

Dynamic and geometric alignment of CS₂ in intense laser fields of picosecond and femtosecond duration

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Abstract

CS₂ is identified as a molecule for which distinction can be made between dynamic and geometric alignment induced by intense laser fields. Measured anisotropic angular distributions of fragment ions arise from (i) dynamic alignment of the S-C-S axes along the laser polarization vector for 35-ps laser pulses and (ii) geometric alignment due to an angle-dependent ionization rate in the case of 100-fs pulses. Results of classical calculations of the alignment dynamics support our observations. By comparing mass spectra obtained with linearly- and circularly-polarized light it is not possible to distinguish between dynamic and geometric alignment.

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Prevailing wisdom on the spatial alignment of molecules in intense laser fields has been challenged in two recent reports [1,2]. The possibility of spatially aligning molecules using strong light has attracted much attention since the pioneering double-pulse experiments of Normand *et al.* and Dietrich *et al.* [3] appeared to firmly establish that the field associated with intense, linearly-polarized, laser light of picosecond duration induces sufficiently strong torques on an initially-randomly oriented ensemble of linear diatomic molecules for reorientation of internuclear axis to occur. Experimental manifestation of such alignment is the anisotropic angular distribution of fragments produced upon subsequent dissociative ionization of molecules: ion intensities are maximum in the direction of the laser polarization vector and minimum (frequently zero) in the orthogonal direction. Earlier work on diatomic molecules has been extended to triatomics and polyatomics [4] and recently for neutrals [5]; much of the interest in the alignment of the internuclear axis (referred to in the current literature as dynamic alignment) in molecules has been generated because of tantalizing possibilities of pendular-state spectroscopy [6] and coherent control experiments [7]. Now, results of experiments conducted by Posthumus *et al.* [1] and by Ellert and Corkum [2] offer indications that when a linearly-polarized light field acts on molecules whose constituent atoms are heavy (such as iodine-containing diatomics and polyatomics), laser-induced dynamic alignment may not occur. The angular distributions of the products of dissociative ionization in such cases might be determined essentially by the dependence of the ionization rate on the angle made by the laser polarization (conventionally referred to as photoionization anisotropy) vector with the molecule's symmetry axis [1,2]. For a given value of laser intensity, the rate of ionization is largest for those molecules whose internuclear axis lies parallel to the direction of the laser polarization vector. The observed anisotropy of the fragment ion angular distribution is therefore determined by a purely geometric effect - namely the angle made by the molecule with the light field direction. Moreover, this increase in ionization rate maximizes at a critical internuclear distance at which the least bound electron localizes on one atomic core and the field of the other core adds to the laser field, causing the elongated molecule to field ionize. Posthumus *et al.* [1] have presented a

classical model for such enhanced ionization in which it is not necessary to invoke dynamic alignment in order to account for anisotropic angular distributions of the products of laser-field-induced dissociative ionization of I_2 . In the light of these developments, it is clearly important to reassess the contribution of dynamic and geometric alignment to the observed anisotropy of angular distributions of fragment ions, especially when femtosecond duration light pulses are used to field ionize molecules.

Proper theoretical insight into the extent of alignment obtained when molecules are irradiated by intense laser fields is difficult to attain due, essentially, to unknown values of polarizabilities and hyperpolarizabilities of the gamut of electronic states that might be accessed in the course of dissociative ionization. As noted by Ellert and Corkum [2], it is of much importance to experimentally assess the extent to which the angular anisotropies measured in earlier picosecond and femtosecond experiments are actually due to dynamic alignment. To this end we report here the results of experiments on the linear triatomic, CS_2 , using picosecond laser beams (35 ps, 532 nm) in the intensity range 10^{13} W cm $^{-2}$ and femtosecond beams (100 fs, 806 nm) in the range 10^{13} W cm $^{-2}$ - 10^{15} W cm $^{-2}$. CS_2 , along with its valence isoelectronic companion, CO_2 , is the archetypal triatomic system that has been subjected to many experimental studies. In the context of the present work, it also represents a species on the boundary between ‘heavy’ molecules (such as I_2 and its derivatives) on the one hand, and lighter species (like H_2 , N_2) on the other. On the basis of our experiments, we identify CS_2 as the molecule that undergoes dynamic alignment when irradiated by long (35-ps) pulses; on the other hand, 100-fs pulses give rise to anisotropic fragment ion distributions that can be accounted for in terms to geometric alignment.

In our femtosecond experiments, light pulses (of wavelength 806 nm) were obtained from a high-intensity, Ti:S, chirped pulse amplified, 100-fs laser operating at 10 Hz repetition rate. The laser light was focused using a biconvex lens, of focal length 10 cm, in an ultrahigh vacuum chamber capable of being pumped down to a base pressure of 3×10^{-11} Torr. We used operating pressures of $\leq 8 \times 10^{-8}$ Torr (i.e. well below the pressure at which space charge effects will alter the results). Ions produced in the laser-molecule interaction zone

were analyzed by a two-field, linear time-of-flight (TOF) spectrometer. To study the spatial distribution of ions produced in the focal zone, apertures of different sizes were inserted before the detector in order to spatially limit the interaction volume being sampled. In the present series of measurements we used circular apertures, of 2 mm and 15 mm diameter, centered about the focal point. In the former case only the Rayleigh range (2.4 mm) was sampled while in the latter instance the lowest intensity accessed was $5 \times 10^{12} \text{ W cm}^{-2}$ for a peak laser intensity of $2 \times 10^{15} \text{ W cm}^{-2}$. Details of our apparatus and methodology are presented elsewhere [9]. Our picosecond experiments used the second harmonic from an Nd:YAG laser producing 35-ps long light pulses. Here, the ions formed were analyzed by either a quadrupole mass spectrometer or a TOF device. This apparatus has also been described in a number of earlier publications [4].

Typical angular distributions measured for S^+ and S^{2+} fragments are shown in Fig.1. The polarization angle was varied by means of a halfwave plate, with on-line monitoring of the laser intensity to ensure a constant value in the course of measurements with different polarizations. The angular distributions for S^+ and S^{2+} (and for higher charge states of S-ions that are not shown in the figure) are clearly very anisotropic, with many more ions being produced in the direction of the laser polarization vector than in an orthogonal direction. This holds for both 35-ps and 100-fs duration laser pulses. *A priori*, it is not possible to deduce whether the observed anisotropy is due to dynamic or geometric effects. Following the prescription articulated by Posthumus *et al.* [1], we distinguish between dynamic alignment on the one hand and the effects of angle-dependent ionization rates (geometric alignment) on the other by probing the ratio of fragment ion yields obtained with orthogonal laser polarizations over a range of laser intensities. Fig. 2 depicts the variation with laser intensity of the ratio of $S_{\parallel}^+/S_{\perp}^+$ (and the corresponding ratio for S^{2+} and S^{3+} ions), where the subscripts \parallel and \perp denote, respectively, the S^+ yield at angles of 0° and 90° between the laser polarization vector and the axis of the TOF spectrometer. In the case of geometric alignment, it would be expected that the \perp -component becomes enhanced as the laser inten-

sity is increased. Consequently, the $S_{\parallel}^+/S_{\perp}^+$ ratio would fall with increasing laser intensity. Our 100-fs results indeed indicate this: significant falls occur in the $S_{\parallel}^+/S_{\perp}^+$, $S_{\parallel}^{2+}/S_{\perp}^{2+}$ and $S_{\parallel}^{3+}/S_{\perp}^{3+}$ ratios as the laser intensity is increased from 10^{13} to 10^{15} W cm $^{-2}$. Geometric alignment clearly dominates the spatial alignment process in this case. However, Fig. 2 also shows that when 35-ps duration laser pulses are used, of intensity in the 10^{13} W cm $^{-2}$ range, the *opposite* effect is observed. The $S_{\parallel}^+/S_{\perp}^+$ ratio now increases with laser intensity. Similar observations were also made for S^{2+} ions. Dynamic alignment of CS $_2$ clearly occurs when we use longer-duration (35-ps) laser pulses.

In order to gain some intuitive insight into the different behavior obtained with short and long pulses, we have carried out calculations of the alignment dynamics by solving the classical equation of motion for a rigid rotor in an electric field (see (1)), for different laser intensities and pulse durations. These calculations provide information on the nature of the torques that are experienced by the molecule in the time evolution of the laser pulse. The interaction of the radiation field with CS $_2$ is, in the first approximation, governed by the molecular polarizability, $\alpha = \alpha_{\parallel} - \alpha_{\perp}$, where the first and second terms refer, respectively, to polarizability components parallel to and perpendicular to the molecular bond. Following Landau and Lifshitz [10] we express the angular acceleration of the internuclear axes as

$$\ddot{\theta} = -\frac{\alpha\epsilon^2}{2I}\sin 2\theta, \quad (1)$$

where θ is the polar angle between the S-C-S axis and the light field, ϵ is the field strength, and I is the moment of inertia of the molecule about its centre of mass. We assume cylindrical symmetry and ignore higher-order terms involving α^2 . There is no permanent dipole contribution since we take CS $_2$ to remain linear even in a strong external field. The alignment dynamics calculated by us are depicted in Fig. 3 for a range of laser intensities. The time-dependent light pulse is taken to be a gaussian multiplied by a cosine function (the intensity envelopes of our 100-fs and 35-ps pulses are shown as the solid lines in Fig. 3). As the light intensity increases, a torque is exerted on the molecule, causing reorientation along the polarization vector. Further increases in intensity lead to ionization, bond stretching

and multiple electron ejection (and consequent dissociation). Since eqn. (1) only accounts for the first of these steps, the reorientation time that is obtained is to be regarded as a lower limit. Using 100-fs pulses at intensities $<10^{14}$ W cm $^{-2}$, our results indicate that no significant reorientation of the S-C-S molecule occurs. For peak intensities in the 10^{14} W cm $^{-2}$ range, there is significant reorientation; the angle changes from 0.75 to 0.45 radians in the time taken for the laser pulse to reach an intensity of $\sim 5 \times 10^{13}$ W cm $^{-2}$. Since this intensity is well above the S $^+$ appearance threshold (Fig. 2), the extent of reorientation is clearly overestimated in our calculations. For higher peak intensities ($\sim 10^{15}$ W cm $^{-2}$), our results indicate that although the torque generated by the laser field is sufficient to bring the molecule in line with the polarization vector, the angular velocity imparted in the process is large enough to cause oscillations about the polarization axis such that there is no overall alignment. Fig. 3b shows the corresponding calculations for 35-ps laser pulses. For peak intensities above 10^{12} W cm $^{-2}$, the molecular axis becomes coincident with the polarization vector very early in the time evolution of the laser pulse. Thereafter, small amplitude oscillations are seen. Such a system would be expected to show dynamic alignment, as is indeed seen in our experiments.

An obvious, but presently unavoidable, shortcoming in our calculations is in our use of α -values that pertain to CS $_2$ in its ground electronic state. The value of α_{\parallel} will increase substantially with applied field, as the bond elongates and the electron density distribution is distorted from its ground-state morphology. No information exists on how, and to what extent, such enhancement occurs. In addition, contributions from the hyperpolarizabilities (which are expected to be substantial at these laser intensities) must also be considered in a proper description [11]. Nevertheless, the qualitative insight that these model calculations yield is encouraging in that there is consistency with our experimental observations.

We note that the prescription used by Ellert and Corkum [2] in order to distinguish between dynamic and geometric alignment in iodine and iodine-containing molecules was to measure the fragmentation pattern using linearly- and circularly-polarized light of intensities such that the same field strengths were obtained in both cases. Identical fragmentation

patterns were taken as evidence against dynamic alignment. An assumption that is implicit in such an approach is that circularly-polarized light can be treated as a combination of two perpendicular, linearly-polarized components. However, on the basis of recent experiments, it is our contention that the dynamics resulting from irradiation of molecules by circularly-polarized light cannot, *a priori*, be expected to be a linear combination of the dynamical effects due to linearly polarized light aligned parallel and perpendicular to the molecular symmetry axis. Circularly-polarized light imparts angular momentum to the molecule that is being irradiated, whereas linearly-polarized light does not. How this might affect molecular dynamics in intense laser fields is an issue that has not been properly addressed. Experiments that we have recently conducted on intense-field-induced multiple ionization of N_2 [12] reveal that the polarization state of the incident light affects the ionization spectrum in the following fashion: when using circularly-polarized light, we observe a distinct *suppression of ionization channels* compared to the situation pertaining to linearly-polarized light of the same field strength. Moreover, an enhancement of lower-energy pathways to dissociation is apparent in the case of circular polarization. We believe that this may reflect the importance of high angular momentum intermediate states that may be accessed when circularly-polarized light is used. Such states present “wider” centrifugal barriers to dissociative ionization; this manifests itself in the increasing importance of longer tunneling time pathways that our data on N_2^{q+} ions [12] indicate.

In the case of CS_2 molecules also, we observe significant differences in the pattern of dissociative ionization between circularly- and linearly-polarized light. By way of example, we show in Fig. 4 the fragmentation pattern obtained, at two laser intensities, using linearly-polarized light that is aligned parallel and perpendicular to the TOF axis, as well as with circularly-polarized light. The ion yield obtained with circularly-polarized light is uniformly lower than that obtained with linear polarization, parallel as well as perpendicular (the CS_2^+ peak at the higher laser intensity is not taken into account in this comparison as the ion signal was saturated). Note that fragment ion yields obtained with parallel polarization are higher than corresponding yields obtained with circular-polarization, even when the

magnitudes of the electric field components in the latter are a factor of three larger than in the former. Hence, comparison of ion yields obtained with linear and circular polarization cannot give unambiguous evidence for or against dynamic alignment, and it is for this reason that we opt to rely on data shown in Fig. 2 to make deductions about geometric alignment being responsible for the anisotropic angular distributions that are obtained for fragment ions when CS₂ molecules are immersed in 100-fs-long laser pulses.

Hitherto, discussions of polarization effects in molecules have tended to focus only on classical aspects of spatial alignment resulting from induced dipole moments in intense light fields. The results shown in Fig. 4 indicate that the polarization state of light is also of fundamental importance in a quantum mechanical sense in that it affects molecular ionization yields and dissociation pathways. It is clear that such considerations need to be incorporated in development of adequate descriptions of molecular dynamics in intense light fields.

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FIGURES

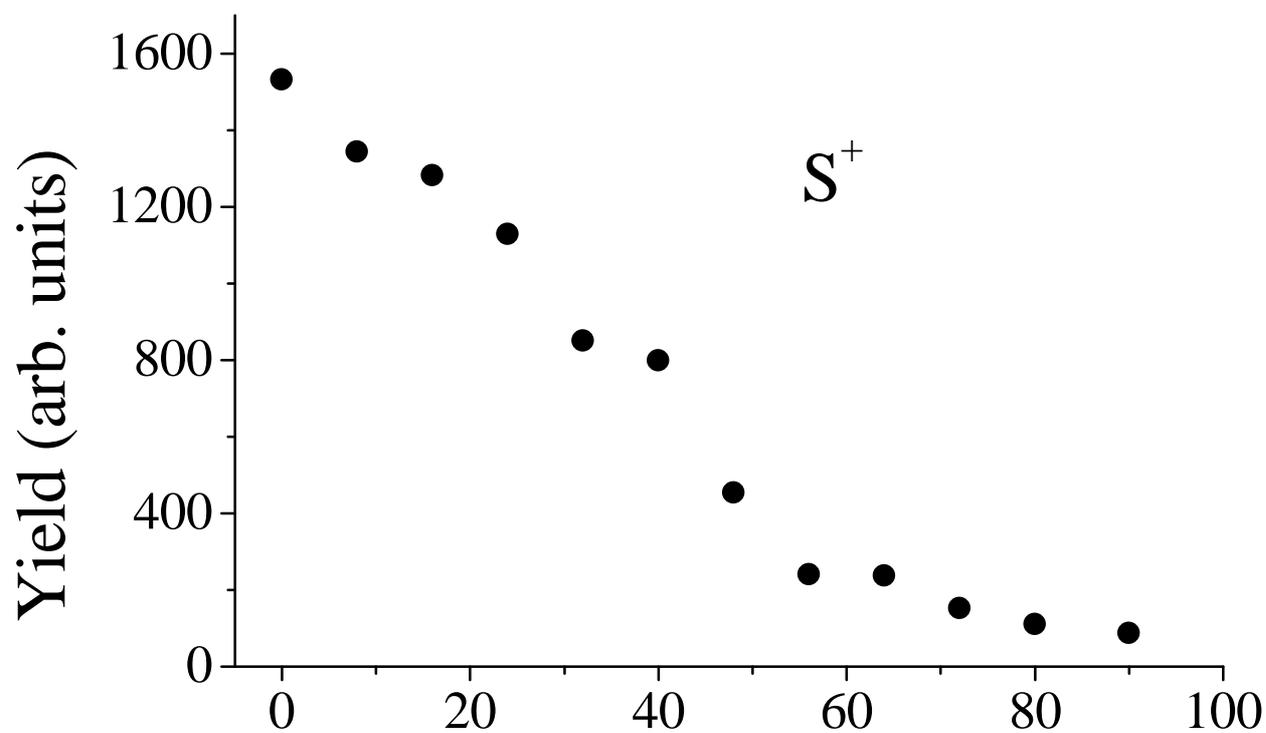
FIG. 1. Variation of (a) S^+ and (b) S^{2+} yield with polarization angle. These measurements were made using 100-fs laser pulses. Similar data was obtained using 35-ps pulses.

FIG. 2. Variation with laser intensity of the ratio, $S_{\parallel}^{q+}/S_{\perp}^{q+}$. \parallel and \perp denote, respectively, the ion yield at angles of 0° and 90° between the laser polarization vector and the TOF axis. Note the different functional dependence obtained in the case of 35-ps and 100-fs pulses. The picosecond ratios have been divided by 2.

FIG. 3. Calculated time dependence of the angle between the S-C-S axis and the laser polarization vector for different values of laser intensity for (a) 100-fs and (b) 35-ps pulses. The temporal profiles of the laser pulses are indicated by the solid curves.

FIG. 4. Mass spectra of CS_2 irradiated by 100-fs pulses at two laser intensities, with linear polarization (pointing parallel and perpendicular to the TOF axis) as well as with circular polarization.

(a)



(b)

