

DESCRIPTION OF MOLECULAR DISTORTIONS
II. INTENSITIES OF THE SYMMETRIC STRETCHING BANDS
OF TETRAHEDRAL MOLECULES

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The symmetry of many molecules in the solid state is lower than that of the free molecule (or in case of ions - of the "free" ion). As a consequence, the selection rules for IR absorption are relaxed and transitions which are forbidden for the free molecule become allowed. Whether the corresponding band would be strong, medium or weak, will depend on the degree of the molecular distortion. In an attempt to describe the distortions of "tetrahedral" molecules in a more rigorous way than this is usually done, a quantity called distortion vector (S) is defined.

A qualitative agreement between the magnitude of S and the intensity of the symmetric stretching band was found for a number of crystalline compounds containing sulfate ions. In cases where both the intensity of the bands has been quantitatively determined and the crystal structure is known, the calculated values of S are fairly well correlated to the measured IR intensities, the correlation coefficient for a function of the $Y = b \cdot X^2$ type being $r = 0.81$.

INTRODUCTION

It is well known that very often the molecular symmetry is lowered on going from gas to solid and the molecule is said to be "distorted" in the crystal. Several approaches have so far been applied in order to describe these distortions in a most appropriate way. Baur [1], in his study of phosphates, introduced the distortion indices as measures for the departures of the P-O and O-O distances and O-P-O angles from their values in an "ideal" tetrahedron. In describing the coordination around metal atoms, Dollase [2] used quantities called absolute and relative distortion of a given polyhedron with respect to an idealized least squares, best-fit polyhedron of the same kind. Murray-Rust et al. [3-5] used symmetry coordinates to define displacement vectors which transform as the irreducible representations of the molecular point group. However, the results obtained by any of these methods could not be easily related to the results derived from spectroscopic measurements e.g. the removal of degeneracies, the non-zero intensity for "forbidden" transitions etc.

In a previous paper [6] we showed that tensors can be successfully applied in describing molecular distortions. Although a

strong correlation was found between the main components of the tensor of distortion and the frequencies (IR or Raman) of the components of the antisymmetric stretching vibration for a series of sulfate compounds, this method [6] could not tell anything about the band intensities.

In this work we present a method (based on simple geometrical arguments) which could be used to estimate the IR band intensities of the symmetric stretching vibrations in tetrahedral ions in crystals (in our case - sulfates) with known structure.

THE METHOD

The idealized "free" sulfate ion has a tetrahedral structure with $R(S-O) = 147.2$ pm [4]. Its symmetric stretch can be visualized as a synphase motion of the four oxygens towards the sulfur atom or away from it. The mode is infrared inactive since the permanent dipole moment is zero and there is no change in its value during the vibration.

Most sulfate ions are, of course, distorted in the crystalline state. If the distortion is such that the ion has a D_2 , S_4 or D_{2d} symmetry, the net dipole moment is still zero and will remain so during the symmetric stretching vibration. For any other type of distortion the ion will possess a net dipole moment and its change during the symmetric stretching vibration could be expected to be proportional to the dipole moment value in the equilibrium state. In other words, the intensity of the symmetric stretch should follow the magnitude of the net dipole moment of the ion, provided that the form of the normal mode is essentially the same as in the case of the undistorted ion (for small distortions such an assumption appears to be a reasonable one).

In an attempt to facilitate the correlation between the crystallographic measures of distortion and its spectroscopic manifestations, we propose to introduce a quantity called "distortion vector" \vec{S} defined as :

$$\vec{S} = (\vec{SO}_1 + \vec{SO}_2 + \vec{SO}_3 + \vec{SO}_4) / \langle SO \rangle \quad (1)$$

where \vec{SO}_i are the bond-vectors and $\langle SO \rangle$ is the mean value of the bond lengths. The quantity thus defined is proportional to the equilibrium value of the dipole moment and, if the assumptions outlined above hold, to the dipole moment change during the symmetric stretching vibration.

RESULTS AND DISCUSSION

The distortion vector values for many different sulfate compounds were calculated from the available crystal structure data. As seen from the examples given in Figs. 1 and 2, it appears that, at least qualitatively, the intensity of the symmetric stretch does indeed increase with the increased distortion vector magnitude.

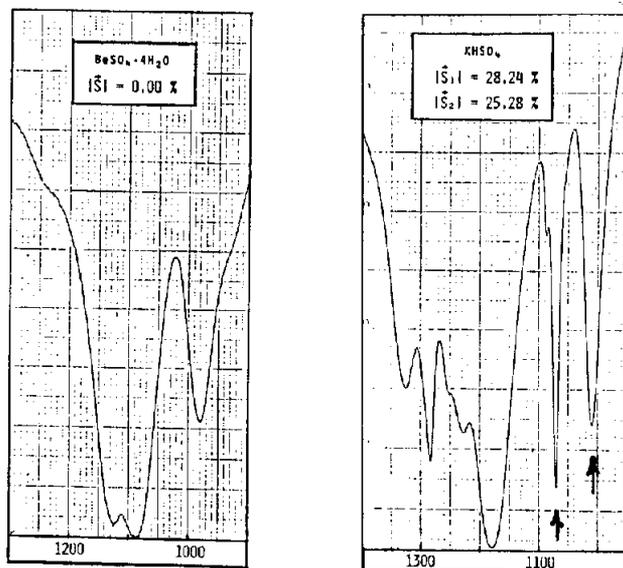


Fig. 1. Examples for the smallest (a) and largest (b) found value for the distortion vector

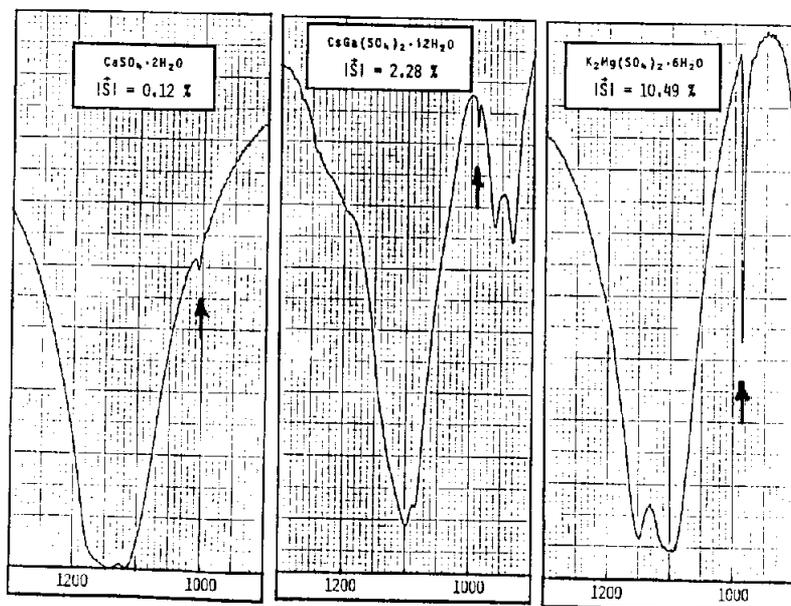


Fig. 2. Infrared spectra and distortion vector values for some simple inorganic compounds

A somewhat more quantitative approach is also possible if the data on the intensity of the symmetric stretch (I) as well as structural data are taken into account. We attempted to correlate the values of the distortion vector (calculated on the basis of available crystallographic data [7-18]) with those for the IR intensity (the latter have been reported [19,20] for a rather limited number of sulfates). The results are given in Fig. 3.

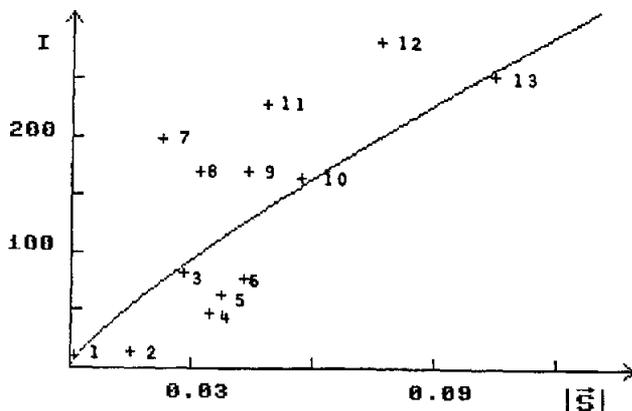


Fig. 3. Regression of the intensity of the symmetric SO_4 stretch (I) on the distortion vector value

- | | |
|--|--|
| 1. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ [7] | 2. CaSO_4 [8] |
| 3. $\text{K}_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ [9] | 4. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ [10] |
| 5. $(\text{NH}_4)_2\text{Mn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ [11] | 6. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ [12] |
| 7. $\text{K}_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ [15] | 8. $(\text{NH}_4)_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ [14] |
| 9. $(\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ [15] | 10. $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ [16] |
| 11. $(\text{NH}_4)_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ [16] | 12. $(\text{NH}_4)_2\text{Cd}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ [17] |
| | 13. $\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ [18] |

Despite the considerable scatter of the points (which may be partly due to inaccuracies in the determination of the intensity values and/or the insufficient refinement of the crystal structures), a clear trend is readily seen. The equation of the best-fit curve was found to be :

$$I = 1569 \cdot |S|^{0.8142} \quad (2)$$

with a correlation coefficient $r = 0.81$. It should be noted that an additional (perhaps quite important) factor may contribute to the observed scatter of the points. The symmetric stretching vibrations of phosphate and sulfate compounds [21,22] are, namely, known to be affected by the so-called "specific cation effects" and these could not be taken into account in our simple model. Because of that, the equation (2) should not be used for predictive purposes, but could help to make a more reliable as-

signment of the infrared bands in some more involved cases, especially when bands due to vibrations other than the sulfate symmetric stretch appear in the same spectral region (e.g. in various types of coordination compounds containing sulfate ions, in organic sulfate compounds etc.).

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