

Note

Hydrogen peroxide dimers and the production of O₂ in icy satellite surfaces

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Received 19 June 2003; revised 8 September 2003

Abstract

Oxygen is seen in the reflectance spectra of the icy surfaces of Ganymede and Europa via absorption bands at 627 and 573 nm. Here we show that the trapped O₂ associated with these spectral features can be produced via radiation-induced decomposition of hydrogen peroxide dimers contained in hydrogen peroxide inclusions in these icy satellite surfaces.

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Keywords: Ganymede; Europa; Ices; Radiation chemistry

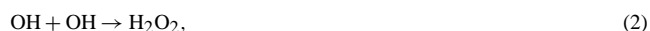
1. Introduction

The atmospheres and the surfaces of the icy Galilean satellites are known to be affected by chemical products formed from the radiolysis and photolysis of their icy surfaces (Johnson and Quickenden, 1997; Johnson et al., 2003a). Molecular oxygen (O₂) is one such product that has been identified in the gas phase and in the reflectance spectra of the icy surfaces of Ganymede and Europa (Spencer et al., 1995; Spencer and Calvin, 2002). These spectra show absorption features at 573 and 627 nm that are consistent with absorption wavelengths of O₂–O₂ dimers present in a condensed phase (Calvin et al., 1996). The relative band strengths and shapes are, however, distorted from that for pure O₂ (Johnson, 1999; Calvin et al., 2003) which may be due to the presence of other species or a perturbing matrix in which the O₂ dimers are embedded. Since the observed features require high local densities of O₂, absorptions originating from O₂ in the tenuous atmospheres of these satellites are ruled out. Therefore, O₂ inclusions are present in the icy regoliths at temperatures at which O₂ has been suggested to diffuse out of ice over relevant periods of time (Baragiola and Bahr, 1998). Such inclusions are also suggested by the observation of ozone trapped in certain icy satellite surfaces (e.g., Noll et al., 1996). On the basis of recent laboratory data, we suggest a new oxygen formation mechanism that is relevant to a surface that has experienced long-term exposure to radiation.

2. Formation and decomposition of hydrogen peroxide

Hydrogen peroxide (H₂O₂) and the hydroperoxy radicals (HO₂) are formed by reactions of hydroxy (OH) radicals formed by radiolytic and

photolytic destruction of H₂O:

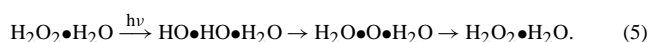


The OH, H₂O₂, and HO₂ formed in UV irradiated ice by the sequence above have all been detected in laboratory studies via their infrared absorptions (Gerakines et al., 1996). The H₂O₂, presumably formed via this reaction pathway, has also been identified in the icy surface of Europa (Carlson et al., 1999).

The photolysis of gas phase H₂O₂ does not yield O or O₂ (Vaghjani et al., 1992), instead the primary products are OH radicals (and H atoms at higher energy). In addition, a summary of the data on the radiolysis and photolysis of ice (Johnson et al., 2003b) indicates that trapped O, and not individual peroxide molecules, is the likely precursor for O₂ formation in fresh ice samples (Matich et al., 1993; Johnson et al., 2003b). The photolysis of H₂O₂ in a matrix also leads to the production of two OH radicals (Khriachtchev et al., 2000). In the gas-phase the OH radicals move away from each other and react with other species leading to the loss of H₂O₂. However, in a solid matrix the OH radicals must escape from the cage in which they were formed for a localized loss of H₂O₂ to occur. If neither OH escapes they can re-react to again form H₂O₂ or the H₂O•O complex (4) identified by Khriachtchev et al. (2000).



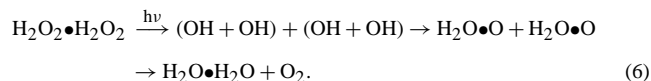
In ice the species H₂O•O may be the trapped O discussed by Matich et al. (1993). Similarly, irradiation of the H₂O₂•H₂O complex results in the formation of an H₂O•O•H₂O intermediate (5) which in turn rapidly photo-decomposes back to H₂O₂•H₂O (Engdahl and Nelander, 2000).



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The photo-decomposition of an H_2O_2 dimer (6), on the other hand, can produce an H_2O dimer and O_2 (Engdahl and Nelander, 2002).



As shown in Eq. (6), this occurs by the dissociation of two H_2O_2 molecules to four OH radicals. These radicals then recombine to form two $\text{H}_2\text{O} \bullet \text{O}$ complexes in the same cage and consequently very rapidly decompose to form an H_2O dimer and O_2 (6). Engdahl and Nelander (2002) also report that H_2O_2 dimer decomposes significantly faster than the H_2O_2 monomer which, in turn, decomposes faster than the $\text{H}_2\text{O}_2 \bullet \text{H}_2\text{O}$ complex.

A primary pathway for O_2 formation in ice is the direct reaction of an O atom with a previously trapped O atom, as discussed, and may be the principal pathway in laboratory studies of fresh ice samples. However, trapped O and freshly produced O are highly reactive. The model proposed here (6) provides an efficient way to produce O_2 after peroxide inclusions are formed. Each peroxide molecule in the dimer contributes an O atom in the same cage, so diffusion of O through the ice lattice to react with another O atom is not required. Therefore, once formed the peroxide inclusions provide a previously unknown, but effective way of producing O_2 .

3. Application of the above to O_2 formation on Ganymede and Europa

The primary radiation products of ice are OH and H (1). H atoms are very mobile within the ice lattice and on forming H_2 are lost from the icy surfaces to the tenuous atmospheres surrounding the satellites (Johnson et al., 2003a, 2003b). The OH radical however can remain trapped in the ice lattice, recombining with H to reform H_2O , or reacting with other species to form secondary and higher order radiation products. One such secondary product is H_2O_2 that is produced from the reaction of two OH radicals.

In low dose laboratory experiments on ice samples the formation of O_2 and H_2O_2 appear to involve competing pathways (Johnson et al., 2003b). It has also been reported that in H_2O ice, H_2O_2 tends to form microcrystals (Gurman et al., 1967). That is, dilute frozen mixtures of ice will tend to have H_2O_2 present in aggregates within the H_2O matrix rather than being uniformly distributed. This work is the only work we are aware of that has reported the structure of H_2O_2 – H_2O ice mixtures. However this result is not entirely unexpected. The binding energy of the H_2O_2 dimer is calculated to be 6.31 kcal/mol (Engdahl et al., 2001) whereas the H_2O dimer has a binding energy of 4.94 kcal/mol (Schütz et al., 1997). Presumably this greater binding energy for the H_2O_2 dimer is due to the additional oxygen atom in H_2O_2 that allows two hydrogen bonds per dimer as opposed to one hydrogen bond per dimer for the H_2O dimer. It is therefore, not unreasonable to think that H_2O_2 molecules will preferably form aggregates in H_2O ices due to this higher binding energy. Segregation of species with different cohesive energies by annealing of solids is well established (e.g., Johnson and Jesser, 1997). Differential thermography was used (Gurman et al., 1967) to establish the presence of microcrystals of H_2O_2 in frozen H_2O_2 / H_2O mixtures. A similar technique could be used on irradiated ice to determine the presence of any such H_2O_2 microcrystals.

We know from the oxygen observations that the absorptions arise from O_2 dimers present at solid-state densities (Calvin et al., 1996, 2003). Due to the low fluxes and long annealing times this O_2 can accumulate and form inclusions in ice (Johnson and Jesser, 1997; Johnson, 1999). Recent work by Chaabouni et al. (2000) has shown that a species can remain trapped in ice at temperatures above its sublimation point. However, the stability of these inclusions over times of the order of years at the temperatures relevant to Ganymede and Europa has been questioned (Baragiola and Bahr, 1998; Baragiola et al., 1999). If these criticisms are correct, then a more stable cage may be needed to obtain the observed absorption bands. This is also suggested by the fact that these bands are considerably distorted from laboratory observations of solid or liquid O_2 (Calvin et al., 2003).

The laboratory data described above suggest that H_2O_2 will form micro-crystalline inclusions (Gurman et al., 1967) in the icy surfaces of

the Galilean satellites and that O_2 may be formed efficiently in such microcrystals (Engdahl and Nelander, 2002). The O_2 formed in these inclusions may also be more stable than O_2 trapped in ice. The higher binding energy between H_2O_2 molecules, compared with H_2O molecules, may reduce the ability of O_2 to diffuse out into the tenuous atmosphere. Under attack by mobile H, the O_2 may form HO_2 and eventually cycle back to H_2O_2 via chemical reactions:



Diffusing O can also trap at such inclusions, enhancing the likelihood of O_2 formation. Since H_2O_2 has been observed in the icy satellite surfaces, it is possible that the stability and density of the trapped O_2 needed to explain the relative band depths and shapes of the 573 and 627 nm absorptions at temperatures that range between ~ 60 – 120 K can be explained by O_2 formation and trapping in H_2O_2 inclusions. Measurements are clearly needed to confirm this and to identify the spectral shifts associated with the peroxide inclusions.

Since the satellite surfaces have been irradiated and annealed at low temperatures for long periods of time, they can be very different from the fresh ice surfaces studied in the laboratory. Whereas O_2 is formed inefficiently in a fresh ice sample, probably requiring the occurrence of pairs of low probability dissociation events of the type $\text{H}_2\text{O} + h\nu \rightarrow \text{H}_2 + \text{O}$ (Johnson et al., 2003b), the situation is very different once H_2O_2 inclusions have been formed. Single excitation events can then efficiently lead to O_2 production. This model could be readily tested in the laboratory by the study of absorption spectra versus dose in the radiolysis or photolysis of peroxide inclusions in ice. In addition, the spectral shifts of the O_2 absorption bands in an H_2O_2 matrix could be measured and compared with the shifts measured in space observations, and the amounts of H_2O_2 and O_2 in the icy surfaces should be related.

The process described here does not impinge upon the discussions of the interesting experiments in which O_2 is produced by irradiation of freshly formed ice samples (Reimann et al., 1984; Matich et al., 1993; Sieger et al., 1998). Rather, the present proposal is a process that would become important on a surface that had experienced long-term irradiation and annealing. Molecular oxygen formed in both fresh ice deposits or in H_2O_2 inclusions could contribute to the ambient O_2 atmospheres seen on Europa and Ganymede (Hall et al., 1998). Here we suggest that the O_2 formed in H_2O_2 inclusions can have a bearing on the visible O_2 bands (Spencer et al., 1995; Spencer and Calvin, 2002) from the icy Galilean satellites.

Models for forming O_2 on the Galilean satellites might be distinguished by observations. Solid O_2 cold trapped from the atmosphere has been suggested (Baragiola and Bahr, 1998). This could be stable in very cold (night time, polar or shaded) regions, but would begin to rapidly evaporate when exposed to the visible light by which it is observed. The presence of O_2 in hydrogen peroxide inclusions suggested here, rather than O_2 trapped as inclusions in ice (Johnson and Jesser, 1997), should show a correlation with the observed distribution of hydrogen peroxide, allowing for differences in absorbance.

4. Summary

We have proposed a new mechanism in which the trapped O_2 seen on the icy satellites is formed by radiolysis or photolysis in H_2O_2 inclusions. This mechanism is based upon two overlapping ideas. Firstly, after long annealing times, even at relatively low temperatures, H_2O_2 is likely to be present as aggregates in ice. Such inclusions have been shown to occur experimentally in pure ice (Gurman et al., 1967) and are in agreement with theoretical calculations (Engdahl et al., 2001). Secondly, dimers of H_2O_2 in a frozen matrix produce O_2 efficiently when irradiated (Engdahl and Nelander, 2002). This relies on the cage effect, which limits the escape of OH radicals from the volume in which they are formed. Therefore, if trapped O_2 and O_2 inclusions in pure ice are unstable at the temperatures of interest, these two observations could explain the source of a high-density form of O_2 thought to account for the visible bands on Ganymede and Europa.

Acknowledgments

R.E.J. acknowledges support by a Gladden Fellowship in Chemistry, School of Biomedical and Chemical Sciences at The University of Western Australia and by grants from NASA's Planetary Geology and Geophysics Program and the NSF Astronomy Program. P.D.C. acknowledges support by an Australian Postgraduate Award.

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