

# Femtosecond multichannel photodissociation dynamics of CH<sub>3</sub>I from the A band by velocity map imaging

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(Received 20 October 2006; accepted 30 November 2006; published online 8 January 2007)

The reaction times of several well-defined channels of the C–I bond rupture of methyl iodide from the A band, which involves nonadiabatic dynamics yielding ground state I(<sup>2</sup>P<sub>3/2</sub>) and spin-orbit excited I\*(<sup>2</sup>P<sub>1/2</sub>) and ground and vibrationally excited CH<sub>3</sub> fragments, have been measured by a combination of a femtosecond laser pump-probe scheme and velocity map imaging techniques using resonant detection of ground state CH<sub>3</sub> fragments. The reaction times found for the different channels studied are directly related with the nonadiabatic nature of this multidimensional photodissociation reaction. © 2007 American Institute of Physics. [DOI: 10.1063/1.2426332]

The study of chemical transformations in real time using ultrashort laser pulses is the aim of femtochemistry.<sup>1,2</sup> Since the late 1980s, a significant number of studies have dealt with time resolved molecular dynamics in systems of increasing complexity (for excellent reviews and reports see, for instance, Refs. 2–14). However, some basic issues concerning the real time dynamics of simple systems have remained elusive. New insight on the detailed mechanisms in these systems can be obtained by the combination of state-of-the-art femtosecond laser systems and detection techniques.

Ultrafast reaction dynamics has been probed by a large variety of detection techniques,<sup>2–4</sup> including laser induced fluorescence, photoelectron spectroscopy, and time-of-flight mass spectrometry, among others. Multiphoton ionization with time-of-flight mass spectrometry presents a number of advantages over other probe methods: Mass resolution permits the direct identification of reaction species and intermediates, and the detection of ions is experimentally straightforward. Zewail and co-workers developed femtosecond time-resolved kinetic energy time-of-flight (KETOF) mass spectrometry using fragment resonant detection to exploit the temporal, velocity, angular, and state dynamics and studied a large variety of uni- and bimolecular reactions in real time.<sup>3</sup> More recently, velocity map imaging<sup>15,16</sup> has been shown to be a powerful technique when combined with femtosecond laser pulses to study the real time dynamics of complex systems,<sup>4,9,17–19</sup> including the use of photoelectron spectroscopy<sup>4,20</sup> and photoion-photoelectron coincidence techniques.<sup>4,6,7,20</sup>

In the present work, we have studied the multichannel photodissociation dynamics of CH<sub>3</sub>I from the A band in real time by combining the velocity map imaging technique,<sup>15,16</sup> which provides selectivity at the detection end, and the use of tunable femtosecond laser radiation, which provides selec-

tivity and resonant enhancement at the probe end.<sup>3,9,21,22</sup> No other polyatomic system has been the subject of as much investigation as CH<sub>3</sub>I. The relatively low number of atoms in the molecule, combined with the richness and complexity of an apparently simple dissociation process, has made it a benchmark where a variety of experimental and theoretical techniques have been tested over more than two decades (see, for instance, Refs. 3, 16, and 23–28, and references therein). Dissociation of CH<sub>3</sub>I in the near UV proceeds via excitation in the A band involving three optically allowed transitions: two weak perpendicular transitions to the <sup>3</sup>Q<sub>1</sub> and <sup>1</sup>Q<sub>1</sub> states that correlate to ground state I(<sup>2</sup>P<sub>3/2</sub>) and a strong parallel transition to the <sup>3</sup>Q<sub>0</sub> state that correlates to spin-orbit excited I\*(<sup>2</sup>P<sub>1/2</sub>). Most of the absorption can be attributed to the <sup>3</sup>Q<sub>0</sub> state, and the I(<sup>2</sup>P<sub>3/2</sub>) fragment observed in the experiments is the result of a nonadiabatic transition at the conical intersection between the <sup>3</sup>Q<sub>0</sub> and <sup>1</sup>Q<sub>1</sub> states (see Fig. 1).

CH<sub>3</sub>I photodissociation was the first system to be studied by ion imaging.<sup>29</sup> Comprehensive velocity map imaging experiments of the A band photodissociation of CH<sub>3</sub>I have been carried out with nanosecond lasers<sup>27,28</sup> and its femtosecond fragmentation has been recently explored as a probe of molecular alignment.<sup>30</sup> The presence of the conical intersection and the influence of fragment vibration on the dynamics makes the multidimensional A-band dissociation of CH<sub>3</sub>I the ultimate candidate for real-time studies. However, experiments using femtosecond laser pulses have been scarce and mostly concerned with Rydberg states.<sup>31,32</sup> In a seminal paper published in 1998, Zewail and co-workers<sup>3</sup> managed to clock the reaction time in the A-band photodissociation of CH<sub>3</sub>I at 277 nm excitation by using gated time-resolved KETOF mass spectrometry. In these experiments, resonant detection of the I(<sup>2</sup>P<sub>3/2</sub>)/I\*(<sup>2</sup>P<sub>1/2</sub>) fragment was carried out allowing the clocking of the reaction which turned out to be as fast as 125 fs.

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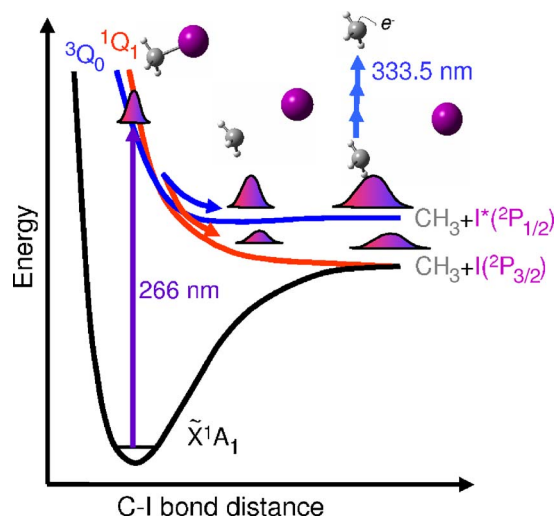


FIG. 1. (Color online) Schematic representation of the relevant potential energy curves along the C–I bond representing the A band photodissociation of CH<sub>3</sub>I. A wave packet on the <sup>3</sup>Q<sub>0</sub> potential curve is produced by the pump (266 nm) femtosecond pulse. Most of the wave packet evolves adiabatically along the <sup>3</sup>Q<sub>0</sub> surface correlating to CH<sub>3</sub>+I\*(<sup>2</sup>P<sub>1/2</sub>), but part of it leaks nonadiabatically to the <sup>1</sup>Q<sub>1</sub> surface correlating to the CH<sub>3</sub>+I(<sup>2</sup>P<sub>3/2</sub>). Clocking of the different reaction channels is carried out by a time-delayed probe (333.5 nm) femtosecond pulse producing the 2+1 REMPI of ground state CH<sub>3</sub> fragment.

In the present work, we have been able to clock different channels of the A-band photodissociation of CH<sub>3</sub>I. Each channel is tagged by the combination of resonant multiphoton ionization of the CH<sub>3</sub> fragment and velocity-resolved detection. We initiate the reaction by a femtosecond pump pulse at 266 nm as sketched in Fig. 1. Once the wave packet is formed in the <sup>3</sup>Q<sub>0</sub> potential surface, the dynamics is probed by a time-delayed femtosecond pulse centered at 333.5 nm, which ionizes the ground-state CH<sub>3</sub> fragments by 2+1 resonance enhanced multiphoton ionization (REMPI) centered on the Q branch of the  $3p_z(^2A_2'' \leftarrow ^2A_2'')$  0<sub>0</sub><sup>0</sup> transition. Interestingly, the broadband nature of the femtosecond pulse gives us the possibility of also probing CH<sub>3</sub> fragments with one quantum in the  $\nu_1$  stretching mode (1<sub>1</sub><sup>1</sup>). Thus, we simultaneously record the appearance of vibrationally excited CH<sub>3</sub> together with vibrationless CH<sub>3</sub> correlating with I(<sup>2</sup>P<sub>3/2</sub>) or I\*(<sup>2</sup>P<sub>1/2</sub>) in a single experiment.

A supersonic molecular beam of CH<sub>3</sub>I seeded in He was produced by a homemade 1 kHz piezoelectric valve.<sup>33</sup> The skimmed molecular beam entered through the repeller plate of an ion lens system working in velocity mapping configuration.<sup>15</sup> Cold CH<sub>3</sub>I molecules were excited with a femtosecond pump pulse at 266 nm obtained by frequency tripling the fundamental of a 1 kHz Ti:sapphire amplified laser system (80 fs, 1 mJ) and the CH<sub>3</sub> fragments were probed with a time-delayed femtosecond pulse at 333.5 nm produced by frequency quadrupling the signal pulse of an optical parametric amplifier (OPA). Pump and probe pulse energies were  $\approx 1$  and  $\approx 3$   $\mu$ J, respectively, with a bandwidth of  $\approx 3$  nm full-width-half-maximum (FWHM). Both pulses were recombined and focussed into the molecular beam. The intensities of the pump and probe lasers in the interaction region are estimated to be 10<sup>11</sup> W/cm<sup>2</sup>. The polarization of the pump and probe beams was set parallel to the detector

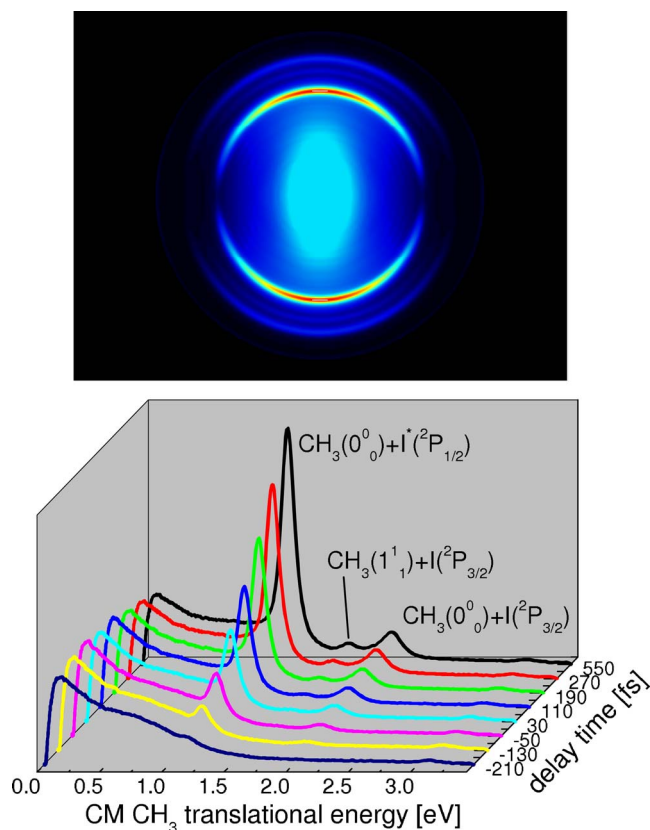


FIG. 2. (Color online) (a) Abel inverted CH<sub>3</sub><sup>+</sup> image at 1 ps pump-probe delay obtained from the raw image by using the pBasex software (Ref. 35). The inner, most intense ring, and the outermost ring correspond, respectively, to vibrationless CH<sub>3</sub>(0<sub>0</sub><sup>0</sup>) formed in correlation with spin-orbit excited I\*(<sup>2</sup>P<sub>1/2</sub>) and ground state I(<sup>2</sup>P<sub>3/2</sub>) fragments. The middle ring corresponds to the channel yielding symmetric stretch mode excited CH<sub>3</sub>(1<sub>1</sub><sup>1</sup>) in correlation with I(<sup>2</sup>P<sub>3/2</sub>) fragment. (b) Center-of-mass kinetic energy distributions of CH<sub>3</sub> fragments as a function of the pump-probe delay time.

face, which consists of a dual microchannel plate (MCP) and a phosphor screen. Mass-selected detection was achieved by gating the gain in the front MCP plate. The 2D images on the phosphor screen were recorded by a CCD camera. Raw images were acquired automatically for series of pump-probe delay times and were Abel inverted<sup>34</sup> using the pBasex method.<sup>35</sup> Both the time overlap and the cross-correlation of the pump and probe pulses were obtained by measuring *in situ* the transient rise of the *N,N*-diethylaniline parent ion by 1+1' REMPI following the procedure described in Ref. 3. Typical cross-correlations were 280 $\pm$ 20 fs FWHM.

Figure 2(a) shows an Abel inverted CH<sub>3</sub><sup>+</sup> image measured at a delay time of 1 ps between the dissociating and the probe laser pulses. Three distinct rings are clear in the image. The outer and inner rings correspond to ionization of vibrationless CH<sub>3</sub>(0<sub>0</sub><sup>0</sup>) correlating respectively with the formation of I(<sup>2</sup>P<sub>3/2</sub>) and I\*(<sup>2</sup>P<sub>1/2</sub>).<sup>27,28</sup> The weaker middle ring is assigned to the production of vibrationally excited CH<sub>3</sub> with one quantum in the  $\nu_1$  symmetric stretch (1<sub>1</sub><sup>1</sup> band), which correlates with I(<sup>2</sup>P<sub>3/2</sub>).<sup>28</sup> The central part of the image corresponds to low-speed ions formed in MPI processes due to both the pump and probe lasers. No rings appear in the images if the probe laser wavelength is tuned off the Q branch of the CH<sub>3</sub>(0<sub>0</sub><sup>0</sup>). Translational energy and angular distributions at different delay times can be extracted from the Abel

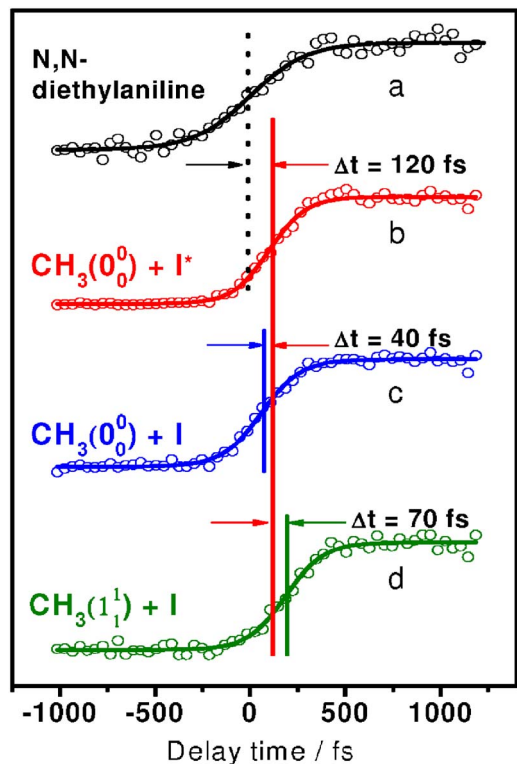


FIG. 3. (Color online) (a) *N,N*-diethylaniline parent ion transient measured *in situ* by 1+1' REMPI (Ref. 3). This transient sets the time zero for our clock. (b) CH<sub>3</sub> transient corresponding to the main dissociation channel yielding CH<sub>3</sub>(0<sub>0</sub><sup>0</sup>) and I\*(<sup>2</sup>P<sub>1/2</sub>). (c) Measurement of the appearance of CH<sub>3</sub>(0<sub>0</sub><sup>0</sup>) correlated with I(<sup>2</sup>P<sub>3/2</sub>). This gives a measurement of the magnitude of the acceleration of the wave packet motion as the <sup>3</sup>Q<sub>0</sub> → <sup>1</sup>Q<sub>1</sub> nonadiabatic leak occurs. (d) Measurement of the appearance of CH<sub>3</sub>(1<sub>1</sub><sup>1</sup>) correlated with I(<sup>2</sup>P<sub>3/2</sub>). Note the long delay (110 fs) between the channels producing vibrationless and symmetric stretch excited CH<sub>3</sub> and ground state I(<sup>2</sup>P<sub>3/2</sub>) fragments.

inverted images. Figure 2(b) shows the coexistence of a broad translational energy distribution due to MPI with three narrow peaks, whose intensities depend on the delay time, corresponding to the resonant processes described above.<sup>36</sup> Anisotropy parameters,  $\beta$ , obtained from the angular distributions were found not to depend on the delay time and have values close to the limiting value for a parallel transition ( $\beta=2$ ).<sup>27,28</sup>

The determination of the reaction times for the different channels is performed by integrating each of the resonant peaks in the CH<sub>3</sub> kinetic energy distributions (corresponding to the rings) as a function of the delay time. Figure 3(a) shows the temporal behavior of *N,N*-diethylaniline measured *in situ* used as reference. The rise of this signal corresponds to the convolution of a step function at a time defined as the zero of time with the pump-probe cross correlation. The transients measured for all channels shown in Fig. 3 exhibit a rise with the same time constant. Figure 3(b) shows the appearance of CH<sub>3</sub>(0<sub>0</sub><sup>0</sup>) fragments in correlation with I\*(<sup>2</sup>P<sub>1/2</sub>). The value of 120 ± 30 fs for the reaction time of this channel (see Table I) is consistent with the result reported by Zewail and co-workers.<sup>3</sup> The error in this appearance time corresponds to dispersion observed for several independent measurements. Figures 3(c) and 3(d) show the appearance of CH<sub>3</sub>(0<sub>0</sub><sup>0</sup>) and CH<sub>3</sub>(1<sub>1</sub><sup>1</sup>) in correlation with I(<sup>2</sup>P<sub>3/2</sub>), respec-

TABLE I. Appearance times,  $\tau_i$ , for the different channels of the A-band photodissociation of CH<sub>3</sub>I. Clocking times ( $\tau_1$ ) for channel (1) are subject to a greater uncertainty due to the need of using an external reference (*N,N*-diethylaniline). Relative appearance times for different channels ( $\tau_1 - \tau_2$  and  $\tau_3 - \tau_1$ ) are obtained from a single set of data for each run and can therefore be measured more accurately.

CH <sub>3</sub> I + hν → CH <sub>3</sub> (0 <sub>0</sub> <sup>0</sup> ) + I*( <sup>2</sup> P <sub>1/2</sub> ) ( $\tau_1$ )		
CH <sub>3</sub> I + hν → CH <sub>3</sub> (0 <sub>0</sub> <sup>0</sup> ) + I( <sup>2</sup> P <sub>3/2</sub> ) ( $\tau_2$ )		
CH <sub>3</sub> I + hν → CH <sub>3</sub> (1 <sub>1</sub> <sup>1</sup> ) + I( <sup>2</sup> P <sub>3/2</sub> ) ( $\tau_3$ )		
$\tau_1$ /fs	$\tau_1 - \tau_2$ /fs	$\tau_3 - \tau_1$ /fs
120 ± 30	43 ± 12	68 ± 14

tively. Since all measurements are performed simultaneously for the three channels from a set of images obtained as a function of delay time, the errors in the relative appearance times are considerably lower than absolute clocking times.

Therefore, we have directly measured the acceleration in the wave packet motion caused by the nonadiabatic crossing between the <sup>3</sup>Q<sub>0</sub> and <sup>1</sup>Q<sub>1</sub> surfaces, which makes the I(<sup>2</sup>P<sub>3/2</sub>) channel faster than the I\*(<sup>2</sup>P<sub>1/2</sub>) channel by about 40 fs (see Table I). This longer dissociation time for the I\*(<sup>2</sup>P<sub>1/2</sub>) channel is consistent with the expected wave packet dynamics on the calculated <sup>3</sup>Q<sub>0</sub> and <sup>1</sup>Q<sub>1</sub> surfaces,<sup>24,26</sup> but this is the first reported measurement for this system. Similar results were also found by Zewail and co-workers<sup>3</sup> for the ICN molecule. The influence of vibrational energy content of CH<sub>3</sub> on the dissociation times is theoretically less obvious. The fact that we simultaneously measure vibrationless and symmetric stretch excited CH<sub>3</sub> in correlation with I(<sup>2</sup>P<sub>3/2</sub>) allows us to determine directly the delay existing between these two channels, which we found to be about 110 fs [see Figures 3(c) and 3(d)]. The only previous (indirect) reference to this phenomenon is the work by Kinsey and co-workers,<sup>23</sup> where, in a frequency domain, Raman spectroscopy experiment, they found evidence suggesting that the extension of the C–I bond temporally precedes the onset of the conversion of CH<sub>3</sub> from its tetrahedral configuration to its ultimately planar geometry (umbrella motion). We have observed this type of behavior, and measured its time delay directly, in the CH<sub>3</sub> symmetric stretch motion.

The combination of resonant probing with velocity map imaging has allowed us to unambiguously clock several dissociation channels in the A band photodissociation of CH<sub>3</sub>I in the femtosecond time scale. New experimental data on this benchmark system have been measured, which should be a stringent test for wave packet theoretical models. Work is in progress to determine the reaction times for other channels of this photodissociation process, i.e., those yielding vibrationally excited CH<sub>3</sub> in the umbrella mode. This work should encourage further work exploiting the nature of broadband femtosecond excitation and the ever more sophisticated charged particle imaging techniques for the study of the many still standing issues in real time reaction dynamics.

We are grateful to Professor F. J. Aoiz, Professor J. Santamaría, and Professor L. Vázquez for their longstanding support and to V. Guadaño (LASING S.A.) for his long hours of technical assistance. We thank Dr. G. García for sharing with us the pBasex software, Dr. H. G. Ballesteros for his

help with the automatization of data acquisition, and J. González-Vázquez for his technical advice. Two of the authors (J.G.I. and J.D.) gratefully acknowledge financial support from the FPI program and the CSIC-Unidades Asociadas program, respectively, of the Spanish Ministry of Education and Science (MEC). This work has been financed by the Spanish MEC through Grant No. CTQ2005-08493-C02-01. This research has been performed within the Unidad Asociada between UCM and CSIC. The facilities provided by the Centro de Asistencia a la Investigación de Espectroscopia Multifotónica y de Femtosegundo (UCM) are gratefully acknowledged.

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