

Mid- and far-infrared spectral links for calcium carbonate polymorphs

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Abstract—We compare mid- and far-infrared attenuated total reflectance spectra for calcite and aragonite, which are two polymorphs of calcium carbonate, CaCO_3 , in order to demonstrate which spectral feature changes can be attributed to phase (crystal structure) differences. These comparisons, together with our recent studies of multi-phase carbonate-containing samples, help to lay the groundwork for distinguishing far-infrared spectral features that are related to crystallinity differences in calcium carbonates.

I. INTRODUCTION

GLASSY materials and their crystalline counterparts have distinct vibrational spectra, but they also share some common features [1,2]. In a similar way, polycrystalline and amorphous forms of calcite (CaCO_3) have characteristic spectral differences the mid-infrared (MIR) range (400-4000 cm^{-1} , equivalent to 12-120 THz). Previous experimental and theoretical studies have identified that MIR peaks are due to vibrational modes that occur within the carbonate moiety (intra-unit-cell modes) [3,4,5]. In contrast, there has been far less attention paid to the lattice (inter-unit cell) vibrational modes of calcium carbonate minerals, which fall in the far-infrared (FIR) range (80-650 cm^{-1} or 2-20 THz). Bridging this knowledge gap between local modes and lattice modes is a first step toward assessing more subtle spectral differences that occur in amorphous and poorly crystalline calcium carbonate. Given this context, the present paper summarizes key differences in the FIR spectra of calcium carbonate polymorphs.

Calcite and aragonite have the same chemical composition (CaCO_3), but they have different crystal structures. In calcite, the carbonate units lie in distinct planes, with layers of Ca ions in between. In aragonite, the carbonate units and the Ca ions are staggered. The net result is that aragonite is slightly more dense (2.9 g/cm^3) relative to calcite (2.7 g/cm^3).

Studies have shown that both calcite and aragonite can crystallize from amorphous precursors [12]. In fact, these amorphous calcite and aragonite precursors – although they have poor long-range order with poor X-ray diffraction peaks – have distinct structural differences on short-range length scales that can be detected with techniques such as solid state nuclear magnetic resonance (NMR). These crystallinity differences – which ultimately reveal which polymorph will crystallize from the amorphous precursor -- are very useful to track when studying biomineralization processes, archaeological material formation and diagenesis pathways, or the curing and aging properties of carbonate-based construction materials [3,4,5,6,7].

Based on these kinds of short-range structural differences, it is not surprising that the vibrational modes of calcite-like and aragonite-like carbonates have energy differences that influence their MIR and FIR spectra. In the MIR range, these differences in the carbonate vibrational modes are very well documented in the literature, having been validated experimentally and theoretically by many groups [3,4,5]. For

the lattice mode vibrations, which fall in the range of 80-400 cm^{-1} (2-12 THz), there is substantially less literature available. There are a growing number of THz studies on carbonate minerals; one of the most recent uses pulsed THz time domain spectroscopy to look at the lowest energy lattice modes for calcite, aragonite, and Mg-containing calcites in the range of 1-6 THz (30-200 cm^{-1}) [8]. Others compared the transmittance FIR spectra for a large number of carbonate minerals, including aragonite and calcite, in the range of 50-650 cm^{-1} (1.5-20 THz) [9]. Earlier work by us compares attenuated total reflectance MIR (for carbonate modes) and FIR (for lattice modes) for mixtures of calcite and related Ca-containing minerals [6].

In this work, we identify FIR spectral differences between calcite and aragonite. These data lay the groundwork for future studies that can address more nuanced structural changes related to crystallinity differences.

II. EXPERIMENT METHODS

We synthesized calcium carbonate samples using a solution-based procedure that involves both concentration and temperature control. The starting solutions were prepared using ACS-grade salts (NaCO_3 and CaCl_2 solutions) dissolved in ultrapure water, with a ratio of 1:1 between calcium and carbonate. Both solutions were held at 70 °C prior to mixing. The resulting precipitate was centrifuged, filtered and dried in ambient conditions to produce a fine white powder. The sample was then hand ground for several iterations in an agate mortar and pestle. The recipe above produces calcite. We triggered aragonite formation by replacing the CaCl_2 solution with a mixture of MgCl_2 and CaCl_2 in a 1:4 ratio. These synthesis conditions produced phase-pure aragonite. However, we note that going to higher solution temperatures (up to 90 °C) or using higher Mg:Ca proportions led to detectable amounts of an undesired secondary phase (dolomite, $(\text{Ca,Mg})\text{CO}_3$).

IR data were collected in an attenuated total reflectance (ATR) geometry by pressing the lightly ground powder against a diamond crystal (Bruker Platinum Diamond ATR attachment) that was integrated into a Bruker Vertex 70v vacuum spectrometer. The advantage of this ATR method is that we can use the same powder – with the same pressing – for both MIR and FIR data collection. In contrast, transmission IR spectra would require a diluting material, such as KBr (transparent in MIR) or polyethylene (transparent in FIR). Preliminary tests showed us that polyethylene is not helpful for calcium carbonate MIR spectra because it has strong peaks that overlap with those of calcite and aragonite.

MIR data (KBr beamsplitter) were collected in separate measurements from the FIR spectra (mylar beamsplitter). All spectra were collected with 2 cm^{-1} resolution. In previous work [6], we demonstrated that repeated ATR spectra re-pressed using the same powder lead to peak position variations +/- 2 cm^{-1} . In this work, we present all spectra using the convention of plotting ATR intensity versus decreasing wavenumber.

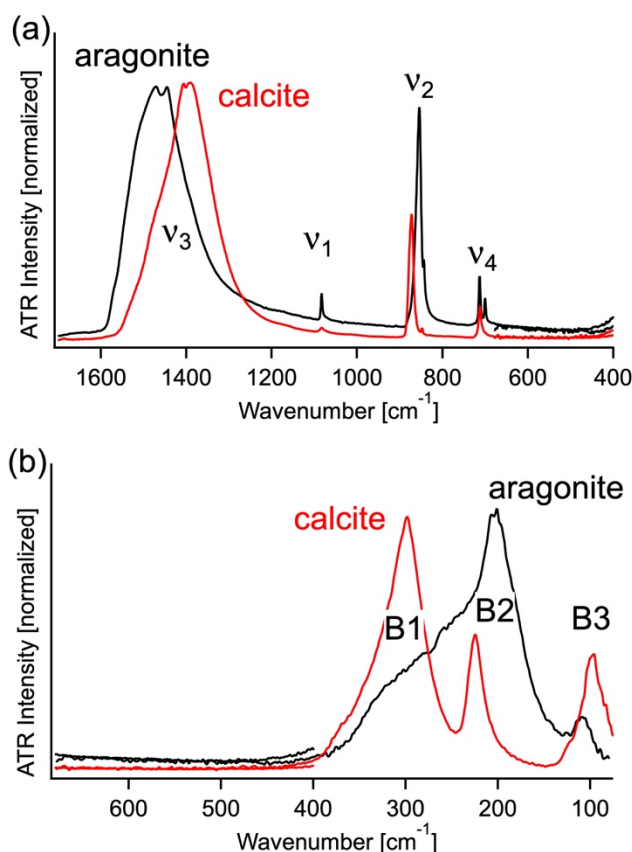


Fig. 1. Representative (a) MIR-range and (b) FIR-range spectra show shifts in peak positions, as well as relative intensity differences, between calcite (red) and aragonite (black). We note that there is overlap between our FIR and MIR spectral ranges (400 and 680 cm^{-1}), but that there are no calcite or aragonite vibrational modes that have energies in this range.

III. RESULTS

The MIR spectral region shows peak shifts between calcite and aragonite, as well as a few other differences (Figure 1b). To summarize, aragonite has two additional peaks: a weak peak at 1090 cm^{-1} (v_1), and another relatively weak peak at 700 cm^{-1} . As mentioned above, these differences are very well documented in the literature, and vibrations that correspond to each peak have been validated experimentally and theoretically [3,4,5]. There is an asymmetric in-plane stretch (v_3), out-of-plane bend (v_2) and in-plane bend (v_4).

We use these MIR spectra to assess phase purity in our samples. For example, the representative calcite spectrum in Figure 1b shows a weak aragonite v_1 peak (1090 cm^{-1}). This indicates a small amount of aragonite as a secondary phase in this specimen, which is a common occurrence using this particular solution-based method to synthesize calcite powders.

The FIR spectral region also shows differences between calcite and aragonite vibrational modes (Figure 1c). Some of these differences have been reported in the literature, but there is less clarity about their origins, due in part to the dearth of theoretical calculations for confirmation. For clarity and consistency with earlier work [6], we refer to FIR spectral features as bands B1, B2, and B3. These are three distinct bands for calcite, but in aragonite the band B1 appears as a shoulder

on the high-wavenumber side of band B2. For aragonite, we assign the B1 shoulder that appears in our aragonite spectra to several “anti-translatory” modes, whereas we assign band B2 and B3 as libration modes by comparisons with earlier experimental work [9]. We note that the small amount of aragonite (detected in the MIR spectrum for the calcite sample) does not affect the position or relative intensity of the FIR peaks to any demonstrable degree, based on comparisons with spectra for pure calcite samples from our earlier work [6].

Comparing our ATR FIR spectra for calcite and aragonite with transmission FIR spectra from the literature [9] shows qualitative similarities, but also some important differences. Most notably, our ATR spectra resolve the aragonite peaks much more clearly than the transmission spectra. In the MIR, others have compared ATR and transmission spectra for calcite [10]. In the FIR, comparisons become more complicated due to enhanced anharmonicity effects; not only does this influence experimental spectra interpretations, but it also impedes accurate mode assignments from theoretical calculations [11].

IV. CONCLUSIONS

We present MIR and FIR spectra, collected using attenuated total reflectance, for calcite and aragonite. Comparing IR spectra for polymorphs is one important step toward our ultimate goal of assessing differences in vibrational spectra for crystalline and amorphous calcium carbonate powders.

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