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D_2^{2+} dication as a probe of spatial alignment of D_2 molecules in intense laser light

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Abstract

The dissociative double ionization of D_2 has been studied in a 532 nm, linearly polarized laser field with intensities in the range 10^{13} – 10^{14} W cm⁻². The laser-field-induced dipole moment gives rise to a torque on D_2 molecules that tends to dynamically align the D–D axis parallel to the laser polarization vector. From measurements of the dependence on polarization angle of the kinetic energy of the $D^+ + D^+$ fragment pairs a simple method, which may be of wide applicability, is developed that yields semiquantitative information on the fraction of molecules that are spatially aligned by the linearly polarized laser field. (Int J Mass Spectrom 192 (1999) 367–377) © 1999 Elsevier Science B.V.

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1. Introduction

It is now established that in interactions of molecules with intense light fields a host of nonlinear processes and dynamics are induced that have no analogue in weak-field or zero-field situations. Many of the light-induced phenomena that have been the subject of investigations appear to be counterintuitive and not easily amenable to conceptualization within the framework of conventional perturbative physics. Amongst them are the observed ejection of several electrons from the molecular core at internuclear separations far from equilibrium (multiple ionization), emission of high-energy photons (harmonic generation), above-threshold dissociation, enhanced ioniza-

tion, and formation of very-high-energy above-threshold ionization electrons and negative ions. Within the context of diatomic molecules, these intense-field-molecule interaction effects continue to attract a great deal of contemporary interest [1–7].

The intensity of the laser field used to probe such phenomena also results in distortions of molecular potential energy (PE) surfaces, and experimental manifestations of field-distorted or “dressed” PE curves include various nonlinear phenomena like above-threshold dissociation (attributable to diabatic or adiabatic crossings of PE curves [8], bond-softening (brought about by suppression of the potential barrier against dissociation in the vicinity of an avoided crossing [9], and vibrational trapping) which occurs if a deep enough potential well is formed at large internuclear separations as a result of an avoided curve crossing [10]. Consideration of field-induced distortions of PE curves has also opened up the

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possibility of exercising some selectivity between competing processes in experiments which utilize phase control in a two-colour optical field [11–13]. Recently, attempts have also been made to probe the dissociation and ionization dynamics of polyatomic molecules by considering field-induced distortions of molecular electron density distributions [14,15].

In order to develop insights into the dynamics governing field-induced behaviour of molecular species exposed to laser pulses, it is also necessary to account for one major distinctive feature of light–matter interactions in the high intensity regime: the spatial alignment of one or more bonds along the direction of the laser polarization vector. The possibility of spatially aligning molecules by means of linearly polarized, intense light fields has attracted much recent attention. It is established that the field associated with linearly polarized laser light of intensity greater than $\sim 10^{12}$ W cm⁻² can induce sufficiently strong torques on an initially randomly oriented ensemble of diatomic and linear triatomic molecules such that dynamic alignment of the internuclear axes occurs. Experimental manifestations of such alignment are the anisotropic angular distributions of fragments produced upon subsequent dissociative ionization of such molecules: ion intensities are maximum in the direction of the laser polarization vector and minimum (frequently zero) in the orthogonal direction [16–19]. Much of the interest in such alignment processes has been generated in the context of pendular-state spectroscopy [20–21] and coherent control [22]. Calculations [23] have indicated that aligned 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 prospect of trapping molecules [23,24], aligning them, and subjecting them to inertial confinement [16,23,25,26] by means of polarization interaction with an intense laser beam opens horizons for a new class of ultra-high-resolution and high-precision spectrometric and collisional experiments of the type hitherto applicable only to charged atoms and molecules in electromagnetic traps.

As stated previously, the experimental signature of dynamic spatial alignment is the markedly anisotropic angular distribution of fragment ions that results from laser-field-induced molecular fragmentation and ionization [16,21,24,27,28]. Following theoretical predictions made by Herschbach and co-workers [23], recent experiments on molecular dissociative ionization induced by strong laser fields have provided ample evidence that laser-field-aligned linear triatomic molecules like CS₂ and CO₂ also undergo pendular motion [21,24]. Experiments on polyatomic molecules possessing nonlinear geometries (like CCl₄ and related species, and ring molecules like C₆H₆) have also indicated that spatial alignment of certain bonds along the light polarization vector can have profound consequences on the fragmentation dynamics [29–31].

Recently, experimental indications have been obtained that if the linearly polarized light field is of sufficiently short duration (say, of the order of 100 fs), dynamic alignment may not occur in molecules that contain heavy atoms (such as iodine-containing diatomics and polyatomics), and the angular distributions of the products of dissociative ionization in such cases might be determined by the dependence of the ionization rate on the angle made by the laser polarization vector with the molecule's symmetry axis (see, for instance, [32,33]). For a given value of laser intensity, the rate for enhanced ionization would be largest for those molecules whose internuclear axis lies parallel to the direction of the laser polarization vector. When the laser polarization vector is aligned perpendicular to the molecule's internuclear axis, the field-induced ionization is very atomlike (see, for instance, [1,34]). In the case of geometric alignment also, one would expect to obtain a fragment ion angular distribution that is anisotropic with respect to the direction of the laser polarization vector. On the other hand, if the intense light fields are of longer duration than ~ 100 fs (say, picoseconds and longer), for most light molecules conventional wisdom dictates that the dynamics of field-induced spatial alignment is 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 . The second-order field–molecule interaction potential $V_\theta(\theta)$ is given by

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

where E is the average field strength and α_{\parallel} and α_{\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 [21,24] has shown that the field–molecule interaction energy overwhelms the field-free rotational energy and can thus induce dynamic alignment.

Although the idea that spatial alignment of molecular axes can be achieved using strong light fields now appears to be established, there exists no information on the *extent* to which molecules, which are initially randomly oriented in space, can be aligned by exposure to intense laser radiation. We report here a possible experimental procedure to estimate, at least semiquantitatively, the percentage of molecules that become spatially aligned when subjected to a 532 nm, linearly polarized laser field with intensities in the range 10^{13} – 10^{14} W cm⁻². Such estimates might be of value in identifying molecular species, particularly those possessing high values of linear and higher-order polarizabilities, that can be spatially aligned with high efficiency; experiments on such species will not only be of intrinsic, fundamental interest but might be of value in diverse applications, ranging from studies of gas-phase catalysis, new energy storage devices and grain chemistry to surface studies, ion propulsion and combustion science. The experimental procedure we propose is based on the utilization of the dissociation properties of molecular dications, and by way of illustration we present preliminary results of experiments we have conducted on the D₂²⁺ dication.

2. Interaction of D₂ (H₂) with intense laser light

Extensive work, both theoretical and experimental, has been reported on the dissociative ionization (DI)

of H₂ and D₂ in intense fields [35]; we use D₂ as a prototype to illustrate our procedure. Ion formation can occur in the following fashion when D₂ molecules interact with an intense light field:



Eq. (2) represents molecular ionization; it is possible that in this case D₂⁺ ions may be formed in electronically excited states which, in turn, interact with the intense field to give rise to dissociation:



Processes (2) and (3) have been established in the above-threshold ionization studies of Bucksbaum and co-workers [36–38] and lead to formation of ions with fairly low values of kinetic energy. Process (5) also yields D⁺ ions whose average kinetic energy content is fairly low. In contrast, the coulomb explosion channel (4) is expected to yield D⁺–D⁺ ion pairs whose average kinetic energy content is expected to be significantly higher, of the order of several electron volts. The branching ratios for the different processes will depend on laser intensity, wavelength and pulse duration. In the present experiments we focus attention only on the high-energy process (4).

Our experiment involves measurement of the kinetic energy of fragment ion pairs resulting from laser-field-induced dissociative double ionization of D₂ molecules [process (4)] as a function of the polarization angle of the incident laser beam. Specifically, we monitor the yield of D⁺–D⁺ ion pairs (using a coincidence time-of-flight technique described in Sec. 3) as we alter the direction of the laser polarization vector while keeping the laser intensity

constant. We determine, from our time-of-flight spectra, the center-of-mass kinetic energy released (KER) when $D^+ - D^+$ ion pairs are produced; such KER data is used to estimate the fraction of D_2 molecules (which are initially randomly oriented in space) that become spatially aligned due to interaction with the intense light field.

3. Experimental considerations

KER values were determined from time-of-flight spectra measured using a crossed-beams apparatus, details of which are described elsewhere [39]. Briefly, a 35-ps-wide pulse of 532 nm radiation from a high-energy Nd:YAG laser (where Nd:YAG denotes neodymium-doped yttrium aluminium garnet) was focused to a spot size of $\sim 40 \mu\text{m}$, where it interacted with an effusive molecular beam of 1 mm diameter. Positively charged ions produced in the interaction zone were electrostatically extracted into a linear, 20 cm long, time-of-flight mass spectrometer (TOF) and detected by a channel electron multiplier (CEM). The size of the ion extraction region was 1.2 cm, the acceleration region was 0.5 cm long while the flight tube had a length of 18 cm. The circular electrodes on either side of the ion extraction zone each had a diameter of 7 cm, with the ion-“puller” electrode having an aperture of 6 mm diameter. The output pulses from the CEM were amplified and fed into a fast digital storage oscilloscope (DSO) coupled to a computer through a fast data bus. Typically, TOF mass spectra were accumulated over $\sim 30\,000$ laser shots (our laser operated at a repetition rate of 10 Hz). Experiments were conducted at different values of D_2 gas pressure; data presented here was acquired at low enough pressures to ensure that space charge saturation effects were minimized [27,28].

Angular distributions of D^+ fragment ions were also measured. A combination of halfwave plate and polarizer was used to obtain the desired polarization at constant intensity. The polarization direction was rotated in steps of $1^\circ - 4^\circ$. The shot-to-shot reproducibility of the laser was monitored on-line by a fast photodiode coupled to the DSO and in the course of

most of the measurements, the shot-to-shot laser intensity variation was $\sim \pm 5\%$.

The dissociation dynamics of doubly charged molecules were probed by detection, in coincidence, of $D^+ + D^+$ fragment ion pairs. At the laser intensities used in these experiments, many ions can be generated with a single laser pulse and under such circumstances, conventional coincidence techniques cannot be applied. We took recourse to covariance mapping, a coincidence technique of measuring temporal correlations between pairs of ions which result from decay of a doubly charged precursor [40]. Covariance mapping has found considerable utility in recent studies of the fragmentation dynamics of multiply charged molecules [41,42]. As in other recent experiments, the measured TOF was represented as $X(t_1)$ at a number of discrete points (typically 1000) where $X(t_1)$ represents a 1000-element vector indexed by t_1 . If $Y(t_2)$ is the same vector, the covariance matrix, $C(t_1, t_2)$, between each pair of TOF points t_1 and t_2 can be obtained from the tensor product:

$$\begin{aligned} C(t_1, t_2) &= \langle (X - \langle X \rangle)(Y - \langle Y \rangle) \rangle \\ &= \langle XY \rangle - \langle X \rangle \langle Y \rangle \\ &= \langle X(t_1)Y(t_2) \rangle - \langle X(t_1) \rangle \langle Y(t_2) \rangle \end{aligned} \quad (6)$$

For averages taken over a total of N laser pulses (typically 30 000),

$$\begin{aligned} C(t_1, t_2) &= \frac{1}{N} \sum_{i=1}^N X_i(t_1)Y_i(t_2) - \left[\frac{1}{N} \sum_{i=1}^N X_i(t_1) \right] \\ &\quad \cdot \left[\frac{1}{N} \sum_{i=1}^N Y_i(t_2) \right] \end{aligned} \quad (7)$$

The covariance map is the small difference between two large correlated ($\langle XY \rangle$) and uncorrelated ($\langle X \rangle \langle Y \rangle$) products. A slice along either axis of the covariance map yields a coincidence spectrum (in this case, a single peak whose shape is analyzed to yield an average value of the kinetic energy released).

An important facet of the present study is that the methodology to be adopted had to be chosen with extreme care because of opposing constraints placed

on experimental conditions by the need to make angle-resolved measurements and covariance maps. It is known that dissociation of singly charged molecular ions gives rise to fragments that possess centre-of-mass kinetic energies of, at most, a few hundred millielectron volts. However, dissociation of dication precursors gives rise to fragment-ion KER values that are considerably larger (several electron volts). The reliability of coincidence measurements using TOF techniques is largely determined by the steps taken to ensure that high-energy fragment ions do not escape detection. Hence, the use of large electrostatic extraction fields in the laser–molecule interaction region is mandatory in TOF configurations. On the other hand, use of large extraction fields leads to reduction of the energy resolution in TOF spectrometers. Furthermore, angular distributions of ions produced upon dissociation of dications may also become distorted by non-uniformities in the electrostatic ion extraction field employed in the TOF spectrometer. Indeed, experimental manifestations of pendular motion in angular distribution measurements have hitherto only been obtained with mass filters other than TOF instruments where it is sometimes possible to use zero ion-extraction fields [21,24].

In angular distribution measurements carried out in TOF instruments, the effective angular resolution of the apparatus is essentially determined by the magnitude of the electrostatic ion extraction field and the KER value associated with each fragment ion. We carried out trajectory simulations through our TOF spectrometer of ions possessing a range of KER values and the results are shown in Fig. 1 for different values of extraction field. For ions possessing low values of KER, the effective acceptance angle of our TOF spectrometer is large. At low values of ion extraction fields ($\leq 100 \text{ V cm}^{-1}$), fragment ions possessing low KER values ($\sim 500 \text{ meV}$) are detected with an acceptance angle as large as 25° whereas for those with larger KER values ($\sim 3 \text{ eV}$) the corresponding acceptance angle is $\sim 7^\circ$. In order to detect high-KER fragments with sufficient efficiency it is clearly necessary to use larger extraction fields. However, this results in degradation of energy resolution.

It is, therefore, clear that whereas for reliable

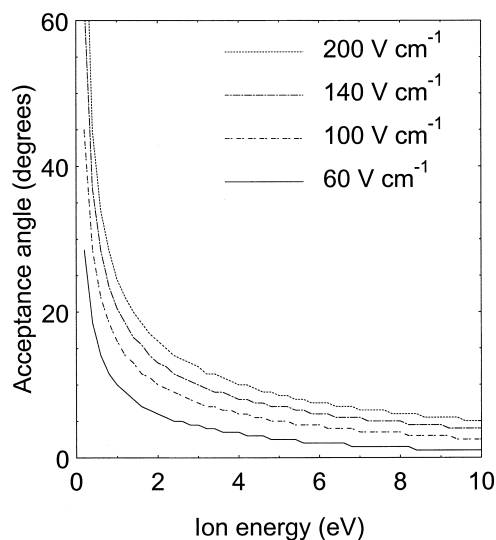


Fig. 1. Computer simulations of ion trajectories showing the dependence of the acceptance angle (half width at half maximum) of our time-of-flight spectrometer on the fragment ion kinetic energy.

energy information from TOF spectra it is necessary to employ low values of ion extraction fields, the present goal of measuring angle-resolved covariance maps of fragments arising from doubly charged precursors necessitated the use of high ion extraction fields. On the basis of a large number of measurements, optimal values in the range $50\text{--}100 \text{ V cm}^{-1}$ were chosen. Recent work on angle-resolved dication formation in CO_2 has indicated to us that such values of extraction field yield angular distribution data whose gross features are consistent with the pristine angular distributions measured using zero extraction fields in an apparatus incorporating a quadrupole mass spectrometer [43].

4. Results and discussion

4.1. Mass spectra and covariance map

A typical “singles” TOF mass spectrum showing D^+ fragments obtained in our experiments on D_2 is shown in Fig. 2. Peaks marked *f* and *b* represent energetic D^+ fragment ions that are ejected in the

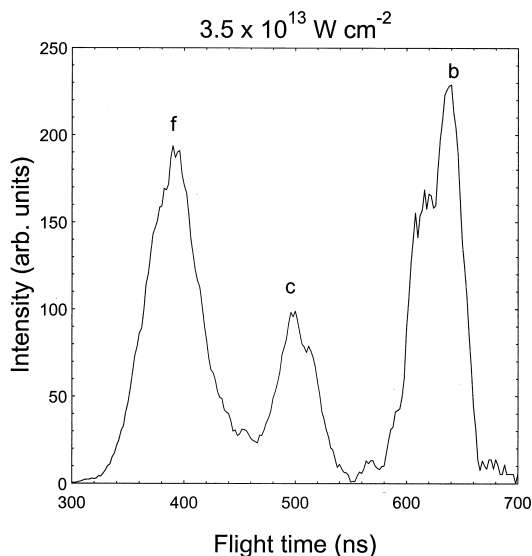


Fig. 2. A typical time-of-flight mass spectrum of D^+ fragment ions obtained upon dissociative ionization of D_2 molecules at a laser intensity of $4 \times 10^{13} \text{ W cm}^{-2}$. The direction of the laser polarization vector was parallel to the axis of the spectrometer in these measurements.

forward and backward direction, respectively. The central peak is due to lower-energy D^+ ions formed by processes (2) and (4); it starts to dominate the spectrum at lower values of laser intensity as contributions from double ionization diminish in importance.

A covariance map obtained when D_2 is exposed to 532 nm laser radiation at an intensity of $4 \times 10^{13} \text{ W cm}^{-2}$ is depicted in Fig. 3. This covariance map, and others in the present series of experiments (not shown), were constructed using a single TOF tube and a single detector. Under these conditions, the covariance $C(t_1, t_2) = C(t_2, t_1)$, and there is, therefore, an “autocorrelation” pair of signals which, in the case of a homonuclear molecule, give an appearance of coincidences between pairs of f - f and b - b peaks. For the sake of clarity, we present our covariance map in the form of a three-dimensional plot in which the autocorrelation features (that lie along the 45° line in the figure) have been subtracted. The two peaks shown in Fig. 3 are the proper time-correlated D^+ - D^+ ion pairs.

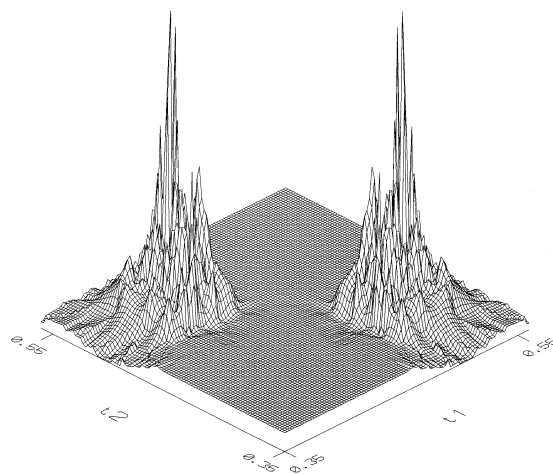


Fig. 3. A covariance map showing temporal correlations of D^+ ion pairs resulting from process (3). t_1 and t_2 are the times-of-flight (in microseconds) of D^+ ions and have the same range of values as the time axis depicted in Fig. 2. The peak intensity was 40 using the same units as in Fig. 2. The autocorrelation features (which lie along the diagonal) have been eliminated for the sake of clarity.

4.2. Angular distributions of D^+ fragments

Determinations of KER values were made at different directions of the laser polarization vector. In order to gain some insight into the angular distributions of D^+ ions, we measured the variation of D^+ intensity with laser polarization angle; Fig. 4 depicts the results in the form of a polar plot. These measurements were made using an extraction field of 60 V

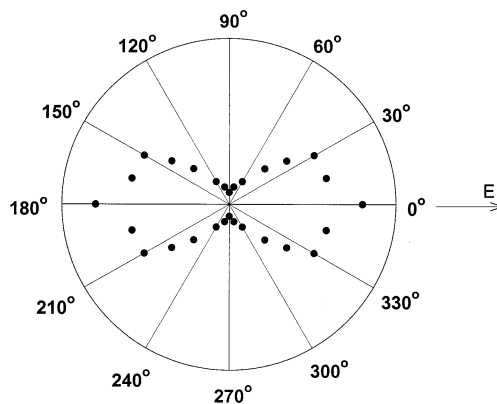


Fig. 4. A typical angular distribution of D^+ ions in the form of a polar plot. The laser polarization vector was along the 0° direction.

cm^{-1} . The radial distance in Fig. 4 represents the D^+ yield at different angles. It is clear that many more D^+ ions are produced in the 0° and 180° directions (where the laser polarization vector was parallel to the TOF axis) than under angular conditions when the polarization axis was orthogonal to the TOF axis. This type of angular distribution is consistent with the earlier illustrations of spatial alignment of diatomic molecules by Normand and co-workers [16]. We have attempted to gain further insight into the effect of the electrostatic field used to extract ions into our TOF spectrometer on the overall shape of the D^+ angular distribution in terms of an empirical parameter Δ which we define as

$$\Delta(\text{D}^+) = \frac{D_{\parallel}^+}{D_{\perp}^+}, \quad (8)$$

where D_{\parallel}^+ and D_{\perp}^+ are the ion intensities when the direction of the laser polarization vector is, respectively, 0° and 90° with respect to the axis of the TOF spectrometer. The value of $\Delta(\text{D}^+)$ is only an approximate measure of the extent of alignment of the D–D internuclear axis along the laser polarization axis as its measurement has been made using an electrostatic ion extraction field that might affect, to some extent, the pristine D^+ ion angular distribution function. However, we believe that it is still a useful parameter for low values of extraction field because our present measurements are made on D^+-D^+ ion pairs which are produced from dissociation of doubly charged D_2^{2+} ions. As discussed in the following section, the mean total kinetic energies released upon such dissociation are very large (~ 5 eV), with an energy distribution extending up to ~ 14 eV [16,39] and such large KER values may be expected to somewhat mitigate the distortions of angular distribution functions induced by the electrostatic extraction field. Values of $\Delta(\text{D}^+)$ were measured for different values of extraction field: at 50 V cm^{-1} it was ~ 11.2 whereas for 200 V cm^{-1} it was ~ 7.5 . Similar measurements were also made for D_2^+ ions. The value of $\Delta(\text{D}_2^+)$ (~ 1) remained invariant over the range of extraction fields from 50 to 200 V cm^{-1} .

We have also explored limitations that might be

imposed on the dynamics of spatial alignment processes by the very nature of the laser–molecule interaction. Specifically, we have addressed the question: is the field-induced alignment disturbed by effects induced by the space charge in the intense plasma that is created in the laser–molecule interaction zone? It has been shown by Delone and Krainov [44] in the context of the ionization of atoms in intense laser fields that space charge effects can give rise to significant distortions of the initial angular and energy distributions of both atomic ions and ejected electrons that are formed in the focal zone of an intense laser beam. Whereas manifestations of space charge effects have been unambiguously observed in electron motion (particularly in above-threshold ionization spectra [45]), the complex dynamics of ion motion has so far precluded corresponding observations in the ion channels. Space-charge saturation effects will arise from the number density of charged particles produced in the laser–molecule interaction. Specifically, such effects are determined by plasma parameters which, in turn, are directly affected by the gas number density, the laser intensity and the size of the laser–molecule interaction zone within which initial plasma formation occurs. We ensured that the focused laser spot size remained invariant in the course of our experiments, and we measured angular distributions and made KER determinations at a number of different gas target densities and laser intensities. Details of the results of experiments on the effect of space charge effects on angular distributions are presented elsewhere [27,28]; the angular distribution and KER results presented here were obtained under experimental conditions that ensured that they are essentially free of artifacts attributable to space charge effects.

4.3. Kinetic energies released upon D^+-D^+ ion-pair formation

If all the D_2 molecules in our experiment have their internuclear axes aligned along the direction of the laser polarization (which is arranged to be parallel to the TOF axis), the ion pairs produced in process (3) would initially either travel in the forward or the

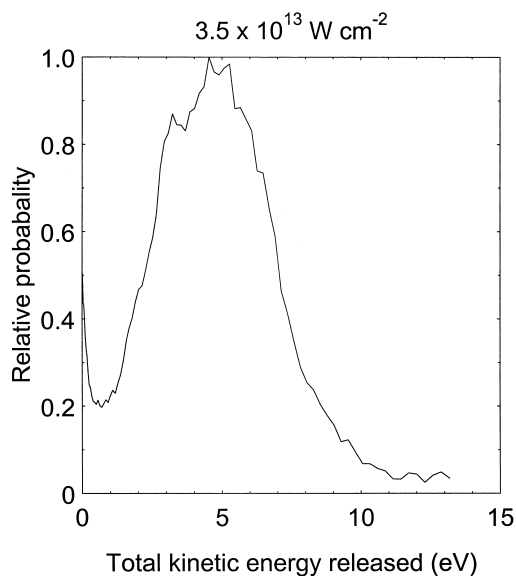


Fig. 5. Distribution of total kinetic energies released (KER) upon dissociative ionization of D_2 molecules at a laser intensity of $4 \times 10^{13} \text{ W cm}^{-2}$. These results are deduced from the TOF spectrum shown in Fig. 2. The kinetic energy of each D^+ fragment is half the total KER value.

backward direction with respect to the CEM. The latter set of ions, after initially traveling away from the TOF, would be reflected back by the electrostatic ion extraction field. The difference in time-of-flight between such forward and backward scattered fragments is $\Delta t = 2mv/(qE)$, where v is the velocity of the fragment, E is the electrostatic ion extraction field in the interaction region, q and m are, respectively, the charge and mass of the fragment. Measurement of the time difference between the forward and backward scattered fragment ion peaks in TOF spectra directly yields information on the average KER. By way of illustration we present in Fig. 5 the D^+D^+ total kinetic energy distribution function obtained from the TOF spectrum shown in Fig. 2. It comprises a low-energy (thermal to ~ 1 eV) contribution, and a substantial contribution from higher-energy ions; the most probable total KER value is ~ 5 eV, with the maximum total KER value extending up to ~ 14 eV.

Values of KER reflect the internuclear separation (r) at which dissociation of the multiply charged molecular precursor occurs. In the case of diatomic

molecules, measured KER distributions can be mapped to the internuclear separation as the potential energy function is usually well known, at least of the initial ground electronic state. Such mapping has, in the recent past, been used to provide evidence that KER values less than those expected from purely coulombic considerations are indicative of enhanced ionization (EI) at internuclear distances larger than equilibrium. EI of molecules in short, intense laser pulses at large critical internuclear separations, R_c , was initially discovered [46] in theoretical simulations of the ionization rates of H_2^+ ; ionization maxima observed in the range of R_c values 2–5 Å were initially interpreted in terms of electron localization effects brought on by large charge exchange radiative resonance couplings between the highest-occupied and lowest-unoccupied molecular orbitals. Theoretical interpretations of EI in terms of extensions of the field-ionization and barrier-suppression ionization models have also been successful [47]. Experimental confirmation of EI has since been obtained in a number of studies of diatomic molecules (see, for instance, [34,35]). The mean value of the total KER that is measured in our experiments leads us to deduce that H–H cleavage appears to occur at an internuclear separation that is approximately a factor of two larger than the equilibrium value for the ground electronic state of the H_2 molecule. This deduction is in consonance with the present understanding of EI processes in intense-field–molecule interactions.

Measurements of KER were made by us over a range of laser polarization angles. For the purposes of the present study, we focus attention on measurements of the time difference, Δt , between the forward and backward scattered D^+ ion pairs formed in process (3). We monitored changes in Δt as a function of laser polarization angle at a fixed value of laser intensity. If the D^+ KER value, at the given laser intensity, were independent of the polarization direction, a $[v \times \cos(\theta)]$ type of distribution would be expected for the time difference, where θ is the angle between the laser polarization vector and the TOF axis, and v is the mean velocity of D^+ ions. This assumes that all D_2 molecules in the interaction zone are perfectly aligned along the polarization direction,

in which case the D^+ signal would be maximum at $\theta = 0^\circ$ and zero at $\theta = 90^\circ$. This is in accord with conventional wisdom on photodissociation dynamics wherein the angular distribution of photofragment ions is expected to be given by a sum of even Legendre functions $P_{2j}(\cos \theta)$: $\sum_{j=1}^n \beta_{2j} P_{2j}(\cos \theta)$, where n represents the number of absorbed photons.

Although our measured angular distribution is very anisotropic, indicating that the D_2 precursors are aligned along the laser polarization vector, all D_2 molecules in the interaction zone are not expected to strictly align along the direction of the applied field. Let n be the fraction of molecules that are aligned along the polarization direction (this fraction would greatly depend on the polarizability of the molecule being studied, and also on the laser intensity and pulse duration). Due to the initial random orientation of the molecules, the orientation being at angles other than θ , say ϕ_i , there would be an additional contribution of $v \times \cos(\phi_i)$ to the angular distribution function. It should be noted here that $\phi_i \neq \theta$, and both vary from 0° to 90° . Let $P(\phi_i)$ represent the number of molecules aligned along any given angle ϕ_i . Thus for a given θ , the contribution to Δt from all the nonaligned molecules would be

$$b = a \sum_{\phi_i \neq \theta} P(\phi_i) \times \cos(\phi_i). \quad (9)$$

So, the time difference between the forward and backward scattered D^+ ions is $\Delta t = a \times [n \times |\cos(\theta)| + b]$, where $a = 2mv/(qE)$ is a measure of the mean velocity of the D^+ fragment ions. In the absence of laser-induced alignment, the contribution to Δt made by the nonaligned molecules would be independent of the direction of the laser polarization vector and dependent only on the acceptance angle of the TOF spectrometer. However, our experiments show that Δt does, indeed, vary with the direction of the laser polarization vector, indicating that dynamic alignment of D_2 is induced by the laser field. In the case of those molecules that do not become aligned but are, nevertheless, doubly ionized, the Δt value would, clearly, not show any dependence on the direction of the laser polarization vector.

The measured dependence of Δt on the laser

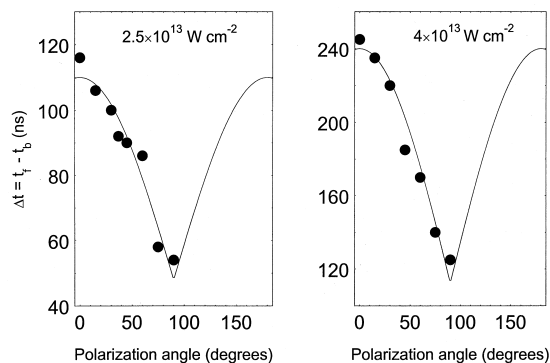


Fig. 6. Plot of the time difference between the forward- and backward-scattered D^+ as a function of the laser-field polarization direction, θ , with respect to the spectrometer axis, at two laser intensities. The solid line is the fit, $a \times [(1 - b)|\cos(\theta)| + b]$, to the experimental data.

polarization angle is depicted in Fig. 6 for two different laser intensities. In the absence of quantitative information on the initial spatial distribution of molecules in a direction other than θ , we have fitted our experimental data with a $[a(1 - b)|\cos(\theta)| + b]$ function. The parameter b , which is given by (8), does not directly yield the fraction of unaligned molecules, but provides an estimate of the lower limit for aligned molecules. Using several data sets of the type depicted in Fig. 6, we obtained in the course of our experiments a value of b which indicates that at least 53% of the D_2 molecules in the interaction zone are aligned in the field direction, over the range of laser intensities employed in the present experiments.

5. Summary

The prospect of trapping molecules and spatially aligning them opens horizons for a totally different class of “complete” gas-phase experiments, perhaps using ultrahigh resolution and high-precision spectrometry, and collisional techniques, which aim to probe dynamical properties of quantal state-selected molecules that are also spatially well characterized. Quantification of the extent of spatial alignment is clearly an important prerequisite before such progress is made. Such quantification has not been reported

previously, and no unambiguous methodology exists at present that offers a proper prescription for making such measurements.

The method that we have outlined here for estimating the degree of spatial alignment of molecules in intense laser fields might be of general utility, at least in the case of linear molecules. It is possible that our reported value of 53% may be apparatus dependent, and also dependent on experimental parameters like field strength, laser pulse duration and ambient gas pressure. Nevertheless, we believe that the data may be of general interest and may contribute to the development of better methodology for making proper measurements of the extent of spatial alignment of molecules in intense laser fields; our suggestion of laser-field-induced dication dissociation as a possible route for a new methodology has not been considered before.

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