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Small steps on the slippery road to life: Molecular synthesis in astrophysical ices initiated by low energy electron impact

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ABSTRACT

We report the synthesis and desorption of new chemical species from simple molecular surface ices irradiated by low energy (<60 eV) electrons. For CD_4 ices we observe the formation and desorption of energetic ions such as D_3^+, CD_5^+, and $C_2D_n^+$ ($n = 2$–5), as well as three carbon containing chains, that are also observed to desorb from C_2D_2 films; for oxygen rich methane ices we observe the synthesis and desorption of H_2O^+, H_3O^+, as well as formaldehyde type cations, *viz.*, H_nCO^+ ($n = 1$–3), among others. The formation of all these pre-biotic molecular species, produced here by low-energy electron-impact-initiated cation-reactions in simple molecular films, suggests that similar mechanisms may lead to the synthesis of life's most basic molecular components in planetary, or astrophysical surface ices that are continuously subjected to the types of space radiations (UV, X- or γ-ray, or heavy ions) that can generate such low energy secondary electrons.

1. Introduction

The question of the origin for the building blocks of life, either synthesized here on earth, or in space [1], has been the subject of much debate, experimental investigation, or astronomical observation, much of it stimulated by the early experiments of Miller [2], and subsequent space radiation related variations thereof [3–5]. And while the precise details of the formation of even the simplest biomolecular elements that make up life on earth still remain shrouded in mystery, one of the notions that persist throughout the debate is that the building blocks of life, such as amino-acids, or even the components of RNA and DNA, where synthesized via radiolysis [6] either in the earths proto-atmosphere, its early oceans, or in the near interstellar space surrounding the early earth.

Here we provide experimental evidence for the hypothesis that the subsequent interactions of low energy secondary electrons and ions, formed during the radiolysis of solid or liquid media, with atoms and molecules in the medium, may have played, and may still play an important role in the chemical transformation of astrophysical or planetary surface ices [7], where they lead to the synthesis of more complex chemical species from less complex, naturally occurring components. It is not surprising that the contexts where such secondary electron and ion reactions occur are those wherever ionizing radiation deposits energy in matter, and thus range from radiation damage to DNA [8,9], to the radiolysis of molecules at the surfaces of extraterrestrial icy grains or particles, or icy regions of some planets and their satellites [7], which are exposed to various space radiations. Many of the previous experiments have probed new products remaining in the films via methods of post-irradiation analysis of the films, e.g., TPD-MS [10], or FTIR in ion irradiation studies [3], while some experiments have investigated the formation of new chemical products that desorb from films or surfaces during radiolysis [7,11].

In this contribution, we present results of cation scattering in, and desorption from, molecular ices initiated by low energy electron (<70 eV) impact. The thin ice layers studied here consist of several monolayer (ML) thick films of small molecules such as $^{16}O_2$, $^{18}O_2$, N_2, CD_4, and C_2D_2 condensed at 20 K under ultra high vacuum conditions, much like those found in interplanetary or interstellar space. The samples are irradiated directly with a low energy ($E(e) \leq 70$ eV) electron beam emanating from a hemispherical monochromator ($\Delta E(e) \approx 80$ meV), and desorbing ionic species are mass selected with a high resolution mass spectrometer, and detected using standard charge sensitive electronics.

We find that low energy electron impact initiates a variety of cation fragment reactions at, or near, the surface of the molecular surface ices, all of which result in the formation and desorption of new, more complex chemical species than those that were initially deposited in the films. Therefore, we propose that similar cation reactions, initiated in planetary or astrophysical surface ices by the abundant secondary electrons generated by the various space radiations (UV, X- or γ-ray, or heavy ions) that impinge on them,

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can provide a mechanism not only for the formation of prebiotic molecules in various space environments, but also for their desorption into the vacuum of interstellar or interplanetary space.

2. Experimental methods

The electron stimulated desorption (ESD) apparatus used in the present study has been described in great detail elsewhere [12,13]. A monochromatic electron beam of about 2×10^{-9} A, with variable incident energy, and a resolution of about 80 meV fwhm, impinges onto a thin polycrystalline Pt foil press-fitted directly onto the tip of a closed cycle cryostat; the latter is held at 20 K during the sample preparation and experiments. The Pt substrate is cleaned by multiple resistive heating cycles at 900 °C. Multilayer films are condensed on the clean Pt by means of a volumetric dosing procedure [14], with an accuracy of about ±30% and an overall repeatability of ±0.2 monolayers (ML). The electron energy scale is calibrated to within ±300 meV with respect to the vacuum level ($E_{vac} \equiv 0$ eV) by measuring the onset of the transmitted current through the film. Since energy shifts of the onset of current transmission relate to charging of the films, it is possible to verify that the present results were obtained from essentially un-charged samples. The entire system is housed in an ultra-high vacuum system held at 10^{-10} Torr, and enveloped by a double μ-metal shield to eliminate stray magnetic fields.

Some of the cations produced during electron impact may desorb and enter an ion lens system (containing a set of retardation grids) which precedes a quadrupole mass spectrometer (QMS). The QMS system may be operated in: (a) the *ion mass* mode, where the mass spectrum of desorbing ions is measured at a fixed incident electron energy, (b) the *ion yield* mode, where the signal of a particular desorbing ion species is monitored as a function of incident electron energy, E(e), or (c) the *ion energy mode*, where the desorbed cation signal is recorded versus the retardation voltage on the grids of the QMS lens system [13], at a fixed E(e) and ion mass to charge ratio.

The present experiments are performed on pure and heterogeneous multilayer films containing $^{16}O_2$, N_2, with stated purities of ca. 99.995%, of 99% for CD_4 and C_2D_2, while the stated isotopic purity of $^{18}O_2$ was >99%.

3. Results and discussion

Starting with simple molecular films, we investigated electron impact initiated cation reactions in mixed films of O_2 and N_2. Shown in Fig. 1 are the ESD yield functions for O^+, N^+, and NO^+ from a mixed film of O_2/N_2, while the inset shows the ESD mass spectrum of these ions. We observe that, while N^+ is only seen to desorb at electron energies above ca. 25 eV, both O^+ and NO^+ are desorbing at electron energies near 21 eV. Therefore, we propose that, based on the different desorption thresholds for these cations, the formation of NO^+ is most likely the result of O^+ scattering from N_2 in the mixed film, leading to the formation and desorption of NO^+ via the following reaction:

$$e^- + O_2 \rightarrow O_2{}^+ + e^- \rightarrow O^+ + O + e^-$$

followed by

$$O^+ + N_2 \rightarrow ON_2{}^+ \rightarrow NO^+ + N$$

Retardation analysis [13] of the O^+ ions desorbing from these films under electron impact, as shown in Fig. 2, demonstrates that the O^+ fragments produced by low energy electron impact have sufficient kinetic energy to abstract N atoms from N_2 prior to desorption from the surface of the films. We note that the formation and desorption of both, $O_2{}^+$ and $N_2{}^+$, in these electron irradiated films is most likely already the result of electron initiated cation fragment reactions, as shown in Fig. 3 for mixed $^{16}O_2/^{18}O_2$ films. Here the observation that similar intensities of $^{16}O_2{}^+$, $^{16}O^{18}O^+$, and $^{18}O_2{}^+$ are seen to desorb from the mixed films containing simi-

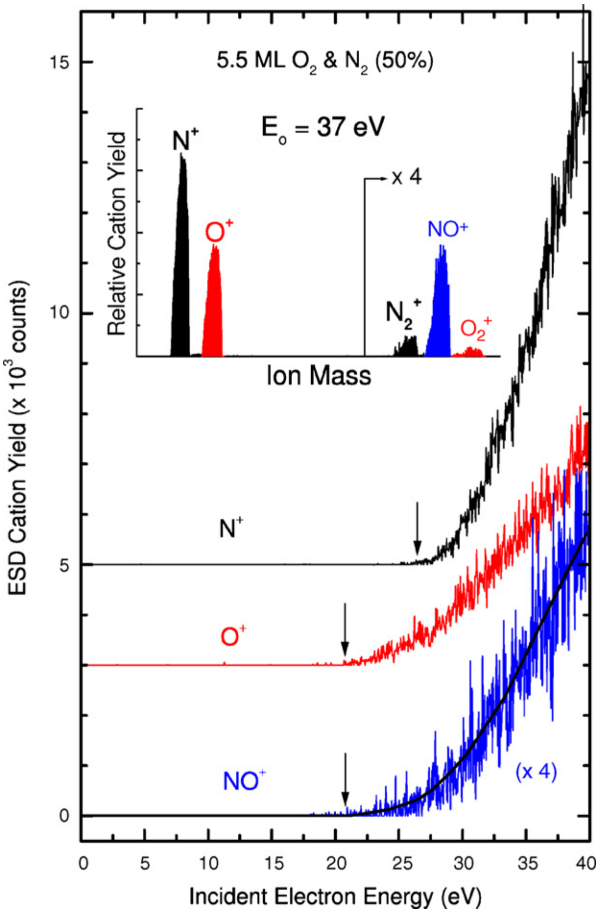

Fig. 1. Electron stimulated desorption (ESD) cation fragment yields as function of incident electron energy for a 5.5. monolayer (ML) mixed O_2/N_2 film (the curves have been displaced vertically for clarity), and the associated ESD mass spectrum obtained at 37 eV is shown in the inset.

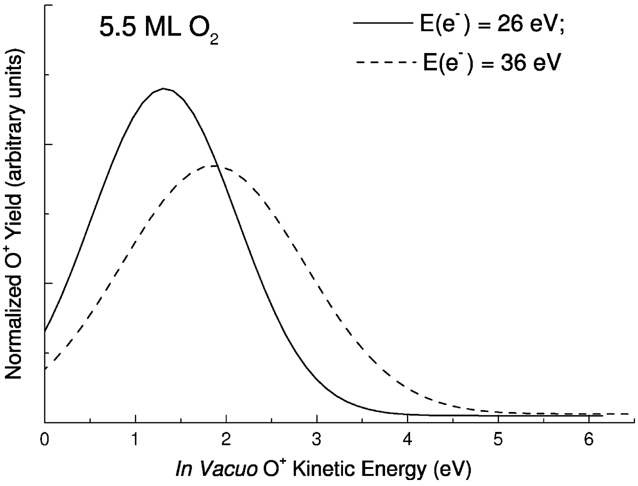

Fig. 2. Smoothed kinetic energy distributions (see Ref. [13] for experimental details) for O^+ produced by ESD from a multilayer O_2 film at two different incident electron energies.