Molecular Focusing and Alignment with Plasmon Fields

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ABSTRACT We show the possibility of simultaneously aligning molecules and focusing their center-of-mass motion near a metal nanoparticle in the field intensity gradient created by the surface plasmon enhancement of incident light. The rotational motion is described quantum mechanically while the translation is treated classically. The effects of the nanoparticle shape on the alignment and focusing are explored. Our results carry interesting implications to the field of molecular nanoplasmonics and suggest several potential applications in nanotechnology.

KEYWORDS Nanoparticles, nanophotonics, surface plasmons, field enhancement, molecular alignment, molecular focusing

Molecular nanoplasmonics—the interaction of molecule/nanostructure systems with light—has been the topic of rapidly growing scientific activity during the past few years. This interest owes in part to a variety of technologically important applications, ranging from metal-enhanced spectroscopies1–5 and photocatalysis6 to nanoparticle-based sensing,7–9 measurement,10,11 and medical diagnostics.12,13 In part it owes to a range of interesting questions in fundamental science, including the competition between radiative and nonradiative decay of the excited molecule,14–17 the interplay of energy18–21 and charge22,23 transfer between the molecule and the nanoparticle, and the response of the molecule to the birefringent properties of the nanoparticle.24–26

A fascinating phenomenon which, to the best of our knowledge, was not explored as yet and which may have implications to all of the above fields, is focusing and alignment of the molecule by the spatially and orientationally inhomogeneous electromagnetic field in the vicinity of the nanoparticle. In the gas phase, both laser alignment and laser focusing of molecules have been studied in detail. The former topic, in particular, has evolved during the past decade into a major tool in optics, molecular physics, and spectroscopy.27,28 Here, a moderately intense laser pulse coherently excites a rotationally broad, spatially aligned superposition of rotational levels via sequential, angular momentum nonconserving transitions. Alignment may be induced at either near- or far-off-resonance frequencies, but most experiments to date have focused on the latter mechanism. The coherence properties of the wavepacket, and hence the quality and time evolution of the alignment, are independent of the frequency regime; they are largely determined by the duration of the alignment pulse (more generally, the duration of the pulse turn-off). In the adiabatic limit, where the pulse duration exceeds the time scale of the rotational periods, the alignment characteristics follow the pulse turn-on and turn-off; the molecules align during the laser pulse but return to their original, isotropic state upon turn-off. More interesting, and the topic of most studies to date, is the nonadiabatic case, where a short (with respect to the rotational periods) pulse impulsively imparts a significant amount of angular momentum to the material system, giving rise to dynamic alignment that survives and is enhanced following the pulse turn-off. The generalization of alignment to 3D alignment29 and its extension to complex systems, including large polyatomic molecules,30 solvated molecules,31 molecular assembly32 and molecular junctions33 are discussed elsewhere.

Molecular focusing34–40 has been the topic of many fewer studies, but is readily understood from the analogy to related topics, including optical trapping, molecular tweezers, Stern–Gerlach magnets, and state selection by a hexapole field. Here, a spatially inhomogeneous field serves to deflect the molecular trajectories in a controllable fashion. In the case of a far-off-resonance laser field, the molecules focus by virtue of the spatial dependence of the Stark shift.

Metal nanoparticles and arrays thereof are known to plasmon enhance an incident light in a manner that depends critically on the particle shape and size and is hence strongly inhomogeneous, both spatially and orientationally. In what follows we show that the plasmon enhanced field can serve to both align and focus molecules that are not chemisorbed onto the particle, giving rise to nanoscale molecular assembly with both orientational and spatial order that are subject to control. This result carries interesting implications to molecular nanoplasmonics, along with potential applications in sensing and spectroscopy.

The concept behind molecular focusing and alignment via the surface plasmon enhanced field is illustrated schematically in Figure 1. The local enhancement of the incident field creates a large gradient in the field intensity, causing the...
molecules to move down the gradient toward the region of the highest intensity. In addition, a combination of the incident field and the field scattered by the nanoparticle produces spatial variations in the field polarization vector and, as a result, variations in the alignment of the molecules in the vicinity of the nanoparticle. Since, in the far-off-resonance limit, the interaction strength is proportional to the field intensity, the alignment of the molecules becomes sharper as their centers of mass approach the nanoparticle. This qualitative picture is quantified in what follows by the field intensity region, of the order of the incident light intensity,

where $x$, $y$, $z$ are the space-fixed (SF) coordinates, and $\alpha$ is the molecular polarizability tensor. The electromagnetic field vector as a function of space and time is determined through solution of the Maxwell equations using a home-developed finite-difference time-domain approach. The molecule–nanoparticle interaction potential is

$$V = \frac{k \zeta_e}{k \zeta_e - 3D} \left\{ \frac{3}{k \zeta_e} \exp\left[-\kappa(\zeta - \zeta_e)\right] - \left(\frac{\zeta_e}{\zeta}ight)^3 \right\}$$  \hspace{1cm} (2)$$

where $\zeta$ is the shortest distance between the center of mass of the molecule and the surface of the nanoparticle, $D$ and $\zeta_e$ are the depth and the position of the minimum of the well, respectively, and the reciprocal range of repulsion, $\kappa$, modifies the curvature of the well thus aiding in fitting of the potential parameters to experimental data. The values of the parameters, $D = 0.5$ eV, $\zeta_e = 3$ Å, and $\kappa = 3.3$ Å$^{-1}$, are similar to those used in the study of scattering of NO molecules from a silver surface. Although not specific to the ethylene–silver system, these parameter values are adequate in capturing the qualitative aspects of the molecule–nanoparticle interaction in the context of the present study.

Since the field intensity varies on length scales that are much larger than the size of the molecules, the center-of-mass translational motion due to the field gradient is considerably slower than the rotational motion. Therefore, the alignment of the molecules adjusts essentially instantaneously to the changes in the electric field, as their centers of mass evolve. Provided that the field remains time invariant relative to the rotational period of the molecules, the rotational motion is adiabatically separable from their center-of-mass translation. In this regime, the centers of mass evolve on the rotational adiabatic potential energy surfaces (PES), $\{ E_{ad}(\epsilon) \}$, which depend parametrically on the field polarization vector at each point in space, and are solutions to the rotational eigenproblem

$$H_{ad}(\epsilon)\psi_{ad}(\epsilon) = E_{ad}(\epsilon)\psi_{ad}(\epsilon)$$

with the adiabatic Hamiltonian

$$H_{ad}(\epsilon) = H_{rot} + H_{ind}(\epsilon)$$

We distinguish two intensity regions with qualitatively different consequences on the molecular dynamics. A low intensity region, of the order of the incident light intensity,
where the interference between the scattered and the incoming source waves creates a diffraction pattern, and a much higher intensity region, in the vicinity of the nanoparticle, where surface plasmon enhancement dominates. The difference in the intensity scales leads to large variations in the magnitude of the minima on the adiabatic PES and ultimately to different alignment and translational dynamics in the corresponding regions. This point is illustrated in Figure 2, where the plotted range of the lowest adiabatic rotational PES \( E_0(\varepsilon) \) is limited to the well depth in the diffraction region. In the areas of constructive interference, the attractive potential wells are expansive but fairly shallow. On the other hand, the potential wells in the plasmon enhancement regions, situated by the lateral corners of the nanoparticle in Figure 2, are spatially localized and of considerably greater depth (vide infra), which goes beyond the scale of the plot.

The trends in the landscape of \( E_0(\varepsilon) \) are reflected in the alignment of molecules approaching the nanoparticle. We quantify the degree of alignment using the expectation values of the squared cosines of the Euler angles \( \theta \) and \( \phi \), i.e., \( \langle \cos^2 \alpha \rangle = \langle \psi_0 | \cos^2 \alpha | \psi_0 \rangle \), \( \alpha = \theta, \phi \). The angles \( \theta \) and \( \phi \) are analogous to the polar and azimuthal angles, respectively, of the polar coordinate system. The third Euler angle, \( \chi \), describes the internal rotation of the molecule about its \( Z \) axis (see Figure 1 for definition of the BF axes). Since for ethylene the difference in the polarizabilities along the \( X \) and \( Y \) axes (out-of-plane, and perpendicularly to the C–C bond, respectively) is very small, and since we only consider the dynamics on the lowest adiabatic rotational PES, the rotation in \( \chi \) remains essentially unaffected even in the plasmon enhancement regions. The values \( \langle \cos^2 \alpha \rangle = 1 \) and \( \langle \cos^2 \alpha \rangle = 0 \) correspond to the cases of perfect alignment and antialignment in the angle \( \alpha \), respectively. The perfect alignment in \( \theta \) indicates that the BF \( Z \) axis and the SF \( z \) axis are parallel, while the two axes are perpendicular in the case of the perfect antialignment in \( \theta \). The most polarizable molecular axis tends to align with the largest component of the electric field envelope vector.\(^{27,28}\) In the present study, the electric field is polarized in the SF \( xy \) plane, and as the most polarizable \( Z \) axis of ethylene is drawn toward the \( xy \) plane, we expect to observe antialignment in \( \theta \). For the azimuthal angle \( \phi \), perfect alignment and antialignment correspond to the projection of the \( Z \) axis onto the \( xy \) plane (\( \theta = 0, \pi \) being parallel to the \( x \) or \( y \) axis, respectively. The interplay between the two most polarizable axes of ethylene and the spatially inhomogeneous polarization of the electric field vector gives rise to areas of preferential alignment and antialignment in \( \phi \) as well as areas with isotropic rotational distribution, where every orientation of the \( Z \) axis projection onto the \( xy \) plane is equally probable. Figure 3 shows cuts through the \( \langle \cos^2 \theta \rangle \) and \( \langle \cos^2 \phi \rangle \) surfaces along the \( y \) axis for several nanoparticle shapes. The \( x \) coordinates of the cuts are chosen to be 2 nm to the left (in the layout of Figure 2) of the leftmost edge of the nanoparticle. Figure 3 illustrates sharp alignment in \( \phi \) and antialignment in \( \theta \) in the plasmon enhancement region, whereas in the diffraction region, the rotational distribution is only slightly perturbed from its isotropic values of 1/3 for \( \theta \) and 0.5 for \( \phi \). Likewise the two regions display different alignment dependence on the nanoparticle shape. All four nanoparticle shapes are very similar in size and consequently produce very similar diffraction patterns, thus, leading to little sensitivity of the alignment on the nanoparticle shape in the diffraction region. Conversely, the surface plasmon excitation depends greatly on the nanoparticle shape, giving rise to the corresponding dependence in the alignment results. Sharp features, e.g., corners, produce stronger field enhancement...
than round features. The alignment in the case of the sphere is thus much weaker than the alignment in the other three cases. The diamond and the L-shape particles produce very similar alignment results along the cut considered, since the L-shape is oriented with its elbow toward the light source and hence the nanoparticle profiles facing the incident light are similar in these two cases. The cube is of the same dimension as the diamond but oriented with its sides parallel to the xy axes. Unlike the diamond, the cube exhibits surface plasmon enhancement of the field at all four corners, with the corners closest to the light source furnishing lesser enhancement. The two areas of increased field intensity along the cut line produce two alignment peaks in Figure 3. Another difference in the alignment results in the case of the cube is observed in the alignment in $\phi$. Both alignment, i.e., $\langle \cos^2 \phi \rangle > 0.5$, and antialignment, $\langle \cos^2 \phi \rangle < 0.5$, occur at each corner of the nanoparticle with the lines of inversion collinear with the diagonals of the square. Figure 3 clearly shows two sharp transitions in the values of $\langle \cos^2 \phi \rangle$ as the cut line crosses the two inversion lines. It is evident that the degree, sense, and spatial extent of alignment can be precisely controlled by choice of the particle size and shape.

The center-of-mass translational motion is modeled by solving the classical Hamilton equations, $\dot{\mathbf{r}} = \mathbf{F}(\mathbf{r}, \mathbf{p})$, $\dot{\mathbf{p}} = -\nabla V(\mathbf{r})$, $\mathbf{p} = x, y, z$, and $\mathbf{F}(x, y, z) = (p_x^2 + p_y^2)/2m + E_0(\phi) + V$. For a number of initial conditions $\{x, y, p_x, p_y\}$, the initial coordinates are taken from the $5 \times 5$ grid uniformly sampling the $xy$ plane in Figure 2 while the initial momenta are set to $p_x = p_y = 0$. The enhanced field intensity is largest at the surface, which, combined with the van der Waals forces acting on the molecule in the immediate vicinity of the nanoparticle, results in the molecule continuing to accelerate toward the nanoparticle and eventually colliding with it. Accurate modeling of the molecule–surface collisions is beyond the scope of this article in large part because mixing of the rotational states during inelastic collisions would break the adiabatic approximation. Instead, we terminate any trajectory that comes closer than 3 Å to the surface of the nanoparticle.

The results of the classical trajectory calculations in the case of the diamond are shown in Figure 4, superimposed on a contour plot of the full potential for a diamond-shaped nanoparticle. The range of the contours is the same as in Figure 2. Trajectories starting out near the troughs on the adiabatic rotational PES in the diffraction region are transiently trapped and, for a period of time, oscillate in the potential well. Several of the trapped trajectories remain confined to the troughs for the duration of the simulation, 3 $\mu$s, while others, in their oscillatory movement, encounter a lower potential ridge and escape. The focusing effect is illustrated by the trajectories starting in the vicinity of the potential wells created by the plasmon enhanced fields. There are two pairs of such trajectories in Figure 4, one pair near each of the two enhancement regions. With their initial coordinates separated by $\sim242$ nm, the trajectories in each pair are steered directly toward the nanoparticle, cross, and collide with the nanoparticle separated by $\sim57$ nm. Similar behavior, of both trapped and focused trajectories, was also observed for the other particle shapes.

As noted above, the trajectories in this study are started with the total energy equal to the rotational energy at the corresponding point on the PES, i.e., with zero initial translational momentum. Molecules in a thermal ensemble possess both rotational and translational momentum distributions, but provided that the initial translational momentum is not exceedingly large, the qualitative aspects found in this study are not modified. Molecules with nonzero initial translational momentum are more likely to overcome the low potential energy barriers in the diffraction region. On the other hand, the much larger field gradients and deeper potential wells in the plasmonic enhancement regions are sufficient to deflect and focus molecules passing through these regions.

In summary, we showed alignment and focusing of molecules in the fields resulting from localized plasmon enhancement on the surface of a nanoparticle. In the nanoparticle vicinity, the alignment quality, sense, and spatial distribution exhibit clear dependence on the nanoparticle shape. Sharp molecular focusing occurs in the plasmon-enhanced fields for all nanoparticle shapes studied. Our results suggest the potential application of metal nanoparticles and their arrays to create molecular nanopatterns with orientational and spatial order that are both subject to control. These results invite also the extension of our approach to trap atoms or ions in the plasmon-enhanced inhomogeneous field, with potential applications in logic and lithography.

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**Supporting Information Available.** Figures are given showing the electric field envelope vector components for...
the four nanoparticle shapes, the lowest adiabatic rotational PES, and the center-of-mass trajectories for the sphere, cube, and the L-shaped nanoparticle. This material is available free of charge via the Internet at http://pubs.acs.org/.

REFERENCES AND NOTES


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