

Vibrational spectra, normal coordinate analysis and thermodynamics of 2-chloro-5-nitrobenzotrile

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The laser Raman (0-3500 cm^{-1}) and FTIR (200-4000 cm^{-1}) spectra (Nujol, KBr, liquid and vapour) of 2-chloro-5-nitrobenzotrile have been recorded. A zero-order normal coordinate analysis has been made for the molecule using force constants derived earlier. On the basis of potential energy distributions and eigen vectors unambiguous vibrational assignments have been made for all the fundamentals of the molecule. The ideal gas state thermodynamic functions of the molecule are also computed in the temperature range 200-1500 K by utilizing the observed fundamental frequencies assuming rigid-rotor harmonic oscillator approximation.

Keywords: Vibrational spectra, Normal coordinate analysis, Thermodynamics, Nitrobenzotrile

1 Introduction

The usefulness of vibrational spectroscopy has expanded rapidly over the last decade with the development of FTIR and Raman instrumentation. A number of investigations concerning the interpretation of the vibrational spectra of benzonitrile and its mono- and di-substituted derivatives have been reported¹⁻¹⁵. Force field calculations have also been made in few cases using the classical method developed by Wilson *et al.*¹⁶ to support the vibrational analysis. Rastogi *et al.*^{7,13} have reported the IR and Raman spectra and planar and non-planar force fields for 2,6-difluoro, and 2,4-dichlorobenzonitriles. Recently, geometry, vibrational wavenumbers, atomic charges, several thermodynamic parameters (total energy, rotational constants and the room temperature entropy) and dipole moments of some di-substituted benzonitriles have been reported¹⁰⁻¹². Other studies on these molecules also appear in literature. Most of the di-substituted benzonitriles so far studied are of the type $\text{C}_6\text{H}_3\text{CNX}_2$, whereas very less study appears on the molecules of the type $\text{C}_6\text{H}_3\text{CNXY}$, where X and Y are different atoms or group of atoms attached to the benzene ring. The reason for this situation may be because the complexity of a molecule increases with increasing number of atoms in it and its decreasing symmetry. It is well known that it is easier to deal with a molecule of lesser complexity than that

which is relatively more complex. This statement is true even with the computational convenience offered by the present day computers. Further, in force field computations one has to start with simpler molecules and then consider relatively more complex molecules in a systematic manner, in order to arrive at physically reasonable set of force constants. This has naturally resulted in comparatively large number of investigations in the case of simpler molecules than those of relatively more complex systems. The di-substituted benzonitriles are no exception (e.g. in *para* substitution, for monoatomic substituents, $\text{C}_6\text{H}_3\text{CNX}_2$ has C_{2v} symmetry, whereas $\text{C}_6\text{H}_3\text{CNXY}$ has C_s symmetry, if planar structure is assumed). To the best of our knowledge the vibrational spectrum of 2-chloro-5-nitrobenzotrile molecule has not been reported completely so far.

The aim of the present study is four fold namely:

- (i) To record infrared and Raman spectra of 2-chloro-5-nitrobenzotrile in its various states of aggregation in order to obtain complete information on its vibrational frequencies. This seems to be lacking in the literature available so far.
- (ii) To make a zero-order normal coordinate analysis (i.e. force constants are not refined) for the molecule under consideration to make the

vibrational assignments unambiguous as emphasized by Fuhrer *et al*¹⁷.

- (iii) To examine the transferability of force constants by getting their initial values from our earlier work on substituted benzonitriles¹⁸ and other related systems^{19,20}. This is the most interesting aspect of the present study.
- (iv) To compute thermodynamic functions of the molecule in the temperature range 200-1500 K by utilizing the observed fundamental frequencies assuming rigid-rotor harmonic oscillator approximation. We do this as a part of our general program of study on substituted benzenes.

2 Experimental Details

Spectrally pure 2-chloro-5-nitrobenzonitrile was purchased from M/s Aldrich Chemical Co, USA and used as such without further purification. The Raman spectrum was excited by the 488.0 nm line of an argon ion laser of 100 mW power and was recorded on Jasco K 500 Raman spectrophotometer. The slit width at the entrance was 380 μ m, the time constant was 0.5s and the scanning speed was 5. The resolution of the Raman spectra is 1 cm⁻¹. These spectra shown in Figs 1 and 2, have several prominent Raman shifts. Their quality is good except for the non-linear baseline in Fig. 1.

The IR spectra in liquid and vapour phases, were recorded by Jasco Spectrophotometer model FTIR/7000 and in KBr and Nujol on Nicolet-DX spectrophotometer. IR spectra in liquid and vapour phases were recorded by warming the powdered substance (2-chloro-5-nitrobenzonitrile) in a variable T cell for gas (SPECAC) and warming the KBr windows of the cell to avoid condensation of the gas. The temperature was controlled by two thermocouples. The FTIR spectra were recorded with a resolution of 1 cm⁻¹. These spectra, shown in Figs 3-6 are of very good quality. However, in order to

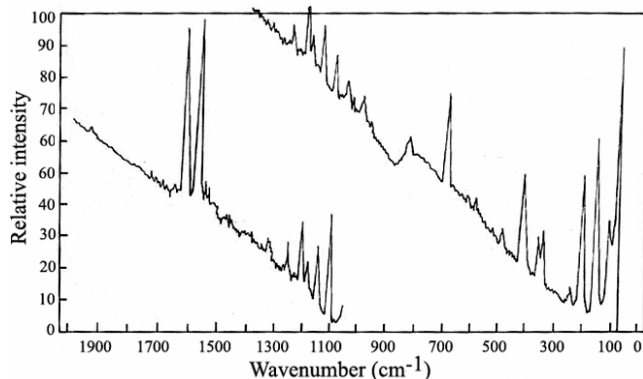


Fig. 1 — Raman spectrum of 2-chloro-5-nitrobenzonitrile (0-2000 cm⁻¹)

record weak bands with sufficient intensity, we used more quantity of the sample in KBr pellet. This explains the reason for the low starting transmittance in this spectrum as shown in Fig. 4.

3 Normal Coordinate Analysis and Results

Wilson's FG matrix method was used for the normal coordinate analysis¹⁶. The molecule under

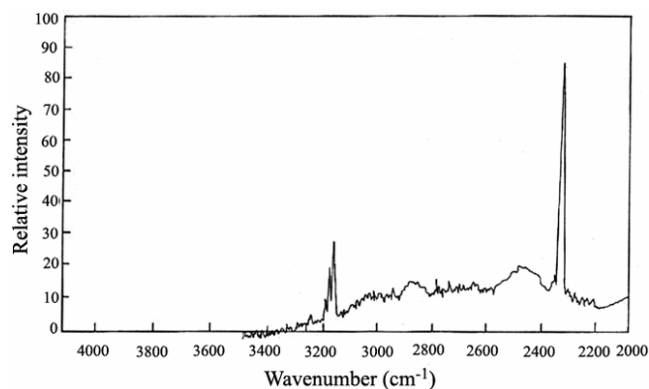


Fig. 2 — Raman spectrum of 2-chloro-5-nitrobenzonitrile (2000-3500 cm⁻¹)

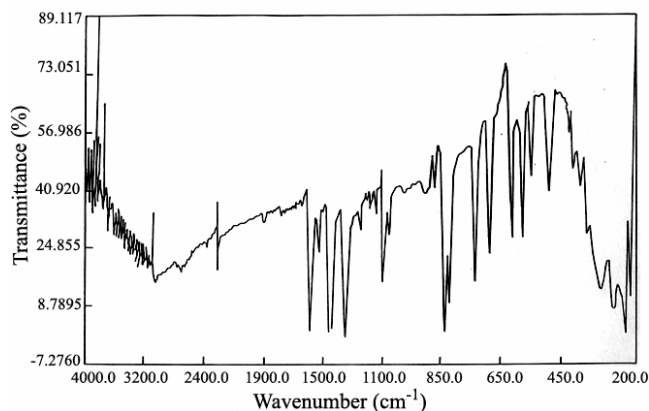


Fig. 3 — FTIR (Nujol) spectrum of 2-chloro-5-nitrobenzonitrile (200-4000 cm⁻¹)

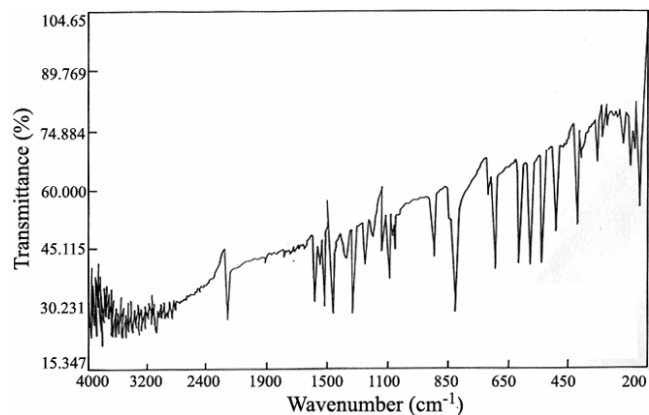


Fig. 4 — FTIR (KBr) spectrum of 2-chloro-5-nitrobenzonitrile (200-4000 cm⁻¹)

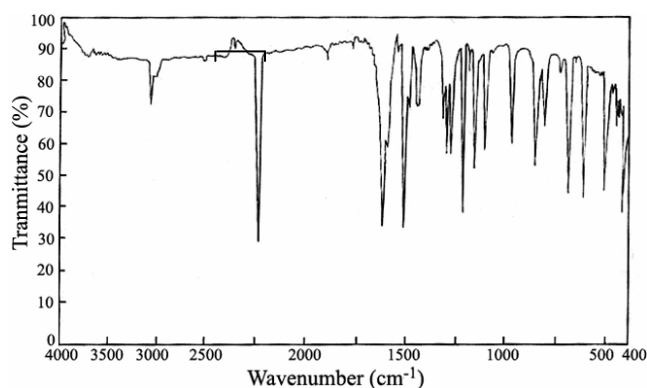


Fig. 5 — FTIR (Liquid) spectrum of 2-chloro-5-nitrobenzonitrile (400-4000 cm^{-1})

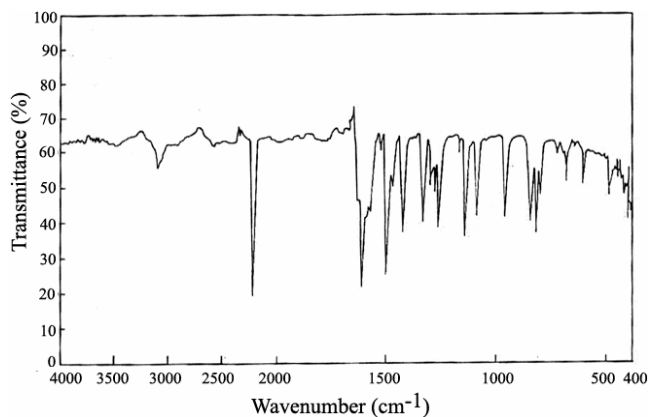


Fig. 6 — FTIR (Vapour) spectrum of 2-chloro-5-nitrobenzonitrile (400-4000 cm^{-1})

consideration, with labeling of atoms is shown in Fig. 7(b). The molecule has C_s symmetry. For C_s structure, the 39 fundamentals of the molecule consist of 27 in-plane (a') vibrations and 12-out-of plane (a'') vibrations. All the vibrations are active in both the infrared and Raman spectra.

The structural parameters, internal coordinate system, method of dealing with redundancies, symmetry coordinates used, process of selecting initial set of force constants and the method of computation in the present case were the same as those employed for substituted benzonitriles¹⁸. In analogy with monohalogenated nitrobenzenes¹⁹ the C-N and N=O bond lengths are taken as 1.426 Å and 1.186 Å, respectively and the corresponding angles (C N O and O N O) were assumed to be 120° each. Thus, a 70-element valence force field was chosen for the normal coordinate analysis of in-plane and out-of-plane vibrational modes. The initial values of all the force constants were obtained from substituted benzonitriles for benzonitrile moiety¹⁸, whereas those

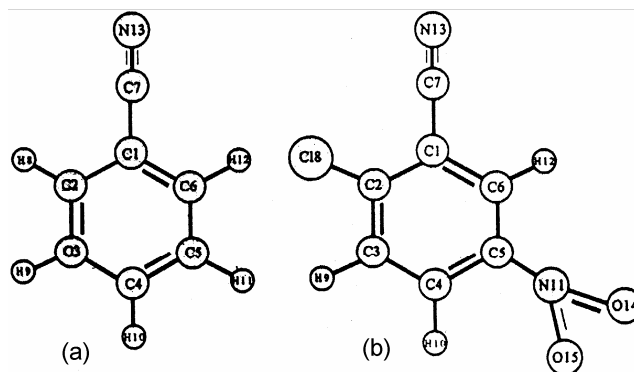


Fig. 7 — Structures of (a) Benzonitrile and (b) 2-chloro-5-nitrobenzonitrile molecules with classical numbering of atoms.

associated with nitro group were taken from monohalogenated nitrobenzenes¹⁹ for in-plane vibrations and chlorinated nitrobenzenes²⁰ for out-of-plane vibrations. We have made use of the above criterion in our earlier publications¹⁸⁻²⁰, from which initial force constants were taken for the present system. The reliability of force constants used in this investigation is beyond any reasonable doubt because it is an established procedure to determine reliability of force constants based on the following five criteria, when an initial set of force constants has been refined:

(i) The calculated and observed frequencies should agree within reasonable limits of experimental error and anharmonicity corrections, (ii) The final values of the force constants, especially those of the diagonal ones, should be close to their initial values, (iii) The dispersions of the constants should be small, (iv) The constants should be comparable to the corresponding ones in related molecules, and (v) The constants should reproduce the frequencies of related molecules with reasonable accuracy in a zero-order calculation.

Therefore, a zero order calculation was made employing this initial set of force constants using Schachtschneiders programme²¹ modified to suit the Hall Mark II mini computer system at National Institute of Technology, Warangal, India. This reproduced 38 observed frequencies with an average error of 17.8 cm^{-1} . This should be considered acceptable, as the force constants are not refined in a zero-order calculation. This supports the transferability of the force constants reported in Refs 18-20. The zero-order force constants are presented in Table 1. Further, as the force constants are reliable that have reproduced the frequencies with reasonable

Table 1 — Zero order force constants

Symbol	Coordinates	Common Involved	Value Atoms	Symbol	Coordinates	Common Involved	Value Atoms
(A) In-plane force constants diagonal force constants Stretch				Stretch-Bend — <i>Contd</i>			
K_R	C–H	—	5.1729	$F_{(d,\epsilon)}$	C–C, NCC	C–C	0.3635
K_d	C–C	—	6.8170	$F_{(M,\psi)}$	N = O, CNO	N = O	0.4705
K_r	C–CN	—	5.3445	$F_{(N,\gamma)}$	C–N, ONO	N	0.1207
K_D	C≡N	—	16.8559	$F_{(d,\alpha)}$	C–C, C–C–CN	C–C	0.2377
K_N	C–N	—	5.0318	$F_{(D,\beta)}$	C≡N, CCN	C≡N	0.0032
K_M	N=O	—	9.0244	$F_{(Rl,\phi_1)}$	C–Cl, CICC	C–Cl	0.7772
K_{Rl}	C–Cl	—	3.3247	$F_{(d,\phi_1)}$	C–C, CICC	C–C	0.0707
Bend				Bend-Bend			
H_ϕ	CCH	—	0.5019	$F_{(\phi,\phi)}$	CCH, CCH	C–C	0.0013
H_θ	CCC	—	1.0536	$F_{(\theta,\theta)}$	CCC, CCC	C–C	0.0152
H_α	C–C–CN	—	0.7464	$F_{(\alpha,\beta)}$	C–C–CN, CCN	C–CN	0.0214
H_β	CCN (nitrile)	—	0.3862	$F_{(\epsilon,\epsilon)}$	NCC, NCC	C–N	0.2098
H_ϵ	NCC (nitro)	—	1.2884	$F_{(\alpha,H)}$	C–C–CN, CCH	C–C	– 0.0387
H_ψ	CNO	—	0.9881	$F_{(\phi_l,\phi)}$	CICC, CCH	C–C	0.0568
H_γ	ONO	—	1.5294	$F_{(\alpha,\phi)}$	C–C–CN, CCCI	C–C	– 0.0196
H_{ϕ_1}	CCCl	—	0.8007	(B) Out-of-Plane Force Constants			
Interaction constants				Diagonal force constants			
Stretch-Stretch				γ_R C–H — 0.4234			
$F_{(d,d)}$	C–C, C–C	C	0.8007	γ_{Rl}	C–Cl	—	0.5070
$F_{(d,d)}$	C–C, C–C	—	– 0.5837	δ	C–C	—	0.3113
$F_{(d,d)}$	C–C, C–C	—	0.2123	γ_M	C–CN	—	0.4049
$F_{(R,d)}$	C–H, C–C	C	0.0269	γ_{Ml}	C≡N	—	0.4857
$F_{(r,d)}$	C–CN, C–C	C	0.2915	γ_N	C–N	—	0.5195
$F_{(r,D)}$	C–CN, C≡N	C	– 0.0923	γ_{Nl}	N=O	—	0.2373
$F_{(N,D)}$	C–N, C–C	C	0.6310	Interaction constants			
$F_{(N,M)}$	C–N, N = O	N	0.3803	$\gamma_R \gamma_R$	C–H, C–H	C–C	– 0.0505
$F_{(M,M)}$	N = O, N = O	N	1.2493	δ_i, δ_{i+1}	C–C, C–C	CCC	– 0.0067
$F_{(R,R)}$	C–H, C–H	C–C	– 0.0104	γ_{Rl}, γ_R	C–Cl, C–H	C–C	– 0.0735
$F_{(R,R)}$	C–H, C–H	—	– 0.0462	γ_M, γ_R	C–CN, C–H	C–C	– 0.0232
$F_{(R,R)}$	C–H, C–H	—	– 0.0775	γ_N, γ_R	C–N, C–H	C–C	0.0166
$F_{(Rl,d)}$	C–Cl, C–C	C	0.0597	γ_R, δ	C–H, C–C	—	0.1383
Stretch-Bend				γ_{Rl}, δ	C–Cl, C–C	—	0.1766
$F_{(d,\theta)}$	C–C, CCC	C–C	0.6001	γ_{Ml}, δ	C–CN, C–C	—	0.1405
$F_{(R,\phi)}$	C–H, CCH	C–H	0.0733	γ_{Nl}, δ	C–N, C–C	—	0.2384
$F_{(r,\alpha)}$	C–CN, C–C–CN	C–CN	0.2643	γ_M, γ_{Rl}	C–CN, C–Cl	—	– 0.0589
$F_{(r,\beta)}$	C–CN, CCN	C–CN	– 0.0735	τ_N	C–N	—	0.0318
$F_{(N,\epsilon)}$	C–N, NCC	C–N	1.0172	γ_R	C–H, C–H	—	0.0047
$F_{(N,\psi)}$	C–N, CNO	C–N	0.6202				
$F_{(M,\gamma)}$	N = O, ONO	N=O	0.9563				
$F_{(d,\phi)}$	C–C, CCH	C–C	0.1932				

accuracy, the resulting potential energy distributions and consequent vibrational assignments should be considered reliable.

4 Discussion

Vibrational assignments — The observed vibrational bands alongwith their assignments are presented in Table 2, whereas the corresponding calculated wavenumbers and the respective potential energy distributions (PEDs) are given in Table 3. Here, the

normal mode description following each fundamental in the last column are due to Wilson²². The results presented in Table 2, are self-explanatory; therefore, the discussion is confined to some of the important modes only.

C–C/C–H Stretching vibrations — The assignments for the three C–H stretching modes (20a, 20b, 2) and two ring C–C stretching modes corresponding to the benzene modes 8 (a, b) and 19 (a, b) are straightforward in light of PEDs.

Table 2 — Vibrational assignments of 2-chloro-5-nitrobenzonitrile

S. No.	Sp	Sym		IR		Raman		Assignment
		Nujol	KBr	Liquid	Vapour			
1.	<i>a'</i>	—	—	3055w	—	3055s	—	v(C-H)2
2.	<i>a'</i>	—	—	—	3090w	3084vw	—	v(C-H)20a
3.	<i>a'</i>	—	3070m	—	—	3070m	—	v(C-H)20b
4.	<i>a'</i>	—	—	1184s	1185vw	1186w	—	v(C-CN)13
5.	<i>a'</i>	—	1099s	1105s	1100s	1096s	—	v(C-C)1
6.	<i>a'</i>	—	1605s	1618s	1618vs	1618vs	—	v(C-C)8a
7.	<i>a'</i>	—	1584w	—	—	1574vs	—	v(C-C)8b
8.	<i>a'</i>	1536m	—	1504s	1506vs	—	—	v(C-C)19a
9.	<i>a'</i>	1250w	1264m	1270s	1270s	1260m	—	v(C-C)14
10.	<i>a'</i>	—	338w	—	—	342m	—	v(C-Cl)7a
11.	<i>a'</i>	1460s	1457s	—	—	—	—	v(C-C)19b
12.	<i>a'</i>	912m	—	—	—	—	—	v(CN)7b
13.	<i>a'</i>	1204w	1216w	1218m	—	1205s	—	β (C-H)3
14.	<i>a'</i>	1134m	1130m	1145s	1146s	1144m	—	β (C-H)18a
15.	<i>a'</i>	1120s	—	—	—	—	—	β (C-H)18b
16.	<i>a'</i>	—	—	—	—	—	—	β (C-CN)15
17.	<i>a'</i>	740s	—	—	742w	—	—	β (C-C-C)6a
18.	<i>a'</i>	488s	480s	500s	500m	486w	—	β (C-C-C)6b
19.	<i>a'</i>	—	—	—	416m	—	—	β (C-C-C)12
20.	<i>a'</i>	292m	—	—	—	—	—	β (C-Cl)9b
21.	<i>a'</i>	220s	218s	—	—	200vs	—	β (CN)9a
22.	<i>a'</i>	—	2236s	2238s	2238s	2235vs	—	v(C \equiv N)
23.	<i>a'</i>	612s	618s	625s	618m	616vw	—	β (C \equiv N)
24.	<i>a''</i>	—	—	856s	860s	—	—	π (C-H)5
25.	<i>a''</i>	816s	826s	—	818m	820w	—	π (C-H)11
26.	<i>a''</i>	—	—	970s	968s	970w	—	π (C-H)17b
27.	<i>a''</i>	—	—	—	—	100m	—	π (C-Cl)17a
28.	<i>a''</i>	242s	252m	—	—	244w	—	π (CN)10a
29.	<i>a''</i>	—	—	—	—	140s	—	π (C-CN)10b
30.	<i>a''</i>	688s	700s	695s	694m	685s	—	τ (C-C-C)4
31.	<i>a''</i>	404m	410s	407s	—	404s	—	τ (C-C-C)16a
32.	<i>a''</i>	358sh	354m	—	—	360m	—	τ (C-C-C)16b
33.	<i>a''</i>	568s	583s	—	—	583w	—	ω (C \equiv N)
Internal modes of the NO ₂ group in 2-chloro-5-nitrobenzonitrile								
34.		1550vs	1549s	—	1552w	1550w	—	ν_{as} NO ₂
35.		1350vs	1349s	—	1350s	1340vs	—	ν_{sym} NO ₂
36.		840vs	—	—	840s	—	—	δ NO ₂
37.		547s	547s	—	—	—	—	γ NO ₂
38.		—	—	—	—	80vs	—	τ NO ₂
39.		—	718m	725w	—	—	—	ω NO ₂

vs-very strong, s-strong, m-medium, w-weak, vw-very weak, v-stretching, β -in-plane-bending, π -out-of-plane-bending, τ -torsion, ω -out-of-plane

In 2-chloro-5-nitrobenzonitrile studied here, modes 8a and 8b are expected to be around 1600 cm⁻¹. The higher wavenumber has 79% C-C stretching character. It exhibits mixing with mode 18a. The lower wavenumber is a C-C stretching mode to the extent of 83%. This mixes with mode 18b. According to the calculations made here, the fundamentals around 1618 and 1584 cm⁻¹ are ascribed to mode 8a and 8b, respectively.

Modes 19a and 19b are expected in the range 1400-1500 cm⁻¹. The higher wavenumber is a C-C stretching mode to the extent of 45%. It has a PED contribution of 49% from C-H in-plane bending mode 18b. The lower frequency exhibits C-C stretching character to the extent of 44%. This mode also mixes with C-H in-plane bending mode 18b. In addition, this mode also mixes with ν_{as} (NO₂). According to computations, the absorptions near 1506

Table 3 — Potential energy distribution (PED) of 2-chloro-5-nitrobenzonitrile

S. No	Mode	Observed Freq. (cm ⁻¹)	Calculated Freq. (cm ⁻¹)	PED in internal Force constants	Vibrational Assignments
a' species					
1.	v(CH)2	3055 ⁺	3054	101K _R	2
2.	v(CH)20a	3084 ⁺	3107	98K _R	20a
3.	v(CH)20b	3070*	3082	99K _R	20b
4.	v(CCl)7a	338*	319	20H _θ , 18K _{RI} , 10K _d	6b+7a+1
5.	v(CN)7b	912*	913	25K _N , 17H _θ , 13K _r , 13K _d	7b+6b+13+19a
6.	v(C–CN)13	1185	1203	32K _d , 21H _θ , 19K _r , 16H _θ	1+18b+13+19a
7.	v(CC)l	1100	1054	42K _d , 25H _θ , 11K _{RI} , 11H _φ	1+12+7a+18b
8.	v(CC)8a	1618	1608	79K _d , 10H _φ	8a+18a
9.	v(CC)8b	1584*	1583	83K _d , 18H _φ	8b+18b
10.	v(CC)14	1270	1278	89K _d , 22H _φ	14+18b
11.	v(CC)19a	1506	1470	49H _φ , 45K _d	18b+19a
12.	v(CC)19b	1457*	1403	44K _d , 26H _φ , 22K _M	19b+18b+v _{as} (NO ₂)
13.	β(CH)3	1218 ^{\$}	1262	61H _φ , 30K _d	3+19b
14.	β(CH)18a	1146	1134	49H _φ , 38K _d	18a+19b
15.	β(CH)18b	1120*	1101	32H _φ , 26K _d , 13K _N , 12K _{RI}	18b+19a+7b+7a
16.	β(CCl)9b	292*	292	33H _φ , 21H _ψ , 18H _β , 15H _ε	9b+γ(NO ₂)+β(C≡N)+9a
17.	β(CN)9a	200 ⁺	165	49H _ε , 34H _φ , 15H _ψ	9a+9b+γ(NO ₂)
18.	β(C–CN)15	—	124	46H _α , 29H _β	15+β(C≡N)
19.	β(CCC)6a	742	698	55H _θ , 14K _{RI} , 12K _d	6a+7a+1
20.	β(CCC)6b	500	518	19H _θ , 16H _β , 12H _α , 10K _d	6b+β(C≡N)+15+1
21.	β(CCC)12	416	423	17K _r , 16H _β , 16H _θ	13+β(C≡N)+12
22.	v(C≡N)	2238	2232	86K _D , 14K _r	v(CN)+13
23.	β(C≡N)	618	618	27H _α , 17H _β , 12H _ε , 12H _ψ	15+β(C≡N)+9a+γ(NO ₂)
24.	v _{as} (NO ₂)	1549*	1534	71K _M , 22K _d	v _{as} (NO ₂)+8b
25.	v _s (NO ₂)	1349*	1346	70K _M , 35K _N	v _s (NO ₂)+7b
26.	δ(NO ₂)	840	809	37H _γ , 16H _θ , 12H _ψ	δ(NO ₂)+6a+γ(NO ₂)
27.	γ(NO ₂)	547*	529	27H _ψ , 17K _{RI} , 13H _ε	γ(NO ₂)+7a+9a
a'' species					
28.	π(CH)5	860	871	104γ _R	5
29.	π(CH)11	818	810	100γ _R	11
30.	π(CH)17b	968	955	108γ _R	17b
31.	π(CCl)17a	100 ⁺	99	78θ, 17γ _{RI}	16b+17a
32.	π(CN)10a	252*	267	65γ _N , 24γ _{RI}	10a+17a
33.	π(C–CN)10b	140 ⁺	139	57γ _M , 19γ _N , 11γ _{MI}	10b+10a+ω(C≡N)
34.	τ(CCCC)4	694	690	44γ, 20γ _M , 13γ _{MI}	4+10b+ω(C≡N)
35.	τ(CCCC)16a	404*	399	78δ, 25γ _{MI}	16+ω(C≡N)
36.	τ(CCCC)16b	358*	362	64δ, 42γ _{MI}	16b+17a
37.	ω(C≡N)	568*	533	53δ, 43γ _{MI}	4+ω(C≡N)
38.	ω(NO ₂)	718*	701	77γ _{MI} , 18γ _N	ω(NO ₂)+10a
39.	τ(NO ₂)	80 ⁺	58	90τ _N	τ(NO ₂)

+ : Raman shift, * : solid phase IR frequency, \$ liquid phase IR frequency others are vapour phase IR frequencies

and 1457 cm⁻¹ are due to mode 19a and mode 19b, respectively.

The assignment of mode 14, which is also known as Kekule mode is usually difficult as one of the C–H bending vibrations appears in its vicinity. According to the calculations, the band at 1270 cm⁻¹ is assigned to mode 14. It is observed to have almost a pure C–C character. It mixes with the C–H in-plane bending mode 18b to the extent of 22%.

Ring vibrations — The ring vibrations 1, 12, 6a and 6b require a careful consideration of their quantitative description for correct assignment and their correlation with benzene ring mode as suggested by Patel *et al.*²³. These modes are characterized by the fact that all the C–C bonds change in length symmetrically in mode 1, alternate $\overline{\text{CCC}}$ angles increase or decrease in mode 12, the $\overline{\text{CCC}}$ angles change in the ratio +2, -1, -1, +2, -1, -1 in mode 6a,

while they change in the ratio 0, +2, -2, 0, +2, -2 in mode *6b* (the +ve and -ve signs indicate increase and decrease, respectively). The above statement is approximately true in the case of asymmetrically substituted benzene of present type. Using this criterion and also the potential energy distributions, the absorptions near 1100, 740, 500 and 416 cm^{-1} have been attributed due to the modes 1, *6a*, *6b*, and 12, respectively.

C-H out-of-plane bending vibrations — As identified from appropriate phase relations and the PED presented in Table 3, the following observations can be made. The bands at 870, 818 and 968 cm^{-1} are due to modes 5, 11 and *17b*, respectively. The order of C-H wagging modes in this molecule is *17b* > 5 > 11. Further, the present calculations show mode 5, 11 and *17b* to be pure.

CCCC torsional vibrations — In accordance with the discussion presented in Ref. (24), in the case of corresponding modes the following assignments are arrived at for the ring torsions 4, *16a* and *16b*. Modes 4, *16a* and *16b* come near 694, 408 and 354 cm^{-1} , respectively.

It is seen that mode 4 is the highest ring torsional vibration in this compound. It mixes with mode *10b* and $\omega(\text{C}\equiv\text{N})$. The present calculations establish that the frequency of mode *16a* is greater than that of *16b*. Mode *16a* mixes with $\omega(\text{C}\equiv\text{N})$, whereas mode *16b* mixes with mode *17a*. Thus, the order of CC torsions is 4 > *16a* > *16b* in this molecule.

Vibrations of nitrile (C≡N) group — The stretching vibration of nitrile group around 2235 cm^{-1} should be the strongest in Raman and it is expected to have considerable intensity in infrared. On this basis, it has been identified near ~ 2238 cm^{-1} in all the phases. As it is separated from other frequencies, it is expected to be almost a pure frequency. The calculations confirm this expectation, as there is about 86% of C≡N stretching character in this frequency. It mixes with C-CN stretching mode 13 to the extent of 14%.

C-CN vibrations — As identified from appropriate phase relations and PED presented in Table 3, the following observations can be made. PED of above molecule shows that the bands at 1185, 124 (calculated value), 140 cm^{-1} are due to the modes 13, 15 and *10b*, respectively. The higher frequency is the (C-CN) stretching mode to the extent of 19%, lower frequency is the (C-CN) in-plane bending mode to the extent of 46%, while the other frequency is the (C-CN) out-of-plane bending mode to the extent of 57%.

C-Cl vibrations — The C-Cl stretching mode appears as mixed mode. It has been observed that in benzene derivatives containing a Cl atom, the C-Cl stretching frequency appears in 600-800 cm^{-1} region²⁵. However, on the basis of PED, the band observed at 338 cm^{-1} in IR and Raman spectra has been identified as C-Cl stretching mode. This assignment is further supported by the literature value¹³. The C-Cl in-plane bending mode may be correlated to the wavenumber 292 cm^{-1} (Nujol). The C-Cl out-of-plane bending mode appears at 100 cm^{-1} in Raman.

Internal vibrations of NO₂ group — The NO₂ group has two stretching frequencies one being symmetric and other asymmetric. The aromatic nitro compounds give strong bands in the region 1570-1500 cm^{-1} and 1370-1300 cm^{-1} . Randle and Whiffen²⁶ assigned the symmetric stretching frequency to a band lying between 1333 and 1370 cm^{-1} and the asymmetric stretching frequency between 1494 and 1539 cm^{-1} in the spectra of nitrobenzene derivatives. Thus, in the present case, the bands at 1350 and 1349 cm^{-1} in IR and at 1340 cm^{-1} in the Raman are assigned to symmetric stretching vibration, while the bands appear at 1550, 1549 and 1552 cm^{-1} in IR and 1550 cm^{-1} in Raman are assigned to asymmetric stretching vibration. These assignments are substantiated by the present calculations. The bands at 840, 547 and 718 cm^{-1} in IR spectrum and at 80 cm^{-1} in Raman spectrum have been assigned to NO₂ deformation, rocking, wagging and torsional vibrations, respectively.

Table 4 — Thermodynamic functions of 2-chloro-5-nitrobenzonitrile

Temp (K)	Enthalpy	(-) Free energy	Entropy	Heat capacity
200.0	12.589	61.848	74.437	21.264
273.0	15.857	67.244	82.101	28.281
298.0	16.995	67.683	84.678	30.563
300.0	17.086	67.797	84.883	30.742
400.0	21.559	73.331	94.690	38.957
500.0	25.730	78.598	104.330	45.614
600.0	29.499	83.630	113.130	50.868
700.0	32.850	88.435	121.290	55.014
800.0	35.843	93.023	128.870	58.321
900.0	38.494	97.401	135.900	60.993
1000.0	40.857	101.580	142.440	63.177
1100.0	42.970	105.580	148.550	64.981
1200.0	44.869	109.400	154.274	66.485
1300.0	46.582	113.060	159.640	67.749
1400.0	48.133	116.570	164.700	68.818
1500.0	49.543	119.940	169.480	69.729

5 Thermodynamic Functions

Thermodynamic functions of 2-chloro-5-nitrobenzonitrile have been calculated by utilizing standard expressions²⁷ and are presented in Table 4. In order to calculate these functions, the result of the present spectroscopic study is used to derive the vibrational contribution to the partition function. For determining rotational contributions, the required structural parameters are the same as those used for normal coordinate analysis. The calculations of total contributions of enthalpy, free energy, entropy and heat capacity at various temperatures were carried out in the rigid rotor harmonic oscillator approximation and these relate to 1 mole of perfect gas at 1 atm. The frequencies used for computation of thermodynamical functions are 3084, 3070, 3055, 2238, 1618, 1584, 1549, 1506, 1457, 1349, 1270, 1218, 1185, 1146, 1120, 1100, 968, 860, 840, 818, 742, 718, 694, 618, 568, 547, 500, 416, 404, 358, 338, 292, 252, 200 cm⁻¹.

6 Conclusions

It is apparent from Table 3 that out of the 39 normal fundamentals, 38 could be observed in the present case. Most of the modes have wavenumbers in the range suggested by previous assignments found in the literature in the case of related molecules. The planar C–CN bending mode is calculated at a lower wavenumber (124 cm⁻¹) than non-planar (140 cm⁻¹) counterpart, contrary to the case of benzonitrile.

From the potential energy distribution, it appears that the wavenumber corresponding to the (C≡N) stretching contains almost 100% contribution from the C≡N stretching force constant. It is also apparent from Table 3 that there is no interaction between the C–Cl and C≡N stretching vibrations. As the difference between the observed and theoretical values of most of the fundamentals is very small, the assignments made by us seem to be correct.

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