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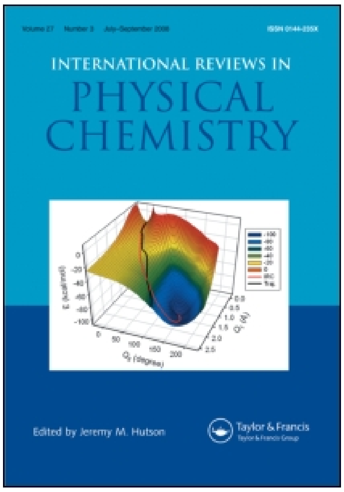

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Hydrated Complexes: Relevance to Atmospheric Chemistry and Climate

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Hydrated Complexes: Relevance to Atmospheric Chemistry and Climate

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Intermolecular interactions in molecular clusters can significantly alter the optical properties and reaction dynamics of the constituent monomers. As a result, both atmospheric chemistry and climate may be affected. We review here the spectroscopy and photochemistry of molecular hydrates and point to their possible relevance to the Earth's atmosphere. Data needed to model the atmospheric effects of hydrates includes calculation of both their abundance and their absorption cross-section. We discuss these issues and examine the potential spectroscopic effects of hydrates in the atmosphere, as well as the fundamental work needed to quantify better the magnitude of these effects.

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1. Introduction

Weak intermolecular interactions responsible for solvation and complexation have been shown to affect the optical properties and reaction dynamics of molecular systems (Robinson 1967, Donaldson *et al.* 1987, 1988a,b, Sapers *et al.* 1988, Prinslow and Vaida 1989, Vaida *et al.* 1989a,b, Gillies *et al.* 1991, Rudich *et al.* 1993,

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Donaldson *et al.* 1998, Hansen and Francisco 2002, Mmereki, B. T. and Donaldson, D. J. 2002, Gimmler, G. and Havenith, M. 2003). These effects have recently been discussed in connection with their relevance to the Earth's atmosphere (Vaida *et al.* 1992, Vaida and Headrick 2000, Vaida *et al.* 2001). This review focuses on molecular complexes of atmospheric chromophores with water (hydrates). The work reviewed includes the spectroscopy and photoreactivity of hydrates and points to their role in climate and in chemistry. Recently, the importance of radical–molecule complexes in atmospheric chemistry has been eloquently reviewed by Francisco and coworkers (Aloisio and Francisco 2000, Hansen and Francisco 2002), and we refer the reader to these reviews. In what follows we discuss the abundance, spectroscopy, photoreactivity and atmospheric relevance of molecular hydrates.

Water vapour is prevalent in the atmosphere, absorbing radiation in the IR and near-IR. Water readily forms hydrogen-bonded complexes with itself and other acids, with bond energies from approximately 5 kcal mol^{-1} for $(H_2O)_2$ (Kim *et al.* 1992, Xantheas and Dunning 1993) to approximately 9–12 kcal mol^{-1} for HNO_3–H_2O and H_2SO_4–H_2O (Kuczkowski *et al.* 1981, Tao *et al.* 1996). Much weaker (less than 1 kcal mol^{-1}) van der Waals interactions with N_2, O_2 or Ar can lead to complexes between abundant atmospheric gases and water.

Intermolecular interactions in condensed phase (Robinson 1967, Vaida *et al.* 1989b, Hansen and Francisco 2002) or in a complex (Donaldson *et al.* 1987, 1988b,c, Sapers *et al.* 1988, Prinslow and Vaida 1989, Vaida *et al.* 1989, Schriver *et al.* 1990, Gillies *et al.* 1991, Rudich *et al.* 1993, Frost and Vaida 1995, Hurwitz and Naaman 1995, Donaldson *et al.* 1998, Aloisio and Francisco 2000, Staikova and Donaldson 2001, Hansen and Francisco 2002) have been shown to stabilize a molecule's potential energy surface (PES) in proportion to its dipole moment and the polarity of the solvent. Differential shifts of the PES involving absorption of radiation and photochemical reaction lead to shifts in the frequency and intensity in the absorption spectra. These are especially important when the shift leads to properties that can be differentiated from those of the constituent monomers. In the atmosphere, such effects can induce changes in the energetics of chemical reactions and in the identity of photo-products.

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The energy source for the Earth's temperature, climate and chemistry is the Sun, providing the top of the atmosphere with radiation characteristic of a blackbody of approximately 6000 K, having a $\lambda_{\max}$ value of approximately 500 nm. Penetration of this radiation through the atmosphere is controlled by atmospheric absorbers: ozone and oxygen determine the high-energy (UV) cut-off, while absorption by H_2O with some contribution from CO_2, O_2, O_3 and other trace gases takes place in the near-IR and IR (Tyndall 1861, Ludlam 1980, Ramanathan and Vogelmann 1997). Any absorbers' spectra falling outside the absorption of these major atmospheric chromophores can have a very significant effect. In this context, we evaluate the effect of molecular hydrates in atmospheric climate and chemistry.

The fundamental physical and chemical parameters needed for this study include determination of atmospheric abundance, spectra and photochemistry of a complex. These have been the object of theoretical and experimental investigations, with recent emphasis on atmospherically relevant complexes (Fellers *et al.* 1999a,b, Vaida and Headrick 2000, Vaida *et al.* 2001). Attempts to observe and experimentally quantify these complexes in the atmosphere have so far failed in all but one case, that of the oxygen dimer (Pfeilsticker *et al.* 1997, Solomon *et al.* 1998). Theoretical predictions of the water dimer abundance and spectra (Chylek and Geldart 1997) prompted field measurements to search for this complex, but these failed to identify spectroscopic features assignable to this dimer (Pfeilsticker *et al.* 1997, Solomon *et al.* 1998). As was pointed out by some of us (Vaida *et al.* 2001), interference from the monomer, the small vibrational overtone cross-sections for the dimer, and the very large expected bandwidth will make such a search difficult both in the field and in the laboratory. It is very likely that spectra of the water clusters and other hydrates contribute to the intensity of empirical continua that have been observed underlying water vapour spectra (Clough *et al.* 1980, 1989, Clough 1995). Clearer spectroscopic signatures for complexes should be found in the IR, where the fundamental intermolecular vibrations are found with no interference from monomer vibrational transitions. Elegant spectroscopic studies have led to the structural characterization of complexes of importance in the atmosphere: $(H_2O)_n$ (Liu *et al.* 1996, Goldman *et al.* 2001, Keutsch and Saykally 2001), HNO_3–H_2O (Canagaratna *et al.* 1998) and H_2SO_4–H_2O (Fiacco *et al.* 2002).

Theoretical studies aimed at understanding the thermodynamic properties of weakly bound molecular hydrates have focused on the water dimer (Kim *et al.* 1992, Slanina and Crifo 1992, Mhin *et al.* 1993, Chylek and Geldart 1997, Munoz-Caro and Nino 1997, Tso *et al.* 1998, Hobza *et al.* 1999, Vaida and Headrick 2000, Goldman *et al.* 2001, Schenter *et al.* 2002). Elucidation of thermodynamic properties remains a challenging problem, even for the water dimer, as for such weakly bound systems at the high temperatures characteristic of the Earth's atmosphere (200–300 K), vibrational energy levels up to the dissociation limit (Fellers *et al.* 1999a,b) for the complex as well as dissociative states (Schenter 1998, Schenter *et al.* 2002) must be treated to obtain the free energy of dimerization and from that, the equilibrium constant needed to determine abundances of atmospheric complexes (Vigasin 1985, 1991, 1995, 1998, Vigasin and Slanina 1998, Vigasin 2001). Fellers *et al.* (1999a,b) and Schenter and colleagues (Schenter 1998, Schenter *et al.* 2002) in elegant theoretical work have recently discussed these issues for the specific case of water dimers and advanced toward a proper statistical mechanics description for weakly bound systems. The estimated abundances presented here do not tackle the problem of excited vibrational states at and above dissociation and can only be taken to give a rough estimate of the range of possible values for the atmospheric abundance of complexes relative to the water dimer. The abundance calculations are accompanied by calculations of frequencies and intensities of vibrational overtones applied to the same molecular hydrates involving atmospheric gases. The result of this work points to the potential spectroscopic effects of hydrates in the atmosphere and the need for further fundamental work to quantify the magnitude of these effects.

2. Atmospheric Abundance of Hydrates

In order to understand the atmospheric implications of the complexes in question, it is necessary to calculate or measure their abundances in the atmosphere. To date, the only molecular complex directly measured in the atmosphere has been the O_2–O_2 complex (Pfeilsticker *et al.* 1997, Solomon *et al.* 1998). Since many complexes have binding energies higher than that of O_2–O_2, it is likely that they will exist in the atmosphere; however, no others have been directly measured. Consequently, laboratory studies and theory are needed to estimate their abundances. In principle, the abundance of such complexes can be estimated from the equilibrium constant, K_p, for the formation of the complex:

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$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{A} \cdot \mathrm{B}, \tag{1}$$

$$K_\mathrm{p} = \frac{P_{\mathrm{A}\cdot\mathrm{B}}}{P_\mathrm{A} P_\mathrm{B}}. \tag{2}$$

Thus, if the equilibrium constant and the partial pressures of the monomers are known, the abundance of the complex can be determined.

While it is possible to measure equilibrium constants experimentally, doing so for these complexes is a challenging process: determining the concentration of the complex requires a temperature- and pressure-controlled environment in which monomers and the complex can be monitored using high-resolution spectroscopy. In addition, the hydrates have many low-frequency modes, which are in a high vibrational state at room temperature, thus causing line broadening and difficulties in discerning such spectra from the background. So far, little progress has been made on the experimental measurement of equilibrium constants, so theory plays a large role in estimating these quantities. The water dimer, however, is an exception in that a good deal of progress has been made examining its properties experimentally (Curtiss *et al.* 1979, Keutsch and Saykally 2001). Nevertheless, recent attempts to measure the water dimer spectrum in the atmosphere have failed (Pfeilsticker *et al.* 1997, Solomon *et al.* 1998).

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It is well known that basic statistical mechanics can provide an estimate for equilibrium constants. However, weakly bound molecular complexes at atmospheric temperatures (200–300 K) present a challenge (Vigasin 1985, 1991, Epifanov and Vigasin 1994, Vigasin 1995, Epifanov and Vigasin 1997, Vigasin 1998, Vigasin and Slanina 1998, Vigasin 2001, Schenter *et al.* 2002). Weakly bound complexes, especially those with lower binding energies, will have very shallow potential wells and will be excited near their dissociation limit at atmospheric temperatures. It is therefore necessary to treat vibrational levels at and above dissociation as has been eloquently pointed out (Vigasin and Slanina 1998, Fellers *et al.* 1999a,b, Schenter *et al.* 2002). Thus, the statistical mechanics implemented here is most likely not accurate at these temperatures because of such effects. Instead, a more rigorous treatment of the system should be implemented, one which defines the difference between bound and metastable species and takes into account the density of ro-vibrational states near the dissociation limit. However, the quantities calculated can be used as estimates, and when possible, as in the case of $(H_2O)_2$ (Curtiss *et al.* 1979), compared with and constrained by experiments. In order to use statistical mechanics, however, certain molecular parameters are required for the construction of partition functions. These include vibrational frequencies of both monomers and complex, rotational constants of both monomers and complex, as well as the binding energy of the complex. Using these quantities in molecular partition functions described in detail elsewhere (McQuarrie 1973, 1976, Vaida and Headrick 2000), thermodynamic quantities including the molar enthalpy, ΔH°, and entropy, ΔS°, can readily be calculated. The molar Gibbs free energy, ΔG°, is then calculated using the following familiar thermodynamic relation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ. \tag{3}$$

The equilibrium constant is related to ΔG° as follows:

$$K(T) = \exp(-\Delta G^\circ / RT), \tag{4}$$

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where R is the ideal gas constant (8.314 J mol^{-1} K^{-1}) and T is the temperature in Kelvins. To calculate the abundance of a complex at a specific altitude, one needs both the temperature at that altitude and the partial pressures or mixing ratios of the two monomers. For all of the molecules in question, these temperatures and mixing ratios have been directly measured (Brasseur and Solomon 1986).

The results of abundance calculations for several molecular complexes with different binding energies are illustrated in figures 1–3. Table 1 provides the molecular parameters and their sources (Millen and Morton 1960, Cook *et al.* 1974, McQuarrie 1976, Dyke *et al.* 1977, Kuczkowski *et al.* 1981, Schriver *et al.* 1990, Gillies *et al.* 1991, Hertzberg 1991, Kim *et al.* 1992, Frost and Vaida 1995, Tao *et al.* 1996, Svishchev and Boyd 1998, Re *et al.* 1999) for each calculation. Examination of figure 1 illustrates the important relation between binding energy and molar enthalpy (ΔH°). N_2–H_2O has a binding energy (Svishchev and Boyd 1998) of 1.55 kcal mol^{-1} whereas H_2SO_4–H_2O has a binding energy (Re *et al.* 1999) of 11.3 kcal mol^{-1} or greater. Note that the larger binding energy results in a more negative molar enthalpy.

At low temperatures, such as those at which the *ab initio* theory, matrix isolation and supersonic expansion experiments are conducted, entropic contributions (i.e., $T\,\Delta S^\circ$) become negligible; however, in the atmosphere, at relatively high temperatures, the molar entropy of complexes becomes quite significant, as illustrated in figure 1. At the tropopause, the entropic effect is at its lowest magnitude. This, of course, is due to the minimum in temperature (212.6 K) (Brasseur and Solomon 1986).

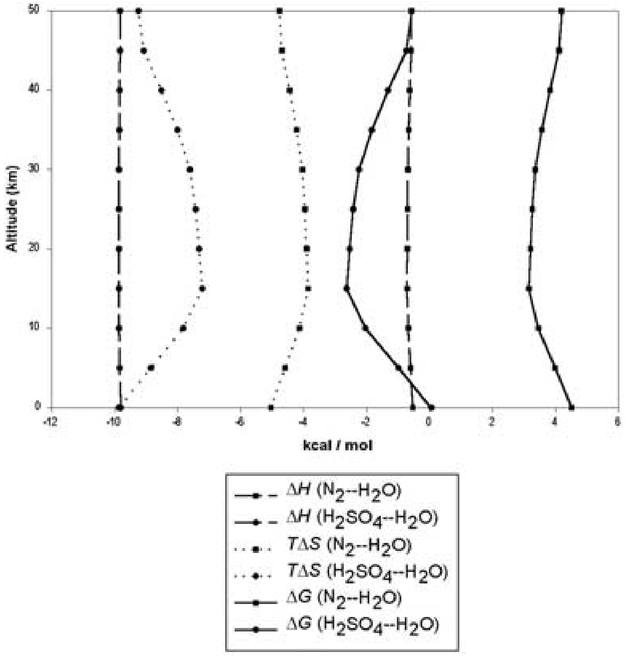

Figure 1. Altitude profiles of thermodynamic quantities (ΔH°, $T\,\Delta S^\circ$, and ΔG°) for two hydrates: N_2–H_2O and H_2SO_4–H_2O.

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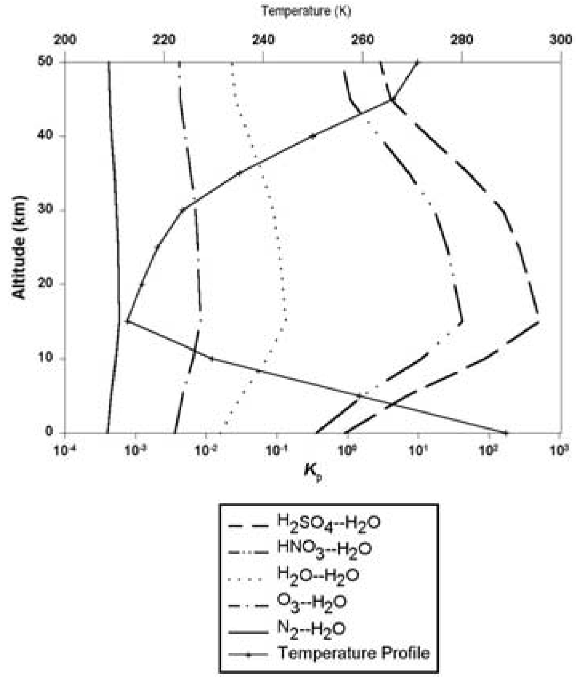

Figure 2. Altitude profile for the equilibrium constant of five hydrates. The altitude profile of the temperature is also plotted.

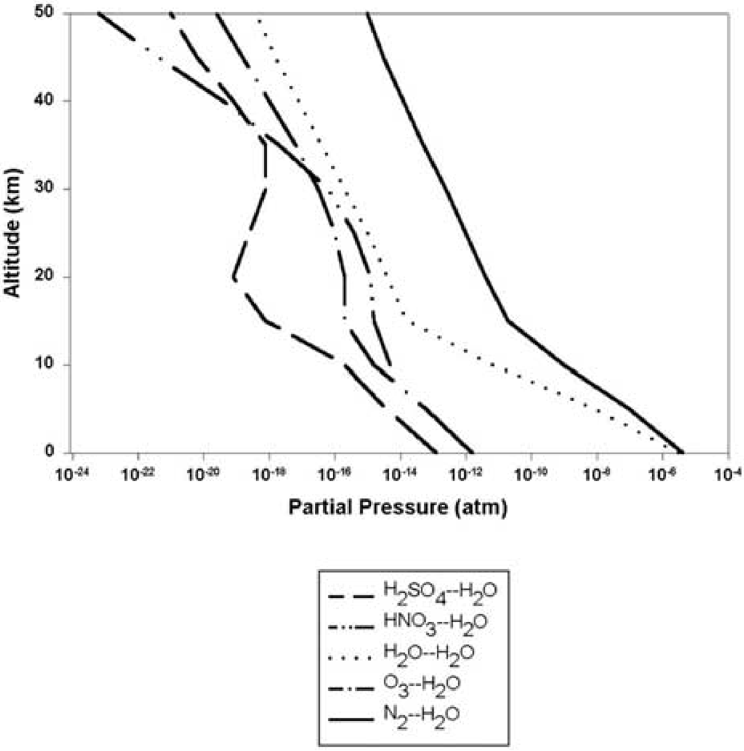

Figure 3. Altitude profile for the partial pressures of five hydrates.

Table 1. Molecular parameters.

	Vibrational frequencies[a] (cm^{-1})	Rotational constants (cm^{-1})
N_2	2179.4	2.001[b]
H_2O	1660.7, 3869.8, 3990.1	9.277 71[c], 14.5218[c], 27.8806[c]
N_2–H_2O BE = -1.55 kcal mol^{-1}[a]	70.1, 81.1, 91.2, 181.1, 269.1, 1668.0, 2182.6, 3867.7, 3985.0	0.0975[d], 0.0979[d], 176[d]
	Vibrational frequencies (cm^{-1})	Rotational constants (cm^{-1})
O_3	709[e], 1042[e], 1103[e]	0.394 79[e], 0.445 25[e], 3.5534[e]
H_2O	1648[f], 3832[f], 3942[f]	9.285[e], 14.512[e], 27.877[e]
O_3–H_2O BE = -2.4 kcal mol^{-1}[h]	50[g], 53[g], 56[g], 70[h], 140[g], 246[g], 708[i], 1046[i], 1107[i], 1645[j], 3806[j], 3911[j]	0.109[h], 0.139[h], 0.399[h]
	Vibrational frequencies[f] (cm^{-1})	Rotational constants (cm^{-1})
H_2O	1640, 3859, 3983	9.277 71[c], 14.5218[c], 27.8806[c]
H_2O–H_2O BE = -4.99 kcal mol^{-1}[f]	130, 137, 146, 182, 362, 637, 1639, 1667, 3765, 3846, 3950, 3967	0.200 138[k], 0.200 138[k], 6.671 28[k]
	Vibrational frequencies[l] (cm^{-1})	Rotational constants (cm^{-1})
HNO_3	464, 576, 651, 743, 885, 1325, 1358, 1872, 3629	0.2088[m], 0.4036[m], 0.4340[m]
H_2O	1681, 3749, 3895	9.277 71[e], 14.5218[e], 27.8806[e]
HNO_3–H_2O BE = -9.5 kcal mol^{-1}[l]	73, 95, 166, 231, 323, 425, 632, 678, 753, 871, 944, 1343, 1511, 1689, 1845, 3290, 3731, 3865	0.073 86[l], 0.089 81[l], 0.4064[l]
	Vibrational frequencies[n] (cm^{-1})	Rotational constants (cm^{-1})
H_2SO_4	248, 317, 348, 411, 457, 499, 507, 764, 819, 1140, 1148, 1155, 1393, 3760, 3764	0.163[p], 0.167[p], 0.172[p]
H_2O	1639[o], 3821[o], 3923[o]	9.277 71[e], 14.5218[e], 27.8806[e]
H_2SO_4–H_2O BE = -11.3 kcal mol^{-1}[n]	49, 125, 214, 230, 258, 342, 375, 403, 476, 502, 516, 531, 774, 840, 866, 1134, 1152, 1322, 1445, 1618, 3110, 3770, 3758, 3903	0.06[o], 0.06[o], 0.15[o]

BE, binding energy. [a] Svishchev and Boyd (1998). [b] McQuarrie (1976). [c] Cook *et al.* (1974). [d] estimated from geometry given by Leung *et al.* (1989). [e] Herzberg (1991). [f] Kim *et al.* (1992). [g] Scaled intermolecular frequencies of the water dimer (from Kim *et al.* (1992)), referenced to the stretching vibration of 70 cm^{-1} (from Gillies *et al.* (1991)). [h] Gillies *et al.* (1991). [i] Schriver *et al.* (1990). [j] Schriver *et al.* (1990), scaled to harmonic value following Ref 13. [k] Dyke *et al.* (1977). [l] Tao *et al.* (1996). [m] Millen and Morton (1960). [n] Re *et al.* (1999) unless otherwise noted. [o] H. G. Kjaergaard provided estimates on the vibrational frequencies of H_2O and rotational constants of H_2SO_4–H_2O. [p] Kuczkowski *et al.* (1981).

Finally, the molar free energy (ΔG°) for N_2–H_2O and H_2SO_4–H_2O is also shown in figure 1. Here it is most evident that entropic effects can begin to dominate enthalpic effects (i.e. $|T\,\Delta S^\circ| > |\Delta H^\circ|$, thus $\Delta G > 0$). For N_2–H_2O, this is the case at all altitudes: because of its low binding energy, and thus low enthalpy, the entropic effects are dominant at atmospheric temperatures. The opposite is true for H_2SO_4–H_2O; here, enthalpy exceeds entropic contributions in magnitude at nearly all altitudes and ΔG° is negative. Again, because of the entropic contribution, ΔG° for both hydrates reaches a minimum at the tropopause.

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Figure 2 shows the altitude profile of the equilibrium constant for five hydrates: N_2–H_2O, O_3–H_2O, H_2O–H_2O, HNO_3–H_2O and H_2SO_4–H_2O. Also shown is the variation of temperature with altitude. The equilibrium constants are correlated to the binding energies of the complexes; N_2–H_2O has the lowest binding energy and the lowest equilibrium constant (K_p), and H_2SO_4–H_2O has the highest binding energy and the highest K_p. Also, hydrates with higher binding energies have equilibrium constants that vary in magnitude with altitude the most: H_2SO_4–H_2O changes by nearly three orders of magnitude, while O_3–H_2O and N_2–H_2O change by no more than a factor of 5. Finally, the temperature profile illustrates the effect of temperature on the equilibrium constants. The minimum in temperature corresponds to a maximum in equilibrium constant for hydrate formation; as expected, low temperatures signify less entropic contribution, and thus more stability for the complexes.

The partial pressures of each complex are graphed versus altitude in figure 3. Note that the maximum partial pressure for all hydrates does not occur at the tropopause like the equilibrium constant, but rather at ground level. This effect is due to the partial pressure of the monomers. For example, the partial pressure of water dimer is affected both by the equilibrium constant as well as the square of the partial pressure of water monomer:

$$P_{\mathrm{H_2 \cdot H_2O}} = (P_{\mathrm{H_2O}})^2 K_{\mathrm{p}}. \tag{5}$$

As altitude increases, the partial pressure of water monomer drops sharply until the tropopause, where the decrease becomes more gradual. This is reflected in figure 3 in the inflection point that can be seen at 15 km for each hydrate. A second inflection point for O_3–H_2O, HNO_3–H_2O and H_2SO_4–H_2O can be seen at approximately 20, 25 and 35 km respectively. This is due to the contributions of the partial pressures of O_3, HNO_3 and H_2SO_4 monomers; each gives the partial pressure profile of the complex its distinct shape.

The use of such a simple, fundamental theory to describe such complexes warrants some discussion. The molecular parameters used have been determined either by theory or often by spectroscopic studies taking place at extremely low temperatures (e.g. supersonic jets and matrix isolation). As a result, detailed information about the system near the bottom of the potential well is obtained; however, the anharmonic portion of the potential remains poorly described. In spite of such shortcomings, estimates based on standard statistical mechanics provide the most information about the atmospheric abundances of complexes. Because of their potential atmospheric importance, even rough estimates of abundances can provide valuable information about the contribution that these complexes will make in the atmosphere (Goldman *et al.* 2001, Vaida *et al.* 2001).

3. Calculated overtone spectra of hydrated complexes

The near-IR spectra of molecules containing OH bonds are dominated by OH stretching overtone vibrations (Henry and Kjaergaard 2003). These overtone transitions are described well by the local mode model (Henry 1977) and are generally found to contain one peak for each of the non-equivalent OH bonds in the molecule (Henry and Kjaergaard 2003). 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 Lawton 1982). Combined

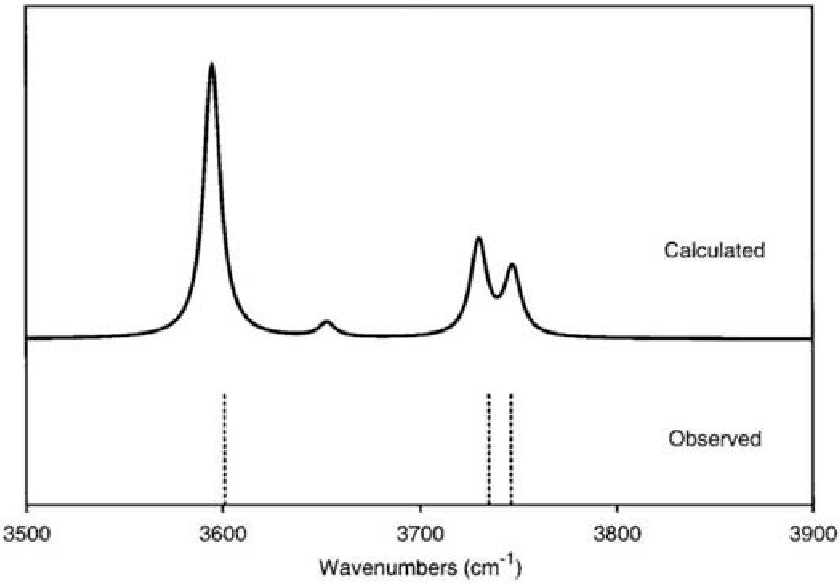

Figure 4. Agreement between HCAO calculated water dimer spectrum and the molecular beam observed positions.

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with an *ab initio* calculated dipole moment function, intensities of these overtone transition are successfully predicted (Kjaergaard *et al.* 1990, Kjaergaard and Henry 1991). Absolute OH stretching overtone intensities of spectroscopic accuracy can be obtained provided that a reasonable quality *ab initio* dipole moment function is used (Kjaergaard *et al.* 1994). We have used the HCAO local mode model to calculate successfully the vibrational band intensities of the water molecule (Kjaergaard *et al.* 1994).

We describe the intensity of an overtone transition by the oscillator strength f, which, for a transition from the vibrational ground state g to a vibrational excited state e, is given by (Kjaergaard *et al.* 1990, Atkins and Friedman 1997)

$$f_{\mathrm{eg}} = 4.702 \times 10^{-7}\,\mathrm{cm}\ \mathrm{D}^{-2} \times \tilde{\nu}_{eg}|\mu_{eg}|^2, \tag{6}$$

where $\tilde{\nu}_{eg}$ is the frequency of the transition in wavenumbers and $\mu_{eg} = \langle e|\boldsymbol{\mu}|g\rangle$ is the transition dipole moment matrix element in debyes (D).

Hydrated complexes come in different classes. The H_2O molecule can act either as a hydrogen donor as in N_2–H_2O or as the hydrogen acceptor as in HNO_3–H_2O. Water typically acts as the donor in the weaker complexes with N_2, O_2 and also in the water dimer. H_2O also acts as the acceptor in water dimer but generally in stronger complexes with acids such as HNO_3, H_2SO_4 and HCOOH. The hydrogen atom involved with the hydrogen bonding is the most perturbed in the complex; however, other OH bonds in the complexes can also be sufficiently perturbed to alter the spectroscopic signature. The water units in hydrated complexes are either symmetric with the two OH bonds equivalent or asymmetric with two non-equivalent OH bonds. The OH bond in the HNO_3 unit of the complex can be described as an isolated local mode.

We use the HCAO local mode model to obtain the vibrational energies and wave functions required in equation (6). The details of the HCAO local mode model for the different number of bonds have been given previously and we give only an outline here for an asymmetric H_bOH_f group. The local mode model zeroth-order Hamiltonian is written (Kjaergaard and Henry 1992)

$$(H - E_{|oo\rangle})/hc = v_b\tilde{\omega}_b - (v_b^2 + v_b)\tilde{\omega}_b x_b + v_f\tilde{\omega}_f - (v_f^2 + \nu^f)\tilde{\omega}_f x_f \tag{7}$$

with each of the two OH-stretching potentials described by Morse potentials. $E_{|00\rangle}$ is the energy of the vibrational ground state, v are the vibrational quantum numbers and $\tilde{\omega}$ and $\tilde{\omega}x$ are the frequencies and anharmonicities of the local mode oscillators. The zeroth-order basis states can be written as products of Morse oscillator wavefunctions. The coupling between the two OH oscillators is limited to the harmonic coupling between states with the same total $v = v_b + v_f$ and gives rise to the perturbation (Kjaergaard and Henry 1992)

$$H'/hc = -\gamma'_{bf}(a_b a_f^\dagger + a_b^\dagger a_f) \tag{8}$$

where $a^\dagger$ and a are the step-up and step-down operators known from harmonic oscillators (Messiah 1961) and γ'_{bf} is the effective intramanifold coupling coefficient:

$$\gamma'_{bf} = (\gamma_{bf} - \phi_{bf})(\tilde{\omega}_b\tilde{\omega}_f)^{1/2}. \tag{9}$$

γ'_{bf} can be determined from the *ab initio* calculated optimized geometry and force constants. Diagonalization of the Hamiltonian, equations (7) and (8), gives the eigenenergies and vibrational wavefunctions.

The Morse oscillator frequency $\tilde{\omega}$ and anharmonicity $\tilde{\omega}x$ required in equation (7) and the dipole moment function required in equation (6) can be obtained from *ab initio* calculations. Expansion of the Morse potential shows that the local mode frequency and anharmonicity can be expressed by the second- and third-order force constants F_{ii} and F_{iii} and the inverse of the reduced mass of the OH bond, G_{ii} (Sowa *et al.* 1991, Low and Kjaergaard 1999):

$$\tilde{\omega} = \frac{\omega}{2\pi x} = \frac{(F_{ii}G_{ii})^{1/2}}{2\pi c}, \tag{10}$$

$$\tilde{\omega}x = \frac{\omega x}{2\pi x} = \frac{hG_{ii}}{72\pi^2 c}\left(\frac{F_{ii}}{F_{ii}}\right)^2. \tag{11}$$

The dipole moment function is approximated by a series expansion in the internal OH displacement coordinates about the equilibrium geometry:

$$\mu(q_b, q_f) = \sum_{i,j} \mu_{ij} q_b^i q_f^j \tag{12}$$

where the coefficients μ_{ij} are given by

$$\mu_{ij} = \frac{1}{i!j!}\frac{\partial^{i+j}\boldsymbol{\mu}}{\partial a_b^i \partial q_f^j}. \tag{13}$$

The summation in equation (12) is usually limited to fifth-order diagonal and third-order mixed terms (Kjaergaard and Henry 1992, Low and Kjaergaard 1999). This usually provides oscillator strengths which are converged for states with $\nu \leq 6$.

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The second- and third-order force constants F_{ii} and F_{iii} and the dipole moment expansion coefficients are determined from grids of *ab initio* calculated potential energies and dipole moments respectively. The grid is calculated by displacing the OH bonds by ± 0.2 Å from the equilibrium position in steps of 0.05 Å to provide good convergence of the potential energy derivatives (force constants) and dipole moment derivatives (Kjaergaard and Henry 1992, Low and Kjaergaard 1999). The mixed expansion coefficients are calculated from a two-dimensional dipole moment grid, $\mu(q_\mathrm{b}, q_\mathrm{f})$, in which the internal displacement coordinates q_b and q_f of the two OH oscillators are displaced by ± 0.2 Å from equilibrium in steps of 0.05 Å (Kjaergaard and Henry 1992, Low and Kjaergaard 1999). We have scaled the *ab initio* calculated local mode parameters, $\tilde{\omega}$ and $\tilde{\omega}x$, of the OH oscillators in the hydrated complexes by the ratio of calculated to experimental local mode parameters for the relevant monomers. Thus, for example, for H_2O units, the H_2O molecule is used.

The geometry optimizations and grid point calculations are performed with use of an *ab initio* program such as Gaussian94 (Frisch *et al.* 1995). Geometries should be optimized with 'tight' convergence limits and confirmed as minima by frequency calculations resulting in zero imaginary frequencies. The dipole moment at each grid point is calculated using the density matrix for the current method, in order to provide dipole moments that are the correct analytical derivatives of the energy.

Recently, the HCAO local mode method has been used to calculate the vibrational band positions and intensities of OH stretching transitions for $(H_2O)_2$ (Low and Kjaergaard 1999), H_2O–N_2 and H_2O–O_2 (Kjaergaard *et al.* 2002), H_2O–HNO_3 (Kjaergaard 2002), and H_2SO_4–H_2O (Hintze *et al.* 2002). These calculations used dipole moment functions calculated with the correlated quadratic configuration interaction including singles and doubles level of theory with a 6-311++G(2d,2p) basis set (QCISD/6-311++G(2d,2p)). With this *ab initio* method the geometric structure of the hydrated complexes is correctly predicted and the calculated dipole moment and binding energy, where measured, are in close agreement with the experimental values. The predicted OH stretching fundamental transitions were in good agreement with the experimentally observed transitions in a molecular beam (Miller 1988, 1990, Huisken *et al.* 1996, Miller 2001) and recent matrix isolation spectra of the fundamental region (Perchard 2001a,b).

The fundamental and first OH stretching overtone also seem to agree well with these calculations (Perchard 2001a,b). Matrix experiments are known to show frequency redshifts and sometimes perturb intensities. The agreement between the HCAO calculations and the Ar matrix isolation spectra of the water dimer (Perchard 2001b) is very good.

In figure 5 we compare the calculated OH-stretching overtone spectra in the region corresponding to $\nu = 4$ of $(H_2O)_2$ and N_2–H_2O with a simulated experimental H_2O spectrum. Rotational structure is not included in the simulated spectra of these complexes. The stronger $(H_2O)_2$ complex shows significant changes compared with the H_2O spectrum whereas the N_2–H_2O spectrum only has small changes, as expected on the basis of the significantly lower binding energy for this complex.

In figure 6, we have compared the calculated spectrum of the HNO_3–H_2O complex with those of the H_2O and HNO_3 molecules. The very large shift of the OH stretching transition in the HNO_3 unit of the complex compared with the monomer is obvious. However, shifts in the OH stretching transitions of the H_2O

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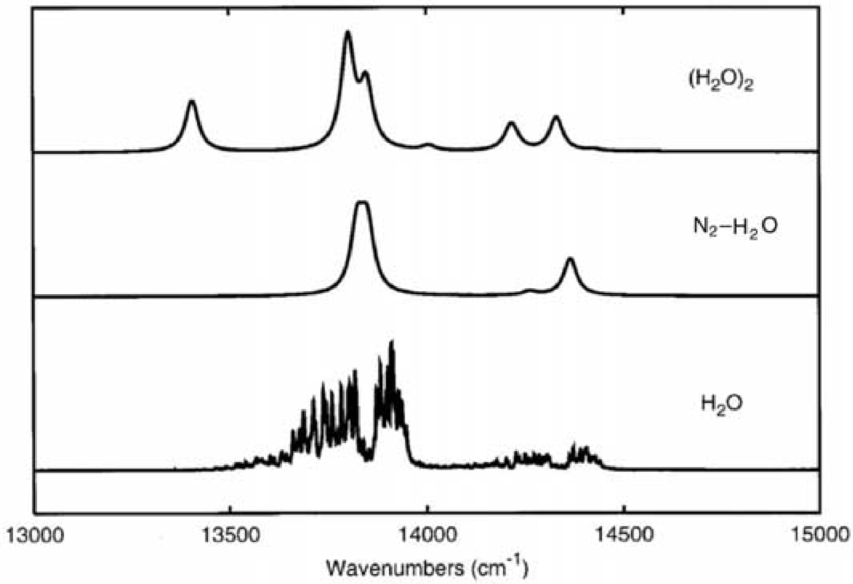

Figure 5. HCAO calculated OH stretching overtone spectrum ($\nu = 4$) of $(H_2O)_2$ and N_2–H_2O, compared with the experimental H_2O spectrum.

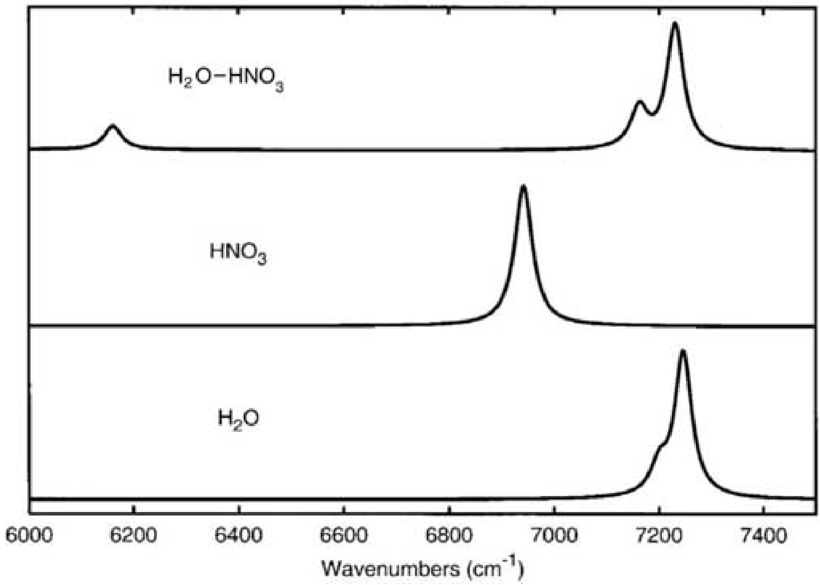

Figure 6. HCAO calculated OH stretching overtone spectrum ($\nu = 4$) of H_2O–HNO_3 compared with those of H_2O and HNO_3.

unit are also apparent. Likewise, intensity shifts are observed, in particular for the OH stretch of HNO_3 in the complex.

The illustrations presented here show that the local mode model can be used to predict frequencies and intensities for these hydrates. The results show significant

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shifts for the OH stretch compared with the monomeric constituents, especially for the more strongly bound hydrates.

4. Atmospheric Implications

The estimates of atmospheric abundance and spectra suggest that the role of hydrates in affecting both climate and chemistry should not be overlooked. The water dimer contributes to the absorption of solar radiation (Goldman *et al.* 2001, Headrick and Vaida 2001, Vaida *et al.* 2001), and other complexes may do the same (Kjaergaard *et al.* 2003); chemistry of weakly bound hydrates in the atmosphere may significantly be altered, as has been shown for O_3–H_2O (Frost and Vaida 1995) and H_2SO_4–H_2O (Vaida *et al.* 2003).

In order to understand the contribution of such complexes to both atmospheric chemistry and climate, it is crucial to understand better their abundance and their spectroscopy. The abundance of a complex may determine to what extent chemical reactions or absorption of radiation may be affected. Currently, experimental spectroscopy of hydrates is limited to low-temperature environments, and abundance calculations are based primarily on theory and comparison with such low-temperature experiments. A few attempts to identify water clusters in the warmer atmosphere and high-temperature laboratory studies (Curtiss *et al.* 1979) of steams provide some means of comparing theory and experiment.

The effect of such complexes on climate has been examined in the case of the water dimer (Vaida *et al.* 2001). Results from theoretical calculations and a line-by-line radiative transfer model indicate that absorption of the dimer in the tropical atmosphere could be as high as $3.3\,\mathrm{W\,m^{-2}}$ ($0.7\,\mathrm{W\,m^{-2}}$ for a global average) (Vaida *et al.* 2001). In addition, global warming would result in a faster increase in dimer absorption than that for monomer absorption, and so could provide positive feedback in such a case. In spite of the extensive spectroscopic and structural data and *ab initio* calculations, the effect of larger water clusters ($(H_2O)_n$, with $n > 2$) on climate could not be included in atmospheric models (Evans and Vaida 2000, Headrick and Vaida 2001).

While $(H_2O)_2$ is the only hydrate that has been shown to contribute to climate effects, others may not be insignificant to this process, and thus should not be overlooked. Despite the fact that spectra of hydrates other than water clusters are not expected to be shifted greatly from those of the monomers, small shifts may be important, especially if the abundances are high. N_2–H_2O is estimated to have an abundance 10 times that of H_2O–H_2O, for example; a change in band profile on its formation could result in significant absorption of radiation (Kjaergaard *et al.* 2003).

Complexes and hydrates have also been shown to alter chemical reactions significantly. For example, the O_3–H_2O complex has been shown to have a role in the tropospheric production of OH (Frost and Vaida 1995). Calculations suggest that photolysis of the complex may account for up to 15% of the OH production in the troposphere (Frost and Vaida 1995). Because of the decreased partial pressure of water monomer at high altitudes, this reaction is most important at low altitudes. Recent *ab initio* theoretical studies are expected to provide a much better estimate of these clusters' atmospheric abundance (Lee 2003, Xantheas 2002).

The solar spectrum contains the highest abundance of photons in the visible region. These photons, while high in abundance, do not contain the energy needed to promote electronic transitions in many atmospheric species, and thus are not considered to contribute greatly to the chemistry taking place in the atmosphere. However, another mechanism acting in the ground electronic state is a possibility using visible radiation (Henry 1997, Crim 1984, Butler *et al.* 1986, Scherer *et al.* 1986, Crim 1987, Henry 1987, Sinha *et al.* 1989, 1990, Crim 1996, Phillips *et al.* 1998). This mechanism involves excitation of vibrational overtones of OH stretching transitions, which are in the visible region for molecules containing an OH bond. Despite the fact that overtone transitions are very low in intensity, their role in atmospheric chemistry may be quite significant. Several examples of this light-initiated chemistry, including atmospheric constituents such as HNO_3, HONO, HO_2NO_2, H_2O and H_2SO_4, which are known HO_x sinks, have recently been discussed (Holland *et al.* 1991, Abel *et al.* 1997, Donaldson *et al.* 1997, 1998, Fono *et al.* 1999, Wennberg *et al.* 1999, Brown *et al.* 2000, Donaldson *et al.* 2000, Zhang *et al.* 2000, Lange *et al.* 2001, Witonsky *et al.* 2001, Roehl *et al.* 2002, Staikova *et al.* 2002). Ground-state photochemistry is most significant when not competing with excited electronic state reactions. Thus, these types of reactions are most important at high zenith angles (where higher-energy UV light is minimized) (Donaldson *et al.* 1997) or for molecules that have very weak or no electronic transitions in the visible and near-UV regions (Vaida *et al.* 2003); the latter is the case for H_2SO_4 and its hydrate.

The photolysis of H_2SO_4–H_2O hydrate has been recently investigated in its role of SO_2 production at high altitudes (Vaida *et al.* 2003). The dehydration reaction that produces SO_3 and H_2O from H_2SO_4 has been found to occur in the ground state of the reactant; OH vibrational overtones are found to be responsible for the reaction, rather than an electronic absorption, which has not been observed for wavelengths as low as 140 nm (Hintze *et al.* 2003). The hydrate could play a significant role in the production of SO_3, primarily because the barrier for its reaction is $25\,\mathrm{kcal\,mol^{-1}}$, as opposed to $40\,\mathrm{kcal\,mol^{-1}}$ for monomer reaction (Morokuma and Muguruma 1994). The barrier for dissociation is lowered for the hydrate because less energy (and hence a lower OH stretching overtone) is required, and thus the absorption cross-section is larger than that of the monomer (Hintze *et al.* 2003). While it is predicted that the primary source of SO_2 is due to reaction by the monomer, it is important not to overlook the effect that the hydrate may have, especially considering its significantly lower reaction barrier.

In conclusion, we show that weakly bound complexes, in spite of their low expected atmospheric, abundance, could play a role in the Earth's atmosphere. The specific examples shown involve clusters of atmospheric chromophores with water (hydrates). For some of these complexes, the case in point being the water dimer, fundamental physicochemical properties have been investigated. Progress towards obtaining the fundamental database needed for atmospheric models is being made with much fundamental work remaining theoretically and confirmed by laboratory experiment and field measurements. The estimates of abundance and spectroscopic cross-sections suggest that molecular hydrates could play an interesting role in affecting the Earth's temperature, climate and chemistry.

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