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Femtosecond observation of a concerted chemical reaction

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Abstract

A time-resolved study is presented of the photodissociation of methylene iodide (CH_2I_2) to produce a carbene diradical and molecular iodine. This reaction pathway occurs only at high excitation energies (vacuum ultraviolet) and is initiated in this case by a two-photon transition at $\lambda_{\text{equivalent}} = 155$ nm. Discrimination over competing pathways is achieved by wavelength-selective monitoring of the nascent I_2 dynamics. The results show clear evidence that breakage of the two carbon–iodine bonds and formation of the iodine–iodine bond is concerted. The reaction takes place in less than 100 fs and is characterized by coherent vibrational motion in the iodine molecule.

1. Introduction

Concerted chemical and biochemical processes have been of great interest, particularly since the publication of Woodward and Hoffmann's work on pericyclic reactions [1]. A concerted reaction is defined as one for which multiple primitive changes (bond formation, charge transfer, etc.) occur in a single kinetic step [1–4]. In practice this means that a reaction is considered to be concerted if there is no evidence of intermediate stages, so that classification necessarily depends on the sensitivity of the method of choice to short-lived intermediates. A reaction that is rapid compared to the detection method used may thus be considered to be concerted. Molecular beam techniques have been used to determine gas phase reaction mechanisms[5]; these methods have a temporal resolution comparable to the rotational period of a molecule ($\approx 10^{-12}$ s), and have been useful in determining the concertedness of chemical reactions by analysis of the momentum and angular distribution of the products [6–8].

The use of femtosecond transition state spectroscopy (FTS) [9] to detect the presence of reaction intermediates has been introduced by Zewail and co-workers. Their time-resolved experiments on the α-cleavage reaction of acetone and on decarbonylation of cyclopentanone, for example, have shown that both reactions proceed by a stepwise (non-concerted) mechanism [10,11].

The motivation for this experiment was to observe a concerted chemical reaction on the time scale of molecular vibrations and to study the dynamics resulting from this type of mechanism. We chose to study the photochemical reaction in which methylene iodide produces a carbene radical and molecular iodine:

$$CH_2I_2 + h\nu_{\text{VUV}} \rightarrow CH_2\left(X\,^3B_1\right) + I_2\left(D'\,^3\Pi_{2g}\right). \tag{1}$$

This reaction has been previously studied without time resolution [12–16]. Fig. 1 schematically illustrates the most likely pathways for photodissociation

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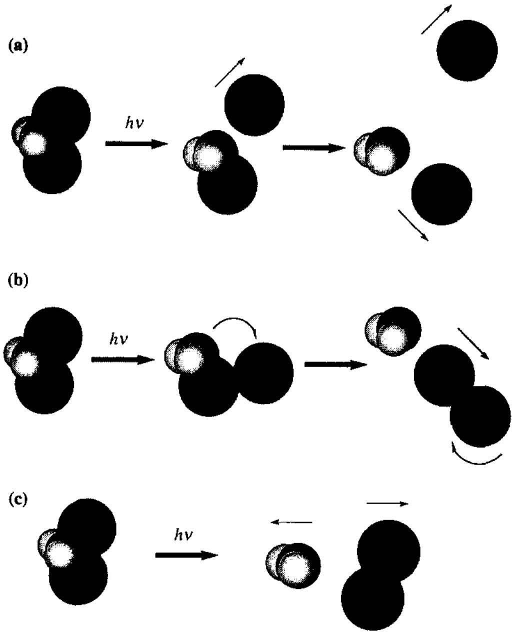


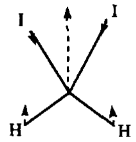
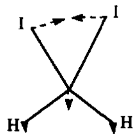
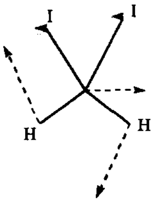
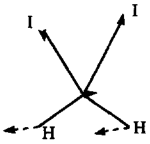
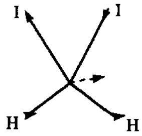
Fig. 1. Schematic of the reaction mechanisms for photodissociation of methylene iodide. All fragments are drawn relative to carbene-fixed coordinates. (a) Stepwise (sequential) dissociation; the first iodine atom released has time to move away from the molecular fragment before the second carbon–iodine bond breaks. Molecular iodine is formed later, by three-body collisions. (b) Mechanism in which the first carbon–iodine bond breaks and an iodine–iodine bond is formed while the second iodine is still part of the molecule, thus forming an ylide. This stage is concerted; subsequent breaking of the second carbon–iodine bond completes the reaction. (c) Concerted bond breaking and formation process; breaking of the two carbon–iodine bonds is simultaneous with formation of an iodine–iodine bond. This mechanism would be expected to produce a molecular iodine product with a large degree of vibrational coherence (see text).

of CH_2I_2. In (a) the two carbon–iodine bonds break sequentially and I_2 forms later by a collisional process; this is the major channel at lower excitation energies [17–21] and is likely to be enhanced by excitation of the asymmetric C–I stretch ν_9. Pathway (b) represents ylide formation followed by elimination of molecular iodine. This process is facilitated by excitation of the CI_2 rocking mode ν_8 of CH_2I_2. In (c) the two carbon–iodine bonds are broken simultaneously with formation of the iodine–iodine bond; excitation of ν_3 and ν_4, the symmetric C–I stretch and the I–C–I bending vibration, respectively, would be expected to favor process (c) (see Table 1) [22].

2. Experimental

The experiments reported here were performed using FTS [9]; the femtosecond laser system used was a home-built colliding pulse mode-locked laser (CPM), pumped by an Ar^+ laser. The output from the CPM was amplified and recompressed, to produce transform limited 60 fs pulses centered at 620 nm, having an energy of 0.5 mJ per pulse and a repetition rate of 30 Hz. The pulses were then split by a Mach–Zhender interferometer arrangement with one fixed and one adjustable arm; 310 nm pulses were generated in the fixed arm by frequency doubling using a 0.1 mm KDP crystal. Pump and probe pulses were collinearly recombined and focused (200 mm) in the sample cell. LIF was detected perpendic-

Table 1
Selected vibrational modes of CH_2I_2 (see Ref. [31])

Mode	Energy (cm^{-1})	Symmetry	
ν_3	1351	a_1	
ν_4	128	a_1	
ν_7	717	b_2	
ν_8	1107	b_1	
ν_9	572	b_1	

ular to the direction of the laser. The signal obtained at each time delay between the pump and probe pulses was averaged for 10 laser shots. Typical transients contained data from 200 different time delays and were averages of 100 scans.

The sample (99% purity) was introduced to a quartz cell and outgassed to 10^{-5} Torr at liquid nitrogen temperature. The purity of the sample was checked using FT-IR and GC–MS. Experiments were carried out at room temperature, at a vapor pressure of 1 Torr and in the presence of iodine scavenging agents (copper and sodium thiosulfate) to ensure that the signal originates from nascent iodine only.

The laser pulse (pump) at 310 nm initiates the reaction by two-photon excitation of methylene iodide to a high-energy electronic state. The molecule then dissociates, producing CH_2 in the $X(^3B_1)$ state and I_2 in the $D'(^3\Pi_{2g})$ state. Selective monitoring of the reaction dynamics of this dissociative pathway is accomplished by exclusive detection of the D′ state fluorescence. Subsequent dynamics of the I_2 product are probed by depletion of the D′ state population using a second pulse (620 nm). As the molecules vibrate, the depletion efficiency varies as a function of time delay between pump and probe lasers. However, for changes to be observed on a macroscopic scale, the nascent I_2 molecules must vibrate in phase.

If the I_2 molecules were formed at the same time, i.e. if the reaction was concerted, the short duration of the laser pulses ensures that a modulation of fluorescence intensity would be observed as the Franck–Condon factors for the depletion transition vary. Coherent vibrational motion in the I_2 product would not, however, be observed from the product of pathway (a) (sequential dissociation followed by collisional association); in that case there would be a statistical distribution of vibrational energy and phase. Sweeping the time delay between pump and probe pulses thus yields a transient that reflects the temporal evolution of the reaction and that of the nascent I_2.

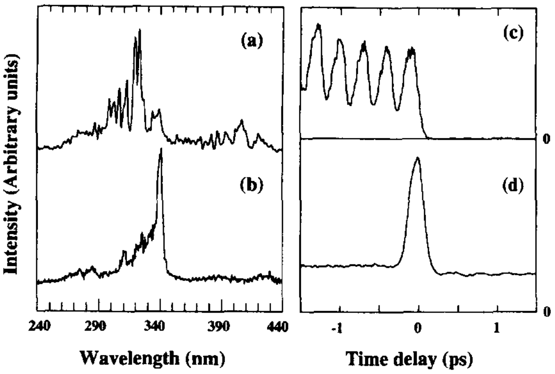


Fig. 2. (a and b) Dispersed fluorescence spectra obtained by excitation of I_2 (a, 0.25 Torr) and CH_2I_2 (b, 1 Torr) by pump and probe lasers overlapped in time. The I_2 spectrum observed in (a) is characteristic of the E → B and f → B transitions [23,24]; (b) is characteristic of the D′ → A′ transition [25–27]. The spectra are scaled; the signal at 340 nm from the I_2 cell is comparable to the signal from the CH_2I_2 cell (c and d). Time-resolved data from I_2 (c) and CH_2I_2 (d) vapor cells. Both were collected at 340 nm. Negative time corresponds in both cases to the 620 nm pulse arriving before the 310 nm pulse. (c) Shows oscillations of the B state of I_2, produced by excitation from the ground state and monitored by f → B fluorescence [28]. (d) Shows the transient obtained from the CH_2I_2 cell; fluorescence from the D′ state is depleted by the 620 nm pulse at positive times. The large feature at time zero is due to a cooperative multiphoton effect (see text).

3. Results and discussion

In order to ascertain that the observed signal was not produced by background iodine, the dispersed fluorescence spectrum and the time resolved dynamics from the CH_2I_2 cell were compared with data from an iodine vapor cell under similar experimental conditions (Fig. 2). The I_2 cell yielded a spectrum characteristic of the $f(^3\Pi_{0g}) \to B(^3\Pi_{0u})$ and $E(^3\Pi_{0g}) \to B(^3\Pi_{0u})$ transitions (Fig. 2a) [23,24]. The spectrum from the CH_2I_2 cell, however, is quite different (Fig. 2b) and can be assigned to the I_2 $D'(^3\Pi_{2g}) \to A'(^3\Pi_{2u})$ transition [25–27]; the $\Delta\Omega = 0$ selection rule makes the D′ state optically inaccessible from molecular iodine in the ground state. The magnitude of the signal at 340 nm from each cell is approximately the same. Clearly, the contribution of background I_2 to the signal from the CH_2I_2 cell is insignificant. The time-resolved dynamics obtained from each cell were also completely different. For the I_2 cell at negative times (620 nm pulse arriving first), vibrational dynamics of the B state as demonstrated by Dantus et al. [28] were obtained (Fig. 2c). No signal was detected at positive times. The CH_2I_2 transient, on the other hand, shows a featureless signal at negative times followed by an intense feature at time zero (when pump and probe lasers

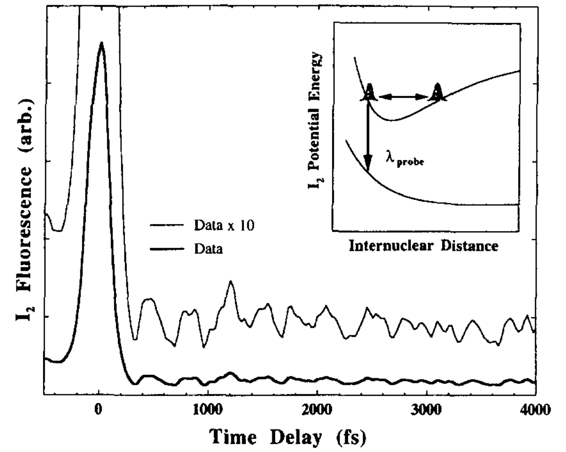


Fig. 3. FTS transient of CH_2I_2 photolysis. Fluorescence of the I_2 product was detected at 341 nm. Negative time corresponds to probe (620 nm) pulse arriving before pump (310 nm) pulse; depletion of the signal can be observed at positive times. Vibrational oscillations of molecular iodine are also visible on this scan (see text). The large signal at time zero is due to multiphoton excitation. The insert shows a schematic of the depletion process from I_2 $D'(^3\Pi_{2g})$. Depletion efficiency is at a maximum when the wavepacket is at the inner turning point, as shown.

coincide in time). At positive times a depletion of the original signal and some vibrational dynamics are observed. From the differences in the frequency- and time-resolved data we conclude that our CH_2I_2 results are free of I_2 contamination.

The transient shown in Fig. 3 was obtained by detecting the $D' \rightarrow A'$ fluorescence from the nascent iodine molecules at 341 nm as a function of delay time between excitation and probe lasers. The feature observed at zero time delay represents an excitation process in which the molecule absorbs one 620 nm and two 310 nm photons, which is equivalent to excitation by a single photon at 124 nm. Because excitation of CH_2I_2 with two 310 nm photons is just below the thermodynamic threshold for production of CH_2 in the X state and I_2 in the D′ state, the yield of I_2 was found to be an order of magnitude greater in the time zero region due to the additional energy provided by the 620 nm photon. This observation is consistent with previous measurements obtained using a hydrogen discharge lamp scanned from 110 to 135 nm [14]. Furthermore, the enhancement is greatest when the 620 nm laser is polarized parallel to the excitation laser, consistent with a cooperative process. This has been confirmed by a three-beam $(620 + 310^2)/620$ experiment [29]. Since time zero enhancement is feasible only for as long as the transition state exists, an upper limit for the dissociation time can be established. Based on the time it takes for the time zero signal to fall to half of its maximum value (see Fig. 3) [30], we estimate that fragment separation occurs in less than 100 fs.

At positive times, a modulation in intensity as a function of time delay can be observed. This is the most significant feature of these data and is caused by coherent vibrational motion of the molecular iodine products (as discussed above). To observe coherence the products must be formed within a very short time of each other (less than the vibrational period of the free product). Since a fragment separation time of ≤ 100 fs can be established for this reaction (vide supra), we would therefore expect to be able to see oscillations of this type. Analysis of the transient was facilitated by Fourier transform of the time-resolved signal; the resulting frequencies are consistent with vibrational energy levels of the D′ state (see Fig. 4) [25]. The phase of the depletion indicates that the probing process selectively depletes those iodine molecules which are found at the inner turning point in their vibration, where the Franck–Condon overlap is greatest (see Fig. 4 insert). The transients at positive times were best modelled by a bimodal distribution of D′ vibrational popula-

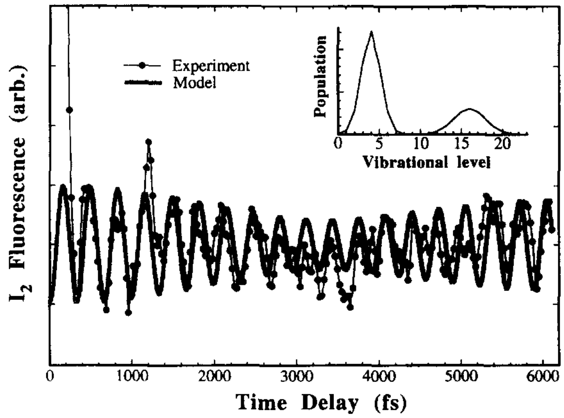


Fig. 4. Fourier transform and fit to vibrational oscillations seen in the temporal data (Fig. 3). The oscillations were found to correspond best to a bimodal distribution of vibrational energy levels, centered at $v' = 4$ and $v' = 16$ as shown. This may indicate that two different processes are producing I_2. The phase of these oscillations is consistent with a depletion of the fluorescent state, as expected.

tions comprised of two Gaussian functions centered at $v' = 4$ and $v' = 16$ with a FWHM of 3 and 4 quanta respectively, as shown in Fig. 4 (insert). We believe that the observed distribution indicates that I_2 is being produced by two different processes.

Since stepwise photodissociation (Fig. 1a) can be ruled out as a source of coherently vibrating I_2 molecules, the processes shown in Fig. 1b and c are the most likely mechanisms. Synchronous dissociation (Fig. 1c) is probably facilitated by thermal population of the I–C–I bend ν_4, which is substantial for a fraction of the parent molecules (46% have two or more quanta in this mode). The difference in energy between the populations centered at $v' = 4$ and $v' = 16$ of the D′ state of I_2 is estimated to be 1200 ± 200 cm^{-1}. Within this energy range we find three possible vibrational modes and combinations: the CI_2 rocking mode ν_8, $\nu_2 + \nu_7$, a combination of the H–C–H bend and the CH_2 rock, and $\nu_4 + \nu_8$, a combination of the I–C–I bend and the CI_2 rock (see Table 1) [31]. Because the distribution of product energies is bimodal it is reasonable to suppose that some of the products arise from parent molecules with a quantum of excitation in one of these modes. Note that two out of three of these possibilities favor mechanism (b), ylide formation. We therefore conclude that the dominant mechanism is represented schematically in Fig. 1c (symmetric elimination of I_2), and that there is also a significant contribution ($\approx 30\%$) from pathway (b). The reason why we are able to resolve these two pathways is that the experiments are carried out just below the thermodynamic threshold of the reaction, making enhancement due to parent vibrational excitation more significant. When the experiment was performed at $\lambda_{\text{equivalent}} = 124$ nm a distinct vibrational distribution was not observed [29]. The products of pathway (b) would be expected to exhibit a greater degree of rotational excitation than those of mechanism (c). Anisotropy data were collected to establish the average angular momentum of the products. Unfortunately, the sensitivity of the time zero signal to the relative polarization of pump and probe lasers prevents us from extracting this information.

In conclusion, we report the observation of a concerted chemical reaction on the time scale of molecular vibrations. The results presented here demonstrate vibrational coherence resulting from the concerted elimination of molecular iodine on photolysis of CH_2I_2. Observation of rotational excitation in the products would help to further resolve the pathway of the reaction. It would be useful to extend the current study to dihalogen analogs of methylene iodide in order to more clearly resolve the processes occurring at the transition state. Application of this type of study to other reactions would also be of interest; when the excitation laser is at the thermodynamic threshold of a concerted reaction, coherent motion of the products should be observed. Coherence in the product channel, observed first for the $HgI_2 \rightarrow HgI + I$ reaction [32], is now common in the gas, liquid and solid phases and in biological systems.

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