



## VIBRATIONAL SPECTROSCOPIC STUDIES AND AB INITIO CALCULATIONS OF p-CHLOROBENZENESULFONIC ACID

HEMA TRESA VARGHESE<sup>a</sup>, C. YOHANNAN PANCIKER<sup>\*</sup>,  
G. MADHAVA WARRIER<sup>b</sup>, MANIKANTAN NAIR<sup>c</sup> and K. RAJU<sup>c</sup>

Department of Physics, T. K. M. College of Arts and Science, KOLLAM (Kerala) INDIA

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

<sup>b</sup>Department of Physics, Govt. Victoria College, PALAKKAD (Kerala) INDIA

<sup>c</sup>Department of Physics, University College, TRIVANDRUM (Kerala) INDIA

### ABSTRACT

A complete vibrational spectrum analysis of p-chlorobenzenesulfonic acid has been performed. The wavenumbers are calculated on the basis of ab initio theory using Hartree-Fock/6-31G\* basis set. The predicted infrared intensities, Raman activities and force constants are reported. 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. The calculated geometrical parameters are also in agreement with reported values.

**Key words:** Sulfonic acid, Hartree-Fock, Hyperpolarizability, IR

### INTRODUCTION

Aromatic sulfonation is an important industrial process, which is used for the manufacture of detergents and surfactants from alkyl benzene on the mega-tonne scale<sup>1</sup>. Sulfones are useful intermediates in a wide range of fields such as agrochemicals<sup>2</sup>, pharmaceuticals<sup>3</sup> and polymers<sup>4,5</sup>. The sulfonyl group is widely used by synthetic organic chemists and sulfones have many industrial applications<sup>6,7</sup>. Computational method is at present widely used for simulating IR spectra. Such simulations are indispensable tools to perform normal coordinate analysis so that modern vibrational spectroscopy is unimaginable without involving them. In the present study, the vibrational frequencies are calculated theoretically and compared with experimental data.

---

\* Author for correspondence

## EXPERIMENTAL

The IR spectrum was recorded on a Bruker IFS 66V FT-IR spectrometer with sample as KBr and polyethylene pellets. The spectral resolution was  $4\text{ cm}^{-1}$ .

### Computational details

Calculations of the title compound were carried out with Gaussian03 program<sup>8</sup> using the HF/6-31G\* basis set 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 at the Hartree-Fock level 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. 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 bands, infrared intensities and Raman activities, force constants and the corresponding assignments are given in Table 1. The spectra of esters of sulfonic acids are dominated by three absorptions with a moderate to strong intensity, due to both  $\text{SO}_2$  stretching vibrations and a S-O stretching. Usually esters of sulfonic acids absorb at  $1350\text{-}1420\text{ cm}^{-1}$  due to asymmetric  $\text{SO}_2$  stretching vibrations<sup>10,11</sup>. The calculated values are  $1386$  and  $1323\text{ cm}^{-1}$ . Sulfonic acid complexes show symmetric  $\text{SO}_2$  stretching vibrations<sup>10</sup> at  $1235\text{-}1165\text{ cm}^{-1}$ . The symmetric  $\text{SO}_2$  stretching vibration appears at  $1155\text{ cm}^{-1}$  in the IR spectrum and at  $1151\text{ cm}^{-1}$  theoretically<sup>10-12</sup>. By comparison with OH bending frequencies in sulfuric acid and other sulfonic acids, the band at  $1117$  (HF) and  $1100\text{ cm}^{-1}$  (IR) is assigned as SOH bend<sup>13</sup>. The  $\nu\text{S-O(H)}$  mode is reported at  $1026\text{ cm}^{-1}$  for sulfamic acid<sup>11</sup>, at around  $1020\text{ cm}^{-1}$  for amino benzenesulfonic acids<sup>14</sup> and at  $1040\text{ cm}^{-1}$  for p-toluene sulfonic acid<sup>15</sup>. For the title compound, the  $\nu\text{S-O}$  is observed at  $1055\text{ cm}^{-1}$  in the IR spectrum and at  $1067\text{ cm}^{-1}$  theoretically<sup>16</sup>. Usually the  $\text{SO}_2$  deformations absorb with a weak to moderate intensity. The  $\text{SO}_2$  scissors<sup>10</sup> absorb in the range  $520\text{-}610\text{ cm}^{-1}$  and observed at  $627\text{ cm}^{-1}$  in the IR spectrum and at  $615, 599\text{ cm}^{-1}$  theoretically. A second  $\text{SO}_2$  deformation, often assigned as a wagging mode is found at  $566\text{ cm}^{-1}$  in IR and at  $545\text{ cm}^{-1}$  theoretically, clearly separated from the scissors. The  $\text{SO}_2$  twisting and rocking vibrations<sup>10,17</sup> are seen in the range  $425 \pm 85$  and  $345 \pm 44\text{ cm}^{-1}$ . The C-S stretching vibration appears moderately to strongly in the region  $760 \pm 25\text{ cm}^{-1}$  for majority of investigated

molecules<sup>10</sup>. The band observed at 762 cm<sup>-1</sup> is assigned to C-S stretching vibration. As seen from Table 1, the HF calculations give this mode at 739 cm<sup>-1</sup>. The CCl bond absorb in the range<sup>18</sup> 830-560 cm<sup>-1</sup> and in the present case, the band at 709 cm<sup>-1</sup> in IR and 704 cm<sup>-1</sup> (HF) is assigned as the stretching mode of CCl.

**Table 1: Calculated vibrational wavenumbers, IR bands and assignments**

$\nu_{\text{(HF)}} \text{ cm}^{-1}$	IR intensities (KM/Mole)	Raman activity (A**4/AMU)	Force constants (mDyne/A),	$\nu_{\text{(IR)}} \text{ cm}^{-1}$	Assignments
3582	232.81	160.26	10.10	3568	$\nu\text{OH}$
3055	1.18	202.99	7.57	3090	$\nu\text{CH}$
3054	0.07	1.00	7.55	3055	$\nu\text{CH}$
3041	1.26	79.12	7.46		$\nu\text{CH}$
3041	0.07	10.28	7.45		$\nu\text{CH}$
1600	77.82	52.00	9.81	1621	$\nu\text{Ph}$
1579	11.04	2.83	12.31	1567	$\nu\text{Ph}$
1483	39.52	0.06	3.50	1481	$\nu\text{Ph}$
1386	36.91	0.01	3.74	1396	$\nu_{\text{as}}\text{SO}_2$
1323	251.31	2.67	20.61	1318	$\nu_{\text{as}}\text{SO}_2$
1292	6.74	0.69	1.58	1295	$\delta\text{CH}$
1189	363.92	9.26	2.60	1192	$\delta\text{CH}$
1165	20.03	4.43	1.18		$\delta\text{CH}$
1151	21.14	0.26	3.28	1155	$\nu_{\text{s}}\text{SO}_2$
1117	25.83	8.58	1.69	1100	$\delta\text{SOH}$
1085	51.97	1.12	2.31	1091	$\nu\text{CX(X)}$
1070	82.47	23.88	6.26	1065	$\delta\text{CH}$
1067	1.90	0.02	1.67	1055	$\nu\text{S-O(H)}$
996	0.03	0.01	1.00	1001	$\gamma\text{CH}$
994	19.62	0.66	2.84		$\gamma\text{CH}$

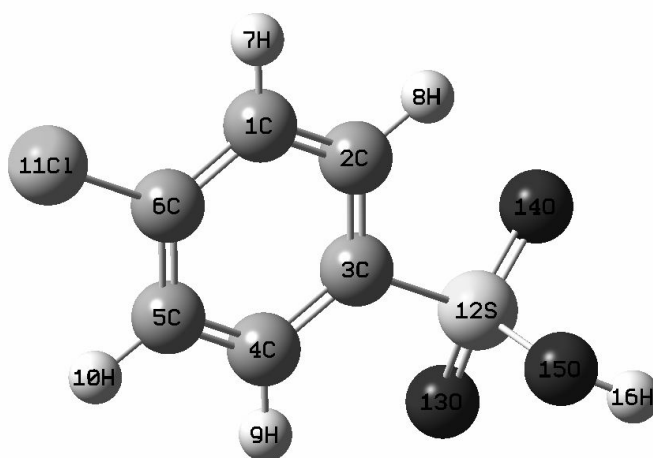
Cont...

$\nu_{(\text{HF})}$ $\text{cm}^{-1}$	IR intensities (KM/Mole)	Raman activity ( $\text{A}^{**4}/\text{AMU}$ )	Force constants (mDyne/A),	$\nu_{(\text{IR})}$ $\text{cm}^{-1}$	Assignments
983	0.20	0.80	0.96		$\gamma\text{CH}$
848	21.50	0.89	0.93	855	$\gamma\text{SOH}$
846	0.13	1.50	0.66	850	$\gamma\text{CH}$
832	383.49	6.03	2.86	837	Ring breath
739	45.29	23.48	2.81	748	$\nu\text{C-S}$
704	2.65	0.14	1.47	709	$\nu\text{C-Cl}$
615	0.05	6.91	1.99	621	$\delta\text{SO}_2$
599	113.39	3.23	2.04		$\delta\text{SO}_2$
545	54.27	1.32	1.00	556	$\omega\text{SO}_2$
498	35.86	1.71	2.11	491	$\gamma\text{Ph(X)}$
476	8.66	1.03	1.01		$\tau\text{SO}_2$
465	71.41	0.58	1.21	452	$\delta\text{Ph(X)}$
406	0.02	0.03	0.36		$\gamma\text{Ph}$
375	12.89	0.71	0.58		$\tau\text{SO}_2$
350	9.24	1.01	0.58		$\delta\text{CX(X)}$
281	4.08	0.04	0.46		$\rho\text{SO}_2$
249	1.05	7.29	0.77		$\rho\text{SO}_2$
192	1.80	1.39	0.21		$\delta\text{CX(X)}$
147	1.07	0.47	0.16		$\gamma\text{CX(X)}$
130	1.62	1.31	0.04		$\gamma\text{CX(X)}$
74	1.15	3.74	0.01		tPh
39	10.72	4.13	0.01		tPh

$\nu$ -stretching;  $\delta$ -in-plane deformation;  $\gamma$ -out-of-plane deformation;  $\tau$ -twisting; rocking;  $\omega$ -wagging; t, torsion; X-substituent sensitive; Ph-Phenyl; subscripts: as – asymmetric, s-symmetric.

The CH stretching vibrations of the phenyl ring<sup>10</sup> occurs above 3000 cm<sup>-1</sup> and in the present case, the ab initio calculations give  $\nu_{\text{CH}}$  in the range 3041-3055 cm<sup>-1</sup>. For parasubstituted phenyl ring, the  $\nu_{\text{Ph}}$  modes<sup>10</sup> are expected in the range 1280-1620 cm<sup>-1</sup> and these bands are identified and assigned (Table 1). The ring breathing mode<sup>19</sup> for the parasubstituted benzenes with entirely different substituents have been reported to be strongly IR active with typical bands in the interval 780-840 cm<sup>-1</sup>. For the title compound, this is confirmed by the strong band in the IR spectrum at 837 cm<sup>-1</sup>, which finds support from the computational results. For 1,4-disubstituted benzenes, the  $\delta_{\text{CH}}$  modes are seen in the range<sup>10</sup> 995-1315 cm<sup>-1</sup>. Bands observed at 1295, 1192 and 1065 cm<sup>-1</sup> in the IR spectrum and at 1292, 1189, 1165 and 1070 cm<sup>-1</sup>, theoretically. The CH out-of-plane deformations<sup>10</sup> are observed below 1000 cm<sup>-1</sup>. Generally, the  $\gamma_{\text{CH}}$  deformations with the highest wavenumbers have a weaker intensity than those absorbing at lower wavenumbers.

Chlorine is highly electronegative and tries to obtain additional electron density. It attempts to draw it from the neighbouring atoms, which move closer together in order to share the remaining electrons more easily as a result. Due to this, the bond angle C<sub>1</sub>-C<sub>6</sub>-C<sub>5</sub> is found to be 121.6° and the exocyclic angles C<sub>1</sub>-C<sub>6</sub>-Cl<sub>11</sub> and C<sub>5</sub>-C<sub>6</sub>-Cl<sub>11</sub> become 119.2°. The C<sub>6</sub>-Cl<sub>11</sub> bond length in the present case is 1.7367 Å which is in agreement with the previous reported value<sup>20</sup>. According to literature, the S=O bond lengths are 1.386 Å for pyridine sulfuric acid complex<sup>21</sup>, 1.446-1.448 Å for sulfuric acid<sup>22</sup> and 1.448-1.472 Å for some monohydrated sulfuric acid<sup>23</sup>. In present case, from ab initio calculations, the S=O bond length is 1.4244 Å. Givan et al.<sup>24</sup> have reported the S=O bond length for sulfuric acid, deuterated sulfuric acid by the X-ray, microwave and ab initio study as 1.426, 1.422 and 1.429 Å and the O=S=O angle as 123.3, 124.77° (experimental), 124.77° (ab initio) respectively. In the present case, the O=S=O bond angle is found to be 119.8°.



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>25</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  $1.67 \times 10^{-30}$  esu, which is comparable with the reported values of similar derivatives<sup>26</sup>. We conclude that the title compound is an attractive object for future studies of non linear optical properties.

## REFERENCES

1. H. Cerfontain, *Mechanistic Aspects in Aromatic Sulfonation and Desulfonation*, Interscience, New York (1968).
2. W. J. Michaely and G. W. Kraatz, U. S. Patent, 4780 127, 1988; Chem. Abstr. 1989, 111, pp. 1290, 17a.
3. A. Padwa, W. H. Bullock and A. D. Dyszlewski, *J. Org. Chem.* **55**, 955 (1990).
4. S. M. Mackinnon and J. Y. Wang, *Macromolecules*, **31**, 7970 (1998).
5. F. Paolo, M. Giorgio, M. Patrizia, P. Concetto and S. Filippo, *Macromol. Chem. Phys.* **197**, 1007 (1996).
6. P. D. Magnus, *Tetrahedron*, **33**, 2019 (1977).
7. K. M. Roy, in, W. Gerharz (Ed.), *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. A25, VCH, Weinheim, Germany, (1985) p. 487.
8. M. J. Frisch, et al., *Gaussian03*, Revision C. 02, Gaussain Inc., Wallingford CT (2004).
9. J. B. Foresman, E. Frisch, in, E. Frisch, (Ed.), *Exploring Chemistry with Electronic Structure Methods, A Guide to Using Gaussian*, Gaussian, Pittsburg PA (1996).
10. N. P. G. Roeges, *A Guide to the Complete Interpretation of Infrared Spectra of Organic Structures*, Wiley, New York (1994).
11. R. M. Silverstein and F. X. Webster, *Spectrometric Identification of Organic Compounds*, Ed. 6, Wiley, Asia (2003).
12. I. Mokhtar, Y. Takakazi and I. Patigul, *J. Zhejian Univ. Sci.*, **6B**, 365 (2005).
13. S. M. Chackalackal and F. E. Stafford, *J. Am. Chem. Soc.*, **88**, 4815 (1996).
14. L. Ganguly, C. I. Jose and A. B. Biswas, *Spectrochim. Acta*, **24A**, 215 (1968).

15. H. G. M. Edwards, D. R. Brown, J. R. Dale and S. Plant, *J. Mol. Struct.* **595**, 111 (2001).
16. C. Y. Panicker, H. T. Varghese, D. Philip and H. I. S. Noguera, *Spectrochim. Acta*, **64A**, 744 (2006).
17. A. Given, H. Rothe, A. Loewenschuss and C. J. Nelson, *Phys. Chem. Phys.*, **4**, 255 (2002).
18. N. B. Colthup, L. H. Daly and S. E. Wiberly, *Introduction to Infrared and Raman Spectroscopy*, Ed. 2, Academic Press, New York (1975).
19. G. Varsanyi, *Assignments of Vibrational Spectra of Seven Hundred Benzene Derivatives*, Wiley, New York (1974).
20. C. H. Endredi, F. Billes and S. Holly, *J. Mol. Struct. Theochem.*, **633**, 73 (2003).
21. J. Baran, Z. Dega-Szafran, M. Jaskolski, M. K. Marchewka, H. Ratajczak and M. Szafran. *J. Mol. Struct.*, **406**, 127 (1997).
22. Y. Miller, G. M. Chaban and R. B. Gerber. *J. Phys. Chem.*, **A 109**, 6565 (2005).
23. S. Re, Y. Osamura and K. Morokuma. *J. Phys. Chem.*, **A 103**, 3535 (1999).
24. A. Givan, L. A. Larsen, A. Loewenschuss and C. J. Nielsen. *J. Mol. Struct.*, **509**, 35 (1999).
25. M. Tommasini, C. Castiglioni, M. Del Zoppo and G. Zerbi, *J. Mol. Struct.*, **480**, 179 (1999).
26. H. T. Varghese, C. Y. Panicker, V. S. Madhavan, S. Mathew, J. Vinsova and C. Van Alsenoy, *J. Raman Spectrosc.*, DOI:10.1002/jrs.2265.

*Accepted : 02.09.2009*