

Structure of vaterite and infrared spectra

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Auszug

Zwei Strukturvorschläge für Vaterit wurden mit Hilfe der Infrarot-Spektroskopie überprüft. Im Strukturvorschlag von MEYER (1959) hat das Carbonat-Ion die Punktsymmetrie C_s , im Strukturvorschlag von KAMHI (1963) die Punktsymmetrie C_{2v} . Die beobachteten Infrarotspektren sind charakterisiert durch die Anregung und Aufspaltung von ν_1 und durch die Aufspaltung von ν_3 , was die Annahme der C_{2v} -Punktsymmetrie stützt.

Abstract

Two structural propositions of vaterite are examined using infrared spectroscopy. The carbonate ion has C_s -site symmetry in the structure presented by MEYER (1959), but C_{2v} according to KAMHI (1963). Observed infrared spectra are characterized by (1) the activation and splitting of ν_1 and (2) the splitting of ν_3 , which support C_{2v} symmetry.

Introduction

It was by MEYER (1959) and KAMHI (1963) that the structure of vaterite (CaCO_3) was determined by x-ray methods. MEYER reported an orthorhombic cell with the dimensions $a = 4.13$, $b = 7.15$, $c = 8.48 \text{ \AA}$, space group $Pnma-V_h^{16}$, whereas KAMHI found a hexagonal cell with the dimensions $a = 4.13$, $c = 8.49 \text{ \AA}$, space group $P6_3/mmc-D_{6h}^4$. MEYER's structure is fairly consistent with KAMHI's in its unit-cell dimensions, but not in its atomic positions, especially in the site symmetry of the carbonate ion.

Many workers such as NAKAMOTO *et al.* (1957), GATEHOUSE *et al.* (1958), ADLER and KERR (1963) examined the infrared spectra of a number of carbonate compounds and showed the spectral differences related to differences in the site symmetry of the carbonate ion. These may give us further knowledge to the vaterite structure.

below. There is no considerable difference between MEYER's and KAMHI's x-ray powder data except for the 101 reflection in MEYER's results.

Site symmetry

Atomic positions and site symmetries are:

Atomic positions Site symmetries

In the structure presented by MEYER:

Ca : (4 <i>a</i>)	<i>C_i</i>
C : (4 <i>c</i>) with $x = 0.67$, $z = 0.157$	<i>C_s</i>
O(1) : (4 <i>c</i>) with $x = 0.67$, $z = 0.471$	<i>C_s</i>
O(2) : (8 <i>d</i>) with $x = 0.67$, $y = 0.118$, $z = 0.0$	<i>C_i</i>

In the structure by KAMHI:

Ca : (2 <i>a</i>)	<i>D_{3d}</i>
C : (6 <i>h</i>) with $x = 0.29$	<i>C_{2v}</i>
O(1) : (6 <i>h</i>) with $x = 0.12$	<i>C_{2v}</i>
O(2) : (12 <i>k</i>) with $x = 0.38$, $z = 0.12$	<i>C_s</i>

where two carbon atoms are randomly distributed over six positions and six oxygen atoms over eighteen positions. From the atomic positions and the site symmetries mentioned above, the site symmetries of the carbon and the carbonate ion of vaterite are derived and shown in Table 2. Those of calcite and aragonite are listed in the same table for reference.

Table 2. *Site symmetries of carbon and carbonate ion in CaCO₃ polymorphs*

	Vaterite		Calcite	Aragonite
	(MEYER)	(KAMHI)		
C	<i>C_i</i>	<i>D_{3d}</i>	<i>C_{3i}</i>	<i>C_s</i>
CO ₃	<i>C_s</i>	<i>C_{2v}</i>	<i>D₃</i>	<i>C_s</i>

Infrared spectra

The infrared spectrum of vaterite is shown in Fig. 1, and compared to these of the two other polymorphs, calcite and aragonite. The wave numbers are listed in Table 3. The characteristic features of the infrared spectrum of vaterite are:

1. the activation and splitting of ν_1 ,
2. the splitting of ν_3 ,
3. the appearance of satellites near the fundamental ν_2 .

The details of both 1 and 3 are shown in Fig. 2.

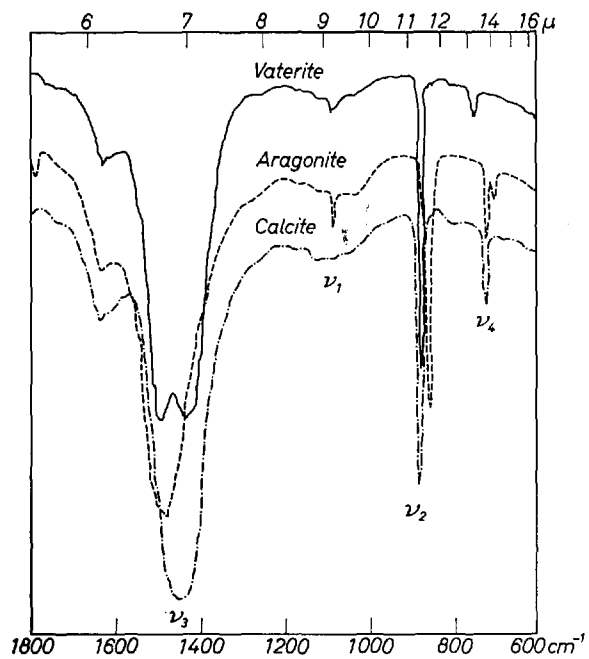
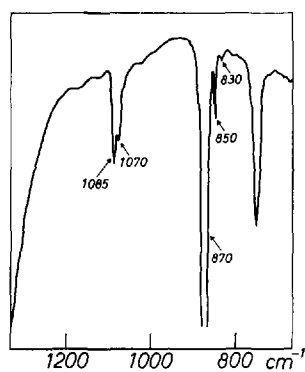


Fig. 1. Infrared absorption spectra of vaterite, aragonite and calcite

Table 3. Infrared spectra of CaCO_3 polymorphs

	ν_3	ν_1	ν_2	ν_4
Vaterite	1490, 1420	1085, 1070	870, 850, 830	750 cm^{-1}
Aragonite	1475	1080	855, 840	715, 700
Calcite	1430		870, 845	715

Fig. 2. Detailed infrared spectra of ν_1 and ν_2 in vaterite

The ideal carbonate ion has the internal symmetry D_{3h} . However, if the site symmetry is considered, D_{3h} is lowered to D_3 in calcite and to C_s in aragonite, while in vaterite it is lowered to C_s (MEYER'S model) and to C_{2v} (KAMHI'S) respectively. Correlation between D_{3h} , D_3 , C_{2v} and C_s is shown in Table 4 (WILSON *et al.*, 1955; NAKAMOTO *et al.*, 1957). We can expect from this table that in both symmetries,

Table 4. Correlation between D_{3h} , D_3 , C_{2v} and C_s

	D_{3h}	D_3	C_{2v}	C_s	assignment
ν_1	A'_1	A_1	$A_1(I)$	$A'(I)$	symmetric stretching
ν_2	$A''_2(I)$	$A_2(I)$	$B_1(I)$	$A''(I)$	out-of-plane bending
ν_3	$E'(I)$	$E(I)$	$A_1(I) + B_2(I)$	$A'(I) + A'(I)$	asymmetric stretching
ν_4	$E'(I)$	$E(I)$	$A_1(I) + B_2(I)$	$A'(I) + A'(I)$	in-plane bending

(I): infrared active.

Table 5. Infrared spectra of carbonate compounds

Compound		Symmetry	ν_3	ν_1	ν_2	ν_4
Free CO_3^{--}	1	D_{3h}	1415		879	680
CaCO_3 (calcite)	1	D_3	1430		874	710
$[\text{Co}(\text{NH}_3)_6]\text{ClCO}_3$	1	D_3	1390--1370		868	688
CaCO_3 (aragonite)	1	C_s	1470	1080	855	710, 696
BaCO_3	2	C_s	1435	1062	860	694
$(\text{Ce, La})(\text{CO}_3)\text{F}$	2	C_s	1443	1086	868	728
$\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$	2	C_{2v}	1488, 1414	1068	869	712--699
$[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{Br}$	1	C_{2v}	1450, 1370	1070	848	750
$[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{Cl}$	1	C_{2v}	1592, 1255	1025	837	752
$\text{Na}_2[\text{Cu}(\text{CO}_3)_2] \cdot 3\text{H}_2\text{O}$	3	C_{2v}	1529, 1326	1066, 1050	850	755
$\text{K}_2[\text{Co}(\text{CO}_3)_2] \cdot 4\text{H}_2\text{O}$	3	C_{2v}	1338	1082, 1049	884	799, 766
$\text{K}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$	3	C_{2v}	1527, 1330	1080, 1037	851	809
$[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{CO}_3)_3]$	3	C_{2v}	1523, 1285	1073, 1031	889	738
$[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{Cl}$	3	C_{2v}	1493, 1297	1057, 1043	873, 848	738

¹ NAKAMOTO *et al.* (1957), ² ADLER and KERR (1963), ³ GATEHOUSE *et al.* (1958).

the ν_1 mode is activated and the degeneracies of both ν_3 and ν_4 are resolved, but we can not distinguish C_{2v} from C_s in this point. Their distinction, however, is possible experimentally. The infrared spectra data of carbonate compounds presented by NAKAMOTO *et al.* (1957), GATEHOUSE *et al.* (1958) and ADLER and KERR (1963) are shown in Table 5.

The ν_1 activation is easily seen in both C_s and C_{2v} site symmetries, though, in addition, C_{2v} symmetry has frequently a characteristic splitting of ν_1 . The resolution of both ν_3 and ν_4 is not complete in C_s symmetry, while that of ν_3 is complete in C_{2v} symmetry. The frequent absence of ν_3 and ν_4 doublets in C_s symmetry has been explained by ADLER and KERR (1963) as caused by accidental degeneracy, which may also explain the absence of ν_4 doublet in C_{2v} symmetry. The satellites near the fundamental ν_2 in vaterite may be due to the coupling of the out-of-plane bending as in aragonite (DECIUS, 1955, 1963). The features in infrared spectrum of vaterite shown in Fig. 1 and Table 3 are fairly consistent with that of C_{2v} symmetry, but not with C_s . Therefore we conclude that the site symmetry of the carbonate ion in vaterite is C_{2v} , which may confirm the structure presented by KAMHI.

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