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Studies on structures, vibrational frequencies of 3-amino-2-bromo pyridine based on density functional theory calculations

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ARTICLE INFO ABSTRACT Article history: The FT-IR and FT-Raman spectra of 3-amino-2-bromo pyridine(ABP) were recorded in the Received: 9 July 2011; regions 4000-400 cm⁻¹ and 4000-100 cm⁻¹. The fundamental vibrational frequencies and Received in revised form: intensity of vibrational bands were evaluated using density functional theory (DFT) and 29 August 2011; standard B3LYP/6-311+G** basis set combination. The vibrational spectra were interpreted, Accepted: 15 September 2011; with the aid of normal coordinate analysis based on a scaled quantum mechanical (SOM) force field. The Infrared and Raman spectra were also predicted from the calculated intensities. Keywords Comparison of simulated spectra with the experimental spectra provides important information Vibrational spectra, about the ability of the computational method to describe the vibrational modes. Unambiguous vibrational assignment of all the fundamentals was made using the total energy distribution FT-Raman spectra, (TED). DFT calculation.

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Introduction

FT-IR,

Pyridine and its derivatives constitute an important class of compounds with several applications in the pharmaceuticals and cosmetics sector as well as being used as pesticides. Bromo pyridines, in particular, are known to be hardly biodegradable and highly toxic to fresh water and marine bacteria and special attention is needed as these compounds can be found not only in the effluents of certain industrial activities but also in raw and drinking water due to spills or fugitive emissions.

Quantum chemical computational methods have proved to be an essential tool for interpreting and predicting the vibrational spectra [1,2]. A significant advancement in this area was made by combining semi empirical quantum mechanical method; ab initio quantum mechanical method and density functional theory (DFT), each method having its own advantage [3-6]. In scaled quantum mechanical (SQM) approach, the systematic errors of the computed harmonic force field are corrected by a few scale factors which are found to be well transferable between chemically related molecules [2,7,8] and were recommended for general use. In the present investigation, the vibrational analysis of ABP using the SQM force field method based on DFT calculation was presented. The infrared and Raman spectra of the title compound were also simulated utilizing the computed dipole derivatives for IR and polarisability derivatives for Raman activities.

Experimental details

Spectroscopically pure ABP was obtained from Lancaster chemical company, U.K., and used as such for the spectral The room temperature Fourier transform measurements. infrared spectra of ABP was recorded in the 4000-400 cm⁻¹ region at a resolution of ± 1 cm⁻¹, using BRUKER IFS-66V vacuum Fourier transform spectrometer, equipped with an MCT detector, a KBr beam splitter and globar source. The FT-Raman spectrum was recorded on the same instrument with FRA-106 Raman accessories in the region 4000-100 cm⁻¹. Nd:YAG laser operating at 200 mW power with 1064 nm excitation was used as source.

Computational details

In order to find the most optimized molecular geometry, the energy and vibrational frequency calculations were carried out for ABP with GAUSSIAN 03W software package [9] using the B3LYP functional [10,11] standard 6-311+G** (large) basis sets.

The Cartesian representation of the theoretical force constants have been computed at optimized geometry by assuming C1 point group symmetry. Scaling of the force field was performed according to the SQM procedure [12,13] using selective scaling in the natural internal coordinate representation [14,15].

Transformation of the force field and subsequent normal coordinate analysis including the least square refinement of the scale factors, calculation of the total energy distribution (TED) and the prediction of IR and Raman intensities were done on a PC with the MOLVIB program (version 7.0-G77) written by Sundius [16,17]. For the plots of simulated IR and Raman spectra, pure Lorentizian band shapes were used with a bandwidth of 10 cm⁻¹.

The symmetry of the molecule was also helpful in making vibrational assignments. By combining the results of the GAUSSVIEW program [18] with symmetry considerations, vibrational frequency assignments were made with a high degree of confidence. The defined local symmetry coordinates form complete set and matches quite well with the motions observed using the GAUSSVIEW program.

Prediction of Raman intensities

The Raman activities (Si) calculated with the GAUSSIAN 98W program and adjusted during the scaling procedure with MOLVIB were subsequently converted to relative Raman intensities (Ii) using the following relationship derived from the basic theory of Raman scattering [19-21].

$$I_{i} = \frac{f(v_{o} - v_{i})^{4} S_{i}}{v_{i} [1 - \exp(-hcv_{i} / KT)]} - \dots - (1)$$





Where v_0 is the exciting frequency (in cm⁻¹), v_i is the vibrational wavenumber of the ith normal mode; h, c and k are fundamental constants, and f is a suitably chosen common normalization factor for all peak intensities.

Results and discussion

Molecular geometry

The optimized molecular structure of ABP was shown in Fig.1. The global minimum energy obtained by the DFT structure optimization was presented in Table 1. The optimized geometrical parameters obtained by the large basis set calculation were presented in Table 2.



Fig. 1. The optimized molecular structure of ABP Table 1. Total energies of ABP, calculated at DFT (B3LYP)/6-31G* and (B3LYP)/6-311+G** level Method **Energies (Hartrees)** -2874.4390 6-31G*

6-311+G**

Table 2. Optimized geometrical parameters of ABP obtained by B3LYP/ 6-311+G** density functional calculations

-2874.7470

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Bond	Value	Bond	Value(Å)	Dihedral	Value(Å)
length	(Å)	angle		angle	
C2-N1	1.31111	C3-C2-N1	125.438883	C4-C3-C2-N1	0.000000
C3-C2	1.41111	C4-C3-C2	115.161521	C5-C4-C3-C2	0.000000
C4-C3	1.40297	C5-C4-C3	120.136330	C6-N1-C2-C3	0.000000
C5-C4	1.39187	C6-N1-C2	118.467542	Br7-C2-N1-C6	-180.000000
C6-N1	1.34016	Br7-C2-N1	116.533239	N8-C3-C2-N1	-180.000000
Br7-C2	1.93444	N8-C3-C2	122.800369	H9-C4-C3-C2	180.000000
N8-C3	1.39672	H9-C4-C3	119.186462	H10-C5-C4-C3	-180.000000
H9-C4	1.08767	H10-C5-C4	120.606785	H11-C6-N1-C2	-180.000000
H10-C5	1.08574	H11-C6-N1	116.355658	H12-N8-C3-C2	-29.999993
H11-C6	1.08681	H12-N8-C3	111.667064	H13-N8-C3-C2	-149.999962
H12-N8	1.01734	H13-N8-C3	111.627324		
H13-N8	1.01664				

Detailed description of vibrational modes can be given by means of normal coordinate analysis (NCA). For this purpose, the full set of 45 standard internal coordinates containing 12 redundancies were defined as given in Table 3.From these, a non-redundant set of local symmetry coordinates were constructed by suitable linear combinations of internal coordinates following the recommendations of Fogarasi et. al [14, 15] are summarized in Table 4. The theoretically calculated DFT force fields were transformed in this later set of vibrational coordinates and used in all subsequent calculations.

Analysis of vibrational spectra

The 33 normal modes of ABP are distributed in agreement with C1 symmetry. All the vibrations were active both in Raman scattering and infrared absorption. The detailed vibrational assignments of fundamental modes of ABP along with calculated IR, Raman intensities and normal mode descriptions (characterized by TED) were reported in Table 5.

For visual comparison, the observed and simulated FT-IR and FT-Raman spectra of ABP are produced in a common frequency scales in Fig. 2 & Fig. 3. Root mean square (RMS) values of frequencies were obtained in the study using the following expression,

$$RMS = \sqrt{\frac{1}{n-1}\sum_{i}^{n} \left(\upsilon_{i}^{calc} - \upsilon_{i}^{exp}\right)^{2}}$$

No(i)	symbol	Туре	Definition
Streching	-		
1-3	ri	C-H(aro)	C4-H9,C5-H10,C6-H11
4-6	Ri	C-N	C2-N1,C6-N1,C3-N8
7-10	Ri	C-C(aro)	C2-C3,C3-C4,C4-C5,C5-C6
11-12	\mathbf{p}_{i}	N-H	N8-H12,N8-H13
13	Pi	C-Br	C2-Br7
Bending	θ_i	C-H	H9-C4-C3,H9-C4-C5,H10-C5-C4,
14-19			H10-C5-C6,
			H11-C6-C5,H11-C6-N1
20-21	βi	C-Br	Br7-C2-N1,Br7-C2-C3
22-23	βi	C-N	N8-C3-C2, N8-C3-C4
24-25	βi	C-N-H	C3-N8-H12,C3-N8-H13
26	γi	N-H-N	H12-N8-H13
27-32	α_i	C-C-	N1-C2-C3,C2-C3-C4,C3-C4-C5,
		C(ring)	C4-C5-C6,C5-C6-N1,C6-N1-C2
Out-of-			H11-C6-C5-N1,
plane	ωi	C-H	H10-C5-C4-C6,
33-35			H9-C4-C3-C5
36	ωi	C-Br	Br7-C2-N1-C3
27		CCN	Nº C2 C2 C4

Table 3. Definition of internal coordinates of ABP

		w1	
38-39	8-H13,C2-C3-N8-H1	ωi	-N8-H12
Torison	3-C4,C2-C3-C4-C5,		C4-C5,
40-45	5-C6,C4-C5-C6-N1,	τ_{i}	C6-N1,
	1-C2,C6-N1-C2-C3		C2-C3
	1-C2,C6-N1-	U 1	ĺ

^{*}for numbering of atom refer Fig. 1

Table 4. Definition of local symmetry coordinates and the value corresponding scale factors used to correct the force Calde for ADD

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No.(i)	Symbol ^a	Definition ^b	Scale factors used in calculation
1-3	C-H(aro)	r1,r2,r3	0.920
4-6	C-N	R4,R5,R6	0.927
7-10	C-C(aro)	R7,R8,R9,R10	0.927
11-12	N-H	p11,p12	0.918
13	C-Br	P13	0.902
14-16	C-H	$(\theta 14 - \theta 15)/\sqrt{2}, (\theta 16 - \theta 17)/\sqrt{2}, (\theta 18 - \theta 19)/\sqrt{2}$	0.942
17	C-Br	$(\theta 20 - \theta 21)/\sqrt{2}$	0.947
18	C-N	$(\theta 22 - \theta 23)/\sqrt{2}$	
19	C-N-H	$(\beta 24 - \beta 25) / \sqrt{2}$	0.947
20	N-H-N	γ26	0.979
21	C-C- C(ring)	$(\alpha 27 - \alpha 28 + \alpha 29 - \alpha 30 + \alpha 31 - \alpha 32)/$ $\sqrt{6}$	0.986
22	C-C- C(ring)	$(2\alpha 27 - \alpha 28 - \alpha 29 + 2\alpha 30 - \alpha 31 - \alpha 32)/\sqrt{12}$	0.986
23	C-C- C(ring)	$(\alpha 28 - \alpha 29 + \alpha 31 - \alpha 32)/2$	0.986
24-26	C-H	ω33, ω34, ω35	0.963
27	C-Br	ω36	0.965
28	C-C-N	ω37	0.935
29-30	C-N-H	ω38, ω39	0.963
31	C-C- C(ring)	$(\tau 40 - \tau 41 + \tau 42 - \tau 43 + \tau 44 - \tau 45)/\sqrt{6}$	0.935
32	C-C- C(ring)	$(\tau 40 - \tau 42 + \tau 43 - \tau 44)/2$	0.935
33	C-C- C(ring)	(-τ40+2τ41-τ42-τ43+2τ44- τ45)/√12	0.935

^a These symbols are used for description of the normal modes by TED in Table 5.

^b The internal coordinates used here are defined in Table 3.



Fig. 2 FT-IR spectra of ABP (a) Observed (b) Calculated with B3LYP/6-311+G**

 Table 5. Detailed assignments of fundamental vibrations of ABP by normal mode analysis based on SQM force field calculation

 Observed frequency
 Calculated frequency (cm⁻¹) with

Na	Symmetry	(cm	1 ⁻¹)	B3LY	B3LYP/6-311+G ^{**} force field		field	TED (%) among type of internal coordinates ^c		
INO.	Species C1	Infrared	Raman	Unscaled	Scaled	IR ^a Ai	Raman ^b I:			
1	А		3693	3663	3580	0.823	3.048	NH(100)		
2	А	3448		3581	3500	1.106	1.138	NH(100)		
3	А		3238	3291	3217	10.281	1.658	CH(99)		
4	А			3270	3196	0.644	6.537	CH(99)		
5	А	2853		3257	3184	32.645	1.927	CH(99)		
6	А	1789	1786	1743	1704	1.929	2.487	bHNH (85), tNH2 (9)		
7	А			1676	1638	2.068	0.687	CC(46), CN(19), bCH(13), bHNH(11), bring(8)		
8	А	1621	1623	1651	1614	2.764	3.518	CC(54), bCH(18), CN(11), bring(9)		
9	А	1555	1500	1533	1499	15.338	5.829	bCH(48), CN(26), CC(20)		
10	А	1457		1515	1481	23.688	7.651	CN(30), bCH(29), CC(20), bCNH(10), bCN(7)		
11	А	1417	1350	1385	1354	31.408	1.240	CN(45), bCH(20), CC(19), bCNH(10)		
12	А	1312		1366	1335	90.911	6.224	CC(40), CN(32), bCH(24)		
13	А	1267		1302	1273	58.978	3.868	CN(48), bCH(30), bCNH(10), CC(6)		
14	А			1202	1175	194.38 3	12.416	bCH(50), CC(26), bCNH (20)		
15	А	1134		1143	1118	13.515	3.823	CC(30), bCNH (29), bCH(12), CN(10), bring(9), CBr(7)		
16	А	1079	1111	1120	1095	1.566	0.142	CC(48), bCH(30), CN(17)		
17	А	1032	1068	1077	1053	54.847	10.136	bring(56), CC(26), CBr(8)		
18	А		986	994	972	1.689	13.162	gCH(88), tring(11)		
19	А		935	943	922	56.213	1.034	gCH(79), tring(6), tNH2 (5), gCN(5)		
20	А	891	894	901	881	11.896	1.346	tNH2 (43), bHNH (25), bring(8), CC(7), gCH(6)		
21	А	841	833	840	821	16.045	8.090	gCH(32), tNH2 (14), bring(13), CN(13), bHNH (8), tring(8)		
22	А	768	803	810	792	4.290	6.363	gCH(31), tNH2 (30), bHNH (20), CN(10), bring(6)		
23	А	711	755	761	744	20.840	6.821	tring(52),tNH2(15),gCBr(14),gCN(11),gCH(6)		
24	А	659	682	687	672	126.69 6	8.081	bring(66), CC(13), CBr(12), CN(7)		
25	А		572	577	564	28.136	6.579	bring(54), tring(10), tNH2(8), gCN(7), CN(6)		
26	А	550	566	570	558	20.030	6.374	tring(35),tNH2 (25),gCN(21),gCH(7),bring(5)		
27	А		470	474	464	8.750	24.095	tring(56), gCBr (23), gCN(10), gCH(9)		
28	А	445	446	450	440	84.684	14.793	bCN(65), bCBr (11), CBr(6), bCNH (5)		
29	А		307	310	303	7.193	90.342	tNH2 (98)		
30	А		293	295	289	15.122	87.655	tNH2 (49), CBr(32), bCBr (6), bring(6)		
31	А		274	276	270	21.232	223.230	tNH2 (80), tring(9)		
32	А		221	223	218	11.347	146.678	tNH2 (61), bCBr (28), bCN(6)		
33	А		134	136	133	11.070	52.458	tring(78), gCBr (12), tNH2 (6)		

Abbreviations used: b, bending; g, wagging; t, torsion; s, strong; vs, very strong; w, weak; vw, very weak; ^a Relative absorption intensities normalized with highest peak absorption

^b Relative Raman intensities calculated by Eq.1 and normalized to 100.

^c For the notations used see Table 4.



The RMS error of the observed and calculated frequencies (unscaled / B3LYP/6-311+G^{**}) of ABP was found to be 116 cm⁻¹. This is quite obvious; since the frequencies calculated on the basis of quantum mechanical force fields usually differ appreciably from observed frequencies. This is partly due to the neglect of anharmonicity and partly due to the approximate nature of the quantum mechanical methods. In order to reduce the overall deviation between the unscaled and observed fundamental frequencies, scale factors were applied in the normal coordinate analysis and the subsequent least square fit refinement algorithm resulted into a very close agreement between the observed fundamentals and the scaled frequencies.

Refinement of the scaling factors applied in this study achieved a weighted mean deviation of 7 cm^{-1} between the experimental and scaled frequencies of the title compound.

C–NH₂ vibrations

The scaled C–NH₂ symmetric and asymmetric stretches in the range 3400–3600 cm⁻¹ is in agreement with experimental symmetric and asymmetric stretching value of 3581 and 3663 cm⁻¹. The NH₂ wagging mode has been identified at 289,303,564,744 cm⁻¹ is in agreement with recorded value of 293,307,572,550,711 cm⁻¹.

The NH₂ twisting vibration calculated to be 1175,1273,1354 cm⁻¹ is very good agreement with recored value of 1267,1350 cm⁻¹ in FT-IR/FT Raman spectrum. The FT-IR/FT Raman stretching mode at 1267,1312 cm⁻¹ corresponding to C-NH₂ moiety was calculated to be 1273,1335 cm⁻¹.The C–NH2 out-of-plane and in-plane bending vibrations at 440 and 464 cm⁻¹, respectively are also in good agreement with the assignment in the experimental data. It should be emphasized that the wave number calculated by B3LYP/6-311 + G(d, p) method for the NH₂ torsion mode at 303 cm⁻¹ is not in agreement with the experimental value of 307 cm⁻¹[22-30].

C–C vibrations

The C–C aromatic stretch, known as semicircle stretching, predicted at 1614 cm⁻¹ is in excellent agreement with experimental observations of 1621/1623 cm⁻¹ in FTIR/FT-Raman spectrum. The ring breathing mode at 881 cm⁻¹ coincides

satisfactorily with medium strong FT-Raman band at 891 cm⁻¹. The theoretically calculated C–C–C out-of- plane and in-plane bending modes have been found to be consistent with the recorded spectral data.

C Br vibrations

The assignments of CBr stretching and deformation vibrations have been made on the basis of the calculated PED and by the halogen-substituted benzene derivatives. C–X group (X = Cl, Br, I) vibrations are assigned in the frequency range of 1100-500 cm⁻¹. In FT-Raman spectrum the strong band at 221 cm⁻¹ is assigned to C–Br stretching vibration coupled with ring deformation. The theoretical wavenumber of this band, 464,289 cm⁻¹ coincides well with the experimental, and the calculated PED confirms this assignment. The C–Br out-of-plane bending and in-plane bending vibrations are assigned to the Raman bands at 221 and 134,293 cm⁻¹, respectively. This is in agreement with the calculated value.

Phenyl ring vibration

The phenyl ring vibrations are not particularly sensitive to the nature of substituent. As revealed by PED, two modes are associated mainly with the CH in-plane bending vibration. These modes are observed at the following wavenumbers, 1032 and 1134 cm⁻¹ in FT-IR and 1068 cm⁻¹ in FT-Raman, respectively. The ring breathing vibration is assigned to the band at 986 cm⁻¹ observed in the FT-IR and FT-Raman spectra. This wavenumber is in excellent agreement with the theoretical predictions, 972 cm⁻¹, and is supported by the literature data [23]. The C C aromatic stretch, known as semicircle stretching, predicted at 1614 cm⁻¹ is in reasonable agreement with that observed in FT IR/FT-Raman spectrum.

C-H vibrations

The assignment of carbon-hydrogen stretching modes is straight forward on the basis of the scaled ab initio predicted frequencies and well known "group frequencies". The hetero aromatic structure shows the presence of C-H stretching vibrations in the region 3100-3000 cm⁻¹ which is the characteristic region for ready identification of C-H stretching vibration. In this region, the bands are not affected appreciably by the nature of the substituents. From Figs. 2 and 3, it could be seen that there is a broad absorption band in the region 3800-3200 cm⁻¹ upon which the C-H stretching frequencies are superimposed.

Hence, the FT-Raman band at 3238 cm⁻¹ have been designated to C–H stretching vibrations. The CH in-plane bending vibrations assigned at 935,986,1079,1134 cm⁻¹ and at 672,711,744,792 cm⁻¹ are assigned for the CH out-of-plane bending mode correlates well with the recorded FT-IR/FT-Raman values.

Hyperpolarizability calculations

The first-order hyperpolarizibility (β_{ijk}) of the novel molecular system of ABP is calculated using 3-21 G (d,p) basis set based on finite field approach. Hyperpolarizibility is a third rank tensor that can be described by a 3 x 3 x 3 matrix. It strongly depends on the method and basis set used. The 27 components of 3D matrix can be reduced to 10 components due to Kleinman [29] symmetry. The calculated first-order hyperpolarizability (β_{total}) of ABP is 1.5132x10⁻³⁰ esu, which is nearly 8 times greater than that of urea (0.1947 x 10⁻³⁰ esu). The calculated dipole moment (μ) and first-order hyperpolarizibility (β) are shown in Table 4.6. The theoretical calculation seems to be more helpful in determination of particular components of β tensor than in establishing the real values of β . Domination of particular components indicates on a substantial delocalization of charges in those directions. It is noticed that in β_{zzz} (which is the principal dipole moment axis and it is parallel to the charge transfer axis) direction, the biggest values of hyperpolarizability are noticed and subsequently delocalization of electron cloud is more in that direction. The higher dipole moment values are associated, in general, with even larger projection of β_{total} quantities. The electric dipoles may enhance, oppose or at least bring the dipoles out of the required net alignment necessary for NLO properties such as β_{total} values. The connection between the electric dipole moments of an organic molecule having donoracceptor substituent and first hyperpolarizability is widely recognized in the literature [30]. The maximum β was due to the behavior of non-zero µ value. One of the conclusions obtained from this work is that non-zero μ value may enable the finding of a non-zero ß value. Of course Hartee-Fock calculations depend on the mathematical method and basis set used for a polyatomic molecule.

Fig. 4 shows the highest occupied molecule orbital (HOMO) and lowest unoccupied molecule orbital (LUMO) of ABP. There is an inverse relationship between hyperpolarizability and HOMO–LUMO.

HOMO energy = -0.327 a.u

LUMO energy = 0.113 a.u HOMO-LUMO energy gap = 0.440 a.u

Table 6. The dipole moment (μ) and first-order hyperpolarizibility (β) of ABP derived from DFT calculations

β_{xxx}	1.3199
β_{xxy}	-10.653
β_{xyy}	29.883
β _{yyy}	-25.793
β _{zxx}	-555.48
β_{xyz}	411.91
β _{zyy}	789.23
β_{xzz}	-12.099
β_{yzz}	15.135
βzz	8120.6
β_{total}	1.5132
μ _x	1.07584234
μ _y	1.06760453
μ _z	0.00107001
μ	1.46441691

Dipole moment (µ) in Debye, hyperpolarizibility $\beta(-2\omega;\omega,\omega) = 10^{-30}$ esu.



Fig. 4. Representation of the orbital involved in the electronic transition for (a) HOMO (b) LUMO (c) HOMO, LUMO (d) Occupied (e) Virtual (f) All

Electronic excitation mechanism

The static polarizability value[31-32] is proportional to the optical intensity and inversely proportional to the cube of transition energy. With this concept, larger oscillator strength (f_n) and $\Delta \mu_{gn}$ with lower transition energy (E_{gn}) is favourable to obtain large first static polarizability values. Electronic excitation energies, oscillator strength and nature of the respective excited states were calculated by the closed-shell singlet calculation method and are summarized in Table 7. Representation of the orbital involved in the electronic transition was shown in Fig. 5.

Fable	7. Comput	ed abs	orption	wavel	ength	(λ_{ng}) , en	ergy
(E _{ng}),	oscillator	streng	th (f _n) ε	and its	major	contribu	tion

n	λ_{ng}	Eng	f _n	Major contribution
1	201.2	6.16	0.1252	H-0->L+0(+70%)
2	194.0	6.39	0.0460	H-0->L+1(+26%),
				H-3->L+0(+22%)
3	190.2	6.52	0.0475	H-0->L+1(+40%),
				H-3->L+0(28%)





Fig. 5. Representation of the orbital involved in the electronic transition for (a) HOMO-0 (b) LUMO+0 (c) LUMO+1 (e) HOMO-3

Conclusion

In this work, the SQM force field method based on DFT calculations at the B3LYP/6-311+ G^{**} level have been carried out to analyze the vibrational frequencies of ABP. Refinement of the scaling factors applied in this study achieved a weighted RMS deviation of 7 cm⁻¹ between the experimental and scaled frequencies. This close agreement established between the experimental and scaled frequencies obtained using large basis set (6-311+ G^{**}) calculations has proved to be more reliable and accurate than the calculations using lower basis sets.

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References

[1] B.A. Hess Jr., J. Schaad, P. Carsky, R. Zahraduik, Chem. Rev. 86, 709 (1986) .

[2] P. Pulay, X.Zhou, G. Fogarasi, in: R. Fransto (Ed.), NATO AS Series, Vol.C, 406, Kluwer, Dordrecht, P.99, (1993).

[3] W. J. Hehre, L. Random, P.V.R. Schleyer, J.A. Pople, Ab Initio Molecular Orbital Theory, Wiley, New York, (1986).

[4] D.N. Shin, J.W. Hahn, K.H. Jung, T.K. Ha, J.Raman Spectrosc. 29,245 (1998).

[5] T. Ziegler, Chem. Rev. 91, 651 (1991).

[6] C.E. Blom, C. Altona, Mol. Phys. 31, 1377 (1976).

[7] G.R. De Mare, Y.N. Panchenko, C.W. Bock, J. Phys. Chem. 98, 1416 (1994).

[8] Y. Yamakita, M. Tasuni, J. Phys. Chem. 99, 8524 (1995).
[9] M.J. Frisch, G.W. Trucks, H.B. Schlega, G.E. Scuseria, M.A. Robb, J.R. Cheesman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, N. Roga, P. Salvador, J.J. Dannenberg, D.K. Malick, A.D. Rabuck, K. Rahavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Penng, A. Nanayakkara, M. Challa-Combe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle and J.A. Pople, Gaussian 98,

Revision A 11.4, Gaussian Inc., Pittsburgh, PA (2002).

- [10] A.D. Becke, J.Chem. Phys.98, 5648 (1993).
- [11] C. Lee, W.Yang, R.G. Parr, Phys. Rev. B.37, 785 (1998).

[12] P. Pulay, G. Fogarasi, G. Pongor, J.E. Boggs, A. Vargha, J.Am. Chem. Soc. 105, 7037 (1983).

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

[14] G. Fogarasi and P. Pulay In: J.R. Durig, Editor, Vibrational Spectra and Structure vol. 14, Elsevier, Amsterdam, p. 125 (Chapter 3), (1985).

[15] G. Fogarasi, X. Xhov, P.W. Taylor and P. Pulay, J. Am. Chem. Soc. p. 8191, 114 (1992).

[16] T. Sundius. J.Mol. Struct. 218, 321 (1990).

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

(b) MOLVIB (v.7.0), Calculation of harmonic force fields and vibrational modes of molecules, QCPE Program No. 807, (2002).

[18] A. Frisch, A.B. Nielson and A.J. Holder, Gaussview Users Mannual, Gaussian Inc., Pittsburgh, PA (2000).

[19] P.L. Polavarapu, J. Phys. Chem. 94, 8106 (1990).

[20] G. Keresztury, S. Holly, J. Varga, G. Besenyei, A.V. Wang, J.R. Durig, Spectrochim. Acta 49A,2007 (1993).

[21] G. Keresztury, in: J.M. Chalmers and P.R. Griffiths(Eds), Handbook of Vibrational Spectroscopy vol.1, John Wiley & Sons Ltd. p. 71, (2002).

[22] H.D. Cohen, C.C.J. Roothan, J. Chem. Phys. S34, 435 (1965).

[23] D.N. Sathyanarayana, Vibrational Spectroscopy—Theory and Applications, second ed., New Age International (P) Limited Publishers, New Delhi, (2004).

[24] George Socrates, Infrared and Raman Characteristic Group Frequencies -Tables and Charts (third ed.), John Wiley & Sons, Chichester (2001).

[25] V. Krishna kumar, R. John Xavier, Indian J. Pure Appl. Phys. 41, 95 (2003).

[26] J. Mohan, Organic Spectroscopy-Principles and Applications, second ed., Narosa Publishing House, New Delhi, (2001).

[27] B. Lakshmaiah, G. Ramana Rao, J. Raman Spectrosc. 20, 439 (1989).

[28] W.O. George, J.E. Goodfield, W.F. Maddams, Spectrochim. Acta A 41A, 1243 (1985).

[29] D.A. Kleinman, Phys. Rev. 126,1977 (1962).

[30] P.N. Prasad, D.J. Williams, Introduction to Nonlinear Optical Effects in Molecules and Polymers, Wiley, New York, (1991).

[31]. K. Wu, C. Liu, C. Mang, Opt. Mater. 29 (2007) 1129– 1137.

[32] S. Iran, W.M.F. Fabian, Dyes Pigments 70 (2006) 91-96.