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Infrared Detection of HO_2 and HO_3 Radicals in Water Ice

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Infrared spectroscopy has been used to detect HO_2 and HO_3 radicals in $H_2O + O_2$ ice mixtures irradiated with 0.8 MeV protons. In these experiments, HO_2 was formed by the addition of an H atom to O_2 and HO_3 was formed by a similar addition of H to O_3. The band positions observed for HO_2 and HO_3 in H_2O-ice are 1142 and 1259 cm^{-1}, respectively, and these assignments were confirmed with $^{18}O_2$. HO_2 and HO_3 were also observed in irradiated $H_2O + O_3$ ice mixtures, as well as in irradiated H_2O_2 ice. The astronomical relevance of these laboratory measurements is discussed.

Introduction

Although the hydroperoxy (HO_2) radical has long been known to be produced in irradiated water ice,[1] its infrared (IR) spectral detection in H_2O is challenging. Because HO_2 is a strong hydrogen-bonding species,[2] with O−H stretching absorption bands likely to occur in the same spectral region as, and be dominated by, strong broad water features, most IR studies of HO_2 have been confined to its trapping in inert gas matrixes.[3] Furthermore, the reactivity of HO_2, coupled with the relative insensitivity of IR spectroscopy, make it difficult to establish an IR-detectable concentration of this radical in solid H_2O-ice. Recent work by Ignatov et al.,[4] has suggested the formation of HO_2 in UV-irradiated $H_2O + O_3$ ices in the 3200−3600 cm^{-1} region, but their results are not conclusive.

The problems that plague the condensed-phase study of HO_2 also apply to HO_3. Recent work has identified HO_3 at ambient temperatures in the gas-phase using neutralization-reionization mass spectrometry[5] and Fourier transform microwave spectroscopy.[6] It was shown that at ambient temperatures HO_3 has an appreciable gas-phase lifetime ($>10^{-6}$ s) and is not merely a momentary complex.[5] HO_3 also has been detected in the infrared, but only when isolated in an Ar matrix.[7] Direct detection in the more-reactive H_2O matrix has not been reported but is desirable because HO_3 has possible roles in atmospheric chemistry[8] and has been implicated as a bactericidal oxidant by Wentworth et al.[9] Previous work suggests that HO_3, as well as HO_2, can form strong hydrogen bonds to water[10,11] and that such bonds might actually stabilize these radicals.[11]

Beyond the areas already mentioned, HO_2 and HO_3 are also of interest in planetary science, and it is on this area that we focus. Frozen water is the dominant ice on surfaces in the outer solar system (e.g., those on the Galilean and Saturnian icy satellites) as well as on interstellar grains. Such bodies range in temperature from ∼100 to ∼10 K, respectively, and exist in a variety of photon-, electron- and ion-radiation environments. IR spectroscopy has played a major role in characterizing the composition of these ices and was the tool used to identify H_2O_2, a radiation product, on the surface of Europa.[12] Small UV and visible signatures of two other radiation products, O_2 and O_3, also have been identified in spectra of the Galilean and Saturnian satellites.[13−16] However, identifying radiation products and unraveling their chemistry remain important challenges for planetary chemists.

Experimental Methods

Ice samples typically were prepared by mixing the appropriate gas-phase components in a vacuum manifold, using standard manometric techniques, followed by deposition onto a polished, cold aluminum substrate. The substrate, situated in a high-vacuum chamber ($\sim 1 \times 10^{-7}$ Torr), could be cooled to 9 K by an APD HC-4 closed-cycle helium refrigerator. The thickness of each ice sample (∼ 3 μm) was determined by laser interferometry. The 0.8 MeV protons used for irradiations were produced from a Van de Graaff accelerator at the Goddard Radiation Facility, and infrared spectra of the ices were measured using a Nicolet Nexus 670 spectrometer at 4 cm^{-1} spectral resolution. Millipore-purified water was degassed by several freeze−pump−thaw cycles before use. Research-grade $^{16}O_2$ (Matheson Tri-Gas) was used as received, as was $^{18}O_2$ (Isotec; purity of >97%). Ozone was synthesized by a Tesla-coil discharge in a glass bulb containing 100 Torr of O_2 and trapped in liquid nitrogen before use. Urea−hydrogen peroxide (Aldrich) was heated to 313 K to produce H_2O_2 vapor. This was deposited directly onto the precooled substrate via an attachment to the outside of the cryostat, therefore avoiding any decomposition of H_2O_2 on the metal surfaces of the vacuum manifold. For additional experimental details, see ref 17.

Results and Discussion

Recent experiments in our laboratory on 0.8 MeV H^+-irradiated $H_2O + O_2$ ice mixtures (H_2O:O_2 ratios of ∼6:1[18]) at 9 K show previously unassigned IR features at 1142 and 1259 cm^{-1} after a dose of 0.6 eV/16 atomic mass units (amu).[19] These

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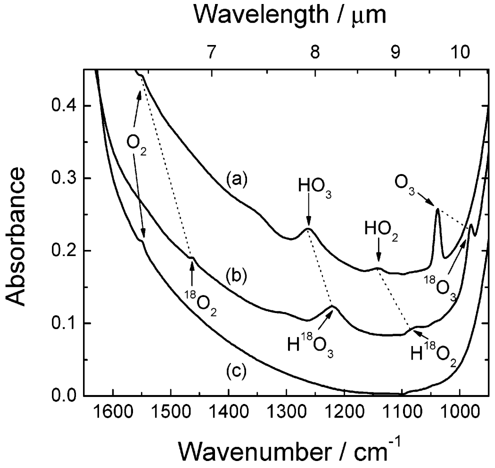

Figure 1. Infrared spectra of (a) 6:1 $H_2O + O_2$ and (b) 6:1 $H_2O + {}^{18}O_2$ ice mixtures irradiated with 0.8 MeV H^+ at 9 K to a dose of 0.6 eV/16 amu. The IR spectrum of unirradiated 6:1 $H_2O + O_2$ is shown in (c).

TABLE 1: Vibrational Frequencies for HO_2 and HO_3 Absorption Bands in Water-Ice Compared with Those in an Argon Matrix (2, 6)

	$\tilde{\nu}_3(H^{16}O_2)$ (cm^{-1})	$\tilde{\nu}_3(H^{18}O_2)$ (cm^{-1})	isotopic shift (cm^{-1})	$\tilde{\nu}_3(H^{16}O_2)/\tilde{\nu}_3(H^{18}O_2)$
in H_2O−ice	1142	1078	64	1.059
in Ar	1101.3	1039.7	61.6	1.0592
matrix shift (cm^{-1})	41	38		

	$\tilde{\nu}(H^{16}O_3)$ (cm^{-1})	$\tilde{\nu}(H^{18}O_3)$ (cm^{-1})	isotopic shift (cm^{-1})	$\tilde{\nu}(H^{16}O_3)/\tilde{\nu}(H^{18}O_3)$
in H_2O−ice	1259	1220	39	1.032
in Ar	1223	1190	33	1.028
matrix shift (cm^{-1})	36	30		

absorptions are shown in Figure 1. H_2O_2 and O_3 were also produced and observed as absorptions at 2850 and 1040 cm^{-1} respectively. The band intensities at 1142 and 1259 cm^{-1} decreased as the irradiated sample was warmed, and disappeared by ~100 K. To help identify these absorptions, the experiment was repeated using $H_2O + {}^{18}O_2$, whereon the bands shifted to 1078 and 1220 cm^{-1}, respectively.

Table 1 summarizes the isotopic shifts for the 1142 and 1259 cm^{-1} features and compares them to data reported for HO_2 and HO_3. The ^{18}O isotopic shifts of 39 and 64 cm^{-1} we observed in H_2O-ice compare favorably with those for HO_2 and HO_3, respectively, in solid argon. Our table's final column shows that the ratios of band positions, $^{16}O/^{18}O$, also agree closely with results for HO_2 and HO_3 in argon. The small discrepancy in the ratio of positions for HO_3 in ice and Ar may be due to the different lattices slightly altering the relative contributions of bending and stretching components[7] in the observed vibrational mode. In any case, the results summarized in Table 1 strongly suggest assignments of the 1142 and 1259 cm^{-1} IR bands to HO_2 and HO_3, respectively.

Supporting these spectral assignments are the matrix shifts, H_2O-ice to argon, of Table 1. These show a consistent value of 35 ± 6 cm^{-1} for all four isotopologues, a similarity suggesting that HO_2 and HO_3 hydrogen bond similarly in H_2O-ice. Furthermore, the absolute values of the matrix shifts are reasonable. In the case of HO_2, this radical bonds to a single water molecule in a cyclic way, similar to that of the water dimer, so that its H atom acts as a hydrogen bond donor (i.e., $OOH\cdots OH_2$) and its terminal O atom acts as a hydrogen bond acceptor (i.e., $HOO\cdots HOH$).[2] Consequently, the ν_3 mode of HO_2 (OO stretch) is sensitive to shifts of vibrational frequency due to hydrogen bond interactions with the ice lattice. Previous work has shown that the ν_3 band of HO_2 shifts ~19 cm^{-1} upon complexation of this radical with a single H_2O molecule.[2] The influence of many H_2O molecules, such as an ice matrix, will enhance the shift so that the values in Table 1 are about as expected.

Our spectral assignments are also consistent with the initial composition of the ice mixture and the known radiation chemistry of water. Ionizing radiation results in, among other things, decomposition of H_2O molecules into H and OH radicals, so that HO_2 can form by an H-addition reaction to O_2 as follows:

$$H + O_2 \rightarrow HO_2 \tag{1}$$

Alternatively, HO_2 might also form through the reaction

$$O + OH \rightarrow HO_2 \tag{2}$$

Here, OH is produced from the dissociation of water molecules and O is produced from the dissociation of O_2. However, in $H_2O + {}^{18}O_2$ experiments reaction 2 would produce an $H^{16}O^{18}O$ molecule and we see no evidence for this.

In pure water, HO_2 is usually considered to be produced from the abstraction of H from H_2O_2, formed previously by OH-radical dimerization:

$$OH + OH \rightarrow H_2O_2 \tag{3}$$

$$H_2O_2 + OH \rightarrow HO_2 + H_2O \tag{4}$$

We do observe H_2O_2 formation in our ices by the growth of an absorption at ~2850 cm^{-1}, but the HO_2 band at 1142 cm^{-1} appears at low doses when the H_2O_2 feature is still very weak. With the high abundance of O_2 molecules in our $H_2O + O_2$ ices, an H-addition reaction to O_2 seems more likely, particularly because H-addition reactions have been observed in other H^+-irradiated ices.[20−22] Previous work in this laboratory[20] found a substantial enhancement of the H_2O_2 yield in irradiated H_2O-ice when O_2 was added, an enhancement presumably due to the sequential addition of two H atoms to O_2 through an HO_2 intermediate. The present observations indicate that HO_2 is forming in this manner, supporting the earlier proposed mechanism for H_2O_2 production in $H_2O + O_2$ mixtures.[20]

An assignment of the 1259 cm^{-1} band to HO_3 suggests that this radical might also form by an H-addition reaction, this time to O_3 produced radiolytically from the O_2 present in the ice mixture.

$$H + O_3 \rightarrow HO_3 \tag{5}$$

To test this possibility, we synthesized ozone and performed radiation experiments with $H_2O + O_3$ ices at 9 K. A 1259 cm^{-1} band was observed after ion irradiation, shifting to 1220 cm^{-1} when $^{18}O_3$ was used. Figure 2 shows that in our $H_2O + O_3$ experiments the intensity of the 1259 cm^{-1} band *decreased* with increasing dose, a behavior consistent with an HO_3 assignment. At higher doses, less HO_3 was produced because much of the O_3 precursor had been destroyed. As expected, HO_2 also was observed (at 1142 cm^{-1}, 1078 cm^{-1} when $^{18}O_3$ was used) in irradiated $H_2O + O_3$ ice mixtures, probably due to H-addition to O_2 made from irradiated O_3. Consistent with the assignments was the observation that the HO_2 band did not decrease in intensity like HO_3. This clearly shows that the two bands are from two different species. The HO_2 and HO_3 bands also were seen after pure H_2O_2 ices (prepared from the thermal decomposition of the urea−H_2O_2 complex) were ion-irradiated at 9

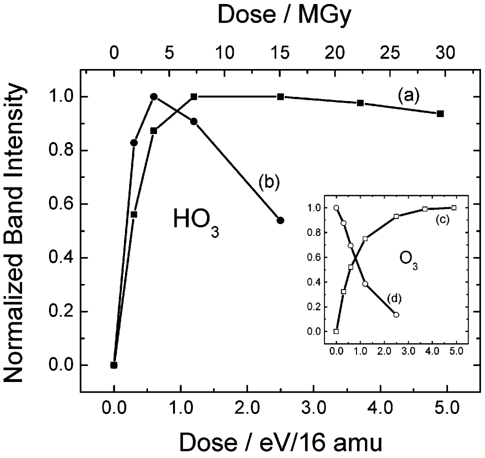

Figure 2. Normalized intensities of the HO_3 absorption band produced from (a) 6:1 $H_2O + O_2$ and (b) 5:1 $H_2O + O_3$ ice mixtures as a function of radiation dose. For comparison, the inset shows normalized intensities vs dose for the 1040 cm^{-1} O_3 absorption band in (c) 6:1 $H_2O + O_2$ and (d) 5:1 $H_2O + O_3$ ice mixtures.

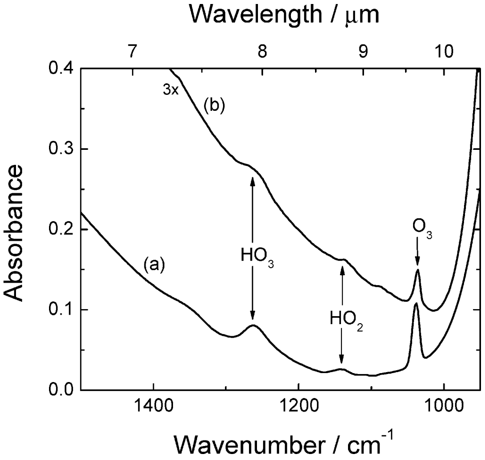

Figure 3. Infrared spectra of 6:1 $H_2O + O_2$ ice mixtures irradiated with 0.8 MeV H^+ at (a) 9 K and (b) 80 K to a dose of 0.6 eV/16 amu.

K. Here, O_2 and O_3 presumably were produced by the radiolytic destruction of H_2O_2, followed by H-addition to form HO_2 and HO_3. It is also possible that some HO_2 was made through reaction 4.

The 9 K low-temperature experiments so far described might not fully represent the radiolytic processes occurring on the surfaces of icy Galilean or Saturnian satellites, which have temperatures in the 65−130 K region. As already stated, the HO_2 and HO_3 we observed was retained when the irradiated H_2O-ice was warmed from 9 to ~100 K, but do these radicals *form and persist* at temperatures typical of the Jovian and Saturnian systems? We repeated our experiments with a 6:1 $H_2O + O_2$ mixture deposited at 9 K but subsequently warmed and irradiated at 80 K. Figure 3 compares spectra from our 9 and 80 K experiments and shows that HO_2 and HO_3 also are produced at the higher temperature, although their band intensities are smaller than at 9 K. At 80 K, hydrogen is lost from the sample more efficiently, as H_2, than at 9 K because the H atom mobility is greater. In addition, above ~30 K, some O_2 is lost from the ice because of sublimation. Evidence for this was seen as an increase in the vacuum chamber pressure at 30 K, and in the disappearance of the 1550 cm^{-1} O_2 absorption above this temperature. The smaller HO_2 and HO_3 intensities at 80 K also might be caused by destruction processes, such as radical−radical reactions with OH, or even other HO_2 and HO_3, which are efficiently trapped at 9 K.

We also note that the present work clears up a minor mystery in the literature. An earlier paper by Gerakines et al.[23] listed band positions for HO_2 in H_2O-ice that are essentially identical to those for HO_2 trapped in argon. However, the data in our Table 1 show that HO_2 undergoes substantial hydrogen-bonding to H_2O, with matrix shifts near 40 cm^{-1}. Thus we believe that the HO_2 reported earlier[23] was actually HO_2 measured in Ar layers that enveloped the ice sample. A similar detection, and an unexpected absence of a matrix effect, was reported for two OH bands,[23] features now known to be from site effects induced by an Ar matrix on the OH stretch of an $H_2O{\cdot}HO$ complex.[24]

Conclusions

In summary, we have assigned spectral bands at 1142 and 1259 cm^{-1} in irradiated $H_2O + O_2$ ices, at both 9 and 80 K, to HO_2 and HO_3, respectively. With a re-interpretation of previous work,[22] this is the first such detection of either radical in H_2O-ice by IR spectroscopy. These species, which persist to ~100 K, are also produced in irradiated $H_2O + O_3$ and H_2O_2 ices, and are formed from H-addition reactions to O_2 and O_3. Consequently, we believe that HO_2 and HO_3 can form on Galilean and Saturnian icy satellites, contributing to the inventory of oxidants. Along with O_2, O_3, and H_2O_2, the HO_2 and HO_3 radicals will have the ability to oxidize other molecules, such as organics, or even provide a source of chemical energy to sustain microbial life.[25] Beyond our solar system, HO_2 and HO_3 probably also form by UV and cosmic-ray bombardment of ice grains in the interstellar medium and in proto-planetary disks.

The HO_2 and HO_3 radicals have been overlooked by astrochemists and planetary scientists but appear to readily form in irradiated water ices containing O_2. Thus these radicals should be considered in future theoretical models of ice radiation processes. For observational astronomers, our experimental results confirm theoretical predictions of the stability of HO_3 in the presence of H_2O molecules,[11] and imply that both HO_2 and HO_3 radicals could exist in extraterrestrial environments. Both species should be sought in astronomical observations of icy bodies.

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(18) A relatively high O_2 fraction has been used to enable the detection of the title radicals. However, although the 6:1 ratio exceeds the abundance of O_2 on any known satellite, there is spectroscopic evidence[13] that O_2 is present at high densities on a small scale, and under such circumstances HO_2 and HO_3 may form.

(19) The radiation dose is standardized to units of eV/16 amu to facilitate meaningful comparison between ice mixtures of varying constituents. Note that 1 eV/16-amu-molecule is ∼600 Mrad or ∼6.00 MGy.

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