*Journal of Fluorine Chemistry*, *30* (1985) 159–170

Received: March 5, 1985; accepted: May 5, 1985

# HARMONIC FORCE FIELD FOR MONOMERIC GALLIUM TRIFLUORIDE WITH APPLICATION OF THE KEATING BENDINGS

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## SUMMARY

A normal coordinate analysis for $GaF_3$ is presented for the first time. Several force field approximations were investigated. The new type of so-called Keating coordinates were applied in addition to the familiar valence and central coordinates. A Coriolis constant was estimated from the theory of its mass dependence. The unobserved $\omega_1(A_1')$ frequency was calculated. A final ('exact') force field was determined with the aid of a reported $\Delta\omega_3$ isotopic frequency shift. Finally the mean amplitudes of vibration and Bastiansen-Morino shrinkage effect at temperatures up to 1000 °C were computed.

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0022-1139/85/$3.30

## INTRODUCTION

Several works have been published on the vibrational spectra of $GaCl_3$, $GaBr_3$ and $GaI_3$ [1-9], and the reported data have been used to carry out normal coordinate analyses for these molecules [7,9-16]. For $GaF_3$ on the other hand, we have found only one spectroscopic work[17] which deals with the infrared spectra in inert gas matrices, and no normal coordinate analysis. In the present vibrational analysis we have derived the force constants of $GaF_3$ and calculated the unobserved (Raman-active) $\omega_1(A_1')$ frequency, the Coriolis constant $\zeta_3(E'\times E')$ [18-20], the mean amplitudes of vibration [20] and Bastiansen -Morino shrinkage effect [20].

A new type of internal coordinates referred to as Keating's bending [21] has been applied in the present work. This coordinate is implied in a potential proposed by Keating [22] 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 [23-27], to which also $GaF_3$ belongs (symmetry $D_{3h}$).

## FORCE FIELD APPROXIMATIONS

In a two-dimensional species it is well known that the two frequencies alone are not sufficient to determine the three independent force constants. If no more additional experimental data are available one must resort to approximations. In the present work we have investigated five different approximations for the $E'$ species of $GaF_3$. Let $(F_{33}, F_{34}, F_{44})$ designate the symmetry force constants in terms of standard coordinates [20], for which the G matrix elements [28] read:

$$G_{33} = \frac{1}{2}(3\mu_X + 2\mu_Y), \qquad G_{34} = \frac{1}{2}\,27^{\frac{1}{2}}\,\mu_X, \qquad G_{44} = 3G_{33} \tag{1}$$

Here $\mu_X$ and $\mu_Y$ denote the inverse masses of the X = Ga and Y = F atoms, respectively. A set of force constants $(F_{33}, F_{34}, F_{44})$ is said to be 'compatible' when it is consistent with two predestined (experimental) frequencies ($\omega_3$, $\omega_4$). The five approximations are listed below in the order of decreasing values of $F_{34}/F_{44}$.

(i) Valence force field [28,29] (VFF)

$$F_{34} = 0 \tag{2}$$

(ii) A special force field from Pandey et al. [30] is defined by

$$F_{33} = \lambda_3/G_{33}, \qquad F_{34} = -\frac{1}{2}\lambda_4 G_{34}/D, \qquad F_{44} = \lambda_4 G_{33}/D \tag{3}$$

Here $\lambda_k$ is the familiar frequency parameter [20,28] ($\lambda_k = 4\pi^2 c^2 \omega_k^2$). $D$ is used to designate the determinant of the appropriate G matrix block, viz.

$$D = G_{33}G_{44} - G_{34}^2 = 3\mu_Y(3\mu_X + \mu_Y) = 3M/(m_X m_Y^2) \tag{4}$$

Here $m_X$ and $m_Y$ are the appropriate atomic masses, and $M = m_X + 3m_Y$ is the total molecular mass. Under the assumptions (3) one has

$$F_{34}/F_{44} = -\frac{1}{2}\,27^{\frac{1}{2}}\; m_Y/(2m_X + 3m_Y) \tag{5}$$

The force constants (3) are not exactly compatible. They give the correct sum of λ's since

$$F_{33}G_{33} + 2F_{34}G_{34} + F_{44}G_{44} = \lambda_3 + \lambda_4 \tag{6}$$

The product of λ's on the other hand is not reproduced exactly. One has

$$(F_{33}F_{44} - F_{34}^2)D = \lambda_3\lambda_4[1 - \frac{9}{16}(\lambda_4/\lambda_3)m_Y^2(m_X M)^{-1}] \tag{7}$$

The right-hand side of eqn. (7) approaches $\lambda_3\lambda_4$ when $m_X/m_Y \rightarrow \infty$. For $GaF_3$ the assumption (3) was found to give very nearly the correct frequencies. The method has also been adopted by others [31]. In the present work we have used a slight modification in order to get exactly compatible force constants: $F_{34}$ was maintained from eqn. (3) while the other two force constants were fitted to the frequencies.

(iii) The kinetic constant method was first proposed by Thirugnanasambandam [32], and used by many investigators in molecular vibrations. References to many works are found elsewhere [33,34]. The method has also been applied to planar symmetrical $XY_3$ molecules [12,16,35,36]. In this case the method amounts to the assumption

$$F_{34}/F_{44} = -G_{34}/G_{33} = -2^{\frac{1}{2}} m_Y/(2m_X + 3m_Y) \tag{8}$$

which is seen to be closely related to eqn. (5).

(iv) Keating force field [23,27] (KFF)

$$F_{34}/F_{44} = -3^{-\frac{1}{2}} \tag{9}$$

(v) Central force field [28,29] (CFF)

$$F_{34}/F_{44} = -3^{\frac{1}{2}} \tag{10}$$

In addition to these five approximations (i)-(v) the mass influence on Coriolis constants [20,37,38] was considered and employed in further force field determinations (see below).

## APPLICATION TO GALLIUM TRIFLUORIDE

### *Observed E' frequencies*

In the present computations we have adopted $\omega_3 = 748$ cm$^{-1}$ and $\omega_4 = 188$ cm$^{-1}$ for $^{69}GaF_3$, as observed by Hastie et al. [17] in an Ar matrix. Although these authors present the $\omega_2$ and $\omega_4$ fundamentals without differentiation, we have chosen the larger value as the out-of-plane ($A_2''$) frequency ($\omega_2 = 193$ cm$^{-1}$) because the sequence $\omega_2 > \omega_4$ has been determined in a number of monomeric trihalides of aluminum [3,4,8,9,39,40,42,43,45,46,48], gallium [3,5,8,9] and indium [3,41,44,47]. The observations for $AlF_3$ [39,40,43] are of special relevance to the present case. Also Perov et al. [4]: assumed $\omega_2 > \omega_4$ in their estimated frequencies for $GaF_3$ (quoted below).

Hastie et al. [17] have also reported the $^{69}Ga/^{71}Ga$ isotopic splitting on the $\omega_3$ band. Their data give $\Delta\omega_3 = 3.0$ cm$^{-1}$, the same shift in the Ar and Ne matrices, although the differences (Ne/Ar) in the absolute values are 11.2 cm$^{-1}$.

### *Isotopic product rule*

The isotopic (Teller-Redlich) product rule predicts

$$\omega_3\omega_4/(\omega_3{*}\omega_4{*}) = 1.0064$$

as the theoretical frequency ratio. Here the starred and unstarred symbols pertain to $^{71}GaF_3$ and $^{69}GaF_3$, respectively. With the adopted experimental data for $\omega_3$, $\omega_4$ and $\omega_3{*} = \omega_3 - \Delta\omega_3$ one obtains the calculated value of $\omega_4{*} = 187.55$ cm$^{-1}$. The corresponding isotopic shift, viz. $\Delta\omega_4 = 0.45$ cm$^{-1}$, is regarded as quite insignificant. This estimate explains why no experimental isotopic shift of the $\omega_4$ band has been observed.

### *Approximate force field computations*

Table 1 shows the calculated $\Delta\omega_3$ isotopic shifts with the approximate force fields (i)-(v) described above. They are all within 3.0 ± 0.2 cm$^{-1}$ through the range of $F_{34}/F_{44}$ from 0.000 to -1.732. Hence, this shift is not very sensitive to the compatible force constants. This is a common experience. Therefore, it is desirable to take other additional data into account, like the Coriolis constant. Table 1 includes the calculated $\zeta_3$ values of $^{69}GaF_3$ from the different force field approximations.

### *Mass influence on Coriolis constants*

Unfortunately, no experimental $\zeta$ value for $GaF_3$ is available. However, its value may be estimated with some confidence from the theory of mass influence on Coriolis constants [20,37,38]. For two planar symmetrical $XY_3$ molecules, the value of $\zeta_3$ has been determined with reasonable accuracy (say ±0.005). We have adopted (a) $\zeta_3 = 0.789$ for $^{11}BF_3$ [49], and (b) $\zeta_3 = 0.474$ for $^{32}S^{16}O_3$ [50,51]. Based on these data we have produced the curves of mass dependence of $\zeta_3$ for planar symmetrical $XY_3$ molecules (Fig. 1). They

TABLE 1

Calculated $\Delta\omega_3$ isotopic frequency shifts ($cm^{-1}$) and the Coriolis Constant $\zeta_3(^{69}GaF_3)$ from different force fields

| Force field[a] | $F_{34}/F_{44}$ | $\zeta_3$ | $\Delta\omega_3$ |
|---|---|---|---|
| (i) VFF | 0.000 | 0.332 | 3.19 |
| (ii) Ref. 30 | -0.253 | 0.312 | 3.14 |
| (iii) Kin. const. | -0.507 | 0.293 | 3.09 |
| $\zeta(SO_3)$ | -0.517 | 0.292 | 3.09 |
| (iv) KFF | -0.577 | 0.287 | 3.08 |
| 'Exact' | -0.996 | 0.254 | 3.00 |
| $\zeta(BF_3)$ | -1.502 | 0.212 | 2.90 |
| (v) CFF | -1.732 | 0.192 | 2.85 |

[a] See explanations in the text.

predict the values of (a) $\zeta_3 = 0.212$ and (b) $\zeta_3 = 0.292$ for $^{69}GaF_3$ in the two cases. The corresponding force fields were determined; the calculated values of $F_{34}/F_{44}$ and $\Delta\omega_3$ are included in Table 1.

### *'Exact' force field*

Table 1 includes also the results from an 'exact' force field for the *E'* species of $GaF_3$. It was determined by means of the observed $\Delta\omega_3$ shift. In view of the above discussion this result should not be accepted without great care. But we find that the corresponding $\zeta_3$ value (0.254 for $^{69}GaF_3$) is very reasonable in this case; it falls in fact in-between the two curves of Fig. 1. Hence this 'exact' force field was accepted as the final one. It reads (in mdyne/Å):

$F_{33} = 4.506$, $F_{34} = -0.1023$, $F_{44} = 0.1026$

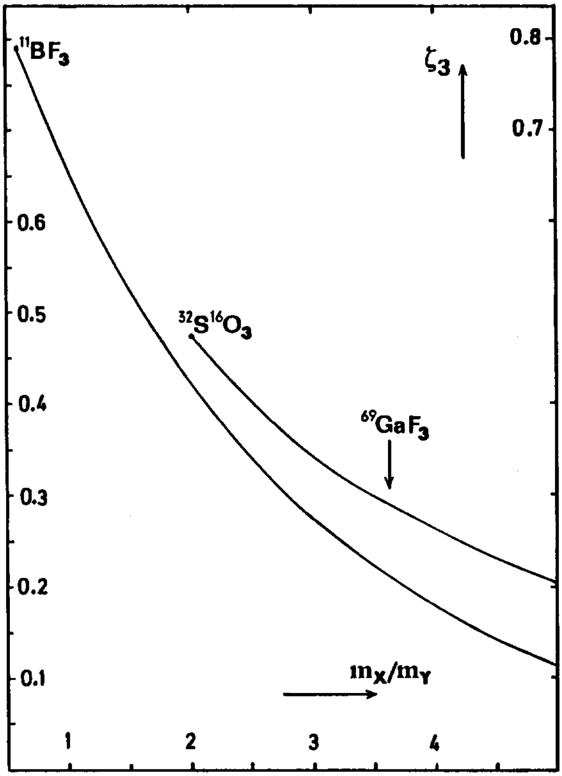

Fig. 1. Mass dependence of $\zeta_3$ for planar symmetrical $XY_3$ molecules, based on (a) $\zeta_3 = 0.789$ for $^{11}BF_3$ and (b) $\zeta_3 = 0.474$ for $^{32}S^{16}O_3$.

*Force fields in terms of different symmetry coordinates*

It is interesting to compare the validities of the VFF, KFF and CFF approximations. Recent studies of different planar symmetrical $XY_3$ molecules [23,24,26,27] tend to conclude with the superiority of the KFF. Also in the present case, Table 1 indicates roughly that KFF comes close to the 'exact' force field. In order to have a quantitative measure of the superiority of the mentioned approximations we have expressed all the eight force fields (Table 1) in terms of the symmetry valence-, Keating- and central coordinates. Table 2 shows the interaction force constants from these representations. For the 'exact' force field we find

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

TABLE 2

Interaction force constants (mdyne/A) from the force fields in terms of different coordinates

| Force field[a] | $F_{34}$ | $F_{34}^{k}$ | $F_{34}^{c}$ |
|---|---|---|---|
| (i) VFF | 0.000 | 0.068 | 0.356 |
| (ii) Ref. 30 | -0.026 | 0.038 | 0.303 |
| (iii) Kin. const. | -0.052 | 0.008 | 0.250 |
| $\zeta(SO_3)$ | -0.053 | 0.007 | 0.248 |
| (iv) KFF | -0.059 | 0.000 | 0.236 |
| 'Exact' | -0.102 | -0.050 | 0.151 |
| $\zeta(BF_3)$ | -0.157 | -0.112 | 0.048 |
| (v) CFF | -0.184 | -0.141 | 0.000 |

[a] See Table 1 and explanations in the text.

TABLE 3

Calculated mean amplitudes of vibration ($l$ in A) and the Bastiansen-Mor Shrinkage Effect (Δ in A) for $^{69}GaF_3$

| Temp. | $l$(Ga-F) | $l$(F···F) | Δ |
|---|---|---|---|
| 0 K | 0.0399 | 0.069 | 0.0027 |
| 25 C | 0.0413 | 0.095 | 0.0063 |
| 250 C | 0.0462 | 0.120 | 0.0106 |
| 500 C | 0.0527 | 0.143 | 0.0155 |
| 750 C | 0.0590 | 0.164 | 0.0205 |
| 1000 C | 0.0649 | 0.182 | 0.0254 |

as an indication that KFF is a better approximation than either VFF or CFF, provided that the 'exact' force field is to be trusted. The same relation holds also for the force fields (iii) and '$\zeta(SO_3)$' (Table 2), which are very close to the KFF approximation.

## *The unobserved $\omega_1$ frequency*

The fundamental of $\omega_1(A_1')$ is inactive in infrared, but would be active in Raman. In order to estimate this frequency we have transferred the value of $f_{rr} = \frac{1}{3}(F_{11} - F_{33}) = -0.049$ mdyne/Å from $AlF_3$ [52]. That resulted in

$F_{11} = 4.359$ mdyne/Å, $\omega_1 = 624.1$ cm$^{-1}$

This estimate is only tentative since it is based on a very uncertain (unobserved) $\omega_1$ frequency of $AlF_3$ [39,52].

For the sake of comparison we quote the $GaF_3$ frequencies (in cm$^{-1}$) estimated by Perov et al. [4]:

$\omega_1 = 650, \quad \omega_2 = 250, \quad \omega_3 = 710, \quad \omega_4 = 225$

In conclusion the following values (for $^{69}GaF_3$) were adopted in the present work.

$\omega_1 = 624.1, \quad \omega_2 = 193, \quad \omega_3 = 748, \quad \omega_4 = 188$

## *Mean amplitudes and shrinkage effect*

The final in-plane force field (see above) was used to calculate the mean amplitudes of vibration [20] for $^{69}GaF_3$. The results at different temperatures are given in Table 3. In order to compute the Bastiansen-Morino shrinkage effect [20] one also needs the out-of-plane frequency ($\omega_2$; see above) and the bond distance, $R$. We adopted $R = 1.88$ Å from the only available experimental works [53,54]. They concern relatively old gas electron diffraction measurements. The present results of calculated $l$ and $\Delta$ (Table 3) would be of great interest in a modern gas electron investigateion of the $GaF_3$ molecule.

## ACKNOWLEDGEMENT

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

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