



VIBRATIONAL SPECTROSCOPIC STUDIES AND *ab initio* CALCULATIONS OF 3-METHYLSULFANILIC ACID

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ABSTRACT

The Fourier transform-infrared spectrum of 3-methylsulfanilic acid was recorded and analyzed. The vibrational wavenumbers of the compound have been computed using the Hartree-Fock/6-31G* basis and compared with the experimental values. The first hyperpolarizability, predicted infrared intensities and Raman activities are reported. The calculated first hyperpolarizability is comparable with the reported values of similar structures and is an attractive object for future studies of non linear optics. Optimized geometrical parameters of the title compound are in agreement with similar reported structures.

Keywords: HF calculations, FT-IR, Sulfanilic acid, Hyperpolarizability

INTRODUCTION

Sulfanilic acid finds a number of applications in the syntheses of organic dyes¹. The amide of sulfanilic acid and certain related substituted amides are of considerable medical importance as sulfa drugs. Sulfa drugs make up a considerable portion of the pharmaceutical industry². The study of sulfanilic acid is important because of its biological significance and selectivity towards the oxidants.³ It is soluble in aqueous bases, nearly insoluble in water and aqueous acids and insoluble in organic solvents. These properties are understandable when we realize that it actually has the zwitter ionic structure that contains the $-\text{NH}_3^+$ and $-\text{SO}_3^-$

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groups.³ Panicker *et al.*⁴ reported the potential dependent surface enhanced Raman scattering profile of sulfanilic acid on silver electrode. Sulfanilamides were the first effective chemotherapeutic agents to be employed systematically for the prevention and cure of bacterial infections in humans.⁵ Further more, sulfa drugs and their complexes have many applications, such as diuretic, antiglaucoma or antiepileptic drugs, among others⁶⁻⁸. The sulfanilamides exert their antibacterial action by the competitive inhibition of the enzyme dihydropterase synthetase towards the substrate p-aminobenzoate⁹. Some metal sulfanilamides get much attention owing to their antimicrobial activity. Nonlinear optics deals with the interaction of applied electromagnetic fields in various materials to generate new electromagnetic fields, altered in wavenumber, phase or other physical properties.¹⁰ Organic molecules, able to manipulate photonic signals efficiently, are of importance in technologies such as optical communication, optical computing and dynamic image processing.^{11,12} Phenyl substituents can increase molecular hyperpolarizability, a result described as surprising.^{13,14} Many organic molecules, containing conjugated π electrons and characterized by large values of molecular first hyperpolarizabilities, were analyzed by means of vibrational spectroscopy.¹⁵ *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 so that modern vibrational spectroscopy is unimaginable without involving them. In the present study, the theoretical calculations of the wavenumbers and first hyperpolarizability of the title compound are reported and compared with experimental data.

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 cm^{-1} .

Computational details

Calculations of the title compound were carried out with Gaussian03 program¹⁶ 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 correlation¹⁷. We therefore, have used the scaling factor value of 0.8929 for HF/6-31G* basis set¹⁷. The absence of imaginary wavenumber on the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum

energy. The spectral assignment was aided by the animation option of MOLEKEL program, which gives a visual presentation of the vibrational modes.

RESULTS AND DISCUSSION

The calculated (scaled) wavenumbers, infrared bands and the corresponding assignments are given in Table 1. The SO₂ asymmetric stretching vibration^{18,19} lies within the region $1415 \pm 85 \text{ cm}^{-1}$ and esters of sulphonic acids absorb at $1385 \pm 35 \text{ cm}^{-1}$. For sodium 5-sulphosalicylate dihydrate²⁰ $\nu_{\text{as}}\text{SO}_2$ is reported at 1300 cm^{-1} . We have observed $\nu_{\text{as}}\text{SO}_2$ at 1313 cm^{-1} in IR and 1315 cm^{-1} in Raman spectrum of sulfanilamide²¹. In the title compound, the band seen at 1314 cm^{-1} in the IR spectrum and at 1315 cm^{-1} by HF calculation is assigned as $\nu_{\text{as}}\text{SO}_2$ mode.^{18,19} The SO₂ symmetric stretching vibration^{18,19} is expected in the region $1195 \pm 60 \text{ cm}^{-1}$. For orthanilic acid²² $\nu_{\text{s}}\text{SO}_2$ is observed around 1208 cm^{-1} . Most of the esters of sulfonic acids¹⁸ show $\nu_{\text{s}}\text{SO}_2$ at $1200 \pm 35 \text{ cm}^{-1}$. For sulfanilamide, $\nu_{\text{s}}\text{SO}_2$ is reported at 1147 cm^{-1} (IR) and 1136 cm^{-1} (Raman)²¹. This mode is seen at 1138 cm^{-1} in the IR spectrum and at 1131 cm^{-1} theoretically for the title compound. Usually absorption of SO₂ deformations appears with weak to moderate intensity. The SO₂ scissors is assigned in the region $570 \pm 60 \text{ cm}^{-1}$ and the SO₂ wagging vibration in the region $520 \pm 40 \text{ cm}^{-1}$, both with medium intensity and clearly separated¹⁸. For orthanilic acid²², δSO_2 is reported at 613 cm^{-1} and ωSO_2 at 565 cm^{-1} . For sulfanilamide²¹, the bands at 626 and 540 cm^{-1} are assigned as δSO_2 and ωSO_2 modes. For the title compound, the SO₂ deformation bands are observed at 537 cm^{-1} in the IR spectrum and at $565, 535 \text{ cm}^{-1}$ theoretically. The C-S stretching band appears moderately to strongly in the region $760 \pm 25 \text{ cm}^{-1}$ for majority of the investigated molecules¹⁸. In the case of pyridine-3-sulfonic acid, $\nu\text{C-S}$ is reported at 742 cm^{-1} experimentally and at 740 cm^{-1} theoretically²³. In the present case, the band observed at 763 cm^{-1} in the IR spectrum and at 743 cm^{-1} (HF) is assigned as $\nu\text{C-S}$ mode. The SO₂ twisting and rocking vibrations^{18,24} are seen in the range $425 \pm 85 \text{ cm}^{-1}$ and $345 \pm 55 \text{ cm}^{-1}$. The $\nu\text{O-S}$ stretching vibration is expected in the region $795 \pm 35 \text{ cm}^{-1}$ according to Roeges¹⁸ and the band at 817 cm^{-1} in IR and 819 cm^{-1} by HF calculation is assigned as this band. The HF calculations give the νOH stretching mode²⁰ at 3587 cm^{-1} .

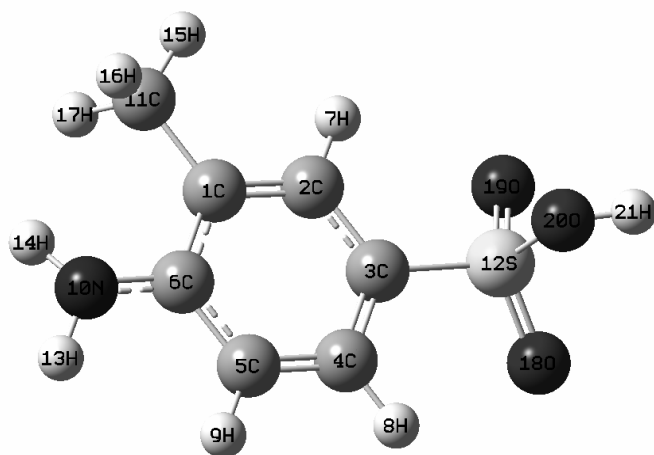
In aromatic compounds, the asymmetric stretching vibrations of CH₃ are expected in the range of $2905\text{-}3000 \text{ cm}^{-1}$ and symmetric CH₃ vibrations in the range of $2860\text{-}2870 \text{ cm}^{-1}$.^{18,25} The asymmetric stretching modes of the methyl group are calculated to be at $2940, 2895 \text{ cm}^{-1}$ and the symmetric mode at 2847 cm^{-1} . Two bending vibrations can occur within a methyl group. The first of these, the symmetrical bending vibration, involves the in-phase bending of the C-H bonds. The second, the asymmetrical bending vibration, involves out-of-

phase bending of the C-H bonds. The asymmetrical deformations are expected in the range¹⁸ of 1400-1485 cm^{-1} . The calculated values of $\delta_{\text{as}}\text{Me}$ modes are 1470 and 1458 cm^{-1} . In many molecules, the symmetric deformation $\delta_{\text{s}}\text{Me}$ are expected in the region¹⁸ $1380 \pm 25 \text{ cm}^{-1}$. The HF calculations give $\delta_{\text{s}}\text{Me}$ at 1397 cm^{-1} . The bands observed at 1451 and 1402 cm^{-1} in the IR spectrum are assigned as deformation bands of the methyl group. Aromatic molecules display a methyl rock¹⁸ in the neighbourhood of 1045 cm^{-1} . The second methyl rock¹⁸ in the region $970 \pm 70 \text{ cm}^{-1}$ is more difficult to find among the C-H out-of-plane deformations. For the title compound, these modes ρMe are calculated at 1047 and 983 cm^{-1} . The band observed at 1038 cm^{-1} in the IR spectrum is assigned as methyl rocking vibration.

The broad band observed in the IR spectrum at 3500 cm^{-1} is assigned to the asymmetric stretching mode²⁶ of NH_2 . The NH_2 stretching modes are expected in the region¹⁸ 3250-3480 cm^{-1} . The HF calculations give 3501 and 3408 cm^{-1} as asymmetric and symmetric NH_2 stretching vibrations. The NH_2 scissoring vibration¹⁸ is expected in the range $1620 \pm 20 \text{ cm}^{-1}$ and the band at 1633 cm^{-1} in IR spectrum and 1650 cm^{-1} (HF) is assigned as this scissoring mode. The NH_2 scissoring modes are reported at 1629 cm^{-1} for sulfanilamide²¹ and at 1637 cm^{-1} in IR, 1634 cm^{-1} in Raman and 1642 cm^{-1} theoretically for orthanilic acid.²² The δNH_2 scissoring modes are reported at 1621, 1597 cm^{-1} (IR), 1621, 1602 cm^{-1} (Raman) for para-substituted halogenoanilines²⁷ and at 1630 cm^{-1} for 2-aminobenzyl alcohol.²⁸ According to Roeges¹⁸, $\rho/\tau\text{NH}_2$ vibration is expected in the region $1070 \pm 50 \text{ cm}^{-1}$ and in the present case, the band observed at 1084 cm^{-1} in IR and 1084 cm^{-1} by HF calculation is assigned as $\rho/\tau \text{NH}_2$ mode. Krishnakumar and Balachandran²⁹ and Altun *et al.*³⁰ reported these modes at 1130, 1126, 1089, 1085 cm^{-1} for dibromo, nitro and methyl thioaniline complexes, and at 1040, 1030, 1008 cm^{-1} for methyl aniline complexes, respectively. Kurt *et al.*³¹ observed the wagging mode ωNH_2 for chloromethylaniline at 667 cm^{-1} in IR spectrum and at 695 cm^{-1} by HF calculation. Tzeng *et al.*³² calculated the wagging mode of amino group at 649 cm^{-1} and experimentally at 665 cm^{-1} . For the title compound, the wagging mode of NH_2 is observed at 688 cm^{-1} in the IR spectrum and at 657 cm^{-1} theoretically.

Primary aromatic amines with nitrogen directly attached to the ring absorb in the region 1330-1260 cm^{-1} due to the stretching vibration of the phenyl carbon-nitrogen bond^{25,32}. We have observed this νCN mode at 1251 cm^{-1} in the IR spectrum and at 1267 cm^{-1} theoretically. Akalin and Akyuz³³ assigned C-N stretching vibration at 1268 cm^{-1} in the Raman spectrum for paraphenylenediamine, at 1226, 1227, 1229 cm^{-1} for paraphenyldiamine complexes and at 1266, 1263, 1216 cm^{-1} theoretically. The torsional modes¹⁸ of NH_2 are expected in the region $230 \pm 70 \text{ cm}^{-1}$.

The phenyl CH stretching vibrations occur above 3000 cm^{-1} and is typically exhibited as multiplicity of weak to moderate bands, compared with the aliphatic CH stretching.³⁴ In the present case, the HF calculations give νCH modes in the range $3004\text{--}3047\text{ cm}^{-1}$. The bands observed at 3108 and 3057 cm^{-1} in the IR spectrum is assigned as phenyl CH stretching modes. For tri-substituted phenyl ring, νPh modes¹⁸ are seen in the range $1640\text{--}1260\text{ cm}^{-1}$. In the present case, the νPh modes are observed at 1604 , 1580 , 1493 cm^{-1} in the IR spectrum and at 1607 , 1582 , 1493 , 1411 and 1295 cm^{-1} theoretically. In asymmetric tri-substituted benzene, when all the three substituents are light, the wavenumber interval of ring breathing mode³⁵ is between 500 and 600 cm^{-1} . In the case of mixed substituents, the wavenumber is expected³⁵ to appear between 600 and 750 cm^{-1} . When all the three substituents are heavy, the ring breathing mode is expected around 1100 cm^{-1} . For the title compound, the band calculated at 743 cm^{-1} is assigned as the ring breathing mode of the phenyl ring. This mode is not pure but contains significant contribution from C-S stretching vibration. The in-plane bending δCH modes¹⁸ are expected above 1000 cm^{-1} . In the present case, these modes are observed at 1111 , 1162 , 1219 cm^{-1} in the IR spectrum and at 1113 , 1171 , 1209 cm^{-1} theoretically. The CH out-of-plane deformations¹⁸ are observed between 1000 and 700 cm^{-1} . Generally, the CH out-of-plane deformations with the highest wavenumbers have a weaker intensity than those absorbing at lower wavenumbers. These γCH modes are observed at 889 , 842 cm^{-1} in the IR spectrum and at 976 , 885 , 829 cm^{-1} theoretically.



The reported values of S=O in SO_2 and SO_3 molecules are 1.4308 , 1.4469 \AA and 1.4173 , 1.4261 \AA , respectively.^{36,37} In the present case, the *ab initio* calculations give S=O bond length as 1.4266 , 1.4265 \AA and S-O as 1.5950 \AA . Clerbaux and Colin³⁸ reported S-O bond length as 1.4811 and 1.4931 \AA , and Demaison *et al.*³⁹ reported S-O in the range

1.5750-1.6119 Å, S=O in the range 1.4111-1.4301 Å and according to Miller *et al.*⁴⁰ S=O =1.446 Å and S-O =1.627 Å. According to Natsheh *et al.*⁴¹ the bond length O-H =0.98, S-O =1.626, S=O =1.441 Å and Hintze *et al.*⁴² gave the corresponding lengths as 0.968, 1.593 and 1.423 Å. According to Anderson *et al.*⁴³, the SO bond lengths lie in the range 1.452-1.5666 Å and the CN bond lengths in the range 1.472-1.467 Å. The O-S-O angles are reported in the range^{39,41} 101.4-102.3° where as in the present case, the O₁₉-S₁₂-O₁₈ = 119.4°, O₁₉-S₁₂-O₂₀ = 107.4°, O₁₈-S₁₂-O₂₀ = 119.4°. The CCN bond angles are reported⁴³ as 118.6-119.5°. For the title compound, the CCN angles C₅-C₆-N₁₀ = 119.7° and C₁-C₆-N₁₀ = 120.2°. For the title compound, the *ab initio* calculations give S₁₂-O₂₀-H₂₁ angle as 109.6° where as the reported values is in the range^{36,39,41} 106.5-108.5°. The differences between the reported experimental and calculated values are observed. It must be due to the fact that experimental results belong to the solid phase and theoretical calculations belong to the gaseous phase of a single molecule.

In the amino group, the nitrogen atom is likely out-of-plane, with a torsional angle C-C-C-N around 178° or (around 2°). Existence of this angle has interpreted to be caused by the asymmetric interaction between the NH₂ group and the benzene ring plane. This interaction is common to all aniline derivatives^{32,44}. The C-N distance in the present case is 1.381 Å, which is similar to the measured value in aniline.⁴⁵

Analysis of organic molecules having conjugated π -electron systems and large hyperpolarizability using infrared and Raman spectroscopy has evolved as a subject of research.⁴⁶ 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. The first hyperpolarizability (β_0) of this novel molecular system is calculated using HF method, based on the finite field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. First hyperpolarizability is a third rank tensor that can be described by a $3 \times 3 \times 3$ matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry.⁴⁷ The calculated first hyperpolarizability of the title compound is 2.69×10^{-30} esu, which is comparable with the reported values of similar derivatives⁴⁸ and experimental evaluation of this data is not readily available.

CONCLUSION

In this work, we have performed the theoretical and experimental vibrational analysis of 3-methylsulfanilic acid. The theoretical study gave a description of the geometry and vibrational wavenumbers of the title compound. The calculated (scaled) wavenumbers

are in good agreement with the experimental values obtained for the investigated molecule. The observed discrepancies between the theory and experiment could be a consequence of the anharmonicity and of the general tendency of the quantum mechanical methods to overestimate the force constants at the exact equilibrium geometry. From the calculated hyperpolarizability value, we conclude that the title compound is an attractive object for future studies of nonlinear optical properties.

Table 1: Calculated vibrational wavenumbers (scaled), measured infrared band positions and assignments for 3-methylsulfanilic acid

$\nu_{(\text{HF})} \text{ cm}^{-1}$	IR Intensity (KM/Mole)	Raman activity (A**4/AMU)	$\nu_{(\text{IR})} \text{ cm}^{-1}$	Assignments
3587	205.92	179.68		νOH
3501	24.98	57.44	3500	$\nu_{\text{as}}\text{NH}_2$
3408	41.29	144.93		$\nu_{\text{s}}\text{NH}_2$
3047	0.95	79.70	3108	νCH
3036	0.68	51.73	3057	νCH
3004	16.19	89.13		νCH
2940	17.40	54.18	2929	$\nu_{\text{as}}\text{Me}$
2895	29.22	84.81		$\nu_{\text{as}}\text{Me}$
2847	40.97	143.83		$\nu_{\text{s}}\text{Me}$
1650	163.83	27.39	1633	δNH_2
1607	56.73	54.31	1604	νPh
1582	51.19	28.13	1580	νPh
1493	79.21	6.61	1493	νPh
1470	18.53	5.67		$\delta_{\text{as}}\text{Me}$
1458	6.71	18.25	1451	$\delta_{\text{as}}\text{Me}$
1411	18.07	3.59		νPh
1397	9.48	8.90	1402	$\delta_{\text{s}}\text{Me}$

Cont...

$\nu_{(\text{HF})} \text{ cm}^{-1}$	IR Intensity (KM/Mole)	Raman activity (A**4/AMU)	$\nu_{(\text{IR})} \text{ cm}^{-1}$	Assignments
1315	228.38	2.71	1314	$\nu_{\text{as}}\text{SO}_2$
1295	47.13	2.11		νPh
1267	53.04	9.98	1251	νCN
1209	23.65	3.73	1219	δCH
1190	321.41	23.65	1195	δOH
1171	93.88	1.01	1162	δCH
1131	16.65	1.90	1138	$\nu_{\text{s}}\text{SO}_2$
1113	96.67	13.25	1111	δCH
1084	41.53	6.35	1084	$\rho/\tau\text{NH}_2$
1047	0.30	1.03	1038	ρMe
1038	2.96	0.84	1030	$\rho/\tau\text{NH}_2$
983	3.16	3.06		ρMe
976	0.15	0.49		γCH
931	5.50	1.06	906	νCC
885	101.81	2.70	889	γCH
829	24.53	2.63	842	γCH
819	297.43	14.42	817	νOS
743	2.65	17.62	763	νCS , Ring breath
717	16.54	0.73	710	γPh
657	55.12	6.31	688	ωNH_2
584	5.72	1.12	599	$\delta\text{Ph(X)}$
565	81.19	3.16		δSO_2
535	277.86	9.24	537	ωSO_2
517	115.55	5.46		$\gamma\text{Ph(X)}$

Cont...

$\nu_{(\text{HF})}$ cm^{-1}	IR Intensity (KM/Mole)	Raman activity ($\text{A}^{**4}/\text{AMU}$)	$\nu_{(\text{IR})}$ cm^{-1}	Assignments
501	59.09	1.98		$\delta\text{Ph(X)}$
488	100.97	5.87		γPh
439	14.26	0.68	443	τSO_2
434	24.66	0.59		$\delta\text{Ph(X)}$
368	19.60	0.82		$\delta\text{CN(X)}$
331	1.58	0.52		ρSO_2
319	37.64	0.76		$\delta\text{CC(X)}$
295	7.715	3.13		$\gamma\text{CN(X)}$
270	1.78	3.91		tNH ₂
237	1.13	1.75		δOS
182	1.25	0.08		tMe
165	0.51	2.41		$\delta\text{CS(X)}$
149	0.07	0.14		$\gamma\text{CC(X)}$
85	3.12	2.76		$\gamma\text{CS(X)}$
59	6.12	1.15		tPh
42	100.80	4.35		tPh

ν -stretching; δ -in-plane deformation; γ -out-of-plane deformation; τ -twisting; rocking; ω -wagging; t- torsion; X-substituent sensitive; Me-methyl; Ph-Phenyl; subscripts: as – asymmetric, s- symmetric

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