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Formation of nitric oxide and nitrous oxide in electron-irradiated $\text{H}_2^{18}\text{O}/\text{N}_2$ ice mixtures—evidence for the existence of free oxygen atoms in interstellar and solar system analog ices†

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We investigated the irradiation of low temperature $\text{H}_2^{18}\text{O}/\text{N}_2$ ice mixtures with energetic electrons in an ultrahigh vacuum chamber. The newly formed species, such as nitric oxide (N^{18}O), nitrous oxide (NN^{18}O), hydrogen peroxide ($\text{H}_2^{18}\text{O}_2$) and hydrazine (N_2H_4), were identified in the experiments with infrared absorption spectroscopy and mass spectrometry. The results suggest that the unimolecular decomposition of water molecules within water ices at 10 K can lead to the formation of transient, suprathreshold oxygen atoms. These oxygen atoms may play an important role in the formation of oxygen-containing biomolecules such as amino acids and sugar, as well as the decomposition of the biomolecules in the ices.

1. Introduction

Water (H_2O) and nitrogen (N_2) are important ice components on the surfaces of Neptune's satellite Triton,^{1–3} Pluto,^{3–6} and on icy objects in the Kuiper Belt.^{7,8} Water ice is also the dominant component of ice-coated interstellar grains in molecular clouds.^{9,10} Solid nitrogen, although it has not been detected in the solid phase in molecular clouds due to its weak infrared absorption, has been found in the gas phase from far ultraviolet observations toward HD 124314—a moderately reddened star in the southern constellation of Centaurus.¹¹ Further, its existence in ices has been suggested by Elsila *et al.* indicating that nitrogen-bearing ice mixtures provided the best fit to the 2140 cm^{-1} carbon monoxide (CO) band embedded in non-polar ices as observed in dense molecular clouds.^{12,13}

The ices in molecular clouds and in the outer solar system are subject to ionizing irradiation by energetic particles and ultraviolet photons from the galactic cosmic radiation field and by the solar wind. Thus, laboratory experiments have been conducted to investigate the physical processes and chemical reactions induced in pure water ice by irradiation

and sputtering.^{14–17} Moore and Hudson¹⁸ and Gomis *et al.*¹⁹ detected the formation of hydrogen peroxide (H_2O_2) in irradiated water ice by infrared absorption spectroscopy. Bahr *et al.*²⁰ monitored the release of molecular oxygen (O_2) and hydrogen peroxide (H_2O_2) from proton-irradiated cubic water ice with a quadrupole mass spectrometer. In our previous work, we reported the formation of molecular hydrogen (H_2), molecular oxygen (O_2), and hydrogen peroxide (H_2O_2) in crystalline and amorphous water ices by energetic electrons at 12 K, 40 K, 60 K, and 90 K.^{21,22}

Nitrogen-bearing ices were studied at cryogenic temperatures as low as 10 K to understand the role of nitrogen in molecular clouds and the outer solar system. Bernstein and Sandford²³ studied the variations of the 2328 cm^{-1} feature of solid molecular nitrogen (N_2) in distinct ice mixtures. Satorre *et al.*²⁴ conducted an infrared spectroscopy study of ice mixtures containing nitrogen, water, and methane. Moore and Hudson investigated²⁵ proton-irradiated nitrogen-rich ices containing methane (CH_4) and carbon monoxide (CO). Jamieson *et al.* detected the formation of nitrous oxide (N_2O) in electron-irradiated nitrogen and carbon dioxide ice mixtures²⁶ and the formation of an azide radical (N_3) in electron-irradiated solid nitrogen.²⁷ Brunetto *et al.*²⁸ measured the near-IR transmittance spectra of nitrogen and methane ice mixtures at a temperature range between 16 and 40 K. Fulvio *et al.*²⁹ studied near-infrared spectra and 200 keV proton irradiation of water trapped in a nitrogen matrix.

Although the previous laboratory experiments on nitrogen-bearing ices and the inherent detection of the azide radical (N_3) suggested unambiguously the release of nitrogen atoms upon interaction of molecular nitrogen with ionizing radiation, in the case of water ice, the situation is less clear. In the gas phase, Yuan *et al.*³⁰ provided compelling evidence that photolysis of water leads to the formation of atomic hydrogen plus the hydroxyl radical (OH). Quantum chemical calculations by van Harreveld and van Hemert³¹ revealed that the formation of molecular hydrogen and electronically excited oxygen atoms (O^1D) should be also an important decomposition pathway as verified experimentally by Yi *et al.*³² via laser induced fluorescence spectroscopy of the decomposition products. Nevertheless, the common picture of the astrochemistry community focuses on the unimolecular decomposition of water ices *via* atomic hydrogen losses, and with the exception

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of Zheng *et al.*^{21,22} and Hama *et al.*³³ the pathway leading to atomic oxygen has achieved little attention so far.

In this work, we report an infrared and mass spectrometry study on the interaction of ^{18}O -water–nitrogen ice mixtures with energetic electrons to elucidate the presence and reactivity of oxygen atoms formed in the unimolecular decomposition of water. By reacting the liberated oxygen atoms with molecular and atomic nitrogen forming dinitrogen monoxide (N_2O^{18}) and nitrogen monoxide (NO^{18}), we aim to extract kinetic profiles of the newly formed products. This in turn assists to derive reaction mechanisms on the decomposition of water and also on the reactivity of the energetic oxygen atoms released in this process. Since water is the dominating component of interstellar grains and of icy objects in the outer Solar System, these findings would provide evidence on a hitherto neglected route to generate highly reactive oxygen atoms from the most dominating ice component—water—which in turn can add to unsaturated bonds³⁴ and insert into single bonds^{35–37} of astrobiologically important molecules embedded inside these ices.

2. Experimental

The experiments were conducted in a contamination-free ultrahigh vacuum chamber ($<10^{-10}$ torr) which has been introduced elsewhere.^{21,38} Briefly, a two-stage closed-cycle helium refrigerator coupled with a rotary platform is attached to the main chamber and holds a polished polycrystalline silver mirror serving as a substrate for the ice condensation. With the combination of the closed-cycle helium refrigerator and a programmable temperature controller, the temperature of the silver mirror can be regulated precisely (± 0.3 K) between 10 and 350 K. A valve and a glass capillary array are used to condense gases on the silver mirror. The actual thickness of the ice samples can be controlled *via* the condensation time and the pressure in the main chamber. The $\text{H}_2^{18}\text{O}/\text{N}_2$ ice samples were formed by depositing a $\text{H}_2^{18}\text{O}/\text{N}_2$ gas mixture (1 : 1) onto the silver mirror at 12 K. To minimize the contamination from air inside the ice, we froze H_2^{18}O (Aldrich, 97% ^{18}O) with liquid nitrogen and repeatedly defrosted it in vacuum. The gas mixing chamber was filled with about 16 torr H_2^{18}O vapor and 17 torr N_2 . The background pressure in the main chamber was 7.6×10^{-11} torr before deposition. During the deposition, the pressure in the main chamber was maintained at 1.4×10^{-8} torr for 30 min. The total sample thickness was measured to be 230 ± 50 nm based on the methodology as described previously.^{21,22,27} The samples were irradiated with 5 keV electrons at 12 K for 180 min at beam currents of 0 nA (blank experiment) and 100 nA by scanning the electron beam over an area of 1.86 ± 0.02 cm². After each irradiation, the sample was kept at the same temperature for 60 min and then warmed up at 0.5 K per minute until all the species on the substrate were sublimed. The infrared spectra of the samples were measured *on-line* and *in situ* by a Fourier Transform infrared spectrometer (Nicolet); the species subliming from the samples were monitored with a quadrupole mass spectrometer (Balzer QMG 420) in the range of 1 to 200 amu.

3. Results

3.1 Infrared spectra

During the irradiation of $\text{H}_2^{18}\text{O}/\text{N}_2$ ice, we detected the formation of N_2^{18}O and N^{18}O in the infrared spectra of the exposed samples. We also identified the infrared absorptions of newly formed $\text{H}_2^{18}\text{O}_2$ and N_2H_4 during the warming up of the ice sample. Fig. 1 presents a comparison of the infrared spectra of $\text{H}_2^{18}\text{O}/\text{N}_2$ ices before (thin line) and after (thick line) the irradiation. Fig. 2 displays the infrared absorption spectra measured at 179 K and 185 K after the sublimation of the ^{18}O -water ice. The infrared features identified in the spectra are summarized in Table 1. In detail, the major absorption features in the spectra belong to the water (H_2^{18}O) ice. The features centered at 3350, 2180, 1650, and 800 cm⁻¹ correspond to the ν_1/ν_3 , $3\nu_L/\nu_L + \nu_2$, ν_2 , and ν_L modes of H_2^{18}O ice, respectively. The sharp peak at 3659 cm⁻¹ corresponds to the vibration of the water dangling OH bond. The existence of 3659 cm⁻¹ peak indicates the $\text{H}_2^{18}\text{O}/\text{N}_2$ ices are in amorphous form. The frequencies of the water features here are slightly shifted from those of pure water ice³⁹ because

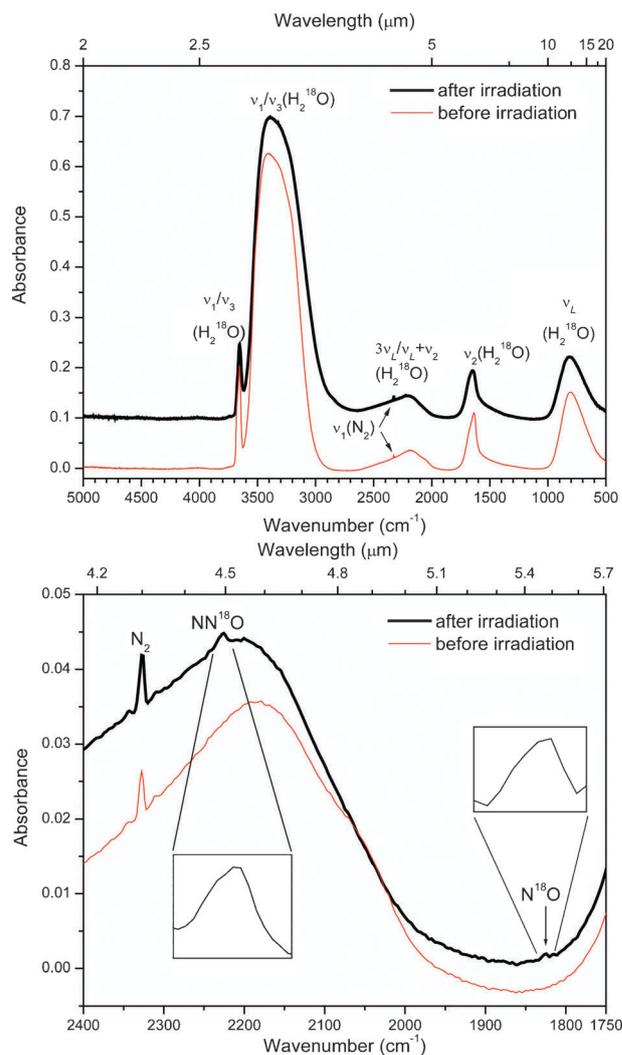


Fig. 1 Infrared spectra of $\text{H}_2^{18}\text{O}/\text{N}_2$ ice before (thin line) and after irradiation (thick line) at 12 K.

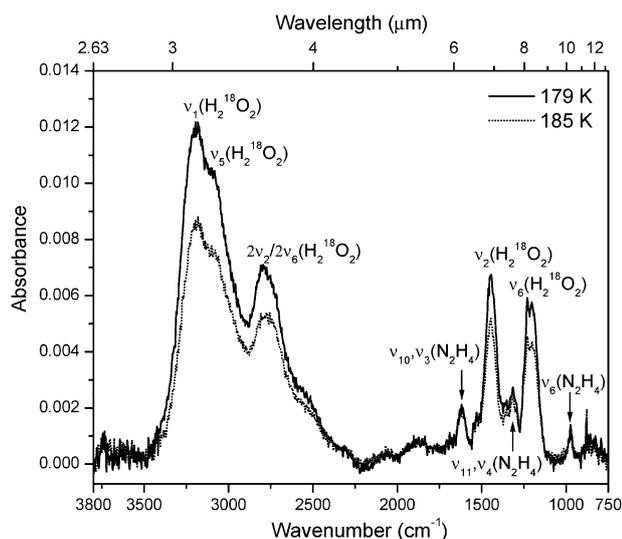


Fig. 2 Infrared spectra of the irradiated sample taken in the warm up phase at 179 and 185 K when most of the ^{18}O -water has sublimed.

H_2^{18}O is used and it is mixed with molecular nitrogen. The sharp peak at 3239 cm^{-1} can be assigned to the ν_1 vibrational mode of molecular nitrogen which is infrared forbidden in the gas phase but active in the solid state.²³ During the irradiation, we observed two new peaks at 2229 and 1827 cm^{-1} . The peak at 2229 cm^{-1} can be assigned to N_2^{18}O ⁴⁰ and that at 1827 cm^{-1} can be attributed to N^{18}O .⁴¹

Additional species cannot be identified in the infrared spectrum during the irradiation since their absorption features were hidden in the strong water (H_2^{18}O) bands. As shown in Fig. 2, these features emerged during the warm up phase when most of the H_2^{18}O ice sublimed. The absorption features at 3193 , 3089 , 1448 , and 1211 cm^{-1} are from the symmetric OH stretching (ν_1), asymmetric OH stretching (ν_5), symmetric HOO bend (ν_2), and asymmetric HOO bend (ν_6) of hydrogen peroxide ($\text{H}_2^{18}\text{O}_2$). The feature at 2787 cm^{-1} probably is due to the overtone of symmetric HOO bend or combination of ν_2 and ν_6 of hydrogen peroxide. The new features at 1620 cm^{-1}

can be assigned to the NH_2 deformation of hydrazine (N_2H_4).^{42,43} The new features at 1318 and 975 cm^{-1} can be assigned to the NH_2 wag⁴² and NH_2 rock⁴⁴ modes of hydrazine (N_2H_4).

3.2 Mass spectra

We monitored the species released into the gas phase with a quadrupole mass spectrometer during and after the irradiation. The products released during the irradiation were below the detection limit of our system. This is consistent with previous investigations of the pure water and nitrogen systems by our group indicating that at 10 K and at our low electron beam current, the samples are not heated, and the radical species generated are trapped inside the low temperature ices during the irradiation. Fig. 3 shows the mass spectral results after irradiation during the warming of the $\text{H}_2^{18}\text{O}/\text{N}_2$ ice. Fig. 3a depicts the blank experiment (no irradiation). Fig. 3b resulted from the irradiation at 100 nA electron current for 180 min . Comparison of the mass signals from the blank and irradiation experiments confirms the infrared spectral results that N_2^{18}O , $\text{H}_2^{18}\text{O}_2$, and N_2H_4 were generated during the irradiation.

In detail, it is important to note that H_2^{18}O ($m/z = 20$) was released into the gas phase at $30\text{--}35\text{ K}$, $35\text{--}45\text{ K}$, and $120\text{--}176\text{ K}$. The intensities of the H_2^{18}O peaks at $30\text{--}35\text{ K}$ and $35\text{--}45\text{ K}$ decreased significantly after irradiation. That probably is related to the change of ice structure caused by irradiation. In the blank experiment, molecular nitrogen ($m/z = 28$) was released into the gas phase at four temperature ranges, $14\text{--}20\text{ K}$, $20\text{--}60\text{ K}$, $140\text{--}155\text{ K}$, and $155\text{--}176\text{ K}$. The N_2 peak at $14\text{--}20\text{ K}$ is the release of weakly bonded N_2 molecules on the ice surface, whereas the N_2 peak at $20\text{--}60\text{ K}$ probably can be attributed to the phase transition of the ice sample and sublimation of N_2 . The N_2 peak at $140\text{--}155\text{ K}$ is produced by release of trapped N_2 in ^{18}O -water ice in the process of water crystallization, and that at $155\text{--}176\text{ K}$ is release of deeply trapped N_2 along with the sublimation of H_2^{18}O . The N_2 peak at $155\text{--}176\text{ K}$ is significantly enhanced after irradiation.

Table 1 Infrared absorption features of the sample and the newly formed species

Absorption (cm^{-1})	Literature value (cm^{-1})	Ref.	Assignment	
			Species	Carrier
Before irradiation (amorphous ice of H_2^{18}O and N_2 mixture)				
3659	—	—	H_2^{18}O	ν_1/ν_3 (dangling OH)
3350	—	—	H_2^{18}O	ν_1/ν_3
2329	—	—	N_2	ν_1
2180	—	—	H_2^{18}O	$3\nu_L/\nu_L + \nu_2$
1650	—	—	H_2^{18}O	ν_2
800	—	—	H_2^{18}O	ν_L
During irradiation				
2228	2229	40	NN^{18}O	ν_3
1825	1827	41	N^{18}O	ν_1
During warming				
3193	—	—	$\text{H}_2^{18}\text{O}_2$	ν_1 (sym. OH stretch)
3089	—	—	$\text{H}_2^{18}\text{O}_2$	ν_5 (asym. OH stretch)
2787	—	—	$\text{H}_2^{18}\text{O}_2$	$2\nu_3/2\nu_6/\nu_2 + \nu_6$
1620	1655, 1603, 1606	42, 43	H_2NNH_2	ν_{10}, ν_3 (NH_2 deform)
1448	—	—	$\text{H}_2^{18}\text{O}_2$	ν_2 (sym HOO bend)
1318	1350, 1304	42	H_2NNH_2	ν_{11}, ν_4 (NH_2 wag)
1211	—	—	$\text{H}_2^{18}\text{O}_2$	ν_6 (asym. HOO bend)
975	975	44	H_2NNH_2	ν_6 (NH_2 rock)

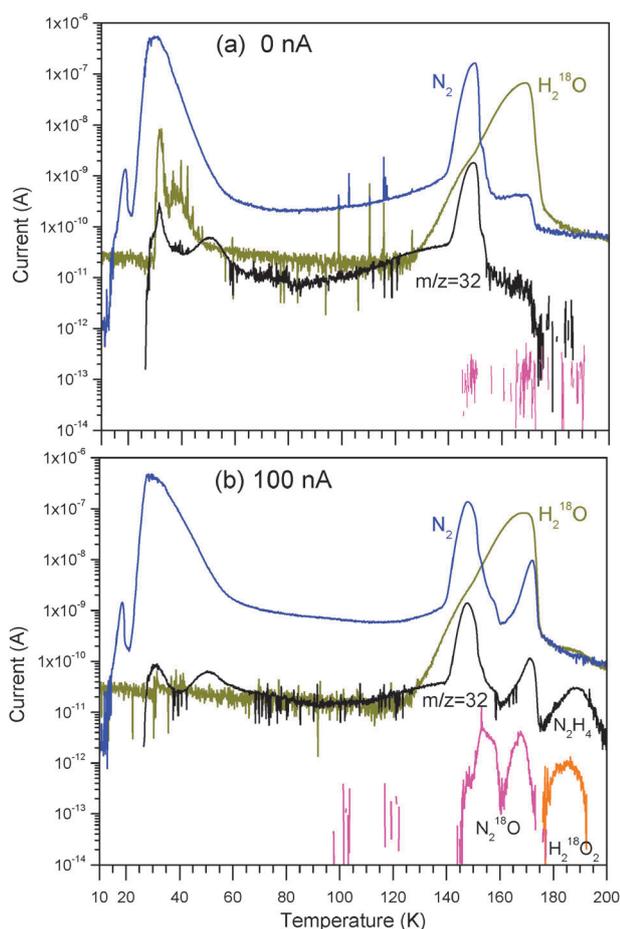


Fig. 3 The temporal evolution of the ion currents during warming up of the $\text{H}_2^{18}\text{O}/\text{N}_2$ ice samples as observed in the mass spectrometer. (a) 0 nA (no irradiation), (b) 100 nA.

The signals of $m/z = 32$ at 26–38 K, 42–60 K and 140–155 K temperature ranges in the blank experiment are mainly from the release of the residual $^{16}\text{O}_2$ in the ice samples. After irradiation (Fig. 3b), new peaks appeared at 160–175 and 175–200 K for $m/z = 32$. These peaks are mainly contributed by newly formed N_2H_4 ($m/z = 32$). N^{18}O also has a mass-charge ratio of 32, but it has much lower sublimation temperature. Thus, it may contribute some to the 160–175 K peak but very little to the 175–200 K peak. The new species N_2^{18}O ($m/z = 46$) was released into the gas phase at 145–160 and 160–173 K. The newly formed $\text{H}_2^{18}\text{O}_2$ ($m/z = 38$) was released at 177–192 K, slightly higher temperature than that in the experiments of pure water ice.²¹ As already shown, the N_2H_4 peak is also at higher temperature than that in the experiments of pure ammonia ice.⁴³ On the other hand, the release temperatures of $\text{H}_2^{18}\text{O}_2$ and N_2H_4 in this work are similar to those observed in ammonia–water ice⁴⁵ in which H_2O_2 and N_2H_4 also coexisted. Based on this information, we propose that the delay of sublimation of $\text{H}_2^{18}\text{O}_2$ and N_2H_4 relative to that in pure water ice and pure ammonia ice probably is caused by the interaction between $\text{H}_2^{18}\text{O}_2$ and N_2H_4 .

4. Discussion

Hydrazine (N_2H_4) is a very important precursor for the production of purines, pyrimidines, and amino acids.

The formation of hydrazine (N_2H_4) in this experiment implies that it might be possible to produce small biological molecules *via* irradiation of interstellar ices that contain very simple molecules such as water, molecular nitrogen, and carbon dioxide or monoxide. In our previous studies, we have detected N_2H_4 and NH_2OH by irradiation of solid ammonia⁴³ and ammonia–water ice,⁴⁵ respectively. The irradiation experiment of $\text{H}_2^{18}\text{O}/\text{N}_2$ ice mixtures suggests that the precursor of purines, pyrimidines, and amino acids can be generated not only in ammonia-rich ice but also in nitrogen-rich ice.

Having identified hydrazine (N_2H_4) and hydrogen peroxide ($\text{H}_2^{18}\text{O}_2$) during the exposure of neat ammonia and water ices, we are focusing our discussion on the formation of the newly formed nitrogen–oxygen products which are unique to the present system. For the decomposition mechanism of water, previous studies suggested that reaction (1) is the major pathway, whereas the unimolecular decomposition into molecular hydrogen and electronically excited oxygen atoms has been proposed as a viable alternative.^{21,22}

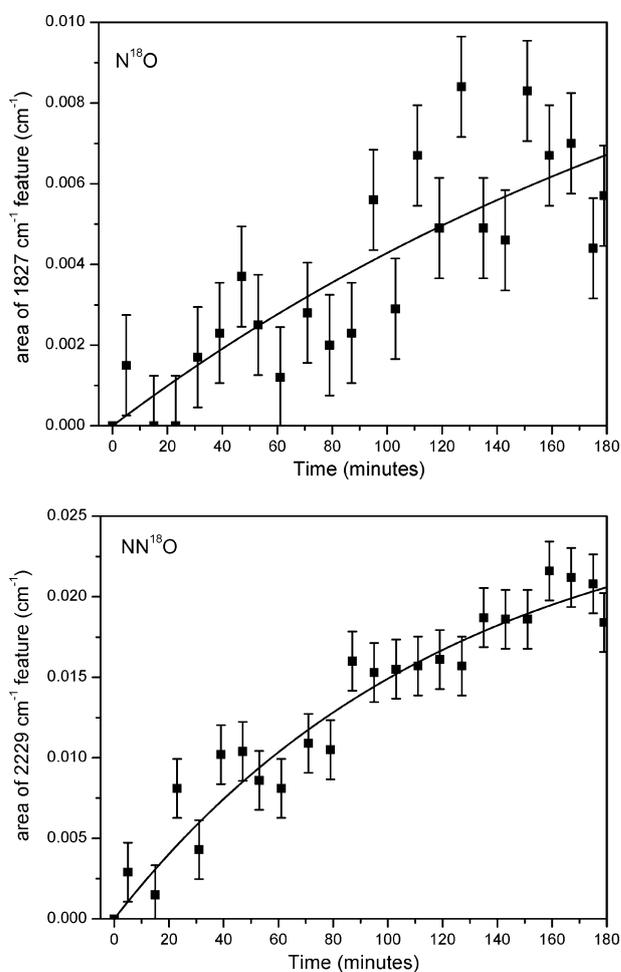


Fig. 4 Temporal evolution of the absorption features of N^{18}O (1827 cm^{-1}) and NN^{18}O (2229 cm^{-1}). The experimental data points were fitted with pseudo first-order kinetics.

Is it feasible to 'trace' the released oxygen atoms and to follow the temporal evolution of the product molecules in which oxygen is incorporated? As a matter of fact, our investigations provided evidence on the formation of N^{18}O (1827 cm^{-1}) and NN^{18}O (2229 cm^{-1}). A detailed analysis of their temporal profiles (Fig. 4) indicates pseudo-first order kinetics. The fit for N^{18}O estimated the a and k values to be $1.4 \times 10^{-2} \pm 1.2 \times 10^{-2}\text{ cm}^{-1}$ and $3.8 \times 10^{-3} \pm 4.3 \times 10^{-3}\text{ min}^{-1}$ respectively, and that for NN^{18}O estimated the a and k values to be $2.6 \times 10^{-2} \pm 0.3 \times 10^{-2}\text{ cm}^{-1}$ and $8.5 \times 10^{-3} \pm 1.8 \times 10^{-3}\text{ min}^{-1}$ respectively. Since the formation of NN^{18}O follows pseudo first order kinetics, NN^{18}O is likely to be formed *via* the reaction of ^{18}O atoms with a neighboring nitrogen molecule (reaction (3)). This process is similar as found in carbon dioxide–nitrogen ices in which carbon dioxide decomposed to form carbon monoxide plus atomic oxygen; the latter was found to react with nitrogen molecules to form N_2O .²⁶ Therefore, the detection and temporal profile of the N_2^{18}O molecule verifies the generation of free ^{18}O atoms generated by electron irradiation of H_2^{18}O molecules and the subsequent reaction with molecular nitrogen.



The N^{18}O molecule more likely is formed by the reaction between N and ^{18}O atoms in the matrix cage. Observation of N^{18}O indicates the existence of free nitrogen and ^{18}O atoms. To summarize, our laboratory studies and temporal fits of the N_2^{18}O and N^{18}O molecules suggest that the unimolecular decomposition of water molecules within water ices at 10 K can also lead to the formation of free oxygen atoms. Since the reaction of ground state $\text{O}(^3\text{P})$ with N_2 has a high energy barrier,⁴⁶ the detection of N_2^{18}O also confirms that the free ^{18}O atoms here are either in their $\text{O}(^1\text{D})$ state or suprathreshold ground state $\text{O}(^3\text{P})$.

5. Conclusions

Nitric oxide (N^{18}O), nitrous oxide (NN^{18}O), hydrogen peroxide ($\text{H}_2^{18}\text{O}_2$) and hydrazine (N_2H_4) were generated in electron-irradiated low temperature $\text{H}_2^{18}\text{O}/\text{N}_2$ ice mixtures. Since nitric oxide (N^{18}O) and nitrous oxide (NN^{18}O) can only be formed *via* the reactions of N and N_2 with free ^{18}O atoms here, the detection of these species verified that free $^{18}\text{O}(^1\text{D})$ atoms were generated from the decomposition of H_2^{18}O . Therefore, our results confirmed that the unimolecular decomposition of water molecules within water ices can also lead to the formation of transient oxygen atoms. That is an evidence for the existence of suprathreshold or electronically excited oxygen atoms in interstellar and solar system analog ices, which is important for our understanding of the formation and decomposition of biomolecules in the interstellar medium and the outer solar system.

6. Astrophysical implications

Detection of the simplest organic sugar and amino acid, glycolaldehyde (CH_2OHCHO) and glycine ($\text{NH}_2\text{CH}_2\text{COOH}$), in the interstellar medium has been reported by Hollis *et al.*⁴⁷ and Kuan *et al.*⁴⁸ respectively. Although the existence of

interstellar glycine is still in controversy,⁴⁹ it has been proposed that amino acids and organic sugar might be able to be generated in the icy interstellar grain mantles by ultraviolet starlight.⁵⁰ Laboratory experiments also show that the formation of glycolaldehyde⁵¹ and amino acids^{52,53} in icy interstellar dust grains is possible. Organic molecules are found to be widespread in the Universe from star dust to the Solar system.⁵⁴ The interstellar dust grain and the icy objects in the solar system are usually water-rich. Therefore, biomolecules probably are formed in water-rich ices. Galactic cosmic rays, UV photons and solar wind particles can generate reactive species such as H, OH and O atoms from the dominating water-rich component. The O atoms at the electronic excited state in particular can add to double bonds in organic molecules and also insert into C–H bonds. Thus, the free $\text{O}(^1\text{D})$ atoms generated in water may play an important role in the formation of oxygen-containing biomolecules such as amino acids and sugar. Recently, amino acetonitrile ($\text{NH}_2\text{CH}_2\text{CN}$) has been detected in Sgr B2(N).⁵⁵ The H, OH and O atoms in the ice may interact with amino acetonitrile to form glycine through multiple-step reactions. On the other hand, the free $\text{O}(^1\text{D})$ atoms might be able to destroy some of the biomolecules already formed. Laboratory experiments suggest that the H, O, and OH resulting from ultraviolet photolysis of water may contribute to the decomposition of amino acid in ice.⁵⁶

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