Available online at www.elixirpublishers.com (Elixir International Journal)

Vibrational Spectroscopy

Elixir Vib. Spec. 97 (2016) 41956-41958

ISSN: 2229-712X

FT-IR and FT-Raman Spectral Investigation of 3-Nitropyrrole

R. Ramasamy
Department of Physics, National College (Autonomous),Trichy – 620 001, Tamil Nadu, India.

ARTICLE INFO
Article history:
Received: 4 July 2016;
Received in revised form:
27 July 2016;
Accepted: 1 August 2016;

Keywords
FT-IR,
FT-Raman,
3-nitropyrrole,
Normal coordinate analysis,
potential energy distribution.

ABSTRACT
Normal coordinate calculations of 3-nitropyrrole have been carried out using Wilson's FG matrix Valence Force Field (GVFF) for both in-plane and out-of-plane vibrations. The potential energy constants obtained in this study are refined using numerical methods.

1.Introduction

Pyrrole is a heterocyclic aromatic organic compound, a five-membered ring with the formula C_4H_4NH. It is a colourless volatile liquid that darkens readily upon exposure to air. Pyrroles are components of more complex macrocycles, including the porphyrins of heme, the chlorins, bacteriochlorins, chlorophyll and porphyrinogens.

Pyrrole is essential to the production of many different chemicals. 3-nitropyrrole has been assessed as universal bases in primers for dideoxy DNA sequencing and in the polymerase chain reaction.

In the present paper, an effort has been made to record spectra and to assign the observed fundamental modes of vibrations.

2. Experimental methods

Pure chemical of 3-nitropyrrole is obtained from Lancaster chemical company and used as such without any further purification.

The FT-IR spectrum of the title compound was recorded in the region 4000-400 cm^{-1} using KBr pellet. The Bruker IFS 66V model FT-IR spectrometer was used for the spectral measurements. The globar and mercury arc sources, KBr beam splitters are used while recording FT-IR spectrum of the title compound.

The FT-Raman spectrum was recorded on a Bruker IFS 66V model interferometer equipped with an FRA-106 FT-Raman accessory. The spectrum was recorded in the stoke's region (4000-100 cm^{-1}) using the 1064 nm line of a Nd:YAG laser for excitation operating at 200 mW of power.

3. Results and Discussion

3.1. Structure and symmetry

The molecular structure of 3-nitroprrole is shown in Fig.1. From the structural point of view the molecule is assumed to have C_s point group symmetry. The 30 fundamental modes of vibrations arising for this molecule are distributed into 21A′ and 9A″ species. The A′ and A″ species represent the in-plane and out-of-plane vibrations.

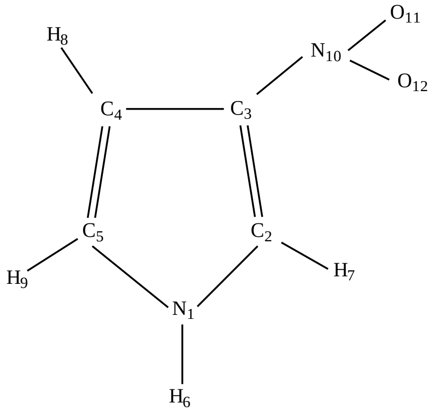

Fig 1. Molecular structure of 3-nitropyrrole.

3.2. Normal coordinate analysis

The evaluation of potential energy constants are made on the basis of GVFF by applying Wilson's FG matrix mechanism [1]. The vibrational secular determinants have been solved using the compute programmes with the SIMPLEX optimization procedure [2]. The structural parameters were taken from the Sutton's table [3]. The initial set of force constants and the vibrational frequencies required for the calculations were taken from the literature [4]. All the force constants have been refined via a non-linear square fit analysis between the calculated and observed frequencies. The refinement converged smoothly in three cycles.

3.3. Symmetry coordinates

Detailed description of vibrational modes can be given by means of normal coordinate analysis. For this purpose, the full set of 41 standard internal valence coordinates (containing 11 redundancies) were defined in Table 1. From these a non-redundant set of local internal coordinates were constructed (Table 2) much like the natural internal coordinates recommended by IUPAC [5, 6]. Theoretically calculated force fields were transformed to the latter set of vibrational coordinates and used in all subsequent calculations.

Tele:
E-mail address: ramasamy_ty@yahoo.co.in

Table 1. Definition of internal coordinates of 3-nitropyrrole.

No (i)	Symbol	Type	Definition
Stretching			
1-3	r_i	C-C	C2-C3, C3-C4, C4-C5
4-6	R_i	C-N	C2-N1, C5-N1, C3-N10
7-9	q_i	C-H	C2-H7, C4-H8, C5-H9
10	Q_i	N-H	N1-H6
11-12	P_i	N-O	N10-O11, N10-O12
In-plane-bending			
13-14	α_i	N-C-H	N1-C2-H7, N1-C5-H9
15-18	α_i	C-C-H	C3-C4-H8, C3-C2-H7, C5-C4-H8, C4-C5-H9
19-20	θ_i	C-N-H	C2-N1-H6, C5-N1-H6
21-22	θ_i	C-C-N	C2-C3-N10, C4-C3-N10
23-24	γ_i	C-N-O	C3-N10-O11, C3-N10-O12
25	γ_i	O-N-O	O12-N10-O11
26-30	β_i	Ring	N1-C2-C3, C2-C3-C4-, C3-C4-C5, C4-C5-N1, C5-N1-C2
Out-of-plane bending			
31-33	ω_i	C-H	H7-C2-N1-C3, H8-C4-C3-C5, H9-C5-C4-N1
34	σ_i	N-H	H6-N1-C5-C2
35	π_i	C-N	N10-C3-C2-C4
Torsion			
36-40	t_i	τ Ring	C2-N1-C5-C4, N1-C5-C4-C3, C5-C4-C3-C2, C4-C3-C2-N1, C3-C2-N1-C5
41	t_i	τC-NO$_2$	C3-N10-O11-O12

For numbering of atoms refer fig.1.

Table 2. Definition of local symmetry coordinates of 3-nitropyrrole.

No (i)	Type	Definition
1-3	CC	r_1, r_2, r_3
4-6	CN	R_4, R_5, R_6
7-9	CH	q_7, q_8, q_9
10	NH	Q_{10}
11	No$_2$ss	$(P_{11}+P_{12}) / \sqrt{2}$
12	No$_2$ass	$(P_{11} – P_{12}) / \sqrt{2}$
13-15	bCH	$(\alpha_{13} - \alpha_{14}) / \sqrt{2}$, $(\alpha_{15} - \alpha_{16}) / \sqrt{2}$, $(\alpha_{17} - \alpha_{18}) / \sqrt{2}$
16	bNH	$(\theta_{19} – \theta_{20}) / \sqrt{2}$
17	bCN	$(\theta_{21} – \theta_{22}) / \sqrt{2}$
18	No$_2$ rock	$(\gamma_{23} – \gamma_{24}) / \sqrt{2}$
19	No$_2$ twist	$(\gamma_{23} + \gamma_{24}) / \sqrt{2}$
20	No$_2$ sciss	$(2\gamma_{25} – \gamma_{23} – \gamma_{24}) / \sqrt{2}$
21	R bend 1	$\beta_{26} + (\beta_{27} + \beta_{30}) + b(\beta_{28} - \beta_{29})$
22	R bend 2	$(a – b) (\beta_{27} - \beta_{30}) + (1 – a) (\beta_{28} + \beta_{29})$
23-25	ωCH	$\omega_{31}, \omega_{32}, \omega_{33}$
26	σNH	σ_{34}
27	πCN	π_{35}
28	R torsion 1	$\tau_{38} + b(\tau_{36} + \tau_{40}) + a(\tau_{37} + \tau_{39})$
29	R torsion 2	$(a – b) (\tau_{39} - \tau_{37}) + (1 – a) (\tau_{40} - \tau_{36})$
30	No$_2$ wag	τ_{41}

a = cos 144° and b = cos 72°

3.4. Vibrational Band Assignments

The FT-IR and FT-Raman spectra of the title compound are shown in Figs. 2-3. The observed frequencies of the title compound together with probable assignment, calculated frequencies and PEDS are presented in Table 3.

Table 3. Vibrational frequencies and assignments of 3-nitropyrrole.

S. No.	Species	Observed frequency (cm-1)		Calculated frequency (cm^{-1})	Assignment (% PED)
		FT-IR	FT-Raman		
1.	A′	3286	-	3275	N-H Stretching (95)
2.	A′	3140	-	3131	C-H Stretching (99)
3.	A′	3130	-	3120	C-H Stretching (97)
4.	A′	3089	-	3081	C-H Stretching (98)
5.	A′	1645	-	1635	No$_2$ sciss (84)
6.	A′	1551	-	1542	C-C Stretching (72)
7.	A′	1509	-	1501	C-C Stretching (70)
8.	A′	1493	-	1482	C-C Stretching (71)
9.	A′	1469	-	1460	C-N Stretching (76)
10.	A′	1434	-	1423	C-N Stretching (75)
11.	A′	1409	-	1401	C-N Stretching (71)
12.	A′	-	1262	1252	No$_2$ass (98)
13.	A′	1232	-	1221	No$_2$ss (90)
14.	A′	1221	-	1211	N-H in-plane bending (73)
15.	A′	1181	-	1173	C-H in-plane bending (71)
16.	A′	1135	-	1126	C-H in-plane bending (70)
17.	A′	1092	-	1100	C-H in-plane bending (72)
18.	A″	-	1086	1095	C-H out-of-plane bending (66)
19.	A″	-	1041	1052	C-H out-of-plane bending (60)
20.	A″	-	962	971	C-H out-of-plane bending (64)
21.	A″	-	887	897	N-H out-of-plane bending (48)
22.	A″	880	-	872	No$_2$ twist (69)
23.	A′	863	-	853	Ring deformation in-plane bending (50)
24.	A′	813	-	804	Ring deformation in-plane bending (51)
25.	A′	759	-	748	C-N in-plane bending (69)
26.	A″	734	-	724	C-N out-of-plane bending (58)
27.	A″	-	655	644	Ring deformation out-of-plane bending (62)
28.	A″	611	-	603	Ring deformation out-of-plane bending (64)
29.	A″	592	-	582	No$_2$ wag (61)
30.	A′	455	-	447	No$_2$ rock (68)

Abbreviations used: ss-symmetric stretching, ass-antisymmetric stretching, ω-wagging, t-torsion.

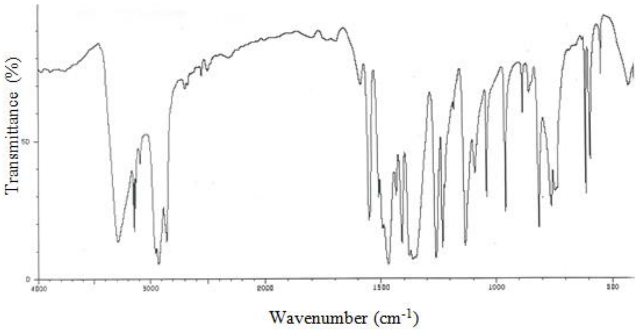

Fig 2.FT-IR spectrum of 3-nitropyrrole.

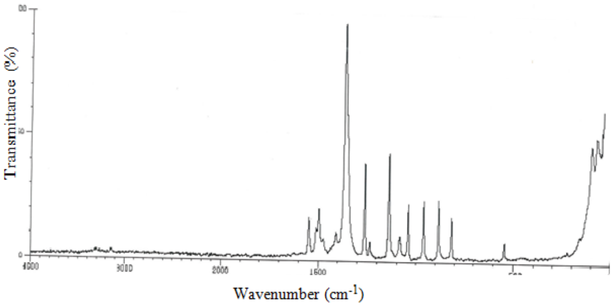

Fig 3. FT-Raman spectrum of 3-nitropyrrole.

3.4.1. N-H vibrations

In all the heterocyclic compounds, the N-H stretching vibrations [7] occur in the region 3500-3000 cm^{-1}. Hence the FT-IR band at 3286 cm^{-1} has been designated to N-H stretching modes of vibrations.

3.4.2. C-H vibrations

The molecular structure shows the presence of C-H stretching vibrations in the region 3000-3100 cm^{-1}, which is the characteristic region for the ready identification of C-H stretching vibrations [8].

Hence, in the present investigation, C-H vibrations have been found at 3140, 3130, 3089 cm^{-1} in IR.

3.4.3. C-C vibrations

The bands between 1400 and 1650 cm^{-1} in benzene derivatives are due to C-C stretching vibrations [9]. Therefore, the C-C stretching vibrations of the title compound are observed at 1551, 1509, 1493 cm^{-1} in IR.

3.4.4. C-N Vibrations

The identification of C-N stretching frequency is very difficult task, since the mixing bands are possible in this region. Hence the FT-IR bands observed at 1469, 1434, 1409 cm^{-1} in IR of the title compound are assigned to C-N stretching modes of vibration. These assignments are made in accordance with the assignments proposed by Krishnakumar et al [10].

3.4.5. Nitro group vibrations

The characteristic group frequencies of the nitro group are relatively independent of the rest of the molecule which makes this group convenience to identify. The asymmetric and symmetric stretching modes of nitro group are at 1262 cm^{-1} in Raman and 1232 cm^{-1} in IR respectively. The FT –IR bands at 1645, 880, 592, 455 cm^{-1} are due to scissoring, twisting, wagging and rocking modes of nitro groups. The nitro group assignments of the title compound are also supported by the literature [11].

4. Conclusion

Based on the normal coordinate analysis a complete vibrational analysis was performed on 3-nitropyrrole. A systematic set of symmetric coordinates have been constructed. The closer agreement obtained between the calculated and observed frequencies and the PED calculations are also supporting the assignments made for various functional groups present in the molecule.

A complete vibrational band assignment of the title compound has been carried out using FT-IR and FT-Raman spectra on the basis of C_s point group symmetry.

References

1. E.B. Wilson, Phys, Rev., 45, 706, 1934.
2. J.A. Nelder and R. Mead, Comput. J., 7, 308, 1965.
3. L.E. Sutton, “The inter atomic band distance and bond analysis in molecules and ions” (chemical society, London), 1958.
4. V. Suryanarayanan, Pavankumar and G. Ramanarao, spectrochim Acta A, 48, 1481, 1992.
5. IUPAC commission on molecular structure on spectroscopy, Pure & Appl chem., 50, 1707, 1978.
6. P. Pulay, G. Fogarasi, F. Prog and J.E. Boggs, J.Am. Chem. Soc., 101, 2550, 1979.
7. V. Krishnakumar and R. Ramasamy, Spectrochim Acta A, 66, 503-511, 2007.
8. V. Krishnakumar and R. Ramasamy Indian J. Pure & Appl. Phys. 41, 258-261, 2003.
9. R. Ramasamy, Journal of Applied Spectroscopy, 80, 506-512, 2013.
10. V. Krishnakumar and R. Ramasamy Indian J. Pure & Appl. Phys., 40, 252-255, 2002.
11. V. Krishnakumar, K. Parasuraman and A. Natarajan, Indian J. Pure & Appl. Phys., 36, 171-176, 1998.