PHYSICAL REVIEW A, VOLUME 63, 045401

Propensity of molecules to spatially align in intense light fields

S. Banerjee, D. Mathur, and G. Ravindra Kumar
Tata Institute of Fundamental Research, Homi Bhabha Road, Mumbai 400 005, India

(Received 26 April 2000; published 6 March 2001)

The propensity of molecules to spatially align along the polarization vector of intense, pulsed light fields is related to readily accessible parameters (molecular polarizability, moment of inertia, peak intensity, and pulse duration of the light). It is possible to predict which molecules can be spatially aligned, and under what circumstances, upon exposure to intense light. Accounting for both enhanced ionization and hyperpolarizability, it is shown that *all* molecules can be aligned, even those with the smallest static polarizability, when subjected to ultrashort pulses of sufficient intensity.

DOI: 10.1103/PhysRevA.63.045401 PACS number(s): 33.80.Rv, 33.90.+h, 42.50.Vk

Studies of the response of matter to intense electromagnetic radiation address the physics of systems driven strongly away from equilibrium. Matter is inherently unstable when subjected to strong electric fields of the type that can be generated in intense laser light. In molecules subjected to light intensities in excess of $\sim 10^{12}\ \mathrm{W\,cm^{-2}}$, distortions of potential energy surfaces, with concomitant changes in electron density distributions, lead to ionization, dissociation, and large dipole moments (μ). With linearly polarized $\mathbf{E}$ fields of magnitudes that equal, or exceed, interatomic binding fields, the induced dipole moments exert torques on the molecular axes $\mu \times \mathbf{E}$ that can be large enough to spatially reorientate molecules and their ions such that the most polarizable axis points along the $\mathbf{E}$ vector. In early experiments, anisotropic angular distributions of fragment ions were obtained when the light polarization vector was rotated relative to the detector axis, and these were taken to be signatures of spatial orientation [1]. Recently, it has been recognized that ionization rates computed using the field ionization Coulomb explosion model [2] also depend on the angle that the internuclear axis makes with the $\mathbf{E}$ vector, the angular dependence arising from the barrier suppression due to $\mathbf{E}\cdot\mathbf{r}$ ($\mathbf{r}$ denotes the molecular axis). This also gives rise to anisotropic angular distributions [3].

Spatial alignment of isolated molecules is a subset of one of the central endeavors of physicists and chemists, namely to control the external degrees of freedom of molecules at the microscopic level. Practical interest in spatial alignment of molecules arises from tantalizing possibilities of entirely new studies on pendular-state spectroscopy [4], coherent control [5], and molecular trapping and focusing [6]. The role of polarization in altering dissociation pathways has also been experimentally established [7]. It is clearly very important, therefore, to establish the extent of spatial alignment that might be achieved both on the basis of the properties of a given molecule and the characteristics of the laser light to be used. Specific insight is also needed on the relative importance of angle-dependent ionization on the one hand, and molecular reorientation on the other, in making sense of measured anisotropies in ion distributions. We report results of a study that enables us to predict the propensity of molecules to spatially align in intense, pulsed, polarized light on the basis of readily accessible parameters. All existing experimental data on spatial alignment is explained by our model. We show that it is possible to align molecules even with ultrashort pulses, irrespective of the polarizability.

In any analysis of spatial alignment three factors play a crucial role: (i) the peak intensity of the laser pulse, (ii) its temporal duration, and (iii) the ratio of the molecular polarizability (ground or excited state) to the moment of inertia ($R = \alpha/I$). At high enough intensities, molecular hyperpolarizabilites may also be significant although their role in the alignment dynamics has not hitherto been explicitly considered. It is also established that field ionization of molecules is ubiquitous with short pulse lasers. The important conclusion of the field ionization model relevant to alignment is the breakup of the molecule at a critical distance R_c that is larger than the equilibrium internuclear separation R_e [8]. The stretching of the internuclear axis increases the moment of inertia, and leads to a slowing down of reorientation; dissociation at R_c implies that the molecule will dissociate before the peak intensity is reached, except for ultrashort light pulses.

We consider a rotor in a time dependent $\mathbf{E}$ field [9]. The interaction Hamiltonian is $H_I = -\mu\cdot\mathbf{E}$, where $\mu = \mu_0 + \frac{1}{2}\alpha\mathbf{E} + \frac{1}{24}\gamma\mathbf{E}\mathbf{E}$. The Lagrangian is:

$$L = \frac{\mathrm{I}}{2}[\dot{\theta}^2 + \sin^2\theta\dot{\phi}^2] + \mu\cdot\mathbf{E}. \tag{1}$$

The equation of motion is then given by

$$\theta = -\frac{\alpha_{\mathrm{eff}}}{2\mathrm{I}}[\mathbf{E}(t)]^2 \sin 2\theta - 2\frac{\dot{r}}{r}\dot{\theta}, \tag{2}$$

where α_{eff} is the effective polarizability. In the low-field limit this is the linear polarizability; its modification in high fields is discussed later. To keep our calculations realistic we use a Gaussian laser pulse, $E(t) = E_0 e^{-(t^2/2\tau^2)}\cos\omega t$. Spatial variations within the laser beam are not taken into account, but note that intensity-selective experiments that minimize focal volume effects are possible [10]. In Eq. (2), the first term causes reorientation while the second term, the so-called damping term, impedes the motion of the molecular axis towards the $\mathbf{E}$ vector. In the field ionization Coulomb explosion model [2], the damping term arises due to the

1050-2947/2001/63(4)/045401(4)/$20.00

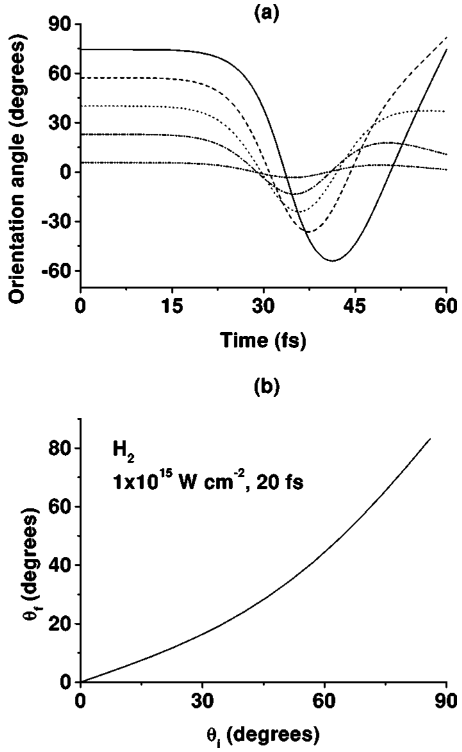

FIG. 1. Time evolution of the molecular orientation for a peak intensity of 10^{15} $\mathrm{W\,cm^{-2}}$ and temporal width of 100 fs.

elongation of the molecular axis from R_e to R_c after the removal of one or two electrons by tunnel/over-the-barrier ionization.

We present our results as follows. We first consider the simplest case where the polarizability is linear and no damping term is present. It is shown that even such a picture is of wide-ranging validity and utility. We then discuss results of calculations that take into account both damping and the hyperpolarizability, and we examine the extent to which our results are modified. Our calculations are compared with experimental observations.

Equation (2) is solved used a fourth-order Runge-Kutta algorithm for the intensity range 10^{12}–10^{15} $\mathrm{W\,cm^{-2}}$, and pulse durations of 40 fs–2 ps. Instead of molecule-specific calculations, the R parameter has been taken to lie in the interval 2×10^4–2×10^7 (covering a wide range of light and heavy species, like H_2, N_2, CS_2 and I_2). The initial direction of the molecular axis θ_0 is taken to be random in space. After the light pulse is switched on, the angular position is calculated as a function of time for various values of θ_0, as shown in Fig. 1(a). From this, one obtains a plot of θ_f versus θ_i, where θ_i is the initial angular position and θ_f is the angular orientation of the molecular axis at a particular instant [see Fig. 1(b)]. It is easy to show that the angular distribution of the molecular axis is proportional to $(d\theta_f/d\theta_i)^{-1}$. This procedure can no longer be used when the applied field is so strong that the molecular axis crosses $\theta=0$. In such cases we have used a counting method by interpolating the relation between θ_f and θ_i to obtain the angular distribution.

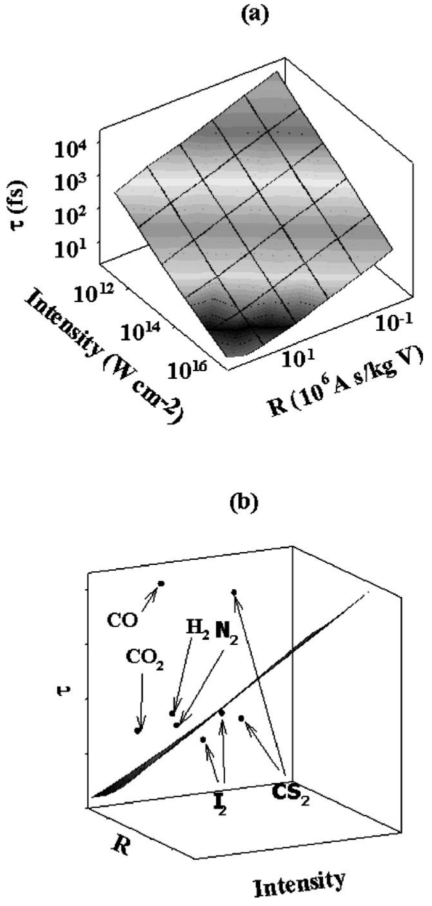

FIG. 2. Alignment of molecules for various conditions of peak intensity, pulse duration and $R=\alpha/I$. Points below the surface correspond to the case of no alignment while all points on the plane and above it lead to the molecular axis lining along the light polarization vector.

The trajectories shown in Fig. 1(a) correspond to H_2 exposed to 20 fs pulses at 10^{15} $\mathrm{W\,cm^{-2}}$. The slope in Fig. 1(b) shows that the extent of reorientation in H_2 is negligible under these conditions. Similar calculations were carried out for a range of parameters specified above and the results are shown in Fig. 2. The hatched surface demarcates the regions where spatial alignment is significant from those where no significant reorientation occurs. All points *above* the surface correspond to molecules that are "tightly" aligned, while the opposite holds for points that lie below the surface. Note that we are dealing here only with linear polarizabilities. The nonlinear polarizability components serve only to strengthen the alignment. Thus, the demarcation based on α alone is very rigorous.

Note that the above calculations pertain to the position of the molecular axis. However alignment is deduced from the anisotropy of fragment ions. To make the connection with experimental data it should be noted that the angular distributions that are shown are those that would practically be measured using a spectrometer with a small acceptance angle. Thus, our calculations are specially relevant to the angular distributions of highly charged ions (that possess large kinetic energies). This is also important in the context of the residual angular momentum as the molecule rotates.

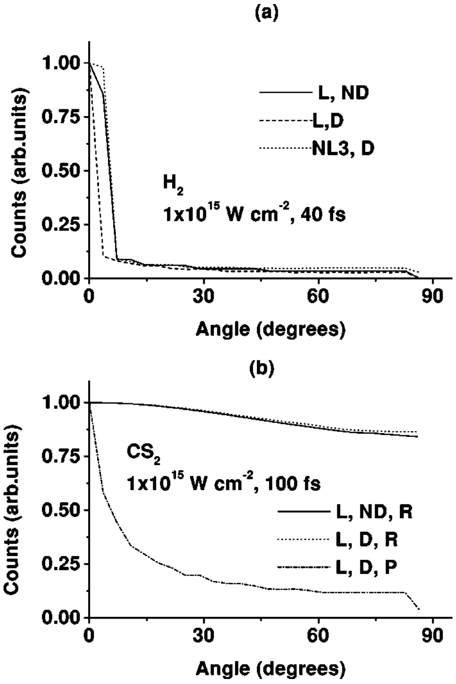

FIG. 3. Alignment dynamics calculated with enhanced ionization taken into account. Only linear polarization is considered.

This is sufficiently large to cause significant rotation on the time scale of the laser pulse, but negligible compared to the energy of the fragment ions (typically >1 eV). Illustrative experimental data are also shown in Fig. 2.

We now consider the damping term. Ignoring this term essentially assumes that the molecule is a rigid rotor in the intense field. However, as already noted, when the field is sufficiently large, the ionization dynamics occur through an enhanced ionization (EI) mechanism wherein one or two electrons are removed at the first ionization step that occurs at the equilibrium internuclear separation; thereafter, the two residual ions repel each other, leading to an increase in the bond length. This results in one or more Stark-shifted electronic levels rising above the potential barrier that separates the atomic cores, at which point multiple electron ejection occurs, leading to molecular fragmentation. EI can modify the reorientation rate in two ways: (i) as the moment of inertia increases, the magnitude of the first term in Eq. (2) will reduce, and (ii) the damping term comes into play, leading to a further decrease in the rate at which the molecule rotates toward the light field vector. Does EI modify our first-order calculations? We have carried out tests for some standard cases for which EI parameters are established. Figure 3(a) shows the angular distribution for H_2 for a pulse duration of 40 fs at a peak laser intensity of 10^{15} $\mathrm{W\,cm^{-2}}$, with and without the damping term. It is clear that the reorientation of H_2 is not significantly affected when the damping term is included. There are two major reasons for this: (i) R is extremely large and the torque experienced by H_2 is sufficient to induce reorientation despite the presence of an opposing force, and (ii) the fact that the ionization energy (and hence, the appearance intensity) of H_2 is quite high, the damping force only comes into play close to the peak of the laser pulse, by which time the molecular axis is already aligned with the **E** vector. Interestingly, the width of the angular distribution with damping included is actually smaller than when no damping is present. This is due to the angular velocity without damping being larger, causing the molecular axis to execute large amplitude oscillations about $\theta=0$; hence, there exist instants at which the peak of the angular distribution is shifted away from zero.

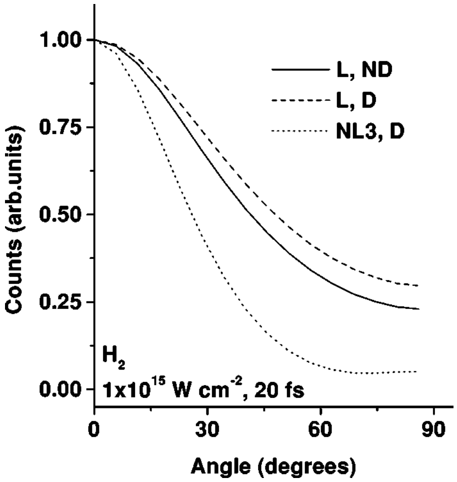

FIG. 4. Reorientation of molecular axis of H_2, with nonlinear contributions to the polarizability.

A contrary situation is depicted in Fig. 3(b) for linear CS_2 exposed to 100 fs pulses. Here, the lower ionization energy, coupled with the relatively small value of R, leads to virtually no reorientation of the S–C–S axes with the direction of the **E** field at the point at which dissociation occurs. Strong alignment can be expected if it is assumed that the molecule survives undissociated until the peak of the laser pulse, a fact contrary to experimental observation, and illustrates the essentiality of EI in any such model. Similar calculations have been carried out for N_2 and I_2. The situation for N_2 is similar to H_2 because of the similarity in the relevant parameters. In the case of I_2, reorientation of the molecule is not significant, either with or without the damping term.

Hitherto, only the polarization response that arises from the linear term has been considered. To what extent is this justified, especially over the intensity range 10^{12}–10^{15} $\mathrm{W\,cm^{-2}}$? We note that hyperpolarizabilites are significant only at the highest intensities. This is obvious if one compares the integrals that define work done by the field on the molecule by each order of the hyperpolarizability. It is expected that for longer pulses, a model based on linear polarizability is sufficient since the dissociation of the molecule occurs on the rising edge of the pulse. However, as the pulse duration becomes shorter (<50 fs), the molecule will survive until the maximum intensity is reached, and the reorientation due to the higher order terms will become comparable to that due to the linear term, and may even exceed it. To incorporate hyperpolarizability in our calculations, certain approximations are needed. The magnitude of second- and higher-order susceptibilities is not known in most cases. Moreover, these quantities are tensors with numerous components, and it is difficult to consider all the components in an exact way.

We consider here H_2, taking into account the third-order term due to the electronic response γ_e. The equation of motion is modified as follows: $\alpha \sin 2\theta E^2 \rightarrow \alpha \sin 2\theta E^2 + \gamma_e \sin 4\theta E^4 + \ldots$. Figure 4 shows the effect of nonlinearity on the reorientation of the molecular axis of H_2 acted on by a 20 fs pulse. There is now a significantly larger reorientation of the H–H axis. As noted above, such effects will be significant only for very short pulses [see results in Fig. 3(a) for a 40 fs pulse; the effect of the third-order term is much smaller there than for the 20 fs case]. We have verified that for longer pulses such higher order terms need not be taken into account. Of course, it is obvious that as the laser pulses get shorter, orders higher than the third become significant. One can speculate that heavy molecules, like I_2, may align with sufficiently short pulses because of the contribution from such terms. It is clearly necessary to test this conjecture experimentally since very little is known about the high order polarizabilities of almost all molecules.

In summary, we have considered molecular reorientation using a classical model. The justification for using a classical model is twofold. In intense field-molecule interactions, classical analyses are found to be extremely fruitful in explaining much of the experimental data. Also, exact time-dependent analysis of the molecular response to a high-intensity pulsed light field is presently not feasible. We show that, despite the obvious limitations of classical models, the results are of considerable utility in understanding a large body of experimental work on alignment, and for enabling predictions to be made on whether or not, and under what circumstances, molecules will be spatially aligned when subjected to intense, polarized, short-duration light fields. The rigor of the model is demonstrated. We have also incorporated, for the first time; (i) the role of enhanced ionization in the reorientation of molecules and (ii) the role of hyperpolarizability. It is shown that *higher-order contributions to the dipole moment are very important for extremely short light pulses*. It is predicted that this will lead to alignment of molecules even for sub-50 fs pulses that are becoming increasingly accessible to experimentalists.

The TIFR high energy, femtosecond laser facility has been set up with substantial funding from the Department of Science and Technology.

---

[1] D. Normand *et al.*, J. Phys. B **25**, L497 (1992); P. Dietrich *et al.*, Phys. Rev. A **47**, 2305 (1993); G. Ravindra Kumar *et al.*, J. Phys. B **29**, L95 (1996); V. R. Bhardwaj *et al.*, Phys. Rev. A **56**, 2455 (1997), and references therein.

[2] L. J. Fraskinski *et al.*, Phys. Rev. Lett. **58**, 2424 (1987).

[3] J. H. Posthumus *et al.*, J. Phys. B **31**, L553 (1998); Ch. Ellert and P. B. Corkum, Phys. Rev. A **59**, R3170 (1999); S. Banerjee *et al.*, *ibid.* **60**, R3369 (1999).

[4] B. Friedrich and D. Herschbach, Phys. Rev. Lett. **74**, 4623 (1995); G. R. Kumar *et al.*, Phys. Rev. A **53**, 3098 (1996).

[5] E. Charron *et al.*, Phys. Rev. A **49**, R641 (1994).

[6] B. Friedrich and D. R. Herschbach, Phys. Rev. Lett. **74**, 4623 (1995); J. D. Weinstein *et al.*, Nature (London) **395**, 148 (1998).

[7] D. Mathur *et al.*, Phys. Rev. A **50**, R7 (1994).

[8] T. Zuo and A. D. Bandrauk, Phys. Rev. A **52**, R2511 (1995); J. H. Posthumus *et al.*, J. Phys. B **29**, L525 (1996).

[9] C. M. Dion *et al.*, Phys. Rev. A **59**, 1382 (1999).

[10] S. Banerjee, G. Ravindra Kumar, and D. Mathur, J. Phys. B **32**, 4277 (1999); Phys. Rev. A **60**, R25 (1999).