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Structural,vibrational spectroscopic investigation and HOMO-LUMO Analysis of substituted toluene

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ABSTRACT
This work deals with themolecular structure and vibrational spectra of 2 - chloro 5 – Nitrotolueneand2 - Iodo 5 – Nitrotoluene(2I5NT) with IR and Raman intensities usingDFT/B3LYP incorporated with the suitable basis set available in Gaussian09 software. We have calculated potential energy distributions (PEDs) for the important assignments. Normal modes assignments of some of the vibrational frequencies of title molecule are in good agreement with the earlier reported experimental frequencies whereas others have been modified. HOMO-LUMO analyses were also performed to analyze the transition profile. The intrinsic electronic properties such as electronegativity, chemical hardness, softness, chemical potential, and electrophilicity index were also calculated.

***Keywords**: IR and Raman spectra, DFT, NCA, NBO.*

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I. INTRODUCTION:

Toluene and substitutedtoluene are very important due to their wide applications in medicine and industry.Toluenehad been used as a coolant for its good heat transfer capabilities in sodium cold traps which was used in nuclear reactor systemloops. Toluene has alsobeen used in the process of removing the cocaine from coca leavesin the production of Coca-Cola syrup [1].Tolueneis a water-insoluble liquid with thetypical smell of paint thinners. It is mono-substituted benzenederivative. It is an aromatic hydrocarbon that is widely used as anindustrial feedstock. Toluene is also capable of dissolving a numberof notable inorganic chemicals such as sulfur. It isused as a solvent to create a solution of carbon nanotubes. Toluenecan be used to break open red blood cells in order to extractshemoglobin in biochemistry experiments [2].There is no theoretical work seems available on the vibrational spectra (IR and Raman) of title molecules. However, Krishnakumar and co-workers have reported the assignment dealing withspectroscopic study of closely similar molecules of title molecules[1, 2]. They reported vibrational assignment of2–bromo 5–Nitrotoluene (BNT), 2– floro 5–Nitrotoluene (FNT), 2-chloro 4–Nitrotoluene (2Cl4NT)and 4–chloro 2–Nitrotoluene (4Cl2NT) [1, 2]. In their study, the authors used DFT/B3LYP level of theory to calculate molecular structure and vibrational spectra of these moleculeswith IR and Raman intensities.

In our present study, we have made an effort to calculated molecular structure and vibrational spectrawith IR and Raman intensities of titlemolecules using Density Functional Theory (DFT) incorporated with the suitable basis set available in Gaussian09 software. We havealso calculated potential energy distributions (PEDs) for the crucial assignment. Some of the vibrational frequencies of title molecules are in goodagreement with the earlier reported experimental frequencies whereas others have modified.HOMO-LUMO analysis is also performed to analyze the transition profile of 2I5NT and 2Cl5NT.

II. COMPUTATIONAL DETAILS:

The bond lengths, bond angles and vibrational frequencies with the IR intensities and Raman scattering activities in 2I5NT and 2Cl5NT molecule was calculated atDFT/B3LYP level with the standard DGDZVP basis set available in the Gaussian09program [3].The potential energy distributions (PEDs) have also calculated to make a conspicuousassignment as animation available in GaussView is not a guarantee for correct normal modeassignment. For the subsequent normal coordinate analysis (NCA), the force fields obtainedin the Cartesian coordinates and dipole derivatives with respect to atomic displacements wereextracted from the archive section of the Gaussian 09 output and transformed to a suitablydefined set of internal coordinates which by means of a modified version of the MOLVIBprogram [4, 5]. The Raman activity obtained by Gaussian09 was converted into Raman intensity using empirical relation of Ramanscattering theory [6,7].

NBO analysis gives information about the interaction between both the filled and virtual orbitalspaces, it could enhance the analysis ofintra and inter–molecular interactions. The interaction between filled and antibondingorbital's represent the deviation of the molecule from the Lewis structure and can be used asthe measure of delocalization. This noncovalent bonding–antibonding interaction can bequantitatively described in terms of the second order perturbation interaction energyE (2) [8–11].This energy represents the estimate of the off–diagonal NBO Fock Matrix elements. It can be deduced from the second–order perturbation approach [12]

$$E^{(2)} = \Delta E_{ij} = q_i \frac{F_{ij}^2}{\varepsilon_j - \varepsilon_i}$$

Where $q_i$is the ithdonor orbital occupancy, ε_i and ε_j are the diagonal elements (orbital energies) and F_{ij} is the off diagonal NBO Fock Matrix element.

III. RESULT AND DISCUSSIONS:

3.1 Molecular structure:

The optimized bond lengths and bond angles in 2I5NTand 2Cl5NT calculated at the B3LYP/ DGTZVP level are collected in Table 1.The optimized molecular structures of title molecules with atomic labeling are shown in **Fig 1**. In our present study for the title molecules, the DFT calculated bond length for the bond C1-C2 is 1.393 and 1.392Å while this bond length for 2Cl4NT and 4Cl2NT was found at 1.391 Å [1]. Therefore, there is a good agreement between present assignment and earlier reported assignment of2Cl4NT and 4Cl2NT molecules [1, 2]. However,Krishnakumarand co-workers reportedthis bond length for BNTalso with a magnitude of 1.392Å[2].The bond length for the C5-C10 bond is calculated at 1.509Å in both the 2I5NT and 2Cl5NT which is longer than ring CC bonds due to conjugation effect. However, this bond length was 1.505Åin 2Cl4NT[1]. The two bond length of bonds N15-O16 and N15-O17 has been optimized at 1.236Å while both of these two bond lengths values were found shorter by 0.048Åin case of4Cl2NTmolecule [1].The bond length between halogen and carbon is optimized at 2.131Å and 1.754Å in 2I5NT and 2Cl5NT respectively.

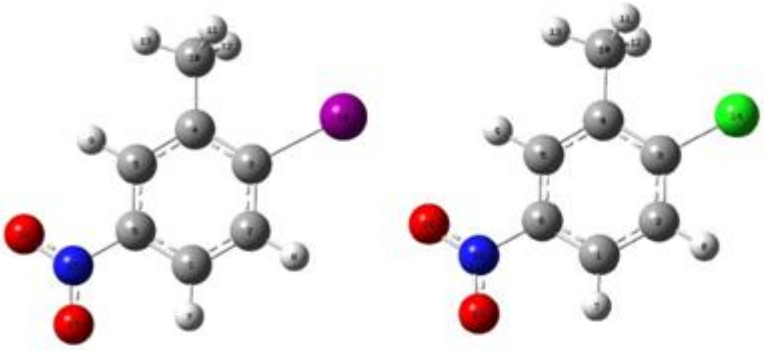

Fig.1

3.2 Vibrational Dynamics:

There are 17 atoms in both the 2I5NTand 2Cl5NT molecules therefore, these possess 45 normal modes. In our present calculation we have done vibrational assignment for 2I5NTand 2Cl5NT which are collected in Tables 2.We have categorized our results into following sections as follows-

3.2.1 CH_3 group vibrations:

As we know that CH_3 group has nine normal modes and in our title molecules one CH_3 group is present therefore, there are nine normal modes correspond to the CH_3 group,which are the symmetrical stretching (CH_3 symmetric stretch) and asymmetrical stretching (CH_3 asymmetric stretch), in-plane stretching modes, and CH_3 symmetric deformation and CH_3 asymmetric deformation modes; in-plane rocking (CH_3ipr), out-of-plane rocking (CH_3opr), and twisting (CH_3twi) modes.

In the earlier works [1, 2], only CH_3 symmetric stretching normal mode could be assigned. However, in our present study the CH_3 symmetric stretching normal mode has been assigned at the scaled frequency 2919cm^{-1} in 2I5NT whereas 2920cm^{-1} in 2Cl5NT.This normal mode is rather a mix mode and contributes to PED in the coupled form of its own out of plane stretching (CH_3ops) in both the molecules.The IR intensity for this mode is weak while Raman intensity is strong. Kumar and Vermareported this mode contribution at 2892cm^{-1} in their study [13].From this it reveals that there is nearly 149cm^{-1} difference between present and earlier reported frequencies for this mode. The two bands assigned at 2984 cm^{-1} and 2938 cm^{-1}were corresponding to CH_3 anti-symmetric stretching normal mode [13]. However,the CH_3 anti-symmetric stretching normal mode could not assigned at any frequency in our present study.Krishnakumarand co-workersreportedCH_3 symmetric stretching normal mode for 2Cl4NT and 4Cl2NTat 2734cm^{-1} and 2861cm^{-1} respectively[1].In addition to this, the authors also predicted this modeat 2970cm^{-1} and 2957cm^{-1} for FNT andBNTmolecules respectively [2].

The band at 3098 cm^{-1}is assigned to the in plane stretching mode of the CH_3 group in2I5NT with weakIR intensity. However, the same mode got shifted to the 3017cm^{-1} in 2Cl5NT.Krishnakumarand co-workers assigned in plane stretching mode of the CH_3 group for 2Cl4NT and 4Cl2NTat 2848 cm^{-1} and 2989 cm^{-1} in their study [1].He also assigned the bands at 3053 cm^{-1} and 3110 cm^{-1} to the in plane stretching mode of the CH_3 group for FNT andBNT respectively [2].The in plane stretching mode of the CH_3 group for FNT,2Cl4NT and 4Cl2NTcontributes to PEDs in pure form while for BNT, this mode contributes to PEDs in coupled form of out of plane stretching mode of the CH_3 group.

The bands at 2966 cm^{-1},2937 cm^{-1} were assigned to the out of plane stretching mode of the CH_3 group for 2Cl4NT and 4Cl2NT respectively [1].In our present study we assigned this modeis at scaled frequency 2989 and 2991cm^{-1}.This mode contributes to PEDs in pure form but this normal mode at 2923 cm^{-1} and 3071 cm^{-1} contributes to PEDs in the coupled form of other mode for FNT andBNT respectively [2].In our study, IR intensity is weak while Raman intensity is strong for this normal mode.The out of plane bending normal mode of the CH_3 group for 2Cl4NT and 4Cl2NT was assigned at 1535 cm^{-1},1516 cm^{-1}respectively while in case of FNT and BNT this mode observed at 1067 cm^{-1} and 1073 cm^{-1} respectively [1,2]. In our present study, we have assigned this normal mode at scaled frequency 1044cm^{-1} in 2I5NT whereas 1045cm^{-1} in case of 2Cl5NT.From this it reveals that our assignment for this mode shows a good agreement with the assignment of FTN and BTN but there is quite difference with the assignment of 2Cl4NT and 4Cl2NT.The assignment of rocking mode is very ambiguous. The out of plane rocking mode of CH_3 group contributes to PEDs at 15620cm^{-1} while in plane rocking normal mode at 1485 cm^{-1} for the 2I5NT molecule in our study. The IR and Raman intensities are weak corresponding to the out of plane rocking mode of CH_3 group while for in plane rocking mode of CH_3 group, the IR intensity is very strong and Raman intensity is weak. V. Krishnakumaret al. assigned out of plane rocking mode of CH_3 group at 1034 cm^{-1} and 1032 cm^{-1} for 2Cl4NT and 4Cl2NT respectively [1] while V. Krishnakumaret al. assigned out of plane rocking mode for FTN and BTN at 1497 and 1509cm^{-1} respectively [2]. From this we can conclude that our assignment has similarities with the assignment of out of plane rocking mode for FTN and BTN but this mode assignment appears wrong for 2Cl4NT and 4Cl2NT.The out of plane rocking mode of CH_3 group contributes to PEDs in coupled form of other modes [1].The inplane rocking normal mode was assigned at 1086 cm^{-1} and 1078 cm^{-1} for 2Cl4NT and 4Cl2NTrespectively [1].

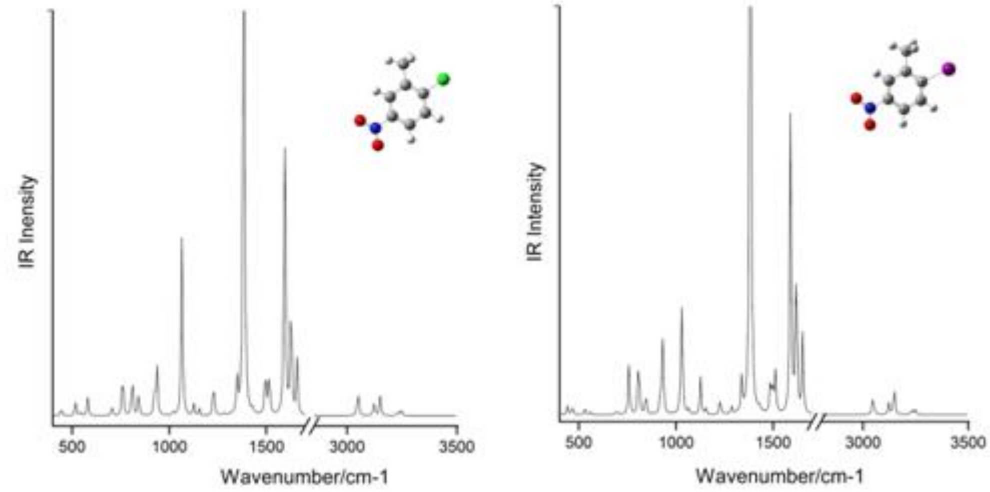

Fig.2

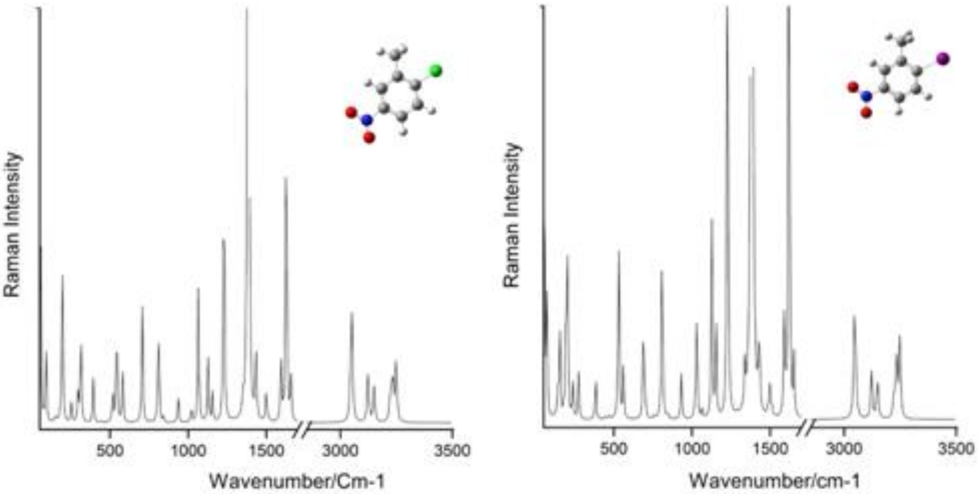

Fig.3

3.2.2 NO_2 group vibrations:

The NO_2 group gives rise to the six internal modes of vibrations as: the symmetric stretching, the anti-symmetric stretching, the symmetric planar deformation or scissoring, the anti-symmetric planar deformation or rocking, the symmetric out-of-plane deformation or wagging (ω) and the anti-symmetric out-of-plane deformation or torsion. The symmetric stretching and anti-symmetric stretching modes are easily assigned.

The NO_2 asymmetric stretchingvibration band range is 1570–1485 cm^{-1} and that of thesymmetric stretching vibration is 1370–1320 cm^{-1} [1]. The NO_2 symmetric stretching has assigned at scaled frequency 1266 and 1359cm^{-1} in our present study for title molecules. The IR and Raman intensities are very strong for this mode. The bands observed at scaled frequencies 1398 cm^{-1} and 1566cm^{-1} have assigned to the NO_2 anti symmetric normal mode. The deformation vibrations(rocking, waggingand twisting) of NO_2 group contribute to several normal modes in the low frequencyregion [2]. Krishnakumaret al. assigned the bands at 739 cm^{-1} and 752 cm^{-1} for 2Cl4NT and 4Cl2NTto the wagging mode of NO_2 group [1].In our present study, we have assigned these normal modeswithin their characteristic frequency region.These modes contribute to the PEDs in the coupled form of other modes. The scissoring normal mode of NO_2 group has been assigned at scaled frequency nearly 793cm^{-1} in both the molecules.This mode is rather a mix mode. The IR and Raman intensities for this mode are weak. The band observed at the frequency 50 cm^{-1} and 21 cm^{-1} were assigned to the NO_2 twisting mode for 2Cl4NT and 4Cl2NT respectively [1].Krishnakumaret al. assigned the bands at 57 cm^{-1} and 188 cm^{-1} to the twisting mode of FNT but the sufficient contribution to PEDs appeared at frequency 57 cm^{-1}[2].In present investigation PED shows that this group twisting is well within their frequency range and are assigned in Table2 and Table3.

3.2.3 Ring and C-I vibrations:

The ring C–C stretching vibrations occur in the region of 1650–1400 cm^{-1}[14]. Many ring normal modes were affected by the substation in aromatic ring.The bands absorbed at 1631,1588, 1510, 1418, 1344, 1194, 1615, 1608, 1475, 1343, 1027,1210 $cm^{-1}$and 320, 260, 527, 380 $cm^{-1}$for FNT and BNT were designated to ring stretching and bending modes respectively [2]. In our study, the overall assignment for ring vibrations is satisfactory in both molecules. The bond which belongs to the ring and halogen atoms are very interesting since mixingof vibrations are possible due to the lowering of the moleculessymmetry and the presence of heavy atoms [2]. The C-I stretching has observed at 188cm^{-1}while C-Cl stretching is calculated at 306cm^{-1}in our present study. The C-I stretching has observed at lower frequency because iodine atom is heavy.

IV. HOMO-LUMO ANALYSIS:

The orbital energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are also calculated to analyze the transition profile of 2I5NT and 2Cl5NT. Highest occupied molecular orbital and lowest unoccupied molecular orbital are very important parameters for quantum chemistry. This is also used by the frontier electron density for predicting the most reactive position in -electron systems and also explains several types of reaction in conjugated system. The conjugated molecules are characterized by a small highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) separation, which is the result of a significant degree of intermolecular charge transfer from the endcapping electron-donating groups to the efficient electron-acceptor groups through conjugated path. Both the highest occupied molecular orbital and lowest unoccupied molecular orbital are the main orbitals that take part in chemical stability [15]. The orbital energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are collected in table 4.The HOMO acts as electron donor while LUMO acts as electron acceptor. In FNT and BNT molecule, the highest occupied molecular orbital energies were -0.270a.u and -0.087a.u and lowest unoccupied molecular orbital energies were -0.266 and -0.094a.u and the energy gap values were 0.182, and0.172a.u respectively [2]. However, in present study the energy gap is 4.26 in 2I5NT whereas 4.62eV in 2Cl5NT. The orbital surfaces are depicted in **Fig- 4**.

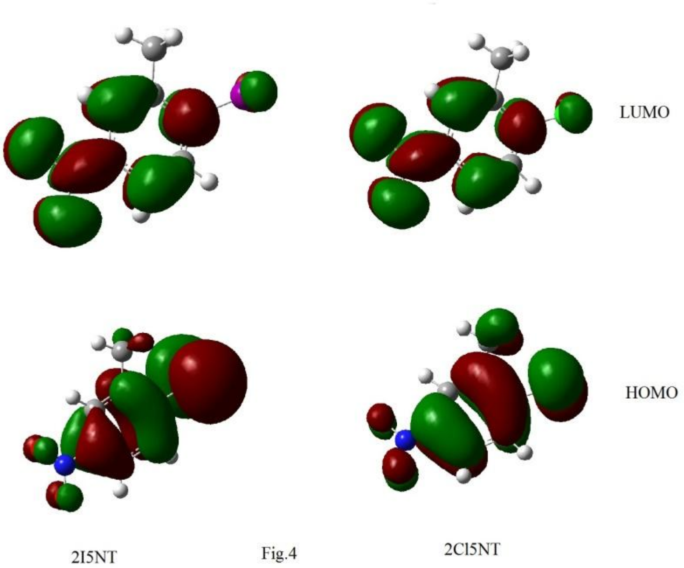

Fig.4

V. INTRINSIC ELECTRONIC PROPERTIES:

Reactivity is an intrinsic electronic property of any system which forecasts its availability for a possible chemical changes. The global reactivity descriptors are of use to illustrate chemical stability and reactivity. Electronegativity represents the capability to attract electrons. Chemical hardness is a measure for resistance to any change or deformation. Molecule with small energy gap is more polarizable and is termed as soft molecule, having high chemical reactivity and low kinetic stability [16]. Since Koopman's[17, 18] theorem states that ionization potential and electron affinity can be linked with the frontier orbitals as follows

$I = -E_{HOMO}$

$A= -E_{LUMO}$

With the help of above values we calculated electronic properties **(**electronegativity, chemical hardness, softness, chemical potential, and electrophilicity index) which are tabulated in table 5. The formula for electronegativity, chemical hardness, softness, chemical potential, and electrophilicity index are

Ionization potential $(I) = -E_{HOMO}$
Electron affinity $(A) = -E_{LUMO}$
Electronegativity $(\chi) = (I + A)/2$
Chemical hardness $(\eta) = (I - A)/2$
Softness $(S) = 1/2\eta$
Chemical potential $(\mu) = -\chi = -(I + A)/2$
Electrophilicity index $(\omega) = \mu^2 S$

VI. APPLICATION AND IMPORTANCE OF THIS VIBRATIONAL SPECTROSCOPIC INVESTIGATION

Since vibrational spectroscopy is an important tool to identify the unknown compounds. The beauty of this method is that the compound does not destroy. This method measures the vibrational energy in compound. The each bond has different vibrational energy. The C-C bond can be different from going to one compound to another which depends on what group or compound each carbon is bound to. Each compound has different fingerprint due to the vibrational energy. Our present study reports the vibrational energy, different geometrical parameters which are important to the identification of these compounds. Moreover, this study may be used by authors who do cluster study of these compounds.

VII. CONCLUSION:

The molecular structure and vibrational spectraof 2I5NT and 2Cl5NTwith IR and Raman intensitieshave been discussed.Normal modes assignments of some of the vibrational frequencies of title molecule are in good agreement with the earlier reported experimental frequencies whereas others have modified. Therefore, results presented in this work show that DFT method is reliable to calculate molecular structure and vibrational spectra with IR and Raman intensities.The calculated HOMO and LUMOenergies show that charge transfer occurs within the molecule.The intrinsic electronic properties such as electronegativity, chemical hardness, softness, chemical potential, and electrophilicity index have also been calculated in order to determine the reactivity of both the molecules.

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Table 1. Optimized geometrical parameters of 2I5NT and 2Cl5NT.

Parameters	**2I5NT**	**2Cl5NT**
C1-C2	1.393	1.392
C2-C3	1.401	1.398
C3-C4	1.410	1.408
C4-C5	1.402	1.4
C5-C6	1.394	1.395
C6-C1	1.394	1.395
C4-C10	1.509	1.509
C6-N15	1.473	1.473
N15-O16	1.236	1.236
N15-O17	1.236	1.236
C3-Cl4	2.131	1.754
C1-C2-C3	120.21	119.85
C2-C3-C4	121.89	122.37
C4-C5-C6	120.70	116.98
C5-C6-C1	121.89	121.93
C6-C1-C2	118.18	118.26
C6-N15-O16	117.82	117.82
C6-N15-O17	117.61	117.64
Energy	-7395.381	-935.688

Table 2. Vibartional Assignment of 2 - Iodo 5 – Nitrotoluene.

Theoretical			**Experimental**^{d}		υ^e	^{f}**PEDs**
υ^a	**A**^{b}	**R**^{c}	IR	Raman		
3247	2.75	93.32			3110	rCH
3234	2.00	64.64			3098	CH_3ips+CH_3ops+rCH
3223	0.86	37.85			3087	rCH
3148	15.18	48.28			3015	rCH
3121	6.14	50.60	3077	3085	2989	CH_3ops
3047	11.47	151.93	3023	3067	2919	CH_3ss+CH_3ops
1652	42.93	17.32	1646	1639	1623	rCC+CHipb+CNipb+CCC
1619	94.15	193.49	1608	1603	1591	rCC+CHipb
1590	176.92	28.83	1510	1516	1562	CH_3opr+CH_3ipr+CH_3ipb
1511	22.55	1.89			1485	CH_3ipr+CH_3opr+CH_3opb
1499	11.69	8.14	1454	1475	1473	rCC+CHipb+CH_3sb
1486	21.20	2.63	1423	1420	1460	CH_3sb+rCC1+CHipb+rCC
1431	3.70	17.57			1406	NO_2as+rCC+CHipb+NO_2roc+CNipb
1423	0.52	5.12	1375	1379	1398	NO_2as+rCC+CHipb
1382	451.15	577.38	1340	1340	1358	rCC
1338	19.58	9.14	1265	1267	1315	CHipb+rCN+NO_2ss+NO_2sci+rCC
1288	3.85	0.38	1254	1255	1266	NO_2ss+rCN+CHipb+NO_2sci
1227	8.97	104.80	1192	1207	1206	rCC1+CHipb+rCC+NO_2ss+CCC
1153	3.44	15.35			1133	CHipb+rCC+NO_2ss
1126	20.72	31.17	1130	1125	1106	CHipb+rCC+rCN+NO_2ss+CH_3ipb
1063	2.60	1.23	1090	1097	1044	CH_3opb+CHopb
1030	66.47	14.65			1012	CH_3ipb+rCC
1020	6.16	2.62	1008	1013	1002	CCC+rCC+rCI+CH_3ipb+CHipb
980	0.61	0.008	992		963	CHopb+CCtwi
932	42.27	5.78	946		916	CHopb+CCtwi+CH_3opb
920	12.72	0.25			904	rCC1+rCN+rCC+CCC+NO_2ss+CHipb
844	12.03	0.54	854		829	CHopb+ CCtwi
807	33.42	20.30	746		793	NO_2sci+NO_2ss+rCC1+CCC+rCC
757	30.04	0.28			744	NO_2wag+CCtwi+CNopb+CHopb+CIopb
700	1.10	1.36			688	NO_2wag+CCtwi+CC1opb+CIopb+CHopb
688	1.19	8.77	669	680	676	CCC+NO2sci+CHipb+rCC+rCI+CNipb
560	1.42	2.91	515	534	550	NO_2roc+CCC+CNipb+CC1ipb+CHipb
530	3.59	10.42			520	CCtwi+CNopb+CC1opb+NO_2wag+CIopb
524	0.01	0.13	477		515	CNipb+NO_2roc+CCC+rCC1+CC1ipb+rCC
466	4.91	0.17	431		458	rCI+rCN+NO_2sci+CC1ipb+NO_2roc+CCC
441	4.68	0.06			433	CCtwi+CC1opb+CIopb+CHopb
383	1.11	1.45	380		376	CC1ipb+NO_2roc+CIipb+rCC+rCN
273	6.12	0.91	273		268	CCtwi+CIopb+NO_2wag+CNopb+CC1opb
236	0.77	0.60	207	211	231	CNipb+CC1ipb+CIipb+NO_2roc+rCI+CCC
203	0.33	1.78	187	185	199	CCtwi+CNopb+CH_3twi+CCC+CC1opb
192	0.006	1.41	167		188	rCI+CCC
153	1.67	0.63	147		150	CIipb+CNipb+rCC
141	0.33	0.14	110		138	CH_3twi+CCtwi
70	2.18	0.21			68	CCC+CCtwi
52	0.22	0.33			51	CCtwi+CCC

^{a}Theoretical frequency (in cm^{-1}) at DFT/b3lyp/DGDZVP

^{b}Theoretical IR Intensity (Km/mol)

^{c} Theoretical Raman Intensity (Å^4/amu)

^{d}Experimental frequenciestaken from ref. [3]

^{e}Scaled frequency at MOLVIB-7.0

^{f} potential energy distributions of normal modes. Contribution less than 5% were not considered.

The abbreviations are – r = stretching, twi = twisting, ωag = wagging, ipb = in-plane bending, roc = rocking, opb= out of plane bending,sci= scissoring.

Table 3. Vibartional Assignment of 2 - Chloro 5 – Nitrotoluene.

Theoretical			υ^e	**^{f}PEDs**
υ^a	**A^b**	**R^c**		
3248	3.01	85.33	3111	rCH
3235	2.14	55.60	3099	rCH
3224	0.75	62.01	3088	rCH
3150	11.72	47.77	3017	CH_3ips
3123	7.64	67.23	2991	CH_3ops
3049	14.70	172.64	2920	CH_3ss+CH_3ops
1657	35.79	16.77	1628	rCC+CNipb+rCC1
1627	80.32	128.40	1599	rCC+CHipb
1594	184.93	22.23	1566	NO_2as+rCC+ CClipb
1514	26.33	1.18	1488	CH_3opr+CH_3ipr
1499	9.24	8.66	1473	CH_3ipr+CH_3opr
1493	21.86	1.12	1467	rCC+CHipb+CH_3sb
1435	0.52	15.57	1410	CH_3sb+CHipb+rCC1
1428	2.54	4.85	1403	CH_3sb
1383	401.81	369.13	1359	NO_2ss+rCN+CHipb
1349	21.25	4.29	1326	rCC +CCC
1283	1.25	0.40	1261	CHipb+rCC
1228	22.77	65.81	1207	CHipb+rCC1
1155	4.02	5.71	1135	CHipb+rCC
1125	7.34	12.81	1105	CHipb+rCC
1065	107.55	23.36	1046	CCC+ CH_3opb
1064	2.84	1.10	1045	CH_3opb+CHopb
1019	2.26	2.37	1001	CH_3ipb+rCC
976	0.70	0.047	959	CHopb+CCtwi
936	33.22	4.06	920	CCC+CN+CC1
922	13.87	0.17	906	CHopb
841	13.42	0.80	826	CHopb+ CH_3opb
809	24.99	13.20	795	NO_2sci+rCC1+CCC
759	29.26	0.14	746	CNopb+CHopb
706	3.10	10.49	693	CCC+ rCCl
703	2.56	1.27	691	CH_3opr+CCtwi
580	11.06	3.72	570	CCC+CNipb
542	2.80	7.75	532	CNipb+NO_2roc+CCC+rCC1
529	0.21	0.05	520	CH_3opr+CCtwi+CHopb
516	8.88	1.83	507	CNipb + CH_3ipb+CCC
444	4.93	0.05	436	CHopb+CCtwi
391	1.35	1.78	384	NO_2roc+CH_3roc
312	0.68	2.90	306	rCCl+rCN+ NO_2sci+CC1ipb
294	4.24	0.75	289	CCtwi+CC1opb+CClopb
251	0.59	0.40	246	CH_3twi+CClipb
194	3.04	0.68	190	CNipb+CC1ipb+CClipb+NO_2roc
194	0.17	1.62	190	CH_3twi+CCtwi
150	0.51	0.054	147	CH_3twi+CCtwi
89	3.09	0.26	87	CH_3twi+ CNipb+CCtwi
55	0.05	0.23	54	NO_2twi+ CCtwi

[a]Theoretical frequency (in cm^{-1}) at DFT/b3lyp/DGDZVP
[b]Theoretical IR Intensity (Km/mol)
[c] Theoretical Raman Intensity (Å^4/amu)
[d]Experimental frequenciestaken from ref. [3]
[e]Scaled frequency at MOLVIB-7.0
[f] potential energy distributions of normal modes. Contribution less than 5% were not considered.

The abbreviations are – r = stretching, twi = twisting, ωag = wagging, ipb = in-plane bending, roc = rocking, opb= out of plane bending,sci= scissoring.

Table 4. HOMO – LUMO energies and their gap.

Orbital	**2I5NT^a**	**2Cl5NT**
HOMO	-0.26873	-0.28145
LUMO	-0.11197	-0.11068
Energy Gap	4.26	4.62

[a]orbital energies are given in eV unit.

Table 5.The intrinsic electronic properties

Molecule	I/eV	A/ev	χ/eV	η/eV	S/eV	μ/eV
2I5NT	7.31	3.04	5.17	2.13	0.234	-5.17
2Cl5NT	7.65	3.01	5.33	2.32	0.215	-5.33

Table S1. Definition of force constants

Force constants	Definition
CC stretching	C1-C2,C2-C3,C3-C4,C4-C5,C5-C6,C6-C1.
CC1 stretching	C5-C10
CC1ipb	C10-C5-C6,C10-C5-C4.
CC1opb	C10-C5-C6-C4.
CN stretching	C1-N15
CNipb	N15-C1-C2,N15-C1-C6
CNopb	N15-C1-C2-C6
CH3ss	C10-H11+ 0.5773 C10-H12+ 0.5773 C10-H13. 0.5773
CH3ips	C10-H11+ 0.8166 C10-H12+ -0.4083 C10-H13, -0.4083
CH3ops	C10-H12, -0.7072 C10-H13. 0.7072
CH3ipr	H11-C10-H12+ 0.8166 H11-C10-H13+ -0.4083 H12-C10-H13. -0.4083
CH3opr	H11-C10-H13+ 0.7072 H12-C10-H13. -0.7072
CH3ipb	H11-C10-C5+ 0.8166 H12-C10-C5+ -0.4083 H13-C10-C5. -0.4083
CH3opb	H12-C10-C5+ 0.7072 H13-C10-C5. -0.7072
CH3sb	H11-C10-C5+ 0.4083 H12-C10-C5+ 0.4083 H13-C10-C5+ 0.4083 H11-C10-H12+ -0.4083 H11-C10-H13+ -0.4083 H12-C10-H13. -0.4083
CH3twi	C6-C5-C10-H11+ 0.4083 C6-C5-C10-H12+ 0.4083 C6-C5-C10-H13+ 0.4083 C4-C5-C10-H11+ 0.4083 C4-C5-C10-H12+ 0.4083 C4-C5-C10-H13. 0.4083
CH stretching	C6-H9,C2-H7,C3-H8
CI stretching	C4-I14
CIipb	C5-C4-I14,C3-C4-I14
CIopb	I14-C4-C5-C3
CHipb	C5-C6-H9,C1-C6-H9,C1-C2-H7,C3-C2-H7,C2-C3-H8,C4-C3-H8
CHopb	H9-C6-C1-C5,H7-C2-C1-C3,H8-C3-C2-C4
NO2ss	N15-O16+ 0.7072 N15-O17.0.7072
NO2as	N15-O16+ 0.7072 N15-O17. -0.7072
NO2sci	O16-N15-O17+ 0.8165 O16-N15-C1+ -0.4082 O17-N15-C1. -0.4082
NO2roc	O16-N15-C1+ 0.7072 O17-N15-C1. -0.7072
NO2wag	O16-N15-O17-C1
NO2twi	O16-N15-C1-C6+ 0.4082 O16-N15-C1-C2+ 0.4082 O17-N15-C1-C6+ 0.4082 O17-N15-C1-C2+ 0.4082
CCC	C6-C1-C2,C1-C2-C3,C2-C3-C4,C3-C4-C5,C4-C5-C6,C5-C6-C1.
CCtwi	N15-C1-C2-H7+ N15-C1-C2-C3+ H7-C2-C1-C6+ C3-C2-C1-C6, H7-C2-C3-H8+ H7-C2-C3-C4+ C1-C2-C3-H8+

	C1-C2-C3-C4, H8-C3-C4-I14+ H8-C3-C4-C5+ C2-C3-C4-I14+ C2-C3-C4-C5, I14-C4-C5-C10+ I14-C4-C5-C6+ C3-C4-C5-C10+ C3-C4-C5-C6, C10-C5-C6-H9+ C10-C5-C6-C1+ C4-C5-C6-H9+ C4-C5-C6-C1, H9-C6-C1-N15+ H9-C6-C1-C2+ C5-C6-C1-N15+ C5-C6-C1-C2.

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