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Disentangling molecular alignment and enhanced ionization in intense laser fields

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Using circular and linear laser polarization for strong-field dissociative ionization we show that iodine molecules are rotationally fixed by their own moment of inertia during the dissociative ionization with a 80-fs pulse. What seems to be alignment of the fragments is created by an enhancement of the ionization rate, which is strongly dependent on the angle between the molecular axis and the laser electric-field vector. By the introduced method we can measure the degree of alignment for I_2, Br_2, Cl_2, and O_2 and independently estimate the enhancement of the ionization rate for I_2. [S1050-2947(99)50105-4]

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It is widely assumed that small molecules in the gas phase rapidly align with the laser polarization when illuminated by intense femtosecond or picosecond pulses [1–4] due to the torque on the laser-induced molecular dipole moment. The experimental justification for this assumption is the strong angular dependence of the exploding fragment distribution [5–7] during dissociative ionization. Pump-probe experiments by others [8] as well as by our group [9] appear to confirm this interpretation. Based on this experimental evidence, theoretical description of molecules in strong fields has concentrated on linear models [3,1,2]. In fact, the evidence has appeared so strong that the angular dependence of the fragments in dissociative ionization experiments has been quantitatively compared with models for orientational trapping of molecules in continuous laser fields [10].

However, several recent findings have raised doubt that the angular dependence of the fragment distribution is caused by a reorientation of the molecule [11]. It has been found experimentally that diatomic molecules appear to Coulomb explode at a critical internuclear separation [5,12], which is about 1.3 to 2 times the equilibrium internuclear separation. Theoretical models [5,13,14], supported by experiments [15,16], explain this anisotropy by an enhancement of the ionization rate for linearly polarized light with electric-field vector parallel to the molecular axis ($\mathbf{E}\|\mathbf{r}$) compared with $\mathbf{E}\perp\mathbf{r}$. This increase peaks at the ''critical distance'': while the molecular ion dissociates it reaches a critical internuclear separation at which the least bound electron localizes on one atomic core and the field of the other atomic ion assists the laser field in tunnel ionization of the elongated molecule. By modeling enhanced ionization classically, it has been shown recently that dynamic alignment is unnecessary to account for the anisotropy in the iodine fragments [17]. It is important to experimentally clarify the degree of molecular alignment, since many phenomena depend on the angle between polarization and molecular axis. Note, inhibition of reorientation of a molecule often seen in solids [18] is equivalent to an inertial confinement (demonstrated below) of heavy molecules in the gas phase.

With the following scheme we distinguish unambiguously between the effects of molecular alignment and angular dependent ionization rate on the observed anisotropic fragment distribution. (i) We select a direction for observation of fragment ions resulting from dissociative ionization via the geometry of the time-of-flight mass spectrometer. (ii) The alignment relative to the laser field is controlled by using either linearly or circularly polarized light. Alignment along a given axis is only possible in linearly polarized light, since in circularly polarized light the field vector rotates too quickly for any molecule to follow, and thus molecules can only align to a plane. The use of circularly polarized light enables the calibration of ionization in the absence of linear alignment. (iii) The differences between the observed fragmentation patterns obtained using linearly polarized light with $\mathbf{E}\|\mathbf{r}$, and circularly polarized light with equal electric field amplitude, are a quantitative measure for the degree of alignment of molecules in the linearly polarized laser field.

First, the measuring scheme is established using a molecule for which alignment is unlikely, due to large moment of inertia and low anisotropic polarizability. We chose diiodomethane (CH_2I_2) since the two iodine atoms have just the critical internuclear separation where the enhancement of the ionization rate peaks for I_2. We confirm that ionization is mainly dependent on the electric-field component parallel to the axis along the I—I bond. That is, the same dissociative ionization signal should be observed for parallel and circularly polarized light, provided they have the same maximum fields.

Second, we study a series of diatomic molecules to determine the influence of mechanical and electronic molecular parameters on alignment. Since I_2 shows little alignment (see below), we also use the opportunity to quantitatively study the ionization enhancement in I_2 (and CH_2I_2) for linearly polarized light with polarization axis parallel (versus perpendicular) to the internuclear axis. Furthermore, we show that laser-induced shielding of Coulomb repulsion by almost ionized electrons [3] cannot be used to explain experimental data on the critical distance [19,12] observed in dissociative ionization experiments.

The experiment is performed [15] with a background pressure of 3×10^{-9} mbar at an operating pressure of about 10^{-7} mbar (i.e., below the pressure at which space-charge effects influence the results). The laser beam (diameter 4 to

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12 mm) enters the vacuum chamber through a 6-mm-thick fused silica window. It is focused by a parabolic mirror of 50-mm focal length into the 3-cm-long acceleration stage of a time-of-flight (TOF) mass spectrometer to a focal spot of 7.5- to 2.5-μm diameter. The molecular fragments enter the 3-cm-long drift region via a 2-mm entrance hole. This results for a TOF voltage of 800 V in an acceptance angle of 24° for the I^{2+}-I^{2+} channel.

The linearly polarized laser pulses (625 nm, 130 μJ, 80 fs) are transformed into circular polarization by a $\lambda/4$ plate. The presence (or absence) of a subsequent polarizer allows us to choose linearly polarized light—either parallel or perpendicular to the detector axis—(or circularly polarized light) with equal field amplitude, which is critical to our approach. If the laser electric-field component parallel to the molecular axis primarily determines the ionization rate in strong-field ionization, then—in the absence of aligment—a pulse linearly polarized with $\mathbf{E}\|\mathbf{r}$ and a circularly polarized pulse (which has an additional field component of equal amplitude but phase shifted by $\pi/2$ and perpendicular to the molecular axis) should produce the same fragment ion signals at the detector. The light intensity for perpendicular polarization was a factor of 1.12 higher than for parallel polarization, i.e., the electric field was 6% larger. This deviation results from the fact that the $\lambda/4$ plate was designed for 610 nm.

Studying ionization without alignment requires a molecule with large moment of inertia and small anisotropic polarizability [Eq. (1)]. CH_2I_2 is such a candidate since (i) it has with $r(\mathrm{I—I})=3.58$ Å [20] a moment of inertia 1.7 times larger than I_2; (ii) it has an anisotropic static polarizability, $\alpha_{\|}-\alpha_{\perp}$ (defined relative to the I—I bond axis), which is equal to that of I_2 at r_{eq} and 30% smaller than that of elongated I_2 at 3.6 Å [21,22]; (iii) this anisotropy of the polarizability of CH_2I_2 should decrease [21] as the carbon-iodine bond length increases, until the $C^{n+}-I^{m+}$ bonds break (electrons localize); (iv) after the carbon and hydrogen fragments leave CH_2I_2, $\alpha_{\|}(\omega_0)-\alpha_{\perp}(\omega_0)$ of the remaining elongated I_2 is small since 3.6 Å is the characteristic distance for electron localization in all charge states of I_2 [13].

Note, that the large mass differences between the constituents of CH_2I_2 separate the time scales of motions involved in dissociative ionization. Hydrogen and carbon depart quickly, leaving the heavier fragments almost in their original position. Assuming Coulomb potentials and unit charge on the carbon and iodine fragments, the C—I bond length doubles within 40 fs. Experimentally we observe C^{2+} fragments with typical explosion velocities of 0.26 Å/fs (≈ 40 eV). Thus for CH_2I_2 molecules in the high-intensity region of the laser focus (labeled by the charge state the fragments reach) isolated iodine ions are produced well before the peak of our 80-fs pulse and close to their original internuclear separation of $R\approx 3.6$ Å. This allows a detailed comparison with iodine since $R\approx 3.6$ Å is also the critical distance for I_2.

Figure 1 shows the kinetic-energy distributions of the I^{2+} fragments of CH_2I_2 for the three laser polarizations. The fragmentation channels are labeled with the charge states of the two ionic fragments. Parallel and circular polarizations yield approximately equal signals for the 2-1, 2-2, 2-3, and even the 3-3 and 3-4 channels (not shown), which confirms that primarily the parallel component of the field is important. In the absence of alignment the large difference in signal between circular (parallel) and perpendicular polarization can only be due to angle-dependent ionization. Thus, alignment can be observed, even in the presence of angle-dependent ionization, by comparing the signal intensities obtained with parallel and circular polarized light.

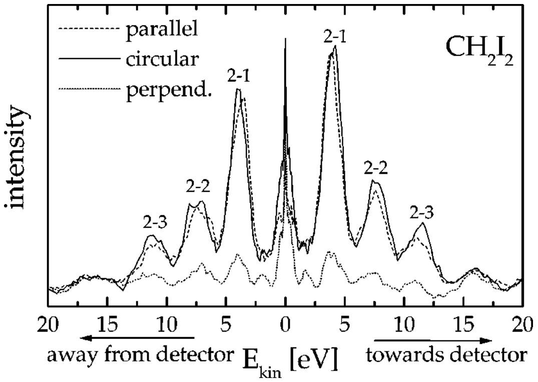

FIG. 1. Kinetic-energy distribution of I^{2+} resulting from the explosion of CH_2I_2 for circular laser polarization as well as for parallel or perpendicular polarization with respect to the molecular axis. The ion signals for parallel and circular polarization are approximately equal.

We study a series of diatomic molecules with decreasing moment of inertia (I_2, Br_2, Cl_2, and O_2). Figure 2 depicts the time-of-flight distributions for I^{n+} and $Cl^{n+}(n=2,3)$ for the three different polarization states. Since the ionization rate is primarily determined by the parallel field component, different strengths of the fragment signals for parallel and circular polarization measure the degree of alignment.

The following observations can be made based on the I_2 data: (i) The kinetic energy of the I^{2+} (and I^{3+}) fragments are nearly identical to the corresponding peaks in the CH_2I_2

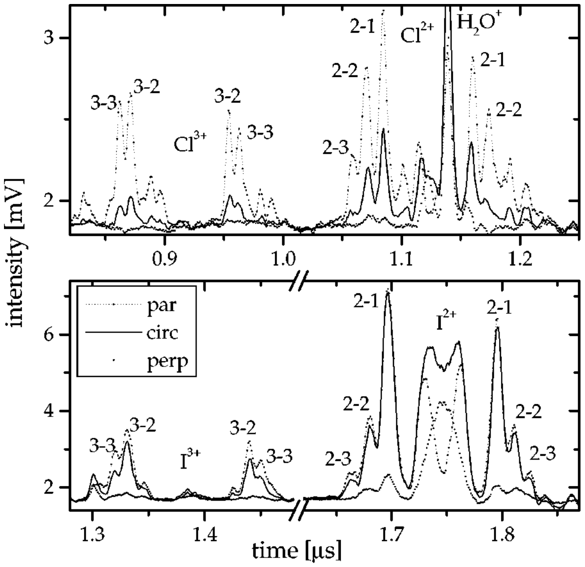

FIG. 2. Flight time distributions of the ionic fragments for chlorine (above) and iodine (below). The I^{2+} intensities for parallel and circular polarization are nearly equal, whereas they differ significantly for Cl^{2+}, showing the absence of alignment for the iodine molecule.

data. For example, the kinetic energy in the 2-1 channel is 5% larger for iodine than for CH_2I_2, and in the 2-2 channel the kinetic energy is 11% larger for the fragments of I_2 than for those of CH_2I_2. (ii) The signal strength of the 2-1 channel is identical for parallel and circular polarization, while for 2-2 only a slight difference can be detected. Diatomic iodine does not significantly align for laser intensities below the threshold for ${I_2}^{5+}$. (iii) The splitting of the peaks of the same fragment channel (and thus the kinetic energy of the fragments) is identical for parallel and circular polarization. This is in contradiction to Brewczyk *et al.* [3], who interpreted their calculated results by a shielding effect due to highly excited ''not quite ionized'' electrons for linearly polarized light. If shielding were important, the electrons would be driven away by the circularly polarized light, making the shielding ineffective and resulting in a larger kinetic energy of the fragment ions. (iv) The I^{3+} portion of the spectrum shows that alignment increases for higher charge states.

Observation (i) above shows that the $I^{2+,3+}$ fragments from both CH_2I_2 and I_2 originate from approximately the same internuclear distance, which is consistent with a critical distance of 3.6 Å [12]. Thus, the two atoms in the iodine molecule must have moved out during the rising edge of the laser pulse, which excites all molecules into mostly dissociative states [23]. The nearly equal ion signal in Fig. 2 at low kinetic energies for $\mathbf{E}\|\mathbf{r}$ as for $\mathbf{E}\perp\mathbf{r}$ shows that the same fraction of molecules is in dissociative states and reaches the critical distance at low laser intensity, either in the outer regions of the focus or in the rising edge of the pulse in the inner regions of the focus.

This excitation of molecules irrespective of their orientation is an alternative interpretation of the pump-probe experiments [8,9], which have so far been claimed as unambiguous evidence for alignment. If the preceding perpendicular pump laser pulse excites almost all molecules, these are largely dissociated by the time the second parallel polarized pulse arrives. Therefore, fewer ions will be observed in the same ionization channel in the pump-probe induced fragment spectrum.

The chlorine data show (a) the same kinetic energy splitting for circular and parallel polarized light, i.e., again no shielding by Rydberg electrons; (b) that the intensity of Cl^{2+} in the 2-1 channel (forward ions) for parallel polarization is a factor of 2 higher than for circular polarization, which is consistent with a higher degree of dynamic alignment; (c) that the angle-dependent ionization causes a factor of 3 in intensity between perpendicular and circular polarization. Based on these quantitative data and those of Br_2 and O_2 (not shown) we see that lighter molecules are partially aligning, even in a pulse as short as 80 fs, with the degree of alignment increasing for higher charge states and for decreasing initial moment of inertia.

Alignment is far from instantaneous, as can be seen by a classical estimate assuming constant angular acceleration during a rectangular 80-fs laser pulse. Using the polarizability components defined relative to the molecular symmetry axis of the neutral $I_2, \alpha_\| - \alpha_\perp = 7.6\times10^{-40}$ A s m^2/V [24], the moment of inertia at r_e, and the maximum field given by the ionization threshold of ${I_2}^{2+}$, $E_{th} = 1.5\times10^{8}$ V/cm, one obtains a total angle change $\Delta\theta = 4.2°$.

A better description is obtained by solving numerically the classical equations of motion for the internuclear distance and for the angle θ between molecular axis and laser polarization. While the internuclear distance is assumed to increase due to Coulomb repulsion, the angular acceleration is given by the torque $\mathbf{M} = \mathbf{d}\times\mathbf{E}$ on the molecular dipole moment $\mathbf{d}$ induced by the laser field $\mathbf{E}$(t). During dissociative ionization, the moment of inertia $I(t) = mr(t)^2/2$ is time dependent, leading to

$$\ddot{\theta} = -\frac{\alpha_\| - \alpha_\perp}{I}\mathbf{E}(t)^2 \cos\theta \sin\theta + 2\frac{\dot{r}}{r}\dot{\theta}. \tag{1}$$

An additional term due to the initial angular-momentum projection on the laser polarization axis, M_z, given by $M_z^2 \cos\theta/I^2 \sin^3\theta$ [25] can be neglected for the strong laser fields considered here. The mass of the molecule has two counteracting effects in the angular acceleration process. A light molecule is easy to accelerate, but the internuclear distance increases quickly, once the molecule reaches a dissociative state. Thus, the increasing moment of inertia leads to a reduced or even negative angular acceleration [second term on right-hand side of Eq. (1)] while the laser field is still on, and leads to an angular deceleration when the laser is off.

Using the measured threshold intensities for ${I_2}^{n+}$ [26] and a Gaussian laser pulse time profile, Eq. (1) overestimates the experimental alignment for iodine by a factor of 2 but underestimates the effect for chlorine by a factor of 2. The accuracy is limited by the uncertainties of the electronic properties (α and the threshold laser fields for ionization). While the ground-state polarizability of a neutral molecule is well known, it is not for elongated and excited molecules or for molecular ions. Note, that (i) for neutral diatomic molecules an increase of $\alpha_\|$ with elongation was found by quantum-chemical calculations [27,21]; (ii) the relation between α and oscillator strength $f_{ij}, \alpha(|j\rangle) \approx \Sigma_i f_{ij}/\omega_{ij}^2$, with transition energies ω_{ij} indicates an overall decrease of α with increasing charge [28]; recent calculations [21] show a decrease of α from neutral iodine to ${I_2}^{6+}$ by a factor of 2; (iii) α can be negative in some excited states; (iv) for increasing laser field the polarizability differs from the zero field value even in the electronic ground state [29]; (v) when r reaches the critical distance, electron localization occurs and the anisotropy in the frequency-dependent polarizability $\alpha(\omega_0)$ must decrease. This can be understood as a consequence of the shallow internal barrier of the double-well potential of the elongated molecule. These severe uncertainties of the polarizability lead to the overestimate of alignment in the former calculations [9] performed in our group.

Since iodine does not align significantly for charge states below 5+, we can use the 2-1 channel to extract a quantitative measure of the increase of the ionization rate between parallel and perpendicular polarization. Since our laser peak intensity exceeds 10^{16} W/cm^2, the ionization into the triply charged state ${I_2}^{3+}$ is saturated, i.e., all ions come from the region of the laser focus where the laser intensity exceeds the threshold for triple ionization but stays below fourfold ionization. The volume of this region increases with the threshold intensity as $I_{th}^{3/2}({I_2}^{3+})$. The observed tenfold increase in ion signal for parallel compared to perpendicular polarization is therefore equivalent to a decrease of the threshold intensity by about 4.5. We measured the same change of threshold intensity by decreasing the laser intensity of the parallel polarization until the ion signal for parallel polarization equaled the ion signal for perpendicular polarization at the previous intensity. Based on Ammosov-Delone-Krainov theory [30] we estimate an increase in intensity of 4.5 changes the ionization rate (in the region of $10^{13}\ \mathrm{s}^{-1}$) by 10^3, while a decrease in intensity of 4.5 changes the rate by 10^6.

In conclusion, we have presented a method to disentangle the contributions of angle-dependent ionization and of alignment, respectively, to the anisotropy of the fragment distribution. For I_2, where alignment is negligible at field strengths below the ionization threshold for ${I_2}^{5+}$, it is now possible to measure the relative ionization rate for parallel and perpendicular light in the nonsaturated regime [31]. Dynamic alignment during an 80-fs laser pulse becomes more significant for higher field strengths and for the lighter molecules. The calculation of alignment in either femtosecond or picosecond pulses is extremely difficult due to uncertainties in polarizability in the multitude of states that the molecule passes through during dissociative ionization. It is therefore important to investigate to what extent the anisotropy of the fragment distribution in picosecond pulse experiments [29,4], for which our proposed method is valid as well, is due to dynamic alignment.

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