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INFRARED SPECTRA, SYMMETRY AND STRUCTURE RELATIONS OF SOME CARBONATE MINERALS

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ABSTRACT

Variations in infrared spectra of carbonate minerals are indicative of changes in symmetry of the ionic carbonate molecule. The point-group symmetry of the ion determined from spectral considerations is generally compatible with its site symmetry. Molecular symmetry does not, however, vary systematically with crystal class. The existence of more than one non-equivalent molecule per unit cell is reflected in certain carbonates by spectral enrichment in the wavelength region of one or more of the fundamental degenerate or non-degenerate vibrations. Alternative causes of spectral multiplicity are also considered; however, the enrichment has been observed only for minerals which are known or suspected from *x*-ray data to contain non-equivalent carbonate ions.

INTRODUCTION

Infrared spectroscopy has been used successfully by chemists and physicists to resolve problems of structural arrangement of organic and inorganic substances. This approach is possible because mechanical vibrations of molecules from which infrared spectra originate are governed by molecular symmetry in such a way that specific sets of vibrations can be correlated with specific symmetry operations. It is possible to treat ions as discrete functional groups because binding forces within ionic molecules in minerals are significantly stronger than forces binding the molecules to the rest of the structure, bearing in mind that the vibrations are dependent on crystal structure. This provides a versatile method for analyzing mineral structures at the molecular level.

In spite of this potential, spectral studies of minerals appearing in earth-science journals have for the most part emphasized descriptive features, and relatively little attention has been accorded effects of molecular environment on frequencies and complexities of molecular vibrations. Some manifestations of this dependency have been indicated by Halford (1946) for calcite and aragonite; by Nakamoto et al. (1957) for carbonate coordination compounds; and by Adler and Kerr (1963) for calcite-group and aragonite-group minerals. For the most part, however, differences among molecular spectra of various carbonate minerals as well as other mineral groups, such as sulfates, phosphates, and silicates, remain unexplained. The lack of adequate understanding of these variations continues to be a deterrent to application of infrared spectroscopy to mineralogical problems.

The purpose of this and other recent papers by the writers is to provide an analysis of infrared spectral data for several carbonate minerals, in terms of factors that have a known or suspected influence on vibrations of the ionic carbonate molecule CO_3^{2-}. The results have led us to an intriguing and rapid means of recognizing, or at least suspecting, non-identical carbonate ions in the unit cell, a task otherwise accomplished only by rigorous x-ray structure analysis.

The point-group notations used here to identify molecular and site symmetries are the usual sets of symmetry operations prescribed by Schoenflies and customarily used by spectroscopists. Although the Hermann-Mauguin notations are equally informative and are in more common usage in mineralogical literature, the Schoenflies notations are preferred for ease of comparison with the character tables identifying symmetry species for various molecular point groups.

The spectral region which includes fundamental vibrations of the carbonate molecule approximately covers the range 6 to 16 microns. The carbonate stretching modes, v_3 and v_1, are found near 7 and 9 microns, and the bending modes, v_2 and v_4, occur at about 11 and 14 microns, respectively. The v_3 and v_4 modes are doubly degenerate, *i.e.* each under certain symmetry conditions may split into two distinct vibrations of different frequency. In the present study only features of absorption bands corresponding to fundamental vibrations are of primary concern.

The internal symmetry of the molecule is established by the configuration of nuclei comprising the molecule. In the carbonate ion, positions of the single carbon and three oxygen atoms determine this symmetry. The site symmetry of the molecule is defined by the arrangement of any molecular ion and extramolecular nuclei to which it is bonded; it is, therefore, a function both of the symmetry of the molecule and its external environment. A simple example may help to clarify this point. The ideal carbonate ion has the internal symmetry D_{3h}. However, if neighboring Ca atoms are also considered, as in calcite, the symmetry elements which define the configuration of one carbon, three oxygen and six calcium atoms are no longer D_{3h} but D_3. For dolomite and aragonite, the divalent metallic ions provide still different site symmetries for the carbonate ion (or carbon atom). In this study, variations in site symmetry have been observed to alter the carbonate absorption spectra, leading us to certain inferences regarding the ionic symmetry.

Much more remains to be learned about the dependence of vibrations of functional molecular groups in crystals on extramolecular environment. Until this knowledge is gained, it is doubtful whether much significance may be attached to interpretations of absorption spectra ascribed to interactions required for crystal cohesion, such as hydrogen bonding, which seems to be the topic of much predictive discourse in recent mineralogical literature.

EXPERIMENTAL TECHNIQUE

Infrared spectra that furnish the data for this paper were recorded on a Perkin-Elmer Model 21 double-beam infrared spectrometer equipped with sodium chloride optics. All samples were prepared using the potassium bromide pellet technique. Ordinarily, 0.85 mg of finely ground mineral was mixed and reground with 300 mg of KBr in a dental amalgamator and the mixture used to form a pellet under vacuum at approximately 19,000 psi.

Mineral specimens were obtained primarily from the mineral collections of the U. S. National Museum through the courtesy of Dr. George S. Switzer, and supplemental material was furnished by Dr. Joseph Fahey, U. S. Geological Survey. Mineral identity was confirmed by *x*-ray diffraction analysis.

The cooperation of Dr. Irving A. Breger and the U. S. Geological Survey in making available the spectrometer for this investigation is gratefully acknowledged. The authors are also indebted to Dr. Howard Evans, U. S. Geological Survey, who kindly provided many helpful suggestions in regard to the crystal-structure data and to Dr. Ralph S. Halford, Columbia University, for suggestions concerning alternative interpretations of the spectral data.

MOLECULAR SYMMETRY AND STRUCTURAL RELATIONS

The structure of the carbonate molecule was established first by Bragg (1914) and more recently has been confirmed by other crystal structure studies. In the model ion, three oxygen atoms are coplanar with a central carbon atom and are situated at the corners of an equilateral triangle at a distance of approximately 1.31 Å from the carbon atom. This form is highly symmetrical and is considered representative of the molecule in its free state undistorted by asymmetrical external forces. In crystal structures, however, one might expect the symmetry of the ion to be modified, because of variable or unequal external forces, and these can be expected to produce differences in infrared spectra.

Previous systematic studies of relationships between molecular symmetry and vibrations of the carbonate ion were accomplished by Halford (1946) and Nakamoto et al (1957). From theoretical considerations, Halford (1946) related spectral differences between calcite and aragonite to the site symmetry of the carbonate ion, the structural transition being accompanied by a lowering of the site symmetry of the carbonate ion from D_3 in calcite to C_s in aragonite; with concomitant removal of the degeneracy of the v_3 and v_4 modes and the appearance of v_1 in aragonite. The spectral differences observed for these minerals at 9 μ and 14 μ are, therefore, related to differences in molecular symmetry brought about by a change in the environment of the carbonate ion.

Subsequently, Nakamoto *et al.* (1957), investigating carbonate coordination compounds, determined that a split in the degenerate v_3 carbonate mode could result from formation of unidentate (in which one C—O bond changes character) or bidentate (in which two C—O bonds change character) bonds between the carbonate and metallic ions. Although effects were found to be qualitatively similar for both bond types, the bidentate structure produces a greater separation of the split bands. In both cases v_1 is activated, but absorption is more intense when a bidentate linkage is formed. The v_4 mode apparently is unaffected, since the degeneracy is not visually resolved. For both unidentate and bidentate complexes the effective symmetry of the ion is lowered to C_{2v}, because the coordinated and uncoordinated oxygens are no longer symmetrically equivalent.

These early works demonstrate the influence of the symmetry of the carbonate ion on spectral complexity and indicate the possibility of applying variations in absorption patterns to elucidating molecular symmetry in carbonate minerals. We have found, however, that fortuitous overlap or coincidence of bands places some limitation on the usefulness of the spectra for this purpose. For example, the absence of a v_4 doublet in spectra of witherite and cerussite (Adler and Kerr, 1963), isotypes of aragonite and strontianite, is most likely caused by accidental degeneracy and restricts the usefulness of these spectra in molecular analysis. Spectra obtained with CsBr optics by Miller *et al.* (1960) show no additional bands assignable to the v_4 vibration beyond the 15-micron region. Furthermore, in no case does the v_3 vibration appear to be resolved into two component bands although, as reported by Halford (1946), degeneracy of this band is removed in the aragonite group. Consequently, it may be inferred that the individual v_3 and v_4 vibrations fortuitously coincide or overlap for these minerals. It should be emphasized, therefore, that molecular symmetry is not always clearly indicated by the absorption pattern, inasmuch as degeneracies may remain unresolved because of overlap or near coincidence of band maxima or for unknown reasons. The absence of spectral bands is not always an indication that a particular molecular configuration may not exist. Nevertheless, when a complex carbonate spectrum contains split degenerate bands with v_1, the symmetry of the molecule is low.

We have observed that hydrous carbonate minerals present another problem. Some of these minerals, including gaylussite and pirssonite (Fig. 1) yield absorption bands in excess of the prescribed number of fundamentals in the 11-, 12- and 14-μ regions. Because similar bands are observed generally in hydrous minerals, these bands may be caused, we believe, by OH torsional vibrations. Since the bands may, in some cases, be mistaken for the v_2 and v_4 carbonate fundamentals, their existence is of

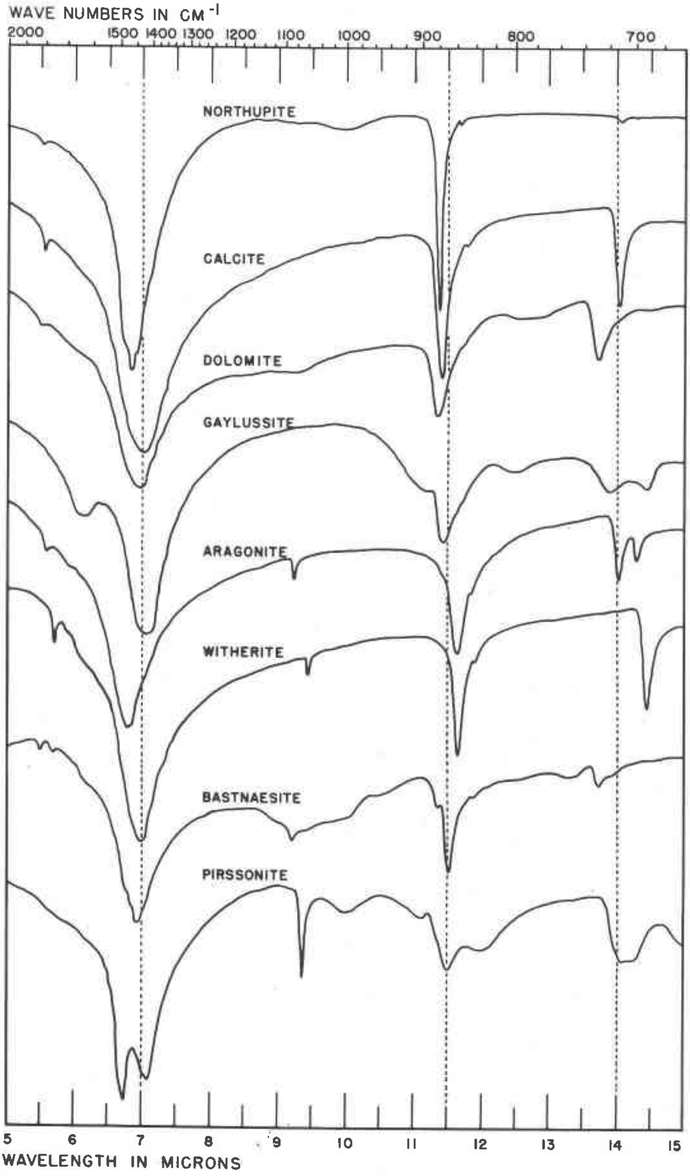

FIG. 1. Infrared spectra of carbonate minerals showing absorptions corresponding to carbonate vibration modes.

some concern in utilizing spectra of hydrous carbonates as an index of molecular symmetry. Although dehydration has been considered, this is also likely to alter the coordination about the carbonate ion and, thus, cause further spectral changes involving carbonate bands. Therefore, deuterated analogs of the hydrous minerals must be synthesized before a more reliable interpretation appears possible. Despite these difficulties tentative interpretations of the spectra of gaylussite and pirssonite are given and tentative molecular symmetries are assigned on the basis of the v_3 and v_1 modes.

TABLE 1. ABSORPTIONS OF THE CO_3^{2-} ION AS A FUNCTION OF MOLECULAR SYMMETRY (FROM DATA IN NAKAMOTO ET AL., 1957)

Molecular Symmetry	Number of Bands Observed			
	v_3	v_1	v_2	v_4
D_{3h}	1 (vs)	—	1 (s)	1 (s)
D_3 (site)	1 (vs)	—	1 (s)	1 (s)
C_s	1 (vs)[1]	1 (w)	1 (s)	2 (m-s)[2]
C_{2v}	2 (s)	1 (vw-m)	1 (s)	1 (w-m)[1]

vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

[1] Two bands are theoretically possible.

[2] A single band is observed for some minerals.

With the aid of tables (Herzberg, 1945) denoting the number of vibrations of each species for point groups with degenerate vibrations and the symmetry types and characters for these point groups, it is possible to establish the nature of the vibrations which may occur for various possible configurations of the carbonate ion. If the symmetry of the carbonate ion (Table 1) in a crystal is identical or similar to that of the free ion, D_{3h}, it is apparent that only single bands should appear for the degenerate v_3 and v_4 modes, and v_1 should remain inactive. Although the site symmetry of the carbonate ion in calcite is D_3, the effective molecular symmetry is apparently D_{3h}. Similarly, the site symmetry for dolomite is C_3, but the apparent molecular symmetry is also D_{3h} (Table 3). The difference in molecular and site symmetry for calcite results from the orientation of the calcium atoms which are doubly coordinated about the oxygen atoms and lie in a plane oblique to the molecular plane, as depicted by Bragg (1937, p. 119). The difference in site symmetries for dolomite and calcite results from substitution of a Mg atom for one of the two Ca atoms about each molecular oxygen atom. This site symmetry change has no effect on the molecular symmetry as determined from the absorption spectra.

The site symmetry for aragonite is C_s, but the vibrations are no longer identical to those of the free molecule; hence, the molecular symmetry appears also to have been modified. Since the appearance of v_1 in the aragonite spectrum indicates a molecular dipole moment, which cannot exist if more than one axis of symmetry is present, the molecule cannot have internal D_{3h} symmetry. It is possible, however, that coordination contributing to site symmetry C_s may produce molecular symmetry C_s, as the latter is compatible with a dipole moment. Moreover, from site-group data (Table 2) it follows that site symmetry C_s is also a sub-group of molecular point groups D_{3h}, C_{2v} and C_{3v}. Therefore, crystals in which carbonate ions occupy a C_s site may conceivably have molecular symmetry D_{3h}, C_s, C_{2v} or C_{3v}. Other site groups compatible with molecular point groups of the carbonate ion are given in Table 2.

TABLE 2. POSSIBLE SITES FOR MOLECULAR POINT GROUPS OF THE CARBONATE ION

Molecular Point Group	Molecular Site Group
D_{3h}	C_1, C_s, C_2, C_3, C_{2v}, C_{3v}, C_{3h}, D_3, D_{3h}
C_{3v}[1]	C_1, C_s, C_3, C_{3v}
C_{2v}[1]	C_1, C_s, C_{2v}
C_s[1]	C_1, C_s

[1] Point groups to which a molecule with a dipole moment might belong.

As previously indicated, with C_{2v} symmetry the carbonate molecule may assume unidentate or bidentate configuration in which one C–O bond is non-equivalent to the other two. This may involve a metal-oxygen bond of different character as in Werner coordination compounds, a hydrogen bond, or a different cation coordination about the non-equivalent oxygen.

The distinction between unidentate and bidentate bonding is important although both configurations produce C_{2v} symmetry in the carbonate molecule. Using H bond formation as an example, only the single non-equivalent oxygen is hydrogen-bonded in the unidentate structure, whereas in the bidentate structure the two equivalent oxygen atoms participate in H bonding. According to Nakamoto *et al.* (1957), the distinction may be possible on the basis of the intensity of the v_1 vibration and the degree of splitting of the two v_3 bands. However, no limiting quantitative criteria have as yet been established for distinguishing between the two structures by infrared spectra. Recognizing one or the other of the two bond types in minerals may be difficult.

Consideration also might be given to the existence in minerals of a non-planar carbonate ion having C_{3v} symmetry in which the carbon atom is displaced slightly from the molecular plane along the three-fold symmetry axis. In this case there are two symmetric vibrations, v_1 and v_2, and two degenerate vibrations, v_3 and v_4. One absorption band should appear, therefore, for each of the four active fundamentals. The degeneracy of v_4 is evidently not always resolved in minerals having C_s molecular symmetry (for example witherite and cerussite). Hence, the existence of a C_{3v}-type ion cannot be confirmed, *i.e.*, distinguished from C_s, on the basis of the fundamental absorption spectrum. However, its existence should be suspect in any carbonate mineral producing a spectrum in which all four fundamentals are present, when v_3 and v_4 are doubly degenerate. From this aspect, the possibility of a molecular symmetry change from C_s, for aragonite and strontianite, to C_{3v}, for witherite and cerussite, should not be overlooked. Such a change might conceivably result from the crowding of electropositive charges about the carbonate molecule as larger cations are introduced in the structure. Molecular symmetry C_1 must also be accorded similar consideration. However, it should be kept in mind that both C_{3v} and C_1 require a non-planar carbonate ion for which there is, as yet, no concrete evidence.

After consideration of the possible symmetry elements involved, a decision about the molecular symmetry may be based first on whether the molecule possesses a dipole moment. In the absence of v_1 the molecule may be assumed to have zero dipole moment. Therefore, carbonate spectra lacking absorption corresponding to v_1 are indicative of molecular point group D_{3h} which has symmetry elements precluding a dipole moment. When v_1 appears in the spectrum the molecule may belong to point group C_s or C_{2v} (and C_{3v} or C_1, if we consider non-planar CO_3^{2-} ions) which have symmetry elements prescribing a dipole moment. The number of bands observed for the normally degenerate vibrations also may be used as an indication of the molecular point group. However, as previously mentioned, the absorptions resulting from removal of degeneracies may overlap in some cases, and the resulting lack of resolution can be misleading. Therefore, the value of v_3 and v_4 alone is limited in determining molecular symmetry. Theoretically, the distinction between C_s and C_{2v} symmetry cannot be made on the basis of the observed presence or absence of the split in the v_3 and v_4 bands, although when the v_3 band is not visibly split C_s symmetry is tacitly assumed. The transition to either symmetry type removes all degeneracies present in the D_{3h} state, since C_s and C_{2v} have only non-degenerate vibrations. Furthermore, all six vibration modes are infrared active for both point groups.

In classifying the carbonate minerals according to indicated molecular symmetry (Table 3), primary consideration is given to the presence or absence of absorption corresponding to the v_1 vibration mode; likewise, a secondary distinction is made on the basis of the degenerate modes. Point-group crystal symmetry data and space-group notations in Table 3 are based upon Palache *et al.* (1951). Infrared mineral spectra yielding the absorption data in this table are shown in Fig. 1, and the absorption data are given in Table 4.

Comparison of molecular with crystal point-group data (Table 3) shows no consistent valid correlation between molecular symmetry and crystal class. For example, D_{3h} molecular symmetry is represented by four minerals crystallizing in the isometric, hexagonal and monoclinic systems and C_s molecular symmetry by two minerals which are respectively hexagonal (trigonal) and orthorhombic. From another standpoint, the hexagonal minerals have both D_{3h} and C_s molecular symmetries, and the orthorhombic minerals have C_s and C_{2v} molecular symmetries. Unfortunately, problems associated with the interpretation of spectra of many hydrous carbonates, which are more numerous than anhydrous species, limit the number of examples.

Although lattice symmetry is not a satisfactory index to molecular symmetry, the molecular site-group determination using space-group data and a knowledge of the population of the unit cell (Halford, 1946), is of some value in this respect. In many cases, however, the atomic arrangement within the unit cell can be determined from crystal structure data, and it is, therefore, not necessary to determine site symmetry by this method. Such information was for the most part obtained from abstracts of structural data in Strukturbericht and Structure Reports. References to original data may be found in these reports as well as in Palache, *et al.* (1951). Site data for bastnaesite were obtained from Donnay (1953).

The atomic arrangement in northupite is compatible with two possible space groups, namely T_h^4 and O_h^7. In each structure the CO_3^{2-} ions are in closely related positions. For space group O_h^7 (see *Strukturbericht*, **II**) the carbonate ion lies on site C_{3v} and for T_h^4 on site C_3, both of which, according to Table 2, are sub-groups of molecular point groups D_{3h} and C_{3v}. The spectrum however, is conformable with the vibrational requirements of D_{3h}, but not C_{3v}, symmetry inasmuch as no dipole moment is evident.

The site symmetry for pirssonite, C_1 (Evans, 1962), is compatible with all possible molecular point groups listed in Table 2.

NON-EQUIVALENT MOLECULAR SITES IN CARBONATES

In the foregoing, the complexity of the carbonate absorption spectrum has been interpreted in terms of molecular symmetry, assuming that all carbonate molecules in the unit cell are identical and that none of the bands results from a coupling or combination effect. The number of per-

TABLE 3. SYMMETRY CLASSIFICATION OF SOME CARBONATE MINERALS

Crystal Point Group	Crystal Space Group	Crystal Class	Mineral or Salt	Composition	Number of Observed Absorption Bands				Suggested Molecular Symmetry
					ν_3	ν_1	ν_2	ν_4	
$T_h(m3)$	$T_h^4(Fd3)$	Isometric-diploidal	Northupite	$Na_3MgCl(CO_3)_2$	1	–	1	1	$D_{3h}(C_3$ site)
$D_{3d}(\bar{3}m)$	$D_{3d}^6(R\bar{3}c)$	Hexagonal-scalenohedral	Calcite	$CaCO_3$	1	–	1	1	$D_{3h}(D_3$ site)
$S_6(\bar{3})$	$C_{3i}^2(R\bar{3})$	Hexagonal-rhombohedral	Dolomite	$Ca(Mg,Fe,Mn)(CO_3)_2$	1	–	1	1	$D_{3h}(C_3$ site)
$C_{2h}(2/m)$	—	Monoclinic-prismatic	Gaylussite	$Na_2Ca(CO_3)_2\cdot 5H_2O$	1	–	1	1	D_{3h}
$D_{2h}(mmm)$	$D_{2h}^{16}(Pmcn)$	Orthorhombic-dipyramidal	Aragonite	$CaCO_3$	1	1	1	2	$C_s(C_s$ site)
$D_{2h}(mmm)$	$D_{2h}^{16}(Pmcn)$	Orthorhombic-dipyramidal	Witherite	$BaCO_3$	1	1	1	1	$C_s(C_s$ site)
$D_{3h}(\bar{6}n2)$	$D_{3h}^2(C\bar{6}c2)$	Ditrigonal-dipyramidal	Bastnaesite	$(Ce,La)(CO_3)F$	1	1	1	1	$C_s(C_s$ site)
$C_{2v}(mm2)$	$C_{2v}^{19}(Fdd2)$	Rhombic-pyramidal	Pirssonite	$Na_2Ca(CO_3)_2\cdot 2H_2O$	2	1	1	1 or 2	$C_{2v}(C_1$ site)

TABLE 4. ABSORPTION BANDS OF THE CARBONATES LISTED IN TABLE 3

Mineral	Locality	Wavelength (microns)			
		v_3	v_1	v_2	v_4
Northupite	Green River, Wyo.	6.83	—	11.37	14.06
Calcite	New Mexico (106158)[1]	7.02	—	11.40	14.02
Dolomite	Guanajuato, Mex. (R2408)	6.95	—	11.35	13.72
Gaylussite	Searles Lake, Calif. (102876)	7.07	—	11.43	13.89 or 14.44
Aragonite	Horschenz, Bohemia (R12050)	6.80	9.22	11.65	14.02, 14.31
Witherite	Cumberland, England (R2560)	6.97	9.42	11.63	14.41
Bastnaesite	Belgian Congo (104097)	6.93	9.21	11.52	13.74
Pirssonite	Searles Lake, Calif. (107403)	6.72, 7.07	9.36	11.50	14.05–14.30

[1] U. S. National Museum Identification Number.

missible fundamental bands is prescribed for non-linear molecules by the relationship

$$3N\text{-}6 = \text{number of normal vibration modes},$$

where N is the number of atoms in the molecule. Hence, there can be only six normal modes for a given carbonate molecule. These are the v_3 (doubly degenerate), v_1 (latent, non-degenerate), v_2 (non-degenerate) and v_4 (doubly degenerate) vibrations. The carbonate minerals already considered give rise to no more than six fundamental carbonate absorption bands, and the appearance of fewer than this number has been related to symmetry restrictions. It can be assumed, therefore, that for these minerals all carbonate ions are identical or occupy more or less identical sites in the crystal lattice.

The features that distinguish one mineral spectrum from another arise from differing influences exerted by the crystal field on the molecule (Adler and Kerr, 1963). If in a single crystal two molecules exist with respect to their cation environments or their symmetries at non-equivalent sites, the observed spectrum may yield evidence of this in the ideal case through the appearance of the simple spectrum of each of the non-identical molecules. Consequently, the mineral spectrum may contain more than the maximum number of bands permissible for an individual mode, and in some cases doubling of the spectral bands may result. Spectra from which two non-equivalent carbonate ions may be postulated on this basis are shown in Fig. 2, and the absorption data are given in Table 5.

Since the basic *x*-ray data indicate that the unit cells of huntite, parisite and shortite contain two non-equivalent carbonate molecules, there is considerable support for our interpretation. The structures of barytocalcite and alstonite are not sufficiently well known to identify such dissimilar molecular groups. Therefore, we point to the data presented here as evidence for the existence of non-equivalent carbonate ions in these two mineral structures.

Unfortunately, alternative mechanisms may account for spectral enrichment observed in the region of the carbonate fundamentals. Nakamoto *et al.* (1957) and Gatehouse *et al.* (1958) have attributed strong absorption bands appearing at about 7 microns in spectra of unidentate and bidentate carbonato-complexes to splitting of the v_3 vibration, which is in accord with removal of its normal degeneracy. Similar splitting has also been observed for basic and organic carbonates by Miller and Wilkins (1952), Hunt, Wisherd and Bonham (1950) and Gatehouse *et al.* (1958). However, further splitting of v_3 has been observed only for the hydrogen carbonates and has been attributed by Gatehouse *et al.* (1958) to interaction between neighboring CO_3 groups which are hydrogen bonded. They also have observed a splitting of v_1 in the hydrogen carbonates and carbonato-complexes that, they suggest, may arise from interaction of neighboring molecular groups or from Fermi resonance of v_1 with lower frequency fundamentals. However, no splitting of v_2 was observed for the carbonate compounds they examined, and the v_4 mode did not give rise

TABLE 5. ABSORPTION DATA ON CARBONATES CONTAINING MORE THAN ONE NON-EQUIVALENT MOLECULAR SITE PER UNIT CELL

Mineral	Composition	Wavelength (microns)			
		v_3	v_1	v_2	v_4
Barytocalcite	$CaBa(CO_3)_2$	6.62, 6.84, 7.11, 7.32	9.20, 9.25	11.37, 11.52	13.83, 14.29, 14.37, 14.74
Huntite	$Mg_3Ca(CO_3)_4$	6.62, 6.92	8.99	11.20, 11.49	13.46
Parisite	$Ce_2Ca(CO_3)_3F_2$	6.90	9.19, 9.27	11.49	13.40, 13.62
Shortite	$Na_2Ca_2(CO_3)_3$	6.57, 6.75, 6.88, 7.09	9.18, 9.35	11.46, 11.54, 11.75	13.69, 13.91, 14.10, 14.42
Alstonite	$CaBa(CO_3)_2$	6.85	9.20, 9.39	11.60, 11.68	14.00, 14.11, 14.26, 14.48

Barytocalcite—Cumberland, England (78839)[1]
Huntite —Crestmore, Calif. (R11367)
Parisite —Colombia, S. A. (R2612)
Shortite —Green River, Wyo.
Alstonite —Northumberland, England (78840)

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[1] U. S. National Museum Identification Number.

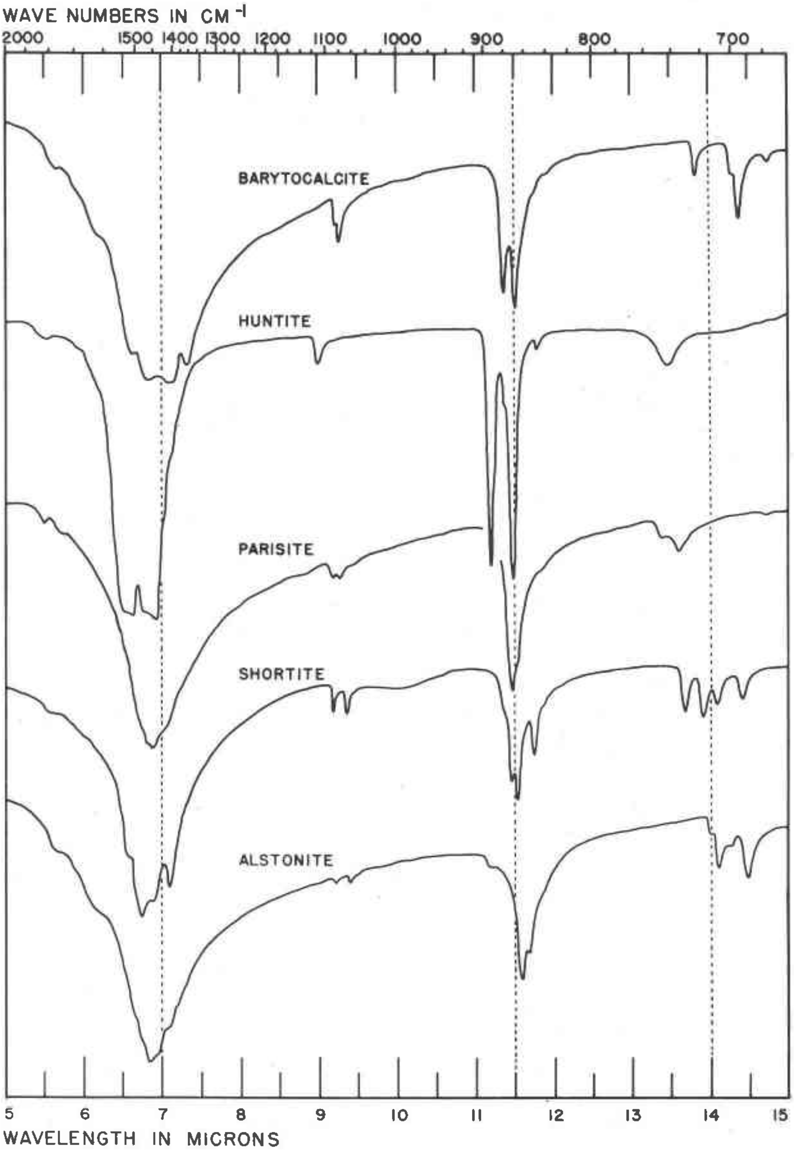

FIG. 2. Infrared spectra of carbonate minerals indicating non-equivalent molecules in the unit cell.

within the NaCl region to more than the number of bands prescribed by removal of the degeneracy.

Consideration must also be given to additive and subtractive combinations with lattice modes to produce satellite bands which are displaced to either side of the molecular frequency. Hexter (1958) has suggested that the 5.7 μ band (1755 cm^{-1}) in the calcite spectrum reported by Schaefer, Bormuth and Matossi (1926) is in accord with the additive combination of the v_3 fundamental (1432 cm^{-1}) and the 323 cm^{-1} lattice mode. Similarly, the band at 6.3 μ (1587 cm^{-1}) may be a combination of the 155 cm^{-1} lattice mode with the v_3 fundamental, and the 8.5 μ (1175 cm^{-1}) band may be a subtractive combination of the 257 cm^{-1} lattice mode with v_3. It should be noted that among these three combination modes only the bands at 5.7 and 6.3 μ are strong enough to be observed in the spectra of powdered samples of calcite-group minerals and none can be readily mistaken for fundamentals. Unassigned satellite bands of similar intensity have been observed also adjacent to v_3 and v_2 (Fig. 1) for various carbonate minerals, but they are certainly not to be confused with the intense bands observed in the spectra of barytocalcite and huntite, which are taken as evidence of their dimolecular character.

Although none of the combination bands observed by Hexter (1958) for calcite is of sufficient intensity to be mistaken for degeneracies of fundamentals, it is noteworthy that Brecher *et al.* (1961) have observed in their study of a single crystal of cyclopropane that combinations of lattice modes with molecular fundamentals can give rise to prominent absorption bands adjacent to the involved fundamental. Therefore, it is necessary to consider this possibility, as well as molecular interaction, to account for the multiplicities of bands which are not attributable to removal of degeneracies. It is interesting, however, that these multiplicities are observed (Fig. 2) for three minerals known from *x*-ray evidence to contain non-equivalent carbonate molecules in their unit cells, and have not been observed for minerals known to possess only identical molecules. Therefore, they appear to furnish empirical evidence of this condition.

Further interpretation of the spectra in Fig. 2 would require considerable detailed investigation of parameters beyond the scope of this paper.

CONCLUSION

Theoretically, infrared spectral analysis of minerals may be used to establish the symmetry of the carbonate ion. The symmetry requirements of the lattice provide a means of verifying the molecular symmetry suggested by the vibrational spectrum. The experimental data herein presented are in good agreement with expectation, but some complications arise from accidental spectral degeneracies. The problems and limitations of the method are reflected in the alternative interpretations that are possible. However, it is clear that the ideal symmetry of the carbonate ion, which has a planar structure belonging to point group D_{3h}, is modified to lower symmetry as a function of its extramolecular environment. This is apparent in the spectra of aragonite, bastnaesite and pirssonite which preclude a highly symmetrical ionic form.

As suggested by curves obtained from carbonate minerals known to contain non-equivalent CO_3^{2-} ions in the unit cell, it is possible on the basis of the presence of spectral enrichment, *i.e.* fundamental bands in excess of the number prescribed by symmetry requirements for a single molecule, to predict the presence of non-equivalent ions in the unit cell. In this application, the infrared method provides a technique that is much simpler and faster than the classical *x*-ray methods.

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