

Infrared Spectra of Amorphous and Crystalline Calcium Carbonate

Flemming A. Andersen^{*a} and Ljerka Brečević^b

^aDepartment of Chemistry, Panum Institute, University of Copenhagen, Blegdamsvej 3, DK-2200 Copenhagen N, Denmark and

^bLaboratory for Precipitation Processes, Ruđer Bošković Institute, YU-41000 Zagreb, Croatia, Yugoslavia

Andersen, F. A. and Brečević, Lj., 1991. Infrared Spectra of Amorphous and Crystalline Calcium Carbonate. – Acta Chem. Scand. 45: 1018–1024.

The infrared spectrum of an amorphous, rather unstable form of calcium carbonate has been obtained in the region 4000–400 cm^{-1} and at the temperature of liquid nitrogen. In addition the IR spectra of the crystalline polymorphs (vaterite, aragonite and calcite) have been measured on powders with higher resolution and precision than previously, in the region 4000–200 cm^{-1} without cooling and in the region 4000–400 cm^{-1} , cooling the samples by liquid nitrogen. The lack of observed pronounced doublet structure of the ν_3 band for CO_3^{2-} in vaterite and aragonite is explained as being due to the overlapping of the two component bands (ν_{3a} and ν_{3b}) by combination bands. A frequency value for the infrared-inactive normal vibration ν_1 of CO_3^{2-} in calcite has been obtained from the observed frequencies of two combination bands. More lattice frequencies than previously reported have been obtained for calcite and aragonite in the region 400–200 cm^{-1} . A revised assignment for calcite is given. For vaterite, lattice bands have been measured for the first time and an assignment of the bands to lattice modes is proposed on the basis of a factor group analysis of the external modes of CO_3^{2-} .

The infrared spectra of the crystalline polymorphs calcite and aragonite of calcium carbonate measured for single crystals and for powders have been reported by many workers.^{1–15}

Most of the investigations have been carried out using prism instruments. The metastable crystalline modification vaterite has only been the subject of a few IR measurements in the mid-infrared on powders.^{1,7,11,12,13} No measurements on single crystals of vaterite have been reported, nor have IR spectra of powders of vaterite in a pure state been published below 400 cm^{-1} . In the case of amorphous calcium carbonate, only two IR spectra have to our knowledge appeared in the literature,^{2,16} except for two frequencies reported by Louisfert and Pobeguain.¹ Brečević and Nielsen¹⁷ have recently studied the solubility of an amorphous rather unstable calcium carbonate. Among the other observations, they showed that its IR spectrum differs from the spectra of the known crystalline polymorphs. Because amorphous calcium carbonates are precursors to the crystalline polymorphs we thought it of interest to study the infrared spectrum of amorphous calcium carbonate in more detail. Furthermore, we have measured the infrared spectra on powders of calcite, aragonite and vaterite in the region 4000–200 cm^{-1} because there are disagreements among the mid-infrared powder data reported previously for these crystalline modifications (see Table 2 later) and because the infrared data published for calcite and aragonite in the region 400–200 cm^{-1} do not seem entirely satis-

factory; finally, data for vaterite have not been reported in this region.

Experimental

Amorphous calcium carbonate. This was prepared at 283 K. Calcium chloride solution was placed in a beaker containing a magnetic stirrer, and a small volume of concentrated sodium carbonate solution was quickly added to make 150 ml of a solution initially 4×10^{-3} mol l^{-1} in calcium and carbonate. The precipitate formed within 20 s and was filtered through a membrane filter (0.22 μm pore diameter) 3–5 min after reactants had been mixed. To prevent its transformation into a more stable form, the substance was immediately freeze-dried and was subsequently kept in liquid nitrogen.

Vaterite. The following procedure yielded the substance in a sufficiently pure form. 250 ml of 5×10^{-3} mol l^{-1} sodium carbonate solution were placed in a beaker immersed in an ultrasound bath at room temperature. From a separation funnel 250 ml of 6×10^{-2} mol l^{-1} calcium chloride solution were added in the course of 1 h. Spherulites of vaterite were formed. The substance was filtered off and dried in a desiccator over silica gel.

Calcite. The method of preparation described for vaterite was followed until the suspension had been obtained. Then the suspension was stirred mechanically for another 24 h at room temperature during which period the precipitate

* To whom correspondence should be addressed.

changed into calcite crystals, which were then filtered off and dried in a desiccator.

Aragonite. Crystals of aragonite were synthesized following the method of Angus *et al.*¹⁸ with slight changes. Artificial sea-water was made by dissolving 23.5 g NaCl, 5.0 g MgCl₂ · 6H₂O, 0.024 g SrCl₂ and 1.5 g CaCl₂ · 6H₂O in 1000 ml of water. 500 ml of this solution were heated to 60 °C and stirred continuously while 100 ml of sodium carbonate solution (0.6 g l⁻¹) were added uniformly during 15 min.

Another 100 ml portion of the same solution was then added at a constant rate during 3 h and the system was stirred overnight. The aragonite crystals adhered to the glass walls. After being scraped off, they were filtered, rinsed with water and dried at 100 °C for 3 h. The product was kept in a desiccator over silica gel.

The IR spectra were recorded in the region 4000–200 cm⁻¹ with a Perkin–Elmer model 225 spectrophotometer purged by CO₂-free dry air. Potassium bromide and caesium iodide pellets containing 0.2–2 mg of the sample in 300 mg alkali halide were used. The spectra were also recorded at low temperature in the region 4000–400 cm⁻¹. During these experiments the KBr pellets were placed in an evacuated Specac P/N 21.000 variable-temperature cell and cooled by liquid nitrogen. A blank pellet mounted in a variable-temperature cell of the abovementioned type served as a reference. During this procedure the spectrometer was not purged with dry CO₂-free air. The resolution in the spectra was 1–2 cm⁻¹ in the 4000–450 cm⁻¹ region and 2–2.5 cm⁻¹ in the 450–200 cm⁻¹ region. The accuracy of the frequencies given is believed to be ± 0.5–1 cm⁻¹ for narrow bands, ± 1–2 cm⁻¹ for broad bands and ± 2–3 cm⁻¹ for shoulders.

Results and discussion

The free carbonate ion belongs to the point group D_{3h} and therefore has four normal vibrations, one of species A'_1 , one of species A''_2 and two of species E' as shown in Table 1.¹⁹ However, for CO₃²⁻ in the solid phase, i.e. for amorphous and crystalline carbonates, the symmetry of CO₃²⁻ will be lowered.

Table 1. Correlation scheme for D_{3h} , D_3 and C_s .^a

D_{3h}	D_3	C_s
$A'_1(R)(\nu_1)$	$A_1(R)(\nu_1)$	$A'(I,R)(\nu_1, 2\nu_3, 2\nu_4)$
$A''_2(I)(\nu_2)$	$A_2(I)(\nu_2)$	
$E'(I,R)(\nu_3, \nu_4)$	$E(I,R)(\nu_3, \nu_4)$	$A''(I,R)(\nu_2)$

^a1, infrared active; R, Raman active; $\nu_1, \nu_2, \nu_3, \nu_4$, the normal vibrations of the carbonate ion. ν_1 , symmetric C–O stretching mode; ν_2 , CO₃ out-of-plane deformation mode; ν_3 , asymmetric C–O stretching mode; ν_4 , OCO bending (in-plane deformation) mode.

In the amorphous phase all four internal normal modes of the carbonate ion are expected to be infrared active. Furthermore, one would expect that the degeneracy of ν_3 and ν_4 for the free carbonate ion is lifted, so that a total of six fundamentals are allowed in the IR spectrum. If the splitting of the ν_3 and ν_4 bands is not resolved, only four fundamental bands will be observed.

In the IR spectrum of the amorphous CaCO₃, which has been shown to be non-crystalline by X-ray powder diffraction,¹⁷ absorption bands appear in the regions 1500–1400, 1100–1000, 900–800 and close to 700 cm⁻¹, just as for the crystalline modifications, (Fig. 1). The two broad bands of medium intensity observed at 1067 and 864 cm⁻¹ are assigned as ν_1 and ν_2 , respectively. Louisfert and Pobeguain¹ report bands at 1073 and 790 cm⁻¹; Pobeguain² and Dupuis *et al.*¹⁶ observed bands at 1078, 1020, 866 and 798 cm⁻¹ and at 1075, 1030, 860, 735, 705 and 690 cm⁻¹, respectively, for amorphous samples of CaCO₃, some of these frequencies being in good agreement with those obtained by us. The strong broad absorption in the 1500–1400 cm⁻¹ region and the very weak absorption around 700 cm⁻¹ must be due to the normal modes ν_3 and ν_4 , respectively. As seen in Fig. 1(A), these bands are split, the band maxima of the components being observed at 1490 and 1425 cm⁻¹ (ν_{3a} and ν_{3b}) and 725 and 690 cm⁻¹ (ν_{4a} and ν_{4b}), respectively. In Fig. 2, the part denoted CR displays an expanded spectrum (900–680 cm⁻¹) showing the broad ν_2 band and the very weak bands corresponding to ν_{4a} and ν_{4b} (indicated by arrows). The two weak bands at 1793 and 1760 cm⁻¹ [Fig. 1(A)] have been assigned to the combinations $\nu_1 + \nu_{4a} = 1792$ cm⁻¹ and $\nu_1 + \nu_{4b} = 1757$ cm⁻¹, respectively. According to Brečević and Nielsen,¹⁷ amorphous calcium carbonate contains less than one molecule of water per molecule of CaCO₃ in its structure. The bands corresponding to the three normal vibrations of the water molecule were found at about 3375 and 3230 cm⁻¹ (antisymmetric and symmetric OH stretches) and at 1640 cm⁻¹ (HOH bending).

For the crystalline modifications of CaCO₃ the number of fundamental bands for the carbonate ion which appear in the IR spectra are governed by the selection rules given in Table 1. The site symmetry for CO₃²⁻ in calcite and aragonite has been given as D_3 and C_s , respectively, by Halford²¹ from the crystal structure as determined by X-ray diffraction measurements. For vaterite the crystal structure has been subject to some argument.^{13,22–24} However, a site symmetry of C_s for the carbonate ion seems compatible with the X-ray diffraction work by Meyer²⁴ because of the placing of CO₃²⁻ around the mirror plane $z = 1/4$. Because the degeneracy of ν_3 and ν_4 is lifted, a splitting of the ν_3 and ν_4 bands as observed for the amorphous CaCO₃ is expected for aragonite and vaterite. Fig. 2 shows that for aragonite the ν_4 band appears as a doublet (ν_{4a} and ν_{4b}) at low temperature as well as at normal temperature. The splitting of the ν_4 mode has been observed in the IR spectra by several investigators (Table 2) but was observed for the first time in Raman spectra by Rives-Arnau *et al.*²⁵ For vaterite the two components are resolved at low temperature, while at nor-

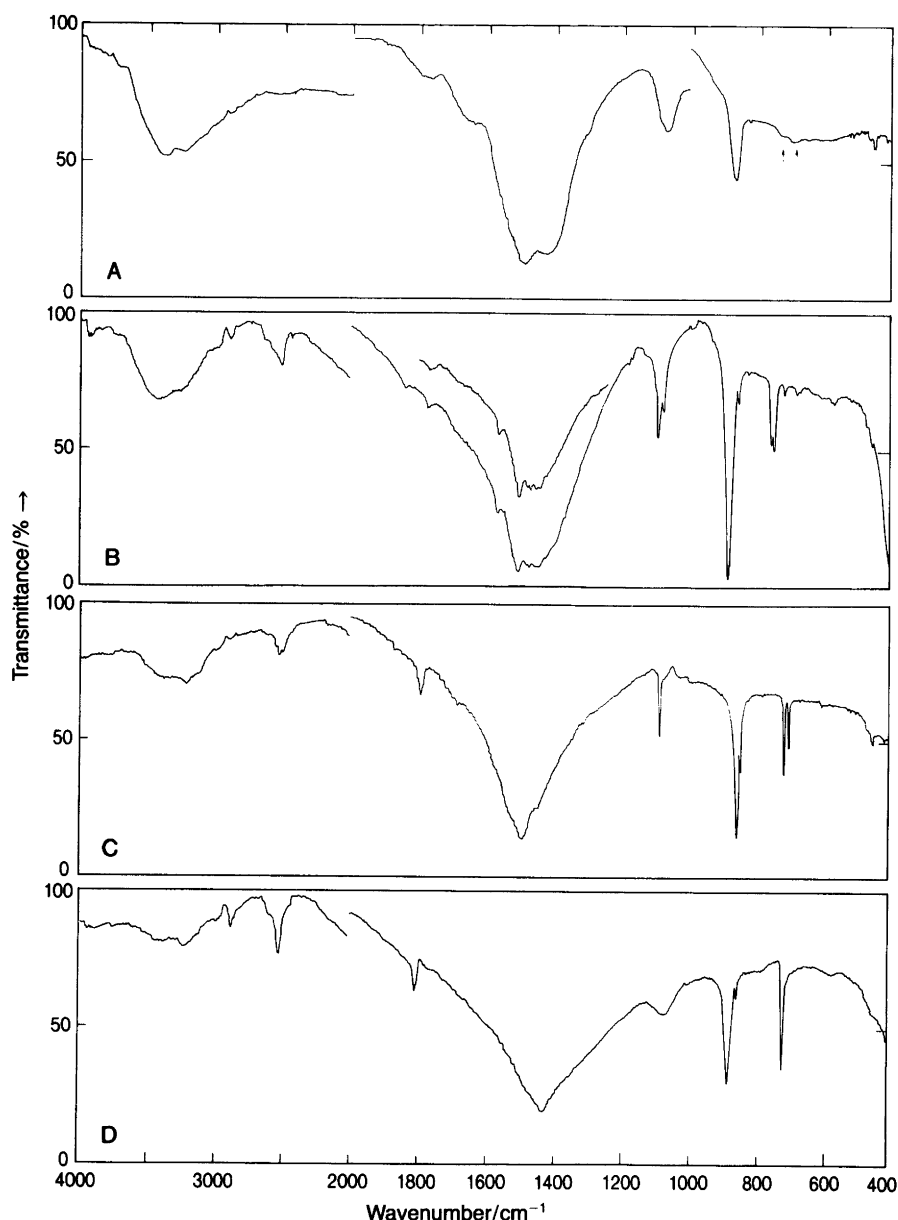


Fig. 1. Infrared spectra of (A) amorphous CaCO_3 , (B) vaterite, (C) aragonite and (D) calcite in KBr pellets cooled by liquid nitrogen with about 0.4–0.6 mg of sample in each pellet.

mal temperature the low-frequency component appears as a shoulder.

For the ν_3 band no distinct splitting is observed at normal temperature either for aragonite or for vaterite. Careful examination of the strong broad absorption in the 1600–1400 cm^{-1} region at normal temperature and at low temperature [Figs. 1(B) and (C)], however, indicates that this absorption originates from several overlapping bands. For aragonite bands have been estimated at 1570, 1525, 1488, 1473 and 1440 cm^{-1} , the bands at 1488 and 1440 cm^{-1} being assigned to the two components of ν_3 . The band observed at 1473 cm^{-1} we have assigned to the combination $220 + 263 + 290 + \nu_{4b} = 1473 \text{ cm}^{-1}$, the 220, 263 and 290 cm^{-1} bands being associated with lattice modes. The 1525 cm^{-1} band may be explained as $2 \times 220 + \nu_1 = 1523 \text{ cm}^{-1}$ and the band at 1570 cm^{-1} as $\nu_2 + \nu_{4a} = 1566 \text{ cm}^{-1}$. In the spectrum of vaterite bands have been found at about 1487, 1470,

1445 and 1418 cm^{-1} . We have assigned the bands at 1487 and 1445 cm^{-1} to ν_{3a} and ν_{3b} , respectively. The two other bands have been explained as due to combinations of a lattice mode and ν_1 , $332 + \nu_1 = 1421 \text{ cm}^{-1}$ and $383 + \nu_1 = 1472 \text{ cm}^{-1}$.

The paper by Sato and Matsuda¹³ includes an IR spectrum of vaterite showing a nicely split band in the region 1500–1400 cm^{-1} , the frequencies of the two component bands being 1490 and 1420 cm^{-1} . It has not been possible for us to obtain such a band structure, either at normal or at low temperature.

The weak band at 1077 cm^{-1} on the low-frequency side of the ν_1 band in the spectrum of vaterite is explained as the combination $332 + \nu_{4a} = 1078 \text{ cm}^{-1}$, while the weak satellite bands on the low-frequency side of the ν_2 bands in the spectra of all three crystalline modifications have been explained by Sterzel and Chorinsky¹² and by Sterzel²⁶ as

Fig. 2. Expanded IR spectra of (A) vaterite, (B) aragonite and (C) calcite at normal temperature (AL, BL and CL) and at low temperature (AR, BR and CR). An IR spectrum of amorphous CaCO_3 is included in CR.

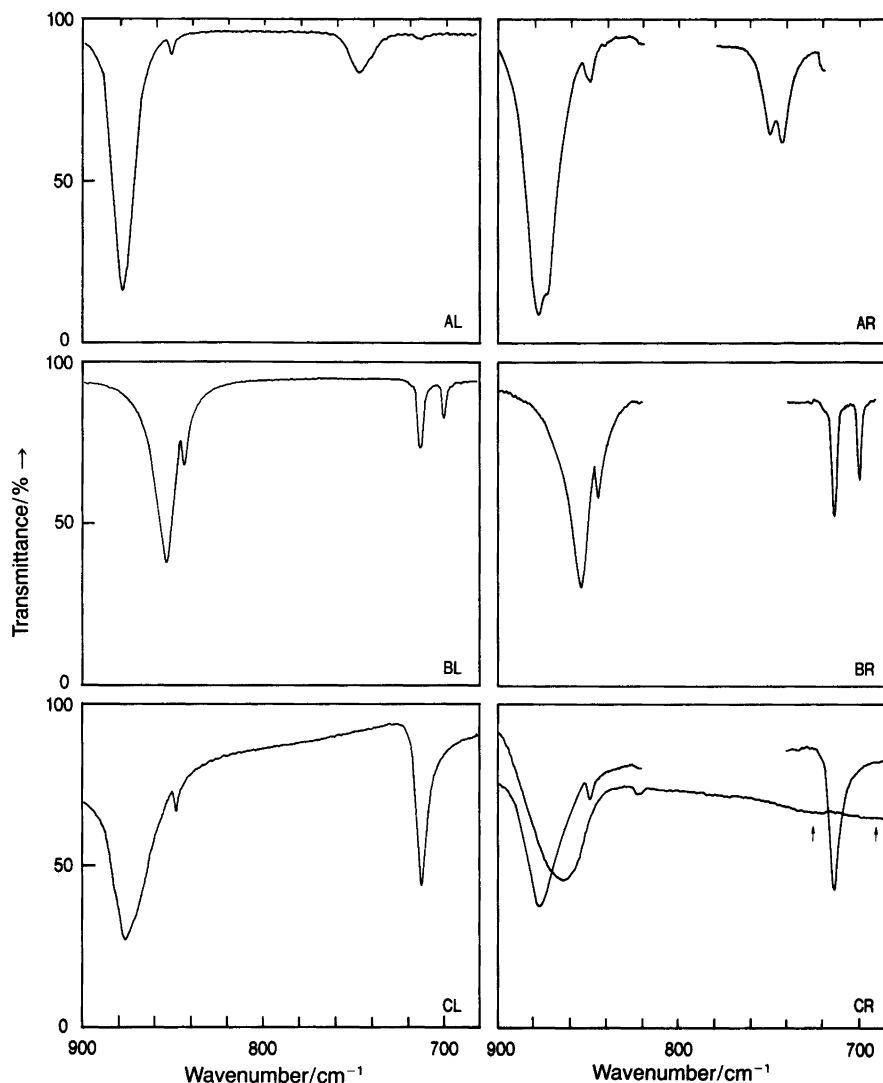


Table 2. Wavenumbers (in cm^{-1}) corresponding to the internal modes of the carbonate ion in calcite, aragonite and vaterite obtained by a number of other investigators from the IR absorption of powders.

Ref.	Calcite				Aragonite				Vaterite			
	1	2	3	4	1	2	3	4	1	2	3	4
3		874	1430	710	1080	855	1470	710				
								696				
6		876	1435	712	1085	875	1470	712				
								699				
7	1087?	881	1432	712	1087	866	1550	715	1090	878	1450	741
							1430	703				
9		877	1422	713	1084	859	1472	713				
								699				
11		877	1435	712	1082	859	1485	712	1088	876	1480	745
								699			1440	
12		877	1419	713	1083	857	1511	713	1089	877	1450	744
							1489	700				
13		870	1430	715	1080	855	1475	715	1085	870	1490	750
								700			1420	
14	1079	876		713	1081	853		712				
								694				

Table 3. Observed normal vibration frequencies (in cm^{-1}) of the carbonate ion in the amorphous form and in the three crystalline forms of calcium carbonate.

Normal vibrations	Amorphous form ^b	Vaterite		Aragonite		Calcite	
		a	b	a	b	a	b
ν_1	1067	1089	1088	1083	1085	—	—
ν_2	864	877 873	878 873	854	854	877	876
ν_3	(ν_{3a}) (ν_{3b})	1490 1425	1487 1443	1488 1440	1490 1442	1420	1423
ν_4	(ν_{4a}) (ν_{4b})	725 690	746 743	713 700	714 700	713	713

^aNo cooling of the KBr pellets. ^bKBr pellets cooled by liquid nitrogen.

being due to the ν_2 mode of $^{13}\text{CO}_3^{2-}$ originating from the natural abundance of the ^{13}C isotope. However, other explanations have also been given.²⁷ The rather intense band at 873 cm^{-1} which appears as a shoulder on the low-frequency side of the ν_2 of vaterite (Fig. 2) may be explained as a summation band ν_4 plus a lattice mode in the frequency range $120\text{--}130\text{ cm}^{-1}$ or it may be the result of factor group splitting.

The values of the fundamental frequencies for CO_3^{2-} in vaterite, aragonite and calcite obtained in the present investigation (Table 3) compares well with the values of Sterzel and Chorinsky¹² except for the fundamentals ν_{3a} and ν_{3b} of CO_3^{2-} in aragonite and vaterite.

A frequency value of the infrared-inactive fundamental ν_1 of calcite has been determined from the frequencies of the two combination bands $\nu_1 + \nu_3$ and $\nu_1 + \nu_4$ observed at 2510 and 1800 cm^{-1} , respectively, for samples at low tem-

perature, resulting in the values 1089 and 1087 cm^{-1} for ν_1 , the average value 1088 cm^{-1} being in perfect agreement with the value (1088 cm^{-1}) obtained from polarized Raman spectra of calcite by Porto *et al.*²⁸

For all three crystalline polymorphs bands due to lattice modes have been observed in the $450\text{--}200\text{ cm}^{-1}$ region (Fig. 3). The observed frequency values are given in Table 4, together with values for aragonite and calcite obtained by other workers. No frequencies for the IR-active lattice modes of vaterite seem to have been published. Liebisich and Rubens²⁹ obtained lattice frequencies for aragonite and calcite using IR reflexion from single crystals, Louisfert³⁰ have reported lattice frequencies for calcite obtained from IR absorption of lamellae, and Morandat *et al.*³¹ have published frequencies for calcite and aragonite obtained from IR spectra of powders. Miller *et al.*³² have reported one IR lattice band for aragonite.

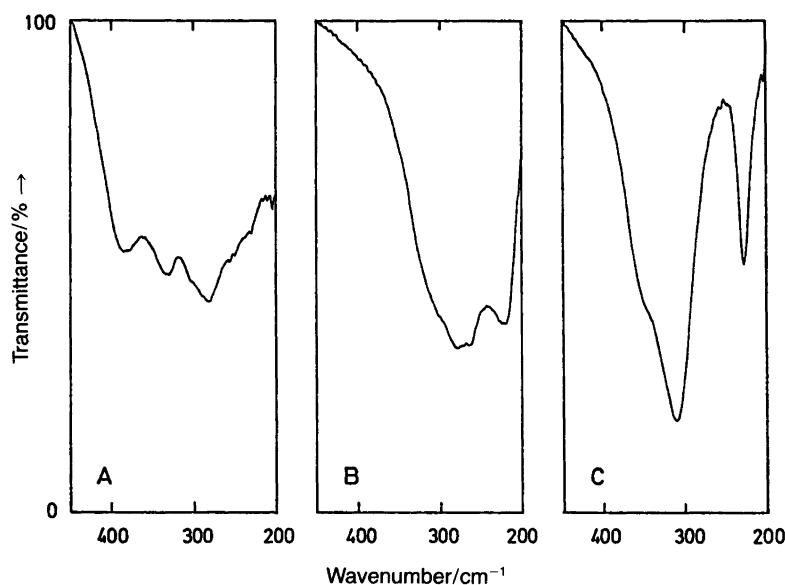


Fig. 3. Infrared spectra of (A) vaterite, (B) aragonite and (C) calcite at normal temperature in the region $450\text{--}200\text{ cm}^{-1}$, with 0.7 ± 0.1 mg of sample in each CsI pellet.

Table 4. Observed lattice frequencies (in cm^{-1}).

Vaterite	Aragonite			Calcite				
	This work	^a	^b	This work	^a	^c	^d	^b
383 (A_{2u})	315	315 ^e		354	312	309 or 342	338 (A_{2u})	360
332 (E_{1u})	290			311	312	342 or 309	310 (E_u)	335
282 (E_{1u})	280		294 (B_{2u})	227	229	229	176 (E_u)	182
250 (E_{1u})	273	267	274 (B_{1u})		106	109	106 (A_{2u})	106
232 (E_{1u})	263		274 (B_{3u})		106	109	86 (E_u)	106
	237	235	(200) (B_{1u})					
	220	216	(200) (B_{2u})					
		165	200 (B_{3u})					
			118 (B_{1u})					
		106	114 (B_{2u})					
			(100) (B_{3u})					

^aIR absorption of powders, Ref. 31. ^bIR reflexion from single crystals, Refs. 29 and 30. ^cIR absorption of powders, Ref. 14. ^dIR absorption of lamellae, Ref. 30. ^eValue from Ref. 32.

Our results for calcite and aragonite provide an extension of the previously published data for these two polymorphs. For calcite the pronounced shoulder observed at 354 cm^{-1} has been assigned as the lattice vibration belonging to species A_{2u} , and the very strong broad absorption at 311 cm^{-1} is therefore due to a lattice vibration of species E_{1u} . For aragonite, having 11 IR-active lattice modes, seven vibrations and four librations, more bands have been observed by us in the region $300\text{--}200 \text{ cm}^{-1}$ than are reported by Morandat *et al.*³¹ The assignment of the lattice bands of aragonite is, however, complicated because of the orthorhombic structure of the crystal. Couture³³ has worked out vector diagrams for the factor group vibrations analogous to those given for calcite. The diagrams for the external modes for calcite as constructed by Cabannes³⁴ are shown in the paper by Morandat *et al.*,³¹ and they are also given by Nakamoto, together with diagrams for the internal modes.²⁰ Morandat *et al.* assign the strong band at 267 cm^{-1} in the IR spectrum of aragonite to three vibrations, $B_{1u} + B_{2u} + B_{3u}$, corresponding to antitranslation of the calcium and carbonate ions. As seen in Table 4, we find at least three bands in this region at 280, 273 and 263 cm^{-1} .

No factor group analysis of the external modes of CO_3^{2-} in vaterite has to our knowledge appeared in the literature. According to Meyer,²⁴ the space group for vaterite is D_{6h}^4 ($= P6_3/mmc$), with the Ca^{2+} ions on the 2(a) sites with D_{3d} symmetry, in agreement with the result of Kamhi.²³ However, the CO_3^{2-} ions seem to be distributed over 12(j) sites with site symmetry C_s , because of the placing of CO_3^{2-} around the mirror plane $z = 1/4$, the carbon atom and the oxygen atom O(1) being on the plane and the two oxygen atoms O(2) being placed over and below the mirror plane on an axis perpendicular to the plane (the z -axis). A factor-group analysis of the lattice modes gave eqns. (1) and (2).

$$\Gamma_{\text{Ca}}^{\text{lib}} + \Gamma_{\text{CO}_3}^{\text{lib}} = A_{2u}^{\text{IR}} + 4E_{1u}^{\text{IR}} + 2A_{1g}^{\text{R}} + 2E_{1g}^{\text{R}} + 4E_{2g}^{\text{R}} \quad (1)$$

$$+ A_{1u} + 2B_{1u} + 3B_{2u} + 3E_{2u} + 2A_{2g} + B_{1g} + B_{2g}$$

$$\Gamma_{\text{CO}_3}^{\text{lib}} = A_{2u}^{\text{IR}} + 2E_{1u}^{\text{IR}} + A_{1g}^{\text{R}} + 4E_{1g}^{\text{R}} + 2E_{2g}^{\text{R}} \quad (2)$$

$$+ A_{1u} + B_{1u} + B_{2u} + 4E_{2u} + A_{2g} + 2B_{1g} + 2B_{2g}$$

This means that there are eight IR-active lattice modes, five vibrations and three librations, and 15 lattice modes which are active in the Raman spectrum. There are 25 modes which are inactive in the IR as well as in the Raman spectrum. Three acoustic modes, $A_{2u} + 2E_u$, have been omitted. In the region $450\text{--}200 \text{ cm}^{-1}$ we have observed five bands (Table 4), three strong and rather broad bands at 383, 332 and 282 cm^{-1} and two shoulders at about 250 and 232 cm^{-1} . The five bands probably correspond to translational oscillations of the ions ($A_{2u} + 4E_{1u}$), the three strong bands at 383, 332 and 282 cm^{-1} probably being due to antitranslational vibrations of the calcium and carbonate ions. The remaining three lattice bands, which then correspond to librations ($A_{2u} + 2E_{1u}$), are expected to be found below 200 cm^{-1} .

Acknowledgements. We thank Professor Arne E. Nielsen, Department of Chemistry, Panum Institute, University of Copenhagen, and Dr. Peter Andersen, The H. C. Ørsted Institute, University of Copenhagen, for helpful discussions.

References

- Louisfert, J. and Pobeguïn, T. C. R. *Hebd. Séanc. Acad. Sci. Paris* 235 (1952) 287.
- Pobeguïn, T. J. *Phys. Radium* 15 (1954) 410.
- Nakamoto, K., Fujita, J., Tanaka, S. and Kobayashi, M. J. *Am. Chem. Soc.* 79 (1957) 4904.
- Baron, G., Caillere, C., La Grange, R. and Pobeguïn, T. *Bull. Soc. Fr. Crist.* 82 (1959) 150.
- Pobeguïn, T. C. R. *Hebd. Séanc. Acad. Sci. Paris* 248 (1959) 2220.
- Huang, C. K. and Kerr, P. F. *Amer. Mineral.* 45 (1960) 311.

7. Weir, C. E. and Lippincott, E. R. *J. Res. Natl. Bur. Stand., Ser. A* 65 (1961) 173.
8. Adler, H. H. and Kerr, P. F. *Amer. Mineral.* 47 (1962) 700.
9. Adler, H. H. and Kerr, P. F. *Amer. Mineral.* 48 (1963) 124.
10. Adler, H. H. and Kerr, P. F. *Amer. Mineral.* 48 (1963) 839.
11. Moencke, H. *Mineralspektren I, Berlin* (1963–66).
12. Sterzel, W. and Chorinsky, E. *Spectrochim. Acta, Part A* 24 (1968) 353.
13. Sato, M. and Matsuda, S. *Z. Kristallogr.* 129 (1969) 405.
14. Donoghue, M., Hepburn, P. H. and Ross, S. D. *Spectrochim. Acta Part A* 27 (1971) 1065.
15. Frech, R., Wang, E. C. and Bates, J. B. *Spectrochim. Acta Part A* 36 (1980) 915.
16. Dupuis, T., Ducloux, J., Butel, P. and Nahon, D. *Clay Miner.* 19 (1984) 605.
17. Brečević, L. and Nielsen, A. E. *J. Cryst. Growth* 98 (1989) 504.
18. Angus, J. G., Raynor, J. B. and Robson, M. *Chem. Geol.* 27 (1979) 181.
19. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th Ed., Wiley, New York 1986, p. 88.
20. Nakamoto, K. *Ibid.*, p. 93.
21. Halford, R. S. *J. Chem. Phys.* 14 (1946) 8.
22. Meyer, H. J. *Angew. Chem.* 71 (1959) 678.
23. Kamhi, S. R. *Acta Crystallogr.* 16 (1963) 770.
24. Meyer, H. J. *Z. Kristallogr.* 128 (1969) 183.
25. Rives-Arnau, V., Munuera, G. and Criado, J. M. *Spectrosc. Lett.* 12 (1979) 733.
26. Sterzel, W. *Z. Anorg. Allg. Chem.* 368 (1969) 308.
27. Farmer, V. C. *The Infrared Spectra of Minerals*, Mineralogical Society, London 1974, Monogr. 4, p. 245.
28. Porto, S. P., Giordmaine, J. A. and Damen, T. C. *Phys. Rev.* 147 (1966) 608.
29. Liebisch, T. and Rubens, H. *Sitzber. Preuss. Akad. Wiss.* 12 (1919) 198.
30. Louisfert, J. C. *R. Hebd. Séanc. Acad. Sci. Paris* 248 (1959) 1150.
31. Morandat, J., Lorenzelli, V. and Le Comte, J. *Physique* 28 (1967) 152.
32. Miller, F. A., Carlson, G. L., Bentley, F. F. and Jones, W. H. *Spectrochim. Acta* 16 (1960) 135.
33. Couture, L. *Ann. Phys., Ser. 12* (2) (1947) 5.
34. Cabannes, J. *Rev. Scientifique* 80 (1942) 407.

Received March 22, 1991.