

## Molecular optics in an intense laser field: A route to nanoscale material design

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It is shown that molecules can be focused in the gradient of a moderately intense laser field under standard molecular-beam conditions. Simple relationships are given for the focal length and the minimum molecular beam size. Both can be controlled and varied over a wide range by choice of the molecular beam and field parameters. Molecular focusing is proposed as a route to nanoscale processing (deposition, etching, doping, etc.) of materials. Molecular trapping is obtained as the strong interaction limit of a general "molecular optics" scheme. [S1050-2947(97)50307-6]

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Optical manipulation of atoms has grown into a major branch of atomic physics [1,2]. Atoms have been trapped, cooled, focused, and accelerated with applications ranging from recoilless spectroscopy and atom optics [1(a)] to the study of cold collisions and of unique quantum effects induced by spatial confinement [1]. The extension of optical matter manipulation to the richer molecular domain could open a range of new possibilities. As discussed below, it could have important applications in nanoscale lithography, molecular-beam technology, novel separation techniques, and the fabrication of new materials.

Reference [3] described the use of light forces to separate atomic and molecular species in a beam and to study long-range molecular potentials. The combination of a laser field with a buffer-gas load is proposed as a potential molecular trap in the conclusion of Ref. [4], and an experimental setup to that end is described. However, a theoretical analysis that would assess the prospect of "molecular optics" and guide possible future experiments is lacking.

By analogy to the way in which laser-induced atomic trapping employs the linear momentum of photons to confine the motion of atoms to a small region of space, laser-induced molecular alignment [4,5] employs the angular momentum of photons to confine the rotational motion of molecular systems to a narrow distribution about the field-polarization direction. Molecular alignment is currently understood theoretically [4,5] and was recently demonstrated experimentally [6].

In the present work we suggest an application of both linear and angular-momentum properties of photons in the molecular domain. We show the possibility of *simultaneously aligning* the molecular axis and *focusing* its center of mass in a moderately intense (below the off-resonance ionization threshold) laser field [7]. The proposed focusing technique differs qualitatively from atomic focusing schemes [2]. It is robust, general, and potentially readily realizable in the laboratory. Molecular trapping [4] is obtained as the strong interaction limit of the molecular focusing scenario.

The possibility of depositing nanoscale strips of atoms using weak-field standing waves has been demonstrated experimentally in Ref. [8]. As discussed in detail in Ref. [8(b)], while suitable to large-scale parallelization, the weak-field standing-wave technique requires an extremely well-collimated, ultracold beam, and is therefore restricted to at-

oms with a simple level structure [9]. The potential well inducing confinement is of the sine form and hence of a relatively weak gradient. We propose the extension of nanoscale deposition [8] to the molecular domain in a way that circumvents cooling, offers potentially a sharper and controllable potential gradient, and allows flexibility in pattern design.

Much research [10] has been devoted recently to high-resolution etching, driven by the urge [11] for a new technology that will bypass the inherent limitations of conventional lithography. We propose laser desorption of reacted nanostructures following nanoscale deposition of reactive molecules as a route to *nanosize etching*. Thus, for instance, laser focusing of  $I_2$  onto silicon and subsequent photodesorption of Si-I would serve to etch nanoscale features on a silicon substrate, currently one of the important goals of applied physics [10]: Removal of monolayers of a substrate through the combination of surface chemistry with photodesorption has already been demonstrated [12]. A possible experimental configuration is shown in Fig. 1(a). Upon passage through the laser beam the molecules align along the polarization axis, and their trajectories are deflected so as to focus at a predetermined (field-free) distance downstream, where a surface is positioned. We show below that the distance of the focus from the laser axis can be controlled and varied in a wide range by choice of the molecular-beam velocity and the laser intensity.

Numerical calculations were carried out within a fully quantum-mechanical framework and within a hybrid quantum-classical approximation, and supplemented by an analytical model. We studied the cases of a near- and a far-off-resonance field and the limits of a light and a heavy molecule. Below we present only a sample of the results obtained via the hybrid quantum-classical approach and applied to the far-off-resonance case. A full account will be given elsewhere.

The system is subject to a laser field of Gaussian intensity profile

$$\vec{\varepsilon}(\vec{y}, \vec{z}; t) = \hat{\varepsilon} \varepsilon_m e^{-(y^2 + z^2)/2f(t)} \cos(\omega_l t), \quad (1)$$

where  $\hat{\varepsilon}$  is a unit vector along the polarization direction,  $\varepsilon_m$  is the field amplitude, distances are measured in units of

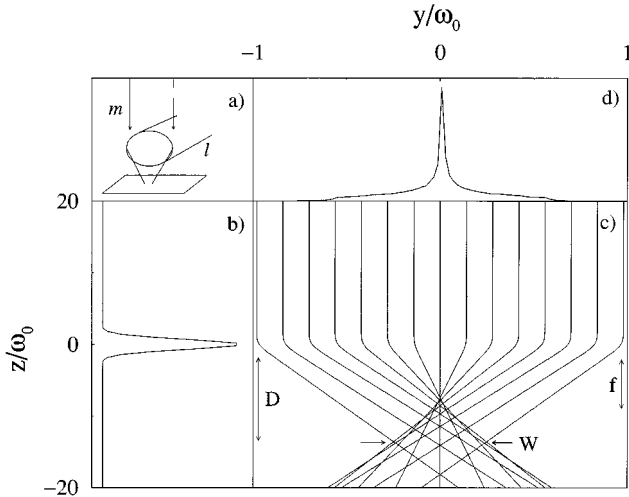


FIG. 1. (a) A possible setup: The molecular beam ( $m$ ) propagates along the  $z$  direction; a  $z$ -polarized laser beam ( $l$ ) propagates along  $x$  and the surface, placed sufficiently far from the laser beam to avoid its damage, defines the  $(x, y)$  plane. Rays impinging upon the laser beam at  $|y_i| > \omega_0$  are blocked by means of an aperture or a laser mask. (The cutoff at  $y_i = \pm \omega_0$  is arbitrary. Different cutoffs give the same qualitative behavior). (b) Effective potential  $E^{00}[\varepsilon(\bar{y}, \bar{z})]$  vs  $\bar{z}$  for peak intensity of  $I_m = 5 \times 10^{12} \text{ W cm}^{-2}$ . The well depth is 1278 K. (c) Corresponding classical trajectories for an initial beam velocity of  $v_{z,i} = 10^3 \text{ m/sec}$ .  $f$  marks the point of highest molecular density (the “focus” of the “molecular lens”),  $D$  marks the distance of the minimum molecular beam size (for a  $2\omega_0$ -wide aperture) from the laser axis and  $W$  is the minimum size. (d) A constant  $z$ -cut of the molecular density at  $z = -f$ .

the laser spot size  $\omega_0$ ,  $\bar{y} = y/\omega_0$ ,  $\bar{z} = z/\omega_0$ ,  $f(t)$  is a smooth envelope, and  $\omega_l$  is the laser frequency. Gaussian optics is neither essential nor optimal (*vide infra*).

In the far-off resonance [13] limit, subsequent to elimination of the free center-of-mass coordinate  $x$ , the complete Hamiltonian is given as

$$H = H_{\text{rel}} + \frac{1}{2m\omega_0^2} \left( \frac{\partial^2}{\partial \bar{y}^2} + \frac{\partial^2}{\partial \bar{z}^2} \right) - \vec{\mu}_{\text{ind}}(\bar{y}, \bar{z}; t) \cdot \vec{\varepsilon}(\bar{y}, \bar{z}; t), \quad (2)$$

where  $H_{\text{rel}}$  is the field-free Hamiltonian for the relative (internal) motion, and the induced dipole is  $\vec{\mu}_{\text{ind}} = \alpha \vec{\varepsilon}(\bar{y}, \bar{z}; t)$ , where  $\alpha$  is the dynamical polarizability tensor. The far-off-resonance condition eliminates a term linear in  $\vec{\varepsilon}$  and is used below to also omit the rapidly oscillating term of the field, proportional to  $\cos(2\omega_l t)$ . Molecular alignment arises from the dependence of the interaction term on the angle between the polarization and molecular axes. Molecular focusing arises from the spatial dependence of the laser intensity. The qualitative difference between the Hamiltonian (2) and the familiar Hamiltonian used in theories of atomic focusing [2] arises from the anisotropy of typical molecular polarizabilities and from the fact that a two-level description [2] cannot be applied to molecules.

Equation (2) shows that both confinement of the angular mode and confinement of the center-of-mass mode are induced by intensity gradients, the system tending to concentrate at the region of highest intensity where energy is minimized. However, while rotational motion is induced by a

gradient of the molecular size scale (several angstroms) translational motion is induced by a gradient of the laser-beam dimension ( $\omega_0 \approx 0.5\text{--}100 \mu\text{m}$ ). Put alternatively,  $(2m\omega_0^2)^{-1}$  in Eq. (2) is smaller by a factor of order  $(\omega_0/R_{\text{eq}})^2 \approx 10^7\text{--}10^{11}$  than the principle rotational constant of the molecule,  $B_e = 1/(2MR_{\text{eq}}^2)$ ,  $R_{\text{eq}}$  and  $M$  being the corresponding equilibrium distance and reduced mass. The center-of-mass translational motion is therefore ca. 4–5 orders of magnitude slower than the rotational motion, and the pulse duration required to focus is correspondingly longer than that required to align molecules [5].

The large time-scale disparity between the rotational and center-of-mass motions and the long pulses required suggests adiabatic separability of the rotational and translational modes. We first solve (quantum mechanically) for the rotational motion at fixed values of the field amplitude ( $\varepsilon$ ) and next use the resulting eigenvalues,  $E^{J_i|M|K}(\varepsilon)$  as effective potentials for the center-of-mass motion. The labeling of the eigenvalues by  $(J_i, |M|, K)$  is a reminder of the fact that in the limit of slow turn-on of the interaction the  $J_i$ th eigenpair of the full Hamiltonian,  $\{E^{J_iMK}(\varepsilon), |J_iMK; \varepsilon\rangle\}$ , correlates adiabatically with the  $J_i$ th free rotor eigenpair  $\{E^{J_iMK}(\varepsilon = 0) \approx B_e[J_i(J_i + 1) - K^2], |J_iMK; \varepsilon = 0\rangle \propto D_{KM}^J\}$  of the conserved quantum numbers  $M$  and  $K$ . In the presence of the laser field the total angular momentum loses its significance as a good quantum number and the  $|J_iMK; \varepsilon\rangle$  are best described as librator states [4], which vibrate about the field axis with decreasing amplitude as the intensity increases.

Since the de Broglie wavelength of the molecule is small with respect to the dimension of the field-induced well,  $\lambda_B = 2\pi\hbar/\sqrt{2mE} \ll \omega_0$ , classical mechanics is generally adequate for description of the center-of-mass translation (as is geometric optics in the analogous limit). We thus proceed by propagating Hamilton's equations for the center-of-mass motion, evolving on the parametrically time- and space-dependent potentials  $E^{J_i|M|K}[\varepsilon(\bar{y}, \bar{z}; t)]$ , where  $J_i$ ,  $M$ , and  $K$  are determined by the mode of preparation of the system.

We consider  $\text{I}_2$  molecules in their ground electronic state; hence  $K = \Omega = 0$ , and the parallel and perpendicular components of the polarizability are  $\alpha_{\parallel} = 114$  and  $\alpha_{\perp} = 54 \text{ bohr}^3$ , respectively [14]. The initial conditions are chosen to correspond to the configuration described in Fig. 1(a):  $\{y_i\}$  is a uniform distribution across the transverse laser beam direction,  $z_i$  is an arbitrary constant (satisfying  $z_i < v_{z,i}\tau$ , where  $\tau$  is the laser pulse duration) and the initial momentum is along the  $z$  axis. The laser is turned on before the system has reached the vicinity of the laser beam axis and kept constant while the molecules are in the beam region. The required pulse duration is thus of order  $\tau \geq 4\omega_0/v$  corresponding to  $\tau \geq 10^{-9}\text{--}10^{-7} \text{ sec}$  for typical spot sizes and beam velocities. The actual turn-on felt by the system is determined by the *spatial*, rather than by the *temporal* profile of the laser and is slow (as compared to rotations), ensuring adiabatic evolution of the eigenstates of the field-free Hamiltonian into the correlating states of the full Hamiltonian.

Figure 1(c) shows several classical trajectories in the  $\{y, z\}$  plane, evolving subject to the adiabatic potential shown in Fig. 1(b). As is evident from Fig. 1(c), the molecular-beam density reaches a sharp peak at  $\{y = 0, z = -f\}$ , the “focus” of the “molecular lens.” A cut across the

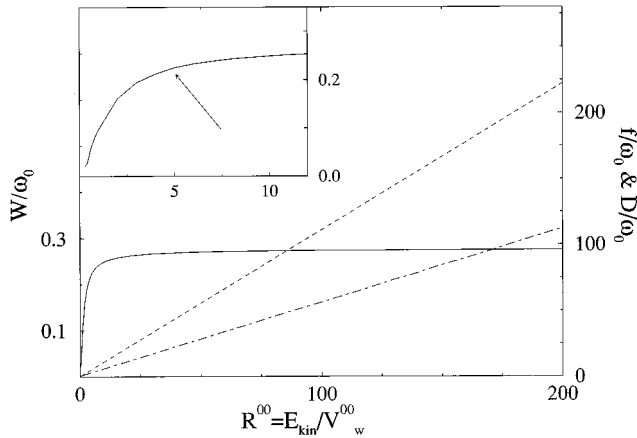


FIG. 2. The focal distance  $f$  (dotted), the width  $W$  (solid), and distance  $D$  (dash) of the minimum beam size vs the energy ratio  $R^{00}$ . The point marked by an arrow corresponds, e.g., to maximum intensity of  $I_m = 10^{12} \text{ W cm}^{-2}$  with velocity  $v_{zi} = 300 \text{ m/sec}$  (or any multiple of  $v_{zi}$  by  $n$  coupled with multiple of  $I_m$  by  $n^2$ ).

beam at  $z = -f$  is shown in Fig. 1(d). An alternative means of characterizing the lens is in terms of the distance and width of the minimum beam size, marked  $D$  and  $W$ , respectively in Fig. 1(c). The focusing parameters are determined by the ratio  $R^{J_i|M|} = E_{\text{kin}}/V_w^{J_i|M|}$  between the molecular energy and the depth of the field-induced effective well. To a good approximation  $V_w^{00} \approx \alpha_{\parallel} \varepsilon_m^2 / 4 - \sqrt{B_e \Delta \alpha \varepsilon_m}$  [4], producing, with the parameters of Fig. 1, an energy ratio of  $R^{00} = 12$ . As  $R^{J_i|M|}$  decreases both the focal length  $f$  and the width and distance parameters decrease until  $W$  shrinks to a point and  $D = f$ .

This behavior is illustrated quantitatively in Fig. 2. Both  $f$  and  $D$  are linear in the energy ratio over most of the considered range while the focal width has a fast turn-on and reaches a nearly flat plateau. In the  $R^{J_i|M|} \rightarrow 0$  limit the system is trapped and at  $R^{J_i|M|} \rightarrow \infty$  the trajectories focus at infinity, as expected from the laws of geometric optics. The simple  $R^{J_i|M|}$  dependence of  $f$  and  $D$  provides a useful relation for the quantities of interest in a focusing experiment in terms of the controllable parameters of the system. Together with the robust plateau structure of  $W$  these curves suggest considerable flexibility in the choice of system parameters to obtain a desired outcome. The possibilities of using non-Gaussian laser optics to enhance the intensity gradient, and of placing two laser beams, one below the other, to double the effect, offer further flexibility. At finite rotational temperatures higher-energy adiabatic potentials ( $J_i, M \neq 0$ ) need be taken into account and the  $J_i = 0$  trajectories broaden. Consequently  $W$  (and to a lesser extent  $D$ ) increases with temperature. The qualitative effect, however, is maintained.

Figure 2 allows the focusing behavior of other systems to be estimated. To zero order  $V_w^{00}$  depends linearly on  $\alpha_{\parallel} \varepsilon_m^2$  and hence a smaller polarizability can be compensated by a proportional increase of the intensity (or, given that  $\varepsilon_m^2$  is upper-bounded by the ionization threshold, by the same decrease in the square of the beam velocity). Figures 1 and 2 suggest also several other means of manipulating the center-of-mass motion of molecules with light. A single laser beam could be used to *collimate* a diverging molecular beam. At

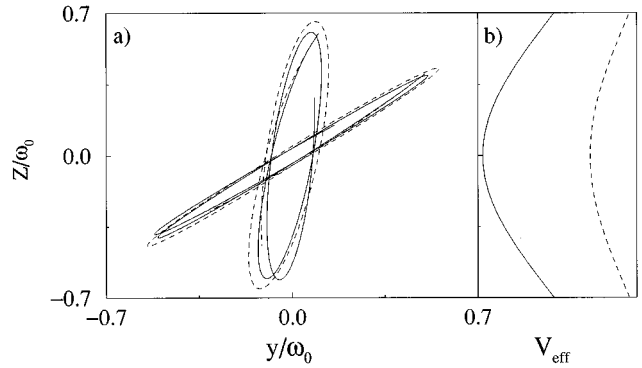


FIG. 3. Classical trajectories (a) and effective potentials  $E^{J_i|M|}[\varepsilon(\bar{y}, \bar{z})]$  (b) for  $J_i = 0$  (solid) and for  $J_i = |M| = J_i^{\text{max}}$  (dash). The temperature is 15 K, the peak intensity is  $I_m = 10^{12} \text{ W cm}^{-2}$  and the well depth ranges from  $V_w^{00} = 253 \text{ K}$  to  $V_w^{J_i^{\text{max}}|J_i^{\text{max}}|} = 104 \text{ K}$ . The (randomly chosen) initial conditions are  $\{y_i, z_i, v_{yi}, v_{zi}\} = \{0.1, 0.6, 14 \text{ msec}^{-1}, 28 \text{ msec}^{-1}\}$  and  $\{0.5, 0.4, 22 \text{ msec}^{-1}, 22 \text{ msec}^{-1}\}$ .

higher intensities it could be used to *reflect* molecules, possibly providing a route to short-pulse molecular beams. The addition of a second laser beam could serve to *steer* a focused molecular beam in a given direction. The use of co-propagating laser and molecular beams could serve to *guide* molecules in space.

Molecular trapping, already proposed in Ref. [4], is obtained in the  $R^{J_i|M|} < 1$  limit, addressed in Fig. 3. In this situation it is appropriate to consider a cold cell, rather than a supersonic jet environment. The initial conditions are then a random distribution of the initial position vector and a random distribution of the initial velocity vector with  $|v_i| = \sqrt{2E_{\text{kin}}/m}$ . The translational energy is equilibrated with the rotational energy and Boltzmann-distributed at the cell temperature. In order to ensure adiabatic evolution of the field-free states into the correlating stages of the full Hamiltonian it is now necessary to switch the field on sufficiently slowly.

Figure 3(a) shows trajectories initiated with two randomly chosen sets of conditions. The corresponding adiabatic potentials are shown in Fig. 3(b). Out of the Boltzmann distribution of populated rotational states we consider the two that give rise to the two most widely spread trajectories,  $\{J_i = M = 0\}$  and  $\{J_i = |M| = J_i^{\text{max}}\}$ , where  $J_i^{\text{max}}$  denotes the largest  $J$  significantly populated at the cell temperature. With the effective wells of Fig. 3(b) and a kinetic energy of 15 K, the energy ratio  $R^{J_i|M|}$  ranges from  $R^{00} = 0.06$  to  $R^{J_i^{\text{max}}|J_i^{\text{max}}|} = 0.14$  as  $J_i$  and  $|M|$  increase. At the small  $R^{J_i|M|}$  values typical of low temperatures the trajectories probe essentially only the harmonic part of the effective potential and the orbits are typical of the Lamb-Dicke regime. For larger  $R^{J_i|M|}$  values,  $R^{J_i|M|} \rightarrow 1$ , the vibrational amplitude is much wider and fills the region where the field amplitude is non-negligible,  $\sqrt{y^2 + z^2} \lesssim 1.5\omega_0$ .

An analogous far-off resonance trap has been demonstrated experimentally for highly polarizable atoms [15]. Figure 3 suggests that its more important potential may be in the molecular domain, both since subkelvin cooling could be

avoided (see note 9) and since molecular, by contrast to atomic, polarizabilities are mostly anisotropic and often possess large parallel components. (The axial polarizabilities of  $\text{CS}_2$ ,  $\text{CHI}_3$ , and  $\text{CCl}_3\text{CN}$ , for instance, are 105, 113, and 72 bohr<sup>3</sup>, respectively. In chainlike molecules delocalized  $\pi$  bonding is mostly linked with high parallel polarizability that rises rapidly with the chain length.)

The possibility of manipulating molecular motions using the mechanical force of light, illustrated above, opens a range of exciting applications of intense lasers. In addition to extending the field of atom optics to the richer molecular domain, our results suggest further applications. These include stereochemical studies under field-free, high-density conditions, high-resolution spectroscopy of pendular states, the study and control of polymerization, trace analysis by means of high-resolution mass spectrometry, and the use of light-based prisms and waveguides to separate molecules

into isotopes and reaction products into electronic branches. Perhaps most importantly, in the arena of device fabrication, the possibility to deposit *aligned nanostructures* proposed here, together with the dependence of electric and magnetic properties on the degree of order, has potential applications in the production of materials possessing predesigned electric and/or magnetic properties. Given the increasing accessibility of intense lasers [13], these opportunities invite further research.

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