

Experimental FT-IR, FT-Raman spectra and theoretical DFT calculations of 3-acetylbenzotrile

A. USHA RANI¹, N. SUNDARAGANESAN^{2*} and S. SEBASTIAN²

¹Avvaiyar Government College for Women, Karikal - 609 602 (India).

¹Research and Development Centre Bharathar University, Coimbatore - 641 046 (India).

²Department of Physics (Engineering), Annamalai University, Annamalai Nagar - 608 002 (India).

(Received: August 08, 2009; Accepted: October 15, 2009)

ABSTRACT

The Fourier transform infrared and Fourier transform Raman spectra of 3-acetylbenzotrile (3ABN) was recorded in the solid phase. The optimized geometry was calculated by B3LYP method using 6-311++G(d,p) basis set. The harmonic vibrational frequencies, infrared intensities, Raman scattering activities and the thermodynamic functions of the title compound were performed at the same level of theory. The theoretical spectrograms for IR and Raman spectra of the title molecule have been constructed.

Key words: FT-IR and FT-Raman spectra:ab initio and DFT (Density Function Theory), 3-acetylbenzotrile; vibrational analysis.

INTRODUCTION

Benzotrile is a phenyl cyanide compound. It is a colourless liquid with a boiling point of 197°C and having a smell of bitter almonds. Many derivatives of benzotrile are widely used in industry and medicinal fields. The main products of benzotrile-benzoic acid are used in medicine as urinary antiseptic in the form of salt and in vapour form for disinfecting bronchial tubes. Benzotrile derivatives are used in dye industry for making aniline blue and also used for preserving food products¹ Because of its wide use and structural simplicity a large number of studies on benzotrile and its derivatives were reported².

Joshi *et al.*,³ reported the Infrared and electronic absorption spectra of 2,6-3,5-dichloro benzotriles and 3-chloro-4methyl benzotrile. The various modes of vibrations were assigned and the

effects of substitution were analysed. The infrared absorption spectra of liquid m- and p-methyl benzotrile have been recorded by Johri *et al.*⁴. The spectra were recorded forming a thin film of compound between KBr plates. They have carried out a complete vibrational assignment of the spectra on the basis of C_s and C_{2v} point group symmetry.

Literature survey reveals that to the best of our knowledge, neither the complete Raman and IR spectra nor the force fields for 3ABN have been reported so far. In our present study Density Functional Theory (DFT) calculations have been performed to support our wavenumber assignment. DFT calculations are reported to provide excellent vibrational frequencies of organic compounds if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation, for basis set deficiencies and for the anharmonicity.

EXPERIMENTAL

The compound (3-acetylbenzotrile)3ABN in the solid form was purchased from the Sigma-Aldrich Chemical Company (USA) with a stated purity of greater than 98% and it was used as such without further purification. The FT-Raman spectrum of 3-ABN has been recorded using 1064 nm line of Nd:YAG laser as excitation wavelength in the region 100-4000 cm^{-1} on a Bruker model IFS 66 V spectrophotometer. The FT-IR spectrum of this compound was recorded in the region 400-4000 cm^{-1} on IFS 66 V spectrophotometer using KBr pellet technique. The spectra was recorded at room temperature, with a spectral resolution of 2.0 cm^{-1} . The observed experimental FT-IR and FT-Raman spectra along with theoretical spectra are shown in Figs. 1-2. The spectral measurements were carried out at Sophisticated Analytical Instrumentation Facility (SAIF), IIT, Chennai.

Method of calculations

All calculations were performed at Hartree-Fock (HF) and B3LYP levels on a Pentium IV/3.02 GHz personal computer using Gaussian 03W⁵ program package, invoking gradient geometry optimization⁶. The geometry was re-optimized at gradient corrected density functional theory (DFT)⁷ with the Becke's three parameter hybrid functional (B3)⁸ for the exchange part and the Lee-Yang-Parr (LYP) correlation function⁹, accepted as a cost effective approach, for the computation of molecular structure, vibrational frequencies and energies of optimized structures.

Density functional theory offers electron correlation frequently comparable to second-order Moller-Plesset theory (MP2). Finally, the calculated normal mode vibrational frequencies provide thermodynamic properties also through the principle of statistical mechanics. By combining the results of the GAUSSVIEW program¹⁰ with symmetry considerations, along with available related molecules vibrational frequency assignments were made with a high degree of accuracy.

RESULTS AND DISCUSSION

Molecular Geometry

The labeling of atoms in 3-acetylbenzotrile is given in Fig. 3. The optimized

geometrical parameters (bond length and angles) by DFT/B3LYP with 6-311++G(d,p) as basis sets are listed in Table 1, along with available experimental data, viz. benzotrile¹¹. It is seen from Table 1, a general priority for reproducing the experimental bond length taken from Ref. ¹¹ is not present in DFT-B3LYP level. However, all the bond lengths and bond angles computed with the DFT-B3LYP levels show excellent agreement with available experimental results when compared with HF levels.

The optimized geometry shows that CN and COCH₃ groups substituted in para and meta positions of phenyl ring are coplanar, which predicts maximum conjugation of the molecule with donor and acceptor groups. The DFT/6-311++G(d,p) calculations also gives shortening of the angle C4-C5-C13 by 2° and increase of the angle C6-C5-C13 by 2.8° from normal 120° at the C5 position, and this asymmetry of exocyclic angles reveals the repulsion between the COCH₃ group and the phenyl ring. The asymmetry of the exocyclic angles C2-C3-C11 and C4-C3-C11 is less at the C3 position, which gives lower repulsion of CN group with phenyl ring. The computed values of above mentioned angles correlate well with experimental results¹¹.

Vibrational assignments

With this assumed structural model, the molecule belongs to Cs point group and the 60 normal modes of fundamental vibrations which span the irreducible representations: 33A' + 15A". All the 48 fundamental vibrations are active in both IR and Raman.

The harmonic-vibrational frequencies calculated for 3ABN at B3LYP level using the triple split valence basis set along with diffuse and polarization functions, 6-311++G(d,p) have been collected in Table 2. Comparison of the frequencies calculated in general at B3LYP with experimental values (Table 2) reveals the overestimation of the calculated vibrational modes due to neglect of anharmonicity in real system. Inclusion of electron correlation in density functional theory to a certain extent makes the frequency values smaller in comparison with the HF frequency data. In order to improve the agreement with the

experiment, vibrational frequencies calculated at B3LYP/6-311++G(d,p) level were scaled by 0.96 [12]. The descriptions concerning the assignment have also been indicated in Table 2. The calculated

IR and Raman spectra of the title compound is shown in Fig. 1-2.

There are six equivalent C-C bonds in

Table 1: Geometrical parameters optimized in (3ABN), bond length (Å), bond angle (°)

Parameters	B3LYP		Experimental ^a	
	Bond length (Å)	6-31G(d,p)		6-311++G(d,p)
C1-C2		1.391	1.389	
C1-C6		1.396	1.394	1.387
C1-H7		1.085	1.083	
C2-C3		1.407	1.405	1.399
C2-H8		1.085	1.083	
C3-C4		1.399	1.397	1.399
C3-C11		1.436	1.433	1.430
C4-C5		1.400	1.398	1.387
C4-H9		1.084	1.083	
C5-C6		1.402	1.400	1.391
C5-C13		1.505	1.507	
C6-H10		1.085	1.083	
C11-N12		1.163	1.155	1.152
C13-O14		1.220	1.215	
C13-C15		1.517	1.515	
C15-H16		1.096	1.094	
C15-H17		1.090	1.088	
C15-H18		1.096	1.094	
Bond angle (°)				
C2-C1-C6		120.2	120.2	
C2-C1-H7		119.8	119.8	
C6-C1-H7		120.0	120.0	
C1-C2-C3		119.7	119.7	
C1-C2-H8		120.7	120.7	
C3-C2-H8		119.6	119.7	
C2-C3-C4		120.1	120.1	120.0
C2-C3-C11		119.8	119.8	119.9
C4-C3-C11		120.2	120.2	119.9
C3-C4-C5		120.2	120.2	119.9
C3-C4-H9		121.1	120.9	
C5-C4-H9		118.7	118.9	
C4-C5-C6		119.3	119.2	120.2
C4-C5-C13		117.7	118.0	
C6-C5-C13		123.0	122.8	
C1-C6-C5		120.5	120.6	120.1
C1-C6-H10		119.2	119.1	

^a Taken from Ref[11]

Table 2: Vibrational wave numbers obtained for 3ABN at B3LYP/6-311++G(d,p) [harmonic frequency (cm⁻¹)] IR intensities (Km mol⁻¹), Raman scattering activities (Å⁴ amu⁻¹), Raman depolarization ratio and reduced masses (amu), force constants (m dyne Å⁻¹)

Mode nos.	Experimental (cm ⁻¹)		Theoretical Frequencies (cm ⁻¹)						Vibrational	
	FT-IR	FT-Raman	B3LYP/6-311++G(d,p)	IR int	Sact	Depratio	Red Mass	Force constants	assignments	
1		96 w	54	1	0	0.75	1.0	0.11	τ CH ₃	
2		139 m	66	4	5	0.74	4.5	0.01	β C-CH ₃ + β C ^o N	
3			97	2	2	0.70	4.7	0.03	γ C ^o N + gC-H	
4			116	8	3	0.75	5.7	0.05	β C ^o N + b C-CH ₃	
5			147	2	2	0.71	4.1	0.06	γ C ^o N	
6		183 w	248	1	1	0.73	8.3	0.33	γ C ^o N	
7	379 w		297	1	2	0.44	3.4	0.19	γ CCC	
8			352	5	4	0.34	7.1	0.56	γ CCC	
9	432 w	428 w	361	0	1	0.70	4.9	0.41	γ CCC + γ C ^o N	
10	480 w	478 vw	407	1	3	0.11	9.4	0.99	β CCC	
11			483	0	3	0.14	4.2	0.63	γ CCC	
12	538 s	532 vw	521	1	5	0.16	6.3	1.10	β C ^o N + β C=O	
13			547	15	8	0.14	4.8	0.93	β C-CN	
14	557 w	554 vw	563	1	13	0.26	4.2	0.86	β C-CN	
15	607 s	603 vw	622	8	2	0.71	7.5	1.86	γ CCC	
16		630 vw	644	9	19	0.10	6.5	1.72	β CCC	
17	680s		683	36	12	0.38	4.9	1.47	β CCC	
18	692 w	691 ms	694	15	0	0.28	3.0	0.93	γ CCC + γ C-H	
19	802 vs		774	4	6	0.68	4.2	1.63	β CCC	
20		860 vw	837	53	0	0.47	1.3	0.59	γ C-H	
21			912	8	5	0.20	1.6	0.83	p CH ₃	
22			929	18	1	0.68	1.4	0.77	g C-H	
23			951	0	0	0.72	1.4	0.78	γ C-H	
24			973	1	43	0.06	6.2	3.76	trigonal bending	
25			985	17	5	0.40	3.8	2.38	γ C-H	
26	965 s	964 vw	1006	0	29	0.24	1.3	0.83	γ C-H	

Table 2. Cont.

27	997 m	996 s	1023	1	4	0.14	2.7	1.83	ring breathing
28	1025 m		1069	32	6	0.12	2.2	1.63	β C-H
29	1088 m	1089 m	1090	3	8	0.30	1.8	1.35	β C-H
30	1187 s	1182 m	1156	2	4	0.09	3.3	2.81	ν C-CN
31			1172	10	12	0.35	1.3	1.10	β C-H
32	1274 s	1275 ms	1266	11	5	0.38	3.3	3.38	ν C-C
33			1275	150	0	0.39	1.2	1.22	ω CH3
34	1313 w	1294 s	1315	8	5	0.73	1.5	1.64	β C-H
35	1369 vs	1368 w	1376	2	7	0.51	1.1	1.32	CH ₃ umbrella mode
36	1481 m		1391	1	0	0.73	2.2	2.76	β C-H + δ CH ₂ in CH ₃
37	1418 s	1422 w	1402	1	0	0.74	1.1	1.38	CH ₃ asym. bending
38	1581 s	1578 m	1456	2	1	0.63	2.0	2.71	ν C=C
39	1598 s	1597 m	1555	2	0	0.66	4.8	7.46	ν C=C (semicircle stretch)
40	1688 vs	1676 vs	1566	18	7	0.71	5.1	8.07	ν C=O
	1747w								overtone/combination
	1820w								overtone/combination
	1930w								overtone/combination
	1981w								overtone/combination
41	2229 vs	2228 vs	2258	11	318	0.27	12.8	41.61	ν C°N
42	2924 vw	2926 m	2912	1	55	0.71	1.1	5.90	ν C-H
43		2963 vw	2923	4	73	0.71	1.1	5.97	ν C-H
44		3005 w	2925	0	40	0.32	1.1	5.98	ν C-H
45	3044 w	3043 vw	2933	7	234	0.13	1.1	6.04	ν C-H
46	3070 m	3080 m	3098	4	182	0.04	1.0	6.32	ν_s C-H in CH ₃
47			3185	10	87	0.62	1.1	7.15	ν_{as} C-H in CH ₃
48		3115vw	3193	9	39	0.71	1.1	7.21	ν_{as} C-H in CH ₃

IR int - IR intensity; Sact -Raman scattering activity; Kmmol⁻¹ w-weak ; vw- very weak ; s-strong ; vs-very strong ; m-medium; br, sh- broad, shoulder ; ν - stretching; ν_{sym} - symmetric stretching ; ν_{asy} - asymmetric stretching ; β - in plane bending ; γ - out-of -plane bending ; ω - wagging ; τ - twisting ; δ -scissoring ; τ -torsion.

benzene and consequently there will be six C-C stretching vibrations. In addition, there are several in-phase and out-of-phase bending vibrations of the ring carbons. However, due to high symmetry of benzene, many modes of vibrations are infrared inactive. In general the bands around 1400 cm^{-1} to 1650 cm^{-1} in benzene derivatives are assigned to skeletal stretching of C-C bonds. The bands observed at 1481 , 1581 and 1598 cm^{-1} of 3-acetylbenzonitrile are identified as C-C stretching vibrations. The theoretically calculated C-C stretching vibrations by B3LYP/6-311++G(d,p) are at 1266 , 1456 and 1555 cm^{-1} show excellent agreement with recorded spectral data. The C-C aromatic stretch known as semicircle stretching, predicted at 1555 cm^{-1} is also in excellent agreement with experimental observations of 1581 cm^{-1} in FT-IR and 1578 cm^{-1} in FT-Raman spectra. In the benzene, fundamental (992 cm^{-1}) and (1010 cm^{-1}) represents the ring breathing mode and carbonal trigonal bending mode. Under the C_s point group both the frequency of vibrations are very close, there is appreciable interaction between these vibrations and consequently their energies will be modified. The ring breathing and trigonal bending modes of 3ABN are assigned at 997 and 1025 cm^{-1} respectively. The theoretically computed values for the above said vibrations are at 1023 and 973 cm^{-1} by B3LYP/6-311++(d,p) method coincides with experimental observations. The theoretically calculated C-C-C out-of-plane and C-C-C in-plane bending modes have been found to be consistent with the recorded spectral values.

The C-H stretching modes usually appear with strong Raman intensity and are highly polarized. May be owing to this high polarization, the C-H stretching vibrations of benzene derivatives generally appear above 3000 cm^{-1} . In FT-IR spectrum of 3ABN, the bands are at 3044 and 3070 cm^{-1} are assigned to the C-H stretching vibrations of aromatic ring respectively. In the FT-Raman spectrum, the bands are observed at 3005 and 3043 cm^{-1} are attributed to C-H stretching vibrations. The vibrations assigned to aromatic C-H stretch in the region 2912 - 2933 cm^{-1} ¹³ are in agreement with experimental assignment 3005 - 3044 cm^{-1} ¹⁴. The expected C-CN stretching vibration is identified in the region 1095 - 1245 cm^{-1} . The C-CN stretching vibration is observed as strong to medium intensity

at 1179 cm^{-1} in 2-chloro-6-methylbenzonitrile¹⁵, 1150 cm^{-1} in m-methylbenzonitrile¹⁶ and 1183 cm^{-1} in p-methylbenzonitrile¹⁶. It is further observed that in many of the 1,2,3-trisubstituted molecules, C-CN stretching has a higher value in cases where the attached substituent is more electron attractive. In our title molecule a strong band at 1187 cm^{-1} in FT-IR and medium band at 1182 cm^{-1} in FT-Raman are assigned to C-CN stretching vibration. The theoretically calculated value by B3LYP/6-311++G(d,p) method at 1156 cm^{-1} shows excellent agreement with experimental observations.

The three in-plane C-H bending vibrations appear in the range 1000 - 1300 cm^{-1} in the substituted benzene and the three out-of-plane bending vibration occur in the frequency range 750 - 1000 cm^{-1} ¹⁷. The C-H in-plane bending vibrations assigned in the region 1069 - 1315 cm^{-1} , while the experimental observation are at 1088 - 1313 cm^{-1} . The calculated frequencies 837 , 929 , 951 and 985 cm^{-1} for the C-H out-of-plane bending falls in FT-IR value at 965 , 692 cm^{-1} and FT-Raman value at 964 , 860 and 691 cm^{-1} .

A nitrile group is associated with three characteristic frequencies. They are stretching, in-plane and out-of-plane bending vibrations. The geometry of the cyano group ($C\equiv N$) is affected insignificantly by a new substituent on the phenyl ring. Hence the vibrational wavenumber on the cyano group remains almost unchanged from the benzonitrile molecules. For the aromatic compound which bears a $C\equiv N$ group attached to the ring, a band of good intensity has been absorbed in the region 2240 - 2221 cm^{-1} ¹⁸ and it is being attributed to $C\equiv N$ stretching. A strong IR band at 2229 cm^{-1} in 3ABN indicates $C\equiv N$ stretching. It is calculated in benzonitrile at 2229 cm^{-1} which is close to the calculated value 2258 cm^{-1} in our molecule 3ABN. Experimentally^{19,20} in mono-substituted benzonitrile, this vibration appears in the 2220 - 2240 cm^{-1} range and in di-substituted benzonitrile at 2230 cm^{-1} , in accordance with scaled values of 2238 cm^{-1} in 4-amino benzonitrile and 2248 cm^{-1} in benzonitrile and with an IR intensity that varies from medium-weak to strong depending on the substituent. As in benzonitrile molecule and its derivative, this stretching mode appears with the strongest Raman intensity in accordance with our present result. The

intensity is enhanced by the conjugation of the aromatic ring.

In-plane and out-of-plane bending modes of C≡N group, by contrast appears with weak IR intensity and with null Raman activity and strongly coupled with CCC bending modes. The C≡N planar and non-planar bending modes appear at 564 and 246 cm^{-1} respectively in 2-aminobenzonitrile²¹. In anthranitrile molecule²² the band observed at

570 cm^{-1} in solid and liquid phase has been assigned to the in-plane C≡N deformation mode. Therefore, in the present case the strong band observed at 538 cm^{-1} in FT-IR and a very weak band at 532 cm^{-1} in FT-Raman spectra has been assigned to in-plane C≡N deformation mode in accordance with the assignments proposed by Mittal²³ in related molecules. The C≡N out-of-plane bending mode is observed at 183 cm^{-1} in FT-Raman spectrum for our title molecule. The theoretically computed values

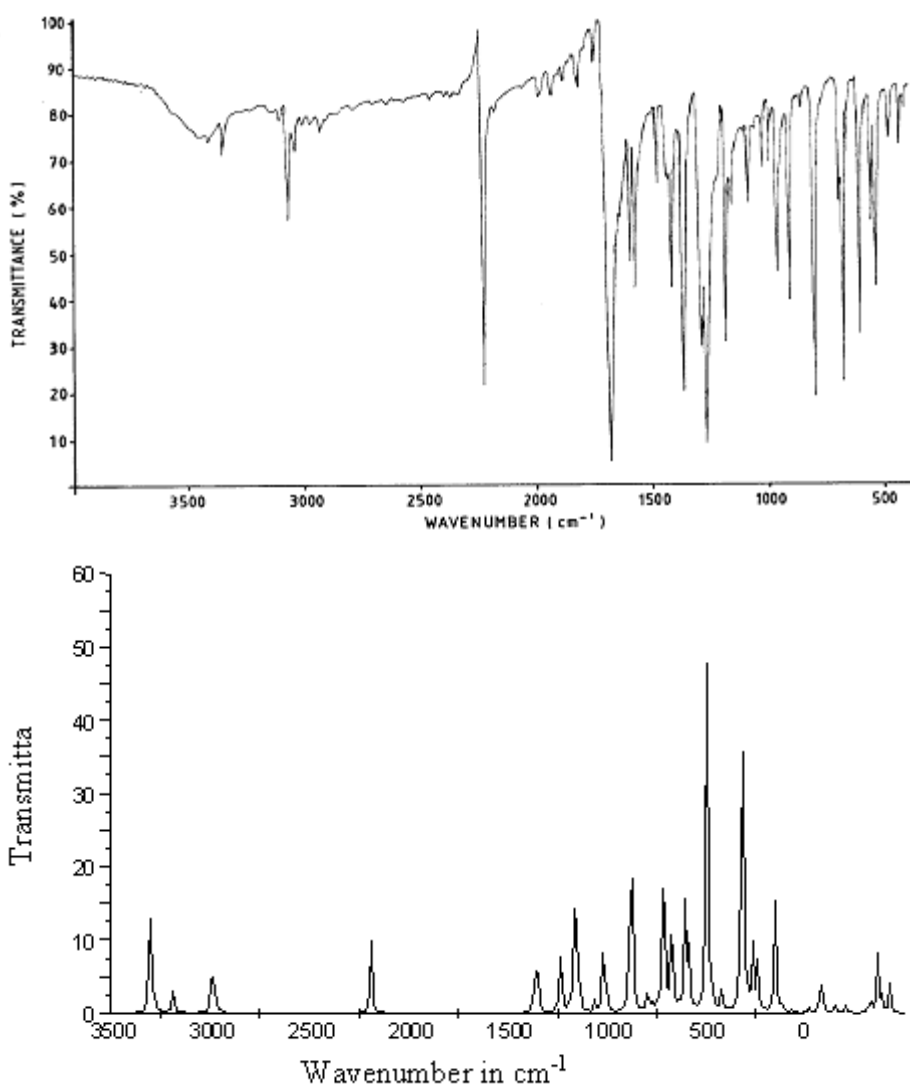


Fig. 1(a): Recorded FT-IR spectrum of 3-acetylbenzonitrile
(b) Theoretical FT-IR spectrum of 3-acetylbenzonitrile

at 521 and 248 cm^{-1} by B3LYP/6-311++G(d,p) method for $\text{C}\equiv\text{N}$ in-plane and out-of-plane bending vibrations respectively shows excellent agreement with experimental observations.

The carbonyl group is important and its characteristic frequency has been extensively used to study a wide range of compounds. If a compound contains a carbonyl group the absorption caused by $\text{C}=\text{O}$ stretching is generally the strongest²⁴. Carbonyl group vibrations in ketones are the best characteristic bands in vibrational spectra and for this reason, such bands have been the subject of extensive studies²⁵. The intensity of

these bands can increase because of conjugation or formation of hydrogen bonds. The increase of conjugation, therefore, leads to the intensification of the Raman lines as well as to the increased infrared band intensities. The carbonyl stretching vibrations in ketones are expected in the region 1715 - 1680 cm^{-1} . In the present investigation the FT-IR band observed at 1688 cm^{-1} and the FT-Raman band observed at 1676 cm^{-1} has been assigned to $\text{C}=\text{O}$ stretching vibration. The theoretically calculated value by B3LYP/6-311++G(d,p) method at 1566 cm^{-1} is deviating negatively by 110 cm^{-1} . This assignment is in good agreement with literature value²⁶.

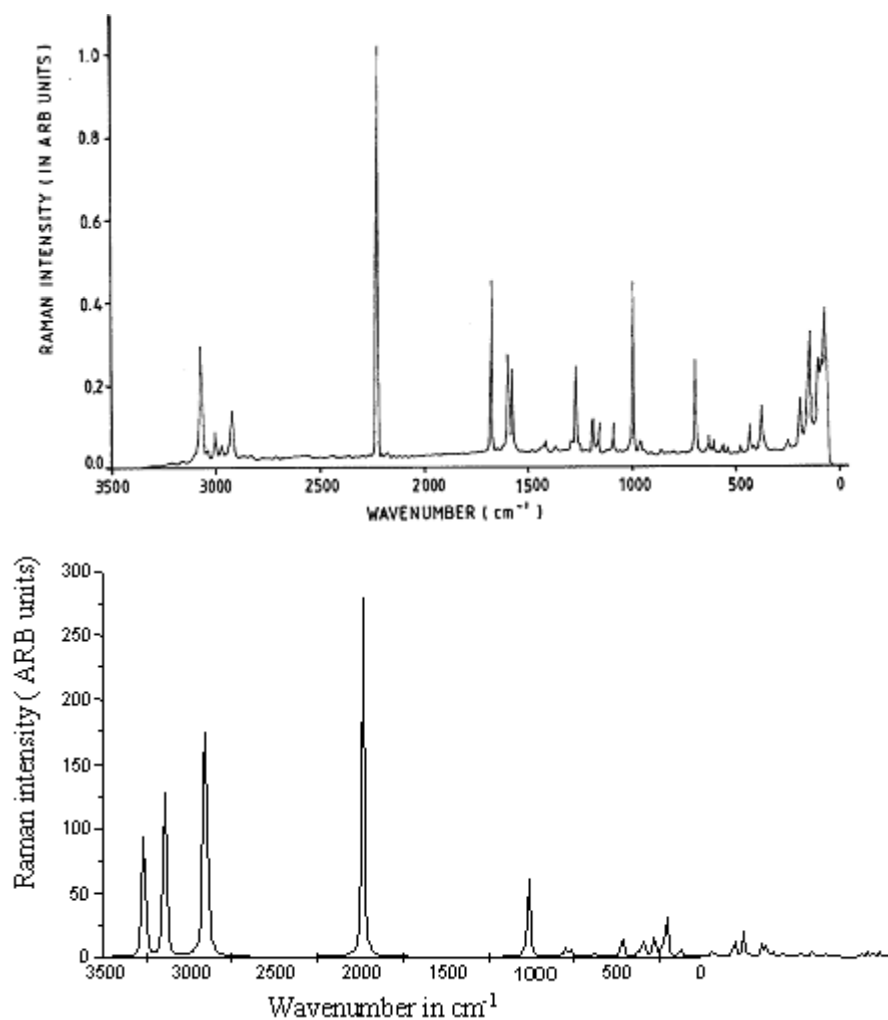


Fig. 2(a): Recorded FT-Raman spectrum of 3-acetylbenzonitrile
(b) Theoretical FT-IR spectrum of 3-acetylbenzonitrile

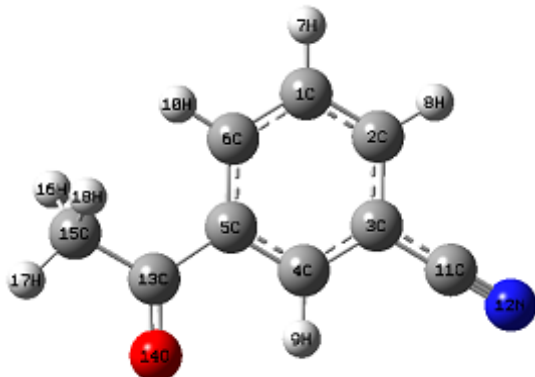


Fig. 3: Numbering system adopted in this study (3-acetylbenzonitrile)

Methyl groups are generally referred to as electron donating substituents in the aromatic ring system. The asymmetric C-H stretching mode of CH_3 group is expected in the region around 2980 cm^{-1} and the symmetric ²⁵ one is expected around the region 2870 cm^{-1} . The CH_3 asymmetric stretching vibrations appears as medium intense bands in the Raman spectrum at 3080 cm^{-1} and weak bands in the IR spectrum at 3070 cm^{-1} , which is coupled with the aromatic C-H stretching mode. The symmetric stretching mode is observed as a medium intense band in the Raman spectrum at

2926 cm^{-1} . The changes in intensity of the CH_3 stretching mode in infrared spectrum and shift to higher wavenumbers are due to the influence of electronic effects resulting from hyperconjugation and induction of methyl group with the aromatic ring system. For the molecule where induction produces stronger polarization of C-H bonds along with the increase of both C-H force constant and charge of the hydrogen atom (q°_{H}) and decrease of C-H stretching infrared intensity and with decrease of C-H bond length can cause enhancement of vibrational wavenumber of C-H stretching modes²⁷. Another electronic effect, hyperconjugation, causes the interaction of the orbital of a methyl group with the p orbital of an aromatic ring system²⁸. This interaction occurs with the releasing of electronic charge from s C-H to the C-C bond that connects the two interacting groups. The most evident effect of this interaction is that the C-C bond decreases in length from its normal value (1.54 \AA) and increase in strength, but hyperconjugation can also have effect on C-H bonds. The different value of the equilibrium charges of hydrogen atoms involved in C-H bonds obtained from infrared intensities have been directly correlated to spectral patterns. When the hydrogen bonds become more acidic (q°_{H} more positive) because of the release of electronic charge, the infrared C-H stretching intensity decreases and the bending intensity increases²⁹. This happens because of hyperconjugation of the

Table 3: Theoretically computed energies (a.u.), zero-point vibrational energies (kcal mol⁻¹), rotational constants (GHz), entropies (cal mol⁻¹ K⁻¹) and dipole moment (D) for 3-acetylbenzonitrile

Parameters	HF/6-31G(d,p)		B3LYP/6-31(d,p)	
	6-31G(d,p)	6-311++G(d,p)	6-31G(d,p)	6-311++G(d,p)
Total energy	-474.2210897	-474.3206492	-477.1477233	-477.1569546
Zero-point energy	91.92	91.22	85.68	83.03
Rotational constants	2.2298	2.2363	2.1884	2.7895
	0.7267	0.7269	0.7192	0.7485
	0.5499	0.5504	0.5432	0.5871
Entropy				
Total	94.590	95.017	96.969	95.441
Translational	40.827	40.827	40.827	40.827
Rotational	30.268	30.264	30.309	30.392
Vibrational	23.495	23.926	25.833	24.222
Dipole moment	6.648	6.795	6.103	6.531

methyl group to the p electron in the aromatic ring, where the injection of negative electronic charge takes place from the CH₃ group to an adjacent portion of the molecule that contains π electrons. In 3ABN, the methyl hydrogen atoms are subjected simultaneously to hyperconjugation and induction, which cause the enhancement of stretching wavenumbers and the decrease of infrared intensities as reported in the literature for similar molecular systems³⁰. Thus, the hyperconjugation and induction of the methyl group, causing changes in intensity in infrared spectrum, clearly indicated the methyl hydrogen are directly involved in the donation of electronic charge which is confirmed by the large q_{H} values.

Other molecular properties

Several calculated thermodynamic parameters are presented in Table 3. Scale factors have been recommended³¹ for an accurate prediction in determining the zero-point vibration energies (ZPVE), and the entropy, $S_{\text{vib}}(T)$. The variations in the ZPVEs seem to be insignificant. The total energies are found to decrease with the increase of the basis set dimension. The changes

in the total entropy of 3-ABN at room temperature at different basis set are only marginal.

CONCLUSIONS

We have carried out ab initio DFT calculations on the structure and vibrational spectrum of 3ABN. Comparison between the calculated and experimental structural parameters indicates that B3LYP results are in good agreement with experimental ones. Vibrational frequencies, infrared intensities and Raman activities calculated by B3LYP/6-311++G(d,p) method agree very well with experimental results. On the basis of agreement between the calculated and observed results, assignments of fundamental vibrational modes of 3ABN were examined and some assignments were proposed. Therefore, the assignments made at higher level of theory with higher basis set with only reasonable deviations from the experimental values, seem to be correct. This study demonstrates that scaled DFT/B3LYP calculations are powerful approach for understanding the vibrational spectra of medium sized organic compounds.

REFERENCES

- Bahl, B.S., Arun Bhal, *Advanced Organic Chemistry*, S. Chand and Company Ltd., 4th ed. (1995) 1117.
- Abramczyk, H. W., *Reimschuessel, Proceedings of the IV International Conference of Raman Spectroscopy*, Tokyo (1984) 174.
- Joshi, A., K. Rao, S., Shasahidar, M.A., *Current Sci.* **57**: 477 (1988).
- Johri, G.K., Prakash, V., Srivastava, C.L., *Ind. J. Pure Appl. Phys.* **14**: 418 (1976).
- Frisch, M.J., et al *Gaussian 03*, Gaussian Inc., Wallingford, CT (2004)
- Schlegel, H.B., *J. Comput. Chem.*, **3**:214 (1982).
- Hohenberg, P., Kohn, W., *Phys. Rev B.* **864**:136(1964).
- Becke, A.D., *J. Chem. Phys.* **98**: 1372 (1993).
- Lee, C., Yang, W., Parr, R.G., *Phys. Rev. B* **37**: 785(1988).
- Frisch, A., Nielson, A.B., Holder, A.J., *GAUSSVIEW User Manual*, Gaussian Inc, Pittsburgh, PA, 2000.
- Rastogi, V.K., Palafox, M.A., Singh, S., Singhal, S.K., *Asian, J. Phys.* **7**:229(1998).
- Pople, J.A., Schlegel, H.B., Krishnan, R., Defrees, D.J., Binkley, J.S., Frish, M.J., Whiteside, R.A., Hout, R.H., Hehre, W.J., *Int. J. Quantum Chem. Symp.* **15** : 269 (1981).
- Ferguson, E.E. et al, *J. Chem. Phys.* (USA) **21**: 1464 (1953).
- Ansari, A.K., Verma, P.K., *Spectrochim. Acta A* **35**: 35 (1979).
- Goel, R.K., Sharma, S.D., Sharma, S.N., *Ind. J. Pure Appl. Phys.* **17**: 55 (1979).
- Sinha, S.P., Chatterjee, C.L., *Ind. J. Pure Appl. Phys.* **14**: 419 (1976).

17. Socrates, G., *Infrared Charectristic Group Frequencies*, John Wiley, New York (1981).
18. Lee, C., Yang, W., Parr, R.G., *Phys. Rev.B* **37**: 785 (1998).
19. Bakiler, M., Maslov, I.V., Akyiiz, S., *J. Mol. Struct.* **475**: 83 (1999).
20. Zlerkiewiez, W., Michalska, D., Zeegers-Huyskens, T. H., *J. Phys. Chem A.* **104**: 11685 (2000).
21. Rastogi, V.K., Mital, H.P., Sharma, S.N., Chattopadhyay, S., *Ind. J. Phys.* **65B**: 356 (1991).
22. Rastogi, V.K., Alcolea Palsfox, M., Lal, B., Vaibhav J., *Ind. J. Pure Appl. Phys.* **38**: 564 (2000).
23. H.P; Mital, *Spectral Studies of Some Polyatomic Molecules and Biologically active Compounds*, Ph.D. Thesis, ChCS University, Meerut, India (1995).
24. Nakkeeran, C. Ph.D., Thesis, Bharathidasan University, Tiruchirapalli, Tamil Nadu, India, 1997.
25. Kleinman, D.A., *Phys. Rev.* **126**: 1977 (1962).
26. Krishnakumar, V., John Xavier, R., *Ind. J. Pure Appl. Phys.* **41**: 597 (2003).
27. Person, W.B., Zerbi, G., *Vibrational Intensities in Infrared and Raman Spectroscopy*, Elsevier, Amsterdam (1982).
28. Gussoni, M., Castiglioni, C., Ramos, M.N., Rui, M.C., Zerbi, G., *J. Mol. Struct.* **224** : 445(1990).
29. Gussoni, M., Castiglioni, C., *J. Mol. Struct.* **521**: 1 (2000).
30. Socrates, G., *Infrared Charectristic Group Frequencies*, Wiley-Interscience Publication, New York (1980).
31. Lister, G.D., Tyler, J.K., Hog, J.H., Larsen, N.W., *J. Mol. Struct.* **23**: 253 (1974).