



## **SPECTROSCOPIC INVESTIGATIONS OF ANILINIUM NITRATE**

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### **ABSTRACT**

The vibrational frequencies of anilinium nitrate were calculated using Gaussian03 software package and the fundamental modes are assigned. The calculated frequencies are in agreement with the reported experimental values. The calculated geometrical parameters are compared with the geometrical parameters of similar derivatives. The calculated first hyperpolarizability is comparable with the reported values of similar derivatives and is an attractive object for future studies of non linear optics.

**Keywords:** Anilinium nitrate, HF, DFT calculations, Hyperpolarizability

### **INTRODUCTION**

Aniline and its derivatives are used in several pharmaceutical and industrial processes as starting materials because they can serve as precursors in the synthesis of dyes and sensitizer molecules, pesticides and antioxidants<sup>1,2</sup>. They are used in electro optical industry, for the synthesis of technological materials with nonlinear optical responses<sup>3</sup>. The structures and vibrational spectra of aniline and substituted aniline complexes are being studied extensively, since elucidation of their molecular properties as well as nature of reaction mechanism is of utmost importance. The structural, electronic and vibrational parameters of aniline molecule change with inclusion of substituent group because it leads to

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the variation of charge distribution in the molecule. The structure and normal vibration of aniline and its derivatives were reported by Tzeng et al.<sup>4,5</sup>. The IR and Raman studies of anilinium nitrate were reported by Marchewka and Pietraszko<sup>6</sup>. There are many examples of nitrates exhibiting structural phase transitions<sup>6</sup>. In the present study, the vibrational frequencies of the title compound are theoretically calculated and compared with reported data.

### Computational details

Calculations of the title compound were carried out with Gaussian03 program<sup>8</sup> using the B3LYP/6-31G\* and HF/6-31G\* levels of theory to predict the molecular structure and wavenumbers. Molecular geometry was fully optimized by Berny's optimization algorithm using redundant internal coordinates. Harmonic vibrational wavenumbers were calculated using the analytic second derivatives to confirm the convergence to minimum on the potential surface. The wavenumber values computed theoretically contain known systematic errors due to the negligence of electron correlation<sup>9</sup>. We therefore, have used the scaling factor value of 0.8929 for HF/6-31G\* basis set and 0.9613 for B3LYP/6-31G\* basis set. The absence of imaginary wavenumber on the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum energy.

## RESULTS AND DISCUSSION

The calculated (scaled) wavenumbers, IR and Raman bands and their assignments are given in Table 1. According to Roeges<sup>10</sup>, NH<sub>3</sub> stretching vibrations are expected in the region 2910-3200 cm<sup>-1</sup>. For anilinium nitrate, the DFT calculations give 3352, 3319, 3248 cm<sup>-1</sup> as stretching modes of NH<sub>3</sub> group, where as the reported values<sup>6</sup> are 3187, 3176 cm<sup>-1</sup>. The DFT calculations give the in-plane deformations of the NH<sub>3</sub> group at 1642, 1615 and 1487. The corresponding values are 1636, 1615, 1499 cm<sup>-1</sup> in the IR spectrum and 1635, 1619 cm<sup>-1</sup> in the Raman spectrum<sup>6</sup>. These modes are expected in the region<sup>10</sup> 1635-1480 cm<sup>-1</sup>. Although the CN stretch and the NH<sub>3</sub> rock can couple, the CN stretching vibration<sup>10</sup> is unambiguously assigned in the neighbourhood of 1050 cm<sup>-1</sup>. The NH<sub>3</sub> rocking mode is expected in the range<sup>10</sup> 1005-1200 cm<sup>-1</sup>. The DFT calculations give 1036 and 975 cm<sup>-1</sup> as rocking modes of NH<sub>3</sub>. The bands at 1038, 995 cm<sup>-1</sup> in IR spectrum and at 1038, 993 cm<sup>-1</sup> in Raman spectrum are assigned as these modes by Marchewka and Pietraszko<sup>6</sup>. The band 1073 cm<sup>-1</sup> is assigned as CN stretching mode. The  $\delta$ CCN mode is coupled with the twisting and skeletal-deformation modes of NH<sub>3</sub>, which are found to be respectively in the ranges<sup>10</sup> 425-535 cm<sup>-1</sup> and 310-370 cm<sup>-1</sup>. The NH<sub>3</sub> torsional modes lie in the region<sup>10</sup> 140-240 cm<sup>-1</sup> and bands at 109 and 6 cm<sup>-1</sup> are assigned as these modes theoretically.

**Table 1: Calculated vibrational wavenumbers and band assignments**

$\nu_{(\text{HF})} \text{ cm}^{-1}$	$\nu_{(\text{DFT})} \text{ cm}^{-1}$	$\nu_{(\text{IR})} \text{ cm}^{-1}$	$\nu_{(\text{Raman})} \text{ cm}^{-1}$	Assignments
3330	3352			$\nu_{\text{as}}\text{NH}_3$
3315	3319.			$\nu_{\text{as}}\text{NH}_3$
3227	3248	3187	3176	$\nu_{\text{s}}\text{NH}_3$
3054	3109	3108	3102	$\nu\text{CH}$
3033	3086	3085	3085	$\nu\text{CH}$
2989	3049		3064	$\nu\text{CH}$
2986	3048	3026	3025	$\nu\text{CH}$
2982	2831	2970	2985	$\nu\text{CH}$
1659	1642	1636	1635	$\delta_{\text{as}}\text{NH}_3$
1649	1615	1615	1619	$\delta_{\text{as}}\text{NH}_3$
1613	1597	1603	1605	$\nu\text{Ph}$
1581	1558	1553	1552	$\nu\text{Ph}$
1526	1487	1499		$\delta_{\text{s}}\text{NH}_3$
1481	1466	1468		$\nu\text{Ph}$
1477	1450	1457		$\nu\text{Ph}$
1353	1442	1450		$\nu\text{Ph}$
1340	1356	1340	1344	$\nu_{\text{as}}\text{NO}_3$
1263	1333			$\nu\text{Ph}$
1241	1310	1306		$\nu_{\text{as}}\text{NO}_3$
1182	1190	1204	1205	$\delta\text{CH}$
1170	1142	1163	1165	$\delta\text{CH}$
1150	1098	1101		$\delta\text{CH}$
1106	1073			$\nu\text{CN}$
1086	1069	1059		$\delta\text{CH}$

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$\nu_{(\text{HF})} \text{ cm}^{-1}$	$\nu_{(\text{DFT})} \text{ cm}^{-1}$	$\nu_{(\text{IR})} \text{ cm}^{-1}$	$\nu_{(\text{Raman})} \text{ cm}^{-1}$	Assignments
1083	1036	1038	1038	$\rho\text{NH}_3$
1055	1026	1031	1029	$\delta\text{CH}$
1015	1003	1005	1004	Ring breath
999	975	995	993	$\rho\text{NH}_3$
987	974	971		$\nu_s\text{NO}_3$
984	958	963		$\gamma\text{CH}$
978	882	890		$\gamma\text{CH}$
861	795	822	838	$\gamma\text{CH}$
794	792	795	794	$\gamma\text{CH}$
774	739	749	750	$\delta\text{NO}_3$
733	727	725	722	$\gamma\text{CH}$
690	689	691	690	$\gamma\text{Ph}$
660	680			$\delta\text{Ph(X)} \delta\text{NO}_3$
650	654	620		$\omega\text{NO}_3$
624	598	617	617	$\delta\text{Ph}$
508	497	527	529	$\delta\text{Ph(X)}$
454	429			$\gamma\text{Ph (X)}$
417	400	402	401	$\gamma\text{Ph}$
338	327			$\tau\text{NH}_3$
223	204	274	273	$\delta\text{CX(X)}$
125	156	179	184	$\gamma\text{CX(X)}$
86	112	147	109	$\text{tNO}_3$
63	77	120	92	$\text{tPh}$
36	57	93		$\text{tPh}$
30	24			$\text{tNH}_3$

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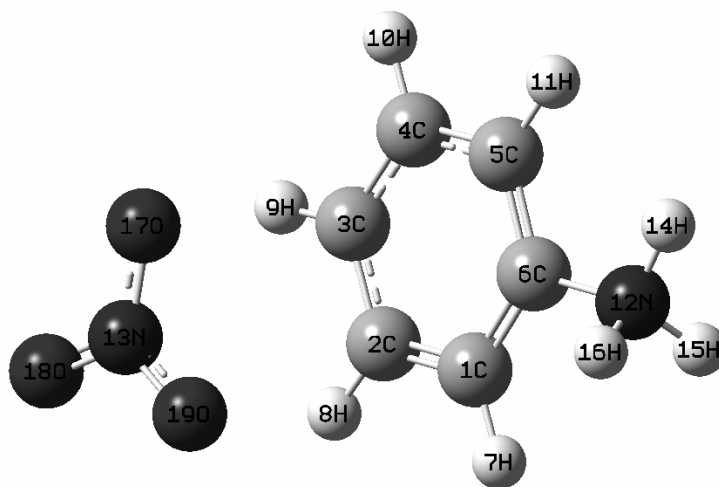
$\nu_{(\text{HF})} \text{ cm}^{-1}$	$\nu_{(\text{DFT})} \text{ cm}^{-1}$	$\nu_{(\text{IR})} \text{ cm}^{-1}$	$\nu_{(\text{Raman})} \text{ cm}^{-1}$	Assignments
27	16			tNO <sub>3</sub>

$\nu$ -stretching;  $\delta$ -in-plane deformation;  $\gamma$ -out-of-plane deformation;  $\tau$ -twisting; rocking;  $\omega$ -wagging; X-substituent sensitive; Ph-Phenyl; t-torsion  
subscripts: as – asymmetric, s- symmetric; experimental frequencies are taken from reference [6].

The DFT calculations give the NO<sub>3</sub> stretching vibrations at 1356, 1310 and 974 cm<sup>-1</sup>. The bands observed at 1340, 1306, 971 cm<sup>-1</sup> in the IR spectrum and at 1344 cm<sup>-1</sup> in the Raman spectrum are assigned as NO<sub>3</sub> stretching vibrations. The deformation bands of NO<sub>3</sub> are observed at 749, 620 cm<sup>-1</sup> in the IR spectrum and at 750 cm<sup>-1</sup> in the Raman spectrum. Correspondingly, the DFT calculations give these modes at 739, 680 and 654 cm<sup>-1</sup>. Brooker and Irish<sup>11</sup> reported stretching vibrations of NO<sub>3</sub> in the range 1045-1071 cm<sup>-1</sup> (Raman), 1045-1051 cm<sup>-1</sup> in IR and in the range 787-838 cm<sup>-1</sup> in IR.

The existence of one or more aromatic rings in a structure is normally readily determined from the C H and C=C-C ring related vibrations. The CH stretching occurs above 3000 cm<sup>-1</sup> and is typically exhibited as a multiplicity of weak to moderate bands compared with aliphatic C-H stretch<sup>12</sup>. In the present case, the DFT calculations predict the  $\nu$ CH modes in the range 3109-2831 cm<sup>-1</sup>. Experimentally observed values are in the range 3108-2970 cm<sup>-1</sup>. The lowering of CH stretching mode is due to the interaction between NO<sub>3</sub> group and the phenyl ring.

The benzene ring possesses six ring stretching vibrations of which the four with the highest wavenumbers occurring near 1600, 1580, 1490 and 1440 cm<sup>-1</sup> are good group vibrations<sup>10</sup>. With heavy substituents, the bands tend to shift to somewhat lower wavenumbers and the greater are the number of substituents on the ring, the broader are the absorption regions<sup>10</sup>. In the case of C=O substitution, the band near 1490 cm<sup>-1</sup> can be very weak<sup>10</sup>. The fifth ring stretching vibration is active near 1315± 65 cm<sup>-1</sup>, a region that overlaps strongly with that of the CH in-plane deformation<sup>10</sup>. The sixth ring stretching vibration, the ring breathing mode appears as a weak band near 1000 cm<sup>-1</sup> in mono-, 1,3-di and 1,3,5-trisubstituted benzenes. In the otherwise substituted benzenes, however, this vibration is substituent sensitive and difficult to be distinguished from other modes. For the title compound, the ring breathing mode appears at 1005 cm<sup>-1</sup> in the IR spectrum, 1004 cm<sup>-1</sup> in the Raman spectrum and at 1003 cm<sup>-1</sup> theoretically. The in-plane and out-of-plane CH deformations of the phenyl ring are expected in the regions 1320-1040 cm<sup>-1</sup> and 990-730 cm<sup>-1</sup>, respectively<sup>10</sup>. All these bands are identified and assigned (Table 1).



Holden and Dickinson<sup>13</sup> reported N-O bond length in the range 1.23-1.27 Å and O-N-O angle as 120°. Lucas<sup>14</sup> reported N-O bond lengths in the range 1.21 -1.29 Å and ONO angle in the range 116-128°. For the title compound, the NO bond lengths are in the range 1.2369-1.2663 Å and ONO angles in the range 119.0 – 120.6°. Marchewka and Pietraszko<sup>6</sup> reported NH bond lengths in the range 0.9129-0.9451 Å, NO bond lengths in the range 1.2295-1.2670 Å and CNH angles in the range 110.4-112.3°, HNH angles in the range 106.6-108.6° and ONO angles in the range 118.5-121.8°. The DFT calculations give CNH angles in the range 110.4-110.8° and HNH angles in the range 108.2-108.4° for the title compound. In the present case, the NH bond lengths are in the range 1.008-1.0087 Å. For the title compound, the C<sub>6</sub>-N<sub>12</sub> bond length is 1.4988 Å whereas the reported value is 1.4662 Å<sup>6</sup>. The DFT calculations give shortening of angles C<sub>5</sub>-C<sub>6</sub>-N<sub>12</sub> by 1.2°, C<sub>1</sub>-C<sub>6</sub>-N<sub>12</sub> by 2.1° and increase of angle C<sub>1</sub>-C<sub>6</sub>-C<sub>5</sub> by 3.3° at C<sub>6</sub> position and this asymmetry reveals the interaction between NH<sub>3</sub> group and the phenyl ring.

Analysis of organic molecules having conjugated  $\pi$ -electron systems and large hyperpolarizability using infrared and Raman spectroscopy has evolved as a subject of research<sup>15</sup>. The potential application of the title compound in the field of non linear optics demands the investigation of its structural and bonding features contributing to the hyperpolarizability enhancement, by analyzing the vibrational modes using the IR and Raman spectrum. The calculated first hyperpolarizability of the title compound is  $110.98 \times 10^{-30}$  esu, which is comparable with the reported values of similar derivatives<sup>16</sup>. We conclude that the title compound is an attractive object for future studies of non linear optical properties.

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