

Dissociation dynamics of CH₃I in electric spark induced breakdown revealed by time-resolved laser induced breakdown spectroscopy

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ABSTRACT

The electric discharge spark dissociation of gas CH₃I is found to be similar to its femtosecond laser photodissociation. The almost identical spectra of the two processes show that their initial ionization conditions are very similar. The initial ionization followed by molecular fragmentation is proposed as the dissociation mechanism, in which the characteristic emissions of I⁺, CH₃, CH₂, CH, H, and I₂ are identified as the dissociation products. The emission band of 505 nm I₂ is clearly observed in the time-resolved laser induced breakdown spectroscopy (LIBS). The dynamic curve indicates that I₂ molecules are formed after the delay time of ~4.7 ns. The formation of I₂ molecule results from the bimolecular collision of the highly excited iodine atom I⁺(⁴P) and CH₃I molecule. This dynamical information can help understand the process of electric discharge spark dissociation of CH₃I.

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1. Introduction

Chemical oxygen iodine laser (COIL) is applied in the military and industry because of its high-power and high-energy output. Electric-COIL (E-COIL) is an improvement direction of COIL [1], where a high-voltage pulse is applied to decompose CH₃I molecule to produce iodine atoms in the excited state as the active laser medium. Given its easy gasification and decomposition properties, the CH₃I molecule has the potential to become an ideal active medium as the iodine-containing compound in E-COIL systems. The CH₃I dissociation dynamics under spark discharge is complex, during which multiple reaction pathways lead to various resultant products. Molecular I₂ is formed after the electric spark dissociation of CH₃I. It is a very strong quencher of atomic iodine in excited state I⁺(²P_{1/2}), which has a negative influence in COIL [2,3]. The mechanism of I₂ formation after the photolysis of A-state CH₃I has been analyzed [4–7], where the mixture of inert gases and low concentration CH₃I are excited by UV laser pulse in the jet expansion system. However, these experimental conditions deviate from the plasma environment of electric spark dissociation. In E-COIL, higher concentrations of CH₃I are used for electric spark dissociation. After a high-voltage pulse is loaded between the

electrodes, the CH₃I molecules are ionized and fragmented into high-temperature plasma because of electron collisions. So far, the mechanism of I₂ molecule formation in a plasma environment after CH₃I breakdown is still unclear. Therefore, the study of I₂ formation under plasma environment is helpful for understanding the actual case in E-COIL system.

In the experiment of electric pulse discharge, due to the long electric pulse, it is difficult to record high time-resolved spectra of the electric spark dissociation. Therefore, the femtosecond (fs) pulsed laser induced breakdown (LIB) is used as a simulation for electric spark dissociation. Laser induced breakdown spectroscopy (LIBS) is a plasma-based atomic emission analytical technique. The initial breakdown is induced optically, and its emission mechanism is very similar to that in the electric spark induced breakdown spectroscopy [8]. The electric spark breakdown process can be considered as a high-voltage breakdown followed by a classic arc discharge. Initially, a high-voltage pulse is applied to the electrodes, causing the sample to ionize into a high-temperature plasma. In the fs LIBS, a hot plasma is produced by multiphoton ionization, which makes the initial plasma condition very similar to that in the electric spark breakdown. In this work, the almost identical breakdown emission spectra are obtained by fs laser and electric spark. This result indicates that it is feasible to use fs laser breakdown to simulate an electric spark breakdown. The fs LIBS possesses high time-resolved property to obtain time-resolved spectra, which provides a better description of I₂ formation and CH₃I dissociation. In fs LIBS, the emissions of the plasma

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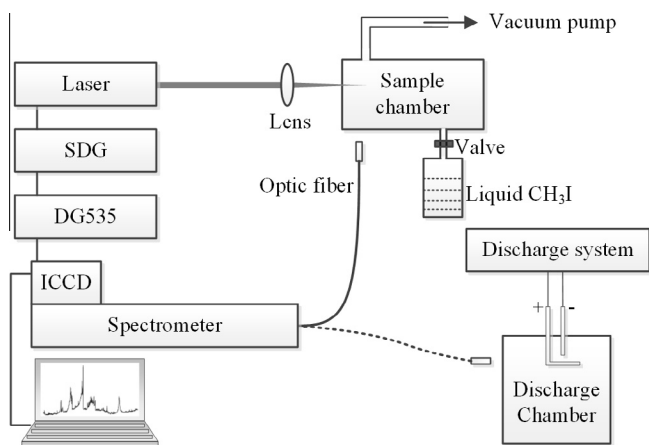


Fig. 1. Experimental setup for the LIBS and the electric spark system.

continuum and the atomic spectral lines emerge as fast decay properties. Therefore, as a secondary emission process, the emission of newly formed I_2 can be distinguished from the spectral line background of the breakdown products. Although the photodissociation dynamics of CH_3I from its A, B, and C excited states have been studied widely [9,10], the studies on the emission spectra of the intermediate species are still scarce. In this work, we utilize fs LIBS to monitor formation process of I_2 molecule and other dissociation products, such as iodine atom I, CH_3 fragment, and CH_2 fragment. In other words, the confirmed emission spectra of intermediate species can be used as the real-time indicators in monitoring the dissociation products in the E-COIL system. In comparison with time-of-flight mass spectrometry, real-time emission spectroscopy is a more practical and convenient technique to monitor the reactions in CH_3I dissociation in E-COIL.

2. Experiment

The LIBS experimental setup is shown in Fig. 1. The fs laser pulse is produced from a Ti: sapphire system (Spectra-Physics)

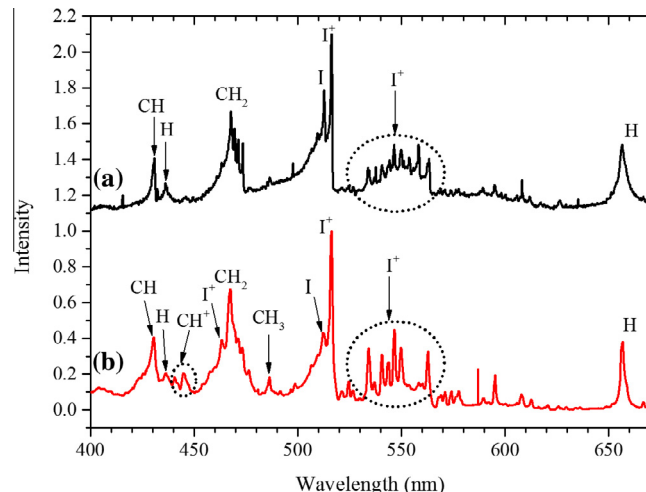


Fig. 2. Time integral emission spectra of CH_3I gas dissociation. (a) 800 nm fs laser photodissociation. (b) Electric spark dissociation.

delivering 110 fs, ~ 0.4 mJ pulse at 800 nm with 1 kHz repetition rate. The laser beam is focused into a sample chamber with a 100 mm focal length lens to provide an excitation intensity of $\sim 2 \times 10^{13}$ W/cm². A straight two-way vacuum stopcock is used as a valve for controlling the flow of CH_3I gas between the chamber and the container of liquid CH_3I . First, the valve is closed to cut off the pipe of liquid CH_3I container, then the air in the sample chamber is pumped out by a vacuum pump. When the air pressure of the chamber is close to that of a vacuum (2 Pa), the valve is opened to release the CH_3I gas into the chamber. The liquid CH_3I is gasified rapidly in the nearly vacuum environment. Hence, the chamber is filled with pure CH_3I gas. In the experiment, the chamber is pumped by a vacuum pump from start to end. Therefore, the liquid CH_3I is gasified all the time, and the chamber is always filled with fresh CH_3I gas for dissociation.

The emission from the sample is collected by a fiber probe connected to a spectrometer (Bruker Optics 250IS/SM) coupled with

Table 1
Observed emission peaks in LIBS and standard spectrum in reference.

Observed spectra (nm)	Identified substance	Standard spectra (nm)	Transition assignment
435.8	H	634.0 ^{a,b}	5 → 2 H-γ line Balmer series
2656.5	H	656.0 ^{a,b}	3D → 2P
512.8	I	511.9 ^a	(³ P ₂)7p 2[1] _{1/2} → (³ P ₂)6s 2[2] _{3/2}
463.2	I*	463.2 ^a	Uncertain
497.7	I*	498.7 ^a	(² D°)6p 3D ₂ → (⁴ S°)5d 3D ₁
516.3	I*	516.0 ^a	(⁴ S)6p 5P → (⁴ S)6s 5S°
533.9	I*	533.8 ^a	Uncertain
537.7	I*	537.0 ^a	Uncertain
540.7	I*	540.7 ^a	(² D°)6p 3D ₂ → (² D°)6s 3D ₂
544.3	I*	543.8 ^a	Uncertain
546.5	I*	546.5 ^a	(⁴ S)6p 5P → (⁴ S)6s 5S°
549.9	I*	549.7 ^a	Uncertain
553.8	I*	552.2 ^a	Uncertain
558.3	I*	559.3 ^a	(² D°)6p 3D ₁ → (⁴ S°)5d 3D ₁
563.3	I*	562.6 ^a	(⁴ S)6p 3P → (⁴ S)6s 3S°
485–512	I ₂	495–512 ^b	D' 3Π _{2g} → 3Δ _{2u}
486.2	CH ₃	485.5 ^c	D ² A ₁ ' → B ² A ₁ '
467.6	CH ₂	461.5 ^d	C → A
430.8	CH	431.0 ^c	A → X
440.6	CH*	439.6 ^d	A → X
444.7	CH*	439.6 ^d	A → X

^a NIST atomic spectra database.

^b Handbook of lasers database.

^c Calculation by energy difference using excited energy level data from reference [16].

^d Excited energy levels are calculated by Gaussian 03 program.

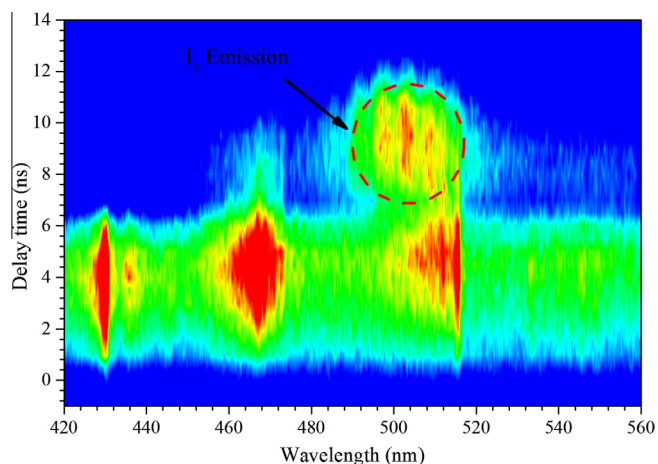


Fig. 3. Contour map of the time-resolved LIBS in fs laser dissociation. The signal of the I_2 molecule emission is clearly observed and marked with a dotted circle.

an intensified charge coupled device (ICCD, iStar DH720, Andor) to record the time-resolved or time-integrated spectra. The synchronization and delay generator (SDG II, Spectra Physics) sends a gate signal to trigger the digital delay pulse generator (DG535). The DG535 is used to control the delay time between the laser pulse and the gate of the ICCD. The time-resolved emission spectra is recorded by the ICCD with a time resolution of ~ 2 ns, and the time integral emission spectra are recorded when the ICCD gate is fully opened.

The homemade spark discharge system produces a ~ 0.5 μ s pulse voltage of about 24 kV. This time scale of the pulse voltage is far greater than that of the CH_3I dissociation process. Hence, only the time integral emission spectra are obtained. The discharge chamber includes the discharge electrodes comprising a plate and a needle with a gap of 1 mm. The discharge chamber has a similar vacuum pump system to that of LIBS to gasify the liquid CH_3I . The electric spark emission from the samples is collected by a fiber probe connected to the spectrometer, and detected by the ICCD.

3. Results and discussion

The time integral emission spectra of 800 nm fs laser photodissociation and electric spark dissociation are presented in Fig. 2. The NIST spectra database [11] and Handbook of lasers database [12] are used to identify the characteristic emissions. The quantum chemical calculations are also performed on CH_2 and CH^+ using Gaussian 03 program [13]. First, the stabilized geometry structures of CH_2 and CH^+ are optimized using the density functional theory (DFT) method of B3LYP/AUG-cc-pVTZ. Second, the excited electronic levels are calculated using time-dependent density functional theory (TD-DFT) method (TD B3LYP/AUG-cc-pVTZ). Hence, the energy differences between excited energy levels are obtained to be used in assigning the electron transitions. The assignments of the spectra are summarized in Table 1. The spectra of 800 nm fs laser photodissociation and the electric spark dissociation have similar spectral structures. The characteristic emissions of the iodine atom, I^+ ion, H atom, CH_3 fragment, CH_2 fragment, and CH fragment exist in both of the two spectra. The characteristic emissions of CH^+ ion only exist in the electric spark dissociation. The emission peaks at 512.8 nm and 516.3 nm coincide with the emission characteristic peaks of iodine atom I and I^+ ion, respectively. These two emission peaks also fit the C_2 molecular emission bands at 513.0 nm and 516.6 nm [14,15]. However, to our knowledge, no observation of C_2 molecule has been reported in the CH_3I photodissociation. In the CH_3I dissociation process, abundant I^+ ions are produced by photoionization or electric ionization. Because of the recombination of I^+ ions and electrons, a large number of iodine atoms should also be produced. Therefore, the assignment of the intense emission peaks at 512.8 nm and 516.3 nm to I atom and I^+ ion is reasonable.

In the usual photodissociation of CH_3I , the molecule can absorb several photons to reach a dissociative state [17]. If the laser pulse duration is shorter than the lifetime of the dissociative state, the molecule can be ionized directly to a CH_3I^+ ion through multiphoton up-pumping. Then the parent ion is decomposed into several fragments. This dissociation process is known as ionization

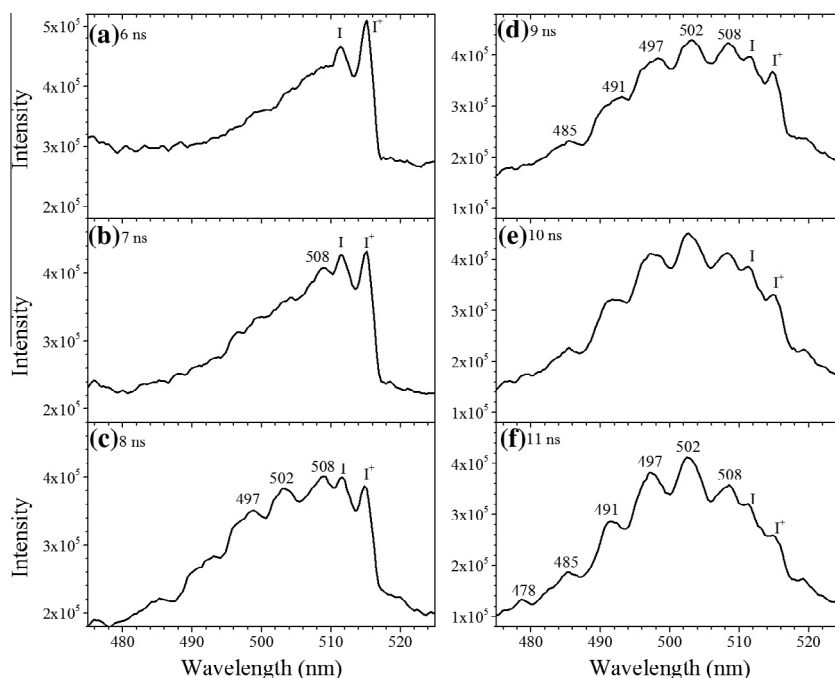


Fig. 4. Time-resolved spectra of I_2 emission at 505 nm band. Some spectral structures begin to emerge after the delay time of 6 ns, and the average energy gap of these emerged peaks from 485 nm to 508 nm is measured as ~ 233 cm^{-1} .

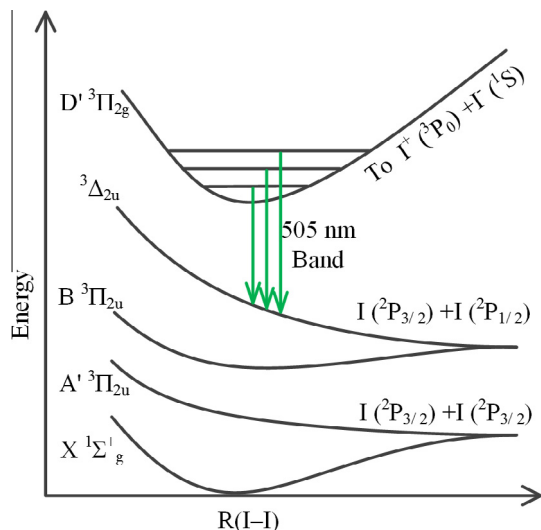


Fig. 5. Energy level diagram of the I_2 molecule. An emission band of 505 nm is assigned to the transition from $D' \ ^3\Pi_{2g}$ to $^3\Delta_{2u}$ [19]. The upper level is a bound ion pair state, whose dissociation limit is a pair of positive and negative ions $I^+(^3P_0) + I^-(^1S_1)$. The lower level is an unbound state.

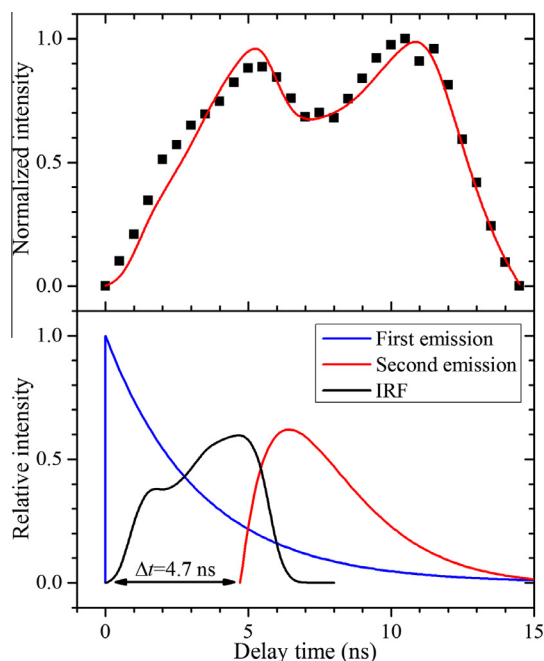


Fig. 6. (a) Measured time-resolved dynamic data and their fitting curve at the wavelength of 497 nm. (b) Model of double-peak dynamic.

followed by dissociation (ID). By contrast, if the laser pulse duration is longer than the lifetime of the dissociative state, the dissociation fragments may absorb more photons within the laser pulse duration to ionize or fragment further. It is named dissociation followed by ionization (DI). In general, ID and DI compete in the photodissociation process, which is usually dependent on the laser pulse duration. DI is more prominent in ns photodissociation, while ID is more prominent in fs/ps photodissociation. In the experiment of Szaflarski and El-Sayed [18], they compare the dissociation products when the pulse durations of 6 ns and 30 ps at 266 nm are used. In the ns laser photodissociation, no CH_3I^+ parent ions are essentially observed, while in the ps laser

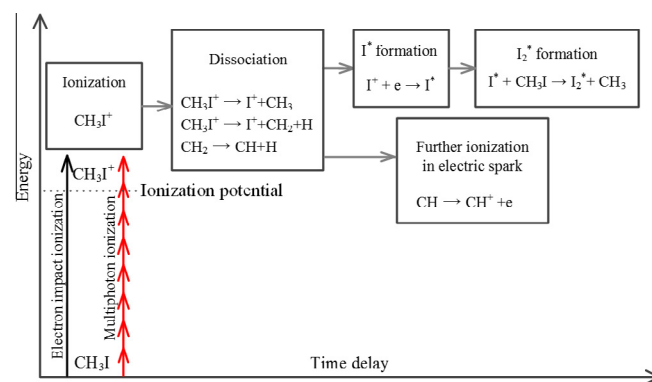


Fig. 7. Schematic mechanism of CH_3I molecule dissociation and I_2 molecule formation. CH_3I molecule is ionized by multiphoton or electron impact, followed by fragmentation.

photodissociation, the CH_3I^+ peak dominates. In the present work, the fs laser pulse provides higher peak power and much shorter pulse duration than those of a ps laser pulse, so the ID mechanism should dominate. Therefore, for the case of the fs laser dissociation, the CH_3I molecule is ionized by multiphoton absorption initially, followed by a fast dissociation process of CH_3I^+ ions. From Fig. 2, it is found that the fs laser photodissociation and the electric spark dissociation have similar spectral structures. In the initial electric discharge process, the CH_3I molecule is ionized initially by electron impact excitation, which resembles the ID process in fs laser dissociation. The CH_3I^+ ions then undergo fast dissociation from its ionization level. It means the CH_3I molecules may experience similar initial ionization process to generate a hot plasma. The only difference between Figs. 2(a) and (b) is that the characteristic emissions of CH^+ ion exist in the electric spark dissociation spectrum. When the discharge proceeds in the longer time duration, the fragments of CH are further ionized to CH^+ by electron impact. Compared to fs laser excitation, the electric discharge process remains for a longer time. The produced electrons can be accelerated by the electric field throughout the electric discharge pulse, until eventually, the cascade ionization with electric spark is observed. Hence, the dissociation fragment can be adequately ionized by cascade ionization in the electric spark dissociation, resulting in further ionization of CH fragments to CH^+ . By contrast, when the ultrafast fs laser pulse is used for the breakdown process, the molecule is ionized directly into the ionization state. Given the very short pulse duration, there is no “pulse tail” to heat the plasma already produced by the pulse front [8]. Thus, no further cascade ionization process can exist in the fs laser dissociation experiment. This result also indicates that the emissions of the plasma continuum and the atomic spectral lines should emerge as fast decay properties in fs laser-induced breakdown.

The photodissociation using strong fs laser pulse provides enough time resolution to monitor the process of I_2 molecule formation. As shown in the contour map of the time-resolved spectra in Fig. 3, the obvious broad emission centered at 505 nm during the delay time of 6–12 ns is assigned to the emission of I_2^* . This emission band is consistent with the fluorescence spectra of I_2 molecule for the transition from the molecular energy level $D' \ ^3\Pi_{2g}$ to $^3\Delta_{2u}$ [19]. After laser excitation, a brown coagulated substance is found in the chamber. The brown coagulated substance is dissolved in alcohol, and it is found that its UV–Vis absorption spectrum is almost identical to that of I_2 molecule alcohol solution. It indicates that the I_2 molecule is formed after CH_3I photodissociation.

The time-resolved spectra provide a detailed evolutionary process of I_2^* , which is shown in Fig. 4. The structure of the 505 nm

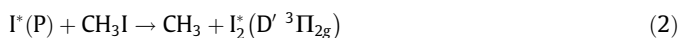
band is evolved with time, showing a secondary emission process. Similar spectral structures of I_2 appear in the 505 nm emission band have been found in the experiment where electron beam is used in exciting mixtures of HI and argon [19], even though the structures of the band are unable to be assigned because of the relatively low spectral resolution. In the present work, the spectral structures are clearly observed in the time-resolved spectra, and the average energy gap of the peaks that emerged from 485 nm to 508 nm is measured as $\sim 233 \text{ cm}^{-1}$, which is assigned to the vibrational levels of $D' \ ^3\Pi_{2g}$ state. As shown in Fig. 5, the emission band of $\sim 505 \text{ nm}$ is assigned to the transition from the bound level $D' \ ^3\Pi_{2g}$ to the free level $^3\Sigma_u$. We propose that the vibrational structure of the upper state $D' \ ^3\Pi_{2g}$ is responsible for the special spectral structures in the 505 nm emission band.

Fig. 6 provides the dynamic curve at the wavelength of 497 nm. A double-peak dynamic process is clearly observed. As shown in Fig. 6(b), two dynamic curves are used for fitting the double-peak dynamic process. The first dynamic curve is an exponential decay, which describes the initial plasma emission. A typical double exponential curve is used for modeling the second emission of I_2^* molecule, which is described as follow:

$$I(t) = b \cdot \frac{1/\tau_1}{1/\tau_2 - 1/\tau_1} \cdot [e^{-(t-\Delta t)/\tau_1} - e^{-(t-\Delta t)/\tau_2}], \quad (1)$$

where $1/\tau_1$ and $1/\tau_2$ are the rate constants of I_2^* molecule formation and decay respectively, and parameter b is the relative intensity about the first emission. The parameter Δt describes the timescale when I_2^* molecules begin to emit light, because the emission of newly formed molecule lags behind the initial plasma emission in LIBS [8]. The instrument response function (IRF) is deduced directly by measuring the pulse width of the fs laser using the ICCD. After convolution of the IRF and the superposition of the two emission curves, the data points are fitted, and the fitting curve is shown in Fig. 6(a). The obtained fitting parameters are $\tau_1 = 1.8 \text{ ns}$, $\tau_2 = 1.6 \text{ ns}$, and $\Delta t = 4.7 \text{ ns}$, and the obtained lifetime of the first mission is $\sim 3.3 \text{ ns}$. The results indicate the second emission of I_2^* molecule begins at the delay time of $\sim 4.7 \text{ ns}$.

In the time-resolved spectra of photodissociation, except for the I_2^* emission around 505 nm, the other emission lines show rapid decay processes and no secondary emission peak appears. As shown in Fig. 5, the upper state ($D' \ ^3\Pi_{2g}$) is an ion pair state (I^+I^-) of positive and negative ions $I^+(^3P_0)$ and $I^-(^1S_1)$. However, only the characteristic emission of I^+ ions is found, but that of the negative iodine ions I^- . Hence, we propose that the I_2^* molecule in $D' \ ^3\Pi_{2g}$ state cannot be produced from the recombination of positive and negative iodine ions. The iodine atoms are formed gradually in the recombination process of iodine ions with electrons. This result can be seen in the time-resolved spectra of Fig. 4 where both the emission intensities of atomic I and ion I^+ decrease with the time delay while the relative signal strength (I^+/I^+) increases. Therefore, a large number of the highly excited iodine atoms are produced in the time scale of 6–12 ns. A high concentration of CH_3I gas makes the molecules collide more easily. Therefore, we propose that the collisional reaction of highly excited I^* and CH_3I molecule is responsible for the production $I_2^*(D' \ ^3\Pi_{2g})$, which can be illustrated as



Although the bimolecular collision reaction, where the electronic ground state I_2 molecule is produced by the collision of $I^*(^2P_{1/2})$ atom and CH_3I molecule, has already been observed in the photolysis of CH_3I [20], the mechanism for producing iodine molecules in higher energy level ($D' \ ^3\Pi_{2g}$) has not been reported. We think the excited $I_2^*(D' \ ^3\Pi_{2g})$ molecule can be produced by collisions of iodine atoms in the higher excited state $I^*(^4P)$. A similar

collisional mechanism for the formation of I_2 in excited state (D') has been studied in iodine-containing molecules HI and CF_3I , where the predominant process has been proposed as the collisional deactivation of the metastable atom $I^*(^4P)$ by iodine-containing molecules [19]. The molecule CH_3I could share the same collisional mechanism. In the present work, because of the recombination of I^+ ions and electrons in the plasma, a large number of highly excited iodine atoms are produced in a time scale of 6–12 ns. Therefore the proposed reaction (2) is the predominant mechanism for the formation of molecule $I_2^*(D' \ ^3\Pi_{2g})$ in this time region.

The electric spark dissociation is initiated by electron impact ionization, and the initial plasma condition is similar to that of fs laser induced breakdown. The similar time integral emission spectra obtained by fs laser photodissociation and electric spark dissociation show the uniformity of the two dissociations. Thus, we propose that the CH_3I molecule is ionized by the electron impact in the process of electric spark dissociation at first, and subsequently fragments from its ionization state to the fragments of I^+ , CH_3 , CH_2 , CH , and H . From the time-resolved spectra of fs laser photodissociation, a more clear reaction mechanism is proposed and shown in Fig. 7. Given the slower discharge process in the electric spark dissociation, the dissociation fragment can be further ionized by electron collisions. Eventually, the cascade ionization is formed. The signal of CH^+ only exists in the electric spark dissociation, which is attributed to the production of cascade ionization. In the dissociation process, a large number of I^+ ions are produced, and after recombination with electrons, the highly excited iodine atoms are formed gradually. The I_2^* molecules are produced simultaneously through the reaction described in Eq. (2).

In this work, relative low laser intensity ($\sim 2 \times 10^{13} \text{ W/cm}^2$) is used for the multiphoton ionization of CH_3I , therefore no signal of multiply charged ions has been found, such as the emission signals of I^{2+} , I^{3+} , C^{2+} , and C^{3+} . It is different from the case of Coulomb explosion. In the studies of CH_3I Coulomb explosion, with the much higher laser intensities (10^{14} – 10^{15} W/cm^2), multiply charged ions are produced [21]. The Coulomb explosion and multiphoton ionization of CH_3I have been reported in the excitation of laser intensity $\sim 10^{13} \text{ W/cm}^2$ [22,23]. The highest laser intensity in our experiment is $\sim 2 \times 10^{13} \text{ W/cm}^2$, which is just below the threshold value of CH_3I coulomb explosion. Therefore, the major process of the LIBS in this work is multiphoton ionization rather than Coulomb explosion.

4. Summary

The dynamics of CH_3I dissociation is evaluated using fs laser-induced breakdown and electric spark-induced breakdown spectroscopy. The almost identical emission spectra obtained by fs laser photodissociation and electric spark dissociation denote that a similar mechanism exists in their initial dissociation processes. With a relative low intensity of $\sim 2 \times 10^{13} \text{ W/cm}^2$, the major process is multiphoton ionization in the fs laser photodissociation. The electrons in the outer orbits of CH_3I are ionized to produce CH_3I^+ , which is very similar to the ionization by electron impact in the electric spark dissociation. Therefore, ID is proposed as the breakdown mechanism in both fs laser breakdown and electric spark breakdown. The CH_3I molecules are ionized to generate hot plasma in the initial processes of both fs laser and electric spark dissociations. The ID mechanism dominates the dissociation process with products of I^+ , CH_3 , CH_2 , CH , and H . The process of I_2 molecule formation is observed by the time-resolved LIBS. The 505 nm emission band shows that I_2 molecules are formed after the delay time of 4.7 ns. The bimolecular collision reaction channel of highly excited iodine atoms $I^*(^4P)$ and CH_3I molecules is responsible for the formation of I_2^* molecules.

The initial ionization process in the electric spark dissociation of CH_3I can be simulated by applying fs laser induced breakdown. The plasma produced by multiphoton ionization under fs laser excitation provides the initial plasma condition similar to that of the initial electron impact breakdown in the electric spark. Furthermore, the fs laser also provides high time resolution to monitor intermediate products. Therefore, a better description of the electric spark dissociation mechanism is obtained. Further studies involving the laser active gases in a real E-COIL system are needed to obtain the further reaction mechanism, such as the dissociation of some mixture gases with CH_3I .

Conflict of interest

This study is helpful in understanding the dynamics of electric discharge spark dissociation of CH_3I , and helpful in designing electric discharge systems to improve reaction efficiency of the E-COIL.

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References

- [1] S.J. Davis, W.E. McDermott, M.C. Heaven, in: B.J. Thompson (Ed.), *Gas Lasers*, 2006.
- [2] J. Kasper, G. Pimentel, *Appl. Phys. Lett.* 5 (1964) 231.
- [3] J. Kasper, J. Parker, G. Pimentel, *J. Chem. Phys.* 43 (1965) 1827.
- [4] Y. Fan, D. Donaldson, *J. Phys. Chem.* 96 (1992) 19.
- [5] Y. Fan, D. Donaldson, *J. Chem. Phys.* 97 (1992) 189.
- [6] K.V. Vidma, A.V. Baklanov, Y. Zhang, D.H. Parker, *J. Chem. Phys.* 125 (2006) 133303.
- [7] K. Vidma, A. Baklanov, E. Khvorostov, V. Ishchenko, S. Kochubei, A. Eppink, D. Chestakov, D. Parker, *J. Chem. Phys.* 122 (2005) 204301.
- [8] A. Miziolek, V. Palleschi, I. Schechter, *Laser-induced breakdown spectroscopy*, Cambridge University Press, 2006.
- [9] M. Janssen, M. Dantus, H. Guo, A. Zewail, *Chem. Phys. Lett.* 214 (1993) 281.
- [10] L. Khundkar, A. Zewail, *Chem. Phys. Lett.* 142 (1987) 426.
- [11] Y. Ralchenko, Kramida, A.E., Reader, J., NIST ASD Team (2008), National Institute of Standards and Technology, Gaithersburg, MD. (2009, December 14).
- [12] M. Weber, *Handbook of Lasers*, CRC, 2001.
- [13] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, et al., *Gaussian 03, Revision E.01*, Gaussian Inc, Wallingford CT, 2004.
- [14] R.K. Thareja, *J. Chem. Phys.* 100 (1994) 4019.
- [15] K. Nyholm, M. Kaivola, C.G. Aminoff, *Appl. Phys. B* 60 (1995) 5.
- [16] G. Herzberg, *Molecular spectrum and molecular structure III. Electronic spectra and electronic structure of polyatomic molecules*, D. Van Nostrand Company, New York, 1966.
- [17] K. Ledingham, R. Singhal, *Int. J. Mass Spectrom. Ion Proc.* 163 (1997) 149.
- [18] D.M. Szaflarski, M. El-Sayed, *J. Phys. Chem.* 92 (1988) 2234.
- [19] K.P. Killeen, J.G. Eden, *Appl. Phys. Lett.* 43 (1983) 539.
- [20] R.T. Meyer, *J. Chem. Phys.* 72 (1968) 1583.
- [21] J. Ford, Q. Zhong, L. Poth, A. Castleman Jr, *J. Chem. Phys.* 110 (1999) 6257.
- [22] G.G. María, E. Corrales, Jesús González-Vázquez, Vincent Lorient, Rebeca de Nalda, Luis Bañares, *J. Phys. Chem. A* 116 (2012) 2669.
- [23] Y. Liu, T. Gerber, P. Radi, Y. Sych, G. Knopp, *Chem. Phys. Lett.* 610–611 (2014) 153.