PHYSICAL REVIEW B VOLUME 22, NUMBER 12 15 DECEMBER 1980

Quantum theory of enhanced Raman scattering by molecules on metals: Surface-plasmon mechanism for plane metal surface

Ting-Kuo Lee
Institute for Theoretical Physics, University of California, Santa Barbara, California 93017

Joseph L. Birman
Department of Physics, The City College of the City University of New York, New York, New York 10031

(Received 7 February 1980)

The enhancement ratio of Raman scattering for adsorbed versus isolated molecules has been calculated quantum mechanically using coupled eigenstates obtained in the preceding paper. There, the surface-plasmon states for a plane surface were coupled with molecular dipole eigenstates by Fano's method; the resulting eigenstates with, or without, consideration of spatial dispersion were discussed. An enhancement ratio 10^6 can be obtained in this theory *only* at an effective resonant frequency ω_L^m: The ratio is sharply peaked about ω_L^m. The location of ω_L^m and the maximum ratio obtainable depend sensitively upon the dielectric function used to describe the metal. The experimentally observed ratio by pyridine on silver *cannot* be obtained using realistic parameter values for the spatially dispersive dielectric function $\epsilon(\omega,\vec{k})$ of silver and the parameters for pyridine. This mechanism, invoking surface plasmons for a plane surface, is most likely responsible for only a small fraction of the total observed enhancement, contrary to what could be anticipated from classical image-field theory.

I. INTRODUCTION

Since the first observation by Fleischmann *et al.*[1] of a "giant" Raman scattering (RS) by pyridine molecules adsorbed on a prepared silver electrode in a solution, much experimental and theoretical work has been devoted to providing an explanation of this phenomenon. Ratios as high as 10^6 have been reported experimentally for molecules adsorbed compared to those free in solution.[2] Some evidence exists for this effect for other molecules on Ag, Cu, and Au.[3] Responding to the challenge of understanding the major mechanisms involved, several workers have proposed theoretical models based on the idea that the enhancement is a resonant effect.[4-7] King *et al.*[4] and Efrima and Metiu[5] proposed that the large image field produced by the induced dipole of the adsorbed molecule produces a large shift and broadening of the molecular electronic excitations, thereby causing resonant RS at a frequency shifted from the isolated molecule excitation energy. These theories are either qualitative[4] or classical.[5] An essential element in both theories is the image-field effect, and it will be recalled that the image field results from the classical, nonretarded limit of the quantum theory of electron-surface-plasmon interaction as shown by Mahan.

One objective of the present work is to test the supposition that the interaction between molecule and surface-plasmon states originating from a plane surface is the major contribution to the observed enhanced Raman scattering. To this end we shall use the results of the preceding paper[8] in which we obtained coupled eigenstates of the composite system by carefully treating the interaction between molecule and surface plasmon including both spatially dispersive and spatially nondispersive metal dielectric functions. Here we use the coupled eigenstates as the intermediate states in a calculation of Raman scattering cross sections.

The results of our calculation is that it is improbable that the surface-plasmon–molecule interaction for a plane surface is the major microscopic source of the enhanced RS. It is found that in order for this mechanism to be the principal operative one, a number of important parameters in the model must have values which disagree by as much as an order of magnitude with known values for systems showing enhancement, such as the pyridine molecule on a silver surface. We find that the enhancement of RS on this mechanism should show typical resonant behavior with a pronounced and well-localized enhancement at an effective resonant frequency ω_L^m. The position of ω_L^m and the resonant enhancement ratio (relative RS intensity of adsorbed and isolated molecules) depends critically on the density of states or the dispersion relation of the surface plasmons. The enhancement ratio also depends sensitively on the relative interband contribution to the dielectric function in the frequency range of interest. Since the enhancement effect is of resonant type, the pronounced enhancement will only occur in a relatively small frequency range.

If all the parameters in the theory have optimal values, enhancements of as much as 10^5–10^6 can be obtained.[9] However, as will be illustrated and discussed below, we consider this to be improbable in general and even in serious contradiction to known parameter values in the cases of pyridine on silver. Most probably, the mechanism investigated here contributes some fraction $\sim 10^3$ of the total $\sim 10^6$ enhancement ratio. A notable omission in the present model is the consideration of the effect of surface roughness.

II. RAMAN SCATTERING INTENSITY RATIO FOR ADSORBED AND/OR ISOLATED MOLECULES

A. Theory

The RS matrix element between an initial state $|i\rangle$ and final state $|f\rangle$ is well known[10] to be of the form

$$M=\sum_j\left(\frac{\langle f|\hat{e}_s\cdot\vec{p}|j\rangle\langle j|\hat{e}_i\cdot\vec{p}|i\rangle}{E_j-E_i-\hbar\omega_L}+\frac{\langle f|\hat{e}_i\cdot\vec{p}|j\rangle\langle j|\hat{e}_s\cdot\vec{p}|i\rangle}{E_j-E_f+\hbar\omega_L}\right), \tag{1}$$

where $|j\rangle$ are the intermediate states, E_i, E_j, and E_f are energies of the initial, intermediate, and final states, respectively, and ω_L is the incident laser frequency. $\hat{e}_i$ and $\hat{e}_j$ are the polarization vectors of the incident and scattered light.

For the system of molecules adsorbed on a semi-infinite metal surface, the initial state $|i\rangle$ is taken to be the ground state of the coupled system, i.e., the molecule in the lowest electronic level and vibrational state, and no surface plasmons are excited. The electronic constituent of the final state $|f\rangle$ is the same as the initial state $|i\rangle$ but now the molecule is in an excited vibrational state: Therefore $E_f-E_i=\hbar\omega_v$. We have restricted ourselves to Stokes processes only, and we have only considered dipole-allowed transitions.

In the absence of the metal, choosing the intermediate states $|j\rangle$ to be all possible dipole-allowed excited electronic states and vibrational states of the molecule, the matrix M gives the usual result for molecular Raman scattering. The vibrational-state overlap integrals are important in determining the relative probability of transitions between different states. In this paper, we shall assume that the molecule has only one vibrational state coupled with the excited electronic level, and vibrational-state overlap integrals will be omitted. We also assume that the molecule has only one excited electronic level as we did in the preceding paper, denoted I.

In the presence of the metal surface, there are several important changes. First, the incident electric field felt by the molecules is changed to the so-called "primary field"[5] which is the combination of incident and reflected optical fields from the metal surface. Depending on the coefficient of reflectivity of the metal, the primary field has angular and polarization dependence.[5] Since we are not interested in angle- and polarization-dependent properties of RS in this paper, the effect of the primary field will be omitted. (All these properties should be the same as those given by Efrime and Metiu[5] in their classical theory.)

The intermediate states $|j\rangle$ are now chosen to be the new eigenstates of the coupled system in which surface plasmons influence excitations of the molecules. These eigenstates have been given in paper I, and here we shall use those results. As given in Eq. (23) of paper I, the states $|j\rangle$ are

$$|j\rangle=|\psi_E\rangle=a(E)|1,g\rangle+\sum_{\vec{q}}b_{\vec{q}}(E)|0,\vec{q}\rangle\,. \tag{2}$$

Since we have assumed that only one vibrational state is coupled to the electronic level, the matrix element M becomes

$$M\propto\int dE\,|a(E)|^2\left(\frac{\langle 0,g|\hat{e}_s\cdot\vec{p}|1,g\rangle\langle 1,g|\hat{e}_i\cdot\vec{p}|0,g\rangle}{E-\epsilon_0-\hbar\omega_L}+\frac{\langle 0,g|\hat{e}_i\cdot\vec{p}|1,g\rangle\langle 1,g|\hat{e}_s\cdot\vec{p}|0,g\rangle}{E-\epsilon_0-\hbar\omega_v+\hbar\omega_L}\right). \tag{3}$$

As mentioned above, the vibrational-state overlap integral is omitted. We remark that Eq. (3) is derived under the assumption that light cannot directly couple to the surface plasmon, thus the terms $b_q(E)$ of Eq. (2) do not appear.

The first matrix element in Eq. (3) is much larger than the second term as the laser frequency approaches the energy $E-\epsilon_0$. Near resonance the ratio of the scattering cross section for the adsorbed molecules and isolated molecules is given by

$$R=\frac{\left|\int dE\,\dfrac{|a(E)|^2}{E-\epsilon_0-\hbar\omega_L}\right|^2}{\left|\dfrac{1}{\epsilon_1-\epsilon_0-\hbar\omega_L}+\dfrac{1}{\epsilon_1-\epsilon_0-\hbar\omega_v+\hbar\omega_L}\right|^2}, \tag{4}$$

where ϵ_1 and ϵ_0 are the two energy levels of the molecule. According to Eq. (30) of paper I, $|a(E)|^2$ is of the form

$$|a(E)|^2=\frac{|V_E|^2}{[E-\epsilon_1-F(E)]^2+\pi^2|V_E|^4}\,. \tag{5}$$

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

$$\Delta(E)=\sum_{\vec{q}}\frac{|V_q|^2}{E-\epsilon_0-\hbar\omega_q-i\delta}, \tag{6}$$

where $\hbar\omega_q$ is the surface-plasmon energy and

$|V_q|^2$ is given in I by Eq. (15) or (8), depending on whether or not spatial dispersion or wave-vector dependence of the dielectric constant of the metal is taken into account. Substitution of Eq. (5) into Eq. (4) yields

$$R=\frac{(\epsilon_1-\epsilon_0-\hbar\omega_L)^2}{[\hbar\omega_L+\epsilon_0-\epsilon_1-F(\epsilon_0+\hbar\omega_L)]^2+\pi^2|V(\epsilon_0+\hbar\omega_L)|^4}\,. \tag{7}$$

The second term in the denominator of Eq. (4) has been neglected in the derivation of Eq. (7). The ratio R can be enormous at the effective resonance frequency ω_L^m such that

$$\hbar\omega_L^m+\epsilon_0-\epsilon_1-F(\epsilon_0+\hbar\omega_L^m)=0 \tag{8}$$

as long as

$$F(\epsilon_0+\hbar\omega_L^m)>|V(\epsilon_0+\hbar\omega_L^m)|^2\,.$$

Without including spatial dispersion, all plasmon states $\hbar\omega_q$ have energies less than $\hbar\omega_{sp}$, which is determined by the equation $\epsilon(\omega_{sp})+1=0$. $\epsilon(\omega)$ is the dielectric constant of the metal. The density of surface-plasmon states diverges at ω_{sp}. Thus by inspecting Eq. (6), we obtain

$$\operatorname{sgn}[F(\epsilon_0+\hbar\omega)]=\operatorname{sgn}[\operatorname{Re}\Delta(\epsilon_0+\hbar\omega)]=\operatorname{sgn}(\omega-\omega_{sp})\,. \tag{9}$$

B. Pyridine adsorbed on silver

We examined the consequences of this theory by applying it to the experimentally well-studied case of pyridine adsorbed on silver. In Fig. 1, we have plotted the logarithm of the function R given by Eq. (7) as a function of laser energy $\hbar\omega_L$.

A number of cases will be illustrated with and without inclusion of spatial dispersion and with and without inclusion of an interband contribution to the dielectric function of Ag. These will be denoted in text and in the figure as follows:

I: interband included, no spatial dispersion;

II: interband absent, no spatial dispersion;

I^s,II^s: spatial dispersion included in I,II, respectively.

For the pyridine molecule we take the electronic excitation energy to be[11] $\epsilon_1-\epsilon_0=4.31$ eV. The oscillator strength for these two levels in the z direction is chosen as $f_{01}^z=1$,[12] but in the perpendicular direction $f_{01}^\perp=0$.

For silver we can roughly estimate the surface-plasmon energy by using the simple Drude expression

$$\epsilon(\omega)=1-\omega_p^2/\omega^2\,, \tag{10}$$

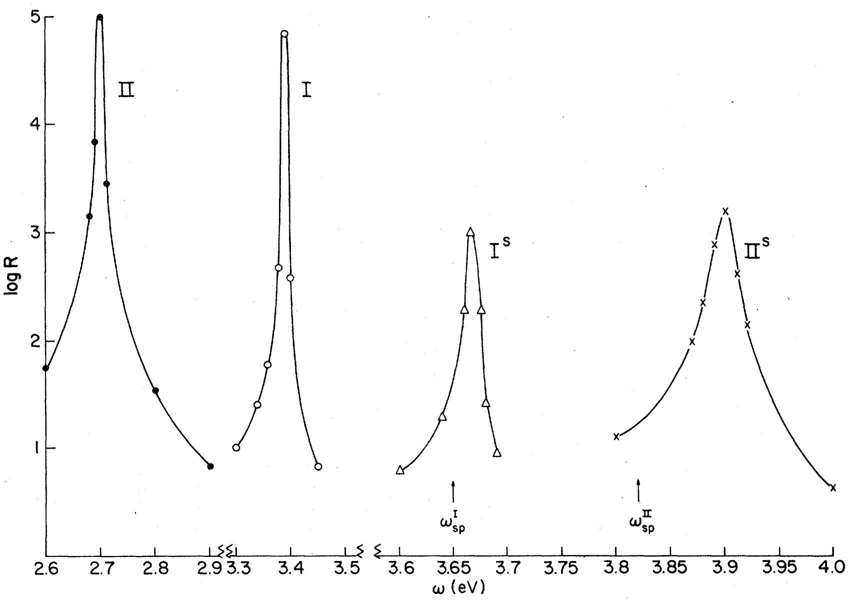

FIG. 1. Logarithm of the ratio of RS intensity R between adsorbed and isolated molecules as a function of frequency. The dielectric function of the metal is given by Eq. (11) for curve I and Eq. (10) for curve II. Curve I^S (II^S) has the same values for the parameters as curve I (II), except the wave-vector dependence is included in the dielectric function in the form given by Eq. (14). Note, for clarity, different scales were used in plotting different frequency regimes. The values of surface-plasmon frequency for simple Drude model (ω_{sp}^{II}) and for the model including background contribution in the dielectric function (ω_{sp}^{I}) are indicated. Parameters are taken to have values appropriate to the system pyridine on silver. Values used for curves are as follows. *No spatial dispersion*: I, Eq. (11), $a=32.48$ eV^2, $\omega_0=4.57$ eV, $\omega_{pf}=9.2$ eV, $\omega_{sp}^{I}=3.66$ eV; II, Eq. (10), $\omega_{pf}=5.4$ eV. *Spatial dispersion included*: I^S, Eqs. (11) and (14), $c/\beta=2.74\times10^2$ (other parameters as for I); II^S, Eqs. (10) and (14), c/β as for I^S (other parameters as for II). *In all cases* $R_z=1.5$ Å and $\Gamma=10^{-3}$.

where the volume-plasmon frequency $\hbar\omega_p = 5.4$ eV. Thus the frequency ω_{sp}, determined by the equation $\epsilon(\omega_{sp}) + 1 = 0$, is $\hbar\omega_{sp} = 3.82$ eV. Including an interband contribution to the dielectric function we have

$$\epsilon(\omega) = 1 - \omega_{pf}^2/\omega^2 + \epsilon_b(\omega) \tag{11}$$

and

$$\epsilon_b(\omega) = \frac{a/\hbar^2}{\omega_0^2 - \omega^2} . \tag{12}$$

The parameters are chosen to approximately fit the measured optical dielectric constant of Ag (Ref. 13): $a = 32.48\ (\mathrm{eV})^2$, $\hbar\omega_0 = 4.57$ eV, and $\hbar\omega_{pf} = 9.2$ eV. Thus $\hbar\omega_{sp} = 3.66$ eV.

We can now calculate the functions given in Eq. (8) and locate the effective resonance frequency ω_L^m. Notice that $F(E)$ and $|V_E|^2$ in Eq. (7) are evaluated using Eqs. (37) and (44) of I, where the lifetime of surface plasmon is chosen as $\Gamma = 10^{-3}$ eV. The consequence of smaller Γ and $|V_E|^2$, as will be seen immediately below, is a higher enhancement ratio (at ω_L^m) but a narrower frequency range over which enhancement occurs. A larger Γ will decrease the calculated enhancement ratio.

In Fig. 1, curves *I* and *II* illustrate the quantitative prediction of the surface-plasmon mechanism for the enhancement ratio in the absence of spatial dispersion in Ag. Both curves show a narrow resonance effect, with 2 orders of magnitude enhancement (10^3 to 10^5) in the ranges 2.7 ± 0.02 eV and 3.39 ± 0.01 eV, respectively. The peak position ω_L^m of curve *I* is greatly shifted from peak of curve *II*, but the height of peak *I* is approximately the same as *II*. This can be understood from Eqs. (7) and (8), since at $\omega = \omega_L^m$, the height of the peak is given by

$$R^m = \left| \frac{F(\epsilon_0 + \hbar\omega_L^m)}{\pi\, |V(\epsilon_0 + \hbar\omega_L^m)|^2} \right|^2 , \tag{13}$$

where the position of the peak, as given by Eq. (8), depends on F only. The presence of ϵ_b reduces the coupling between the surface plasmon and dipole, i.e., $V_{\vec q}$ of Eq. (8) in I, thus reducing the values of $F(E)$ and $|V_E|^2$. But the ratio of $F(E)$ and $|V_E|^2$ is relatively unchanged.

For both curves *I* and *II* in Fig. 1, the distance between the molecule and the surface is chosen as $R_z = 1.5$ Å. As discussed in paper I, Eqs. (39) and (44), the functions $F(E)$ and $|V_E|^2$ are proportional to R_z^{-3}. Therefore the positions of the peaks ω_L^m of curves *I* and *II* are very sensitive to the parameter R_z [Eq. (8)]. However, it follows from Eq. (13) that the height of the peak is independent of R_z.

We emphasize that R is not the Raman intensity of the adsorbed molecule but the ratio between the adsorbed molecule and the isolated molecule. Equation (13) has meaning only where we are in resonance and where there exists a solution ω_L^m to Eq. (8). For large R_z, thus small $F(E)$, Eq. (8) may or may not have a solution ω_L^m, depending upon the parameters $\epsilon_1 - \epsilon_0$ and ω_{sp}.

We now turn to include the effect of spatial dispersion which we include (as in I) in the longitudinal dielectric function of the metal in the form

$$\epsilon(\omega, \vec{k}) = 1 + \epsilon_b(\omega) - \frac{\omega_{pf}^2}{\omega^2 - \beta^2 k^2} . \tag{14}$$

As shown by Fuchs and Kliewer,[14] the dispersion relation for surface plasmons and density of states obtained from Eq. (14) are quite different from those obtained from Eq. (11) in which the wave-vector dependence is omitted. Including the effect of spatial dispersion, surface-plasmon states possessing large wave vectors have energies above ω_{sp}, contrary to the case without consideration of spatial dispersion. Thus Eq. (9) is no longer correct, and ω_L^m may be larger than ω_{sp}. For Ag the parameter β in Eq. (14) is chosen as $c/\beta = 2.741 \times 10^2$, where c is the velocity of light.

In Fig. 1 curves I^s and II^s show the effect of spatial dispersion on the predicted enhancement ratio. First, note the significant shift of the effective resonance frequency ω_L^m due to the mentioned consequences of change in density of states. Second, the effect of spatial dispersion not only changes the position ω_L^m of the peak but also reduces the maximum ratio R^m by an order of magnitude. This reduction of R^m is caused by the increase of $|V(\epsilon_0 + \hbar\omega_L^m)|^2$ which is much larger for $\omega_L^m > \omega_{sp}$ than for $\omega_L^m < \omega_{sp}$ in the absence of spatial dispersion. Note that besides β, all other parameters are the same between curves II^s (I^s) and *II* (*I*), which are to be compared.

III. SUMMARY

Using the eigenstates of the coupled system, surface plasmons for a plane surface and molecular excitations of the adsorbed molecules as intermediate states in evaluating the RS matrix element, we calculated the RS intensity ratio between adsorbed and isolated molecules. The ratio R has a resonance denominator, producing a very sharp and narrow peak as function of laser frequency. The maximum ratio R^m, which is at the resonant frequency ω_L^m, may achieve a value of order of 10^3 to 10^6 depending upon the parameters and various approximations used.

Two functions $F(E)$ and $|V_E|^2$ were derived in paper I; these determine the resonant frequency

ω_L^m, the width, and the maximum ratio R^m. There are several important parameters needed to evaluate these two functions. The two most important parameters, in our opinion, are the distance R_z between the molecule and the surface and the oscillator strength f_{01} of the bare molecular levels. Both $F(E)$ and $|V_E|^2$ are directly proportional to f_{01} and R_z^{-3} in the case of neglect of the effect of spatial dispersion of the metal. Including the effect of spatial dispersion $F(E)$ and $|V_E|^2$ is still very sensitive to R_z though not proportional to R_z^{-3} as shown in I.

Besides the intrinsic lifetime Γ of the surface-plasmon states, all other parameters can be more or less determined from the experimental values of optical dielectric constants of the metal and the energy levels of the molecule. The value of Γ, which is the lifetime of surface plasmon in the absence of adsorbed molecules, is given a value of 10^{-3} eV in our numerical calculation. The "real" value of Γ is most likely larger than 10^{-3} eV and has been given as $\Gamma \sim 0.08$ eV.[15] The corresponding enhancement ratio would decrease by an order of magnitude.

By using a fictitious dielectric constant for Ag, i.e., neglecting the large interband dielectric constant, we obtain the enhanced RS intensity (curve *II* of Fig. 1) in the visible frequency range where experimental results are reported.[2] As expected, this result is in qualitative agreement with the result of the classical image-field theory given by Efrima and Metiu.[5] But such a result is obtained if we assume $R_z \lesssim 1.5$ Å and $f_{01} \gtrsim 1$. The large oscillator strength is unphysical; the value of R_z is questionable. Much more serious is the required neglect of spatial dispersion and of the interband dielectric coefficient ϵ_b: Both need to be included if one is to obtain agreement with known optical properties of Ag. If ϵ_b is included, then R_z has to be less than 1 Å and f_{01} to be greater than 1 to have enhanced RS intensity in the visible frequency region. But the inclusion of spatial dispersion will completely shift the enhanced RS intensity out of the visible frequency range.

Thus to have the resonant RS in the experimentally reported frequency range, we have to use very restricted values of parameters R_z and f_{01} and must neglect spatial dispersion in the theory given above (this is also true for Efrima and Metiu).[5] In our opinion, choosing the value of the oscillator strength f_{01} to be equal to or larger than 1 is unjustified. Efrima and Metiu[5] have obtained a large value for f_{01} from the measured static polarizability α_0 of pyridine. But this polarizability α_0 includes contributions from *all* the excited levels of pyridine instead of just the lowest excited states as was the case considered by Efrima and Metiu[5] and us. The real value of the oscillator strength between the lowest excited value of the oscillator strength between the lowest excited state and the ground state of pyridine could be of the order of 10^{-1} or less.[11] Thus neglecting spatial dispersion, the resonant RS will not occur at the visible frequency range. Hexter and Albrecht[6] have also considered using new states of the coupled surface plasmons and molecular levels as intermediate states in resonant RS. But explicit expressions for the coupled states were not given. Their final RS matrix elements disagree with our result.

Before we give conclusions, we shall briefly review the many approximations used in our calculation:

(1) The molecule is assumed to be a two-level system. Since surface plasmons only couple strongly to states with energies close to their energies, the assumption of the two-level molecule is a good approximation provided that other excited states have much higher energy.[11]

(2) As discussed in paper I, a dipole approximation is used in calculating the coupling matrix element between the surface plasmon and molecular levels. This approximation can be easily improved to include multipole terms.

(3) The molecule is assumed to be weakly adsorbed on a metal surface. The energy levels and oscillator strength of the molecule are not strongly influenced by the metal. The surface-plasmon dispersion relation of the metal is also unchanged by the presence of the molecule.

(4) Surface roughness has been completely neglected. Surface roughness will change the surface-plasmon dispersion relation. It will also provide a direct coupling between light and surface plasmons; thus the RS matrix element will be modified to include extra terms. However, the position of the RS peak ω_L^m should not be affected.

(5) A simple hydrodynamical approximation is used for the wave-vector-dependent dielectric function. Specular reflection is used for the boundary condition. The density of surface-plasmon states and dispersion relation will be changed quantitatively when a different form of dielectric function is used or a different boundary condition is applied. This simple form of dielectric function is used as an example to show the importance of spatial dispersion.

On the basis of our work reported here we conclude that surface-plasmon–molecule excitation coupling for a plane surface using reasonable values of parameters, may be responsible for some fraction of the enhancement in RS due to adsorption of molecules on the metal surface, but the major mechanism probably resides in other couplings.

Note added. After this work was completed and this paper was submitted, compelling evidence has been amassed on the effect of metal surface roughness on enhanced Raman scattering from pyridine on Ag surfaces.[16] While there had been many reports[17] of surface roughness effects from the very beginning of work on the surface-enhanced Raman scattering phenomenon,[1-3] the popularity and relative simplicity of the proposed classical "image-dipole mechanism" of a molecular dipole above a plane metal surface[4,6,7] led us to formulate the present quantum approach in this paper and the preceding as an attempt to quantitatively test the model. It is now evident that a theory of the surface-enhanced Raman scattering requires system eigenstates for which proper account is taken *a priori* of the surface roughness. Work along these lines is in progress.

ACKNOWLEDGMENTS

We thank Professor R. Birke, Dr. O. Genack, Professor J. Gersten, Professor J. Lombardi, Dr. D. N. Pattanayak, and Dr. D. Weitz for discussions. Special thanks are given to Professor N. Tzoar for discussion of the importance of spatial dispersion effects. This work was supported by the Army Research Office Grant No. DAAG29-79-G-0040, the National Science Foundation Grant No. DMR78-12399, and the PSC-BHE Faculty Research Award No. 13084.

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