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Enhanced dissociative electron attachment to CF_2Cl_2 by transfer of electrons in precursors to the solvated state in water and ammonia ice

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We present direct evidence that the presence of polar molecules greatly enhances dissociative electron attachment (DEA) of ~0 eV electrons to CF_2Cl_2. The absolute DEA cross sections are found to be $\sim 1.3 \times 10^{-14}$ and $\sim 9.7 \times 10^{-14}\,\mathrm{cm}^2$ for 0.1 monolayer (ML) CF_2Cl_2 on 5 ML H_2O and 5 ML NH_3 ice grown on Kr, respectively. They are ~130 and ~970 times larger than the gaseous values. This enhancement is due to the transfer of electrons in the precursor states, rather than the transfer of solvated electrons in water or ammonia ice.

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Electron trapping in dielectric media can occur via various mechanisms, such as resonance stabilization and dissociative electron attachment (DEA).[1] Recently, Nagesha and Sanche[2] observed a large enhancement in attachment of near 0 eV electrons to molecules adsorbed on glassy *n*-hexane layers condensed on Pt. This enhancement is attributed to coupling of molecular anion states with image states; the negative-electron-affinity band structure of the dielectric layer, with the band-gap edge lying above the vacuum level, enhances the lifetime of electrons trapped in image states.

Another type of electron trapping exists for excess electrons in polar media composed of molecules with permanent dipole moments, such as ammonia and water. It was first observed in the liquid phase,[3] and then in clusters[4] and condensed films.[5] Electron trapping in H_2O and NH_3 and the related chemistry are issues of wide interest,[6,7] due to the abundance of H_2O in biological systems and in the Earth's environment, and the high efficiency of NH_3-enhanced chemical reactions. Transfer of trapped electrons is a fundamental and challenging theoretical issue[8,9] of great relevance to such diverse areas as environmental sciences,[10] radiobiology,[11] biochemistry,[12,13] and stratospheric ozone depletion.[14]

Recently, Lu and Madey[15] observed that F^- and Cl^- yields produced by the impact of 250 eV electrons on CF_2Cl_2 (CFC-12, a major ozone-depletion substance) adsorbed on a metal Ru surface are enhanced by several orders of magnitude upon coadsorption with polar molecules such as H_2O and NH_3. It was postulated that the giant anion enhancement is due to transfer of self-trapped (solvated) electrons in polar molecule clusters to CF_2Cl_2 molecules that then dissociate, following the production of low-energy secondary electrons from the metal substrate. However, direct evidence for this mechanism involving near 0 eV electrons could not be obtained due to the inaccessibility of an electron beam in the very-low-energy range.[15] In addition metal-substrate effects, such as dielectric screening and work-function lowering induced by coadsorbates, could influence the anion yields in previous experiments.[16] Thus, evidence for the existence of an isolated enhancement mechanism involving DEA to chlorofluorocarbons (CFC's) adsorbed on ice films (i.e., without the presence of a metal substrate) could not be obtained and the related absolute DEA cross sections could not be determined.

In this Brief Report, (1) we present direct evidence that DEA of near 0 eV electrons to physisorbed CF_2Cl_2 is strongly enhanced with the presence of a water or ammonia ice film; (2) absolute cross sections for DEA to CF_2Cl_2 are measured to be $\sim 1.3 \times 10^{-14}$ and $\sim 9.7 \times 10^{-14}\,\mathrm{cm}^2$ for 0.1 monolayer (ML) CF_2Cl_2 adsorbed on a 5 ML H_2O and a 5 ML NH_3 film grown on Kr, respectively, which are ~130 and ~970 times the gas-phase values; (3) the results indicate that the enhancement is due to transfer of electrons to CFC's from the precursors of the solvated state, prior to their full solvation (self-trapping) in the water or ammonia ice film. These are key factors in evaluating the relevance of laboratory findings to atmospheric ozone depletion, namely, in evaluating the magnitude of ozone depletion via dissociative electron transfer from ice in polar stratospheric clouds.

The experiments were conducted in an ultrahigh-vacuum chamber with a base pressure of $\sim 5 \times 10^{-11}$ torr. A polycrystalline Pt foil is used as a substrate, which is cleaned by resistive heating in oxygen and can be cooled to ~20 K with a closed-cycle helium refrigerator. High-purity Kr, H_2O or NH_3, and CF_2Cl_2 gases are condensed in sequence onto the Pt surface with two separate directional dosers. Their coverages are determined from temperature-programmed desorption spectra.[17] Electron trapping in a dielectric film is measured by the low-energy electron transmission (LEET) method.[18] A magnetically collimated electron beam (0–10 eV) having an energy resolution of 40 meV is produced by a trochoidal monochromator. A LEET spectrum records the electron current transmitted through a dielectric film as a function of incident electron energy, which has a sharp onset at the vacuum level defined as zero eV. If electrons are trapped in the film with a lifetime longer than the detection limit of milliseconds,[18] the onset curve shifts to a higher energy by ΔV. An electron trapping coefficient A_s is defined as $d(\Delta V)/dt$ at $t=0$. For charging by a submonolayer of CF_2Cl_2 on the H_2O or NH_3 film surface, the system can be considered as a parallel-plate capacitor.[18] Then the electron-trapping cross section $\sigma(E)$ is obtained from

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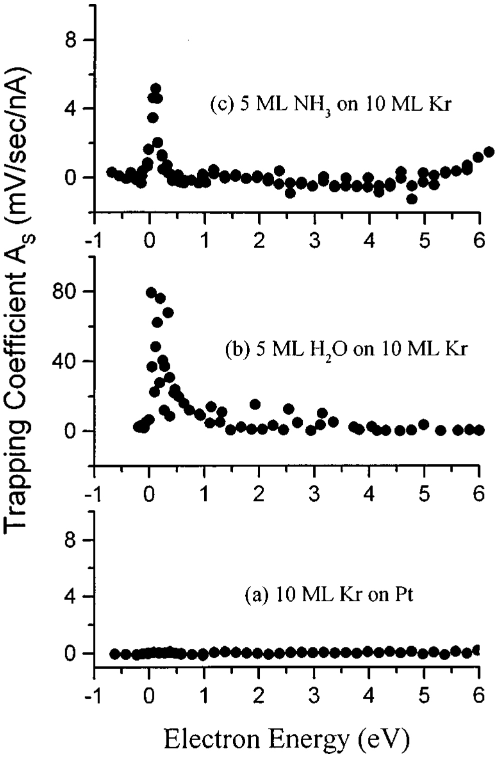

FIG. 1. Trapping coefficient A_s as a function of incident electron energy for (a) 10 ML Kr condensed on Pt; (b) 5 ML H_2O on 10 ML Kr condensed on Pt; and (c) 5 ML NH_3 on 10 ML Kr condensed on Pt.

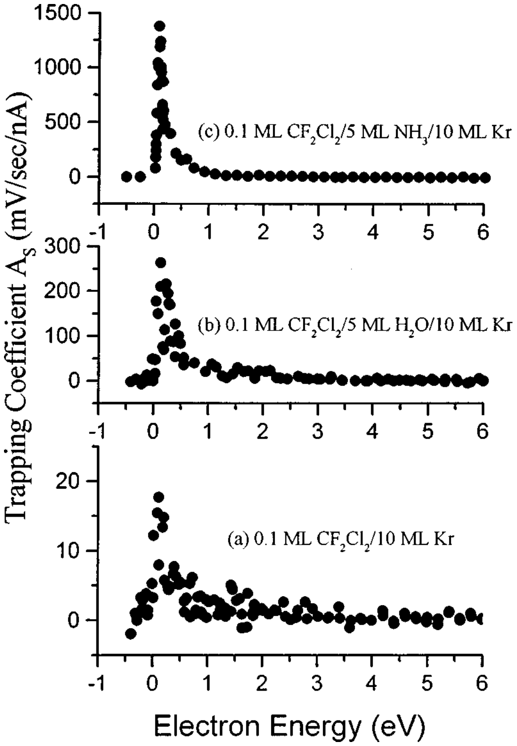

FIG. 2. Trapping coefficient A_s versus incident electron energy for $0.1\,\mathrm{ML}\,CF_2Cl_2$ on (a) 10 ML Kr, (b) $5\,\mathrm{ML}\,H_2O$, and (c) $5\,\mathrm{ML}\,NH_3$. The polar H_2O or NH_3 film is isolated from the Pt substrate by a 10 ML Kr film.

$$A_s(E)=\frac{\sigma(E)\rho_0 J_0}{\epsilon_0}\left(\frac{L_1}{\epsilon_1}+\frac{L_2}{\epsilon_2}\right). \tag{1}$$

Here, E is the incident electron energy, ρ_0 the surface density of electron-trapping molecules, J_0 the incident electron density, and ϵ_0 the vacuum permittivity. ϵ_1 (1.91) and ϵ_2 [3.3 and 3.4, respectively, for H_2O and NH_3 (Ref. 19)] are the dielectric constants of the Kr and polar molecular films. $L_1=32.6\,\text{Å}$ is the film thickness for 10 ML Kr and $L_2=13.0$ and 11.7 Å for $5\,\mathrm{ML}\,H_2O$ and $5\,\mathrm{ML}\,NH_3$, respectively. In the present experiments, $A_s(E)$ was measured for $0.1\,\mathrm{ML}\,CF_2Cl_2$ [$\rho_0\sim 6\times 10^{13}/\mathrm{cm}^2$ (Ref. 17)] condensed on a 10 ML Kr film with and without the presence of a 5 ML H_2O or NH_3 spacer layer. Finally, the installation of an ultrafine vacuum valve to control the dosing of small amounts of electron-trapping molecules reduced the uncertainty in the measured $\sigma(E)$ from ~50% (Ref. 18) to ~30%.

Shown in Fig. 1 are the incident-electron energy dependencies of $A_s(E)$ for (a) a 10 ML pure Kr, and (b) a $5\,\mathrm{ML}\,H_2O$ and (c) a $5\,\mathrm{ML}\,NH_3$ film condensed on top of the Kr film. No electron trapping occurs in the Kr film, and electron trapping near 0 eV is observed for H_2O on Kr, in agreement with previous measurements.[20,21] In contrast, NH_3 on Kr exhibits a very small electron-trapping probability at ~0 eV. Electron solvation was first observed in liquid NH_3, but few studies have been made of electron trapping in the solid phase or clusters of NH_3, compared with H_2O. Nevertheless, both experiments[4] and quantum-mechanical calculations[22] have demonstrated a dramatic difference between solvated electrons in $(H_2O)_m$ and in $(NH_3)_n$ clusters. $(H_2O)_m^-$ cluster anions are observed for all sizes with $m\geqslant 2$, while $(NH_3)_n^-$ cluster anions are seen only for $n\geqslant 36$. This substantial difference is interpreted as due to the energetic instability of electrons localized at $(NH_3)_n$ states, in essential agreement with the present observation: almost no well-bound trapped electrons with a lifetime longer than milliseconds are detected in the NH_3 film. However, electrons trapped in transient states with shorter lifetimes are expected to exist in the polar film.[22]

Shown in Fig. 2(a) is $A_s(E)$ for $0.1\,\mathrm{ML}\,CF_2Cl_2$ adsorbed on a 10 ML Kr surface, from which a trapping cross section $\sigma=1.4\times 10^{-15}\,\mathrm{cm}^2$ at nearly 0 eV is derived. In the gas phase, CF_2Cl_2 has a maximum DEA cross section of $\sim 1\times 10^{-16}\,\mathrm{cm}^2$ at ~0 eV leading exclusively to Cl^-, $e^-(\sim 0\ \mathrm{eV})+CF_2Cl_2\rightarrow Cl^-+CF_2Cl$, which is about one order of magnitude larger than that for F^- production peaking at ~3 eV.[23] Thus, the measured σ at ~0 eV is predominantly due to the DEA leading to Cl^-. The larger σ value by about one order of magnitude for the condensed phase is reasonably explained by the polarization of the Kr film induced by the dissociating anion, as seen for other halomethanes.[20,21] Due to the low kinetic energy of the Cl^- fragment and the image force, most Cl^- ions from the DEA at ~0 eV cannot desorb and are captured at the surface.[17] Strictly speaking, the present measurements cannot distinguish whether the electron is trapped as the Cl^- fragment or a stabilized $CF_2Cl_2^-$. However, it has been pointed out that for CFC molecules with DEA resonances near 0 eV the dissociation probability lies near unity once an electron is attached.[23] Thus, the measured charges are due to electrons trapped as Cl^- ions, i.e., σ corresponds to the DEA cross section.[20,21]

The results of $A_s(E)$ for $0.1\,\mathrm{ML}\,CF_2Cl_2$ condensed on $5\,\mathrm{ML}\,H_2O$, or $5\,\mathrm{ML}\,NH_3$ predosed onto the 10 ML Kr surface are shown in Figs. 2(b) and 2(c), respectively. Evidently, the presence of H_2O increases the electron-trapping cross section near 0 eV. However, the trapping coefficient in Fig. 2(b) should include a contribution from well-bound electrons trapped in the H_2O film shown in Fig. 1(b). After subtracting the data for A_s in Fig. 1(b) from those in Fig. 2(b), we obtained from Eq. (1) a trapping cross section $\sigma = 1.3\times10^{-14}\,\mathrm{cm}^2$ at $\sim$0 eV for $0.1\,\mathrm{ML}\,CF_2Cl_2$ on $5\,\mathrm{ML}\,H_2O$, which is about one order of magnitude larger than that on Kr [Fig. 2(a)] or two orders higher than the gaseous cross section. The case for the electron solvent NH_3 is clearer and more direct, as almost no well-bound electrons are detected in the NH_3 film [Fig. 1(c)]. Most significantly, NH_3 causes a giant enhancement of DEA to CF_2Cl_2, as seen in Fig. 2(c). The cross section σ at $\sim$0 eV reaches $\sim 9.7\times10^{-14}\,\mathrm{cm}^2$ for $0.1\,\mathrm{ML}\,CF_2Cl_2$ on $5\,\mathrm{ML}\,NH_3$, which is nearly three and two orders of magnitude larger than the corresponding peak values for gaseous CF_2Cl_2 and CF_2Cl_2 on Kr, respectively. Here, the measured σ's near 0 eV for CF_2Cl_2 on a H_2O or NH_3 film are smaller than the estimated values reported earlier.[14] However, the values given in Ref. 14 were the total dissociation cross sections with an incident beam of 250 eV electrons, which produce copious amounts of low-energy secondary electrons. Moreover, in those experiments the molecules were coadsorbed on a metal (Ru) surface, where the effects of the substrate induced by coadsorbates could influence the anion yields,[16] as mentioned earlier. In the present experiments, we obtain absolute DEA cross sections for CF_2Cl_2 adsorbed on the H_2O or NH_3 film deposited onto a Kr surface. At first glance, one might attribute the enhancement in σ to an effect of the polar molecular film on the direct DEA to CF_2Cl_2 (i.e., without electron transfer). However, it has been shown that direct DEA is significantly *reduced* for molecules deposited on H_2O and NH_3 films.[24]

In the past decade, femtosecond time-resolved laser studies have provided instructive information on the dynamics of electron trapping and solvation in polar media.[25–27] It has been observed that in polar liquids electron solvation occurs in two stages. Before it becomes solvated, the electron is weakly bound in the ''preexisting trap,'' a precursor of the fully solvated state, with a lifetime on the scale of picoseconds. The precursor can be a transient state in an energy level above or near the vacuum level, an excited state of the solvated electron or a ''hot solvated electron.''[25–27] In the case of solids, the solvation time, i.e., the lifetime of electrons in a precursor, is greatly increased; it is proportional to the dielectric relaxation time of the medium.[28] The latter increases from the scale of picoseconds for the liquid water to microseconds for ice below 200 K.[29] Indeed, the solvation time of ice near the melting point 269 K has been observed to be on the time scale of nanoseconds.[28] Thus, the lifetime of precursor electrons in ice at $\sim$20 K is expected to lie in the range of microseconds. It has long been predicted that radiation-induced electrons in a precursor state (so-called dry electrons) are highly reactive due to their large mobility; these electrons will react rapidly with electron-attaching molecules, if the latter are present in the medium.[28] For DEA to CF_2Cl_2 via electron transfer from fully solvated traps, we can take as an upper limit of A_s the value in the pure polar film plus that due to direct DEA to CF_2Cl_2 on Kr (i.e., $\sim$100 $\mathrm{mV\,s^{-1}\,nA^{-1}}$ for H_2O and $\sim 25\ \mathrm{mV\,s^{-1}\,nA^{-1}}$ for NH_3. However, the measured values of $A_s(0\,\mathrm{eV})$ for CF_2Cl_2 on H_2O and NH_3 are much larger, by a factor of 3 and 70, respectively (Fig. 2). Thus, we must conclude that transfer of electrons from precursor states to CF_2Cl_2 is the major mechanism responsible for the observed increase in σ near 0 eV. The electron energy threshold E_{min} for the DEA of CF_2Cl_2 leading to Cl^- is equal to the bond dissociation energy of CF_2Cl-Cl minus the electron affinity of Cl.[23] E_{min} is -0.4 eV in the gas phase, and is reduced to about -1.4 eV for CF_2Cl_2 adsorbed on the film surface due to the effect of the polarization potential ($\sim$1.0 eV). This indicates that, despite their long lifetimes, the fully solvated electrons with a binding energy of 3.2 eV in H_2O bulk[27] can hardly contribute to the DEA of CF_2Cl_2, as deduced from our experiments. For the pure H_2O or NH_3 film (Fig. 1), electrons temporarily localized at precursor states can transmit through the Kr spacer layer into the metallic substrate without being detected, as their lifetime is far shorter than the detection limit (milliseconds). As a result, the trapping cross section is low, corresponding to electron residence in the solvated state. However, the case can be dramatically different when a CF_2Cl_2 molecule, which has a large probability to attach a precursor electron, is adsorbed on the surface. Because of the rapidity of electron transfer ($\leqslant$20 fs),[8] which occurs in a time far shorter than the lifetime (microseconds) of an electron trapped in a precursor state in the H_2O or NH_3 film, there is a large probability for transfer of the electron to CF_2Cl_2 followed by dissociation. As a result, the DEA cross section of CF_2Cl_2 is significantly enhanced, as shown in Fig. 2.

A large number of experimental data[30] have demonstrated that the mobility (μ_e) of an excess electron in a polar liquid is inversely proportional to the viscosity (η) of the solvent, which indicates that the migration of excess electrons in polar liquids is diffusion controlled. In particular, this conclusion was verified for reactions of solvated electrons in liquid ammonia with halogenated compounds.[10] In the present case, the ratio of the measured DEA cross sections for CF_2Cl_2 on NH_3 and H_2O ice is $\sim$7.5. This value is very close to the viscosity ratio of the two electron solvents: $\eta(H_2O)/\eta(NH_3)=6.6$.[30] This good agreement within the experimental error suggests that the electron transfer reaction in the solid phase also follows a diffusive mechanism. Such a conclusion is consistent with the theoretical prediction for electron transport in water and ammonia clusters.[22]

NH_3 as a reagent gas to enhance DEA of organic and inorganic molecules has led to important applications such as in the analysis of human blood[12] and human milk triacylglycerols,[13] although the role of NH_3 is not clear. The mechanism revealed here sheds light on the principle of these applications; it can also be of considerable significance for radiation-induced damage to cellular DNA that lies in a water environment.[31] Moreover, the observed enhancement in DEA of CFC molecules by water ice can have far-reaching significance in relation to the creation of the ozone hole(s) over the Antarctic and Arctic poles, where polar stratospheric clouds (PSC's) composed of water ice are found. According to our findings, low-energy electrons produced by the continuous cosmic-ray radiation and momentarily trapped in PSC's must cause a significant enhancement of the DEA of CFC molecules reaching the surface of PSC's.[14]

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