

Superinelastic Electron Transfer: Electron Trapping in H₂O Ice via the N₂⁻(²Π_g) Resonance

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We present measurements on the trapping of 0–3 eV electrons in H₂O ice films covered with a submonolayer of N₂ molecules. At the energy of the N₂⁻(²Π_g) shape resonance, the absolute cross section for electron trapping in ice is $\sim 5.5 \times 10^{-16}$ cm², similar to that for vibrational excitations of gaseous N₂ via the resonance. This result, indicating that nearly all electrons from autoionization of N₂⁻(²Π_g) are transferred to electron traps in ice, is explained by superinelastic electron transfer from N₂⁻(²Π_g) into preexisting traps in polar ice, leaving N₂ in high vibrational excited states.

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Resonances in electron-molecule collisions are highly efficient energy transfer processes, in which an incident electron is captured by a target molecule to form a temporary negative ion [1]. The decay of the resonance may lead to dissociative electron attachment (DEA), vibrational and rotational excitation, or electronic excitation of the molecule [1]. This process has also been observed for many molecules adsorbed on surfaces [2,3], following the first observations by Sanche and Michaud [4] and Demuth *et al.* [5]. In gaseous N₂, the electron scattering cross sections exhibit a shape resonance of symmetry ²Π_g around 2.3 eV, which decays by autoionization into vibrational states of N₂: $e^- + N_2 \rightarrow N_2^-(^2\Pi_g) \rightarrow N_2(\nu = 0, 1, 2, \dots) + e^-$; DEA does not occur [1]. In the condensed phase, for N₂ molecules adsorbed on a metal or dielectric surface, the N₂⁻(²Π_g) resonance is also observed in electron scattering experiments, but its energy is lowered by ~ 1.0 eV due to its polarization of the medium [5–7]. On a metal, the vibrational excitation cross sections were found to be smaller than in the gas phase; this feature was first attributed to a decrease of the resonance lifetime for adsorbed molecules [5]. Moreover, for N₂ coadsorption with a submonolayer of H₂O, the N₂⁻(²Π_g) resonance was found to be almost completely “quenched” in electron scattering experiments [8]. However, the resonance may still be efficient for N₂ molecules physisorbed on a surface, as predicted theoretically by Djamo *et al.* [9,10]. These authors showed that the autoionization of N₂⁻(²Π_g) on a surface mostly leads to electrons finally going into the substrate that cannot be observed in reflected electron scattering experiments. In this Letter, we present a method to detect this process by measuring the electron trapping in a H₂O layer on which N₂ molecules are physisorbed.

Trapped electrons in H₂O have special significance in biological systems [11] and in the Earth’s environment [12]. Enhanced dissociation of chlorofluorocarbons (major ozone-depleting molecules) adsorbed on H₂O and NH₃ ice via transfer of trapped electrons has recently been observed [13,14]. Electron trapping in polar media occurs via thermalization of low-energy electrons [15–17]. It is

of significance to explore if these processes can occur via charge transfer in heterogeneous systems.

In this Letter, we report the first observation of electron trapping in a dielectric medium via autoionization of a transient molecular anion. Electron trapping in N₂-adsorbed H₂O ice is shown to occur by direct electron transfer from the N₂⁻(²Π_g) shape resonance at ~ 1.0 eV to a preexisting trap of the polar medium. The electron is then trapped in a deep trap by relaxation of the medium. The absolute cross section for this process is measured to be $\sim 5.5 \times 10^{-16}$ cm². This value is similar to the sum of the vibrational excitation cross sections due to autoionization of the N₂⁻(²Π_g) state in the gas phase, indicating a highly efficient electron transfer. This phenomenon is absent when N₂ is isolated from the H₂O film by a Kr layer. This novel process is termed a “superinelastic” electron transfer, since the electron autoionizing from the N₂⁻(²Π_g) state is transferred to a trapping state of energy below the vacuum level, which causes formation of a vibrationally excited N₂^{*} of energy higher than the N₂⁻(²Π_g) state.

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, H₂O, and N₂ gases are in sequence condensed onto the Pt surface with two separate directional dosers. Water molecules are incident at an angle of $\sim 20^\circ$ from the surface normal, ensuring the growth of amorphous layers of low porosity [18]. Their coverages are determined from temperature programmed desorption spectra, where one monolayer (ML) of H₂O refers to a bilayer with a density of $\sim 1.0 \times 10^{15}$ molecules · cm⁻². Electron trapping in a dielectric film is measured by the low-energy electron transmission (LEET) method [19]. A magnetically collimated electron beam (0–10 eV) with an energy resolution of 40 meV is produced by a trochoidal monochromator. A LEET spectrum is obtained by measuring the current transmitted through a dielectric film as a function of incident electron energy; this spectrum has a sharp onset at

the vacuum level defined as 0 eV. If electrons are trapped in the film, the onset curve shifts to a higher energy by ΔV . An electron-trapping coefficient $A_s(E)$ is defined as $d(\Delta V)/dt$ at $t = 0$ for an incident electron energy E . For charging by a submonolayer of N_2 adsorbed on the surface of a H_2O film predosed on a Kr film, the electron-trapping cross section $\sigma(E)$ is obtained by [14]

$$A_s(E) = \frac{\sigma(E)\rho_0 J_0}{\varepsilon_0} \left(\frac{L_1}{\varepsilon_1} + \frac{L_2}{\varepsilon_2} \right). \quad (1)$$

E is the incident electron energy, ρ_0 the surface density of electron-trapping molecules ($1.66 \times 10^{14} \text{ cm}^{-2}$ for 0.2 ML N_2), J_0 is the incident electron density, and ε_0 is the vacuum permittivity. $\varepsilon_1 = 1.91$ and $\varepsilon_2 = 3.3$ are the dielectric constants of Kr and H_2O , respectively. $L_1 (= 32.6 \text{ \AA}$ for 10 ML Kr) and $L_2 (= n \times 2.6 \text{ \AA}$ for n ML H_2O) are the film thicknesses. Should some N_2 adsorb at the pores of the H_2O film, some uncertainty in the value of L_2 in Eq. (1) could arise. This, however, should not give rise to a significant error in the calculated value of σ via Eq. (1) for measurements with ultrathin H_2O films (≤ 5 ML) because $L_1/\varepsilon_1 \gg L_2/\varepsilon_2$.

Shown in Fig. 1 are the energy dependencies of $A_s(E)$ for (a) 0.2 ML N_2 , (b) 0.2 ML N_2 on a 3 ML H_2O film, and (c) 0.2 ML N_2 on a 1 ML H_2O film; each is condensed over a 10 ML Kr film. $A_s(E)$ for the pure H_2O films on Kr are also shown in Figs. 1b and 1c. As shown and discussed previously [17], no electron trapping occurs in the Kr film; electrons emitted from the autoionization of the $N_2^- (^2\Pi_g)$ resonance transmit quickly through Kr into the metallic substrate. In contrast, trapping of near 0 eV incident electrons has been observed for H_2O ice [17,20]. It is seen clearly in Figs. 1b and 1c that, in addition to the trapping peak near 0 eV, the presence of N_2 on the polar molecular films gives rise to a new structure peaking at an energy of about 1.0 eV. The peak near 0 eV results from direct thermalization of incident electrons followed by self-trapping in the polar film [17]. The new peak at ~ 1.0 eV is similar to the envelope shape of the $N_2^- (^2\Pi_g)$ resonance observed in the electron scattering spectra for N_2 adsorbed on a rare gas film or on a metal, where the lowest energy peak is shifted from the gas-phase energy of 1.9 eV to about 1.0 eV due to the polarization energy of the condensed film or the image potential of the metal [5–7]. Similar to the case for N_2 adsorbed on a metal surface, the boomerang oscillations visible in gaseous vibrational cross sections are absent for N_2 adsorbed on ice. This absence may be explained by the shortening of the resonance lifetime [9,10] and/or potential fluctuations on the surface at the ice film.

From the difference spectrum (see the insets of Figs. 1b and 1c) between the $A_s(E)$ spectra with and without the adsorption of 0.2 ML N_2 , we can obtain the absolute cross section σ for electron trapping in ice caused by adsorbed N_2 molecules with the use of Eq. (1). Shown in Fig. 2 is the obtained σ as a function of the H_2O film thick-

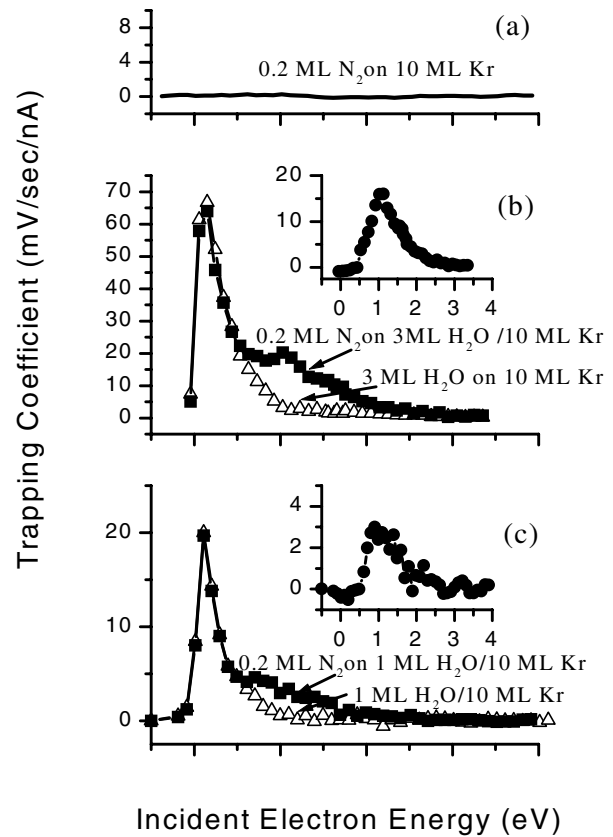


FIG. 1. Trapping coefficient $A_s(E)$ as a function of incident electron energy E for 0.2 ML of N_2 on (a) 10 ML Kr; (b) 3 ML H_2O ; and (c) 1 ML H_2O . The polar H_2O film is isolated from the Pt substrate by a 10 ML Kr film. The insets in (b) and (c) are the $A_s(E)$ difference between the spectra for the polar molecular film with and without the presence of 0.2 ML N_2 .

ness. The measured σ value increases from the lowest H_2O thickness and then reaches a nearly saturation value of $\sigma \approx 5.5 \times 10^{-16} \text{ cm}^2$ for film thicknesses ≥ 4 ML. This value is very similar to the sum ($\approx 5 \times 10^{-16} \text{ cm}^2$) of the vibrational cross sections for excitations of the $\nu = 1$ to five levels of N_2 via resonant scattering at ~ 1.9 eV in the gas phase [1]. The trapping peak at ~ 1.0 eV is therefore interpreted as due to electron transfer from the $N_2^- (^2\Pi_g)$ resonance. At first glance, this result seems contradictory to the observation of strong quenching of the resonance in electron scattering experiments by Jacobi *et al.* [8]. However, in those experiments any electron scattered inelastically into surrounding ice was not detected. Indeed, our results show that the $N_2^- (^2\Pi_g)$ resonance is not quenched for N_2 adsorbed on a H_2O ice surface, but remains a very efficient process with most of the electrons finally being trapped in the polar molecular film. In other words, the electron transfer process from the $N_2^- (^2\Pi_g)$ to the ice is so efficient that nearly all electrons from the shape resonance are trapped in the ice film. This observation is in good agreement with the theoretical prediction for the case of N_2 adsorbed on a metal surface: most electrons via the resonance are scattered into the metal and are thus

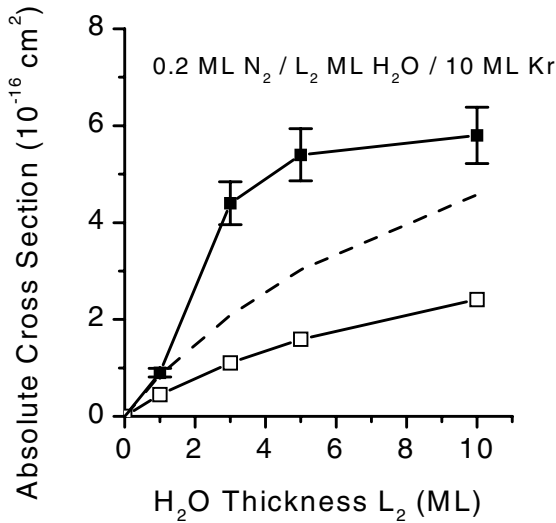


FIG. 2. The solid squares are the measured absolute cross section σ for electron trapping in H_2O ice via the $\text{N}_2^- (^2\Pi_g)$ resonance near 1.0 eV (the maximum) as a function of the H_2O film thickness. The open squares are the calculated (σ_{in}) of the total electron-trapping cross sections in H_2O films for all possible vibrational decay channels of the $\text{N}_2^- (^2\Pi_g)$ state (see text). The dashed line is the upper limits of the total trapping cross sections, assuming that gaseous values are increased by a factor of $1/E_i$ and that no decrease in anion lifetime occurs on ice.

unobservable in scattering experiments [9,10]. According to this analysis, the total vibrational excitation cross section is close to that in the gas phase due to two competing effects: the decrease in the resonance lifetime and the lowering in the resonance energy [10]. The present observation is thus also consistent with this prediction. The question remains, however, as to how electrons are transferred from $\text{N}_2^- (^2\Pi_g)$ to the solvated state in the polar film.

Two possible mechanisms could lead to the final trapping of electrons in H_2O ice: (i) $\text{N}_2^- (^2\Pi_g)$ autoionizes to produce a low-energy electron, which is then thermalized and trapped in ice via inelastic scattering. (ii) the electron in $\text{N}_2^- (^2\Pi_g)$ is transferred directly into a trap in the ice. To distinguish between these mechanisms, we present further experimental and calculation results. First, the electron-trapping spectrum was measured with the H_2O layer isolated from adsorbed N_2 molecules by a Kr spacer, which from LEET measurements is known to allow the efficient transmission of normally incident electrons with energies ≤ 2 eV [21]. The result is shown in Fig. 3 the trapping peak around 1.0 eV almost completely disappears. In this case, the electron from the autoionization of $\text{N}_2^- (^2\Pi_g)$ can transmit through the top Kr film and reach the H_2O layer. Mechanism (i) is therefore still effective, whereas mechanism (ii) is prohibited. Thus, the observation in Fig. 3 is clearly inconsistent with the mechanism (i). Second, we can estimate the electron trapping cross section via the mechanism (i). For incident electrons of energies

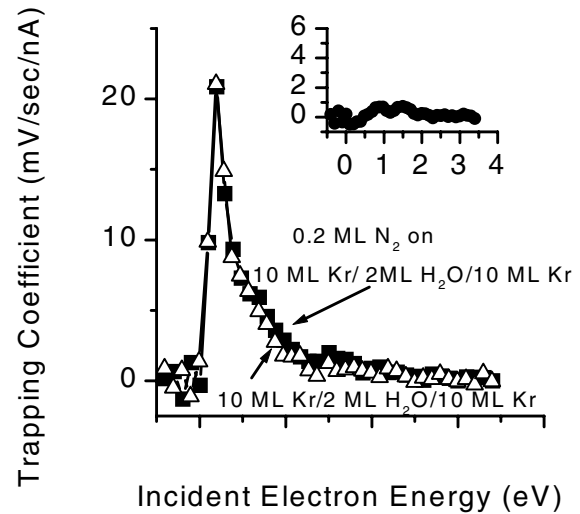


FIG. 3. Trapping coefficient $A_s(E)$ as a function of incident electron energy E for 0.2 ML N_2 adsorbed on a 10 ML Kr/2 ML H_2O /10 ML Kr sandwich film. The inset is the $A_s(E)$ difference between the spectra for the film with and without the presence of 0.2 ML N_2 .

E_i , resonant scattering by N_2 produces electrons of energies ($E_i - E_\nu$) with cross sections $\sigma_\nu(E_i)$ for excitation of the ν th vibrational level of N_2 . The maximum probability $p(E)$ of electrons being trapped by 1 ML H_2O layer is the product of the electron-trapping cross section $\sigma_e(E)$ per a H_2O molecule in ice and the molecular density of 1 ML H_2O , i.e., $p(E) = \sigma_e(E) \times 1.0 \times 10^{15}$. If we assume that autoionization of $\text{N}_2^- (^2\Pi_g)$ results only in electrons scattered into the H_2O film, the upper limit for the total cross section of the electrons being trapped via inelastic scattering in a N ML H_2O film is given by

$$\sigma_{in} = \sum_{\nu=1}^4 \sum_{j=1}^N [1 - p(E_i - E_\nu)]^{j-1} \times p(E_i - E_\nu) \sigma_\nu(E_i). \quad (2)$$

For electron impact at $E_i = 1.0$ eV, vibrational excitation produces scattered electrons with energies E of 0.71, 0.42, 0.13, and 0 eV, respectively [6–8]. With the experimental values for $\sigma_e(E)$ obtained from Ref. [20] and the gaseous vibrational excitation cross sections σ_ν at $E_i = 1.9$ eV from Ref. [1], we can estimate σ_{in} . Our calculation thus assumes that, as for N_2 on a metal surface [10], any increase in the vibrational excitation cross section from the lowering in energy of the resonance, is canceled by a decrease in anion lifetime. The result is shown in Fig. 2 and deviates significantly from the measured data. For comparison we have also calculated σ_{in} assuming that the gas-phase cross sections are increased by a factor $1/E_i$, with no decrease in anion lifetime (dashed line in Fig. 2). We expect, however, that the interaction of N_2^- with the dipole moment of the water will produce a decrease in the lifetime of the resonance so that the results of more physically realistic calculations will always lie below this limit.

Based on the above observations, we propose that the mechanism (ii), i.e., direct electron transfer from the $N_2^-(^2\Pi_g)$ shape resonance into a trap in the polar film is responsible for the electron-trapping peak near 1.0 eV. It is known that there exist "preexisting traps," the precursors to the fully solvated state, in polar media [22–24]. The precursor states can be a state in an energy level just below the vacuum level [23,24]. The extra electron in $N_2^-(^2\Pi_g)$ can make a superinelastic transition to a preexisting trap in the polar film, leaving N_2 with excess vibrational energy. The electron in the preexisting trap can then become more deeply trapped via relaxation of the medium, and be detected in the present measurements. For N_2 on H_2O ice, direct transfer of an electron from N_2^- into a deep trap is unlikely, since this would require reorienting the surrounding water molecules, which can occur only on a time scale much longer than that for autoionization. The solvation time is proportional to the dielectric relaxation time of the medium, which increases from the scale of picoseconds for the liquid water to microseconds for ice below 200 K [25]. Superinelastic electron transfer should depend on the availability of the preexisting traps in the H_2O film, which increases from the lowest H_2O coverages and saturates as the film changes to bulk ice at high coverages (≥ 4 bilayers). Thus, the electron-trapping cross section via the $N_2^-(^2\Pi_g)$ resonance shows a corresponding behavior (Fig. 2). The superinelastic decay of the $N_2^-(^2\Pi_g)$ resonance is very different from the autoionization occurring in the gas phase. The latter process ends with a vibrationally excited N_2^* state which is below the $N_2^-(^2\Pi_g)$ intermediate state in energy, while the superinelastic electron transfer leads to an opposite situation, i.e., the N_2^* state is above the N_2^- state.

In cluster experiments, by mixing N_2 with positive-electron-affinity molecules such as SF_6 and O_2 , the SF_6^- and O_2^- yields via the $N_2^-(^2\Pi_g)$ resonance at ~ 2.3 eV have recently been observed [26]. In interpreting their results, Matejcik *et al.* [26] suggested that the electronic energy of the $N_2^-(^2\Pi_g)$ resonance is quickly dispersed in clusters; the subsequent autoionization of the resonance emits a very low energy electron, which is easily accepted by a SF_6 or O_2 , leading to SF_6^- and O_2^- anions. However, the $N_2^-(^2\Pi_g)$ shape resonance is a short-lived state, which has only time enough to vibrate once before autoionization takes place in the gas phase [1]. Thus, the energy dispersion of the $N_2^-(^2\Pi_g)$ resonance prior to autoionization in clusters is very limited. Rather, we suggest that direct electron transfer from $N_2^-(^2\Pi_g)$ to the unoccupied affinity level of O_2 or SF_6 may occur, similar

to the electron transfer to a preexisting trap in ice in the present case.

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