

# Theoretical and experimental studies of vibrational spectra and thermal analysis of 2-nitroaniline and its cation

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Received: 26 January 2009 / Accepted: 23 March 2009 / Published online: 6 June 2009  
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**Abstract** The FTIR spectrum of 2-nitroaniline was recorded in the regions 4000–400  $\text{cm}^{-1}$ . The optimized molecular geometry, bond orders, atomic charges, harmonic vibrational wave numbers and intensities of vibrational bands of 2-nitroaniline and its cation were calculated at DFT levels invoking two different basis sets 6-31G\*\* and 6-31+G\*\* using Gaussian 03W program. The X-ray geometry and FTIR vibrational frequencies were compared with the results of DFT calculations. The thermal stability of 2NA is studied by the thermo gravimetric analysis (TGA). Experimental degradation process of 2-nitroaniline was interpreted with the bond order analysis. The Mulliken atomic charge analysis was also made in the present study. Based on the molecular geometry and Mulliken charge analysis, intra molecular hydrogen bonding was identified.

**Keywords** DFT calculations · FTIR · 2-nitroaniline and its cation · TGA · Vibrational frequencies

## Introduction

Research in the field of designing NLO materials has gained momentum in the recent past on account of its role in optical parametric amplifiers, optical parametric oscillators, etc. [1–3]. Aniline based compounds play a very important role in designing organic materials for molecular electronics. The high second order hyperpolarizabilities of many nitro aniline molecules have led to describe them as prototypes for second harmonic generation. Poly aromatic hydrocarbons and their cations are believed to be the carriers of the unidentified infrared emission bands (UIR) and diffuse interstellar bands (DIB). Hence, the vibrational spectra of cations are of considerable interest. The comparison of the interstellar emission, information of the vibrational modes of ionized molecule is also needed. Many researchers studied the correlation between static hyperpolarizabilities and ground state geometries in terms of bond length alteration parameter. Hence we made an attempt to study the vibrational spectra of 2-nitroaniline and its cation in the present study. Dhaneshwar *et al.* studied the crystal structure of and twinning in  $\gamma$ -O-nitroaniline [4], Plough-Sorensen *et al.* reported the structure of O-nitroaniline hydrochloride [5] and recently Bharathikannan *et al.* established the NLO property of 2-nitroaniline with picric acid [6]. 2-Nitroaniline or O-nitroaniline is one of the isomeric family of nitroaniline. The main objective of this paper is to present, more accurate vibrational assignments

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and a comparison of the high-level theoretical vibrational spectra of neutral and ionized 2-nitroaniline (2NA). The evolution of density function theory that includes electron correlation in an alternative way has affording opportunities of performing vibrational analysis of moderately large organic molecules [7]. The results from DFT theory with results obtained from experiments has shown that the methods using B3LYP are the most promising in providing correct vibrational wave numbers. A scan of literature survey reveals that to the best of our knowledge, no DFT calculations of  $C_6H_6N_2O_2$  and  $C_6H_6N_2O_2^+$  have been reported so far. Hence, a systematic study on the vibra-

tional spectra and structure of 2NA and its positive ion with the aid of DFT has been carried out.

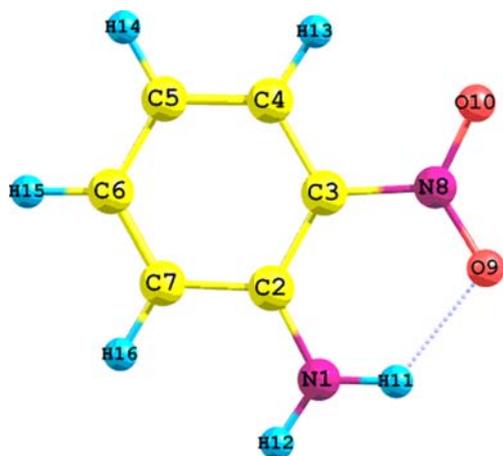
### Experimental methods

Fourier transform infrared spectrum is recorded using Nexus 670 spectrometer with a resolution of  $4\text{ cm}^{-1}$  at 298 K in the wavenumber region from  $4000 - 400\text{ cm}^{-1}$ . The spectrometer is fitted with XT-KBr beam splitter and DTGS detector. A base line correction is carried for the spectrum recorded. The thermal analysis studies was made

**Table 1** Selected geometrical parameters of 2NA and its cation

Geometrical parameters	Lit		B3LYP/6-31G(d,p)			B3LYP/6-31+G(d,p)		
	[Ref. 5]	[Ref.4]	Neutral	Cation	$\Delta$	Neutral	Cation	$\Delta$
Bond length (Å)								
N1–C2	1.455	1.371	1.355	1.327	0.028	1.358	1.328	0.030
C2–C3	1.402	1.355	1.425	1.447	–0.022	1.425	1.447	–0.022
C2–C7	1.379	1.415	1.419	1.440	–0.021	1.420	1.442	–0.022
C3–C4	1.387	1.435	1.405	1.372	0.033	1.407	1.374	0.033
C3–N8	1.451	1.490	1.448	1.481	–0.033	1.448	1.482	–0.034
C4–C5	1.374	1.371	1.381	1.416	–0.035	1.382	1.417	–0.035
C5–C6	1.380	1.380	1.406	1.408	–0.002	1.408	1.409	–0.001
C6–C7	1.383	1.358	1.380	1.377	0.003	1.382	1.378	0.004
N8–O9	1.217	1.223	1.247	1.239	0.008	1.248	1.239	0.009
N8–O10	1.226	1.216	1.232	1.216	0.016	1.234	1.217	0.017
N1–H11	–	0.74	1.009	1.023	–0.014	1.010	1.025	–0.015
N1–H12	–	0.94	1.006	1.015	–0.009	1.007	1.016	–0.009
C4–H13	–	0.93	1.082	1.084	–0.002	1.083	1.085	–0.002
C5–H14	–	0.97	1.084	1.085	–0.001	1.084	1.085	–0.001
C6–H15	–	0.93	1.086	1.085	0.001	1.086	1.085	0.001
C7–H16	–	1.050	1.087	1.086	0.001	1.087	1.086	0.001
O9...H11	–	2.64	1.895	1.831	0.064	1.914	1.854	0.060
Bond angle (°)								
N1–C2–C3	123.6	127.4	124.0	122.5	1.5	124.3	122.8	1.5
N1–C2–C7	117.9	116.2	119.7	119.5	0.2	119.3	119.2	0.1
C3–C2–C7	118.4	116.4	116.3	118.0	–1.7	116.4	117.9	–1.5
C2–C3–C4	121.5	121.3	121.2	120.3	0.9	121.2	120.3	0.9
C2–C3–N8	121.3	124.2	121.8	121.9	–0.1	121.8	121.9	–0.1
C2–C7–C6	120.1	120.1	121.8	120.8	1.0	121.8	120.9	0.9
C4–C3–N8	117.1	114.5	117.0	117.8	–0.8	117.0	117.8	–0.8
C3–C4–C5	118.8	122.7	120.8	120.3	0.5	120.8	120.3	0.5
C3–N8–O9	117.5	114.2	118.9	117.6	1.3	118.8	117.5	1.3
C3–N8–O10	117.7	120.0	118.7	117.3	1.4	118.8	117.5	1.3
C4–C5–C6	120.3	113.6	118.8	120.7	–1.9	118.9	120.7	–1.8
C5–C6–C7	120.9	125.9	121.0	119.9	1.1	120.9	119.8	1.1
O9–N8–O10	124.7	125.7	122.4	125.1	–2.7	122.5	125.0	–2.5
N1–H11...O9	–	150.0	126.5	129.7	–3.2	125.2	128.3	–3.1

$\Delta$  - Difference between neutral and cation values



**Fig. 1** Atom numbering scheme of 2-nitroaniline

using SDT Q600 Model TA instrument. The mass losses and heat response of the changes in the sample were measured from 0 °C to 1000 °C. The heating rate is 20 K per minute in air atmosphere.

### Computational details

The DFT calculations are performed on a Pentium IV personal computer using the Gaussian-03W program package [8]. The geometries are optimized in 6-31G\*\* and 6-31+G\*\* basis sets using density functional theory employing the B3LYP keyword, which invokes Becke's three parameter hybrid method [9] using the correlation

function of Lee *et al.* [10]. Since the molecule possesses amino and nitro groups, we used diffuse and polarization functions for better description of these bonds. The optimized geometrical structures were utilized in the calculations of harmonic vibrational wave numbers to characterize all stationary points as minima. The calculated vibrational frequencies of normal mode provide thermodynamic parameters by way of statistical mechanics.

## Results and discussion

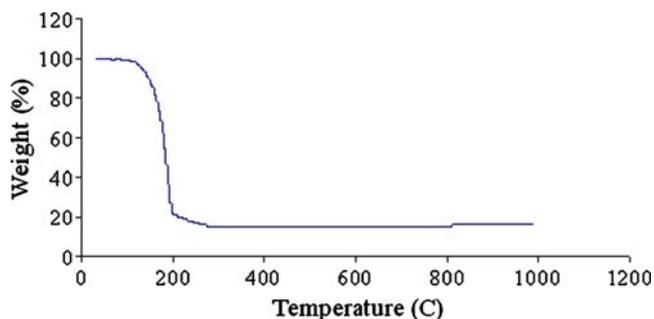
### Molecular geometry

2NA and its positive ion are subjected to geometry optimizations in their ground state. For each method, geometry optimizations are performed. The requested convergence on the maximum density matrix was  $10^{-6}$  a.u.; the threshold value of the maximum displacement is 0.0018 Å and that of the maximum force is 0.00045 Hartree/Bohr using the Bery analytical gradient optimization routine [11, 12]. The nature of stationary points is checked by diagonalizing the Hessian matrix to determine the number of imaginary frequencies (zero for local minimum). The self consistent field (SCF) energy of 2-NA at B3LYP level with the basis sets 6-31G\*\* and 6-31+G\*\* is found to be -492.123 a.u. and -491.83 a.u. respectively and for its positive ion is found to be -492.146 a.u. and -491.844 a.u. respectively.

The optimized structural parameters of 2NA and its positive ion calculated by DFT levels with two different basis sets (6-31G\*\* and 6-31+G\*\*) are listed in Table 1 in

**Table 2** Bond orders of 2NA and its cation

Bond	B3LYP/6-31G(d,p)			B3LYP/6-31+G(d,p)		
	Neutral	Cation	$\Delta$	Neutral	Cation	$\Delta$
N1–C2	1.0165	1.0908	-0.0743	1.0377	1.1126	-0.0749
C2–C3	1.0734	1.0131	0.0603	1.0971	1.0380	0.0591
C2–C7	1.0755	1.0146	0.0609	1.0896	1.0252	0.0644
C3–C4	1.1012	1.1909	-0.0897	1.1279	1.2120	-0.0841
C3–N8	0.8597	0.8037	0.0560	0.8804	0.8189	0.0615
C4–C5	1.1698	1.0617	0.1081	1.1945	1.0782	0.1163
C5–C6	1.0973	1.0899	0.0074	1.1101	1.1050	0.0051
C6–C7	1.1808	1.1818	-0.0010	1.2036	1.2010	0.0026
N8–O9	1.0416	1.0582	-0.0166	1.0876	1.0979	-0.0103
N8–O10	1.0842	1.1232	-0.0390	1.1251	1.1525	-0.0274
N1–H11	0.6705	0.6454	0.0251	0.6682	0.6427	0.0255
N1–H12	0.6835	0.6641	0.0194	0.6816	0.6610	0.0206
C4–H13	0.7679	0.7599	0.0080	0.7648	0.7556	0.0092
C5–H14	0.7738	0.7669	0.0069	0.7717	0.7660	0.0057
C6–H15	0.7715	0.7646	0.0069	0.7705	0.7627	0.0078
C7–H16	0.7730	0.7677	0.0053	0.7699	0.7657	0.0042



**Fig. 2** Thermogram of 2-nitroaniline

accordance with the atom numbering scheme given in Fig. 1. Table 1 also gives the bond length and bond angle difference ( $\Delta$ ) between neutral and positive ion of 2NA. The calculated bond distances and angles for the title compound are in agreement with experimental data [4, 5]. The optimized structure shows that only one intramolecular hydrogen bond is formed between NH<sub>2</sub> and NO<sub>2</sub> fragments, in such a way that only one N1-H11 bond is connected by an H bond to oxygen atom (O9) of the NO<sub>2</sub> fragment. The calculated O9...H11 bond distance of neutral and positive ion is found to be 1.895 Å and 1.831 Å in 6-31G\*\* & 1.914 Å and 1.854 Å in 6-31+G\*\* basis set respectively. The comparison of bond length values between the two different basis sets does not show any remarkable differences. However after ionization, the bond distances vary within the range  $\pm 0.03$  Å (except O9...H11 bond) in both the basis sets. The bond length of C4-C5 and C6-C7 support the double bond character whereas C3-C4, C5-C6 supports single bond character. The slightly longer bond distances of C2-C3 and C2-C7 are due to the presence of amino groups. It is observed that C3-N8 bond distance is longer than that of N1-C2 may be due to intra-molecular hydrogen bonding. The hydrogen bonding angle N1-H11...O9 calculated by DFT method is also included in Table 1. The experimental and computed bond angles are in good agreement. A remarkable deviation of calculated hydrogen bonding distance and angles with experimental value is noticed. It is due to the fact theoretical calculation was done for the isolated molecule whereas experimental study includes neighborhood interaction also.

#### Bond order and TA analysis

Thermogravimetric analysis is used to provide quantitative information on weight losses due to decomposition and/or evaporation of low molecular material as a function of time and temperature, thus greatly facilitating the interpretation of thermal degradation processes. Computational quantum chemistry provides additional data, which can be utilized successfully for the interpretation of experimental results

which may be used in the description and prediction of primary fragmentation processes.

Table 2 presents the bond order of neutral and cation charged species of 2NA. Bond order is related to bond strength. The weakest bonds, which are assumed to be, cleaved preferentially and relatively low pi bond character. For neutral and charged molecular species of 2NA, the bond order of N-H is lower than that of C-H bond. The C3-N8 bond is the weak bond refers to the possible starting decomposition of the neutral as well as cation. The thermal stability of 2NA is studied by the thermo gravimetric analysis (TGA). It was carried out by employing SDT Q600 TA instruments between the temperatures 0 °C to 1000 °C at a heating rate of 20 K per minute in air atmosphere. The 2NA sample weighing 2.275 mg is taken for the analysis and the thermo gram is depicted in the Fig. 2. The major weight loss occurs in the low region from 110 °C to 199 °C with the elimination of NO<sub>2</sub> gaseous product. The loss of NO<sub>2</sub> gas molecules from the entity of 2-nitroaniline (both neutral and charged molecular ion) were observed in thermo gravimetric analysis. Table 2 shows that the C3-N8 has the smallest bond order and refers to the possible starting decomposition site in 2-nitroaniline. So, the theoretical bond order analysis was applied to declare TGA observation. This bond breaks at low temperature and hence the gaseous product like NO<sub>2</sub> eliminated is reflected in the thermo gram of 2NA.

**Table 3** Mulliken atomic charges

S.No	Atoms	B3LYP/6-31G(d,p)		B3LYP/6-31+G(d,p)	
		neutral	cation	neutral	cation
1	N1	-0.6713	-0.5529	-0.6152	-0.4488
2	C2	0.3321	0.3427	-0.1523	-0.1171
3	C3	0.2388	0.2895	0.2840	0.2198
4	C4	-0.0965	-0.0799	-0.0860	-0.0358
5	C5	-0.1096	-0.0471	-0.0875	0.0115
6	C6	-0.0721	-0.0603	-0.2064	-0.2013
7	C7	-0.1290	-0.0659	0.1069	0.2352
8	N8	0.3674	0.4172	-0.2933	-0.2109
9	O9	-0.4486	-0.4009	-0.1260	-0.0836
10	O10	-0.4059	-0.3193	-0.0314	0.0654
11	H11	0.3086	0.3704	0.3460	0.3890
12	H12	0.2696	0.3410	0.3087	0.3671
13	H13	0.1367	0.2120	0.1681	0.2217
14	H14	0.0953	0.1923	0.1339	0.2051
15	H15	0.0982	0.1847	0.1338	0.1999
16	H16	0.0862	0.1763	0.1165	0.1825
Dipole moment ( $\mu$ )		4.725	7.128	5.192	7.443

Dipole moment is in Debye (D).

**Table 4** Experimental and theoretical vibrational assignments of neutral 2-nitroaniline

Mode	FTIR (cm <sup>-1</sup> )	B3LYP/6-31G**		B3LYP/6-31+G**		Assignment
		wave number (cm <sup>-1</sup> )	Intensity (km/mol)	wave number (cm <sup>-1</sup> )	Intensity (km/mol)	
1		35	85	65	5	τNO2
2		82	25	107	32	γNH2
3		175	105	200	153	βC-NO2+βC-NH2
4		246	0	242	0	βC-NH2+γC-C-C
5		301	2	297	2	τNH2+γC-N+γC-NH2
6		388	3	386	2	ρNO2
7		406	1	406	1	γCC
8	412	435	0	432	0	γC-C-C
9		537	13	536	18	βC-NH2
10	523	546	1	543	2	γCCN
11		569	1	567	2	βNH2+τC-NH2
12	554	604	16	609	21	γNH
13		683	8	679	7	γCH+γNH+γCN
14	663	703	2	687	3	βC-C-C+βC-NO2+βNH2
15		752	43	739	37	ωNO2+γCH
16	739	783	10	778	32	γNCH+γNCC
17	783	832	5	827	4	γCN+Ring def.
18		852	1	850	0	δNO2
19	877	883	16	880	14	ωNH2
20		971	0	976	1	Ring breathing
21		987	0	992	0	γCH
22		1030	8	1024	9	γCH
23		1077	2	1073	3	βCH
24	1097	1116	42	1112	51	βCH+βC-NH2
25		1184	19	1181	25	ρNH2
26	1165	1195	20	1192	24	βCH+νNH
27	1244	1305	56	1296	241	tNH2
28		1314	215	1306	73	βNH+βCH+νCC
29		1394	170	1382	203	νCN+νCC+νNO2
30	1344	1403	28	1398	11	νCC+βCH
31	1427	1490	56	1478	72	νNO2+νCC+βCH+βNH
32		1525	18	1517	14	νCC+βNH+βCH+δNH2
33	1505	1582	222	1565	273	νNO2+νCC+βCH+βNH
34		1621	138	1611	80	βNH+νNO2+δNH2
35	1567	1630	8	1619	69	νNO2+γCC+δNH2+βNH
36	1629	1685	234	1672	249	δNH2+βNH+νCN
37		3179	6	3180	6	νCH
38		3197	15	3198	13	νCH
39		3217	8	3217	6	νCH
40	3171	3247	3	3244	3	νCH
41	3346	3579	89	3580	84	νNH
42	3474	3741	74	3734	80	νNH

ν-stretching, β -in plane bending, γ -out of plane bending, τ-torsion, ω-wagging, ρ-rocking, δ-scissoring, and t-twisting.

**Table 5** Calculated vibrational frequency assignments of 2-nitroaniline cation

Mode	B3LYP/6-31G**		B3LYP/6-31+G**		Assignment
	Wave number (cm <sup>-1</sup> )	Intensity (km/mol)	Wave number (cm <sup>-1</sup> )	Intensity (km/mol)	
1	61	0	58	0	τNO <sub>2</sub>
2	130	4	128	5	γNH <sub>2</sub>
3	228	2	226	2	βC-NO <sub>2</sub> +βC-NH <sub>2</sub>
4	296	10	292	9	βC-NH <sub>2</sub> +γC-C-C
5	374	15	373	15	τNH <sub>2</sub> +γC-N+γC-NH <sub>2</sub>
6	393	2	391	4	ρNO <sub>2</sub>
7	397	3	392	2	γCC
8	464	1	460	1	γC-C-C
9	535	0	533	1	βC-NH <sub>2</sub>
10	556	2	554	2	γCCN
11	617	32	610	9	βNH <sub>2</sub> +τC-NH <sub>2</sub>
12	649	54	635	61	γNH
13	657	1	654	1	γCH+γNH+γCN
14	741	0	714	6	βC-C-C+βC-NO <sub>2</sub> +βNH <sub>2</sub>
15	786	38	782	126	ωNO <sub>2</sub> +γCH
16	805	131	791	39	γNCH+γNCC
17	829	13	826	13	γCN+Ring def.
18	875	40	872	39	δNO <sub>2</sub>
19	897	0	891	1	ωNH <sub>2</sub>
20	997	3	993	4	Ring breathing
21	1016	2	1011	1	γCH
22	1017	8	1012	7	γCH
23	1045	9	1043	8	βCH
24	1102	16	1096	17	βCH+βC-NH <sub>2</sub>
25	1167	9	1166	10	ρNH <sub>2</sub>
26	1193	0	1191	0	βCH+νNH
27	1316	0	1314	0	tNH <sub>2</sub>
28	1353	183	1348	187	βNH+βCH+νCC
29	1399	4	1397	5	νCN+νCC+νNO <sub>2</sub>
30	1410	47	1404	46	νCC+βCH
31	1483	0	1479	0	νNO <sub>2</sub> +νCC+βCH+βNH
32	1499	24	1496	21	νCC+βNH+βCH+δNH <sub>2</sub>
33	1552	7	1547	8	νNO <sub>2</sub> +νCC+βCH+βNH
34	1593	326	1589	364	βNH+νNO <sub>2</sub> +δNH <sub>2</sub>
35	1628	0	1624	3	νNO <sub>2</sub> +γCC+δNH <sub>2</sub> +βNH
36	1681	40	1662	40	δNH <sub>2</sub> +βNH+νCN
37	3208	1	3206	1	νCH
38	3225	0	3223	0	νCH
39	3235	8	3232	12	νCH
40	3241	18	3237	16	νCH
41	3382	327	3400	316	νNH
42	3616	176	3613	178	νNH

ν-stretching, β -in plane bending, γ -out of plane bending, τ-torsion, ω-wagging, ρ-rocking, δ-scissoring, and t-twisting.

## Mulliken atomic charges

It is known that the atomic charges are very much dependent on how the atoms are defined. It also plays an important role in the application of quantum chemical calculations to molecular systems. The Mulliken charges calculated at B3LYP level with two different basis sets are given in Table 3. In the present study, our interest is to compare different basis sets to describe the electron distribution in 2NA as broadly as possible, and assess the sensitivity of the calculated charges to changes in the choice of the basis set. From Table 3, it is observed that change to charge distribution by a change in basis set may be due to polarization [13]. Table 3 agrees that after ionization of 2NA its atomic charges are electron deficient in both basis set. Kolandaivel *et al.* [14], Summerhays *et al.* [15] and Roy *et al.* [16] confirmed that Nitrogen atom is the preferred site for protonation in aniline. In the present work, we also concluded that the Nitrogen atom N1 of the amino group is the preferred site for protonation. It is due to the fact that the hydrogen atoms of N1 involved in intramolecular hydrogen bonding with Oxygen atom O9 which is double bonded with N8. In Mulliken population analysis shows that all hydrogen atoms in molecules have lost electrons. Charge migration to heavy atoms can be related to molecular interactions. The hydrogen atoms attached with N1 atom, H11 has more electron deficient than H12 atom. This is in good agreement with the criterion for hydrogen bond formation and hence loss of charge by the hydrogen atom. The dipole moment of the neutral molecule of 2NA and its cation were calculated at 6-31G\*\* and 6-31+G\*\* levels and it is shown in Table 3. The dipole moment value of positive ion of 2NA shows only a 10% increase. It indicates that the change in molecular geometry when going from neutral to cation form. It is also reflected in changing the geometrical parameters slightly (see Table 1)

## Vibrational assignments

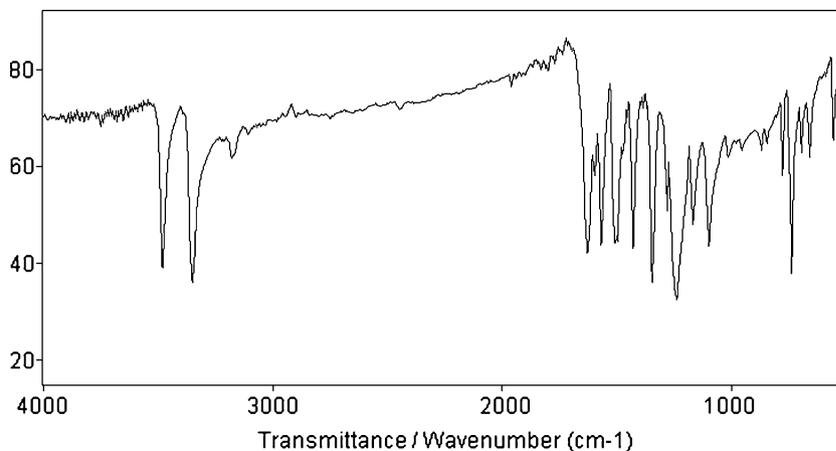
The molecule 2NA as well as its positive ion has 16 atoms. The 42 normal vibrations are distributed as 29A' + 13A'' species considering Cs point group symmetry. The SCF energy and geometrical parameters of 2NA and its positive ion in C1 symmetry has lower values rather in Cs symmetry. Therefore we ignored the Cs symmetry of the molecule. The calculated vibrational frequencies are numbered from the smallest to the largest fundamental wave number. The calculated and experimental wave numbers and intensities of the normal mode of vibrations and corresponding vibrational assignments for all of the 42 fundamental modes of vibration for the 2NA and its positive ion are given in Tables 4 and 5 respectively.

Experimental wave numbers and intensities obtained from FTIR spectrum (Fig. 3) have been compared with corresponding DFT values. The bands observed at 3346 and 3474  $\text{cm}^{-1}$  in our FTIR spectrum of the title compound correspond to N-H stretching vibrations mode. The assignments agree with the reported results of Bharathikannan *et al.* [6]. The DFT calculations for the 2-nitroaniline cation predict the NH stretching frequencies are found to be slightly decreased after ionization. It can be seen that there is a dramatic increase in the intensity of vibration.

The band at 3171  $\text{cm}^{-1}$  is due to C-H stretching vibration [17]. There are four stretching vibrations predicted by DFT calculations in the range 3180 – 3250  $\text{cm}^{-1}$  which were assigned for CH stretching vibrations. The intensity of CH stretching vibration after ionization remains unchanged. However, the stretching frequencies are found to be slightly increased after ionization.

The NH<sub>2</sub> scissoring mode is observed by the absorption at 1629  $\text{cm}^{-1}$  is in excellent agreement with expected value 1625  $\text{cm}^{-1}$  [18]. It is fairly matching with the calculated values at 1685 and 1672  $\text{cm}^{-1}$  in 6-31G\*\* and 6-31+G\*\*

**Fig. 3** B3LYP/6-31+G(d,p)  
Experimental FTIR spectrum of  
2-nitroaniline



methods respectively. The NH<sub>2</sub> twisting vibration calculated to be 1296 cm<sup>-1</sup> and 1305 cm<sup>-1</sup> is observed in the FTIR spectrum at 1244 cm<sup>-1</sup>. The NH<sub>2</sub> wagging vibration at 880 cm<sup>-1</sup> is satisfactorily agreeing with the observed value 877 cm<sup>-1</sup> in the FTIR spectrum.

The stretching vibration of NO<sub>2</sub> group falls in the region 1570–1485 cm<sup>-1</sup> [19]. The bands at 1567 and 1505 cm<sup>-1</sup> corresponds to NO stretching vibrations. Our DFT computed values of 1619 and 1565 cm<sup>-1</sup> exactly coincides with the experimental results. The results are in agreement with the literature value [20].

The computed frequency at 35 cm<sup>-1</sup> is assigned for NO<sub>2</sub> torsional vibration. The deformation vibration of NO<sub>2</sub> group, i.e., rocking, wagging, and scissoring contribute several normal modes in the low frequency region. The theoretically calculated values at 386, 739, and 850 cm<sup>-1</sup> corresponds to rocking, wagging, and scissoring of NO<sub>2</sub> vibrations. The above findings are in good agreement with the results of Sundaraganesan *et al.* [21]. The CH in plane and out of plane bending vibrations assigned in the region are in the range found in the literature [17]. It is found that these modes are contaminated by NH<sub>2</sub> and NO<sub>2</sub> groups. Silverstein *et al.* [20] assigned C-N stretching vibration in the region 1382–1266 cm<sup>-1</sup> for aromatic amines. In the present study, the computed bands at 1382 cm<sup>-1</sup> are assigned to be due to C-N stretching.

The calculated bands in the region 1398–1565 cm<sup>-1</sup> are assigned for CC stretching mode and are in good agreement with the literature values [19]. The ring breathing mode is predicted at 976 cm<sup>-1</sup> and satisfactorily coincides with the literature values.

## Conclusions

The optimized molecular geometry, bond orders, atomic charges, harmonic vibrational wave numbers, and intensities of vibrational bands of 2-nitroaniline and its cation were calculated at DFT levels invoking two different basis sets 6-31G\*\* and 6-31+G\*\* using Gaussian 03W program. We have investigated the effect of ionization in the optimized geometries and IR spectrum and atomic charges of 2NA with the aid of high level DFT calculations. Ionization causes a small change in the optimized geometry and vibrational frequencies but significant change in the intensity of the neutral 2NA.

**Acknowledgments** The authors are grateful and express the deepest sense of gratitude to Sophisticated Analytical Instrument Facilities Centre at Central Electro Chemical Research Institute, Karaikudi, for extending the facilities to record FTIR and Thermo Gravimetric Analysis. The authors are also grateful to Dr. C. K. Lakshmanaperumal, Reader and Head, and Dr. K. Chitra, Department of Physics, L. N. Government College for their fruitful discussion during the preparation of manuscript.

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