

1 **The near-infrared spectra of the alkali carbonates**

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19

20 **Abstract**

21

22 This study presents the first account of the near-infrared (NIR) spectra of the alkali carbonates:
23 [Cs₂CO₃] [Rb₂CO₃] [K₂CO₃] [Na₂CO₃] and [Li₂CO₃]. Seven NIR bands (labelled [A] to [G] inclusive) within
24 the [4000-6000cm⁻¹] (2.5 – 1.66μm) region of interest are common to the five spectra examined, of
25 which six bands [A-C] and [E-G] proved amenable to quantitative study. The first three occur in the
26 range 4067-4493cm⁻¹ (2.458-2.226μm) and are assigned to a [CO₃²⁻] 3ν₃ overtone, Bands [E] and [F]
27 are centred at *ca* 4902cm⁻¹ (2.04 μm) and *ca* 5034cm⁻¹ (1.98 μm) respectively and are assigned to a
28 (2ν₁ + 2ν₃) combination. Band [G] centred at *ca* 5190 cm⁻¹ (1.92 μm) is assigned to a (ν₁ + 3ν₃)
29 combination. One additional band (Band [X]) centred in the vicinity of *ca* 4080cm⁻¹ (2.45μm) in all
30 spectra other than [Cs₂CO₃] is assigned to (2ν₃ + 2ν₄). The data is compared with the corresponding
31 additive sum of the mid-infrared (MIR) fundamental, or in the case of combinations, Raman and MIR
32 fundamentals. The quantified differences between NIR band frequency and that of the
33 corresponding MIR derived overtone or combination in the case of [Li₂CO₃] and [Rb₂CO₃] closely
34 coincide with Raman active lattice modes of rotary origin. From which it is argued that vibration -
35 libration combinations may operate across a range of NIR frequencies for these mineral types. NIR
36 data from [K₂CO₃], [Cs₂CO₃] and [Na₂CO₃] are discussed in the light of these findings. The influences
37 of differences in atomic mass and space group effects on the NIR spectra of the alkali carbonates are
38 also demonstrated.
39

40 **1. Introduction**

41

42 Anhydrous carbonates number sixty-five mineral types in which the $[\text{CO}_3^{2-}]$ radical provides all the
43 negative charge [1]. The group 1 alkali metal carbonates ($[\text{Li}_2\text{CO}_3]$, $[\text{Na}_2\text{CO}_3]$, $[\text{K}_2\text{CO}_3]$, $[\text{Rb}_2\text{CO}_3]$ and
44 $[\text{Cs}_2\text{CO}_3]$) constitute an important group of minerals which find application in a range of chemical
45 processes [2]. All alkali carbonates are highly hygroscopic and water soluble [3]. The alkali
46 carbonates have been investigated in a number of studies [4 - 8]. It is established that three types of
47 anhydrous alkali carbonate mineral structures exist: $[\text{Li}_2\text{CO}_3]$ (space group $C2/c$); $[\text{Na}_2\text{CO}_3]$ (space
48 group $c2/m$); and $[\text{K}_2\text{CO}_3]$ (space group $p2_1/c$). The potassium carbonate is isostructural with
49 $[\text{Rb}_2\text{CO}_3]$ and $[\text{Cs}_2\text{CO}_3]$ [4-7].

50

51 In common with other carbonate mineral groups [9,10] the $[\text{CO}_3^{2-}]$ internal modes occur across a
52 range of mid-infrared (MIR) wavenumber intervals (table 1). The Raman active ν_1 (totally symmetric
53 C-O stretching mode) appears at *ca* 1080cm^{-1} , the MIR active ν_2 (out-of-plane bending mode) occurs
54 at *ca* 880cm^{-1} , the MIR and Raman active ν_3 doubly degenerate (anti-symmetric stretching mode)
55 occurs around *ca* 1430cm^{-1} , while the doubly degenerate ν_4 in-plane bending mode occurs around
56 715cm^{-1} . The ν_4 internal mode is split in all of the alkali carbonates [4-7]. In the case of $[\text{Li}_2\text{CO}_3]$ and
57 the isostructural carbonates the remaining internal modes of the carbonate ion (ν_1 , ν_2 and ν_3) occur
58 as single bands. The exception is $[\text{Na}_2\text{CO}_3]$ which displays a doublet structure for each of the internal
59 modes (Table 1), interpreted in terms of two non-equivalent orientations of the $[\text{CO}_3^{2-}]$ ion within
60 the primitive unit cell [4,10].

61

62 For carbonate minerals the near-infrared region contains bands due to overtone and combination
63 tones of the $[\text{CO}_3^{2-}]$ anion, also where present evidence of $[\text{H}_2\text{O}]$ [9]. However we can find no
64 published accounts of the near-infrared spectra of any of the alkali carbonates although it seems
65 certain that the differing crystal structures will find expression in the resultant spectra as will any
66 evidence of hydration. Further, studies of other anhydrous carbonate mineral groups indicate that
67 correlations between specific near-infrared wavelengths and different metal cations exist and that
68 combinations between external (lattice) modes and the internal modes of molecular origin may exist
69 [11]. To this end this study presents the near-infrared (NIR) spectra of the alkali carbonates and
70 explores crystal chemical correlations between the spectra with Raman and MIR findings.

71

72 **2. Materials and Methods**

73

74 The powdered alkali metal carbonates examined in this study were sourced from international
75 suppliers: lithium carbonate (Acros Organics, lot number (lot. n.) A0231490), sodium carbonate
76 (Honeywell Fluka, lot. n. SLBQ8163V), potassium carbonate (Fisher Scientific, lot. n. 0886824),
77 rubidium carbonate (Sigma Aldrich, lot.n. MKBW4880V) and cesium carbonate (Sigma Aldrich, lot.n.
78 MKBZ2431V). Samples were oven-dried at 100°C for twenty four hours and immediately placed in a
79 desiccator and then placed in the standard reflectance glass tubes supplied with the NIR instrument
80 by Perkin Elmer. The tubes were filled 2cm deep with the powders. A small bag containing desiccant
81 was placed on top of the sample before sealing the tube with a plastic stopper. The spectra were
82 then measured immediately. Several repeat measurements were taken for each powder sample
83 type. NIR analyses were conducted with a Perkin Elmer Spectrum 100N spectrometer. The powdered
84 samples were measured at room temperature in the range 4000-10000cm⁻¹. The samples were
85 measured using NIRA (near-infrared reflectance accessory) which is used to collect diffuse
86 reflectance spectra of solids and powders. The measurements were done in absorbance. The NIR
87 measurement protocol is as follows. A background scan is taken and a scan type is selected to be
88 interleaved (i.e. the shuttle automatically moves to the rear position to take background scan before
89 moving to the front position to scan the sample and display the ratioed sample spectrum). The
90 number of scans collected was 8, resolution 16cm⁻¹, INGAAS detector selected, optical path
91 difference velocity 1.00 cm/sec.

92

93 Raman analyses were performed with a Perkin Elmer Raman Identichex fitted with a 785nm laser, a
94 CCD detector and a fibre-optic probe with 70mW laser power. The probe spot size is 100µm,
95 working distance is 7.5mm. The samples were measured in the spectral range 2000-100cm⁻¹, with
96 2cm⁻¹ resolution. Each spectrum was collected from 8 scans for 2 seconds. Data manipulation was
97 performed using the software Spectrum (Perkin Elmer) and PeakFit (Jandel, Scientific Software). First
98 derivative (Gaussian) peak-fitting was employed on all spectroscopic data using Jandel Scientific
99 PeakFit software. All values reported show $r^2 > 0.995$. All data was collected at the University of
100 Brighton (United Kingdom).

101 **3. Experimental results**

102

103 **3.1 The near-infrared spectra of the alkali carbonates**

104 In common with all NIR spectra which emerge from overtones and combinations of fundamental
105 MIR absorptions [12] the alkali carbonates show a range of broad variably resolved overlapping

106 bands in the [4000-6000cm⁻¹] region, which are qualitatively similar in appearance to those of the
107 alkaline earths carbonates [9]. Figure 1 shows the spectra and associated Peak-Fit software results
108 for the five alkali carbonate mineral powders examined. Bands [A] to [G] inclusive are common to
109 the five spectra and are central to this study (table 2). Those bands which are not common to all
110 spectra are labelled [V] to [Z] inclusive. Band [V] is singular to [Na₂CO₃]. Band [W] may fall below the
111 lower wavenumber detection range for [Rb₂CO₃] and [Cs₂CO₃], is close to 4000cm⁻¹ for [Na₂CO₃], at
112 4020cm⁻¹ for [K₂CO₃] and 4022cm⁻¹ for [Li₂CO₃]. Band [X] is absent from the [Cs₂CO₃] spectrum. Bands
113 [Y] and [Y¹] are singular to [Rb₂CO₃]. Peak-Fit software identified an additional weak band (band [Z])
114 in the vicinity of 5490cm⁻¹ [Li₂CO₃], 5232cm⁻¹ [Rb₂CO₃] and 5210cm⁻¹ [Cs₂CO₃]. In other spectra the
115 band was too poorly resolved relative to background to accurately position or analyse (marked [Z*]
116 on figure 1), as were variably resolved extremely broad bands in the 5500-5800cm⁻¹ region (marked
117 [Z^{1,2*}] on figure 1). Band(s) in the vicinity of ca 5260cm⁻¹ (1.9μm) theoretically could originate at
118 least in part from the combination of H-O-H band with the antisymmetric OH stretch [9]. However
119 near-infrared spectra do not show an accompanying asymmetric OH stretch at 7140cm⁻¹ (1.49μm).
120 Hence all bands listed in table 2 and displayed in figure 1 are interpreted as [CO₃²⁻] radical-related
121 spectral features although bands [Z^{*1,2}] proved too poorly resolved and broad in nature for
122 meaningful quantitative study and are hereafter excluded from this study.

123

124 **3.2 Bands [A] to [G], atomic mass and space group considerations**

125

126 Figure 2 shows bands [A-G] inclusive plotted against the corresponding atomic mass (amu) of each
127 co-ordinating cation. The figure shows that for each band [Na₂CO₃] occurs at higher wavenumbers
128 than [Li₂CO₃]. Bands [A-C] and [E-G] show reasonable *r*² power-trend type fits for the isostructural
129 carbonates with [Cs₂CO₃] occurring at lower wavenumbers than [K₂CO₃] while the [Rb₂CO₃]
130 wavenumber values are intermediate with respect to [K₂CO₃] and [Cs₂CO₃]. Similar 'mass effects' on
131 fundamental vibrations of internal modes in other carbonate mineral types have been assigned to
132 small changes in the bending and stretching force constants, reflecting differences in the chemical
133 bonding of the carbonate ion [10]. It is also evident from figure 2 that the relationship between
134 increasing atomic mass and decreasing wavenumber does extend to [Na₂CO₃] and [Li₂CO₃] i.e. the
135 [Na₂CO₃] bands occur at marginally higher wavenumbers than those of the [Li₂CO₃] powders,
136 consistent with differing space group effects also exerting influence on band wavenumber positions.

137

138 In contrast to bands [A-C] and [E-G] band [D] shows no correlation between wavenumber and
139 atomic mass for the isostructural carbonates. The reason for the singular absence of any correlation

140 is unclear. However, the spectrum of $[\text{Rb}_2\text{CO}_3]$ shows a shoulder to band [D], marked [Y] and $[\text{Y}^1]$ on
141 figure 1. Hence, it is possible that band [D] in at least some of the other spectra is composite in
142 nature but have gone either unresolved or partially resolved with Peak-Fit software, thereby
143 accounting for the seemingly random nature of band [D] data. For this reason band [D] is not
144 considered further in this study.

145

146 **3.3 Band assignments [A-C]**

147

148 In order to investigate relationships between the NIR data with MIR fundamental vibrations
149 experimental data were plotted against the additive sums of overtones and combinations derived
150 from data listed in table 1. For example, for each alkali carbonate the ν_3 frequency listed in table 1
151 was multiplied by three to yield the overtone denoted $M(3\nu_3)$ etc. For $[\text{Na}_2\text{CO}_3]$ in which each
152 fundamental appears twice (with a small wavenumber separation between each) the average of the
153 two band wavenumbers for each fundamental were taken (table 1).

154

155 In utilizing the MIR internal mode data it is important to note that the degenerate ν_3 fundamental of
156 carbonate minerals measured from powders are broad in MIR spectra with the measured
157 wavenumber falling somewhere between the transverse and longitudinal components of ν_3 .
158 Consequently measurements are generally considered less accurate than for other fundamentals. In
159 the case of powdered calcite, a ($\pm 12.5\text{cm}^{-1}$) variation in the frequency of ν_3 has been reported from
160 seven separate studies [10]. Nevertheless, previous studies have successfully employed the infrared-
161 active component of ν_3 to document linear trends in a range of carbonate mineral compounds [13].

162

163 In comparison with the NIR spectra of other carbonate mineral groups [9] bands [A-C] occur across a
164 wavenumber interval consistent with a $[\text{CO}_3^{2-}] 3\nu_3$ overtone. Figure 3a shows the NIR data for bands
165 [A-C] plotted against $M(3\nu_3)$. Band [A] $[\text{Cs}_2\text{CO}_3]$, $[\text{Rb}_2\text{CO}_3]$ and $[\text{Li}_2\text{CO}_3]$ data are marginally lower than
166 the corresponding $M(3\nu_3)$ values. Band [A] $[\text{K}_2\text{CO}_3]$ data plus all band [B] and [C] data are greater
167 than $M(3\nu_3)$. The three isostructural carbonates show linear trends of increasing wavenumber in the
168 general order $[\text{K}_2\text{CO}_3] > [\text{Rb}_2\text{CO}_3] > [\text{Cs}_2\text{CO}_3]$. The best-fit trend tie-lines for bands [A], [B] and [C] are
169 all angled oblique to the tie line linking the $M(3\nu_3)$ data points. The quantified number (cm^{-1}) to
170 which separate NIR band data points deviate from $M(3\nu_3)$ wavenumber are given in figure 3a.

171

172 **3.4 Band assignments [E-F]**

173

174 Bands [E] and [F] are centred at *ca* 4902cm⁻¹ (2.04 μm) and *ca* 5034cm⁻¹ (1.98 μm) respectively (fig.
175 1). The wavelength intervals are both consistent with a (2ν₁ + 2ν₃) combination band [9]. Figure 3b
176 shows bands [E] and [F] plotted against the corresponding additive sum M(2ν₁ + 2ν₃). In common
177 with bands [A],[B] and [C] the isostructural carbonates in bands [E] and [F] show increase in
178 wavenumber [K₂CO₃] > [Rb₂CO₃] > [Cs₂CO₃]. For both bands the projected tie-lines linking the data
179 points are oblique to the tie-line linking M(2ν₁ + 2ν₃) data points. Band [E] [Na₂CO₃] data point
180 closely coincides with the corresponding M(2ν₁ + 2ν₃) value, whereas [Li₂CO₃] is offset 90cm⁻¹ from
181 its corresponding M(2ν₁ + 2ν₃) total. All band [F] data exhibits NIR wavenumbers greater than M(2ν₁
182 + 2ν₃). The greatest offset (167cm⁻¹) is shown by [K₂CO₃]. Conversely [Li₂CO₃] is practically coincident
183 with its corresponding M(2ν₁ + 2ν₃) total. Also plotted on figure 3b is the band [V] data point for
184 [Na₂CO₃], which is offset 207cm⁻¹ wavenumbers from the corresponding M(2ν₁ + 2ν₃) total.

185

186 **3.5 Band assignment [G]**

187

188 Band [G] is centred at *ca* 5190 cm⁻¹ (1.92 μm) (fig.1), consistent with a (ν₁ + 3ν₃) assignment [9]. All
189 band [G] NIR data plots at lower wavenumbers than the corresponding M(ν₁ + 3ν₃) totals (Fig. 3c).
190 The isostructural carbonates show the same sequential ordering of increasing NIR wavenumber as
191 previously described for bands [A-C] and [E-F]. The tie-line connecting them is orientated at a low
192 oblique angle or sub parallel to that connecting M(ν₁ + 3ν₃) totals. The [Li₂CO₃] data point is made
193 conspicuous by its 194cm⁻¹ offset from its corresponding M(ν₁ + 3ν₃) total.

194

195 **3.6 Band assignment [X]**

196

197 Band [X] is centred in the vicinity of *ca* 4080cm⁻¹ (2.45μm) in all spectra other than [Cs₂CO₃] (fig.1).
198 Because the wavenumber of band [X] decreases from [Li₂CO₃] (4140cm⁻¹) to 4007cm⁻¹ for [Rb₂CO₃] it
199 may follow that band [X] for [Cs₂CO₃] may occur at <4000cm⁻¹. The wavenumber interval of band [X]
200 data is consistent with a (2ν₃ + 2ν₄) assignment [9]. Band [X] NIR data is plotted against M(2ν₃ + 2ν₄)
201 in figure 3d. All data plots at lower values than corresponding M(2ν₃ + 2ν₄) totals.

202

203 **4. Interpretation**

204

205 It is well documented that overtones are the whole number multiples of the fundamentals only to a
206 first approximation and, because of the anharmonicity of vibration overtones are usually less than
207 the additive sum the fundamental frequency [14]. Thus, the presence of differences between the

208 NIR band data and additive sums of MIR vibration fundamentals is not striking in the sense that
209 anharmonicity of vibration implies that it should be so. What is apparent is that individual NIR band
210 data sets are either greater or less than the whole number additive sum of the assigned overtone /
211 combination, or else contain data which is both greater and less than that of the assignment (fig. 3).
212 Further, the NIR data for the isostructural carbonates is sequentially ordered with respect to atomic
213 mass, while different space group effects evidently exert influence on $[\text{Na}_2\text{CO}_3]$ and $[\text{Li}_2\text{CO}_3]$ spectra
214 (fig. 2).

215

216 It has been demonstrated that lattice modes of rotatory origin can combine with internal modes of
217 molecular origin to shift the pure molecular vibrational transition to higher and or lower frequencies
218 [15,16]. Figure 4 shows the Raman spectra of the five carbonate powders in the $100\text{-}300\text{cm}^{-1}$ lattice
219 mode region. $[\text{Li}_2\text{CO}_3]$ differs significantly from the other spectra by virtue of possessing sharp high
220 intensity Raman bands which suggests a far higher degree of ordering than the other alkali
221 carbonates [4,10]. In contrast the $[\text{Na}_2\text{CO}_3]$ powder exhibits Raman bands which are broad and
222 diffuse. This difference is interpreted to indicate that $[\text{Na}_2\text{CO}_3]$ is far less well ordered [4].
223 Broadening of lattice modes provides evidence of translational disorder in the stacking of $[\text{CO}_3^{2-}]$ ions
224 [10]. The Raman spectra of the three isostructural carbonates are characterised by broad
225 overlapping bands similar in appearance to $[\text{Na}_2\text{CO}_3]$ (fig. 4). However the width of the room
226 temperature lattice modes of $[\text{K}_2\text{CO}_3]$ and $[\text{Rb}_2\text{CO}_3]$ are ascribed to thermal broadening distinct from
227 the true disordering of $[\text{Na}_2\text{CO}_3]$ [5]. Presumably thermal broadening also exerts influence on
228 $[\text{Cs}_2\text{CO}_3]$ as its Raman spectrum is qualitatively similar to that of the other isostructural carbonates
229 (fig. 4).

230

231 Selection rules indicate that for $[\text{Li}_2\text{CO}_3]$ twenty one lattice modes are expected which involve
232 motions of the anion and cation sub lattices [7], of these the $[\text{Li}_2\text{CO}_3]$ Raman spectrum shows three
233 distinct sharp high intensity bands at 194 , 157 and 128cm^{-1} (fig.4) which are believed to result from
234 rotary motion of the carbonate groups [4]. A fourth high intensity band situated at slightly less than
235 100cm^{-1} wavenumbers is suggested by the asymmetric rise in background intensity towards the
236 100cm^{-1} detection limit and is in keeping with reports of a lattice mode at 96cm^{-1} [4]. Also evident is
237 an undocumented band at 103cm^{-1} which is presumably another lattice mode (fig. 4). The 194cm^{-1}
238 difference between NIR band [G] $[\text{Li}_2\text{CO}_3]$ data and the corresponding $M(\nu_1 + 3\nu_3)$ total coincides
239 precisely in wavenumber with that of a Raman active lattice mode. Band [C] 103cm^{-1} offset from
240 $M(3\nu_3)$ total coincides exactly with that of another lattice mode. Band [E] offset from $M(2\nu_1 + 2\nu_3)$
241 total (90cm^{-1}) is six wavenumbers from another known lattice mode. Band [X] is offset 184cm^{-1} from

242 the ($2\nu_3 + 2\nu_4$) assignment MIR total, placing the data point 10cm^{-1} wavenumbers from the $[\text{Li}_2\text{CO}_3]$
243 194cm^{-1} lattice mode (fig.6) and 8cm^{-1} from a second (very weak) lattice mode calculated at 176cm^{-1}
244 [8]. Given that no polarization dependence can be determined from powders, meaning that different
245 lattice modes of similar wavenumber may appear as a single band [10] the $[\text{Li}_2\text{CO}_3]$ data is
246 interpreted to provide evidence that lattice modes of rotatory origin do combine with overtones and
247 combinations of internal modes of molecular origin in the case of the $[\text{Li}_2\text{CO}_3]$ powder.

248

249 Any search for evidence of lattice modes combining with internal modes of molecular origin within
250 the NIR spectra of the remaining alkali carbonates is difficult. The structural disorder of $[\text{Na}_2\text{CO}_3]$
251 means that Raman peak positions are likely to be less precise than for $[\text{Li}_2\text{CO}_3]$, plus additive sums of
252 the $[\text{Na}_2\text{CO}_3]$ fundamentals are based on the average of each doubled fundamental wavenumber
253 pair (table 1). Thermal broadening of the isostructural carbonates means that significant numbers of
254 lattice modes are only resolved by Raman spectroscopy at very low temperature [5,7]. In addition
255 the lattice modes of $[\text{K}_2\text{CO}_3]$ and $[\text{Rb}_2\text{CO}_3]$ have been described as exceptionally complicated because
256 forty five lattice modes are allowed by C_{2h} unit cell group selection rules [5]. Further, analytical
257 constraints commonly mean that very few studies report lattice modes at $<100\text{cm}^{-1}$ from mineral
258 powders. This fact may explain why we could find no published accounts of $[\text{Rb}_2\text{CO}_3]$ lattice modes
259 at less than 75cm^{-1} wavenumbers and no documented accounts of $[\text{Na}_2\text{CO}_3]$ lattice modes at less
260 than 98cm^{-1} wavenumbers.

261

262 Table 3 shows the wavenumber differences between NIR data from the five alkali carbonate
263 powders relative to each band's mid-infrared additive sum of the overtone or combination
264 assignment, together with the closest published account of a lattice mode frequency. Boxes within
265 the table shaded grey indicate the absence of published accounts of low wavenumber lattice modes.
266 Of the remaining data points twenty of the twenty one data points fall within 11cm^{-1} of a known
267 lattice mode frequency. The outlier is band [F] $[\text{Cs}_2\text{CO}_3]$ (97cm^{-1}) which shows a 17cm^{-1} separation
268 from the nearest known lattice mode frequency (table 3). However peak-fitting of the Raman
269 spectrum of $[\text{Cs}_2\text{CO}_3]$ suggests the presence of a strong (previously unreported) band at $\text{ca } 101\text{cm}^{-1}$,
270 i.e. within 4cm^{-1} of the band [F] $[\text{Cs}_2\text{CO}_3]$ data point (fig. 4). In addition the $[\text{Rb}_2\text{CO}_3]$ band [X] 121cm^{-1}
271 wavenumber difference with the corresponding $\text{M}(2\nu_3 + 2\nu_4)$ additive sum is close to a peak-fit
272 resolved Raman band at 117cm^{-1} (fig. 4) i.e. within 4cm^{-1} of the band [X] data point. Further, band [F]
273 and [C] $[\text{Rb}_2\text{CO}_3]$ data also closely coincide with additional high intensity Raman bands (fig. 4),
274 suggesting that there is some evidence of lattice modes combining with internal modes of molecular
275 origin in $[\text{Rb}_2\text{CO}_3]$. Data from $[\text{Cs}_2\text{CO}_3]$ and $[\text{K}_2\text{CO}_3]$ are open to interpretation as is $[\text{Na}_2\text{CO}_3]$. In the

276 case of the sodium carbonate a Raman active lattice mode at $\approx 90\text{cm}^{-1}$ has been reported [4] which
277 is broadly coincident with three NIR bands data points (table 3). Further, band [V] data which is
278 singular to the $[\text{Na}_2\text{CO}_3]$ powder coincides with a weak Raman active band (fig. 3). However further
279 research is required to corroborate these findings, in this respect THz spectroscopy may hold future
280 promise.

281

282 5. Conclusions

283

284 Previous work has demonstrated that the vibrational spectra of molecular crystals may comprise
285 pure vibration transitions of molecular origin enveloped by vibration - libration combinations which
286 can shade individual bands to a higher and or lower frequency than in the pure vibrational transition
287 [15]. Further, it has been shown that high frequency overtone and combination bands in the 3000
288 cm^{-1} to 5000 cm^{-1} region of calcite register lattice modes combining with ν_3 overtones [9,16].
289 Because the difference in wavenumber of four $[\text{Li}_2\text{CO}_3]$ bands with a $3\nu_3$ overtone and three
290 combinations (calculated as additive sum of the fundamentals involved) closely coincide with that of
291 Raman active rotary lattice modes it is argued that vibration - libration combinations occur across a
292 variety of NIR wavelengths in $[\text{Li}_2\text{CO}_3]$ and $[\text{Rb}_2\text{CO}_3]$ alkali carbonate spectra. It is also suggested that
293 data presented here is at least in part qualitatively in keeping with vibration - libration combinations
294 operating within the NIR spectra of other alkali carbonates across a range of frequencies.

295

296 Isostructural carbonate data from bands [A-C] and [E-G] repeatedly fall in a sequential ordered
297 pattern of NIR wavenumber decreasing with increasing atomic mass from $[\text{K}_2\text{CO}_3]$ to $[\text{Rb}_2\text{CO}_3]$ to
298 $[\text{Cs}_2\text{CO}_3]$ (fig. 2). This trend closely resembles that observed from calcite and aragonite group mineral
299 powders [11], in which compression of the carbonate ion by its packing increases with decreasing
300 cation size. In this respect of note $[\text{K}_2\text{CO}_3]$ data from bands [B,C] and [E,F] consistently show the
301 greatest disparity from the corresponding additive sum of the vibration fundamentals relative to
302 $[\text{Rb}_2\text{CO}_3]$ and $[\text{Cs}_2\text{CO}_3]$. Given that the same quantified disparities closely match that of a lattice
303 mode it appears conceivable that librational anharmonicity may increase as cation size decreases in
304 these four NIR bands.

305

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307

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310

311 **References**

312

313 [1] L.B. Railsback . Carbonates and Evaporites. 14 (1999) 1-20.

314 [2] C.F. Windisch, J.L. Cox, E.N. Greenwell. Spectrochim. Acta A53 (1997) 1981-1993.

315 [3] C.J.H Schutte, K. Buis (1961) Spectrochim. Acta A17 (1961) 921-924.

316 [4] M.H. Brooker, J.B. Bates. J. Chem. Phys. 54 (1971) 4788-4796.

317 [5] M.H. Brooker, J.B. Bates. Spectrochim. Acta 30A (1974) 2211-2220.

318 [6] Y. Hase. An. Acad. Brasil. 52 (1980) 520-525.

319 [7] M.H. Brooker, J. Wang J. (1992) Spectrochim. Acta 48A (1992) 999-1008.

320 [8] N. Koura, S. Kohara, K. Takeuchi, S. Takahashi, L.A. Curtiss, M. Grimsditch, M. Saboungi. J. Mol.
321 Struct. 382, (1996) 163-169.

322 [9] G.R. Hunt, J.W. Salisbury. Mod. Geol. 2 (1971) 23-30.

323 [10] W.B. White (1974), Farmer V.C (ed) The infrared spectra of minerals. Mineral Soc. Monogr. 4
324 (chap. 12) (1974) 227-282.

325 [11] L. Hopkinson, K. Rutt. Spectrochim. Acta A162 (2016) 105-108.

326 [12] F. Westad, A. Schmidt, M. Kermit M (2008). J. Near-Infrared Spec. 16 (2008) 265-273.

327 [13] H.H. Adler, P.F. Kerr P.F. Am. Miner. 48 (1963) 124-137.

328 [14] M. Reichenbacher, J. Popp. Challenges in Molecular Structure Determination. Springer-Verlag
329 Berlin Heidelberg (2012) DOI 10.1007/978-3-642-24390-5_2.

330 [15] R.M. Hexter, D.A. Dows. J. Chem. Phys. 25 (1956) 504-509.

331 [16] R.M. Hexter. Spectrochim. Acta 10 (1958) 281-290.

332

333 **Captions**

334

335 **Table 1.** The wavenumbers (cm^{-1}) of internal modes (Int.) of $[\text{CO}_3^{2-}]$ in the alkali carbonates. The
336 $[\text{Li}_2\text{CO}_3]$ and $[\text{Na}_2\text{CO}_3]$ data is from [4]. Note that the ν_1 vibration of the sodium carbonate is split as
337 are all ν_4 measurements (given in brackets). The mean of the wavenumbers for each split
338 fundamental were taken for each carbonate mineral type for the purposes of the present study.
339 Note that the $[\text{Na}_2\text{CO}_3]$ data for the ν_3 internal mode (marked with an asterix *) were measured
340 through thin films at 80K. The $[\text{K}_2\text{CO}_3]$ and $[\text{Rb}_2\text{CO}_3]$ data are from [5]. The $[\text{Cs}_2\text{CO}_3]$ internal mode
341 data is from [6].

342

343 **Table 2.** Near-infrared data for bands [A-G] inclusive, plotted as wavenumbers cm^{-1} . The wavelength
344 range for each band is given in microns (μm) beneath the band label title.

345

346 **Table 3.** All lattice mode (L. mode) data marked with an asterisk was acquired at 80K, all other data
347 was acquired at room temperature. Data marked with a superscript (^a) is from [8]. L. mode data
348 marked (^b) is from [5]. L. mode marked (^c) is from [4]. L. mode data marked (^d) is from [7].. No data is
349 available for areas shaded grey.

350

351 **Figure 1.** Near-infrared absorption spectra of: $[\text{Li}_2\text{CO}_3]$; $[\text{Na}_2\text{CO}_3]$; $[\text{K}_2\text{CO}_3]$; $[\text{Rb}_2\text{CO}_3]$; and $[\text{Cs}_2\text{CO}_3]$
352 with peak-fit overlays. See text for details.

353

354 **Figure 2.** Bands [A-G] inclusive plotted against atomic mass units (amu). The best fit trend lines are
355 constructed for the three isostructural carbonates.

356

357 **Figure 3.** NIR data plotted against the assigned overtone or combination derived from the additive
358 sum of the MIR fundamentals data. Isostructural carbonate data points are shaded grey, $[\text{Li}_2\text{CO}_3]$ and
359 $[\text{Na}_2\text{CO}_3]$ data points are plotted black. The wavenumber separation between the NIR data from
360 each alkali is reported in brackets. Isostructural carbonate data points against which r^2 values are
361 derived are shaded grey. **a)** NIR bands [A] (diamonds), [B] (triangles) and [C] (circles) plotted against
362 the corresponding $M(3\nu_3)$ value. **b)** Near-infrared bands [E] (diamonds) and [F] (triangles) plotted
363 against the corresponding $M(2\nu_1 + 2\nu_3)$ combination wavenumber. Band [V] data point is marked
364 with an open circle. **c)** NIR band [G] plotted against the corresponding $M(\nu_1 + 3\nu_3)$ combination
365 wavenumber. **d)** NIR band [X] plotted against the corresponding $M(2\nu_3 + 2\nu_4)$ combination
366 wavenumber.

367

368 **Figure 4.** Raman spectra of the alkali carbonates in the $100 - 300\text{cm}^{-1}$ wavenumber region of interest,
369 y-axis is Raman intensity. NIR data giving the wavenumber difference with that of the MIR derived
370 additive sum of the overtone or combination assignment are presented in square brackets giving the
371 relevant band letter label and wavenumber total.

372

373

374 **Table 1**

Alkali carbonate	Int. mode ν_1 (cm ⁻¹) Raman	Int. mode ν_2 (cm ⁻¹) Infrared	Int. mode ν_3 (cm ⁻¹) Infrared	Int. mode ν_4 (cm ⁻¹) Infrared
[Li ₂ CO ₃]	1092	865	1430	732 (741,723)
[Na ₂ CO ₃]	1081 (1083 1079)	(886,880)	1419 (1425, 1413*)	697 (701,694)
[K ₂ CO ₃]	1063	880	1400	686 (690,683)
[Rb ₂ CO ₃]	1053	879	1380	684 (688,681)
[Cs ₂ CO ₃]	1042	878	1367	676 (679, 674)

375

376

377 **Table 2**

	Band [A] (cm ⁻¹) (2.359-2.458μm)	Band [B] (cm ⁻¹) (2.321-2.416μm)	Band [C] (cm ⁻¹) (2.226-2.339μm)	Band [D] (cm ⁻¹) (2.174-2.227μm)	Band [E] (cm ⁻¹) (2.004-2.102μm)	Band [F] (cm ⁻¹) (2.004-2.102μm)	Band [G] (cm ⁻¹) (1.969-1.881μm)
Li ₂ CO ₃	4238	4308	4393	4506	4954	5049	5188
Na ₂ CO ₃	4252	4345	4493	4599	4990	5080	5315
K ₂ CO ₃	4234	4313	4407	4518	4996	5093	5205
Rb ₂ CO ₃	4125	4194	4292	4490	4815	4996	5144
Cs ₂ CO ₃	4067	4139	4275	4582	4757	4915	5078

378

379

380 **Table 3**

Assignment Band	$(3\nu_3)$				$(2\nu_1 + 2\nu_3)$				$(\nu_1 + 3\nu_3)$		$(2\nu_3 + 2\nu_4)$			
	[A]	L. mode	[B]	L. mode	[C]	L. mode	[E]	L. mode	[F]	L. mode	[G]	L. mode	[X]	L. mode
[Li ₂ CO ₃]	52	-	18	-	103	97 ^a	90	95 ^a	5	-	194	194 ^a	184	176,194 ^a
[Na ₂ CO ₃]	5	-	88	-	236	228 ^{c*}	10	-	80	-	23	-	100	98 ^c
[K ₂ CO ₃]	34	-	113	109 ^{b*}	207	201 ^{b*}	70	76 ^a	167	159,176 ^{b*}	58	52 ^a	45	52 ^a
[Rb ₂ CO ₃]	15	-	54	-	152	153 ^b	51	-	130	132 ^b	49	-	121	132 ^b
[Cs ₂ CO ₃]	34	43 ^{d*}	38	43 ^{d*}	174	170 ^d	61	65 ^d	97	72,114 ^d	65	65 ^d	No data	-

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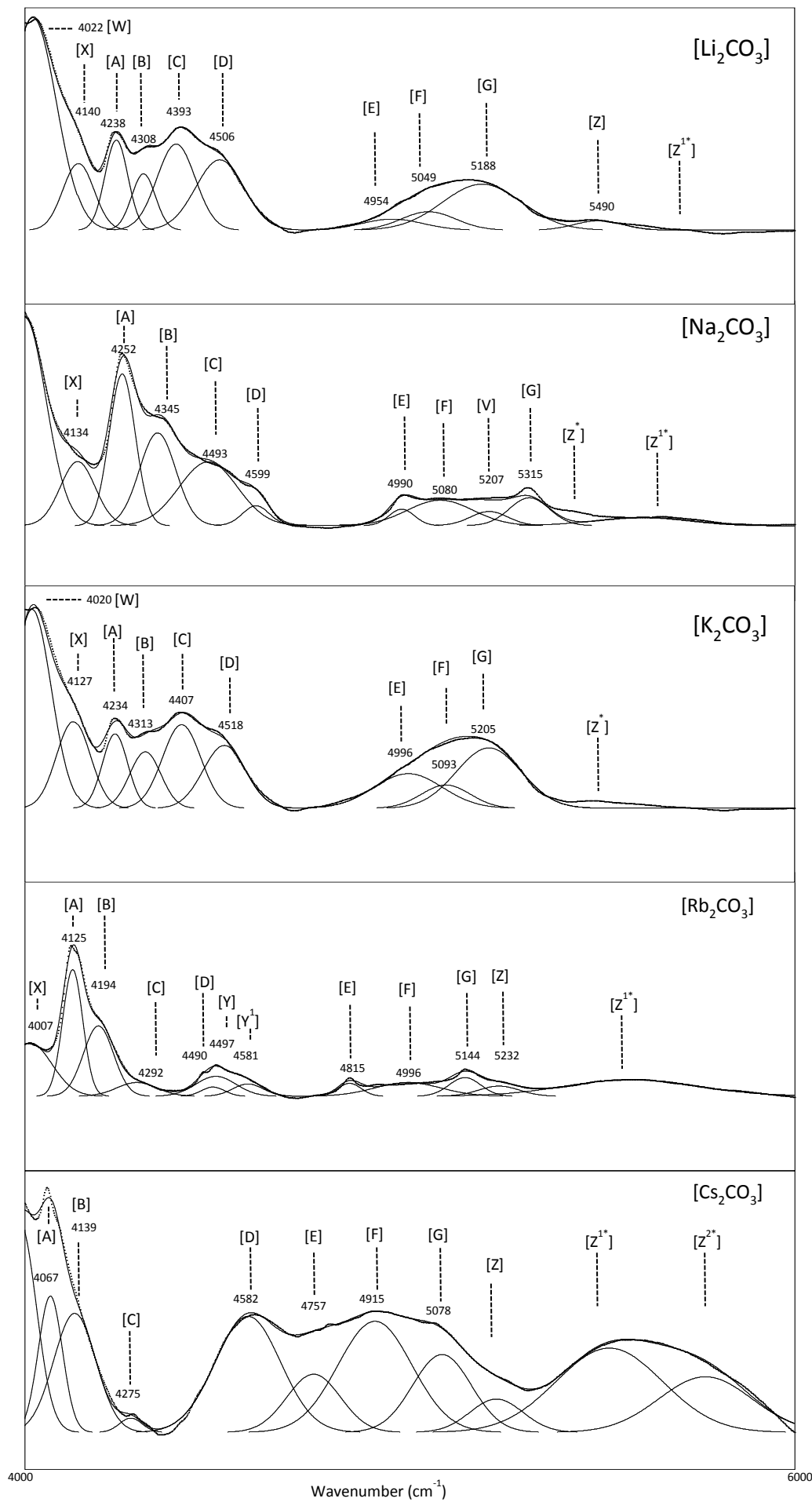
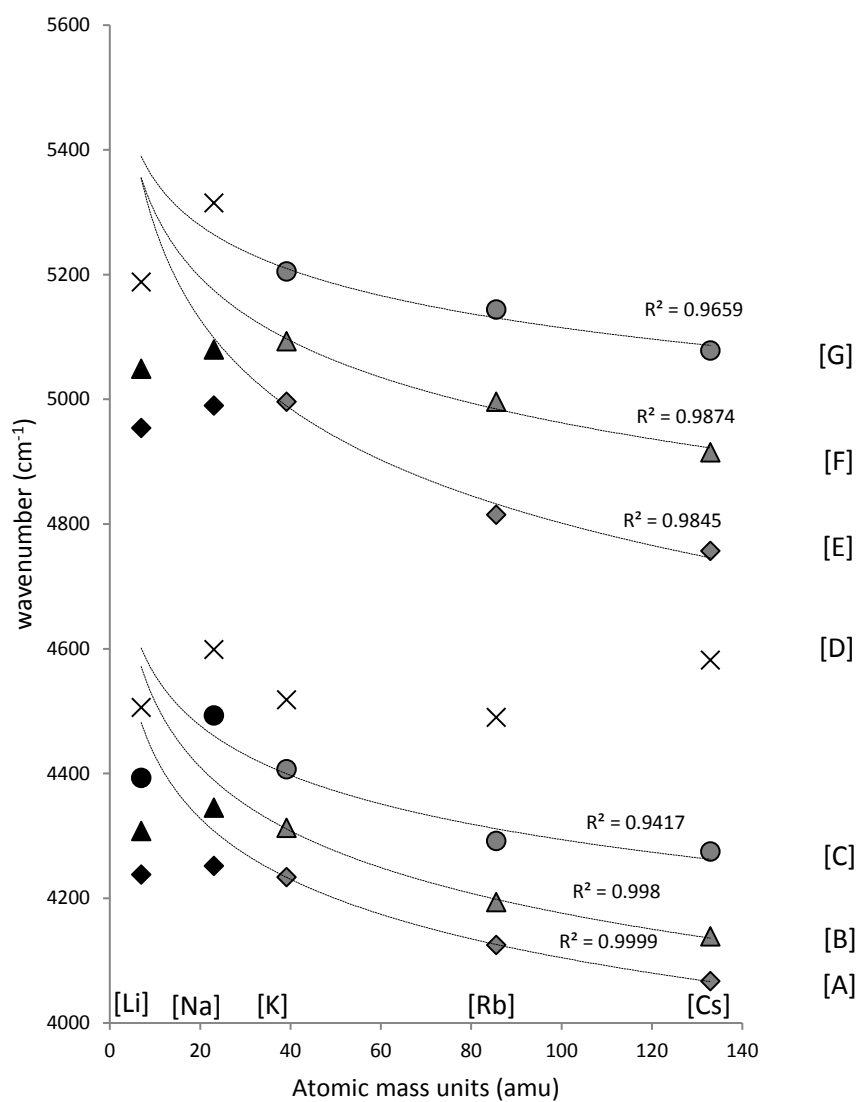


Figure 1

387 Figure 2.

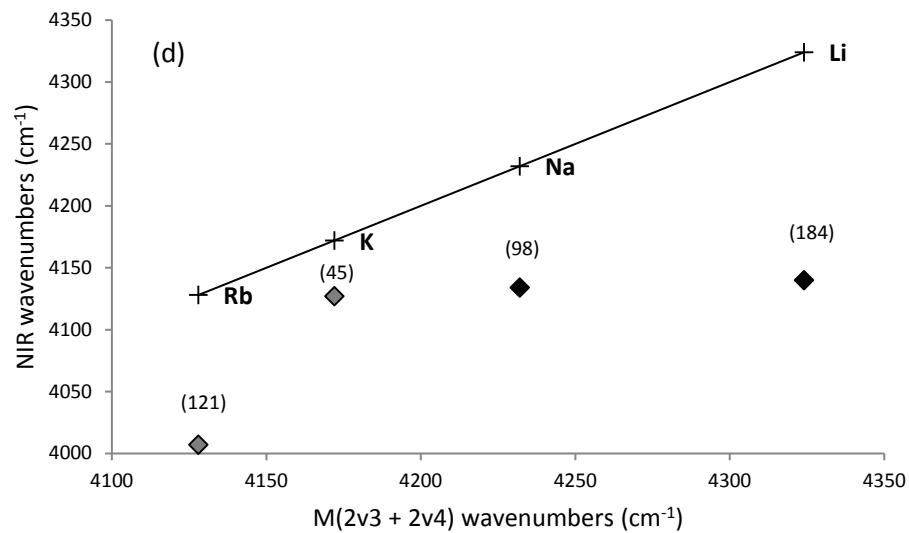
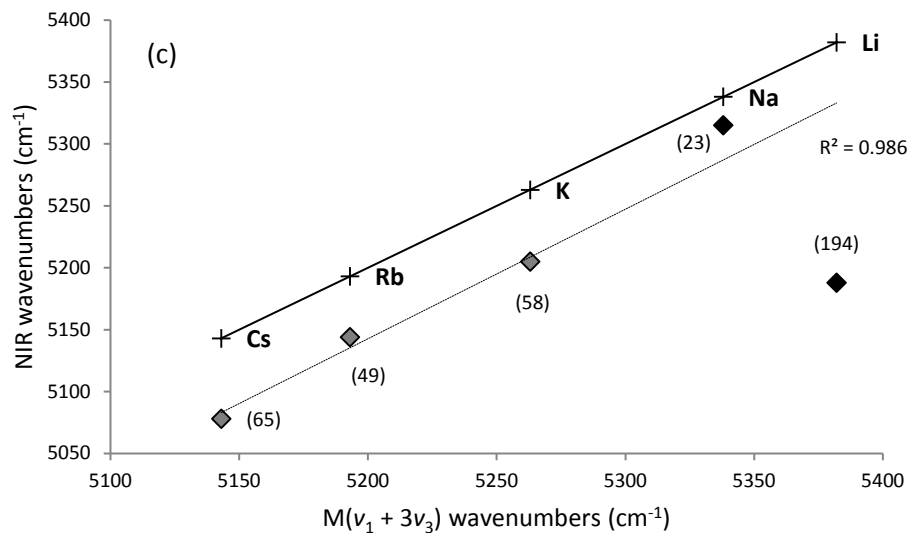
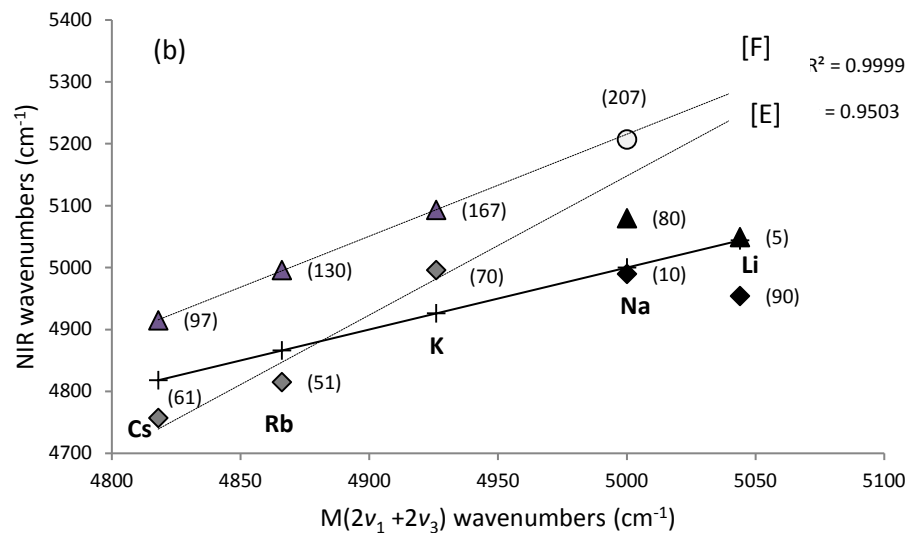
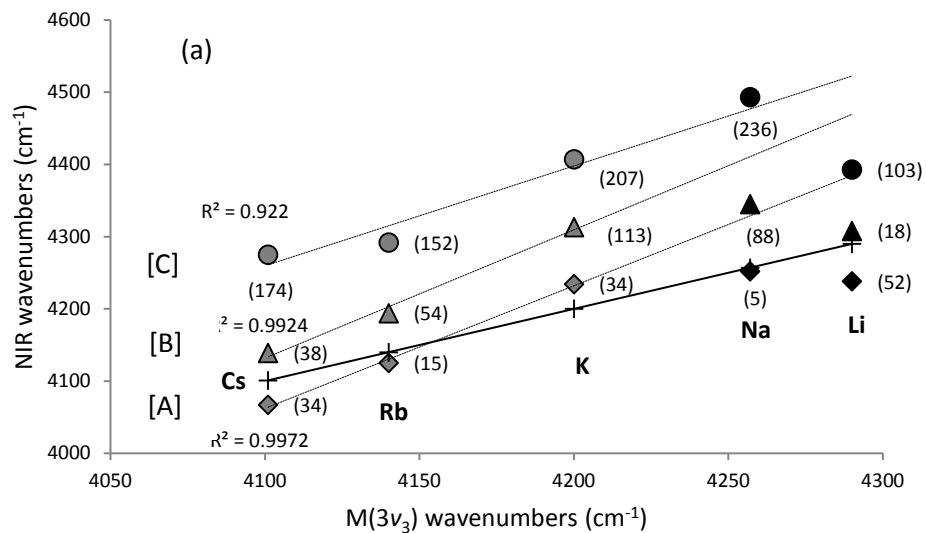


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Figure 3



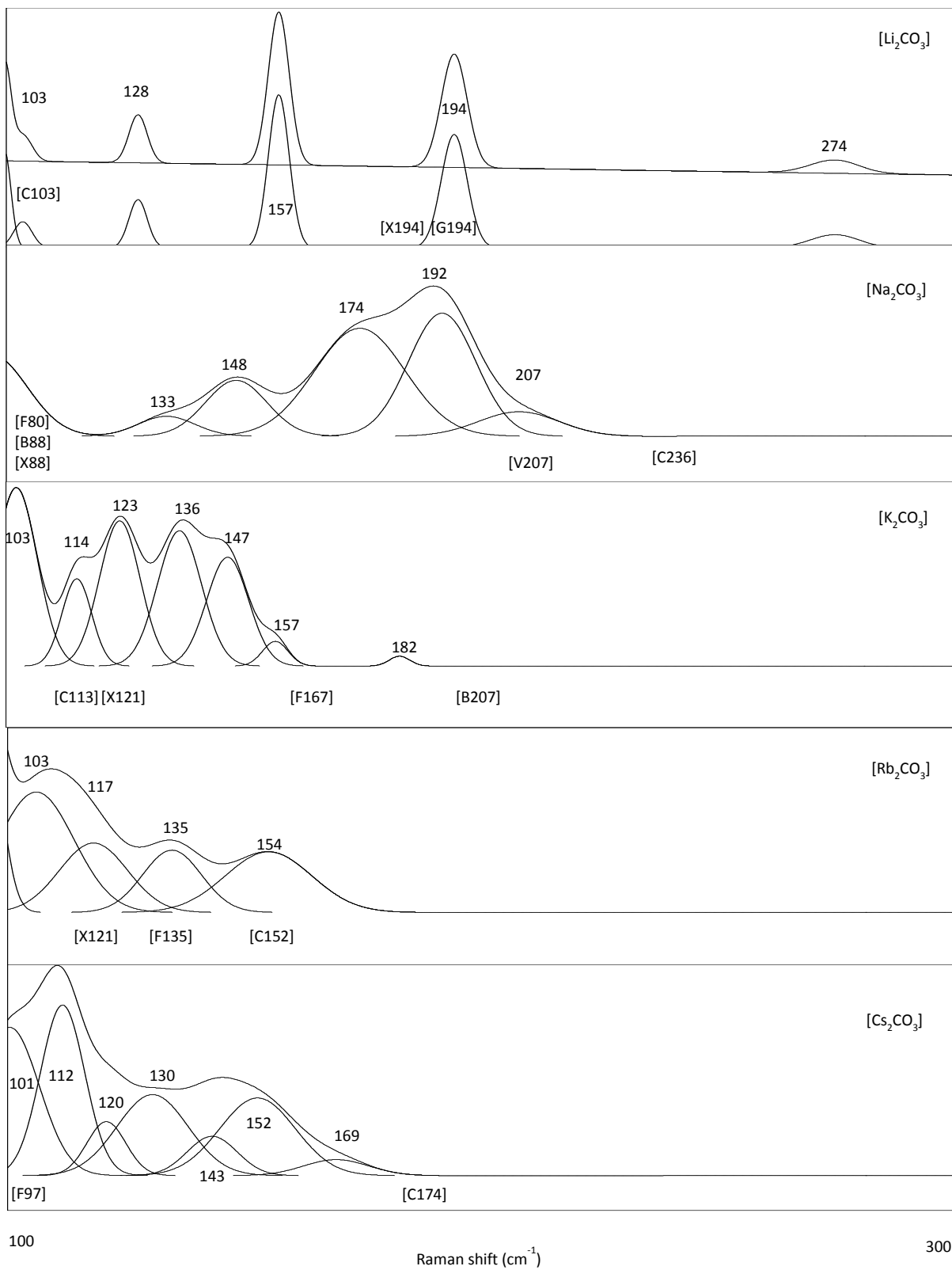


Figure 4

