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

William B. Grant

December 15, 1987

Prepared for
U.S. Air Force
and
National Aeronautics and Space Administration
by
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California
The research described in this publication was carried out by the Jet Propulsion Laboratory, California Institute of Technology, and was sponsored by the U. S. Air Force and the National Aeronautics and Space Administration.

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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, CO₂ laser with a White cell, CO₂ 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 N₂ 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 CO₂ 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 CO² 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 CO² 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 CO² laser lines considered to not be affected by
water vapor line or ammonia absorption.) Data are included for more CO²
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 CO₂ 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 12C₁₆O₂ laser (925-1088 cm⁻¹), but Ryan et al. extended the range to 840 cm⁻¹ by using 1₃C₁₆O₂ and 1₄C₁₆O₂ 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) CO₂ 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) CO₂ laser line yielded a value of 35.0 ±2.2 atm⁻¹ cm⁻¹ (Grant et al., 1987). When the reported measurements for CO₂ 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 N₂ 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 H₂O line absorptions in this spectral region are mainly pure rotational or ν₂ vibrational band transitions with large values of ΔKₙ. 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 H₂O 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 CO₂ 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) CO₂ 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 CO₂ laser lines for 100% N₂, 80% N₂:20% O₂ and 60% N₂:40% O₂. For the two CO₂ 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 N₂ 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 N₂ 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 N₂-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 ±10 to ±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$^{-1}$.

VI. Acknowledgments

The author would like to thank J. S. Margolis, R. T. Menzies, C. B. Farmer, G. L. Loper (Aerospace Corp.), S. A. Clough (AFGL), and M. E. Thomas (Johns Hopkins University) for helpful discussions. This work was performed at the Jet Propulsion Laboratory, California Institute of Technology, with support from the National Aeronautics and Space Administration and the U.S. Air Force. The author would like to specifically acknowledge the J. F. Kennedy Space Center and the Air Force Engineering and Services Center, Tyndall AFB, Florida.
VII. References


S. A. Clough, 1987, AFGL, private communication.


<table>
<thead>
<tr>
<th>Source</th>
<th>Cell</th>
<th>Path length (m)</th>
<th>Spectral region (cm⁻¹)</th>
<th>Water vapor partial pressure (torr)</th>
<th>Buffer Gas</th>
<th>Temperature (K)</th>
<th>Reference</th>
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<td>White</td>
<td>707</td>
<td>700-100 2400-2800</td>
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<td>White</td>
<td>1500</td>
<td>944-980</td>
<td>6-14</td>
<td>N₂ 80%N₂:20%O₂ 60%N₂:40%O₂</td>
<td>296</td>
<td>Nordstrom et al., 1978</td>
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<td>N₂</td>
<td>297.5</td>
<td>Peterson et al., 1979</td>
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<td>800-1250 2000-3300</td>
<td>5-20</td>
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<td>5-25</td>
<td>Air</td>
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<td>800-1280 1800-2300</td>
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<td>Air</td>
<td>298-299</td>
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Table 2. $^{12}\text{C}^{16}\text{O}_2$ Laser Lines Thought Not to Be Affected Significantly by Water Vapor Line or Ammonia Absorption$^a$

<table>
<thead>
<tr>
<th>Designation</th>
<th>Frequency$^b$ (cm$^{-1}$)</th>
<th>Designation</th>
<th>Frequency$^b$ (cm$^{-1}$)</th>
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<tbody>
<tr>
<td>10P (38)</td>
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<td>9P (36)</td>
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<td>931.0014</td>
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<td>1033.4880</td>
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<td>932.9604</td>
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<td>945.9802</td>
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<td>1052.1955</td>
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<td>951.1923</td>
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<td>1053.9235</td>
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<td>6</td>
<td>954.5451</td>
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<td>1057.3002</td>
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<td>9R (6)</td>
<td>956.1850</td>
<td>8</td>
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<tr>
<td>10R (24)</td>
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<tr>
<td>26</td>
<td>978.4723</td>
<td>20</td>
<td>1070.4623</td>
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<td>28</td>
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<td>32</td>
<td>980.9132</td>
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<td>1079.8523</td>
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<td>983.2522</td>
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<td>38</td>
<td>985.4883</td>
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<td>1083.4788</td>
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<td>986.5674</td>
<td>38</td>
<td>1086.8698</td>
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</table>

$^a$To the 1-2% level for water vapor line absorption.
$^b$Bradley et al., 1986.
Table 3. Spectrophone Measurement Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Peterson</th>
<th>Hinderling</th>
<th>Shumate</th>
<th>Ryan</th>
<th>Loper</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mechanical</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cell length</td>
<td>29.5 cm</td>
<td>16 cm</td>
<td>20 cm</td>
<td>30 cm</td>
<td>14.9 cm</td>
</tr>
<tr>
<td>Cell Volume</td>
<td>30 cm³</td>
<td>1810 cm³</td>
<td>3530 cm³</td>
<td>11.5 cm³</td>
<td>11.5 cm³</td>
</tr>
<tr>
<td>Cell Volume/Surface Ratio</td>
<td>0.3 cm</td>
<td>2.18 cm</td>
<td>3.16 cm</td>
<td>0.17 cm</td>
<td>0.24 cm</td>
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<tr>
<td>Cell Wall Material</td>
<td>Stainless Steel</td>
<td>Copper</td>
<td>Pyrex</td>
<td>Glass</td>
<td>Stainless Steel</td>
</tr>
<tr>
<td>Number of Compartments</td>
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<td>3</td>
<td>1</td>
<td>1</td>
<td>2</td>
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<tr>
<td>Resonant Frequency</td>
<td>NA</td>
<td>3460 Hz</td>
<td>2750 Hz</td>
<td>695 Hz</td>
<td>NA</td>
</tr>
<tr>
<td>Q</td>
<td>NA</td>
<td>340</td>
<td>200</td>
<td>17</td>
<td>NA</td>
</tr>
<tr>
<td>Window Effects Reduction</td>
<td>Dual cell, laser beam alignment</td>
<td>3 cells</td>
<td></td>
<td></td>
<td>Dual cell</td>
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<tr>
<td><strong>Experimental</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O Partial Pressure</td>
<td>4-15 torr</td>
<td>10 torr</td>
<td>5,10, 15 torr</td>
<td>3-11 torr</td>
<td>3-10 torr</td>
</tr>
<tr>
<td>Source of Water</td>
<td>Triple Distilled</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Flowing gas or static?</td>
<td>Static</td>
<td>Static</td>
<td>Static</td>
<td>Flowing</td>
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</tr>
<tr>
<td><strong>Calibration</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Original Value Used for Ethylene Absorption</td>
<td>NA</td>
<td>34.76 atm⁻¹ cm⁻¹</td>
<td>29.1 atm⁻¹ cm⁻¹</td>
<td>33 atm⁻¹ cm⁻¹</td>
<td>34.76 atm⁻¹ cm⁻¹</td>
</tr>
<tr>
<td>Correction Factor for Ethylene</td>
<td>NA</td>
<td>1.007</td>
<td>1.20</td>
<td>1.06</td>
<td>1.002</td>
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</tbody>
</table>
Table 4. Spectrophone Measurements of Strong Water Vapor Line Absorption Coefficients at 300 K, 10-Torr Partial Pressure, in Synthetic Air, and (α) C₂H₄ = 34.76 atm⁻¹ cm⁻¹, for Selected CO₂ Laser Lines

<table>
<thead>
<tr>
<th>CO₂ laser line</th>
<th>Shumate ((10^{-6}\text{ cm}^{-1}))</th>
<th>Nordstrom ((10^{-6}\text{ cm}^{-1}))</th>
<th>Ryan ((10^{-6}\text{ cm}^{-1}))</th>
<th>Loper ((10^{-6}\text{ cm}^{-1}))</th>
<th>Average ((10^{-6}\text{ cm}^{-1}))</th>
<th>Relative uncertainty (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10P(40)</td>
<td>1.02</td>
<td>1.09</td>
<td>12.4</td>
<td>0.93 ± 0.15</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>10P(20)</td>
<td>1.09</td>
<td>0.98</td>
<td>2.07</td>
<td>1.05 ± 0.05</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>10P(16)</td>
<td>2.07</td>
<td>1.66</td>
<td>1.37 ± 0.17</td>
<td>0.95 ± 0.08</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>10R(14)</td>
<td>1.70</td>
<td>1.8</td>
<td>1.30 ± 1.3</td>
<td>11.60</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>10R(16)</td>
<td>1.60</td>
<td>1.24</td>
<td>9.09</td>
<td>11.35 ± 0.15</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>10R(18)</td>
<td>0.97</td>
<td>0.89</td>
<td>0.88</td>
<td>2.93 ± 0.17</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>9P(28)</td>
<td>2.76</td>
<td>3.10</td>
<td>3.62</td>
<td>2.97 ± 0.32</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>9R(10)</td>
<td>2.86</td>
<td>2.65</td>
<td>3.49</td>
<td>0.98 ± 0.16</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>9R(14)</td>
<td>0.93</td>
<td>0.84</td>
<td>0.89 ± 0.05</td>
<td>2.78</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>9R(30)</td>
<td>0.97</td>
<td>1.13</td>
<td>1.05 ± 0.08</td>
<td>8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*aAmmonia interference possible for this CO₂ 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, (a) C$_2$H$_4$ = 35.0 atm$^{-1}$ cm$^{-1}$

<table>
<thead>
<tr>
<th>CO$_2$ laser line designation</th>
<th>CO$_2$ laser line frequency$^a$ (cm$^{-1}$)</th>
<th>CO$_2$ laser value$^b$ (10$^{-6}$ cm$^{-1}$)</th>
<th>AFGL value$^c$ (10$^{-6}$ cm$^{-1}$)</th>
<th>H$_2$O Center Frequency (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10P(40)</td>
<td>924.9740</td>
<td>12.40 ± 1.5</td>
<td>20.5 ± 4.1</td>
<td>924.9882</td>
</tr>
<tr>
<td>10P(20)</td>
<td>944.1940</td>
<td>0.93 ± 0.16</td>
<td>0.88 ± 0.10</td>
<td>944.4210</td>
</tr>
<tr>
<td>10P(16)</td>
<td>947.7420</td>
<td>1.05 ± 0.08</td>
<td>1.05 ± 0.11</td>
<td>948.2635</td>
</tr>
<tr>
<td>10R(12)</td>
<td>970.5472</td>
<td>2.11 ± 0.15</td>
<td>2.03 ± 0.25</td>
<td>970.5705</td>
</tr>
<tr>
<td>10R(14)</td>
<td>971.9303</td>
<td>1.72 ± 0.12</td>
<td>0.88 ± 0.10</td>
<td>971.6561</td>
</tr>
<tr>
<td>10R(16)</td>
<td>973.2885</td>
<td>1.37 ± 0.19</td>
<td>1.08 ± 0.12</td>
<td>973.2528</td>
</tr>
<tr>
<td>10R(18)</td>
<td>974.6219</td>
<td>0.95 ± 0.10</td>
<td>0.79 ± 0.08</td>
<td>973.9833</td>
</tr>
<tr>
<td>10R(20)</td>
<td>975.9304</td>
<td>11.30 ± 1.5</td>
<td>10.4 ± 2.1</td>
<td>975.9436</td>
</tr>
<tr>
<td>10R(22)</td>
<td>977.2139</td>
<td>1.35 ± 0.17</td>
<td>1.04 ± 0.11</td>
<td>977.4314</td>
</tr>
<tr>
<td>9P(28)</td>
<td>1039.3693</td>
<td>2.93 ± 0.25</td>
<td>1.63 ± 0.18</td>
<td>1039.5441</td>
</tr>
<tr>
<td>9P(10)</td>
<td>1055.6251</td>
<td>2.97 ± 0.38</td>
<td>2.28 ± 0.29</td>
<td>1055.5177</td>
</tr>
<tr>
<td>9R(12)</td>
<td>1073.2785</td>
<td>0.98 ± 0.17</td>
<td>1.57 ± 0.18</td>
<td>1073.2807</td>
</tr>
<tr>
<td>9R(14)</td>
<td>1074.6465</td>
<td>3.56 ± 0.23</td>
<td>1.87 ± 0.21</td>
<td>1074.4071</td>
</tr>
<tr>
<td>9R(16)</td>
<td>1075.9878</td>
<td>0.89 ± 0.07</td>
<td>1.00 ± 0.10</td>
<td>1075.3781</td>
</tr>
<tr>
<td>9R(30)</td>
<td>1084.6351</td>
<td>2.78 ± 0.28</td>
<td>0.62 ± 0.06</td>
<td>1084.8271</td>
</tr>
<tr>
<td>9R(32)</td>
<td>1085.7654</td>
<td>1.05 ± 0.11</td>
<td>0.75 ± 0.08</td>
<td>1085.5502</td>
</tr>
</tbody>
</table>

$^a$ 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 (Glough, 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

<table>
<thead>
<tr>
<th>Problems</th>
<th>Advantages</th>
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<tbody>
<tr>
<td><strong>Spectrophone</strong></td>
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</tr>
<tr>
<td>Sample and cell purity</td>
<td>Small cell size</td>
</tr>
<tr>
<td>Non-tunability of source</td>
<td>Temperature can be easily varied</td>
</tr>
<tr>
<td>Volume-to-surface ratio</td>
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</tr>
<tr>
<td>Calibration</td>
<td>Uniform gas mixture</td>
</tr>
<tr>
<td>Maintaining resonant frequency</td>
<td>Easy to calibrate</td>
</tr>
<tr>
<td>Window effects</td>
<td></td>
</tr>
<tr>
<td>Laser beam alignment</td>
<td></td>
</tr>
<tr>
<td>Water vapor concentration</td>
<td></td>
</tr>
<tr>
<td>Laser kinetic cooling of CO₂</td>
<td></td>
</tr>
<tr>
<td>Knowledge of water vapor line absorption</td>
<td></td>
</tr>
<tr>
<td>Adsorption and desorption of water vapor to walls</td>
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</tr>
<tr>
<td><strong>White cell</strong></td>
<td></td>
</tr>
<tr>
<td>Low spectral resolution with spectrometer</td>
<td>Large volume-to-surface ratio</td>
</tr>
<tr>
<td>Non-tunability of CO₂ laser</td>
<td></td>
</tr>
<tr>
<td>Knowledge of water vapor line absorption</td>
<td>Impurities less of a problem</td>
</tr>
<tr>
<td>Definition of continuum</td>
<td>Continuous tunability</td>
</tr>
<tr>
<td>Coating of mirror surfaces</td>
<td></td>
</tr>
<tr>
<td>Calibration</td>
<td></td>
</tr>
<tr>
<td>Adsorption of water vapor to walls</td>
<td></td>
</tr>
<tr>
<td>Water vapor concentration uniformity</td>
<td></td>
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<tr>
<td>Sample purity</td>
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</tr>
<tr>
<td><strong>Atmospheric long-path</strong></td>
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<td>Aerosols</td>
<td>No window effects</td>
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<td>Water vapor inhomogeneity</td>
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<td>Other absorbing gases</td>
<td>No wall adsorption</td>
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<tr>
<td>Water vapor line absorption</td>
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<td>Calibration</td>
<td></td>
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<tr>
<td>Low resolution</td>
<td></td>
</tr>
<tr>
<td>Lack of control of temperature and pressure</td>
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</table>
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/m³.
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 spectrophotometer, 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.
A Critical Review of Measurements of Water Vapor Absorption in the 840 to 1100 cm⁻¹ Spectral Region

William B. Grant

JET PROPULSION LABORATORY
California Institute of Technology
4800 Oak Grove Drive
Pasadena, California 91109

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Washington, D.C. 20546

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, CO₂ laser with a White cell, CO₂ 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 N₂ 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.