The force constants in the isoelectronic series CF₃SO₂X (X = F, OH, NH₂, CH₃): a study based on DFT calculations and experimental data

L.E. Fernández[a], A. Ben Altabef[a,1], E.L. Varetti[b,1,*]

[a]*Facultad de Bioquímica, Química y Farmacia, Instituto de Química y Física, Universidad Nacional de Tucumán, San Lorenzo 456, 4000 S.M. de Tucumán, Argentina*
[b]*Facultad de Ciencias Exactas, Departamento de Química, CEQUINOR (Centro de Química Inorgánica, CONICET, UNLP), Universidad Nacional de La Plata, C.Correo 962, 1900 La Plata, Argentina*

Abstract

Density functional theory calculations at the B3LYP/6-31G(d,p) level of theory were performed on the members of the isoelectronic series CF₃SO₂X (X = F, OH, NH₂, CH₃), in order to obtain the optimized geometric parameters and conformations for the four molecules, as well as the wavenumbers corresponding to the normal modes of vibration and the associated force constants. The original force field was transformed to local symmetry coordinates and scaled to reproduce the experimental wavenumbers. The trends observed in geometrical parameters and force constants along the isoelectronic series could be explained making use of the calculated atomic charges. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The isoelectronic molecules CF₃SO₂X (X = F, OH, NH₂, CH₃) were studied as part of a more comprehensive vibrational study of chemical species containing the CF₃SO₂ moiety [1 and references therein]. The Raman spectrum of trifluoromethanesulfonyl fluoride, CF₃SO₂F, was published by other authors [2], whereas the vibrational properties of triflic acid, CF₃SO₂OH [3,4], trifluoromethanesulfonamide, CF₃SO₂NH₂ [5]

and methyl trifluoromethyl sulfone, CF₃SO₂CH₃ [6], were studied experimentally and theoretically in this laboratory. A quantum chemistry study of CF₃SO₂OH, in which the fundamental wavenumbers were calculated by means of HF and MP2 methods, was also published by other authors [7].

The combination of experimental data and quantum chemistry calculations to define the molecular force constants by means of the scaled quantum mechanical (SQM) method, proposed in its primitive form by Blom and Altona [8] and later developed by Pulay et al. [9], has proven to be a powerful tool. In this method, the harmonic force constants derived from the calculations are scaled by a limited number of factors to reproduce the experimental vibrational wavenumbers, correcting for deficiencies of the

* Corresponding author. Tel.: +54-221-4240-172; fax: +54-221-4259-485.
E-mail address: varetti@quimica.unlp.edu.ar (E.L. Varetti).
[1] Members of the Carrera del Investigador Científico, CONICET (Argentina).

Table 1
Optimized geometric parameters for the series CF_3SO_2X and experimental parameters for CF_3SO_2OH

	CF_3SO_2F	CF_3SO_2OH		$CF_3SO_2NH_2$	$CF_3SO_2CH_3$
		Calcd	Exp. [17]		
Bonds (Å)					
C–F$_{trans}$[a]	1.329	1.330	1.332	1.332	1.327
C–F$_{cis}$[a,b]	1.327	1.329	1.332	1.333	1.339
C–S	1.872	1.869	1.833	1.867	1.880
S=O[b]	1.445	1.452	1.418	1.459	1.464
S–X	1.611	1.630	1.558	1.671	1.805
X–H	–	0.974	0.960	1.015	1.090
Angles (°)					
S–C–F$_{trans}$[a]	107.4	108.4	110.3	108.5	109.2
S–C–F$_{cis}$[a,b]	109.4	109.5	110.3	109.8	109.5
O=S=O	124.1	123.8	122.0	123.6	122.1
C–S–X	95.65	99.02	102.3	100.4	101.1
C–S=O	109.0	107.5	105.4	106.3	106.5
X–S=O	107.6	108.2	109.9	108.9	109.3
S–X–H[b]	–	107.8	115.0	111.4	107.9
H–X–H[b]	–	–	–	113.8	111.0
C–S–X–H	–	100.4	180.0	± 115.8	± 61.1, 180.0

[a] Bond C–F *trans* or *cis* to the S–X bond.
[b] Mean value.

computational methods. That approach works quite well because of the fairly systematic character of the errors in the initially calculated force constants, caused by the use of a limited basis set, the harmonic approximation usually assumed and, in the Hartree–Fock approximations, the neglect of electron correlation.

In the present work, the measured wavenumbers corresponding to the normal modes of vibration of the four studied isoelectronic molecules constitute the basis for the scaling of their force constants, calculated by means of density functional theory (DFT) methods. The variation of some force constants along the series reflect the bond changes caused by the change of the X group.

2. Calculation methodology

The optimized molecular geometries and conformations, wavenumbers corresponding to the normal modes of vibration, Cartesian harmonic force constants and infrared and Raman intensities were calculated by means of the DFT techniques, as provided by the GAUSSIAN 98 set of programs [10]. The B3LYP [11,12] functional was employed,

together with the 6-31 G (d,p) basis set, a combination which is being extensively used in the calculation of molecular properties.

The Cartesian force constants were converted to a set of local symmetry coordinates or 'natural coordinates' as defined by Fogarasi et al. [13] for each molecule of the series through the corresponding B matrix [14], calculated with a standard program. The resulting force field was subsequently scaled using the scheme of Pulay et al. [9,15], in which the main force constants are multiplied by scale factors f_i, f_j,… and the corresponding interaction constants are multiplied by $(f_i f_j)^{1/2}$, adjusting the scale factors to reproduce as well as possible the experimental wavenumbers. The resulting SQM force field served to calculate the Potential Energy Distribution for each molecule. The mathematical treatment of the Cartesian force constants leading to the SQM force field was performed with the program FCARTP, developed by Collier [16].

3. Molecular geometries

The optimized geometrical parameters calculated for the four studied molecules are compared in
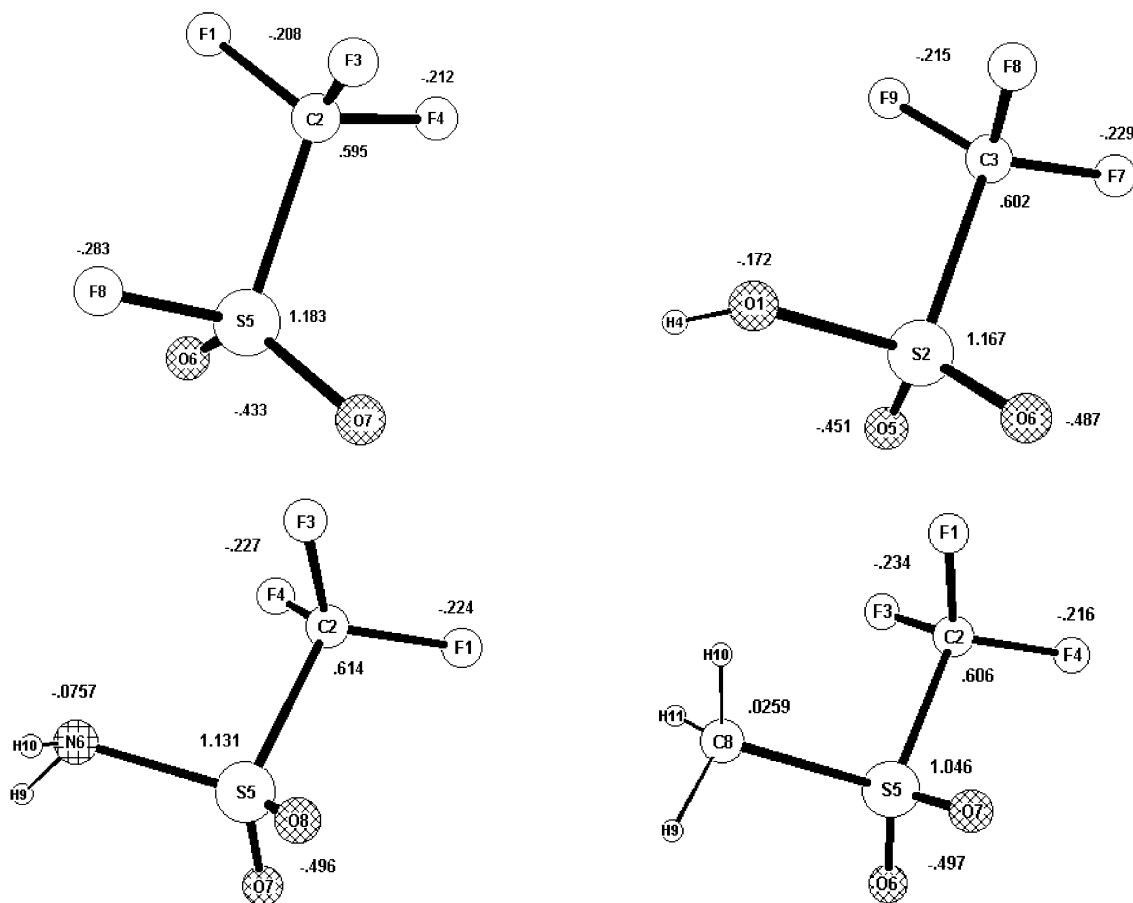
Fig. 1. The molecular structures of the CF_3SO_2X species. Atomic charges are indicated with hydrogen summed into heavy atoms in the X groups.

Table 1. The molecular structure of CF_3SO_2OH was already studied by the electron diffraction technique [17]. These experimental results were included in Table 1 for comparison purposes. It can be seen that the S–O(H) distance is the least accurately reproduced by the calculations, which gives a bond 0.072 Å too long. In fact, it has been shown that the single S–O bond of covalent sulfonates of the type $XOSO_2Y$ are predicted to be systematically too long by 0.04–0.07 Å by the B3LYP/6-31G(d) method [18].

The conformations obtained for the four molecules of the series can be appreciated in Fig. 1. A plane of symmetry locates three of the molecules in the point group C_s, being CF_3SO_2OH an exception, with a CSOH angle of 100.4° (calculated). Such *gauche*

conformation for the acid is also shown by other $XOSO_2Y$ sulfonates [18]. It should be mentioned that the angle in question could not be determined in the electron diffraction study and that its value was fixed at 180° [17].

Calculations made on the sulfonamide group with ab initio techniques at the RHF/6-31G(d) level of theory [19] reveal the existence of two stable conformers of C_s symmetry, one similar to that shown in Fig. 1 (*cis*) and the other resulting from a 180° rotation around the NS bond (*trans*). Another interesting result of such study is that the barrier to conversion between the two conformers is much lower by inversion at the nitrogen than by conventional rotation around the NS bond. The existence of a second C_s conformer was confirmed in the present study at the B3LYP/6-31G(d,p) level of theory,

Table 2
Natural internal coordinates for CF_3SO_2F

Definition (according to Fig. 1)	Description[a]
a′	
$S_1 = d(2-1) + d(2-3) + d(2-4)$	ν CF_3 symm.
$S_2 = 2d(2-4) - d(2-1) - d(2-3)$	ν CF_3 antisymm.
$S_3 = r(5-6) + r(5-7)$	ν SO_2 symm.
$S_4 = l(5-8)$	ν S–F
$S_5 = \epsilon(1-2-4) + \epsilon(3-2-4) + \epsilon(1-2-3) - \beta(1-2-5) - \beta(3-2-5) - \beta(4-2-5)$	δ CF_3 symm.
$S_6 = \psi(2-5-6) + \psi(2-5-7) - \gamma(8-5-6) - \gamma(8-5-7)$	Wag. SO_2
$S_7 = 2\epsilon(1-2-3) - \epsilon(1-2-4) - \epsilon(3-2-4)$	δ CF_3 antisymm.
$S_8 = 4\phi(6-5-7) - \psi(2-5-6) - \psi(2-5-7) - \gamma(8-5-6) - \gamma(8-5-7)$	δ SO_2
$S_9 = 4\theta(2-5-8) - \psi(2-5-7) - \psi(2-5-6) - \gamma(8-5-7) - \gamma(8-5-6)$	δ CSF
$S_{10} = t(2-5)$	ν S–CF_3
$S_{11} = 2\beta(4-2-5) - \beta(1-2-5) - \beta(3-2-5)$	ρ CF_3
a″	
$S_{12} = r(5-6) - r(5-7)$	ν SO_2 antisymm.
$S_{13} = d(2-1) - d(2-3)$	ν CF_3 antisymm.
$S_{14} = \epsilon(1-2-4) - \epsilon(3-2-4)$	δ CF_3 antisymm.
$S_{15} = \psi(2-5-7) - \psi(2-5-6) + \gamma(8-5-7) - \gamma(8-5-6)$	Rock. SO_2
$S_{16} = \psi(2-5-7) - \psi(2-5-6) - \gamma(8-5-7) + \gamma(8-5-6)$	Tw. SO_2
$S_{17} = \beta(1-2-5) - \beta(3-2-5)$	ρ CF_3
$S_{18} = \sum \tau [F_i - C_2 - S_5 - F_8(O_6, O_7)]$	Torsión CF_3

[a] ν, stretching; δ, deformation; ρ, rocking.

Table 3
Natural internal coordinates for CF_3SO_2OH

Definition (according to Fig. 1)	Description[a]
a′	
$S_1 = h(1-4)$	ν OH
$S_2 = d(3-7) + d(3-8) + d(3-9)$	ν CF_3 symm.
$S_3 = 2d(3-7) - d(3-8) - d(3-9)$	ν CF_3 antisymm.
$S_4 = r(2-5) + r(2-6)$	ν SO_2 symm.
$S_5 = \alpha(2-1-4)$	δ SOH
$S_6 = l(1-2)$	ν S–OH
$S_7 = \epsilon(8-3-9) + \epsilon(7-3-8) + \epsilon(7-3-9) - \beta(7-3-2) - \beta(8-3-2) - \beta(9-3-2)$	δ CF_3 symm.
$S_8 = \psi(3-2-5) + \psi(3-2-6) - \gamma(1-2-5) - \gamma(1-2-6)$	Wag. SO_2
$S_9 = 2\epsilon(8-3-9) - \epsilon(7-3-8) - \epsilon(7-3-9)$	δ CF_3 antisymm.
$S_{10} = 4\phi(5-2-6) - \psi(3-2-5) - \psi(3-2-6) - \gamma(1-2-5) - \gamma(1-2-6)$	δ SO_2
$S_{11} = 4\theta(1-2-3) - \psi(3-2-5) - \psi(3-2-6) - \gamma(1-2-5) - \gamma(1-2-6)$	δ CSO
$S_{12} = t(2-3)$	ν S–CF_3
$S_{13} = 2\beta(7-3-2) - \beta(8-3-2) - \beta(9-3-2)$	ρ CF_3
a″	
$S_{14} = r(2-5) - r(2-6)$	ν SO_2 antisymm.
$S_{15} = d(3-8) - d(3-9)$	ν CF_3 antisymm.
$S_{16} = \epsilon(7-3-8) - \epsilon(7-3-9)$	δ CF_3 antisymm.
$S_{17} = \psi(3-2-5) - \psi(3-2-6) + \gamma(1-2-5) - \gamma(1-2-6)$	Rock. SO_2
$S_{18} = \psi(3-2-5) - \psi(3-2-6) - \gamma(1-2-5) + \gamma(1-2-6)$	Tw. SO_2
$S_{19} = \sum \tau[H_4 - O_1 - S_2 - C_3(O_5, O_6)]$	Torsión SOH
$S_{20} = \beta(8-3-2) - \beta(9-3-2)$	ρ CF_3
$S_{21} = \sum \tau[F_i - C_3 - S_2 - O_1(O_5, O_6)]$	Torsión CF_3

[a] ν, stretching; δ, deformation; ρ, rocking.

being located 0.75 kcal/mol higher than the *cis* conformer shown in Fig. 1.

4. Vibrational spectra and force constants

4.1. Experimental data

The calculation of the force field for the molecules of the studied series was based on the following experimental data:

CF_3SO_2F: The published data from a Raman study of the liquid substance was used [2]. The set of fundamental wavenumbers appear in Tables 6 and 12, in which the 1140 and 1270 cm^{-1} bands are assigned to the symmetric SO_2 stretching and the symmetric CF_3 stretching, respectively, inverting the previous assignment.

CF_3SO_2OH: A study of the infrared spectra of triflic

acid in the gas, liquid and solid phases, as well as isolated in an Ar matrix, has been published [3]. That study allowed the identification of several bands due to the monomeric molecule, an important consideration in view of the strong intermolecular association present in the condensed phases. An additional infrared spectrum in the 700–50 cm^{-1} region of the gas mantained at ca. 60 °C helped to define other monomer bands [4], leading to the set of fundamental wavenumbers shown in Tables 7 and 12, in which the values measured for the gaseous substance were included when available.

$CF_3SO_2NH_2$: This substance is a solid at room temperature, a fact which points to a strong intermolecular association. An infrared and Raman study followed by the calculation of its optimized molecular structure and vibrational wavenumbers

Table 4
Natural internal coordinates for $CF_3SO_2NH_2$

Definition (according to Fig. 1)	Description[a]
a'	
$S_1 = h(6-9) + h(6-10)$	ν NH$_2$ symm.
$S_2 = \alpha(9-6-10)$	δ NH$_2$
$S_3 = d(2-1) + d(2-4) + d(2-3)$	ν CF$_3$ symm.
$S_4 = 2d(2-1) - d(2-4) - d(2-3)$	ν CF$_3$ antisymm.
$S_5 = r(5-8) + r(5-7)$	ν SO$_2$ symm.
$S_6 = l(5-6)$	ν S–NH$_2$
$S_7 = \epsilon(3-2-4) + \epsilon(1-2-3) + \epsilon(1-2-4) - \beta(1-2-5) - \beta(3-2-5) - \beta(4-2-5)$	δ CF$_3$ symm.
$S_8 = 4\phi(8-5-7) - \psi(2-5-8) - \psi(2-5-7) - \gamma(6-5-8) - \gamma(6-5-7)$	δ SO$_2$
$S_9 = 2\epsilon(3-2-4) - \epsilon(1-2-3) - \epsilon(1-2-4)$	δ CF$_3$ antisymm.
$S_{10} = \psi(2-5-8) + \psi(2-5-7) - \gamma(6-5-8) - \gamma(6-5-7)$	Wag. SO$_2$
$S_{11} = \delta(9-6-5) + \delta(10-6-5)$	Wag. NH$_2$
$S_{12} = 4\theta(2-5-6) - \psi(2-5-8) - \psi(2-5-7) - \gamma(6-5-8) - \gamma(6-5-7)$	δ CSN
$S_{13} = t(2-5)$	ν S–CF$_3$
$S_{14} = 2\beta(1-2-5) - \beta(3-2-5) - \beta(4-2-5)$	ρ CF$_3$
a''	
$S_{15} = h(6-9) - h(6-10)$	ν NH$_2$ antisymm.
$S_{16} = r(5-8) - r(5-7)$	ν SO$_2$ antisymm.
$S_{17} = d(2-4) - d(2-3)$	ν CF$_3$ antisymm.
$S_{18} = \delta(9-6-5) - \delta(10-6-5)$	Rock. NH$_2$
$S_{19} = \epsilon(1-2-3) - \epsilon(1-2-4)$	δ CF$_3$ antisymm.
$S_{20} = \psi(2-5-8) - \psi(2-5-7) + \gamma(6-5-8) - \gamma(6-5-7)$	Rock. SO$_2$
$S_{21} = \psi(2-5-8) - \psi(2-5-7) - \gamma(6-5-8) + \gamma(6-5-7)$	Tw. SO$_2$
$S_{22} = \sigma\tau[H_i-N_6-S_5-C_2 \ (O_7, O_8)]$	Torsión NH$_2$
$S_{23} = \beta(3-2-5) - \beta(4-2-5)$	ρ CF$_3$
$S_{24} = \sigma\tau[F_i-C_2-S_5-N_6(O_7, O_8)]$	Torsión CF$_3$

[a] ν, stretching; δ, deformation; ρ, rocking.

Table 5
Natural internal coordinates for $CF_3SO_2CH_3$

Definition (according to Fig. 1)	Description[a]
a'	
$S_1 = 2h(8-9) - h(8-10) - h(8-11)$	ν CH$_3$ antisymm.
$S_2 = h(8-9) + h(8-10) + h(8-11)$	ν CH$_3$ symm.
$S_3 = 2\alpha(10-8-11) - \alpha(9-8-10) - \alpha(9-8-11)$	δ CH$_3$ antisymm.
$S_4 = \alpha(9-8-10) + \alpha(9-8-11) + \alpha(10-8-11) - \delta(9-8-5) - \delta(10-8-5) - \delta(11-8-5)$	δ CH$_3$ symm.
$S_5 = d(1-2) + d(2-3) + d(2-4)$	ν CF$_3$ symm.
$S_6 = 2d(2-4) - d(2-1) - d(2-3)$	ν CF$_3$ antisymm.
$S_7 = r(5-6) + r(5-7)$	ν SO$_2$ symm.
$S_8 = 2\delta(9-8-5) - \delta(10-8-5) - \delta(11-8-5)$	ρ CH$_3$
$S_9 = l(8-5)$	ν S–CH$_3$
$S_{10} = \epsilon(1-2-3) + \epsilon(1-2-4) + \epsilon(3-2-4) - \beta(4-2-5) - \beta(1-2-5) - \beta(3-2-5)$	δ CF$_3$ symm.
$S_{11} = 2\epsilon(1-2-3) - \epsilon(1-2-4) - \epsilon(3-2-4)$	δ CF$_3$ antisymm.
$S_{12} = 4\phi(6-5-7) - \psi(2-5-6) - \psi(2-5-7) - \gamma(8-5-6) - \gamma(8-5-7)$	δ SO$_2$
$S_{13} = \psi(2-5-6) + \psi(2-5-7) - \gamma(8-5-6) - \gamma(8-5-7)$	Wag. SO$_2$
$S_{14} = t(2-5)$	ν S–CF$_3$
$S_{15} = 4\theta(2-5-8) - \psi(2-5-6) - \psi(2-5-7) - \gamma(8-5-6) - \gamma(8-5-7)$	δ CSC
$S_{16} = 2\beta(4-2-5) - \beta(1-2-5) - \beta(3-2-5)$	ρ CF$_3$
a''	
$S_{17} = h(8-11) - h(8-10)$	ν CH$_3$ antisymm.
$S_{18} = \alpha(9-8-10) - \alpha(9-8-11)$	δ CH$_3$ antisymm.
$S_{19} = r(5-6) - r(5-7)$	ν SO$_2$ antisymm.
$S_{20} = d(2-1) - d(2-3)$	ν CF$_3$ antisymm.
$S_{21} = \delta(10-8-5) - \delta(11-8-5)$	ρ CH$_3$
$S_{22} = \epsilon(1-2-4) - \epsilon(3-2-4)$	δ CF$_3$ antisymm.
$S_{23} = -\psi(2-5-6) + \psi(2-5-7) - \gamma(8-5-6) + \gamma(8-5-7)$	Rock. SO$_2$
$S_{24} = \psi(2-5-6) + \gamma(8-5-7) - \psi(2-5-7) - \gamma(8-5-6)$	Tw. SO$_2$
$S_{25} = \beta(3-2-5) - \beta(1-2-5)$	ρ CF$_3$
$S_{26} = \sigma\tau[H_i-C_8-S_5-C_2(O_6, O_7)]$	Torsión CH$_3$
$S_{27} = \sigma\tau[F_i-C_2-S_5-C_8 \ (O_6, O_7)]$	Torsión CF$_3$

[a] ν, stretching; δ, deformation; ρ, rocking.

at the HF/6-31G(d,p) level resulted in the assignment of all but two of the spectral bands, which could not be observed [5]. The measured wavenumbers for this molecule appears in Tables 8 and 12.

$CF_3SO_2CH_3$: The infrared and Raman spectra of the liquid substance as well as the infrared spectrum of the gas provided a set of bands due to the normal modes of vibration, of which only the CF$_3$ torsional band could not be measured. The HF, MP2 and DFT quantum chemical methods were used to calculate the optimized geometry, whereas the vibrational wavenumbers were calculated using the B3LYP/6-31G(d,p) procedure [6]. The experi-

mental (mainly gas values) wavenumbers given in [6] are reproduced in Tables 9 and 12.

4.2. Calculation of force constants

The harmonic force constants expressed in Cartesian coordinates, as given by the GAUSSIAN 98 set of programs, were transformed to the 'natural coordinates' or local symmetry coordinates defined in

Table 6
Experimental and calculated wavenumbers, infrared and Raman intensities and potential energy distribution for CF_3SO_2F

Mode	Exp.	Calcd[a]	Calcd SQM[b]	IR int.[c]	Raman int.[d]	P.E.D. (contributions ≥10%)
a'						
ν_1	1270	1234	1263	36.66	10.89	$54S_3 + 17S_5 + 16S_{10} + 16S_1$
ν_2	1235	1281	1221	265.78	0.37	$96S_2 + 20S_7$
ν_3	1140	1131	1147	276.25	5.59	$36S_1 + 38S_3 + 31S_5 + 13S_{10}$
ν_4	829	811	830	133.61	1.20	$67S_4 + 17S_6 + 17S_1$
ν_5	771	760	773	43.81	12.96	$35S_1 + 27S_5 + 12S_{10} + 15S_4$
ν_6	611	591	623	125.40	1.97	$31S_6 + 25S_8 + 20S_5$
ν_7	564	549	565	0.75	2.37	$51S_7 + 11S_2$
ν_8	488	460	482	12.43	1.76	$50S_8 + 25S_6 + 15S_7$
ν_9	333	310	334	0.36	2.56	$36S_{11} + 30S_8 + 26S_9 + 14S_7$
ν_{10}	301	285	302	3.06	4.94	$48S_{10} + 14S_6 + 11S_{11}$
ν_{11}	196	182	182	2.75	0.37	$87S_9 + 51S_{11}$
a''						
ν_{12}	1467	1418	1447	234.35	3.62	$99S_{12}$
ν_{13}	1235	1288	1230	194.96	0.64	$95S_{13} + 20S_{14}$
ν_{14}	564	553	568	0.07	2.52	$51S_{14} + 12S_{13}$
ν_{15}	463	433	448	14.80	1.67	$54S_{15} + 16S_{14}$
ν_{16}	333	318	333	0.49	3.13	$44S_{16} + 37S_{17} + 15S_{14}$
ν_{17}	196	174	193	3.04	0.09	$55S_{17} + 51S_{16} + 40S_{15}$
ν_{18}	–	38	38	0.03	0.04	$102S_{18}$
RMSD (cm^{-1})		23.01	8.62			

[a] DFT with B3LYP approximation and 6-31G** basis set.
[b] From Scaled Quantum Mechanics force field (see text).
[c] Infrared intensities in km mol^{-1}.
[d] Raman activities in Å^4 (amu)$^{-1}$.

Table 7
Experimental and calculated wavenumbers, infrared and Raman intensities and potential energy distribution for CF_3SO_2OH

Mode	Exp.	Calcd[a]	Calcd SQM[b]	IR int.[c]	Raman int.[d]	P.E.D. (contributions ≥10%)
a'						
ν_1	3585	3755	3587	130.44	63.31	$100S_1$
ν_2	1256	1223	1252	62.67	8.99	$23S_2 + 39S_4 + 23S_7 + 20S_{12}$
ν_3	1226	1265	1219	223.63	0.58	$49S_3 + 44S_{15} + 10S_9$
ν_4	1157	1138	1150	186.02	3.85	$50S_4 + 26S_2 + 23S_7$
ν_5	1120	1124	1122	155.89	6.38	$87S_5$
ν_6	859	815	864	181.10	2.84	$81S_6 + 14S_8 + 11S_2$
ν_7	771	755	771	41.13	14.07	$43S_2 + 24S_7 + 13S_{12}$
ν_8	613	590	624	131.01	2.08	$38S_8 + 21S_7 + 18S_{10}$
ν_9	571	551	568	0.59	3.15	$44S_9 + 11S_3$
ν_{10}	496	470	494	19.93	2.03	$51S_{10} + 21S_8 + 22S_9$
ν_{11}	344	321	337	1.82	3.13	$34S_{13} + 30S_{10} + 25S_{11} + 14S_9$
ν_{12}	307	288	306	1.42	5.45	$48S_{12} + 14S_8 + 10S_7$
ν_{13}	160	180	189	4.25	0.42	$84S_{11} + 45S_{13}$
a''						
ν_{14}	1456	1405	1431	239.10	2.77	$94S_{14}$
ν_{15}	1208	1277	1206	218.49	0.33	$49S_{15} + 45S_3 + 11S_{16}$
ν_{16}	571	549	564	0.46	2.38	$52S_{16} + 13S_{15}$
ν_{17}	463	430	438	23.65	2.37	$54S_{17} + 14S_{16} + 11S_{18}$
ν_{18}	351	334	344	23.79	1.95	$45S_{18} + 31S_{20} + 15S_{16}$
ν_{19}	200	259	209	63.04	1.87	$43S_{20} + 42S_{17} + 20S_{19} + 17S_{18}$
ν_{20}	160	176	158	11.07	0.73	$92S_{19} + 32S_{18} + 11S_{20}$
ν_{21}	86	47	86	1.42	0.04	$110S_{21} + 25S_{19}$
RMSD (cm^{-1})		48.27	11.20			

[a] DFT with B3LYP approximation and 6-31G** basis set.
[b] From Scaled Quantum Mechanics force field (see text).
[c] Infrared intensities in km mol^{-1}.
[d] Raman activities in Å^4 (amu)$^{-1}$.

Table 8
Experimental and calculated wavenumbers, infrared and Raman intensities and potential energy distribution for $CF_3SO_2NH_2$

Mode	Exp.	Calcd[a]	Calcd SQM[b]	IR int.[c]	Raman int.[d]	P.E.D. (contributions $\geq$10%)
a'						
ν_1	3280	3530	3280	55.61	94.31	$100S_1$
ν_2	1522	1585	1528	46.38	5.26	$78S_2 + 10S_{11}$
ν_3	1235	1216	1242	76.06	7.32	$31S_3 + 24S_5 + 31S_7 + 25S_{13}$
ν_4	1190	1263	1207	199.89	0.46	$57S_4 + 12S_9 + 34S_{17}$
ν_5	1153	1117	1154	213.59	6.97	$58S_5 + 12S_3 + 10S_7 + 15S_6$
ν_6	957	871	960	158.88	4.40	$64S_6 + 11S_5 + 11S_3$
ν_7	767	757	771	10.45	10.42	$47S_3 + 23S_7 + 14S_{13}$
ν_8	628	603	630	191.16	7.70	$40S_{10} + 12S_8 + 19S_7 + 10S_6$
ν_9	568	555	571	58.44	4.15	$41S_9 + 11S_4$
ν_{10}	495	545	499	98.23	1.68	$46S_8 + 20S_{10} + 27S_9$
ν_{11}	432	467	444	4.89	2.59	$109S_{11} + 26S_6 + 27S_2$
ν_{12}	337	336	337	9.25	1.82	$36S_{14} + 31S_{12} + 35S_8 + 14S_9$
ν_{13}	311	292	309	1.76	5.33	$47S_{13} + 14S_{10} + 11S_7$
ν_{14}	204	183	191	4.88	0.33	$86S_{12} + 52S_{14}$
a''						
ν_{15}	3392	3656	3397	65.83	51.11	$100S_{15}$
ν_{16}	1357	1379	1403	240.21	2.17	$95S_{16}$
ν_{17}	1190	1263	1207	251.77	0.45	$60S_{17} + 13S_{19} + 32S_4$
ν_{18}	1046	1076	1053	0.05	5.26	$84S_{18}$
ν_{19}	568	548	562	0.05	1.86	$55S_{19} + 13S_{17}$
ν_{20}	382	407	417	0.01	1.88	$49S_{20} + 14S_{19} + 14S_{18} + 12S_{23}$
ν_{21}	–	320	352	0.72	3.09	$43S_{21} + 23S_{23} + 14S_{19}$
ν_{22}	–	252	246	25.28	1.44	$76S_{22} + 46S_{20} + 17S_{23}$
ν_{23}	204	175	184	0.96	1.01	$68S_{21} + 48S_{23} + 40S_{22}$
ν_{24}	85	50	87	3.26	0.00	$118S_{24} + 33S_{22} + 19S_{21}$
RMSD (cm^{-1})		82.30	15.04			

[a] DFT with B3LYP approximation and 6-31G** basis set.
[b] From Scaled Quantum Mechanics force field (see text).
[c] Infrared intensities in km mol^{-1}.
[d] Raman activities in $\mathring{A}^4$ $(amu)^{-1}$.

Tables 2 (CF_3SO_2F), 3 (CF_3SO_2OH), 4 ($CF_3SO_2NH_2$) and 5 ($CF_3SO_2CH_3$). Although these definitions were already published for the amide [5] and the sulfone [6], the definitions for S_{12} (δ CSN) and S_{22}, S_{24} (torsions) were modified for sulfonamide in the present work, whereas the table for the sulfone is repeated here for the sake of completeness.

In the molecules now studied as well as in the related molecule $CF_3SO_2OSiH_3$ [1] the relative ordering of the symmetric CF_3 stretching mode and of the pair of non-degenerate CF_3 antisymmetric modes which results from the experimental evidence (symmetric ν CF_3 > antisymmetric ν CF_3), is inverted by the calculated values (symmetric ν CF_3 < antisymmetric ν CF_3), at least at the level of theory used in the present work. The calculated wavenum-

bers were brought to the proper ordering using the appropriate factors in the SQM force field.

The scaling factors, defined according to Pulay et al. [9], were calculated independently for each molecule. Besides, the root mean square deviations (RMSD) were determined as a measure of the difference between the experimental wavenumbers and those calculated with the corresponding SQM force field. All these values appear in Table 10. It can be seen that the scaling factors in general do not differ much for each coordinate. However, a notable difference is observed in the RMSD's, which show substantially higher values for the substances which were studied experimentally in the condensed phases, namely CF_3SO_2F (liquid) and $CF_3SO_2NH_2$ (solid). It seems evident that larger deviations from the

Table 9

Experimental and calculated wavenumbers, infrared and Raman intensities and potential energy distribution for $CF_3SO_2CH_3$

Mode	Exp.	Calcd[a]	Calcd SQM[b]	IR int.[c]	Raman int.[d]	P.E.D. (contributions ≥10%)
a'						
ν_1	3018	3188	3028	1.03	61.57	$100S_1$
ν_2	2938	3081	2926	0.64	98.66	$100S_2$
ν_3	1420	1470	1426	10.52	10.05	$93S_3$
ν_4	1330	1360	1322	5.98	0.43	$100S_4$
ν_5	1241	1206	1241	49.55	5.69	$26S_5 + 21S_6 + 24S_{10} + 18S_{14} + 16S_7$
ν_6	1207	1274	1203	245.84	0.86	$72S_6 + 15S_{11}$
ν_7	1140	1109	1128	235.79	7.85	$66S_7 + 19S_5 + 16S_{10}$
ν_8	955	981	954	48.61	4.62	$69S_8$
ν_9	776	764	775	15.21	1.48	$27S_9 + 11S_{13} + 32S_5$
ν_{10}	739	721	739	56.79	16.75	$23S_{10} + 17S_5 + 38S_9$
ν_{11}	561	542	561	11.47	5.50	$33S_{11} + 17S_{13} + 14S_9$
ν_{12}	538	524	544	58.09	2.73	$37S_{12} + 20S_{11} + 11S_8$
ν_{13}	483	461	483	35.34	5.67	$34S_{12} + 19S_{11} + 27S_{13} + 18S_9$
ν_{14}	322	309	325	0.52	3.28	$20S_{14} + 24S_{12} + 30S_{16} + 21S_{15} + 10S_{11}$
ν_{15}	291	273	289	1.03	4.44	$33S_{14} + 23S_{13} + 19S_{16} + 10S_{15}$
ν_{16}	195	175	179	7.41	0.25	$90S_{15} + 49S_{16}$
a''						
ν_{17}	3038	3198	3037	0.04	46.95	$100S_{17}$
ν_{18}	1420	1462	1418	2.36	13.49	$89S_{18}$
ν_{19}	1393	1350	1373	230.91	3.66	$94S_{19}$
ν_{20}	1201	1237	1182	171.14	0.59	$94S_{20} + 22S_{22}$
ν_{21}	961	985	953	1.06	6.28	$80S_{21}$
ν_{22}	561	541	554	0.03	1.58	$56S_{22} + 14S_{20}$
ν_{23}	387	374	386	2.33	1.63	$47S_{23} + 26S_{25} + 21S_{22} + 10S_{21}$
ν_{24}	310	286	304	0.03	2.47	$60S_{24} + 18S_{23} + 15S_{25} + 15S_{21}$
ν_{25}	204	187	198	2.65	0.32	$54S_{25} + 42S_{24} + 22S_{23} + 12S_{26}$
ν_{26}	165?	164	166	0.16	0.00	$92S_{26} + 13S_{23}$
ν_{27}	–	40	40	1.96	0.00	$117S_{27}$
RMSD (cm^{-1})		57.42	7.93			

[a] DFT with B3LYP approximation and 6-31G** basis set.
[b] From Scaled Quantum Mechanics force field (see text).
[c] Infrared intensities in $km\ mol^{-1}$.
[d] Raman activities in $Å^4\ (amu)^{-1}$.

theoretical gas state wavenumbers were caused by intermolecular interactions in these substances. Probably for the same reasons, the scaling factors obtained for the S–X, SO_2 and CF_3 coordinates in sulfonamide deviate appreciably from the factors calculated for the other molecules.

The set of calculated factors for the four substances suggests that such values are transferable between molecules for the same internal coordinate, as happens for molecules formed by C, N, O and H atoms [20]. In order to prove this assertion, the normal modes were calculated for each molecule using the mean value of the factors obtained for coordinates which are common to the four molecules, which appear in the last column of Table 10. When these mean values of factors were used, the calculated wavenumbers appearing in Tables 6–9 were obtained. The corresponding RMSD values, also included in these Tables, were larger as those of Table 10, as expected, but considerably lower than the values resulting from the comparison of experimental wavenumbers with the wavenumbers initially calculated with GAUSSIAN.

The obtained matrices of SQM force constants are available as supplementary material. The internal force constants, as a characteristic parameter of each

Table 10
Scaling factors for the force field of the isoelectronic molecules CF_3SO_2X

Coordinates[a]	CF_3SO_2F	CF_3SO_2OH	$CF_3SO_2NH_2$	$CF_3SO_2CH_3$	Mean values
ν CF_3 symmetric	1.015	0.924	0.914	0.945	0.950
ν CF_3 antisymm.	0.880	0.882	0.840	0.902	0.876
ν SO_2 symmetric	0.983	1.074	1.042	1.076	1.044
ν SO_2 antisymm.	1.040	1.074	0.977	1.076	1.042
ν S–X	1.042	1.160	1.450	1.039	
δ CF_3	1.031	1.120	1.140	1.087	1.094
δ SO_2	1.147	1.143	1.000	1.028	1.080
ρ SO_2	1.147	1.210	0.758	1.028	1.036
Wag. SO_2, twist. SO_2	1.114	1.135	1.157	1.260	1.166
δ C–S–X	1.114	0.707	1.164	1.260	1.061
ν C–S	1.250	1.160	1.092	1.039	1.135
ρ CF_3	1.223	1.170	1.030	1.163	1.146
ν X–H	–	0.912	0.863	0.902	
δ H–X–H	–	–	1.042	0.943	
ρ H–X–H	–	–	0.944	0.919	
RMSD (cm^{-1})	8.59	4.99	7.40	4.62	

[a] ν, stretching; δ, deformation; ρ, rocking.

chemical bond, were calculated for each molecule in order to compare such bonds along the isoelectronic series. These values were collected in Table 11.

5. Discussion of the results

Rather monotonic trends in the calculated geometric parameters (Table 1) and in the experimental normal mode wavenumbers (Table 12) are observed for the three first members of the isoelectronic series, CF_3SO_2F, CF_3SO_2OH and $CF_3SO_2NH_2$. Such trends are, however, in general not followed by the sulfone, $CF_3SO_2CH_3$. Some numbers which serve to illustrate these facts are also included in Table 12 and will be used to

Table 11
Internal force constants for the isoelectronic molecules CF_3SO_2X

Force constant[a]	CF_3SO_2F	CF_3SO_2OH	$CF_3SO_2NH_2$	$CF_3SO_2CH_3$
Bond stretchings				
f (C–F)	6.17	6.05	5.98	5.90
f (C–F/C–F)	0.87	0.87	0.87	0.86
f (C–S)	3.02	3.08	3.14	2.89
f (S=O)	10.93	10.54	10.17	9.93
f (S–X)	4.67	4.98	6.23	3.06
f (X–H)	–	7.19	6.19	4.95
Deformations				
f (F–C–F)	1.31	1.31	1.32	1.31
f (F–C–S)	0.96	0.96	0.96	0.92
f (C–S=O)	0.97	1.01	1.05	1.06
f (O=S–X)	1.24	1.29	1.30	1.06
f (O=S=O)	1.11	1.12	1.11	1.14
f (C–S–X)	0.95	0.96	1.03	0.99
f (S–X–H)	–	0.64	0.41	0.46
f (H–X–H)	–	–	0.54	0.42

[a] Units are mdyn $Å^{-1}$. Bending constants were normalized with the factor $(r_1 r_2)^{-1}$, being r_1 and r_2 the lengths of the bonds forming the angle.

Table 12
Experimental wavenumbers and additional data for the isoelectronic molecules CF_3SO_2X

Mode[a]	CF_3SO_2F	CF_3SO_2OH	$CF_3SO_2NH_2$	$CF_3SO_2CH_3$
ν SO_2 antisymm.	1467	1456	1357	1393
ν CF_3 symmetric	1270	1256	1235	1241
ν CF_3 antisymm.	1235	1226	1190	1207
ν CF_3 antisymm.	1235	1208	1190	1201
ν SO_2 symmetric	1140	1157	1153	1140
ν S–X	829	859	957	776
δ CF_3 symmetric	771	771	767	739
Wagging SO_2	611	613	628	483
δ CF_3 antisymm.	564	571	568	561
δ CF_3 antisymm.	564	571	568	561
δ SO_2	488	496	495	538
ρ SO_2	463	463	382	387
Twisting SO_2	333	351	(320, calcd)	310
δ CSX	196	160	204	195
ν S–CF_3	301	307	311	291
Torsion S–X	–	160	(252, calcd)	165?
ρ CF_3	333	344	337	322
ρ CF_3	196	200	204	204
Torsion CF_3	–	86	85	–
ν SO_2 (mean val.)[b]	1314	1299	1259	1273
f S=O (mdyn Å^{-1})	10.93	10.54	10.17	9.93
d S=O (Å, Gauss.)	1.445	1.452	1.459	1.464
f SX (mdyn Å^{-1})	4.67	4.98	6.23	3.06
d SX (Å, Gauss.)	1.61	1.63	1.67	1.81
d SX (Å, $\sum$cov. rad.)	1.55	1.67	1.74	1.79

[a] ν, stretching; δ, deformation; ρ, rocking.
[b] $\nu SO_2 = [\frac{1}{2}(\nu_a^2 + \nu_s^2)]^{\frac{1}{2}}$.

explain these trends with simple arguments. The following considerations can be made, always with reference to Table 12:

The mean value of both SO_2 stretching wavenumbers decrease along the CF_3SO_2X series, although it shows an increase for the sulfone. Such a decreasing trend is more clearly shown by the corresponding force constant and should be associated with the decreasing electronegativity of the substituents X. In fact, the negative charges on the X central atoms (Fig. 1) decrease along the series whereas the S atom become less positive, opposing the delocalization over the S=O bonds of the lone pairs belonging to the oxygen atoms which form the SO_2 group and decreasing therefore their bond orders and force constants. At the same time, the negative charge on these oxygen atoms increase, as expected. Such dependence of the S=O stretching wavenumbers with electro-

negativity of the substituents in $XYSO_2$ compounds has been shown by Hargittai [21].

The SX stretching wavenumber show initially an increasing trend but falls for the sulfone and the corresponding valence force constants follow the same trend. Looking for a connection between these vibrational data and the geometrical parameters, it can be seen that the theoretical SX distances show an increasing trend, and that such increase is particularly large for $CF_3SO_2CH_3$, eventually explaining the lower vibrational parameters (stretching wavenumber and force constant) observed for the SC stretching. The increasing trend of GAUSSIAN calculated SX distances is approximately reproduced by the sum of covalent atomic radii, corrected by the difference in electronegativity between the atoms S and X [22], included also in Table 12. Both sets of distance values are practically coincident for the sulfone, but for the acid and the amide the GAUSSIAN values are lower

than the sum of covalent radii. Such observation, summed to the still lower experimental value of the SO distance (1.56 Å) in triflic acid, suggests that the SO and SN bonds (and probably also the SF bond) have partial double character resulting from the delocalization of the X lone electron pairs on the SX bond. (A similar proposal was made to explain the barrier of rotation around a SN bond in sulfonamides resulting from an ab initio calculation [19]). The decreasing electronegativity of X along the series should favor such delocalization and a reinforcing of the SX bonds, explaining in principle the increasing trend of stretching wavenumbers and force constants and its abrupt fall for the sulfone, for which no electron delocalization is possible. Such an argument could also explain the low value obtained for the force constant associated with the O=S–X deformation (Table 11).

6. Supplementary data

The SQM matrices of force constants have been deposited with the British Library at Boston Spa, Wetherby, West Yorks, UK as Supplementary Publication No. SUP 26689 (8 pages). Persons wishing to obtain copies of deposited material should contact Service Enquiries, British Lending Library, Boston Spa, Wetherby, West Yorks, LS23 7BQ, UK citing the SUP number. Tel.: +44-1937-546-060; fax: +44-1937-546-333; e-mail: dsc-customer-services@bl.uk.

Acknowledgements

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