

## Chapter I

### INTRODUCTION



Many new experimental techniques have been developed recently for the investigation of the vibrational properties of crystals. These methods are: infra-red spectroscopy, Raman spectroscopy, edge emission and absorption, and electron tunnelling effect.

In crystalline state, pronounced differences from the isolated molecular spectrum can occur, not only in the frequency shift but also in their splitting into a number of components and in the appearance of new absorption. These features are not satisfactorily interpreted by point group theory. Two approaches, site group approximation(1) and factor group approximation(2) have been advanced to account for these phenomena. Then it is possible to distinguish several types of effects that lead to a multiplet structure.

#### Factor Group Splitting(or the Correlation Field Splitting)

A nondegenerate vibration in an isolated species may exhibit a multiplet structure in a multiply occupied unit cell of a crystal due to correlation field effects which result from the correlation (or coupling) between the vibrational motions of each molecular species in a unit cell through intermolecular forces.

#### Site Group Splitting

A potential energy environment of lowered symmetry in a crystal may lift the degeneracy of a degenerate mode of an isolated species and lead to a multiplet structure.

It is possible to study these two types of splitting individually. Factor group splitting can be eliminated from the spectra by studying molecules in matrix isolation(3), isotopic solid solutions(4) and in dilute solid solutions with isomorphous molecules(5). These techniques eliminate correlation field effects which may dominate and complicate the spectra so the spectral bands become simplified and sharpened. Therefore, they reflect more directly the nature of the site group effects. The resultant splitting of spectra is site group splitting.

The crystalline alkali halides have been employed as host matrices for the study of vibrational energy levels of molecular ions(6,7). They are favorite host matrices because of the infrared transparency and because the character of the sites occupied by the impurity ions in these host matrices is readily known. Glassy alkali halides, glassy and crystalline alkali oxyanion(8) are also used as matrices.

In crystals containing polyatomic molecular units, the optical modes consist of internal modes and external modes. There is a wide energy gap between the internal and external modes. The external modes fall in low frequencies which are determined by intermolecular van der Waals or ionic forces. The internal modes fall in high frequencies because of the intramolecular covalent forces.

There have been numerous vibrational studies of  $AB_xC_{1-x}$  mixed crystal systems in which ions B and C are randomly distributed on a sublattice (9,10). For the most part of these studies the ions are monatomic, and the vibrational modes are external optical modes, but the very few involve systems in which B and C are molecular ions (11-14). In these systems, molecular ions give rise to the internal

optical modes. When they have a multiply occupied unit cell, the internal modes exhibit a rich vibrational multiplet structure through factor group correlations. In the very dilute samples, the guest ion may be matrix isolated and therefore vibrationally decoupled and sensitive only to site group effects.

Vibrational spectra in different state of potassium chromate and potassium sulphate have been reported; in solution(15,16), in crystal(17-21) and in inert gas matrix-isolation(22,23).

The tetrahedral chromate ion has 4 normal modes of vibration:  $\nu_1$  Raman active  $847\text{ cm}^{-1}$ ,  $\nu_2$  Raman active  $348\text{ cm}^{-1}$ ,  $\nu_3$  and  $\nu_4$  both Raman and infra-red active  $884, 368\text{ cm}^{-1}$ , respectively.

The tetrahedral sulphate ion also has 4 normal modes of vibration:  $\nu_1$  Raman active  $983\text{ cm}^{-1}$ ,  $\nu_2$  Raman active  $450\text{ cm}^{-1}$ ,  $\nu_3$  and  $\nu_4$  both Raman and infra-red active  $1105, 611\text{ cm}^{-1}$ , respectively.

For crystal spectra of potassium chromate and potassium sulphate, the complications arise due to crystal effects. The single bands ( $\nu_3, \nu_4$ ) which are degenerate in the free ions are replaced by multiplets. Bands due to  $\nu_1$  and  $\nu_2$  which are infra-red inactive in the free ions happen to appear in the crystal spectra. Some very low frequency bands appear below  $200\text{ cm}^{-1}$  in the Raman spectra. These features of the crystal spectra result from the existence of a different symmetry environment within the crystal and the presence of significant intermolecular forces in the crystal.

In this work vibrational modes of the mixed crystal system potassium chromate/ potassium sulphate are studied. Potassium chromate and potassium sulphate are isomorphous and they form a continuous range of mixed crystals. Their internal vibrational modes fall in different frequency regions. These two characters mean that a study of the infra-red and Raman spectra of polycrystalline samples with a variety of compositions should enable a distinction between site and factor group effects. In the low concentration of potassium chromate in potassium sulphate host or the low concentration of potassium sulphate in potassium chromate host, each vibrational unit of the low concentration component will be vibrationally uncoupled and sensitive only to site group effects.

In summary, this work is intended to:

1. Prepare potassium chromate/ potassium sulphate mixed crystals
2. Compare infra-red, Raman spectra of mixed crystals with their mixtures.
3. Determine the unit cell parameters and composition of mixed crystals.
4. Apply the site group approximation and the factor group approximation for interpreting the spectral phenomena.