

1 **Crystal chemical correlations between the mid and near-infrared in carbonate minerals**

2 Laurence Hopkinson ^{1*}, Ken J. Rutt ²

3 ¹(*Corresponding author) School of the Environment and Technology, University of
4 Brighton, Cockcroft Building, Lewes Road Brighton BN2 4GJ, United Kingdom.

5 Tel: +44(0)1273 642239

6 E-mail address: l.hopkinson@brighton.ac.uk

7
8 ² School of Pharmacy and Biomolecular Sciences, University of Brighton, Cockcroft
9 Building, Lewes Road Brighton BN2 4GJ, United Kingdom.

10 Tel: +44(0)1273 642239

11 E-mail address: k.r.rutt@brighton.ac.uk

12

13

14

15 **Abstract**

16

17 Near-infrared (NIR) spectra of carbonates have proved important in many disciplines
18 including planetary exploration. Classically bands in the $4000\text{-}6000\text{cm}^{-1}$ ($2.5 - 1.67\mu\text{m}$)
19 region are assigned to $[\text{CO}_3^{2-}]$ internal mode combinations and overtones. However band
20 assignments remain equivocal. This study examines three prominent bands ((*ca* 4505 cm^{-1}
21 ($2.219\mu\text{m}$), 4900cm^{-1} ($2.041\mu\text{m}$) and 5145cm^{-1} ($1.944\mu\text{m}$)) from powdered calcite and
22 aragonite group minerals. Results indicate that the bands originate from anharmonic coupling
23 of degenerate internal mode(s) with external (lattice) modes. On this basis it is suggested that
24 NIR data may provide an untapped source of detailed information on lattice mode
25 frequencies and information on the type(s) of the environmental cation(s) in carbonate
26 minerals.

27

28 **Key words:** Infrared observations, mineralogy, spectroscopy

1. Introduction

Carbonate minerals are of appreciable interest in many disciplines including planetary exploration [1-5]. The mid-infrared (MIR) spectra of the $[\text{CO}_3^{2-}]$ internal modes of the aragonite (orthorhombic) and calcite (trigonal) groups are well documented as is intra-group wavenumber sensitivity of the carbonate radical to the coordinating divalent cation(s) [6-8]. Although no single physical property of the environmental cation is considered directly responsible for absorption band positions [3] it is widely considered that small shifts of internal modes from the free ion wavenumber reflect small changes in the chemical bonding of the carbonate ion [8]. Various near-infrared (NIR) reflectance and absorption bands have been reported in separate studies in the $4000\text{-}6000\text{cm}^{-1}$ ($2.5 - 1.67\mu\text{m}$) region [9-10] and a range of assignments for calcite and aragonite have been suggested based primarily on combination and overtones of the carbonate radical [1,9,11] although anharmonicity is expected to have quite a large effect on multiple combination tones [11]. To this end this study explores three prominent bands in NIR spectra in an attempt to elucidate the precise relationship between the NIR bands, anharmonicity and, the MIR spectra from which the overtones and combinations emanate.

2. Materials and Methods

Fourier Transform mid-infrared (MIR) analyses were performed using a Perkin Elmer Spectrum 65. Raman analyses were conducted on lightly ground carbonate mineral powders employing a Perkin Elmer IdentiCheck Raman spectrometer, fitted with a 785nm laser and continuous (dispersive) CCD detector. The samples were measured in the spectral range $2000\text{-}200\text{ cm}^{-1}$. Each spectrum was collected from 8 scans for 2s using 70mW laser power at room temperature. Both techniques show a resolution of 2cm^{-1} for sharp spectral bands. Near-infrared (NIR) analyses were conducted using a Perkin Elmer Spectrum 100N spectrometer. Samples were measured in glass vials using NIR reflectance accessory in the range $4000\text{-}6000\text{cm}^{-1}$ region with resolution 16 cm^{-1} . Each spectrum was collected from 5 scans as an interleaved measurement and displayed in absorbance mode. For all three spectroscopic techniques first derivative peak fitting was performed using PeakFit (Jandel, Scientific Software) all values reported show $r^2 > 0.995$.

Six calcite group and four aragonite group powders were analyzed. The MIR and Raman band positions of the internal modes of the carbonate powders agree well with previous reports (Table S1). Hereon experimental band positions are reported in favor of

62 previously published band positions merely to minimize potential uncertainties in band
63 frequencies related to particle size effects and cation substitution schemes within specific
64 powders [21,22] when reporting complementary NIR data. All data was collected at room
65 temperature and acquired at the University of Brighton (United Kingdom).

66

67 **3. Results and Discussion**

68

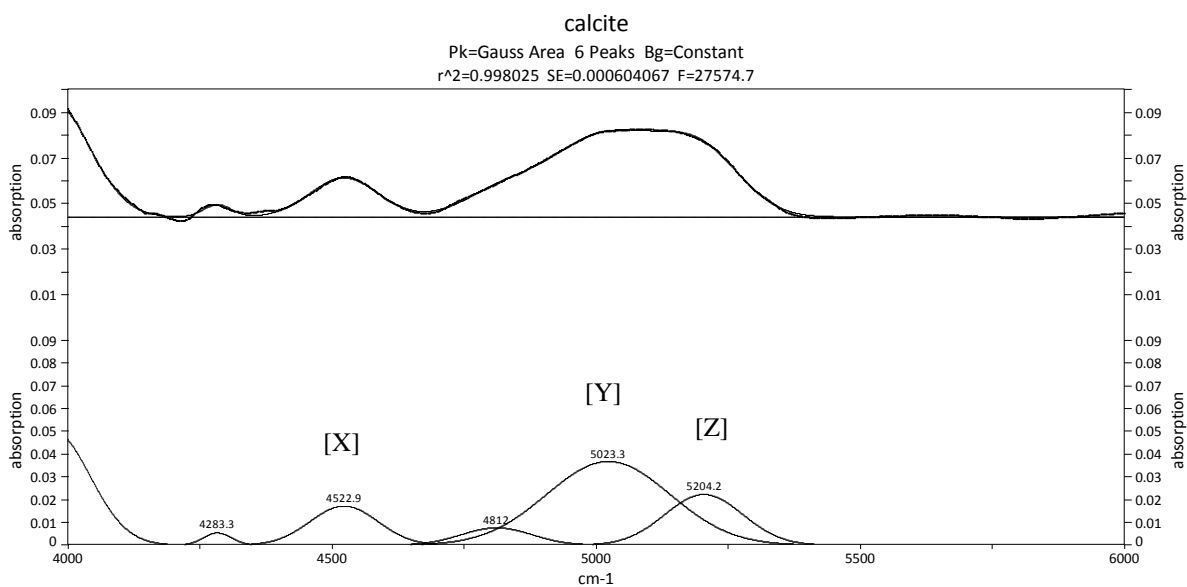
69 The NIR spectra consist of a series of variably resolved and commonly overlapping
70 broad bands (Fig. 1) with peaks within wavenumber ranges in which reflectance and
71 absorbance bands have previously been reported [2,9]. Bands in the region of (*ca* 4505, 4900
72 and 5145 cm^{-1}) labelled [X],[Y],[Z] respectively were resolved for all minerals examined, the
73 relative strengths of absorbance and frequencies varied from spectrum to spectrum (Table 1).
74 The three bands are the focus of this study. The calcite NIR band [Y] wavenumber (5023 cm^{-1} ,
75 1.99 μm) closely coincides with the 2 μm band reported from calcite assigned as ($2\nu_1 + 2\nu_3$)
76 combination band [9]. The closest match to the calcite band [X] wavenumber (measured at
77 4523 cm^{-1} (2.21 μm)) is reported at 2.16 μm assigned to ($\nu_1 + 2\nu_3 + \nu_4$) [1,9]. The calcite band
78 [Z] at 5204 cm^{-1} (1.92 μm) closely coincides with the 1.9 μm band assigned to a ($\nu_1 + 3\nu_3$)
79 combination [9].

80

81

82

83



84

85

86 **Figure 1.** Peak-fitted NIR spectrum of calcite powder ($r^2 = 0.998$). Labels [X], [Y] and [Z] indicate the relative
87 positions of the three bands examined in this study.

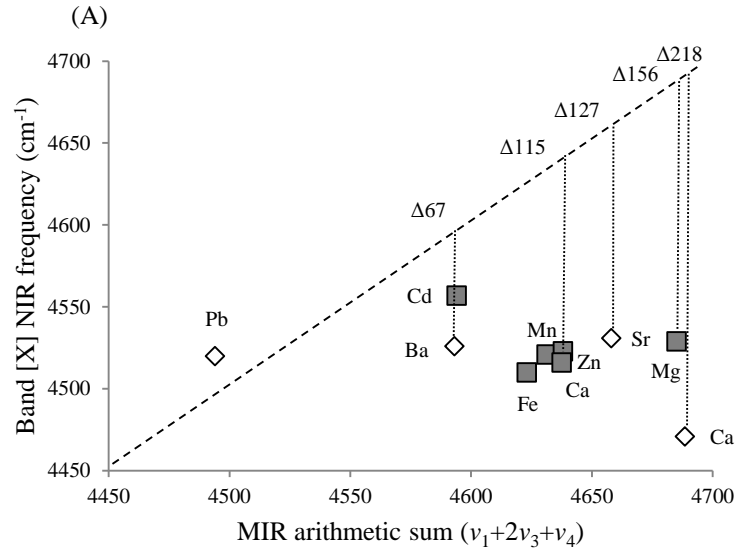
88

89 Figure 2 shows the calculated values of the combination bands derived from simple
90 summation of MIR data plotted against the NIR frequencies of bands [X], [Y] and [Z]. For all
91 three bands the NIR data deviates variably from a simple harmonic approximation to the
92 MIR-derived values. Further, the disposition of data is such that the divalent cations with the
93 greatest and least atomic masses define the two extremes in wavenumber values for each
94 mineral group and, for bands [X] and [Z] the greatest and least atomic masses for each
95 mineral group coincides with the largest and smallest offset of the NIR wavenumber from the
96 MIR arithmetic totals (Fig. 2).

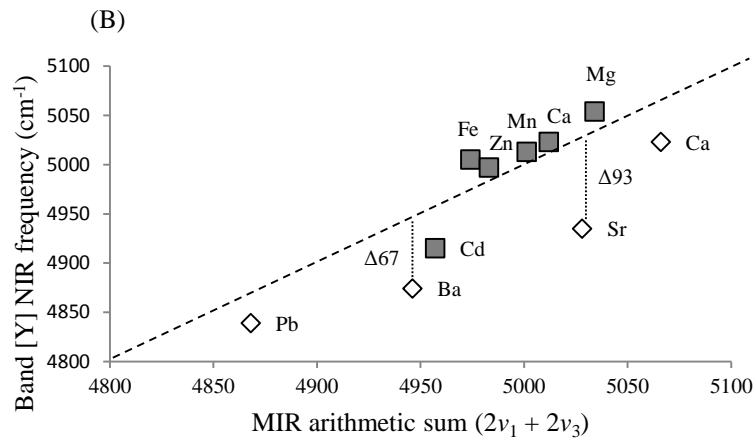
97 The wavenumber difference ($\Delta x \text{ cm}^{-1}$) between values attained by summation of MIR
98 combination band totals and that recorded by NIR for bands [X], [Y], and [Z] respectively are
99 tabulated in Table 2. In total thirteen NIR band ($\Delta x \text{ cm}^{-1}$) values fall within 16cm^{-1} of
100 published values for a given mineral-specific lattice mode, with eight readings within $\leq 4\text{cm}^{-1}$
101 of a published lattice mode. For example (Band [X]) the mineral aragonite ($\Delta 217\text{cm}^{-1}$)
102 exactly coincides with the $217\text{cm}^{-1} A_{1g}$ Raman mode [8]; strontianite ($\Delta 127\text{cm}^{-1}$) coincides
103 with a lattice mode at 128.6 cm^{-1} [24]; magnesite ($\Delta 162\text{cm}^{-1}$) very closely coincides with an
104 E_u lattice mode reported at 158cm^{-1} [8]; otavite ($\Delta 124\text{cm}^{-1}$) is close to a E_u lattice mode
105 reported at 120cm^{-1} [8]; calcite ($\Delta 115 \text{ cm}^{-1}$) closely matches the A_{2u} lattice mode reported
106 between 106cm^{-1} and 109cm^{-1} [8,25]. Band [Y] witherite [BaCO_3] ($\Delta 72\text{cm}^{-1}$) closely
107 coincides with a lattice mode reported at 76cm^{-1} [8]; strontianite [SrCO_3] ($\Delta 93\text{cm}^{-1}$) closely
108 coincides with a lattice mode reported at 105cm^{-1} [24]. Band [Z] ($\Delta x \text{ cm}^{-1}$) values in seven
109 cases (Fig. 1c) closely match reported translational and librational lattice mode frequencies
110 (Table 2).

111 MIR-measurement of the degenerate ν_3 mode from powders is less accurate than the
112 sharper ν_1 , ν_2 and ν_4 internal modes. For instance, values obtained from powdered calcite at
113 room temperature show a spread of almost 30cm^{-1} in separate studies (mean 1422.5cm^{-1} ($n =$
114 $7) \pm 12.5\text{cm}^{-1}$) [8]. Evidently many NIR analyses show $\Delta x \text{ cm}^{-1}$ values which exceed
115 analytical uncertainty related to MIR measurement of ν_3 and also coincide exactly or closely
116 with established lattice modes (Table 2). This is interpreted to indicate that subtractive lattice
117 mode components to combinations which contain overtones of the ν_3 fundamental exist in the
118 NIR spectra as a consequence of interaction of the motions of the carbonate ion with motion
119 of the entire lattice cell, with the separation in wavenumber due to anharmonic coupling of
120 the internal and lattice fundamentals [26].

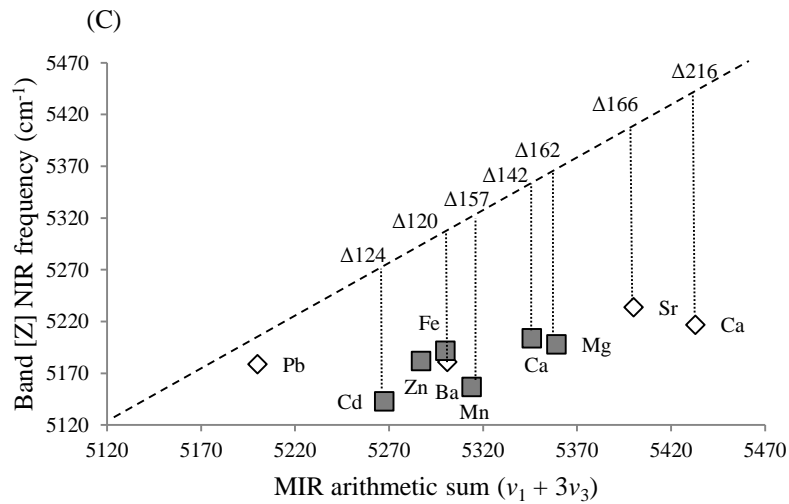
121



122



123



124

125 **Figure 2.** MIR derived frequencies of combination bands plotted against NIR frequencies for (a) band [X], (b)

126 band [Y], and (c) band [Z]. Combination band assignments are taken from [9]. Diamonds represent aragonite

127 group minerals, squares calcite – group minerals.

128 Band [Y] calcite group data approximates to the MIR derived arithmetic sum of ($2\nu_1$
129 $+ 2\nu_3$) suggesting minimal mixing of lattice modes with combinations of internal mode
130 overtones (Figure 1b) with the highest wavenumber internal mode combination band
131 occurring in compounds with the smallest cation, consistent with compression of the
132 carbonate ion by its packing being largest for small cations and decreasing as the size of the
133 coordinating cation increases [8]. The aragonite group data show a similar trend but all occur
134 at lower frequencies consistent with greater anharmonicity and potentially greater degrees of
135 mixing of internal modes with lattice modes as a function of environmental cation and
136 mineral group structure. The greatest $\Delta \text{ cm}^{-1}$ values of bands [X] and [Z] coincide with the
137 smallest cation mass of the calcite and aragonite groups, i.e. the minerals magnesite and
138 aragonite respectively, suggesting that the wavenumber of the lattice mode active in mixing
139 with internal modes may increase with decreasing cation size.

140

141 **4. Conclusions**

142 The majority of MIR studies do not present data at $ca < 600\text{cm}^{-1}$. Similarly Raman
143 studies do not commonly report bands at $ca < 200\text{cm}^{-1}$. Moreover no polarization dependence
144 can be determined from powders which means that different external modes of similar
145 wavenumber may appear as a single band [8]. Hence unassigned low-wavenumber $\Delta x \text{ cm}^{-1}$
146 values reported in Fig.2 and table 2 may include or consist of undocumented lattice modes
147 and or regions within which lattice modes of similar wavenumber reside.

148

149 **References**

150

- 151 [1] S.J. Gaffey, Am. Mineral. 71 (1986) 151-162.
152 [2] S.J. Gaffey, J. Geophys. Res. 92 (1987) 1429-1440.
153 <http://dx.doi.org/10.1029/JB092iB02p01429>.
154 [3] M.D. Lane, P.R. Christensen, J. Geophys. Res. 102 (1997) 25581-25592.
155 <http://dx.doi.org/10.1029/97JE02046>.
156 [4] Ehlmann, B.L., et al., 2008. Science 322 (2008) 1828-1832.
157 <http://dx.doi.org/10.1126/science.1164759>.
158 [5] P.L. Harner, M.S. Gilmore, Icarus, 250 (2015) 204-214.
159 <http://doi.org:10.1016/j.icarus.2014.11.037>.
160 [6] C.K. Huang, P.F. Kerr, 1960. Am. Mineral. 45 (1960) 311-324.

- 161 [7] H. Elderfield, R. Chester, *Am. Mineral.* 56 (1971) 1600-1606.
- 162 [8] W.B. White, Farmer V.C., Ed. *The infrared spectra of minerals*, Mineral. Soc. Mono. 4.
163 (1974) Chap. 12. 227-282.
- 164 [9] G.R. Hunt, J.W. Salisbury, *Mod. Geol.* 2 (1971) 23-30.
- 165 [10] E. Palomba, A. Zinzi, E.A. Cloutis, M. D'Amore, D. Grassi, A. Maturilli, *Icarus*, 203
166 (2009) 58-65. <http://dx.doi.org/10.1016/j.icarus.2009.04.013>.
- 167 [11] R.M. Hexter, *Spectrochim. Acta* 10 (1958) 281-290.
- 168 [12] M.E. Böttcher, P-L Gehlken, D.F. Steele, *Solid State Ionics.* 103 (1997) 1379-1385.
- 169 [13] H.G.M Edwards, S.E. Villar, J. Jehlicka, T. Munshi, *Spectrochim. Acta* A61 (2005)
170 2273-2280. <http://dx.doi.org/10.1016/j.saa.2005.02.026>.
- 171 [14] J. Santillán, Q. Williams, *Phys. Earth Planet. Int.* 143 (2004) 291-304.
- 172 [15] M.C. Hales, R.L. Frost, *Polyhedron.* 26 (2007) 4955-4962.
173 <http://dx.doi.org/10.1016/j.poly.2007.07.002>.
- 174 [16] C-C. Lin, L-G. Lui, *J. Phys. Chem. Solids*, 58 (1997) 977-987.
- 175 [17] R.L. Frost, W.N. Martens, D.L. Wain, M.C. Hales, *Spectrochim. Acta* A70 (2008) 1120-
176 1126. <http://dx.doi.org/10.1016/j.saa.2007.10.027>.
- 177 [18] F. Zhou, C. Yan, H. Wang, Q. Sun, Q. Wang, A. Alshameri, *Min. Eng.* 78 (2015) 15-20.
- 178 [19] R. Minch, D.H. Seoung, L. Ehm, B. Winkler, K. Knorr, L. Peters, L.A. Borkowski, J.B.
179 Parise, Y. Lee, L. Dubrovinsky, W. Depmeier, *Alloys and Comp.* 508 (2010) 251-257.
180 <http://dx.doi.org/10.1016/j.jallcom.2010.08.090>.
- 181 [20] M. Marocchi, H. Bureau, G. Fiquet, F. Guyot, *Chem. Geol.* 290 (2011) 145-155.
182 <http://dx.doi.org/10.1016/j.chemgeo.2011.09.010>.
- 183 [21] J.V. Dubrawski, A-L. Channon, S. St. Warne, 1989. *Am. Mineral.* 79 (1989) 187-190.
- 184 [22] P. Kristova, L.J. Hopkinson, K.R. Rutt, *J. Phys. Chem. A.* 119 (2015) 4891-4897.
185 <http://dx.doi.org/10.1021/acs.jpca.5b02942>.
- 186 [23] A.K. Sood, A.K. Arora, V. Umadevi, G. Venkataraman, *Solid State Phys.* 16 (1981) 1-
187 16.
- 188 [24] J.M. Alía, Y. Díaz de Mera, H.G.M. Edwards, P. González Martín, S. López-Andres,
189 *Spectrochim. Acta* A53 (1997) 2347-2362. [http://dx.doi.org/10.1016/S1386-1425\(97\)00175-](http://dx.doi.org/10.1016/S1386-1425(97)00175-3)
190 [3](http://dx.doi.org/10.1016/S1386-1425(97)00175-3).
- 191 [25] F.A. Andersen, L. Brečević, *Acta Chem. Scan.* 45 (1991) 1018-1024.
- 192 [26] R.M. Hexter, D.A. Dows, *J. Chem. Phys.* 25 (1956) 504-509.

194 **Acknowledgments**

195

196 The University of Brighton is thanked for financial support. The reviewers are thanked for
197 their input. The data and samples are archived at the University of Brighton.

198

199 **Table captions**

200

201 **Table 1.** Near-infrared peak-fitted bands, all reported values are in (cm^{-1}) units. Band [X]
202 wavenumbers corresponds to 2.267 - 2.174 μm wavelength range, band [Y] to 2.092 -
203 1.992 μm and, band [Z] to the 1.968 - 1.919 μm range.

204

205 **Table 2.** Frequencies of NIR data and MIR calculated values for bands: [X] ($\nu_1 + 2\nu_3 + \nu_4$);
206 [Y] ($2\nu_1 + 2\nu_3$); [Z] ($\nu_1 + 2\nu_3$) compared with published lattice mode frequency data. Lattice
207 mode data from [8, 16, 23-24].

208

209 **Supplementary Material table caption**

210

211 **Table S1.** MIR Internal mode frequencies of the powdered carbonate minerals (bold)
212 compared to published values. Data from: [8,12-20]. The ν_2 frequency of the natural siderite
213 and magnesite specimens investigated in the present study are consistent with essentially pure
214 iron-rich siderite and impure Fe-Mn bearing magnesite [21].

215

216

217

218

219

Table 1

220

221

222

	4050-4180	4250-4419	[X] 4410-4600	[Y] 4780-5020	[Z] 5080-5210	5475-5750
Cerrusite	4144	4307	4520	4839	5179	5615
Witherite	4182	4391	4526	4874	5181	5538
Strontianite	4097	4256	4531	4935	5234	5597
Aragonite	4062	4343	4471	5059	5217	-
Calcite	-	4283	4523	5023	5204	-
Rhodacrosite	-	4402	4521	5013	5157	-
Otavite	4093	-	4557	4919	5146	5765
Magnesite	4076	4417	4529	5056	5197	-
Siderite	4016	4318	4510	5005	5182	5605
Smithsonite	-	4293	4516	4997	5192	5683

223

224

225

Table 2

226

	band	MIR	NIR	$\Delta(\text{MIR} - \text{NIR})$	Assignment
Magnesite [MgCO₃]	X	4685	4529	156	158cm ⁻¹ [8]
	Y	5034	5056	-22	
	Z	5359	5197	162	158cm ⁻¹ [8]
Calcite [CaCO₃]	X	4638	4523	115	106cm ⁻¹ (powder), <i>ν_r</i> 102cm ⁻¹ , <i>ν_l</i> 123cm ⁻¹ (single crystal) [8]
	Y	5012	5023	-11	
	Z	5346	5204	142	156cm ⁻¹ [23]
Rhodochrosite [MnCO₃]	X	4631	4521	110	
	Y	5001	5013	-12	
	Z	5314	5157	157	157cm ⁻¹ [8]
Siderite [FeCO₃]	X	4623	4510	113	
	Y	4974	5005	-31	
	Z	5287	5182	105	
Otavite [CdCO₃]	X	4594	4557	38	
	Y	4957	4919	42	
	Z	5267	5143	124	120cm ⁻¹ [8]
Smithsonite [ZnCO₃]	X	4637	4516	122	
	Y	4983	4997	-14	
	Z	5300	5192	108	
Aragonite [CaCO₃]	X	4689	4471	218	217cm ⁻¹ [8] 215.6cm ⁻¹ [24] 214cm ⁻¹ [16]
	Y	5066	5023	43	
	Z	5433	5217	216	217cm ⁻¹ A1g [8] 215.6 [24] 214cm ⁻¹ [16]
Strontianite [SrCO₃]	X	4658	4531	127	128.6cm ⁻¹ [24]
	Y	5028	4935	93	102cm ⁻¹ [24]
	Z	5400	5234	166	170.8cm ⁻¹ [24]
Witherite [BaCO₃]	X	4593	4526	67	75, 76cm ⁻¹ [8]
	Y	4946	4874	72	75, 76cm ⁻¹ [8]
	Z	5301	5181	120	136cm ⁻¹ [8]
Cerrusite [PbCO₃]	X	4494	4520	-26	
	Y	4868	4839	29	
	Z	5200	5179	21	

227

228

229

Supplementary Material Table S1

230

	ν_1 cm ⁻¹	ν_2 cm ⁻¹	ν_3 cm ⁻¹	ν_4 cm ⁻¹	notes
Magnesite	1096 1094 ^[13]	878 884.5 ^[12] 887 ^[8] 885 ^[14]	1421 1456 ^[12] 1450 ^[8] 1446 ^[14]	747 747 ^[13] 748 ^[8] 749 ^[14]	Natural magnesite, University of Brighton collection
Calcite	1086 1084 ^[12] 1086 ^[8]	871 875.71 ^[12]	1420 1419-1428 ^[12] 1420-1435 ^[8]	712 712 ^[8]	Synthetic
Rhodochrosite	1094 1088 ^[8]	862 867 ^[8] 868 ^[18] 862 ^[14]	1407 1433 ^[8] 1431 ^[18] 1450 ^[14]	724 727 ^[8] 735 ^[14]	Natural rhodochrosite University of Brighton collection
Siderite	1087 1090 ^[20]	861 866 ^[8] 861 ^[14]	1400 1422 ^[8] 1412 ^[14]	736 737 ^[8] 734 ^[14]	Natural siderite University of Brighton collection
Otavite	1084 1088 ^[19]	859 862 ^[8]	1395 1462 ^[8]	721 722 ^[8]	Synthetic
Smithsonite	1088 1093 ^[8] 1092 ^[15]	866 870 ^[8] 864 ^[15] 864-867 ^[17]	1408 1440 ^[8] 1392,1424 ^[15]	742 743 ^[8] 743 ^[15] 743-744 ^[17]	Natural University of Brighton collection
Aragonite	1083 1085 ^[8]	854* 875, 870 ^[8] 853 ^[16]	1450 1490 ^[8]	712,699 712,699 ^[8]	Natural University of Brighton collection
Strontianite	1072 1075 ^[8]	856 860 ^[8]	1443 1470 ^[8]	705,699 707,699 ^[8]	Synthetic
Witherite	1060 1064 ^[8]	856 860 ^[8]	1420 1435 ^[8]	693 693 ^[8]	Natural University of Brighton collection
Cerrusite	1059	856	1414 1422 ^[8]	682,676 677 ^[8]	Synthetic

231