a third body is needed to stabilize the reaction complex. In this instance the Ar buffer gas would serve as a third body to remove excess energy from the newly formed transient product. Although our present data do not give positive proof that a third body is needed for stabilization, in view of the discrepancy between the present results and those obtained in ref 4, it may be likely. Further, the results of Tiee et al. are in closer agreement with the results of this study, and it is apparent that total pressure differences lead to different rate constants. To resolve this conflict, reaction rate experiments may be carried out utilizing other buffer gases. It is known that different buffer gases lead to different atom and free-radical recombination rate constants. These same effects should occur for termolecular molecule–molecule reactions as well.

Conclusion

The overall vibrational relaxation rate constant in the bending manifold for CFCl in Ar was found to be $k_v = (6.8 \pm 0.7) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. This rate constant may prove to be useful in the correlation of vibrational relaxation studies. However, state-to-state relaxation studies should be performed to determine the exact mechanism for this relatively fast relaxation. Finally, it is hoped that the rates of reaction of CFCl with the nitrogen–oxygen compounds will aid in the formulation of more accurate models for stratospheric chemistry.

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Dielectric Environment Effects on Surface Enhanced Resonant Electromagnetic Processes

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When a thick layer of Raman active molecules is deposited on a rough metal surface, on metal colloid particles, or on a metal island film, in a surface enhanced Raman scattering (SERS) experiment, the dielectric properties of the molecular layer should affect the observed scattering. This effect is expected to be large for resonance Raman scattering, where the dielectric function of the molecular layer is appreciably different from unity. This effect is studied within the coated-sphere model. A rich structure is predicted for the frequency dependence of the enhancement ratio in the resonant case. In addition, the coverage dependence of SERS is predicted to be substantially different in the resonant and nonresonant cases.

Introduction

The discovery of surface enhanced Raman scattering (SERS)[1] and the realization that at least part of the effect is due to intensified local electromagnetic field experienced by the adsorbed molecules[2] have led several workers to consider surface effects on other electromagnetic phenomena involving adsorbed molecules. The effect of smooth metal surfaces on the lifetime of excited adsorbed molecules (shortening of lifetime due to energy transfer to surface plasmons) has been known for some time,[3] and recent theoretical work has considered similar effects on the lifetime of molecules adsorbed on dielectric particles.[4] Enhanced adsorption and luminescence by molecules adsorbed on metal island films have been recently reported[5-8] and theoretically investigated.[3,9] Nonlinear optical processes are also expected to be enhanced on appropriate surfaces, and, indeed, enhanced second harmonic generation has been recently observed.[10] Finally, it has been suggested that enhanced photochemistry may be observed under appropriate conditions.[11]

It has been pointed out[11,12] that important differences exist between processes like SERS, which are nonresonant as far as the adsorbed molecule is concerned, and processes in which the incident radiation is in resonance with the molecule, e.g., adsorption and consecutive processes involving the excited molecule. One such difference arises from the role played by the adsorbed molecules in modifying the dielectric environment of the substrate. In nonresonant processes this modification is small and only weakly frequency dependent, and therefore the molecular layer covering the substrate behaves approximately as an inert dielectric; in fact, the dielectric properties are determined mostly by the solvent (e.g., water or rare gas solid). Indeed, all theories of SERS disregard the contribution of the optically active adsorbate to the dielectric function of the medium surrounding the substrate.

(1) R. P. Van Duyne in "Chemical and Biochemical Applications of Lasers", Vol. 4, C. B. Moore, Ed., Academic Press, New York, 1978; E. Burstein, C. Y. Chen, and S. Lindquist, "Proceedings of the US–USSR Symposium on the Theory of Light Scattering in Condensed Matter", Plenum Press, New York, 1979; T. E. Furtak and J. Reyes, *Surf. Sci.*, **93**, 351 (1980); S. Efrima and H. Metiu, *Isr. J. Chem.*, **17**, 18 (1979).

(2) J. Gersten and A. Nitzan, *J. Chem. Phys.*, **75**, 1139 (1981), and references therein.

(3) R. R. Chance, A. Prock, and R. Silbey, *Adv. Chem. Phys.*, **37**, 1 (1978).

(4) See: ref 2 and R. Rupin, *J. Chem. Phys.*, submitted for publication.

(5) A. M. Glass, P. F. Liao, J. G. Bergman, and D. H. Olson, *Opt. Lett.*, **5**, 368 (1980); H. G. Craighead and A. M. Glass, *ibid.*, **6**, 248 (1981); A. M. Glass, A. Wokaun, J. P. Heritage, J. G. Bergman, P. F. Liao, and D. H. Olson, *Phys. Rev. B*, in press.

(6) S. Garoff, D. A. Weitz, T. J. Gramila, and C. D. Hanson, *Opt. Lett.*, **6**, 245 (1981); D. A. Weitz, S. Garoff, C. D. Hanson, T. J. Gramila, and J. I. Gersten, Proceedings of the International Conference on Luminescence, West Berlin, 1981, to be published in *J. Lumin.*

(7) G. Ritchie, C. Y. Chen, and E. Burstein, Proceedings of the 7th International Conference on Raman Spectroscopy, Ottawa, Canada, 1980.

(8) A. Harstein, J. R. Kirtley, and J. C. Tsang, *Phys. Rev. Lett.*, **45**, 301 (1980).

(9) C. F. Eagen, "Nature of the Enhanced Optical Absorption of Dye-Coated Ag Island Films", submitted for publication.

(10) C. K. Chen, A. R. B. de Castro, and Y. R. Shen, *Phys. Rev. Lett.*, **46**, 145 (1981); C. K. Chen, T. F. Heinz, D. Ricard, and Y. R. Shen, *ibid.*, **46**, 1010 (1981); A. Wokaun, J. G. Bergman, J. P. Heritage, A. M. Glass, P. F. Liao, and D. H. Olson, *Phys. Rev. B.*, in press.

(11) A. Nitzan and L. E. Brus, *J. Chem. Phys.*, **75**, 2205 (1981).

(12) S. Garoff, D. A. Weitz, J. Gersten, and A. Nitzan, to be submitted for publication.

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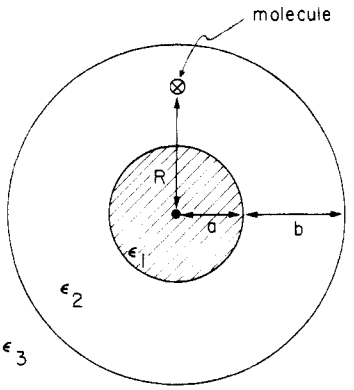

Figure 1. Coated-sphere model.

When the incident radiation is close to resonance with the molecular transition, this contribution can no longer be disregarded, unless adsorbate concentration is very small. Indeed, it has been demonstrated both theoretically and experimentally[5,6] that the spectral behavior of dye-coated metal particles is profoundly different from that of the free metal particles.

In this paper we study the effect of the dielectric properties of the adsorbate layer on local field, absorption, and Raman scattering in this layer. We focus attention on the difference between resonant and nonresonant optical processes, and we demonstrate that the dielectric properties of the molecular coating may have a dramatic effect on surface enhanced resonance Raman scattering as well as on other resonance optical processes.

Model and Analytical Solutions

With the aim to demonstrate the effect of adsorbate dielectric properties on resonant electromagnetic phenomena in the simplest way, we chose the coated-sphere model (Figure 1) in the electrostatic (particle small relative to wavelength) limit. The same model, as well as its generalization, the coated-spheroid model, has been used by others to interpret the absorption spectrum of dye-coated silver islands.[5,6,9] In most calculations reported below, we use for the dielectric function of the sphere the bulk dielectric function of silver. The coating is represented by the Clausius Mossotti function

$$\epsilon_2(\omega) = \frac{1 + (8\pi/3)N\alpha}{1 - (4\pi/3)N\alpha} \tag{1}$$

where N is the number density of the optically active adsorbate molecules and where $\alpha = \alpha(\omega)$ is the molecular dynamic polarizability, taken to be

$$\alpha(\omega) = \alpha_0\omega_0^2/(\omega_0^2 - \omega^2 - i\omega\Gamma) \tag{2}$$

α_0 is the static molecular polarizability, ω_0 is the molecular resonance frequency, and Γ is the associated molecular damping rate. The use of eq 1 for the dielectric function of the molecular layer as well as the use of the bulk dielectric function of silver to represent a small silver sphere are obviously only very rough approximations. Conventionally introduced corrections—modifying the imaginary part of the dielectric function of the metal core to account for finite size effects and adding a constant to the right-hand side of eq 2—do not affect our qualitative conclusions. (More important is the anisotropy expected in the dielectric response of the thin molecular coating which is not accounted for in the model given by eq 1 and 2.)

In the electrostatic approximation, the electromagnetic properties of this model are obtained by solving the Laplace equation with the proper boundary conditions at the two interfaces. Here, we present only the final relevant results.

The local field within the dielectric shell averaged over the volume of the shell is given by

$$\frac{\langle|E|^2\rangle_{\text{shell}}}{|E_0|^2} = \left|\frac{3q^3}{\epsilon_2/\epsilon_3 + 2}\right|^2 \frac{1 + 2|s|^2/q^3}{|q^3 + 2sr|^2} \tag{3}$$

where

$$s = \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + 2\epsilon_2} \qquad r = \frac{\epsilon_2 - \epsilon_3}{\epsilon_2 + 2\epsilon_3} \tag{4a}$$

and where

$$q = (a + b)/b \tag{4b}$$

The same local field at the surface of the sphere averaged over this surface is given by

$$\frac{\langle|E|^2\rangle_{\text{surf}}}{|E_0|^2} = \left|\frac{3q^3}{\epsilon_2/\epsilon_3 + 2}\right|^2 \frac{1 + 2|s|^2}{|q^3 + 2sr|^2} \tag{5}$$

The absorption cross section within the shell,[13] per molecule, is given by

$$\sigma_a^{\text{shell}} = \frac{1}{2}\frac{\omega}{cN}\,\text{Im}\,(\epsilon_2)\frac{\langle|E|^2\rangle_{\text{shell}}}{|E_0|^2} \tag{6}$$

where c is the speed of light.

The result (6) may be compared to the absorption cross section per molecule of a small sphere characterized by the dielectric function ϵ_2 (eq 1). This is obtained from eq 6 by replacing $\langle|E|^2\rangle/|E_0|^2$ by the corresponding expression for a sphere, i.e., $|3/(\epsilon_2 + 2)|^2$. The result is

$$\sigma_a^{\text{sph}} = \frac{2\pi\omega^2}{C^2}\frac{\alpha_0\omega_0^2\Gamma}{(\omega_0^2 - \omega^2)^2 + (\omega\Gamma)^2} \tag{7}$$

which is the same as the absorption cross section of a single isolated molecule.

Finally, we may use eq 1 and 2 to obtain the absorption cross section, per molecule, obtained from bulk measurement on the adsorbate medium. The result is (see, e.g., ref 14, eq 7.55)

$$\sigma_a^{\text{bulk}} \simeq \frac{\text{Im}\,\epsilon_2}{(\text{Re}\,\epsilon_2)^{1/2}}\frac{\omega}{Nc} \tag{8}$$

Next, we consider Raman and resonance Raman scattering. We consider a molecule located at a distance R, $a < R < a + b$, from the center of the spherical core of Figure 1. The molecule is taken to have a scalar polarizability α (α is taken to be a scalar to be consistent with the use of eq 1 and 2 for $\epsilon_2(\omega)$). We also assume that the Raman scattering process is incoherent; i.e., the total scattering intensity is assumed to be the sum of intensities associated with the individual molecules. In evaluating the latter, we take account of the fact that each molecule is imbedded in a medium of dielectric function $\epsilon_2(\omega)$.

Even though the problem may be solved exactly within the classical theory in the electrostatic limit, we simplify things further by neglecting image terms arising from the interaction of the molecular dipole with the field associated with the polarization of the rest of the system by the same dipole. Image contribution to the SERS effect is usually quite small. The calculation then consists of first evalu-

(13) Note that this is the absorption by the molecular coating only (not by the dielectric core), which may be followed in principle by monitoring the fluorescence excitation line shape.

(14) J. D. Jackson, "Classical Electrodynamics", Wiley, New York, 1975.

ating, at the molecule position, the local field resulting from the incident field at frequency ω. This local field gives rise to a dipole $\mu = \alpha E_{loc}$ at the molecule. Secondly, assuming that μ oscillates with the emission frequency ω', we calculate the total dipole $\mu^{tot}(\omega')$ induced by μ in the coated-sphere system. The light scattering associated with μ^{tot} is the desired Raman scattering intensity.

The calculation described above is quite similar (though involving a somewhat different boundary value problem) to other calculations of the electromagnetic theory of SERS.[2] The result of the total dipole induced in the system for a molecule located in region 2 on the z axis is

$$\mu_z^{tot} = \frac{\epsilon_2(\omega')}{\epsilon_3(\omega')} A^{\perp}(\omega)\, A^{\perp}(\omega') \alpha E_{0z}$$

$$\mu_n^{tot} = \frac{\epsilon_2(\omega')}{\epsilon_3(\omega')} A^{\parallel}(\omega)\, A^{\parallel}(\omega') \alpha E_{0n} \qquad n = x, y \qquad (9)$$

where

$$A^{\perp}(\omega) = \frac{3q^3}{(\epsilon_2/\epsilon_3 + 2)(q^3 + 2sr)}\left[1 + 2s\left(\frac{R}{a}\right)^{-3}\right] \qquad (10a)$$

$$A^{\parallel}(\omega) = \frac{3q^3}{(\epsilon_2/\epsilon_3 + 2)(q^3 + 2sr)}\left[1 - s\left(\frac{R}{a}\right)^{-3}\right] \qquad (10b)$$

The enhancement ratio ρ associated with the total Raman scattering is obtained from $\rho = |\mu^{tot}|^2/|\alpha E_0|^2$. Averaging over all directions, we get

$$\rho(R) = |\epsilon_2(\omega')/\epsilon_3(\omega')|^2(\tfrac{1}{3}|A^{\perp}(\omega)\, A^{\perp}(\omega')|^2 + \tfrac{2}{3}|A^{\parallel}(\omega)\, A^{\parallel}(\omega')|^2) \qquad (11)$$

$\rho(R)$ is the enhancement ratio for a molecule located at a distance R ($a < R < a + b$) from the sphere center, averaged over all angular directions. The enhancement ratio averaged over the molecular shell is

$$\rho = \frac{3\int_a^b dR\, R^2 \rho(R)}{(a + b)^3 - a^3} \qquad (12)$$

Numerical Results and Discussion

In the calculations reported in this section, we use a silver sphere of radius a and a spherical coating of thickness b, characterized by the density of optically active molecules N, and their static polarizability α_0, resonance frequency ω_0, and resonance width Γ. Unless otherwise stated, we take $N = 2 \times 10^{21}$ cm^{-3}, $\gamma = 0.003$ eV (a reasonable homogeneous level width for a large molecule in condensed phases), and $\alpha_0 = 10^{-24}$ cm^3. The dielectric function of silver is taken from the results of Johnson and Christy.[15]

In Figure 2 we display the surface average of the local field on the sphere surface for several coating thicknesses. In Figure 2A $\omega_0 = 3.5$ eV (which is the same as the frequency of the dipolar resonance of a small silver sphere) and in Figure 2B $\omega_0 = 3.25$ eV. The main points to notice are (a) the damping of the local field enhancement at $\omega = 3.5$ eV for increasing coating thickness in the resonance case (Figure 2A) and (b) the double-peak nature of the local field at the molecular resonance (most pronounced in Figure 2A), which is related to the splitting in the absorption spectrum shown below.

Figure 3 shows the absorption cross section (per molecule) for an isolated molecule, for a small dielectric sphere,

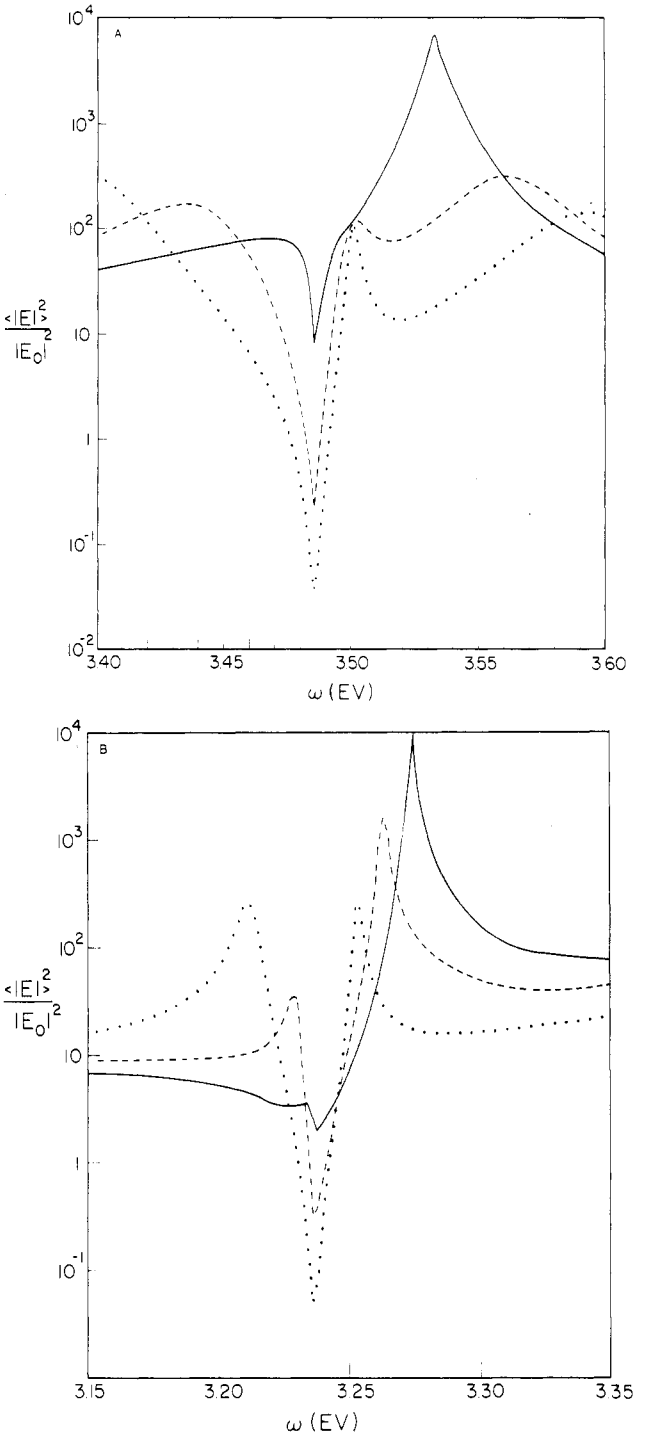

Figure 2. Surface average of the local field on the sphere surface in the coated-sphere model. ϵ_1 is taken as the bulk dielectric function of silver; ϵ_2 is calculated from eq 1 and 2 with the molecular parameters given in the text. $\epsilon_3 = 1$. Coating thickness: $b = 0.01a$ (—); $b = 0.1a$ (– – –); $b = 0.4a$ (···). A: $\omega_0 = 3.5$ eV. B: $\omega_0 = 3.25$ eV.

for a dielectric bulk, and a dielectric shell ($\epsilon_1 = \epsilon_3 = 1$; $b/a = 0.1$). In all of these cases the dielectric medium is characterized by $\epsilon = \epsilon_2$ (eq 1), and $\omega_0 = 3.5$ eV. Figure 4 depicts the absorption cross section (per molecule) of a molecular shell ($b/a = 0.1$; ϵ_2 given by eq 1) around the silver sphere, for two molecular concentrations. Note that the low concentration limit is equivalent to the calculation done for a single molecule near a sphere.

It is seen that (a) the enhancement of the absorption cross section observed for the isolated molecule near the silver particle is damped in the coated-sphere system, particularly in the resonant case, and (b) the splitting in

(15) P. B. Johnson and R. W. Christy, *Phys. Rev. B*, 6, 4370 (1972).

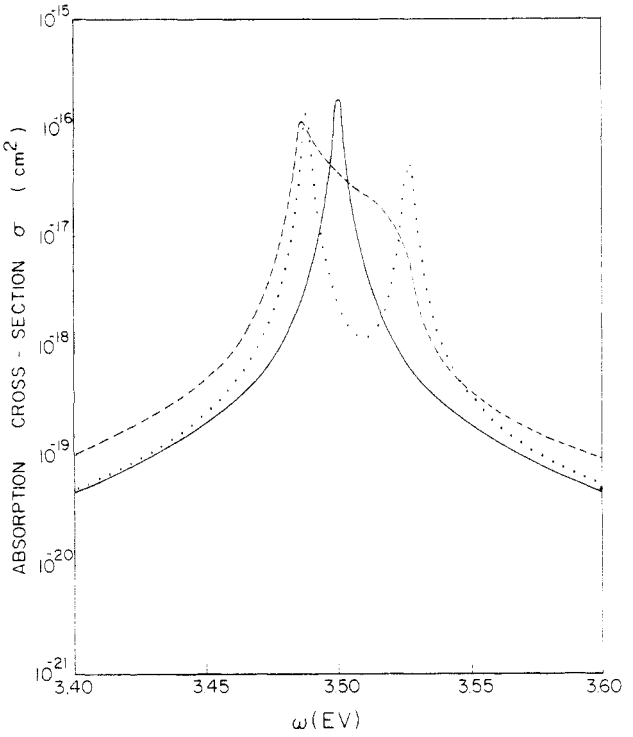

Figure 3. Absorption cross section (per molecule) for a small dielectric sphere (—), a dielectric hollow shell (···), and a dielectric bulk (– – –) made of these molecules. $N = 2 \times 10^{21}$ cm^{-3}, $\alpha_0 = 10^{-4}$ cm^3, $\gamma = 0.003$ eV, $\omega_0 = 3.5$ eV.

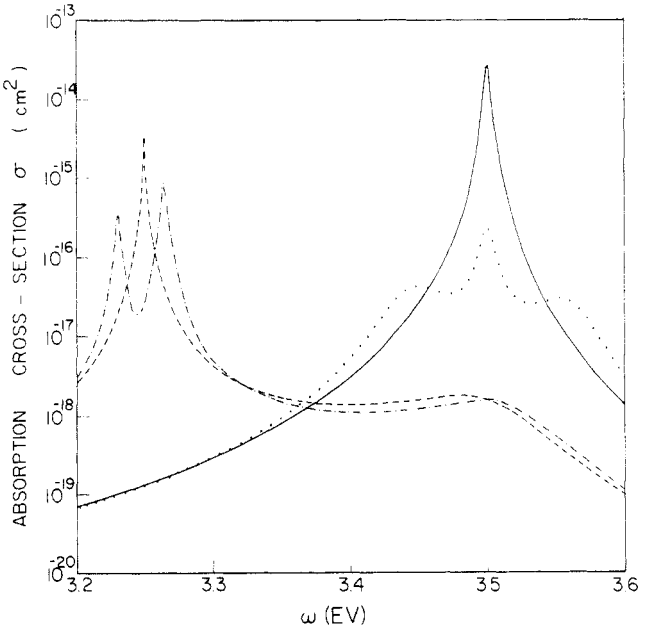

Figure 4. Absorption cross section (per molecule) of a molecular shell ($b = 1.1a$) on a silver sphere: (—) $\omega_0 = 3.5$ eV and $N = 1 \times 10^{19}$ cm^{-3}; (– – –) $\omega_0 = 3.25$ eV and $N = 1 \times 10^{19}$ cm^{-3}; (···) $\omega_0 = 3.5$ eV and $N = 2 \times 10^{21}$ cm^{-3}; (–·–) $\omega_0 = 3.25$ eV and $N = 2 \times 10^{21}$.

the absorption spectrum of dye-coated silver particles observed experimentally and theoretically in earlier works[5,6,9] is a property of the shell geometry rather than of the molecular shell–metal sphere interaction.[16] Indeed,

(16) Professor M. Kerker has informed us of similar observations obtained in the coated-sphere and coated-spheroid models. It is interesting to note that in ref 9, where $\epsilon_2(\omega)$ is taken to be linear in $\alpha(\omega)$ of eq 2, a double-peak absorption is obtained even for a sphere with $\epsilon = \epsilon_2(\omega)$ and is associated with two solutions to the equation $\epsilon_2(\omega) = -2$ for the resonance frequency. If eq 1 is used for $\epsilon_2(\omega)$, the equation $\epsilon_2(\omega) = -2$ has no solution.

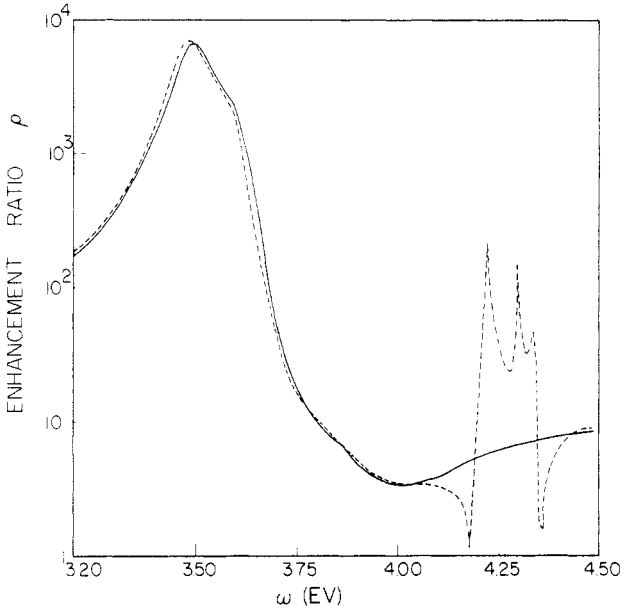

Figure 5. Raman enhancement ratio for a single molecule located at $R = 1.02a$ under vacuum ($\epsilon_2 = \epsilon_3 = 1$) outside a silver sphere (—) and for the same molecule embedded in a dielectric shell ($b = 0.1a$) (– – –), $\omega_0 = 4.2$ eV; $\omega' = \omega - 0.125$ eV. $N = 2 \times 10^{21}$ cm^{-3}.

a closer examination of eq 3 reveals two poles in this expression as a function of ϵ_2 even when $\epsilon_1 = \epsilon_3 = 1$.

Turning our attention to the Raman scattering, we note that the enhancement factors $A(\omega)$ (eq 10a,b) become for $\epsilon_2 = \epsilon_3$

$$A^{\perp} = 1 + 2s(R/a)^{-3} \tag{13a}$$

$$A^{\parallel} = 1 - s(R/a)^{-3} \tag{13b}$$

These factors have the same form as in the case of a single molecule located at a distance R from the sphere center (in the absence of a molecular coating). Note, however, that, when the coating is present, s is associated with the polarizability of the spherical core if this core is imbedded in an infinite medium made of the molecular dielectric. Another modification of the Raman enhancement ratio results from the second factor

$$\lambda \equiv 3q^3/[(\epsilon_2/\epsilon_3 + 2)^2 + (q^3 + 2sr)] \tag{14}$$

which is related to the local field seen by the Raman active molecules (compare eq 3 and 5). Resonance effects associated with this factor are similar to those discussed above in relation to the field enhancement. It is seen, for example, that the factor r (which is essentially the molecular line shape) appears in the denominator of λ and may thus lead to reduction in the scattering intensity if $|2sr| \gg q^3$. It should be kept in mind, however, that the total magnitude of the ratio ρ results from several contributions. The resonance Raman scattering from a hollow molecular shell (without the metal core) already shows the peculiar features associated with the double-peaked field enhancement ratio discussed above. This is the main contribution to the structure seen near 4.2 eV in the dashed line of Figure 5. When the molecule is close to resonance with the dipolar plasmon of the inner core, a rich structure is obtained as seen in the dashed line of Figure 6.

Another interesting observation is related to the coverage dependence of SERS. When the calculation is done disregarding the dielectric function of the molecular coating, the coverage dependence is determined by the distance dependence for a single molecule as given by eq 13. When the factor λ is taken into account (eq 11 is proportional

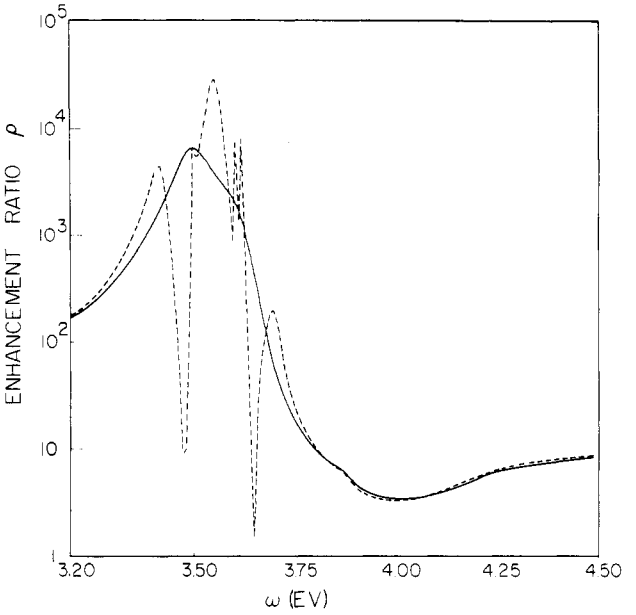

Figure 6. Same as Figure 5 for $\omega_0 = 3.5$ eV.

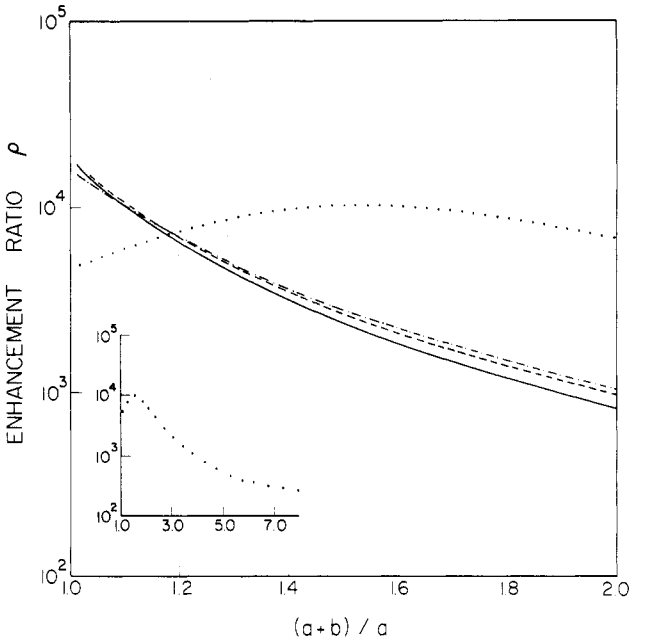

Figure 7. Raman enhancement ratio ρ for a spherical shell of thickness b around a small silver sphere as a function of coating thickness: (—) $\omega_0 = 3.5$ eV and $N = 1 \times 10^{18}$ cm^{-3}; (– – –) $\omega_0 = 4.2$ eV and $N = 1 \times 10^{18}$ cm^{-3}; (···) $\omega_0 = 3.5$ eV and $N = 2 \times 10^{21}$ cm^{-3}; (–·–) $\omega_0 = 4.2$ eV and $N = 2 \times 10^{21}$ cm^{-3}. Other molecular parameters are the same as in the former figures. The insert shows the high thickness behavior of the $\omega_0 = 3.5$ eV and $N = 2 \times 10^{21}$ cm^{-3} case. In all cases $\omega = 3.5$ eV and $\omega' = \omega - 0.125$ eV.

to $|\lambda(\omega)\ \lambda(\omega')|$), there is an additional contribution to the coverage dependence in the factors q^3. Far from resonance, $q^3 \gg 2sr$, these factors cancel. However, close to resonance, when $q^3 \ll 2sr$, λ is proportional to q^3 which increases with coverage. This behavior is seen in Figure 7, where the enhancement ratio ρ as inferred from the total Raman scattering from the molecular shell (eq 12) is plotted as a function of the shell thickness. For molecule resonant ($\omega_0 = 3.5$ eV) and nonresonant ($\omega_0 = 4.2$ eV) with the dipolar plasmon of the silver core, we compare the results obtained for two molecular concentrations: $N = 1 \times 10^{18}$ cm^{-3} and $N = 2 \times 10^{21}$ cm^{-3}. In the low-concentration case $\epsilon_2 \simeq 1$ in both the resonant and the nonresonant cases (so they are equivalent to the single molecule near a sphere model) and both lead to almost the same coverage dependence which is similar to that observed experimentally.[17] In the high-concentration case, the nonresonant molecules behave similarly to those discussed above. However, for resonant molecules we predict an initial rise in the coverage dependence of ρ and a much slower reduction in higher coverages. Note that the limiting value of ρ at $(a + b)/a \to \infty$ is not unity but a value which is related to the difference between the Raman scattering of an isolated molecule and that of a molecule imbedded in a medium with dielectric function ϵ_2. The predicted difference between the coverage dependence of SERS in the resonant and nonresonant cases should be amenable to experimental verification.

Conclusion

Surface effects on Raman scattering by adsorbed molecules are expected to be different for resonance Raman scattering compared to the usually studied regular Raman phenomenon. Our results indicate that part of the difference between resonant and nonresonant electromagnetic phenomena involving adsorbed molecules may result from the influence of the adsorbate layer on the dielectric environment of the substrate. The structured frequency dependence of the internal field in the adsorbate shell leads to a highly structured frequency dependence of the resonant Raman cross section. Large differences in the enhancement ratio may be observed at slightly different frequencies. Furthermore, the coverage dependence of SERS is predicted to have a different qualitative behavior in resonance and nonresonance cases.

The effects discussed here are not the only ones by which resonance and nonresonance SERS differ from each other. Other effects, related to surface induced damping of the molecular resonance, are discussed elsewhere.[11,12]

Note Added in Proof. Wang and Kerker (*Phys. Rev. B* (1982)) have very recently used a model similar to the one presented here (with some calculations done also on spheroidal shapes) to study the extinction cross section and the luminescence of small dye-coated metal particles. Similar models have been used in other contexts (H. Chew, M. Kerker, and P. J. McNulty, *J. Opt. Soc. Am.*, **66**, 440 (1976); M. Kerker, *ibid.*, **65**, 376 (1975)). Earlier works on concentric spheres is cited in these references.

Acknowledgment. This research was supported by the Commission of Basic Research of the Israel Academy of Sciences. We are grateful to Professor J. Gersten for many helpful discussions and to Professor M. Kerker for helpful comments.

(17) J. E. Rowe, C. V. Shank, D. A. Zwemer, and C. A. Murray, *Phys. Rev. Lett.*, **44**, 1770 (1980); D. A. Zwemer, C. V. Shank, and J. E. Rowe, *Chem. Phys. Lett.*, **73**, 201 (1981); C. A. Murray, D. L. Allara, and M. Rhinewine, *Phys. Rev. Lett.*, **46**, 57 (1981).