Polarization-state dependence of the ionization dynamics of a chiral molecule in intense laser light

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Circular dichroism of a chiral molecule, S(+)2-butanol, is investigated in intense laser light. Although theory suggests the possibility of enhanced differences in absorption (leading to ionization) of circularly polarized light of a particular handedness by a random ensemble of chiral molecules, we report results of experiments that fail to observe such effects. While the ionization probability does not significantly change with the ellipticity of the incident light, fragmentation decreases with enhanced ellipticity. The kinetic-energy release accompanying CH^+ formation decreases as the laser light becomes more intense, a possible manifestation of bond softening.

I. INTRODUCTION

Following its discovery in 1825 by Fresnel, and studies by Pasteur in 1850 [1], chirality has remained an important concept in diverse areas of scientific activity that range from microscopic investigations of elementary particles, molecules, and crystals to considerations of large-scale properties of living matter and the open question of biological homochirality. Contemporary interest in chirality also stems from tantalizing possibilities of molecule-level engineering using chiral molecules. For instance, Mao *et al.* have recently reported a device that is based on the transition of right-handed to left-handed DNA and Koumura *et al.* have produced the first light-driven monodirectional molecular rotor using a chiral helical alkene [2]. Chirality and its manifestation in the interaction of photons has renewed interest not only for possible applications in switching and storage devices but also from a fundamental viewpoint. The possibilities of controlling laser pulse shapes and widths provide new impetus for exploring the possibilities of controlling molecular excitation and dissociation. Theoretical advancements are also being made on the design of pulse widths to achieve selective excitation of chiral molecules of a particular handedness using circularly polarized laser pulses [3,4].

It is known that in chiral molecules, which have a nonzero magnetic moment, the electromagnetic radiation brings forth optical activity due to the combined polarization contribution from the electric and magnetic transition moments [5]. The inversion symmetry associated with the magnetic moment in chiral molecules leads to circular dichroism (CD), which causes the absorption rates for left- and right-circularly polarized light to be different for a molecule of a particular handedness. Linear optical activity is a well-understood phenomenon and is now a widely applied tool for structure determination. Its manifestation in electron scattering [6,7] and single-photon ionization [8] have also been studied recently. Nonlinear optical activity, on the other hand, is studied very little experimentally, though there has been considerable theoretical interest [9].

Theoretical arguments suggest that molecular transition probabilities associated with the $\boldsymbol{\mu} \cdot \mathbf{m}$ interaction carry information about both the ''degree'' as well as the ''sense'' of structural handedness in absorbing systems. Quantitatively, both semiclassical radiation theory and quantum electrodynamics predict the two-photon CD to be at least as probable as the single-photon CD [10,11]. Though predictions have been made on the possibility of observing circular dichroism in randomly oriented molecules under two- or three-photon absorption, there has been very little experimental work. Similar predictions for circular dichroism in two- or three-photon absorption have also been made for molecules possessing a permanent dipole moment [12]. Extending these arguments, it may also be expected that in the case of multiphoton ionization, there might be a possibility of observing circular dichroism.

Circular dichroism in the interaction of chiral molecules with intense laser light has not so far been explored, either theoretically or experimentally. Intense electric fields that are produced by short laser pulses result in the production of very large induced dipoles in molecules, and these can influence molecular dissociation and alignment [14]. The large magnetic fields associated with intense electromagnetic pulses can also induce transitions due to the magnetic moment in asymmetric chiral molecules. Furthermore, such magnetic fields can couple electric-dipole and magnetic-dipole transitions, leading to the possibility that $\boldsymbol{\mu} \cdot \mathbf{m}$ interaction terms might result in selective enhancement of the absorption of circularly polarized light of a particular handedness. For instance, there is the intriguing possibility that a chiral molecule that is dextrorotary might absorb an intense, left-circularly polarized (LCP) pulse much more effectively than a right-circularly polarized (RCP) pulse.

In this paper, we report results of an attempt to probe circular dichroism in multiphoton ionization and dissociation of a gas-phase chiral molecule. Specifically, we report here the results of ionization studies of optically active S(+)2-butanol using LCP and RCP infrared light in the intensity regime 10^{12}–10^{14} W cm^{-2}. Alas, the ionic fragmentation patterns obtained in our experiments with LCP and RCP light are identical. A more sensitive test is to measure the kinetic energies with which different fragment ions are formed, and these too reveal no dissimilarities. These measurements also explore the possibility that different angular-

momentum states accessed by LCP and RCP light might yield changes in the shapes of peaks observed in time-of-flight spectra, reflecting changes in the energetics accompanying the resulting dissociation dynamics. Interestingly, we find evidence that, counterintuitively, the kinetic energies released (KER) upon fragmentation decrease as the laser intensity increases. This is possibly indicative of a transition between molecular bond softening and above-threshold dissociation.

II. EXPERIMENT

In our experiments, light pulses of 35-ps duration, of wavelength 1064 nm, were obtained from a high-intensity, Nd:YAG laser operating at a repetition rate of 10 Hz. The laser light was focused using a biconvex lens of 10 cm focal length in an ultra-high-vacuum chamber capable of being pumped down to a base pressure of 8×10^{-11} Torr. The vapor of chirally pure S(+)2-butanol was leaked into the chamber, resulting in operating pressures of $\leq 8 \times 10^{-8}$ Torr. These pressures were low enough to ensure that space-charge effects did not alter the results. Ions produced in the laser-molecule interaction zone were analyzed by a two-field, linear time-of-flight (TOF) spectrometer. A more detailed illustration of the apparatus used in these experiment can be found elsewhere [15].

In measurements of fragmentation patterns, we ensured 100% collection efficiency into our TOF spectrometer by using large (>100 V cm^{-1}) electrostatic extraction fields. However, measurements of kinetic-energy spectra were typically carried out at extraction fields of ~ 20 V cm^{-1} to ensure sufficiently high-energy resolution. The polarization state of the laser light was changed by using a quarter-wave plate, and mass spectra were collected for LCP and RCP light interacting with the chiral molecules under otherwise identical conditions.

III. RESULTS AND DISCUSSION

The S(+)2-butanol mass spectrum was found to be dominated by $CH_2CH_3^+$ and H^+ fragments, with small contributions from CH^+ and $C_3H_7O^+$ ions. Peaks corresponding to single and double ionization of the parent 2-butanol were also observed. The fragmentation pattern remained unchanged with the polarization state of the laser light. These results are depicted in Fig. 1, where the yield of a particular ion using LCP light pulses is plotted as a function of the corresponding yield with RCP light. Since the yields in both experiments were identical, the points fall on a 45° line. The experiment was repeated over a wide range of sample pressures and laser intensities (spanning the regime of multiphoton ionization, at the lower end of the range, to tunnel ionization at the higher end). A much more sensitive search for differences between LCP-induced and RCP-induced effects involved the measurement of kinetic energies released upon fragmentation. Identical spectra were obtained with LCP and RCP light. Differences in the kinetic-energy release with the polarization of the incident light would manifest themselves
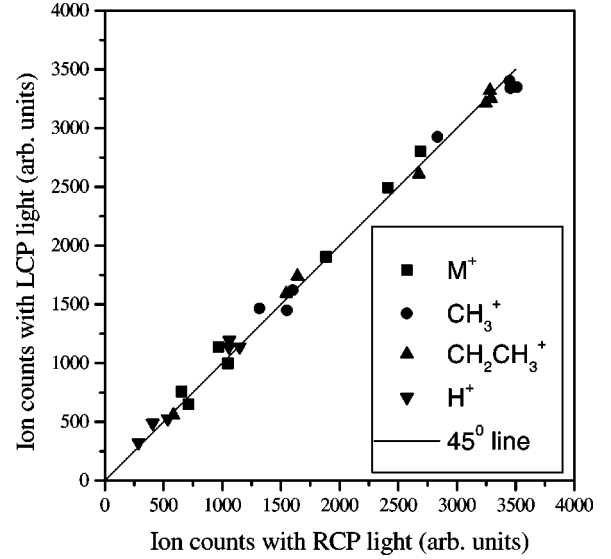

FIG. 1. Comparison of ion yields obtained with LCP and RCP light. The different data points show results obtained at several laser intensities spanning the range 10^{12}–10^{14} W cm^{-2}. The points trace a 45° line showing that the ion intensities are independent of the handedness of the interacting circularly polarized light field.

as changes in the shape of the fragment ion peaks. No such changes were observed.

The chiral asymmetry in the molecules should, in principle, make a difference in multiphoton absorption (ionization) for LCP and RCP laser light. For two-photon absorption, theory [13] suggests that the difference in absorption coefficient should go as

$$\delta_L - \delta_R \propto \text{Im}[(D_2^2)^*_{ng}(G_2^2)_{ng} + (B_2^2)_{ng}(G_2^2)^*_{ng}], \quad (1)$$

where $(D_2^2)_{ng}$ is the molecular transition tensor due to the electric-dipolar ($\boldsymbol{\mu} \cdot \mathbf{d}$) interaction

$$(D^2)^*_{ng} = \langle n|T^{\mu\mu}|g\rangle = \sum_i \frac{\langle n|\boldsymbol{\mu}|i\rangle\langle i|\boldsymbol{\mu}|g\rangle}{E_{ig} - h\nu}. \quad (2)$$

$(B^2)_{ng}$ is the molecular transition tensor due to the magnetic-dipolar ($\mathbf{m} \cdot \mathbf{d}$) interaction

$$(B^2)^*_{ng} = \langle n|T^{\mathbf{mm}}|g\rangle = \sum_j \frac{\langle n|\mathbf{m}|j\rangle\langle j|\mathbf{m}|g\rangle}{E_{jg} - h\nu}. \quad (3)$$

$(G^2)_{ng}$ is the molecular transition tensor due to both electric-dipolar and magnetic-dipolar ($\mathbf{m} \cdot \mathbf{d}$) interaction

$$(G^2)^*_{ng} = \langle n|T^{\mu\mathbf{m}} + T^{\mathbf{m}\mu}|g\rangle$$

$$= \sum_k \frac{\langle n|\boldsymbol{\mu}|k\rangle\langle k|\mathbf{m}|g\rangle + \langle n|\mathbf{m}|k\rangle\langle k|\boldsymbol{\mu}|g\rangle}{E_{kg} - h\nu}. \quad (4)$$

The three-photon absorption [12] is expected to go as

$$\delta_L - \delta_R \propto (\boldsymbol{\mu} \cdot \text{Im } \mathbf{m})|\boldsymbol{\mu}|^4. \quad (5)$$
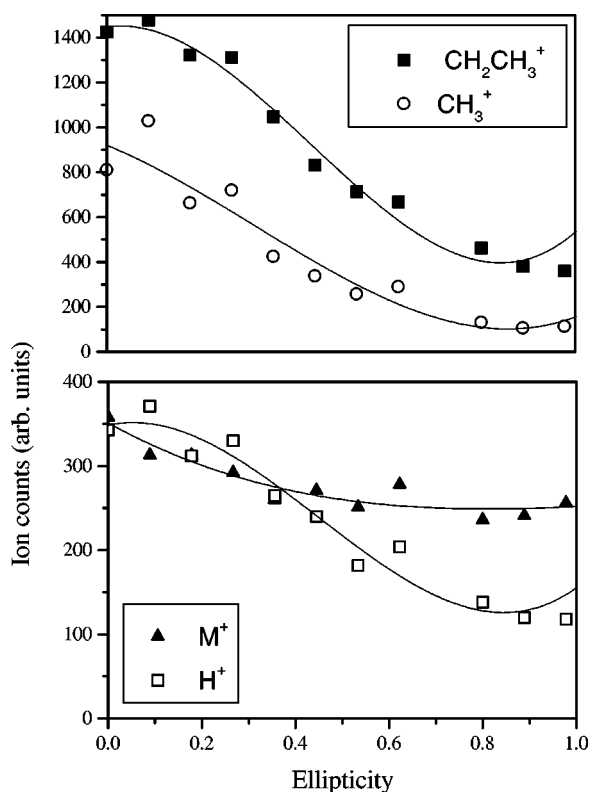
FIG. 2. Change in ion intensities as a function of the ellipticity of the incident laser radiation. The solid lines are guides to the eye. M^+ denotes the parent $C_4H_{10}O^+$ ion. Ellipticity$=0$ denotes linearly polarized light, with the electric-field vector parallel to the axis of the time-of-flight spectrometer. Ellipticity$=1$ denotes circularly polarized light.

These arguments can be extended to multiphoton absorption (ionization) of molecules and are expected to yield absorption rates that depend on the handedness of the laser polarization. However, the present results do not show any difference in the ionization and fragmentation probability with the handedness of the laser polarization.

With present laser technology, absorption-rate differences of the order of 1% can realistically be measured in experiments of the type reported here. The present results indicate that differences are of smaller magnitude than this. In order to carry out experiments in the multiphoton regime that are equivalent, in terms of sensitivity, to conventional single-photon CD, it would be necessary to have the ability to switch laser polarization states at a very rapid rate (of the order of at least a few tens of kHz). On any intense field experiment of the type we report here, a serious limitation is placed by present-day technology. Our laser operated at a repetition rate of 10 Hz. It is currently possible to have high-intensity lasers operating at repetition rates of, at most, 1 kHz. Advances in laser technology that enhance this rate by a factor of 10 will lead to better sensitivity, which might help the development of intense-field CD.

We have also measured the ionization rates as a function of the ellipticity of the interacting light; Fig. 2 shows the measured variation. As is seen, the intensity of the fragment ions decreases, almost by a factor of 3, in changing the po-larization state of the laser from linear to circular. The parent ion intensity, on the other hand, shows much less variation with laser polarization. It is of interest to note that an overall decrease in the total ionization rate has recently been observed when simple molecules (like N_2, CS_2) are irradiated by circularly polarized, intense laser fields [16]. The change in ionization and fragmentation patterns arising from the interaction with circularly polarized (CP) and linearly polarized (LP) light may be attributed to two main factors:

(i) At the same intensity of the laser pulse, in changing from LP to CP, the electric-field amplitude decreases. The decrease in the effective electric-field component in the direction of the TOF spectrometer can result in a decrease in the ionization signal rate that is measured as the ellipticity goes from linear polarization to circular polarization.

(ii) Selection rules for excitation by LP light and CP light are expected to be different. The excited states accessed when CP light is used will be different from those accessed using LP light and, consequently, the resulting fragmentation pattern would be expected to exhibit differences when compared to that obtained using LP light.

If the ionization probability were solely dependent on the electric-field amplitude, then one would expect the intensity of the parent molecular ion to decrease with an increase in the ellipticity to the *same* extent as in the case of fragment ions. This is not so, as Fig. 2 shows. So, it is probable that access to different electronic states in the excitation manifold is responsible for the different degree of fragmentation observed with an increase in ellipticity. It is intriguing that the fragmentation pattern remains unchanged in going from linear to circular polarized light; all fragment ions merely decrease in intensity as the transition from LP to CP light is made. If the excitation manifold that is accessed is, indeed, different, in terms of orbital angular momenta, one might expect the gross fragmentation pattern to change in that certain fragmentation channels might be more favored over others. This, however, is not the case here, since *all* the fragment ions decrease with ellipticity. A more detailed analysis is clearly required in order to understand the observed fact that the relative cross section for fragmentation is affected to a substantial extent while the overall ionization probability remains essentially unchanged as the polarization properties of the incident light are altered. With large molecules like S(+)2-butanol, the large density of states as well as large Stark shifts and dressing of the potentials induced by the intense laser field preclude a detailed analysis at present.

We have also probed the laser-field-induced spatial alignment of chiral S(+)2-butanol. Using a half plate, the plane of polarization of the laser light was rotated with respect to the direction of the axis of our TOF spectrometer. Spectra collected with the polarization vector parallel to the TOF axis, or perpendicular to it, were very similar. No decrease in the intensity of any fragment ion was observed. If there were any preferential axis of alignment for the irradiated molecules, one would expect, on the basis of considerable recent experience of the spatial alignment of different classes of molecules irradiated by picosecond laser fields, that certain fragment ion intensities would be larger when the polarization vector was parallel to the TOF axis than when it was
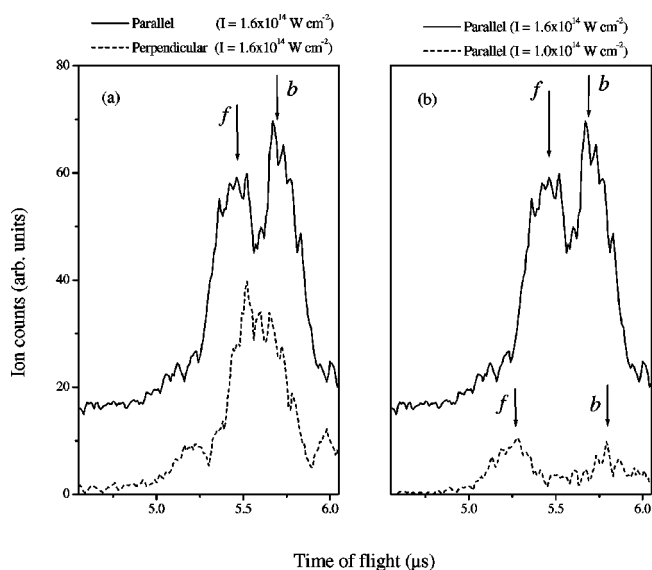
FIG. 3. (a) TOF spectra depicting the kinetic-energy release in the center-of-mass frame for the CH^+ fragment ion. *f* and *b* indicate the forward- and backward- scattered ion peaks (see text). The solid curve shows the spectrum obtained with the laser polarization parallel to the TOF axis and the dashed curve shows the corresponding spectrum obtained with the polarization vector perpendicular to the TOF axis. (b) KER spectra of CH^+ at two different energies, as indicated in the figure, with the laser polarization vector parallel to the TOF axis.

orthogonal to it [14]. The anisotropy of the molecular polarizability is clearly such that no bond is preferentially aligned along the laser polarization vector in the present case.

When the kinetic energy released upon formation of certain fragment ions is large, it is possible to observe forward-backward splittings of ion peaks in a TOF spectrum measured with relatively low ion extraction fields [15,17]. In the case of CH^+ fragments observed in our spectra, KER values were sufficiently large to enable us to resolve such splittings (see Fig. 3). The solid curve shown in Fig. 3(a) depicts such forward-backward peaks recorded when the laser polarization vector was parallel to the TOF axis. The dashed curve shows the TOF spectrum obtained with the polarization vector perpendicular to the TOF axis. As expected with perpendicular polarization, a single, broad peak appears at the center of the twin peaks obtained using parallel polarization. Using such spectra, it is possible to deduce the KER distribution function. We have done this at different values of laser intensity and we find that the mean KER value is inversely proportional to the laser intensity. Figure 3(b) shows the spectra (obtained with parallel polarization) at two different laser intensities. The dashed curve, obtained using lower laser intensity, shows TOF peaks that have a larger

separation between the forward and backward components, indicating a larger KER value than in the case of measurements using higher laser intensity. This appears counterintuitive, as one might expect that as the magnitude of the light field is enhanced, the KER distribution would shift toward higher energies, as channels leading to higher degrees of excitation become accessible.

Our observations are reminiscent of theoretical predictions that have been made of the dependence upon laser intensity of the competition between bond softening and above-threshold dissociation (ATD) in H_2^+ [18]. Irradiation of the zeroth vibrational level of H_2^+ by low values of laser intensity ($\sim 3 \times 10^{12}$ W cm^{-2}, 300 nm wavelength) leads to three-photon ATD. This is brought about by a crossing of the $1s\sigma_g$ potential-energy (PE) curve by the $1s\sigma_u$ curve dressed by three photons. This leads to the formation of H^+ fragments possessing a mean KER value of ~ 4.25 eV. At somewhat higher values of laser intensity ($\sim 5 \times 10^{13}$ W cm^{-2}), two-photon ATD dominates the KER distribution, with a mean H^+ energy of ~ 2.5 eV. This process involves an initial three-photon transition to the repulsive $1s\sigma_u$ curve followed by one-photon emission accompanying an adiabatic transition to the $1s\sigma_g$ PE curve dressed by two photons. At laser intensities in excess of 1.5×10^{14} W cm^{-2}, the single-photon bond-softening process dominates, producing 1-eV protons. Experimental evidence for bond softening in two- and three-photon ATD in H_2^+ has been obtained [19], but we believe that the data shown in Fig. 3 probably represent the first experimental manifestation of the competition between such processes as a function of light intensity in a more complex molecular system. As in the case of theoretical predictions that higher laser intensities favor more adiabatic behavior of the fragmentation process in H_2^+, it appears from our results that the propensity for more adiabatic behavior as the strength of the irradiation field increases might be more generally applicable than hitherto anticipated.

In summary, we have measured the polarization-state dependence of ionization and fragmentation of chiral S(+)2-butanol in intense, 1064-nm laser fields of 35-ps duration. No circular dichroism was observed in multiphoton or intense field absorption (ionization). Fragmentation rates were found to decrease as the incident laser radiation became more elliptical. At the same time, ionization of the parent molecule was little affected. Kinetic energies released upon fragmentation showed an unexpected inverse dependence on laser intensity; this was possibly due to bond softening.

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