Vibrational Spectra and Force Constants of Symmetric Tops, XLVII. Rovibrational Spectra of Three Monoisotopic H_3GeCl Species in the ν_6 Region

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Fourier transform spectra of the monoisotopic species $H_3{}^{70}Ge^{35}Cl$ and $H_3{}^{74}Ge^{37}Cl$ have been recorded in the ν_6 region near 600 cm^{-1} with a resolution of 0.04 cm^{-1}. Rotational analyses based on ~ 700 data for each isotopomer have been performed, and the excited state parameters ν_6^0, A_6, B_6, $A\zeta_6$, η_{6J}, η_{6K}, D_K^6 and F_6 have been determined. The previously reported analysis of ν_6 data of $H_3{}^{74}Ge^{35}Cl$ has been repeated employing improved ground state constants, and a r.m.s. deviation of $\sim 4 \times 10^{-3}$ cm^{-1} has been achieved for the three different isotopic combinations, which show fully consistent excited state parameters.

1. Introduction

In a recent contribution from our laboratories (for part XLVI of this series cf. [1]) we have reported on the infrared spectrum recorded with a resolution of 0.04 cm^{-1} of $H_3{}^{74}Ge^{35}Cl$ (abbreviated (7435) in the following) near 600 cm^{-1} and the rovibrational analysis of the ν_6 fundamental [2]. The investigation of the ν_1/ν_4 fundamental of (7435) has revealed that the combination level $\nu_5^{\mp 1} + 2\nu_6^{\pm 2}$ interacts with ν_4 by Fermi resonance, $W_{4566} = 0.513\,(7)$ cm^{-1} [3]. The analysis of the ν_1/ν_4 vibrational levels of other isotopic combinations such as $H_3{}^{70}Ge^{35}Cl$ (7035) and $H_3{}^{74}Ge^{37}Cl$ (7437) in progress now therefore requires secure information concerning the ν_6 fundamental of the respective species. We have therefore initiated a complementary study of the ν_6 band of (7035) and (7437) and report in the following briefly on the results of the rovibrational analysis. Since the ν_6 analysis of (7435) was undertaken, the ground state constants of (7435) have been improved tremendously by means of ground state combination differences obtained from nearly Doppler-limited spectra and the observation of perturbation-allowed transitions [4]. Furthermore, it has been possible to increase the relative accuracy of the line position measurements of the previously recorded spectra by means of a peak-finder routine (kindly supplied by I. M. Mills and P. J. Turner). For these two reasons repeating of the reduction of the previously reported data promised improvement of the $v_6 = 1$ state parameters and better consistency with (7035) and (7437).

2. Experimental

The different H_3GeCl species were prepared as described previously [2]. Isotopic purities were: ^{70}Ge, 97.1%; ^{74}Ge, 98.9%; ^{35}Cl, 99.1%, ^{37}Cl, 98.2%. Fourier Transform spectra were recorded with a resolution of 0.04 cm^{-1} and calibrated with CO_2 [5] and N_2O lines [6]; frequency accuracy of peak-finder evaluated lines $< 5 \times 10^{-3}$ cm^{-1}. For further details see Ref. [2].

3. Rotational Analysis

Experimental line positions were fitted to upper state parameters as given by

$$E(v, l, J, k) = (A_v - B_v)\,k^2 + B_v\,J(J+1) - D_J^v\,J^2(J+1)^2 - D_{JK}^v\,J(J+1)\,k^2 - D_K^v\,k^4 - [2A\zeta_v - \eta_{vJ}\,J(J+1) - \eta_{vK}\,k^2]\,k\,l \qquad (1)$$

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Table 1. Molecular parameters of H_3GeCl for the ground and the $v_6 = 1$ excited state (cm^{-1})

	$H_3{}^{70}Ge^{35}Cl$	$H_3{}^{74}Ge^{35}Cl$	$H_3{}^{74}Ge^{37}Cl$
A_0	2.632453 [a]	2.632453 [a]	2.632453
B_0	0.146826	0.14454622	0.13935058
$D_J^0 \times 10^8$	6.60	6.416	5.976
$D_{JK}^0 \times 10^6$	1.11	1.085	1.015
$D_K^0 \times 10^5$	2.144 [a]	2.144	2.144 [a]
ν_6^0	602.69032 (28)	602.13356 (33)	601.78190 (30)
$(A_6 - A_0) \times 10^2$	1.1271 (6)	1.1236 (6)	1.1189 (8)
$(B_6 - B_0) \times 10^4$	− 2.5857 (14)	− 2.5473 (24)	− 2.4445 (30)
$(D_K^6 - D_K^0) \times 10^5$	0.0802 (25)	0.0836 (22)	0.074 (4)
$(A\zeta)_6$	0.557618 (22)	0.558914 (24)	0.556290 (28)
$\eta_{6J} \times 10^6$	2.358 (19)	2.479 (26)	2.42 (4)
$\eta_{6K} \times 10^5$	1.633 (25)	1.640 (25)	1.60 (4)
$F_6 \times 10^5$	− 2.176 (17)	− 2.232 (31)	− 2.05 (7)
No. of fitted lines	696	591	701
$\sigma \times 10^3$	3.71	3.73	4.10

[a] Constrained.

for a fixed ground state and employing a computer program [7]. The essential $\Delta l = \Delta k = \pm 2$ resonance was treated in the usual way with the sign conventions of Ref. [8], $F_6 = \frac{1}{4} q_6^{(+)}$. The J dependent ground state parameters up to quartic terms, Table 1, of (7435) and (7437) have been determined by a fit of ground state combination differences measured in FT spectra [4] which are more than one order of magnitude more precise than those on which the present analysis is based. For (7035), the adopted B_0 value is from Ref. [9], while D_J^0 and D_{JK}^0 are extrapolated from those of (7435) and (7437) by means of the relation predicted from the harmonic molecular force field [3]. A unique A_0 value which has been obtained from perturbation-allowed transitions in (7437) [4] was adopted, and similarly the D_K^0 values of the three different species were constrained to the value of (7435). The latter was obtained according to Aliev and Watson [10] from data of the present analysis and of Ref. [3] and [4].

A total of ca. 700 mostly unblended transition frequencies were included in the fit for each species, and many more lines which turned out to be blended were rejected. Transitions ranged to K'' and J'' values up to 18/82, 18/60 and 15/52 for (7035), (7435) and (7437), respectively. The observation made for (7435) [2] that only the eight refined parameters listed in Table 1, as determined from the experimental data, are physically meaningful, has been confirmed for (7035) and (7437). The greater accuracy of the frequency measurements in this study is reflected by the smaller σ values, $\sim 4 \times 10^{-3}$ cm^{-1}, compared to the previously reported 7.7×10^{-3} cm^{-1}. We note, however, that owing to the previous larger number (1667) of transition frequencies, the standard deviations of the refined parameters are very similar. We confirmed that, with the present ground state, the previous refined data yield excited state parameters for (7435) which do not differ significantly from those quoted in Table 1.

The excited state parameters for the different species are consistent. While the changes of the typical J-dependent parameters B_6 and F_6 are significant and correspond to those of B_0, the changes of η_{6J} are smaller than three standard deviations. The K^n-dependent quantities ($n = 0-4$) are correlated, and small changes may well be due to a slightly different composition of the refined data. The isotopic shifts of ν_0 with respect to (7435), + 0.557 for (7035) and − 0.352 cm^{-1} for (7437), may be compared with those computed from the harmonic force field [4], + 0.566 and − 0.352 cm^{-1} respectively.

4. Hot bands

The ν_6 band is accompanied by hot bands, of which $(\nu_3 + \nu_6) - \nu_3$ (A), $2\nu_6^{\pm 2} - \nu_6^{\pm 1}$ (B) and $2\nu_6^0 - \nu_6^{\pm 1}$ (C) are strongest with predicted intensities at 298 K relative to ν_6 of ~ 13, ~ 11 and ~ 5%, respectively. Owing to the density of our spectra, only Q branches of these hot bands were discernible, and in order to improve the visibility of these Q branches, we have used, as previously described [2], spectra

Table 2. Coefficients of polynomial fit $\nu_K = a + b(K\Delta K) + c(K\Delta K)^2 + d(K\Delta K)^3$ to Q_K peak maxima (cm^{-1}) for ν_6 and hot bands $(\nu_3 + \nu_6) - \nu_3$ (*A*) and $2\,\nu_6^{\pm 2} - \nu_6^{\pm 1}$ (*B*) for H_3GeCl.

		a	*b*	$c \times 10^2$	$d \times 10^5$	$\sigma \times 10^3$
(7035)	ν_6	603.898 (49)	3.8596 (38)	1.042 (36)	–	102
		603.879 (10)	3.8792 (12)	1.074 (8)	– 8.0 (8)	21
	A	602.303 (37)	3.8851 (32)	1.072 (35)	–	69
		602.298 (17)	3.9015 (24)	1.073 (16)	– 11.1 (19)	31
	B	604.687 (30)	3.9084 (53)	0.986 (54)	–	44
(7435)	ν_6	603.383 (20)	3.8694 (19)	1.081 (20)	–	37
		603.384 (5)	3.8789 (7)	1.081 (5)	– 6.5 (5)	8
	A	601.773 (18)	3.8917 (21)	1.092 (24)	–	18
		601.774 (5)	3.8997 (8)	1.079 (7)	– 9.8 (9)	5
	B	604.114 (23)	3.9034 (47)	0.862 (59)	–	37
(7437)	ν_6	602.989 (36)	3.8824 (29)	1.059 (31)	–	69
		602.975 (12)	3.8971 (16)	1.078 (11)	– 8.1 (11)	23
	A	601.451 (37)	3.9039 (35)	1.085 (37)	–	69
		601.450 (14)	3.9196 (19)	1.090 (14)	– 11.0 (15)	25
	B	603.766 (27)	3.9278 (46)	1.003 (46)	–	45

Derived parameters (cm^{-1})[a]

	x_{36}	$x_{66} + g_{66}$
(7035)	– 1.576 (17)	0.954 (15)
(7435)	– 1.608 (6)	0.924 (12)
(7437)	– 1.518 (17)	0.956 (12)

[a] From fit of measured *Q* branch shifts.

with a sufficiently low resolution to suppress rotational $\Delta J = \pm 1$ structure, 0.5, 0.24 and 0.5 cm^{-1} for (7035), (7435) and (7437), respectively, for the assignment and evaluation of the hot band *Q* branches. As was mentioned previously and illustrated in Ref. [2] in Fig. 1, only *Q* branches of (*A*) and (*B*) were detectable, while (*C*) is buried under the strong *Q* branches of ν_6.

The positions of the peak maxima as evaluated by the peakfinder routine were fitted to the polynomial

$$\nu_K = a + b(K\Delta K) + c(K\Delta K)^2 + d(K\Delta K)^3 \quad (2)$$

to yield the coefficients set out in Table 2.

It should be pointed out that the peak maxima differ systematically from subband origins, and therefore only the anharmonic shifts x_{36} and $x_{66} + g_{66}$ rather than molecular quantities related to the hot bands have been derived by comparison. The results quoted for (7435) are in full agreement with those quoted in Table 2 of Ref. [2], though a slightly higher accuracy has been achieved in the present study. Lists with observed and calculated transition frequencies of ν_6 and the correlation matrices of free parameters have been deposited as supplementary material [11].

Acknowledgement

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[11] Lists of observed and calculated transition frequencies and 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. IRD-10016.