Vibrational Spectroscopy at Very High Pressures. Part 26.[†] An Infrared Study of the Metastable Phases of Ca[CO₃]

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Infrared and far-i.r. spectra of $Ca[CO_3]$ have been recorded under hydrostatic conditions in a diamond anvil cell to 40 kbar. The new data are analysed in conjunction with the Raman results of Fong and Nicol. The spectra of $Ca[CO_3]$(II) are shown to be consistent with a recent *X*-ray single-crystal structure, with site rather than factor-group selection rules accounting for most features. For $Ca[CO_3]$(III) a structure is postulated in which there are two crystallographically-distinct sets of anions in a primitive cell with *Z* being at least four and probably eight.

AT ambient conditions the thermodynamically stable phase of calcium carbonate adopts the calcite$\equiv Ca[CO_3]$(I) structure. In 1939 Bridgman [1] found, from *P–V* measurements, that phase transitions occurred at room temperature at 14 and 17 kbar (1 kbar = 0.1 GPa = 10^8 N m^{-2}) yielding, successively, $Ca[CO_3]$(II) and $Ca[CO_3]$(III). These new phases lie within the stability field of aragonite (which is denser [2]) and are believed to be metastable with respect to it. Values for the transition pressures have recently been revised to 15 and 22 kbar.[3] Calcite and aragonite are directly interconvertible at elevated pressures combined with temperatures of 200—600 °C.[4]

TABLE 1

Structural data for the solid phases of $Ca[CO_3]$

Phase	Calcite $Ca[CO_3]$ (I)	$Ca[CO_3]$ (II)	$Ca[CO_3]$ (III)	Aragonite	Vaterite
Crystal system	Rhombohedral	Monoclinic	Not known	Orthorhombic	Hexagonal
Space group	$R\bar{3}c \equiv D^6_{3d}$	$P2_1/c \equiv C^5_{2h}$		$Pnma \equiv D^{16}_{2h}$	$P6_3/mmc \equiv D^4_{6h}$
Z	2	4		4	12 [a]
Atom sites	Ca 2*b* C 2*a* O 6*e*	All on 4*e* (general)		Ca 4*c* C 4*c* O 4*c*, 8*d*	
CO_3^{2-} site symmetry	D_3	C_1		C_s	
Reference	*b*	3		*b*	*c*, *d*

[a] The structure is complex with a sub-cell having *Z* = 2. [b] R. W. G. Wyckoff, ' Crystal Structures,' 2nd edn., Interscience, New York, 1967, vol. 2. [c] H. J. Meyer, *Z. Kristallogr.*, *Kristallgeom.*, *Kristallphys.*, *Kristallchem.*, 1969, **128**, 183. [d] M. Sato and S. Matsuda, *Z. Kristallogr*, *Kristallgeom.*, *Kristallphys. Kristallchem.*, 1969, **129**, 405.

A definitive *X*-ray diffraction study of single-crystal $Ca[CO_3]$(II) by Merrill and Bassett [3] showed it to be monoclinic, $P2_1/c$, with a tetramolecular cell. On the basis of *X*-ray powder diffraction data it has been suggested that $Ca[CO_3]$(III) and $K[NO_3]$(IV) are isostructural. However, the single-crystal work on $Ca[CO_3]$(II) showed how unreliable conclusions drawn from powder data only can be: on this basis alone the structure of $Ca[CO_3]$(III) must be considered indeterminate but we also note that the high-pressure Raman spectra of $Ca[CO_3]$(III) are inconsistent with the $K[NO_3]$(IV) structure type.[5] Structural data for the various solid phases of $Ca[CO_3]$ are shown in Table 1.

An *X*-ray powder pattern investigation showed that up to 24 kbar there is no phase transition in either aragonite or vaterite.[2]

The metastable phases of $Ca[CO_3]$ have been investigated previously by i.r. spectroscopy using diamond anvil cells (d.a.c.s).[6-8] However, the work suffers from two serious deficiencies. (i) In none of it was the sample material contained within a gasket: hence, due to the large shear stresses present, pure phases were not obtained. (ii) The far-i.r. region was not investigated. The only extant Raman work on $Ca[CO_3]$(II), (III) is that of Fong and Nicol.[5]

EXPERIMENTAL

Fine Calcite powder was loaded into the d.a.c. without grinding since that process would probably have induced transformation to aragonite. The inconel gasket had a hole initially of 0.5 mm diameter and was 0.05 mm thick. Nujol was used as the pressure transmitting medium. Pressures were estimated by use of the ruby *R*-line method.

Far-i.r. spectra were obtained using a Beckman-RIIC FS-620 interferometer modified by conversion to off-axis optics. Mid-i.r. spectra were studied by use of a Perkin-Elmer 580 spectrophotometer, with a beam condenser using KBr lenses.

RESULTS AND DISCUSSION

Data are given in Tables 2 and 3 and Figures 1 and 2. Selection rules for CO_3^{2-} internal modes in $Ca[CO_3]$(I) and (II) are given in Table 4 and factor group analyses in Table 5 (obtained by the method of Adams and Newton [9]).

[†] Part 25, D. M. Adams and A. D. Williams, *J. Phys. and Chem. Solids*, in the press.

TABLE 2

Mid-i.r. wavenumbers (cm^{-1}) for $\mathrm{Ca[CO_3]}$ at ambient temperatures and various pressures; u = unresolved

Pressure/kbar	$\nu_1 + \nu_4$	ν_1	ν_2	ν_4	Phase
0.001					Calcite/I
4.7	1 795vw		877s,br	715s	
10.0	1 802vw	1 090vw	880s,br	717s	
16.6	1 802vw	1 088m	875s,br	712s	II
18.0	1 805w	1 092m	874s,br	735 (sh), 713s	II/III intergrowths
22.3	*ca.* 1 815w,br	1 090ms 1 080 (sh)	875s,br	738s, 722s, 712s, 685m	
23.3	*ca.* 1 815w,br	1 090s 1 080 (sh)	875s,br	737s, 722s, 710s, 685m	
32.7	*ca.* 1 835vw *ca.* 1 780vw	1 092s ush	876s,br	740s, 727 (sh), 685ms	III
39.0	*ca.* 1 835vw *ca.* 1 780vw	1 094s ush	876s,br	740s, 730 (sh), 685s	III

Mid-i.r. Spectra.—The ν_1 region. The transition from $\mathrm{Ca[CO_3](I)}$ = calcite to $\mathrm{Ca[CO_3](II)}$ is heralded by appearance of a strong band in the ν_1 region at 1 088 cm^{-1} in the 16.6 kbar spectrum. This is particularly dramatic as ν_1 is i.r.-forbidden in $\mathrm{Ca[CO_3](I)}$, see Table 4, although in fact there is very weak absorption *ca.* 1 090 cm^{-1} in the 10.0 kbar spectrum. Appearance of weak, formally forbidden, i.r. absorption in the ν_1 region has been found for many materials which adopt the calcite structure but the reason for it is not yet established. The ν_1 absorption appears as a single sharp band, within the limits of our resolution (3.7 cm^{-1}). In the 22.3 kbar spectrum a second component is clearly present; as this is just within the $\mathrm{Ca[CO_3](III)}$ region, and as the structure then persists to higher pressures, we consider that it is properly attributed to the higher pressure phase.

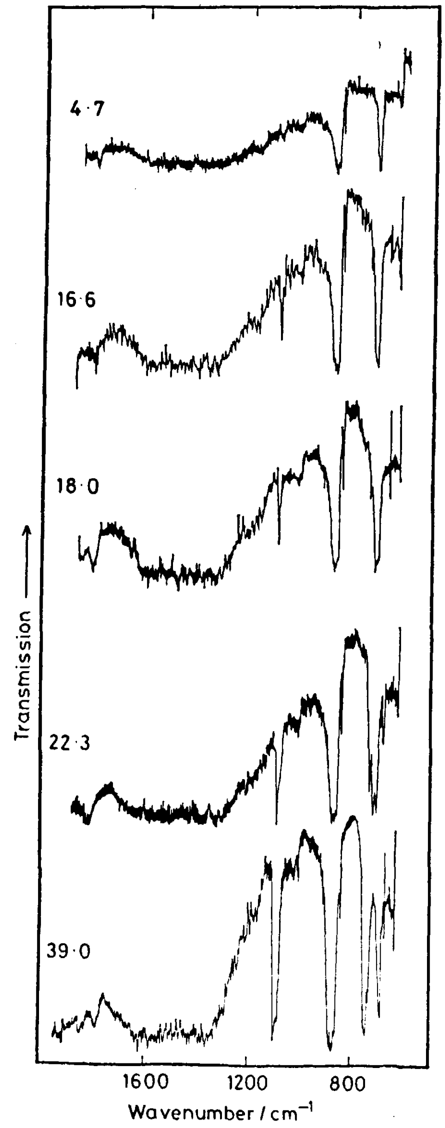

FIGURE 1 Mid-i.r. spectra of $\mathrm{Ca[CO_3]}$ at various pressures (kbar). Spectral slit width 3.7 cm^{-1}

In their Raman study of $\mathrm{Ca[CO_3]}$ at high pressures, Fong and Nicol also found ν_1 to be a single band. Comparison of their results with our own on a semi-quantitative basis is subject to two uncertainties. Firstly, the Drickamer cell design (which they used) is known to subject the sample to a small shear stress in addition to compression and this may well affect the frequencies of the vibrational modes. Secondly, although there is no reason to doubt their pressure estimates, they were not made using the now almost universal ruby *R*-line technique (which they pre-dated). However, useful comparisons between our two sets of data can still be made.

For $\mathrm{Ca[CO_3](II)}$ both Raman and i.r. spectra should exhibit a doublet in the ν_1 region, Table 4, if full factor-group splitting occurs. As this is plainly not the case, we

TABLE 3

Far-i.r. wavenumbers (cm^{-1}) for $\mathrm{Ca[CO_3]}$ at ambient temperature and various pressures [a]

Pressure/kbar	0.001	9.6	15.9	20.0	29.1
	103 [b]	105 [b]	102 113	117	117
					133
				163	*ca.* 160 *ca.* 172
			188	192	
	222	231	232		
	>250 [c]	>270	*ca.* 280	>200	>200
			>300		
Phase	I	I	II	II	III

[a] To be read in conjunction with Figure 2(*b*). Bands below 100 cm^{-1} are considered to be unreliable and may be artefacts. [b] Known to be the average of two bands. [c] Indicates several unresolved bands above this value.

TABLE 4

Selection rules for the internal modes of Ca[CO$_3$](I) and (II)

			Ca[CO$_3$] (I) ≡ Calcite			Ca[CO$_3$] (II)	
	D_{3h} Ion			$D_3 \xrightarrow{\times 2}$ Site	D_{3d} [a,b] Crystal	$C_1 \xrightarrow{\times 4}$ Site	C_{2h} [b] Crystal
ν_1	a_1' (Raman)	$\nu_{sym}(CO_3)$	A_1 (Raman)	A_1 (Raman) 1 088	$A_{1g}+A_{1u}$ (inactive)	A	6($A_g + B_g + A_u + B_u$)
ν_2	a_2'' (i.r.)	$\pi(CO_3)$	A_2 (i.r.)	A_{2g} (inactive)	+ A_{2u} (i.r.) 872	A	
ν_3	e' (Raman, i.r.)	$\nu_{asym}(CO_3)$	E (Raman, i.r.)	E_g (Raman) 1 432	+ E_u (i.r.) 1 407	2A	
ν_4	e' (Raman, i.r.)	$\delta(CO_3)$	E (Raman, i.r.)	E_g (Raman) 714	+ E_u (i.r.) 712	2A	

[a] Frequencies from ref. 10. [b] These columns sum to give the rows $\Gamma_{vib.}$ of Table 5(a) and (b).

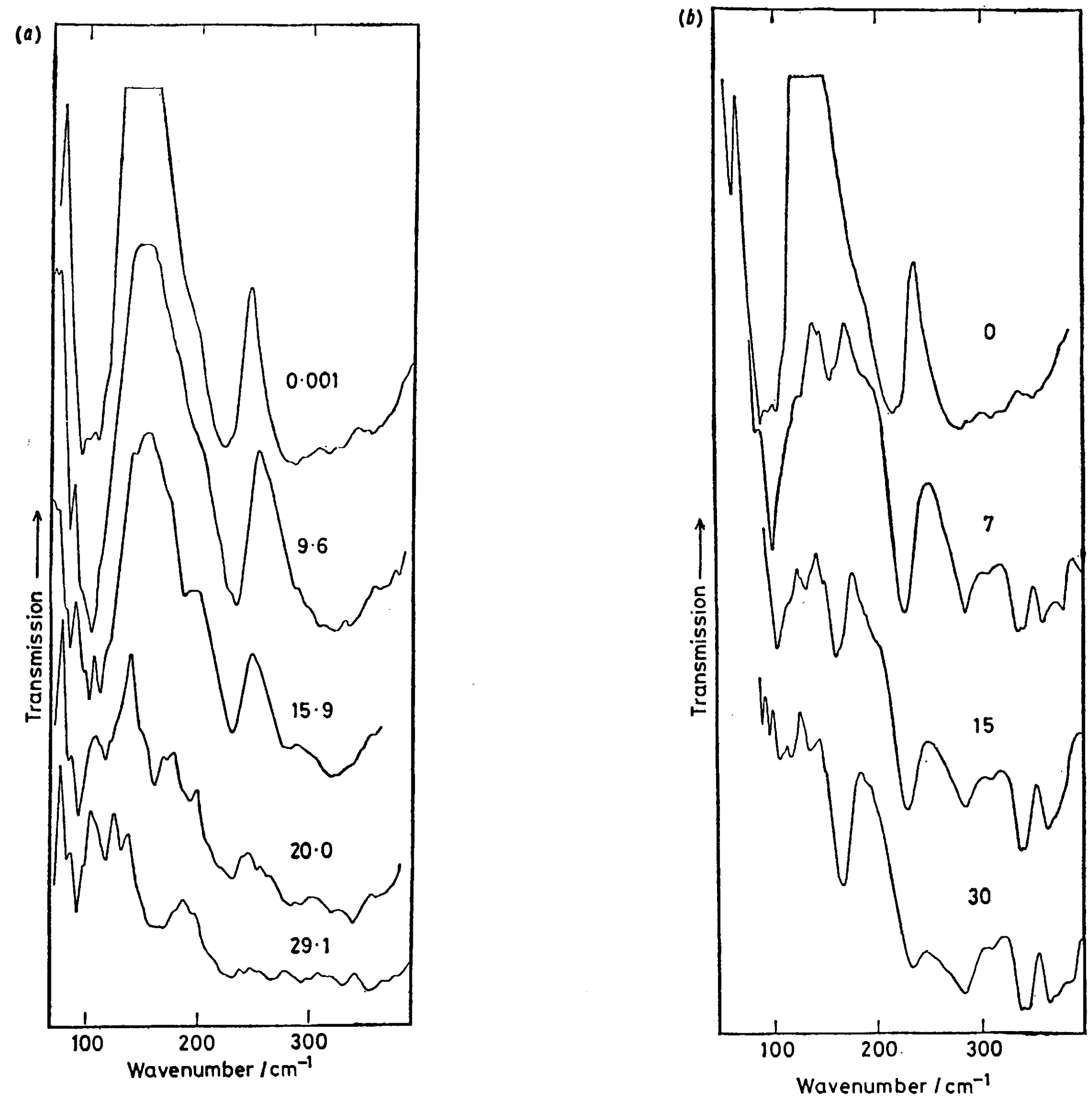

FIGURE 2 Far-i.r. spectra of Ca[CO$_3$] at various pressures. (a) In a gasketed d.a.c. under hydrostatic pressures (kbar). (b) In a d.a.c. without a gasket ($i.e.$ under shear stress); values (kbar) are the approximate average applied pressures.

enquire whether the site-symmetry group rules are a better approximation. Carbonate is on general sites; the single ν_1 mode must therefore be active and coincident in both i.r. and Raman spectra. Fong and Nicol found ν_1 at 1 096 cm^{-1} at 14 kbar whereas at 16.6 kbar we find it at 1 088 cm^{-1}. It is probable that their pressures are slight underestimates. Thus, $\mathrm{Ca[CO_3]}$(III), which they indicate as having examined at 18 kbar, is now known not to be formed until 22 kbar. Add to this point the slight increase in frequency of ν_1 with increase of pressure, Table 2, and it is probable that the Raman and i.r. frequencies are coincident within experimental error. Nevertheless, direct experimentation is required to settle the matter.

On entering $\mathrm{Ca[CO_3]}$(III), ν_1 becomes a doublet in the i.r. spectra, as was also found for the Raman spectra by Fong and Nicol. If we take their 18 kbar spectrum as comparable to ours at 23.3 kbar (*i.e.* just within phase III in each case) then the Raman bands are *ca.* 8 cm^{-1} higher than the i.r. ones. This difference is probably significant and, if so, indicates that $\mathrm{Ca[CO_3]}$(III) has a centrosymmetric cell. Non-coincident i.r.-Raman doublets also imply that the cell has, at least, $Z = 4$.

The ν_2 region. This region is singularly uninformative in structural terms. The ν_2 absorption appears and remains as a single band in all three phases and is, moreover, remarkably insensitive to increase of pressure. Both Fong and Nicol and ourselves found that there was no significant increase in frequency in ν_2 in $\mathrm{Ca[CO_3]}$(III) over a 20 kbar range. ν_2 is, however, rather broad in all three phases. In phase I this is undoubtedly due to the longitudinal optic–tranverse optic splitting[10] of 19 cm^{-1} which is large relative to that of ν_4 and ensures that the presence of a reflectance component overlaying the transmission spectrum will give the appearance of breadth. We consider this to be the most likely explanation of the ν_2 region spectra for phases II and III also. It is certainly possible that unresolved components lie within the ν_2 envelopes, especially for $\mathrm{Ca[CO_3]}$(III), but we note that the Raman spectra of Fong and Nicol likewise show no splitting here.

The difference between our 16.6 kbar value for ν_2 in $\mathrm{Ca[CO_3]}$(II), 875 cm^{-1}, and that of ref. 5 at a nominal 14 kbar, 866 cm^{-1}, is too large to be accounted for by the errors considered under the ν_1 discussion. Whatever the experimental factors which affect the absolute frequencies reported from our two studies, the *difference* $\nu_1 - \nu_2$ is 230 cm^{-1} for ref. 5 and 213 cm^{-1} for our own data at the pressures quoted. It appears, therefore, that the i.r. and Raman components of ν_2 are genuinely non-coincident but that the remaining factor-group component expected in each spectrum is vanishingly weak.

The ν_4 region. This is a particularly informative region, structurally speaking, as was recognised by Cifrulak.[8] Theory permits, Table 4, a single band (E_u) in the i.r. spectrum for phase I (calcite), as is observed. It is raised modestly in frequency with increase of pressure, as is also the case for the sole (E_g) Raman analogue.[5] There are signs of ν_4 splitting in the i.r. spectra of phase II at 16.6 and 18.0 kbar but nothing was clearly resolved until phase III had been entered.

The new feature most characteristic of $\mathrm{Ca[CO_3]}$(III) is a prominent i.r. band at 685 cm^{-1}, accompanied by a Raman-active analogue[5] at 695 cm^{-1}. The clear (Figure 1) and substantial separation of these bands from the now characteristically complex part of the ν_4 spectrum $>$710 cm^{-1}, together with the rather small factor-group splittings accompanying ν_1 and ν_2, strongly argue for the presence of a second, crystallographically distinct, anion in the unit cell. This, together with the other internal and external mode evidence, leads us to suggest that $\mathrm{Ca[CO_3]}$(III) is formed from (II) by cell doubling in one direction to give $Z = 8$.

Our probable ν_4 splitting for $\mathrm{Ca[CO_3]}$(II), together with that found in the Raman spectra by Fong and Nicol, appears to be consistent with site rather than factor-group rules. Thus, the site rules require ν_4 to be a doublet ($2A$) which is i.r.-Raman coincident. This is what is observed, within the limits of experimental error.

The i.r. spectra obtained at 22.3 and 23.3 kbar appear to be of II/III intergrowths as judged by the other ν_4 region spectra: this is not surprising as we are still very close to the transition pressure. However, above 30 kbar a simpler spectrum is established consisting of bands centred near 685 and 740 cm^{-1} with a clearly resolved shoulder on the higher one. There is no longer any sign of the band near 712 cm^{-1} which appears to be from residual $\mathrm{Ca[CO_3]}$(II): this band was present even at 61 kbar in Cifrulak's i.r. spectra[8] because use of a d.a.c. without a gasket allows concurrent presence of polymorphs in the large pressure gradients which then exist. The Raman data for phase III are closely similar to these from the i.r. spectra.

TABLE 5

Factor group analyses for $\mathrm{Ca[CO_3]}$(I) and (II)

(*a*) $\mathrm{Ca[CO_3]}$(I) $D^6_{3d} \equiv R3c$, $Z = 2$

D_{3d}		A_{1g}	A_{2g}	E_g	A_{1u}	A_{2u}	E_u
Ca	2*b*	0	0	0	1	1	2
C	2*a*	0	1	1	0	1	1
O	6*e*	1	2	3	1	2	3
N_T		1	3	4	2	4	6
T_A					0	1	1
T		0	1	1	1	1	2
R		0	1	1	0	1	1
$\Gamma_{\mathrm{vib.}}$		1	1	2	1	1	2
Activity		Raman		Raman		i.r.	i.r.

(*b*) $\mathrm{Ca[CO_3]}$(II) $C^5_{2h} \equiv P2_1/c$, $Z = 4$

All atoms on 4*e*

C_{2h}	A_g	B_g	A_u	B_u
N_T	15	15	15	15
T_A			1	2
T	6	6	5	4
R	3	3	3	3
$\Gamma_{\mathrm{vib.}}$	6	6	6	6
Activity	Raman	Raman	i.r.	i.r.

N_T = Total number of unit-cell modes, T_A = acoustic branch modes, T = optic-branch translatory modes, R = librational modes, and $\Gamma_{\mathrm{vib.}}$ = internal modes.

Finally, we note that the changes in the ν_4 region which are so characteristic of $\mathrm{Ca[CO_3]}$(III) are reflected in the $\nu_1 + \nu_4$ combination which splits into a doublet. In

$Ca[CO_3](I)$ this combination must originate from A_{1g} (1 088) + E_u(712.5) = E_u(1 800.5). Retention of the centre of symmetry in passing to phase II requires an analogous selection rule based upon C_{2h} labels, and an equivalent but more complex result is obtained for $Ca[CO_3](III)$ if the centre of symmetry is, again, retained.

The external-mode region. The lattice-mode assignment for calcite = $Ca[CO_3](I)$ is well established.[10] Selection rules are in Table 5(*a*) but it is instructive to consider also how the modes of individual ions on their sites couple. The point to be emphasised is that, in general, the coupling which leads to factor-group selection rules is relatively weak and that lattice modes of a given basic origin (*e.g.* libratory) will be found in similar positions in both i.r. and Raman spectra (see diagram below). The known assignment is: E_g 156, 283; A_{2u} 92, 303; E_u 102, 223, and 297 cm^{-1}. The modes at 283, 297, and 303 cm^{-1} are considered to be mainly libratory in type.

$$\begin{array}{llll}
 & & & \xrightarrow{\times 2}\ D_{3d}^{6}\text{ crystal}\\
CO_3^{2-} & D_3\text{ site} & \left\{\begin{array}{l}R(z)\ A_2\\ R(x,y)\ E\end{array}\right. & \begin{array}{c}A_{2g}+A_{2u}\\ E_g+E_u\end{array}\\
 & & \left\{\begin{array}{l}T(z)\ A_2\\ T(x,y)\ E\end{array}\right. & \begin{array}{c}A_{2g}+A_{2u}\\ E_g+E_u\end{array}\\
Ca^{2+} & S_6\text{ site} & \left\{\begin{array}{l}T(z)\ A_u\\ T(x,y)\ E_u\end{array}\right. & \begin{array}{l}A_{1u}+A_{2u}\\ 2E_u\end{array}
\end{array}$$

In $Ca[CO_3](II)$ each libratory or translatory degree of freedom at a general site generates a full vector (A_g + A_u + B_g + B_u). Thus, in this phase the lattice-mode spectrum is expected to consist of groups of two i.r. plus two Raman bands in close proximity which, themselves, will be grouped near the positions already located for $Ca[CO_3](I)$.

Far-i.r. spectra of $Ca[CO_3](I)$, Figure 2, show three major absorption features. Two nearly coincident bands, for which $\omega_{t.o.}$ (t.o. = transverse optic) takes values of 297 and 303 cm^{-1} respectively, form a broad region of intense absorption from *ca.* 250 to 400 cm^{-1}. Below *ca.* 100 cm^{-1} very little energy passes through the gasketed d.a.c. and the spectra are considered to be unreliable in this region. They were supplemented by a few runs without gaskets. The E_u mode with $\omega_{t.o.}$ = 223 cm^{-1} moves under pressure (p) with $\Delta\omega/\Delta p = 0.57$ cm^{-1} kbar^{-1}. Increases of frequency with pressure are also evident for the higher-frequency bands but severe overlap precludes measurement.

Phase II is most clearly characterised by appearance of two new bands which are at 163 and 192 cm^{-1} at 20.0 kbar. Additional adsorption near 260 cm^{-1} also fills in the region between the E_u mode (at 223 cm^{-1} at ambient pressure) and the higher-energy bands. These new features are close to the Raman bands reported for $Ca[CO_3](II)$ at 14 kbar by Fong and Nicol, *viz*, 155, 204, 240 cm^{-1}, in agreement with the selection rules. Nevertheless, the total numbers of i.r. and Raman lattice-mode bands found are substantially less than the predictions of factor-group analysis. As in $Ca[CO_3](I)$, it is almost certain that bands of both A_g and B_g symmetry are overlaid in the Raman spectra and similarly for A_u and B_u modes in the i.r.

On entering phase III the far-i.r. spectra become yet more complex, as is to be expected from the evidence of the internal modes and the work of Fong and Nicol. The latter found no less than 13 lattice-mode bands between 100 and 360 cm^{-1}. Whilst, in our far-i.r. spectra of phase III at 29.1 kbar, Figure 2, it is clear that very many absorption bands are present, few can be measured with any accuracy as they form almost a continuum.

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