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Electron irradiation of solid nitrous oxide

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ABSTRACT

We report the results of chemical processing induced by 1 keV electron irradiation of a solid N₂O ice sample formed at 25 K. Ozone and several oxides of nitrogen (NO₂, N₂O₂, N₂O₃, N₂O₄ and N₂O₅) were observed to form during the irradiation period. Such reactions have important implications for the ice chemistry of outer solar system planets/satellites and interstellar ices.

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1. Introduction

Nitrous oxide (N₂O) is an important gaseous species in the terrestrial atmosphere [1]. First detected by Adel, through its characteristic absorption band at 7.8 μ m [2], it is one of the most important greenhouse gases in the terrestrial troposphere. In the stratosphere, N₂O plays a key role in ozone depletion chemistry being a natural source for the nitric oxide (NO) that destroys ozone in a catalytic NO_x reaction. Significant amounts of N₂O are released into the atmosphere as a result of biological activity at Earth's surface but chemical production of N₂O is also possible via the reaction of molecular nitrogen (N₂) either with atomic oxygen (O) or with O₃ [3]. However, research has shown that non-biological formation pathways are less significant [4,5] than biological.

N₂O was the third molecule to be detected in space that contains the NO bond therefore demonstrating the universality of basic chemistry that, on Earth at least, led to evolution of life. Significant concentrations of nitrous oxide (a relative fractional abundance of 10^{-9} to molecular hydrogen H₂) have been observed in the SgrB2(M) [6] and is believed to have been produced by neutral-neutral reactions [7]. Although N₂O has not yet been detected in any of the outer solar system planets/satellites it is nevertheless likely that it will be formed by irradiation of common ices like N₂, CO_2 and CO_2 . Indeed irradiation of N_2 and carbon dioxide (CO_2) ice by energetic electrons at 5 keV [8] and protons at 0.8 MeV [9] have shown that N₂O will be easily formed in astrochemical ices. Therefore it is important to study irradiation of N₂O ices to determine subsequent chemical products. One earlier experiment [10] has revealed that, contrary to expectations, ozone is formed when solid nitrogen oxides are bombarded using 4 keV argon atoms and ions. Since ozone is widely suggested as a biomarker in extrasolar planets, the mechanisms and probability of ozone being formed by such abiotic processes should be investigated.

In order to understand such ozone formation it is necessary to investigate the dissociation dynamics of N_2O within the irradiated ice. To date there have been no definitive experiments on dissociation of N_2O in condensed multilayers however some information on possible chemical pathways may be obtained by reviewing gaseous phase photochemistry.

Photo-dissociation reactions of N₂O include the production of atomic oxygen and molecular nitrogen and nitric oxide via the following reactions [11]:

$$N_2O + h\nu \rightarrow N_2 + O(^1D) \text{ or } O(^1S)$$

 $(\lambda < 337 \text{ nm or } 210 \text{ nm}, \text{ respectively}),$ (1)

$$\rightarrow \mathrm{NO} + \mathrm{N}(^{4}\mathrm{S}) \ (\lambda < 250 \ \mathrm{nm}). \tag{2}$$

Atomic oxygen can combine to form molecular oxygen and then react with atomic oxygen to form O_3

$$O(^{3}P) + O(^{3}P) \rightarrow O_{2}, \tag{3}$$

$$O(^{3}P) + O_{2} + M \rightarrow O_{3} + M \text{ (where } M = N_{2} \text{ or } O_{2}),$$
 (4)

while $O(^{1}D)$ can further dissociate $N_{2}O$ to form NO or $N_{2} + O_{2}$:

$$O(^1D) + N_2O \rightarrow NO + NO, \tag{5}$$

$$\rightarrow N_2 + O_2. \tag{6}$$

Hence in any dissociation of N_2O in a dense media, such as an ice we might expect to observe formation of O_3 and NO as well as N_2 and O_2 .

2. Experimental method

The apparatus used in this experiment has been described in detail before [12] so only a brief description is given here. The apparatus is comprised of an ultra high vacuum (UHV) chamber (base pressure less than 10^{-9} mbar) with a liquid helium cooled cryostat which cools the zinc selenide (ZnSe) substrate placed at the cryostat to 25 K. N₂O (stated purity 99.5% from Argo International) was deposited at a pressure of 10^{-7} mbar for about 90 s at



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 ${\sim}25$ K. After deposition an IR spectrum of the solid N₂O ice was recorded using a Fourier Transform InfraRed (FTIR) spectrometer over the 4000–600 cm⁻¹ region using 4 cm⁻¹ resolution. Ten micro ampere of 1 keV electrons (beam spot size ${\sim}$ 3 mm) produced by a conventional electron gun irradiated the ice sample for about 90 min. IR spectra were recorded continuously throughout the irradiation period in order to detect the formation of new molecules.

3. Results

Fig. 1 shows an infrared spectrum of a N₂O ice sample maintained at ~25 K before irradiation. Fundamental bands corresponding to vibrational modes v_1 and v_3 were found to be at 1292.2 cm⁻¹ and 2237 cm⁻¹, respectively [13–15]. Eight other bands were observed at 1164.8 cm⁻¹, 2580.2 cm⁻¹ and 3861 cm⁻¹ (correspond-



Fig. 1. Infrared bands recorded in a thin film of nitrous oxide ice cooled to ${\sim}25$ K.

Table 1	
Infrared band positions for solid N2O at different temperature	s

Mode	Wavenumber, cm ⁻¹				
	This work 25 K	Lapinski et al. [13] 6 K	Dows [15] 70 K	Smith et al. [14] 15 K	
2v ₂	1164.8	1166.6	1165.6	1166.5	
v ₁	1292.2	1291.2	1293.4	1291.3	
$v_1 + v_2$	1887.9	1885.3	1888.1 ^a	1885.9	
v ₃	2237.0	2235.6	2238.0	2235.9	
$v_1 + 2v_2$	2468.7	2466.5	2468.5 ^a	2466.9	
2v ₁	2580.2	2575.3	2579.5	2576.0	
$v_2 + v_3$	2813.6	2809.3	2813.7	2809.2	
$2v_2 + v_3$	3379.5	3374.5	-	3373.8 [°]	
$v_1 + v_3$	3508.0	3499.3	3508	3499.9	
3v ₁	3861.0	3853.7	-	-	

^a Calculated values.

ing to the overtone bands $2v_2$, $2v_1$ and $3v_1$) and 1887.9 cm^{-1} , 2468.7 cm⁻¹, 2813.6 cm⁻¹, 3379.5 cm⁻¹ and 3508 cm⁻¹ (assigned to combination bands $v_1 + v_2$, $v_1 + 2v_2$, $v_2 + v_3$, $2v_2 + v_3$ and $v_1 + v_3$). Table 1 shows a comparison of our measured band positions with those recorded by earlier authors at different temperatures. At higher temperatures a phase change may occur forming a highly ordered crystal ice matrix leading to new spectral signatures. In a



Fig. 2. IR spectra of the new bands observed in solid N₂O during irradiation. (a) 1039.6 cm⁻¹ (ν_3) band of O₃ and (b) details of the spectral region between 1950 and 1550 cm⁻¹ showing formation of several oxides of nitrogen.

high density ice N_2O dimers may also be formed and identified through their four distinctive absorption bands at 2213.1, 2214.3, 2220.7 and 2221.9 cm⁻¹ [16]. In our spectrum a shoulder around 2219.6 cm⁻¹ may therefore be attributed to $(N_2O)_2$.

During irradiation several new infrared bands appeared in the measured IR spectrum (Fig. 2) indicating the synthesis of new molecules under the influence of electron irradiation. A band at 1039.6 cm⁻¹ was observed to appear in the IR spectrum immediately and is identified as the v_3 O–O asymmetric stretch of O_3 (Fig. 2a). Several new bands were found to be grouped within the 1950–1550 cm^{-1} region (Fig. 2b and Table 2) and may be assigned to several nitrogen oxides e.g. that at 1614.9 cm⁻¹ is ascribed to NO₂, 1594 cm⁻¹ (N₂O₃), 1741.2 cm⁻¹ (*trans*-N₂O₂, N₂O₅), 1763.4 cm⁻¹ (*cis*-N₂O₂, *sym*-N₂O₄), 1702.4 cm⁻¹ (N₂O₅), 1718.2 cm⁻¹ (O_2N-NO_2), 1855.7 cm⁻¹ (*trans*- N_2O_2 , cis- N_2O_2 , $asym-N_2O_4$) and 1832.1 cm⁻¹ ($asym-N_2O_3$). Several additional vibrational modes of newly formed products might be present in the saturated regions of the N₂O spectrum and therefore can not be distinguished, whilst any N₂ or O₂ formed as the result of N₂O dissociation cannot be observed since neither species is IR active.

Table 2

Assignments of new IR bands that are observed during 1 keV electron irradiation upon solid N_2O at temperature ${\sim}25~K$

New bands in wavenumbers (cm^{-1})	Molecule	Mode	References
1039.6	03	<i>v</i> ₃	А
1594.0	N_2O_3	?	В
1614.9	NO ₂	V3	Α
1702.4	N_2O_5	V9	А
1718.2	N_2O_4	?	В
1741.2	trans-N ₂ O ₂	V ₅	А
	N_2O_5	V1	А
1763.4	cis-N ₂ O ₂	V5	А
	sym-N ₂ O ₄	V9	А
1832.1	asym-N ₂ O ₃	v_1	А
1855.7	trans-N ₂ O ₂	v_1	А
	cis-N ₂ O ₂	v_1	А
	asym-N ₂ O ₄	v_1	А
1867.0	N_2O_3	?	В

?, Unable to assign the vibrational mode.

A – Jamieson et al. [8] and references therein.

B – Fateley et al. [21].



Fig. 3. Ozone growth during irradiation by 1 keV electrons in solid N₂O at ~25 K. The column density is calculated using the absorption coefficient value of 1.4×10^{-17} cm molecule⁻¹ for v₃ band of O₃ [22].

4. Discussion

Electron impact dissociation of N_2O may, as in the case of photodissociation, be expected to produce molecular nitrogen and atomic oxygen:

$$N_2O + e^- \rightarrow N_2 + O({}^3P/{}^1D).$$
 (7)

Since it requires only 1.67 eV for dissociation of N–O bond in N₂O all the incident electrons and most of the secondary electrons induced by ionization will have enough energy to dissociate any N₂O molecules with which they interact. Piper and Rawlins [17] have shown that, although a spin forbidden process, electron impact dissociation of N₂O is dominated by the production of oxygen in its ground state (³P) rather than the excited O(¹D). Ozone production, observed as a characteristic IR feature at 1039 cm⁻¹, can then form via a two step process, generating molecular oxygen in the first step and addition of another O(³P) producing O₃ in the second step (reactions (3) and (4)). Fig. 3 shows the growth of ozone during irradiation; ozone production is observed as soon as electron irradiation begins.

In an ice matrix, kept at 25 K, O₃ production can also be explained by the formation of the complex ($N_2O \cdots O_2$). Once molecular oxygen is generated such a complex is easily stabilized within the ice. The interaction of such a complex with another free oxygen atom ($N_2O \cdots O_2$) would then lead to a localised reaction within the matrix cage resulting in ($N_2O \cdots O_3$):

$$N_2 O \cdots O_2 + O({}^3P) \to N_2 O + O_3.$$
 (8)

The possibility of such reactions occurring within N_2O molecular cages is supported by spectroscopic identification of complex $(N_2O...O_2)$ [18,19].

The formation of $O(^{1}D)$ atoms not only provides an alternative source of $O(^{3}P)$ atoms but may lead to the formation of the nitric oxide dimer [20] known as dinitrogen dioxide (N_2O_2) :

$$N_2 O + O(^1 D) \to (NO)_2. \tag{9}$$

NO dimers were clearly identified both in the *cis* and *trans* isomeric forms (Fig. 2b, Table 2) in our spectrum.

Due to the weak bond between N–N in the $(NO)_2$ dimer they provide a source for NO monomers. Atomic oxygen reacts with the NO monomer to produce NO₂ (10), which was observed in the spectrum at 1614.9 cm⁻¹:

$$NO + O \rightarrow NO_2.$$
 (10)

Further reactions then generate the heavier molecular products N_2O_3 , N_2O_4 and N_2O_5 . Dinitrogen trioxide (N_2O_3) can be formed in two ways: (i) a reaction of NO_2 with NO (11) and (ii) addition of atomic oxygen to N_2O_2 . During irradiation both these reactions might compete in forming N_2O_3 molecules in the N_2O ice but reaction (i) was observed to be very efficient due to the growth of 1594 cm⁻¹ N_2O_3 signature and a corresponding decrease in the NO_2 signature at 1614.9 cm⁻¹:

$$NO_2 + NO \rightarrow N_2O_3, \tag{11}$$

$$2NO + O_2 \rightarrow 2NO_2, \tag{12}$$

$$2NO_2 \to N_2O_4. \tag{13}$$

 NO_2 dimers produced via reaction Eq. (12) or due to the close proximity of two NO_2 molecules produced via reaction Eq. (10) may in turn dimerize to form N_2O_4 (13). A very weak band at

$$2NO_2 + O_3 \to N_2O_5 + O_2. \tag{14}$$

5. Conclusion

Electron irradiation of a 25 K sample of N₂O ice has been shown to generate a rich chemistry with the synthesis of both ozone and a large number of nitric oxides from N₂O₂ up to N₂O₅ being formed from intermediate product such as NO, NO₂, O₂. Formation of N₂O₅ during irradiation revealed the reaction of O₃ molecules with NO₂. Most of the reactions are common to those observed in the Earth's atmosphere where they are initiated by photo-dissociation of nitrous oxide. Although N₂O has to date only been detected in interstellar medium it is highly likely that it is formed in several of the solar system's icy bodies. The present experiments would then suggest that irradiation of such N₂O containing ices by the solar wind, sunlight and/or magnetospheric ion bombardment will quickly lead to abiotic ozone formation as well as a large number of nitric oxides which may subsequently react with hydrocarbon species and water to form even more complex species. Therefore, future experiments will explore the irradiation of $N_2O/H_2O/CO_2/$ hydrocarbon ice mixtures by various sources of irradiation, also using isotopic composition to deduce the kinetics behind the formation of new molecules observed in this preliminary experiment.

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References

- [1] L.E. Miller, J. Chem. Educ. (1954) 112.
- [2] A. Adel, ApJ 88 (1938) 168.
- [3] P. Harteck, S. Dondes, Phys. Rev. 95 (1954) 320.
- [4] R.M. Goody, C.D. Walshaw, Q. J. Royal Meteorol. Soc. 79 (1953) 496.
- [5] W. Demore, O.F. Roper, J. Chem. Soc. 37 (1962) 2048.
- [6] L.M. Ziurys, A.J. Apponi, J.M. Hollis, L.E. Snyder, ApJ 436 (1994) L181.
- [7] T.J. Millar, J.M. C Rawlins, A. Bennett, P.D. Brown, S.B. Charnley, A&AS 87 (1991) 585.
- [8] C.S. Jamieson, C.J. Bennett, A.M. Mebel, R.I. Kaiser, ApJ 624 (2005) 436.
- [9] M.H. Moore, B. Donn, R. Khanna, M.F. A'Hearn, Icarus 54 (1983) 388.
- [10] J. Liang, J. Michl, J. Am. Chem. Soc. 106 (1984) 5039.
- [11] D.R. Bates, P.B. Hays, Planet. Space Sci. 15 (1967) 189.
- [12] A. Dawes, et al., J. Chem. Phys. 126 (2007) 244711.
- [13] A. Lapinski, J. Spanget-Larsen, J. Waluk, J.G. Radziszewski, J. Chem. Phys. 115 (2001) 1757.
- [14] D.F.J. Smith, J. Overend, R.C. Spiker, L. Andrews, Spectrochim. Acta 28A (1971) 87.
- [15] D.A. Dows, J. Chem. Phys. 26 (1957) 745.
- [16] J.R. Sodeau, R. Withnall, J. Phys. Chem. 89 (1985) 4484.
- [17] L.G. Piper, W.T. Rawlins, J. Phys. Chem. 90 (1986) 320.
- [18] M. Bahou, L. Schriver-Mazzuoli, C. Camy-Peyret, A. Schriver, J. Chem. Phys. 108 (1998) 6884.
- [19] M. Bahou, L. Schriver-Mazzuoli, C. Camy-Peyret, A. Schriver, T. Chiavassa, J.P. Aycard, Chem. Phys. Lett. 265 (1997) 145.
- [20] H.H. Michels, J.A. Montgomery Jr., J. Chem. Phys. 88 (1988) 7248.
- [21] W.G. Fateley, H.A. Bent, B. Crawford, J. Chem. Phys. 31 (1959) 204.
- [22] C.J. Bennett, R.I. Kaiser, ApJ 635 (2005) 1362.