Atmospheric absorption of near infrared and visible solar radiation by the hydrogen bonded water dimer

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SUMMARY

Based on the physico-chemical properties of water dimers, their near infrared and visible absorption of solar radiation in the earth’s atmosphere is calculated. The calculation uses equilibrium constants determined by statistical mechanics, and a vibrational absorption spectrum determined by a coupled oscillator quantum mechanics model and *ab initio* quantum chemistry. The resulting total atmospheric absorption was calculated using a line-by-line radiative-transfer model, and depends significantly on the dimer abundance, as well as on the frequency and line width given to vibrational transitions. The best estimate achieved for the possible range of total absorption from 400 nm to 5000 nm by water dimer in the tropics is 1.6–3.3 W m\(^{-2}\). In a global-warming scenario, the increased temperature and water vapour partial pressure result in a nonlinear increase in the absorption of solar radiation by water clusters. Most of the energy from water dimer absorption is deposited in the lower troposphere, particularly in the tropics, tending to make it more convective.

KEYWORDS: Near-infrared absorption Radiative transfer Water dimer absorption

1. INTRODUCTION

Infrared (IR) and near infrared (NIR) radiation is absorbed by rotational transitions associated with the vibrational modes in water vapour. These water bands are the cause of the intense and extensive atmospheric absorption; they are by far the largest contributors to the greenhouse effect (Tyndall 1861; Ludlam 1980; Ramanathan and Vogelmann 1997). The importance of water in the atmosphere, and the suggestions from recent field measurements that its properties are not appropriately modelled, led to a re-examination of the available information and the search for additional absorption features that may contribute to the overall spectroscopy of water (Stephens and Tsay 1990; Cess et al. 1995; Kiehl et al. 1995; Pilewskie and Valero 1995; Ramanathan et al. 1995; Arking 1996; Crisp 1997; Francis et al. 1997; Han et al. 1997; Zender et al. 1997; Fu et al. 1998; Jing and Cess 1998; Pilewskie et al. 1998; Smith et al. 1998; Walden et al. 1998; Cess et al. 1999; Yu et al. 1999). Improved potential energy surfaces for the water molecule have become available (Polyansky et al. 1996; Xantheas and Dunning Jr 1998) making it possible to re-examine the HITRAN database with input from both theory and experiment (Reimers and Watts 1983; Carleer et al. 1999).

Water molecules bind easily to one another by forming hydrogen bonded complexes. These weak interactions (approximately 5 kcal mol\(^{-1}\)) (Kim et al. 1992; Xantheas 1996) perturb the rovibronic and electronic states of individual molecules, and are expected to alter the spectroscopy of gaseous water. The structure and energetics of these complexes have recently become available as a result of studies by experimental methods and theoretical techniques.

The question we are examining here is whether NIR absorptions of water binary complexes are sufficiently intense, broad and shifted by hydrogen bonding that they are not completely overlapped by the monomer absorption bands and become significant absorbers of solar radiation. We specifically investigate absorptions arising from water

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dimers due to vibrational overtones and combinations in the 500 nm to 5000 nm wavelength range. The possible involvement of water complexes in the atmosphere has been proposed for a long time (Bignell 1970; Lee 1973; Coffey 1977; Wolynes and Roberts 1978; Carlon 1979; Bohlender et al. 1980; Gebbie 1980; Dias-Lalcaca et al. 1984) and, more recently, the role of water complexes in absorption of solar radiation in the NIR has been explored (Goss and Vaida 1996; Chylek and Geldart 1997; Daniel et al. 1999; Chylek et al. 1999). These suggestions were not sufficiently supported by fundamental physical chemistry. This study relies on our recent theoretical (Low and Kjaergaard 1999) and experimental results (Goss et al. 1999) to evaluate the abundance and the vibrational spectrum of the water dimer. The radiative effects were obtained by use of the physico-chemical properties of the hydrogen bonded water dimer in a line-by-line radiative-transfer model of the propagation of sunlight through the atmosphere to the earth's surface. The model results show a significant contribution from the water dimer to absorption of solar radiation while explaining the difficulties in observing its spectral features in atmospheric spectra (Daniel et al. 1999; Hill and Jones 2000).

By way of the radiative-transfer model, the contribution to absorption of solar radiation by water dimer in a global-warming scenario was calculated. The calculated value establishes the existence of an anthropogenic feedback by the contribution of hydrogen bonded water dimers to absorption of solar radiation.

2. ATMOSPHERIC ABUNDANCE OF WATER DIMERS

The extent to which water complexes affect the radiative balance of the atmosphere is determined, in part, by their atmospheric abundance. A search for water dimers, (H$_2$O)$_2$, failed to give any positive results (Daniel et al. 1999; Hill and Jones 2000). In the absence of direct atmospheric measurements, we employ computational methods and laboratory model studies to estimate the atmospheric abundance of hydrogen bonded water complexes.

In order to evaluate the role of water cluster absorptions in the atmosphere, the abundance of these clusters has to be estimated as a function of altitude, temperature and water vapour partial pressure. The procedure we use relies on computing the standard free-energy change ($\Delta G^\circ$) for formation of the cluster, from which the equilibrium constant $K_{eq} = \exp(-\Delta G^\circ/RT)$, where $R$ is the universal gas constant and $T$ is temperature, can be obtained. The partial pressure of the water dimer can be calculated from $K_{eq}$ at the relevant temperatures: $p(\text{H}_2\text{O})_2 = K_{eq} [p(\text{H}_2\text{O})]^2$.$^2$

In accordance with low temperature supersonic jet experiments, theory predicts that the minimum energy structures for water clusters (H$_2$O)$_n$ with $n > 2$ are cyclic (Vaida and Headrick 2000). Experimental equilibrium constants are not available for (H$_2$O)$_n$ with $n > 2$. Elegant spectroscopic experiments in low-temperature supersonic jets provided the minimum energy structures for these complexes which have been calculated using high-level ab initio theory. Given the information to date, we calculate (Vaida and Headrick 2000) that the equilibrium constants increase as a function of cluster size with the number of hydrogen bonds. This increase is not sufficient to compensate for the nonlinear dependence on the water vapour pressure in the atmosphere, $p(\text{H}_2\text{O})_n = K_{eq} [p(\text{H}_2\text{O})]^n$. Consequently, the calculated vapour pressure for (H$_2$O)$_n$, with $n > 2$, is too small to be of interest here and, due to their low abundance, these water clusters are not expected to contribute to absorption of solar radiation in the NIR and visible (Evans and Vaida 2000; Vaida and Headrick 2000). Evaluation of the contribution of (H$_2$O)$_n$ with $n > 2$ to absorption of solar radiation awaits fundamental studies of all the water cluster isomers. For these reasons, in what follows, we concentrate on calculations
of the atmospheric abundance of water dimer by determining the temperature-dependent equilibrium constant.

As shown above, the partial pressure of the dimer is proportional to the equilibrium constant, and scales with the square of the water vapour pressure. The standard free-energy change is calculated from the change in the reaction standard enthalpy ($\Delta H^\circ$) and the reaction entropy ($\Delta S^\circ$) as $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. In the light of the small binding energy for the dimer, the free-energy change is very sensitive to the balance between the enthalpic and entropic contributions, both of which are temperature dependent. We obtained the translational, rotational, vibrational and electronic contributions to $\Delta H^\circ$ and $\Delta S^\circ$ using standard procedures of statistical mechanics (Vaida and Headrick 2000). The calculations involved obtaining canonical ensemble partition functions in terms of the molecular partition functions for the various degrees of freedom. The inputs required for these statistical mechanical expressions include vibrational frequencies, rotational constants, cluster mass and temperature. The dimer abundance profiles were determined using standard statistical mechanics procedures described elsewhere (Vaida and Headrick 2000), harmonic vibrational frequencies from Kim et al. (1992) and rotational constants from Dyke et al. (1977). We investigated the effect of anharmonicity of molecular vibrations using the work of Jung and Gerber (1996) and found that the values of $K_{eq}$ in the anharmonic cases lie between the limiting cases given in Fig. 1. Consistent with our calculations, we choose, in this study, two limiting cases from the literature, for the upper and lower dimer abundance. The low-abundance profile shown in Fig. 1 comes from the work of Mhin et al. (1993), while the high-abundance profile shown in the same figure is taken from the work of Munoz-Caro and Nino (1997). The equilibrium constants used to construct the dimer abundance shown in Fig. 1 are those.
we believe most consistent with experiment (Curtiss et al. 1979). The resulting dimer concentrations are different by about a factor of three at all altitudes considered for the 'low' and 'high' equilibrium constants used.

3. Calculation of the Vibrational Absorption Spectrum for Water Dimer

To estimate the magnitude of the atmospheric absorption by water dimers in the NIR region, the frequency, intensity and line widths of the vibrational transition of \((\text{H}_2\text{O})_2\) must be known. Insufficient information is available from experiment which gives only the frequencies and line widths for a few of the fundamental vibrational transitions in the IR and low-energy NIR region to about 4000 cm\(^{-1}\). Thus, we have to calculate or estimate empirically the frequencies, intensities and line widths of all vibrational transitions in \((\text{H}_2\text{O})_2\).

The NIR spectra of molecules containing \(XH\) bonds \((X = C, N, O, \ldots)\) are dominated by the transitions which involve \(XH\)-stretching overtone vibrations. These overtone transitions are well described by the local mode model (Henry 1977) and are generally found to contain one Lorentzian peak for each of the non-equivalent \(XH\) bonds in the molecule. The harmonically coupled anharmonic oscillator (HCAO) local mode model has proven successful in the prediction of the overtone peak positions (Mortensen et al. 1981; Child and Halonen 1984), and combined with an \textit{ab initio} calculated dipole-moment function (DMF) intensities of overtone transition are successfully predicted (Kjaergaard et al. 1990). We have found that nonlinearity in the DMF is essential for the calculation of overtone intensities (Kjaergaard and Henry 1992) and that a reasonable quality \textit{ab initio} DMF is required to give absolute overtone intensities of spectroscopic accuracy (Kjaergaard and Henry 1994). We have previously used the HCAO local mode model with an \textit{ab initio} calculated DMF to calculate the vibrational band intensities of the water monomer (Kjaergaard et al. 1994, 1999) and found good agreement with experimental intensities in the HITRAN database (Rothman et al. 1998).

We have recently used the HCAO local mode model and \textit{ab initio} methods to calculate OH-stretching vibrational band positions and oscillator strengths (intensities) for the water dimer and trimer (Low and Kjaergaard 1999). Details of the calculations and their dependence on the choice of \textit{ab initio} method are given elsewhere (Low and Kjaergaard 1999). In the following, we describe briefly how the HCAO local mode can be used to investigate the water dimer, and discuss our results.

To calculate the OH-stretching band positions and oscillator strengths both a potential energy surface and a DMF for the water dimer are required. Within the HCAO local mode model, the \((\text{H}_2\text{O})_2\) water dimer is modelled as two \(\text{H}_2\text{O}\) units with each unit treated as two harmonically coupled anharmonic OH-stretching oscillators. The anharmonic oscillators are approximated by Morse oscillators which are described by a local mode frequency, \(\omega\), and anharmonicity, \(\omega x\). The harmonic coupling between the two OH-stretching oscillators in each of the \(\text{H}_2\text{O}\) units is described by the effective local mode coupling parameter \(\gamma'\). Our HCAO local mode model calculation of the water dimer includes the four OH-stretching vibrational modes but no lower-frequency modes.

We have used the correlated quadratic configuration interaction including singles and doubles (QCISD) level of theory with the 6-311++G(2d,2p) basis set (QCISD/6-311++G(2d,2p)) in the \textit{ab initio} calculations. With this \textit{ab initio} method the structure of the water dimer is correctly predicted and the calculated permanent dipole moment, bond lengths, and binding energy are all in very close agreement with the experimentally known values (Low and Kjaergaard 1999). We have used the QCISD/6-311++G(2d,2p) \textit{ab initio} method to calculate both a potential energy surface and a DMF as functions
of the four OH-stretching coordinates of the water dimer. The local mode parameters are determined from the ab initio calculated potential energy surface. It is common to scale ab initio calculated IR frequencies and we have determined suitable scaling factors of local mode parameters calculated with the QCISD/6-311++G(2d,2p) method by comparison of calculated and measured local mode parameters for the water monomer (Low and Kjaergaard 1999). The scaling factors are 0.984 and 0.851 for the local mode frequency and anharmonicity, respectively. The DMF is expanded to fourth order in the OH-stretching coordinates, and to third order in the mixed terms which depend on two coordinates. The DMF expansion coefficients are not given here but can be obtained from the authors. We have used ‘Gaussian 94’ (Frisch et al. 1995) for all the ab initio calculations. The water dimer consists of an acceptor (H₂O_H₃) and a donor unit (H₆OH₇), where the subscripts a, b and f represent the OH bond in the acceptor unit, the hydrogen bond and the free OH bond in the donor unit. The local mode parameters used in our present calculation are given in Table 1.

Solutions of the Schrödinger equation associated with the local mode Hamiltonian will provide the vibrational energy levels and wave functions. These vibrational energy levels provide the peak positions. The oscillator strengths of the vibrational transitions depend on the square of the transition dipole-moment matrix element (Fermi’s Golden rule), which can be calculated from the vibrational wave functions and the DMF. We have used the local mode parameters in Table 1 and the QCISD/6-311++G(2d,2p) DMF to calculate all OH-stretching transitions in water dimer.

In Fig. 2, we compare the calculated total oscillator strength of the OH-stretching transitions in the water dimer and monomer. The expected rapid drop off in intensity with increasing overtone is clearly visible in Fig. 2. We find that the intensity of the dimer is approximately twice the intensity of the water monomer, except in the fundamental region where the dimer intensity is somewhat larger. The water dimer is two loosely held water units and, intuitively, we would expect the dimer intensity to be approximately twice the intensity of water monomer, as previously suggested by Chylek and Geldart (1997).

The increased fundamental intensity of the water dimer compared with the monomer is due to the hydrogen bonded OH-stretching vibration, OH₃. Hydrogen bonds are
known to exhibit a frequency red shift and increased fundamental intensity compared with the non-bonded bonds. The intensity of the hydrogen bonded OH-stretching transitions varies significantly with spectral regions. In the fundamental region it is the strongest of the OH-stretching transitions and as intense as all the non-bonded transitions. In the first OH-stretching overtone region, \( v = 2 \), where \( v \) is the vibrational quantum number, it has an intensity several orders of magnitude less than the non-bonded transitions, and for \( v \geq 3 \) its intensity is roughly half of the sum of the non-bonded transitions (Low and Kjaergaard 1999). The hydrogen-bonded OH\(_b\)-stretching vibration in the water dimer also exhibits a significant frequency red shift, as is directly evident from the local mode parameters in Table 1. The other OH bonds in the water dimer, OH\(_F\) and OH\(_a\), have very similar local mode parameters to the water monomer and thus a significant portion of the water dimer overtone intensity will fall in the region of the water monomer. However, the hydrogen bonded OH-stretching bands will be significantly red shifted, about 300 cm\(^{-1}\) for the \( v = 3 \) region around 1000 nm (Low and Kjaergaard 1999), and will occur in regions with little absorption from water monomer.

The only other calculation of overtone intensities in the water dimer is by Tso et al. (1998), who used a semi-empirical potential to describe all the vibrational modes in the water dimer. We would expect some uncertainty of the vibrational peak positions with a semi-empirical potential. They give an accuracy of their calculated fundamental frequencies to observed frequencies as 4%, but presumably it is somewhat less for the dominant OH-stretching vibrations in the IR. In comparison, our HCAO calculated frequencies show a maximum error of 7 cm\(^{-1}\) or 0.2% compared with the experimentally observed OH-stretching bands (Huang and Miller 1989; Huiskan et al. 1996). We expect the error in calculated frequency to increase with increasing overtone in both calculations. We estimate our maximum uncertainty in the calculated frequencies to be about 1%, or about 100 cm\(^{-1}\) (5 nm) for the highest overtone, \( v = 7 \), region and less for the lower overtones. This uncertainty arises mainly from uncertainty in the calculated frequency and to a lesser degree, the anharmonicity.
To our knowledge the calculation by Tso et al. (1998) lacks a suitable DMF which depends on the vibrational coordinates and where the dipole moment has been determined from the molecular orbital wave function. We have previously clearly shown that the DMF and, in particular, its nonlinear dependence on the internal coordinates is essential for the calculation of spectroscopically accurate OH-stretching intensities (Kjaergaard and Henry 1992). Thus we would expect the intensities calculated by Tso et al. to be significantly in error. It is common and suitable to use the double harmonic (DH) approximation (linear dipole and vibrational normal modes) to calculate IR spectra. This method is implemented in most ab initio programs like Gaussian 94. It is unfortunate that Tso et al. do not compare their calculated intensities with any of the many calculated DH fundamental IR spectra for water dimer (Xantheas and Dunning Jr 1993).

Fundamental intensities calculated with the DH approximation and with our HCAO method agree well (Low and Kjaergaard 1999). However, the fundamental spectra calculated by Tso et al. (1998) show different peak positions as well as significantly different intensities of the OH-stretching transitions. The most significant difference is the intensity of the OH\textsubscript{b}-stretching vibration, which Tso et al. predict to be weak, whereas both DH and HCAO calculations predict it to be the strongest transition in the \( v = 1 \) region. The uncertainty in our calculated intensities is believed to be less than a factor of 2 for the dominant features, and possibly somewhat higher for the weaker transitions in each overtone region. The uncertainty will certainly be lower for the lower overtones, the regions we find contribute most to the absorption of solar radiation.

The simulated overtone absorption spectrum for the water dimer by Tso et al. (1998) shows clearly that the NIR spectrum is dominated by the OH-stretching vibrations. Their spectrum shows very little intensity outside the OH-stretching region; most notable is the lack of intensity in the stretch–bend combination regions, which we know are present in spectra of water monomer. The calculation by Tso et al. predicts overtone intensities that are significantly larger than the intensities we have calculated with our HCAO local mode model, and larger than the intuitive factor of two compared with the water monomer intensities. Based on the calculations by Tso et al., Daniel et al. (1999) recently attempted to measure OH-stretching transitions from water dimer in the atmosphere in the 624–686 nm region. They conclude that the water dimer intensities predicted by Tso et al. are at least a factor of ten too large, unless they are shifted outside the range of their measurement.

In another recent experiment on water clusters the \( v = 2 \) total OH-stretching intensity is estimated to be less than 2% of the \( v = 1 \) intensity (Goss et al. 1999). This also suggests that the Tso et al. (1998) calculated intensities are very high, as they predict a \( v = 2 \) intensity of about one third of the \( v = 1 \) intensity. We predict the intensity of the \( v = 2 \) region to be 1.4% of the \( v = 1 \) region for the water dimer and about 0.7% for the water trimer; both values are between the monomer result of 12% and liquid-water result of 0.4%, and are in good agreement with the water cluster experiment by Goss et al. (1999). Thus we believe that our HCAO local mode calculated OH-stretching provides a good basis for assessing the atmospheric absorption of NIR and visible solar radiation by the water dimer. We urge caution in the use of the results by Tso et al., partly for the high uncertainty in peak positions but more so for the very high uncertainty in the intensities.

We have used our HCAO calculated OH-stretching transitions as a basis in our simulation of the water dimer spectrum. No overtone or combination bands of the HOH-bending and lower-frequency intermolecular modes have been observed (Goss
et al. 1999). It is complicated to model all of the 12 vibrational modes in a six-atom molecule like the water dimer. We have included the HOH-bending modes in an empirical way and have neglected all lower-frequency intermolecular vibrational modes. These lower-frequency modes have vibrational frequencies of the order of 100 cm\(^{-1}\) and contribute very little to the overtone intensities, but could contribute to an increase in the overall width of the transitions. It is generally believed that these lower-frequency transitions gain most of their intensity by stealing intensity of the pure OH-stretching transitions (Child and Halonen 1984). For the water monomer the bend–stretch combination bands (ν quanta in stretch and one in bend) are observed to have an intensity that is approximately one tenth the intensity of the parent OH-stretching (ν quanta in stretch) transition (Kjaergaard and Henry 1994; Rothman et al. 1998). Thus for the dimer we have approximated the bending regions based on the calculated OH-stretching transition. For each OH-stretching transition we have added a stretch–bend combination transition which is located 1580 cm\(^{-1}\) higher in frequency (approximate bending frequency) and with an intensity one tenth of the pure OH-stretching vibration.

The remaining spectroscopic parameters necessary to simulate a water dimer spectrum are the line width and line shape. No experimental or theoretical information is available concerning the line width or line shape of vibrational overtone transitions of water clusters. The low-temperature supersonic jet expansion fundamental OH-stretching spectra of water dimer (Huang and Miller 1989; Huiskens et al. 1996) have observed line widths (full width at half maximum (FWHM)) of 11.5 cm\(^{-1}\) and 13 cm\(^{-1}\) for the OH\(_{\text{b}}\) and OH\(_{\text{t}}\)-stretching vibrations, respectively. Tso et al. employ a reasonable rigid rotor model to simulate rotation, although the uncertainty in peak positions and intensities of their calculation is large. Their simulation leads to a line width of about 15 cm\(^{-1}\) for the ν = 1 region, increasing to about 50 cm\(^{-1}\) at ν = 3. Vibrational overtones are expected to be somewhat broader than the fundamental transitions. In spectra of polyatomic molecules of similar size to the water dimer, Lorentzian line shapes of tens of cm\(^{-1}\), increasing in widths by factors of 2 to 3 between ν = 2 and ν = 5, have been measured (Kjaergaard et al. 1991, 1993). Based on this information we estimate 15 cm\(^{-1}\) as the minimum width of the vibrational transitions in water dimer at atmospheric temperatures, and use 200 cm\(^{-1}\) as an upper bound on the width. We have not imposed an unknown gradual increase in bandwidth but rather have used these two widths as limiting cases. We estimate that the effect will be intermediate between these two and have used an average FWHM of 40 cm\(^{-1}\) as our best estimate. We await new experimental information to provide better line width to input to the model. Based on the line shape observed in vapour phase overtone spectra of molecules we have used a Lorentzian line shape in all simulations (Kjaergaard et al. 1993).

The simulated vibrational absorption spectrum for the water dimer is shown in Fig. 3, with each vibrational transition given a Lorentzian line shape with a FWHM width of 15, 40, and 200 cm\(^{-1}\), respectively. The spectrum is reasonably simple with basically one peak for each of the non-equivalent OH bonds, and a stretch–bend combination band between the pure OH-stretching transitions, as expected. This is very similar to what is observed in overtone spectra of other molecules (Child and Halonen 1984; Kjaergaard et al. 1993).

Comparison of our simulated spectrum in Fig. 3 with that of Tso et al. (1998) shows resemblance at first glance. However, this is partly due to the compressed nature of the axis, in particular the logarithmic scale. It is important to realize that the intensity of a transition is the integrated cross-section (the area of a band) not the cross-section. The cross-section depends significantly on the width of the peak.
Figure 3. Absorption cross-sections of the water dimer. Cross-sections are for assumed vibrational spectral widths of 200 cm\(^{-1}\), 40 cm\(^{-1}\) and 15 cm\(^{-1}\). The full curve (40 cm\(^{-1}\) width) is the most likely case.

4. **LINE-BY-LINE MULTIPLE SCATTERING MODELS**

The dimer absorption cross-sections discussed in section 3 demonstrate significant spectral overlap with absorption features of other atmospheric gases, the most important being the H\(_2\)O monomer. This overlap leads to a significantly reduced impact of including H\(_2\)O dimers in radiative-transfer calculations. To quantify this impact we have used the line-by-line multiple scattering model described by Daniel et al. (1999). In this work, the model atmosphere is divided into 50, 1 km thick homogeneous layers. Calculations are made for both a ‘global average’ case at a solar zenith angle of 60° and for a tropical case with an overhead sun. The 1976 standard atmosphere is adopted for the global average temperature profile. The monomer vertical column is prescribed to be the global mean of 24.5 mm of precipitable water from the water vapour data-set of Randel et al. (1996). The water profile is generated from a constant relative humidity from the ground up to 11 km. The tropical case is assumed to have a surface temperature of 298 K with a lapse rate of 4.9 K km\(^{-1}\) up to 18 km. The monomer column, 45 mm, is taken from a representative July tropical average of Randel et al. (1996), again with a constant relative humidity throughout the troposphere. In each case, above the troposphere the water vapour mixing ratio is reduced to 5 parts per million by volume, its assumed lower-stratosphere mixing ratio. Absorption coefficients are calculated for H\(_2\)O, O\(_2\), and CO\(_2\) every 0.01 cm\(^{-1}\) using the HITRAN 1996 list (Rothman et al. 1998), and including the revised H\(_2\)O suggested by Giver et al. (2000). Pressure and temperature broadening are considered throughout the calculated region with wing contributions considered out to 10 cm\(^{-1}\) on either side of the line centres. In addition to the structured absorption of H\(_2\)O, O\(_2\), and CO\(_2\), ozone absorption is
considered although it has a minor effect on the results. Ozone cross-sections are
taken from World Meteorological Organization (1995) and a vertical column amount
of 350 Dobson units is assumed. Absorption optical depths as a function of altitude
are calculated at the same resolution and then binned to a resolution varying with
wavelength from 0.025 nm at 400 nm to 0.1 nm at 5.0 μm, before being used in the
two-stream multiple scattering part of the calculation. Rayleigh scattering and a surface
albedo of 0.15 are also included in the calculations. Sensitivity cases were run at higher
resolution, 0.001 nm at 400 nm to 0.01 nm at 5.0 μm, which demonstrated differences
in the dimer absorption of less than 1%.

5. RESULTS AND DISCUSSION

The results of this modelling study are based on the dimer’s calculated atmospheric
abundance, calculated vibrational frequencies and intensities, and empirically estimated
band-shapes for vibrational transitions of water dimers. The vertical profile range of
the dimer, calculated from the equilibrium coefficients discussed in section 2, is shown
in Fig. 1, along with the monomer profile. The conditions where water dimers would
make the most contribution to absorption of solar radiation are found in the tropical
atmosphere. Under tropical humidity conditions, an upper limit of approximately
3 W m⁻² is calculated. In the lower-humidity situation modelled for the globally av-
eraged atmosphere at 60° zenith angle, the effect ranges from 0.3 to 0.7 W m⁻², de-
 pending on the dimer abundance profile used. It is evident that the dimer is present
in much less abundance than the monomer (>3 orders of magnitude at low altitude)
and that it decreases with increasing altitude with a scale height roughly half that of
the monomer. Consequently, the majority of the clear-sky water dimer absorption must
occur in the lower part of the troposphere. For these calculations, the vertical column
dimer abundance falls between 4.7 × 10¹⁸ and 1.0 × 10¹⁹ molecules cm⁻². Figures 4
and 5 show the direct solar radiation incident on the ground when water dimers (and the
other atmospheric absorbers) are present. A comparison of these figures with the dimer
absorption cross-sections (Fig. 3) illustrates the importance of the overlap of the dimer’s
absorption features with those of the monomer. Specifically, although the dimer exhibits
strong absorption features around 1.4 and 1.9 μm, the water monomer absorbs most of
the light in these regions, causing the addition of the dimer to absorption calculations to
have a much reduced effect than a simple inspection of the cross-section would suggest.

Figure 6 shows the modelled spectral absorption (W m⁻² nm⁻¹) by water dimer clusters
along with the cumulative absorption (integrated from 400 nm) in W m⁻² as a function
of wavelength. Figure 6 illustrates that additional dimer absorption occurs primarily
in monomer ‘windows’, particularly from 1.5 to 1.8 μm and from 1.9 to 2.5 μm. A
comparison of Fig. 6 with Fig. 3 also shows that most of the absorption features which
might be observed in the atmosphere to detect the water dimer are due not exclusively
to the dimer absorption cross-section but, instead, in large part to the interaction of the
dimer absorption features with those of the monomer. The precise appearance of these
absorption features will therefore depend on the exact spectral position of the dimer
absorption cross-section, thus making positive identification of dimer absorption very
difficult. On the other hand, it is this absorption overlap with the monomer that makes
the dimer’s atmospheric absorption of reduced significance.

Because of the importance of the dimer absorption in the far wings of the vibrational
overtone bands compared with the band centres, and because of the uncertainty in the
spectral width of the bands, three absorption cases have been calculated. In the first,
Figure 4. Calculated clear-sky direct solar intensity reaching the surface at wavelengths between 500 and 2500 nm.

Figure 5. Same as Fig. 4 but for wavelengths between 2500 and 5000 nm.
the Lorentzian FWHM is assumed to be 15 cm$^{-1}$, in the second it is assumed to be 40 cm$^{-1}$, and in the third 200 cm$^{-1}$. The 15 and 200 cm$^{-1}$ cases represent extremes in the likely values of the vibrational bandwidth and are meant to illustrate the importance of an accurate understanding of the spectral width to the absorption calculations. The 40 cm$^{-1}$ Lorentzian is expected to more closely approximate the real atmospheric dimer vibrational shape. There are two primary reasons for the spectral width to affect the absorption of the water dimer. The first is due to spectral overlap with the monomer absorption features. As stated above, the strong dimer absorption features around 1.4 and 1.9 μm occur at wavelengths coincident with saturated monomer bands. The monomer has already absorbed most of the solar radiation, leaving little to be absorbed by the addition of the dimer to the calculation. However, if the dimer vibrational spectral bandwidths were larger, although the total integrated cross-section would be unchanged, more of the absorption would be moved out of the region of overlap with the monomer into the window regions where significant absorption could occur. The second reason for the importance of the vibrational bandwidth is the saturation of the dimer absorption itself. For the 15 cm$^{-1}$ case the centres of the dimer absorption bands between 1.8 μm and 3.0 μm are heavily saturated; hence, an increase in dimer amount will have relatively less impact on the total absorption than in the optically thin case. Therefore, as the vibrational widths are made larger, more absorption is transferred to the wings of the distribution, and the total absorption increases. Both of these effects lead to the expectation that, for a given dimer abundance, broader dimer features will lead to increased absorption. As shown in the dimer absorption totals displayed in Table 2, this is indeed the case. Our best estimate for dimer absorption using the previously discussed equilibrium constants and cross-sections assuming a FWHM of 40 cm$^{-1}$

Figure 6. Cumulative and spectral absorption due to water dimer. Cumulative absorption is calculated by integrating the spectral absorption from 400 nm to the plotted wavelength.
TABLE 2. CALCULATED WATER DIMER ABSORPTIONS. THREE VIBRATIONAL BAND WIDTH (FULL-WIDTH-HALF-MAXIMUM OF 15, 40, AND 200 cm⁻¹) RESULTS ARE SHOWN FOR LORENTZIAN BAND SHAPES.

<table>
<thead>
<tr>
<th>Lorentzian full-width-half-maximum</th>
<th>Low equilibrium constants (W m⁻²)</th>
<th>High equilibrium constants (W m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tropical case, overhead sun</td>
<td>1.6</td>
<td>3.3</td>
</tr>
<tr>
<td>40 cm⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Global average case, 60° solar zenith angle</td>
<td>0.3</td>
<td>0.7</td>
</tr>
<tr>
<td>40 cm⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15 cm⁻¹</td>
<td>0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>200 cm⁻¹</td>
<td>1.4</td>
<td>3.0</td>
</tr>
</tbody>
</table>

is 0.3–0.7 W m⁻² for a clear sky and a solar zenith angle of 60°. When the spectral profile width is decreased to 15 cm⁻¹ the absorption decreases to 0.1–0.3 W m⁻². Conversely, when the profile width is increased to 200 cm⁻¹, the absorption increases to 1.4–3.0 W m⁻².

We performed model calculations for a global-warming scenario when an increased temperature is expected to lead to an increase in water vapour partial pressure and therefore a nonlinear increase in the water cluster concentrations, using the best estimate FWHM line width of 40 cm⁻¹. An increase in the tropospheric dew-points of about 2 K leads to an increase in our best guess dimer instantaneous absorption values of 0.05 W m⁻² from 0.32 to 0.37 W m⁻² for the global mean case. In the clear sky, tropical case with overhead sun, the increase ranged from 0.3 W m⁻² at the low end of the range to 0.5 W m⁻² at the high end. The absorption of solar radiation by water dimers will therefore increase nonlinearly as the temperature increases, and the resulting positive feedback will be concentrated in the lower tropical troposphere.

6. CONCLUSIONS

We have used recent experimental and theoretical information describing bimolecular water complexes to evaluate the necessary input parameters for a line-by-line atmospheric radiative-transfer model. The model results give a range of values for the expected absorption of solar radiation in the clear atmosphere when water dimers are included. The results are sensitive to uncertainties in the abundance and the spectra of (H₂O)₂. The atmospheric absorption due to water bimolecular complexes in the tropical atmosphere is estimated to be 1.6 to 3.3 W m⁻², while only 0.3–0.7 W m⁻² is estimated in the ‘global average’ case at a solar zenith angle of 60°. This result suggests the need for laboratory studies and theoretical calculations to characterize fundamental physicochemical properties of water complexes better, as well as field studies to search for spectroscopic signatures of these complexes in the atmosphere.

Field studies to date have failed to identify structured absorptions due to water dimers in the atmosphere (Daniel et al. 1999). A significant result of the present study is the realization that the expected absorption features of the dimer are of small size and/or demonstrate significant overlap with the H₂O monomer, rendering spectroscopic identification difficult. Examination of the results of Fig. 6 also points to the need for more extended wavelength coverage (e.g. 1.5–2.5 μm) to access the most auspicious regions where the water dimers are expected to absorb and not be fully obscured by monomer transitions.
In a global-warming scenario, given the assumed abundance and cross-sections of this work, it should be remembered that as water monomer increases in response to higher temperatures, the impact of water dimers in absorbing solar radiation increases faster relative to the monomer, and should provide a positive feedback to anthropogenic climate change. The deposition of energy is primarily in the lowest layers of the troposphere, and will therefore tend to make it more convective, particularly in the tropics.

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REFERENCES


Curtiss, L. A., Frurip, D. J. and Blander, M.

Daniel, J. S., Solomon, S., Sanders, R. W., Portmann, R. W., Miller, D. C. and Madsen, W.

Diaz-Lacaca, P., Packham, N. J. C. and Gebbie, H. A.

Dyke, T. R., Mack, K. M. and Muenster, J. S.

Evans, G. T. and Vaida, V.

Francis, P. N., Taylor, J. P., Hignett, P. and Slingo, A.


Fu, Q., Lesins, G., Higgins, J., Charlock, T., Chylek, P. and Michaelsky, J.

Gebbie, H. A.

Giver, L. P., Chackerian, C. and Varanasi, P.

Goss, L. and Vaida, V.

Goss, L. M., Sharpe, S. W., Blake, T. A., Vaida, V. and Brault, J. W.

Han, Y., Shaw, J. A., Chemsishe, J. H., Brown, P. D. and Clough, S. A.

Henry, B. R.

Hill, C. and Jones, R. L.

Huang, Z. S. and Miller, R. E.

Huisken, F., Kaloudis, M. and Kulicke, A.


1984 The effect of ultraviolet radiation on water vapour absorption between 5 and 50 cm⁻¹. *Infrared Phys.*, 24, 437–441


1995 ‘Gaussian 94 (Revision D.4)’. Gaussian, Inc., Pittsburgh, PA, USA


Tyndall, J. 1861 On the absorption and radiation of heat by gases and vapours, and on the physical connection of radiation, absorption and conduction. Phil. Trans. R. Soc. London, A151, 1–36


