Cation Vibrations in Solvent Cages, Co-ordination Compounds, Glasses, Crystals, and Related Systems

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Summary Lithium and magnesium ions in solvent cages, co-ordination compounds, glasses, and crystalline salts exhibit bands around 400 cm^{-1} characteristic of the cation–oxygen polyhedra; similar bands are also found with nitrogen-donors.

ALKALI-METAL salts dissolved in oxygen-donor solvents like ethers, ketones, and amides exhibit broad low-frequency i.r. absorption bands characteristic of alkali-metal ions.[1–3] For lithium salts, this band appears around 400 cm^{-1}. This band is essentially independent of anion and solvent in polar solvents, and the solvation number is four.[2,4] Edgell and his co-workers[1] have observed that the vibrations of alkali-metal ions responsible for these solvent-cage bands are somewhat analogous to lattice modes in crystals. We show here that the alkali-metal cation–solvent cage bands as well as similar bands in alkali metal oxide glasses indeed arise from vibrations of specific cation–oxygen co-ordination polyhedra similar to those found in the spectra of crystalline oxyanion salts by Tarte.[5,6] We have extended these studies to the vibration of Mg^{2+} in oxygen polyhedra present in different systems and also to cation vibrations in nitrogen-donor solvents.

Solid 1 : 4 co-ordination compounds of Li^+ with various amides show a sharp band around 400 cm^{-1} due to vibration involving the Li^+ ion.[7] Lithium borate glasses of various compositions give broad bands in the 350—500 cm^{-1} region due to Li^+ vibration and the corresponding crystalline phases show two or three sharp bands in this region.† The region of absorption due to Li^+ vibration in these different systems closely corresponds to the characteristic region of absorption (400—500 cm^{-1}) of LiO_4 tetrahedra reported by Tarte[5,6] for oxyanion salts of lithium. Bands in this region have been recently reported for the asymmetric stretching vibration of the Li_2O_6 unit in $LiMeCO_2$,-$2H_2O$ where again each lithium is surrounded by four oxygens.[9] We conclude, therefore, that the absorption band around 400 cm^{-1} in solutions, co-ordination compounds, glasses, and other systems[10] is due to the stretching vibration of the LiO_4 polyhedron.‡ The corresponding bands around 200, 160, and 108 cm^{-1} due to vibrations of Na^+, K^+, and Cs^+ found in oxygen-donor solvents,[12] oxide glasses,[11] and crown-ether complexes[12] are also likely to be characteristic of such cation–oxygen polyhedra. The bands in solutions and glasses are generally broad possibly because they are composite bands arising from the presence of different polyhedra with a variety of cation–oxygen distances.

CNDO/2 MO calculations on 1 : 1, 1 : 2, and 1 : 4 complexes of Li^+ with ethers, ketones, and amides show that the interaction is uniformly strong in all these systems with nearly the same $Li \cdots O$ distance (*ca.* 2·3 Å) and stretching force constant. Based on these calculations, we predict an LiO_4 asymmetric stretching vibration around 500 cm^{-1}. These calculations also predict the expected changes in bond distances in the donor molecules consistent with the observed changes in n.m.r. and i.r. spectra.[7] Thus, interaction with Li^+ increases the $C{=}O$ distance in carbonyl compounds and hence lowers the $C{=}O$ stretching frequency.§

We have also studied the i.r. spectra of solutions of magnesium salts in several amide solvents as well as solid 1 : 6 co-ordination complexes of Mg^{2+} with amides. In all these systems, and in magnesium borate glasses, we have found a band around 400 cm^{-1}. Similar bands are also reported in hexa-aquo-complexes of magnesium.[14] We feel that the 400 cm^{-1} band is characteristic of the MgO_6 octahedron since bands in this region are found in silicates and germanates where the presence of MgO_6 octahedron is definitely known.[5] Based on these studies, it appears likely that the bands around 260 and 145 cm^{-1} in calcium and barium oxide glasses[11] are also characteristic of the corresponding cation–oxygen polyhedra.

We have examined the presence of characteristic cation vibration bands in nitrogen-donor media. CNDO/2 calculations show that the interaction of Li^+ with N-donors like pyridine and MeCN is comparable to that with oxygen donors. We have found a band around 400 cm^{-1} in solutions of lithium salts in MeCN; this band has already been reported in pyridine.[1,15] Mg^{2+} in pyridine also gives a band in this region. In the case of MeCN, the $C{\equiv}N$ stretching frequency increases owing to interaction with Li^+, consistent with theoretical predictions; a similar increase of $\nu(C{\equiv}N)$ is found in interactions with hydroxylic solvents or Lewis acids.[16]

The remarkable constancy of the low-frequency bands characteristic of quantised vibrations of cations in different systems indicates their usefulness as probes in the study of co-ordination of cations in solutions, glasses, crystals, and other systems and also of ion–solvent interactions. It is interesting that the only requirement to observe these bands is the short-range order of the first co-ordination sphere.

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† B_2O_3 has no absorption bands below 500 cm^{-1}.[8]

‡ LiO_6 octahedra[5] are known to show bands below 300 cm^{-1}.

§ In some respects, interaction of Li^+ with oxygen donors is comparable to protonation.[13]

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