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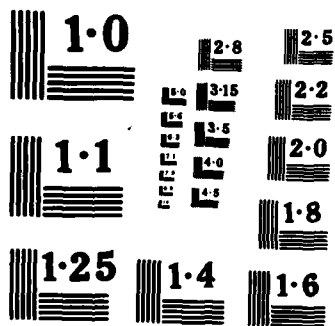
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THE ENHANCEMENT OF MOLECULAR FLUORESCENCE AND
PHOTOCHEMISTRY BY SMALL METAL PARTICLES

by

P. Das and H. Metiu

University of California
Department of Chemistry
Santa Barbara, CA 93106

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The Enhancement of Molecular Fluorescence and Photochemistry by Small Metal Particles

Purna Das and Horia Metiu

Department of Chemistry
University of California
Santa Barbara, California 93106

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ABSTRACT

We examine a quantum mechanical model for the enhancement
of fluorescence yield and photochemical rates by the presence of
small particle capable to sustain electromagentic resonances.
The sphere lowers the absorption and emission efficiency by
taking energy from the molecule and storing it into nonradiative
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studies how the interplay of these effects modifies fluorescence
intensity and the rate of photo-chemical reactions.

I.   INTRODUCTION

The spectroscopy and the relaxation dynamics of vibrational and electronic excitations of molecules and atoms adsorbed on metal surfaces have received a great deal of attention lately since they are involved in many surface processes such as surface photochemistry[1-4], surface photoemission[5], surface enhanced Raman scattering (SERS),[6,7] and photoluminescence.[8-10] In the present article we examine molecular fluorescence and photochemistry in the presence of a surface.

Qualitatively these phenomena are fairly well understood.[7a] In all surface enhanced processes the local field acting on the molecule is increased by reflection of the incident radiation. This increase is substantial if surface curvature is large,[11] if the incident light excites surface electromagnetic resonances,[11-16] or if solid particles are used to polarize each other.[17] This local field enhancement increases the rate of photochemical processes and the intensity of adsorbate fluorescence. The presence of the surface however causes energy transfer from the molecule to surface excitations, such as plasmons,[18-19] electron-hole pairs or phonons.[20-21] This results in a decrease of the excited population which causes a decrease of the photo-chemical rate. The total rate is established through the competition of these opposing effects.

In the case of fluorescence an additional complication arises because the excited molecule polarizes the surface[7a,8,9,18,19] and this emits at the molecular frequency, thus enhancing the emission intensity. This enhancement is particularly strong if the emission frequency matches that of a radiative surface resonance.

Recently several theoretical models[2,14-16,22-23] predicting and/or explaining observed fluorescence[8-10] and photochemistry[24]

of adsorbates have appeared in the literature.

Our purpose in this article is twofold: to provide a more
systematic derivation of the quantum mechanical behavior of the
molecule-sphere system, and to carry out a more extensive
numerical study of fluorescence and photochemical rates.
Previous work included surface effects in an intuitive manner by
replacing the oscillator strength and width appearing in the
quantum theory for an isolated molecule with surface dependent
expressions suggested by the classical theory. The intuitive
arguments are quite reasonable, but we prefer to derive the rate
equations by using a detailed quantum model. Our results confirm
those of previous work.

The theory uses a small (Rayleigh limit) sphere as a model
of the surface. This can be experimentally realized in colloidal
systems[25] or by preparing matrix isolated metal spheres.[26-27] To
some extent a small sphere is a crude model of a rough surface;
however such extrapolations must be made with care since all the
effects mentioned above could depend strongly on the shape of the
surface.[11-16,28]

II.   THE MODEL

We develop a quantum mechanical model for the steady state
fluorescence or photochemistry of molecules adsorbed on a metal
substrate. The system we have in mind consists of a small
metallic particle or a rough metal surface covered with
adsorbates and irradiated with an external light source. We are
concerned with the influence of the substrate on photochemistry
of adsorbates. To this end we consider the incoherent light
scattering from a molecule, idealized as a three level system,
adsorbed on a dielectric substrate.

II.1   The Three-Level System

The schematic diagram of the adsorbate-substrate system is
shown in Fig. 1. State |I> is the initial state (ground
electronic level) and the states |II> and |III> are excited
electronic states. These are molecular states "dressed" by the
presence of the substrate.

State |II> is populated by absorption of energy from the
light source. This is accompanied by a radiationless relaxation
to state |III> and radiative relaxations to state |I>. If state
|III> is a dissociative continuum the molecule undergoes
photochemical decomposition. If |III> is a bound, discrete
electronic level it can decay radiatively to the ground state
|I>. The presence of the surface modifies the transition |I> →
|II> and |II> → |III> but leaves |II> → |III> unchanged. The
latter assumption excludes the chemical effects of the surface
and it might be inaccurate for molecules chemisorbed at the
surface. This is not a serious limitation here since we are
concerned with long range electromagnetic effects taking place
many A away from the surface.

II.2 Absorbing System: Spontaneous Emission

We consider the interaction of the external radiation with the molecule (only absorbing system $|I> \leftrightarrow |II>$ is considered) to determine the rate of absorption and the induced molecular dipole. The latter must be determined by a self consistent procedure which includes self-polarization caused by the fact that the induced dipole polarizes the surface and interacts with that polarization field.

The incident field $\vec{E}_o(\omega,t)$ is reflected by the surface and this produces a new field denoted here $\overleftrightarrow{R}(\omega,t)\cdot\vec{E}_o(t,\omega)$[14], and called the reflection field. A large number of formulae for the reflection tensor $\overleftrightarrow{R}(\omega)$ for various surface geometries are given in Reference 7a. The molecular dipole induced by $\vec{E}_o(\omega,t)$ polarizes the surface and the polarization field at the point where the molecule is located is denoted[7a,14]

$$\overleftrightarrow{G}(\omega,t) \cdot <\vec{\mu}(t,\omega)> \qquad .$$

$\overleftrightarrow{G}(\omega,t)$ is called here the image tensor and

$$<\vec{\mu}(t,\omega)> \equiv \frac{1}{2} [\vec{\mu}_-(\omega)e^{-i\omega t} + c.c.] \qquad (II.1)$$

is the expectation value of the induced molecular dipole. To calculate the induced dipole self-consistently we include the field $\overleftrightarrow{G}(\omega,t)\cdot<\vec{\mu}(t,\omega)>$ in the expression of the local field

$$\vec{E}_1(\omega,t) = \frac{1}{2} [(\overleftrightarrow{I} + \overleftrightarrow{R}(\omega))\cdot\vec{E}_o(\omega)$$

$$+ \overleftrightarrow{G}(\omega) \cdot <\vec{\mu}_-(\omega)>]e^{-i\omega t} + c.c. \qquad , \qquad (II.2)$$

which is responsible for the polarization of the molecule. In this expression $\overleftrightarrow{I}$ is the unit tensor. The Hamiltonian therefore contains a term of the form

$$V_I(t) = (i \sum_{\vec{k}} (\frac{2\pi\hbar\omega_{\vec{k}}}{V})^{\frac{1}{2}} [|2><1|\vec{\mu}_{21} \cdot (\overleftrightarrow{I} + \overleftrightarrow{R}(\omega_{\vec{k}})) \cdot \vec{\epsilon}_{\vec{k}} a_{\vec{k}} e^{-i(\omega_{\vec{k}} - \omega_{21})t}$$

$$-|1><2|\vec{\mu}_{12} \cdot (\overleftrightarrow{I} + \overleftrightarrow{R}^*(\omega_{\vec{k}})) \cdot \vec{\epsilon}_{\vec{k}}^* a_{\vec{k}}^+ e^{i(\omega_{\vec{k}} - \omega_{21})t}]$$

$$- \frac{1}{2}[|2><1|\vec{\mu}_{21} \cdot \overleftrightarrow{G}(\omega) \cdot <\vec{\mu}_-(\omega)> e^{-i(\omega-\omega_{21})t} + c.c.]\} \quad , \quad (II.3)$$

where V is the volume of the cavity used for field quantization;
the sum is carried over all the photon modes in the cavity; $a_{\vec{k}}$ is
the annihilation operator for a photon of frequency $\omega_{\vec{k}}$ and
polarization denoted by σ; $\vec{\epsilon}_{\vec{k}}$ is the unit polarization vector.
$\vec{\mu}_{ji}$ is the transition dipole moment corresponding to a molecular
transition $|i> \rightarrow |j>$, and $\omega_{ji} \equiv (E_j - E_i)/\hbar$. In writing $V_I(t)$ (see
Equation II.3), which is the molecule field coupling in the
interaction representation, we use the rotating wave
approximation which neglects small, non-linear terms. The image
field has been treated semi-classically while the incident and
the reflected fields are quantized. The quantization is needed
only to make sure that spontaneous emission is treated properly;
other quantum electrodynamic effects, are not expected to play a
role in surface spectroscopy where working at intensities where
the statistical properties of the photon become important is not
practical. The "image" term was treated semiclassically for
convenience, since otherwise we would have to quantize the
electrons and phonons in the solid to get the correct expression
for the manner in which the polarized solid renormalizes the
photon field.[21] Note that in treating the semiclassical term we
must disregard the photon states in the wave function. Thus in
dealing with the quantized field we have $|I> = |1>|n_k+1>$ and $|II>$
$= |2>|n_k>$ where $|1>$ and $|2>$ are the molecular wave functions and
$|n_k+1>$ and $|n_k>$ are field wave functions in the occupation number
representation (a coherent state would be more adequate in
describing laser radiation). However, in dealing with the

semiclassical term $|I\rangle = |1\rangle$ and $|II\rangle = |2\rangle$.

The equations of motion for the matrix elements of the density operator[29] are

$$\dot{\rho}_{ii}(t) = -\frac{i}{\hbar}\langle i|[V(t),\rho(t)]|i\rangle + \sum_{n\neq i} W_{in}\rho_{nn} , \qquad (II.4)$$

$$\dot{\rho}_{ij}(t) = (-i\omega_{ij}-\Gamma_{ij})\rho_{ij}(t) - \frac{i}{\hbar}\langle i|[V(t),\rho(t)]|j\rangle, \quad i \neq j \qquad (II.5)$$

where $\{|i\rangle, |j\rangle\} \equiv \{|I\rangle, |II\rangle\}$. $V(t)$ is the interaction potential given by (II.3), but taken in Schrodinger representation; Γ_{ij} is a phenomenological parameter, that characterizes depopulation induced by interaction with the medium. In the interaction representation, Eqs. (II.4)-(II.5) can be written as

$$\rho^I_{21}(t) = \rho^I_{21}(\omega)e^{-i(\omega-\omega_{21})t} , \qquad (II.6a)$$

$$\rho^I_{12}(t) = \rho^I_{21}(t)^* . \qquad (II.6b)$$

Since $\langle\vec{\mu}(t)\rangle = Tr(\vec{\mu}\rho(t))$, the induced dipole $\langle\vec{\mu}(t)\rangle$ depends on itself through $\rho(t)$. However, Eqs. (II.5), (II.6) and (II.3) can be solved to obtain self-consistent expressions for $\rho_{21}(\omega)$ and $\langle\vec{\mu}_{\pm}(\omega)\rangle$:

$$\rho_{21}(\omega) = \frac{i}{\hbar}(\rho_{11}-\rho_{22})\frac{(2\pi\hbar\omega/V)^{1/2}\sqrt{n+1}}{(\omega-\omega_{21}+i\Gamma_{21})} [\vec{\mu}_{21}\cdot(\overleftrightarrow{I}+\overleftrightarrow{R}(\omega))\cdot\hat{\epsilon}] .$$

$$(1 - \frac{(\rho_{11}-\rho_{22})}{\hbar} \vec{\mu}_{21}\cdot\overleftrightarrow{G}(\omega) . \qquad (II.7a)$$

$$[\overleftrightarrow{I}(\omega-\omega_{21}+i\Gamma_{21}) + \frac{(\rho_{11}-\rho_{22})}{\hbar} \vec{\mu}_{12}\vec{\mu}_{21}\cdot\overleftrightarrow{G}(\omega)]^{-1}\cdot\vec{\mu}_{12}\} ;$$

$$\rho_{21}(t) = \rho_{21}(\omega)e^{-i\omega t}; \; \rho_{12}(t) = \rho_{21}^*(t) \; ; \qquad (II.7b)$$

$$\langle\vec{\mu}_-(\omega)\rangle = \frac{2i}{\hbar} (\rho_{11}-\rho_{22}) (\frac{2\pi\hbar\omega}{V})^{1/2} \sqrt{n+1} \; [\vec{\mu}_{21}\cdot(\overleftrightarrow{I}+\overleftrightarrow{R}(\omega))\cdot\hat{\epsilon}]$$

$$(II.8a)$$

$$[\overleftrightarrow{I}(\omega-\omega_{21}+i\Gamma_{21}) + \frac{(\rho_{11}-\rho_{22})}{\hbar} \vec{\mu}_{12}\vec{\mu}_{21}\cdot\vec{G}(\omega)]^{-1}\cdot\vec{\mu}_{12} \; ;$$

and

$$\langle\vec{\mu}_+(\omega)\rangle = \langle\vec{\mu}_-(\omega)\rangle^* \; . \qquad (II.8b)$$

In these expressions the intensity of the light source appears through the factor n+1, where n is the photon occupation number of the incident field, which is given by

$$n+1 = V|\vec{E}_o|^2(8\pi\hbar\omega)^{-1} \; . \qquad (II.8c)$$

The term $\overrightarrow{R}(\omega)$ is particularly large if the light excites a radiative electromagnetic resonance of the surface. The polarization of the surface by the <u>induced molecular dipole</u> appears through $\overrightarrow{G}(\omega)$. This quantity acts as a molecular self-energy[21,30a] since, by polarizing the surface and interacting with the polarization charge, the molecule polarizes itself. As in any other areas of many body theory the self-energy shifts and broadens the original state. Note that even though we treated the sphere by classical electrodynamics the structure of the theory is the same as the one obtained by a full quantum treatment of the electrons in the sphere and the two level system. The numerical values of the self-energy are however different; a full quantum theory for the sphere introduces non-local electromagnetic effects, which are important at small (i.e. about 5Å[30]) distances. A detailed comparison between local and non-local theories can be found in Ref. 30b. Throughout this paper we use for $\overrightarrow{G}(\omega)$ a local theory. In this theory $\overrightarrow{G}(\omega)$ is

enhanced whenever the dipole couples to the <u>radiative or the non-radiative</u> resonances of the surface. Note that if $\vec{G} = \vec{R} = 0$ the expressions derived above reduce to those for a two level system in the absence of the sphere. The width Γ_{21} contains the dephasing and/or the depopulation caused by intramolecular and/or radiative transitions and the interaction with the medium.

It is interesting to note that the term

$$\{(\omega - \omega_{21} + i\Gamma_{21}) \overset{\leftrightarrow}{I} + ((\rho_{11} - \rho_{22})/\hbar)\vec{\mu}_{12}\vec{\mu}_{21} \cdot \overset{\leftrightarrow}{G}(\omega)\}^{-1}$$

is a 3 x 3 tensor since the symbol

$\vec{\mu}_{12}\vec{\mu}_{21} \cdot \overset{\leftrightarrow}{G}(\omega)$ is a 3 x 3 tensor whose xy component is

$$(\mu_{12})_x[(\mu_{21})_x G_{xy} + (\mu_{21})_y G_{xy} + (\mu_{21})_z G_{zy}] \ .$$

This is introduced in the theory by the presence of the image field in the self-consistent calculation of $\langle\vec{\mu}\rangle$ and ρ_{21}. The tensorial character of this quantity does not mean that the life-time is tensor. If one performs all the tensor inversion and multiplication operations required in (II.7a) the consequence of this formula is that the life-time depends on the orientation of the transition dipole with respect to the surface. In particular, parallel and perpendicular dipoles have different life-times. Since the life-time depends on the rate of energy transfer from the dipole to the surface, the existence of the above effect in the theory is reasonable.

The induced dipole $\langle\vec{\mu}_-(\omega)\rangle$ and the off-diagonal element ρ_{21} depend on the population difference $(\rho_{11} - \rho_{22})$. When the populations of the ground and excited states become equal, the induced dipole moment of the molecule vanishes and so does the surface induced broadening and frequency shift. This is the well known saturation effect caused by intense radiation. If the

external field is weak enough, we can approximate $(\rho_{11}-\rho_{22}) \simeq$ $(\rho_{11}^{o} - \rho_{22}^{o})$ where $\rho_{11}^{o} \simeq 1$ and $\rho_{22}^{o} \simeq 0$ are thermal equilibrium values of the populations. We shall not resort to this approximation since the strength of the surface enhanced local field can be large for certain choices of parameters.

The above calculations provide us with self-consistent expressions for $<\mu>$ and ρ_{12}. To compute the rate of change of population we take the external field to be $[\vec{\vec{I}} + \vec{\vec{R}}(\omega)]\cdot\vec{E}_{o}(\omega)$. This expression does not contain the field $\vec{\vec{G}}\cdot<\vec{\mu}>$ since the latter is already included, by the use of the self-consistent procedure, in the self-energy of the two level system. Using the expression of $V_I(t)$, modified as indicated above, and Eqs. (II.4) and (II.7) we obtain

$$[\dot{\rho}_{22}(t)]_{rad} = (n+1)(4\pi\omega/\hbar V)(\rho_{11}-\rho_{22})\ |\vec{\mu}_{21}\cdot(\vec{\vec{I}}+\vec{\vec{R}}(\omega))\cdot\bar{\epsilon}|^{2}$$

$$[(1-\hbar^{-1}\vec{\mu}_{21}\cdot\vec{\vec{G}}(\omega)\cdot(\vec{\vec{I}}(\omega-\omega_{21}+i\Gamma_{21}) \qquad (II.9)$$

$$+ \hbar^{-1}\vec{\mu}_{12}\vec{\mu}_{21}\cdot\vec{\vec{G}}(\omega))^{-1}\cdot\vec{\mu}_{12})\ (\omega-\omega_{21}+i\Gamma_{21})^{-1}]$$

and $\dot{\rho}_{11}(t) = -\dot{\rho}_{22}(t)$. Eq. (II.9) gives the the rate of change of the population of state $|II>$ by the emission of a photon of frequency ω, polarization $\bar{\epsilon}$ and wave-vector $\vec{k}$. In addition to radiative contributions to $\rho_{22}(t)$ there will be non-radiative decay channels which are not included in Eq. (II.9).

Although not necessary in principle, we shall make certain simplifications in the mathematics assuming that both the induced dipole and the incident field have the form $\vec{\mu} = \mu\ \bar{z}$ and $\vec{E}_{o} = E_{o}\ \bar{z}$, where $\bar{z}$ is the unit vector along the z axis. Then the image-field due to the dipole induced in the surface, at the location of the dipole, picks up only the z-component of the induced dipole. So only $G_{zz}(\omega) \equiv G(\omega)$ is non-zero.

Thus we can rewrite the equations derived here as

$$\rho_{21}(\omega) = \frac{1}{\hbar} \left(\frac{2\pi\hbar\omega}{V}\right)^{1/2} \sqrt{n+1} \; [\vec{\mu}_{21} \cdot (\overleftrightarrow{I} + \overleftrightarrow{R}(\omega)) \cdot \hat{\epsilon}]$$

$$(\rho_{11} - \rho_{22})/(\omega - \omega_{21} + \gamma_{21}) \quad , \tag{II.10}$$

$$\langle \vec{\mu}_-(\omega) \rangle = \frac{2i}{\hbar} (\rho_{11} - \rho_{22}) \left(\frac{2\pi\hbar\omega}{V}\right)^{1/2} \sqrt{n+1}$$

$$(\vec{\mu}_{21} \cdot (\overleftrightarrow{I} + \overleftrightarrow{R}(\omega)) \cdot \hat{\epsilon}) \; \vec{\mu}_{12}/(\omega - \omega_{21} + i\gamma_{21}) \quad , \tag{II.11}$$

and

$$\left[\dot{\rho}_{22}(t)\right]_{rad} = \Gamma_{sa}\rho_{11} - (\Gamma_{se} + \Gamma_{sp}^{(2)})\rho_{22} \quad . \tag{II.12}$$

where

$$\gamma_{21}(\omega) \equiv \Gamma_{21} - \frac{1}{\hbar} (\rho_{11} - \rho_{22}) |\vec{\mu}_{21}|^2 [\text{Re} G(\omega) + i\,\text{Im} G(\omega)] \quad , \tag{II.13}$$

Γ_{sa} and Γ_{se} are the stimulated absorption and emission rates for the transition $|I\rangle \leftrightarrow |II\rangle$, and $\Gamma_{sp}^{(2)}$ is the corresponding spontaneous photon emission rate. The explicit expressions for various rates of absorption and emission are obtained by inspection of Eq. (II.9):

$$\Gamma_{sa} = \Gamma_{sp}^{(2)}(n+1) \quad , \tag{II.14}$$

$$\Gamma_{se} = \Gamma_{sp}^{(2)} n \quad , \tag{II.15}$$

$$\Gamma_{sp}^{(2)} = \left(\frac{4\pi\omega}{\hbar V}\right) \frac{|\vec{\mu}_{21} \cdot (\overleftrightarrow{I} + \overleftrightarrow{R}(\omega)) \cdot \hat{\epsilon}|^2 \; \gamma_{21}'(\omega)}{[(\omega - \omega_{21} - \gamma_{21}''(\omega))^2 + \gamma_{21}'(\omega)^2]} \quad , \tag{II.16}$$

where

$$\gamma_{21}(\omega) \equiv \gamma_{21}'(\omega) + i\gamma_{21}''(\omega) \quad , \tag{II.17}$$

and $\gamma_{21}'(\omega)$ and $\gamma_{21}''(\omega)$ are real. For large n, $\Gamma_{sa} \simeq \Gamma_{se}$ as expected. They depend on the incident laser intensity through the relation $n = V|\vec{E}_o|^2/8\pi\hbar\omega$.

The total spontaneous emission rate is obtained by summing Eq. (II.16) over all wave vectors $\vec{k}$ and polarizations σ. Using the fact that the number of modes per unit frequency interval and per unit solid angle is (for a given polarization)

$$\frac{d^2No}{d\omega d\Omega} = \frac{V\omega^2}{(2\pi)^3 c^3} .$$

(II.19)

we obtain the spontaneous emission rate per unit solid angle (about the propagation direction) and per unit frequency range:

$$\frac{d^2\Gamma_{sp}^{(2)}}{d\omega d\Omega} = \frac{2\omega^3}{\pi\hbar c^3} \frac{|\vec{\mu}_{21}\cdot(\overleftrightarrow{I}+\overleftrightarrow{R}(\omega))\cdot\hat{\epsilon}|^2 \; \gamma'_{21}(\omega)}{[(\omega-\omega_{21}-\gamma''_{21}(\omega))^2+\gamma'_{21}(\omega)^2]} ,$$

(II.20)

In order to get the total spontaneous emission rate $\Gamma_{sp}^{(2)T}$ we integrate the right hand side of Eq. (II.20) with respect to ω and Ω. Approximating, as customary, $\gamma_{21}(\omega)\simeq\gamma_{21}(\omega_{21})$, where ω_{21} is the transition frequency, the total spontaneous emission rate is

$$\Gamma_{sp}^{(2)T} \simeq \frac{4}{\hbar c^3} \; \tilde{\omega}_{21}^3 \; | \; \vec{\mu}_{21}\cdot(\overleftrightarrow{I}+\overleftrightarrow{R}(\tilde{\omega}_{21}))\cdot\hat{\epsilon}|^2$$

(II.21)

where $\tilde{\omega}_{21} \equiv \omega_{21} + \gamma''_{21}(\omega_{21})$; $\gamma''_{21}(\omega)$ is the shift of the upper level due to the presence of the surface. This shift is usually small compared to ω_{21} and hence may be neglected. When γ''_{21} is neglected, the effect of the sphere on the spontaneous emission (within the approximations made here) appears through $\overleftrightarrow{R}(\omega_{21})$ and we recover the usual formula when the sphere is absent:

$$\Gamma_{sp}^{(2)T} = \frac{4}{\hbar c^3} \; \omega_{21}^3 |\vec{\mu}_{21}\cdot\hat{\epsilon}|^2$$

(II.22)

which is identical with Einstein's A-coefficient. A similar inspection of Eq. (II.15) in the absence of the surface and in the limit $\Gamma_{21}\to0$ gives Einstein's B-coefficient[31], implying that the presence of a polarizable object renormalizes the Einstein coefficients via $\tilde{\omega}_{ij}$ and $(\overline{\overleftrightarrow{I}+\overleftrightarrow{R}(\tilde{\omega}_{ij})})$.

II.3 STEADY STATE POPULATION

So far we have focused our attention on the absorbing
system ($|I\rangle \leftrightarrow |II\rangle$) alone and established expressions for the
power absorption by the molecule in the presence of the sphere as
well as the rate of spontaneous emission of photons via the $|II\rangle$
$\rightarrow |I\rangle$ transition. These formulae contain the level populations,
which we now set out to determine. The emitting system consists
of levels $|III\rangle$ and $|I\rangle$ and fluorescence emission takes place via
the spontaneous transition $|III\rangle \rightarrow |I\rangle$. Since the fluorescence
intensity is low we do not include stimulated processes in the
$|III\rangle \leftrightarrow |I\rangle$ transition. The absorbing and emitting systems are
coupled only through the radiationless transition $|II\rangle \rightarrow |III\rangle$.

We denote by Γ_2 and Γ_3 the rates of decay of populations of
levels $|2\rangle$ and $|3\rangle$, respectively, for an isolated molecule
modeled as a three level system. They include both radiative and
nonradiative parts, such that we can write $\Gamma_i = \Gamma_i^{(R)} + \Gamma_i^{(NR)}$ ($i = 2,3$), and treat the full Γ_i as an empirical molecular
parameter of the theory. The presence of the sphere simply
renormalizes these decay rates, by adding to them the surface
induced terms discussed in Section II.1. We therefore denote
their values when the sphere is present by $\tilde{\Gamma}_2$ and $\tilde{\Gamma}_3$. Written
out explicitly these quantities are

$$\tilde{\Gamma}_2 = \Gamma_2 + \frac{2|\vec{\mu}_{21}|^2}{\hbar} (\rho_{11} - \rho_{22}) \, \mathrm{Im}G(\omega) \qquad\qquad (\text{II.31a})$$

$$\tilde{\Gamma}_3 = \Gamma_3 + \frac{2|\vec{\mu}_{31}|^2}{\hbar} (\rho_{11} - \rho_{33}) \, \mathrm{Im}G(\omega') \qquad\qquad (\text{II.31b})$$

where ω is the frequency of the incident laser and ω' that of the
fluorescent emission. Further, let us write $\Gamma_{se} = \Gamma_{sa}$. Then the
equations of motion for the populations are

$$\dot{\rho}_{11} = \Gamma_{se}(\rho_{22}-\rho_{11}) + \tilde{\Gamma}_2\rho_{22} + \tilde{\Gamma}_3\rho_{33} \qquad\qquad \text{(II.32a)}$$

$$\dot{\rho}_{22} = \Gamma_{se}(\rho_{11}-\rho_{22}) - \tilde{\Gamma}_2\rho_{22} - K\rho_{22} \qquad\qquad \text{(II.32b)}$$

$$\dot{\rho}_{33} = K\rho_{22} - \tilde{\Gamma}_3\rho_{33} \qquad\qquad \text{(II.32c)}$$

Steady state solutions for ρ_{ii} ($i = 1,2,3$) are obtained by requiring that $\dot{\rho}_{11} = \dot{\rho}_{22} = \dot{\rho}_{33} = 0$:

$$\rho_{11} = (\Gamma_{se}+K+\tilde{\Gamma}_2)/[K+\tilde{\Gamma}_2+\Gamma_{se}(2+K/\tilde{\Gamma}_3] \qquad\qquad \text{(II.33a)}$$

$$\rho_{22} = \Gamma_{se}\rho_{11}/(\Gamma_{se}+K+\tilde{\Gamma}_2) \qquad\qquad \text{(II.33b)}$$

$$\rho_{33} = (\frac{K}{\tilde{\Gamma}_3})\ \rho_{22} \qquad\qquad \text{(II.33c)}$$

The level populations are dependent on the molecule-surface separation through Γ_{se} and $\tilde{\Gamma}_i$ ($i = 2,3$). These steady state values of the level populations can be used to compute $\gamma_{21}(\omega)$ (Eq. (II.13)).

II.4 ENHANCEMENT OF FLUORESCENCE

The spontaneous radiative decay of state $|III\rangle$ causes a fluorescence signal of frequency ω'. The polarization dipole induced in the sphere by the emitting molecular dipole radiates at the source frequency ω'. Thus the radiation from the system consists of the coherent sum of the radiation for both molecular dipole and the dipole induced in the sphere. However, instead of going through the complications of determining the molecular (emitting) dipole moment at ω', and computing the fluorescence from the classical radiation formula, we write the power emitted by the molecule due to a spontaneous transition $|III\rangle \rightarrow |I\rangle$ as

$$P_{Fl} = N\rho_{33}\, \hbar\omega'\, \Gamma_{sp}^{(3)T} , \qquad (II.34)$$

where N is the total number of molecules in the system and Γ_{sp} is the total rate of decay due to spontaneous emission from state $|III\rangle$, and is given by

$$\Gamma_{sp}^{(3)T} = \frac{4}{\hbar c^3}\, \tilde{\omega}_{31}^3\, |\vec{\mu}_{31}\cdot(\overleftrightarrow{I} + \overleftrightarrow{R}\,(\tilde{\omega}_{31}))\cdot\bar{\epsilon}|^2 \qquad (II.35a)$$

or

$$\Gamma_{sp}^{(3)T} = \frac{4}{3\hbar c^3}\, \omega_{31}^3\, |\vec{\mu}_{31}|^2 |1+R(\omega_{31})|^2 \qquad (II.35b)$$

In writing Eq. (II.35b) we neglected the frequency shift caused by the sphere and averaged over the random orientations of the polarization direction $\bar{\epsilon}$. If we denote the power emitted by isolated molecules by P_{Fl} then the enhancement ratio for fluorescence is

$$R_{Fl} = \frac{P_{Fl}}{P_{Fl}^{(0)}} = |1+R(\omega_{31})|^2 (\rho_{33}/\rho_{33}^{(0)}) \qquad (II.36a)$$

where $\rho_{33}^{(0)}$ is the population of level 3 in the absence of the

sphere. Since $(\rho_{33}/\rho_{33}^{(0)}) = (\rho_{22}/\rho_{22}^{(0)})(\Gamma_3/\tilde{\Gamma}_3)$ we can write

$$R_{F1} = |1+R(\omega)|^2 \; |1+R(\omega_{31})|^2 (\frac{\Gamma_3}{\tilde{\Gamma}_3})(\frac{\gamma_{21}'(\omega)}{\Gamma_{21}})(\frac{[(\omega-\omega_{21})^2+((\Gamma_{21})^2]}{[(\omega-\tilde{\omega}_{21})^2+\gamma_{21}'(\omega)^2]})$$

$$(\frac{K+\Gamma_2+\Gamma_{se}^{(0)}(2+K/\Gamma_3)}{K+\tilde{\Gamma}_2+\Gamma_{se}(2+K/\tilde{\Gamma}_3)}) \qquad\qquad (II.36b)$$

In a resonance situation ($\omega \simeq \omega_{21}$ and $\omega' \simeq \omega_{31}$) we neglect the level shifts and assume $\Gamma_{se} << \Gamma_2^{(R)}$, to obtain

$$R_{F1} \simeq |1+R(\omega)|^2|1+R(\omega')|^2 (\frac{\Gamma_3}{\tilde{\Gamma}_3}) (\frac{\Gamma_{21}}{\gamma_{21}'(\omega)}) [\frac{K+\Gamma_2}{K+\tilde{\Gamma}_2+\Gamma_{se}(2+\frac{K}{\tilde{\Gamma}_3})}] .$$

$$(II.36c)$$

Here $\Gamma_{21} = (\Gamma_2+K)/2$.

Let us now analyse Eqs. (II.36). $|1+R(\omega)|^2$ is strongly enhanced when the incident laser field is in resonance with a radiative (i.e. dipolar) electromagnetic resonance of the sphere. This implies enhanced absorption and consequently enhanced emission. Another source of enhancement of emission is through $|1+R(\omega')|^2$, which is large when the emission frequency is resonating with a radiative electromagnetic resonance of the sphere. If the separation between the excitation and the fluorescence frequency is much smaller than the width of the electromagnetic resonance a double resonance condition can be achieved. On surfaces having more than one electromagnetic resonance (e.g. ellipsoidal particles) one can try to use one resonance for enhancing excitation efficiency and another to enhance emission.

As noted earlier, the enhancement is limited by the broadening of the upper level due to the presence of the

substrate. Due to the bradening of state $|II>$ absorption is decreased as reflected by the factor $(\Gamma_{21}/\gamma_{21}(\omega))$. Similarly, the broadening of state $|III>$ brings in a factor $(\Gamma_3/\tilde{\Gamma}_3)$ which counteracts in part the enhancement caused by $|1+R(\omega')|^2$. The remaining factors are presumably due to the decrease in the transfer of population from $|II>$ to $|III>$. Such qualitative conclusions can be, of course, anticipated on the basis of simple classical models.[7a]

II.5   Photochemical reactions and radiationless transitions for adsorbates

Photochemical reactions and radiationless transitions are very similar processes in which the molecule excited in state |II> undergoes a transition to a continuum or another bound state, respectively. We consider here cases in which the presence of the surface does not affect the transition rate, thus excluding catalytic processes. The surface affects the observed yield by modifying the primary process, i.e. the population of the level |II>.

It is therefore sufficient to consider a two level model with the equation of motion[29]

$$\rho_{11}(t) = -\Gamma_{sa}\rho_{11}(t) + (\Gamma_{se} + \tilde{\Gamma}_2 + K_{pc})\rho_{22} , \qquad \text{(II.37a)}$$

$$\rho_{22}(t) = -\rho_{11}(t) . \qquad \text{(II.37b)}$$

We have assumed that the reagent concentration is high enough for the photochemical reaction to have any effect on the steady state kinetics, so that $\rho_{11} + \rho_{22} = 1$. The steady state solution of Eq. (II.37) yields

$$\rho_{22} = \frac{\Gamma_{se}}{\tilde{\Gamma}_2 + K_{pc} + \Gamma_{se}} , \qquad \text{(II.38a)}$$

$$\dot{\rho}_{11} = (1-\rho_{22}) , \qquad \text{(II.38b)}$$

where $\Gamma_{sa} = \Gamma_{se}$. Since K_{pc} is the number of times a molecule undergoes photochemical reaction per second, the number of molecules decaying per second by photochemical decomposition is given to be $NK_{pc}\rho_{22}$. In units of N, the photochemical rate is

$$r_{pc} = K_{pc}\rho_{22}$$

$$\text{(II.39)}$$

$$= \frac{K_{pc}\Gamma_{se}}{(\tilde{\Gamma}_2 + K_{pc} + 2\Gamma_{se})}$$

The enhancement factor for this rate is the ratio $R_{pc} = r_{pc}/r_{pc}$. Here Γ_{21}, which enters through Γ_{se} and $\tilde{\Gamma}_2$, is $(\Gamma_2 + K_{pc})/2$.

III. NUMERICAL RESULTS

We shall now present numerical results for a molecule
located at a distance d from a spherical Ag particle of radius a.
The dielectric constant of the sphere is taken from Ref. 32. The
molecular parameters are the widths Γ_2 and Γ_3, the oscillator
strengths f_{21} and f_{31} ($f_{ij} = 2m\omega_{ij}|\vec{\mu}_{ij}|^2/e^2\hbar$, e and m are the
electron charge and mass respectively), and the rate K for the
radiationless transition $|II> \rightarrow |III>$ or K_{pc} for photochemical
reaction. Γ_2 and f_{21} correspond to the absorption system ($|I>$
$\longleftrightarrow |II>$) and Γ_3 and f_{31} correspond to the emitting system ($|III>$
$\rightarrow |I>$. Other parameters are the transition frequencies ω_{21}, ω_{31}
and the frequencies ω and ω' of the incident and emitted
radiation respectively. We assume throughout that $\omega = \omega_{21}$ and ω'
$= \omega_{31}$. Our aim is to find the best conditions for the
enhancement of fluorescence or the photochemical decomposition
rates.

In most of the calculations presented here we use the
following values for the parameters: $a = 200$ A, $f_{21} = f_{31} = 0.1$,
$\omega_{21} = 3.48$ eV, $\omega_{31} = 3.46$ eV $= \omega'$, $\Gamma_2 = \Gamma_3 = 10^9$ sec^{-1},
$K = 10^{12}$ sec^{-1} and the incident laser power of 10^3W/m^2. We call
this the basic parameter set and mention explicitly only the
parameters whose value differs from that given in the basic set.

For a small sphere the reflection tensor $R(\omega)$ is

$$R(\omega) = 2a^3(a + d)^{-3}(\epsilon(\omega) - 1)(\epsilon(\omega) + 2)^{-1} \qquad (III.1)$$

Since we assume a transition dipole perpendicular to the surface
and along the z axis only one component of the tensor is needed.

In Fig. (2a) we plot $|R(\omega)|^2$ and $|1+R(\omega)|^2$ as a function of
ω, for several values of d. The curves show that the local field
enhancement factor $|1+R(\omega)|^2$ peaks at frequencies which are

slightly lower than the resonance frequency of the sphere where $|R(\omega)|^2$ peaks).

For a small sphere the image tensor is

$$G(\omega) = \sum_{n=1}^{\infty} (n+1)^2 a^{2n+1} (a+d)^{-(2n+4)} (\epsilon(\omega)-1)[\epsilon(\omega)+(n+1)/n]^{-1}.$$

(III.2)

Since we assume that the transition dipole is perpendicular to the surface and lies along the z axis, no other component of the tensor is needed. While the reflection tensor $R(\omega)$ has a resonance at a frequency given by Re $\epsilon(\omega) = -2$. (For Ag this is at $\omega = 3.49$ eV, if the dielectric constants of Ref. 32 are used), $G(\omega)$ has an infinite number of resonances whose frequencies are given by Re $\epsilon(\omega) = (n+1)/n$. Since the resonant terms are weighted (in Eq. (III.2)) by the factors $(n+1)^2[a/(a+d)]^{2n+1}$, their relative importance depends on the molecule-sphere distance d. If d is very small only the resonance corresponding to very large n can enhance $G(\omega)$;[7] this gives for the resonance frequency Re $\epsilon(\omega) = -1$ which is the condition for a flat surface. Physically this makes sense since if d/a << 1 the surface appears flat to the emitting dipole. At large values of d the dipole field becomes spatially smooth and only the dipolar resonance n = 1 (i.e Re $\epsilon = -2$) is coupled to the dipole. Thus we expect that the line width is resonantly enhanced through $\text{Im}G(\omega)$ at frequencies depending on d. This is illustrated in Fig. 2b where we plot the surface induced line width $\Gamma_{2S} = (e^2 f_{21}/2m\omega_{21})(\rho_{11} - \rho_{22})\text{Im}G(\omega)$ as a function of ω, for several surface-molecule distances. We calculated the steady state values of $\rho_{11} - \rho_{22}$, instead of using, the customary assumption that $\rho_{11} - \rho_{22} \simeq 1$, to test whether the enhancement of the local field causes any build up in ρ_{22}; we find that this is not the case. The calculation was done for the three level system, that is for K $\neq$ 0.

The enhancement factor for the absorption by the transition $|I\rangle \rightarrow |II\rangle$, when the transition $|II\rangle \rightarrow |III\rangle$ is turned on with the rate constant K, is the ratio of the power absorbed in the presence of the sphere P_{abs} ·to the power absorbed when the sphere is absent P^o_{abs} and it is given by

$$R_{abs} = P_{abs}/ P^o_{abs} =$$

$$= (\rho_{11} - \rho_{22}) \frac{|1+R(\omega)|^2 [(\omega-\omega_{21})^2 + ((\Gamma_2+K)/2)^2}{[(\omega-\omega_{21})^2 + \gamma'_{21}(\omega)^2]} \left(\frac{\gamma'_{21}(\omega)}{\Gamma_{21}}\right)$$

$$(III.3)$$

The populations ρ_{11} and ρ_{22} are given by the steady state equations (II.33), while $\gamma'_{21}(\omega)$ is the real part of $\gamma_{21}(\omega)$ given by Eq. (II.13). The enhancement factor R_{F1} for fluorescence is given by Eq. (II.36c). In Fig. 3 we plot R_{abs} and R_{F1} as functions of surface-molecule distance. Curve (a) has Γ_2 and Γ_3 equal to 10^9 sec^{-1} and the rate coefficient K for the $|I\rangle \rightarrow |III\rangle$ transition is $10^{\cdot 1}$ sec^{-1}. Curve (b) has an increased rate $K = 10^{12}$sec^{-1}. Since this increases the fluorescence of the molecule at the surface and that of the molecule in vacuum we do not expect a dramatic increase of the enhancement factor. Some increase is achieved because the rate K of the transition $|II\rangle \rightarrow |III\rangle$ competes more successfully with the surface quenching of the level $|II\rangle$ through $|II\rangle \rightarrow |I\rangle$. Curve (c) shows the effect of increasing Γ_3, which increases the fluorescence rate (the scale for curve (c) is on the right hand side of Fig. 3) and the rate of absorption.

The enhancement of the steady state population ρ_{22} (given in Eq. (II.33)) is shown in Fig. 4, for the same parameters as in Fig. 3. In Fig. 5 we show the relative magnitude of the molecular line width Γ_2 in vacuum with respect to the line width in the presence of the surface, for various values of d and for K $= 10^{12}$ sec^{-1}. Once the ratio equals 1, i.e. once Γ_2 exceeds

substantially the surface induced width, the fluorescence damping by the surface is no longer an important factor; however, the surface still can enhance fluorescence through enhanced absorption ($|I\rangle \to |II\rangle$) and emission ($|III\rangle \to |I\rangle$).

In Fig. 6 we show the dependence of the absorption and fluorescence enhancement factors on the surface-molecule distance for several choices of the absorption and emission frequencies ω and ω', respectively. For all cases, $K = 10^{12}$ sec^{-1} and $\omega = \omega_{21}$ and $\omega' = \omega_{31}$, i.e. the molecule is on resonance with the incident light and the resonance emission is detected. Curve (a) has ω and ω' close to each other and in resonance with the sphere. In curve (b) the emission frequency is off resonance. This diminishes the enhanced emission (i.e. $|1+R(\omega')|^2$) but it also diminishes the rate of quenching of level $|III\rangle$ by the surface; the overall effect is an enhancement of the fluorescence for the smaller values of d. The other curves show the decrease of R_{F1} and R_{abs} as both frequencies are off resonance.

In Fig. 7 we show the enhancement factor R_{pc} for the photochemical rate, (obtained from Eq. (II.39)), for various values of the rate in vacuum K_{pc}. The enhancement of slow rates is fairly marginal at all distances, essentially because surface quenching of state $|II\rangle$ is more efficient than its depletion by the photochemical process. For the curve (c), having the highest value of K_{pc}, the quenching process prevails at low distances d, but is overcome at roughly 20 Å. The reason for this is that the enhancement factor $|1+R(\omega)|^2$ decays with the distance slower than the quenching rate; therefore at some intermediate distance it prevails and yields an enhancement factor of 50.

In Fig. 8 we show the dependence of the photochemical enhancement factor on the incident power, for $K_{pc} = 10^{11}$ sec^{-1} and $I_{inc} = 10^3$, 10^8, and 10^{10} W/m^2. Increased power diminishes the enhancement factor, essentially because in vacuum the process

is proportional to the power. The slight decrease of the enhancement is caused by the fact that the stimulated emission from level |II> is enhanced by the presence of the sphere and this increases the radiative energy loss from level |II>. So while the absolute photochemical rate goes up with power, the enhancement by the sphere goes down. For high powers one must also be concerned with the effects of heating and multiphoton processes.

In concluding we emphasize that we have considered here only the quenching caused by energy transfer, as given by local electrodynamics. The non-local effects[30] are short ranged and are important only at the distances at which the enhancement factors are very low. Therefore, unless one is specifically interested in monolayers or bilayers the non-local effects can be disregarded. Another short range quenching mechanism is the charge transfer from the excited molecule to the metal.[33] This seems to be the predominant mechanism [33] whenever the ionization potential of the excited state exceeds the work function of the surface by less than[34] approximately 1 eV. We have made no attempt to include this effect here.

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FIGURE CAPTIONS

Figure 1.   Schematic diagram of a three level system. ω and ω'
              are the incident and emitted light frequencies,
              respectively. E_1, E_2, and E_3 are the respective
              level energies. Solid vertical lines indicate
              stimulated transitions; dashed vertical lines
              indicate spontaneous (radiative) transitions; the
              wavy line indicates a radiationless transition.

Figure 2(a). $|R(\omega)|^2$ (-.-.-) and $|1+R(\omega)|^2$ (———) as a function
              of frequency ω for various d. The basic parameter
              set is used in computation. Curves a, b, and c are
              for d = 10 Å, 50 Å, and 150 Å respectively.

Figure 2(b). Surface induced width Γ_{2s} as a function of frequency
              for various d. The basic parameter set is used in
              computation. Curves a, b, and c refer to the same
              situation as in Figure 2(a).

Figure 3.   Absorption (---) and fluorescence (——) enhancement
              ratios, R_{abs} and R_{F1}, as functions of distance d
              from the surface. We use the basic parameter set,
              and: (a) K = 10^{11} sec^{-1}; (b) $\omega' = \omega_{31}$ = 3.45 eV; and
              (c) $\Gamma_3 = 10^{10}$ sec^{-1} and ω' as in curve (b). The
              scale for curve c is on the right hand side of the
              graph.

Figure 4.   The ratio of the population of level 2 in the
              presence of the sphere to that in the absence of the
              sphere, as a function of d. We use the parameters of
              curves (a), (b), and (c) of Fig. 3.

Figure 5.   The ratio of the natural width to the surface induced
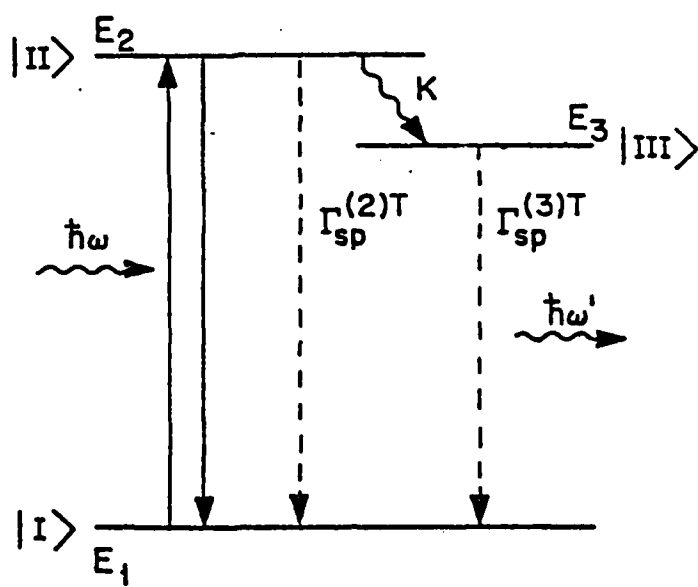   width as a function of the natural width. Here the

basic parameter set, with Γ_2 varying is used. Curves
a, b, and c are for d = 20 Å, 50 Å, and 100 Å,
respectively.

Figure 6.   Absorption (----) and fluorescence (——) enhancement
ratios as functions of the distance d. The various
curves are obtained by using the basic parameter set
with the following changes:
a. $\omega = \omega_{21}$ = 3.48 eV, $\omega' = \omega_{31}$ = 3.45 eV;
b. $\omega = \omega_{21}$ = 3.48 eV, $\omega' = \omega_{31}$ = 3.0 eV;
c. $\omega = \omega_{21}$ = 4.0 eV, $\omega' = \omega_{31}$ = 3.48 eV;
d. $\omega = \omega_{21}$ = 3.30 eV, $\omega' = \omega_{31}$ = 3.0 eV.

Figure 7.   The enhancement factor (R_{pc}) for the photochemical
rate as a function of distance d. The basic
parameter set with the replacement of K by K_{pc} is
used. Here $I_{inc} = 10^4 \omega/m^2$.
For curve (a) K_{pc} = 10^9 sec^{-1};
for (b) K_{pc} = 10^{10} sec^{-1};
for (c) $_{pc}$ = 10^{12} sec^{-1}.

Figure 8.   The enhancement factor (R_{pc}) for the photochemical
rate as a function of distance d for various I_{inc}.
The parameters a = 200 Å, f_{21} = .1,
$\omega = \omega_{21}$ = 3.48 eV, $\Gamma_2 = 10^9$ sec^{-1}, $K_{pc} = 10^{11}$ sec^{-1}
are used for all the curves. For curve (a) I_{inc} =
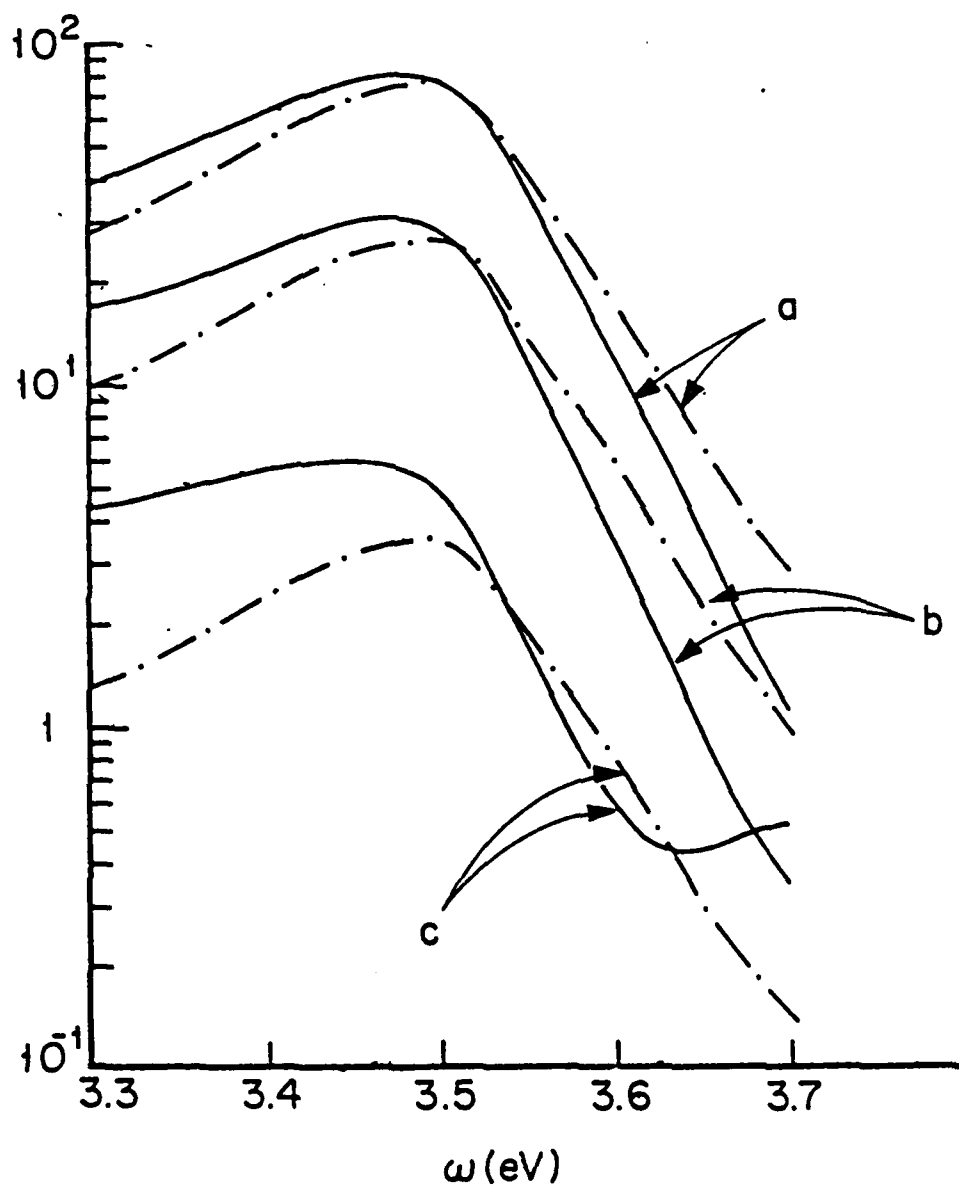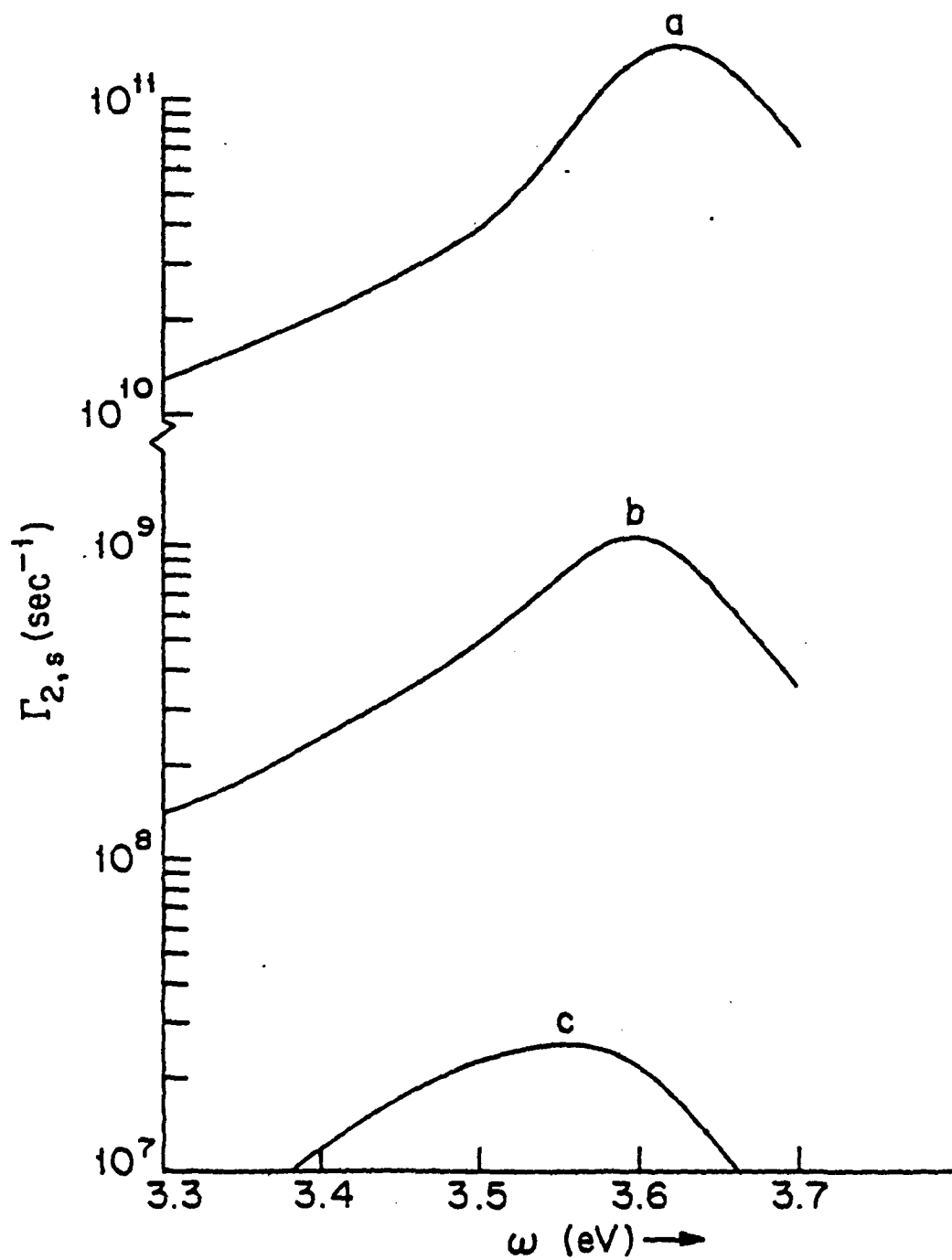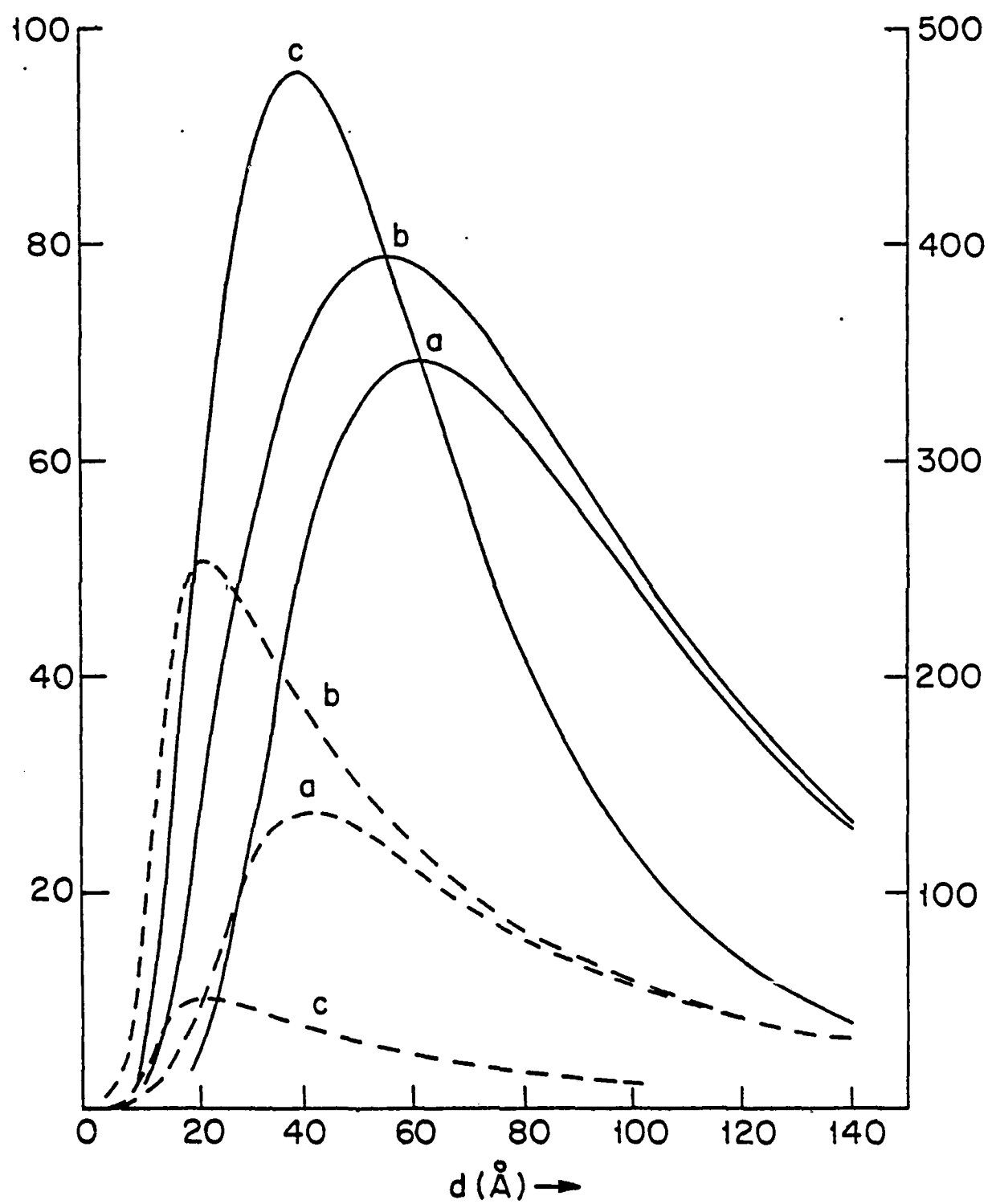10^3 W/m^2; for curve (b) $I_{inc} = 10^8$ W/m^2; for curve
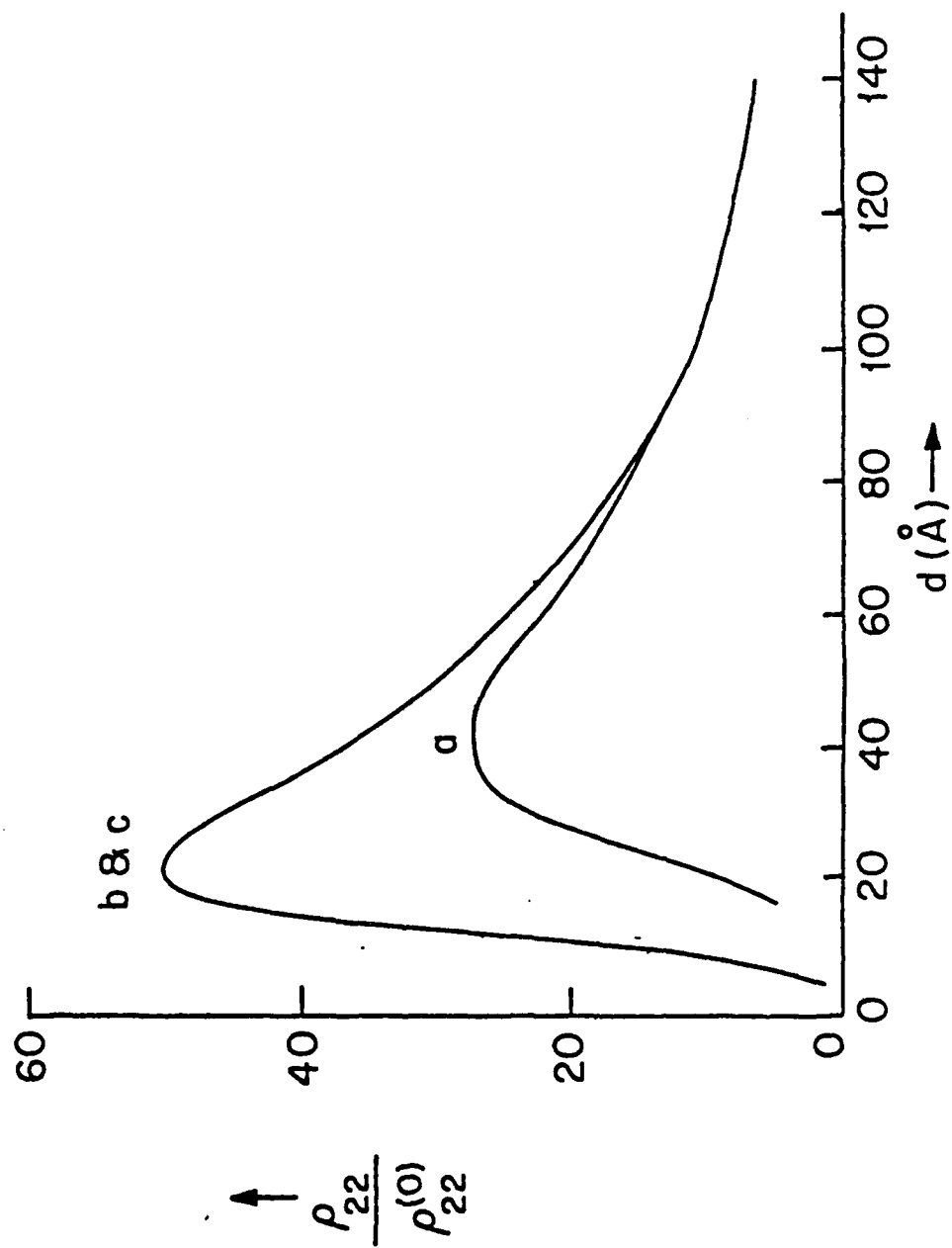(c) I_{inc} = 10^{10} W/m^2.

FIG. 2 (a

FIG. 2(b)

FIG. 3

FIG 4

FIG. 5

Figure axes: vertical axis $\dfrac{\Gamma_2}{\Gamma_{2,s}}$ with values 1, 10^{-1}, 10^{-2}, 10^{-3}; horizontal axis $\Gamma_2 \ (\text{sec}^{-1})(\times 1.6)$ with values 10^8, 10^9, 10^{10}, 10^{11}. Curves labeled a, b, c.
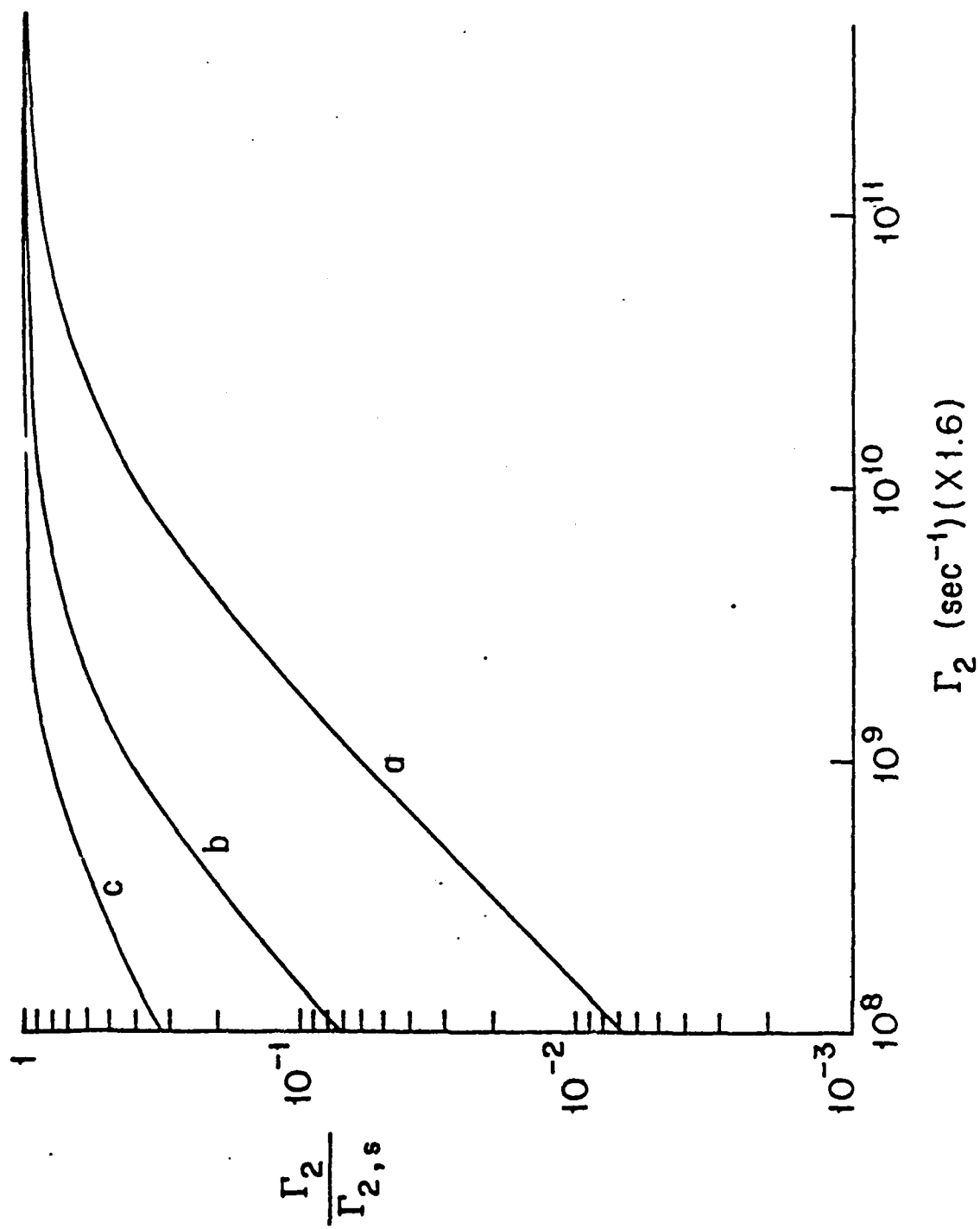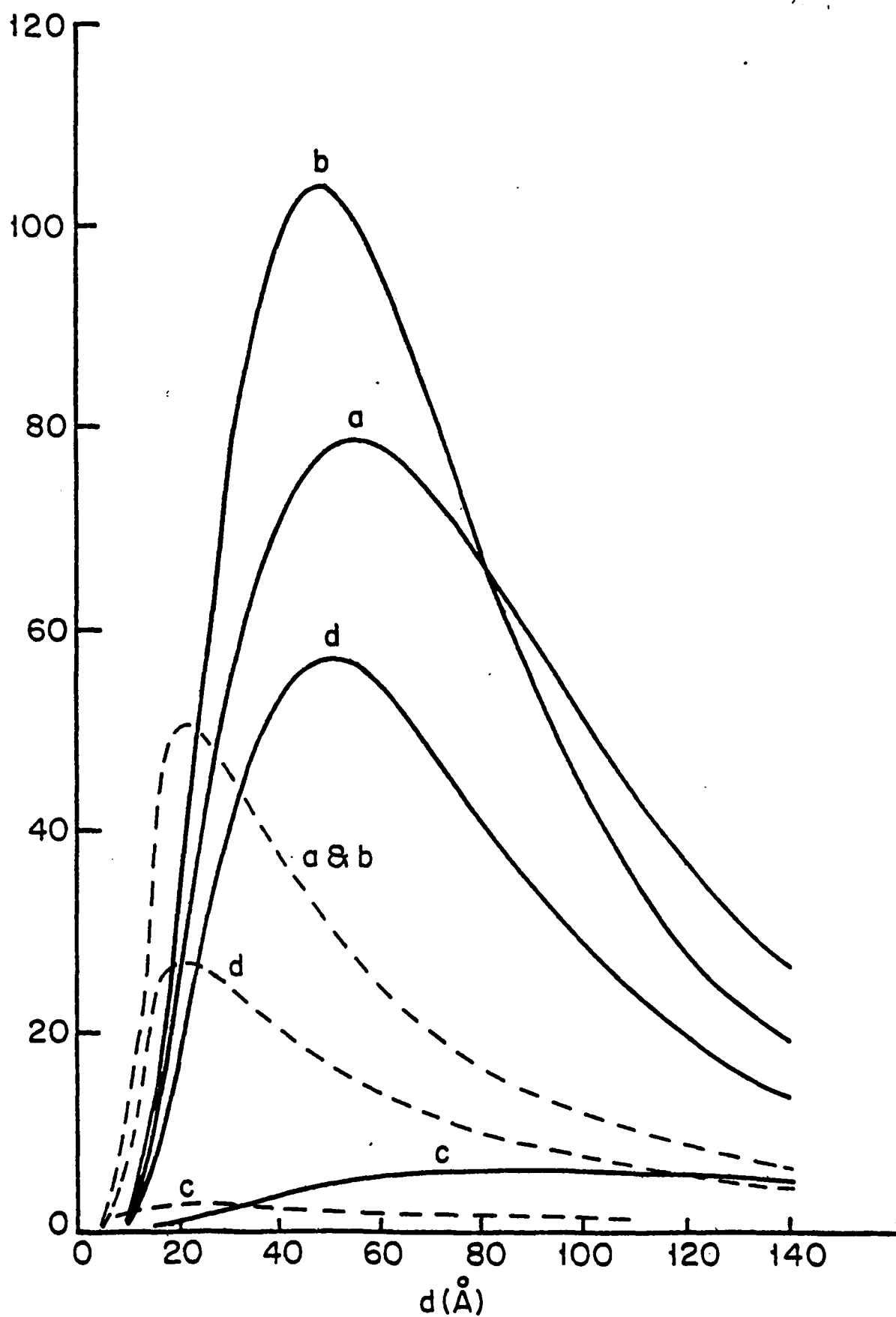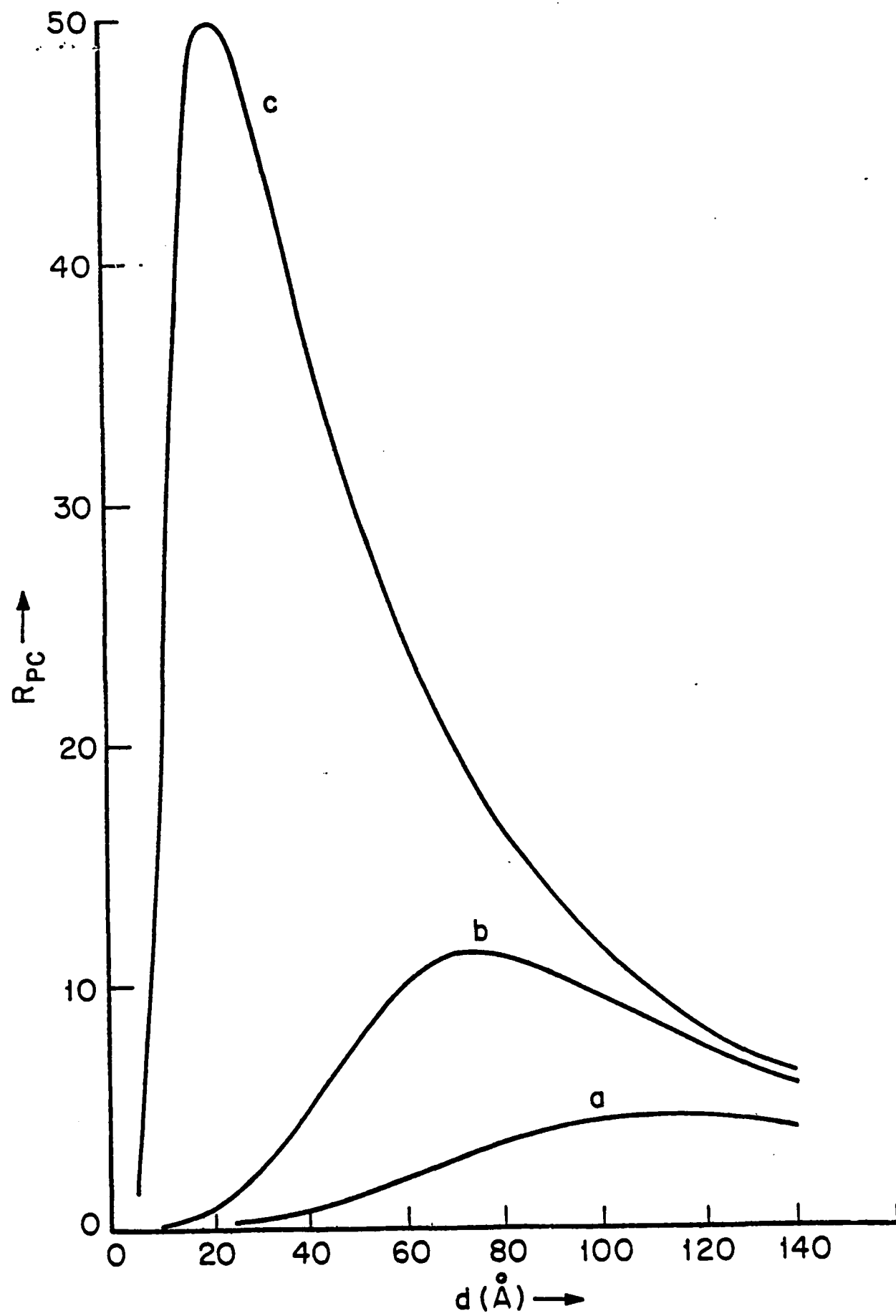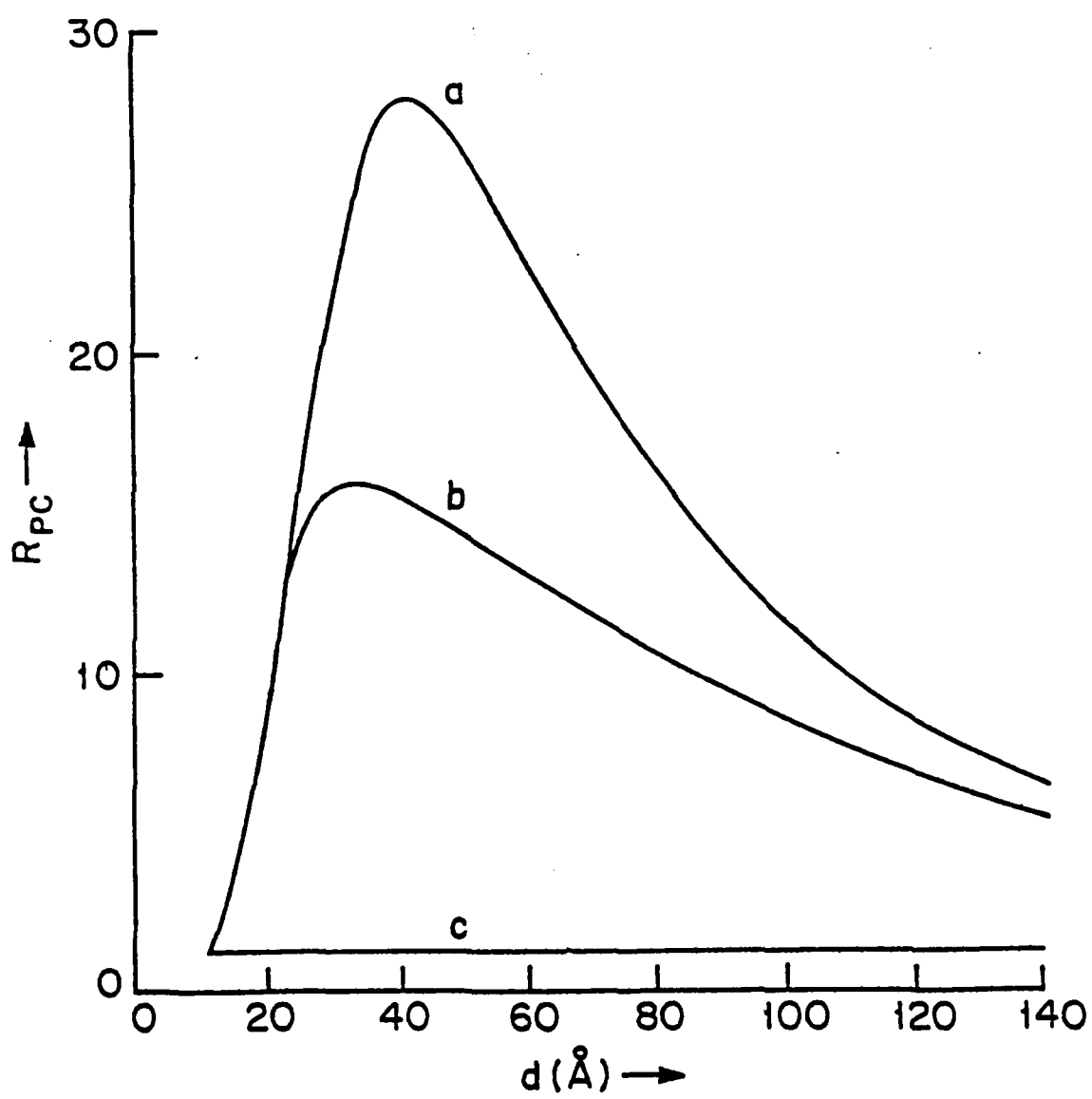
FIG 6

FIG. 7

FIG. 8

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