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Spectrochimica Acta Part A 62 (2005) 221–225

SPECTROCHIMICA ACTA PART A

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# A scaled quantum mechanical force field for the sulfuryl halides
# II. The $SO_2XF$ (X = Cl, Br) halides

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Received 7 December 2004; accepted 16 December 2004

## Abstract

Force fields and vibrational wavenumbers were calculated for the molecules $SO_2XF$ (X = Cl, Br) using DFT techniques. The previously available experimental data and assignments for $SO_2ClF$ and $SO_2BrF$ were partially confirmed by the theoretical results. These data were subsequently used in the definition of scaled quantum mechanics force fields for such molecules. A comparison of the obtained force constants is made with results previously published for the $SO_2X_2$ molecules.

*Keywords:* Sulfuryl halides; Infrared; Raman; DFT calculations; Force constants

## 1. Introduction

A revision of the vibrational assignments published for the symmetric sulfuryl halides $SO_2X_2$ (X = F, Cl) and a calculation of the corresponding quantum mechanical force fields (including that of the still unknown $SO_2Br_2$) was the object of a previous work [1]. The mixed halides $SO_2XF$, of which only these having X = Cl or Br are known, are now considered.

The sulfuryl chloride fluoride, $SO_2ClF$, was studied before in many opportunities, being known the Raman spectrum of the liquid [2–4], the infrared spectrum of the gas [3,4] and the microwave spectrum [5]. This last study furnished a set of geometrical parameters for that molecule. The measured normal vibrational wavenumbers were used for the calculation of force fields in the Urey-Bradley approximation [6,7] or in terms of a general harmonic force field [5,8,9]. A theoretical calculation of geometrical parameters and vibrational wavenumbers was also performed as part of a study on the enthalpy of formation [10].

Less studied was the sulfuryl bromide fluoride, $SO_2BrF$, for which infrared and Raman spectra [11,12] or a discussion of previous results [13] were published. Force constants calculations were also reported for this molecule, either in the Urey-Bradley approximation [7] or as a general force field [9].

In the present study density functional theory (DFT) calculations were made on $SO_2ClF$ and $SO_2BrF$ in order to obtain optimized geometrical structures, wavenumbers of the normal modes of vibration and force constants. Scaled quantum mechanical (SQM) force fields were defined for each molecule, based on the wavenumbers reported in the literature.

## 2. Calculations

The optimized structures and vibrational wavenumbers were calculated at different levels of theory and with several basis sets, following the methodology previously used for

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doi:10.1016/j.saa.2004.12.030

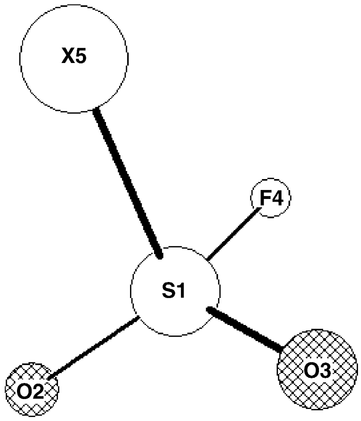

Fig. 1. The calculated molecular structure for the $SO_2XF$ species.

Table 1
Optimized geometric parameters for the molecules $SO_2ClF$ and $SO_2BrF$ and experimental values for $SO_2ClF$

| | $SO_2ClF$ | | $SO_2BrF$ |
|---|---|---|---|
| | Calculated[a] | Experimental[b] | Calculated[a] |
| Bonds (Å) | | | |
| S=O | 1.437 | 1.409 | 1.439 |
| S—F | 1.592 | 1.540 | 1.596 |
| S—X | 2.034 | 1.986 | 2.200 |
| Angles (°) | | | |
| O=S=O | 124.2 | 123.3 | 123.9 |
| F—S—X | 97.2 | 98.1 | 97.4 |
| O=S—F | 107.1 | 107.3 | 107.0 |
| O=S—X | 108.9 | 109.0 | 109.1 |

[a] B3PW91/6-31G* calculation.

[b] Ref. [5].

the $SO_2X_2$ molecules (see [1]). Here again, the combination of the B3PW91 functional and the 6-31G* basis set allowed the best approximation to the experimental wavenumbers and therefore these results were used for subsequent calculations.

For the $SO_2XF$ molecules, as observed before for the symmetrical $SO_2X_2$ species [1], the introduction of polarization functions in the used basis sets improved the agreement between calculated and observed wavenumbers, whereas the introduction of diffuse functions was detrimental for such calculation. An inverse behaviour, i.e. best results with diffuse functions and worst results with polarization functions, were observed when the central atom in similar simple species is a transition metal, as in the case of the $VO_2X_2{}^-$ anions [14] and $VOX_3$ molecules [15]. Both situations were observed in the theoretical study of the cation (non-metallic central atom) and anion (transition metal central atom) present in the salt $PCl_4{}^+VOCl_4{}^-$ [16].

The results obtained in the exploratory calculations at the Hartree–Fock level or using the B3LYP and B3PW91 functionals at the DFT level, with different basis sets, are available as Supplementary Material. These results show also the effect which the introduction of polarization and/or diffuse functions have on the predicted wavenumbers.

Scaling of the theoretical force field was made according to the scheme of Pulay et al. [17], as detailed in the previous work [1].

## 3. Structural results

The calculations produced the expected pseudo-tetrahedral structures with $C_s$ symmetry depicted in Fig. 1. Structural geometrical parameters were reported only for $SO_2ClF$, after a microwave study by Müller and Gerry [5]. These experimental parameters are compared with the theoretical ones in Table 1. Calculated distances resulted larger by 0.052 Å or less whereas calculated angles do not differ in more than 0.94° from the experimental values. Here again, as in the case of the $SO_2X_2$ molecules, the lowest level exploratory calculation (HF/6-31G*) reproduced notably well the known molecular geometry, with differences not greater than 0.009 Å for distances and 0.37° for angles (see the Supplementary Material).

## 4. Vibrational results

The normal modes of vibration of the $SO_2XF$ molecules, with $C_s$ symmetry, are classified as $6A' + 3A''$. The mea-

Table 2
Natural internal coordinates for $SO_2XF$

| Definition (according to Fig. 1) | Description[a] |
|---|---|
| $A'$ | |
| $S_1 = r(1\text{-}2) + r(1\text{-}3)$ | $\nu SO_2$ symmetric |
| $S_2 = d(1-4)$ | $\nu$S—F |
| $S_3 = \alpha(4\text{-}1\text{-}2) + \alpha(4\text{-}1\text{-}3) - \alpha(5\text{-}1\text{-}2) - \alpha(5\text{-}1\text{-}3)$ | Wag. $SO_2$ |
| $S_4 = 4\theta(2\text{-}1\text{-}3) - \alpha(4\text{-}1\text{-}2) - \alpha(4\text{-}1\text{-}3) - \alpha(5\text{-}1\text{-}2) - \alpha(5\text{-}1\text{-}3)$ | $\delta SO_2$ |
| $S_5 = l(1\text{-}5)$ | $\nu$S—X |
| $S_6 = 4\phi(4\text{-}1\text{-}5) - \alpha(4\text{-}1\text{-}2) - \alpha(4\text{-}1\text{-}3) - \alpha(5\text{-}1\text{-}2) - \alpha(5\text{-}1\text{-}3)$ | $\delta$FSX |
| $A''$ | |
| $S_7 = r(1\text{-}2) - r(1\text{-}3)$ | $\nu SO_2$ antisymmetric |
| $S_8 = \alpha(4\text{-}1\text{-}2) - \alpha(4\text{-}1\text{-}3) + \alpha(5\text{-}1\text{-}2) - \alpha(5\text{-}1\text{-}3)$ | $\rho SO_2$ |
| $S_9 = \alpha(4\text{-}1\text{-}2) - \alpha(4\text{-}1\text{-}3) - \alpha(5\text{-}1\text{-}2) + \alpha(5\text{-}1\text{-}3)$ | Twist. $SO_2$ |

[a] $\nu$, stretching; $\delta$, deformation; $\rho$, rocking.