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Model for Raman and fluorescent scattering by molecules embedded in small particles*

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A model for Raman and fluorescent scattering by molecules embedded in small particles is described. This takes into account the effect of the particle's geometrical and optical properties upon the unshifted field which excites the molecular transitions within the particle, and upon the shifted field. Formulas are given which relate the angular distribution of the scattered radiation to the nature of the molecular scatterers and to the size and refractive index of the particle. These results are relevant for current problems in cell biology and atmospheric physics.

I. INTRODUCTION

Many problems of practical importance involve fluorescent and Raman scattering by molecules embedded in a dielectric particle whose dimensions are comparable to the wavelength, yet much larger than molecular dimensions, or by such particles consisting entirely of scattering molecules. For example, the dielectric particle may be a biological cell which has been tagged with fluorescent molecules that attach to the DNA, the cytoplasm, or the cell membrane. The fluorescence can be used to monitor specific cell functions, or in cell identification and sorting systems.[1] As another example, the particle may be part of the atmospheric aerosol. This case is of considerable interest in studies employing LIDAR (light detecting and ranging) for remote sensing of both molecular and particulate constituents of the atmosphere.[2]

In a quantitative treatment of the scattering problem the geometrical and optical properties of the particle must be taken into account, but to the best of our knowledge this paper represents the first attempt to do so. These properties strongly influence both the local field which excites the molecular transitions and the angular distribution and polarization of the emitted field. The angular distribution and the polarization of the emitted fluorescence and Raman radiation will be shown to be different from that of elastically scattered light and from the corresponding distributions for the inelastic scattering by free molecules. In addition, measurement of this inelastically scattered radiation may provide useful information regarding the size, shape, and refractive index of the particle and also regarding the distribution of the inelastically scattering molecules within the particle. We develop in this paper a formalism that can be used to express the experimentally observed quantities in terms of the concentration and distribution of the relevant molecules in a particle of arbitrary shape and refractive index. Explicit results are derived for spherical particles.

The point of view here is classical. The particle affects the local exciting field and the angular distribution of the emitted radiation but not the molecular transitions. The model is described in Sec. II. The induced field due to a single dipole at an arbitrary position within the particle is expanded in vector spherical harmonics in Appendix A. The unshifted transmitted field is given in Appendix B. In Sec. III the scattered field and the internal field are similarly expanded, and the expansion coefficients of the scattered field are determined by the boundary conditions for the case of a dielectric sphere. The more general case of an arbitrary distribution of dipoles inside the particle can be obtained by superposition. Extension to any other shape for which the boundary value problem can be solved is straightforward in principle, but involves much labor. The limiting case for small radius is considered in Sec. IV.

II. MODEL

If an electromagnetic wave of angular frequency ω_0 is incident on a dielectric particle, the scattered radiation will consist of an elastic part (at angular frequency ω_0) and an inelastic part at other frequencies. We consider here only inelastic scattering which arises from molecular transitions and omit consideration of quasielastic Brillouin scattering. The electromagnetic field inside the particle likewise consists of a transmitted part (at frequency ω_0) and secondary fields at other frequencies. For a particular frequency ω, we represent the secondary field as being generated by a collection of classical dipoles, arbitarily distributed within the particle, which undergo forced oscillations at frequency ω induced by the transmitted field. The strength of the induced dipoles may be described by an effective polarizability α, which in general may be a tensor, multiplying the transmitted electric field. The transmitted field is derived in the present notation in Appendix B.

At the shifted frequency ω, the field inside the particle is the sum of the induced dipole field and an internal field due to the dielectric. This internal field is a secondary field which must be postulated in order to account for the effect of the boundary upon the dipolar field. Outside the particle, there is only an outgoing field at this frequency. This outgoing field is determined in terms of the dipole field by the standard boundary conditions, which state that at frequency ω the tangential components of $\vec{E}$ and $\vec{H}$ must be continuous at the boundary of the particle.

III. BOUNDARY CONDITIONS AND SCATTERED FIELD

We now carry out the calculations outlined in Sec. II. Consider a spherical particle embedded in a homogeneous medium. Let a plane wave of angular frequency ω_0 be incident on the particle. This will give rise to forced oscillations of free and bound charges synchronous with the incident field, as well as to molecular transitions that result in the emission of radiation at different frequencies. The electric field inside the particle consists of the transmitted field $\vec{E}_1^0(\vec{r}, \omega_0)$ at the incident frequency (see Appendix B) and induced fields $\vec{E}_1(\vec{r}, \omega)$ at other frequencies. Similar statements can be made regarding the magnetic fields. As indicated in Sec. II, the induced fields will be approximated by a distribution of induced dipoles oscillating at frequency ω. We work out the fields for a single induced dipole in this section. The result for the general case may then be obtained in a straightforward way by superposition.

Let the media inside and outside the sphere be labeled 1 and 2 with dielectric constants ϵ_1 and ϵ_2, magnetic permeabilities μ_1 and μ_2, wave numbers k_1 and k_2, and indices of refraction n_1 and n_2, respectively. These material constants depend upon the particular frequency ω or ω_0 under consideration; ω is used for the calculations in Sec. III. We require the fields outside to approach outgoing spherical waves at large distances,[3]

$$\vec{E}_2(\vec{r}) = \sum_{l,m} \left(\frac{ic}{n_2^2\omega} c_E(l,m) \nabla \times [h_l^{(1)}(k_2 r) \vec{Y}_{llm}(\hat{r})] + c_M(l,m) h_l^{(1)}(k_2 r) \vec{Y}_{llm}(\hat{r}) \right), \tag{1}$$

$$\vec{B}_2(\vec{r}) = \sum_{l,m} \left(c_E(l,m) h_l^{(1)}(k_2 r) \vec{Y}_{llm}(\hat{r}) - \frac{ic}{\omega} c_M(l,m) \nabla \times [h_l^{(1)}(k_2 r) \vec{Y}_{llm}(\hat{r})] \right). \tag{2}$$

The fields $\vec{E}_1(\vec{r})$ and $\vec{B}_1(\vec{r})$ inside the sphere will be the dipole fields $\vec{E}_{\rm dip}$ and $\vec{B}_{\rm dip}$ plus the fields due to the dielectric

$$\vec{E}_1(\vec{r}) = \vec{E}_{\rm dip}(\vec{r}) + \sum_{l,m} \{ (ic/n_1^2\omega) b_E(l,m) \nabla \times [j_l(k_1 r) \vec{Y}_{llm}(\hat{r})] + b_M(l,m) j_l(k_1 r) \vec{Y}_{llm}(\hat{r}) \}, \tag{3}$$

$$\vec{B}_1(\vec{r}) = \vec{B}_{\rm dip}(\vec{r}) + \sum_{l,m} \{ b_E(l,m) j_l(k_1 r) \vec{Y}_{llm}(\hat{r}) - (ic/\omega) b_M(l,m) \nabla \times [j_l(k_1 r) \vec{Y}_{llm}(\hat{r})] \}, \tag{4}$$

with

$$\vec{E}_{\rm dip}(\vec{r}) = \sum_{l,m} \{ (ic/n_2^2\omega) a_E(l,m) \nabla \times [h_l^{(1)}(k_1 r) \vec{Y}_{llm}(\hat{r})] + a_M(l,m) h_l^{(1)}(k_1 r) \vec{Y}_{llm}(\hat{r}) \}, \tag{5}$$

$$\vec{B}_{\rm dip}(\vec{r}) = \sum_{l,m} \{ a_E(l,m) h_l^{(1)}(k_1 r) \vec{Y}_{llm}(\hat{r}) - (ic/\omega) a_M(l,m) \nabla \times [h_l^{(1)}(k_1 r) \vec{Y}_{llm}(\hat{r})] \}, \tag{6}$$

where $a_E(l,m)$ and $a_M(l,m)$ are given by (A14) and (A19). It should be understood that these fields refer to one specific dipole localized at $\vec{r}'$ and that the coefficients in each of the expansions (3)–(6) are functions of $\vec{r}'$. The coefficients $c_E(l,m)$ and $c_M(l,m)$ of the outgoing field are determined in terms of the known dipole coefficients $a_E(l,m)$ and $a_M(l,m)$ by the boundary conditions

$$\hat{r} \times \vec{E}_1 = \hat{r} \times \vec{E}_2 \tag{7}$$

and

$$\hat{r} \times \vec{H}_1 = \hat{r} \times \vec{H}_2 \tag{8}$$

evaluated at $r = a$. In view of (A16), of the vector identity

$$\hat{r}\times\{\nabla\times[g_l\vec{Y}_{llm}(\hat{r})]\}=\hat{r}\times\left(\frac{1}{r}\frac{d}{dr}(rg_l)\hat{r}\times\vec{Y}_{llm}(\hat{r})+\frac{i[l(l+1)]^{1/2}}{r}g_l\hat{r}Y_{lm}(\hat{r})\right)=-\frac{1}{r}\frac{d}{dr}(rg_l)\vec{Y}_{llm}(\hat{r}),\tag{9}$$

where g_l denotes either j_l or $h_l^{(1)}$, and also of the orthogonality of the $\vec{Y}_{l\gamma m}$'s for different γ, the boundary conditions give

$$\frac{1}{n_2^2}\frac{d}{da}[ah_l^{(1)}(k_2a)]\,c_E(l,m)=\frac{1}{n_1^2}\frac{d}{da}[ah_l^{(1)}(k_1a)]\,a_E(l,m))+\frac{1}{n_1^2}\frac{d}{da}[aj_l(k_1a)]\,b_E(l,m),\tag{10}$$

$$h_l^{(1)}(k_2a)c_M(l,m)=h_l^{(1)}(k_1a)a_M(l,m)+j_l(k_1a)b_M(l,m);\tag{11}$$

$$\frac{1}{\mu_2}h_l^{(1)}(k_2a)c_E(l,m)=\frac{1}{\mu_1}h_l^{(1)}(k_1a)a_E(l,m)+\frac{1}{\mu_1}j_l(k_1a)b_E(l,m),\tag{12}$$

$$\frac{1}{\mu_2}[k_2ah_l^{(1)}(k_2a)]'c_M(l,m)=\frac{1}{\mu_1}[k_1ah_l^{(1)}(k_1a)]'a_M(l,m)+\frac{1}{\mu_1}[k_1aj_l(k_1a)]'b_M(l,m),\tag{13}$$

where

$$[xf(x)]'\equiv\frac{d}{dx}[xf(x)].\tag{14}$$

Solving Eqs. (11)–(13), we find

$$c_E(l,m)=\frac{\mu_2n_2^2\{h_l^{(1)}(k_1a)[k_1aj_l(k_1a)]'-j_l(k_1a)[k_1ah_l^{(1)}(k_1a)]'\}\,a_E(l,m)}{\mu_1n_2^2h_l^{(1)}(k_2a)[k_1aj_l(k_1a)]'-\mu_2n_1^2j_l(k_1a)[k_1ah_l^{(1)}(k_1a)]'}=\frac{(in_2^2/\mu_1k_1a)a_E(l,m)}{\epsilon_1j_l(k_1a)[k_2ah_l^{(1)}(k_2a)]'-\epsilon_2h_l^{(1)}(k_2a)[k_1aj_l(k_1a)]'}\tag{15}$$

and

$$c_M(l,m)=\frac{(i\mu_2/k_1a)a_M(l,m)}{\mu_1j_l(k_1a)[k_2ah_l^{(1)}(k_2a)]'-\mu_2h_l^{(1)}(k_2a)[k_1aj_l(k_1a)]'},\tag{16}$$

where we have used the properties of the Wronskians of the spherical Bessel functions to simplify the numerators. At large distances

$$h_l^{(1)}(k_2r)\to(-i)^{l+1}e^{ik_2r}/k_2r,\tag{17}$$

$$\nabla\times[h_l^{(1)}(k_2r)\vec{Y}_{llm}(\hat{r})]\to(-i)^l(e^{ik_2r}/r)\,\hat{r}\times\vec{Y}_{llm}(\hat{r}),\tag{18}$$

and

$$\vec{B}_2(\vec{r})\to\frac{e^{ik_2r}}{k_2r}\sum_{l,m}(-i)^{l+1}[c_E(l,m)\vec{Y}_{llm}(\hat{r})+n_2c_M(l,m)\,\hat{r}\times\vec{Y}_{llm}(\hat{r})],\tag{19}$$

$$\vec{E}_2(\hat{r})\to(1/n_2)\vec{B}_2(\vec{r})\times\hat{r}.\tag{20}$$

The time-averaged power radiated per solid angle is

$$\frac{dP}{d\Omega}=\frac{cr^2}{8\pi n_2^2}|\vec{B}_2(\vec{r})|^2=\frac{c^3}{8\pi n_2^4\omega^4}\left|\sum_{l,m}(-i)^{l+1}[c_E(l,m)\vec{Y}_{llm}(\hat{r})+n_2c_M(l,m)\,\hat{r}\times\vec{Y}_{llm}(\hat{r})]\right|^2,\tag{21}$$

where $n_2=1$ if the outside medium is vacuum, and where the coefficients $c_E(l,m)$ and $c_M(l,m)$ are given by Eqs. (15), (16), (A14), and (A19).

IV. LIMITING CASE

If both k_1a and k_2a are much less than unity, we have

$$c_E(l,m)\to(2l+1)\left(\frac{n_2}{n_1}\right)^{l+1}\frac{\mu_2n_2^2a_E(l,m)}{l\mu_2n_1^2+(l+1)\mu_1n_2^2},$$
$$=\frac{3a_E(1,m)}{n_1^2(n_1^2+2\mu_1)}\quad\text{for } n_2=1,\ \mu_2=1,\ \text{and } l=1;\tag{22}$$

$$c_M(l,m) \to (2l+1)\left(\frac{n_2}{n_1}\right)^{l+1} \frac{\mu_2 a_M(l,m)}{l\mu_1+(l+1)\mu_2},$$
$$= \frac{3a_M(1,m)}{n_1^2(\mu_1+2)} \quad \text{for } n_2=1\,,\ \mu_2=1\,,\ \text{and } l=1\,. \tag{23}$$

Since $r' \leq a$, Eq. (A14) shows that the leading nonvanishing values of $a_E(l,m)$ correspond to $l=1$ and

$$a_E(1,1) = (\tfrac{4}{3}\pi)^{1/2} ik_1^3(p_x - ip_y)\,, \tag{24}$$
$$a_E(1,-1) = -(\tfrac{4}{3}\pi)^{1/2} ik_1^3(p_x + ip_y)\,, \tag{25}$$
$$a_E(1,0) = -(\tfrac{8}{3}\pi)^{1/2} ik_1^3 p_z\,. \tag{26}$$

To this order $a_M(1,m)=0$, as can be seen from Eq. (A19). Thus according to Eq. (21) the angular distribution of the radiated power P is (setting $n_2=1$)

$$\frac{dP}{d\Omega} \cong \frac{c^3}{8\pi\omega^3}\left|\sum_m c_E(1,m)\vec{\mathrm{Y}}_{11m}(\hat{r})\right|^2$$
$$= \frac{9\omega^4 n_1^2}{8\pi c^3(n_1^2+2\mu_1)^2}[p_x^2\sin^2\phi + p_y^2\cos^2\phi + p_z^2 + (p_x^2\cos^2\phi + p_y^2\sin\phi - p_z^2)\cos^2\theta$$
$$- 2\sin\theta(p_x p_y \sin\theta\cos\phi\sin\phi + p_y p_z\cos\theta\sin\phi + p_x p_z\cos\theta\cos\phi)]\,, \tag{27}$$

and the total radiated power is

$$P = \int \frac{dP}{d\Omega} = \frac{3\omega^4 n_1^2 \vec{\mathrm{p}}^2}{c^3(n_1^2+2\mu_1)^2}\,. \tag{28}$$

For a dipole along the z axis the angular distribution reduces to the simple form

$$\frac{dP}{d\Omega} = \frac{9\omega^4 n_1^2 \vec{\mathrm{p}}^2}{8\pi c^3(n_1^2+2\mu_1)^2}\sin^2\theta. \tag{29}$$

In this limit the radiation depends upon the strength of the induced dipole but not on the radius of the particle. In general, the angular distribution involves more terms in the series expansion. These additional terms will contain information about the radius a, and this will be of interest in applications to cell biology and atmospheric physics.

V. DISCUSSION

The angular distribution of the radiation emitted by a dipole in a dielectric sphere is represented in terms of a multipole expansion in Eq. (21). The expansion coefficients $c_E(l,m)$ and $c_M(l,m)$ are given in terms of the dipole strength by Eqs. (15), (16), (A14), and (A19). The effects of the particle boundary are immediately obvious when, as in Eqs. (15) and (16), the expansion coefficients for the inelastically scattered field are expressed in terms of the corresponding expansion coefficients for the dipole alone. The strength and orientation of the dipole depends, in turn, upon the transmitted field (at the unshifted frequency ω_0) at that location within the particle and upon the polarizability tensor. Finally, the transmitted field is a linear function of the radiation field incident on the particle. For the reader's convenience we rederive the (unshifted) transmitted field in our notation in terms of the incident field in Appendix B. For many important cases the polarizability α is a scalar and the angular distribution is completely determined by the transmitted field.

Problems involving distributions of more than one scattering molecule can be obtained from the above solution by superposition. For coherent scattering the expression for the electric field given in Eq. (20) can be multiplied by the appropriate distribution function and integrated over the relevant region of the particle. For incoherent scattering it is the time average power per unit solid angle given in Eq. (21) that is weighted and integrated.

In neither case is it reasonable to expect either the angular distribution or the polarization to be identical to the elastic case when the expression in Eq. (21) is integrated over the distribution of fluorescent particles, even in the special case where the fluorescent molecules comprise the entire particle.

Most problems of practical interest will require computer calculations similar to those now used in the standard Lorenz-Mie scattering calculations.[4] Raman and fluorescent scattering are currently used to identify specific molecules and to estimate their concentrations. When the scattering molecules are embedded in particles that are large compared to molecular dimensions the angular distribution and polarization of the inelastically scattered radiation can be used to extract information on the size and shape of the particle. When used in conjunction with Lorenz-Mie scattering, information on the distribution of the relevant molecules can be obtained.

Most important, the effect of particle size and refractive index on the angular distribution of the fluorescent or Raman scattering must be considered in any quantitative description of that scattering.

APPENDIX A: VECTOR SPHERICAL HARMONICS EXPANSION OF DIPOLE FIELD

We shall use the same units and notation as Jackson[3] except for the vector spherical harmonics. For the latter we follow the notations of Edmonds.[5]

Let the vector potential at the coordinate $\vec{r}$ due to an oscillating electric dipole at $\vec{r}'$ with dipole moment $\vec{p}$ be $\vec{A}_{dip}$. Suppressing the factor $e^{-i\omega t}$, we have

$$\vec{A}_{dip} = -ik\vec{p}\frac{e^{ik|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|} = 4\pi k^2\vec{p}\sum_{l,m} j_l(kr')h_l^{(1)}(kr)Y_{lm}^*(\hat{r}')Y_{lm}(\hat{r}), \tag{A1}$$

so that

$$\vec{B}_{dip} = \nabla\times\vec{A}_{dip} = 4\pi k^3\sum_{l,m} j_l(kr')h_l^{(1)\prime}(kr)\,\hat{r}\times\vec{p}\,Y_{lm}^*(\hat{r}')Y_{lm}(\hat{r}) + \frac{4\pi ik^2}{r}\sum_{l,m} j_l(kr')h_l^{(1)}(kr)Y_{lm}^*(\hat{r}')[\hat{r}\times\vec{L}\,Y_{lm}(\hat{r})], \tag{A2}$$

where $j_l(x)$ denotes the spherical Bessel function regular at the origin,

$$h_l^{(1)\prime}(x) = \frac{d}{dx}h_l^{(1)}(x), \quad \text{and} \quad \vec{L} = -i\vec{r}\times\nabla.$$

To avoid complications in writing we assume $r' < r$. This is justified in the case of a sphere which we work out in detail because the fields are eventually evaluated for $\vec{r}$ at the surface of the sphere.

To fit the boundary conditions, we need an expansion of $\vec{B}_{dip}$ of the form

$$\vec{B}_{dip} = \sum_{l,m}\{a_E(l,m)h_l^{(1)}(kr)\vec{Y}_{llm}(\hat{r}) - (ic/\omega)a_M(l,m)\nabla\times[h_l^{(1)}(kr)\vec{Y}_{llm}(\hat{r})]\}. \tag{A3}$$

The coefficients $a_E(l,m)$ and $a_M(l,m)$, which depend on the coordinate $\vec{r}'$, are obtained from (A2) using the orthogonal properties of the vector spherical harmonics. We have

$$\begin{aligned} a_E(l',m')h_{l'}^{(1)}(kr) &= \int \vec{Y}_{l'l'm'}^*(\hat{r})\cdot\vec{B}_{dip}\,d\Omega \\ &= \frac{4\pi ik^2}{r}\vec{p}\cdot\Big(-i\sum_{l,m} j_l(kr')Y_{lm}^*(\hat{r}')krh_l^{(1)\prime}(kr)\int\vec{Y}_{l'l'm'}^*(\hat{r})\times[\hat{r}Y_{lm}(\hat{r})]\,d\Omega \\ &\qquad - \sum_{l,m}[l(l+1)]^{1/2}j_l(kr')Y_{lm}^*(\hat{r}')h_l^{(1)}(kr)\int\hat{r}[\vec{Y}_{l'l'm'}^*(\hat{r})\cdot\vec{Y}_{llm}(\hat{r})]\,d\Omega\Big). \end{aligned} \tag{A4}$$

To evaluate the first integral in the last statement of (A4), we use the identity[6]

$$\hat{r}Y_{lm}(\hat{r}) = -\left(\frac{l+1}{2l+1}\right)^{1/2}\vec{Y}_{l,l+1,m}(\hat{r}) + \left(\frac{l}{2l+1}\right)^{1/2}\vec{Y}_{l,l-1,m}(\hat{r}). \tag{A5}$$

The integral then reduces to a sum of integrals of cross products of vector spherical harmonics. The latter can be evaluated by expanding the vector spherical harmonics in terms of the ordinary spherical harmonics Y_{lm}. Inserting the appropriate Clebsch-Gordan coefficients, we find

$$\vec{Y}_{l'l'm'}^* = \sum_{\mu,q}[Y_{l'\mu}\hat{e}_q(l',\mu,1,q|l',1,l',m)]^* \equiv \Big(\sum_q \alpha_q\hat{e}_q\Big)^*, \tag{A6}$$

$$\vec{Y}_{l,l+1,m} = \sum_{\mu',q'}[Y_{l+1,\mu'}\hat{e}_{q'}(l+1,\mu',1,q'|l+1,1,l,m)] \equiv \sum_{q'}(\beta_{q'}\hat{e}_{q'}), \tag{A7}$$

$$\begin{aligned} \int\vec{Y}_{l'l'm'}(\hat{r})\times\vec{Y}_{l,l+1,m}(\hat{r})\,d\Omega &= \int[-(\alpha_{-1}^*\beta_0+\alpha_0^*\beta_1)\hat{e}_1 + (\alpha_1^*\beta_1-\alpha_{-1}^*\beta_{-1})\hat{e}_0 + (\alpha_1^*\beta_0+\alpha_0^*\beta_{-1})\hat{e}_{-1}]\,d\Omega \\ &= \frac{\delta_{l',l+1}}{2l'}\left(\frac{l'+1}{2l'+1}\right)^{1/2}\vec{F}, \end{aligned} \tag{A8}$$

where

$$F_x = i\{[(l'-m)(l'-m'-1)]^{1/2}\delta_{m',\,m-1} + [(l'+m')(l'+m'-1)]^{1/2}\delta_{m',\,m+1}\}, \tag{A9}$$

$$F_y = [(l'-m')(l'-m'-1)]^{1/2}\delta_{m',\,m-1} + [(l'+m')(l'+m'-1)]^{1/2}\delta_{m',\,m+1},$$

$$F_z = -2i[(l'+m')(l'-m')]^{1/2}\delta_{m'm}.$$

The other cross product can be evaluated in the same way; the result is

$$\int \vec{\mathrm{Y}}^{*}_{l'l'm'}(\hat{r}) \times [\hat{r}\, Y_{lm}(\hat{r})]\, d\Omega = -\tfrac{1}{2}\delta_{l',l+1}\left(\frac{l'+1}{l'(2l'+1)(2l'-1)}\right)^{1/2}\vec{\mathrm{F}} - \tfrac{1}{2}\delta_{l',l-1}\left(\frac{l'}{(l'+1)(2l'+1)(2l'+3)}\right)^{1/2}\vec{\mathrm{G}}, \tag{A10}$$

where $\vec{\mathrm{F}}$ is given by Equation (A7) and

$$G_x = i\{[(l'-m'+1)(l'-m'+2)]^{1/2}\delta_{m',\,m+1} - [(l'+m'+1)(l'+m'+2)]^{1/2}\delta_{m',\,m-1}\}, \tag{A11}$$

$$G_y = [(l'-m'+1)(l'-m'+2)]^{1/2}\delta_{m',\,m+1} + [(l'+m'+1)(l'+m'+2)]^{1/2}\delta_{m',\,m-1},$$

$$G_z = 2i[(l'+m'+1)(l'-m'+1)]^{1/2}\delta_{m'm}.$$

To evaluate the second integral in (A4),

$$\int \hat{r}\,[\vec{\mathrm{Y}}^{*}_{l'l'm'}(\hat{r}) \cdot \vec{\mathrm{Y}}_{llm}(\hat{r})]\; d\Omega \equiv \vec{\mathrm{R}},$$

we first express the quantity inside the brackets as a sum of spherical harmonics times their complex conjugates (of different orders in general). This is then multiplied by

$$\hat{r} = (\tfrac{2}{3}\pi)^{1/2}(Y_{1,-1} - Y_{11},\, iY_{1,-1} + iY_{11},\, \sqrt{2}\,Y_{10}) \tag{A12}$$

and integrated over $d\Omega$ using well-known results for integrals of products of three spherical harmonics.[6] Thus

$$R_x = \frac{\delta_{l',l+1}}{2l'}\left(\frac{(l'+1)(l'-1)}{(2l'+1)(2l'-1)}\right)^{1/2}\{[(l'-m')(l'-m'-1)]^{1/2}\delta_{m',\,m-1} - [(l'+m')(l'+m'-1)]^{1/2}\delta_{m',\,m+1}\}$$

$$+\frac{\delta_{l',l-1}}{2(l'+1)}\left(\frac{l'(l'+2)}{(2l'+1)(2l'+3)}\right)^{1/2}\{-[(l'+m'+1)(l'+m'+2)]^{1/2}\delta_{m',\,m-1} + [(l'-m'+1)(l'-m'+2)]^{1/2}\delta_{m',\,m+1}\},$$

$$R_y = \frac{i\delta_{l',l+1}}{2l'}\left(\frac{(l'+1)(l'-1)}{(2l'+1)(2l'-1)}\right)^{1/2}\{[(l'-m')(l'-m'-1)]^{1/2}\delta_{m',\,m-1} + [(l'+m')(l'+m'-1)]^{1/2}\delta_{m',m+1}\} \tag{A13}$$

$$-\frac{i\delta_{l',l-1}}{2(l'+1)}\left(\frac{l'(l'+2)}{(2l'+1)(2l'+3)}\right)^{1/2}\{[l'+m'+1)(l'+m'+2)]^{1/2}\delta_{m',\,m-1} + [(l'-m'+1)(l'-m'+2)]^{1/2}\delta_{m',\,m+1}\},$$

$$R_z = \frac{1}{l'}\left(\frac{(l'+1)(l'-1)(l'+m')(l'-m')}{(2l'+1)(2l'-1)}\right)^{1/2}\delta_{m'm}\delta_{l',l+1} + \frac{1}{l'+1}\left(\frac{l'(l'+2)(l'-m'+1)(l'+m'+1)}{(2l'+1)(2l'+3)}\right)^{1/2}\delta_{m'm}\delta_{l',l-1}.$$

We now insert (A13) and (A10) into (A4), using the recursion relations of the spherical Bessel functions[7] to eliminate the derivatives of $h_l^{(1)}(kr)$. After considerable algebra, we find on dividing out $h_{l'}^{(1)}(kr)$ and dropping the primes that

$$a_E(l,m) = \frac{2\pi i k^3}{[l(l+1)(2l+1)]^{1/2}}\,\vec{\mathrm{p}}\cdot\left(\frac{(l+1)j_l(kr')}{[2l-1]^{1/2}}\vec{\epsilon}^{\,-} + \frac{l j_{l+1}(kr')}{[2l+3]^{1/2}}\vec{\epsilon}^{\,+}\right), \tag{A14}$$

where

$$\epsilon_x^- = [(l+m)(l+m-1)]^{1/2}Y^*_{l-1,m-1}(\hat{r}') - [(l-m)(l-m-1)]^{1/2}Y^*_{l-1,m+1}(\hat{r}'),$$

$$\epsilon_y^- = -i\{[(l+m)(l+m-1)]^{1/2}Y^*_{l-1,m-1}(\hat{r}') + [(l-m)(l-m-1)]^{1/2}Y^*_{l-1,m+1}(\hat{r}')\},$$

$$\epsilon_z^- = -2[(l+m)(l-m)]^{1/2}Y^*_{l-1,m}(\hat{r}');$$

$$\epsilon_x^+ = [(l+m+1)(l+m+2)]^{1/2}Y^*_{l+1,m+1}(\hat{r}') - [(l-m+1)(l-m+2)]^{1/2}Y^*_{l+1,m-1}(\hat{r}'),$$

$$\epsilon_y^+ = i\{[(l+m+1)(l+m+2)]^{1/2}Y^*_{l+1,m+1}(\hat{r}') + [(l-m+1)(l-m+2)]^{1/2}Y^*_{l+1,m-1}(\hat{r}')\},$$

$$\epsilon_z^+ = -2[(l+m+1)(l-m+1)]^{1/2}Y^*_{l+1,m}(\hat{r}').$$

The evaluation of $a_M(l,m)$ is similar. Taking the scalar product of Eq. (A2) with $\{\nabla\times[g_{l'}\vec{\mathrm{Y}}_{l'l'm'}(\hat{r})]\}^*$ [here

$g_{l'}$ denotes $h_{l'}^{(1)}(kr)$] and integrating we have

$$
\begin{aligned}
-\frac{ick^2}{\omega} a_M(l',m') &\left[|g_{l'}|^2 + \frac{1}{k^2r^2}\frac{d}{dr}\left(rg_{l'}^*\frac{d}{dr}rg_{l'}\right)\right] \\
&= 4\pi k^3 \sum_{l,m} j_l(kr')g_l' Y_{lm}^*(\hat{r}') \int \{\nabla\times[g_{l'}\vec{\mathrm{Y}}_{l'l'm'}(\hat{r})]\}^* \cdot (\hat{r}\times\vec{\mathrm{p}}) Y_{lm}(\hat{r})\, d\Omega \\
&\quad + \frac{4\pi i k^2}{r} \sum_{l,m} j_l(kr')g_l Y_{lm}^*(\hat{r}') \int \{\nabla\times(g_{l'}\vec{\mathrm{Y}}_{l'l'm'}(\hat{r})]\}^* \cdot \{\vec{\mathrm{p}}\times[\vec{\mathrm{r}}\times\vec{\mathrm{L}}Y_{lm}(\hat{r})]\}\, d\Omega \\
&= 4\pi k^2 \vec{\mathrm{p}} \cdot \left[\sum_{l,m} j_l(kr')g_l' Y_{lm}^*(\hat{r}')\frac{1}{r}\frac{d}{dr}(rg_l^*) \int \vec{\mathrm{Y}}_{l'l'm'}^*(\hat{r}) Y_{lm}(\hat{r})\, d\Omega \right. \\
&\quad \left. + r^{-2}[l(l+1)]^{1/2}\left([l'(l'+1)]^{1/2}g_l^* \int Y_{l'm'}^*(\hat{r})\vec{\mathrm{Y}}_{llm}(\hat{r})\, d\Omega - i\frac{d}{dr}(rg_l^*) \int [\hat{r}\times\vec{\mathrm{Y}}_{l'l'm'}^*(\hat{r})]\times[\hat{r}\times\vec{\mathrm{Y}}_{llm}(\hat{r})]\, d\Omega\right)\right] .
\end{aligned} \tag{A15}
$$

The first two integrals in the last form of Eq. (A15) can be easily evaluated by expressing the $\vec{\mathrm{Y}}_{Jlm}$'s in terms of Y_{lm}'s, while the last one can be evaluated by noting that

$$\hat{r}\times\vec{\mathrm{Y}}_{llm}(\hat{r}) = i(2l+1)^{-1/2}[\sqrt{l}\,\vec{\mathrm{Y}}_{l,l+1,m}(\hat{r}) + (l+1)^{1/2}\vec{\mathrm{Y}}_{l,l-1,m}(\hat{r})], \tag{A16}$$

which can be verified by using the identities given in Ref. 5. Proceeding in the same way as for the electric term, we find

$$
\begin{aligned}
\int [\hat{r}\times\vec{\mathrm{Y}}_{l'l'm'}^*(\hat{r})]&\times[\hat{r}\times\vec{\mathrm{Y}}_{llm}(\hat{r})]\, d\Omega \\
&= [2l'(l'+1)]^{-1}\delta_{ll'}\big(i\{\delta_{m',m+1}[(l'+m')(l'-m'+1)]^{1/2} + \delta_{m',m-1}[(l'-m')(l'+m'+1)]^{1/2}\}\hat{i} \\
&\quad + \{\delta_{m',m+1}[(l'+m')(l'-m'+1)]^{1/2} - \delta_{m',m-1}[(l'-m')(l'+m'+1)]^{1/2}\}\hat{j} + 2m\delta_{mm'}\hat{k}\big)
\end{aligned} \tag{A17}
$$

and

$$
\begin{aligned}
\int \vec{\mathrm{Y}}_{l'l'm'}^*(\hat{r}) Y_{lm}(\hat{r}) d\Omega &\\
&= \tfrac{1}{2}[l'(l'+1)]^{-1/2}\delta_{l'l}\big(\{\delta_{m',m-1}[(l'-m')(l'+m'+1)]^{1/2} + \delta_{m',m+1}[(l'+m')(l'-m'+1)]^{1/2}\}\hat{i} \\
&\quad + i\{\delta_{m',m-1}[(l'-m')(l'+m'+1)]^{1/2} - \delta_{m',m+1}[(l'+m')(l'-m'+1)]^{1/2}\}\hat{j} + 2m\delta_{m'm}\hat{k}\big),
\end{aligned} \tag{A18}
$$

where $\hat{i}$, $\hat{j}$, $\hat{k}$, are the Cartesian unit vectors. Together with an analogous expression for $\int Y_{l'm'}^*(\hat{r})\vec{\mathrm{Y}}_{llm}(\hat{r}) \times d\Omega$, we finally get

$$a_M(l,m) = \frac{-2\pi i(k^2\omega/c)j_l(kr')\vec{\mathrm{p}}\cdot\vec{\mathrm{M}}}{[l(l+1)]^{1/2}}, \tag{A19}$$

where

$$
\begin{aligned}
\vec{\mathrm{M}} = \big(&\{[(l-m)(l+m+1)]^{1/2}Y_{l,m+1}^*(\hat{r}') + [(l+m)(l-m+1)]^{1/2}Y_{l,m-1}^*(\hat{r}')\}\hat{i} \\
&+ i\{[(l-m)(l+m+1)]^{1/2}Y_{l,m+1}^*(\hat{r}') - [(l+m)(l-m+1)]^{1/2}Y_{l,m-1}^*(\hat{r}')\}\hat{j} + 2mY_{lm}^*(\hat{r}')\hat{k}\big).
\end{aligned} \tag{A20}
$$

In arriving at (A19) we have used various identities for the spherical Bessel functions[7] to simplify (A15), divided out a factor involving g_l, and dropped the primes on l and m.

We note the following properties of the coefficients a_E and $a_{M'}$ which are helpful for numerical work:

$$a_E^*(l,m) = (-1)^{m+1}a_E(l,-m), \tag{A21}$$

$$a_M^*(l,m) = (-1)^m a_M(l,-m). \tag{A22}$$

APPENDIX B: TRANSMITTED FIELD

In our model the induced dipole moment $\vec{\mathrm{p}}$ in Eq. (A1) is equal to the polarizability α times the transmitted electric field at the unshifted frequency ω_0. This is the field that stimulates the molecular transitions that ultimately result in the emission at the shifted frequency (fluorescence, Raman scattering, etc.). It can be calculated in the same way as the scattered fields for Lorenz-Mie scattering. Let a circularly polarized plane wave of frequency ω_0 moving along the z axis be incident on a sphere of radius a (as in Sec. III, the inside of the sphere is called medium 1 and the outside medium 2; also, $\omega_0=k_2c$); then

$$\vec{E}_{\rm inc}=(\hat{\epsilon}_1\pm i\hat{\epsilon}_2)e^{ik_2z}=\sum_{l,m}\{(ic/n_2^2\omega_0)\alpha_E(l,m)\nabla\times[j_l(k_2r)\vec{Y}_{llm}(\hat{r})]+\alpha_M(l,m)j_l(k_2r)\vec{Y}_{llm}(\hat{r})\}, \tag{B1}$$

$$\vec{B}_{\rm inc}=\hat{\epsilon}_3\times\vec{E}_{\rm inc}=\mp i\vec{E}_{\rm inc}=\sum_{l,m}\{\alpha_E(l,m)j_l(k_2r)\vec{Y}_{llm}(\hat{r})-(ic/\omega_0)\alpha_M(l,m)\nabla\times[j_l(k_2r)Y_{llm}(\hat{r})\}, \tag{B2}$$

where

$$\alpha_M(l,m)=i^l[4\pi(2l+1)]^{1/2}\delta_{m,\pm1}, \tag{B3}$$

$$\alpha_E(l,m)=\mp i\alpha_M(l,m). \tag{B4}$$

Outside the particle the electric field $\vec{E}_2$ is the sum of $\vec{E}_{\rm inc}$ and an elastically scattered field $\vec{E}_{\rm sc}$, which can be expanded as

$$\vec{E}_{\rm sc}=\sum_{l,m}\{(ic/n_2^2\omega_0)\beta_E(l,m)\nabla\times[(h_l^{(1)}(k_2r)\vec{Y}_{llm}(\hat{r})]+\beta_M(l,m)h_l^{(1)}(k_2r)\vec{Y}_{llm}(\hat{r})\}. \tag{B5}$$

Similarly $\vec{B}_2=\vec{B}_{\rm inc}+\vec{B}_{\rm sc}$, with

$$\vec{B}_{\rm sc}=\sum_{l,m}\{\beta_E(l,m)h_l^{(1)}(k_2r)\vec{Y}_{llm}(\hat{r})-(ic/\omega_0)\beta_M(l,m)\nabla\times[h_l^{(1)}(k_2r)\vec{Y}_{llm}(\hat{r})]\}. \tag{B6}$$

Inside the particle the transmitted fields at frequency ω_0 may be written

$$\vec{E}_1=\sum_{l,m}\{(ic/n_1^2\omega_0)\gamma_E(l,m)\nabla\times[j_l(k_1r)\vec{Y}_{llm}(\hat{r})]+\gamma_M(l,m)j_l(k_1r)\vec{Y}_{llm}(\hat{r})\}, \tag{B7}$$

$$\vec{B}_1=\sum_{l,m}\{\gamma_E(l,m)j_l(k_1r)\vec{Y}_{llm}(\hat{r})-(ic/\omega_0)\gamma_M(l,m)\nabla\times[j_l(k_1r)\vec{Y}_{llm}(\hat{r})]\}. \tag{B8}$$

Unlike the familiar case of Lorenz-Mie scattering, we are interested in the fields $\vec{E}_1$ and $\vec{B}_1$. As usual, these are determined by the boundary conditions

$$\hat{r}\times\vec{E}_1=\hat{r}\times\vec{E}_2, \tag{B9}$$

$$\hat{r}\times\vec{H}_1=\hat{r}\times\vec{H}_2, \tag{B10}$$

together with the orthogonal properties of the vector spherical harmonics. These provide the following equations for the coefficients $\gamma_E(l,m)$ and $\gamma_M(l,m)$:

$$n_1^2\alpha_E(l,m)[k_2aj_l(k_2a)]'+n_1^2\beta_E(l,m)[k_2ah_l^{(1)}(k_2a)]'=n_2^2\gamma_E(l,m)[k_1aj_l(k_1a)]', \tag{B11}$$

$$\alpha_M(l,m)j_l(k_2a)+\beta_M(l,m)h_l^{(1)}(k_2a)=\gamma_M(l,m)j_l(k_1a), \tag{B12}$$

and

$$\mu_1\alpha_E(l,m)j_l(k_2a)+\mu_1\beta_E(l,m)h_l^{(1)}(k_2a)=\mu_2\gamma_E(l,m)j_l(k_1a), \tag{B13}$$

$$\mu_1\alpha_M(l,m)[k_2aj_l(k_2a)]'+\mu_1\beta_M(l,m)[k_2ah_l^{(1)}(k_2a)]'=\mu_2\gamma_M(l,m)[k_2aj_l(k_2a)]'. \tag{B14}$$

Solving these gives the expansion coefficients of the required transmitted fields

$$\gamma_E(l,m)=\frac{(i\mu_1n_1^2/k_2a)\alpha_E(l,m)}{n_1^2\mu_2j_l(k_1a)[k_2ah_l^{(1)}(k_2a)]'-n_2^2\mu_1h_l^{(1)}(k_2a)[k_1aj_l(k_1a)]'}, \tag{B15}$$

$$\gamma_M(l,m)=\frac{-(i\mu_1/k_2a)\alpha_M(l,m)}{\mu_2h_l^{(1)}(k_2a)[k_1aj_l(k_1a)]'-\mu_1j_l(k_1a)[k_2ah_l^{(1)}(k_2a)]'}. \tag{B16}$$

These expressions have a somewhat different appearance from those given in Ref. 8 because we have used the properties of the Wronskians of the spherical Bessel functions to simplify the numerators. To facilitate comparison with works that employ different notations we list also the standard Mie scattering coefficients:

$$\beta_E(l,m)=\frac{\epsilon_2 j_l(k_2a)[k_1aj_l(k_1a)]'-\epsilon_1 j_l(k_1a)[k_2aj_l(k_2a)]'\}\alpha_E(l,m)}{\epsilon_1 j_l(k_1a)[k_2ah_l^{(1)}(k_2a)]'-\epsilon_2 h_l^{(1)}(k_2a)[k_1aj_l(k_1a)]'}, \tag{B17}$$

$$\beta_M(l,m)=\frac{\{\mu_1 j_l(k_1a)[k_2aj_l(k_2a)]'-\mu_2 j_l(k_2a)[k_1aj_l(k_1a)]'\}\alpha_M(l,m)}{\mu_2 h_l^{(1)}(k_2a)[k_1aj_l(k_1a)]'-\mu_1 j_l(k_1a)[k_2ah_l^{(1)}(k_2a)]'}. \tag{B18}$$

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[1]See, for example, P. F. Mullaney and P. N. Dean, Biophys. J. 10, 764 (1970); L. A. Kamentsky, H. R. Melamed, and H. R. Derman, Science 150, 630 (1965); W. A. Bonner, H. R. Hulett, R. G. Sweet, and L. A. Herzenberg, Rev. Sci. Instrum. 43, 404 (1972); X. Yataganas and B. D. Clarkson, J. Histochem. Cytochem, 22, 651 (1974).

[2]See, for example, J. Cooney, J. Orr, and C. Tomasetti, Nature 224, 1098 (1969); S. H. Melfi, J. D. Lawrence, Jr., and M. P. McCormick, Appl. Phys. Lett. 15, 295 (1969); J. Gelbwachs and M. Birnbaum, Appl. Opt. 12, 2442 (1973); G. J. Rosasco, E. S. Etz, and W. A. Cassatt, Appl. Spectrosc. 29, 396 (1975). This last reference verifies experimentally for Raman scattering our assumption that the molecular transitions are not affected by virtue of the molecules being embedded in a small particle.

[3]We are using the notation of J. D. Jackson [*Classical Electrodynamics* (Wiley, New York, 1962)] modified so that the expansions are valid for arbitrary dielectric media.

[4]See, for example, M. Kerker, *The Scattering of Light and Other Electromagnetic Radiation* (Academic, New York, 1969).

[5]A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton U. P., Princeton, N. J., 1957). Edmonds's $\vec{Y}_{llm}$ is the same as Jackson's $\vec{X}_{lm}$.

[6]M. E. Rose, *Elementary Theory of Angular Momentum* (Wiley, New York, 1957).

[7]See, for example, *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. Stegun (Natl. Bur. of Stand., U.S. GPO, Washington, D.C., 1965).

[8]M. Kerker and D. Cooke, Appl. Opt. 12, 1379 (1973).