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Modification of an NF_3 film by sub-excitation electrons

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Abstract

By applying the IRAS technique (infrared-absorption-reflection spectroscopy) and electron stimulated desorption (ESD) of negative ions we demonstrate that a 10 monolayer (ML) film of NF_3 is degraded in the course of low-energy electron irradiation in the range 0–5 eV which is far below the electronic excitation of NF_3. Degradation is accompanied by the desorption of F^- fragment ions from the film and formation of NF_2 radicals and N_2F_4 molecules in the film. The energy dependence of the degradation cross-section follows that for resonant (dissociative) electron attachment in the low-energy region ($\approx$ 0–5 eV) and increases above 6 eV. We therefore identify (dissociative) electron capture at low energy as the only initial reaction responsible for the chemical changes in the NF_3 film. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

In this contribution we study the reactions induced by a beam of energy selected electrons interacting with a 10 monolayer (ML) film of NF_3 deposited on a cryogenically cooled (25 K) Au substrate under UHV conditions. The reactions are monitored by infrared-absorption-reflection-spectroscopy (IRAS) and electron stimulated desorption (ESD) of negative ions, both recorded as a function of the primary electron energy. By comparing with data from the gas phase it can be concluded that in the energy range 0–5 eV resonant dissociative electron capture is responsible for the degradation of the NF_3 film, the desorption of F^- ions and the formation of new species in the film. The relevant energy range (<5 eV) is considerably below the threshold for electronic excitation in NF_3($\approx$ 7 eV [1]) .

The electron impact behaviour of gas phase NF_3 (single molecules and clusters) has attracted considerable interest in the last years as this compound is used as feed gas in various plasma etching processes [2–5] and also as a fluoride source in excimer gas laser media [6,7]. Owing to the comparatively high dissociative electron attachment (DA) cross-section it is also used to generate F^- in the course of ion–molecule reactions [8,9]. The DA cross-section in NF_3 generating F^- is 2.2×10^{-16} cm^2 and thus more than two orders of magnitude larger than that in CF_4 (1.6×10^{-18} cm^2 [11,12]). In the gas phase, the DA products F_2^- and NF_2^- are also observed [10,13], however, with cross-sections about two orders of magnitude below that of F^-.

The present study is a continuation of our previous investigation of electron stimulated desorption of F^- from condensed NF_3 [14] where it was shown that F^- desorption is driven by DA to

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NF_3 molecules at or near the surface within a resonant low-energy feature (0.5–4 eV).

Reactions in condensed material initiated by low-energy electrons have been observed before and we mention here electron-induced synthesis of ozone in a dioxygen matrix [15], activation of adsorbed cyclopropane [16], bond selective dissociation of alkanethiol-based self-assembled monolayers [17] and DNA strand breaks by low-energy (3–20 eV) electrons [18]. In the last two studies the explicit energy dependence of the corresponding reactions has been studied resulting in a resonant-like behaviour peaking around 10 eV. In particular the findings on DNA strand breaks present a fundamental challenge to the traditional notion that genotoxic damage by secondary electrons can only occur at energies above the onset of ionization [18]. While all the above-mentioned reactions are induced by *sub-ionization* electrons it is also clear that in each case electronic excitation was involved, either electronically excited neutral states or electronically excited resonances.

In the present contribution we study reactions induced by *sub-excitation electrons* where any reaction pathways involving the associated electronically excited neutrals can be excluded. To our knowledge this is the first example of a reaction in condensed material initiated by electrons appreciable below the threshold for electronic excitation. In that case, only one single possible process, namely (resonant) dissociative electron attachment via the electronic ground state of the negative ion is responsible for the observed reaction.

2. Experimental

The present experiments were carried out in a UHV apparatus (Fig. 1) consisting of a trochoidal electron monochromator (TEM), a cryogenic-cooled monocrystalline Au substrate mounted on a manipulator and a commercial quadrupole mass spectrometer with an ion extraction system [12]. The substrate can be cooled down to approximately 25 K by means of a closed cycle He refrigerator and resistively heated up to several 100 K. The molecules are condensed on the metallic substrate by exposing it to a volumetrically cali-

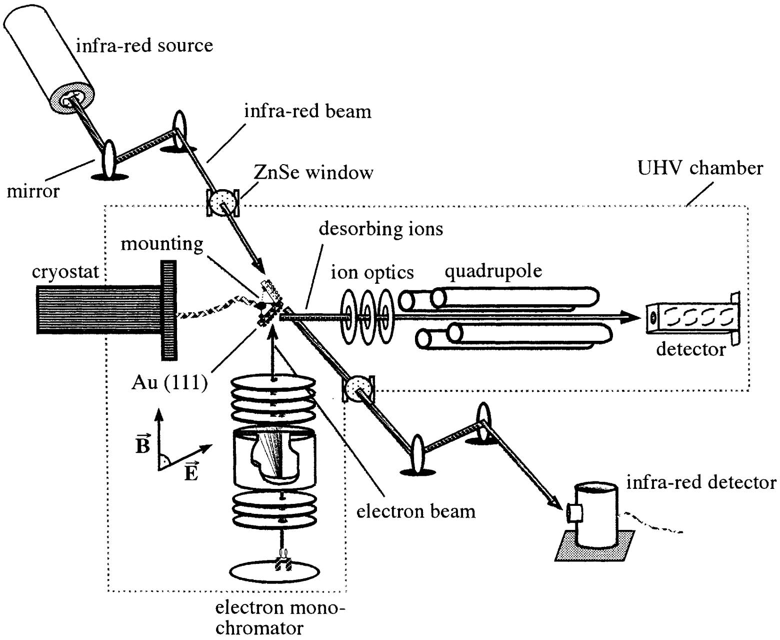

Fig. 1. Scheme of the experimental setup to study electron initiated reactions in an NF_3 film by means of the IRAS technique and electron stimulated desorption of fragment anions.

brated gas quantity effusing from a capillary located 0.7 cm from the gold crystal.

The TEM operates with a weak homogeneous magnetic field (≈ 30 Gauss) which aligns the electrons thus preventing spreading of the beam. The instrument has thereby proven to be particularly suited to study electron-induced processes in the low-energy domain. The base pressure in the chamber is in the 10^{-10} mbar range.

After electron bombardment, the target can be rotated into a position where an infrared beam is transmitted through the adsorbate and reflected at a grazing angle (85°) for applying the IRAS technique which has recently been established in our laboratory [19]. As a consequence of the dielectric properties of the metallic substrate only vibrational modes having a component of the dynamic dipole moment perpendicular to the surface can be excited and only at grazing angles of incidence one can expect appreciable IRAS intensities [20].

The electron energy is calibrated by the onset of the electron injection curve into the substrate (0 eV, vacuum level). In the course of the desorption experiments the energy resolution of the electron beam was 0.2 eV (fwhm) at a current of 40 nA while the IRAS experiments were performed at a much higher electron intensity (≈ 0.8 μA) and lower energy resolution (≈ 0.5 eV).

3. Results and discussion

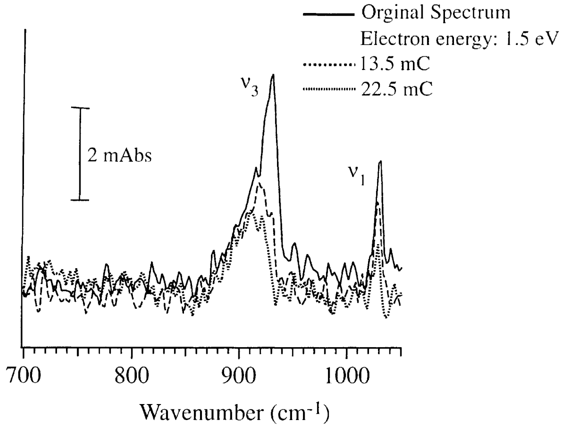

Fig. 2. IRAS signature of the ν_3 (asymmetric stretch) and ν_1 (symmetric stretch) vibration from a 10 ML NF_3 film before and after electron irradiation at an energy of 1.5 eV. The ordinate is in units of milliabsorbance (mAbs).

Fig. 2 shows the IRAS spectrum of a 10 ML film of NF_3 before and after exposition to the electron beam for different times (i.e., exposed charge in mC) at an energy of 1.5 eV. Clearly visible is the ν_1 (symmetric stretch) and ν_3 (asymmetric stretch) vibration at 1030 and 931 cm^{-1}, respectively. While the ν_3 vibration has components of the dynamical dipole moment perpendicular to the C_{3v} axis of the molecule, that of the ν_1 vibration is oriented parallel to it. From the facts that the method is only sensitive to dipole moments oriented perpendicular to the substrate and that both modes are active in IRAS and we conclude that there is no preferential orientation of the NF_3 molecule in the film. The ν_3 mode is shifted with respect to the gas phase value (908 cm^{-1} [21]) but corresponds to that obtained from Raman spectroscopy (930 cm^{-1}) recorded on condensed NF_3 at 62 K [22]. It should be noted that we do not observe a measurable degradation when the IR spectrum of the NF_3 film is recorded *without* electron exposure but for times exceeding those of electron irradiation. At an electron exposure above 35–40 mC degradation reaches saturation. The ν_3 intensity is then dropped to about 20% of the initial value. The residual intensity is due either to an incomplete overlap between the surface area covered by the electron beam and that by the IR beam or to the fact that electron-induced degradation is not operative through *the entire* 10 ML film. While electrons are transmitted through the entire film (as recorded by the electron injection curve) it is not obvious whether DA reactions are restricted to molecules at or near the surface. While the lowest DA channel generating F^-, viz,

$$e^- + NF_3 \rightarrow NF_2 + F^- \tag{1}$$

is exothermic by 0.76 eV [13], electron attachment is only operative for energies above ≈ 0.4 eV due to the disposition of the relevant neutral and anionic potential energy surface with the corresponding Franck–Condon Factors [14]. It is hence a question of the kinetic energy of the electrons within the film. It is likely that electron transport through the NF_3 film occurs via an electronic conduction band like in rare gas films [23] or in non-polar insulating liquids [24].

The degradation of the NF_3 film is studied by monitoring the ν_3 signal for different electron beam exposure times and at different electron energies. This is shown in Fig. 3 for an electron energy of 1.5 eV. The ordinate corresponds to the change of absorbance (Δ) in units of milliabsorbance (mAU). The time dependence of Δ can be approximated [25] by an exponential saturation function of the form

$$\Delta = \Delta_\infty[1 - \exp(-\sigma Q/eA)], \tag{2}$$

with Q the charge quantity corresponding to a particular electron beam exposure time, σ the *degradation parameter*, A the interaction area between the electron beam and the molecular film, e the elementary charge and Δ_∞ the asymptotic change of the absorbance. Note that both Δ and Δ_∞ are *negative numbers*. For one single monolayer the degradation parameter directly corresponds to the degradation cross-section.

An evaluation of data sets shown in Fig. 3 obtained at different electron energies yields the energy dependence of the (relative) degradation cross-section. Fig. 4 indicates that this degradation cross-section peaks at low energy (near 4 eV) and increases again at energies above 6 eV. Although Fig. 4 contains only four data points it must be emphasized that each of these data points is obtained from a series of independent measurements (see Fig. 3). This behaviour can directly be related to the electron scattering and electron capture properties of the target molecule as can be seen by comparing with gas phase studies [10,13] and studies on electron stimulated desorption of anions from an NF_3 film [14].

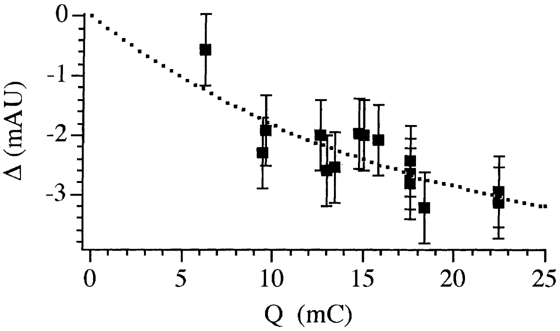

Fig. 3. Change of absorbance (Δ) as a function of electron irradiation time (corresponding to a charge Q in mC) at an electron energy of 1.5 eV. The dotted curve corresponds to a fit using the saturation function (Eq. (2)).

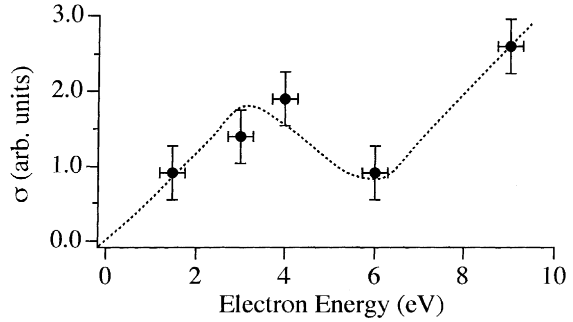

Fig. 4. Relative degradation cross-section as a function of the electron energy extracted from the fitting procedure (Fig. 3). Note that each of the four data points are obtained from a series of independent measurements according to Fig. 3.

Fig. 5a shows the F^- yield from gas phase NF_3 obtained in a previous study from our laboratory

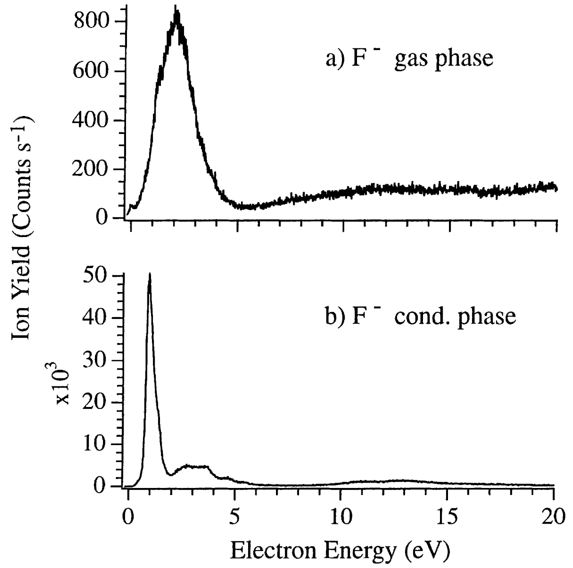

Fig. 5. Comparison of F^- formation from (a) gas phase NF_3 (reproduced from Ref. [11]), and (b) from an NF_3 film at a thickness (10 ML) also used for the IRAS studies. The desorption feature is narrower than the gas phase ion yield due to the kinetic energy filter for desorption (see the text).

[14] and the desorption yield obtained from a 10 monolayer film recorded in the course of the present experiments. While degradation observed by IRAS is operative through the entire molecular film, desorption of ions is probably restricted to reactions at or near the surface (vida supra). F^- formation exhibits pronounced resonant structures in the low-energy region, both from gas phase NF_3 and as desorption product from condensed molecules. This signal is due to resonant dissociative electron attachment. In the gas phase the precursor ion $NF_3^{-\#}$ (the resonance) decomposes into the ionic fragments F^-, F_2^- and NF_2^- (plus the corresponding neutrals) with F^- by far the dominant channel. While gas phase NF_3 yields a broad and unresolved signal in the energy range 0.4–5 eV this feature splits into two energetically separated resonances in the desorption yield. As previously discussed in detail [14] NF_3 possesses two energetically overlapping resonances in this energy range. It is very likely that both resonances are associated with the electronic ground state of the anion as electronically excited states of the neutral are located above 7 eV. While the low-energy resonance *impulsively* decomposes into $F^- + NF_2$ thereby releasing an appreciable amount of kinetic energy, the second resonance decomposes less directly yielding a kinetic energy distribution with a comparably low value of the mean energy. On the other hand, desorption of an ion from a surface requires a minimum of translational energy to overcome the solvation energy. It is in fact this *kinetic energy filter* which produces the two separated features in the desorption yield [14]. While F^- is by far the dominant ion in gas phase DA to NF_3, there is no direct information on the neutral fragments formed. From thermodynamics, however, it is clear that only above 2.12 eV the multiple fragmentation channel $F^- + F + NF$ becomes accessible while below that energy only the NF_2 radical can be formed.

From the energy dependence we conclude that the degradation cross-section can directly be related to *resonant electron capture* as the only initial process. This is in fact the only process which can initiate chemical changes in this energy domain. Another process operative in this energy range is *vibrational excitation* of the neutral molecule. Since the vibrational *excitation functions* also exhibit a low-energy resonance [26] one can conclude that effective vibrational excitation also proceeds via *resonant inelastic scattering*, i.e. the transient negative ion can either dissociate (formation of F^-) or eject the extra electron with some energy loss recovering the neutral molecule in a vibrationally excited state. In a condensed environment, this energy will immediately dissipate and no chemical change can occur. It should also be noted that *undissociated neutrals* can in fact desorb via short-lived negative ion resonances: once an ion is formed at or near the surface, it will first be accelerated towards the surface and after electron detachment the neutral system may eventually find itself in the desorption continuum [27]. By performing thermal desorption spectroscopy, however, we can safely say that the amount of material in the adsorbate does not significantly change upon electron exposition and desorption of neutral molecules can hence be excluded as a major source of the degradation observed by IRAS.

In contrast to the low-energy domain the increase of the degradation cross-section at higher energies can no longer be associated with one single process as at these energies electronic excitation associated with inelastic electron scattering contributes. The electronically excited states can, e.g., dissociate into neutral fragments and the *inelastic*ally scattered electrons can be captured by further NF_3 molecules.

We have also performed an extended IR analysis of the NF_3 film after electron irradiation in order to get information on new species formed in the course of degradation. Although these measurements still suffer from a weak signal to noise level, there is evidence that irradiation at 1.5 eV creates NF_2 radicals and N_2F_4 molecules. The latter may be formed by the exothermic association of two adjacent NF_2 radicals. In contrast to this exposure of 8 eV electrons gives evidence for NF and NF_2 but not N_2F_4. This may indicate that N_2F_4 which is eventually formed at 8 eV is degraded by subsequent electron collisions and that degradation is not (or less) operative at low electron energies.

We finally note that in a condensed environment the relaxed NF_3^- can certainly be formed in the course of electron capture. Density Functional Theory (DFT) calculations predict an appreciable adiabatic electron affinity of EA (NF_3) = 1.71 eV and a strong geometry change on going to the anion (C_s symmetry with one N–F bond considerably enlarged) [13]. Since so far only calculated gas phase vibrational frequencies of the anion are available, we were not successful to unambiguously identify this ion in the molecular film.

Acknowledgements

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