

Controlling the Lifetime of Adsorbate Negative Ion States

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We demonstrate theoretically that the lifetime of molecular or atomic negative ions can be controlled by adsorption onto a metallic thin film, a phenomenon that is analogous to the electromagnetic enhancement/inhibition of the lifetime of electronically excited atomic states which decay by spontaneous photon emission. Specifically, we show that by coupling the $^2\Pi_g$ negative ion state of adsorbed N_2 to the quantum well states of a thin film of Ag(111) supported on a Pd(111) the ionic lifetime can be significantly increased or decreased by changing the thickness of the thin film.

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Resonant electronic states in adsorbed molecules are believed to be responsible for a variety of electron-induced dynamical processes at surfaces [1–3] including dissociation [1], desorption [4], and the excitation of intramolecular and surface-molecule vibrational modes [5–13]. Recent studies have revealed the importance of resonant electron-molecule interactions in surface photochemistry [14–16], molecular beam scattering [5,17,18], and dissociative molecular adsorption [19,20], where the electrons originate in the substrate. According to the Franck-Condon picture, the cross sections and product distributions for such processes are strongly dependent upon the lifetime of the intermediate state [5]. Indeed, it has long been recognized that the ability to control the lifetime of the resonant electronic states of adsorbed molecules would be “synonymous with the control of surface chemical dynamics” [5]. In this paper we show, theoretically, that the lifetime of a particular type of molecular resonant state, the negative ion resonance, can be controlled by adsorption of the molecule onto an epitaxial metallic thin film. This is the first attempt to use a quantitative theory of adsorbate lifetimes to *design* a specific type of controlled surface structure that changes, in a predictable manner, the lifetime of an adsorbate negative ion.

Molecular and atomic negative ion states are resonant electronic states in which an incident electron is temporarily trapped by the molecule or atom [21–23]. The idea presented in this Letter is based upon a tunneling picture of the subsequent decay of the negative ion by electron detachment [24,25]. According to that viewpoint, the lifetime of the captured electron is (inversely) related to the time dependent probability current that flows away from the molecule through the barrier that confines the electron. In the case of negative ion formation *via* a shape resonance the electron tunnels through a centrifugal barrier. Then, the corresponding probability current is proportional to the penetrability of the barrier that traps the electron and the local density of unoccupied electronic states (LDOS) in the vicinity of the molecule [24,25]. The barrier penetrability is usually increased when the molecule

is adsorbed onto a surface, because the surface breaks the molecular symmetry and allows the electron to “leak” out through lower angular momentum channels that have lower effective barrier heights [23]. This effect tends to reduce the resonance lifetime of an adsorbed molecule, because the barrier penetrability is increased by the presence of the surface. However, there is another important contribution to the alteration of the lifetime of the negative ion upon adsorption. Compared to a free atom or molecule, the presence of the substrate may substantially increase or decrease the local density of unoccupied electronic states into which the trapped electron detaches [24–27]. It is this effect that permits the control of the resonance lifetime by adsorption of a molecule onto a metallic thin film.

In order to demonstrate this phenomenon, we have performed detailed calculations for the specific case of the $^2\Pi_g$ shape resonance of N_2 . In free N_2 this resonance is responsible for negative ion formation for an incident electron energy of approximately 2.3 eV. This resonance survives physisorption of the molecule and electron attachment *via* this negative ion state has been observed experimentally in vibrational spectroscopy of N_2 physisorbed on Ag(111) [5,28–31]. Figures 1 and 2 show the results of a layer-KKR (Korringa-Kohn-Rostoker) calculation [26,27] of the resonance energy and lifetime of the $^2\Pi_g$ state of an isolated N_2 molecule physisorbed on an epitaxial thin film of N layers of Ag on Pd(111) [32]. The adsorption height is 3.2 Å, and the molecule is oriented parallel to the surface above the top site [26,27]. As $N \rightarrow \infty$, this adsorption geometry reproduces the experimentally observed energy (~ 1.2 eV) and lifetime of this state for N_2 physisorbed polycrystalline Ag [28].

In Fig. 1 we plot the calculated energy of the $^2\Pi_g$ negative ion state as a function of the number of layers N in the Ag thin film. The energy of the state is reduced to approximately 1.2 eV compared to the gas phase value of 2.3 eV and is almost independent of the film thickness. This behavior is consistent with the image screening of the negative ion by the metallic substrate which simply

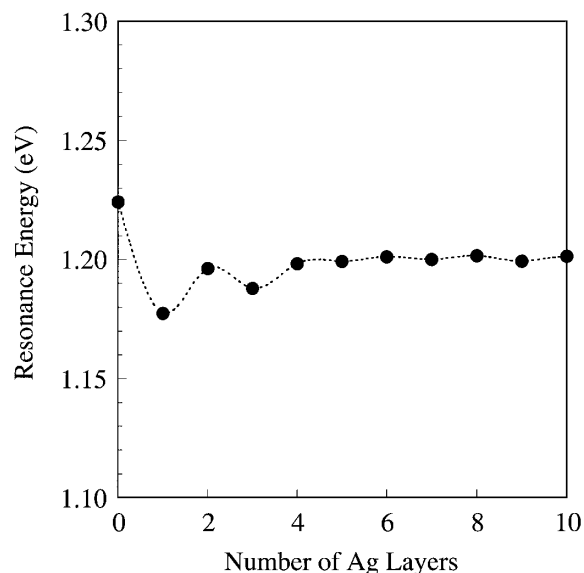


FIG. 1. The calculated energy of the ${}^2\Pi_g$ negative ion state of an isolated N_2 molecule physisorbed on an epitaxial thin film of Ag on Pd(111) (solid circles). The resonance energy is plotted as a function of the number of Ag layers in the thin film, N . The adsorption height is fixed at 3.2 Å, and the molecule is oriented parallel to the surface above the top site. The dashed line is a guide to the eye only.

lowers the resonance energy as the molecule approaches the surface.

In Fig. 2 the calculated lifetime of the ${}^2\Pi_g$ negative ion state is plotted as a function of the number of layers in the Ag thin film (solid circles). We observe an oscillatory modulation of the lifetime that is strongly correlated with the thickness of the Ag film. If the Ag film is removed from the calculation, and the lifetime is computed as a function of the height of the N_2 molecule above Pd(111) (Fig. 2, dashed curve), then lifetime modulation is suppressed, and we observe an essentially monotonic decrease of the lifetime of the negative ion state as the molecule approaches the surface.

The behavior shown in Fig. 2 can be explained by considering the unoccupied electronic structure of the Pd(111) substrate and the Ag(111) thin film. Pd(111) has a projected band gap with edges at approximately -4.6 and $+2.1$ eV relative to the vacuum level. The energy of the adsorbed N_2 ${}^2\Pi_g$ state ($+1.2$ eV) lies well within this gap, so that the Pd(111) substrate acts as an efficient reflector of electrons detaching from the ${}^2\Pi_g$ state of the molecule. By contrast, the corresponding L gap in Ag(111) $\bar{\Gamma}$ lies between $L_2 \approx -4.4$ and $L_1 \approx -0.8$ eV relative to the vacuum level, below the energy of the ${}^2\Pi_g$ state. Consequently, the Ag/Pd(111) thin film behaves as a lossy electronic waveguide that supports quantum well states produced by multiple scattering of electrons between the Ag/Pd interface and the surface barrier (i.e., the Ag/vacuum interface) [33]. The modulation of the resonance lifetime observed in Fig. 2 results from the cou-

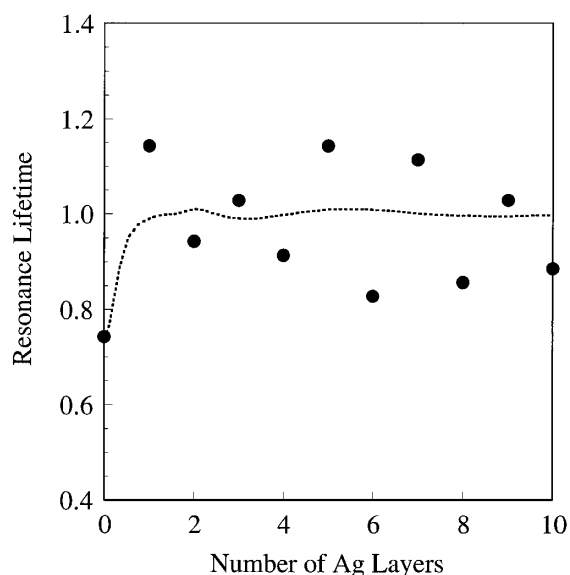


FIG. 2. Solid circles: The calculated lifetime of the ${}^2\Pi_g$ negative ion state of an isolated N_2 molecule physisorbed on an epitaxial thin film of Ag on Pd(111). The lifetime is plotted as a function of the number of Ag layers in the thin film and is normalized to the lifetime of ${}^2\Pi_g$ negative ion state of the free molecule. Dashed curve: As for the solid curve but with the Ag layers removed from the calculation. In this case, the resonance lifetime is plotted as a function of the N_2 -Pd(111) spacing [i.e., the adsorption height on clean Pd(111)].

pling of the negative ion of the adsorbed molecule to the quantum well states of the thin film. The electronic mode structure of the thin film and, consequently, the LDOS just outside of the surface are strongly dependent upon the film thickness. Therefore, the lifetime of the adsorbate negative ion state can be altered by varying the film thickness to change the density of unoccupied electronic states into which the trapped electron may detach.

This physical picture is consistent with the results presented in Fig. 3. Figure 3 shows the reciprocal unoccupied LDOS [$\rho^{-1}(\mathbf{r}_M)$] evaluated above a model surface consisting of the Pd(111) substrate under an empty potential well equal in depth to the surface barrier height of Ag(111) and having a width equal to the thickness of the film. This quantity was evaluated for states at the resonance energy. The LDOS was evaluated by the layer-KKR method at a position corresponding to the center of mass of the N_2 molecule (\mathbf{r}_M) when physisorbed on the surface. Since, in this calculation, the Ag layers are represented by a simple potential well, this model allows us to display the LDOS modulations for films of arbitrary thickness. According to a simple tunneling theory, we expect the lifetime of the negative ion to be inversely proportional to the unoccupied LDOS in the vicinity of the molecule. This picture is confirmed by Fig. 3 in which we observe a modulation of the reciprocal LDOS that is quite similar to the discrete layer-by-layer lifetimes obtained for the actual Ag/Pd(111) surface. Of course, the

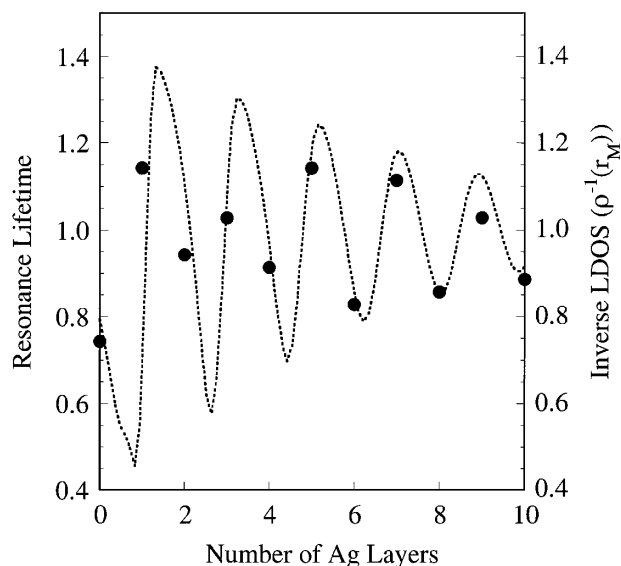


FIG. 3. A comparison of the normalized lifetime of the $2\Pi_g$ negative ion state of N_2 on Ag/Pd(111) (solid circles) and the reciprocal of the local density of unoccupied electronic states, $\rho^{-1}(r_M)$, computed for the model potential described in the text (dashed line). Both quantities were calculated by the layer-KKR method and were normalized to their values far from the surface.

locations of the maxima and minima for the layer-KKR method and model calculations are not perfectly aligned, because the model potential cannot exactly reproduce the propagation of electrons through the Ag layer or the shape of surface barrier at the Ag/vacuum interface [34–36]. Nevertheless, Fig. 3 clearly illustrates that it is the alteration of the LDOS by the electronic waveguide formed by the thin film that is the physical origin of the modulation of the lifetime.

It is of interest to note that the model presented in this paper is analogous to a phenomenon recently studied in the field of photonics: cavity QED. It has been shown that the lifetime of electronically excited states of molecules which decay by the spontaneous emission of a photon can be altered by placing the molecule in an environment where the local density of photonic states is substantially different from the vacuum [37]. This has been achieved in practice by confining dye molecules between two parallel planar Si mirrors separated by a fraction of the wavelength of the emitted photon [37]. The mirrors form a planar waveguide, the electromagnetic modes of which can be altered by changing the spacing of the mirrors. In this case the excited dye molecules occupy the interior of the waveguide and couple directly to the electromagnetic modes of the waveguide. In our electronic analog the thin film waveguide is lossy and therefore coupling to the modes is achieved by placing the molecule on the surface corresponding to the exterior of the guide.

The behavior we have reported in this paper is not confined to the N_2 -Ag/Pd(111) system we have considered

here in detail. Instead, our model demonstrates that one way to manipulate the lifetime of an adsorbate negative ion state is the control the local density of unoccupied electronic states into which the trapped electron is emitted. Presumably, the metallic waveguide described in this paper is not the only way of achieving this effect; adsorption onto a quantum dot where the electronic states are confined more effectively might result in a more dramatic modulation of the lifetime of an atomic or molecular negative ion.

In conclusion, we have shown how the lifetime of a negative ion state can be altered by adsorption onto a specific surface structure consisting of an electronic waveguide formed by an epitaxial metallic thin film. Such a structure can be used to control the lifetime of an adsorbate negative ion by simply changing the thickness of the film. Therefore we have shown, theoretically, how it may be possible to achieve direct control of a class of electron induced dynamical processes that proceed *via* negative ion formation.

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