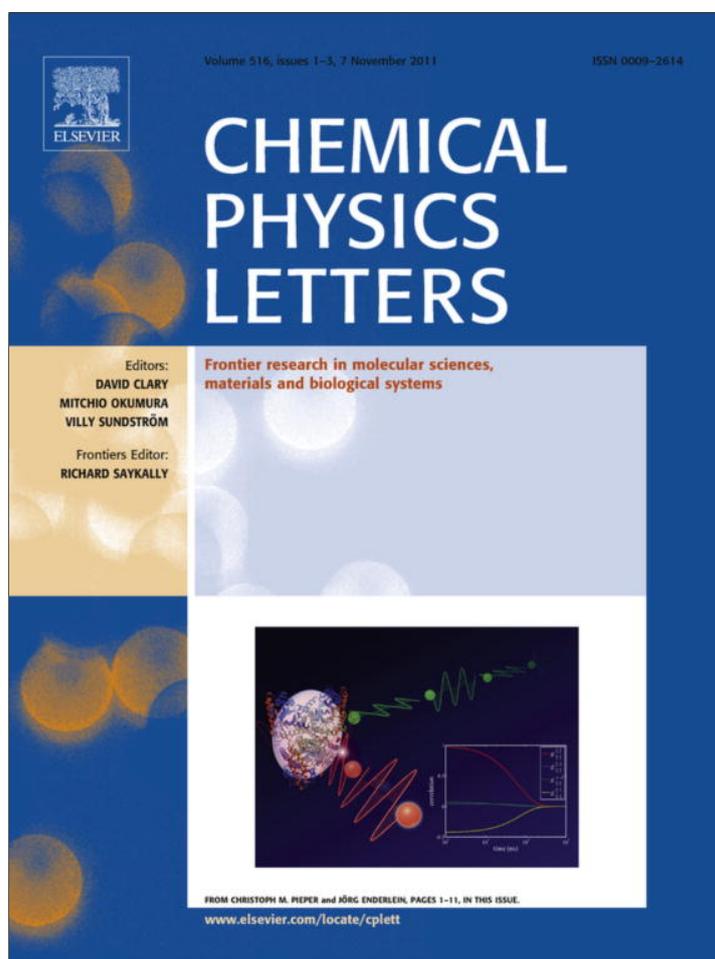


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Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplettTwo-dimensional REMPI of CF₃Br: Rydberg states and photofragmentation channels

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ABSTRACT

Mass spectra were recorded for $(2 + n)$ REMPI of CF₃Br as a function of resonance excitation energy in the 71 320–84 600 cm⁻¹ region to obtain two-dimensional REMPI data. CF₃⁺, Br⁺ ($i = 79, 81$) and C⁺ ions were detected. Laser power dependence experiments were performed for ion signals. CF₃⁺ signals due to resonance transitions from the ground state CF₃Br to number of Rydberg states and various vibrational states followed by CF₃⁺ and Br⁻ ion-pair formation via intersystem crossings, were identified. Bromine atom production by predissociation channels via two-photon excitation to the Rydberg states is proposed, based on detecting bromine atom $(2 + 1)$ REMPI.

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1. Introduction

CF₃Br and its related counterparts CF₃Cl and CF₃I are all important industrial compounds with wide ranging applications. The freon CF₃Br (Halon 1301) has been used in aircrafts for fuel inerting and as a fire suppressor whereas CF₃Cl (CFC-13) has been used as a refrigerant. The production and use of these two compounds has been banned under the terms of the Montreal Protocol since 2000 [1], due to their significant ozone depletion and global warming properties. More recently CF₃I, which is considered less environmental unfriendly, has been considered as a possible replacement compound for CF₃Br and CF₃Cl. All in all the possible uses or discarding of these compounds rely on their photochemical and photoabsorption properties.

Rather limited detailed information are available on the photoabsorption and photochemistry of CF₃Br as well as of CF₃Cl and CF₃I. Although the vacuum UV spectrum of CF₃Br was reported as early as 1973 [2] only recently reliable absorption cross sections at energies above the lowest lying electronic transitions have appeared [3]. The UV absorption spectroscopy of these compounds is similar. Weak continua due to $n \rightarrow \sigma^*$ C–X (X = Cl, Br, I) transitions (A bands) appear at low energies. More intense structures due to $\sigma \rightarrow \sigma^*$ C–X transitions and transitions from lone pair orbitals with dominant X character (p to sp^3 character) to ns and np Rydberg states appear at higher energies [3,4]. Rydberg states identified, are either believed to belong to series converging to the two spin-orbit components of the ground state ions, $X^2E_{3/2}$ and $X^2E_{1/2}$, or the first excited ionic state $A^2E_{1/2}$ [3,5]. Spectra due to transitions to ns Rydberg states are generally found to be more intense than those due to transitions to np states as one might expect from the basic selection rule $\Delta l = \pm 1$.

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In terms of photochemistry studies main emphasis has been on the effect of absorption in the low energy A band corresponding to transitions to several repulsive states followed by dissociation to form CF₃ + Br(²P_{3/2})/Br*(²P_{1/2}) [6–8]. The same products are believed to be the main result of photodissociation via higher energy states [4,9]. Fluorescence studies of CF₃Cl and CF₃Br reveal emissions from CF₃⁺ for excitations above the energy thresholds for CF₃⁺ + X; X = Cl, Br formations [4,10,11] with maximum quantum yields of about 20% and 7% at 112.5 nm (CF₃Cl) and 125.0 nm (CF₃Br), respectively. Judging from negative photoion spectroscopy studies of CF₃X; X = Cl, Br and I insignificant ion-pairs, CF₃⁺ + X⁻ are formed via excitations to the high energy Rydberg state region despite being energetically allowed [9]. This is surprising and contradicts with observations for related compounds such as methyl halides [12,13], hydrogen halides [14–17], halogens [18,19] and interhalogens [20,21] where Rydberg doorway states in ion-pair formations have been evidenced.

Whereas resonance enhanced multiphoton ionization (REMPI) studies have been performed for CF₃Cl [11] and CF₃I [22,23] to our best knowledge no analogous studies have been reported for CF₃Br. 4p and 6p Rydberg states are found to be excited by two-photon resonance excitations of CF₃Cl and CF₃I, respectively. Spectra due to transitions to Rydberg states with total electronic angular momentum quantum numbers $\Omega = 0, 1$ and 2 in the series converging to both ion states, $X^2E_{3/2}$ and $X^2E_{1/2}$, have been identified for CF₃I [22]. The fragment ions CF₃⁺ and CF⁺ and $(2 + 1)$ REMPI of the Cl atoms are detected in REMPI of CF₃Cl, whereas no parent ions have been seen [11]. The CF₃⁺ ions are believed to be formed by ionization of CF₃⁺ after dissociation of the resonance excited Rydberg states and the strong Cl atom resonances are mainly attributed to dissociation channels which form the species CF₃ + Cl(²P_{3/2})/Cl*(²P_{1/2}). CF₃⁺ and CF₃I⁺ ions are detected in REMPI of CF₃I. It has been argued that structure distortions observed in Rydberg states of CF₃I could possibly be due to interactions with ion-pair states [22].

The Rydberg and ion-pair state structures of the unfluorinated counterparts CH_3X ; $\text{X} = \text{Cl}, \text{Br}$ and I have been studied more extensively than the corresponding fluorinated compounds [24] and limited comparison of spectra structures is available. Considerable differences, however, have been observed in certain Rydberg spectra structures for CF_3I and CH_3I [22].

In this Letter we present $(2+n)$ REMPI studies of CF_3Br . Two-photon resonance excitations to Rydberg states are observed and characterized. Ion-pair formations and predissociation channels are identified.

2. Experimental

Two dimensional (2D) REMPI data for jet cooled CF_3Br gas were recorded. Ions were directed into a time-of-flight (TOF) tube and detected by a micro-channel plate (MCP) detector to record the ion yield as a function of mass and laser radiation wavenumber. The apparatus used is similar to that described elsewhere [25–27]. Tunable excitation radiation in the 562–475 nm wavelength region was generated by Excimer laser-pumped dye laser systems, using a Lambda Physik COMPex 205 Excimer laser and a Coherent ScanMatePro dye laser. The dyes C-540A, C-503, and C-480 were used and frequency doubling obtained with a BBO-2 crystal. The repetition rate was typically 10 Hz. The bandwidth of the dye laser beam was about 0.095 cm^{-1} . Typical laser intensity used was 0.1–0.3 mJ/pulse. The radiation was focused into an ionization chamber between a repeller and an extractor plate. An undiluted, pure CF_3Br gas sample (Pfaltz & Bauer Inc.) was used. It was pumped through a 500 μm pulsed nozzle from a typical total backing pressure of about 2.0–2.5 bar into the ionization chamber. The pressure in the ionization chamber was lower than 10^{-6} mbar during experiments. The nozzle was kept open for about 170 μs and the laser beam was typically fired 500 μs after opening the nozzle. Ions were extracted into a TOF tube and focused onto a MCP detector, of which the signal was fed into a LeCroy WaveSurfer 44MXs-A, 400 MHz storage oscilloscope as a function of flight time. Average signal levels were evaluated and recorded for a fixed number of laser pulses (typically 30 pulses) to obtain the mass spectra. Mass spectra were typically recorded in 0.05 or 0.1 cm^{-1} laser wavenumber steps to obtain 2D REMPI spectra. REMPI spectra for certain ions as a function of excitation wavenumber (1D REMPI) were obtained by integrating mass signal intensities for the particular ion. Care was taken to prevent saturation effects as well as power broadening by minimising laser power. Laser calibration was performed by recording an optogalvanic spectrum, obtained from a built-in Neon cell, simultaneously with the recording of the REMPI spectra. Line positions were also compared with the bromine lines [28]. The accuracy of the calibration was found to be about $\pm 1.0 \text{ cm}^{-1}$ on a two-photon wavenumber scale. Intensity drifts during the scan were taken into account, and spectral intensities were corrected for accordingly. Overall spectra are composed of several shorter scans, each of which were normalized. These scans were then normalized to each other using the intensities of bands that are common to neighbouring sections.

3. Results and analysis

2D-REMPI data recorded for the two-photon excitation region 71 320–84 600 cm^{-1} revealed ion signals for CF_3^+ , ${}^i\text{Br}^+$ ($i = 79, 81$) and C^+ only. The CF_3^+ 1D-REMPI showed weak broad features ranging from about 74 300 cm^{-1} to 84 600 cm^{-1} (see Figure 1). The atom ion signals consisted of ${}^i\text{Br}({}^2P_{3/2})/{}^i\text{Br}({}^2P_{1/2})$ (Figure 2) and $\text{C}({}^3P_j)/\text{C}({}^1D)$ atom $(2+n)$ REMPI's only. The ${}^i\text{Br}$ atom $(2+n)$ REMPI signals observed, were very weak in the lowest wavenumber region (70 987–72 012 cm^{-1} ; $\text{Br}^*({}^3P_{2c} 5p) \leftarrow \text{Br}^*({}^4p^5; {}^2P_{1/2})$ tran-

sitions) whereas the ${}^i\text{Br}$ atom resonance signals above 74 300 cm^{-1} were significantly stronger, overall, and very strong signals were observed in the high energy region for the two resonance transitions from $\text{Br}^*({}^4p^5; {}^2P_{1/2})$ to $\text{Br}^*({}^1D]_c 5p; {}^2F_{5/2})$ (83 376.99 cm^{-1}) and $\text{Br}^*({}^1D]_c 5p; {}^2P_{1/2})$ (83 814.79 cm^{-1}), respectively (see Figure 2). The C/C^* atom REMPI signals all are very weak.

Comparison of the 1D-REMPI spectrum for CF_3^+ and the relative single-photon absorption spectrum derived from Ref. [3] (Figure 1) shows that the strongest features in the REMPI spectrum match the broad absorption peak, near 76 550 cm^{-1} , which has been assigned to a transition from the ground state CF_3Br to a $5p$ Rydberg state which belongs to a Rydberg series converging to the ground ionic state ($\text{CF}_3\text{Br}^+, X^2E$) [3]. No CF_3^+ signal, on the other hand, was found for excitation in the lower energy region corresponding to excitations to the $5s$ Rydberg states (peak near 70 750 cm^{-1}) and the overall CF_3^+ signal in the high energy region gradually decreases with energy between 80 000–84 600 cm^{-1} where an excitation to a $5s$ Rydberg state, which belongs to a Rydberg series converging to the excited ionic state ($\text{CF}_3\text{Br}^+ 2A_1$), is predicted to occur. We therefore conclude that negligible contribution to the CF_3^+ REMPI spectrum is associated with initial two-photon excitations to $5s$ Rydberg states but that significant contribution to the spectral features can be due to initial transitions to $5p$ Rydberg states. This is what might be expected for a two-photon excitation of a nonbonding electron localized on the halogen atom with dominating p -orbital character according to the selection rule $\Delta l = 0$. Assignments of CF_3^+ REMPI spectra features are shown in Figure 1 and listed in Table 1. These were guided by the following.

- (i) Rydberg states were assumed to follow the standard expression

$$E([\Omega_c]nl; \omega) = IE([\Omega_c] - R/(n - \delta_l)^2) \quad (1)$$

where $E([\Omega_c]nl; \omega)$ is the energy of the Rydberg state $[\Omega_c]nl; \omega$, IE is the ionization limit to which the series converges ($[\Omega_c]$), R is the Rydberg constant, n is the principal quantum number and δ_l is the relevant quantum defect, depending on l (see Table 2). A search was made for consistent fits of the major spectra peaks to expression [1] for ionization limits of spin-orbit components of the ground ionic state (Table 1) for realistic quantum defect values (see Table 2).

- (ii) Assuming that the potential energy surfaces for the Rydberg states closely resembles those for the ground state $\text{CF}_3\text{Br}(\text{X})$ there is a reason to believe that the strongest spectral features are due to transitions corresponding to unaltered vibrational energy, i.e. that $\Delta v_i = 0$ transitions are the most Franck-Condon-factor favourable for all i . Furthermore frequencies of vibrational modes for Rydberg states are expected to be close to those in the ground state. v_i ($i = 1, 2, 3$) notations corresponding to a_1 symmetry (valid for $\text{CF}_3\text{Br}(\text{X})$) are assumed.
- (iii) By analogy with Rydberg state assignments and observations for the unfluorinated counterpart CH_3Br [12,13] p and d Rydberg states, both $\omega' = 0$ and $\omega' = 2$ components are expected to be observable with $E(\omega = 2) < E(\omega = 0)$. Whereas $\Delta E_\omega (= E(\omega = 0) - E(\omega = 2))$ is uncertain its value is expected to decrease with the principal quantum number n [12].

Transitions to four p Rydberg states ($[X^2E_{3/2}]5p$, $[X^2E_{3/2}]6p$, $[X^2E_{1/2}]5p$ and $[A^2E_{3/2}]6p$) and one d state ($[X^2E_{3/2}]4d$) are identified. Generally the strongest features for each transition are assigned to $\omega = 0$ states, vibrational bands (0,0) whereas spectral features on the long wavenumber side of these, within about 1000 cm^{-1} wave-

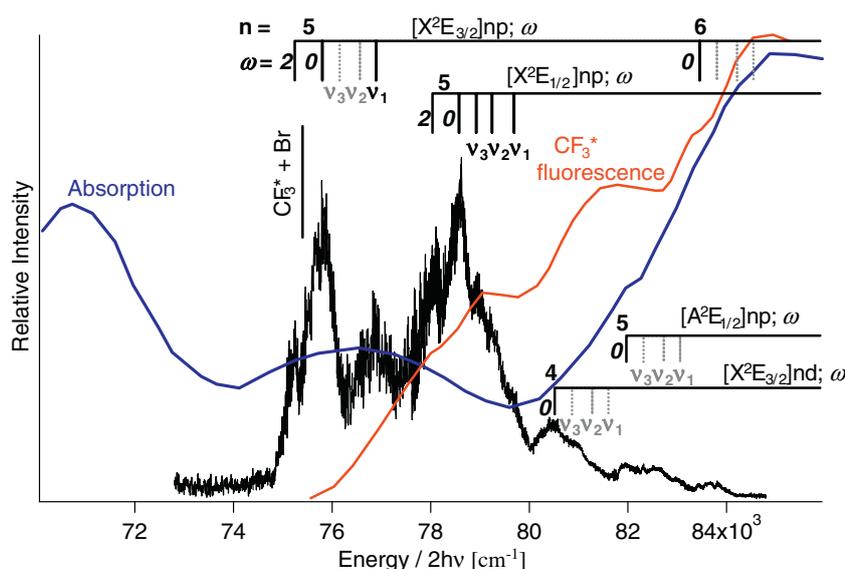


Figure 1. CF_3^+ 1D REMPI spectrum, relative absorption spectrum from Ref. [3] (blue curve) and relative CF_3^+ fluorescence spectrum from Ref. [4] (red curve). Assignments of Rydberg states are shown as unbroken sticks. Dotted sticks are estimated vibrational bands based on vibrational frequencies for the ground state. Threshold for $\text{CF}_3^+ + \text{Br}$ formation is marked. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

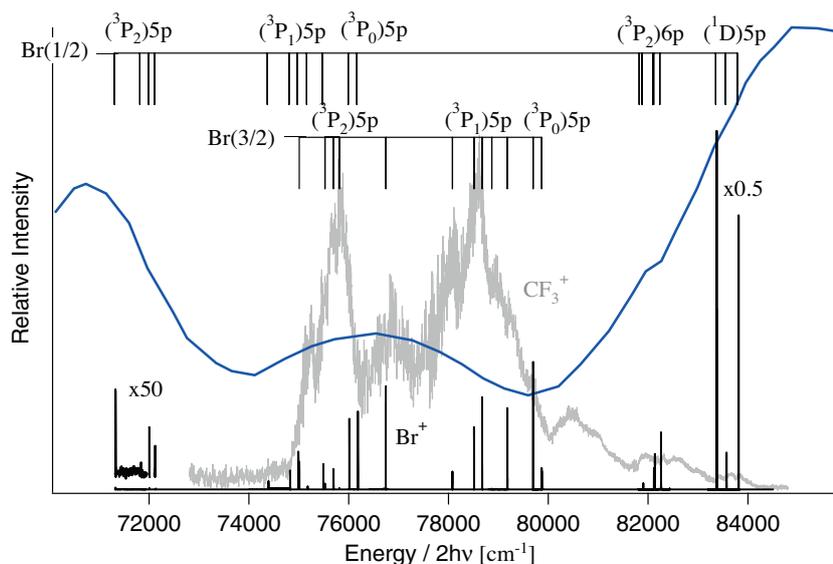
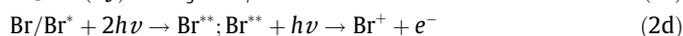


Figure 2. Br^+ 1D REMPI spectra (bold) along with the CF_3^+ 1D REMPI spectrum (Figure 1) (grey) and the absorption spectrum from Ref. [3] (blue curve). Assignments of Br atomic lines are indicated. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

number region, are attributed to transitions to $v_i = 1$ and $v_j = 0$ ($j \neq i$). $\omega = 2$ components were identified for the $[X^2E_{3/2}]5p$ and $[X^2E_{1/2}]5p$ states with $\Delta E_\omega = 560$ and 540 cm^{-1} , respectively. Quantum defect values derived from the analysis and IE 's used are listed in Table 1.

Whereas the very weak bromine atomic REMPI signals observed between $70987\text{--}72012 \text{ cm}^{-1}$ are in the region where no significant Rydberg state excitation is found to occur the medium to strong bromine atomic lines between 74300 and 84600 cm^{-1} are observed where the transitions to the p and d Rydberg states are observed (Figure 2). The strong lines at 83376.99 and 83814.79 cm^{-1} are associated with transitions to the $[X^2E_{3/2}]6p$ state. We therefore believe that the corresponding Br atoms ($\text{Br}(^2P_{3/2})$ and $\text{Br}^*(^2P_{1/2})$) are formed via predissociation of the excited Rydberg states ($\text{CF}_3\text{Br}^{**}(\text{Ry})$) followed by $(2 + 1)$ REMPI, as



The predissociation can either occur by channel (2b) for all energy excitations or by channel (2c) for energies larger than 75332 cm^{-1} [4]. According to Suto and Lee [4] the maximum fluorescence quantum yield for CF_3^+ is only 7% (for $125.0 \text{ nm}/80000 \text{ cm}^{-1}$ one-photon excitation) suggesting that channel (2b) dominates over (2c). Log–log plots of signal intensities as a function of the laser power showed typical ‘levelling off curvature’ [13], which makes it hard to determine the number of photons required for the ionization. This is characteristic of saturation effect, as may be expected for a multiple step $(2 + 2 + 1)$ REMPI [13,29].

Table 1

 Transition wavenumbers, assignments, quantum defect values (δ_i) and ionization energies (IE) relevant for bands due to transitions from ground state CF_3Br to Rydberg states.

Peaks/shoulders (cm^{-1})	Assignments [$\Omega_c n ; \omega (v_1, v_2, v_3)$]	δ_i	IE/cm^{-1}
75243	$[X^2E_{3/2}]5p; 2 (0,0,0)$		91979.4 ^a
75803	$[X^2E_{3/2}]5p; 0 (0,0,0)$	2.40	91979.4 ^a
76890	$[X^2E_{3/2}]5p; 0 1,0,0$		
78036	$[X^2E_{1/2}]5p; 2 (0,0,0)$		94366.8 ^b
78576	$[X^2E_{1/2}]5p; 0 (0,0,0)$	2.36	94366.8 ^b
78922	$[X^2E_{1/2}]5p; 0 (0,0,1)$		
79244	$[X^2E_{1/2}]5p; 0 (0,1,0)$		
79692	$[X^2E_{1/2}]5p; 0 (1,0,0)$		
81967	$[A^2E_{1/2}]5p; 0 (0,0,0)$	2.39	98077.0 ^c
83455	$[X^2E_{3/2}]6p; 0 (0,0,0)$	2.38	91979.4 ^a
80515	$[X^2E_{3/2}]4d; 0 (0,0,0)$	0.91	91979.4 ^a

^a From Ref. [5].

^b Based on Ref. [5]: $IE([X^2E_{3/2}]c) = IE([X^2E_{3/2}]c) + \Delta E_{SO}(CF_3Br^+(X))$; $\Delta E_{SO}(CF_3Br^+(X))$ is the spin-orbit splitting in $CF_3Br^+(X)$ (0.30 eV).

^c Based on Ref. [5]: $IE([A^2E_{1/2}]c) = IE([X^2E_{1/2}]c) + \Delta E_{SO}(Br)$; $\Delta E_{SO}(Br)$ is the spin-orbit splitting in Br (0.46 eV).

Table 2

 Quantum defect values (δ_i) for Rydberg states of bromine atoms and bromine containing compounds.

Atom/molecular species	δ_i		
	s-States	p-States	d-States
Br	3.14 ^a	2.69 ^a	1.30 ^a
Br ₂	2.96 ^b		1.29 ^b
CH ₃ Br		2.57 ^c	0.97 ^c
CF ₃ Br	2.97 ^d , 3.10 ^d	2.71 ^d , 2.38 ^e	0.91 ^e

^a Average values derived from fitting expression (1) to bromine atom Rydberg state energy values [28] vs. principal quantum numbers n .

^b Average values derived from reference [30].

^c Average values derived from reference [12].

^d Values from reference [3].

^e Average values from this work; see Table 1.

CF_3^+ ions could either be formed by one-photon ionization of CF_3^+ after its minor formation by (2c), or, more likely, by state-transfer from the Rydberg states to an inner wall of an ion-pair state above its dissociation limit to form CF_3^+ and Br^- ion pairs (see Figure 3),



(3b) is analogous to many observations reported for related halogen containing compounds [12,21]. Comparison of the CF_3^+ 1D REMPI spectral structure and the relative fluorescence spectrum from reference [4] (see Figure 1) shows no clear correlation between the two. Furthermore, we performed careful power dependence experiments for the CF_3^+ signals as a function of the laser power for several wavenumber excitations in the region 77 200–81 600 cm^{-1} to derive consistent slope values of about 2 (1.9 ± 0.3) from log–log plots of signal intensities as a function of the laser power suggesting that only two photons are needed to form CF_3^+ . All in all we therefore conclude that the major channel for the CF_3^+ formation is (3b).

Energetically C/C^* atoms can not be formed by dissociation of excited CF_3Br states formed by the initial two-photon excitation of concern. The very weak C/C^* atom (2 + 1) REMPI signals, observed, therefore must follow a minimum of initial three-photon excitation.

4. Conclusions

(2 + n) REMPI of CF_3Br reveals weak CF_3^+ , medium to strong $^iBr^+$ ($i = 79.81$) and very weak C^+ ion signals, only, in the two-photon excitation region 71 320–84 600 cm^{-1} . The CF_3^+ signal shows

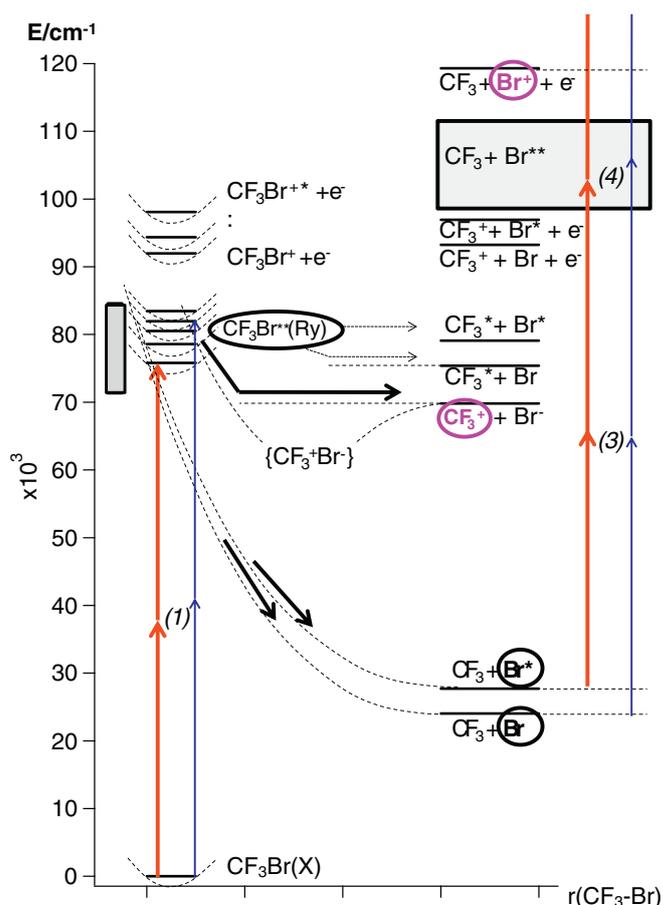


Figure 3. (2 + n) REMPI of CF_3Br : energetics, excitations (red and blue arrows) and photofragmentation processes. The excitation region studied is marked by a shaded area to left. Numbers inside brackets in italic indicate number of photons needed for the particular excitations shown in red and blue. Intermediate species of major importance in the photoexcitation and photofragmentation processes are highlighted with black circles. The major photodissociation processes are indicated by bold arrows. The shaded area on the right marks the range for bromine atomic energy levels excited in (2 + 1) REMPI. Major ion species detected are highlighted in purple. See text for further clarification. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

molecular structures whereas only (2 + 1) atom REMPI signals for $^iBr^+$ and C^+ are observed. The CF_3^+ signals are associated with initial two-photon excitation to p and d Rydberg states followed by crossing to ion-pair states and formation of CF_3^+ and Br^- ion pairs in agreement with general observations for large number of halogen containing reagents. This is further supported by laser power dependence of CF_3^+ signals. The CF_3^+ spectra peaks observed are assigned to transitions to Rydberg states, $\omega = 0$ and 2 and various vibrational states, v_i ($i = 1-3$). The $^iBr^+$ (2 + 1) REMPI observed most probably follows predissociation of the excited Rydberg states of concern. More than two-photon initial excitation is needed prior to C/C^* formation and (2 + 1) C atom REMPI.

Acknowledgements

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