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Molecular structure, FT-IR and FT-Raman spectra and HOMO-LUMO analysis of 2-methoxy-4-nitroaniline using ab initio HF and DFT (B3LYP/B3PW91) calculations

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ABSTRACT

Fourier-Transform infrared and Fourier-Transform Raman spectra of 2-methoxy-4-nitroaniline(2M4NA) was recorded in the region 4000 – 400 cm^{-1} and 3500 – 100 cm^{-1} .Quantum chemical calculations of energies, geometrical structure and vibrational wavenumbers of 2M4NA were carried out by ab initio HF/6-311G(d,p) and DFT (B3LYP/6-311G(d,p) and B3PW91/6-311G(d,p)) levels of theory with complete relaxation in the potential energy surface.The vibrational frequencies are calculated and scaled values are compared with FT-IR and FT-Raman experimental values. The difference between the observed and scaled wavenumber values of most of the fundamentals is very small in DFT than HF. The calculated HOMO-LUMO energies show that charge transfer occurs in the molecule. 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 2M4NA.. The experimental spectra also coincide satisfactorily with those of theoretically constructed simulated spectrograms.

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

INTRODUCTION

In chemical industry and in the field of biology aromatic amines play a major role. 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, pharmaceutical products, rubber, plastic additives, photographic antifogging agents and coccidiosis. 2-Methoxy-4-nitroaniline is used in dyeing textiles, in the printing industry, and as an intermediate in the synthesis of azo dyes that have applications in tattoo inks, emulsion paints, toy enamels and also used in the test systems with synthetic peptide substrates in haemostaseology[3]. It is also used in the preparation of β-Amino carbonyl compounds which are extremely important as biologically active molecules [4].It plays an important role in detection of advanced solid tumors in patients[5]. Vibrational assignments based on FT-IR in the vapour, solution,liquid phases and the Raman spectra in the liquid state were reported for aniline [6]. Rai *et al*. performed IR and Raman spectral measurement and DFT calculations of chlorine substituted anilines [7]. Ploug-Sorensen *et al* reported the structure of o- nitro aniline hydrochloride [8]. The Vibrational spectra of the 2,6 dibromo-4-nitroaniline and 2-(methylthio) aniline applying DFT calculation based on B3LYP level with 6-31G* basis set was reported by Krishnakumar *et al.* [9]. The theoretical and experimental studies of vibrational spectra and thermal analysis of 2-nitroaniline and its cation have reported by S.Azhagiri *et al.* [10]. Shankar *et al.* [11] studied 2-chloro-6-methylaniline with polarized Raman and infrared spectra. E Kavitha *et al* have studied the molecular structure and HOMO – LUMO studies of 4-nitroaniline [12]. Molecular modeling by quantum chemical calculation of 2-chloro-5-nitrotoluene was studied by PM Anbarasan *et al* [13].

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 [14,15] 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 2-methoxy-4-nitroaniline have been reported so far. In this study, molecular geometry,optimized parameters and vibrational frequencies are computed and the performance of the computational methods for ab initio (RHF), hybrid density functional methods (B3LYP and B3PW91) at 6-311G(d,p) basis set is compared. In particular, for polyatomic molecules the DFT methods lead to the prediction of more accurate molecular structure and vibrational frequencies than the conventional ab initio Hartree-Fock calculations.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 treatment of electron correlation, for the deficiencies and for the anhormanicity [16-17]. Ab initio HF and Density Functional Theory (DFT) calculations have been performed to support our wave number assignments.

MATERIALS AND METHODS

2. Experimental details

The compound (2M4NA) was purchased from Sigma-Aldrich Chemical Company, USA with more than 98 % purity and was used as such without further purification to record FTIR and FT Raman spectra. A projection of 2-methoxy-4-nitroaniline is shown in the Figure 1. 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 (2M4NA) is presented in the Figures 2 & 3.

3. Computational details

The entire calculations conducted in the present work were performed at Hartree-Fock (HF), B3LYP and B3PW91 levels included in the Gaussian 03W package [18] program together with the 6-311G(d,p) basis set function of the density functional theory (DFT) utilizing gradient geometry optimization [19]. 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) [20] employing the Becke's three-parameter hybrid functional (B3) [21] combined with gradient –corrected Lee-Yang and Parr(LYP) correlation [22] functional (B3LYP) and Perdew and Wang (PW91) [23,24] which present the best predicting results for molecular geometry and vibrational wave numbers for moderately larger molecule[25-27]. 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 [28]. 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 2M4NA is used for harmonic vibrational frequency calculations resulting in IR and Raman frequencies. The DFT hybrid B3LYP,B3PW91 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 [29], a scaling factor of 0.96 has been uniformly applied to the B3LYP with 6-311G(d,p) and 0.9631 for B3PW91 with 6-311G(d,p) calculated wavenumbers [30]. Similarly, the vibrational modes studies through HF method were scaled by a value of 0.89 [31]. 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 [32] 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.

RESULTS AND DISCUSSION

4.1 Molecular geometry

The optimized structure parameters of 2M4NA calculated by ab initio HF and DFT-B3LYP, B3PW91 levels with the 6-311G(d,p) basis set are listed in the Table 1. 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 2-methoxy-4-nitroaniline [33] . 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 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 [34,35]. 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 and B3PW91 with those of HF, as a whole the formers are on higher side than the latter and the DFT 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, molecular and thermodynamic properties.

4.2 Vibrational assignments

The vibrational analysis of 2M4NA is performed on the basis of the characteristic vibrations of methoxy,nitro and amino modes. The molecule under consideration belongs to the Cs point group. It has 20 atoms, so 54 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 2M4NA at HF and B3LYP, B3PW91 levels using the 6-311G(d,p) basis set 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 and B3PW91 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 2-methoxy-4-nitroaniline is presented in a common wavenumber scale in Figures 2&3.

C-H Vibrations

The 2M4NA 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 2-methoxy-4-nitroaniline is a trisubstituted aromatic system it has two adjacent and one isolated C-H moieties. The aromatic structure 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 [36]. The expected three C-H stretching vibrations correspond to (mode nos. (52-50) stretching modes of C1-H, C4-H and C6-H units. The vibrational mode nos: (52-50)assigned to aromatic C-H stretching computed by B3PW91/6-311G(d,p) method at 3124, 3117 and 3067 cm^{-1} shows good agreement with recorded FT-Raman spectrum which shows peak at 3131, 3097and 3089cm^{-1} .

The aromatic C-H in- plane bending modes of benzene and its derivatives are observed in the region 1300-1000cm^{-1}. The bands are sharp but are weak to medium intensity. The C-H in-plane bending vibrations computed in the region at 1300,1240 and 1213 cm^{-1} (mode nos: 35,34,33) by B3PW91/6-311G(d,p) method shows good agreement with FT-Raman spectral region at 1282 and 1230 and 1195cm^{-1}. The C-H out-of-plane deformation modes of benzene [37,38] are expected to occur in the region 1000-600cm^{-1} . The out-of-plane bending vibration falls in the FT-IR, FT-Raman spectrum as a medium bands at 958, 916 and 881 cm^{-1} and 922,914 and 852cm^{-1} shows good agreement with theoretically computed B3PW91/6-311G(d,p) and B3LYP/6-311G(d,p) methods at 921,918 and 858 cm^{-1},and 919,897 and 858cm^{-1} (mode nos: 26,25 and 24). The same vibrations computed by HF/6-311G (d,p) also shows good agreement with experimental data.

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}[39]. The FT-IR band observed at 1600, 1554 and 1500cm^{-1} assigned to C-C stretching vibration shows good agreement with theoretically computed B3PW91/6-311G (d,p) method in the region at 1604,1558 and 1500 cm^{-1} (mode nos: 45,43 and 42). The same vibration computed by HF method also shows the same kind of result. The ring breathing mode observed as medium strong band at 829cm^{-1} in FT-IR spectrum and 813cm^{-1} in FT-Raman show good agreement with theoretically computed B3PW91/6-311G(d) method at 807 cm^{-1} (mode no:23). For the in-plane deformation vibration Shimanouchi *et al.* [40] 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. 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.

O-CH_3 group vibrations

The compound 2M4NA has only one methoxy group at 2nd position; therefore there will be only one O-CH_3 stretching mode. In case of computed HF/6-311G(d,p) the O-C stretching vibration observed at 1053cm^{-1} and at 1035 and 1045cm^{-1} by DFT/B3LYP/6-311G(d,p) and B3PW91/6-311G(d,p) methods nearly coincides with the experimental FT-IR peak at 1047 and FT-Raman at 1049cm^{-1}.This is supported by bandana sharma *et al* [41] in their study of the same kind of vibration at 1041 cm^{-1} in HF and 1069cm^{-1} in DFT study. Each CH_3 or OCH_3 group give rise to three C-H valance oscillations (2800-3000 cm^{-1}) and three C-H deformation as suggested by Bellamy[42]. Bandana Sharma *et al* [41] has assigned C-H asymmetric stretching at 2983,3045 cm^{-1} and C-H symmetric stretching at 2914 cm^{-1}. Meganathan *et al* [43] has assigned 2929,2971cm^{-1} for C-H asymmetric and 2838 cm^{-1} for C-H symmetric vibration in their study. Based on the above litereature data the very strong band observed at 2952,3037cm^{-1} and 2870 cm^{-1} in FT-IR spectrum is assigned to C-H asymmetric and symmetric stretching vibration. The theoretically computed B3PW91/ 6-311G(d,p) at 2953,3038 and 2875cm^{-1} coincides exactly with the experimental results.The B3LYP/6-311G(d,p) value nearly coincides with this.

The very strong band observed at 1122cm^{-1} in FTIR and 1118 cm^{-1} in FT Raman assigned as CH_3 twisting vibration is in excellent agreement with the theoretically calculated value by HF/6-311G(d,p) method at 1100 cm^{-1}, B3LYP/6-311G(d,p) method at 1119 cm^{-1} and B3PW91/6-311G(d,p) method also at 1119 cm^{-1}. The vibrational wavenumbers 251cm^{-1} and 189 cm^{-1} in FT Raman are assigned to CH_3 in plane bending vibration and CH_3 out of plane bending vibration. The same vibration computed theoretically at 252,246 and 250cm^{-1} and 187,184 and 185cm^{-1} by HF and DFT methods. The O-CH_3 vibration mode assigned at 1040cm^{-1} for anisole[44] and in the region of 1000-1100cm^{-1} for its derivatives [45-48]. Singh and Yadav[49] assigned the C-O-CH_3 angle bending mode at 341,382 and 340 cm^{-1} for o,m and p-methoxy benzaldehyde respectively. In accordance with the above conclusion, we have assigned the theoretically predicted value 324, 326 and 327cm^{-1} by HF and DFT methods as the C-O-CH_3 angle bending mode which coincides with the band at 322 cm^{-1} observed in the FT-Raman spectrum. Balafour[44] assigned the torsional mode of O-CH_3 group at 82cm^{-1}, Lakshmaiah and Rao[46] calculated this mode to be at 58cm^{-1} for anisole. Some researchers assigned this mode at 100 cm^{-1} [50,51]. In our study this mode is assigned theoretically at 71,89,91cm^{-1} in HF and DFT methods.

NO_2 Vibration:

The deformation vibration of NO_2 group (scissoring,wagging,rocking and twisting) contributes to several modes in the low frequency region[52]. The NO_2 scissoring mode of vibration occurs in the region 794,791cm^{-1} in thoreticlly computed DFT (B3PW91/B3LYP)methods is well supported by 796cm^{-1} in FT-IR and 806cm^{-1} in FT-Raman. In aromatic compounds the wagging mode of ωNO_2 is assigned at 740±50 cm^{-1} with a moderate to strong intensity, a region in which γCH is also active[53]. For the present compound ωNO_2 assigned at 710, 722 cm^{-1} in B3LYP/6-311G(d,p) and B3PW91/6-311G(d,p) methods coincides exactly with 727,721cm^{-1} in FT-IR and FT-Raman experimental spectra. The rocking mode ρNO_2 is active in the region 545±45 cm^{-1} in aromatic compounds. In the present case, the rocking mode of NO_2 at 558, 555cm^{-1} in DFT methods is supported by experimental observation at 555cm^{-1} in FT-Raman. The frequency computed theoretically by B3LYP/6-311G(d,p) and B3PW91/6-311G(d,p) methods at 57 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 [54,55]. Based on the above literature data the very strong band observed at 1319 cm^{-1} in FT-Raman spectrum is assigned to NO_2 symmetric stretching vibration. The theoretically computed by B3LYP/6-311G(d,p) at 1310cm^{-1} (mode no: 36) The computed value for NO_2 asymmetric stretching vibration by B3PW91/6-311G(d,p) at 1558cm^{-1} nearly coincides with experimental FT-IR at 1554 and FT-Raman at 1566cm^{-1}.

NH_2 Vibration

The title molecule 2M4NA 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 [57] the corresponding bands were observed at lower frequencies 3499 and 3414 cm^{-1}. Honda *et al* [56] 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. Kavitha *et al* [12] has assigned 3578,3475cm^{-1} for N-H asymmetric and symmetric vibration. The asymmetric (ν_{as}) stretching mode appears to be calculated at the higher wavenumber 3572cm^{-1} than the symmetric (ν_s) one 3478 cm^{-1} by B3PW91/6-311G(d,p) method (mode nos. 54,53) are related to the FT-IR band as strong and very strong bands at 3571,3502 cm^{-1}. The counter part of the FT-Raman spectrum shows 3569, 3475cm^{-1}.

The NH_2 group of molecule under investigation 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 region 1615-1650 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 [57]. The computed NH_2 scissoring vibration by B3PW91/6-311G(d,p) method at 1604cm^{-1} (mode no.45) nearly coincides with the experimental FT-IR value at 1600cm^{-1}. The NH_2 rocking mode predicted at 1020 cm^{-1} in the theoretical value is in good agreement with 1022 cm^{-1} band at FT-Raman. The NH_2 wagging mode computed by theoretical DFT methods to be at 372,375 cm^{-1} shows good agreement with recorded FT-Raman at 359cm^{-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[58,59]. 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 movement from the donor to acceptor can make the molecule highly polarized through the single –double bond 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 transition 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 = -0.22345 a.u.
LUMO energy = -0.07643 a.u.
HOMO–LUMO energy gap = 0.14702 a.u.

The calculated self-consistent field (SCF) energy of 2-methoxy-4-nitroaniline is -606.56022256 a.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 2M4NA 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 [60]. 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.

5.3 Thermodynamic properties

On the basis of vibrational analysis of DFT studies at B3LYP/ 6-311G(d,p), B3PW91/ 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 2-methoxy-4-nitroaniline at room temperature at different methods are only marginal.

CONCLUSION

The results of the study lead to the following conclusions. (i) The proper frequency assignments for the compound 2M4NA is performed for the first time from the FTIR and FT Raman spectra. The experimental FTIR and FT Raman spectra were compared with the theoretical ab initio and DFT calculations of the vibrational spectra of the molecule. (ii) The equilibrium geometries of 2M4NA was determined and analyzed both at HF and DFT levels of theories utilizing 6-311G(d, p) basis set. The scaled DFT(B3LYP/B3PW91) calculations are powerful approach for understanding the vibrational spectra of medium sized organic compounds. (iii) The HOMO-LUMO energy gap and other related molecular properties were discussed and reported.

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

Bond length (Å)	Experimental	HF/6-311G(d,p)	B3LYP/ 6-311G(d,p)	B3PW91/ 6-311G(d,p)
C_1-C_2	1.337	1.386	1.401	1.399
C_1-C_6	1.337	1.385	1.388	1.386
C_1-H_7	1.100	1.075	1.084	1.085
C_2-C_3	1.337	1.412	1.422	1.420
C_2-N_{10}	1.266	1.374	1.373	1.368
C_3-C_4	1.337	1.369	1.381	1.379
C_3-O_{13}	1.355	1.352	1.367	1.361
C_4-C_5	1.377	1.394	1.400	1.397
C_4-H_8	1.100	1.069	1.079	1.081
C_5-C_6	1.337	1.372	1.388	1.385
C_5-N_{18}	1.248	1.453	1.461	1.456
C_6-H_9	1.100	1.071	1.080	1.082
N_{10}-H_{11}	1.050	0.994	1.008	1.007
N_{10}-H_{12}	1.050	0.994	1.007	1.006
O_{13}-C_{14}	1.402	1.402	1.424	1.416
C_{14}-H_{15}	1.113	1.086	1.095	1.096
C_{14}-H_{16}	1.113	1.080	1.088	1.089
C_{14}-H_{17}	1.113	1.085	1.095	1.095
N_{18}-O_{19}	1.310	1.188	1.227	1.222
N_{18}-O_{20}	1.310	1.190	1.229	1.224
Bond angle(°)				
C_2-C_1-C_6	120.0	121.2	121.2	121.2
C_2-C_1-H_7	120.0	119.2	119.0	119.0
C_1-C_2-C_3	120.0	118.8	118.5	118.5
C_1-C_2-N_{10}	120.0	122.1	122.7	122.8
C_6-C_1-H_7	120.0	119.6	119.8	119.8
C_1-C_6-C_5	120.0	118.7	119.0	118.9
C_1-C_6-H_9	120.0	121.0	121.6	121.6
C_3-C_2-N_{10}	120.0	119.1	118.8	118.6
C_2-C_3-C_4	120.0	120.4	120.6	120.6
C_2-C_3-O_{13}	120.0	114.6	114.1	114.1
C_2-N_{10}-H_{11}	120.0	115.6	116.5	116.5
C_2-N_{10}-H_{12}	120.0	116.3	118.0	118.2
C_4-C_3-O_{13}	120.0	125.0	125.3	125.3
C_3-C_4-C_5	120.0	119.2	119.1	119.1
C_3-C_4-H_8	120.0	121.9	122.4	122.4
C_3-O_{13}-C_{14}	120.0	119.6	118.2	117.8
C_5-C_4-H_8	120.0	118.9	118.5	118.5
C_4-C_5-C_6	120.0	121.7	121.6	121.7
C_4-C_5-N_{18}	120.0	118.6	118.7	118.6
C_6-C_5-N_{18}	120.0	119.7	119.7	119.7
C_5-C_6-H_9	120.0	120.2	119.5	119.5
C_5-N_{18}-O_{19}	120.0	117.9	118.0	117.9
C_5-N_{18}-O_{20}	120.0	117.8	117.8	117.8
H_{11}-N_{10}-H_{12}	120.0	114.5	116.1	116.3
O_{13}-C_{14}-H_{15}	109.5	111.2	111.2	111.3
O_{13}-C_{14}-H_{16}	109.5	106.2	105.9	106.1
O_{13}-C_{14}-H_{17}	109.4	111.2	111.1	111.2
H_{15}-C_{14}-H_{16}	109.5	109.3	109.5	109.4
H_{15}-C_{14}-H_{17}	109.4	109.6	109.5	109.5
H_{16}-C_{14}-H_{17}	109.4	109.3	109.5	109.4
O_{19}-N_{18}-O_{20}	120.0	124.4	124.2	124.3

Table2. Comparison of the observed(FT-IR and FT-Raman) and calculated (HF/B3LYP and B3PW91) vibrational frequencies of 2-methoxy-4-nitroaniline [harmonic frequency (cm^{-1})]

	Experimental frequency		Calculated frequency			
Vibrational mode nos.	FT-IR	FT-Raman	HF/ 6-311G(d,p)	B3LYP/ 6-311G(d,p)	B3PW91/ 6-311G(d,p)	Vibrational assignments
1			48	57	57	ω(O-CH_3)+ ι(NO_2)
2			71	89	91	ω(O-CH_3)
3		107	111	110	110	γ(CH_3)$_+$ ι((NH_2)
4		158	162	161	162	(O-CH_3) bending
5		189	187	184	185	ω(NH_2)+ γ (CH_3)
6		251	252	246	250	β (CH_3)
7		254	255	252	251	ring torsional
8		322	324	326	327	(C-O-C) bending
9		329	327	328	328	(C-O-C) bending
10		349	349	348	350	ν(C-C-C)
11		359	352	375	372	ω(NH_2)
12	407	430	439	428	430	ω(NH_2)
13		449	475	446	446	ν(NH_2)
14		489	489	478	482	ι(O-CH_3)
15	516	521	525	519	521	γ(C-O-C)
16	553	544	543	541	544	ρ (NO_2)
17	595	555	553	555	558	ρ (NO_2)+ γ(C-O-C)
18	619	632	630	630	632	β(C-H)+β(C-C-C)
19	659	696	705	692	695	γ (C-H)
20	727	721	752	710	722	ω(NO_2)
21	765	790	771	774	783	β(C-C-C)+ν(C-O)
22	796	806	814	791	794	δ(NO_2)
23	829	813	822	800	807	ring breathing
24	881	852	900	858	858	γ (C-H)
25	916	914	918	897	918	γ (C-H)
26	958	922	957	919	921	γ (C-H)
27		1022	1020	1011	1020	ρ(NH_2)+ν (O-CH_3)
28	1047	1049	1053	1035	1045	ν (O-CH_3)
29		1080	1088	1070	1080	ν(C-N)+ βC-H
30	1122	1118	1100	1119	1119	CH_3 twisting
31		1141	1141	1125	1128	ν(C-H)
32	1172	1168	1176	1163	1166	ν(C-H)
33		1195	1187	1206	1213	β (C-H)
34	1251	1230	1236	1243	1240	β (C-H)
35		1282	1257	1284	1300	β (C-H)+ν(C-N)
36	1367	1319	1305	1310	1342	ν_s (NO_2)
37		1384	1404	1351	1375	ν (C-C-C)+ω (NO_2)
38	1405	1430	1429	1402	1410	CH_3 sym.bending
39		1446	1440	1427	1432	CH_3 sym.bending
40		1469	1443	1432	1433	CH_3 asym.bending

contd…

Table2. Comparison of the observed(FT-IR and FT-Raman) and calculated (HF/B3LYP and B3PW91) vibrational frequencies of 2-methoxy-4-nitroaniline [harmonic frequency (cm^{-1})]

	Experimental frequency		Calculated frequency			
Vibrational mode Nos.	FT-IR	FT Raman	HF/ 6-311G(d,p)	B3LYP/ 6-311G(d,p)	B3PW91/ 6-311G(d,p)	Vibrational assignments
41			1452	1447	1447	CH_3 asym. bending
42	1500	1492	1493	1485	1500	ν(C-C)
43	1554	1566	1569	1519	1558	ν (C-C)+ν_{as}(NO_2)
44		1585	1575	1558	1567	δ (NH_2)
45	1600		1607	1579	1604	δ(NH_2)+ν(C-C)
46			1635	1593	1608	δ (NH_2)
47	2870		2821	2891	2875	ν(C-H)
48	2952		2878	2950	2953	ν(C-H)
49	3037	3019	2928	3014	3038	ν(C-H)
50		3089	2968	3045	3067	ν(C-H)
51		3097	3024	3099	3117	ν(C-H)
52	3114	3131	3041	3111	3124	ν(C-H)
53	3502	3475	3390	3447	3478	ν_s(NH_2)
54	3571	3569	3490	3557	3572	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

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

Molecular properties	HF/6-311G(d,p)	B3LYP/6-311G(d,p)	B3PW91/6-311G(d,p)
ε_{HOMO}	-0.31204	-0.22186	-0.22345
ε_{LUMO}	0.07169	-0.07656	-0.07643
Energy gap	0.38373	0.1453	0.14702
Ionisation Potential (I)	0.31204	0.22186	0.22345
Electron affinity(A)	-0.07169	0.07656	0.07643
Global Hardness (η)	0.19187	0.07265	0.07351
Chemical potential (μ)	-0.12018	-0.14921	-0.14994
Global Electrophilicity (ω)	0.03763	0.15320	0.15291

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-methoxy-4-nitroaniline

Parameters	HF / 6-311G(d,p)	B3LYP / 6-311G(d,p)	B3PW91/ 6-311G(d,p)
Total energy	-603.23664919	-606.79776416	-606.56022256
Zero point energy	102.60999	95.29991	95.72729
Rotational constants			
	1.61430	1.58356	1.59369
	0.67945	0.66851	0.67290
	0.47978	0.47158	0.47467
Entropy			
Total	99.981	102.111	101.989
Translational	41.265	41.265	41.265
Rotational	30.791	30.844	30.824
Vibrational	27.924	30.002	29.899
Dipole moment	6.1154	6.6911	6.7082

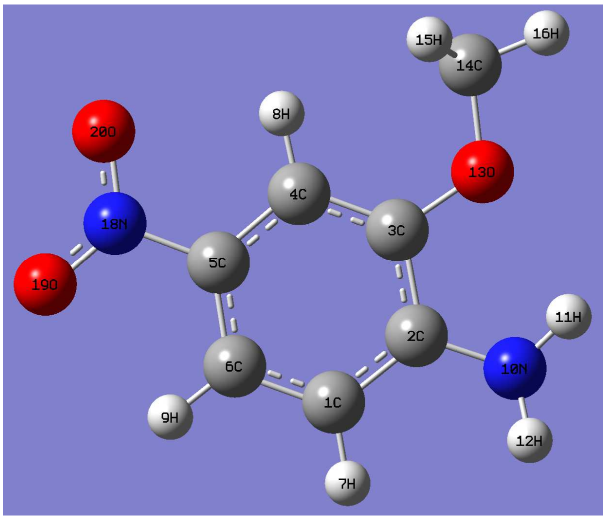

Fig. 1 The atom numbering for 2-methoxy-4-nitroaniline molecule

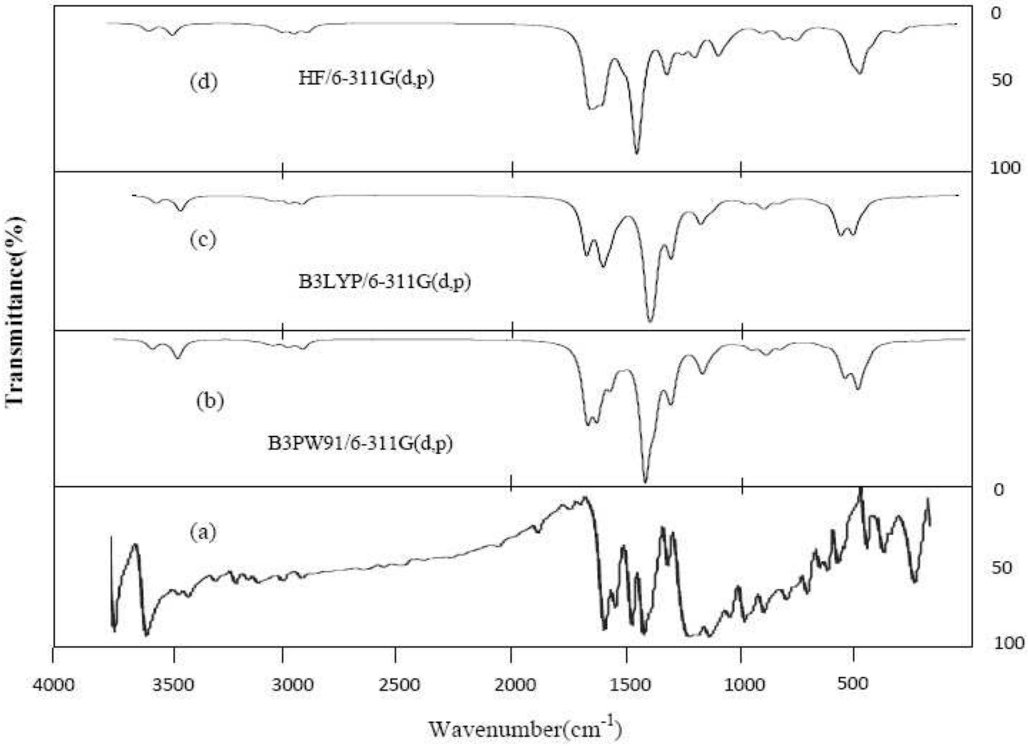

Fig. 2 Experimental (a), calculated (b,c), (d) FT-IR Spectra of 2-methoxy-4-nitroaniline

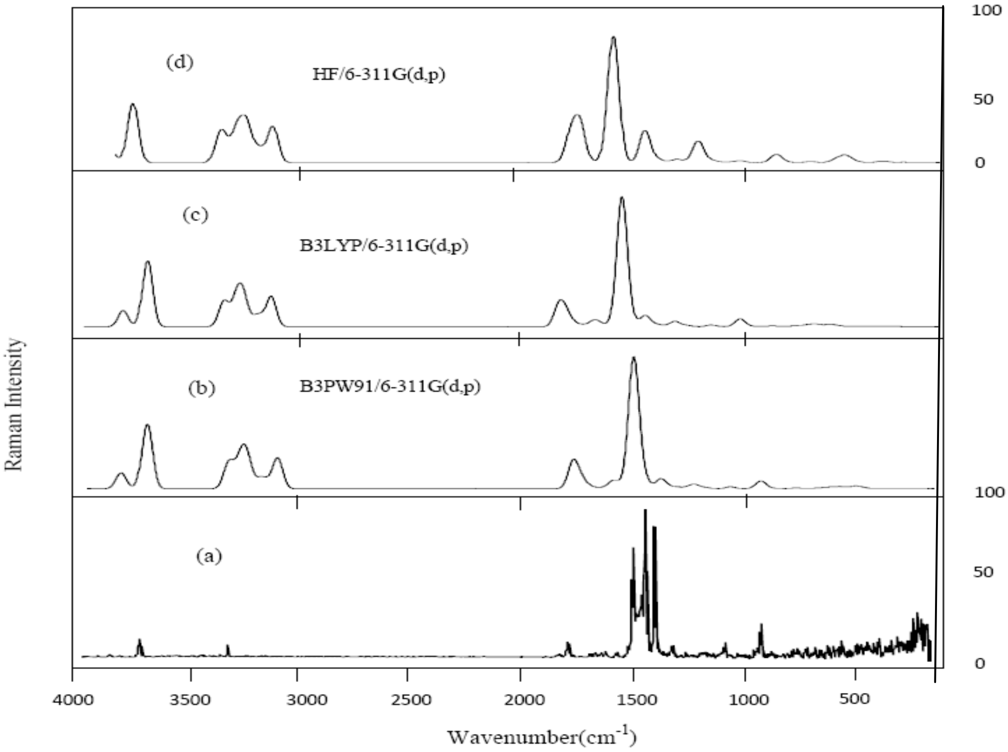

Fig. 3 Experimental (a), calculated (b,c), (d) FT-Raman Spectra of 2-methoxy-4-nitroaniline

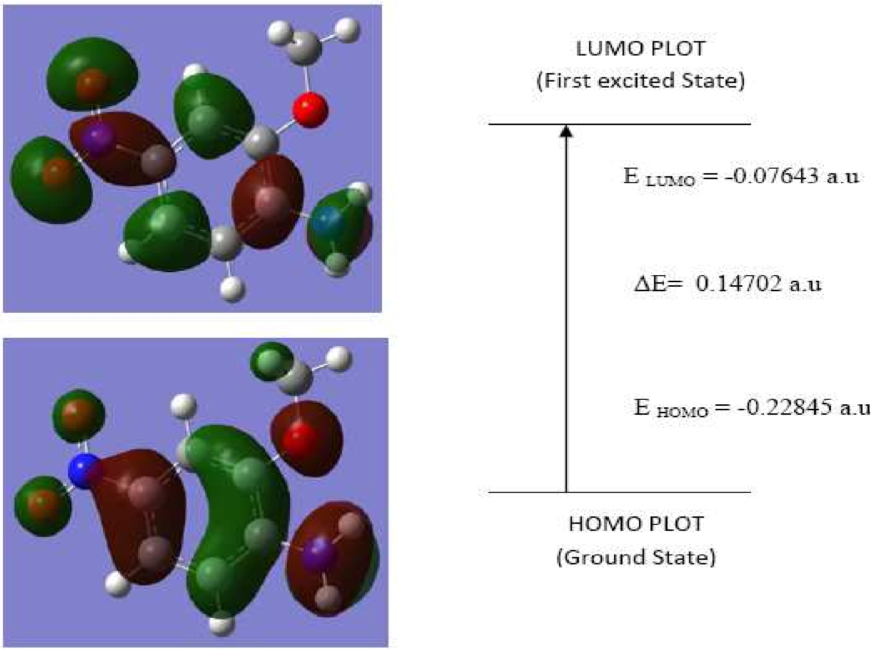

Fig. 4 Atomic orbital composition of the frontier molecule for 2-methoxy-4-nitroaniline

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