

## The near-infrared (NIR) spectra of powdered calcite in the 3 to 121 $\mu$ m mode particle size range

Laurence Hopkinson<sup>1\*</sup> (\* corresponding author), Petra Kristova<sup>2</sup>, Ken Rutt<sup>2</sup>

<sup>(1)</sup> School of the Environment and Technology,

University of Brighton

Cockcroft Building, Lewes Road, Brighton.BN2 4GJ.

United Kingdom.

Tel +44(0) 1273 642239, Fax: +44 (0) 642285, e.mail: [l.hopkinson@brighton.ac.uk](mailto:l.hopkinson@brighton.ac.uk)

<sup>(2)</sup> School of Pharmacy and Biomolecular Sciences,

University of Brighton.

Huxley Building, Lewes Road, Brighton BN2 4GJ.

United Kingdom.

Tel: +44 (0)1273 642065, Fax: +44 (0)1273 642285, e.mail:

[p.kristova@brighton.ac.uk](mailto:p.kristova@brighton.ac.uk)

Tel: +44 (0)1273 642076, Fax: +44 (0)1273 642285, e.mail: [k.j.rutt@brighton.ac.uk](mailto:k.j.rutt@brighton.ac.uk)

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## Abstract

The near-infrared (NIR) spectra of powdered carbonate minerals is of significant multidisciplinary interest. However, there is a paucity of accounts of the behaviour of NIR bands as a function of particle size in well-constrained experimental settings, although such studies may hold promise in revealing band-specific traits and identifying spectral features amenable to quantified measurement of particle size fractions. To these ends, this study examines the NIR spectral response in the 2.5 to 1.66 $\mu\text{m}$  wavelength (4000-6000 $\text{cm}^{-1}$  wave number) region from powdered calcite in size fractions ranging from 3 to 121 $\mu\text{m}$  mode particle sizes.

Results show that the behavioural response of the NIR spectra is varied. Those assigned to  $3\nu_3$ : 2.34 $\mu\text{m}$  (4270 $\text{cm}^{-1}$ ) and 2.3 $\mu\text{m}$  (4350 $\text{cm}^{-1}$ ) wavelengths show a linear relationship ( $r^2 = 0.9992$ ), with decreasing particle size and absorption intensity. Bands at 2 $\mu\text{m}$  (5007 $\text{cm}^{-1}$ ), 1.96 $\mu\text{m}$  (5109 $\text{cm}^{-1}$ ) and 1.87 $\mu\text{m}$  (5336 $\text{cm}^{-1}$ ) assigned to combinations between  $\nu_3$  overtones and  $\nu_1$  and its overtone show an initial decrease in absorption intensity, but an increase in absorption intensity in the 3 $\mu\text{m}$  mode particle size powder relative to the 5 $\mu\text{m}$  mode powder. The differing behaviours of  $3\nu_3$  overtone related bands with respect to combinations containing  $\nu_1$  or its overtone occur at particle size ranges in which the optical thick to thin transition occurs at mid-infrared (MIR) frequencies. The separate NIR behavioural responses of specific bands are qualitatively reminiscent of MIR types 1 and 2 behaviour of  $[\text{CO}_3^{2-}]$  anion internal modes at the optical thick to thin transition.

## 1. Introduction

Utilizing near-infrared (NIR) spectroscopy as a tool to assess particle sizes of powdered materials in general and carbonate minerals in particular spans many fields of scientific endeavour including planetary exploration [1-4]. It is generally accepted that NIR bands in the  $4000\text{-}6000\text{cm}^{-1}$  ( $2.5\text{-}1.67\mu\text{m}$ ) region stem from overtones and combinations of the different internal modes of the  $[\text{CO}_3^{2-}]$  anion although comprehensive assignments of NIR bands are incomplete [1,2,5,6] and, there is a paucity of documented experimental accounts of the NIR spectral response from carbonate mineral powders as a function of grain size. Although it is known that absolute intensities of carbonate bands are a function of particle size and packing it has been suggested that relative intensities, shapes and positions of bands are not significantly affected by grain size or packing [1].

Mid-infrared (MIR) reflectance studies [7,8] show that the spectral response from carbonate powders is sensitive to powder grain size because of the competing effects of the specular and diffuse components of the reflected radiation. Pore space plays a role in the decrease in spectral contrast through separation of fine particles so that they incoherently volume scatter. However, theoretically compaction of the same powdered sample could subsequently serve to enhance coherent scattering [7,8]. MIR emissivity studies demonstrate that variation in spectral behaviour as a function of grain size is specific to the separate internal modes of the carbonate  $[\text{CO}_3^{2-}]$  anion as a function of the intrinsic absorption coefficient and particle size [9-11]. The  $\nu_3$  antisymmetric stretching mode undergoes a progressive decrease in spectral contrast with decreasing particle size, labelled 'type-1' behaviour [9,11,12]. The  $\nu_2$  and  $\nu_4$   $[\text{CO}_3^{2-}]$  bending modes initially follow the same trend as  $\nu_3$  until a critical particle size at which point the original emissivity trough becomes a peak, 'type-2' behaviour. Type-3 behaviour is characterised by a spectral feature that increases in spectral contrast with decreasing particle size [9,11,12]. Particle size effects on the Raman spectra of calcite powders are far less well documented, although a decrease in intensity of all bands below  $24\mu\text{m}$  mode size powders has been reported [13].

Given that NIR bands ultimately stem from the separate behaviours of the  $[\text{CO}_3^{2-}]$  internal modes it seems likely that varied trends in the NIR spectral response as a function of grain

size may exist. To this end, this study examines the NIR spectral response of calcite powders across eight separate particle size intervals. The MIR and Raman response of the exact same powders are published elsewhere [13].

## **2. Materials and methods**

The mode sizes of the powdered calcite (Iceland spar) examined in this study and associated particle size distributions for each size fraction (performed by laser diffraction using a Malvern Mastersizer 2000 particle size analyser) are presented in Figure 1. Details on particle size fraction preparation, scanning electron microscopic analysis and, the mid infrared and laser Raman spectral responses for the exact same powders as those examined in this present study are presented in detail elsewhere [13]. It is important to note that the 121 $\mu\text{m}$  to 19 $\mu\text{m}$  powders were dry milled, washed in absolute alcohol and the 3 $\mu\text{m}$  and 5 $\mu\text{m}$  powders prepared from the supernatant from washing the samples [13]. Hence the potential for fines clinging to surfaces of coarser particles was minimized, as even a very small amount of fine particles adhered to the surfaces of large particles can have a significant influence on the volume component of spectral response [8].

Near-infrared (NIR) spectra of solids are most commonly measured using a reflectance technique. It is this area that was intended for investigation, particularly the effect of porosity in packed powders. Transmission measurements involving dilution with KBr would not be appropriate. NIR analyses in the present study were conducted using a Perkin Elmer Spectrum 100N spectrometer. Each modal grain size fraction was divided into six subsamples, which were then poured (to a depth of *ca* 7mm) into 4ml clear glass vials, which were then lightly tapped against the work surface to level powder within each vial. The vials (Perkin Elmer product number L9001029) are designed for NIR analysis. The samples were then measured sequentially to monitor sample homogeneity and analytical performance. Samples were measured in the range 10000-4000  $\text{cm}^{-1}$  with resolution 16 $\text{cm}^{-1}$  as an interleaved measurement. The laser beam goes vertically through the tube bottom and collects the reflected radiation. Each spectrum was collected from 8 scans. First derivative peak fitting was performed using PeakFit (Jandel, Scientific Software) all values

reported show  $r^2 > 0.995$ . The peak fit procedure utilizes zero crossing points and a Savitsky-Golay smoothing function. All data was collected at the University of Brighton (United Kingdom).

### 3. Results and discussion

Nine overlapping bands were resolved using peak fit software, two of which occur close to the  $4000\text{cm}^{-1}$  limit of coverage, hence the remaining seven labelled [A-G] in figure 2 form the basis of this study (Figure 2). The bands exist at wave number intervals comparable with previous studies [1,2]. The bands are documented in table 1 alongside possible band assignments offered from the literature [1,5,6,14]. The wave numbers of the bands do not undergo any significant wave number shift as a function of powder grain size other than perhaps band [F], although this band is very broad (Fig.2). However, significant band-specific changes in absorption are evident. Qualitative comparison of the spectra of the coarsest ( $121\mu\text{m}$ ) and finest fractions indicates overall reduction in peak definition and broadening of spectral features. The weakest band (band [D]) is not resolved in powders with mode sizes  $\leq 24\mu\text{m}$ .

Figure 3 shows absorption for the seven bands plotted against particle mode size. Bands [A] and [B] decrease in absorption intensity with decreasing particle size. Bands [C] and [D] show no significant relationship between absorption and particle size except possibly the low absorption of the  $3\mu\text{m}$  modal size in band [C]. Bands [E],[F] and arguably [G] show similar progressive reduction in absorption intensity, barring the finest  $3\mu\text{m}$  fraction which shows absorption intensity comparable to the  $19$  and  $24\mu\text{m}$  fractions (Figure 3).

Physical compaction of powder unavoidably formed a component of inserting powder into glass vials. However, it is difficult to envisage how inhomogeneous sample compaction could explain the various attributes of the data set shown in figure 3. Namely, the strong correlation between particle size and spectral contrast of bands [A] and [B] are distinguished from that shown by bands [E] and [F] because the latter two bands show a decided increase in absorbance at  $3\mu\text{m}$  mode size relative to the  $5\mu\text{m}$  mode samples. Hence data suggests

that particle size dependent band-specific behaviour outweighs the potential influence of any arbitrary differential sample compaction.

Bands [A] and [B] display extensively similar behaviour as a function of grain size, undergoing a 67.93% and 66.05% reduction in absorption intensity of the 3 $\mu\text{m}$  mode size fraction relative to the 121 $\mu\text{m}$  mode size fraction respectively. The bands intensities are strongly correlated ( $r^2 = 0.9992$ ) and, appear highly sensitive to calcite powder particle size fraction (Figure 4). Bands [A] and [B] are both assigned to  $3\nu_3$  overtones in separate studies [1,5,14]. Presumably the existence of two  $3\nu_3$  overtones at differing wave numbers registers the imprecise representation of longitudinal and transverse components of  $\nu_3$  in measurements taken from powders, similar to that described in MIR studies of calcite group mineral powders [15]. MIR studies show that  $\nu_3$  is the internal mode most affected by particle size [13] and, the protracted decrease in NIR absorption intensity with decreasing particle size of both  $3\nu_3$  overtone bands reported here is compatible with type-1 like behaviour. Hence, it is suggested that  $\nu_3$  overtone bands show similar effects in the NIR to the  $\nu_3$  internal mode at MIR wave lengths.

The origins and behaviour of bands [C] and [D] are questionable. A band in the vicinity of Band [D] reported at 2.16 $\mu\text{m}$  has previously been assigned to either  $\nu_1 + 2\nu_3 + \nu_4$  or  $3\nu_1 + 2\nu_4$  (2.16 $\mu\text{m}$ ) [5], and the separation of the two bands (*ca* 132 $\text{cm}^{-1}$ ) could indicate a relation between the two bands through coupling of an external lattice mode. However, the loss of resolution of band [D] at  $\leq 24\mu\text{m}$  mode size prohibits any interpretation of the band in fine fractions. Band [C] results are also equivocal because there is no significant correlation between particle size and absorbance, other than possibly the 3 $\mu\text{m}$  fraction which shows absorption lowered relative to the rest of the data set.

Bands [E], [F] and possibly [G] show an abrupt increase in the strength of absorbance of the 3 $\mu\text{m}$  mode fraction relative to 5 $\mu\text{m}$  mode fraction. Band [E] has been assigned to the combination  $2\nu_1 + 2\nu_3$  [5] and, band [G] to a  $\nu_1 + 3\nu_3$  combination with anharmonic coupling to an external (lattice mode) [6]. The origin of band [F] is uncertain. However, the band occurs at a *ca* 102 $\text{cm}^{-1}$  wave number offset from band [E], which closely coincides with a calcite external (lattice) mode reported at 106 $\text{cm}^{-1}$  [15]. Hence band [F] may represent  $2\nu_1 +$

$2\nu_3$  coupled to an external (lattice) mode. Accepting this it follows that the common link between bands [E], [F] and possibly [G] are overtones of the degenerate  $\nu_3$  combined with the non-degenerate  $\nu_1$  or its overtone. Interestingly, the apparent increase in NIR absorbance strength in the  $3\mu\text{m}$  mode powder fraction relative to the  $5\mu\text{m}$  mode fraction is qualitatively reminiscent of type-2 behaviour observed in MIR studies [9,11,12] and, the majority of the particulate constituents of the  $3\mu\text{m}$  mode powder are at size ranges which make  $\nu_1$  and  $\nu_3$  optically thin at MIR wavelengths.

## Conclusions

Results show that the behaviour of near-infrared bands in relation to particle size is varied. Bands at  $2.34\mu\text{m}$  ( $4270\text{cm}^{-1}$ ) and  $2.3\mu\text{m}$  ( $4350\text{cm}^{-1}$ ) wavelength decrease in absorbance strength with decreasing particle size in a highly systematic fashion over the 3 to  $121\mu\text{m}$  mode particle size range. The band at  $2.22\mu\text{m}$  ( $4500\text{cm}^{-1}$ ) appears to undergo a decrease in absorbance in the  $3\mu\text{m}$  mode particle size fraction relative to all other particle size fractions. Over the same ( $121\text{-}3\mu\text{m}$ ) particle size range bands at  $2\mu\text{m}$  ( $5007\text{cm}^{-1}$ ),  $1.96\mu\text{m}$  ( $5109\text{cm}^{-1}$ ) and  $1.87\mu\text{m}$  ( $5336\text{cm}^{-1}$ ) wavelengths show an initial decrease in absorption intensity, but an increase in absorption intensity in the  $3\mu\text{m}$  mode particle size powder relative to the  $5\mu\text{m}$  mode powder. Hence, data suggests that the bands show trends reminiscent of mid-infrared type-1 and type-2 behaviours of  $[\text{CO}_3^{2-}]$  internal modes in the vicinity of the particle size optical thick to thin transition.

## Acknowledgements

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## Figure captions

**Figure 1.** Particle size analysis of powdered calcite size fractions, modified from [13].

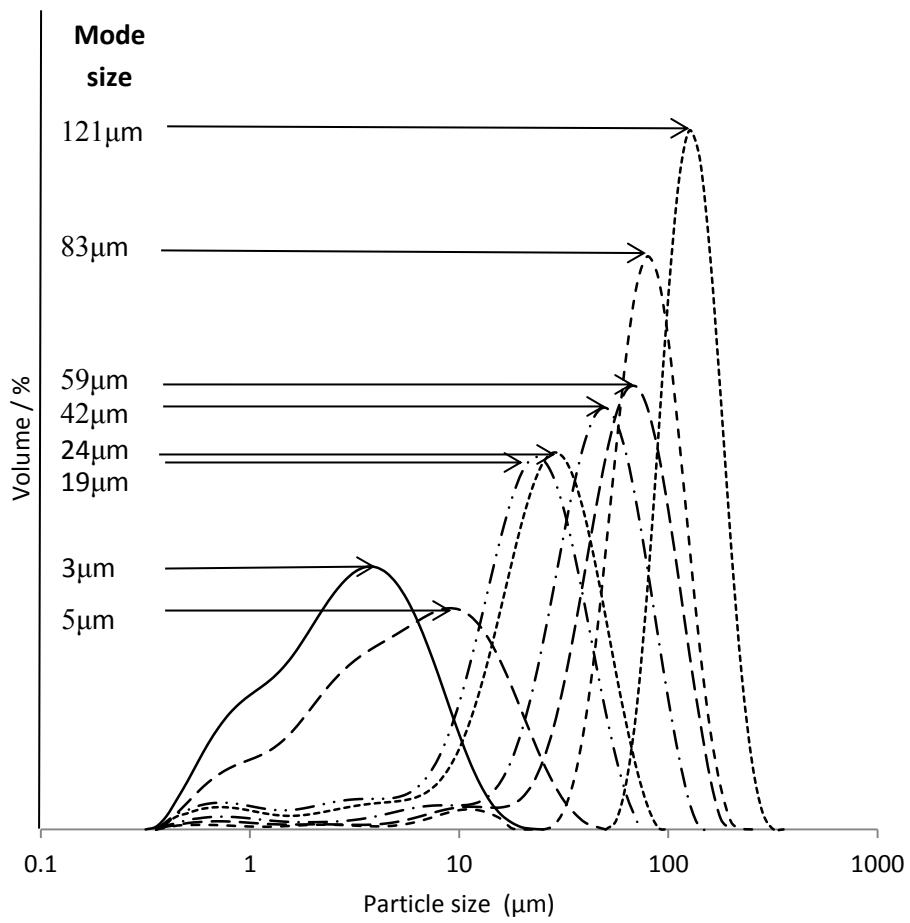
**Figure 2.** NIR spectrum of a 120 $\mu\text{m}$  mode particle size calcite powder, bands are labelled [A] to [G] respectively, with corresponding first derivative peak fit ( $r^2 = 0.998$ ).

**Figure 3.** Absorption plotted against particle size fraction ( $\mu\text{m}$ ) for bands [A] to [G]. Grey diamonds represent the mean absorption intensity of six replicate analyses represented by white diamonds. Error bars represent the standard deviation relative to the mean analysis, where not shown the error bar is smaller than the grey (mean) diamond symbol.

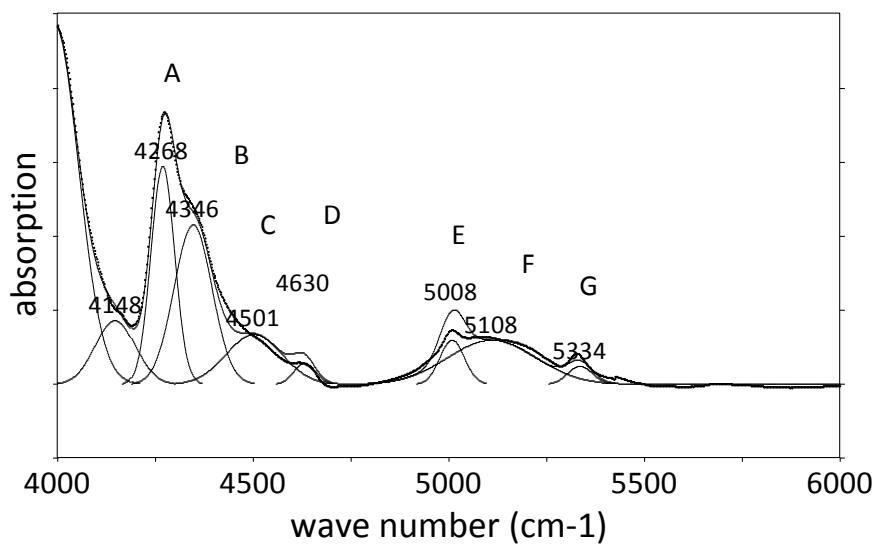
**Figure 4.** Band [A] mean absorption plotted against band [B] mean absorption. The mode grain sizes of the eight powders are given in microns.

## Table Caption

**Table 1.** The mean wave number for the seven bands (labelled [A] to [G]) for eight particle mode size fractions, together with mean wavelength and previously published band assignments. Symbol  $\bar{\nu}$  denotes the mean wave number ( $\text{cm}^{-1}$ ) of six replicate analyses.

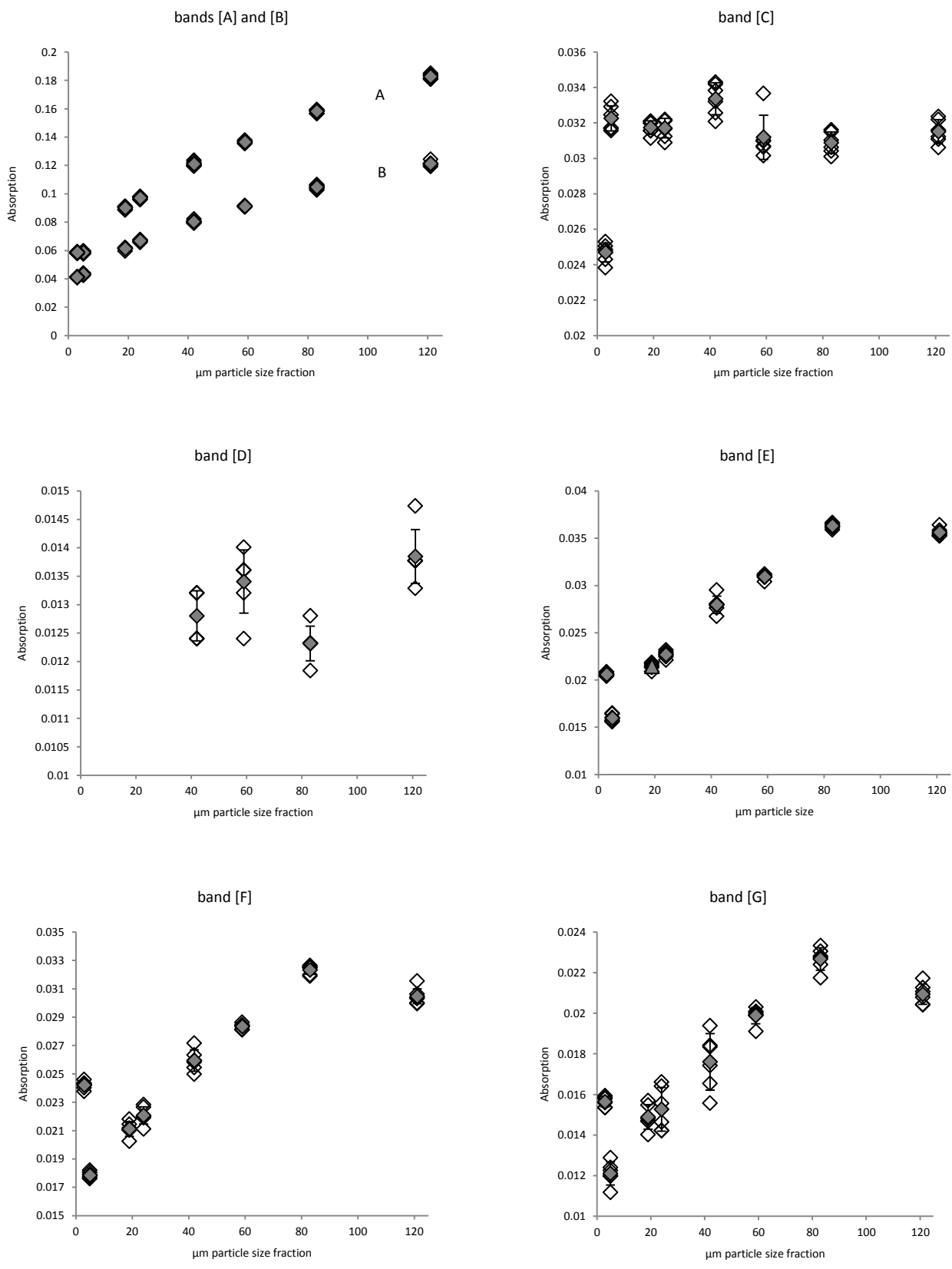


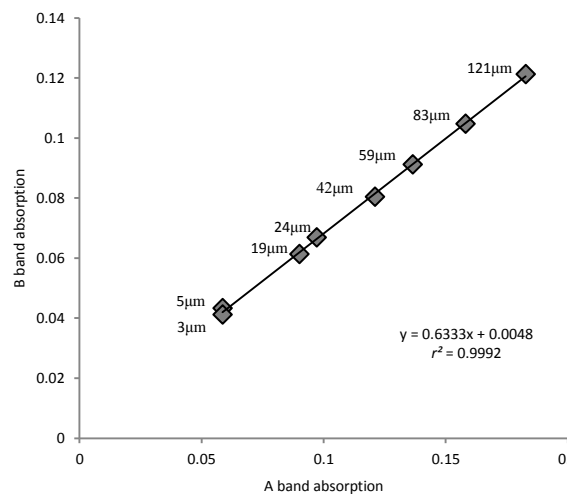
**Figure 1.**



**Figure 2.**

**Figure 3**





**Figure 4.**

	A	B	C	D	E	F	G	$\mu\text{m}$ size
$\dot{x}$	4271	4351	4503	-	4991	5162	5320	3
$\dot{x}$	4272	4349	4500	-	5006	5146	5317	5
$\dot{x}$	4270	4349	4498	-	5007	5123	5332	19
$\dot{x}$	4269	4348	4512	-	5009	5120	5332	24
$\dot{x}$	4271	4353	4509	4632	5009	5111	5334	42
$\dot{x}$	4270	4353	4510	4633	5008	5113	5335	59
$\dot{x}$	4271	4352	4494	4622	5006	5110	5337	83
$\dot{x}$	4269	4346	4499	4631	5007	5109	5336	121
Wavelength ( $\mu\text{m}$ )	2.34	2.30	2.22	2.16	2.00	1.96	1.87	
Assignment	$3v_3$ (2.35 $\mu\text{m}$ ) [5].	$3v_3$ (2.30 $\mu\text{m}$ ) [1,14].		$v_1 + 2v_3 + v_4$ or $3v_1 + 2v_4$ (2.16 $\mu\text{m}$ ) [5]. Coupled to lattice mode [6].	$2v_1 + 2v_3$ (2.0 $\mu\text{m}$ ) [5].		$v_1 + 3v_3$ (1.9 $\mu\text{m}$ ) [5]. Coupled to lattice mode [6].	

**Table 1.**