



## VIBRATIONAL SPECTROSCOPIC STUDY OF 2-AMINOETHYLSULFONIC ACID

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### ABSTRACT

The vibrational wavenumbers of 2-aminoethylsulfonic acid 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. 2-Aminoethylsulfonic acid is an attractive object for future studies of non-linear optics. The calculated geometrical parameters (DFT) are in agreement with the reported experimental values.

**Key words:** Sulfonic, HF, DFT, Hyperpolarizability.

### INTRODUCTION

Amino acids, which constitute a very important class of biomolecules, can act as potential sulfur and nitrogen donor ligands. It has been found that they utilize their functional groups as fully as possible in metal conduction.<sup>1</sup> Copper complexes of amino acids present important pharmacological interest as several of them show a wide spectrum of effects, including anti-inflammatory, antiulcer, anticonculsant and antitumoral activities.<sup>2-4</sup> Summayya *et al.*<sup>5</sup> reported the vibrational spectroscopic studies and *ab initio* calculations of L-glutamic acid -5- amide. The vibrational and Raman spectrum of aspartic acid dipeptide and glutamic acid dipeptide were reported by Navarrete *et al.*<sup>6</sup> Taurine (2-aminoethylsulfonic acid) is a substance found in several organs of the human body such as heart, brain, liver, muscle and fluids such as bile.<sup>7</sup> It is believed that the 2-aminoethylsulfonic acid (taurine) plays a fundamental role in neuronal mechanisms and its low concentration in the body can be associated with neurological abnormalities.<sup>8</sup> Lima *et al.*<sup>9</sup> reported the high pressure Raman study of taurine crystal. In the present study, we have calculated the vibrational wavenumbers by using HF and DFT methods and compared with

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the reported experimental values. 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>10</sup> In this context, the hyperpolarizability of the title compound was calculated theoretically.

### COMPUTATIONAL DETAILS

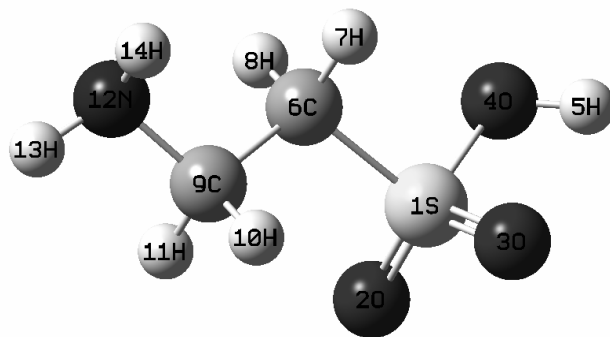
Calculations of the title compound were carried out with Gaussian03 program<sup>11</sup> using the Hartree-Fock and DFT (B3LYP) levels of theory predict the molecular structure and vibrational wavenumbers. Molecular geometry (Fig. 1) was fully optimized by Berny's optimization algorithm using redundant 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>12</sup> The absence of imaginary wavenumbers of the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum energy. The optimized geometrical parameters (DFT) are given in Table 1.

**Table 1: Optimized geometry of the molecule, atom labeling according to Fig. 1.**

Bond lengths (Å)		Bond angles (°)		Dihedral angles (°)	
S <sub>1</sub> -O <sub>2</sub>	1.4575	A(2,1,3)	120.8	D(2,1,4,5)	-116.8
S <sub>1</sub> -O <sub>3</sub>	1.4655	A(2,1,4)	108.7	D(3,1,4,5)	14.9
S <sub>1</sub> -O <sub>4</sub>	1.6509	A(2,1,6)	109.0	D(6,1,4,5)	129.6
S <sub>1</sub> -C <sub>6</sub>	1.8043	A(3,1,4)	106.6	D(2,1,6,7)	-178.5
O <sub>4</sub> -H <sub>5</sub>	0.9762	A(3,1,6)	110.5	D(2,1,6,8)	-61.8
C <sub>6</sub> -H <sub>7</sub>	1.0940	A(4,1,6)	98.9	D(2,1,6,9)	59.4
C <sub>6</sub> -H <sub>8</sub>	1.0926	A(1,4,5)	106.2	D(3,1,6,7)	46.5
C <sub>6</sub> -C <sub>9</sub>	1.5333	A(1,6,7)	106.2	D(3,1,6,8)	163.1
C <sub>9</sub> -H <sub>10</sub>	1.1022	A(1,6,8)	107.3	D(3,1,6,9)	-75.7
C <sub>9</sub> -H <sub>11</sub>	1.0939	A(1,6,9)	111.1	D(4,1,6,7)	-65.1
C <sub>9</sub> -N <sub>12</sub>	1.4645	A(7,6,8)	109.2	D(4,1,6,8)	51.6
N <sub>12</sub> -H <sub>13</sub>	1.0178	A(7,6,9)	112.1	D(4,1,6,9)	172.8

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Bond lengths (Å)		Bond angles (°)		Dihedral angles (°)	
N <sub>12</sub> -H <sub>14</sub>	1.0190	A(8,6,9)	110.8	D(1,6,9,10)	54.9
		A(6,9,10)	109.3	D(1,6,9,11)	-61.8
		A(6,9,11)	108.5	D(1,6,9,12)	-179.4
		A(6,9,12)	108.3	D(7,6,9,10)	-63.8
		A(10,9,11)	107.3	D(7,6,9,11)	179.5
		A(10,9,12)	114.7	D(7,6,9,12)	61.9
		A(11,9,12)	108.5	D(8,6,9,10)	174.0
		A(9,12,13)	109.7	D(8,6,9,11)	57.3
		A(9,12,14)	110.1	D(8,6,9,12)	-60.3
		A(13,12,14)	106.2	D(6,9,12,13)	166.2
				D(6,9,12,14)	-77.3
				D(10,9,12,13)	-71.4
				D(10,9,12,14)	45.1
				D(11,9,12,13)	48.5
				D(11,9,12,14)	165.1



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

## RESULTS AND DISCUSSION

In associated aliphatic and alicyclic primary amines, the NH<sub>2</sub> stretching vibration<sup>13,14</sup> occurs in the range 3390 - 3260 cm<sup>-1</sup>. In the vibrational spectra of amino acids, the NH<sub>2</sub>

stretching modes<sup>5,15</sup> are reported at around 3400 and 3200  $\text{cm}^{-1}$ . In the present case, the DFT calculations give  $\text{NH}_2$  stretching modes at 3423 and 3340  $\text{cm}^{-1}$ . The  $\text{NH}_2$  scissoring vibration<sup>14</sup> gives rise to a broad band in the region  $1600 \pm 50 \text{ cm}^{-1}$  and the rocking/twisting  $\text{NH}_2$  mode is expected in the region  $1160 \pm 140 \text{ cm}^{-1}$ . Associated primary amines show a characteristic broad  $\omega\text{NH}_2$  band between 1000 and 700  $\text{cm}^{-1}$ , with a maximum absorption<sup>14</sup> at  $840 \pm 55 \text{ cm}^{-1}$ . The  $\text{NH}_2$  torsion is expected in the low wavenumber region.<sup>14</sup> For the title compound, the theoretical calculations give the  $\text{NH}_2$  deformation bands at 1635, 1142, 773  $\text{cm}^{-1}$ . The CN stretching vibration<sup>16</sup> is expected in the region 1250-1020  $\text{cm}^{-1}$  and the band at 1104  $\text{cm}^{-1}$  is assigned as this mode.

The vibrations of the  $\text{CH}_2$  group, the asymmetric stretch, symmetric stretch, scissoring vibrations, and wagging vibrations appear in the regions  $3000 \pm 50$ ,  $2965 \pm 30$ ,  $1455 \pm 55$  and  $1350 \pm 85 \text{ cm}^{-1}$ , respectively.<sup>14,17</sup> All these vibrations are identified and assigned (Table 2). The rocking modes<sup>14</sup> of  $\text{CH}_2$  is expected in the range  $895 \pm 85 \text{ cm}^{-1}$  and the torsional modes are seen in the low wavenumber range. Baran *et al.*<sup>15</sup> reported the CC stretching bands in the range 870 - 1117  $\text{cm}^{-1}$  and CC bending modes below 400  $\text{cm}^{-1}$ . Summayya *et al.*<sup>5</sup> reported these bands at 999, 899, 399, 347, 272, 231 and 211  $\text{cm}^{-1}$ . In the present case, the CC stretching mode is assigned at 1009  $\text{cm}^{-1}$ .

**Table 2: Calculated wavenumbers (scaled) and assignments**

HF/6-31G*			HF/6-311G*			B3LYP/6-31G*			Assignments
$\nu$ ( $\text{cm}^{-1}$ )	IR Intensity	Raman activity	$\nu$ ( $\text{cm}^{-1}$ )	IR Intensity	Raman activity	$\nu$ ( $\text{cm}^{-1}$ )	IR Intensity	Raman activity	
3606	223.02	61.18	3671	195.64	66.04	3554	114.59	91.01	$\nu\text{OH}$
3413	3.37	82.66	3418	1.51	80.34	3423	0.25	95.43	$\nu_{\text{as}}\text{NH}_2$
3336	1.67	105.31	3351	0.52	105.74	3340	0.57	130.04	$\nu_{\text{s}}\text{NH}_2$
2977	4.29	37.96	2960	6.58	36.57	3042	2.67	39.92	$\nu_{\text{as}}\text{CH}_2$
2939	13.76	55.49	2919	15.60	53.12	2996	9.68	43.14	$\nu_{\text{as}}\text{CH}_2$
2916	2.96	83.41	2900	3.77	89.70	2977	1.81	90.93	$\nu_{\text{s}}\text{CH}_2$
2853	45.06	76.00	2839	47.09	79.46	2883	45.33	79.09	$\nu_{\text{s}}\text{CH}_2$
1644	33.36	6.68	1660	38.61	4.69	1635	22.69	9.78	$\delta\text{NH}_2$
1490	0.63	9.20	1481	1.57	7.37	1486	1.11	9.28	$\delta\text{CH}_2$

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HF/6-31G*			HF/6-311G*			B3LYP/6-31G*			Assignments
$\nu$ ( $\text{cm}^{-1}$ )	IR Intensity	Raman activity	$\nu$ ( $\text{cm}^{-1}$ )	IR Intensity	Raman activity	$\nu$ ( $\text{cm}^{-1}$ )	IR Intensity	Raman activity	
1432	10.28	10.95	1424	10.71	8.76	1428	5.72	13.04	$\delta\text{CH}_2$
1412	15.88	1.18	1409	15.68	0.95	1390	11.31	1.85	$\omega\text{CH}_2$
1345	276.86	2.61	1336	237.83	3.52	1320	108.45	6.28	$\omega\text{CH}_2$
1322	21.76	6.98	1321	81.40	4.70	1307	85.47	6.23	$\nu_{\text{as}}\text{SO}_2$
1288	14.91	6.58	1285	22.43	4.51	1266	18.92	5.69	$\tau\text{CH}_2$
1239	10.94	2.38	1238	10.58	1.55	1216	5.56	2.23	$\tau\text{CH}_2$
1170	283.16	2.46	1161	303.37	2.31	1142	197.05	4.37	$\tau/\rho\text{NH}_2$
1118	30.26	4.56	1115	15.41	4.36	1104	8.03	5.22	$\nu\text{CN}$ , $\delta\text{SOH}$
1110	22.18	5.34	1107	27.42	5.10	1078	39.60	7.25	$\nu_{\text{s}}\text{SO}_2$
1053	11.89	8.41	1046	12.14	7.42	1057	5.66	7.50	$\nu\text{SO}(\text{H})$
1027	14.37	9.70	1023	15.57	8.12	1009	4.42	8.77	$\nu\text{CC}$
940	5.72	3.96	939	4.15	3.76	943	1.63	1.91	$\gamma\text{OH}$ , $\rho\text{CH}_2$
854	182.20	2.32	853	151.39	1.53	838	149.84	4.38	$\rho\text{CH}_2$
848	270.63	5.70	843	320.14	4.29	773	123.81	3.11	$\nu\text{OS}$ , $\omega\text{NH}_2$
778	11.70	11.90	772	7.26	10.73	763	98.95	1.52	$\nu\text{CS}$
762	7.57	1.20	757	6.43	1.88	721	44.88	20.11	$\delta\text{SO}_2$
564	138.69	4.15	567	148.03	4.10	524	87.76	5.39	$\omega\text{SO}_2$
497	41.47	3.28	499	47.07	3.44	464	19.06	4.73	$\rho\text{SO}_2$
426	16.01	1.27	433	19.12	1.52	396	11.18	1.68	$\delta\text{CC}$
342	15.87	0.64	345	17.44	0.91	333	19.00	1.22	$\delta\text{CSO}_3\text{H}$
316	1.72	4.69	316	1.20	4.65	310	3.35	6.21	$\delta\text{CN}$
312	2.95	1.34	313	1.61	1.22	292	2.87	1.81	$\text{tCH}_2$

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HF/6-31G*			HF/6-311G*			B3LYP/6-31G*			Assignments
$\nu$ ( $\text{cm}^{-1}$ )	IR Intensity	Raman activity	$\nu$ ( $\text{cm}^{-1}$ )	IR Intensity	Raman activity	$\nu$ ( $\text{cm}^{-1}$ )	IR Intensity	Raman activity	
236	59.75	1.91	229	57.82	1.28	238	55.24	2.39	tCH <sub>2</sub>
176	113.79	1.48	156	57.88	0.69	172	83.77	1.71	tNH <sub>2</sub>
145	7.04	0.46	127	84.57	1.58	136	11.02	0.85	tSOH
89	2.90	0.30	88	2.69	0.27	90	3.60	0.35	tCH <sub>2</sub> NH <sub>2</sub>
78	6.51	0.22	79	8.72	0.21	66	3.98	0.30	tSO <sub>2</sub>

$\nu$ -stretching;  $\delta$ -in-plane deformation;  $\gamma$ -out-of-plane deformation;  $\omega$ -wagging;  $\tau$ -torsion;  $\tau$ -twisting;  $\rho$ -rocking; subscripts: as-asymmetric, s-symmetric.

The spectra of esters of sulfonic acids are dominated by SO<sub>2</sub> stretching and SO stretching vibrations and expected in the range<sup>14,16</sup> 1165-1410  $\text{cm}^{-1}$ . By comparison with OH bending frequencies in sulfuring acid and other sulfonic acids SOH bend<sup>18</sup>, the band at around 1118  $\text{cm}^{-1}$  is assigned as SOH bending. The SO(H) stretching mode is reported at 1026  $\text{cm}^{-1}$  for sulfamic acid<sup>19</sup> and at around 1020  $\text{cm}^{-1}$  for aminobenzene sulfonic acids<sup>20</sup> and at 1035  $\text{cm}^{-1}$  for pyridine-3-sulfonic acid.<sup>21</sup> For the title compound. The SO<sub>2</sub> and SO stretching vibrations are assigned at 1307, 1078 and 1057  $\text{cm}^{-1}$ . Usually the SO<sub>2</sub> deformations absorb with a weak to moderate intensity. The SO<sub>2</sub> scissors<sup>14</sup> absorb in the range  $565 \pm 45 \text{ cm}^{-1}$ . The SO<sub>2</sub> twisting and rocking vibrations<sup>14,22</sup> are seen in the range  $425 \pm 85$  and  $345 \pm 55 \text{ cm}^{-1}$ . In the present case, the DFT calculations give the deformation bands of SO<sub>2</sub> at 721, 524, 464  $\text{cm}^{-1}$  and at 333  $\text{cm}^{-1}$ .

The reported values of S=O in SO<sub>2</sub> and SO<sub>3</sub> molecules are 1.4308, 1.4469Å and 1.4173, 1.4261Å, respectively.<sup>23</sup> In the present case, the DFT calculations give the S=O bond length as 1.4575, 1.4655Å and S-O bond length as 1.6509Å. Demaison *et al.*<sup>24</sup> reported S-O in the range 1.5750-1.6119Å, S=O in the range 1.4111-1.4301Å and according to Miller *et al.*<sup>25</sup> S=O is 1.446Å and S-O is 1.627Å. In the amino group, the nitrogen atom is likely to be in the plane with a torsion angle S<sub>1</sub>-C<sub>6</sub>-C<sub>9</sub>-N<sub>2</sub> = -179.4° and the oxygen atom O<sub>4</sub> is likely to be out-of-plane with a torsion angle O<sub>4</sub>-S<sub>1</sub>-C<sub>6</sub>-C<sub>9</sub> = 172.8° (or 7.2°). The C-N distance in anilinium sulfate<sup>23</sup> is 1.4196Å where as in the present case, C-N = 1.4645Å. The O=S=O angles are reported as<sup>23</sup> 121° and for the title compound, the corresponding value is 120.8°. The O-S=O angle is reported in the range<sup>23</sup> 105.2-108.5° and in the present case, the range is 106.6-108.7°.

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>26</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  $0.45 \times 10^{-30}$  esu, which is comparable with the reported values of similar derivatives.<sup>27</sup> It is concluded that the title compound is an attractive object for future studies of non-linear optics.

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