

Theoretical And Vibrational Study of Tetraethylammonium Hexafluorosilicate of [(C₂H₅)₄N]₂SiF₆

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Abstract— Systematically study of crystal structures and molecules of compounds R₂MX₆ type of the general formula R₂MX₆ or R: cation substitute Ammonium, M: tetravalent metal and X: Halogène have a big importance for interpretation of certain number of basic physical propriety of crystals of this family [1]. In this study we determined in advance the structure of compounds tetraethyl ammonium hexafluorosilicate of formula [(C₂H₅)₄N]₂SiF₆ by using the technique of diffraction RX in powder which is calculated in normal temperature and after resolution of principal peak, we have seen that this compound is crystallized in monoclinic system with a space group P2₁[2]. Theoretical analysis of cation [(C₂H₅)₄N]⁺ displays that the outnumbering of vibration in the molecular group D_{2d}, we have 177 modes of internal vibrations and 6 modes of vibration for anion SiF₆²⁻[2].

Experimentally results [2] are comparable with those obtained theoretically by the HF method with STO-3G basis [7].

Keywords—tetraethylammonium; hexafluorosilicate; Crystal; Theoretical analysis; IR spectra.

I. INTRODUCTION

The IR vibrational spectra of hexachlorostannate alkylammonium compounds of the general formula where is R₂MX₆: ammonium cation substituted, M: tetravalent metal (M = Re, Te, Sn, U, Sb, Si, Pt, Zr, Pd) and X: halogen (X = Cl, F, I, and Br) has been widely reported in the literature have been classified into various structural types. Their classification depends mainly: methods of synthesis, nature and size of the organic groups [1]. In terms of crystal symmetry, the compounds of this type generally have a kinship with anti-fluorite structure of the compound (NH₄)₂SnCl₆[1], in these compounds the symmetry of tetrahedral site occupied by the cation is the same as cation of free Td (43m), the vertices and centres of faces of the mesh cube are occupied by anion MX₆²⁻ with orientation compatible with the symmetry Fm3m. Generally, the compounds of the types [(R₄N)₂N]₂MCl₆ antifluorines keep their network, they sometimes suffer distortions and become a different symmetry in certain

compounds, the observation of reflections not indexed in the Fm3m symmetry (Z=4) shows that the symmetry is exactly Fd3c [6, 5]. Maximum when the symmetry of the cation does not reach Td, the crystal is much lower than Fm3m, SnCl₆²⁻ anions can suffer distortions and rotational movements around the central atom Sn. such a situation is observed for hexachlorostannate of CH₃NH₃⁺ and (CH₃)₃NH⁺ trigonal symmetry [4].

The IR spectroscopy of [(C₂H₅)₄N]₂SiF₆ was performed on the basis of a C1 symmetry for cations and anions [7] it was concluded that these groups are located on general positions compatible with the group space P2₁.

Our objective is to study quantum compound of formula [(C₂H₅)₄N]₂SiF₆ aim to make an identification with the experimental results [2].

Characterization of [(C₂H₅)₄N]₂SiF₆ by X-ray diffraction powder has enabled us to provide a better structure for this compound.

The study vibrational spectroscopic IR is developed to achieve additional information from those determined by X-ray diffraction for this compound. This study is supported by calculations of vibrational spectra from the theoretical optimized geometry obtained by calculating HF/STO-3G [8], allowing us to achieve a more rigorous assignment of the bands observed in the experimental IR spectrum.

II. EXPERIMENTAL

The single crystals of formula [(C₂H₅)₄N]₂SiF₆ is obtained by slow evaporation, at room temperature, of a hydrofluoride acid solution containing stoichiometric amounts of tetraethylammonium (C₂H₅)₄N⁺, (acidified with (HF) and SiCl₄.

The characterization by X-ray diffraction of tetraethyl ammonium hexachlorosilicate was performed using a diffractometer system "XPRT-PRO" menu of a Goniometry "PW3050/60" to counter, anticathode copper (Cu) lengths wave K-Alpha 1.54 Å [2].

Infrared spectra is recorded at room temperature in the 400–4000 cm^{-1} spectral range with 8 cm^{-1} resolution with Bruker Tensor 27 FTIR spectrometer and the application of the KBr pellet technique [2].

III. RESULTS AND DISCUSSIONS

A. Crystallography

The x-ray crystallographic data obtained at ambient temperature $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{SiF}_6$ indicated that it belongs to the monoclinic system with the space group $\text{P}2_1$ shows that this compound crystallizes in the monoclinic system with its setting: $a = 13.430\text{\AA}$, $b = 13.825\text{\AA}$, $c = 12.940\text{\AA}$, $\beta = 90.942^\circ$, Cell volume: $V = 2402.24$ and space group $\text{P}2_1$ [2].

B. Quantum Calculations

The quantum calculations have allowed us to optimize the geometry of this compound [8] and to establish the infrared spectra of a vibrational frequency calculation [8]. This was achieved using HF method and STO-3G basis (HF/STO-3G).

1) optimized geometry

Optimized geometry of the complex of formula $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{SiF}_6$ is obtained by the method HF/STO-3G using the program GAUSSIAN 07 (Figure 1) [8].

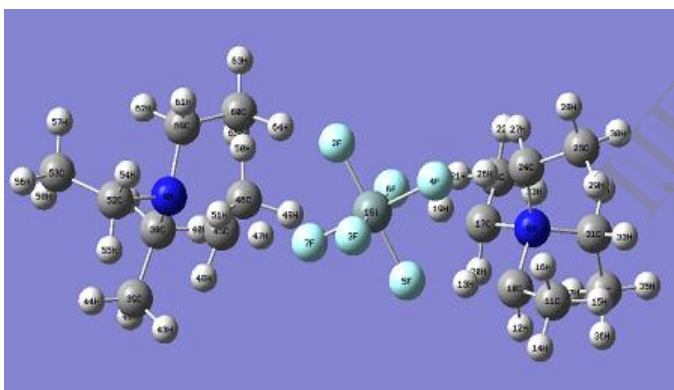


Figure 1: The optimized Geometry of complex $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{SiF}_6$ method HF/STO-3G

2) Geometric theoretical and experimental parameters of $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{SiF}_6$

The theoretical geometric parameters are comparable with those obtained experimental in the case of compounds same family (Table 1) [1, 2,3].

Parameters	Theoretical values	experimental values
Si-F	1.6484- 1.6873	2.680 - 2.668
N-C	1.5309- 1.5639	1.528 - 1.548
C-C	1.5362- 1.5411	1.513 - 1.561
CNC	107.65- 112.535	107.0 - 113.5
NCC	114.75- 116.35	112.5 - 114.3

Table1: Interatomic distances (\AA) in angstroms and bond angles in degrees ($^\circ$) of $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{SiF}_6$

Geometrical parameters of the angles that which we no have experimental values for the family compound $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{SiF}_6$ are grouped in the table below (Table 2).

Values of the compound geometric dihedral of compound $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{SiF}_6$ confirms the XRD results leave theoretical analysis and can also be made by the interpretation made the CH_3 and CH_2 groups are distorted and rotational displacements around the central atom if those who will lead a lowering of symmetry crystalline compound (Table 3).

Tableau 2: Angles in degrees of connection the complex $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{SiF}_6$

A	V/U(Degré)	A	V/U(Degré)
C-C-H	112.25-114.24	F-F-F	108.5
Si-F-H	69.10-138.75	F-F-C	63.84-116.86
F-Si-H	70.35-114.22	Si-F-C	123.59
H-Si-H	20.64-67.50	F-H-H	57.03
F-Si-C	94.1134	F-H-C	154.90-177.7
C-F-H	44.74-64.47	F-C-N	108.4907
F-C-H	164.0229	N-H-F	61.3245
H-F-H	49.94-60.34	N-H-C	114.3288
F-Si-F	87.80-91.68	N-C-H	104.60-109.70
H-C-H	107.27-112.08	Si-H-H	120.309
		F-F-C	63.83-116.86

A : Angles ; V : Valeurs ; U : unités

Tableau 3: Deidre of connection the complex
[(C₂H₅)₄N]₂SiF₆

D	V/U(Degré)	D	V/U(Degré)
H-C-C-H	(-177,9)- (178,17)	H-F-H-C	(-27,89)-(49,90)
C-C-H-F	(-158,8)-(178,5)	C-F-H-C	(-22,28)-(21,89)
N-C-C-H	(-178,31)- (178,11)	Si-F-H-C	(-22,80)-(19,86)
C-N-C-H	(-179,22)- (179,23)	F-Si-F-H	(-173,06)- (158,74)
C-N-C-C	(-176,80)- (173,54)	H-F-H-F	(-176,70)- (107,91)
F-C-C-H	(-176,11)- (65,11)	F-Si-F-C	(-122,05)- (149,56)
N-C-H-F	(-56,27)-(77,46)	C-F-F-H	(-170,68)- (156,58)
H-F-C-C	(-15,11)- (146,25)		

A : Angles ; V : Valeurs ; U : unités

3) Theoretical and Experimental vibrationnal spectra of [(C₂H₅)₄N]₂SiF₆

The infrared spectra experimental of [(C₂H₅)₄N]₂SiF₆ (Figure II), the latter is mixed with 95% KBr, is recorded at T=25°C in the frequency range between 400 and 4000 cm⁻¹, and with a spectral resolution of 8 cm⁻¹ the different peaks observed and their assignment will be reported in (Table IV) [2].

Theoretical and experimental Infrared Spectra of [(C₂H₅)₄N]₂SiF₆ are similar to how they show (figure 2 and 3).

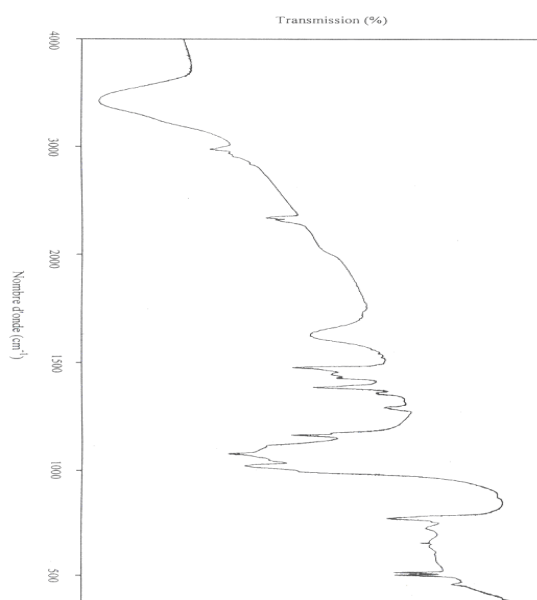


Figure 2: Experimental Infrared Spectra of [(C₂H₅)₄N]₂SiF₆

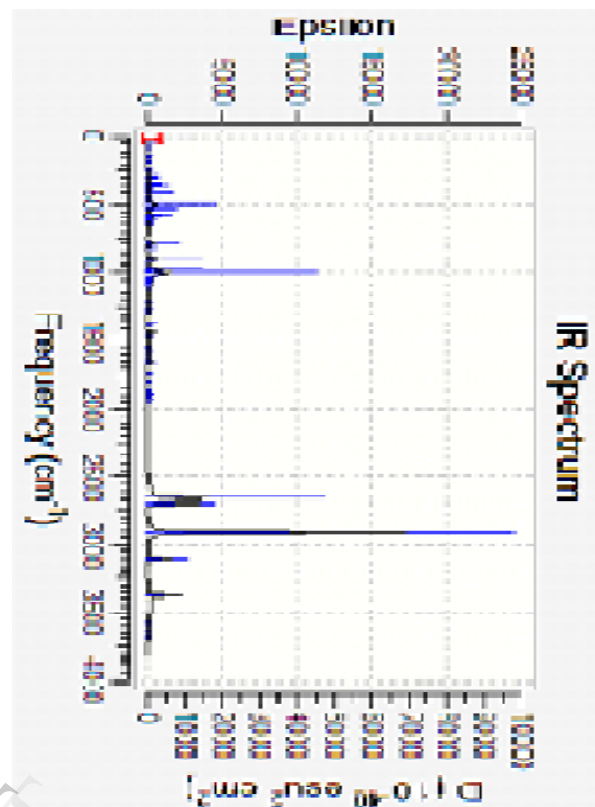


Figure 3 : Theoretical Infrared Spectra of [(C₂H₅)₄N]₂SiF₆

4) Identification and interpretation the IR spectrum experimental and theoretical of [(C₂H₅)₄N]₂SiF₆

Experimental and Theoretical spectra of tetraethyl ammonium hexafluorosilicate studied are comparable, which we shared in the areas mentioned below:

a) Domain in which these frequencies below 533 cm⁻¹:

These frequencies are assigned to the whole molecule of vibration and movement Roking CH₃ and CH₂ groups.

b) Frequency range 533-1100 cm⁻¹:

These piks we attributed to the stretching of the Si-N bonds and F (ν CN) / (ν Si-F), and deformation of entities CH₃ CH₂ and torsion symmetrical DC link shown respectively to the frequencies 1083, 1060 and 1029 cm⁻¹ asymmetrical deformation of the CH₃ group CH₂ and CN bond torsion asymmetric and CC are located about 1100 cm⁻¹.

c) Frequency range 1174-1396 cm⁻¹:

In this area we have allocated these frequencies to asymmetric deformation modes of CH₂ and CH₃ groups, Roking CH₃ and torturers of liason CC.

d) Frequency range 1450-1750 cm^{-1}

Frequencies that appear vers 1450 cm^{-1} are attributed to deformation of the angles HCH and CNC groups CH_3 , CH_2 and CH_3 deformation, CH_2 and CH_3 group of Roking are located vers 1620 cm^{-1} and finally twisting motion appears around 1750 cm^{-1} .

e) Frequency range 2750 -3250 cm^{-1} .

The piks that appear in this area are attributed to CH stretching of liaison.

Tableau 4: Experimental and Theoretical Frequency of $[(C_2H_5)_4N]_2SiF_6$

$\nu_{Exp}(Cm^{-1})$		$\nu_{th}(Cm^{-1})$		Assignment
		50	f	Roking (molécule)
		150	tf	Vibration (molécule)
		250	f	Vibration (cation)
		300	f	Vibration (molécule)
471	f	450	f	Vibration (molécule)
		400	f	
533	m	500	f	Vibration (molécule)
521	m	550	f	
671	f	650-670	f	δ (F-Si-F) / δ (C-N-C) / δ (C-C-N)
787	m	800	f	(vs C-N) / (vs Si-F)
741	f			
1029	m	950	f	$\delta_s(CH_3)$ $\delta_s(CH_2)$ / (tsC-C)
		900	f	
1083	F			$\delta_s(CH_3)$ / $\delta_s(CH_2)$ / (tsC-C)
1060	ep	1050	tf	
1100	ep	1100	tf	$\delta_s(CH_3)$ $\delta_s(CH_2)$ / r(CH ₃) / (va C-N) / (taC-C)
1180	ep			
1174	m	1200	tf	$\delta_a(CH_3)$ $\delta_a(CH_2)$ / r(CH ₃) / (taC-C)
1305	f	1300	tf	$\delta_a(CH_3)$ $\delta_a(CH_2)$
1365	f	1440	tf	$\delta_a(CH_3)$ $\delta_a(CH_2)$
1396	m	1460	f	$\delta_a(CH_3)$ $\delta_a(CH_2)$
1450	f	1489	m	δ (H-C-H) δ (C-N-C) / $\delta_a(CH_3)$ $\delta_a(CH_2)$

ν_{Exp} : Experimental frequency ; ν_{th} : Theoretical Frequency

1620	f	1650	tf	$\delta_a(CH_3)$ $\delta_a(CH_2)$ / r(CH ₃) / r(CH ₂)
1750	m L	1850	tf	Twisting (CH ₃)
2750	ep	2650-2700	f	ν (C-H)
2985	f	2900	TF	ν (C-H)
2960	f			
3250	TF L	3150-3350	f	ν (C-H)

IV-CONCLUSION

The interpretation of the IR spectrum of $[(C_2H_5)_4N]_2SiF_6$ was done satisfactorily on the basis of a C_1 symmetry for cations and anions, it can be concluded that these groups are located on general positions consistent with space group $P2_1$.

The calculation of vibrational frequencies by the method HF/STO-3G values provided in good agreement with the experimental values that allowed us to establish a detailed allocation of the IR spectrum. Frequencies of the entities constituting the crystal show no significant difference compared to their frequencies in the free state, thus reflecting the ionic character of this compound and the individuality of the entities that constitute it.

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