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Dynamics of Solvated Electron Transfer in Thin Ice Film Leading to a Large Enhancement in Photodissociation of $CFCl_3$

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Since the blue color of the liquid ammonia solution of sodium was first explained,[1] solvated electron has been extensively studied as a prototypical system of solvation. With the advent of ultrafast laser spectroscopy,[2] the transient life cycle of solvated electron in water is now quite well-established. Although general features of solvated electron have been addressed in detail,[2,3] its transfer dynamics to target molecules is still poorly understood[4] due to the presence of the countercations and the uncontrollable transfer distance in bulk solution.

Such complications can be largely avoided by using a well controlled thin molecular layer, to which two-photon photoemission (2PPE) spectroscopy is typically applied, often in time-resolved manner using a pump−probe scheme.[5,6] The low energy electrons generated in 2PPE have wide-ranging implications in many electron-driven phenomena, such as surface photochemistry and biotoxicity.[7−12] In particular, a self-trapped electron in the ice particles of a polar stratospheric cloud has been proposed as the culprit for the dissociation of atmospheric chlorofluorocarbons via facile dissociative electron attachment,[11] which still remains a subject of debate as to its actual role in polar ozone depletion.[7−9]

Although the phenomenon of electron solvation itself can now be investigated in detail in a thin molecular layer, as has been demonstrated in a recent study of an ice film grown on Cu(111),[5] the chemistry initiated by it has not been addressed at a corresponding level. In this paper, we report observation by 2PPE of solvated electrons in a thin ice film of water grown on Ag(111) and, for the first time, its transfer to neighboring molecules of trichlorofluoromethane ($CFCl_3$). A distinctive aspect of the present work is that we made a direct observation of the transient state of the electron in its transfer process to a molecular adsorbate.

Details of experimental apparatus and procedures[13] are given in the Supporting Information section. Figure 1a shows time-resolved 2PPE spectra of 5 ML H_2O on Ag(111) at 90 K obtained at different time delays. The energy along the abscissa refers to the intermediate state energy above the Fermi level, $E - E_F = E_{kin} + \Phi - h\nu_2$, where E_F, Φ, and $h\nu_2$ denote, respectively, the Fermi level, the work function, and the probe photon energy (see inset of Figure 1a). The prominent peak denoted e_{sol} at 2.9 eV is tentatively attributed to the photoinjected electron undergoing solvation in the ice film, based on the following observations: (1) the position of the e_{sol} peak moves to a lower energy with an increasing time delay, indicating that the photoinjected electron becomes more strongly bound with relaxation, and (2) the relaxation rate at a low coverage of 1 ML is much faster than at higher coverages (see Supporting Information). Due to the lattice mismatch between Ag(111) and the molecular layer of water,[14] the degree of coordination among water is smaller at a lower coverage,[5] which allows for more facile molecular reorientation to accommodate the photoinjected electron than in a highly coordinated bulk-like multilayer. In Figure 1b, the integrated photoelectron intensity of the e_{sol} band at 5 ML is plotted as a function of the time delay. When deconvoluted against the pump−probe cross-correlation, the decay curve gives a time constant of 120 fs, which amounts to the lifetime of the e_{sol} state before it decays back to the metal. The energetics and dynamics of the e_{sol} state in this study are in good agreement with those on Cu(111).[5]

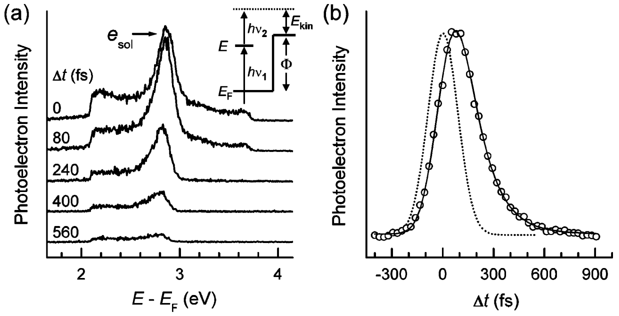

Figure 1. (a) Time-resolved 2PPE spectra of 5 ML H_2O/Ag(111) at $h\nu_1 = 3.70$ eV and $h\nu_2 = 1.85$ eV. The inset shows the pertinent energy levels. (b) Integrated intensity of the e_{sol} band as a function of the time delay (Δt). Dotted line, cross-correlation curve between the pump and probe; circles, experimental data; solid line, theoretical fit to the data. The exponential decay time is 120 fs.

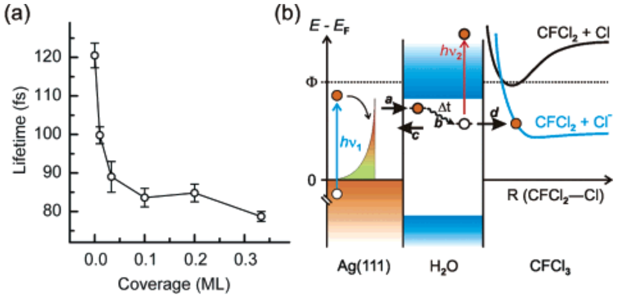

Figure 2. (a) Lifetime of the e_{sol} state as a function of the coverage of $CFCl_3$ adsorbed on 5 ML H_2O/Ag(111). (b) Schematic diagram for the life cycle of the photoinjected electrons in $CFCl_3$/H_2O/Ag(111): photoinjection of electron into the loosely bound e_{sol} state residing below the vacuum level (***a***); solvation in the ice layer leading to energy relaxation (***b***); back transfer of the photoinjected electron to the metal (***c***); electron transfer to coadsorbed $CFCl_3$ (***d***).

When adsorbed on the ice film, $CFCl_3$ was found to exert little perturbation to the ice layers, as revealed by thermal desorption spectroscopy, and also to induce little change in the 2PPE spectra (not shown). However, the lifetime of the e_{sol} state decreased markedly, even with as little $CFCl_3$ as 0.01 ML (Figure 2a). The accelerated decay implies that a new decay channel becomes operative for the solvated electron. Furthermore, photodissociation of C−Cl bonds and buildup of Cl^- ions on the ice surface were deduced from thermal desorption spectra and work function change obtained after photoirradiation at $h\nu = 3.49$ eV (see Supporting Information). While the photon energy used is considerably less than the photodissociation threshold of $CFCl_3$[15] (∼5 eV) or the work function of the surface (∼4.1 eV), it is enough to excite the substrate

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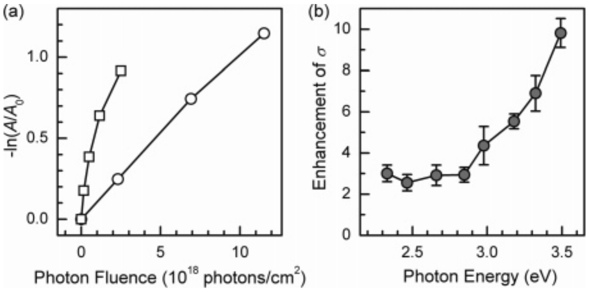

Figure 3. (a) Semilogarithmic plot for the fractional number density (A/A_0) of 1 ML $CFCl_3$/Ag(111) with (squares) and without (circles) water overlayer (8 ML) as a function of the photon fluence at $h\nu = 3.49$ eV. (b) Enhancement of the effective photodissociation cross-section (σ) of 1 ML $CFCl_3$/Ag(111) due to 8 ML water overlayer as a function of the photon energy.

electron into the e_{sol} state. Since the spatial extent of the electronic wave function for the e_{sol} state has been estimated to be of the order of 10−20 Å,[5] electron transfer to the coadsorbed $CFCl_3$ is highly likely.

The observed drop in the lifetime of the e_{sol} state in Figure 2a should be a direct result of facile dissociative electron transfer to the coadsorbed $CFCl_3$. Halogenated hydrocarbons are known to have enormous capture cross-sections for low energy electrons. In Figure 2b, the fate of the photoexcited electron is depicted schematically. After photoinjection of electrons from metal to ice (***a***), the loosely bound electrons in the e_{sol} state undergo solvation or self-trapping through the polarization of the surrounding water molecules, which lowers the energy of the e_{sol} state (***b***). While some of the electrons in the e_{sol} state return to the metal (***c***), others are transferred by tunneling into the anionic state of $CFCl_3$ represented by the blue potential energy curve (***d***), which itself is much lower in energy than in the gas phase due to the image charge interaction and the dielectric polarization force.[16] The resulting transient anion quickly undergoes dissociation into a $CFCl_2$ radical and a Cl^- ion.

To better understand the role of water molecules in turn, the photodissociation yield of $CFCl_3$/Ag(111) at $h\nu = 3.49$ eV was measured as a function of the photon fluence with and without water overlayer. As shown in Figure 3a, the fractional number density (denoted A/A_0) of intact $CFCl_3$ decreases (shown by a positive slope in $-\ln(A/A_0)$) with increasing photon fluence due to the dissociative hot electron transfer from the metal, whose effect is much more dramatic with an overlayer of water (squares) than without (circles). Provided that the reaction follows a first-order kinetics, the reaction cross-section (σ) can be calculated from the equation $-\ln(A/A_0) = \sigma F t$, where F is the photon flux and t is the irradiation time.[17] Since the slope decreases as the reaction proceeds, the effective photodissociation cross-section was determined from the initial slope (see Supporting Information for detailed coverage dependence of σ). In Figure 3b, the water-induced enhancement of σ, defined as $\sigma(H_2O/CFCl_3)/\sigma(CFCl_3)$, is presented as a function of the photon energy. While the enhancement remains constant at lower photon energies, it increases rather abruptly at $h\nu = \sim 2.9$ eV, which is the minimum energy required to excite a substrate electron into the e_{sol} state. Once the electron is formed in the e_{sol} state, its extended lifetime as a bound state leads to a higher probability for transfer to the neighboring $CFCl_3$ molecule. On the other hand, the water overlayer itself can accelerate the reaction even at a photon energy lower than the energy of the e_{sol} state by stabilizing the anion state of $CFCl_3$ through a decrease in work function and the polarization effects.[16] Since the photoexcited hot electron has an increasing population distribution at lower energies, the stabilization of the anionic state means that more electrons become available for electron transfer, thereby increasing its rate.[17] The additional enhancement at the higher photon energy, which should be attributed to the long-lived e_{sol} state as pointed out earlier, is quite consistent with the recent work of Madey et al.,[18] which showed that the enhancement caused by coadsorption of water in electron-stimulated dissociation of halocarbons is by a factor of 2−4. Our findings constitute direct observation of a solvated electron state in a thin ice film of water that promotes an electron-driven chemical reaction by providing a transient bound state for the excited electron, which is otherwise subject to ultrafast decay to the substrate.

In summary, we found that photoexcitation of substrate electrons from a metal can bring about a solvated electron state in an ice film above the metal surface. The lifetime of the photoinjected e_{sol} state is markedly decreased with coadsorption of $CFCl_3$ as a result of electron transfer from the ice to $CFCl_3$. The two-step electron transfer by way of ice (***a*** and ***d*** in Figure 2b) is in accord with the observed photochemistry. In addition, the water overlayer was found to greatly promote the photodissociation of $CFCl_3$ by extending the lifetime of the excited electron through solvation. The water-induced enhancement of photoreaction demonstrates an active role of water as an electron solvent, which should have far-reaching implications for many electron-driven chemical reactions.

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Supporting Information Available: Detailed experimental procedures, temporal shift of the e_{sol} state energy, thermal desorption spectra after photoirradiation, photoinduced work function change, and water coverage dependence of σ. This material is available free of charge via the Internet at http://pubs.acs.org.

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