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Surface-Plasmon-Enhanced Optical Forces in Silver Nanoaggregates

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We use extended Mie theory to investigate optical forces induced by and acting on small silver nanoparticle aggregates excited at surface plasmon resonance. It is shown that single molecules can be trapped at junctions between closely spaced nanoparticles, which are simultaneously pulled together by optical forces. These effects could significantly influence surface-enhanced Raman scattering and related spectroscopies under normal experimental conditions and contribute to single-molecule sensitivity.

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The recent discovery of single-molecule sensitivity in surface-enhanced Raman scattering (SERS) [1–4] has caused a renewed interest in optical phenomena associated with resonantly excited metal nanoparticles. It is generally believed that SERS arise at certain "hot sites," where the optical interactions are locally enhanced due to excitation of surface plasmon resonances (SPR) [5]. Such sites could be located at junctions between closely spaced nanoparticles, at sharp edges or in crevices, at certain positions in fractal aggregates, etc. [6,7]. The surface enhancement M can be treated as the product of three factors, $M = M_1M_2M_3$, where M_1 is the local enhancement of the incident intensity at a certain cite, $M_2 \approx M_1$ is the enhancement at the Raman frequency, and M_3 describes the chemical interaction between the molecule and the metal surface. Extended Mie theory models indicate that the total electromagnetic enhancement $\approx M_1^2$ can reach 10^{11} in hot nanojunctions [6] and account for the dominant part of the experimentally estimated enhancement, which ranges between $M = 10^{10}$ and $M = 10^{15}$ in recent single-molecule studies [1–4]. However, as the hot sites implicated in SERS are all of nanoscopic dimensions, the local intensity, through M_1, vary by orders of magnitude over very short distances. In this Letter, we investigate to what extent the intensity gradients associated with hot nanojunctions between silver particles may lead to optical forces that influence SERS, as proposed in [4]. We find that single-molecule optical trapping effects and optical forces between closely spaced particles can be expected under *normal* experimental conditions. Elucidating the effects of such optically induced dynamic processes not only benefits SERS, but nanoparticle SPR spectroscopy and sensing in general. There is also the possibility of novel optical trapping technologies for the life sciences, as already pointed out in [8].

In the following approximate treatment, we consider the single molecule as a pointlike object characterized by an isotropic complex polarizability [9]:

$$\alpha(\omega) = \alpha'(\omega) + i\alpha''(\omega) = \alpha_1 \frac{\omega_1^2}{\omega_1^2 - \omega^2 - i\omega\Gamma_1} + \alpha_\infty. \tag{1}$$

Here the lowest lying electronic transition (HOMO ⇒ LUMO) is described as a two-level system, with strength α_1, transition frequency ω_1, and linewidth Γ_1, while contributions from higher transitions are included in the constant α_∞. The static polarizability is thus $\alpha_0 = \alpha_1 + \alpha_\infty$. As shown in Fig. 1(a), we choose parameters in order to mimic the optical response of the chromophore Rhodamine 6G (R6G) [10]. Since the molecule is

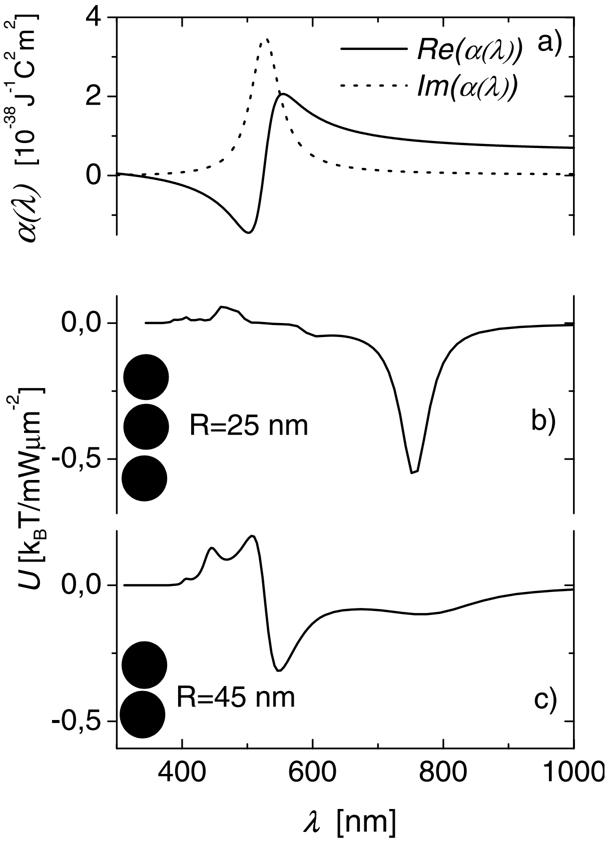

FIG. 1. (a) Wavelength dependence of the molecular polarizability [10]; (b),(c) variation in optical potential $U(\lambda)$ in units of k_BT ($T = 300$ K) at the junction between Ag particles ($d = 1$ nm) for a three-sphere and a two-sphere system in water illuminated with a plane wave polarized parallel to the symmetry axes.

considered pointlike, the electric field acting on it can be locally approximated by a plane wave $\mathbf{E}_L(\mathbf{r}, \omega) = \mathbf{E}_L(\mathbf{r})e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}$. The time-averaged optical force is then the sum of a conservative force $\langle \mathbf{F}_C \rangle = -\nabla\langle U \rangle$, where $\langle U \rangle = -\langle \mathbf{P} \cdot \mathbf{E}_L \rangle = -\frac{1}{2}\alpha' E_L^2$ is the optical potential and $\mathbf{P}$ is the induced molecular dipole moment, and a dissipative force $\langle \mathbf{F}_D \rangle = \frac{1}{2}\mathbf{k}\alpha'' E_L^2$ [9]. Using $M_1 = |\mathbf{E}_L|^2/|\mathbf{E}_0|^2$, where $\mathbf{E}_0$ is the incident field, we can then rewrite the total force as:

$$\langle \mathbf{F} \rangle = \frac{I_0 n}{c\epsilon_0}\{\alpha' \nabla M_1 + \alpha'' \mathbf{k} M_1\}, \tag{2}$$

where n is the refractive index of the surrounding medium and I_0 is the incident intensity. From Eq. (2), it is clear that a nonresonant ($\alpha' \gg \alpha''$) molecule tends to move towards the position with highest enhancement factor M_1, i.e., lowest optical potential. However, a drift should not occur unless the conservative force manages to overcome the temperature dependent Brownian motion of the molecule. Thus, if the molecule is sufficiently mobile, the probability to find it at a point $\mathbf{r}$ with optical potential $U(\mathbf{r})$ is

$$P(\mathbf{r}, U) \propto P(\mathbf{r})e^{-[\langle U(\mathbf{r})\rangle/k_B T]}, \tag{3}$$

where $P(\mathbf{r})$ is the corresponding probability "in the dark."

We now consider a model based on nearly touching silver spheres illuminated with a plane wave incident perpendicular to an axis through the particles' centers and with the electrical field parallel to this axis. This polarization configuration is the most favorable for optical trapping and SERS, since an enormous field enhancement occurs at the junction between the metal particles. The local field $\mathbf{E}_L$, and the corresponding M_1, is evaluated according to generalized Mie theory [11]. In brief, the incident and scattered fields are described as a series of vector spherical harmonics of order l, m, where the multipole index $l \in [1, \infty]$ and $m \in [-l, l]$, using the appropriate expansion coefficients for each particle. For practical reasons, the multipole expansion is truncated at an order $l = L$, which is chosen large enough to ensure convergence. The fields emanating from the different spheres in the aggregate are then coupled self-consistently, using a technique similar to the order-of-scattering method [12], which allows one to calculate the retarded total local field $\mathbf{E}_L$ at an arbitrary point in space [13]. Calculations of $M_1(\lambda)$ for several dimer configurations, and other SERS active particle shapes, can be found in [6].

In order to estimate the optical forces and potentials, we need to specify the radius (R) and the surface separation (d) of the Ag particles. In Figs. 1(b) and 1(c) we show $U(\lambda)$ within a $d = 1$ nm gap [14] for a trimer ($R = 25$ nm) and a dimer ($R = 45$ nm) in water. The variation with λ is governed by two resonance effects: the surface plasmons, via $M_1(\lambda)$, and the molecular resonance, via $\alpha'(\lambda)$. Dimers composed of small Ag particles in general exhibit plasmon resonances in the blue-green, i.e., in the same region as the absorption bands of many chromophores, such as rhodamine 6G as shown in Fig. 1(a). For larger aggregates, such as the trimer system in Fig. 1(b), the main SPR is pushed towards the near-infrared region where the molecular polarizability is real valued and out of resonance. This case is similar to those investigated by Kneipp and co-workers [1]. From Fig. 1(b), and for an incident intensity of 10 mW/μm^2 as used in [1], one finds that the optical potential well reaches a depth of $\sim 6k_B T$ [15]. According to Eq. (3), this implies that the average probability to find the molecule in the gap between the spheres increases by more than 2 orders of magnitude due to the external illumination. In Fig. 2(a), we show the spatial variation of the optical potential for the trimer system at resonance. The trapping volume, defined by $|U| > k_B T$, is very small, of the order 100 nm^3, which implies that the conservative force is correspondingly large (in the pN range). A molecule that resides within, or passes through, the trapping volume under those circumstances will thus instantaneously be forced to the position of highest SERS efficiency, i.e., at the particle junction.

For illumination close to the molecular absorption band, $\alpha'(\lambda)$ varies greatly and may take negative values depending on the ratio α_∞/α_1; see Eq. (1). Although the optical potential is resonantly enhanced at the red side of the absorption band, one now also needs to consider the dissipative force, which tends to push the molecule in the direction of the local photon wave vector $\mathbf{k}$. In Fig. 2(b), we show $\langle \mathbf{F}_C \rangle$ and $\langle \mathbf{F}_D \rangle$ at $\lambda = 550$ nm for a dimer system. For this particular wavelength, where $\alpha' \approx \alpha''$, $|\langle \mathbf{F}_C \rangle| > 10|\langle \mathbf{F}_D \rangle|$, which means that the optical trap is stable despite the dissipative force.

As shown in Fig. 3(a), molecular trapping is effective only for extremely small interparticle distances d: from electrostatics one finds $U \propto M_1 \propto d^{-2}$ [6]. The reason is that evanescent multipolar contributions dominate the optical near fields in the gap region, as can be seen from Fig. 3(b) [13]. However, the multipole fields that produce the optical trap between particles also induce a force that pulls these particles together. This is a long-range force, which thus creates molecular traps and promotes SERS.

From a microscopic point of view, the total optical force acting on a given particle is obtained from Maxwell's stress tensor $T_{ij} = \varepsilon E_i E_j + \frac{1}{\mu} B_i B_j - \frac{1}{2}(\varepsilon E^2 + \frac{1}{\mu} B^2)\delta_{ij}$ through an integration over the particle surface [16]:

$$\langle \mathbf{F} \rangle = \oint_S \langle \mathbf{T} \cdot \mathbf{n} \rangle ds. \tag{4}$$

The corresponding optical potential can be obtained from the work needed to move the particle from position $\mathbf{r}_0$ to infinity:

$$U = -\int_\infty^{r_0} \mathbf{F}(\mathbf{r}) \cdot d\mathbf{r}. \tag{5}$$

Figure 4(a) shows a near-field calculation of the force component parallel to the surface normal $\mathbf{n}$ for the lower

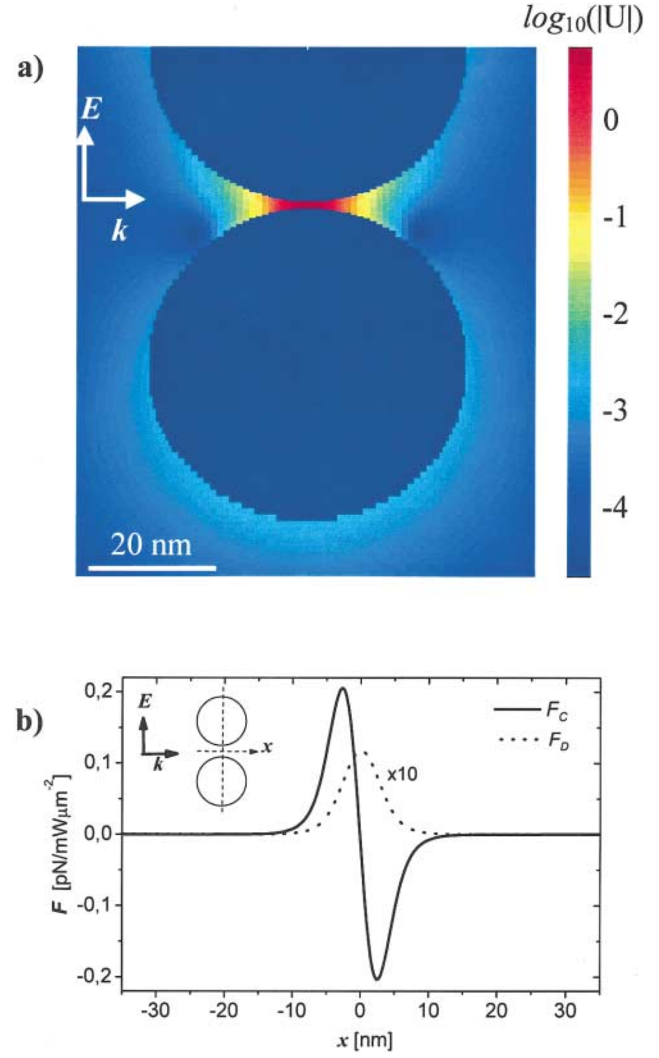

FIG. 2 (color). (a) Spatial variation of optical potential U in units of k_BT ($T = 300$ K) around a three-sphere system ($R = 25$ nm, $d = 1$ nm, $I_0 = 10$ mW/μm^2) in water excited at a collective surface plasmon resonance [$\lambda = 760$ nm, see Fig. 1(b)]. (b) The conservative (gradient) force and the dissipative force along the x axis through a dimer gap (see inset, $R = 45$ nm, $d = 1$ nm, $\lambda = 550$ nm). The intensity enhancement factors M_1 in the gap are 9.2×10^5 in (a) and 1.7×10^5 in (b). Molecular polarizability according to Fig. 1(a).

particle in a symmetrical dimer configuration. It is clear that the force field is heavily concentrated to the position of the hot site (the upper pole). For an incident intensity of 1 mW/μm^2, the net optical force, i.e., after surface integration, is 62 pN in the direction pointing towards the other particle in the dimer. This can be compared to the force in the k direction, i.e., the radiation pressure force, which is only 0.3 pN.

Figure 4(b) shows the variation in optical potential with interparticle distance for a few different sphere radii. It is clear that the attractive interaction have a fairly long range, in particular, for the larger particles. Note that the interaction turns repulsive for large separations, when the dipole fields of the individual particles are no longer in phase. This is also the case for short separations, if the incident field is polarized perpendicular to the dimer axis (not shown).

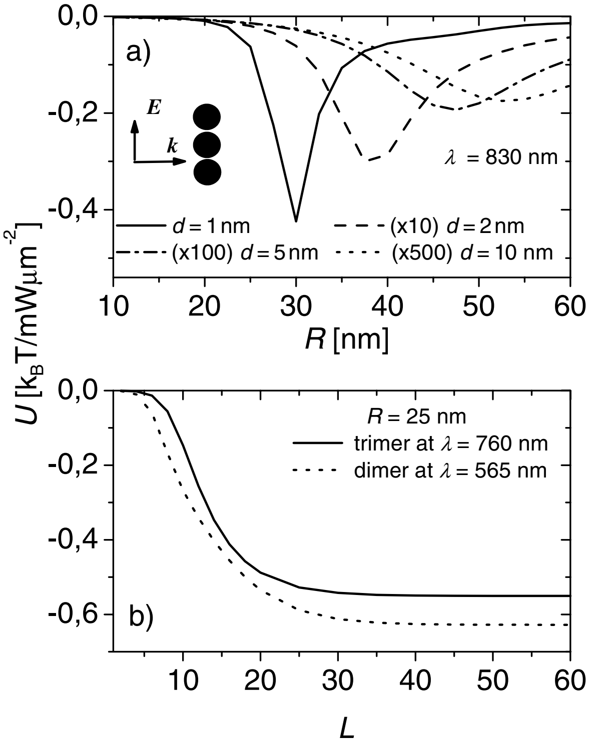

FIG. 3. (a) Variation in optical potential in a nanogap for a trimer system as a function of particle radius R and interparticle separation d. (b) Variation in optical potential in nanogaps ($d = 1$ nm) at SPR as a function of the number of multipoles L included in the Mie expansion.

Although there are no reported experimental observations of SPR induced optical forces in SERS, the results presented above indicate that such effects can be important even at moderate illumination intensities (mW/μm^2). An important observation is that the optical interactions tend to increase the "contrast" between different SERS active sites, i.e., molecules are attracted to sites with high surface enhancement and properly aligned particles are pulled closer together, and vice versa. One way to test for these kinds of interactions would be to measure the variation in SERS intensity at a certain fixed wavelength and laser power while the intensity and/or wavelength of a separate laser beam is varied, as indicated by the results in Fig. 1. We should also point out that SPR induced optical trapping effects should be equally effective for single particles, provided that sharp edges or tips with sufficiently high ∇M_1 values exist. In the case of many-particle systems, e.g., the large fractal aggregates discussed in [7], retarded dipole fields induced by particles some distance away from a particular hot site could increase the depth and range of the optical potential well further.

Finally, the preceding results suggest that surface plasmon enhanced optical forces due to coupled

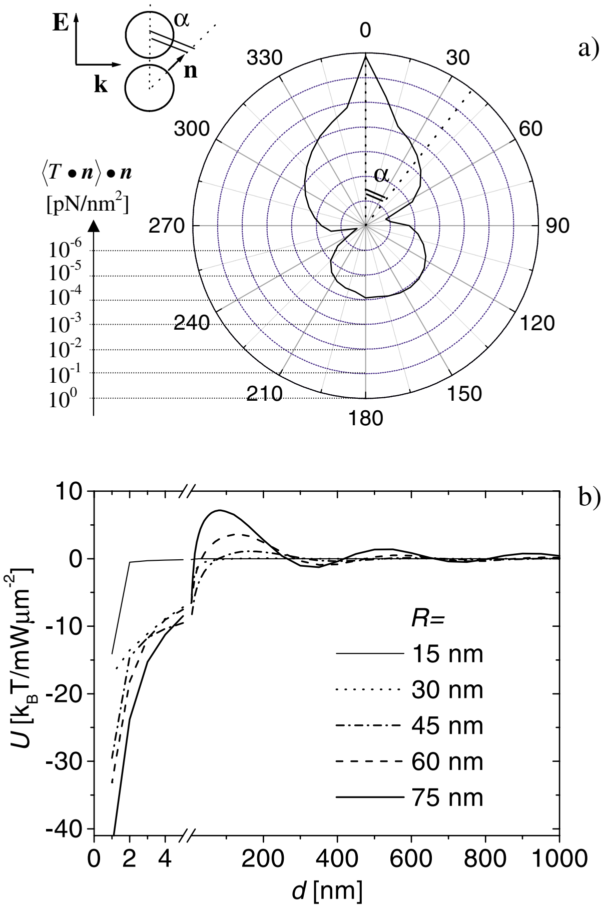

FIG. 4 (color online). (a) Polar plot of the optical force per area unit, $^{10}\log(\langle \mathbf{T} \cdot \mathbf{n} \rangle \cdot \mathbf{n})$, for the lower particle in a dimer (see inset, $I_0 = 1$ mW/μm^2, $\lambda = 514.5$ nm, $R = 45$ nm, $d = 1$ nm); (b) interparticle optical potential $U(d, R)$ for dimers in water ($T = 300$ K, polarization configuration shown in inset).

nanoparticles can be used for *controlled* manipulation of single molecules. One possibility is a scheme similar to the one proposed by Novotny *et al.* [8], but instead of a sharp metal tip, use a tip with a nanoscopic crevice, analogous to a dimer junction, which optically attracts a weakly adsorbed (macro)molecule. A more novel approach would be to use a probe that contains two closely spaced flexible protrusions, similar to the nanotweezers recently constructed by Bøggild *et al.* [17]. If the probe is coated with Au or Ag, an incident light field could force the protrusions together, similar to Fig. 4, so that an object on the surface can be gripped and moved.

In summary, we have performed quantitative electrodynamic calculations of optical forces associated with surface plasmon resonances in small Ag nanoparticle aggregates. The results indicate that single molecules can be trapped and particle aggregates can be deformed even for incident intensities of the order mW/μm^2. Such effects could play an important role in surface-enhanced Raman scattering and contribute to single-molecule sensitivity.

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[1] K. Kneipp *et al.*, Phys. Rev. Lett. **76**, 2444 (1996); **78**, 1667 (1997); Phys. Rev. E **56**, R6281 (1998).
[2] S. Nie and S. R. Emory, Science **275**, 1102 (1997).
[3] H. Xu *et al.*, Phys. Rev. Lett. **83**, 4357 (1999).
[4] A. M. Michaels, J. Jiang, and L. Brus, J. Phys. Chem. B **104**, 11 965 (2000).
[5] For SERS reviews, see M. Moskovits, Rev. Mod. Phys. **57**, 783 (1985); K. Kneipp *et al.*, Chem. Rev. **99**, 2957 (1999).
[6] H. Xu *et al.*, Phys. Rev. E **62**, 4318 (2000).
[7] M. I. Stockman *et al.*, Phys. Rev. B **46**, 2821 (1992).
[8] L. Novotny, R. X. Bian, and X. S. Xie, Phys. Rev. Lett. **79**, 645 (1997); P. C. Chaumet, A. Rahmani, and M. Nieto-Vesperinas, *ibid.* **88**, 123601 (2002); J. R. Arias-Gonsáles, M. Nieto-Vesperinas, and M. Lester, Phys. Rev. B **65**, 115402 (2002).
[9] K. D. Bonin and V. V. Kresin, *Electric-Dipole Polarizabilities of Atoms, Molecules and Clusters* (World Scientific, Singapore, 1997).
[10] The static polarizability of R6G was estimated to $\bar{\alpha}_0 \approx 347$ a.u. from *ab initio* calculations (GAUSSIAN 98, HF/6-31G*; [Patrik Johansson (private communication)]). The two-level parameters in Eq. (1) are taken from experimental absorption data for R6G in water, yielding a resonance at ~528 nm with full width of ~40 nm and an absorption cross section of $\sim 5 \times 10^{-16}$ cm^2. These data yield $\alpha_1 \approx 3.5 \times 10^{-39}$ J^{-1} C^2 m^2 and $\alpha_\infty = \alpha_0 - \alpha_1 \approx 2.2 \times 10^{-39}$ J^{-1} C^2 m^2.
[11] U. Kreibig and M. Vollmer, *Optical Properties of Metal Clusters* (Springer, New York, 1995).
[12] K. A. Fuller, Appl. Opt. **30**, 4716 (1991).
[13] H. Xu, Ph.D. thesis, Department of Applied Physics, Chalmers University of Technology, Göteborg, Sweden, 2002. This thesis contains a preprint version of this Letter.
[14] For $d = 1$ nm, the midpoint between the spheres should be outside the spillout region of the Ag s electrons; see A. Liebsch, *Electronics Excitations at Metal Surfaces* (Plenum, New York, 1997). For smaller separations, there will be an interparticle current that reduces the local field below that calculated by classical electrodynamics. Experiments indicate that this occurs at $d \approx 0.5$ nm; see C. P. Collier *et al.*, Science **277**, 1978 (1997).
[15] Because of the low absorption cross section, the illumination induced temperature rise of the nanoparticles in water is negligible for the wavelength and power ranges considered here [13].
[16] J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1998), 3rd ed.
[17] P. Bøggild *et al.*, Nanotechnology **12**, 331 (2001).