Vibrational Study of the Trifluoromethanesulfonate Anion: Unambiguous Assignment of the Asymmetric Stretching Modes

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Introduction

The trifluoromethanesulfonate anion, $CF_3SO_3^-$, is widely employed in inorganic chemistry as a weakly coordinating anion that lacks the treacherous redox properties of perchlorate and is more resistant to hydrolysis than BF_4^-. Vibrational spectra of polyatomic anions, including the trifluoromethanesulfonate (triflate) anion, have been used to identify the mode of anion coordination in transition metal complexes,[1] to probe cation–anion interactions in electrolytes,[2] and to determine the extent of dissociation of the corresponding acid.[3] Clearly, such studies require unambiguous assignments for the vibrational modes of the triflate anion. In spite of several detailed investigations,[4-8] however, the assignments for some of the fundamentals of $CF_3SO_3^-$ in the CF and SO stretching region (which are critical to the interpretation of $CF_3SO_3^-$ coordination to cations) remain in dispute.

In the present work we investigate the infrared and Raman spectra of the trifluoromethanesulfonate anion in which one or more of the oxygen atoms were isotopically enriched with oxygen-18. The infrared and Raman spectra of the isotopically labeled triflate anion allow unambiguous identification of the bands which involve significant motion of the oxygen atoms. We have also performed a normal coordinate analysis to confirm the magnitude of the observed shifts.

Experimental and Calculation Section

Synthesis. Freshly distilled trifluoromethanesulfonic anhydride (1.00 mL, 5.94 mmol) was vigorously stirred in a Schlenk tube with an excess (250 μL, 13.9 mmol) of deionized water. The ^{18}O-labeled sample was prepared by using 96.5% $H_2^{18}O$ instead of deionized water. Initially the reaction mixture was biphasic, with the less dense water beading on the top of the triflic anhydride. As the reaction progressed (~1 h) three distinct layers could be seen and upon completion (several hours), the reaction mixture consisted of a single clear layer with a small amount of excess water.

An aqueous solution (40% by weight) of tetrabutylammonium hydroxide (9.0 mL, 13.7 mmol) was added to the Schlenk tube and stirred. The excess water was decanted by syringe and the remaining cloudy suspension was isolated and dried in vacuo. Recrystallization was accomplished by redissolution in a minimal amount of dichloromethane followed by addition of diethyl ether and cooling to yield white crystals. The crystals were dried for several hours on a high vacuum line.

Spectroscopy. Mid-IR (400–4000 cm⁻¹) spectra were collected using a Bomem MB-100 fourier transform infrared spectrometer equipped with a DTGS detector operating at a resolution of 1 cm⁻¹. Spectra were collected as Nujol mulls using KBr plates. Far-IR (100–400 cm⁻¹) spectra

Table I. Infrared and Raman Frequencies[a] of Tetrabutylammonium Trifluoromethanesulfonate and Tetrabutylammonium Iodide

[Bu₄N][CF₃SO₃]			[Bu₄N]I[b]	
unlabeled	¹⁸O-labeled			
IR	IR	Raman	IR	Raman
1269 vs	1270	1276		
	1247	1248		
1223 s	1221	1223		
1145 vs	1145	1153		
1113 wsh	1113	1111	1108	1111
1063 wsh	1064	1066	1066	
1056 w	1057	1059	1055	1060
1032 vs	1032	1032		
	1015	1016		
	999	1000		
993 vw	992 sh		990	
925 w	925	927	922	927
894 m	894	903	896	907
882 m	882	878	880	881
799 vw	799		793	
751 m	751	753		
736 m	737		737	
722 w	722		722	
637 vs	637			
	633			
	628			
629 m				
		599		600
572 m	571	572		
		533	531	532
517 m	516	518		
	510			
393	395		398	
346	346	346		
309	308			
		263		264
206	206			

[a] All frequencies are cm⁻¹. [b] Features are listed only if they overlap important regions for the $CF_3SO_3^-$ vibrational spectra.

were collected on a BIO-RAD Digilab Model FTS-40 FIR with a Model 3200 data station at a resolution of 2 cm⁻¹. Spectra were collected as Nujol mulls between polyethylene plates.

Raman spectra were obtained from solid crystalline samples in 5 mm Pyrex tubes. The sample was illuminated with the 488.0 nm line of an argon ion laser and scattered light was collected in a 90° geometry for stationary samples or in the 180° geometry (backscattering) for spinning samples. All spectra were run at a bandpass of 2.0 cm⁻¹.

Calculations. Vibrational calculations were carried out using a computer program for the nonlinear least-squares refinement of force constants and other associated programs.[9] The $CF_3SO_3^-$ molecule was assumed to have a staggered geometry and C_{3v} symmetry. All angles were assumed to be tetrahedral. The problem was set up using C_{3v} symmetry coordinates, which have been tabulated previously.[10] Two symmetry force fields were constructed by correction and refinement of the force field of Bürger et al.[5] and of Varetti et al.[11] to fit the present data and assignments. The two problems were set up identically using the bond distances as listed in the original papers.[5,8]

The force field of Varetti et al. was modified in the following manner. Initially the values of F_{66} and F_{77} were adjusted and refined to give the proper assignments of $\nu_{as}(SO_3)$ and $\nu_{as}(CF_3)$. The values of all eleven diagonal force constants were then refined to fit the frequencies for [Bu₄N][CF₃SO₃] listed in Table I. In this process the off-diagonal force constants were not modified or refined.

The published force field of Bürger et al. appears to contain an error. The frequencies calculated using the "set I" force constants for the asymmetric deformations (ν_8 and ν_{11}) disagreed with the observed values by as much as 70 cm⁻¹. To ensure that the problem was set up correctly, the elements of the G matrix calculated by the vibrational analysis package

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(9) Program QCMP 012, Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN.
(10) Clark, E. A.; Weber, A. *J. Chem. Phys.* **1966**, *45*, 1759–1766.
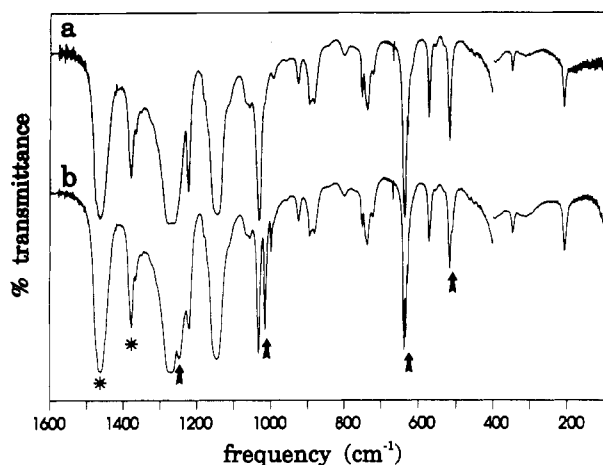(11) Varetti, E. L. QUINOR, Argentina, personal communication, Universidad Nacional de La Plata, 1992.

Figure 1. IR spectra from 100 to 1600 cm⁻¹ for unlabeled (a) and partially ¹⁸O-labeled (b) [Bu₄N][CF₃SO₃]. Peaks which shift upon isotopic labeling are marked with an arrow. Peaks due to the Nujol mulling agent are marked with asterisks.
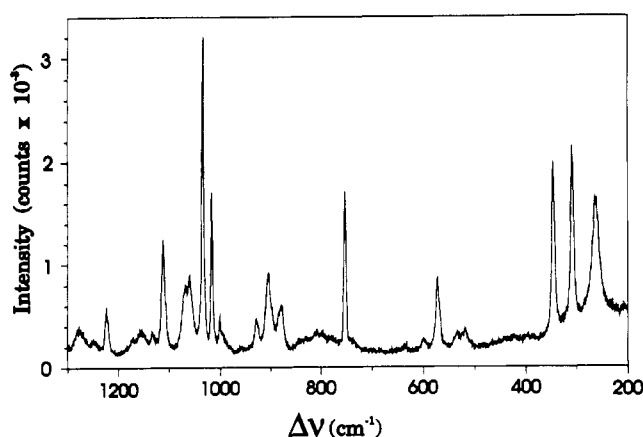

Figure 2. Raman spectrum from 200 to 1300 cm⁻¹ of partially ¹⁸O-labeled [Bu₄N][CF₃SO₃].

were checked against the listing tabulated for C_{3v} molecules by Clark and Weber.[10] To correct this apparent error, the values of F_{88} and $F_{11\ 11}$ were modified to fit the observed frequencies. This modified force field was then refined, varying only the diagonal force constants, to fit the frequencies observed for [Bu₄N][CF₃SO₃].

The calculation of vibrational frequencies for the partially ¹⁸O-labeled anion presented a problem as the symmetry of the anion is reduced upon isotopic labeling from C_{3v} to C_s symmetry. To maintain consistency with the published force fields the C_{3v} symmetry force constants were employed along with a G matrix reflecting the lower symmetry of the isotopically substituted species. Due to the reduced symmetry of the problem, the calculation was performed with no block factoring. This procedure enabled the calculation of vibrational frequencies for the partially labeled molecule without the construction of yet another force field. A minor disadvantage of this procedure is that it does not lead to a simple representation of the eigenvectors for the partially ¹⁸O-labeled anion.

Results

The infrared and Raman data collected for solid [Bu₄N]-[CF₃SO₃] and [Bu₄N]I is compiled in Table I. Figure 1 shows a comparison of IR traces for both unlabeled and partially ¹⁸O-labeled [Bu₄N][CF₃SO₃]. Since the isotopically enriched sample contains approximately 50% of the unlabeled trifluoromethanesulfonate anion, the IR trace shown in Figure 1b displays bands for both the labeled and unlabeled anion. Figure 2 shows the Raman spectrum obtained for partially ¹⁸O-labeled [Bu₄N]-[CF₃SO₃]. Observed frequencies for the normal isotopic species along with calculated and observed frequency shifts for ¹⁸O-isotopic substitution of one and two oxygen atoms are listed for both modified force fields in Table II. Tables of symmetry force

Table II. Comparison of Calculated and Observed Frequency Shifts (cm⁻¹) for Isotopically Substituted Trifluoromethanesulfonate

normal isotopic band (cm⁻¹)	[CF₃S¹⁶O₂¹⁸O]⁻			[CF₃S¹⁶O¹⁸O₂]⁻		
	$\Delta_{calc}{}^a$	$\Delta_{calc}{}^b$	Δ_{obs}	$\Delta_{calc}{}^a$	$\Delta_{calc}{}^b$	Δ_{obs}
1273	24	25	26	39	39	
1222	0	0		0	0	
1149	0	0		0	0	
1032	16	17	17	31	31	33
752	0	2		0	5	
637	7	5	5	14	10	9
572	1	2		2	3	
517	4, 12ᶜ	3, 10ᶜ	7	12, 20	10, 18	
346	8	5		12	9	
308	2	3		4	5	
206	1	3		2	5	

ᵃ Calculated using modified Varetti force field. ᵇ Calculated using modified Bürger force field. ᶜ Observed shoulder is presumably a superposition of both shifts.

constants and calculated potential energy distributions for the modified Varetti and Bürger force field are available as supplementary material.

Discussion

The trifluoromethanesulfonate anion has been the subject of many vibrational spectroscopic studies using polarized Raman and infrared spectroscopy on both powders and single crystals.[4–8] The data and assignments for CF₃SO₃⁻ in the literature and the current work are compiled in Table III.[4–8] Also, normal coordinate analyses have been reported; however, some of the assignments, especially for the asymmetric stretching modes, are not firmly established. The major ambiguities in the assignments for the vibrational bands of the triflate anion are in the stretching region between 1000 and 1300 cm⁻¹, where the CF and SO stretching modes overlap.

In the present research, the tetrabutylammonium cation was chosen because of its large size and attendant weak ion pairing and also because of the relatively weak IR and Raman spectra of this cation in the range of the CF₃SO₃⁻ vibrational spectra. The bands in the infrared and Raman spectra due to the tetrabutylammonium cation were readily eliminated by inspection of the absorptions observed for tetrabutylammonium iodide (Table I). No attempt was made to assign the vibrational modes of the cation.

In order to experimentally distinguish the assignment of bands for SO₃ and CF₃ we carried out vibrational spectroscopic measurements on ¹⁸O-labeled triflate. The labeled material was prepared by hydrolysis of the anhydride CF₃SO₂–O–SO₂CF₃ with H₂¹⁸O to produce equimolar amounts of CF₃S¹⁶O₃H and CF₃S¹⁶O₂¹⁸OH (reaction 1). The triflic acid was then converted

$$(CF_3S^{16}O_2)_2{}^{16}O + H_2{}^{18}O \rightarrow$$

$$CF_3S^{16}O_3H + CF_3S^{16}O_2{}^{18}OH \quad (1)$$
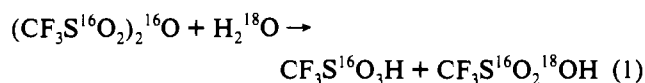
to the tetrabutylammonium salt via reaction with tetrabutylammonium hydroxide.

The vibrational data for the product indicate that a significant percentage of the [Bu₄N][CF₃SO₃] was isotopically labeled at two of the oxygen atoms. This double labeling may result from the reaction between the ¹⁸O-labeled CF₃SO₃H and the remaining triflic anhydride (Scheme I), which is only slowly consumed in the reaction. The postulated multiple exchange leading to doubly labeled triflate is likely to be promoted by the triphasic nature of the reaction which provides high local concentrations of the anhydride. The alternate possibility that direct exchange of triflic acid occurs with ¹⁸O-enriched water was ruled out because a mixture of excess ¹⁸O-labeled water and triflic acid stirred for approximately 2 days showed no evidence of isotopic exchange.

The spectral data in the 1000–1300-cm⁻¹ region (Figure 1) clearly show that the bands located at 1270 and 1032 cm⁻¹ in the

Table III. Comparison of Trifluoromethanesulfonate Anion Vibrational Bands and Assignments[a]

Ag[CF₃SO₃][b]		Na[CF₃SO₃][c]		[NH₄][CF₃SO₃][d]		[NH₄][CF₃SO₃][e]		[Bu₄N][CF₃SO₃][f]	
1270	$\nu_{as}(SO_3)$[g]	1285	$\nu_{as}(CF_3)$	1251	$\nu_{as}(SO_3)$	1260	$\nu_{as}(CF_3)$	1273[h]	$\nu_{as}(SO_3)$
1237	$\nu_s(CF_3)$	1230	$\nu_s(CF_3) + \nu_s(CS)$	1227	$\nu_s(CF_3)$	1236	$\nu_s(CF_3)$	1222	$\nu_s(CF_3)$
1167	$\nu_{as}(CF_3)$[g]	1188	$\nu_{as}(SO_3)$	1180	$\nu_{as}(CF_3)$	1181	$\nu_{as}(SO_3)$	1149	$\nu_{as}(CF_3)$
1043	$\nu_s(SO_3)$	1038	$\nu_s(SO_3)$	1035	$\nu_s(SO_3)$	1035	$\nu_s(SO_3)$	1032[h]	$\nu_s(SO_3)$
760	$\delta_s(CF_3) + \nu_s(CS)$	766	$\delta_s(CF_3) + \nu_s(CS)$	760	$\delta_s(CF_3)$	770	$\delta_s(CF_3)$	752	$\delta_s(CF_3)$
647	$\delta_s(SO_3)$			649, 640	$\delta_s(SO_3)$	648	$\delta_s(SO_3)$	637[h]	$\delta_s(SO_3)$
582	$\delta_{as}(CF_3)$	580	$\delta_s(SO_3), \delta_{as}(SO_3)$	575		581	$\delta_{as}(CF_3)$	572	$\delta_{as}(CF_3)$
525	$\delta_{as}(SO_3)$	520	$\delta_{as}(CF_3)$	518		520	$\delta_{as}(SO_3)$	517[h]	$\delta_{as}(SO_3)$
351	$\rho(SO_3)$	353	$\rho(SO_3)$	347		352	$\rho(SO_3)$	346	$\rho(SO_3)$
320	$\nu_s(CS) + \delta_s(CF_3)$	321	$\nu_s(CS) + \delta_s(CF_3)$	320	$\nu_s(CS)$	326	$\nu_s(CS)$	308	$\nu_s(CS)$
217	$\rho(CF_3)$	208	$\rho(CF_3)$	220		228	$\rho(CF_3)$	206	$\rho(CF_3)$

[a] Key to assignments: ν = bond stretch, δ = group angle deformation, ρ = group angle rock; subscript "s" for totally symmetric (A) vibrations and subscript "as" for degenerate asymmetric (E) vibrations. All frequencies are cm⁻¹. [b] Data and assignments from ref 5. [c] Data and assignments from ref 4. [d] Data and assignments from ref 6. [e] Data and assignments from ref 8. [f] Data and assignments from this work. [g] Assignments listed are for the "set I" force constants from ref 5. An alternate assignment [reversing $\nu_{as}(SO_3)$ and $\nu_{as}(CF_3)$] is also given. [h] Band displays shift upon ¹⁸O isotopic labeling.

Scheme I
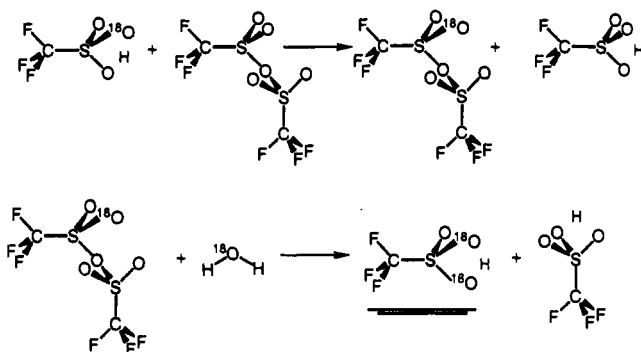
unlabeled material shift significantly upon isotopic labeling. These bands may be assigned, taking into account their previously determined symmetry,[6,8] as the asymmetric and symmetric SO₃ stretching modes, respectively. The asymmetric and symmetric CF₃ stretching modes can then be assigned to the remaining bands at 1149 and 1222 cm⁻¹. These assignments are in accord with the "set I" assignments of Bürger et al.,[5] along with those of Gänswein and Behm[6] and Katsuhara et al.[7] They disagree, however, with the frequently quoted assignments of Miles et al.[4]

Spectral data show that the bands at 637 and 517 cm⁻¹ in the unlabeled material display a shift upon labeling. The single crystal Raman and infrared polarization data of other authors[8] indicate these may be assigned as the symmetric and asymmetric deformations of the SO₃ group, respectively. The remaining bands at 752 and 572 cm⁻¹ are then assigned as the CF₃ symmetric and asymmetric deformations with a significant amount of C–S stretching character in the band at 752 cm⁻¹.

In recent papers the C–S stretching mode has been assigned to the band at 308 cm⁻¹, with negligible contributions from SO₃ deformation. In keeping with this assignment, oxygen-18 labeling did not shift the 308-cm⁻¹ feature, but this should not be construed as confirmation of the assignment.

The doubly degenerate (E) vibrational bands in the 200–400-cm⁻¹ range have been given equivalent qualitative descriptions of SCF and CSO deformations[5] or CF₃ and SO₃ rocking modes.[7,8] The remaining bands at 346 and 206 cm⁻¹ were assigned as indicated by previous authors as SO₃ and CF₃ rocking modes. In

our normal coordinate analysis, it was found that a reasonable force field resulted for either assignment. Inspection of the infrared data show no obvious shifts, however, both peaks broaden by approximately 25%. Therefore, the assignments in Table III of the SO₃ and CF₃ rocking modes reflect the reasoning of previous authors.

The calculated vibrational frequency shifts for the partially ¹⁸O-labeled trifluoromethanesulfonate anion listed in Table II match the observed shifts very well. There are only small differences in the shifts calculated using either of the modified force fields. The largest and most significant difference is in the isotopic shift calculated for the mode at 346 cm⁻¹ which is assigned as an SO₃ rocking mode. The shifts calculated for the modified Varetti and Bürger force fields are 8 and 5 cm⁻¹, respectively. As mentioned earlier, the only two bands assignable to the SO₃ rocking motion are at 346 and 206 cm⁻¹. Neither band displays an observable shift in the infrared spectrum, but both broaden by approximately 25%.

The measured fwhh (full width at half-height) for the peak at 346 cm⁻¹ is approximately 5.3 cm⁻¹. For this peak width, a shift of at least 6.0 cm⁻¹ would be required in order to resolve the normal isotopic peak from the partially ¹⁸O-labeled peak. The isotopic shift calculated for the modified Bürger force field is smaller than 6.0 cm⁻¹ and therefore, it is reasonable that the isotopic shift is not clearly observed. These data therefore, favor the higher degree of mixing between the two low-frequency rocking modes found in the potential energy distribution for the modified Bürger force field. A vibrational study of the fully ¹⁸O isotopically substituted trifluoromethanesulfonate anion may clarify the assignments in this low frequency region.