

Spectroscopic investigations of p-nitroanilinium perchlorate A computational study

C.YOHANNAN PANICKER^{1*}, HEMA TRESA VARGHESE²,
K. MADHUSOODANANA PILLAI³, MANIKANTAN NAIR³, K. RAJU³ and M. LAILA³

¹Department of Physics, TKM College of Arts and Science, Kollam-691 005 (India).

²Department of Physics, Fatima Mata National College, Kollam-691 001 (India).

³Department of Physics, University College, Trivandrum, (India).

(Received: May 25, 2009; Accepted: July 03, 2009)

ABSTRACT

The vibrational frequencies of p-nitroanilinium perchlorate parent molecules were calculated using Gaussian03 software package and the fundamental modes are assigned. The predicted infrared intensities and Raman activities are reported. The calculated geometrical parameters are in agreement with reported values. The differences between experimental and calculated vibrational modes are observed. It must be due to the fact that hydrogen bond vibrations present in the crystal lead to strong perturbation of the IR wavenumbers and intensities of many other modes. Also, we state that the experimental results belong to the solid phase and the theoretical calculations belong to the gaseous phase of parent molecules. The calculated first hyperpolarizability is comparable with the reported values of similar derivatives and is an attractive object for future studies of non linear optics.

Key words: Hartree-Fock ab initio calculations, perchlorate, hyperpolarizability, nonlinear optics

INTRODUCTION

The structure, spectra and phase transition in p-nitroanilinium perchlorate crystal was reported by Marchewka et al.¹. Perchlorates are interesting due to structural phase transitions connected with the ordering of perchlorate anions. Aniline and its derivatives are used in several pharmaceutical and industrial processes as starting materials because they can serve as precursors in the synthesis of dye and sensitizer molecules, pesticides and antioxidants^{2,3}. They are used in electro optical industry, for the synthesis of technological materials with nonlinear optical responses⁴. The structures and vibrational spectra of aniline and substituted aniline complexes are being studied extensively, since elucidation of their molecular properties as well as nature of reaction mechanism is of utmost importance. The structural, electronic and vibrational

parameters of aniline molecule change with inclusion of substituent group because it leads to the variation of charge distribution in the molecule. The structure and normal vibration of aniline and its derivatives were reported by Tzeng et al.^{5,6}. Among crystals comprising perchlorate anions, the most interesting are non-centrosymmetric; due to non linear properties. In this work, the vibrational frequencies and other parameters of the parent molecules are calculated theoretically.

Computational details

Calculations of the title compound were carried out with Gaussian03 program⁷ using the HF/6-31G* basis set to predict the molecular structure and wavenumbers. Molecular geometry (fig. 1) was fully optimized by Berny's optimization algorithm using redundant internal coordinates. Harmonic vibrational wavenumbers were calculated using the

analytic second derivatives to confirm the convergence to minimum on the potential surface. The wavenumber values computed at the Hartree-Fock level contain known systematic errors due to the negligence of electron correlation⁸. We therefore, have used the scaling factor value of 0.8929 for HF/6-31G* basis set. The absence of imaginary wavenumber on the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum energy.

RESULTS AND DISCUSSION

The geometrical parameters of p-nitroanilinium are given in table 1 and vibrational frequencies of p-nitroanilinium are given in table 2. For comparison, the experimental IR and Raman frequencies of p-nitroanilinium perchlorate crystal¹

are also included in table 2. The reported values of Cl-O bond lengths are in the range¹ 1.4134-1.4421 Å while in the present calculation for isolated perchlorate, the bond length is 1.4503 Å. Also the present calculation gives the O-Cl-C bond angle as 109.5° while the reported values are in the range¹ 107.4-110.2°. In the present study, for perchlorate, the ab initio calculations give the vibrational frequencies as 1061, 1061, 871, 597, 597, 427 cm⁻¹. The corresponding reported values¹ are 1077, 1052, 928, 630, 620, 452 cm⁻¹. The variation found in the experimental and calculated vibrational modes must be due to the fact that experimental results belong to solid phase and theoretical calculations belong to gaseous phase of isolated perchlorate molecule.

According to Roeges⁹ NH₃ stretching

Table 1: Geometrical parameters of p-nitroanilinium

C ₁ -C ₂	1.3845	A(2,1,6)	118.7	D(6,1,2,8)	-180.0
C ₁ -C ₆	1.3815	A(2,1,7)	121.1	D(7,1,2,3)	-179.8
C ₁ -H ₇	1.0711	A(6,1,7)	120.2	D(7,1,2,8)	0.1
C ₂ -C ₃	1.3792	A(1,2,3)	118.2	D(2,1,6,12)	-179.9
C ₂ -H ₈	1.0753	A(1,2,8)	120.0	D(7,1,6,5)	179.9
C ₃ -C ₄	1.3793	A(3,2,8)	121.8	D(1,2,3,4)	-0.2
C ₃ -N ₁₁	1.4828	A(2,3,4)	123.4	D(1,2,3,11)	-179.0
C ₄ -C ₅	1.3845	A(2,3,11)	118.3	D(8,2,3,4)	179.9
C ₄ -H ₉	1.0753	A(4,3,11)	118.3	D(8,2,3,11)	1.1
C ₅ -C ₆	1.3815	A(3,4,5)	118.2	D(2,3,4,5)	0.2
C ₅ -H ₁₀	1.0711	A(3,4,9)	121.8	D(2,3,4,9)	-179.9
C ₆ -N ₁₂	1.4660	A(5,4,9)	120.0	D(11,3,4,5)	179.0
N ₁₁ -H ₁₃	1.0122	A(4,5,6)	118.7	D(11,3,4,9)	-1.1
N ₁₁ -H ₁₄	1.0122	A(4,5,10)	121.1	D(2,3,11,13)	-150.3
N ₁₁ -H ₁₅	1.0136	A(6,5,10)	120.2	D(2,3,11,14)	-30.7
N ₁₂ -O ₁₆	1.1887	A(1,6,5)	122.8	D(2,3,11,15)	89.5
N ₁₂ -O ₁₇	1.1887	A(1,6,12)	118.6	D(4,3,11,13)	30.8
		A(5,6,12)	118.6	D(4,3,11,14)	150.4
		A(3,11,13)	111.7	D(4,3,11,15)	-89.4
		A(3,11,14)	111.7	D(3,4,5,6)	-0.1
		A(3,11,15)	111.7	D(3,4,5,10)	179.8
		A(13,11,14)	106.9	D(9,4,5,6)	180.0
		A(13,11,15)	107.3	D(4,5,6,12)	179.9
		A(14,11,15)	107.3	D(10,5,6,1)	-179.9
		A(6,12,16)	116.8	D(1,6,12,16)	179.9
		A(6,12,17)	116.8	D(1,6,12,17)	-0.1
		A(16,12,17)	126.4	D(5,6,12,17)	-180.0

Table 2 Frequencies and assignments of IR and Raman spectral data

$\nu_{(\text{HF})}$ cm^{-1}	$\nu_{(\text{IR})}$ cm^{-1}	$\nu_{(\text{Raman})}$ cm^{-1}	IR Intensity (KM/Mole)	Raman activity (A**4/AMU)	Assignments
3315	3155		119.21	35.79	$\nu_{\text{as}}\text{NH}_3$
3301	3135		158.09	44.99	$\nu_{\text{as}}\text{NH}_3$
3219	3103		122.09	99.89	$\nu_{\text{s}}\text{NH}_3$
3076	3089	3090	19.45	20.97	νCH
3076	3068		10.77	95.41	νCH
3019	3029		0.01	52.24	νCH
3019			1.25	102.04	νCH
1695	1683		427.50	0.31	$\nu_{\text{as}}\text{NO}_2$
1634	1632		115.28	10.48	$\delta_{\text{as}}\text{NH}_3$
1623	1605	1604	66.60	7.41	$\delta_{\text{as}}\text{NH}_3$
1609	1591		7.99	32.33	νPh
1599	1539	1538	0.21	0.71	νPh
1515	1510	1509	162.17	7.18	$\delta_{\text{s}}\text{NH}_3$
1496	1496		11.28	4.94	νPh
1468	1468		269.74	37.90	νPh
1421	1425	1432	0.13	0.16	$\nu_{\text{s}}\text{NO}_2$
1302	1312	1310	0.4673	0.54	νPh , δCH
1193	1203	1204	86.65	0.02	νCN
1162	1147	1148	5.24	2.48	δCH
1130	1139		6.49	10.81	δCH
1116	1121	1120	2.28	9.22	δCH
1068	1077		3.69	2.46	νCN
1066	1052	1052	32.29	1.44	ρNH_3 , νCN
1005	1016	1013	0.01	0.045	δCH
995			5.19	1.81	γCH
992			0.62	1.14	ρNH_3
991	980		8.20	0.57	γCH
861	863	864	65.90	15.81	δNO_2
855	850		24.06	0.26	γCH
833	831		0.00	1.75	γCH
759		775	7.60	12.86	Ring breath
746	739	741	52.52	3.71	ωNO_2
660	680		7.47	0.04	δPh
615	618	620	0.90	6.56	$\delta\text{Ph(X)}$
601			2.19	0.53	γPh
518	536	534	2.88	0.83	ρNO_2
463	472	472	16.73	0.17	γPh
408			0.00	0.05	δCCN
353	357		8.61	0.45	$\delta\text{Ph(X)}$
348			16.75	5.70	δPh
286		303	25.49	3.44	δCCN
217	195	235	0.21	0.97	γCCN
109			3.91	0.14	tNH_3
47			0.00	0.07	tNO_2
6			0.05	0.38	tNH_3

ω -stretching; δ -in-plane deformation; γ -out-of-plane deformation; τ -torsion; rocking; ω -wagging; X-substituent sensitive; Ph-Phenyl; subscripts: as - asymmetric, s- symmetric.

vibrations are expected in the region 2910-3200 cm^{-1} . For p-nitroanilinium, we have obtained 3219-3315 cm^{-1} where as the reported values¹ are 3103-3155 cm^{-1} . The HF calculations give the in-plane deformations of the NH_3 group at 1634, 1623 and 1515. The corresponding values are 1632, 1605, 1510 in the IR spectrum and 1604, 1503 cm^{-1} in the Raman spectrum¹. These modes are expected in the region⁹1635-1480 cm^{-1} . Although the CN stretch and the NH_3 rock can couple, the CN stretching vibration⁹ is unambiguously assigned in the neighbourhood of 1050 cm^{-1} . The NH_3 rocking mode is expected in the range⁹ 1005-1200 cm^{-1} . The abinitio calculations give 1066 and 992 cm^{-1} as rocking modes of NH_3 . The band at 1052 cm^{-1} in both spectra is assigned as this mode by Marchewka *et al.*¹. The band 1066 cm^{-1} is not pure but it contains significant contribution from CN stretching mode. The δCCN mode is coupled with the twisting and skeletal-deformation modes of NH_3 which are found to be respectively in the ranges 425-535 cm^{-1} and 310-370 cm^{-1} . The deformation bands of CCN are calculated to be at 408, 286 and 217 cm^{-1} . The NH_3 torsional modes lie in the region⁹ 140-240 cm^{-1} and bands at 109 and 6 cm^{-1} are assigned as these modes theoretically.

The most characteristic bands in the spectra of nitro compounds are due to NO_2 stretching vibrations, which are the two most useful group wavenumbers, not only because of their spectral position but also for their strong intensity⁹.

The symmetric and antisymmetric NO_2 stretching vibrations of nitro compounds are expected respectively in the ranges 1360-1400 and 1500-1660 cm^{-1} . In substituted nitrobenzenes, $\delta_s\text{NO}_2$ appears strongly in the range 1345 \pm 30 cm^{-1} , in 3-nitropyridine¹⁰ in the range 1350 \pm 20 cm^{-1} and in conjugated nitroalkenes¹¹ at 1345 \pm 15 cm^{-1} . In the present case the bands at 1695 (HF), 1683 (IR) and 1421 (HF), 1425 (IR), 1432 (Raman) are assigned as asymmetric and symmetric NO_2 stretching modes, respectively. The NO_2 scissoring^{9,12-14} occur in the region 850 \pm 60 cm^{-1} when conjugated to C=C or aromatic molecules, with a contribution of the νCN , which is expected to be near 1120 cm^{-1} . The δNO_2 vibration is reported to be at 852 cm^{-1} for nitrobenzene, at 890 cm^{-1} for $\text{H}_2\text{C}=\text{CHNO}_2$, and at 904 and 834 cm^{-1} for 1,3-dinitrobenzene. In aromatic compounds, the wagging mode, ωNO_2 is assigned at 740 \pm 50 cm^{-1} with a moderate to strong intensity, a region in which $\tilde{\alpha}\text{CH}$ is also active⁹. The ωNO_2 is reported at 701 and 728 cm^{-1} for 1,2-dinitrobenzene and at 710 and 772 cm^{-1} for 1,4-dinitrobenzene⁹. In aromatic compounds, the rocking mode ρNO_2 is active in the region 545 \pm 45 cm^{-1} . Nitrobenzene⁹ shows this rocking mode at 531 cm^{-1} . Sundaraganesan *et al.*¹⁵ reported the NO_2 deformation bands at 839,744 and 398 cm^{-1} (experimental), and at 812, 716, 703 and 327 cm^{-1} theoretically. For the title compound the deformation bands are assigned at 861, 746, 518 (HF), 863, 739, 536 cm^{-1} (IR) and 864, 741, 534 cm^{-1} (Raman).

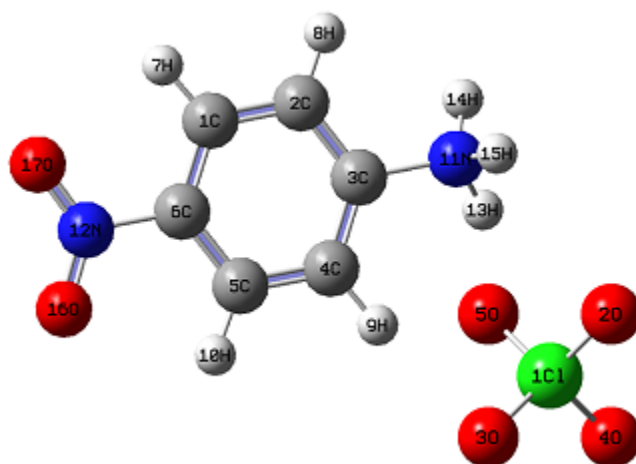


Fig. 1: Optimized geometry

For parasubstituted benzenes the ring stretching modes ν_{Ph} is expected in the region 1280-1620 cm^{-1} and the aromatic CH stretching vibrations⁹ absorb weakly to moderately between 3120 and 3000 cm^{-1} . The ring breathing mode for the parasubstituted benzenes with different substituents¹⁶ have been reported in the range 780-840 cm^{-1} . The HF calculation give the ring breathing mode at 759 cm^{-1} . The in-plane and out-of-plane CH deformations⁹ are seen in the range 995-1315 cm^{-1} and 700-1000 cm^{-1} , respectively, and all these bands are assigned in table 3.

Marchewka *et al.*¹ reported the bond lengths $\text{C}_3\text{-N}_{11}=1.4703$, $\text{C}_6\text{-N}_{12}=1.4756$, $\text{N}_{12}\text{-O}_{16}=1.2147$, $\text{N}_{12}\text{-O}_{17}=1.2092$, $\text{N}_{11}\text{-H}_{13-15}=0.7931\text{-}0.9012$ Å whereas in the present case, the corresponding values are 1.4828, 1.4660, 1.1887, 1.1887 and 1.0122 -1.0136Å. In the present case the HF calculations give the bond angles $\text{O}_{16}\text{-N}_{12}\text{-O}_{17}=126.4$, $\text{O}_{17}\text{-N}_{12}\text{-C}_6=116.8$, $\text{O}_{16}\text{-N}_{12}\text{-C}_6=116.8$,

$\text{N}_{12}\text{-C}_6\text{-C}_5=118.6$, $\text{N}_{12}\text{-C}_6\text{-C}_1=118.6$, $\text{C}_5\text{-C}_6\text{-C}_1=122.8$, $\text{C}_3\text{-N}_{11}\text{-H}_{13}=111.7$, $\text{C}_3\text{-N}_{11}\text{-H}_{14}=111.7$, $\text{C}_3\text{-N}_{11}\text{-H}_{15}=111.7^\circ$ whereas the corresponding reported values¹ are 123.5, 118.4, 118.1, 118.7, 119.2, 122.1, 114.7, 110.0 and 109.5°.

Analysis of organic molecules having conjugated π -electron systems and large hyperpolarizability using infrared and Raman spectroscopy has evolved as a subject of research¹⁷. The potential application of the title compound in the field of non linear optics demands the investigation of its structural and bonding features contributing to the hyperpolarizability enhancement, by analyzing the vibrational modes using the IR and Raman spectrum. The calculated first hyperpolarizability of the title compound is 0.6×10^{-30} esu, which is comparable with the reported values of similar derivatives¹⁸. We conclude that the title compound is an attractive object for future studies of non linear optical properties.

REFERENCES

1. Marchewka, M.K., Drozd, M., and Pietraszko, A., *Mat. Sci. Eng.* **100B**: 225 (2003).
2. Whysner, J., Vera, L., and Williams, G.M., *Pharmacol. Ther.* **71**: 107 (1996).
3. Hohenberg, P., and Kohn, W., *Phys. Rev.B* **136**: 864 (1964).
4. Altun, A., Golsuk, K., and Kumru, M., *J. Mol. Struct. Theochem.* **625**: 17 (2003).
5. Tzeng, W.B., Narayanan, K., Shieh, K.C., and Tung, C.C., *J. Mol. Struct. Theochem.* **428**: 231 (1998).
6. Tzeng, W.B., and Narayanan, K., *J. Mol. Struct. Theochem.* **434**: 247 (1998).
7. Frisch, M.J., et al. *Gaussian03*, Revision C.02, Gaussain Inc., Wallingford CT(2004).
8. Foresman, J.B., Frisch, E., in: Frisch, E., (Ed.), *Exploring Chemistry with Electronic Structure Methods, A Guide to Using Gaussian*, Gaussian, Pittsburg PA, (1996).
9. Roeges, N.P.P.G., *A Guide to the Complete Interpretation of Infrared Spectra of Organic Structures*, Wiley, New York, (1994).
10. Perjessy, A., Rasala, D., Tomasik, P., and Gawinecki, R., *Collect. Czech. Chem. Commun.* **50**: 244 (1985).
11. Brown Jr, J.F., *J. Am. Chem. Soc.* **77**: 6341 (1955).
12. Green, J.H.S., Kynanston, W., and Lindser, A.S., *Spectrochim. Acta* **17**: 486 (1961).
13. Exner, O., Kovac, S., and Solcaniova, E., *Collect. Czech. Chem. Commun.* **37**: 2156 (1972).
14. Rao, D.S.R., and Thyagarajan, G., *Indian J. Pure Appl. Phys.* **16**: 941 (1978).
15. Sundaraganesan, N., Ayyappan, S., Umamaheswari, H., and Joshua, B.D., *Spectrochim Acta* **66A**: 17 (2007).

16. Varsanyi, G., *Assignments of Vibrational Spectra of Seven Hundred Benzene Derivatives*, Wiley, New York (1974).
17. Tommasini, M., Castiglioni, C., Del Zoppo, M., and Zerbi, G., *J. Mol. Struct.* **480**: 179 (1999).
18. Varghese, H.T., Panicker, C.Y., Madhavan, V.S., Mathew, S., Vinsova, J., and Van Alsenoy, C., *J. Raman Spectrosc.* DOI:10.1002/jrs.2265.