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High-resolution slice imaging of quantum state-to-state photodissociation of methyl bromide

M. Laura Lipciuc and Maurice H. M. Janssen^{a)}

Laser Centre, Vrije Universiteit, de Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

and Department of Chemistry, Vrije Universiteit, de Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

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The photodissociation of rotationally state-selected methyl bromide is studied in the wavelength region between 213 and 235 nm using slice imaging. A hexapole state selector is used to focus a single ($JK=11$) rotational quantum state of the parent molecule, and a high speed slice imaging detector measures directly the three-dimensional recoil distribution of the methyl fragment. Experiments were performed on both normal (CH_3Br) and deuterated (CD_3Br) parent molecules. The velocity distribution of the methyl fragment shows a rich structure, especially for the CD_3 photofragment, assigned to the formation of vibrationally excited methyl fragments in the ν_1 and ν_4 vibrational modes. The CH_3 fragment formed with ground state $\text{Br}(^2P_{3/2})$ is observed to be rotationally more excited, by some $230\text{--}340\text{ cm}^{-1}$, compared to the methyl fragment formed with spin-orbit excited $\text{Br}(^2P_{1/2})$. Branching ratios and angular distributions are obtained for various methyl product states and they are observed to vary with photodissociation energy. The nonadiabatic transition probability for the $^3Q_{0+} \rightarrow ^1Q_1$ transition is calculated from the images and differences between the isotopes are observed. Comparison with previous non-state-selected experiments indicates an enhanced nonadiabatic transition probability for state-selected $K=1$ methyl bromide parent molecules. From the state-to-state photodissociation experiments the dissociation energy for both isotopes was determined, $D_0(\text{CH}_3\text{Br})=23\,400\pm133\text{ cm}^{-1}$ and $D_0(\text{CD}_3\text{Br})=23\,827\pm94\text{ cm}^{-1}$. © 2007 American Institute of Physics. [DOI: 10.1063/1.2813350]

I. INTRODUCTION

The UV photochemistry of halocarbons has received much attention because of their important role in the destruction of the ozone layer. Methyl bromide is the most important carrier of bromine to the stratosphere, where bromine atoms are about 50–60 times more effectual on a per atom basis than chlorine atoms in exhausting ozone.¹ The photodissociation of methyl iodide has been studied in great detail as it represents a benchmark system for polyatomic dissociation dynamics, see, e.g., Ref. 2 and references therein. The photodissociation of methyl bromide appears to have various similarities to methyl iodide but has been studied much less.

Methyl bromide photodissociation via excitation to the $\tilde{A}$ band (first absorption continuum) leads to two dissociation channels: $\text{CH}_3 + \text{Br}(^2P_{1/2})$ with the bromine atom in the spin-orbit excited state, referred to as the Br^* channel, and $\text{CH}_3 + \text{Br}(^2P_{3/2})$ with the bromine atom in the ground state, referred to as the Br channel. Five dissociative excited states correlate to these two dissociation channels and, in Mulliken's notation,³ they are referred to as 3Q_2 , 3Q_1 , $^3Q_{0+}$, $^3Q_{0-}$, and 1Q_1 (in ascending energy order). Only three of these states, 3Q_1 , $^3Q_{0+}$ and 1Q_1 , are electric dipole allowed from the ground state. The excited 3Q_1 and 1Q_1 states, which are accessed through a perpendicular transition, asymptotically correlate to the Br^* channel, while the excited $^3Q_{0+}$ state, which is accessed through a parallel transition, asymptoti-

cally correlates to the Br^* channel. A curve crossing takes place between the 1Q_1 and $^3Q_{0+}$ states.^{4–7} In C_{3v} molecular geometry the symmetries of these three dissociative excited states are A_1 for the $^3Q_{0+}$ state and E for 3Q_1 and 1Q_1 states. In C_{3v} geometry the $^3Q_{0+}$ and 1Q_1 states are of different symmetry and allowed to cross. A reduction to C_s molecular symmetry causes the $^1Q_1(E)$ state to split into two states of A' and A'' symmetries and the $^3Q_{0+}(A_1)$ state reduces to A' symmetry. In C_s geometry nonadiabatic transitions between the $^1Q_1(A')$ and the $^3Q_{0+}(A')$ state can take place allowing branching into both Br^* and Br channels.⁸ Methyl bromide in the ground state and in the excited state near the Franck-Condon region has C_{3v} geometry. A reduction to C_s symmetry may occur if a bending mode or a similar motion is excited in the dissociating molecule. In case of methyl iodide the parent molecule has a propensity to bend in the vicinity of the conical intersection.⁴ The Jahn-Teller effect together with the zero-point vibration of the ν_6 rocking motion of the parent distorts the C_{3v} symmetry enabling nonadiabatic transitions between the two energy surfaces mentioned above.

If the dissociation time of methyl bromide is much shorter than the rotational period, the dissociation is prompt and axial recoil will preserve C_{3v} symmetry. The lifetime of the $\tilde{A}$ band of CH_3Br has not been determined directly, but it was estimated to be about 120 fs.⁹ The end-over-end rotational period for methyl bromide is estimated by $\tau_{\text{rot}} = 1/2BJ \approx 52\text{ ps}$, for $J=1$ ($B=0.3192\text{ cm}^{-1}$), so $\tau_{\text{diss}} \ll \tau_{\text{rot}}$, even for initial rotational states up to $J=10$.

The $\tilde{A}$ absorption band of CH_3Br has a maximum near

^{a)}Author to whom correspondence should be addressed. Electronic mail: mhmmj@chem.vu.nl

~ 200 nm (see, e.g., Fig. 2 in Ref. 10). Magnetic-circular-dichroism data¹¹ show that the 3Q_1 and $^3Q_{0+}$ components are weaker relative to the 1Q_1 component for methyl bromide compared to methyl iodide, where the total intensity distribution is $^3Q_{0+}:^1Q_1:^3Q_1=75:25:1$. From the partial absorption cross section of the $\tilde{A}$ band of CH_3Br ,⁹ we can see that all three components contribute, more or less, to the dissociation process, and the Br/Br^* branching can be produced through both direct excitation and nonadiabatic transitions between the 1Q_1 and $^3Q_{0+}$ energy surfaces. Methyl bromide photodissociation studies have been performed at 193 and 222,¹² 205 nm,¹³ between 218–245 nm,⁹ and between 240–280 nm.¹⁴ It has been found by photofragment imaging and time-of-flight experiments that nonadiabatic processes play an important role in methyl bromide dissociation dynamics through the $\tilde{A}$ band. Studies which probe both Br atoms and methyl fragments using a nonresonant ionization scheme⁹ as well as resonant detection¹⁴ show that both the branching ratio and the anisotropy parameters for each channel depend on the photolysis wavelength. All studies agree that the internal state distribution is hot for both channels, but is hotter for the methyl in the Br channel. Most of the methyl vibrational excitation is assigned to ν_2 umbrella mode.⁹ Evidence of rotationally hot ($E_{\text{rot}} \sim 0.1$ eV) CH_3 ($\nu_2=0,1$) for both Br^* and Br channels was found by Underwood and Powis.¹⁴ The deuterated methyl bromide dissociation was investigated only by Hess *et al.*¹³ at 205 nm and they found that the dissociation dynamics is very similar to the normal methyl bromide.

In this paper we present slice imaging results for photolysis of rotationally state-selected CH_3Br and CD_3Br at 213 nm and in the red wing of the absorption band near 230 nm. Angular and translational energy distributions of state-selectively detected CH_3/CD_3 fragments are obtained using the slice imaging technique.^{15–17} The paper is organized as follows. In Sec. II we provide a short description of the experimental setup. In Sec. III we present images, velocity distributions, and angular distributions for methyl from the photodissociation of normal and deuterated methyl bromide. We present a discussion of the results in Sec. IV and summarize the observations in Sec. V.

II. EXPERIMENT

The molecular beam setup has been described in great detail elsewhere.^{18–20} A mixture of 15% CH_3Br or CD_3Br seeded in Kr is expanded supersonically through a pulsed nozzle and is skimmed before it enters the buffer chamber. The buffer chamber contains a metal sphere of 1 mm diameter, also known as the beamstop, and is positioned on the molecular beam axis. The beamstop eliminates molecules with vanishing first-order Stark interaction, which otherwise would travel in straight lines along the center of the hexapole. The third chamber contains the hexapole. The hexapole focuses the molecules which are off axis and have passed the beamstop onto a final collimator, a 1 mm conically shaped hole in the repeller plate located in the fourth chamber, the imaging chamber. The imaging chamber contains the ion optics—three cylindrical plates: repeller, extractor, and one

FIG. 1. Hexapole focusing spectrum of CH_3Br . The hexapole voltage is the total voltage difference between the positive and the negative rods. The assigned (JKM) rotational states are indicated.

extra plate for slice imaging.^{19,20} The state-selected molecular beam of methyl bromide molecules, focused by the hexapole, is intersected at right angle, in between the repeller and extractor plate, by two counter propagating laser beams separated in time by about 5 ns. The photolysis laser has a wavelength of either 212.8 nm, the fifth harmonic of a Nd:YAG laser (YAG denotes yttrium aluminium garnet), or a wavelength in the 227–235 nm region, the frequency doubled output of a Nd:YAG pumped tunable dye laser. The photolysis laser is focused on the molecular beam with a 25 cm focal length lens and is linearly polarized with the polarization vector perpendicular to the molecular beam propagation direction. The second laser beam with a wavelength between 333–334 nm is focused on the molecular beam with a 25 cm lens and ionizes the methyl photofragment through a (2+1) resonantly enhanced multiphoton ionization (REMPI) scheme. Two photons are used to resonantly excite the methyl photofragment via the 0_0^0 band of the $3p_z\ ^2A_2'' \leftarrow \leftarrow 2p_z\ \tilde{X}\ ^2A_2''$ electronic transition, and the third photon is used to ionize the excited methyl fragment. The ionization laser is also linearly polarized and has the polarization vector either perpendicular or parallel to the molecular beam propagation direction.

The $\text{CH}_3^+/\text{CD}_3^+$ ions are velocity mapped onto a position sensitive detector, a microchannel plate (MCP) with phosphor screen and charge coupled device (CCD) camera. The detector is positioned at the end of a 34 cm time-of-flight tube, which is in line with the molecular beam propagation direction. In order to slice the middle part of the methyl ion cloud the MCP detector is gated with a homebuilt fast high-voltage pulser. We used either a pulser based on metal oxide semiconductor field effect transistor technology, with an effective slice width of about 12 ns, or a pulser based on avalanche transistor technology, with an effective slice width of about 4.5 ns.²⁰ The forward-backward spread in the arrival time of the methyl ion cloud was about 80 ns, which means that we were able to take slices with a width of about 8%–15% of the total spread in arrival time. The light from the phosphor screen is imaged on a 2048×2048 pixels large frame CCD camera (PCO2000). To obtain the position of the

TABLE I. Rotational constants and vibrational frequencies of the ground ($\tilde{X}^2A_2''$) and excited ($3p_z^2A_2''$) states of the CH₃ radical (all in cm⁻¹).

$\tilde{X}^2A_2''$					
Vibrational mode	(0000)	(1000)	(0100)	(0010)	(0001)
ν		3004.43 ^a	606.45 ^a	3160.82 ^a	1398 ^a
B	9.578 ^b	9.492 ^c	9.258 ^b	9.471 ^d	9.831 ^e
C	4.724 ^b	4.693 ^c	4.812 ^b	4.702 ^d	4.885 ^f
$3p_z^2A_2''$					
Vibrational mode	(0000)	(1000)	(0100)	(0010)	(0001)
ν		2931 ^g	1323 ^g	3087 ^h	1428 ^g
B	9.51 ⁱ	...	...	...	...
C	4.62 ⁱ	...	...	...	...

^aReference 37.^bReference 38.^cReference 39.^dReference 40.^eReference 41.^fCalculated assuming the approximate formula $C = B/2$.^gReference 26.^hReference 27.ⁱReference 42.

individual ion events on the phosphor screen, we used centroiding techniques to read out the CCD camera.²⁰

III. RESULTS

A. Parent quantum state selection and fragment quantum state-selective detection

The hexapole focusing spectrum of CH₃Br is shown in Fig. 1. All data presented here were taken with a total hexapole voltage of 880 V, which corresponds to state selecting the ($JKM=111$) state of the CH₃Br parent molecule. The focusing spectrum of CD₃Br (not shown here) is similar to CH₃Br and all our data on photolysis of CD₃Br were taken with the hexapole set to focus the ($JKM=111$) state.

For the detection of the CH₃ and CD₃ photofragments we used the $3p_z^2A_2'' \leftarrow \leftarrow 2p_z^2\tilde{X}^2A_2''$ two-photon transition and recorded (2+1) REMPI spectra in the region of the 0₀⁰ origin band. The $3p_z^2A_2''$ intermediate state is predissociative.^{21–23} For both fragments we only observed the strong Q branch. In the case of CD₃ photofragments the sideband structures of O , P , R , and S transitions, which are

easily observed in the state-to-state photodissociation of CD₃I near 266 nm,¹⁸ were not observed in the experiments reported here on methyl bromide. Ion images were recorded at several positions inside and outside of the Q branch. The spectroscopic data available for both the normal and deuterated methyl radicals are summarized in Tables I and II.

B. Calibration of kinetic energy of slice images

For the analysis of the slice images a conversion from pixel to velocity or energy needs to be made. This conversion depends on the actual settings of the voltages on the electrodes of the ion lens. We calibrated this conversion on the state-to-state photodissociation of methyl iodide at 235 nm. The state-to-state photodissociation of methyl iodide has been very well studied in the past and much is known about the energetics of the photodissociation dynamics.^{6,18,23} We recorded under the same experimental conditions of voltages, on our ion lens, the slice images of CH₃ from photodissociation of CH₃I ($JK=11$) at 235 nm, and CH₃ from photodissociation of CH₃Br ($JK=11$) at 212.8 nm. In Fig. 2 a typical raw data image is shown of methyl after photodisso-

TABLE II. Rotational constants and vibrational frequencies of the ground ($\tilde{X}^2A_2''$) and excited ($3p_z^2A_2''$) states of the CD₃ radicals (all in cm⁻¹).

$\tilde{X}^2A_2''$					
Vibrational mode	(0000)	(1000)	(0100)	(0010)	(0001)
ν		2157.5 ^a	457.8 ^a	2381.09 ^a	1026 ^a
B	4.802 ^b	4.759 ^c	4.7 ^d	4.759 ^c	...
C	2.401 ^b	2.373 ^c	2.429 ^d	2.373 ^c	...
$3p_z^2A_2''$					
Vibrational mode	(0000)	(1000)	(0100)	(0010)	(0001)
ν		2106 ^f	1065 ^f	2346 ^f	1048 ^f
B	4.76 ^d	...	5.23 ^d	...	...
C	2.38 ^d	...	2.83 ^d	...	...

^aReference 37.^bReference 43.^cSame as $\nu_3=1$.^dReference 22.^eReference 44.^fReference 26.

FIG. 2. Ion slice image of CH_3 after photolysis at 212.8 nm of CH_3Br ($JKM=111$). The probe laser was set at $\tilde{\nu}_{\text{probe}}=59\,971.22\text{ cm}^{-1}$. The polarization of the photolysis laser was vertical and in the plane of the image, and the polarization of the ionization laser was perpendicular (normal) to the plane of the image. The total number of ion events is 12 511.

ciation of CH_3Br ($JK=11$) at 212.8 nm. We use a software program¹⁹ which reads out the large frame CCD camera every five laser shots (repetition rate of laser is 10 Hz). Each large frame image is analyzed on-the-fly for ion events and the center of gravity of each ion event is obtained. For each event the centroided coordinates as well as the coordinates of the pixel with the maximum intensity are stored. By accumulating a sufficient number of events we obtain a centroided image and a peak image. The image presented in Fig. 2 is a peak image. The typical number of events per frame (500 ms data acquisition corresponding to five laser shots) was between 7–10, of which about 2–4 were background ions (mostly visible near the center of the image) produced by the photolysis laser, especially for photolysis at 212.8 nm.

The $\text{CH}_3(NK)$ fragment is detected on the Q branch of the 0_0^0 band of the $3p_z\ ^2A_2'' \leftarrow 2p_z\ \tilde{X}\ ^2A_2'$ two-photon transition. In Table III we list the rotational energies, spectroscopic transition frequencies, and predissociation linewidths for rotational levels $N=1-15$ and $K=1$ of the methyl radical. The probe laser was set at a frequency corresponding to a two-photon energy of $59\,971.2\text{ cm}^{-1}$, the transition frequency for detection of $\text{CH}_3(NK=31)$. Note, however, from Table III that the predissociation width of methyl can be very large, so that in effect, depending on the population distribution over the different rotational states (NK), at the same two-photon frequency also other rotational states may be detected besides the level that is spectroscopically closest to the laser frequency.

In Fig. 3 we show the kinetic energy distribution of the methyl fragment from dissociation of CH_3I ($JK=11$) at 235 nm and CH_3Br ($JK=11$) at 212.8 nm. In the distribution of methyl from CH_3I ($JK=11$) three peaks are seen, which can be readily assigned. The small peak at low kinetic energy near $11\,000\text{ cm}^{-1}$ is from dissociation with the probe laser near 333 nm, the other two peaks are from dissociation at 235 nm and correlating with spin-orbit excited I^* or ground state I atoms. We calibrated the kinetic energy on the methyl peak correlating with spin-orbit excited I^* from dissociation of CH_3I ($JK=11$) at 235 nm. We used the following quantities to calibrate the kinetic energy axis of the CH_3I system: $E_{\text{photolysis}}=42\,533.75\text{ cm}^{-1}$, $E_{\text{rot}}[\text{CH}_3\text{I} (JK=11)]=5.369\text{ cm}^{-1}$, and $D_0(\text{CH}_3\text{I})=19\,067\text{ cm}^{-1}$.²⁴ It has been calculated by Xie *et al.*⁶ that the photodissociation of state-selected CH_3I ($JK=11$) at 266 nm produces a relatively cold methyl rotational distribution in the I^* channel peaking around $N=3$. We assume, in the absence of other information, that this N value is also the peak in the distribution for photolysis of CH_3I ($JK=11$) at 235 nm for the I^* channel. In Table III we list the rotational energy for levels $N=1-15$ and $K=1$ for the normal

TABLE III. Rotational energies, transition frequencies, and predissociation linewidths (all in cm^{-1}) for CH_3 and CD_3 for $N=1-15$ and $K=1$.

N	CH_3			CD_3		
	E_{rot}	ν^a	$\Delta\nu^b$	E_{rot}	ν^a	$\Delta\nu^c$
1	14.31	59 971.82	4.2	7.20	59 885.94	0.76
2	52.61	59 971.57	5	26.40	59 885.77	0.8
3	110.00	59 971.21	6.2	55.20	59 885.50	0.86
4	186.44	59 970.72	7.8	93.56	59 885.14	0.94
5	281.84	59 970.11	9.8	141.48	59 884.68	1.04
6	396.13	59 969.38	12.2	198.94	59 884.10	1.16
7	529.18	59 968.53	15	265.91	59 883.38	1.3
8	680.87	59 967.55	18.2	342.34	59 882.53	1.46
9	851.05	59 966.46	21.8	428.22	59 881.50	1.64
10	1039.56	59 965.24	25.8	523.49	59 880.30	1.84
11	1246.20	59 963.90	30.2	628.10	59 878.89	2.06
12	1470.78	59 962.44	35	742.02	59 877.25	2.3
13	1713.08	59 960.85	40.2	865.18	59 875.36	2.56
14	1972.85	59 959.15	45.8	997.52	59 873.18	2.84
15	2249.83	59 957.32	51.8	1138.97	59 870.69	3.14

^aTwo-photon transition frequency for the Q branch of the 0_0^0 rovibronic band.

^bTotal predissociation linewidth $\Delta\nu=\Delta\nu_0+s[N(N+1)-K^2]$, with $\Delta\nu_0=4\text{ cm}^{-1}$ and $s=0.2\text{ cm}^{-1}$ (Ref. 23).

^cSame as superscript "b" but with $\Delta\nu_0=0.75\text{ cm}^{-1}$ and $s=0.01\text{ cm}^{-1}$ (Ref. 18).

FIG. 3. Kinetic energy distribution for photolysis of state-selected CH₃I ($JK=111$) at 235 nm (solid line) and CH₃Br ($JK=11$) at 213 nm (dotted line) using the same voltages on the ion lenses. The probe laser was set at $\tilde{\nu}_{\text{probe}}=59\,971.22\text{ cm}^{-1}$. The small peak near $11\,000\text{ cm}^{-1}$ is from photolysis of CH₃I ($JK=11$) at 333 nm with the probe laser.

and deuterated methyl fragments. Using $E_{\text{rot}}[\text{CH}_3(NK=11)]=110\text{ cm}^{-1}$, we find that the total kinetic energy in the I^* channel is $E_{\text{kin}}=E_{\text{photolysis}}+E_{\text{rot}}[\text{CH}_3\text{I}(JK=11)]-E(\text{I}^*)-E_{\text{rot}}[\text{CH}_3(NK=11)]-D_0=42\,533.8+5.37-7603.4-110-19\,067=15\,758.9\text{ cm}^{-1}$. With this value we can calibrate the conversion of pixel ρ to kinetic energy: $E_{\text{kin}}=C_{\text{CH}_3\text{I}}\rho^2$. Subsequently, we can calculate the conversion factor for photolysis of CH₃Br, at the same ion lens voltages, from the mass factors: $C_{\text{CH}_3\text{Br}}=C_{\text{CH}_3\text{I}}(1+m_{\text{CH}_3}/m_{\text{Br}})/(1+m_{\text{CH}_3}/m_{\text{I}})=1.062\,305C_{\text{CH}_3\text{I}}$.

In Fig. 3 we see that for photolysis at 212.8 nm of CH₃Br ($JK=11$) (dotted line) two peaks separated by an energy difference of $\Delta E_{\text{kin}}=3480\text{ cm}^{-1}$ are found. This energy difference is slightly less, about 205 cm^{-1} , than the Br–Br^{*} spin-orbit energy of 3685 cm^{-1} . This indicates that the internal rotational energy of the methyl in the Br channel is slightly more than the rotational energy of the Br^{*} channel. A similar observation was made for photolysis of CH₃I ($JK=11$) at 266 nm, where the rotational distribution for vibrational ground state methyl correlating with ground state I peaks around $N=4-5$, whereas for the I^* channel the distribution peaks at $N=3$.^{6,25} In Fig. 3 we find that the kinetic energy of the methyl channel correlating with ground state I is about 7102 cm^{-1} higher than the I^* channel. This energy difference is lower than the spin-orbit splitting of 7603.4 cm^{-1} . It can be concluded that at 235 nm the average rotational energy of the methyl correlating with ground state I from photodissociation of CH₃I ($JK=11$) is some 500 cm^{-1} more than the channel correlating with spin-orbit excited I^* .

C. Photodissociation of CH₃Br

The photodissociation of rotationally state-selected CH₃Br ($JKM=111$) was studied at the following photolysis wavelengths: 212.8, 229, 229.5, 230, 230.5, and 231 nm. We used the calibration as described in the previous section to obtain the kinetic energy distribution from the slice images. The kinetic energy release spectra at three photolysis wave-

FIG. 4. The kinetic energy release after photolysis of CH₃Br ($JKM=111$) at three different wavelengths. The probe laser was set at $\tilde{\nu}_{\text{probe}}=59\,971.22\text{ cm}^{-1}$ to detect CH₃ for the panels (a) and (b), and at $\tilde{\nu}_{\text{probe}}=59\,978.64\text{ cm}^{-1}$ in panel (c). Note that the vertical scale in panel (c) is expanded and clipped.

lengths are shown in Fig. 4. Two strong peaks and two much weaker bumps in between the strong peaks can be observed. We assign the first and strongest peak in all spectra to CH₃ released in the ground vibrational state and Br(²P_{1/2}) in the spin-orbit excited state (Br^{*} channel). The fourth and second strongest peak is assigned to CH₃ in the ground vibrational state with the Br(²P_{3/2}) atom in the ground state (Br channel). These two strong peaks are well separated by an energy varying between 3350 and 3480 cm^{-1} , close to but slightly less than the bromine spin-orbit splitting of 3685.24 cm^{-1} . This small difference with the spin-orbit splitting suggests that the methyl fragment correlating with ground state Br may have a slightly higher rotational excitation relative to the methyl fragment born in coincidence with Br^{*}.

Two weak extra peaks appear in between the two strong peaks. These two weaker peaks in the upper panel of Fig. 4 appear near 1270 and 2550 cm^{-1} lower kinetic energy releases, relative to the vibrationless (0000) CH₃ peak in the Br channel. The peak with an energy difference near 1270 cm^{-1} is assigned to CH₃ with one quantum of vibrational excitation in the ν_4 mode. The (0001) rotationless energy level is at 1398 cm^{-1} , see Table I. The intensity of this (0001) methyl peak is larger when CH₃ is probed outside at the blue side of the Q branch of the 0_0^0 vibronic transition. This is shown in panel (c) of Fig. 4, where a blowup of the kinetic energy release spectra is presented for photolysis at 229 nm. In the wavelength region where the 0_0^0 band appears, the 1_1^1 , 3_1^1 and 4_1^1 bands have been assigned recently.^{26,27} In panel (c) the methyl fragment was detected at $59\,985.8\text{ cm}^{-1}$, towards the origin of the 4_1^1 band which is predicted near $\sim 60\,002\text{ cm}^{-1}$ using isotope shifts for the vibrational frequencies of the observed 4_1^1 origin band in deuterated CD₃.²⁶ In panels (a) and (b) methyl was probed at $59\,971.2\text{ cm}^{-1}$, which is the peak of the Q branch of the 0_0^0 band. The shoulder labeled with X in Fig. 4 has not been explicitly assigned. The energy difference of about 2550 cm^{-1} is less than the internal energy of a vi-

TABLE IV. The Br^* yield of CH_3 and CD_3 final vibrational channels as measured within the Q branch of the 0_0^0 transition after photolysis of state-selected $\text{CH}_3\text{Br}/\text{CD}_3\text{Br}$.

$\lambda_{\text{photolysis}}$ (nm)	CH_3 vibrational mode		CD_3 vibrational mode	
	(0000)	(0000)	(1000) ^a	
212.8	0.72	0.93	0.54	
227	... ^b	0.89	0.46	
229	0.67	... ^b	... ^b	
231	0.65	0.84	0.40	
235	... ^b	0.77	0.33	

^aMost likely assignment, see text.

^bNot measured at this wavelength.

brationally excited methyl fragment in the ν_1 mode, (1000) at about 3004 cm^{-1} , or the ν_3 mode, (0010) at 3161 cm^{-1} , see Table I.

From the kinetic energy release spectra the Br^* yield was obtained ranging from 0.72 at photolysis of 212.8 nm to about 0.65 at photolysis wavelengths near 230 nm, see Table IV.

We obtain the angular distributions by integrating the intensity centered around the peak of the radial velocity distribution, as determined from Fig. 4, within the full width at half maximum of the velocity peak. The angular distribution was fitted with the following expression:

$$I(\theta) = \frac{\sigma}{4\pi} [1 + \beta P_2(\cos \theta)], \quad (1)$$

where σ is the total dissociation cross section, P_2 is the second order Legendre polynomial, and β is the anisotropy parameter. In Fig. 5 we show the angular distribution extracted from the images for the state-to-state photolysis at 212.8 nm

FIG. 5. The angular intensity distribution of CH_3 from the photolysis of CH_3Br ($JKM=111$) at 212.8 nm [panel (a)] and at 231 nm [panel (b)]. The solid lines, in both panels, represent fits through the measured angular intensity distribution with the following anisotropy parameter: in panel (a) $\beta=1.41$ for CH_3 in the excited Br^* channel (open circles) and $\beta=-0.52$ for CH_3 in the ground state Br channel (solid dots); in panel (b) $\beta=1.79$ for CH_3 in the excited Br^* channel (open circles) and $\beta=-0.23$ for CH_3 in the ground state Br channel (solid dots).

TABLE V. Measured anisotropy parameter β after photolysis of CH_3Br ($JKM=111$) at several dissociation and probe laser wavelengths.

$\lambda_{\text{photolysis}}$ (nm)	Probe transition	β	
		$\text{CH}_3 + \text{Br}^*$	$\text{CH}_3 + \text{Br}$
	0_0^0	(0000)	(0000)
212.8	$Q3$	1.41	-0.52
	$Q4$	1.40	-0.60
	$Q5$	1.16	-0.70
229.5	$Q3$	1.74	-0.37
	$Q5$	1.82	-0.12
230	$Q3$	1.70	-0.38
	$Q5$	1.82	-0.12
231	$Q3$	1.79	-0.23
	$P3$	1.51	-0.22

[panel (a)] and 231 nm [panel (b)] of CH_3Br . The β parameter that we obtain, see Table V, indicates that the angular recoil of CH_3 ($\nu_1=0, \nu_2=0, \nu_3=0, \nu_4=0$) changes from a parallel recoil with a positive β for the Br^* channel to a perpendicular-type recoil with a negative β for the ground state Br channel, at both photolysis wavelengths. The anisotropy parameter for the Br^* channel is larger at longer photolysis wavelength, increasing from a value of $\beta=1.2-1.4$ at 212.8 nm to $\beta=1.8$ around 230 nm. In the Br channel with CH_3 in the ground vibrational state, the anisotropy parameter increases from $\beta=-0.60$ at 212.8 nm, which reflects a strong anisotropic perpendicular-type recoil, to $\beta=-0.2$ around 230 nm. A discussion regarding the origin of those changes will be given in Sec. IV.

D. Photodissociation of CD_3Br

The photolysis of rotationally state-selected CD_3Br ($JK=11$) was studied at the following wavelengths: 212.8, 227, 231, and 235 nm. In Fig. 6 we show two typical data images of CD_3 after photolysis at 212.8 nm [panel (a)] and at 231 nm [panel (d)]. The size of the images in panels (a) and (d) is 2048×2048 pixels. In the panels (b) and (c) cuts of the image in panel (a) are taken for regions near the top and equator, respectively. In the panels (e) and (f) similar bottom and equator cuts of the image in panel (d) are shown. Both images were taken with the probe laser set at $\tilde{\nu}_{\text{probe}} = 59\,885.22\text{ cm}^{-1}$ to detect CD_3 through the Q branch of the 0_0^0 band. In the image in panel (a) we can see several rings with varying angular intensity distribution. In the image in panel (d) even more rings appear and again all these rings have a different angular intensity distribution.

In Fig. 7 we show the total kinetic energy release spectra obtained for photolysis at 212.8, 231, and 235 nm and various different probe energies indicated by the two-photon energy in cm^{-1} . We used the calibration procedure as discussed in Sec. III B to convert the velocity axis from CCD pixels to energy.

The weak peak, labeled 5 in panel (a), of the fastest CD_3 fragment near 2.76 eV is assigned to vibrationless $\text{CD}_3(0000)+\text{Br}$, and the stronger peak, labeled 3 near 2.37 eV, to $\text{CD}_3(0000)+\text{Br}^*$. The energy difference of

FIG. 6. Ion slice images of CD₃ after photolysis of CD₃Br ($JKM=111$) at 212.8 nm [panel (a)] and 231 nm [panel (d)]. (b) Top cut of the image in panel (a) of size 525 × 350 pixels. (c) Right side cut of the image in panel (a) of 350 × 525 pixels. (e) Bottom cut of the image in panel (d) of 525 × 350 pixels. (f) Right side cut of the image in panel (d) of 350 × 525 pixels. The probe laser was set at $\tilde{\nu}_{\text{probe}}=59\,885.22\text{ cm}^{-1}$. The polarization of the photolysis laser was vertical and in the plane of the image, and the polarization of the ionization laser was perpendicular (normal) to the plane of the image. In panels (a)–(f) various rings are visible. The total number of ion events is 8353 for image (a) and 13 465 for image (d).

3120 cm⁻¹ between peaks 3 and 5 is slightly lower than the Br^{*}–Br spin-orbit splitting of 3685 cm⁻¹, indicating that the CD₃(0000) fragment formed with Br in the spin-orbit ground state is somewhat more rotationally excited than CD₃(0000) fragment formed with Br^{*}. The peak labeled 4 appears at a kinetic energy release of about 1600 cm⁻¹ lower than the

fastest CD₃(0000)+Br peak. Most closely in energy would be a combination excitation of one quantum in the ν_2 and one quantum in the ν_4 ; the CD₃(0101) energy level is near 1483 cm⁻¹, see Table II. However, this is quite unlikely as the ν_2 has a very different frequency in the intermediate $3p_z\ ^2A_2''$ REMPI state and the ν_4 is very similar in frequency in both states. This makes efficient detection at this laser wavelength of the (0101) combination band much more difficult. A more likely possibility is that peak 4 is vibrationally excited CD₃ with either one quantum in the ν_1 or one quantum in the ν_3 . The CD₃(1000) level is at 2157 cm⁻¹ and the CD₃(0010) level is at 2381 cm⁻¹. So in both cases it would mean that these vibrationally excited levels would have much less rotational energy than the CD₃(0000) fragment. Because energetically the CD₃(1000) level is closest in energy, we think that peak 4 is most likely the CD₃(1000)+Br channel. The strong peak, labeled 1, near 2.13 eV is shifted by about 3470 cm⁻¹ to lower energy relative to peak 4. This is again close to the spin-orbit splitting, so we assign peak 1 to the same CD₃ fragment as peak 4, most probably CD₃(1000) but with spin-orbit excited Br^{*} as a cofragment.

The second peak near 2.29 eV, labeled 2 in panel (a) of Fig. 7, appears at an energy of ~654 cm⁻¹ lower than peak 3 assigned to CD₃(0000)+Br^{*}. The most likely assignment for this peak is the CD₃(0001)+Br^{*} channel. The CD₃(0001) energy level is at 1026 cm⁻¹. We observe when we change the probe laser two-photon energy from 59 901 cm⁻¹ [panel (a)] to 59 885 cm⁻¹ [panel (b)] i.e., from the blue side of the 0₀⁰ Q branch to the center of the 0₀⁰ Q branch, that peak 2 is reduced in intensity. If we tune the probe laser even further to the red near 59 872 cm⁻¹ [panel (c)], both peak 2 and the CD₃(0000)+Br^{*} peak 3 are reduced in intensity compared to panel (a). This agrees with an assignment of peak 2 to the CD₃(0001) fragment, as the 4₁¹ origin band was assigned spectroscopically at an energy shifted by 22 cm⁻¹ to the blue relative to the energy of the 0₀⁰ band.²⁶ The reduction of the relative intensity of peaks 2 and 3 in panel (c), by shifting the probe energy to the red, agrees with the assignment of the relative positions of the 0₀⁰, 4₁¹, 3₁¹, and 1₁¹ bands.

In panels (d) and (e) of Fig. 7 we present the kinetic energy release obtained from CD₃Br photolysis at 231 nm and with the detection through the Q branch [$\tilde{\nu}_{\text{CD}_3\text{detection}}=59\,885.22\text{ cm}^{-1}$, panel (d)] and about 13 cm⁻¹ to the red side of the 0₀⁰ band [$\tilde{\nu}_{\text{CD}_3\text{detection}}=59\,872.45\text{ cm}^{-1}$, panel (e)]. We basically see the same structure as in panels (b) and (c), however, the CD₃(0000)+Br channel (peak 5) is more pronounced at this lower dissociation wavelength. Again, when moving the wavelength to the red the peaks assigned to CD₃(0000)+Br^{*} and CD₃(0000)+Br become reduced in intensity, in agreement with a reduced detection efficiency of CD₃(0000) when moving the probe laser energy away from the peak of the 0₀⁰ Q band.

The kinetic energy release from the photolysis of rotationally state-selected deuterated methyl bromide at 235 nm is shown in panel (f) of Fig. 7. The CD₃ photofragments were detected at the Q branch of the 0₀⁰ band. Again we see the main structure as discussed above for the other wave-

FIG. 7. The kinetic energy release obtained from images taken at photolysis wavelengths of 212.8, 231, and 235 nm and different probe laser positions inside and outside the Q branch of the $3p_z\ ^2A_2'' \leftarrow 2p_z\ \tilde{X}^2A_2''\ 0_0^0$ transition. The peaks are labeled 1–5, see the text for a discussion of the assignment. In panel (f) various extra shoulders appear at positions indicated by the arrows.

FIG. 8. The angular intensity distribution of CD_3 obtained from the image in Fig. 6(d) from the photolysis of CD_3Br ($JKM=111$) at 231 nm. The solid lines represent fits through the measured angular intensity distributions with the following anisotropy parameters: (a) for CD_3 in the vibrational excited $\nu_1=1$ in the Br^* channel (open circles) $\beta=1.70$ and in the Br channel (solid dots) $\beta=-0.51$; (b) for CD_3 vibrational ground state in the Br^* channel (open circles) β is 1.88 and in the Br channel (solid dots) is 0.09.

lengths. However, at this lower wavelength we observe more small peaks and shoulders, indicated by the arrows, suggesting more vibrationally excited species.

In Table IV we present the Br^* yield of CD_3 measured through the Q branch of the 0_0^0 band. The Br^* yield for $\text{CD}_3(0000)$ decreases with longer photolysis wavelength, from $\sim 93\%$ at 212.8 nm to $\sim 77\%$ at 235 nm. This is also observed for the Br^* yield for $\text{CD}_3(1000)$, in this case, the quantum yield decreases from $\sim 54\%$ to $\sim 33\%$. As a general observation we can say that the Br^* yield for CD_3 in the ground vibrational state or in the excited vibrations do not change much by probing different rotational states, showing small variations around the values listed in Table IV.

In Fig. 8 the angular distribution of CD_3 is shown after photolysis of CD_3Br at 231 nm. The angular distribution in Fig. 8 was obtained from the image of Fig. 6(d). The measured angular distributions were fitted to Eq. (1). In Table VI we present the results of the fits of the measured angular distributions of the deuterated methyl photofragments at the photolysis and probe wavelengths listed in the table. The photolysis at 212.8 nm leads, as discussed above, to CD_3 in the vibrational ground state and in some excited vibrational states in both Br^* and Br channels. The anisotropy parameters that we measure are $\beta=1.74$ for $\text{CD}_3(1000)$ in the Br^* channel and $\beta=-0.86$ in the Br channel. The Br^* channel for CD_3 in the ground vibrational state has a large positive $\beta=1.63$ corresponding to a parallel-type recoil. For the peak labeled 2 $\beta=0.88$. We attributed this channel to $\text{CD}_3(0001)$ released in the Br^* channel. For photolysis at 231 nm the anisotropy parameters that we measure are as follows: $\beta=1.70$ for $\text{CD}_3(1000)+\text{Br}^*$ and $\beta=-0.51$ for the $\text{CD}_3(1000)+\text{Br}$ channel. For ground state $\text{CD}_3(000)$ we find $\beta=1.88$ for the Br^* channel and $\beta=0.09$ for the Br channel.

TABLE VI. Measured anisotropy parameter β after photolysis of CD_3Br ($JKM=111$) at several dissociation and probe laser wavelengths.

$\lambda_{\text{photolysis}}$ (nm)	Probe transition 0_0^0	β^a				
		CD_3+Br^*			CD_3+Br	
		(0000)	(1000) ^b	(0001) ^b	(0000)	(1000) ^b
212.8	$R1$	1.35	1.39	0.75	... ^c	-0.8
	$Q4$	1.63	1.74	0.88	... ^c	-0.86
	$Q11$	1.40	1.73	0.52	... ^c	-0.92
	$P2$	1.53	1.77	0.47	... ^c	-0.83
227	$Q4$	1.86	1.78	... ^c	0.01	-0.63
231	$R2$	1.60	1.58	... ^c	0.19	-0.80
	$R1$	1.79	1.68	... ^c	-0.07	-0.56
	$Q4$	1.88	1.70	... ^c	0.09	-0.51
	$Q11$	1.84	1.82	... ^c	-0.12	-0.57
	$P2$	1.80	1.86	... ^c	0.12	-0.50
235	$Q4$	1.77	1.70	... ^c	0.01	-0.64

^a β is the coefficient of the second order Legendre polynomial. For CD_3 detection through the Q branch it is the classical anisotropy parameter, but for the detection through individual rotational lines of O , P , R , and S branches this coefficient might also contain some alignment information.

^bMost likely, see text.

^cNo analysis due to very low or absent signal.

IV. DISCUSSION

As was mentioned in the Introduction there are three repulsive excited electronic states which are optically allowed in the $\tilde{A}$ band, namely, $^3Q_1(E)$, $^3Q_{0+}(A_1)$, and $^1Q_1(E)$. The $^3Q_{0+}(A_1) \leftarrow \tilde{X}(A_1)$ is a parallel transition. The transition dipole moment is oriented parallel to the C–Br bond, and therefore molecules with the bond axis parallel to the polarization direction of the photolysis laser are preferentially excited and dissociate along the laser polarization direction. The $^3Q_1(E) \leftarrow \tilde{X}(A_1)$ and $^1Q_1(E) \leftarrow \tilde{X}(A_1)$ are perpendicular transitions. The transition dipole moments are oriented perpendicular to the C–Br bond, and the molecules oriented like this will dissociate perpendicular to the polarization direction of the photolysis laser. In the limit of fast axial recoil the anisotropy parameter will be $\beta=2$ for a transition to the $^3Q_{0+}$ state and $\beta=-1$ for a transition to 3Q_1 or 1Q_1 states. Deviations from these limiting values can be due to several processes such as a long lifetime for the dissociative excited state which will allow rotation of the parent molecule during dissociation. Other possibilities are the simultaneous excitation to multiple surfaces or nonadiabatic transitions between the $^3Q_{0+}$ and 1Q_1 states which will smear out both the $\cos^2 \theta$ and $\sin^2 \theta$ distributions. A good measure for the nonadiabatic transitions between the two energy surfaces is the Br^* quantum yield.

A. Br^* quantum yield and the angular distribution of methyl

The measurement of the photofragment anisotropy parameter, together with the Br^* yield, provides us with insight in the dissociation dynamics in the $\tilde{A}$ -band. In the case of CH_3I photolysis at 266 nm, the absorption is mostly to the

$^3Q_{0+}$ state and the population is expected predominantly in the I^* channel.^{23,28–30} The population in the I channel has been attributed to nonadiabatic transitions between the $^3Q_{0+}$ and 1Q_1 states and the I^* yield has been used as a measure of the nonadiabatic interaction between these two surfaces.^{5,6} However, recent calculations by Alekseyev *et al.*³⁰ suggest that for non- C_{3v} geometries, with small H₃–C–I bending angles near 10°, the μ_z component of the 3Q_1 , $^1Q_1 \leftarrow ^3Q_{0+}$ transitions may have significant excitation strength, even exceeding the strength of the perpendicular $\mu_{x,y}$ transitions.

For CH₃Br/CD₃Br photolysis in the 213–235 nm region, the Br^{*} yield is not a direct measure of the nonadiabatic interaction between the two surfaces due to the fact that the dissociation takes place through absorption to all three energy surfaces mentioned above.⁹ The Br channel can be populated by both direct absorption to the 1Q_1 and 3Q_1 states and by nonadiabatic transitions from the $^3Q_{0+}$ state. The measured Br^{*} yield for photolysis of rotationally state-selected CH₃Br and CD₃Br at several wavelengths ranges between 0.65–0.93 for CH₃(000) and CD₃(000), see Table IV. The Br^{*} yield decreases with increasing photolysis wavelength for both methyl and deuterated methyl, and is somewhat higher for the deuterated methyl. The Landau-Zener model^{9,14,31} predicts a lower Br^{*} quantum yield in CD₃Br than in CH₃Br. Based on the fact that the coupling potential between the two (1Q_1 and $^3Q_{0+}$) diabatic surfaces, the difference in the slopes of the potentials and the internuclear separation at the crossing point is the same for CH₃Br and CD₃Br, the quantum yield can be predicted from the asymptotic recoil velocities. The higher Br^{*} yield that we obtain for CD₃Br photolysis suggests that this model fails here as it does in the case of CH₃I/CD₃I photolysis.

Townsend *et al.*³² estimated curve crossing probabilities for photodissociation of CH₃Cl at 193 nm, i.e., on the red side of the absorption band centered around 170 nm. They assumed that there is only direct excitation to two surfaces at 193 nm, the $^3Q_{0+}$ and 1Q_1 states. However, normally, on the red side of the maximum of the absorption band, the 3Q_1 is located. Recent calculations by Ajitha *et al.*³³ suggest that the $^3Q_{0+}$ and 3Q_1 surfaces are very similar in energy, and the $^3Q_{0+}$ surface is calculated to be centered at 52 019 cm^{−1}, 192 nm (see Fig. 4 and Table V in Ref. 33). Under the assumption of absorption to only the $^3Q_{0+}$ and 1Q_1 states, Townsend *et al.* can directly infer from the observed β parameter for the two Cl and Cl^{*} channels the contributions of perpendicular and parallel excitation. We cannot follow this same approach directly for the photodissociation of CH₃Br as it was shown by Gougousi *et al.*⁹ that at our photolysis wavelengths in the region of 213–230 nm we have contributions from all three optically allowed transitions. Therefore, we estimate the probability of curve crossing, in a similar way as Gougousi *et al.*,⁹ from the velocity distribution of CH₃ and CD₃ by integrating the intensities at the polar and equator parts of the images within an angular range of 20°. Under the assumption that the z component of the transition dipole moment to the perpendicular surfaces is vanishing,³⁰ the direct production of ground state Br is through perpendicular transitions to the 1Q_1 and 3Q_1 states. Therefore, all events in the Br channel that we find at the poles will be due

to the nonadiabatic transitions via the conical intersection of the $^3Q_{0+}$ and 1Q_1 states. Similarly, the direct production of excited state Br^{*} is through a parallel transition to the $^3Q_{0+}$ state and any events we find at the equator will be due to nonadiabatic transitions. The (Br)_{indirect} represents the amount of Br produced at the poles of the image by nonadiabatic transitions, and the (Br^{*})_{direct} represents the amount of Br^{*} produced at the pole by direct excitation to the $^3Q_{0+}$ state. The ratio (Br)_{indirect}/[(Br^{*})_{direct} + (Br)_{indirect}] $\equiv P_{NA}(^3Q_{0+} \rightarrow ^1Q_1) = P_{01}$ gives us the probability of nonadiabatic transitions from the $^3Q_{0+}$ to the 1Q_1 state. For CH₃Br photolysis at 212.8 nm leading to CH₃(0000), we find $P_{01}=0.08$, and for photolysis at 231 nm $P_{01}=0.17$. For CD₃Br photolysis leading to CD₃(0000) at 212.8 nm, we find $P_{01}=0.05$ and for photolysis at 235 nm $P_{01}=0.08$. For CD₃Br photolysis leading to CD₃(1000) at 212.8 nm we find $P_{01}=0.12$, and for photolysis at 231 nm $P_{01}=0.36$.

The ratio (Br^{*})_{indirect}/[(Br)_{direct} + (Br^{*})_{indirect}] $\equiv P_{NA}(^1Q_1 \rightarrow ^3Q_{0+}) = P_{10}$ gives us the probability of nonadiabatic transitions from the 1Q_1 to the $^3Q_{0+}$ state. Here the (Br)_{direct} represents the amount of ground state Br produced at the image's equator by direct excitation to the 1Q_1 state. As we mentioned above the direct population of the ground state Br channel results from absorption to both 1Q_1 and 3Q_1 states. Absorption to the 3Q_1 state is important in the red wing of the $\tilde{A}$ band and cannot be neglected. We use the deconvolution of the absorption cross section of the $\tilde{A}$ band⁹ in order to separate the contributions of absorption to 1Q_1 and 3Q_1 states to the direct population of the ground state Br channel. For CH₃Br photolysis leading to CH₃(0000), we find the following values for the nonadiabatic transition probability, $P_{NA}(^1Q_1 \rightarrow ^3Q_{0+})$, as a function of the photolysis wavelength: $P_{10}=0.47$ (212.8 nm), 0.74 (229 nm), 0.92 (230 nm), and 0.92 (231 nm). For CD₃Br photolysis leading to CD₃(0000) we find the following values for the nonadiabatic transitions probabilities as a function of the photolysis wavelength: $P_{10}=0.71$ (212.8 nm), 0.81 (227 nm), 0.94 (231 nm), and ~ 1 (235 nm). For the CD₃Br photolysis leading to CD₃(1000): $P_{10}=0.17$ (212.8 nm), 0.29 (227 nm), 0.72 (231 nm), and 0.98 (235 nm).

The nonadiabatic transition probability from the $^3Q_{0+}$ to the 1Q_1 state (P_{01}) is higher in the case of CH₃Br vs CD₃Br photolysis at all studied wavelengths and increases with increasing photolysis wavelength. Interestingly, the probability of nonadiabatic transitions from 1Q_1 to the $^3Q_{0+}$ state (P_{10}) is smaller for CH₃Br vs CD₃Br, but again the curve crossing probability P_{10} increases with increasing wavelength as does (P_{01}) for both isotopes. The values that we observe for a specific vibrational channel (0000) in the methyl fragment are generally somewhat smaller (about 50%) than the overall nonadiabatic transition probability values that Gougousi *et al.*⁹ extracted from the total Br^{*}/Br yield correlating with all vibrational channels of the methyl cofragment. However, we photolyze a K -selected initial parent molecule ($J=K=1$). It has been discussed before that the breaking of the C_{3v} symmetry in methyl iodide leads to an enhanced nonadiabatic transition probability.^{6,23} As Gougousi *et al.* did their experiments in a supersonic cold molecular beam with $K=0$ states,

it suggests that the nonadiabatic transition probability for other vibrational channels than the ground state (0000) must be higher. This is in agreement with our observations for the vibrationally excited $\text{CD}_3(1000)$, where a substantially higher nonadiabatic transition probability is observed than for ground state $\text{CD}_3(0000)$. Unfortunately, there are no dynamical theoretical calculations available for the methyl bromide system as for the photodissociation of methyl iodide.⁶ Recently, one dimensional electronic potential curves were reported by Ajitha *et al.*³³ but no dynamical calculations are available. In the case of CD_3I vs CH_3I photolysis at 266 nm, a higher I^* yield was found for CD_3I photolysis, indicating that the nonadiabatic transition probability is higher for methyl iodide than for deuterated methyl iodide,²³ similar to what we observe here for methyl bromide.

The β parameters that we observe for $\text{CD}_3(0000)$ in the two Br/Br^* channels are somewhat closer to the limiting (-1 vs 2) values than the values for $\text{CH}_3(0000)$. This is consistent with a lower nonadiabatic transition probability for the deuterated system. The β parameters that we observe for a single vibrational $\text{CH}_3(0000)$ state in the Br^* channel ($\beta = 1.4$ – 1.8) are somewhat smaller than the values reported by Gougousi *et al.*⁹ in the same wavelength region ($\beta = 1.86$ – 1.94), and also smaller than the values in the red wavelength region (240–280 nm) as reported by Underwood and Powis¹⁴ ($\beta = 1.9$). This may again be reflecting the enhanced nonadiabatic transition probability for $K=1$ initial parent states, as the experiments of Gougousi *et al.* and Underwood and Powis both have $K=0$ initial parent states in their expansions. Interestingly, the β parameter that we observe for the vibrationally excited state $\text{CD}_3(1000)+\text{Br}$ channel is much more negative than the ground state channel. Even though the nonadiabatic transition probability for this channel is higher, see above, the Br^* yield is much lower for this channel and this leads eventually to a larger negative β parameter, closer to the limiting value of -1 .

B. Vibrational and rotational excitations of the methyl fragment

Previous studies^{9,12–14} of photolysis of $\text{CH}_3\text{Br}/\text{CD}_3\text{Br}$ through the A band concluded that the CH_3 and CD_3 fragments have internal state distributions that are significantly hot for both Br and Br^* channels. The studies agreed on the fact that the methyl fragments are more vibrationally excited in the Br channel than in the Br^* channel. van Veen *et al.*,¹² Hess *et al.*,¹³ and Gougousi *et al.*⁹ suggested that the available internal energy goes mainly in the methyl vibrational excitation, especially in the ν_2 umbrella mode. Gougousi *et al.*⁹ also concluded that the fragment rotational excitation should be relatively low, about $T=50$ K [$E_{\text{rot}}=(3/2)$ kT ≈ 52 cm⁻¹]. On the other hand, Underwood and Powis¹⁴ concluded that the lack of rotational structure in methyl (2 + 1) REMPI spectra from photodissociation of CH_3Br in the red wing (240–280 nm) was evidence for highly rotationally excited methyl fragments. They observed that the rotational excitation is on the order of ~ 0.1 eV (800 cm⁻¹), this corresponds to rotational levels up to $N=9$, see Table III. Theoretical *ab initio* calculations for the photodissociation of

CH_3I reported a small bending anisotropy (≈ 43 cm⁻¹) for the A' surface near the conical intersection between the $^3Q_{0+}(A_1)$ and $^1Q_1(E)$ energy surfaces.^{4,5} From imaging experiments of photodissociation of $\text{CH}_3\text{I}/\text{CD}_3\text{I}$ near 266 nm, a rotational excitation of about 90 and 120 cm⁻¹ for CH_3 and CD_3 photofragments, respectively, was measured for methyl fragments in the I^* channel.^{34,35}

We performed rovibrationally resolved experiments and detect the methyl fragments through the 0_0^0 rovibronic band. As was reported in Sec. III A we also do not observe any rotational structure in our (2+1) REMPI spectra for neither the CH_3 fragments nor the CD_3 fragments. From our analysis, see also Sec. IV C, we observe that photolysis of CH_3Br at 212.8 nm produces more rotationally excited CH_3 fragments, up to $N=9$, than photolysis around 230 nm, where we see excitation up to $N=6$. For CD_3Br photolysis at 212.8 nm we found CD_3 fragments rotationally excited up to $N=8$. We also consistently observe that the methyl born with the spin-orbit ground state Br has more rotational energy, some 230–340 cm⁻¹, than the methyl fragment correlating with spin-orbit excited Br^* .

In the kinetic energy release distribution of the photodissociation of CH_3Br , we mainly see the methyl peaks assigned to ground state methyl $\text{CH}_3(0000)$, see Fig. 4. Small extra peaks are observed when the probe wavelength is slightly tuned to the blue side of the 0_0^0 rovibronic band, especially for photolysis near 229 nm. This small peak is assigned to $\text{CH}_3(0001)$. For the photodissociation of CD_3Br much more vibrational activity is observed. Remarkably, the peaks assigned to vibrationally excited $\text{CD}_3(1000)$ are very strong and the ground state $\text{CD}_3(0000)+\text{Br}$ channel is barely visible for photolysis at 212.8 nm. According to the deconvolution of the absorption profiles of the $^3Q_{0+}$, 1Q_1 , and 3Q_1 surfaces by Gougousi *et al.*,⁹ the peak of the parallel $^3Q_{0+}$ band is near 210 nm (5.9 eV). The deconvolution suggests that the strength of the parallel absorption at 212.8 nm is about 60% of the total absorption and a substantial contribution remains from excitation to the perpendicular surfaces correlating to ground state Br . It appears from our data that the population of the vibrationless $\text{CD}_3(0000)+\text{Br}$ channel is much lower than the $\text{CD}_3(0000)+\text{Br}^*$ channel, contrary to photodissociation of normal CH_3Br . At this moment we do not have a clear explanation of the strong isotope effect on the distribution of vibrational states observed in the kinetic energy release of methyl. Theoretical calculations of the dynamics on *ab initio* surfaces are needed to give insight in the physical mechanism.

C. C–Br bond dissociation energy in CH_3Br and CD_3Br

We determine the bond dissociation energy for $\text{CH}_3\text{Br}/\text{CD}_3\text{Br}$ in a similar way as reported before for the OCS molecule.^{20,36} We calibrate our images as described in Sec. III B. For photolysis at a given wavelength we can write the following energy equation:

$$E_{\text{photolysis}} + E_{\text{int}}^{\text{CH}_3\text{Br}} = D_0 + E_{\text{vib,rot}}^{\text{CH}_3} + E_{\text{kinetic}}^{\text{total}} + E_{\text{spin-orbit}}^{\text{Br}} \quad (2)$$

where $E_{\text{photolysis}}$ is the photolysis energy, $E_{\text{int}}^{\text{CH}_3\text{Br}}$ is the internal rotational and vibrational energy of CH₃Br, D_0 is the bond dissociation energy, $E_{\text{vib,rot}}^{\text{CH}_3}$ is the rotational and vibrational energy of the CH₃ fragment, $E_{\text{kinetic}}^{\text{total}}$ is the total translational energy of CH₃ and Br photofragments, and $E_{\text{spin-orbit}}^{\text{Br}}$ is the Br spin-orbit energy. If we express the kinetic energy as $E_{\text{kinetic}}^{\text{total}} = a_1 \rho^2$, where ρ is the radial pixel position of the photofragments in the slice image, we can rewrite the energy balance as

$$\begin{aligned} E_{\text{initial}} &= E_{\text{photolysis}} + E_{\text{int}}^{\text{CH}_3\text{Br}} - E_{\text{vib,rot}}^{\text{CH}_3} - E_{\text{spin-orbit}}^{\text{Br}} \\ &= D_0 + a_1 \rho^2. \end{aligned} \quad (3)$$

The photolysis energy $E_{\text{photolysis}}$ is known to within 0.1 cm⁻¹. The internal energy of the hexapole state-selected parent molecule $E_{\text{int}}^{\text{CH}_3\text{Br}}$ is known to spectroscopic precision, i.e., $E_{\text{int}}^{\text{CH}_3\text{Br}}(J=K=1) = 5.58$ cm⁻¹ and $E_{\text{int}}^{\text{CD}_3\text{Br}}(J=K=1) = 2.86$ cm⁻¹.

For the extraction of the dissociation energy we used the experimental data taken with the probe laser set at the same position, near the peak of the *Q* branch, for all photolysis wavelengths used. Because of the large predissociation width of the REMPI transition, see Table III, we do not detect a single rotational state of the methyl fragment. Furthermore, because of small but significant changes of rotational energy with changing photolysis wavelength or spin-orbit channel, we accounted for the internal rotational energy as follows. We compared the change in kinetic energy release at various dissociation wavelengths with the change in photodissociation energy relative to the dissociation at 212.8 nm. Furthermore, we compared the difference in kinetic energy of the Br and Br* channel with the difference in the Br–Br* spin-orbit energy. For CH₃Br we find that the CH₃(0000)+Br* channel has some 440 cm⁻¹ more internal rotational energy for photolysis at 212.8 nm than around 230 nm. The CH₃(0000)+Br channel at 212.8 nm has about 340 cm⁻¹ more internal rotational energy than the CH₃(0000)+Br* channel, this difference between spin-orbit energy and observed kinetic energy difference reduces to about 230 cm⁻¹ near 230 nm. We compared these energies to the nearest rotational energy levels (*NK*) in CH₃(0000), listed in Table III, and used these nearest energy levels to represent the average internal energy of the CH₃(0000) fragments. Specifically, we used, for photolysis at 212.8 nm, $E_{\text{vib,rot}}^{\text{CH}_3}(NK=91) = 851$ cm⁻¹ for the CH₃(0000)+Br channel, and $E_{\text{vib,rot}}^{\text{CH}_3}(NK=71) = 529$ cm⁻¹ for the CH₃(0000)+Br* channel. For photolysis around 230 nm we used $E_{\text{vib,rot}}^{\text{CH}_3}(NK=61) = 396$ cm⁻¹ for CH₃(0000)+Br, and $E_{\text{vib,rot}}^{\text{CH}_3}(NK=31) = 110$ cm⁻¹ for CH₃(0000)+Br*. For photolysis at 212.8 nm of CD₃Br we used $E_{\text{vib,rot}}^{\text{CD}_3}(NK=81) = 342$ cm⁻¹ for CD₃(0000)+Br*, and for photolysis at 235 nm $E_{\text{vib,rot}}^{\text{CD}_3}(NK=41) = 94$ cm⁻¹ for CD₃(0000)+Br*. The probe REMPI energies of the levels (*NK*)=(91) and (*NK*)=(31) in CH₃(0000) are spectroscopically separated by about 5 cm⁻¹, whereas the predissociation widths of the REMPI transitions range from 6–22 cm⁻¹, see Table III. For CD₃(0000) the probe energy difference is about 2.5 cm⁻¹ between (*NK*)=(81) and (*NK*)=(41), and the predissociation

FIG. 9. Plot of the square of the radii of the CH₃(0000) peaks in the velocity distribution [panel (a)] or CD₃(0000) [panel (b)]. For CH₃Br(*JKM*=111) data from five different photolysis wavelengths were used, for CD₃Br(*JKM*=111) we used data from four photolysis wavelengths. The line represents a fit of a straight line from which we obtain the dissociation energy, $D_0(\text{CH}_3\text{Br}) = 23\,400 \pm 133$ cm⁻¹ and $D_0(\text{CD}_3\text{Br}) = 23\,827 \pm 94$ cm⁻¹.

widths are about 1–1.5 cm⁻¹. Therefore, we think it is very probable to detect slightly different (average) *N* states at the same probe wavelength when changing the photolysis wavelength.

Taking these internal rotational energies into account we can plot the total E_{initial} vs the square of the radii of the peaks, see Fig. 9. Each point corresponds to an individual dissociation channel of either methyl+Br or methyl+Br*. The square of the radii of the peaks were fit to a straight line. The intersection with the vertical axis gives the bond dissociation energy D_0 . The fit gives $D_0(\text{CH}_3\text{Br}) = 23\,400 \pm 133$ cm⁻¹ and $D_0(\text{CD}_3\text{Br}) = 23\,827 \pm 94$ cm⁻¹. The value that we find for the CH₃Br bond dissociation energy is close to the value of (2.87 ± 0.2) eV, $(23\,150 \pm 160$ cm⁻¹) reported by van Veen *et al.*¹² Furthermore, we can compare the experimentally obtained dissociation energies for the two isotopes with a theoretical estimate of this difference assuming that to first order $D_e(\text{CH}_3\text{Br}) = D_e(\text{CD}_3\text{Br})$. If we calculate the zero-point energies (ZPE) of the two isotopes of the parent molecules and the methyl fragments from the vibrational frequencies, we find $\text{ZPE}(\text{CH}_3\text{Br}) = 7880$ cm⁻¹, $\text{ZPE}(\text{CH}_3) = 6362$ cm⁻¹, $\text{ZPE}(\text{CD}_3\text{Br}) = 5930$ cm⁻¹, and $\text{ZPE}(\text{CD}_3) = 4715$ cm⁻¹. This gives a theoretical value for the difference in the D_0 of the two isotopes, $D_0(\text{CD}_3\text{Br}) - D_0(\text{CH}_3\text{Br}) = 302$ cm⁻¹. This agrees quite well with the experimentally obtained difference of 427 cm⁻¹.

V. CONCLUSIONS

In this paper we reported the photodissociation of rotationally (*JK*=11) state-selected methyl bromide in the wavelength region of 213–235 nm. The newly developed high speed slice imaging detector gives an improved velocity resolution, and the kinetic energy release distribution shows various excited methyl fragments in ν_1 and ν_4 vibrational

modes, besides the ground state channel. We see a strong effect of the *D*-isotope substitution on the enhanced production of methyl with one quantum of vibration in ν_1 . For all wavelengths studied the increase of the kinetic energy of methyl in the Br channel is less than the increase in available energy from the spin-orbit energy. This means that the methyl in the Br channel typically has some 230–340 cm⁻¹ more rotational energy than methyl in the Br* channel. From the images estimates of the nonadiabatic transition probability for transitions from the $^3Q_{0+}$ to the 1Q_1 state are calculated. A comparison with earlier data from non state-selected experiments indicates that the *K*=1 state selection enhances the nonadiabatic transition probability, as was also observed for photodissociation of methyl iodide. From the wavelength dependence of the kinetic energy release, we obtain new values for the dissociation energy, $D_0(\text{CH}_3\text{Br}) = 23\,400 \pm 133 \text{ cm}^{-1}$ and $D_0(\text{CD}_3\text{Br}) = 23\,827 \pm 94 \text{ cm}^{-1}$.

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