FT-IR and FT-Raman Spectra, HOMO-LUMO and NBO Analysis of 2-Bromo-4-Nitrotoluene: an *Ab Initio* and DFT Approach

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Abstract–The FT-IR and FT-Raman spectra of 2-bromo-4-nitrotoluene (BNT) have been recorded in the region 4000-400 cm^{-1} and 3500-100 cm^{-1}, respectively. The optimized molecular geometry, vibrational frequencies, Infrared intensities, Raman intensities and thermodynamic parameters in ground state were calculated using *ab initio* Hartree-Fock (HF) and density functional B3LYP methods (DFT) with 6-311++G(d,p) basis set. The observed FT-IR and FT-Raman vibrational frequencies are analysed and compared with theoretically predicted vibrational frequencies. The geometries and normal modes of vibration obtained from HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) methods are reliable compared with the experimental data. The Mulliken charges, the natural bonding orbital (NBO) analysis and thermodynamic functions of the investigated molecule were computed using HF and DFT calculations. The calculated HOMO and LUMO energies show that charge transfer occurs within molecule. The influences of bromine and nitrogen atoms and methyl group on the geometry of benzene and its normal modes of vibrations have also been discussed.

Keywords–Vibrational Spectra; HF; DFT; HOMO-LUMO; NBO; 2-Bromo-4-Nitrotoluene

I. INTRODUCTION

Toluene, also known as methyl benzene or phenylmethane, is a clear, water-in soluble liquid with the typical smell of paint thinners, redolent of the sweet smell of the related compound benzene. It is an aromatic hydrocarbon that is widely used as an industrial feed-stock and as a solvent. Like other solvent, toluene is also used as an inhalent drug for its intoxicating properties [1, 2]. Toluene reacts as a normal hydrocarbon towards electrophitic aromatic substitution [3, 4]. The methyl group around 25 times is more reactive than benzene in such reaction. It undergoes Bromination by Br_2 in the presence of Fe to give *ortho* and *para* isomers. The shift to higher frequencies in the case of BNT is due to the high electron withdrawing effect of nitro group which on further nitration yield *o*-bromo-*p*-nitrotoluene (2-bromo-4-nitrotoluene). It is also used as a carbon source for marking multi wall carbon nanotubes. Toluene can be used to break open red blood cells in order to extract hemoglobin in bichemistry experiments [5]. The complete vibrational analysis at 2-bromo-4-nitrotoluene was performed by combining the experimental and theoretical information using Pulay's

density functional theory (DFT) based on scaled quantum chemical approach [6]. It is expected that both *ab initio* HF and DFT levels are reliable for predicting vibrational spectra of BNT. More recently, the experimental vibrational spectra at α-chlorotoluene, α, α-chlorotoluene and 2-bromo-4-methylaniline [7, 8] have been investigated in comparison with *ab inito* and DFT studies. However, the comparative studies on the complete FT-IR and FT-Raman spectra of BNT have not been reported so far. In this study, molecular geometry, optimized parameters and vibrational frequencies are computed and the performance of the computational methods for HF/B3LYP/6-311++G (d, p) basis set is compared.

II. EXPERIMENTAL DETAILS

The compound under investigation namely 2-bromo-4-nitrotoluene (BNT) is provided from the Lancaster Chemical Company (UK) which is at spectroscopic grade and hence used for recording the spectra of such without any purification. The room temperature FT-IR spectrum of the BNT was measured in the region 4000-400 cm^{-1} on BRUKER IFS 66V spectrometer using KBr pellet. The spectral resolution is $\pm 1 cm^{-1}$.

The FT-Raman spectrum of BNT was also recorded in the region 3500-100 cm^{-1} with BRUKER RFS 100/s Raman module equipped with Nd: YAG laser source operating at 1064 nm line width 150 mw power. The spectra were recorded with scanning speed of 50 cm^{-1} min^{-1} of spectral width 4 cm^{-1}. The reported wave numbers are believed to accurate within $\pm$ 1 cm^{-1}.

III. COMPUTATIONAL DETAILS

Quantum chemical density functional calculations have been carried out for BNT with the 2009 version of the Gaussian program package [9] using HF and B3LYP function [10, 11] combined with the standard 6-311++G(d,p) basis set. The Cartesian representation of the theoretical force constants have been computed at the fully optimized geometry by assuming the model belongs to C_1 point group symmetry. The optimized geometrical parameters, fundamental vibrational frequencies, IR intensity, Raman intensity, the atomic charges and other thermodynamic parameters were also calculated.

Scaling of the force field was performed according to the SQM procedure [12, 13] using selective scaling in the natural internal coordinate representation [6, 14]. The transformation and the subsequent normal coordinate analysis (NCA) including the least squares refinement of the scaling factors, calculation of potential energy distribution work done on PC with the MOLVIB program written (version 7.0–G77) by Sundius [15-17].

From the intensity theory of Raman scattering [18] the relative Raman intensities (I_i) and Raman activities (S_i) were calculated.

$$I_i = \frac{f(\nu_o - \nu_i)^4 S_i}{\nu_i (1 - \exp - ((hc_{vi})/KT))}$$

where ν_o is the exciting frequency (in cm^{-1}), ν_i is the vibrational wavenumber of the ith normal mode, h, c and k are fundamental. Constants and f is suitably chosen common normalization factor for all peak intensities.

IV. RESULT AND DISCUSSION

A. Molecular Geometry

The molecular structure of BNT is shown in Fig. 1. The global minimum energy obtained by HF and DFT structure optimization are calculated –916.365 Hartrees and –919.865 Hartrees, respectively. The calculated optimized geometrical parameters obtained in this study for the title compound are compared with the experimental values [19, 20] are presented in the Table I.
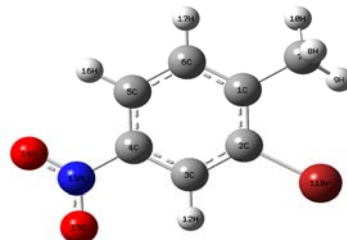

Fig. 1 Molecular structure of 2-bromo-4-nitroaniline

TABLE I OPTIMIZED MOLECULAR GEOMETRIES OF 2-BROMO-4-NITROTOLUENE BASED ON HF/6-311++G (D, P) AND B3LYP/6-311++G (D, P)

Parameters	HF/6-311++G(d,p)	B3LYP/6-311++G(d,p)	Exp^a	Expl^b
Bond length (Å)				
C1 – C2	1.394	1.404	1.400	1.403
C1 – C6	1.392	1.402	1.391	1.403
C1 – C7	1.506	1.503	1.501	1.507
C2 – C3	1.380	1.388	1.392	1.395
C2 – Br11	1.901	1.919	1.873	1.911
C3 – C4	1.380	1.390	1.391	1.394
C3 – H12	1.070	1.080	1.080	1.083
C4 – C5	1.379	1.389	1.390	1.393
C4 – N13	1.464	1.478	-	-
C5 – C6	1.381	1.388	1.393	1.395
C5 – H16	1.071	1.080	-	-
C6 – H17	1.074	1.084	-	-
C7 – H8	1.084	1.093	1.073	1.095
C7 – H9	1.084	1.093	1.074	1.093
C7 – H10	1.082	1.090	1.071	1.095
N13 – O14	1.187	1.225	-	-
N13 – O15	1.871	1.224	-	-
Bond angle (°)				
C2 – C1 – C6	117.313	117.003	121.5	116.5
C2 – C1 – C7	122.573	122.547	-	122.8
C6 – C1 – C7	120.113	120.448	-	120.7
C1 – C2 – C3	121.986	128.282	119.2	122.6
C1 – C2 – Br11	120.619	120.175	120.1	119.9
C3 – C2 – Br11	117.393	117.542	-	117.4
C2 – C3 – C4	118.373	118.217	120.3	118.6
C2 – C3 – H12	121.301	121.755	120.1	120.7
C4 – C3 – H12	120.323	120.027	-	120.6
C3 – C34 – C5	121.920	121.935	120.5	120.9
C3 – C4 – N13	118.771	118.728	-	-
C5 – C4 – N13	119.307	119.336	-	-
C4 – C5 – C6	118.349	118.330	120.5	118.7
C4 – C5 – H16	120.323	119.922	-	-
C6- C5 – H16	121.326	121.747	-	-
C1 – C6 – C5	122.055	122.231	117.8	122.5
C1 –C6 – H17	118.957	118.611	-	-
C5 – C6 – H17	118.987	119.156	-	-

C1 – C7 – H8	110.857	111.078	109.5	111.4
C1 – C7 – H9	110.857	111.076	-	110.5
C1 – C7 – H10	110.408	110.753	-	114
H8 – C7 – H9	107.510	106.797	109.5	108.2
H8 – C7 – H10	108.558	108.500	-	106.8
H9 – C7 – H10	108.552	108.497	-	108.2
C4 – N13 – O14	117.455	117.491	-	-
C4 – N13 – O15	117.632	117.701	-	-
14 – N13 – O15	124.911	124.806	-	-

Detailed description of vibrational modes can be given by means of normal coordinate analysis. For this purpose, the full set of 58 standard internal coordinates (containing 13 redundancies) was defined in Table II. From these, a non-redundant set of local symmetry coordinates was constructed by suitable linear combination of internal coordinates following the recommendations of Fogarasi and Pulay [11, 12] are summarized in Table III. The theoretically calculated DFT force field were transformed to the later set of vibrational coordinates and used in all the subsequent calculations.

TABLE II DEFINITION OF INTERNAL COORDINATES OF 2-BROMO-4-NITRO TOLUENE

No.	Symbol	Type	Definition
Stretching			
1-6	r_i	CC	C1–C2, C2–C3, C3–C4, C4–C5, C5–C6, C6–C1
7	R_i	CC	C1–C7
8-10	Q_i	CH	C3–H12, C5–H16, C6–H17
11	q_i	CN	C4–H13
12	T_i	CBr	C2–Br
13-14	t_i	NO	N13–O14, N13–O15
15-17	S_i	CH (methyl)	C7–H8, C7–H9, C7–H10
In-plane bending			
18-23	α_i	CCC	C1–C2–C3, C2–C3–C4, C3–C4–C5, C4–C5–C6, C5–C6–C1, C6–C1–C2
24-29	β_i	CCH	C2–C3–H12, C4–C3–H12, C1–C6–H17, C5–C6–H17, C4–C5–H16, C6–C5–H16
30-31	α_i	CCC	C6–C1–C7, C2–C1–C7
32-33	γ_i	CCBr	C1–C2–Br11, C3–C2–Br11
34-35	ϕ_i	CCN	C5–C4–N13, C3–C4–N13
36-37	δ_i	CNO	C4–N13–O15, C4–N13–O14
38	σ_i	ONO	O14–N13–O15
39-41	β_i	CCH	C1–C7–H8, C1–C7–H9, C1–C7–H10
42-44	π_i	HCH	H8–C7–H10, H10–C7–H9, H9–C7–H10
Out-of-plane bending			
45-50	τ_i	CC	C1–C2–C3–C4, C2–C3–C4–C5, C3–C4–C5–C6, C4–C5–C6–C1, C5–C6–C1–C2, C6–C1–C2–C3
51	ω_i	CC	C7–C1–C6–C2
52-54	ω_i	CH	H12–C3–C2–C4, H16–C5–C4–C6, H17–C6–C5–C1
55	ω_i	CBr	Br11–C2–C3–C1
56	ω_i	CN	N13–C4–C5–C3
57	ω_i	NO	C4–N13–O14–O15
58	ω_i	CH	C6(C2)–C1–C7(H8, H9, H10)

B. Vibrational Assignments

The title compound belongs to C_1 symmetry consists of 17 atoms have its 45 normal vibrational modes, 17 stretching modes, 14 of these modes should be in-plane vibrations and 14 out-of-plane vibrations with respect to the reflection on the symmetry plane (see Tables II and III).

The detailed vibrational assignments of fundamental modes of BNT along with observed and calculated frequencies, Raman intensities, infrared intensities and normal mode of descriptions are reported in Table IV. The observed FT-IR and FT-Raman spectra of the title compound are shown in Figs. 2 and 3, respectively.

TABLE III DEFINITION OF LOCAL SYMMETRY CO-ORDINATES OF 2-BROMO-4-NITRO TOLUENE

No.	Symbol[a]	Definition[b]
1-6	CC	$r_1, r_2, r_3, r_4, r_5, r_6$
7	CC	R_7
8-10	CH	Q_8, Q_9, Q_{10}
11	CN	q_{11}
12	CBr	T_{12}
13	NO_2ss	$(t_{13} + t_{14})/\sqrt{2}$
14	NO_2ass	$(t_{13} - t_{14})/\sqrt{2}$
15-17	CH_3 ss	$(s_{15} + s_{16} + s_{17})/\sqrt{2}$
	CH_3 ips	$(2s_{15} - s_{16} - s_{17})/\sqrt{6}$
	CH_3 ops	$(s_{16} - s_{17})/\sqrt{2}$
18	R trigd	$(\alpha_{18} - \alpha_{19} + \alpha_{20} - \alpha_{21} + \alpha_{22} - \alpha_{23})/\sqrt{6}$
19	R symd	$(-\alpha_{18} - \alpha_{19} + \alpha_{20} - \alpha_{21} + \alpha_{22} + \alpha_{23})/\sqrt{2}$
20	R asymd	$(\alpha_{18} - \alpha_{19} + \alpha_{22} + \alpha_{23})/\sqrt{2}$
21-23	bCH	$(\beta_{24} - \beta_{25})/\sqrt{2}$, $(\beta_{26} - \beta_{27})/\sqrt{2}$, $(\beta_{28} - \beta_{29})/\sqrt{2}$
24	CCC	$(\alpha_{30} - \alpha_{31})/\sqrt{2}$
25	CCBr	$(\pi_{32} - \pi_{34})/\sqrt{2}$
26	CCN	$(\alpha_{34} - \alpha_{35})/\sqrt{2}$
27	NO_2 (sci)	$(2\sigma_{36} - \sigma_{37} - \sigma_{38})/\sqrt{2}$
28	NO_2 (rock)	$(\sigma_{37} - \sigma_{38})/\sqrt{2}$
29	NO_2 (twisting)	$(\sigma_{37} + \sigma_{38})/\sqrt{2}$
30	CH_3 (sb)	$(-\sigma_{39} - \sigma_{40} - \sigma_{41} + \pi_{42} + \pi_{43} + \pi_{44})/\sqrt{6}$
31	CH_3 (ipb)	$(-\pi_{42} - \pi_{43} + 2\pi_{44})/\sqrt{6}$
32	CH_3 (opb)	$(-\pi_{42} - \pi_{43})/\sqrt{2}$
33	CH_3 (ipr)	$(-2\sigma_{39} - \sigma_{40} - \sigma_{41})/\sqrt{2}$
34	CH_3 (opr)	$(\sigma_{40} - \sigma_{41})/\sqrt{2}$
35	τring	$(\tau_{45} - \tau_{46} + \tau_{47} - \tau_{48} + \tau_{49} - \tau_{50})/\sqrt{6}$
36	τsymd	$(\tau_{45} - \tau_{46} - \tau_{48} + \tau_{49})/\sqrt{2}$
37	τasymd	$(-\tau_{45} + 2\tau_{46} - \tau_{47} - \tau_{48} + 2\tau_{49} - \tau_{50})/\sqrt{2}$
38	ωCC	ω_{51}
39-41	ωCH	$\omega_{52}, \omega_{53}, \omega_{54}$
42	ωCBr	ω_{55}
43	ωCN	ω_{56}
44	ωNO	ω_{57}
45	ωCH	ω_{58}

[a]These symbols used for description of the normal modes by assignment in Table IV

[b]The internal coordinates used here are defined in Table II

TABLE IV OBSERVED AND CALCULATED VIBRATIONAL FREQUENCIES (IN CM^{-1}), IR INTENSITIES, RAMAN INTENSITIES OF BNT

S. NO.	Observed frequency (cm^{-1})		Unscaled frequency (cm^{-1})		Scaled frequency (cm^{-1})		Assignments (% PED)
	FT-IR	FT-Raman	a	b	a	b	
1.	3108		3405	3232	3121	3110	νCH (98)
2.	3083		3395	3225	3096	3088	νCH (98)
3.	3042		3345	3180	3045	3038	νCH (97)
4.		3060	3263	3118	3058	3038	CH_3 ips (99)

5.	2966		3243	3086	2968	2965	CH$_3$ ops (98)
6.		2926	3183	3034	2930	2925	CH$_3$ ss (98)
7.	1594	1599	1825	1633	1603	1593	νCC (75) δCH (22)
8.	1589		1776	1623	1591	1588	νCC (74) δCC (20)
9.		1549	1739	1575	1553	1545	NO$_2$ ips (68) νCC (20)
10.			1640	1500	1475	1470	CH$_3$ ipb (86)
11.	1471		1617	1489	1468	1465	CH$_3$ opb (85)
12.	1469		1609	1479	1453	1452	νCC (68) δCH (24)
13.	1382		1602	1419	1385	1380	νCC (65) δCN (12)
14.	1348		1543	1411	1355	1343	νCC (64)δCBr (20) δCC (10)
15.			1528	1368	1348	1352	δCH (65) νCC (22) δRing (10)
16.	1299		1397	1330	1307	1300	δCH (65) νCC (23)
17.	1267	1270	1316	1287	1270	1264	NO$_2$ ss (66) νCC (25)
18.	1211	1214	1333	1227	1214	1210	δCH (62) νCC (22) δRing (12)
19.	1143		1280	1160	1148	1147 2	νCC (63) δCN (18) δCH (10)
20.	1129		1229	1129	1135	1133	νCC (64) δCBr (16) δCN (12)
21.	1119		1159	1120	1120	1120	ωCH (78) δRing (12)
22.		1130	1186	1052	1044	1040	CH$_3$ sb (88)
23.			1152	1016	1005	1007	CH$_3$ ipr (85)
24.			1094	981	978	972	CH$_3$ opr (86)
25.	891	892	1032	918	894	890	ωCH (82)
26.	884		990	893	888	882	δRing 1 (68) νCC (20) δCH (10)
27.			930	840	822	822	νCN (70) νCC (12) δCC (10)
28.		717	874	808	717	715	δRing 2 (62) δRing 3 (20)
29.		701	816	725	706	700	ωCH (86)
30.			742	693	660	661	NO$_2$ wagging (68)
31.	634	638	723	661	642	635	NO$_2$ scissoring(72)
32.			692	642	630	627	δCC (64) δCBr (22)
33.			593	548	545	540	δCN (66) νCC (22) δCH ( )
34.		457	561	518	458	455	νCBr (75) δCH (22)
35.			480	439	431	428	NO$_2$ rocking (78)
36.			457	425	415	413	δCBr (73) δCC (20)
37.		310	392	361	316	312	ωCN (58) δRing 1 (20) δRing 2 (12)
38.		258	326	296	295	291	δRing 1 (54) ωCC (20) ωCH (10)
39.			320	294	284	282	ωCBr (38) ωCN (27)
40.		174	253	234	263	260	ωCC (62) ωCH (21)
41.			172	154	178	174	NO$_2$ twisting (62)
42.			169	148	143	140	δRing 3 (54) νCH (20) νCN (10)
43.			162	147	138	135	δRing 2 (54) ωCC (20)
44.			117	106	102	100	δRing 3 (55) ωCC (18) ωCBr (10)
45.			43	44	44	40	t CH$_3$ (75)

[a]Calculated by HF/6-311++G(d,p); [b]Calculated by B3LYP/6-311++G(d,p)
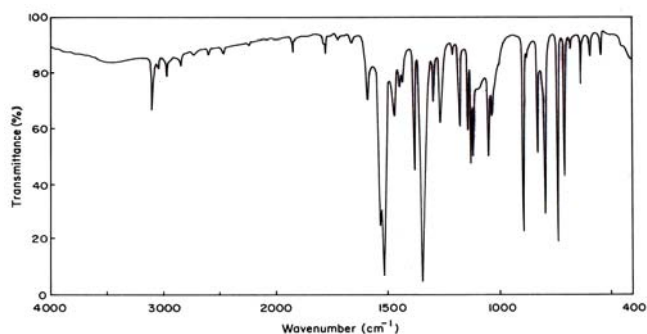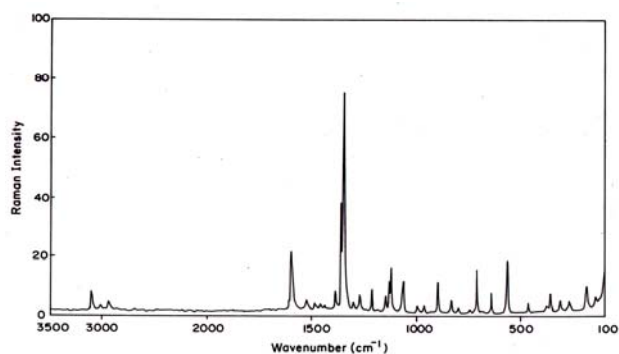
Fig. 2 FT-IR spectrum of 2-bromo-4-nitrotoluene

Fig. 3 FT-Raman spectrum of 2-bromo-4-nitrotoluene

C. C – H Vibrations

Aromatic compounds commonly exhibit multiple weak bands in the region 3100–3000 cm^{-1} due to aromatic C–H stretching vibration [21]. Since the BNT is a trisubstituted aromatic system, it has two adjacent and one isolates C–H moieties. Accordingly, in the present study, C_3–H_{12}, C_5–H_{16} and C_6–H_{17} stretching vibrations are observed at 3108, 3083 and 3042 cm^{-1}, respectively. The theoretically computed values at 3405, 3395 and 3345 cm^{-1} in HF/6-311++G(d,p) and 3232, 3225 and 3180 cm^{-1} in B3LYP/6-311++G(d,p) methods are assigned to C–H stretching vibrations.

The C–H in-plane and out-of-plane bending vibrations generally lie in the regions 1300-1000 cm^{-1} and 1000-675 cm^{-1} [22, 23], respectively. In accordance with above literature data in our present study, the band observed at 1299 and 1211 cm^{-1} in FT-IR spectrum and 1214 cm^{-1} in FT-Raman are assigned to C–H in-plane bending vibrations. The C–H in-plane bending vibrations of the present compound are calculated at 1397 and 1333 cm^{-1} in HF/6-31++G (d,p) and 1330 and 1227 cm^{-1} in B3LYP/6-311++G(d,p) methods are assigned to C–H in-plan bending vibrations.

The bands observed at 1119, 891 cm^{-1} in the FT-IR spectrum and 892, 701 cm^{-1} in the FT-Raman are assigned to C–H out-of-plane bending vibrations for BNT. The theoretically computed values at 1159, 1032 and 816 cm^{-1} in HF/6-311++G(d,p) and 1120, 918 and 725 cm^{-1} in B3LYP/6-311++G(d,p) methods are assigned to C–H out-of-plan bending vibrations.

D. NO$_2$ Vibrations

The aromatic nitro compound have strong absorption due to the asymmetric and symmetric vibrations of the NO$_2$ group at 1570 – 1480 cm^{-1} and 1370 – 1320 cm^{-1} [24, 25], respectively.

The bands appeared at 1267 cm^{-1} in FT-IR and 1549, 1270 cm^{-1} in FT-Raman spectra are assigned to NO$_2$ symmetric and asymmetric stretching vibrations. The bands observed at 634 cm^{-1} in FT-IR spectrum and 638 cm^{-1} in FT-Raman spectrum assigned to NO$_2$ scissoring vibration. The NO$_2$ rocking and wagging modes of the present compound are calculated at 480, 439 cm^{-1} in HF and 742, 698 cm^{-1} in B3LYP methods. The NO$_2$ twisting vibration is observed at 174 cm^{-1} in FT-Raman spectrum. According to the Literatures [26, 27], all these vibrations are found to be within their characteristic region.

E. CH$_3$ Vibrations

The title molecule under consideration possesses a CH$_3$ group in the side substituted chain. For the assignments of CH$_3$ group frequencies one can expect the nine fundamentals can be associated to each CH$_3$ group. The vibrations are CH$_3$ss (symmetric stretching), CH$_3$ ips (in-plane stretching). CH$_3$ipb (in-plane bending), CH$_3$sb (symmetric bending), CH$_3$ipr (in-plane rocking), CH$_3$opr (out-of-plane rocking), tCH$_3$(twist), CH$_3$ops(out-of-plane stretching), CH$_3$opb (out-of-plane bending) vibrations, respectively.

The CH methyl group stretching vibrations are highly localized and generally observed in the range 3000-2800 cm^{-1} [28]. In the present investigation, the bands observed at 2966 cm^{-1} in FT-IR spectrum and 3060, 2926 cm^{-1} in FT-Raman spectrum assigned to CH$_3$ stretching vibrations. The bands identified at 3263, 3243 and 3183 cm^{-1} in HF/6-311++G(d,p) and 3118, 3086, and 3034 cm^{-1} in B3LYP/6-311++G(d,p) method are assigned to CH$_3$ stretching vibrations. For BNT, the values observed at 1471 and 1469 cm^{-1} FT-IR spectrum are assigned to in-plane and out-of-plane bending vibrations, respectively.

The computed values are 1152, 1016 cm^{-1} by HF/6-311++G(d,p) and 1094, 981 cm^{-1} by B3LYP/6-311++G(d,p) are assigned to CH$_3$ in-plane rock and out-of-plane rock of BNT molecule. The computed values at 43 cm^{-1} and 44 cm^{-1} are assigned to CH$_3$ twisting vibrations by HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) methods, respectively.

F. C–Br Vibrations

The assignments of C–Br vibrations have been made by comparison with halogen substituted benzene derivatives. The stretching vibrations of C–X group (X – Br, Cl, F) lies in the frequency range 480-800 cm^{-1}. Bromine compounds absorb strongly in the region 650-450 cm^{-1} due to the C–Br stretching vibrations [29].

In the present work, FT-Raman spectrum observed at 457 cm^{-1} assigned to C–Br stretching vibration. The theoretically computed values at 516 cm^{-1} in HF/6-

311++G(d,p) and 518 cm⁻¹ in B3LYP/6-311++G(d,p) methods are assigned to C–Br stretching vibrations.

The C–Br in-plane bending vibrations of the present compound are calculated at 457 cm⁻¹ HF/6-311++G(d,p) and 425 cm⁻¹ in B3LYP/6-311++G(d,p) are assigned to C–Br in-plane bending vibrations. The computed values at 320 cm⁻¹ and 294 cm⁻¹ are assigned to C–Br out-of-plane bending vibrations by both HF/6-311++G(d,p) and DFT/6-311++G(d,p) methods, respectively. These assignments are in line with the Literature [30].

G. C–N Vibrations

C–N stretching vibrations are a difficult task, since the mixing of vibrations is possible in this region. Silverstein *et al* [31] assigned the C–N stretching absorption in the region 1388 – 1266 cm⁻¹. In benzotrizole, the C–N stretching bands are found to be present at 1307 and 1387 cm⁻¹. Shanmugam *et al* [32], reported C–N stretching frequency observed at 1368 cm⁻¹. The same stretching vibration has predicated at 1335 cm⁻¹ in 2,4-dinitro phenyl hydrogen [33]. Mani *et al* [34], assigned C–N stretching absorption at 1169 cm⁻¹ in FT-IR and 1120 cm⁻¹ in FT-Raman.

The C–N stretching vibrations of the present compound are calculated at 930 cm⁻¹ in HF/6-311++G(d,p) and 840 cm⁻¹ in B3LYP/6-311++G(d,p) methods are assigned to C–N stretching vibrations. According to the Literature [35], C–N stretching vibrations are found to be well within their characteristic regions. The C–N in-plane bending vibrations of the present compound are computed at 593 cm⁻¹ in HF and 548 cm⁻¹ in B3LYP method are assigned to C–N in-plane bending vibrations. The C–N out-of-plane bending vibration is observed at 310 cm⁻¹ in FT-Raman spectrum.

H. C–C Vibrations

The ring C–C and C=C stretching vibrations [36] known as semicircular stretching usually occur in the region 1380–1280 cm⁻¹ and 1625–1430 cm⁻¹. In our present investigation C–C stretching vibrations of BNT are observed at 1594, 1589, 1382, 1348, 1143 and 1289 cm⁻¹ in FT-IR spectrum and 1599 and 1130 cm⁻¹ in FT-Raman spectrum. In our present investigation, the FT-IR bands observed at 884 cm⁻¹ in FT-IR spectrum and 717 cm⁻¹ in FT-Raman spectrum are assigned to C–C in-plane bending vibrations. The values calculated at 990, 874 and 169 cm⁻¹ in HF and 893, 808 and 148 cm⁻¹ in B3LYP methods are assigned to C–C in-plane bending vibrations. The C–C out-of-plane bending is observed at 258 cm⁻¹ in FT-Raman spectrum. These assignments are in good agreement with the Literatures [37, 38].

I. Other Molecular Properties

1) Mulliken Population Analysis:

The charge distribution calculated by the Mulliken method [39,40] for the equilibrium geometry of BNT is given in Table V. The charge distribution on the molecule has an important influence on the vibration spectra. From the result it is clear that the substitution of CH₃ atoms in the aromatic ring leads to decrease of electron density on C₇ atom. The

atomic charges in the CH₃ group are almost identical. The atomic charge obtained from HF/6-311++G(d,p) basis set shows that C1 atom is more acidic due to more positive charge. Also the substitution of NO₂ charge changes are presented in Table V.

TABLE V THE CHARGE DISTRIBUTION CALCULATED BY THE MULLIKEN METHOD FOR BNT

S. No.	Atoms	Atomic charges	
		HF/6-311++G(d,p)	B3LYP/6-311++G(d,p)
1.	C₁	0.374406	0.332400
2.	C₂	0.284509	0.215969
3.	C₃	-0.371107	-0.250900
4.	C₄	-0.208636	-0.224193
5.	C₅	-0.196369	-0.152815
6.	C₆	-0.496566	-0.3484400
7.	C₇	-0.816871	-0.391337
8.	H₈	0.176138	0.179240
9.	H₉	0.176256	0.176736
10.	H₁₀	0.176913	0.177215
11.	Br₁₁	-0.255064	-0.156213
12.	H₁₂	0.343445	0.277803
13.	N₁₃	-0.102671	-0.181944
14.	O₁₄	-0.058740	-0.007148
15.	O₁₅	-0.055103	-0.003797
16.	H₁₆	0.294264	0.240251
17.	H₁₇	0.201146	0.177133

2) HOMO-LUMO Analysis:

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are the main orbital part that takes part in chemical stability [41]. The HOMO represents the ability to donate an electron, LUMO as an electron acceptor, represents the ability to obtain an electron. The HOMO and LUMO energies calculated by B3LYP/6-311++G(d,p) method are as shown in Fig. 4 The electronic transition absorption Corresponds to the transition from the ground to the first excited state and mainly described by an electron excitation from the HOMO to LUMO. The HOMO-LUMO transition implies an electron density transfer to ring from nitro group moreover, the orbital significantly overlaps in their position for BNT. The calculated self-consistent field (SCF) energy of BNT is -3049.73603912 a.u. According to B3LYP/6-311++G(d,p) calculation, the energy band gap (ΔE) (translation form HUMO to LUMO) of the molecule is about -0.17172 a.u.
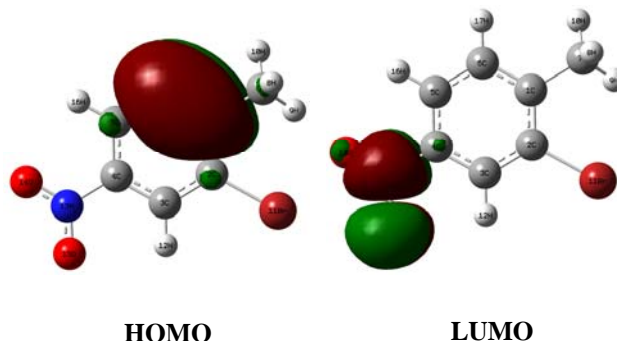

HOMO   **LUMO**

Fig. 4 HOMO-LUMO structure of 2-bromo-4-nitrotoluene

3) Natural Bond Orbital Analysis:

The natural bonding orbital calculation [42] was performed at the B3LYP level in order to investigate the electronic structure of the optimized geometry correspond to the formation of N–O .... H hydrogen bond. The hyperconjugative interaction energy was deduced from the second-order perturbation approach [43].

$$E^{(2)} = -n \frac{\langle \sigma|F|\sigma \rangle^2}{\varepsilon_{\sigma*} - \varepsilon_{\sigma*}} = -n\sigma \frac{F_{ij}^2}{\Delta E} \qquad (13)$$

where $\langle \sigma|F|\sigma \rangle^2$, or F_{ij}^2 is the Fock matrix element between the i and j NBO orbital, ε_{σ} and $\varepsilon_{\sigma*}$ are the energies of σ and $\sigma*$ NBO's, and n_{σ} is the population of the donor σ orbital.

Natural bond orbital analysis provides an efficient method for studying intra and intermolecular bonding and interaction among bonds, and also provides a convenient basis for investigating charge-transfer or conjugative interaction in molecular systems. Some electron donor orbital, acceptor orbital and the interacting stabilization energy resulted from the second-order micro-disturbance theory are reported [44]. The larger the $E^{(2)}$ value is, the more intensive the interaction between electron donor and electron acceptors will be, i.e. the more donating tendency from electron donors to electron acceptors and the greater the extent of conjugation of the whole system.

NBO analysis has been performed on the molecular BNT to identify and explain the formation of the strong intramolecular hydrogen bonding between toluene group and carbon in the molecule. The corresponding results have been tabulated in Tables VI and VII. The importance of hyperconjugative interaction and electron density transfer (EDT) from lone electron pairs of the Y atom to the (X–H) antibonding orbital in the X–H ...Y system have been reported by Reed et al [45].

TABLE VI NATURAL BOND ORBITAL ANALYSIS OF BNT AT B3LYP/6-311++G(D,P) LEVEL OF THEORY

Bond (A–B)	ED/ Energy (a.u)	ED_A (%)	ED_B (%)	NBO	S (%)	P (%)
BD(C_4–N_{13})	1.98801	37.26	62.74	0.61040(SP$^{3.05}$)C+ 0.7921(SP$^{1.82}$)N	24.65 35.41	75.22 64.55
BD(C7–H18)	1.97408	60.83	39.17	0.7799(SP$^{3.17}$)C+ 0.6259(SP$^{0.00}$)H	23.95 99.97	75.99 0.03
BD(C_7–H_9)	1.98482	61.09	8.91	0.7816(SP$^{3.04}$)C+ 0.6238(SP$^{0.00}$)H	24.75 99.96	75.19 0.04
BD(C_7–H_{10})	1.98703	60.39	39.61	0.7771(SP$^{3.16}$)C+ 0.6294(SP$^{0.00}$)H	24.03 94.97	75.91 0.03
BD(N_{13}–O_{14})	1.99554	48.80	51.20	0.6985(SP$^{2.10}$)N+ 0.7156(SP$^{2.75}$)O	32.21 26.61	67.66 73.24
BD(N_{13}–O_{15})	1.99563	48.80	511.20	0.6986(SP$^{2.10}$)N+ 0.7155(SP$^{2.75}$)O	24.65 35.41	75.22 64.55
BD*(C_4–N_{13})	0.10946	62.71	37.26	0.7921(SP$^{3.05}$)C– 0.6104(SP$^{1.82}$)N	24.65 35.41	75.22 64.55
BD*(C_7–H_8)	0.00723	39.17	60.83	0.6259(SP$^{3.17}$)C– 0.7799(SP$^{0.00}$)H	23.95 99.97	75.99 0.03
BD*(C_7–H_9)	0.00743	38.91	61.09	0.6238(SP$^{3.04}$)C– 0.7816(SP$^{0.00}$)H	24.75 99.96	75.19 0.04
BD*(C_7–H_{10})	0.00579	39.61	60.39	0.6294(SP$^{3.16}$)C– 0.7771(SP$^{0.00}$)H	24.03 99.97	75.91 0.03
BD*(N_{13}–O_{14})	0.05345	51.20	48.80	0.7156(SP$^{2.10}$)N– 0.6985(SP$^{2.75}$)O	32.21 26.61	67.66 73.24
BD*(N_{13}–O_{15})	0.5365	51.20	48.80	0.7155(SP$^{2.10}$)N– 0.6986(SP$^{2.7}$)O	32.19 26.61	67.69 73.24

TABLE VII SECOND ORDER PERTURBATION THEORY ANALYSIS OF FOCK MATRIX IN NBO BASIS FOR BNT AT B3LYP/6-311++G(D,P) LEVEL OF THEORY

Donor NBO(i)	Acceptor NBO(j)	$^a E^{(2)}$ (KCal/mol)	E(i)– E(j) (a.u)	F(i,j) (a.u)
BD(C_4–N_{13})	BD*(C_2–C_3)	1.38	1.36	0.039
BD(C_7–H_{10})	BD*(C_1–C_2)	3.19	1.07	0.052
BD(C_7–H_9)	BD*(C_1–C_6)	3.23	1.08	0.053
BD(C_7–H_8)	BD*(C_1–C_0)	4.14	0.54	0.046
BD(N_{13}–O_{15})	BD*(C_4–C_5)	4.04	0.47	0.043
LP(O_{14})	BD*(C_4–N_{13})	4.23	1.06	0.061
LP(O_{14})	BD*(C_4–N_{13})	14.738	0.56	0.081
LP(O_{14})	BD*(N_{13}–O_{15})	19.629	0.77	0.0111
LP(O_{14})	BD*(N_{13}–O_{15})	172.0911	0.15	0.146
LP(O_{15})	BD*(C_4–N_{13})	14.61	0.56	0.081
LP(O_{15})	BD*(N_{13}–O_{14})	19.69	0.77	0.112

Table VI shows calculated natural orbital occupancy (number of electron (or) "natural population" of the orbital). It is noted that the maximum occupancies 1.9956, 1.9955 and 1.9880 are obtained for BD(N13–O15), BD(N13–O14), and BD(C4–N13), respectively, and corresponding sp composition is also tabulated. Therefore, the results suggest

that the N13–O15, N13–O14, and C4–N13 bond lengths of these compounds are essentially controlled by the p

character of these hybrids orbital's and also by the nature of the N13–O15, N13–O14 and C4–N13 bonds.

4) Perturbation Theory Analysis:

Delocalization of the electron density between occupancies Lewis type (bond (or) lone pair) NBO orbital and formally unoccupied (anti-bond (or) Rydberg) non-Lewis NBO orbital corresponding to a stabilizing donor-acceptor interaction have been performed at B3LYP/6-311++G(d,p) level. The energy of these interactions can be estimated by the second order perturbation theory [46]. Table VII lists the calculated second-order interaction energies ($E^{(2)}$) between the donor-acceptor orbital in BNT.

The most important interaction energies, related to the resonance in the Aromatic ring, are electron donating from the LP(O14), LP(O15) to the anti-bonding acceptor BD*(N13–O15), BD*(N13–O14) and BD*(N13–O15) orbital. These energies are 172.09, 19.69 and 19.62 (Kcal/mol) respectively. These interactions clearly indicate the increase of π-electron delocalization occurs due to substitution of the molecule.

5) Thermodynamic Properties:

The total energy of a molecule is the sum of translational, rotational, vibrational and electronic energies. ie, E = Et + Er + Ev + Ee. The statistical thermo chemical analysis of BNT is carried out considering the molecule to be at room temperature of 298.15 K and one atmospheric pressure. The thermodynamic parameters, like rotational constant, zero point vibrational energy (ZPVE) of the molecule by DFT method (B3LYP level) were presented in Table VIII for BNT. The title molecule is considered as an asymmetric top having rotational symmetry Number 1 and the total thermal energy has been arrived as the sum of electronic, translational, rotational and vibrational energies. The variations in the zero point vibrational energy seem to be insignificant. The thermodynamic functions are determined from spectroscopic data by statistical methods. The thermodynamic quantities such as entropy S_{vib}, heat capacity at constant pressure (C_p), enthalpy (H−E)/T, Gibb's free energy (G−E)/T and internal thermal energy(E) for various range (100K-700K) of temperatures are determined using the vibrational wave numbers and these results are presented in the Table VIII. The correlation equations between these thermodynamic properties and temperatures were fitted by parabolic formula. All the thermodynamic data provide helpful information for the further study on the title compound. From the Table VIII it can be observed that the thermodynamic parameters are increasing with temperature ranging from 100 K to 700 K, (Fig. 5) due to the fact that the vibrational intensities of molecule with temperature.

TABLE VIII THERMODYNAMIC PROPERTIES AT DIFFERENT TEMPERATURES AT THE B3LYP/6-311+G(D,P) LEVEL FOR 2-BROMO-4-NITROTOLUENE

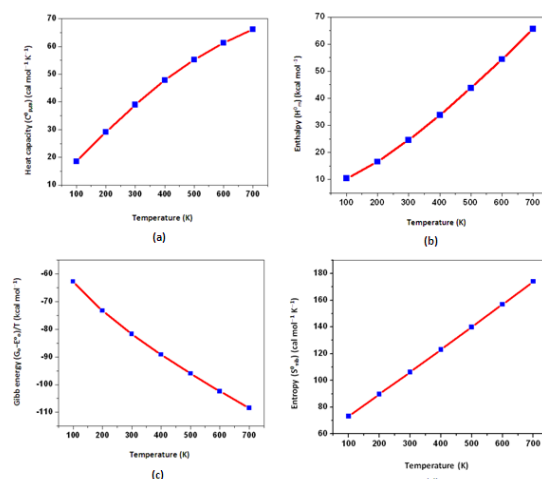| T (K)	$C^0_{p,m}$ (cal mol^{-1} K^{-1})	H^0_m (kcal mol^{-1})	G^0_m (kcal mol^{-1})	S^0_m (kcalmol^{-1}K^{-1})
100	18.5367	10.3661	-62.6878	73.0540
200	29.1655	16.5671	-73.2207	89.7878
300	38.9754	24.6112	-81.6504	106.2617
400	47.8385	33.7952	-89.1238	122.9190
500	55.2731	43.7931	-96.0016	139.7947
600	61.2866	54.4193	-102.4300	156.8494
700	66.1383	65.5500	-108.4820	174.0321

Fig. 5 Correlation graphic representations of BNT
(a) heat capacity and temperature
(b) entropy and temperature
(c) enthalpy and temperature
(d) Gibb energy and temperature

V. CONCLUSIONS

In the present study the FT-IR and FT-Raman spectra of 2-bromo-4-nitrotoluene (BNT) have been recorded. The optimized molecular geometry, vibrational frequencies, Infrared intensities, Raman intensities and thermodynamic parameters in ground state were calculated using *ab initio* Hartree-Fock (HF) and density functional B3LYP methods (DFT) with 6-311++G(d,p) basis set. The observed vibrational frequencies are analysed and compared with theoretically predicted vibrational assignments using PED calculations. The geometries and normal modes of vibration obtained from B3LYP/6-311++G (d, p) methods are reliable compared with the experimental data. The Mulliken charges, the natural bonding orbital (NBO) analysis and thermodynamic functions of the investigated molecule were computed using DFT calculations. The calculated HOMO and LUMO energies show that charge transfer occurs within molecule. The influences of bromine and nitrogen atoms and methyl group on the geometry of benzene and its normal modes of vibrations have also been discussed. Thermodynamic analysis reveals that all the thermodynamic parameters calculated are directly proportional to temperature.

REFERENCES

[1] H.Z., Streicher, P.A. Gabow, A.H. Moss, D. Kono, W.D. Kaehny, Syndromes of toluene sniffing in adults, Ann. Intern. Med. 94(6) (1981) 758 – 762, PMID 7235417.

[2] G. Devathasan, D. Low, P.C. Teoch, S.H. Wan, P.K. Wong, Complications of Chronicglue (toluene) abuse in adolescents, Aust. N.Z. J. Med. 14(1) (1984) 39 – 43, PMID 6087782.

[3] B.S. Furnell, et. al., Vogel's Text Book of Practical Organic Chemistry, 5th ed. Longman/Wiley, New York, 1989.

[4] LG. Wade, Organic Chemistry, 5th ed., Prentice Hall, New Jersey, 2003, p. 871.

[5] P.B. Nagabalasubramanian, S. Periandy, S. Mohan, M. Govindarajan, Spectrochim. Acta A 73 (2009) 277 – 280.

[6] G. Fogarasi, P. Pulay, in: J.R. During (Ed.), Vibrational Spectra and Structure, Vol. 14, Elsevier, Amsterdam, 1985, p. 125 (Chapter 3).

[7] S. Ramalingam, S. Periandy, B. Narayanan, S. Mohan, Spectrochim. Acta A 76 (2010) 84 – 92.

[8] P.B. Nagabalasubramanian, S. Periandy, S. Mohan, Spectrochim. Acta A 77 (2010) 150 – 159.

[9] Gaussian09W Program, Gaussian Inc., Wallingford, CT, 2009.

[10] A.D. Becke, J. Chem. Phys. 98 (1993) 5648 – 5652.

[11] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1998) 785 – 789.

[12] P. Pulary, G. Forgarasi, G. Pongor, J.E. Bogg, A. Vargha, J. Am. Chem. Soc. 105 (1983), 7073 – 7047.

[13] G. Rauhut, P. Pulay, J. Phys. Chem. 99 (1995) 3093 – 3100.

[14] G. Fogarasi, X. Zhou, P.W. Taylor, P. Pulay, J. Am. Chem. Soc. 14 (1992) 8191 – 8201.

[15] T. Sundius, J. Mol Struct. 218 (1990) 321 – 326.

[16] T. Sundius, MOLVIB (v.7.0); Calculation of Harmonic Force Fields and Vibraional Modes of Molecules, QCPE Program No. 807, 2002.

[17] T. Sundius, Vib. Spectrosc, 29 (2002) 89 – 95.

[18] V. Krishnakumar, S. Dheviamalar, Raman Spectrosc. 40 (2009) 411 – 415.

[19] P.L. Soni, H.M. Chawia, Text book of Organic Chemistry, 26th revised ed., Sultan Chand and Sons, New Delhi, 1995.

[20] C. Aruna Giri, M. Arivazhagan, A. Subashini, Spectrochim Acta A 79 (2011) 1747– 1759.

[21] G. Varsanyi, Vols. 1 and 2 Assignments for Vibratonal Spectra of Seven Hundered Benzene Derivatives, Academia Kiado, Budapest, 1973.

[22] V. Krishnakumar, N. Prabavathi, Spectrochim, Acta 71 (2008), 449 – 457.

[23] A. Altun, K. Goluck, M. Kumru, J. Mol. Struct. (Theochem) 155 (2003) 637–639.

[24] V.A. Sholyapochnikov, L.S. Khaihin, O.E. Grikina, C.W. Bock, L.V. Vilkov, J. Mol. Struct. 1994, 326, 1.

[25] J. Clarkson, W.E. Smith, J. Mol. Struct, 2003, 655, 413.

[26] G. Socrates, Intra red and Raman Characteristic Group Frequencies, John Wiley, New York, 2000.

[27] D.N. Sathyanarayana, Vibrational Spectroscopy – Theory and Applications, 2nd ed., New Age International Publishers, New Delhi, 2004.

[28] F.R. Dollish, W.G. Fateley, F.F. Bentely, Characteristic Raman Frequencies on Organic Compounds, Willey, New York, 1997.

[29] J. Arthur, L. Plante, D.H. Stidham, Spectrochim, Acta A 74 (2009) 808 – 818.

[30] M. Karaback, M. Cinar, S. Ermec, M. Kurt, J. Raman Spectro SC. 41 (2010) 98 – 105.

[31] M. Silverstein, G. Clayton Bessaler, C. Morill, Spectrometric identification of orgain compounds, John Willey, New York, 1981.

[32] R. Shan Mugam, D. Sathya Narayana, Spectrochim Acta A 40 (1984) 764.

[33] P. Mani, H. Umamaheswari, B. Dominic Jo Shua, N. Sundaraganesan, J. Mol. Struc. (Therochem), 863 (2008) 44.

[34] N. Sundaraganesan, S. Ayyappan, H. Umamaheswari, B. Dominic Joshua, Spectrochim Acta A 66 (2007) 17.

[35] B. Smith, Infrared Spectral Interpretation, A Systamatic Approach, CRC Press, Washington, DC, 1999.

[36] V. Krishnakumar, R. John Xavier, Indian J. Pure. Appl. Phys. 41 (2003) 95 - 98.

[37] R.L. Pessole, L.D. Shield, I.C. Mcwilliam, Modern Method of Chemical Analysis, Wiley, New York, 1976.

[38] G. Socrates, Infrared and Raman Characteristic Group Frequencies – Tables and Charts, Third ed., Wiley, Chichester, 2001.

[39] D. Arul Dhas, I. Hubert Joe, S.D.D. Roy, T.H. Freeda, Spectrochim. Acta A77 (2010) 36 – 44.

[40] R.S. Mulliken, J. Chem. Phys. 23 (1955) 1833 – 1840.

[41] J.R. During, T.S. Little, T.K. Gounev, J. K. Gardnerjr, J.F. Sullivan, J. Mol. Struct, 375 (1996) 83 – 84.

[42] E.D. Glendening, A.E. Reed, J.E. Carpender, F.W. Wein Hold, NBO version 3.1 TCI, University of Wisconsin, Madison, 1998, 65.

[43] J. Chocholousoua, V. Spirko, P. Hobza, Phys. Chem. Phys. 6(1) (2004) 37 – 41.

[44] J.N. Liv, Z.R. Chem, S.F. Yuan, J. Zheji ang unit, Sci. B 6(2005) 584 – 589.

[45] A.E. Reed, L.A. Curtiss, F. Weinhold, Chem. Rev. 88 (1988) 896 – 926.

[46] L. Hubert Joe, J. Kostoua, C. Ravikumar, M. Amalanathan, S.C. Pinzaru, J. Rama Spectro Sc. 40 (2009) 1033 – 1038.