Effects of Band Structure on Electron Attachment to Adsorbed Molecules: Cross Section Enhancements via Coupling to Image States

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Near-zero-energy electrons at the surface of glassy n-hexane (nHg) are strongly trapped by adsorbed molecules, with a cross section 10^2-10^4 larger than those on the solid Kr surface. This enhancement is attributed to the difference in the band structures of solid nHg and Kr near the vacuum level. [S0031-9007(98)08056-9]

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In recent studies, it has been shown [1] that there are three basic mechanisms responsible for electron trapping within dielectrics and at their surfaces: resonance stabilization, dissociative electron attachment (DEA), and intermolecular stabilization. In the latter process, an electron is trapped in a preexisting potential created by a cluster of molecules, whereas, in the other two, an electron is temporarily captured by a molecule. DEA occurs when the transient anion dissociates before autoionization, producing a neutral fragment and a stable anion. For molecules with a positive electron affinity, resonance stabilization occurs when an anion formed in high vibrational levels of its ground state is stabilized by transferring vibrational energy to the surrounding medium. This Letter reports the first experimental study on the role of substrate band structure (BS) and image states in the above processes. The coupling of a molecular transient anion to image states of a substrate has been investigated theoretically by Rous [2]. In the case of N_2 physisorbed on Ag (111), he found a strong increase in the magnitude of the vibrational excitation cross section of N_2 due to the coupling of $N_2^-({}^2\Pi_g)$ to the image states of Ag (111).

Image states result from the Coulombic interaction between an extra electron and condensed matter at a vacuum interface. A wide range of metallic surfaces and low dielectric constant dielectrics are known to support a progression of image states, each with well characterized binding energies and lifetimes [3–5]. At the surface of some thin-film linear alkane solids having a band gap edge above the vacuum level, these states have been observed at cryogenic temperatures by UV-photoemission spectroscopy and their lifetimes measured [5]. In this Letter, we show that when molecules possessing one of the previously mentioned charging mechanism near zero energy are adsorbed on such substrates, they exhibit huge electron trapping cross sections. Our results further indicate that this phenomenon can be explained by invoking coupling between long lived image states and molecular or cluster anionic states. These findings may have far reaching implications in molecular damage induced by ionizing radiation [6] at surfaces and interfaces, in the charging properties of polymers [7], and in the dielectric aging of high-voltage insulators [1].

We have chosen to study electron attachment to CH_3Cl, O_2, H_2O, and CF_4. These molecules have different electron stabilization properties near zero energy and their absolute cross sections for stable anion formation (SAF) have recently been measured on the surface of solid Kr [8–11]. CH_3Cl yields exclusively Cl^- with a peak cross section of 1.3×10^{-17} cm^2 around 0.5 eV [8]. SAF occurs via formation and dissociation of the ground ${}^2A_1$ state of CH_3Cl^-. Below 1 eV, O_2 undergoes resonance stabilization to form $O_2^-({}^2\Pi_g)$ with a cross section of 2.7×10^{-17} cm^2 [9] and H_2O molecules trap thermal electrons via intermolecular stabilization with a cross section of 3×10^{-16} cm^2 [10]. CF_4 does not trap electrons near zero energy but has DEA channels around 6 eV with a maximum cross section of 5.8×10^{-18} cm^2 [11]. On the surface of glassy solid n-hexane (nHg) SAF cross sections for CH_3Cl, O_2, and H_2O are found to be 10^2-10^4 times more intense. This difference is attributed to the different BS of nHg and Kr. *Contrary to solid Kr, nHg has a band gap edge lying about 0.8 eV above the vacuum level [12] which favors the formation of and trapping into image states.*

Our experiments were conducted using an improved low energy electron transmission (LEET) method [13]. In a LEET experiment, a magnetically collimated monochromatic (40 meV FWHM) electron beam of variable energy impinges on a solid film condensed onto a metallic substrate (in our case, polycrystalline Pt cleaned by resistive heating in O_2). A LEET spectrum is obtained by measuring the electron current transmitted through the film as a function of the potential applied between the electron source and the substrate. The LEET current rises sharply at the zero energy reference of the vacuum level, producing a sharp structure called the injection curve (IC). If electrons are trapped on the film surface, the IC is displaced to a higher energy by a potential barrier ΔV arising from the charges. The displacement of the IC is a measure of the height of ΔV which can be related to the absolute charging cross section $\sigma(E)$, by considering the charged film as a parallel plate capacitor. For charging caused by the adsorption of a submonolayer of molecules onto the surface of a dielectric spacer film, $\sigma(E)$ can be related to the potential ΔV by a charging coefficient

$$A_s(E) = \frac{d\Delta V}{dt} = \frac{\sigma(E)\rho_0 J_0 L}{\kappa\varepsilon_0} \qquad (1)$$

in the limit of small charging [13]. In Eq. (1), E is the electron energy, ρ_0 the initial density of electron trapping molecules per unit area, J_0 the electron beam current density, κ the dielectric constant of the spacer film, ε_0 the permittivity of free space, and L the thickness of the spacer (i.e., the distance between the metal and the film vacuum interface). For n-hexane, κ and the thickness of a monolayer (ML) are, respectively, 2.15 [14] and 4.17 Å [15]. In the present experiments, $A_s(E)$ was measured within the 0–10 eV range for submonolayers (~0.1 ML) of CH_3Cl, O_2, H_2O, and CF_4 condensed on multilayer n-hexane spacer films which were irradiated with an electron beam ($J_0 \sim 25\ \mathrm{nA/mm^2}$) normal to the surface, for a known duration (several ms), at specific energies. $A_s(E)$, determined by measuring the shift of the IC for each of the energies, was accurate within 10%; $\sigma(E)$, evaluated using Eq. (1) had an absolute and relative uncertainty of 47% and 10%, respectively [13]. The n-hexane spacer was condensed at 25 and 80 K, at which temperatures it had amorphous and crystalline (*nHc*) morphologies, respectively [16,17]. The temperature dependence of LEET spectra [1,17] shows that *nHc* has a BS distinctly different from that of *nHg* [1].

We show in Fig. 1(a) $A_s(E)$ for a 10 ML pure *nHg* film. It reveals that *nHg* films do not trap charges on direct electron bombardment up to about 7 eV. Above this energy, H^- is formed via DEA [1]. Similarly, for 13-ML *nHc* appreciable charging below 7 eV is not observed as shown in Fig. 1(b). This condition allows us to study SAF by dopant molecules on n-hexane films up to ~7.0 eV. Figure 1(c), shows $A_s(E)$ for 0.1 ML CH_3Cl on the surface of a 5-ML *nHg* film. The sharp (FWHM ~50 meV) and intense peak near zero energy is shown on an extended energy scale in the inset (d). The maximum in A_s corresponds to a SAF cross section of $2 \times 10^{-13}\ \mathrm{cm}^2$ which is ~10^4 times larger than that for DEA on the Kr film surface [8] shown in Fig. 1(e). Charging by 0.1 ML CH_3Cl on the *nHc* film surface is shown in Fig. 1(f). It reveals that the strong electron trapping seen on *nHg* vanishes on *nHc* producing an $A_s(E)$ similar to that in (b). The CH_3Cl DEA peak expected around 0.5 eV, similar to that on the Kr surface, is hidden by the background signal in (f).

We show in Fig. 2(a), $A_s(E)$ for 0.1 ML O_2 on the surface of a 5 ML *nHg* film and in (b) the $A_s(E)$ for 0.05 ML H_2O on a 10-ML *nHg* surface. Both figures exhibit extremely large $\sigma(E)$ of $2 \times 10^{-13}\ \mathrm{cm}^2$ and $4 \times 10^{-14}\ \mathrm{cm}^2$ A_s, *near zero energy,* indicating that charging via resonance stabilization (O_2) and intermolecular stabilization by clusters of H_2O are also strongly affected by the *nHg* surface. Charging at higher energies, however, is unaffected by condensation on *nHg* [17]. This is illustrated in Fig. 2(c), which represents the A_s of 0.1 ML CF_4 on the surface of 13-ML *nHg* and in (d), which represents 0.1 ML CF_4 on the surface of 10 ML Kr. The A_s peak near 6 eV for CF_4 seen in (d), is buried under the base line in (c). The results on CF_4 show that not all molecules give huge A_s peaks near zero energy on *nHg*; for observing such an effect, the dopant molecule must possess a mechanism to trap electrons near zero eV. In summary, Figs. 1 and 2 illustrate that (1) the asymmetrical shapes of the peaks in $\sigma(E)$, which extend from 0 to 1 eV for CH_3Cl, O_2, and H_2O on Kr [see Fig. 1(e) and Refs. [9] and [10], respectively] are squeezed into a sharp nearly symmetrical peak (e.g., inset Fig. 1) near zero energy; (2) this modification of peak line shapes and the huge enhancement in $\sigma(E)$ does not depend on the mechanism of electron stabilization and (3) the strong enhancement in $\sigma(E)$ is observed for different types of dopant molecules.

A priori, there are three possible scenarios in which BS changes can intervene to enhance $\sigma(E)$: (1) the incoming electron is first captured by the dopant molecule to form a transient anion which couples to the surface BS and dissociates or stabilizes to its ground state; (2) same

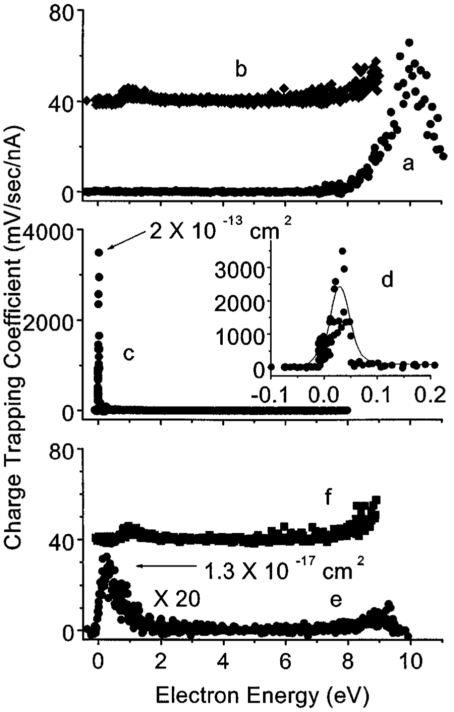

FIG. 1. Charging coefficient as a function of incident electron energy for (a) a 10-ML film of glassy n-hexane (*nHg*); (b) a 13-ML film of crystalline n-hexane (*nHc*); (c) 0.1 ML CH_3Cl on a 5-ML *nHg* surface; (d) the peak near zero energy in (c) shown on an extended scale; (e) 0.1 ML CH_3Cl on a 10-ML Kr surface; (f) 0.1 ML CH_3Cl on 13 ML *nHc* surface. All compounds were condensed on a Pt substrate. Relevant cross sections evaluated using Eq. (1) are shown in (c) and (e).

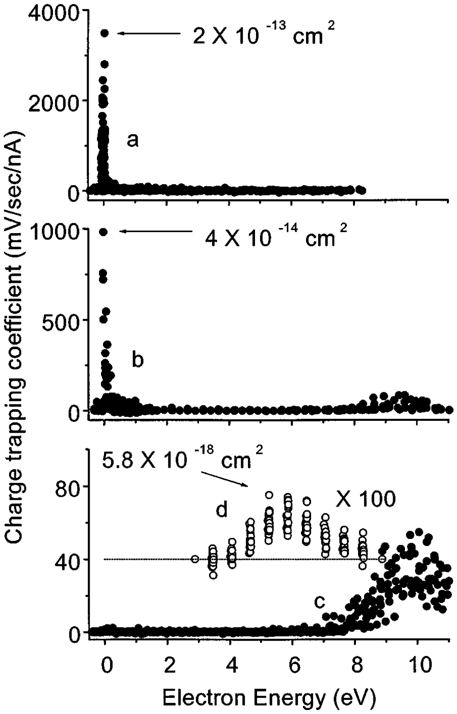

FIG. 2. Charging coefficient as a function of electron energy for (a) 0.1-ML O_2 on 5 ML *nHg* surface; (b) 0.05-ML H_2O on 10-ML *nHg* surface; (c) 0.1-ML CF_4 on the surface of 13-ML *nHg*; and (d) 0.1-ML CF_4 on a 10-ML Kr surface. Relevant cross sections evaluated using Eq. (1) are shown in each plot.

as (1), but the transient anion decays into vibrational excitation leaving the outgoing electron in an image state [2]; afterwards, the electron is captured by the dopant molecule; and (3) a near-0-eV electron normally incident on *nHg* changes momentum by scattering from the surface. For any final momenta other than specular, the electron is captured at the surface by the image force which pulls the electron toward the solid, but it cannot penetrate the latter due to the band gap which extends up to 0.8 eV above the vacuum level [12]. In this case, the electron can occupy an image state. Via scenario (1) coupling of the molecular anion state to the density of states provided by an admixture of an incoming plane wave and a backscattered vacuum wave function is unlikely to give an appreciable increase electron capture cross section [18] nor does it provide a mechanism to increase the lifetime of the anion [19]. Also, scenario (1) does not apply to the intermolecular stabilization mechanism [e.g., Fig. 2(b)]. Furthermore, since the dopant molecule first captures the electron, the line shape of the resonance profile and the energy of the maximum in $\sigma(E)$ should be the same on both *nHg* and Kr; *this is contrary to all experimental observations.* Similarly, scenario (2) cannot explain the results of Fig. 2(b) and the changes in the resonance energy and line shapes [Figs. 1(c) and 2(a)]. On the other hand, *trapping via scenario (3) provides a maximum in $\sigma(E)$ at 0 eV, a line shape unrelated to that of an electron resonance and applies to all dopants that can trap an electron at 0 eV or below* (e.g., CH_3Cl, O_2, and H_2O but not CF_4). Scenario (3) is expected to provide huge cross sections since in this case the entire surface is available for electron capture and near 0 eV electrons are likely to change momentum to other than specular when scattering from an amorphous surface. However, this implies that image states exist with lifetimes sufficiently long to allow for stabilization into localized anion states.

A schematic diagram of the BS of *nHg* deduced from the information contained in the LEET spectra of *nHg* [1,12,17] is shown in Fig. 3. The *nHg* film has a band gap at the vacuum level and the lowest conduction band edge lying at $V_0 \sim 0.8$ eV [1,12]. For such a dielectric film deposited on a metal, the image potential of an electron at a distance z from the metal perpendicular to the film surface may be written [5] as

$$V(z) = V_0 = (1/4z)/4\pi\kappa\varepsilon_0 \qquad z < L \tag{2a}$$

$$= V_v(L + b, L) \qquad L \leqslant z \leqslant L + b \tag{2b}$$

$$= V_v(z, L) \qquad z > L + b \tag{2c}$$

In Eq. (2), $V_v(z, L)$ is the potential in the vacuum region; i.e.,

$$V_v(z, L) = \left\{ -\beta e^2/4(z - L) + [(1 - \beta^2)e^2/4\beta] \times \sum_{n=0}^{\infty} [(-\beta)^n/(z - L + nL)] \right\} \Big/ 4\pi\varepsilon_0 ,$$

where, $\beta = (\kappa - 1)/(\kappa + 1)$. Since V_v is not valid at $z = L$, a cutoff parameter "b" (0.75 Å, see Fig. 3) is employed and V_v is chosen to be a constant for $L \leqslant z \leqslant L + b$. For a 5-ML *nHg* film on a Pt (111) surface, we solved the Schrödinger equation with the potential of Eq. (2) and the boundary conditions of vanishing wave function at $z = 0$ and at infinity [5], by numerically diagonalizing the Hamiltonian using a discrete variable representation algorithm with Fourier functions as the basis set [20]. We obtained two bound image states with eigenenergies $E_1 = -0.42$ eV and $E_2 = -0.1$ eV, shown in Fig. 3.

Electrons in image states usually have long lifetimes [3–5]. For an electron trapped in the E_1 image state our calculations, for a 5-ML *nHg* film, using WKB approximation of Cole [5] yielded a lifetime of ~ 0.4 μs against its decay via tunneling into the metal. This value does not, however, represent a realistic lifetime because the electron can reach the metal via hopping diffusion through gap states [12]. Following the method described in Ref. [12], we obtained a lifetime of ~ 3 ns for decay via diffusion through gap states for a 5-ML *nHg* film; this is orders of magnitude larger than phonon vibrational periods and hence sufficiently long for electron stabilization [9]. Electrons in image states eventually propagate into the metal faster than the experimental time scale and cannot be observed in the charging spectrum

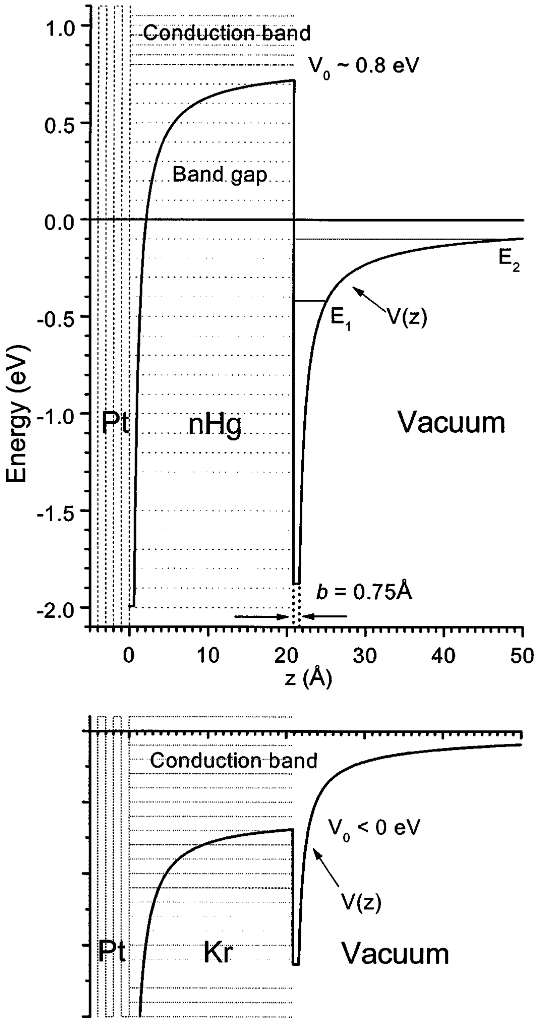

FIG. 3. Schematic diagram of simplified one-dimensional band structure for a *nHg* (top) and Kr (bottom) spacer layer film.

of pure *nHg* [Fig. 1(a)]. The introduction of a dopant molecule at the surface having an electron attachment mechanism near zero energy, however, dramatically alters this scenario. Image states can couple to negative ion states of the dopant [2] lying below the vacuum level or having energy and/or Franck-Condon widths extending below the vacuum energy; this coupling leads to the transfer of the electron into the molecular trap when the energy of the final (i.e., relaxed) anionic state is lower than that of the initial image state. This mechanism increases the probability of electron attachment to the dopant as seen in the Figs. 1(c), 2(a), and 2(b). The image potential of an electron entering into a Kr film is shown at the bottom of Fig. 3. In this case, the electron enters directly from vacuum into the conduction band; it does not remain at the surface and immediately propagates across the dielectric into the metal. Thus, the time of interaction between the anion and image states (if any) is drastically reduced causing the intense charging to vanish on the Kr surface. The disappearance of this intense charging effect on the *nHc* surface corroborates the inference from LEET spectra, that the BS of *nHc* is much different than that of *nHg* [1,17], causing unhindered electron transmission to occur as in the Kr film and/or strong specular reflection due to long-range order.

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[1] L. Sanche, IEEE Trans. Dielectr. Electr. Insul. **4**, 507 (1997); Scanning Microsc. **9**, 619 (1995).
[2] P. J. Rous, Phys. Rev. Lett. **74**, 1835 (1995).
[3] R. W. Schoenlein *et al.*, Phys. Rev. Lett. **61**, 2596 (1988).
[4] R. M. Osgood, Jr. and X. Wang, Solid State Phys. **51**, 1 (1998).
[5] R. L. Lingle, Jr. *et al.*, Chem. Phys. **205**, 191 (1996); M. W. Cole, Phys. Rev. B **3**, 4418 (1971).
[6] C. von Sonntag, *The Chemical Basis of Radiation Biology* (Taylor and Francis, New York, 1987).
[7] G. Damamme *et al.*, IEEE Trans. Dielectr. Electr. Insul. **4**, 558 (1997).
[8] L. Sanche *et al.*, Phys. Rev. Lett. **75**, 3568 (1995); P. Ayotte *et al.*, J. Chem. Phys. **106**, 749 (1997).
[9] L. Sanche and M. Deschênes, Phys. Rev. Lett. **61**, 2096 (1988).
[10] A. D. Bass and L. Sanche, J. Chem. Phys. **95**, 2910 (1991); W. C. Simpson *et al.*, J. Chem. Phys. **108**, 5027 (1998).
[11] A. D. Bass *et al.*, J. Phys. Chem. **99**, 6123 (1995).
[12] L. G. Caron *et al.*, Phys. Rev. B **33**, 3027 (1986).
[13] K. Nagesha *et al.*, Rev. Sci. Instrum. **68**, 3883 (1997).
[14] A. D. Sen *et al.*, J. Phys. D **25**, 516 (1992).
[15] N. Norman and H. Mathisen, Acta Chem. Scand. **15**, 1755 (1961); L. E. Firment and G. A. Somorjai, J. Chem. Phys. **66**, 2901 (1977).
[16] S. L. Hager and J. E. Willard, J. Chem. Phys. **63**, 942 (1975); K. Takeda, M. Oguni, and H. Suga, J. Phys. Chem. Solids **52**, 991 (1991).
[17] K. Nagesha and L. Sanche (to be published).
[18] H. Sambe *et al.*, Phys. Rev. Lett. **59**, 505 (1987).
[19] A. Gerber and A. Herzenberg, Phys. Rev. B **31**, 6219 (1985).
[20] D. T. Colbert and W. H. Miller, J. Chem. Phys. **96**, 1982 (1992).