Molecular Vibrations of Aluminum Trichloride Monomer with Application of the Keating Bendings

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The vibrational spectra and previous normal coordinate analyses of $AlCl_3$ are reviewed. The valence force field (VFF), central force field (CFF) and Keating force field (KFF) are tested. KFF is found to be the best one of these approximations with regard to the agreement with an observed isotopic frequency. A final force field is taken from a very recent work. It confirms that KFF is superior to both CFF and KFF. The data of a Coriolis constant, mean amplitudes of vibration and the Bastiansen-Morino shrinkage effect are calculated and discussed.

The vibrational frequencies and harmonic force constants of $AlCl_3$ seem now to be well established [1]. Consequently we find this molecule to be well suited for testing the applicability for 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 BF_3 [4], the other boron trihalides [5] and SO_3 [6]. A preliminary communication [7] shows that also an application to $AlCl_3$ is promising.

Valence-, Central- and Keating Coordinates

Keating's bending, $\varkappa$ [2], involves three atoms like the ordinary (Decius') bending [8, 9]. The ***s*** vector [9] of $\varkappa$ for a terminal atom is parallel to the opposite bond; cf. Figure 1. For one atom the figure also shows the ***s*** vectors of $R\alpha$ (perpendicular to the adjacent bond) and d, the nonbond (Urey-Bradley type [10]) interatomic distance deviation.

A standard set of symmetry coordinates for the planar symmetrical XY_3 molecular model [11] is given in Figure 1. These coordinates are referred to as the symmetry valence coordinates. On substituting the Decius bendings ($R\alpha$'s) by d's the symmetry

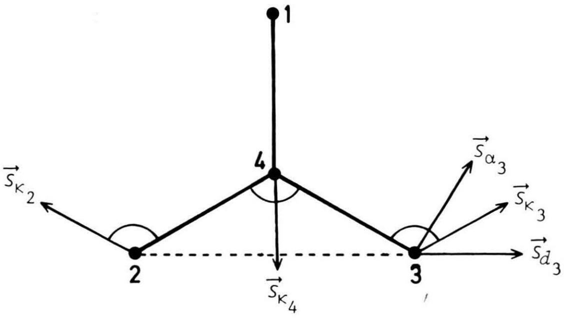

Fig. 1. The planar symmetrical XY_3 molecular model; symmetry D_{3h}. ***s***-vectors are shown for one of the Keating bendings, viz. $\varkappa_1$. For $R\alpha_1$ and d_1 the ***s***-vectors are given only for one atom, viz. No. 3. R denotes the equilibrium bond length. Symmetry coordinates are given. The alternative degenerate pairs (species E') are the symmetry valence (VAL)-, central (CEN)- and Keating (KEA) coordinates.

$$(A_1') \quad \frac{1}{\sqrt{3}}(r_1 + r_2 + r_3)$$

$$(A_2') \quad R\gamma \text{ (out-of-plane coordinate)}$$

$$(E')$$

$$\text{VAL}\begin{cases} \frac{1}{\sqrt{6}}(2r_1 - r_2 - r_3)\,, & \frac{1}{\sqrt{2}}(r_2 - r_3) \\ \frac{R}{\sqrt{6}}(2\alpha_1 - \alpha_2 - \alpha_3)\,, & \frac{R}{\sqrt{2}}(\alpha_2 - \alpha_3) \end{cases}$$

$$\text{CEN}\begin{cases} \frac{1}{\sqrt{6}}(2r_1 - r_2 - r_3)\,, & \frac{1}{\sqrt{2}}(r_2 - r_3) \\ \frac{1}{\sqrt{6}}(2d_1 - d_2 - d_3)\,, & \frac{1}{\sqrt{2}}(d_2 - d_3) \end{cases}$$

$$\text{KEA}\begin{cases} \frac{1}{\sqrt{6}}(2r_1 - r_2 - r_3)\,, & \frac{1}{\sqrt{2}}(r_2 - r_3) \\ \frac{1}{\sqrt{6}}(2\varkappa_1 - \varkappa_2 - \varkappa_3)\,, & \frac{1}{\sqrt{2}}(\varkappa_2 - \varkappa_3) \end{cases}$$

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central coordinates [11, 12] emerge. In an analogous way we define the symmetry Keating coordinates [4, 6] by means of the Keating bendings; cf. Figure 1.

The **G** matrix block of species E' in terms of the standard coordinates is given by Cyvin [11] and at many other places. In terms of the symmetry central- and Keating coordinates one has

$$G^{c}_{33} = \tfrac{3}{2}\mu_X + \mu_Y = G_{33}, \quad G^{c}_{34} = -\tfrac{1}{2}\,3^{1/2}\mu_Y, \quad G^{c}_{44} = \tfrac{3}{2}\mu_Y \tag{1}$$

and

$$G^{k}_{33} = G_{33}, \quad G^{k}_{34} = \tfrac{1}{2}(3\mu_X - \mu_Y), \quad G^{k}_{44} = \tfrac{1}{2}(3\mu_X + 5\mu_Y), \tag{2}$$

respectively. Here μ_X and μ_Y denote as usual the inverse atomic masses of the appropriate atoms.

Let the usual force constants of the E' species be given by (F_{33}, F_{34}, F_{44}). When this set is transferred to the two other coordinate sets considered here one obtains

$$F^{c}_{33} = F_{33} + 12^{1/2}F_{34} + 3F_{44}, \quad F^{c}_{34} = 2(F_{34} + 3^{1/2}F_{44}), \quad F^{c}_{44} = 4F_{44} \tag{3}$$

and

$$F^{k}_{33} = F_{33} + \tfrac{1}{3}(12^{1/2}F_{34} + F_{44}), \quad F^{k}_{34} = \tfrac{2}{3}(3^{1/2}F_{34} + F_{44}), \quad F^{k}_{44} = \tfrac{4}{3}F_{44}. \tag{4}$$

Experimental Works and Previous Normal Coordinate Analyses

The experimental works of vibrational spectroscopy are reviewed here in order to show the long way it took to establish the frequencies with confidence and to give an idea about the experimental uncertainties.

Three vibrational frequencies of $AlCl_3$ are found in the tables of Landolt-Börnstein [13] from 1951. They are quoted in Table 1. However, we have not been able to locate the original sources of these data in spite of the references [14, 15] cited in Landolt-Börnstein. Later research has shown these frequencies to be completely wrong. Before that they had been used in some normal coordinate analyses [16–20], which of course only have historical interest today. One of these works [17] gives calculated mean amplitude of vibration [11].

In a mainly thermodynamic work published in 1951 by Heise and Wieland [21] the investigators estimated the $AlCl_3$ vibrational frequencies (cf. Table 1) from related compounds with astonishing intuition (see below). Their estimates for $AlBr_3$, however, seem to be somewhat dubious when compared with later experimental evidence [22].

The first reliable observed frequencies for $AlCl_3$ are: ν_3 from the infrared spectrum of Klemperer [23] in 1956, along with ν_1 and ν_4 from Raman spectra of

Table 1. Experimental (and estimated) vibrational frequencies (cm^{-1}) for $AlCl_3$.

$\nu_1(A_1')$	$\nu_2(A_2'')$	$\nu_3(E')$	$\nu_4(E')$	Method[a]; Reference
541	–	808	348	Compiled; Landolt-Börnstein (1951) [13]
350	215	615	130	Estd.; Heise and Wieland (1951) [21]
–	–	610	–	IR; Klemperer (1956) [23]
345	230	–	135	Estd.; JANAF (1962) [24]
400	245	–	150	Estd.; JANAF (1963) [25]
415 ± 15	95 ± 15	–	–	ED; Zasorin and Rambidi (1967) [26]
–	110	–	–	ED; Cyvin and Brunvoll (1969) [30]
371	–	–	146	Ra; Beattie and Horder (1969) [22]
–	185	–	–	Estd.; JANAF (1971) [36]
382 ± 0.5	182.8	594.7	149.2	IR(Ar); Lesiecki and Shirk (1972) [37]
–	160 – 170	615	–	IR; Selivanov and Maltsev (1973) [43]
–	174	–	142	IR(Xe); Perov et al. (1974) [44]
375	183	595	150	Selected; Shimanouchi (1974) [45]
–	–	619.1	–	IR(Ar); Schnöckel (1976) [42]
393.5	–	618.8	150	Ra, IR(Ar); Beattie et al. (1976) [46]
–	137.84	–	–	Calcd.; Goel et al. (1977) [49]
–	183.0	618.6	151.1	IR(Ar); Pong et al. (1978) [47], (1979) [48]
391 ± 6	164 ± 10	643 ± 2	154 ± 9	ED; Spiridonov et al. (1981) [50]
375	214	616	148	Ra, IR; Tomita et al. (1983) [1], Klaeboe et al. (1984) [54]

[a] Abbreviations: Calcd. calculated; ED electron diffraction; Estd. estimated; IR infrared; Ra Raman.

Beattie and Horder [22] in 1969 (cf. Table 1). The ν_2 frequency still remained unobserved at that time. In the period between these two measurements different estimates of the unknown frequencies have been suggested with the aid of non-spectroscopical evidence. Different versions are found in the JANAF Thermochemical Tables, as estimated by means of thermodynamical data. For ν_2 in particular the values 230 cm^{-1} [24] and 245 cm^{-1} [25] were proposed (cf. Table 1). Zasorin and Rambidi [26] employed the experimental mean amplitudes and shrinkage effect from a gas electron diffraction investigation [27] in their determination of the $AlCl_3$ frequencies. Their data (cf. Table 1) include $\nu_2 = 95 \pm 15\ cm^{-1}$. One set of frequencies from JANAF Tables [24] have been applied in some normal coordinate analyses [28, 29] with calculated Coriolis constants [29], mean amplitudes [11, 28] and shrinkage effect [28]. The frequencies from Zasorin and Rambidi [26] have also been used in different vibrational analyses [30, 31]. In one of these works [30] the higher limit of ν_2 (viz. 110 cm^{-1}) is advocated. Revised normal coordinate analyses were later performed [32, 33] by taking into account the Raman ν_1 frequency from Beattie and Horder [22]. Some of the authors have erroneously referred to the estimated ν_3 and ν_4 frequencies from Heise and Wieland [21] as spectroscopical ones [30] and even as infrared frequencies [33].

The three observed frequencies [22, 23] for the in-plane vibrations of $AlCl_3$ were adopted in some normal coordinate analyses with calculations of mean amplitudes [34, 35], as well as in a new edition of JANAF Tables [36]. In the latter work [36] the out-of-plane frequency of $\nu_2 = 185\ cm^{-1}$ was estimated by fitting to thermodynamical data.

The next major event in the vibrational spectroscopy of $AlCl_3$ is due to Lesiecki and Shirk [37], who reported the infrared spectrum of matrix-isolated $AlCl_3$ in solid Ar. The report includes $\nu_2 = 182.8\ cm^{-1}$. Its conclusion about a pyramidal equilibrium structure for $AlCl_3$ aroused some discussion [38–42]. This was a short intermezzo, which ended in a general agreement about the planarity.

In the meantime a new infrared work [43] appeared, which (in addition to an observed ν_3) estimated $\nu_2 = 160-170\ cm^{-1}$ for $AlCl_3$. Also some additional infrared matrix-isolation spectra were studied: by Perov et al. [44] in a Xe matrix and Schnöckel [42] in Ne-, Ar- and N_2 matrices. In Table 1 only the ν_3 value from the Ar-matrix spectrum of the latter work [42] is quoted. It was attributed to $Al^{35}Cl_3$. It may also be of interest to quote the frequency values selected by Shimanouchi [45] in 1974 (cf. Table 1). This set includes some values from Lesiecki and Shirk [37], which later have been revised.

The mentioned discussion about planarity contains some preliminary communications [40, 41] on detailed spectroscopic investigations of matrix-isolated $AlCl_3$. The full papers appeared later: the Raman and infrared studies of Beattie et al. [46] and infrared studies of Pong et al. [47, 48], all in Ar matrices. The modern matrix-isolation works [42, 46–48] contain $^{35}Cl/^{37}Cl$ isotopic splittings of some bonds, viz. ν_1 [46] and ν_3 [42, 46–48]. The values quoted in Table 1 pertain to $Al^{35}Cl_3$. Force-constant calculations are also included [42, 46–48]. The observation of $\nu_2 = 183\ cm^{-1}$ by Pong et al. [47, 48] was not confirmed by the other workers [42, 46], who were not able to observe this frequency. The frequencies of Beattie et al. [46] were used in a normal coordinate analysis including mean amplitude calculations by Goel et al. [49]. These investigators calculated $\nu_2 = 137.84\ cm^{-1}$ from a force-field approximation.

In a noteworthy work by Spiridonov et al. [50] the harmonic force field of $AlCl_3$ was determined by new techniques of interpreting gas electron diffraction data. The work contains accurate determinations of the mean amplitudes from electron diffraction at two temperatures. Recent normal coordinate analyses [51–53] have been used to calculate mean amplitudes (or mean-square amplitudes [51, 52]) and Coriolis constants along with other molecular constants of $AlCl_3$.

The most recent contribution to the vibrational spectroscopy of $AlCl_3$ is due to Tomita et al. [1] and Klaeboe et al. [54]. Their work includes a Raman and infrared investigation of gaseous $AlCl_3$, along with a normal coordinate analysis [54] with calculated mean amplitudes. These investigators have reported an observation in infrared of $\nu_2 = 214\ cm^{-1}$ (cf. Table 1). Incidentally, this value coincides almost exactly with the estimate of Heise and Wieland [21] as early as in 1951 (see above).

Calculated and observed mean amplitudes along with the shrinkage effect for $AlCl_3$ from literature are given in Table 2. In Table 3 the literature data of a calculated Coriolis constant (ζ_3) are given.

Table 2. Mean amplitudes (l in Å) and shrinkage effect (Δ in Å) for $AlCl_3$ from literature. The temperature is 298 K when not otherwise indicated. Values at higher temperatures are entered in *italics*.

l (Al–Cl)	l (Cl ··· Cl)	Δ	Method [a]; Reference
0.0515	0.0560	–	VS; Nagarajan (1962) [17]
0.0504	0.1103	0.00608	VS; Nagarajan (1966) [28]
0.060 ± 0.005	*0.180 ± 0.010*	*0.04*	ED 800 K; Zasorin and Rambidi (1967) [27]
0.0658	*0.1758*	–	VS 800 K; Zasorin and Rambidi (1967) [26]
0.0494	0.1088	–	VS; Cyvin (1968) [11]
0.047_0	0.108_9	0.019_6	VS; Cyvin and Brunvoll (1969) [30], Cyvin (1969) [31]
0.064_5	*0.173_7*	*0.051_5*	VS 800 K; Cyvin and Brunvoll (1969) [30], Cyvin (1969) [31]
0.048_1	0.099_9	–	VS; Avasthi and Mehta (1971) [34]
0.048	0.107	–	VS; Cyvin et al. (1974) [32]
0.048_1	0.110_3	–	VS; Phongsatha and Cyvin (1974) [33]
0.066_4	*0.175_9*	–	VS 800 K; Phongsatha and Cyvin (1974) [33]
0.0481	0.0997	–	VS; Sarkar and Singh (1977) [35]
0.0473	0.0969	–	VS; Goel et al. (1977) [49]
0.0743(3)	*0.187(6)*	–	ED 1150 K; Spiridonov et al. (1981) [50]
0.0472	0.0967	0.0078	VS; Dhanalakshmi et al. (1982) [53]
0.048	0.100	–	VS; Tomita et al. (1983) [1]
0.066	*0.158*	–	VS 800 K; Tomita et al. (1983) [1]

[a] Abbreviations: ED electron diffraction; VS vibrational spectroscopy.

Table 3. Calculated Coriolis constant of $AlCl_3$ from literature.

ζ_3	Reference
0.734	Cyvin et al. (1964) [29]
0.7 ± 0.1	Cyvin and Brunvoll (1969) [30]
0.69286	Natarajan and Somasundaram (1980) [51]
0.6673	Dhanalakshmi et al. (1982) [53]

The VFF, CFF and KFF Approximations

The valence force field (VFF) and central force field (CFF) approximations are well known [9, 55]. They imply $F_{34} = 0$ and $F^{\mathrm{c}}_{34} = 0$, respectively, where F^{c}_{34} is defined by (3). In an analogous way the Keating force field (KFF) was defined by putting F^{k}_{34} of (4) equal to zero [4, 6].

The validity of these force field approximations for $AlCl_3$ was investigated. Table 4 shows the force constants of the three approximations when consistent with the $Al^{35}Cl_3$ frequencies of Pong et al. [47, 48]; cf. also Table 1. Table 4 includes the calculated ω_3 frequency of the isotopic $Al^{37}Cl_3$ (designated ω_3^*) in each case. These results may be compared with the experimental value of $\omega_3^* = 613.2\ \mathrm{cm}^{-1}$ [47, 48]. Hence the conclusion of this test: KFF is the best one of the three approximations, while CFF is the worst. The same conclusion was reached on the basis of the experimental data from Beattie et al. [46]; cf. Table 1. This feature is demonstrated by a slightly different approach in the following.

An "exact" force field for the E' species is determined by means of ω_3, ω_4 and ω_3^*. Table 5 shows the results, both using the data of Pong et al. [47, 48], and those of Beattie et al. [46] (cf. Table 1). The latter set was supplemented by $\omega_3^* = 613.3\ \mathrm{cm}^{-1}$ [46]. The conventional (F_{33}, F_{34}, F_{44}) force constants were converted to F^{c}_{ij} and F^{k}_{ij} according to (3) and (4). The results are found in Table 5. In both cases we find the relations

$$|F^{\mathrm{k}}_{34}| < |F_{34}| < |F^{\mathrm{c}}_{34}| . \quad (5)$$

This is taken as an indication that VFF is a better approximation than CFF and KFF is still better.

Final Force Field

Tomita et al. [1] determined a harmonic force field of species E' for $AlCl_3$ from their own infrared gas frequencies and seven isotopic shifts from the matrix-isolation spectra of Beattie et al. [46]. These shifts seem to have been measured with great accuracy. The values 5.5 and 5.4 cm^{-1} are deduced for the $^{35}Cl/^{37}Cl$ shift of $\Delta\omega_3$ from the data of Beattie et al. [46] and of Pong et al. [47, 48], respectively. Schnöckel has reported $\Delta\omega_3 = 5.55 \pm 0.15\ \mathrm{cm}^{-1}$ [42]. But all these data refer to infrared spectra in an Ar matrix. The computations of Tomita et al. [1] imply that the values are appropriate for gas data too.

Table 4. The E' species force constants (in mdyne/Å) of simple force field approximations, consistent with $\omega_3 = 618.6$ cm^{-1} and $\omega_4 = 151.1$ cm^{-1} for $Al^{35}Cl_3$ [47, 48]. Calculated ω_3^* ($Al^{37}Cl_3$) in cm^{-1}.

Force field	F_{33}	F_{34}	F_{44}	ω_3^*
VFF	2.5388	0.0000	0.09960	613.47
CFF	2.9296	−0.1657	0.09569	612.61
KFF	2.6770	−0.0552	0.09560	613.18

Table 5. "Exact" E' species force fields[a] in mdyne/Å, deduced with the isotopic ω_3^* frequency as additional information.

Coordinates[b]	$F_{33}(\Omega)$	$F_{34}(\Omega)$	$F_{44}(\Omega)$	Ref.[c]
VAL	2.713	−0.0686	0.0936	[46]
CEN	2.756	0.1872	0.3746	
KEA	2.665	−0.0168	0.1249	
VAL	2.668	−0.0513	0.0958	[47, 48]
CEN	2.777	0.2291	0.3831	
KEA	2.640	0.0046	0.1277	

[a] $F_{ij}(\Omega)$ equals F_{ij}, F^c_{ij} and F^k_{ij} for $\Omega = \pi/2$, $5\pi/6$ and $2\pi/3$, respectively [6].

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

[c] References to applied experimental frequencies.

Table 6. Calculated and observed mean amplitudes (l in Å) and calculated Bastiansen-Morino shrinkage effect ($\varDelta$ in Å) for $Al^{35}Cl_3$.

Temperature (K)	l (Al−Cl)	l (Cl···Cl)	$\varDelta$ (Cl···Cl)	Calc. or Obs. [50]
0	0.0443	0.0645	0.0029	Calc.
298.15	0.0480	0.0997	0.0067	Calc.
800	0.0662	0.1580	0.0168	Calc.
800	0.060(5)[a]	0.180(10)	–	Obs.
1150	0.0779	0.1889	0.0239	Calc.
1150	0.074(3)	0.187(6)	–	Obs.
1410	0.0857	0.2089	0.0293	Calc.
1410	0.083(2)	0.198(7)	–	Obs.

[a] Values in parentheses are estimated total errors (×10^3).

Table 7. Final E' species force field [1] in terms of different coordinates[a].

Coordinates	$F_{33}(\Omega)$	$F_{34}(\Omega)$	$F_{44}(\Omega)$
VAL	2.692	−0.0682	0.0912
CEN	2.729	0.1795	0.3648
KEA	2.644	−0.0180	0.1216

[a] See footnote to Table 5.

This is probably a reasonable assumption, although the absolute values of ω_3 vary considerably; it has been reported for ω_3 of $Al^{35}Cl_3$ (in cm^{-1}): 595.3 in N_2-matrix [42]; 610−616 in gas [1, 23, 43, 54]; 618.6 [47, 48], 618.8 [46] and 619.1 [42] in Ar-matrix; 622.4 in Ne-matrix [42]. In conclusion we believe that the force field of Tomita et al. [1] is about as good as it can be with the experimental evidence available at present. Our recalculation with the reported force field [1] gave $\varDelta\omega_3 = 5.48$ cm^{-1}.

The adopted force field [1] was used to calculate the $E' \times E'$ Coriolis constant (ζ_3) for $Al^{35}Cl_3$; the result was $\zeta_3 = 0.688$. No experimental value is available. The calculated value is very reasonable, however. It falls within the estimate ($\zeta_3 = 0.7 \pm 0.1$) of Cyvin and Brunvoll [30] made on the basis of the theory of mass influence on Coriolis constants [29]. In this analysis the experimental value $\zeta_3(^{11}BF_3) = 0.7438$ [56] was employed. The application of a slightly more recent value, viz. 0.789 [57], does not alter the conclusion. It has been used in an analysis of the mass influence on ζ_3 for boron trihalides [5] and results in $\zeta_3 = 0.726$ for $Al^{35}Cl_3$.

Calculated mean amplitudes of vibration [11] for $AlCl_3$ are reported by Tomita et al. [1]. The results were found to be in good correspondence with the experimental data of Spiridonov et al. [50] from gas electron diffraction investigations. The Bastiansen-Morino shrinkage effect [11] is also of interest in modern gas electron diffraction studies. Our calculated values for $Al^{35}Cl_3$ are found in Table 6, along with recalculated and observed [50] mean amplitudes. In these computations we have applied, in addition to the E' species force field: $\omega_1 = 375$ cm^{-1} [1], $\omega_2 = 214$ cm^{-1} [1], $R = 2.068$ Å [50].

The final force field of $AlCl_3$ [1] was expressed in terms of the symmetry valence-, central- and Keating coordinates of the present definitions. The force constants of the E' species are given in Table 7. We find the same relation (5) as above, indicating that KFF is a better approximation than either CFF or VFF.

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