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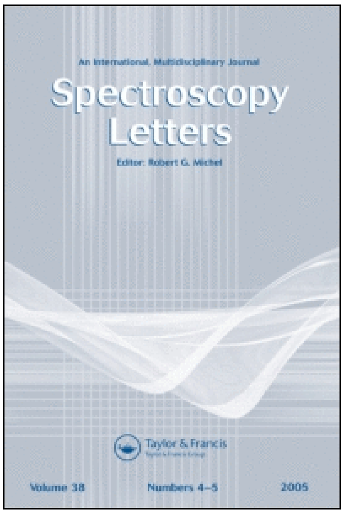

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Molecular Vibrations of Fe_2Cl_6 (g) and $AlFeCl_6$ (g)

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MOLECULAR VIBRATIONS OF $Fe_2Cl_6(g)$ AND $AlFeCl_6(g)$

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ABSTRACT

Normal coordinate analyses were performed for Fe_2Cl_6 and $AlFeCl_6$ on the basis of new Raman data. Calculated mean amplitudes of vibration are reported.

INTRODUCTION

Recent high temperature Raman spectroscopic studies were able to establish most of the Raman active vibrational frequencies of the $Fe_2Cl_6(g)$[1,2] and $AlFeCl_6(g)$[2] gaseous molecules. With the aid of the IR[3] and Raman[4] matrix isolation studies for the $Fe_2Cl_6(g)$ as well as of the extensive studies for the $Al_2Cl_6(g)$[5], an assignment of the measured vibrational frequencies for both the $Fe_2Cl_6(g)$ and the $AlFeCl_6(g)$ molecules was possible[2].

The purpose of the present work is to derive an appropriate force field for the $Fe_2Cl_6(g)$. The analogy with the $Al_2Cl_6(g)$ was exploited and the force field approximation of reference 5 was adopted. Furthermore the derived force field for $Fe_2Cl_6(g)$ is combined with that for

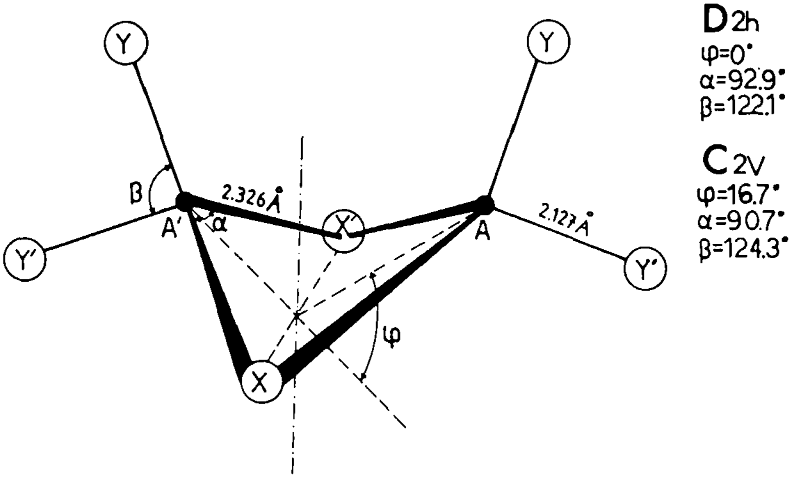

Fig. 1. The $A_2X_2Y_4$ molecular model for the pure dimer $Fe_2Cl_6(g)$.

$Al_2Cl_6(g)^5$ to calculate the vibrational frequencies for the vapor complex $AlFeCl_6(g)$. A good agreement between the calculated and experimentally measured Raman frequencies of the vapor complex has been found.

THE $Fe_2Cl_6(g)$ MOLECULE

The structure of the $Fe_2Cl_6(g)$ has been determined by accurate electron diffraction measurements[6,7]. The molecule consists of two tetrahedrally bonded Fe atoms with two common bridging Cl atoms thus forming a four member ring as shown in Fig. 1. There are two proposed structures for this molecule. In the first, angle $\varphi=0$ (Fig. 1), the ring is planar and the molecular symmetry is D_{2h} as for the $Al_2Cl_6(g)$. In the second, $\varphi=16{,}7°$, the ring is puckered and the symmetry is C_{2v}. The electron diffraction data are more consistent with the puckered-ring structure but it has been pointed out that the deviation from the planar-ring structure may be due to the

Table 1. Distribution and correlations of the normal modes of vibration for the AA' X_2Y_4 molecules

A. Puckered - (C_{2v}) and planar-ring (D_{2h}) models (pure dimer).

Symmetry group	Species							
C_{2v}	$7A_1$(R,IR)		$3A_2$(R)		$3B_1$(R,IR)		$5B_2$(R,IR)	
	↗	↖	↗	↖	↗	↖	↗	↖
D_{2h}	$4A_g$(R)	$3B_{1u}$(IR)	A_u(IA)	$2B_{1g}$(R)	$2B_{2u}$(IR)	B_{3g}(R)	$2B_{2g}$(R)	$3B_{3u}$(IR)

B. Planar-ring models for the complex (C_{2v}) and the pure dimer (D_{2h}).

Symmetry group	Species							
C_{2v}	$7A_1$(R,IR)		$2A_2$(R)		$5B_1$(R,IR)		$4B_2$(R,IR)	
	↗	↖	↗	↖	↗	↖	↗	↖
D_{2h}	$4A_g$(R)	$3B_{3u}$(IR)	A_u(IA)	B_{3g}(R)	$3B_{1u}$(IR)	$2B_{2g}$(R)	$2B_{1g}$(R)	$2B_{2u}$(IR)

large amplitude vibration around the axis connecting the two bridged Cl atoms[6,7].

In our analysis we consider both structures, starting with the D_{2h}, because of its similarity with the Al_2Cl_6(g).

Planar-ring model, D_{2h}. The geometrical parameters[6] are given in Fig. 1. For D_{2h} symmetry, the distribution of the 18 normal modes of vibration are given in Table 1. A complete set of independent symmetry coordinates was used in the analysis. Tomita et al[5]. have given the symmetry - adapted linear combinations of valence coordinates, which also were employed here. In contrast to these researchers[5] we have removed the redundant coordinates at an early stage of the analysis so that our transformation matrix (U) from valence to symmetry coordinates (S=UR) is not orthogonal. The problem was handled in a standard way through the T matrix[8], which pertains to the opposite transformation, i.e. from symmetry coordinates to valence coordinates: R = TS. This matrix is unique in spite of the presence of redundancies among the valence

Table 2. Valence force constants.[a]

	Coordinate(s) involved	Al_2Cl_6[b]	Fe_2Cl_6
Stretch and stretch/stretch (mdyne Å^{-1})			
	A-Y	2.759	2.490
	A-X	1.177	1.025
	A-Y/A-X	0.200	0.177
	A-Y/A-Y'	0.295	0.400
	A-X/A'-X	0.295	0.31
Stretch/bend (mdyne rad^{-1})			
	A-X/XAX	0.227	0.181
Bend and bend/bend (mdyne Å rad^{-2})			
	YAY'	0.654	0.55
	XAX' AXA'	0.595	0.400
	XAY	0.474	0.3785
	YAY'/XAY XAY/XAY'	0.165	0.171
	XAY/X'AY	0.073	0.0524
Torsion (mdyne Å rad^{-2})			
	X'AXA'	0.08075	0.04325

[a] For conversion to SI units: 1 Å = 100 pm, 1 mdyne Å^{-1} = 100 N m^{-1}.

[b] From Tomita et al[5]. Their ring deformation constant was converted to torsion.

coordinates (R). Another difference from the previous work[5] concerns the choice of the ring deformation coordinate. Since we intended to transform the force constants to a model with puckered four-membered ring we chose a coordinate which is applicable to both cases, viz. (1/2) $(\tau_1 - \tau_2 + \tau_3 - \tau_4)$, where τ designates a torsion of a bond in the ring. In the planar-ring case this coordinate is proportional with the ring deformation coordinate used by Tomita et al[5]. Their force constant value for this coordinate could therefore easily be transferred to the force constant associated with the coordinate of our choice.

The force-field approximation of Tomita et al.[7] was used; the force-constant values of this investigation of Al_2Cl_6 are quoted in Table 2. These values were modified by an elaborate trial and error procedure in our adaptation to Fe_2Cl_6. In the course of this procedure we computed the T matrix and used it to determine the contributions of the different valence-coordinate force constants to the symmetry force constants. These transformations could be used to control to some extent the influence of the different force constants on the vibrational frequencies. It was aimed at a best possible fit to the experimental Raman gas frequencies, which are given in Table 3.

The force constants of Fe_2Cl_6 shown in Table 2 are considered as the final set, which gave satisfactory agreement with the mentioned Raman frequencies (Table 3). The measured in Ar matrix infrared frequencies[3], are included in the table. We find a general qualitative agreement with our calculated values amounting to quantitative agreement in some places. We would not expect a greater quantitative accuracy in the reproduction of these data, especially because of matrix shifts when having in mind that the force constants were fitted to Raman frequencies in the gas phase. In conclusion our computations completely confirm the previous assignments of the infrared frequencies[3].

Puckered-ring model (C_{2v}). The geometrical parameters for this structure are also given in Fig. 1. The distribution of the normal modes of vibration can be found in Table 1. The vibrational frequencies for this model have been calculated by transferring the final force constant values described above (and given in Table 2). The frequency shifts due to the ring puckering (see Table 3) are relatively small so that the new calculated frequencies are still compatible with the experimental data. This is due to the fact that the distortions of the puckered ring

Table 3. Observed and calculated vibrational frequencies (cm^{-1}) for Al_2Cl_6 and Fe_2Cl_6.

		Al_2Cl_6[a]		Fe_2Cl_6			
D_{2h}		Obs.	Calc.	Obs.[b]	Calculated		C_{2v}
					D_{2h}	C_{2v}	
A_g	ν_1	511	510	422	421.3	417.5	A_1
	ν_2	337	341	305	304.9	305.8	A_1
	ν_3	219	219	150	155	155	A_1
	ν_4	98	100	78	78	78.7	A_1
A_u	ν_5	-	55	-	44	43.2	A_2
B_{1g}	ν_6	281	282	-	223.1	223	A_2
	ν_7	168	168	-	123.3	126.7	A_2
B_{1u}	ν_8	626	623	467.5	451.1	453.6	A_1
	ν_9	178	178	118.5	133.7	133.9	A_1
	ν_{10}	-	33	24.3	23.5	24.5	A_1
B_{2g}	ν_{11}	614	617	450	449.6	451.9	B_2
	ν_{12}	115	115	92	82.7	83.3	B_2
B_{2u}	ν_{13}	418	415	328.0	331.6	328.3	B_1
	ν_{14}	123	125	98.7	105.1	105.8	B_1
B_{3g}	ν_{15}	-	105	82	81.7	79	B_1
B_{3u}	ν_{16}	483	483	406.0	414.6	411.1	B_2
	ν_{17}	320	318	280.2	255.9	255.6	B_2
	ν_{18}	143	142	115.7	105.7	106.4	B_2

[a] From Tomita et al[5].

[b] For the *g* species Raman gas data[1,2]; *u* species infrared Ar matrix data[3,4].

(C_{2v}) model from the planar-ring (D_{2h}) model are small ($\varphi = 16.7°$).

Furthermore it should be noticed that the Raman and IR intensity of the modes that became active because of the change in symmetry (Table 1) are also expected to be small.

Finally, there seems to be no evidence for distinguishing between the planar and puckered-ring models from the observed spectra. A further modification of the derived force constants is certainly not warrant at the present case.

THE $AlFeCl_6(g)$ MOLECULE

The $AlFeCl_6(g)$ molecule has been found[2,9] in the vapor phase, only in equilibrium with relatively large amounts of $Fe_2Cl_6(g)$ and $Al_2Cl_6(g)$ and thus structural electron diffraction data are very difficult to obtain. However, for the purpose of the normal coordinate analysis and in comparison with other vapor complex species[1], we have assumed that the molecule consists of a $FeCl_4$ distorted tetrahedron bound by an edge with a $AlCl_4$ distorted tetrahedron. As shown in Fig. 2, two bridging chlorine atoms are present, forming a planar four-membered ring. From the structural similarities of the complex molecule with $Al_2Cl_6(g)$[10] and $Fe_2Cl_6(g)$[6,7] the bond lengths and angles given on Fig. 2 have been estimated by assuming that:

i. the bond lengths of the $FeCl_4$ and $AlCl_4$ "tetrahedra" in the vapor complex remain the same as in the corresponding $Fe_2Cl_6(g)$ and $Al_2Cl_6(g)$ molecules.

ii. the terminal chloride bond angles are also the same as in the two pure dimers.

iii. the γ angle (Fig. 2) of the complex is the arithmetic mean of the γ angles of the two dimers.

The symmetry group of the complex is C_{2v} and the distribution of the normal modes is given in Table 1.

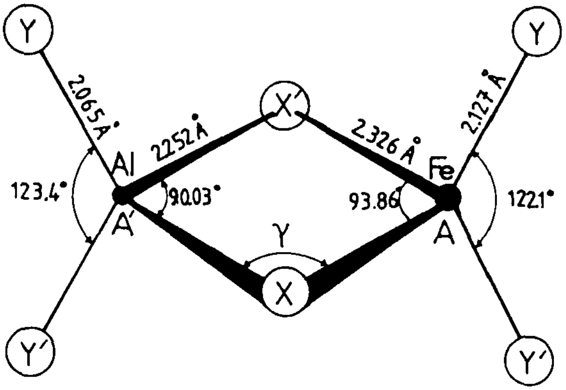

Fig. 2. The AA'X_2Y_4 planar-ring model for the complex molecule $AlFeCl_6$(g).

The force field approximation is the same as that used for Al_2Cl_6(g)[5] and Fe_2Cl_6(g). The force constant values from Al_2Cl_6(g) and Fe_2Cl_6(g) (Table 2) were combined into the force field for $AlFeCl_6$. In two cases, where both Al and Fe are involved we had to assume intermediate values: for f(AXA') and the f(A-X/A'-X) interaction constant the values were estimated to be 0.50 mdyne Å rad^{-2} and 0.30 mdyne $Å^{-1}$, respectively.

The vibrational frequencies calculated from this force field are displayed in Table 4, where they are compared with Raman gas frequencies. This agreement is seen to be excellent.

In Table 4 we have included a correlation of the $AlFeCl_6$(g) frequencies with the calculated values for Al_2Cl_6(g) and Fe_2Cl_6(g) (planar-ring model). As expected we find the $AlFeCl_6$(g) values as intermediate between appropriate frequencies of Al_2Cl_6(g) and Fe_2Cl_6(g). Only in two cases, viz. ν_{16} and ν_{18} of $AlFeCl_6$(g), the calculated frequencies failed to follow this scheme. A splitting has

Table 4. Observed and calculated vibrational frequencies for $AlFeCl_6$. Calculated frequencies for Al_2Cl_6 and Fe_2Cl_6 (see also Table 3); cm^{-1} units.

C_{2v}		$AlFeCl_6$		Al_2Cl_6 (calc.)	Fe_2Cl_6 (calc.)
		Obs.	Calc.		
A_1	ν_1	496	495.2	510(ν_1) 483(ν_{16})	
	ν_2	413	417.4		421.3(ν_1) 414.6(ν_{16})
	ν_3	330	328.5	341(ν_2)	304.9(ν_2)
	ν_4	289	283.4	318(ν_{17})	255.9(ν_{17})
	ν_5	190	187.3	219(ν_3) 142(ν_{18})	
	ν_6	-	121.4		155(ν_3) 105.7(ν_{18})
	ν_7	88	86.5	100(ν_4)	78(ν_4)
A_2	ν_8	-	94.7	55(ν_5) 105(ν_{15})	
	ν_9	52	47.9		44(ν_5) 81.7(ν_{15})
B_1	ν_{10}	620	618.1	623(ν_8) 617(ν_{11})	
	ν_{11}	461	450.7		451.1(ν_8) 449.6(ν_{11})
	ν_{12}	-	159.9	178(ν_9) 115(ν_{12})	
	ν_{13}	-	94.46		133.7(ν_9) 82.7(ν_{12})
	ν_{14}	-	28.3	33(ν_{10})	23.5(ν_{10})
B_2	ν_{15}	-	365.2	415(ν_{13})	331.6(ν_{13})
	ν_{16}	-	320.9	282(ν_6)	223.1(ν_6)
	ν_{17}	151	155.0	168(ν_7) 125(ν_{14})	
	ν_{18}	-	91.5		123.3(ν_7) 105.1(ν_{14})

occurred so that ν_{16} is too high and ν_{18} too low in relation to the frequencies of the pure compounds.

It is clear that the above type of correlations can not be executed with exactness because it is based on the possibility of an approximate description of the normal modes. In principle all frequencies within the same species are mixed. We have in particular confirmed the existence of a considerable mixing for the ν_{16} and ν_{18} frequencies of $AlFeCl_6(g)$, as revealed by the potential ener-

Table 5. Calculated mean amplitudes of vibration (Å units) for Al_2Cl_6, $AlFeCl_6$ and Fe_2Cl_6, planar-ring models.

Distance[a]	Al_2Cl_6 [c] 420 K	$AlFeCl_6$ 440 K	Fe_2Cl_6 463 K
Al···Al	0.091		
Al···Fe		0.100	
Fe···Fe			0.111
$Al-Cl_b$	0.077	0.078	
$Fe-Cl_b$		0.081	0.086
$Al-Cl_t$	0.053	0.053	
$Fe-Cl_t$		0.054	0.055
$Al\cdots Cl_t$	0.202	0.240	
$Fe\cdots Cl_t$		0.227	0.276
$Cl_b\cdots Cl_b$	0.095	0.104	0.116
$Cl_t\cdots Cl_b$	0.156	0.161 0.205	0.198
com $Cl_t\cdots Cl_t$	0.120	0.123 0.150	0.153
trans $Cl_t\cdots Cl_t$	0.164	0.187	0.211
cis $Cl_t\cdots Cl_t$	0.451	0.532	0.664

[a] Abbreviations: b bridged; t terminal.

[c] From Tomita et al.[5]

gy distribution. Nevertheless we are not able to give a good explanation of why the splitting should occur for these frequencies and none of the others. Unfortunately there is no experimental evidence for this phenomenon since neither ν_{16} or ν_{18} have been observed.

MEAN AMPLITUDES OF VIBRATION

The force constants (Table 2) were used to calculate the mean amplitudes of vibration[11] for Fe_2Cl_6(g) and $AlFeCl_6$(g). The results for the planar ring models are shown in Table 5 together with the corresponding data for Al_2Cl_6(g) from literature[5].

Table 6. Calculated and observed mean amplitudes of vibration (Å units) for Fe_2Cl_6 at 463 K.

	D_{2h}		C_{2v}	
Distance[a]	Calculated	Obs.[b]	Calculated	Obs.[b]
Fe···Fe	0.111	0.129(8)	0.116	0.143(6)
$Fe\text{-}Cl_b$	0.086	0.084(2)	0.086	0.084(2)
$Fe\text{-}Cl_t$	0.055	0.059(2)	0.055 0.055	0.059(1)
$Fe\cdots Cl_t$	0.276	0.312(13)	0.319 0.224	0.316(29) 0.190(11)
$Cl_b\cdots Cl_b$	0.116	0.127	0.121	0.141
$Cl_t\cdots Cl_b$	0.198	0.178(5)	0.199 0.199	0.170(5)
com $Cl_t\cdots Cl_t$	0.153	0.162	0.149	0.154
trans $Cl_t\cdots Cl_t$	0.211	0.211(24)	0.240	0.212(20)
cis $Cl_t\cdots Cl_t$	0.664	0.470	0.693 0.540	0.530 0.420

[a] See footnote to Table 5.

[b] Hargittai et al.[6]

A more detailed investigation of Fe_2Cl_6(g) is presented in Table 6, since observed mean amplitude data from gas electron diffraction[6] exist for this molecule. Our calculated values are compared with observed values for both possible structures (planar and puckered-ring models).

The correspondence between the calculated and the electron diffraction values is good within the expected uncertainty limits, except for the cis $Cl_t....Cl_t$ and possibly, the $Fe....Cl_t$ distances. The same discrepancy has been observed for the Al_2Cl_6(g) molecule[5]. The reasoning given in ref. 5 refers to the strong influence of the torsional force constant on these two amplitudes.

Since the corresponding normal mode has a very low frequency, it is notobserved at all for $Al_2Cl_6(g)$[5], or its observation is quite uncertain for $Fe_2Cl_6(g)$[3]. Thus it is possible to fix the torsional force constant such as to take the appropriate value for the mean amplitude without altering the value of the frequency very much. However we believe that this should be avoided because of the unreasonably high value obtained by the torsional force constant in that case. It is possible that the observed disagreement is due to the limits posed in the accuracy of the normal coordinate analysis by the assumption of small harmonic vibrations. This assumption should be invalid for the torsional mode because of its large amplitude.

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