Vibrational Spectra and Force Constants of Symmetric Tops, XLIII [1] Fourier Transform Infrared Spectra of Monoisotopic H$_3$GeBr Species in the $v_1/\nu_4$ and $v_6$ Region

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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 $v_1/\nu_4$ region near 2100 cm$^{-1}$ with a resolution of 0.015 cm$^{-1}$ and in the $v_6$ and 2 $\nu_6$ regions near 800 and 1150 cm$^{-1}$ with a resolution of 0.04 cm$^{-1}$. Rotational analyses based on $\sim 1500$, $\sim 1100$ and $\sim 300$ data of $v_1/\nu_4$, $v_6$ 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. $v_1$, 2115.815 0(2)/2115.813 4(2) cm$^{-1}$, and $\nu_4$, 2126.016 5(4)/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, $\nu_4\approx-0.021(1)$, $577.601(2)/577.541(7)$ cm$^{-1}$, and $v_6$ are affected by $/ (\pm 2, \pm 2)$ resonance. Furthermore, the hot bands ($v_1 + v_3$) - $v_3$, ($v_3 + \nu_4$) - $v_3$, ($v_1 + v_6$) - $v_3$, 2 $v_6$ - $v_6$ and 2 $\nu_6$ - $\nu_6$ have been detected and analyzed.

1. Introduction

Recently we have reported on the rovibrational investigation of the fundamental $v_3$ (a$_1$ $\nu$ GeBr) near 300 cm$^{-1}$ [2] and of the a$_1$/e/E triade $v_2/v_3/\nu_6$ of H$_2$GeBr 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$^{80}$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 $v_1$ to $v_3$ while $K$ structure of the perpendicular fundamentals $\nu_4$ to $v_8$ was indicated.

Continuation of the rovibrational study of H$_3$GeBr seemed desirable for several reasons. First, only a complete set of vibration-rotation interaction parameters allows the equilibrium structure to be computed. Second, such a complete study promised to supply the full set of ground state centric constants, the centrifugal distortions $D_{ij}^{k}$, $D_{jk}^{i}$ 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 $v_2/v_3/\nu_6$ and $v_4$ of H$_2$GeBr [3] and play an important role by the GeH stretching fundamentals $v_1$ and $\nu_4$ of H$_2$GeCl [6].

In the following contribution we deal with the fundamentals $v_1/\nu_4$ near 2100 and $\nu_6$ 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 $v_6$ with 2 $\nu_6$ cannot be ruled out, the GeH$_3$ stretching vibrations are expected to be weakly coupled by Coriolis $x,y$ resonance, $B_{\nu_4}\approx0.002$ cm$^{-1}$ being predicted from the harmonic force field. In addition, $v_1/\nu_4$ may well interact with several vibrational combinations in the 2100 cm$^{-1}$ region. While the $v_6$ 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 $v_1$ and $\nu_4$.

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2. Experimental

Monoisotopic H$_3$GeBr 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$_2$O and CO$_2$ lines [8], frequency accuracy $3 \times 10^6$ cm$^{-1}$ for $v_6$ and $6 \times 10^5$ cm$^{-1}$ for the $2v_6$ and $v_1/v_4$ regions. The $v_1/v_4$ 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 $2 \times 10^6$ cm$^{-1}$ for $v_5$ and $1 \times 10^5$ cm$^{-1}$ for $v_5'$. 3. Vibrational analysis

The vibrational transitions $v_1$, $v_4$ and $v_6$ 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:

$$
(v_1 + v_3) - v_3,
$$
$$
(v_3 + v_4) - v_3,
$$
$$
(v_3 + v_6) - v_3 23\%,
$$
$$
(v_1 + v_6) - v_6,
$$
$$
2v_6 - v_1^{2},
$$
$$
\Sigma (v_4 + v_6) - v_6 12\%,
$$
$$
2v_1 - v_6^{2} 6\%.
$$

$p = 1$ and $p = -1$ intensity alternation of $K \Delta K$ subbands, $p = 0, \pm 1, \pm 2, \ldots$ is expected to appear for the hot bands $2v_6 - v_1^{2}$ and $2v_1 - v_6^{2}$ respectively. Analogous behaviour is expected for the two components of $(v_4 + v_6) - v_6$ which however have not been observed. Additional information concerning the $(2v_6 - v_1)$ hot bands comes from the overtones $2v_1^{2}$ and $2v_1'2$ which have been observed in the spectra. Thus it is confirmed that the Q branches of $2v_1 - v_6^{2}$ are partly hidden by Q branches of $v_6$. Unresolved Q branches of the hot bands $(v_1 + v_3) - v_3$, $(v_3 + v_4) - v_3$ and $(v_3 + v_6) - v_6$ have been identified, rotational $\Delta J = \pm 1$ lines being buried under the cold bands. Indication was found for Q branches of $(v_1 + 2v_3) - 2v_3$ and $(2v_3 + v_4) - 2v_1$. The Q branch edges corresponding to first Q branch lines[$^{0}Q_K(K),^{R}Q_K(K),^{P}Q_K(K + 1)$] are listed in Tables 1 to 3. While the hot bands $(v_1 + n v_3) - n v_3$ and $(v_3 + v_4) - v_3$ are blue-shifted from the cold bands and follow regular patterns, Figs. 1 and 2, the hot band $(v_3 + v_6) - v_3$ is perturbed due to Fermi resonance between $v_3 + v_6$ and $v_5$, Figure 3 [3]. Therefore a polynomial analysis of the Q branch positions of $(v_3 + v_6) - v_3$ 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 $(v_1 + v_3) - v_3$, Table 1, and $(v_3 + v_4) - v_3$ and $(2v_3 + v_4) - 2v_3$, 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 $v_1 + v_3$ and $v_3 + v_4$ are not significantly perturbed. No indication was found for hot bands with $v_6$ as lower level.

4. Rotational analysis

4.1. Theory

The $v_1$, $v_4$ systems coupled by Coriolis $x$, $y$ resonance with additional essential $I(\pm 2, \pm 2)$ resonance within $v_1(t = 4)$ were treated as described previously [9] with the conventions of [10] and [11]. $q_i^{(4)} = 4F_i$. Conventional diagonal matrix elements and the following off-diagonal terms were adopted:

$$
\langle r_1 = 1, r_4 = 0; J, k | H | r_1 = 0, r_4 = 1, l_4 = \pm 1; J, k \pm 1 \rangle = \pm 2^{1/2} B \Omega_{1,4,4} \zeta_{K} \zeta_{4} |J(J + 1) - k(k \pm 1)|^{1/2}
$$

$$
\Omega_{1,4,4} = \frac{1}{2} \left[ (v_1/v_4)^{1/2} + (v_4/v_1)^{1/2} \right]
$$

$$
\langle r_1 = 1, l_4 = 0, J, k + 1 | H | r_1 = 1, l_4 = -1, J, k - 1 \rangle = -2F_{r}J(J + 1) - k(k + 1)]^{1/2}
$$

$$
\Omega_{1,4,4} = \frac{1}{2} \left[ (v_1/v_4)^{1/2} + (v_4/v_1)^{1/2} \right]
$$

<table>
<thead>
<tr>
<th>$K$</th>
<th>$H_{3}^{74}$Ge$^{79}$Br</th>
<th>$H_{3}^{74}$Ge$^{81}$Br</th>
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<tr>
<td>3</td>
<td>2115.779 6</td>
<td>2115.777 2</td>
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<tr>
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<td>4.843 7</td>
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<td>3.160 0</td>
</tr>
<tr>
<td>10</td>
<td>2.618 5</td>
<td>2.618 5</td>
</tr>
</tbody>
</table>
Table 2. Q branch edges of the hot bands $(v_3 + v_4) - v_3$ and $(2v_3 + v_4) - 2v_3$ of $^7\text{Ge}^{79}\text{Br}$ and $^7\text{Ge}^{81}\text{Br}$ (cm$^{-1}$).

<table>
<thead>
<tr>
<th>$K \Delta K$</th>
<th>$^7\text{Ge}^{79}\text{Br}$</th>
<th>$^7\text{Ge}^{81}\text{Br}$</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>$(v_3 + v_4) - v_3$</td>
<td>$(v_3 + v_4) - v_3$</td>
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<td>74.134 1</td>
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<tr>
<td>-13</td>
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<td>62.748 9</td>
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</tbody>
</table>

The fundamental $v_6$ 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 $D_3\text{GeBr}$ and $HD_2\text{GeBr}$ [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 $(A\zeta_6)_{66} = -2(A\zeta_6)$ and from $v_6^{\pm 1}$, $2v_6^{\pm 2}$ and $(2v_6^{\pm 2} - v_6^{\pm 1})$ according to the procedure described previously [16, 17].
Table 3. Q branch edges of the hot bands \((v_3 + v_6) - v_3, 2v_6^\perp - v_6^\perp\) and \(2v_6^\perp - v_6^\perp\) (cm\(^{-1}\)) of \(\text{H}_3\text{Ge}^{79}\text{Br}\) and \(\text{H}_3\text{Ge}^{81}\text{Br}\).

<table>
<thead>
<tr>
<th>(K,\Delta K)</th>
<th>((v_3 + v_6) - v_3)</th>
<th>(2v_6^\perp - v_6^\perp)</th>
<th>(2v_6^\perp - v_6^\perp)</th>
</tr>
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<tbody>
<tr>
<td>(\text{H}_3\text{Ge}^{79}\text{Br})</td>
<td>(\text{H}_3\text{Ge}^{81}\text{Br})</td>
<td>(\text{H}_3\text{Ge}^{79}\text{Br})</td>
<td>(\text{H}_3\text{Ge}^{81}\text{Br})</td>
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<tr>
<td>(v_{\text{obs}})</td>
<td>(\Delta)</td>
<td>(v_{\text{obs}})</td>
<td>(\Delta)</td>
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<tr>
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<tr>
<td>6</td>
<td>-</td>
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</table>

Coefficients of polynomial fit \(a_0 + a_1 (K\,\Delta K) + a_2 (K\,\Delta K)^2\):

\[
a_0 = 579.666 (17) \\
a_1 = 4.120 (9) \\
a_2 = 0.64 (4) \\
\sigma(K) \times 10^3 = 20 (18) \\
v_0 = 577.089 (5) \\
\sigma(v_0) = 0.398 (6) \\
\sigma(v_6) = 0.655 (5)
\]

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 \(D_J\) and \(D_{JK}\) was not physically meaningful. The ultimate fit parameters are set out in Table 5. Figure 4 illustrates a section of...
Infrared Spectra of H$_3$GeBr (v$_1$ + v$_3$) and some rotational lines.

Table 4. Ground state molecular parameters of H$_3^{74}$Ge$^{81}$Br/H$_3^{74}$Ge$^{81}$Br (cm$^{-1}$).

| Parameter | 2.632 5 [13] | 2.631 7/2.631 4$^a$ | 2.632 9/2.633 0$^c$ | 2.632 5/2.632 5 | 7.925 02/7.830 22 [13] | 7.924 73 (18)/7.830 26 (16)$^d$ | 7.925 02/7.830 22 | 2.13/2.00 [2] | 2.08/2.03$^b$ | 2.05 (4)/2.046 (24)$^d$ | 2.08/2.03 | 3.3/3.3 [15] | 3.62/3.54$^b$ | 3.9 (7)/3.9 (4)$^d$ | 3.62/3.54 | 2.24/2.24$^b$ | 2.26/2.26$^c$ | 2.26/2.26$^d$
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<td>$A_0$</td>
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<td></td>
<td></td>
<td>$B_0 \times 10^3$</td>
<td>$D_0 \times 10^7$</td>
<td>$D_0 \times 10^7$</td>
<td>$D_0 \times 10^7$</td>
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<td>$K$</td>
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<tr>
<td>$B_0 \times 10^3$</td>
<td>7.925 02/7.830 22 [13]</td>
<td>7.924 73 (18)/7.830 26 (16)$^d$</td>
<td>7.925 02/7.830 22</td>
<td>2.05 (4)/2.046 (24)$^d$</td>
<td>2.08/2.03</td>
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</tr>
</tbody>
</table>
| $D_0 \times 10^7$ | 3.3/3.3 [15] | 3.62/3.54$^b$ | 3.9 (7)/3.9 (4)$^d$ | 3.62/3.54 | 2.24/2.24$^b$ | 2.26/2.26$^c$ | 2.26/2.26$^d$

$^a$ From (A$_Q$)$_{10} = -2$ (A$_Q$)$_{12}$.
$^b$ From harmonic force field [3].
$^c$ From v$_{10}^{-1}$, 2 v$_{10}^{-2}$ and (2 v$_{10}^{-1}$ - v$_{10}^{-1}$).
$^d$ From ground state combination differences, this study.
$^e$ From $\eta$ sum rule, see text.
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 \((v_3 + v_6) - v_3\) is due to the Fermi perturbation of the upper state \(v_3 + v_6\). The \((\pm 2, \pm 2)\) interaction which only affects the \(k l = 1\) level is significant. Possible interactions of \(v_6\) with \(2v_3\) \([2]\) 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 \((J' \approx 70)\). From the absence of any significant shifts of those \(v_6\) lines which should be most affected by a rotational resonance with \(2v_3\) we conclude that any possible interaction must be very weak.

4.4. The \(v_6 = 2\) states

Transitions to both the \(2v_6^2\) and \(2v_6^2\) 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 \(H_3^{34}Ge\) \([16]\), and their evaluation which was mainly aimed to determine \(x_{66}, \theta_{66}\), and \(A_0\) was extended approximately to the level achieved for \(H_3Ge\) \([16]\). A total of 186/134 \(R\) and \(P\) lines of \(2v_6^2\) and 120/120 peaks due to sharp \(Q\) branches and \(Q\) and \(P\) clusters of \(2v_6^2\) have been used to numerically evaluate the parameters listed in Table 5. No interaction of \(2v_6^2\) with \(2v_6^2\) 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 \(v_1\) and \(v_4\)

The central part of the \(v_1/v_4\) band of (81) is illustrated in Fig. 2. \(Q\) branches of \(v_1\) are sharp and well pronounced for \(K \geq 3\). Their sharpness implies a small \((B_1 - B_0)\) value. \(Q\) and \(P\) clusters can be decoded by means of ground state combination differences, but on a whole, \(v_1\) tends to be buried under
more intensive $v_4$ absorptions. In particular, strong overlap of $Q_{R_3}(J)$ and $Q_{R_6}(J+4)$ lines is found in (81).

The Q branches of $v_4$ 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 straightforward from missing lines. Both (79) and (81) do not show any indication of resonance perturbation of $v_4$, transition frequencies being unshifted and Q branches regularly shaped. The absence of any resonance affecting $v_4$ is somewhat surprising because, at comparable sensitivity, the $v_1$, $v_4$ rovibrational bands of all silyl and germyl halides so far studied showed evidence for local perturbations. Unperturbed appearance is also noted for $(v_3 + v_4) - v_3$ and, as far as visible, for $(2v_3 + v_4) - 2v_3$.

The Coriolis $x$, $y$ resonance is weak and essentially restricted to interactions of the $kl = -1$ and $-2$ levels of $v_4$ with $K = 2$ and 3 levels of $v_1$. A total of 168/362 and 1032/1280 $v_1$ and $v_4$ 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 $\sigma$ 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 \(v_1/v_4\) 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 \(v_1/v_4\) of H\(_3\)SiCl [9]. Lists of observed and calculated transition frequencies and correlation matrices of free parameters have been deposited as supplementary material [20].

5. Discussion

The present study concludes the rovibrational investigation of the fundamentals of H\(_3\)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 \(v_5\) and \(v_3 + v_6\), has been established. Obviously the large mass of the H\(_3\)GeBr molecule tends to suppress significant

\[\text{Table 5. Molecular parameters of the } \nu_6 = 1 \text{ and } 2 \text{ states of } H_3^{74}Ge^{79}Br \text{ and } H_3^{74}Ge^{81}Br \text{ (cm}^{-1})^d.\]

\[
\begin{array}{cccc}
\nu_6^0 & H_3^{74}Ge^{79}Br & H_3^{74}Ge^{81}Br \\
(A_6 - A_0) \times 10^2 & 577.6012(4) & 577.5417 (4) \\
(B_6 - B_0) \times 10^4 & -1.3665(15) & -1.3382(17) \\
(D^e_6 - D^e_0) \times 10^5 & 0.0597(7) & 0.067(5) \\
(A_C - A_0) & 1.0592(1) & 1.079(26) \\
\eta_6 A_{6} A_{6} & 1.64(8) & 1.89(5) \\
F_6 \times 10^5 & 8.98(18) & 8.32(15) \\
\text{No. of fitted lines} & 1011 & 1071 \\
\sigma(J, K) \times 10^3 & 5.7 & 6.0 \\
\end{array}
\]

\[\text{Table 6. Molecular parameters of the } \nu_1, \nu_4 \text{ excited states of } H_3^{74}Ge^{79}Br \text{ and } H_3^{74}Ge^{81}Br \text{ (cm}^{-1})^a.\]

\[
\begin{array}{cccc}
\nu_1^0 & H_3^{74}Ge^{79}Br & H_3^{74}Ge^{81}Br^b & H_3^{74}Ge^{81}Br \\
(A_1 - A_0) \times 10^2 & 2115.81498(23) & 2115.81337(16) & 2115.81337(16) \\
(B_1 - B_0) \times 10^5 & -2.3384(5) & -2.3352(4) & -2.3352(4) \\
(\nu_1^0)^0 & 2126.01652(13) & 2126.01638(9) & 2126.01667(8) \\
(A_4 - A_0) \times 10^2 & -1.66739(25) & -1.66525(28) & -1.66707(9) \\
(B_4 - B_0) \times 10^5 & 5.027(6) & 4.953(4) & 4.953(4) \\
(D^e_1 - D^e_0) \times 10^5 & 1.753(11) & 1.739(6) & 1.738(6) \\
(A_C - A_0) & 2.3057(9) & 2.284(26) & 2.280(26) \\
\eta_1 A_{4} A_{4} & 0 \text{ fixed} & 0 \text{ fixed} & 0 \text{ fixed} \\
\eta_1 A_{4} & 0.142909(11) & 0.142748(8) & 0.142752(8) \\
F_1 \times 10^5 & -1.323(17) & -1.163(13) & -1.175(13) \\
(\frac{1}{2} B \Omega \Omega A_{1} A_{1} A_{1}) \times 10^3 & -2.45(5) & -2.284(26) & -2.280(26) \\
\text{No. of fitted data} & 1200 & 1642 & 1642 \\
\sigma(J, K) \times 10^3 & 1.57 & 1.55 & 1.56 \\
\end{array}
\]

\[a \text{ Ground state values were adopted for unquoted centrifugal distortion coefficients.} \]

\[b \text{ (} D^e_1 - D^e_0 \text{) refined.} \]
Table 7. Rounded molecular parameters for $\text{H}_3\text{Ge}^{74}\text{Br}/\text{H}_3\text{Ge}^{81}\text{Br}$ (cm$^{-1}$).

<table>
<thead>
<tr>
<th>$i$</th>
<th>$(v)$</th>
<th>$(A_i - A_0) \times 10^2$</th>
<th>$(B_i - B_0) \times 10^4$</th>
<th>$(v_v)$</th>
<th>$(A_i - A_0) \times 10^2$</th>
<th>$(B_i - B_0) \times 10^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2115.815 0/2115.813 4</td>
<td>- 2.336/- 2.335</td>
<td>0.175/0.174</td>
<td>2126.016 5/2126.016 7</td>
<td>- 1.667/- 1.667</td>
<td>0.503/0.495</td>
</tr>
<tr>
<td>2</td>
<td>831.825/831.796</td>
<td>- 1.35/- 1.25</td>
<td>- 0.13/- 0.14</td>
<td>872.612/872.601</td>
<td>- 1.240/- 1.242</td>
<td>- 0.356 1/- 0.355 9</td>
</tr>
<tr>
<td>3</td>
<td>306.585/304.729</td>
<td>- 2.82/- 2.77</td>
<td>- 0.2</td>
<td>0.353 1/0.532 7</td>
<td>1.193/1.192</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>577.601/577.542</td>
<td>1.367/- 1.348</td>
<td>- 0.13/- 0.14</td>
<td>1.6/1.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>0.2</td>
<td>1.06/1.08</td>
<td>1.367/-1.348</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.9/0.93</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$(\Omega_{\alpha} \zeta_{\alpha} \chi_{\alpha}) \times 10^3$

- $x_{13}$ : 0.17/0.17
- $x_{34}$ : 0.45/0.45
- $x_{33}$ : - 0.77/- 0.76 [2]
- $x_{36}$ : - 1.64/- 1.63 [3]
- $x_{66}$ : 0.40/0.41
- $g_{66}$ : 0.664/0.676

Acknowledgement

We wish to express our gratitude to Professor M. Quack for recording spectra with the BOMEM instrument. The Deutsche Forschungsgemeinschaft is thanked for financial support through the Sonderforschungsbereich 42. Support by the Fonds der Chemie is gratefully acknowledged.

[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.