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$_2$O + 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$_2$O-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$_2$O + O$_3$ ice mixtures, as well as in irradiated H$_2$O$_2$ 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$_2$O 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 matrices.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$_2$O-ice. Recent work by Ignatov et al.,⁴ has suggested the formation of HO$_3$ in UV-irradiated H$_2$O, 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 spectrometry⁵ 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$_2$O matrix has not been reported but is desirable because HO$_3$ has possible roles in atmospheric chemistry⁸ 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 water¹⁰,¹¹ 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.

References

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IR spectroscopy has played a major role in characterizing the composition of these ices and was the tool used to identify H$_2$O$_2$, 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 (~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 $^{16}$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$_2$O$_2$ vapor. This was deposited directly onto the precooled substrate via an attachment to the outside of the cryostat, therefore avoiding any decomposition of H$_2$O$_2$ 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$_2$O + O$_2$ ice mixtures (H$_2$O:O$_2$ ratios of ~6:1) 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
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 when 18 O3 was used. Figure 2 shows that in our H2O–ice when O2 was added, an enhancement presumably due to the sequential addition of two H atoms to O2 through an HO3 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.

\[ H + O2 \rightarrow HO2 \]  

\[ O + OH \rightarrow HO2 \]  

\[ H2O2 + OH \rightarrow HO2 + H2O \]  

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 HO3 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.

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To test this possibility, we synthesized ozone and performed radiation experiments with H2O + O2 ices at 9 K. A 1259 cm−1 band was observed after ion irradiation, shifting to 1220 cm−1 when 18O2 was used. Figure 2 shows that in our H2O + O2 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 O2 precursor had been destroyed. As expected, HO2 also was observed (at 1142 cm−1, 1078 cm−1 when 18O2 was used) in irradiated H2O + O2 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
form and persist at temperatures typical of the Jovian and destruction of H₂O₂, followed by H-addition to form HO₂ and HO₃. In Figure 3, infrared spectra of 6:1 H₂O + O₃ and (d) 5:1 H₂O + O₃ ice mixtures are compared to show 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,²⁴ features now known to be from site effects induced by an Ar matrix on the OH stretch of an H₂O-HOcomplex²⁴.

Conclusions

In summary, we have assigned spectral bands at 1142 and 1259 cm⁻¹ in irradiated H₂O + O₃ 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 + O₂ 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, O₁, 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.²² 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 HO₂ 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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References and Notes


(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 $\sim$600 Mrad or $\sim$6.00 MGy.


