

Molecule adsorbed on plane metal surface: Coupled system eigenstates

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As part of a test of the surface plasmon mechanism for surface-enhanced Raman scattering by molecules adsorbed on plane metal surfaces, we have developed the quantum-mechanical theory of the interaction between physisorbed molecules and the plane surface of a metal. Particular attention was given to the coupling between a discrete dipole-allowed excitation on the molecule and the continuum of excitations of the surface plasmons at a plane metal surface. Coupled system eigenstates were obtained by Fano's method for cases where the metal was nonspatially dispersive and where spatial dispersion was included. The interaction energy V_q was computed in both cases. In this absence of spatial dispersion the classical image-field-theory result is obtained in the nonretarded limit. In the presence of spatial dispersion a significantly different result is found. The results were used (see following paper) to calculate the cross section for enhanced Raman scattering.

I. INTRODUCTION

Strongly enhanced Raman scattering by molecules adsorbed at a metal-solution interface has been observed recently.¹⁻³ The scattering cross section of the adsorbed molecules has been reported to be as much as 6 orders of magnitude larger than that for the same molecule in solution. This great enhancement has stimulated many investigators to produce models suggesting that this is a type of resonance scattering.⁴⁻⁷ Most of these models are either qualitative or classical; the intermediate states involved in the scattering processes are not clearly specified.

In this and the following paper we investigate a new quantum theory of the eigenstates and Raman scattering cross section of the composite system of molecule adsorbed on a plane metal surface. Our theory is based on a simple model for the surface of the metal assumed flat, and for the electronic structure of the molecule assumed to be a two-level system with allowed transitions. We allow the metal to be characterized by a frequency-dependent dielectric function $\epsilon(\omega)$, or a more general frequency- and wave-vector-dependent function $\epsilon(\omega, \vec{k})$ including spatial dispersion. The metal can sustain elementary excitations such as those that originate in surface plasmons, volume plasmons, and interband and intraband electronic transitions. The molecule is idealized as a two-level system with a discrete dipole-allowed excitation and is assumed to be weakly physisorbed on the metal surface. The excitations in the metal related to both electron-hole polarization given by interband and intraband transitions, and the macroscopic electric field external to the metal surface produced by the plasmons, will in-

fluence the electronic excitations in the adsorbed molecules.

The coupling between the discrete excitation of the adsorbed molecule and the continua of electronic excitations in the metal is of decisive importance. We investigate the new coupled eigenstates of the composite inhomogeneous molecule-metal system quantum mechanically, using Fano's general theory⁸ of discrete-continua coupling, and we are able to make quantitative statements about these states. Because the surface plasmons produce a large macroscopic electric field outside the metal, we only consider the surface-plasmon contribution in these two papers.

Mahan⁹ has shown that the interaction between surface plasmons and an electron outside the metal is equivalent to that of the image field, in the classical limit. The proper dynamical nature of the interaction between the electrons and metal can only be taken into account by working in a quantum picture of surface plasmons. The macroscopic electric field due to surface plasmons depends sensitively on the dielectric function of the metal and the boundary conditions on the interface.^{10,11} Another important factor is the presence of spatial dispersion: If this effect is included, a drastically different density of states of surface plasmons will result compared to neglect of the effect of wave-vector dependence in the dielectric function. The density of plasmon states affects the coupled eigenstates in an important manner.

In Sec. II of this paper we investigate carefully the coupling coefficient between surface plasmon and molecule for both cases: spatial dispersion absent and present. In Sec. III, the Hamiltonian for the coupled systems is set up and the eigenstates are obtained. In Sec. IV, the eigenstates of

the coupled systems are analyzed—presence and absence of spatial dispersion are contrasted. In Sec. V, we discuss our results and compare with various simpler limiting cases: classical (non-retarded) limit of the image charge and a picture in which shifted and broadened molecular levels are invoked. The merit of basing a theory of Raman scattering on a quantum theory of the coupled system should be evident. The theory presented here is capable of being applied to arbitrary surface configuration; in the particular applications reported in this and the following paper, the metal surface is taken as plane.

II. COUPLING COEFFICIENT $V_{\vec{q}}$

We model the composite system as a semi-infinite metal outside of which are molecules. The metal occupies the half-space $z < 0$ and has dielec-

tric coefficient $\epsilon(\omega, \vec{k})$. Molecules are affixed at distance $R_z > 0$ from the interface $z = 0$. We assume the dielectric function is $\epsilon_0 = 1$ for the half-space $z > 0$ taken as vacuum. The metal surface is an ideal plane, and roughness is ignored in this model. We proceed to compute the interaction energy of metal and molecule.

A. Absence of spatial dispersion in the metal

In the case of a nonspatially dispersive metal for which the dielectric function is assumed to be independent of wave vector \vec{k} , the quantized polarization field of a surface plasmon has been derived by many authors.¹²⁻¹⁴ Here we shall follow Nkoma¹³ *et al.*

The quantized vector potential field for the surface plasmon outside the metal is given by

$$\vec{A}(\vec{r}, z) = \sum_{\vec{q}} f_{\vec{q}} \frac{1}{(1 + q^2/\gamma^2)^{1/2}} \left[\left(\hat{q} + \frac{iq}{\gamma} \hat{z} \right) e^{-i\omega t + i\vec{q} \cdot \vec{r} - \gamma z} a_{\vec{q}} + \left(\hat{q} - \frac{iq}{\gamma} \hat{z} \right) e^{-i\omega t - i\vec{q} \cdot \vec{r} - \gamma z} a_{\vec{q}}^\dagger \right], \quad (1)$$

where \vec{q} and \vec{r} are two-dimensional vectors parallel to the surface and \hat{q} and \hat{z} are unit vectors. The normalization constant $f_{\vec{q}}$ is given by

$$f_{\vec{q}} = - \left(\frac{4\pi\hbar c^2 \gamma}{\omega A} \right)^{1/2} \epsilon(\omega) \left(\epsilon(\omega) [1 + \epsilon(\omega)] + \frac{\omega}{2} \frac{\partial \epsilon(\omega)}{\partial \omega} \right)^{-1}, \quad (2)$$

where A is the area of the surface. The variables γ , q , and ω are related by the equation

$$\gamma^2 = q^2 - \frac{\omega^2}{c^2}, \quad (3)$$

and the surface-plasmon-dispersion relation is

$$\frac{c^2 q^2}{\omega^2} = \frac{\epsilon(\omega)}{1 + \epsilon(\omega)}. \quad (4)$$

In the nonretarded limit, i.e., $cq/\omega \gg 1$, the surface plasmon frequency ω_{sp} is determined by the equation

$$\epsilon(\omega_{sp}) + 1 = 0. \quad (5)$$

Equations (1)–(4) were also derived by Elson and Ritchie¹² for the special case of the Drude dielectric function:

$$\epsilon(\omega) = 1 - \omega_p^2/\omega^2, \quad (6)$$

The electric field outside the metal is given by

$$\vec{E} = -\frac{1}{c} \frac{\partial \vec{A}}{\partial t}.$$

This electric field can cause an electronic transi-

tion in the molecules adsorbed on the metal surface. Generally the dielectric function of the metal will be assumed to include both interband and free-electron contributions, i.e.,

$$\epsilon(\omega) = 1 + \epsilon_b(\omega) - \omega_{pf}^2/\omega^2, \quad (7)$$

where ω_{pf} is the free-electron plasmon frequency.

We shall assume the molecule has only two electronic levels, 0 and 1, and the dipole approximation will be used for the transition matrix element. Thus the interaction between surface plasmons and molecules is given by a coupling coefficient $V_{\vec{q}}$ of the form

$$|V_{\vec{q}}|^2 = |f_{\vec{q}}|^2 \left(\frac{1}{1 + q^2/\gamma^2} \right) \left(\frac{\omega^2}{c^2} \right) \times \left(|\vec{\mu}_1 \cdot \hat{q}|^2 + \frac{q^2}{\gamma^2} \mu_z^2 \right) e^{-2\gamma R_z}, \quad (8)$$

where $\vec{\mu}_1$ and μ_z are the electric dipole moments of the molecules in the direction perpendicular and parallel to \vec{z} , respectively. In the limit $cq/\omega \gg 1$, Eq. (8) reduces to the simple form

$$|V_{\vec{q}}|^2 = \frac{\pi\hbar\omega q}{A} (|\vec{\mu}_1 \cdot \hat{q}|^2 + \mu_z^2) e^{-2\gamma R_z}. \quad (9)$$

We have used Eq. (6) to derive Eq. (8). This result was also given by Gersten and Tzoar.¹⁵

Instead of using the Drude form equation (6) and if we use the more general form of dielectric function given in Eq. (7), then in the nonretarded limit $|V_{\vec{q}}|^2$ is given by

$$|V_q|^2 = \frac{2\pi\hbar\omega q}{A} \left(\frac{\omega}{2} \frac{\partial \epsilon(\omega)}{\partial \omega} \right)^{-1} (|\vec{\mu}_1 \cdot \hat{q}|^2 + \mu_z^2) e^{-2qR_z}. \quad (10)$$

B. Effect of spatial dispersion in the metal

When spatial dispersion or the wave-vector dependence is included in the dielectric function $\epsilon(\omega, \vec{k})$, the surface-plasmon-dispersion relation is no longer given by Eq. (4) and depends on the boundary conditions used.

Fuchs and Kliever¹⁰ have used several forms of dielectric function to calculate the surface-plasmon-dispersion relation, assuming specular reflection as the boundary condition. It turns out that the simple hydrodynamical form of $\epsilon(\omega, \vec{k})$ gives a result similar to the more complicated Lindhard dielectric function, so we shall use the hydrodynamical form of $\epsilon(\omega, \vec{k})$ given by Fuchs and Kliever.¹⁰

We shall restrict ourselves to the nonretarded limit in the derivation of $|V_q|^2$. It will be apparent below that the important region of (ω, \vec{k}) space is far away from the light line. In the hydrodynamical approximation, the longitudinal dielectric function is of the form¹⁰

$$\epsilon_l(\omega, \vec{k}) = 1 + \epsilon_b(\omega) - \frac{\omega_{pf}^2}{\omega^2 - \beta^2 k^2}, \quad (11)$$

where ω_{pf} is the free-electron plasmon frequency

$$|V_q|^2 = |\vec{\mu} \cdot \vec{\nabla} \phi|^2 = \frac{4\pi\hbar\omega q}{A} \omega_{pf}^2 (|\vec{\mu}_1 \cdot \hat{q}|^2 + \mu_z^2) e^{-2qR_z} \left[\omega^2 \left(7 + 5\epsilon_b + \frac{1}{1 + \epsilon_b} \right) + \epsilon_b^2 \left(\omega^2 - \frac{\omega_{pf}^2}{1 + \epsilon_b} \right) \right]^{-1}. \quad (15)$$

Having obtained the interaction constant V_q , we can now proceed to set up the Hamiltonian for the coupled systems and obtain the new eigenstates.

III. HAMILTONIAN AND EIGENSTATES OF THE COUPLED SYSTEM

Since the molecule is assumed to be a two-level system, the Hamiltonian of the molecule in the absence of interaction is taken as

$$H_m = \sum_{n=0,1} \epsilon_n C_n^\dagger C_n, \quad (16)$$

where 0 and 1 denote the ground and excited states; C_n are Fermion operators. The surface plasmons are described by the Hamiltonian

$$H_{sp} = \sum_q \hbar \omega_q a_q^\dagger a_q, \quad (17)$$

where the frequency ω_q is given by Eq. (4) or Eq. (14). In the dipole approximation, the interaction between molecule and surface plasmons is given

and $\beta^2 = \frac{3}{5} v_F^2$, v_F is the Fermi velocity. Equation (11) agrees with Eq. (7) in the long-wavelength limit.

Following the result of Fuchs and Kliever¹⁰ it is easy to show that outside the metal the potential field due to the surface plasmon is given by

$$\phi = E_q e^{-qz + i\vec{q} \cdot \vec{r}}, \quad (12)$$

where

$$E_q^2 = \frac{4\pi\hbar\omega}{Aq} \omega_{pf}^2 \left[\omega^2 \left(7 + 5\epsilon_b + \frac{1}{1 + \epsilon_b} \right) + \epsilon_b^2 \left(\omega^2 - \frac{\omega_{pf}^2}{1 + \epsilon_b} \right) \right]^{-1}. \quad (13)$$

A derivation of Eq. (13) is given in the Appendix.

Here ω and q are related by the surface-plasmon-dispersion relation

$$\frac{\beta^2 q^2}{\omega^2} = \frac{\left(2 + \epsilon_b - \frac{\omega_{pf}^2}{\omega^2} \right)^2}{(2 + \epsilon_b) \left(2 + \epsilon_b - \frac{\epsilon_b}{1 + \epsilon_b} \frac{\omega_{pf}^2}{\omega^2} \right)}. \quad (14)$$

In the limit $\beta = 0$ and $\epsilon_b = 0$, Eq. (14) reduces to the well known surface-plasmon-dispersion relation (in the nonretarded limit), $\omega^2 = \frac{1}{2} \omega_{pf}^2$.

In the dipole approximation and with spatial dispersion included, the coupling constant V_q is given by

by

$$H_{int} = \sum_q V_q C_1^\dagger C_0 a_q + \text{H.c.}, \quad (18)$$

where H.c. is the Hermitian conjugate. The ground eigenstate for the uncoupled Hamiltonian $H_m + H_{sp}$ is denoted $|0, g\rangle$. The excited states that will be considered are given by

$$|1, g\rangle = C_1^\dagger C_0 |0, g\rangle, \quad |0, \vec{q}\rangle = a_q^\dagger |0, g\rangle,$$

and

$$|1, \vec{q}\rangle = C_1^\dagger C_0 a_q^\dagger |0, g\rangle.$$

Thus the matrix elements of the total Hamiltonian

$$H = H_m + H_{sp} + H_{int} \quad (19)$$

are given by

$$\langle i, g | H | j, g \rangle = \epsilon_i \delta_{ij}, \quad (20)$$

$$\langle 0, \vec{q} | H | 0, \vec{q}' \rangle = \hbar \omega_q \delta_{\vec{q}\vec{q}'}, \quad (21)$$

and

$$\langle 0, \vec{q} | H | 1, g \rangle = V_{\vec{q}}^*, \quad (22)$$

all other matrix elements are zero. We are neglecting two plasmon excitations because their contribution to the Raman scattering matrix element is negligible.

Equations (20)–(22) in effect describe the coupling between a discrete state $|1, g\rangle$ and a continuum $|0, \vec{q}\rangle$. The coupling between ground discrete state $|0, g\rangle$ and the upper continuum $|1, \vec{q}\rangle$ has been neglected¹⁶ in Eq. (18), since the energy difference $\epsilon_1 + \hbar\omega_q - \epsilon_0$ for states $|0, g\rangle$ and $|1, \vec{q}\rangle$ is much larger than $\epsilon_1 - \hbar\omega_q - \epsilon_0$ for $|1, g\rangle$ and $|0, \vec{q}\rangle$.

Fano⁸ has solved the problem of interacting discrete states and continuum given by Eqs. (20)–(22). Following his analysis the eigenstates of the total Hamiltonian H are given by

$$|\psi_E\rangle = a(E)|1, g\rangle + \sum_{\vec{q}} b_{\vec{q}}(E)|0, \vec{q}\rangle, \quad (23)$$

where $a(E)$ and $b_{\vec{q}}(E)$ are given by

$$|a(E)|^2 |V_E|^2 = [\pi^2 + Z^2(E)]^{-1} \quad (24)$$

and

$$b_{\vec{q}}(E) = \left(\phi \frac{1}{E - \epsilon_0 - \hbar\omega_q} + Z(E)\delta(E - \epsilon_0 - \hbar\omega_q) \right) V_{\vec{q}}^* a(E). \quad (25)$$

In Eq. (25), ϕ denotes the principle part. The function $Z(E)$ is defined by the equation

$$Z(E) |V_E|^2 = E - \epsilon_1 - F(E) \quad (26)$$

and functions $F(E)$ and $|V_E|^2$ are given by

$$F(E) = \sum_{\vec{q}} \phi \frac{1}{E - \epsilon_0 - \hbar\omega_q} |V_{\vec{q}}|^2 \quad (27)$$

and

$$|V_E|^2 = \sum_{\vec{q}} |V_{\vec{q}}|^2 \delta(E - \epsilon_0 - \hbar\omega_q). \quad (28)$$

Evidently, $F(E)$ and $\pi |V_E|^2$ are the real and imaginary parts of the function $\Delta(E)$,

$$\Delta(E) \equiv \sum_{\vec{q}} \frac{|V_{\vec{q}}|^2}{E - \epsilon_0 - \hbar\omega_q - i\delta}, \quad (29)$$

where $\delta \rightarrow 0+$.

Using Eqs. (26) and (29), $|a(E)|^2$ can be rewritten in the form

$$|a(E)|^2 = \frac{|V_E|^2}{[E - \epsilon_1 - F(E)]^2 + \pi^2 |V_E|^4} \quad (30)$$

or

$$|a(E)|^2 = \frac{1}{\pi} \text{Im}[E - \epsilon_1 - \Delta(E)]^{-1}. \quad (31)$$

$|a(E)|^2$ has a resonant behavior near $E^R = \epsilon_1 + F(E^R)$ for very small values of $|V(E^R)|^2$. This property is thoroughly analyzed by Fano⁸ and it will not be discussed here. In the following paper,¹⁷ we used $|a(E)|^2$ to investigate the possibility of resonant Raman scattering.

Here we wish to emphasize that the states $|\psi_E\rangle$ [Eq. (23)] represent a new set of eigenstates of the entire system. They have properties of both surface-plasmon states and molecular states. They should not be identified as shifted and broadened original molecular states as discussed, for example, by Philpott.¹⁸ In fact, if $\hbar\omega_q < \epsilon_1 - \epsilon_0$ for all surface plasmons, besides the continua given by Eq. (23) which have energies less than $\epsilon_1 - \epsilon_0$, there exists a discrete state whose energy $E > \epsilon_1 - \epsilon_0$ and satisfies the equation $E - \epsilon_1 = F(E)$. Thus these new states are more like bonding and antibonding states than shifted levels.

IV. FUNCTIONS $F(E)$ AND $|V_E|^2$

The function $\Delta(E)$, or $F(E)$ and $|V_E|^2$, completely specifies the new eigenstates of the coupled system. In the case of no spatial dispersion, substitution of Eq. (8) into Eq. (27) yields

$$F(E) = \int q dq \frac{2\hbar c^2 \gamma}{\omega} \epsilon^2(\omega) \left(\epsilon(\omega)[1 + \epsilon(\omega)] + \frac{\omega}{2} \frac{\partial \epsilon(\omega)}{\partial \omega} \right)^{-1} \frac{1}{1 + q^2/\gamma^2} \frac{\omega^2}{c^2} \left(\frac{1}{2} \mu_1^2 + \frac{q^2}{\gamma^2} \mu_z^2 \right) e^{-2\gamma R_z} \phi \frac{1}{E - \epsilon_0 - \hbar\omega}. \quad (32)$$

Using Eq. (4), we obtain

$$q dq = \frac{\omega d\omega}{c^2} \left(\frac{1}{1 + \epsilon(\omega)} \right)^2 \left(\epsilon(\omega)[1 + \epsilon(\omega)] + \frac{\omega}{2} \frac{\partial \epsilon}{\partial \omega} \right). \quad (33)$$

Using Eqs. (3), (4), and (33), Eq. (32) is reduced to the form

$$F(E) = \int_0^{\omega_{sp}} d\omega (2\hbar) \left(\frac{\omega}{c} \right)^3 \frac{\epsilon^2(\omega)}{[1 - \epsilon(\omega)][-1 - \epsilon(\omega)]^{5/2}} \left[\frac{1}{2} \mu_1^2 - \epsilon(\omega) \mu_z^2 \right] \exp\left(-\frac{2\omega R_z}{c[-1 - \epsilon(\omega)]^{1/2}}\right) \phi \frac{1}{E - \epsilon_0 - \hbar\omega}, \quad (34)$$

where ω_{sp} is the surface-plasmon frequency defined by Eq. (5). Equation (34) can be further reduced by introducing the oscillator strength of the molecules for the transition:

$$f_{01}^z = \frac{2m(\epsilon_1 - \epsilon_0)}{e^2 \hbar^2} \mu_z^2 \quad (35)$$

and

$$f_{01}^{\pm} = \frac{m(\epsilon_1 - \epsilon_0)}{e^2 \hbar^2} \mu_1^2. \quad (36)$$

Equation (34) then simplifies to the form

$$F(E) \simeq \frac{e^2 \hbar^3}{m(\epsilon_1 - \epsilon_0)} \frac{1}{c^3} \int_0^{\omega_{sp}} d\omega \mathcal{G}\left(\frac{\omega^3}{E - \epsilon_0 - \hbar\omega}\right) [f_{01}^{\pm} - \epsilon(\omega)f_{01}^{\mp}] \frac{\epsilon^2(\omega)}{[-1 - \epsilon(\omega)]^{5/2}[1 - \epsilon(\omega)]} \exp\left(-\frac{2\omega R_z}{c[-1 - \epsilon(\omega)]^{1/2}}\right). \quad (37)$$

Inspecting the integral in Eq. (37), we can easily see that $F(E) \propto (R_z)^{-3}$. Equation (37) can also be evaluated approximately by using the fact that the integrand in Eq. (37) is heavily weighted near the region $1 + \epsilon(\omega) = 0$ or $\omega = \omega_{sp}$. Using the approximation $\omega \sim \omega_{sp}$ in Eq. (37), we obtain

$$F(E) \simeq \frac{e^2 \hbar^3}{m(\epsilon_1 - \epsilon_0)} \frac{1}{c^3} \int_0^{\omega_{sp}} d\omega \frac{\omega_{sp}^3}{E - \epsilon_0 - \hbar\omega_{sp}} (f_{01}^{\pm} + f_{01}^{\mp}) \frac{1}{2[-1 - \epsilon(\omega)]^{5/2}} \exp\left(-\frac{2\omega_{sp} R_z}{c[-1 - \epsilon(\omega)]^{1/2}}\right). \quad (38)$$

If we choose the Drude dielectric function, Eq. (6), the integral in Eq. (38) can be easily evaluated, and the result is

$$F(E) \simeq \frac{1}{8R_z^3} (\mu_z^2 + \frac{1}{2}\mu_1^2) \frac{\hbar\omega_{sp}}{E - \epsilon_0 - \hbar\omega_{sp}}. \quad (39)$$

At $E = \epsilon_0$, Eq. (39) gives the well-known expression for the self-energy of a dipole and its image field.¹⁹

Since R_z is usually a few angstroms, $F(E)$ of Eq. (37) is very large. When spatial dispersion is included the value of $F(E)$ is greatly reduced and it will not depend on R_z in the functional form $F(E) \propto R_z^{-3}$.

Substitution of Eq. (15) into Eq. (27) yields $F(E)$ for the spatially dispersive medium. It is of the form

$$F(E) = \frac{e^2 \hbar^2}{m(\epsilon_1 - \epsilon_0)} \left(\frac{\omega_{pt}}{c}\right)^3 \int_0^{Q_c} Q^2 dQ (f_{01}^{\pm} + f_{01}^{\mp}) \exp\left(-\frac{2\omega_{pt} R_z Q}{c}\right) \times \left[\epsilon_b^2 \left(\Omega^2 - \frac{1}{1 + \epsilon_b} \right) + \Omega \left(7 + 5\epsilon_b + \frac{1}{1 + \epsilon_b} \right) \right]^{-1} \mathcal{G} \frac{\Omega}{(E - \epsilon_0)/\hbar\omega_{pt} - \Omega}, \quad (40)$$

where

$$Q = \frac{cq}{\omega_{pt}}, \quad \Omega = \frac{\omega}{\omega_{pt}},$$

and q and ω in Eq. (40) satisfy the dispersion relation Eq. (14). The finite cutoff Q_c was taken to be $Q_c \cong c/\beta$.

For the special case $\epsilon_b = 0$ and $E = \epsilon_0$, $F(E)$ of Eq. (40) reduces to the self-energy of a dipole and its image field (in the presence of spatial dispersion). In other words, $F(E = \epsilon_0)$ reduces to the form

$$F(E = \epsilon_0) = -\frac{1}{2} (\mu_z^2 + \frac{1}{2}\mu_1^2) \int_0^{Q_c} q^2 dq e^{-2qR_z} \left[1 + \frac{q^2 \beta^2}{\omega_{pt}^2} - \frac{q^2 \beta^2}{\omega_{pt}^2} \left(1 + \frac{2\omega_{pt}^2}{q^2 \beta^2} \right)^{1/2} \right]. \quad (41)$$

Without spatial dispersion, i.e., $\beta = 0$, Eq. (41) reduces to Eq. (39) for $E = \epsilon_0$. In the limit of very small R_z , the leading term of Eq. (41) is proportional to R_z^{-1} . Equation (41) is much smaller than the value given by Eq. (39). Thus the effect of spatial dispersion, even using simplest hydrodynamic form equation (11), greatly reduces the strength of image field obtained classically.

Not only are there quantitative differences for $F(E)$ between spatially dispersive and nonspatially dispersive media but also a qualitative change. Without spatial dispersion, $F(E)$ is positive for $E > \hbar\omega_{sp}$, since there are no surface-plasmon states with energy larger than $\hbar\omega_{sp}$. This is clearly shown in Eq. (39). In the presence of spatial dispersion as in Eq. (11), most surface-plasmon states with large wave vectors are above ω_{sp} . Thus $F(E)$ is still negative for values of E immediately above $\hbar\omega_{sp}$.

The quantity $|V_E|^2$, defined by Eq. (28), is easily calculated using Eq. (8). Without spatial dispersion, $|V_E|^2$ is given by

$$|V_E|^2 = \frac{e^2 \hbar^2}{m(\epsilon_1 - \epsilon_0)} \frac{1}{c^3} \omega^3 [f_{01}^{\pm} - \epsilon(\omega)f_{01}^{\mp}] \frac{\epsilon^2(\omega)}{[-1 - \epsilon(\omega)]^{5/2}[1 - \epsilon(\omega)]} \exp\left(-2\frac{\omega}{c} R_z \frac{1}{[-1 - \epsilon(\omega)]^{1/2}}\right), \quad (42)$$

where $\omega = (E - E_0)/\hbar$. Equation (42) has also been derived by Philpott¹⁸ in discussing the decay rate of ex-

cited molecules interacting with surface plasmons.

We remark that Eqs. (28) and (42) are correct using the assumption that the surface-plasmon energy $\hbar\omega_q$ is real. It is obvious that if \hbar/Γ is the intrinsic lifetime of the surface plasmon, $|V_E|^2$ is changed to the form

$$|V_E|^2 = \frac{1}{\pi} \sum_q |V_q|^2 \frac{\Gamma}{(E - \epsilon_0 - \hbar\omega_q)^2 + \Gamma^2}. \quad (43)$$

Substitution of Eq. (7) into Eq. (43) yields

$$|V_E|^2 = \frac{e^2 \hbar^2}{m(\epsilon_1 - \epsilon_0)} \frac{1}{c^3} \frac{1}{\pi} \int_0^{\omega_{sp}} d\omega \omega^3 \frac{\Gamma}{(E - \epsilon_0 - \hbar\omega)^2 + \Gamma^2} [f_{01}^L - \epsilon(\omega) f_{01}^Z] \\ \times \frac{\epsilon^2(\omega)}{[1 - \epsilon(\omega)][-1 - \epsilon(\omega)]^{5/2}} \exp\left(-\frac{2\omega R_z}{c[-1 - \epsilon(\omega)]^{1/2}}\right). \quad (44)$$

Equation (44) is the same as Eq. (37) after replacing the factor

$$\rho \frac{1}{E - \epsilon_0 - \hbar\omega}$$

in Eq. (37) by

$$\frac{1}{\pi} \frac{\Gamma}{(E - \epsilon_0 - \hbar\omega)^2 + \Gamma^2}.$$

Note that $|V_E|^2$ given by Eq. (40) is also proportional to R_z^{-3} . By using the same method $|V_E|^2$ for the spatially dispersive medium can be obtained from Eq. (40). It is of the form

$$|V_E|^2 = \frac{e^2 \hbar^2}{m(\epsilon_1 - \epsilon_0)} \left(\frac{\omega_{pt}}{c}\right)^3 \int_0^{\omega_c} Q^2 dQ (f_{01}^L + f_{01}^Z) \exp\left(-\frac{2\omega_{pt} R_z Q}{c}\right) \left[\epsilon_b^2 \left(\Omega^2 - \frac{1}{1 + \epsilon_b}\right) + \Omega \left(7 + 5\epsilon_b + \frac{1}{1 + \epsilon_b}\right)\right]^{-1} \\ \times \frac{1}{\pi} \Omega \left(\frac{\Gamma}{\hbar\omega_{pt}}\right) / \left[\left(\frac{E - \epsilon}{\hbar\omega_{pt}} - \Omega\right)^2 + \left(\frac{\Gamma}{\hbar\omega_{pt}}\right)^2\right]. \quad (45)$$

$|V_E|^2$ for the spatially dispersive medium [Eq. (45)] is much larger than $|V_E|^2$ for the medium without spatial dispersion [Eq. (44)]. Note $|V_q|^2$ of Eq. (43) increases with q and ω provided that $qR_z < 1$. In the integration of Eq. (44) without spatial dispersion ω is restricted to values less than ω_{sp} . In contrast, by including spatial dispersion as in Eq. (45) ω can be larger than ω_{sp} .

V. CONCLUSIONS

A new approach was used to study the interaction between a weakly adsorbed molecule and a plane metal surface. Special emphasis was given to the coupling between discrete electronic levels of the molecule and continuous levels of the surface plasmons of the metal. A set of new eigenstates was obtained for the coupled systems. These eigenstates are combinations of the bare surface-plasmon states and the excited level of molecules.

Since the polarization field and the density of states of surface plasmons depend on the dielectric function of the metal, the eigenstates of the coupled systems are quite different for a spatially dispersive metal, where the wave-vector depen-

dence is included in the dielectric function of the metal, and a nonspatially dispersive metal.

Without taking spatial dispersion into account, the interaction between surface plasmons and molecules reduces to the classical image field in the nonretarded limit. The eigenstates are shifted from the bare energy levels of the molecule. The separation is proportional to the inverse cube of R_z , the distance between molecules and the metal. When spatial dispersion is included, for example, by using the hydrodynamic approximation, the separation between the eigenstates and the bare levels of the molecule is greatly reduced and is not proportional to R_z^{-3} .

Since we have used the simplest hydrodynamic form of dielectric function for the metal and have neglected the variation of electronic density near the surface, the conclusion drawn above for the effect of spatial dispersion on the eigenstates serves as an indication of the importance of the surface-plasmon-dispersion relation.

Efrima and Metiu⁷ used classical image-field theory to explain the observed enhanced Raman scattering for adsorbed molecules on metals. In the following paper¹⁷ on the eigenstates for Raman

scattering, we show that without spatial dispersion and using a simple Drude dielectric function for the metal, the result is similar to that found in Ref. 7. Inclusion of spatial dispersion will drastically change the result.

Philpott¹⁸ was the first to point out that resonant Raman scattering could occur at energies far away from the bare molecular levels due to interaction with surface plasmons. As pointed out at the end of Sec. IV, his description of the new eigenstates as shifted and broadened molecular levels are misleading. Hexter and Albrecht⁴ have discussed this problem recently, but their eigenstates are not derived explicitly and the final Raman scattering matrix elements seem incorrect (see Ref. 17).

We remark that in this paper we emphasized the surface plasmons as the primary excitations interacting with the molecules. In general, other excitations, such as inter- and intraband transitions and volume plasmons, could also contribute. But the coupled systems can still be classified by interactions between discrete states and continua. The result given in Sec. III will still be correct but with different V_q . Gersten *et al.*⁵ have investigated the tunneling interaction between molecule and metal in a perturbative approach. Since their system involved interaction between the discrete state of the molecule and all the electronic states above the Fermi level in the conduction band of the metal, their result can be obtained by the theory given here.

In this paper, for convenience of calculation, we have made several important assumptions: The metal surface is taken plane, and roughness is neglected; the molecule is taken as a two-level system, and the dipole approximation is used to evaluate the induced electronic transition in the molecule due to surface-plasmon polarization field. Results for multilevel molecules could be obtained by extending the theory as described by Fano.⁸ Since the distance between molecule and metal R_z is only a few angstroms, the wave vector involved in the calculation of V_q is very large. The dipole approximation assuming $e^{i\vec{q}\cdot\vec{r}} \sim 1 + i\vec{q}\cdot\vec{r}$ in evaluating the matrix element should not be used; instead, the exact matrix element of $e^{i\vec{q}\cdot\vec{r}}$ should be used. At present the magnitude of such effects is not known and they may indeed be very important and change results based on the two-level and dipole approximations. However, we restricted ourselves here to a careful quantum-mechanical treatment of one particular model.

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APPENDIX

By using the longitudinal dielectric function of the form given by Eq. (11), Fuchs and Kliever¹⁰ have shown that in the nonretarded limit the electric field inside the metal ($z < 0$) is given by

$$E_x(z) = i \frac{E_q}{\pi} \int_{-\infty}^{\infty} \frac{dq_z}{k^2} e^{-iq_z z} \frac{q^2}{\epsilon_l(k, \omega)} \quad (\text{A1})$$

and

$$E_z(z) = -\frac{iE_q}{\pi} \int_{-\infty}^{\infty} \frac{dq_z}{k^2} \frac{q_z q}{\epsilon_l(k, \omega)}, \quad (\text{A2})$$

where

$$k^2 = q_z^2 + q^2.$$

Note that the total electric field is proportional to $e^{+i\vec{q}\cdot\vec{r}}$ where $\vec{r}\cdot\hat{z} = 0$. Substitution of Eq. (11) into (A1) and (A2) yields

$$E_x(z) = iE_q \frac{q}{1 + \epsilon_b(\omega)} \times \left(\frac{\omega^2}{\beta^2 q_L^2} e^{qz} - \frac{\tilde{\omega}_p^2}{\beta^2 q_L^2} \frac{q}{(q^2 - q_L^2)^{1/2}} e^{(q^2 - q_L^2)^{1/2} z} \right) \quad (\text{A3})$$

and

$$E_z(z) = E_q \frac{q}{1 + \epsilon_b(\omega)} \left(\frac{\omega^2}{\beta^2 q_L^2} e^{qz} - \frac{\tilde{\omega}_p^2}{\beta^2 q_L^2} e^{(q^2 - q_L^2)^{1/2} z} \right), \quad (\text{A4})$$

where

$$\tilde{\omega}_p^2 = \omega_{pT}^2 / [1 + \epsilon_b(\omega)] \quad (\text{A5})$$

and

$$\frac{\beta^2 q_L^2}{\omega^2} = 1 - \frac{\tilde{\omega}_p^2}{\omega^2}. \quad (\text{A6})$$

The potential associated with the electric field \vec{E} is given by

$$\vec{E} = -\vec{\nabla}\phi$$

and

$$\phi(z) = -\frac{E_q}{1 + \epsilon_b} \left(\frac{\omega^2}{\beta^2 q_L^2} e^{qz} - \frac{\tilde{\omega}_p^2}{\beta^2 q_L^2} q / (q^2 - q_L^2)^{1/2} e^{(q^2 - q_L^2)^{1/2} z} \right) e^{i\vec{q}\cdot\vec{r}}. \quad (\text{A7})$$

All the fields above are in the metal, i.e., $z < 0$. The potential in the region $z > 0$ is

$$\phi(z) = E_q e^{-qz + i\tilde{q}\cdot\tilde{r}}. \quad (\text{A8})$$

The boundary condition that ϕ is continuous at $z = 0$ yields the dispersion relation

$$\frac{q}{(q^2 - q_L^2)^{1/2}} = \frac{\omega^2}{\tilde{\omega}_b^2} \left(2 + \epsilon_b - \frac{\omega_b^2 t}{\omega^2} \right) \quad (\text{A9})$$

Equation (A9) is equivalent to Eq. (14).

The charge density is given by the equation

$$\begin{aligned} \rho &= \frac{1}{4\pi} \nabla \cdot \vec{E} \\ &= \frac{E_q}{4\pi} q \left(1 - \frac{1}{1 + \epsilon_b} \right) \delta(z=0) e^{i\tilde{q}\cdot\tilde{r}} \\ &\quad + \frac{E_q \tilde{\omega}_b}{4\pi \beta^2} \frac{q}{1 + \epsilon_b} \frac{1}{(q^2 - q_L^2)^{1/2}} e^{(q^2 - q_L^2)^{1/2} z} e^{i\tilde{q}\cdot\tilde{r}} \Theta(-z), \end{aligned} \quad (\text{A10})$$

where $\Theta(z)$ is the step function. It is interesting to observe that in the case $\epsilon_b = 0$ there is no surface charge density but only volume charge density associated with evanescent volume plasmon.¹⁹

Without spatial dispersion i.e., $\beta = 0$ in Eq. (11), there is only surface charge density:

$$\rho = \frac{E_q}{2\pi} q e^{i\tilde{q}\cdot\tilde{r}} \delta(z=0). \quad (\text{A11})$$

The normalization constant E_q in Eq. (A8) can be determined by quantizing the potential field. The quantization is done by following Stern and Ferrell.²⁰ The ϕ and ρ given by Eqs. (A7), (A8), and (A10) satisfy the equation

$$\frac{1}{2} \hbar \omega = \int \rho \phi dz A. \quad (\text{A12})$$

Thus E_q is obtained and given by Eq. (13).

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