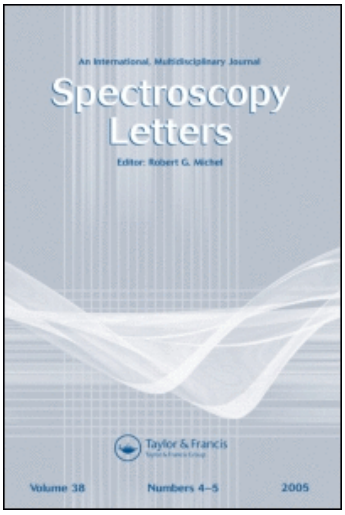

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Group Theoretical Analysis of the v_1 (CO_3^{2-}) Vibration in Crystalline Calcium Carbonate

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GROUP THEORETICAL ANALYSIS OF THE ν_1 (CO_3^{2-}) VIBRATION IN CRYSTALLINE CALCIUM CARBONATE

Key Words: Raman and infrared spectra; calcium carbonate; calcite; aragonite; vaterite; group theory; correlation method.

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ABSTRACT

A group theoretical analysis, based on the correlation method, is presented for the symmetric stretch vibration of the carbonate ion in three crystalline forms of calcium carbonate: calcite, aragonite and vaterite. Numbers of Raman and infrared active components are calculated and compared with experimental data, including those from a recent Raman study of vaterite. It is shown that the splitting observed for ν_1 in vaterite is compatible with two of the proposed crystal structures for this compound.

INTRODUCTION

In a recent paper in this journal[1], Behrens et al. reported on the Raman spectra of three different crystalline forms of calcium carbonate: calcite, aragonite and vaterite. They observed a splitting of ν_1, the symmetric stretch of

the carbonate ion in vaterite, and claimed that this implies two (or more) distinct site symmetries for the (CO_3^{2-}) groups. Since none of the three proposed structures for vaterite [2-4] show such a feature, they concluded that all three must be incorrect. In this note, it is shown that when coupling between ions in the unit cell is considered, by use of the group theoretical correlation method, multiple Raman active components of this mode are expected for two of these proposed structures. For comparison and completeness, similar analyses for calcite and aragonite are also presented.

The correlation method was introduced by Hornig[5] and developed by Winston and Halford[6] and by Bhagavantam and Venkatarayudu[7]. A compilation by Fateley et al.[8] conveniently provides the necessary tables, procedures and many useful examples in a single volume. In principle, by comparing the character tables for the point groups representing the symmetries of an isolated molecule or ion, its site in the unit cell and the unit cell as a whole, correlations are developed which allow one to predict the number of Raman and infrared active modes for any crystal of known structure.

The correlation is in two stages: the first links the symmetry species of the isolated molecular ion to those of the site. The point group of the site is normally a sub-group of that of the isolated unit, and this lower symmetry sometimes leads to the splitting of degenerate modes and to changes in optical (Raman or infrared) activity, the result of what Hornig termed the "static field" of the crystal. The second stage links the symmetry species of the site to those of the unit cell group. The latter, also known as the factor group, is obtained from the space group by subtracting the translational operations. The site group is also a subgroup of the factor group, unless there is only one molecule in the primitive unit cell, in which case they are identical. In fact, the number of branches from the site species to those of the unit cell is a measure of the occupancy number of the unit cell. Physically, this stage represents coupling of

units in the primitive cell through intermolecular or interionic forces. For a given normal mode, all units oscillate similarly but with various relative phases, and this leads to multiple components with slightly different frequencies. This phenomenon, analogous to the coupled pendulum experiment in many undergraduate physics laboratories, was termed the "correlation field" effect by Hornig, but is also known as factor group or Davydov splitting in the literature.

APPLICATION TO CALCITE

The structure of calcite is trigonal[9], with space group #167: $R\bar{3}c$ or D_{3d}^6. There are two formula units in the centrosymmetric cell, with site symmetries D_3 for the carbonate ions and S_6 for the calcium ions. The symmetric stretch ν_1 CO_3^{2-} belongs to the A_1' species of the point group D_{3h} for the isolated ion and to the A_1 species of the point group D_3 for the site. Correlation to the factor group D_{3d} gives two modes, one of A_{1g} species which is Raman active, and the other of A_{1u} species which is inactive. The Raman mode has been observed near 1086 cm^{-1} in a number of studies[1,10,11] including one by Porto et al.[12] who also confirmed that only diagonal elements of the polarizability tensor were involved. Infrared studies by Adler and Kerr[13] and by Steizel[14] showed no absorption in this region for pure calcite samples, in full agreement with group theoretical predictions.

APPLICATION TO ARAGONITE

Aragonite has centrosymmetric orthohombic structure with four formula units in the primitive cell[9]. The space group is #62: Pmcn or D_{2h}^{16}. Both types of ion are on sites with C_s symmetry. The mirror plane for the carbonate ion is a vertical plane of symmetry of the point group D_{3h} for the isolated ion. The correlation of the ν_1 (CO_3^{2-}) mode for this structure gives an A' representation at

the site and the following four species for the unit cell:

$$\Gamma(\upsilon_1) = A_g\ (R) + B_{2g}\ (R) + B_{1u}(ir) + B_{3u}(ir)$$

Hence, four components are predicted, two in each spectrum. A Raman peak at 1087cm^{-1} was reported by Griffith[11] and recently confirmed by Behrens et al.[1] Weak infrared absorption in the ν_1 region has been observed at 1085 cm^{-1} by Adler and Kerr[13] and by Sterzel[14]. However, we have not found in the literature any evidence of two components being observed for ν_1 in either Raman or infrared spectra. This indicates that coupling between the carbonate ions is too small to result in resolvable splittings, probably because their separation in this structure is quite large, with the calcium ions providing some screening. Low temperature measurements might, however, allow the peaks to be resolved.

APPLICATION TO VATERITE

A definitive crystal structure determination of vaterite is not yet available, but three possible hexagonal cells have been proposed[2-4]. Of these, the one discussed by Meyer[4] involves considerable disorder in the carbonate sublattice and is therefore, less amenable to analysis by group theoretical techniques. In all three structures, the normals to the carbonate planes are perpendicular to the hexagonal axis, rather than parallel to it as in calcite and aragonite. The one proposed by Kamhi[2] has a centrosymmetric unit cell containing six ions of each type. The space group is #194: $P6_3/mmc$ or D^4_{6h}. The carbonate ions are on C_{2v} sites, with two calcium ions on D_{3d} sites and the other four on D_{3h} sites. The correlation for the ν_1 (CO_3^{2-}) mode gives an A_1 representation at the site and the following four species for the unit cell:

$$\Gamma(\upsilon_1) = A_{1g}\ (R) + E_{2g}\ (R) + B_{1u}(-) + E_{1u}(ir)$$

Hence two Raman peaks and one non-coincident infrared peak are predicted.

The unit cell proposed by Lippman[3] also contains six formula units but is non-centrosymmetric. The space group is #182: $P6_322$ or D_6^6. The carbonate ions are on C_2 sites and the calcium ions are on three sets of D_3 sites. The resulting correlation diagram shows that the ν_1 (CO_3^{2-}) mode has an A representation at the site and the following four species for the unit cell:

$$\Gamma(\upsilon_1) = A_1(R) + B_1(-) + E_1\ (Rir) + E_2(R)$$

Hence three Raman peaks are predicted, one of them being coincident in frequency with a single infrared active peak.

In a recent study, Behrens et al.[1] reported on the Raman spectra of the ν_1, ν_4 and lattice regions of calcite, aragonite and vaterite. For vaterite, a triplet was observed for ν_1 and a doublet for ν_4, and at least six lattice modes were detected. This spectrum of vaterite is characteristic of an ordered crystal. The structure proposed by Meyer[4], with its disorder in the CO_3^{2-} sublattice, would likely lead to single broad peaks in each of the internal mode regions and broad overlapping features in the lattice region. It therefore appears unlikely that this structure is the correct one.

Of the other two structures, that proposed by Kamhi[2] predicts a Raman doublet in the ν_1 region, whereas that of Lippmann[3] predicts a triplet, just as observed. However, Behrens et al.[1] state that the third component at 1080 cm^{-1} is probably due to some calcite impurity in the vaterite sample. If this were the case, one would also expect some evidence of a calcite peak in the ν_4 region (near 711 cm^{-1}), well separated from the vaterite peaks at 740 and 750 cm^{-1}. Since none is observed, it appears more likely that the three components of ν_1 in the vaterite spectrum are genuine, and that therefore the non-centrosymmetric structure proposed by Lippmann[3] is the preferred one. To the best of our knowledge, no infrared data on vaterite is available in the literature. If it could

be verified that there is a single infrared peak in the ν_1 region, coincident with one of the Raman components (at 1074, 1080 and 1090 cm^{-1}), then confirmation of this structure would be assured.

In asserting that the observed splitting in the ν_1 region is the result of the carbonate ions possessing two distinct site symmetries, Behrens et al.[1] appear to have overlooked the possibility that it could result from the correlation field effect. The fact that the splittings were observable in vaterite but not in aragonite indicates that the coupling between carbonate ions in the former crystal is stronger, probably as a result of the ions being closer together in this structure. In any case, the conclusion of Behrens et al.[1] that all three proposed structures must be incorrect does not appear to be justified.

CONCLUDING REMARKS

In this note, it has been shown that the splitting observed in the Raman spectrum of the ν_1 region of vaterite[1] is compatible with two of the three proposed structures for this crystal, provided that account is taken of coupling between carbonate ions in the unit cell. If all three observed components are genuine, than the non-centrosymmetric structure proposed by Lippmann[3] is the most likely. If, on the other hand, one component is the result of calcite impurity, then the centrosymmetric structure proposed by Kamhi[2] would be favoured. Complementary infrared spectra of vaterite crystals would allow a resolution of this ambiguity, as would, of course, a definitive X-ray or neutron diffraction crystal structure determination.

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REFERENCES

1. Behrens G., Kuhn L.T., Ubic R., Heuer A.H. *Spectrosc. Lett. 1995*; 28:983.

2. Kamhi S.R. *Acta Cryst. 1963*; 16:770.

3. Lippmann F. *Sedimentary Carbonate Materials*, New York: Springer, 1973.

4. Meyer H.J. *Zeit. Kryst. 1969*; 128:183.

5. Hornig D.F. *J. Chem. Phys. 1948*; 16:1063.

6. Winston H., Halford R.S. *J. Chem. Phys. 1949*; 17:607.

7. Bhagarantam S., Venkatarayudu T. *Theory of Groups and its Application to Physical Problems*, Bangalore Press, India, 1951.

8. Fateley W.G , Dollish F.R., McDevitt N.T., Bentley F.F. *Infrared and Raman Selection Rules for Molecular and Lattice Vibrations: The Correlation Method*, New York: Wiley, 1972.

9. Donnay J.D.H. *Crystal Data Determinative Tables*, American Crystallographic Association, 1963.

10. Rutt H.N., Nicola J.H. *J. Phys. C: Solid State Phys. 1974*; 7:4522.

11. Griffith W.P. *J. Chem. Soc. A. 1970*; 286.

12. Porto S.P.S., Giordmaine J.A., Damen T.C. *Phys. Rev 1966*; 147:608.

13. Adler H.H., Kerr P.F. *Amer. Mineralogist 1962*; 47:700.

14. Sterzel W. *Zeit Anorg. Allgem. Chem. 1969*; 368:309.

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