

CO₂ laser induced IRMPD of 2-bromo-2-chloro-1,1,1-trifluoroethane: time-resolved luminescence studies

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Abstract

The IRMPD of 2-bromo-2-chloro-1,1,1-trifluoroethane gives rise to an intense visible light emission between 350 and 750 nm due to various carbenes. The effect of various experimental parameters such as laser energy, pulse duration and substrate pressure on the emission has been studied. Infrared fluorescence studies have also been carried out to explore the vibrational excitation of the photoproducts. A self-consistent mechanism is proposed explaining the complex photodissociation dynamics of the system.

1. Introduction

The consequences of the atmospheric photodegradation of CFC compounds have necessitated the search for suitable alternative chemicals. In this context, hydrochlorofluorocarbons (HCFC) and hydrofluorocarbons (HFC) may be better substitutes. In the light of significant photodissociation in the environment, it is of relevance to study the photodissociation dynamics of these compounds [1–3]. 2-bromo-2-chloro-1,1,1-trifluoroethane (BCTFE) falls under the general category of HCFC. Further, BCTFE is commonly used as an anaesthetic. It has the potential application as a working medium for hydrogen halide

lasers and also as a working molecule for the laser isotope separation of deuterium [2]. Therefore, it is important to investigate the primary dissociation channels of BCTFE along with the spectral and kinetic information on transients and stable products. In the present work, infrared multiphoton dissociation (IRMPD) of BCTFE has been carried out using a CO₂ laser.

This work is a continuation of our efforts to investigate the laser induced photodissociation dynamics of halocompounds [3]. In our earlier studies of IRMPD of 1,2-dibromo-1,1-difluoroethane (DBDFE), a strong UV-visible luminescence was observed. The formation of CF₂Br- $\dot{\text{C}}\text{H}$ carbene was suggested to be a primary step. To substantiate this mechanism, the IRMPD of BCTFE has now been investigated. In addition, it will be of interest to have

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a comparative study of our results with that of Ref. [2] and with those of the sensitized decomposition [1] and the thermal dissociation [4] of BCTFE. However, the present system BCTFE having three different halogen atoms would involve more complex photodissociation dynamics compared to that of DBDFE.

In thermolysis, the major products are reported to be halobutenes whose formation is explained by invoking the carbene mechanism. In Ref. [2], BCTFE was excited by the collision induced vibrational energy transfer from excited CF_3CDBrCl molecules. The primary dissociation channels were suggested to be Br, Cl elimination leading to $\text{CF}_3\ddot{\text{C}}\text{H}$ carbene and C–Cl bond cleavage. These primary products were responsible for the formation of all the other stable products. In the SF_6 sensitized photodissociation of BCTFE under cw CO_2 laser excitation [1], the primary step was proposed to be homolytic C–Br bond cleavage.

In the current study, we report the IR and visible luminescence from the photoproducts of IRMPD of BCTFE. A dissociation mechanism is proposed with carbenes as primary photoproducts and visible light emitters.

2. Experimental

A pulsed CO_2 laser (Lumonics 103-2), tuned to the 9R(40) or 9R(32) line was used for irradiation. The beam was focused with a BaF_2 lens of 25 cm focal length in a 250 cm^3 pyrex cell equipped with four windows. The energy and the temporal profile of the laser pulse were measured by a pyroelectric detector (Gentec ED-500) and a room temperature fast IR detector (Edinburgh Instruments), respectively. The progress of the dissociation was ascertained by FTIR (Nicolet Magna 550) and the stable products were characterized by GC, GCMS and FTIR techniques. In GC, most of the products were separated on 10% silicon grease column at room temperature, while products such as C_2F_4 , C_3F_6 , $\text{C}_2\text{F}_3\text{H}$, CF_3Br were separated on a Porapak Q column at 80°C .

BCTFE (PCR Inc.) as obtained was used since there was no appreciable impurity seen by GC analysis and FTIR spectrum. The sample was subjected to

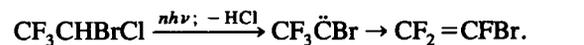
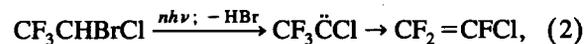
several freeze–pump–thaw cycles before it was admitted to the reaction cell. The experimental apparatus for the infrared fluorescence (IRF) and visible luminescence studies is described in detail elsewhere [3]. Briefly, the wavelength resolved (5 nm resolution) visible emission was detected and processed with a digital storage oscilloscope and IBM PC. The time constant of the complete detection system was found to be less than 100 ns.

The IRF, originated under the same experimental conditions, was monitored perpendicular to the laser beam with a liquid nitrogen cooled InSb detector (Judson, J-10D) equipped with a preamplifier. IRF spectra were obtained by a circular variable filter (OCLI 902, bandwidth $\approx 100\text{ cm}^{-1}$ fwhm). The time constant of the complete set-up was found to be about 1.2 μs .

3. Results and discussion

On irradiation, BCTFE undergoes dissociation yielding $\text{CF}_2=\text{CHF}$, $\text{CF}_2=\text{CFCl}$, CF_3CHCl_2 and $\text{CF}_2\text{Br}-\text{CF}_2\text{Br}$ as major photoproducts (yield decreasing in that order). In addition, numerous other minor products such as C_2F_4 , C_3F_6 , CF_3Br , $\text{CF}_3\text{CH}=\text{CF}_2$, $\text{CF}_3\text{CF}_2\text{Br}$, $\text{CF}_3\text{CCl}=\text{CF}_2$, $\text{CF}_3\text{CCl}=\text{CHCF}_3$, $\text{CF}_2\text{Cl}-\text{CF}_2\text{Br}$, CF_3CFBrCl , HBr and HCl were also obtained.

The possible primary steps in the decomposition of BCTFE are the homolytic scission of the C–F, C–H, C–C, C–Cl and C–Br bonds together with the molecular elimination of HF, HCl and HBr. However, the threshold energies for the homolytic scission of the bonds are generally higher than those for molecular elimination [5]. In the majority of haloethanes, the principle dissociation process involves the molecular elimination of hydrogen halide via a four-centered or three-centered transition state [6,7]. Keeping these observations and the stable products analysis in view, the following dissociation mechanism is suggested:



The carbenes are proposed to be primary dissociation products, which can explain the formation of almost all stable photoproducts. The intermediate carbenes $\text{CF}_3\dot{\text{C}}\text{H}$, $\text{CF}_3\dot{\text{C}}\text{Cl}$ and $\text{CF}_3\dot{\text{C}}\text{Br}$ are formed by the elimination of Br and Cl, HBr and HCl, respectively, which subsequently rearrange to the corresponding olefins by 1,2-fluorine atom migration (reactions (1)–(3)).

3.1. The intermediate carbenes and their reactions

The carbene $\text{CF}_3\dot{\text{C}}\text{H}$ can be generated in the IRMPD of BCTFE either by successive or simultaneous elimination of Br and Cl. However, the molecular elimination is expected to be a lower activation energy channel, and thus BrCl molecular elimination is probably the predominant channel leading to $\text{CF}_3\dot{\text{C}}\text{H}$. The $\text{CF}_3\dot{\text{C}}\text{Cl}$ and $\text{CF}_3\dot{\text{C}}\text{Br}$ carbenes are generated by α,α -HBr and α,α -HCl elimination, respectively. Masuda et al. [2] have suggested that the carbene $\text{CF}_3\dot{\text{C}}\text{H}$ is formed in the sensitized dissociation of BCTFE either by successive elimination of Br and Cl or by molecular elimination of BrCl, and this carbene isomerizes to a stable product $\text{CF}_2=\text{CHF}$. Pola and Chvatal [1] have also observed a minor yield of $\text{CF}_2=\text{CHF}$ in the sensitized dissociation of BCTFE. Also in the thermal dissociation a $\text{CF}_3\dot{\text{C}}\text{H}$ carbene intermediate is formed which is dimerized or recombined to give halobutenes [4].

In the IRMPD of BCTFE, HBr and HCl elimination takes place through a three-centered transition state. The support for the carbene mechanism comes from the observation of HCl and HBr through IRF. HCl was also detected by its rovibrationally resolved FTIR absorption spectra (Fig. 1). However, HBr could not be detected by FTIR, probably due to its reaction with other products and adsorption on the photolysis cell. Earlier investigators [1,4] have also given evidence for HCl and HBr elimination. However, HBr elimination is suggested to be a secondary channel. BCTFE can also eliminate HF through a four-centered transition state giving rise to $\text{CF}_2=\text{CBrCl}$. This would be similar to the case of chemically activated 1,1,1-trifluoro-2-chloroethane [8]. The presence of a small IR absorption band in the photolysed sample at 1030 cm^{-1} due to SiF_4 (the reaction product of HF with silica of the reaction cell), indicates that HF elimination is taking place to

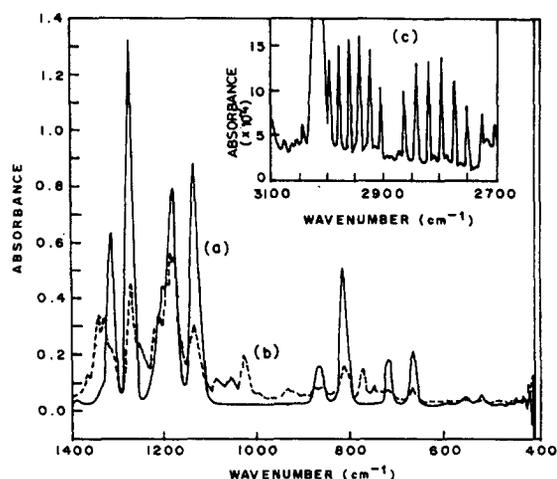


Fig. 1. FTIR absorption spectra of $\text{CF}_3\text{-CHBrCl}$ (5.0 Torr), (a) prior to IRMPD, (b) after IRMPD. (c) (inset) Rovibrationally resolved FTIR spectrum of the HCl photoproduct in IRMPD of $\text{CF}_3\text{-CHBrCl}$.

a small extent. However, there was no evidence for CF_2CBrCl , the co-product of HF.

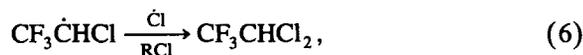
It is well known that carbenes such as from (1) to (3) can undergo one or more of the following reactions: (i) isomerization to alkenes by 1,2-fluorine atom migration, (ii) dimerization, (iii) addition to the C=C bond and (iv) insertion into the C-H bonds. The relative importance of these reactions depends on the energy of the carbene and the experimental conditions, such as pressure, fluence, etc. At low pressures, the importance of 1,2-fluorine migration increases. Although 1,2-fluorine atom migration is more difficult than other halogen atom migration in the rearrangement of carbenes, such fluorine atom migration is reported in trifluoromethyl carbenes [8,9]. At high pressures, all the above-mentioned reactions have been reported to occur [10,11], but in the liquid phase photolysis of the precursors to these carbenes, no isomer products could be observed. In addition to the above-mentioned reactions, these carbenes were also found to undergo cross reactions among themselves. The isomerization channel is strongly dependent on the energy of the carbene because of an energy barrier of $\approx 30\text{ kcal/mol}$ [8]. As the IRMPD of BCTFE leads to the formation of carbenes with a broad energy distribution, only those carbenes with energy greater than the energy barrier for isomerization will be converted to respective

olefins, and the remaining will undergo dimerization and other reactions. In our experiments at low pressure, isomerization to alkenes by 1,2-fluorine migration is observed to be the major reaction channel for the carbenes. These isomerized products have a lot of internal energy permitting the molecule to be probed through IRF. Thus in these experiments, a major fraction of the carbenes is produced with energy higher than the activation barrier for isomerization. However, in the case of thermal excitation and cw CO₂ laser pyrolysis, the energy deposition is not sufficient for isomerization and, therefore, dimerization or recombination of the carbenes become important. Unlike thermal dissociation where halobutenes are favoured on the basis of energetics, the yield was found to be negligible in our runs.

Besides the two major stable products viz. CF₂=CHF and CF₂=CFCl which could be explained as isomerization products of the carbenes, two additional products CF₃CHCl₂ and CF₂BrCF₂Br in substantial amounts were observed. The product CF₃CHCl₂ may be formed in two ways: the carbene transient, CF₃ĊCl may add to HCl to yield the product CF₃CHCl₂,



or by



where the radical CF₃ĊHCl, generated by C–Br bond cleavage, can easily extract a chlorine atom from another molecule or can combine with a free chlorine atom.

The formation of CF₂Br–CF₂Br in substantial quantity is somewhat surprising. The precursor for this product could be the secondary product C₂F₄, which is identified as one of the minor products. Bromination of C₂F₄ can lead to the formation of CF₂Br–CF₂Br as the addition product. A similar explanation has been given for the formation of CF₂Br–CFHBr from CF₂=CFH by Masuda et al. [2] in the IRMPD of BCTFE.

Therefore, in summary, the stable products characterization suggests that there are two primary channels of dissociation (reactions (1) and (2)) in the IRMPD of BCTFE. The other stable products are

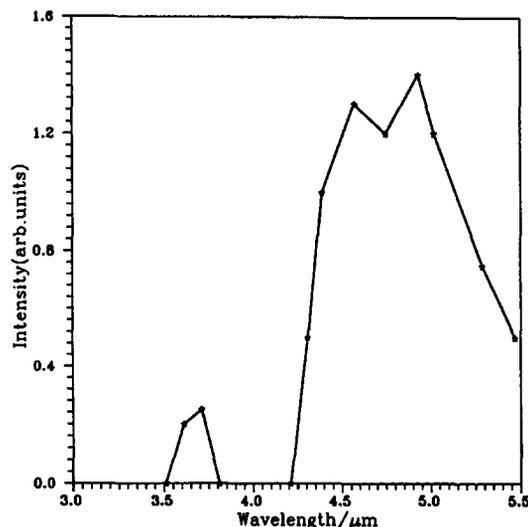
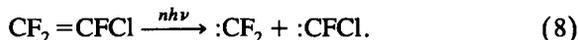
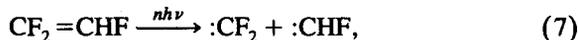


Fig. 2. Infrared fluorescence spectrum of the vibrationally excited photoproduct in the IRMPD of CF₃–CHBrCl.

due to secondary or tertiary reactions involving these precursors. The carbenes can isomerize to give the corresponding olefins and these olefins can also absorb further photons from the same laser pulse to undergo IRMPD to yield different carbenes [12],



These secondary carbenes can undergo dimerization and recombination to give a variety of stable products, a few of which are observed by us.

3.2. Infrared fluorescence study

During BCTFE photolysis, IRF was observed around 3.7 μm and between 4.4 and 5.4 μm as shown in Fig. 2. Since the IRF was observed at laser fluences higher than the dissociation threshold of BCTFE, it is believed that the IRF contribution is mainly from photoproducts and not from the parent molecule. The band around 3.7 μm is assigned to vibrationally hot HBr [3,13] and HCl [14]. The band between 4.4 and 5.4 μm can probably be attributed to overtones and combination bands of the photoproducts CF₂=CFCl and CF₂=CHF, which are expected to have a large internal energy originating from intramolecular energy release during their pro-

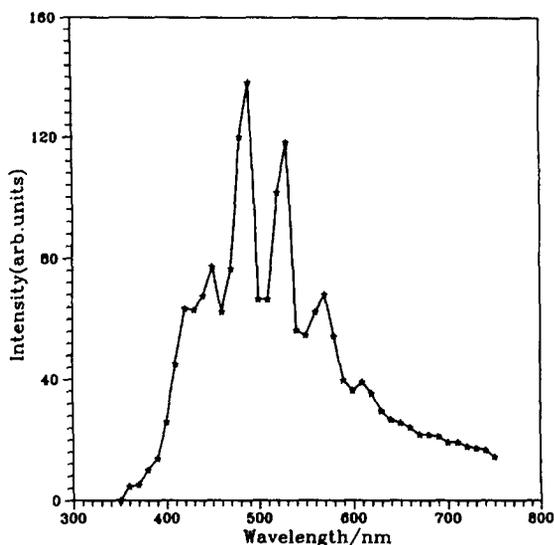


Fig. 3. A spectrum of the UV/visible luminescence from carbenes in the IRMPD of $\text{CF}_3\text{-CHBrCl}$.

duction via rearrangement of the carbenes. Kinetic study could not be carried out since the dispersed fluorescence was not very strong.

3.3. UV/visible luminescence in the IRMPD of BCTFE

A streak of visible emission was observed along the irradiation axis during the IRMPD of BCTFE. This visible emission was observed over a broad wavelength range of 350–750 nm with bands around 480 and 520 nm (Fig. 3). In our earlier IRMPD studies of DBDFE, a similar visible emission was observed, which was assigned to the $\text{CF}_2\text{Br}\ddot{\text{C}}\text{H}$ carbene. In the present study, we suggest that the carbenes, $\text{CF}_3\ddot{\text{C}}\text{Cl}$ and $\text{CF}_3\ddot{\text{C}}\text{H}$, are responsible for this emission and it is not due to the inverse electronic relaxation of the parent molecule since the visible fluorescence is observed above the energy threshold for dissociation. Moreover, the UV absorption of BCTFE lies below 200 nm, and thus it is not expected to give any emission between 350 and 750 nm. Similarly, the stable photoproducts of BCTFE are not expected to emit in this region.

The emission can be ascribed to the electronically excited carbenes, $\text{CF}_3\ddot{\text{C}}\text{Cl}$, $\text{CF}_3\ddot{\text{C}}\text{H}$, $:\text{CHF}$ and $:\text{CFCl}$ on the basis of spectral information. The electronic

absorption spectra of the matrix isolated chloro(trifluoromethyl) carbene has been reported to have two bands between 530 and 740 nm ($\lambda_{\text{max}} = 640$) and below 340 nm ($\lambda_{\text{max}} = 235$), the latter being much stronger [9]. The electronic absorption and emission spectroscopy of chlorofluoromethylene, $:\text{CFCl}$, is well known [12,15], and its absorption and emission bands lie between 340 and 390 nm and 385 and 645 nm, respectively. The CHF carbene is reported to have an adsorption between 430 and 600 nm. To our knowledge, the electronic spectra of trifluoromethyl carbene ($\text{CF}_3\ddot{\text{C}}\text{H}$) are not known, but in analogy with $:\text{CHF}$ and $:\text{CFCl}$, the absorption spectrum of $\text{CF}_3\ddot{\text{C}}\text{H}$ is expected to be red-shifted with respect to that of $\text{CF}_3\ddot{\text{C}}\text{Cl}$. Thus, all the four carbenes are potential emitters between 350 and 750 nm in the IRMPD of BCTFE. However, $:\text{CHF}$ and $:\text{CFCl}$ result from the IRMPD of secondary photoproducts $\text{CF}_2 = \text{CFH}$ and $\text{CF}_2 = \text{CFCl}$, respectively. This will lead to a small yield of these secondary carbenes. This observation is reflected in minor yields of stable photoproducts arising from these secondary carbenes. Therefore, the primary carbenes, $\text{CF}_3\ddot{\text{C}}\text{Cl}$ and $\text{CF}_3\ddot{\text{C}}\text{H}$, are suggested to be the major emitters of the UV/visible fluorescence.

As in our earlier studies [3], the generation of electronically excited carbenes, $\text{CF}_3\ddot{\text{C}}\text{Cl}$ and $\text{CF}_3\ddot{\text{C}}\text{H}$, is explained by the absorption of additional photons from the laser pulse by the nascent carbenes. If the carbenes are produced in the quasi-continuum, they can have resonant or near-resonant absorption of IR radiation of any frequency [16]. The observed isomerization of the carbenes to olefins suggest that the former is produced with an excess internal energy and probably in the quasi-continuum state. Therefore, these highly vibrationally excited carbenes in the ground electronic state can relax to a higher electronic state from which UV/visible emission can take place. Alternatively, the carbenes can be produced in the higher electronic state in the primary step itself acquiring sufficient energy from the partitioning of the available energy with the parent molecules. This possibility appears to be difficult on the basis of a large energy requirement.

3.4. Time-resolved studies

On excitation with a CO_2 laser pulse consisting of a spike (≤ 150 ns) followed by a tail of μs duration,

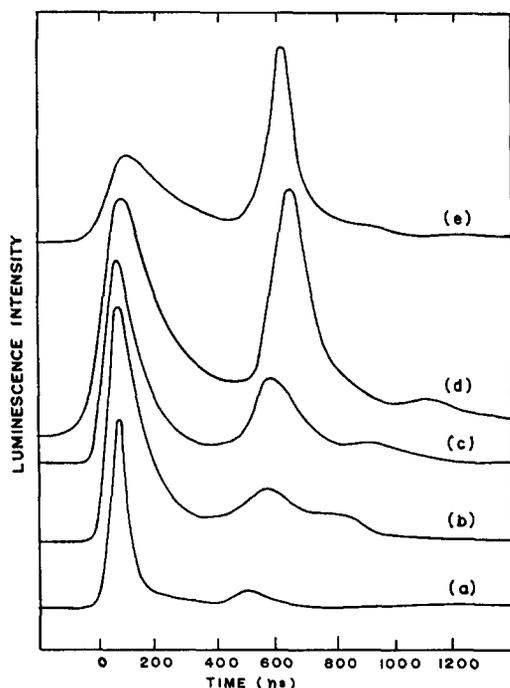


Fig. 4. Effects of substrate pressure on the relative intensity of the first and second luminescence peaks observed in the IRMPD of $\text{CF}_3\text{-CHBrCl}$ at constant laser pulse energy. Traces (a)–(e) are in decreasing order of pressures of 7.6, 4.9, 2.7, 2.0 and 1.4 Torr and sensitivities are (a) 200 mV/div, (b), (c) and (e) 100 mV/div and (d) 50 mV/div.

a typical optical emission signal was obtained which consists of two peaks (Fig. 4). The temporal profile of the optical emission was found to be strongly dependent on various experimental conditions such as laser pulse shape, pulse energy, excitation frequency and substrate pressure. On excitation with a laser pulse from N_2 -free gas mixture, where the tail portion is absent, the signal consists of only the first peak. Thus, it implies that the excitation of BCTFE with the spike region of the laser pulse is responsible for the first peak and the tail region leads to the second emission peak. IRMPE by the spike region of the laser pulse leads to a broad distribution of vibrationally excited BCTFE molecules of which a fraction with energy greater than the dissociation threshold undergoes dissociation. The tail region of the pulse can subsequently excite the remaining excited but undissociated molecules along with vibrationally ground state molecules.

On increasing the laser energy of tail-free pulses,

we have observed that the temporal profile of the first peak changes with the appearance of an additional peak on a 300 ns timescale. This feature also grows with increasing pulse energy and can be ascribed to the different emitting species at higher laser energy. Alternatively, it can originate from the excitation by the tailing part of the spike, and can become observable as the laser energy increases. The use of band-pass filters, centered around 480 and 520 nm, eliminates the second temporal peak (around 300 ns) indicating this emission to be at different wavelengths, which may be due to the secondary carbenes $:\text{CFCl}$ and $:\text{CFH}$ (reactions (7) and (8)). It is expected that these secondary carbenes will be important at higher laser energies. It was observed that the decay of the first peak is dependent on the substrate pressure, showing faster decay with increasing pressure. On the basis of the decay curves, we assign a lifetime of about 150 ns for emitting species.

The time evolution of the emission peaks and their relative intensities were found to be significantly affected by varying the pressure of BCTFE (Fig. 4). The relative intensity of the second peak to that of the first peak was found to decrease with increasing pressure of BCTFE. This can be explained by the vibrational deexcitation of BCTFE and primary carbenes because the collisional effects gain more importance on a longer timescale for the second peak compared to the first emission peak [17]. This observation is in contrast with our earlier work on the IRMPD of 1,2-dibromo-1,1-difluoroethane (DBDFE) where the relative intensity of the second peak was found to increase with increasing pressure of DBDFE. The appearance of second peak at an earlier timescale with increasing substrate pressure can possibly be due to enhanced collisional excitation and also vibrational energy pooling. A more detailed study on the kinetics of emission from this molecule, and the difference in collisional effects on emission from DBDFE and BCTFE will be reported [18].

4. Conclusion

The IRMPD of 2-bromo-2-chloro-1,1,1-trifluoroethane yields the stable products, $\text{CF}_2 = \text{CFH}$,

$\text{CF}_2=\text{CFCl}$, CF_3CHCl_2 , $\text{CF}_2\text{BrCF}_2\text{Br}$ besides various minor products. A strong UV/visible emission between 350 and 750 nm and IRF at 3.7 μm and 4.4–5.4 μm are observed. The array of products arising out of the complex photodissociation dynamics of BCTFE is explained with a suitable mechanism as corroborated by the visible luminescence and the IRF investigations. The temporal profile of the luminescence consisting of two components shows a strong dependence on the laser and molecular parameters highlighting the contribution from collision assisted phenomena.

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