

# DFT based computational study on the molecular conformation, NMR chemical shifts and vibrational transitions for *N*-(2-methylphenyl) methanesulfonamide and *N*-(3-methylphenyl) methanesulfonamide

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## ABSTRACT

This paper presents a DFT quantum chemical investigation of the molecular conformation, NMR chemical shifts and vibrational transitions of *N*-(2-methylphenyl)methanesulfonamide and *N*-(3-methylphenyl)methanesulfonamide (C<sub>8</sub>H<sub>11</sub>NO<sub>2</sub>S) employing B3LYP exchange correlation. The vibrational wave-numbers were calculated and the complete assignments were performed on the basis of the total energy distribution (TED) of the vibrational modes, calculated with scaled quantum mechanics (SQM) method. The <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts of the compounds were calculated in CDCl<sub>3</sub> and DMSO using the GIAO method. Finally, calculations were compared with experimental values.

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## 1. Introduction

Amides, sulfonamides and their derivatives have been the subject of investigation for many reasons. The amides are important constituent of many biologically significant compounds. The chemistry of sulfonamides is of interest as they show distinct physical, chemical and biological properties. The sulfonamide derivatives are known for their numerous pharmacological activities, antibacterial, antitumor, insulin-release stimulation and antithyroid properties [1]. In addition, the unsubstituted aromatic/heterocyclic sulfonamides act as carbonic anhydrase inhibitors [2,3] whereas other types of derivatives show diuretic activity (high-ceiling diuretics or thiazidiazine diuretics), hypoglycemic activity and anticancer properties [4]. Although sulfonamides are best known as bacteriostatic [5] and antimalarial agents [6], there is now a range of drugs, possessing very different pharmacological activities, in which the sulfonamide group is present [7]. Several of these drugs suffer from bioavailability problems or adverse secondary effects [8–10]. Due to their significant pharmacology applications and widespread use in medicine, these compounds have gained attention in bio-inorganic and metal-based drug chemistry.

Jayalakshmi and Gowda reported Infrared and <sup>1</sup>H and <sup>13</sup>C NMR spectra of *N*-(substituted phenyl)-methanesulphonamides in-

cludes *N*-(2-methylphenyl)methanesulfonamide (2MPMSA) and *N*-(3-methylphenyl)methanesulfonamide (3MPMSA) [11]. They also analyzed the X-ray crystallographic structure of these two compounds [12,13]. Dodoff studied the Infrared spectra (in solid state and CCl<sub>4</sub>) and the conformational features of *N*-3-pyridinylmethanesulfonamide (PMSA) using molecular mechanics and HF ab initio calculations [14]. The crystal structure of PMSA and *trans*-diiodobis(PMSA)platinum(II) were also reported by Dodoff and coworkers [15]. Recently we initiated a spectroscopic study supported by ab initio and density functional theory calculations of some *para*-halogen benzenesulfonamides, 4-X-C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>NH<sub>2</sub> (X = F, Cl or Br) [16]. To our knowledge, no density functional (DFT) study has been performed on the conformation, vibrational and NMR spectra of the title compounds yet. We believe that the potentially active sulfonamide derivatives deserve more detailed and systematic theoretical studies using updated computer programs and recently available knowledge on structure activity relations. The purpose of this work is to investigate theoretically structural and spectroscopic properties of 2MPMSA and 3MPMSA.

## 2. Quantum chemical calculations

Geometry optimization was started from the X-ray experimental atomic position [12,13]. The molecular structure of two compounds in the ground state (in vacuo) was optimized. The optimized structural parameters were used in the vibrational

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frequency calculations at DFT levels to characterize all stationary points as minima. Polarization functions have been added for the better treatment of the position effect of substituent group. Analytic frequency calculations at the optimized geometry were done to confirm the optimized structure to be an energy minimum and to obtain theoretical vibrational spectra. These values were scaled by corresponding scaling factors. The fundamental vibrational modes were characterized by their TEDs which were calculated by using the SQM program [17,18].

For NMR calculations, after optimization,  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts ( $\delta\text{H}$  and  $\delta\text{C}$ ) were calculated in dimethylsulfoxide (DMSO) and chloroform ( $\text{CDCl}_3$ ) using the gauge-invariant atomic orbital (GIAO) method [19,20] which is one of the most common approaches for calculating nuclear magnetic shielding tensors. Based on our previous experience [16,21], we selected the B3LYP [22,23] hybrid functional and a fairly large and flexible basis set 6-311++G(d,p) to perform accurate calculations on the title molecules. The entire calculations were performed on a Pentium IV/3.02 GHz personal computer using Gaussian 03 [24] program package, invoking gradient geometry optimization.

### 3. Results and discussion

#### 3.1. Molecular geometries

The optimized structure of compounds is shown in Fig. 1 with numbering of the atoms. The optimized structure parameters of studied molecules are listed in Table 1, in accordance with the atom numbering scheme given in Fig. 1. The available experimental data [12,13] obtained by the X-ray study for two compounds are also given in Table 1 for comparison. As can be noticed from Table 1, all of the computed bond lengths and most of the bond angles are slightly larger than experimental ones. These discrepancies can be explained by the fact that the calculations assume an isolated molecule where the intermolecular Coulombic interaction with the neighboring molecules are absent, whereas the experimental result corresponds to interacting molecules in the crystal lattice. It is well known that DFT methods predict bond lengths which are systematically too long, particularly the C–H bond lengths. Since, large deviation from experimental C–H bond lengths may arise from the low scattering factors of hydrogen atoms in the X-ray diffraction experiment. This overestimation is also verified in our calculation as represented in Table 1. The theoretical values of C–H bonds are greater than 1.0 Å while the values in the experimental result are shorter. The overestimation can be seen for other bond lengths, i.e. the deviation for N–S and S–C bonds is quite high. However, it's well known that the B3LYP method, which includes electron correlation effects, overestimates

strongly all bond lengths around sulphur atom [25–27]. The biological activity of alkyl sulfonamides is thought to be due to the H atom of the phenyl N–H portion of the sulfonamide molecule, as it can align itself in relation to a receptor site [12]. The conformation of the N–H bond in the structures of 2MPMSA and 3MPMSA are obtained syn to the ortho-methyl substituent and anti to the meta-methyl substituent [12,13]. In our study the positions of N–H group are determined with dihedral angles given in Table 1. The C–N–S–C dihedral angles are computed at 60.2° and 55.9° for 2MPMSa and 3MPMSA, respectively. As analyzed from geometric parameters these values are deviated ca. 2° from experimental results. The predicted CNS bond angle for each molecule is in a good agreement with observed values. To make comparison with experimental data, we present RMS values based on the calculations (bottom of Table 1). As can be seen there, the average deviation of bond lengths and bond angles is obtained at 0.109, 0.113 Å and 1.7, 1.8° for 2MPMSA and 3MPMSA, respectively.

#### 3.2. Vibrational analysis

The present molecules have 23 atoms and 63 normal modes of vibrations. The fundamental vibrational wavenumbers of 2MPMSA and 3MPMSA as calculated by DFT (B3LYP) are given in Tables 2 and 3. The resulting vibrational wavenumbers for the optimized geometries as well as IR intensities, Raman scattering activities and available experimental IR frequencies are also given in the tables. Vibrational modes are numbered from smallest to largest wavenumbers. In the last columns are given a detailed description of the normal modes based on TED. The calculated IR and Raman spectra are shown in Fig. 2, where the calculated intensity and activity is plotted against the harmonic vibrational wavenumbers. We know that DFT potential symmetrically overestimate the vibrational wavenumbers. These discrepancies are corrected either by computing anharmonic corrections explicitly or by introducing a scaled field or by directly scaling the calculated wavenumbers with a proper factor. Considering systematic errors we calibrated the vibrational wavenumbers calculated by B3LYP method with two scaling factors of 0.983 up to 1700  $\text{cm}^{-1}$  and 0.958 for greater than 1700  $\text{cm}^{-1}$ .

The Raman activities ( $S_{\text{Ra}}$ ) calculated with Gaussian 03 program [26] converted to relative Raman intensities ( $I_{\text{Ra}}$ ) using the following relationship derived from the intensity theory of Raman scattering [28–30].

$$I_i = \frac{f(\nu_0 - \nu_i)^4 S_i}{\nu_i [1 - \exp(-hc\nu_i/kT)]}$$

where  $\nu_0$  is the laser exciting wavenumber in  $\text{cm}^{-1}$  (in this work, we have used the excitation wavenumber  $\nu_0 = 9398.5 \text{ cm}^{-1}$ , which cor-

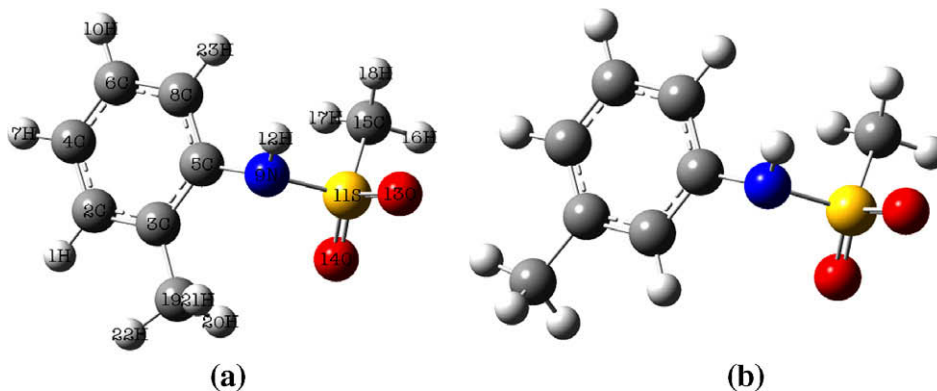


Fig. 1. The theoretical geometric structure and atoms numbering of 2MPMSA (a) and 3MPMSA (b).

**Table 1**  
Comparison of the theoretical and experimental geometric parameters of 2MPMSA and 3MPMSA according to atom numbers given in Fig. 1, bond lengths in angstrom, bond angles and dihedral angles in degrees.

| Bond lengths (Å)     | 2MPMSA             |       | 3MPMSA             |       | Bond Angles (°)       | 2MPMSA             |       | 3MPMSA             |        |
|----------------------|--------------------|-------|--------------------|-------|-----------------------|--------------------|-------|--------------------|--------|
|                      | X-ray <sup>a</sup> | B3LYP | X-ray <sup>b</sup> | B3LYP |                       | X-ray <sup>a</sup> | B3LYP | X-ray <sup>b</sup> | B3LYP  |
| H(1)–C(2/3)          | 0.940              | 1.085 | 0.870              | 1.083 | C(3)–C(5)–N(9)        | 120.1              | 119.8 | 120.0              | 120.9  |
| C(2)–C(3)            | 1.392              | 1.400 | 1.389              | 1.398 | C(8)–C(5)–N(9)        | 118.9              | 119.4 | 119.4              | 119.1  |
| C(2)–C(4)            | 1.374              | 1.392 | 1.370              | 1.400 | C(4)–C(6)–C(8)        | 119.9              | 119.2 | 119.5              | 120.5  |
| C(3)–C(5)            | 1.395              | 1.407 | 1.378              | 1.398 | C(4)–C(6)–H(10)       | 120.6              | 120.7 | 121.0              | 120.0  |
| C(3/2)–C(19)         | 1.495              | 1.506 | 1.500              | 1.510 | C(8)–C(6)–H(10)       | 119.5              | 120.1 | 119.0              | 119.5  |
| C(4)–C(6)            | 1.366              | 1.393 | 1.380              | 1.392 | C(5)–C(8)–C(6)        | 120.2              | 120.8 | 119.2              | 119.5  |
| C(4)–H(7)            | 0.950              | 1.084 | 0.870              | 1.085 | C(5)–C(8)–H(23)       | 120.3              | 119.2 | 118.0              | 120.1  |
| C(5)–C(8)            | 1.386              | 1.399 | 1.375              | 1.399 | C(6)–C(8)–H(23)       | 119.5              | 120.1 | 123.0              | 120.4  |
| C(5)–N(9)            | 1.434              | 1.437 | 1.446              | 1.424 | C(5)–N(9)–S(11)       | 123.02             | 122.4 | 121.2              | 124.3  |
| C(6)–C(8)            | 1.377              | 1.391 | 1.385              | 1.392 | C(5)–N(9)–H(12)       | 122.6              | 115.2 | 111.0              | 115.4  |
| C(6)–H(10)           | 0.960              | 1.084 | 0.900              | 1.084 | S(11)–N(9)–H(12)      | 108.0              | 109.4 | 114.0              | 109.8  |
| C(8)–H(23)           | 0.930              | 1.085 | 0.920              | 1.085 | N(9)–S(11)–O(13)      | 105.4              | 104.8 | 106.1              | 104.4  |
| N(9)–S(11)           | 1.617              | 1.694 | 1.618              | 1.692 | N(9)–S(11)–O(14)      | 109.1              | 107.7 | 108.1              | 108.2  |
| N(9)–H(12)           | 0.848              | 1.014 | 0.856              | 1.013 | N(9)–S(11)–C(15)      | 107.3              | 106.9 | 107.8              | 105.8  |
| S(11)–O(13)          | 1.429              | 1.459 | 1.436              | 1.459 | O(13)–S(11)–O(14)     | 118.2              | 121.9 | 118.1              | 121.7  |
| S(11)–O(14)          | 1.423              | 1.457 | 1.426              | 1.457 | O(13)–S(11)–C(15)     | 109.2              | 107.9 | 109.1              | 108.5  |
| S(11)–C(15)          | 1.749              | 1.809 | 1.749              | 1.807 | O(14)–S(11)–C(15)     | 107.2              | 106.8 | 107.2              | 107.1  |
| C(15)–H(16)          | 0.960              | 1.090 | 0.960              | 1.090 | S(11)–C(15)–H(16)     | 106.0              | 106.0 | 109.5              | 106.4  |
| C(15)–H(17)          | 0.910              | 1.089 | 0.960              | 1.089 | S(11)–C(15)–H(17)     | 107.0              | 108.9 | 109.5              | 108.6  |
| C(15)–H(18)          | 0.990              | 1.089 | 0.960              | 1.089 | S(11)–C(15)–H(18)     | 108.0              | 108.9 | 109.5              | 108.7  |
| C(19)–H(20)          | 0.900              | 1.092 | 0.960              | 1.092 | H(16)–C(15)–H(17)     | 110.0              | 110.4 | 109.5              | 110.5  |
| C(19)–H(21)          | 0.950              | 1.092 | 0.960              | 1.096 | H(16)–C(15)–H(18)     | 112.0              | 110.5 | 109.5              | 110.8  |
| C(19)–H(22)          | 0.900              | 1.092 | 0.960              | 1.092 | H(17)–C(15)–H(18)     | 114.0              | 111.8 | 109.5              | 111.7  |
| RMS                  |                    | 0.109 |                    | 0.113 | C(3/2)–C(19)–H(20)    | 112.0              | 111.2 | 109.5              | 111.3  |
| Bond angles (°)      |                    |       |                    |       | C(3/2)–C(19)–H(21)    | 111.0              | 110.8 | 109.5              | 110.8  |
| H(1)/C(19)–C(2)–C(3) | 117.6              | 118.5 | 120.2              | 120.2 | C(3/2)–C(19)–H(22)    | 110.0              | 110.4 | 109.5              | 111.4  |
| H(1)/C(19)–C(2)–C(4) | 120.3              | 119.4 | 122.0              | 120.8 | H(20)–C(19)–H(21)     | 107.0              | 106.6 | 109.5              | 107.4  |
| C(3)–C(2)–C(4)       | 122.1              | 122.0 | 117.8              | 119.0 | H(20)–C(19)–H(22)     | 108.0              | 108.8 | 109.5              | 108.3  |
| C(2)–C(3)–C(5)       | 116.9              | 117.3 | 120.8              | 120.6 | H(21)–C(19)–H(22)     | 109.0              | 108.9 | 109.5              | 107.4  |
| C(2)–C(3)–C(19)/H(1) | 121.2              | 120.5 | 118.0              | 120.3 | RMS                   |                    | 1.7   |                    | 1.8    |
| C(5)–C(3)–C(19)/H(1) | 121.9              | 122.2 | 121.0              | 119.1 | Dihedral angles (°)   |                    |       |                    |        |
| C(2)–C(4)–C(6)       | 119.9              | 119.9 | 122.0              | 120.5 | C(8)–C(5)–N(9)–S(11)  | –65.4              | –96.2 | –114.3             | –130.7 |
| C(2)–C(4)–H(7)       | 116.0              | 119.9 | 118.0              | 119.7 | C(5)–N(9)–S(11)–O(13) | 179.2              | 174.6 | 174.6              | 170.4  |
| C(6)–C(4)–H(7)       | 123.7              | 120.2 | 120.0              | 119.8 | C(5)–N(9)–S(11)–O(14) | –51.3              | –54.2 | –57.7              | –58.6  |
| C(3)–C(5)–C(8)       | 120.9              | 120.7 | 120.6              | 119.9 | C(5)–N(9)–S(11)–C(15) | 64.5               | 60.2  | 57.9               | 55.9   |

<sup>a</sup> From Ref. [12].

<sup>b</sup> From Ref. [13].

responds to the wavelength of 1064 nm of a Nd:YAG laser),  $\nu_i$  the vibrational wavenumber of the  $i$ th normal mode ( $\text{cm}^{-1}$ ), while  $S_i$  is the Raman scattering activity of the normal mode  $\nu_i$ .  $f$  (is a constant equal to  $10^{-12}$ ) is a suitably chosen common normalization factor for all peak intensities.  $h$ ,  $k$ ,  $c$  and  $T$  are Planck and Boltzmann constants, speed of light and temperature in Kelvin, respectively.

The hetero aromatic structure shows the presence of C–H stretching vibrations in the region  $3100\text{--}3000\text{ cm}^{-1}$  which is the characteristic region for the ready identification of C–H stretching vibrations. In this region, the bands are not affected appreciably by the nature of substituents [31,32]. The modes 53–62 are due to C–H stretching of hydrogen bonded carbon atoms of phenyl ring, methyl substituent of ring and  $\text{SO}_2$ . Except modes 57 and 58 for 2MPMSA all remaining modes are pure stretching vibrations contributing nearly 100%. The aromatic C–H in-plane bending modes of benzene and its derivatives are observed in the region  $1300\text{--}1000\text{ cm}^{-1}$ . The bands observed in the FT-IR spectrum [11] at  $1045$  and  $1111\text{ cm}^{-1}$  are assigned to aryl C–H in-plane bending vibration for 2MPMSA. The theoretically computed by B3LYP method at  $1119$ ,  $1165$  and  $1287\text{ cm}^{-1}$  (modes nos. 35, 36 and 40) for 2MPMSA and  $1101$ ,  $1161$ ,  $1174$  and  $1328\text{ cm}^{-1}$  (modes nos. 35–37, 42) for 3MPMSA show good agreement with recorded data. The C–H out-of-plane bending vibrations occur in the range  $750\text{--}1000\text{ cm}^{-1}$  in the aromatic compounds. The bands observed at  $627$  and  $743\text{ cm}^{-1}$  in FT-IR spectrum are assigned to aryl C–H out-of-plane bending vibrations for title compounds. We com-

puted four pure bands for each molecule assigned to out-of plane ring C–H bending which show excellent agreement with the region given for this mode. The TED for in-plane bending vibrations suggests that these are mixed modes. In general, the calculated aromatic C–H vibrations (stretching, in-plane and out-of-plane bending) are in good agreement with experimentally accepted values given in literature [31–35].

It is stated that the N–H stretching vibrations occur in the region  $3300\text{--}3500\text{ cm}^{-1}$  [36]. Experimentally, the strong bands at  $3280$  and  $3250\text{ cm}^{-1}$  are assigned to N–H stretching for 2MPMSA and 3MPMSA [11]. In this study, we computed this band at  $3406$  and  $3422\text{ cm}^{-1}$  which shows high difference with the observed ones. However, it's known that calculations in high frequency region are not reliable with experimental data due to the anharmonic effects and difference between experiment and calculations media. The same band was recorded at  $3383\text{ cm}^{-1}$  for PMSA in  $\text{CCl}_4$  solution [14]. As expected, these modes for both of molecules, are pure stretching modes as it is evident from TED column, they are almost contributing 100%. The pure N–H in-plane-bending vibrations are calculated at  $1380$  and  $1385\text{ cm}^{-1}$  for 2MPMSA and 3MPMSA while the observed bands correspondence at  $1400$  and  $1390\text{ cm}^{-1}$ . The out-of-plane bending vibrations of N–H are contaminated with other vibrations, as seen in Tables 2 and 3.

Empirical assignments of vibrational modes for peaks in the fingerprint region are difficult. In the wavenumber region of  $600\text{--}1660\text{ cm}^{-1}$ , the spectrum observed in the experiments closely

Table 2

Comparison of the calculated and experimental vibrational spectra and proposal assignments of 2MPMSA.

| No | Exp. <sup>a</sup> | Experimental assignments <sup>a</sup> | Unscaled freq. | Scaled freq. | $I_{IR}$ | $S_{Ra}$ | Assignments (TED)                                                                                                              |
|----|-------------------|---------------------------------------|----------------|--------------|----------|----------|--------------------------------------------------------------------------------------------------------------------------------|
| 1  |                   |                                       | 38             | 37           | 4.150    | 1.499    | $\tau(\text{SO}_2\text{-CH}_3)$ (76) + $\tau(\text{CH}_3)_{\text{methyl}}$ (11)                                                |
| 2  |                   |                                       | 72             | 71           | 2.147    | 3.441    | $\beta(\text{CNS})$ (30) + $\tau(\text{CH}_3)_{\text{methyl}}$ (25)                                                            |
| 3  |                   |                                       | 93             | 91           | 3.019    | 1.548    | $\beta$ ring-N-S (58) + $\tau(\text{CH}_3)_{\text{methyl}}$ (20) + $\beta\text{CNS}$ (11)                                      |
| 4  |                   |                                       | 139            | 137          | 1.165    | 0.857    | $\tau(\text{CH}_3)_{\text{methyl}}$ (69)                                                                                       |
| 5  |                   |                                       | 184            | 181          | 0.215    | 0.788    | $\tau(\text{CH}_3)_{\text{methane}}$ (45) + $\tau(\text{CH}_3)_{\text{methyl}}$ (30)                                           |
| 6  |                   |                                       | 195            | 192          | 1.105    | 0.675    | $\tau(\text{CH}_3)_{\text{methane}}$ (66)                                                                                      |
| 7  |                   |                                       | 222            | 218          | 1.302    | 2.141    | $r\text{C-CH}_3$ + $\beta\text{CCN}$ (20)                                                                                      |
| 8  |                   |                                       | 257            | 253          | 1.248    | 3.386    | $r\text{SO}_2$ (29)                                                                                                            |
| 9  |                   |                                       | 280            | 275          | 1.513    | 3.649    | $\nu\text{CNS}$ (19) + $\beta\text{N-S-CH}_3$ (16)                                                                             |
| 10 |                   |                                       | 333            | 327          | 0.234    | 1.327    | $r\text{S-CH}_3$ (62) + $r\text{C-CH}_3$ (14)                                                                                  |
| 11 |                   |                                       | 367            | 361          | 4.851    | 4.087    | $r\text{C-CH}_3$ (24) + $\gamma\text{CNS}$ (22) + $r\text{S-CH}_3$ (20) + $\nu\text{CNS}$ (11)                                 |
| 12 | 428 w             | C=C ( $\gamma$ Ar)                    | 420            | 413          | 4.636    | 1.027    | $r\text{C-CH}_3$ (22) + $\beta\text{CCN}$ (15) + $\gamma\text{CCC}$ (10)                                                       |
| 13 | 446 w             | C=C ( $\gamma$ Ar)                    | 456            | 448          | 24.671   | 6.891    | $\gamma\text{NH}$ (21) + $\rho\text{SO}_2$ (14) + $\gamma\text{CCC}$ (11)                                                      |
| 14 |                   |                                       | 469            | 461          | 2.459    | 6.629    | $\gamma\text{NH}$ (39) + $\gamma\text{CCC}$ (17)                                                                               |
| 15 |                   |                                       | 484            | 476          | 21.260   | 3.834    | $\gamma\text{NH}$ (33) + $\rho\text{SO}_2$ (17) + $\nu\text{S-CH}_3$ (11)                                                      |
| 16 |                   |                                       | 515            | 506          | 91.170   | 9.136    | $\gamma\text{NH}$ (17) + $w\text{SO}_2$ (12) + $\nu\text{S-CH}_3$ (11) + $\beta\text{CCC}$ (11)                                |
| 17 |                   |                                       | 539            | 530          | 8.809    | 1.128    | $\gamma\text{CCC}$ (45)                                                                                                        |
| 18 |                   |                                       | 572            | 562          | 19.811   | 21.382   | $\beta\text{CCC}$ (21) + $\beta\text{CNS}$ (21)                                                                                |
| 19 | 627 w             | C-H ( $\gamma$ Ar)                    | 633            | 622          | 7.956    | 6.680    | $\beta\text{CCC}$ (46)                                                                                                         |
| 20 |                   |                                       | 703            | 691          | 28.076   | 16.434   | $\nu\text{S-CH}_3$ (26) + $\gamma\text{CCC}$ (21)                                                                              |
| 21 | 710 w             | N-H ( $\gamma$ )                      | 729            | 717          | 83.235   | 3.906    | $\nu\text{C-CH}_3$ (38) + $\gamma\text{CCC}$ (15)                                                                              |
| 22 | 743 s             | C-S ( $\nu$ )                         | 751            | 738          | 19.845   | 3.368    | $\gamma$ $\text{CH}_{\text{ring}}$ (57)                                                                                        |
| 23 |                   |                                       | 779            | 766          | 10.628   | 7.140    | ring breath. (35) + $\nu\text{C-CH}_3$ (13)                                                                                    |
| 24 | 833 m             | C-H ( $\beta$ Ar)                     | 831            | 817          | 45.095   | 4.814    | $\nu\text{SN}$ (32) + $\beta(\text{C-NH-S})$ (18)                                                                              |
| 25 |                   |                                       | 877            | 862          | 4.253    | 1.022    | $\gamma$ $\text{CH}_{\text{ring}}$ (79)                                                                                        |
| 26 |                   |                                       | 881            | 866          | 22.437   | 13.140   | $\nu(\text{CNS})$ (32) + $\beta\text{CCC}_{\text{ring}}$ (31)                                                                  |
| 27 | 914 w             | S-N ( $\nu_{\text{sym}}$ )            | 958            | 942          | 1.473    | 0.152    | $\gamma$ $\text{CH}_{\text{ring}}$ (85)                                                                                        |
| 28 |                   |                                       | 976            | 959          | 31.463   | 4.208    | $r\text{S-CH}_3$ (85)                                                                                                          |
| 29 |                   |                                       | 982            | 965          | 30.273   | 2.246    | $r\text{S-CH}_3$ (83)                                                                                                          |
| 30 |                   |                                       | 995            | 978          | 0.059    | 0.077    | $\gamma$ $\text{CH}_{\text{ring}}$ (85)                                                                                        |
| 31 |                   |                                       | 1010           | 993          | 0.831    | 3.115    | $r\text{C-CH}_3$ (58) + $\nu$ $\text{CC}_{\text{ring}}$ (23)                                                                   |
| 32 | 1045 w            | C-H ( $\beta$ Ar)                     | 1068           | 1050         | 2.468    | 1.011    | $r\text{C-CH}_3$ (84)                                                                                                          |
| 33 |                   |                                       | 1070           | 1052         | 7.143    | 28.452   | $\nu$ $\text{CC}_{\text{ring}}$ (58) + $\beta\text{CH}_{\text{ring}}$ (20)                                                     |
| 34 |                   |                                       | 1115           | 1096         | 250.346  | 9.611    | $\nu_{\text{sym}} \text{SO}_2$ (85)                                                                                            |
| 35 | 1111 m            | C-H ( $\beta$ Ar)                     | 1138           | 1119         | 11.482   | 3.277    | $\beta\text{CH}_{\text{ring}}$ (36) + $\nu$ $\text{CC}_{\text{ring}}$ (19) + $\nu\text{CC}_{\text{ring}}$ (10)                 |
| 36 | 1153 s            | S=O ( $\nu_{\text{sym}}$ )            | 1185           | 1165         | 0.564    | 5.100    | $\beta\text{CH}_{\text{ring}}$ (81) + $\nu$ $\text{CC}_{\text{ring}}$ (17)                                                     |
| 37 |                   |                                       | 1210           | 1189         | 4.776    | 5.301    | $\nu$ $\text{CH}_3$ (20) + $\beta\text{CH}_{\text{ring}}$ (20) + $\nu$ $\text{CN}$ (15) + $\nu$ $\text{CC}_{\text{ring}}$ (14) |
| 38 |                   |                                       | 1234           | 1213         | 23.687   | 56.878   | $\nu$ $\text{CC}_{\text{ring}}$ (28) + $\nu$ $\text{CN}$ (27) + $\beta\text{CH}_{\text{ring}}$ (13)                            |
| 39 | 1238 w            | C-N ( $\nu$ )                         | 1287           | 1265         | 57.731   | 30.635   | $\nu_{\text{asym}} \text{SO}_2$ (32) + $\beta\text{CH}_{\text{ring}}$ (19) + $\beta\text{NH}$ (11)                             |
| 40 | 1281 w            | C-N ( $\nu$ )                         | 1309           | 1287         | 95.341   | 3.490    | $\nu_{\text{asym}} \text{SO}_2$ (40) + $\beta\text{CH}_{\text{ring}}$ (31)                                                     |
| 41 |                   |                                       | 1324           | 1301         | 56.157   | 3.303    | $\nu_{\text{asym}} \text{CCC}_{\text{ring}}$ (71) + $\nu_{\text{asym}} \text{SO}_2$ (11)                                       |
| 42 | 1317 s            | S=O ( $\nu_{\text{asym}}$ )           | 1346           | 1323         | 10.965   | 0.427    | $w(\text{CH}_3)_{\text{methane}}$ (96)                                                                                         |
| 43 |                   |                                       | 1404           | 1380         | 66.991   | 15.168   | $\beta\text{NH}$ (61)                                                                                                          |
| 44 | 1400 m            | N-H ( $\beta$ )                       | 1421           | 1397         | 4.854    | 9.280    | $w(\text{CH}_3)_{\text{methyl}}$ (96)                                                                                          |
| 45 |                   |                                       | 1451           | 1426         | 5.581    | 4.946    | $\rho(\text{CH}_2)_{\text{methane}}$ (89)                                                                                      |
| 46 |                   |                                       | 1457           | 1432         | 4.323    | 5.774    | $\rho(\text{CH}_2)_{\text{methane}}$ (80)                                                                                      |
| 47 |                   |                                       | 1471           | 1446         | 5.667    | 2.809    | $\beta\text{CH}_{\text{ring}}$ (36) + $\rho(\text{CH}_2)_{\text{methane}}$ (21) + $\nu\text{CC}_{\text{ring}}$ (18)            |
| 48 |                   |                                       | 1479           | 1454         | 8.316    | 6.809    | $\rho(\text{CH}_2)_{\text{methane}}$ (87)                                                                                      |
| 49 | 1468 w            | C=C ( $\nu$ Ar)                       | 1505           | 1479         | 21.529   | 5.170    | $\{\beta\text{CH}_2$ (58) + $\gamma\text{CH}$ (10)}_{\text{methane}}                                                           |
| 50 | 1497 m            | C=C ( $\nu$ Ar)                       | 1523           | 1497         | 27.923   | 3.929    | $\beta\text{CH}_{\text{ring}}$ (47) + $\nu\text{CC}_{\text{ring}}$ (26)                                                        |
| 51 | 1583 m            | C=C ( $\nu$ Ar)                       | 1617           | 1590         | 1.687    | 21.304   | $\nu\text{CC}_{\text{ring}}$ (65) + $\beta\text{CH}_{\text{ring}}$ (12)                                                        |
| 52 |                   |                                       | 1639           | 1611         | 3.438    | 36.455   | $\nu\text{CC}_{\text{ring}}$ (66) + $\beta\text{CH}_{\text{ring}}$ (11)                                                        |
| 53 |                   |                                       | 3043           | 2915         | 19.605   | 190.477  | $\nu\text{CH}_{\text{methyl}}$ (100)                                                                                           |
| 54 | 2931 w            | C-H ( $\nu$ Alk)                      | 3060           | 2931         | 0.658    | 152.810  | $\nu\text{CH}_{\text{methane}}$ (100)                                                                                          |
| 55 |                   |                                       | 3105           | 2975         | 5.188    | 51.023   | $\nu\text{CH}_{\text{methyl}}$ (100)                                                                                           |
| 56 | 2980 w            | C-H ( $\nu$ Alk)                      | 3114           | 2983         | 13.746   | 56.811   | $\nu\text{CH}_{\text{methyl}}$ (100)                                                                                           |
| 57 | 3010 w            | C-H ( $\nu_{\text{sym}}$ Ar)          | 3158           | 3025         | 5.500    | 41.819   | $\nu\text{CH}_{\text{ring}}$ (61) + $\nu_{\text{asym}} \text{CH}_{\text{methane}}$ (39)                                        |
| 58 | 3026 w            | C-H ( $\nu_{\text{sym}}$ Ar)          | 3159           | 3026         | 3.522    | 53.208   | $\nu_{\text{asym}} \text{CH}_{\text{methane}}$ (61) + $\nu\text{CH}_{\text{ring}}$ (39)                                        |
| 59 |                   |                                       | 3164           | 3031         | 2.457    | 115.339  | $\nu\text{CH}_{\text{ring}}$ (99)                                                                                              |
| 60 |                   |                                       | 3168           | 3035         | 0.691    | 30.492   | $\nu_{\text{asym}} \text{CH}_{\text{methane}}$ (99)                                                                            |
| 61 |                   |                                       | 3178           | 3045         | 17.546   | 72.682   | $\nu\text{CH}_{\text{ring}}$ (100)                                                                                             |
| 62 |                   |                                       | 3191           | 3057         | 13.979   | 263.732  | $\nu\text{CH}_{\text{ring}}$ (99)                                                                                              |
| 63 | 3280 s            | N-H ( $\nu_{\text{sym}}$ )            | 3555           | 3406         | 33.645   | 83.887   | $\nu\text{NH}$ (100)                                                                                                           |

<sup>a</sup> From Ref. [11], s, strong; m, medium; w, weak; Alk, alkyl; Ar, aryl;  $I_{IR}$ , IR intensity;  $S_{Ra}$ , Raman scattering activity;  $\nu$ , stretching;  $\beta$ , in-plane bending;  $\gamma$ , out-of-plane bending;  $\omega$ , wagging;  $r$ , rocking;  $\rho$ , scissoring;  $t$ , twisting;  $\tau$ , torsion.

resembles the calculated spectrum, except for differences in details. The ring carbon-carbon stretching vibration occurs in the region 1625–1430  $\text{cm}^{-1}$ . In general, the bands are of variable intensity and observed at 1468–1583 625–1590, 1590–1575, 1540–1470, 1460–1430 and 1380–1280  $\text{cm}^{-1}$  from the frequency ranges given by Varsanyi [33] for the five bands in the region. In the present work, the frequencies observed in the FT-IR spectrum

at 1468, 1497, 1583 and 1493, 1589  $\text{cm}^{-1}$  were assigned to C–C stretching vibrations. The predicted values are coincident with all observed values. The in-plane deformations are at higher frequencies than the out-of-plane vibrations. Shimanouchi et al. [37] gave the frequency data for these vibrations for different benzene derivatives as a result of normal coordinate analysis. The calculated bands at 562, 622, 866 and 514, 740  $\text{cm}^{-1}$  are assigned to in-plane

**Table 3**  
Comparison of the calculated and experimental vibrational spectra and proposal assignments of 3MPMSA.

| No. | Exp. <sup>a</sup> | Experimental assignments <sup>a</sup> | Unscaled freq. | Scaled freq. | $I_{IR}$ | $S_{Ra}$ | Assignments (TED)                                                                                                                                 |
|-----|-------------------|---------------------------------------|----------------|--------------|----------|----------|---------------------------------------------------------------------------------------------------------------------------------------------------|
| 1   |                   |                                       | 28             | 28           | 0.742    | 1.124    | $\tau(\text{CH}_3)_{\text{methyl}}$ (61) + $r(\text{ring-methanesulfanamide})$ (27)                                                               |
| 2   |                   |                                       | 33             | 32           | 1.529    | 2.280    | $r(\text{ring-methanesulfanamide})$ (50) + $\tau(\text{CH}_3)_{\text{methyl}}$ (34)                                                               |
| 3   |                   |                                       | 61             | 60           | 4.950    | 3.277    | $\gamma\text{CNS}$ (95)                                                                                                                           |
| 4   |                   |                                       | 104            | 102          | 3.659    | 0.463    | $\beta\text{CNS}$ (29) + $\beta\text{CCN}$ (16)                                                                                                   |
| 5   |                   |                                       | 197            | 194          | 1.599    | 0.301    | $\tau(\text{CH}_3)_{\text{methane}}$ (70)                                                                                                         |
| 6   |                   |                                       | 204            | 201          | 2.124    | 0.757    | $\tau(\text{CH}_3)_{\text{methane}}$ (34) + $\gamma\text{C-CH}_3$ (16)                                                                            |
| 7   |                   |                                       | 217            | 213          | 0.712    | 1.778    | $\gamma\text{C-CH}_3$ (33) + $\gamma\text{C-CH-C}$ (23)                                                                                           |
| 8   |                   |                                       | 246            | 242          | 0.489    | 2.232    | $\tau(\text{CH}_3)_{\text{methane}}$ (38) + $t\text{SO}_2$ (27) + $\beta\text{CCN}$ (19) + $\beta\text{C-CH}_3$ (14)                              |
| 9   |                   |                                       | 285            | 280          | 0.835    | 5.160    | $\beta\text{S-CH}_3$ (27) + $\nu\text{SN}$ (13)                                                                                                   |
| 10  |                   |                                       | 323            | 318          | 0.581    | 1.681    | $t\text{SO}_2$ (45) + $\beta\text{C-CH}_3$ (16) + $\beta\text{S-CH}_3$ (16)                                                                       |
| 11  |                   |                                       | 350            | 344          | 4.137    | 5.621    | $r\text{S-CH}_3$ (62)                                                                                                                             |
| 12  | 409 w             | C=C ( $\gamma$ Ar)                    | 388            | 381          | 1.228    | 0.479    | $\beta\text{C-CH}_3$ (46) + $\beta\text{CCN}$ (19)                                                                                                |
| 13  | 447 w             | C=C ( $\gamma$ Ar)                    | 450            | 442          | 11.964   | 0.234    | $\beta\text{C-CH-C}$ (74)                                                                                                                         |
| 14  |                   |                                       | 480            | 472          | 27.857   | 6.301    | $\rho\text{SO}_2$ (66) + $\nu\text{S-CH}_3$ (17)                                                                                                  |
| 15  |                   |                                       | 506            | 497          | 19.506   | 2.018    | $\gamma\text{NH}$ (40) + $r\text{S-CH}_3$ (15)                                                                                                    |
| 16  |                   |                                       | 523            | 514          | 54.873   | 6.157    | $\beta\text{CCC}$ (24) + $\gamma\text{NH}$ (10)                                                                                                   |
| 17  |                   |                                       | 536            | 527          | 40.919   | 14.747   | $\gamma\text{CCC}$ (32) + $\gamma\text{NH}$ (17) + $\nu\text{C-CH}_3$ (12)                                                                        |
| 18  |                   |                                       | 568            | 558          | 4.837    | 2.808    | $\gamma\text{CCC}$ (60)                                                                                                                           |
| 19  | 644 w             | C-H ( $\gamma$ Ar)                    | 627            | 616          | 12.706   | 7.552    | ring breath. (36)                                                                                                                                 |
| 20  | 692 m             | N-H ( $\gamma$ )                      | 700            | 688          | 3.796    | 8.611    | $\gamma\text{C-CH-C}$ (58) + $\nu\text{S-CH}_3$ (15)                                                                                              |
| 21  |                   |                                       | 719            | 707          | 104.317  | 10.244   | $\nu\text{S-CH}_3$ (45)                                                                                                                           |
| 22  | 743 m             | C-H ( $\gamma$ Ar)                    | 753            | 740          | 0.620    | 5.979    | $\beta\text{CCC}$ (31) + $\nu\text{C-CH}_3$ (12)                                                                                                  |
| 23  | 771 m             | C-S ( $\nu$ )                         | 791            | 778          | 31.986   | 0.698    | $\gamma\text{CH}_{\text{ring}}$ (67)                                                                                                              |
| 24  |                   |                                       | 840            | 826          | 82.168   | 13.409   | $\nu\text{SN}$ (46) + $\beta\text{CNS}$ (14)                                                                                                      |
| 25  |                   |                                       | 889            | 874          | 1.572    | 0.320    | $\gamma\text{CH}_{\text{ring}}$ (85)                                                                                                              |
| 26  | 912 w             | S-N ( $\nu$ )                         | 921            | 905          | 17.306   | 0.566    | $\gamma\text{CH}_{\text{ring}}$ (79)                                                                                                              |
| 27  |                   |                                       | 955            | 939          | 27.519   | 7.631    | $\nu\text{CC}_{\text{ring}}$ (28) + $\nu\text{CN}$ (15) + $\nu\text{C-CH}_3$ (12) + $r\text{C-CH}_3$ (11)                                         |
| 28  |                   |                                       | 979            | 962          | 54.776   | 5.391    | $r\text{S-CH}_3$ (83)                                                                                                                             |
| 29  |                   |                                       | 983            | 966          | 0.817    | 0.189    | $\gamma\text{CH}_{\text{ring}}$ (82)                                                                                                              |
| 30  |                   |                                       | 985            | 968          | 22.616   | 1.830    | $r\text{S-CH}_3$ (82)                                                                                                                             |
| 31  |                   |                                       | 1013           | 996          | 0.507    | 53.167   | Ring breath. (78)                                                                                                                                 |
| 32  |                   |                                       | 1028           | 1011         | 13.640   | 1.491    | $r(\text{CH}_3)_{\text{methyl}}$ + $\nu\text{CC}_{\text{ring}}$ (11)                                                                              |
| 33  |                   |                                       | 1063           | 1045         | 6.819    | 0.755    | $r\text{C-CH}_3$ (60) + $\gamma\text{CCC}$ (30)                                                                                                   |
| 34  |                   |                                       | 1114           | 1095         | 296.723  | 5.759    | $\nu_{\text{sym}}\text{SO}_2$ (84)                                                                                                                |
| 35  |                   |                                       | 1120           | 1101         | 1.873    | 6.051    | $\nu\text{CC}_{\text{ring}}$ (40) + $\nu\text{CH}_{\text{ring}}$ (39)                                                                             |
| 36  | 1146 s            | S=O ( $\nu_{\text{sym}}$ )            | 1181           | 1161         | 5.156    | 15.306   | $\nu\text{CH}_{\text{ring}}$ (33) + $\nu\text{CN}$ (18) + $\nu\text{C-CH}_3$ (17) + $\nu\text{CC}_{\text{ring}}$ (11)                             |
| 37  |                   |                                       | 1194           | 1174         | 1.645    | 1.900    | $\nu\text{CH}_{\text{ring}}$ (76) + $\nu\text{CC}_{\text{ring}}$ (16)                                                                             |
| 38  | 1252 w            | C-N ( $\nu$ )                         | 1264           | 1243         | 41.151   | 23.300   | $\nu\text{CC}_{\text{ring}}$ (23) + $\nu_{\text{asym}}\text{SO}_2$ (14) + $\beta\text{NH}$ (14) + $\nu\text{CN}$ (10)                             |
| 39  | 1271 w            | C-N ( $\nu$ )                         | 1289           | 1267         | 56.564   | 59.263   | $\nu_{\text{asym}}\text{SO}_2$ (30) + $\nu\text{CC}_{\text{ring}}$ (16) + $\nu\text{CN}$ (15)                                                     |
| 40  |                   |                                       | 1323           | 1301         | 109.577  | 4.775    | $\nu_{\text{asym}}\text{SO}_2$ (40) + $\nu\text{CC}_{\text{ring}}$ (38)                                                                           |
| 41  | 1317 s            | S=O ( $\nu_{\text{asym}}$ )           | 1349           | 1326         | 10.312   | 0.511    | { $\text{wCH}_3$ (99)} <sub>methane</sub>                                                                                                         |
| 42  |                   |                                       | 1351           | 1328         | 5.885    | 2.427    | $\beta\text{CH}_{\text{ring}}$ (64) + $\nu\text{CC}_{\text{ring}}$ (19)                                                                           |
| 43  |                   |                                       | 1409           | 1385         | 123.178  | 16.398   | $\beta\text{NH}$ (38)                                                                                                                             |
| 44  | 1390 m            | N-H ( $\beta$ )                       | 1417           | 1393         | 4.818    | 16.708   | { $\text{wCH}_3$ (91)} <sub>methylene</sub>                                                                                                       |
| 45  |                   |                                       | 1452           | 1427         | 3.060    | 4.903    | { $\beta\text{CH}_2$ (91)} <sub>methane</sub>                                                                                                     |
| 46  |                   |                                       | 1459           | 1434         | 2.942    | 5.145    | { $\beta\text{CH}_2$ (58) + $\gamma\text{CH}$ (31)} <sub>methane</sub>                                                                            |
| 47  |                   |                                       | 1475           | 1450         | 5.770    | 4.965    | { $\beta\text{CH}_2$ (39)} <sub>methylene</sub> + $\beta\text{NH}$ (13) + $\beta\text{CH}_{\text{ring}}$ (13) + $\nu\text{CC}_{\text{ring}}$ (10) |
| 48  |                   |                                       | 1490           | 1465         | 7.695    | 9.292    | { $\beta\text{CH}_2$ (94)} <sub>methylene</sub>                                                                                                   |
| 49  |                   |                                       | 1507           | 1481         | 15.706   | 1.341    | $\beta\text{CH}_{\text{methyl}}$ (46) + $\beta\text{CH}_{\text{ring}}$ (16) + $\nu\text{CC}_{\text{ring}}$ (14)                                   |
| 50  | 1493 m            | C=C ( $\nu$ Ar)                       | 1525           | 1499         | 61.903   | 3.439    | $\beta\text{CH}_{\text{ring}}$ (44) + $\nu\text{CC}_{\text{ring}}$ (24)                                                                           |
| 51  | 1589 w            | C=C ( $\nu$ Ar)                       | 1625           | 1597         | 35.063   | 36.020   | $\nu\text{CC}_{\text{ring}}$ (64) + $i\text{CH}_{\text{ring}}$ (12)                                                                               |
| 52  |                   |                                       | 1645           | 1617         | 52.731   | 42.753   | $\nu\text{CC}_{\text{ring}}$ (62) + $\beta\text{CH}_{\text{ring}}$ (13)                                                                           |
| 53  |                   |                                       | 3024           | 2897         | 23.355   | 239.049  | $\nu_{\text{sym}}\text{CH}_{\text{methyl}}$ (100)                                                                                                 |
| 54  | 2929 w            | C-H ( $\nu$ Alk)                      | 3061           | 2932         | 0.484    | 151.519  | $\nu_{\text{sym}}\text{CH}_{\text{methane}}$ (100)                                                                                                |
| 55  |                   |                                       | 3079           | 2950         | 17.229   | 83.643   | $\nu_{\text{asym}}\text{CH}_{\text{methyl}}$ (100)                                                                                                |
| 56  |                   |                                       | 3108           | 2977         | 13.444   | 60.081   | $\nu_{\text{asym}}\text{CH}_{\text{methyl}}$ (100)                                                                                                |
| 57  | 3018 w            | C-H ( $\nu_{\text{sym}}$ Ar)          | 3159           | 3026         | 1.570    | 61.619   | $\nu\text{CH}_{\text{ring}}$ (99)                                                                                                                 |
| 58  |                   |                                       | 3161           | 3028         | 0.116    | 65.869   | $\nu_{\text{asym}}\text{CH}_{\text{methane}}$ (100)                                                                                               |
| 59  |                   |                                       | 3167           | 3034         | 15.628   | 59.109   | $\nu\text{CH}_{\text{ring}}$ (98)                                                                                                                 |
| 60  |                   |                                       | 3168           | 3035         | 1.132    | 47.672   | $\nu_{\text{asym}}\text{CH}_{\text{methane}}$ (96)                                                                                                |
| 61  |                   |                                       | 3185           | 3051         | 14.285   | 209.617  | $\nu\text{CH}_{\text{ring}}$ (99)                                                                                                                 |
| 62  |                   |                                       | 3200           | 3066         | 1.093    | 48.726   | $\nu\text{CH}_{\text{ring}}$ (99)                                                                                                                 |
| 63  | 3250 s            | N-H ( $\nu_{\text{sym}}$ )            | 3572           | 3422         | 37.760   | 79.509   | $\nu\text{NH}$ (100)                                                                                                                              |

<sup>a</sup> From Ref. [11], s, strong; m, medium; w, weak; Alk, alkyl; Ar, aryl;  $I_{IR}$ , IR intensity;  $S_{Ra}$ , Raman scattering activity;  $\nu$ , stretching;  $\beta$ , in-plane bending;  $\gamma$ , out-of-plane bending;  $\omega$ , wagging;  $r$ , rocking;  $\rho$ , scissoring;  $t$ , twisting;  $\tau$ , torsion.

CCC and the bands at 530, 691, 717 and 527, 588  $\text{cm}^{-1}$  are assigned to out-of-plane CCC deformation of phenyl ring for 2MPMSA and 3MPMSA, respectively. The TEDs of these vibrations are not pure modes as it is evident from the last columns of TED.

The symmetric and asymmetric  $\text{SO}_2$  stretching vibrations occur in the region 1125–1150 and 1295–1330  $\text{cm}^{-1}$  [36]. The intense signals appearing at 1418  $\text{cm}^{-1}$  and 1217  $\text{cm}^{-1}$  (IR) and

1414  $\text{cm}^{-1}$  and 1228  $\text{cm}^{-1}$  (Ra) were attributed to the  $\text{SO}_2$  anti-symmetric and symmetric stretching fundamental modes for sulfamoyl fluoride substance [25]. For molecules of 2MPMSA and 3MPMSA symmetric S=O stretching vibrations were calculated at 1096 and 1095  $\text{cm}^{-1}$  as pure modes while obtained at 1153 and 1146  $\text{cm}^{-1}$  in FT-IR spectrum [11]. For the asymmetric S=O vibrations two bands were computed at 1265, 1287  $\text{cm}^{-1}$  (2MPMSA)

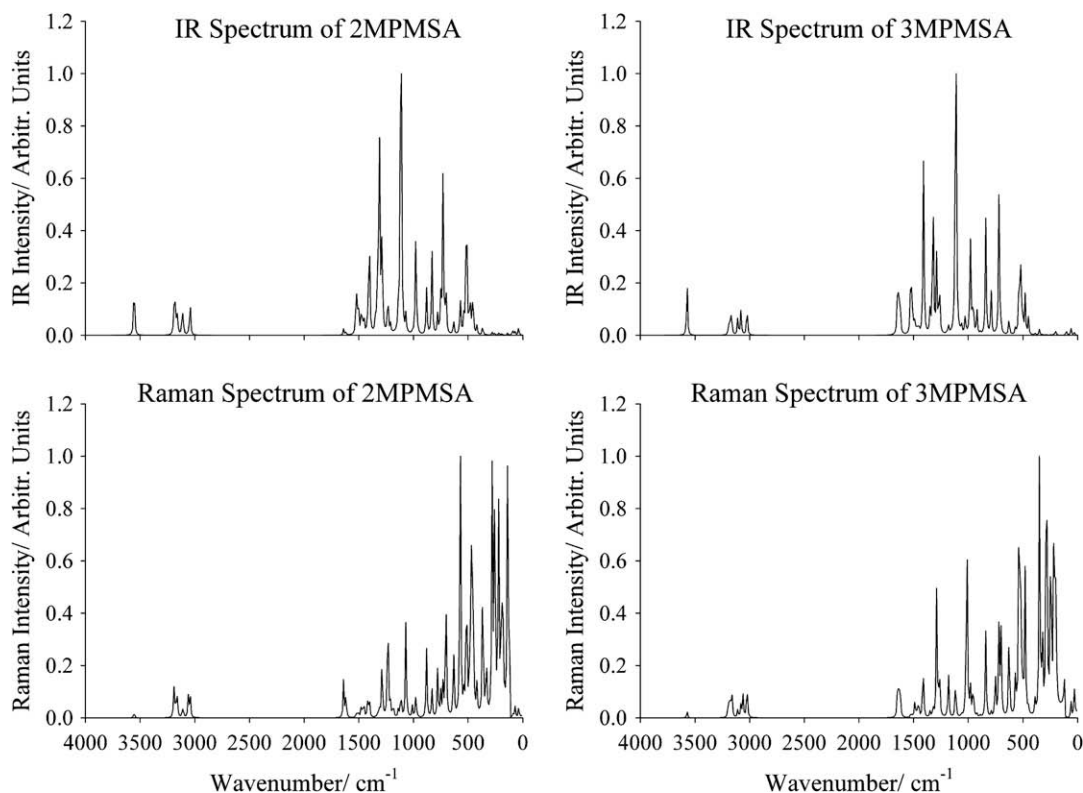


Fig. 2. The simulated Infrared and Raman spectra of 2MPMSA and 3MPMSA.

and 1267, 1301  $\text{cm}^{-1}$  (3MPMSA) which are contaminated with other vibrations, and this mode was recorded at 1317  $\text{cm}^{-1}$  for both molecules. For PMSA the symmetric stretching mode was recorded at 1150  $\text{cm}^{-1}$  as strong peak, where the asymmetric mode was obtained at 1341 and 1351  $\text{cm}^{-1}$  [14]. It's noticed that the calculated symmetric vibration is deviated negatively while the asymmetric one positively. As mentioned before, B3LYP method overestimates strongly all bond lengths around sulphur atom due to includes electron correlation effects [25–27]. Thus, the prediction of force constants and vibrational wavenumbers show difference with experimental results. The other in-plane deformation of  $\text{SO}_2$  (scissoring, wagging and torsion) are shown in Tables 2 and 3.

The bands at 914 and 912  $\text{cm}^{-1}$  obtained in FT-IR spectrum and calculated at 817 and 826  $\text{cm}^{-1}$  are due to S–N stretching mode. The S–CH<sub>3</sub> stretching mode is predicted at 691, 707  $\text{cm}^{-1}$  and recorded at 743, 771  $\text{cm}^{-1}$ . The effect of sulphur atom can be seen for these vibration modes too. It should be noted that the unscaled values are more reliable than scaled ones.

### 3.3. NMR spectra

The isotropic chemical shifts are frequently used as an aid in identification of reactive ionic species. It is recognized that accurate predictions of molecular geometries are essential for reliable calculations of magnetic properties. The NMR spectra calculations were performed for chloroform ( $\text{CDCl}_3$ ) and in dimethylsulfoxide (DMSO) solvent. It is necessary to consider the solvent effects because the spectral data available are obtained in different solutions. The isotropic shielding values were used to calculate the isotropic chemical shifts  $\delta$  with respect to tetramethylsilane (TMS), ( $\delta_{\text{iso}}^X = \sigma_{\text{iso}}^{\text{TMS}} - \sigma_{\text{iso}}^X$ ). Besides X-ray crystallography,  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectroscopy can provide the required structural data for the investigated compound [11–13]. The calculated  $^{13}\text{C}$  and  $^1\text{H}$

chemical shifts in the solution are summarized in Table 4 in comparison with the experimental data. The atom positions were numbered as in Fig. 1. Comparison between experimental and theoretical NMR chemical shifts provides practical information on the chemical structure and conformation of compounds. This usefulness is largely due to empirical structure chemical shift correlations. Taking into account that the range of  $^{13}\text{C}$  NMR chemical shifts for a typical organic molecule usually is >100 ppm [38,39],

Table 4

The experimental and calculated  $^1\text{H}$  and  $^{13}\text{C}$  isotropic chemical shifts (with respect to TMS, all values in ppm) for 2MPMSA and 3MPMSA.

| Atom  | 2MPMSA            |       |                 | 3MPMSA            |       |                 |
|-------|-------------------|-------|-----------------|-------------------|-------|-----------------|
|       | Exp. <sup>a</sup> | DMSO  | $\text{CDCl}_3$ | Exp. <sup>a</sup> | DMSO  | $\text{CDCl}_3$ |
| C(2)  | 131.2             | 136.0 | 136.4           | 139.7             | 147.2 | 147.4           |
| C(3)  | 134.8             | 147.9 | 148.7           | 121.4             | 123.9 | 124.4           |
| C(4)  | 126.2             | 133.9 | 133.7           | 126.1             | 130.5 | 130.3           |
| C(5)  | 131.2             | 141.2 | 141.1           | 136.8             | 145.0 | 145.0           |
| C(6)  | 127.1             | 131.6 | 131.0           | 129.4             | 134.7 | 134.2           |
| C(8)  | 123.4             | 133.8 | 132.9           | 117.8             | 120.9 | 120.1           |
| C(15) | 39.8              | 44.0  | 43.8            | 39.0              | 44.6  | 44.4            |
| C(19) | 18.0              | 20.2  | 20.4            | 21.3              | 21.9  | 22.0            |
| RMS   |                   | 7.9   | 7.9             |                   | 5.2   | 5.1             |
| H(1)  | 7.13              | 7.67  | 7.60            | 7.21              | 7.72  | 7.77            |
| H(7)  | 7.13              | 7.65  | 7.56            | 6.98              | 7.44  | 7.34            |
| H(10) | 7.21              | 7.67  | 7.55            | 7.08              | 7.65  | 7.52            |
| H(12) | 6.80              | 6.33  | 5.91            | 7.32              | 6.47  | 6.05            |
| H(16) | 3.00              | 2.74  | 2.71            | 3.00              | 2.87  | 2.83            |
| H(17) | 3.00              | 2.94  | 2.90            | 3.00              | 2.82  | 2.78            |
| H(18) | 3.00              | 2.63  | 2.48            | 3.00              | 2.49  | 2.36            |
| H(20) | 2.33              | 2.95  | 3.04            | 2.32              | 2.31  | 2.28            |
| H(21) | 2.33              | 2.75  | 2.78            | 2.32              | 2.59  | 2.57            |
| H(22) | 2.33              | 2.00  | 1.95            | 2.32              | 2.20  | 2.23            |
| H(23) | 7.43              | 7.59  | 7.39            | 7.21              | 6.98  | 6.77            |
| RMS   |                   | 0.42  | 0.48            |                   | 0.42  | 0.52            |

<sup>a</sup> From Ref. [11].

the accuracy ensures reliable interpretation of spectroscopic parameters. Table 4 indicates that the carbons of the phenyl ring have signals of from 123.4 to 134.8 ppm and from 117.8 to 139.7 ppm for 2MPMS and 3MPMSA, respectively [11]. The chemical shifts of alkyl carbon atoms are recorded at 39.8, 18.0 ppm and 39.0, 21.3 ppm [11], as shown in Table 4.

Hydrogen attached or nearby electron-withdrawing atom or group can decrease the shielding and move the resonance of attached proton towards to a higher frequency. By contrast electron-donating atom or group increases the shielding and moves the resonance towards to a lower frequency. In this study, the chemical shifts obtained and calculated for the hydrogen atoms of methyl groups are quite low. All values are  $\leq 3.00$  ppm due to the shielding effect. Likewise, the chemical shift of N bonded hydrogen atom is lower than ring atoms. The H atom is the smallest of all atoms and mostly localized on the periphery of molecules; therefore their chemical shifts would be more susceptible to intermolecular interactions in the aqueous solutions as compared to that for other heavier atoms. As can be seen in Table 4, the calculated chemical shifts for  $^1\text{H}$  are more sensitive as compared to that of  $^{13}\text{C}$ .

#### 4. Conclusion

The molecular conformation,  $^1\text{H}$ ,  $^{13}\text{C}$  NMR chemical shifts, vibrational transitions of *N*-(2-methylphenyl) methanesulfonamide and *N*-(3-methylphenyl) methanesulfonamide molecules were examined by DFT (B3LYP) method and 6-311++G(d,p) basis set. Optimized geometric structure is found to be in agreement with experimental results. The vibrational wavenumbers were calculated and the complete assignments were performed on the basis of the total energy distribution (TED) of the vibrational modes. Results are compared with experimental observed FT-IR spectrum. After scaling down, the calculated wavenumbers show good agreement with FT-IR. The positions of hydrogen and carbon atoms of title molecules are determined with help of computed  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts. The chemical shift values (with respect to TMS) were also compared with the published experimental data, showing a very good agreement both for  $^1\text{H}$  and  $^{13}\text{C}$ .

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