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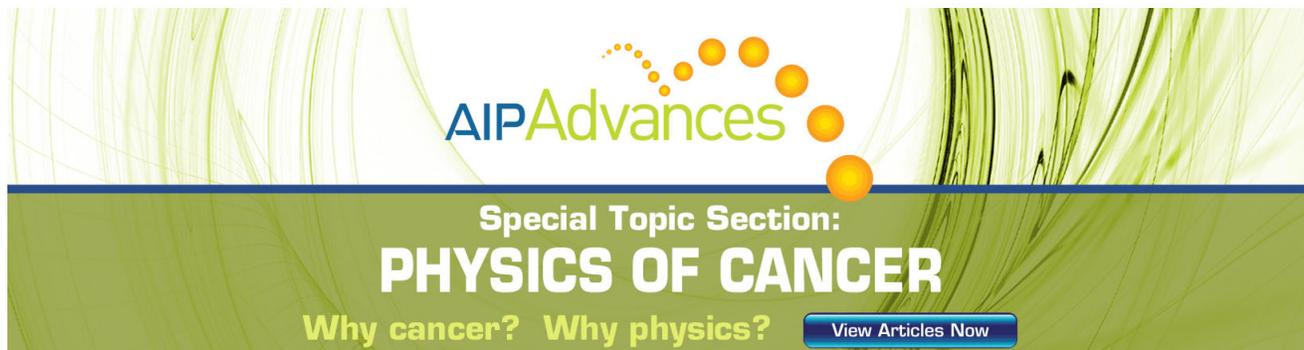
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The infrared spectrum of HOOH^+ trapped in solid neon

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When a $\text{Ne:H}_2\text{O}_2$ mixture is codeposited at 4.3 K with a beam of neon atoms that have been excited in a microwave discharge, three new, photosensitive absorptions appear which can be assigned to the three infrared-active vibrational fundamentals of *trans*- HOOH^+ . When the $\text{Ne:H}_2\text{O}_2$ deposition system is pretreated with the vapors of D_2O , the product absorptions include new peaks which can be attributed to vibrational fundamentals of *trans*- HOOD^+ and *trans*- DOOD^+ . Density functional calculations of the vibrational fundamentals of the three hydrogen peroxide cation isotopologues support the proposed assignments. Broad, photosensitive product absorptions also appear near the positions of vibrational transitions of O_3^- , and may be contributed by a weakly bound complex of that species with H_2O . [<http://dx.doi.org/10.1063/1.4757389>]

I. INTRODUCTION

Because of the ease with which hydrogen peroxide decomposes, studies of the properties of this molecule—of fundamental interest—have been especially difficult. Much also remains to be learned about the properties of the ions produced from it in high-energy processes such as those which occur during combustion and in the terrestrial ionosphere, planetary atmospheres, and interstellar matter.

Measurement of the photoelectron spectrum of hydrogen peroxide by Osafune and Kimura¹ provided the first information about the electronic energy levels of HOOH^+ . Their observations determined that the first excited state of HOOH^+ lies approximately $16\,800\text{ cm}^{-1}$ above the onset of ionization and its second excited state approximately $38\,400\text{ cm}^{-1}$ above that onset. Later photoelectron studies by Brown² and by Ashmore and Burgess³ confirmed those values and yielded an adiabatic ionization energy of 10.62 eV for the uncharged molecule. More recently, photoionization measurements by Litorja and Ruscic⁴ refined the value for the first ionization energy of HOOH to 10.631(7) eV. Using their measurements together with known thermochemical quantities, these workers determined the appearance energy of HO_2^+ from H_2O_2 and calculated the appearance energies of H_2O^+ and OH^+ from H_2O_2 . Ruscic and co-workers⁵ subsequently reanalyzed the appearance energy of HO_2^+ from H_2O_2 , obtaining a slightly revised value.

Molecular orbital calculations have provided a powerful tool for further advancing our understanding of the structure and energy levels of HOOH^+ and its fragment ions. Takeshita and Mukherjee⁶ obtained an ionization energy that was reasonably close to the observed value for H_2O_2 and a planar structure with the *trans*- configuration for the $\tilde{X}^2\text{B}$ ground state of the cation. Later calculations on HOOH^+ by Xie and co-workers⁷ using a wide variety of computational procedures

reaffirmed the *trans*- structure for the ground-state cation. Subsequent refinements in the *ab initio* calculations of the vibrational energy levels of *trans*- HOOH^+ were reported by Hrušák and Iwata,⁸ and density functional calculations were conducted by Litorja and Ruscic.⁴

Following on experimental studies and preliminary calculations suggesting that oxywater, H_2OO , might be stable, Huang and co-workers⁹ performed high-level calculations which yielded a potential minimum for a C_s structure, with the plane of symmetry bisecting the HOH angle. They also calculated vibrational frequencies for oxywater. At about the same time, calculations by Xie and co-workers⁷ found an H_2OO^+ isomer with C_s symmetry approximately 23 kcal/mol (96 kJ/mol) above the ground state of *trans*- HOOH^+ . Collisional activation, charge reversal, and neutralization-reionization experiments by Schröder and co-workers¹⁰ support the occurrence of oxywater. A more recent collisionally activated dissociation mass spectrometry study by de Petris and co-workers¹¹ suggested the presence of oxywater cation, but direct observation of that species—like that of oxywater—has not yet been achieved.

A series of experiments in this laboratory has succeeded in stabilizing sufficient concentrations of a wide variety of small molecular ions trapped in solid neon at 4.3 K for detection of their infrared absorptions.^{12,13} Among the earliest of this series of experiments was one in which prominent infrared absorptions of O_4^+ and O_4^- were identified when a dilute Ne:O_2 gas mixture was codeposited with a beam of neon atoms that had been excited in a microwave discharge.¹⁴ Experiments conducted using partial O-18 enrichment demonstrated that with our experimental configuration backstreaming of the O_2 into the discharge region is minimal. Similar experiments on H_2O and on O_3 samples have led to the spectroscopic identification of H_2O^+ and O_3^- , respectively.^{15,16} The ion products observed in all of the experiments are consistent with the predominant role of neon atoms in their first excited states, between 16.6 and 16.85 eV, in leading to molecular ionization. Electrons produced on cation formation are captured in various ion traps in the solid deposit. The

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results of a search for the ions produced from hydrogen peroxide are presented in this paper.

II. EXPERIMENTAL DETAILS

Following on the report by Cooper and co-workers¹⁷ that the vapor over a complex of urea with hydrogen peroxide (UHP) provides a safe, convenient source of anhydrous H₂O₂, Pettersson and co-workers¹⁸ used UHP for studies of the spectroscopy and photochemistry of hydrogen peroxide trapped in rare-gas matrices. For the present studies, we obtained UHP in pellet form from Fisher Scientific Co.¹⁹ The outer surface was trimmed from a pellet, and a portion of the interior material was pulverized. In the early experiments, the UHP powder was transferred to a freezeout tube, placed on the vacuum manifold, heated to the desired temperature using a water bath, and pumped on for a prolonged period of time. During the ensuing deposition, a constant pressure of neon (Spectra Gases, Inc., Research Grade, 99.999%) was introduced into the manifold, where it mixed with the UHP vapor over the warmed solid. The resulting Ne:UHP mixture flowed through a metering valve into the deposition line and was codeposited with a beam of pure neon that had been excited in a microwave discharge. A revised procedure for sampling the UHP was found to give a more consistent yield of ion products. The pulverized UHP was introduced into a 54-cm length of 1/4 in. o.d. perfluoroalkoxy tubing, which is very nonreactive and is usable for low-pressure systems over a relatively large temperature range. The tube was then fashioned into a “U” and connected to a straight length of similar tubing using a pair of nylon vacuum T-couplings. One end of the straight length was attached to a neon reservoir maintained at a constant pressure and the other to a metering valve, which then led to the cryostat deposition inlet. The U-tube was maintained at 60 ± 5 °C during sample outgassing but was cooled to room temperature before starting the deposition. Deuterium enrichment was achieved by repeated exposure of the manifold, prepurified solid in the U-tube, and deposition line to approximately 10 Torr of D₂O for times ranging from minutes to hours, followed by heating and pumping on the solid, cooling to room temperature, and codeposition with the discharged neon.

The Ne:H₂O₂ mixtures were codeposited at 4.3 K with a similar amount of pure neon that had been excited by a microwave discharge before streaming through a 1 mm pinhole in the end of a quartz discharge tube. Details of the deposition procedure and of the discharge configuration have been described previously.²⁰

The absorption spectra of the sample deposits were obtained using a Bomem DA 3.002 Fourier-transform interferometer with transfer optics that have been described previously.²¹ All of the observations were conducted at a resolution of 0.2 cm^{-1} between 450 and 5000 cm^{-1} using a globar source, a KBr beamsplitter, and a wide-band HgCdTe detector cooled to 77 K. Data were accumulated for each spectrum over a period of at least 15 min. The resulting spectrum was ratioed against a similar one taken without a deposit on the cryogenic mirror. Under these conditions, the positions of the prominent, nonblended atmospheric water vapor lines between 1385 and 1900 cm^{-1} and between 3620 and

3900 cm^{-1} , observed in a calibration scan, agreed to within 0.01 cm^{-1} with the high-resolution values reported by Toth.²² Based on previous investigations, with this experimental configuration the standard uncertainty (type B) in the determination of the absorption maxima for molecules trapped in solid neon is $\pm 0.1 \text{ cm}^{-1}$ (coverage factor, $k = 1$, i.e., 1σ).

Information on photoinduced changes in the matrix sample was obtained by exposing the deposit to various wavelength ranges of near infrared, visible, and ultraviolet radiation. A tungsten background source was used with a filter of Corning glass type 2403 to exclude radiation of wavelength shorter than 630 nm. Irradiations were also conducted using a medium-pressure mercury arc source with a filter of Corning glass type 3389, 7380, 7740, or 7058 to exclude radiation of wavelength shorter than 420, 345, 280, or 260 nm, respectively. Irradiations were also conducted using unfiltered medium-pressure mercury arc emission, estimated to have a cutoff wavelength near 240 nm.

III. RESULTS AND DISCUSSION

A. Infrared spectrum of H₂O₂

As in studies reported by other workers, the hydrogen peroxide produced from UHP was free from major contaminants, except that some of it decomposed into water and oxygen in the stainless steel deposition line used for our experiments. With a constant neon pressure of approximately 80 Torr over the UHP sample, maintained at approximately 60 °C, a suitable amount of Ne:H₂O₂ was deposited in 3 h for the appearance of very prominent H₂O₂ fundamental absorptions. The positions of these H₂O₂- d_n absorptions are compared in Table I with the gas-phase positions summarized by Koput and co-workers,²³ with a recent helium droplet study,²⁴ and with argon-matrix values.¹⁸ Some of the frequencies in Table I were from gas-phase²⁵ and argon-matrix²⁶ Raman studies by Giguère and Srinivasan.

As in the experiments of Pettersson and co-workers,¹⁸ absorptions of dimeric hydrogen peroxide were also present. These have been the subject of a detailed argon-matrix study by Engdahl and co-workers.²⁷ Absorptions of the complex of water with hydrogen peroxide, previously studied by Engdahl and Nelander,²⁸ also appeared near the more prominent absorptions of isolated water and hydrogen peroxide.

B. Products of the discharge experiments

In all of the discharge experiments, weak absorptions of O₃, HO₂,²⁹ H₂O⁺,¹⁵ and *trans*- and *cyc*-O₄⁺^{14,30} appear. All but one of the remaining absorptions, which have a photodestruction threshold near 345 nm, are shown in Figure 1. These absorptions fall into two classes. A set of broad absorptions (marked by open circles) is more prominent, and sharp absorptions at 857.4 and 3237.0 cm^{-1} (marked by filled circles) are less prominent in experiment (a) than in experiment (b). The remaining sharp absorption contributes a 1273-cm^{-1} shoulder-marked by an arrowhead-on the high-frequency side of the very strong H₂O₂ absorption shown in trace (a) of Figure 2. This shoulder reproducibly disappears on

TABLE I. Ground-state vibrational transitions (cm^{-1}) of HOH-d_n between 450 and 4000 cm^{-1} .

Isotopologue	Vib. No.	Gas phase ^a	Helium droplet ^b	Neon matrix ^c	Argon matrix ^d	
HOOH	1	3617.95	3617.1		3593 ^e	
		3609.8				
	2	1393.5 ^f	865.0		1385 ^e	
	3	877.93				
	5	865.94	3619		3597.0	
		3618.84				
6	3610.66	3610.22	3609	3587.8		
	1273.68					
DOOD	6	1264.58		1271.2	1277.0	
		981		981.2	1266.9	1270.9
DOOD	1	2668 ^f			2653.5 ^e	
		2				1029 ^f
	3	867 ^f			871 ^e	
	5	2661			2655.7	2651.3
					2645.3	2645.3
	6	947			948.8	951.3

^aUnless otherwise noted, studies summarized by Ref. 23.

^bReference 24.

^cThis work. Based on previous investigations, the standard uncertainty is 0.1 cm^{-1} (1σ) except for the absorptions at 3609 and 3619 cm^{-1} , which have an estimated uncertainty of 1 cm^{-1} .

^dUnless otherwise noted, Ref. 18.

^eReference 26.

^fReference 25.

irradiation of the deposit through a 345 nm cutoff filter. As is shown in traces (b) and (c) of Figure 2, successive increase in the extent of deuterium enrichment results in the appearance of the labeled OD-bending absorptions of HOOD and D_2O_2 between 940 and 990 cm^{-1} and in alteration of the absorption pattern between 1260 and 1300 cm^{-1} because of the contribution of absorption by the OH-bending fundamental of HOOD. Figure 3 shows other spectral regions in which new photosensitive absorptions appear on deuterium enrichment, observed in the same three experiments for which portions of the spectrum are shown in Figure 2. Several new absorptions are marked by filled circles. The broad absorptions of Figure 1 show little change in the deuterium enrichment studies.

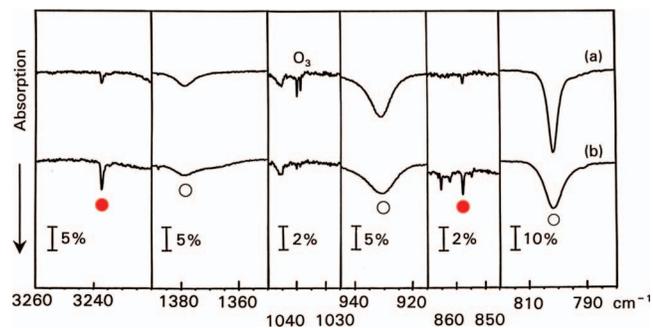


FIG. 1. Product absorptions in studies of the infrared spectra of Ne:UHP samples that were codeposited with a beam of discharged neon atoms. ●, ○ Peaks with photodestruction threshold near 345 nm. See text. (a) 7.43 mmol Ne:UHP mixture prepared using the freezeout tube setup (see text) and codeposited at 4.3 K over a period of 142 min with 7.49 mmol neon that had been excited in a microwave discharge. (b) 3.68 mmol Ne:UHP mixture prepared using the U-tube configuration (see text) and codeposited at 4.3 K over a period of 65 min with 3.79 mmol neon that had been excited in a microwave discharge.

In discharge experiments such as this, studies of the photolysis of the initial deposit by filtered near infrared, visible, and ultraviolet light often yield valuable information for identification of the products of discharge excitation. Because H_2O_2 is photolyzable, possible contributions from its photolysis must also be considered. The photoproduction of OH from

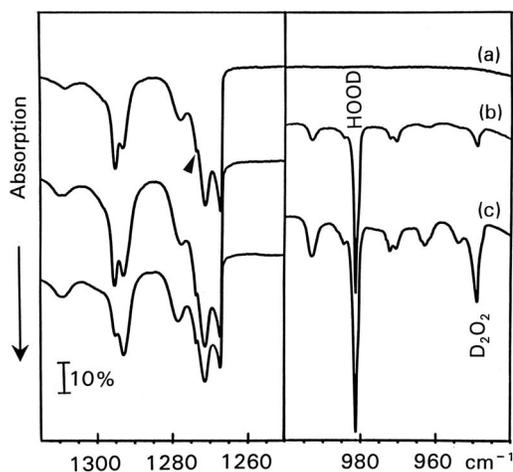


FIG. 2. Absorptions of normal and deuterium-enriched H_2O_2 deposits in a neon matrix. The shoulder at 1273.5 cm^{-1} , marked by an arrowhead, is photosensitive, and is attributed to the product marked in Figure 1 by red circles. (a) 3.68 mmol Ne:UHP mixture prepared using the U-tube configuration (see text) and codeposited at 4.3 K over a period of 65 min with 3.79 mmol neon that had been excited in a microwave discharge. (b) 6.44 mmol Ne:UHP mixture prepared using the U-tube configuration (see text) after repeated exposure to D_2O and codeposited at 4.3 K over a period of 151 min with 5.43 mmol neon that had been excited in a microwave discharge. (c) 14.45 mmol Ne:UHP mixture prepared using the U-tube configuration (see text) after repeated exposure to D_2O and codeposited at 4.3 K over a period of 354 min with 11.95 mmol neon that had been excited in a microwave discharge.

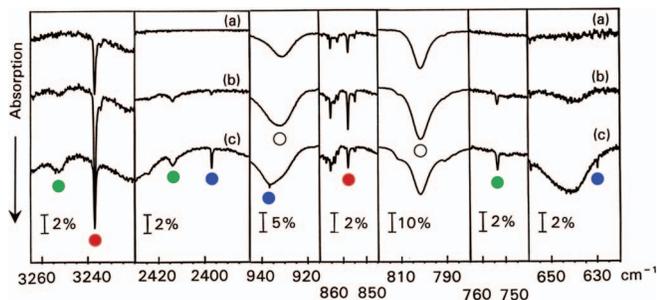


FIG. 3. Photosensitive product absorptions in studies of the infrared spectra of Ne:UHP samples with successively greater deuterium enrichment that were codeposited with a beam of discharged neon atoms. (a)–(c) For experimental conditions, see captions to Figures 2(a)–2(c). ● (Red) *trans*- HOOH^+ ; ● (green) *trans*- HOOD^+ ; ● (blue) *trans*- DOOD^+ ; open circles, weakly bound complex of O_3^- with H_2O (tentative).

H_2O_2 is well known and is an important first step in the oxidation of atmospheric molecules during the daylight hours. Recent observations by Kahan and co-workers³¹ have extended the range of gas-phase H_2O_2 absorption to wavelengths as long as 410 nm. In rare-gas matrices, this photodecomposition process would be severely inhibited by cage recombination of the resulting OH.

An argon-matrix study by Khriachtchev and co-workers³² using photolysis wavelengths ranging from 193 to 380 nm reported the production of OH and of the complex of an O atom with H_2O . No absorptions of HO_2 were detected. The OH evidently is formed with sufficient kinetic energy for some of it to escape the cage in which it is produced. They propose that cage recombination of pairs of OH results in the formation of H_2O and O atoms, which form a photosensitive van der Waals complex with infrared absorptions at 3731 and 3633 cm^{-1} . On prolonged irradiation, its absorptions and those of H_2O_2 decrease, and the OH absorption continues to grow. The gas-phase photoelectron spectrum of $\text{H}_2\text{O} \cdots \text{O}^-$ obtained by Arnold and co-workers³³ showed a band separation of 3629 cm^{-1} , consistent with the argon-matrix assignment. Photosensitive absorptions which correspond to those reported for $\text{H}_2\text{O} \cdots \text{O}$ were not detected in the present study. The infrared band centers for the absorptions of gas-phase OH and OD were reported by Amano³⁴ at 3569.64 and 2632.06 cm^{-1} , respectively. The corresponding transitions for those species trapped in a neon matrix, obtained in the emission spectra studied by Tinti,³⁵ lie at 3572.8 and 2632.7 cm^{-1} . They did not appear in the infrared spectra of our initial deposits, but a small amount of OH may have been formed upon unfiltered mercury-arc irradiation of the deposit.

Later infrared studies^{36,37} extended the results to observations of the photolysis of H_2O_2 trapped in the heavier rare gases. Although they found matrix-dependent variation in the products, none of the infrared studies show the absorption pattern obtained in the high-level *ab initio* vibrational frequency calculations for oxywater conducted by Huang and co-workers.⁹

Pehkonen and co-workers³⁶ reported that ultraviolet photolysis of dimeric (or multimeric) HOOH in an argon matrix results in stabilization of the $\text{HOO} \cdots \text{HOH}$ complex.

TABLE II. Appearance energies at 0 K of various cations from hydrogen peroxide.

Cation	eV	Reference
HOOH^+	10.631(7)	4
H_2O^+	13.728(3)	4
HO_2^+	15.095(26)	5
OH^+	15.174(4)	4

The spectrum of that species agrees with that reported by Nelander,³⁸ who found that in an argon matrix the absorptions of the H_2O moiety in that complex lie at 3691 and 3501.5 cm^{-1} and fundamental absorptions of the HOO moiety at 3236.2, 1479.3, and 1120.4 cm^{-1} . There is no evidence in the present study for the stabilization of this complex.

Irradiation of an ion-containing deposit with visible and near-ultraviolet light is especially useful for finding infrared absorptions of ion products. In addition to possible photodissociation, both cations and anions are susceptible to destruction by photoinduced charge recombination. Most anions possess low electron photodetachment thresholds. The electrons released by their photodetachment may diffuse through the rare-gas solid, resulting in cation neutralization.

Litorja and Ruscic⁴ reported the values summarized in Table II for the appearance energies of HOOH^+ and of several of its fragment ions. Even at 73.6 nm (16.85 eV), the effective high energy cutoff in the present experiments, they found that H_2O_2^+ remains the predominant cation product.

Most of our understanding of the spectroscopic properties of H_2O_2^+ has arisen from *ab initio* calculations. An early study performed by Takeshita and Mukherjee⁶ at the SCF level, including configuration interaction, indicated that the $\tilde{X}^2\text{B}$ ground state of the cation is planar, with the *trans*- configuration. The onset of ionization of H_2O_2 was estimated to occur at about 10.5 eV, in reasonable agreement with the currently accepted value. The onset of the $\tilde{A}^2\text{A}$ state, which is also planar but has the *cis*- configuration, lies at an energy about 2 eV higher. Using a wide variety of sophisticated computational procedures, Xie and co-workers⁷ again found the *trans*- structure of H_2O_2^+ to be lowest in energy, with the *cis*-structure approximately 8 kcal/mol (33 kJ/mol) higher in energy. The *trans*- to *cis*- torsional barrier was approximately 32 kcal/mol (134 kJ/mol). Because of symmetry breaking, *ab initio* calculations on H_2O_2^+ at several levels encountered difficulty, surmounted by using Brueckner methods. A subsequent study by Hrušák and Iwata⁸ further explored the problem of symmetry breaking and found that the most satisfactory results were obtained for the BD(T), CASSCF, and B3LYP calculations. A short time later, Litorja and Ruscic⁴ also obtained similar results from their density functional calculations at the B3LYP level for *trans*- HOOH^+ .

The first information about the vibrational spectrum of H_2O_2^+ was obtained from the photoelectron spectroscopic experiments of Brown and co-workers² and of Ashmore and co-workers,³ who assigned structure in the ground-state photoelectron band to a progression in the totally symmetric deformation fundamental with a spacing of 1080(50) cm^{-1} .

TABLE III. Structures calculated for *trans*-HOOH⁺.

Coordinate	BD(T)/cc-pVTZ ^a	CASSCF(13,10)/cc-pVDZ ^a	UB3LYP/cc-pVTZ ^{a,b}
R _{OH} (Å)	1.001	1.005	0.996
R _{OO} (Å)	1.322	1.332	1.310
α _{HOO}	103.2°	102.7°	104.5°
τ _{HOOH}	180°	180°	180°

^aReference 8.^bThis work.

Analysis of the infrared study of H₂O₂⁺-*d_n* reported in this paper was facilitated by calculations of the isotopic substitution behavior of the vibrational fundamentals of *trans*-HOOH⁺ using the GAUSSIAN 09 program package.³⁹ The positions of the ground-state fundamentals were obtained by density functional calculations using the unrestricted B3LYP procedure⁴⁰ together with the correlation-consistent polarized valence triple-zeta basis set (cc-pVTZ) developed by Dunning.⁴¹

The calculated structures of *trans*-HOOH⁺ obtained by Hrušák and Iwata⁸ and in this work are compared in Table III. A similar structure was also obtained by Litorja and Ruscic.⁴ The OH bond lengths are unusually large, consistent with OH-stretching fundamentals which are anomalously low in frequency. The vibrational frequencies which resulted on scaling the presently calculated values by a factor of 0.965 (a typical scaling factor for UB3LYP/cc-pVTZ calculations) are summarized in Table IV.

Proton sharing of hydride cations with rare-gas atoms or matrices may lead to a large shift in the stretching vibration fundamental of the participating H atom. The phenomenon

TABLE IV. Observed^a and calculated^b vibrational fundamental absorptions (cm⁻¹) of ground-state *trans*-HOOH⁺-*d_n*.

Isotopologue	Vibration	Calculated	Observed
HOOH ⁺	ν ₁ (a _g)	3319.4(0)	
	ν ₂ (a _g)	1534.7(0)	
	ν ₃ (a _g)	1199.8(0)	1080 ± 50 ^c
	ν ₄ (a _u)	834.7(321)	857.4 wm
	ν ₅ (b _u)	3298.3(645)	3237.0 m
	ν ₆ (b _u)	1267.0(238)	1273.5 sh ^d
HOOD ⁺	ν ₁	3308.9(316)	3252.8 wm
	ν ₂	2414.3(164)	2413.4 wm
	ν ₃	1437.1(64)	
	ν ₄	1198.3(0.2)	
	ν ₅	1002.8(107)	1014.6 w
	ν ₆	730.0(235)	753.1 wm
DOOD ⁺	ν ₁ (a _g)	2426.3(0)	
	ν ₂ (a _g)	1197.2(0)	
	ν ₃ (a _g)	1155.3(0)	
	ν ₄ (a _u)	607.7(148)	629.6 w
	ν ₅ (b _u)	2401.2(312)	2396.5 wm
	ν ₆ (b _u)	922.4(108)	936.3 vw

^aNeon matrix. This work. Based on previous investigations, the standard uncertainty is 0.1 cm⁻¹ (1σ). The approximate relative intensities observed in the experiment of Figure 3(c) are included. (vw—very weak; w—weak; wm—weak to medium; m—medium).

^bUB3LYP/cc-pVTZ. Scaled by 0.965. Calculated infrared absorption intensities (km/mol) are given in parentheses.

^cReferences 2 and 3.

^dShoulder on H₂O₂ absorption. Tentative identification.

has been discussed by Bieske and Dopfer⁴² and by Jacox.¹² The proton affinity of HO₂, 660 kJ/mol, is large compared to that of neon, 198.8 kJ/mol.⁴³ Their difference, 461 kJ/mol, lies in the region of the plot given by Jacox where the expected frequency shift due to proton sharing by the cation with the neon matrix approaches zero.

Table IV includes the positions of the product absorptions marked by filled circles or by an arrowhead in Figures 1–3. The agreement is sufficiently good to support the assignment of these absorptions to *trans*-HOOH⁺ and its deuterium-substituted isotopologues. As predicted by the calculations, the position of the infrared-active OH-stretching fundamental is anomalously low. The appearance of the OH- and OD-stretching fundamentals of *trans*-HOOD⁺ slightly above the infrared-active OH- and OD-stretching fundamentals of *trans*-HOOH⁺ and *trans*-DOOD⁺ is consistent with the relative positions predicted by the calculations. The appearance of the 1273.5 cm⁻¹ absorption, tentatively assigned to ν₆ of *trans*-HOOH⁺, very near the calculated frequency, is consistent with that assignment. The appearance of a weak absorption at 936.3 cm⁻¹ in the most heavily deuterium-enriched deposit, close to the calculated position of ν₆ of *trans*-DOOD⁺ and of a weak absorption at 1014.6 cm⁻¹ (not shown in the figures) of the closely related absorption of *trans*-HOOD⁺ are consistent with the assignment given in Table IV. The large frequency shift of the 857.4-cm⁻¹ absorption supports its assignment to the torsion vibration of *trans*-HOOH⁺, rather than to an OO-stretching vibration of some other product, for which the expected shift on deuterium enrichment should be small. The breadth of the absorptions of *trans*-HOOD⁺ is greater than that of the absorptions assigned to *trans*-HOOH⁺ and *trans*-DOOD⁺, possibly because of the lower symmetry of *trans*-HOOD⁺.

Conceivably, the oxywater cation may contribute to the product spectrum in the present experiments. Xie and co-workers⁷ located a pyramidal H₂OO⁺ structure with C_s symmetry approximately 23 kcal/mol (96 kJ/mol) above the ground state of *trans*-HOOH⁺. They also calculated the spectral positions of the ground-state oxywater cation at several different levels with various basis sets. Their calculations suggest that the relatively prominent OH-stretching fundamentals of H₂OO⁺ should lie in the spectral region typical for OH-stretching vibrations, where they may be obscured by prominent absorptions of H₂O, H₂O₂, and molecular complexes involving those two species. Two other oxywater fundamentals have somewhat lower calculated intensities. With allowance for anharmonicity, one of them may be obscured by the prominent ν₂ absorption of water between about 1595 and 1635 cm⁻¹. An approximately equally intense oxywa-

ter absorption should lie between about 650 and 700 cm^{-1} . The remaining two fundamental absorptions should be weak. There is little evidence to support the stabilization of oxywater cation in the present experiments.

Another possible cation product is HO_2^+ . Although Dyke and co-workers⁴⁴ assigned a progression in the first photoelectron band of HO_2 to the OO-stretching absorption of HO_2^+ , beyond the first band the structure was blurred. The bands were also indistinct in the photoionization spectrum obtained by Litorja and Ruscic,⁴ suggesting that autoionization occurs in that region of excitation energy. The low-lying \tilde{a}^1A' state of HO_2^+ may play a significant role in the observed broadening. Their B3LYP calculations of the positions of the fundamental vibrations of ground-state HO_2^+ yielded values which agreed well with the values ($\nu_1 = 3066.6$, $\nu_2 = 1071.5$, $\nu_3 = 1361.6 \text{ cm}^{-1}$) subsequently obtained in the anharmonic MRCI calculations by Robbe and co-workers.⁴⁵ The multi-reference configuration interaction (MRCI) study also determined that the origin of the \tilde{a}^1A' state of HO_2^+ should lie only about 1185 cm^{-1} above the ground-state origin.

The proton affinity of O_2 is only 421 kJ/mol,⁴³ sufficiently close to that of neon or helium for proton sharing with the rare gas to cause a substantial shift in the OH-stretching fundamental of HO_2^+ . Nizkorodov and co-workers⁴⁶ observed a difference of 144 cm^{-1} between the OH-stretching frequency of HO_2^+ complexed with helium and that of HO_2^+ complexed with neon. A linear plot of the positions of the OH-stretching mode of HO_2^+ complexed with a neon atom and with a helium atom against the polarizability of the rare-gas atom suggested that ν_1 of gas-phase HO_2^+ should lie at 3020(40) cm^{-1} , in reasonable agreement with the value calculated by Robbe and co-workers.⁴⁵ The ν_1 fundamental of HO_2^+ complexed with a single neon atom appeared at 2761 cm^{-1} . It is likely that this absorption would appear at a somewhat higher frequency when the HO_2^+ is surrounded by neon atoms in a cryogenic solid. In the present experiments, no absorption attributable to HO_2^+ appeared near 1072 or 1362 cm^{-1} or between 2750 and 2850 cm^{-1} .

Another possible fragment cation in these experiments is OH^+ . Its high-resolution ultraviolet emission spectrum was studied by Merer and co-workers.⁴⁷ A subsequent infrared absorption study by Crofton and co-workers⁴⁸ located the OH^+ band center at 2956.37 cm^{-1} , in close agreement with the position found in the earlier study. The proton affinity of the O atom is 485.2 kJ/mol,⁴³ sufficiently low to predict that OH^+ will engage in significant proton sharing when it interacts with a neon atom. The gas-phase infrared predissociation spectroscopy of OH^+ complexed to a single atom of helium or of neon was studied by Roth and co-workers,⁴⁹ who found a shift to a frequency below that of the diatomic cation of 66 or 170 cm^{-1} on complex formation with helium or neon, respectively. This places the $\text{OH}^+ \cdots \text{Ne}$ absorption at 2786.5 cm^{-1} . No absorption near that position appeared in the present series of experiments.

Still another fragment cation which could be produced from H_2O_2 in the present experiments is H_2O^+ . Weak absorptions of that species are present, but may have resulted from ionization of H_2O in the deposit.

In order to preserve overall charge neutrality of the solid deposit when cations are trapped, anions must also be present. The simplest likely infrared-active molecular anion is OH^- . Two laboratories⁵⁰ have reported a gas-phase photodetachment threshold of 1.827 eV for this species. The gas-phase OH^- band center was located by Owrutsky and co-workers⁵¹ at 3555.59 cm^{-1} . Subsequently, Rehfuss and co-workers⁵² located the OD^- band center at 2625.33 cm^{-1} . These positions are only slightly different from those for the corresponding uncharged species, 3569.64 and 2632.06 cm^{-1} , respectively. Several prominent OH- and OD-stretching vibrations of other species appear near these two anion absorptions in the neon-matrix experiments. Therefore, definitive identification of OH^- and OD^- is not presently possible.

Another potential anion in these experiments is HO_2^- . Because the electron affinity of HO_2 is 1.078(6) eV,⁵³ in solid neon it is estimated that ready photodestruction of HO_2^- should occur on irradiation of the deposit through a 420-nm cutoff filter. The positions calculated at the restricted coupled-cluster singles and doubles with triples included perturbatively (RCCSD(T)) level by Horn and co-workers⁵⁴ for the vibrational fundamentals of HO_2^- , corrected for anharmonicity, are $\nu_1 = 3585.1$, $\nu_2 = 1072.8$, and $\nu_3 = 727.7 \text{ cm}^{-1}$. Identification of the OH-stretching absorption of HO_2^- , like that for OH^- , is not feasible in these experiments. Absorptions that correspond to the two lower frequency fundamentals have not been identified.

In a comparative density functional and *ab initio* study of the $[\text{H}_2\text{O}_2]^-$ potential surface, Hrušák and co-workers⁵⁵ found that attachment of an electron to ground-state uncharged hydrogen peroxide is endothermic by approximately 58 kcal/mol (243 kJ/mol). The global potential minimum on the surface being studied is for the $\text{H}_2\text{O} \cdots \text{O}^-$ complex. The potential barrier between it and the ion-dipole complex, $\text{OH} \cdots \text{OH}^-$ is small, implying that the latter structure would be difficult to characterize. These results are consistent with those obtained in an earlier experimental study by Lifshitz.⁵⁶ The photoelectron spectroscopic study by Arnold and co-workers³³ obtained a vertical detachment energy of 2.94 eV for $\text{H}_2\text{O} \cdots \text{O}^-$.

Finally, since a small amount of O_3 is detected in these experiments, O_3^- may also be present. The gas-phase photodetachment threshold for that anion lies at 2.10 eV,⁵⁷ a value sufficiently high to be consistent with onset of its photodestruction in solid neon with a threshold near 345 nm. The photoelectron study by Arnold and co-workers,⁵⁸ as well as the earlier studies, are consistent with values of $\nu_1 = 975(50) \text{ cm}^{-1}$ and of $\nu_2 = 550(50) \text{ cm}^{-1}$ for gas-phase O_3^- . Several workers have identified the ν_3 absorption of O_3^- trapped in rare-gas matrices very near 800 cm^{-1} . Lugez and co-workers¹⁶ have summarized these studies. They found that in a neon matrix O_3^- has a sharp, very prominent absorption at 796.3 cm^{-1} , with a less intense satellite at 795.0 cm^{-1} and considerably weaker peaks at 793.7 and 792.9 cm^{-1} . A weak to moderately intense peak at 800.0 cm^{-1} is attributed to a complex of O_3^- with an unidentified species. Subsequently, Lee and co-workers⁵⁹ conducted CCSD(T) calculations for O_3^- using basis sets up to aug-cc-pVQZ. These calculations yield a harmonic vibrational frequency for the antisymmetric

stretching fundamental, ν_3 , that is 70 cm^{-1} or more higher than the neon-matrix value, and the anharmonic frequency correction increases the disparity. Arnold and co-workers had determined a value of $880(50)\text{ cm}^{-1}$ from sequence bands observed in an unpublished study of the spectrum of vibrationally excited O_3^- cited in their photoelectron spectroscopy paper, noted above. Lee and colleagues suggested that this fundamental may be exceptionally sensitive to the environment of the anion. Recently, Bopp and co-workers⁶⁰ obtained the vibrational predissociation spectra between 700 and 2400 cm^{-1} for O_3^- complexed with an argon atom. Absorption of that complex was found at $797(5)\text{ cm}^{-1}$. Their spectra of larger O_n^- anions for which n is an odd number gave absorption maxima within 1 cm^{-1} of that value, indicating that complexation of O_3^- with one or more O_2 molecules shifts this fundamental of O_3^- very little.

Assignment of the three broad, photosensitive absorptions shown in Figure 1 to vibrational transitions of a weakly bound complex of O_3^- with H_2O or another species trapped in the solid is proposed. The suitability of the observed photodestruction threshold to this assignment has already been discussed. The positions of these three absorptions are insensitive to the introduction of deuterium into the system. The two lower frequency absorptions correspond well with the positions found for ν_3 and ν_1 of O_3^- , and the weaker absorption near 1380 cm^{-1} lies close to the anticipated position of the $\nu_3 + \nu_2$ combination band.

IV. CONCLUSIONS

The interaction of $16.6\text{--}16.85\text{ eV}$ neon atoms with H_2O_2 followed by rapid quenching of the products in a neon matrix leads to the appearance of two distinct sets of infrared absorptions. One set of absorptions is contributed by *trans*- HOOH^+ . The positions observed for the three infrared-active vibrational fundamentals of *trans*- HOOH^+ are consistent with the values obtained from *ab initio* and density functional calculations. On deuterium enrichment of the sample, absorptions characteristic of the corresponding fundamentals of *trans*- HOOD^+ and *trans*- DOOD^+ also appear. Consideration of the properties of other potential ion products suggests that the second set of absorptions is contributed by a weakly bound complex of O_3^- with H_2O or another species in the solid.

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