Theoretical Modeling of the Surface-Enhanced Raman Optical Activity

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ABSTRACT: Surface-enhanced Raman optical activity (SEROA) is a new technique combining the sensitivity of the surfaceenhanced Raman scattering (SERS) with the detailed information about molecular structure provided by the chiral spectroscopies. So far, experimental SEROA spectra have been reported in several studies, but the interpretation and theoretical background are rather limited. In this work, general expressions for the electromagnetic contribution to SEROA are derived using the matrix polarization theory and used to investigate the enhancement in model systems. The results not only reveal a strong dependence of the enhancement on the distance between the molecule and a metal part but also the dependence of the ratio of ROA and Raman intensities (circular intensity difference, CID) on the distance and rotational averaging. For a ribose model, an optimal molecule–colloid distance was predicted which provided the highest CIDs. However, the CID maximum disappeared after a rotational averaging. For cysteine zwitterion, the simulated SEROA and SERS spectra provided a qualitative agreement with previous experiments.

INTRODUCTION

Surface-enhanced Raman optical activity (SEROA) is a fastdeveloping spectroscopic technique that measures a tiny difference in scattering of right and left circularly polarized light on molecules in the vicinity of metal surfaces or colloids. Similar to the surface-enhanced Raman scattering (SERS)¹ which uses unpolarized light, the SEROA method attracts attention of experimentalists^{2–4} and theoretical chemists⁵ because of the possibility to increase the sensitivity of the spectroscopic techniques. In addition, the Raman optical activity (ROA) is extremely sensitive to molecular structure, for example, to absolute configuration⁶ or conformation.⁷ Unlike the traditional ROA, the SEROA variant would not need excessive amounts of sample or too concentrated solutions.

The theoretical foundations of the SERS phenomena including SEROA are not complete. Observed enhancements are believed to be caused by a combination of large evanescent electromagnetic fields at the metal surface resulting from surface plasmon excitation, resonance Raman enhancement via metal-molecule charge-transfer states, and changes in the molecule's ground-state electronic structure.^{5,8,9} Encouraging results, for example, were obtained with modeling using clusters of a molecule and a few metal atoms.^{8,10,11}

We concentrate on the enhancement caused by the electromagnetic mutual polarization of system components (e.g., colloid and a molecule), as this contribution is always present in the scattering and well comprises the geometrical arrangement of molecules on colloid surfaces.⁵ The colloid dimension is supposed to be smaller than the wavelength;¹² however, because of the fine fractal-like structure of electrolytically roughened surfaces,^{3,12} the theory can potentially be applied in a limited way also to molecules absorbed on metal plates. According to the theory, excitation laser light induces multipole moments in the molecule, which in turn polarizes the metal particles, which are sensed by the molecule, and so forth.⁵ The laborious perturbational expressions can be efficiently

avoided using the matrix polarization theory (MPT).¹³ MPT provides total effective polarizations of the modeled system in a well tractable form and can be easily extended to multiparticle systems. We should nevertheless note that the theory so far approximates the colloid by a polarizable sphere only, the same polarizabilities are assumed for the initial and scattered light, and the chemical and plasmon parts of the enhancement are neglected. Higher order polarizability terms, such as frequencydependent magnetic susceptibility, are also neglected in this study as they are supposedly small;¹⁴ in principle, however, they can be included within MPT via the generalized polarizability matrix as well.

Previously, only general MPT expressions were given and applied to a limited number of simple systems.¹³ The dependence of polarizabilities on atomic coordinates and molecular vibrations was not discussed. In this work, we derive explicit formulas comprising derivatives of the polarization tensors with respect to nuclear coordinates. Then the theory is verified on a system of three chirally arranged water molecules, where its performance could be compared to an exact result and a perturbation approach. As an example of a more realistic system, backscattering Raman and ROA spectra of the ribose molecule in the vicinity of a polarizable metal sphere are discussed, with respect to their dependence on molecular orientation and distance. Finally, cysteine zwitterion surfaceenhanced spectra are calculated by MPT and compared to previous experimental results.

THEORY

Let us consider a cluster of N polarizable particles, for example, including molecules and colloids, exposed to a laser light. The electric dipoles, magnetic dipoles, and electric quadrupoles induced at each particle *i* are, respectively,¹⁴

Received: February 21, 2012 Published: April 10, 2012

$$m_{i,\alpha} = -\omega^{-1} \mathbf{G}'_{i,\beta\alpha} \dot{\mathbf{E}}_{i,\beta}$$
(1b)

$$\Theta_{i,\alpha\beta} = \mathbf{A}_{i,\gamma,\alpha\beta} \mathbf{E}_{i,\gamma} \tag{1c}$$

where **E** and **B** are the electric and magnetic field vectors, ω is the light frequency, α_{ij} \mathbf{G}'_{ij} and \mathbf{A}_i are the respective electric dipole–electric dipole, electric dipole–magnetic dipole, and electric dipole–electric quadrupole polarizability. The variables connected with the particles are always written in local coordinate systems (e.g., \mathbf{G}'_i and \mathbf{G}'_j are written in systems with origins translated to *i* and *j*, respectively). In MPT, we define respective generalized molecular moment (\mathbf{M}_i), polarizability (\mathbf{P}_i), and field (\mathbf{F}_i) as

$$\begin{split} \mathbf{M}_{i} &= \begin{pmatrix} \mu_{i} \\ \omega^{-1}\dot{\mu}_{i} \\ m_{i} \\ \omega^{-1}\dot{m}_{i} \\ \Theta_{i}/3 \\ \omega^{-1}\dot{\Theta}_{i}/3 \end{pmatrix} \qquad \mathbf{P}_{i} &= \begin{pmatrix} \alpha_{i} & 0 & 0 & \mathbf{G}_{i}' & \mathbf{A}_{i}/3 & 0 \\ 0 & \alpha_{i} & -\mathbf{G}_{i}' & 0 & 0 & \mathbf{A}_{i}/3 \\ 0 & -\mathbf{G}_{i}'^{t} & 0 & 0 & 0 & 0 \\ \mathbf{G}_{i}^{t} & 0 & 0 & 0 & 0 & \mathbf{O} \\ \mathbf{G}_{i}^{t}/3 & 0 & 0 & 0 & 0 & \mathbf{O} \\ \mathbf{A}_{i}^{t}/3 & 0 & 0 & 0 & 0 & \mathbf{O} \\ 0 & \mathbf{A}_{i}^{t}/3 & 0 & 0 & 0 & \mathbf{O} \\ \end{pmatrix} \\ \mathbf{F}_{i} &= \begin{pmatrix} \mathbf{E}_{i} \\ \omega^{-1}\dot{\mathbf{E}}_{i} \\ \mathbf{B}_{i} \\ \omega^{-1}\dot{\mathbf{E}}_{i} \\ \nabla \mathbf{E}_{i} \\ \omega^{-1}\nabla \dot{\mathbf{E}}_{i} \end{pmatrix} \tag{2}$$

For practical computations, because there are only 6 unique quadrupolar components, the dimension of these tensors can be set to $24 (= 4 \times 3 + 2 \times 6)$, instead of the full number of 30. For example, we can define an " $(\alpha\beta)$ " index comprising *xx*, *xy*, *xz*, *yy*, *yz*, and *zz*. Further collection of variables in the generalized moment (**M**), field (**F**), and polarizability (**P**) of the whole system allows one to write eqs 1a-1c in a compact form:

$$\mathbf{M} = \begin{pmatrix} \mathbf{M}_{1} \\ \mathbf{M}_{2} \\ \vdots \\ \mathbf{M}_{N} \end{pmatrix} = \begin{pmatrix} \mathbf{P}_{1} & 0 & \dots & 0 \\ 0 & \mathbf{P}_{2} & \dots & 0 \\ \vdots & \vdots & \cdots & \cdots & \vdots \\ 0 & 0 & \dots & \mathbf{P}_{N} \end{pmatrix} \begin{pmatrix} \mathbf{F}_{1} \\ \mathbf{F}_{2} \\ \vdots \\ \mathbf{F}_{N} \end{pmatrix} = \mathbf{P} \cdot \mathbf{F}$$
(3)

The local field \mathbf{F}_i at each particle is composed of the laser field \mathbf{F}_0 and a radiation coming from the moments induced in other particles, so that

 $\mathbf{F} = \mathbf{F}_0 + \mathbf{X} \cdot \mathbf{M} \tag{4}$

 $\mathbf{X} = \begin{pmatrix} 0 & \mathbf{X}_{12} & \dots & \mathbf{X}_{1N} \\ \mathbf{X}_{21} & 0 & \dots & \mathbf{X}_{2N} \\ \dots & \dots & \dots & \dots \\ \mathbf{X}_{N1} & \mathbf{X}_{N2} & \dots & 0 \end{pmatrix}$ $\mathbf{X}_{ij} = \begin{pmatrix} \mathbf{T}_{ij} & 0 & 0 & 0 & -\nabla_i \mathbf{T}_{ij} & 0 \\ 0 & \mathbf{T}_{ij} & 0 & 0 & 0 & -\nabla_i \mathbf{T}_{ij} \\ 0 & 0 & \mathbf{T}_{ij}/c & 0 & 0 \\ 0 & 0 & \mathbf{T}_{ij}/c & 0 & 0 \\ \nabla_i \mathbf{T}_{ij} & 0 & 0 & 0 & -\nabla_i \nabla_i \mathbf{T}_{ij} \\ 0 & \nabla_i \mathbf{T}_{ij} & 0 & 0 & 0 & -\nabla_i \nabla_i \mathbf{T}_{ij} \end{pmatrix}$

 $\mathbf{T}_{ij,\alpha\beta} = (4\pi\varepsilon_0)^{-1}(3r_{ij,\alpha}r_{ij,\beta} - \delta_{\alpha\beta}r_{ij}^{-2})r_{ij}^{-5}$, $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, $\nabla_i = \partial/\partial \mathbf{r}_i$, and ε_0 is vacuum permittivity. Note that the X and T tensors are origin independent as they depend on the position differences only.

Eliminating F from eqs 3 and 4, we can obtain the local moments as

$$\mathbf{M} = (\mathbf{P} \cdot \mathbf{E} - \mathbf{X} \cdot \mathbf{P})^{-1} \cdot \mathbf{F}_0 = \mathbf{P}_t \cdot \mathbf{F}_0$$
(5)

For vibrational Raman and ROA intensities, we will need derivatives of the total effective polarizability \mathbf{P}_t with respect to a coordinate q_{λ} ($\lambda = 1, ..., 3 \times N_{\text{atoms}}$), which can be obtained from eq 5 as

$$\mathbf{P}_{t}^{(\lambda)} = (\partial \mathbf{P}_{t}) / (\partial q_{\lambda}) \approx \mathbf{P}^{(\lambda)} \cdot (\mathbf{E} - \mathbf{X} \cdot \mathbf{P})^{-1} + \mathbf{P} \cdot (\mathbf{E} - \mathbf{X} \cdot \mathbf{P})^{-1} \cdot \mathbf{X} \cdot \mathbf{P}^{(\lambda)} (\mathbf{E} - \mathbf{X} \cdot \mathbf{P})^{-1}$$
(6)

where we neglected the term $(\partial \mathbf{X})/(\partial q_{\lambda})$, as it is rather small for multiatom molecules.

Induced momenta of the whole system, written in the common origin gauge, are

$$\mu_{t,\alpha} = \sum_{i=1,\dots,N} M_{i,\alpha} \tag{7a}$$

$$m_{t,\alpha} = \sum_{i=1,\dots,N} \left(\mathbf{M}_{i,\alpha+6} + \omega \varepsilon_{\alpha\beta\gamma} r_{i\beta} \mathbf{M}_{i,\gamma+3} / 2 \right)$$
(7b)

and

$$\Theta_{t,\alpha\beta} = \sum_{i=1,\dots,N} (3M_{i,(\alpha\beta)+12} + (3/2)(M_{i,\alpha}r_{i\beta} + M_{i,\beta}r_{i\alpha}) - \delta_{\alpha\beta}r_{i\gamma}M_{i,\gamma})$$
(7c)

so that polarizabilities $\alpha_{v} G_{t}$, and A_{t} of the whole system can be written in the common origin system as

$$\alpha_{t,\alpha\beta}^{(\lambda)} = \frac{\partial \mu_{t,\alpha}^{(\lambda)}}{\partial E_{0,\beta}} = \sum_{i=1}^{N} P_{t,i,\alpha,\beta}^{(\lambda)}$$
(8a)

$$G_{t,\beta\alpha}^{\prime(\lambda)} = -\frac{\partial m_{t,\alpha}^{(\lambda)}}{\omega^{-1}\partial \dot{\mathbf{E}}_{0,\beta}} = -\sum_{i=1}^{N} \left(\mathbf{P}_{t,i,\alpha+6,\beta+3}^{(\lambda)} + \omega \varepsilon_{\alpha\beta\gamma} r_{i\beta} \mathbf{P}_{t,i,\gamma+3,\beta+3}^{(\lambda)}/2 \right)$$
(8b)

where **X** is the distance matrix:

COMPUTATIONS

Ab initio computations of the polarizabilities $\boldsymbol{\alpha}_{i}$, $\mathbf{G}_{i'}$, and \mathbf{A}_{i} and their derivatives for studied molecules were performed with the Gaussian program.¹⁵ The MPT expressions were implemented in a separate code. Thus for molecular complexes, the Gaussian tensors, obtained for each molecule were used as an input, providing the dressed tensor derivatives 8a–8c. Intensities of various ROA experimental setups can be obtained by the usual procedures given elsewhere.^{14,16,17} For the backscattered (180°) SCP arrangement and the harmonic approximation investigated in this study, we get the respective ROA and Raman intensities for each vibrational normal mode *J* as

$$I_{J,ROA} = I_J^R - I_J^L = (8K/c) [12\beta_J (G')^2 + 4\beta_J (A)^2]$$
(9a)

$$I_{J,\text{Raman}} = I_J^R + I_J^L = 4K[45\alpha_J^2 + 7\beta_J(\alpha)^2]$$
(9b)

where *K* is a constant, *c* is the velocity of light, and the tensor invariants are defined from the normal mode polarizability derivatives $(\alpha_{\alpha,\beta}^{(J)} = \partial \alpha_{\alpha,\beta} / \partial Q_p$ etc.) as^{17,18}

$$\beta_{J}(G')^{2} = (1/2)(3\alpha_{\alpha\beta}^{(J)}G_{\alpha\beta}^{(J)} - \alpha_{\alpha\alpha}^{(J)}G_{\beta\beta}^{(J)})$$

$$\beta_{J}(A)^{2} = (1/2)\omega\alpha_{\alpha\beta}^{(J)}\varepsilon_{\alpha\gamma\delta}A_{\gamma,\delta\beta}^{(J)}$$

$$\alpha_{J}^{2} = (1/9)\alpha_{\alpha\alpha}^{(J)}\alpha_{\beta\beta}^{(J)}$$

$$\beta_{I}(\alpha)^{2} = (1/2)(3\alpha_{\alpha\beta}^{(J)}\alpha_{\alpha\beta}^{(J)} - \alpha_{\alpha\alpha}^{(J)}\alpha_{\beta\beta}^{(J)})$$

The Einstein summation convention is used, and $\varepsilon_{\alpha\beta\gamma}$ is the antisymmetric tensor. From the intensities (eqs 9a and 9b), the Stokes spectra were calculated as sums of the normal mode contributions with a temperature correction factor and a convolution with Lorenztian curves:

$$S(\omega) = \sum_{J} I_{J} \left[1 - \exp\left(-\frac{\omega_{J}}{kT}\right) \right]^{-1} \frac{1}{\omega_{J}} \left[4\left(\frac{\omega - \omega_{J}}{\Delta}\right)^{2} + 1 \right]^{-1}$$
(10)

where *k* is the Boltzmann constant, *T* is temperature (298 K), ω_l is the normal-mode frequency, and $\Delta = 15 \text{ cm}^{-1}$.

For a test of the MPT polarizability derivative expressions, a water trimer geometry was constructed from three parallel water molecules; the neighboring ones being separated by 4 Å and rotated by 30°. The monomer geometries were optimized at the HF/6-31G* level, and monomer and trimer dynamic polarizability tensors calculated at the HF level with the 6-31++G** basis set using the laser excitation wavelength of 532 nm. Then the trimer polarizabilities, in addition to the exact result, were calculated (1) as a plain sum from monomer tensors obtained for isolated H₂O molecules; (2) using the perturbational mutual polarization correction;^{14,19} and (3) with the MPT expressions above.

As a more realistic example, we chose a colloid particle and a ribose molecule. The colloid was approximated by a polarizable sphere of isotropic polarizability $\alpha = 1 \times 10^6$. A randomly chosen ribose conformation was selected and optimized by energy minimization by Gaussian at the B3LYP²⁰/6-31+G**/CPCM²¹(water) level; with this approximation, the dynamic polarizability tensor derivatives (α , G', and A, with the frequency corresponding to 532 nm) and harmonic force

field were computed as well. Using the MPT expressions above, the atomic derivatives of the total polarizability and the Raman and ROA SCP backscattered intensities were calculated. Spectra averaged over molecular rotation, $\overline{S} = (4\pi)^{-1} \int S d\Omega$, were also calculated, Ω is the spatial angle, and the integration was performed on a variable spherical grid so that the numerical error could be kept under desired limit (0.1%).

As a third example, we chose the cysteine zwitterion, for which SEROA was reported lately.³ Conformational search was done on 27 initial geometries, generated by 120° increment rotations around the ${}^{\alpha}C-C_{O}$, ${}^{\alpha}C-{}^{\beta}C$, and ${}^{\beta}C-S$ bounds, using the B3LYP/6-311++G**/CPCM(H₂O) level as implemented in Gaussian. The solvent model was also applied. The search provided nine stable conformers, from which the Raman, ROA, SERS, and SEROA spectra were calculated by Boltzmann averaging, using the excitation wavelength of 532 nm. For the surface enhancement, the metal part was replaced by a polarizable sphere of $\alpha = 3 \times 10^6$, separated by 100 Å from the cysteine. Because we suppose a large rotational freedom of the molecule in the SEROA experiment,³ the spectra were averaged (in addition to the Boltzmann averaging) over the molecular rotation, as for the ribose.

EXPERIMENTAL SECTION

D- and L-Cysteine obtained from Sigma-Aldrich (CZ) were dissolved in water (16 mg/120 μ L), and the spectra were measured with the backscattering SCP Biotools μ -ChiralRA-MAN-2X instrument using the excitation laser wavelength of 532 nm.²² Laser power was set to 600 mW (power at the sample was 300 mW), with total acquisition time 4 h. The presented experimental ROA spectrum was obtained after subtraction of D- and L-cysteine spectra and division by 2. Solvent bands were subtracted from the Raman spectra, and minor baseline corrections were made.

RESULTS AND DISCUSSION

Water Trimer Test System. As a simple test, for the water trimer, we calculated average error between the exact and transferred tensor (t = derivatives of α , G', and A) derivatives, $\delta = \left[\sum_{i=1}^{m} (t_i - t_{\text{exact},i})^2/m\right]^{1/2}$, where the group index *i* runs over all possible indices 1, ..., *m*. The errors are plotted in Figure 1. For all the approximations (plain sum, perturbational, and MPT), the error is quite small, in agreement with the behavior of similar systems observed previously.¹⁹ For example, for the magnitude of the polarizability derivatives of ~1 atomic units



Figure 1. Root-mean-square errors of the dipole (α), magnetic (G'), and quadrupole (A) polarizability tensor derivatives of the water trimer, obtained (a) without and with (b) the perturbational and (c) MPT interaction corrections.

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Figure 2. The ribose molecule in a vicinity of polarizable particle (not in scale), and the calculated Raman $(I^R + I^L)$ and ROA $(I^R - I^L)$ spectra for the distances of 6, 15, and 1000 nm.

(au), $\delta \sim 0.05$ au, i.e., 5%. By other words, the trimer polarizabilities can be fairly well approximated by a plain sum of the monomers.

Still, when the mutual polarization is turned on by the classical perturbation scheme (red bars in Figure 1), the error can be further reduced by $\sim 10\%$. The MPT (green bars) provides consistent and slightly better results than the perturbation, in particular for the **A** tensor. The small difference between the perturbational and MPT treatment corresponds to the small contribution of the mutual polarizabilities to the total response of molecular systems. For systems like the water trimer, the perturbational approach is thus adequate to correct the plain sum approximation of the polarizability tensors; however, in this example, we could verify that the MPT scheme was implemented correctly.

Ribose Surface-Enhanced Spectra. Raman and ROA surface (colloid) enhanced spectra of the D-ribose molecule simulated for the ribose—colloid distances of 6, 15, and 1000 nm are plotted in Figure 2. At the largest distance (R), the spectra are obviously identical to those of a free molecule. For R = 15 nm on average only a minor intensity increase is apparent for the Raman bands, whereas the ROA signal is enhanced much more, although the sign and relative intensity pattern is largely conserved. At the lowest distance, both the Raman and ROA enhancement is approaching 10^3 , and

significant redistribution of intensities occurs. Many ROA bands change their signs.

The average relative Raman and ROA intensities and circular intensity difference (CID) ratio¹⁴ of the ROA and Raman signal as dependent on the distance are plotted in Figure 3. The trend indicated in Figure 2, i.e., that for some distances ROA enhances more than Raman, is confirmed for a wide range of *R*. At R = 150 Å, the MPT model provides the largest CID ratio, about 10 times bigger than for the free molecule. To the best of our knowledge, this aspect of the enhancement has never been discussed before and provides a potential way of efficient experimental setup for the ROA measurement. Yet in a vicinity of the sphere (R < 100 Å) the unpolarized Raman signal becomes too large, and CID almost vanishes if compared with the free molecule limit.

In the bottom part of Figure 3, CIDs obtained for the A and G' tensor derivative contributions to ROA are plotted separately, in addition to the total ratios. As often observed for ROA,²³ the electric quadrupolar (A) contribution is small and so is the corresponding CID ratio. Nevertheless, it also exhibits a maximum for a similar distance as the total or G'-based CID enhancement. As another computational experiment displayed in Figure 3, we calculated CID ratios when a second colloid was added to ribose at the same distance but in an opposite direction. This causes maximal CID enhancement at a somewhat large distance (~200 Å) than with one particle only,



Figure 3. At the top, the dependence of the average Raman and ROA intensities $(|S| = \int_a^b |S(\omega)| d\omega/(b - a)$, $a = 0 \text{ cm}^{-1}$ and $b = 4000 \text{ cm}^{-1}$, ROA intensities were multiplied by 10^4) on the ribose–colloid distance is plotted. The bottom panel shows the average CID intensity ratio and CIDs for individual G' and A derivative contributions and when another colloid was added at the same distance but opposite direction from the ribose.

and for very short distances the ratios rise again. Finally, we introduced an asymmetry into the colloid shape via its nonzero A and G' elements (not shown), which, however, provided almost identical result to the spherical case. From this, we can deduce that colloidal aggregates may provide larger SEROA than asymmetry of individual metal particles.

The effect of molecular isomerization and orientation on the Raman and ROA enhancement is explored in Figure 4. The α and β -ribose forms provide a very similar response in the vicinity of the colloidal particle. However, the averaging of the spectra over molecular rotation has a dramatic effect on the CID ratio. In fact, the flexible system behaves in an opposite way to the "rigid" one (Figure 3), at $R \sim 150$ Å providing the smallest, not the highest CIDs; these do not vanish for shorter distances but return to values similar as to the free molecule. Quite unexpected is also the ROA absolute intensity drop around $R \sim 150$ Å, consistent, however, with the dramatic effect of the rotational averaging. The overall decrease of the ROA signal due to the molecule–colloid orientational averaging (Figure 4) is consistent with previous theoretical predictions.⁵ This can be further modified by chemical effects, not included in MPT.¹¹

Although detailed comparison to experiment cannot be done due to unknown experimental geometry, noise, and complexity of the system (hydration, many conformations), we can note that the modeled behavior is consistent with the SERS and SEROA spectra of L- and D-ribose measured with silver citrate colloids and a polycarbopol separator reported in literature.⁴ The necessity to control the colloid–sugar distance (and possibly also orientation) in experiment is consistent with the steep dependence of CID on these parameters (Figures 3 and 4). Also the ROA sign flipping for the majority of ribose bands (Figure 2) was observed in the SEROA spectra.⁴

Cysteine Silver Plate Enhancement. We apply the same model for the D-cysteine zwitterion, as this amino acid is supposed to have an increased affinity to silver surfaces, it can be modeled at a high approximation level, and its SEROA spectrum was reported recently.³ Although no experimental signal was observed with colloids, electrolytically roughened silver plate did provide SEROA. The porous silver surface confirmed by scanning electron microscopy is much closer to a colloidal dust (with features smaller than ~100 nm) than a smooth plane. Thus we consider a rough approximation of the silver by the polarizable sphere being adequate at least for a qualitative modeling of the influence of the silver surface on cysteine scattering properties.

Indeed, qualitative comparison of the experimental changes of the Raman and ROA spectra of cysteine upon vicinity of the metal surface in Figure 5 reveals encouraging similarities. For the plot, a baseline was subtracted from the experimental SEROA and SERS spectra of the D-isomer from ref 4. Note, however, that the SEROA and SERS spectra are from different experiments, and a reproducibility of the surface-enhanced spectra is often problematic.⁴ The changes in the experimental relative Raman intensities (Figure 5C,D) are not very specific; the band at ~800 cm⁻¹ becomes smaller, and the signal around 1400 cm⁻¹ becomes sharper at the presence of the surface, which both are predicted by the computation.

For ROA, the signal above 1400 cm^{-1} is not well reproduced by the calculation, and the experiment can be also affected by artifacts coming from impurities and the aqueous environ-



Figure 4. The dependence of the average ROA/Raman intensities and CID ratios on the ribose–colloid distance for averaged molecular orientation (as indicated by the Euler angles) for randomly chosen conformers of the α - and β -ribose forms.

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Figure 5. ROA (top) and Raman (bottom) spectra of D-cysteine: (A) experimental ROA of free molecule, this work, obtained as "(D - L)/2"; (B) experimental SEROA, ref 3; (C) experimental Raman, this work; (D) experimental SERS, ref 3; and (E–H) B3LYP/CPCM/6-311++G** computed Boltzmann and rotationally averaged spectra. The lowest-energy conformer geometry is the inset.

ment.⁴ However, a reasonable pattern appears in most parts of the measured wavenumber region. For the free molecule, the basic sign pattern ("+ + - +" for the experimental bands at 1216, 885, 703, and 628 cm⁻¹, Figure 5A) is reproduced by the computation (at 1231, 845, 661, and 582 cm^{-1} , Figure 5E). The vicinity of the silver surface makes the relative intensity of the positive ROA signal around 1216 cm^{-1} weaker (cf. Figure 5B), which is in rough agreement with the predicted spectrum (Figure 5F), where even negative components appear around this wavenumber. At 885 cm^{-1} (free molecule, Figure 5A), the positive signal changes to a couplet, with the negative lobe at 838 cm⁻¹ for SEROA (Figure 5B), which is all in agreement with the simulation (the calculated band at 845 cm⁻¹, Figure 5E,F). The most prominent change is apparent for the free molecule negative experimental ROA at 703 cm⁻¹, being reversed in SEROA to the strongest positive band at 715 cm⁻¹. This is provided by the MPT as well at 661 cm^{-1} . Finally, a new band appears in experimental SEROA at 530 cm⁻¹ if compared to the free molecule, which might well correspond to the calculated signal at 489 cm⁻¹. The intensities below 400 cm⁻¹ are not reliable⁴ and affected by molecular flexibility and solvent interactions not included in CPCM.²⁴

Because of the complexity of the surface-enhanced mechanisms and the many factors that cannot be currently controlled (molecular motion, silver-cysteine interaction, distance and orientation, etc.), the agreement between the computed and experimental SEROA spectra can be to a large degree accidental. Nevertheless, we can conclude that the matrix perturbation theory based on the electromagnetic interactions between the molecule and a metal particle is able to describe important molecule-metal interactions. It provides the changes in the enhanced Raman and ROA spectra as dependent on the system geometry. As such, it can become a useful tool in Raman spectroscopy and material science.

CONCLUSIONS

On the basis of the matrix polarization theory, which unlike the perturbational approach, can also be used for strongly mutually polarized systems, we derived analytical expressions for effective polarizability derivatives of the Raman and ROA tensors. The equations were implemented so that they could be used with molecular polarizability derivatives obtained by quantum chemical computations and verified on the water trimer, where MPT provided slightly better results than the perturbation approximations. Then, using force field and polarizability derivatives of ribose and cysteine molecules obtained by DFT, we approximated the metal part by a polarizable sphere and computed the SERS and SEROA spectra. For ribose, this procedure revealed an interesting dependence of the CID ROA/Raman intensity ratio on the distance and molecular orientation that was in a qualitative agreement with previously reported experiment and can potentially serve as a hint for experimental setups providing large ROA signals. For cysteine, the simulated results provided nearly band-to-band agreement to the surface enhancement observed on a silver plate. This suggests that the model is realistic and provides important information about molecular geometry and interaction with the metal.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The work was supported by the Grant Agency (P208/11/ 0105) and Ministry of Education (LH11033) of the Czech Republic. We thank Prof. Magdalena Pecul for providing us with the SEROA cysteine spectra.

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