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Infrared spectroscopy at the surface of carbonates

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IR spectroscopy has been extensively employed to characterize the structural and vibrational properties of carbonates, yet its application in studying adsorption capacity of carbonate surfaces remains limited. This short review presents the use of FTIR as a powerful tool for investigating the structure and surface chemistry of carbonates, which is relevant to several environmental and industrial applications (such as CO₂ capture and storage). Several FTIR techniques provide detailed analysis of the structure of carbonate polymorphs (calcite, aragonite, vaterite, and amorphous phases) alongside their phase transformation kinetics. In addition, adsorption studies of various molecules (CO, CO₂, H₂O, acids and several HCs) were performed to identify the adsorption sites, mechanisms and intermediates. These insights highlight the significance of IR spectroscopy for understanding carbonate structure and surface properties, and guide future research in several environmental and industrial processes where carbonates are involved.

Introduction

The surface chemistry of solid carbonates recently gained particular interest in the fight against greenhouse effect and climate global warming, for CO₂ capture and storage as well as for its further use (e.g. in methanation reactions ⁶). Carbonates are also increasingly considered as adsorbent materials for various chemicals such CO ¹, H₂O ¹, CO₂ ² and HCs. ^{3,4,5}

Mastering surface chemistry of carbonates is not possible without a good understanding of the possible adsorption modes and of the various possible reaction mechanisms on the surface of carbonates. One of the most powerful methods for monitoring adsorption phenomena is infrared spectroscopy ⁶ and it has been used extensively to study the formation of surface carbonates by adsorption of CO₂ on various oxides. ⁷ Carbonates themselves have been studied by IR spectroscopy but a systematic study of adsorbed species on solid carbonates is still missing.

This work reviews literature information and data obtained by IR spectroscopy on the various chemical species found on the surface of carbonates, together with the basic information on carbonate structure where relevant.

The infrared spectrum of the core structure of carbonates

Before it was used to study adsorbed species on carbonates, IR was largely employed in all spectral regions, from near to far IR, for characterising the composition, structure and crystalline phases of carbonates.

Vibration bands of the structure of the carbonate ion

Isolated planar ions of the form XO₃ with trigonal symmetry such as CO₃²⁻ exhibit four fundamental modes of vibration. ^{8,9} The frequencies of these vibration modes, as reported in the literature ^{10,11}, are shown in Table 1. An interesting feature is the progressive increase of the frequency of the ν₄ vibration with the radius of the counter cations. ¹²

Table 1 Approximate IR frequency ranges of the four fundamental vibration modes of carbonate. ^{10,11}

Vibration mode	ν ₁	ν ₂	ν ₃	ν ₄
Assignment	symmetric in-plane stretch	out-of-plane bend	asymmetric in-plane stretch	in-plane bend
Wavenumber (cm ⁻¹)	1070-1090	850-880	1400-1500	700-750

Carbonates also display, between 2900 and 4000 cm⁻¹, some other IR absorption bands due to overtones and combinations of the fundamental bands ¹³, including some weak combination bands at 1795 and 2514 cm⁻¹. ³ Interestingly, for studying surface species, some combination bands around 3000 cm⁻¹, indeed due to the carbonate structure, are sometimes mistaken for C-H stretch absorption bands.

The different IR techniques such as IRRAS, DRIFTS, transmission IR and ATR display differences in the spectra measured for the same sample. Figure 1 ¹⁴ shows IR spectra of BaCO₃ measured by four IR techniques. The figure shows the higher surface-sensitivity of DRIFTS and transmission IR as evidenced by the surface bands observed (2400-3000 cm⁻¹) and assigned to O-H stretching of hydrogen carbonate species ¹⁵, while ATR and IRRAS are rather bulk-sensitive. Interestingly, there are noticeable band ν₃ position shifts between

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all four techniques, mostly due to instrument configuration. IRRAS spectrum displayed a significant blueshift, which could be due to a change in the refractive index while scanning over the band range.

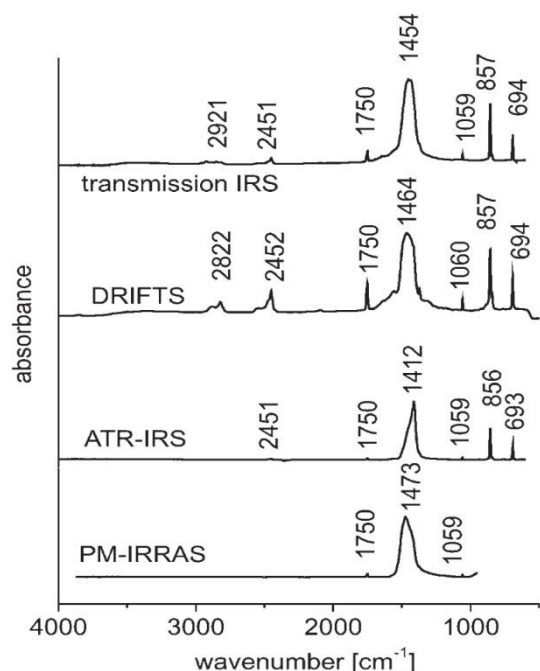


Fig. 1 IR spectra of BaCO_3 measured by different IR techniques. Adapted from reference ¹⁴ with permission from Royal Society of Chemistry, copyright 2008.

Identification of crystalline phases in calcium carbonate

Calcium carbonate is the most abundant natural carbonate. It amounts for 4% of Earth's crust ¹⁶ and is the main component in chalk, coral skeleton, and limestone.

IR spectroscopy is informative for the structure and properties of CaCO_3 polymorphs ^{17,18,19}, displayed in Figure 2.¹⁸ The relative intensities of the ν_1 ($\sim 1100 \text{ cm}^{-1}$) and ν_4 ($\sim 700 \text{ cm}^{-1}$) and the splitting of the ν_4 and ν_3 ($1400\text{--}1500 \text{ cm}^{-1}$) can be used to identify the varieties (amorphous CaCO_3 , vaterite, aragonite or calcite), especially with noticeable low intensity of the ν_1 vibration band for calcite.

In the Near-IR, several absorption bands are present due to overtones and combinations of the fundamental bands. The spectral region between 3920 and 28600 cm^{-1} (Figure 3) was used to identify and distinguish calcite, aragonite and dolomite using seven characteristic bands for carbonates in the range of ($3900\text{--}6250 \text{ cm}^{-1}$) ²⁰, with major bands at 4000 cm^{-1} ²¹ and $4250\text{--}4350 \text{ cm}^{-1}$.^{13,21}

Spectral features in the near IR and higher end of the MIR were used to determine carbonate content in arid soil samples.²² However, the PLSR (partial least-squares regression) efficiency of the method was found to be only 52% due to the overlapping of other soil components (illite, chlorite) with similar spectral features. The accuracy would have been improved by extending the measurement range to lower frequency MIR and FIR.

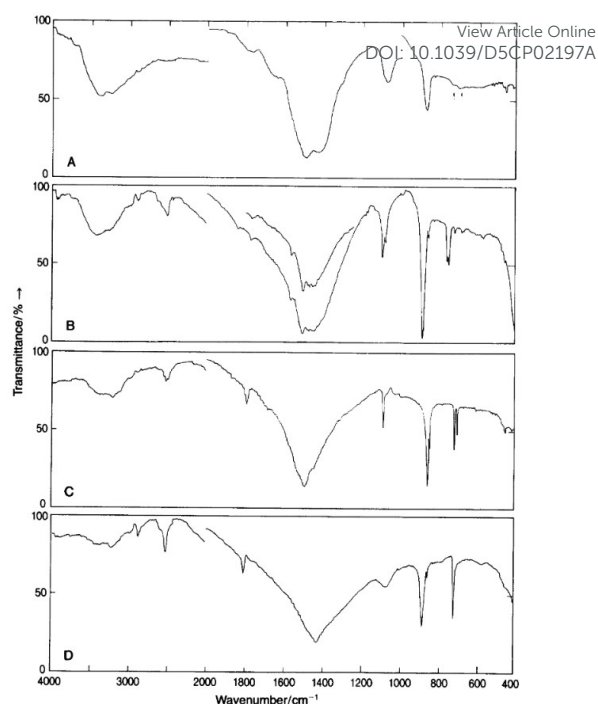


Fig. 2 IR spectra of (A) amorphous CaCO_3 , (B) vaterite, (C) aragonite, and (D) calcite. Adapted from reference ¹⁸ with permission from Scandinavian Society of Chemistry, copyright 1991.

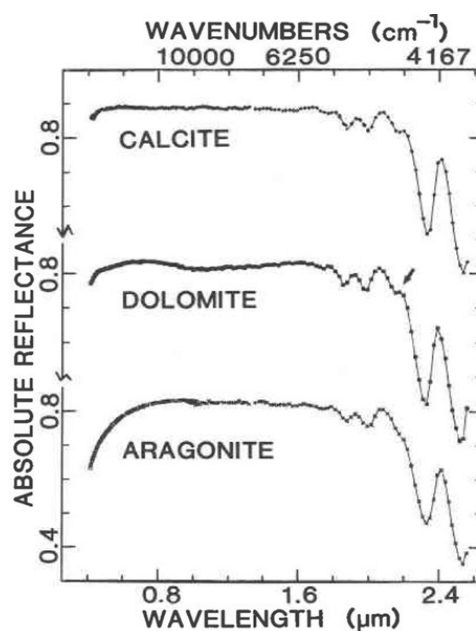


Fig. 3 Vis-NIR reflectance spectra of CaCO_3 minerals. Adapted from reference ²⁰ with permission from Mineralogical Society of America, copyright 1986.

Similarly, the spectral range $28600\text{--}2000 \text{ cm}^{-1}$ was used to detect anhydrous carbonate minerals using bands at ~ 4350 , 4000 , 2940 , 2560 and 2130 cm^{-1} (Figure 4).²¹ In addition, water related spectral features were detected at 10000 , 8330 , $7140\text{--}6670$, 5260 , and 3570 cm^{-1} . However, some typical characteristic carbonate IR bands were shifted, weak or absent in the case of hydrous carbonates and these



minerals may be difficult to identify or distinguish from other hydrous minerals such as sulphates or chlorides.

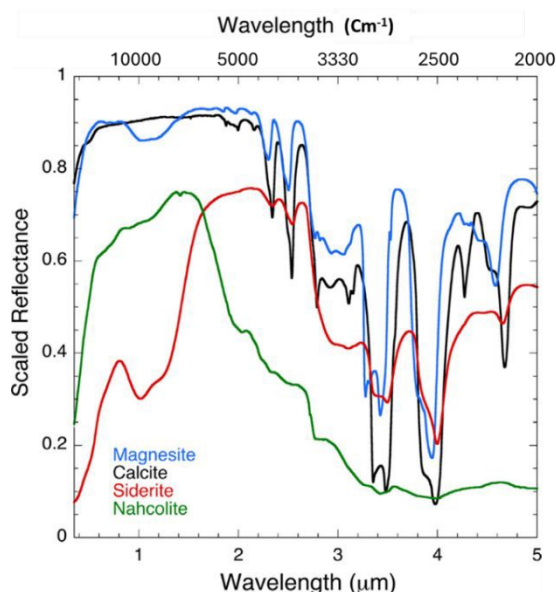


Fig. 4 NIR reflectance spectra (at 2000-28571 cm^{-1}) for anhydrous carbonates: calcite, magnesite, siderite, and nahcolite. Adapted from reference ²¹ with permission from Elsevier B. V., copyright 2015.

Using IR to monitor stability and phase change kinetics

Amorphous CaCO_3 (ACC) is a thermodynamically unstable phase, and various parameters influence its transformation into CaCO_3 crystalline phases.¹¹ These parameters include impurities, pH and temperature. However, the amorphous phase can be stabilized at low particle sizes (< 100 nm), using surfactants, or when contained in overbased (highly alkaline) detergent additives. An example is presented in Figure 5²³ where the amorphous phase was synthesized and stabilized by AOT (dioctyl sodium sulfosuccinate). However, heating to 70 °C, calcite or vaterite were obtained depending on the heating ramp. CaCO_3 polymorphs (including ACC) were also sometimes used as additives for lubricants and grease.¹¹

ACC transformation into calcite (via thermal treatment and by exposure to water at RT) was monitored by IR, XRD and TGA.²⁴ Heating ACC resulted in the removal of adsorbed water above 100 °C with the formation of calcite at 270-400 °C. Similarly, exposure to a water/ethanol solution resulted in the crystallization of ACC. However, the product varied depending on the amount of water and the duration of exposure. Small water amount and/or short exposure time led to the formation of aragonite and/or vaterite, while more water and/or prolonged exposure led to the formation of calcite. The authors studied the influence of adding anionic polyelectrolytes, mimicking soluble proteins for inhibition of crystallization.

Similarly, the transformation of ACC to calcite was shown, using IR monitoring, to proceed via vaterite as a transition state.²⁵ A two-step mechanism was suggested starting with the formation of vaterite particles followed by a much slower step of redissolution and

precipitation into calcite. Figure 6 shows the XRD patterns corresponding to each step as well as the IR spectra of the initial and final materials.

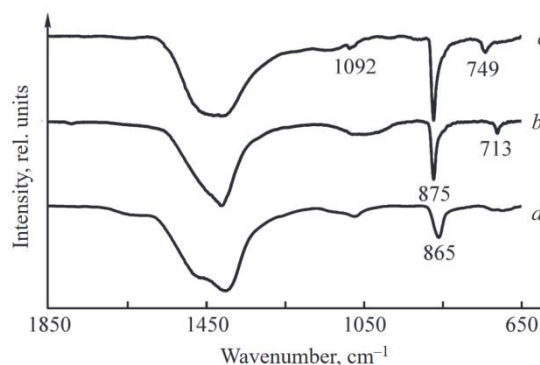


Fig. 5 IR spectra of (a) AOT-ACC, (b) calcite (heating ramp = 10 °C/min), and (c) vaterite (ramp = 1 °C/min). Adapted with permission from reference ²³ with permission from Royal Society of Chemistry, copyright 2013.

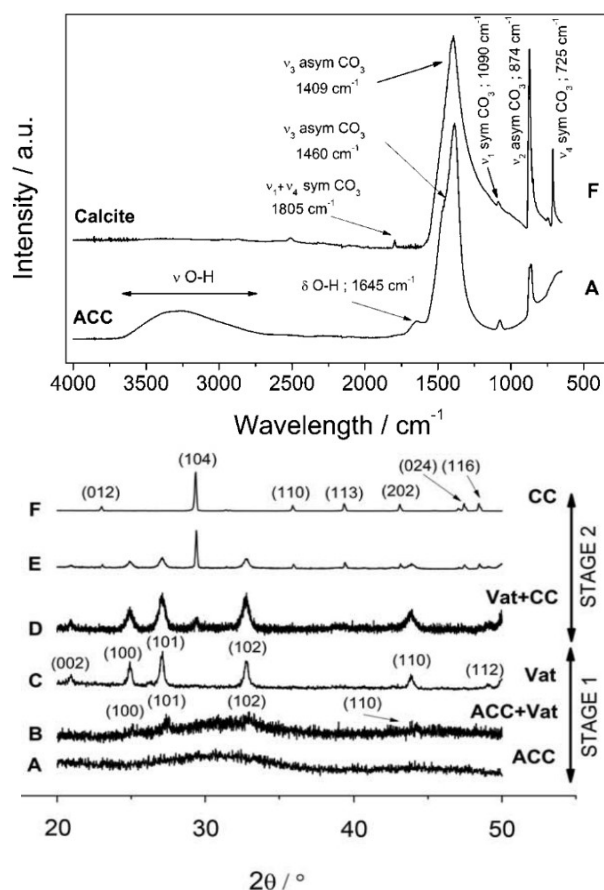


Fig. 6 Infrared spectra of ACC and calcite (top) showing the change in water content from the amorphous hydrated precursor to the non-hydrated crystalline calcium carbonate phases. 'A' and 'F' represent the same samples shown in the XRD patterns (bottom) of solids collected at different elapsed times during the off-line experiments, showing ACC, vaterite and calcite. Adapted from reference ²⁵ with permission from Royal Society of Chemistry, copyright 2011.



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IR was used to study naturally occurring spicules, skeletal elements in marine animals consisting of stable ACC entirely (in the ascidian *Pyura pachydermatina*) or of a composite of ACC and calcite (in the sponge *Clathrina*) (Figure 7). In both cases, the presence of ACC was associated with proteins rich in glutamic acid (and/or glutamine), serine, glycine and polysaccharides²⁶, while calcite was associated with proteins rich in aspartic acid (and/or asparagine).

Aragonite and vaterite transformation by heating into the more stable phase calcite was followed by IR spectroscopy.^{19,27} The least stable phase vaterite was first prepared and its transformation into the other two phases was controlled. These transformations were clearly demonstrated by the significant changes in IR spectra at 650–1200 cm⁻¹ (Figure 8).

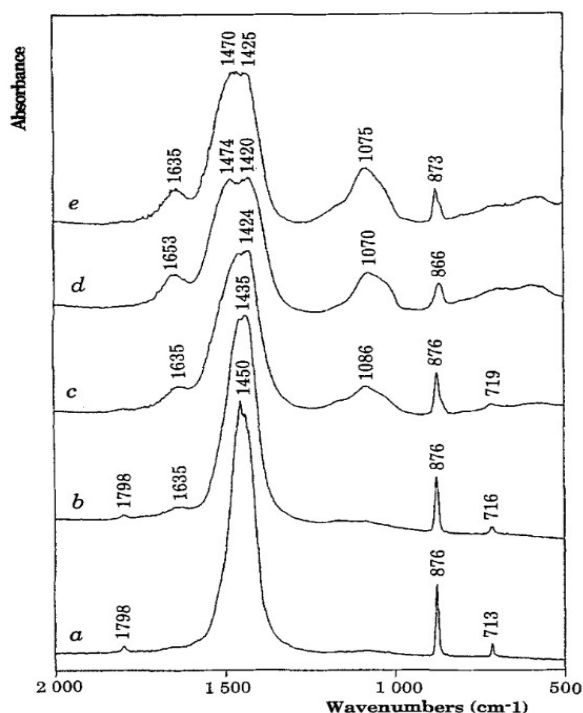


Fig. 7 IR spectra of calcium carbonates from: a) geological calcite; b) separated calcitic cores from the *Clathrina* spicules; c) intact *Clathrina* spicules (note the atypical broadening of the calcitic peaks and the additional absorption at 1080 cm⁻¹); d) *P. pachydermaha* spicules; e) synthetic amorphous CaCO₃ grown in the presence of the macromolecules extracted from the amorphous layer of *Clathrina* spicules. Adapted from reference²⁶ with permission from Wiley Online Library, copyright 1996.

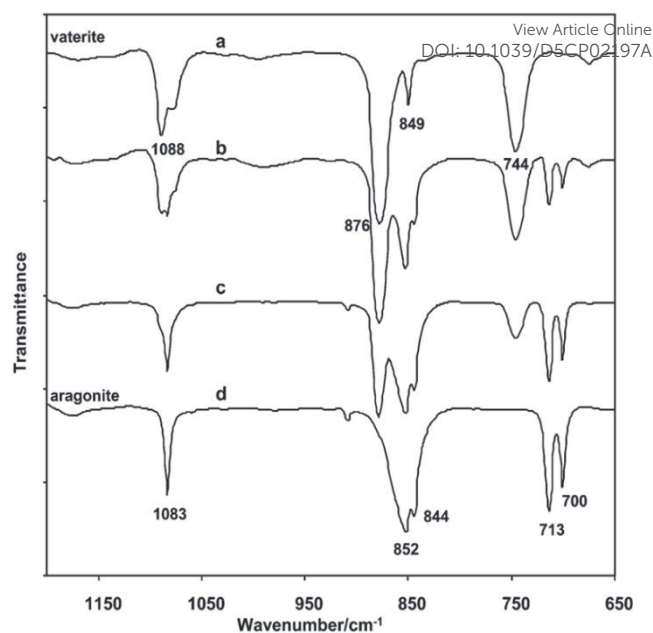


Fig. 8 FTIR spectra (650–1200 cm⁻¹) of (a) the vaterite sample, and when it was refluxed in distilled water for (b) 30 min, (c) 60 min, and (d) 75 min. Adapted from reference²⁷ with permission from American Chemical Society, copyright 2010.

Identification of carbonate composition: hydration of magnesium carbonate

The compositions and structure of several hydrous magnesium carbonates were studied by various techniques and IR spectroscopy which provided significant information.²⁸ Combining IR data published by several groups, a relation was established between the infrared band frequencies and the lengths of H-bonds of various hydrated solids (including carbonates) (Figure 9).²⁸ Moreover, Figure 10²⁸ shows FTIR spectra of three hydrated magnesium carbonate minerals where the bands due structural hydrogen bonds varied significantly depending on the mineral structure.

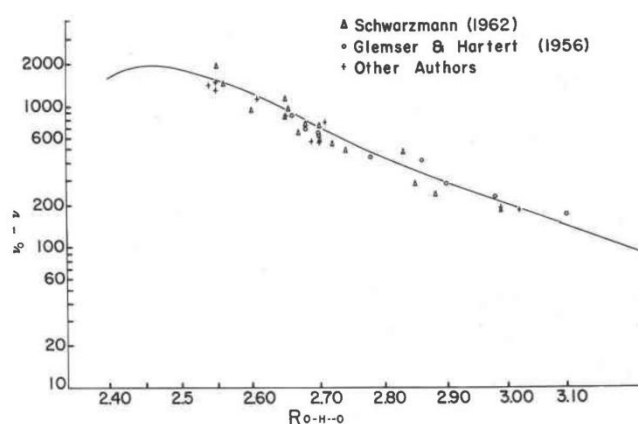


Fig. 9 Relationship between O-H frequency (ν) and O-H...O distance in H-bonds ($R_{O-H...O}$); where $\nu_0=3756$ cm⁻¹ on the Y-axis. Adapted from reference²⁸ with permission from Mineralogical Society of America, copyright 1971.



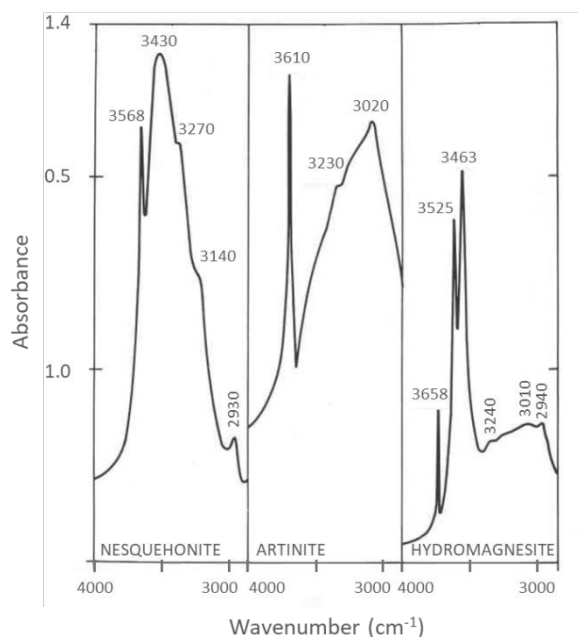


Fig. 10 Spectra of the hydrous magnesium carbonate minerals in the near infrared. Adapted from reference ²⁸ with permission from Mineralogical Society of America, copyright 1971.

IR studies of adsorbed species

The interaction of solid carbonates with small molecules and organic compounds is important for several concerns. Organic compounds govern the crystallization of biogenic carbonates in shells and marine organisms. In the field of oil extraction, understanding the way hydrocarbons and naphtha derivatives are adsorbed on carbonates is the key to extracting the maximum amount of oil from limestone deposits. Organics and probe molecules can also be adsorbed on the surface of solid carbonates for understanding surface sites on possible catalysts or on materials for sorption purposes.

Adsorption sites on carbonates

Adsorption sites vary depending on the type of molecules. Cationic metal sites are expected to be the preferential adsorption sites for most molecules such as CO ¹, H₂O ¹ and HCs.^{3,4,5} Carbonate groups, rather than the cations, were reported to be the preferential adsorption sites for CO₂.² Adsorbed water also leads to the formation of a surface intermediate Ca(OH)HCO₃ ^{1,29,30} where SO₂ adsorbs on the hydrogen carbonate group, whereas CO₂ and inorganic acids adsorb on -OH groups.

Co-adsorption with water was found to strengthen CO adsorption on some solids and red-shift its absorption band ³¹ and similarly CO₂ adsorption on carbonate was enhanced due to adsorbed water ²⁹. Several adsorption models also explained the relation between heats of adsorption, temperature and coverage. Temkin model ^{32,33} suggests that heat of adsorption is inversely proportionally to

coverage, and coverage is inversely proportional to temperature with a plateau of full coverage at relatively low temperatures.

Adsorption of CO

CO adsorbed on Calcite yielded an IR absorption band at 2173-2176 cm⁻¹ at CO coverage of 2-0 L (Figure 11). This indicates the rather weak adsorption, considering that gaseous CO absorption bands are located at 2114 and 2176 cm⁻¹ (rotovibrational P and R branches respectively). CO adsorption happens over Ca cations.^{34,35,36} Further infrared investigation of other carbonate minerals and different adsorption conditions is lacking.

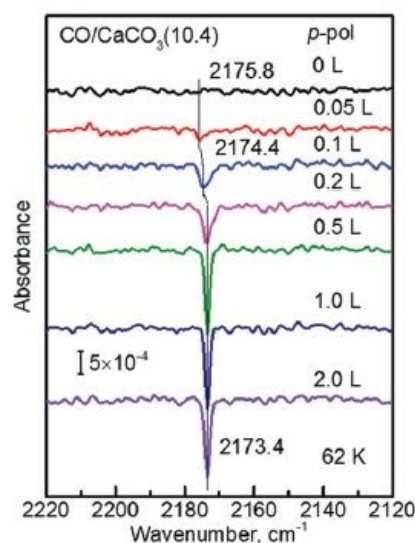


Fig. 11 IRRAS spectra with p-polarized light for CO adsorbed on calcite(10.4) surface at 62 K with increasing exposures (0-2 L). Adapted from reference ³⁴ with permission from Royal Society of Chemistry, copyright 2021.

The heat of adsorption and the vibrational spectrum were satisfactorily reproduced by DFT calculations for CO on calcite, with 2177 cm⁻¹ (theoretically) for 2175 cm⁻¹ (measured) at a coverage of 0.5 ML ³⁴.

Adsorption of CO₂

CO₂ methanation over Ni/Dolomite was followed by *in situ* and *operando* DRIFTS and was found to proceed via CO₂ adsorption followed by the formation of formates, resulting finally in the formation of CH₄ and H₂O and not CO (Figure 12-top) ³⁷. Formates were observed after heating to 300 °C onwards as evidenced by the bands at 1393, 1484, 1524 cm⁻¹ (Figure 12-bottom). At 400 °C, a new band was detected at 1107 cm⁻¹ and was ascribed to the formation of methoxy group and an increased activity. At 500 °C, the intense carbonate ν₃ band at ~1440 cm⁻¹ disappeared due to thermal decomposition.

CO₂ was similarly found by FTIR to adsorb over hydrotalcite based catalysts during CO₂ methanation ³⁸ or during surface activation by plasma glow discharge.³⁹ IR absorption bands of several carbonate



species were detected upon introducing CO₂ over the hydrotalcite based catalyst (Figure 13).

CO₂ adsorption was reported (without infrared data) to be positively affected by humidity, and H₂O leads to the formation of hydrogen carbonate species where CO₂ is adsorbed through -OH groups. Hydrogen carbonate was also formed during CO₂ adsorption over oxides depending on surface hydroxylation.⁷

CO₂ adsorption and reactivity were studied on several carbonate minerals and under different adsorption conditions including the presence of co-adsorbents. Adsorption sites and band positions were identified. Yet, FTIR studies are not abundant, and further works could bring about more insights.

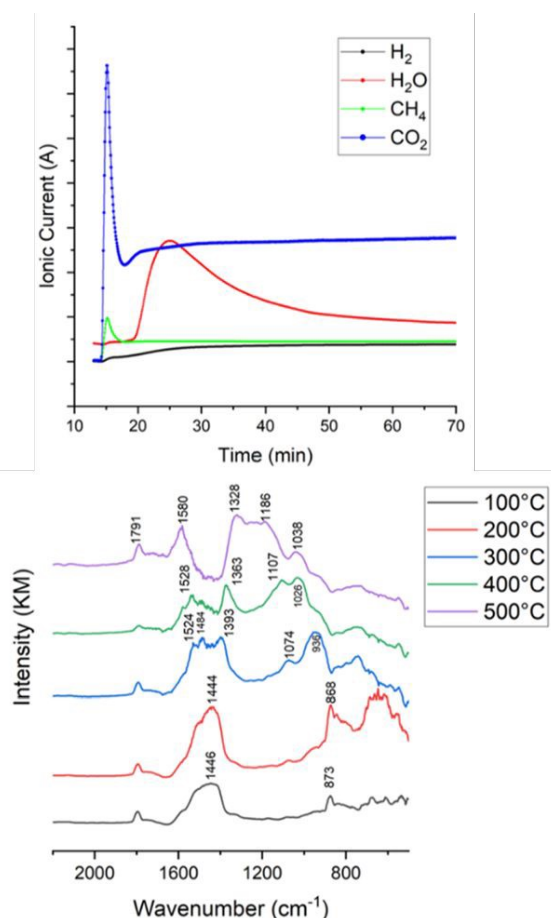


Fig. 12 Operando CO₂ methanation at 400°C on Ni/Dolomite: (Top) Evolution of Mass spectroscopy signal with reaction time. (Bottom) *In situ* DRIFT spectra as a function of catalyst temperature. Adapted from reference³⁷ with permission from Elsevier B. V., copyright 2024.

As a matter of fact, CO₂ and CO adsorption represent a major carbon capture and storage (CCS) methodology which aims at reducing greenhouse gases in the atmosphere. Yet, this approach was sparingly followed by FTIR measurement in literature reports despite its significance.

In this context, samples from naturally occurring carbonate reservoirs were reported to be efficient for CO₂ storage. For instance, CO₂-saturated brine was transported through the core sample and lead to changes in the permeability and porosity by creating conductive flow channels enhancing the rock's storage capacity.^{40,41} Moreover, industrial projects were operated by applying CO₂ injections into carbonate rock reservoirs worldwide^{42,43}, and indeed reported CO₂ storage efficiency.

On the other hand, over other CCS materials such as metal oxides⁷, Mg minerals⁴⁴ and cementitious materials^{45–47}, upon adsorption of carbon oxides, carbonate formation was observed which in turn took part in further adsorption. Moreover, an electrochemical process was developed and efficiently capture CO₂ and form various carbonate salts⁴⁸ where carbonate structure was evidenced by FTIR and XRD. This process represents a simulation of naturally occurring carbonate formation in sea water by the reaction of dissolved CO₂ with metal ions.

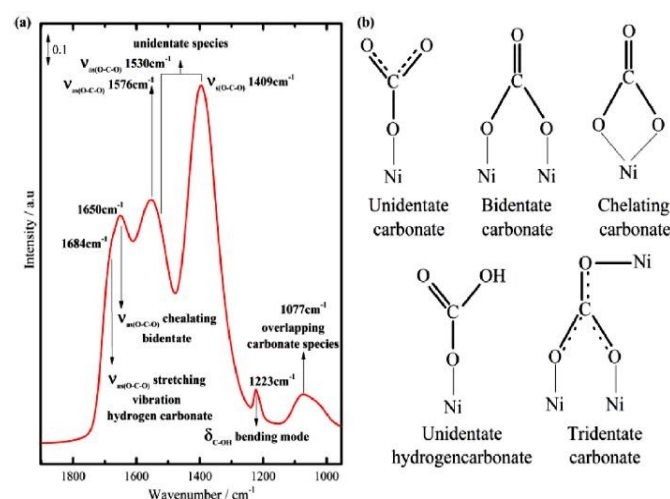


Fig. 13 (a) Infrared spectra of CO₂ adsorbed on Ni-hydrotalcite derived catalyst and (b) Possible species appeared in the CO₂ adsorption experiment. Adapted from reference³⁸ with permission from Elsevier B. V., copyright 2023.

Adsorption of H₂O

Water adsorption on CaCO₃ forms a surface hydrogen carbonate species.³⁰ Consequently, CO₂ and HNO₃ are adsorbed through the -OH groups, whereas SO₂ is adsorbed via the hydrogen carbonate groups. This adsorption mechanism is consistent with a positive effect of H₂O on CO₂ adsorption on calcite.²⁹ In contrast, surface solvation (by H₂O) had a negative effect on the adsorption of aromatic hydrocarbons on calcite.⁴⁹ Figure 14³⁰ shows the evolution of ATR spectra of CaCO₃ during the exposure to a range of relative humidity. Increasing humidity induced an increased intensity for the IR bands due to adsorbed water around 1640 and 3000-3700 cm⁻¹.

Over hydrotalcites¹, H₂O adsorption similarly leads to the formation of hydrogen carbonate and to the liberation of CO₂. This is accompanied by the formation of -OH groups detected by IR at 1490 and 3500 cm⁻¹ (Figure 15) and by the loss of carbonyl bond



absorption bands at 1340 and 1570 cm^{-1} . Water is suggested to adsorb on cationic metal sites. The formation of hydrogen carbonates was also observed²⁹ as mentioned before.

Although there are few reports on H_2O adsorption on carbonates, valuable information is available about adsorption sites and reactivity. These works also demonstrated the positive effect of humidity on CO_2 adsorption and the negative effect of water on the adsorption of aromatic hydrocarbons.

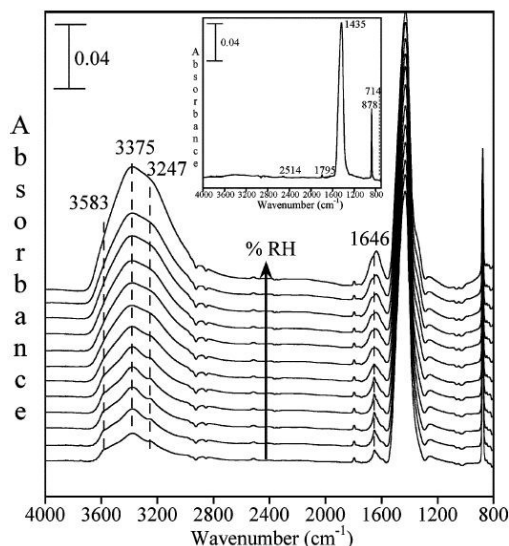


Fig. 14 Evolution of ATR-FTIR spectra during water adsorption on calcium carbonate as a function of relative humidity from 10.6 to 95.3% RH (10.6, 20.2, 29.8, 41.6, 50.1, 55.8, 60.1, 65.6, 70.7, 77.3, 81.5 and 95.3% RH). Inset: ATR-FTIR spectrum of calcium carbonate under dry conditions (<5% RH). Adapted from reference³⁰ with permission from Royal Society of Chemistry, copyright 2005.

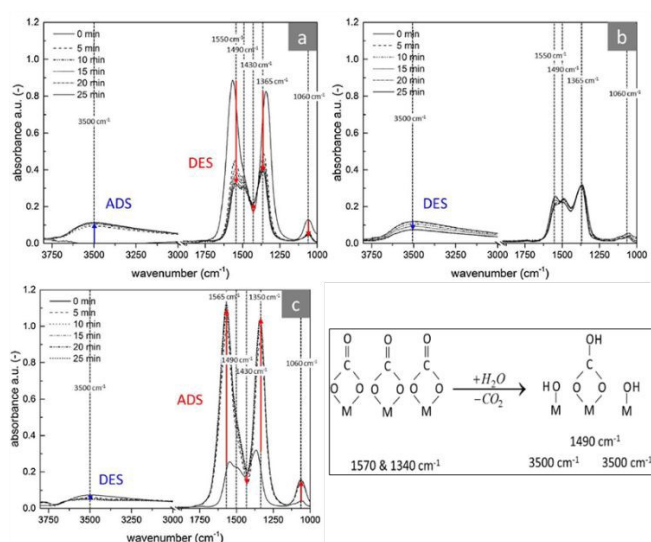


Fig. 15 IR spectra of hydrotalcite after (a) Adsorption of H_2O at 400 °C (b) Desorption of H_2O at 400 °C with N_2 (c) Adsorption of CO_2 at 400 °C after desorption with H_2O and N_2 . The equation shows H_2O adsorption and CO_2 liberation. Adapted from reference¹ with permission from Elsevier B. V., copyright 2018.

Adsorption of hydrocarbons and functional molecules

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The infrared spectrum of adsorbed probe molecules gives key information on surface sites and possible chemical reactions on the surface, for example with aromatics which are important for oil extraction purposes. Characteristic bands for the probe molecule are shifted upon adsorption, and more for the first monolayer than for the subsequent layers. An example of adsorbed benzene on calcite is shown in Figure 16, where liquid benzene displayed a characteristic band at 667 cm^{-1} whereas it was shifted to 680 cm^{-1} in the case of a monolayer adsorbed on calcite and to 673 cm^{-1} in the case for extended adsorption layers.

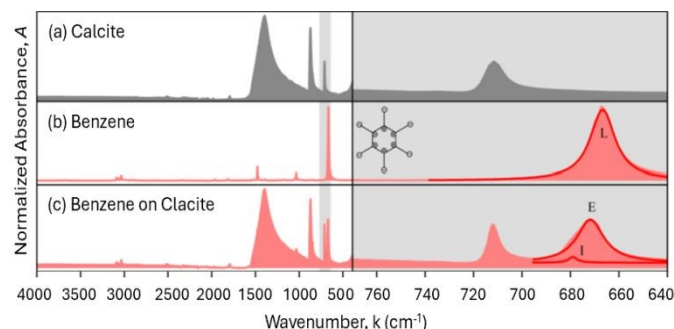


Fig. 16 [Left] IR spectra at 400–4000 cm^{-1} of (a) calcite, (b) benzene, and (c) benzene on calcite. [Right] Expanded view of 640–770 cm^{-1} . L: liquid, E: extended adsorption layers, I: first adsorption layer. Adapted from reference⁵⁰ with permission from American Chemical Society, copyright 2015.

Combining FTIR and DFT investigations proved useful to explain the interaction of calcite with four aromatic compounds.⁵¹ Ionic bonds were formed as Ca–O (between calcite and benzoic acid, with the formation of –OH groups via oxygen atoms of calcite) and Ca–N (between Calcite and Pyridine). Thiophene was adsorbed via O–H bond formation, whereas toluene showed no interaction.

Combined MD and DFT computed a stronger CO_2 adsorption on CaCO_3 polymorphs compared to CH_4 adsorption², in agreement with the previously mentioned observations.⁵² Adsorption strengths of CH_4 and CO_2 were computed on vaterite, aragonite and calcite.²

Adsorption energies were also computed for benzene and hexane on calcite and dolomite⁵ and Ca cations were suggested as the most energetically favorable adsorption sites. This is consistent with some experimental studies^{4,52} but could easily be checked in detail with IR.

Tert-butyl cyanide (TBC) was used as a probe for acidity on carbonated MgO (containing MgCO_3).⁴ The cyanide group attached itself to Mg cations acting as weak Lewis acid sites. The $\nu(\text{CN})$ absorption band is observed at 2234 cm^{-1} when TBC is only physisorbed, with no strong interaction. When the probe molecule is adsorbed on carbonate-free MgO, it is slightly shifted to 2240 cm^{-1} . On the carbonated solid, the stronger interaction leads to an upward shift to 2262 cm^{-1} , which indicates a stronger electron depletion on the cation because of the carbonate moiety (Figure 17).



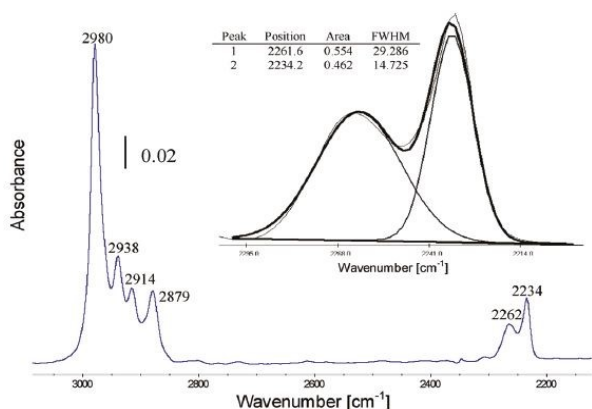


Fig. 17 tert-Butyl cyanide adsorption on carbonated MgO activated at 240 °C. The zoom-in region of 2300–2150 cm⁻¹. The deconvolution results are shown in the inset. Adapted from reference ⁴ with permission from American Chemical Society, copyright 2011.

CH₄ desorption and recovery from carbonate natural gas reservoirs was improved by hot CO₂ gas injections due to a favorable adsorption competition between CO₂ and methane ⁵², (Figure 18). Detailed information on the molecular interactions by IR is, however, missing. With aminoacids, experimental information is clearly missing. It was computed that anhydrous ACC favored the adsorption of basic/neutral aminoacids, whereas co-adsorbed water improved the adsorption of acidic aminoacids.⁵³ The study also suggested a faster diffusion of surface Ca²⁺ compared to the bulk ions. Experimental studies are needed to validate these findings.

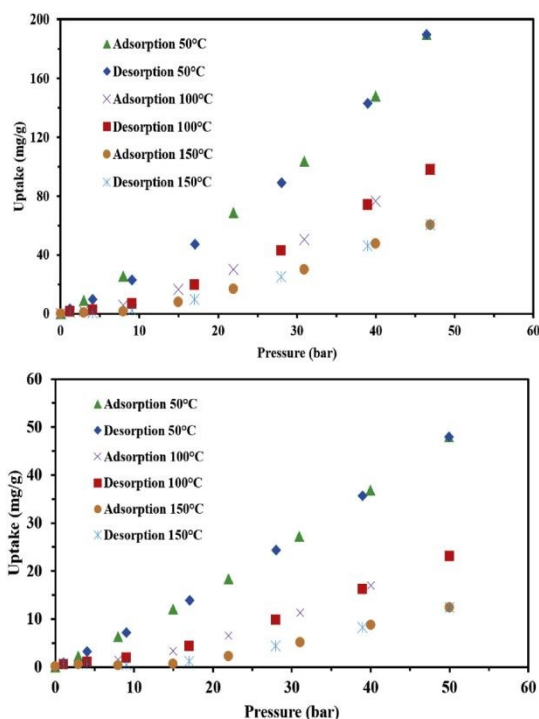


Fig. 18 Evolution with temperature and pressure of the adsorption and desorption of CO₂ (top) and CH₄ (below) on carbonate rocks. Adapted from reference ⁵² with permission from Elsevier B. V., copyright 2018.

Conclusions

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Infrared spectroscopy has proven to be a versatile, facile and inexpensive technique for studying carbonate minerals. FTIR techniques offer valuable information on their structural features, phase transitions, and on the remarkable adsorption capacities. This review builds up on the use of FTIR for studying carbonate structure and the differentiation between its polymorphs, monitoring dehydration and rehydration processes, aiming at studying the adsorption mechanisms and adsorption sites for several molecules such as CO, CO₂, H₂O, and several HCs on carbonates. Some authors reported theoretical modeling and validated the results via experimental data, but FTIR remains underutilized in literature for studying surface properties of carbonates. Therefore, future works should target integrating FTIR (alongside computational modeling) to deepen our understanding of these surface properties including the nature of surface acidity. This, in turn, would be beneficial for several processes where carbonates are heavily involved such as CO₂ capture and storage and natural gas extraction.

Author contributions

All authors contributed to the conceptualization, bibliographic survey and design of the review. The original draft was written by Taha Elgayyar. Further modification and comments were performed by all authors. All authors approved of the final version of the review.

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Sincerely,

Taha Elgayyar, Federico Azzolina-Jury, and Frédéric Thibault-Starzyk

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