Vibrational Spectra and Force Constants of Symmetric Tops, XLIII [1] Fourier Transform Infrared Spectra of Monoisotopic H_3GeBr Species in the ν_1/ν_4 and ν_6 Region

H. Bürger, R. Eujen, A. Rahner, and P. Schulz

FB 9 – Anorganische Chemie, Universität-Gesamthochschule, Wuppertal, West Germany

S. Cradock

Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ,
Scotland

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Fourier transform infrared spectra of the monoisotopic species $H_3{}^{74}Ge^{79}Br$ and $H_3{}^{74}Ge^{81}Br$ have been recorded in the ν_1/ν_4 region near 2100 cm^{-1} with a resolution of 0.015 cm^{-1} and in the ν_6 and $2\,\nu_6$ regions near 580 and 1150 cm^{-1} with a resolution of 0.04 cm^{-1}. Rotational analyses based on ~ 1500, ~ 1100 and ~ 300 data of ν_1/ν_4, ν_6 and $2\,\nu_6$ respectively for each isotopomer have been performed, and ground state and excited state vibrational, rotational and rovibrational parameters have been determined. ν_1, 2115.815 0(2)/2115.813 4(2) cm^{-1}, and ν_4, 2126.016 5(1)/2126.016 7(1) cm^{-1} ($H_3{}^{74}Ge^{79}Br/H_3{}^{74}Ge^{81}Br$), are weakly coupled by Coriolis x, y resonance, $\zeta_{1,4} \simeq -0.021$. ν_6, 577.601 2(4)/577.541 7(4) cm^{-1}, and ν_4 are affected by l $(\pm 2, \pm 2)$ resonance. Furthermore, the hot bands $(\nu_1 + \nu_3) - \nu_3$, $(\nu_3 + \nu_4) - \nu_3$, $(\nu_3 + \nu_6) - \nu_3$, $2\,\nu_6^{\pm 2} - \nu_6^{\pm 1}$ and $2\,\nu_6^0 - \nu_6^{\pm 1}$ have been detected and analyzed.

1. Introduction

Recently we have reported on the rovibrational investigation of the fundamental ν_3 (a_1 ν GeBr) near 300 cm^{-1} [2] and of the a_1/e/E triade $\nu_2/\nu_5/\nu_3 + \nu_6$ of H_3GeBr in the GeH_3 bending region near 850 cm^{-1} [3]. For this purpose spectra were recorded with a resolution of 0.04 cm^{-1}. In order to avoid complications inevitably caused by the isotopic effect of Ge and Br, monoisotopic material $H_3{}^{74}Ge^{79}Br$ and $H_3{}^{74}Ge^{81}Br$, abbreviated in the following (79) and (81), was used. These investigations were aimed to update previous low-resolution studies of natural material [4, 5]. These had not revealed any details of the parallel fundamentals ν_1 to ν_3 while K structure of the perpendicular fundamentals ν_4 to ν_6 was indicated.

Continuation of the rovibrational study of H_3GeBr seemed desirable for several reasons. First, only a complete set of vibration-rotation interaction parameter allows the equilibrium structure to be computed. Second, such a complete study promised to supply the full set of ground state rotational constants, the centrifugal distortions D_J^0, D_{JK}^0 and D_K^0 included. Third, precise knowledge of fundamental vibrational frequencies and isotopic shifts is essential for the evaluation of the molecular force field. Finally the analysis of vibrational and rotational resonances requires secure knowledge of the rovibrational parameters of possible perturbers. Such resonances have been established for $\nu_2/\nu_5/\nu_3 + \nu_6$ of H_3GeBr [3] and play an important role by the GeH stretching fundamentals ν_1 and ν_4 of H_3GeCl [6].

In the following contribution we deal with the fundamentals ν_1/ν_4 near 2100 and ν_6 near 600 cm^{-1} of (79) and (81) associated with the species a_1/e GeH_3 stretching and species e GeH_3 rocking vibrations, respectively. While the latter is supposed to be isolated and unperturbed, though coupling of ν_6 with $2\,\nu_3$ cannot be ruled out, the GeH_3 stretching vibrations are expected to be weakly coupled by Coriolis x, y resonance, $B\,\zeta_{1,4}^y \simeq 0.002$ cm^{-1} being predicted from the harmonic force field. In addition, ν_1/ν_4 may well interact with several vibrational combinations in the 2100 cm^{-1} region. While the ν_6 and $2\,\nu_6$ regions are studied with an experimental resolution of 0.04 cm^{-1}, a resolution of 0.015 cm^{-1} was necessary for the analysis of the dense spectrum in the region of the overlapping fundamentals ν_1 and ν_4.

Reprint requests to Prof. Dr. H. Bürger, Universität-Gesamthochschule, Gaußstraße 20, D-5600 Wuppertal 1.

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2. Experimental

Monoisotopic H_3GeBr samples were prepared as described previously [2] from $^{74}GeO_2$ (98.9% ^{74}Ge), $Na^{79}Br$ (98.6% ^{79}Br) and $Na^{81}Br$ (97.8% ^{81}Br) and purified by repeated trap to trap condensation employing a vacuum line with greaseless stopcocks.

18.6 cm cells fitted with KBr windows were used, and pressures between 1.5 and 25 mbar were chosen. Spectra in the 2100, 1150 and 600 cm^{-1} ranges were recorded with a resolution of 0.04 cm^{-1} employing a NICOLET type 7199 interferometer. Calibration was with CO [7], H_2O and CO_2 lines [8], frequency accuracy 3×10^{-3} cm^{-1} for ν_6 and 6×10^{-3} cm^{-1} for the $2\nu_6$ and ν_1/ν_4 regions. The ν_1/ν_4 range was also studied with a BOMEM DA 002 instrument operating with a resolution (fwhm) of 0.015 cm^{-1}. Calibration was with CO lines [7]; frequency accuracy 2×10^{-3} cm^{-1} for (79) and 1×10^{-3} cm^{-1} for (81).

3. Vibrational analysis

The vibrational transitions ν_1, ν_4 and ν_6 are accompanied by satellites which are due to hot bands. At room temperature the following intensities relative to the cold bands are expected for the major hot bands:

$$\begin{array}{llll} (\nu_1+\nu_3)-\nu_3, & (\nu_3+\nu_4)-\nu_3, & (\nu_3+\nu_6)-\nu_3 & 23\%, \\ (\nu_1+\nu_6)-\nu_6, & 2\,\nu_6^{\pm 2}-\nu_6^{\pm 1}, & \Sigma(\nu_4+\nu_6)-\nu_6 & 12\%, \\ 2\,\nu_6^{0}-\nu_6^{\pm 1} & & & 6\%. \end{array}$$

$3p+1$ and $3p-1$ intensity alternation of $K\,\Delta K$ subbands, $p = 0, \pm 1, \pm 2, \ldots$, is expected to appear for the hot bands $2\,\nu_6^{\pm 2}-\nu_6^{\pm 1}$ and $2\,\nu_6^{0}-\nu_6^{\pm 1}$ respectively. Analogous behaviour is expected for the two components of $(\nu_4+\nu_6)-\nu_6$ which however have not been observed. Additional information concerning the $(2\nu_6-\nu_6)$ hot bands comes from the overtones $2\,\nu_6^{\pm 2}$ and $2\,\nu_6^{0}$ which have been observed in the spectra. Thus it is confirmed that the Q branches of $2\,\nu_6^{0}-\nu_6^{\pm 1}$ are partly hidden by Q branches of ν_6.

Unresolved Q branches of the hot bands $(\nu_1+\nu_3)-\nu_3$, $(\nu_3+\nu_4)-\nu_3$ and $(\nu_3+\nu_6)-\nu_6$ have been identified, rotational $\Delta J = \pm 1$ lines being buried under the cold bands. Indication was found for Q branches of $(\nu_1+2\,\nu_3)-2\,\nu_3$ as well as for $(2\,\nu_3+\nu_4)-2\,\nu_3$. The Q branch edges corresponding to first Q branch lines [$^{Q}Q_K(K)$, $^{R}Q_K(K)$, $^{P}Q_K(K+1)$] are listed in Tables 1 to 3. While the hot bands $(\nu_1+n\,\nu_3)-n\,\nu_3$ and $(\nu_3+\nu_4)-\nu_3$ are blue-shifted from the cold bands and follow regular patterns, Figs. 1 and 2, the hot band $(\nu_3+\nu_6)-\nu_3$ is perturbed due to Fermi resonance between $\nu_3+\nu_6$ and ν_5, Figure 3 [3]. Therefore a polynomial analysis of the Q branch positions of $(\nu_3+\nu_6)-\nu_6$ listed in Table 3 is not practicable. The anharmonicity constants x_{36} have been determined, − 1.641 and − 1.627 cm^{-1} for (79) and (81), respectively [3]. The Q branch frequencies of the hot bands $(\nu_1+\nu_3)-\nu_3$, Table 1, and $(\nu_3+\nu_4)-\nu_3$ and $(2\,\nu_3+\nu_4)-2\,\nu_3$, Table 2, were subjected to a polynomial analysis to yield the quoted anharmonicity constants. From the regular pattern of the hot band Q branches we conclude that the upper levels $\nu_1+\nu_3$ and $\nu_3+\nu_4$ are not significantly perturbed. No indication was found for hot bands with ν_6 as lower level.

Table 1. $^{Q}Q_K$ peak positions of the hot band $(\nu_1+\nu_3)-\nu_3$ of $H_3{}^{74}Ge^{79}Br$ and $H_3{}^{74}Ge^{81}Br$ (cm^{-1}).

K	$H_3{}^{74}Ge^{79}Br$	$H_3{}^{74}Ge^{81}Br$
3	2115.779 6	2115.777 2
4	–	–
5	5.407 0	5.405 6
6	5.149 4	5.146 6
7	4.843 7	4.842 9
8	4.492 2	4.491 8
9	4.097 1	4.094 4
10		–
11		3.160 0
12		2.618 5

4. Rotational analysis

4.1. *Theory*

The ν_1, ν_4 systems coupled by Coriolis x, y resonance with additional essential $l(\pm 2, \pm 2)$ resonance within $\nu_t (t = 4)$ were treated as described previously [9] with the conventions of [10] and [11], $q_t^{(+)} = 4F_t$. Conventional diagonal matrix elements and the following off-diagonal terms were adopted:

$$\begin{aligned} &\langle v_1 = 1,\ v_4 = 0;\ J, k \,|\, H \,|\, v_1 = 0, \\ &\quad v_4 = 1,\ l_4 = \pm 1;\ J, k \pm 1 \rangle \\ &\qquad = \pm\, 2^{1/2}\, B\, \Omega_{1,4}\, \zeta_{1,4}^{y}\, [J(J+1) - k(k \pm 1)]^{1/2} \\ &\Omega_{1,4} = \tfrac{1}{2}\,[(\nu_1/\nu_4)^{1/2} + (\nu_4/\nu_1)^{1/2}] \end{aligned} \tag{1}$$

$$\begin{aligned} &\langle v_t = 1,\ l_t = 1,\ J, k+1 \,|\, H \,|\, v_t = 1,\ l_t = -1.\ J, k-1 \rangle \\ &\qquad = -\,2\,F_t\,[J(J+1) - k(k+1)]^{1/2} \\ &\qquad\quad \cdot [J(J+1) - k(k-1)]^{1/2}. \end{aligned} \tag{2}$$

Table 2. Q branch edges of the hot bands $(\nu_3 + \nu_4) - \nu_3$ and $(2\,\nu_3 + \nu_4) - 2\,\nu_3$ of $H_3{}^{74}Ge^{79}Br$ and $H_3{}^{74}Ge^{81}Br$ (cm^{-1}).

$K\,\Delta K$	$H_3{}^{74}Ge^{79}Br$		$H_3{}^{74}Ge^{81}Br$	
	$(\nu_3 + \nu_4) - \nu_3$	$(2\,\nu_3 + \nu_4) - 2\,\nu_3$	$(\nu_3 + \nu_4) - \nu_3$	$(2\,\nu_3 + \nu_4) - 2\,\nu_3$
15	2205.528 8			
14	–			
13	2195.885 1			
12	90.987 2		2190.992 1	
11	86.067 3		86.066 5	
10	81.087 2		81.102 9	
9	76.080 5	2176.494 7	76.099 7	2176.544 7
8	71.032 9	–	71.036 1	–
7	65.958 9	66.374 7	65.981 2	–
6	60.829 7	61.244 3	60.824 6	61.251 6
5	55.650 1	56.084 6	55.654 0	–
4	50.463 5	50.876 5	50.460 6	–
3	45.218 7	45.657 3	45.223 7	45.668 8
2	39.949 2	–	39.942 9	–
1	34.643 0	–	34.649 9	–
0	29.313 8	29.719 8	29.301 7	–
− 1	23.933 0		23.920 3	–
− 2	18.522 7		18.506 5	–
− 3	13.079 1		13.073 3	–
− 4	07.595 4		07.598 9	–
− 5			02.092 9	–
− 6			2096.559 6	2097.019 0
− 7			90.985 8	–
− 8			85.399 3	85.863 2
− 9			79.786 3	
− 10			74.134 1	
− 11			–	
− 12			62.748 9	

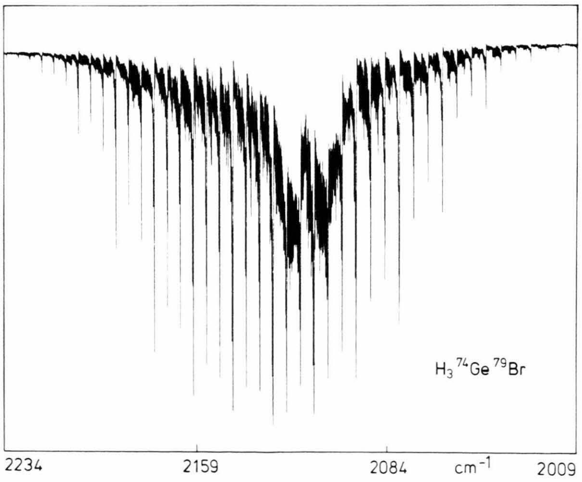

Fig. 1. Survey spectrum of $H_3{}^{74}Ge^{79}Br$ in the ν_1/ν_4 region. 18.7 cm cell, 2.5 mbar, resolution 0.04 cm^{-1}.

The fundamental ν_6 was treated similarly, only $l(\pm 2, \pm 2)$ resonance according to (2) being considered. A program was used [12] which fitted upper state parameters from observed transitions for a fixed ground state.

4.2. *Ground state*

The ground state parameters used in this study are set out in Table 4. A deduced A_0 value comes from a combined IR and mw study of D_3GeBr and HD_2GeBr [13] using additional mw data from [14], while B_0 originates from corrected [13] mw data [15]. A_0 was also calculated using the relation $(A\,\zeta)_{66} = -2(A\,\zeta)_6$ and from $\nu_6^{\pm 1}$, $2\,\nu_6^{\pm 2}$ and $(2\,\nu_6^{\pm 2} - \nu_6^{\pm 1})$ according to the procedure described previously [16, 17].

Table 3. Q branch edges of the hot bands $(\nu_3+\nu_6)-\nu_3$, $2\nu_6^0-\nu_6^{\pm 1}$ and $2\nu_6^{\pm 2}-\nu_6^{\pm 1}$ (cm^{-1}) and differences $\Delta = \nu_{obs} - \nu_{fit}$ (10^{-3} cm^{-1}) of $H_3{}^{74}Ge^{79}Br$ and $H_3{}^{74}Ge^{81}Br$.

$K\Delta K$	$(\nu_3+\nu_6)-\nu_3$		$2\nu_6^0-\nu_6^{\pm 1}$				$2\nu_6^{\pm 2}-\nu_6^{\pm 1}$			
	$H_3{}^{74}Ge^{79}Br$	$H_3{}^{74}Ge^{81}Br$	$H_3{}^{74}Ge^{79}Br$		$H_3{}^{74}Ge^{81}Br$		$H_3{}^{74}Ge^{79}Br$		$H_3{}^{74}Ge^{81}Br$	
	ν_{obs}	ν_{obs}	ν_{obs}	Δ	ν_{obs}	Δ	ν_{obs}	Δ	ν_{obs}	Δ
13	631.143	630.814								
12	26.793	26.352								
11	22.392	21.898								
10	17.940	17.445								
9	13.689	13.000								
8	–	–			613.169	29	613.754	– 17	613.844	8
7	–	–	608.850	31	08.867	– 5	09.497	9	09.506	– 13
6	–	–	04.601	– 14	04.606	– 22	05.243	14	05.217	– 11
5	–	–	00.393	– 31	00.394	– 13	00.987	– 6	00.959	– 6
4	597.833	597.882	–		596.201	– 8	596.790	10	596.748	20
3	93.032	93.676	592.086	4	92.050	16	92.587	– 3	92.549	30
2	88.381	88.843	87.883	– 44	87.868	– 14	–		88.316	– 20
1	83.229	84.193	83.781	– 11	83.744	– 9	–		84.183	2
0	80.028	79.689	79.677	11	–		–		80.044	– 9
– 1	–	–	75.581	28	–		576.058	– 3	75.943	– 8
– 2	–	–	–		71.541	36	71.974	– 12	71.881	4
– 3	66.765	–	67.372	6	67.489	22	67.937	2	67.827	– 2
– 4	62.673	62.737	63.271	– 20	63.438	– 15	63.903	– 4	63.824	16
– 5	58.522	58.543			59.456	– 7	59.911	9	59.806	– 9
– 6	54.521	54.531			55.485	– 10	55.920	1	55.836	– 12
– 7	50.370	50.506								
– 8	46.518	46.550								
– 9	42.621	42.608								
– 10	38.566	38.730								
– 11	34.665	34.841								
Coefficients of polynomial fit $a_0 + a_1\,(K\Delta K) + a_2\,(K\Delta K)^2$										
	a_0		579.666 (17)		579.647 (14)		580.158 (7)		580.052 (9)	
	a_1		4.120 (9)		4.094 (5)		4.109 (3)		4.115 (3)	
	$a_2 \times 10^2$		0.64 (4)		1.15 (3)		1.16 (1)		1.35 (2)	
	$\sigma(K) \times 10^3$		20		18		9		13	
	ν_0		577.089		577.069		579.708		579.614	
	x_{66}		0.398 (6)		0.400 (6)					
	g_{66}		0.655 (5)		0.636 (4)					

The centrifugal distortions may be computed from the reported harmonic force field [3]. Independently, $1/2(D_J^0 + D_J^3)$ is available from the ν_3 analysis [2] while an estimate for D_{JK}^0 comes from the mw study [15]. Presumably the most precise values for D_J^0 and D_{JK}^0, at least for (81), were obtained in this study from a least squares fit of ground state combination differences performed on ν_1 and ν_4 data.

D_K^0 has been computed from the molecular force field [3], but since all ($t = 4$ to 6) η_{tJ} and η_{tK} values as well as D_J^0 and D_{JK}^0 constants are now experimentally available, D_K^0 may be determined from the relation (η sum rule) [18, 19]

$$\sum_{t=4}^{6} [(D_K - 1/4\,\eta_{tK}) - 1/4\,\eta_{tJ}] = 3\,D_K - 1/4\,D_{JK} - 1/2\,D_J\,. \quad (3)$$

Relation (3) is quite insensitive to uncertainties of the comparatively small D_J and D_{JK} values. The least squares analyses were performed with the ground state parameters set out in the last column of Table 4. These are assumed to be the best values for (79) and (81) at present.

4.3. *The $v_6 = 1$ state*

The assignment of the spectra is straightforward from first lines and the observed intensity alternation. A total of 1039 and 1104 transitions have been fitted for (79) and (81), $K\Delta K$ ranging from -15 to $+15$ and J'' up to 71. Refinement of the excited state centrifugal distortions D_J^6 and D_{JK}^6 was not physically meaningful. The ultimate fit parameters are set out in Table 5. Figure 4 illustrates a section of

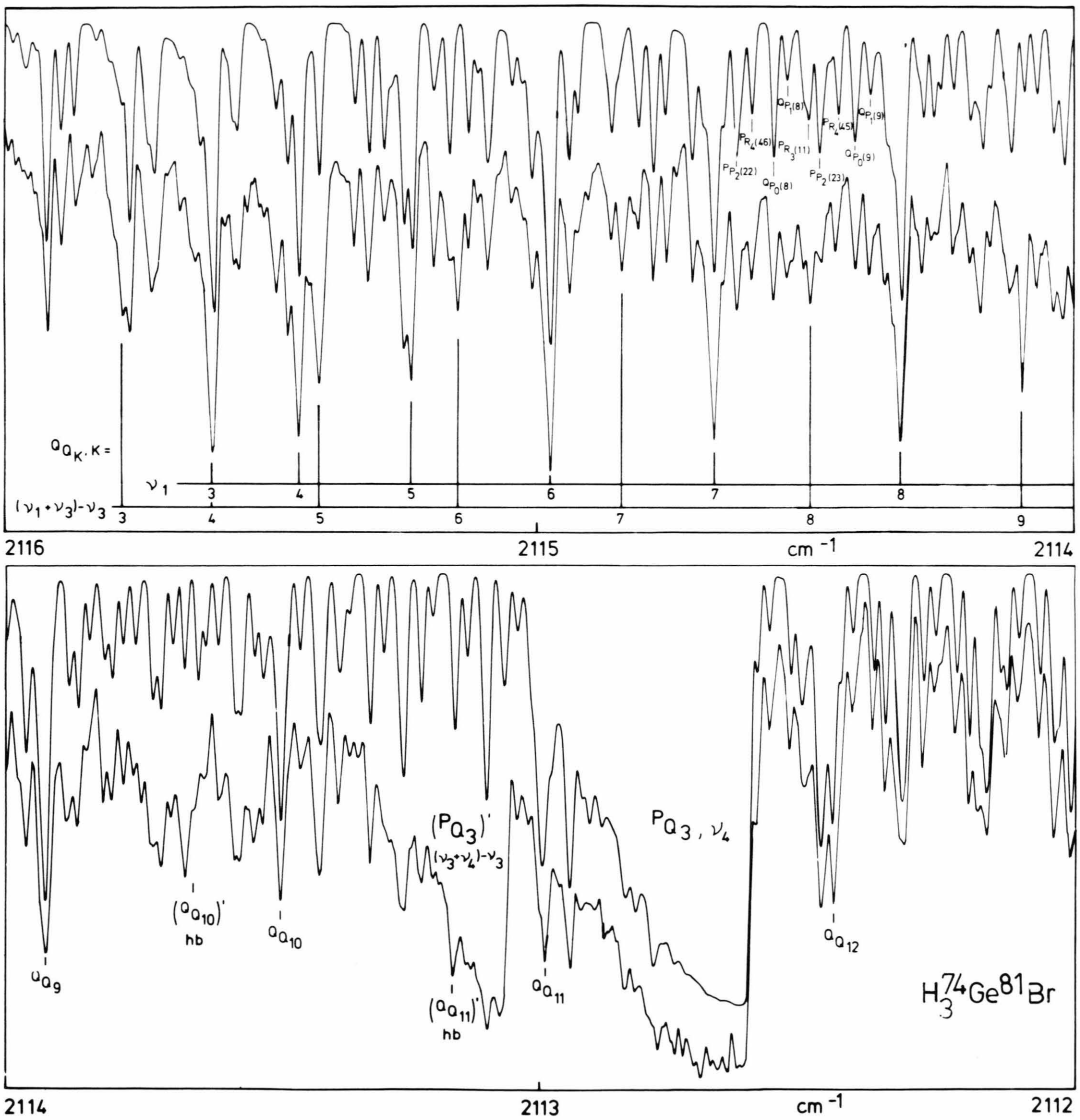

Fig. 2. Detail of the ν_1/ν_4 spectrum of $H_3{}^{74}Ge^{81}Br$. Upper trace: simulated spectrum, hot bands omitted. Lower trace: observed spectrum, 18.7 cm cell, 2.5 mbar, resolution 0.015 cm^{-1}. Assignments are given for ^QQ branches of ν_1, $(\nu_1+\nu_3)-\nu_3$ and some rotational lines.

Table 4. Ground state molecular parameters of $H_3{}^{74}Ge^{79}Br/H_3{}^{74}Ge^{81}Br$ (cm^{-1}).

				Adopted:
A_0	2.632 5 [13]	2.631 7/2.631 4 [a]	2.632 9/2.633 0 [c]	2.632 5/2.632 5
$B_0 \times 10^2$	7.925 02/7.830 22 [13]		7.924 73 (18)/7.830 26 (16) [d]	7.925 02/7.830 22
$D_J^0 \times 10^8$	2.13/2.00 [2]	2.08/2.03 [b]	2.05 (4)/2.046 (24) [d]	2.08/2.03
$D_{JK}^0 \times 10^7$	3.3/3.3 [15]	3.62/3.54 [b]	3.9 (7)/3.9 (4) [d]	3.62/3.54
$D_K^0 \times 10^5$		2.24/2.24 [b]	2.26/2.26 [e]	2.26/2.26

[a] From $(A\zeta)_{66} = -2(A\zeta)_6$. [b] From harmonic force field [3]. [c] From $\nu_6^{\pm1}$, $2\nu_6^{\pm2}$ and $(2\nu_6^{\pm1} - \nu_6^{\pm1})$. [d] From ground state combination differences, this study. [e] From η sum rule, see text.

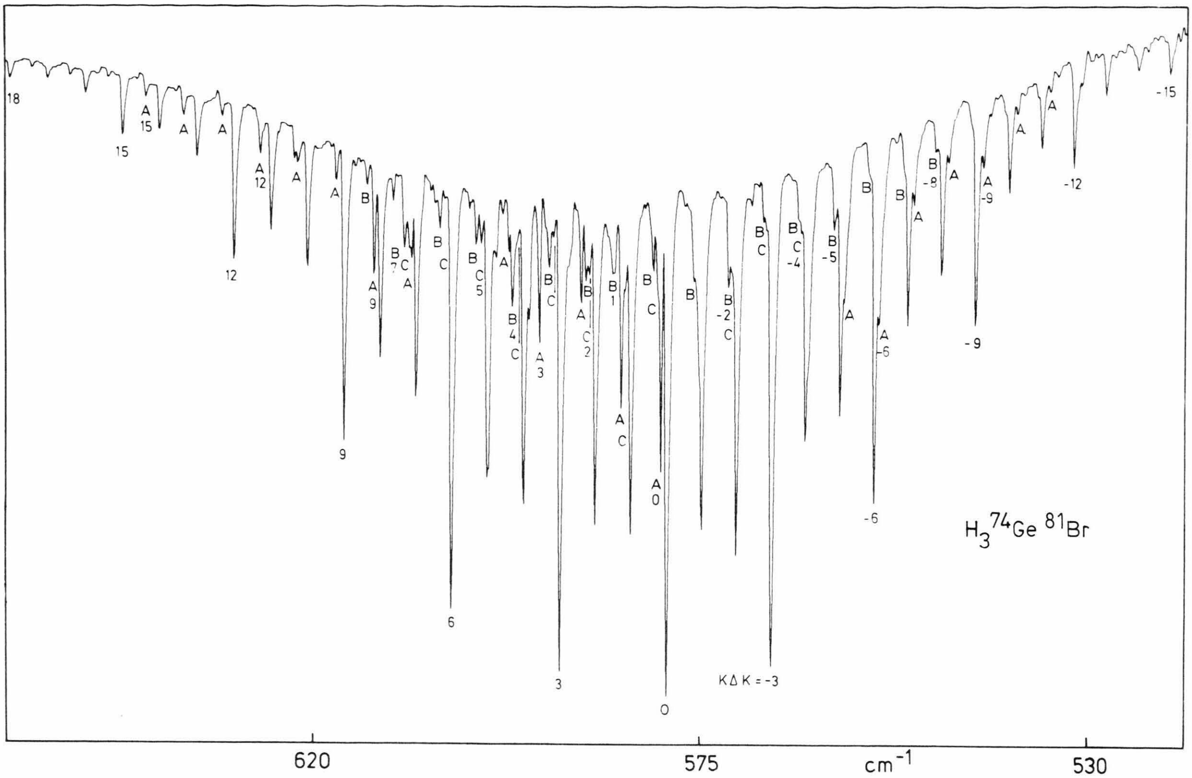

Fig. 3. Survey spectrum of $H_3{}^{74}Ge^{81}Br$ in the ν_6 region, 18.7 cm cell, 19 mbar, resolution 0.24 cm^{-1}. Q branches with double intensity are assigned. A: $(\nu_3+\nu_6)-\nu_6$, B: $2\nu_6^{\pm2}-\nu_6^{\pm1}$, C: $2\nu_6^{0}-\nu_6^{\pm1}$.

the experimental spectrum of (81) and its band contour simulation, hot bands omitted. The contribution of the hot bands is particularly evident from this comparison. The sharpness of the Q branches of the hot band $(\nu_3+\nu_6)-\nu_3$ is due to the Fermi perturbation of the upper state $\nu_3+\nu_6$. The $l(\pm 2, \pm 2)$ interaction which only affects the $k\,l = 1$ level is significant. Possible interactions of ν_6 with $2\,\nu_3$ [2] were searched with particular care. For (79) the $K = 8$ and $k\,l = 9$ levels and for (81) the $K = 7$ and $k\,l = 8$ levels are close for low J while the $(K-1)$ and $(k\,l-1)$ levels respectively come close for high J values ($J' \geqq 70$). From the absence of any significant shifts of those ν_6 lines which should be most affected by a rotational resonance with $2\,\nu_3$ we conclude that any possible interaction must be very weak.

4.4. *The $v_6 = 2$ states*

Transitions to both the $2\,\nu_6^0$ and $2\,\nu_6^{\pm2}$ levels have been observed, but due to the limited amount of available material the intensity of the spectra was quite low. They resemble those of $H_3{}^{74}GeI$ [16], and their evaluation which was mainly aimed to determine x_{66}, g_{66} and A_0 was extended approximately to the level achieved for H_3GeI [16]. A total of 186/134 ^{R}R and ^{P}P lines of $2\,\nu_6^{\pm2}$ and 120/120 peaks due to sharp ^{Q}Q branches and ^{Q}R and ^{Q}P clusters of $2\,\nu_6^0$ have been used to numerically evaluate the parameters listed in Table 5. No interaction of $2\,\nu_6^{\pm2}$ with $2\,\nu_6^0$ has been detected. The agreement of the $v_6 = 2$ parameters with those obtained for the $v_6 = 1$ level is satisfactory, and both the $l = 0$ and $l = \pm 2$ levels are evidently unperturbed.

4.5. *Analysis of ν_1 and ν_4*

The central part of the ν_1/ν_4 band of (81) is illustrated in Fig. 2. ^{Q}Q branches of ν_1 are sharp and well pronounced for $K \geqq 3$. Their sharpness implies a small $(B_1 - B_0)$ value. ^{Q}R and ^{Q}P clusters can be decoded by means of ground state combination differences, but on a whole, ν_1 tends to be buried under

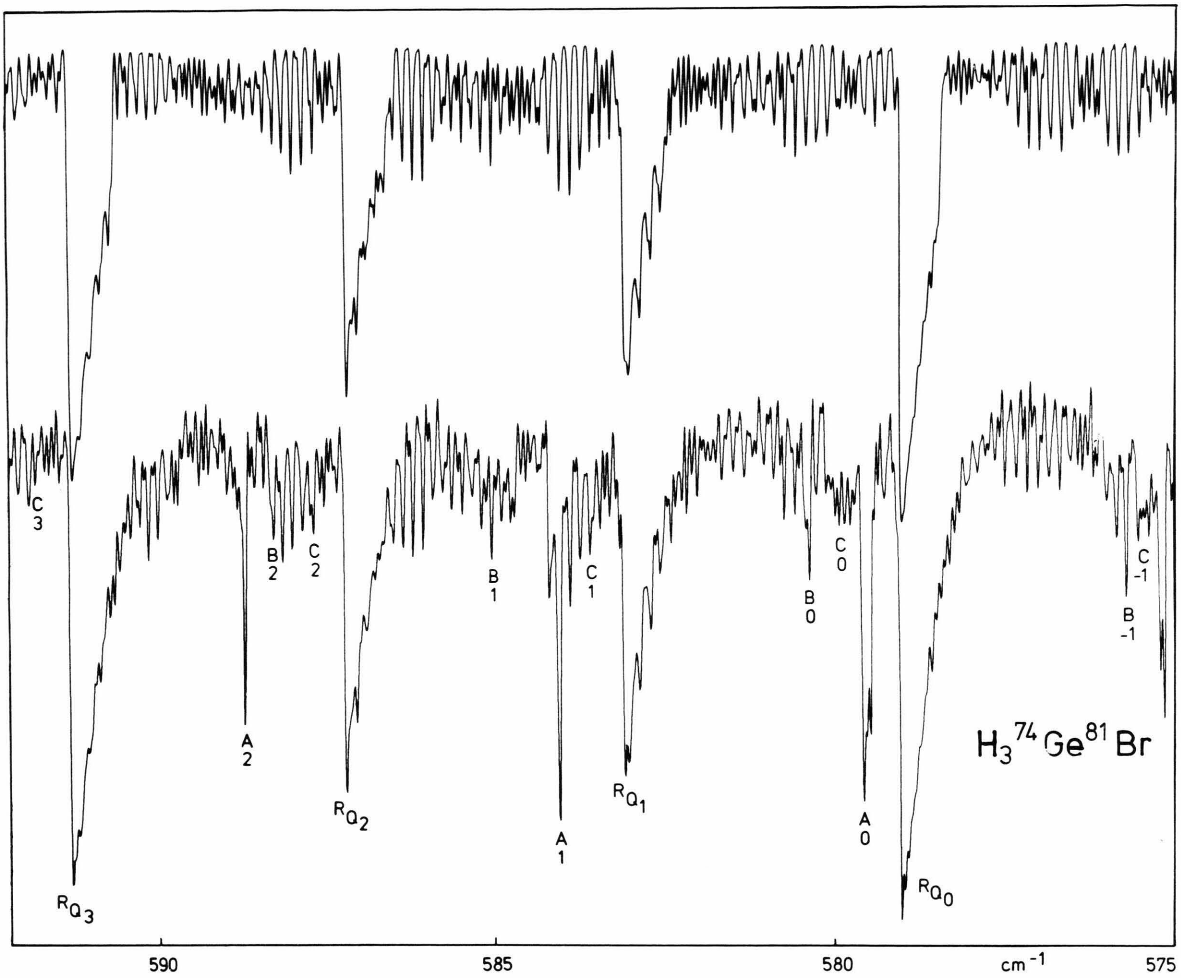

Fig. 4. Detail of the IR spectrum of $H_3{}^{74}Ge^{81}Br$ in the ν_6 region. Upper trace: Simulated spectrum, hot bands omitted. Lower trace: Experimental spectrum, 18.7 cm cell, 19 mbar, resolution 0.04 cm^{-1}. Given assignments are as in Figure 3.

more intensive ν_4 absorptions. In particular, strong overlap of $^QR_3\,(J)$ and $^QR_6\,(J+4)$ lines is found in (81).

The Q branches of ν_4 are reasonably sharp, evenly spaced and show regular, blue-degraded envelopes indicative of a small positive $(B_4 - B_0)$ value. The K assignment is straightfoward from missing lines. Both (79) and (81) do not show any indication of resonance perturbation of ν_4, transition frequencies being unshifted and Q branches regularly shaped. The absence of any resonance affecting ν_4 is somewhat surprising because, at comparable sensitivity, the ν_1, ν_4 rovibrational bands of all silyl and germyl halides so far studied showed evidence for local perturbations. Unperturbed appearance is also noted for $(\nu_3+\nu_4)-\nu_3$ and, as far as visible, for $(2\,\nu_3+\nu_4)-2\,\nu_3$.

The Coriolis x, y resonance is weak and essentially restricted to interactions of the $k\,l=-1$ and -2 levels of ν_4 with $K=2$ and 3 levels of ν_1. A total of 168/362 and 1032/1280 ν_1 and ν_4 data of (79)/(81) respectively were subjected to a least squares fit. The final excited state molecular parameters are set out in Table 6. Refinement of excited state centrifugal distortions was not physically meaningful; the standard deviation σ of the measured transition frequencies is of the order of one tenth of the resolution. The independently determined (79) and (81) parameters are consistent, the (81) data being more precise because of the superior quality of the appropriate spectrum. In particular the substantial amount of lower resolution data for (79) which were used in the refinement curtails the quality of the ν_1/ν_4 parameters for this isotopomer. Consistency of the observed with the computed spectrum, Fig. 2, is apparent except for the features which are due to the hot bands omitted in the simulation. The simulation was performed with a transition moment ratio $M_1 : M_4 = 1.0$, negative intensity perturbation by the Coriolis resonance being clearly favoured. This is in agreement with the force field predictions and analogous to ν_1/ν_4 of H_3SiCl [9]. Lists of observed and calculated transition frequencies and correlation matrices of free parameters have been deposited as supplementary material [20].

Table 5. Molecular parameters of the $v_6 = 1$ and 2 states of $H_3{}^{74}Ge^{79}Br$ and $H_3{}^{74}Ge^{81}Br$ (cm^{-1}) [a].

	$H_3{}^{74}Ge^{79}Br$	$H_3{}^{74}Ge^{81}Br$
$(\nu_6)^0$	577.601 2 (4)	577.541 7 (4)
$(A_6 - A_0) \times 10^2$	1.193 0 (9)	1.192 0 (9)
$(B_6 - B_0) \times 10^4$	− 1.366 5 (15)	− 1.348 2 (17)
$(D_K^6 - D_K^0) \times 10^5$	0.059 (7)	0.067 (5)
$(A\zeta^z)_6$	0.533 08 (4)	0.532 70 (4)
$\eta_{6J} \times 10^6$	1.059 (21)	1.079 (26)
$\eta_{6K} \times 10^5$	1.64 (8)	1.89 (5)
$F_6 \times 10^6$	8.98 (18)	8.32 (15)
No. of fitted lines	1011	1071
$\sigma(J, K) \times 10^3$	5.7	6.0
$l = 0$		
$(2\nu_6)^0$	1154.674 3 (19)	1154.550 6 (17)
$(A_{66} - A_0) \times 10^2$	2.375 (9)	2.381 (7)
$(B_{66} - B_0) \times 10^4$	− 2.708 (5)	− 2.679 (4)
$l = \pm 2$		
$(2\nu_6)^0$	1157.329 8 (16)	1157.253 9 (19)
$(A_{66} - A_0) \times 10^2$	2.131 (5)	2.231 (6)
$(B_{66} - B_0) \times 10^4$	− 2.800 (8)	− 2.811 (11)
$(A\zeta^z)_{66}$	− 1.062 47 (9)	− 1.069 74 (9)
$\eta_{66J} \times 10^6$	− 2.138 fixed	− 2.138 fixed
$\eta_{66K} \times 10^5$	− 3.527 fixed	− 3.527 fixed
No. of fitted lines	288	254
$\sigma(J, K) \times 10^3$	8.8	8.8
x_{66}	0.400 (10)	0.409 (10)
g_{66}	0.663 9 (6)	0.675 8 (6)

[a] Ground state values were adopted for unquoted centrifugal distortion coefficients.

5. Discussion

The present study concludes the rovibrational investigation of the fundamentals of $H_3{}^{74}GeBr$ studied with a resolution of 0.04 cm^{-1} or better. Table 7 quotes rounded excited state molecular parameters for comparison. Surprisingly only a single resonance, the Fermi resonance between ν_5 and $\nu_3 + \nu_6$, has been established. Obviously the large mass of the H_3GeBr molecule tends to suppress significant

Table 6. Molecular parameters of the ν_1, ν_4 excited states of $H_3{}^{74}Ge^{79}Br$ and $H_3{}^{74}Ge^{81}Br$ (cm^{-1}) [a].

	$H_3{}^{74}Ge^{79}Br$	$H_3{}^{74}Ge^{81}Br$ [b]	$H_3{}^{74}Ge^{81}Br$
$(\nu_1)^0$	2115.814 98 (23)	2115.813 37 (16)	2115.813 37 (16)
$(A_1 - A_0) \times 10^2$	− 2.336 4 (5)	− 2.335 2 (4)	− 2.335 2 (4)
$(B_1 - B_0) \times 10^5$	1.753 (11)	1.739 (6)	1.738 (6)
$(\nu_4)^0$	2126.016 52 (13)	2126.016 38 (9)	2126.016 67 (8)
$(A_4 - A_0) \times 10^2$	− 1.667 39 (25)	− 1.665 25 (28)	− 1.667 07 (9)
$(B_4 - B_0) \times 10^5$	5.027 (6)	4.953 (4)	4.953 (4)
$(D_K^4 - D_K^0) \times 10^5$	0 fixed	0.0123 (18)	0 fixed
$(A\zeta^z)_4$	− 0.142 909 (11)	− 0.142 748 (8)	− 0.142 752 (8)
$\eta_{4J} \times 10^7$	− 1.66 (7)	− 1.45 (6)	− 1.42 (6)
$\eta_{4K} \times 10^5$	− 1.323 (17)	− 1.163 (13)	− 1.175 (13)
$F_4 \times 10^7$	− 0.654 (30)	− 0.564 (30)	− 0.593 (31)
$(\sqrt{2} B \Omega_{1,4} \zeta^y_{1,4}) \times 10^3$	− 2.45 (5)	− 2.284 (26)	− 2.280 (26)
No. of fitted data	1200	1642	1642
$\sigma(J, K) \times 10^3$	1.57	1.55	1.56
x_{13}	+ 0.172 (5)	+ 0.171 (2)	
x_{34}	+ 0.453 (4)	+ 0.447 (6)	
$(2x_{34})$	+ 0.884 (6)	+ 0.87 (2)	

[a] Ground state values were adopted for unquoted centrifugal distortion coefficients. [b] $(D_K^4 - D_K^0)$ refined.

Table 7. Rounded molecular parameters for $H_3{}^{74}Ge^{79}Br/H_3{}^{74}Ge^{81}Br$ (cm^{-1}).

	$i = 1$	$i = 2$ [3]	$i = 3$ [2]
$(\nu_i)^0$	2115.815 0/2115.813 4	831.825/831.796	306.585/304.729
$(A_i - A_0) \times 10^2$	− 2.336/− 2.335	1.01/1.00	− 0.2
$(B_i - B_0) \times 10^4$	0.175/0.174	− 1.35/− 1.25	− 2.82/− 2.77
	$i = 4$	$i = 5$ [3]	$i = 6$
(ν_i)	2126.016 5/2126.016 7	872.612/872.601	577.601/577.542
$(A_i - A_0) \times 10^2$	− 1.667/− 1.667	− 1.240/− 1.242	1.193/1.192
$(B_i - B_0) \times 10^4$	0.503/0.495	− 0.13/− 0.14	− 1.367/−1.348
$(A\zeta^z)_i$	− 0.142 91/− 0.142 75	− 0.356 1/− 0.355 9	0.533 1/0.532 7
$\eta_{iJ} \times 10^6$	− 0.17/− 0.14	− 0.9	1.06/1.08
$\eta_{iK} \times 10^5$	− 1.32/− 1.18	− 0.6[a]	1.6/1.9
$F_i \times 10^6$	− 0.065/− 0.059	20	9.0/9.3

$(\sqrt{2}\, B\, \Omega_{1,4}\, \zeta^y_{1,4}) \times 10^3$	− 2.5/− 2.3	$(B\, \Omega_{2,5}\, \zeta^y_{2,5}) \times 10^2$	5.11/5.11 [3]	W_{356}	4.407/4.406 [3]
x_{13}	0.17/0.17	x_{34}	0.45/0.45	x_{66}	0.40/0.41
x_{33}	− 0.77/− 0.76 [2]	x_{36}	− 1.64/− 1.63 [3]	g_{66}	0.664/0.676

[a] Assuming $D^0_K = 2.24 \times 10^5$.

interactions even if appropriate rovibrational levels suited to interact are close. From the data set out in Table 7 possible interactions may be predicted. Furthermore, molecular parameters of H_3GeBr species not investigated in this "pilot" study should be predictable, e.g. by means of the molecular force field.

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[1] For Part XLII see K. Burczyk and H. Bürger, Spectrochim. Acta, in press.
[2] H. Bürger, K. Burczyk, R. Eujen, A. Rahner, and S. Cradock, J. Mol. Spectrosc. **97,** 266 (1983).
[3] F. Lattanzi, C. di Lauro, H. Bürger, R. Eujen, P. Schulz, and S. Cradock, Mol. Phys. **51,** 81 (1984).
[4] D. E. Freeman, K. H. Rhee, and M. K. Wilson, J. Chem. Phys. **39,** 2908 (1963).
[5] K. H. Rhee and M. K. Wilson, J. Chem. Phys. **43,** 333 (1965).
[6] F. Lattanzi, C. di Lauro, H. Bürger, R. Eujen, and S. Cradock, J. Mol. Spectrosc. in press (1984).
[7] A. R. H. Cole, "Tables of Wavenumbers for the Calibration of Infrared Spectrometers", 2nd ed., Pergamon, Oxford 1977.
[8] J. Kauppinen, K. Jolma, and V. M. Horneman, Appl. Optics **21,** 3332 (1982).
[9] H. Bürger and P. Schulz, J. Mol. Spectrosc. **103,** 160 (1983).
[10] C. di Lauro and I. M. Mills, J. Mol. Spectrosc. **21,** 386 (1966).
[11] G. J. Cartwright and I. M. Mills, J. Mol. Spectrosc. **34,** 415 (1970).
[12] C. Betrencourt-Stirnemann, G. Graner, D. E. Jennings, and W. E. Blass, J. Mol. Spectrosc. **69,** 179 (1978).
[13] S. Cradock, D. C. McKean, and W. M. MacKenzie, J. Mol. Struct. **74,** 265 (1981).
[14] L. C. Krisher and S. N. Wolf, J. Chem. Phys. **58,** 396 (1973).
[15] S. N. Wolf and L. C. Krisher, J. Chem. Phys. **56,** 1040 (1972).
[16] H. Bürger, R. Eujen, A. Rahner, P. Schulz, J. E. Drake, and S. Cradock, Z. Naturforsch. **38 a,** 740 (1983).
[17] H. Bürger, G. Schippel, A. Ruoff, H. Essig, and S. Cradock, J. Mol. Spectrosc. in press (1984).
[18] M. R. Aliev and J. K. G. Watson, J. Mol. Spectrosc. **75,** 150 (1979).
[19] H. Matsuura and H. Murata, J. Mol. Spectrosc. **100,** 449 (1983).
[20] Lists of observed and calculated transition frequencies and the correlation matrices may be obtained from Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen, West Germany, on submission of the name of the authors, the literature reference and the registry Nr. 10009.