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Contribution of Infrared Spectroscopy to the Vibrational Study of Ethylenediammonium Chloride Thiocyanate: (C₂H₁₀N₂) (Cl NCS)

Sahel Karoui and Slaheddine Kamoun

Abstract

The C₂H₁₀N₂ Cl NCS (EDCT) compound is characterized by using infrared spectroscopy. The infrared spectrum of the title compound was recorded (400–4000 cm⁻¹) at room temperature and discussed, essentially in terms of vibrational modes of [C₂H₁₀N₂]²⁺ cations and [SCN]⁻ and [Cl]⁻ anions. Ethylenediammonium thiocyanate chloride crystallizes, at room temperature, in the triclinic system, space group P1 (C_i). The entities [C₂H₁₀N₂]²⁺, [SCN]⁻ and [Cl]⁻ occupy sites of symmetry (C₁). Several ground state thermodynamic parameters were calculated using the ab initio Hartree-Fock (HF) and DFT (B3LYP) methods with 6-31++G (d, p) and 6-311++G (d, p) basic sets such as vibration frequencies, rotation constants, and optimized molecular geometry. The comparison between the theoretical and experimental infrared spectrum showed good agreement.

Keywords: ethylenediammonium chloride thiocyanate, IR, vibrational spectra, DFT calculations

1. Introduction

This chapter is devoted to the characterization of C₂H₁₀N₂ Cl NCS by infrared vibrational spectroscopy. These studies make it possible to highlight the structural analogies and to possibly provide some additional information to those obtained by X-ray diffraction. In this chapter, we used group theory; indeed, this valuable tool allows both to count the normal vibration modes of vibration of a crystal and to describe these vibrations in symmetrical coordinate terms. In addition, an attempt is made to assign the various modes of vibration to all the bands that have appeared. It is based on predictions theories and previous work carried out on similar compounds. Infrared is a research tool can also provide exquisite structural insights into the molecule and characterizes the vibrational modes of the molecules and has enfolded within it much information on chemical structure [1]. The combined use of FT-IR spectroscopy extracts most of the obtainable information and these are the popular tools in the chemist and physicist. Amine, amino acid and Schiff bases [2–6] have recently been the focus of coordination chemists due to their

preparative accessibilities, structural varieties, and varied denticities. With those purposes, first, the EDCT was synthesized [7] and then characterized it by Infrared Spectroscopy. Simultaneously, to obtain the ground state optimized geometries and the vibrational wavenumbers of the different normal modes, we carried out the *ab initio* HF and DFT calculations. Here, the hybrid B3LYP method was used together with the 6-31++G (d, p) and 6-311++G (d, p) basis sets [8].

2. Experimental details

2.1 Synthesis

The title compound has been obtained by mixing, in stoichiometric proportions, a solution of ethylenediamine, a freshly prepared solution of thiocyanic acid HSCN and a solution of potassium halide. KX (X = Cl) [7].

2.2 IR spectroscopy

Infrared absorption spectrum was recorded at room temperature in the 400–4000 cm^{-1} frequency range on a Perkin-Elmer spectrometer equipped with a Universal ATR Accessory (UATR).

2.3 Computational details

Numerous studies [9–12] have shown that the method DFT-B3LYP in combination with the bases 6-31++G (d, p) and 6-311++G (d, p) allowed to determine with precision energies, molecular structures and infrared vibratory frequencies. In the ground state the molecular structure of the $\text{C}_2\text{H}_{10}\text{N}_2\text{Cl NCS}$ (EDCT) phase calculated was optimized by the use of the DFT/B3LYP methods with the methods 6-31++G (d, p) and 6-311++G (d, p) base set, and the calculated optimized structure was used in vibrational frequency calculations. The calculated harmonic vibratory frequencies and the minimal energy of the geometric structure were scaled by (B3LYP) with the base set 6-31++G (d, p) and 6-311++G (d, p). HF/DFT calculations for EDCT are performed using GAUSSIAN 03W program [13, 14]. On the other hand, the energies of the frontier orbital's were used to calculate the gap energy values and some interesting descriptors in order to predict their reactivities and behaviors at the same level of theory [14–17].

3. Results and discussion

3.1 Molecular geometry

The structure of the EDCT belongs to C_i point group symmetry and its molecular structure is obtained from GAUSSAN 03W and GAUSSVIEW programs are shown in **Figure 1**. The molecule contains one diprotonated ethylenediammonium cation, one Cl^- and one SCN^- anions. The comparative optimized structural parameters such as bond lengths and bond angles are presented in **Table 1**. The comparative graphs of bond lengths and bond angles of ethylenediammonium chloride thiocyanate for two sets are presented in **Figures 2** and **3** respectively. Most of the optimized bond lengths are slightly higher than the experimental values, depending on the theoretical values, because the theoretical calculations belong to isolated molecules in the gas phase and the experimental results to solid state molecules. The

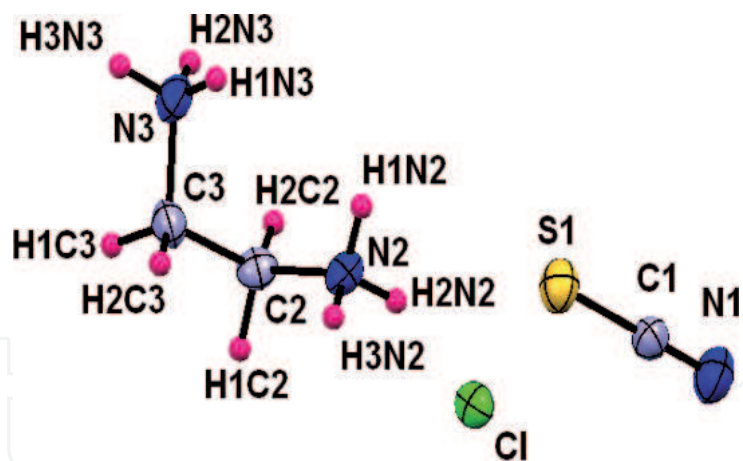


Figure 1.
Molecular structure of ethylenediammonium chloride thiocyanate.

Geometrical parameters	Methods			
	HF/6-311++G (d. p)	B3LYP/6-31++G (d. p)	B3LYP/6-311++G (d. p)	Experimental value [12]
Bond length (Å)				
S(1)–C(1)	1.6314	1.6324	1.6324	1.6358(12)
C(1)–N(1)	1.1651	1.1687	1.1651	1.1573(16)
C(2)–N(2)	1.4847	1.4284	1.4847	1.4798(14)
C(3)–N(3)	1.4817	1.5107	1.4817	1.4834(15)
C(2)–C(3)	1.5066	1.5334	1.5066	1.5054(15)
C(2)–H(1C2)	0.9763	1.0926	0.9763	0.9700
C(2)–H(2C2)	1.0059	1.0927	1.0059	0.9700
C(3)–H(1C3)	0.9694	1.0971	0.9694	0.9700
C(3)–H(2C3)	1.0299	1.0930	1.0299	0.9700
N(2)–H(1N2)	0.9048	1.0333	0.9048	0.8900
N(2)–H(2N2)	0.8967	1.0357	0.8967	0.8900
N(2)–H(3N2)	0.8660	1.0264	0.8660	0.8900
N(3)–H(1N3)	0.8665	1.0202	0.8665	0.8900
N(3)–H(2N3)	0.8639	1.0540	0.8639	0.8900
N(3)–H(3N3)	0.8715	1.0219	0.8715	0.8900
Bond angle (°)				
N(1)–C(1)–S(1)	173.60	170.71	171.76	178.48(11)
N(2)–C(2)–C(3)	114.00	115.16	114.16	113.06(9)
N(3)–C(3)–C(2)	113.46	113.75	113.72	112.98(9)
C(2)–N(2)–H(1N2)	109.86	111.45	111.44	109.5
C(2)–N(2)–H(2N2)	107.14	111.99	112.00	109.5
C(2)–N(2)–H(3N2)	110.63	112.81	112.83	109.5

Geometrical parameters	Methods			
	HF/6-311++G (d. p)	B3LYP/6-31++G (d. p)	B3LYP/6-311++G (d. p)	Experimental value [12]
C(3)–N(3)–H(1N3)	112.06	113.78	113.77	109.5
C(3)–N(3)–H(2N3)	111.40	112.73	112.77	109.5
C(3)–N(3)–H(3N3)	107.78	107.37	107.38	109.5
N(2)–C(2)–H(1C2)	107.63	106.91	106.89	109.0
N(2)–C(2)–H(2C2)	105.68	105.49	105.65	109.0
N(3)–C(3)–H(2C3)	106.94	107.64	107.64	109.0
N(3)–C(3)–H(1C3)	107.95	105.96	105.94	109.0
C(2)–C(3)–H(1C3)	107.81	108.17	108.14	109.0
C(2)–C(3)–H(2C3)	111.33	111.69	111.62	109.0
C(3)–C(2)–H(1C2)	111.34	111.77	111.73	109.0
C(3)–C(2)–H(2C2)	107.22	108.54	108.49	109.0
H(1C2)–C(2)–H(2C2)	109.25	107.86	107.81	107.8
H(2C3)–C(3)–H(1C3)	110.86	108.27	108.30	107.8
H(1N2)–N(2)–H(2N2)	106.29	103.41	103.45	109.5
H(1N2)–N(2)–H(3N2)	108.76	108.24	108.27	109.5
H(2N2)–N(2)–H(3N2)	108.54	108.53	108.59	109.5
H(1N3)–N(3)–H(2N3)	112.15	112.78	112.80	109.5
H(1N3)–N(3)–H(3N3)	106.29	103.84	103.89	109.5
H(2N3)–N(3)–H(3N3)	107.41	107.83	107.88	109.5
N(2)–C(2)–C(3)–N(3)	74.53	74.32	74.36	72.09 (12)

Table 1.
Optimized geometrical parameters for ethylenediammonium chloride thiocyanate computed at HF/6-311++G (d. p), B3LYP/6-31++G (d. p) and B3LYP/6-311++G(d. p) basis sets.

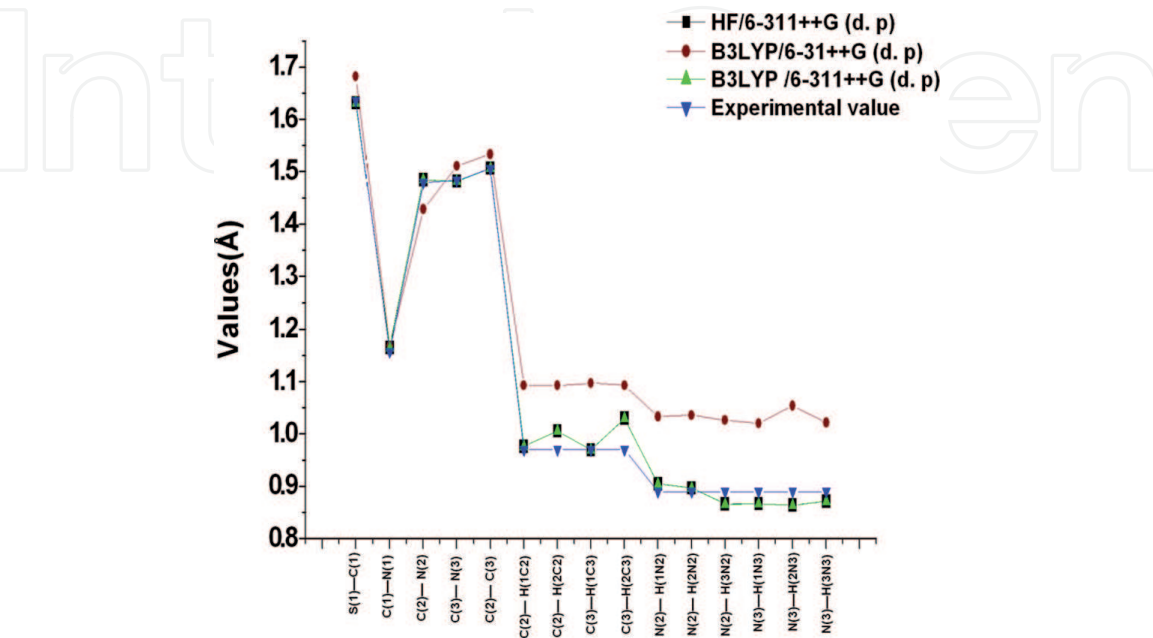


Figure 2.
Bond length differences between theoretical (HF and DFT) approaches.

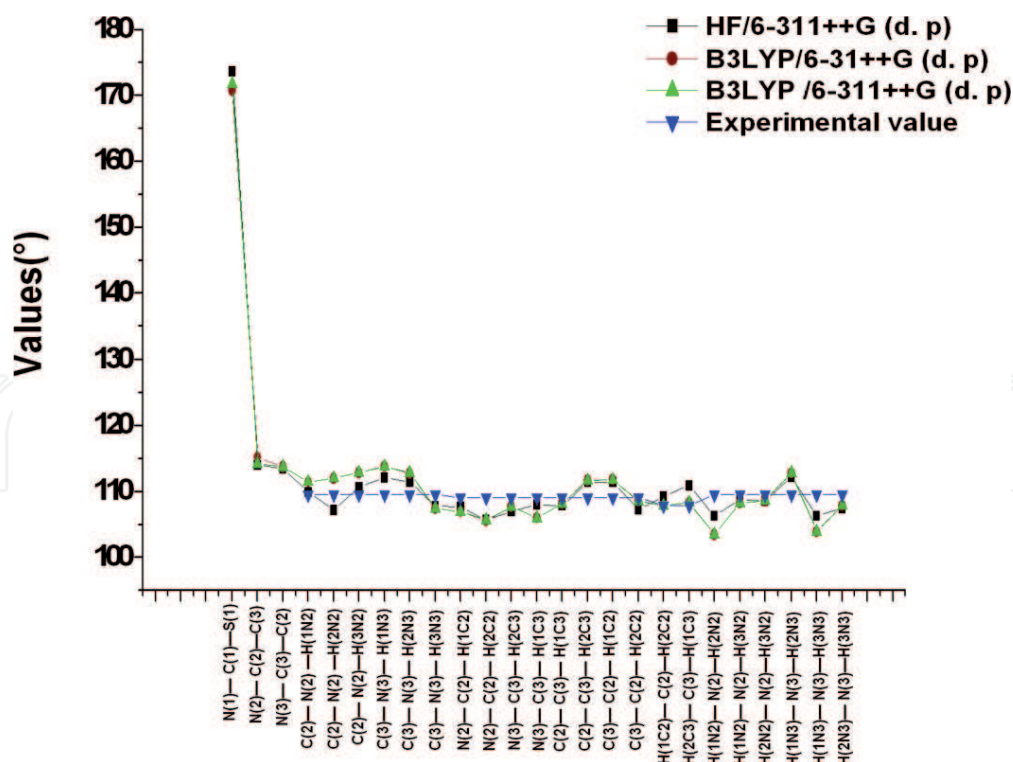


Figure 3.
Bond angle differences between theoretical (HF and DFT) approaches.

angles and binding lengths of B3LYP are compared with those of HF, the formers are generally larger than later and the values calculated by B3LYP are well correlated with the experimental data. The parameters (the vibration frequencies and the thermodynamic properties) represent a good approximation. The data presented in **Table 1** show that the theoretical HF and DFT levels (B3LYP/6-311++G (d, p)) generally estimate the same values for some link lengths and angles. The calculated C—N bond lengths are found same at two positions (C2—N2 and C3—N3) is 1.4847 and 1.5066 Å (HF and DFT), 0.0049 and 0.0012 Å, respectively, differed from the experimental value 1.4798(14) and 1.5054(15) Å [15–17]. The $[C_2H_{10}N_2]^{2+}$ dication shows an eclipsed conformation. The calculated N—C—C—N torsion angle is 74.53° (HF and DFT), 2.44° differed from the experimental value 72.09(12)° [7]. The thiocyanate ion, present as a monodentate ligand, is almost linear. The calculated angle is 173.60° but the experimental value 178.48 (11)° and an average calculated and experimental C—S and C—N bond lengths are 1.6314 and 1.1651, 1.6358 (12) and 1.1573 (16) Å [7], respectively.

3.2 Vibrational analysis

3.2.1 Contribution of IR spectrometry to the vibrational study of $C_2H_{10}N_2$ Cl NCS

3.2.1.1 Theoretical analysis of $C_2H_{10}N_2$ Cl NCS vibrations

The factor group method of classifying fundamental vibrational modes of crystals, as developed by Bhagavantam and Venkatarayudu [18], is certainly the most powerful method of treating $C_2H_{10}N_2$ Cl NCS crystal structure. The unit cell of $C_2H_{10}N_2$ Cl NCS contains 18 atoms which correspond to 54 degrees of vibrational freedom. To simplify the discussion of the IR data, the vibrational modes will be considered in two groups: the internal modes of SCN^- anions and $(C_2H_{10}N_2)^{2+}$ cations. Ethylenediammonium thiocyanate chloride crystallizes, at room temperature,

in the triclinic system, space group P1 (C_1). The entities $[C_2H_{10}N_2]^{2+}$, $[SCN]^-$ and $[Cl]^-$ occupy sites of symmetry (C_1).

3.2.1.2 Counting by the factor group method

The number of normal modes of vibration of the group SCN^- isolated of ideal symmetry $C_{\infty v}$ is given by the representation:

$$\Gamma_{SCN} = 2A_1 + E_1 \quad (1)$$

While that of an isolated group $[C_2H_{10}N_2]^{2+}$ of symmetry C_{2v} is given by the irreducible representation:

$$\Gamma_{[C_2H_{10}N_2]^{2+}} = 11A_1 + 8A_2 + 9B_1 + 8B_2 \quad (2)$$

The correlation diagram is given in **Table 2**. The counting of the main vibrations of this compound by the factor group method leads to the following results:

- Overall vibration representation: $\Gamma_{(ni)} = 54Ag + 54Au$
- Translation modes: $\Gamma_{(T')} = 9Ag + 9Au$
- Rotation mode: $\Gamma_{(R')} = 5Ag + 5Au$
- The representation of the internal vibrations is: $\Gamma_{(ni)} = 40Ag + 40Au$

The analysis in terms of internal vibrations, rotation R' and translation T' , is given in **Table 3** with their activities in IR.

3.2.1.3 Enumeration by the site group method

This method was used in order to have a detailed description of the symmetry and the nature of the internal vibrations (deformation in the plane or out of the plane, symmetrical or asymmetrical elongation, torsion, etc.).

3.2.1.3.1 Vibrations of $[C_2H_{10}N_2]^{2+}$ in group (C_1)

To describe the vibrations of the organic cation, we considered separately the vibrations of the groups ($-NH_3$) and ($-CH_2-$) and the skeleton $(C_2N_2)^{2+}$.

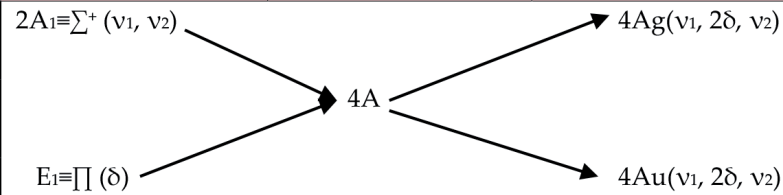
a. Description of the normal modes of vibration of the grouping ($-NH_3$)

The group ($-NH_3$) supposed free, has the symmetry $3m$ (C_{3v}), it presents nine internal vibrations schematized in **Figure 4**.

$$2A_1 + A_2 + 3E \quad (3)$$

Each group ($-NH_3$) occupies a site (C_1) in the cation. The use of correlation tables allows us to describe the symmetry of these vibrations in the molecular group of the cation (**Table 4**). The result is:

$$\Gamma_{NH_3} = 18Ag + 18Au \quad (4)$$

	Molecular group (G.M)	Group of site (G.S)	Factor group (G.F)
	C _{∞v}	C ₁	C _i
Anion (SCN) ⁻ (C _{∞v})			

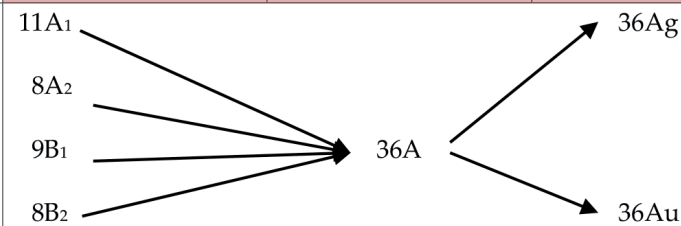
	Molecular group (G.M)	Group of site (G.S)	Factor group (G.F)
	C _{2v}	C ₁	C _i
Cation (C ₂ H ₁₀ N ₂) ²⁺ (C ₁)			

Table 2.
Internal mode correlation diagrams of C₂H₁₀N₂ Cl NCS in C_i.

b. Description of the normal modes of vibration of the grouping (—CH₂—)

The group (—CH₂—) supposed free, has the symmetry mm2 (C_{2v}), it has six internal vibrations schematized in **Figure 5**.

$$2A_1 + A_2 + B_1 + 2B_2 \tag{5}$$

The (—CH₂—) groups occupy E(C₁) sites in the cation, the correlation method allows us to determine their vibrational symmetry in the C₁ molecular group of the cation (**Table 5**). The result is:

$$\Gamma_{CH_2} = 12Ag + 12Au \tag{6}$$

C _i	n _i	n _i	R'					T'			Activity	
		EDA (C _{2v})	SCN ⁻ (C _{∞v})	Cl ⁻ (C ₁)	EDA (C _{2v})	SCN ⁻ (C _{∞v})	Cl ⁻ (C ₁)	EDA (C _{2v})	SCN ⁻ (C _{∞v})	Cl ⁻ (C ₁)	IR	R
Ag	54	36	4	0	3	2	0	3	3	3	-	+
Au	54	36	4	0	3	2	0	3	3	3	+	-

Table 3.
Enumeration of internal and external modes of C₂H₁₀N₂ Cl NCS in C_i.

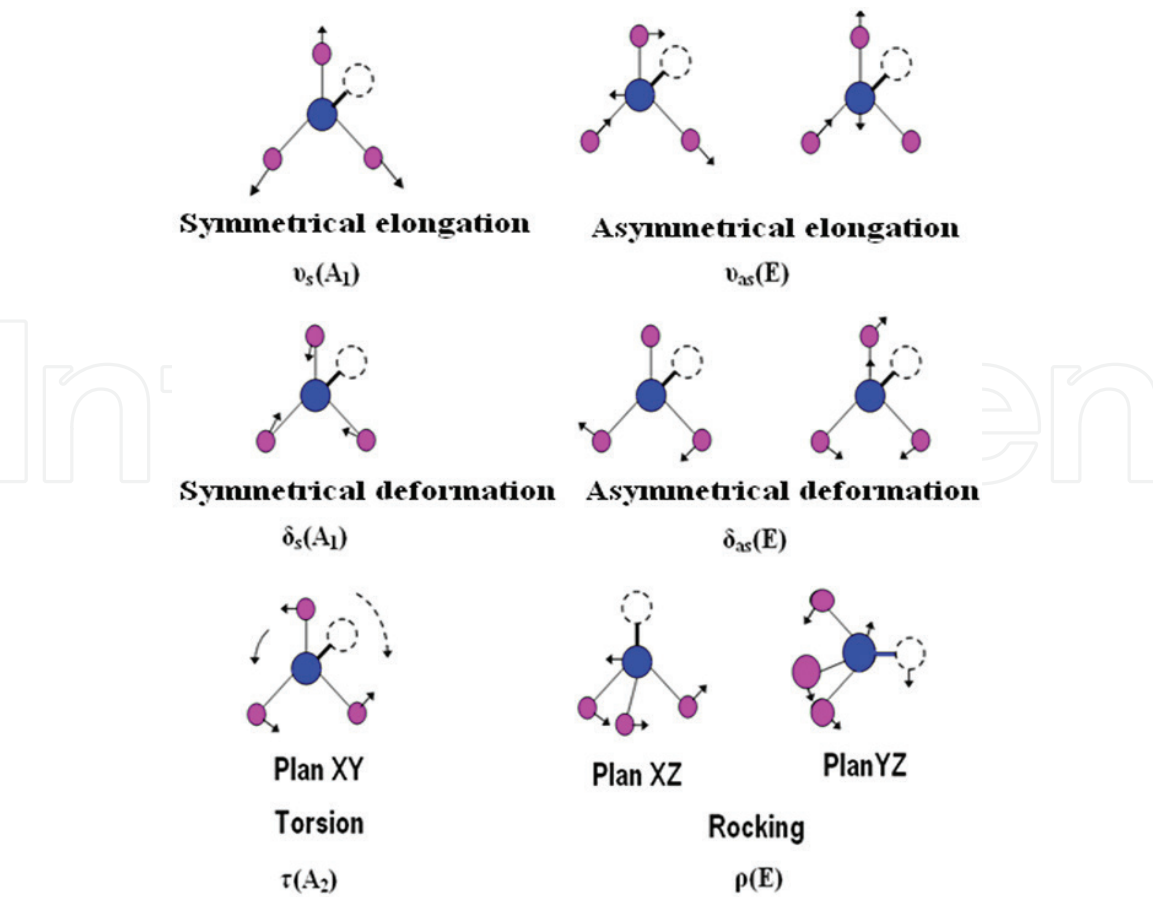


Figure 4. Normal modes of vibration of groups (-NH₃) of symmetry 3m (C_{3v}).

c. Description of the vibration modes of the skeleton (NC₂N)

To describe the vibrations of the skeleton (NC₂N), the corresponding symmetrical coordinates as a function of the internal coordinates have been calculated as follows:

- Increased C—N bonds: Δr_i (i = 1, 2)
- Increased C—C bonds: Δr₃
- Increase of the CCN bond angles: Δφ_i (i = 1, 2)
- Torsion of DC links: τ_{CC}

GM (-NH ₃)	(-NH ₃)	GM (-NH ₃)	GS (-NH ₃)	GF (Crystal)
3m C _{3v}	m C _s	2mm C _{2v}	C _i	C _i
(v _s , δ _s) 2A ₁	5A'	5A ₁	18A	18Ag (2v _s , 2δ _s , 4v _a , 4δ _a , 2δτ, 4δ _θ)
(δτ) A ₂	4A''	4A ₂		18Au (2v _s , 2δ _s , 4v _a , 4δ _a , 2δτ, 4δ _θ)
(v _a , δ _a , δ _θ) 3E		5B ₁		
		4B ₂		

Table 4. Internal modes of (-NH₃) in (C_i).

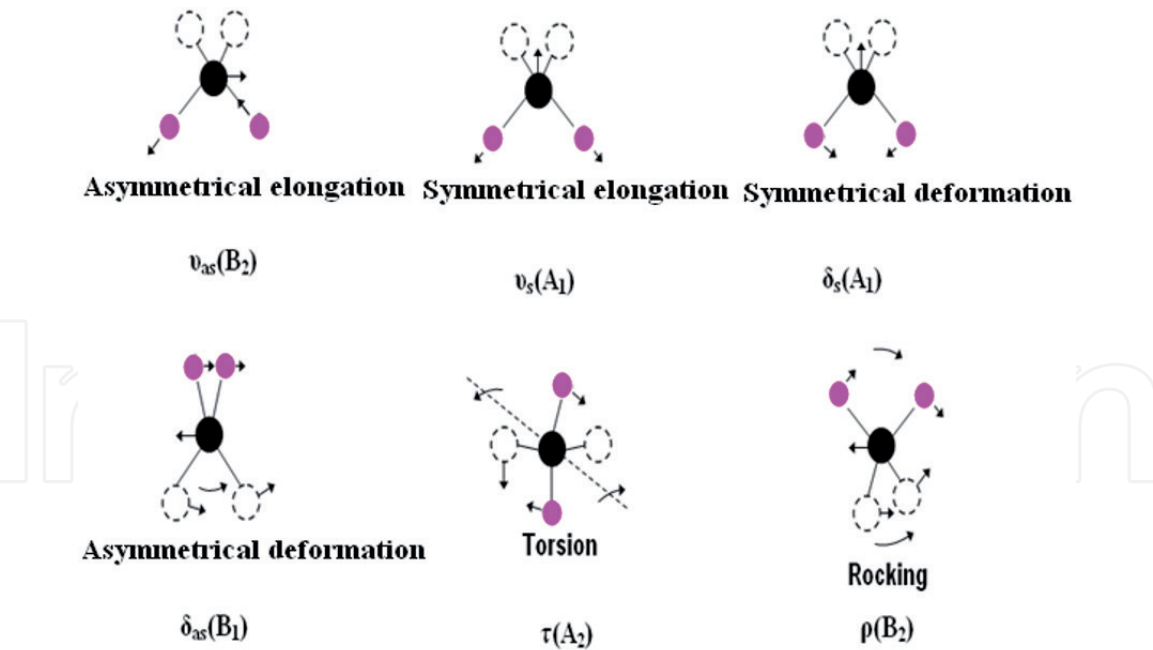


Figure 5.
Normal modes of vibration of (-CH₂-) of symmetry mm₂, (C_{2v}).

The number of coordinates is 6 = 3 N-6 (N: number of atoms in the backbone, here N = 4). Using the transforms of each coordinate under the symmetry operations of the point group C_s corresponding to the cation, six symmetrized coordinates were calculated (**Table 6**). At each coordinate a vibration mode has been assigned. These vibrations are shown schematically in **Figure 6**. The description of the normal modes of the NC₂N backbone and their activities in IR are shown in **Table 7**. The irreducible representation of the internal vibration modes of the skeleton in C_i is:

$$\text{Skeletal} = 6\text{Ag} + 6\text{Au} \tag{7}$$

d.Description of the vibration modes of SCN⁻

The internal vibrations of the SCN⁻ anion have already been studied [2], they are described in terms of symmetrized coordinates as a function of the internal coordinates. These modes are divided in the group C_{∞v} as follows:

$$\Gamma_{(\text{SCN}^-)} = 2\text{A}_1(\Sigma^+) + \text{E}_1(\Pi) \tag{8}$$

GM (-CH ₂)	(-CH ₂)	GM (-CH ₂)	GS (-CH ₂)	GF (Crystal)
mm2 C _{2v}	m C _s	mm2 C _{2v}	E C ₁	C _i
<div><div><div><div><div><div>(v_s, δ_s)2A₁</div><div>(δ_τ) A₂</div><div>(δ_a)B₁</div><div>(v_a, δ_q)B₂</div></div><div><div>3A'</div><div>3A''</div></div><div><div>3A₁</div><div>3A₂</div><div>3B₁</div><div>3B₂</div></div><div><div>12A</div><div>12A</div></div><div><div>12Ag (2v_s, 2δ_s, 2v_a, 2δ_a, 2δ_τ, 2δ_q)</div><div>12Au (2v_s, 2δ_s, 2v_a, 2δ_a, 2δ_τ, 2δ_q)</div></div></div></div></div></div>				

Table 5.
Internal modes of (-CH₂-) in (C_i).

Class	Symmetric coordinate	Vibration modes
A ₁	$S_{1\ 1}^A = \frac{1}{\sqrt{2}} (\Delta r_1 + \Delta r_2)$ $S_{2\ 1}^A = \Delta r_3$ $S_{3\ 1}^A = \frac{1}{\sqrt{2}} (\Delta \varphi_1 + \Delta \varphi_2)$	Symmetrical elongation C-N: ν_s (C-N) Symmetrical elongation C-C: ν_s (C-C) Symmetrical deformation in the plane CCN: δ_s (CCN)
B ₁	$S_{6\ 2}^B = \tau_{cc}$	Twist out of the plane CCN: τ_{cc}
B ₂	$S_{4\ 1}^B = \frac{1}{\sqrt{2}} (\Delta r_1 - \Delta r_2)$ $S_{5\ 1}^B = \frac{1}{\sqrt{2}} (\Delta \varphi_1 - \Delta \varphi_2)$	Asymmetrical elongation C-N: ν_{as} (C-N) Asymmetrical deformation in the plane CCN: δ_{as} (CCN)

Table 6.
Symmetric vibrational coordinates of NC₂N in (C_{2v}).

These vibrations are shown schematically in **Figure 7**. The vibrational analysis in terms of internal vibrations is given in **Table 8**. The distribution of normal SCN group modes and their IR activity are shown in **Table 9**. The irreducible representation of the internal vibration modes of SCN⁻ in C_i is:

$$\Gamma_{\text{SCN}^-} = 4\text{Ag} + 4\text{Au} \tag{9}$$

3.3 Group theory analysis

The comparisons of the experimental infrared spectra for EDCT, by using HF/6-311++G (d, p), (B3LYP) 311++G (d, p) and (B3LYP)/6-31++G (d, p) theory level, with the corresponding average predicted demonstrate good correlations as observed in **Figure 8**. Using the split triple valence base as well as the diffuse and polarization functions for computed harmonic vibratory frequencies of EDCT, 6-31++G (d, p) and 6-311++G (d, p), the frequencies FT-IR observed for various vibration modes were presented in **Table 10**. The comparative values of IR intensities activities are presented in **Table 11** and their corresponding graph given in **Figure 9**. The comparative graph of vibratory frequencies calculated by the HF and

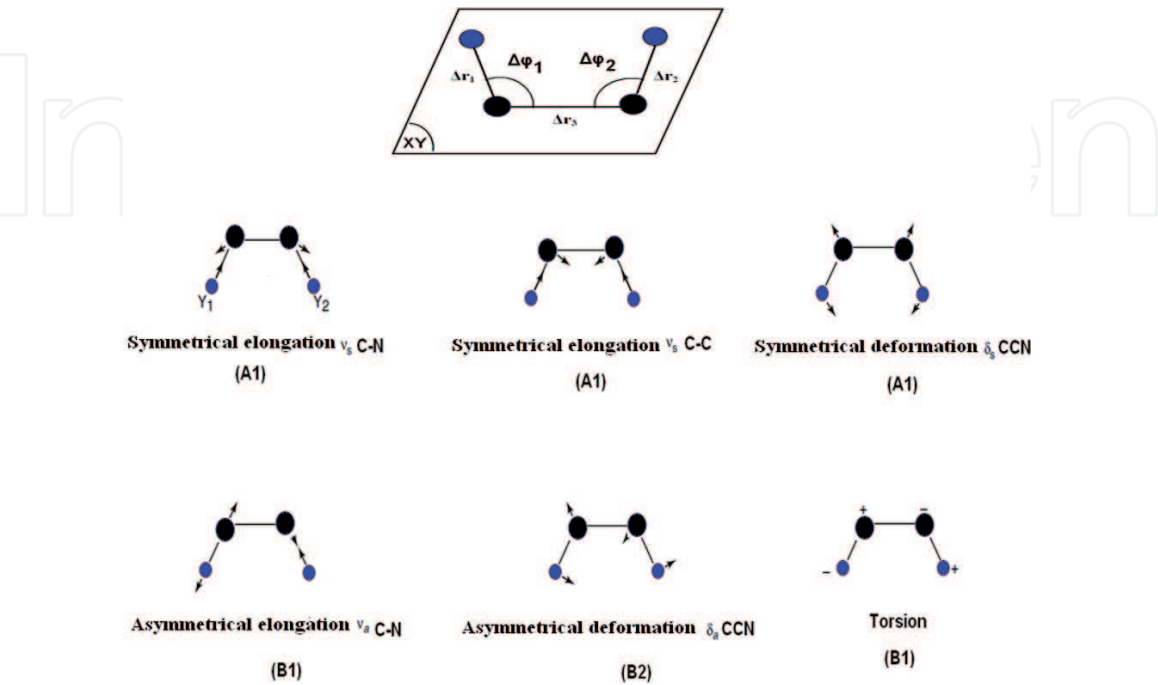


Figure 6.
Normal modes of NC₂N skeleton vibration in (C_{2v}).

Description of mnv	C _{2v}	C ₁ (site group)	C _i (factor group)
Valence			
$\nu_s(\text{CN})$	A ₁ (IR, R)	A(IR, R)	Ag(R) + Au(IR)
$\nu_{as}(\text{CN})$	B ₁ (IR, R)	A(IR, R)	Ag(R) + Au(IR)
$\nu_s(\text{CC})$	A ₁ (IR, R)	A(IR, R)	Ag(R) + Au(IR)
Deformation			
$\delta_s(\text{CCN})$	A ₁ (IR, R)	A(IR, R)	Ag(R) + Au(IR)
$\delta_{as}(\text{CCN})$	B ₁ (IR, R)	A(IR, R)	Ag(R) + Au(IR)
Torsion			
τ_{CC}	B ₂ (IR, R)	A(IR, R)	Ag(R) + Au(IR)

Table 7.
Distribution of normal skeleton vibration modes in C₂H₁₀N₂ Cl NCS.

DFT methods to HF/6-311++G (d, p), B3LYP/6-31++G (d, p) and B3LYP/6-311++G (d, p). The basic sets for the EDCT are shown in **Figure 10**. It appears from the figure that the frequencies calculated by B3LYP with 6-31++G (d, p) of basis sets are closer to the experimental frequencies as HF method with 6-311++G (d, p) base set.

3.4 Bands assignments

3.4.1 NH₃ modes

The asymmetric stretching $\nu_{as}(\text{NH}_3)$ of symmetries (Ag + Au) are observed in IR at 3325 and 3326 cm⁻¹. The symmetric stretching $\nu_s(\text{NH}_3)$ of symmetries (Ag + Au) are observed in IR at 3210 cm⁻¹. The asymmetric deformation $\delta_{as}(\text{NH}_3)$ of symmetry (Ag + Au) observed IR at 1500 and 1570 cm⁻¹. The symmetric deformation $\delta_s(\text{NH}_3)$ of symmetries (Ag + Au) are observed in IR at 1467 cm⁻¹. The Rocking $\delta_p(\text{NH}_3)$ of symmetries (Au) are observed only in IR at 493 and 498 cm⁻¹. The torsion $\delta_\tau(\text{NH}_3)$ of symmetries (Au) observed in IR at 483 cm⁻¹. The rocking and twisting modes are assigned as predicted by the calculations and in accordance with the expected regions for similar compounds [7, 8, 19, 20], as observed in **Table 10**.

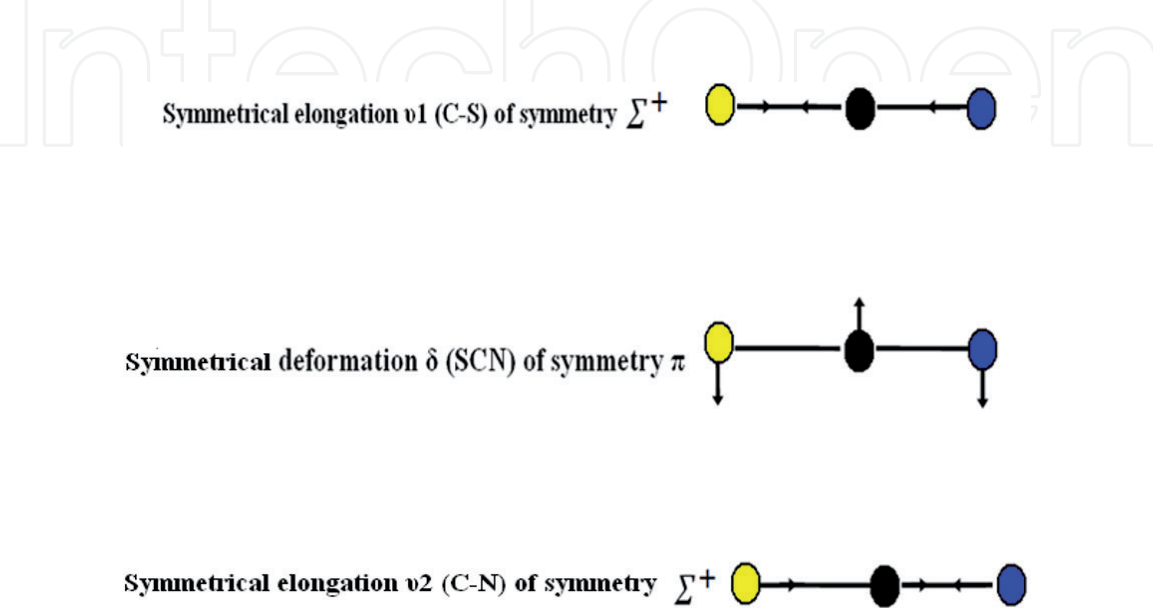


Figure 7.
Normal modes of vibration of the anion SCN⁻ in (C_{∞v}).

	Mode	Molecular group (G.M)	Group of site (G.S)	Factor group (G.F)	Activity	
		$C_{\infty v}$	C_1	C_i	IR	R
Anion (SCN) ⁻ ($C_{\infty v}$)	(ν_1, ν_2)	$2\Sigma^+$	4A	4Ag($\nu_1, 2\delta, \nu_2$)	-	+
	(δ)	Π		4Au($\nu_1, 2\delta, \nu_2$)	+	-

Table 8.
Internal modes of (SCN)⁻ in ($C_{\infty v}$).

3.4.2 CH₂ modes

By comparison with previous works reported on similar compounds containing [C₂H₁₀N₂]²⁺ [21], we have attributed the bands observed in IR at 3222 and 2427 cm⁻¹ to asymmetric stretching $\nu_{as}(CH_2)$ and symmetric $\nu_s(CH_2)$ of symmetries (Ag + Au), respectively. The asymmetric deformation $\delta_{as}(CH_2)$ and symmetric $\delta_s(CH_2)$ is observed at 1452 and 1200 cm⁻¹ in IR spectrum at 1341 and 1454 cm⁻¹. The calculated frequencies of B3LYP/6-31++G (d, p) and B3LYP/6-311++G (d, p) methods for CH₂ asymmetric and as asymmetric vibrations showed excellent agreement with recorded spectrum as well as literature data. The Rocking $\delta_p(CH_2)$ of symmetries (Ag + Au) are observed in IR at 1000 cm⁻¹. The torsion $\delta_t(CH_2)$ of symmetry (Ag + Au) observed in IR at 1124 cm⁻¹. The rocking and twisting modes are assigned as predicted by calculations, as indicated in **Table 10**.

3.4.3 Skeletal modes

The NCCN skeleton gives six normal modes of vibration that may be described as three skeleton stretching ($2\nu_{CN} + 1\nu_{CC}$), two NCCN deformation modes and one torsional mode around the C—C bond. The symmetrical elongations of the symmetry skeleton $\nu_s(CC)$ of symmetries (Ag + Au) appear in IR at 750 cm⁻¹. The asymmetric stretching $\nu_{as}(CN)$ of symmetries (Ag + Au) observed in IR at 544 cm⁻¹. The symmetric stretching $\nu_s(CN)$ of symmetries (Au) observed in IR at 532 cm⁻¹. The asymmetric deformation $\delta_{as}(CCN)$ of symmetry (Ag + Au), is observed in IR at 435 cm⁻¹. The symmetric deformation $\delta_s(CCN)$ of symmetry (Au) observed only in IR at 430 cm⁻¹.

3.4.4 Internal modes of the thiocyanate group (SCN⁻)

The thiocyanate group (SCN⁻) has four vibrations in the $C_{\infty v}$ group: two of valence denoted [$\nu_1(CS), \nu_2(CN)$] of symmetry (Σ^+) and a doubly degenerate deformation

Description of mnv	$C_{\infty v}$	G.S (C_1)	C.G (G.F)
Valence			
$\nu_1(CS)$	A ₁ (IR, R)	A(IR, R)	2A _g (R) + 2A _u (IR)
$\nu_2(CN)$	A ₁ (IR, R)	A(IR, R)	2A _g (R) + 2A _u (IR)
Deformation			
$\delta(SCN)$	E ₁	A(IR, R)	2Ag(R) + 2Au(IR)

Table 9.
Description of the normal modes of SCN⁻ in C₂H₁₀N₂ Cl NCS.

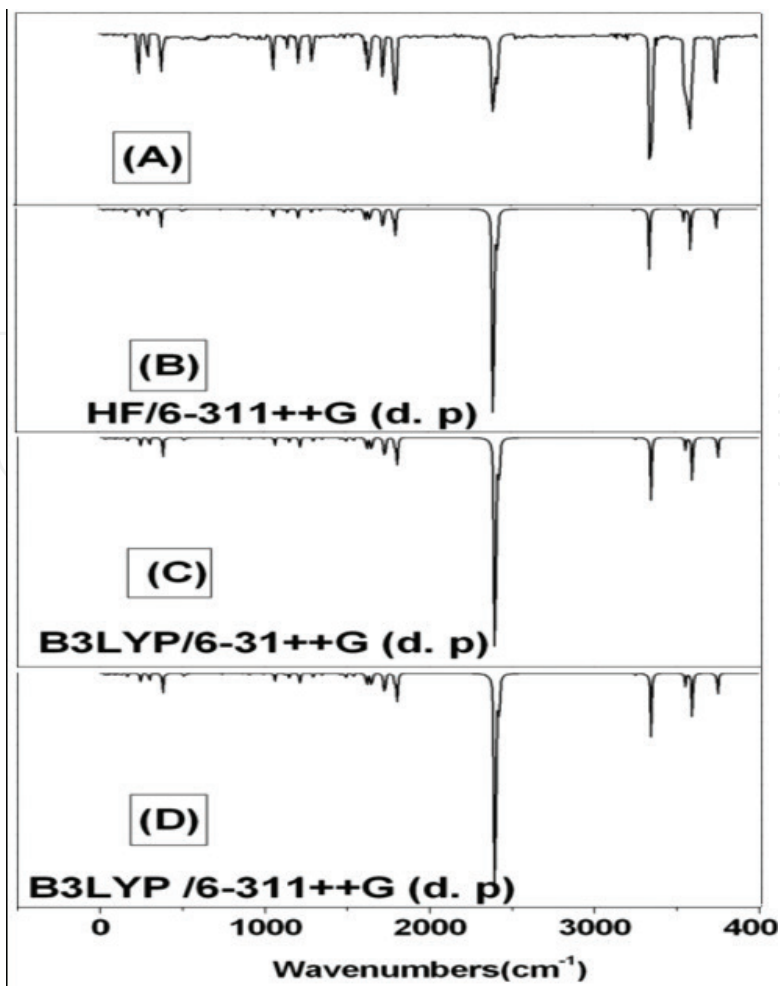


Figure 8.
(A) Experimental infrared spectrum of $C_2H_{10}N_2$ Cl NCS in the solid phase compared with the calculated with: (B) (HF)/6-311++G (d, p), (C) B3LYP/6-31++G (d, p) and (D) B3LYP/6-311++G (d, p).

Mode nos.	Theoretical wavenumbers (cm ⁻¹)				Vibrational assignments
	FT-IR	HF/ 6-311++G (d,p)	B3LYP/ 6-31++G (d,p)	B3LYP/ 6-311++G(d,p)	
1	-	3746	3746	3749	Combination bands + 2 x $\delta_{as}(NH_3)$
2	-	3740	3740	3742	
3	-	3590	3590	3593	
4	-	3537	3536	3551	
5	3365(ep)	3341	3343	3349	$\nu_{as}(NH_3)$
6	3326(m)	3318	3320	3332	
7	3325(m)	3311	3307	3302	
8	3210(m)	3250	3259	3262	
9	-	3262	3241	3247	$\nu_{as}(CH_2)$
10	2427(m)	2404	2409	2413	$\nu_s(CH_2)$
11	2400(F)	2400	2399	2390	2x $\delta_{as}(CH_2)$ Combination bands + 2x $\delta_s(CH_2)$ 2x $\nu_{as}(CC)$
12	-	1805	1800	1809	
13	1787(ep, f)	1791	1797	1801	
14	-	1785	1784	1782	
15	1718(ep, f)	1726	1727	1734	
16	1710(f)	1719	1723	1718	
17	1638(f)	1629	1643	1636	
18	1616(m)	1629	1623	1623	$\nu_2(C=N)$

19	1617(f)	1619	1613	1611	Combination bands
20	1570	1587	1582	1580	$\delta_{as}(\text{NH}_3)$
21	1500(m)	1532	1533	1539	$\delta_{as}(\text{NH}_3)$
22	1467(F)	1474	1486	1491	$\delta_s(\text{NH}_3)$
23	1452(m)	1458	1452	1453	$\delta_{as}(\text{CH}_2)$
24	-	1341	1345	1340	$\delta_{as}(\text{CH}_2)$
25	-	1287	1289	1292	$\delta_s(\text{CH}_2)$
26	1200(TF)	1204	1208	1211	$\delta_s(\text{CH}_2)$
27	-	1135	1146	1126	$\delta_t(\text{CH}_2)$
28	1124(TF)	1122	1122	1121	$\delta_t(\text{CH}_2)$
29	-	1050	1057	1061	$\delta_o(\text{CH}_2)$
30	1000 (F)	990	990	996	$\delta_o(\text{CH}_2)$
31	906(f)	909	901	921	Combination bands
32	818 (m)	831	864	874	Combination bands
33	758(f)	741	738	739	$\nu_s(\text{CC})$
34	544(f)	551	536	530	$\nu_{as}(\text{CN})$
35	532(TF)	504	508	512	$\nu_s(\text{CN})$
36	498(F)	499	488	481	$\delta_o(\text{NH}_3)$
37	493(m)	496	487	482	$\delta_o(\text{NH}_3)$
38	483(m)	473	475	471	$2^* \delta_t(\text{NH}_3)$
39	450 (f)	458	450	451	$\nu_1(\text{C}=\text{S})$
40	448(f)	441	449	449	$\nu_1(\text{C}=\text{S})$
41	435(ep, f)	436	431	429	$\delta_{as}(\text{CCN})$
42	430(f)	429	421	428	$\delta_s(\text{CCN})$
43	424(f)	426	424	424	$\delta(\text{SCN})$
44	409(f)	402	406	402	$\delta(\text{SCN})$
45	-	88	83	81	$\delta_t(\text{NH}_3)$
46	-	76	72	72	Modes externes de ($\text{C}_2\text{H}_{10}\text{N}_2$) ⁺ + Cl ⁻ + SCN ⁻
47	-	42	44	48	
48	-	30	28	36	

Table 10.
Observed, HF/6-31++G (d, p), B3LYP/6-31++G (d, p) and B3LYP/6-311++G (d, p) level calculated vibrational frequency of ethylenediammonium chloride thiocyanate.

vibration denoted $\delta_1(\text{SCN})$ of symmetry (π). From the bibliographic results [22–28] and the analysis by group theory, an attempt to attribute these vibrations observed in IR is illustrated in **Table 10**. The deformation $\delta_1(\text{SCN})$ of symmetry (1Au) is observed in IR at 409 and 424 cm^{-1} . The calculated frequencies of B3LYP/6-31++G (d, p) and

Calculated with HF/6-311++G (d. p)				Calculated with B3LYP/6-31++G (d. p)		Calculated with B3LYP/6-311++G (d. p)	
Mode nos.	IR intensity	Mode nos.	IR intensity	IR intensity	IR intensity	IR intensity	IR intensity
1	14.48	25	12.72	13.50	19.57	15.30	14.59
2	15.73	26	24.56	9.27	18.75	10.22	22.15
3	7.17	27	32.62	6.33	36.54	4.37	34.14
4	20.26	28	30.24	12.70	33.84	10.60	31.04
5	13.87	29	0.11	13.85	1.40	17.22	0.40
6	9.54	30	23.90	9.61	131.09	7.91	129.89
7	28.49	31	12.19	27.24	9.80	27.24	9.09
8	45.53	32	176.12	73.75	149.02	70.95	141.72
9	111.58	33	199.40	87.48	190.70	87.08	188.76
10	29.05	34	82.23	6.61	48.96	8.11	42.56
11	2.12	35	13.39	166.12	62.76	186.03	62.76
12	6.16	36	65.01	12.53	99.11	13.63	99.11
13	31.58	37	64.34	3.41	161.00	5.11	159.11
14	12.29	38	194.80	37.30	83.40	35.20	83.40
15	18.08	39	955.17	5.35	398.06	3.15	518.06
16	2.11	40	595.05	7.87	173604	8.07	102.36
17	0.73	41	5.95	3.34	2.72	1.04	1.79
18	25.97	42	190.52	17.59	189.07	12.09	199.17
19	41.46	43	2.82	9.63	4.62	10.03	4.32
20	2.43	44	0.69	67.12	523.90	61.02	503.60
21	55.16	45	1.88	12.97	118.46	10.17	111.16
22	66.06	46	9.01	42.44	380.52	41.01	370.12
23	93.86	47	121.09	79.33	117.71	89.83	115.51
24	28.19	48	111.24	32.91	90.63	27.11	77.83

Table 11.
Comparative values of IR intensities activities between HF/6-31++G (d. p), B3LYP/6-31++G (d. p) and B3LYP/6-311++G (d. p) of ethylenediammonium chloride thiocyanate.

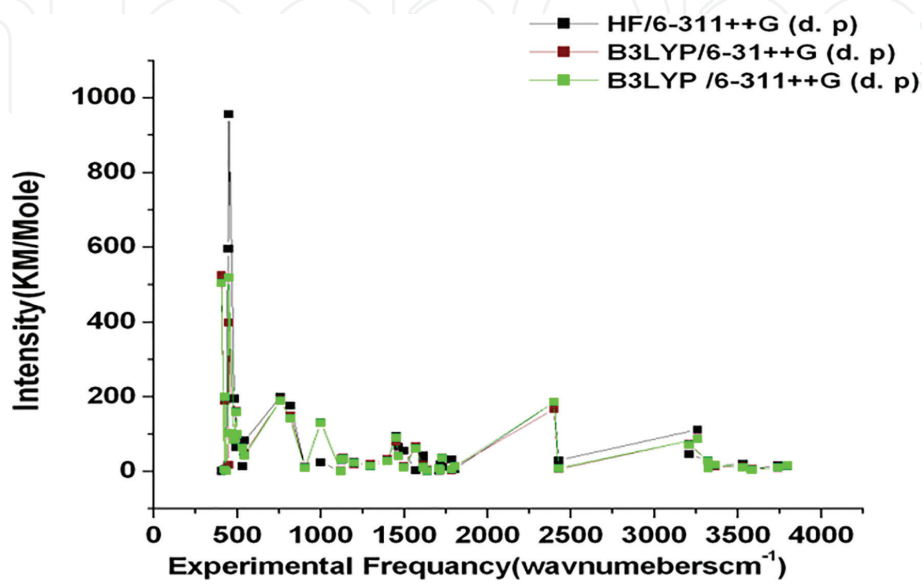


Figure 9.
Comparative graph of IR intensities by HF and DFT (B3LYP).

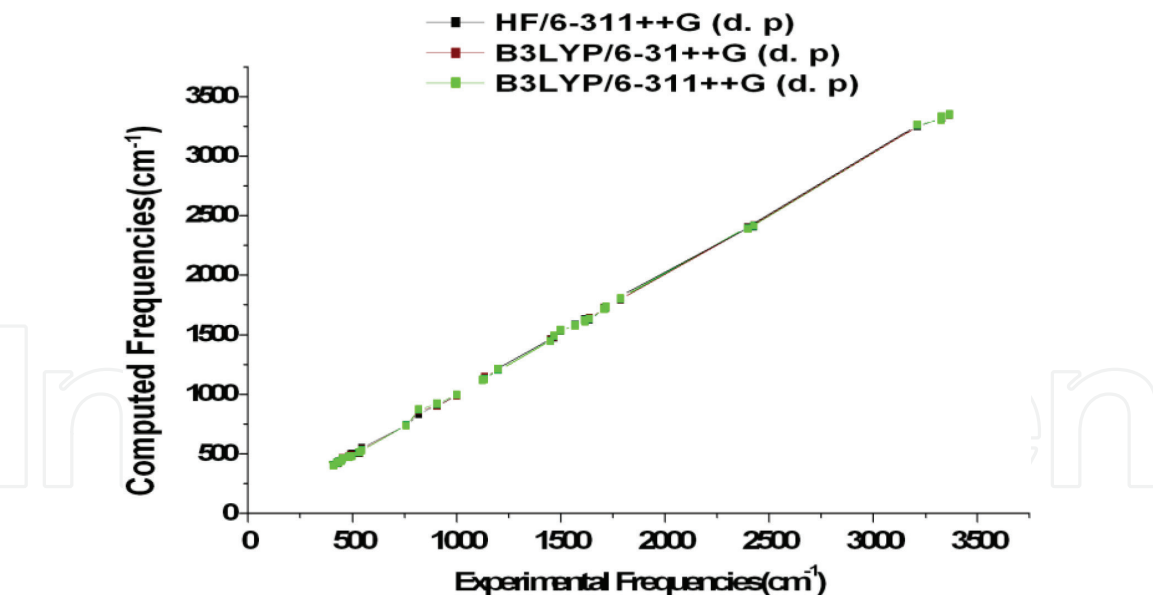


Figure 10.
Comparative graphs of computed frequencies (HF and DFT) with experimental frequencies.

B3LYP/6-311++G (d, p) methods for SCN deformation symmetric vibrations showed excellent agreement with recorded spectrum as well as literature data. We note a rise of degeneracy of the symmetry π of δ_1 (SCN) with a burst of 33 cm^{-1} . The symmetric stretching ν_1 (C=S) of symmetries (1Ag + 1Au) are observed in IR at 450 and 484 cm^{-1} . The calculated frequencies of B3LYP/6-31++G (d, p) and B3LYP/6-311++G (d, p) methods for C=S symmetric vibrations showed excellent agreement with recorded spectrum as well as literature data. The symmetric stretching ν_2 (C=N) of symmetries (1Ag + 1Au), predicted by the group theory, are observed in IR at 1616 cm^{-1} .

3.5 Other molecular properties

Several calculated thermodynamic parameters are presented in **Table 12**. Scale factors have been recommended [29] for an accurate prediction in determining the

Parameters	HF/6-311++ (d, p)	B3LYP/6-31++(d, p)	B3LYP/6-311++G (d. p)
Zero point vibration energy	105.84889	100.34649	98.57158
Rotational constants	1.55409	1.63393	1.55409
	0.47626	0.52535	0.47626
	0.37522	0.46146	0.37522
Rotational temperature	0.07458	0.07842	0.07458
	0.02286	0.02521	0.02286
	0.01801	0.02215	0.01801
Energy			
Translational	0.889	0.889	0.889
Rotational	0.889	0.889	0.889
Vibrational	108.982	105.524	105.017
Total	110.759	107.302	107.394
Molar capacity at constant volume			
Translational	2.981	2.981	2.981
Rotational	2.981	2.981	2.981
Vibrational	19.092	29.415	17.227
Total	25.054	25.377	23.189

Parameters	HF/6-311++ (d, p)	B3LYP/6-31++(d, p)	B3LYP/6-311++G (d, p)
Entropy			
Translational	41.025	41.025	41.025
Rotational	31.426	31.426	31.074
Vibrational	15.540	15.594	15.589
Total	87.792	87.546	87.587
Dipole moment	39.4045	38.6462	38.6426

Table 12.
Theoretically computed zero point vibrational energy (kcal mol⁻¹), rotational constants (GHz), rotational temperature (K), thermal energy (kcal mol⁻¹), molar capacity at constant volume (cal mol⁻¹ K⁻¹) entropies (cal mol⁻¹ K⁻¹) and dipole moment (Debye) for ethylenediammonium chloride thiocyanate.

zero-point vibration energies, and the entropy. It can be seen that the total energies decrease with the increase of the size of the basic set. Changes in the total entropy of EDCT at room temperature and in different basic sets are only marginal.

4. Conclusions

The present document attempts to define the appropriate frequency assignments for the thiocyanate ethylenediammonium chloride compound from the FT-IR spectrum. Vibrational frequencies and infrared intensities are calculated and analyzed by the theoretical HF and DFT (B3LYP) levels, using the 6-31++G (d, p) and 6-311++G (d, p)base sets.. The comparison between the calculated vibrational frequencies and the experimental values indicates that both methods can predict the FT-IR spectra of the title compound. The results of DFT-B3LYP method indicate better fit to experimental ones than ab initio HF upon evaluation of vibrational frequencies. Several thermodynamic parameters of the title molecule are comparatively discussed. The observed and the calculated wavenumbers are found to be in good agreement with majority modes.

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