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AN EXPERIMENTAL AND THEORETICAL STUDY OF THE VIBRATIONAL PROPERTIES OF CF_3SO_2Cl

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Dedicated to Professor Dr. Enrique J. Baran for his important contributions to Inorganic Chemistry

Abstract

The infrared and Raman spectra of CF_3SO_2Cl were obtained and analyzed. An assignment of the observed bands is proposed, based in a comparison with similar molecules and with a theoretical calculation of frequencies and normal modes of vibration made by means of density functional theory (DFT) techniques. The original force field in Cartesian coordinates was transformed to local symmetry coordinates and subsequently scaled to reproduce the experimental frequencies.

Keywords: CF_3SO_2Cl, infrared, Raman, DFT, force constants.

Resumen

Se obtuvieron y analizaron los espectros de infrarrojo y Raman de CF_3SO_2Cl. Se propone una asignación de las bandas observadas en base a la comparación con moléculas similares y con el cálculo teórico de las frecuencias y modos normales de vibración realizado por medio de las

técnicas de la teoría del funcional de la densidad (DFT). El campo de fuerzas original en coordenadas cartesianas fue transformado a coordenadas de simetría local y posteriormente fue escalado para reproducir las frecuencias experimentales.

Palabras clave: CF_3SO_2Cl, infrarrojo, Raman, DFT, constantes de fuerza.

Introduction

Several studies were made in this laboratory on molecules of general formula SO_2XY, where the substituents were monoatomic as in SO_2X_2 (X = F, Cl, Br) [1] and SO_2XF (X = Cl, Br) [2], or simple polyatomic groups as in the isoelectronic series CF_3SO_2X (X = F, OH, NH_2, CH_3) [3]. Now, the infrared and Raman spectra of CF_3SO_2Cl were obtained and interpreted using theoretical techniques similar to those used in the mentioned previous studies. The resulting data are compared with those obtained previously for CF_3SO_2F [3,4], a member of the above mentioned series.

Experimental

CF_3SO_2Cl (Sigma-Aldrich) is a liquid with relatively high vapour pressure at room temperature. The infrared spectra of the gas was obtained at several pressures in a 10 cm glass cell provided with KBr windows, using Bruker FTIR instruments, models IFS66 and Equinox 55. The Raman spectrum of the liquid was obtained with the FRA-106 accessory mounted on the IFS66 instrument, using 1064 nm light from a Nd/YAG laser for excitation.

Calculations

The optimized molecular geometries, frequencies 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 03 set of programs [5].

Some exploratory calculations showed that a good approximation to the experimental vibrational frequencies could be obtained using the B3PW91 functional [6, 7] combined with the 6-311G(d) basis set. Such combination was also used for SO_2X_2 [1] and SO_2XF [2]. The Cartesian force constants given by the calculation were converted to a set of local symmetry coordinates or "natural coordinates" as defined by Fogarasi et al. [8] through the corresponding B matrix [9], calculated with a standard program. The resulting force field was subsequently scaled using the scheme of Pulay et al. [10, 11], in which the main force constants are multiplied by scale factors *fi, ff,…* and the corresponding interaction constants are multiplied by *(fi.fj)$^{1/2}$*, adjusting the scale factors to reproduce as well as possible the experimental frequencies. The resulting scaled quantum mechanics (SQM) force field served to calculate the Potential Energy Distribution of the molecule. The mathematical treatment of the Cartesian force constants leading to the SQM force field was performed with the program FCARTP, developed by Collier [12], whereas the atomic displacement vectors corresponding to each molecular vibration were visualized by means of the program Moldraw [13].

Results and discussion

Molecular structure

The structure of CF_3SO_2Cl as calculated with the above mentioned quantum chemistry method appear in Fig. 1, showing a *gauche,* non-eclipsed conformation. The geometrical parameters are presented in Table 1, together with the experimental structure obtained by electron diffraction techniques [14]. The corresponding data for CF_3SO_2F was added to the Table and includes also the set of experimental data [15], not mentioned in the previous work [3]. As can be seen the

experimental data are reproduced rather well for both molecules, with differences in the bond lengths ≤ 0.041 Å (with the notable exception of the S-X bond, reproduced with a difference ≤ 0.070 Å). Angles are predicted with differences generally less than 1º, with the exception of O=S=O for CF₃SO₂Cl, which shows a difference of 1.4º.
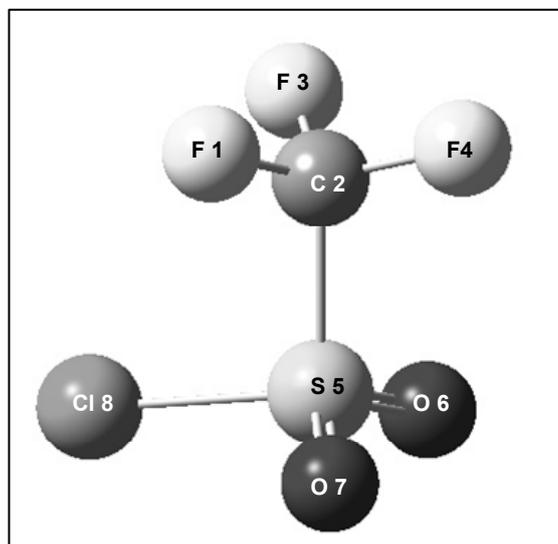
Figure 1. Structure of the CF_3SO_2Cl molecule.

Table 1. Optimized and experimental geometric parameters for the molecules CF_3SO_2X (X= F, Cl).

	CF_3SO_2F		CF_3SO_2Cl	
	Exp. [a]	Calc.	Exp. [b]	Calc.
Bonds (Å)				
C-F$_{trans}$	1.325(2)	1.322	1.326(4)	1.321
C-F$_{cis}$		1.319		1.317
C-S	1.835(5)	1.876	1.857(6)	1.895
S=O	1.410(3)	1.431	1.416(7)	1.439
S-X	1.543(3)	1.610	2.016(5)	2.086
Angles (º)				
F$_{cis}$-C-F$_{trans}$	109.8	110.2	109.9(3)	110.3
F$_{cis}$-C-F$_{cis}$		110.3		110.6
S-C-F$_{trans}$	-	107.3	109.1(4)	106.6
S-C-F$_{cis}$		109.4		109.5
O=S=O	124.1(10)	124.6	122.4(10)	123.8
C-S-X	95.4	95.5	98.7(4)	98.6
C-S=O	108.5(6)	109.0	108.3(7)	107.5
X-S=O	-	107.4	108.3(3)	108.2

[a] Ref. 15; [b] Ref. 14.

Vibrational results

The studied molecule have C_s symmetry and 18 normal modes of vibration, which span the representation 11 A' + 7 A'', all active in infrared and Raman. The experimental spectra are reproduced in Fig. 2, in which the calculated spectra were also added for comparison purposes. A reasonable coincidence can be seen between both sets of data.
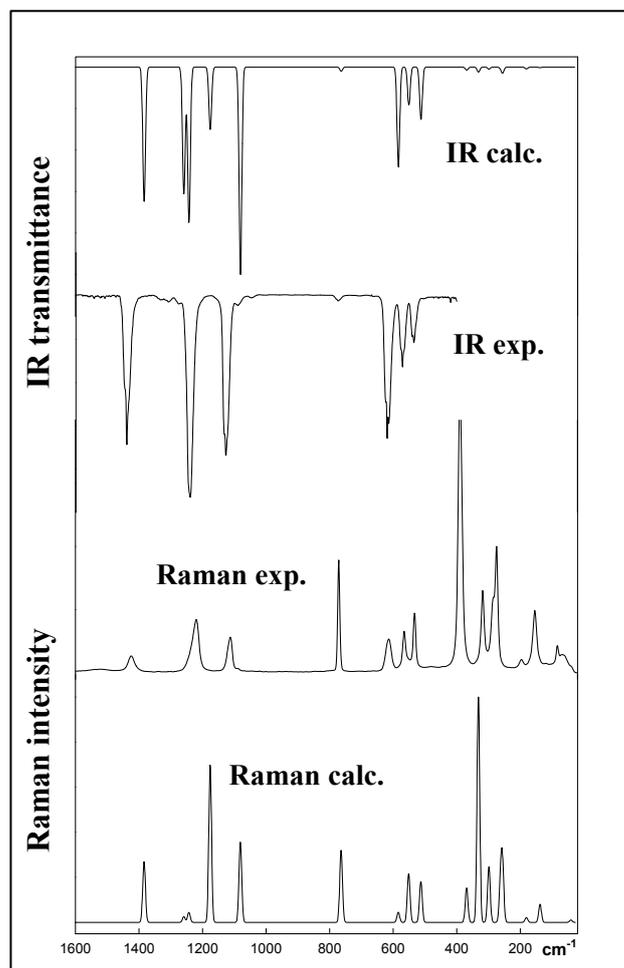
Figure 2. The experimental and calculated infrared and Raman spectra of CF_3SO_2Cl. Infrared spectrum: gas phase; path length 10 cm; pressure 6 torr; resolution 2 cm^{-1}. Raman spectrum: liquid phase; resolution 2 cm^{-1}.

The assignment of bands.

The atomic displacement vectors corresponding to each of the calculated vibrational modes and the previous studies made on CF_3SO_2F [3] and other molecules were used as a basis for the proposed assignment of the observed bands to the different modes of vibration. The measured frequencies for these bands appear in Table 2 whereas the calculated frequencies are included in Table 5.

Six of the bands measured in the infrared spectrum of the gaseous substance show a PQR structure resulting of the unresolved rotational structure. The moments of inertia of the molecule are 251.9, 392.3 and 450.7 uma.Å^2, giving CF_3SO_2Cl the character of an asymmetrical top with the largest moment normal to the molecular symmetry plane. Therefore, those vibrations having A''

symmetry (antisymmetric with respect to that plane) are expected to have a band envelope of the C type, with a prominent Q branch.

Table 2. Frequency of the observed bands in the infrared and Raman spectra of CF$_3$SO$_2$Cl (units are cm^{-1}).

Infrared (gas)	Band type	Raman (liquid)[a]	Assignment
1445			
1438.1 s	C	1425 (6)	ν_{12}
1431 sh			
1245 s [b]		ca. 1232 sh	ν_1, ν_{13}
1238 vs [b]		1220 (19)	ν_2
1131.5			
1126.5	AB	1113 (13)	ν_3
1121 sh			
ca. 778 sh.			
772.9	AB	771.5 (41)	ν_4
ca. 766 sh.			
623.7			
619.1	AB	614.3 (12)	ν_5
614.1			
575.6			
570.8	C	565.7 (14)	ν_{14}
ca. 565 sh.		ca. 557	ν_6
539.5			
535.0	AB	533.0 (20)	ν_7
ca. 528 sh.			
		390.0 (100)	ν_8, ν_{15}
		318.3 (27)	ν_{16}
		286 (25)	ν_9
		275.3 (44)	ν_{10}
		196.8 (3)	ν_{17}
		154.9 (20)	ν_{11}
		83 br (8)	ν_{18}

Abbreviations: v, very; w, weak; s, strong; br, broad; sh, shoulder.
[a] Relative band heights in parentheses.
[b] Components resulting from a curve fit analysis.

CF₃ vibrations.

The three bands due to the CF_3 stretching vibrations should appear in the 1100-1300 cm^{-1} region, generally strong in the infrared and weak in the Raman spectra. A relatively strong and asymmetric band at 1239 cm^{-1} and a weaker band with PQR structure located at 1126.5 cm^{-1} appear in that region in the infrared spectrum of gaseous CF_3SO_2Cl (Fig. 2). Using curve fitting procedures it was possible to decompose the stronger band in two components centered at 1245 and 1238 cm^{-1}, being the last one the stronger of the pair. The corresponding Raman band is also asymmetric, confirming such overlapping. A comparison of the Raman spectrum with that of CF_3SO_2F [4] leads to the assignment of the 1245 cm^{-1} component and the 1126.5 cm^{-1} band to the two antisymmetric and the symmetric CF_3 stretching modes, respectively.

Comparison with CF_3SO_2F [3] and with the calculated data allow the immediate assignment of the 772.9 and 570.8 cm^{-1} bands to the symmetric and one of the antisymmetric CF_3 deformations, respectively. The last mentioned band shows a C contour and therefore should be due to the deformation of A" species, as mentioned above. That band appears at 565.7 cm^{-1} in the Raman spectrum and shows a shoulder at ca. 557 cm^{-1} which is assignable to the antisymmetric deformation of A' species.

The 286 and 196.8 cm^{-1} Raman bands are assigned to the pair of non-degenerated CF_3 rocking modes after comparison with the theoretically calculated frequencies (Table 5).

SO₂ vibrations.

The strong bands located at 1438.1 and 1238 cm^{-1} are immediately assigned to the antisymmetric and symmetric SO_2 stretching modes, respectively. The 1438.1 cm^{-1} band, as happens also with the already mentioned 570.8 cm^{-1} band, shows a very prominent Q branch in the envelope of the rotational structure which is typical of the C-type bands, associated with dipolar moment changes ($\Delta\mu$) parallel to the higher inertial moment of the molecule.

The band centered at 535.0 cm^{-1} is assigned to the SO_2 angular deformation, a mode which appears in the range 488-538 cm^{-1} [3]. The vibrations comprising the group as a whole should now be considered. A simple comparison with the calculated frequencies and previous experimental results indicate the assignment of the 619.1 cm^{-1} band to the SO_2 wagging and the 318.3 cm^{-1} band to the SO_2 twisting. The band due to the SO_2 rocking mode, predicted by the calculations at 375 cm^{-1} (Table 5), does not appear in the Raman spectrum; that missing band is considered overlapped by the strong band centered at 390 cm^{-1}.

Skeletal modes and torsion.

The C-S stretching mode appears always around 300 cm^{-1} in the CF_3SO_2X molecules [3] and therefore the 275.3 cm^{-1} Raman band is assigned to it. This mode and the SO_2 twisting mode give rise to relatively prominent Raman bands separated by 30-40 cm^{-1} in the molecules having the CF_3SO_2 moiety [3]; such difference amounts to 43 cm^{-1} in CF_3SO_2Cl. The intense Raman band located at 390.0 cm^{-1} is assigned to the S-Cl stretching mode, which appears at 422 cm^{-1} in SO_2ClF [2].

A weak band centered at 83 cm^{-1} in the Raman spectrum of the liquid substance is assigned to the CF_3 torsional mode.

Calculation of force constants.

The force field in Cartesian coordinates, as given by the Gaussian programs, was transformed to the set of non-redundant, natural internal coordinates defined in Table 3. Such coordinates take into account the local symmetry of the CF_3 group and follow the proposals of

Fogarasi et al. [8]. The resulting force constants were subsequently scaled according with the methodology mentioned above (Calculations) in order to reproduce as well as possible the experimental frequencies.

The calculated scale factors corresponding to each force constant appear in Table 4, whereas the resulting frequencies, infrared and Raman predicted intensities and potential energy distribution appear in Table 5. The SQM force field was used to calculate the internal force constants appearing in Table 6.

Table 3. Natural internal coordinates for the CF_3SO_2Cl molecule.

Definition (according to Fig. 1)	Description[a]
A′	
$S_1 = 2d\ (2\text{-}4) - d\ (2\text{-}3) - d\ (2\text{-}1)$	ν CF$_3$ antisym.
$S_2 = r\ (5\text{-}6) + r\ (5\text{-}7)$	ν SO$_2$ sym.
$S_3 = d\ (2\text{-}4) + d\ (2\text{-}3) + d\ (2\text{-}1)$	ν CF$_3$ sym.
$S_4 = \alpha\ (1\text{-}2\text{-}3) + \alpha\ (1\text{-}2\text{-}4) + \alpha\ (3\text{-}2\text{-}4) - \beta\ (4\text{-}2\text{-}5) -$ $\beta\ (3\text{-}2\text{-}5) - \beta\ (1\text{-}2\text{-}5)$	δ CF$_3$ sym.
$S_5 = \psi\ (2\text{-}5\text{-}6) + \psi\ (2\text{-}5\text{-}7) - \gamma\ (8\text{-}5\text{-}6) - \gamma\ (8\text{-}5\text{-}7)$	Wag. SO$_2$
$S_6 = 2\alpha\ (1\text{-}2\text{-}3) - \alpha\ (1\text{-}2\text{-}4) - \alpha\ (3\text{-}2\text{-}4)$	δ CF$_3$ antisym.
$S_7 = 4\phi\ (6\text{-}5\text{-}7) - \psi\ (2\text{-}5\text{-}6) - \psi\ (2\text{-}5\text{-}7) -$ $\gamma\ (8\text{-}5\text{-}6) - \gamma\ (8\text{-}5\text{-}7)$	δ SO$_2$
$S_8 = t\ (5\text{-}8)$	ν S-Cl
$S_9 = 2\beta\ (4\text{-}2\text{-}5) - \beta\ (1\text{-}2\text{-}5) - \beta\ (3\text{-}2\text{-}5)$	ρ CF$_3$
$S_{10} = l\ (2\text{-}5)$	ν C-S
$S_{11} = 4\theta\ (2\text{-}5\text{-}8) - \psi\ (2\text{-}5\text{-}7) - \psi\ (2\text{-}5\text{-}6) - \gamma\ (8\text{-}5\text{-}7) - \gamma\ (8\text{-}5\text{-}6)$	δ C-S-Cl
A″	
$S_{12} = r\ (5\text{-}6) - r\ (5\text{-}7)$	ν SO$_2$ antisym.
$S_{13} = d\ (2\text{-}3) - d\ (2\text{-}1)$	ν CF$_3$ antisym.
$S_{14} = \alpha\ (1\text{-}2\text{-}4) - \alpha\ (3\text{-}2\text{-}4)$	δ CF$_3$ antisym.
$S_{15} = \psi\ (2\text{-}5\text{-}7) - \psi\ (2\text{-}5\text{-}6) + \gamma\ (8\text{-}5\text{-}7) - \gamma\ (8\text{-}5\text{-}6)$	ρ SO$_2$
$S_{16} = \psi\ (2\text{-}5\text{-}7) - \psi\ (2\text{-}5\text{-}6) - \gamma\ (8\text{-}5\text{-}7) + \gamma\ (8\text{-}5\text{-}6)$	Twist. SO$_2$
$S_{17} = \beta\ (1\text{-}2\text{-}5) - \beta\ (3\text{-}2\text{-}5)$	ρ CF$_3$
$S_{18} = \Sigma\ \tau\ [X_i\text{-}C_2\text{-}S_5\text{-}Cl_8\ (O_6, O_7)]$	torsion CF$_3$

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

Table 4. Scaling factors for the force field of the CF_3SO_2Cl molecule.

Coordinates [a]	Factors
ν CF_3 sym.	0.939
ν CF_3 antisym.	0.936
ν SO_2 sym.	1.085
ν SO_2 antisym.	1.040
ν S-Cl	1.340
δ CF_3	1.081
Wag. SO_2, Twist. SO_2, δ C-S-Cl	1.074
ν C-S	0.980
δ SO_2, ρ SO_2	0.973
ρ CF_3	1.183
torsion CF_3	3.552

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

Comparison with the CF_3SO_2F molecule.

The values of Table 1 shows clearly that, on passing from CF_3SO_2Cl to CF_3SO_2F, the increasing in electronegativity of the halogen substituent causes a decrease of the C-S and S=O distances, whereas the corresponding force constants show an increase, as expected (Table 6). Such change of bond distances should be associated to the increasing positive charge on the S atom, which varies from +0.906 for the Cl compound to +1.127 for the F compound. In fact, it is expected that a larger positive charge in the central atom causes a displacement of electrons from the substituents, reinforcing the corresponding bonds.

Table 5. Experimental and calculated frequencies, infrared and Raman intensities and potential energy distribution for CF_3SO_2Cl.

Mode	Experim.	Calcd.[a]	Calcd. SQM[b]	IR int.[c]	Raman int.[d]	P.E.D. (contributions $\geq$ 10 %)	Main comp.
A'							
ν_1	1245	1264	1243	269.18	1.00	$53\ S_1 + 38\ S_2 + 11\ S_6$	ν CF$_3$ antisym.
ν_2	1238	1200	1230	102.44	15.23	$41\ S_2 + 46\ S_1$	ν SO$_2$ sym.
ν_3	1126.5	1101	1109	344.56	7.36	$54\ S_3 + 45\ S_4 + 18\ S_1 + 16\ S_{10}$	ν CF$_3$ sym.
ν_4	772.9	775	775	6.02	6.49	$31\ S_4 + 44\ S_3 + 12\ S_{10}$	δ CF$_3$ sym.
ν_5	619.1	595	628	182.89	1.21	$48\ S_5 + 29\ S_8 + 10\ S_4$	Wag. SO$_2$
ν_6	563	559	568	62.09	2.83	$33\ S_6 + 18\ S_7 + 12\ S_5$	δ CF$_3$ antisym.
ν_7	535.0	522	537	83.44	4.11	$44\ S_7 + 30\ S_6 + 19\ S_8$	δ SO$_2$
ν_8	390.0	349	382	7.40	20.74	$58\ S_8 + 21\ S_7 + 17\ S_5$	ν S-Cl
ν_9	286	305	318	2.41	4.87	$46\ S_9 + 24\ S_7 + 14\ S_{11} + 13\ S_{10} + 12\ S_6$	ρ CF$_3$
ν_{10}	275.3	261	269	8.74	4.46	$47\ S_{10} + 24\ S_9 + 21\ S_5$	ν C-S
ν_{11}	154.9	140	146	0.95	1.59	$100\ S_{11} + 22\ S_9$	δ C-S-Cl
A"							
ν_{12}	1438.1	1411	1437	235.58	5.82	$99\ S_{12}$	ν SO$_2$ antisym.
ν_{13}	1245	1279	1252	215.89	0.54	$98\ S_{13} + 20\ S_{14}$	ν CF$_3$ antisym.
ν_{14}	570.8	558	575	0.21	2.05	$61\ S_{14} + 10\ S_{13}$	δ CF$_3$ antisym.
ν_{15}	390.0	375	389	5.49	3.32	$35\ S_{15} + 36\ S_{17} + 21\ S_{14}$	Rock. SO$_2$
ν_{16}	318.3	269	276	1.54	4.13	$52\ S_{16} + 24\ S_{15} + 13\ S_{17}$	Twist. SO$_2$
ν_{17}	196.8	182	189	2.98	0.46	$49\ S_{17} + 50\ S_{16} + 39\ S_{15}$	ρ CF$_3$
ν_{18}	83	44	83	0.09	0.20	$105\ S_{18}$	τ CF$_3$
RMSD (cm^{-1})		24	7				

[a] DFT with B3PW91 approximation and 6-311G* 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 6. Internal force constants for the molecules CF_3SO_2X (X = F, Cl).

Force constant [a]	CF_3SO_2F [b]	CF_3SO_2Cl [c]
Bond stretchings		
f(C-F)	6.34	6.34
f(C-F / C-F)	0.76	0.76
f(C-S)	3.31	2.34
f(S-X)	4.85	2.65
f(S=O)	11.22	11.07
Deformations		
f(F-C-F)	1.21	1.32
f(F-C-S)	0.97	0.99
f(C-S-X)	1.48	0.95
f(C-S=O)	0.95	0.92
f(X-S=O)	1.25	0.96
f(O=S=O)	1.19	0.97

[a] Units are mdyn $Å^{-1}$ for stretchings and stretch/stretch interactions and mdyn $Å$ rad^{-2} for angular deformations.
[b] Recalculated values after Ref. 3.
[c] This work.

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