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Computation and interpretation of vibrational spectra, thermodynamical and HOMO-LUMO analysis of 2-chloro-4-nitroaniline

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Abstract: The FT-IR (4000-400 cm^{-1}) and FT- Raman (4000-100 cm^{-1}) spectra of 2-chloro-4-nitroaniline (2Cl4NA) have been recorded using Bruker IFS 66 V spectrometer. An ab initio HF(HF/6-311G(d,p) and DFT(B3LYP/6-311G(d,p)) calculations have been performed giving energies, optimized structures, harmonic vibrational frequencies,IR intensities and Raman activities. The study is extended to the HOMO - LUMO analysis to calculate the energy gap, ionization potential, electron affinity, global hardness,chemical potential and global electrophilicity and thermodynamic properties of 2Cl4NA . A complete vibrational assignment aided by the theoretical harmonic frequency analysis has been proposed. The calculated HOMO and LUMO energies show the charge transfer occurs in the molecule. The harmonic vibrational frequencies calculated have been compared with experimental FTIR and FT Raman spectra. The observed and the calculated frequencies are found to be in good agreement. The experimental spectra also coincide satisfactorily with those of theoretically constructed simulated spectrograms.

Keywords: FTIR and FT Raman spectra; ab initio and DFT; 2-chloro-4-nitroaniline; vibrational analysis; HOMO-LUMO energy.

1. Introduction

Aromatic amines are very important in chemical industry and in the field of biology . Aniline and substituted anilines are widely used as a starting material in a vast amount of pharmaceutical and many other industrial processes. They have attracted considerable attention over the years (1,2). Nitroaniline is used in the synthesis of dyes, agrochemicals, pharmaceuticals, rubber and plastic additives, photographic antifogging agents and coccidiosis. 2Cl4NA is used in the demonstration of skin-sensitizing power in guinea-pigs (3). It is also used as a nitrogen reduction agent in the study of mutagenicity (4). Vibrational assignments based on FT-IR in the vapour, solution,liquid phases and the Raman spectra in the liquid state were reported for aniline (5). Rai *et al*. performed IR and Raman spectral measurement and DFT calculations of chlorine substituted anilines (6). Ploug-Sorensen *et al* reported the structure O- nitro aniline hydrochloride (7).

S.Azhagiri *et al* have reported the theoretical and experimental studies of vibrational spectra and thermal analysis of 2-nitro aniline and its cation (8). E Kavitha *et al* have studied the molecular structure and HOMO – LUMO studies of 4-nitroaniline (9). Molecular modeling by quantum chemical calculation of 2-chloro-5-nitrotoluene have studied by PM Anbarasan *et al* (10).

Density functional theory (DFT), accepted by the ab initio quantum chemistry community is a cost-effective general procedure for studying physical properties of the molecules. DFT calculations of vibrational spectra of many organic systems (11,12) have shown promising conformity with experimental results. Therefore, in this present investigation ab initio and DFT techniques are employed to study the complete vibrational spectra of the title compound and to identify the various normal modes with greater wave number accuracy. Literature survey reveals that to the best of our knowledge no ab initio HF/DFT frequency calculations of 2Cl4NA have been reported so far. The main objective of this paper is to present, more accurate molecular geometry and molecular vibrational assignment of title molecule. For that purpose quantum chemical computations were carried out on 2Cl4NA using HF/DFT with basis set 6-311G(d,p).The calculated HOMO (Highest occupied molecular orbitals)–LUMO (Lowest unoccupied molecular orbitals) energies show that charge transfer occur in the title molecule. DFT calculations are reported to provide excellent vibrational frequencies of organic compounds, if the calculated frequencies are scaled to compensate for the approximate treatement of electron correlation, for the deficiencies and for the anhormanicity (13-14). Ab initio HF and Density Functional Theory (DFT) calculations have been performed to support our wave number assignments.The theoretically predicted IR and Raman intensities are well in agreement with that of experimental spectral data.

2. Experimental details

The compound under investigation namely 2Cl4NA **(Fig.1)** is purchased from Sigma-Aldrich Chemical Company, U.S.A. which is of spectroscopic grage and hence used for recording the spectra as such without further purification. The FTIR spectra of the compound is recorded in the region 4000 – 400 cm^{-1} in evacuation mode on Bruker IFS 66V spectrophotometer using KBr pellet technique (solid phase) with 4.0 cm^{-1} resolutions. The FT Raman spectra are recorded using 1064 nm line of Nd: YAG laser as excitation wavelength in the region 3500 – 100 cm^{-1} on Bruker IFS 66V spectrometer equipped with FRA 106 FT Raman module accessory. The spectral measurements were carried out at Central Electro Chemical Research Institute(CECRI), Karaikudi (Tamil Nadu), India. The experimental FTIR and FT Raman spectra of 2Cl4NA is presented in the **Figs. 2 & 3.**

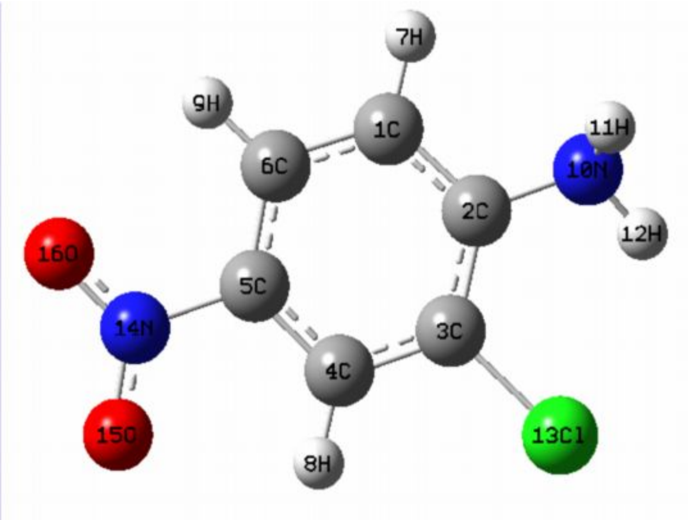
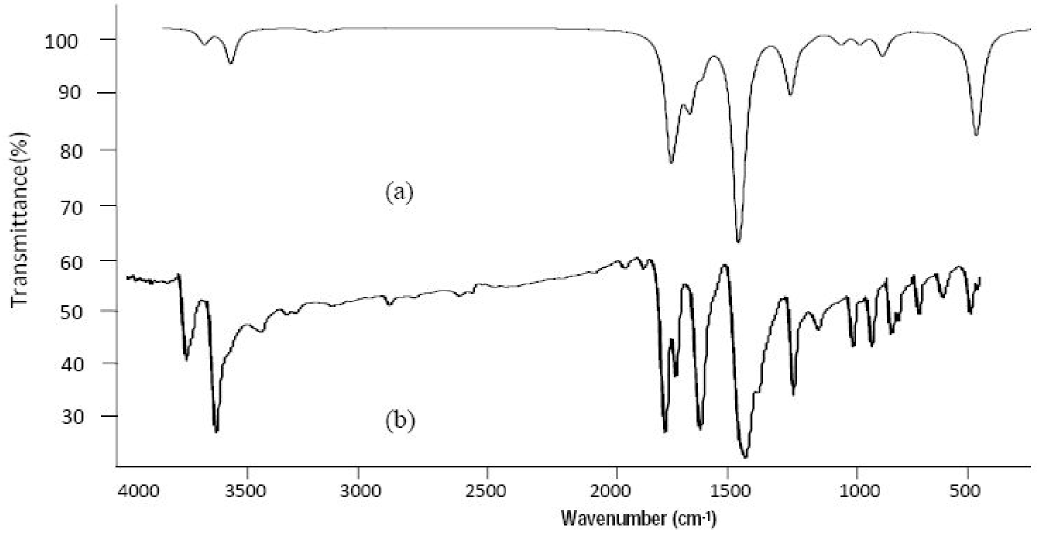


Fig.1. The atom numbering for 2-chloro-4-nitroaniline molecule

B3LYP/6-311G(d,p)



HF/6-311G(d,p)

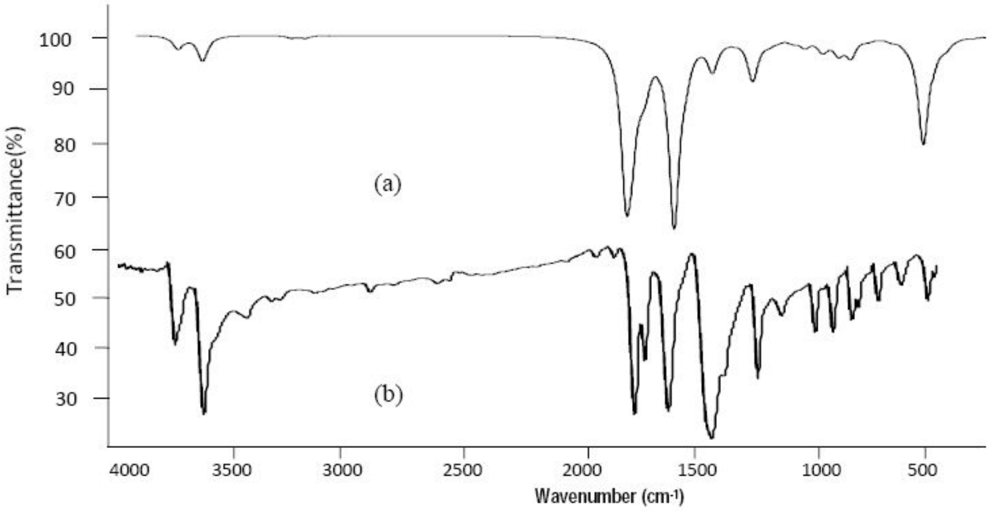


Fig. 2. FTIR Spectra of 2-chloro-4-nitroaniline (a) calculated and (b) observed

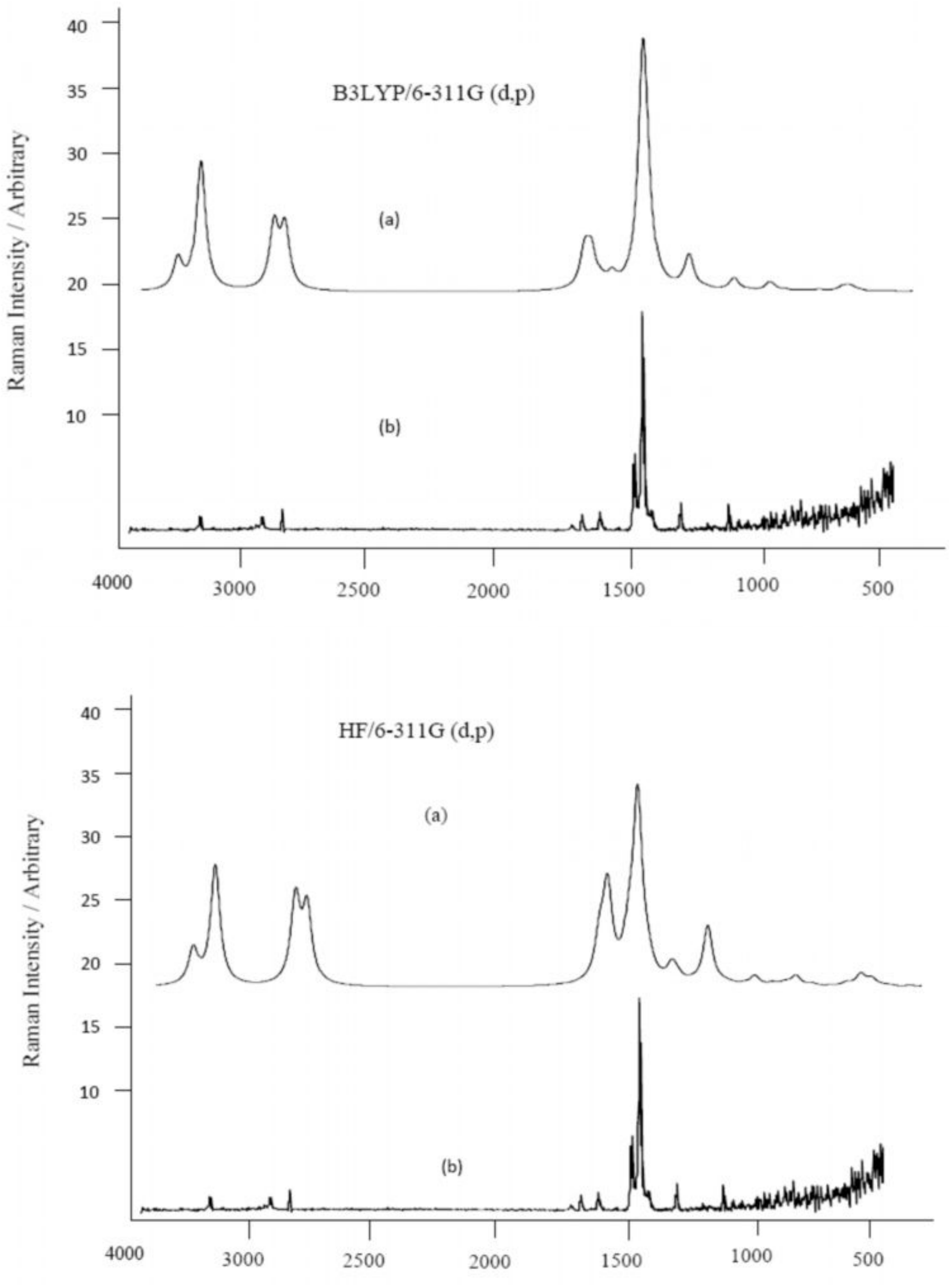


Fig. 3. FT Raman Spectra of 2-chloro-4-nitroaniline (a) calculated and (b) observed

3. Computational details

The entire calculations conducted in the present work were performed at Hartree-Fock (HF) and B3LYP levels included in the Gaussian 03W package (15) program together with the 6-311G basis set function of the density functional theory (DFT) utilizing gradient geometry optimization (16). The geometries were first determined at the Hartree Fock level of theory employing 6-311G (d,p) basis set. All the geometries were then optimized using 6-311G (d,p) basis sets using density functional theory (DFT) (17) employing the Becke's three-parameter hybrid functional (18) combined with Lee-Yang-Parr correlation (19) functional (B3LYP) method. The DFT partitions the electronic energy as $E = E_T+E_V+E_J+E_{XC}$, where E_T, E_V, and E_J are the electronic kinetic energy, the electron nuclear attraction and the electron-electron repulsion terms respectively. The electron correlation is taken into account in DFT via the exchange correlation term E_{XC}, which includes the exchange energy arising from the antisymmetry of the quantum mechanical wavefunction and the dynamic correlation in the motion of individual electrons; it makes DFT dominant over the conventional HF procedure (20). The optimized structural parameters were used in the vibrational frequency calculations at the HF and DFT levels to characterize all stationary points as minima. Then vibrationally averaged nuclear positions of 2Cl4NA is used for harmonic vibrational frequency calculations resulting in IR and Raman frequencies together with intensities and Raman depolarization ratios. The DFT hybrid B3LYP functional also tends to overestimate the fundamental modes in comparison to the other DFT methods; therefore, scaling factors have to be used to obtain considerably better agreement with experimental data. Thus according to the work of Rauhut and Pulay (21), a scaling factor of 0.96 has been uniformly applied to the B3LYP calculated wavenumbers. Similarly, the vibrational modes studies through HF method were scaled by a value of 0.89 (22). Finally, calculated normal mode vibrational frequencies, provide thermodynamic properties by way of statistical mechanics. Zero point vibrational energy was also calculated in the present work. By combining the results of the Gaussview program (23) with symmetry considerations, vibrational frequency assignments were made with high degree of accuracy. 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. For the plots of simulated IR and Raman spectrum, pure Lorentzian band shapes were used with a bandwidth of 10 cm^{-1}. HOMO-LUMO analysis and energy gaps has been computed and other related molecular properties are calculated.

4. Results and Discussion

4.1 Molecular geometry

The optimized structure parameters of 2Cl4NA calculated by ab initio HF and DFT-B3LYP levels with the 6-311G(d,p) basis set are listed in the **Table1.** in accordance with the atom numbering scheme given in **Fig.1**. Our optimized structural parameters are now compared with the exact experimental X-ray study for 2Cl4NA (24) . From the structural data shown in Table 1, it is known that the various bond lengths are greater than the experiment. The over estimation can be explained that the theoretical calculations belong to isolated molecule in gaseous phase and the experimental results belong to similar molecule in solid state.

The changes in the frequency or bond length of the C-H bond on substitution is due to a change in the charge distribution on the carbon atom of the benzene (25,26). The substituents may be either of electron withdrawing type(F,Cl,Br,NO_2,etc.) or electron donating type (CH_3 ,C_2H_5, NH_2, etc). The carbon atoms are bonded to the hydrogen atoms with σ bond in benzene and substitution of a NO_2 group for hydrogen reduces the electron density at the ring carbon atom. The ring carbon atom in substituted benzenes exert a large attraction on the hydrogen atom resulting in an increase in the C-H force constant and a decrease in the corresponding bond length. The reverse holds well on substitution with electron donating group.

Comparing bond angles and lengths of B3LYP with those of HF, as a whole the formers are on higher side than the latter and the HF calculated values correlates well compared with the experimental results. In spite of the differences, calculated geometric parameters represent a good approximation and they are the bases for calculating other parameters, such as vibrational frequencies and thermodynamic properties.

4.2 Vibrational assignments

The vibrational analysis of 2Cl4NA is performed on the basis of the characteristic vibrations of chloro,nitro and amino modes. The molecule under consideration would belongs to the Cs point group. It has 16 atoms, so 42 normal modes of fundamental vibrations. The computed vibrational wavenumbers, their IR and Raman activities corresponding to the different normal modes are used for identifying the vibrational modes unambiguously. The harmonic vibrational frequencies calculated for 2Cl4NA at HF and B3LYP levels using the 6-311G(d,p) basis set along with polarization functions have been summarized in **Table 2.** It can be noted that the calculated results are harmonic frequencies while the observed frequencies contain anharmonic contribution. The latter is generally lower than the former due to anharmonicity. The reproductions of observed fundamental frequencies are more desirable because they are directly observable in a vibrational spectrum. Comparison between the calculated and the observed vibrational spectra helps us to understand the observed spectral features. Inclusion of electron correlation in density functional theory to a certain extend makes the frequency values smaller in comparison with the HF frequency data. Comparison of the frequencies calculated by B3LYP with experimental values reveals the overestimation of the calculated vibrational modes due to neglect of anharmonicity in real system. Inclusion of electron correlation in density functional theory to a certain extent makes the frequency values smaller in comparison with experimental values

For visual comparison, the observed and calculated (simulated) FTIR and FT Raman spectra of 2Cl4NA is presented in a common wavenumber scale in **Figs. 2&3.**

Table 1. Optimized geometrical parameters of 2-chloro-4-nitroaniline, bond length(Å), Interaxial angles(°)

Bond length(Å)	Experimental	HF/6-311G(d,p)	B3LYP/ 6-311G(d,p)
C1-C2	1.420	1.401	1.411
C1-C6	1.337	1.372	1.381
C1-H7	1.100	1.075	1.084
C2-C3	1.337	1.399	1.413
C2-N10	1.266	1.365	1.366
C3-C4	1.337	1.374	1.380
C3-Cl13	1.719	1.746	1.761
C4-C5	1.377	1.380	1.392
C4-H8	1.100	1.071	1.080
C5-C6	1.337	1.384	1.393
C5-N14	1.444	1.453	1.465
C6-H9	1.100	1.071	1.081
N10-H11	1.050	0.993	1.006
N10-H12	1.050	0.993	1.007
N14-O15	1.310	1.188	1.226
N14-O16	1.310	1.188	1.226
Bond angle(°)			
C2-C1-C6	120.0	121.4	121.5
C2-C1-H7	120.0	118.9	118.7
C1-C2-C3	120.0	117.5	117.2
C1-C2-N10	120.0	120.4	121.1
C6-C1-H7	120.0	119.7	119.8
C1-C6-C5	120.0	119.3	119.3
C1-C6-H9	120.0	120.9	121.4
C3-C2-H10	120.0	122.0	121.7
C2-C3-C4	120.0	121.6	121.9
C2-C3-Cl13	118.0	119.7	118.9
C2-N10-H11	120.0	117.1	118.6
C2-N10-H12	120.0	118.1	118.8
C4-C3-Cl13	118.0	118.7	119.1
C3-C4-C5	120.0	119.1	118.9
C3-C4-H8	120.0	120.6	121.2
C5-C4-H8	120.0	120.3	119.8
C4-C5-C6	120.0	121.1	121.1
C4-C5-N14	120.0	119.2	119.1
C6-C5-N14	120.0	119.8	119.8
C5-C6-H9	120.0	119.9	119.3
C5-N14-O15	120.0	117.7	117.8
C5-N14-O16	120.0	117.6	117.6
O11-N10-H12	118.0	115.0	116.5
O15-N14-O16	120.0	124.7	124.6

Table2. Comparision of the observed (FT-IR and FT-Raman) and calculated vibrational frequencies of 2-chloro-4-nitro aniline [harmonic frequency (cm^{-1}) IR intensities(km mol^{-1}), Raman scattering activities (Å amu $^{-1}$),

	Experimental		Calculated				
Vibrational Mode nos.	FT-IR	FT-Raman	HF/6-311G(d,p)	B3LYP/ 6-311G(d,p)	IR Intensity	Raman Intensity	Vibrational Assignment
1			51	54	0.228	0.427	γ C-Cl +ιNO_2
2		108	109	107	0.096	1.478	ωNH_2
3		158	167	166	0.197	1.171	γ NH_2
4		188	175	174	1.752	0.752	lattice vibration
5		262	262	263	2.497	2.170	βC- NH_2
6		302	303	298	121.1.2	2.417	β C-Cl + ωNH_2
7		318	345	313	192.078	7.316	ω NH_2
8		345	351	342	3.185	6.016	νC-C-C
9		358	356	356	6.888	3.162	νC-C-C+ β NH_2
10	406	397	397	400	12.315	0.673	ωNH_2
11		429	440	431	6.314	0.293	βC-C-C
12		458	465	463	3.172	3.284	β C-NH_{2+} βC-C-C
13	516	516	520	519	1.380	0.402	βC-C-C
14	553	536	535	534	2.665	1.897	βC-C-C+βNO_2
15	619	632	627	628	4.581	3.219	βC-C-C+νNO_2
16	660	682	699	686	0.310	1.073	νC-C+νC-Cl
17		696	702	701	48.421	13.693	νC-Cl
18	727	721	751	710	2 4.268	2.298	ν NH_2
19	796	806	809	796	24.037	0.735	γC-H
20	829	806	821	801	9.155	1.063	γC-C
21	874	872	892	873	23.428	22.355	ring breathing
22	916	890	940	892	14.939	0.884	γC-H
23	958	937	976	938	0.744	0.393	γC-H
24		1002	1007	1004	6.128	2.399	βC-H
25	1047	1029	1041	1027	11.7567	1.249	ρNH_2
26	1068	1091	1103	1091	163.291	60.647	βC-C-C
27	1122	1118	110	1124	16.222	3.850	β C-H
28	1172	1141	1185	1228	3.377	0.994	νC-NH_2
29	1252	1275	1247	1292	227.307	91.792	ν C-C+ωNH_2+ β C-H+νC-NO_2
30	1274	1305	1275	1312	217.517	196.997	νsyNO_2+ν C-C+νC-NO_2
31		1319	1388	1316	215.837	211.071	β C-H
32	1392	1384	1436	1394	3.509	1.035	νC-NH_2
33	1438	1467	1477	1465	68.612	21.307	ν C-C
34	1529	1540	1554	1523	160.881	8.079	ν C-C+$\nu_{as}NO_2$
35	1546	1546	1574	1564	14.340	61.387	ν C-C+ δNH_2
36	1552	1552	1612	1569	83.409	3.404	ν C-C+ $\nu_{as}NO_2$
37	1600	1606	1636	1596	299.225	65.697	δ NH_2 + ν C-C
38	3014	3034	3047	3046	8.773	111.787	νC-H
39	3081	3081	3076	3097	2.414	75.002	νC-H
40	3101	3100	3101	3102	7.327	42.854	νC-H
41	3432	3446	3400	3454	96.160	236.575	ν_s NH_2
42	3571	3569	3553	3563	41.204	55.723	ν_{as} NH_2

Abbrevations used τ- torsion; γ- out of plane bending; β- in plane bending; ρ- rocking; δ- scissoring; υ- stretching; υ_{s}- symmetric stretching; υ_{as}- asymmetric stretching; ω- wagging

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C-H Vibrations

Normally, aromatic compounds commonly shows the presence of C-H stretching vibrations in the region 3000–3100 cm^{-1} which is the characteristic region for the ready identification of C-H stretching vibration (27).The 2Cl4NA molecule give rise to three C-H stretching, three C-H in-plane bending vibrations and three C-H out-of-plane bending vibrations. Since 2Cl4NA is a trisubstituted aromatic system it has two adjacent and one isolated C-H moieties. The expected three C-H stretching vibrations correspond to (mode nos. 40-38) stretching modes of C1-H, C4-H and C6-H units. The vibrational (mode nos: 40-38) assigned to aromatic C-H stretching computed by B3LYP/6-311G(d,p) method at 3102, 3097 and 3046 cm^{-1} shows good agreement with recorded FT-IR spectrum at 3101, 3081and 3014cm^{-1} and the FT-Raman spectrum shows peak at 3100, 3081and 3034 cm^{-1} is assigned to C-H stretching vibration.

The aromatic C-H in- plane bending modes of benzene and its derivatives are observed in the region 1300-1000 cm^{-1}. The bands are sharp but are weak to medium intensity. The C-H in-plane bending vibrations computed in the region at 1292,1124 and 1004 cm^{-1} (mode nos: 29,27,24) by B3LYP/6-311G(d,p) method shows good agreement with FT-IR spectral region at 1252 and 1122 cm^{-1} and 1275,1118 and 1002cm^{-1} in FT-Raman spectral region respectively. The C-H out-of-plane deformation modes of benzene (28,29) are expected to occur in the region 1000-600cm^{-1} bending vibration falls in the FT-IR spectrum as a medium bands at 958, 916 and 796 cm-^{1} shows good agreement with theoretically computed B3LYP/6-311G(d,p) method at 938, 892 and 796 cm^{-1} (mode nos: 23, 22 and 19). The same vibrations computed by HF/6-311G (d,p) also shows good agreement with experimental data.

C-Cl vibrations:

The vibrations belonging to the bond between the ring and the halogen atoms are worth to discuss here, since mixing of vibrations are possible due to the lowering of the molecular symmetry and the presence of heavy atoms on the periphery of molecule (30). The assignments of C-Cl stretching and deformation vibration have been made by comparison with halogen substituted benzene derivatives (31). Mooney (32,33) assigned vibrations of the C-X group (X= Cl, Br, I) in the frequency range of 1129-480cm^{-1}. Based on the above literature data, the theoretically computed by B3LYP/ HF 6-311G (d,p) method at 701/702 cm^{-1} (mode no: 17) is assigned to C-Cl stretching vibration and shows good agreement with experimental FT-Raman bands at 696 cm^{-1}. The C-Cl in-plane bending vibration computed by B3LYP/6-311G(d,p) method at 298 cm^{-1} (mode no:6) correlate well with FT-Raman band at 302 cm^{-1}. The C-Cl out-of- plane bending vibration computed by B3LYP/6-311G(d,p) method at 54 cm^{-1} (mode no:1) shows good agreement with HF method.

C-C vibrations

There are six equivalent C-C bonds in benzene and consequently there will be six C-C stretching vibrations. In addition, there are several C-C-C in-plane and out of – plane bending vibrations of the ring carbons. However, due to symmetry of benzene, many modes of vibrations are infrared inactive. In general the C-C stretching vibrations in aromatic compounds give the bands in the region of 1430 to 1650 cm^{-1}(34). The FT-IR band observed at 1600, 1552, 1546, 1529cm^{-1} and 1606, 1552, 1546, 1540cm^{-1} in FT-Raman spectrum are assigned to C-C stretching vibration shows good agreement with theoretically computed B3LYP/ 6-311G (d,p) method in the region at 1596- 1523 cm^{-1} (mode nos: 37-34). The same vibration computed by HF method also shows the same kind of result. The ring breathing mode observed as medium strong band at 874cm^{-1} in FT-IR spectrum and 872cm^{-1} in FT-Raman show good agreement with theoretically computed B3LYP/6-311G(d) method at 873 cm^{-1} (mode no:21). For the in-plane deformation vibration Shimanouchi *et al.* (35) gave the frequency data for different benzene derivatives as a result of normal coordinate analysis. The theoretically calculated C-C-C in plane bending vibration i.e. on viewing the vibration we found that C6-C1-C2 and C3-C4-C5 angle vary in the opposite direction, coupled with C2-NH_2 and C5-NO_2 stretching modes. The pairs C2-C5 and C3-C6 of the phenyl ring move radially such that when C2 and C5 come closer, C3 and C6 move away. In general, the C-C-C out- of plane and in- plane - bending vibrational wavenumber observed in FT-IR spectrum and FT-Raman spectrum shows good agreement with theoretically computed wavenumber.

NO_2 Vibration:

The deformation vibration of NO_2 group (rocking) contributes to several modes in the low frequency range. The frequency computed theoretically by B3LYP/6-311G(d,p) method at 54 cm^{-1} (mode no: 1) is assigned to torsion mode of NO_2 group. In all nitro substituted benzene, two strong bands are observed near 1530 and 1340 cm^{-1} which are the asymmetric and symmetric stretching vibrations of NO_2 groups and provide an unmistakable identity for the existence of NO_2 group in the molecule (36, 37). Based on the above literature data the very strong band observed at 1305 cm^{-1} in FT-Raman spectrum is assigned to NO_2 symmetric stretching vibration. The theoretically computed B3LYP/6-311G(d,p) at 1312cm^{-1} (mode no: 30) is assigned to NO_2 symmetric stretching vibration. The NO_2 asymmetric stretching vibration computed by B3LYP/6-311G(d,p) method 1523 cm^{-1} also coincides exactly with very strong FT-IR band at 1529 $cm^{-1}$and 1540cm^{-1} in FT-Raman.

NH_2 Vibration

In all the primary aromatic amines, the N-H stretching frequencies occur in the region 3300-3500 cm^{-1}.The fundamental modes involving the amino group are stretching and bending of NH bond, torsion and inversion. The title molecule under investigation possess one NH_2 group and hence we expect one symmetric and one asymmetric N-H stretching vibrations. In the IR spectrum of aniline , the asymmetric and symmetric NH_2 stretching vibrations were assigned the bands at 3508 and 3412 cm^{-1} respectively, while in p-fluroaniline (38) the corresponding bands were observed at lower frequencies 3499 and 3414 cm $^{-1}$. The NH_2 stretching vibrations show the characteristic frequency shift caused by halogen substituent. Honda *et al* (38) in their studies of the jet-cooled neutral molecules of aniline and 4-floroaniline demonstrated the F substituent caused a slight decrease of the N-H stretching frequencies. The antisymmetric (ν_{as}) stretching mode appears to be calculated at the higher wavenumber 3563cm^{-1} than the symmetric (ν_s) one 3454 cm^{-1} by B3LYP/6-311G(d,p) method having mode nos. 41,42 are related to to the FT-IR band as strong and very strong bands at 3571,3432 cm^{-1}. The counter part of the FT-Raman spectrum shows 3569, 3446cm^{-1}.

The NH_2 group of molecule under investigating also has scissoring (δ NH_2) rocking (ρNH_2) and wagging (ωNH_2) modes. The scissoring mode of the NH_2 group appears in the region1615-1650 cm^{-1} in benzene derivatives with NH_2 substituents. JP Abraham *et al* has assigned IR band at 1608 cm^{-1} and the Raman band at 1620 cm^{-1} in their compound p-amino acetanilide (39). The computed NH_2 scissoring vibration by B3LYP/6-311G(d,p) method at 1596cm^{-1}(mode no.37).The NH_2 rocking mode predicted at 1027 cm^{-1} in the theoretical value is good agreement with 1029 cm^{-1} band at FT-Raman. The NH_2 wagging mode computed by theoretical method B3LYP/6-311G(d,p) to be at 400 cm^{-1} shows good agreement with recorded FT-IR 406 and FT-Raman 397cm^{-1}.

5. Other molecular properties

5.1 HOMO LUMO analysis

Many organic molecules that contain conjugated π electrons are characterized as hyperpolarizabilities and were analysed by means of vibrational spectroscopy(40,41). In most of the cases , even in the absence of inversion symmetry , the strongest band in the Raman spectrum are weak in the IR spectrum and vice -versa. The π electron cloud moment from the donor to acceptor can make the molecule highly polarized through the single –double path when it changes from the ground state to the first excited state. The analysis of wave function indicates that the electron absorption corresponds to the transition from the ground to the first excited state and is mainly described by one electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied orbital (LUMO). The LUMO: of π nature (ie. benzene ring) is delocalized over the whole C-C bond. By contrast the HOMO is located over NH_2 atom, consequently the HOMO $\longrightarrow$ LUMO transtition implies an electron density transfer to aromatic part and NO_2 of π conjugated system from NH_2 group. The atomic orbital compositions of the frontier molecule orbital are sketched in **fig. 4.**

HOMO energy = −0.24406 a.u.
LUMO energy = −0.08751 a.u.
HOMO–LUMO energy gap = 0.15655a.u.
The calculated self-consistent field (SCF) energy of 2-chloro-4-nitroaniline is -951.86302067a.u. Moreover, the lowering in the HOMO and LUMO energy gap explains the eventual charge transfer interactions that take place within the molecule.

5.2 HOMO-LUMO energy gap and related molecular properties

The HOMO, LUMO and HOMO-LUMO energy gap of 2Cl4NA in the HF and DFT level in 6-311G(d,p) basis set has been calculated. The HOMO–LUMO energy gap reveals that the energy gap reflects the chemical activity of the molecule. Associated within the framework of SCF MO theory the ionization energy and electron affinity can be expressed through HOMO and LUMO orbital energies as I = $-E_{HOMO}$ and A= $-E_{LUMO}$.The hardness corresponds to the gap between the HOMO and LUMO orbital energies. The larger the HOMO-LUMO energy gap the harder the molecule (42). The global hardness, $\eta = 1/2(E_{LUMO} - E_{HOMO})$. The hardness has been associated with the stability of chemical system. The electron affinity can be used in combination with ionization energy to give electronic chemical potential, $\mu = 1/2(E_{HOMO} + E_{LUMO})$. The global electrophilicity index, $\omega = \mu^2/2\eta$ is also calculated and listed in **Table 3.**

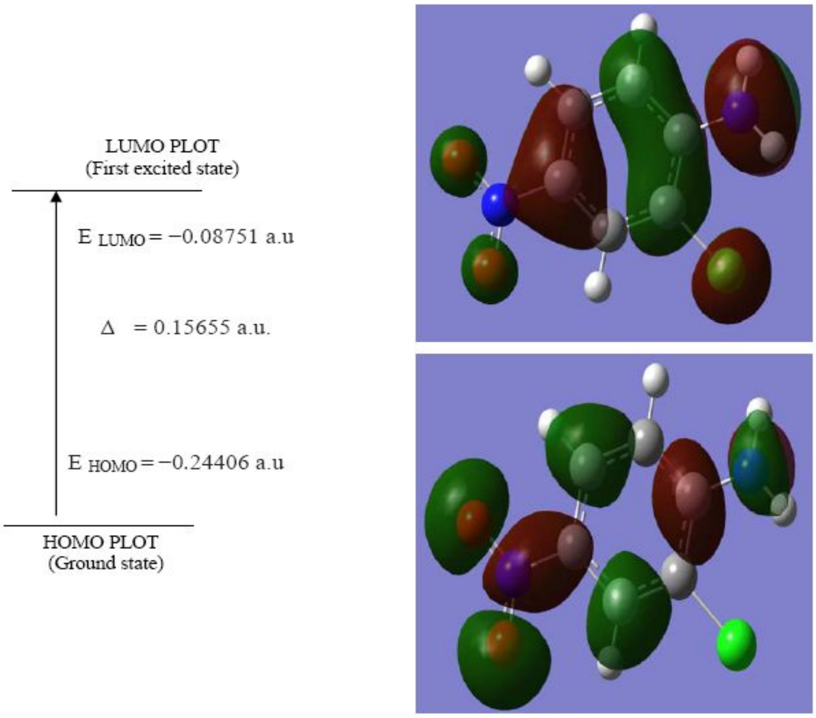

Fig. 4. Atomic orbital composition of the frontier molecule for 2-chloro-4nitroaniline

Table 3.
Comparison of HOMO, LUMO, energy gaps (*e*HOMO –LUMO), and related molecular properties of 2-chloro-4-nitroaniline (eV)

Molecular properties	HF/6-311G(d,p)	B3LYP/6-311G(d,p)
ε_{HOMO}	-0.33505	-0.24406
ε_{LUMO}	0.06245	-0.08751
Energy gap	0.3975	0.15655
Ionisation Potential (I)	0.33505	0.24406
Electron affinity(A)	-0.06245	0.08751
Global Hardness (η)	0.19875	0.078275
Chemical potential (μ)	-0.1363	0.165785
Global Electrophilicity (ω)	0.0467361	0.1755643

Table 4.
Theoretically computed energies (a,u), zero point vibrational energies (kcal mol^{-1}), rotational constants (GHz) entropies (cal mol^{-1} k^{-1}) and Dipole moment (D) (Kcal Mol^{-1} Kelvin^{-1}) of 2-chloro-4-nitroaniline

Parameters	HF – 6-311G(d,p)	B3LYP – 6-311G(d,p)
Total energy	-948.2468662	-951.86302067
Zero point energy	74.32440	68.81707
otational constants	1.87501	1.84774
	0.62776	0.61544
	0.47040	0.46173
Entropy		
Total	94.378	96.852
Translational	41.335	41.335
Rotational	30.741	30.794
Vibrational	22.302	24.723
Dipole moment	6.2997	6.5533

5.3 Thermodynamic properties

On the basis of vibrational analysis at B3LYP/ 6-311G(d,p) and HF/6-311G(d,p) levels, several thermodynamic parameters are calculated and are presented in Table 4 . The zero point vibration energy (ZPVE) and the entropy, S_{vib} (T) are calculated to the extent of accuracy and the variations in ZPVE seem to be insignificant. The total energy and the change in the total entropy of 2Cl4NA at room temperature at different methods are only marginal.

6. Conclusion

Based on the ab initio HF calculations at HF/6-311G(d,p) and DFT with B3LYP/6-311G(d,p) levels,complete vibrational properties of 2-chloro-4-nitroaniline have been investigated by FT-IR and FT-Raman spectroscopies. The assignment of fundamental frequencies are confirmed by the qualitative agreement between the calculated and observed frequencies. The experimental FTIR and FT Raman spectra were compared with the theoretical ab initio and DFT calculations of the vibrational spectra of the molecule. The vibrational frequencies made by quantum mechanical calculation of B3LYP method agree satisfactoriliy with FT-IR and FT-Raman experimental results. Assignments of all the fundamental vibrational modes were examined and proposed in this investigation and also the comparision with the literature support the validity of the background theory.The HOMO-LUMO energy gap and other related molecular properties were discussed and reported.

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