
Molecular Dynamics in Chlorine Compounds Using X-Ray Thermal Parameters and Nuclear Quadrupole Resonance Data

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Molecular dynamics (torsional frequencies) in several chlorine compounds were evaluated on the basis of X-ray thermal parameter data and nuclear quadrupole resonance data using Bayer's and Brown's approximation. It was found that the values obtained in both cases are in good agreement. The above approach is a good illustration of the supplementary nature of the data from X-ray studies in relation to nuclear quadrupole resonance studies of compounds in solid state.

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1. Introduction

Study of nuclear quadrupole resonance (NQR) in molecular solids gives useful information about the molecular dynamics (torsional frequencies) and phase transitions in solids [1]. Usually the torsional frequencies, namely f_x and f_y , are calculated using NQR frequency and crystal structure data, by numerical analysis [2]. The values will be compared with Fourier transformed IR/IR data.

Here an approach has been made to evaluate torsional frequencies at room temperature in number of chlorine compounds using crystal structure and the available X-ray thermal parameters. In order to evaluate the torsional frequencies the mean square angular displacements of various C-Cl bond directions and the available X-ray thermal parameter has been utilized.

2. Method of calculation

The temperature factor of an atom for any set of lattice planes (hkl) depends on the interplanar spacing and on the magnitude of vibration perpendicular to the

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planes. The expression for general temperature factor is given as

$$T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*b^* + 2U_{23}hllb^*c^*)], \quad (1)$$

where a^* , b^* , and c^* are the reciprocal lattice parameters and U_{ij} are called thermal parameters expressed in terms of mean square amplitudes of vibration in pm^2 . The off-diagonal thermal parameters have been neglected, since they are relatively small compared to the diagonal terms. The mean square angular displacement $\langle\theta^2\rangle$ is evaluated using the thermal parameters in the following manner.

TABLE I

Mean square atomic displacements of carbon and chlorine atoms in certain chlorine compounds.

Sl. No.	Compound	Atom	U_{11} [pm^2]	U_{22} [pm^2]	U_{33} [pm^2]	$\langle U \rangle$ [pm^2]
1	2,5-dichlorophenol line I	Cl(1)	23	38	05	22.000
		C(4)	17	28	02	15.666
	line II	Cl(2)	23	37	03	21.000
		C(7)	17	27	03	15.666
2	2,6-dichlorophenol line I	C(4)	74	60	316	150.00
		Cl(1)	94	71	416	193.66
	line II	C(8)	58	62	381	165.66
		Cl(2)	64	100	468	210.66
3	3,5-dichlorophenol line I	C(5)	62	635	54	250.33
		Cl(1)	82	1010	64	385.33
	line II	C(7)	68	676	39	261.00
		Cl(2)	88	1005	46	379.66
4	2,5-dichloro-3,6-dihydroxy <i>p</i> -benzoquinine	C	222	265	153	213.33
		Cl	271	320	166	252.33
5	aniline-2,4,5-trichlorophenol	C(8)	111	115	27	80.333
		Cl(1)	166	155	37	119.66
	line I	C(10)	183	92	42	105.66
	line II	Cl(2)	211	115	43	123.00
	line III	C(11)	122	133	29	94.666
		Cl(3)	172	181	37	130.00
6	2-amino-5-chloropyridine	C(5)	360	2101	1424	1295.0
		Cl(1)	391	2930	2412	1911.0
7	monochloro acetic acid	C(2)	479	662	414	518.33
		Cl(1)	407	522	378	435.67

Let us suppose that the mean square displacements of two atoms forming a bond are given by $\langle U_1^2 \rangle$ and $\langle U_2^2 \rangle$ and the length of the bond is l_{12} , then the mean square displacements of the bond direction would be approximately given by

$$\langle \theta^2 \rangle = (\langle U_1^2 \rangle - \langle U_2^2 \rangle) / l_{12}. \quad (2)$$

The mean square angular displacement values calculated using the above equation are given in Table I.

The NQR motional averaging has been shown to arise from temperature dependent tilting of the z -axis of the electric field gradient (EFG) tensor. One can therefore estimate $\langle \theta^2 \rangle$ for various C-Cl bond directions with the respective EFG z -directions through the NQR data. The torsional frequencies of the molecules are evaluated using the formula

$$\nu_T = \nu_0 \left\{ 1 - \frac{3h}{8\pi^2} \frac{1}{Af_T^2} \left[\frac{1}{2} + \frac{1}{\exp(hf_T/kT) - 1} \right] \right\}. \quad (3)$$

Using high temperature approximation [3, 4], $hf_T/kT \ll 1$, Eq. (3) can be written as

$$\nu_T = \nu_0 (1 - 3kT/8\pi^2 Ac^2 f_T^2). \quad (4)$$

TABLE II
Parameters used for torsional frequency calculations (A is moment of inertia).

Sl. No.	Compound	Atom	A_x [10^{-40} g cm ²]	A_y [10^{-40} g cm ²]	$A = (A_x + A_y)/2$ [10^{-40} g cm ²]
1	2,5-dichlorophenol				
	line I	Cl(1)	478.721	351.688	415.207
	line II	Cl(2)	478.721	351.688	415.207
2	2,6-dichlorophenol				
	line I	Cl(1)	1283.95	753.556	1018.75
	line II	Cl(2)	1306.08	787.538	1046.81
3	3,5-dichlorophenol				
	line I	Cl(1)	1505.0	863.897	1184.44
	line II	Cl(2)	1515.0	863.897	1189.44
4	2,5-dichloro-3,6-dihydroxy <i>p</i> -benzoquinone	Cl(1)	2210.28	1499.04	1854.66
5	aniline-2,4,5-trichlorophenol				
	line I	Cl(1)	2201.27	5119.23	3660.23
	line II	Cl(2)	2201.27	5119.23	3660.23
	line III	Cl(3)	2178.39	5335.97	3757.18
6	2-amino-5-chloropyridine	Cl(1)	978.960	839.930	909.445
7	monochloro acetic acid	Cl(1)	11918.3	5755.07	8836.50

Equation (4) can be expressed in terms of mean square angular displacement as

$$\nu_T = \nu_0[1 - (3/2)\langle\theta^2\rangle]. \quad (5)$$

Comparing Eq. (4) and Eq. (5), the mean square angular displacement $\langle\theta^2\rangle$ is given by

$$\langle\theta^2\rangle = kT/4\pi^2c^2Af_T^2. \quad (6)$$

Therefore

$$f_T = [kT/4\pi^2c^2A\langle\theta^2\rangle]^{1/2}, \quad (7)$$

where $A = (A_x + A_y)/2$ — average value of the moment of inertia and f_T — the torsional frequency. Estimated values of moment of inertia (A) and the torsional frequency (f_T) values are given in Table II and Table III.

TABLE III

Estimated mean square angular amplitudes $\langle\theta^2\rangle$ of the C–Cl directions and corresponding effective torsional frequencies f_T at $T = 300$ K in the following compounds.

Sl. No.	Compound	Atom	C–Cl bond length [pm]	$\langle\theta^2\rangle$ [rad ²]	Torsional frequency(f_T)	
					X-ray data [cm ⁻¹]	NQR data [cm ⁻¹]
1	2,5-dichlorophenol					
	line I	Cl(1)	172.0	0.0080705	58.90	60
	line II	Cl(2)	174.0	0.0062486	67.00	62
2	2,6-dichlorophenol					
	line I	Cl(1)	171.0	0.0051312	47.13	38
	line II	Cl(2)	174.0	0.0055935	44.53	40
3	3,5-dichlorophenol					
	line I	Cl(1)	176.6	0.002750	59.71	65
	line II	Cl(2)	176.9	0.002424	63.50	66
4	2,5-dichloro-3,6-dihydroxy <i>p</i> -benzoquinone	Cl(1)	171.7	0.001610	62.45	58
5	aniline-2,4,5-trichlorophenol					
	line I	Cl(1)	172.9	0.0026469	34.69	33
	line II	Cl(2)	174.5	0.0013021	49.47	47
	line III	Cl(3)	174.7	0.0026010	34.54	42
6	2-amino-5-chloropyridine	Cl(1)	173.6	0.0065500	44.15	42
7	monochloro acetic acid	Cl(1)	177.0	0.0025170	22.56	20.5

3. Results and discussion

Generally, the torsional frequencies of the molecules lie in the range 20 cm^{-1} to 100 cm^{-1} [5]. In the present case, the values obtained by X-ray thermal parameters, were compared with those obtained by NQR data [6–8]. It was found that the values obtained in both cases are in good agreement. The above approach is a good illustration of the supplementary nature of the data from X-ray studies [9–12] in relation to NQR studies of compounds in solid state. It is also interesting to compare this value with the Raman data and infrared data.

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