IR, Raman and computational study
of lithium trifluoromethanesulfonate

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ABSTRACT

The vibrational wavenumbers of Lithium trifluoromethanesulfonate were calculated using Gaussian03 software package at different levels and the fundamental modes are assigned. The predicted infrared intensities, Raman activities and first hyperpolarizability are reported. The calculated wavenumbers and geometrical parameters are in agreement with the reported experimental values.

INTRODUCTION

In the field of polymer electrolyte materials with suitable conducting and mechanical properties for application in electrochemical systems, gel polymer electrolytes are widely used.[1,2] Usually gel polymer electrolytes is formed by dissolving a lithium salt in a plasticizer and adding them to a polymer network. For a plasticizer to play the role as a conductivity enhancer, it should have a high dielectric constant to dissociate ions and low viscosity to facilitate the ion transport. Mixed solvents which are composed of a main solvent with high dielectric constant and viscosity but small dielectric constant are preferred as it brings about a marked conductivity enhancement of the electrolytes.[3] Lithium trifluoromethane sulfonate can be used as such a solvent.[4] Winie and Arof[4] reported the FT-IR studies on interactions among components in hexanoyl chitosan-based polymer electrolytes. Ab initio quantum mechanical method

is at present widely used for simulating the IR spectrum. Such simulations are indispensable tools to perform normal coordinate analysis that modern vibrational spectroscopy is unimaginable without involving them. In the present study, we have calcualted the vibrational wavenumbers of the title compound by using Hartree-Fock and DFT methods and compared with the IR and Raman bands. The IR and Raman spectra are downloaded from www.aist.jp.go and www.sigmaaldrich.com.

EXPERIMENTAL

Computational details

Calculations of the title compound were carried out with Gaussian03 program[5] using the Hartree-Fock and DFT (B3LYP) levels of theory using the standard 6-31G* set to predict the molecular structure and vibrational wavenumbers. Molecular geometry (Fig. 1) was fully optimized by Berny's optimization algorithm using redundant

internal coordinates. Harmonic vibrational wavenumbers were calculated using the analytic second derivatives to confirm the convergence to minima of the potential surface. The wavenumber values computed contain known systematic errors and hence we have used scaling factors 0.8929 for HF and DFT method.[6] For DFT calculated wavenumbers, so scaling factor is used since the values agree with the experimental wavenumbers. The absence of imaginary wavenumbers of the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum energy. The optimized geometrical parameters (DFT) are given in Table 1.

RESULTS AND DISCUSSION

The calculated scaled wavenumbers, experimental IR and Raman wavenumbers and the assignments are given in Table 2. According to Roeges[7] the CF_3 stretching vibrations are expected in the range 1165-1340 cm^{-1}, CF_3 deformation bands in the region 540-780 cm^{-1} and rocking modes of CF_3 in the region 260-390 cm^{-1}. The DFT calculations give the CF_3 stretching modes at 1234, 1197, 1098 cm^{-1} and CF_3 deformation bands at 761, 571, 560 and 521 cm^{-1}. Characteristic frequencies of the title compound are reported at 1293, 1252, 1044 cm^{-1} (SO_3) , 1224, 1188, 776 cm^{-1} (CF_3).[4] Panicker *et al.*[8] reported the SO_3 bands at 1176, 1033, 697, 492,

356, 138 cm^{-1} in the IR spectrum and at 1180, 1044, 360, 170 cm^{-1} in the Raman spectrum for sulfanilic acid sodium salt. Ganguly *et al.*[9] reported SO_3 modes at 1157, 1124, 1034, 682, 558 cm^{-1} and Panicker *et al.*[10] reported SO_3 modes at 1156, 1035, 686, 560 cm^{-1} in IR spectrum and at 1156, 1128, 1035, 693 cm^{-1} in Raman spectrum for sulfanilic acid. The SO_3 stretching mode is seen at 1048 cm^{-1} in benzene sulfonate[11] and at 1035 cm^{-1} for sulfanilic acid.[12] In the present case, the SO_3 modes are assigned at 1324, 1265, 963 cm^{-1} (stretching) and 633, 504, 377, 221 cm^{-1} (deformation). The CS stretching vibration is reported at 640 cm^{-1} (IR), 644 cm^{-1}(Raman) and at 642 cm^{-1} theoretically[13-15] and for the title compound the band at 618 cm^{-1} is assigned as CS stretching mode. The torsional modes are usually seen in the low wavenumber region.[7,16]

According to Kaduk[17] the Li-O bond distance span in a wide range and the average distance of Li-O is 1.969 Å. For the title compound the Li-O bond length (DFT) is found to be 1.8867 Å. The DFT calculations give the SO bond lengths in the range 1.4538-1.5138 Å. Clerbaux and Colin[18] reported the S-O bond length as 1.4811 and 1.4931 Å. In the present case the CS bond length is 1.8637 Å which is in agreement with the reported values.[19] Mary *et al.*[20] reported the CF bond length as 1.3242 Å whereas in the present calculation the CF bond lengths lie in the range 1.3319-1.3469 Å.

Table 1: Geometrical parameters (DFT) of the title compound

| Bond lengths (Å°)		Bond Angles (°)		Dihedral Angles (°)	
S_1–O_2	1.4538	A(2,1,3)	118.0	D(2,1,5,6)	-180.0
S_1–O_3	1.5138	A(2,1,4)	118.0	D(2,1,5,7)	60.7
S_1–O_4	1.5138	A(2,1,5)	107.4	D(2,1,5,8)	-60.6
S_1–C_5	1.8637	A(2,1,9)	144.5	D(3,1,5,6)	54.8
S_1–Li_9	2.3675	A(3,1,4)	105.4	D(3,1,5,7)	-64.6
O_3–Li_9	1.8867	A(3,1,5)	103.0	D(3,1,5,8)	174.1
O_4–Li_9	1.8867	A(4,1,5)	103.0	D(4,1,5,6)	-54.7
C_5–F_6	1.3469	A(5,1,9)	108.1	D(4,1,5,7)	-174.0
C_5–F_7	1.3319	A(1,5,6)	108.7	D(4,1,5,8)	64.7
C_5–F_8	1.3319	A(1,5,7)	110.4	D(9,1,5,6)	0.0
		A(1,5,8)	110.4	D(9,1,5,7)	-119.3
		A(6,5,7)	108.9	D(9,1,5,8)	119.4
		A(6,5,8)	108.9		
		A(7,5,8)	109.6		
		A(3,9,4)	79.3		
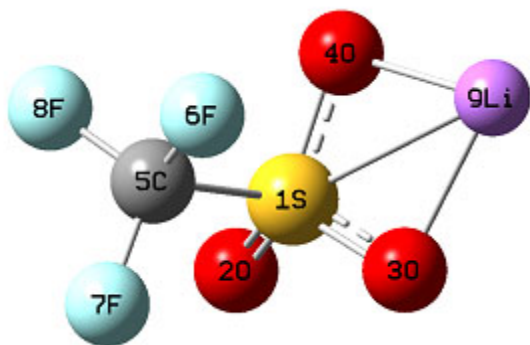
Fig. 1: Optimized geometry of the molecule

The first hyperpolarizability (β_0) of this novel molecular system is calculated using theoretically, based on the finite field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. First hyperpolarizability is a third rank tensor that can be described by a 3×3×3 matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry.[21] The calculated first hyperpolarizability of the title compound is $3.18 10^{-30}$ esu (B3LYP/6-31G* method). We conclude that the title compound is an attractive object for future studies of non linear optical properties.

Table 2: Calculated (scaled) wavenumbers, IR, Raman frequencies and assignments

HF/6-31G*			B3LYP/6-31G*			$\upsilon_{(IR)}$	$\upsilon_{(Raman)}$	Assign
υ (cm^{-1})	IR Intensity	Raman Activity	υ (cm^{-1})	IR Intensity	Raman Activity	(cm^{-1})	(cm^{-1})	ments
1314	439.58	2.56	1324	295.88	4.49	1322	1329	υSO_3
1271	326.81	0.57	1265	268.73	0.34	1257	1268	υSO_3
1255	105.02	3.44	1234	126.87	1.61	1224	1240	υCF_3
1237	196.13	1.99	1197	167.07	3.73	1196	1205	υCF_3
1117	322.24	2.92	1098	253.30	4.15	1089	1085	υCF_3
985	237.04	13.48	963	196.54	20.05			υSO_3
769	13.12	7.67	761	1.42	10.77	777	769	δCF_3
649	201.91	0.68	633	128.67	1.63			δSO_3
599	94.87	1.66	618	163.66	0.37			υCS
563	12.18	2.91	571	65.29	3.14	551	577	δCF_3
545	108.55	0.79	560	7.49	3.75	547		δCF_3
507	67.27	0.29	521	13.33	0.44	521		δCF_3
502	38.70	0.25	504	26.16	0.32		495	δSO_3
343	7.65	1.99	377	8.90	0.10		368	δSO_3
342	18.81	0.25	336	4.15	2.87		338	ρCF_3
331	2.67	1.40	321	0.01	2.32			γSCF_3
320	5.80	3.26	306	5.62	4.81		298	γCSO_3
222	13.59	0.23	221	9.57	0.62		218	ρSO_3
190	0.24	0.01	187	0.37	0.01			ρCF_3
112	46.52	0.24	99	39.55	0.61			tCF_3
61	6.15	0.05	55	4.91	0.11			$t SO_3$

υ-stretching; δ-in-plane deformation; γ-out-of-plane deformation; ρ-rocking; t-torsion; subscripts: as-asymmetric, s-symmetric.

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