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FEATURE ARTICLE

Physicochemical Properties of Hydrated Complexes in the Earth's Atmosphere

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Theoretical and experimental studies have recently attempted to investigate the role of molecular complexes in the Earth's atmosphere. The extent to which these weakly bound molecular species affect atmospheric chemistry and the climate is ultimately determined by their abundance. In this paper, we discuss the standard statistical procedures that are used in calculating equilibrium constants and dimer abundances. We also highlight the competition that arises between energy and entropy when complexation is considered at atmospherically relevant temperatures. For illustration, the abundance of select hydrated complexes, namely, O_2-H_2O, O_3-H_2O, H_2O-H_2O, and HNO_3-H_2O, are estimated. Using the results of our calculations, we evaluate and compare the physicochemical properties of these hydrated complexes and discuss how monomer concentrations, temperature, and dimer binding energies influence their calculated atmospheric abundances. We further examine the shortcomings of our estimates and include a short analysis outlining the inherent sensitivity of our computational method to discrepancies that exist in the available database for hydrated complexes.

Introduction

The Earth's atmosphere is a highly complex and dynamic system whose thermal and chemical balance were once thought to be maintained primarily by gas-phase processes. Certain atmospheric phenomena, such as the polar ozone hole[1,2] and the cloud absorption anomaly,[3−11] have since challenged this belief. Ultimately, the discrepancies between atmospheric observations and theoretical model calculations led to the recognition of the atmospheric importance of heterogeneous processes.[1,2,6,12−16] To understand this new atmospheric chemistry, research efforts began to focus on bridging the gap between pure gas-phase processes and those that occurred in the condensed phase. In that aim, we focus this paper on the role of weakly bound molecular complexes. These species, regarded as precursors to the condensed phase, are small molecular clusters bound by weak intermolecular interactions.[17−25] By perturbing the ro-vibronic and electronic states of the individual molecules, these forces alter the spectroscopy and photoreactivity of the monomeric constituents and give rise to new avenues of chemistry.[19,25−27] The shifting and broadening of monomer spectral features, the appearance of new absorption bands, intensity enhancement of forbidden electronic transitions, modification of existing monomer dissociation pathways, and the appearance of entirely new photodissociation channels represent a few of the known consequences of complexation.[16,25,26,28−42] Since the Earth's temperature, climate, and chemistry are fueled by the absorption of solar radiation in the atmosphere and at the surface, any one of these could have significant atmospheric consequences.[16,19,27,43−50]

Weakly bound complexes containing water have generated substantial scientific interest.[37,45,51−67] Water, in all of its phases, is a major player in the absorption of solar and terrestrial radiation.[68,69] Because of this, complexes that contain water have great potential to alter the radiative balance and chemistry of our atmosphere. It is well-known that water is able to form complexes with both itself and with other atmospheric chromophores.[28,30,37,39,45,49−51,56,58,61−63,65−67,70−168] Some of these complexes, such as H_2O-H_2O and HNO_3-H_2O, are bound by

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substantial intermolecular hydrogen bonding. As a result, these complexes have much larger binding energies (4.99 kcal/mol[67,128] for H_2O-H_2O and 9.5 kcal/mol[66] for HNO_3-H_2O) than those which are bound by weak van der Waal interactions. Through the use of innovative experimental techniques and complex ab initio calculations, a wealth of structural, dynamical, and energetic information has been generated for numerous hydrated complexes. Recent studies have focused on O_2-H_2O,[49,70-72] N_2-H_2O,[49,73-75] H_2-H_2O,[75-77] $CO-H_2O$,[74,75,78-82] Cl_2-H_2O,[83] CO_2-H_2O,[84,85] NH_3-H_2O,[58,65,86,87] NO_x-H_2O,[88] ClO_x-H_2O,[61,83] $HOCl-H_2O$,[30,83] O_3-H_2O,[39,45,89,90] $(H_2O)_n$,[50,56,62,63,65,67,91] H_2S-H_2O,[161] HO_x-H_2O,[28,51] SO_3-H_2O,[37,162,163] HNO_3-H_2O,[66,164] H_2CO-H_2O,[165-167] and $(CH_3)_2CO-H_2O$.[168]

In this paper, we use standard thermodynamics and statistical mechanics[169,170] to approximate the atmospheric abundance of select hydrated molecular complexes. Our analysis includes specific application of these computational methods to hydrated complexes which have been under experimental study in our laboratories, namely O_2-H_2O,[171] O_3-H_2O,[45] H_2O-H_2O,[172] and HNO_3-H_2O. We use the results of these calculations to evaluate and compare the physicochemical properties of these complexes and discuss the factors that are important in controlling their atmospheric abundance. Choosing these four complexes was not without intent. Each has a potentially important role in the atmosphere, and collectively, they display a wide range of the physicochemical properties inherent to molecular complexes. This allows for a concise, yet comprehensive, comparison. Since the abundance of molecular complexes scales with both the concentration of the individual cluster molecules and with the intermolecular binding energy, we purposely selected species where these particular factors varied significantly. Considering the atmospheric pressures of molecular oxygen are 3−6 orders of magnitude larger than those of nitric acid,[173] and the binding energies of their respective hydrates range from 0.32 kcal/mol[49] to 9.5 kcal/mol,[66] it is clear that O_2-H_2O and HNO_3-H_2O make prime candidates for our study. As we will illustrate, structural and energetic information for each complex is essential for our calculations and analyses. The number of hydrated molecular complexes having a complete database of this information is minimal, further restricting our options.

Using experimental and theoretical results from our lab and others, we are able to construct dimer altitude profiles by estimating thermodynamic equilibrium constants and dimer partial pressures at atmospherically relevant temperatures (200−300 K). We subsequently examine how monomer concentrations, temperature, and dimer binding energies influence the degree to which each complex contributes to atmospheric processes. In this context, the competition between the energetic and entropic effects of complexation is highlighted. Following this is a short analysis describing the sensitivity of our equilibrium constant calculations to the inconsistencies that exist in the available structural and energetic information.

Atmospheric Abundance of Hydrated Complexes

A. Procedure. The extent to which molecular complexes affect the thermal and chemical balance of the atmosphere is ultimately determined by their atmospheric abundance. Although many weakly bound molecular complexes have been isolated and identified in laboratory studies, the only one that has been identified experimentally in the atmosphere is the oxygen dimer.[48,174] Although other complexes, such as $(ClO)_2$,[47,175] are known to have binding energies much higher than that of the oxygen dimer, there still has been no direct experimental evidence of their existence in our atmosphere. Until this unfortunate absence of experimental data is remedied, researchers must rely on computational methods and laboratory modeling studies in order to determine atmospheric concentrations of molecular complexes. The traditional method through which these atmospheric abundances have been determined involves the application of standard thermodynamic and statistical mechanic procedures.[169,170] Although we use this method in our analysis, it is important to question whether this procedure is appropriate and germane given the system to which it is being applied. Atmospheric conditions pose a constraint that clearly challenges modern statistical procedures for determining abundances. In particular, the relatively high atmospheric temperatures (200−300 K) threaten the stability of weakly bound molecular complexes, making their characterization particularly difficult. At atmospheric temperatures, the value of k_BT is comparable to, or will even exceed, the weak binding energies inherent to molecular complexes. (For example, the value of k_BT at 250 K is 0.50 kcal/mol, whereas binding energies of weakly bound molecular complexes typically range from 0.2 to 10 kcal/mol.) If they do exist, as evidenced in the O_2-O_2 findings,[174] it is not known whether they are stable species having a substantial lifetime or whether they are better described as short-lived, collisional complexes. Furthermore, the actual structures of the individual complexes become ill-defined once free rotations and high-amplitude vibrations become important. Atmospheric temperatures are often difficult to access in the laboratory. Consequently, much of our experimental knowledge of molecular complexes comes from work done not at the atmospherically relevant 200−300 K, but rather in a cold, matrix environment[53-60,65,73,83,86,90,165,166,168,176] or in a supersonic molecular jet.[16,22,35,77,78,105,113,145,148,163,177] Whether or not the low-temperature structures determined from these experimental techniques provide an accurate model for atmospheric complexes has yet to be conclusively determined. Theoretical treatments of these same systems, while checked by the above-mentioned low-temperature structures, may also extrapolate to inadequate atmospheric structures. For example, theory predicts that the minimum energy structures for water clusters, $(H_2O)_n$, of $n = 3$ and higher are cyclic in nature.[56,96-98,116,117,134,137,138,152,155,156,158,160] These structures, however, may not be the most important at atmospheric conditions. Instead, the linear and branched-chain structures may be more favorable. Without an accurate molecular description, it is difficult to quantitatively evaluate the abundance of these species via traditional methods. Therefore, the probability exists that these standard procedures are simply ill-equipped to handle weakly bound complexes at atmospheric conditions. Nevertheless, assuming that thermal equilibrium holds, we use these established conventions as a useful guide for estimating atmospheric abundances and equilibrium constants. As we have shown in our work on O_3-H_2O[45] and $(H_2O)_2$,[172] these estimates are an indispensable precursor for establishing spectroscopic and chemical consequences of complexation in the atmosphere. In concession to the previous arguments, we add the caveat that our results are better seen as an approximation rather than an absolute.

The procedure used to determine pressure-dependent equilibrium constants and atmospheric abundances is detailed here. A more extensive description can be found in Donald A. McQuarrie's *Statistical Mechanics* and *Statistical Thermodynamics*.[169,170] Using equilibrium statistical thermodynamics,[169,170] available monomer and dimer vibrational and rotational constants,[45,49,66,89,90,94,105,128,178-181] dimer binding energies[49,66,89,127] and atmospheric inputs,[173] we calculated ΔH° and ΔS° for the four hydrated complexes. It can be shown that the enthalpy change for the formation of clusters from nonlinear monomeric constituents is given by

$$\Delta H^\circ_{\mathrm{T}} = -4\mathrm{RT} + \Delta E^\circ_{T,vib} + BE \tag{1}$$

where $\Delta E^\circ_{T,vib}$ is the change in the vibrational contribution to internal energy upon complexation and BE is the binding energy of the complex. For complexes comprised of one linear monomer, such as $O_2{-}H_2O$, this relationship remains unchanged except for the $-4RT$ term, which becomes $-7/2\ RT$. For the general dimerization reaction of the form

$$\mathrm{M(g)} + \mathrm{H_2O(g)} \leftrightarrows \mathrm{M} - \mathrm{H_2O(g)} \tag{2}$$

$\Delta E^\circ_{T,vib}$ can be calculated by determining $E^\circ_{T,vib}$ for the dimer and the individual monomers and then subtracting these quantities in the following manner:

$$\Delta E^\circ_{T,vib} = E^\circ_{T,vib}\,(\mathrm{M} - \mathrm{H_2O}) - E^\circ_{T,vib}\,(\mathrm{M}) - E^\circ_{T,vib}\,(\mathrm{H_2O}) \tag{3}$$

For a nonlinear polyatomic molecule, the vibrational contribution to the internal energy is given bywhere h is Planck's

$$E^\circ_{T,vib} = \frac{hcR}{k_{\mathrm{B}}} \sum_{j=1}^{3n-6} \left\{ \tilde{\nu}_j \left[\frac{1}{2} + \left(e^{\frac{hc\tilde{\nu}_j}{k_{\mathrm{B}}T}} - 1\right)^{-1} \right] \right\} \tag{4}$$

constant, c is the speed of light in a vacuum, R is the universal gas constant, k_{B} is Boltzmann's constant, T is temperature, n is the number of atoms in the molecule, and $\tilde{\nu}_j$ is the jth vibrational constant in units of wavenumbers. When calculating $E^\circ_{T,vib}$ for linear, polyatomic molecules, the only modification to eq 4 is in the limits of the summation. Instead of $3n{-}6$ vibrations, there will only be $3n{-}5$. Calculating the entropy change for complexation, ΔS°, is slightly more complicated and requires knowing the rotational constants for both monomers and the dimer. The thermodynamic quantity ΔS° is defined as

$$\Delta S^\circ = \Delta S^\circ_{T,trans} + \Delta S^\circ_{T,rot} + \Delta S^\circ_{T,vib} + \Delta S^\circ_{T,elec} \tag{5}$$

which explicitly illustrates the translational, rotational, vibrational, and electronic contributions to the change in entropy. In general terms, $\Delta S^\circ_{T,x}$ (x = trans, rot, vib, or elec) can be written as

$$\Delta S^\circ_{T,x} = S^\circ_{T,x}\,(\mathrm{M} - \mathrm{H_2O}) - S^\circ_{T,x}\,(\mathrm{M}) - S^\circ_{T,x}\,(\mathrm{H_2O}) \tag{6}$$

The individual $S^\circ_{T,x}$ terms, summarized in eq 7−11, are calculated using both structural and spectroscopic information.[170]

$$S^\circ_{T,trans} = \mathrm{R}\ln\left[\left(\frac{2\pi m k_{\mathrm{B}} T}{h^2}\right)^{3/2} \cdot \frac{e^{5/2} k_{\mathrm{B}} T}{P^{\mathrm{o}}}\right] \tag{7}$$

$$S^\circ_{T,rot}\ (\text{linear molecule}) = \mathrm{R}\ln\left(\frac{Te}{\sigma\Theta_r}\right),\ \text{where } \Theta_r = \frac{\tilde{B}}{k_{\mathrm{B}}} \tag{8}$$

$$S^\circ_{T,rot}\ (\text{nonlinear molecule}) = \mathrm{R}\ln\left[\left(\frac{T^3}{\Theta_A\Theta_B\Theta_C}\right)^{1/2} \cdot \frac{\pi^{1/2}e^{3/2}}{\sigma}\right],\ \text{where } \Theta_A = \frac{\tilde{A}}{k_{\mathrm{B}}},\ \text{etc.} \tag{9}$$

$$S^\circ_{T,vib} = R \sum_{j=1}^{3n-5 \text{ or } 3n-6} \left\{ \frac{hc\tilde{\nu}_j}{k_{\mathrm{B}}T} \cdot \left(e^{\frac{hc\tilde{\nu}_j}{k_{\mathrm{B}}T}} - 1\right)^{-1} - \ln\left(1 - e^{\frac{-hc\tilde{\nu}_j}{k_{\mathrm{B}}T}}\right) \right\} \tag{10}$$

$$S^\circ_{T,elec} = R\ln\omega_{\mathrm{el}} \tag{11}$$

The variables introduced in these equations are defined as follows: m is the mass of the molecule, P° is the standard reference pressure of 1 atm, σ is the molecular symmetry number, $\tilde{B}$ and $\tilde{A}$ are the characteristic rotational constants in wavenumbers, and ω_{e1} is the molecular ground-state degeneracy.

Since the standard Gibb's free energy change, ΔG°, for the dimerization reaction is given by

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{12}$$

we were able to determine ΔG° by inserting our calculated values of ΔS° and ΔH° at different temperatures. The temperature-dependent thermodynamic equilibrium constant, $K(T)$, is related to ΔG° in the following manner:

$$K(T) = e^{-\frac{\Delta G^\circ}{RT}} \tag{13}$$

In a dimerization reaction, the pressures of the monomers are related to that of the dimer via this thermodynamic equilibrium constant. The exact relationship between these quantities is shown in the following expression:

$$K(T) = \frac{\left(\frac{P_{(\mathrm{M-H_2O})}}{P^\circ}\right)}{\left(\frac{P_{\mathrm{M}}}{\mathrm{P}^\circ}\right)\left(\frac{P_{\mathrm{H_2O}}}{P^\circ}\right)} = \frac{P_{(\mathrm{M-H_2O})}}{(P_{\mathrm{M}})(P_{\mathrm{H_2O}})} \cdot P^\circ = K_p(T) \cdot P^\circ \tag{14}$$

where $K_p(T)$ is the equilibrium constant for complexation (in units of atm^{-1}), $P_{\mathrm{H_2O}}$ and P_{M} are the monomer pressures, and $P_{(\mathrm{M-H_2O})}$ is the partial pressure of the dimer. Using known atmospheric monomer partial pressures[173] and calculated values of $K(T)$ at different altitudes (and temperatures), we were able to determine the desired atmospheric abundance of the four hydrated complexes.

B. Results and Discussion. The spectroscopic data used in calculating ΔH°, ΔS°, ΔG°, and $K_p(T)$ for the four hydrates came primarily from previous theoretical work.[45,49,66,89,90,94,105,128,178−181] Tables 1−4, and the references therein, provide a detailed summary of the specific sources from which all of the spectroscopic input was derived. Using equilibrium statistical mechanics and thermodynamics[169,170] coupled with atmospheric inputs,[173] including temperature, pressure, and monomer concentrations, we estimated the atmospheric abundance of four hydrated complexes and generated their atmospheric profiles. Figure 1 gives a graphic summary of our results by showing the calculated dimer mixing ratios (or mole fractions) and partial pressures as a function of altitude. Although each of the hydrated complexes has a unique atmospheric profile, a cursory comparison reveals some notable similarities. For example, all of the profiles exhibit a general decrease in mixing ratio with increasing altitude. This is easily explained by the analogous behavior demonstrated in the atmospheric profile of the water monomer (see Figure 2a). Another trait that is clearly apparent in all of the dimer profiles is an inflection in the mixing ratios at the tropopause. The dominant factor influencing this trend is the temperature inversion that also occurs in this region of the atmosphere.[69,173,182−185] Beyond these general trends, the similarities

TABLE 1. Spectroscopic Data Used in the O_2-H_2O Abundance Calculation

	vibrational frequencies,[a] cm^{-1}	rotational constants, cm^{-1}
O_2	1435.8	1.44566[b]
H_2O	3990.1, 3869.8, 1660.7	27.8806,[c] 14.5218,[c] 9.27771[c]
O_2-H_2O	3981.25, 3872.4, 1664.4, 1482.2, 133.2, 95.7, 57.8, 43.5, 39.5	3.1741,[d] 0.08247,[d] 0.08038[d]

[a] Ref 49. [b] Ref 179. [c] Ref 94. [d] Ref 180.

TABLE 2. Spectroscopic Data Used in the O_3-H_2O Abundance Calculation[a]

	vibrational frequencies, cm^{-1}	rotational constants, cm^{-1}
O_3	1103,[b] 1042,[b] 709[b]	3.5534,[b] 0.44525,[b] 0.39479[b]
H_2O	3942,[c] 3832,[c] 1648[c]	27.877,[b] 14.512,[b] 9.285[b]
O_3-H_2O	3911,[d] 3806,[d] 1645,[d] 1107,[e] 1046,[e] 708,[e] 246,[f] 140,[f] 70,[g] 56,[f] 53,[f] 50[f]	0.399,[g] 0.139,[g] 0.109[g]

[a] All values were taken from ref 45 with specific references given in footnotes b−g. [b] Ref 178. [c] Ref 128. [d] Ref 90, scaled to harmonic value following ref 128. [e] Ref 90. [f] Scaled intermolecular vibrational frequencies of the water dimer (from ref 128), referenced to the stretching vibration of 70 cm^{-1} (from ref 89). [g] Ref 89.

TABLE 3. Spectroscopic Data Used in the H_2O-H_2O Abundance Calculation

	vibrational frequencies,[a] cm^{-1}	rotational constants, cm^{-1}
H_2O	3983, 3859, 1640	27.8806,[b] 14.5218,[b] 9.27771[b]
H_2O-H_2O O	3967, 3950, 3846, 3765, 1667, 1639, 637, 362, 182, 146, 130, 137	6.67128,[c] 0.200138,[c] 0.200138[c]

[a] Ref 128. [b] Ref 94. [c] Ref 105.

TABLE 4. Spectroscopic Data Used in the HNO_3-H_2O Abundance Calculation

	vibrational frequencies,[a] cm^{-1}	rotational constants, cm^{-1}
HNO_3	3629, 1872, 1358, 1325, 885, 743, 651, 576, 464	0.4340[b], 0.4036,[b] 0.2088[b]
H_2O	3895, 3749, 1681	27.8806,[c] 14.5218,[c] 9.27771[c]
HNO_3-H_2O	3865, 3731, 3290, 1845, 1689, 1511, 1343, 944, 871, 753, 678, 632, 425, 323, 231, 166, 95, 73	0.4064,[a] 0.08981,[a] 0.07386[a]

[a] Ref 66. [b] Ref 181. [c] Ref 178.

between the complexes dissolve in terms of both the magnitudes of the mixing ratios and the rates at which the mixing ratios decrease with elevation. Dimer abundance, and therefore the shape of the dimer altitude profile, is controlled by many factors. These include not only atmospheric variables, such as monomer mixing ratios and atmospheric temperatures, but also thermodynamic variables, such as changes in free energy ($\Delta G°$) via contributions from both $\Delta H°$ and $\Delta S°$. Our ability to determine and fully characterize the extent to which complexation occurs in our atmosphere is ultimately limited by the availability of both experimental and theoretical data on the structure and energetics of the individual hydrated complexes.

As previously mentioned, dimer abundance is influenced by parent monomer concentrations. Figure 2a shows the mixing ratio of O_2, O_3, H_2O, and HNO_3 as a function of altitude. Since the composition of our atmosphere is approximately 21% oxygen,[173] it is no surprise that it is the most abundant species of those depicted. O_2 mixing ratios remain fairly constant throughout the troposphere (which extends from the Earth's surface to the tropopause at ∼15 km) and upward through the next 30 km, known as the stratosphere. To maintain this uniform mixing ratio, O_2 concentrations must decrease with altitude to accompany the likewise decrease in atmospheric pressure.[186] This is explicitly shown in Figure 2b where the monomer altitude profiles of O_2, O_3, H_2O, and HNO_3 are given in absolute pressures.

Near the surface, water vapor is the next most abundant constituent. Unlike O_2, the atmospheric mixing ratios of H_2O are highly variable and dependent upon altitude. As shown in Figure 2, water vapor levels decrease rapidly in the lower atmosphere and to a lesser extent above the troposphere. In fact, H_2O mixing ratios actually exhibit a minimum at the tropopause. The dominant factor controlling this behavior is temperature. The troposphere is characterized by a decrease in temperature with increasing altitude.[69,173,182−184 185] This thermal declination causes water vapor to essentially "freeze" out of the air as it rises above the Earth's surface. Due to the minimal temperatures (∼212 K) accessible at the tropopause, the water vapor mixing ratio in that region is essentially reduced to the ice saturation value.[183] In the stratosphere, the opposite thermal trend is evident, but very little water vapor (only about 5 to 6 ppm) is transported above the "cold trap" at the tropopause.[183]

The atmospheric abundance of O_3 exhibits an entirely different altitude profile. Unlike H_2O, ozone mixing ratios are higher in the upper atmosphere than near the surface of the Earth, reaching a maximum of about 10 ppm at an altitude of 25−30 km.[183,185] It is within this region of relatively high ozone concentrations that O_3 absorbs nearly all wavelengths between 240 and 290 nm and causes the stratospheric temperature inversion.[183] The altitude profile of O_3 can be qualitatively explained by the chemical pathways and precursors leading to its production. Ozone formation in our atmosphere occurs via the following reaction:[187]

$$O(^3P) + O_2 + M \rightarrow O_3 + M \tag{15}$$

Since $O(^3P)$ is formed photochemically, it is the available solar radiation that dictates its atmospheric source. In the upper stratosphere, $O(^3P)$ formation is due to photolysis of O_2 ($\lambda < 242$ nm). The relatively high O_2 concentrations in this region, combined with atmospheric transport processes, explain the elevated ozone mixing ratios observed in the stratosphere. In the troposphere and lower stratosphere, where accessible solar radiation is limited to wavelengths above 290 nm, the primary source of $O(^3P)$ is from the photolysis of NO_2 ($\lambda < 420$ nm).[182] Atmospheric NO_2 is much less abundant than O_2, leading to much lower concentrations of ozone in the troposphere.

The nitric acid altitude profile diverges greatly from that of the others. Nitric acid is an oxidation product of NO_2 in the atmosphere and is formed by the three-body process shown in eq 16:

$$NO_2 + OH + M \rightarrow HNO_3 + M \tag{16}$$

N_2O_5 hydrolysis and the abstraction of hydrogen from organics by NO_3 also provide pathways to HNO_3 production. Because nitric acid undergoes absorption into water droplets and rapid deposition at the Earth's surface, very little tropospheric HNO_3 is observed.[173,182]

These monomer profiles provide invaluable insight into the trends seen in the atmospheric abundance of the corresponding hydrated dimers. Since the oxygen mixing ratio remains fairly uniform through both the troposphere and the stratosphere, the

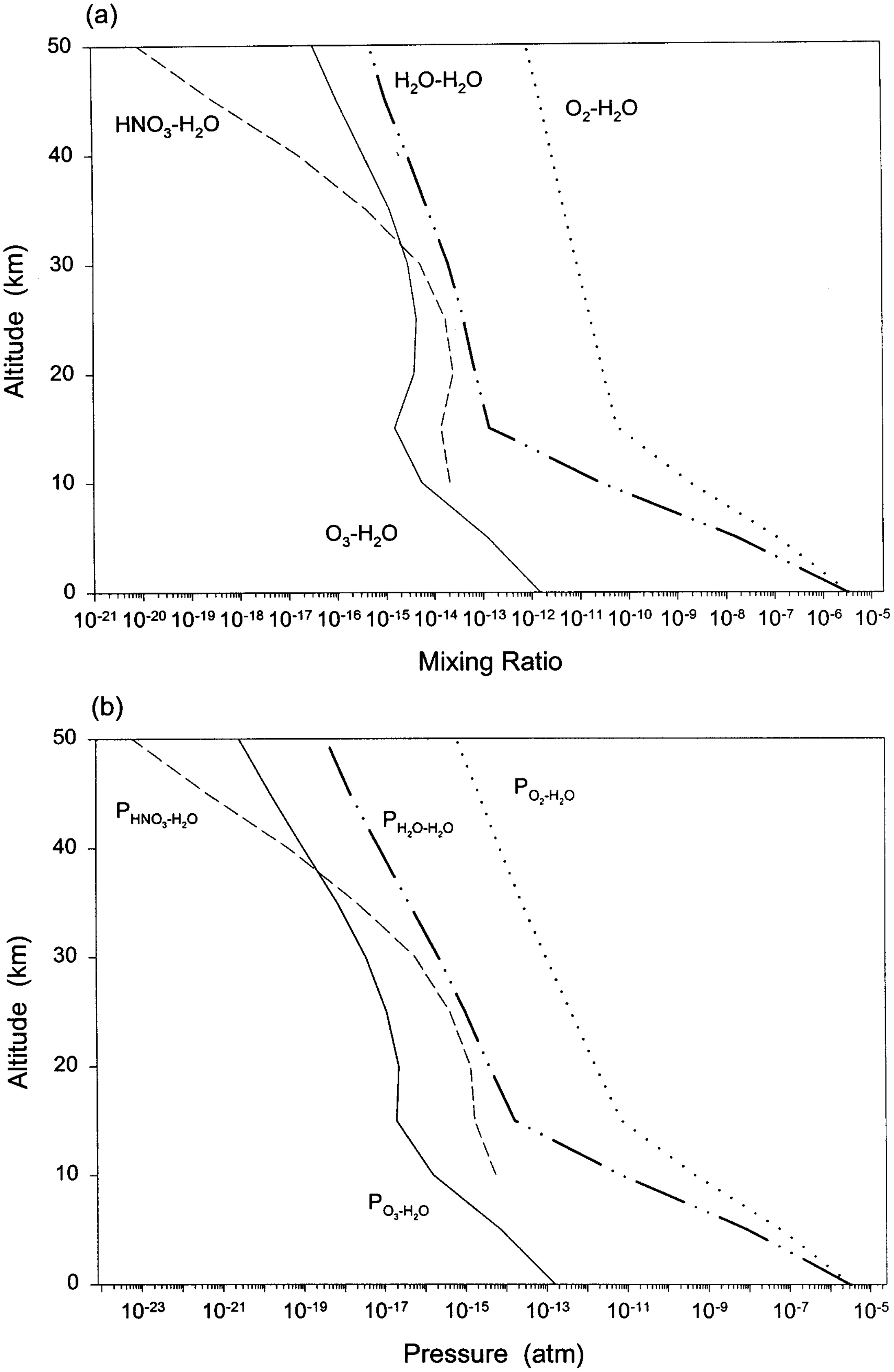

Figure 1. Estimated (a) mixing ratios and (b) atmospheric pressures of O_2−H_2O, O_3−H_2O, H_2O−H_2O, and HNO_3−H_2O as a function of altitude.

O_2−H_2O profile is clearly controlled by the amount of accessible water vapor. This is readily apparent at the surface where the O_2−H_2O mixing ratio is almost equal to that of the water dimer. The vertical profiles of both O_2−H_2O and H_2O−H_2O exhibit rapidly decreasing mixing ratios throughout the troposphere. This decrease, however, is much more severe for the water dimer since both monomeric species, as opposed to only one in O_2−H_2O, display an accelerated attenuation in abundance with altitude. As illustrated in Figure 2a, the mixing ratios of H_2O and O_2 remain relatively constant above the tropopause. Because

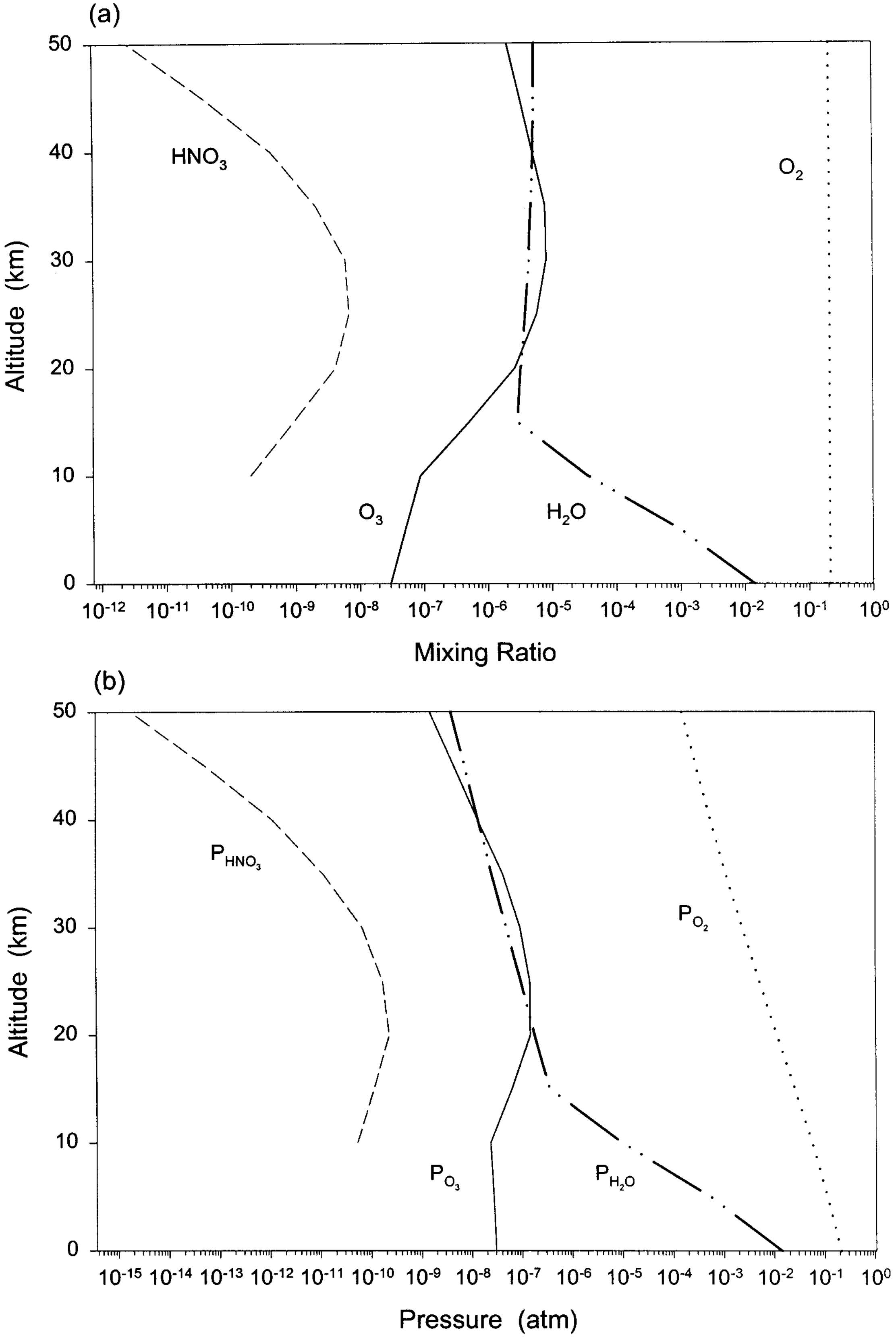

Figure 2. O_2, O_3, H_2O, and HNO_3 (a) mixing ratios and (b) partial pressures as a function of altitude.

of this, the shapes of the O_2-H_2O and H_2O-H_2O altitude profiles are very similar in this region. Atmospheric pressures of O_2 are much higher than those of H_2O (see Figure 2b), resulting in water dimer mixing ratios which are orders of magnitude less than those calculated for the O_2-H_2O complex. Since both ozone and nitric acid are less abundant than atmospheric O_2 or H_2O, their hydrated complexes would be expected to have even smaller atmospheric mixing ratios. Our results are consistent with this prediction.

The O_3-H_2O profile is somewhat more complex. Throughout most of the troposphere, H_2O concentrations seem to dictate not only the amount of O_3-H_2O present, but also the shape of its atmospheric profile. Up to 10 km, the O_3-H_2O mixing ratios, like those of water vapor, decrease with elevation. It is interesting to note the effect that the rising O_3 mixing ratio has on the abundance of its hydrated complex. In this region, the O_3 mixing ratios increase enough to slightly offset the extent to which the diminishing H_2O concentrations affect the weakly bound complex. In contrast, the uniform O_2 mixing ratios do little to alter water's influence on O_2-H_2O abundance. Therefore, the O_2-H_2O mixing ratios appear to decrease more rapidly with altitude than those of O_3-H_2O. In the lower stratosphere, O_3-H_2O mixing ratios begin to increase with altitude until about 25 km. Once again, this is due to the increasing ozone mixing ratio. The altitude profiles for both O_3 and its hydrated complex display the same characteristics above ∼20 km.

Like ozone, nitric acid mixing ratios increase between 10 and 20 km. This, coupled with the opposing behavior of water vapor, causes the HNO_3-H_2O mixing ratio to remain relatively constant. Above these altitudes, the availability of HNO_3 becomes the significant factor controlling HNO_3-H_2O formation. Thus, in this region the HNO_3-H_2O profile takes on the general appearance of the nitric acid profile.

One striking feature evidenced in the calculated, dimer altitude profiles is the relatively high HNO_3-H_2O concentrations below 40 km. Of the monomers discussed, nitric acid is by far the least abundant. Despite this observation, our calculations predict a higher abundance of HNO_3-H_2O than O_3-H_2O below 40 km. Understanding this seemingly contradictory behavior requires a deeper investigation into additional factors which affect complexation, namely dimer binding energies and thermodynamic factors, such as enthalpy and entropy, which dictate the magnitude of the equilibrium constant.

At 9.5 kcal/mol,[66] the binding energy of HNO_3-H_2O is the largest of the complexes under discussion. H_2O-H_2O is predicted to have a binding energy of 4.99 kcal/mol,[128] which is a little more than half that of HNO_3-H_2O, while the binding energy of O_3-H_2O (2.4 kcal/mol[89]) is roughly one-fourth that of HNO_3-H_2O. O_2-H_2O is characterized by very weak intermolecular forces and has an estimated binding energy of only 0.32 kcal/mol.[49] As shown in eq 1, binding energy has a large effect on the temperature-dependent equilibrium constant of dimerization via the enthalpy term, $\Delta H°$. The other two factors which affect $\Delta H°$ are a translation−rotation term ($-4RT$ or $-7/2\ RT$) and a vibrational term ($\Delta E^{\circ}_{T,vib}$). Except for O_2-H_2O, all of the hydrated complexes have the same translational−rotational contribution ($-4RT$) to $\Delta H°$ at a given temperature. The O_2-H_2O complex has a slightly smaller contribution ($-7/2\ RT$) due to the linear oxygen monomer. At a given temperature, the $\Delta E^{\circ}_{T,vib}$ term is different for each complex due to the unique vibrational frequencies of both the nonwater component of each hydrate and the individual dimers themselves. At most, these differences are several kcal/mol, which is not especially significant when one considers the effect the binding energy has on $\Delta H°$.

Figure 3a graphically illustrates the calculated enthalpies of O_2-H_2O, O_3-H_2O, H_2O-H_2O, and HNO_3-H_2O as a function of altitude. As predicted via binding energies, the calculated $\Delta H°$ values of HNO_3-H_2O are much greater (more exothermic) than those of the other three hydrates. Since the HNO_3-H_2O complex is more energetically favored, the calculated values of $K_p(T)$ for this dimer are much greater than those determined for the remaining three hydrates (see Figure 4). These “large” $K_p(T)$ values explain the relatively high HNO_3-H_2O concentrations seen in Figure 1b.

Enthalpy is not the only thermodynamic factor influencing the magnitude of the equilibrium constant. Entropy, or more importantly the product of temperature and $\Delta S°$, also plays an important role. Complexation is not an entropically favored process, and at low temperatures, such as those produced in supersonic jets and matrix experiments, the $T\Delta S°$ term has very little effect on the magnitude of $\Delta G°$, and therefore, on the equilibrium constant. This is a different story at atmospheric temperatures. The $T\Delta S°$ term becomes exceedingly more important at higher temperatures. At 200−300 K, the contribution of $T\Delta S°$ to free energy can even dominate the enthalpic contribution.

Figure 3b depicts the calculated values of $T\Delta S°$ as a function of altitude for the four hydrated complexes. As expected, the altitude profile of this thermodynamic quantity closely resembles that of the atmospheric temperature profile. However, it is the magnitude of the $T\Delta S°$ values which is the most notable feature of this graph. Comparison between parts a and b of Figure 3 quickly reveals the comparable magnitude of $\Delta H°$ and $T\Delta S°$ values at atmospheric temperatures. For most of the depicted atmospheric temperatures (and altitudes), the $T\Delta S°$ term clearly dominates the enthalpic term at that same temperature and, consequently, it becomes the prevailing factor affecting both the magnitude and the sign of the free energy change. Figure 3c shows the calculated values of $\Delta G°$ as a function of altitude. The shape of the $\Delta G°$ altitude profile is essentially the inverse of the $T\Delta S°$ profile with a small magnitude variance corresponding to the very small difference between $\Delta H°$ and $T\Delta S°$.

While abundance and equilibrium constant calculations can give invaluable information about molecular complexes, it is extremely important to acknowledge the inherently sensitive nature of these computational methods. An impressive body of theoretical and experimental work has been conducted on many hydrated complexes in order to elucidate their structures and energetics. In the process, an extensive database has been generated. While this is a true testament to the significance of this field, the inconsistencies that exist in this database provide some confusion when one attempts to address the possible atmospheric abundance of such species. Specifically, small discrepancies in vibrational and rotational constants, and certainly dimer binding energies, become a source of large discrepancies in equilibrium constant estimates. This is clearly illustrated when the water dimer is used as an example. Using data from several theoretical groups, we estimated equilibrium constants for the water dimer at atmospherically relevant temperatures. From our analysis it was estimated that a 10% increase in the dimer binding energy has the effect of increasing the calculated equilibrium constant by a factor of 5.[67,140] The inclusion of anharmonic effects in the calculated potentials was estimated to increase the value of $K_p(T)$ by roughly half this amount.[62,67,140,160] Not only do these estimates illustrate the large uncertainties that still remain in the theoretical database for hydrated complexes, they also show the need for experimental validation of the theoretical potentials.

Conclusion

In this paper we estimated the atmospheric abundance of hydrates and discussed factors, such as monomer partial pressures, cluster binding energy, altitude, temperature, and pressure, which influence the equilibrium constant. Specifically, we focused on the O_2-H_2O, O_3-H_2O, H_2O-H_2O, and HNO_3-H_2O complexes in order to illustrate the formidable challenge of estimating dimer abundances at the relatively high atmospheric temperatures where entropic factors become important. The available experimental database for relevant conditions is

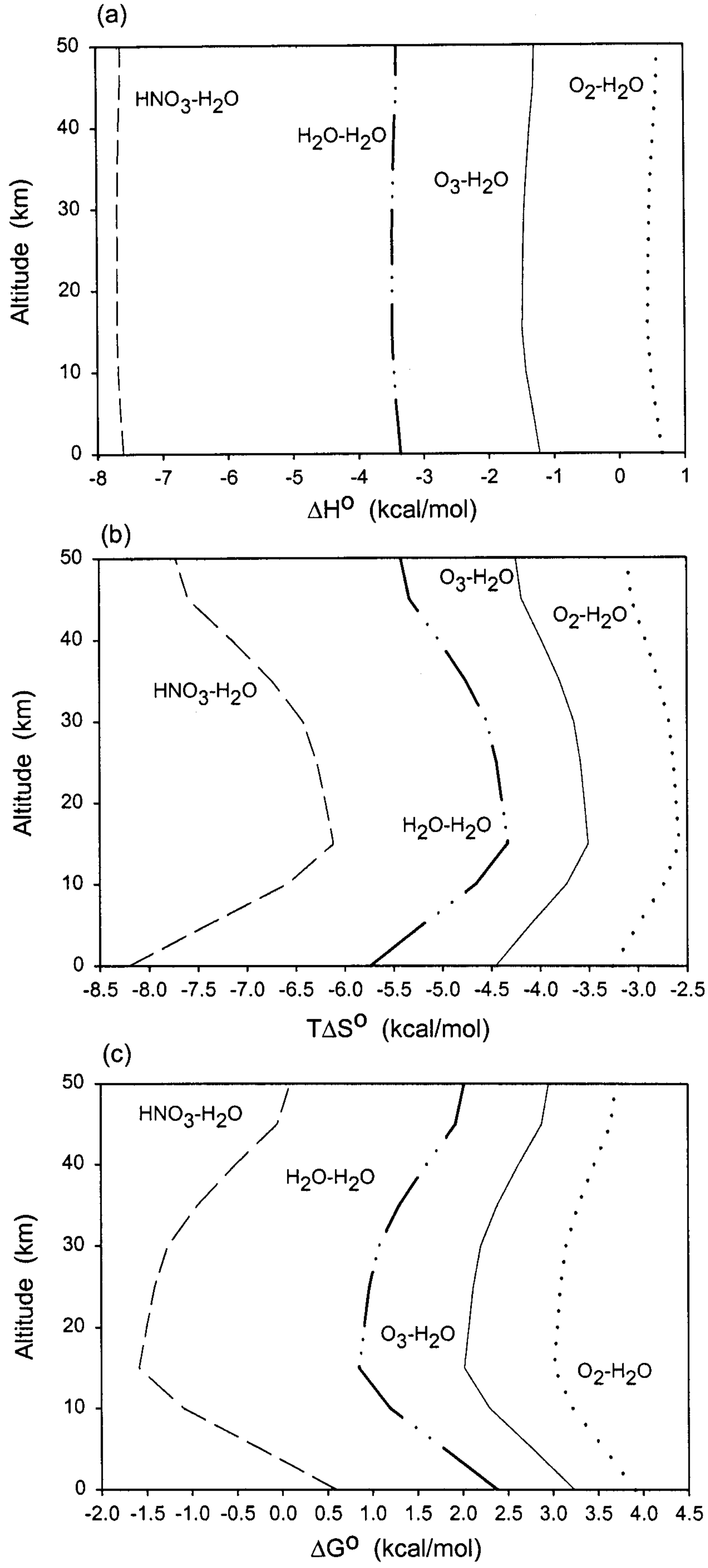

Figure 3. Calculated values of (a) ΔH°, (b) TΔS° and (c) ΔG° for O_2-H_2O, O_3-H_2O, H_2O-H_2O, and HNO_3-H_2O as a function of altitude.

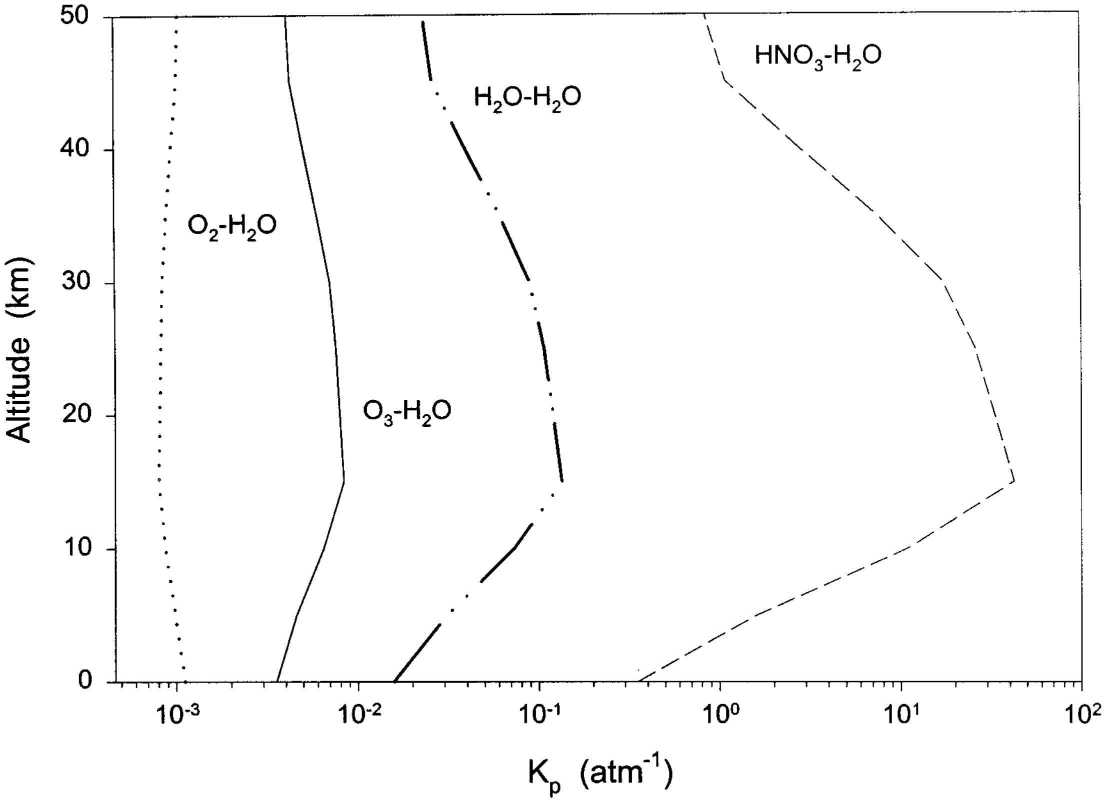

Figure 4. Estimated equilibrium constants (K_p) for O_2-H_2O, O_3-H_2O, H_2O-H_2O, and HNO_3-H_2O as a function of altitude.

extremely scarce, providing little guidance for the extrapolation of low-temperature results where ab initio structures and binding energies are well calculated. Laboratory and field measurements at atmospheric conditions would be beneficial in extending the fundamental database used to evaluate the properties of bimolecular complexes in the atmosphere.

In addition to providing estimates of atmospheric abundance, we discussed the ambiguities involved in these estimates. Allowing for large uncertainties, the range of plausible values for the partial pressures and mixing ratios of these complexes is very small. Nevertheless, these bimolecular complexes could play a role in the chemical and radiative balance of the atmosphere if their spectroscopic and photochemical properties are sufficiently different from those of their monomeric constituents. Our group[45,172] and others[43,49,174] have shown this.

As previously mentioned, weak intermolecular interactions lead to shifts in the absorption spectra, increases in intensities of forbidden transitions, and increases in spectroscopic bandwidths.[16,25,26,28−42] These effects combine to "fill in" atmospheric windows and may, therefore, influence the Earth's temperature and climate. For example, we estimate that water dimers absorb several W/m^2 of solar radiation.[172] This amount is potentially measurable, even if measurements to date have failed to identify water dimers in the atmosphere.[188] Because of the effect water partial pressures $p^2_{H_2O}$ have on the equilibrium constant, it is anticipated that in a global warming scenario water dimer concentrations will increase as $p^2_{H_2O}$ rather than in a linear manner as anticipated for water vapor.[172] Due to the abundance and spectroscopic properties of $(H_2O)_n$, O_2-H_2O, and N_2-H_2O,[43,44,49] these hydrated complexes are the ones most likely to affect the Earth's climate via absorption of solar and terrestrial radiation.

Weakly bound molecular complexes may have a role to play in the atmosphere even when their absorption cross sections and abundances are too small to significantly affect the Earth's radiative balance. In particular, photochemical radical production in the atmosphere may be influenced by light-initiated chemical reactions of complexes. In previous work, we discussed such chemistry using O_3-H_2O as an example.[45] Despite the very low estimated O_3-H_2O abundance, the contribution of O_3-H_2O photolysis to OH production could be significant. This is especially true at dusk and dawn when only low-energy solar radiation is available to overlap the red-shifted dimer cross section.

Further development of experimental and theoretical techniques able to investigate the fundamental physical chemistry of molecular complexes in the atmosphere is clearly needed. Atmospheric problems bring into focus the special environment for which little information is available. As described here, even the very low and inaccurate abundance estimates for water complexes are sufficient to suggest their involvement in the atmosphere.

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