Density Functional Theory and ab initio Hartree-Fock Calculations of Molecular Structure and Vibrational Spectra of Anilinium Nitrate

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Z. Naturforsch. **63a,** 712 – 720 (2008); received February 1, 2008

The molecular geometry, vibrational frequencies, infrared intensities, Raman scattering activities and several thermodynamic parameters of anilinium nitrate in the ground state have been calculated by both Hartree-Fock (HF) and three density functional theory (DFT) methods (B3LYP, BLYP and B3PW91) using the 6-31G(d) basis set. The results of the optimized molecular structure are presented and compared with the experimental X-ray structure. The optimized geometric bond lengths are described very well by the HF method while bond angles are reproduced more accurately by the DFT methods. Comparison between the observed fundamental vibrational frequencies of anilinium nitrate and the results of DFT and HF methods indicates that B3LYP is superior to the scaled HF, BLYP and B3PW91 approaches for molecular vibrational problems. The computed vibrational frequencies are used to determine the types of molecular motions associated with each of the experimental bands observed. In addition, calculated results are related to the linear correlation plot of computed data versus experimental geometric parameters and IR data.

Key words: Anilinium Nitrate; DFT; HF; IR and Raman Spectra; Structure Elucidation; Vibrational Assignment; Thermodynamic Parameters.

1. Introduction

In the literature, there is a number of papers about experimental vibrational assignments, the harmonic force field, vibrational spectra, and infrared and Raman vibrational spectroscopic studies of metal(II) complexes of anilinium nitrate [1].

Density functional theory (DTF) calculations are reported to provide excellent vibrational frequencies of organic compounds if the calculated frequencies are scaled to compensate the approximate treatment of electron correlation, the basis set deficiencies and the anharmonicity [2, 3]. Rauhut and Pulay [4] calculated the vibrational spectra of thirty one molecules using the B3LYP method with the 6-31G(d) basis set. In their work, they calculated also vibrational frequencies of twenty smaller molecules, whose experimental vibrational frequencies were well assigned, and derived transferable scaling factors by using the least-square method. The scaling factors were successfully applied to other eleven larger molecules. Thus, vibrational frequencies calculated by the B3LYP method with the 6-31G(d) basis set can be utilized to eliminate the uncertainties in the fundamental assignments of infrared and Raman vibrational spectra [5].

Marchewka and Pietraszko studied X-ray diffraction (XRD) as well as vibrational spectra of anilinium nitrate ($C_6H_8N^+ \cdot NO_3^-$) [1]. To the best of our knowledge, no estimates of theoretical results for anilinium nitrate have been reported yet. In this study, we have calculated the vibrational frequencies of the ground state of anilinium nitrate to distinguish the fundamental frequencies from the experimental vibrational frequencies and geometric parameters, using HF and DFT (B3LYP, BLYP and B3PW91) methods. These calculations are valuable for providing insight into the vibrational spectrum and molecular parameters.

2. Computational Details

The molecular structures of anilinium nitrate in the ground state (in vacuo) are optimized by HF and B3LYP, BLYP and B3PW91 methods with the 6-31G(d) basis set. Density functionals for all studies reported in this paper are

$$E_{XC} = (1-a_0)E_X^{\mathrm{LSDA}} + a_0 E_X^{\mathrm{HF}} + a_X \Delta E_X^{\mathrm{B88}} + a_C E_C^{\mathrm{LYP}} + (1-a_C)E_C^{\mathrm{VWN}}.$$

Here the energy terms are the Slater exchange, the HF

exchange, Becke's exchange functional correction, the gradient-corrected correlation functional of Lee, Yang and Parr, and the local correlation functional of Vosko, Wilk and Nusair [6], respectively.

Similarly, the B3PW91 model is obtained by replacing the VWN and LYP correlation functionals with the PW91 one [7]. For the purpose of comparison, computations were performed with standard density functional (DF) methods. In particular we have used the Becke exchange [8] in conjunction with either the PW91 [7] or the LYP [9] correlation functionals to obtain the BPW91 and BLYP procedures, respectively. Finally, the influence of the HF/DF exchange ratio has been examined by some computations using a 'half-and-half' approach in combination with the LYP correlation functional [10].

Default optimization specifications were used in general. If symmetry constraints let to transition state or hilltop instead of minimum, this would show as the presence of one or more imaginary frequencies not belonging to the totally symmetric irreducible representation. Four sets of vibrational frequencies for these species were calculated by these methods and then scaled by 0.8929, 0.9613, 0.9940 and 0.9772 [11], respectively. Molecular geometry is not restricted and all the calculations were performed by using the GaussView molecular visualization program [12] and Gaussian 98 program package [13].

3. Results and Discussion

3.1. Geometrical Structure

The atomic numbering scheme, the hydrogen bonds [1] and the theoretical geometric structure of anilinium nitrate are shown in Figs. 1a–c. Its geometric structure is orthorhombic, and the space group is *Pbca* with the cell dimensions $a = 10.158(2)$ Å, $b = 9.277(2)$ Å, $c = 16.177(3)$ Å and the volume $V = 1524.5(5)$ Å^3. The primitive unit cell contains eight molecules [1].

The parameters of anilinium nitrate bond (lengths and angles) optimized by HF, B3LYP, BLYP and B3PW91 methods with 6-31G(d) as the basis set are listed in Table 1; they are compared with the experimental crystal structure data of anilinium nitrate. Positively charged anilinium cations and NO_3^- anions are present in the structure. The N(1)-O(3), N(1)-O(2), N(1)-O(1) were found to be 1.2294 Å, 1.2414 Å and 1.2669 Å [1]. Herein these bond lengths have been calculated to be 1.228 Å, 1.209 Å, 1.260 Å (HF); 1.209 Å, 1.230 Å, 1.270 Å (B3LYP); 1.225 Å, 1.215 Å, 1.247 Å (BLYP); and 1.225 Å, 1.205 Å, 1.259 Å (B3PW91). Moreover, we took into account positively charged anilinium cations with the bond length N(0)-H(1N), N(0)-H(2N), N(0)-H(3N); these bond lengths were observed to be 0.912 Å, 0.937 Å, 0.945 Å [1]. In the present study, we have calculated 1.065 Å, 1.006 Å, 1.012 Å using HF; 1.018 Å, 1.017 Å, 1.027 Å using B3LYP; 1.025 Å, 1.071 Å, 1.026 Å using BLYP; and

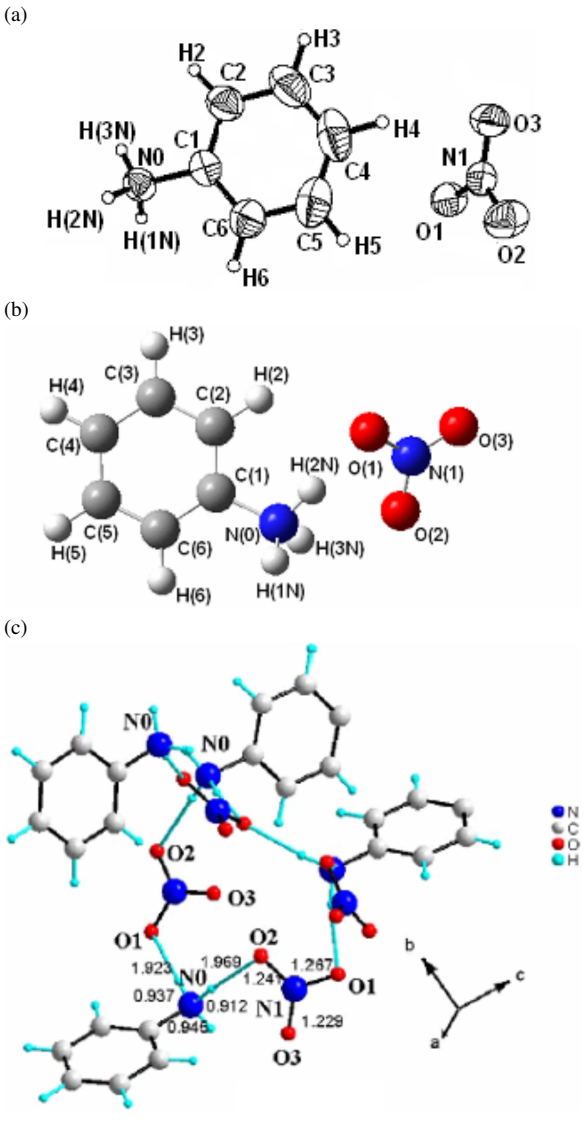

Fig. 1. (a) The experimental geometric structure of anilinium nitrate taken from [1]. (b) The theoretical geometric structure of anilinium nitrate. (c) The hydrogen bonds in anilinium nitrate taken from [1].

Table 1. Optimized and experimental geometries of the ground state of anilinium nitrate.

Parameter	Exp. [1]	Calculated [6-31G(d)]			
		HF	B3LYP	BLYP	B3PW91
Bond lengths (Å)					
N(0)-C(1)	1.4662(10)	1.458	1.430	1.441	1.424
N(0)-H(1N)	0.912(9)	1.065	1.018	1.025	1.016
N(0)-H(2N)	0.937(10)	1.006	1.017	1.071	1.017
N(0)-H(3N)	0.945(10)	1.012	1.027	1.026	1.067
N(1)-O(3)	1.2294(9)	1.228	1.209	1.225	1.225
N(1)-O(2)	1.2414(9)	1.209	1.230	1.215	1.205
N(1)-O(1)	1.2669(9)	1.260	1.270	1.247	1.259
C(1)-C(2)	1.3723(12)	1.382	1.398	1.410	1.398
C(1)-C(6)	1.3748(12)	1.381	1.400	1.408	1.396
C(2)-C(3)	1.3870(13)	1.384	1.395	1.403	1.391
C(2)-H(2)	0.985(10)	1.076	1.088	1.094	1.087
C(6)-C(5)	1.3900(14)	1.386	1.393	1.405	1.392
C(6)-H(6)	0.972(10)	1.074	1.086	1.095	1.088
C(4)-C(3)	1.3666(16)	1.386	1.395	1.406	1.394
C(4)-C(5)	1.3675(16)	1.385	1.396	1.405	1.393
C(4)-H(4)	0.976(11)	1.074	1.086	1.093	1.086
C(5)-H(5)	0.928(12)	1.074	1.086	1.093	1.086
C(3)-H(3)	0.976(12)	1.074	1.086	1.093	1.086
Bond angles (°)					
C(1)-N(0)-H(1N)	112.2(6)	112.8	112.2	112.2	112.3
C(1)-N(0)-H(2N)	111.3(6)	112.5	112.2	112.1	112.3
H(1N)-N(0)-H(2N)	108.5(8)	108.9	109.0	109.0	109.1
C(1)-N(0)-H(3N)	110.3(6)	112.2	112.4	112.1	111.8
H(1N)-N(0)-H(3N)	106.5(8)	104.2	105.3	108.0	108.0
H(2N)-N(0)-H(3N)	107.8(8)	108.2	108.3	106.8	106.0
O(3)-N(1)-O(2)	121.83(7)	122.4	120.1	123.0	122.5
O(3)-N(1)-O(1)	119.72(7)	117.8	118.2	118.3	118.2
O(2)-N(1)-O(1)	118.46(6)	119.8	120.5	117.6	117.8
C(2)-C(1)-C(6)	121.80(8)	121.8	121.8	119.8	119.7
C(2)-C(1)-N(0)	119.35(7)	119.8	120.5	119.5	119.6
C(6)-C(1)-N(0)	118.85(7)	118.2	119.5	120.5	120.5
C(4)-C(3)-C(2)	120.34(10)	120.0	120.4	120.6	120.6
C(4)-C(3)-H(3)	120.7(7)	120.2	120.1	120.1	120.1
C(1)-C(2)-C(3)	118.66(9)	118.9	119.9	119.7	119.8
C(1)-C(2)-H(2)	119.6(5)	120.6	119.8	119.5	119.6
C(3)-C(2)-H(2)	121.7(5)	120.3	120.1	120.6	120.5
C(1)-C(6)-C(5)	118.39(9)	118.6	119.7	119.9	119.9
C(1)-C(6)-H(6)	121.1(6)	121.8	120.5	119.8	119.9
C(5)-C(6)-H(6)	120.4(6)	121.2	120.6	120.1	120.3
C(3)-C(4)-C(5)	120.41(9)	120.1	120.3	119.3	119.3
C(3)-C(4)-H(4)	118.2(6)	119.8	119.3	120.3	120.3
C(5)-C(4)-H(4)	121.3(6)	119.9	120.3	120.5	120.3
C(4)-C(5)-C(6)	120.39(10)	120.3	120.6	120.4	120.4
C(4)-C(5)-H(5)	123.8(7)	121.2	122.1	122.1	122.6
C(6)-C(5)-H(5)	115.8(7)	117.4	117.2	117.3	117.3
C(2)-C(3)-H(3)	118.9(7)	119.6	119.3	119.2	119.2
Torsion angles (°)					
C(6)-C(1)-C(2)-C(3)	−0.66(13)	−0.2	−0.2	−0.5	−0.5
N(0)-C(1)-C(2)-C(3)	179.19(8)	−179.2	−177.1	−177.2	−177.4
C(2)-C(1)-C(6)-C(5)	0.81(14)	0.2	0.5	0.2	0.3
N(0)-C(1)-C(6)-C(5)	−179.05(8)	179.1	177.4	−179.8	177.1
C(3)-C(4)-C(5)-C(6)	−0.58(17)	−0.05	−0.01	−0.2	−0.2
C(1)-C(6)-C(5)-C(4)	−0.18(16)	−0.10	−0.4	−0.1	−0.09
C(5)-C(4)-C(3)-C(2)	0.73(16)	0.11	0.3	0.01	0.02
C(1)-C(2)-C(3)-C(4)	−0.12(15)	−0.2	−0.1	−0.3	−0.3

1.016 Å, 1.017 Å, 1.067 Å using B3PW91 methods. Furthermore, the H(1N)-N(0)-H(2N) bond angle was observed to be 108.5° [1]; this angle has been calculated to be 108.9°, 109.0°, 109.0° and 109.1° by using HF, B3LYP, BLYP and B3PW91 methods, respectively (see Table 1). Additionally, the N(0)-C(1)-C(2)-C(3) and N(0)-C(1)-C(6)-C(5) torsion angles were found to be 179.19° and −179.05° [1]; these angles have been calculated to be −179.2°, 179.1° by HF; −177.1°, 177.4° by B3LYP; −177.2°, 179.8° by BLYP; and −177.4°, 177.1° by B3PW91 methods (see Table 1). The differences result from the crystal structure of anilinium nitrate (Fig. 1). The hydrogen bond in anilinium nitrate [1], shown in Fig. 1c, is consistent with the theoretical geometric structure of anilinium nitrate (Fig. 1b). The other optimized geometric parameters of anilinium nitrate are shown in Table 1. For the optimized geometric parameters, various methods including the HF method estimated some bond lengths to some extent [14 – 17]. It has noted that the experimental results belong to the solid phase, and theoretical calculations belong to the gaseous phase. The correlations between the experimental and calculated geometric parameters are obtained by several methods (Fig. 2). According to our calculations, the HF method correlates well for the bond length with the other methods (Table 1, Fig. 2). The largest difference between experimental and calculated HF, BLYP and B3PW91 bond lengths are about 0.154 Å, 0.166 Å, 0.159 Å, respectively. The B3LYP method leads to geometric parameters, which are much closer to experimental ones. The bond angles provided by the B3LYP method are the closest to the experimental values (Table 1). The largest difference is about 3.6° at the second angle. As a result, the optimized bond lengths by the HF method and bond angles by the DFT (B3LYP) method give the best agreement with the experimental values.

3.2. Assignments of the Vibrational Modes

We have not found any theoretical results for anilinium nitrate in the literature, and the experimental vibrational spectra of anilinium nitrate used in this study have been taken by Marchewka and Pietraszko [1]. We have calculated the theoretical vibrational spectra of anilinium nitrate by using HF, B3LYP, BLYP and B3PW91 methods with the 6-31G(d) basis set. We have compared our calculations of anilinium nitrate with the experimental results. The bands calculated in the measured region 4000 – 80 cm^{-1} arise from the vi-

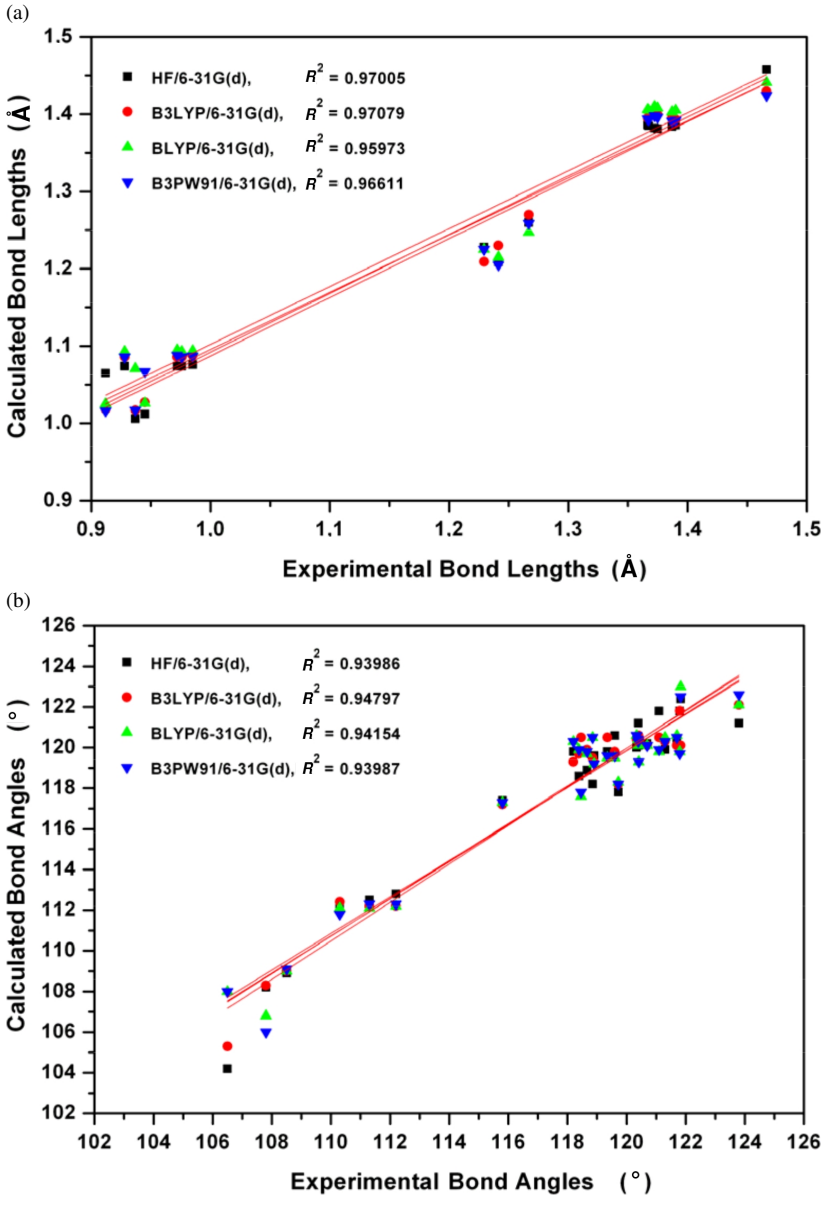

Fig. 2. (a) Correlation graphs of calculated and experimental molecular bond lengths of anilinium nitrate. (b) Correlation graphs of calculated and experimental molecular bond angles of anilinium nitrate.

brations of protons in the hydrogen bonds, the internal vibrations of the mono-protonated anilinium cations and nitrate anions, and the vibrations of the lattice. The vibrational band assignments have been made by using the Gauss-View molecular visualization program [12]. Theoretical and experimental results of anilinium nitrate are tabulated in Table 2. Some new bands were observed too. These features corroborate the complex formation. The new bands at 1636 and 795 cm^{-1} appeared in the spectrum of anilinium nitrate [1]. These bands have been calculated at 1631 and 773, 781, 805, 799 cm^{-1}.

The proton transfer from nitric acid to the amino group of the aniline molecule is vibrationally proved by the presence of strong infrared bands at 1586 and 1553 cm^{-1}. We have calculated these bands (NH_3 asym./sym. def.) at 1592 cm^{-1} (weak band), 1550 cm^{-1} (medium band) by the HF method, 1593 cm^{-1} (weak band) by the B3LYP method, 1592 cm^{-1} (very weak band), 1554 cm^{-1} (weak band)

Table 2. Comparison of the observed and calculated vibrational spectra of anilinium nitrate.

Assignment	Exp. [1] (cm^{-1}) IR with powder	Exp. [1] (cm^{-1}) Raman with powder	Scaled frequencies [6-31G(d)] (cm^{-1}) HF	I_{IR}[a]	I_{Raman}[b]	B3LYP	I_{IR}[a]	I_{Raman}[b]	BLYP	I_{IR}[a]	I_{Raman}[b]	B3PW91	I_{IR}[a]	I_{Raman}[b]
NH_3 asym. str.	3187 vssh	3176 vw	3260	137.2	71.8	3259	16.4	125.8	3357	11.2	155.0	3439	20.4	122.5
NH_3 sym. str.	3108 m	3102 vw	3040	8.9	219.3	3092	13.6	262.5	3110	16.4	280.7	3154	11.9	255.4
C-H str.	3085 m	30 85 vw	3034	5.0	47.4	3080	23.3	18.9	3099	30.0	19.0	3142	21.4	23.3
C-H str.	–	3064 m	–	–	–	–	–	–	–	–	–	–	–	–
C-H str.	–	3056 wsh	–	–	–	–	–	–	–	–	–	–	–	–
C-H str.	3026 m	3025 vw	3026	15.6	85.4	3073	9.8	122.0	3092	13.2	129.1	3135	6.9	125.3
C-H str.	–	–	3015	2.9	73.2	3065	0.3	62.5	3083	0.5	68.4	3126	0.9	56.9
C-H str.	–	–	3001	6.0	58.3	3052	11.7	58.7	3070	13.6	68.4	3114	10.5	57.8
N-H...O str.	2744 s	2985 vw	–	–	–	2702	2224.7	266.6	2655	2174.8	374.3	2708	2416.9	270.2
N-H...O str.	2336 w	–	2361	1805.5	121.2	–	–	–	–	–	–	–	–	–
NH_3 rock.	–	–	1667	9.0	27.7	1709	241.2	1.9	1670	152.8	1.7	1766	269.4	2.2
NH_2 sci.	1636 w	1635 vw	1631	45.6	3.9	–	–	–	–	–	–	1631	92.8	22.7
Ring str.	1620 w	1619 vw	1617	43.6	12.9	1621	78.6	14.5	1627	73.5	12.1	1628	33.0	20.3
Ring str.	1603 w	–	1611	100.7	6.9	1602	41.6	28.9	–	–	–	1611	3.8	5.3
NH_3 asym. def.	1586 s	1605 w	1592	33.5	5.3	1593	4.0	6.4	1592	49.0	36.1	–	–	–
NH_3 sym. def.	1553 s	1522 vw	1550	1413.9	5.4	–	–	–	1554	5.0	6.7	1537	34.4	0.8
Ring str.	1499 s	–	1494	62.2	0.6	–	–	–	–	–	–	1504	292.7	1.4
Ring str.	1468 m	–	–	–	–	1469	223.8	2.1	1492	42.0	0.4	1486	13.6	0.9
Ring rock.	1457 m	–	1457	11.5	0.9	1459	77.1	0.8	1467	23.2	1.7	–	–	–
N-H...O in-plane def.	1396 vs	–	1378	546.3	2.7	–	–	–	1402	268.9	3.6	1363	256.6	14.7
NO_3^- asym. str.	1340 vssh	1344 vw	1331	3.1	0.7	1329	0.9	0.2	1339	1.2	0.8	1358	44.7	7.2
Ring bend.	–	–	–	–	–	1315	37.0	1.7	1329	1.0	1.9	1343	0.3	0.8
N-H...O in-plane def.	1306 vs	–	–	–	–	1308	226.7	21.4	–	–	–	1252	86.7	14.2
C-N str.	1204 m	1205 w	1208	6.9	0.7	1220	83.2	12.5	1213	138.0	10.8	1185	2.7	5.9
C-H in-plane def.	–	1181 w	–	–	–	–	–	–	–	–	–	–	–	–
C-H bend.	1163 m	1165 vw	1162	0.9	6.8	1166	2.5	6.2	1175	4.2	6.6	1166	0.4	5.4
NH_3 bend.	–	–	1121	7.6	4.5	1121	3.9	5.3	1129	4.0	8.3	1138	3.9	4.6
C-H in-plane def.	1109 w	–	1088	59.4	15.6	–	–	–	–	.	.	–	–	–
C-H in-plane def.	1101 w	–	1080	98.2	4.9	–	–	–	–	.	.	1075	11.1	0.5
C-H bend.	1059 w	1061 vw	1058	2.3	0.3	1055	4.8	0.2	1058	4.7	0.3	1051	202.5	14.8
NO_3^- asym. str.	1038 s	1038 vs	1022	6.9	0.7	1019	32.6	16.3	1019	5.2	12.8	1038	0.6	12.2
NO_3^- asym. str.	1031 m	1029 w	1017	20.0	1.6	1014	211.1	9.6	–	–	–	1013	1.0	23.4
6(A_1) mode of benzene ring	1005 vw	1004 s	1008	5.4	7.1	–	–	–	1002	210.8	17.1	979	116.8	6.7
C-C and C-N str.	995 w	993 vw	995	0.6	0.1	–	–	–	980	10.7	33.4	970	2.5	0.9
NO_3^- out-of-plane bend.	835 vw	838 vw	854	3.3	2.4	849	64.1	6.2	842	69.5	9.7	864	70.6	6.0
NO_3^- out-of-plane bend.	822 w	812 vw	–	–	–	810	0.8	6.2	805	0.5	7.5	822	0.4	5.5
Sym. ring breath.	795 vw	794 m	773	6.6	14.2	781	69.8	7.7	805	0.5	7.5	799	73.7	7.5
In-plane ring def.	749 vs	750 vw	749	56.6	0.5	754	18.2	0.2	759	97.3	6.5	753	16.4	0.3
NO_3^- in-plane bend.	725 m	722 vw	722	40.7	2.1	728	18.1	3.4	728	26.8	3.4	739	22.2	3.5
Sym. ring breath.	716 w	716 vw	720	0.2	1.1	–	–	–	720	4.9	1.8	–	–	–
In-plane ring def.	691 s	690 vw	681	15.9	0.2	680	19.1	0.2	680	16.1	0.2	691	24.0	0.1

Table 2 (continued).

Assignment	Exp. [1] (cm^{-1}) IR with powder	Exp. [1] (cm^{-1}) Raman with powder	Scaled frequencies [6-31G(d)] (cm^{-1}) HF	I_{IR}[a]	I_{Raman}[b]	B3LYP	I_{IR}[a]	I_{Raman}[b]	BLYP	I_{IR}[a]	I_{Raman}[b]	B3PW91	I_{IR}[a]	I_{Raman}[b]
O-NO-O sci.	620 vw	–	–	–	–	632	4.3	5.6	624	4.1	5.4	684	5.1	3.4
In-plane ring def.	617 w	617 w	605	4.3	5.8	611	0.1	5.1	615	0.1	4.8	617	0.1	4.9
Out-of-plane C-N bend.	527 w	529 vw	514	27.8	4.7	518	2.9	3.0	521	4.2	2.7	526	3.1	3.0
Out-of-plane C-N bend.	478 s	479 vw	467	18.8	1.0	494	21.7	0.8	494	22.3	1.2	502	23.7	0.8
NH_3 rock.	–	–	–	–	–	458	16.1	0.4	457	17.3	0.6	466	11.8	0.4
Skeletal def.	402 w	401 vw	409	1.2	0.1	402	0.1	0.1	402	0.01	0.1	405	0.01	0.1
NH_3 rock.	–	–	341	4.3	2.1	350	3.9	1.4	348	5.2	2.4	350	3.8	1.3
Skeletal def.	274 w	273 vwbr	211	23.4	3.1	267	25.5	0.2	265	25.5	0.1	275	26.8	0.1
Lattice	179 w	184 w	204	66.3	0.3	177	23.5	4.1	176	25.1	4.1	182	24.4	4.1
Lattice	147 w	–	137	2.2	2.0	–	–	–	–	–	–	–	–	–
Lattice	120 vw	109 s	–	–	–	116	4.0	0.9	116	3.3	1.2	114	3.5	1.2
Lattice	93 vw	92 s	91	6.8	1.0	87	0.1	0.8	86	0.2	1.4	90	0.06	0.9

[a] IR intensities (km/mol). [b] Raman scattering activities (Å^4/amu). vs, very strong; s, strong; m, medium; br, broad; w, weak; sh, shoulder; vw, very weak.

by the BLYP method and 1537 cm^{-1} (medium band) by the B3PW91 method using the 6-31G(d) basis set.

Most bands observed in the infrared and Raman spectra of the title compound belong to benzene ring modes. Only some of them may be assigned to the NH_3 group [1]. The in-plane ring deformation, 8(B1), gives the infrared bands at 749 and 691 cm^{-1} [1]. These bands have been calculated at 749, 681 cm^{-1} by the HF/6-31G(d) level; 754, 680 cm^{-1} by the B3LYP/6-31G(d) level; 759, 680 cm^{-1} by the BLYP/6-31G(d) level; and 753, 691 cm^{-1} by the B3PW91/6-31G(d) level.

Other reliable group vibrations of the benzene ring are the stretching ones [18]. The bands at 1620, 1603, 1499 and 1468 cm^{-1} have weak, strong and medium intensity, respectively. They are observed also in the spectrum of the deuterated analogue [1]. The bands corresponding to the ring stretching type of vibrations appeared at 1617, 1611, 1494 cm^{-1} with very weak intensity (by HF); 1621, 1602, 1469 cm^{-1} with very weak intensity (by B3LYP); 1627, 1492 cm^{-1} with weak (by BLYP); and 1628, 1611, 1504, 1486 cm^{-1} with weak and very weak (by B3PW91). Other assignment of internal vibrations of the anilinium cation can be seen in Table 2.

The planar NO_3^- ion (D_{3h}) has six vibrational degrees of freedom [1]. They form four fundamental modes: antisymmetric stretching (υ_3) at approximately 1330 cm^{-1} (doubly degenerated, both IR- and Raman-active), symmetric stretching (υ_1) at 1040 cm^{-1} (Raman-active), out-of-plane bending (υ_2) at 800 cm^{-1} (IR-active) and in-plane bending (υ_4) at 730 cm^{-1} (doubly degenerated, both IR- and Raman-active) [19].

Two bands in the infrared spectrum are observed at 835 and 822 cm^{-1} with very weak and weak intensity, respectively [1]. From the vibrational data of nitrate anions, vibrational bands have been calculated at 854 cm^{-1} (very weak) using HF; 849, 810 cm^{-1} (very weak) using B3LYP; 842, 805 cm^{-1} (medium and weak) using BLYP; and 864, 822 cm^{-1} (medium and very weak) using B3PW91 methods. They originate from the bending type of vibrations of nitrate anions. The splitting of this mode into a doublet may be ascribed to a lowering of symmetry of the NO_3^- ion from D_{3h} to C_{2v} or C_s [1].

Two infrared bands, one with strong and the other with medium intensity, were observed at 1038 and 1031 cm^{-1}, respectively [1]. These infrared bands have been calculated at 1022 and 1017 cm^{-1} with

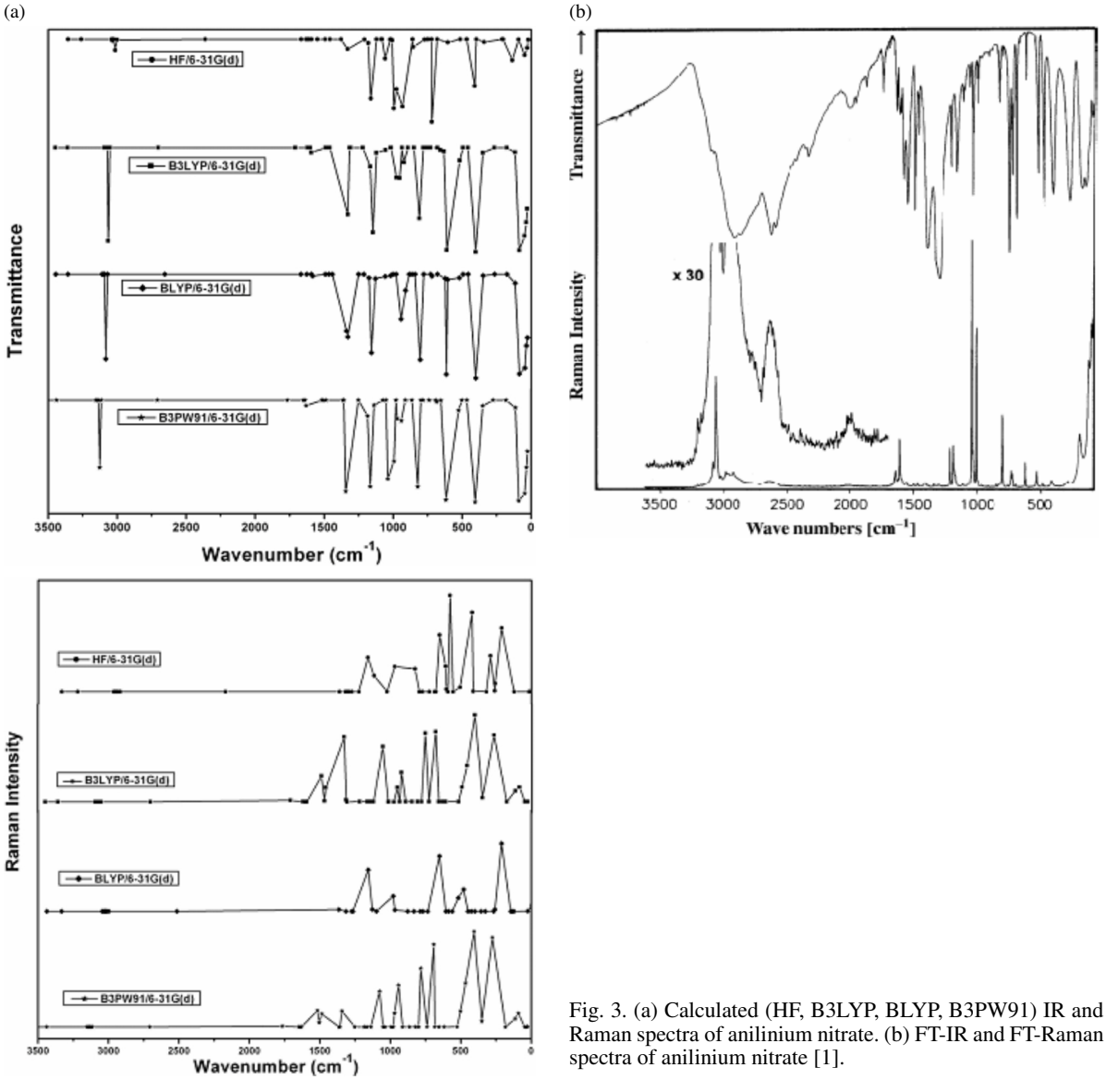

Fig. 3. (a) Calculated (HF, B3LYP, BLYP, B3PW91) IR and Raman spectra of anilinium nitrate. (b) FT-IR and FT-Raman spectra of anilinium nitrate [1].

weak and medium intensity for HF level, for B3LYP level at 1019 and 1014 cm^{-1} with medium and strong intensity, for BLYP level at 1019 cm^{-1} with weak intensity and for B3PW91 level at 1038, 1013 cm^{-1} with very weak intensity. These bands were assigned to asymmetric stretching vibrations of NO_3^- anions. The observed splitting may correspond to the crystal-field effect, as there are eight crystallographically equivalent ions in the elementary unit cell [1].

All hydrogen atoms of the protonated amino group of the anilinium residue participate in this type of interaction. The vibrations of N–H...O type manifest themselves as perturbed amino group vibrations of the mono-protonated anilinium cations. In the case of the title crystal, almost every N–H bond would be to some extent independent having the transition dipole moments parallel to the N–H vectors [1]. The position of infrared bands originating from the absorption of a particular hydrogen bond strongly depends on its length [20]. The two submaxima observed at 2930 and 2873 cm^{-1} at the above mentioned multicomponent broad band could be explained by the ex-

Parameter		HF	B3LYP	BLYP	B3PW91
			6-31G(d)		
Dipole moment		11.13	4.92	4.68	5.06
Zero-point vibrational energy		90.83	89.94	89.44	90.03
Total energy		−565.18	−568.50	−568.35	−568.29
Rotational constants		3.11	2.56	2.57	2.59
		0.46	0.47	0.46	0.47
		0.42	0.44	0.43	0.44
Entropy	Rotational	27.51	30.82	32.91	30.53
	Translational	36.85	41.11	43.79	40.72
	Vibrational	28.99	33.95	37.79	34.15
	Total	93.35	105.88	114.49	105.40

Table 3. Dipole moment (D), zero-point vibrational energies (kcal mol^{-1}), calculated energies (a. u.), rotational constants (GHz), and entropies (cal mol^{-1} K^{-1}) of anilinium nitrate.

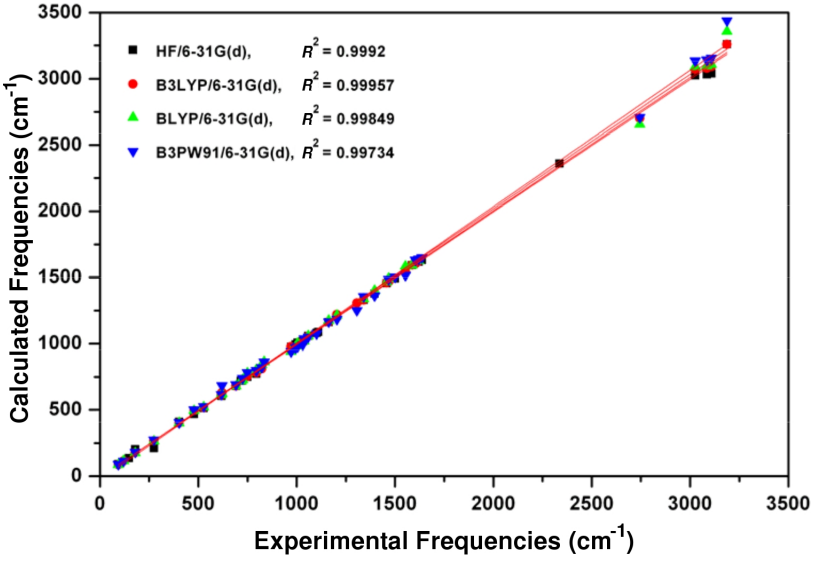

Fig. 4. Correlation graphs of calculated and experimental frequencies of anilinium nitrate.

istence of these two groups of hydrogen bonds [1]. Additionally, the N–H...O hydrogen bond stretching vibrations were observed at 2744, 2736 cm^{-1} with strong and weak intensity. Herein N–H...O hydrogen bonds' stretching vibrations have been calculated by HF at 2361 cm^{-1} with very strong intensity, by B3LYP at 2702 cm^{-1} with very strong intensity, by BLYP at 2655 cm^{-1} with very strong intensity and by B3PW91 methods at 2708 cm^{-1} with very strong intensity.

The system of weak hydrogen bonds of N–H...O type has a characteristic feature for anilinium salts. The position of the infrared bands originating from the antisymmetric stretching type of vibrations was analyzed in other complexes of aniline [21] and *p*-nitroaniline [22, 23]. The other bands of anilinium nitrate are given in Table 2 and in Figure 3. The theoretical and experimental IR and Raman spectra of anilinium nitrate are shown in Figure 3. To make a comparison with the experiment, we present the correlation plot in Fig. 4 based on our calculations. As one can easily see from this figure, the experimental fundamentals agree much with the scaled fundamentals and are found to have a better correlation for the B3LYP ones than for the HF, BLYP and B3PW91 ones.

3.3. Thermodynamic Parameters of Anilinium Nitrate

Several thermodynamic parameters have been calculated using HF, B3LYP, BLYP and B3PW91 methods with the 6-31G(d) basis set. The calculated parameters of anilinium nitrate are given in Table 3. An accurate prediction of the zero-point vibrational energy (ZPVE) and the entropy $[S_{\mathrm{vib}}(T)]$ are multiplied by the data [11]. The total energy and the change in the total entropy of anilinium nitrate calculated by the different theoretical methods are also presented.

4. Conclusions

In this study, we have calculated the geometric parameters, vibrational frequencies and thermodynamic parameters of anilinium nitrate by using HF, B3LYP, BLYP and B3PW91 methods with the 6-31G(d) basis set. To fit the theoretical results with the experimental ones for these methods, we have multiplied the data by 0.8929, 0.9613, 0.9940 and 0.9772, respectively. Multiplication factor results seemed to be in good agreement with the experimental ones. In particular, the results of the B3LYP method have shown to better fit with the experimental ones than those of the HF, BLYP and B3PW91 methods in terms of the evaluated vibrational frequencies and bond angles. On the other hand, geometric parameters (only bond lengths) calculated by the HF method have shown to better fit with the experimental ones than those calculated by the B3LYP, BLYP and B3PW91 methods.

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