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Predissociation Dynamics of B State of Methyl Iodide with Femtosecond Pump-probe Technique[†]

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The predissociation dynamics of B Rydberg state of methyl iodide is studied with femtosecond two-color pump-probe time-of-flight spectra at pump pulse of 400 nm and probe pulse of 800 nm. The dominant product channels are the CH_3I^+ and CH_3^+ formation. The time-dependent signals for CH_3I^+ and CH_3^+ ions are obtained. Both of the signal curves can be fitted by biexponential decays with time constants of τ_1 and τ_2 , τ_1 is assigned to the lifetimes of high Rydberg states, which can be accessed by absorbing three 400 nm pump pulses and τ_2 reflects the dynamics of B Rydberg state, which is accessed with two pump pulses. The lifetime of B Rydberg state is determined to be about 1.57 ps, which is incredibly consistent with the previous studies. The results were interpreted as a multiphoton dissociative ionization processes.

Key words: Methyl iodide, Predissociation, Pump-probe, Femtosecond

I. INTRODUCTION

With the recent development of ultra-short-pulse laser technology [1], pump-probe technique can be applied to investigate the ultrafast phenomena in real time [2,3]. Typically in pump-probe experiment, a short laser pulse prepares an excited state and a second pulse probes the change of population in the excited state by multiphoton ionization, fluorescence depletion, or other spectroscopic techniques. The time-dependent population can reflect the internal vibrational energy redistribution (IVR) dynamics or photodissociation dynamics in real time. Therefore, the studies of the evolution of molecular excited states in real time scale have been realized via pump-probe scheme.

Methyl iodide as a prototype molecule has been extensively studied in a wide range of areas, such as clusters [4], gas phase conditions [5], surface [6], intense laser field [7], solution [8], and so on. The absorption spectra of methyl iodide have shown several obvious bands [9], which were assigned to A, B, C, and D bands, respectively. Lots of experiments have been carried out to reveal the nature of excited states. But, there is still some disagreement among them.

The A state is a broad absorption band without observed vibronic structure, which arises from an electronic transition involving a nonbonding 5p electron excitation to a C–I antibonding orbital. A lifetime of 70 fs was deduced by Bersohn from anisotropy parameter β of I^+ [10]. Knee's study showed that the photodis-

sociation lifetime is less than 500 fs using picosecond real-time method [11]. In 1998, Zewail and co-workers measured the A band lifetime using time-resolved kinetic energy time of flight (KETOF) mass spectrometry [12], and the reaction time was determined to be 125 fs. A recent work [5] was done to measure the reaction times of several channels of the C–I bond rupture of methyl iodide from the A state, by a combination of a femtosecond laser pump-probe scheme and velocity map imaging techniques. This work revealed unprecedented details about the A state.

The Rydberg states of methyl iodide arise from electronic transitions from a 5p iodide orbital to a higher atomic Rydberg orbital, such as the 6s or 6p of the iodide atom. The Rydberg series start at 200 and 184 nm with two distinct bands termed as the B and C states. As the first Rydberg state, the dynamics of B state has been studied by many groups. From the absorption spectra of the B state [13], we can know that the origin transition is remarkable stronger than others. Using spontaneous resonance Raman scattering, the lifetime of the electronic origin band was measured to be 0.5 ps [13]. Through resonance enhanced multiphoton ionization linewidth measurement [14], the lifetime of B state is determined to be 0.87 ps (origin). Baronavski directly measured the lifetime of B state using tunable deep UV femtosecond photoionization spectroscopy; the lifetime of origin band is 1.38 ps [15,16]. The next Rydberg states result from a promotion to the 6p orbital, and these are also split into the $^2\text{E}_{3/2}$ at 170 nm (the D state) [17] and the $^2\text{E}_{1/2}$ state at 157 nm [18]. Janssen *et al.* reported time and mass resolved femtosecond studies of CH_3I [19,20], the 6p and 7s Rydberg states are accessed using two photon excitation near 310 nm followed by multiphoton ionization. The lifetimes for the 6p and 7s vibrationless levels are 166 and 131 fs,

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respectively.

In this paper, we report the time-resolved measurement of the decay dynamics of excited methyl iodide using femtosecond multiphoton ionization, the B Rydberg state is reached by two pump pulses, the high Rydberg states is also achieved by three pump pulses, the evolution of these states is monitored in real time by probe pulse, the lifetimes of origin band of B state and the high Rydberg states are determined, the first one shows great agreement with the previous direct measurement and the high Rydberg states display a fast decay dynamics, this work reveals more details about the Rydberg states of methyl iodide.

II. EXPERIMENTS

The experiments were performed using an ion velocity imaging system, which has been described elsewhere [21]. This system is very similar to that Eppink and Parker reported [22,23]. It consists of two stainless steel chambers that are pumped with separate turbomolecular pumps. The first chamber houses a pulsed valve with a 0.6 mm nozzle. The samples (99.9%) were purchased commercially without additional purification. The sample mixture was prepared with methyl iodide seeded in helium. The laser enters the second chamber in a direction that is perpendicular to the molecular beam and intercepts the molecular beam. The ion optics of the time of flight (TOF) mass spectrometer (TOF-MS) consists of three plates: a repeller, an accelerator, and a ground plate, which is the entrance to the flight tube. High voltages of the appropriate ratio for ion imaging are applied to the repeller and accelerator to focus the ions into the flight tube that followed the molecular beam flight direction. The typical voltages in our experiment are 1700 and 1260 V to obtain good focus. The detector assembly consists of a dual microchannel plate (MCP) and a fast P47 phosphor screen. A charge coupled device (CCD) camera and a photomultiplier tube are mounted behind the screen to collect images and TOF mass spectra, respectively.

Our femtosecond laser system consists of an oscillator and a chirped regenerative amplifier with a stretcher and compressor. The femtosecond laser seed pulse is generated in a self-mode-lock Ti:sapphire oscillator pumped by a diode solid state laser, this oscillator provides a narrow femtosecond pulse (~ 20 fs) with average power 450 mW and repetition rate 76 MHz. The output pulse is temporally stretched before admitting into a chirped regenerative amplifier pumped by a Q-switched Nd:YLF laser with an average power 8 W at working frequency 1 kHz. The chirped regenerative amplifier outputs a femtosecond pulse with 1.4 mJ/pulse at working frequency 1 kHz. The amplified pulse is subsequently compressed to obtain short femtosecond pulse with 1 mJ/pulse.

The fundamental light is frequency doubled by a beta

barium borate crystal (BBO type I) to produce the second harmonic generation (SHG) pulse, centered at about 400 nm, the output of BBO is separated into SHG and fundamental pulses by a dichroic mirror, which reflects the 400 nm laser pulse and transmits the fundamental one. The fundamental pulse subsequently passes a step-motor-controlled optical delay stage as a probe pulse and the SHG pulse works as pump pulse, both pump and probe laser pulses are coaxially aligned with another dichroic mirror and focused ($f=250$ mm) onto the molecular beam. The diagram of the experimental apparatus is shown in Fig.1.

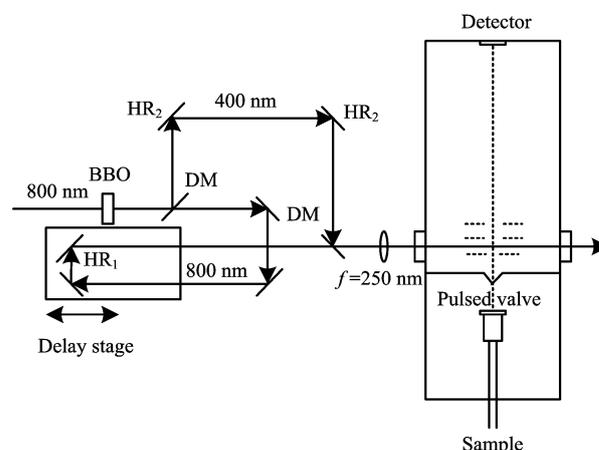


FIG. 1 Diagram of the experimental apparatus. HR₁=high reflectivity mirror of 800 nm; HR₂: high reflectivity mirror of 400 nm; DM: dichroic mirror, 400 nm reflection and 800 nm transmission; BBO: BBO crystal for second harmonic generation.

The pulse width of the fundamental laser is measured to be 80 fs. The power of two pulses is optimized to obtain a good two-color signal. The typical pump laser power was used about 30 μ J/pulse. The probe laser power was 103 μ J/pulse. To avoid space charge effects, care was taken to avoid both laser pulses focusing on the molecular beam. The formation of cluster is also minimized by performing the photolysis on the rising edge of the molecular beam pulse. The time delay between the pump and probe pulse varies with a micrometer driven optical delay stage, which is controlled by the computer.

III. RESULTS AND DISCUSSION

In Fig.2 a typical mass spectrum is shown, which is obtained by interaction of methyl iodide with pump and probe pulses at the same time. The ion signal intensity obtained at zero delay time is 50 times stronger than that produced by the pump or probe pulse, individually. Three peaks are observed corresponding to the CH₃⁺ fragment, the CH₃I⁺ parent ion and the very weak I⁺ fragment, respectively. The absolute magnitude of the

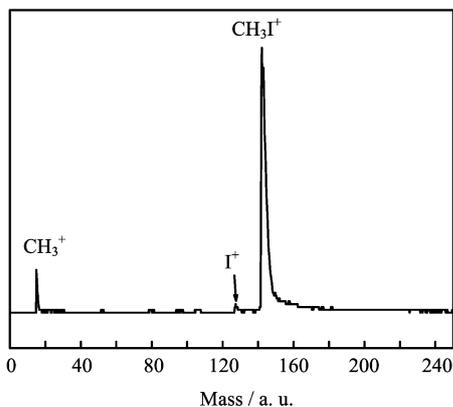


FIG. 2 The TOF spectrum of CH_3I obtained for pump (400 nm) and probe (800 nm) pulses at zero delay time.

CH_3I^+ and CH_3^+ fragment peaks are about several orders stronger than the I^+ fragment peak. Therefore, the dominant channels are the formation of CH_3I^+ and CH_3^+ fragment. The ratio of the area of the CH_3I^+ peak to that of the CH_3^+ peak is $I(\text{CH}_3\text{I}^+)/I(\text{CH}_3^+)=17$. Because the ionization potential of CH_3I is 9.538 eV [24], which is lower than the appearance energies of CH_3^+ and I^+ [25,26], thus, the formation of CH_3I^+ is energetically more favorable than others. This is similar to the previous results, that the signals of fragments are up to two orders of magnitude smaller than the signal of parent ions [20].

The time-dependent ion signals of CH_3I^+ and CH_3^+ are represented in Fig.3. The signal of I^+ is too weak to extract the pump-probe signal. In negative time-delay direction, which means that the fundamental light (800 nm) is used as the pump pulse, no any enhancement of signals was observed. On the contrary, the signals show strong enhancement in positive time-delay direction when the SHG pulse serves as the pump source. So, in this experiment the molecules are excited by the SHG pulse and subsequently ionized by the fundamental pulse.

The ion signal is the convolution result of instrumental response function with the actual dynamical delay signal [27]. The instrumental response function can be written in Gaussian shape, under this experimental condition that the width of instrumental response function is 300 fs. The actual dynamical delay signal can be represented by several exponential functions.

For the time-dependent ion signals of CH_3I^+ and CH_3^+ in Fig.3, as the delay time increases from the zero delay point, the signals decreases very rapidly just during the beginning 400 fs, after that, the signals show slow decreasing. The decay presents the time-dependent population of the excited state, the population relates with the dynamics such as intramolecular vibration energy distribution, intersystem crossing, dissociation, and so on. The time constant of exponential decay displays the lifetime of the excited states reached

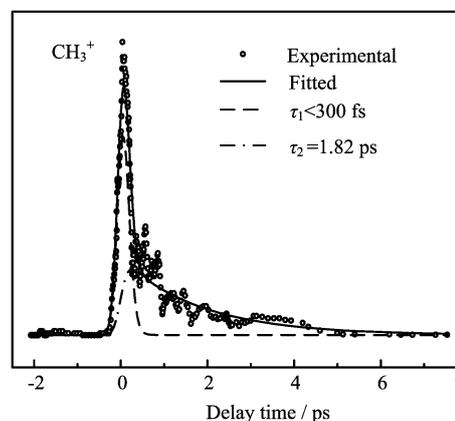
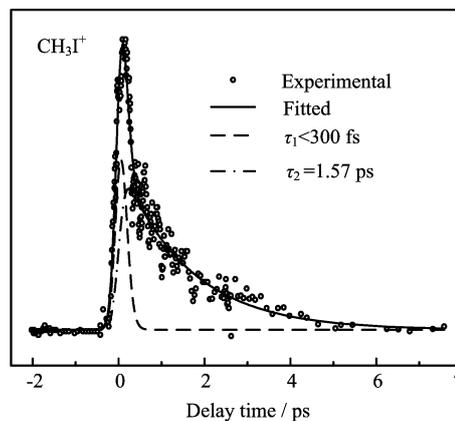


FIG. 3 Time-dependent signals of CH_3I^+ and CH_3^+ .

by the pump pulses.

The time-dependent signals of CH_3I^+ and CH_3^+ are fitted by biexponential decays with time constants τ_1 and τ_2 , both of the fragments exhibit significant enhancement at the zero overlap of the two laser pulses typically associated with strong field effects. Figure 4 shows the energy level diagram of methyl iodide and its cation, only those states relevant to this study are shown. With the wavelength employed in this study, ions can be produced through the multiphoton absorption of the pump and probe pulses. There are two mechanisms that can produce the CH_3I^+ and CH_3^+ ions. Channel (1): the B Rydberg state is accessed by two pump pulses, subsequent absorbing three probe pulses will produce the CH_3I^+ parent ion, addition absorbing of a probe pulse will reach the ionic \tilde{A} state, which correlates to the $\text{CH}_3(^2\text{A}_2'')+\text{I}^+(^3\text{P}_2)$ dissociation products, this state can undergo an internal conversion to the \tilde{X} state and a vibrational predissociation takes place to reach the channel $\text{CH}_3^+(^1\text{A}_1)+\text{I}^+(^2\text{P}_{3/2})$ [28]. Channel (2): the molecules are excited by three pump pulses and another probe pulse to produce the CH_3I^+ parent ion, subsequent absorbing one more probe pulse to reach $\text{CH}_3^+(^1\text{A}_1)+\text{I}^+(^2\text{P}_{3/2})$ fragmental channel. For both of the channels, in order to produce I^+ fragment,

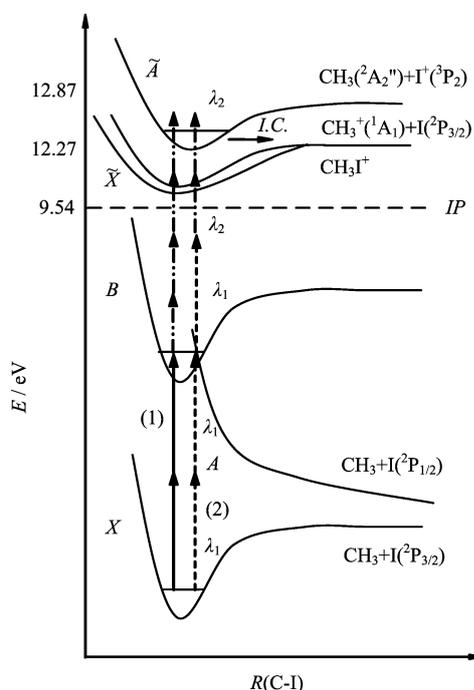


FIG. 4 Energy level diagram of methyl iodide and its cation, Channel (1) and (2) represent the two possible ways to form CH_3I^+ and CH_3^+ , λ_1 and λ_2 denote the pump and probe pulses, respectively. The diagram is based on energy level diagram in Ref.[25,29,30].

more probe pulses absorption are necessary. Apparently, CH_3^+ fragmental channel is easy to reach than I^+ fragmental channel.

As all the above fittings are convoluted with the instrumental response function (300 fs). Therefore, the fast dissociation, τ_1 has a lifetime short than 300 fs, which was described as pulse width limited lifetime in Ref.[32]. τ_1 was assigned to a dissociative ionization process by absorbing three 400 nm pump pulses and sequent one or two 800 nm probe pulses, as shown in Channel (2) of Fig.4, the parent ions and CH_3^+ fragment could be produced, respectively. Under this experiment condition, due to the high pump power, the multiphoton absorption is easy to happen. The methyl iodide can be excited to very high Rydberg state after three photons absorption. These Rydberg states being just under the ionization potential of methyl iodide, might be $8s'$, $6d'$ in addition to $7p'$ and $8p'$ which were assigned by Wang *et al.* [31], these Rydberg states converge on the $^2E_{1/2}$ ionization limit. Due to the bandwidth inherent to the femtosecond pulse, and the high density of highly excited Rydberg states, more than one of these states can be accessed simultaneously. There are few reports about this region. As for the short lifetime corresponding to a fast dynamics of the Rydberg states, similar phenomena have also been observed in study of acetone, its high Rydberg states have a lifetime shorter than 150 fs, which have been assigned to

the interaction of these states with the neighboring valence states [32,33]. The Rydberg states of CH_3I and CD_3I were studied [19,20] using two-photon femtosecond excitation, the dynamics of the 3_0^0 transitions of the 6p state, and the 0_0^0 transition of the 7s state were determined, the decay time were $\tau(6p3_0^0)=141\pm 3$ fs, and $\tau(7s0_0^0)=115\pm 11$ fs.

The decay time, τ_2 , was considered ionization through the origin of B state. The room temperature B state absorption spectrum of CH_3I vapor is in the 195-202 nm region [13], the strongest vibronic bands are the origin band and progressions in the ν_2 mode, the band positions for origin and ν_2 mode are at 201.2 and 196.7 nm, respectively. Since the bandwidth of our pump pulse is less than 5 nm, hence, only the origin band could be accessed in the excitation of two 400 nm pump pulses. This state is a bound state, but a strong coupling to the repulsive A band leads to predissociation and can be accessed by absorbing two pump pulses (400 nm), the subsequent dissociation is monitored by the probe pulse (800 nm), which ionizes the excited molecule by absorbing three or four probe pulses, as shown in Channel (1) of Fig.4. The observed decay times are 1.57 and 1.82 ps for CH_3I^+ and CH_3^+ , respectively. The lifetimes of CH_3I^+ and CH_3^+ are close but with a discrepancy of about 0.25 ps. The lifetime of CH_3I^+ shows great consistency with the previously results obtained by Baronavski *et al.* [15,16]. They measured the lifetime of B state directly, the difference maybe comes from the discrepancy of excitation method, they used single photon excitation but we used multiphoton excitation. Generally, the results obtained by direct measurement are longer than the indirect results from Wang and Syage [11,12], these indirect methods are influenced by many factors, such as the spectral width of the excited light, pressure, Doppler and laser power broadening, line shape, and so on. It is extremely difficult to obtain the lifetime via measure of the line widths. There are some theoretical studies about the Rydberg state predissociation dynamics. Quantum time-dependent wavepacket method was used to calculate the transients of CH_3I and CD_3I [34], it was found that the deuterated methyl iodide has longer lifetime due to the mass effect, which was in agreement with the experimental results. Donaldson *et al.* presented a theoretical model for the predissociation of methyl iodide [35], empirical B state potential energy surfaces were derived, and the intersections between B state and the dissociative state were calculated, the results suggested that methyl iodide might exhibit mode-specific photofragmentation.

The time-dependent ion signals of CH_3I^+ and CH_3^+ show the similar kinetics which confirms our assumption that they are both formed by ionization from the same state as discussed above. The same trend was also observed in the study of aryl halides by Kadi *et al.* [36]. The only difference is the number of probe pulse for ionization of the molecule. The fast dissociation, τ_1 is the

same for CH_3I^+ and CH_3^+ ions, for τ_2 , the decay time of CH_3^+ just shows a little longer than the decay time of CH_3I^+ . We suggest that it may be due to the propagation of a wave packet in the CH_3I^+ ground state. The wave packet moves from the region initially excited by probe pulses into a region where the Franck-Condon (FC) factors are more favorable for the $\text{CH}_3^+ + \text{I}$ fragmentation. Absorption of another probe pulse would then lead to the formation of CH_3^+ . The lifetime of CH_3^+ then reflects both the parent CH_3I ionization and subsequent ion fragmentation.

We exclude the possibility that ions come from the ionization of neutral radical or atom, there are two reasons, first, if the ion is formed from neutral radical or atom, it should be an exponential increase, we just observe exponential decrease in our experiment condition. Therefore, the ion formed from ionization of neutral radical or atom is very rare. Second, the ionization potential for CH_3 radical is 9.838 eV [37], this means to ionize them, seven probe pulses absorbing is necessary. This channel is unfavorable in energy. This conclusion can be supported by the work of Chen *et al.* [38,39]. They studied the photodissociation dynamics of the acetone S_2 (n,3s) Rydberg state using femtosecond pump-probe mass-selected multiphoton ionization spectroscopy. In their experiment, they found that the ions coming from the ionization of the neutral CH_3 radical is sensitive to the probe wavelengths. When the wavelengths of probe pulse is off-resonance, the signals of CH_3^+ ion are dominated by a nearly wavelength-independent component that arise from dissociative ionization of initial state and acetyl intermediate.

Compared to the previous results, our study confirms the previous direct results, we also observe a fast dynamics of the high Rydberg states due to the multiphoton absorption of the pump pulses, this study further demonstrates the complex nature of Rydberg states, and reveals more information about the predissociation of B Rydberg state.

IV. CONCLUSION

The predissociation dynamics of B Rydberg state of methyl iodide has been studied with femtosecond two-color pump-probe time-of-flight spectrum at pump pulse of 400 nm and a probe pulse of 800 nm. The dominant channels are the formation of CH_3I^+ and CH_3^+ fragments. The time-dependent signals for both fragments are obtained, each of them can be fitted by bi-exponential decays with time constants τ_1 and τ_2 , τ_1 is assigned to the excitation of high Rydberg states by three 400 nm pump pulses and displayed a fast dynamics. And τ_2 reflects the dynamics of B Rydberg state, which is accessed with two pump pulses. The lifetime of B Rydberg state is determined to be 1.57 ps, which shows incredible consistent with the previous work. By the way, the two possible channels to produce CH_3I^+

and CH_3^+ fragments are assumed to interpret the experimental results, Channel (1): the B Rydberg state is accessed by two pump pulses, subsequent absorbing three probe pulses will produce the CH_3I^+ parent ion, in additional absorbing of another probe pulse will reach the ionic \tilde{A} state, which correlates to the CH_3 ($2A_2''$)+ I^+ (3P_2) dissociation products, this state can undergo an internal conversion to the \tilde{X} state and a vibrational predissociation takes place to reach the channel CH_3^+ (1A_1)+ I ($^2P_{3/2}$). Channel (2): the molecules are excited by three pump pulses and another probe pulse to produce the CH_3I^+ parent ion, subsequent absorbing another probe pulse to reach CH_3^+ (1A_1)+ I ($^2P_{3/2}$) fragmental channel. Our work confirms the previous results and provides more details about the Rydberg states of methyl iodide.

V. ACKNOWLEDGMENTS

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