PHYSICAL REVIEW A VOLUME 56, NUMBER 3 SEPTEMBER 1997

Spatial alignment of gas-phase polyatomic molecules by an intense laser field

V. R. Bhardwaj, K. Vijayalakshmi, and D. Mathur
Tata Institute of Fundamental Research, Homi Bhabha Road, Mumbai 400 005, India

(Received 11 February 1997; revised manuscript received 16 May 1997)

Angular distributions have been measured of Cl^+ fragment ions resulting from dissociative ionization of polyatomic molecules CCl_4, $CHCl_3$ and CH_2Cl_2 induced by linearly polarized laser pulses of intensity 10^{13} W cm^{-2}. Pronounced anisotropy is exhibited in all cases, with Cl^+ detected mainly along the direction of the laser's polarization axis, indicative of field-induced spatial alignment of the precursor molecules. The directional properties of the average linear polarizability of the precursors appear to play a key role in determining the extent to which such alignment occurs.

[S1050-2947(97)03609-3]

PACS number(s): 33.80.Wz, 33.90.+h, 34.90+q, 33.15.Ta

Large dipole moments can be induced in molecules by intense, linearly polarized light fields. Such dipole moments exert torques on molecules that can swamp rotational motion such that, independently of the initial spatial orientation of the molecule, the molecular axis is rotated and spatial alignment of linear molecules occurs along the direction of the light polarization vector. Such movement can occur even in the low-intensity, rising edge of a laser pulse. As the applied field continues to increase, bond lengths can also increase until an instant is reached at which bond cleavage occurs.

The possibility of spatially aligning gas-phase molecules broadens the horizons for spectroscopy [1] and chemical reaction dynamics [2] as well as being of intrinsic interest in studies of laser-matter interactions. Experimental evidence for the preferential alignment of the internuclear axes of molecules along the polarization axis of linearly polarized laser beams has been obtained in measurements of angular distributions of fragment ions produced in intense-field-induced dissociative ionization experiments involving diatomic molecules [3] as well as some linear triatomics [4]. Friedrich and Herschbach [1] have shown theoretically that pendular states that arise out of laser-field-induced dipole moments are directional superpositions of field-free molecular states, corresponding to oblate spheroidal wave functions, whose eigenenergies are inversely proportional to field strength. The experimental manifestation of field-induced pendular motion has been demonstrated recently in the case of the linear triatomics CO_2 and CS_2 [4].

Are polyatomic molecules also spatially aligned by intense laser fields? If so, can such alignment be probed by measuring the angular distributions of fragment ions resulting from field-induced dissociative ionization (DI)? We have attempted to provide answers to these questions by conducting DI experiments on a series of polyatomic molecules, CCl_4, $CHCl_3$, and CH_2Cl_2, using linearly polarized laser fields whose wavelength, pulse duration, and intensity are, respectively, 532 nm, 35 ps, and $(2–8)\times10^{13}$ W cm^{-2}. Laser-field-induced DI is a complex nonperturbative, dynamical problem of spatially aligned molecules that may be undergoing pendular motion and the prospects of rigorous theoretical treatments are remote. Consequently, we have also attempted to provide guideposts for further work by trying to relate the measured angular distributions to ground-state linear molecular polarizabilities.

Our experiments were conducted using apparatus and methodology that have been described in recent reports of DI and angular distribution measurements of a number of triatomic molecules [5,4,6]. In brief, linearly polarized, 35-ps-wide, 532-nm pulses from a Nd:YAG laser (where YAG denotes yttrium aluminum garnet), focused to a spot size of 40 μm [7], interacted with the vapor of each polyatomic species in an UHV chamber pumped to a base vacuum of 2×10^{-8} Torr. The pumping geometry employed in the laser-molecule interaction zone ensured target gas pressures ($\sim10^{-6}$ Torr) that corresponded to target molecule number densities of $\leqslant10^9$ cm^{-3}. Typical laser intensities used were in the range $(2–8)\times10^{13}$ W cm^{-2}. Ions produced in the laser-molecule interaction were mass analyzed by a quadrupole mass spectrometer; ion detection was by an off-axis channel electron multiplier operating in the particle counting mode. The angular distribution of fragment ions was measured by rotating the polarization direction of the incoming laser field with respect to the spectrometer axis; a combination of a half wave plate and linear polarizer was used to obtain the desired polarization at constant intensity. The shot-to-shot reproducibility of the laser intensity was $\pm5\%$; this was ensured by on-line monitoring of the laser energy. Only those ions whose initial velocity vector lay within the acceptance angle set by the entrance aperture of the mass filter were detected; the angular resolution was $\pm4°$ in the present measurements.

Such angular distributions were made under conditions where *no* ion extraction fields were used; earlier experiments [4,8] have yielded evidence that even relatively small fields can lead to distortion of angular distributions. A detailed discussion has been recently presented of how fragment ion angular distributions are affected by ion extraction voltage and by charge saturation effects [9] when high target gas number densities are used [10]. The effect of the extraction field on the angular distributions of Cl^+ fragment from CCl_4 was studied by measuring the ratio (ϵ) of the Cl^+ ion signal at $\theta=0°$ (when the final polarization direction is parallel to the spectrometer axis) and at $\theta=90°$ as a function of the extraction electric field. It was observed that the angular distribution pattern remains essentially undistorted with ap-

TABLE I. Components of the polarizability of different bonds in directions parallel to ($\alpha_{\parallel}$) and perpendicular to ($\alpha_{\perp}$) the bond. Also indicated are the bond polarizability (α') averaged over all spatial orientations. α is the average polarizability of the molecule in its ground electronic state (see the text) and Δ is the ratio of $\alpha_{\parallel}$ for the C-Cl bond to α. All polarizability values are in units of Å^3 and half width at half maximum (HWHM) values are in degrees. ϵ is the ratio of Cl$^+$ ion yield at $\theta=0°$ and $\theta=90°$.

Bond	$\alpha_{\parallel}$	$\alpha_{\perp}$	α'	Molecule	α	Δ	HWHM	ϵ
C-Cl	3.67	2.08	2.61					
C-H	0.79	0.58	0.65					
				CCl_4	10.44	0.35	50	4.8
				$CHCl_3$	8.48	0.43	38	7.9
				CH_2Cl_2	6.52	0.56	33	∞

plication of extraction fields of up to 4 V cm^{-1} ($\epsilon=5$), but drastic effects start to manifest themselves when the extraction field is larger ($\epsilon=1$) under our experimental conditions [8]. To study the saturation effects angular distributions of S$^+$ fragment from CS_2 were measured at two different number densities in the interaction region. For large number densities (10^{10}–10^{11} cm^{-3}, produced in a molecular beam) the ratio of ion yields at $\theta=0°$ and $\theta=90°$ was of the order of 15 and the corresponding ratio at $\theta=0°$ and $\theta=50°$ was ~ 2, resulting in a broader angular distribution. On the other hand, when the number densities were small ($\leqslant 10^9$ cm^{-3}, as produced in an effusive gas target) the ratio of ion yields at $\theta=0$ ° and $\theta=90°$ was infinity. The ion signal became zero at angles larger than $\sim 70°$. The S$^+$ signal ratio at $\theta=0°$–$50°$ was 30, resulting in a tighter angular distribution.

In its ground electronic state, carbon tetrachloride possesses tetrahedral geometry (T_d symmetry) with a central carbon atom and four peripheral chlorine atoms. In the absence of any external field, the electronic charge is concentrated around the peripheral Cl atoms, which is to be expected on electronegativity grounds by considering the relative positions of the C and Cl atoms in the Periodic Table. The molecule $CHCl_3$ has a similar structure to CCl_4 with C_{3v} symmetry but with one of the chlorine atoms replaced by a hydrogen atom; the C-Cl bond is more dipolar in nature than the C-H bond. The substitution of two chlorine atoms with two hydrogen atoms yields CH_2Cl_2, which has C_{2v} symmetry. Now the two chlorine atoms and the carbon atom are located in a plane that is orthogonal to the plane formed by the two hydrogen atoms and the carbon atom (in contrast to the situation in CCl_4 where any two planes formed by two Cl atoms and the C atom will be mutually inclined at 120°). The bond angles and bond lengths of each of the three molecules were calculated *ab initio* using the all-electron molecular-orbital electronic-structure code GAMESS [11]. The optimized values of bond angles and bond lengths that we obtained were in good agreement with values that are well established using various spectroscopic techniques [12].

When each of the three molecules is placed in a polarized laser field, the electronic charge cloud is distorted; induced dipole moments are generated and each molecule tends to become spatially aligned with one of the C-Cl bonds along the direction of the applied field [13] and this manifests itself

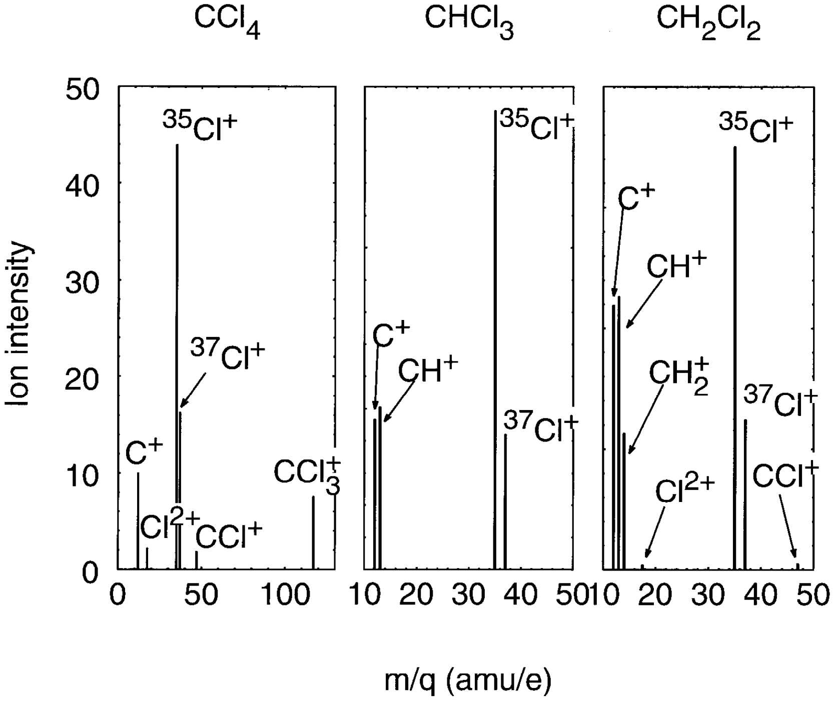

FIG. 1. Typical mass spectra of CCl_4, $CHCl_3$, and CH_2Cl_2. The linearly polarized electric field [intensity approximately (3–5)$\times 10^{13}$ W cm^{-2}] was applied along the mass spectrometer axis in all cases.

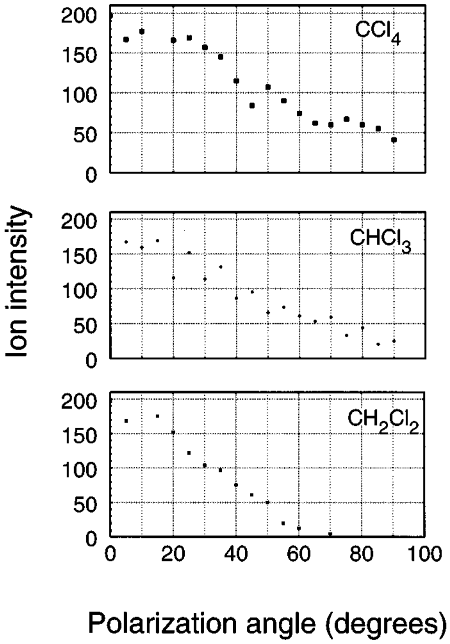

FIG. 2. Angular distributions of Cl^+ fragments resulting from intense-field-induced dissociative ionization of CCl_4, CHCl_3, and $\mathrm{CH}_2\mathrm{Cl}_2$. The linearly polarized electric field was applied along the 0° direction in all cases.

in the angular distributions of Cl^+ fragment ions produced upon DI of each molecule. It is appropriate to assume that the molecules tend to align with one of the C-Cl bonds along the polarization direction. This is consistent with the high polarizability of this bond (see Table I). Moreover, as the parallel component of the polarizability is greater than the perpendicular component [1] the interaction potential, defined below, has a minimum when the C-Cl bond is along the field direction and this results in the spatial alignment that is indicated by the anisotropic Cl^+ angular distribution. Indications of this are also observed in the measured fragmentation pattern. Figure 1 depicts typical mass spectra measured in the 0° direction using intense 532-nm, 35-ps laser radiation. The laser polarization vector kept aligned along the spectrometer axis defines the 0° direction. It is evident that Cl^+ is the dominant fragment in all three molecules, in marked contrast to the fragmentation pattern obtained when electron-impact mass spectrometry is employed (see, for instance, [8]). The dominance of the Cl^+ ion in laser-induced fragmentation is a manifestation of the spatial alignment of the C-Cl bond along the laser polarization vector. An unambiguous manifestation of such alignment is observed in the variation of Cl^+ intensity as the polarization axis is altered.

The measured angular distributions of Cl^+ ions are shown in Fig. 2. Identification of the different fragmentation channels is not possible with the present experimental setup as, unlike studies performed using time-of-flight techiques [3], a quadrupole mass spectrometer does not yield information on the temporal correlation between different ion fragments, nor does it provide energy information. The angular distribution measurements of the Cl^+ fragment from all the three molecules reported here are the integrated Cl^+ intensity over different possible channels.The most noteworthy feature is the nonisotropic nature of all the angular distributions, with maximum number of Cl^+ ions produced along the direction of the laser polarization; the corresponding Cl^+ intensity was at least a factor of 4 less in the orthogonal direction in all three instances. It is also noteworthy that the overall shapes of the angular distribution functions is different in the three molecules, with the ''tightest'' (narrowest) distribution being obtained in the case of $\mathrm{CH}_2\mathrm{Cl}_2$.

The observed anisotropic angular distributions manifest the spatial alignment of the three molecules. Elegant two-pulse experiments on diatomic molecules by Corkum and co-workers and others [3] have clearly established that the angular dependence of ionization rates cannot explain the observed anisotropic distributions. The laser-molecule interaction responsible for spatial alignment is essentially governed by the molecular polarizability α, which in turn is governed by a $\cos^2\theta$ potential as opposed to a $\cos\theta$ potential applicable in the case of permanent dipoles. The total angular momentum of each molecule is coupled to the laser field through α. For linear molecules, the second-order field-molecule interaction potential $V_\theta(\theta)$ is given by

$$V_\theta(\theta) = -\frac{1}{2}E^2(\alpha_\parallel \cos^2\theta + \alpha_\perp \sin^2\theta), \tag{1}$$

where E is the average field strength and $\alpha_\parallel$ and $\alpha_\perp$ are the polarizability components parallel to and perpendicular to the molecular bond. The $V_\theta(\theta)$ term is, in general terms, the cause of the spatial alignment and earlier work [4] has shown that the field-molecule interaction energy overwhelms the field-free rotational energy and can thus induce alignment.

For a polyatomic molecule the total polarizability α can be expressed as a sum of polarizabilities of the constituent groups [14]:

$$\alpha = \alpha_A + \alpha_B + \alpha_C + \cdots, \tag{2}$$

where each of the constitutuent polarizabilities $\alpha_A, \ldots$ consists of two direction-dependent components $\alpha_\parallel$ and $\alpha_\perp$. If the applied electric field is at an angle θ with a given bond in a polyatomic molecule, the polarizability α_θ is

$$\alpha_\theta = \alpha_\parallel \cos^2\theta + \alpha_\perp \sin^2\theta. \tag{3}$$

Averaging over all possible solid angles (spatial orientations) leads to an average value of the bond polarizability

$$\alpha' = \frac{1}{3}(\alpha_\parallel + 2\alpha_\perp). \tag{4}$$

The average polarizability α of a polyatomic molecule is then the sum of the average polarizabilities α' of its bonds. For the molecules studied in the present experiments, the values of $\alpha_\parallel$ and $\alpha_\perp$ for the C-Cl bond are 3.67 Å^3 and 2.08 Å^3, respectively; for the C-H bond, the corresponding values are 0.79 Å^3 and 0.58 Å^3 [14]. Values of α' and α for the three molecules are listed in Table I. The parameter of importance in determining the extent to which spatial alignment occurs is the torque that is generated on the molecule as the highly polar C-Cl bond aligns along the direction of the applied electric field. A measure of the magnitude of this torque is the parameter Δ, which we define as

$$\Delta=\frac{\alpha_{\parallel}(\text{C-Cl})}{\alpha}. \tag{5}$$

Values of Δ are also shown in Table I and indicate a direct relationship between the ''tightness'' of the Cl^+ ion angular distribution and the value of Δ for the precursor molecule: the highest Δ value is for the CH_2Cl_2 molecule and the Cl^+ ion angular distribution in this instance also indicates the highest degree of spatial alignment of the precursor molecule in the sense that the fragment ion intensity falls to zero at angles larger than $\sim 60°$. The tightness of the angular distribution can also be seen, apart from the Δ value, from the indicated values of the half-width at half maximum and the value of ϵ as shown in Table I, where the ratio of ion yield at $\theta=0°$ and $\theta=90°$ is represented by ϵ. Minimum Cl^+ yield occurs at larger angles in the case of the other two molecules. At an angle of 90°, the Cl^+ yield is significantly smaller in the case of the $CHCl_3$ molecule than for the CCl_4 precursor. It may be noted that Δ parametrizes very complicated dynamics: as one of the C-Cl bonds aligns along the field direction, the remaining (out-of-plane) bonds also interact with the applied field, but in such manner as to give rise to ''drag'' forces that result in angular distributions of different widths. Under such circumstances, a more quantitative estimate of the resultant torque exerted by the applied field on each molecule is difficult to make. It would clearly be of much interest to carry out molecular-dynamics simulations on such systems.

Is it possible to present semiquantitative estimates of the torque exerted by the laser field on each of the molecules studied here? Although estimates have been made by Dietrich *et al.* [3] in the case of diatomic molecules such as I_2 and model calculations have been carried out by us in the case of linear triatomic molecules such as CS_2 and CO_2 [4], a similar exercise is not feasible at present for the large nonplanar polyatomic molecules studied here. We are exploring an alternative approach in which we consider the field-induced distortions of electron density distributions in such polyatomic species and relate such distortions to the angular distributions and fragmentation patterns; preliminary results are presented elsewhere [13].

In summary, measurements of the angular distributions of the most intense fragment ion peak in the mass spectrum obtained upon intense-field-induced DI of CCl_4, $CHCl_3$, and CH_2Cl_2 show that spatial alignment does occur in the case of polyatomic molecules possessing nonlinear geometries. The average ground-state linear polarizability of such molecules might be a reasonable parameter with which to predict the extent to which such alignment occurs. We take no account of higher-order polarizabilities that might be expected to become fairly significant at the laser intensities used in our experiments. We find that the magnitude of a molecule's linear polarizability is in itself not a sufficiently useful parameter for predicting the degree of spatial alignment; the directional properties of the polarizability play a key role. This is exemplified by the Δ parameter in the present study that is related, in complex fashion, to the torque that might be expected to be exerted on the molecule as a result of the interaction of the applied laser field with the most polarizable of the many bonds in a polyatomic molecule.

---

[1] B. Friedrich and D. R. Herschbach, Chem. Phys. Lett. **262**, 41 (1996); Phys. Rev. Lett. **74**, 4623 (1995).

[2] B. Friedrich, H.-G. Rubahn, and N. Sathyamurthy, Phys. Rev. Lett. **69**, 2487 (1992).

[3] D. Normand, L. A. Lompré, and C. Cornaggia, J. Phys. B **25**, L497 (1992); P. Dietrich, D. T. Strickland, B. Laberge, and P. B. Corkum, Phys. Rev. A **47**, 2305 (1993); D. T. Strickland, Y. Beaudoin, P. Dietrich, and P. B. Corkum, Phys. Rev. Lett. **68**, 2755 (1992).

[4] G. R. Kumar, P. Gross, C. P. Safvan, F. A. Rajgara, and D. Mathur, J. Phys. B **29**, L95 (1996); Phys. Rev. A **53**, 3098 (1996).

[5] G. R. Kumar, C. P. Safvan, F. A. Rajgara, and D. Mathur, Chem. Phys. Lett. **217**, 626 (1994).

[6] C. P. Safvan, K. Vijayalakshmi, F. A. Rajgara, G. R. Kumar, V. R. Marathe, and D. Mathur, J. Phys. B **29**, L481 (1996).

[7] G. R. Kumar, C. P. Safvan, F. A. Rajgara, and D. Mathur, J. Phys. B **27**, 2981 (1994).

[8] K. Vijayalakshmi, V. R. Bhardwaj, C. P. Safvan, and D. Mathur, J. Phys. B **30**, L339 (1997).

[9] M. V. Ammosov, F. A. Il'kov, M. G. Malakhov, and Ch. K. Mukhtarov, J. Opt. Soc. Am. B **6**, 1961 (1989).

[10] D. Mathur, V. R. Bhardwaj, P. Gross, G. R. Kumar, F. A. Rajgara, C. P. Safvan, and K. Vijayalakshmi, Laser Phys. (to be published).

[11] M. W. Schmitdt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, J. Comput. Chem. **14**, 1347 (1993).

[12] *CRC Handbook of Chemistry and Physics*, 54th ed. (CRC, Boca Raton, FL, 1973), p. F-199.

[13] K. Vijayalakshmi, V. R. Bhardwaj, and D. Mathur, J. Phys. B (to be published).

[14] J. O. Herschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), p. 949.