Structure and Vibrational Spectra of the Vapour Molecules Fe_2Cl_6 and $AlFeCl_6$

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Melting of aluminium and iron trichloride crystals is accompanied by a structural transition from octahedral to tetrahedral coordination of the metal ions, and a widely accepted interpretation of their liquid structure is that it mainly consists of strongly correlated dimeric units. Such Al_2Cl_6 and Fe_2Cl_6 molecules are stable in the vapour phase and coexist in gaseous mixtures together with $AlFeCl_6$ molecules. In this work we extend to Fe_2Cl_6 and $AlFeCl_6$ our earlier study of the ionic interactions in Al_2Cl_6 [Z. Akdeniz and M. P. Tosi, Z. Naturforsch. **54a,** 180 (1999)], using a model which accounts for ionic deformability through (i) effective valences and (ii) electrostatic and overlap polarizabilities. The main disposable parameters of the model are adjusted to the Fe–Cl bond length in $FeCl_3$ monomer molecule and to the Fe–Fe bond length and a bond-stretching frequency in the Fe_2Cl_6 molecule. The results are used to evaluate the structure of the $AlFeCl_6$ molecule, which has so far only been inferred from the observed Raman spectrum in mixed vapours. Extensive comparisons with data on molecular vibrational frequencies are also presented for Fe_2Cl_6 and $AlFeCl_6$.

Key words: Ionic Clusters; Molecular Vapours; Molten Salts.

1. Background from Molten-salt and Molecular-vapour Studies

Aluminium trichloride and iron trichloride are two of the very few binary materials whose local structure is known to markedly change on melting (for recent reviews see [1, 2]). It is especially striking to contrast their melting behaviour with those of yttrium trichloride and aluminium tribromide. YCl_3 and $AlCl_3$ crystals are isomorphous and are formed from slightly distorted cubic-close-packed arrangements of the chlorines, inside of which the metal ions occupy alternate layers of octahedral sites. Such a layer structure is also present in crystalline $FeCl_3$, except that the layer stacking is hexagonal rather than cubic. In $AlBr_3$ crystals the packing of the bromines is also hexagonal, but the metal ions occupy tetrahedral sites such that the crystal may be viewed as formed from Al_2Br_6 dimeric units in the shape of edge-sharing bitetrahedra.

YCl_3 retains on melting a closely packed structure with octahedral-type coordination [3, 4]. Instead, melting of $AlCl_3$ and $FeCl_3$ is accompanied by a cooperative structural transition bringing the metal ions from octahedral into tetrahedral sites [5] and yielding a liquid which is primarily composed of Al_2Cl_6 or Fe_2Cl_6 molecular dimers [6, 7]. The dimeric structure of the $AlBr_3$ crystal is preserved in the melt [8]. These melting mechanisms are reflected in the values of the macroscopic melting parameters (in the sequence YCl_3, $AlCl_3$, $FeCl_3$ and $AlBr_3$, the relative volume change $\Delta V/V_\ell$ equals 0.0045, 0.47, 0.39 and 0.18, and the entropy change ΔS equals 7.56, 18.1, 17.8 and 7.3 e.u.). Some residual differences between the $AlCl_3$ and $FeCl_3$ melts are revealed by macroscopic data [9], in particular by the values of the ionic conductivity σ (in $\Omega^{-1}\,cm^{-1}$, $\sigma = 5 \times 10^{-7}$ in $AlCl_3$ and $\sigma = 0.04$ in $FeCl_3$, against $\sigma = 0.39$ in YCl_3 and $\sigma = 1 \times 10^{-8}$ in $AlBr_3$). A partial ionization equilibrium resulting from chlorine ion transfer between dimeric units appears to be established in molten $FeCl_3$ near freezing [10].

The Raman scattering spectra of these systems show prominent peaks, reflecting the local structures around the metal ion and their lifetime [11]. By following the Raman spectrum from the crystal into the liquid and the vapour, evidence is obtained on whether such local structures persist or are altered across phase changes (see e.g. [12]). The similarity of $AlCl_3$ and $FeCl_3$ in melting behaviour and local liquid structure extends into their vapour phase. Here the Al_2Cl_6 and Fe_2Cl_6 molecular dimers are the stable structures and indeed coexist in gaseous mixtures with $AlFeCl_6$ molecules [13].

Relatively sophisticated models of the microscopic interactions in the ionic assembly are needed to account for the presence and the stability of such local structures in the melt in classical simulation studies (see e.g. [14]). In this work we extend to the Fe_2Cl_6 and $AlFeCl_6$ molecules our earlier study of aluminium trichloride clusters, which was based on a pseudoclassical deformation-dipole model [15]. The plan of the paper is briefly as follows. The essential aspects of the model are recalled in § 2, which also presents the determination of the model parameters from data on iron trichloride clusters and some results on the $FeCl_3$ monomer. The results for the structure of the Fe_2Cl_6 and $AlFeCl_6$ molecules are presented in § 3, while § 4 report our results for their vibrational frequencies. Comparisons are made throughout the paper with similar theoretical results on the Al_2Cl_6 molecule [15] and with the available experimental data. Some concluding remarks are made in § 5.

2. Interionic Force Model and its Parameters for Iron Trichloride

We describe each molecule at zero temperature by means of a potential energy function $U(\{\boldsymbol{r}_{ij}\}, \{\boldsymbol{p}_i\})$, which depends on all interionic bonds $\boldsymbol{r}_{ij}$ and all electronic dipoles $\boldsymbol{p}_i$ on the halogens. The molecule is handled by a computer program which performs two basic tasks: (i) from a given starting configuration we search for zero-force structures corresponding to extrema in $U(\{\boldsymbol{r}_{ij}\}, \{\boldsymbol{p}_i\})$, and (ii) we examine deformations of each zero-force structure in order to assess its mechanical stability and to evaluate its vibrational frequencies.

The form of $U(\{\boldsymbol{r}_{ij}\}, \{\boldsymbol{p}_i\})$ is

$$U(\{\boldsymbol{r}_{ij}\},\{\boldsymbol{p}_i\}) = \sum_{i<j}\left[\frac{z_i\, z_j e^2}{r_{ij}} + \Phi_{ij}\,(r_{ij}) - \frac{C_i\, C_j}{r_{ij}^6}\right] + U_{\mathrm{pol}}^{\mathrm{cl}}\,(\{\boldsymbol{r}_{ij}\},\{\boldsymbol{p}_i\}) + U_{\mathrm{shell}}\,(\{\boldsymbol{r}_{ij}\},\{\boldsymbol{p}_i\}). \tag{1}$$

The sum in (1) includes (i) the Coulombic energy of the ionic point charges having effective valences z_i subject to overall charge compensation, (ii) the overlap repulsive energy as described by the Busing form [16]

$$\Phi_{ij}(r) = f\,(\rho_i + \rho_j)\,\exp\,[(R_i + R_j - r)/(\rho_i + \rho_j)], \tag{2}$$

and (iii) the van der Waals energy. A crucial point of the model in (1) is to allow for the electronic polarization of the halogens through both the classical polarization energy $U_{\mathrm{pol}}^{\mathrm{cl}}$ and the shell deformation energy U_{shell}, the latter being patterned after the so-called shell model (or deformation-dipole model) in lattice dynamics of ionic and semiconducting crystals [17]. Minimization of (1) with respect to the dipoles yields the dipole $\boldsymbol{p}_{\mathrm{h}}$ on the h-th halogen as

$$\boldsymbol{p}_{\mathrm{h}} = \alpha_{\mathrm{h}}\,\boldsymbol{E}_{\mathrm{h}}\,(\{\boldsymbol{r}_{ij}\},\{\boldsymbol{p}_i\}) + \alpha_{\mathrm{s}} \sum_{i_{\mathrm{h}}} \hat{\boldsymbol{r}}_{i\mathrm{h}} \left|\frac{\mathrm{d}\Phi_{i\mathrm{h}}\,(r_{i\mathrm{h}})}{\mathrm{d}r_{i\mathrm{h}}}\right|. \tag{3}$$

Here, $\boldsymbol{E}_{\mathrm{h}}$ is the self-consistent electric field on the halogen, α_{h} and α_{s} are its electrical and short-range polarizabilities and the sum is restricted to run over its first-neighbour metal ions. The last term on the RHS of (3) is the deformation dipole from changes in the state of near-neighbour overlap and leads to saturation of the net dipoles as the ions deform in reaching their equilibrium positions.

A very helpful aspect of the model (1) is that transferability of the parameters describing the halogen ion and direct proportionality between the characteristic radius R_{m} and the hardness parameter ρ_{m} of the metal ion are approximately valid. Thus from our earlier results on Al_2Cl_6 [15] and bearing in mind that the Fe–Cl bond lengths tend to be longer than the Al–Cl ones by 0.06–0.08 Å, we immediately obtain a first estimate of the model parameters for Fe_2Cl_6. We have then refined this initial assessment by re-adjusting the radius of the Fe ion, the polarizability of the Cl ion (at constant $\alpha_{\mathrm{s}}/\alpha_{\mathrm{h}}$ ratio) and the effective valence in Fe_2Cl_6 to the Fe–Cl bond length in the $FeCl_3$ monomer [18], to the Fe–Fe bond length in the Fe_2Cl_6 molecule [19] and to the stiffest bond-stretching frequency of the Fe_2Cl_6 molecule [13].

We briefly mention at this point our results for the $FeCl_3$ monomer and delay a discussion of the structure of Fe_2Cl_6 to the next section. We reproduce the equilibrium shape of $FeCl_3$, which is reported [18] to be an equilateral triangle of chlorines centred on the Fe ion (D_{3h} symmetry) and having an Fe–Cl bond length of 2.14 Å. We also estimate that an energy of about 0.9 eV is needed to break the dimer into two monomers at zero temperature. This estimate is not inconsistent with the fact that the dimer still is the dominant species in the vapour at 550 K [13].

Table 1 reports the values of the model parameters that we have obtained for Fe_2Cl_6 and compares them with those obtained for Al_2Cl_6 in our earlier work [15]. This comparison illustrates the extent to which the halogen

Table 1. Interionic force parameters in Fe_2Cl_6 and Al_2Cl_6 (m denotes the metal ion and h denotes the halogen)

	f (e^2/Å^2)	z_m	z_h	R_m (Å)	r_m (Å)	R_h (Å)	r_h (Å)	C_h (eÅ$^{5/2}$)	α_h (Å^3)	α_s (Å^3/e)
Al_2Cl_6	0.05	2.47_2	$-.82_4$	0.948	0.044	1.71	0.238	5.5	2.05	0.46
Fe_2Cl_6	0.05	2.30_4	$-.76_8$	0.959	0.041_5	1.71	0.238	5.5	2.72	0.66

parameters are transferable between different isomorphic compounds.

Table 2. Equilibrium structure of Fe_2Cl_6 (bond lengths in Å, bond angles in degrees). Underlined values have been fitted to the diffraction data on the iron trichloride vapour. The notations Cl^B and Cl^T denote bridging and terminal chlorines, respectively.

	Fe–Cl^B	Fe–Cl^T	Fe–Fe	Cl^B–Cl^B	Cl^T–Cl^T	$\angle Cl^B \cdot Fe \cdot Cl^B$	$\angle Cl^T \cdot Fe \cdot Cl^T$
This work	2.33	2.15	$\underline{3.20}$	3.40	3.72	93.6	119.7
Expt. [19]	2.326	2.127	3.20	3.272	3.723	92.9	122.1

3. Results for Molecular Structures

3.1. The Fe_2Cl_6 Dimer

In an extensive search for stable configurations of the Fe_2Cl_6 molecule in the potential energy hyperspace, we have only met with the D_{2h}-symmetry shape consisting of two tetrahedrally bonded Fe ions which share two chlorines and form with them a planar ring. This is the same equilibrium structure as for the Al_2Cl_6 dimer. *Ab initio* calculations carried out at the Hartree-Fock level by Scholz and Curtiss (unpublished) also find the D_{2h} symmetry for the equilibrium structure of Fe_2Cl_6.

The electron diffraction data on the Fe_2Cl_6 molecule [19] are consistent with this structure but also admit the possibility of a puckered-ring structure with C_{2v} symmetry, which is obtained through a 16.7° rotation around the axis formed by the two bridging chlorines. This deviation from a planar-ring structure may actually reflect large-amplitude oscillations around the aforementioned axis [19]. Normal-coordinate analyses of molecular vibrations have been carried out for both structures and show that a set of force constants fitted to the modes of the D_{2h} one predict small frequency shifts on ring puckering [20]. The observed Raman spectra of Fe_2Cl_6 have subsequently been interpreted in terms of a D_{2h} molecular symmetry [13].

Table 2 reports our results for the equilibrium structural parameters of Fe_2Cl_6 and compares them with the electron diffraction data. There evidently is good quantitative agreement between model and experiment.

3.2. The $AlFeCl_6$ Molecule

In transferring the parameters reported in Table 1 for Al_2Cl_6 and Fe_2Cl_6 to calculations on the $AlFeCl_6$ molecule, we have chosen to attribute (i) the parameters in the first row to Al and its terminal chlorines, (ii) those in the second row to Fe and its terminal chlorines, and (iii) average values from the two rows to the bridging chlorines. We have checked that alternative reasonable choices do not alter to a relevant extent the results that we report below.

A tetrahedron centred on Al and a second tetrahedron centred on Fe are very well suited to join up in forming the $AlFeCl_6$ molecule, because of their similarity in bond lengths and bond angles. Their matching only requires opening up of the $\angle Cl^B \cdot Al \cdot Cl^B$ angle by a few degrees and a closing down of the $\angle Cl^B \cdot Fe \cdot Cl^B$ angle by a similar amount, with the some minor adjustments of the bond lengths. In fact, we have found two mechanically stable structures for the $AlFeCl_6$ molecule at zero temperature, which are almost degenerate in energy. From our calculations the ground state is a puckered-ring structure, which is obtained by a rotation of only 3° around the axis joining the two bridging chlorines. The first excited state is a planar-ring structure. These structures are referred to in the following as distorted (d) and undistorted (u), respectively. Since the energy difference between them is only 0.04 eV, at a temperature of a few hundred degrees the molecule will be seen as being in the undistorted structure and executing oscillations around the bridging-chlorines axis.

Our results for the structural parameters of $AlFeCl_6$ in both configurations are reported in Table 3 together with the corresponding results for Al_2Cl_6 [15] and Fe_2Cl_6 (Table 2). It will be seen that matching of the two tetrahedra requires an inversion in the relative magnitude of the $\angle Cl^B \cdot Al \cdot Cl^B$ and $\angle Cl^B \cdot Fe \cdot Cl^B$ bond angles relative to the pure dimers [21]. Our calculations also predict an inversion in the relative magnitude of the $\angle Cl^T \cdot Al \cdot Cl^T$ and $\angle Cl^T \cdot Fe \cdot Cl^T$ bond angles.

Table 3. Equilibrium structure of Al_2Cl_6, $AlFeCl_6$(d), $AlFeCl_6$(u) and Fe_2Cl_6 (bond lengths in Å, bond angles in degrees). The notations Cl^B, Cl^T and $Cl^{T'}$ denote bridging, Al-terminal and Fe-terminal chlorines. Small differences in the metal-chlorine bond lengths in $AlFeCl_6$(d), at the level of 0.01 Å, have been ignored.

	$Al–Cl^B$ $Fe–Cl^B$	$Al–Cl^T$ $Fe–Cl^{T'}$	M–M	$Cl^B–Cl^B$	$Cl^T–Cl^T$ $Cl^{T'}–Cl^{T'}$	$\angle Cl^B \cdot Al \cdot Cl^B$ $\angle Cl^B \cdot Fe \cdot Cl^B$	$\angle Cl^T \cdot Al \cdot Cl^T$ $\angle Cl^{T'} \cdot Fe \cdot Cl^{T'}$
Al_2Cl_6	2.276	2.065	3.20	3.23	3.59	90.5	120.8
$AlFeCl_6$(d)	2.26 2.36	2.08 2.14	3.25	3.28	3.59 3.73	93.1 88.0	119.5 121.6
$AlFeCl_6$(u)	2.25 2.36	2.08 2.14	3.20	3.32	3.59 3.73	94.9 89.4	119.5 121.4
Fe_2Cl_6	2.33	2.15	3.20	3.40	3.72	93.6	119.7

$(AlCl_4)^-$	$Al_2Cl_6(D_{2h})$	$AlFeCl_6$(d)		$AlFeCl_6$(u)	$Fe_2Cl_6(D_{2h})$	$(FeCl_4)^-$
466 (490: ν_3)	$\underline{625}$ (625)	606	(620: B_1, ν_{10})	591	$\underline{467}$ (467: B_{1u}, ν_3)	356 (370)
	616 (614)	503	(496: A_1, ν_1)	497	463 (450: B_{2g}, ν_{11})	
	529 (611)	489	(461: B_1, ν_{11})	487	422 (422: A_g, ν_1)	
	484 (483)	425	(413: A_1, ν_2)	424	404 (406: B_{3u}, ν_{16})	
355 (351: ν_1)	428 (418)	389	(365*: B_2, ν_{15})	404	341 (328: B_{2u}, ν_{13})	331 (330)
	349 (337)	341	(330: A_1, ν_3)	353	330 (305: A_g, ν_2)	
	309 (320)	279	(321*: B_2, ν_{16})	284	269 (280: B_{3u}, ν_{17})	
	235 (281)	212	(289: A_1, ν_4)	217	217 (225: B_{1g}, ν_6)	
170 (186: ν_4)	226 (219)	201	(190: A_1, ν_5)	204	182 (150: A_g, ν_3)	140 (136)
	166 (178)	156	(151: B_2, ν_{17})	156	138 (118: B_{1u}, ν_9)	
	153 (168)	135	(121*: A_1, ν_6)	136	110 (112: B_{1g}, ν_7)	
	134 (143)	122	(113: B_1, ν_{12})	121	113 (116: B_{3u}, ν_{18})	
	124 (123)	106	(95*: A_2, ν_8)	106	106 (99: B_{2u}, ν_{14})	
103 (121: ν_2)	109 (115)	96	(91*: B_2, ν_{18})	96	90 (82: B_{2g}, ν_{12})	92 (114)
	96 (105*)	92	(89: B_1, ν_{13})	92	85 (82*: B_{3g}, ν_{15})	
	95 (98)	89	(88: A_1, ν_7)	90	85 (78: A_g, ν_4)	
	53 (55*)	49	(52: A_2, ν_9)	49	48 (44*: A_u, ν_5)	
	18 (33*)	17	(28*: B_1, ν_{14})	15	14 (24: B_{1u}, ν_{10})	

Table 4. Frequencies of vibrational modes (in cm^{-1}). The underlined values have been fitted to spectral data on the vapour. Experimental values on dimeric molecules are from [13] and are reported in parentheses (starred values are from force-field fits). Experimental values on the $(MCl_4)^-$ anions (in parentheses) are from [11] and [23].

4. Results for Vibrational Frequencies

Table 4 shows our results for the vibrational frequencies of the Al_2Cl_6 and Fe_2Cl_6 dimers and of the $AlFeCl_6$ molecule, in comparison with the experimental values reported by Nalbandian and Papatheodorou [13] (whenever experimental values are not available, we show the results of a force-field fit by the same authors). The modes have been listed in the order of decreasing frequency, but the assignments proposed in [13] for D_{2h} and C_{2v} symmetry are also shown.

Following the discussion given in our earlier work on Al_2Cl_6 [15], we have tried in Table 4 to display correlations between the modes of the dimeric molecules and the four mode frequencies of the $(AlCl_4)^-$ and $(FeCl_4)^-$ tetrahedra. The latter frequencies have been calculated with the model parameters shown in Table 1 and are reported in the side columns of Table 4. The calculated metal-halogen bond lengths are 2.15 Å in $(AlCl_4)^-$ and 2.23 Å in $(FeCl_4)^-$.

The ν_3 and ν_1 modes of the tetrahedron are associated with the stretching of a metal-halogen bond and with the symmetric stretching of the four metal-halogen bonds, respectively. The other modes, conventionally denoted by ν_2 and ν_4, are associated with deformations and torsions. As discussed by Manteghetti and Potier [22] in relation to their study of the vibrational spectrum of the $(Al_2Cl_7)^-$ complex, the ν_d vibration of a pyramidal $AlCl_3$ group is split by the loss of ternary symmetry and by the coupling between groups, giving rise to four terminal asymmetric modes at frequencies higher than that of the ν_3 mode in $(AlCl_4)^-$. This accounts for the top quadruplet of modes in the three central columns in Table 4. These arguments then suggest that the next quadruplet is mainly related to bond stretching and that the lower modes are mainly related to bond bendings and torsions in the dimeric molecule.

It is seen from Table 4 that our results are in very reasonable agreement with all the available data on both bond stretching and bond deformation modes. This indicates that the model should describe rather reliably all the structural fluctuations taking place at equilibrium in the melts of these materials.

5. Concluding Remarks

In conclusion, we should like to comment on the model of ionic interactions that we have used to evaluate structural and dynamical properties of dimeric trihalide molecules. The model accounts for quantal effects associated with electron-shell deformability of the halogens through the introduction of (i) effective valences and (ii) electrical and overlap polarizabilities. Main attention in determining the effective valences is paid to the metal-halogen bond stretching mode as a precursor to halogen stripping. The polarizability of the halogen ions plays instead a main role in determining molecular bond angles.

We expect that such a model should be most appropriate for ionic systems containing s and p valence electrons. Indeed, a number of tests against first-principles calculations from molecular-orbital and density-functional methods were successfully made in our earlier study of Al trichloride clusters [15]. However, we have seen in the present work that the model also gives a reasonably accurate account of the properties of molecules containing ions with an incomplete d-shell such as trivalent Fe. We should recall in this connection that from molecular-orbital calculations by Scholz and Curtiss (unpublished) the ground state of both $FeCl_3$ and Fe_2Cl_6 is a high-spin state. How precisely such a property of the quantum-mechanical ground state is incorporated into a pseudoclassical picture seems worthy of further study.

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