Pure water vapor continuum measurements between 3100 and 4400 cm\(^{-1}\): Evidence for water dimer absorption in near atmospheric conditions

D. J. Paynter, 1 I. V. Ptashnik, 2,3 K. P. Shine, 1 and K. M. Smith 4

Received 8 January 2007; revised 7 April 2007; accepted 9 May 2007; published 23 June 2007.

[1] Despite the potentially important role that water dimers may play in the Earth’s energy balance, there is still a lack of firm evidence for absorption of radiation by dimers in near-atmospheric conditions. We present results of the first high-resolution laboratory measurements of the water vapor continuum absorption within the 3100–4400 cm\(^{-1}\) spectral region at a range of near-room temperatures. The analysis indicates a large contribution of dimer absorption to the water vapor continuum, significantly in excess of that predicted by other modern representations of the continuum. The temperature dependence agrees well with that expected for dimers. Citation: Paynter, D. J., I. V. Ptashnik, K. P. Shine, and K. M. Smith (2007), Pure water vapor continuum measurements between 3100 and 4400 cm\(^{-1}\): Evidence for water dimer absorption in near atmospheric conditions, Geophys. Res. Lett., 34, L12808, doi:10.1029/2007GL029259.

1. Introduction

[2] Water vapor is the most important radiatively active gas in the Earth’s atmosphere [Kiehl and Trenberth, 1997], absorbing across visible and infrared wavelengths. Its spectrum consists of thousands of broadened lines associated with rotational and rotational-vibrational transitions. In addition to these lines, it has long been recognized that water vapor possesses a continuum absorption which varies relatively slowly with wavelength. It was initially proposed [Elsasser, 1938] that this continuum was due to the cumulative absorption by the distant wings of the spectral lines; later it was also suggested [Penner and Varanasi, 1967] that a component of the continuum was the absorption by the water dimer – (H\(_2\)O)\(_2\) - a complex consisting of two weakly-bonded water molecules.

[3] The origin of the continuum has remained controversial ever since; in many applications of radiative transfer, the semi-empirical Clough-Kneizys-Davies (CKD) continuum model is used [Clough et al., 1989]. The CKD continuum is essentially defined as the difference between observed absorption/emission and that predicted using line-by-line simulations due to the spectral lines; it uses a plausible physical model to predict the continuum to wave-lengths or conditions that have not been observed. By contrast Ma and Tipping [2002] (MT) use theoretical calculations of the departure of water monomer spectral lines from a Lorentzian shape to estimate the continuum. In recent years, however, the possible role of the dimer in explaining the continuum has re-emerged [e.g., Ptashnik et al., 2004; Daniel et al., 2004; Cormier et al., 2005] as a result of modern ab-initio prediction of its spectrum [Lov and Kjaergaard, 1999; Vaida et al., 2001; Schofield and Kjaergaard, 2003] and temperature dependence [Vigasin, 2000]; these allow a more targeted approach to detecting the resulting spectral features in laboratory or atmospheric spectra. However, the theoretical calculations of the water dimer spectrum are subject to an ongoing debate. It can be inferred from Brown and Tipping [2003] that their calculations indicate no significant dimer absorption.

[4] The spectroscopic properties of the dimer, like other clusters, are usually studied in non-equilibrium or non-gaseous conditions like expanded molecular beams [e.g., Huiski, 1996; Nizkorodov et al., 2005] or in solid matrices [e.g., Perchard, 2001] at very low temperatures. These investigations cannot give information about either the abundance of dimers or the strength of their absorption in atmospheric conditions.

[5] Initial attempts to detect direct dimer absorption in the atmosphere proved unsuccessful [Daniel et al., 1999; Hill and Jones, 2000]. The first reports claiming detection of dimer absorption in the atmosphere [Pfeilsticker et al., 2003] (near 13400 cm\(^{-1}\)) and in equilibrium room-temperature laboratory conditions [Ptashnik et al., 2004] (within the 5300 cm\(^{-1}\) water vapor band) appeared only recently. The conclusion of Pfeilsticker et al. [2003], however, was criticized by Suhm [2004] and has not been confirmed by repeat measurements [Lotter, 2006], while the result obtained by Ptashnik et al. [2004] still requires independent verification.

[6] To choose the spectral region suitable for dimer detection and to derive its abundance, both these works used the recent ab-initio prediction by Schofield and Kjaergaard [2003] (henceforth SK) for dimer band intensities and positions. These theoretical predictions agree well with solid matrices non-equilibrium dimer measurements of Perchard [2001]. Since the results of Ptashnik et al. [2004] seems to confirm the SK prediction for the dimer stretching + bending vibrations near 5300 cm\(^{-1}\), it seemed logical to test the validity of this theory for another spectral region, in which an alternative set of measurements was available to provide important supporting evidence.

[7] Comparing the theoretical prediction of SK for the dimer spectrum with that of the water monomer (Figure 1b)
Figure 1. The absorption spectra calculated (a) for a mixture of 15 mbar water vapor with 1000 mbar of N₂ (T = 293K), and (b) for pure water vapor. The water monomer spectrum (WM) is simulated using HITRAN-2004 line catalogue with the MT_CKD continuum included. The water dimer (WD) absorption is plotted according to ab-initio intensities and the SK band positions, using a band HWHM of 25 cm⁻¹ and equilibrium constant Kᵣₑᵣ = 0.041 atm⁻¹ according to Curtiss et al. [1979] extrapolation (see Figure 4).

shows that the region 3100–4200 cm⁻¹ is the most promising for laboratory detection of dimer absorption from 1000–8000 cm⁻¹. Additionally, recent literature reviews [Ptashnik, 2005; I. V. Ptashnik, Evaluation of suitable spectral intervals for near-IR laboratory detection of water vapour continuum absorption, submitted to Journal of Quantitative Spectroscopy & Radiative Transfer, 2007, hereinafter referred to as Ptashnik, submitted manuscript, 2007] reveal that the only known room-temperature measurement of continuum absorption in this spectral region, made by Burch [1985], has spectral features similar to those predicted by SK.

[8] We present results of modern high-resolution water vapour continuum measurements in this spectral region at near-room temperatures; firstly to verify the 20-year-old low-resolution experiment of Burch [1985], secondly to compare our new results with modern continuum models and dimer ab-initio prediction, and thirdly, and crucially, to ascertain for the first time the temperature dependence of the continuum between 3100 cm⁻¹ and 4200 cm⁻¹, which can provide important evidence of the physical origin of the absorption.

2. Deriving the Continuum

[9] Near-infrared spectra of pure water vapor were obtained at the Rutherford Appleton Laboratory Spectroscopy Facility using a high-resolution Fourier transform spectrometer at a resolution of 0.03 cm⁻¹ with a short-path-length absorption cell [Remedios, 1990] at an optical path length of 17.2 m. The experiment was carried out at vapor pressures between 20 and 266 mbar and temperatures between 296 and 351 K. Further details of the experimental setup can be found in Ptashnik et al. [2004].

[10] The pure water vapor continuum is defined as the difference between the measured absorbance spectra and one calculated using parameters from the HITRAN-2004 spectral line database [Rothman et al., 2005] and a line-by-line code (A. Dudhia, Reference Forward Model version 4: Software user manual, 2005, http://www.atm.ox.ac.uk/RFM), calculating each line profile to 25 cm⁻¹ either side of the line center.

[11] In order to increase the accuracy of the continuum retrieval, two constraints were imposed to select data points to be used in this analysis: the measured optical depth is required to be less than 4 and the optical depth of two adjacent points each at higher and at lower wavenumber must vary by a value of less than 0.03 from that mid-point. The first constraint ensures that the optical depths used in the analysis are not taken from highly saturated absorption lines. The second constraint excludes the spectral regions near monomer line centers where errors in the line-center wavenumber, strength and width of catalogued HITRAN-2004 lines will have greatest effect. It was discovered that a HITRAN-2004 line at 3732.13 cm⁻¹ had a self broadened half width which was wrongly categorized. For this reason the self broadened half width from the Toth line list (available at http://mark4sun.jpl.nasa.gov/data/spec/H2O/) was used for this line only.

3. Results and Fitting

[12] Derived spectra were analyzed at 296, 304, 317, 337 and 351 K; the 296 and 351 K spectra are shown in Figures 2 and 3 respectively. The results indicate that for this temperature range the most recent versions of the CKD continuum model (MT_CKD-1.10 (E. J. Mlawer et al., A revised perspective on the water vapor continuum: The MT_CKD model, manuscript in preparation, 2007) and the MT continuum [Ma and Tipping, 2002] both fail to describe the main features of the derived continuum.

[13] Our high-resolution measurements at 296 K (Figure 2) confirm the 20-year-old experiment of Burch [1985] (which was performed only at this temperature), demonstrating similar distinct spectral features near 3615 and 3730 cm⁻¹. Our measurements at 351 K (Figure 3), where a higher obtainable vapour pressure allowed for better determination of weaker areas of the continuum, also showed an additional feature at 3215 cm⁻¹.

[14] The continuum derived by Burch [1985] has been modified for Figure 2. Burch [1985] calculates the monomer
absorption using an old AFGL spectral line database, while our work uses HITRAN-2004. Therefore, to compare the two continua it was necessary to recalculate the Burch [1985] continuum using HITRAN-2004. This caused a decrease of about 10% in the Burch continuum.

A theoretical dimer absorption fitted to the derived continuum spectra is also shown in Figures 2 and 3. To simulate the dimer absorption spectra, the band strength, position, shape, halfwidth and dimerization equilibrium constant ($K_{eq}$) must be determined. There is uncertainty in all these parameters; for example, the \textit{ab initio} calculations by SK of dimer band intensities and positions are subject to uncertainty. Hence, after making reasonable assumptions, some fitting of the theoretical spectrum and $K_{eq}$ is justified to achieve better agreement between theory and observations; indeed, the fitting can then contribute to refined theoretical models of the dimer spectrum.

Figure 2 and 3 show that assuming a Lorentzian band shape for the dimer transitions, with half-width at half-maximum (HWHM) of about 28 cm$^{-1}$ leads to a good fit of the main features in the derived continuum. The positions of these features, as was shown earlier [Ptashnik, 2005; Ptashnik, submitted manuscript, 2007] in the analysis of Burch's experiment, correlate well with the SK prediction for the dimer band centers at 3215, 3598 and 3730 to 3745 cm$^{-1}$ (formed mainly by $|0\rangle_i|0\rangle_n|2\rangle_f$, $|0\rangle_i|1\rangle_n|0\rangle_f$, $|1\rangle_i|0\rangle_n|0\rangle_f$ and $|10\rangle_i|0\rangle_n$ dimer transitions respectively). We find that both the band positions and widths remain constant over the temperature range at which the measurements were conducted.

By obtaining the spectra of these features over a range of temperatures, it has been possible to define the temperature dependence of $K_{eq}$ for near-atmospheric conditions. However, this process is far less straightforward than assigning the band positions, because the derived water dimer spectra is the product of both dimer abundance and spectroscopic band strengths, and our measurements alone are unable to separate out these two components. Therefore, in order to obtain the value of either quantity from the derived continuum, we assume a value for one of the parameters.

Initially we assumed that the SK band strengths were correct, and then determined the values of $K_{eq}$ from the measurements at different temperatures. However, the value of $K_{eq}$ at 3615 cm$^{-1}$ was two thirds that at 3730 cm$^{-1}$ band, a physically impossible result. This signifies that the predicted relative intensities of these bands need to be altered, but gives no information about which, if any, is correct. Assuming the 3730 cm$^{-1}$ band strength to be correct, yields a value of $K_{eq}$ in best agreement with previous work (see Figure 4). This then requires that SK band strengths of the 3215 and 3615 cm$^{-1}$ dimer bands be scaled by factors of 0.40 and 0.72 respectively to achieve agreement between dimer theory and the derived continuum. The same scaling factors were then found to be appropriate at all measured temperatures: this signifies that all the dimer features have a
compared to 3615 cm
which is too small
We acknowledge the UK Natural Environ-
PAYNTER ET AL.: WATER DIMER ABSORPTION
33
Weakly Interacting
Ptashnik et al.
Scribano et al.
Slanina and Crifo
78
87
J. Geophys. Res.
band). This may explain
Acknowledgments.
104
[1985] and
[1997] calculation;
[2004] and this work by fitting to
are shown in Figure 4. For
Burch
Temperature dependence of the dimerization
at different near-room temperatures.
Harvey and Lemmon
2
[2004] second virial coefficients
using SK dimer band strengths;
experimental residual (with MT continuum subtracted)
VRT-MCYf potential energy surface.
3730 cm
subtracted off, because of its stronger contribution around
MT is subtracted are almost identical to when no continuum
is subtracted. However, when the MT_CKD continuum
is subtracted off, because of its stronger contribution around
3730 cm\(^{-1}\) compared to 3615 cm\(^{-1}\), no scaling factor
is needed for the 3615 cm\(^{-1}\) dimer band.

[20] The fitted values of \(K_{eq}\) are shown in Figure 4. For
each temperature the top of the error bars represents \(K_{eq}\)
fitted with neither continuum model subtracted, the mid
value with MT subtracted and the lower value with
MT_CKD continuum subtracted. It is not clear which of
the derived values in Figure 4 is the best estimate for \(K_{eq}\),
because both continua models have their shortcomings. The
MT continuum is formulated to improve the monomer
Lorentzian line shape mainly in far wings, but it does not
make any significant adjustments to the line shape nearer
the line center. The MT_CKD continuum model, on the
other hand, is semi-empirical with line shape parameters
being chosen to fit the experimentally determined contin-
um, including the continuum measurements of Burch
[1985]. This means that some part of the MT_CKD contin-
um is likely to include dimer absorption; therefore its
subtraction could result in a value of \(K_{eq}\) which is too small
(a similar result was obtained in our earlier work [Ptashnik
et al., 2004] for the 5300 cm\(^{-1}\) band). This may explain
why the larger estimated value of \(K_{eq}\) obtained when either
MT or no continuum are subtracted, is in better agreement
with other work (see Figure 4).

[21] Given the uncertainty still present in the SK strengths it can only presently be stated that regardless of
which, if any, continuum model is subtracted, the dimer-like
features discovered in the spectrum have the same expo-

Figure 4. Temperature dependence of the dimerization
equilibrium constant by different authors: Curtiss et al.
[1979] from thermal conductivity measurements in hot
vapor; Slanina and Crifo [1992] prediction using BGH/G
pair potential; Munoz-Caro and Nino [1997] calculation;
Ptashnik et al. [2004] and this work by fitting to
experimental residual (with MT continuum subtracted)
using SK dimer band strengths; Harvey and Lemmon
[2004] second virial coefficients \(B(T)\); Scribano et al. [2006] calculation using flexible
VRT-MCYf potential energy surface.

similar temperature dependence and that the derived con-
tinuum is robust.

In order to account for the monomer line far wing
contributions from water monomers to the continuum, this
fitting procedure is performed with either the MT or the
MT_CKD continua subtracted from the derived continuum.
Due to its small contribution, the scaling factors found when
MT is subtracted are almost identical to when no continuum
is subtracted. However, when the MT_CKD continuum
is subtracted off, because of its stronger contribution around
3730 cm\(^{-1}\) compared to 3615 cm\(^{-1}\), no scaling factor
is needed for the 3615 cm\(^{-1}\) dimer band.

[20] The fitted values of \(K_{eq}\) are shown in Figure 4. For
each temperature the top of the error bars represents \(K_{eq}\)
fitted with neither continuum model subtracted, the mid
value with MT subtracted and the lower value with
MT_CKD continuum subtracted. It is not clear which of
the derived values in Figure 4 is the best estimate for \(K_{eq}\),
because both continua models have their shortcomings. The
MT continuum is formulated to improve the monomer
Lorentzian line shape mainly in far wings, but it does not
make any significant adjustments to the line shape nearer
the line center. The MT_CKD continuum model, on the
other hand, is semi-empirical with line shape parameters
being chosen to fit the experimentally determined contin-
um, including the continuum measurements of Burch
[1985]. This means that some part of the MT_CKD contin-
um is likely to include dimer absorption; therefore its
subtraction could result in a value of \(K_{eq}\) which is too small
(a similar result was obtained in our earlier work [Ptashnik
et al., 2004] for the 5300 cm\(^{-1}\) band). This may explain
why the larger estimated value of \(K_{eq}\) obtained when either
MT or no continuum are subtracted, is in better agreement
with other work (see Figure 4).

[21] Given the uncertainty still present in the SK strengths it can only presently be stated that regardless of
which, if any, continuum model is subtracted, the dimer-like
features discovered in the spectrum have the same expo-

4. Conclusion

[22] High-resolution measurements of pure water vapor
absorption have been performed in the spectral region
3100–4400 cm\(^{-1}\) at different near-room temperatures.
The continuum part of the absorption spectra was derived
by subtracting the monomer line contribution. The retrieved
continuum absorption agrees well (within 20%) with the
previous low-resolution measurements of Burch [1985] and
consists of distinct broad features (HWHM \(\approx 25–30\) cm\(^{-1}\))
near 3215, 3615 and 3730 cm\(^{-1}\), that correspond rather well
to the absorption predicted for water dimer bands [Schofield
and Kjaergaard, 2003]. On the other hand, the most widely
used water vapour continuum models significantly under-
estimate the self-continuum absorption in this spectral
region. The temperature dependence of the continuum
absorption, derived for the first time in this spectral region,
corresponds well with that expected for the dimer equilib-
rium constant. The results confirm previous suggestions
[e.g., Ptashnik et al., 2004; Daniel et al., 2004; Vaida et al.,
2001], that there is a significant dimer contribution to the
water vapor continuum absorption within the strongest near-
IR bands. However, it is evident from Figures 2 and 3, that
not all features in our observed continuum can be explained
by current dimer models.

[23] Acknowledgments. We acknowledge the UK Natural Environ-
ment Research Council for funding a studentship to DJP and providing
access to the Rutherford Appleton Laboratory Molecular Spectroscopy
Facility. We also wish to thank Henrik Kjaergaard and an anonymous
reviewer for their comments.

References
Brown, A., and R. H. Tipping (2003), Collision induced absorption in
dipolar molecule-homonucleic diatomic pairs, in Weakly Interacting
Molecular Pairs: Unconventional Absorbers of Radiation in the Atmo-
sphere, edited by C. Camy-Peyret and A. A. Vagasin, pp. 93–99,
Base, Mass.
Cornier, J. G., J. T. Hodges, and J. R. Drummond (2005), Infrared water
vapor continuum absorption at atmospheric temperatures, J. Chem. Phys.,
Clough, S. A., F. X. Kneizys, and R. W. Davies (1989), Line shape and the
Curtiss, L. A., D. J. Frurip, and M. Blander (1979), Studies of molecular
association in H2O and D2O vapors by measurement of thermal-
Daniel, J. S., S. Solomon, R. W. Sanders, R. W. Portmann, D. C. Miller, and
W. Madsen (1999), Implications for water monomer and dimer solar
absorption from observations at Boulder, Colorado, J. Geophys. Res.,
104, 16,785–16,792.
Atmospheric water vapor complexes and the continuum, Geophys. Res.
Elsasser, W. M. (1938), Far infrared absorption of atmospheric water vapor,
Harvey, A. H., and E. W. Lemmon (2004), Correlation for the second virial
Hill, C., and R. L. Jones (2000), Absorption of solar radiation by water
vapor in clear and cloudy skies: Implications for anomalous absorption,
Huisken, F., M. Kaloudis, and A. Kulcke (1996), Infrared spectroscopy of
Kiehl, J. T., and K. E. Treberth (1997), Earth’s annual global mean energy


— D. J. Paynter, I. V. Ptashnik, and K. P. Shine, Department of Meteorology, University of Reading, Earley Gate, Reading RG6 6BB, UK. (d.j.paynter@reading.ac.uk)

K. M. Smith, Space Science and Technology Department, Rutherford Appleton Laboratory, Chilton OX11 0QX, UK.