Molecular Vibrations of Gallium Trichloride Monomer with Application of the Keating Bending

B. N. Cyvin and S. J. Cyvin
Division of Physical Chemistry, The University of Trondheim, Norway

G. Díaz Fleming
Departamento de Química, Universidad Católica de Valparaíso, Chile

T. Mogstad and E. Rytter
Laboratory of Inorganic Chemistry, The University of Trondheim, Norway

Z. Naturforsch. **40a,** 714–718 (1985); received May 10, 1985

The vibrational spectra and previous normal coordinate analyses of $GaCl_3$ are reviewed. The valence force field (VFF), Keating force field (KFF) and central force field (CFF) are investigated, taking into account isotopic frequency shifts and the mass influence on Coriolis constants. It seems that KFF is an appropriate force field approximation. In its definition a new type of internal coordinates, the Keating's bending, is invoked. A final force field is tentatively determined and used to calculate the mean amplitudes of vibration.

Introduction

The vibrational frequencies of $GaCl_3$ seem now to be well established [1] after a great deal of efforts (see below). Consequently we find this molecule to be suited for testing the applicability of a new type of internal coordinates, referred to as Keating's bending [2]. This coordinate is implied in a potential proposed by Keating [3] in the theory of lattice dynamics. In the context of molecular vibrations of isolated species Keating's bendings have been successfully applied to different planar symmetrical XY_3 molecules [4–8], to which also $GaCl_3$ belongs (symmetry D_{3h}).

Previous Work

In an infrared study of dimeric gallium trichloride Beattie et al. [9] attributed two bands to the monomeric species with a question mark (see Table 1). Some years later certain fundamentals belonging undoubtedly to the monomeric form were observed in both Raman [10] and infrared [11] spectra of superheated vapours. Avasthi and Mehta [12] considered the Raman frequency of ν_1 (382 cm^{-1}) [10] as unreliable, but it has been confirmed by later measurements. Table 1 continues with the quotation of the first infrared spectrum of $GaCl_3$ in an Ar matrix [13]. These workers have reported isotopic splittings of the ν_3 band. The calculated

Table 1. Vibrational frequencies (cm^{-1}) of monomeric gallium trichloride from literature.

$\nu_1(A_1')$	$\nu_2(A_2'')$	$\nu_3(E')$	$\nu_4(E')$	Method * and reference
–	–	548?	170?	IR; Beattie et al. (1967) [9]
382	–	–	128	Ra; Beattie and Horder (1969) [10]
358	–	–	–	Empirical rule; Avasthi and Mehta (1971) [12]
–	145	450	128	IR; Selivanov and Maltsev (1973) [11]
–	136.2	470	132.1	IR (Ar); Pong et al. (1975) [13]
–	–	514	–	Calculated; Cyvin and Phongsatha (1975) [14]
381	–	457	128	Ra; Drake and Rosenblatt (1976) [15]
384	–	467	132	IR (Ar), Ra (Ar); Beattie et al. (1976) [16]
–	137.84	–	–	Calculated; Goel et al. (1977) [17]
–	143	464	131	IR; Klaeboe et al., Sjøgren et al. (1984) [18, 1]

* Abbreviations: IR infrared; Ra Raman; (Ar) argon matrix isolation (all the other experimental works pertain to the gas phase).

Reprint requests to Prof. S. J. Cyvin, Division of Physical Chemistry, The University of Trondheim, N-7034 Trondheim-NTH, Norway.

0340-4811 / 85 / 0700-0714 $ 01.30/0. – Please order a reprint rather than making your own copy.

Table 2. Mean amplitudes of vibration (l in Å units) for $GaCl_3$ at 298 K from literature.

l(Ga–Cl)	l(Cl ... Cl)	Reference
0.043	0.106	Cyvin and Phongsatha (1975) [14]
0.0453	0.1047	Goel et al. (1977) [17]
0.0431	misprint	Sarkar and Singh (1978) [19]
0.0458	0.1048	Goel and Sharma (1980) [20]
0.0434	0.1050	Sengodan and Srinivasacharya (1980) [21]

frequency of ν_3 from Cyvin et al. [14] is apparently too high. Drake et al. [15] observed for the first time ν_3 in the Raman spectrum. The same year (1976) an excellent work by Beattie et al. [16] appeared, where both infrared and Raman spectra in Ar matrix isolation are reported for different compounds including $GaCl_3$. Isotope splitting of both ν_1 and ν_3 for this molecule had been observed. Table 1 also shows a calculated frequency of ν_2 [17]. Very recently new high-temperature infrared spectra were reported [1, 18].

Several ones of the works cited above contain force constant calculations [1, 12–14, 16, 17]. Additional works on force constants exist [19–21]. Some of these works contain calculated mean amplitudes of vibration; cf. Table 2. Very little information is available on the Coriolis coupling in $GaCl_3$. One of the cited works [21] gives the calculated value of $\zeta_3 = 0.4320$. A similar value ($\zeta_3 = 0.4314$) was obtained from an empirical relation [22].

Valence, Keating and Central Coordinates

Keating coordinates emerge when the ordinary (Decius') bendings [23, 24] are substituted by the corresponding Keating's bendings [2, 3]. Their application to the planar symmetrical XY_3 model has been treated in detail elsewhere [4, 8]. Let (F_{33}, F_{34}, F_{44}) designate the force constants of the degenerate (E') block in terms of the (ordinary) symmetry valence coordinates [25]. They are converted into the force constants in terms of the symmetry Keating coordinates by

$$F_{33}^{k} = F_{33} + \tfrac{1}{3}(12^{\frac{1}{2}} F_{34} + F_{44}),$$

$$F_{34}^{k} = \tfrac{2}{3}(3^{\frac{1}{2}} F_{34} + F_{44}),$$

$$F_{44}^{k} = \tfrac{4}{3} F_{44}.$$

In a similar way one obtains the central coordinates [25, 26] on substituting Decius' bendings by the nonbond interatomic displacements. The corresponding symmetry force constants of the E' block of planar symmetrical XY_3 are given by

$$F_{33}^{c} = F_{33} + 12^{\frac{1}{2}} F_{34} + 3F_{44},$$

$$F_{34}^{c} = 2(F_{34} + 3^{\frac{1}{2}} F_{44}),$$

$$F_{44}^{c} = 4F_{44}.$$

The well-known valence force field (VFF) and central force field (CFF) approximations [24, 27] are characterized by $F_{34} = 0$ and $F_{34}^{c} = 0$, respectively. In an analogous way the Keating force field (KFF) is defined by $F_{34}^{k} = 0$ [4, 8].

Application to Gallium Trichloride

Introduction

The Keating (as well as central) coordinates have previously been applied to BF_3 [4], the other boron trihalides [5], $AlCl_3$ [7] and SO_3 [7, 8].

Here the theory is applied to $GaCl_3$. All the force constant sets of the present work are "compatible", i.e. exactly consistent with the experimental frequencies for $^{69}Ga^{35}Cl_3$. The adopted numerical wave numbers of the E' species are $\omega_3 = 464\ cm^{-1}$ and $\omega_4 = 131\ cm^{-1}$ [1]. In the cited work [1] a force field was produced by means of these frequencies along with seven isotopic frequency shifts [16]. We have slightly modified this force field in order to make it compatible, and transferred the force constants to our definition [25], which implies scaled bendings. Table 3 shows the value of F_{34} and the calculated $\Delta\omega_3$ frequency shifts for the symmetrically substituted molecules, along with the calculated Coriolis constant ζ_3 (for $^{69}Ga^{35}Cl_3$).

Approximate Force Fields

The same data (ζ_3 and $\Delta\omega_3$) are given in Table 3 for calculations with the VFF, KFF and CFF approximations. It is found that the literature force field (ii) [1] happens to come very close to the CFF (i). Another useful approach to the studies of force fields is to express a given force field in terms of the different coordinates. In Table 4 the force field (ii) is given in terms of the symmetry valence-, Keating- and central coordinates. We find that F_{34}^{c} (= 0.010

Table 3. Calculated $\Delta\omega_3$ isotopic frequency shifts (cm^{-1}) and the Coriolis constant $\zeta_3(^{69}Ga^{35}Cl_3)$ from different force fields (F_{34} in mdyne/Å), along with the observed frequency shifts.

Force field	F_{34}	ζ_3	$\Delta\omega_3(^{71}Ga^{35}Cl_3)$	$\Delta\omega_3(^{69}Ga^{37}Cl_3)$	$\Delta\omega_3(^{71}Ga^{37}Cl_3)$
(i) CFF	− 0.148	0.327	2.62	7.57	10.24
(ii) $\Delta\omega$ [a]	− 0.142(22)	0.334	2.64	7.54	10.23
(iii) $\zeta(BF_3)$ [b]	− 0.063	0.430	2.83	7.17	10.05
(iv) KFF	− 0.048	0.449	2.87	7.10	10.01
(v) $\zeta(SO_3)$ [b]	− 0.024	0.478	2.92	6.99	9.96
(vi) VFF	0.000	0.507	2.98	6.88	9.91
Observed $\Delta\omega_3$ (cm^{-1}) [13]			2.7	7.3	10.0
[16]			2.8	7.5	10.3

[a] Slightly modified force field from literature [1]. The value in parentheses represents the estimated standard deviation $\times 10^3$ based on 18 calculated shifts.

[b] $\zeta_3(^{69}Ga^{35}Cl_3)$ estimated from the mass influence on Coriolis constants.

Table 4. Force constants (mdyne/Å) of the E' species for $GaCl_3$ in different coordinates.

Force field [a]	Coordinates [b]	$F_{33}(\Omega)$ [c]	$F_{34}(\Omega)$	$F_{44}(\Omega)$
(ii)	VAL	2.677	− 0.142	0.085
	KEA	2.542	− 0.108	0.113
	CEN	2.440	0.010	0.340
(iii)	VAL	2.567	− 0.063	0.082
	KEA	2.522	− 0.018	0.110
	CEN	2.595	0.158	0.329
(iv)	VAL	2.544	− 0.048	0.082
	KEA	2.516	0.000	0.110
	CEN	2.625	0.190	0.329
(v)	VAL	2.506	− 0.024	0.083
	KEA	2.506	0.028	0.111
	CEN	2.673	0.240	0.332

[a] See Table 3.

[b] Symmetry valence (VAL)-, Keating (KEA)- and central (CEN) coordinates.

[c] $F_{ij}(\Omega)$ equals F_{ij}, F^{k}_{ij} and F^{c}_{ij} for $\Omega = \pi/2$, $2\pi/3$ and $5\pi/6$, respectively [8].

mdyne/Å) is smaller in absolute magnitude than either F_{34} or F^{k}_{34}. This situation is usual. For most molecules CFF is a worse approximation than VFF [24, 27].

A detailed inspection of Table 3, where some of the observed isotopic shifts [13, 16] are included, demonstrates that these shifts are not very sensitive to the force constants. This is a common experience. It is seen (Table 3) that the whole range of F_{34} from 0 to -0.148 mdyne/Å is consistent with the observed frequency shifts roughly within ± 0.5 cm^{-1}. Therefore, other types of additional information, like the Coriolis constant, need to be considered.

Mass Influence on Coriolis Constants

Table 3 shows also that the Coriolis constant (ζ_3) would fix the force field better than the frequency shifts. Unfortunately no experimental ζ value for $GaCl_3$ is available. But we have tried to estimate the value of ζ_3 by means of the theory of mass influence on Coriolis constants [25, 28]. For two planar symmetrical XY_3 molecules the value of ζ_3 has been determined with reasonable accuracy (say ± 0.005). We have adopted (a) $\zeta_3 = 0.789$ [29] for $^{11}BF_3$ and (b) $\zeta_3 = 0.474$ [30, 31] for $^{32}S^{16}O_3$. Based on these data we have produced the curves of mass dependence of ζ_3 for planar symmetrical XY_3 molecules; cf. Figure 1. They predict the values (a) $\zeta_3 = 0.430$ and (b) $\zeta_3 = 0.478$ for $^{69}Ga^{35}Cl_3$ in the two cases; see also Table 3. The former value is supported by the previously calculated [21] and estimated [22] values; see above. We have used our two values to determine the corresponding $GaCl_3$ force fields, which are designated (iii) and (iv) in the cases (a) and (b), respectively. It is interesting to note that these force fields are clustered around the Keating force field, KFF (iv); cf. Table 3. In Table 4 the force constants are expressed in terms of the symmetry valence-, Keating- and central coordinates. In the case (iii) one finds

$$|F^{k}_{34}| < |F_{34}| < |F^{c}_{34}| .$$

If this force field was the true one it would indicate that VFF is a better approximation than CFF, and KFF still better. In case (v) one has

$$|F_{34}| < |F^{k}_{34}| < |F^{c}_{34}|$$

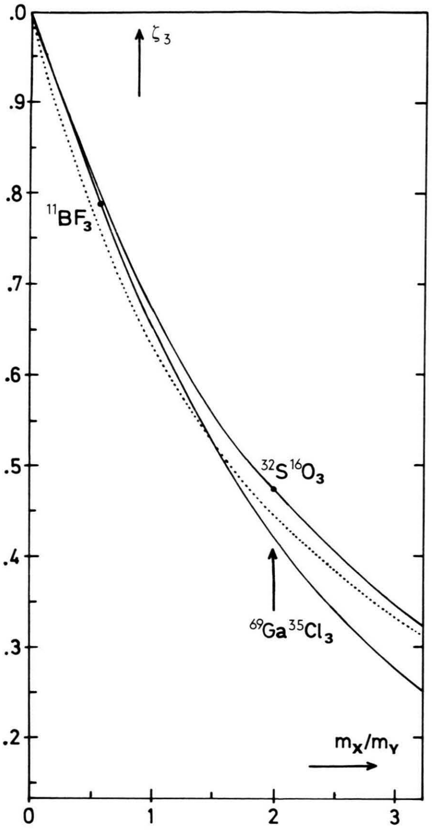

Fig. 1. Mass dependence of ζ_3 for planar symmetrical XY_3 molecules, based on (a) $\zeta_3 = 0.789$ for $^{11}BF_3$ and (b) $\zeta_3 = 0.474$ for $^{32}S^{16}O_3$. The dotted curve (c) corresponds to KFF for $GaCl_3$. When $m_X/m_Y \to \infty$ one has in the three cases: (a) $\zeta_3 \to -0.250$, (b) $\zeta_3 \to -0.126$, (c) $\zeta_3 \to -0.072$.

Table 5. Calculated mean amplitudes of vibration (l in Å units) and Bastiansen-Morino shrinkage effect (Δ in Å) for $^{69}Ga^{35}Cl_3$.

Temperature	l(Ga–Cl)	l(Cl ... Cl)	Δ
0 K	0.0405	0.065	0.0023
25 °C	0.0457	0.104	0.0072
250 °C	0.0551	0.134	0.0123
500 °C	0.0651	0.162	0.0180
750 °C	0.0740	0.185	0.0238
1000 °C	0.0821	0.207	0.0296

but the difference between $|F_{34}|$ and $|F_{34}^{k}|$ is not large.

It is hard to decide which one of the force fields (iii) and (v) is better. We are inclined to give preference to (iii) because $GaCl_3$ is chemically more related to BF_3 than to SO_3.

Keating Force Field

The above computations and discussion seem to indicate that KFF (iv) is a good approximation for $GaCl_3$. The E' species force constants in the three types of coordinates are included in Table 4. The calculated Coriolis constant for $^{69}Ga^{35}Cl_3$ is $\zeta_3 = 0.449$, i.e. in-between the values consistent with the force fields (iii) and (v). The curve of mass dependence of ζ_3 from KFF of $GaCl_3$ is dotted in Figure 1 (c). It is seen to follow nicely the two full-drawn curves for small mass ratios, say $m_X/m_Y < 2$. For $m_X/m_Y > 2$ the curves (a) and (b) separate significantly, while (c) tends to approach the curve (b). The legend of Fig. 1 gives the limiting values of ζ_3 when $m_X/m_Y \to \infty$.

Final Force Field

In conclusion the experimental evidence seems not to be sufficient to determine with confidence which one of the force fields is best. In view of the above discussion we have chosen (iii) as the final force field as an alternative to (ii). It reproduces the isotopic frequency shifts with sufficient accuracy and gives a reasonable value of ζ_3; cf. Table 3.

The final force field was used to calculate the mean amplitudes of vibration [25] for $^{69}Ga^{35}Cl_3$. In species A_1' the frequency value $\omega_1 = 382\ cm^{-1}$ [1, 10] was applied. It gives the force constant $F_{11} = 3.006$ mdyne/Å. The results are shown in Table 5. Those of 25 °C are comparable with the previous literature values. In order to compute the Bastiansen-Morino shrinkage effect [25] one needs also $\omega_2(A_2'')$ and the bond distance (R). The value of $\omega_2 = 143\ cm^{-1}$ [1] was adopted along with $R = 2.09$ Å [1, 32]. The results are included in Table 5.

Remark on the Coriolis Constant Variation

Coriolis constants have been used several times to fix the force constants in small molecules with degenerate two-dimensional blocks. Until recently this problem has been attacked either by a graphical ("display diagram") method [33, 34] or an iteration method employing Jacobi elements [35]. Cyvin [4] in his analysis of BF_3 applied an analytical method. For planar symmetrical XY_3 molecules, display diagrams have been drawn for BF_3 [36, 37], SO_3 [38]

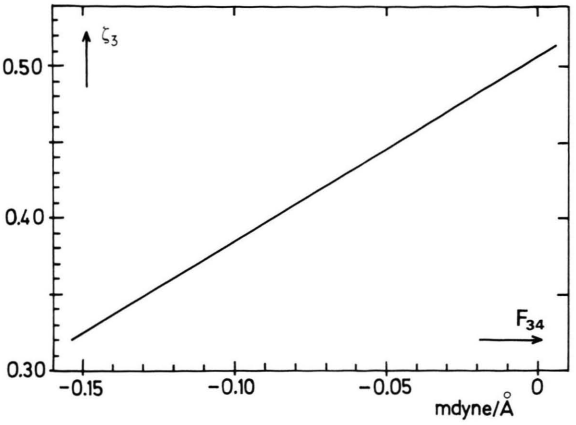

Fig. 2. ζ_3 of $^{69}Ga^{35}Cl_3$ as a function of F_{34}. The dependence is exactly linear.

and $AlCl_3$ [39]. These are curves of ζ_3 as a function of F_{34}, the interaction force constant of a compatible force field. In all cases [36–39] the curves look as straight lines, and indeed they are exactly linear. From Cyvin's formula [4] one obtains explicitly

$$\zeta_3 = \frac{3\mu_X(\lambda_3 + \lambda_4) + 48^{\frac{1}{2}} F_{34}\mu_Y(3\mu_X + \mu_Y)}{(\lambda_3 - \lambda_4)(3\mu_X + 2\mu_Y)}.$$

Here the λ's are the familiar frequency parameters (proportional to the squared wave numbers), while μ_X and μ_Y are the inverse masses of the X and Y atoms, respectively. Figure 2 shows graphically this linear dependence for $^{39}Ga^{35}Cl_3$. The slope of the line is easily obtained by differentiation:

$$\frac{d\zeta_3}{dF_{34}} = \frac{48^{\frac{1}{2}}\mu_Y(3\mu_X + \mu_Y)}{(\lambda_3 - \lambda_4)(3\mu_X + 2\mu_Y)}.$$

This expression was derived by Cyvin and Brunvoll [39] in a much more complicated way.

Acknowledgement

Financial support to BNC from The Norwegian Research Council for Science and the Humanities is gratefully acknowledged.

[1] C. E. Sjøgren, P. Klaeboe, and E. Rytter, Spectrochim. Acta **40 A,** 457 (1984).
[2] S. J. Cyvin, Spectroscopy Letters **17,** 489 (1984).
[3] P. N. Keating, Phys. Rev. **145,** 637 (1966).
[4] S. J. Cyvin, Spectroscopy Letters **17,** 493 (1984).
[5] S. J. Cyvin, B. N. Cyvin, and J. Brunvoll, Spectroscopy Letters **17,** 511 (1984).
[6] S. J. Cyvin and B. N. Cyvin, Spectroscopy Letters **17,** 525 (1984).
[7] S. J. Cyvin, B. N. Cyvin, T. Mogstad, J. Brunvoll, and G. Díaz Fleming, Spectroscopy Letters **17,** 537 (1984).
[8] S. J. Cyvin, B. N. Cyvin, and G. Díaz Fleming, Spectrochim. Acta **41 A,** 351 (1985).
[9] I. R. Beattie, T. Gilson, and P. Cocking, J. Chem. Soc. (A) **1967,** 702.
[10] I. R. Beattie and J. R. Horder, J. Chem. Soc. (A) **1969,** 2655.
[11] G. K. Selivanov and A. A. Maltsev, Zh. Strukt. Khim. **14,** 943 (1973).
[12] M. N. Avasthi and M. L. Mehta, J. Mol. Struct. **8,** 49 (1971).
[13] R. G. S. Pong, R. A. Stachnik, A. E. Shirk, and J. S. Shirk, J. Chem. Phys. **63,** 1525 (1975).
[14] S. J. Cyvin and A. Phongsatha, Spectroscopy Letters **8,** 71 (1975).
[15] M. C. Drake and G. M. Rosenblatt, J. Chem. Phys. **65,** 4067 (1976).
[16] I. R. Beattie, H. E. Blayden, S. M. Hall, S. N. Jenny, and J. S. Ogden, J. Chem. Soc. Dalton **1976,** 666.
[17] R. K. Goel, S. D. Sharma, and A. N. Pandey, Spectroscopy Letters **10,** 915 (1977).
[18] P. Klaeboe, E. Rytter, and C. E. Sjøgren, J. Mol. Struct. **113,** 213 (1984).
[19] P. C. Sarkar and G. C. Singh, Indian J. Pure Appl. Phys. **16,** 1077 (1978).
[20] R. K. Goel and S. D. Sharma, Acta Phys. Polon. **A 57,** 251 (1980).
[21] V. Sengodan and K. G. Srinivasacharya, Indian J. Pure Appl. Phys. 620 (1980).
[22] V. Sengodan and P. Ramalingam, Bull. Soc. Chim. Belg. **92,** 691 (1983).
[23] J. C. Decius, J. Chem. Phys. **17,** 1315 (1949).
[24] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, Molecular Vibrations, McGraw-Hill, New York 1955.
[25] S. J. Cyvin, Molecular Vibrations and Mean Square Amplitudes, Universitetsforlaget, Oslo and Elsevier, Amsterdam 1968.
[26] R. Teranishi and J. C. Decius, J. Chem. Phys. **22,** 896 (1954).
[27] G. Herzberg, Infrared and Raman Spectra of Polyatomic Molecules, D. van Nostrand, Princeton 1945.
[28] B. N. Cyvin, S. J. Cyvin, and L. A. Kristiansen, Z. Naturforsch. **19 a,** 1148 (1964).
[29] S. G. W. Ginn, D. Johansen, and J. Overend, J. Mol. Spectr. **36,** 448 (1970).
[30] J. B. Milne and A. Ruoff, J. Mol. Spectr. **23,** 408 (1967).
[31] A. J. Dorney, A. R. Hoy, and I. M. Mills, J. Mol. Spectr. **45,** 253 (1973).
[32] P. A. Akishin, V. A. Naumov, and V. M. Tatevskii, Kristallografiya **4,** 194 (1959).
[33] I. M. Mills, Spectrochim. Acta **16,** 35 (1960).
[34] J. L. Duncan and I. M. Mills, Spectrochim. Acta **20,** 1089 (1964).
[35] I. M. Mills, J. Mol. Spectr. **5,** 344 (1960); erratum: ibid. **17,** 164 (1965).
[36] J. L. Duncan, J. Mol. Spectr. **13,** 338 (1964).
[37] D. C. McKean, Spectrochim. Acta **22,** 269 (1966).
[38] R. Stølevik, B. Andersen, S. J. Cyvin, and J. Brunvoll, Acta Chem. Scand. **21,** 1581 (1967).
[39] S. J. Cyvin and J. Brunvoll, J. Mol. Struct. **3,** 453 (1969).