric path. Where possible, the data were selected at a water vapor partial pressure of ten torr buffered to 760 torr with N_2 or synthetic air and a temperature of between 296 and 300K.

The intercomparison of the data leads to several observations and conclusions. First, there are four sets of laboratory data taken with nitrogen as the buffer gas which generally agree well mutually and with AFGL's HITRAN code. Second, there is one set of laboratory data that shows that using air as the buffer gas gives a few percent decrease in the water vapor continuum compared with using nitrogen as the buffer gas. Third, the atmospheric long-path measurements for water vapor partial pressures below about 12 torr are roughly grouped within 20% of the HITRAN value. For higher water vapor partial pressures, ther is an apparent decrease in the water vapor absorption coefficient compared to the models. This is attributed here to aerosol effects at high relative humidities. Fourth, there are three sets of spectrophone data for water vapor in synthetic air which are significantly higher than any of the other measurements. This discrepancy is attributed here to the effects of impurity gases in the cell.

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