



DFT Application to the Analysis of Quadrupole Coupling Constant of Aluminum Methyl Chloride Dimers

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Abstract: The analysis of the ^{27}Al and ^{35}Cl quadrupole coupling parameters of aluminum methyl chloride dimers were carried out on the basis of the density functional theory (DFT). The available experimental values of quadrupole coupling constants were compared with their calculated ones. In this investigation, the correlations were made between calculated ^{27}Al and ^{35}Cl nuclear quadrupole coupling constant, χ , and dihedral angles θ , of dimers. These θ s were produced through the ring puckering motions about the hinge line which joins the two bridge atoms. χ s of ^{27}Al and ^{35}Cl were used as probes for monitoring the departure of the symmetry of these dimers from a high symmetry point group to the lower one. It was also found that the common symmetry point group attributed to aluminum methyl chloride dimers is valid only up to dihedral angle, 20° . After this point, puckering motions can cause further break down of symmetry. Moreover, the replacement of bridged chloride by methyl can apparently decrease χ values of ^{27}Al atom. This could be due to the alteration of the orbital density in aluminum atoms.

Key words: DFT; ^{27}Al and ^{35}Cl NQR; aluminum methyl chloride dimers.

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1. Introduction

The molecular structures of organo-aluminum halides were studied by experimental Far-IR and Raman spectroscopy [1,2]. These studies suggest that organo-aluminum halides preferably occur in the form of dimers and the bridge atom might be formed either by alkyl or by chloride (Fig.1) [3,4]. The anticipated model for these compounds is their rigid

form. However, in Al_2X_6 ($\text{X}=\text{Cl}, \text{Br}$), dimers undergo ring puckering motion through the hinge line which joins the bridge halogens [5,6]. A consequence of the ring puckering motion is the conversion of higher symmetry into lower symmetry [5]. Among these, the more favorable structure is the one which is more capable to accommodate large amplitude of ring puckering motions. These dimers are relevant to

Ziegler-Natta catalysis [7,8]. It is shown that spectroscopic methods especially when they coupled with theoretical calculations have the potential to achieve a detailed understanding of the active sites at the molecular level [7]. Theoretical calculations have been used to investigate Ziegler-Natta catalysts [9-16]. Theoretical investigation of the role of AlR_3 ($\text{R}=\text{CH}_3, \text{Cl}$) as cocatalyst for the Ziegler-Natta reaction reveals that AlR_3 facilitates the reduction of the Ti atoms by means of an exchange between the R and Cl ligands [17].

The study of molecular structures of non-transition metal halogenides with the help of nuclear magnetic resonance (NMR) spectra can be complicated by the possibility of rapid interchange of terminal and bridging groups. However, these complexes are particularly interesting from the point of view of nuclear quadrupole resonance spectroscopy (NQR) [18-24]. Our previous study shows that NQR is an efficient method for the recognition of dimers with different conformers [25]. The important physical properties that can be determined both experimentally and theoretically are the nuclear quadrupole coupling constant, χ and the asymmetry parameter, η . χ is sensitive to the shape of electronic charge distribution in molecules and η measures the departure of the electric field gradient (EFG) from axial symmetry. Density functional theory (DFT) was employed to calculate ^{27}Al and ^{35}Cl EFG tensors for six aluminum methyl chloride dimers. The EFG tensors were converted into the χ . The results are summarized in Tables 1-6.

2. Theory

Quadrupolar nuclei ($I > 1/2$) are associated with nuclear quadrupole coupling constant, χ :

$$\chi = \frac{e^2 Q q_{zz}}{h} \quad (1)$$

Where the unit of electrostatic charge is e , h is the plank constant and eQ is the nuclear electric quadrupole moment. χ values are proportional to EFG tensor which originates from the internal electrostatic charges at the site of the quadrupolar nucleus [26,27]. Electric quadrupole moments of ^{27}Al ($I=5/2$) and ^{35}Cl ($I=3/2$) are taken as $Q = -81.65 \times 10^{-27} \text{ cm}^2$ and $Q = 146 \times 10^{-27} \text{ cm}^2$, respectively [28]. Equation 1 was used to direct the relation of the calculated EFG tensors changes with the ring puckering motion and available experimental nuclear quadrupole coupling constant. The χ values of ^{27}Al and ^{35}Cl were calculated by equations 2 and 3, respectively:

$$\chi(^{27}\text{Al}) = 34.454 \times q_{zz} \quad (\text{MHz}) \quad (2)$$

$$\chi(^{35}\text{Cl}) = 19.189 \times q_{zz} \quad (\text{MHz}) \quad (3)$$

2.1. Computational Methods

The EFG at a nucleus, q_{zz} , produced by electron distribution in the molecule, can be obtained with a reasonable effort from DFT calculations. Since it involves only the ground state wave function, it is calculated more readily than, for instance, the chemical shift in NMR. The DFT molecular orbital calculations were carried out with the *Gaussian 98* program [29]. Six conformers of aluminum methyl chloride were selected (Fig.1).

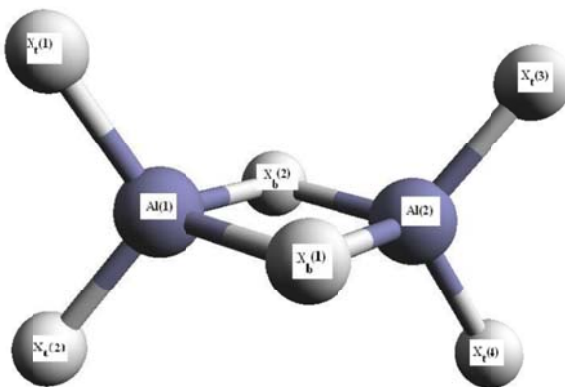


Fig.1. Molecular structure of a-f aluminum methyl chloride compounds.

a: $\text{AlCl}_3, \text{AlCl}_1\text{met}_2(\text{t})$	b: $\text{AlCl}_1\text{met}_2(\text{t}), \text{AlCl}_1\text{met}_2(\text{t})$	c: $\text{AlCl}_2\text{met}_1(\text{t}), \text{AlCl}_2\text{met}_1(\text{t})$
d: $\text{AlCl}_3, \text{AlCl}_2\text{met}_1(\text{b})$	e: $\text{AlCl}_2\text{met}_1(\text{t}), \text{AlCl}_1\text{met}_2(\text{t})$	f: $:\text{AlCl}_3, \text{AlCl}_2\text{met}_1(\text{t})$

The partially geometry optimization at constant dihedral angles, $\theta < \text{dih}(X_{b1}\text{Al}_1-\text{Al}_2X_{b2})$ ($X_b = \text{Cl}$ or CH_3) and the computation of the components of EFG tensors, eq_{xx} , eq_{yy} and eq_{zz} in principal axis system (PAS) were done at B3LYP/6-311G* level of theory. The relevant study also applied B3LYP method with the 3-21G and 6-311G* basis sets of NQR parameters for the dimers of transition and non-transition metal halogenides [30]. Their research has proved the reliability of DFT method for the description of the geometry and NQR frequencies of these dimers. Further investigation established a correlation coefficient between experimental and theoretical ^{27}Al χ s of aluminum chloride compounds [31]. The results of the calculations are summarized in Tables 1-6.

3. Results and Discussion

The nuclear quadrupole coupling constants was performed to differentiate between different conformers of six aluminum methyl chloride compounds. These conformers were generated by

varying the ring puckering angle, θ . The angle was varied from 0° up to 40° , using 10° increments. Our pervious study shows that nuclear quadrupole coupling constant is a better alternative than geometrical parameters for distinguishing between different conformers of Al_2Cl_6 as well as Al_2Br_6 [25].

I: $\text{AlCl}_3, \text{AlCl}_1\text{met}_2(\text{t})$

At equilibrium, Fig.1a, the point group symmetry, C_{2v} shows two kinds of aluminum and chloride (Table 1). Changing the dihedral angle from 0° to 20° , apparently cause no significant variations in the χ values of this dimer. After 20° , there is no symmetry element(s) to convert the bridge chlorides into each other. However, for terminal chlorides this happens after 30° . As Table 1 shows, the χ value of $^{27}\text{Al}(2)$ is about 30 MHz higher than the one of $^{27}\text{Al}(1)$. One may conclude that replacement of one terminal electronegative group, chloride, by methyl group increases the electron density in a bridged $^{27}\text{Al}(2)$ atom.

Table 1. Calculated χ_s , MHz, (^{27}Al , ^{35}Cl) of (AlCl_3 , $\text{AlCl}_1\text{met}_2(\text{t})$)

θ^a	Al(1)	Al(2)	Cl(b1)	Cl(b2)	Cl(t1)	Cl(t2)
0	13.461	43.100	22.489	22.505	26.470	26.470
10	13.434	43.134	22.560	22.590	26.531	26.410
20	13.365	43.055	22.783	22.906	26.600	26.482
30	13.511	42.453	23.287	23.737	26.700	26.842
40	15.967	42.053	23.978	24.926	26.883	27.404

^a Dihedral angle ($\text{Cl}_{b1}\text{-Al}_1\text{-Al}_2\text{-Cl}_{b2}$)**Table 2.** Calculated χ_s , MHz, (^{27}Al , ^{35}Cl) of ($\text{AlCl}_1\text{met}_2(\text{t})$, $\text{AlCl}_1\text{met}_2(\text{t})$)

θ^a	Al(1)	Al(2)	Cl(b1)	Cl(b2)	Exp. $^{27}\text{Al}^b$
0	39.062	39.033	20.765	20.763	36.4
10	38.996	39.014	20.785	20.789	
20	38.369	38.873	20.877	20.911	
30	38.315	39.169	21.249	21.323	
40	37.348	40.174	21.764	21.579	

^a Dihedral angle ($\text{Cl}_{b1}\text{-Al}_1\text{-Al}_2\text{-Cl}_{b2}$) ^b M. J. S. Dewar, D. B. Patterson, W. I. Simpson, J. Am. Chem. Soc., 93 (1971), 1030.**II: $\text{AlCl}_1\text{met}_2(\text{t})$, $\text{AlCl}_1\text{met}_2(\text{t})$**

($\text{AlCl}_1\text{met}_2(\text{t})$, $\text{AlCl}_1\text{met}_2(\text{t})$), Fig. 1b, has D_{2h} symmetry in its static form. This means that there is an identical χ for bridge chlorides. Also, it implies having the same χ for aluminums. Changing the dihedral angle from 0° to 10° appears not to cause any significant deviation from the assigned D_{2h} symmetry. Within the range of $10\text{-}20^\circ$, there is a correlation between the χ_s of bridge chlorides.

In this range, the symmetry point group is reduced to C_{2v} . After 20° , puckering motions lead to further reduction of the symmetry, Table 2. From this point on, the χ_s of two chlorides change appreciably. At equilibrium, the calculated χ of ^{27}Al , 39.0 MHz, is in

agreement with experimental ones, 36.4 MHz [23].

III: $\text{AlCl}_2\text{met}_1(\text{t})$, $\text{AlCl}_2\text{met}_1(\text{t})$

($\text{AlCl}_2\text{met}_1(\text{t})$, $\text{AlCl}_2\text{met}_1(\text{t})$), Fig. 1c, is expected to have C_{2h} symmetry at equilibrium. Therefore, it has identical χ values for both aluminums and chlorides. Table 3 shows that the two bridge chlorides have similar chemical environment up to 20° . The calculated χ of ^{27}Al , 27.4 MHz, is in agreement with experimental ones, 25.6 MHz [23]. The χ of bridged chloride is 90.5% of the χ value of terminal chloride. This is in agreement with studies of RAlCl_2 dimer which indicate that the bridging halogens exhibit NQR transitions which are at 91.5-92.5% of the values for the terminal ones [23,32].

Table 3. Calculated χ_s , MHz, (^{27}Al , ^{35}Cl) of $(\text{AlCl}_2\text{met}_1(\text{t}), \text{AlCl}_2\text{met}_1(\text{t}))$.

θ°	Al(1)	Al(2)	Cl(b1)	Cl(b2)	Cl(t1)	Cl(t2)	Exp. ^{27}Al	^{27}Al
							$^{27}\text{Al}^b$	6-311G*/3-21G ^c
0	27.426	27.421	22.511	22.514	24.879	24.877	25.6	27.8
10	27.717	27.449	22.420	22.425	24.483	24.393		
20	27.817	27.336	22.691	22.744	24.500	24.419		
30	27.658	27.236	23.256	23.411	24.456	24.662		
40	27.492	27.931	24.081	24.299	24.401	24.980		

^a Dihedral angle (Cl_{b1}-Al₁-Al₂-Cl_{b2}).

^b M. J. S. Dewar, D. B. Patterson, W. I. Simpson, J. Am. Chem. Soc., 93 (1971), 1030.

^c O. Kh. Polechuk, E.L. Kalinina, J.N. Latosin'ska, J. Koput, J. Mol. Struct. (Theochem), 574 (2001), 233.

Table 4. Calculated χ_s , MHz, (^{27}Al , ^{35}Cl) of $(\text{AlCl}_3, \text{AlCl}_2\text{met}_1(\text{b}))$.

θ°	Al(1)	Al(2)	Cl(b)	Cl(t1)	Cl(t2)	Cl(t3)	Cl(t4)
0	11.390	11.480	22.937	25.718	25.719	25.729	25.727
10	11.449	11.490	22.974	25.814	25.640	25.664	25.810
20	11.562	12.237	23.063	26.020	25.590	25.635	26.027
30	11.651	14.208	23.369	26.413	25.523	25.622	26.422
40	12.299	19.536	23.603	26.947	25.501	25.639	26.877

^a Dihedral angle (Al₁-Cl_b-(CH₃)_b-Al₂).

IV: $\text{AlCl}_3, \text{AlCl}_2\text{met}_1(\text{b})$

This is a dimer in which one of the bridge halogens is replaced by a $-\text{CH}_3$ group (Fig.1.d). The symmetry point group of this molecule at equilibrium is C_{2v} . So, one expects that all terminal chlorides have identical chemical environment. According to Table 4, their χ values are the same up to 10° .

After 10° , the terminal chlorides are clearly divided into two groups. The difference between their χ_s gradually increases. The χ values of two aluminums are the same up to 10° . From this point on, the χ_s of two aluminums differ considerably. A closer look at the χ values of ^{27}Al presented in Tables 1-4 shows a

meaningfully decrease of ^{27}Al χ_s in this dimer.

V. $\text{AlCl}_2\text{met}_1(\text{t}), \text{AlCl}_1\text{met}_2(\text{t})$ & $\text{AlCl}_3, \text{AlCl}_2\text{met}_1(\text{t})$

Both of these dimers possess C_s point group at equilibrium. Tables 5 and 6 indicate that the bridge chlorides in these molecules have identical χ values up to 30° . After this point on, the χ_s of bridge chlorides are disintegrated. Consequently, their plane of symmetry disappears. According to NQR, the spectra for a number of aluminum alkyl halides, each replacement of one terminal chloride in dimer by methyl, can increase χ of Al by ca.12 MHz [23]. The results of Tables 1 and 5 confirm this conclusion.

Table 5. Calculated χ_s , MHz, (^{27}Al , ^{35}Cl) of ($\text{AlCl}_2\text{met}_1(\text{t}), \text{AlCl}_1\text{met}_2(\text{t})$)

θ^a	Al(1)	Al(2)	Cl(b1)	Cl(b2)	Cl(t)
0	26.022	41.166	21.462	21.452	24.303
10	25.994	40.975	21.552	21.548	24.266
20	25.883	40.863	21.756	21.754	24.287
30	25.470	40.909	22.254	22.207	24.248
40	25.339	42.034	22.946	22.405	24.244

^a Dihedral angle ($\text{Al}_1\text{-Cl}_{\text{b1}}\text{-Cl}_{\text{b2}}\text{-Al}_2$)**Table 6.** Calculated χ_s , MHz, (^{27}Al , ^{35}Cl) of ($\text{AlCl}_3, \text{AlCl}_2\text{met}_1(\text{t})$)

θ^a	Al(1)	Al(2)	Cl(b1)	Cl(b2)	Cl(t1)	Cl(t2)	Cl(t3)
0	15.043	28.880	23.358	23.382	24.805	26.714	26.861
10	14.887	29.002	23.502	23.495	26.657	26.882	24.830
20	14.651	29.208	23.810	23.811	26.618	26.910	24.865
30	14.237	29.517	24.381	24.392	26.781	26.966	24.869
40	14.647	30.585	25.330	24.731	26.932	26.914	24.920

^a Dihedral angle ($\text{Cl}_{\text{b1}}\text{-Al}_1\text{-Al}_2\text{-Cl}_{\text{b2}}$)

4. Conclusion

Nuclear quadrupole coupling constants of ^{27}Al and ^{35}Cl in different conformers of six aluminum methyl chloride dimers were calculated using DFT method. These conformers were created through the hinge line which joins the two bridge atom.

According to the results, the calculated χ values are in good agreement with available experimental ones. Also, the correlations between nuclear quadrupole coupling constants, χ_s and dihedral angles, θ_s were meaningful (Table 1-6). It was also found that the common symmetry point group attributed to

aluminum methyl chloride dimers is valid only up to dihedral angle, 20° . After this point, puckering motions can cause further break down of symmetry. Moreover, the replacement of bridged chloride by methyl can apparently decrease χ values of ^{27}Al atom. This could be due to the alteration of the orbital density in aluminum atoms.

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