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**High resolution FTIR spectrum of CH₂D⁷⁹Br:
the ground, $\nu_5 = 1$ and $\nu_9 = 1$ state constants**

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Abstract

The first high resolution infrared spectrum of $\text{CH}_2\text{D}^{79}\text{Br}$ has been investigated in the range $710 - 1080 \text{ cm}^{-1}$ by Fourier transform infrared spectroscopy employing a synchrotron radiation source at an unapodized resolution of 0.0025 cm^{-1} . This spectral region accounts for the fundamental bands ν_5 ($\nu_0 = 768.809 \text{ cm}^{-1}$) and ν_9 ($\nu_0 = 930.354 \text{ cm}^{-1}$) having the structure of hybrid a-/b- and c-type bands of near prolate asymmetric tops, respectively. The rovibrational analysis has been performed over a wide range of transitions with quantum numbers $J \leq 72$ and $K_a \leq 16$. The experimentally determined ground state constants including four sextic coefficients have been obtained for the first time by merging the ground state combination-differences of the two bands. The A-reduced Watson Hamiltonian in the I^r representation has been adopted to fit the data. Only weak interaction effects ascribed to a-type Coriolis coupling were influencing the $K_a = 10 - 14$ stacks of the bands. The residuals were adjusted by including in a dyad model one higher order interaction term.

Keywords: Monodeutero methyl bromide; $\text{CH}_2\text{D}^{79}\text{Br}$; Rovibrational analysis; FTIR spectroscopy.

1. Introduction

Methyl bromide, CH_3Br , is currently object of experimental [1–3] and theoretical [4] investigations due to environmental problems connected to the atmospheric transformation processes involving photolysis and chemical reactions with ozone, hydroxyl and nitrate radicals [5, 6]. Harmonic and *ab initio* anharmonic force fields were performed by Schneider and Thiel [7–9]. The molecular parameters calculated *ab initio* at different levels of theory, including the symmetric and asymmetric deuterium isotopologues, were given by Venkatraman et al. [10]. Absolute integrated infrared intensities of the fundamental bands were determined by Van Staten and Smit [11].

Raman and microwave data of the partially deuterium isotopologues are unavailable from literature whereas IR measurements were mainly confined to the regions of the fundamental bands [12]. Only very recently IR studies on CH_2DBr , performed in a large spectral range, provided the assignment of an extensive number of vibrational states with the support of an improved anharmonic force field [13]. From the partially resolved rotational structure of b- and c-type bands, a number of spectroscopic parameters was also evaluated.

In this paper, we report for the first time the results obtained from the high resolution IR spectrum of the ν_5 and ν_9 fundamental bands of $\text{CH}_2\text{D}^{79}\text{Br}$. The pure sample has been prepared in our laboratory for spectroscopic purposes. The choice of selecting one of the 79/81 bromine species is motivated by the near coincidence of the band origins which produce high density spectral lines in particular near the band centres. The ground state constants were obtained through suitable combination

differences (GSCDs) from the rovibrational transitions of ν_5 (a / b-hybrid band) and ν_9 (c-type band) fundamentals. The dataset of each band was initially treated using the classical Hamiltonian model of Watson for asymmetric top molecules. Indeed these levels, separated by about 160 cm^{-1} , are weakly perturbed by Coriolis resonance. Only in the last fits a high order interaction term was introduced in a dyad model to take into account the systematic displacements observed in the higher K_a stacks of both bands.

2. Experimental details

2.1 Synthesis of the sample

$\text{CH}_2\text{D}^{79}\text{Br}$ was prepared by brominating CH_2DOH (CDN Isotopes, 99.2 atom % D) using Na^{79}Br (O.R.N.L., 98.82 atom % ^{79}Br) and dilute H_2SO_4 [14]. The reaction took place in an evacuated Pyrex tube, provided with a HP Rotaflo stopcock placed in a oven at $250\text{ }^\circ\text{C}$ for 24 h. The product was separated from the excess of CH_2DOH by low temperature distillation under dynamic vacuum. No evidence of organic impurities was found in the sample by standard IR techniques. However the high resolution spectrum showed weak lines due to the perpendicular band ν_6 (955 cm^{-1}) of $\text{CH}_3^{79}\text{Br}$.

2.2 Recording of the spectrum

The high resolution (0.0025 cm^{-1}) infrared absorption spectrum of the isotopically enriched $\text{CH}_2\text{D}^{79}\text{Br}$ sample has been recorded at 296 K in the spectral region between 650 and 1100 cm^{-1} with the Bruker IFS 120 HR Fourier transform infrared spectrometer located at the infrared beam-line at MAX-lab (Lund University, Sweden). The highly brilliant synchrotron radiation source offered from the MAX-I electron storage ring was employed as an external radiation source [15, 16]. MAX-I is a 550 MeV electron storage ring with a 300 mA maximum ring current and a mean lifetime of about 4 h. The synchrotron beam is practically an infrared point source and an aperture was solely employed to limit the amount of thermal background radiation. The Michelson interferometer was equipped with a Ge/KBr beam splitter, the detector was a narrowband MCT and selected optical and electronic filters were employed to reduce the photonic noise level, detector nonlinearity effects and eliminate aliasing. The sample of 0.433 kPa $\text{CH}_2\text{D}^{79}\text{Br}$ was kept in 0.5-L multipass absorption cell with a total optical path length of 184 cm. The collected interferograms (210 co-added scans) were post-zero-filled and the absorption line positions were fitted using the Microcal Origin Pro 8 software package. The absolute wave number scale of the resulting transmittance spectrum was subsequently calibrated against absorption lines of CO_2 reported by V.-M. Horneman [17]. The accuracy of the line positions is estimated to $\sim 0.0015\text{ cm}^{-1}$ for unblended lines.

3. Results and discussion

The $\text{CH}_2\text{D}^{79}\text{Br}$ molecule is a near prolate asymmetric rotor ($\kappa = -0.997$) belonging to the C_s point group. All nine fundamental modes (six of A' and three of A'' symmetry species) are infrared-active. The bands arising from the normal vibrations are summarized in Table 1. The survey IR spectrum of the region investigated is shown in Figure 1. The ν_5 hybrid band exhibits a prominent central Q -branch typical of an a-type contour and a rotational profile in the wings of the P , R branches due to the weaker b-type component whereas ν_9 manifests the rotational structure of a c-type band. On the whole the contours approach to the parallel (a-type) and perpendicular bands (b- and c-type) of prolate symmetric rotors. In order to interpret the well resolved rovibrational structure, initial spectral predictions were performed using the spectroscopic parameters of [13] obtained from the analysis of the partially resolved structure identified in the IR spectrum of CH_2DBr in natural abundance.

The rovibrational analysis of ν_5 begun by considering the a-type component. From a preliminary scrutiny of the spectrum it was found, as expected from the medium resolution data [13], that the Q -branch is moving to the blue and within each multiplet a series of lines degrading to lower wavenumbers could be followed until they merge into the next one. Correspondingly group of regularly spaced lines decreasing their intensity were also readily apparent in the P - and R -branches near the band centre. The assigned transitions were used for initial calculation of the ground state constants through GSCDs then fixed for a rough evaluation of the upper state parameters. Correlation diagrams, which combine P , Q , and R -transitions reaching the same upper sublevels, were adopted according to the method early described by Nakagawa and Overend [18].

These plots display line position and relative intensity for each K_a subband occurring in the P , Q , and R branches. When significant and systematic deviations from a vertical set of transitions were reproduced, the progression of assignment was provided by refining the spectroscopic constants of the ground and upper levels. Figure 2 displays a picture of the rotational structure of the ${}^qQ_K(J)$ -subbranches. The assignment was performed from the weak lines with $K_a = 2$ and proceeded up to $K_a = 15$ with $J \leq 25$ for the stronger subbranches. Conversely the sequences of the ${}^q(P,R)_K(J)$ multiplets are almost completely mixed up. In this case the assignment reached $K_a = 14$ and $J \leq 71$. Lines undergoing to asymmetry splitting were found up to $K_a = 3$ with the even ($K_a'' + K_c'' = J''$) component located at lower and higher wavenumbers in the P - and R -branches, respectively, compared to the odd ($K_a'' + K_c'' = J'' + 1$) one. At this point of analysis the identified transitions provided comparable centrifugal distortion constants for the lower and upper states.

In the b-type component the ${}^{p,r}Q_K(J)$ clusters regularly degrade to lower wavenumbers. They can be easily distinguished in spectral regions where the a-type lines show negligible line strength. In absence of asymmetry splitting, observed for transitions with $K_a' \leq 4$, the clusters are completely resolved even at the band heads. The rovibrational assignment was computer assisted by graphical correlation plots where in this case a large number of transitions showing different line intensities, sharing a common upper state sublevel, can be combined. When the new data were added in a bootstrap procedure by refining the lower and upper state parameters, the A rotational and the Δ_K centrifugal distortion constants greatly improved in accuracy. However, as also shown in Figure1, the line strengths in the P - and R -branches differ significantly.

As a result the ${}^r(R,Q)_K(J)$ and ${}^p(P,Q)_K(J)$ subbranches up to $K_a' = 15$ and 8, respectively, with $J \leq 60$ were positively identified.

The rovibrational analysis of ν_9 was accomplished in a similar fashion to that described for the b-type component of ν_5 . Predictions were performed using the information of Ref. [13] together with the determined ground state constants from ν_5 . Just as for the perpendicular component of ν_5 , the ${}^{p,r}Q$ -subbranches are evenly spaced and approximately separated by the term value $2(A - \bar{B}) = 7.36 \text{ cm}^{-1}$, where $\bar{B} = (B + C) / 2$. The rotational structure, with partial exclusion of the ${}^pQ_J(J)$ manifold, is fully resolved. In absence of asymmetry splitting each K_a manifold degrades to lower wavenumbers as J increases thus indicating that, as for ν_5 , $\bar{B}$ of $\nu_9 = 1$ is comparatively smaller than that of the ground state. An example of a typical multiplet is illustrated in Figure 3. The ${}^pP_K(J)$ and ${}^rR_K(J)$ -subbranches widely spread out all over the spectral region where the P -wing merges into the R -branch extremity of ν_5 . Within each sequence, the J lines are regularly spaced by about $2\bar{B} = 0.59 \text{ cm}^{-1}$. The weaker ${}^rP_K(J)$ and ${}^pR_K(J)$ transitions with K_a values up to medium quantum numbers were also identified and included in the dataset. Asymmetry splitting was observed up to $K_a' = 5$. Assignment was extended up to $K_a = 16$ and $J \leq 72$ in both P - and R -branches which show comparable line intensity.

As mentioned the ground state spectroscopic constants of $\text{CH}_2\text{D}^{79}\text{Br}$ are unavailable in the literature. However they can be provided with a high level of accuracy by merging the large number of GSCDs produced from the dataset of ν_5 and ν_9 . This was done by excluding the transitions ascribed to broad lines due to overlapping or to partially unresolved features for the asymmetry splitting. More than 12400 GSCDs ($K_a \leq 16$ and $J \leq 71$) with $\Delta K_a = 0, \pm 1, \pm 2$ were calculated and weighted

according to the number of transitions sharing a common upper level. In detail they were weighted with the reciprocal of the number of differences carried out in each group [19]. In the least-squares procedure the ground state constants were determined by computing the rotational energy levels with Watson's A-reduction Hamiltonian in the I' representation [20]. The preliminary fits were performed by varying the constants up to fourth order; then a number of higher order centrifugal distortion terms were tested to take into account the significant systematic deviations in the residuals. The determined ground state constants which include four sixth order term values are listed in Table 2.

The rovibrational structure of the ν_5 and ν_9 bands could be fitted separately within the accuracy of measurements for a large number of transitions. However systematic deviations from the calculated values were observed for $K_a' = 12$ of ν_5 and $K_a' = 10$ of ν_9 . The residuals (observed – calculated values) of the transitions involving the two sublevels increasing with J were similar in magnitude but different in sign. This suggested the presence of a local perturbation between the upper states. The ν_5 and ν_9 levels are of A' and A'' symmetry species, respectively; hence they can interact through a- ($\Delta K_a = 0, \pm 2, \dots$) and / or b-type ($\Delta K_a = \pm 1, \pm 3, \dots$) Coriolis resonance. The approximate energy level diagram shows that in our range of assignment the perturbation can locally affect sublevels differing by two units in K_a ; the interaction is therefore of a-type Coriolis with $\Delta K_a = \pm 2$.

Taking into account the perturbation term, about 14000 assigned transitions were simultaneously fitted by fixing the ground state constants at the values determined in the present work. Calculation was carried out using the ATIRS package software [21] and in particular the VCALPGM program, a graphical interface to the Pickett's SPFIT /

SPCAT program [22]. The starting parameters of the fit were those obtained from the treatment of the apparently unperturbed transitions whereas the initial estimated value of the a-type Coriolis term ($\eta_{5,9}^{bc} = 0.79 \times 10^{-4} \text{ cm}^{-1}$) was calculated by considering the maximum energy shift observed for $K_a' = 10$ and $J' = 62$ of ν_5 . In the least squares fit only apparently single lines were considered.

The excited state spectroscopic parameters are included in Table 2. They represent the best set of constants obtained with a standard deviation of $0.44 \times 10^{-3} \text{ cm}^{-1}$. Statistically only five randomly distributed assigned transitions revealed displacements higher than $\pm 0.0020 \text{ cm}^{-1}$ from the calculated values. The standard deviation of the fit is more than three times lower than the estimated accuracy of measurements. The quartic centrifugal distortion constants are all comparable with the ground state values as well as the less accurate sextic terms with exclusion of the Φ_{KJ} constant of ν_5 . The observed discrepancy is probably due to the existence of further weak Coriolis resonances between $\nu_5 = 1$ and $\nu_6 = 1$ levels. The comparison of the vibration-rotation interaction constants of ν_5 and ν_9 with the computed values predicted from the anharmonic force field [23], given in Table 3, shows a general good agreement thus indicating that additional interactions are only marginal. It should be lastly mentioned that many weak unassigned features are present in the spectrum. Most of them belong to transitions due to hot bands from the low lying $\nu_6 = 1$ state: the Boltzmann population at room temperature of this level is predicted about 6% of the ground vibrational state.

The list of assigned transitions and the (obs.-calc.) values resulting from the spectroscopic parameters of Table 2 are available upon request from one of the authors (P.S.).

4. Conclusion

A detailed high resolution IR study of the ν_5 and ν_9 fundamentals of the near prolate asymmetric top $\text{CH}_2\text{D}^{79}\text{Br}$ has been performed. The fully resolved rotational structure of the a-, b-hybrid ν_5 and c-type ν_9 bands allowed an accurate determination of the ground state constants through GSCDs. They should be of great help in studies concerning more complex band systems of the molecule. The precise value of the rotational constant A_0 is important for the structure determination whereas the evaluation of the centrifugal distortion constants of the asymmetric species are useful for an improvement of the force field of methyl bromide. A local perturbation affecting the ν_5 and ν_9 bands due to the near coincidence of the K_a sublevels differing by two units has been detected. The upper state spectroscopic parameters have been obtained by fixing the ground state constants and using a higher order a-type Coriolis interaction term in a dyad model. The unassigned weak lines mainly belong to hot bands with $\nu_6 = 1$ as lower state. In order to interpret this additional structure, the rovibrational analysis of the low lying fundamental is in progress.

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Table 1. Gas Phase Infrared Fundamental Bands of CH₂D⁷⁹Br^a

Symmetry species	Mode	Wavenumber / cm ⁻¹	Relative Intensity ^b	Approximate description
A'	v ₁	3001.04(1) ^c	s	CH ₂ sym. stretch
	v ₂	2243.80(1)	m	CD stretch
	v ₃	1424.94(1)	s	CH ₂ deformation
	v ₄	1225.21(5)	s	CH ₂ wag
	v ₅	768.80852(8)	m	D–C–Br deformation
	v ₆	595.0(2)	s	CBr stretch
A''	v ₇	3052.96(2)	m	CH ₂ antisym. stretch
	v ₈	1252.55(3)	w	CH ₂ twist
	v ₉	930.35379(8)	m	CH ₂ rock

^a Ref. 13.
^b Abbreviations used are as follows: s = strong, m = medium, w = weak.
^c The experimental error in parentheses is on the last significant digit.

Table 2. Spectroscopic constants (cm^{-1}) for the ground, $v_5 = 1$ and $v_9 = 1$ states of $\text{CH}_2\text{D}^{79}\text{Br}^a$

		Ground state	$v_5 = 1$	$v_9 = 1$
v_0			768.808516(82)	930.353789(82)
A		3.97445755(114)	3.9862648(39)	4.0006428(31)
B		0.29756678(20)	0.29658963(29)	0.29668616(32)
C		0.29232654(20)	0.29128939(29)	0.29137974(35)
Δ_J	$\times 10^6$	0.272868(92)	0.272223(99)	0.273700(104)
Δ_{JK}	$\times 10^5$	0.330164(113)	0.31944(31)	0.35180(25)
Δ_K	$\times 10^4$	0.562090(102)	0.56476(44)	0.59830(27)
δ_J	$\times 10^8$	0.47691(84)	0.4290(27)	0.5160(33)
δ_K	$\times 10^6$	0.5525(154)	0.445(65)	0.617(77)
Φ_J	$\times 10^{13}$	−0.764(128)	−0.914(147)	−0.827(160)
Φ_{JK}	$\times 10^{11}$	0.347(28)	0.258(67)	0.478(52)
Φ_{KJ}	$\times 10^{10}$	0.517(38)	−0.460(127)	0.902(84)
Φ_K	$\times 10^8$	0.2727(28)	0.2288(137)	0.3465(65)
$\eta_{5,9}^{bc}$	$\times 10^4$		0.8182(100)	
No.	of data	12462	6765	7070
J_{max}		71	71	72
$K_{\text{a max}}$		16	15	16
σ	$\times 10^3$	0.472		0.439

^a Quoted uncertainties in parenthesis are one standard deviation in units of the last significant digits.

Table 3. Vibration-rotation interaction constants α (cm⁻¹) for CH₂D⁷⁹Br

	v ₅		v ₉	
	Experimental	Calculated ^a	Experimental	Calculated ^a
$\alpha^A \times 10^3$	-11.807	-11.891	-26.185	-26.821
$\alpha^B \times 10^3$	0.977	0.935	0.880	0.857
$\alpha^C \times 10^3$	1.037	1.000	0.947	0.907

^a Calculated from the anharmonic force field predicted from coupled cluster CCSD(T) with cc-pVTZ basis set [23].

Figure captions

Fig. 1 Overview of the medium resolution (0.2 cm^{-1}) transmission spectrum of $\text{CH}_2\text{D}^{79}\text{Br}$ in the region of the ν_5 and ν_9 fundamentals (room temperature, pressure: 22 hPa, optical path length: 16 cm)

Fig. 2 The high resolution spectrum of the ν_5 fundamental of $\text{CH}_2\text{D}^{79}\text{Br}$ showing the fine structure of the a-type Q -branch.

Fig. 3 The ${}^rQ_9(J)$ subbranch of the ν_9 fundamental of $\text{CH}_2\text{D}^{79}\text{Br}$. This typical line sequence has also been found for the perpendicular component of ν_5 .

FIGURE 1

Overview of the medium resolution (0.2 cm⁻¹) transmission spectrum of CH₂D⁷⁹Br in the region of the v₅ and v₉ fundamentals (room temperature, pressure: 22 hPa, optical path length: 16 cm).
288x201mm (600 x 600 DPI)

FIGURE 2

The high resolution spectrum of the ν_5 fundamental of CH₂D⁷⁹Br showing the fine structure of the a-type Q-branch.
288x201mm (600 x 600 DPI)

FIGURE 3

The rQ₉(J) subbranch of the v₉ fundamental of CH₂D₇₉Br. This typical line sequence has also been found for the perpendicular component of v₅.
288x201mm (600 x 600 DPI)