The propensity of molecules to spatially align in intense light fields

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Abstract

The propensity of molecules to spatially align along the polarization vector of intense, pulsed light fields is related to readily-accessible parameters (molecular polarizabilities, moment of inertia, peak intensity of the light and its pulse duration). Predictions can now be made of which molecules can be spatially aligned, and under what circumstances, upon irradiation by 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 the shortest available laser pulses (of sufficient intensity).

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Studies of the response of matter to very intense fluxes of electromagnetic radiation address fundamental physics issues 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 the case of molecules subjected to laser light of intensity in excess of $\sim 10^{12}$ W cm^{-2}, distortions of potential energy surfaces, with concomitant alterations in electron density distributions, lead to ionization, dissociation, and formation of strong 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 molecular axis points along the light field vector. In early experiments, anisotropic angular distribution of fragment ions were obtained when the light polarization vector was rotated relative to the detector axis, and these were taken to be unambiguous signatures of spatial orientation [1,2]. In recent studies, it has been recognized that the molecular ionization rate depends on the angle that the internuclear axis makes with the light field vector, and that this also leads to anisotropic angular distributions [3]. Indeed, the ionization rate has to be computed using the field ionization Coulomb explosion model [4], whose angular dependence arises from the fact that the barrier suppression is given by $\mathbf{E} \cdot \mathbf{r}$, where $\mathbf{r}$ denotes the molecular axis.

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 atomic and molecular species at the microscopic level. The polarizability interaction of an intense, linearly-polarized light field with the induced dipole moment of molecules gives rise to a double-well potential; the resulting angular reorientation of molecular axes is akin to the interconversion of left- and right-handed enantiomers that was considered by Hund over 3 decades ago in terms of similar potentials [5]. Spatial alignment of individual molecules can also justifiably be considered a special facet of the optical Kerr effect [6]. On a more practical level, interest in studies of spatial alignment of molecules has been generated because of tantalizing possibilities of entirely new studies on pendular-state spectroscopy [7], coherent control experiments [8], and molecular trapping and focusing [9]. The crucial role of polarization in choosing or altering dissociation pathways has also been experimentally established [10]. It is clearly very important, therefore, to establish, both on the basis of the properties of the molecule under investigation and the characteristics of the laser light that is used, the extent of spatial alignment that occurs. 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 fragment ion distributions. In this Letter we present results of a comprehensive study that enables predictions to be made of the propensity of molecules to spatially align in intense, pulsed, polarized light on the basis of parameters that are readily accessible. We show that existing experimental data, spanning work done over the past decade by several groups including our own is explained by our model. We also show that it is possible to align molecules even with extremely short light pulses irrespective of the polarizability.

In any given 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 ($R = \frac{\alpha}{\mathrm{I}}$). 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 well 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$_e$ [12]. 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.

The process of alignment is modeled by considering a rotor in a time dependent **E** field [13]. In this case the interaction Hamiltonian is given by H$_I$ = -$\mu.\mathbf{E}$ where $\mu = \mu_{\mathbf{0}} + \frac{1}{2}\alpha\mathbf{E} + \frac{1}{24}\gamma\mathbf{E}\mathbf{E}$. The Lagrangian is:

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

The equation of motion is then given by

$$\frac{\mathrm{d}^2\theta}{\mathrm{dt}^2} = -\frac{\alpha_{\mathrm{eff}}}{2\mathrm{I}}\mathbf{E}(t)^2 sin2\theta - 2\frac{\dot{\mathrm{r}}}{\mathrm{r}}\dot{\theta}, \tag{2}$$

where α_{eff} is the effective polarizability. In the low-field limit this is the linear polarizability. The modification of this in high fields is discussed later. To keep our calculations as realistic as possible we have used a Gaussian laser pulse, $E(t) = E_0 e^{-\frac{\mathrm{t}^2}{2\tau^2}} cos\omega t$. Spatial variations within the laser beam are not taken into account since it has been shown recently that intensity selective experiments minimize focal volume effects [11]. In Eq. (1), the first term causes reorientation while the second term, the so-called damping term, impedes the motion of the molecular axis towards the light field vector. In the field ionization Coulomb explosion model [4], the damping term arises due to the 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.

Eq. (2) is solved used a 4th-order Runge-Kutta algorithm for a range of light field parameters. We consider the laser intensity range 10^{12} - 10^{15} W cm^{-2}, and pulse durations from 40 fs to 2 ps. In the linear case, molecule-specific calculations have not been done. Instead the A-parameter has been taken to lie in the interval 2×10^4 - 6×10^7 (covering a wide range of light and heavy species, amongst them 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 figure 1(a). From this one obtains a plot of θ_f vs. 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. This is shown in figure 1(b). It is easy to show that the angular distribution of the molecular axis is proportional to $(\frac{\mathrm{d}\theta_\mathrm{f}}{\mathrm{d}\theta_\mathrm{i}})^{-1}$. This procedure can no longer be used when the applied field is so strong that the molecular axis crosses θ=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.

The trajectories shown in figure 1 (a) correspond to H_2 exposed to 20 fs pulses at 10^{15} W cm^{-2}. As can be seen from the slope in figure 1(b) the extent of reorientation in H_2 is negligible under these conditions. Similar calculations were carried out for a range of parameters as specified above, and results are shown in figure 2. The surface demarcates the regions where spatial alignment is significant from those where no significant reorientation occurs. All points *above* the surface, i.e. in regions of larger intensity, polarizability and pulse duration correspond to molecules that are significantly 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.

It is to be noted 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. 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 which are typically in excess of 1 eV. Illustrative experimental data for various molecules are also shown in the figure and we note the excellent agreement that is obtained between our model and measured data.

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. Subsequent to the first ionization step that occurs at the equilibrium internuclear separation, the two residual atomic ions mutually 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. Firstly, as the moment of inertia increases, the magnitude of the first term in Eq. (1) will reduce. In addition, the damping term will come into play, leading to a further decrease in the rate at which the molecule rotates towards the light field vector. It is important to investigate the extent EI might modify our first-order calculations. Since EI parameters are available only for a few molecules, we have carried out these calculations for some standard cases. These can be extended to any other molecule once the relevant parameters are known either by calculation or experiment.

Fig. 3 (a) shows the angular distribution for H_2 for a pulse duration of 40 fs at a peak laser intensity of 10^{15} 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. Firstly, R is extremely large and the torque experienced by H_2 is sufficient to induce reorientation despite the presence of an opposing force. Secondly, 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 light polarization vector. Interestingly, the width of the angular distribution with damping included is actually smaller than when no damping is present. This arises due to the fact that the angular velocity without damping is larger, causing the molecular axis to execute large amplitude oscillations about θ=0; hence, there will exist instants at which the peak of the angular distribution will shift away from zero.

A contrary situation is depicted in Fig. 3(b) when linear CS_2 molecules are exposed to 100 fs light fields. In this case, the lower ionization energy of the molecule coupled with the relatively small value of A, leads to a situation where there is 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 till 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 other molecules like 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 even without the damping term. Once the damping term is included there is only a small deflection of the molecular axis.

Hitherto, only the polarization response that arises from the linear term has been considered. To what extent is this justified, especially at intensities in the range of 10^{12} - 10^{15} W cm^{-2}? It is important to note that hyperpolarizabilites are significant only at the highest intensities. This is obvious when we compare the integrals which define the work done by the field on the molecule by each order of the hyperpolarizability. It can be 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 till 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 need to be made. Firstly, the magnitude of the second- and higher-order susceptibilities is not known in most cases [14]. Moreover, these quantities are tensors with numerous components and it is difficult to consider all the components in an exact way. We consider here the case for H_2 taking into account the third order term due to the electronic response γ_e. The equation of motion is modified as follows: $\alpha sin 2\theta E^2 \rightarrow \alpha sin 2\theta E^2 + \gamma_e sin 4\theta E^4 + \ldots$

Fig. 4 shows the effect of nonlinearity on the reorientation of the molecular axis for H_2 acted on by a 20 fs pulse.The inclusion of only the third order term [14] leads to a significantly larger reorientation of the H-H axis as compared to the case when only the linear term is considered. As noted previously, such effects will be significant only for very short pulses. This is shown in figure 3(a) for the case of a 40 fs pulse wherein the effect of the third order term is much smaller than that for the 20 fs case. We have verified that for longer pulses such higher order terms need no longer be taken into account. Of course, it is obvious that as the laser pulses get shorter even higher order terms will begin to play a significant role. One can speculate that heavy molecules, like I_2, may align with sufficiently short pulses because of the contribution from higher order 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 two-fold. In intense field-molecule interactions, classical analysis have been shown 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 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.

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REFERENCES

[1] D. Normand *et al.*, J. Phys. B **25**, L497 (1992), P. Dietrich *et al.*, Phys. Rev. A **47**, 2305 (1993), J. H. Sanderson *et. al.*, J. Phys. B **31**, L599 (1998).

[2] 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.

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

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

[5] F. Hund, Z. Phys. **43**, 805 (1927), see also B. Friedrich and D. Herschbach, Z. Phys. D **36**, 221 (1996).

[6] J. H. Williams, Adv. Chem. Phys. **85**, 361 (1993).

[7] B. Friedrich and D. Herschbach, Phys. Rev. Lett. **74**, 4623 (1995), G. R. Kumar *et al.*, Phys. Rev. A **A53**, 3098 (1996), W. Kim and P. M. Felker, J. Chem. Phys. **108**, 6763 (1998), J. Ortigoso *et al.*, J. Chem. Phys. **110**, 3870 (1999).

[8] E. Charron, A. Giusti-Suzor, and F. H. Mies, Phys. Rev. A **49**, R641 (1994).

[9] B. Friedrich and D. R. Herschbach, Phys. Rev. Lett. **74**, 4623 (1995), J. D. Weinstein *et al.*, Nature **395**, 148 (1998), H. Stapelfeldt *et al.*, Phys. Rev. Lett. **79**, 2787 (1997).

[10] D. Mathur *et al.*, Phys. Rev. A **50**, R7 (1994), J. Phys. B **27**, L603 (1994).

[11] S. Banerjee, G. Ravindra Kumar, and D. Mathur, J. Phys. B **32**, 4277 (1999), Phys. Rev. A **60**, R3369 (1999).

[12] T. Zuo and A. D. Bandrauk, Phys. Rev. A **52**, R2511 (1995), T. Seideman *et al.*, Phys. Rev. Lett. **75**, 2819 (1995), J. H. Posthumus *et al.*, J. Phys. B **29**, L525 (1996), K. C. Kulander *et al.*, Phys. Rev. A **53**, 2562 (1996).

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

[14] C. C. Wang, Phys. Rev. B **2**, 2045 (1970), D. P. Shelton, Mol. Phys. **60**, 65 (1987).

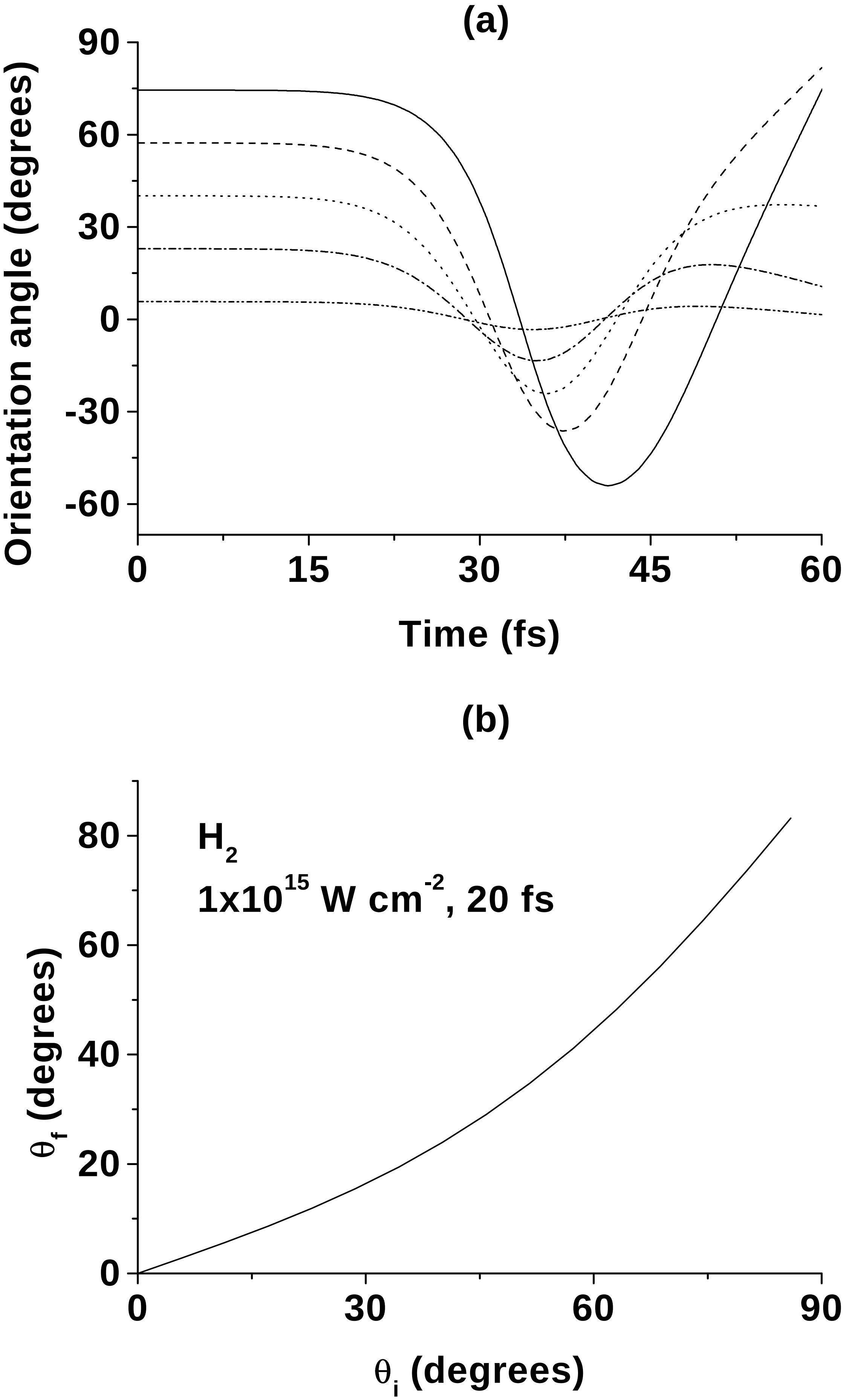
FIGURES

FIG. 1. (a) Time evolution of the molecular alignment for various initial orientations at a peak intensity of 10^{15} W cm^{-2} and temporal width of 20 fs. (b) Alignment of the molecular axis at the point of breakup predicted by the EI model as a function of initial orientation.

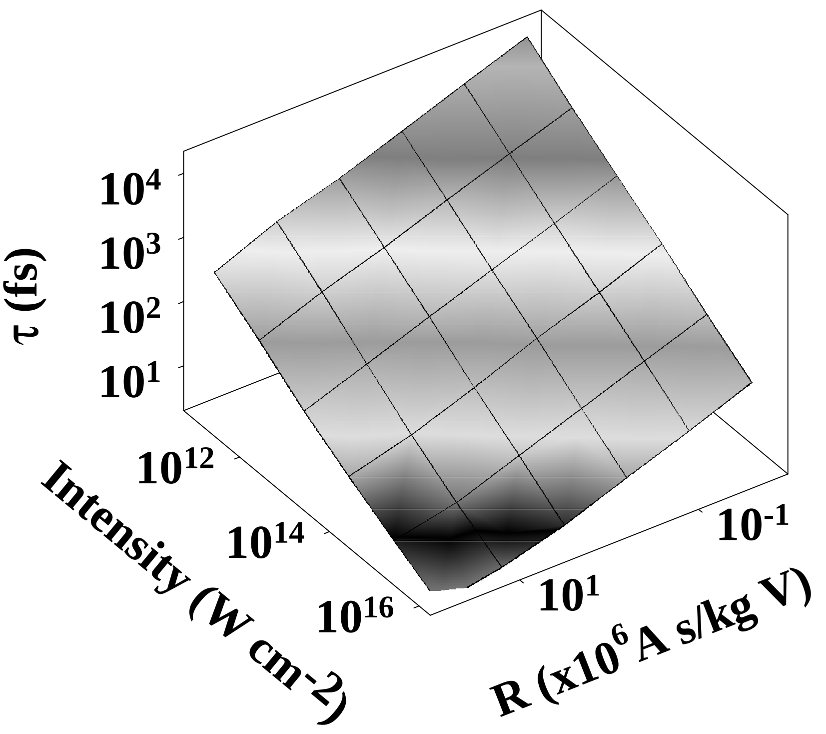
FIG. 2. (a) Alignment of molecules for various conditions of peak intensity, pulse duration and R (see text). Points lying below the surface correspond to the case of no alignment while all points lying on the surface, and above it, lead to the molecular axis being aligned along the light polarization vector. (b) Experimental data for some typical molecules: CO [1], CO_2 [1], H_2, N_2 [3], I_2 [3], CS_2 (picosecond data [2], femtosecond data [11]). The axes ranges are the same as in (a).

FIG. 3. Alignment dynamics calculated with enhanced ionization taken into account (a) H_2 (b) CS_2. L≡linear polarizability, ND≡no damping, D≡damped rotation, NL3≡linear and third order polarizability.

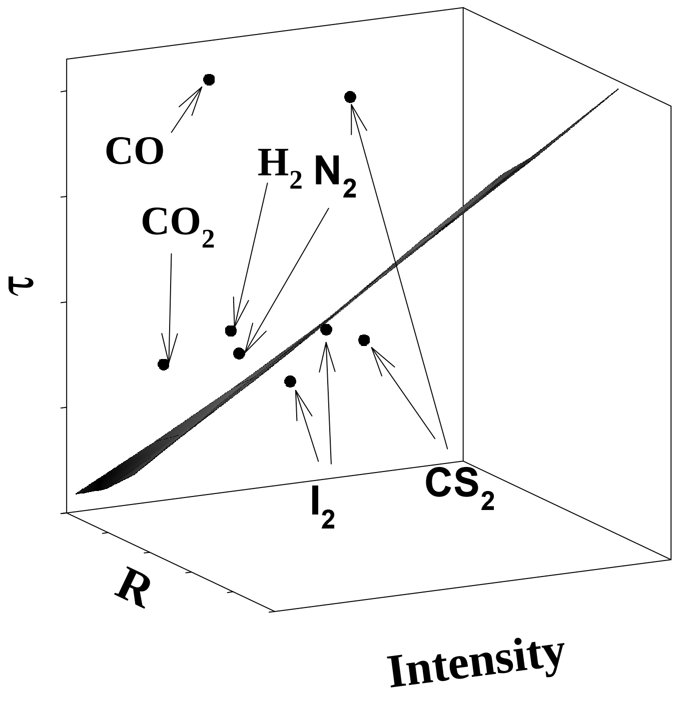
FIG. 4. Alignment of molecular axes for H_2 assuming nonlinear contributions to the polarizability at a peak intensity of 10^{15} W cm^{-2} and temporal duration of 20 fs. The symbols are explained in fig.3


(a)
90
60
30
0
-30
-60
Orientation angle (degrees)
0
15
30
45
60
Time (fs)
(b)
H_2
$1x10^{15}$ W cm^{-2}, 20 fs
80
60
40
20
0
θ_f (degrees)
0
30
60
90
θ_i (degrees)

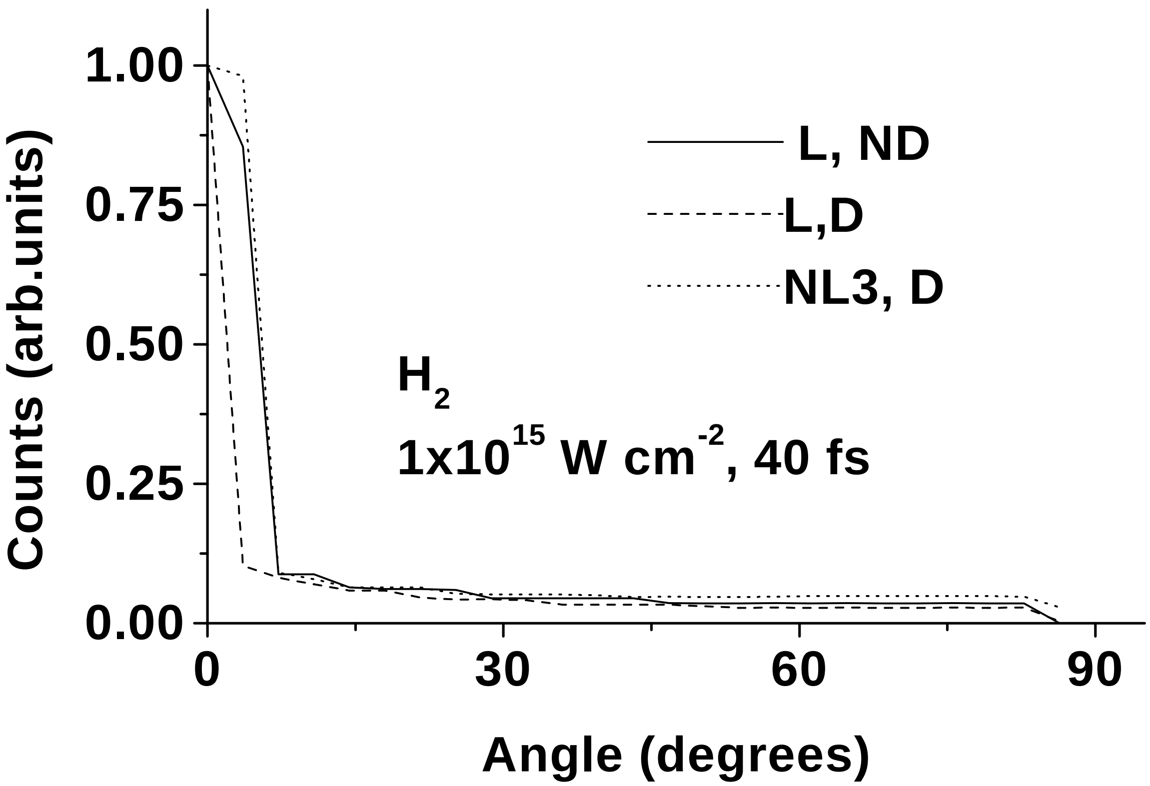
(a)


10^4
10^3
10^2
10^1
τ (fs)
10^{12}
10^{14}
10^{16}
Intensity (W cm-2)
10^{-1}
10^1
R (x10^6 A s/kg V)

(b)

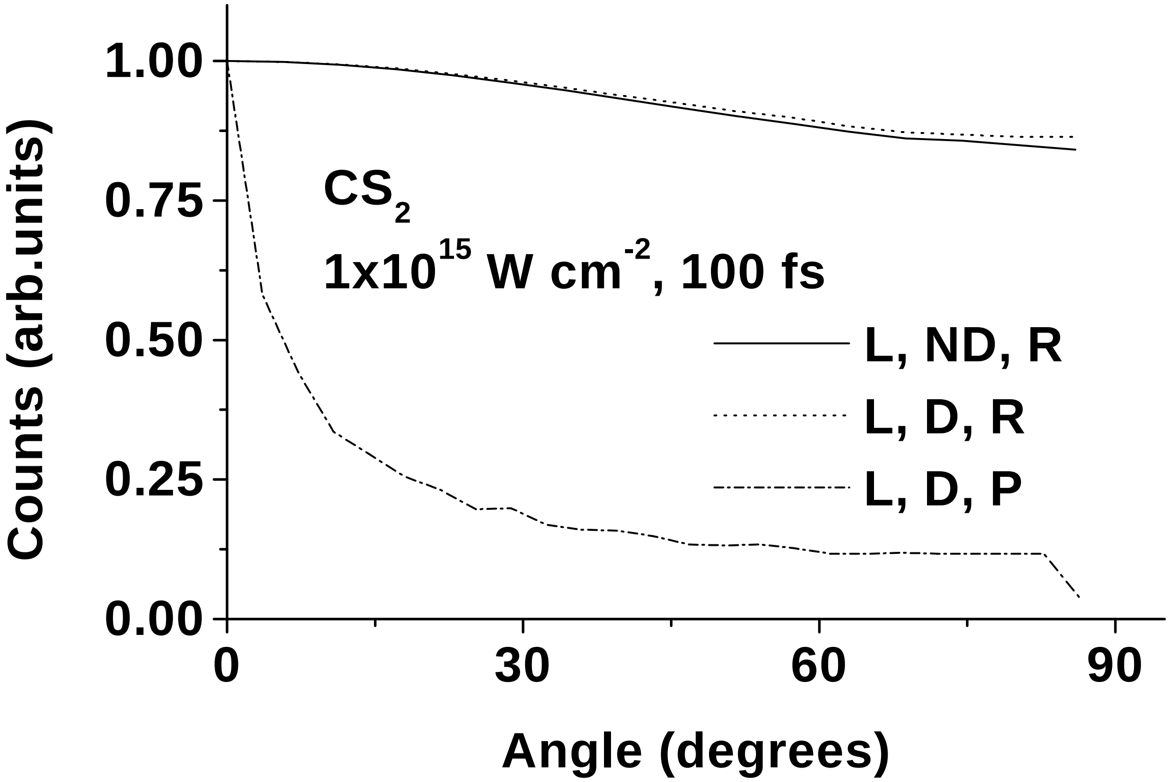

CO
H_2
N_2
CO_2
τ
I_2
CS_2
R
Intensity

(a)



Counts (arb.units)
1.00
0.75
0.50
0.25
0.00
0
30
60
90
Angle (degrees)
L, ND
L,D
NL3, D
H_2
$1x10^{15}$ W cm^{-2}, 40 fs

(b)



Counts (arb.units)
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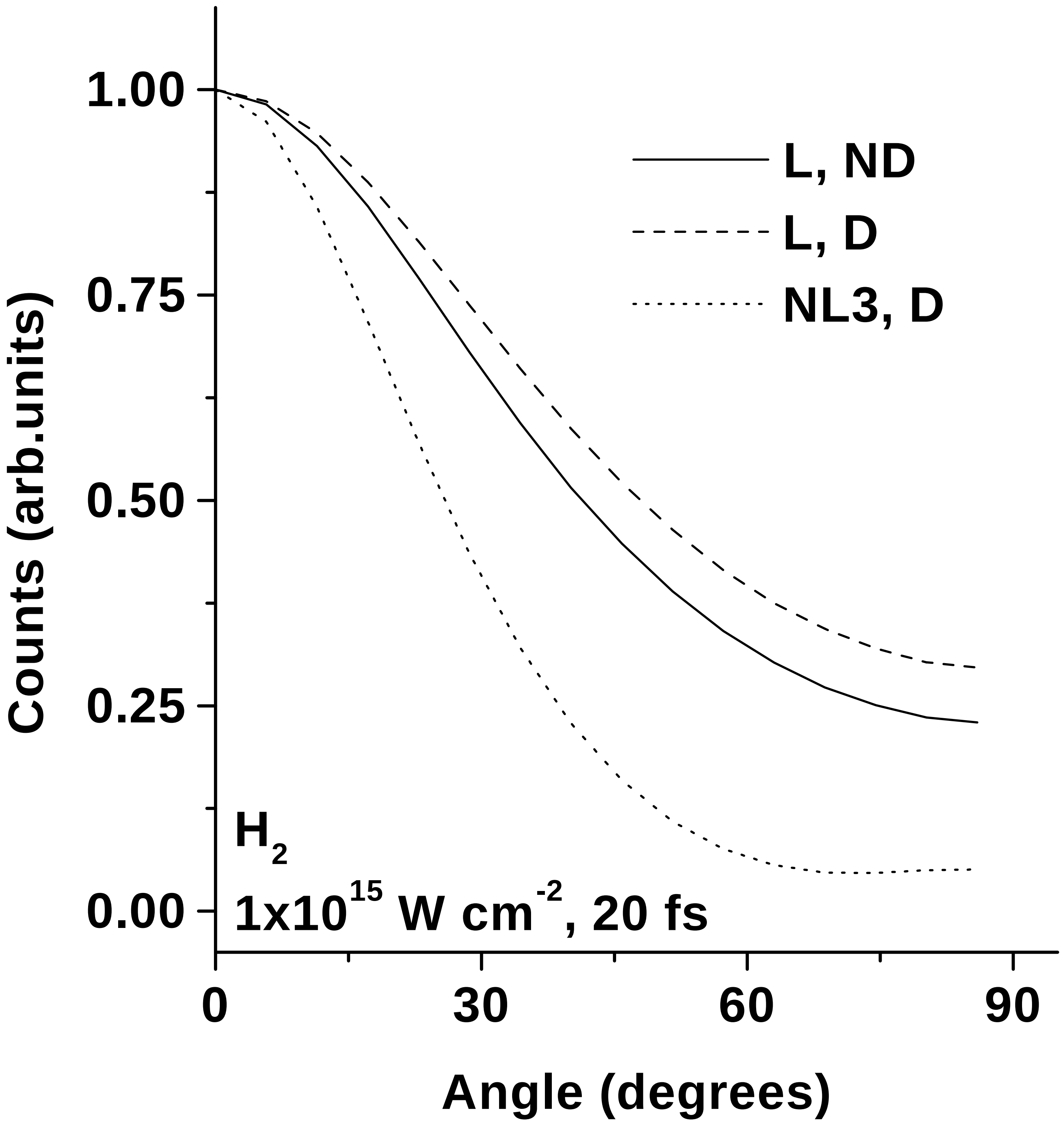
0.75
0.50
0.25
0.00
0
30
60
90
Angle (degrees)
CS_2
$1x10^{15}$ W cm^{-2}, 100 fs
L, ND, R
L, D, R
L, D, P



1.00
0.75
0.50
0.25
0.00
Counts (arb.units)
0
30
60
90
Angle (degrees)
L, ND
L, D
NL3, D
H_2
1×10^{15} W cm^{-2}, 20 fs