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Raman line shifts of adsorbed molecules in surface Raman spectroscopy

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A general electromagnetic formulation for the calculation of the Raman line shifts in surface Raman scattering from adsorbed molecules is given. These shifts in our model arise from the electromagnetic interaction between the molecules and the metal. Assuming a Thomas-Fermi model for the metal, explicit results for shifts as a function of the distance of the molecules from the spherical metallic surface are presented. The deviations from the classical $1/d^3$ dependence are also discussed.

I. INTRODUCTION

Most of the work[1–3] on the surface-enhanced Raman scattering has been concerned with large enhancements of Raman cross sections of molecules adsorbed on metals, including the investigation of various possible mechanisms, such as electromagnetic,[1] conduction-electron tunneling,[1] resonant charge-transfer, etc., that could lead to large cross sections. However, questions like the shape of the resonance Raman lines of the adsorbed molecules and their frequency shifts compared to the corresponding free molecular values have been only partially investigated,[4] partly because such questions can only be answered completely if one can examine a realistic microscopic model for the molecule-substrate system. At atomic distances d from the surface, both the classical electrodynamic self-image renormalization of the vibrational frequencies due to the presence of the polarizable substrate as well as the exact nature of the charge redistribution in possible metal-molecule chemical bonding may play the essential roles in governing the line shapes and frequency shifts.

In a recent work,[3] an explicit two-oscillator electromagnetic model for the surface-enhanced Raman scattering was proposed. Apart from the calculation of the overall integrated enhancement factor, this model also enables one to calculate the Raman line-shape function, including the frequency shift, by explicitly taking into account the electromagnetic interaction between the molecule and the metal. Since experimentally one can measure both the total enhancement of the cross section and the frequency shift simultaneously, it is of importance to calculate both these quantities using the same model and compare them with experimental results in a given situation. Investigations of such correlations should be quite significant in this field. As far as the electromagnetic mechanism is concerned, the two-oscillator model of Ref. 3 is capable of providing a simple framework for calculating the line shape and frequency shift. In this paper we plan to use this model to calculate such shifts by including spatial dispersion of the metal dielectric function, which cannot be ignored for small d.

The organization of this paper is as follows. In Sec. II we briefly describe the two-oscillator model for the surface Raman scattering and discuss the factors which determine the Raman line-shape function. In Sec. III we calculate the shifts for molecules adsorbed on metallic spheres, in which the spatial dispersion of metallic dielectric function has been included. In Sec. IV the results of the numerical calculations are given for a wide range of parameters such as the radius a of the sphere, distance d of the molecule from the surface, etc. The inclusion of spatial dispersion is shown to lead to a considerable deviation from the classical $1/d^3$ dependence for the frequency shift.

II. THE MODELS FOR SURFACE RAMAN SCATTERING AND THE RAMAN LINE SHAPE FUNCTION

In a previous paper two of us have proposed a two-oscillator model[3] for the surface Raman scattering. In this model the electronic motion (relative amplitude $\mathbf{x}$) and ionic motion (amplitude $\mathbf{Q}$) in the adsorbed molecule are assumed to be represented by interacting oscillators in the presence of the polarizable substrate. The interaction between the electronic oscillator and the ionic oscillator with charge Z, in the molecule, was taken to be of the form

$$V^{(3)}_{\text{Raman}} = C_{ijk} x_i x_j Q_k , \quad i,j,k = 1,2,3 , \tag{2.1}$$

where summations over repeated indices are implied. This is the part of the trilinear interaction responsible for Raman scattering. These two charged oscillators also interact with the electromagnetic field distribution in the presence of the substrate medium and the molecule. The net electromagnetic field distribution consists of the incident field at the frequency ω_l, the fields produced by the substrate medium, and the additional self-field of the molecule because of the presence of the substrate. The external field $\mathbf{E}^{(0)}$ on the molecule is defined as the field produced at the molecular site $\mathbf{r}_0$ by the incident field $\mathbf{E}^{\text{inc}}$, in the presence of the substrate medium but without the molecule. This obviously depends on the characteristics of the polarizable substrate and plays the role of the external field acting on the molecule. Of course, the additional self-fields produced by the molecular motion in the presence of the substrate renormalize the electronic, ionic, and Raman polarizabilities of the molecule. The renormalization and $\mathbf{E}^{(0)}$ depend critically on the characteristics of the substrate and its geometrical shape. For spontaneous Raman scattering at frequency ω_s, in the limit of large ionic mass M and in the limit of diagonal (linear) electronic polarizability $\alpha_{ii}(\omega)$ of the molecule, we found that the ratio $F(\omega_s)$ of the cross section in the presence and in the absence of substrate medium is

$$F(\omega_s)=\frac{[G(\mathbf{r}\rightarrow\infty,\mathbf{r}_0,\omega_s)\cdot R(\omega_s,\omega_l):\mathbf{E}^{(0)}(\omega_l)\mathbf{Q}^*(\omega)]^2}{\{\underline{G}_0(\mathbf{r}\rightarrow\infty,\mathbf{r}_0,\omega_s)\cdot\underline{R}^{(0)}(\omega_s,\omega_l):\mathbf{E}^{\text{inc}}(\omega_l)[\mathbf{Q}^{(0)}(\omega)]^*\}^2}\ . \tag{2.2}$$

Here $G(\mathbf{r},\mathbf{r}_0,\omega_s)$ is the electromagnetic Green's dyadic which depends on the shape and the dielectric function of the material medium and $\underline{G}_0$ is the free-space Green's dyadic

$$\left[-\nabla^2+\boldsymbol{\nabla}\boldsymbol{\nabla}\cdot-\frac{\omega^2}{c^2}\right]\underline{G}_0(\mathbf{r},\mathbf{r}_0,\omega)=4\pi\delta(\mathbf{r}-\mathbf{r}_0)\underline{I}\ . \tag{2.3}$$

The equation for $\underline{G}$ is more involved and will be given in Sec. III. In Eq. (2.2), $\mathbf{R}^{(0)}$ is the free-space Raman tensor, whereas $\underline{R}$ is in the presence of the medium and is given by

$$R_{ijk}(\omega_s,\omega_l)=\frac{R_{ijk}^{(0)}(\omega_s,\omega_l)}{\left[1-\frac{\omega_s^2}{c^2}\alpha_{ii}(\omega_s)G_{ii}^{(s)}(\omega_s)\right]\left[1-\frac{\omega_l^2}{c^2}\alpha_{jj}(\omega_l)G_{jj}^{(s)}(\omega_l)\right]}\ . \tag{2.4}$$

In Eq. (2.4), $\underline{G}^{(s)}(\omega)$ $[=\underline{G}^{(s)}(\mathbf{r}_0,\mathbf{r}_0,\omega)=\underline{G}-\underline{G}_0]$ depends on the substrate medium and $\underline{G}^{(s)}\rightarrow 0$ in the absence of the medium. Because of thermal motion, $Q(\omega)$ is a fluctuating quantity and its correlation function can be obtained from the fluctuation-dissipation theorem and the linear-response theory. As shown in Ref. 3, we have the result

$$\langle Q_i^*Q_j\rangle_\omega=\frac{\hbar}{\pi}[1+n(\omega)]\text{Im}\left[M(-\omega^2+\omega_0^2-i\omega\gamma)I-\frac{Z^2\omega^2}{c^2}\underline{G}^{(s)}(\omega)\right]_{ij}^{-1}\ , \tag{2.5}$$

where $n(\omega)$ is the thermal occupation number and γ is the damping associated with the ionic motion. The fluctuation is related to the ionic polarizability $\beta^{(0)}(\omega)$

$$\beta^{(0)}(\omega)=\frac{Z^2}{M(\omega_0^2-\omega^2-i\omega\gamma)}\underline{I}\ , \tag{2.6}$$

which is renormalized due to the self-fields produced by the presence of the substrate. The renormalized polarizability $\beta(\omega)$ is

$$\beta(\omega)=\left[1-\frac{\omega^2}{c^2}\underline{\beta}^{(0)}(\omega)\cdot\underline{G}^{(s)}(\omega)\right]^{-1}\cdot\underline{\beta}^{(0)}(\omega)\ . \tag{2.7}$$

The renormalization of the ionic polarizability is similar to the renormalization of the electronic polarizability which has been previously discussed.[3]

The Raman line shape is determined from (2.5). Compared to the isolated molecule case, we now see from (2.5) that the interaction of the molecule with the medium results in the characteristic shifts and the widths of the Raman line. These shifts and widths obviously depend on the real and imaginary parts of the surface-dependent Green's function. An estimate of the shifts and widths can be made for specific models of the medium shape and its dielectric properties. In the next section we calculate such shifts by assuming metal particles to be spherical and by taking the Thomas-Fermi model of the metal.

III. RAMAN LINE SHIFTS FOR MOLECULES ADSORBED ON METALLIC SPHERES

We will now evaluate the Raman line shifts for a specific model, viz., molecules adsorbed on metallic spheres; the geometrical arrangement is sketched in Fig. 1. It is known that if the molecules are located along the z axis and if the incident field is polarized along the z axis, then the most significant component of the Raman tensor is R_{zzz}. Hence the Raman line shape will be determined from $\langle Q_z^*Q_z\rangle_\omega$. Assuming that $\omega\approx\omega_0$, and that $\underline{G}^{(s)}(\omega)$ is *diagonal* [cf. (3.8)], we can write (2.5) as

$$\langle Q_z^*Q_z\rangle_\omega=\frac{\hbar}{\pi}[1+n(\omega)](2\omega_0M)^{-1}\,\text{Im}(-\omega+\omega_R-i\gamma_R)^{-1}\ , \tag{3.1}$$

where

$$\omega_R \approx \omega_0 - \frac{Z^2\omega_0^2}{2Mc^2\omega_0}\mathrm{Re}G_{zz}^{(s)}(\omega_0) \ , \tag{3.2}$$

$$\gamma_R \approx \frac{Z^2\omega_0^2}{2Mc^2\omega_0}\mathrm{Im}G_{zz}^{(s)}(\omega_0) + \frac{\gamma}{2} \ . \tag{3.3}$$

Our further analysis depends on the structure of the Green's function $G^{(s)}$, which in turn depends on the characteristics of the substrate medium. In the previous work,[3] the substrate was characterized by a local dielectric function. However, we will now use a nonlocal dielectric function for the medium. This choice is necessary because of the closeness of the molecule to the surface and because we essentially need the zero-frequency dielectric function in the calculation of Raman shifts. Our basic results of Sec. II remain valid even when we characterize the medium by nonlocal dielectric function, provided we correctly calculate $\mathbf{E}^{(0)}$ and $\underline{G}$.

The Green's function $\underline{G}$ for $\mathbf{r},\mathbf{r}_0$ outside the substrate medium, satisfies

$$\left[\nabla\times\nabla\times\underline{G}(\mathbf{r},\mathbf{r}_0,\omega) - \epsilon_0(\omega)\frac{\omega^2}{c^2}\right]\underline{G}(\mathbf{r},\mathbf{r}_0,\omega) = 4\pi\delta(\mathbf{r}-\mathbf{r}_0)\underline{I} \ . \tag{3.4}$$

The boundary value problem can be solved by giving Green's-function equations for r inside the medium and the boundary conditions. Such a boundary value problem is solved in detail in Ref. 5 for the following model for the nonlocal dielectric function

$$\epsilon_t(\mathbf{k},\omega) \approx \epsilon_t = 1 - \frac{\omega_p^2}{\omega^2 + i\omega\Gamma} \ , \tag{3.5}$$

$$\epsilon_l(\mathbf{k},\omega) \approx 1 - \frac{\omega_p^2}{\omega^2 + i\omega\Gamma - \beta k^2} \ . \tag{3.6}$$

In the hydrodynamical approximation $\beta = \frac{3}{5}$(Fermi velocity)^2. Eventually we will take the low-frequency limit when β will be related to the Thomas-Fermi wave vector

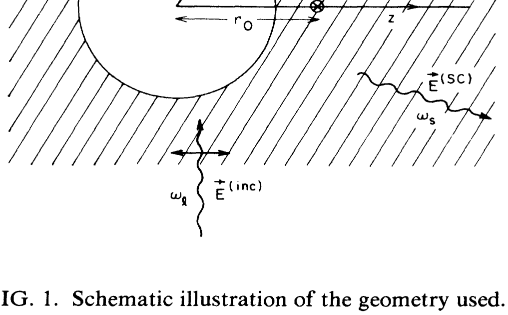

FIG. 1. Schematic illustration of the geometry used.

$$\epsilon_l(\mathbf{k},\omega) \rightarrow 1 + \frac{k_{\mathrm{TF}}^2}{k^2} \quad \text{as } \omega \rightarrow 0 \ . \tag{3.7}$$

In practice, one is dealing with small spheres and with molecules lying close to the surface, i.e., with sizes and distances which are much smaller than a wavelength. In such cases it is sufficient to ignore the retardation effects. In a previous paper[5] it has been shown that for a sphere of radius a contained in a medium with dielectric constant ϵ_0

$$\lim_{c\rightarrow\infty}\left[\frac{\omega^2}{c^2}\underline{G}^{(s)}(\mathbf{r}_0,\mathbf{r}_0,\omega)\right] = \frac{1}{\epsilon_0}\sum_{n=1}^{\infty}\frac{a^{2n+1}}{r_0^{2n+4}}nX_n\left[(n+1)\hat{z}\hat{z} + \frac{n}{2}(\hat{x}\hat{x}+\hat{y}\hat{y})\right] , \tag{3.8}$$

where, in terms of spherical Bessel function j_n,

$$X_n = \frac{\left[\dfrac{(k_l a)j_n'(k_l a)}{n j_n(k_l a)}\right]\left[1-\dfrac{\epsilon_0}{\epsilon_t}\right] - \left[\epsilon_0 - \dfrac{\epsilon_0}{\epsilon_t}\right]}{\left[\dfrac{k_l a j_n'(k_l a)}{n(n+1)j_n(k_l a)}\right]\left[n + \dfrac{\epsilon_0}{\epsilon_t}(n+1)\right] + \left[\epsilon_0 - \dfrac{\epsilon_0}{\epsilon_t}\right]} , \tag{3.9}$$

$$k_l^2 = (\omega^2 - \omega_p^2 + i\omega\Gamma)/\beta \ . \tag{3.10}$$

Raman line shifts can now be calculated by using (3.8) in (3.2). However, one can obtain a simplified expression by taking the low-frequency limit of (3.9), whence we get

$$X_n \rightarrow \frac{[bj_n'(b)/nj_n(b) - \epsilon_0]}{[bj_n'(b)/(n+1)j_n(b) + \epsilon_0]} \ ,$$

$$b = iak_{\mathrm{TF}} \ . \tag{3.11}$$

One can easily see that such a limit is justified, e.g., for Pyridine A_1 on Ag, $\omega_p/\omega_0 = \lambda_0/\lambda_p = (1/\lambda_p)/(1/\lambda_0) = 1/(1365\times10^{-8})(992) \sim 10^2$ and then

$$k_l^2 = \frac{-\omega_p^2}{\beta}\left[1 - \frac{\omega^2}{\omega_p^2}\right] \sim -\frac{\omega_p^2}{\beta} \sim -k_{\mathrm{TF}}^2 \ .$$

Note that X_n is real and hence, in this limit, the corrections to the width of the Raman line are unimportant. The relative shift $\Delta = (\omega_R/\omega_0 - 1)$ can now be written as

$$\Delta = \frac{Z^2 k_{\mathrm{TF}}^3}{2M\omega_0^3}S = -\frac{\beta^{(0)}(0)}{2}k_{\mathrm{TF}}^3 S \ , \tag{3.12}$$

where

$$S = \frac{1}{\epsilon_0}\sum_{n=1}^{\infty}\frac{(k_{\mathrm{TF}}a)^{2n+1}}{(k_{\mathrm{TF}}r_0)^{2n+4}}n(n+1)X_n \ . \tag{3.13}$$

The relative shift has been expressed in terms of the static ionic polarizability $\beta^{(0)}$ and the function S which depends on (i) the size of the sphere, (ii) distance of the molecule from the surface, and (iii) ϵ_0—the dielectric constant of the medium in which molecules and substrate are embedded.

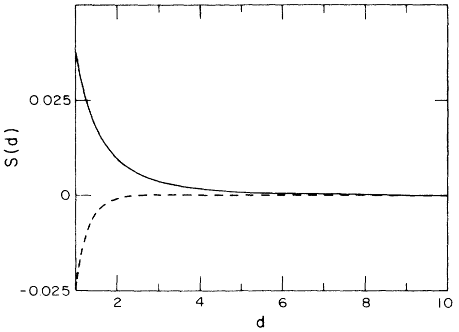

FIG. 2. The shift S ($\Delta \propto S$) as a function of the distance $d = k_{\mathrm{TF}}(r_0 - a)$ of the molecule from the surface. The radius of the sphere is taken as $\Delta_0(k_{\mathrm{TF}})^{-1}$. The embedding medium is taken either as a vacuum (solid curve) or a dielectric with $\epsilon_0 = 2.25$ (dotted curve).

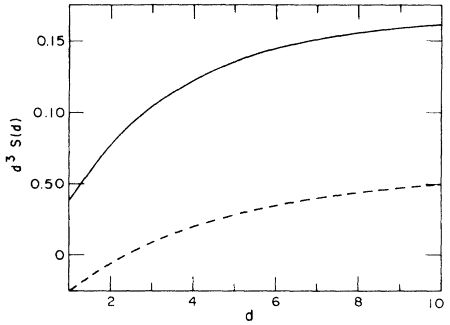

FIG. 3. Behavior of $d^3S(d)$ as a function of d. Other parameters are the same as in Fig. 2.

IV. NUMERICAL RESULTS FOR RAMAN LINE SHIFTS

In this section we present some estimates of the Raman shifts for typical cases such as CO on Ag and Pyridine A_1 on Ag—we introduce a frequency scale in terms of the proton mass M_p, electronic charge e, and Bohr radius a_0,

$$\Omega_p^2 = e^2 / M_p a_0^3 \ , \tag{4.1}$$

and then rewrite (3.12) as

$$\Delta = -\frac{Z^2 M_p}{2e^2 M}(k_{\mathrm{TF}} a_0^3) S(\lambda_0/\lambda_p)^2 \ . \tag{4.2}$$

Note that λ_p corresponds to 5100 cm^{-1} and for Ag, $k_{\mathrm{TF}} a_0 \approx 0.9$. Making then rough estimates for Z^2M_p/e^2M, we find the following.

(i) For Pyridine A_1 on Ag: $\lambda_0^{-1} = 992$ cm^{-1}, $Z^2M_p/e^2M \sim 0.04$,

$$\Delta \cong -0.4S \ . \tag{4.3}$$

Note that the reported shift is of the order of 1006 cm^{-1} -992 cm$^{-1} \approx 14$ cm^{-1}.

(ii) For CO (2035 cm^{-1}) mode on Ag: $\lambda_0^{-1} = 2135$ cm^{-1}, $Z^2M_p/e^2M \sim 0.1$,

$$\Delta \approx = 0.21S \ . \tag{4.4}$$

The experimentally reported shift is of the order of 2142 cm^{-1} $-$ 2135 cm^{-1} $=$ 7 cm^{-1}. Our theoretical results already show that for the CO (2035 cm^{-1}) mode on Ag, the shifts are smaller, in agreement with experiment.

The actual relative shift will depend on the magnitude of S. We have evaluated S numerically for several values of $k_{\mathrm{TF}}a$ and $k_{\mathrm{TF}}r_0$ and the results for some typical cases are shown in Figs. 2 and 3. The convergence of the series for S is rather poor for molecules too close to the sphere or for larger sphere sizes. In such cases, we have used a Padé summation technique. Figure 2 shows the variation of S with the distance $k_{\mathrm{TF}}(r_0 - a) \equiv (d)$ of the molecule from the surface for two different values of the dielectric function of the embedding medium. The sign of Δ depends on the distance of the molecule and the dielectric properties of the embedding medium. Our analysis shows that the shifts are much smaller[6] unless the molecule is within an angstrom or so from the surface. For example, for $d = 1$, $\epsilon_0 = 2.25$ and for the CO mode we find that $\Delta\omega_0 \approx 10$ cm^{-1}. A similar result holds for Pyridine (A_1 mode) adsorbed or Ag. Note that $\Delta < 0$ for $\epsilon_0 = 1$. We emphasize that a detailed comparison with experimentally reported values is difficult since the shifts are going to be affected by a variety of other factors such as the presence of other molecules. Moreover, at such small distances other mechanisms such as charge transfer may also contribute to the shifts. Our electromagnetic model shows how a reasonable order-of-magnitude estimate for shifts can be made. Such an estimate is similar to the observed values. Finally, in Fig. 3, we plot $d^3 s(d)$ as for the case of a medium without spatial dispersion; the shifts are expected to have the dependence[7] $S \sim (d^{-3})$. Thus Fig. 3 gives the deviations due to our use of the Thomas-Fermi model of the metal. Our analysis shows that the deviations from the classical d^{-3} dependence are quite significant.

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[1] The literature on this subject is very exhaustive. We refer to the review papers by H. Metiu; J. I. Gersten and A. Nitzan; S. S. Jha; M. Moskovits and D. P. Dilella; M. Fleischmann and J. R. Hill; B. Pettinger and H. Wetzel; J. A. Creighton; E. Burstein, S. Lundquist, and D. L. Mills; and P. F. Liao, in *Surface Enhanced Raman Scattering*, edited by R. K. Chang and T. E. Furtak (Plenum, New York, 1982). Also, see D. S. Wang, M. Kerker, and H. Chew, Appl. Opt. **19**, 2315 (1980);

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[2] Cf. review articles by K. Arya and R. Zeyher, and A. Otto, in *Light Scattering in Solids IV,* Vol. 54 of *Topics in Applied Physics,* edited by M. Cardona and G. Güntherot (Springer, Heidelberg, 1984); also see M. E. Lippitsch, Phys. Rev. B **29**, 3101 (1984); S. S. Jha and J. C. Tsang, *ibid.* **28**, 4216 (1983); S. S. Jha, Surf. Sci. **158**, 190 (1985).

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[4] R. F. Willis, A. A. Lucas, and G. D. Mahan, in *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis, Vol. 2, Adsorption at Solid Surfaces,* edited by D. A. King and D. P. Woodruff (Elsevier, Amsterdam, 1983), p. 58.

[5] G. S. Agarwal and S. V. ONeil, Phys. Rev. B **28**, 487 (1983).

[6] It must be noted that the shifts reported in this work are much smaller than those reported in Ref. 5, where shifts at optical frequencies were computed. This difference arises as optical frequencies shifts become fairly large due to the excitation of surface plasmons, whereas at the frequencies of Raman transitions, such surface plasmon resonances do not contribute.

[7] The corresponding function S for a molecule close to a plane surface is $\int_0^\infty dx\, x^2 e^{-2xd}[(1+x^2)^{1/2}-x]^2$ [cf. J. Heinrich, Phys. Rev. B **8**, 1346 (1973)]. The behavior of $d^3S(d)$ found for a sphere is similar to that for a plane (cf. Heinrich's Fig. 2 curve marked γ_{sda}).