Controlling the Branching Ratio of Photodissociation Using Aligned Molecules

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Using a sample of iodine molecules, aligned by a strong, linearly polarized laser pulse, we control the branching ratio of the I + I and I + I* photodissociation channels by a factor of 26. The control relies on selective photoexcitation of two potential curves that each correlate adiabatically with one of the product channels. The selectivity is achieved by irradiating the aligned molecules with light polarized parallel or perpendicular to the polarization axis of the alignment laser.

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Using lasers to control photoinduced processes in molecules and atoms is a subject of intense activity [1–3]. Of particular interest is controlling the outcome of photochemical reactions in which the photoexcited reactant molecules yield at least two distinct final products. Two main approaches to control, termed active and passive control, have been developed [1]. Active control utilizes the coherent properties of light to steer reactions into the desired products. This is performed in frequency resolved schemes as demonstrated by Gordon and co-workers [4] using quantum mechanical interference between three photon and one photon absorption in HI molecules to control whether the molecules are preferentially dissociated or ionized. Active control is also carried out in the time domain with tailored ultrashort laser pulses manipulating the outcome of the reaction. A recent experimental demonstration, reported by Gerber and co-workers [5], showed how the branching ratios of different organometallic photodissociation channels can be controlled with phase-shaped femtosecond laser pulses. Passive control relies on the ability to selectively excite an electronically excited state that is repulsive in the bond that one wants to break. The state selection is controlled by the wavelength of the exciting radiation and has been used to achieve selective bond breaking in CH_2IBr [6] and CH_3SH [7].

In this paper we demonstrate a control method that allows both state selectivity in photoexcitations and control of the branching ratio of photodissociation processes. The selective excitation is obtained by controlling the spatial orientation of the molecules with respect to the polarization of the exciting light so that either perpendicular transitions are enhanced and simultaneously parallel excitations suppressed or vice versa. The orientation of the molecules is controlled by a strong, nonresonant laser field since the interaction between the induced dipole moment of the molecules and the strong, linearly polarized laser field forces the molecules to align along the polarization axis [8–10]. We show how the branching ratio between two photodissociation channels can be controlled by irradiating the aligned molecules with light polarized either parallel or perpendicular to the polarization axis of the alignment laser provided that the two channels correlate adiabatically with two excited potential energy surfaces accessed through a parallel and a perpendicular transition, respectively.

For the first demonstration of our control method we choose a molecule and a photoexcitation energy that leads to dissociation via two different channels with approximately the same probability. Such a situation exists when I_2 molecules are irradiated by 485 nm light. The molecules are either excited to the B $^3\Pi\, 0_u^+$ state that dissociates into I + I*, or to the $^1\Pi\, 1_u^+$ state that dissociates into I + I (see Fig. 1), where I and I* denote iodine atoms in the $^2P_{3/2}$ and the $^2P_{1/2}$ states, respectively. The extinction coefficients for the two transitions are approximately equal at 485 nm [11], and the B $^3\Pi\, 0_u^+$ state is connected to the $X\ ^1\Sigma\, 0_g^+$ ground state with a parallel transition moment,

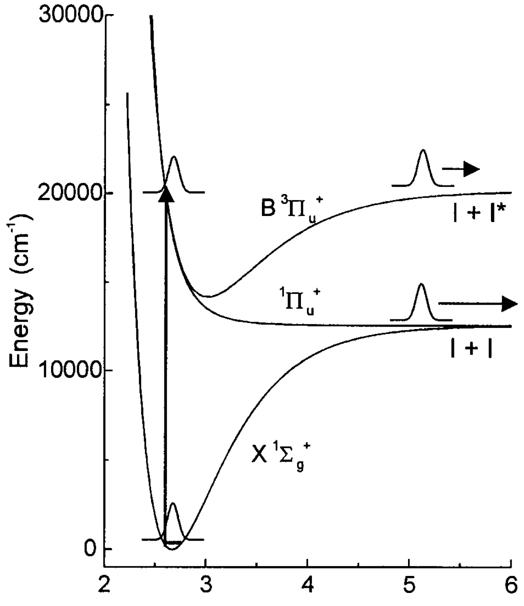

FIG. 1. Simplified potential energy diagram of I_2 showing the excitation of the B $^3\Pi\, 0_u^+$ state (parallel transition) leading to I + I* dissociation, and the excitation of the $^1\Pi\, 1_u^+$ state (perpendicular transition) leading to I + I dissociation.

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whereas the transition moment from the ground state to the $^1\Pi\, 1_u^+$ state is perpendicular [12]. Our aim is now to show that the branching ratio of the dissociation channels, $(\mathrm{I} + \mathrm{I})/(\mathrm{I} + \mathrm{I}^*)$, can be controllably varied over a broad range of values, i.e., be made much smaller as well as much larger than the natural value of 2 [13].

To carry out the experiment a pulsed supersonic beam, formed by expanding 1 Torr of I_2 gas in 4 bars of helium through a 0.5 mm nozzle [14], is crossed by three focused laser beams (more experimental details are given in Ref. [15]). The first laser beam originates from a pulsed single-longitudinal mode Nd:YAG laser ($\lambda = 1064$ nm). The 3.5 ns long pulses align the I_2 molecules along the laser polarization axis [9]. The second laser beam, used to photodissociate the molecules, comes from a femtosecond (fs) optical parametric amplifier. These "pump" pulses are $\sim$150 fs long with a peak intensity of $\sim 1.5 \times 10^{12}$ W/cm^2, and centered at 485 nm. The pump pulses are synchronized to the maximum intensity of the yttrium-aluminum-garnet (YAG) pulse to ensure that the I_2 molecules are dissociated when they are most strongly aligned [16]. To determine the production of the two different dissociation channels we measure the number of iodine atoms emerging with the energy characteristic of each of the two channels. Since our detector is sensitive only to ions, we ionize the photofragments without changing their direction or their kinetic energy. This is done by firing a second, intense fs laser "probe" pulse after the dissociation is complete. The probe pulses are 100 fs long with a peak intensity of $\sim 7 \times 10^{13}$ W/cm^2. They originate from a Ti-sapphire based regeneratively amplified fs laser system operating at 800 nm. The ionized fragments are accelerated by a static field towards a position sensitive ion detector mounted on-line with the molecular beam. The detector consists of a microsphere plate backed by a phosphor screen. Each ion detected leads to emission of a localized flash of light which is recorded by a CCD camera. Fast electronic gating of the CCD camera allows us to record mass and charge selected ion images.

Figure 2 shows the I^+ ion images when the molecules are irradiated with the pump pulses polarized parallel to [Fig. 2(a)], perpendicular to [Fig. 2(c)], or at an angle of 45° with [Fig. 2(b)] the fixed YAG polarization (horizontal in Fig. 2). The intensity of the YAG pulse is 7×10^{10} W/cm^2. In all three images the angular distribution of the I^+ ions is localized around the polarization direction of the YAG laser. This is a manifestation of the molecules being aligned by the YAG pulse along its electric field vector as reported previously [9]. Each ion image exhibits one or two pairs of radially narrow half rings with diameters 4.3 and 14.4 mm, and a more diffuse, radially broad, distribution of I^+ ions. The half rings result from those I_2 molecules that are photodissociated by the pump pulse and subsequently ionized by the probe pulse. The radially broad distribution originates from fragmentation of multiply charged molecular ions formed when the intense probe pulse interacts with those I_2 molecules that did not undergo excitation by the pump pulse [15]. The diameters of the inner and the outer pair of half rings correspond to kinetic energies of the I^+ fragments that identify the $d = 4.3$ mm half rings as the $\mathrm{I} + \mathrm{I}^*$ dissociation channel and the $d = 14.4$ mm half rings as the $\mathrm{I} + \mathrm{I}$ dissociation channel. For the parallel geometry the 4.4 mm half rings are very strong while the 14.4 mm half rings are nearly absent; i.e., photodissociation proceeds essentially only through the $\mathrm{I} + \mathrm{I}^*$ channel. For the perpendicular geometry the situation is reversed. Here, the 14.4 mm half rings become very intense, whereas the 4.3 mm half rings almost disappear showing that now the $\mathrm{I} + \mathrm{I}$ dissociation channel is strongly dominating. Finally, when the pump pulse is polarized at 45° with respect to the YAG polarization both pairs of half rings are present. This behavior demonstrates how laser induced alignment makes it possible to control the branching ratio between the $\mathrm{I} + \mathrm{I}^*$ and $\mathrm{I} + \mathrm{I}$ photodissociation channels.

To quantify the degree of control we measure the yield of the two dissociation channels at a series of angles, α, between the YAG polarization and the polarization of the

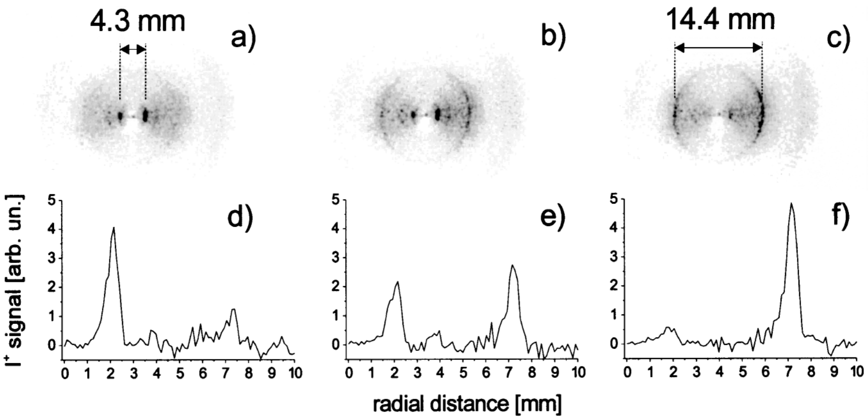

FIG. 2. Ion images, and the corresponding radial distributions of I^+ ions, resulting from photodissociation of aligned I_2 molecules. In all images the YAG polarization is horizontal. The angle α between the polarization of the pump pulse and the YAG polarization is (a) and (d): $\alpha = 0°$; (b) and (e): $\alpha = 45°$; (c) and (f): $\alpha = 90°$. Each ion image is accumulated over 3000 laser shots.

pump pulse. This is done in the following way. For each value of α an ion image is recorded and the radial distribution of I^+ ions is determined by an angular integration of the image. For each radial distribution recorded with all three laser pulses present we subtract the radial distribution of an ion image recorded with the pump pulse blocked [15]. Hereby, it is possible to isolate those ions that originate from the two dissociation channels. The resulting radial distributions for $\alpha = 0°$, 45°, and 90° [Figs. 2(d), 2(e), and 2(f)] are shown below the three ion images in Fig. 2. The area of each of the narrow peaks at radius $r = 2.15$ and 7.2 mm equals the yield of the $I + I^*$ and the $I + I$ dissociation channels, respectively. In Fig. 3 we show the results for α between 0° and 90°. The production of the $I + I^*$ channel decreases gradually while the production of the $I + I$ channel increases gradually as the angle is varied from 0° to 90°. This is consistent with the expectations of the parallel dissociation channel dominating when the molecules are aligned parallel to the polarization of the pump pulse and the perpendicular channel gradually taking over as the pump pulse polarization is changed towards an angle of 90° with the aligned molecules.

We also calculate the yield of the two dissociation channels for a sample of aligned molecules irradiated by a linearly polarized laser field at 485 nm. For that purpose we assume that the probability P of finding a molecule with an orientation (θ, φ) is [10]

$$P(\theta, \varphi) = N \exp\left(-\frac{\sin^2\theta}{2\sigma^2}\right), \tag{1}$$

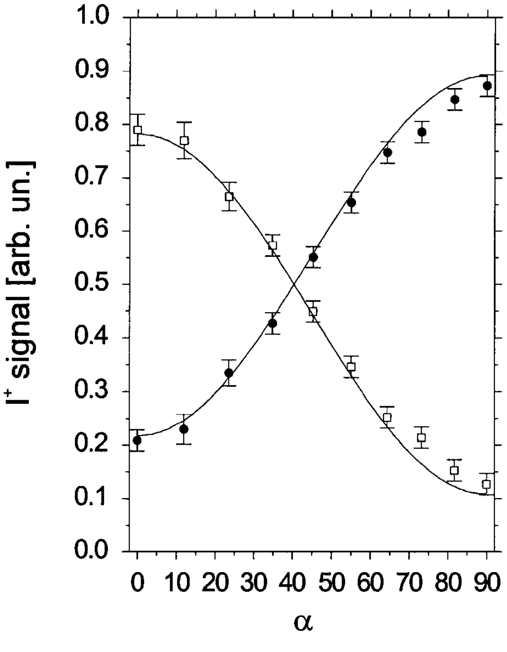

FIG. 3. The yield of the $I + I$ (filled circles) and the $I + I^*$ (open squares) dissociation channels as a function of the angle α between the polarizations of the YAG pulse and the pump pulse. The full curves represent the calculated yield of the two dissociation channels (see text).

where θ is the angle between the molecular axis and the YAG polarization, φ is the azimuthal angle, N is a normalization factor, and σ is the parameter describing the degree of alignment. The yield of the $I + I^*$ channel is found by calculating the expectation value of $\cos^2\beta$ using the probability distribution from Eq. (1), β being the angle between the polarization of the pump pulse and the molecular axis [17]. Similarly, the yield of the $I + I$ channel is determined by the expectation value of $\sin^2\beta$. As seen in Fig. 3 good agreement between the experimental results and the calculations (full curve) is obtained for $\sigma = 0.30$. For comparison, σ is determined from the angular distribution of the perpendicular $I + I$ channel in the ion image where $\alpha = 90°$ [9]. This yields $\sigma = 0.30 \pm 0.02$, in excellent agreement with the σ value used in the calculations shown in Fig. 3.

The branching ratio between the two dissociation channels reaches its extreme values at $\alpha = 0°$ and 90°:

$$\frac{I + I}{I + I^*}(\alpha = 0°) = 0.27 \pm 0.02$$

$$\frac{I + I}{I + I^*}(\alpha = 90°) = 6.9 \pm 0.5 .$$

Stronger control of the branching ratio, i.e., lower value at $\alpha = 0°$ and higher value at $\alpha = 90°$, requires a more aligned sample of molecules. This can be obtained by either increasing the intensity of the YAG pulse, I_{YAG}, or by lowering the rotational temperature of the molecules. Unfortunately, increasing I_{YAG} also increases the probability of the dissociating molecules absorbing additional photons from the YAG pulse. In particular, at $I_{\mathrm{YAG}} > 2 \times 10^{11}\ \mathrm{W/cm^2}$ we observe that a significant fraction of the molecules excited to either the B $^3\Pi\, 0_u^+$ or the $^1\Pi\, 1_u^+$ state are further excited to a higher lying molecular state, by absorption of a YAG photon. This leads to dissociation into two I^* atoms, and we therefore lose both state selectivity and the degree of dissociation control at too high intensities of the YAG pulse. Although it is possible that more infrared alignment pulses, for instance, CO_2 laser pulses, couple the molecular electronic states more weakly, and therefore allow use of higher intensities, the best approach to a stronger control is a lowering of the rotational temperature.

The spatial orientation of molecules can also be controlled by the application of an electric hexapole field [18,19] or a strong static electric field [19,20], the latter method often termed the brute force method. These techniques arrange polar molecules in a head-versus-tail order (orientation) and are therefore particularly suited for studies of orientational effects in bimolecular reactions. Recently, Kong and co-workers [21] showed that brute force oriented molecules also allow for some selectivity in photochemical processes. They observed that the yield of I^* atoms can be enhanced by 30% when oriented ICN molecules are photodissociated by light polarized parallel rather than perpendicular to the orientation field. In general, brute force oriented molecules are much less angularly confined than laser aligned molecules and a much higher degree of selectivity in photoinduced reactions can therefore be achieved with the laser induced alignment method. Furthermore, laser induced alignment does not require a permanent dipole moment of the molecules so the technique allows control of photoinduced processes in both polar and nonpolar molecules.

State selective photoexcitation of aligned molecules should be applicable to a large number of molecules. The degree to which the branching ratio of different photodissociation channels can be controlled depends on the specific molecular system. In those cases where the excited states correlate adiabatically with the final product states a control similar to that demonstrated for I_2 should be possible. In the more general case where nonadiabatic effects [22], such as curve crossings, become important, the degree of control will be reduced. Still, the selective excitation of a subset of potential energy surfaces in combination with the fixed molecular geometry could provide new insight in studies of photochemical processes in large molecules.

In conclusion, high selectivity in photoexcitation of laser aligned molecules can be achieved by controlling the angle between the polarization of the alignment laser and the polarization of the exciting light. This was used to control the branching ratio of the $\mathrm{I} + \mathrm{I}$ and $\mathrm{I} + \mathrm{I}^*$ photodissociation channels by a factor of 26. Aligned molecules might also prove to be useful for other control methods of chemical reactions. Most active (coherent) control schemes involve resonant transitions induced by linearly polarized light. Thus, for a sample of randomly oriented molecules the coherent control will be effective only for those molecules where the direction of their rotational angular momentum falls within a certain range. By contrast, for a sample of aligned molecules the active control can be extended to all molecules within the focal volume of the alignment laser. In addition, aligned molecules offer an alternative method to selective excitation of parallel type or perpendicular type vibrational modes of polyatomic molecules. This might have applications for that part of mode selective chemistry where the outcome of bimolecular reactions is controlled by the initial vibrational modes of the reagents [23].

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