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Double Resonance in Fluorescent and Raman Scattering by Molecules in Small Particles

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It is pointed out that in fluorescent and Raman scattering by molecules in or near a small particle, large enhancements in the scattered signals are obtained when both the incident and the fluorescent frequencies coincide with eigenfrequencies of the particle. Numerical results are presented for spherical particles with a refractive index 2.2 + 0.409× $10^{-2}i$ uniformly filled with fluorescent scatterers. The effects are found to be substantial.

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There has been considerable interest recently in fluorescent and Raman scattering by molecules embedded in small particles,[1-3] particularly resonant effects. A classical model[3] for these processes has been formulated by one of us (H.C.) with Kerker and McNulty which takes into account the influence of the physical properties of the host particle on the scattered radiation. Benner and co-workers[1,2] observed striking resonances when the fluorescent frequency coincided with one of the eigenfrequencies of the host particles, which may be spherical or cylindrical. The purpose of this paper is to draw attention to the possibility of double resonances, which occur when both the incident frequency and the fluorescent/Raman frequency coincide with eigenfrequencies of the host particle. This effect is a consequence of our model,[3] and has a simple physical interpretation. We will present the results of some numerical calculations based on our model, which show that the effect is substantial.

Consider a fluorescent scattering molecule located at $\vec{r}'$ inside a spherical particle of radius a (medium 1), with dielectric constant ϵ_1 and magnetic permeability μ_1. Let a plane electromagnetic wave of angular frequency ω be incident on the particle from the outside (medium 2, dielectric constant ϵ_2 and magnetic permeability μ_2), causing the molecule to emit fluorescent radiation at a shifted frequency ω'. In our model,[3] the local field $\vec{E}_L(\vec{r}',\omega)$ induces in the molecule a dipole moment $\vec{p}=\alpha\vec{E}_L(\vec{r}',\omega)$ (α is the polarizability, a tensor in general), which oscillates and radiates at the fluorescent frequency ω'. The fluorescent radiation field $\vec{E}(\vec{r},\omega')$ at an outside point $\vec{r}$ is computed from an exact solution of the appropriate boundary value problem. The local field $\vec{E}_L(\vec{r}',\omega)$ is assumed to be given by the transmitted field at frequency ω as computed in Mie theory.[4] Specifically, if a right circularly polarized plane wave traveling along the z axis is incident on the sphere (radius a) centered at the origin, the local field at an interior point $\vec{r}'$ is given by[3]

$$\vec{E}_L(\vec{r}',\omega)=\sum_l\{(ic/n_1^2\omega)\gamma_E(l,1)\nabla'\times[j_l(k_1r')\vec{Y}_{l l 1}(\hat{r}')]+\gamma_M(l,1)j_l(k_1r')\vec{Y}_{l l 1}(\hat{r}')\}, \tag{1}$$

where

$$\gamma_E(l,1)=\frac{(\mu_1\epsilon_1/\mu_2k_2a)i^l[4\pi(2l+1)]^{1/2}}{\epsilon_1j_l(k_1a)[k_2ah_l^{(1)}(k_2a)]'-\epsilon_2h_l^{(1)}(k_2a)[k_1aj_l(k_1a)]'}, \tag{2a}$$

$$\gamma_M(l,1)=\frac{(\mu_1/k_2a)i^{l+1}[4\pi(2l+1)]^{1/2}}{\mu_1j_l(k_1a)[k_2ah_l^{(1)}(k_2a)]'-\mu_2h_l^{(1)}(k_2a)[k_1aj_l(k_1a)]'}, \tag{2b}$$

n_1 being the index of refraction of the sphere (medium 1), and the quantities k_α, μ_α, ϵ_α ($\alpha=1,2$) being evaluated at frequency ω. Note that the denominators of the local-field coefficients are the same as those of the Mie scattering coefficients. These coefficients become large when the frequency ω approaches one of the eigenfrequencies of the sphere. Thus when the incident frequency ω is near one of the resonant frequencies of the sphere, the local field becomes resonantly enhanced, resulting in a larger induced dipole moment $\vec{p}=\alpha\vec{E}_L(\vec{r}',\omega)$ which produces enhanced fluorescent radiation. The fluorescent radiation field (frequency ω') at an outside point $\vec{r}$ is shown in Ref. 3 to be given by

$$\vec{E}(\vec{r},\omega')=\sum_l\{(ic/n_2'^2\omega')c_E(l,1)\nabla'\times[h_l^{(1)}(k_2r)\vec{Y}_{ll1}(\hat{r})]+c_M(l,1)h_l^{(1)}(k_2r)\vec{Y}_{llm}(\hat{r})\}, \tag{3}$$

where

$$c_E(l,1)=\frac{(in_2'^2/\mu_1'k_1'a)(4\pi k_1'^2)\vec{p}\cdot\{\nabla'\times[j_l(k_1'r')\vec{Y}_{ll1}{}^*(\hat{r}')]\}}{\epsilon_1'j_l(k_1'a)[k_2'ah_l^{(1)}(k_2'a)]'-\epsilon_2'h_l^{(1)}(k_2'a)[k_1'aj_l(k_1'a)]'}, \tag{4a}$$

$$c_M(l,1)=\frac{(i\mu_2'/k_1'a)(4\pi ik_1'^2\omega'/c)j_l(k_1'r')\vec{p}\cdot\vec{Y}_{ll1}{}^*(\hat{r}')}{\mu_1'j_l(k_1'a)[k_2'ah_l^{(1)}(k_2'a)]'-\mu_2'h_l^{(1)}(k_2'a)[k_1'aj_l(k_1'a)]'}, \tag{4b}$$

with the quantities n_2', k_α', μ_α', ϵ_α' $(\alpha=1,2)$ being evaluated at the fluorescent frequency ω'. These coefficients also have denominators like the Mie coefficients, but they are evaluated at the fluorescent frequency ω'. If the fluorescent frequency ω' coincides with an eigenfrequency of the particle, the fluorescent field will be enhanced through a small resonant denominator in an expansion coefficient in (3). These (single) resonances may be identified with those observed by Benner *et al.*[1] Double resonances arise when the dipole moment $\vec{p}$ entering (4a) and (4b) is also resonantly enhanced as discussed above.

These effects have a simple physical interpretation if the particle is pictured as a resonator with a set of eigenfrequencies. When the incident frequency is near one of these eigenfrequencies, the internal field is resonantly enhanced, inducing a magnified fluorescent dipole moment $\vec{p}$. This dipole moment generates an oscillating field at the fluorescent frequency ω' which is refracted by the particle before reaching the outside. If this frequency ω' is also at an eigenfrequency of the particle, a second enhancement results because the particle is being driven at a resonant frequency. A similar interpretation also applies to the case when the molecule is in the vicinity of the particle instead of being inside. In this case the local field is the sum of the incident field and the elastically scattered field from the particle at the incident frequency ω. If ω is near an eigenfrequency, the resonantly scattered field will be large and may even dominate over the incident field. Again, a second enhancement occurs when the fluorescent radiation (frequency ω') is resonantly scattered off the particle if ω' is near an eigenfrequency. All the above considerations are also valid for Raman scattering. Moreover, it is clear from our discussion that a double resonance

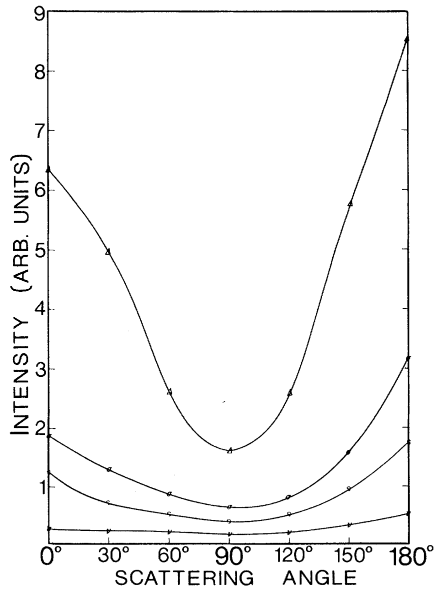

FIG. 1. Horizontal incidence ($\vec{E}_{\text{inc}}$ in the scattering plane). Δ = double resonance; σ = single resonance, SR I; s = single resonance, SR II; ν = nonresonant.

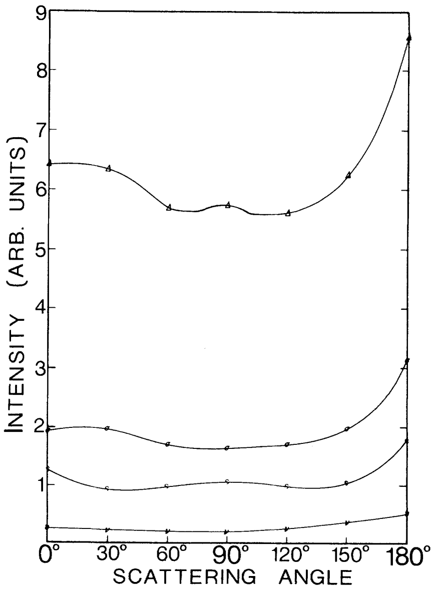

FIG. 2. Vertical incidence ($\vec{E}_{\text{inc}}$ perpendicular to the scattering plane). Same notation as in Fig. 1.

will also occur if a resonance is so broad that both the incident and the fluorescent/Raman frequencies lie within the resonant peak. This is, in fact, the case for Raman scattering by pyridine molecules adhering to small silver particles at an incident wavelength of about 450 nm.[5-7] A detailed discussion of this special case in connection with surface-enhanced Raman scattering has been given in Ref. 5.

To illustrate the effects of double resonances, we have computed the intensity of the fluorescent radiation as a function of scattering angle for a spherical particle of refractive index[8] $2.2+0.409\times10^{-2}i$ (for both incident and fluorescent frequencies) uniformly filled with incoherently radiating fluorescent molecules. The incident beam is along the z axis, and the scattering plane is the x-z plane. We give results for incident polarization along the x axis (H polarization, Fig. 1) and along the y axis (V polarization, Fig. 2). Four angular distributions are shown in each figure: one at double resonance (DR), two at single resonance (SR I and SR II), and one for nonresonance (NR). All the frequencies are taken to be in the region where there are two neighboring resonances at $ka\equiv2\pi a/\lambda=3.04$ and 3.6, respectively. The DR curve corresponds to $ka=3.6$ and $k'a=3.04$ (k and k' being the vacuum incident and fluorescent wave numbers, respectively), the SR I curve to $ka=3.75$ (nonresonant) and $k'a=3.6$, the SR II curve to $ka=3.2$ (nonresonant) and $k'a=3.04$, and the NR curve to $ka=3.2$ and $k'a=2.77$. The intensity units are arbitrary but the same in both figures, which are also normalized to the same particle radius. The intensities were computed for a scalar polarizability α and summed over 6400 uniformly distributed sites.[9]

It will be seen that for both polarizations the intensities at double resonance are sharply higher than at single resonance, which are in turn much larger than at nonresonant frequencies. Because the local fields are quite different at different sites, the double resonance effects are reduced by the averaging process.[9] Nevertheless, the effects are sufficiently significant to make experimental study interesting and desirable. As the computer time needed to perform the calculations increases steeply with ka, we are unable to investigate the experimental situation of Ref. 1, which involves values of ka in excess of 100. However, we believe that the examples and physical arguments here show that double resonances should exist for higher values of ka as well as for cylindrical particles (in fact, for particles of arbitrary shape). For higher values of ka, the width of the resonances become narrower and the spacing Δka between successive resonances decreases in relation to ka.[10] Since the frequency shifts in Raman scattering are in general small compared to the incident frequency, we expect double resonances to be observable for Raman scattering for large values of ka. The effects are probably smaller for large ka, as a large number of terms will then contribute to the scattered field, so that resonance in one or two terms will have a smaller effect on the total intensity. Thus it appears that the effect of double resonances will be most pronounced for small ka and large refractive indices.[11]

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[11] For a striking example of a double resonance as a mechanism for SERS see the case $ka\ll1$ discussed in Ref. 5.