On the Internal Motion of Iron Chloride Molecules

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The vibrationally averaged structures of the iron chloride molecules may considerable differ from their equilibrium structure as a consequence of low-frequency large amplitude vibrations. Mean amplitudes of vibration and perpendicular amplitude correction terms have been calculated for $FeCl_2$ and $FeCl_3$. Mean amplitudes of vibration have also been calculated for D_{2h} (equilibrium structure) and C_{2v} (vibrationally averaged structure) symmetry forms of Fe_2Cl_4 and Fe_2Cl_6. The applicability of normal coordinate analysis for high temperature systems with large amplitude motion is discussed.

Introduction

As part of our research program on low volatile metal halides we have recently carried out electron diffraction structure analyses on $FeCl_2$, $FeBr_2$, Fe_2Br_4 [1] and Fe_2Cl_6 [2], while the monomeric $FeCl_3$ is under investigation at the moment. A normal coordinate analysis has already been performed on the dimeric iron trichloride [3, 4], but there was none on either of the other iron chlorides. Several spectroscopic investigations have been reported so far on different kinds of iron chlorides (gas-phase infrared of Fe_2Cl_6 [5], gas-phase infrared [6] and matrix isolation infrared [7] of $FeCl_2$ and Fe_2Cl_4, matrix isolation infrared of all the four iron chloride species i.e. $FeCl_2$, $FeCl_3$, Fe_2Cl_4 and Fe_2Cl_6 [8] and finally matrix isolation Raman of Fe_2Cl_6 and $FeCl_3$ [9]).

As a number of geometrical data and experimental frequencies are available for these molecules it was felt worthwhile to calculate the mean amplitudes of vibration for $FeCl_2$, $FeCl_3$, Fe_2Cl_4 and Fe_2Cl_6. The reason of recalculating these amplitudes for the dimeric iron trichloride is (a) to have them for the exact temperature of the electron diffraction experiments; (b) in the earlier calculation [4] D_{2h} symmetry was assumed for the molecule, whereas the electron diffraction investigation yielded a puckered ring average structure with C_{2v} symmetry.

Analyses

Approximate diagonal valence force fields were constructed and the valence force constants were transformed to symmetry force constants. These were used to find the L transformation matrix ($S = L\,Q$) by means of the well known secular equation method [10]. The mean amplitudes of vibration (l-values) and the perpendicular correction terms (K-values) have been computed by means of the L matrix and the frequencies. The experimental frequencies were used when available, otherwise theoretical values calculated from the approximate valence force field were used. Since the set of experimental frequencies is not complete (particularly for the dimeric species) the calculated force constants can be considered to be tentative only. An other source of uncertainty is the fact that all frequencies refer to matrices and not to gas phase. It is very difficult to judge the sign and magnitude of the matrix shifts but their effect is certainly important for the lower frequencies. Since the computed values of the mean amplitudes of vibration are not very sensitive to small changes of the force field (or of the frequencies) they are hoped to be reliable. Unfortunately this is not the case with the K-values and therefore they will only be given for the monomeric species where the normal coordinate analysis is more straightforward.

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Results and Discussion

Monomers

The geometrical data of $FeCl_2$ were taken from [1], while for $FeCl_3$ the preliminary data of an electron diffraction investigation being in progress in the Budapest laboratory were used. In case of $FeCl_2$ the frequencies from Refs. [7] and [8] were used while for $FeCl_3$ the frequencies and assignement of [8] were used. There is a disagreement between the interpretation of the spectra in the two works on $FeCl_3$ [8, 9] as to the symmetry of the molecule. According to the infrared spectroscopic investigation [8] the molecule has D_{3h} symmetry, while according to the Raman study [9] the molecule is pyramidal (C_{3v}) with a bond angle of 115°. Since our electron diffraction investigation yields a flat pyramidal vibrationally averaged structure with a larger bond angle, we prefer to believe that the equilibrium structure of the molecule is planar rather than pyramidal.

For the $FeCl_2$ molecule the valence force constants $f_r = 224$ N/m, $f_{rr} = 0.47$ N/m and $f_p = 0.166$ N·m give computed frequenxies that are in agreement with the experimental ones. Using the value of the shrinkage effect from electron diffraction ($\delta_g = 11.9$ pm [1]), the bending frequency of $FeCl_2$ was estimated to be 72 cm^{-1} (between 66 and 81 cm^{-1}, taking into account all the uncertainties of the ED experiment)*.

Valence force constants $f_r = 226$ N/m, $f_{rr} = 0.34$ N/m, $f_\alpha = 22.4$ N·m and $f_\gamma = 3.21$ N/m, with all the others being zero, reproduce the experimental frequencies for planar $FeCl_3$. The calculated l and K values for both molecules are listed in Table 1.

Table 1. Mean amplitudes of vibration, perpendicular correction terms and calculated shrinkages for $FeCl_2$ and $FeCl_3$.

	$FeCl_2$		$FeCl_3$	
	Fe-Cl	Cl ... Cl	Fe-Cl	Cl ... Cl
r, pm	215.9	431.8	213.3	369.4
l, pm				
0 K	4.28	5.41	4.28	7.29
298 K	4.92	6.64	4.90	13.24
723 K			6.83	20.23
893 K	7.56	10.61		
K, pm				
0 K	0.29	0.0	0.21	0.05
298 K	1.37	0.0	0.79	0.21
723 K			1.88	0.49
893 K	4.04	0.0		
δ, pm				
0 K		0.58		0.31
298 K		2.74		1.16
723 K				2.77
893 K		8.08		

Dimers

For both dimers two sets of amplitudes have been calculated. One for D_{2h} symmetry corresponding to the equilibrium structure and one for C_{2v} symmetry that is compatible with the average structure determined by electron diffraction. Since the geometry of the dimeric iron dichloride is not known we assumed it on the basis of the structure of the monomeric $FeCl_2$ and the dimeric Fe_2Br_4 [1]. For the dimeric iron trichloride molecule the geometry determined by electron diffraction at 185 °C [2] was used for all temperatures. Figures 1 and 2 shows the numbering of the atoms and the models of Fe_2Cl_4 and Fe_2Cl_6, respectively. Because of their approximate nature, the force constants of the dimeric species are not given here. Tables 2 and 3 contain the calculated l values for the D_{2h} and C_{2v} symmetry species of Fe_2Cl_4, respectively. The corresponding values for Fe_2Cl_6 are collected in Tables 4 and 5, respectively. In every case the amplitudes are given for absolut zero Kelvin, for room temperature and for the temperature of the electron diffraction experiment. Where available, the corresponding experimental amplitudes are also

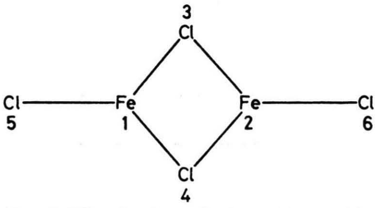

Fig. 1. Numbering of atoms in Fe_2Cl_4 molecule.

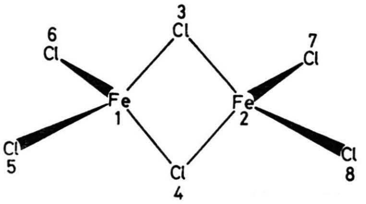

Fig. 2. Numbering of atoms in Fe_2Cl_6 molecule.

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* This frequency was found to be 88 cm^{-1} in [7].

Table 2. Mean amplitudes of vibration for Fe_2Cl_4; D_{2h} symmetry.

Atomic pair	*r*, pm	*l*, pm		
		0 K	298 K	893 K
Fe(1)-Cl(5)	215.9	4.4	5.3	8.2
Fe(1)-Cl(3)	235.9	5.1	6.6	10.6
Fe(1) ... Fe(2)	331.6	5.9	11.0	18.6
Cl(3) ... Cl(4)	335.6	6.7	10.6	17.8
Cl(3) ... Cl(5)	417.0	7.0	11.7	19.7
Fe(1) ... Cl(6)	547.5	6.7	12.3	20.9
Cl(5) ... Cl(6)	763.4	7.4	13.5	23.0

Table 3. Mean amplitudes of vibration for F_2Cl_4; C_{2v} symmetry.

Atomic pair	*r*, pm	*l*, pm		
		0 K	298 K	893 K
Fe(1)-Cl(5)	215.9	4.4	5.2	8.1
Fe(1)-Cl(3)	235.9	5.1	6.5	10.6
Fe(1) ... Fe(2)	327.9	5.4	9.1	15.3
Cl(3) ... Cl(4)	336.5	6.6	9.7	16.3
Cl(3) ... Cl(5)	416.7	6.9	11.4	19.2
Fe(1) ... Cl(6)	542.6	6.2	11.2	18.9
Cl(5) ... Cl(6)	756.0	7.3	16.7	28.5

listed. The agreement between the experimental and calculated values is quite satisfactory. Some of the amplitudes are unusually large as a consequence of the very low frequency torsional motion of the dimeric molecules. These values have been assumed from the spectroscopic calculations in the electron diffraction structure refinement.

In conclusion there is one important thing to be mentioned. Although the calculated mean amplitudes agree well with the experimental ones and they greatly facilitate the electron diffraction investigation, the very low frequencies and the large amplitude motion of these molecules pose some problems. As is well known the normal coordinate analysis is performed under the assumption of small harmonic vibrations. However, many of the inorganic halides have unusually low deformation frequencies and in addition their electron diffraction study often re-

Table 4. Mean amplitudes of vibration for the D_{2h} symmetry form of Fe_2Cl_6.

Atomic pair	*r*, pm	l_{calc}, pm				l_{exp}, pm
		0 K	298 K	461 K	723 K	461 K
Fe (1)-Cl (5)	212.7	4.3	4.9	5.7	6.9	5.9 (2)
Fe (1)-Cl (3)	232.6	4.9	6.1	7.3	8.9	8.4 (2)
Fe (1) ... Fe (2)	320.7	6.0	11.3	13.9	17.4	12.9 (8)
Cl (3) ... Cl (4)	337.1	6.6	10.9	13.3	16.5	12.7 *
Cl (3) ... Cl (5)	363.9	8.1	16.2	20.0	25.0	17.8 (5)
Cl (5) ... Cl (6)	372.3	7.0	12.4	15.2	18.9	16.2 *
Fe (1) ... Cl (7)	462.8	8.1	19.2	23.8	29.7	31.2 (13)
Cl (5) ... Cl (8)	526.7	12.8	38.5	47.8	59.8	[47.8] **
Cl (5) ... Cl (7)	645.0	8.3	17.5	21.6	27.0	21.1 (24)

* Refined together with other parameters. ** Not refined.

Table 5. Mean amplitudes of vibration for Fe_2Cl_6; C_{2v} symmetry.

Atomic pair	*r*, pm	l_{calc}, pm				l_{exp}, pm
		0 K	298 K	461 K	723 K	461 K
Fe (1)-Cl (5)	212.7	4.3	4.9	5.7	6.9	5.9 (1)
Fe (1)-Cl (3)	232.6	4.9	6.1	7.2	8.9	8.4 (2)
Fe (1) ... Fe (2)	323.4	6.1	12.0	14.7	18.4	14.3 (6)
Cl (3) ... Cl (4)	331.0	6.9	11.7	14.4	17.9	14.1 *
Cl (3) ... Cl (5)	363.2	8.0	16.1	19.8	24.7	17.0 (5)
Cl (5) ... Cl (6)	376.1	7.0	12.4	15.2	18.9	15.4 *
Fe (1) ... Cl (8)	442.5	8.6	21.9	27.1	33.9	31.6 (29)
Fe (1) ... Cl (7)	480.9	7.7	17.1	21.1	26.3	19.0 (11)
Cl (5) ... Cl (8)	465.5	13.7	42.5	53.0	66.1	[53.0] **
Cl (6) ... Cl (7)	575.0	11.8	33.9	42.0	52.6	[42.0] **
Cl (5) ... Cl (7)	639.6	8.5	18.8	23.3	29.1	21.2 (20)

* Refined together with other parameters. ** Not refined.

quires high-temperature experimental conditions. Accordingly, the anharmonicity should not be completely ignored.

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