



# The near-infrared spectra of the alkali carbonates

Laurence Hopkinson<sup>a,\*</sup>, Ken J. Rutt<sup>b</sup>, Petra Kristova<sup>b</sup>

<sup>a</sup> School of the Environment and Technology, University of Brighton, Cockcroft Building, Lewes Road, Brighton BN2 4GJ, United Kingdom

<sup>b</sup> School of Pharmacy and Biomolecular Sciences, University of Brighton, Huxley Building, Lewes Road, Brighton BN2 4GJ, United Kingdom

## ARTICLE INFO

### Article history:

Received 13 February 2018

Received in revised form 6 April 2018

Accepted 9 April 2018

Available online 11 April 2018

### Keywords:

Alkali carbonates

Overtones

Combinations

Vibration

Libration

## ABSTRACT

This study presents the first account of the near-infrared (NIR) spectra of the alkali carbonates:  $[\text{Cs}_2\text{CO}_3]$   $[\text{Rb}_2\text{CO}_3]$   $[\text{K}_2\text{CO}_3]$   $[\text{Na}_2\text{CO}_3]$  and  $[\text{Li}_2\text{CO}_3]$ . Seven NIR bands (labelled [A] to [G] inclusive) within the  $[4000\text{--}6000\text{ cm}^{-1}]$  ( $2.5\text{--}1.66\text{ }\mu\text{m}$ ) region of interest are common to the five spectra examined, of which six bands [A–C] and [E–G] proved amenable to quantitative study. The first three occur in the range  $4067\text{--}4493\text{ cm}^{-1}$  ( $2.458\text{--}2.226\text{ }\mu\text{m}$ ) and are assigned to a  $[\text{CO}_3^{2-}] 3\nu_3$  overtone, Bands [E] and [F] are centred at  $ca\ 4902\text{ cm}^{-1}$  ( $2.04\text{ }\mu\text{m}$ ) and  $ca\ 5034\text{ cm}^{-1}$  ( $1.98\text{ }\mu\text{m}$ ) respectively and are assigned to a  $(2\nu_1 + 2\nu_3)$  combination. Band [G] centred at  $ca\ 5190\text{ cm}^{-1}$  ( $1.92\text{ }\mu\text{m}$ ) is assigned to a  $(\nu_1 + 3\nu_3)$  combination. One additional band (Band [X]) centred in the vicinity of  $ca\ 4080\text{ cm}^{-1}$  ( $2.45\text{ }\mu\text{m}$ ) in all spectra other than  $[\text{Cs}_2\text{CO}_3]$  is assigned to  $(2\nu_3 + 2\nu_4)$ . The data is compared with the corresponding additive sum of the mid-infrared (MIR) fundamental, or in the case of combinations, Raman and MIR fundamentals. The quantified differences between NIR band frequency and that of the corresponding MIR derived overtone or combination in the case of  $[\text{Li}_2\text{CO}_3]$  and  $[\text{Rb}_2\text{CO}_3]$  closely coincide with Raman active lattice modes of rotary origin. From which it is argued that vibration-libration combinations may operate across a range of NIR frequencies for these mineral types. NIR data from  $[\text{K}_2\text{CO}_3]$ ,  $[\text{Cs}_2\text{CO}_3]$  and  $[\text{Na}_2\text{CO}_3]$  are discussed in the light of these findings. The influences of differences in atomic mass and space group effects on the NIR spectra of the alkali carbonates are also demonstrated.

© 2018 Elsevier B.V. All rights reserved.

## 1. Introduction

Anhydrous carbonates number sixty-five mineral types in which the  $[\text{CO}_3^{2-}]$  radical provides all the 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  $[\text{Cs}_2\text{CO}_3]$ ) constitute an important group of minerals which find application in a range of chemical processes [2]. All alkali carbonates are highly hygroscopic and water soluble [3]. The alkali carbonates have been investigated in a number of studies [4–8]. It is established that three types of anhydrous alkali carbonate mineral structures exist:  $[\text{Li}_2\text{CO}_3]$  (space group C2/c);  $[\text{Na}_2\text{CO}_3]$  (space group c2/m); and  $[\text{K}_2\text{CO}_3]$  (space group p2<sub>1</sub>/c). The potassium carbonate is isostructural with  $[\text{Rb}_2\text{CO}_3]$  and  $[\text{Cs}_2\text{CO}_3]$  [4–7].

In common with other carbonate mineral groups [9,10] the  $[\text{CO}_3^{2-}]$  internal modes occur across a range of mid-infrared (MIR) wavenumber intervals (Table 1). The Raman active  $\nu_1$  (totally symmetric C–O stretching mode) appears at  $ca\ 1080\text{ cm}^{-1}$ , the MIR active  $\nu_2$  (out-of-plane bending mode) occurs at  $ca\ 880\text{ cm}^{-1}$ , the MIR and Raman active  $\nu_3$  doubly degenerate (anti-symmetric stretching mode) occurs around  $ca\ 1430\text{ cm}^{-1}$ , while the doubly degenerate  $\nu_4$  in-plane bending mode

occurs around  $715\text{ cm}^{-1}$ . The  $\nu_4$  internal mode is split in all of the alkali carbonates [4–7]. In the case of  $[\text{Li}_2\text{CO}_3]$  and the isostructural carbonates the remaining internal modes of the carbonate ion ( $\nu_1$ ,  $\nu_2$  and  $\nu_3$ ) occur as single bands. The exception is  $[\text{Na}_2\text{CO}_3]$  which displays a doublet structure for each of the internal modes (Table 1), interpreted in terms of two non-equivalent orientations of the  $[\text{CO}_3^{2-}]$  ion within the primitive unit cell [4,10].

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

## 2. Materials and Methods

The powdered alkali metal carbonates examined in this study were sourced from international suppliers: lithium carbonate (Acros

\* Corresponding author.

E-mail addresses: [l.hopkinson@brighton.ac.uk](mailto:l.hopkinson@brighton.ac.uk), (L. Hopkinson), [k.j.rutt@brighton.ac.uk](mailto:k.j.rutt@brighton.ac.uk), (K.J. Rutt), [p.kristova@brighton.ac.uk](mailto:p.kristova@brighton.ac.uk), (P. Kristova).

**Table 1**

The wavenumbers ( $\text{cm}^{-1}$ ) of internal modes (Int.) of  $[\text{CO}_3^{2-}]$  in the alkali carbonates. The  $[\text{Li}_2\text{CO}_3]$  and  $[\text{Na}_2\text{CO}_3]$  data is from [4]. Note that the  $\nu_1$  vibration of the sodium carbonate is split as are all  $\nu_4$  measurements (given in brackets). The mean of the wavenumbers for each split fundamental were taken for each carbonate mineral type for the purposes of the present study. Note that the  $[\text{Na}_2\text{CO}_3]$  data for the  $\nu_3$  internal mode (marked with an asterisk \*) were measured through thin films at 80 K. 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 data is from [6].

Alkali carbonate	Int. mode $\nu_1$ ( $\text{cm}^{-1}$ ) Raman	Int. mode $\nu_2$ ( $\text{cm}^{-1}$ ) Infrared	Int. mode $\nu_3$ ( $\text{cm}^{-1}$ ) Infrared	Int. mode $\nu_4$ ( $\text{cm}^{-1}$ ) Infrared
$[\text{Li}_2\text{CO}_3]$	1092	865	1430	732 (741, 723)
$[\text{Na}_2\text{CO}_3]$	1081 (1083, 1079)	(886, 880)	1419 (1425, 1413*)	697 (701, 694)
$[\text{K}_2\text{CO}_3]$	1063	880	1400	686 (690, 683)
$[\text{Rb}_2\text{CO}_3]$	1053	879	1380	684 (688, 681)
$[\text{Cs}_2\text{CO}_3]$	1042	878	1367	676 (679, 674)

Organics, lot number (lot. n.) A0231490), sodium carbonate (Honeywell Fluka, lot. n. SLBQ8163V), potassium carbonate (Fisher Scientific, lot. n. 0886824), rubidium carbonate (Sigma Aldrich, lot.n. MKBW4880V) and cesium carbonate (Sigma Aldrich, lot.n. MKBZ2431V). Samples were oven-dried at 100 °C for 24 h and immediately placed in a desiccator and then placed in the standard reflectance glass tubes supplied with the NIR instrument by Perkin Elmer. The tubes were filled 2 cm deep with the powders. A small bag containing desiccant was placed on top of the sample before sealing the tube with a plastic stopper. The spectra were then measured immediately. Several repeat measurements were taken for each powder sample type. NIR analyses were conducted with a Perkin Elmer Spectrum 100 N spectrometer. The powdered samples were measured at room temperature in the range 4000–10,000  $\text{cm}^{-1}$ . The samples were measured using NIRA (near-infrared reflectance accessory) which is used to collect diffuse reflectance spectra of solids and powders. The measurements were done in absorbance. The NIR measurement protocol is as follows. A background scan is taken and a scan type is selected to be interleaved (i.e. the shuttle automatically moves to the rear position to take background scan before moving to the front position to scan the sample and display the ratioed sample spectrum). The number of scans collected was 8, resolution 16  $\text{cm}^{-1}$ , INGAAS detector selected, optical path difference velocity 1.00 cm/s.

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

### 3. Experimental Results

#### 3.1. The Near-infrared Spectra of the Alkali Carbonates

In common with all NIR spectra which emerge from overtones and combinations of fundamental MIR absorptions [12] the alkali carbonates show a range of broad variably resolved overlapping bands in the [4000–6000  $\text{cm}^{-1}$ ] region, which are qualitatively similar in appearance to those of the alkaline earths carbonates [9]. Fig. 1 shows the spectra and associated Peak-Fit software results for the five alkali carbonate mineral powders examined. Bands [A] to [G] inclusive are common to the five spectra and are central to this study (Table 2). Those bands which are not common to all spectra are labelled [V] to [Z] inclusive. Band [V] is singular to  $[\text{Na}_2\text{CO}_3]$ . Band [W] may fall below the lower

wavenumber detection range for  $[\text{Rb}_2\text{CO}_3]$  and  $[\text{Cs}_2\text{CO}_3]$ , is close to 4000  $\text{cm}^{-1}$  for  $[\text{Na}_2\text{CO}_3]$ , at 4020  $\text{cm}^{-1}$  for  $[\text{K}_2\text{CO}_3]$  and 4022  $\text{cm}^{-1}$  for  $[\text{Li}_2\text{CO}_3]$ . Band [X] is absent from the  $[\text{Cs}_2\text{CO}_3]$  spectrum. Bands [Y] and [Y<sup>1</sup>] are singular to  $[\text{Rb}_2\text{CO}_3]$ . Peak-Fit software identified an additional weak band (band [Z]) in the vicinity of 5490  $\text{cm}^{-1}$   $[\text{Li}_2\text{CO}_3]$ , 5232  $\text{cm}^{-1}$   $[\text{Rb}_2\text{CO}_3]$  and 5210  $\text{cm}^{-1}$   $[\text{Cs}_2\text{CO}_3]$ . In other spectra the band was too poorly resolved relative to background to accurately position or analyse (marked [Z\*] on Fig. 1), as were variably resolved extremely broad bands in the 5500–5800  $\text{cm}^{-1}$  region (marked [Z<sup>1,2\*</sup>] on Fig. 1). Band(s) in the vicinity of ca 5260  $\text{cm}^{-1}$  (1.9  $\mu\text{m}$ ) theoretically could originate at least in part from the combination of H—O—H band with the antisymmetric OH stretch [9]. However near-infrared spectra do not show an accompanying asymmetric OH stretch at 7140  $\text{cm}^{-1}$  (1.49  $\mu\text{m}$ ). Hence all bands listed in Table 2 and displayed in Fig. 1 are interpreted as  $[\text{CO}_3^{2-}]$  radical-related spectral features although bands [Z<sup>1,2\*</sup>] proved too poorly resolved and broad in nature for meaningful quantitative study and are hereafter excluded from this study.

#### 3.2. Bands [A] to [G], Atomic Mass and Space Group Considerations

Fig. 2 shows bands [A–G] inclusive plotted against the corresponding atomic mass (amu) of each co-ordinating cation. The figure shows that for each band  $[\text{Na}_2\text{CO}_3]$  occurs at higher wavenumbers than  $[\text{Li}_2\text{CO}_3]$ . Bands [A–C] and [E–G] show reasonable  $r^2$  power-trend type fits for the isostructural carbonates with  $[\text{Cs}_2\text{CO}_3]$  occurring at lower wavenumbers than  $[\text{K}_2\text{CO}_3]$  while the  $[\text{Rb}_2\text{CO}_3]$  wavenumber values are intermediate with respect to  $[\text{K}_2\text{CO}_3]$  and  $[\text{Cs}_2\text{CO}_3]$ . Similar ‘mass effects’ on fundamental vibrations of internal modes in other carbonate mineral types have been assigned to small changes in the bending and stretching force constants, reflecting differences in the chemical bonding of the carbonate ion [10]. It is also evident from Fig. 2 that the relationship between increasing atomic mass and decreasing wavenumber does extend to  $[\text{Na}_2\text{CO}_3]$  and  $[\text{Li}_2\text{CO}_3]$  i.e. the  $[\text{Na}_2\text{CO}_3]$  bands occur at marginally higher wavenumbers than those of the  $[\text{Li}_2\text{CO}_3]$  powders, consistent with differing space group effects also exerting influence on band wavenumber positions.

In contrast to bands [A–C] and [E–G] band [D] shows no correlation between wavenumber and atomic mass for the isostructural carbonates. The reason for the singular absence of any correlation is unclear. However, the spectrum of  $[\text{Rb}_2\text{CO}_3]$  shows a shoulder to band [D], marked [Y] and [Y<sup>1</sup>] on Fig. 1. Hence, it is possible that band [D] in at least some of the other spectra is composite in nature but have gone either unresolved or partially resolved with Peak-Fit software, thereby accounting for the seemingly random nature of band [D] data. For this reason band [D] is not considered further in this study.

#### 3.3. Band Assignments [A–C]

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

In utilizing the MIR internal mode data it is important to note that the degenerate  $\nu_3$  fundamental of carbonate minerals measured from powders are broad in MIR spectra with the measured wavenumber falling somewhere between the transverse and longitudinal components of  $\nu_3$ . Consequently measurements are generally considered less accurate than for other fundamentals. In the case of powdered calcite, a ( $\pm 12.5 \text{ cm}^{-1}$ ) variation in the frequency of  $\nu_3$  has been reported from seven separate studies [10]. Nevertheless, previous studies have successfully employed the infrared-active component of  $\nu_3$  to document linear trends in a range of carbonate mineral compounds [13].

Download English Version:

<https://daneshyari.com/en/article/7668649>

Download Persian Version:

<https://daneshyari.com/article/7668649>

[Daneshyari.com](https://daneshyari.com)