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Tip-enhanced Raman scattering in epsilon-near-zero nanocavity

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Observation of molecular optomechanical effects is complicated by the need to localize electromagnetic energy in metal gaps about 1 nm in size. We propose to use a nanocavity with an epsilon-near-zero medium so that the conditions required for optomechanical coupling are less stringent. In this work, we simulate the enhancement of Raman scattering depending on the permittivity of the material and the polarization of the near field of the nanoparticle. It is shown that when the real part of dielectric permittivity close to zero, Raman scattering demonstrates an additional enhancement.

Keywords: molecular optomechanics, epsilon-near-zero, tip-enhanced Raman scattering, optical cooling, plasmonic nanocavity.

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Advances in manufacturing and digital technologies and the design of new materials are now closely linked to developments in the fields of nanophotonics and optoelectronics. Nanostructures in which plasmonic resonances are excited allow to localize the energy of the electromagnetic field and enhance the optical response of single molecules by several orders of magnitude. Plasmonic nanoresonators are proposed as the basis for various sensors and optoelectronic light-capturing devices to enable enhanced optical spectroscopy, photochemistry, optical materials design, and super-resolution microscopy [1–3]. The simplest example of a plasmonic nanocavity is a slit formed between two metal particles or between a particle and a substrate, in which well-localized slit modes can be excited. Optomechanical coupling in such nanocavities allows to obtain a nonlinear vibrational response of a single molecule [4]. In contrast, single plasmonic particles have a low Q factor due to the fact that metals have ohmic losses in the visible and near-infrared regions. Therefore, at room temperatures, for vibrational spectromicroscopy, plasmonic particles are used in combination with dielectric resonators, in which the mode volume is much larger than the localization region of the molecule. Nanocavities are of particular importance in the optomechanics of molecules, in particular for optical cooling using anti-Stokes Raman scattering (RS) [4,5].

In this work, we propose to reduce optical losses in a nanocavity by using media with an epsilon-near-zero (ENZ) dielectric permittivity. They have such unusual properties as a near-zero group velocity, a huge phase velocity, large optical nonlinearity, and an enhancement of field strength components normal to the interface [6]. These properties of the medium appear at frequencies of incident light close to a certain frequency ω_{ENZ} (let us call it the ENZ frequency), at which $\mathrm{Re}[\varepsilon(\omega_{\mathrm{ENZ}})] = 0$. Due to the low group velocity, these media themselves can be used as a resonant cavity. The enhancement of the electric field and the density of electromagnetic states by continuous ENZ films was shown in works [6,7]. Moreover, the advantage of ENZ materials is the ability to tune the ENZ frequency during synthesis [8].

In contrast to previous works, we study the influence of the ENZ medium on the optomechanics of the molecule by simulating enhanced Raman scattering in a resonant cavity of a plasmonic nanoparticle located near a film of such a medium. In this work, enhanced Raman spectra are analyzed depending on the dielectric constant of the film and the polarization of the optical near field of the nanoparticle. It is shown that when the condition of its real part being equal to zero is reached, an additional strengthening of the RS occurs. Simulation of forced Raman scattering for a molecule inside a layer of ENZ material was also performed.

Let us review a system consisting of a molecule on a substrate and playing the role of an optical nanoantenna of an elongated gold spheroidal nanoparticle, the major axis of which determines the orientation of the nanoantenna. The dielectric substrate is coated with a thin layer of ENZ material. Optomechanical coupling occurs due to the feedback effect of the molecular oscillation on the optical field inside the resonant cavity Let us write down the Hamiltonian of the optomechanical system [9]

$$\hat{H} = \hat{H}_{\mathrm{em}} + \hbar\Omega_0 \hat{a}^\dagger \hat{a} - \frac{1}{2}\hat{\mathbf{E}}\frac{\partial \overleftrightarrow{\alpha}}{\partial Q}\hat{\mathbf{E}} Q_0(\hat{a}^\dagger + \hat{a}), \qquad (1)$$

where $\hat{H}_{\mathrm{em}}$ — the Hamiltonian of the electromagnetic field in the medium, Ω_0 — natural frequency of the harmonic oscillator corresponding to a given normal oscillation, $\hat{a}^\dagger$ and $\hat{a}$ — bosonic creation and annihilation operators,

Q_0 — amplitude of zero-point oscillations and $\partial\overset{\leftrightarrow}{\alpha}/\partial Q$ — Raman- tensor of a given normal oscillation. Obviously, the expression

$$\mathrm{F} = (1/2)\hat{\mathbf{E}}[\partial\overset{\leftrightarrow}{\alpha}/\partial Q]\hat{\mathbf{E}}$$

represents the optical force acting on the harmonic oscillator. The nature of this force, generally speaking, can be different depending on the type of molecule. To simplify the picture, we will assume that the optical force is generated by electrostriction, i. e. the influence of the electron shells of a molecule, deformed under the influence of an electric field, on its vibrational motion. In the Born-Oppenheimer approximation, we can assume that there are separate oscillations of the field and oscillations of the molecule, which is why the field and bosonic operators commute.

Using Hamiltonian (1), the Heisenberg equations of motion can be obtained for both operators. In this case, the equations of motion of the electromagnetic field after mathematical transformations can be reduced to the Helmholtz equation

$$\nabla \times \nabla \times \hat{\mathbf{E}}(\mathbf{r}, \omega) - \varepsilon(\omega)\,\frac{\omega^2}{c^2}\,\hat{\mathbf{E}}(\mathbf{r}, \omega) = \frac{\omega^2}{\varepsilon_0 c^2}\,\hat{\mathbf{P}}(\mathbf{r}, \omega). \quad (2)$$

Here $\varepsilon(\omega)$ — dielectric permittivity of the medium in which the molecule is placed. If the molecule lies on a layer of ENZ material, then $\varepsilon(\omega) = 1$. In general, if the width of the space between the top of the nanoparticle and the surface of the ENZ layer is comparable to the dimensions of the molecule itself, then it is required to take into account the heterogeneous distribution of currents inside this molecule [10]. We will review the case of a small molecule for which the polarization currents can be considered concentrated:

$$\hat{\mathbf{P}}(\mathbf{r}, \omega) = [\partial\overset{\leftrightarrow}{\alpha}/\partial Q]Q_0(\hat{a}^\dagger + \hat{a})\hat{\mathbf{E}}(\mathbf{r}, \omega)\delta(\mathbf{r} - \mathbf{r}_m).$$

It is convenient to write the solution to equation (2) through the tensor Green's function, considering the polarization $\hat{\mathbf{P}}(\mathbf{r}, \omega)$ to be an external source and separating the components at the frequency of the incident field $\mathbf{E}_L$ and shifted frequencies (Stokes field $\mathbf{E}_S$ and anti-Stokes field $\mathbf{E}_A$):

$$\hat{\mathbf{E}}_R(\mathbf{r}) = \frac{\omega_R^2}{\varepsilon_0 c^2}\overset{\leftrightarrow}{\mathbf{G}}(\mathbf{r}, \mathbf{r}_m; \omega_R)\,\frac{\partial\overset{\leftrightarrow}{\alpha}}{\partial Q}\,Q_0\hat{b}\mathbf{E}_L(\mathbf{r}_m), \quad (3)$$

where $R = S, A$, and the operator $\hat{b} = \hat{a}$ for the anti-Stokes field and $\hat{b} = \hat{a}^\dagger$ for the Stokes field. Substituting this into the equation of motion of the oscillator and averaging, we obtain the solution

$$a(\Omega) = \sqrt{(n(T))}\,\frac{1}{-i(\Omega - \Omega_1) + \Gamma + \Gamma_{\mathrm{opt}}}, \quad (4)$$

where $n(T)$ — average vibrational population,

$$\Omega_1^2 = \Omega_0^2 - \frac{1}{\varepsilon_0 c^2}\,\mathrm{Re}\Big[\mathbf{E}_L^*\frac{\partial\overset{\leftrightarrow}{\alpha}}{\partial Q}\Big(\omega_S^2\overset{\leftrightarrow}{\mathbf{G}}(\mathbf{r}_m, \mathbf{r}_m; \omega_S) + \times\omega_{aS}^2\overset{\leftrightarrow}{\mathbf{G}}(\mathbf{r}_m, \mathbf{r}_m; \omega_{aS})\Big)\frac{\partial\overset{\leftrightarrow}{\alpha}}{\partial Q}\,\mathbf{E}_L\Big], \quad (5)$$

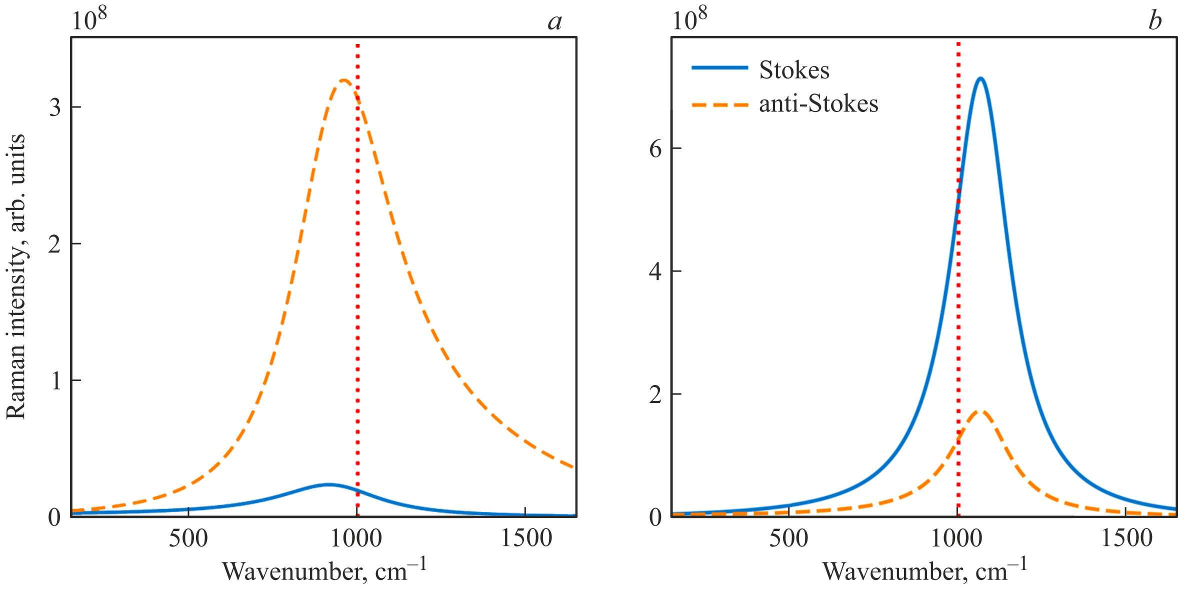
$$\Gamma_{opt} = \frac{1}{\varepsilon_0 c^2\Omega_0}\,\mathrm{Im}\Big[\mathbf{E}_L^*\,\frac{\partial\overset{\leftrightarrow}{\alpha}}{\partial Q}\,\Big(\omega_S^2\overset{\leftrightarrow}{\mathbf{G}}(\mathbf{r}_m, \mathbf{r}_m; \omega_S) + \times\omega_{aS}^2\overset{\leftrightarrow}{\mathbf{G}}(\mathbf{r}_m, \mathbf{r}_m; \omega_{aS})\Big)\frac{\partial\overset{\leftrightarrow}{\alpha}}{\partial Q}\,\mathbf{E}_L\Big] \quad (6)$$

— shifted natural frequency of oscillations („optical spring") [9] and induced relaxation rate, respectively. The latter quantity can be expressed in terms of the local density of electromagnetic states in the vicinity of the molecule [5].

The simulation was carried out using the tensor Green's function method using formulas (3)–(6). From them, knowing the Green's function, the field values at the Stokes, anti-Stokes frequencies and at the frequency of the incident field can be obtained. When determining the Green's function itself, we used the approach described in detail in the works [5,11,12]. This approach is similar to the discrete-dipole approximation (DDA) method with the difference that the Green's function in an extended homogeneous medium is taken as a basis and the far-field components are discarded. The dielectric permittivity of the ENZ medium is described by the Drude model: the plasma frequency $\omega_p \approx \omega_{\mathrm{ENZ}}$ varies within the range of the RS spectrum, the collision frequency is assumed to be $\gamma_p = 0.05\omega_p$. The interaction of the nanoantenna with the substrate is simulated using the image method. The result is a self-consistent system of equations, solving which we obtain the components of the complete tensor Green's function at the localization point of the molecule. Having found the local field at the frequency of the incident field, the Stokes and anti-Stokes fields were then calculated using formula (3).

The figure shows the dependence of the line intensity in the Stokes and anti-Stokes spectra on the wave number. The simulation was carried out for the case when the molecule is inside the ENZ layer, and the incident radiation has a frequency lower (Figure, *a*) or higher (Figure, *b*) than the ENZ frequency. It can be seen that the enhancement of anti-Stokes scattering occurs when the frequency of the incident field is lower than the frequency of the nanocavity, and vice versa. This corresponds to optomechanical cooling and heating modes, respectively. This effect is confirmed by the visible linewidth in the RS spectrum. In the cooling mode, the induced relaxation rate (6) is greater than zero, so the line in the RS spectrum broadens. In contrast, in the heating mode, the induced relaxation rate Γ_{opt} is less than zero, and vibrational pumping occurs. The RS lines narrow as in forced RS. In the figure, *a* and *b* the red dotted line indicates the position of the line in the spectrum of conventional RS radiation without optomechanical coupling. Let us note that the line in the spectrum shifts from its original position, which corresponds to the effect of an optical spring. The line shift is described by equation (5).

In this simulation, we limited to the case of an isotropic Raman tensor. However, in the case of an asymmetric molecule, its Raman tensor may have principal components that are significantly different from each other [11]. The analysis developed in this work allows to take into account



Line in the RS spectrum of a molecule optomechanically coupled to an ENZ nanocavity at an incident field frequency lower than (*a*) and higher (*b*) than the ENZ frequency. Simulation parameters: wavelength of the incident field $\lambda = 632$ nm, radius of the nanoantenna vertex $r = 10$ nm, thickness of the ENZ film $d = 50$ nm, frequency $\Omega_0 = 1000\,\text{cm}^{-1}$ (shown by the dotted line), $\Gamma = 20\,\text{cm}^{-1}$, incident field strength $\mathbf{E} = 1\,\text{V}/\lambda$.

and describe the phenomena associated with this. They can be assessed by analyzing formula (6). In order for the relaxation rate to be greatest, the matrix element of the Raman tensor $\mathbf{E}_L^*(\partial\overleftrightarrow{\alpha}/\partial Q)^2\mathbf{E}_L$ be maximal, and the $\mathbf{E}_L$ local field vector is determined to a significant extent by the orientation of the nanoantenna relative to the substrate. This means that to optimize the effect, it is required that the polarization direction of the near field coincides with the largest (in the sense of eigenvalue) principal axis of the squared Raman tensor. This result allows, under real experimental conditions, to select the orientation of the nanoantenna in order to increase the magnitude of optomechanical effects.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] J. Liu, M. Jalali, S. Mahshida, S. Wachsmann-Hogiu. Analyst, **145** (2), 364 (2020). DOI: 10.1039/C9AN02149C

[2] G.-C. Li, Q. Zhang, S.A. Maier, D. Lei. Nanophotonics, **7** (12), 1865 (2018). DOI: 10.1515/nanoph-2018-0162

[3] J. Lee, K.T. Crampton, N. Tallarida, V.A. Apkarian. Nature, **568**, 78 (2019). DOI: 10.1038/s41586-019-1059-9

[4] P. Roelli, C. Galland, N. Piro, T.J. Kippenberg. Nat. Nanotechnology, **11**, 164 (2016). DOI: 10.1038/nnano.2015.264

[5] A.R. Gazizov, M.Kh. Salakhov, S.S. Kharintsev. JETP Lett., **117** (9), 668 (2023). DOI: 10.1134/S0021364023601021

[6] I. Liberal, N. Engheta. Nature Photonics, **11**, 149 (2017). DOI: 10.1038/nphoton.2017.13

[7] A.R. Gazizov, M.Kh. Salakhov, S.S. Kharintsev. Bull. Russ. Acad. Sci.: Phys., **86**, S71 (2022). DOI: 10.3103/S1062873822700411

[8] A.V. Kharitonov, S.S. Kharintsev. Bull. Russ. Acad. Sci.: Phys., **86**, S92 (2022). DOI: 10.3103/S1062873822700459

[9] M. Aspelmeyer, T.J. Kippenberg, F. Marquardt. Rev. Mod. Phys., **86**, 1391 (2014). DOI: 10.1103/RevModPhys.86.1391

[10] X. Chen, P. Liu, Z. Hu, L. Jensen. Nat. Commun., **10**, 2567 (2019). DOI: 10.1038/s41467-019-10618-x

[11] A.R. Gazizov, M.Kh. Salakhov, S.S. Kharintsev. J. Raman Spectrosc., **51**, 442 (2020). DOI: 10.1002/jrs.5795

[12] A.R. Gazizov, M.Kh. Salakhov, S.S. Kharintsev. J. Phys.: Conf. Ser., **2015**, 012044 (2021). DOI: 10.1088/1742-6596/2015/1/012044

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