

direct lithium atom-molecule complexes, of the type characterized here, which undergo subsequent reactions with other molecules.

**Acknowledgment.** We thank C. Trindle and M. Tranquille for helpful discussions and communication of preliminary results, M.

Hawkins for preliminary experiments, and the NSF for financial support.

**Registry No.** Li, 7439-93-2;  $^7\text{Li}$ , 13982-05-3;  $^6\text{Li}$ , 14258-72-1;  $\text{C}_2\text{H}_4$ , 74-85-1;  $^{13}\text{C}_2\text{H}_4$ , 51915-19-6;  $\text{C}_2\text{H}_2\text{D}_2$ , 6755-54-0;  $\text{C}_2\text{D}_4$ , 683-73-8.

## A Vibrational Study of Lithium Sulfate Based Fast Ionic Conducting Borate Glasses

E. I. Kamitsos,\* M. A. Karakassides, and G. D. Chryssikos†

Theoretical and Physical Chemistry Institute, The National Hellenic Research Foundation, Athens 116-35, Greece (Received: January 27, 1986)

The influence of the sulfate anion on the structure of the  $x\text{Li}_2\text{O} \cdot y\text{Li}_2\text{SO}_4 \cdot \text{B}_2\text{O}_3$  fast ionic conducting glasses has been studied by Raman and Fourier-transform infrared spectroscopies, for compositions probing the whole glass-forming region ( $x = 0.20, 0.56; y = 0-0.50$ ). Difference spectra are presented to elucidate the  $\text{SO}_4^{2-}$ -induced structural changes. Thus, for the  $x = 0.20$  series, combined Raman and infrared results showed that  $\text{Li}_2\text{SO}_4$  additions induce the formation of  $\text{BO}_4$  tetrahedra. However, for high lithium oxide content ternary glasses ( $x = 0.56$ ), while Raman spectra did not show obvious changes of the glass structure upon increasing  $y$ , infrared spectra clearly indicated that the numbers of  $\text{BO}_4$  tetrahedra and nonbridging oxygen-containing borate groups both increase. It was concluded that the presence of  $\text{SO}_4^{2-}$  anions, in the glass melt, favors the formation of borate groups, which are more polar than those of the corresponding binary glasses.

### Introduction

Studies of inorganic glasses with high ionic conductivity have attracted much interest due to their advantageous characteristics, for energy conversion and storage applications, over the crystalline conductive solids.<sup>1</sup>

Fast ionic conducting glasses (FIC) are usually presented by the formula  $x\text{M}_2\text{O} \cdot y\text{M}_n\text{X} \cdot \text{A}_p\text{O}_q$ , where  $\text{A}_p\text{O}_q$  is the glass former (i.e.,  $\text{SiO}_2$ ,  $\text{B}_2\text{O}_3$ , etc.), M is a metal, usually Li, Na, Ag, and  $\text{X}^n$  is an anion, usually halogen,  $\text{S}^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{MoO}_4^{2-}$ , etc. Although fast ion conduction in glasses is a general phenomenon, the mechanism of ion transport in glasses is not well understood, contrary to transport in crystalline solids. This is partly because no detailed knowledge is available about the local glass structure and the way this is affected by the anion,  $\text{X}^n$ . It is obvious that understanding the structural characteristics of such technologically important FIC glasses is critical not only in explaining the mechanism of ionic conduction but also in designing systems with improved characteristics appropriate for the current needs.

There are contradictory reports for the effect of  $\text{X}^n$  on the glass structure and, to an extent, on the mechanism of conduction. For instance, on the basis of Raman, infrared reflectance,<sup>2,3</sup> and  $^{11}\text{B}$  NMR<sup>4</sup> data, it was concluded that the only factor affecting  $N_4$ , the fraction of 4-coordinated boron atoms, in ternary  $x\text{Li}_2\text{O} \cdot y\text{LiCl} \cdot \text{B}_2\text{O}_3$  glasses, is the O/B ratio. However, Uhlmann and co-workers were able to conclude on the basis of density, conductivity, and glass transition temperature measurements that the halide indeed causes major network modifications.<sup>5-7</sup> These conclusions are supported in part by new Raman results based on careful control of the O/B ratio<sup>8</sup> and by NMR results as well.<sup>9</sup>

While halogens can either sit in an interstitial position and/or coordinate boron atoms, there are anions, like  $\text{SO}_4^{2-}$ , that can only occupy interstitial sites. A very interesting FIC glass system based on  $\text{SO}_4^{2-}$ , i.e.,  $x\text{Li}_2\text{O} \cdot y\text{Li}_2\text{SO}_4 \cdot \text{B}_2\text{O}_3$ , was reported by Levasseur and co-workers.<sup>3,10</sup> Very stable, easily prepared, high lithium content glasses were obtained in this system. The high lithium content of these glasses is an important feature, since binary  $x\text{Li}_2\text{O} \cdot \text{B}_2\text{O}_3$  glasses with lithium content up to ca.  $x = 1.8$  are very difficult to obtain, besides the fact that they are very hygroscopic.<sup>11</sup>

The effect of the  $\text{SO}_4^{2-}$  anion on the glass structure was studied by Raman spectroscopy in the systems  $0.71\text{Li}_2\text{O} \cdot y\text{Li}_2\text{SO}_4 \cdot \text{B}_2\text{O}_3$ .<sup>10</sup>

TABLE I: Compositions of Ternary  $x\text{Li}_2\text{O} \cdot y\text{Li}_2\text{SO}_4 \cdot \text{B}_2\text{O}_3$  Glasses Studied in This Work

	$x$	$y$		$x$	$y$
A	0.20	0	E	0.56	0
B	0.20	0.01	F	0.56	0.15
C	0.20	0.02	G	0.56	0.30
D	0.20	0.03	H	0.56	0.50

It was concluded that  $\text{SO}_4^{2-}$  anions are diluted in the glass network without any detectable interactions with it. These observations are very reasonable, since for such a large  $x$  value ( $x = 0.71$ ) the boron-oxygen network is greatly affected by  $\text{Li}_2\text{O}$ . Large interstices are created which can easily accommodate the  $\text{SO}_4^{2-}$  ions, without any important interactions, at least to a degree detectable by Raman spectroscopy. What remained to be investigated is whether the large and ionic  $\text{SO}_4^{2-}$  groups can induce changes to borate networks modified to a lesser extent by  $\text{Li}_2\text{O}$  and thus more compact. Besides Raman spectroscopy, such changes could effectively be probed by infrared spectroscopy, which, due to differences in selection rules, is known to be complementary to Raman, especially when  $N_4$  values are to be estimated.<sup>12</sup> Thus, we have studied by both infrared and Raman spectroscopy the system  $0.56\text{Li}_2\text{O} \cdot y\text{Li}_2\text{SO}_4 \cdot \text{B}_2\text{O}_3$  and compared the spectra. For

(1) For review articles in fast ionic conducting glasses, see: (a) Tuller, H. L.; Button, D. P.; Uhlmann, D. R. *J. Non-Cryst. Solids* **1980**, *40*, 93. (b) Tuller, H. L.; Barsoum, M. W. *J. Non-Cryst. Solids* **1985**, *73*, 331. (c) Ravaine, D. *J. Non-Cryst. Solids* **1985**, *73*, 287. (d) Minami, T. *J. Non-Cryst. Solids* **1985**, *73*, 273.

(2) Irion, M.; Couzi, M.; Levasseur, A.; Reau, J. M.; Brethous, J. C. *J. Solid State Chem.* **1980**, *31*, 285.

(3) Levasseur, A.; Brethous, J. C.; Reau, J. M.; Hagenmuller, P.; Couzi, M. *Solid State Ionics* **1980**, *1*, 177.

(4) Geissberger, A. E.; Bucholtz, F.; Bray, P. J. *J. Non-Cryst. Solids* **1982**, *49*, 117.

(5) Button, D. P.; Tandon, R. P.; Tuller, H. L.; Uhlmann, D. R. *J. Non-Cryst. Solids* **1980**, *42*, 297.

(6) Button, D. P.; Tandon, R. P.; Tuller, H. L.; Uhlmann, D. R. *Solid State Ionics* **1981**, *5*, 655.

(7) Button, D. P.; Tandon, R. P.; King, C.; Velez, M. H.; Tuller, H. L.; Uhlmann, D. R. *J. Non-Cryst. Solids* **1982**, *49*, 129.

(8) Turcotte, D. E.; Risen, Jr., W. M.; Kamitsos, E. I. *Solid State Commun.* **1984**, *51*, 313.

(9) Kline, D.; Bray, P. J. *Phys. Chem. Glasses* **1966**, *7*, 41.

(10) Levasseur, A.; Kbal, M.; Brethous, J. C.; Reau, J. M.; Hagenmuller, P.; Couzi, M. *Solid State Commun.* **1979**, *32*, 839.

(11) Martin, S. W.; Angell, C. A. *J. Non-Cryst. Solids* **1984**, *66*, 429.

(12) *Glass Structure by Spectroscopy*; Wong, J., Angell, C. A., Eds.; Marcel Dekker: New York, 1976.

\* On leave of absence from the Chemistry Department, Brown University, Providence, RI 02912.

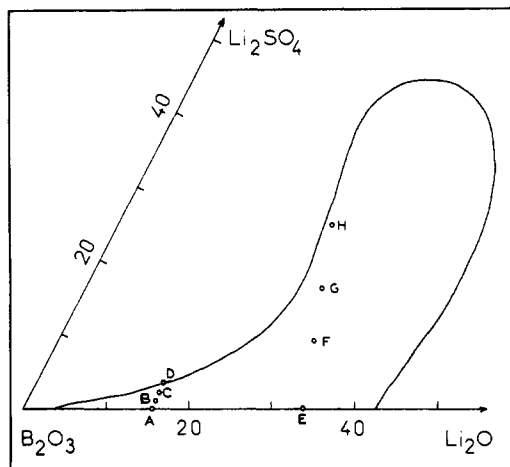


Figure 1. Glass formation region of the system  $x\text{Li}_2\text{O}-y\text{Li}_2\text{SO}_4-\text{B}_2\text{O}_3$ . The ternary glasses studied in this work are indicated; for exact compositions see Table I.

a better understanding of any possible effect of  $\text{SO}_4^{2-}$  ions on the glass structure, we have also studied by infrared (IR) and Raman spectroscopy a system with low  $\text{Li}_2\text{O}$  content, i.e.,  $0.20\text{Li}_2\text{O}-y\text{Li}_2\text{SO}_4-\text{B}_2\text{O}_3$ . In doing so the "effectiveness" of  $\text{SO}_4^{2-}$  could be examined with respect to the nature of its surroundings, that is, the nature of B-O network, which is surely different for the  $x = 0.20$  and  $x = 0.56$  glass systems.

### Experimental Section

Reagent grade powders of anhydrous  $\text{B}_2\text{O}_3$ ,  $\text{Li}_2\text{CO}_3$ , and  $\text{Li}_2\text{SO}_4$  were used in the preparation of the glasses. To ensure that the  $\text{Li}_2\text{O}/\text{B}_2\text{O}_3$  ratio is exactly the same in the ternary and the corresponding binary glasses, the following glass-making procedure was established. First, the binary glasses were prepared by thoroughly mixing the appropriate amounts of  $\text{Li}_2\text{CO}_3$  and  $\text{B}_2\text{O}_3$  and then melting in Pt crucibles until a clear, bubble-free melt was obtained. Melting temperatures in the range of  $900\text{--}950^\circ\text{C}$  and melting times of ca. 20 min were adequate to obtain clear, homogeneous glasses. The ternary glasses were then obtained by mixing the appropriate amounts of  $\text{Li}_2\text{SO}_4$  and the powdered form of the binary glass and then melting the mixture at  $950\text{--}1050^\circ\text{C}$  for 20 min. Clear glass fibers were drawn from the melt and used for Raman measurements without any further treatment. For infrared measurements glass fibers were grounded in a vibrating mill, and the glass powder was used for preparation of KBr pellets, containing about 2 wt % glass. The compositions of the ternary glasses that we prepared are shown in Table I and correspond to points A through H of the glass formation region presented in Figure 1.

Raman spectra were measured on a Ramanor HG2S Jobin-Yvon spectrometer. The  $514.5\text{-nm}$  line of a Spectra-Physics 165 argon ion laser operating at 500 mW was used for excitation. A  $90^\circ$  scattering geometry was employed, with the glass fiber oriented such that its cross section was perpendicular to the laser beam. The resolution of the Raman spectra was  $2\text{ cm}^{-1}$ . The infrared spectra were recorded on a Fourier-transform Bruker 113v vacuum spectrometer. Each spectrum is the result of a signal averaging of 100 scans at  $2\text{-cm}^{-1}$  resolution.

### Results and Discussion

**Raman Spectra.** Glassy  $\text{B}_2\text{O}_3$  consists of randomly oriented boroxol rings ( $\text{B}_3\text{O}_3$ ) interconnected by B-O-B bridges.<sup>13,19</sup> Its

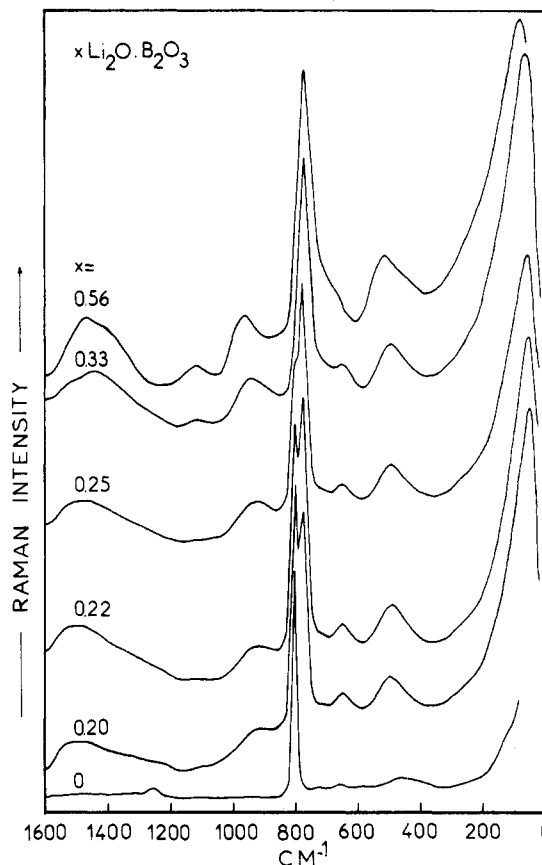


Figure 2. Raman spectra of the binary borate glasses:  $x\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ .

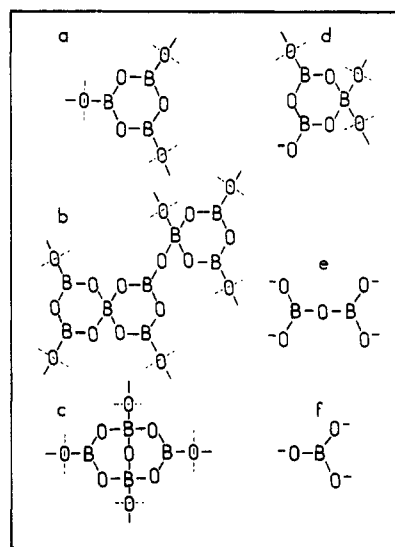


Figure 3. Polyborate groups postulated for borate glasses: (a) boroxol ring, (b) tetraborate, (c) diborate, (d) triborate with one NBO, (e) pyroborate, and (f) orthoborate. Note that O with a slash indicates a bridging oxygen and  $\text{O}^-$  indicates a nonbridging oxygen.<sup>19</sup>

Raman spectrum is dominated by a sharp and highly polarized peak at  $805\text{ cm}^{-1}$ , which is assigned to the boroxol ring-breathing vibration<sup>17</sup> and involves motion of the oxygen rather than the boron atoms.<sup>20</sup>

According to the pioneering work of Krogh-Moe<sup>16,22,23</sup> and Bray and O'Keefe,<sup>21</sup> substantial structural changes are induced to the

- (13) Strong, S. L.; Kaplow, R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1968**, *24*, 1032.
- (14) Mozzi, R. L.; Warren, B. E. *J. Appl. Crystallogr.* **1970**, *3*, 251.
- (15) Sinclair, R. N.; Desa, J. A.; Etherington, G.; Johnson, P. A.; Wright, A. C. *J. Non-Cryst. Solids* **1980**, *42*, 107.
- (16) Krogh-Moe, J. *Phys. Chem. Glasses* **1965**, *6*, 46.
- (17) Brill, T. W. *Philips Res. Rep., Suppl.* **1976**, No. 2.
- (18) Konijnendijk, W. L. *Philips Res. Rep., Suppl.* **1975**, No. 1.

- (19) Konijnendijk, W. L.; Stevels, J. M. *J. Non-Cryst. Solids* **1975**, *18*, 307.
- (20) Windisch, C. F.; Risen, Jr., W. M. *J. Non-Cryst. Solids* **1982**, *48*, 307.
- (21) Bray, P. J.; O'Keefe, G. *Phys. Chem. Glasses* **1963**, *4*, 37.
- (22) Krogh-Moe, J. *Phys. Chem. Glasses* **1960**, *1*, 26.
- (23) Krogh-Moe, J. *Phys. Chem. Glasses* **1962**, *3*, 101.

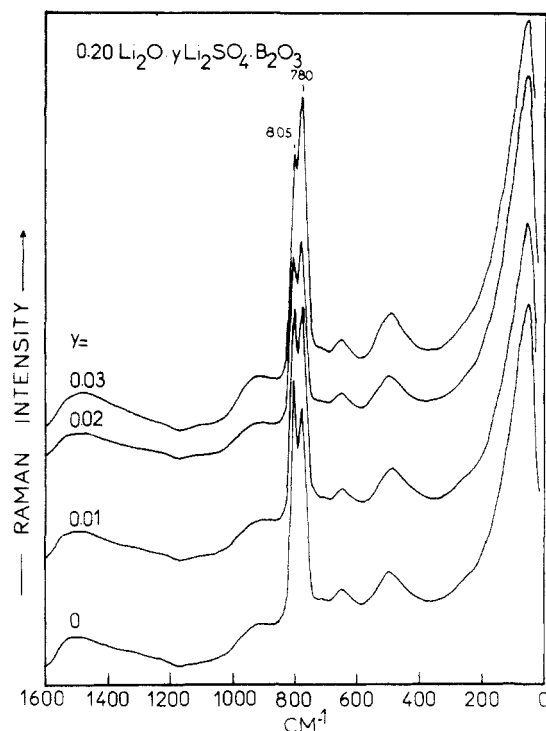


Figure 4. Raman spectra of the ternary glasses:  $0.20\text{Li}_2\text{O} \cdot y\text{Li}_2\text{SO}_4 \cdot \text{B}_2\text{O}_3$ .

$\text{B}_2\text{O}_3$  glass network upon addition of alkali metal oxide. Konijnendijk and Stevels demonstrated that Raman spectroscopy can effectively probe these changes.<sup>18,19</sup> Thus, for  $0 < x < 0.33$ , the  $805\text{-cm}^{-1}$  peak decreases in intensity and a new peak at ca.  $780\text{ cm}^{-1}$ , which is attributed to six-membered rings with one or more 4-coordinated boron atoms,<sup>17</sup> grows in intensity. The  $805\text{-cm}^{-1}$  peak disappears at  $x = 0.33$ , and subsequent additions of alkali metal oxide hardly shift the  $780\text{-cm}^{-1}$  band to lower frequencies. Figure 2 presents Raman spectra of several lithium borate glasses. It is very clear that, for  $0.20 < x < 0.25$ , the intensity ratio of the  $805\text{-}$  and  $780\text{-cm}^{-1}$  peaks is very sensitive to very small changes in modification. A variety of boron-oxygen units with smaller scattering cross section give rise to secondary features in the Raman spectra. Some of these groups, thought to be present in borate glasses, are shown in Figure 3, although combinations of various other groups can occur as well.<sup>14,24</sup>

It is clear that the  $\text{M}_2\text{O}/\text{B}_2\text{O}_3$  ratio is an important determinant of the borate glass structure, since both the relative number of 3- and 4-coordinated boron and the types of groups present in binary borates depend strongly on this ratio. For this reason we have kept the  $\text{Li}_2\text{O}/\text{B}_2\text{O}_3$  ratio fixed and changed the amount of  $\text{Li}_2\text{SO}_4$ , in order to detect its effect on the glass structure. Two ternary glass series were selected for this study, i.e.,  $0.20\text{Li}_2\text{O} \cdot y\text{Li}_2\text{SO}_4 \cdot \text{B}_2\text{O}_3$  and  $0.56\text{Li}_2\text{O} \cdot y\text{Li}_2\text{SO}_4 \cdot \text{B}_2\text{O}_3$ . The former system was selected for two reasons: first, because the corresponding binary glass contains tetraborate units, close to their maximum concentration, as well as boroxol and diborate groups, and second, because at least three ternary glasses could be prepared for a comparative study. Attempts to prepare ternary glasses with  $x < 0.20$  were limited to one ternary glass, because these compositions are close to the glass-forming boundaries (Figure 1). The  $x = 0.56$  system was selected because its corresponding binary glass contains both diborate groups, at the maximum concentration, as well as groups containing nonbridging oxygens NBO's.<sup>24</sup>

The Raman spectra of the  $0.20\text{Li}_2\text{O} \cdot y\text{Li}_2\text{SO}_4 \cdot \text{B}_2\text{O}_3$  ternary glasses are shown in Figure 4. The effect of  $\text{Li}_2\text{SO}_4$  addition is clearly manifested by a continuous change in the relative intensity of the  $780\text{-}$  and  $805\text{-cm}^{-1}$  peaks. Moreover, the very small additions of  $\text{Li}_2\text{SO}_4$  cause changes that are similar to those observed

in the spectra of binary glasses with the same total lithium content. No new peaks attributed to  $\text{SO}_4^{2-}$  are observed in the spectra of the ternary glasses, due of course to the very small concentration of  $\text{SO}_4^{2-}$ .

To ensure that the observed changes in the spectra of the ternary glasses are not artifacts originating from  $\text{B}_2\text{O}_3$  losses, due to the longer melting time of ternary glasses, we have devised the following experiment. Binary  $0.20\text{Li}_2\text{O} \cdot \text{B}_2\text{O}_3$  glass was prepared as described in the Experimental Section. Glass fibers were drawn at 20-, 40-, and 60-min melting time. The Raman spectra of these fibers were measured and compared. No obvious changes were detected, indicating that possible losses should not cause any significant deviation from the nominal compositions. Similar observations were recently reported by Kuppinger and Shelby.<sup>25</sup>

Next we examine the possible ways that  $\text{SO}_4^{2-}$  can influence the B-O network, as manifested by the Raman spectra. Direct participation of  $\text{SO}_4^{2-}$  in network formation is excluded, and thus  $\text{SO}_4^{2-}$  ions should sit in interstitial sites and affect the B-O network by their size and/or charge. The relative increase of the intensity of the  $780\text{-cm}^{-1}$  peak with  $y$  implies an increase of the number of boroxol rings with at least one  $\text{BO}_4$  tetrahedron. This could result from an increase of  $N_4$ , that is, an increase of the number of  $\text{BO}_4$  units relative to the number of  $\text{BO}_3$  units. However, if we assume that the  $\text{Li}_2\text{O}/\text{B}_2\text{O}_3$  ratio is the main determinant of the glass structure, something widely accepted for binary glasses, the  $N_4$  should be the same for the ternary and binary glasses. Under the assumption of invariant  $N_4$ , the effect of  $\text{Li}_2\text{SO}_4$  would be to cause a redistribution of polyborate units. Such a reorganization would tend to place a fixed number of  $\text{BO}_4$  tetrahedra among a greater number of boroxol rings, in ternary glasses. This implies a greater number of boroxol rings with  $\text{BO}_4$  units and thus an increase of the  $780\text{-cm}^{-1}$  band. Such a model is opposite to that proposed by Uhlmann and co-workers, in an effort to explain the variations in density and glass transition temperature, in lithium chloroborate FIC glasses.<sup>7</sup> Thus, starting with the assumption that  $N_4$  is independent of  $y$ , we can advance so far as to postulate that introduction of  $\text{SO}_4^{2-}$  causes a better "dispersion" of  $\text{BO}_4$  tetrahedra in the B-O network.

It is interesting to note that a similar effect can be observed in the Raman spectra of  $x\text{Li}_2\text{WO}_4 \cdot \text{B}_2\text{O}_3$  glasses, reported by Lavasseur and co-workers.<sup>26</sup> For  $x = 0.14$  it seems that additions of  $\text{Li}_2\text{WO}_4$  cause an increase of the  $780\text{-cm}^{-1}$  peak relative to that at  $806\text{ cm}^{-1}$ . The authors of this work focused mainly on the changes of the part of the spectrum due to  $\text{WO}_4^{2-}$  anions and did not discuss changes of the part of the spectrum which is due to B-O network.

We now turn our attention to the Raman spectra of the  $x = 0.56$  ternary series, shown in Figure 5. The spectra of polycrystalline  $\text{Li}_2\text{SO}_4$  and aqueous solution of  $\text{Li}_2\text{SO}_4$  (0.5 M) are also included for comparison. The spectra of the ternary glasses are essentially superpositions of the spectrum of the binary glass and that of the  $\text{SO}_4^{2-}$  anion. Specifically, the four Raman-active modes of the tetrahedral  $\text{SO}_4^{2-}$  anions are observed at  $1125\text{ cm}^{-1}$  ( $\nu_3$ ),  $1005\text{ cm}^{-1}$  ( $\nu_1$ ),  $635\text{ cm}^{-1}$  ( $\nu_4$ ), and  $460\text{ cm}^{-1}$  ( $\nu_2$ ). The  $\nu_3$ ,  $\nu_4$ , and  $\nu_2$  bands of  $\text{SO}_4^{2-}$  in glass are quite similar in bandshape with those of aqueous solution of  $\text{Li}_2\text{SO}_4$ ; i.e., they appear as envelopes of the corresponding bands of polycrystalline  $\text{Li}_2\text{SO}_4$ . This suggests that  $\text{Li}_2\text{SO}_4$  is completely diluted in the boron-oxygen network and no microcrystalline domains of  $\text{Li}_2\text{SO}_4$  are formed, for the compositions studied.

From early work on molten alkali metal sulfates it is known that the frequency of the  $\nu_1$  mode is sensitive to cation-sulfate interactions.<sup>27</sup> This mode appears at  $1005\text{ cm}^{-1}$  in the glass,  $1006\text{ cm}^{-1}$  in polycrystalline  $\text{Li}_2\text{SO}_4$ , and  $983\text{ cm}^{-1}$  in aqueous solutions, indicating that the  $\text{Li}^+ \cdots \text{SO}_4^{2-}$  interactions in glass and polycrystalline  $\text{Li}_2\text{SO}_4$  are comparable. We also note that the  $\nu_1$  mode has a bandwidth of  $30\text{ cm}^{-1}$  in glass and  $10\text{ cm}^{-1}$  in both poly-

(24) For a review article on the structure of borate glasses, see: Griscom, D. L. In *Borate Glass: Structure, Properties, Applications*; Pye, L. D., Frechette, V. D., Kreidl, N. K., Eds.; Plenum: New York, 1978.

(25) Kuppinger, C. M.; Shelby, J. E. *J. Am. Ceram. Soc.* **1985**, *68*, 463.

(26) Lavasseur, A.; Kbal, M.; Sanz, M.; Couzi, M. *J. Solid State Chem.* **1983**, *47*, 256.

(27) Walrafen, G. E. *J. Chem. Phys.* **1965**, *43*, 479.

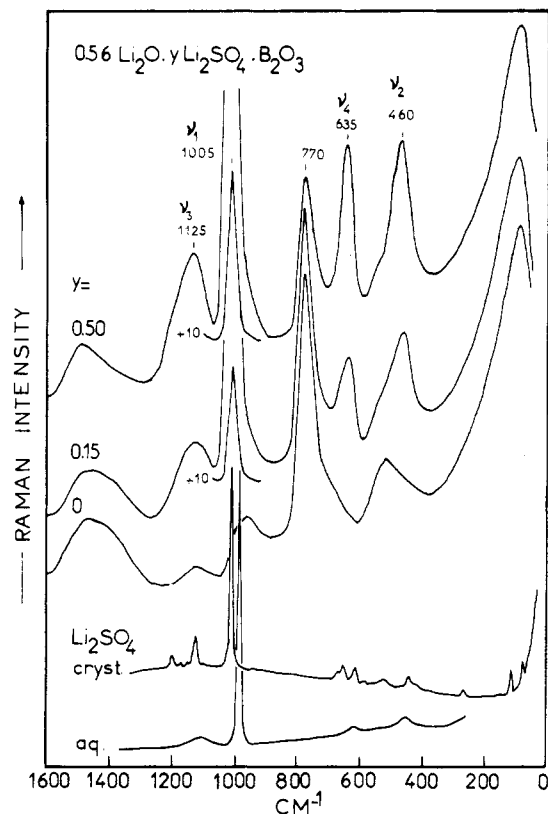


Figure 5. Raman spectra of the ternary glasses:  $0.56\text{Li}_2\text{O} \cdot y\text{Li}_2\text{SO}_4 \cdot \text{B}_2\text{O}_3$ .

crystalline  $\text{Li}_2\text{SO}_4$  and aqueous solution. This can be taken as an indication of a wider distribution of environments of  $\text{SO}_4^{2-}$  in the glass and/or a greater symmetry reduction.

The broad band structure that extends from 1300 to  $1600\text{ cm}^{-1}$ , and which is due to the B–O network, seems to be affected by  $\text{SO}_4^{2-}$  in the  $y = 0.50$  glass. Thus, there is an intensity enhancement for this composition, relative to the binary glass. The origin of this band can be attributed to B–O<sup>-</sup> bond stretching, which involves NBO's.<sup>19,28</sup>

Overall, the Raman study of the  $x = 0.56$  ternary glasses shows that  $\text{SO}_4^{2-}$  is completely diluted in the glass network and interacts weakly with it. These results are similar to those obtained for the  $x = 0.71$  series,<sup>10</sup> with the additional observation that for the  $y = 0.50$  glass an increase of the number of NBO's seems to be effected by  $\text{SO}_4^{2-}$ .

At this point we should note that Raman spectroscopy gives information about the relative number of borate groups containing  $\text{BO}_4$  units, which is true mostly for low  $x$  values, but gives no direct information on the absolute numbers of 3- and 4-coordinated boron atoms. This is because the  $\text{BO}_3$  units that are present in highly modified compositions are not necessarily part of the ring structures that scatter in the  $800\text{--}760\text{ cm}^{-1}$  region. However, infrared spectroscopy probes all  $\text{BO}_3$  units in the glass, regardless of their environment, under a single envelope between 1500 and  $1150\text{ cm}^{-1}$ . This envelope is clearly distinct from a second feature, in the  $1100\text{--}890\text{ cm}^{-1}$  region, that contours all the stretching modes of  $\text{BO}_4$  units. Thus, despite the fact that extinction coefficients of the various species are undetermined, the infrared spectra of the borate glasses are more valuable in showing a relative change of the number of tetrahedral boron units vs. that of triangular ones.<sup>29,30</sup>

**Infrared Spectra.** Infrared studies in borate glasses were originally advanced by Krogh-Moe and co-workers<sup>16,31</sup> by a sys-

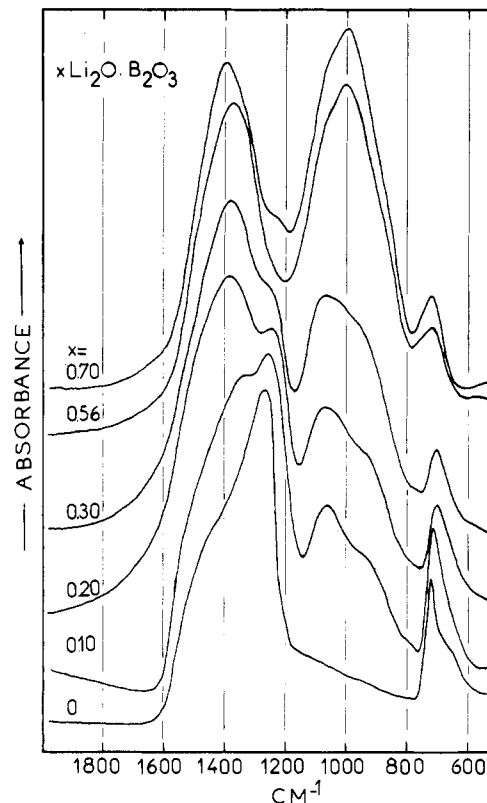


Figure 6. Infrared spectra of the binary borate glasses:  $x\text{Li}_2\text{O} \cdot \text{B}_2\text{O}_3$ .

tematic study and comparison of the spectra of crystalline borate compounds and the corresponding borate glasses. It was demonstrated that remarkable similarities exist between the two series of spectra, and this was taken to indicate the presence of the same type of borate groups in the glassy state and the corresponding crystals. Subsequently, the infrared spectra of borate glasses, including those modified by alkali metal oxides,<sup>18,32,33</sup> alkaline earth,<sup>18,34–36</sup> and various other oxides,<sup>29,30,37,38</sup> have been studied in an effort to elucidate the borate glass structure.

In infrared studies, like in Raman studies, it is useful to consider first the spectra of the binary glasses before studying those of the ternary systems. Thus, the spectra of  $x\text{Li}_2\text{O} \cdot \text{B}_2\text{O}_3$  glasses are shown in Figure 6, where the spectrum of  $\text{B}_2\text{O}_3$  glass is also included for comparison. Attempts to record the IR spectrum of  $\text{B}_2\text{O}_3$  by the KBr technique were not successful due to rapid hydrolysis, and so the spectrum of a thin blown film of  $\text{B}_2\text{O}_3$  was recorded. This spectrum is almost identical with that reported by Tenney and Wong<sup>39</sup> for a vapor-deposited  $\text{B}_2\text{O}_3$  film. The effect of  $\text{Li}_2\text{O}$  additions can be followed by the systematic changes shown in the IR spectra of the series. A new broad band structure in the  $850\text{--}1100\text{ cm}^{-1}$  region is growing in intensity upon increasing  $x$ . In addition, changes of relative intensities of bands at ca. 1250 and  $1380\text{ cm}^{-1}$  are observed. A detailed interpretation of the infrared spectra of borate glasses had not been accomplished yet, due to the complexity of the spectra originating from the glass nature of the materials. However, it is by now widely accepted that the broad band structure in the region  $1150\text{--}1500\text{ cm}^{-1}$  is attributed to the B–O bond stretching of  $\text{BO}_3$  units, while that in the region  $850\text{--}1100\text{ cm}^{-1}$ , appearing upon modification, is

(31) Kristiansen, L. A.; Krogh-Moe, J. *Phys. Chem. Glasses* **1968**, 9, 96.

(32) Borrelli, N. F.; McSwain, B. D.; Su, G.-J. *Phys. Chem. Glasses* **1963**, 4, 11.

(33) Selvaraj, U.; Rao, K. J. *Spectrochim. Acta, Part A* **1984**, 40A, 1081.

(34) Krogh-Moe, J. *Ark. Kemi* **1958**, 12, 475; **1958**, 14, 567.

(35) Quan, J. T.; Adams, C. E. *J. Phys. Chem.* **1966**, 70, 340.

(36) Hogarth, C. A.; Ahmed, M. M. *J. Mater. Sci. Lett.* **1983**, 2, 649.

(37) Boulou, E. N.; Kreidl, N. J. *J. Am. Ceram. Soc.* **1971**, 54, 368.

(38) Chrysikos, G. D.; Turcotte, D. E.; Mulkern, R. V.; Bray, P. J.; Risen, Jr., W. M. *J. Non-Cryst. Solids*, in press.

(39) Tenney, A. S.; Wong, J. J. *Chem. Phys.* **1972**, 56, 5516.

(28) White, W. B.; Brawer, S. A.; Furukawa, T.; McCarthy, G. J. In *Borate Glasses: Structures, Properties, Applications*; Pye, L. D., Frechette, V. D., Kreidl, N. J., Eds.; Plenum: New York, 1978.

(29) Minami, T.; Ikeda, Y.; Tanaka, M. *J. Non-Cryst. Solids* **1982**, 52, 159.

(30) Minami, T.; Shimizu, T.; Tanaka, M. *Solid State Ionics* **1983**, 9+10, 577.

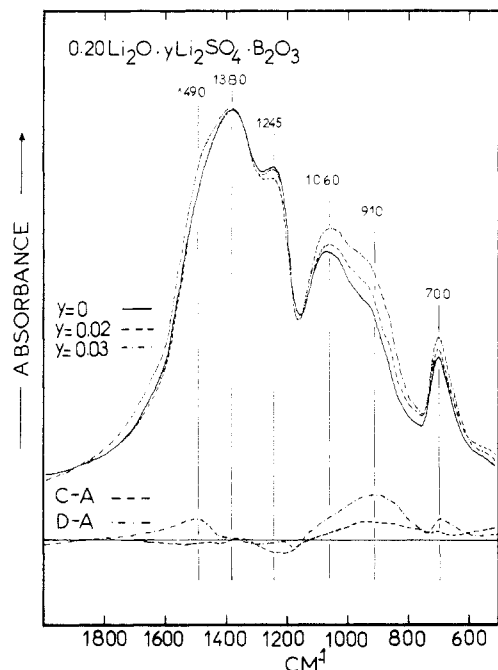


Figure 7. Infrared spectra of the ternary glasses:  $0.20\text{Li}_2\text{O} \cdot y\text{Li}_2\text{SO}_4 \cdot \text{B}_2\text{O}_3$ .

attributed to the B–O stretching of  $\text{BO}_4$  units. The band at ca.  $720\text{ cm}^{-1}$  is assigned to the bond-bending vibration of B–O–B linkages of the B–O network.<sup>16,18,29</sup> On the basis of the above assignments it is obvious that, upon increasing modification, the number of  $\text{BO}_4$  units is increased relative to that of  $\text{BO}_3$  units. Thus, infrared spectroscopy can probe the relative numbers of  $\text{BO}_4$  and  $\text{BO}_3$  units more directly than Raman does. In fact, the intensity ratio of the broad bands, characteristic of  $\text{BO}_4$  and  $\text{BO}_3$  units, has been utilized to indicate the extent of modification.<sup>29,30</sup>

In Figure 7 we have plotted the IR spectra of the  $x = 0.20$  binary and ternary glasses. To demonstrate clearly the differences caused by the very small additions of  $\text{Li}_2\text{SO}_4$ , the spectra have been scaled to give  $\text{BO}_3$  envelope bands of the same intensity. It is evident that a systematic increase of the intensity of the band attributed to  $\text{BO}_4$  is induced upon increasing  $y$ . The band at  $1245\text{ cm}^{-1}$  does not change in a systematic manner throughout the series, while that at  $700\text{ cm}^{-1}$  increases in intensity upon  $\text{Li}_2\text{SO}_4$  addition. Also, the  $y = 0.03$  glass shows an additional weak shoulder at ca.  $1450\text{ cm}^{-1}$ .

In order to speak in a more quantitative way about the changes of the numbers of  $\text{BO}_4$  and  $\text{BO}_3$  units, deduced from the IR spectra, it is useful to subtract the spectrum of the binary glass from that of the ternary glasses and to study the difference spectra. For spectral subtraction, subroutines provided by Bruker are utilized. Thus, the difference,  $D(\nu) = T(\nu) - [C_1 B(\nu) + C_2]$ , of the absorbance spectra  $T(\nu)$  of the ternary and  $B(\nu)$  of the binary glass is calculated by minimizing the sum of the squares  $D(\nu)^2$ , with respect to the variables  $C_1$  and  $C_2$ . The difference spectra calculated by this method are shown in Figure 7, designated by C–A and D–A, where A indicates the spectrum of the binary and C, D indicate those of the ternary glasses, with  $y = 0.02$  and  $y = 0.03$ , respectively. The broad band peaking at ca.  $910\text{ cm}^{-1}$  in the difference spectra shows clearly the formation of  $\text{BO}_4$  units, at the expense of  $\text{BO}_3$  units. Also, the increasing intensity at  $700\text{ cm}^{-1}$ , upon increasing  $y$ , indicates an increasing number of B–O–B bridges, which is a consequence of the formation of additional  $\text{BO}_4$  tetrahedra. The difference spectrum for  $y = 0.03$  shows another interesting feature at ca.  $1490\text{ cm}^{-1}$ , which appears shifted by more than  $100\text{ cm}^{-1}$  from the main  $\text{BO}_3$  peak at  $1380\text{ cm}^{-1}$ . The presence of a new peak in this region can be attributed to  $\text{BO}_3$  units containing NBO's.<sup>29,35</sup> An analogous peak at the same frequency region is identified in the Raman spectrum of this glass. Thus, the difference spectra indicate an increase of the number of  $\text{BO}_4$  units, upon addition of  $\text{Li}_2\text{SO}_4$ . Furthermore, for the  $y$

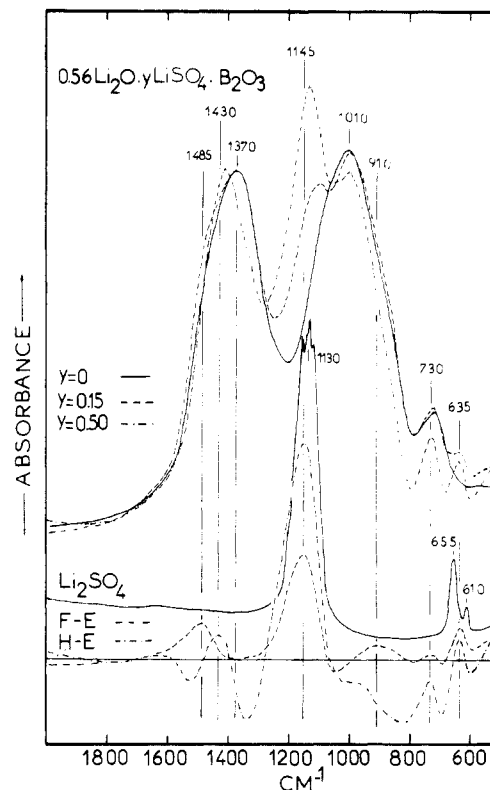


Figure 8. Infrared spectra of the ternary glasses:  $0.56\text{Li}_2\text{O} \cdot y\text{Li}_2\text{SO}_4 \cdot \text{B}_2\text{O}_3$ .

$= 0.03$  glass a conversion of some  $\text{BO}_3$  units into ones containing NBO's is observed as well.

The infrared spectra of the high lithium oxide content glasses ( $x = 0.56$ ), also properly scaled, are shown in Figure 8. If the  $\text{Li}_2\text{SO}_4$  content is increased, several effects are observed in the IR spectra. The main ones are the appearance of two new bands at  $1130$  and  $635\text{ cm}^{-1}$  and the shift of the  $\text{BO}_3$  band to  $1420\text{ cm}^{-1}$  for the  $y = 0.50$  glass. To better illustrate these effects, the difference spectra have also been calculated and plotted in Figure 8. For comparison, the IR spectrum of polycrystalline  $\text{Li}_2\text{SO}_4$  is also shown in Figure 8. This shows peaks at  $1130$ ,  $655$ , and  $610\text{ cm}^{-1}$ , which are assigned to the asymmetric  $\nu_3$  stretching ( $1130\text{ cm}^{-1}$ ) and to  $\nu_4$  bending ( $655$  and  $610\text{ cm}^{-1}$ ). This split of  $\nu_4$  has been observed in other sulfate salts as well.<sup>40,41</sup> The difference spectra show the  $\text{SO}_4^{2-}$  bands at  $1145\text{ cm}^{-1}$  ( $\nu_3$ ) and  $635\text{ cm}^{-1}$  ( $\nu_4$ ). The  $\nu_3$  in the glass is broader than that in  $\text{Li}_2\text{SO}_4$ , and both  $\nu_3$  and  $\nu_4$  appear as single bands, in agreement with the results obtained from the Raman study.

The difference spectrum for  $y = 0.15$  exhibits a considerable intensity at  $910\text{ cm}^{-1}$ , indicating the formation of  $\text{BO}_4$  units, and also a peak at  $1485\text{ cm}^{-1}$ , implying the formation of  $\text{BO}_3$  units with NBO. Thus, some  $\text{BO}_3$  units are converted into  $\text{BO}_4$  tetrahedra and  $\text{BO}_3$  units with nonbridging oxygen. The  $y = 0.50$  difference spectrum shows a negligible intensity in the  $\text{BO}_4$  region and a peak at  $1430\text{ cm}^{-1}$ , attributed to triangles with NBO's. It is evident that, for this glass, NBO's are formed at the expense of  $\text{BO}_3$  and  $\text{BO}_4$  units.

## Conclusions

The Raman and infrared spectra of binary lithium borate and ternary lithium borosulfate FIC glasses have been measured and analyzed. It was shown that unique conclusions cannot be drawn on the basis of the Raman spectra alone, at least for the  $x = 0.20$  series. This is due to the nature of the vibrations involved. Thus, for  $x = 0.20$  the Raman spectra indicate that the number of six-membered borate groups with  $\text{BO}_4$  tetrahedra increases with

(40) Hester, R. E.; Krishnan, K. *J. Chem. Phys.* **1968**, *49*, 4356.

(41) Schroeder, R. A.; Lippincott, E. P.; Weir, C. E. *J. Inorg. Nucl. Chem.* **1966**, *28*, 1397.

$\text{Li}_2\text{SO}_4$  additions. Infrared spectra showed that this is the result of a direct increase of the number of  $\text{BO}_4$  units, i.e.,  $N_4$  increases. Both infrared and Raman results for the  $x = 0.56$  series showed that  $\text{SO}_4^{2-}$  anions are completely dispersed in the boron-oxygen network, which is affected by their presence. This is manifested by an increase of  $\text{BO}_4$  units and NBO's for the  $y = 0.15$  glass and by an increase of NBO's mainly for the  $y = 0.50$  glass. The presence of  $\text{Li}_2\text{SO}_4$  in the melt seems to favor the formation of  $\text{BO}_4$  tetrahedra, in the  $x = 0.20$  series, and the formation of NBO's, in the  $x = 0.56$  series. Even though this may lead to the thought that the effect of  $\text{SO}_4^{2-}$  is different for the two series, the actual trend is the same. To understand this point, we may recall that the  $x = 0.20$  binary glass contains mostly boroxol rings and tetraborate groups. So,  $\text{SO}_4^{2-}$  anions cause the destruction of boroxol rings in favor of the more polar tetraborate groups. The

$x = 0.56$  binary glass contains mostly diborate groups and groups having NBO's. By analogy,  $\text{SO}_4^{2-}$  anions favor the formation of the latter, i.e., the more polar groups, at the expense of diborate groups. The trend appears to be the same; that is, the presence of  $\text{SO}_4^{2-}$  favors the formation of more polar borate groups than the ones found in the binary glasses.

**Acknowledgment.** Continuous and enthusiastic support of the work on FIC glasses by Professor C. A. Nicolaides, Director of the Institute of Theoretical and Physical Chemistry, is very gratefully acknowledged. G.D.C. expresses his thanks to Professor W. M. Risen, Jr., of Brown University and Professor C. A. Nicolaides for making his collaboration to this work possible.

**Registry No.**  $\text{Li}_2\text{SO}_4$ , 10377-48-7;  $\text{Li}_2\text{O}$ , 12057-24-8.

## Matrix Isolation Infrared Spectra of the 1:1 Molecular Complexes of Sulfur Trioxide with Selected Oxygen-Containing Bases

Craig S. Sass and Bruce S. Ault\*

Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221 (Received: February 3, 1986)

The 1:1 molecular complexes between  $\text{SO}_3$  and a series of oxygen-containing bases have been isolated and characterized in nitrogen matrices. The spectra of the complexes all showed a red shift and splitting of the antisymmetric stretching mode of the  $\text{SO}_3$  subunit in the complex, typified by product bands at 1362 and 1378  $\text{cm}^{-1}$  in the complex with dimethyl ether. A number of perturbed vibrational modes of the base subunit were observed as well, and generally arose from vibrations involving motion of the oxygen atom of the base. A comparison of the shift of the perturbed base modes in these complexes with previously studied complexes indicated that  $\text{SO}_3$  is a very strong Lewis acid, although only small shifts were observed for the  $\text{SO}_3$  subunit, and the symmetric stretching mode was not activated to a detectable degree.

### Introduction

The development of new techniques in recent years has increased interest in the study of molecular complexes, involving both Lewis and Brønsted acids.<sup>1-3</sup> Complexes involving strong Lewis acids such as  $\text{BF}_3$  have been known for years,<sup>4-6</sup> and much of the current attention has been focused on relatively weakly bound complexes. Sulfur trioxide,  $\text{SO}_3$ , is both a strong Lewis acid and a potent oxidizing agent and is known to form a few stable room temperature complexes with strong Lewis bases such as  $(\text{CH}_3)_3\text{N}$ .<sup>7-9</sup> More often, however, reaction with  $\text{SO}_3$  is sufficiently rapidly that possible intermediate complexes are not observed. The reaction of  $\text{SO}_3$  with  $\text{H}_2\text{O}$  has been of particular interest as it is one step in the formation of acid rain. Castelman has shown<sup>10</sup> that this reaction proceeds through a 1:1 complex in the gas phase, prior to conversion to  $\text{H}_2\text{SO}_4$ . This complex has also been observed in cryogenic matrices.<sup>11,12</sup> Workers have reported the formation of a highly reactive species during the reaction of formaldehyde with  $\text{SO}_3$ , which they postulated might be due to a 1:1 complex.<sup>13</sup>

Matrix isolation<sup>14-17</sup> has been a very effective approach to the study of highly reactive chemical species, including Lewis acid-base complexes. Recently, the study of a series of 1:1 complexes of  $\text{SO}_3$  with amine bases isolated in nitrogen matrices was reported,<sup>18</sup> marking the first observation of a number of these species in a nonperturbing environment. With the continuing interest in the chemistry of  $\text{SO}_3$  and the current lack of knowledge about the interaction of  $\text{SO}_3$  with weak bases, a study was undertaken to characterize the complexes of sulfur trioxide with oxygen bases in inert matrices.

### Experimental Section

All of the experiments in this study were conducted on a conventional matrix isolation system which has been described previously,<sup>19</sup> including modifications for the handling of  $\text{SO}_3$ .<sup>18</sup> Briefly, solid  $\text{SO}_3$  was placed in an all glass/Teflon vacuum system, and the vapor mixed with  $\text{N}_2$  to a ratio of approximately 1000/1. This sample was then deposited onto the 14 K cold window through a Teflon needle valve.

The oxygen bases employed in this study were dimethyl ether (Matheson), dimethyl- $d_6$  ether (ICON), methanol (M. J. Daley),

(1) Bowden, K. H.; Leopold, K. R.; Chance, K. V.; Klemperer, W. J. *Chem. Phys.* **1980**, *73*, 137.

(2) Leopold, K. L.; Bowen, K. R.; Klemperer, W. J. *Chem. Phys.* **1980**, *74*, 7211.

(3) Jensen, W. G. *The Lewis Acid Base Concepts, an Overview*; Wiley-Interscience: New York, 1980.

(4) Swanson, B.; Shriver, D. F. *Inorg. Chem.* **1979**, *9*, 1406.

(5) Amster, R. L.; Taylor, R. C. *Spectrochim. Acta* **1964**, *20*, 1487.

(6) Grundes, J.; Christian, S. D. *J. Am. Chem. Soc.* **1968**, *90*, 2239.

(7) Watari, F. Z. *Anorg. Allg. Chem.* **1964**, *322*, 322.

(8) Kanda, F. A.; King, A. J. *J. Am. Chem. Soc.* **1951**, *73*, 2315.

(9) Sass, R. L. *Acta Crystallogr.* **1960**, *13*, 320.

(10) Holland, P. M.; Castelman, A. W. *Chem. Phys. Lett.* **1978**, *56*, 511.

(11) Tso, T.; Lee, E. K. C. *J. Phys. Chem.* **1984**, *88*, 2776.

(12) Bondybey, V. E.; Nglish, J. H. *J. Mol. Spectrosc.* **1985**, *107*, 221.

(13) Nooi, J. R.; Martens, R. J.; Kemper, H. C. *Rec. Trav. Chim. Pays-Bas* **1972**, *91*, 367.

(14) Craddock, S.; Hinchcliffe, A. J. *Matrix Isolation*; Cambridge University: New York, 1975.

(15) Andrews, L. *Annu. Rev. Phys. Chem.* **1971**, *22*, 109.

(16) Ault, B. S. *Acc. Chem. Res.* **1982**, *15*, 103.

(17) Barnes, A. J. In *Molecular Interactions*; Ratajczak, H., Orville-Thomas, W. J., Eds.; Wiley: New York, 1980.

(18) Sass, C. S.; Ault, B. S. *J. Phys. Chem.* **1986**, *90*, 1547.

(19) Ault, B. S. *J. Am. Chem. Soc.* **1978**, *100*, 2426.