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Simulation of IR and Raman spectra based on scaled DFT force fields: a case study of 4-nitro-o-toluidine, with emphasis on band assignment

M.K.Subramanian* and S.Ramya

Post Graduate and Research Department of Physics, Thiruvalluvar Government Arts College, Rasipuram, India.

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ABSTRACT

The FT-IR and FT-Raman spectra of 4-nitro-o-toluidine (4NOT) were recorded in the region 4000–400 cm⁻¹ and 4000–100 cm⁻¹ respectively. Quantum chemical calculations of energies, geometrical structure and vibrational wavenumbers of 4NOT were carried out by density functional theory (DFT/B3LYP) method with 6-31G* and 6-311+G** basis sets. The difference between the observed and scaled wavenumber values of most of the fundamentals is very small. The values of the total dipole moment (μ) and the first order hyperpolarizability (β) of the compound were investigated. The calculated results show that 4NOT have non-linear optical (NLO) behavior. A detailed interpretation of Infrared and Raman spectra of 4NOT is also reported. The calculated HOMO–LUMO energy gap shows that charge transfer occurs within the molecule. Electronic excitation energies, oscillator strength and nature of the respective excited states were calculated by the closed-shell singlet calculation method for the molecule.

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Introduction

Toluidine is a synthetic chemical used primarily in the manufacture of dyestuffs, although it is also used in the production of rubber, chemicals, and pesticides and as a curing agent for epoxy resin systems. Toluidine is of moderate to low acute toxicity and has the potential to produce minimal skin irritation and mild eye irritation. Toluidine is also used as a corrosion inhibitor in paint formulations and possibly has limited uses in analytical laboratory procedures.

In this study, the vibrational spectra of the 4-nitro-otoluidine (4NOT) have been studied by applying DFT calculations based on 6-31G* and 6-311+G** basis set. The infrared and Raman intensities were also predicted theoretically. Based on that, the simulated IR and Raman spectra were also obtained. The experimentally observed spectral data of the 4NOT is found to be well comparable to that of spectral data obtained by quantum chemical methods. Density functional theory calculations were performed for the title compound to evaluate the first order hyperpolarizability value. The calculated HOMO and LUMO energies shows that charge transfer occur within the molecule. Electronic excitation energies, oscillator strength and nature of the respective excited states were calculated by the closed-shell singlet calculation method were also calculated for the molecule.

Experimental details

The sample of 4NOT was purchased from Lancaster chemical company U.K., and used as such for the spectral measurements. The room temperature Fourier transform infrared spectrum of the title compound was measured in the 4000–400 cm⁻¹ region at a resolution of 1 cm⁻¹ using BRUKER IFS 66v FTIR spectrometer equipped with a cooled MCT detector for the mid-IR range. Boxcar apodization was used for the 250 averaged interferograms collected for the sample and background. The FT-Raman spectrum was recorded at a BRUCKER IFS-66v model interferometer equipped with an FRA–106 FT-Raman accessory. The spectrum was recorded in

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the 4000–100 cm^{-1} stokes region using 1064 nm line of a Nd:YAG laser for excitation operating at 200mW power.

Computational details

The molecular geometry optimizations, energy and vibrational frequency calculations were carried out for 4NOT with the GAUSSIAN 03W software package [69] using the B3LYP functionals [67,68] combined with the standard 6-311+G** basis sets. The Cartesian representation of the theoretical force constants have been computed at optimized geometry by assuming Cs point group symmetry. Scaling of the force field was performed according to the SQM procedure [97,98] using selective scaling in the natural internal coordinate representation [99]. Transformations of the force field and the subsequent normal coordinate analysis including the least square refinement of the scaling factors, calculation of the potential energy distribution, and the prediction of IR and Raman intensities were done on a pc with the MOLVIB program (version V 7.0-G77) written by Sundius [100,101]. For the plots of simulated IR pure Lorentizian band shapes were used with a band width (FWHM) of 10 cm^{-1} .

The symmetry of the molecule was also helpful in making vibrational assignments. The symmetries of the vibrational modes were determined by using the standard procedure [102] of decomposing the traces of the symmetry operation into the irreducible representation. The symmetry analysis for the vibrational modes of 4NOT is presented in order to describe the basis for the assignments.

By combining the results of the GAUSSVIEW program [103] with symmetry considerations, vibrational frequency assignments were made with a high degree of confidence. There is always some ambiguity in defining internal coordination. However, the defined coordinate form complete set and matches quite well with the motions observed using the GAUSSVIEW program.

Prediction of Raman intensities

The prediction of Raman intensities was carried out by following the procedure outlined below. The Raman activities

calculated by the GAUSSIAN 03W program and adjusted during scaling procedure with MOLVIB were converted to relative Raman intensities using the following relationship derived from the basic theory of Raman scattering [104,105].

$$I_{i} = \frac{f(v_{o} - v_{i})^{4} S_{i}}{v_{i} [1 - \exp(-hcv_{i} / KT)]}^{------(4.1)}$$

Where v_0 is the exciting frequency (in cm⁻¹), v_i is the vibrational wavenumber of the ith normal mode; h, c and k are fundamental constants, and f is a suitably chosen common normalization factor for all peak intensities.

Results and discussion

Molecular geometry

The global minimum energy obtained by the DFT structure optimization was presented in Table 4.1. The optimized geometrical parameters obtained by the large basis set calculation were presented in Table 4.2. The optimized molecular structure of 4NOT was shown in Fig. 4.1.



Fig. 4.1. The optimized molecular structure of 4NOT

Table 4.1. Total energies of 4NOT, calculated at DFT (B3LYP)/6-31G* and (B3LYP)/6-311+G** level

Method	Energies (Hartrees)
6-31G*	-531.3958476
6-311+G**	-531.4278134

Analysis of vibrational spectra

The optimized structural parameter were used to compute vibrational frequencies of the compound 4NOT at the 6-311+G** level of calculation. The 51 normal modes of 4NOT are distributed among the symmetry species as Γ_{3N-6} = 35 A' (inplane) + 16 A" (out-of-plane), and in agreement with C_s symmetry. All the vibrations were active both in Raman scattering and infrared absorption. In the Raman spectrum the in-plane vibrations (A') give rise to polarized bands while the out-of-plane ones (A") to depolarized band.

Detailed description of vibrational modes can be given by means of normal coordinate analysis (NCA). For this purpose, the full set of 66 standard internal coordinates containing 15 redundancies were defined as given in Table 4.3. From these, a non-redundant set of local symmetry coordinates were constructed by suitable linear combinations of internal coordinates following the recommendations of Fogarasi et. al [106] are summarized in Table 4.4. The theoretically calculated DFT force fields were transformed in this later set of vibrational coordinates and used in all subsequent calculations.

The detailed vibrational assignments of fundamental modes of 4NOT along with calculated IR, Raman intensities and normal mode descriptions (characterized by TED) were reported in Table 4.5. For visual comparison, the observed and simulated FT-IR and FT-Raman spectra of 4NOT are produced in a common frequency scales in Fig. 4.2 & Fig. 4.3.

Root mean square (RMS) values of frequencies were obtained in the study using the following expression,

$$RMS = \sqrt{\frac{1}{n-1}\sum_{i}^{n} \left(\upsilon_{i}^{calc} - \upsilon_{i}^{exp}\right)^{2}}$$

The RMS error between unscaled and experimental frequencies is 125 cm^{-1} . However, for reliable information on the vibrational properties the use of a selective scaling is necessary. The calculated frequencies are scaled using the set of transferable scale factors recommended by Rauhut and Pulay [107] and resulted in a RMS deviation of 8.34 cm⁻¹.





Fig. 4.3. FT-Raman spectra of 4NOT (a) Observed (b) Calculated with B3LYP/6-311+G**

Table 4.2. Optimized geometrical parameters of 4NOT obtained by B3LYP/ 6–311+G** density functional calculations

Bond length	Value(Å)	Bond angle	Value(Å)	Dihedral angle	Value(Å)
C2-C1	1.38599	C3-C2-C1	120.00023	C4-C3-C2-C1	0.00000
C3-C2	1.38600	C4-C3-C2	120.00023	C5-C4-C3-C2	0.00000
C4-C3	1.38599	C5-C4-C3	119.99953	C6-C1-C2-C3	0.00000
C5-C4	1.38599	C6-C1-C2	119.99953	H7-C2-C1-C6	179.42797
C6-C1	1.38599	H7-C2-C1	120.00089	H8-C3-C2-C1	179.42800
H7-C2	1.12192	H8-C3-C2	120.00081	H9-C5-C4-C3	179.42805
H8-C3	1.12197	H9-C5-C4	119.99903	N10-C1-C2-C3	179.42806
H9-C5	1.12205	N10-C1-C2	119.99899	N11-C4-C3-C2	179.42810
N10-C1	1.44595	N11-C4-C3	119.99899	C12-C6-C1-C2	-179.42861
N11-C4	1.44605	C12-C6-C1	120.00214	O13-N11-C4-C3	-139.43027
C12-C6	1.54002	O13-N11-C4	120.00070	O14-N11-C4-C3	41.14520
O13-N11	1.13177	O14-N11-C4	119.99831	H15-N10-C1-C2	60.56974
O14-N11	1.31602	H15-N10-C1	120.00242	H16-N10-C1-C2	-118.85345
H15-N10	1.02799	H16-N10-C1	119.99756	H17-C12-C6-C1	119.99613
H16-N10	1.02795	H17-C12-C6	109.49822	H18-C12-C6-C1	-0.06545
H17-C12	1.12194	H18-C12-C6	109.49891	H19-C12-C6-C1	-119.92360
H18-C12	1.12201	H19-C12-C6	109.50298		
H19-C12	1.12189				

*for numbering of atom refer Fig. 4.1

Table 4.3. Definition of internal coordinates of 4NOT

No(i)	No(i) symbol Type		Definition			
Stretching						
1-6	r _i	C-C	C1-C2, C2-C3,C3-C4,C4-C5,C5-C6,C6-C1.			
7-9	p _i	С-Н	С2-Н7,С3-Н8,С5-Н9			
10	Si	C-C(m)	C6-C12			
11-12	s _i	C-N	C1-N10,C4-N11			
13-14	N _i	N-H	N10-H15, N10-H16			
15-17	Pi	C-H(m)	C12-H17,C12-H18,C12-H19			
18-19	Φ_{i}	N-O	N11-O13, N11-O14			
Bending 20-25	α_i	C-C-C	C1-C2-C3,C2-C3-C4,C3-C4-C5, C4-C5-C6,C5-C6-C1,C6-C1-C2			
26-31	θ_{i}	C-C-H	C1-C2-H7, C3-C2-H7, C2-C3-H8, C4-C3-H8, C4-C5-H9, C6-C5-H9			
32-33	β_i	C-C-N	C6-C1-N10, C2-C1-N10			
34-35	n _i	C-N-H	C1-N10-H15, C1-N10-H16			
36	ε	H-N-H	H15-N10-H16			
37-38	γ_i	C-C-N	C3-C4-N11, C5-C4-N11			
39-40	μ _i	C-C-C	C1-C6-C12, C5-C6-C12			
41-43	ν_i	H-C-H	H17-C12-H18,H18-C12-H19, H19-C12-H17			
44-46	ϕ_i	C-C-H	C6-C12-H17, C6-C12-H18, C6-C12-H19			
47-48	ι _i	C-N-O	C4-N11-O13, C4-N11-O14			
49	$\overline{\omega}_i$	O-N-O	O13-N11-O14			
Out-of-plane 50-52	ω	С-Н	H7-C2-C1-C3, H8-C3-C2-C4, H9-C5-C4-C6			
53	ξi	C-N-H	C1-N10-H15-H16			
54-56	$\Omega_{\rm i}$	C-N-O	C4-N11-O13-O14,N10-C1-C2-C6, N11-C4-C5-C3.			
57	Vi	C-C	C12-C6-C5-C1			
Torsion			C1-C2-C3-C4,C2-C3-C4-C5,			
58-63	τ_{i}	C-C	C3-C4-C5-C6,C4-C5-C6-C1,			
61		C C U(m)	C1-C6-C12-(H17-H18-H10)			
04	τ _i	$V = C - \Pi(III)$	$C_1 - C_0 - C_1 $			
60	τ	IN-U				
66	τ	N-H	C6-C1-N10-(H15,H16)			

^{*}for numbering of atom refer Fig.4.1

No.(i)	Symbol ^a	Definition ^b	Scale factors used in calculation
1-6	C-C	r1,r2,r3,r4,r5,r6	0.914
7-9	C-H	p8, p9, p10	0.992
10	C-C(m)	S7	0.914
11-12	C-N	s11,s12	0.992
13-14	N-H	N13, N14	0.995
15	mss	(P15+P16+P17)/ \sqrt{3}	0.995
16	mips	(2P16-P15-P17)/ √6	0.992
17	mps	(P15-P17)/ V2	0.919
18-19	N-O	Ф18, Ф19	0.992
20	C-C-C	$(\alpha 20 - \alpha 21 + \alpha 22 - \alpha 23 + \alpha 24 - \alpha 25)/\sqrt{6}$	0.992
21	C-C-C	$(2\alpha 20 - \alpha 21 - \alpha 22 + 2\alpha 23 - \alpha 24 - \alpha 25)/\sqrt{12}$	0.992
22	C-C-C	$(\alpha 21 - \alpha 22 + \alpha 24 - \alpha 25)/2$	0.992
23-25	С-С-Н	$(\theta 26 - \theta 27)/\sqrt{2}, (\theta 28 - \theta 29)/\sqrt{2}, (\theta 30 - \theta 31)/\sqrt{2}$	0.916
26	C-C-N	(β32-β33)/√2	0.923
27	C-N-H	(n34-n35)/√2	0.923
28	H-N-H	ε36	0.923
29	C-C-N	(y37-y38)/√2	0.923
30	C-C-C	(µ39- µ40)/√2	0.923
31	msb	(v41+v42+v43-φ44-φ45-φ46)/√6	0.990
32	mipb	(2v43-v41-v42)/ \sqrt{6}	0.990
33	mopb	(v41-v43)/ v2	0.990
34	mipr	(2φ45-φ44-φ46)/ √6	0.990
35	mopr	(φ44-φ46)/ ¹ / ₂	0.990
36	NO2sc	(2ϖ49-ι47-ι48)/√6	0.990
37	NO2r	(147-148)/√2	0.990
38-40	C-H	ω50,ω51,ω52	0.994
41	C-N-H	ξ53	0.994
42-44	C-N-O	$\Omega 54, \Omega 55, \Omega 56$	0.962
45	C-C	V57	0.962
46	tring	$(\tau 58 - \tau 59 + \tau 60 - \tau 61 + \tau 62 - \tau 63)/\sqrt{6}$	0.994
47	tring	(\tag{58-t60+t63-t63})/2	0.994
48	tring	$(-\tau 58+2\tau 59-\tau 60-\tau 61+2\tau 62-\tau 63)/\sqrt{12}$	0.994
49	C-C-H(m)	τ64/3	0.979
50	N-O	τ65/4	0.979
51	N-H	τ66/4	0.979

Table 4.4. Definition of local symmetry coordinates and the value corresponding scale factors used to correct the force fields for 4NOT

^a These symbols are used for description of the normal modes by TED in Table 4.5. ^b The internal coordinates used here are defined in Table 4.3.

Table 4.5. Detailed assignments of fundamental vibrations of 4NOT by normal mode analysis based on SQM force field calculation

S.	Symmetry species	Symmetry species C (cm ⁻¹)		Calculated frequency (cm ⁻¹) with B3LYP/6-311+G ^{**} force field				TED (%) among type of internal coordinates ^c
NO.	C _s	Infrared	Raman	Unscaled	Scaled	IR ^a A _i	Raman ^b I _i	
1	A'	3680		3686	3684	19.376	66.986	NH(100)
2	Α'	3585		3583	3581	43.833	241.590	NH(100)
3	Α'		3240	3238	3236	0.887	69.478	CH(99)
4	Α'	3220		3225	3223	0.724	48.360	CH(99)
5	Α'		3188	3189	3186	13.372	67.259	mips(92),mops(7)
6	Α'	3175		3173	3171	15.149	101.090	CH(99)
7	A'		3085	3082	3079	18.172	78.768	mops(58),mss(33),mips(8)
8	Α'	3019	3017	3016	3015	31.679	159.729	mss(64),mops(35)
9	Α'			1698	1697	169.024	40.959	bHNH(79),CN(9),CC(7)
10	Α'	1669	1666	1668	1665	64.550	33.967	CC(48),NOas(16),bCH(10),bring(8)
11	Α'	1655		1652	1650	117.764	62.101	CC(46),NOas(23),bCH(7),bring(7)
12	A'		1610	1609	1607	97.366	13.429	NOas(45),CC(37),bring(5)
13	Α'	1549		1550	1548	51.287	3.771	bCH(34),CC(31),bmipb(16),CN(12)
14	A'		1538	1535	1533	7.821	7.895	bmipb(72),CC(9),bmopb(6),bCH(5)
15	A'	1520		1522	1518	8.163	18.922	bmopb(61),bmipb(38)
16	Α'	1466	1478	1475	1473	1.676	15.058	CC(41),bmipb(14),bCH(13),CCm(5)

17	A'			1447	1445	1.258	21.126	bmsb(86),CC(5),CCm(5)
18	A'	1399		1398	1396	527.344	447.042	NOss(63),CN(17),bNO2sc(15)
19	A'		1392	1395	1390	0.136	1.772	CC(84),bCNH(6)
20	A'	1347		1345	1344	152.850	45.663	CN(46),bCH(23),CC(17),bring(6)
21	A'		1319	1322	1317	1.483	0.148	bCH(69),CC(9),bCNH(6)
22	A'			1235	1231	14.864	35.309	CCm(32),bring(28),CC(13),CN(9),bCNH(8)
23	A'	1187		1185	1183	17.215	2.127	bCH(68),CC(18),bCNH(7)
24	Α'		1129	1132	1130	77.750	18.143	bCH(32),CC(30),CN(19)
25	Α'	1085		1082	1080	2.211	1.346	<pre>bmipr(42),bmopb(14),bmipb(12),bmopr(10),gCC(6),tring(5)</pre>
26	Α'		1073	1076	1075	2.675	3.602	bCNH(44),CC(26),bmopr(11),bring(7),bCH(6)
27	Α'	1028		1029	1027	4.363	2.281	bmopr(44),CC(19),bmipr(14),bring(9)
28	A"	975		970	969	2.347	1.799	gCH(82),tring(14)
29	Α'		952	956	954	12.740	7.897	bring(27),CC(19),CN(19),CCm(13),bNO2sc(8),NOss(5)
30	A"	932		935	932	7.641	1.676	gCH(82),tring(8)
31	A"		842	839	837	24.204	3.552	gCH(68),gCN(13),tring(12)
32	Α'	826		830	826	16.281	2.018	bNO2sc(48),bring(26),CN(7),NOss(6)
33	Α'		785	786	783	4.777	28.728	CC(46),CCm(16),bring(10),CN(10),bNO2sc(8)
34	A''	753		759	758	26.388	1.483	gCNO(38),tring(30),gCN(26)
35	A"	716	725	723	722	2.661	0.965	tring(49),gCN(21),gCC(11),gCH(9),gCNO(8)
36	Α'			665	660	4.407	2.994	bring(59),bNO2sc(14),CN(12),CC(6)
37	Α'			559	557	2.911	3.031	bNO2r(39),bCN(20),bCCN(10),bCC(9),CC(7)
38	A"	555		557	552	17.900	2.328	tring(39),gCN(27),bring(9),gCNH(6)
39	A''		548	546	544	3.933	4.613	tring(25),bring(24),gCN(18),CCm(7),bCCN(6)
40	A''			498	496	338.089	22.301	gCNH(56),bHNH(19),CN(8),tring(5)
41	A''	447	454	455	452	50.971	2.388	tring(54),gCC(20),gCN(7),gCNH(6),gCH(6)
42	A'			419	417	2.769	2.705	bNO2r(25),bCC(24),bCCN(21),bring(12),CC(7)
43	A"		315	380	379	39.174	2.003	tNH2(68),gCNH(10),tring(7)
44	A'			369	367	0.598	1.828	bring(46),CN(32),CC(10),bNO2sc(6)
45	A"			323	322	7.703	0.694	gCN(27),tring(26),gCC(14),gCH(8),bCCN(8),bCC(6)
46	A"			313	311	2.139	0.809	gCC(29),bCC(22),gCN(11),tring(9),tNH2(7), bCCN(6)
47	A'		215	212	211	0.900	0.292	bCN(63),bNO2r(10),bCC(9),CC(7)
48	A"			199	197	1.521	2.265	tCH3(54),gCN(13),tring(11)
49	A''		194	196	193	0.337	0.505	tring(28),tCH3(27),gCC(21),gCN(9),gCH(5)
50	A"			115	112	0.543	1.069	tring(65),gCN(13),gCH(11)
51	A''			70	67	0.032	0.120	tNO(85),tring(12)

Abbreviations used: b, bending; g, wagging; t, torsion; s, strong; vs, very strong; w, weak; vw, very weak;

^a Relative absorption intensities normalized with highest peak absorption

^b Relative Raman intensities calculated by Eq.4.1 and normalized to 100.

^c For the notations used see Table 4.4.

Table 4.6. The dipole moment (μ) and first-order <u>hyperpolarizib</u>ility (β) of 4NOT derived from DFT calculations

β_{xxx}	1.3885
β_{xxy}	409.27
β_{xyy}	-965.06
β_{vvv}	894.6
β_{zxx}	1.2363
β_{xyz}	365.59
β_{zyy}	-44.88
β_{xzz}	48.925
β_{yzz}	19.408
β_{zzz}	-417.51
β_{total}	1.9581
μ_{x}	4.05670959
μ_{y}	0.10126002
μ_z	2.69653051
μ	2.61811003

Table 4.7. Computed absorption wavelength (λ_{ng}) , energy (E_{ng}) , oscillator strength (f_n) and its major contribution

n	λ_{ng}	Eng	f _n	Major contribution
1	259.1	4.79	0.0083	H-5->L+0(+34%),
				H-4->L+0(21%)
2	220.9	5.61	0.0250	H-4->L+0(+27%),
				H-5->L+0(+26%)
3	207.1	5.99	0.0341	H-1->L+0(+28%),
				H-0->L+0(23%)

C-H vibrations

The aromatic structure shows the presence of C–H stretching vibrations around 3250-3100 cm⁻¹. In 4NOT these modes were observed at 3240, 3238, 3236, 3225, 3223, 3220, 3175, 3173 and 3171 cm⁻¹. A number of spikes observed throughout the broad absorption is indicative of Fermi resonance. In C–H in-plane bending vibrations are observed in the region 1000–1300 cm⁻¹ and are usually weak. The C–H outof-plane bending modes arise in the region 600–900 cm⁻¹. In the present study, the bands observed at 1655, 1652, 1609, 1549, 1550, 1538, 1535, 1347, 1322 and 1319 cm⁻¹ in 4NOT were assigned to C–H in-plane bending vibrations. The C–H out-of-plane bending modes for 4NOT are also assigned within characteristic region and were presented in Table 4.5.

C-C vibrations

The bands between $1400-1650 \text{ cm}^{-1}$ in Toluidine derivatives are assigned to C-C stretching modes. Accordingly, in the present study, the carbon-carbon vibrations of the title compound are observed at 1669, 1655, 1549 and 1466cm⁻¹ in the FT-IR spectrum and 1666, 1610, 1609, 1607, 1538, 1535, and 1533 cm⁻¹ in the FT-Raman.

C-N vibrations

The identification of C-N stretching frequency is a very difficult task, since the mixing of bands are possible in this region. The FT-IR bands observed at 1399, 1347, 1345, 1344, 1187, 1185 and 1183 cm⁻¹ and FT-Raman bands observed at 1395, 1392, 1390, 1322, 1319, 1317, 1132, 1130 and 1129 cm⁻¹ have been designated to C-N stretching modes of vibrations. These assignments are made in accordance with the assignments proposed by Roy [108].

Amino group vibrations

According to Socrates [109] the frequencies of amino group appear around $3500-3300 \text{ cm}^{-1}$ for NH₂ stretching, 1700–1600 cm⁻¹ for scissoring and 1150–900 cm⁻¹ for rocking deformations. The antisymmetric and symmetric stretching modes of NH₂ group are found at 3585, 3583 and 3581 cm⁻¹ in 4NOT. The bands appeared at 1698 and 1697 cm⁻¹ in infrared are assigned unambiguously to the scissoring modes of the NH₂ group and the NH₂ rocking modes have been assigned to 1347, 1345, 1344, 1322, 1319, 1187, 1185 and 1183 cm⁻¹ respectively for 4NOT. The IR bands for wagging and twisting NH₂ modes of 4NOT are identified at 557, 555, 552, 447, 455, 380, 379 and 315 cm⁻¹ respectively.

Ring vibration

In the present study the bands ascribed at 1085, 1082, 1080, 1076, 1075, 1073, 1029, 1028 and 1027 cm⁻¹ are assigned to ring in-plane and 759, 758, 753, 557, 555, 548, 546, 455 and 447 cm⁻¹ have been designated to ring out-plane bending modes, respectively. Small changes in frequencies observed for these modes are due to the changes in force constant/reduced mass ratio, resulting mainly due to electro negativity of nitrogen atom and the presence of methyl group.

Nitro group vibrations

Aromatic nitro compounds have strong absorptions due to asymmetric and symmetric stretching vibrations of the nitro group at 1570–1485 and 1370–1320 cm⁻¹. Usually, the symmetric vibration is stronger than antisymmetric one in the Raman spectra and the contrary holds in infrared. This could be due to the electron withdrawing substituent adjacent to the nitro group tend to increase the frequency of asymmetric vibration and decrease that of the symmetric vibration. The symmetric stretching vibrations of this group were found intense at 1669,1665, 1652, 1650 and 1399 cm⁻¹ in FT-IR and 1666, 1607, 1609 and 1610 cm⁻¹ in FT-Raman. The ring stretching vibrations are interesting, as the double bond is in conjugation with the ring and are well found in the characteristic regions. **Methyl group vibrations**

For the assignments of CH₃ group frequencies, basically nine fundamentals can be associated to each CH₃ group namely, m ss, symmetric stretch; m ips, inplane stretch (ie, in-plane hydrogen stretching modes); m ipb, in-plane-bending (i.e., hydrogen deformation modes); m sb, symmetric bending; m ipr, in-plane rocking; m opr, out-of-plane rocking and tCH₃, twisting hydrogen bending modes. In addition to that, m ops, out-ofplane stretch and m opb, out-of plane bending modes of the CH₃ group would be expected to be depolarised for A' symmetry species. The m ss frequency is established at 3019 cm⁻¹ in IR and m ips is assigned at 3188, 3189, 3085 and 3082 cm⁻¹ in IR and Raman, respectively, for 4NOT. We have observed the symmetrical methyl deformation mode m sb, at 1447 and 1445 cm⁻¹ in the infrared and Raman, and in-plane-bending methyl deformation mode m ipb, at 1478 cm⁻¹ in the Raman. The band at 3189, 3188, 3085 and 3082 cm^{-1} in infrared is attributed to m ops and m opb, respectively, in the A species. The methyl deformation modes mainly coupled with the in-plane-bending vibrations. The assignment of the band at 195 cm⁻¹ in Raman is attributed to methyl twisting mode.

Hyperpolarizability calculations

The first-order hyperpolarizibility (β_{iik}) of the novel molecular system of 4NOT is calculated using 3-21 G (d,p) basis set based on finite field approach. Hyperpolarizibility is a third rank tensor that can be described by a 3 x 3 x 3 matrix. It strongly depends on the method and basis set used. The 27 components of 3D matrix can be reduced to 10 components due to Kleinman [110] symmetry. The calculated first-order hyperpolarizability (β_{total}) of 4NOT is 1.9581x10⁻³⁰ esu, which is nearly 10 times greater than that of urea (0.1947 x 10^{-30} esu). The calculated dipole moment (μ) and first-order hyperpolarizibility (β) are shown in Table 4.6. The theoretical calculation seems to be more helpful in determination of particular components of β tensor than in establishing the real values of β . Domination of particular components indicates on a substantial delocalization of charges in those directions. It is noticed that in β_{yyy} (which is the principal dipole moment axis and it is parallel to the charge transfer axis) direction, the biggest values of hyperpolarizability are noticed and subsequently delocalization of electron cloud is more in that direction. The higher dipole moment values are associated, in general, with even larger projection of β_{total} quantities. The electric dipoles may enhance, oppose or at least bring the dipoles out of the required net alignment necessary for NLO properties such as β_{total} values. The connection between the electric dipole moments of an organic molecule having donoracceptor substituent and first hyperpolarizability is widely recognized in the literature [111]. The maximum β was due to the behavior of non-zero u value. One of the conclusions obtained from this work is that non-zero μ value may enable the finding of a non-zero ß value. Of course Hartee-Fock calculations depend on the mathematical method and basis set used for a polyatomic molecule.

Fig. 4.4 shows the highest occupied molecule orbital (HOMO) and lowest unoccupied molecule orbital (LUMO) of 4NOT. There is an inverse relationship between hyperpolarizability and HOMO–LUMO.

HOMO energy = -0.343 a.u

LUMO energy = 0.072 a.u HOMO-LUMO energy gap = 0.415 a.u



Fig. 4.4. Representation of the orbital involved in the electronic transition for (a) HOMO (b) LUMO (c) HOMO, LUMO (d) Occupied (e) Virtual (f) All Electronic excitation mechanism

The static polarizability value[112-113] is proportional to the optical intensity and inversely proportional to the cube of transition energy. With this concept, larger oscillator strength (f_n) and $\Delta \mu_{gn}$ with lower transition energy (E_{gn}) is favourable to obtain large first static polarizability values. Electronic excitation energies, oscillator strength and nature of the respective excited states were calculated by the closed-shell singlet calculation method and are summarized in Table 4.7. Representation of the orbital involved in the electronic transition was shown in Fig. 4.5.



Fig. 4.5. Representation of the orbital involved in the electronic transition for (a) HOMO-5 (b) LUMO+0 (c) HOMO-4 (e) HOMO-1 (d) HOMO-0

Conclusion

The FT-IR and FT-Raman spectra have been recorded and the detailed vibrational assignment is presented for 4NOT. The equilibrium geometries, harmonic vibrational frequencies, IR and Raman spectra of 4NOT were determined and analyzed by B3LYP/ 6-31G* and B3LYB/6-311+G level of theory. The difference between the corresponding wave numbers (observed and calculated) is very small, for most of fundamentals. Therefore, the results presented in this work for 4NOT indicate that this level of theory is reliable for prediction of both infrared and Raman spectra of the title compound. The optimized geometrical parameters calculated at B3LYB/6-311+G** level are slightly larger than those calculated at B3LYP/6-311+G* level. The first-order hyperpolarizability (β_{total}) of 4NOT was calculated and found to be 1.9581×10^{-30} esu, which is nearly 10 times greater than that of urea (0.1947 x 10^{-30} esu). It is noticed that in β_{yyy} (which is the principal dipole moment axis and it is parallel to the charge transfer axis) direction, the biggest values of hyperpolarizability are noticed and subsequently delocalization of electron cloud is more in that direction. Hence these materials have been motivated by their wide range of potential applications such as second harmonic generation (SHG), electro-optic modulation, sum and difference frequency doubling of lasers, etc. Such materials have large nonlinear optical coefficients, suitable transparency and excellent comprehensive properties. Electronic excitation energies, oscillator strength and nature of the respective excited states were calculated by the closed-shell singlet calculation method. References

1. L.A. Woodeard, Introduction to the Theory of Molecular Vibration and Vibrational Spectroscopy, Oxford University Press, London, 1972.

2. W.A. Guillory, Introduction to Molecular Structure and Spectroscopy, Allyn and Bacon Inc., Boston, 1977.

3. G. Herzberg, Infrared and Raman Spectra of Polyatomic Molecules, Van Nostrand, New York, 1966.

4. G. Turrell, Infrared and Raman Spectra of Crystals, Academic Press, London, 1972.

5. D.N. Sathyanarayanan, Vibrational Spectroscopy Theory and Application, New Age International publishers, New Delhi, 1996.

6. G.F.Dyke, A.J.Floyd, M.Sainsbyrg, R.S.Theobald, Organic Spectroscopy: An Introduction, Longman Inc., New York, 1981.

7. D.M. Nair, A.P.B. Sinha, K.Venkataraman, Curr. Sci., 40 (1971) 239.

8. R.E. Dpdd. Chemical Spectroscopy, Elsevier Publishing Company, New York, 1962.

9. N.B. Colthup, L.H. Daly, S.E.Wiberely, Introduction to Infrared and Raman Spectroscopy, Academic Press, New York, 1964.

10. S.D. Ross, inorganic Infrared and Raman Spectra, Mc Graw-Hill, London, 1972.

11. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Fifth Edition, Part A, John Wiley & Sons Inc.,New York,1997.

12. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Fifth Edition, Part B, John Wiley & Sons Inc.,New York,1997.

13. I.A. Degen, G.A. Newman, Spectrochim. Acta Part A, 49 (1995) 859.

14. R.S. Krishnan, Source Book on Raman Effect, Publication and Information Directorate CSIR, New Delhi, 1 (1989) 1928.

15. R.S. Krishnan, Source Book on Raman Effect, Publication and Information Directorate CSIR, New Delhi, 2 (1992) 1958.

16. R.S. Krishnan, Source Book on Raman Effect, Publication and Information Directorate CSIR, New Delhi, 3 (1994) 1971.

17. R.S. Krishnan, Source Book on Raman Effect, NISCOM, CSIR, New Delhi, 4 (1998) 1975.

18. C.N.R. Rao, Chemical Application of Infrared Spectroscopy, Academic Press, New York, 1963.

19. G.H. Beaven, E.A. Johnson, H.A. Willis, R.G. Miller, Molecular Spectroscopy-Methods and Applications in Chemistry, Heywood and Company Ltd., London, 1961.

20. F.A. Cotton, Chemical Applications of Group Theory, Wiley Interscience, New York, 1971.

21. L.J. Bellamy, The Infrared Spectra of Complex Molecules-Advances in Infrared Group Frequencies, Vol. 2, Chapman and Hall, London, 1980.

22. R.N. Jones, C. Sandorfy, Chemical Applications of Spectroscopy, Wiley Interscience, New York, 1956.

23. E.G. Brame, I.G. Grasselli, Infrared and Raman Spectroscopy, Marcel Dekker Inc., New York, 1976.

24. E.B. Willson, J.C. Decius, P.C. Cross, Molecular Vibrations: The Theory of Infrared and Raman Vibrational Spectra, McGraw Hill, New York, 1955.

25. R.S. Drago, Physical Methods in Chemistry, W.B. Saaunders Co., Philadelphia, 1977.

26. G.W. King, Spectroscopy and Molecular Structure, Rinehart and Winsten, Inc., New York, 1964.

27. D.M. Dennison, J. Astro.Phy., 62 (1925) 84.

28. N. Bjerrum, Verh, dd. Phys. Ges., 16 (1914) 737.

- 29. T. Shimanouchi, I. Nakagawa, J. Hiraishi, M.Ishil, J. Mol. Specry., 19 (1966) 78.
- 30. H.C. Urey, C.A, Bradley, Phy. Rev., 38 (1931) 1969.
- 31. T. Shimanochi, Physical Chemistry: An Advanced Treatise

Vol. IV, D. Henderson (Ed.), Academic Press, New York, 1970.

32. P. Labonville, J.R. Ferraro, M.C. Wall, L.J. Basile, Coord, Chem. Rev., 7 (1972) 257.

33. T. Shimanouchi, J. Chem. Phys., 26 (1957) 594.

34. T. Shimanouchi, I.S. Zuki, J. Mol. Spectry., 6 (1961) 277; 8 (1962) 222.

35. J.R. Scherer, J. Overend, J. Chem. Phys., 33 (1960) 1681.

36. J.R. Scherer, J. Overend, Spectrochim. Acta Part A, 17 (1961) 719.

37. J.R. Scherer, J. C. Evans, J. Overend, Spectrochim. Acta Part A, 18 (1962) 57.

38. J.R. Scherer, Spectrochim. Acta Part A, 20 (1964) 345.

39. T. Shimanouchi, International Symposium on Molecular Structure and Spectroscopy, Tokyo, 1962.

40. Perisean, E. L. Wu, J. Overend, J.Chem.Phys., 39 (1963) 217.

41. D.F. Health, J.W. Linnett, Trans. Faraday Soc, 44 (1948) 873, 878, 884.

42. L. Pauling, The Nature of the Chemical Bonds, Cornell Univ. Press, Itheca, 1970.

43. H. Kim, P.A. Souder, H. Classen, J. Mol. Spectry, 26 (1968) 46.

44. J. N. Rai, S.Tewari, S.N. Rai, Z. Naturforsch., 279 (1972) 867.

45. D. K. Sharma, Studies in Molecular Constants from Spectral Data, Ph.D. Thesis, Meerut University, Meerut, 1975.

46. N. K. Sanyal, R.K. Goel. A.N. Pandey, Indian J. Pure Appl. Phys., 14 (1976)244.

47. Krebs, A. Muller, Spectrochim. Acta Part A, 22 (1966) 1532; J. Mol. Spectry.,22 (1967) 290.

48. N. Mohan, K. H. Schmidt, A. Muller, J. Mol. Struct., 13 (1972) 155.

49. N. K. Sanyal, A.N. Pandey, H. S. Singh, J. Mol. Spectry., 30 (1969) 144.

- 50. N. K. Sanyal, H.S. Singh, A.N. Pandey, B.P. Singh, Indian J. Pure Appl. Phys., 8 (1970) 72.
- 51. T.G. Harrison, H.H. Patterson, J.J.Godfrey, Inorg, Chem., 15 (1976) 1271.
- 52. Z. Gburski, Acta Phys. Pol., A43 (1973) 237; A44 (1973) 211.

53. J. Overand, J. R. Scherer, J. Chem. Phys., 32 (1960) 1289, 1296; 33, 446: 34, 574.

54. I.M. Mills, Spectrochim. Acta Part A, 19 (1963) 1585.

55. J. Aldous, I.M. Mills, Spectrochim. Acta Part A, 19 (1963) 1567.

56. J. L. Duncan, Spectrochim. Acta Part A, 20 (1964) 1197, 1807.

- 57. L. Nemes, Acta. Chim. Acad. Sci. Hung, 52 (1967) 179.
- 58. W.H. Fletcher, W.T. Thomson, J. Mol. Spectry., 25 (1968) 240.

59. B.K. Sharma, Spectroscopy, GOEL Publishing House, Meerut, Eleventh Editions, 1995.

60. B.P. Stranghan. S. Walker, Spectroscopy, Vol.2, Chapman and Hall, London, 1976.

61. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, second Edition, Wiley- Interscience, New York, 1970.

62. Y.R. Shrma, Elementary Organic Spectroscopy, S.Chand & Company Ltd, New Delhi, 1999.

63. M. castella-Ventura, E. Kassab, G. Buntinx, O. Poizat, Phys. Chem. Chem. Phys., 2(2000) 4682.

64. D.N. Shin, J.W. Hahn, K.H. Jung, T.K. Ha, J.Raman Spectrosc., 29 (1998)245.

65. B. Giese, D. McNaughton, Phys. Chem. Chem. Phys., 4 (2002) 5161.

66. R.G. Parr, W. Yang, Density Functional Theory of Atoms and Molecules, Oxford University Press, New York, 1989.

67. A.D. Becke, J. Chem. Phys., 98 (1993) 5648.

68. C. Lee, W. Yang, R.G. Parr, Phys. Rev., B37 (1988) 785.

69.M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria,

M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2003.

70. Yu. N. Panchenko, N.F.Stepanov, Russ. J. Phys. Chem., 69 (1995) 535.

- 71. Yu. N. Panchenko, J.Mol. Struct., 410/411 (1997) 327.
- 72. Yu. N. Panchenko, Russ. Chem. Bull., 45 (4) (1996) 753.
- 73. P.Hohenberg and W.Kohn, Phys. Rev., 136(1964) B864.
- 74. W. Kohn and L. J. Sham, Phys. Rev., 140 (1965) A 1133.

75. P. J. Stephens, F.J. Devlin, C.F. Chabalowski, and M. J. Frish, J. Phys. Chem., 98 (1994) 11623.

76. P. Pulay, G. Fogarasi, G.Pongor, J. E. Boggs, A. Vargha, J. Am. Chem. Soc., 105 (1983) 7037.

77. P.Pulay, W. Meyer, Mol. Phys., 27 (1974) 473.

78. P.Pulay, Mol. Phys., 17 (1969) 197.

79. G. Fogarasi, P. Pulay, Annu. Rev. Phys. Chem., 35 (1984) 191.

80. C. E. Blom, C. Altona, Mol. Phys., 31 (1976) 1377.

81. T.Shimanouchi, Physical Chemistry; An Advanced Treatise Vol.IV, D.Henderson(Ed.) Academic Press, New York,(1970).

82. Mehmet Karabacak, Dilek Karagöz, Mustafa Kurt, Journal of Molecular Structure, Volume 892, Issues 1–3, 15 December 2008, Pages 25-31.

83. N. Sundaraganesan, S. Kalaichelvan, C. Meganathan, B. Dominic Joshua, J. Cornard, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Volume 71, Issue 3, 1 December 2008, Pages 898-906

84. J. Swaminathan, M. Ramalingam, V. Sethuraman, N. Sundaraganesan, S. Sebastian, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, *Volume 73, Issue* 4, 15 August 2009, Pages 593-600.

85. S. Sudha, N. Sundaraganesan, M. Kurt, M. Cinar, M. Karabacak, *Journal of Molecular Structure, Volume 985, Issues 2–3, 31 January 2011, Pages 148-156*

86. M. Govindarajan, K. Ganasan, S. Periandy, M. Karabacak, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Volume 79, Issue 3, August 2011, Pages 646-653

87. T. Prabhu, S. Periandy, S. Ramalingam, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Volume 79, Issue 5, September 2011, Pages 948-955

88. D. Mahadevan, S. Periandy, S. Ramalingam, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Volume 79, Issue 5, September 2011, Pages 962-969

89. P.B. Nagabalasubramanian, Mehmet Karabacak, S. Periandy, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Volume 82, Issue 1, November 2011, Pages 169-180

90. M. Karabacak, Z. Cinar, M. Kurt, S. Sudha, N. Sundaraganesan, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Volume 85, Issue 1, January 2012, Pages 179-189

91. Mehmet Karabacak, Mehmet Cinar, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Volume 86, February 2012, Pages 590-599

92. M. Govindarajan, M. Karabacak, A. Suvitha, S. Periandy, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Volume 89, April 2012, Pages 137-148

93. S. Sylvestre, S. Sebastian, K. Oudayakumar, T. Jayavarthanan, N. Sundaraganesan, *Spectrochimica Acta Part A:*

Molecular and Biomolecular Spectroscopy, Volume 96, October 2012, Pages 401-412

94. N. Udaya Sri, K. Chaitanya, M.V.S. Prasad, V. Veeraiah, A. Veeraiah, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Volume 97, November 2012, Pages 728-736

95. V. Karunakaran, V. Balachandran, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Volume 98, December 2012, Pages 229-239

96. M. Arivazhagan, D. Anitha Rexalin, J. Geethapriya, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Volume 113, September 2013, Pages 236-249.

97. G. Foragarasi, P. Pulay, in: J.R. Durig (Ed.), Vibrational Spectra and Structure, vol. 14, Elsevier, Amsterdam, 1985, pp. 125–219.

98. P. Pulay, in: H.F. Schaefer III (Ed.), Application of Electronic structure Theory, Modern Theoretical Chemistry, vol. 4, Plenum press, New York, 1997, p. 153.

99. G. Forgarasi, X. Zhou, P.W. Taylor, P. Pulay, J. Am. Chem. Soc. 114 (1992) 8191.

100. T. Sundius, MOLVIB: a program for harmonic force field calculations. QCPE Program no. 604, J. Mol. Struct. 218 (1990) 321.

101. T. Sundius, Vib. Spectrosc. 29 (2002) 89.

102. F.A. Cotton, Chemical Applications of Group Theory, Wiley Interscience, New York, 1971.

103. A. Frisch, A.B. Nielson, A.J. Holder, GAUSSVIEW Users Manual, Gaussian Inc., Pittsburgh, PA, 2000.

104. G. Keresztury, S. Holly, J. Varga, G. Besenyei, A.Y. Wang, J.R. Durig, Spectrochim. Acta 49A (1993) 2007.

105. G. Keresztury, in: J.M. Chalmers, P.R. Griffiths (Eds.), Raman Spectroscopy: Theory in Handbook of Vibrational Spectroscopy, vol.1, John Wiley & Sons Ltd., 2002.

106. P. Pulay, G. Fogarasi, F. Pong, J.E. Boggs, J. Am. Chem. Soc., 101 (1979) 2550.

107. P. Pulay, G. Rauhut, J. Phys. Chem. 99 (1995) 3093.

108. J.N. Roy, Indian J. Phys. B 65 (1991) 364.

109. G. Socrates, Infrared and Raman characteristic Group Frequencies, Tables and Charts, third ed., John Wiley & Sons, Chichester, 2001.

110. D.A. Kleinman, Phys. Rev. 1962;126,1977.

111. P.N. Prasad, D.J. Williams, Introduction to Nonlinear Optical Effects in Molecules and Polymers, Wiley, New York, 1991.

112. K. Wu, C. Liu, C. Mang, Opt. Mater. 29 (2007) 1129-1137.

113. S. Iran, W.M.F. Fabian, Dyes Pigments 70 (2006) 91-96.