DENSITY FUNCTIONAL STUDIES, STRUCTURE, STABILITY AND VIBRATIONAL SPECTRA OF THIOPHENE-2-ACETONITRILE

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Abstract : **The conformational behaviour and structural stability of Thiophene-2-acetanitrile in liquid phase were investigated by utilizing density functional theory calculations with the B3LYP method employing the 6-31G* and 6-311+G** basis sets. Scale factors, which bring computational frequencies in closer agreement with the experimental data, have been calculated for predominant vibrational motions of the normal modes. Complete vibrational assignments were made on the basis of normal coordinate calculations for stable conformer of the molecules. The infrared and Raman spectra were also predicted from the calculated intensities. The observed and the calculated spectra were found to be in good agreement.**

Keywords **- Thiophene-2-acetonitrile; Structural stability; Vibrational spectra; Density functional theory calculations Component.**

I. INTRODUCTION

Thiophene and its derivatives are the main constituents of polyatomic ‘organic conductors’ [1-3]. Polythiophene, like a variety of other conjugated organic polymers, shows a remarkable high electrical conductivity in the oxidized form. The discovery of conducting polymers has become ever more significant due to the fact that this class of materials has proven to be both of great scientific and practical interest [1-7]. Conducting polymers have been put to use in such fields of materials science as electromagnetic shielding, the antistatic coating on photographic films, and windows with changeable optical properties [7-10]. Although the properties have been extensively studied over the last three decades, superconductivity has not been reported for this class of materials. Hence, the investigation on the structures and the vibrations of thiophene and its derivatives are still being carried out, increasingly. The inclusion of substituent groups in thiophene leads to the variation of the charge distribution in the molecule and consequently, this greatly affects the structural and vibrational parameters. Considerations of these factors motivated to undertake the vibrational spectroscopic studies of the title compound.

The philosophy of computational methods of vibrational spectroscopy [11-13] changed significantly when quantum mechanical programs for optimization of the geometry of a molecule and for analytical determination of its force field appeared. Harmonic force fields derived from quantum mechanics are widely used for the calculation of frequencies and the modes of normal vibrations. Indeed, applying current quantum mechanical methods have opened up the way for calculating the frequencies and intensities of spectral bands with a minimum degree of arbitrariness (although the degree depends on the level of the quantum-mechanical treatment) and finding a rational explanation for a number of chemical and physical properties of substances.

However, for a proper understanding of IR and Raman spectra, a reliable assignment of all vibrational bands is essential. Recently, computational methods based on density functional theory are becoming widely used. These methods predict the relatively accurate molecular structure and vibrational spectra with moderate computational effort. In particular, for polyatomic molecules (typically normal modes exceeding 50) the DFT methods lead to the prediction of more accurate molecular structure and vibrational frequencies than the conventional *ab initio* restricted Hartree-Fock (RHF) and Moller-Plesset second-order perturbation theory (MP2) calculations [14-17]. To our best of knowledge, there have been no theoretical calculation to understand the structures and the fundamental vibrational frequencies of the Thiophene-2-acetonitrile (hereafter called as TAN) in liquid phase have been studied by applying the density functional theory (DFT) calculations based on Becke3-Lee-Yang-Parr (B3LYP) level with 6-31G* and 6-311+G** basis sets. The two anticipated stable conformers of TAN have been carried out for the energy calculations at small (6-31G*) and large (6-311+G**) basis sets. The most optimized geometry obtained for the title compounds were used for the DFT calculations. Based on these calculations, the simulated FTIR and FT-Raman spectra of TAN were obtained. The experimentally observed spectral data of the title compounds were found to be well comparable to that of the spectral data obtained by quantum chemical methods.

II. Experimental details

The fine sample of TAN was obtained from Lancaster Chemical Company, UK and used as such for the spectral measurements. The FT-Raman spectra were recorded on a computer interfaced BRUKER IFS model interferometer equipped with FRA 106 FT-Raman accessories. The spectra were recorded in the region 3500 - 100 cm^{-1} with Nd: YAG laser operating at 200 mW power continuously with 1064 nm excitation. The room temperature mid-infrared spectra of the title compounds were measured in the region 4000-400 cm^{-1} at a resolution of ±1 cm^{-1} using BRUKER IFS 66V vacuum Fourier transform spectrometer equipped with an MCT detector, a KBr beam splitter, and globar source.

III. Computational procedure

Quantum chemical density functional calculations were carried out with the 1998 versions of the GAUSSIAN suite of programs [18] using the B3LYP functional [19,20] supplemented with the standard 6-31G* and 6-311+G** basis sets (referred to as DFT calculations). The normal grid (50, 194) was used for numerical integration. The Cartesian representation of the theoretical force constants has been computed at the fully optimized geometry by assuming C_{2v} point group symmetry. The multiple scaling of the force constants was performed by the quantum chemical method with selective scaling in the local symmetry coordinate representation [21] using transferable scale factors available in the literature [22]. The transformation of force field from Cartesian to symmetry coordinate, the scaling, the subsequent normal coordinate analysis, calculations of total energy distribution (TED) and IR and Raman intensities were done on a PC with the version. V7.0 - G77 of the MOLVIB program written by Tom Sundius [23, 24]. To achieve a close agreement between observed and calculated frequencies, the least square fit refinement algorithm was used. The force field obtained this way was then used to recalculate the normal modes, TEDs and the corresponding theoretically expected IR and Raman intensities to predict the full IR and Raman spectra. For the plots of simulated IR and Raman spectra pure Lorentzian band, shapes were used with a bandwidth (FWHM) of 10 cm^{-1}.

The prediction of Raman intensities was carried out by following the procedure outlined below. The Raman activities (S_i) calculated by the GAUSSIAN -98 program and adjusted during the scaling procedure with MOLVIB were converted by relative Raman intensities (I_i) using the following relationship derived from the basic theory of Raman scattering[25-27].

$$I_i = \frac{f(\nu_0-\nu_i)^4 S_i}{\nu_i[1-\exp(-hc\nu_i/kT)]} \qquad \ldots 1$$

where ν_o is the exciting frequency (in cm^{-1} units), ν_i is the vibrational wave number of the i^{th} normal mode, *h*,*c*, and *k* are the universal constants and *f* is a suitability chosen common normalization factor for all peak intensities.

IV Results and discussion

4.1 *Molecular geometry*

The title compound belongs to C_{2v} point group symmetry. The labeling of atoms of two anticipated stable conformers of TAN was shown in Fig.1. The global minimum energy calculations were carried out using small and large basis sets for two stable conformers of the title compound. The total energies obtained for these conformers were listed in Table 1. The DFT structure optimizations of TAN have shown that the conformer a (*s-trans*) has a significantly lower energy than the conformer b (*s-cis*). Subsequent force field and vibrational frequency calculations performed at the B3LYP/6-31G* and B3LYP/6-311+G** level of theory for both optimized structures of TAN have revealed that conformer b (*s-cis*) has a large imaginary frequency corresponding to the internal rotation around the C_{ar} – C bond. DFT predicted bond lengths, and bond angles of the molecules TA and TAN were gathered in Table 2. The DFT calculations depicted C=C bond lengths (atoms C2-C3) were about 0.01Å smaller than the corresponding lengths in Thiophene and 3-methylthiophene [25]. Similarly, the DFT calculated C-H values were smaller by 0.01Å; due to the substitution of thiophene hydrogen atom by an acetonitrile group at C2 because fairly small changes in ring interatomic distance (Table 2). The bond length of S1-C2 is slightly longer (by 0.05 Å) and a larger (by 0.13Å) of an interatomic distance was observed for the C3-C4 bond.

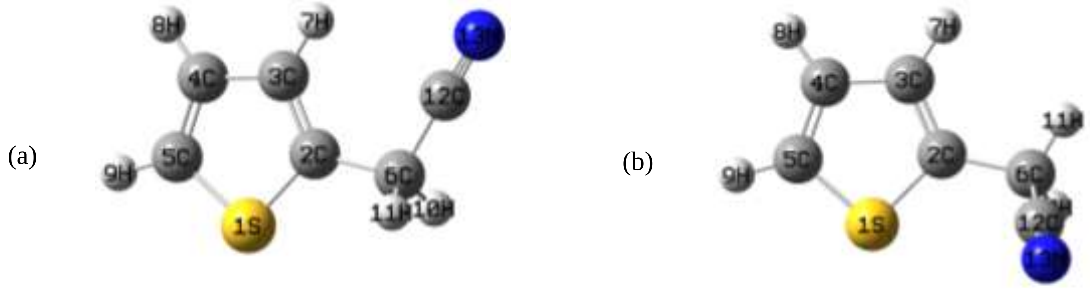

Fig. 1 - The conformers considered and numbering of atoms of thiophene-2-acetonitrile
(a) stable s-trans conformation (b) s-cis conformation

Table 1 - Total energies (in Hartrees) of thiophene-2-acetamide and thiophene-2-acetonitrile obtained employing DFT-B3LYP level with the 6-31G* and 6-311G** basis sets

Conformer	Total energies			
	TA		TAN	
	6-31G*	6-311+G**	6-31G*	6-311+G**
a	-760.7911	-760.9389[#]	-684.4198	-684.5204[#]
b	-760.8077	-760.9371	-684.4197	-684.5201
[#]Global minimum energy				

Table 2 - Optimized geometrical parameters of thiophene-2-acetamide and thiophene-2-acetonitrile obtained by B3LYP/6-311+G** density functional calculations

PARAMETERS	TA	TAN	Thiophene[a]	3-Methylthiophene[a]
Bond length / Bond angle (Å / deg)				
S1-C2	1.77	1.77	1.72	1.72
C2-C3	1.35	1.35	1.36	1.36
C3-C4	1.54	1.55	1.42	1.43
C4-C5	1.37	1.36		1.36
C5-S1	1.77	1.77		1.72
C2-C6	1.54	1.53		
C_{ar}-H[b]	1.07	1.07	1.08	
C6-H (methylene) [b]	1.06	1.06		
C6-C12	1.35	1.35		
C12-O13 (N13)	1.43	2.59		
C12-N14	1.46			
N14-H (amino) [b]	0.99			
S1-C2-C3	110.64	110.64	111.50	112.40
C2-C3-C4	111.86	111.86	112.50	111.30
C3-C4-C5	111.97	111.95		
C4-C5-S1	110.39	110.39		111.50
C5-S1-C2	92.61	92.61	92.20	91.40
C3-C2-C6	124.41	124.41		
S1-C2-C6	124.27	124.27		
C2-C3-H7	124.24	124.24		
C4-C3-H7	123.75	123.75		
C3-C4-H8	124.10	124.10		
C5-C4-H8	124.21	124.21		
C4-C5-H9	124.42	124.42		
S1-C5-H9	124.43	124.43		
C6-C12-O13	119.90			
O13-C12-N14	120.00			
C12-N14-H(amino)[b]	109.47			
H15-N14-H16	109.47			
C2-C6-H(methylene)[b]	109.48			
H10-C6-H11	109.48			

The atoms indicated in the parenthesis belongs to TAN; [a] Taken from Ref[25]; [b] Average value

4.2 Vibrational analysis

The compound Thiophene-2-acetonitrile belongs to C_{2v} point group symmetry. The 33 normal modes of vibrations of TAN were distributed among the symmetry species $\Gamma_{vib}=12A_1+6A_2+4B_1+11B_2$. A final general comment about the normal vibrations the molecule TAN will have 15 stretching vibrations, 8 in-planes bending, and 10 out-of-plan bending vibrations.

A detailed description of vibrational modes can be given by means of normal coordinate's analysis. For this purpose, the full sets of 43 standard internal coordinates (10 redundancies) were defined as given in Table 3. From these, a non-redundant set of local symmetry coordinates were constructed by suitable linear combinations of internal coordinates following the recommendations of Fogarasi and Pulay [26] and they were presented in Table 4. The theoretically calculated DFT force fields were transformed to this later set of vibrational coordinates and used in all subsequent calculations.

The observed and calculated frequencies and normal mode descriptions (characterized by TED) for the conformers (Fig.1(a)) of TAN were depicted in Table 5. For visual comparison, the observed and simulated FT-IR and FT-Raman spectra of TAN were presented in Figs 2 and 3, which helped to understand the observed spectral features.

Root mean square values were obtained in this study using the following expression

$$RMS = \sqrt{\frac{1}{n-1}\sum_{i}^{n} \nu_i^{cal} - \nu_i^{\exp})^2} \qquad \ldots 2$$

The RMS error of the frequencies (unscaled) observed for TAN was found to be 88.49 cm^{-1}. In order to reproduce the observed frequencies, refinement of scaling factors was applied and optimized via least square refinement algorithm which resulted in a weighted RMS deviation of 6.2 and 4.3cm^{-1} for TAN.

C-H and CH_2 vibrations

The C-H stretching frequency is normally placed between 3100 and 3000 cm^{-1}. The infrared bands which appear at 3109 cm^{-1} and the Raman bands 3149, 3110 and 3091cm^{-1} for TAN have been assigned to the C-H stretching mode, as the corresponding force constant contributes almost 99% of the TED of this mode. The carbon-hydrogen in-plane and out-of-plane bending vibrations occur between 1000 and 800 cm^{-1}, respectively. The C-H in-plane and out-of-plane bending vibrations were attributed to 1301, 1251 and 1202 cm^{-1} in IR and 1078, 1041cm^{-1} in the infrared while this is placed at 853 cm^{-1} in the Raman spectrum, respectively. For the assignments of methylene group frequencies, one can expect asymmetric stretching (CH_2 as) to be much more intense than symmetric stretching (CH_2 ss). Thus, detailed investigations of the asymmetric and symmetric stretching internal modes of the CH_2 groups have been established. The bands identified at 3183 and 2922cm^{-1} were assigned to asymmetric and symmetric stretching vibrations of the CH_2 group of the title compound, respectively.

Similarly, it is well established that the deformation vibrations of CH_2 give rise to absorption in the region 1500 – 1400 cm^{-1}. It may, therefore, be assumed that the strong band at 1412 cm^{-1} was designated to the scissoring mode of CH_2 group for TAN. The rocking modes of the CH_2 group of the title compound, give rise to the band at 1128 cm^{-1} in the IR spectra. The assignments of the remaining active fundamentals, the CH_2 wagging, and the twisting, occur over a frequency range centered about 800 and 600 cm^{-1}, respectively. They were weaker than the scissoring and rocking vibrations in the infrared and moderately prominent in the Raman spectra. The CH_2 wagging, mode of TAN was observed at 842 cm^{-1}. The peaks at 591 in the IR were considered to be the CH_2 twisting mode of the title compound.

C ≡ N Vibration

In Thiophene-2-acetonitrile, the spectra of nitriles (R-C≡N) are characterized by medium absorption in the triple-bond stretching region of the spectrum. The assignment of the highly characteristic nitrite stretching mode (C≡N) to the band at 2254 cm^{-1} is quite obvious in all calculations. The degenerate pair of linear bending vibrations of the C-C≡N moiety is split into in-plane and out-of-plane components both strongly mixed with several other in-plane and out-of-plane vibrations, respectively, and contribute to several normal modes in the 600-100 cm^{-1} range. In the final force field, the in-plane linear bend has a small force constant than the out-of-plane counterpart, which may be due to the stronger interaction of the latter with the π-electrons of the aromatic ring [27].

V.Conclusion

Density functional theory calculations have been carried out on the structures and vibrational spectrum of Thiophene-2-acetonitrile. Vibrational frequencies calculated by B3LYP/6-31G* and B3LYP/6-311+G** levels agree very well with experimental results. The assignment of most of the fundamentals provided in this work is believed to be unambiguous. Infrared and Raman intensities were also calculated and reported. The simulated and observed spectra of the title compound agree well. This study demonstrates that scaled DFT/B3LYP calculations are a powerful approach for understanding the vibrational spectra of medium-sized organic compounds.

Table 3 - Definition of internal coordinates of thiophene-2-acetonitrile

No. (i)	Symbol	Type	Definition
		Stretching	
1 – 3	r_i	C – H	C3 – H7, C4 – H8, C5 – H9
4 - 6	R_i	C – C	C2 – C3, C3 – C4, C4 - C5
7 – 8	P_i	C – S	C2 – S1, C5 – S1
9 – 10	q_i	C – C	C2 – C6, C6 – C12
11	Q_i	C ≡ N	C12 – N13
12 – 13	r_i	C – H (methylene)	C6 – H10, C6 – H11
		Bending	
14-17	β_i	C – C – H	C5 – C4 – H8, C3 – C4 – H8
			C2 – C3 – H7, C4 – C3 – H7
18	β_i	C – C – H	C4 – C5 – H9
19	γ_i	S – C – H	S1 – C5 – H9
20	P_i	S – C – C	S1 – C2 – C6
21	θ_i	C – C – C	C3 – C2 – C6
22	θ_i	C – C – C	C2 – C6 – C12
23	δ_i	C – C – N	C6 – C6 – N13
24 - 27	β_i	C – C – H (methylene)	C2 – C6 – H10, C9 – C6 – H10
			C2 – C6 – H11, C9 – C6 – H11
28 - 29	α_i	Ring	C4 – C3 – C2, C3 – C2 – S1
30 – 31			C3 – C4 – C5, C2 – S1 – C5, C4 – C5 – S1
32			
		Out-of-plan bending	
33 – 35	ω_i	C – H	C4 – C2 – C3 – H7, C3 – C5 – C4 – H8 S1 – C4 – C5 – H9
36	ω_i	C – C	C6 – C2 – S1 – C3
37	ω_i	C – N	C2 – C6 – C12 – N13
38	ω_i	C – C	C12 – C6 – C2 – C3 (S1)
		Torsion	
39 – 43	τ_i	tring	C2 – S1 – C5 – C4, C4 – C3 – C2 – S1
			C5 – C4 – C3 – C2, C3 – C2 – S1 – C5
			S1 – C5 – C4 – C3
For numbering atoms refer to Fig. 2			

Table 4 - Definition of local symmetry coordinates and the values of corresponding scale factors used to correct the B3LYP/6–31G* (scaled) and B3LYP/6–311 + G** (refined) force fields for thiophene-2-acetonitrile

No (i)	Symbol	Definition	Scale factors used in calculations	
			B3LYP/ 6-31G*	B3LYP/ 6-311+G**
1 – 3	CH	r_1, r_2, r_3	0.924	0.928
4 – 6	CC	R_4, R_5, R_6	0.904	0.935
7 – 8	CS	p_7, p_8	0.983	0.089
9 – 10	CC	q_9, q_{10}	0.903	0.913
11	CN	Q_{11}	0.917	0.926
12	CH_2 ss	$r_{12}+r_{13}$	0.922	0.930
13	CH_2 as	$r_{12}-r_{13}$	0.922	0.930
14-15	bCH	$(\beta_{14}-\beta_{15})/\sqrt{2}$, $(\beta_{16}-\beta_{17})/\sqrt{2}$	0.945	0.978
16	bCH	$(\beta_{18} - \gamma_{19}) / \sqrt{2}$	0.945	0.978
17	bCC	$(\rho_{20} - \theta_{21}) / \sqrt{2}$	0.876	0.886
18	bCC	θ_{22}	0.876	0.886
19	bCN	δ_{23}	0.990	0.948
20	CH_2 (sciss.)	$\beta_{24} +\beta_{25} +\beta_{26} +\beta_{27}$	0.976	0.982
21	CH_2 (rock)	$\beta_{24} +\beta_{25} -\beta_{26} -\beta_{27}$	0.976	0.982
22	CH_2 (wag)	$\beta_{24} -\beta_{25} +\beta_{26} -\beta_{27}$	0.976	0.982
23	CH_2 (twist)	$\beta_{24} -\beta_{25} -\beta_{26} +\beta_{27}$	0.976	0.982
24	Ring 1	$\alpha_{28} -a(\alpha_{29}+\alpha_{32})+b(\alpha_{30}+\alpha_{31})$	0.967	0.951
25	Ring 2	$(a-b)(\alpha_{29}-\alpha_{32})-(1-a)(\alpha_{30}-\alpha_{31})$	0.967	0.951
26 –28	ωCH	ω_{33}, ω_{34}, ω_{35}	0.965	0.902
29	ωCC	ω_{36}	0.935	0.932
30	ωCN	ω_{37}	0.831	0.834
31	ωCC	ω_{38}	0.935	0.932
32	τRing1	$b (\tau_{39}+\tau_{43}) + a (\tau_{40}+\tau_{42}) + \tau_{41}$	0.923	0.888
33	τRing2	$(a-b) (\tau_{43}-\tau_{39}) + (1-a) (\tau_{42}-\tau_{40})$	0.923	0.888
a = cos144° and b = cos 72°				

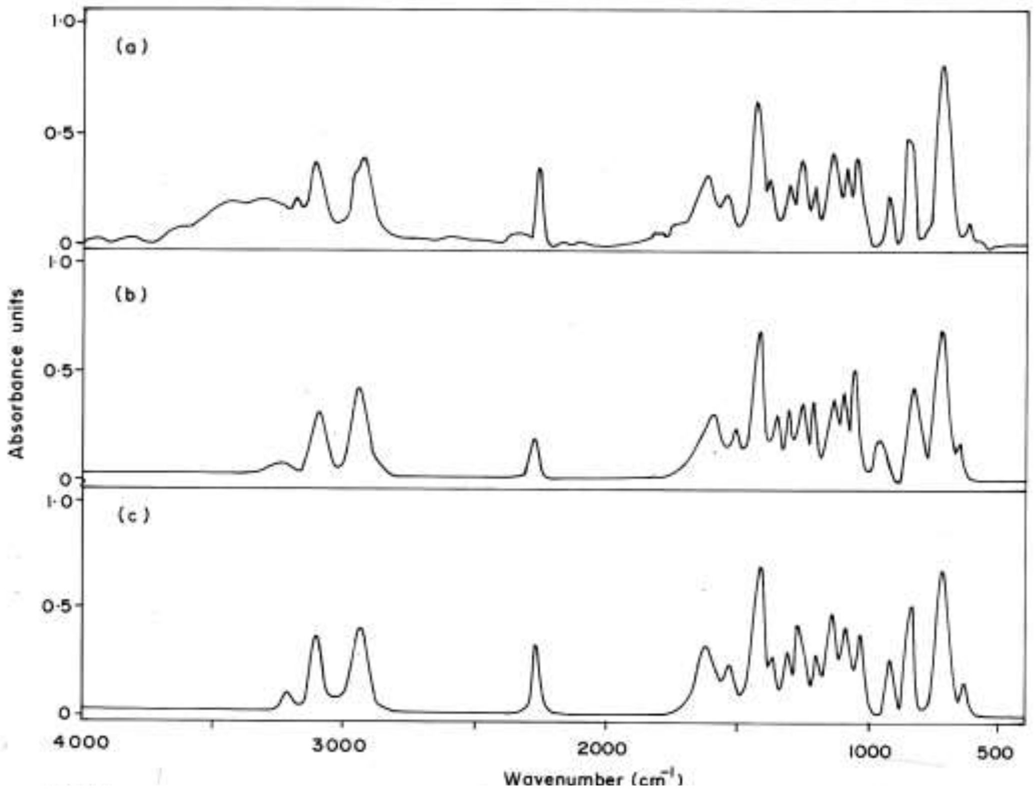

Fig.2 – Comparison of observed and calculated infrared spectra of thiophene-2- acetonitrile
a) observed in liquid phase (b) calculated with B3LYP/6-31G*
c) calculated with B3LYP/6-311+G**

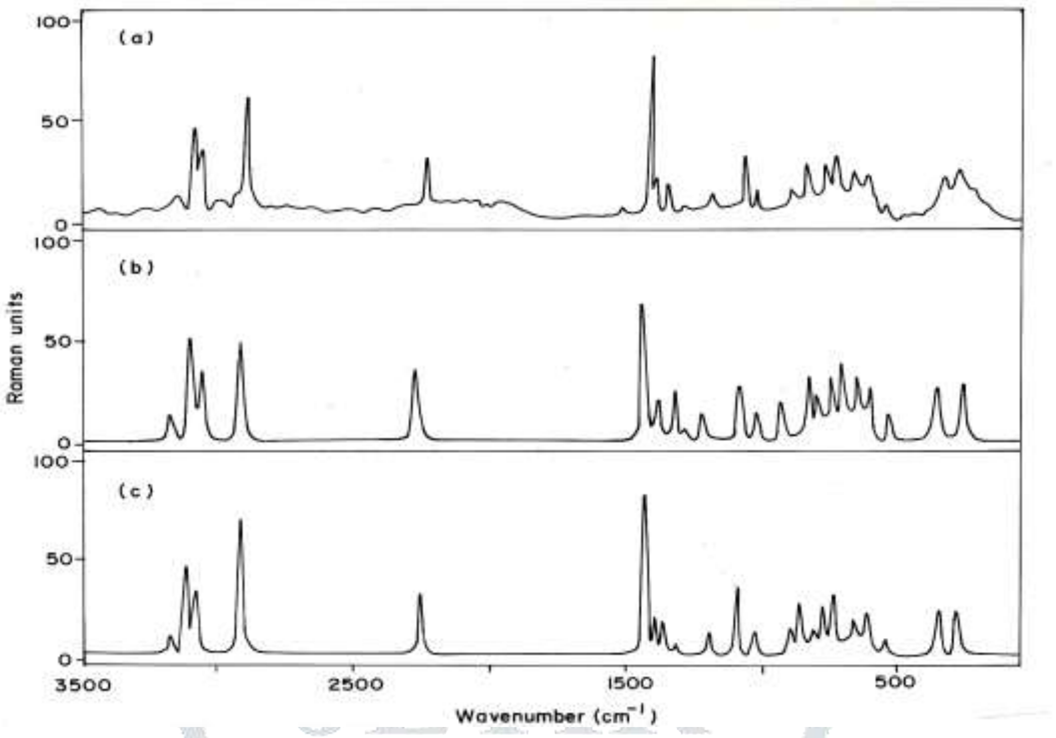

Fig.3 – Comparison of observed and calculated Raman spectra of thiophene-2- acetonitrile
(a) observed in liquid phase (b) calculated with B3LYP/6-31G*
c) calculated with B3LYP/6-311+G**

Table 5 - Assignment of fundamental vibrations of thiophene-2-acetonitrile by normal mode analysis based on SQM force field calculations

No. (i)	Symmetry species C_{2v}	Observed fundamental[a] (cm^{-1})		Calculated frequencies (cm^{-1})			TED (%) among types of internal coordinates[d]
				Unscaled	Scaled		
		FTIR	FT Raman	B3LYP/ 6-31G*	B3LYP/ 6-31G*	B3LYP/ 6-311+G**	
1	A_1	3183 vw		3371	3202	3193	CH_2 as (99)
2	A_1		3149 vw	3328	3161	3157	CH (99)
3	A_1	3109 ms	3110 s	3274	3118	3116	CH (99)
4	B_2		3091 ms	3239	3087	3083	CH (99)
5	B_2	2922 ms	2916 vs	3073	2924	2920	CH_2 ss (98)
6	A_1	2254 ms	2254 ms	2391	2261	2260	CN (68) CC (24)
7	A_1	1610 ms		1735	1607	1613	CC (67) bCH (23)
8	A_1	1538 w		1674	1530	1536	CC (67) bCH (23)
9	B_2		1438 vs	1555	1443	1444	CC (66) bCH (23)
10	A_1	1412 vs	1413 ms	1499	1408	1408	CH_2 (sciss) (80) CC (18)
11	B_2		1363 ms	1455	1356	1366	CC (65) CS (28)
12	B_2		1316 vw	1396	1318	1316	CC (65) CN (23)
13	A_1	1301 w		1372	1300	1301	bCH (66) CC (23)
14	B_2	1251 ms		1318	1249	1253	bCH (66) CC (23)
15	A_1	1202 w	1200 w	1260	1206	1199	bCH (65) CS (22)
16	B_2	1128 ms		1077	1124	1133	CH_2 (rock) (44) CC (20)
17	A_2	1078 ms	1080 s	1122	1084	1082	ωCH (87)
18	B_1	1041 ms	1042 w	1003	1044	1039	ωCH (85)

19	A_1	920 ms		969	928	916	CC (48) CC (36) bRing 1 (12)
20	B_2		905 w	935	914	900	CC (48) bCH (35) bRing 2 (13)
21	B_1		853 ms	881	850	854	ωCH (83)
22	A_2	842 ms		824	835	838	CH_2 (wag.) (61)
23	A_1		825 vw	845	831	822	bRing 1 (69) ωCC (21)
24	B_2		788 ms	772	784	784	bRing 2 (42) CC (22) bCH (11)
25	A_1	706 s		717	706	706	CS (71) bCH (15)
26	A_2		717 ms	725	706	711	ωCC (39), τRing 1 (29), CH_2 (twist) (20)
27	B_2		667 ms	679	660	664	CS (38), τRing 2 (27), ωCH (20)
28	B_2	623 vw		615	626	622	bCN (37), CC (28), CH_2 ss (12)
29	A_2		600 ms	595	598	599	ωCC (37), ωCH (31), τRing 1 (12)
30	A_2		567 vw	572	564	567	CH_2 (twist), (61), τRing 2 (25)
31	B_1		358 w	356	360	355	ωCN (57), ωCC (14)
32	A_2		289 w	292	289	289	τRing 1 (57), ωCH (17)
33	B_1		258 vw	255	256	258	τRing 2 (54) ωCH (10)

s- strong; m – medium; vs – very strong; w – weak; vw – very weak

ss-symmetric stretching; as-asymmetric stretching; b-bending; ω-out of plane bending τ-torsion

[a] Values are taken from liquid phase IR and Raman Spectra

[b] Relative absorption intensities normalized with highest peak absorbance equal to 1.0

[c] Relative Raman intensities calculated by Eq (1) and normalized to 100

[d] For the notation used see Table 4

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