# Preliminary Note

## The effect of temperature on the concentration of ionic species in liquid bromine trifluoride*

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The electrical conductivity of liquid $BrF_3$ decreases with increasing temperature, in contrast to the behavior of virtually all other ionic liquids [1–3]. This unusual effect could be explained if the concentrations of the ions in solution decreased with an increase in temperature, possibly through the simultaneous presence of an alternative equilibrium.

This note describes the determination of the concentrations of the solvo-cation and solvo-anion in pure $BrF_3$ as a function of temperature. An attempt has also been made to determine the concentration of monomer in liquid bromine trifluoride.

Raman measurements were made on samples of bromine trifluoride in Kel-F tubing between 30° and 61°. Assignments of bands have been based upon chemical and spectral considerations [4]. Table 1 lists the vibrational assignments

TABLE 1

RAMAN SPECTRUM OF LIQUID BROMINE TRIFLUORIDE

| Band location (cm$^{-1}$) | Assignment | Change in intensity with increasing temperature | Change in intensity with addition of acid | Change in intensity with addition of base |
|---|---|---|---|---|
| 673 | $\nu_1(a_1)$ $BrF_3$ | inc.* | | |
| 625 | $\nu_1(a_1)$ $BrF_2^+$ | dec.* | inc. | dec. |
| 581 | Polymer | dec. | dec. | dec. |
| 531 | $\nu_2(a_1)$ $BrF_3$ | inc. | | |
| 528 | $\nu_1(a_{1g})$ $BrF_4^-$ | dec. | dec. | inc. |
| 490 | Possible dimer | inc. | dec. | dec. |
| 455 | $\nu_5(b_{2g})$ $BrF_4^-$ | dec. | dec. | inc. |
| 428 | Polymer | dec. | dec. | dec. |
| 341 | $\nu_5(b_1)$ $BrF_3$ | inc. | | |
| 265 | $\nu_6(b_2)$ $BrF_3$ | | | |
| 249 | $\nu_3(b_{1g})$ $BrF_4^-$ | | dec. | inc. |
| 236 | $\nu_3(a_1)$ $BrF_3$ | | | |

* inc. = increased; dec. = decreased.

together with the direction of change noted for the integrated area of each band as the temperature increased. Also included is a comparison of the change in band area in relation to the addition of either an acid, such as antimony pentafluoride, or a base, such as potassium fluoride.

Since the concentration of $BrF_2^+$ equals that of $BrF_4^-$ and since the band in which changes were most easily noted is due to the $\nu_1$ vibration of the $BrF_4^-$ anion, the change in the integrated area under this band was followed with change in temperature in order to calculate the concentration of the ions at each temperature. The concentrations of $BrF_2^+$ and $BrF_4^-$ in pure liquid $BrF_3$ have previously been determined[5] to be $0.9 \pm 0.1$ mol $l^{-1}$. The concentrations of the ions at different temperatures are listed in Table 2. From this table, it may seen that the concentrations of the ions progressively decrease as the temperature increases although little can be said about the concentration of the polymers. The integrated intensity of the bands at 581 and 428 cm$^{-1}$ obviously decreases, although the integrated intensity of the band at 490 cm$^{-1}$ seems to increase with increasing temperature. This observation agrees with that of Selig[6]. An explanation has been offered[2] which states that increasing the temperature favors the formation of a $BrF_3$ dimer, or a lower polymer, at the expense of the higher polymers.

TABLE 2

CONCENTRATION OF IONIC SPECIES IN LIQUID $BrF_3$ AT DIFFERENT TEMPERATURES

| Temperature (°C) | Species | Concentration (mol l$^{-1}$) |
|---|---|---|
| 30 | $BrF_4^-$ | $0.90 \pm 0.1$ |
| 45 | $BrF_4^-$ | $0.84 \pm 0.1$ |
| 51 | $BrF_4^-$ | $0.82 \pm 0.1$ |
| 62 | $BrF_4^-$ | $0.74 \pm 0.1$ |

The concentration of the monomer is more difficult to assess. The integrated area of the band at 673 cm$^{-1}$ increases as the temperature increases. This well-defined band was attributed to the $\nu_1$ vibration in the monomer in careful studies of the vapor spectrum[7]. However, Frey et al.[8] have noted in low-temperature matrix-isolation studies that a band which grows with increasing concentration of $BrF_3$ in the matrix and attributed by them to a dimer is found very close to the monomer peak. For this reason, it is not possible to state unequivocally that the monomer concentration increases with the temperature for the increase in the integrated area of the 673 cm$^{-1}$ band may instead be due to increasing dimer concentration with increasing temperature.

As part of our effort to obtain an idea of the concentration of the $BrF_3$ monomer in liquid $BrF_3$, we dissolved $BrF_3$ in Freon 113 with the view to comparing the integrated intensities of $BrF_3$ bands in Freon 113 with those in pure $BrF_3$.

Bromine trifluoride is soluble in 1,1,2-trichlorotrifluoroethane to an extent somewhat greater than 0.5 mol l$^{-1}$ at room temperature. The spectrum of a 0.50 mol l$^{-1}$ solution of BrF$_3$ in 1,1,2-trichlorotrifluoroethane is shown in Figure 1. The only band observed not attributable to the solvent is that at 673 cm$^{-1}$ which is the $\nu_1$ vibration of the BrF$_3$ monomer. A Raman spectrum of this particular solution was taken 3 weeks after the initial preparation of the solution. No changes in the spectrum were noted. Thus, 1,1,2-trichlorotrifluoroethane does not appear to be reactive towards BrF$_3$. A 0.48 mol l$^{-1}$ solution of BrF$_3$ in trichlorotrifluoro-ethane had a conductivity of 4.8 $\times$ 10$^{-11}$ $\Omega^{-1}$ cm$^{-1}$ in comparison to a conductivity of 4.4 $\times$ 10$^{-11}$ $\Omega^{-1}$ cm$^{-1}$ for the pure solvent thus indicating that ionization of BrF$_3$ in this solvent is negligible. No bands were found in the Raman spectrum of this solution which corresponded to those attributed to a dimer or a higher polymer in either the vapor or pure liquid spectra. It should be noted that there is no Raman intensity near 490 cm$^{-1}$ in that portion of the spectrum where bands attributable to the dimer would be anticipated. Frey et al.[8] have located a band at 480 cm$^{-1}$ in the solid. This band is probably due to the Br–F–Br stretching vibration of the dimer which we have observed both in the infrared and Raman spectra of liquid BrF$_3$. Unfortunately, we were unable to determine unequivocally whether any portion of the integrated area of the band at 673 cm$^{-1}$ is due to the dimer or whether it is all due to the monomer. For this reason, we were unable to establish that the intensity of the 673 cm$^{-1}$ band may be used as a reliable indicator of the concentration of the monomer in liquid BrF$_3$.



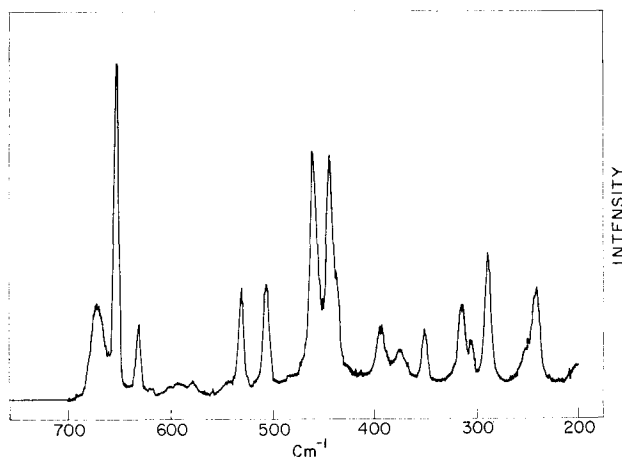Fig. 1. Raman spectrum of a 0.50 mol l$^{-1}$ solution of BrF$_3$ in 1,1,2-trichlorotrifluoroethane.

*Experimental*

Raman spectra were obtained using the 5145 Å exciting line from a Carson argon-ion laser. The apparatus included a Spex spectrometer which has been described elsewhere[9]. Measurements were made on solutions contained in pieces

of sealed, thin-walled Kel-F tubing which were filled on a vacuum line. The resulting spectra were analyzed with the aid of a DuPont Model 310 curve resolver.

Conductivity data were obtained on a Wayne Kerr Autobalance Precision Bridge B331. The conductivity cells used in the experiment have been described previously[2].

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