

Vibrational spectra and thermodynamics of anthranilonitrile molecule

V K Rastogi, M Alcolea Palafox*, B Lal & Vaibhav Jain

Department of Physics, L R College, Sahibabad 201 005

*Departamento de Química-Física I (Espectroscopia) Facultad de Ciencias Químicas

Universidad Complutense, Madrid 28040, Spain

Received 14 February 2000, revised 13 July 2000

The infrared spectra of anthranilonitrile molecule have been recorded in different phases (solid, liquid and gas). The spectra have been analysed assuming C_s point group symmetry for the molecule and the assignments for fundamental vibrations have been made. The thermodynamic functions have been computed in the temperature range 200-1500 K by utilizing the fundamental frequencies obtained from infrared spectra and assuming a rigid rotor-harmonic oscillator.

Introduction

The vibrational spectra of mono-, and di-substituted benzonitriles have been studied in detail by many workers¹⁻¹³. Ultraviolet absorption spectra of benzonitrile and substituted benzonitriles have also been reported¹⁴. Other studies on these molecules also appear in the literature¹⁵⁻³⁰. Recently Rastogi *et al.*¹⁰ have reported the infrared spectra of *o*-aminobenzonitrile in solid phase. As the compound was highly fluorescent, its Raman spectrum could not be recorded and hence the assignments made by them could not be compared with the Raman data. Therefore, in order to have a consistent interpretation of the vibrational wavenumbers of this molecule, we have recorded the FTIR spectrum of this compound in different phases (solid, liquid and gas) in the region 400–4000 cm^{-1} and the results are reported in this paper. It is hoped that our assignments will be useful in the study of vapour phase electronic spectrum and for evaluating the force fields of this molecule. An attempt was also made to record the Raman spectrum of the compound by varying the laser power, however, it is not worth mentioning. Further the observed wavenumbers are used to evaluate the thermodynamic functions, following the standard procedure²¹.

2 Experimental Details

The spectrally pure sample of anthranilonitrile ($\text{H}_2\text{NC}_6\text{H}_4\text{CN}$; F W = 118.14; m.p. = 47–49 °C; bp = 267.268 °C) was obtained from Aldrich Chemical Co, USA and was used as such without further purification.

The FTIR spectra in the region 400–4000 cm^{-1} (in different phases) were recorded on Jasco spectro-

photometer model FTIR/7000. IR spectra in liquid and vapour phases were recorded by warming the powdered substance 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 resolution of the IR spectrometer was of the order of 2 cm^{-1} . The spectra are shown in Fig. 1.

3 Results and Discussion

Fig. 2 shows the structures of benzonitrile and anthranilonitrile (2-aminobenzonitrile) molecules with classical numbering of the atoms. If we assume $-\text{CN}$ and $-\text{NH}_2$ groups as single mass points and coplanar with ring, the molecule under consideration would belong to the C_s point group symmetry. The 39 normal modes of vibrations of this molecule will be distributed as 27 a' (planar) and 12 a'' (non-planar) ones. According to selection rules, both planar, as well as non-planar vibrations are allowed in Raman as well as in IR spectra. The

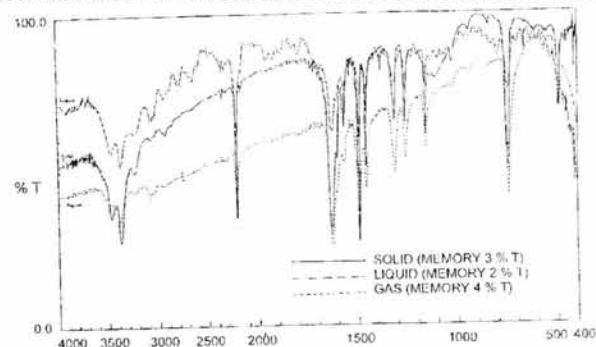


Fig. 1 — Infrared spectra of anthranilonitrile in different phases

species a' gives rise to polarized lines while species a'' to depolarized lines in the Raman spectrum. Since all the vibrations are IR and Raman active, the absence of Raman spectra presents no serious difficulty in the assignments of different types of vibrations. The vibrational assignments have been made essentially on the basis of magnitudes and relative intensities of the observed IR bands in different phases and the help has also been taken from the data available for related molecules. The wavenumbers of the observed fundamental bands and their assignments are given in Table I. As the Table I is self explanatory, we shall therefore, discuss here only some important assignments. For the sake of completeness and comparison we have also included the IR data on 2-aminobenzonitrile in KBr-matrix¹⁰ in the first column of Table I.

3.1 Skeleton vibrations

The ring stretching vibrations are very much prominent in the spectrum of benzene derivatives and are highly characteristic of the aromatic ring itself. In all substituted benzenes, four bands are usually observed in the region of 1400-1650 cm^{-1} , which represent the characteristic skeletal stretching modes of the semi-unsaturated carbon-carbon bonds^{3,4,22}. These bands arise from the degenerate e_{2g} (1596 cm^{-1}) and e_{1g} (1485 cm^{-1}) C-C stretching vibrations of benzene⁵⁻⁶ i.e. vibrations 8 and 19, according to Wilson's notation, respectively. The actual positions of these bands are determined to some extent by the nature of substituents but their magnitude differs appreciably as the position of the substituents changes around the ring. The benzene double degenerate vibration e_{2g} consists of lateral dilation and contraction of the ring, produced mainly by stretching and compressing of the bonds. On the removal of the degeneracy, the components of this vibration appear separately. The double degenerate e_{1g} mode of benzene is basically a ring deformation, since it involves both stretching and

bending of the carbon bonds. Under reduced symmetry the two components appear separately which are active in both IR and Raman spectra. It is usually observed that one of the two components of these two frequencies is lowered while the other component retains the energy of the degenerate vibration in benzene. On the basis of this criterion the IR bands observed at 1575 cm^{-1} (in all the three phases) and 1600 cm^{-1} (in liquid and solid phases) have been assigned as the two components of the e_{2g} vibration of benzene. Similarly the pair of IR wavenumbers 1495 and 1450 cm^{-1} have been assigned as two components of the e_{1g} (1485 cm^{-1}) mode of vibration of benzene. These assignments are in full conformity with the existing literature on the assignment of these fundamentals^{5, 17-23}.

The C-C vibration 14, b_{2u} (1310 cm^{-1}) known as the Kekule mode has been identified at 1312 cm^{-1} in all the phases.

The ring breathing (mode-1) and the trigonal planar ring bending (mode-12) are the most widely discussed modes in the literature. These modes are drastically affected in magnitudes upon substitution. As pointed out by several workers the C-C ring breathing a_{1g} (995 cm^{-1}) and C-C-C trigonal bending b_{1u} (1010 cm^{-1}) vibrations of benzene gives rise to combined modes in molecules belonging to the reduced symmetry. As a result of this, one of the modified modes is considerably reduced and lies between 700-900 cm^{-1} depending upon the mass, nature, number and position of substituents, while the other keeps itself around 1000 cm^{-1} . The frequency of the breathing vibration in aminobenzonitrile depends, in fact, on the number and positions of amino group substituents, which should be considered at a time of choosing the key bands to be used in the analysis of these compounds. These two vibrations (C-C ring breathing and C-C-C trigonal bending) have been identified by Rastogi *et al.*¹⁰ at 1008 and 827 cm^{-1} in *m*-aminobenzonitrile and at 1016 and 819 cm^{-1} in *p*-aminobenzonitrile. In the present case, the bands observed at 1020 cm^{-1} (in all the phases) and at 845 (solid and vapour)/820 cm^{-1} (liquid) have been assigned to these two modes respectively. On account of the higher intensity of 845 cm^{-1} we prefer it to associate to the ring breathing mode-1.

C-C in-plane and out-of-plane bending modes are the modes associated with smaller force constants than the stretching ones, and hence assigned to lower frequencies. Corresponding to the planar carbon bending vibration e_{2g} (608 cm^{-1}) of benzene, there occurs two vibrations in substituted benzenes, one of which with

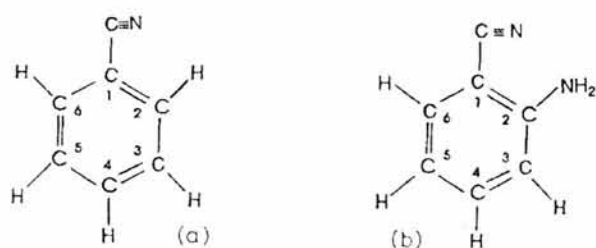


Fig. 2 — Structures of (a) benzonitrile and (b) anthranilonitrile

Table 1 — Assignments of fundamental vibrations

Sym	KBr	Solid	Liquid	Gas	Vib no.	Assignment
a'	3462 vs	3490	3490	3492	—	$\nu_{\text{asym}}(\text{NH}_2)$
a'	3369 vs	3385	3385	3385	—	$\nu_{\text{sym}}(\text{NH}_2)$
—	3328 s	3236	3236	3236	—	$\nu(\text{N-H})$ associated
a'	—	3220	—	—	—	—
a'	3080 s	—	—	3060	2	$\nu(\text{C-H})$
a'	3045 s	3045	3045	—	20a	$\nu(\text{C-H})$
	—	3020	3020	3020	20b	$\nu(\text{C-H})$
	—	2920	2920	—	—	3490–570
	—	2912	—	—	—	1600 + 1312
	—	2772	—	—	—	1600 + 1172
	—	—	2620	2620	—	2210 + 410
	—	2340	—	—	—	3490–1150
a'	2236 vs	2210	2210	2210	—	$\nu(\text{C}\equiv\text{N})$
	—	—	1940	—	—	1450 + 490
	—	—	1905	—	—	1495 + 410
	—	1882	—	—	—	1312 + 570
	—	—	1860	—	—	1450 + 410
	—	1770	—	—	—	1360 + 410
	—	1750	—	—	—	1260 + 490
a'	1634 vvs	1635	1635	1635	—	NH_2 scissor
a'	1592	1600	1600	—	8 b	$\nu(\text{C-C})$
a'	1568 vvs	1575	1575	1575	8 a	$\nu(\text{C-C})$
a'	1496 vvs	1495	1495	1495	19 b	$\nu(\text{C-C})$
a'	1460 vvs	1450	1450	1450	19 a	$\nu(\text{C-C})$
a'	1346 s	1360	—	—	7 b	$\nu(\text{C-NH}_2)$
a'	1316 vs	1312	1312	1312	14	$\nu(\text{C-C})$ kekuley
a'	1268 vvs	1260	1260	1260	3	$\beta(\text{C-H})$
a'	1226 s	—	1205	—	9 a	$\beta(\text{C-H})$
a'	1208 s	—	—	1200 sh	9 b	$\beta(\text{C-H})$
a'	1172 s	1172	1172	1172	13	$\nu(\text{C-CN})$
a'	1154 s	1150	1150	1150	15	$\beta(\text{C-H})$
a''	1068 m	1105 sh	1100 w	—	—	NH_2 twisting
a'	1020 m	1020	1020	1020	12	$\phi(\text{C-C-C})$
a''	968 m	930	960	930	5	$\gamma(\text{C-H})$
a''	912 w	—	900	—	17 b	$\gamma(\text{C-H})$
a''	878 m	—	860	—	10 a	$\gamma(\text{C-H})$
a'	860 s	845	820	845	1	$\nu(\text{C-C})$ (ring breath)
a''	750 vvs	—	793	—	10 b	$\gamma(\text{C-H})$
a'	738 sh	745	745	745	4	$\delta(\text{C-C-C})$
a'	—	—	615	—	—	NH_2 wagging
a'	582 m	—	595	—	6 b	$\phi(\text{C-C-C})$
a'	564 m	570	570	—	—	$\beta(\text{C}\equiv\text{N})$
		530	—	—	—	1635 + 1105
a'	498 vvs	490	490	490	6 a	$\phi(\text{C-C-C})$
		435	—	—	—	845–410
a''	410 vs	410	410	410	16 a	$\delta(\text{C-C-C})$
	380 s	—	—	—	18 a	$\beta(\text{C-NH}_2)$
a'	278 sh	—	—	—	18 b	$\beta(\text{C-CN})$
a''	246 sh	—	—	—	—	$\gamma(\text{C}\equiv\text{N})$
a''	233 sh	—	—	—	17 a	$\gamma(\text{C-NH}_2)$
a''	222 vs	—	—	—	11	$\gamma(\text{C-CN})$
a''	212 vvs	—	—	—	—	NH_2 torsion
a''	—	—	—	—	16 b	$\gamma(\text{C-C-C})$

ν = stretching; β and ϕ = in-plane bending; γ and δ = out-of-plane bending; asym = asymmetric; sym = symmetric

considerably reduced wavenumbers. These two vibrations have been observed at 595 (liquid) and 490 cm^{-1} (in all phases). However, we could not observe any band in solid and vapour phases corresponding to 595 cm^{-1} band in liquid phase. The ring out-of-plane bending vibrations in substituted benzenes owe their origin to the non-degenerate 4, b_{2g} (703 cm^{-1}) and the degenerate 16, e_{2u} (404 cm^{-1}) modes of benzene. The IR bands observed at 745 cm^{-1} and 410 cm^{-1} in all the phases, in the case of present molecule have been assigned to these C–C out-of-plane bending vibrations. These assignments find support from literature values in the case of related molecules¹⁰.

It has been suggested in literature²¹ that C–H stretching vibrations appear in the region 3100–3000 cm^{-1} in all the aromatic compounds. The C–H stretching wavenumbers in benzene derivatives arise from two non-degenerate modes a_{1g} (3073 cm^{-1}) and b_{1u} (3060 cm^{-1}) and two degenerate modes e_{2g} (3046 cm^{-1}) and e_{1u} (3080 cm^{-1}), i.e. vibrations 2, 13, 7 and 20 respectively. In disubstituted benzenes, four of these modes would give rise to four C–H stretching wavenumbers which almost retain the frequencies of benzene and lie in the region of 3000–3100 cm^{-1} , while the other two modes transform into C–X (X = substituent) stretching vibrations, which depend on the mass and nature of substituents and decrease considerably. In the present investigation, only three bands at 3020 (all phases), 3045 (solid and liquid) and 3060 cm^{-1} (gas) could be observed due to C–H stretching vibrations.

In anthranilonitrile two C–X stretching vibrations are expected. It has been reported in literature²¹ that in all primary aromatic amines, a strong band appears in the region 1250–1360 cm^{-1} and the intensity of this band appears to be variable and probably it is associated with substituent and has been assigned to C–NH₂ stretching vibration. Goel *et al.*²³ have assigned the strong bands observed at 1312 and 1302 cm^{-1} , in 2,3-, and 3,5-dichloroanilines respectively to this mode of vibration. Rastogi *et al.*¹⁰ identified the bands observed at 1332 and 1340 cm^{-1} in *m*- and *p*-aminobenzonitriles respectively as C–NH₂ stretching vibration. However, in the present study this mode could appear only in solid phase at 1360 cm^{-1} . This assignment is in accordance with the assignment made on the basis of isotopic frequency shifts²⁴. This seems to be supported further by the fact that the frequency of this band should be higher in anthranilonitrile than in *p*- and *m*- amino-benzonitriles, as indeed occurs²⁴.

Rastogi *et al.*²⁵ have assigned a band at 1172 cm^{-1} to the C–CN stretching mode in the case of 2,4-difluorobenzonitrile. In the present study this mode has also been identified at 1172 cm^{-1} (all the phases), in accordance with assignments proposed by Mohan *et al.*¹¹ in 2-chloro-6-methyl- benzonitrile, by Chandra *et al.*¹³ in 2-amino-5-chloro- benzonitrile and by Rastogi *et al.*^{9,25,26} in 4-amino-2-chlorobenzonitrile, 2,6- difluorobenzonitrile and 2,3-di-fluoro-benzonitrile.

3.2 Group vibrations

–C≡N group vibrations : The nitrile stretching frequency is highly localized within the C≡N group because the PED for this frequency contains contributions from the C–CN and C≡N stretching force constants only. Saito *et al.*²⁹ have suggested that a band at 2223 cm^{-1} (a calculated value) in benzonitrile is the band characteristic of the C≡N stretching vibration. They have also shown by a study on several *m*- and *p*-benzonitriles that the position of this band is not affected much by the kind of substituents. Rastogi *et al.*¹⁰ have assigned a frequency 2236 cm^{-1} to this mode in the case of 2-aminobenzonitrile (KBr matrix), whereas in the present study this mode strongly appears at 2210 cm^{-1} in all the phases. This assignment finds further support by literature values in the case of related molecules³⁰.

The C≡N planar and non-planar bending modes appear at 564 and 246 cm^{-1} respectively in KBr-matrix. Therefore, in the present case the band observed at 570 cm^{-1} in solid and liquid phases has been assigned to the in-plane C≡N deformation mode in accordance with the assignments proposed by Mital²¹ in related molecules. As the C≡N out-of-plane bending mode is observed below 400 cm^{-1} , and therefore could not be assigned in the present study.

NH₂ group vibrations — The molecule anthranilonitrile contains one NH₂ group attached to the carbon atom of the ring at 2nd position. It is, therefore, expected to have the vibrations associated with this group. The NH₂ group has two (N–H) stretching frequencies, one being symmetric and other asymmetric. The frequency of asymmetric vibration is higher than that of symmetric one. In the case of nearly all the primary aromatic amines, two bands^{10,21} occur in the region 3300–3500 cm^{-1} . The bands around 3500 cm^{-1} have been assigned by a large number of workers as asymmetric and that appearing around 3400 cm^{-1} as symmetric stretching vibration. Both of these are subject to small changes with alteration of polarity of the solvent and to rather large

changes in concentrated solutions in which intermolecular association can occur. Intermolecular bonding also lowers these frequencies. In view of these considerations, the strong IR bands observed at 3490 (in solid and liquid)/3492 cm^{-1} (gas) and 3385 cm^{-1} (in all phases) have been assigned to the N–H(NH₂) asymmetric and symmetric stretching vibrations respectively.

It has been pointed out in the literature that in N-octamide in CHCl₃ solution, the NH₂ free absorption occurs at 3530 and 3415 cm^{-1} , but it also shows additional bands at 3498, 3345, 3300 and 3180 cm^{-1} , suggesting different types of simultaneous association of free and bonded N–H bonds. Therefore, the additional bands observed at 3236 (in all phases) and 3220 cm^{-1} (solid) may be assigned to such NH₂ bonded absorption.

The NH₂ group has scissoring, rocking, twisting and wagging modes of bending vibrations.

The NH₂ scissoring frequency has been suggested to lie in the region 1590–1650 cm^{-1} in nearly all primary aromatic amines²¹. The band observed at 1635 cm^{-1} in all the phases has been assigned to this mode, which finds support from literature values in the case of various substituted anilines^{9,10}.

NH₂ rocking vibration²¹ appears in the range 1380–1450 cm^{-1} . However, this vibration may be involved in the 19a mode, where the benzene ring also takes part, so it is also very difficult to unambiguously identify this vibration.

The band appearing at 615 cm^{-1} in liquid phase has been assigned to NH₂ wagging mode. The wagging mode of NH₂ is analogous to the inversion mode of ammonia¹⁰. The IR band corresponding to the inversion mode of ammonia is observed at 950 cm^{-1} (mean of two bands). In methylamine²¹ this band is located at 783 cm^{-1} and in aniline at 660 cm^{-1} . In the present case this vibration is observed at 615 cm^{-1} in liquid phase only.

It is apparent from Table 1 that most of the fundamentals appear in expected range. The symmetric and asymmetric stretching vibrations which appear at 3462 and 3369 cm^{-1} in KBr matrix have shifted to 3490 and 3385 cm^{-1} respectively in all the phases, whereas the characteristic C≡N stretching frequency which has been identified at 2236 cm^{-1} in KBr-matrix appears at 2210 cm^{-1} in all the phases.

4 Thermodynamic Functions

The energy of a molecule consists partly of translational energy, partly of rotational energy, partly of vibrational energy, and partly of electronic energy. For a first approximation these energy contributions can be

Table 2 — Thermodynamic functions of anthranilonitrile

Temp K	Enthalpy	–Free Energy	Entropy	Heat Capacity
200.0	14.688	60.982	74.660	23.960
273.0	18.047	65.741	82.785	30.439
298.0	19.173	67.289	85.459	31.495
300.0	19.262	67.503	85.669	31.659
400.0	23.557	73.259	95.912	39.998
500.0	27.457	78.718	105.175	45.890
600.0	30.933	83.859	118.795	50.549
700.0	34.006	88.708	121.715	54.219
800.0	36.772	93.291	129.025	57.145
900.0	39.128	97.649	135.775	59.529
1000.0	41.269	101.789	142.045	61.490
1100.0	43.138	105.715	147.895	63.109
1200.0	44.902	109.455	153.359	64.450
1300.0	46.451	113.035	158.485	65.609
1400.0	47.859	116.459	163.305	66.571
1500.0	49.137	119.735	167.869	67.400

treated separately. Once the vibrational frequencies of a molecule are known it is possible to calculate the contribution of the vibrational energy to the total energy possessed by a molecule. In like manner the rotational energy contribution can be calculated if the moments of inertia of the molecule are known²¹. Thus the observed frequencies and the moments of inertia are the important variables in determining the thermodynamic functions e.g. enthalpy [$(H^\circ - E^\circ_0)$], heat capacity (C_p°), free energy function [$(F^\circ - E^\circ_0)/T$] and entropy (S°). However, direct experimental measurements of vibrational contribution of thermodynamic quantities of a molecule are difficult and sometimes impossible. But, thermodynamical quantities of a molecule can be calculated more accurately than measured using fundamental wavenumbers of the molecule. Therefore, in this section we report the thermodynamic properties of this molecule at 1 atmospheric pressure in the temperature range 200–1500 K under the rigid rotor-harmonic oscillator approximation and using the observed fundamental wavenumbers. The numerical values for the thermodynamical functions have been obtained following the standard procedure as given in literature²¹ (Table 2). For

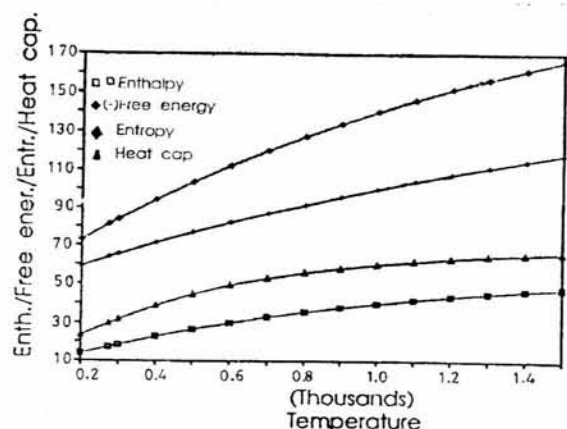


Fig. 3 — Temperature versus enthalpy/(–) free energy / entropy/heat capacity of anthranilonitrile

determining the rotational contribution, the structural parameters were taken from literature.

The computation have been done on a IBM -PC/AT computer. The thermodynamical quantities are plotted as functions of temperature (Fig. 3) and it was found that the thermodynamic functions rise more rapidly in the low temperature range and less rapidly in the high temperature range.

References

- Pathak A N & Sinha B K, *Indian J Pure & Appl Phys.* 18 (1980) 619.
- Pathak A N & Sinha B K, *Indian J Pure & Appl Phys.* 19 (1981) 678.
- Ram S, Gupta B K & Yadav J S, *Indian J Pure & Appl Phys.* 19 (1981) 1110.
- Aquil Rashid & Verma P K, *Indian J Pure & Appl Phys.* 20 (1982) 672.
- Goel R K & Agarwal M L, *Spectrochim Acta*, 38A (1982) 583.
- Sinha B K, *Indian J Pure & Appl Phys.* 22 (1984) 51.
- Huded E V, Ayachit N H, Shashidhar M A & Suryanarayana K Rao, *Indian J Pure & Appl Phys.* 25 (1987) 289.
- Joshi Arun, Suryanarayana K Rao & Shashidhar M A, *Curr Sci.* 57 (1988) 477.
- Rastogi V K, Jain D K & Sharma Y C, *Asian J Chem.* 3 (1991) 113.
- Rastogi V K, Mital H P, Sharma S N & Chattopadhyay S, *Indian J Phys.* 65B (1991) 356.
- Mohan S, Vasuki G & Chandra Rajesh, *Asian J Phys.* 1 (1992) 148.
- Bottura G, Arora S, Gupta J K & Rastogi V K, *Asian J Phys.* 1 (1992) 58.
- Chandra Rajesh, Singh A & Singh T P, *Asian J Phys.* 2 (1993) 50.
- Ramu K, Rao C G R & Santhamma C, *Spectrochim Acta*, 49A (1993), 223.
- Rastogi V K, Sangal J, Goel J P & Singh L, *Proc 9th Int Conf on Fourier Transform Spectroscopy*, Canada, 1993.
- Rao R, Aralakkanavar M K, Rao K S & Shashidhar M A, *Spectrochim Acta*, 45A (1989) 103.
- (a) Lal B, Singh S K & Sharma Y C, *Asian J Phys.* 5 (1996) 219; (b) Lal B, Jyotishi A P, Gupta J K & Pandey A N, *Asian J Phys.* 5 (1996) 265.
- Sharma S D & Doraiswamy S, *J Mol Spectrosc.* 180 (1996) 7.
- (a) Maiti S, Jaman A I, Datta A & Nandi R N, *J Mol Spectrosc.* 140 (1990) 416; (b) Dutta A, Jaman A I & Nandi R N, *J Mol Spectrosc.* 124 (1987) 486; (c) Dutta A, Jaman A I & Ghosh D K & Nandi R N, *J Mol Spectrosc.* 118 (1986) 232.
- Draeger J A, *Spectrochim Acta*, 39A (1983) 809.
- Mital H P, *Spectral studies of some polyatomic molecules and biologically active compounds*, PhD thesis, Ch C S University, Meerut, India, 1995.
- Rastogi V K, Mital H P, Jain D K & Sharma S N, *Acta Physica Polonica*, 79 (1991) 603.
- Goel R K, Gupta S K & Sharma S N, *Pramana*, 11 (1978) 541.
- Carmona P, Molina M & Escobar R, *Spectrochim Acta*, 49A (1993) 1.
- Rastogi V K, Palafox M A, Singh S & Singhal S K, *Asian J Phys.* 7 (1998) 229.
- Rastogi V K, Arora C B, Singhal S K, Singh D N & Yadav R A, *Spectrochim Acta*, 53A (1997) 2505.
- Rastogi V K, Palafox M A, Singh C & Jain V, *J Mol Struct.* 2000 (Communicated).
- Rastogi V K, Vaibhav Jain, M Alcolea Palafox, D N Singh & Yadav R A, *Spectrochimica Acta*, (in press).
- Saito T, Yamakawa M & Takasuka M, *J Mol Spectrosc.* 90 (1981) 359.
- Sharma Y C, *Spectroscopic investigations of some compounds and new complexes*, PhD thesis, Ch C S Univ, Meerut, 1996.
- Baran J, Malarski Z, Sobczyk L & Grech E, *Spectrochim Acta*, 44A (1988) 933.