

Energy flow and fluorescence near a small metal particle

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We examine the classical energy-balance equation for a fluorescing system consisting of a molecule near a small, spherical metal particle capable of sustaining electromagnetic resonances and irradiated with laser light. From the energy-flow distribution in the entire system, we obtain the enhancement factor for the fluorescence emission of the adsorbed molecule. Numerical results demonstrate that the electromagnetic interactions of the molecule and the surface can be understood in terms of energy flow through the entire system and applied to investigate spectroscopic properties of adsorbates in similar systems. Absorption and emission rates of the adsorbed molecule are determined considering the energy-flow distribution and its dependence on the substrate as well as molecular parameters. Such understanding is useful in predicting spectroscopic responses of adsorbates.

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I. INTRODUCTION

Surface processes such as surface-enhanced Raman scattering (SERS),¹ second harmonic generation,² surface photoemission,³ surface fluorescence,⁴ and surface photochemistry⁵ have received considerable attention in the literature since their understanding is important for the development of modern surface-spectroscopic techniques. Modification of photomolecular processes at surfaces is a well-explored field of research. In this paper we present a detailed analysis of molecular fluorescence in the presence of a small, spherical metal particle, based on energy balance in the fluorescing system.

It is widely accepted that the mechanism for surface-enhanced processes is predominantly electromagnetic in nature. The strong local electromagnetic field experienced by the nearby molecules plays an important role.¹ The local field increases by reflection of the incident radiation and the increase is substantial if, as in the case of a small sphere, the surface to volume ratio is large⁶ and if the incident light excites surface electromagnetic resonances.^{6,7} However, if the molecule is very close to the particle surface, nonradiative energy transfer from the molecule to the surface may be significant.⁸ In addition, the emitting state of the molecule may couple strongly to the radiative resonances of the particle. Therefore, a small metal particle capable of sustaining electromagnetic resonances can enhance molecular absorption (hence fluorescence) by increasing the local field, lower absorption, and emission efficiency of the molecule by stealing energy from it, and may increase fluorescence by emitting efficiently the energy transferred from the emitting state of the molecule to a radiative electromagnetic resonance.

The surface effects discussed above are well founded and explained by classical electrodynamics. Staying within the bounds of local electromagnetics, we present a different approach to understanding surface fluorescence and photochemical effects. Our goal is to investigate the energy-flow distribution in the system and apply the energy-conservation

theorem to study the dynamics of the electromagnetic processes involved.

In Sec. II, a treatment of the energy flow in a coupled dipole-sphere system is given. Section III is devoted to understanding molecular fluorescence in the context of energy flow through the system. The study leads to expressions for the fluorescence yield and enhancement ratio and its dependence on surface parameters. A discussion of the numerical results is presented in Sec. IV.

II. ENERGY FLOW IN DIPOLE-SPHERE SYSTEM

We will briefly review the energy-balance procedure for a dipole (Sec. II A) and for a spherical particle (Sec. II B), before treating the coupled dipole-sphere system. Throughout the paper, a near-resonance condition is assumed where the radiation frequency ω , the molecular transition frequency ω_0 , and the resonance frequency ω_s of the spherical particle are nearly the same.

A. Dipole in external electromagnetic field

In the absence of free charges and in a nonmagnetic medium the energy-balance equation in MKS units is given by^{9,10}

$$\int \mathbf{S} \cdot \hat{\mathbf{r}} ds = -\frac{d}{dt} \int \frac{1}{2} (\epsilon_0 \mathbf{E} \cdot \mathbf{E} + \mu_0 \mathbf{H} \cdot \mathbf{H}) dV - \int \mathbf{E} \cdot \dot{\mathbf{P}} dV, \quad (1)$$

where \mathbf{S} is the Poynting vector, \mathbf{E} and \mathbf{H} are the electric- and magnetic-field vectors, and \mathbf{P} is the electric-polarization vector. ϵ_0 and μ_0 are the electric permittivity and magnetic permeability of free space, respectively. The integrals are evaluated by enclosing the dipole in a large sphere of volume V and surface S , with $\hat{\mathbf{r}}$ representing a radially outward unit vector. Equation (1) is time-averaged to yield

$$\bar{W}_e^{\text{dip}} = \frac{d}{dt} \bar{\mathcal{E}}_{\text{field}} + \langle \mathbf{E} \cdot \dot{\mathbf{P}} dV \rangle, \quad (2)$$

where “ $\langle \rangle$ ” denotes time average.

$$\frac{d}{dt} \bar{\mathcal{E}}_{\text{field}} \equiv \left\langle \frac{d}{dt} \int \frac{1}{2} (\epsilon_0 \mathbf{E} \cdot \mathbf{E} + \mu_0 \mathbf{H} \cdot \mathbf{H}) dV \right\rangle$$

is the time-averaged rate of energy storage in the radiation fields and $\bar{W}_e^{\text{dip}} \equiv -\langle \int \mathbf{S} \cdot \hat{\mathbf{r}} ds \rangle$ is the power extinct from the radiation field by the dipole. $\langle \int \mathbf{E} \cdot \dot{\mathbf{P}} dV \rangle$ is the power removed from the radiation field by the dipole and a Drude-Lorentz-type calculation, with the dipole at \mathbf{r}_0 , yields¹⁰

$$\left\langle \int \mathbf{E} \cdot \dot{\mathbf{P}} dV \right\rangle = \left(\frac{e^2 f}{2m} \right) \frac{\omega^2 \Gamma |\mathbf{E}(\mathbf{r}_0, \omega)|^2}{(\omega_0^2 - \omega^2)^2 + \omega^2 \Gamma^2}, \quad (3)$$

where, e and m are the electron charge and mass, respectively, Γ is the gas-phase decay rate, and f is the oscillator strength of the molecular dipole. This power is either stored in the dipole or dissipated to friction,¹⁰ i.e.,

$$\left\langle \int \mathbf{E} \cdot \dot{\mathbf{P}} dV \right\rangle = \frac{d}{dt} \bar{\mathcal{E}}_{\text{dip}} + \bar{W}_{\text{diss}}^{\text{dip}},$$

where

$$\bar{\mathcal{E}}_{\text{dip}} = \frac{f(m/4)(e/m)^2(\omega_0^2 + \omega^2) |E(\mathbf{r}_0, \omega)|^2}{(\omega_0^2 - \omega^2)^2 + \omega^2 \Gamma^2} \quad (4)$$

and

$$\bar{W}_{\text{diss}}^{\text{dip}} = \frac{2\omega^2 \Gamma}{(\omega_0^2 + \omega^2)} \bar{\mathcal{E}}_{\text{dip}}. \quad (5)$$

Thus, at steady state, the power extinct from the radiation field by the dipole is fully dissipated in the dipole,

$$\bar{W}_e^{\text{dip}} = \bar{W}_{\text{diss}}^{\text{dip}} \quad (6)$$

Also, an explicit evaluation of the time-averaged Poyting integral (with $\mathbf{E} = \mathbf{E}_i + \mathbf{E}_\mu$ and $\mathbf{H} = \mathbf{H}_i + \mathbf{H}_\mu$) leads to

$$\bar{W}_e^{\text{dip}} = -\bar{W}_i - \bar{W}_{\text{sc}}^{\text{dip}} - \bar{W}_{\text{int}}, \quad (7)$$

where

$$\bar{W}_i = \int \frac{1}{2} \text{Re}(\mathbf{E}_i \times \mathbf{H}_i^*) \cdot \hat{\mathbf{r}} ds, \quad (8a)$$

$$\bar{W}_{\text{sc}}^{\text{dip}} = \int \frac{1}{2} \text{Re}(\mathbf{E}_\mu \times \mathbf{H}_\mu^*) \cdot \hat{\mathbf{r}} ds, \quad (8b)$$

and

$$\bar{W}_{\text{int}} = \int \frac{1}{2} \text{Re}(\mathbf{E}_i \times \mathbf{H}_\mu^* + \mathbf{E}_\mu \times \mathbf{H}_i^*) \cdot \hat{\mathbf{r}} ds. \quad (8c)$$

$(\mathbf{E}_i, \mathbf{H}_i)$ and $(\mathbf{E}_\mu, \mathbf{H}_\mu)$ are the incident and dipole fields in the region. $\bar{W}_{\text{sc}}^{\text{dip}}$ is the power scattered by the dipole and \bar{W}_{int} is interpreted as the power lost to interference between the incident and the scattered fields. $-\bar{W}_i$ represents the power loss from the incident beam and is set to zero since there is no loss of incident power at steady state. Therefore, at steady

state, $-\bar{W}_{\text{int}}$ can be interpreted as the power *absorbed*, $\bar{W}_{\text{abs}}^{\text{dip}}$, by the dipole from the incident beam.

Following Born and Wolf¹¹ and noting that the electric field of the dipole may be written as⁹

$$\mathbf{E}_\mu(\mathbf{r}, t) = \frac{k^2}{4\pi\epsilon_0} \boldsymbol{\mu}_T \left(\frac{e^{ikr}}{r} \right) e^{-i\omega t},$$

one obtains

$$\bar{W}_{\text{abs}}^{\text{dip}} = (\omega/2) \text{Im}(\boldsymbol{\mu} \cdot \mathbf{E}_i^*). \quad (9)$$

and the power radiated from the dipole⁹

$$\bar{W}_{\text{sc}}^{\text{dip}} = \frac{\omega^4 |\boldsymbol{\mu}(\mathbf{r}_0, \omega)|^2}{12\pi\epsilon_0 c^3}. \quad (10)$$

Here $\vec{\boldsymbol{\mu}}_r \equiv (\vec{\mathbf{I}} - \hat{\mathbf{r}}\hat{\mathbf{r}}) \cdot \boldsymbol{\mu}$, the propagation vector $\mathbf{k} \equiv (\omega/c)\hat{\mathbf{n}}_0$, and c is the speed of light in vacuum.

From a quantum point of view,¹⁰ one may interpret $\bar{W}_{\text{abs}}^{\text{dip}}/\hbar\omega \equiv \Gamma_{\text{sa}}$ as the rate for stimulated absorption, $\bar{W}_{\text{diss}}^{\text{dip}}/\hbar\omega \equiv \Gamma^{(NR)}$ as the rate for nonradiative decay (due to frictional damping), and $\bar{W}_{\text{sc}}^{\text{dip}}/\hbar\omega \equiv \Gamma^{(R)}$ as the rate for radiative decay (emission), for a two-level system. Thus, in a two-level system, the energy-conservation equation may be written as

$$N_0 \frac{\bar{W}_{\text{abs}}^{\text{dip}}}{\hbar\omega} = N_1 \frac{\bar{W}_{\text{diss}}^{\text{dip}}}{\hbar\omega} + N_1 \frac{\bar{W}_{\text{sc}}^{\text{dip}}}{\hbar\omega}. \quad (11)$$

N_0 and N_1 are the populations of the ground and excited states, respectively. As expected, the total decay rate is the sum of the radiative and nonradiative decay rates.

B. Sphere in external electromagnetic field

Consider a single spherical particle in an external radiation field $(\mathbf{E}_i, \mathbf{H}_i)$. The dissipated energy is computed, as before, by surrounding the particle by a large, imaginary sphere. The fields within this spherical region outside the particle are: $\mathbf{E} = \mathbf{E}_i + \mathbf{E}_s$ and $\mathbf{H} = \mathbf{H}_i + \mathbf{H}_s$, where $\mathbf{E}_s \equiv \vec{\mathbf{R}} \cdot \mathbf{E}_i$ and $\mathbf{H}_s \equiv \vec{\mathbf{R}} \cdot \mathbf{H}_i$ are the fields scattered by the particle. The reflection tensor $\vec{\mathbf{R}}$ depends on the geometry and the dielectric property of the spherical particle.¹ If \bar{W}_e^{sph} denotes the power extinct from the radiation field by the sphere, then the energy-balance condition at steady state becomes $\bar{W}_e^{\text{sph}} = \bar{W}_{\text{diss}}^{\text{sph}}$, where

$$\begin{aligned} \bar{W}_e^{\text{sph}} \equiv & \int ds \frac{1}{2} \{ \text{Re}(\mathbf{E}_i \times \mathbf{H}_i^*) \cdot \hat{\mathbf{r}} + \text{Re}(\mathbf{E}_s \times \mathbf{H}_s^*) \cdot \hat{\mathbf{r}} \\ & + \text{Re}[(\mathbf{E}_i \times \mathbf{H}_s^*) + (\mathbf{E}_s \times \mathbf{H}_i^*)] \cdot \hat{\mathbf{r}}. \end{aligned} \quad (12)$$

and

$$\bar{W}_{\text{diss}}^{\text{sph}} \equiv \left\langle \int_{\text{sph}} \mathbf{E}_t \cdot \dot{\mathbf{P}} dV \right\rangle = \epsilon_0 \frac{\omega}{2} \text{Im} \epsilon(\omega) \int_{\text{sph}} |\mathbf{E}_i|^2 dV, \quad (13)$$

$\varepsilon(\omega)$ is the dielectric function of the material of the particle, $\mathbf{E}_t = \mathbf{E}_t(\omega, t)e^{-i\omega t}$ is the electric field inside the particle, and the usual time-scale separation, $d\vec{\mathbf{E}}_t/dt \ll \omega\mathbf{E}_t$, has been applied. Obviously, $\bar{W}_{\text{diss}}^{\text{sph}}$ is related to the energy stored in the sphere,

$$\bar{\mathcal{E}}_{\text{sph}} = \frac{1}{2} \text{Re}[\varepsilon(\omega)] \int_{\text{sph}} |\mathbf{E}_t|^2 dV. \quad (14)$$

Further, since the incident field does not lose power at steady state, we write $\bar{W}_e^{\text{sph}} = -\bar{W}_{\text{sc}}^{\text{sph}} - \bar{W}_{\text{int}}^{\text{sph}}$, where

$$\bar{W}_{\text{sc}}^{\text{sph}} = \int \frac{1}{2} \text{Re}(\mathbf{E}_s \times \mathbf{H}_s^*) \cdot \hat{r} ds$$

is the power scattered by the particle and

$$\bar{W}_{\text{int}}^{\text{sph}} = \int \text{Re} \frac{1}{2} [(\mathbf{E}_i \times \mathbf{H}_s^*) + (\mathbf{E}_s \times \mathbf{H}_i^*)] \cdot \hat{r} ds$$

is the power lost to interference between the incident and the scattered fields. As in the case of a dipole, interpreting $-\bar{W}_{\text{int}}^{\text{sph}}$ as the power absorbed by the particle, one may write $\bar{W}_{\text{abs}}^{\text{sph}} = \bar{W}_{\text{sc}}^{\text{sph}} + \bar{W}_{\text{diss}}^{\text{sph}}$, where¹¹

$$\bar{W}_{\text{abs}}^{\text{sph}} = (\varepsilon_0/\mu_0)^{1/2} (2\pi/k) \text{Im}[\mathbf{E}_s(\omega) \cdot \mathbf{E}_t^*(\omega)] \quad (15)$$

and

$$\bar{W}_{\text{sc}}^{\text{sph}} = \frac{1}{2} (\varepsilon_0/\mu_0)^{1/2} \text{Re} \int |\vec{\mathbf{E}}_s(\omega)|^2 \frac{ds}{r^2}. \quad (16)$$

C. Sphere and dipole in external electromagnetic field

The system now involves both the molecular dipole and the spherical particle in the presence of external fields (\mathbf{E}_i and \mathbf{H}_i). One has to look at energy balance in both components in order to understand the energy flow through the entire system. The electric field at the dipole of moment $\boldsymbol{\mu}$ (at \mathbf{r}_0 relative to the origin at the center of the particle), is given by^{4(b)}

$$\mathbf{E}_{\text{loc}}(\mathbf{r}_0, t) = \mathbf{E}_i(\mathbf{r}_0, t) + \mathbf{E}_s(\mathbf{r}_0, t) + \mathbf{E}_{\mu s}(\mathbf{r}_0, t), \quad (17)$$

where $\mathbf{E}_s \equiv \vec{R}(\mathbf{r}_0, \omega) \cdot \mathbf{E}_i(\omega)$ is the incident field scattered by the sphere and $\mathbf{E}_{\mu s} \equiv \vec{G}_s(\mathbf{r}_0, \mathbf{r}_0; \omega) \cdot \boldsymbol{\mu}(\omega)$ is the dipole field scattered by the sphere. \vec{R} and \vec{G}_s are the reflection and image tensors, respectively,^{1(a),4(b)} and the time dependence of all fields is assumed harmonic. Since $\mathbf{E}_{\mu s}$ simply broadens and shifts the excited level of the molecule, the dipole is driven to a steady state by the *primary field* $\mathbf{E}_p = \mathbf{E}_i + \mathbf{E}_s$. A self-consistent expression for the *dressed dipole moment* $\boldsymbol{\mu}$ at steady state is given by^{1(a),4(b)}

$$\boldsymbol{\mu}(\omega) = \left(\frac{e^2 \tilde{f}}{m} \right) [\tilde{\omega}_0^2 - \omega^2 - i\omega\tilde{\Gamma}]^{-1} \mathbf{E}_i(\mathbf{r}_0, \omega), \quad (18)$$

where

$$\tilde{\omega}_0^2 = \omega_0^2 - \left(\frac{e^2 f}{m} \right) \text{Re}[G_s(\mathbf{r}_0, \mathbf{r}_0; \omega)],$$

$$\tilde{f} = [1 + R(\omega)]f,$$

$$\tilde{\Gamma} = \Gamma + \left(\frac{e^2}{m\omega} \right) \text{Im}[fG_s(\omega)],$$

and the dipole orientation is taken along the direction of the incident field \mathbf{E}_i . For the dipole, the emitted and the dissipated energies are derived from the *primary field*. At steady state, the power “extinct” by the dipole from the *primary field*, $\bar{W}_{e,p}^{\text{dip}}$, is balanced by the power dissipated to friction in the dipole,

$$\bar{W}_{e,p}^{\text{dip}} = \bar{W}_{e,i}^{\text{dip}} + \bar{W}_{e,s}^{\text{dip}} = \bar{W}_{\text{diss}}^{\text{dip}}. \quad (19)$$

Here, $\bar{W}_{e,i}^{\text{dip}}$ is the power extinct by the dipole from the *incident field* and $\bar{W}_{e,s}^{\text{dip}}$ the power extinct by the dipole from the *incident field scattered by the sphere*.

If one encloses the molecular dipole alone by an imaginary spherical volume and evaluates the Poynting integral of Eq. (2) over its surface, one can obtain the power extinct by the dipole, $\bar{W}_{e,p}^{\text{dip}}$. As before, we write $-\bar{W}_{e,s}^{\text{dip}} = \bar{W}_{\text{trans}}^{\text{sph}}$, the power transferred from the dipole to the particle. This interpretation is the consequence of the balance that must exist for the power transfer between the dipole and the particle at steady state. Thus $\bar{W}_{e,i}^{\text{dip}} = \bar{W}_{\text{diss}}^{\text{dip}} + \bar{W}_{\text{trans}}^{\text{sph}}$.

The power transferred from the dipole to the particle can be obtained from the difference between the time-averaged rate of energy storage in the dipole in the presence of the particle $[(d\bar{\mathcal{E}}_{\text{dip}}/dt) = -\tilde{\Gamma}\bar{\mathcal{E}}_{\text{dip}}]$ and that in the absence of the particle $[(d\bar{\mathcal{E}}_{\text{dip}}^{(0)}/dt) = -\Gamma\bar{\mathcal{E}}_{\text{dip}}^{(0)}]$, i.e., $\bar{W}_{\text{trans}}^{\text{sph}} \approx (\tilde{\Gamma} - \Gamma)\bar{\mathcal{E}}_{\text{dip}}^{(0)}$. Further, if we enclose the particle alone by an imaginary sphere and evaluate the Poynting integral over its surface, we can also obtain the energy transfer per unit time from the dipole to the particle. At steady state, this is same as the power extinct from the *dipole field* by the sphere, $\bar{W}_{e,d}^{\text{sph}}$. With fields $(\mathbf{E}_\mu, \mathbf{H}_\mu)$ and $(\mathbf{E}_{\mu s}, \mathbf{H}_{\mu s})$ inside an imaginary sphere surrounding the particle only, the Poynting integral gives $\bar{W}_{\text{trans}}^{\text{sph}} \equiv \bar{W}_{e,d}^{\text{sph}} = -\bar{W}_{\text{sc},d}^{\text{sph}} - \bar{W}_{\text{int},d}^{\text{sph}}$, where $\bar{W}_{\text{sc},d}^{\text{sph}}$ is the power carried by the dipole field scattered by the particle and $\bar{W}_{\text{int},d}^{\text{sph}}$ is the energy lost per unit time to interference between the fields $(\mathbf{E}_\mu, \mathbf{H}_\mu)$ and $(\mathbf{E}_{\mu s}, \mathbf{H}_{\mu s})$. Interpreting $-\bar{W}_{\text{int},d}^{\text{sph}}$ as the power *absorbed by the particle from the dipole field*, we may write

$$\bar{W}_{\text{abs},d}^{\text{sph}} = \bar{W}_{e,d}^{\text{sph}} + \bar{W}_{\text{sc},d}^{\text{sph}}. \quad (20)$$

This means the power absorbed by the particle from the dipole equals the sum of the powers transferred to the particle and carried by the dipole field scattered by the particle.

Let us now look at the total situation by enclosing the dipole-particle system by a large, imaginary sphere over whose surface the Poynting integral may be evaluated. The net energy flowing into the volume is balanced by the sum of

the energies stored in the fields, in the dipole, and dissipated to friction in both the dipole and the particle. The energy stored in the fields includes the energy stored in the particle, $\bar{\mathcal{E}}_{\text{sph}}$, which is computed from Eq. (14) by replacing \mathbf{E}_t by \mathbf{E}'_t , that includes the additional contribution due to the polarization of the particle by the near field of the dipole. At steady state,

$$\bar{W}_{\text{diss}}^{\text{sph}} = \bar{W}_{\text{trans}}^{\text{sph}} = \epsilon_0 \frac{\omega}{2} \text{Im} \epsilon(\omega) \int_{\text{sph}} |\mathbf{E}'_t|^2 dV. \quad (21)$$

$\bar{W}_{\text{diss}}^{\text{dip}}$ and $\bar{\mathcal{E}}_{\text{dip}}$ are obtained from Eqs. (4) and (5) by replacing \mathbf{E} by \mathbf{E}_i , f by \tilde{f} , ω_0 by $\tilde{\omega}_0$, and Γ by $\tilde{\Gamma}$. Similarly, from Eq. (10), we obtain

$$\bar{W}_{\text{sc}}^{\text{dip}} = \frac{(\omega^4/12\pi)\mu_0(\epsilon_0\mu_0)^{1/2}(e^2/m)^2\tilde{f}^2|\mathbf{E}_i|^2}{(\tilde{\omega}_0^2 - \omega^2)^2 + \omega^2\tilde{\Gamma}^2}. \quad (22)$$

The energy balance condition for the total system can be written as

$$-\left\langle \int (\mathbf{E} \times \mathbf{H}) \cdot \hat{\mathbf{r}} ds \right\rangle = \bar{W}_e = \bar{W}_{\text{diss}}^{\text{dip}} + \bar{W}_{\text{diss}}^{\text{sph}} + \frac{d\bar{\mathcal{E}}_{\text{dip}}}{dt} + \frac{d\bar{\mathcal{E}}_{\text{field}}}{dt}. \quad (23)$$

Since the fields in the region surrounding the coupled system are $\mathbf{E} = \mathbf{E}_i + \mathbf{E}_s + \mathbf{E}_\mu + \mathbf{E}_{\mu_s}$ and $\mathbf{H} = \mathbf{H}_i + \mathbf{H}_s + \mathbf{H}_\mu + \mathbf{H}_{\mu_s}$, the total power extinct, \bar{W}_e , from the fields by the coupled system is given by

$$\bar{W}_e = \bar{W}_{\text{abs}} - \bar{W}_{\text{sc}} - \bar{W}_{\text{int}} = \bar{W}_{\text{diss}}^{\text{dip}} + \bar{W}_{\text{diss}}^{\text{sph}} + \frac{d\bar{\mathcal{E}}_{\text{dip}}}{dt} + \frac{d\bar{\mathcal{E}}_{\text{field}}}{dt}, \quad (24)$$

where

$$\bar{W}_{\text{abs}} = -\left\langle \int \{(\mathbf{E}_i \times \mathbf{H}_s + \mathbf{E}_s \times \mathbf{H}_i) + (\mathbf{E}_i \times \mathbf{H}_\mu + \mathbf{E}_\mu \times \mathbf{H}_i) + (\mathbf{E}_i \times \mathbf{H}_{\mu_s} + \mathbf{E}_{\mu_s} \times \mathbf{H}_i)\} \cdot \hat{\mathbf{r}} ds \right\rangle, \quad (25a)$$

$$\bar{W}_{\text{sc}} = \left\langle \int \{(\mathbf{E}_\mu \times \mathbf{H}_\mu) + (\mathbf{E}_s \times \mathbf{H}_s) + (\mathbf{E}_{\mu_s} \times \mathbf{H}_{\mu_s})\} \cdot \hat{\mathbf{r}} ds \right\rangle, \quad (25b)$$

and

$$\bar{W}_{\text{int}} = \left\langle \int \{(\mathbf{E}_s \times \mathbf{H}_\mu + \mathbf{E}_\mu \times \mathbf{H}_s) + (\mathbf{E}_s \times \mathbf{H}_{\mu_s} + \mathbf{E}_{\mu_s} \times \mathbf{H}_s) + (\mathbf{E}_\mu \times \mathbf{H}_{\mu_s} + \mathbf{E}_{\mu_s} \times \mathbf{H}_\mu)\} \cdot \hat{\mathbf{r}} ds \right\rangle. \quad (25c)$$

The term involving $(\mathbf{E}_i \times \mathbf{H}_i)$ has been set equal to zero since there is no loss of incident flux. Hence, at steady state, the true extinction by the dipole-sphere system consists of the absorption power \bar{W}_{abs} minus the scattered power \bar{W}_{sc} , and

the power lost to interference, \bar{W}_{int} , between the scattered fields of the two coupled dipoles (molecule-sphere system). The various terms in \bar{W}_{abs} , \bar{W}_{sc} , and \bar{W}_{int} have specific meanings. The first term in \bar{W}_{abs} represents the power removed by the particle from the incident beam; the second term is the power removed by the dipole from the incident beam; and the last term is the power removed from the incident beam by a dipole induced in the particle by the molecule. Terms in \bar{W}_{sc} can also be interpreted similarly. The first term of \bar{W}_{sc} clearly represents the power scattered by the molecular dipole, the second term represents the power scattered by the sphere polarized by the incident beam, while the third term is the power scattered by the dipole induced in the sphere by the molecule.

III. STEADY-STATE FLUORESCENCE

We now apply the energy-balance condition to steady-state fluorescence of molecules adsorbed on a spherical particle and irradiated with an external laser source. We consider a three level system^{4(b)} (Fig. 1) for the molecule with ground state $|G\rangle$ and excited states $|A\rangle$ and $|B\rangle$. The fluorescing system can be thought of as consisting of two dipoles coupled to the particle. Dipole A ($|G\rangle \leftrightarrow |A\rangle$) absorbs and dipole B ($|B\rangle \leftrightarrow |G\rangle$) emits. The interdipolar coupling is through the radiationless transition $|A\rangle \rightarrow |B\rangle$, characterized by the rate constant K , assumed to be unaffected by the presence of the substrate particle. If state $|B\rangle$ is a dissociative continuum then the molecule undergoes photochemical decomposition.

Let f_A , ω_A , Γ_A , and f_B , ω_B , Γ_B be the gas-phase natural parameters for dipoles A and B, respectively. The interplay of energy between the dipoles and the particle appears through the renormalized parameters \tilde{f}_A , \tilde{f}_B , $\tilde{\omega}_A$, $\tilde{\omega}_B$, $\tilde{\Gamma}_A$, and $\tilde{\Gamma}_B$. If the steady state populations of the ground and excited states are taken to be N_0 , N_A , and N_B , respectively,

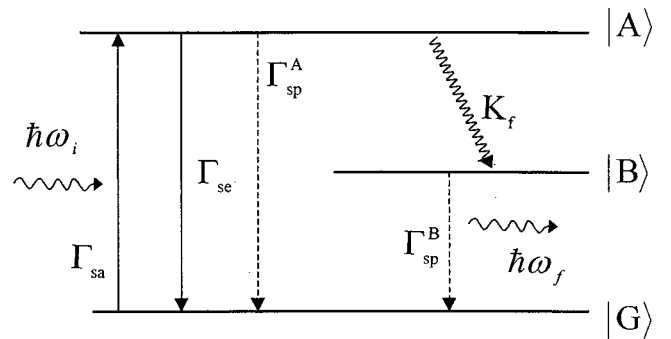


FIG. 1. Schematic diagram of a three-level system. ω_i and ω_f are the incident and emitted light frequencies, respectively. $|G\rangle$, $|A\rangle$, and $|B\rangle$ are the ground and excited states, respectively, of the molecule. Solid vertical lines indicate stimulated transitions and the dashed vertical lines indicate spontaneous (radiative) transitions. The radiationless transition ($|A\rangle \rightarrow |B\rangle$) is indicated by a wavy line.

then in the presence of chemical transformations, the energy-balance equation becomes

$$-\left\langle \int (\mathbf{E} \times \mathbf{H}) \cdot \hat{\mathbf{r}} ds \right\rangle = \bar{W}_{\text{diss}}^A + \bar{W}_{\text{diss}}^B + \bar{W}_{\text{diss}}^{\text{sph}} + \frac{d\bar{\mathcal{E}}_A}{dt} + \frac{d\bar{\mathcal{E}}_B}{dt} + \frac{d\bar{\mathcal{E}}_{\text{field}}}{dt} + \hbar K(\omega_i - \omega_f)(N_B/N), \quad (26)$$

where the last term represents the loss of power to the radiationless relaxation process ($|A\rangle \rightarrow |B\rangle$) and N is the total number of molecules. ω_i and ω_f are the exciting and emitting frequencies. $\bar{\mathcal{E}}_A$ and $\bar{\mathcal{E}}_B$ are the stored energies in the dipoles A and B , respectively. Under steady-state conditions,

$$\bar{W}_e = \bar{W}_{\text{diss}}^A + \bar{W}_{\text{diss}}^B + \bar{W}_{\text{diss}}^{\text{sph}} + \hbar K(\omega_i - \omega_f)(N_B/N). \quad (27)$$

The effects of the substrate on fluorescence are obtained through the determination of both the lifetime of the molecule (in relaxation experiments) and the intensity of emission (in steady-state experiments). If \mathcal{E} is the energy gain or loss in any process, the probability of that process occurring is given by $\mathcal{E}/\hbar\omega$, where $\hbar\omega$ is the photon energy involved in the process. Therefore, the time evolution of the level populations (rate equations) is written as:¹⁰

$$\frac{dN_A}{dt} = N_0 \frac{\bar{W}_{\text{abs}}^A}{\hbar\omega_i} - N_A \frac{\bar{W}_{\text{diss}}^A}{\hbar\omega_i} - N_A \frac{\bar{W}_{\text{sc}}^A}{\hbar\omega_i} - K_f N_A, \quad (28)$$

$$\frac{dN_B}{dt} = K_f N_A - N_B \frac{\bar{W}_{\text{diss}}^B}{\hbar\omega_f} - N_B \frac{\bar{W}_{\text{sc}}^B}{\hbar\omega_f}, \quad (29)$$

$$\frac{dN_0}{dt} = -N_0 \frac{\bar{W}_{\text{abs}}^A}{\hbar\omega_i} + N_A \left(\frac{\bar{W}_{\text{diss}}^A + \bar{W}_{\text{sc}}^A}{\hbar\omega_i} \right) + N_B \left(\frac{\bar{W}_{\text{diss}}^B + \bar{W}_{\text{sc}}^B}{\hbar\omega_f} \right), \quad (30)$$

where, K has been replaced by K_f for fluorescence. These equations are subject to the constraint that N remains constant and superscripts A and B refer to the dipoles A and B , respectively. At steady state the level populations are obtained as

$$\frac{N_A}{N} = \bar{W}_{\text{abs}}^A (\bar{W}_{\text{diss}}^B + \bar{W}_{\text{sc}}^B) / [(\bar{W}_{\text{diss}}^B + \bar{W}_{\text{sc}}^B) \times (\bar{W}_{\text{abs}}^A + \bar{W}_{\text{diss}}^A + \bar{W}_{\text{sc}}^A + \hbar\omega_i K_f) + \hbar\omega_f K_f \bar{W}_{\text{abs}}^A], \quad (31)$$

$$\frac{N_B}{N} = \hbar\omega_f K_f \bar{W}_{\text{abs}}^A / [(\bar{W}_{\text{diss}}^B + \bar{W}_{\text{sc}}^B) \times (\bar{W}_{\text{abs}}^A + \bar{W}_{\text{diss}}^A + \bar{W}_{\text{sc}}^A + \hbar\omega_i K_f) + \hbar\omega_f K_f \bar{W}_{\text{abs}}^A]. \quad (32)$$

As usual, the effect of the substrate is determined by computing the absorption-enhancement factor $\mathbf{r}_A = N_A \bar{W}_{\text{sc}}^A / N_A^{(0)} \bar{W}_{\text{sc}}^{A(0)}$ and the fluorescence-enhancement factor $\mathbf{r}_{\text{FL}} = N_B \bar{W}_{\text{sc}}^B / N_B^{(0)} \bar{W}_{\text{sc}}^{B(0)}$, where $\bar{W}_{\text{sc}}^{A(0)}$ and $\bar{W}_{\text{sc}}^{B(0)}$ are the powers scattered by dipoles A and B , respectively, in the absence of the substrate.

For dipole A of moment $\boldsymbol{\mu}_A$, the power absorbed from the incident beam by is given by

$$\bar{W}_{\text{abs}}^A = -\frac{1}{2} \text{Re} \int [(\mathbf{E}_i \times \mathbf{H}_{\boldsymbol{\mu}_A}^*) - (\mathbf{H}_i^* \times \mathbf{E}_{\boldsymbol{\mu}_A})] \cdot \hat{\mathbf{r}} ds. \quad (33)$$

Using plane waves for the incident fields and spherical waves for the dipole fields, we obtain¹¹

$$\bar{W}_{\text{abs}}^A = \frac{\omega_i}{2} \text{Im}\{\boldsymbol{\mu}_A(\omega_i) \cdot \mathbf{E}_i^*(\omega_i)\}, \quad (34)$$

where the dipole is assumed oriented along the incident field direction \hat{n}_0 , and $\boldsymbol{\mu}_A$ is obtained from Eq. (18). The scattered [see Eq. (10)] and dissipated [see Eqs. (4) and (5)] powers are given by

$$\bar{W}_{\text{sc}}^A = \frac{\omega_i^4 |\boldsymbol{\mu}_A|^2}{12\pi\epsilon_0 c^3}, \quad (35)$$

$$\bar{W}_{\text{diss}}^A = \left(\frac{e^2 \omega^2 \tilde{\Gamma}_A \tilde{f}_A}{2m} \right) \frac{|\vec{\mathbf{E}}_i(\mathbf{r}_0, \omega_i)|^2}{(\tilde{\omega}_A^2 - \omega_i^2)^2 + \omega_i^2 \tilde{\Gamma}_A^2}. \quad (36)$$

The determination of \bar{W}_{diss}^B and \bar{W}_{sc}^B , however, does not proceed along the same lines as \bar{W}_{diss}^A and \bar{W}_{sc}^A . Dipole B is driven by the power gained [$K_f N_A \hbar(\omega_i - \omega_f)$] from dipole A , and does not separately obey Drude-Lorentz equation. At steady state, we may write $K_f N_A \hbar(\omega_i - \omega_f) = \bar{W}_{\text{diss}}^B + \bar{W}_{\text{sc}}^B$. We parametrize \bar{W}_{diss}^B to be a mere fraction of \bar{W}_{sc}^B , which is computed from the spontaneous decay rate Γ_{sp}^B , for the transition $|B\rangle \rightarrow |G\rangle$ [see Ref. 4(b)]:

$$\bar{W}_{\text{sc}}^B = \left(\frac{2}{3} \right) \frac{e^2 \hbar f_B \omega_f^3}{m c^3} |1 + R(\omega_f)|^2. \quad (37)$$

As is well known, the increase in the scattering by oscillator B is significant through $R(\omega_f)$, when the emitting frequency matches that of a radiative surface resonance.

IV. NUMERICAL RESULTS

The fluorescing molecule is positioned at a distance H from a spherical silver particle of radius a . The molecular-transition dipoles are assumed perpendicular to the sphere surface and oriented along the z direction. The dielectric constant for the silver sphere is taken from Ref. 12. The parameters in the calculation are the widths Γ_A and Γ_B , oscillator strengths f_A and f_B [$f_{A,B} = 2m\omega_{A,B} |\vec{\boldsymbol{\mu}}_{A,B}|^2 / e^2 \hbar$, where e and m are the electron charge and mass, respectively, and $\omega_{A,B} = (E_{A,B} - E_G)/\hbar$], and the rate K_f for the radiationless transition $|A\rangle \rightarrow |B\rangle$. We assume throughout that $\omega_i = \omega_A$ and $\omega_f = \omega_B$.

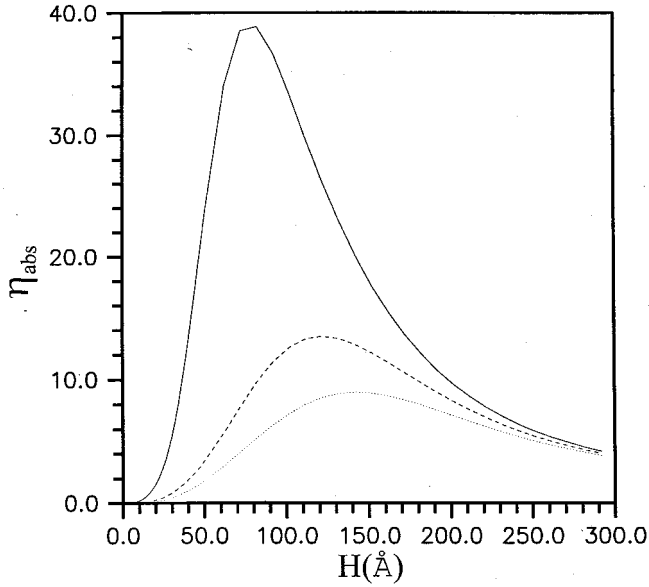


FIG. 2. The enhancement factor for the rate of absorption $\eta_{\text{abs}} = \bar{W}_{\text{abs}}^A / \bar{W}_{\text{abs}}^{A(0)}$ as a function of the molecule-surface distance H for various values of the parameter K_f . The basic parameter set is used in computations. For the dotted curve (\cdots) $K_f = 10^8 \text{ s}^{-1}$, for the dashed curve ($---$) $K_f = 10^9 \text{ s}^{-1}$, and for the solid curve ($---$) $K_f = 10^{10} \text{ s}^{-1}$.

In most of the computations we use the following basic parameter set: $a = 200 \text{ \AA}$, $f_A = f_B = 0.1$, $\omega_A = 3.48 \text{ eV}$, $\omega_B = \omega_f = 3.45 \text{ eV}$, $\Gamma_A = \Gamma_B = 10^9 \text{ s}^{-1}$, $K_f = 10^{10} \text{ s}^{-1}$, and an incident laser power of 10^6 W/m^2 . Parameters whose values differ from those given in the basic set are mentioned separately. The total number of molecules N is obtained by assuming monolayer coverage ($10^{-1} \text{ molecules/\AA}^2$).

It is well known that, for silver, $R(\omega)$ has a resonance at a frequency of 3.48 eV and $G(\omega)$ has an infinite number of resonances with frequencies given by $\varepsilon(\omega) = -(n+1)/n$, whose relative importance depends on the molecule-sphere separation.^{1(a),1(b)} While absorption by dipole A and, consequently, fluorescence emission by dipole B , are increased due to enhanced local field and excitation of surface electromagnetic resonances, both processes are mitigated by energy transfer from the molecule to surface excitations such as plasmons,⁸ electron-hole pairs, or phonons.¹³ Additionally, the polarization of the substrate by the excited molecule causes fluorescence enhancement, which is particularly strong if the emission frequency matches that of a radiative surface resonance.^{1,6}

The absorption-enhancement factor, $\eta_{\text{abs}} \equiv \bar{W}_{\text{abs}}^A / \bar{W}_{\text{abs}}^{A(0)}$, as a function of the molecule-surface distance H for various values of K_f , is shown in Fig. 2. For a typical molecule (basic parameter set), $\eta_{\text{abs}} \approx 40$ at $H \approx 80 \text{ \AA}$. This is in reasonable agreement with previous surface-fluorescence studies.^{4(b)} The ratio falls off in both directions with varying H , as expected, and converges to 1 at a large distance, where surface effects become negligible. The peak enhancement increases and shifts toward smaller H with increasing K_f , an indication that the transition $|A\rangle \rightarrow |B\rangle$ competes more suc-

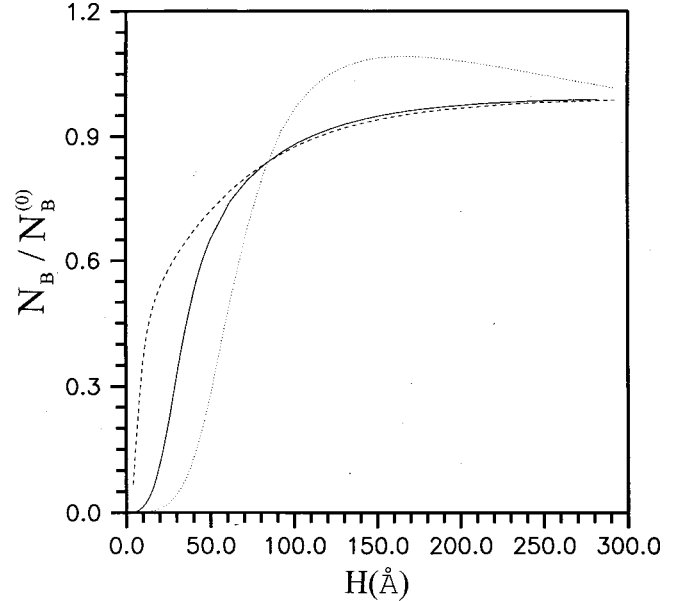


FIG. 3. The population enhancement factor $N_B/N_B^{(0)}$ for oscillator B as a function of molecule-surface distance H for various incident power levels P . The basic parameter set is used. For the dotted curve (\cdots) $P = 10^4 \text{ W/m}^2$, for the solid curve ($---$) $P = 10^6 \text{ W/m}^2$, and for the dashed curve ($---$) $P = 10^8 \text{ W/m}^2$.

cessfully with the quenching of $|A\rangle$ at closer molecule-surface separations.

The population-enhancement ratios $N_A/N_A^{(0)}$ and $N_B/N_B^{(0)}$ are expected to depend on incident power. At higher incident-power levels one expects state $|B\rangle$ to be heavily populated and thus give rise to strong fluorescence emission. At the same time, at large distances from the surface, the surface effects on the rate of emission from $|B\rangle$ through the coupling of oscillator B to the particle may not be able to keep pace with the high rate of population transfer from $|A\rangle$. This would lead to population buildup in state $|B\rangle$. This is shown in Fig. 3, where $N_B/N_B^{(0)}$ is plotted as a function of H for various incident-power levels P . It is seen that for high power levels the ratio $N_B/N_B^{(0)}$ does not show the usual fall off at large distances, rather there is a gradual convergence toward 1 as H increases.

We show the channeling of energy through the three-level system in the presence of the surface by plotting the powers absorbed (\bar{W}_{abs}^A) and scattered (\bar{W}_{sc}^A) by oscillator A and the power scattered (\bar{W}_{sc}^B) by oscillator B as functions of H in Fig. 4. \bar{W}_{abs}^A ($---$) and \bar{W}_{sc}^A ($---$) exhibit familiar behavior. Closer to the substrate particle energy transfer from the molecule to the surface excitations dominates and the result is a quenching of absorption near the surface. With increasing H , the fall off is due to negligible radiative-resonance effects. Dipole B , however, is not coupled to the incident radiation. \bar{W}_{sc}^B is determined from the spontaneous-emission rate Γ_{sp}^B of state $|B\rangle$ and depends on $|1 + R(\omega_f)|^2$, which is large when the emission frequency resonates with a radiative electromagnetic resonance of the sphere. Even if $(\omega_i - \omega_f)$ is much smaller than the width of the electromagnetic resonance, one would expect significant increase in fluorescence emission

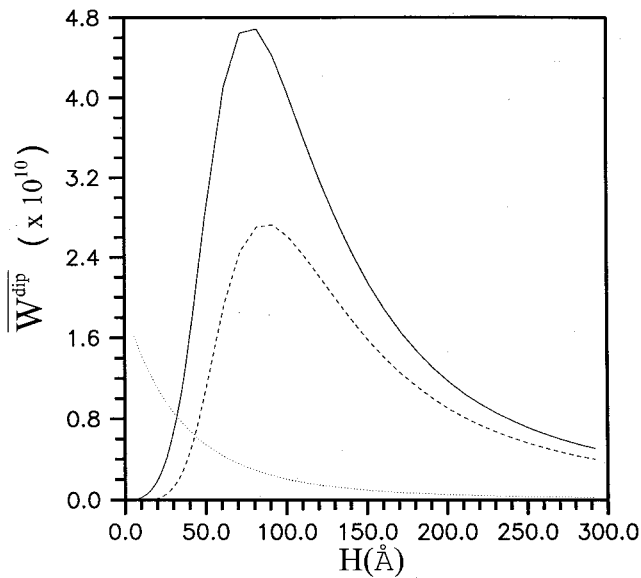


FIG. 4. The absolute absorbed and scattered powers of oscillator A [\bar{W}_{abs}^A (—) and $10^3 \times \bar{W}_{\text{sc}}^A$ (---)] and the absolute scattered power from oscillator B [\bar{W}_{sc}^B (· · ·)] versus distance H from the surface. The basic parameter set is used for all curves. Note that \bar{W}_{sc}^A (---) is scaled up by a factor of 10^3 .

near the surface. So, close to the surface, \bar{W}_{sc}^B (· · ·) is large and falls off gradually as distance increases. The high rate of population transfer K_f from $|A\rangle$ to $|B\rangle$ also helps in increasing \bar{W}_{sc}^B while keeping \bar{W}_{sc}^A low.

The enhancement factor, $r_A = N_A \bar{W}_{\text{sc}}^A / N_A^{(0)} \bar{W}_{\text{sc}}^{A(0)}$, for emission by oscillator A is plotted in Fig. 5 as a function of H for various values of the parameter K_f . The curves refer to the same situation as in Fig. 2. For $K_f = 10^{10} \text{ s}^{-1}$ the peak

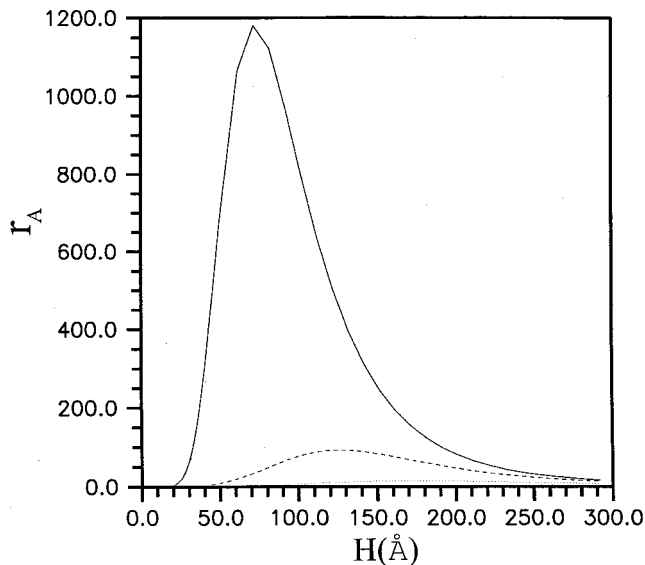


FIG. 5. The enhancement factor r_A for emission by oscillator A as a function of molecule-surface distance H for various values of the parameter K_f . The basic parameter set is used and the curves are for the same values of K_f as in Fig. 2.

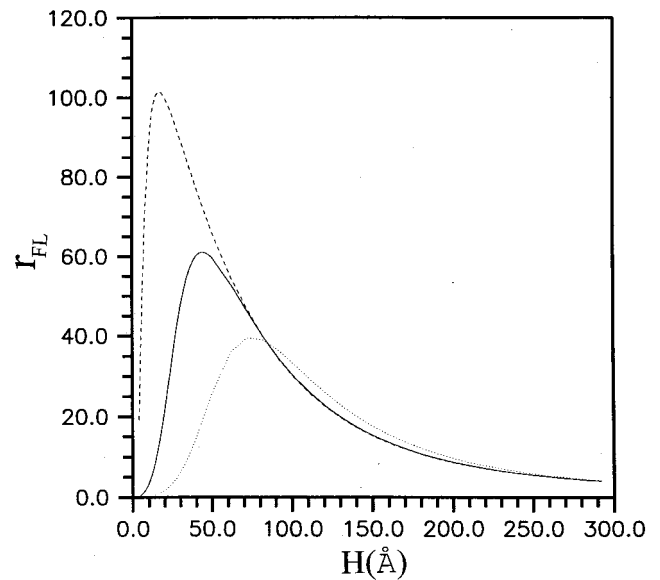


FIG. 6. The fluorescence enhancement factor r_{FL} as a function of distance H for various incident powers. The basic parameter set is used and the curves are for the same incident powers as in Fig. 3.

emission-enhancement factor is about 1200 at about 70 Å from the surface. Also, we note that for greater K_f the enhancement ratio is larger. The rate K_f is unaffected by the presence of the surface. Thus, even though there is a decrease in the population of $|A\rangle$ and consequently of \bar{W}_{sc}^A with increasing K_f , the decrease is even greater in the absence of the surface. This is why the emission-enhancement factor of oscillator A is larger for larger values of K_f . The fluorescence-enhancement factor $r_{FL} = N_B \bar{W}_{\text{sc}}^B / N_B^{(0)} \bar{W}_{\text{sc}}^{B(0)}$ is given in Fig. 6 for various incident-power levels. The curves are for the same situation as in Fig. 3. As expected, this graph exhibits a peak enhancement factor of about 40 at a molecule-surface separation of about 70 Å for an incident power of $P = 10^4 \text{ W/m}^2$ (· · ·). Increase in the incident-power level increases absorption and hence fluorescence, as shown. The shift in the peak enhancement value with increasing incident power indicates that closer to the surface the nonradiative energy transfer from the molecule to the surface cannot be as effective as it would at lower incident-power levels. However, it should be remembered that higher power levels may give rise to nonlinear effects and, therefore, are not desired for linear spectroscopic investigations.

In conclusion, we have considered energy flow as a means of gaining insight into the spectroscopic properties of an irradiated molecule-sphere system. Although the effects of a surface on spectroscopic properties of adsorbed molecules have been studied extensively, in this paper we present yet another viewpoint to the local electromagnetic nature of the problem through a detailed calculation of enhancement factors using energy balance. Starting from an energy-balance equation we have derived expressions for the absorbed and scattered powers of a molecule adsorbed on a small metal particle. These results are then utilized to determine the enhancement factor for fluorescence by considering the time evolution of population in a three-level molecule. Quantities

not strictly obtainable from the energy-balance equation are determined either by extending the dipole-only results to the coupled dipole-sphere system or are introduced to confirm to energy conservation. In spite of the fact that radiation from

the dipole (oscillator A or B) is not strictly determined from energy balance, there is reasonable agreement between our results and those obtained previously from a semiclassical density-matrix treatment of the problem.^{4(b)}

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