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Nicolas Thiré, Raluca Cireasa, David Staedter, Steven Pratt, Valérie Blanchet. Time-resolved predissociation of the vibrationless level of the B state of CH₃I. *Physical Chemistry Chemical Physics*, 2011, submit. hal-00567795v1

HAL Id: hal-00567795

<https://hal.science/hal-00567795v1>

Submitted on 21 Feb 2011 (v1), last revised 11 Jul 2011 (v2)

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Time-resolved predissociation of the vibrationless level of the B state of CH₃I

N. Thiré, R. Cireasa, D. Staedter, V. Blanchet*

¹Université de Toulouse, UPS, 118 route de Narbonne, F-31062 Toulouse, France

²CNRS, Laboratoire Collisions Agrégats Réactivité, IRSAMC, F-31062 Toulouse, France

and

S.T. Pratt

Argonne National Laboratory, Argonne, IL 60439, US

Corresponding author :

V. Blanchet, fax # : 00 (33) 561 558 317, val@irsamc.ups-tlse.fr

ABSTRACT

The predissociation dynamics of the vibrationless level of the first Rydberg state $6s$ (B^2E) state of CH_3I has been studied by femtosecond-resolved velocity map imaging of both the CH_3 and I photofragments. The kinetic energy distributions of the two fragments have been recorded as a function of the pump-probe delay, and as a function of excitation within the umbrella and stretching vibrational modes of the CH_3 fragment. These observations are made by using (2+1) Resonant Enhanced MultiPhoton Ionization (REMPI) via the $3p_z^2A_2''$ state of CH_3 to detect specific vibrational levels of CH_3 . The vibrational branching fractions of the CH_3 are recovered by using the individual vibrationally state-selected CH_3 distributions to fit the full kinetic energy distribution obtained by using nonresonant multiphoton ionization of either the I or CH_3 fragment. The angular distributions and rise times of the two fragments differ significantly. These observations can be rationalized through a consideration of the alignment of the CH_3 fragment and the effect of this alignment on its detection efficiency. A dissociation channel associated with the Rydberg fingerprint observed previously in the photoelectron studies is also detected around 9.2 eV.

Keywords: predissociation, femtosecond spectroscopy, methyl iodide, velocity map imaging
Date: 04 February 2011

1. Introduction

Time-domain studies of the predissociation of Rydberg states of methyl iodide have primarily been performed by monitoring the decay of the parent ion signal produced by photoionization of the Rydberg states. Using this approach, the origin band of the first optically active Rydberg state, namely the B 6s[2] state, was found to have a picosecond lifetime,^{1, 2} while higher vibrational levels of this state were found to have significantly shorter lifetimes.³⁻⁵ Recently, we have studied the predissociation of the origin band of the B 6s[2] state by time-resolved photoelectron spectroscopy,⁶ and in the present paper, we extend this work by using fs-REMPI (Resonant Enhanced Multiphoton Ionization) to study the fragment branching fractions and translational energy distributions. The present results can be compared with the recent results of Gitzinger et al., which were obtained by using a very similar experimental set-up.⁷

The B 6s[2] state is derived from the promotion of 5p π electron into a 6s Rydberg orbital, leaving a ground state CH₃I⁺ ²E_{3/2} ion core. Predissociation of the 6s Rydberg state may occur by spin-orbit interaction with the continuum of the anti-bonding σ^* lowest unoccupied molecular orbital (LUMO) localized on the C-I bond. This σ^* orbital is responsible for the well-known A band. Two dissociation channels are energetically allowed, leading to a ground state CH₃ radical and an iodine atom in either the ²P_{3/2} ground state or the ²P_{1/2} spin-orbit excited state. Hereafter, these two states are labeled I and I*, respectively. The corresponding dissociation thresholds have been determined to be 2.366 ± 0.013 eV and 3.309 ± 0.013 eV by a state of the art experiment that combined a hexapole to select the initial state and a velocity map imaging spectrometer to measure the distribution of the fragments.⁸ The energetics of the neutral and ionic states of the CH₃I parent and its fragments are illustrated schematically in Figure 1, along with the excitation schemes used to prepare the CH₃I and to detect its fragments. Vibrational excitation of the CH₃ is expected to populate the umbrella mode (ν_2

$\sim 607\text{ cm}^{-1}$) preferentially, owing to the transition from the nearly tetrahedral geometry of the CH_3 in CH_3I to the planar structure of the free CH_3 ground state. CH_3 fragments produced by photodissociation within the A band also show some activity in the ν_1 symmetric stretching mode ($\sim 3004\text{ cm}^{-1}$) produced by photodissociation within the A band,^{9, 10} and this may also occur following excitation to the B state.

Here we examine the predissociation of the B-6s[2] origin band by using time-resolved photoion velocity map imaging. The CH_3 and I fragments were selectively ionized by a REMPI scheme that allows the determination of the vibrational distribution of the CH_3 fragment. The remainder of the paper is organized as follows. A brief description of the experimental setup is given in Section 2, and the choice of probe wavelength is discussed in Section 3-1. Next, the time-resolved photoion signals integrated over energies and angle are presented in Section 3-2, and the CH_3 vibrational energy distribution is given in Section 3-3. The time dependences of the fragments as a function of their energies are summarized in Section 3.4. All the results are discussed in Section 4.

2. Experimental Details

The experimental setup is a standard combination of a continuous molecular beam coupled to a Velocity Map Imaging (VMI) spectrometer and has been described previously.⁶ The laser is a 1kHz-3mJ/p Ti:Sapphire regenerative-amplified system (Amplitude System), delivering pulses with a central wavelength of $\sim 805\text{ nm}$ and a Fourier-transform-limited full width at half-maximum (FWHM) duration of $\sim 70\text{ fs}$. The 1.8 mJ/pulse dedicated to femtochemistry is divided into two parts. One part is used to generate the pump beam by using crystals to produce the fourth harmonic at 201.2 nm with a pulse energy of 1.5 μJ . The second part is used to generate the probe beam by using a home-made Non-collinear Optical Parametric Oscillator (NOPA) with three stages of amplification. The NOPA delivers compressed pulses with 25 μJ of energy that are tunable between 510 and 700 nm. This output is then mixed

with the 805 nm fundamental to generate tunable pulses between 313 and 340 nm with 7 μJ of energy, allowing the state-selective ionization of CH_3 with different numbers of quanta in the umbrella mode. The FWHM spectral bandwidths of 150 and 120 cm^{-1} for the pump and probe, respectively, result in a correlation time around ~ 160 fs, somewhat shorter than the experimental FWHM of $\sim 300 \pm 50$ fs, depending on the probe wavelength. The light is focused onto the molecular beam by using 500 and 200 mm lenses for the pump and probe, respectively. By measuring the spatial mode of the light pulses with a UV-CCD camera, the intensities of the two beams are found to be $< 6 \times 10^{11}$ W/cm^2 . Iodine detection is accomplished simply by photoionizing with the second harmonic of the fundamental pulse, i.e., at 403 nm. The 403 nm light has a FWHM of 120 cm^{-1} , and a pulse energy of 35 μJ , corresponding to 3×10^{12} W/cm^2 . In most of the experiments, the linear polarizations of the pump and probe are parallel to each other, and are also parallel to the face of the detector.

The continuous molecular beam is composed of a 10% $\text{CH}_3\text{I}/\text{Ar}$ mixture, obtained by flowing 350 Torr of Ar through a CH_3I sample held at -30 C. This mixture expands through a 250 μm nozzle, and the resulting molecular beam is collimated by two skimmers. Under these expansion conditions, there is no evidence for the formation of CH_3I clusters or I_2 in the mass spectrum or as additional features in the ion images, indicating that dimer formation is negligible.^{5, 11-13}

In the interaction region, the molecular beam is crossed at right angles by the laser beams. The charged species created in this region are extracted perpendicular to the plane defined by the laser and the molecular beams, passing through a 40 cm time-of-flight tube and onto the detector, which consists of two micro channels plates (MCP) of 40 mm coupled to a phosphor screen. Transient ion signals are recorded by integrating the signal from the phosphor, whose output was preamplified and sent to a gated boxcar integrator. At each pump-probe delay, the signal is averaged over 3×10^3 laser shots. The raw images, recorded by a 12 bit digital video

camera, are reconstructed by using Abel transformations to provide the 3-D distributions. At selected pump-probe delays, higher quality images were recorded by averaging over 2×10^5 laser pulses. The CH_3 images have been recorded with 4 kV applied to the repeller, which typically results in a resolution of ~ 100 meV at a fragment translational energy of 2 eV. The iodine fragments were also recorded at a repeller voltage of 4 kV to allow a direct comparison to CH_3 distribution. In addition, the I fragment distributions were also recorded at a repeller voltage of 2 kV to improve the resolution (~ 20 meV at 0.5 eV).

3. Results

The absorption spectrum of CH_3I is dominated by a single sharp peak at 6.16 eV (201.2 nm), and there is no evidence for a background continuum within the laser bandwidth (150 cm^{-1}).¹⁴ This situation ensures that only the $v=0$ level of B-6s[2] is excited by one photon of the pump. The probe wavelengths are chosen to photoionize selectively the methyl fragments as a function of their internal energy, while the atomic I fragments are ionized nonresonantly by using 403 nm photons. Before presenting the results, we discuss the energetics of the ionization schemes at these different probe wavelengths.

3.1 Choice of the probe wavelength

Our optical set-up does not produce pulses of sufficient intensity at 304 nm to allow the state-selective ionization of I^* , in contrast to the experiments of Gitzinger et al.⁷ Instead, the iodine fragments are photoionized nonresonantly by using four photons at 403 nm. Several near resonances at three-photon energy could enhance this ionization process. These three-photon resonances include $^3\text{P}_16\text{d}[1]_{1/2} \leftarrow \text{I}^* \text{ } ^2\text{P}_{1/2}$ at 74425 cm^{-1} , $^1\text{D}_25\text{d}[2]_{1/2} \leftarrow \text{I}^* \text{ } ^2\text{P}_{1/2}$ at 74632 cm^{-1} , and $^3\text{P}_15\text{d}[1]_{3/2} \leftarrow \text{I} \text{ } ^2\text{P}_{3/2}$ at 74587 cm^{-1} .

The CH₃ fragment is produced in the 2p_z ²A₂" electronic ground state and is probed by (2+1) REMPI via the 3p_z ²A₂" Rydberg state. The wavelength was tuned to resonance with the Q branch band heads, corresponding to absorption of two-photons at 333.45 nm for the 0₀⁰ band, at 329.5 nm for the 2₁¹ band (ν₂ is the umbrella mode), at 326.1 nm for the 2₂² band, and at 322.8 nm for the 2₃³ band.^{15, 16} The effective FWHM bandwidth for the two-photon absorption is 170 cm⁻¹, which is significantly smaller than the offset between successive sequence bands, thus allowing vibrational state selective ionization. This probe bandwidth is also sufficiently broad to overlap the entire rotational profile within each umbrella band, and its duration is short enough to compete efficiently with the predissociation of the intermediate 3p_z ²A₂" Rydberg state into CH₂ + H. Note, however, that the bandwidth of the probe at the wavelength for the 0₀⁰ band does overlap the 1₁¹ symmetric stretch band and the 3₁¹ degenerate asymmetric stretch band, both of which occur at 2x333.9 nm.¹⁷

3.2 Time-resolved integrated photoion signals.

Figure 2 shows the femtosecond transients of the parent and fragment peaks observed in the time-of-flight mass spectrum recorded by using the current collected from the phosphor screen. Each ion signal is thus integrated over the translational energy and angular distributions. Figure 2a shows that the decay times of the CH₃I⁺ signal recorded with the probe centred at 333.5 nm or 403 nm are the same even though a different number of probe photons is required for ionisation at these two wavelengths. This decay time corresponds to 1.31 ± 0.07 ps. These measurements are consistent with the 1.38 ± 0.2 ps lifetime measured in one-photon transitions;^{1, 3} the 1.57 ps lifetime measured by using two photon excitation at 400 nm and multiphoton excitation at 800 nm;^{2, 18} and the 1.5 ± 0.1 ps lifetime obtained by photoionization of the vibrationless level with 304 nm photons.⁷

At short time delays, the transients observed for the I^+ and CH_3^+ masses arise from two components. In particular, these transients have a similar rise time to the parent ion signal, but decay to a non-zero plateau at longer times. The rapid rise and fast fall off are due to dissociative ionization to either $CH_3^+ + I$ or $CH_3 + I^+$, with energetic thresholds of 12.248 ± 0.003 eV¹⁹ and 12.82 ± 0.02 eV,²⁰ respectively. The slower rise producing the plateau at longer times can be assigned to the photoionization of neutral fragments produced by the predissociation of the B-6s[2] state. This assignment is discussed in more detail below, and confirmed by using the velocity distributions determined in the imaging experiments. At this point, the transients are simply fit by assuming two components, one for the dissociative ionization process, and a second rising component for the predissociation, and assuming that both processes have the same time constant, T_e . As we will discuss further, this later assumption is not justified for all the fragments. This waveform is given by:

$$S_{frag^+}(\Delta t) = a_0 + \left(1 + erf(\phi(\Delta t))\right) \times \left[b_0 e^{-\frac{\Delta t}{T_e}} + c_0 \left(1 - e^{-\frac{\Delta t}{T_e}}\right) \right] \quad \text{Eq. 1}$$

with the error function, $\phi(\Delta t)$, defined as

$$\phi(\Delta t) = \frac{2\sqrt{\ln 2}}{T_{cc}} \left(\Delta t - \frac{T_{cc}^2}{8 \ln 2 \times T_e} \right). \quad \text{Eq. 2}$$

The cross-correlation time T_{cc} fixed to the measured value of 300 ± 50 fs and the Δt a shift of appearance relative to the “zero delay” are determined by a non-resonant pump-probe ionization of NO. The main parameters obtained by the least squares fitting procedure are summarized in Table 1. All the rise times (~ 1.07 ps) extracted for the nascent fragments in these fits are slightly shorter than the parent decay time, even if Δt is taken into account.

However, as seen below, a more precise determination of this predissociation time can be made by selecting only the contributions arising from the neutral fragment ionisation.

3.3 Energy distribution of photofragments at 8 ps

Figure 3 shows velocity-map ion images for I and CH₃ recorded with a pump-probe delay of 8 ps. The single-color background has been subtracted from these images. Figure 3 also shows reconstructed slices of the three-dimensional velocity distribution obtained by using the Abel transformation. With an energy of excitation at 6.16 eV,²¹ the maximum available energy is 3.8 eV in the I channel, and 2.86 eV in the I* channel. The transition from the ground state to the B-6s[2] state is a perpendicular transition. Thus, for prompt dissociation, the fragments are expected to be preferentially ejected perpendicular to the polarization axis of the pump beam, as it can be seen for the image recorded for I fragments shown in Figure 3a.

In contrast, independent of the probe wavelength, the CH₃ images exhibit different angular distributions (Figures 3b and 3c). These distributions are far more anisotropic than the I* image with minimum intensity at the poles and equators. This observation is at first surprising because the conservation of momentum in the dissociation process requires the true angular distribution of the CH₃ fragments to mirror that of the I* fragment. Because the I* fragment has $J = 1/2$, it cannot be aligned. The I* detection efficiency should then be independent of angle, and the observed I⁺ angular distribution should reflect the true angular distribution. The different observed angular distribution for the CH₃⁺ image thus indicates the presence of an angular dependence of the detection efficiency of the CH₃. The lack of intensity at the poles of the CH₃ distribution suggests a lower detection probability for the fragments flying perpendicularly to the probe laser polarisation axis due to an unfavourable alignment of the CH₃ transition dipole moment and rotational angular momentum relative to the probe polarization. This alignment can be confirmed by recording an image with the probe polarization perpendicular to the pump polarization. An image recorded in this configuration

is shown in Figure 3e, in which a strong CH_3^+ signal is observed perpendicular to the pump polarization. No such angular distributions were mentioned in the recent work of Gitzinger et al.⁷ Alignment of the CH_3 fragment rotational angular momentum has been observed previously for photodissociation of CH_3I within the A band,^{22, 23} and similar angular distributions were also attributed to alignment effects in the two-photon dissociation of Rydberg states in CH_3Br .²⁴ To our knowledge, the observations reported here represent the first detection of angular momentum alignment using broad band fs lasers and imaging techniques. These effects will be discussed in more detail in a forthcoming paper.

All of the CH_3 images that employed the 403 nm light display a saturated central feature, which corresponds to dissociative ionization and is shown in grey in Figure 3. However, with an 8 ps delay, this process is not observed in the CH_3 image when using a resonant probe wavelength (Figure 3b), or in the I image (Figure 3a).

Figure 4 shows the total translational energy distributions extracted from the images for nonresonant ionization of I and CH_3 (4a and 4b, respectively), and for resonant ionization of CH_3 $v_2 = 0, 1,$ and 2 (4e, 4d, and 4c, respectively), at a pump-probe delay of 8 ps. Both our previous work⁶ and the work of others⁷ indicate that the dominant dissociation channel for the B 6s[2] state is to $\text{CH}_3 + \text{I}^*$. The images for state-selective ionization of CH_3 allow us to assign the dominant peak in the corresponding translational energy distributions and thus internally calibrate Figures 4 c-e in a straightforward fashion. An accurate value for that dissociation threshold ($D_0 = 3.309 \pm 0.013$ eV.) has been determined from studies of the A band.⁸ With this assignment, the calibration of the nonresonant CH_3 and I translational energy distributions follows directly. While the absolute accuracy of the internal calibration is not expected to be as good as that obtained by using an external standard, for the present study the

most important aspect is the relative calibration. This relative calibration is expected to be quite good, as all of the images were recorded under the same conditions. With this calibration, it is also clear from Figure 4 that there is no obvious contribution from dissociation to the lower energy $\text{CH}_3 + \text{I}(^2\text{P}_{3/2})$ products. This observation is consistent with our earlier results obtained from photoelectron spectra.⁶

The comparison of the translational energy distributions from the nonresonant I and CH_3 images is revealing. In particular, the I distribution in Figure 4a extends to significantly higher energy than the CH_3 distribution in Figure 4b, exceeding the thermodynamical threshold. Although Gitzinger et al.⁷ plot their I and CH_3 distributions as a function of the translational energy of the individual fragments rather than the total translational energy of both fragments, transforming their I distribution to a total translational energy axis reveals behavior analogous to that of our data. The present CH_3 distributions recorded with probe wavelengths of 400 nm and 800 nm are similar, indicating that these two detection schemes are nonresonant. Interestingly, the translational energy distributions of iodine are different if the angular integration is limited to angles close to the direction parallel or perpendicular to the pump polarisation (see Figure 4a). Because the I^* fragment cannot be aligned, this difference indicates that two processes with different angular distributions are contributing to the I image and its translational energy distribution. Figure 5 shows the angular distributions obtained from images recorded with a pump-probe delay of 8 ps and corresponding to different translational energies of Figure 4a. The anisotropy parameters thus extracted from the I image are $\beta = -0.549 \pm 0.005$ for total translational energy between 2.2 eV and 3.0 eV, and $\beta = +0.89 \pm 0.02$ for energies between 3 eV and 3.8 eV. While the process corresponding to lower translational energies clearly corresponds to the ionization of I^* produced by predissociation of the B-6s[2], the nature of the process producing higher translational energies is discussed further below.

Figure 4c-e shows the energy distributions recorded using probe wavelengths of 326.1, 329.5 and 333.5 nm corresponding to the 2_2^2 , 2_1^1 and 0_0^0 bands, respectively, of the (2+1)REMPI transition involving the $3p_z$ $^2A_2''$ Rydberg state as a resonant step.^{15, 25} Attempts to record an image with the probe wavelength tuned to the 2_3^3 band at 322.8 nm were unsuccessful, which is consistent with the CH_3 distribution recorded with a nonresonant probe, suggesting that the predissociation process does not generate detectable amounts of $CH_3(v_2=3)$. The typical widths of the translational energy distributions in Figures 4c-e vary between 165 and 85 meV. The vertical full lines in Figure 4 indicate the energy threshold expected for the fragment vibrational energy corresponding to bending excitation (v_2 progressions). The v_1 contribution is probed by (2+1)REMPI via 1_1^1 band using 333.9 nm wavelength, which lies within the bandwidth of the 333.5 nm light used for the 0_0^0 band. As already observed at 193.3 nm, in the predissociation of the $v_2=2$ level of the $6s[2]$ state,²⁶ the CH_3 distribution is characterized by significant excitation of the symmetric stretching mode v_1 . In Figure 4, the dashed lines indicate the threshold for excitation to the v_1+v_2 combination mode, which was observed and assigned in previous fs studies of A and B band dissociations by Nalda et al.¹⁰ and Gitzinger et al.⁷ Nevertheless, transitions involving the v_1+v_2 bands are not spectroscopically known.

The vibrationally state-selected translational energy distributions of Figure 4c-e have been used to fit the translational energy distributions from both the I and CH_3 images (Figure 4a-b) recorded nonresonantly, and thus provide a determination of the CH_3 vibrational distribution. This distribution is summarized in Table 2 and Figure 6. The vibrational distribution found for CH_3 recorded off resonance at 403 nm or 800 nm is the same. In contrast to Gitzinger et al. who directly used translational energy distribution measured resonantly as only one component, we have used normalised functions resulting from the fit of each vibrational

component observed in Figure 4. This approach completely decouples the contributions of each vibration and thus eliminates the possible artifacts in the relative intensities produced by variations in the detection efficiencies of the ν_1 and ν_2 components. The $\nu_2 = 1$ feature is the largest component of both vibrational distributions presented in Figure 6, but there is also significant intensity in the $\nu_2 = 0$ component. In contrast, in the vibrational distribution reported by Gitzinger et al., the $\nu_2 = 0$ component is dominant. This difference might just result from the fitting procedure.

3.4 Rise time of the neutral fragments.

Figure 7 shows the time dependence of the fragment signals as a function of the pump-probe delay. The curves for I and CH₃ have been recorded in two and three independent scans, respectively. These time-dependences are fitted by the rising function of Eq.1 (i.e., the term that includes c_0), except for that from Fig. 7-b. The latter decay process is fitted by a cross-correlation function and a decaying exponential similar to term in b_0 of Eq.1. The time constants and time shifts extracted by fitting the data are summarized in Table I.

Iodine fragment

The iodine translational energy distribution is characterized by three different contributions: one corresponding to fragments emitted perpendicular to the pump polarisation at 2.8 eV and two corresponding to fragments emitted parallel to the pump polarisation at 3 eV and 6.4 eV. These three components have different time-dependences, as shown in Figure 7a, 7c and 7b respectively.

Perpendicular component around 2.8 eV – Figure 7a

The iodine fragments emitted between 80°-100° (perpendicular to the pump polarisation) appear within 1.17 \pm 0.06 ps and have a translational energy of about 2.8 eV (Figure 7a). As

expected by taking into account the shift of appearance, these fragments have an overall appearance time corresponding to the decay time of the parent ion (Figure 2a-Table 1). The I* fragment distribution integrated over 360° (Figure 7f) and between 2.2 to 3.5 eV has a time-dependence that agrees with the rising function extracted from the angular- and energy-integrated ion signals from Figure 2b. Indeed the shortest lifetime and time shift are associated with the iodine emitted parallel to the pump polarisation (Figure 7c).

Parallel component around 3 eV – Figure 7c

The time dependence of the iodine fragments emitted parallel to the pump polarisation within a 20° angle and with an energy around 3 eV (see Figure 7c) can be split in two parts: a step function with a rising edge corresponding to the laser cross-correlation and an increasing function with a rise time on the picosecond scale. Note that in Figure 8, the maximum of the kinetic energy distribution of this component shifts from 3.7 eV at 400 fs to 2.9 eV at 8 ps without any broadening. This component has a FWHM of 650 meV (or 70 meV when expressed as fragment kinetic energy). This shift primarily occurs in the first 3 ps, and it is not observed in the perpendicular component of the translational energy distribution. Note that the perpendicular contribution with $\beta=-0.549$ will lead to a contribution in the 20° parallel distribution around 36% of what is emitted perpendicular but centered on 2.75 eV. Figure 4a recorded at 8 ps shows a percentage roughly 27% at 2.75 eV to compare to the 36% expected, while at 3 eV, around 2.5 more iodine are produced parallel instead of perpendicular. This observation leads us to conclude that another process besides the predissociation from the $v=0$ of B-6s[2] state, takes place on a picosecond time scale, and that this process is not observed in the CH₃ product channel.

Parallel component around 6.4 eV –figure 7b

The iodine emitted parallel at 6.4 eV can be fitted by a cross-correlation function with an exponential decay on time scale 1.65 \pm 0.05 ps slightly longer than the CH₃I⁺ decay 1.31 ps

(Figure 7b). We assigned this component to iodine fragment produced around 9.24 eV by the absorption of one probe photon from the $v=0$ level of B 6s[2] state. This (1+1') excitation path was already identified in the photoelectron spectrum via a Rydberg fingerprint onto the 6p[2,4] and 7s[2,4] states.⁶ The vibrational energies in these Rydberg states are 1.92 eV in 6p[2] and 1.21 eV in 7s[2], and these states are expected to have very short lifetimes. Indeed the lifetime of their origin band has been measured to be shorter than 150 fs.²⁷ These two ultrafast radiationless transitions would produce fragments with total available energies of 5.93 eV for the I* channel and 6.88 eV for the I channel, respectively. The production of iodine in its ground state can come from the interaction with the repulsive $^1Q(E)$ as predicted by the calculations for energy larger than 6.8 eV.²⁸ The anisotropy parameter obtained by fitting the angular dependence of the iodine translational distribution between 4.5 and 7 eV at 700 fs is $\beta = 1.89 \pm 0.05$. The kinetic energy of the CH₃ fragments associated with this process is so high that the corresponding ring in the image is larger than the diameter of the detector, and is thus not observed. To a first approximation, the lifetime of this component should reflect the lifetime of the $v=0$ of B 6s[2] state, since this state is an intermediate on the way to reaching the 9.4 eV resonances. It is noteworthy that this process occurs within the probe pulse duration and requires five photons of the probe with two resonant steps.

Methyl fragment

Only the methyl produced in $v_2=1$ and detected with a probe pulse centered at 329.5 nm has been recorded as a function of the pump-probe delay. This time dependence results in the distribution shown in Figure 4d, which was fitted by two Gaussian distributions: one peaking at 2.7 eV and corresponding to $v_2=1$ (REMPI (2+1) transition at 329.5 nm) and the second one around 2.35 eV that we suppose to be due to an excitation of the combination mode (v_1, v_2)=(1,1). As noted above, because of the broad bandwidth of the probe pulse, we may expect

a REMPI (2+1) transition via this band in this wavelength region, but this has never been identified experimentally. Surprisingly both of these components have rise times that are considerably longer than any other timescales measured, especially when taking into account the shift of appearance time. The increase in the rise time is not an experimental artefact, as the same time dependence was obtained for three different experimental runs.

4. Discussion.

In general, our data are in good agreement with the recently published results of Gitzinger et al. The observation that only I* fragments are detected from the predissociation of $v=0$ of the B 6s[2] state also confirms the conclusions of the previous works.^{7, 26, 29, 30} This conclusion can be understood for the B-6s[2] vibrationless level by considering the crossing of the potential surfaces of the B-6s[2] state and the $4E(^3A_1)$ and $^2A_2(^3A_1)$ valence states along the C-I stretching coordinate. Both the $4E$ and 2A_2 valence states cross the B 6s[2] state near its equilibrium geometry, and both are diabatically correlated with the CH_3+I^* dissociation limit.^{28, 31} The predissociation is caused by the spin-orbit coupling. The present vibrational state distribution differs slightly from the one of Gitzinger et al., but can be understood in terms of the different fitting procedures for the CH_3 translational energy distributions. Although all of the predissociation times are in the range of 1.3 ps, these times are systematically longer when neutral CH_3 fragments are detected and fitted (Figure 7), as compared to when the ion transients are detected and fitted with a single timescale (Figure 2).

4.1 The CH_3 Distributions

The rise time for the CH_3 ($v_2 = 1$) signal is 2.2 ps, which is considerably longer than expected based on the corresponding I signal. No rising time for this fragment has been measured in the past for the B-6s[2] $v=0$. This observation can be rationalized by taking into account the relative alignments of dipole moments of transition used to photodissociate the CH_3I and to photoionize the CH_3 fragment when the pump and the probe polarizations are parallel to each other. In the following discussion, CH_3I is assumed to remain in the C_{3v} symmetry group. The transition dipole moment of the B 6s[2] \leftarrow $^1\text{A}_1'$ transition at 201.2 nm is perpendicular to the C_3 axis of the CH_3I and thus selects molecules in a plane perpendicular to the pump polarisation and parallel to the time-of-flight. Thus, if the dissociation is prompt, the C_3 axis of CH_3 fragment is (at least initially) parallel to the C_3 axis of CH_3I , and perpendicular to the polarization axis of the probe light. Alignment of the CH_3 fragment rotational angular momentum has the potential to preserve this relative geometry. However, the transition dipole moment of the two-photon $3p_z$ $^2\text{A}_2'' \leftarrow 2p_z$ $^2\text{A}_2''$ step in the (2+1) REMPI used to detect the CH_3 is parallel to the C_3 axis of the CH_3 . Consequently, for a prompt dissociation, the ionization probability is expected to be extremely weak because the probe polarisation is perpendicular to the dipole moment of detection transition. However, the present dissociation is not a prompt process, but rather a predissociation taking place over 1.3 ps. This process is thought to involve a slow crossing onto the σ^* surface, followed by rapid (<100 fs) dissociation on that surface. Therefore, one factor that can diminish this C_3 alignment effect is the rotation of the parent molecule before the dissociation takes place. In this case, the C_3 axis of the CH_3I will be no longer perpendicular to the probe polarisation, and the CH_3 fragments will be ejected over a greater range of angles relative to the probe polarization. Our main hypothesis is that the resulting position of the C_3 axis relative to the polarization of the probe laser has the potential to modify the appearance of this fragment. We will now discuss this in more detail.

Although the sample is cooled in a molecular beam, the rotational temperature can not be ignored. We will label T_{rot}^* the temperature corresponding to the angular energy causing CH_3I to leave the plane selected by the pump transition and this corresponds to rotation about a C_2 axis. This rotation is the one that contributes most to the loss of anisotropy in the detection process. This T_{rot}^* can be deduced from the angular distribution of the I^* fragment. If it is assumed that the $B\ 6s[2] \leftarrow ^1A_1'$ transition is purely perpendicular, we assume that the deviation of the value of β from the limiting value of -1 to -0.549 ± 0.005 (Figure 5) is due to rotation of the parent molecule outside of this plane selected by the pump transition. By treating classically the parent rotation, the angular distribution of the iodine fragment for a one-photon perpendicular transition can be written:^{32, 33}

$$\Gamma(\theta) = \frac{1}{4\pi} (1 + \beta(T_e) P_2(\cos \theta)) \quad (3)$$

$$\text{with } \beta(T_e) = \beta(0) \frac{1 + (\omega T_e)^2}{1 + 4(\omega T_e)^2} \text{ and } \beta(0) = -1$$

For which the rotational energy is $E_{rot} = \frac{I_b \omega^2}{2}$ with the main moment of inertia for the C-I rotation $I_b = 111.8 \times 10^{-47} \text{ kg.m}^2$ and the predissociation time T_e fixed to 1.3 ps in agreement with the decay time of the parent. Once integrated over the possible rotational energies taking into account their Boltzmann distributions, we get

$$\Gamma(\theta) \propto \frac{\sqrt{\pi} (3 - \cos^2(\theta))}{16T_e \mu} + \frac{\pi [1 - \phi(\mu/2)] \exp(\mu^2/4)}{8T_e} \left(\sin^2(\theta) - \frac{(3 - \cos^2(\theta))}{4} \right) \quad (4)$$

With $\mu^2 = \frac{I_b}{2T_e^2 k_B T_{rot}^*}$ and $\phi(x)$ is the error function. This angular dependency can be then

fitted as done for the experimental results by $\left[1 + \frac{\beta}{2} (3 \cos^2(\theta) - 1) \right]$. Figure 9 gives the

anisotropy parameter β for the predissociation time 1.3 ps. The anisotropy parameter $\beta = -$

0.549 result from $T_{rot}^* = 62$ K to which we can associate an averaged rotational period over

the C_2 axis $\left(\frac{2\pi\sqrt{\pi I_b}}{\sqrt{2k_b T_{rot}^*}} \right)$ of 9 ps. Note that the extracted rotational period is not particularly

sensitive to the predissociation time, and the rotational period changes by only ~ 1 ps for an increase in predissociation time of 100 fs.

Assuming that the predissociation time is 1.3 ps, the C_3 axis will start to be aligned with the probe polarization after a quarter of a rotational period, i.e., ~ 2.25 ps. The observed rise time of the $CH_3(v_2=1)$ of 2.24 ps is consistent with this process. As far as we know the only angular dependence reported for the methyl fragments resulting from the Rydberg excitation is the study by Van Veen et al. with an excitation at 193 nm that populated the $v_2=2$ of the $B6s[2]$ state- 2_0^2 .³⁰ The reported anisotropy parameter of the methyl fragment was measured to be around $\beta = -0.36 \pm 0.05$ while that for the iodine was around $\beta = -0.72$, as expected for a shorter lifetime of 760 fs.³

To measure the predissociation time correctly using the rise time function of the CH_3 fragments for a perpendicular pump transition, the rotational period of the parent needs to be extremely long and the probe polarization needs to be rotated perpendicular to the pump. However this is not compatible with an Abel transform to inverse the data. On the contrary, a slice imaging experiment in which the raw image gives the velocity and angular distribution directly will be a relevant strategy. However slicing experiments have never been done on the small signals typical of femtosecond pump-probe experiments.

The bandwidths measured for the translational distributions of fragments $v_2=1$ (160 meV) and $v_2=2$ (121 meV) in Figure 4 c-d, are significantly narrower than the translation distributions measured by Gitzinger et al.⁷ This observation might be related to their slightly smaller value

$\beta = -0.5$ for the anisotropy of the I* fragment. In particular, both observations are consistent with the conclusion that the expansion of the molecular beam reflecting in a different rotational temperature of the parent (here a continuous beam and in Gitzinger work a pulsed beam) can affect the time-scale of detection of the methyl and the observed angular distribution.

4.2 The I* Fragment emitted parallel around 3 eV.

The iodine distributions of Figure 4 show that some fragments are produced with translational energies that exceed the available energy for dissociation to CH₃ + I* following excitation at 201.2 nm. For example, the fragments with translational energy of 3.50 eV observed in Figure 4a exceed the available energy of 2.86 eV by approximately 22%. This unexpectedly high translational energy is only observed in the iodine, and similar behavior is observed in the data of Gitzinger et al., where an excess energy of 23% is seen in Figure 2a of their paper.⁷ We can decompose the present iodine distribution integrated over 360° with 61 % emitted perpendicular to the pump polarisation and 30% emitted parallel (see Figure 4a). The perpendicular component is associated with the predissociation of the B 6s[2] state, and is consistent with the CH₃ distribution. The surprisingly high kinetic energy fragments are associated with the parallel component. The time dependence of this parallel iodine is shown in Figure 7c, as well as in Figure 8. We will examine now the possible assignment of this contribution.

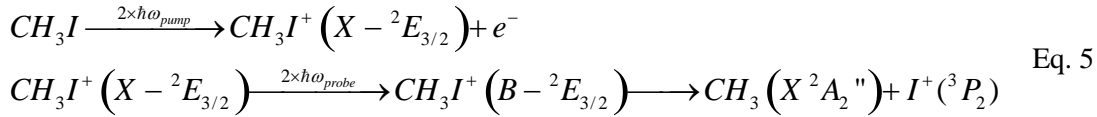
If this fast I signal resulted from dissociation into CH₃ + I, rather than I*, following excitation at 201.2 nm, the available energy would be sufficient to explain the observation. However, the observed kinetic energy of the I would indicate that it is produced in conjunction with CH₃ ($v_2 = 6,7$), which would then be observed in the nonresonant CH₃ image (Figure 4b). The absence of this CH₃ eliminates this potential explanation for the fast I signal.

One way to produce iodine ions without methyl cations is via the dissociation of CH_3I^+ into $\text{CH}_3(X^2A_2'') + \text{I}^+(^3P_2)$ with a (0 K) threshold 12.82 \pm 0.02 eV above the CH_3I ground state.²⁰

The energetics of the cation are summarized in Figure 1. Photoionization of CH_3I by 2 photons at 201.2 nm is known to leave the cation mostly in the $v=0$ of the ground state $X^+E_{3/2}$ (at 9.538 eV).⁶ One probe photon will then reach an energy of 12.61 eV, just 355 meV above the threshold for dissociation to $\text{CH}_3^+ + \text{I}(^2P_{3/2})$. The first electronic excited state of CH_3I^+ is the $A(^2A_1)$ state whose minimum lies 2.4074 eV above the cation ground state. Transitions to the $A(^2A_1)$ state from the ground state are allowed with a transition dipole moment perpendicular to C-I bond.³⁴ This $A(^2A_1)$ state correlates diabatically to the $\text{CH}_3(X^2A_2'') + \text{I}^+(^3P_2)$ asymptote. However, for low vibrational levels, fast internal conversion takes place back to the ground state, leading to the dissociation of the cation into $\text{CH}_3^+ + \text{I}$.

Excitation taking place at two probe photons will reach 15.7 eV ($2+2'-E_{\text{kin}}(e^-)$). The first excited state of CH_3I^+ with 2A_1 symmetry lies around 15.22 eV, and is described as an excitation from the HOMO to a Rydberg orbital.²⁰ A second state occurs in this energy range, corresponding to the $B^2E_{3/2}$ state at about 15 eV, which is populated by a valence transition into the HOMO.²⁰ The $B^2E_{3/2}$ state undergoes Jahn-Teller distortion, and the transition from the ground state of CH_3I^+ is also broadened by predissociation to $\text{I}^+ + \text{CH}_3$ following internal conversion to the $A(^2A_1)$ state.^{35, 36} The fragmentation branching fractions measured in PEPICO experiment (photoelectron-photoion coincidence) performed at 15.7 eV are 40 % to $\text{CH}_3 + \text{I}^+$ and 60% to $\text{CH}_2\text{I}^+ + \text{H}$,³⁵ while the total energy released in the dissociation taking place at 15.8 eV has been found to be 2.93 eV.³⁶ Photodissociation of CH_3I^+ by two photons has been already studied for wavelengths ranging from 427-720 nm.^{34, 37-40} These studies focused primarily on the low energy part of the A state by detecting CH_3^+ fragment. Only Goss have discussed the I^+ fragments appearance.³⁷ The two-photon transition $B(^2E_{3/2}) \leftarrow$

$X(^2E_{3/2})$ can populate the B state via a dipole transition $A_1 \times A_1$ or either $E \times E$. The first will lead to I^+ emitted parallel to the probe polarisation while the second to I^+ emitted perpendicular to the probe polarisation; the latter will thus be hidden by the dominant contribution of the predissociation from the B-6s[2] state. Halogen atoms emitted parallel to the C-X axis following absorption into the B state has been already observed in the photodissociation of CH_3Br^{+41} and CH_3Cl^{+42} cations. Note as well that in Figure 5, the angular dependence of I^+ emitted parallel to the polarization axis is better fitted by assuming a two photon transition (blue line) than a one photon transition (black line): this fit supports our conclusion that the fast I^+ is produced by:



Because the resonant step in the 1 + 1 ionization of CH_3I is a perpendicular transition, the C-I axis of the CH_3I^+ will initially be aligned perpendicular to the probe axis, and thus the two-photon parallel transition to the B state will not be efficiently excited until the rotation of the ion has brought the C-I axis parallel to the probe polarization. As in the case of the CH_3 (2+1) REMPI detection discussed above, this rotation will take a quarter of the rotational period of the parent namely 2.25 ps, as observed on Figure 7(c). The maximum translational energy expected for this channel is 2.9 eV, exactly the energy observed at long delay for iodine emitted parallel to the probe (see figure 8). We explain the energy decrease of this component as a function of the delay until 3 ps as resulting from parent ions produced with vibrational energy. (Figure 3a of 6) Indeed a small number of ions are produced with at least 1 eV of vibrational energy after 1+1 ionization at 201.2 nm. These ions could possibly be photodissociated before rotation of the ion occurs because their total symmetry removes the constraint of having the C-I axis parallel to the probe polarisation. Consequently, the energy of iodine appears higher at earlier times than at later times. These conditions on the dipole of

the photodissociation transition allow the observation of contributions from vibrationally excited cations. At later times, these contributions are hidden by the signal from ions with lower internal energy, which ultimately yield the 2.9 eV translational energy expected for the origin band of the cation.

IV. CONCLUSION

We have investigated the predissociation of CH₃I from the vibrationless level of the B[2] 6s Rydberg state by imaging as a function of time the angular and translational energy distributions of the fragments. The dipole moment of this transition is perpendicular to the C-I axis leading to iodine emitted perpendicularly to the pump polarisation. The multiphoton ionization of the fragments is resonant for CH₃ that allows to determine the energy distribution. No I fragment has been detecting leading us to conclude that the quantum yield of I* is close to 1 from the origin band of the B state. The final-state products have excitation primarily in the CH₃ umbrella mode as expected and observed in most of the dissociations of methyl halide. This distribution is peaked at $\nu_2=1$, with some minor activity in the ν_1 symmetric stretching as well. While the iodine appears on a timescale in agreement with the decay time of the parent, the rise time of the main CH₃ fragment ($\nu_2=1$) is almost twice longer. We explain this by parent molecule that needs to rotate before to dissociate to get a C₃ axis of CH₃ parallel to the probe polarization and thus a favorable configuration to ionize resonantly the CH₃ fragment. Two other contributions are observed with iodine emitted along the pump polarization. They appear on different timescale and multiphoton excitation. One corresponds to the signature of Rydberg states 6p and 7s populated in (1+1') and detected on the photoelectron spectrum.⁶ Both I and I* seem to be emitted from one of these highly vibrationally excited Rydberg states. The present measurement gives an upper limit of the dissociation lifetime for one of these states of 100 fs, namely the duration of the probe pulse. The second contribution comes from the ionization of the CH₃I⁺ produced with two photons

of the pump and then its dissociation by two probe photons onto CH_3+I^+ . As with the detection of the methyl fragment resonantly, this dissociation channel is as well affected by the rotational temperature of the parent molecule. In a forthcoming paper, we will discuss the unusual angular distribution observed on the CH_3 fragments.

Acknowledgments

This work was supported financially by the ANR COCOMOUV, the ANR HARMODYN and L'Université Paul Sabatier via three different BQR. S.T.P. thanks the CNRS for supporting invited research position in the LCAR. S.T.P. was also supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences under contract No. DE-AC02-06CH11357. R.C. gratefully acknowledges the European Union for the award of an Intra-European Marie Curie fellowship through the contract MOLCOTUV-041732. D.S. acknowledges the European Union for its PhD fellowship from the ITN-ICONIC. We thank Elsa Baynard, Laurent Polizzi and Stéphane Faure for their expert technical assistance and Dr. Lionel Poisson for lending us his image analysis software.

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TABLE 1 Time dependences extracted from the fits of the integrated signal of Figure 2 and the energy resolved signals of Figure 7. The fits have been performed with a cross-correlation time around 300 ± 50 fs..

	Time constant T_e /ps	Shift of the appearance t_0 /fs from $\Delta t=t-t_0$
Figure 2 : integrated signal		
(a) CH ₃ I	1.31+/-0.07	0+/-6
(b) Iodine	1.09+/-0.06	100+/-5
(c) CH ₃ $v_2=0$	1.04+/-0.2	50+/-11
(d) CH ₃ $v_2=1$	1.07+/-0.09	0+/-10
Figure 8 : energy resolved signals		
(a) I perp ~2.8 eV	1.17+/-0.06	193+/-20
(b) I para ~6.4 eV	Decay:1.65+/-0.05	164 +/-10
(f) I over 360°	1.05+/-0.05	83+/-19
(d) CH ₃ $v_2=1$	2.24 +/-0.12	307+/-52
(e) CH ₃ v_2+v_1 ?	1.57+/- 0.11	910 +/- 60

TABLE 2 Vibrational distribution at 8 ps resulting from the fit performed on the iodine and CH₃ translational energy distributions recorded with a probe centered 403 nm or 800 nm. The translational energy distribution of the iodine fragments that is fitted is the one obtained by integrating over the angles within 20° of the perpendicular to the pump polarization.

%	origin	ν_2	$2\nu_2$	ν_1	$\nu_1 + \nu_2$
I _{perp}	30±3	30±3	15±2	10±2	4±2
CH ₃ at 403nm	36±1	44±1	9±1	7±1	-
CH ₃ at 800nm	28±2	56±2	4±2	10±2	2±1

FIGURE CAPTIONS

Figure 1. Schematic diagram of the electronic states, dissociation limits, and photoionization thresholds encountered after excitation of the origin band of the B state at 201.2 nm. The nascent CH₃ fragments are probed by (2+1) REMPI (green arrows) and iodine fragment is probed by four-photon ionization (red arrows).

Figure 2. Time-resolved transients recorded after excitation of the origin band of the B state at 201.2 nm: (a) the parent CH₃I⁺ with the probe centered at 403 nm (red triangles) and 333.5 nm (blue crosses). The cross-correlation time is determined from the signal for the photoionization of NO. (b) I⁺ produced by ionization at 403 nm. CH₃⁺ produced by ionization (c) at 333.5 nm that allows REMPI via 2₀⁰ and (d) at 329.5 nm via 2₁¹. See the text for more details on the fits.

Figure 3. Abel transformations at 8 ps delay of (a) iodine fragments recorded with a 403 nm probe with the probe polarization parallel to that of the pump. The repeller voltage is fixed at 2 kV. Raw images of CH₃ collected with a repeller voltage at 4 kV recorded at 8ps with a probe centered at (b) 333.5 nm and (c) 403 nm, both with the probe polarization parallel to that of the pump. Fragment of CH₃ recorded with a 403 nm probe with (d) probe polarization parallel or (e) perpendicular to the pump polarization. The image (d) is an Abel transformation while the image (e) is a raw image. The images have all been symmetrized and the background has been subtracted.

Figure 4. Normalized energy distributions plotted as a function of the translational energy of the center of mass and recorded for different probe wavelengths at 8 ps pump-probe delay.

(a) Full square: Iodine fully integrated over 360°. Circle: Iodine integrated over a 20° range around the perpendicular to the pump polarisation with a weight of 0.61. Triangle: Iodine integrated over a 20° range around the direction parallel to the pump polarisation with a weight of 0.3. The full line corresponds to the sum of the perpendicular and parallel contributions, and should be compared to the full integration over 360°. The vertical line at 2.86 eV corresponds to the threshold limit at one photon for CH₃+I*.

(b) CH₃ ionized by four photons at 403 nm off resonance (empty circle) or seven photons at 800 nm (filled square).

(c-e) CH₃ detected by (2+1) ionization (c) at 326.1 nm via the 2₂² resonance of the 3p_z 2A₂^{''} state, (d) at 329.5 nm via the 2₁¹ resonance of the 3p_z 2A₂^{''} state, (e) at 333.5 nm via the 0₀⁰ resonance of the 3p_z 2A₂^{''} state. The Gaussian fits in red and blue are used in the fit of the vibrational distributions shown in Figure 6. The full vertical lines correspond to the translational energy expected for (n×v₂) while the dashed ones correspond to (n×v₂+v₁) progressions, respectively.

Figure 5. Angular distribution of iodine at 8 ps pump-probe delay and recorded at the translational energy corresponding to the maximum of signal between 2.2-3 eV ($\beta=-0.549\pm 0.005$), and at higher energy between 3 to 3.8 eV (black line with $\beta=+0.89\pm 0.02$ or blue line $\beta_2=+1.02\pm 0.01$ and $\beta_4=-0.33\pm 0.01$).

Figure 6. Fits of the vibration distribution recorded at 8 ps delay using (a) iodine integrated over 20° perpendicular to the pump polarization (Figure 4a) and (b) CH₃ recorded off-resonance at 403 nm (Figure 4b). The vibrational distributions are summarized in Table 1.

Figure 7. Time dependence of the fragments.

(a) Iodine fragments integrated over 20° around the perpendicular to the pump polarization and for translational energies between 2.3 and 3.3 eV. These data have been recorded in two scans.

(b-c) Iodine fragments recorded over 20° around the direction parallel to the pump polarization and for translational energies within a 2 eV window centered (b) at 6.4 eV and (c) at 3 eV

(d) CH_3 fragments recorded with a probe centered at 329.5 nm. The y-scale corresponds to the intensity of the component $\nu_2=1$ recorded via the REMPI 2_1^1 and extracted from a fit of the energy distribution performed for each delay. These data have been recorded in three scans.

(e) CH_3 fragments recorded with a probe centered at 329.5 nm. The y-scale corresponds to the intensity of the component assigned energetically to $\nu_2+\nu_1$ and extracted from a fit of the energy distribution done for each delay.

(f) Iodine fragments integrated over 360° and within a 2 eV window centered at 3 eV.

Figure 8. The translational energy distribution recorded for iodine fragments ejected within a 20° angle of the pump polarization as a function of the pump-probe delay.

Figure 9. The left axis shows the anisotropy parameter β as a function of T_{rot}^* of CH_3I for a predissociation time of 1.3 ps. The horizontal line at $\beta=-0.549$ corresponds to the anisotropy measured in Figure 5 for iodine emitted with $E_T=2.2-3$ eV. The right axis shows the rotational period of CH_3I as a function of T_{rot}^* . For $T_{\text{rot}}^*=62\text{K}$, the period is 9 ps.

Figure 1

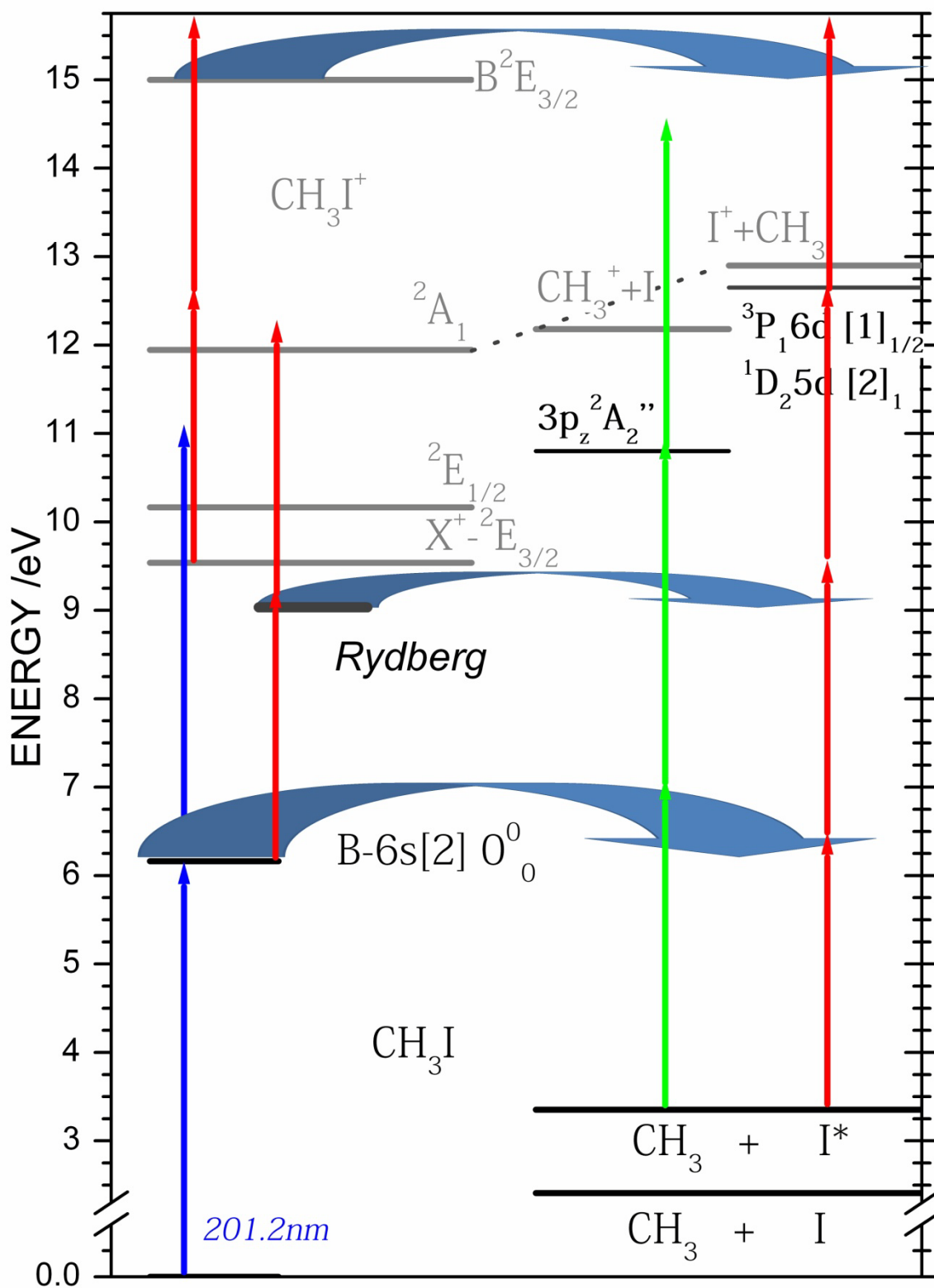


Figure 2

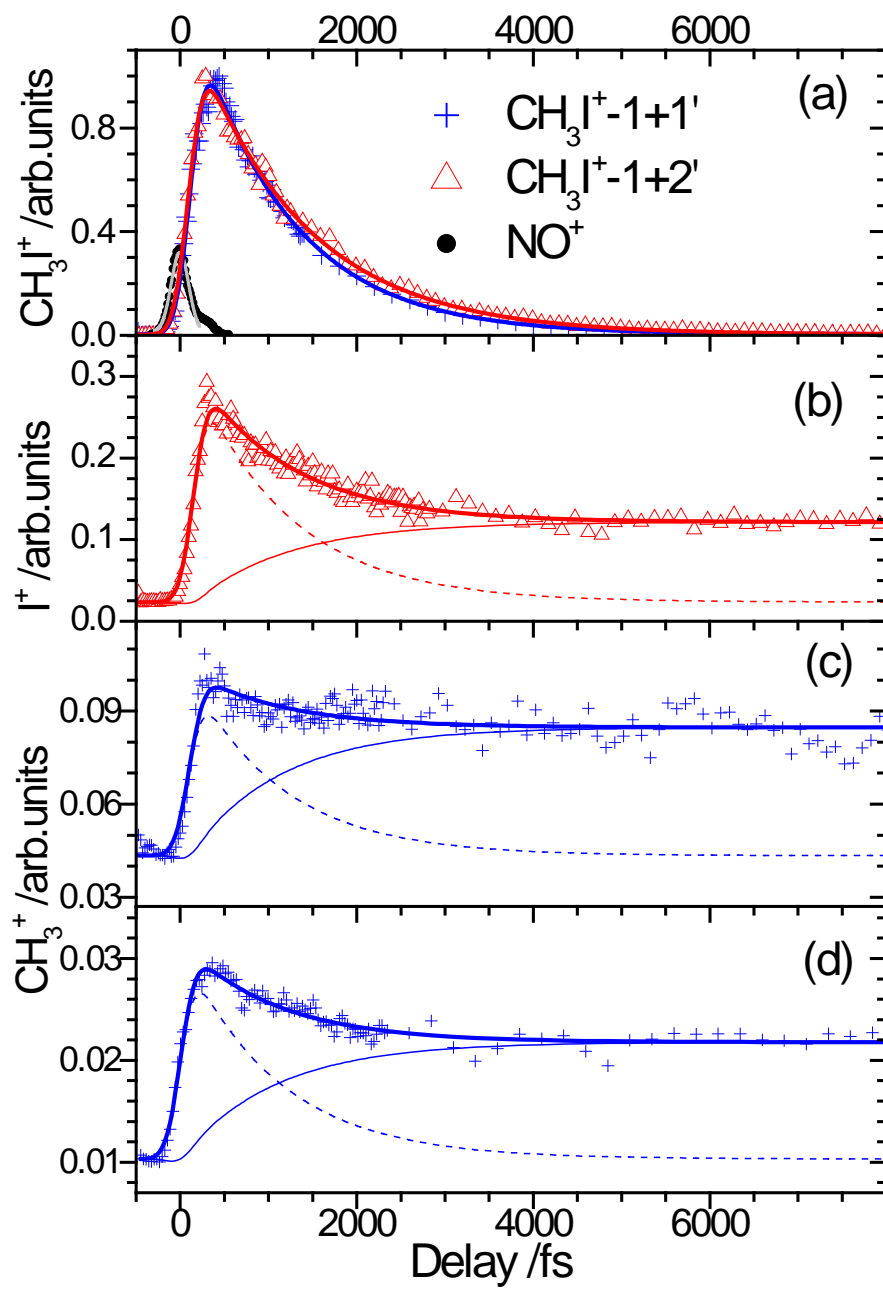


Figure 3

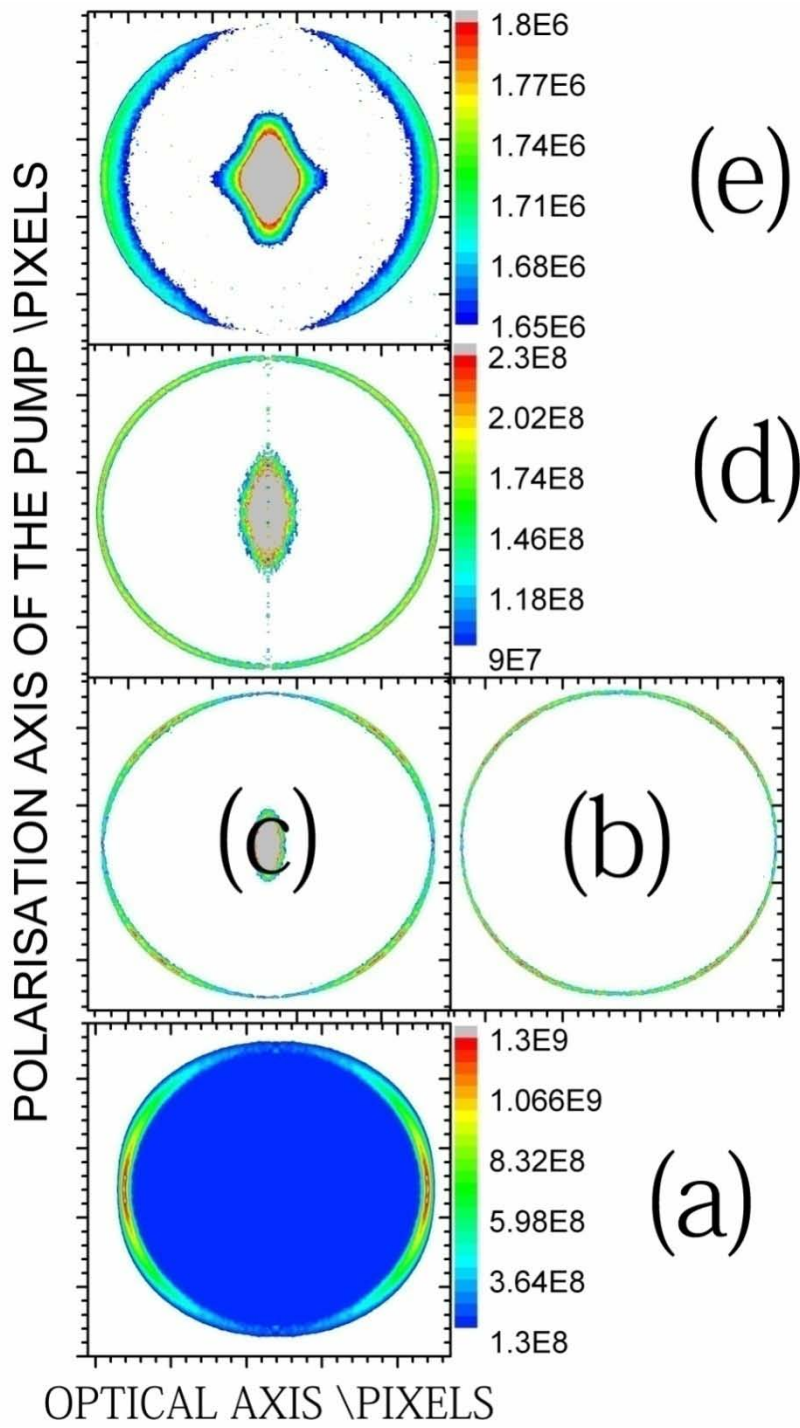


Figure 4

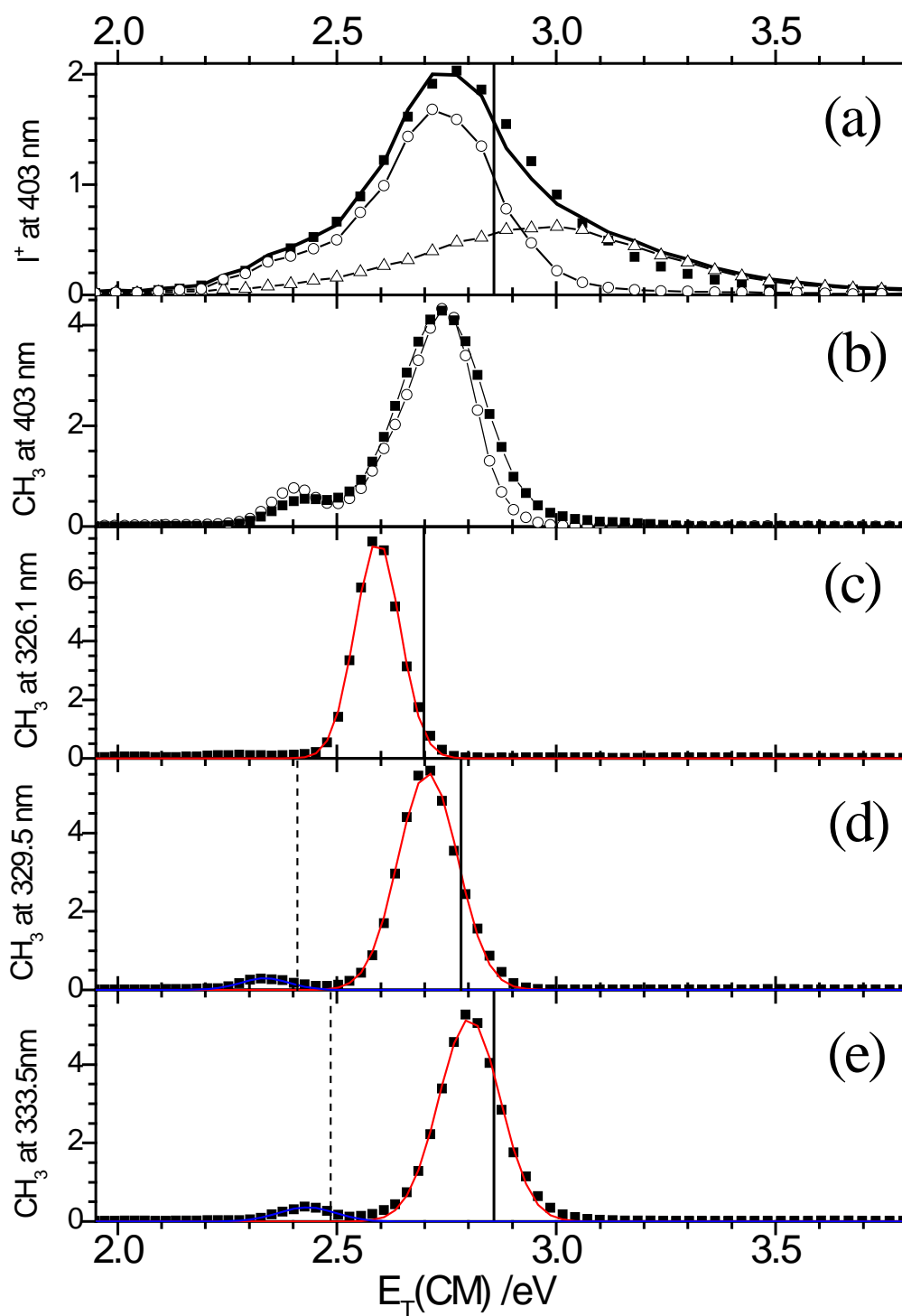


Figure 5

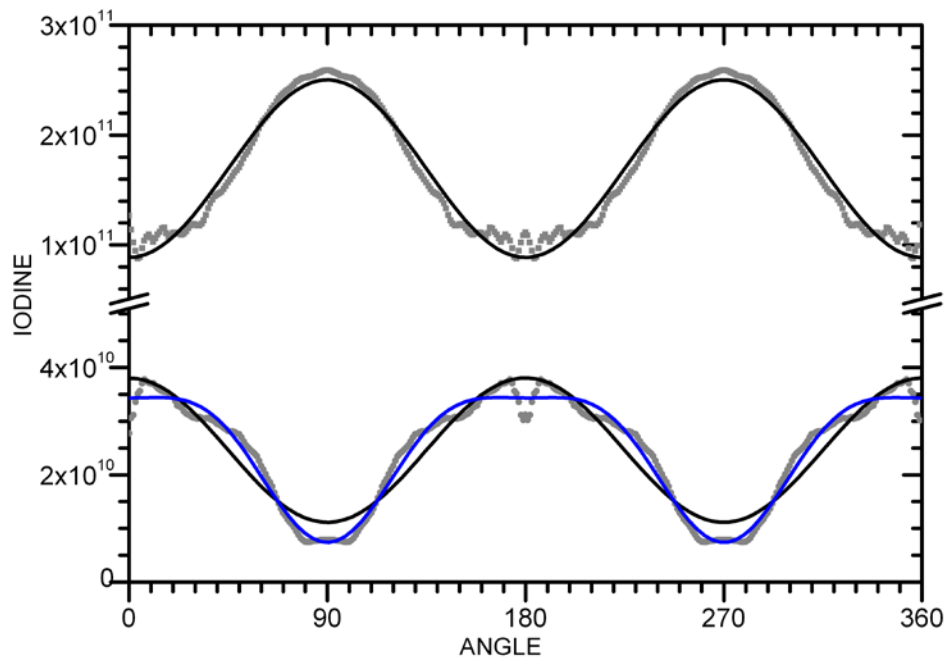


Figure 6

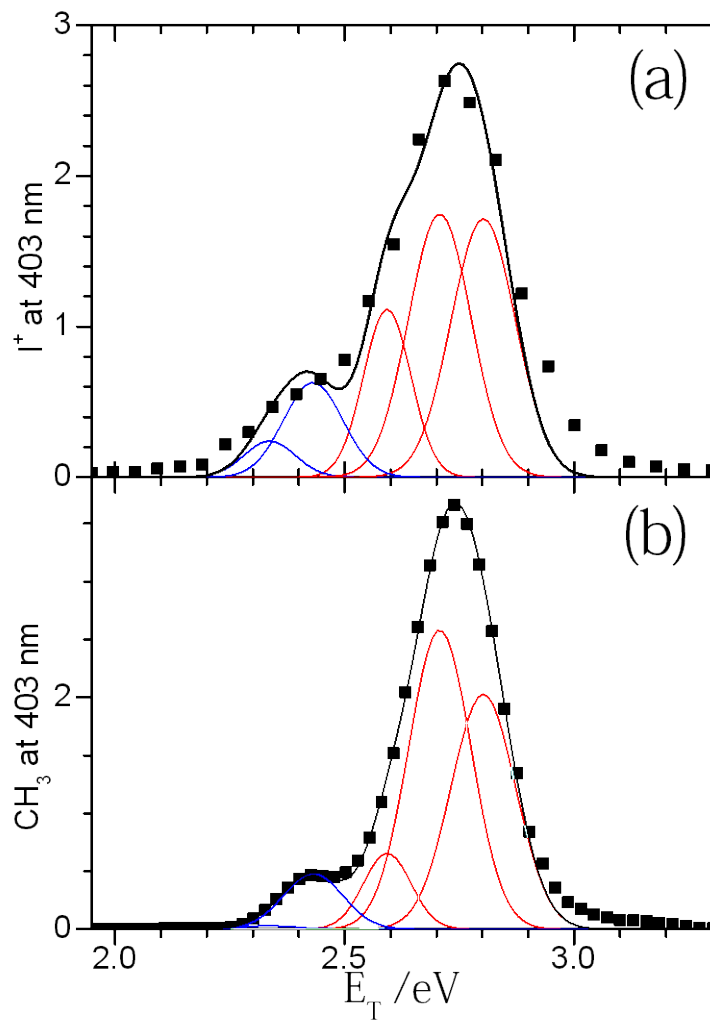


Figure 7

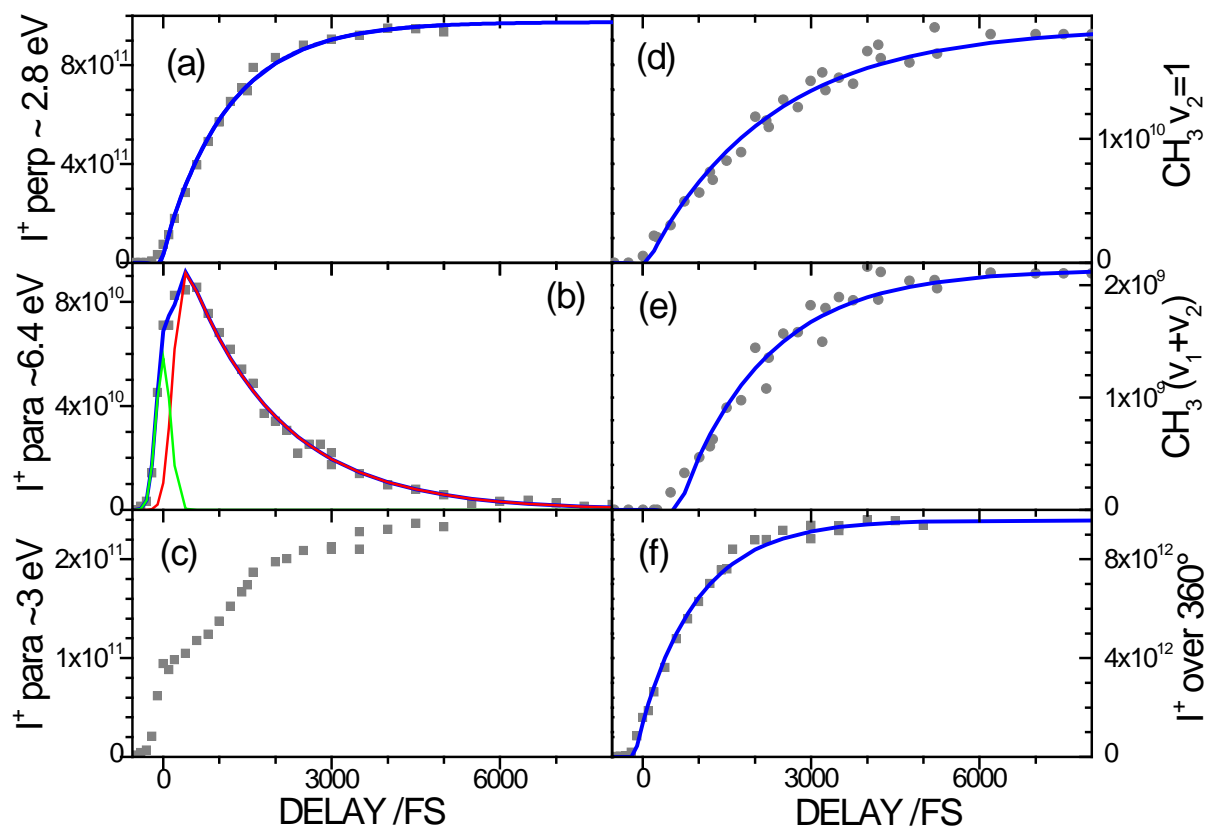


Figure 8

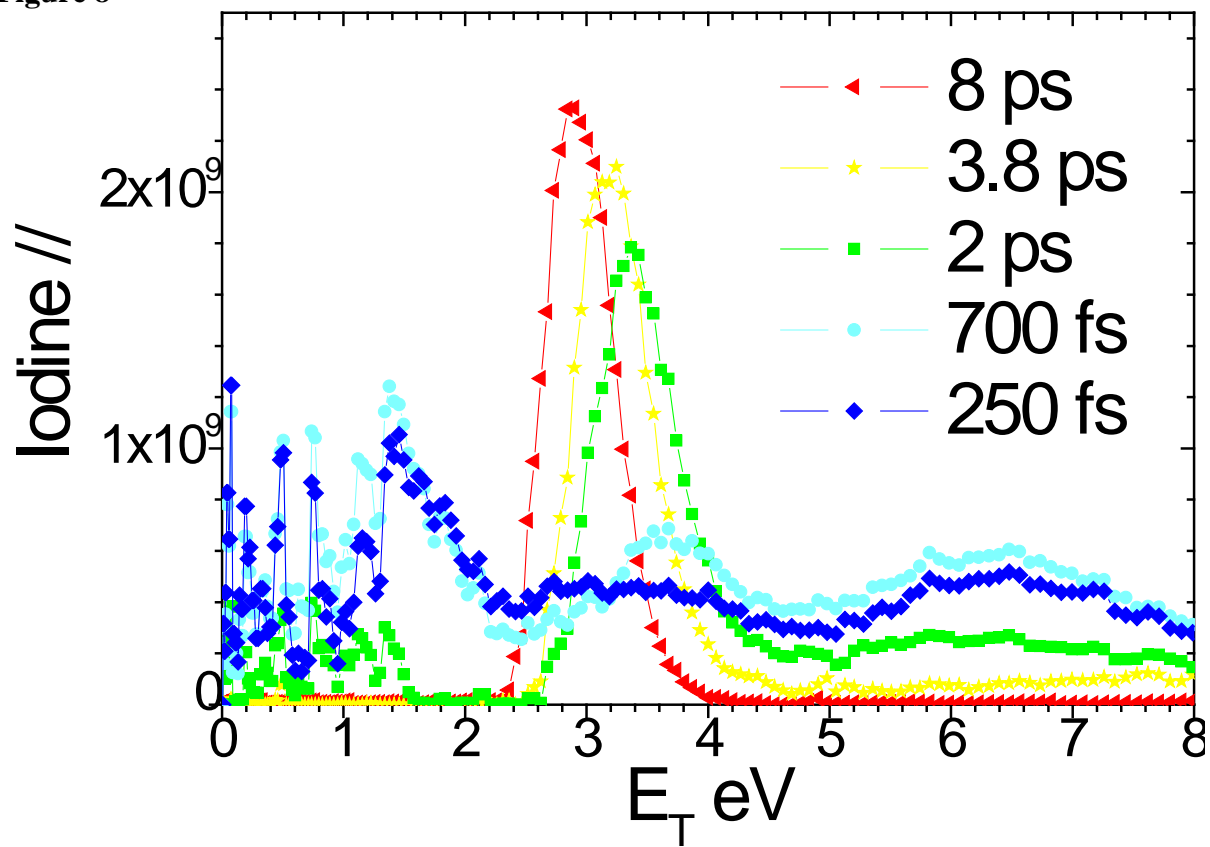


Figure 9

