Infrared Spectra and Intensities of the H_2O and N_2 Complexes in the Range of the ν_1- and ν_3-Bands of Water

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The IR spectra of complexes of water with nitrogen molecules in the range of the symmetric (ν_1) and antisymmetric (ν_3) bands of H_2O have been studied in helium droplets. The infrared intensities of the ν_3 and ν_1 modes of H_2O were found to be larger by factors of 1.3 and 2, respectively, in the N_2-H_2O complexes. These factors are smaller than those obtained in recent theoretical calculations. The conformation of the N_2-H_2O complex was estimated. Spectra and IR intensities of the $(N_2)_2-H_2O$ and $N_2-(H_2O)_2$ complexes were also obtained and their structures are discussed.

Introduction

IR and microwave spectroscopic studies of molecular complexes have been used to provide detailed information on their structures and intermolecular interactions.[1−4] Binary complexes with water molecules have often been treated as prototype systems because the strength of the intermolecular interaction spans a wide range from weak van der Waals to strong hydrogen bonding, depending on the binding partner. For example, the binding energies (D_e) were calculated to be 0.32[5] and 5 kcal/mol[5,6] for the $Ar-H_2O$ and $(H_2O)_2$ complexes, respectively. The N_2-H_2O complex has been calculated to have an intermediate binding energy of about $D_e = 1.3$ kcal/mol[5,7] or $D_0 = 0.55$ kcal/mol.[8] A microwave spectroscopic study[9] has shown that the internal rotation of H_2O in the complex is largely quenched. The $1_{01} \leftarrow 0_{00}$ line of the complex was observed[9] to have four components, which span a frequency range of about 15 MHz. The splitting was ascribed to tunneling motions of water and nitrogen molecules in the complex. According to ref 9, one of the hydrogen atoms of water points toward the N_2 molecule, making a nearly linear N−H−O bond. Similar results were obtained for the equilibrium structure of the complex in a number of ab initio calculations.[5,7,10,11] N_2-H_2O complexes have also been studied by IR spectroscopy in rare-gas matrices.[11−14]

Recently, concentrations of the complexes of water molecules with other species such as CO_2, N_2, O_2, Ar, and water itself in the Earth's atmosphere have been calculated.[5,15] Calculations show that the N_2-H_2O complex is the most abundant in the Earth's atmosphere[5,16] because of its relatively strong binding and the large abundance of nitrogen in the air. Since water is one of the strongest absorbers of solar radiation in the IR spectral region, knowledge of the spectra of the complexes is important to estimate the effect of their absorption on the radiation balance of the Earth. The absorption strength of the vibrational bands, which is usually referred to as infrared intensity (IRI), is instrumental in such an estimate.

There are only few measurements of IRI of molecular complexes, largely because of the difficulties in determining the absolute number densities. Exceptions are the strongly bound species, which have sizable equilibrium fractions of complexes in the gas phase, such as dimers of carboxylic acids.[17] IRI can also be obtained from the laser power saturation dependence of the intensities of spectral lines, which, however, requires the knowledge of the homogeneous line widths. Therefore, this method has so far only been applied to a few simple dimers obtained in a free jet, such as $(HF)_2$,[18] N_2-HF, and CO−HF.[19] At present, theoretical calculations are the main sources of our information on IRI in molecular complexes. Recent calculations[5,7,10,11,16,20] gave a factor of about 2.5 larger IRI for the OH-stretching vibrations in the N_2-H_2O complexes as compared to that in single water molecules. This enhancement was explained by the formation of a weak hydrogen bond.[10] The prediction of the large enhancement of the IRI in N_2-H_2O complexes is, however, surprising in view of the rather weak bonding in the complexes.[5,7,8]

In this work, we have obtained spectra of the N_2-H_2O, $(N_2)_2-H_2O$, and $N_2-(H_2O)_2$ complexes in the region of the symmetric stretch (ν_1) and antisymmetric stretch (ν_3) fundamental bands of water molecules in He droplets. We used the He droplet isolation technique to obtain IR intensities for the complexes studied. IR intensities of the $(N_2)_2-H_2O$ and $N_2-(H_2O)_2$ complexes were also obtained and their structures are discussed.

Experimental Section

Complexes of water and nitrogen molecules were prepared by sequential pickup of single molecules by helium droplets and studied via IR laser depletion spectroscopy. The He droplet experiment has been described in detail previously.[21−23] Helium droplets were obtained upon expansion of the ^{4}He gas through a 5-μm nozzle at a source pressure of $P_0 = 20$ bar at a temperature of $T_0 = 16$ K. The resulting droplet beam passed through a 5-cm long, differentially pumped, pickup chamber,

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which was filled with a gas mixture of nitrogen and water molecules. The pressure in the pickup chamber was measured by an ionization pressure gauge. The IR pulsed laser beam obtained from the optical parametric oscillator−amplifier (Laser Vision, repetition rate, 20 Hz; laser pulsed energy, 5 mJ; spectral resolution, 1.0 cm^{-1}) was aligned antiparallel to the He droplet beam. The absorption of a laser photon is followed by rapid energy transfer to the host droplets and by the subsequent evaporation of He atoms. The average number of evaporated He atoms per droplet is proportional to the energy of the absorbed photon, the IRI of the embedded species, and the abundance of these species in the droplet beam. The total flux of the He droplet beam was detected by a quadrupole mass filter equipped with an electron beam ionizer, which was installed about 80 cm downstream from the source of the droplet beam. The mass filter was adjusted to transmit all masses larger than $M = 6$ amu. The absorption leads to a transient decrease of the mass spectrometer signal, which was recorded by a fast digitizer. To avoid laser power saturation effects, a divergent laser beam was used in the spectral region of the strong ν_3 band of water. In the spectral region of the weaker ν_1 band, the divergent laser beam was collimated by a 1-m f.l. lens, which was placed in front of the entrance window of the vacuum apparatus. In both cases, linear dependence of the depletion signal vs laser pulse energy was verified. The laser cabinet was purged continuously by dry nitrogen, and the optical path between the laser cabinet and the entrance window of the apparatus was evacuated. The depletion spectra were normalized on the laser pulse energy, which varied in the studied range by about 20%. The spectra were calibrated relative to the spectrum of water vapor in an optoacoustic cell.

Results

Figure 1a shows a depletion spectrum in the range of the ν_3 band obtained when water vapor was introduced into the pickup chamber at a pressure of 3×10^{-6} mbar, which approximately corresponds to an average number of water molecules captured per droplet of $z(H_2O) = 0.25$ (see eq 1). The spectrum contains rovibrational lines of the ν_3 fundamental band of single H_2O molecules[24] and bands of the $(H_2O)_2$ dimers, which were assigned to the vibration of the dangling hydrogen atoms of the H-donor molecules and to the ν_3 fundamental band of the acceptor molecules. The spectrum (b) was measured when nitrogen was introduced into the pickup chamber at a pressure of 9×10^{-6} mbar, which corresponds to an average number of nitrogen molecules captured per droplet of $z(N_2) = 0.5$. Trace (c) was obtained from trace (b) by subtraction of the spectra of water molecules and clusters, that is, scaled trace (a). The bands at 3749.8 and 3755.5 cm^{-1} are ascribed to the N_2-H_2O complexes; the band at 3746.2 cm^{-1} to the $(N_2)_2-H_2O$ complexes; and the band at 3728.3 cm^{-1} to the $N_2-(H_2O)_2$ complexes. These assignments are based on the pressure dependences of the intensity of the bands as described below.

The relative abundance of single molecules and complexes in a He droplet is given by the Poisson distribution.[23] For heterogeneous complexes, the abundance $N_{m,n}$ of the complexes $(N_2)_m-(H_2O)_n$ is given by

$$N_{m,n} = \frac{(z(N_2))^m}{m!}\frac{(z(H_2O))^n}{n!}\exp(-z(N_2) - z(H_2O)) \qquad (1)$$

where $z(N_2) = \chi_1 \times P(N_2)$ and $z(H_2O) = \chi_2 \times P(H_2O)$ are the average numbers of the captured N_2 and H_2O molecules per droplet and $P(N_2)$ and $P(H_2O)$ are the partial pickup pressures of nitrogen and water molecules, respectively. The coefficient χ_M is approximately equal to[25]

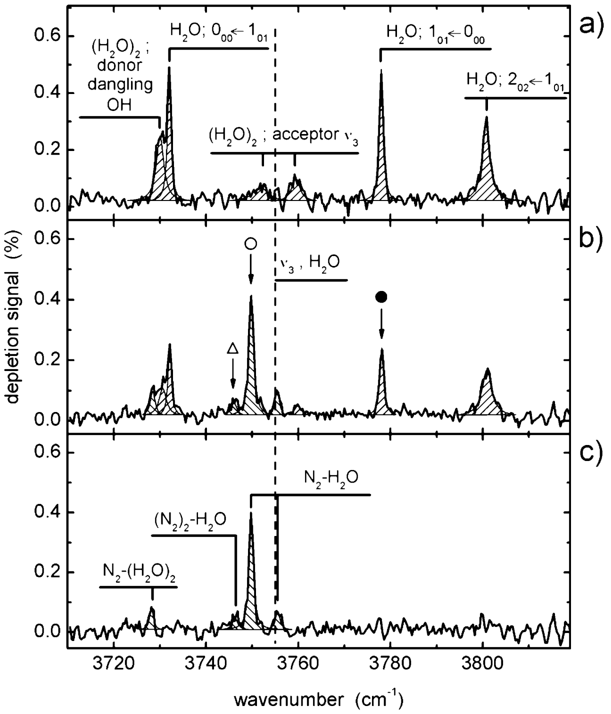

Figure 1. Depletion spectra of the N_2-H_2O complexes in the range of the ν_3 band of H_2O in He droplets. Pickup pressures: panel (a) $P_{H_2O} = 3 \times 10^{-6}$ mbar, $P_{N_2} = 0$; panel (b) $P_{H_2O} = 3 \times 10^{-6}$ mbar, $P_{N_2} = 9 \times 10^{-6}$ mbar. Panel (c) shows spectrum (b) with the contribution of spectrum (a) subtracted. This has been scaled to eliminate H_2O lines from the spectrum. Smooth curves are Gaussian fits as described in the text. The origin of the ν_3 band of H_2O in He droplets is marked by the vertical dashed line. Pickup pressure dependences of the intensity of the peaks marked in panel (b) by arrows are shown in Figure 2.

$$\chi_M = \frac{\sigma_{cap} l}{k_B T} \frac{\sqrt{\langle v_M{}^2\rangle + \langle v_B{}^2\rangle}}{\sqrt{\langle v_B{}^2\rangle}} \qquad (2)$$

where σ_{cap} is the capture cross section of the droplet, l is the length of the pick up region, k_B is the Boltzmann constant, T is the temperature of the pickup chamber, and $\langle v_M{}^2\rangle$ and $\langle v_B{}^2\rangle$ are the mean square velocities of the molecules in the chamber and of the droplet beam, respectively. The velocity of the He droplet beam at $T_0 = 16$ K is known to be about 380 m/s.[25] Figure 2 shows the nitrogen pickup partial pressure dependences of the depletion signal for three peaks in spectrum (b) of Figure 1, that is, $\nu = 3778.0$ cm^{-1}, $\nu = 3749.8$ cm^{-1}, and $\nu = 3746.2$ cm^{-1}. The solid curves in Figure 2 are fits to the experimental dependences using eq 1 with $m = 0$, 1, and 2, respectively. The good quality of the fits supports the assignments of the peaks at $\nu = 3749.8$ and 3746.2 cm^{-1} to N_2-H_2O and $(N_2)_2-H_2O$ clusters, respectively. This assignment is consistent with the results of some very recent work,[26] where the absorption peak of N_2-H_2O in helium droplets has been observed at 3749.40 cm^{-1}. The band at 3755.5 cm^{-1} was assigned to the N_2-H_2O complexes, based on its constant intensity relative to the band at 3749.8 cm^{-1} in the spectra measured at different N_2 pressures. The peak at 3778.0 cm^{-1} corresponds to the $1_{01} \leftarrow 0_{00}$ line of the ν_3 band of single water molecules in He droplets.[24] The values of the χ_1 parameters in the fits for the peaks of H_2O monomers, N_2-H_2O and $(N_2)_2-H_2O$, were determined to be 0.55×10^5, 0.50×10^5, and 0.46×10^5

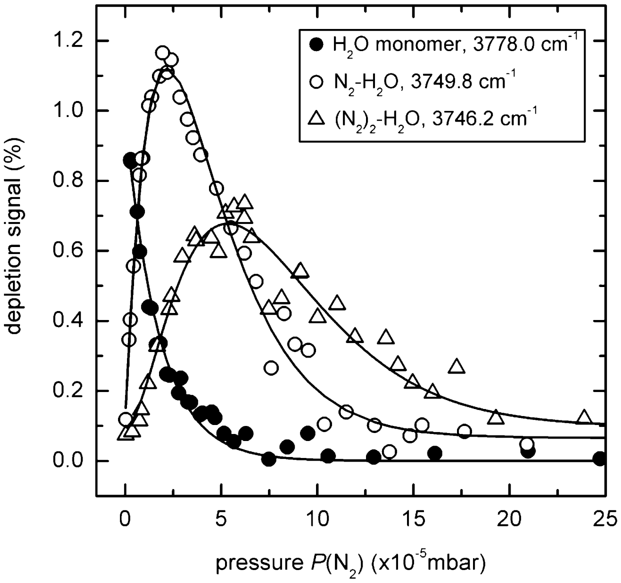

Figure 2. Depletion signal vs N_2 pickup pressure for three bands in Figure 1b: ●, ν = 3778.0 cm^{-1}; ○, ν = 3749.8 cm^{-1}; and △, ν = 3746.2 cm^{-1}. The bands were assigned to H_2O monomers, N_2−H_2O and $(N_2)_2$−H_2O, respectively, according to their pickup pressure dependence. Solid curves are Poisson fits as described in the text. The H_2O pickup pressure was kept constant at 0.3×10^{-5} mbar throughout the measurements. The results for the complexes have slight offsets for clarity.

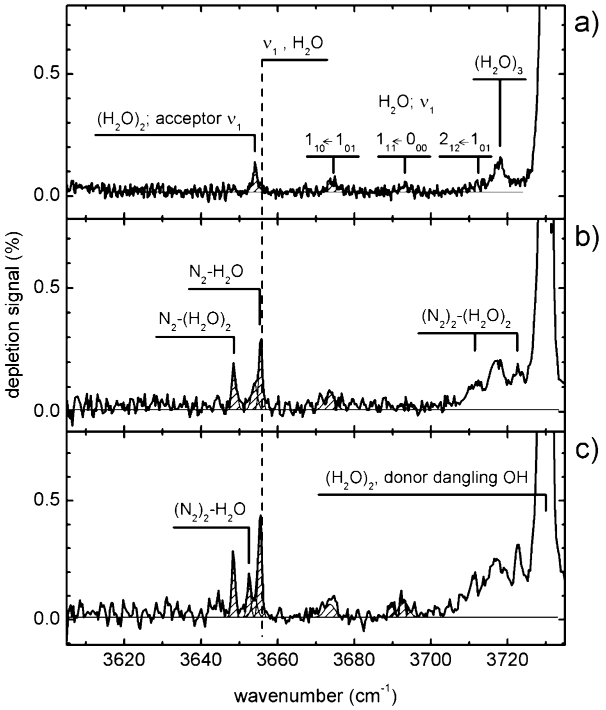

Figure 3. Depletion spectra of the N_2−H_2O complexes in the range of the ν_1 band of H_2O in He droplets. Pickup pressures: panel (a) $P(H_2O) = 6 \times 10^{-6}$ mbar, $P(N_2) = 0$; panel (b) $P(H_2O) = 6 \times 10^{-6}$ mbar, $P(N_2) = 9 \times 10^{-6}$ mbar; panel (c) $P(H_2O) = 6 \times 10^{-6}$ mbar, $P(N_2) = 1.8 \times 10^{-5}$ mbar. Smooth curves are Gaussian fits as described in the text. The spectra were measured with a collimated laser beam, which gave about a factor of 5 larger effective laser energy flux, as compared with measurements in Figure 1. The origin of the ν_1 band of H_2O in He droplets is marked by the vertical dashed line.

mbar^{-1}, respectively. Using the liquid droplet model and $\chi_1 = 0.55 \times 10^5$ mbar^{-1}, the average size of the He droplets was estimated to be 3000 atoms, which is in good agreement with the previous measurements under similar experimental conditions.[23] Somewhat smaller values of χ for the complexes, as compared with single water molecules, most probably indicate partial overlap of the bands of the complexes having different numbers of nitrogen molecules. Although H_2O and N_2 were backfilled in the same pickup chamber, the concentration of the N_2−H_2O complexes preformed in the gas is negligible because of the low pressure of the gas in the chamber. The decrease of the pickup cross section of the droplets upon the capture of the H_2O and N_2 molecules could be neglected, based on the fact that an energy of about 300 K causes evaporation of about 40 He atoms from the droplet, that is, much less than the droplet size of about 3000 atoms.

Figure 3a shows the depletion spectrum in the range of the ν_1 band of water molecules, when water vapor was introduced into the pickup chamber at a pressure of 6×10^{-6} mbar, that is, $z(H_2O) = 0.5$. The strong peaks in the high-frequency part of the spectrum are the same as those in the low-frequency part of Figure 1. The weak band at 3654.4 cm^{-1} is assigned to the ν_1 band of the acceptor molecules in water dimers. Additional weak peaks in Figure 3a are assigned to the rovibrational transitions of the ν_1 band of single water molecules in He droplets.[24] Rovibrational lines of the ν_1 band of water molecules in He have widths of about 3 cm^{-1}, which were ascribed to lifetime broadening, due to rotational relaxation within the ν_1 state.[24] Spectra (b) and (c) were measured with nitrogen molecules introduced into the pickup chamber at pressures of 9×10^{-6} and 1.8×10^{-5} mbar, respectively, which correspond to average numbers of captured N_2 molecules, $z(N_2) = 0.5$ and 1.0, respectively. The band at 3655.6 cm^{-1} is ascribed to N_2−H_2O complexes, the band at 3652.5 cm^{-1} to the $(N_2)_2$−H_2O complexes, and the band at 3648.6 cm^{-1} to the N_2−$(H_2O)_2$ complexes, based on the pressure dependence of their intensity.

The integrated depletion signal of the bands of the $(N_2)_m$−$(H_2O)_n$ complexes, $I_{m,n}$, is proportional to the energy of the absorbed photons ($h\nu_{m,n}$), the IR intensity ($A_{m,n}$), and the probability of finding the complex in the droplet ($N_{m,n}$)

$$I_{m,n} \propto h\nu_{m,n}A_{m,n}N_{m,n} \qquad (3)$$

From eqs 1 and 2, the ratio of $A_{1,1}$ to $A_{0,1}$ is

$$\frac{A_{1,1}}{A_{0,1}} = \frac{\nu_{0,1}}{\nu_{1,1}}\frac{1}{z(N_2)}\frac{I_{1,1}}{I_{0,1}} \qquad (4)$$

where $I_{1,1}$ and $I_{0,1}$ are the integrated band intensities of the N_2−H_2O and H_2O transitions in He droplets, respectively. Because of the very similar frequencies of $\nu_{0,1}$ and $\nu_{1,1}$, the frequency ratio in eq 4 was taken to be unity. $A_{0,1}$ is known to be 44.6 and 2.25 km/mol for the ν_3 and ν_1 bands, respectively.[27,28] In the case of the ν_3 band, $I_{0,1}$ was calculated as a sum of the integrated intensities of the $0_{00} \leftarrow 1_{01}$, $1_{01} \leftarrow 0_{00}$, and $2_{02} \leftarrow 1_{01}$ lines. In the case of the ν_1 band, the sum of the intensities of the $1_{10} \leftarrow 1_{01}$ and $1_{11} \leftarrow 0_{00}$ lines was multiplied by a factor of 1.3 to take into account the intensity of the $2_{12} \leftarrow 1_{01}$ line, which was taken from the HITRAN database described in ref 29. To obtain values of $I_{m,n}$, the spectral peaks were fitted by Gaussians, as shown in Figures 1 and 3 by smooth curves. The values of $I_{m,n}$ were then taken as the areas under the corresponding Gaussians, as shown by the shaded areas in Figures 1 and 3. The resulting values of the IRIs are listed in Table 1 as ratios to corresponding bands of H_2O molecules or $(H_2O)_2$ dimers. The accuracy of the intensity of the ν_3 band of N_2−H_2O is estimated to be about ±25%. The error bars include the effects

TABLE 1: Band Center Frequencies and IRIs of the Complexes of Water and Nitrogen Molecules in He Droplets

complex	band assignment	frequency (cm^{-1})[a]	intensity relative to the corresponding band of H_2O or $(H_2O)_2$[b]	
H_2O	ν_3	3755.1[c]	1[d]	
	ν_1	3655.8[c]	1[d]	
N_2-H_2O	ν_3, parallel	3749.8	1.1 (0.2)[d]	1.3 (0.3)[d]
	ν_3, perpendicular	3755.5	0.2(0.1)[d]	
	ν_1, perpendicular	3655.6	1.6 (0.8)[d]	1.9 (0.9)[d]
	ν_1, parallel	3649.9[e]	0.3 (0.15)[d,e]	
$(N_2)_2-H_2O$	ν_3	3746.2	1.2 (0.4)[d]	
	ν_1	3652.5	1.1 (0.5)[d]	
$(H_2O)_2$	dangling OH stretch of H-donor molecule	3729.9[c]	1.6(0.5)[d,f]	
	ν_1 of H-acceptor	3654.4[c]	1.5 (0.7)[d,f]	
$N_2-(H_2O)_2$	H-donor dangling	3728.3	1.1 (0.7)[g]	
	ν_1 of H-acceptor	3648.6	2.7 (1.3)[g]	

[a] Absolute accuracy ±0.5 cm^{-1} (relative accuracy is ±0.1 cm^{-1}). [b] Numbers in parentheses are error limits (1σ). [c] Reference 24. [d] Ratio relative to the corresponding band of H_2O molecules. [e] Predicted from the splitting and intensity ratio of the parallel and perpendicular components of the ν_3 band of the N_2-H_2O complexes. [f] Reference 39. [g] Ratio relative to the corresponding band of $(H_2O)_2$.

of the droplet size distribution, scattering of the droplet beam at high pickup pressure, and the decrease of the droplet size upon multiple pickup events, which could not be precisely quantified at present. The estimated errors (1σ) are also listed in Table 1. In the range of the ν_1 bands, the error bars are estimated to be ±50% which are larger because of the weakness of the signal. In the spectral range of the ν_3 band, some additional error may be introduced by partial overlap of the bands of the N_2-H_2O and the $(N_2)_2-H_2O$ complexes. In this case, the IR intensity of the N_2-H_2O complexes would be somewhat overestimated. IRIs of the $N_2-(H_2O)_2$ and $(N_2)_2-H_2O$ complexes were obtained in a similar way and compiled in Table 1. To study the accuracy of the method, we performed a similar study of the $Ar-H_2O$ complexes, which will be described in a forthcoming paper.[30] The measured value of the IRI of the Ar complexes of water in the range of the ν_3 mode was found to be the same as that of single water molecules, to within 30% accuracy. This result is expected for $Ar-H_2O$ complexes bound by weak van der Waals forces and therefore serves as an additional proof of the accuracy of the intensity measurements in He droplets.

Discussion

It is seen that the ν_3 band of the N_2-H_2O complexes has two peaks at 3749.8 and 3755.5 cm^{-1} with an intensity ratio of about 5.5:1. Theoretical calculations[5,7,10,11] and microwave spectroscopic studies[9] show that the nitrogen molecule in the complex is bonded to an H-atom of the water molecule in an approximately collinear configuration. Therefore, the complex is expected to have a large rotational constant A. Thus, we assign the two peaks to the parallel (a-type) and perpendicular (b-type) component bands of the N_2-H_2O complexes. The frequency of the parallel band approximately equals the position of the band origin of the transition. The splitting of the two components of 5.7 cm^{-1} approximately equals the rotational constant A of the complex in helium. From the intensity ratio of the subbands, the angle of the transition dipole moment of the ν_3 mode with respect to the inertial a-axis of the complex was determined to be 25 ± 5°. The value of $(B + C)/2$ for the free complex was obtained previously[9] to be somewhat less than 0.1 cm^{-1}. Therefore, the rotational structure of the bands due to the end-over-end rotation of the complex could not be resolved in the present work. We did not observe any additional spectral splitting. This indicates that the internal rotational motion of the H_2O molecule in the complex is quenched, and the splitting due to tunneling motion of either H_2O or N_2 is smaller than the laser line width of 1.0 cm^{-1}, in agreement with previous studies.[9] In contrast, spectra of the $Ar-H_2O$ and O_2-H_2O complexes in helium droplets indicate internal rotation of water molecules in the complex,[30] which is, in the case of the $Ar-H_2O$ complex, in agreement with previous studies.[31,32]

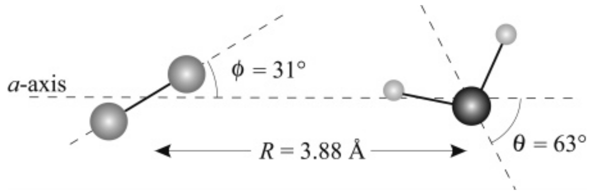

Figure 4. Structure of the N_2-H_2O complex obtained in this work. The N_2 and H_2O units are fixed to their equilibrium structures. The horizontal dashed line gives the a-inertial axis of the complex.

Leung et al.[9] deduced the angle θ between the a-axis of the complex and the C_2 axis of the water molecule in the complex from two different microwave measurements. An angle of $\theta = 63°$ was derived from the results of the Stark experiments. A different angle of $\theta = 43°$ was obtained from the value of the quadrupole coupling constants eQq of the ^{17}O atom in the $N_2-H_2{}^{17}O$ complex. Our result of $\theta = 65°$ ($\theta = 90° - 25°$) is in good agreement with the former. This is reasonable since the result of this work is based on the average of the dipole moment, which must be compared with the value determined by the Stark experiments, but not with that determined by eQq. It should be noticed that experiments cannot distinguish between the four structures with $\pm\theta$ and $180° \pm \theta$. Theoretical calculations[5,7,11] predict that the complex has a planar structure, and the nearest H- and N-atoms are on the same side of the line connecting the center of mass of the N_2 and H_2O units whereas the oxygen atom is on the opposite side.

The structure of the complex, which is in agreement with the Stark measurements,[9] is shown in Figure 4. The angle ϕ between the a-axis and the N_2 molecular axis, and the distance R between the centers of mass of the N_2 and H_2O molecules, were deduced from the rotational constant $A = 5.7$ cm^{-1}, which was obtained in this work, and the rotational constant $(B + C)/2 = 0.0955$ cm^{-1} from ref 9. The angle θ was fixed at 63°. We determined the angle ϕ as 31° and the center of mass separation of the molecules in the complex R as 3.88 Å. By comparison, two configurations, $\phi \approx 0°$ and $R = 3.86$ Å and $\phi \approx 21°$ and $R = 3.91$ Å, both for $\theta = 43°$, were estimated in ref 9. A value $\phi = 24°$ was estimated from quadrupole splitting due to N_2 molecules.[1] The rotational constant A could not be obtained in ref 9. A rigid complex having $\phi = 24°$ and $\theta = 63°$ has a rotational constant $A = 8.6$ cm^{-1}. This is about 34% larger than the value $A = 5.7$ cm^{-1} obtained in this work in He. This discrepancy could be caused by the effect of the He environment. Rotational constants of light molecules with $B_{gas} > 2$ cm^{-1} in He were found to be only a few percent smaller than those in the free molecules.[22,23] However, the effect of He on the magnitude of the rotational constants of molecular complexes has not been extensively studied. It is conceivable that the effect is larger in complexes. In particular, interaction with helium may change the average relative orientation of the molecules in the complex. Therefore, we concluded that the agreement of the ϕ values obtained in this work and in ref 1 is satisfactory. Note also that the alternative structure with angle $\theta = 43°$, which was discussed in ref 9, will give an intensity ratio of the parallel and perpendicular bands of 0.9, much smaller than the value of 5.5 observed in this work. Therefore, this alternative structure can be rejected. The geometry of the complex obtained in this work is quite similar to that obtained by theoretical calculations in refs 5, 7, 10, and 11. More recent calculations[5,10] predict a nearly linear N−N−H−O configuration in disagreement with the structure obtained in this work (see Figure 4). A linear complex must have a much larger rotational constant, $A = 21$ cm^{-1}, as compared to $A = 5.7$ cm^{-1} obtained in this work. Of course, this comparison is subject to certain approximations, because equilibrium configuration is obtained in calculations, whereas a configuration averaged over the zero-point motion is obtained in an experiment. Diffusion Monte Carlo calculations of the N_2-H_2O complex[8] show that the distribution of the N−N−H angle peaks toward 0° and has a width (HWHM) of about 20°.

Because the transition dipole moments are perpendicular in the ν_3 and ν_1 modes of water molecules, the ν_1 band of the N_2-H_2O complex must have parallel and perpendicular components similar to the ν_3 band but with an inverted intensity ratio. Therefore, we assigned the band at 3655.6 cm^{-1} to the perpendicular component of the ν_1 band of the N_2-H_2O complex. The parallel component is expected to be shifted to lower frequencies by 5.7 cm^{-1} and to be a factor of about 5.5 weaker. Due to the smaller signal-to-noise ratio in the ν_1 region and overlap with the band of the $N_2-(H_2O)_2$ complex, we were not able to identify the parallel component of the ν_1 band of the N_2-H_2O complex. According to the above discussion, the frequencies of the origins of the ν_1 and ν_3 bands of the N_2-H_2O complexes in He were obtained as 3649.9 and 3749.8 cm^{-1}, respectively. The bands are shifted toward low frequency with respect to the corresponding band origins of single water molecules in He by 5.9 and 5.3 cm^{-1}, respectively. The similar magnitude of the shift is in accord with the similar amplitude of the OH stretch in the ν_1 and ν_3 modes of water molecules. The shifts of the frequency of the ν_1 and ν_3 modes of water molecules in N_2-H_2O complexes are compared with the results of matrix isolation studies in Table 2. It is seen that the formation of complexes in the matrix leads to a shift of the ν_3 band by about 3 to 5 cm^{-1} toward low frequency, in accord with the present results. On the other hand, the ν_1 band shifts by about 2 to 3 cm^{-1} toward higher frequency. If the complex in a matrix retains the ability to rotate around the a-axis, then matrix measurements will give the perpendicular component of the band, which will have a frequency about 5.7 cm^{-1} above the band origin of the ν_1 band of the N_2-H_2O complexes, as observed in this work, and would be shifted toward higher frequency relative to the frequency of single water molecules.

In this work, the enhancement factor of the IRI in the N_2-H_2O complexes, as compared with that in single water molecules, has been obtained as 1.3 ± 0.3 and 1.9 ± 0.9 for the ν_3 and ν_1 bands, respectively. The agreement of the angle between the Stark measurements in the gas phase and our present experiments in He droplet indicates that the structure of the N_2-H_2O complex in He droplets and in the gas phase is very similar. Therefore, the IRIs obtained in He droplets essentially correspond to the gas-phase values. It is believed that the IRIs obtained in this work are not greatly perturbed by encapsulation in He droplets. This conjecture is supported by the fact that the vibrational frequencies[22,23] and permanent dipole moments[33] of molecules in He droplets remain the same as in free molecules within about 0.01% and 1% accuracy, respectively.

TABLE 2: Frequencies (cm^{-1}) of OH-stretch Band Origins of H_2O and N_2-H_2O in Various Media

	ν_1			ν_3		
medium	H_2O	N_2-H_2O	$\Delta\nu_1$[a]	H_2O	N_2-H_2O	$\Delta\nu_3$[a]
gas[29]	3657.053			3755.929		
in He droplets	3655.8[b]	3649.9	−5.9	3755.1[b]	3749.8	−5.3
in solid Ar[40]	3636.91[c]			3733.9[d]		
in solid Ar[41]	3637.3[c]			3734.0[d]		
in solid Ar[42]	3638.0			3734.3		
in solid Ar[12]		3639.8				
in solid Ar[11]		3640.2			3729.6	
in solid Ar[13]	3637.0[c]	3640.1	3.1	3734.0[d]	3731.2	−2.8
in solid Ar[14]					3731.8	
in solid Kr[13]	3626.6[c]	3630.2	3.6	3724.1[d]		

[a] The difference $\Delta\nu_\iota = \nu_\iota(N_2-H_2O) - \nu_\iota(H_2O)$. [b] Reference 24. [c] The origin is estimated from the frequency of the $1_{10} \leftarrow 1_{01}$ line by subtracting the frequency difference between the $1_{10} \leftarrow 1_{01}$ and $1_{11} \leftarrow 0_{00}$ lines. [d] The origin is estimated as an average of the frequencies of the $1_{01} \leftarrow 0_{00}$ and $0_{00} \leftarrow 1_{01}$ lines.

Larger enhancement factors of 2.0 and 3.6 (ref 10), 2.1 and 4.9 (ref 7), and 2.0 and 4.3 (ref 11) have been obtained in theoretical calculations for the ν_3 and ν_1 bands of the N_2-H_2O complexes, respectively. The comparison with the experimental results of Table 1 indicates that ab initio calculations overestimate IR intensities in clusters by about a factor of 2. Here, we are not able to evaluate the origin of this discrepancy. Some error is introduced by the use of the double harmonic approximation. Moreover, the calculations of the IRI were made for the fixed cluster geometry, whereas the diffusion Monte Carlo study of the N_2-H_2O complex[8] shows a rather broad distribution of the N−H−O angles of about 40° (HWHM) and of the N−H distances of about 0.5 Å (FWHM). Another potential source of error might be the neglect of basis set superposition errors in the course of calculations of the IRI in clusters. The large calculated enhancement of the intensity of the ν_3 band in N_2-H_2O complexes has been explained by the formation of a weak hydrogen bond.[10] In hydrogen bonded complexes such as the water dimer, the frequency of the ν_1 band of the hydrogen donor molecule decreases by about 60 cm^{-1} as compared with that in single water molecules, and its intensity increases by about a factor of 50.[34] The absence of a significant shift and the enhancement of the ν_1 band in the N_2-H_2O complex is evidence against the formation of a hydrogen bond. Nevertheless, the interaction in the complex is strong enough to quench the internal rotation of the water molecules and to give a nearly collinear N−H−O geometry for the complex.

This small increase of the IRI of the ν_3 band of the N_2-H_2O complexes could be explained by polarization of the N_2 molecule of the complex, which oscillates in phase with the H_2O molecule. The induced transition dipole moment μ_{ind} can be estimated as

$$\mu_{\text{ind}} = \alpha E_{\text{ind}} = \begin{pmatrix} \alpha_{zz}E_z \\ \alpha_{xx}E_x \end{pmatrix} = \begin{pmatrix} \alpha_{zz}\dfrac{\mu_{\text{w}}}{R^3}(2\sin\theta\cos\phi - \cos\theta\sin\phi) \\ \alpha_{xx}\dfrac{\mu_{\text{w}}}{R^3}(2\sin\theta\sin\phi + \cos\theta\cos\phi) \end{pmatrix} \quad (5)$$

where α is the polarizability tensor of the N$_2$ and $\alpha_{zz} = 2.22$ Å^3 ($\alpha_{xx} = 1.53$ Å^3)[35] is its component parallel (perpendicular) to the molecular axis; $\mathbf{E}_{\text{ind}}$ is the oscillating electric field at the N$_2$ position induced by the transition dipole moment of water μ_{w}, E_z is its component along the N$_2$ molecular axis, and E_x is its component perpendicular to the axis on the plane containing the complex. R, θ, and ϕ are the same as in Figure 4. An estimate gives the ratio of $A_{1,1}/A_{0,1} = 1.1$ for the structure in Figure 4, in reasonable agreement with the experimental value of 1.3 ± 0.3.

Table 1 shows that the IRI of the ν_1 mode increases by a factor of 1.9 ± 0.9 with respect to that in single water molecules. Although the error bars are larger than in the case of the ν_3 mode, the somewhat larger effect of the complex formation on the intensity of the ν_1 mode of the N$_2$−H$_2$O complexes is in agreement with the weakness of the ν_1 band in water molecules. The attachment of the N$_2$ molecules to one of the hydrogen atoms of the water molecule will induce an asymmetry in the ν_1 vibration, which is equivalent to mixing of the ν_1 mode with the ν_3 mode, which has a factor of about 20 larger IR intensity.

Finally, we will comment on the spectra of the larger $(N_2)_m-(H_2O)_n$ complexes. The addition of an N$_2$ molecule to the N$_2$−H$_2$O complex does not lead to any substantial increase of the IRI for the two vibrational modes as compared with single water molecules. In particular, the lack of enhancement of the ν_1 mode suggests that the two nitrogen molecules are attached to the two H-atoms of water molecules making a symmetric (C_{2v}) complex. In such a complex, the intensities of the ν_3 and ν_1 bands are expected to be very similar to those of single water molecules. The IRI of the ν_3 band of the $(N_2)_2-H_2O$ complexes was found to be a factor of 1.2 stronger than that in single water molecules, in agreement with results for N$_2$−H$_2$O complexes.

The IRI of H$_2$O dimers will be discussed in detail elsewhere.[34] The $(H_2O)_2$ dimer has C_s symmetry with the symmetry plane containing the H-donor H$_2$O monomer and the C_{2v} axis of the H-acceptor monomer.[36,37,38] The bands of the $N_2-(H_2O)_2$ complexes are weak, which explains large error bars for their IRIs. The IRI of the ν_1 mode of the acceptor water molecules of the $N_2-(H_2O)_2$ complexes is a factor of 2 larger than that of the ν_1 mode of H$_2$O dimers. At the same time, no significant increase is observed in the intensity of the dangling stretching mode of the donor water molecules of the complex. This pattern is consistent with the structure of the $N_2-(H_2O)_2$ complex where the N$_2$ molecule is attached to one of the hydrogen atoms of the acceptor molecule of the water dimer. DFT calculations[11] show that this structure has a total dissociation energy of 6.14 kcal/mol, which is about 0.5 kcal/mol larger than those of the other possible conformers of the complex, in agreement with the above assignment. On the other hand, a recent study of the $(N_2)_m-(H_2O)_n$ complexes in the Ar matrix[12] attributed spectra of the $N_2-(H_2O)_2$ complex to a cyclic structure.

Conclusions

In this work, IR depletion spectra of complexes of nitrogen and water in the OH-stretch region have been obtained in He droplets. We have demonstrated the utility of the He droplet technique for measurements of the IR intensities in complexes. The IR intensity of the ν_3 band in N$_2$−H$_2$O complexes was found to be about 30% larger than that in single water molecules. The observed enhancement is smaller than that obtained previously in ab initio calculations. The IR intensity of the ν_1 transition of H$_2$O increases in complexes by about a factor of 2, again smaller than that obtained in calculations. The small degree of the IRI enhancement obtained in this work is consistent with the weak binding energy of the N$_2$−H$_2$O complexes. These results suggest that the effect of the absorption of the N$_2$−H$_2$O complexes in the atmosphere[5] is smaller than that estimated from the calculated values of the IRI.

The origins of the ν_1 and ν_3 bands of the N$_2$−H$_2$O complexes are shifted by about 5 cm^{-1} toward low frequency relative to the corresponding bands of single water molecules. The orientation of the water molecule in the complex with respect to its inertial a-axis was obtained from the intensity ratio of the parallel and perpendicular subbands. The structures of the $(N_2)_2-H_2O$ and $N_2-(H_2O)_2$ complexes have been discussed on the basis of changes of their IRIs from that of H$_2$O.

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