

Infrared Detection of HO₂ and HO₃ Radicals in Water Ice

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Infrared spectroscopy has been used to detect HO₂ and HO₃ radicals in H₂O + O₂ ice mixtures irradiated with 0.8 MeV protons. In these experiments, HO₂ was formed by the addition of an H atom to O₂ and HO₃ was formed by a similar addition of H to O₃. The band positions observed for HO₂ and HO₃ in H₂O-ice are 1142 and 1259 cm⁻¹, respectively, and these assignments were confirmed with ¹⁸O₂. HO₂ and HO₃ were also observed in irradiated H₂O + O₃ ice mixtures, as well as in irradiated H₂O₂ ice. The astronomical relevance of these laboratory measurements is discussed.

Introduction

Although the hydroperoxy (HO₂) radical has long been known to be produced in irradiated water ice,¹ its infrared (IR) spectral detection in H₂O is challenging. Because HO₂ 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 HO₂ have been confined to its trapping in inert gas matrixes.³ Furthermore, the reactivity of HO₂, coupled with the relative insensitivity of IR spectroscopy, make it difficult to establish an IR-detectable concentration of this radical in solid H₂O-ice. Recent work by Ignatov et al.,⁴ has suggested the formation of HO₂ in UV-irradiated H₂O + O₃ ices in the 3200–3600 cm⁻¹ region, but their results are not conclusive.

The problems that plague the condensed-phase study of HO₂ also apply to HO₃. Recent work has identified HO₃ at ambient temperatures in the gas-phase using neutralization-reionization mass spectrometry⁵ and Fourier transform microwave spectroscopy.⁶ It was shown that at ambient temperatures HO₃ has an appreciable gas-phase lifetime (>10⁻⁶ s) and is not merely a momentary complex.⁵ HO₃ also has been detected in the infrared, but only when isolated in an Ar matrix.⁷ Direct detection in the more-reactive H₂O matrix has not been reported but is desirable because HO₃ has possible roles in atmospheric chemistry⁸ and has been implicated as a bactericidal oxidant by Wentworth et al.⁹ Previous work suggests that HO₃, as well as HO₂, can form strong hydrogen bonds to water^{10,11} and that such bonds might actually stabilize these radicals.¹¹

Beyond the areas already mentioned, HO₂ and HO₃ 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 H₂O₂, a radiation product, on the surface of Europa.¹² Small UV and visible signatures of two other radiation products, O₂ and O₃, 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 (~1 × 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 ¹⁶O₂ (Matheson Tri-Gas) was used as received, as was ¹⁸O₂ (Isotec; purity of >97%). Ozone was synthesized by a Tesla-coil discharge in a glass bulb containing 100 Torr of O₂ and trapped in liquid nitrogen before use. Urea–hydrogen peroxide (Aldrich) was heated to 313 K to produce H₂O₂ vapor. This was deposited directly onto the precooled substrate via an attachment to the outside of the cryostat, therefore avoiding any decomposition of H₂O₂ 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 H₂O + O₂ ice mixtures (H₂O:O₂ ratios of ~6:1¹⁸) 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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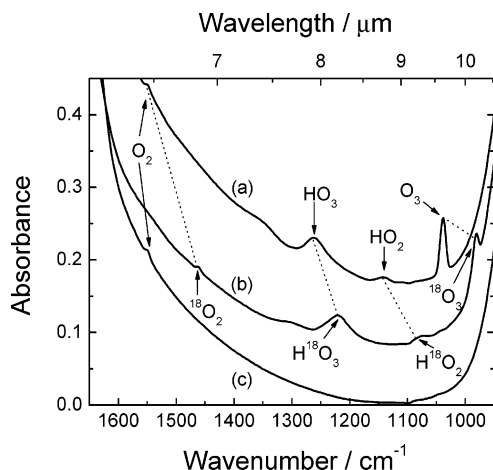


Figure 1. Infrared spectra of (a) 6:1 H₂O + O₂ and (b) 6:1 H₂O + ¹⁸O₂ ice mixtures irradiated with 0.8 MeV H⁺ at 9 K to a dose of 0.6 eV/16 amu. The IR spectrum of unirradiated 6:1 H₂O + O₂ is shown in (c).

TABLE 1: Vibrational Frequencies for HO₂ and HO₃ Absorption Bands in Water-Ice Compared with Those in an Argon Matrix (2, 6)

| | $\tilde{\nu}_3(\text{H}^{16}\text{O}_2)$ (cm ⁻¹) | $\tilde{\nu}_3(\text{H}^{18}\text{O}_2)$ (cm ⁻¹) | isotopic shift (cm ⁻¹) | $\tilde{\nu}_3(\text{H}^{16}\text{O}_2)/$ $\tilde{\nu}_3(\text{H}^{18}\text{O}_2)$ |
|----------------------------------|---|---|---------------------------------------|---|
| in H ₂ O-ice | 1142 | 1078 | 64 | 1.059 |
| in Ar | 1101.3 | 1039.7 | 61.6 | 1.0592 |
| matrix shift (cm ⁻¹) | 41 | 38 | | |
| | $\tilde{\nu}(\text{H}^{16}\text{O}_3)$ (cm ⁻¹) | $\tilde{\nu}(\text{H}^{18}\text{O}_3)$ (cm ⁻¹) | isotopic shift (cm ⁻¹) | $\tilde{\nu}(\text{H}^{16}\text{O}_3)/$ $\tilde{\nu}(\text{H}^{18}\text{O}_3)$ |
| in H ₂ O-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. H₂O₂ and O₃ 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 H₂O + ¹⁸O₂, 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 HO₂ and HO₃. The ¹⁸O isotopic shifts of 39 and 64 cm⁻¹ we observed in H₂O-ice compare favorably with those for HO₂ and HO₃, respectively, in solid argon. Our table's final column shows that the ratios of band positions, ¹⁶O/¹⁸O, also agree closely with results for HO₂ and HO₃ in argon. The small discrepancy in the ratio of positions for HO₃ in ice and Ar may be due to the different lattices slightly altering the relative contributions of bending and stretching components⁷ 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 HO₂ and HO₃, respectively.

Supporting these spectral assignments are the matrix shifts, H₂O-ice to argon, of Table 1. These show a consistent value of 35 ± 6 cm⁻¹ for all four isotopologues, a similarity suggesting that HO₂ and HO₃ hydrogen bond similarly in H₂O-ice. Furthermore, the absolute values of the matrix shifts are reasonable. In the case of HO₂, 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...OH₂) and its terminal O atom acts as a hydrogen bond acceptor (i.e., HOO...HOH).² Consequently, the ν_3 mode of HO₂ (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 HO₂ shifts ~19 cm⁻¹ upon complexation of this radical with a single H₂O molecule.² The influence of many H₂O 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 H₂O molecules into H and OH radicals, so that HO₂ can form by an H-addition reaction to O₂ as follows:

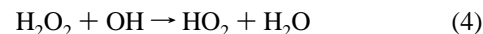
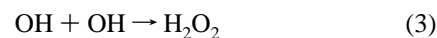


Alternatively, HO₂ might also form through the reaction



Here, OH is produced from the dissociation of water molecules and O is produced from the dissociation of O₂. However, in H₂O + ¹⁸O₂ experiments reaction 2 would produce an H¹⁶O¹⁸O molecule and we see no evidence for this.

In pure water, HO₂ is usually considered to be produced from the abstraction of H from H₂O₂, formed previously by OH-radical dimerization:



We do observe H₂O₂ formation in our ices by the growth of an absorption at ~2850 cm⁻¹, but the HO₂ band at 1142 cm⁻¹ appears at low doses when the H₂O₂ feature is still very weak. With the high abundance of O₂ molecules in our H₂O + O₂ ices, an H-addition reaction to O₂ seems more likely, particularly because H-addition reactions have been observed in other H⁺-irradiated ices.²⁰⁻²² Previous work in this laboratory²⁰ found a substantial enhancement of the H₂O₂ yield in irradiated H₂O-ice when O₂ was added, an enhancement presumably due to the sequential addition of two H atoms to O₂ through an HO₂ intermediate. The present observations indicate that HO₂ is forming in this manner, supporting the earlier proposed mechanism for H₂O₂ production in H₂O + O₂ mixtures.²⁰

An assignment of the 1259 cm⁻¹ band to HO₃ suggests that this radical might also form by an H-addition reaction, this time to O₃ produced radiolytically from the O₂ present in the ice mixture.



To test this possibility, we synthesized ozone and performed radiation experiments with H₂O + O₃ ices at 9 K. A 1259 cm⁻¹ band was observed after ion irradiation, shifting to 1220 cm⁻¹ when ¹⁸O₃ was used. Figure 2 shows that in our H₂O + O₃ experiments the intensity of the 1259 cm⁻¹ band *decreased* with increasing dose, a behavior consistent with an HO₃ assignment. At higher doses, less HO₃ was produced because much of the O₃ precursor had been destroyed. As expected, HO₂ also was observed (at 1142 cm⁻¹, 1078 cm⁻¹ when ¹⁸O₃ was used) in irradiated H₂O + O₃ ice mixtures, probably due to H-addition to O₂ made from irradiated O₃. Consistent with the assignments was the observation that the HO₂ band did not decrease in intensity like HO₃. This clearly shows that the two bands are from two different species. The HO₂ and HO₃ bands also were seen after pure H₂O₂ ices (prepared from the thermal decomposition of the urea-H₂O₂ complex) were ion-irradiated at 9

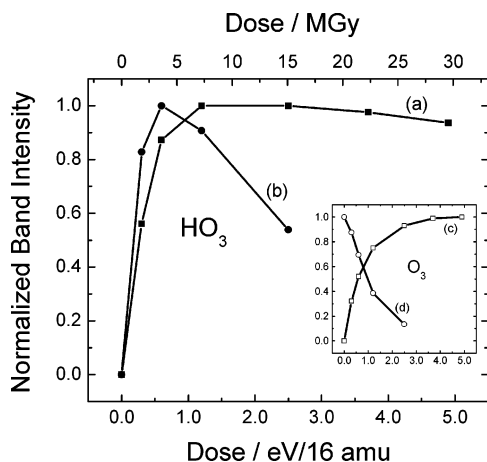


Figure 2. Normalized intensities of the HO₃ absorption band produced from (a) 6:1 H₂O + O₂ and (b) 5:1 H₂O + O₃ ice mixtures as a function of radiation dose. For comparison, the inset shows normalized intensities vs dose for the 1040 cm⁻¹ O₃ absorption band in (c) 6:1 H₂O + O₂ and (d) 5:1 H₂O + O₃ ice mixtures.

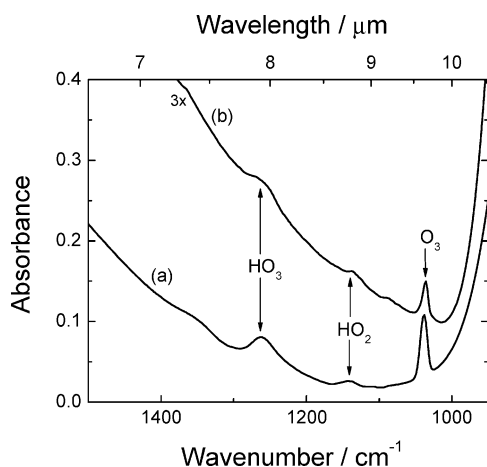


Figure 3. Infrared spectra of 6:1 H₂O + O₂ ice mixtures irradiated with 0.8 MeV H⁺ at (a) 9 K and (b) 80 K to a dose of 0.6 eV/16 amu. Here, O₂ and O₃ presumably were produced by the radiolytic destruction of H₂O₂, followed by H-addition to form HO₂ and HO₃. It is also possible that some HO₂ was made 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 HO₂ and HO₃ we observed was retained when the irradiated H₂O-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 H₂O + O₂ 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 HO₂ and HO₃ 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 H₂, than at 9 K because the H atom mobility is greater. In addition, above ~30 K, some O₂ 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 O₂ absorption above this temperature. The smaller HO₂ and HO₃ intensities at 80 K also might be caused by destruction processes, such as radical-radical reactions with OH, or even other HO₂ and HO₃, 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 HO₂ in H₂O-ice that are essentially identical to those for HO₂ trapped in argon. However, the data in our Table 1 show that HO₂ undergoes substantial hydrogen-bonding to H₂O, with matrix shifts near 40 cm⁻¹. Thus we believe that the HO₂ reported earlier²³ was actually HO₂ 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 H₂O·HO complex.²⁴

Conclusions

In summary, we have assigned spectral bands at 1142 and 1259 cm⁻¹ in irradiated H₂O + O₂ ices, at both 9 and 80 K, to HO₂ and HO₃, respectively. With a re-interpretation of previous work,²² this is the first such detection of either radical in H₂O-ice by IR spectroscopy. These species, which persist to ~100 K, are also produced in irradiated H₂O + O₃ and H₂O₂ ices, and are formed from H-addition reactions to O₂ and O₃. Consequently, we believe that HO₂ and HO₃ can form on Galilean and Saturnian icy satellites, contributing to the inventory of oxidants. Along with O₂, O₃, and H₂O₂, the HO₂ and HO₃ 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, HO₂ and HO₃ probably also form by UV and cosmic-ray bombardment of ice grains in the interstellar medium and in proto-planetary disks.

The HO₂ and HO₃ radicals have been overlooked by astrochemists and planetary scientists but appear to readily form in irradiated water ices containing O₂. 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 HO₃ in the presence of H₂O molecules,¹¹ and imply that both HO₂ and HO₃ 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 O₂ fraction has been used to enable the detection of the title radicals. However, although the 6:1 ratio exceeds the abundance

of O₂ on any known satellite, there is spectroscopic evidence¹³ that O₂ is present at high densities on a small scale, and under such circumstances HO₂ and HO₃ 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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