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Revisiting the electron stimulated desorption of anions from thin films of CF_2Cl_2

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This work is dedicated to Professor Eugen Illenberger on the occasion of his 65th birthday.

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ABSTRACT

A recently constructed TOF mass spectrometer was used to measure the electron-stimulated desorption of anions from thin films of vapor-deposited CF_2Cl_2 in the 0–20 eV energy range. In addition to the previously observed signals of F^- and Cl^-, the anions CF^-, $F_2{}^-$, $CF_2{}^-$, ClF^-, and $Cl_2{}^-$ are detected. Measurements as a function of both incident current and CF_2Cl_2 coverage on a Kr substrate indicate that all desorbed ions are the result of unimolecular dissociation, initiated by the impact of a single electron. Both dissociative electron attachment (DEA) and dipolar dissociation (DD) processes are found to contribute to the desorption yield, but to an extent that is anion dependent. The DEA and DD derived yields of the anions demonstrate distinctly different dependencies on molecule–metal distance, as has been observed in other molecular solids. As previously reported, prolonged bombardment of the CF_2Cl_2 film leads to the production of Cl_2 molecules as evidenced by an enhanced desorption signal of Cl^- at incident electron energies near 5 eV. We have used this effect used to measure the relative cross-section for production of Cl_2 as a function of energy and observe a threshold energy for this process of 7 eV.

1. Introduction

The chemically inert chlorofluorocarbon molecules (CFCs), of which CF_2Cl_2 (Freon 12) is probably the best known example, were widely used in applications ranging from refrigerants to anesthetics, despite eventual concern that they, via photodissociation, were a potential source of Cl atoms that would damage stratospheric ozone [1]. It was not until the observations of the seasonal destruction of the ozone layer near polar regions in the late 1980s [2] that CFCs were definitively linked to such damage and international treaties implemented to limit their manufacture and use.

Aside from UV photolysis, there has been considerable interest in the interactions of low energy electrons (LEEs) with CFCs particularly because they are efficiently dissociated by LEEs via formation of transient negative ions (TNIs) and the process of dissociative electron attachment (DEA). Such reactions, for the molecule CF_2Cl_2, are of the type:

$$e^- + CF_2Cl_2 \rightarrow CF_2Cl_2{}^- \rightarrow Cl^- + CF_2Cl \qquad (1)$$

$$e^- + CF_2Cl_2 \rightarrow CF_2Cl_2{}^- \rightarrow F^- + CFCl_2 \qquad (2)$$

Indeed the earliest *high-resolution* electron impact studies of DEA to gas phase CFCs were undertaken in Professor Illenberger's laboratory [3], where for CF_2Cl_2, the following ions were observed (in order of decreasing yield) via resonances at incident electron energies (E_i) less than ~4 eV: Cl^-, F^-, CF_2Cl^-, FCl^-, and $Cl_2{}^-$. The cross-section for production of Cl^- via reaction (1) at an incident electron energy (E_i) of 0 eV has been measured as 6×10^{-16} cm^2 for a supersonically expanded beam of the gas [4]. This value has been shown, however, to increase by a factor of ~4 as the gas temperature is increased from 300 to 420 K [5].

DEA to condensed CF_2Cl_2 has also been observed by the electron stimulated desorption (ESD) of the anions Cl^- and F^- [6] and has been compared to results from gas and cluster phase [7]. At incident energies less than ~10 eV, anion desorption proceeds via TNI formation, although states observed in the gas phase at $E_i < 3$ eV do not appear to contribute to the ESD yield, quite possibly because ions created at these energies do not possess sufficient kinetic energy to escape from the CF_2Cl_2 film. These same states, however, are observed to persist into the cluster phase [7]. Recently, we have observed, using post-irradiation temperature programmed desorption (TPD) (M. Rajappan et al., unpublished data) the signature of the DEA process, in the synthesis of $C_2F_2Cl_4$ and $C_2F_3Cl_3$ within multilayer CF_2Cl_2 following irradiation with 2–5 eV LEE. Above ~10 eV, desorption of Cl^- and F^- is attributed to the dipolar dissociation (DD) processes [6,7]:

$$e^- + CF_2Cl_2 \rightarrow CF_2Cl^+ + Cl^- \qquad (3)$$

$$e^- + CF_2Cl_2 \rightarrow CFCl_2{}^+ + F^- \qquad (4)$$

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Although this designation of DD by earlier authors was made despite an absence of information concerning the ESD of cations from CF_2Cl_2, it should be noted that aside from DD, no other non-resonant process has been advanced to explain anion desorption at energies above ~10 eV.

The ESD technique has additionally been used to identify and monitor the synthesis of Cl_2 within LEE irradiated multilayer films of CF_2Cl_2 [6]. DEA to condensed CF_2Cl_2 has also been invoked to explain a "giant enhancement" (10^2 to 10^4) in Cl^- and F^- desorption yields observed when sub-monolayer quantities of the molecule, co-deposited with either H_2O or NH_3 on Ru(0 0 0 1) substrate, are bombarded by 250 eV electrons [8,9].

A new time-of-flight (TOF) mass spectrometer for ESD studies was recently constructed in the Sherbrooke laboratory and has already demonstrated superior sensitivity over other instruments [10]. In the work described herein, we present state-of-the-art data on the ESD of anions from CF_2Cl_2 films of varying preparation. In particular we have identified new desorption channels and observed a very marked difference in the variation with film thickness of the anion signals attributable to DEA and DD. We have additionally measured with improved energy resolution, relative cross-section for Cl_2 synthesis.

2. Experimental

ESD measurements were performed under ultrahigh vacuum (UHV) conditions within a chamber, ion-pumped to a base pressure of 5×10^{-11} Torr. The TOF mass analyzer has been described earlier [11]. In the present experiments, sample films were vapor deposited onto a platinum foil substrate, the temperature of which can be stabilized between 10 and 300 K using a closed cycle He cryostat and resistive heating elements. Film temperatures were measured with a Ag–Ni thermocouple attached to the cold-tip of the cryostat. The foil was cleaned by resistive heating to 900 K. The number of layers condensed onto the clean Pt was determined by means of a volumetric dosing procedure [12] with an accuracy of about ±30% and an overall repeatability of ±0.25 monolayer (ML). In the present experiments, high purity CF_2Cl_2 and Kr gases were obtained from Matheson.

Sample films were bombarded with a 2–20 eV electron beam produced by a Kimball Physics ELG-2 electron gun (energy resolution ~0.5 eV FWHM). Electrons impinged onto the sample in the horizontal plane at an incident angle of 45° with respect to the surface normal and focused on a 2 mm^2 spot at 20 mm working distance. For time-of-flight measurements, the electron gun was operated in a pulsed mode and was typically pulsed "on" for 800 ns at a rate of 5000 Hz. The time-averaged incident electron current for most of the present measurements was 0.5 nA at 10 eV, as measured on the clean Pt foil. The absolute electron energy scale of the incident beam was calibrated from the onset energy of electron transmission through multilayer films of CF_2Cl_2 (and Kr when appropriate) and has an estimated uncertainty of about ±0.3 eV. The incident electron energy was controlled by computer.

Anion detection was performed by applying a negative potential pulse (−2 kV, rise/fall time 30 ns, pulse width of 2 μs) to the Pt substrate a short time (~10 ns) after application of the electron beam pulse. The desorbed ions are propelled into the entrance optics of a Reflectron TOF mass analyzer (Kore Technology R-500) positioned along the surface normal at a distance of 10 mm from the sample surface. The variation of anion yields with E_i (i.e., *anion yield functions*) are obtained by recording a sequence of mass spectra at different E_i. This experimental set-up allows ions to be detected with high sensitivity while inflicting a minimum amount of damage to the condensed molecular film.

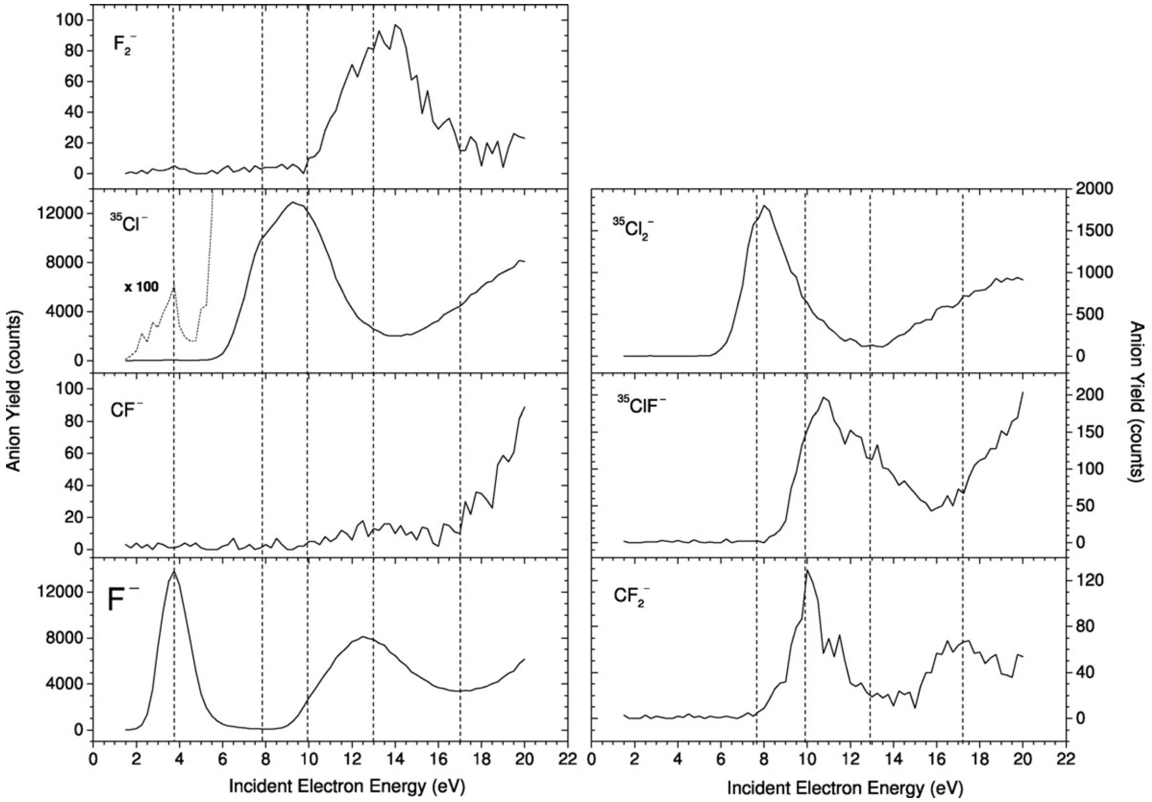

Fig. 1. Anion yield functions from eight monolayers (ML) of CF_2Cl_2 measured at a temperature of 30 K. The incident current was 0.5 nA (as measured on clean Pt at 10 eV) and 25,000 electron pulses (=5 s exposure) were used to accumulate each point. Vertical dashed lines indicate the approximate energies of resonances seen in several yield functions.

Table 1
Resonance energies (±0.5 eV) observed in the anion yield functions of Fig. 1 together with the associated ion channels

Resonance energy (eV)	Decay channels
3.7	F^-, Cl^-
7.5–8.0	Cl^-, $Cl_2{}^-$
9.5–10.0	Cl^-, $CF_2{}^-$, ClF^-, (F^-)
12.5–13	F^-, CF^-, (Cl^-), $F_2{}^-$, ClF^-
17.0	$CF_2{}^-$, ClF^-

Parentheses indicate that the channel is only very weakly present.

3. Results and discussion

3.1. Anion yield functions

Fig. 1 presents anion yield functions obtained from an 8-ML thick film of CF_2Cl_2 at a temperature of 30 K. In addition to the previously reported F^- and Cl^- signals [6,7], we observe measurable yields of the ions: CF^-, $F_2{}^-$, $CF_2{}^-$, ClF^-, and $Cl_2{}^-$. No other desorbed anion signals were seen. By comparing these yield functions, it is possible to identify TNI at five energies (to within ±0.5 eV) that appear to drive desorption by DEA. The energies of these resonances and the identities of final anionic channel are reported in Table 1.

It should be noted that the relative intensity of desorbed anions may not be indicative of the relative cross-sections for the formation of each species, since the probability that an anion desorbs depends on the details of the dissociation dynamics (which determine its initial kinetic energy) and is modulated by (anion specific) scattering processes occurring within the film [13]. Moreover, the sensitivity of the present TOF mass analyzer is dependent on the initial kinetic energy of desorbed ions, and faster (usually less massive) ions are detected less efficiently than the slower (typically more massive) ones [11]. However, since the mass ratio between the lightest (F^-) and heaviest fragment ($Cl_2{}^-$) is only ~3.5 this effect is unlikely as pronounced as in our earlier measurements involving the detection of H^- [11].

Below 12 eV, the present F^- and Cl^- yield functions are in broad agreement with those published earlier [6,7]. A strong resonance is seen in the F^- yield function at an energy of 3.7 eV; the signal then falls to a minimal value, and increases again at energies greater than ~8 eV. The present data reveal near 13 eV a resonance, which is hinted in the measurements of Langer et al. at a slightly higher energy (13.5 eV) [7]. The F^- measurements of Hedhili et al. [6] do not extend above 12 eV. The Cl^- yield function presented herein most closely resembles that reported by Langer et al. [7]. It exhibits a very weak resonance structure at ~4 eV and a broad structure from 6 to about 14 eV that consists of a resonance at ~8 eV and another stronger resonance at ~10 eV. The relative intensities of these last two resonances are reversed in the higher electron energy resolution data by Hedhili et al. [6]. Though varying widely over the entire 2–20 eV incident energy range, the relative signals of F^- and Cl^- are broadly consistent with the earlier studies.

The other desorbed anions have been observed previously only when CF_2Cl_2 films of varying preparation (i.e., deposited with Xe and with NH_3 on Ru(0 0 0 1)) were exposed to ~170 eV electrons [14]. The exact mechanisms underlying their appearance in these experiments are unclear. In the gas phase, the formation of ClF^- and $Cl_2{}^-$ has been reported via DEA involving resonances at $E_i < 4$ eV [3,7], i.e., at energies significantly lower than those observed in the present experiments. In addition, we do not observe the desorption of CF_2Cl^-, which has been reported as a gas-phase dissociation product [3,7]. It is very likely that such ions, if formed by electron impact on CF_2Cl_2 films, would possess insufficient kinetic energy to desorb.

Additional measurements (see supplemental materials) performed in our laboratory show that the desorbed yield of each anion is proportional to the incident current (in the range 0.02–5 nA) and indicate that *even the weak anion signals are generated by single electron scattering events and should not be attributed to the dissociation of any product synthesised in the film by electron irradiation* [15]. Moreover, measurements as a function of CF_2Cl_2 coverage on a 3-ML thick Kr film (supplemental material), reveal that all anion signals increase linearly with coverage (at low coverage) and gradually approach saturation at about 3–4 ML, as is commonly seen in ESD experiments [16,17]. This result is a clear indication that the weaker anion signals do not derive from multiple electron scattering events nor reactive scattering by either the F^- or Cl^- ions [18–20]. As can be seen from Fig. 1, the general shape of the yield functions for the weaker signals indicates that anion desorption is dominated by the DEA process in the 2–20 eV energy range.

3.2. Effect of substrate on DEA and DD processes

Although the shape of anion yield functions (i.e., the relative contributions of different desorption pathways) obtained from CF_2Cl_2 films grown on "thick" Kr films (i.e., of 3 ML or more) varies little with CF_2Cl_2 coverage, the same is not true for films deposited directly onto the Pt substrate. For example, Fig. 2a shows how yield functions for both Cl^- and F^- desorption are modulated by the quantity of CF_2Cl_2 deposited on Pt, whereas Fig. 2b demonstrates how the anion signal at particular energies (indicated with arrows in Fig. 2a and attributable to different dissociation mechanisms, varies with coverage.

Desorption signals associated predominately with TNI formation and DEA (e.g., Cl^- near 7.5 and 9.5 eV, F^- near 4 eV) are strongly suppressed at sub-monolayer coverage. We attribute this decrease in the anion signal to two reasons: (1) the large polarization energy close to the metal represents a significant energetic barrier to anion desorption [21], (2) TNI lifetime is thought to be decreased close to the metal [22]. In contrast, anion signals linked to DD, e.g., Cl^- at 14 eV and F^- at 16 eV, are strongest in the first monolayer; the intermediate $CF_2Cl_2{}^*$ state for DD is neutral and its energy and lifetime much less affected by local polarization [21]. However and as explained for the case of O^- desorption from O_2 films [21], local polarization does affect (lower) the dissociation limits for the DD process and effectively increases the energy available for desorption. Note that the maximal DD desorption signals are observed at different coverages for Cl^- and F^-, indicating that the desorption yield is modulated by a complex interplay of factors including the cross-section for exciting the relevant DD intermediate, the dissociation dynamics (i.e., potential surface of the dissociative state) and post-dissociation interactions of fragment ions. These effects are so strong in the case of F^- that the DD process and its variation with film thickness completely mask those of the TNI/DEA process observed near 12 eV (Fig. 2b).

To exclude the possible role of CF_2Cl_2 coverage effects in the experimental data of Fig. 2 and to demonstrate conclusively how proximity to the metal substrate modulates the desorption processes, we compare in Fig. 3 yield functions for Cl^-, F^-, and $Cl_2{}^-$ from 0.25 ML of CF_2Cl_2 deposited directly on Pt and on 1–3 ML of Kr. As the molecule–metal distance is increased, we observe essentially the same behavior illustrated in Fig. 2; DEA-linked contributions to the desorption yield are enhanced and those associated with DD are suppressed. We note that desorption of the $Cl_2{}^-$, and other anions with weaker signals (data not shown), is dominated by DEA below 16 eV. The data of Figs. 2 and 3 further indicate that the anion signals derive essentially from the film–vacuum interface.

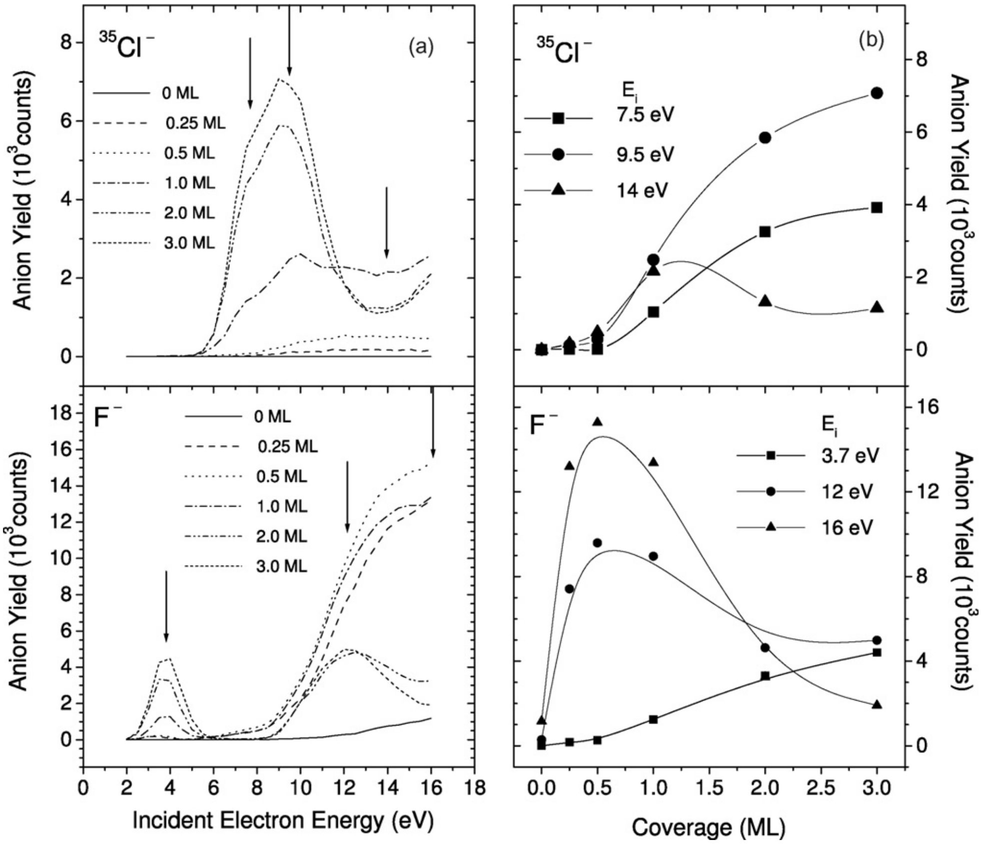

Fig. 2. (a) Variation of Cl$^-$ and F$^-$ yield functions with thickness of CF_2Cl_2 film deposited onto Pt substrate. A film temperature of 30 K and 12,500 electron pulses per point at 0.5 nA (measured at 10 eV on Pt) were used. (b) Variation of Cl$^-$ and F$^-$ desorption signal at the indicated energies (identified by vertical arrows in panel (a)).

3.3. Electron induced synthesis of Cl_2

Hedhili et al. observed that prolonged irradiation of CF_2Cl_2 films by LEEs at temperatures below 75 K gave rise to a new desorption signal of Cl$^-$ at incident electron energies around 5 eV, and attributed its origin to the electron-induced synthesis of Cl_2 [6]. By recording the Cl$^-$ signal at $E_i = 6$ eV before and after *extended electron irradiation* at five other energies, these authors presented initial data on the dependence of Cl_2 formation on electron irradiation energy, though *definitive* information on the synthesis mechanism and its energetic threshold were not presented.

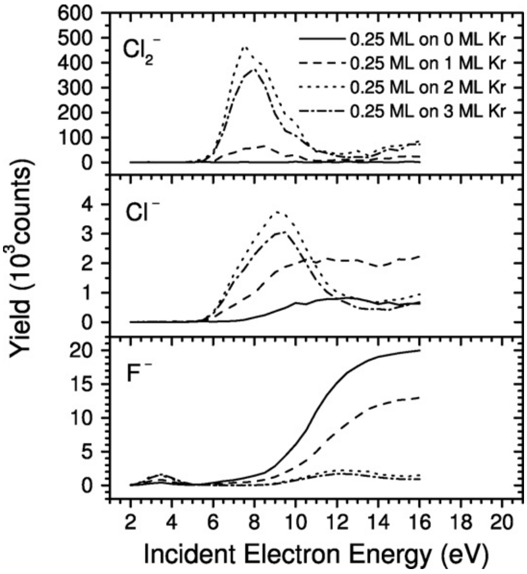

Fig. 3. Variation of Cl$^-$ and F$^-$ yield functions with thickness of CF_2Cl_2 film deposited onto Kr substrate. A film temperature of 30 K and 10,000 electron pulses per point were used.

We have attempted to improve on these earlier measurements using a method previously employed to study electron-induced degradation of thiophene films [11]. The data in Fig. 4 (upper panel) show how the Cl$^-$ signal at 5.5 eV (attributable to Cl_2 synthesis and measured during 2 s at an average incident current of 0.5 nA) varies with time of irradiation at three other (indicated) electron energies. These measurements were made using 3-ML thick films of CF_2Cl_2 at 34 K. A new film was prepared for each irradiation energy. For all irradiation energies studied, a linear variation of Cl$^-$ signal with irradiation time was initially observed, indicating that in the low dose limit, Cl_2 production is initiated by the interaction of a single electron with CF_2Cl_2. Such a result would seem to refute the earlier suggestion [6] that the recombination of Cl$^-$ atoms (created via a number of processes, including quite possibly DEA) to form Cl_2 may play an important role in Cl_2 production. We note that while it is possible that the impact of LEE on CF_2Cl_2 films could, in addition to forming Cl_2, degrade both the CF_2Cl_2 and the synthesised Cl_2 molecules via various processes, such effects would become apparent only after degrading a considerable fraction of CF_2Cl_2 or producing sufficient Cl_2 to make e-Cl_2 scattering likely. However, the observed linear increase in Cl-signal (and hence Cl_2 concentration) with time, indicates that degradation of CF_2Cl_2 and/or Cl_2 are insignificant during measurement and thus that the energy dependence presented in Fig. 4b *cannot* be attributed to the combined effects of Cl_2 formation and loss. Indeed as discussed

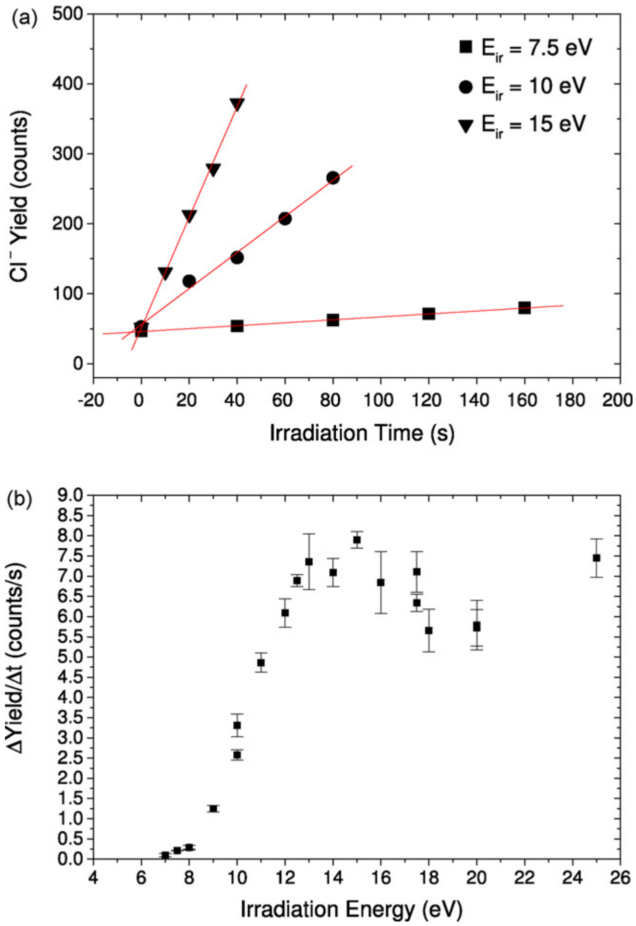

Fig. 4. (a) Sample data showing variation of the ESD signal of Cl^- from a 3-ML thick film of CF_2Cl_2 as measured at 5.5 eV during 10,000 electron pulses, after prolonged, repetitive exposure to electrons of the indicated irradiation energies. In each case the dependencies are well approximated by straight lines; (b) the slopes of these lines (and those obtained at other energies) are plotted against irradiation energy.

elsewhere [11], the linear slopes of each data set presented in Fig. 4a are proportional to the cross-section for Cl_2 production at the relevant energy.

These gradients are plotted as a function of irradiation energy in Fig. 4b. We observe a threshold energy for Cl_2 production between 7 and 7.5 eV; no Cl_2 production is observed when films are irradiated with electrons of lower energy (e.g., 5.4 eV). A maximum in Cl_2 production is reached at about 14 eV, consistent with the earlier experiments [6], and suggests that the synthesis pathway involves formation of a TNI. Interestingly, this maximum appears at roughly the same energy as maxima in the F^-, CF^-, F_2^-, and ClF^- yield functions (Fig. 1). The maximum in Cl_2 formation is not as well defined (narrow) as that reported by Hedhili et al. [6], but since the present results were obtained at a low fluence the measurements presented herein must be considered more accurate.

The theoretical minimum energy for the production of molecular chlorine is considerably lower than the observed threshold because the reaction, $e^- + CF_2Cl_2 \rightarrow Cl_2 + CF_2$ is endothermic by 3.2 eV [6]. It is thus likely that Cl_2 synthesis proceeds via excitation of one or more of the manifold CF_2Cl_2 electronic and ionic states observed above ~6 eV in electron energy loss spectra of the isolated molecule [23].

4. Conclusion

The enhanced sensitivity of the present TOF mass spectrometer reveals the ESD of anions to be even richer than previously reported; the desorption of anions F_2^-, CF_2^-, ClF_2, Cl_2^- at E_i below 20 eV were observed for the first time and to proceed via formation of previously unobserved TNI. The instrument has additionally permitted an accurate identification of the onset energy for Cl_2 synthesis. The DEA and DD anion yields were found to be strongly modulated by proximity of the supporting metal surface, particularly in the cases of F^- and Cl^- desorption at $E_i > 10$ eV attributable to DD. Whether this effect has contributed to previously observed “giant enhancement” in anion desorption [8,9] is a question worthy of further study.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ijms.2008.05.030.

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