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Matrix formulation of the surface-enhanced Raman optical activity theory

Petr Bouř[a)]
Institute of Organic Chemistry and Biochemistry, Academy of Sciences, Flemingovo náměstí 2, 16610 Prague 6, Czech Republic

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The previously formulated surface-enhanced (SE) Raman optical activity (ROA) theory[1] is based on a multipole electromagnetic field expansion. The field of molecule and colloid particles is induced by the excitation light. Although this semistatic polarization is not the only enhancement mechanism,[1,2] it provides a good basis for understanding of the phenomenon. However, the mathematical expressions become rather tedious due to the high degree of expansion (quadrupole and magnetic dipole) and mutual particle-molecule and molecule-particle polarizations. The huge differences between the molecular and colloid polarizabilities make iterative intuitive solutions difficult. Therefore, we propose to rewrite the formulas in a matrix form leading to direct noniterative solutions. This formulation can also be easily extended to multiparticle systems.

Particularly, let us consider N polarizable particles, typically a molecule and S colloids ($N=S+1$). By default, we express variables in *local* coordinate systems connected with the particle centers. The induced electric and magnetic dipole, and electric quadrupole are, respectively,[3]

$$\mu_{i,\alpha}=\alpha_{i,\alpha\beta}E_{i,\beta}+\frac{1}{\omega}G'_{i,\alpha\beta}\dot{B}_{i,\beta}+(1/3)A_{i,\alpha,\beta\gamma}\nabla E_{i,\beta\gamma}, \tag{1a}$$

$$m_{i,\alpha}=-\frac{1}{\omega}G'_{i,\beta\alpha}\dot{E}_{i,\beta}, \tag{1b}$$

and

$$\Theta_{i,\alpha\beta}=A_{i,\gamma,\alpha\beta}E_{i,\gamma}, \tag{1c}$$

for $i=1,\ldots,N$; $\mathbf{E}$ and $\mathbf{B}$ are the electric and magnetic field vectors. In Eqs. (1a)–(1c), the expansion up to the magnetic dipole and electric quadrupole contributions is necessary for inclusion of the optical activity phenomena. Local fields at each particle are composed of the external (light) fields $\mathbf{E}_0$ and $\mathbf{B}_0$, and contributions from the other particles:

$$E_{i,\alpha}=E_{0,\alpha}+\sum_{j=1,\ldots,N,j\neq i}(T_{ij,\alpha\beta}\mu_{j,\beta}-\nabla_{i\alpha}T_{ij,\beta\gamma}\Theta_{j,\beta\gamma}), \tag{2a}$$

$$\nabla E_{i,\alpha\delta}=\nabla E_{0,\alpha\delta}+\sum_{j=1,\ldots,N,j\neq i}(\nabla_{i\delta}T_{ij,\alpha\beta}\mu_{j,\beta}-\nabla_{i\delta}\nabla_{i\alpha}T_{ij,\beta\gamma}\Theta_{j,\beta\gamma}), \tag{2b}$$

$$B_{i,\alpha}=B_{0,\alpha}+(1/c)\sum_{j=1,\ldots,N,j\neq i}T_{ij,\alpha\beta}m_{j,\beta}, \tag{2c}$$

where

$$T_{ij,\alpha\beta}=\frac{1}{4\pi\varepsilon}\frac{3r_{ij,\alpha}r_{ij,\beta}-\delta_{\alpha\beta}r_{ij}^2}{r_{ij}^5},\quad \mathbf{r}_{ij}=\mathbf{r}_i-\mathbf{r}_j,\nabla_i=\frac{\partial}{\partial\mathbf{r}_i}.$$

The expansions are meaningful only if the light wavelength is larger than the system size, which, however, can still be true for colloid systems.[4] Similarly, the same (generally frequency-dependent) polarizabilities are assumed for the initial and scattered light, because the frequency shifts in usual Raman experiments are relatively minor. Instead of an iterative solution by inserting Eqs. (1a)–(1c) into Eqs. (2a)–(2c) and back, we will write the formulas in a matrix form. Realizing that $\ddot{\mathbf{B}}=-\omega^2\mathbf{B}$ and $\ddot{\mathbf{E}}=-\omega^2\mathbf{E}$, where ω is the light frequency, we define the respective generalized moment, polarizability, and field for each particle i as

$$\mathbf{M}_i=\begin{pmatrix}\boldsymbol{\mu}_i\\ \omega^{-1}\dot{\boldsymbol{\mu}}_i\\ \mathbf{m}_i\\ \omega^{-1}\dot{\mathbf{m}}_i\\ \boldsymbol{\Theta}_i/3\\ \omega^{-1}\dot{\boldsymbol{\Theta}}_i/3\end{pmatrix},$$

$$\mathbf{P}_i=\begin{pmatrix}\boldsymbol{\alpha}_i & \mathbf{0} & \mathbf{0} & \mathbf{G}'_i & \mathbf{A}_i/3 & \mathbf{0}\\ \mathbf{0} & \boldsymbol{\alpha}_i & -\mathbf{G}'_i & \mathbf{0} & \mathbf{0} & \mathbf{A}_i/3\\ \mathbf{0} & -\mathbf{G}'^t_i & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0}\\ \mathbf{G}'^t_i & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0}\\ \mathbf{A}^t_i/3 & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0}\\ \mathbf{0} & \mathbf{A}^t_i/3 & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0}\end{pmatrix}\ \text{and}$$

$$\mathbf{F}_i=\begin{pmatrix}\mathbf{E}_i\\ \omega^{-1}\dot{\mathbf{E}}_i\\ \mathbf{B}_i\\ \omega^{-1}\dot{\mathbf{B}}_i\\ \nabla\mathbf{E}_i\\ \omega^{-1}\nabla\dot{\mathbf{E}}_i\end{pmatrix}. \tag{3}$$

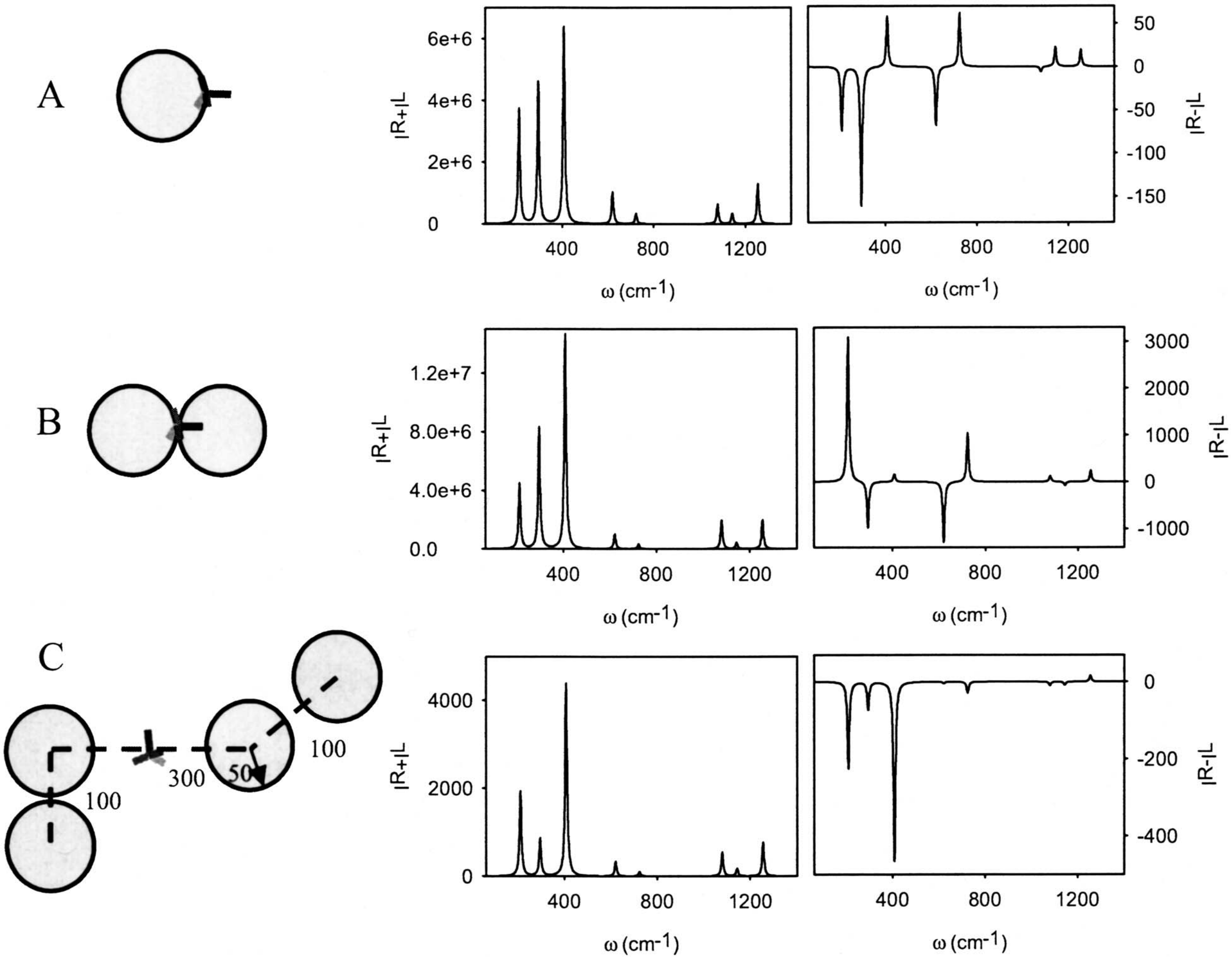

FIG. 1. Calculated Raman and ROA backscattering intensities of CHFClBr (A) on the surface of a conductive dipolar sphere, (B) between two identical and (C) four chirally arranged spheres. The dimensions are indicated in Å.

Because of the symmetry of the quadrupolar indices ($\Theta_{\beta\gamma} = \Theta_{\gamma\beta}$) the dimension of the generalized vectors (3) can be practically set to 24 (3+3+3+3+6+6). Equations (1a)–(1c) then become

$$\mathbf{M} = \mathbf{P} \cdot \mathbf{F}, \tag{4}$$

where $\mathbf{M}$, $\mathbf{P}$, and $\mathbf{F}$ are the generalized moment, polarizability, and field for the entire system, $\mathbf{M}=(\mathbf{M}_1, \mathbf{M}_2, \ldots, \mathbf{M}_\mathbf{N})$, etc. We can analogously define a generalized distance tensor,

$$\mathbf{X}_{ij} = \begin{pmatrix} \mathbf{T}_{ij} & \mathbf{0} & \mathbf{0} & \mathbf{0} & -\nabla_i \mathbf{T}_{ij} & \mathbf{0} \\ \mathbf{0} & \mathbf{T}_{ij} & \mathbf{0} & \mathbf{0} & \mathbf{0} & -\nabla_i \mathbf{T}_{ij} \\ \mathbf{0} & \mathbf{0} & \mathbf{T}_{ij}/c & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{T}_{ij}/c & \mathbf{0} & \mathbf{0} \\ \nabla_i \mathbf{T}_{ij} & \mathbf{0} & \mathbf{0} & \mathbf{0} & -\nabla_i \nabla_i \mathbf{T}_{ij} & \mathbf{0} \\ \mathbf{0} & \nabla_i \mathbf{T}_{ij} & \mathbf{0} & \mathbf{0} & \mathbf{0} & -\nabla_i \nabla_i \mathbf{T}_{ij} \end{pmatrix}$$
$$\text{for}(i \neq j), \mathbf{X}_{ii} = 0, \tag{5}$$

and write local fields (2a)–(2c) as

$$\mathbf{F} = \mathbf{F}_0 + \mathbf{X} \cdot \mathbf{M}. \tag{6}$$

Inserting the moment (4) into the field (6), we obtain $\mathbf{F} = \mathbf{F}_0 + \mathbf{X} \cdot \mathbf{P} \cdot \mathbf{F}$, and, finally, the vector $\mathbf{F}$ describing the local electromagnetic field at each particle

$$\mathbf{F} = (\mathbf{1} - \mathbf{X} \cdot \mathbf{P})^{-1} \cdot \mathbf{F}_0. \tag{7}$$

Local moments are then obtained after substitution of Eq. (7) into Eq. (4). From the total dipole moment $\mu_\alpha = \Sigma_{i=1,\ldots,N} M_{i\alpha}$ we can get the electric-dipole polarizability of the whole system as $\boldsymbol{\alpha}_T = \partial \boldsymbol{\mu} / \partial \mathbf{E}_0$, after considering contributions of desired normal mode derivatives. Total magnetic ($\mathbf{m}$) and quadrupole moments ($\boldsymbol{\theta}$) in *laboratory* coordinates can also be obtained from *local* $\mathbf{M}$ when origin-dependent terms are added, $m_\alpha(\text{lab}) = \Sigma_{i=1,\ldots,N}(M_{i\alpha+6} + \varepsilon_{\alpha\beta\gamma} r_{i\beta} \dot{\mu}_{i\gamma}/2) = \Sigma_{i=1,\ldots,N}(M_{i\alpha+6} + \omega \varepsilon_{\alpha\beta\gamma} r_{i\beta} M_{i,\gamma+3}/2)$ and $\theta_{\alpha\beta}(\text{lab}) = \Sigma_{i=1,\ldots,N}(3M_{i,(\alpha\beta)+12} + (3/2)(\mu_\alpha r_{i\beta} + \mu_\beta r_{i\alpha}) - \delta_{\alpha\beta} \mathbf{r}_i \cdot \boldsymbol{\mu}_i)$. The total optical activity tensors are then calculated as $\mathbf{G}'_T = -\partial \mathbf{m} / \partial(\dot{\mathbf{E}}_0/\omega)$ and $\mathbf{A}_T = \partial \boldsymbol{\theta} / \partial \mathbf{E}_0$. If desired, various molecular orientations with respect to the colloid particles can be averaged numerically in the current implementation.

In Fig. 1 Raman and SE ROA spectra of CHClFBr are given as an example. The molecular polarizability tensors were obtained at the density functional theory PBEPBE/cc-pVDZ level by the GAUSSIAN software[5] according to Ref. 1.

At part A where the C–F bond is oriented outside one sphere center practically the same Raman and ROA spectra are obtained as in Ref. 1, except for the highest-energy ROA peak sign, which is very dependent on the balance of the dipole and quadrupole contributions.[1] In the middle (B), the positioning of the same molecule between two identical spheres increases both Raman enhancement and circular intensity difference ratio (CID) $\mathrm{CID}=(I^R-I^L)/(I^R+I^L)$. Such enhancement increase due to the "nonspherical" quadrupolar terms was suggested in latest nanoparticle experiments.[6] When in the bottom part C the molecule is placed among chirally arranged spheres, the chiral signal is dominated by the molecular environment and the CID ratio increases even more.

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[a] Electronic mail: bour@uochb.cas.cz

[1] B. G. Janesko and G. E. Scuseria, J. Chem. Phys. **125**, 124704 (2006).
[2] L. Zhao, L. Jensen, and G. C. Schatz, J. Am. Chem. Soc. **128**, 2911 (2006).
[3] L. D. Barron, *Molecular Light Scattering and Optical Activity* (Cambridge University Press, Cambridge, 2004).
[4] K. Kneipp, H. Kneipp, S. Abdali, R. W. Berg, and H. Bohr, Spectroscopy (Amsterdam) **18**, 433 (2004).
[5] M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 03, Revision C.02, Gaussian, Inc., Wallingford, CT, 2004.
[6] C. E. Talley, J. B. Jackson, C. Oubre, N. K. Grady, C. W. Hollars, S. M. Lane, T. R. Huser, P. Nordlander, and N. J. Halas, Nano Lett. **5**, 1569 (2005).