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Probing Ultrafast Dissociation Dynamics of Chloroiodomethane in the B Band by Time-Resolved Mass Spectrometry *

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Ultrafast dissociation dynamics of chloroiodomethane (CH_2ICl) in the B band is studied by femtosecond time-resolved time-of-flight (TOF) mass spectrometry. Time-resolved TOF mass signal of parent ion (CH_2ICl^+) and main daughter ion (CH_2Cl^+) are obtained. The curve for the transient signal of CH_2ICl^+ is simple and can be well fitted by an exponential decay convoluted with a Gaussian function. The decay constant determined to be less than 35 fs reflects the lifetime of the B band. Significant substituent effects on photodissociation dynamics of CH_2ICl compared with CH_3I are discussed. The dissociation time from the parent ion CH_2ICl^+ to the daughter ion CH_2Cl^+ is determined in the experiment. The optimized geometry of the ionic state of CH_2ICl and the ionization energy are calculated for further analysis of the measurements. In addition, compared with the parent ion, a new decay component with time constant of ∼596 fs is observed for CH_2Cl^+, and reasonable mechanisms are proposed for the explanation.

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The photochemistry of alkyl halides has attracted substantial attention in recent years, since it has been realized that halogen atoms and halogen-containing radicals are efficient chemical species for the destruction of stratospheric ozone.[1] Alkyl halides may release halogen atoms, like Cl, Br and I atoms, or produce halogen-containing radicals following UV absorption. The decay of these harmful pollutants in the atmosphere depends largely on their photodissociation rates and product channels in the UV region. Thus it is significant to determine their photophysical and photochemical behavior for assessing their environmental impact.

Alkyl iodides are particularly interesting since they offer a unique opportunity to understand the effect of size and structure of the alkyl radicals on the dynamics of dissociation. As the simplest alkyl iodide, photodissociation of CH_3I in the A and B bands has been the active focus and serves as a paradigm for research into photodissociation processes that occur along a repulsive potential surface of the excited state.[2−4]

As an alternative molecule with chlorine-substituted, CH_2ICl has received less attention mainly because the dissociation pathways become more complicated. Most of the research on CH_2ICl is focused on dissociation dynamics of the A band[5] while photolysis of the B band has been seldom investigated so far. However, CH_2ICl, as a typical dihalomethane, is an interesting molecule to examine how the presence of the second C–X chromophore perturbs the states associated with the C–I chromophore. Kwok *et al.* have investigated the B-band short time dissociation dynamics of CH_2ICl in solution by the resonance Raman spectra. Their experimental result suggests that the dissociation or motion of the initially excited wave packet out of the Franck–Condon region for the B-band of CH_2ICl is substantially faster than solvent dephasing collision times.[6] However, to the best of our knowledge, there is still no any exact data on how fast this dissociation or motion for the B-band is.

In this Letter, we study the photodissociation dynamics of CH_2ICl in the B-band by femtosecond time-resolved TOF mass spectroscopy. With the advent of the femtosecond pump-probe technique,[7−13] the lifetime of CH_2ICl in the B-band is first measured. Time-resolved characters of the main daughter ion (CH_2Cl^+) are also obtained and discussed. The results are compared with CH_3I to obtain more insights into photodissociation dynamics of alkyl iodides.

The seed beam of the femtosecond (fs) laser system was generated by a commercial Ti:sapphire oscillator pumped by a cw second harmonic of an Nd:YVO_4 laser, and then amplified by an Nd:YLF pumped regenerative amplifier to generate a 1 kHz pulse train centered at 800 nm (35 fs pulse width) with the maximum energy of 1 mJ/pulse. This light was split into

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two beams, one of which was used to pump an optical parameter amplification (OPA) system to produce the pump light (384 nm). The other beam was served as the probe beam, which was temporally delayed relative to the pump beam by a computer-controlled linear translation stage (PI, M-L01.4A1). The two laser beams were introduced into the vacuum chamber collinearly with a dichroic mirror, and were focused with fused silica lens of $f = 500$ and 350 mm, respectively. During experiments, typical pulse energies were 3μJ for the pump pulse and 20 μJ for the probe pulse. The cross-correlation of 180 fs FWHM for the pump and probe beams was measured. The cross-correlation function was used in the subsequent deconvolution of the time-resolved data and generally permits unambiguous determination of time constants down to about 20% of the cross-correlation FWHM,[14] i.e., ∼35 fs in the current measurement.

The velocity map imaging (VMI)-TOF setup was introduced previously,[15] which is similar to that designed by Eppink *et al.*[16] It consists of a molecular-beam source chamber and an ionization-flight detection chamber. The detection chamber was kept below 5×10^{-5} Pa with the molecular beam on. The sample CH_2ICl (99.8% purity) seeded in helium was expanded into the source chamber with a stagnation pressure of 2 atm through a pulsed nozzle (general valve, with a 0.49 mm orifice) with the repetition rate of 10 Hz. The supersonic molecular beam is collimated by a conical skimmer and intersects perpendicularly with the two laser beams in a two-stage ion lens region. Ions are extracted into a 50 cm field-free region. At the end of the time-of-flight tube, the ions strike a two-stage microchannel plate (MCP) detector backed by a phosphor screen. The signals on screen are taken by a photomultiplier tube connected with an oscilloscope. Each TOF mass spectrum is counted 300 times by the labview acquisition program.

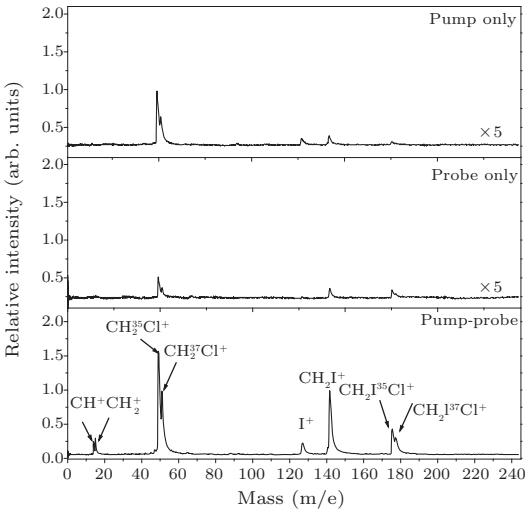

Fig. 1. Typical TOF mass spectra obtained by interaction with the pump beam, probe beam and pump-probe beams at the delay time of zero, respectively.

The peak of the B band of CH_2ICl is estimated to be at 6.46 eV from the absorption spectrum.[17] In our experiment, CH_2ICl was pumped to the B band by two-photon absorption at 384 nm, and then was photoionized by further absorption of 800 nm photons. Figure 1 shows the typical TOF mass spectra obtained by interaction with pump beam, probe beam and pump-probe beams (at zero delay time), respectively. Isotopes of chlorine (Cl^{35} and Cl^{37}) can be well resolved in mass spectra. Several peaks are clearly observed, corresponding to CH^+, CH_2^+, CH_2Cl^+, I^+, CH_2I^+ and CH_2ICl^+, respectively. It can be characterized by multichannel dissociation. However, CH_2Cl^+ is the most dominant fragment ion generated in the B-band photodissociation induced by the femtosecond ultrashot pulse. Here we concentrate on this main dissociation channel. For the other fragments, like CH_2I^+, the time transient signal would also be interesting, and we will probably investigate in the further plan. It is noted that the yield of CH_2Cl^+ is much higher than that of the parent ion, i.e. cation CH_2Cl^+, which indicates that the molecule in such a measurement absorbs more photons than ionization energy and arrives at the high excited states in the cation.

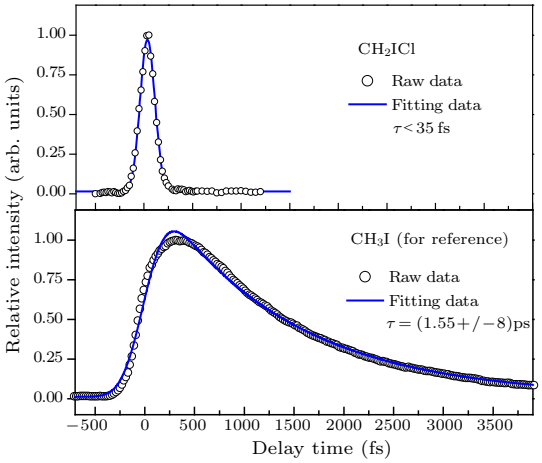

Fig. 2. Comparison of time constant of the B band of CH_2ICl and CH_3I.[3]

Figure 2(a) shows the time-resolved parent ion signal (CH_2ICl^+) after two-photon excitation of the B-band at 384 nm as a function of the pump-probe delay. For CH_2ICl^+, the decay profiles can be well fitted with single exponential with time constant of <35 fs convoluted with a Gaussian describes the instrument response function. The time constant of <35 fs reflects the lifetime of the B-band. The break time for the C–I bond or the C–Cl bond is less than 35 fs. It is reasonable to propose that the B-band dissociation is a typical direct dissociation of electronically excited state. It is greatly different from our previous work on the dissociation dynamics of the B-band of CH_3I.[3] For reference, the time-dependent ion signal for the B-band of CH_3I is also shown in Fig. 2 as reference. The dissociation dynamics of the B-band is attributed to predissociation induced by the crossing between the

B-band and the repulsive A-band. The predissociation lifetime was measured to be ∼1.55 ps.

The molecular structure of CH_2ICl is the product of Cl-substituted of CH_3I. The dissociation dynamics of the A-band of CH_2ICl are similar to CH_3I, both being direct dissociation on repulsive potential energy surface (PES). However, the dissociation dynamics of their B-band are totally different. Kwok *et al.* have investigated the B-band short time dissociation dynamics of CH_2ICl and CH_3I by the resonance Raman spectra.[6] Their experimental and calculation results show that CH_2ICl B-band short-time photodissociation dynamics have significant substituent effects relative to the B-band of CH_3I. It is attributed to the presence of the C–CI chromophore n(X) *(C–X) transitions (peak at ∼170 nm) that are close to the B-band absorption of CH_2ICl but absent in CH_3I. As mentioned above, these substituent effects do not influence the A band dissociation dynamics too much. This is likely due to the C–CI chromophore n(X) *(C–X) transitions (∼170 nm) closer to the B-band absorption (∼192 nm) of CH_2ICl than the A-band absorption (∼270 nm). Here it is also reasonable to propose that the molecules in the B band undergo a fast internal conversion to the A band and then dissociate.

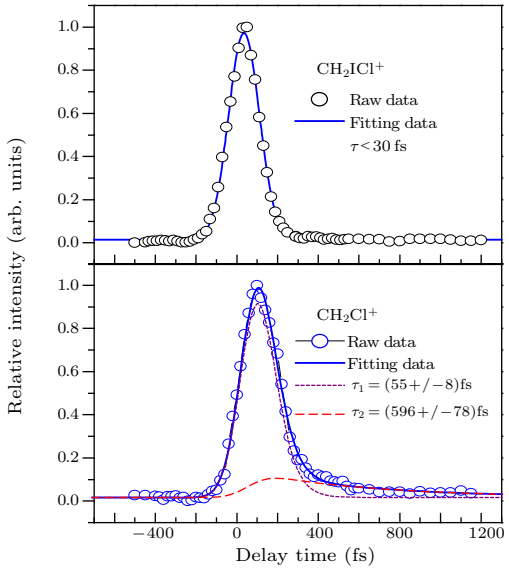

Fig. 3. Transient signals of parent ion (CH_2ICl^+) and main daughter ion (CH_2Cl^+).

In Fig. 3, we also show the time-resolved mass signal of the dominant fragment ion (CH_2Cl^+) as a function of the pump-probe delay. The decay profiles cannot be simply fitted with a single curve. It is the sum of two exponentials with lifetimes of ∼55 fs and ∼596 fs convoluted with a Gaussian which describes the instrument response function. The dynamics of the short component of ∼55 fs is due to the dissociative ionization of parent ion CH_2ICl^+ since it has a similar trend with parent ions. After the pump-probe process, the parent ion of CH_2ICl^+ is generated first,

$$CH_2ICl + 2h\nu_{pump} + nh\nu_{probe} \rightarrow CH_2ICl^+. \quad (1)$$

Due to the high excess energy, CH_2ICl^+ ions dissociate soon and generate fragment ions CH_2Cl^+ and I atoms,

$$CH_2ICl^+ \rightarrow CH_2Cl^+ + I. \quad (2)$$

The time for this dissociation process can be obtained by calculating the time shift of time-dependent ion signals of parent and daughter ions.

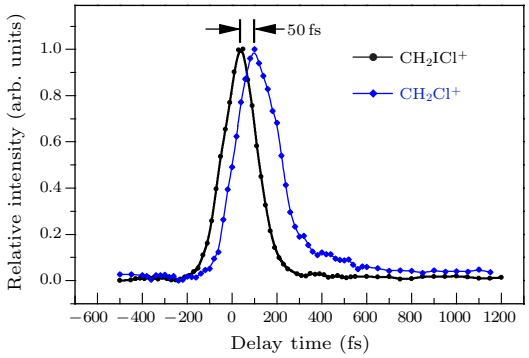

Fig. 4. The time shift of time-dependent ion signals of parent ion (CH_2ICl^+) and main daughter ion (CH_2Cl^+).

According to Fig. 4, the time shift of time-dependent ion signals of CH_2ICl^+ and CH_2Cl^+ is measured to be about ∼50 fs. Therefore the dissociation time for parent ion CH_2ICl^+ to daughter ion CH_2Cl^+ is determined to be ∼50 fs in this experiment. Density functional theory (DFT) calculations are also performed for further analysis and discussion of the cations. The optimized geometry of ground state and ionic state of CH_2ICl are obtained on the level of B3LYP/LANL2DZ via Gaussian program.[18] The obtained ionization energy is 10.12 eV, which is very close to the experimental value of 10.30 eV via MATI measurements.[19] The difference of the calculation with the chosen basis is only 1.7% away from the measurements that indicates the accuracy of the calculation. After the preparation of the B state with absorption of two photons at 384 nm, the probing with three photons at 800 nm is enough to ionize the molecules. The optimized geometry of the ground and the ionic states are also obtained. It is found that the ionization changes the geometry obviously. The C–I bond length prolongs from 0.2179 nm of the neutral CH_2ICl to 0.2276 nm of the cation CH_2ICl^+. The calculated results support that the cations are prior to fragmentation via the C–I bond compared with the neutrals.

Interestingly, as shown in Fig. 3, compared with the parent ion, a new decay component with time constant of ∼596 fs is observed for the fragment ion CH_2Cl^+. It is very elusive. Knopp *et al.* have found similar phenomenon in the photodissociation of C_2H_5I induced by femtosecond ultrashort pulse.[20] They attributed this channel to the dissociation of C_2H_5 radicals. Here we also give one reasonable explanation to this new decay component. After two-photon absorption of the pump beam, CH_2ICl is pumped to the

B-band. Then the B-band excited CH_2ICl undergo ultrafast dissociation to the radical CH_2Cl and I atoms,

$$CH_2ICl + 2h\nu_{pump} \rightarrow CH_2Cl + I. \quad (3)$$

The dissociation time constant is less than 35 fs, the pump beam duration. Therefore, the radical CH_2Cl can still absorb pump beam to excited-state CH_2Cl^*,

$$CH_2Cl + 2h\nu_{pump} \rightarrow CH_2Cl^*. \quad (4)$$

This excited state can be probed by the probe beam

$$CH_2Cl + n'h\nu_{probe} \rightarrow CH_2Cl^+. \quad (5)$$

Therefore this channel also has a contribution to the ion signal of CH_2Cl^+, which corresponds to the new component. The time constant of this component is determined to be ∼596 fs. The decay is attributed to the secondary dissociation process of CH_2Cl radical

$$CH_2Cl^* \rightarrow CH_2 + Cl. \quad (6)$$

All the dissociation mechanisms discussed here are shown in Fig. 6.

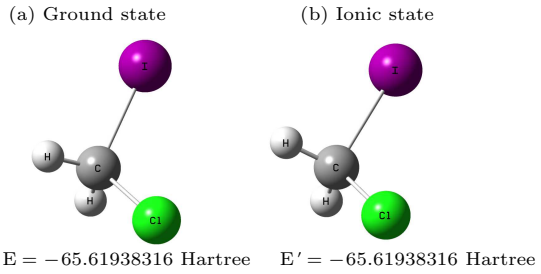

Fig. 5. The optimized geometry of CH_2ICl in the ground (a) and the ionic state (b).

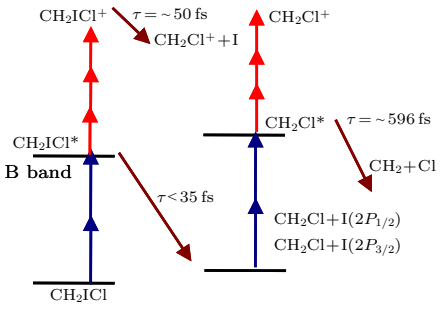

Fig. 6. Dissociation mechanism of CH_2ICl in the B-band.

In conclusion, ultrafast dissociation dynamics of chloroiodomethane in the B band have been studied by femtosecond time-resolved TOF mass spectroscopy. The main results can be concluded to the following three points. (1) Time-dependent signals of the parent ion (CH_2ICl^+) and the main daughter ion (CH_2Cl^+) are obtained. The curve for CH_2ICl^+ is quite simple and can be well fitted by an exponential decay convolution with a Gaussian function. The decay constant reflects the lifetime of the B band, which is determined to be less than 35 fs. Photodissociation dynamics have significant substituent effects relative to the B band of CH_3I, due to the presence of the C-CI chromophore n(X)←*(C–X) transitions (peak at ∼170 nm) that are close to the B-band absorption. (2) The optimized geometry of the ionic state of CH_2ICl and the ionization energy of 10.12 eV are obtained on the level of B3LYP/LANL2DZ via Gaussian program. DFT calculation supports that the cations are prior to fragmentation via the C–I bond compared with the neutrals. The dissociation time from parent ion CH_2ICl^+ to daughter ion CH_2Cl^+ is determined to be ∼50 fs in the experiment. (3) A new decay component with time constant of ∼596 fs is observed for CH_2Cl^+. It is attributed to a secondary dissociation process of CH_2Cl radical generated in the dissociation.

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