

***Ab initio* Hartree-fock calculations of sulfamic acid**

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ABSTRACT

The molecular geometry and vibrational wavenumbers of sulfamic acid have been calculated using the Hartree-Fock method with 6-31G* basis set. Comparison of the observed fundamental vibrational wavenumbers of sulfamic acid with calculated results by *ab initio* method are found in agreement with the experimental data. Predicted infrared intensities, Raman activities and force constants are reported.

Key words: Sulfamic acid, Hartree-Fock, Vibrational assignment, IR

INTRODUCTION

The study of the structure of sulfamic acid, has been of interest as its physical properties are considerably different from those of other substituted sulfuric acids¹⁻⁵. In the Raman spectrum of sulfamic acid⁵ the bands in the 2800-3200 cm⁻¹ region are assigned to hydrogen bonded NH stretching vibrations. However, Vuagnant and Wagner⁴ assigned some of the IR bands in this region to overtones of in-plane bending of NH. Philip *et al.*,⁶ reported the vibrational and surface enhanced Raman scattering spectrum of sulfamic acid. Sulfamic acid crystallizes in the orthorhombic system Pbca (D_{2h}^{15}) with eight formula units in the unit cell¹⁻². All the atoms are in general positions⁶. *Ab initio* quantum mechanical method is at present widely used for simulating IR spectrum. Such simulations are indispensable tools to perform normal coordinate analysis so 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 the Hartree-Fock method and compared it with IR and Raman bands observed by Philip *et al.*,⁶. These calculations are valuable for providing insight into the vibrational spectrum and related molecular parameters.

Computational details

Vibrational wavenumbers of sulfamic acid are calculated by HF/6-31G* basis using Gaussian03 software on a personal computer⁷. The vibrational wavenumbers are calculated using analytic second derivatives to confirm the convergence to minima on the potential surface and to evaluate the zero point vibrational energies. The wavenumber values computed at the HF level contain known systematic errors due to the negligence of electron correlation⁸. Therefore, we have used the scaling factor value of 0.8929 for the HF/6-31G* basis set.

Parameters corresponding to optimized geometry of sulfamic acid (Fig.1) are given in Table 1. The calculated vibrational spectrum has no imaginary wavenumbers, which helped to confirm that the structure of the title compound deduced following optimization corresponds to energy minimum. The optimum geometry was determined by minimizing the energy with respect to all geometric parameters without imposing molecular symmetry constraints. The assignments of the calculated wavenumbers are aided by the animation option of MOLEKEL program, which gives a visual presentation of the vibrational modes⁹⁻¹⁰.

Table 1: Optimized geometrical parameters of Sulfamic acid, atom labeling is according to Fig. 1

Bond lengths (Å)	Bond angles (°)	Dihedral angles (°)
S ₁ -N ₂ 1.6162	A(2,1,5) 109.2	D(5,1,2,3) -50.0
S ₁ -O ₅ 1.4189	A(2,1,6) 107.7	D(5,1,2,4) 175.5
S ₁ -O ₆ 1.4156	A(2,1,7) 101.5	D(6,1,2,3) 175.9
S ₁ -O ₇ 1.5937	A(5,1,6) 121.7	D(6,1,2,4) 41.4
N ₂ -H ₃ 0.9996	A(5,1,7) 106.4	D(7,1,2,3) 62.1
N ₂ -H ₄ 0.9997	A(6,1,7) 108.4	D(7,1,2,4) -72.4
O ₇ -H ₈ 0.9546	A(1,2,3) 114.5	D(2,1,7,8) -155.3
	A(1,2,4) 113.9	D(5,1,7,8) -41.1
	A(3,2,4) 114.5	D(6,1,7,8) 91.4
	A(1,7,8) 109.9	

Table 2: Calculated wavenumbers and band assignments for Sulfamic acid

ν_{HF} (cm ⁻¹)	ν_{IR} (cm ⁻¹) ^a	ν_{Raman} (cm ⁻¹) ^a	IR Intensity (KM/Mole)	Raman activity (A**4/AMU)	Force constants (mDyne/A)	Assignments
3601	-	-	188.30	65.78	10.22	ν_{OH}
3479	-	-	86.10	47.87	9.86	$\nu_{\text{as}}\text{NH}_2$
3372	3361	3380	64.29	77.20	8.80	$\nu_{\text{s}}\text{NH}_2$
1583	1570	1566	76.59	3.84	2.07	δNH_2
1371	-	1385	380.20	1.71	15.57	$\nu_{\text{as}}\text{SO}_2$
1193	1191	-	370.10	2.97	2.80	δOH
1127	1130	-	13.10	5.84	1.84	$\nu_{\text{s}}\text{SO}_2$
1092	1070	1061	1.21	3.18	1.13	$\rho/\tau\text{NH}_2$
880	890	-	182.24	5.33	3.06	$\nu\text{N-S}$
823	798	-	238.99	10.44	4.00	$\nu\text{S-O(H)}$
638	607	-	264.00	4.66	0.60	ωNH_2
523	535	-	52.22	3.96	1.55	δSO_2
515	-	-	39.10	2.23	1.09	ωSO_2
475	-	-	52.68	2.17	0.89	γOH
416	-	-	1.70	0.36	0.34	τSO_2
334	335	-	56.67	2.14	0.19	ρSO_2
261	-	251	48.75	1.49	0.07	$\text{tNH}_2, \delta\text{S-O(H)}$
71	-	84	93.53	2.78	0.00	tOH

ν -stretching; δ -in-plane deformation; γ -out-of-plane deformation; ρ -rocking; ω -wagging; τ -twisting; t -torsion;
as-asymmetric; s-symmetric. a:ref.6

RESULTS AND DISCUSSION

The spectra of sulfonic acids are dominated by three absorptions with a moderate to strong intensity due to both SO_2 stretching vibrations and a S-O stretch¹¹. The asymmetric and symmetric stretching modes of SO_2 group appear in the regions 1330-1500 and 1135-1255 cm^{-1} respectively¹¹. According to ab initio calculations the bands at 1371 and 1127 cm^{-1} are assigned as asymmetric and symmetric SO_2 stretching modes, respectively. Philip et al.⁶ reported these vibrations at 1385 cm^{-1} in the Raman spectrum and 1130 cm^{-1} in the IR spectrum. The S-O(H) stretching vibration¹¹ is expected in the range $795 \pm 35 \text{ cm}^{-1}$. The HF calculations give this mode at 823 cm^{-1} . Usually the SO_2 deformations absorb with a weak to moderate intensity. The SO_2 scissors is expected in the range $565 \pm 45 \text{ cm}^{-1}$ and a second SO_2 deformation, often assigned as a wagging mode, is found in the neighbouring region $535 \pm 35 \text{ cm}^{-1}$, but clearly separated from the scissors. The HF calculations give this scissoring and wagging modes at 523 and 515 cm^{-1} . The twisting and rocking modes of SO_2 group are

expected in the region 425 ± 85 and $345 \pm 55 \text{ cm}^{-1}$, respectively¹¹. The in-plane deformation of S-O(H) group is obtained at 261 cm^{-1} which is in agreement with the literature¹¹.

The competition between steric hindrance and inter- and intra-molecular hydrogen bridges makes it possible that, in the system of R-OH compounds in the liquid or solid state, the OH stretching vibration¹¹ appears in the extensive region $3275 \pm 370 \text{ cm}^{-1}$. In the present case, the HF calculations give the ν_{OH} mode at 3601 cm^{-1} . The OH deformation bands are calculated to be at 1193 and 475 cm^{-1} .

In primary amines containing two equivalent NH bonds, the change of force constant has the same influence on the symmetric and asymmetric NH_2 stretching vibrations. Bellamy and Williams¹² found a correlation between the two vibrations as $\nu_s = 0.876 \nu_{\text{as}} + 345.5$ and in the present study, the calculated value of symmetric NH_2 stretching vibration deviates from this relation by 21 cm^{-1} only. The NH_2 scissoring vibration¹¹ gives

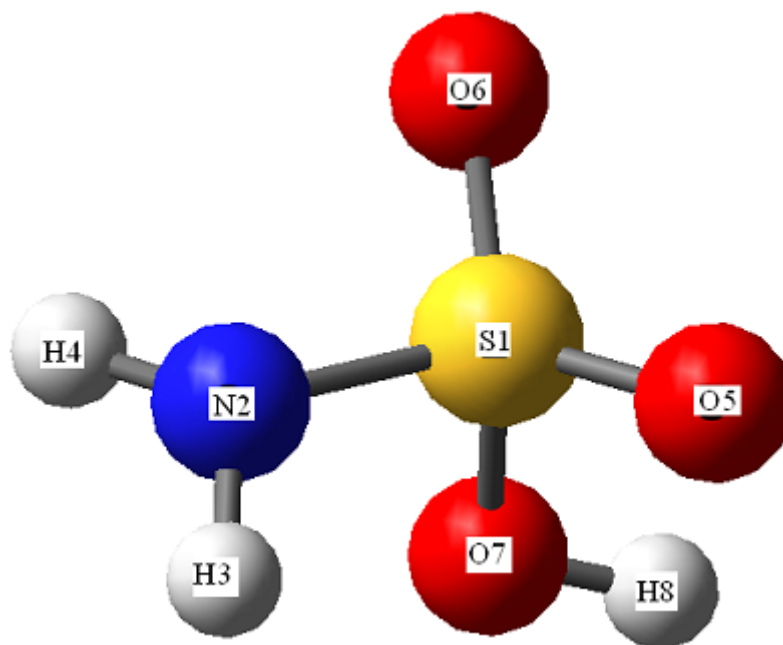


Fig. 1: Optimized geometry of sulfamic acid

rise to a broad strong band in the region 1600 ± 50 cm^{-1} and the band calculated at 1583 cm^{-1} is assigned as δNH_2 band. The rocking/twisting NH_2 band¹¹ is assigned at 1092 cm^{-1} theoretically which is expected in the region 1160 ± 140 cm^{-1} . The wagging mode¹¹ WNH_2 is expected in the region 620 ± 100 cm^{-1} . For the title compound this mode is obtained at 638 cm^{-1} . According to available data¹³⁻¹⁴ the NH_2 torsion is in the region 280 ± 70 cm^{-1} . The band at 334 cm^{-1} is assigned as this mode which is not pure but contains contributions from the rocking mode of SO_2 . The VS-N provides a band¹¹ in the region 905 ± 70 cm^{-1} . The S-N stretching vibrations exhibits a strong band in the IR spectrum and a weak band in the Raman spectrum. Theoretically we have obtained a value 880 cm^{-1} . In the spectra of N-substituted 2 thiophenesulfo-

namides, Arcoria et.al.,¹⁵ assigned VS-N in the region 900 ± 65 cm^{-1} . The majority of the investigated secondary sulfonamides were found to give this stretching frequency¹¹ at 910 ± 35 cm^{-1} .

The reported⁶ average S-N distance is 1.76 Å, the S-O bond length varies from 1.42 to 1.45 Å and the NH bond lengths are 1.013 and 1.032 Å. According to literature⁶ sulphur atom is approximately tetrahedrally coordinated to three oxygen atoms and a nitrogen atom and each nitrogen atom has six oxygen neighbours. In the present study, no such coordination is considered and the *ab initio* calculations give S-N bond length as 1.76 , S-O as 1.4156 , 1.4189 , 1.5937 and NH bond lengths as 0.9996 , 0.9997 Å.

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