Nonradiative relaxation of electronically excited N2 on Al(111). Comparison with nonlocal optical theory

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(Received 31 January 1983; accepted 25 March 1983)

The contribution of surface electron-hole pair creation processes to the nonradiative relaxation of the $C\,^3\Pi_u$ electronically excited state of N_2 on Al(111) is investigated using electron energy loss spectroscopy. The homogeneous broadening of the spectral lines is found to be ~ 140 meV, corresponding to a lifetime of $\sim 5 \times 10^{-15}$ s. We compute the contributions of surface and bulk electron-hole pair generation processes to the lifetime broadening, utilizing a theory for the *nonlocal* dielectric response of the metal based on the Lang–Kohn model for the surface potential. The theory predicts correctly the observed overall decay rate and shows that surface processes make an order of magnitude higher contribution to that rate than the bulk processes. The physical conditions which determine the relative importance of surface and bulk processes are discussed.

INTRODUCTION

In recent years there has been a growing interest in understanding the nature and the decay mechanisms of the electronic excitations of adsorbates.[1] Such information is important in a variety of research areas such as photon and electron-stimulated desorption,[2-5] photoluminescence[6,7] and photochemistry[8,9] of adsorbates, resonance photoemission,[10] and the surface-enhanced Raman effect.[11,12] However, there is still little information regarding the electronic excitations of adsorbates and even less understanding of their decay.

Decay mechanisms of excited species near a metal surface involve bulk and surface plasmon excitations,[13-15] electron-hole (e-h) pair excitations,[16,17] and resonance electron tunneling.[18-20]

Various groups have performed experiments on the quenching of the luminescence of excited molecules as a function of their distance d from a metal surface down to ~ 10 Å.[21-26] The nonradiative decay of molecules in *direct* contact with the surface has also been determined via the lifetime broadening of the spectra.[27] In all cases it was found that the presence of the metal results in strong quenching of the excitations and the findings were interpreted in the context of the classical (local) response) theory.[13] Classical theory, however, puts too much emphasis on bulk loss processes and neglects potentially important e-h pair creation processes near the surface. In several recent publications the use of the *nonlocal* dielectric response for the proper description of surface relaxation phenomena has been considered.[28-32] However, as it has been pointed out,[33] it is important to use a realistic model for the surface potential in order to correctly assess the importance of surface losses. Such a potential is provided by the model of Lang and Kohn[34,35] which is based on the jellium approximation. Using the above surface model, a theory for the nonradiative decay of excitations near a metal has been proposed by Persson and Lang.[36]

In this work we investigate the importance of the decay mechanism involving the creation of e-h pairs in the surface region of a metal. For this purpose we use high resolution electron energy loss spectroscopy (EELS) to study the lifetime broadening of the electronic excitation spectra of N_2 adsorbed on Al(111) at 15 K. This system, for a variety of reasons, appears appropriate for comparisons with theoretical predictions on the nonradiative decay near the surface. The N_2 is weakly adsorbed on the surface with minor perturbations of its electronic structure as seen by ultraviolet photoemission spectroscopy (UPS) of its valence orbitals. Based on the observed (by UPS) valence orbital energies and the observed (by EELS) excitation energies, the $1\pi_g^*$ orbital, common to all observed excitations, lies (in the presence of a valence hole) below the Fermi level of Al. Therefore contributions to the observed broadening from a decay channel involving resonant tunneling of the excited electron to the vacant states of the metal are not present.[19,37] Al itself is a simple free electron metal in the energy range of interest and can be accurately treated within the jellium model. We thus use the theory of Persson and Lang[36] to calculate the broadening resulting from decay paths involving creation of the e-h pair in the bulk and near the metal surface. The theory predicts that, in our case, surface contributions to the decay rate are an order of magnitude higher than bulk contributions, which demonstrates the importance of the nonlocal dielectric response in surface dynamical processes. There is a reasonable agreement between the experimentally obtained (~ 140 meV) lifetime broadening of the $C\,^3\Pi_u$ state and the total lifetime broadening predicted by the Persson–Lang theory (~ 155 meV). The excited state lifetime of the $C\,^3\Pi_u$ state of N_2 on the Al(111) surface is $\sim 5 \times 10^{-15}$ s.

EXPERIMENTAL

The experimental system used in these studies has been described in some detail before,[27,37,38] so only a few points need to be mentioned here. The electron energy loss spectrometer is of the hemispherical deflector type, operating at a resolution of ~ 20 meV in the present study. The UV photoelectron spectra were obtained using He I (21.2 eV) radiation. Both spectrom-

eters are contained in a turbo-molecular and ion pumped UHV chamber with base pressures of 6×10^{-11} Torr. The Al(111) sample was mounted on a Cu block cooled by liquid He to ~15 K. The sample was cleaned by Ar$^+$ sputtering and annealed to ~200 °C.

RESULTS AND DISCUSSION

The interaction of ground state N$_2$ with Al(111)

The ground state ($^1\Sigma_g^+$) of N$_2$ has the orbital configuration $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)^2$. In the gas phase the first three vertical ionization potentials occur at 15.60 (from $2\sigma_u$), 16.98 (from $1\pi_u$), and 18.78 eV (from $3\sigma_g$).[39] When about two layers of N$_2$ are deposited on Al [Fig. 1(a)] the UPS maxima are observed at 9.85, 11.15, and 13.06 eV (with respect to the Fermi level). At sub-monolayer coverage [Fig. 1(b)] there is a further shift to higher binding energies with the emission bands at about 10.46, 11.85, and 13.73 eV, respectively [the work function of Al(111) is 4.25 eV]. The most important fact obtained from the UPS results is that the relative energy separations of the photoemission bands are essentially the same, independent of the N$_2$ phase. This behavior is completely different from that observed for N$_2$ on transition metals (e.g., Ni and W). In the latter case the photoemission peaks from $3\sigma_g$ and $1\pi_u$ merge into a single broad band at ~7.6 eV, while emission from $2\sigma_u$ is seen at 5 eV higher binding energy.[40,41] On these surfaces N$_2$ is *chemisorbed* with the internuclear axis
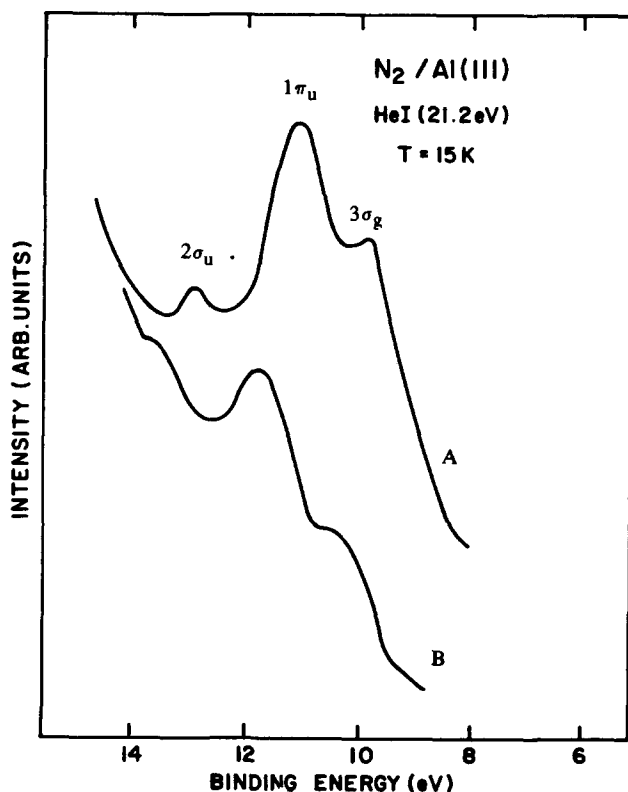

FIG. 1. Ultraviolet ($\hbar\omega = 21.2$ eV) photoemission spectra of N$_2$ on Al(111) at 15 K. A: ~2 monolayers of N$_2$ and B: sub-monolayer coverage. The binding energies are referred to the Fermi level.
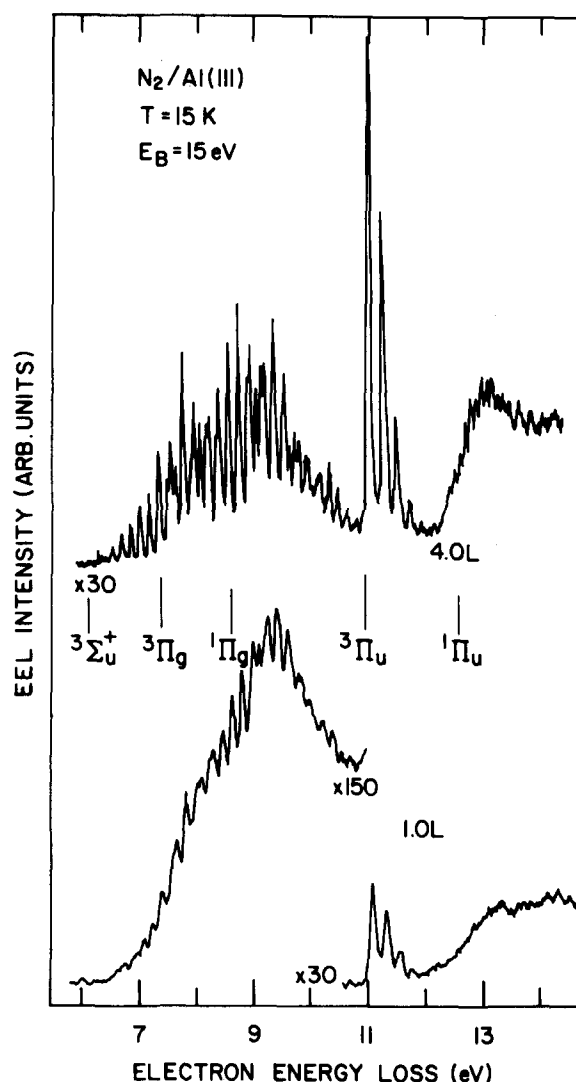

FIG. 2. Electron energy loss spectra of N$_2$ on Al(111) at 15 K. Electron beam energy $E_B = 15$ eV. Upper spectrum: multilayer N$_2$ film. Lower spectrum: monolayer coverage.

perpendicular to the surface. For N$_2$/Al(111), however, the rigid shift of the photoelectron spectrum as a whole implies that the N$_2$ molecule is *physisorbed* and that the observed shifts are associated mostly with final (valence hole) state relaxation effects. The N$_2$ molecule is expected to have its axis parallel to the Al surface so as to maximize the van der Waals interaction. An analogous geometry has been proposed for CO/Al(111)[42] where the binding energy was determined to be ~0.2 eV/molecule. On the basis of its lower polarizability and absence of dipole moment N$_2$ should be even more weakly bound.

Excited states of N$_2$ on Al(111)

At the top of Fig. 2, we show the EEL spectrum of a multilayer film of N$_2$ on Al(111) in the loss range of 6–15 eV. Several electronic transitions with discrete vibronic structure are observed. These transitions can be correlated with the $^1\Sigma_g^+ \rightarrow {}^3\Sigma_u^+$, $^1\Sigma_g^+ \rightarrow {}^{1,3}\Pi_g$, and $^1\Sigma_g^+ \rightarrow {}^{1,3}\Pi_u$ gas phase transitions whose origins (0, 0 band energies) in the gas phase are indicated.[43] These

transitions involve excitation of an electron to the $1\pi_g^*$ unoccupied orbital from the $1\pi_u$, $3\sigma_g$, and $2\sigma_u$ orbitals, respectively. The spin-forbidden singlet-triplet transitions are excited via exchange scattering.[44] In particular the intensity of the $^1\Sigma_g^+ \rightarrow {}^3\Sigma_u$ excitation varies with electron beam energy and angle of observation as expected for exchange scattering.[45]

The monolayer (lower) spectrum shows the same excitations but is significantly broadened by the interaction with the metal surface. The $X\,^1\Sigma_g^+ \rightarrow C\,^3\Pi_u$ transition at 11 eV is particularly suitable for the evaluation of relaxation rates via line broadening because of the absence of spectral congestion. Since the $C\,^3\Pi_u \rightarrow X\,^1\Sigma_g^+$ transition is forbidden (for example, we do not observe significant lifetime broadening of the $^3\Sigma_g^- \rightarrow {}^1\Delta_g$ and $^1\Sigma_g^+$ transitions of O$_2$ physisorbed on Ag[46]), the homogeneous linewidth of the $C\,^3\Pi_u$ state will be determined by the decay rate via the dipole active transition to the lower energy excited $B\,^3\Pi_g$ state. The origin of the $C\,^3\Pi_u \rightarrow B\,^3\Pi_g$ transition (second positive system of N$_2$) is at 3.68 eV.[43]

The linewidth of the 11 eV band ($v = 0$ level of $^3\Pi_u$) is found to be about 80 meV (FWHM) in multilayer N$_2$ films (e.g., by exposing Al at 15 K to 10 L N$_2$; 1 L = 1×10^{-6} Torr s). This width represents the convolution of the instrumental width (~20 meV) and the inhomogeneous width due to the disoriented nature of the N$_2$ film. For monolayer coverage the observed width (FWHM) is about 200 meV. It has been argued that for weakly physisorbed systems on single crystal surfaces, as in this case, the inhomogeneous contribution to the observed width is small.[27] If we assume that the inhomogeneous broadening on the surface is the same as in the bulk, we obtain a homogeneous (lifetime) broadening for $C\,^3\Pi_u(v=0)$ molecules in the first layer of $\Gamma \cong 140$ meV which corresponds to a nonradiative lifetime of ~5×10^{-15} s.

Nonlocal optical theory predictions

The problem of calculating the lifetime broadening of the excited state near the metal surface translates into the problem of the damping of a screened, oscillating (with frequency Ω) dipole above a metal due to the excitation of e-h pairs. In the energy transfer process both energy and momentum need to be conserved. Energy conservation requires that only electrons within a shell $E_F - \hbar\Omega < E < E_F$ at the Fermi surface can be excited. The momentum required for the excitation of e-h pairs in the *bulk* via *intraband* transitions can be provided by electron-phonon or impurity scattering. Scattering by the crystal potential allows *interband* transitions to take place. In our study of the decay of the $^1B_{2u}$ (4.8 eV) state of pyrazine on Ag(111) we found that bulk e-h pair generation can account for the observed decay rate. This is understandable since the excited state energy lies in a region of interband transitions.[27]

Another important source of momentum is provided by the metal surface (the spatial variation of the near field of the dipole, at short distances, also provides momentum). To properly assess the importance of the surface processes, a realistic model for the surface potential is needed. As mentioned in the introduction the model of Persson and Lang[36] satisfies the re-

quirement. In the Persson-Lang model the damping rate due to surface losses of a dynamical dipole $\langle i|\hat{\mu}|f\rangle$ of frequency Ω situated at a distance d from the image plane of the metal is, for $\Omega \ll \omega_p$, given by

$$\frac{1}{\tau_{surf}} = \frac{3|\langle i|\hat{\mu}|f\rangle|^2}{4\hbar d^3} \cdot \frac{1}{k_F d} \cdot \frac{\Omega}{\omega_p} \, \xi(r_s)\beta(r_s, k_F d) \, . \tag{1}$$

The corresponding expression for decay via creation of e-h pairs in the bulk of the metal is

$$\frac{1}{\tau_{bulk}} = \frac{|\langle i|\hat{\mu}|f\rangle|^2}{4\hbar d^3} \, \text{Im} \, \frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 1} \, . \tag{2}$$

By assuming a Drude form for the bulk dielectric function $\epsilon(\omega) = 1 - \omega_p^2/\omega(\omega + i/\tau')$ and that $1/\tau' \ll \Omega \ll \omega_p$, Eq. (2) can be cast[36] in a more informative form (3):

$$\frac{1}{\tau_{bulk}} = \frac{|\langle i|\hat{\mu}|f\rangle|^2}{\hbar d^3} \cdot \frac{1}{k_F l} \cdot \frac{\Omega}{\omega_p} \cdot \left(\frac{\omega_F}{\omega_p}\right)^2 \, . \tag{3}$$

In Eqs. (1)-(3) k_F: Fermi wave vector; ω_F: Fermi frequency; ω_p: bulk plasmon frequency; $l(= v_F \tau')$: electron mean free path. The parameter $\xi(r_s)$ is related to the centroid ($d_\perp$) of the induced surface charge density and is a function of the electron gas density (ρ) parameter $r_s(\frac{4}{3}\pi r_s^3 \equiv \rho^{-1})$. Finally, $\beta(r_s, k_F d)$ is a correction factor which allows the asymptotic form of the original Persson-Lang model to be applicable to all distances.[47] It should be noted that in principle the surface and bulk contributions to the relaxation [Eqs. (1) and (2)] are not simply additive but they will interfere. However, the wave vector dependence of the respective scattering amplitudes is quite different. Bulk damping is rather isotropic in k space while the surface contribution is sharply peaked in the direction of the surface since only electrons moving in this direction can be scattered. As a result the interference (overlap) term is expected to be small.

It is first worth considering the general features of Eqs. (1)-(3). From Eqs. (2) and (3) is seen that decay via creation of bulk excitations falls off with distance as d^{-3}, while, decay via surface e-h pairs [Eq. (1)] falls off faster, as d^{-4}. Therefore, surface contributions become important only at short distances. From the previous discussion, the relative contribution of bulk and surface excitations also depends on the availability of momentum for intraband transitions in the bulk. A measure of the efficiency of such processes is provided by the electron mean free path l [Eq. (3)]. For transition metals which possess a high density of states near the Fermi level and for $\hbar\Omega$ of a few eV, l is small ($k_F l \sim 1$) so that bulk losses can dominate even at the closest distances. On this basis we can understand the observed d^{-3} distance dependence of the phosphorescence lifetime of pyrazine as close as 10 Å above a Ni surface.[21] On the other hand, $k_F l$ is large (~100) for free electron metals and for noble metals below the onset of transitions from the d band (e.g., for Ag below ~3.5 eV) one has $k_F l \sim 100$ and bulk processes are less important.[53] It should be noted that, in general, not only single particle excitations, i.e., e-h pairs, but also collective excitations, i.e., plasmons, contribute to the nonradiative decay of the dynamic dipole. Bulk plasmon contributions to the relaxation rate are not included in the classical theory

[Eq. (2)]. In the nonlocal treatment bulk plasmons can be excited by an external field. However, in the present case since $\hbar\Omega(=3.6\ \text{eV}) < \hbar\omega_p(=15.5)$ no such contribution is present. Contributions from surface plasmons are included in Eq. (2). However, since $\hbar\omega_{sp} = \hbar\omega_p/\sqrt{2} \cong 11$ eV the density of "nonresonant" surface plasmons at 3.6 eV is low so that this decay channel also is unimportant.

Using Eqs. (1) and (2) we can now estimate the relative contributions of surface and bulk e-h pair formation to the lifetime broadening ($\Gamma = \hbar/\tau$) of the $C\,^3\Pi_u(v=0)$ level of N₂ on Al(111). Al is characterized by a $r_s = 2$ electron density parameter so $\xi(r_s=2) = 2$ and $\beta(r_s=2, k_F d = 1.75) = 0.5.$[47] Also $\hbar\omega_p = 15.5$ eV, $\hbar\omega_F = 11.7$ eV, $k_F = 1.75$ Å, and $\epsilon(3.6\ \text{eV}) = -17.288 + i3.035.$[49] The distance between the N₂ and the Al surface (jellium edge) should be about 2 Å, i.e., about 1 Å measured from the image plane.[34,35] The dipole matrix element $\langle i|\hat{\mu}|f\rangle$ where $|i\rangle = |^3\Pi_u\rangle$ and $|f\rangle = |^3\Pi_g\rangle$ can be obtained from the oscillator strength of the transition through the relation

$$|\langle i|\hat{\mu}|f\rangle|^2 = f\frac{\hbar e^2}{2m_e \hbar\Omega}. \qquad (4)$$

The oscillator strength of the 0,0 band at 3.68 eV, $f_{0,0}$, has been determined by electron beam studies as $f_{0,0} = 0.04$[50] and by shock tube studies as 0.057.[51] Using the above $f_{0,0}$ values and the relative transition probabilities of the $0 \to v''$ vibronic bands of Ref. 52 we obtain, $(\sum_{v''} f_{0,v'} \equiv f)$, $f = 0.083$ or 0.112. If we use the mean value of the above two f numbers we calculate that $\Gamma(\text{surface}) \simeq 140$ meV and $\Gamma(\text{bulk}) \simeq 15$ meV. That is at the physisorption distance the surface contribution to the relaxation rate is about an order of magnitude higher than that of the bulk. The two contributions become equal at about 70 Å from the Al surface. The calculated total $(\Gamma_s + \Gamma_b)$ lifetime broadening is ~155 meV which is in agreement with the experimentally deduced lifetime broadening of ~140 meV.

CONCLUSIONS

In previous studies of nonradiative damping of electronic excitations near metal surfaces, it has been concluded that classical theory describes adequately the quenching process. However, most of these studies have been performed under conditions (large distances from the surface, transition metal, or noble metal substrates in the energy range of interband transitions) where quenching via bulk excitations dominates. As we have shown here, however, under the appropriate conditions, damping via surface e-h pair creation can dominate the quenching. The quenching of the $C\,^3\Pi_u$ state of N₂ physisorbed on Al(111) provides a good example of such a case. The observed lifetime broadening is ~140 meV, corresponding to a lifetime of ~5×10^{-15} s (i.e., a lifetime ~10^6 times shorter than that of free N₂). The theory of Persson and Lang predicts comparable overall broadening (~155 meV) and that surface e-h pair creation makes an order of magnitude larger contribution to the decay rate than the corresponding bulk process. Consideration of the *nonlocal* dielectric response of the metal would appear to be essential in the theoretical analysis of dynamical processes on metal surfaces.

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[53] Another point suggested by Eq. (3) is that the bulk contribution to the relaxation rate should be a function of temperature due to the T dependence of l. Under conditions where electron–phonon coupling is the dominant scattering mechanism (i.e., away from interband transitions, and for high purity metals) the creation of bulk e–h pairs should decrease strongly with decreasing T (for low T, $l \sim T^{-5}$ while for high T, $l \sim T^{-1}$) (Ref. 48). Therefore, estimates of the contributions of the bulk to observed low temperature relaxation rates using high T dielectric data are, in this regard, upper limits.