Symmetry-Based Vibrational Analysis of Polyatomic Ionic Species in Polymer Electrolytes: Application to the Compounds Poly(ethylene oxide)$_3$LiCF$_3$SO$_3$ and Poly(ethylene oxide)NaCF$_3$SO$_3$

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ABSTRACT: A symmetry-based vibrational analysis of the compounds (PEO)$_3$LiCF$_3$SO$_3$ and (PEO)NaCF$_3$SO$_3$ is described which preserves the distinct identity of the $CF_3SO_3^-$ intramolecular vibrational modes in the one-dimensional and three-dimensional space groups appropriate to each compound. The infrared and Raman spectra in the $\delta_s(CF_3)$ spectral region of the two compounds are discussed in terms of this formalism, although a similar analysis of the $\nu_s(SO_3)$ region is limited to the (PEO)$_3$LiCF$_3$SO$_3$ compound. A one-dimensional space group is sufficient to describe the $\delta_s(CF_3)$ spectral region in both compounds and the $\nu_s(SO_3)$ region in (PEO)$_3$LiCF$_3$SO$_3$.

1. Introduction

Polymer−salt systems are ionically conducting[1] and therefore of interest for their technological importance as electrolytes in a variety of applications.[2,3] These systems also have interesting structural properties, in particular at high salt concentrations some polymer−salt systems form crystalline compounds.[4,5] In a few cases the crystal structures of these compounds have been solved by X-ray diffraction techniques, yielding a precise picture of the cation and anion coordination and structural details of the cation−polymer interaction. Examples include (PEO)$_3$NaClO$_4$,[6] (PEO)$_3$LiCF$_3$SO$_3$,[7] (PEO)$_3$LiN(SO$_2$CF$_3$)$_2$,[8] and (PEO)NaCF$_3$SO$_3$.[9] Knowledge of the local structure present in a crystalline compound can provide insight into the local structure present in the amorphous phase of the compound above the melting temperature.[10]

Vibrational spectroscopy has been used to study cation−anion interactions[11−14] and cation−polymer interactions[15,16] in polymer electrolytes. This has been a particularly powerful technique to examine cation−anion interactions in systems where the frequencies of anion intramolecular vibrations are sensitive to perturbation by the cations, resulting in bands due to distinct associated ionic species that are reasonably well-separated in frequency. Examples include studies of polyethers containing dissolved salts of trifluoromethanesulfonate, $CF_3SO_3^-$, [13,17] or perchlorate, ClO_4^-.[14,18] Early spectroscopic studies of NaCF$_3$SO$_3$ in poly(propylene oxide) led to the identification of "free" ions and contact ion pairs,[13,19] with evidence for the existence of ionic aggregates observed at high NaCF$_3$SO$_3$ and LiCF$_3$SO$_3$ concentrations in poly(propylene oxide).[19,20] The ionic aggregate was identified as the triple ion $[Li_2CF_3SO_3]^+$ in both PPO−LiCF$_3$SO$_3$ [21] and PEO−LiCF$_3$SO$_3$.[22]

Recent vibrational spectroscopic studies of PEO-MCF$_3$SO$_3$ (M = Li, Na) systems have included some attention to the crystalline compounds (PEO)$_3$LiCF$_3$SO$_3$ and (PEO)NaCF$_3$SO$_3$ which are observed at high salt concentrations.[23,24] To take full advantage of the detailed picture of local structure available from crystal structures of polymer−salt compounds, it is necessary to apply the methods of group theory to the classification of normal modes in those compounds. The development of an appropriate symmetry-based analysis for polymer−salt compounds is greatly aided by previous analyses of crystalline polymers. Crystalline polymers have been extensively studied using vibrational spectroscopy, and many of the group theoretical techniques developed to characterize their normal modes can be applied to polymer electrolytes.

It is a straightforward matter to use a factor group analysis to characterize the vibrations of a crystal in terms of the irreducible representations of the space group. However in crystalline polymers, a factor group analysis predicts a far richer vibrational spectrum than is observed in either the Raman or the infrared spectrum. This observation argues that the vibrations of the polymer chains are often highly decoupled within a unit cell because the intermolecular forces between polymer chains in a crystal are significantly weaker than the intramolecular forces of a single chain; consequently, only the vibrational motion of a single polymer chain in the cell need be considered.[25] The vibrations of a single polymer chain are conveniently described using one-dimension space groups. In a very early application of this method, symmetry-based selection rules were derived for polymer chains by utilizing line group irreducible representations to label the normal modes.[26] This analysis was used to interpret the infrared spectrum of poly(ethylene) and compare with the results predicted from a factor group analysis of the full unit cell.[26,27] The use of a one-dimensional space group was extended to the case of a helical polymer by Liang and Krimm,[28] who described the vibrational modes of poly(tetrafluoroethylene) in terms of helical group irreducible representations. The application of a helical group analysis to the calculation of vibrational frequencies by the Wilson GF-matrix method has been described and applied to poly(oxymethylene).[29] Helical groups have been used to simplify the vibrational analysis of other helical polymers, most notably poly(ethylene oxide).[30]

We have previously extended a helical group analysis to the polymer−salt compound (PEO)$_3$LiCF$_3$SO$_3$ and a line group analysis to (PEO)NaCF$_3$SO$_3$ by assuming the cations and anions of the salt to be an integral part of the polymer chain.[24] In those analyses it was necessary to make specific assumptions about the nature of the

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internal coordinates of the triflate anion to separate the vibrational modes intrinsic to the polymer host and the modes of a polyatomic ionic species present in the polymer electrolyte. To take advantage of the very high degree of vibrational decoupling between the intramolecular modes of the polyatomic ionic species and the modes of the polymer, it would be very useful, from a spectroscopic point of view, to develop a *general* method that correlates the vibrational symmetry species of an isolated polyatomic ion to the symmetry species of the helical group or line group under which the polymer electrolyte can be classified. This would provide a description of the intramolecular vibrations of the polyatomic ions present in a polymer−salt compound that preserves the essentially independent nature of such modes. The development of such a method is the goal of this paper, which will focus on the two compounds $(PEO)_3LiCF_3SO_3$ and $(PEO)NaCF_3SO_3$ as examples.

2. Crystalline Compound $(PEO)_3LiCF_3SO_3$

2.1. Structure. $(PEO)_3LiCF_3SO_3$ crystallizes in the $P2_1/a$ (C_{2h}^5) space group with two polymer chains in the unit cell.[7] Each lithium ion is coordinated by three ether oxygen atoms from adjacent monomer units in a helical PEO chain and two triflate oxygen atoms, one from each of two adjacent triflate anions. The third oxygen atom of each triflate anion is uncoordinated. Consequently, each triflate anion in the compound vibrates essentially as an $[Li_2CF_3SO_3]^+$ species.[10,24]

2.2. Symmetry-Based Analysis. 2.2.1. Isolated Molecular Group. It is useful to begin the analysis by considering the vibrations of an isolated triflate anion, considered here to have a eclipsed geometry and belonging to the C_{3v} point group. There are 18 intramolecular vibrational degrees of freedom which can be classified under the irreducible representations of the point group as

$$\Gamma(\text{intra vib}) = 5A_1 + A_2 + 6E \tag{1}$$

Attention will be focused on the CF_3 symmetric deformation mode, $\delta_s(CF_3)$, and the SO_3 antisymmetric stretching mode, $\nu_{as}(SO_3)$, as examples of intramolecular modes belonging to the A_1 and E symmetry species, respectively. The symmetry species of the two modes under the C_{3v} point group would then be written

$$\Gamma(\delta_s(CF_3)) = A_1 \tag{2}$$

$$\Gamma(\nu_{as}(SO_3)) = E \tag{3}$$

Although the analysis that now follows will be cast in terms of the SO_3 antisymmetric stretching mode and the CF_3 symmetric deformation mode, it is important to note that this treatment is valid for *any* mode belonging to either the A_1 or E symmetry species in the isolated triflate anion.

2.2.2. Local Molecular Group. In the next step of the analysis the triflate ion is allowed to interact with its static potential energy environment. This could be formally done by using the point symmetry of the center of mass of the anion, which in the case of $(PEO)_3LiCF_3SO_3$ is a Wyckoff 4(e) site of C_1 symmetry. In that case the symmetry species of the two kinds of intramolecular modes would be

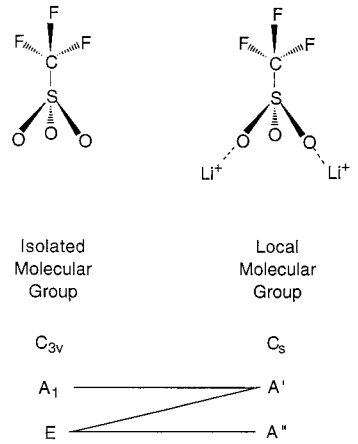

Figure 1. Correlation of the isolated triflate ion symmetry species with those of the local molecular (effective site) group in $(PEO)_3LiCF_3SO_3$.

$$\Gamma(\delta_s(CF_3)) = A \tag{4}$$

$$\Gamma(\nu_{as}(SO_3)) = 2A \tag{5}$$

It is more illustrative and useful to write the approximate site symmetry (or effective site symmetry) by considering the dominant perturbation of the triflate ion by its static environment. In $(PEO)_3LiCF_3SO_3$, two of the three triflate oxygen atoms are each coordinated by a lithium ion, effectively lowering the triflate ion symmetry from C_{3v} to C_s. The vibrations must be now classified under the latter point group, yielding

$$\Gamma(\delta_s(CF_3)) = A' \tag{6}$$

$$\Gamma(\nu_{as}(SO_3)) = A' + A'' \tag{7}$$

The point group which describes the approximate or effective site symmetry will be designated as the local molecular group to distinguish it from the group describing the true site symmetry, i.e., the site group. Nearest-neighbor cation−anion interactions are responsible for the most significant perturbation of the isolated polyatomic ions in polymer−salt systems. In amorphous polymer−salt systems these interactions result in distinct ionic species, and the phenomenon is commonly referred to as "ionic association". Therefore, eqs 4 and 5, or alternatively eqs 6 and 7, describe the effects of ionic association in polymer−salt compounds. These correlations are schematically illustrated in Figure 1.

Although the correlations between the group describing the true site symmetry, or alternatively the effective site symmetry, and the factor group of the crystal can be written down using standard methods,[31] it is more useful to proceed through a correlation with the helical group of the polymer before proceeding on to the factor group. This will permit the distinct identity of the anion intramolecular modes to be preserved in the helical group analysis, the goal of this paper.

2.2.3. Helical Group. If a single polymer chain contains more than one polyatomic ion in the unit cell and the ions are defined as an integral part of the polymer chain, then the helical group can be used to describe the collective vibrations of the polyatomic ions. In other words, the vibrations of individual, perturbed polyatomic ions are dynamically coupled through the helical group, resulting in modes that transform according to the various irreducible representations of the

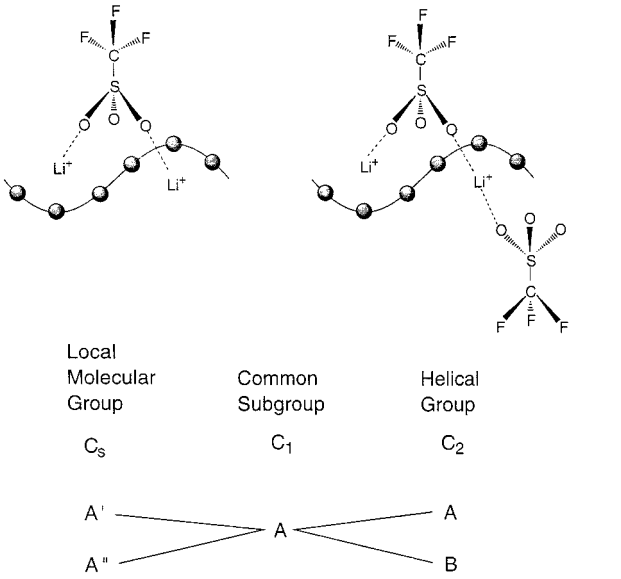

Figure 2. Correlation of the local molecular group symmetry species with those of the helical group via the common C_1 subgroup in $(PEO)_3LiCF_3SO_3$.

helical group. The helical structure of the compound $(PEO)_3LiCF_3SO_3$ has the conformation (TTG TTG $\bar{T}\bar{T}G$)$_2$ for the bond sequence −C−O−C−C− and belongs to the helical group C(2π/2). The *b*-axis of the unit cell coincides with the fiber axis and with the 2/1 screw axis of the helix. There are two triflate anions in each chain running through the unit cell; these two anions (and their coupled vibrations) are related by the 2-fold screw axis.

The key step in this analysis is the correlation the symmetry species of the perturbed polyatomic ion to the symmetry species of the helical group. This is accomplished by identifying the set of all symmetry operations common to the local molecular group and the helical group. These operations are a subgroup of the two groups and provide the required correlation between the irreducible representations of the local molecular group (or alternatively the site group of the polyatomic anion) and the corresponding irreducible representations of the helical group. In $(PEO)_3LiCF_3SO_3$ the only symmetry operation common to the local molecular group and the helical group is the identity. Therefore, the vibrations of the local molecular group are correlated through the common C_1 subgroup to the helical group as illustrated in Figure 2. The C(2π/2) helical group is isomorphous to the C_2 point group; consequently, the irreducible representations of C_2 are the irreducible representations of C(2π/2). The resulting vibrational modes of the triflate anion under the helical group are

$$\Gamma(\delta_s(CF_3)) = A + B \tag{8}$$

$$\Gamma(\nu_{as}(SO_3)) = 2A + 2B \tag{9}$$

The intramolecular vibrational modes of the triflate anions in the chain have now been classified in terms of the irreducible representations of the helical group. This greatly simplifies the next step, because the correlation between a helical group (or, alternatively, a line group) of a polymer and the factor group of the crystal containing the polymer has been previously described in the literature.[26,27]

2.2.4. Factor Group. The most general symmetry-based analysis of the vibrational motion considers only

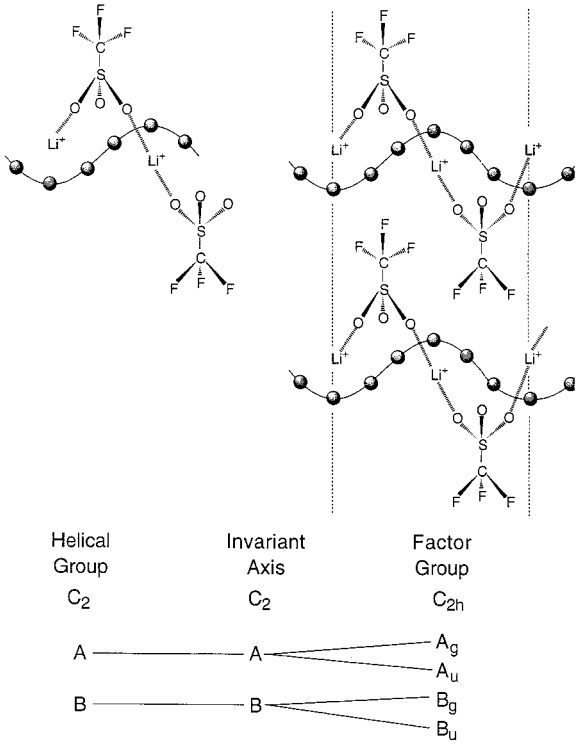

Figure 3. Correlation of the helical group symmetry species with those of the factor group in $(PEO)_3LiCF_3SO_3$.

atoms or monatomic ions, ignoring the bonding interactions among these which form molecular entities such as polyatomic ions or polymer chains. All that is required for a factor group analysis is knowledge of the space group, the occupancy of the Wyckoff sites by the various atoms and ions, and the symmetries of those sites. In the compound $(PEO)_3LiCF_3SO_3$ all atoms occupy Wyckoff 4(e) sites with site symmetry C_1. It has been previously shown[24] that the irreducible representations of the triflate ion intramolecular normal modes in the unit cell are

$$\Gamma(CF_3SO_3^-) = 24A_g + 24B_g + 24A_u + 24B_u \tag{10}$$

while the symmetry species of the modes originating in the $\delta_s(CF_3)$ and $\nu_{as}(SO_3)$ vibrations respectively are

$$\Gamma(\delta_s(CF_3)) = A_g + B_g + A_u + B_u \tag{11}$$

$$\Gamma(\nu_{as}(SO_3)) = 2A_g + 2B_g + 2A_u + 2B_u \tag{12}$$

The A_g and B_g modes are Raman-active and infrared-inactive; the A_u and B_u modes are infrared-active and Raman-inactive. The correlations between the helical group and the factor group are illustrated in Figure 3.

3. Crystalline Compound (PEO)$NaCF_3SO_3$

3.1. Structure. Sodium triflate forms a 1:1 compound with PEO, crystallizing in the $P2_1/c$ (C_{2h}^5) space group with two polymer chains in the unit cell.[9] The triflate ion is extensively coordinated by the cations, with two oxygen atoms from a triflate anion each coordinated to different sodium ions, while the third oxygen atom is coordinated to another two sodium ions. The most significant difference between the two compounds is that in $(PEO)NaCF_3SO_3$ two of the sodium ions coordinated to each triflate anion are in turn coordinated to

neighboring PEO chains, resulting in anionic intermolecular cross-linking. In contrast, there is neither cation nor anion cross-linking in $(PEO)_3LiCF_3SO_3$, where each chain is associated with its own set of ions.

3.2. Symmetry-Based Analysis. 3.2.1. Isolated Molecular Group/Local Molecular Group. The analysis of the isolated ion vibrations is identical in all triflate ion-containing polymer electrolyte compounds. Therefore, the discussion of (PEO)NaTf begins with the symmetry species of the triflate ion perturbed by its static potential energy environment. In $(PEO)NaCF_3SO_3$ the triflate anion is highly coordinated by four sodium ions in an asymmetric arrangement; the effective site group and the true site group are identical and described by the C_1 point group. Consequently, the equations analogous to eqs 6 and 7 are

$$\Gamma(\delta_s(CF_3)) = A \tag{13}$$

$$\Gamma(\nu_{as}(SO_3)) = 2A \tag{14}$$

3.2.2. Line Group. The structure of a single chain in a unit cell of the compound $(PEO)NaCF_3SO_3$ has the conformation $(\overline{TGG}\ \overline{TGG})_2$ for the bond sequence −C−O−C−C− and should properly be described as a distorted zigzag rather than a helical structure, with the sodium ions lying outside the zigzag. The polymer axis is parallel to the *c* axis and does not coincide with the 2-fold screw axis of space group. Therefore, a line group analysis will be used to describe the intramolecular coupling of the triflate anions "belonging" to a single chain. The identity and the *c* glide reflection operation leave the polymer chain axis invariant; hence, the line group is C_s. As in the case of the lithium triflate compound, only the identity operation is common between the effective site group and the line group. Therefore, the C_1 point group provides the correlations between the effective site group and the line group, resulting in the line group symmetry species of the triflate anion given below.

$$\Gamma(\delta_s(CF_3)) = A' + A'' \tag{15}$$

$$\Gamma(\nu_{as}(SO_3)) = 2A' + 2A'' \tag{16}$$

3.2.3. Factor Group. In the compound $(PEO)NaCF_3SO_3$ all atoms occupy Wyckoff 4e sites, as in the case of the lithium triflate compound. Because both compounds crystallize in the C_{2h}^5 space group with the same number of triflate ions per unit cell on the same Wyckoff sites, the triflate anion vibrations in the sodium triflate compound are described by the same factor group irreducible representations as in the lithium compound, i.e., eqs 11 and 12.

4. Comparison with Experimental Data

The infrared and Raman spectra in the $\delta_s(CF_3)$ region have been previously given[24] and are summarized as an energy level diagram in Figure 4. In the infrared spectrum of $(PEO)_3LiCF_3SO_3$ there is a strong band at 761 cm^{-1} and a weak band at 766 cm^{-1}, while in the Raman spectrum there is only a strong band at 766 cm^{-1}. The analysis of the spectra in this region is greatly simplified because there are no interfering PEO bands present. These data can be discussed in terms of the predictions of a helical group analysis. Equation 8 states that for $(PEO)_3LiCF_3SO_3$ under the $C(2\pi/2)$ helical

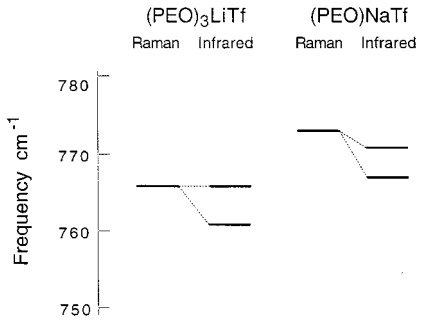

Figure 4. Vibrational modes in the infrared and Raman spectra of the $\delta_s(CF_3)$ region in $(PEO)_3LiCF_3SO_3$ summarized as an energy level diagram.

group there should be two $\delta_s(CF_3)$ modes, an A mode and a B mode. Both modes are formally predicted to be simultaneously infrared- and Raman-active. Because Raman scattering from modes belonging to the totally symmetric irreducible representation of the appropriate group is usually strong relative to other symmetry species present in the system, the band at 766 cm^{-1} is assigned as the A mode, which is strongly Raman-active and weakly infrared-active. Therefore, the mode at 761 cm^{-1} is the B mode whose Raman activity is assumed to be too weak to be observed.

An alternative interpretation of these data can be made in terms of a factor group analysis, which predicts four modes as described in eq 11. In this point of view, one of the Raman-active modes (presumably the A_g mode) and one of the infrared-active modes are coincident at 766 cm^{-1}. The 761 cm^{-1} band is due to the second infrared-active mode, and the remaining Raman-active mode (presumably B_g) is too weak to be observed in the spectrum.

In $(PEO)NaCF_3SO_3$ there is a strong and a weak band in the infrared spectrum at 767 and 771 cm^{-1}, respectively, and a strong mode in the Raman spectrum at 773 cm^{-1}. There is an experimental uncertainly of ±1 cm^{-1} in the frequency of the Raman-active mode, while the infrared-active mode at 771 cm^{-1} has an error of ±1.5 cm^{-1} derived from the curve-fitting procedure which yielded its frequency. Therefore, the two modes may well be coincident, and a line group analysis, which predicts only two modes in this region, is appropriate. In that case, again using the argument that modes belonging to the totally symmetric representation are usually strong Raman scatterers, the mode at 773 cm^{-1} is assigned as the A′ mode and the mode at 767 cm^{-1} is the A″ mode. In a factor group analysis, the strong Raman-active band at 773 cm^{-1} is assigned as the A_g mode, while the B_g mode is too weak to observe. The two infrared active bands are assigned to the A_u and B_u modes, but it is not possible to determine which mode belongs to which symmetry species.

The SO_3 symmetric stretching mode, $\nu_s(SO_3)$, can also be analyzed in the $(PEO)_3LiTf$ compound, although the analysis is somewhat complicated by the presence of bands originating in PEO vibrations. The infrared spectrum of $(PEO)_3LiTf$ has a strong band at 1044 cm^{-1} and a weak band at 1053 cm^{-1}. The infrared spectrum of pure PEO has a weak band at 1061 cm^{-1}, and the gradual disappearance of this band and the corresponding growth of the band at 1053 cm^{-1} in the compound suggests that the latter band is a PEO vibration in the compound. The fact that the 1053 cm^{-1} band is absent in the infrared spectrum of deuterium-substituted

$(PEO)_3LiTf$ strongly supports this view. Therefore, the strong band at 1044 cm^{-1} originates in the triflate ion and is assigned as a $\nu_s(SO_3)$ mode. The Raman spectrum of the compound also contains two bands: a strong band at 1051 cm^{-1} and a band of medium intensity at 1061 cm^{-1}. The observation of two Raman-active bands at 1072 and 1063 cm^{-1} in pure PEO suggests that the band at 1061 cm^{-1} in the compound is actually a PEO band. Therefore, only the 1051 cm^{-1} band is assigned to a $\nu_s(SO_3)$ mode in the compound.

An interpretation of the $\nu_s(SO_3)$ data in terms of a helical group analysis would argue that the infrared-active band at 1044 cm^{-1} is a B mode which is Raman-inactive, while the strongly scattering mode at 1051 cm^{-1} is the A mode which is infrared-inactive. Alternatively, a factor group analysis would assign the 1044 cm^{-1} band to either the A_u or B_u mode, and the Raman-active band to the A_g representation, based on its scattering intensity.

Unfortunately, it is not possible to perform a similar analysis of $\nu_s(SO_3)$ in the $(PEO)NaCF_3SO_3$ compound. The infrared spectrum in this region consists of a broad feature extending from about 1060 to 1030 cm^{-1}, with a second band at about 1020 cm^{-1}. The breadth of the first feature appears to originate in highly coupled vibrations of the triflate ion and precludes an unambiguous assignment of band frequencies in this region.

5. Conclusions

A symmetry-based vibrational analysis of the compounds $(PEO)_3LiCF_3SO_3$ and $(PEO)NaCF_3SO_3$ has been given that focuses on the intramolecular vibrational modes of the triflate anion. Using the experimental observation that these modes are highly decoupled from the vibrations of the PEO backbone, a formalism has been developed which preserves the identity of these modes in a one-dimensional space group analysis appropriate to a single chain running through the unit cell.

The infrared and Raman spectra in the $\delta_s(CF_3)$ spectral region of the compounds $(PEO)_3LiCF_3SO_3$ and $(PEO)NaCF_3SO_3$ are discussed in terms of a helical group analysis and a line group analysis, respectively. In both cases the correlations to a full factor group description are given. The strong Raman scattering intensity of one of the $\delta_s(CF_3)$ bands in each compound allows a mode assignment to the totally symmetric symmetry species of the appropriate group. The $\nu_s(SO_3)$ region of the $(PEO)_3LiTf$ compound is also discussed in terms of a helical group analysis and a factor group analysis. A one-dimensional space group is sufficient to describe the $\delta_s(CF_3)$ modes in both compounds and the $\nu_s(SO_3)$ modes in the lithium-containing compound. However, in other triflate ion spectral regions, significant dynamical coupling between the adjacent chains in the unit cell may result in a more complex vibrational multiplet which must be analyzed using the three-dimensional space group of the crystal.

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