

THE EFFECT OF PERIODICITY ON THE INFRARED
ABSORPTION FREQUENCY ν_4 OF ANHYDROUS
NORMAL CARBONATE MINERALS

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ABSTRACT

An empirical study of the infrared absorption spectra of isomorphous anhydrous carbonates between 13 and 15 microns suggests that frequency trends in the ν_4 carbonate ion vibration are related to the electronic periodicity of cations in external lattice sites.

INTRODUCTION

The vibrational spectra of carbonates over the fundamental infrared range have been much studied and it is now recognised that two distinct differences exist in the spectral characteristics of anhydrous normal carbonate minerals. Firstly, the trigonal carbonates (magnesite, dolomite, calcite, rhodochrosite, smithsonite, and siderite) differ from the orthorhombic carbonates (aragonite, strontianite, witherite, and cerussite) in the number of absorption bands present for each mineral group. These intergroup variations are due to differences in lattice symmetry. In the orthorhombic carbonates the molecular symmetry has been distorted from the ideal D_{3h} configuration of the free carbonate ion to such an extent that centres of positive and negative charge on the ion no longer coincide. A change in dipole moment is, therefore, produced resulting in the appearance of an absorption band at approx. 9.2 μm . corresponding to the symmetric stretching mode (ν_1), a mode which apparently does not give rise to absorption in the spectra of trigonal carbonates of higher symmetry. In addition, restrictions on the inherently doubly degenerate ν_3 (approx. 7 μm .) and ν_4 (approx. 14 μm .) modes are removed in the orthorhombic minerals enabling two bands to appear in each of these spectral regions; in fact the ν_3 band is only resolved in the spectrum of cerussite and the ν_4 band in the spectra of aragonite and strontianite also (Huang and Kerr, 1960; Adler and Kerr, 1963). The ν_2 mode at approx. 11.5 μm . is non-degenerate so is unaffected by changes in symmetry.

As well as variations between carbonates of different structures, intragroup spectral variations also occur in that carbonate minerals of the same structure exhibit differences in the frequencies of their absorption bands. It has been shown empirically (Hunt *et al.*, 1950; Adler *et al.*, 1950; Huang and Kerr, 1960; Weir and Lippincott, 1961; Adler and Kerr, 1963) that these characteristic group frequencies are influenced by sur-

rounding environmental metallic ions. This sensitivity to cationic substitution has been related to changes in the ionic radius and mass of the substitutional ions bonded to the vibrating carbonate ion through a mutual oxygen atom. Weir and Lippincott (1961) have explained the "radius" effect in terms of a decreasing cation-oxygen distance, due to substitution of ions of decreasing cation radius, causing increased oxygen-oxygen repulsion in the unit cell and hence shortening of the C-O bond and an increase in frequency of the carbonate ion vibration. The "mass" effect, however, has not been successfully explained and there is some evidence (Adler, 1965; Adler, personal communication, 1970) that it is essentially non-existent. Absorption trends exhibiting both "radius" and "mass" effects are irregular and sometimes inconsistent with either factor. These inconsistencies have been suggested (Adler and Kerr, 1963) as being due to comparisons being made between elements having similar ionic radii but belonging to different periodic groups. For this reason an empirical investigation was made of the effect of periodicity on the vibrational spectra of the carbonate minerals.

PROCEDURE

In order to consider the significance of periodicity effects, spectral variations have been examined for the ν_4 mode of the anhydrous normal carbonates. The ν_4 mode was chosen since no frequency shift occurs on transition from trigonal to orthorhombic structure when there is no cationic substitution (*i.e.*, transition from calcite to aragonate); shifts occur in ν_2 and ν_3 frequencies but the ν_4 mode remains unchanged apart from splitting due to the removal of degeneracy. It was thought, therefore, that any effects due to structural changes would be less significant than for other modes. The wavelengths of the ν_4 absorption bands of the carbonates studied are listed in Table 1. Apart from the common anhydrous minerals mentioned earlier, data for anhydrous CdCO_3 is included. Cadmium (period 5 group IIB) was added so as to provide a comparison with the spectra of the carbonates of Sr (period 5) and Zn (group IIB). Mineral specimens were obtained from the collections of the Departments of Oceanography and Geology, The University of Liverpool; CdCO_3 was synthesised from reagent grade chemicals. The identity of all samples was confirmed and their purity checked by Dr. M. P. Atherton of the Department of Geology, The University of Liverpool, using X-ray powder methods, and as a further check, chemical analyses were carried out by the authors. Infrared spectra were obtained using a sampling technique and instrumentation previously described (Chester and Elderfield, 1967).

MASS AND RADIUS EFFECTS

From the classical model of a harmonic oscillator it is evident that the frequencies of vibration of a particular molecular group are influenced by the reduced mass of the participating atoms (u) and the restoring forces (k) between these atoms. Hooke's Law relates vibrational frequency (ν) and u and k .

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{k}{u}} \quad (1)$$

This expression relates to a diatomic molecule but as an approximation can be qualitatively applied to the CO_3^{2-} ion. Badger (1934) has derived an equation relating the force constant k (in millidyne/Ångstrom) in equation (1) to the equilibrium inter-atomic distance (R), namely,

$$k = 10[a_{ij}(R - b_{ij})]^{-3} \quad (2)$$

where a_{ij} and b_{ij} are constants that depend on the rows in the Periodic Table in which the atoms i and j are found. This equation similarly relates to a single vibration involving two atoms and cannot directly be

TABLE 1. ν_4 ABSORPTIONS OF THE CO_3^{2-} ION IN ANHYDROUS NORMAL CARBONATE MINERALS AND SYNTHESISED CdCO_3

Carbonate	Wavelength (μm)	
Magnesite	13.40	
Dolomite	13.76	
Calcite	14.08	
Rhodochrosite	13.75	
Smithsonite	13.46	
Siderite	13.56	
Aragonite	14.08	14.39
Strontianite	14.24	14.34
Witherite	14.56	
Cerussite	14.78	14.97
CdCO_3	13.99	14.56

applied to cation substitution effects. However, according to the theory proposed by Weir and Lippincott (1961), the equilibrium C-O distance in carbonates will be modified by changes in the external environment of the CO_3^{2-} ion and intragroup variations indeed infer sensitivity of vibrational modes to external influence.

The effect of cation radius and mass on the ν_4 mode is illustrated in Figure 1. It is apparent that a relationship exists between cation radius and the shifting frequency of the carbonate vibrations for all carbonates except cerussite. Similarly, there is, in general, a relationship of increasing ν_4 wavelength with increasing cation mass; however, Mn, Fe, Zn, and Cd carbonates are anomalous as regards this "mass" effect. Hence, for the majority of carbonate cations there is a relationship between ν and cation radius (r) in agreement with the trend predicted by equations (1)

and (2) for substitution of atoms within the carbonate ion. For the external cations, with the exception of Mn, Fe, Zn, and Cd, the relationship between ν and cation mass (m) similarly reflects the trend predicted between ν and u for substitution of atoms participating in the carbonate ion vibration. The trend for Mn, Fe, and Zn is antipathetic with the "mass" effect observed for the other cations except Cd which does not fit either trend line. It is these differences in systematic trends exhibited, for example, by carbonates of Ca, Sr, and Ba on the one hand and those of Fe and Mn on the other that Adler and Kerr (1963) suggest are due to

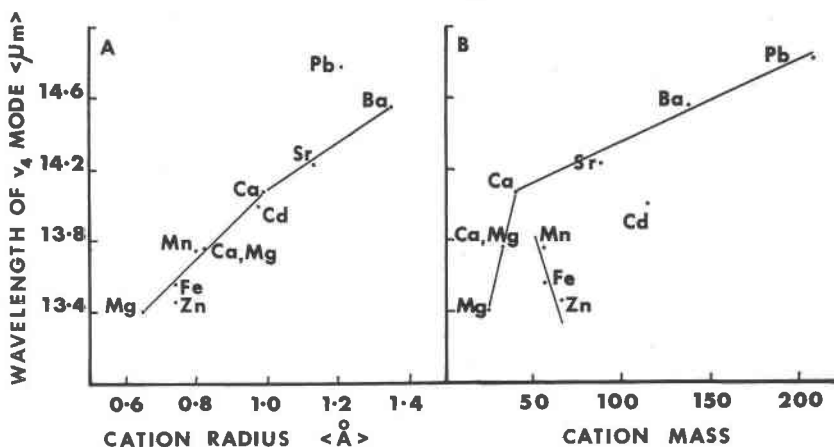


FIG. 1. Variation in the wavelength of the ν_4 carbonate mode with (A) cation radius, (B) cation mass.

differences in electronic configuration of the two groups of cations, *i.e.*, are due to a "periodicity effect."

PERIODICITY EFFECTS

Comparison of the results illustrated in Figure 1 with equations (1) and (2) has shown that the spectral effects of adjustment of the CO_3^{2-} ion in relation to its external environment are qualitatively in agreement with predicted trends for internal environment adjustments. On this basis, a combination of equations (1) and (2)

$$\frac{1}{\nu^2} = \frac{2}{5} \pi^2 c^2 [a_{ij}(R - b_{ij})]^3 \quad (3)$$

would seem to imply a relationship between the square of the wavelength of the ν_4 mode (λ_4) and $m\nu^2$. This relationship is illustrated in Figure 2. A logarithmic scale was adopted for the abscissa since the ν^2 term tends to

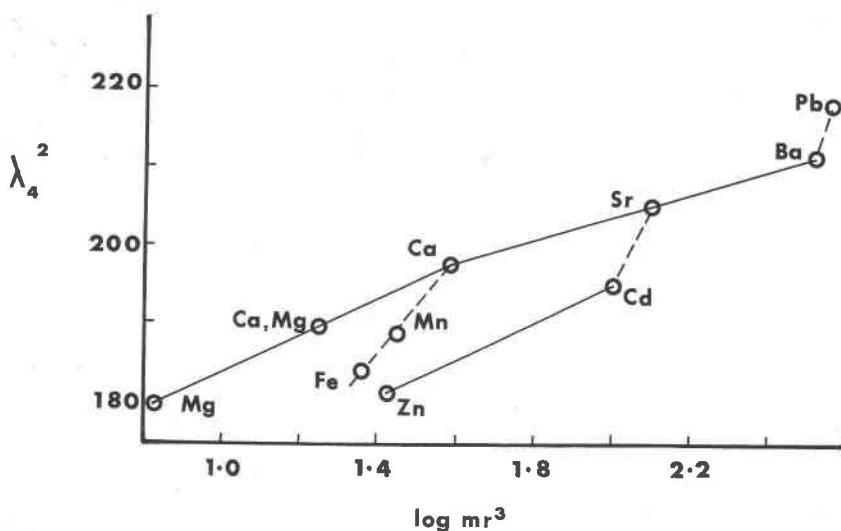


FIG. 2. Plot of $(\nu_4 \text{ wavelength})^2$ versus $\log [\text{cation mass} \times (\text{cation radius})^3]$ for carbonate absorptions.

contract the plotted data for small, light cations with respect to the others.

It can be seen from Figure 2 that trend lines exist for cations of the same group (full lines, Fig. 2) and also of the same period (dashed lines, Fig. 2) of the form:

$$\lambda_4^2 = \alpha \log mr^3 + \beta$$

where α and β are constants depending on group and period, and carbonate structure. α and β were calculated from the graphical data and are listed in Table 2. Several observations can be made with regard to this data:

- (1) For the elements studied from the same groups in the periodic table, the relationship between λ_4^2 and $\log mr^3$ depends on carbonate structure; there is a change in slope between plotted data for the group IIA elements Mg and Ca, and Ca, Sr, and Ba corresponding to a change from calcite to aragonite structure. It cannot be determined whether or not this effect occurs for elements of the same period since there is no divalent cation in the 5th period with an atomic weight less than that of Ca.
- (2) The slope of the Zn→Cd trend line is almost identical to that for Mg→Ca.Mg→Ca. It appears, therefore, that for carbonates of

TABLE 2. VALUES OF PERIODICITY CONSTANTS RELATING ν_4 WAVELENGTH OF CO_3^{2-} ION AND MASS RADIUS AND OF EXTERNAL CATION

group/period	External cation(s)			α	β
group IIIA ^a	Mg	Ca, Mg	Ca	24.46	158.4
IIIA ^b	Ca	Sr	Ba	14.60	175.1
IIB	Zn	Cd		24.41	146.4
VIIA	Mn				153.7
VIII	Fe				150.8
period 4	Ca	Mn	Fe	65.16	94.7
5	Sr	Cd		110.4	-26.5
6	Ba	Pb		176.6	-232.8

^aTrigonal symmetry

^bOrthorhombic symmetry

the same symmetry, differences in the group of the external cation are only reflected in the constant β .

- (3) Contrary to the group effect suggested in (2) the slopes of the trend lines joining elements of the same period are not identical. On comparison of the slopes (α_p) of the trend lines for Ca→Mn→Fe, Sr→Cd and Pb→Ba it can be shown that there is an increase in slope with increasing period number (n) of the form:

$$\alpha_p = 0.73n^3 + 19.2$$

- (4) The data for Zn on Figure 2 is such that it does not fall on the trend line for elements of the 4th period, but to a slightly higher value of $\log mr^3$. This may be due to the fact that zinc is a d^{10} cation whereas Mn and Fe have incomplete M shells. Adler and Kerr (1963) when discussing frequency trends used an ionic radius for Zn slightly less than that of Fe although published data indicates them to be identical. They justify this choice in that "it is desirable for spectroscopic considerations to utilise empirical data which approximately reflect the lattice constants." If this value for the ionic radius of Zn is used, the data falls on the trend line for elements of the 4th period. However, the effects of this is that the slope of the Zn→Cd trend line decreases to a value less than that for Mg→CaMg→Ca; so while this choice places Zn on its correct trend line, its use also means that the constant α will be influenced not only by carbonate symmetry but also by differences in the group of the external cation.

CONCLUSION

The fundamental vibrational frequencies of the carbonate minerals are largely controlled by the nature of the internal C-O bonds and the lattice cations exhibit only a secondary effect on infrared band positions. The data presented above tends to confirm the suggestion of Adler and Kerr (1963) that these secondary effects are influenced by the electronic structure of the carbonate cations. A quantitative assessment is difficult with the limited data available and the calculated constants relating λ_4^2 and $\log mr^3$ are, of necessity, tentative. Only when similar information is evaluated for the ν_2 and ν_3 carbonate modes and for frequency trends on cation substitution in other simple inorganic crystals can the magnitude and significance of the factors determining secondary effects be unambiguously demonstrated. Previous studies have established that cation radius is significant in its effect on the C-O internuclear distance while there is some doubt as to the effect, if any, of cation mass on frequency trends (H. H. Adler, personal communication 1970). The mr^3 term in the periodicity effect illustrated in Figure 2 would imply that the "mass" effect is small compared to the "radius" effect.

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