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Luminescence and nonradiative energy transfer to surfaces

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Luminescent molecules near metal surfaces can have dramatically decreased quantum efficiencies and lifetimes. For example, decreases of $\sim 10^3$ in quantum efficiency and in lifetime occur for nitrogen atoms within 3 nm of potassium surfaces. This paper presents experimental decay curves for light emission from nitrogen atoms in a N_2 matrix of varying thickness (3 to 1000 nm) on sapphire, silver, and potassium substrates. Theoretical decay curves are derived and found to be in agreement with the experimental curves. Both experiment and theory agree that for potassium there is near-resonant coupling between excited nitrogen atoms and potassium surface plasmons. For metal films, both film thickness and surface roughness affect the decay curves.

I. INTRODUCTION

The study of nonradiative energy transfer from an excited molecule to a nearby metal or dielectric surface is a topic of current interest[1-15] with a long history. In 1909, Sommerfeld[16] pointed out the possibility of the existence of a surface wave propagating along the earth's surface if an antenna were close enough to the earth. By analogy[5,17,18] a radiating molecule may act as an oscillating dipole (antenna) near a partially absorbing and partially reflecting metal surface (earth) and setup surface plasmon oscillations in the metal (surface wave).

Here we present studies of the α emission of N atoms ($^2D \rightarrow {}^4S$, $\lambda = 523.0$ nm) in solid nitrogen matrices deposited on Ag, K, and sapphire substrates. The nitrogen matrix is irradiated with electrons and we study the time dependence of the intensity of the emission from the excited N atoms formed by bombardment.

The study of the emission from solid nitrogen began with the work of Vegard,[19] McLennan and Shrum,[20] and Broida and Pellam.[21] More recent work has been reviewed by Oehler, Smith, and Dressler[22] and Sayer, Prince, and Duley.[23] These studies show that the green α emission has a radiative lifetime of about 39 ± 2 sec; the transition arises from N atoms at centrosymmetric sites in which phonons act to dynamically induce the $^2D \rightarrow {}^4S$ transition.[22,24] The concentration of N atoms in the matrix is approximately 0.2 at. %.[25,26]

The interaction between an emitting molecule and metal surface has been studied by following the decay of luminescence from an excited molecule.[1-4] The experimental conditions were such that the molecule-surface plasmon coupling was relatively weak.[5] The dependence of the intensity of luminescence on the molecule surface separation, the type of the metal, film thickness, and surface preparation have been little studied experimentally, although some theoretical work has been done.[5,6] Here we show experimental results demonstrating that the molecule-surface plasmon coupling is a strong function of the surface dielectric constant at the emission wavelength of the molecule. In addition, effects of the surface roughness, metal film thickness, and molecule-surface separation are presented. The theoretical work of Chance, Prock, and Silbey,[5] Lukosz and Kunz,[6] Efrima and Metiu,[7] Kuhn,[8] and Morawitz and Philpott[9] is adapted to the conditions of our experiments.

It should be noted that previous studies were concerned with a single layer of fluorescent molecules coupling to surfaces. Our study of the phosphorescent α emission was performed in an N_2 matrix rather than a very thin N_2 layer separated from the metal surface by an inert solid. Ar, Kr, and Xe all have large interatomic spacings compared to the size of an N_2 molecule or N atom so migration of nitrogen molecules or atoms through the rare-gas matrix would likely be a problem, especially during electron bombardment.[27]

II. EXPERIMENTAL

The experiments were carried out in a bakeable ion-pumped and titanium sublimation-pumped ultrahigh vacuum system with typical operating pressures below 7×10^{-8} Pa ($\sim 5 \times 10^{-10}$ Torr). This pressure corresponds to the order of one impurity monolayer or less striking the substrate per hour. This rate of impurity buildup was considered to have a negligible effect on the experiments, even if the sticking coefficient of the residual gases was unity.

All components mounted on the ultra-high vacuum (UHV) chamber were bakeable to at least 200 °C, although 24-h, 80 °C bakeouts were usually adequate. An electron gun, ion gun, residual gas analyzer, two metal evaporation furnaces, two variable leak gas inlets, and quartz observation windows were all directed at the chemically cleaned single-crystal sapphire substrate which was attached to a UHV modified two-stage helium recirculating refrigerator. To bake the refrigerator above ~100 °C, the internal parts of the refrigerator had to be removed. A Chromel resistance heater was evaporatively deposited on the back of the sapphire substrate. Temperature was measured by a calibrated iron-doped gold vs Chromel thermocouple. The experiments were performed at 11.0 ± 1.0 K. A photoelectric detection system, quartz optics, 1-m monochromator (0.4-mm slits) and chart recorder were used to measure luminescence intensity and decay curves of the electron-beam excited nitrogen matrix.

The thickness of the N_2 film deposited on the substrate was determined by counting interference fringes from specularly reflected Hg pen lamp light ($\lambda = 253.63$ nm) directed at 15° from the substrate normal into the monochromator and PMT for a given exposure (pressure × time) of the substrate to N_2 gas. The measured points fell on a straight line with slope 1100 nm/Pa sec. This thickness vs exposure calibration factor was independent of deposition rate over the range 0.07 to 1.5 nm/sec (7×10^{-5} to 130×10^{-5} Pa). We used this measured calibration factor at the lower exposure rates to estimate the thickness of our thinner films of N_2. Previous work[28] has shown the sticking coefficient of nitrogen on a 10 K surface to be approximately unity.

The thickness of K films was found using the interference fringe method (thin films of K are nearly transparent at $\lambda = 253.65$ nm).[29] Silver thickness estimates were made by visually comparing the Ag film to calibrated Ag films made in another system. The estimates were thought to be reliable to ±4 nm for Ag film thicknesses less than 20 nm. Greater Ag film thicknesses were estimated by assuming a constant deposition rate. The theoretical results were not strongly dependent on Ag thickness for thicknesses greater than about 40 nm.

The following was typical of many experiments. The UHV system was pumped below 7×10^{-8} Pa and the residual gases checked to be sure there were no leaks and that hydrogen and nitrogen were the principal residual gases. The refrigerator was turned on and at 40 K a known thickness of metal (Ag or K) evaporated onto the target. The evaporated metal surface was then heated to 165 K to desorb any residual gases and then cooled to 11 K. Before cooling, Ag films were sometimes annealed at 300 K. Pressures during metal deposition were never above 1×10^{-5} Pa. On the first run, 3 nm of research grade N_2 was deposited. Thicker layers were deposited in subsequent runs after first desorbing the previous N_2 layer by heating to 100 K. The electron gun excited the N_2 with 200-eV electrons (0.6 μA). The energy flux over the approximately 0.2-cm^2 excited area was 0.6 mW/cm^2, slightly smaller than used by other workers.[22,23] The intensity and decay curves of the N, $^2D \rightarrow {}^4S$ transition were measured as a function of N_2 matrix thickness after manually turning off the electron gun. Turn off times of less than 0.1 sec were achieved.

III. THEORETICAL

We consider the system described in Fig. 1 in which the electrons strike the nitrogen layer forming metastable atoms which radiate. We assume that the electron beam is turned off at the time $t = 0$ and the intensity of the fluorescent emission is monitored as a function of $t > 0$. We denote by $I(t - t_0, \vec{r})$ the intensity, measured at time $t > 0$, of the fluorescent emission by an excited atom located at $\vec{r}$, and formed at $t_0 < 0$. The probability that the atom is

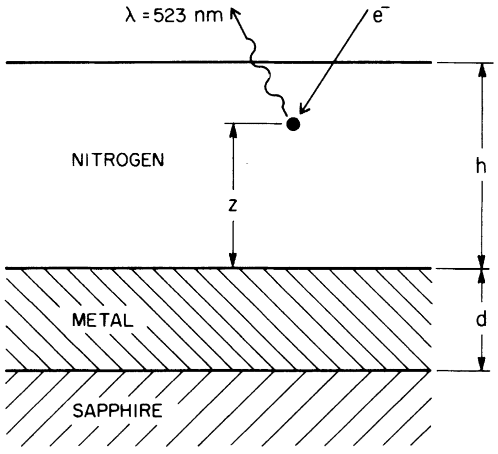

FIG. 1. Experimental geometry showing the sapphire substrate, metal film of thickness d, and nitrogen film of thickness h. The black dot represents a matrix isolated N atom, a distance z from the metal film, being excited by an electron, and its subsequent radiation at $\lambda = 523.0$ nm.

formed at $\vec{r}$ is taken to be

$$P(\vec{r}) = Ce^{-a(h-z)}dz\,dA \qquad (1)$$

where a^{-1} is the penetration depth of the electron in the nitrogen matrix, A is the area, z is the distance to the metal surface, h is the nitrogen layer thickness, and C is an unknown constant.

The probability that the atom was formed at time t_0 is given by $K\,dt_0$, where K is the rate constant for the N_2 dissociation which generates the metastable atoms.

The total intensity collection by the detector at the time $t > 0$ is

$$I(t) = \int_V d\vec{r}\, P(\vec{r}) \int_{-\infty}^{0} dt_0\, K I(t - t_0; z) \quad . \qquad (2)$$

Here V is the volume of the nitrogen sample. We have assumed, in writing down this equation, that the dipoles radiate incoherently.

To complete the calculation we need to estimate $I(t - t_0; z)$. One can derive the result heuristically by using known facts about the process of interest in the absence of the metal surface and then making corrections for the role of the metal.

The electron prepares an excited atom which begins radiation with a time dependent intensity. To compute this intensity, we use the Drude equation to obtain the oscillating dipole of the excited atom. Then, a straightforward electrodynamic calculation gives the intensity of the radiation emitted by the dipole. The results are:

$$\vec{\mu}(t - t_0) = e^{-\Gamma_0(t-t_0)}\left(\alpha e^{-i\omega_0(t-t_0)} + \alpha^* e^{i\omega_0(t-t_0)}\right) \quad , \qquad (3)$$

and

$$I(t - t_0) = Be^{-2\Gamma_0(t-t_0)} \quad . \qquad (4)$$

Here $\vec{\mu}(t - t_0)$ is the value of the dipole moment at the time t, for an atom excited at time t_0. $I(t - t_0)$ is the intensity emitted by this dipole at t. The constants α and B are not of interest since we do not measure the absolute intensity.

The frequency of the radiation, ω_0, and the radiative lifetime $\tau_0 = \Gamma_0^{-1}$ appear in the final result since they enter in the Drude equation

$$\delta\ddot{\vec{r}} + \omega_0^2 \delta\vec{r} + 2\Gamma_0 \delta\dot{\vec{r}} = 0 \quad . \qquad (5)$$

Here $\vec{\mu}(t) \equiv e\,\delta\vec{r}(t)$, and $\delta\vec{r}(t)$ is the "displacement of the electronic charge" due to the excitation of the atom.

The above results are computed for the case of free space. If a "device" such as that described in Fig. 1 is present the Drude equation is modified since the dipole $\vec{\mu}(t)$ interacts with its image field $\vec{E}(\vec{x}, t)$. Thus, for such a case

$$\delta\ddot{\vec{r}}(t) + \omega_0^2 \delta\vec{r}(t) + 2\Gamma(z)\delta\dot{\vec{r}}(t) = \left(\frac{e}{m}\right)\vec{f} \cdot \vec{E}(\vec{x}, t) \qquad (6)$$

Here $\Gamma(z)^{-1}$ is the position dependent radiative lifetime. The presence of the image field will cause a small change in the vibrational frequency and a substantial change in the radiative lifetime.[5–9]

To compute this change we assume for simplicity that the radiating dipole moment is perpendicular to the surface since the experiment should be most sensitive to perpendicular dipoles. Our calculations of radiation patterns of perpendicular and parallel dipoles near a surface show that the intensity of parallel dipoles should be smaller than that of perpendicular dipoles at an observation angle of 15° for $h \leq 200$ nm, though the total integrated intensity of the parallel dipoles is larger. Also, the intensity of the perpendicular dipoles at an observation angle of 15° should be proportional to the total integrated intensity (to within ~5%) for $h \leq 100$ nm, the region of most interest. This assumption gives for the inverse lifetime the equation

$$2\Gamma(z) = 2\Gamma_0 + \left(\frac{e^2 f}{m}\right)\left(\frac{\omega_0 \mu_0}{4\pi}\right) K_1^{-2} \times \mathrm{Re}\left[\int_0^\infty d\lambda \frac{\lambda^3}{\eta_1} \frac{(\Delta_1 \eta_1 \epsilon_2 - \eta_2 \epsilon_1)}{(\Delta_1 \eta_1 \epsilon_2 + \eta_2 \epsilon_1)} e^{2i\eta_1 z}\right] \quad . \qquad (7)$$

Here

$$\eta_j = \left[\left(\frac{\omega_0}{c}\right)^2 \epsilon_j - \lambda^2\right]^{1/2} \quad , \quad j = 1, 2, 3 \quad , \qquad (8)$$

$$\Delta_1 = [\eta_2 \epsilon_3 - i\eta_3 \epsilon_2 \tan(\eta_2 d)][\eta_3 \epsilon_2 - i\eta_2 \epsilon_3 \tan(\eta_2 d)]^{-1} \qquad (9)$$

and

$$K_1 = \left(\frac{\omega_0}{c}\right)(\epsilon_1)^{1/2} \quad . \qquad (10)$$

The symbols ϵ_1, ϵ_2, and ϵ_3 represent the experimental frequency dependent dielectric constants of the solid N_2, metal film, and sapphire, respectively. μ_0 is the magnetic constant of the vacuum, h is the thickness of the N_2 film, and d is that of the metal film.

The equation for the quantity $I(t - t_0)$ in the presence of the device [which we denote $I(t - t_0; z)$] becomes

$$I(t - t_0; z) = B' e^{-2\Gamma(z)(t-t_0)} \quad . \qquad (11)$$

We obtain this from Eq. (4) by assuming that the time evolution of the fluorescence of the molecule in the presence of the device is obtained from the free space expression Eq. (4) by replacing Γ_0 with the corresponding quantity in the presence of the metal film. The constant B' differs from B but this is not relevant to the present work since the intensity is measured in arbitrary units.

The quantity $\Gamma(z)$ depends on the distance to the surface, the thickness of the films involved in the device, the dielectric constants of the materials, and the frequency of the emission.

Inserting Eq. (11) in Eq. (2) we get

$$I(t)=c\int_0^h e^{-a(h-z)}\frac{e^{-2\Gamma(z)t}}{2\Gamma(z)}\,dz \ . \tag{12}$$

This gives the detected intensity in arbitrary units.

The surface plasmon enters in the calculation through the expression for $\Gamma(z)$. Its properties and role in fluorescence depends on the dielectric constants and the dimensions of the layers.

In this calculation we have assumed that the metal surface is smooth. Inclusion of roughness will relax the requirements imposed by the momentum conservation and as a result the surface plasmon is more likely to radiate. The lifetime of the plasmon is likely to be different from that of the excited atom and if plasmon emission is detectable, one may observe two different lifetimes. Such an effect is not included in the present calculation.

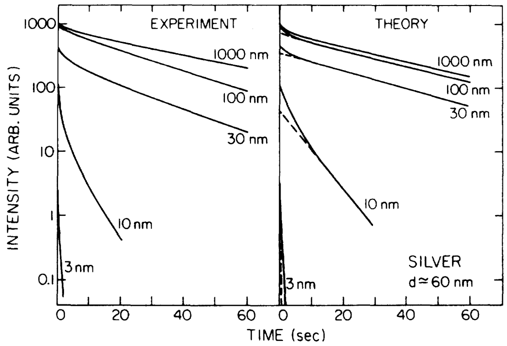

FIG. 3. Experimental and theoretical decay curves of nitrogen deposited on an ~60-nm-thickness silver film. The silver substrate was deposited at 40 K and then annealed at 300 K for 12 h. The dashed theory lines neglect the 2.5-sec lifetime components contribution to the total intensity.

IV. RESULTS AND DISCUSSION

Figures 2–6 show both experimental and theoretical decay curves ($\ln I$ vs t) for a number of substrates and N_2 matrix thicknesses. Decay curves with small initial intensities and steep slopes indicate strong nonradiative coupling between N atoms and the substrate. The theoretical curves predict the slope and relative initial intensities of the experimental curves well.

For very thick N_2 matrices where the effect of the substrate is negligible, the decay curves are described by the sum of two exponentials:

$$I(t)=(0.2e^{-t/2.5}+e^{-t/39})I_0 \ , \tag{13}$$

where the time, t, is measured in seconds. The amplitude and lifetime of the shorter lifetime intensity component are dependent on the exciting electron energy density. It has been observed and discussed by others,[22] though it is probably fair to say that it is not fully understood. At any rate it is easy to include two decay times in the theory.

The 2.5-sec lifetime contribution to the theoretical decay curves was added to the 39-sec lifetime contribution (dashed lines on sapphire and 60-nm silver theory figures) to obtain their weighted sum (solid line on theory figures). Because of its shorter lifetime, the 2.5-sec lifetime component couples less strongly to the substrate than does the 39-sec lifetime component (because of its shorter lifetime it is more likely to radiate) and so it contributes relatively more to thin N_2 matrix initial intensity predictions than it does to thick N_2 initial intensity predictions.

Table I lists the values of the quantities used in the

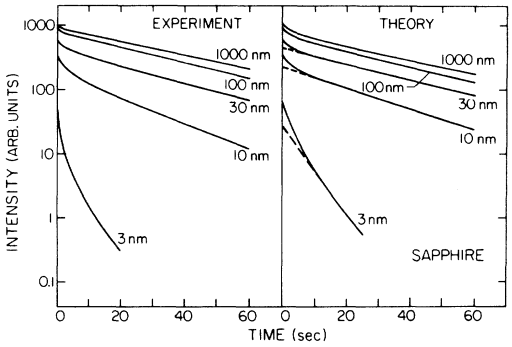

FIG. 2. Experimental and theoretical decay curves ($\ln I$ vs t) of the α emission of N atoms in 3, 10, 30, 100, and 1000-nm-thickness nitrogen matrices deposited on sapphire. The dashed theory lines neglect the "short-lifetime" 2.5-sec contribution to the total intensity.

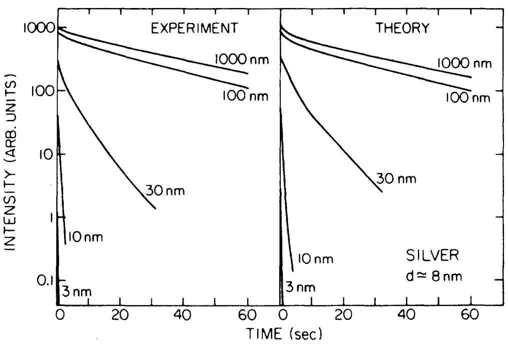

FIG. 4. Experimental and theoretical decay curves for nitrogen on an ~8-nm-thickness, 300-K annealed, silver film. The intensity drops much faster on thin silver than on thick silver for $h=3$, 10, and 30 nm indicating stronger N atom coupling to thin silver.

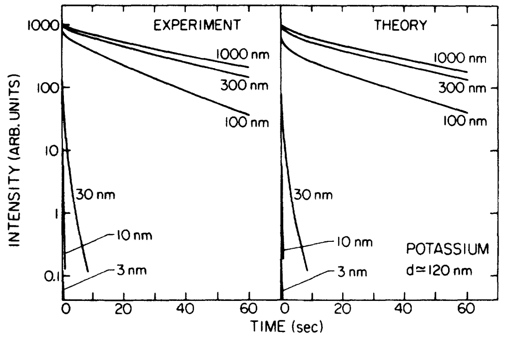

FIG. 5. Experimental and theoretical decay curves for nitrogen on an ~120-nm-thickness potassium substrate annealed at 165 K. Compare the rapid intensity decrease for $h = 30$ nm on potassium substrates with the slower decrease shown on sapphire and silver substrates.

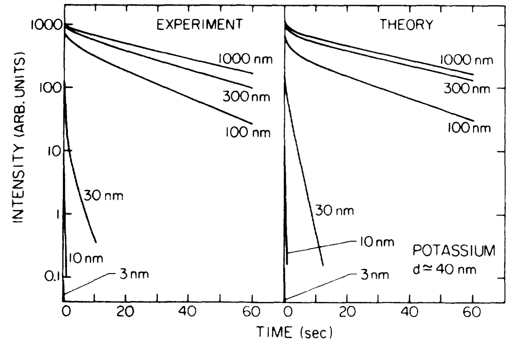

FIG. 6. Experimental and theoretical decay curves for nitrogen on an ~40-nm-thickness potassium substrate annealed at 164 K. These curves fall slightly slower than the curves for thicker potassium (Fig. 5). This effect is most apparent for $h = 30$ nm.

theoretical calculations. Of the several choices available for Ag and K, we use the most recent dielectric constants published. The electron penetration depth in solid nitrogen, a^{-1}, was obtained directly by measuring the fluorescence intensity of the sapphire Cr^{3+} ion impurity ($\lambda \simeq 694$ nm) as a function of solid nitrogen thickness; $\ln(I)$ is proportional to $-ha$ so a^{-1} can be determined by measuring I for several different h's. The oscillator strength was estimated from

$$f_{ik} = 1.499 \times 10^{-14} \lambda^2 g_k / g_i A_{ik} ,$$

where λ is measured in nm, A_{ik} is the transition probability in $\sec^{-1}$, and $g_k(g_i)$ is the statistical weight of the upper (lower) state.[30] For the α transition, $g_k/g_i = \frac{6}{4}({}^2D_{5/2} \rightarrow {}^4S)$ or $\frac{4}{4}({}^2D_{3/2} \rightarrow 4S)$. Because of the larger statistical weight and hence larger oscillator strength, only $g_k/g_i = \frac{6}{4}$ was used. Inclusion of a $g_k/g_i = \frac{4}{4}$ term in f_α slightly decreased the theoretical coupling. From a theoretical calculation of A_{ik} for the α transition[24] it was shown that at low temperatures there is only one significant A_{ik} component. Then $\tau_i^{-1} = \sum_k A_{ik} = A_{ik}$ implies $A_{ik} = \frac{1}{39}$ $\sec^{-1}$, so $f_\alpha \simeq 1.58 \times 10^{-10}$. This estimate neglects crystal-field splitting of the ${}^2D$ state which, we expect, would slightly change g_k/g_i.

Comparison of the decay curves shows that N atoms do not couple as strongly to the sapphire as to the metals (sapphire does not support resonant surface polaritons with energies corresponding to the visible region). Thin silver films couple more strongly to thin layers of N_2 ($h < 50$ nm) than thick silver films. The surface plasmon resonance of thick silver films occurs in the middle ultraviolet ($E \simeq 3.5$ eV, $\lambda \simeq 350$ nm) far from the green α emission. However, if the silver film is thin enough, the surface plasmon is split into higher-energy (normal mode) and lower-energy (tangential mode) resonances due to the interactions of the electron density oscillations on each surface.[31] It is the lower-energy resonance of the thin silver film that is interacting strongly with α.

The thin (40 nm) and thick (120 nm) potassium

TABLE I. Physical quantities used in theoretical calculations of molecule-surface coupling.

Fig.	Substrate	d (nm)	ϵ	a^{-1} (nm)	f	τ_1 (sec)	τ_2 (sec)
2	sapphire[a]	∞	$3.1 + i3 \times 10^{-3}$	3	1.58×10^{-10}	39	2.5
3	silver[b]	60	$-11.56 + i1.673$				
4		8					
5	potassium[c]	120	$-1.882 + i0.1051$				
6		40					
7		10					

[a] References 32 and 33. [b] Reference 32. [c] Reference 29.

substrate decay curves indicate coupling much stronger than for silver or sapphire substrates. The surface plasmon resonance of potassium occurs at about 2.6 eV ($\lambda \simeq 480$ nm) which is near the α emission at about 2.4 eV ($\lambda = 523$ nm) and so the coupling is strong. There is not much difference between thin and thick K since the N atom emission is nearly resonant with the K surface plasmon. However, both experimental and theoretical decay curves for thin K indicate slightly less coupling than in the case of thick K. Theory predicts that if the K film had been thinner ($d \lesssim 10$ nm) then the coupling would have been much less (Fig. 7) than for thick K due to the splitting of the surface plasmon modes and their subsequent movement away from near resonance with the N atom emission.

Figure 8 shows the decay curves for thick unannealed Ag. The thick Ag film ($d \simeq 600$ Å) was deposited at 40 K, heated briefly to 165 K to desorb any deposits that may have accrued during deposition, and then cooled to 10 K. The coupling of N atoms to the Ag surface as indicated by the decay curves is considerably larger for unannealed Ag than it is for annealed Ag and is comparable to that observed with thin Ag. The extra coupling shown in unannealed Ag may be due to roughness effects. Ion bombardment of very thick silver films to produce rough silver films showed similar increases in coupling. The magnitude of the effect clearly indicates that more work needs to be done on atomic and molecular systems coupling to rough metal surfaces.

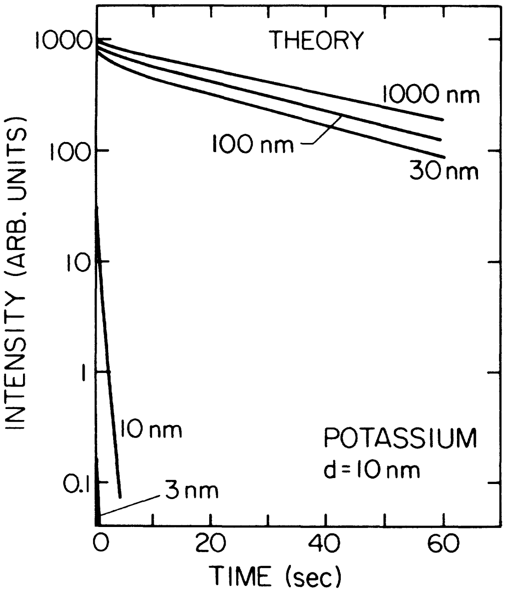

FIG. 7. Theoretical decay curves for nitrogen on a 10-nm-thickness potassium substrate. Note the predicted very slow (as compared to Figs. 5 and 6) intensity decrease of the $h = 30$-nm curve.

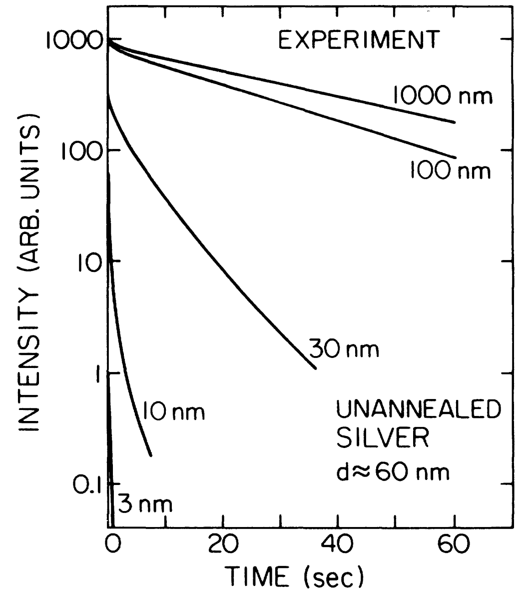

FIG. 8. Experimental decay curves for nitrogen on an ~60-nm silver substrate that has only been heated to 165 K (unannealed). Compare to Fig. 6 which shows data taken on the same film after heating to 300 K. Note the faster intensity decrease of the $h = 30$-nm curve indicating stronger nonradiative surface-N atom coupling for this unannealed film.

The data taken in Figs. 3 and 8 were from the same Ag film, Fig. 3 after annealing and Fig. 8 before annealing. Other experimental runs with Ag indicated that heating to temperatures of about 200 K or less caused no annealing effects whereas heating to over 200 K for different lengths of time gave decreased coupling dependent on both annealing time and temperature. The self-annealing of the Ag film seemed to go to completion after a few hours at 300 K. The data in Fig. 3 were taken after annealing at 300 K for 12 h.

V. SUMMARY

Lifetime and intensity measurements of the N, $^2D \rightarrow {}^4S$ α transition ($\lambda \simeq 523.0$ nm) have been performed as a function of N_2 matrix thickness under UHV conditions on sapphire, silver, and potassium substrates. Theoretical decay curves based on nonradiative energy transfer from excited N atoms to resonant and nonresonant surface plasmon modes of the nearby substrate were compared to the data. The slopes and relative initial intensities of the theoretical decay curves reproduced the experimentai decay curves. This was the first time, to our knowledge, that emission intensities have been checked against theory for molecules coupling to various metal surfaces of various thicknesses in the near surface region. However we have recently become aware of measurements by Harris *et al.*[34] showing that the fluorescence intensity of an excited monolayer of pyrazine separated from a nickel (111) single crystal by an argon spacer layer was proportional to the inverse cube of the pyrazine-Ni separation for separations of 0.7 to 10 nm.

Both theory and experiment have shown that nonradiative coupling to the surface can increase or decrease as the metal film thickness decreases. For Ag films the coupling increased; for K films the coupling decreased. The position of the film's surface plasmon resonance energy relative to the atom (or molecule) emission energy is important to surface-atom (molecule) coupling.

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