



## **SPECTROSCOPIC INVESTIGATIONS OF 2-AMINOPYRIDINE**

**Y. SHEENA MARY<sup>a</sup>, C. YOHANNAN PANICKER\* and  
HEMA TRESA VARGHESE<sup>a</sup>**

Department of Physics, TKM College of Arts and Science, KOLLAM (Kerala) INDIA

<sup>a</sup>Department of Physics, Fatima Mata National College, KOLLAM (Kerala) INDIA

### **ABSTRACT**

The vibrational wavenumbers of 2-aminopyridine were calculated using Gaussian03 software package at different levels and the fundamental modes are assigned. The predicted infrared and Raman activities are reported. The first hyperpolarizability is calculated and the 2-aminopyridine is an attractive object for future studies of non-linear optics. The calculated wavenumbers are in agreement with the reported experimental values.

**Keywords:** HF, DFT calculations, Hyperpolarizability, Amino.

### **INTRODUCTION**

Pyridine has been extensively studied spectroscopically, due to its applications in many chemical structures of high interest in a variety of biomedical and industrial fields.<sup>1</sup> Pyridine has the intrinsic interest of being the azine nearest to benzene. Amino pyridines attracts the attention of many spectroscopists due to their wide applications in pharmacology and agro-chemistry. They serve as a good anesthetic agent and hence, are used in the preparation of drugs for certain brain diseases. Jose and Mohan<sup>2</sup> reported the vibrational spectra and normal coordinate analysis of 2-aminopyridine. *Ab initio* quantum mechanical method is at present widely used for simulating the IR spectrum. Such simulations are indispensable tools to perform normal coordinate analysis that modern vibrational spectroscopy is unimaginable without involving them. In the present study, we have calculated the vibrational wavenumbers of the title compound by using Hartree-Fock and DFT methods and compared with the IR and Raman bands observed by Jose and Mohan.<sup>2</sup>

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\* Author for correspondence; E-mail: cyhyp@rediffmail.com

Many organic molecules containing conjugated  $\pi$  electrons and characterized by large values of molecular first hyperpolarizabilities have been analyzed by means of vibrational spectroscopy.<sup>3</sup> In this context, the hyperpolarizability of the title compound was calculated theoretically.

## COMPUTATIONAL DETAILS

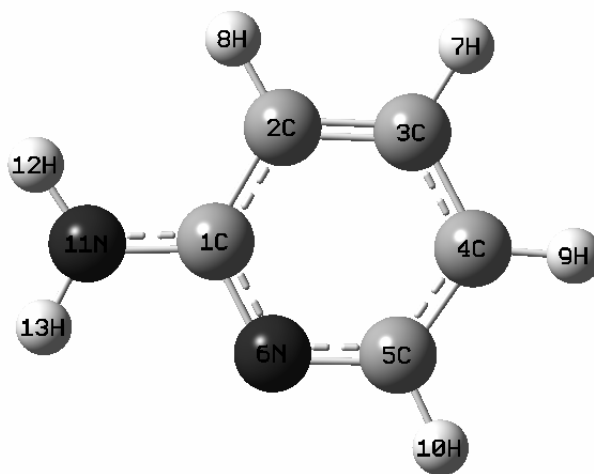
Calculations of the title compound were carried out with Gaussian03 program<sup>4</sup> using the Hartree-Fock and DFT (B3LYP) levels of theory using the standard 6-31G\* set to predict the molecular structure and vibrational wavenumbers. Molecular geometry (Fig. 1) was fully optimized by Berny's optimization algorithm using redundant internal coordinates. Harmonic vibrational wavenumbers were calculated using the analytic second derivatives to confirm the convergence to minima of the potential surface. The wavenumber values computed contain known systematic errors and hence, we have used scaling factors 0.8929 and 0.9613 for HF and DFT methods.<sup>5</sup> The absence of imaginary wavenumbers of the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum energy.

## RESULTS AND DISCUSSION

The calculated scaled wavenumbers, experimental wavenumbers<sup>2</sup> and the assignments are given in Table 1. The  $\text{NH}_2$  stretching modes are expected in the region<sup>6</sup> 3250-3480  $\text{cm}^{-1}$  and the DFT calculation give 3611 and 3489  $\text{cm}^{-1}$  as asymmetric and symmetric  $\text{NH}_2$  stretching modes. Jose and Mohan<sup>2</sup> reported bands at 3442 and 3300  $\text{cm}^{-1}$  as  $\text{NH}_2$  stretching modes. The  $\text{NH}_2$  scissoring vibrations, expected<sup>6</sup> around 1650  $\text{cm}^{-1}$  appear at 1628  $\text{cm}^{-1}$  in Raman spectrum and at 1617  $\text{cm}^{-1}$  in the IR spectrum. The DFT calculations give this mode at 1611  $\text{cm}^{-1}$ . The  $\delta\text{NH}_2$  scissoring vibrations are reported at 1629  $\text{cm}^{-1}$  for sulfanilamide<sup>7</sup> and at 1637  $\text{cm}^{-1}$  in IR, 1634  $\text{cm}^{-1}$  in Raman and 1642  $\text{cm}^{-1}$  in HF for orthanilic acid.<sup>8</sup> According to Roeges<sup>6</sup>,  $\rho/\tau\text{NH}_2$  vibration is expected in the region  $1070 \pm 50$   $\text{cm}^{-1}$  and in the present case, the DFT calculation gives this mode at 1033  $\text{cm}^{-1}$ , which is not pure, but contains significant contributions from other modes. Kurt et al.<sup>9</sup> observed the  $\omega\text{NH}_2$  vibration at 667  $\text{cm}^{-1}$  in the IR spectrum and at 695  $\text{cm}^{-1}$  theoretically. Tzeng et al.<sup>10</sup> calculated the wavenumber of the wagging vibration of amino group at 649  $\text{cm}^{-1}$  and experimentally at 665  $\text{cm}^{-1}$ . For the title compound, the DFT calculation gives the wagging mode of amino group at 751  $\text{cm}^{-1}$ . Primary aromatic amines with nitrogen directly attached to the ring absorb in the region 1330-1260  $\text{cm}^{-1}$  due to the stretching of the ring carbon-

nitrogen bond.<sup>10,11</sup> The band observed at  $1328\text{ cm}^{-1}$  in both spectra and  $1315\text{ cm}^{-1}$  (DFT) is assigned as C-N stretching mode.

The pyridine CH stretching vibrations<sup>12-14</sup> are observed in the range  $3000\text{-}3100\text{ cm}^{-1}$ . Jose and Mohan<sup>2</sup> reported CH stretching vibrations at  $3066, 3049\text{ cm}^{-1}$  in the IR spectrum and at  $3070, 3053, 3028\text{ cm}^{-1}$  in the Raman spectrum. The DFT calculations give these modes at  $3095, 3074, 3058$  and  $3042\text{ cm}^{-1}$ . The pyridine ring stretching vibrations<sup>15</sup> occur in the general region  $1600\text{-}1300\text{ cm}^{-1}$ . These vibrations involve stretching and contraction of all the bonds in the ring and interaction between the stretching modes. In the present case, the DFT calculations gives  $\nu_{\text{Py}}$  modes at  $1580, 1563, 1476, 1436$  and  $1305\text{ cm}^{-1}$ . The pyridine ring breathing mode is assigned at  $988\text{ cm}^{-1}$  (DFT).<sup>16</sup> The in-plane and out-of-plane CH deformations are expected above  $1000$  and below  $1000\text{ cm}^{-1}$  and all these bands (Table 1) are assigned.<sup>6</sup>



**Fig. 1: Optimized geometry (DFT) of the molecule**

Analysis of organic molecules having conjugated  $\pi$ -electron systems and large hyperpolarizability using infrared and Raman spectroscopy has been evolved as a subject of research.<sup>17</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  $2.1 \times 10^{-30}$  esu, which is comparable with the reported values of similar derivatives.<sup>18</sup> We conclude that the title compound is an attractive object for future studies of non-linear optics.

**Table 1: Calculated (scaled) wavenumbers and assignments**

HF/6-31G*			B3LYP/6-31G*			$\nu_{(\text{IR})}$ ( $\text{cm}^{-1}$ )	$\nu_{(\text{Raman})}$ ( $\text{cm}^{-1}$ )	Assignments
$\nu$ ( $\text{cm}^{-1}$ )	IR Intensity	Raman activity	$\nu$ ( $\text{cm}^{-1}$ )	IR Intensity	Raman activity			
3569	54.23	50.00	3611	36.76	59.75	3442	3442	$\nu_{\text{as}}\text{NH}_2$
3452	93.03	114.18	3489	74.42	151.25	3300	3300	$\nu_{\text{s}}\text{NH}_2$
3036	17.47	174.67	3095	15.59	177.29			$\nu\text{CH}$
3017	30.52	72.91	3074	26.18	92.37	3066	3070	$\nu\text{CH}$
3002	17.96	117.07	3058	8.14	87.44		3053	$\nu\text{CH}$
2998	22.02	53.65	3042	33.18	102.04	3049	3028	$\nu\text{CH}$
1623	455.28	35.60	1611	392.43	24.73	1617	1628	$\delta\text{NH}_2$
1602	41.12	0.22	1580	18.19	0.66	1584	1584	$\nu\text{Py}$
1588	73.61	8.96	1563	40.33	6.42	1549	1545	$\nu\text{Py}$
1486	91.02	1.08	1476	70.15	3.41	1473	1470	$\nu\text{Py}$
1438	133.96	2.14	1436	76.78	1.20	1428	1442	$\nu\text{Py}$
1308	52.03	2.50	1315	25.84	2.93	1328	1328	$\nu\text{C-N}$
1306	26.76	5.67	1305	13.34	2.90	1314	1311	$\nu\text{Py}$
1191	12.68	8.13	1283	14.98	4.45	1263	1263	$\delta\text{CH}$
1103	2.26	8.64	1139	11.89	3.77	1142	1147	$\delta\text{CH}$
1094	42.73	4.67	1102	0.50	8.33	1110	1117	$\delta\text{CH}$
1024	1.93	7.84	1033	3.22	13.19	1028	1028	$\delta\text{CH}, \rho/\tau\text{NH}_2$
999	0.59	0.84	988	4.57	0.22	973	970	$\nu\text{Py}$
993	9.39	2.08	959	7.36	14.95			$\gamma\text{CH}$
990	0.00	1.72	947	0.02	0.67	942	949	$\gamma\text{CH}$
962	15.59	17.16	933	0.12	2.74		914	$\gamma\text{CH}$
844	8.82	1.28	835	4.19	18.57	842	840	$\delta\text{Py(X)}$
828	7.30	14.86	821	2.70	2.66	831		$\gamma\text{CH}$

HF/6-31G*			B3LYP/6-31G*			$\nu_{(\text{IR})}$ ( $\text{cm}^{-1}$ )	$\nu_{(\text{Raman})}$ ( $\text{cm}^{-1}$ )	Assignments
$\nu$ ( $\text{cm}^{-1}$ )	IR Intensity	Raman activity	$\nu$ ( $\text{cm}^{-1}$ )	IR Intensity	Raman activity			
771	75.15	0.40	751	42.60	1.18	756	767	$\omega\text{NH}_2$
741	5.87	1.16	722	5.03	1.70			$\gamma\text{Py}$
615	1.93	3.84	616	1.43	3.88	617	621	$\delta\text{Py}$
545	0.35	4.51	546	0.17	5.80	553	545	$\delta\text{Py}(\text{X})$
523	6.21	0.18	519	2.51	0.63			$\gamma\text{Py}(\text{X})$
428	13.94	1.62	441	10.75	1.64	478		$\gamma\text{Py}$
410	2.83	0.23	403	4.05	0.37	400	403	$\delta\text{CN}(\text{X})$
379	8.42	0.50	377	7.18	0.89			$\gamma\text{CN}(\text{X})$
206	5.80	1.33	196	5.81	0.89			tPy
180	23.92	0.57	168	2.83	0.63			tNH <sub>2</sub>

$\nu$ -stretching;  $\delta$  -in-plane deformation;  $\gamma$ -out-of-plane deformation;  $\omega$ -wagging; t-torsion;  $\tau$ -twisting;  $\rho$ -rocking; Py-pyridine ring; X-Substituent sensitive; subscripts: asymmetric, s-symmetric. IR and Raman spectral data are taken from reference 2.

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