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# The vibrational spectra of molecular ions isolated in solid neon.

## X. $\text{H}_2\text{O}^+$ , $\text{HDO}^+$ , and $\text{D}_2\text{O}^+$

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When a  $\text{Ne}:\text{H}_2\text{O} \geq 200$  sample is codeposited at approximately 5 K with a beam of neon atoms that have been excited in a microwave discharge, new infrared absorptions appear close to the gas-phase band centers of the three vibrational fundamentals of  $\text{H}_2\text{O}^+$ . Detailed isotopic substitution studies confirm this assignment and provide assignments for all of the vibrational fundamentals of  $\text{HDO}^+$  and  $\text{D}_2\text{O}^+$ . When ions are present in the neon matrix, rotation of a significant fraction of the water molecules is inhibited. Electrons produced by the photodetachment of anions, which must be present to maintain overall charge neutrality of the deposit, accelerate nuclear spin equilibration of water in the matrix. As the concentration of  $\text{H}_2\text{O}^+$  is decreased by capture of the photodetached electrons, the absorptions assigned to nonrotating water are also reduced in intensity. The nature of the other ionic species which may be present in the sample is considered.

## INTRODUCTION

Although water is present in a wide variety of high energy systems, our knowledge of the spectroscopic properties of its ions is meager. The first report of emission bands of  $\text{H}_2\text{O}^+$  between 400 and 750 nm, assigned to the  $\tilde{A}^2A_1-\tilde{X}^2B_1$  transition, was given by Lew and Heiber<sup>1</sup> in 1973. Shortly thereafter, Herzberg, Lew, and co-workers<sup>2,3</sup> assigned bands observed in the spectrum of Comet Kohoutek to this transition of  $\text{H}_2\text{O}^+$ . Lew<sup>4</sup> subsequently reported a more detailed analysis of the bands, including the determination of the bending frequencies of  $\text{H}_2\text{O}^+$  in both the  $\tilde{X}$  and  $\tilde{A}$  states. Only in 1987 was the corresponding emission spectrum of  $\text{D}_2\text{O}^+$  reported and analyzed by Lew and Groleau.<sup>5</sup> Very recently, Das and Farley<sup>6</sup> obtained the first absorption spectrum of  $\text{H}_2\text{O}^+$ . The  $\tilde{X}$  and  $\tilde{A}$  states of  $\text{H}_2\text{O}^+$  correlate with a  $^2\Pi$  state of linear  $\text{H}_2\text{O}^+$ , split by Renner-Teller interaction. The valence angle of ground-state  $\text{H}_2\text{O}^+$  is only slightly larger than that of  $\text{H}_2\text{O}$ , but the ion becomes linear in its  $\tilde{A}$  state. The position of the origin is not yet certain. Jungen and co-workers<sup>7</sup> obtained a value of  $9187\text{ cm}^{-1}$  from a detailed fit of the experimental data, but the *ab initio* studies of Reuter and co-workers<sup>8</sup> suggest revisions to the interpretation of the data.

Even before the first emission spectra of  $\text{H}_2\text{O}^+$  were reported, studies of the photoelectron spectrum of  $\text{H}_2\text{O}$  by Brundle and Turner<sup>9</sup> had yielded low resolution data for the  $\tilde{X}$  and  $\tilde{A}$  states of  $\text{H}_2\text{O}^+$  and had determined that the origin of the  $\tilde{B}$  state of the cation should lie near  $37\,000\text{ cm}^{-1}$ . Several more recent studies<sup>10-12</sup> have yielded higher resolution photoelectron spectral data for  $\text{H}_2\text{O}^+$ . The experiments of Dixon and co-workers<sup>11</sup> gave the first experimental data on the  $\tilde{A}$  state of  $\text{HDO}^+$ . Reutt and co-workers<sup>12</sup> obtained values for the symmetric stretching and bending fundamentals of  $\text{H}_2\text{O}^+$  and  $\text{D}_2\text{O}^+$  in both the  $\tilde{X}$

and  $\tilde{A}$  states with uncertainties on the order of  $10\text{ cm}^{-1}$ . These workers also estimated vibrational data for the  $\tilde{B}$  state based on a fit of a simulated spectrum to their observations.

Further information on the spectrum of  $\text{H}_2\text{O}^+$  has been obtained from high resolution infrared studies. Dinelli and co-workers<sup>13</sup> used a tunable difference frequency spectrometer to observe the two stretching fundamentals,  $\nu_1$  and  $\nu_3$ , of the cation, and Brown and co-workers<sup>14</sup> used a tunable diode laser to study the  $\nu_2$  absorption. However, no high resolution infrared studies of either  $\text{HDO}^+$  or  $\text{D}_2\text{O}^+$  have been reported.

Recently, we have used Penning ionization and/or photoionization of small molecules by excited neon atoms and their resonance radiation as a means of forming small molecular cations, which are then trapped in a large excess of solid neon for infrared and near-infrared absorption studies. The first in this series of experiments used  $\text{CO}_2$  as the test molecule.<sup>15</sup> The  $\nu_3$  absorption of the resulting  $\text{CO}_2^+$  was shifted by only  $1.4\text{ cm}^{-1}$  from the gas-phase band center, and the  $\nu_3$  absorption of  $\text{CO}_2^-$  was identified. Subsequent studies of samples containing oxygen<sup>16</sup> and nitrogen<sup>17</sup> led to the assignment of infrared absorptions to the dimer ions  $\text{O}_4^+$ ,  $\text{O}_4^-$ , and  $\text{N}_4^+$ . Because the ionization potential of  $\text{H}_2\text{O}$  is  $12.61\text{ eV}$ ,<sup>18,19</sup> well below the  $16.6\text{--}16.8\text{ eV}$  first group of excited states of neon,  $\text{H}_2\text{O}$ , which is always present in small concentration in our experiments, can also ionize. Indeed, the  $\nu_2$  absorption of  $\text{H}_2\text{O}^+$  was identified tentatively in the  $\text{CO}_2$  study.<sup>15</sup> Recently, we have conducted a systematic study of normal and isotopically substituted  $\text{H}_2\text{O}$  in order not only to understand the contribution of water ions to other ion production experiments, but also to determine the infrared spectra of  $\text{HDO}^+$  and  $\text{D}_2\text{O}^+$ .

## EXPERIMENTAL DETAILS (REF. 20)

The unsubstituted  $\text{H}_2\text{O}$  sample and the  $\text{H}_2\text{ }^{18}\text{O}$  (97.2%  $^{18}\text{O}$ ),  $\text{D}_2\text{ }^{16}\text{O}$ , and  $\text{D}_2\text{ }^{18}\text{O}$  (98.2%  $^{18}\text{O}$ , 84% D) samples

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(Merck and Co./Isotopes) used in these experiments were freed of traces of atmospheric gases by repeated freezing at 77 K and pumping on the resulting solid. Isotopic exchange with water adsorbed on the walls of the sampling system occurred readily, limiting the extent of isotopic enrichment obtained in typical experiments. Because the order of the experiments was  $\text{H}_2^{16}\text{O}$ ,  $\text{H}_2^{18}\text{O}$ ,  $\text{D}_2^{18}\text{O}$ ,  $\text{D}_2^{16}\text{O}$ , not only were prominent absorptions of HDO and weaker absorptions of  $\text{H}_2\text{O}$  present in the experiments on the  $\text{D}_2\text{O}$  samples, but also absorptions of  $\text{HD}^{18}\text{O}$  and  $\text{D}_2^{18}\text{O}$  were present in the spectra of  $\text{D}_2^{16}\text{O}$  samples. The neon matrix gas (Spectra Gases, Research Grade) was not subjected to purification.  $\text{Ne}:\text{H}_2^{16}\text{O}$  mixtures of mole ratio 200 (used for the near-infrared studies) and  $\text{Ne}:\text{water}$  mixtures of mole ratio between 400 and 3200 (used for the mid-infrared studies) were prepared using standard manometric procedures.

The  $\text{Ne}:\text{water}$  samples were codeposited at approximately 5 K with an approximately equal amount of pure neon that had been excited by a microwave discharge before streaming from the pinhole in the end of a quartz discharge tube. Details of this deposition procedure and of the discharge configuration have been described previously.<sup>21</sup> A Helitran (APD Cryogenics, Inc.) continuous transfer liquid helium cell was used.

The absorption spectra of the resulting sample deposits were obtained using a Bomem DA3.002 Fourier transform interferometer with transfer optics which have been described previously.<sup>22</sup> Observations of normal and isotopically enriched  $\text{Ne}:\text{water}$  samples were conducted at a resolution of  $0.1\text{ cm}^{-1}$  between 700 and  $5000\text{ cm}^{-1}$  using a globar source, a KBr beam splitter, and a  $\text{HgCdTe}$  detector cooled to 77 K. Observations of  $\text{Ne}:\text{H}_2^{16}\text{O}=200$  samples were conducted at a resolution of  $0.2\text{ cm}^{-1}$  between 1900 and  $8000\text{ cm}^{-1}$  using a tungsten source, a  $\text{CaF}_2$  beam splitter, and an InSb detector cooled to 77 K. Data were accumulated for each spectrum over a period of at least 7.5 min. The resulting spectrum was ratioed against a similar one taken without a deposit on the cryogenic mirror.

In order to obtain additional information on photoinduced changes in the matrix sample, after the infrared spectrum of the initial deposit had been recorded, the sample was subjected to various ranges of visible and ultraviolet radiation. A tungsten lamp was used with a Corning filter of glass type 2403 to provide radiation with a short wavelength cutoff (1% transmission) of approximately 630 nm. A medium-pressure mercury arc was used unfiltered or with Corning filters of glass type 3384, 3389, or 7380 to provide radiation with short wavelength cutoffs of 490, 420, or 345 nm, respectively.

## OBSERVATIONS

The infrared absorption spectrum in the regions in which the three fundamentals of  $\text{H}_2^{16}\text{O}^+$  appear in the gas phase<sup>13,14</sup> is shown in traces (b) of Fig. 1 and traces (a) of Fig. 2 for a  $\text{Ne}:\text{H}_2^{16}\text{O}=400$  sample codeposited with a beam of excited neon atoms. When the sample was exposed to mercury-arc radiation of wavelength longer than 345 nm for approximately 15 min, all of the absorptions shown

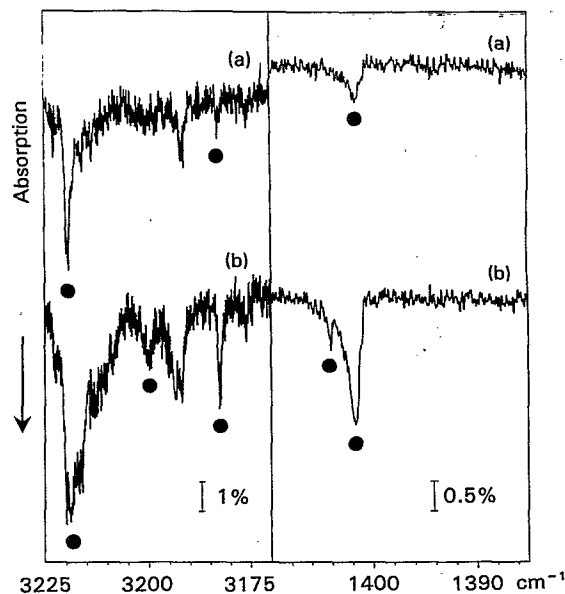


FIG. 1. Concentration dependence of  $\text{H}_2^{16}\text{O}^+$  absorptions. (a) 8.6 mmol  $\text{Ne}:\text{H}_2^{16}\text{O}=1600$  codeposited at  $\sim 5\text{ K}$  over a period of 149 min with 8.4 mmol discharged  $\text{Ne}$ ; (b) 10.4 mmol  $\text{Ne}:\text{H}_2^{16}\text{O}=400$  codeposited at  $\sim 5\text{ K}$  over a period of 210 min with 9.9 mmol discharged  $\text{Ne}$ . ● — diminishes in intensity on mercury-arc irradiation of the deposit  $\lambda > 345\text{ nm}$ .

in those traces except a weak absorption with maxima at  $3192.1$  and  $3193.6\text{ cm}^{-1}$  and a very weak absorption near  $3176\text{ cm}^{-1}$  decreased considerably in intensity. The positions of these latter absorptions may be compared with the  $2\nu_2(1_{1,1}-0_{0,0})$  and  $2\nu_2(1_{1,0}-1_{0,1})$  transitions of gas-phase

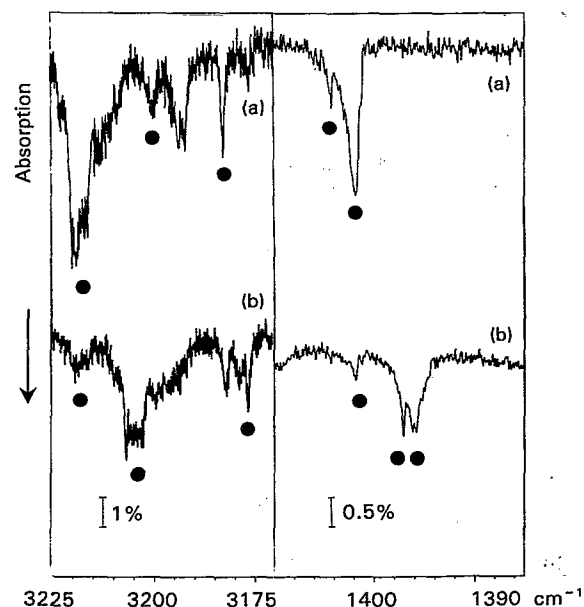


FIG. 2. Oxygen-isotopic dependence of  $\text{H}_2\text{O}^+$  absorptions. (a) 10.4 mmol  $\text{Ne}:\text{H}_2^{16}\text{O}=400$  codeposited at  $\sim 5\text{ K}$  over a period of 210 min with 9.9 mmol discharged  $\text{Ne}$ ; (b) 7.3 mmol  $\text{Ne}:\text{H}_2^{18}\text{O}=400$  codeposited at  $\sim 5\text{ K}$  over a period of 128 min with 6.9 mmol discharged  $\text{Ne}$ . ● — diminishes in intensity on mercury-arc irradiation of the deposit,  $\lambda > 345\text{ nm}$ .

$\text{H}_2^{16}\text{O}$  (Ref. 23), at 3196.09 and 3178.12  $\text{cm}^{-1}$ , respectively. Since it is well known that  $\text{H}_2\text{O}$  can rotate in rare-gas matrices and since the positions of the gas-phase absorptions correspond closely with those of the matrix peaks, the assignment of the unchanged absorptions to the lowest energy transitions associated with  $2\nu_2$  of the *para* and *ortho* nuclear spin isomers of  $\text{H}_2^{16}\text{O}$  trapped in solid neon is suggested.

As is shown in traces (a) of Fig. 1, there was comparatively little change in the pattern of the product absorptions in a study in which the  $\text{H}_2^{16}\text{O}$  concentration was reduced by a factor of 4. The low frequency shoulders on the highest frequency product absorption, at 3219.5  $\text{cm}^{-1}$ , were less prominent, and the very weak, photosensitive absorption near 3200  $\text{cm}^{-1}$  could not be detected. However, the peaks at 1401.7 and 3182.7  $\text{cm}^{-1}$  were still present. These two peaks were below the detection threshold in an experiment on a  $\text{Ne}:\text{H}_2^{16}\text{O}=3200$  sample.

In the study of a  $\text{Ne}:\text{H}_2^{18}\text{O}=400$  sample shown in traces (b) of Fig. 2, the product absorptions characteristic of the  $\text{Ne}:\text{H}_2^{16}\text{O}$  samples were detectable, although greatly reduced in intensity. Each of these absorptions of products formed from  $\text{H}_2^{16}\text{O}$  was accompanied by a new absorption at somewhat lower frequency. Although there are two absorption maxima for the peak near 1396  $\text{cm}^{-1}$ , a second photosensitive absorption was also present on the high frequency shoulder of the 1401.7  $\text{cm}^{-1}$  absorption of the  $\text{H}_2^{16}\text{O}$  experiments. A pair of absorptions near 3180  $\text{cm}^{-1}$ , contributed by a photolytically stable species, lies close to the  $2\nu_2$  ( $1_{1,1}-0_{0,0}$ ) transition of gas-phase  $\text{H}_2^{18}\text{O}$ , reported<sup>23</sup> at 3183.00  $\text{cm}^{-1}$ .

Trace (a) of Fig. 3 shows the  $\text{H}_2^{16}\text{O}$  bending absorption pattern for a small  $\text{Ne}:\text{H}_2^{16}\text{O}$  sample codeposited with undischarged neon, and trace 3(b) shows the absorption pattern which resulted on codeposition of additional  $\text{Ne}:\text{H}_2^{16}\text{O}$  with discharged neon. The positions<sup>23</sup> of the gas-phase band origin and of the low- $J$  rotational transitions for  $\nu_2$  of gas-phase  $\text{H}_2^{16}\text{O}$  are shown at the top of Fig. 3. The correspondence between the neon-matrix absorption frequencies and those characteristic of gas-phase  $\text{H}_2^{16}\text{O}$  is evident. Further details of the assignment of the rotational structure of normal and isotopically substituted  $\text{H}_2\text{O}$  isolated in solid neon are given in a separate paper.<sup>24</sup> The rate of growth in the intensity of the 1595.6  $\text{cm}^{-1}$  absorption in the deposition with discharged neon was greater than that of the other absorptions in this spectral region. When the sample was later exposed to mercury-arc radiation of wavelength longer than 345 nm, that absorption and those assigned to the  $\nu_2$  ( $1_{1,0}-1_{0,1}$ ) and  $\nu_2$  ( $2_{1,2}-1_{0,1}$ ) transitions of  $\text{H}_2^{16}\text{O}$  diminished in intensity, while the already very prominent peak assigned to the  $\nu_2$  ( $1_{1,1}-0_{0,0}$ ) transition of  $\text{H}_2^{16}\text{O}$  grew.

Similar phenomena were noted in the region of the  $\text{H}_2\text{O}$  stretching fundamentals, shown in Fig. 4. The positions<sup>23</sup> of the band origins and of the low- $J$  transitions of gas-phase  $\text{H}_2^{16}\text{O}$  are shown at the top. Traces 4(a) show the absorptions typical of  $\text{Ne}:\text{H}_2^{16}\text{O}$  samples between 3625 and 3825  $\text{cm}^{-1}$ . In this spectral region, the spectra of samples codeposited with undischarged and discharged neon

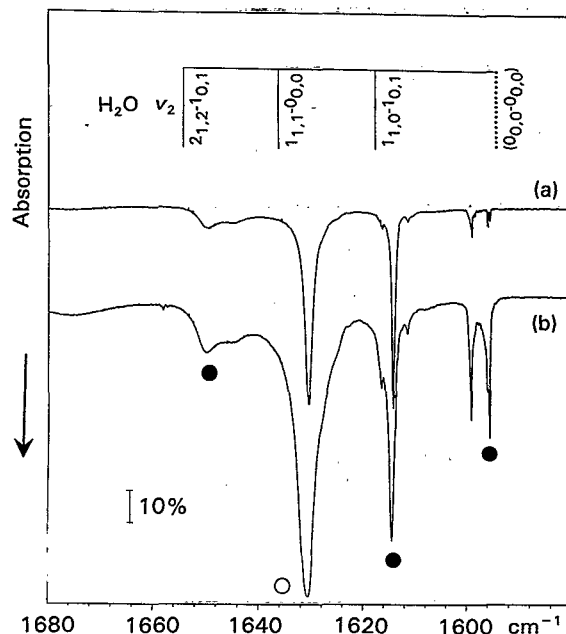


FIG. 3. Dependence of rotational absorptions of  $\nu_2$  of  $\text{H}_2^{16}\text{O}$  on the presence of  $\text{H}_2^{16}\text{O}^+$  in the deposit. (Positions of gas-phase rotational transitions are shown at the top.) (a) 4.28 mmol  $\text{Ne}:\text{H}_2^{16}\text{O}=800$  codeposited at  $\sim 5$  K over a period of 84 min with 4.75 mmol undischarged Ne; (b) 8.45 mmol additional  $\text{Ne}:\text{H}_2^{16}\text{O}=800$  codeposited at  $\sim 5$  K over a period of 170 min with 8.01 mmol discharged Ne. ○—grows in intensity on mercury-arc irradiation of the deposit,  $\lambda > 345$  nm; ●—diminishes in intensity on mercury-arc irradiation of the deposit,  $\lambda > 345$  nm.

were similar except for the appearance of a weak absorption at 3665.3  $\text{cm}^{-1}$  when the neon was discharged. Traces 4(b) show portions of the difference spectrum obtained after the deposit of traces 4(a) had been exposed to

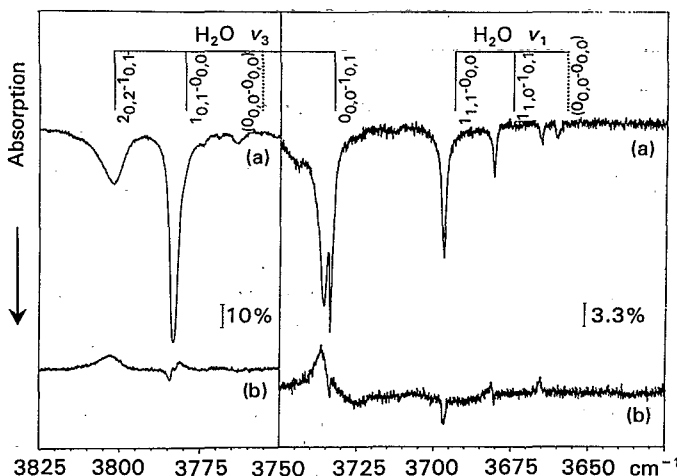


FIG. 4. Dependence of rotational absorptions of  $\nu_1$  and  $\nu_3$  of  $\text{H}_2^{16}\text{O}$  on the presence of  $\text{H}_2^{16}\text{O}^+$  in the deposit. (Positions of gas-phase rotational transitions are shown at the top.) (a) 4.28 mmol  $\text{Ne}:\text{H}_2^{16}\text{O}=800$  codeposited at  $\sim 5$  K over a period of 84 min with 4.75 mmol undischarged Ne, then 8.45 mmol additional  $\text{Ne}:\text{H}_2^{16}\text{O}=800$  codeposited at  $\sim 5$  K over a period of 170 min with 8.01 mmol discharged Ne. (b) Changes after 15 min mercury-arc irradiation of the deposit,  $\lambda > 345$  nm. (Difference spectrum—increase plotted downward.)

TABLE I. Absorptions<sup>a</sup> ( $\text{cm}^{-1}$ ) which change in intensity on mercury-arc irradiation ( $\lambda > 345$  nm) of Ne:H<sub>2</sub>O samples which were codeposited with a beam of discharged neon.

H <sub>2</sub> <sup>16</sup> O	H <sub>2</sub> <sup>18</sup> O	Species	Vibration	Rotation assignment
	1395.9w	H <sub>2</sub> <sup>18</sup> O <sup>+</sup>	$\nu_2$	
	1397.0w	H <sub>2</sub> <sup>18</sup> O <sup>+</sup>	$\nu_2$	
1401.7w	1401.8vw	H <sub>2</sub> <sup>16</sup> O <sup>+</sup>	$\nu_2$	
	1589.2s	H <sub>2</sub> <sup>18</sup> O	$\nu_2$	(0 <sub>0,0</sub> -0 <sub>0,0</sub> )
1595.6ms	1595.6m	H <sub>2</sub> <sup>16</sup> O	$\nu_2$	(0 <sub>0,0</sub> -0 <sub>0,0</sub> )
	1607.0s	H <sub>2</sub> <sup>18</sup> O	$\nu_2$	1 <sub>1,0</sub> -1 <sub>0,1</sub>
1614.3s		H <sub>2</sub> <sup>16</sup> O	$\nu_2$	1 <sub>1,0</sub> -1 <sub>0,1</sub>
	1623.2vs, +	H <sub>2</sub> <sup>18</sup> O	$\nu_2$	1 <sub>1,1</sub> -0 <sub>0,0</sub>
1630.6vs, +	1630.7sh, +	H <sub>2</sub> <sup>16</sup> O	$\nu_2$	1 <sub>1,1</sub> -0 <sub>0,0</sub>
	1642.2sh, br	H <sub>2</sub> <sup>18</sup> O	$\nu_2$	2 <sub>1,2</sub> -1 <sub>0,1</sub>
1649.8m, br		H <sub>2</sub> <sup>16</sup> O	$\nu_2$	2 <sub>1,2</sub> -1 <sub>0,1</sub>
	3176.8w	H <sub>2</sub> <sup>18</sup> O <sup>+</sup>	$\nu_1$	
3182.7w		H <sub>2</sub> <sup>16</sup> O <sup>+</sup>	$\nu_1$	
	3206.5wm	H <sub>2</sub> <sup>18</sup> O <sup>+</sup>	$\nu_3$	
3219.5wm	3219.1w	H <sub>2</sub> <sup>16</sup> O <sup>+</sup>	$\nu_3$	
	3657.9wm	H <sub>2</sub> <sup>18</sup> O	$\nu_1$	
3665.3wm	3665.4w	H <sub>2</sub> <sup>16</sup> O	$\nu_1$	
3680.6wm		H <sub>2</sub> <sup>16</sup> O	$\nu_1$	1 <sub>1,0</sub> -1 <sub>0,1</sub>
	3688.0m, +	H <sub>2</sub> <sup>18</sup> O	$\nu_1$	1 <sub>1,1</sub> -0 <sub>0,0</sub>
3696.9m, +		H <sub>2</sub> <sup>16</sup> O	$\nu_1$	1 <sub>1,1</sub> -0 <sub>0,0</sub>
3735.6m		H <sub>2</sub> <sup>16</sup> O	$\nu_3$	0 <sub>0,0</sub> -1 <sub>0,1</sub>
	3769.0vs, +	H <sub>2</sub> <sup>18</sup> O	$\nu_3$	1 <sub>0,1</sub> -0 <sub>0,0</sub>
3783.3vs, +	3783.3vs, +	H <sub>2</sub> <sup>16</sup> O	$\nu_3$	1 <sub>0,1</sub> -0 <sub>0,0</sub>
	3786.4sh	H <sub>2</sub> <sup>18</sup> O	$\nu_3$	2 <sub>0,2</sub> -1 <sub>0,1</sub>
3801.7m, br	3801.7wm	H <sub>2</sub> <sup>16</sup> O	$\nu_3$	2 <sub>0,2</sub> -1 <sub>0,1</sub>
5358.5m, +		H <sub>2</sub> <sup>16</sup> O	$\nu_2 + \nu_3$	1 <sub>0,1</sub> -0 <sub>0,0</sub>
7285.0wm, +		H <sub>2</sub> <sup>16</sup> O	$\nu_1 + \nu_3$	1 <sub>0,1</sub> -0 <sub>0,0</sub>

<sup>a</sup>vw—very weak; w—weak; m—medium; s—strong; vs—very strong; sh—shoulder; br—broad. Peaks which grow on mercury-arc irradiation are designated by +. Other peaks diminish on irradiation.

mercury-arc radiation with a 345 nm short wavelength cut-off for 15 min. The 3665.3  $\text{cm}^{-1}$  peak was completely destroyed, and all of the peaks which originated in the 1<sub>0,1</sub> rotational level of the ground vibrational state of H<sub>2</sub> <sup>16</sup>O were diminished in intensity. The sharp peak at 3733.7  $\text{cm}^{-1}$ , assigned to (H<sub>2</sub> <sup>16</sup>O)<sub>2</sub>, and the  $\nu_1$  (1<sub>1,1</sub>-0<sub>0,0</sub>) peak of H<sub>2</sub> <sup>16</sup>O grew on irradiation of the deposit. The very prominent  $\nu_3$  (1<sub>0,1</sub>-0<sub>0,0</sub>) absorption, at 3783  $\text{cm}^{-1}$ , also grew, but its behavior was more complex. As is apparent from the difference plot, there was a change in the contour of this absorption on irradiation; the position of the absorption maximum shifted upward by 0.3  $\text{cm}^{-1}$ . The change in intensity of such a strong absorption is not well shown by a per cent absorption plot. The maximum absorbance of this peak was 2.39 in the initial plot and 2.61 after irradiation, representing a growth of approximately 10%.

The positions and approximate relative intensities of all of the absorptions which changed in intensity on near ultraviolet irradiation of Ne:H<sub>2</sub> <sup>16</sup>O and Ne:H<sub>2</sub> <sup>18</sup>O samples that had been codeposited with discharged neon are summarized in Table I. In addition to the data observed in the regions of the H<sub>2</sub>O fundamentals, data for two absorptions arising from combination bands of H<sub>2</sub> <sup>16</sup>O in the near-infrared spectral region, both of which grew on irradiation, are included. The assignment of the 5358.5  $\text{cm}^{-1}$  absorption is based on its close correspondence with the gas-phase data.<sup>25,26</sup> Similarly, the assignment of the 7285.0  $\text{cm}^{-1}$  ab-

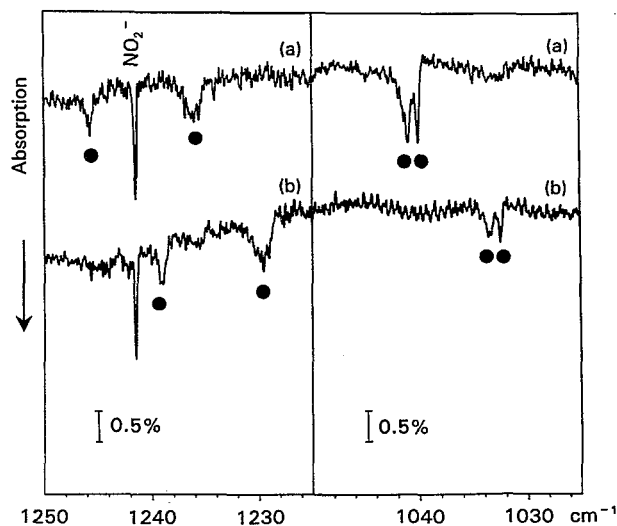


FIG. 5. Oxygen-isotopic dependence of bending fundamental absorptions of HDO<sup>+</sup> and D<sub>2</sub>O<sup>+</sup>. (a) 10.1 mmol Ne:D<sub>2</sub> <sup>16</sup>O=400 codeposited at ~5 K over a period of 188 min with 9.2 mmol discharged Ne; (b) 8.6 mmol Ne:D<sub>2</sub> <sup>18</sup>O=400 codeposited at ~5 K over a period of 157 min with 9.0 mmol discharged Ne. ● — diminishes in intensity on mercury-arc irradiation of the deposit,  $\lambda > 345$  nm.

sorption is derived from the addition of the appropriate rotational energy to the position reported<sup>27</sup> for the gas-phase band center.

When Ne:D<sub>2</sub>O samples were codeposited with discharged neon, a number of new peaks appeared which were readily destroyed by near-ultraviolet radiation. Absorptions near 1040 and 1240  $\text{cm}^{-1}$  for typical Ne:D<sub>2</sub> <sup>16</sup>O and Ne:D<sub>2</sub> <sup>18</sup>O samples are shown in Fig. 5. A pair of closely spaced peaks near 1040  $\text{cm}^{-1}$  was shifted downward by about 7.5  $\text{cm}^{-1}$  on <sup>18</sup>O substitution of the sample. Two approximately equally intense peaks separated by almost 10  $\text{cm}^{-1}$  appeared near 1240  $\text{cm}^{-1}$  and were shifted by about 7  $\text{cm}^{-1}$  on <sup>18</sup>O substitution. Other new peaks, shown in Fig. 6, appeared between 2300 and 2400  $\text{cm}^{-1}$  and near 3200  $\text{cm}^{-1}$ . All of these peaks were weak or very weak, but were reproducibly present. The weak 3206.9  $\text{cm}^{-1}$  absorption of a photolabile species shown in Fig. 6(b) corresponds sufficiently closely with the 3206.5  $\text{cm}^{-1}$  product absorption in the Ne:H<sub>2</sub> <sup>18</sup>O discharge experiments to suggest that the carrier of the absorption in Fig. 6(b) is formed from H<sub>2</sub> <sup>18</sup>O in the sample. The sharp  $\nu_3$  absorption of CO<sub>2</sub>, always present in discharge experiments, can also be seen in Fig. 6, and in Fig. 6(b) sharp absorptions at 2330.8 and 2312.8  $\text{cm}^{-1}$  can be assigned to the  $\nu_3$  absorptions of <sup>16</sup>O <sup>12</sup>C <sup>18</sup>O and <sup>12</sup>C <sup>18</sup>O<sub>2</sub>, respectively, which were impurities in the D<sub>2</sub> <sup>18</sup>O sample. The relatively prominent 2359.7  $\text{cm}^{-1}$  absorption of a photolytically stable species and a satellite absorption at a slightly higher frequency, shown in Fig. 6(a), can be assigned to the 2 $\nu_2$  (1<sub>1,1</sub>-0<sub>0,0</sub>) transition of D<sub>2</sub> <sup>16</sup>O, which also occurs in the gas phase<sup>28</sup> at 2359.7  $\text{cm}^{-1}$ . This absorption, like its H<sub>2</sub>O counterpart, is split by the matrix. In a neon matrix,<sup>24</sup> the <sup>18</sup>O-isotopic shift in  $\nu_2$  of D<sub>2</sub>O amounts to 8.8  $\text{cm}^{-1}$ . Thus, 2 $\nu_2$  (1<sub>1,1</sub>-0<sub>0,0</sub>) of D<sub>2</sub> <sup>18</sup>O should appear near 2342.1  $\text{cm}^{-1}$ . As is

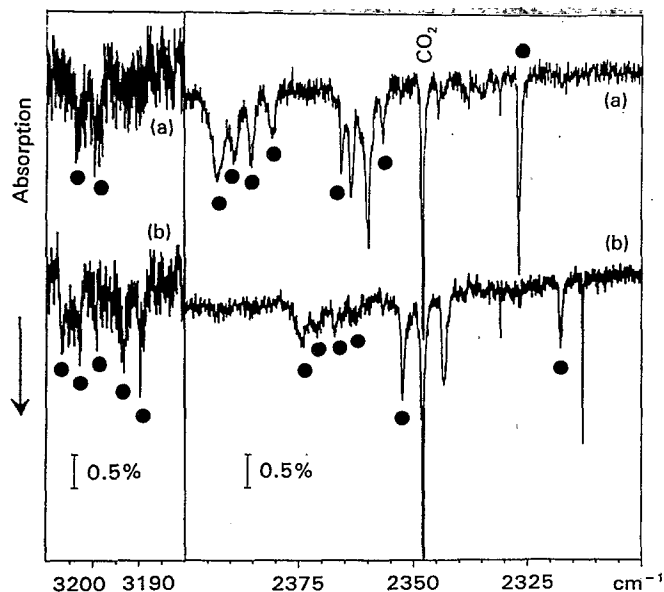


FIG. 6. Oxygen-isotopic dependence of stretching fundamental absorptions of  $\text{HDO}^+$  and  $\text{D}_2\text{O}^+$ . (a) 10.1 mmol  $\text{Ne:D}_2^{16}\text{O}=400$  codeposited at  $\sim 5$  K over a period of 188 min with 9.2 mmol discharged Ne; (b) 8.6 mmol  $\text{Ne:D}_2^{18}\text{O}=400$  codeposited at  $\sim 5$  K over a period of 157 min with 9.0 mmol discharged Ne. ● — diminishes in intensity on mercury-arc irradiation of the deposit,  $\lambda > 345$  nm.

shown in Fig. 6(b), an absorption of a photolytically stable species appears at  $2343.2\text{ cm}^{-1}$ , in satisfactory agreement. Presumably, the high-frequency satellite of this absorption underlies the very prominent  $^{12}\text{C}^{16}\text{O}_2$  peak.

As in the experiments on  $\text{H}_2\text{O}$  samples, a complex pattern of intensity changes in absorptions in the regions of the  $\text{D}_2\text{O}$  and  $\text{HDO}$  fundamentals occurred on near-ultraviolet irradiation of  $\text{Ne:D}_2\text{O}$  samples which had been codeposited with discharged neon. The  $\text{D}_2\text{O}$  and  $\text{HDO}$  bending vibration regions are shown for a  $\text{Ne:D}_2^{16}\text{O}$  sample codeposited with undischarged neon in traces (a) of Fig. 7 and for another sample codeposited with discharged neon in traces 7(b). At the top of Fig. 7, the positions and assignments of low- $J$  rotational transitions associated with  $\nu_2$  of gas-phase  $\text{D}_2^{16}\text{O}$  (Ref. 29) and  $\text{HD}^{16}\text{O}$  (Ref. 30) are indicated. The major change in the spectrum of the discharged sample is the great intensification of the absorptions near the gas-phase band origins of the bending fundamentals of  $\text{D}_2^{16}\text{O}$  and  $\text{HD}^{16}\text{O}$ . When the sample was subsequently exposed to mercury-arc radiation of wavelength longer than 345 nm, these two peaks were greatly reduced in intensity. Much less dramatic changes also occurred in the regions of the stretching fundamentals of  $\text{D}_2\text{O}$  and  $\text{HDO}$ . The positions and approximate relative intensities of all of the photosensitive absorptions characteristic of  $\text{Ne:D}_2^{16}\text{O}$  and  $\text{Ne:D}_2^{18}\text{O}$  samples are summarized in Table II. The rotational assignments given for the two stretching fundamentals of  $\text{D}_2\text{O}$  are based on the gas-phase data of Papineau and co-workers,<sup>28</sup> those for  $\nu_1$  of  $\text{HDO}$  on other gas-phase data of Papineau and co-workers,<sup>31</sup> and those for  $\nu_3$  of  $\text{HDO}$  on the gas-phase data of Toth and Braut.<sup>32</sup>

Although mercury-arc irradiation through a 345 nm

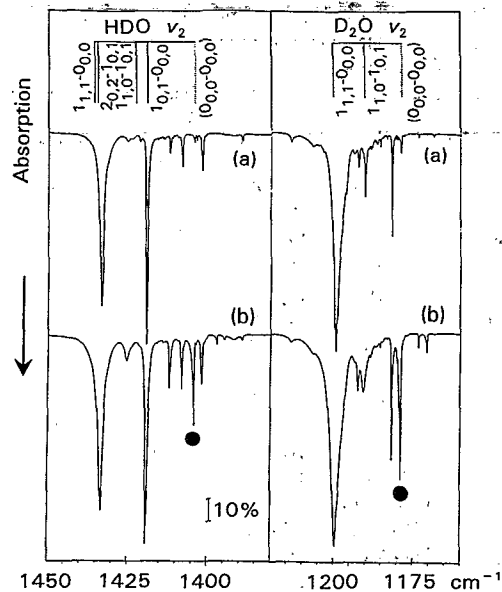


FIG. 7. Dependence of rotational absorptions of  $\nu_2$  of  $\text{HD}^{16}\text{O}$  and  $\text{D}_2^{16}\text{O}$  on the presence of ions in the deposit. (Positions of gas-phase rotational transitions are shown at the top.) (a) 7.24 mmol  $\text{Ne:D}_2^{16}\text{O}=400$  codeposited at  $\sim 5$  K over a period of 138 min with 7.86 mmol undischarged Ne; (b) 10.1 mmol  $\text{Ne:D}_2^{16}\text{O}=400$  codeposited at  $\sim 5$  K over a period of 188 min with 9.2 mmol discharged Ne. ● — diminishes in intensity on mercury-arc irradiation of the deposit,  $\lambda > 345$  nm.

short wavelength cut-off filter was commonly used, several experiments were conducted using irradiation of the deposit through a sequence of filters in order to determine the threshold for the occurrence of the changes in the absorption spectrum summarized in Tables I and II. The onset of all of the changes here reported was observed between 490 and 420 nm. There was no change in the intensities of the water absorptions on filtered or unfiltered mercury-arc irradiation of neon-matrix deposits made without the discharge.

As an aid in determining whether various product absorptions are contributed by cations or anions, a supplementary experiment was conducted in which a  $\text{Ne:H}_2^{16}\text{O:NO}_2=1600:4:1$  sample was codeposited with discharged neon. In addition to the absorptions of  $\text{H}_2^{16}\text{O}$  and  $\text{NO}_2$  and to the product absorptions summarized in the first column of Table I, the spectrum of this sample showed a very strong absorption at  $1241.5\text{ cm}^{-1}$ , readily assigned to  $\text{NO}_2^-$ .<sup>33,34</sup> (Because of the presence of traces of nitrogen and oxygen in the discharge region, this peak appears with weak to moderate intensity in many of the ion generation experiments, including those shown in Fig. 5.) The photodetachment threshold of  $\text{NO}_2^-$  is  $2.273(5)\text{ eV}$ ,<sup>35</sup> considerably higher than that of most anions which contain only hydrogen and oxygen. In this study, there was no change in the intensities of the product absorptions when the sample was exposed to mercury-arc radiation of wavelengths longer than 420 or 345 nm, and only a small change in the product absorptions when a 280 nm cut-off filter (Corning 7740 glass) was used. The absorption of  $\text{NO}_2^-$  and the absorptions which diminished in intensity

TABLE II. Absorptions<sup>a</sup> (cm<sup>-1</sup>) which change in intensity on mercury-arc irradiation ( $\lambda > 345$  nm) of Ne:D<sub>2</sub>O samples which were codeposited with a beam of discharged neon.

D <sub>2</sub> <sup>16</sup> O	D <sub>2</sub> <sup>18</sup> O	Species	Vibration	Rotation assignment
	1032.4vw	D <sub>2</sub> <sup>18</sup> O <sup>+</sup>	$\nu_2$	
	1033.4vw	D <sub>2</sub> <sup>18</sup> O <sup>+</sup>	$\nu_2$	
1040.0w		D <sub>2</sub> <sup>16</sup> O <sup>+</sup>	$\nu_2$	
1040.9w		D <sub>2</sub> <sup>16</sup> O <sup>+</sup>	$\nu_2$	
1170.6m	1170.6s	D <sub>2</sub> <sup>18</sup> O	$\nu_2$	(0 <sub>0,0</sub> -0 <sub>0,0</sub> )
1178.7vs	1178.7wm	D <sub>2</sub> <sup>16</sup> O	$\nu_2$	(0 <sub>0,0</sub> -0 <sub>0,0</sub> )
1190.5wm, +	1190.5vs, +	D <sub>2</sub> <sup>18</sup> O	$\nu_2$	1 <sub>1,1</sub> -0 <sub>0,0</sub>
1199.3vs, +	1199.3m, +	D <sub>2</sub> <sup>16</sup> O	$\nu_2$	1 <sub>1,1</sub> -0 <sub>0,0</sub>
	1229.6w	HD <sup>18</sup> O <sup>+</sup>	$\nu_2$	
	1239.0w	HD <sup>18</sup> O <sup>+</sup>	$\nu_2$	
1236.1w		HD <sup>16</sup> O <sup>+</sup>	$\nu_2$	
1245.7w		HD <sup>16</sup> O <sup>+</sup>	$\nu_2$	
1397.0wm	1397.0s-vs	HD <sup>18</sup> O	$\nu_2$	(0 <sub>0,0</sub> -0 <sub>0,0</sub> )
1404.2s	1404.2wm	HD <sup>16</sup> O	$\nu_2$	(0 <sub>0,0</sub> -0 <sub>0,0</sub> )
	1419.2ms, +	HD <sup>16</sup> O	$\nu_2$	1 <sub>0,1</sub> -0 <sub>0,0</sub>
	2317.7w	D <sub>2</sub> <sup>18</sup> O <sup>+</sup>	$\nu_1$	
2326.4sh		D <sub>2</sub> <sup>16</sup> O <sup>+</sup>	$\nu_1$	
2326.7wm		D <sub>2</sub> <sup>16</sup> O <sup>+</sup>	$\nu_1$	
	2352.3w	HD <sup>18</sup> O <sup>+</sup>	$\nu_1$	
2356.5vw		HD <sup>16</sup> O <sup>+</sup>	$\nu_1$	
2365.6w		HD <sup>16</sup> O <sup>+</sup>	$\nu_1$	
	2367.2w	D <sub>2</sub> <sup>18</sup> O <sup>+</sup>	$\nu_3$	
	2371.0vw	D <sub>2</sub> <sup>18</sup> O <sup>+</sup>	$\nu_3$	
	2374.4w	D <sub>2</sub> <sup>18</sup> O <sup>+</sup>	$\nu_3$	
2380.7vw		D <sub>2</sub> <sup>16</sup> O <sup>+</sup>	$\nu_3$	
2385.2w		D <sub>2</sub> <sup>16</sup> O <sup>+</sup>	$\nu_3$	
2388.8vw		D <sub>2</sub> <sup>16</sup> O <sup>+</sup>	$\nu_3$	
2392.7w		D <sub>2</sub> <sup>16</sup> O <sup>+</sup>	$\nu_3$	
	2620.0w			
2635.8w				
2666.0w	2666.0wm			
2676.8m				
	2684.5m, +	D <sub>2</sub> <sup>18</sup> O	$\nu_1$	1 <sub>1,1</sub> -0 <sub>0,0</sub>
2695.9m, +		D <sub>2</sub> <sup>16</sup> O	$\nu_1$	1 <sub>1,1</sub> -0 <sub>0,0</sub>
	2713.1wm			
	2727.7vs, +	HD <sup>18</sup> O	$\nu_1$	1 <sub>0,1</sub> -0 <sub>0,0</sub>
	2781.4vs, +	D <sub>2</sub> <sup>18</sup> O	$\nu_3$	1 <sub>0,1</sub> -0 <sub>0,0</sub>
	2801.5m, +	D <sub>2</sub> <sup>16</sup> O	$\nu_3$	1 <sub>0,1</sub> -0 <sub>0,0</sub>
	3189.7w	HD <sup>18</sup> O <sup>+</sup>	$\nu_3$	
	3193.4w	HD <sup>18</sup> O <sup>+</sup>	$\nu_3$	
3199.7w	3199.2vw	HD <sup>16</sup> O <sup>+</sup>	$\nu_3$	
3202.9w	3202.9w	HD <sup>16</sup> O <sup>+</sup>	$\nu_3$	
	3206.9w	HD <sub>2</sub> <sup>18</sup> O <sup>+</sup>	$\nu_3$	
	3717.7vs, +	HD <sup>18</sup> O	$\nu_3$	1 <sub>1,1</sub> -0 <sub>0,0</sub>

<sup>a</sup>vw—very weak; w—weak; m—medium; s—strong; vs—very strong; sh—shoulder; br—broad. Peaks which grow on mercury-arc irradiation are designated by +. Other peaks diminish on irradiation.

when the 345 nm filter was used in the Ne:H<sub>2</sub>O studies decreased rapidly in intensity when the sample was exposed to unfiltered mercury-arc radiation. In the presence of NO<sub>2</sub> in the sample, the threshold for the growth of some of the H<sub>2</sub>O absorptions also shifted to approximately 280 nm.

## DISCUSSION

### Infrared spectrum of H<sub>2</sub>O<sup>+</sup>-d<sub>n</sub>

There is considerable evidence to support the assignment of the absorptions at 1401.7, 3182.7, and 3219.5 cm<sup>-1</sup> to the three vibrational fundamentals of H<sub>2</sub> <sup>16</sup>O<sup>+</sup>. As

already noted, the energies of the lowest excited states of the neon atom exceed the ionization potential of H<sub>2</sub>O by approximately 4 eV. The persistence of the three infrared absorptions in studies on samples with a large Ne:H<sub>2</sub> <sup>16</sup>O mole ratio supports their assignment to isolated molecules of an ionic species rather than to an ion complex. The absorption at 1401.7 cm<sup>-1</sup> corresponds closely to the 1408.42 cm<sup>-1</sup> gas-phase band center<sup>14</sup> for ground-state H<sub>2</sub> <sup>16</sup>O<sup>+</sup>. The absorption at 3219.5 cm<sup>-1</sup> deviates by 1.2% from the 3259.03 cm<sup>-1</sup> gas-phase band center<sup>13</sup> of  $\nu_3$  of H<sub>2</sub> <sup>16</sup>O<sup>+</sup>, and the 3182.7 cm<sup>-1</sup> absorption deviates by 0.9% from the 3212.57 cm<sup>-1</sup> gas-phase band center<sup>13</sup> of  $\nu_1$ . Although these deviations are among the largest heretofore observed for molecular ions trapped in solid neon, they are close to the value of 1% within which the ground-state fundamentals of most transient molecules isolated in solid neon fall. The very weak, structured absorption at 1040.0–1040.9 cm<sup>-1</sup> in the Ne:D<sub>2</sub> <sup>16</sup>O experiments also lies close to the 1044.27 cm<sup>-1</sup> gas-phase band center<sup>5</sup> for  $\nu_2$  of D<sub>2</sub> <sup>16</sup>O<sup>+</sup>. Furthermore, in the Ne:D<sub>2</sub> <sup>16</sup>O experiments, there was a product absorption at 2326.7 cm<sup>-1</sup>, which may be compared with the gas-phase value of 2344(6) cm<sup>-1</sup> obtained for  $\nu_1$  of ground-state D<sub>2</sub> <sup>16</sup>O<sup>+</sup> in the relatively high resolution photoelectron spectroscopy study of Reutt and co-workers.<sup>12</sup>

The results of the experiment on a Ne:H<sub>2</sub> <sup>16</sup>O:NO<sub>2</sub> sample are consistent with the contribution of the absorptions at 1401.7 and near 3200 cm<sup>-1</sup> by a cation species. In that study, electrons are readily captured by NO<sub>2</sub> and the energy threshold for their detachment is relatively high. The gas-phase photodetachment threshold for NO<sub>2</sub><sup>-</sup> corresponds to a wavelength of 545 nm. However, the Coulombic interaction between cations and anions in the matrix provides additional stabilization to the ion pair, and the NO<sub>2</sub><sup>-</sup> absorption does not decrease significantly until the sample is exposed to radiation of wavelength near 280 nm. If the three other absorptions are contributed by an anion, their photodetachment threshold should be independent of the presence of NO<sub>2</sub><sup>-</sup>. On the other hand, if they are contributed by a cation which is stable to photodecomposition, the predominant photodestruction mechanism must be electron capture. When most of the electrons are provided by photodetachment of NO<sub>2</sub><sup>-</sup> rather than of an anion with a lower energy photodetachment threshold, the onset of cation photodestruction will occur at the higher NO<sub>2</sub><sup>-</sup> photodetachment threshold, as is observed.

Additional support for the identification not only of H<sub>2</sub>O<sup>+</sup> but also D<sub>2</sub>O<sup>+</sup> and of HDO<sup>+</sup> has been obtained from the results of least-squares force constant adjustment calculations using the program FADJ, developed by Schachtschneider.<sup>36</sup> The structure of H<sub>2</sub>O<sup>+</sup> derived by Dinelli and co-workers<sup>13</sup> was used in the preliminary *G*-matrix calculations, and the four force constants which they calculated for H<sub>2</sub>O<sup>+</sup> were used as the starting point for the adjustment to provide the best fit to the neon-matrix frequencies observed for all three fundamentals of H<sub>2</sub> <sup>16</sup>O<sup>+</sup> and H<sub>2</sub> <sup>18</sup>O<sup>+</sup> and for  $\nu_2$  of the other species. The results of the fit are summarized in Table III. (Most of the absorptions of water cation show complicated structure,



TABLE III. A comparison of observed and calculated<sup>a</sup> fundamentals (cm<sup>-1</sup>) of isotopically substituted H<sub>2</sub>O<sup>+</sup>.

Species	$\nu_1$		$\nu_2$		$\nu_3$	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
H <sub>2</sub> <sup>16</sup> O <sup>+</sup>	3182.7	3182.3	1401.7	1406.8	3219.5	3220.1
H <sub>2</sub> <sup>18</sup> O <sup>+</sup>	3176.8	3177.6	1396.4 <sup>c</sup>	1400.0	3206.5 <sup>c</sup>	3206.0
HD <sup>16</sup> O <sup>+</sup>	2365.6 <sup>b</sup>	2326.3	1236.1	1235.3	3199.7 <sup>b</sup>	3199.4
			1245.7 <sup>b</sup>		3202.9 <sup>b</sup>	
HD <sup>18</sup> O <sup>+</sup>	2352.3 <sup>b</sup>	2313.7	1229.6	1227.7	3189.7 <sup>b</sup>	3189.6
			1239.0 <sup>b</sup>		3193.4 <sup>b</sup>	
D <sub>2</sub> <sup>16</sup> O <sup>+</sup>	2326.7 <sup>b</sup>	2280.9	1040.5 <sup>c</sup>	1035.5	2392.7 <sup>b</sup>	2365.8
D <sub>2</sub> <sup>18</sup> O <sup>+</sup>	2317.7 <sup>b</sup>	2274.2	1032.9 <sup>c</sup>	1026.9	2374.4 <sup>b</sup>	2346.5

<sup>a</sup> $F_{\text{OH}}=5.72 \times 10^2 \text{ N m}^{-1}$ ,  $F_{\text{OH,OH}}=0.05 \times 10^2 \text{ N m}^{-1}$ ;  $F_{\text{HOH}}=0.57 \times 10^{-18} \text{ N m}$ ;  $F_{\text{OH,HOH}}=0.17 \times 10^{-8} \text{ N}$ .

<sup>b</sup>Not used in the fit.

<sup>c</sup>Average of two values separated by 1 cm<sup>-1</sup>.

attributed to multiple trapping sites in the neon matrix. Except where otherwise indicated, the position of the most prominent absorption was used in the fit.) The agreement between the observed and calculated positions of the absorptions which were fitted is excellent, as is that between the observed and calculated positions of the OH-stretching fundamentals of HD<sup>16</sup>O<sup>+</sup> and HD<sup>18</sup>O<sup>+</sup>. Because the anharmonic contributions to OD-stretching fundamentals differ considerably from those to OH-stretching fundamentals, generally the calculated positions of OD-stretching fundamentals are appreciably lower than the observed positions. The deviations shown in Table III for these fundamentals are typical in magnitude and sign. The <sup>18</sup>O-substitution *shift* in the OD-stretching fundamentals should be close to the calculated values, as is observed. Except for the OH-stretching force constant, the final values obtained for the force constants, summarized in a footnote to Table III, agree within the fitting uncertainty with the values obtained for the gas-phase ion by Dinelli and co-workers.<sup>13</sup>

### Intensity changes in H<sub>2</sub>O-*d<sub>n</sub>* absorptions

The assignment of rotational structure to water trapped in the heavier rare-gas matrices has been established for many years. Recently, this assignment has been extended<sup>24</sup> to water trapped in neon matrices. The deviations of the positions of the neon-matrix absorptions from those of the corresponding gas-phase transitions are much smaller than the deviations characteristic of the heavier rare gases. In an argon-matrix study of the photodestruction of ionic species derived from chloroform, Jacox<sup>37</sup> noted a marked dependence of the relative intensities of the  $\nu_2$  rotational transitions of H<sub>2</sub>O on the presence of ions in the system. This phenomenon has since been observed in many other systems and has come to provide a diagnostic for the presence and photodestruction of ions in rare-gas matrices.

In both argon and neon matrices, as ions are destroyed by irradiation of the deposit the absorptions assigned to  $\nu_2$  (<sub>1,1</sub>-0<sub>0,0</sub>) and  $\nu_3$  (<sub>1,0</sub>-0<sub>0,0</sub>) of H<sub>2</sub>O increase significantly in intensity. As shown in Fig. 4(b), the much weaker  $\nu_1$

(<sub>1,1</sub>-0<sub>0,0</sub>) absorption of H<sub>2</sub>O also grows at that stage of the experiment. All of these absorptions arise from the lowest energy nuclear spin configuration (*para*) of H<sub>2</sub>O. On the other hand, the absorptions which arise from H<sub>2</sub>O in the <sub>1,0</sub> rotational state, the lowest rotational level of *ortho*-H<sub>2</sub>O, diminish in intensity. Similar phenomena are noted for D<sub>2</sub>O, although the intensity changes are less marked. The acceleration of nuclear spin conversion in heavier rare-gas matrices when O<sub>2</sub> is added to the sample has been studied by Redington and Milligan<sup>38,39</sup> and by Hopkins and co-workers.<sup>40</sup> Since paramagnetic impurities are effective in this conversion, it is proposed that the interaction of photodetached electrons, which are relatively mobile in the matrix environment, with H<sub>2</sub>O or D<sub>2</sub>O results in rapid nuclear spin equilibration.

In the presence of water cations, the H<sub>2</sub><sup>16</sup>O absorption at 1595.6 cm<sup>-1</sup>, only 0.8 cm<sup>-1</sup> above the gas-phase band origin<sup>23</sup> of the H<sub>2</sub><sup>16</sup>O  $\nu_2$  transition, is greatly intensified. A similar phenomenon is associated with  $\nu_2$  of all of the isotopic species of H<sub>2</sub>O. As ions are removed from the system by near ultraviolet irradiation of the deposit, these absorptions diminish in intensity. The 1595.6 cm<sup>-1</sup> absorption and its counterparts associated with the  $\nu_2$  fundamentals of the isotopic water species have been assigned to "nonrotating" H<sub>2</sub>O trapped in the matrix. Ayers and Pullin<sup>41</sup> have attempted to characterize such nonrotating monomers by adding xenon to Ar:H<sub>2</sub>O samples, thereby introducing lattice disorder without electrostatic effects. This absorption of H<sub>2</sub>O was greatly enhanced when xenon was present. In the Ne:H<sub>2</sub>O experiments considered here, the decrease in the absorption of nonrotating H<sub>2</sub>O as the ions are destroyed, resulting in the formation of uncharged H<sub>2</sub>O, can be attributed to a reduction in the extent of lattice disorder. Molecular rotation may also be inhibited by the ion field, which is strongest before irradiation of the deposit. Since HDO does not possess nuclear spin isomers, the growth in the intensity of the 1419.2 cm<sup>-1</sup> absorption assigned to the HD<sup>16</sup>O  $\nu_2$  (<sub>1,0</sub>-0<sub>0,0</sub>) transition on irradiation of the sample must be attributed to the increase in the fraction of HD<sup>16</sup>O molecules which are able to rotate. (This growth could only be detected when the HD<sup>16</sup>O absorption was of moderate intensity, as in the studies on heavily <sup>18</sup>O-enriched samples. The corresponding absorption in the studies on D<sub>2</sub><sup>16</sup>O samples—and that absorption of HD<sup>18</sup>O in the studies on D<sub>2</sub><sup>18</sup>O samples—were too strong for this intensity change to be seen.)

In the studies of water codeposited with undischarged neon,<sup>24</sup> a weak absorption at 3660.6 cm<sup>-1</sup> was attributed to the  $\nu_1$  transition of nonrotating H<sub>2</sub><sup>16</sup>O. The corresponding transition of H<sub>2</sub><sup>18</sup>O appeared at 3653.3 cm<sup>-1</sup> and that of D<sub>2</sub><sup>16</sup>O appeared at 2672.7 cm<sup>-1</sup>. These absorptions also appeared when the Ne:H<sub>2</sub>O or Ne:D<sub>2</sub>O sample was codeposited with discharged neon, but, as is illustrated in Fig. 4(b), they did not change in intensity on near-ultraviolet irradiation of the deposit. However, a new photosensitive peak appeared at 3665.3 cm<sup>-1</sup>. This peak shifted downward by 7.8 cm<sup>-1</sup>, to 3657.5 cm<sup>-1</sup>, in the Ne:H<sub>2</sub><sup>18</sup>O experiment. The <sup>18</sup>O-isotopic shift for  $\nu_1$  of H<sub>2</sub>O is 7.4 cm<sup>-1</sup>, whereas that for  $\nu_3$  is 14.4 cm<sup>-1</sup>. Thus, the new absorption



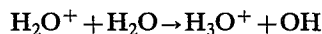
at  $3665.3\text{ cm}^{-1}$  must be assigned to a small perturbation in the  $\nu_1$  vibration of  $\text{H}_2^{16}\text{O}$  rather than to the  $\nu_3$  vibration of the  $\text{H}_2^{16}\text{O}$  moiety in a neutral or ion complex.

Since  $\text{H}_2\text{O}$  can rotate in rare-gas matrices, conceivably  $\text{H}_2\text{O}^+$  may also rotate in that environment. In order to avoid the buildup of a large repulsive potential for deposition of cations in the solid, anions must also be trapped, leading to approximate charge neutrality of the deposit. The resulting cation-anion interactions are likely to inhibit rotation of the ions. These interactions may also contribute to the occurrence of multiple sites in the solid, as evidenced by the broad absorption on the low-frequency side of the  $\nu_3$  peak of  $\text{H}_2^{16}\text{O}^+$  at  $3219.5\text{ cm}^{-1}$  in all but the most dilute samples and by splittings of the absorptions of  $\text{D}_2\text{O}^+$  and  $\text{HDO}^+$ .

### Other products

Several other species which might be expected to appear in these experiments were not detected. Among these are OH and  $\text{OH}^+$ , with gas-phase band centers<sup>42</sup> at  $3568$  and  $2956.3\text{ cm}^{-1}$ , respectively. Because the appearance potential for the formation of  $\text{OH}^+$  from  $\text{H}_2\text{O}$  is  $18.12\text{ eV}$ ,<sup>43</sup> above the  $16.6\text{--}16.8\text{ eV}$  energy range which constitutes most of the output of the neon discharge, that product could not be formed directly from  $\text{H}_2\text{O}$ .  $\text{OH}^-$ , with gas-phase<sup>44</sup> and argon-matrix<sup>45</sup> band centers at  $3555.6$  and  $3554\text{ cm}^{-1}$ , respectively, also was not identified. Furthermore, there was no evidence for the presence of  $\text{H}_3\text{O}^+$ , for which the gas-phase band centers of the three infrared-active vibrational fundamentals have been identified<sup>46-48</sup> at  $954.4$ ,  $1625.95$ , and  $3535.96\text{ cm}^{-1}$ .

The reaction



occurs very rapidly in the gas phase. However, molecular beam studies by Lee and co-workers<sup>49</sup> have established that the dimer ion,  $(\text{H}_2\text{O})_2^+$ , is bound by  $1.58(13)\text{ eV}$  with respect to  $\text{H}_2\text{O}^+ + \text{H}_2\text{O}$  and that this dimer ion requires  $0.52(12)\text{ eV}$  of internal excitation in order to dissociate into  $\text{H}_3\text{O}^+$  and OH. Thus, it is conceivable that  $(\text{H}_2\text{O})_2^+$  might be stabilized in the matrix. In the experiment of Fig. 4, the sharp water dimer absorption on the low frequency shoulder of the  $\text{H}_2\text{O}$   $\nu_3$  ( $0_{0,0}\text{--}1_{0,1}$ ) transition, near  $3735\text{ cm}^{-1}$ , grew as  $\text{H}_2\text{O}^+$  was destroyed. This behavior may have resulted either from electron capture by  $(\text{H}_2\text{O})_2^+$  or from local heating of the sample as a result of exothermic electron capture processes. In a recent theoretical study<sup>50</sup> of  $\text{H}_2\text{O}\cdots\text{Na}^+$  and an experimental study<sup>51</sup> of  $\text{H}_2\text{O}\cdots\text{Mg}^+$ , which might serve as models for the behavior of the  $\text{H}_2\text{O}$  moiety in complexes with small cations, the  $\nu_3$  transition of the  $\text{H}_2\text{O}$  moiety was lowered to a value near  $3665\text{ cm}^{-1}$ . However, as already noted, the photosensitive absorption which we have observed at that position must be assigned to  $\nu_1$  of the  $\text{H}_2\text{O}$  moiety, implying that there is only a very weak interaction of  $\text{H}_2\text{O}$  with the perturbing or complexing species.

The nature of the anion species in these experiments has not been definitively established. Although the Fourier transform ion cyclotron resonance measurements of de

Koning and Nibbering<sup>52</sup> gave a signal for  $\text{H}_2\text{O}^-$ , subsequent *ab initio* calculations<sup>53</sup> indicated that the most stable structure should be linear  $\text{H}_2\cdots\text{O}^-$ , bound by approximately  $0.2\text{ eV}$ . Recent theoretical<sup>54</sup> and experimental<sup>55-58</sup> studies suggest that  $(\text{H}_2\text{O})_2^-$  may be stable by about  $0.1\text{ eV}$ . In order to explain the relatively high photolytic stability of  $\text{H}_2\text{O}^+$  in the neon-matrix experiments, other anions with higher photodetachment thresholds must be present. Among these might be  $\text{OH}^-$ , with a photodetachment threshold<sup>59</sup> of  $1.83\text{ eV}$ . As already noted, the concentration of this species was below the threshold for detection of its infrared absorption. Another possible anion would be  $\text{O}^-$ , with a photodetachment threshold<sup>60,61</sup> of  $1.46\text{ eV}$ . This species is infrared-inactive. Since small atomic species can diffuse to some extent through the rare-gas lattice,  $\text{O}^-$  may react relatively readily in the matrix. Among the possible reaction products would be  $\text{O}_2^-$ , which has a photodetachment threshold<sup>62</sup> of  $0.44\text{ eV}$ . In a neon matrix, all of these anions would be further stabilized by Coulombic interaction with nearby cations. The threshold for the photodestruction of  $\text{H}_2\text{O}^+$  isolated in solid neon is similar to that previously observed<sup>16</sup> for  $\text{O}_4^+$  in a neon matrix. In the latter system,  $\text{O}_2^-$  must be the predominant anion.

### CONCLUSIONS

A sufficient concentration of  $\text{H}_2\text{O}^+$  was stabilized in these experiments for detection of all three of its vibrational fundamentals. Furthermore, deuterium-substitution studies have led to the first definitive identification of all three vibrational fundamentals of  $\text{HDO}^+$  and of  $\nu_3$  of  $\text{D}_2\text{O}^+$ . Although the bending fundamentals of  $\text{H}_2^{16}\text{O}^+$  and  $\text{D}_2^{16}\text{O}^+$  appear close to the gas-phase band centers, the two stretching fundamentals of  $\text{H}_2^{16}\text{O}^+$  isolated in solid neon appear approximately  $1\%$  below the gas-phase band centers, suggesting that there should be a similar matrix shift for the stretching fundamentals of  $\text{HDO}^+$  and  $\text{D}_2\text{O}^+$ . Under the sampling conditions of these experiments, the formation of  $\text{H}_3\text{O}^+$  is inhibited. Photodestruction of  $\text{H}_2\text{O}^+$  is accompanied by growth in the absorptions of rotating  $\text{H}_2\text{O}$  which arise from the  $0_{0,0}$  rotational level of the ground vibrational state. This phenomenon is attributed to acceleration of nuclear spin equilibration by the relatively mobile electrons photodetached from anions. In the presence of  $\text{H}_2\text{O}^+$ , rotation of  $\text{H}_2\text{O}$  in the neon matrix is partially inhibited. The nature of the anion species which provide for overall charge neutrality of the sample has not been definitively established.

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