Negative-Ion Enhancements in Electron-Stimulated Desorption of CF_2Cl_2 Coadsorbed with Nonpolar and Polar Gases on Ru(0001)

Q.-B. Lu and Theodore E. Madey
*Laboratory for Surface Modification, and Department of Physics and Astronomy, Rutgers,
The State University of New Jersey, Piscataway, New Jersey 08854-8019*

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Electron-stimulated desorption of F^- and Cl^- from submonolayer CF_2Cl_2-covered Ru(0001) is strongly affected by coadsorption of polar molecules (H_2O and NH_3) and nonpolar rare-gas atoms (Xe, Kr, and Ar). Giant anionic enhancements (up to 10^2-10^4) are observed for polar molecules, which are several orders of magnitude higher than by nonpolar atoms. The giant enhancements are attributed to enhanced dissociation of CF_2Cl_2 by attachment of self-trapped electrons in polar molecules.
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The study of chlorofluorocarbons (CFCs) is a subject of widespread interest. Because of industrial activities, CFCs, mainly $CFCl_3$ (CFC-11) and CF_2Cl_2 (CFC-12), have been emitted into the atmosphere and are believed to cause depletion of the ozone layer via production of Cl atoms from photodissociation [1].

Dissociative electron attachment (DEA) to produce negative ions is an extremely efficient process in collisions of low-energy electrons with gas- and condensed-phase CFC molecules [2,3]. For condensed-phase molecules, negative-ion yields may be increased by changes in the surrounding medium. There are several mechanisms proposed to explain anionic enhancements observed in various experiments. The F^- yield from electron-stimulated desorption (ESD) of ~1 monolayer (ML) of PF_3 adsorbed on a Ru(0001) is enhanced by 1.5–4 when a ~1 ML rare gas (RG) (Xe, Kr) or water film is deposited on the PF_3 monolayer [4]. This enhancement was attributed to a dielectric screening effect [5]: The dielectric layer on the surface induces a potential barrier that increases the ion survival probability. Moreover, in ESD of fractional-monolayer molecules (ABs) absorbed on top of thick RG films, negative-ion enhancements due to the formation of anionic excitons (RG^{*-}) were observed [6]. A resonant coupling between a *core-excited* AB^{*-} and an anionic exciton (RG^{*-}) has been proposed [6]: $RG^{*-} + AB \rightarrow AB^{*-} + RG$, followed by dissociation of AB^{*-}. In addition, Nagesha and Sanche [7] have recently reported an increase by ~2.5 of the DEA cross section when 0.1 ML CF_3Cl is sandwiched between two 13 ML Kr layers relative to absorption on a 13 ML Kr surface; this is interpreted in terms of the R-matrix model: The added Kr layer enhances the polarization energy on CF_3Cl^- to increase the survival probability of the resonance against autodetachment. In their experiments, they measured the charge trapped in the dielectric films, rather than desorption of negative ions, and could not distinguish whether the charge is trapped in a stabilized CF_3Cl^- or a dissociated Cl^- fragment [8].

In this Letter, we report the effect of coadsorbed polar molecules (H_2O and NH_3) and nonpolar rare-gas atoms (Ar, Kr, and Xe) on F^- and Cl^- yields in ESD of CF_2Cl_2-covered Ru(0001) with various coverages. A striking difference between polar and nonpolar coadsorbates is found: For polar molecules the maximum F^- and Cl^- enhancements are huge, up to factors of 10^2 and 10^4, respectively, which are several orders of magnitude higher than for nonpolar coadsorbates. The giant anionic enhancements are attributed to enhanced dissociation of CF_2Cl_2 by the capture of self-trapped electrons by polar molecules. In addition, the resonant coupling (RC) mechanism is manifest in the difference of the Cl^- enhancements between nonpolar RGs. It is also observed that anionic enhancements increase strongly with decreasing CF_2Cl_2 coverage, which is attributed to intermolecular deexcitation effects. Giant Cl^- enhancements caused by the attachment of self-trapped electrons to CF_2Cl_2 on the surface of polar stratospheric clouds (PSCs) may be of great importance to the creation of the Antarctic ozone hole [9], as PSCs of water ice are formed over Antarctica [10] and Cl^- can be converted into Cl atoms which then destroy O_3.

The experiments were conducted in an ultrahigh vacuum (UHV) chamber with a base pressure $\sim 4 \times 10^{-11}$ torr [4,11]. An electron-stimulated desorption ion angular distribution (ESDIAD) detector with time-of-flight capability permits a direct measurement of the total yield and the angular distribution of a specific ion species. The Ru(0001) crystal can be cooled to 25 K with a closed-cycle helium refrigerator and heated to 1600 K by electron bombardment. Purified CF_2Cl_2 and other gases (Ar, Kr, Xe, H_2O, and NH_3) are, respectively, dosed onto the surface at 25 K with two separate directional dosers. Their coverages are determined using thermal desorption spectroscopy (TDS); one monolayer is defined as the coverage corresponding to the saturation of the monolayer peak in TDS spectra [4,11]. The energy of the electron beam is 250 eV. During electron bombardment, the metal substrate is a source of low-energy secondary electrons, which have a maximum yield at 0–2 eV and a high-energy tail extending to ≥10 eV. Low-energy electrons play a dominant role in the electron-induced dissociation of CFCs [2,3,11]. The electron current is adjustable between 0.05 and 20 nA with a beam size ~1 mm and the collection time for each data point is 5 sec, to avoid detector saturation and to minimize beam damage. The anionic enhancements are independent of the electron current (and dose).

ESDIAD patterns of F^- and Cl^- ions from adsorbed CF_2Cl_2 show that desorption of both F^- and Cl^- is along the surface normal [11]. The emission direction of F^- and Cl^- is not changed by coadsorption. The variations of the F^- and Cl^- yields as functions of Xe coverage for various CF_2Cl_2 precoverages are shown in Figs. 1(a) and 1(b). For the lowest CF_2Cl_2 coverages both F^- and Cl^- yields increase greatly with the initial Xe deposition, exhibit a maximum about 10 times their initial value at nearly 1.5 ML of Xe, and finally decrease to zero intensity at ~3.5 ML of Xe. Similar enhancements of F^- and Cl^- are observed for respective coadsorption with Kr and Ar, but the enhancement of Cl^- is in the order Xe > Kr ≥ Ar. The decrease of F^- and Cl^- with high coadsorbate coverage is due to elastic and inelastic scattering as the desorbed ions pass through the overlayer [4]. Both the F^+ and Cl^+ yields show a monotonic attenuation and quickly disappear with increasing coadsorbate coverage [12], suggesting that coadsorption results in neither the aggregation of CF_2Cl_2 molecules (the formation of islands) nor an exchange of adsorption sites of CF_2Cl_2 with coadsorbates [12]. Shown in Fig. 2(a) is the maximum value of enhancement of the F^- and Cl^- yields as a function of CF_2Cl_2 precoverage on Ru(0001) with coadsorption of Xe, Kr, and Ar, respectively. The Cl^- data for CF_2Cl_2 coverages <0.3 ML are not available, as the initial Cl^- yield prior to RG deposition is too low for reliable measurements [11]. For three RGs in Fig. 2(a), the F^- and Cl^- enhancements are similar, with one exception: The Cl^- enhancement for Xe coadsorption is appreciably larger than for the other cases.

For coadsorption of CF_2Cl_2 with polar H_2O and NH_3, much stronger enhancements of F^- and Cl^- are observed, as shown in Fig. 2(b). For H_2O coadsorption, F^- and Cl^- exhibit maximum enhancements by nearly 2 orders of magnitude at about 1 ML of H_2O. Qualitatively similar results are observed for the coadsorption of NH_3, but the magnitudes of enhancements of F^- and Cl^- are much larger: The maximum NH_3-induced F^- enhancement for 0.1 ML CF_2Cl_2 is ~200 times; the Cl^- enhancement for 0.3 ML CF_2Cl_2 is a factor of $\sim 3 \times 10^4$. The corresponding Cl^- desorption cross section for the maximum enhancement

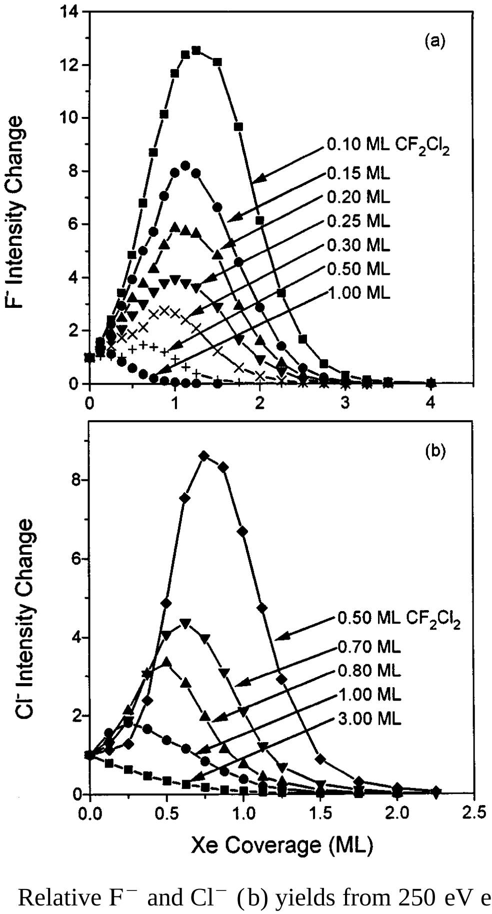

FIG. 1. Relative F^- and Cl^- (b) yields from 250 eV electrons incident onto various coverages of CF_2Cl_2 on Ru(0001) as a function of Xe coverage, where the data in each set are normalized to the initial value at 0 Xe coverage.

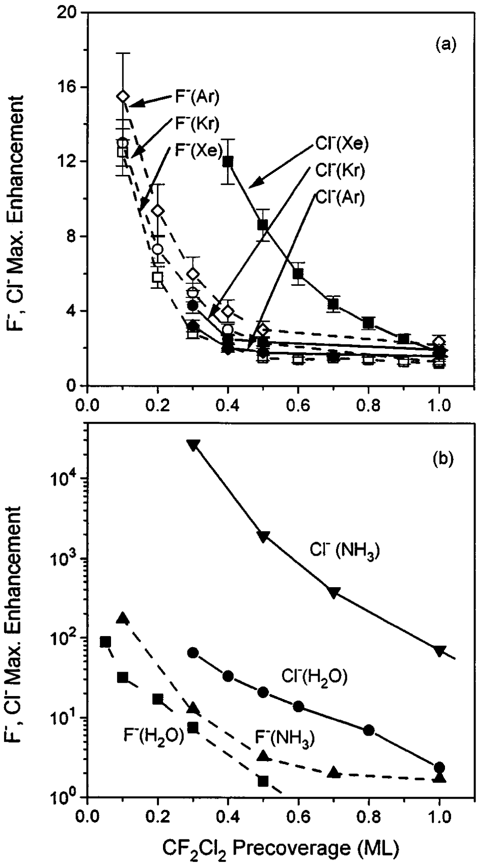

FIG. 2. Maximum magnitude of F^- and Cl^- enhancements versus CF_2Cl_2 coverage (a) for nonpolar Xe, Kr, and Ar coadsorption; (b) for polar H_2O and NH_3 coadsorption.

is ~6×10^{-18} cm^2. However, the total cross section for Cl^- formation induced by electrons is much greater than the Cl^- desorption cross section, since most of the dissociated Cl^- ions are captured at the surface due to the image potential [11]. For an identical CF_2Cl_2 precoverage, the enhancement of Cl^- is much larger than that of F^- for either H_2O or NH_3 coadsorption. From Fig. 2, it is seen that the magnitudes of F^- and Cl^- enhancements rapidly decrease with increasing CF_2Cl_2 coverage.

Before we discuss the above results, it is useful to summarize the DEA results of CF_2Cl_2. Gas- and condensed-phase experiments have established that there are two single-particle resonances at electron energies of nearly 0 and 3.0 eV associated with two vibrationally excited states of the molecule, leading to the ejection of Cl^- and F^-, respectively [2,3]. For the condensed phase, there is an additional core-excited Feshbach resonance centered around 7.0 eV associated with the first electronically excited state of the molecule, which leads exclusively to Cl^- [2]. We have recently studied the ESD of adsorbed CF_2Cl_2 on Ru(0001) from 0 to 5 ML [11]. At an incident electron energy of hundreds of eV, the dominant product is F^-; the Cl^- yield is much smaller.

Consider the mechanisms for the observed negative-ion enhancement. First, we note that neither the dielectric screening effect [5] nor the R-matrix model [7] can account for the observed strongly CF_2Cl_2-precoverage-dependent enhancements of F^- and Cl^-; molecular precoverage is not an input parameter in these model calculations [5,7]. Moreover, the dielectric screening effect would predict greater anionic enhancements for H_2O than for NH_3 coadsorption, as the dielectric constant ε of H_2O is greater than that of NH_3 [13]. This is not consistent with the observed results. Second, the observed anionic enhancements cannot be attributed to the increases in secondary electron emission (SEE) from the substrate caused by coadsorbates. In fact, it is observed that coadsorption of either 1 ML H_2O or 1 ML NH_3 with 0.3 ML CF_2Cl_2 results in a smaller increase (by a factor of ~1.3 ± 0.1) of the SEE yield than 1 ML Xe coadsorption (by a factor of ~1.6 ± 0.1) [12].

The trends for Cl^- enhancements with coadsorption of three RGs are consistent with the RC mechanism, in which anionic excitons (RG^{*-}) couple with varying degrees of effectiveness to core-excited $CF_2Cl_2{}^{*-}$ resonance at ~7.0 eV leading to Cl^- desorption [2]. Here, RG^{*-} excitons are created by secondary electrons from the metal substrate during electron bombardment. One can expect a strong coupling of the 7.0 eV $CF_2Cl_2{}^{*-}$ resonance with a Xe^{*-} exciton (~7.7 eV), a weak coupling with Kr^{*-} (9.7 eV), and a negligible coupling with Ar^{*-} (11.6 eV) [6], although the energies of both the $CF_2Cl_2{}^{*-}$ resonance and the RG^{*-} excitons near the metallic surface are expected to be lowered by the image potential. This prediction is in agreement with the observed results. However, the RC mechanism is not helpful in predicting the great difference of negative-ion enhancements between polar and nonpolar coadsorbates. Negative-ion resonances in gas-phase water and ammonia are observed at 6.5 and 5.6 eV, respectively, and their cross sections are $\sigma(NH_3{}^{*-}) < \sigma(H_2O^{*-})$ [14]. Based on the energy matching requirement [6], RC would predict a strong enhancement of Cl^- for CF_2Cl_2 coadsorption with H_2O than with NH_3. This is not consistent with the observed results. Most significantly, the $CF_2Cl_2{}^{*-}$ resonance at ~3.0 eV resulting in the production of F^- is a *single-particle* resonance associated with the electronic ground state of the molecule. Thus, RC would lead to no F^- enhancement for both polar and nonpolar coadsorbates. These facts lead to the conclusion that RC may be operative, but is not the major mechanism responsible for the giant Cl^- enhancements observed for coadsorption with polar molecules, and is not the mechanism for the F^- enhancements for all coadsorbates.

Liquid ammonia and water are both very efficient electron solvents [15,16]. Each excess (solvated) electron in these polar media is momentarily trapped within an attractive potential well created by orienting the molecules that surround it, and is called a self-trapped electron. Similar "bubblelike" structures to induce electron self-trapping are also found in liquid helium and neon with negative electron affinities (the conduction-band minimum is above the vacuum level) [17]. In contrast, an excess electron in most nonpolar liquids with positive electron affinities, such as heavier rare gases (Ar, Kr, or Xe) and CH_4, has a high mobility, remaining in a quasifree state. A similar proposal has been made quite recently by Nagesha and Sanche [18]. In the case of solids, self-trapped carriers are often described as small polarons [19,20].

In the present case, secondary electrons from the substrate are injected into the water or ammonia molecular layer, where some of them become self-trapped and thus have long lifetimes. When a CF_2Cl_2 molecule is also present on the surface, a trapped electron tunneling to the molecule is expected to form a vibrationally excited intermediate state which then dissociates

$$e^- + m\mathrm{NH_3}(n\mathrm{H_2O}) \rightarrow e_S{}^-(\mathrm{NH_3})_m \text{ or } e_S{}^-(\mathrm{H_2O})_n\,, \tag{1a}$$

$$e_S{}^- + \mathrm{CF_2Cl_2} \rightarrow \mathrm{CF_2Cl_2}{}^{*-} \rightarrow \mathrm{Cl^-} + \mathrm{CF_2Cl}\,, \tag{1b}$$

$$\quad\quad\quad\quad \mid \rightarrow \mathrm{F^-} + \mathrm{CFCl_2}\,, \tag{1c}$$

where, $e_S{}^-$ denotes a self-trapped electron. It is well known that the cross section for Cl^- formation [Eq. (1b)] is much larger than for F^- [Eq. (1c)] in the gas phase [2,3]. In fact, the generation of solvated electron by dissolving alkali-metal atoms in liquid solvents has been applied to dehalogenation of environmentally hazardous halogenated organic compounds, in which halogen atoms are reduced to halogen ions [21,22] and dechlorination can be much more efficient than defluorination. This qualitatively agrees with the present observation that the magnitude of enhancement of Cl^- is much larger than that of F^- for H_2O or NH_3 coadsorption. Mackenzie *et al.*

[22] have achieved a high dehalogenation efficiency of halogenated hydrocarbons by using liquid ammonia as a solvent at a low temperature (223 K) and extended the method to dehalogenation of solids. An important implication is that the dehalogenation of contaminated solids is a diffusion-controlled reaction, depending on the mobility of the solvated electrons [22].

The electric dipole moment of water (1.84 D) is larger than that of ammonia (1.47 D) [23]. As a result, the excess electrons are more easily self-trapped in water than in ammonia due to the stronger electron-dipole interaction in water, and the mobility of electrons in water is much lower than in ammonia at the same temperature [23]. For nondiffusion-controlled reactions, the reaction rate constant of solvated electrons in water with neutral molecules is typically several orders of magnitude higher than in ammonia [13]. For diffusion-controlled reactions, in contrast, the reaction rate constant in liquid ammonia is much higher than in water due to the higher diffusion coefficient of electrons in ammonia [13]. Thus, the present observation that anionic enhancement by ammonia is much higher than by water is consistent with what is expected for diffusion-controlled electron transfer from water or ammonia molecules to CF_2Cl_2.

The above assignment of giant anionic enhancements as due to the dissociative attachment of self-trapped electrons in the condensed-phase polar molecules is supported by the fact that *for CF_2Cl_2 on Ru coadsorbed with polar molecules, the F^- and Cl^- enhancements are 1–3 orders of magnitude larger than for coadsorption with nonpolar RG atoms (Ar, Kr, and Xe); the enhancements by coadsorption with nonpolar molecules (e.g., CH_4, which is isoelectronic with NH_3 and H_2O) are also small, comparable to those by RG atoms [12].* Although the processes expressed in Eq. (1) can also occur for nonpolar coadsorbates, excess electrons injected into most nonpolar media remain in quasifree states and thus have short lifetimes, as mentioned above. Most excess electrons quickly decay into the substrate with a small probability of capture by CF_2Cl_2 leading to F^- and Cl^- enhancements much smaller than those caused by polar molecules.

Finally, we briefly discuss why the magnitude of negative-ion enhancement always decreases with increasing CF_2Cl_2 coverage (Fig. 2). It has long been recognized that among electron attachment processes, a transient ion AB^{*-} (a vibrationally excited state or an electronically excited state) may release its excess internal energy by collisions with another body to become a nondissociative low-lying AB^- state if the electron affinity of AB is positive [14]. The process can be expressed as

$$e_S^- + AB \rightarrow AB^{*-} + M \rightarrow AB^- + M + \text{energy}, \tag{2}$$

where M is a third body (another AB molecule or a different species). This is the well-known three-body attachment; an example is the formation of O_2^- by electron impact with O_2 in the upper atmosphere. A three-body process may transfer a dissociative $CF_2Cl_2^{*-}$ state into a stabilized $CF_2Cl_2^-$ state, since CF_2Cl_2 has a positive electron affinity of 0.4 eV [24], the same as that of O_2. Moreover, charge transfer between neighboring molecules may also occur as coverage increases, reducing the lifetime of the transient AB^{*-} state. For $CF_2Cl_2^{*-}$, these processes are expected to show a strong dependence on the availability of neighboring CF_2Cl_2, and hence on the surface density. Intermolecular deexcitation effects may therefore explain the strong dependence of the F^- and Cl^- enhancements on CF_2Cl_2 coverage.

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