Parent bending effects on nonadiabatic transition dynamics: Isotopomer-resolved imaging of photodissociation of CF$_3$Br at two source temperatures

Fangfang Li, Yujie Ma, Jiaxing Liu, and Fengyan Wang

Citation: The Journal of Chemical Physics 149, 124303 (2018); doi: 10.1063/1.5047927
View online: https://doi.org/10.1063/1.5047927
View Table of Contents: http://aip.scitation.org/toc/jcp/149/12
Published by the American Institute of Physics

Articles you may be interested in
A detailed experimental and theoretical study of the femtosecond A-band photodissociation of CH$_3$I
The Journal of Chemical Physics 128, 244309 (2008); 10.1063/1.2943198

Femtosecond multichannel photodissociation dynamics of CH$_3$I from the A band by velocity map imaging
The Journal of Chemical Physics 126, 021101 (2007); 10.1063/1.2426332

DAVIS: A direct algorithm for velocity-map imaging system
The Journal of Chemical Physics 148, 194101 (2018); 10.1063/1.5025057
Parent bending effects on nonadiabatic transition dynamics: Isotopomer-resolved imaging of photodissociation of CF$_3$Br at two source temperatures

Fangfang Li, Yujie Ma, Jiaxing Liu, and Fengyan Wang$^{a)}$

Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Collaborative Innovation Centre of Chemistry for Energy Materials, Fudan University, Shanghai 200433, People’s Republic of China

(Received 10 July 2018; accepted 6 September 2018; published online 26 September 2018)

Nonadiabatic transition between electronic states plays a critical role in the photodissociation of the CX$_3$Y (X = H and F; Y = Cl, Br, and I) system, and the transition probability was considered to be closely related to the X–C–Y bending motion. Hereby the effect of F–C–Br bending vibration on the nonadiabatic transition dynamics is studied by time-sliced ion velocity imaging of Br(2P$_{1/2,3/2}$) isotopomers produced from the photodissociation of title molecules at two source temperatures, 298 K and 473 K, respectively. At the photolysis wavelength 234 nm, the anisotropy parameter ($\beta$) of the Br(2P$_{3/2}$) products decreases from 1.3 at 298 K to 0.9 at 473 K, while the $\beta$ of Br(2P$_{1/2}$) remains at almost 2 at two temperatures, indicating the significant effect of bending excitation on the ground channel. Two nonadiabatic dissociation pathways are suggested in the Br(2P$_{3/2}$) channel. One of them is the parallel excitation from the ground state to the $^3Q_0$ state in C$_{3v}$ symmetry, and then transition to the $^1Q_1$ state via conical intersection, and the other is the perpendicular excitation to the 3$\Sigma^+$ state in C$_s$ symmetry and then decomposition along this state in the presence of the avoided crossing between 3$\Delta'$ and 4$\Delta'$ states. Closely related to the F–C–Br bending vibration of CF$_3$Br is the latter transition. Published by AIP Publishing. https://doi.org/10.1063/1.5047927

I. INTRODUCTION

For decades, many groups have studied the photodissociation dynamics of the CX$_3$Y (X = H and F; Y = Cl, Br, and I) system, an important class of light-induced molecular dynamics that the nonadiabatic transitions between excited electronic states play a critical role in the reaction pathways.\textsuperscript{1–16} For the title CF$_3$Br, three repulsive states, $^3Q_1$ (2E in C$_{3v}$ symmetry), $^3Q_0$ (2A$_1$), and $^1Q_1$ (3E), are involved in the UV photodissociation, which originates from the $\sigma^*(C–Br)\leftrightarrow n(Br)$ type of electronic transition.\textsuperscript{17–23} As shown in the correlation diagram of Fig. 1(a), the $^3Q_0$ state is reached via a parallel transition and correlates adiabatically with the CF$_3$ + Br$^*$ (2P$_{3/2}$) products, while the $^3Q_1$ and $^1Q_1$ states are reached via perpendicular transitions and correlate adiabatically with the Br(2P$_{3/2}$) channel. From the anisotropy measurements by photofragment translational spectroscopy\textsuperscript{20} and velocity imaging,\textsuperscript{18,21} the strong parallel distribution of Br(2P$_{3/2}$) was contributed to the nonadiabatic transition between the $^3Q_0$ and $^1Q_1$ states. These studies suggested that the transition occurred through the distortion of CF$_3$Br from C$_{3v}$ to C$_s$ symmetry evolving from the F–C–Br bending vibration.

Here, the effect of F–C–Br bending vibration on the nonadiabatic transition dynamics is studied by time-sliced ion velocity imaging of Br(2P$_{1/2,3/2}$) isotopomers produced from the photodissociation of CF$_3$$^{79}$Br/CF$_3$$^{81}$Br molecules at two source temperatures, 298 K and 473 K, respectively. The accessibility of the F–C–Br bending modes with different population would help clarify the influence of the bending mode on the coupling between two repulsive states. As schemed in Fig. 1(b), when the C$_{3v}$ symmetry of CF$_3$Br molecules is distorted to C$_s$ symmetry, the E state is split into A$'$ and A$''$ states, and the 2A$_1$ state is reduced to the A$'$ state, resulting in an avoided crossing between 3$\Delta'$ and 4$\Delta'$ states. The direction of the transition dipole moment with respect to the C–Br bond is shown in Fig. 1. The transition of 3$\Delta'$ $\leftrightarrow$ 1A$'$ in the F–C–Br plane can be differentiated along the C–Br bond or perpendicular to the C–Br bond, in which only the parallel transition was suggested to be related to the parallel features observed in the Br(2P$_{3/2}$) channel.\textsuperscript{17–23}

In addition, we notice that in the previous velocity mapping experiments, the inability to resolve the two bromine isotopomers, $^{79}$Br and $^{81}$Br, with natural abundances of 50.7% and 49.3%, respectively, would cause system deviations in anisotropy measurements.\textsuperscript{21} In the conventional velocity mapping, the inverse Abel transformation, which assumes that there is only a Newton sphere projected onto the detector, had to be carefully used in the analysis of angular distributions in one image with the presence of two isotopomers.\textsuperscript{24,25} The present photodissociation study of CF$_3$$^{79}$Br and CF$_3$$^{81}$Br in respective isotopomer channels,

\[
\text{CF}_3^{79}\text{Br}/\text{CF}_3^{81}\text{Br} \xrightarrow{hv} \text{CF}_3^{+}+^{79}\text{Br}(2\text{P}_{3/2})/^{81}\text{Br}(2\text{P}_{3/2}), \quad (1)
\]
\[
\text{CF}_3^{79}\text{Br}/\text{CF}_3^{81}\text{Br} \xrightarrow{hv} \text{CF}_3^{+}+^{79}\text{Br}^+(2\text{P}_{1/2})/^{81}\text{Br}^+(2\text{P}_{1/2}), \quad (2)
\]
by using the slice imaging technique demonstrates the advantage of directly measuring the scattering species without cylindrical symmetry.26–29

As shown below, the paper is organized as follows: Sec. II describes how we obtain isotopomer-resolved speed and angular distributions in the time-sliced ion velocity imaging. Section III presents the experimental results at two source temperatures. Section IV discusses the detailed dissociation dynamics in the two Br(2P3/2,1/2) channels by comparing the energy distributions and recoil anisotropies of fragments between the two source temperatures. Then Sec. V concludes the important results about the dissociation dynamics in CF3Br molecules.

II. APPARATUS AND EXPERIMENT

A. Slice imaging for isotopomers

As seen in Fig. 2, in our time-sliced ion velocity imaging apparatus, the ion optics consists of 23 circular electrode plates with a diameter of 86 mm and an aperture diameter of 2 mm, 30 mm, or 52 mm, respectively, and projects scattered ions through the electrodes to a position sensitive detector. Figures 2(a) and 2(b) show the ion flight trajectories of 79Br+ and 81Br+ born ions, represented by eight directions at the same initial kinetic energy of 0.75 eV and an initial speed |v| show relative stretching time or time width ts ∝ vz/V. As shown in Fig. 2(c) for the 79Br+ and 81Br+ ion packets, the center slice of the 79Br ions with vz ≈ 0 can be recorded simultaneously with the front of the 81Br ion packet with vz > 0.

The position sensitive detector consists of two microchannel plates (MCP, 75 mm diameter, Photek) and a phosphor screen (P43, Photek). The front MCP is set at 900 V and the rear MCP remains at 1300 V plus 500 V gate voltage with a pulse of ∼30 ns for a slice of the ion cloud. A Lavision Elite CCD camera captures the light emitted from the P43 and transmits it to the computer with improved software “Davis 8.2” for image acquisition.

B. Experimental scheme on photodissociation of CF3Br molecules

The photodissociation experiment was conducted in our crossed-beam setup, and only one of the molecular beams

![FIG. 2. Simulated ion trajectories of (a) 79Br+ and (b) 81Br+ born ions, represented by eight directions at the same initial kinetic energy of 0.75 eV, and a snapshot of the center slice of the 79Br+ ion clouds together with the front slice of 81Br+ ion clouds shown in (c). The potential contour spacing is 58.1 V with a total voltage of 1800 V on the ion optics. The expansion of the ion clouds is shown with the 2.12 µs divisions along the time of flight direction (defined as the Z axis). The velocity distributions of 79Br+ and 81Br+ isotopomers in the XY plane are obtained from the slice images.](image-url)
was used in the present study. Briefly, the supersonic beam of 5% CF$_3$Br in He buffer gas was expanded from the Even-Lavie value with backing pressure about 10 atm, passed the skimmer (Beam Dynamics No. 50), and crossed the laser beam in the center area of the ion optics. Two source temperatures 298 K and 473 K were chosen to change the population of the F–C–Br bending excited CF$_3$Br relative to the ground CF$_3$Br from roughly $P_{\text{bend}} \approx 0.23$ at $T_s = 298$ K to 0.54 at 473 K, corresponding to the vibrational temperature of the molecular beam at $\sim 269$ K and $\sim 424$ K, respectively. To determine the CF$_3$Br internal energy distribution, we measured the speed distribution of the molecule beam along its propagation via ion imaging of parent ions produced from the multiphoton ionization at 193 nm and obtained the translational temperature $T_t \approx 2–3$ K at $T_s = 298$ K and $\sim 16$ K at 473 K, respectively. For an expanding jet of polyatomic molecules, the rotational temperature follows the translational temperature, i.e., $T_r \approx T_t$ in the collision-free region. Thus according to the conservation of enthalpy, the vibrational temperatures are determined and more details are shown in the Appendix.

The laser beam (1-2 mJ/pulse) was generated by a Nd:YAG laser pumped narrow band optical parametric oscillator/optical parametric amplifier (OPO/OPA) laser system (Continuum Sunlite) and then focused by a cylindrical lens with a focal length of 500 mm to the intersection area. The Br($^2P_{3/2}$) produced by the photodissociation of CF$_3$Br at 233.68 nm is ionized at the same wavelength via the (2 + 1) REMPI scheme through the intermediate state $6p^4P_{3/2}$. Likewise, the Br($^2P_{1/2}$) formed by the photodissociation of CF$_3$Br at 234.02 nm is ionized at the same photon energy via the (2 + 1) REMPI scheme through $6p^4P_{1/2}$. The energy range of $\pm 0.46$ cm$^{-1}$ was scanned to cover ions with various kinetic energy components.

We obtained the time evolution of the isotopic ion clouds by scanning the time delay $t$ between the photolysis laser and the pulse gate on the detector. The time of flight is approximately $t \sim 0.605$ microseconds ($\mu$s), where 0.605 $\mu$s is the time lag of the laser pulse to the trigger.

III. EXPERIMENTAL RESULTS

A. Time evolution of the two-bromine isotopomers scattering process

At the total voltage of the ion optics $V = 1800$ V, the temporal evolution of the $^{79}$Br$^*$/$^{81}$Br$^*$($^2P_{1/2}$) time-sliced images expands over $\sim 700$ ns, as shown in Fig. 3 in the region of $t = 15.17–15.88$ $\mu$s. Clearly, as $t$ increases, the $^{79}$Br$^*$($^2P_{1/2}$) ring first appears at 15.17 $\mu$s, and reaches its maximum at 15.41 $\mu$s, and then contracts to a tiny spot at $\sim 15.67$ $\mu$s; Concomitantly, the $^{81}$Br$^*$($^2P_{1/2}$) ring appears at 15.37 $\mu$s and extends to 15.88 $\mu$s, reaching the maximum at 15.61 $\mu$s. The temporal spread ($t_c$) for each isotopic Newton sphere is about 500 ns, and the overlap time $\Delta t_c$ between two ion clouds is about 300 ns ($\Delta t_c = 15.67–15.37$ $\mu$s). The center slices of the two isotopomers are clearly separated at an interval of approximately 200 ns, with the $^{79}$Br$^*$’s center slice at 15.41 $\mu$s and the $^{81}$Br$^*$’s center slice at 15.61 $\mu$s, respectively. The speed and angular distributions of the bromine isotopomers would be obtained from the corresponding center slices.

When the total voltage on the ion optics was increased to 3200 V, the slice images of the $^{79}$Br$^*$ and $^{81}$Br$^*$ isotopomers are shown in Fig. 4. The ion cloud of the $^{79}$Br$^*$ fragments expands from 11.55 $\mu$s to 11.835 $\mu$s with the center slice at 11.69 $\mu$s, while the $^{81}$Br$^*$ fragments expand from 11.69 $\mu$s to 11.97 $\mu$s with the center slice at 11.83 $\mu$s. The center slices of the two isotopomers are separated by 145 ns, with $t_c$ and $\Delta t_c$ to be 285 ns and 145 ns, respectively.

FIG. 3. Time evolution of the raw time-sliced velocity images of $^{79}$Br$^*$($^2P_{1/2}$) and $^{81}$Br$^*$($^2P_{1/2}$) fragments from the photodissociation of respective CF$_3$Br/CF$_3$Br molecules, at a function of time delay $t$ between the photolysis laser and the detection gate. The total applied voltage on the ion optics is 1800 V. The assignments of isotopomers are shown on the top. The linear polarization direction of the laser is vertical in the imaging plane.
FIG. 4. The same as Fig. 3 but at a high voltage of 3200 V.

Figures 5(a) and 5(b) show the time expansion of the $^{79}$Br* and $^{81}$Br* Newton spheres obtained from the original images of Figs. 3 and 4 at two voltages. The pixel-to-speed calibration is based on the well-studied photolysis process of the O$_2$ molecules. 24, 30 Two split peaks, indicated by the vertical dashed lines, represent the center slices for the two isotopomers with $v_z \approx 0$. As seen from Figs. 5(a) and 5(b), the speed for the bromine isotopomers at the center slice is independent of the applied voltage to the ion optics, whereas the speed of the overlapping isotopomer at the none-center slice changes with voltage. A high voltage gives the center slice better mass-resolved velocity profile.

B. Speed and angular distributions of Br*(2P$_{1/2}$) isotopomers at $T_s \approx 298$ K

By integrating ion counts in the center slice images, we obtained the speed distributions of each bromine isotopomer in consideration of the weighting factor of $v^2 \sin \theta$, where $\theta$ is the angle between the laser polarization direction and the recoil velocity $v$ of Br atoms. Figure 6(a) shows the speed distribution of the $^{79}$Br* fragments peaked at $\sim 1360$ m/s, with the speed ratio $\Delta v/v = 0.09 \pm 0.01$ at 1800 V and $0.11 \pm 0.01$ at 3200 V, and the overlapped $^{81}$Br* fragments at 880 m/s at 1800 V and 450 m/s at 3200 V. Meanwhile, Fig. 6(b) shows the speed distribution of the $^{81}$Br* fragments peaked at $\sim 1320$ m/s, with $\Delta v/v = 0.09 \pm 0.01$ at 1800 V and $0.11 \pm 0.01$ at 3200 V, respectively, and the overlapped $^{79}$Br* peaked at a lower speed at the two voltages. The speed distributions of isotopomers in the center slices were well separated from each other in the two voltages, but the high voltage shows much better isotopomer separation at the center slice with slightly reducing the speed ratio $\Delta v/v$.

Figures 6(c) and 6(d) show the angular distributions of the $^{79}$Br* and $^{81}$Br* isotopic fragments, which are, respectively, derived from the corresponding center slice images at two voltages. Top-bottom asymmetry in the angular distributions is related to the density-to-flux effect. 27 The angular distribution of photofragments is generally described by the formula

$$I(\theta) = I_0 [1 + \beta (3 \cos^2 \theta - 1)/2],$$

where the parameter $\beta$ characterizes the anisotropy of the distribution in the range of $[-1, 2]$. 33 As shown in Figs. 6(c) and 6(d), the fitting of Eq. (3) to the angular distributions of bromine isotopomers gives the same limit value of $\beta = 2.0 \pm 0.1$, which is significantly larger than the previous reported value $\beta = 1.83 \pm 0.05$. 19 The discrepancy between our value...
and the previous $\beta$ can be attributed to the inability to distinguish isotopomers in previous imaging experiments, which shows the isotopomer-overlapped time-of-flight spectra in dissociation of CF$_3$Br at 225 nm.\textsuperscript{18,21} This is clearly demonstrated from a lower $\beta$ (1.5 ± 0.1) obtained in the slice image of the two overlapped bromine isotopomers at 1800 V (at 15.49 $\mu$s) or at 3200 V (at 11.76 $\mu$s). Besides, previous studies estimated the rotational temperature in their molecular beam about 50 K,\textsuperscript{18,21} which is larger than the present rotational temperature $\sim$2–16 K. A higher rotational temperature may bring a more isotropic angular distribution.

C. Distributions of Br($^2P_{3/2}$) fragments at $T_s \approx 298$ K

Figures 7(a) and 7(b) show the center slice images of the $^{79}$Br($^2P_{3/2}$) and $^{81}$Br($^2P_{3/2}$) fragments recorded at 3200 V.
Figure 7(c) shows the derived speed distribution of $^{79}$Br fragments with a peak at $\sim 1470$ m/s and speed ratio $\Delta v/v = 0.12 \pm 0.02$, and the distribution of $^{81}$Br products with a peak at $\sim 1450$ m/s and $\Delta v/v = 0.14 \pm 0.02$, respectively. In consistency with the conservation of energy and recoil momentum, the speed distributions between $^{79}$Br and $^{81}$Br fragments show a slight shift. Figure 7(d) shows the angular distributions of the ground $^{79}$Br and $^{81}$Br fragments with the same $\beta = 1.3 \pm 0.2$, which is again larger than the previous result ($\beta = 0.66 \pm 0.05$). The unresolved bromine isotopomers and the high rotational temperature in the previous conventional imaging experiment can together lead to an isotropic angular distribution.

D. Distribution of bromine fragments at a high source temperature

Figure 8(a) shows the center slice image of the $^{79}$Br($^2P_{1/2}$) fragments and (b) shows the $^{79}$Br($^2P_{3/2}$) when the Even-Lavie valve was heated up to 473 K. To directly view the temperature effect on product energy distributions, Figs. 8(c) and 8(d) present the speed distributions of bromine fragments in spin-orbit split states of $^2P_{3/2}$ and $^2P_{1/2}$, obtained at 473 K and 298 K, respectively, which show the negligible difference in the $^{79}$Br or $^{79}$Br* product speed distributions between the two source temperatures. Figures 8(e) and 8(f) display the angular distributions of $^{79}$Br fragments at $T_s \approx 473$ K in $^2P_{3/2}$ and $^2P_{1/2}$ states, respectively. The anisotropy parameters $\beta = 1.9 \pm 0.1$ for Br($^2P_{1/2}$) and $0.9 \pm 0.1$ for Br($^2P_{3/2}$) are obtained at a high source temperature of 473 K. The anisotropy for the Br($^2P_{1/2}$) channel at the high temperature is almost the same to that at the low source temperature within our error bars (one standard deviation), indicating that the parent rotational motion at $T_r \approx 20$ K does not significantly reduce the anisotropy of the excited parent CF$_3$Br. But, for the Br($^2P_{3/2}$) fragments, the distribution at 473 K is more isotropic than that at 298 K. The large change of anisotropy of Br($^2P_{3/2}$) at a high source temperature suggests that the bending excitation plays an important role in the relevant dissociation dynamics.

IV. DISCUSSION

The ground CF$_3$Br in $C_{3v}$ symmetry has six normal vibrational modes, in which $v_3$ ($a_1$) = 4.17 kJ/mol (349 cm$^{-1}$), C–Br stretch, and $v_6$ ($e_1$) = 3.66 kJ/mol (306 cm$^{-1}$), F–C–Br bend, can thermally be excited into relatively large vibrational population at a high source temperature. Excitation of the F–C–Br bending mode can distort CF$_3$Br from $C_{3v}$ symmetry to $C_s$ symmetry, enabling us to study the bending effect on the coupling between the two repulsive states. From the perspective of energy distribution and recoil anisotropy, the discussion on the dissociation dynamics of CF$_3$Br at the two source temperatures is given as below.

A. Energy partitioning

Based on energy conservation, the available energy $E_{avl}$ for Br$^*$($^2P_{1/2}$) and Br$^*$($^2P_{3/2}$) channels from the photodissociation of CF$_3$Br molecules is obtained from the photon energy $hv$ ($\sim 511$ kJ/mol) plus the average excited internal energy of CF$_3$Br($E_{int}$) (about 1.4 kJ/mol at 298 K and 4.4 kJ/mol at 473 K obtained from the relative vibrational population of CF$_3$Br at the two source temperatures) and minus the C–Br bond dissociation energy $D_0$ ($\sim 287$ kJ/mol) and the electronic energy of bromine radicals [0 for Br($^2P_{3/2}$) and 44.1 kJ/mol for Br$^*$($^2P_{1/2}$)]. From the analysis of speed distributions of Br fragments, the partitioning results of $E_{avl}$ into the
translational energy of CF₃ + Br products and the internal energy of \(E_{\text{CF3}}\) are summarized in Table I. It is seen that 82%–86% of \(E_{\text{avl}}\) is disposed into the translation energy of products in the Br*\(^{(2P_{1/2})}\) or Br\(^{(2P_{3/2})}\) channels. The vibration excitation of CF₃Br at a high source temperature has negligible effect on the energy distributions of the CF₃ + Br products.

The direct model for triatomic molecules (F₁)–C–Br estimates that \(\mu_{\text{Br–CF}}/\mu_{\text{Br-CF₃}} = 28\%\) of the available energy is disposed into the translational energy of CF₃ + Br fragments, which is substantially below that we observe. In the direct model, \(E_{\text{avl}}\) is first partitioned between the kinetic energies of C and Br by conservation of linear momentum, \(M_{C}V_{C} = M_{Br}V_{Br}\). Then when the recoiling atom C collides its partner three F atoms, the recoil velocity becomes \(V\) under the premise of linear momentum conservation, \(M_{C}V_{C} = (M_{C} + 3M_{F})V\). Here, we assume that each of the F atom gains velocity along the direction of the C–F bond, and its projection on the axis of symmetry is \(V\). Then the lost kinetic energy \(\Delta E_{T}\), which equals the internal energy of CF₃ fragments, will be

\[
\Delta E_{T} = \frac{1}{2}M_{C}V_{C}^{2} - \frac{1}{2}M_{C}V^{2} - \frac{1}{2}3M_{F}(V/\cos \alpha)^{2},
\]

where \(\alpha\) is the bond angle of F–C–Br at the moment of dissociation. Using \(\alpha \approx 115°\), the F–C–Br bond angle about 4° larger than the optimized geometry for CF₃Br, we calculate about 86% of the available energy disposed into the translational energy of products.

### B. Recoil anisotropy

Table II summarizes the photofragment anisotropy parameters in the current work and previous reports at 234 nm. Comparatively, large \(\beta\) values are present in the current isotopomer resolved studies for both of the Br\(^{(2P_{3/2})}\) and Br\(^{(2P_{1/2})}\) channels. When \(T_{s} = 298\) K, \(\beta = 2.0 \pm 0.1\) of Br\(^{(2P_{1/2})}\) reaches the classical limit, indicating a sudden C–Br cleavage along the \(3Q_{0}\) state after the initially parallel transition. Based on Kim et al.’s density functional calculation and the recoil velocity \(\sim 2870\) m/s measured between Br* and CF₃ in our experiment, it would take about 75 fs to dissociate along the \(3Q_{0}\) curve from 1.920 Å at the ground-state equilibrium geometry to 3.0 Å between the separated CF₃ and Br* fragments. The strong positive \(\beta = 1.9 \pm 0.1\) for the Br\(^{(2P_{1/2})}\) channel at the high source temperature confirms the direct dissociation in a collinear geometry along the \(3Q_{0}\) state and indicates that the F–C–Br bending excitation has little effect on the direct dissociation path to the Br\(^{(2P_{1/2})}\) channel.

The maximum parallel anisotropy (\(\beta \sim 2\)) obtained in the Br\(^{(2P_{1/2})}\) channel rules out the possibility of the initial excitation to the \(1Q_{1}\) state, which would decrease \(\beta\) of Br\(^{(2P_{1/2})}\) by crossing to the surface of \(3Q_{0}\). Then the contribution from the initial \(1Q_{1}\) state to the Br\(^{(2P_{3/2})}\) channel can also be eliminated. Only the low state \(1Q_{1}\), energetically accessible at the current wavelength, can adiabatically form Br\(^{(2P_{3/2})}\) with \(\beta = -1\). In fact, the positive \(\beta = 1.3\) at \(T_{s} = 298\) K and \(\beta = 0.9\) at \(T_{s} = 473\) K measured in our experiment suggest that the initial parallel transition to \(3Q_{0}\) followed by the curve crossing to the \(1Q_{1}\) state is dominant in the formation of the Br\(^{(2P_{3/2})}\) channel. The contributions of the involved parallel and perpendicular transitions can be obtained from \(\beta(\text{Br})\),

\[
\beta(\text{Br}) = a_{||}\beta_{||} + a_{\perp}\beta_{\perp} ,
\]

where \(a_{||}\) and \(a_{\perp}\) are the weighting factors for the purely parallel (\(a_{||} = 2\)) and perpendicular (\(a_{\perp} = -1\)) transitions. From the combined equations, we solve that at \(T_{s} = 298\) K, \(a_{||}\) and \(a_{\perp}\) are 0.77 and 0.23, respectively, while at \(T_{s} = 473\) K, they are 0.63 and 0.37, respectively. Non-zero contributions from parallel transition \(a_{||}\) at two source temperatures confirm the nonadiabatic transition of \(1Q_{1} \rightarrow 3Q_{0}\) in leading to Br\(^{(2P_{3/2})}\). In addition, the large ratio of \(a_{||}/a_{\perp}\) in the Br\(^{(2P_{3/2})}\) channel at a higher source temperature indicates that the perpendicular transition of \(3A' \rightarrow 1A'\) in the F–C–Br plane participates in the dissociation of the CF₃Br in the \(v_{6}\) mode and leads to Br\(^{(2P_{3/2})}\) via the avoided crossing between \(3A'\) and \(4A'\) states.

The relative quantum yields at two source temperatures are used along with the anisotropies to understand the nonadiabatic transition dynamics. When the relative population of F–C–Br bending excited states, which is normalized to the

### Table I. Information on speed distributions and energy distributions in respective Br\(^{(2P_{1/2})}\) and Br\(^{(2P_{3/2})}\) isotopomer channels.

<table>
<thead>
<tr>
<th>Channel</th>
<th>(T_{s}) (K)</th>
<th>(E_{\text{avl}}) (kJ/mol)</th>
<th>(v_{pk}) (m/s)</th>
<th>(⟨E_{F}\rangle) (kJ/mol)</th>
<th>(⟨E_{avr}\rangle) (kJ/mol)</th>
<th>(⟨E_{F}/E_{avr}\rangle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{79})Br* (^{(2P_{1/2})})</td>
<td>298</td>
<td>181</td>
<td>1360 ± 14</td>
<td>155 ± 8</td>
<td>26 ± 1</td>
<td>0.86 ± 0.05</td>
</tr>
<tr>
<td>(^{81})Br* (^{(2P_{1/2})})</td>
<td>298</td>
<td>181</td>
<td>1320 ± 13</td>
<td>155 ± 8</td>
<td>26 ± 1</td>
<td>0.86 ± 0.04</td>
</tr>
<tr>
<td>(^{79})Br* (^{(2P_{3/2})})</td>
<td>473</td>
<td>184</td>
<td>1335 ± 13</td>
<td>153 ± 8</td>
<td>31 ± 2</td>
<td>0.83 ± 0.04</td>
</tr>
<tr>
<td>(^{79})Br (^{(2P_{3/2})})</td>
<td>298</td>
<td>226</td>
<td>1470 ± 15</td>
<td>186 ± 10</td>
<td>40 ± 2</td>
<td>0.82 ± 0.04</td>
</tr>
<tr>
<td>(^{81})Br (^{(2P_{3/2})})</td>
<td>298</td>
<td>226</td>
<td>1450 ± 15</td>
<td>187 ± 10</td>
<td>39 ± 2</td>
<td>0.83 ± 0.04</td>
</tr>
<tr>
<td>(^{79})Br (^{(2P_{3/2})})</td>
<td>473</td>
<td>229</td>
<td>1460 ± 15</td>
<td>189 ± 10</td>
<td>40 ± 2</td>
<td>0.83 ± 0.04</td>
</tr>
</tbody>
</table>

### Table II. Summary of the anisotropy parameters of bromine fragments in the two spin-orbit states. The grey region shows the current results for bromine isotopomers obtained at the two source temperatures and the last row shows the earlier results at the same photoysis wavelength with the reference marked at the upper right of the values.

<table>
<thead>
<tr>
<th>(\lambda) (nm)</th>
<th>Temp. (K)</th>
<th>Isotopomers</th>
<th>(\beta(\text{Br}^{(2P_{3/2})}))</th>
<th>(\beta(\text{Br}^{(2P_{1/2})}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>234</td>
<td>298</td>
<td>(^{79})Br</td>
<td>1.3 ± 0.2</td>
<td>2.0 ± 0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(^{81})Br</td>
<td>1.3 ± 0.2</td>
<td>2.0 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>473</td>
<td>(^{79})Br</td>
<td>0.9 ± 0.1</td>
<td>1.9 ± 0.1</td>
</tr>
<tr>
<td>607</td>
<td>~298</td>
<td>Br</td>
<td>0.66 ± 0.05(^{10})</td>
<td>1.83 ± 0.05(^{10})</td>
</tr>
</tbody>
</table>
ground state of CF$_3$Br, increases from $P_{\text{bend}} \approx 0.23$ at $T_s = 298$ K to 0.54 at 473 K, the relative signal intensities of $^{39}$Br($^2\Pi_{3/2}$)/$^{79}$Br($^2\Pi_{1/2}$) increase from 0.11 ± 0.01 at 298 K to 0.16 ± 0.01 at 473 K. That is, the yield of Br($^2\Pi_{3/2}$) from the high temperatures source is 1.4 ± 0.2 times of that at the low temperature. Then the relative contributions of $a_{||}$ and $a_{\perp}$ to the Br($^2\Pi_{3/2}$) channel are increased to 0.88 and 0.52 at a high temperature, as 1.1 ± 0.2 and 2.3 ± 0.3 times of $a_{||}$ and $a_{\perp}$ at a low temperature, respectively. The different trends of $a_{||}$ and $a_{\perp}$ at the two source temperatures indicate that two nonadiabatic dissociation pathways are involved in the formation of Br($^2\Pi_{3/2}$). The large increase of $a_{\perp}$ at 473 K can be attributed to the increase in the vibrational excitation population in the F–C–Br bending ($v_6$) mode thermally prepared at a high source temperature. The perpendicular feature of the path closely related to the F–C–Br bending vibration is expected to result from the perpendicular excitation to the 3$A'$ state under C$_s$ symmetry and the avoided crossing between 3$A'$ and 4$A'$ states. The direct dissociation along the 3$Q_1$ state can also contribute to $a_{\perp}$ in the Br($^2\Pi_{3/2}$) channel but has no correlation with the binding mode. Meanwhile, another dissociation path as represented by $a_{||}$, which has little to do with the F–C–Br bending mode, would mainly follow the parallel transition to the 3$Q_0$ state in the C$_v$ symmetry and then form Br($^2\Pi_{3/2}$) with the subsequent conical intersection between 1$Q_1$ and 3$Q_0$ states.

The above results and discussions shed new insights into the X–C–Y bending effect on the nonadiabatic photodissociation dynamics of CX$_3$Y (X = H and F; Y = Cl, Br, and I) systems. In contrast to the explanation given in many previous experimental studies, our photodissociation study of thermally excited CF$_3$Br molecules indicates that when F–C–Br bending excitation deforms the molecule symmetry to C$_v$, a perpendicular transition rather than a parallel one occurs to the 3$A'$ state, followed by an avoided crossing between 3$A'$ and 4$A'$ states to form Br($^2\Pi_{3/2}$). The perpendicular feature for the nonadiabatic transition has also been observed in the I($^2\Pi_{3/2}$) channel from the photodissociation study of CH$_3$I molecules in the $v_6$ mode. Meanwhile, we suggest that the molecules undistorted in the C$_v$ symmetry can undergo the parallel transition to the 3$Q_0$ state and then dissociate to the Br($^2\Pi_{3/2}$) fragments along the 1$Q_1$ state via the conical intersection between 3$Q_0$ and 1$Q_1$. These new findings require the assistance of theoretical calculations for better understanding of the nonadiabatic transition dynamics in different symmetries.

V. CONCLUSION

Through the time-sliced ion velocity imaging of photodissociation dynamics of CF$_3$Br molecules, we obtained the isotopomer-resolved speed and angular distributions of the bromine fragments in the two spin-orbit split channels. Taking into account the F–C–Br bending angle, we developed the impulsive model to predict over 80% of available energy into the translational energy of products in the two channels. From the anisotropies of bromine fragments at the two source temperatures, we proposed that the Br($^2\Pi_{1/2}$) products arise adiabatically from the 3$Q_0$ state in a collinear geometry, while the Br($^2\Pi_{3/2}$) fragments are mainly produced from the nonadiabatic transition from the 3$Q_0$ state to the 1$Q_1$ state. The nonadiabatic transitions in the formation of the Br($^2\Pi_{3/2}$) channel can take place in two symmetries: the parallel transition to the 3$Q_0$ state in C$_s$ symmetry with the subsequent conical intersection to 1$Q_1$, and the perpendicular transition to the 3$A'$ state in C$_v$ symmetry followed by the avoided crossing between 3$A'$ and 4$A'$ states. The former transition has little relationship with the F–C–Br bending excitation, while the latter one is closely related to the F–C–Br bending vibration of CF$_3$Br.

In addition, the isotope experiment demonstrates the applicability and reliability of the slice imaging approach in isotopomer-related scattering studies. Although time-sliced images become more complex for imaging of isotopomers with more than one ring, the evolution of the time-sliced images as a function of time of flight and voltage would help to distinguish the scattering distributions of species in any complex system with abundant isotopes and obtain isotopomer-specific scattering dynamics.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Nos. 21673047 and 21327901), the Shanghai Key Laboratory Foundation of Molecular Catalysis and Innovative Materials (Grant No. 16DZ2270100), and the Program for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning.

There are no conflicts of interest to declare.

APPENDIX: DETERMINATION OF THE VIBRATIONAL TEMPERATURE OF A SUPERSONICALLY EXPANDED AND MIXED CF$_3$Br/He BEAM

To determine the vibrational temperature of the supersonically expanded CF$_3$Br/He molecule beam, we used the same procedure as shown in the previous work with the references therein. In the case of the mixed CF$_3$Br/He beam, the mean molecular weight and mean specific heat were considered under the condition of enthalpy conservation. We measured the beam speed distribution in the two source temperatures via ion imaging of CF$_3$Br ions from the multiphoton ionization process at 193 nm. The CF$_3$Br beam speed distributions are shown in Fig. 9, peaking at ~1066 m/s at 298 K and ~1327 m/s at 473 K, respectively. According to $S = \sqrt{2\ln 2 P_{\text{FWHM}}}$, the speed ratio $S$ changes from ~20 to 298 K to ~10 at 473 K. Then the translational temperature $T_t$ can be obtained from $T_t = T_t/(1 + \frac{v}{v_p})^2$, where the specific heat ratio $\gamma = \frac{C_p}{C_v}$, with $C_p$ as the average constant-pressure heat capacity and $C_v$ as the average constant-volume heat capacity in the CF$_3$Br/He beam. Then $T_t$ is calculated to be ~2–3 K at $T_t = 298$ and ~16 K at $T_t = 473$ K (comparatively, $T_t \sim 20–20$ K in the pure CD$_4$ beam). In the formation of the supersonic molecular beam, frequent intermolecular collisions ensure that the rotational temperature follows the translational temperature as it cools, so when the molecule leaves the jet and enters the collision-free region, we assume that $T_r \approx T_t$. 

Then, the vibrational temperature $T_v$ of the supersonic expansion beam of $\sim 5\% \text{CF}_3\text{Br}$ in He is determined by the enthalpy conservation, $-\dot{m}v \text{d}v = (k + C_r) \text{d}T + 0.05(C_v + C_r) \text{d}T$, where $\dot{m}$ is the mean molecular weight, the heat capacity $C_r = C_v = 3k/2$ (subscript $t$ for translation and $r$ for rotation), and $C_v$ for the vibrational capacity of $\text{CF}_3\text{Br}$ molecules. Then, $\frac{1}{2} \dot{m}v^2 = 2.575k(T_s - T_v) + 0.05 \int_{T_s}^{T_v} C_v \text{d}T$.

Among them, $\int_{T_s}^{T_v} C_v \text{d}T = \sum_i k \theta_i \left[\frac{1}{e^{\Delta_i} - 1} - \frac{1}{e^{	heta_i} - 1}\right]$, where $\theta_i = h\nu_i/k$ and $\nu_i$ is the vibrational frequency of $\text{CF}_3\text{Br}$. Finally, $T_v$ is obtained to be $\sim 269$ K and $\sim 424$ K at two source temperatures 298 K and 473 K, respectively.


