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Surface-enhanced Raman scattering in Ag-pyridine sols

Thomas L. Ferrell

Health and Safety Research Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

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The coupled system of an adsorbed atom and a spherical surface plasmon is considered. Application to surface-enhanced Raman scattering is shown by regarding the coupled system's eigenstates as intermediate states in the scattering process.

Lee and Birman have recently analyzed certain features of coupled molecule-surface states for a plane surface.¹ For the simple case of nonretarded electrodynamics and a purely frequency-dependent dielectric response function, one may easily extend their results to the interesting case of a spherical surface. This is accomplished in the present paper.

Also, Birman and Lee have given some consideration to surface-enhanced Raman scattering² (SERS). Their approach, while not directly applicable to SERS (due to their use of a plane surface), provides a basis for further work, as they indicated by their comments on surface roughness. The early observations of SERS from Ag sols in aqueous pyridine by Creighton, Blatchford, and Albrecht³ show that the spherical geometry is also important. Working with the aforementioned simplifications, the spheres being small enough (~ 10 nm) for a nonretarded approach to be effective, it is possible to obtain a relevant analysis. That is, one may use the eigenstates of the coupled molecule-sphere system as intermediate states in SERS. Unlike the planar case, the spherical case has no selection rule preventing coupling of the light and surface plasmons.

As in the treatment given by Ref. 2, the eigenenergy appears in the denominator of the perturbative analysis of SERS in second order, and one finds the ratio of this denominator to the denominator obtained in the second-order treatment of ordinary Raman scattering. This ratio is then related to the Raman enhancement. While the present paper omits the effects due to the alterations in the numerator of the second-order perturbation analysis, it shows there is a resonance which strongly af-

fects the above ratio with reasonable choices of the experimental parameters.

For spherical surface plasmons, one has a Hamiltonian⁴

$$H = \sum_{l=0}^{\infty} \sum_{m=0}^l \sum_{p=\pm 1} \hbar \omega_l b_{lmp}^\dagger b_{lmp}, \quad (1)$$

where the surface plasmon frequency of the l th mode of oscillation is found in terms of the bulk plasmon resonance ω_p from the dispersion relation. For a medium with dielectric constant ϵ_0 outside the sphere, and with $\epsilon_b(\omega)$ the bound-electron contribution to the dielectric function of silver, one has

$$\omega_l^2 = \frac{\omega_p^2 l}{l + l\epsilon_b(\omega) + \epsilon_0(l+1)}, \quad (2)$$

which is independent of the azimuthal indices m and p .

If one models the electronic states of an adsorbed molecule as a two-level system, the Hamiltonian for this is

$$H_M = \sum_{n=0,1} E_n C_n^\dagger C_n = E_0 |0\rangle\langle 0| + E_1 |1\rangle\langle 1|, \quad (3)$$

where E_0 and E_1 are the ground-state and excited state energies, respectively, and C_n^\dagger and C_n create and destroy state n , respectively.

The Hamiltonian for the interaction between the atom and the surface plasmon field may be written with the SERS intermediate states in mind. The interaction Hamiltonian is here taken to be

$$H_{\text{int}} = \sum_{l,m,p} \Gamma_{lm}^p (b_{lmp}^\dagger C_0^\dagger C_1 + b_{lmp} C_1^\dagger C_0), \quad (4)$$

where

$$\Gamma_{lm}^p = \left[\frac{\hbar\omega_l p^2 a^{2l+1}(l+1)}{6b^{2l+4}} \right]^{1/2} \times \left[-\sqrt{l+1}\delta_0^m \delta_1^p + \left[\frac{l}{2} \right]^{1/2} \delta_1^m (\delta_1^p + \delta_{-1}^p) \right], \quad (5)$$

with p^2 the spatial average of the absolute square of the dipole moment. Here b is the distance of the atom from the center of the sphere of radius $a < b$.

The following kets are used.

(i) $|0, n\rangle$: plasmon ground state, atom n th state.

(ii) $b_{lmp}^\dagger |0, n\rangle$: one plasmon in state l, m, p , atom n th state.

An eigenket of

$$H = H_{sp} + H_m + H_{int} \quad (6)$$

belonging to the energy eigenvalue E is

$$|E\rangle = \cos\theta |0, 1\rangle + \sum_{l,m,p} f_l^{-1} \Gamma_{lm}^p b_{lmp}^\dagger |0, 0\rangle. \quad (7)$$

where f_l^{-1} is a superposition coefficient and

$$\tan^2\theta = \sum_{l,m,p} \frac{(\Gamma_{lm}^p)^2}{(\hbar\omega_l - E + E_0)^2}, \quad (8)$$

while

$$\cos\theta = f_l^{-1} (\hbar\omega_l - E + E_0). \quad (9)$$

The ket $|E\rangle$ is normalized, and its energy eigenvalue is found from the relation

$$E = E_1 - \sum_{l,m,p} \frac{(\Gamma_{lm}^p)^2}{\hbar\omega_l - E + E_0}. \quad (10)$$

Substituting for Γ_{lm}^p from (5) gives

$$E = E_1 - \frac{p^2}{6b^3} \sum_{l=0}^{\infty} \frac{\hbar\omega_l (l+1)(2l+1)}{\hbar\omega_l - E + E_0} \left[\frac{a}{b} \right]^{2l+1}. \quad (11)$$

If $d = b - a \ll a$, then (11) reduces for $\omega_{sp} = \omega_p / \sqrt{2}$ to

$$E - E_1 = \frac{-p^2 \hbar\omega_{sp}}{12d^3 (\hbar\omega_{sp} - E + E_1)}, \quad (12)$$

which is a quadratic in E .

One may compare the right-hand side of (12) with the quantum image energy⁵

$$V = \frac{-\hbar\omega_{sp} p^2}{12d^3 (\hbar\omega_{sp} + E_1 - E_0)}. \quad (13)$$

Assuming as in Ref. 2 that the scattering matrix elements in second-order perturbation theory involve the eigenstates of (6) as intermediate states, one has the Raman enhancement factor

$$R = \frac{(E_1 - E_0 - \hbar\omega_0)^2}{E'^2 + \hbar^2 \gamma^2}, \quad (14)$$

where, if Γ is the surface plasmon damping, then the damping of the intermediate state is

$$\gamma = \frac{\Gamma \hbar\omega_{sp} p^2 / 12d^3}{(\hbar\omega_{sp} - \hbar\omega_0)^2}. \quad (15)$$

Only the major contribution to the various second-order matrix elements is used in (14), and the numerator of (14) comes from the appropriate perturbation theory energy denominator for ordinary scattering. The value of E' is given by

$$E' = \frac{E_1 - E_0 + \hbar\omega_{sp}}{2} - \hbar\omega_0 - \hbar\Omega. \quad (16)$$

where

$$(\hbar\Omega)^2 = \left[\frac{\hbar\omega_{sp} - E_1 + E_0}{2} \right]^2 + \frac{\hbar\omega_{sp} p^2}{12d^3}. \quad (17)$$

Notice that $R = 1$ if the classical (Lennard-Jones) image energy $p^2/12d^3$ vanishes.

For the value of $\hbar\omega_0$ for which E' vanishes, one may eliminate $p^2/12d^3$ from R to obtain at the resonance condition

$$R_{\max} = \frac{(\omega_{sp} - \omega_0)^2}{\Gamma^2}. \quad (18)$$

This result takes no account of alterations in the matrix elements appearing in the second-order cross section. As such it would be multiplied by an enhancement in these matrix elements due to the surface plasmon field. However, the foregoing analysis gives one a simple set of formulas for determining the position of the maximum with regard to the incident light (the $E' = 0$ point). Also, it allows the data to be used as an indirect measurement of the image energy. Finally, it gives a major portion of the enhancement.

For pyridine on silver one may take $E_1 - E_0 = 4.31$ eV, $\hbar\omega_{sp} = 3.63$ eV, $\hbar\Gamma = 10^{-2}$ eV, and $\hbar\omega_0 = 2.18$ eV to obtain $R = 10^4$. An additional factor of 10^2 is not unreasonable to expect from other effects.

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¹T. K. Lee and J. L. Birman, Phys. Rev. B 22, 5953 (1980).

²T. K. Lee and J. L. Birman, Phys. Rev. B 22, 5961 (1980).

³J. A. Creighton, C. G. Blatchford, and M. G. Albrecht,

J. Chem. Soc. Faraday II 75, 790 (1979).

⁴J. C. Ashley, T. L. Ferrell, and R. H. Ritchie, Phys. Rev. B 10, 554 (1974).

⁵T. L. Ferrell and R. H. Ritchie, Phys. Rev. A 21, 1305 (1980).