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FEATURE ARTICLE

Carbonic acid: molecule, crystal and aqueous solution

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Carbonic acid (CA) is a crucial species in the equilibrium between carbon dioxide, water and many minerals. Yet many of its properties have either not been studied at all, or have been misunderstood. Its short lifetime in the presence of moisture has been a major stumbling block in efforts to studying it. Over the last two decades, there has been a sustained, albeit slow progress in the detection, synthesis and investigations of CA in its various phases – as a molecule in gas phase, in its crystalline state, as an adsorbate on mineral surfaces and in aqueous solutions. For instance, ultrafast time resolved spectroscopic experiments as well as molecular dynamics based free energy calculations using Kohn–Sham density functional theory have shown the pK_a of CA to be around 3.5 which makes its acidity comparable to that of formic acid. The composition of its gas phase in terms of its conformer and oligomer population have also been examined. Thin films of crystalline carbonic acid polymorphs have been synthesized and characterized using infrared and Raman spectra. Given the difficulties associated in the conduct of experiments to investigate CA, computational modelling has played a significant role. Using a multi-tiered modelling approach, we have been able to examine several model crystal structures possessing distinctive hydrogen bonding motifs. Their vibrational spectra were compared against those obtained from experiments. A model crystal consisting of hydrogen bonded molecules in a chain-like fashion fits the experimental vibrational spectra of β-carbonic acid better than one in which the motif is two-dimensional (sheet-like). Under dry conditions, we predict such a crystal to be stable below 359 K at 1 atm. In this feature article, we provide a summary of our work on carbonic acid as well as review contributions from others.

1 Introduction

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Alongside water, carbon dioxide is the triatomic molecule that has attracted intense interest. In the recent past, much attention

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has been devoted to CO_2 due to its vital role in many atmospheric chemical processes. Being the most oxidized form of carbon, efforts to mitigate the large amount of carbon dioxide released to the atmosphere are challenging;[1–5] these include sequestration and storage using physical as well as chemical means with the ultimate aim of converting it to inorganic carbonates. While the kinetics of the associated individual chemical processes are quite important, even the thermodynamic equilibrium of various species involved are only now being established. The objective of this feature article is to generate attention on a vital component in this equilibrium, carbonic acid.

The main sources for the increase of CO_2 levels in the atmosphere are combustion of fossil fuels to generate electricity, for transportation and to run industries. While about half of emitted anthropogenic CO_2 stays in the atmosphere, the remainder participates in the natural carbon cycle involving the exchange of CO_2 (or species derived from it) between the atmosphere, ocean and the land biosphere.[2] One of the many possible advocated solutions of CO_2 sequestration is to capture CO_2 at point sources such as coal plants and inject it into deep oceans at great depths.[3] This could lead to the acidification of ocean surface and lower the concentration of carbonate ions which can substantially impact the marine ecosystem.[4,6] Thus, understanding the microscopic details of CO_2-rich water is crucial not only from an academic point of view but is vital for biogeochemistry.

The interaction of carbon dioxide with water is weak (binding energy of around -1.9 kcal mol^{-1}) with CO_2 acting as a Lewis acid; a weak hydrogen bonding in which water is the donor is also likely.[7] CO_2-rich water contains low amounts of carbonic acid (H_2CO_3) which can dissociate into bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) anions. Carbonic acid has often been inaccurately pictured as a very weak acid arising out of (i) its short lifetime in water and (ii) the presence of undissociated carbon dioxide in aqueous solution.[8,9] This article is an attempt to summarize recent findings on many aspects of carbonic acid in varied situations – as a crystalline solid, in gas phase, in aqueous solutions and as a species adsorbed on solid surfaces.

This article is divided as follows. In the next section, we discuss the conformers of CA, and later proceed to review the solid phase of carbonic acid. Studies of the molecule in the gas phase and in aqueous solutions are described subsequently. Carbonic acid as a adsorbed species on solid surfaces is discussed later. The article concludes with a summary and an outlook for the future.

2 Conformers of carbonic acid

Carbonic acid (CA) is a diprotic acid with its ability to exchange two protons in aqueous solution. It possesses both hydrogen bond donor (hydroxyl) and acceptor (carbonyl) groups. Strong intermolecular hydrogen bonds leading to stable homodimers can thus be formed. Three stable conformers of CA are known, namely *anti–anti*, *anti–syn* and *syn–syn*. Quantum chemical calculations at the CBS-QB3 level show the *anti–anti* conformer to be the most stable in gas phase,[10,11] while the other two are higher in energy by 1.53 and 9.85 kcal mol^{-1} respectively
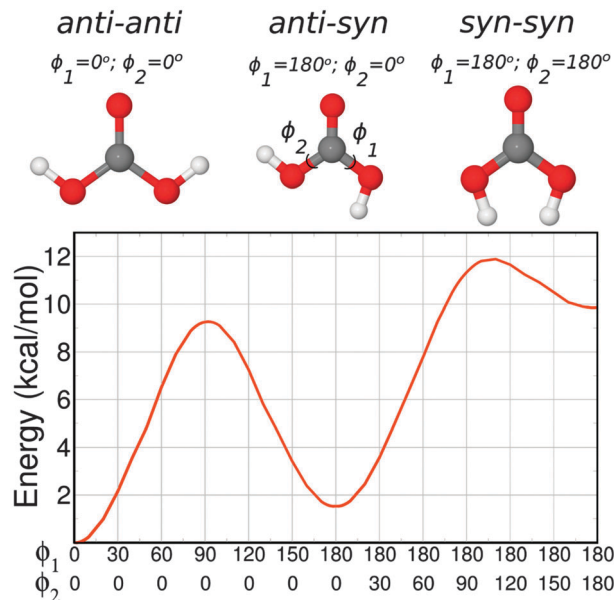

Fig. 1 Three conformers of carbonic acid located on the potential energy surface drawn as a function of the two dihedral angles. Energies are calculated at CBS-QB3 level of theory.[10,11]

(including zero point energy). These values are similar to those reported by Endo *et al.* using the CCSD(T) method.[12] Fig. 1 shows the potential energy of CA plotted as a function of the dihedrals ϕ_1 and ϕ_2.

3 Existence in solid phase

The notion that CA cannot be isolated in pure form either in gas or condensed phase was held for a long time; the molecule was considered elusive. Moore and Khanna condensed mixtures of gaseous CO_2 and H_2O to form thin films which were irradiated with high energy protons to expedite protonation.[13] CA was identified using both infrared (IR) and mass spectroscopy. Carbonic acid was also observed to form by the proton bombardment of pure CO_2 ice, even in the absence of H_2O.[14] These experiments mimic conditions present in outer space and thus indicate the plausibility of either solid (amorphous or crystalline) or gaseous CA to exist therein.

Mayer and co-workers demonstrated the possibility of synthesizing carbonic acid in a crystalline form without employing any radiation sources.[15] By successive injections of potassium bicarbonate and hydrogen chloride on a cold substrate within a cold finger setup, they were able to prepare thin films of crystalline CA. The initially cold layers were warmed gradually from liquid nitrogen temperature and the infrared spectrum was recorded *in situ*. They observed evidence for the presence of individual layers of the salt and the acid up to a temperature of 180 K; however upon increasing the temperature further, protons migrated from the acid layers to react with bicarbonate to form crystalline CA. The use of a methanolic bicarbonate solution yielded the α-polymorph of CA, while an aqueous one yielded β-carbonic acid.[16,17] They were differentiated based on

infrared vibrational spectroscopy and their distinctive thermal stabilities.

Although crystalline thin films of CA can be synthesized, these have been characterized only through vibrational spectroscopy so far. The crystal structures have not been determined yet as single crystals could not be grown and the powder X-ray diffraction patterns are not good enough for the purpose of refinement.[18,19] The mass density of the crystals has not been reported as well. Vibrational spectroscopy has been used to identify the building blocks present in these crystals.

Mayer's (and currently, Loerting's) group have studied the phase transition from amorphous to crystalline carbonic acid by monitoring the spectral changes within a narrow temperature range – from 200 to 230 K. For instance, the protonation of an aqueous solution of $KHCO_3$ with HCl leads to an amorphous CA film at 200 K which transforms to the β-form upon heating. However, protonation with HBr (instead of HCl) leads to the direct generation of the crystalline phase. The changes in the IR spectrum due to amorphization in the former scenario include shifts in peak positions, broadening and splitting of bands. Interestingly, they observed that the amorphous samples, upon heating crystallize to either the α or β polymorphs. Thus, the amorphous films themselves can be distinguished. One can conclude that the structural synthon present in the crystalline phase of the two polymorphs is already developed in the corresponding distinct amorphous states.[19] The X-ray diffraction pattern of amorphous compounds synthesized from each of these polymorphs too were different, indicating that the building blocks in these two crystal structures are different.[19]

Interestingly, on heating the samples above 200 K, both polymorphs sublime without decomposition, indicating the stability of carbonic acid in gas phase. The stability is likely due to the high energy barrier for its decomposition into CO_2 and H_2O, as calculations have shown.[20,21] This observation is instrumental in providing an insight into the possible presence of CA in outer space. The existence of CA in many extraterrestrial systems has been proposed.[22] The two polymorphs of CA can be differentiated by their IR spectra. Recently, CA formation was reported from the surface reactions of non-energetic OH radicals with CO molecules at conditions relevant to astrophysical environments.[23] Based on the peak position of the C=O stretching mode, its structure was expected to be different compared to either α or β-polymorphs.[23]

4 Crystal structure modelling

Hydrogen bonding is the primary interaction present in crystals of carboxylic acids as they have both donor and acceptor functionalities. Conformational isomerism adds another dimension to intermolecular interaction, as a particular conformer can form a stronger hydrogen bond than another. In fact, in α-carbonic acid, the stretching of the OH bond shows two sharp peaks at 2585 and 2694 cm^{-1} while the β-form shows a very broad peak extended in the region 2600–3200 cm^{-1},[16,17] implying stronger hydrogen bonding in the former polymorph. The α-form is thus presumed

to be more stable than the β-form, however sublimation data shows opposite behaviour. At a base pressure of 10^{-7} mbar, α- and β-forms are stable up to 210 and 230 K respectively, beyond which they sublime. Sublimation rates though, can be sensitive to sample morphology as well,[16] so the relative thermodynamic stability of these polymorphs need to be ascertained using other methods also.

The ability of carboxylic acid molecules to possess multiple stable conformations and to further exhibit tautomerism, makes them versatile to exhibit crystal polymorphism. The cyclic hydrogen-bonded dimer and the catemer are the main building blocks found in many crystal structures of carboxylic acids. Such motifs could also constitute the polymorphs of CA. A crucial clue on the identification of the symmetry of the building unit in CA came from Raman spectra of these compounds. The Raman- and IR-active modes of β-carbonic acid were mutually exclusive, suggesting it to have a centrosymmetric building block, whereas no such symmetry was observed in α-carbonic acid.[24] Quantum chemical calculations have shown the high stability of cyclic dimers, made either of two anti–anti conformer molecules or of two anti–syn conformer molecules. Both possess an inversion center and hence are ideal candidates for consideration as building blocks for β-carbonic acid.[25–27] Although the building unit for α-carbonic acid is much less clear, a catemer, i.e., two molecules which are singly hydrogen bonded with each other, has been suggested.[25]

4.1 Oligomers – gas phase calculations

Computational prediction of the crystal structure of a compound, especially an organic one, is a challenging task. Conformational isomerism and weak interactions such as hydrogen bonding, and those involving the π orbitals make the problem a complex one. As mentioned before, many competing and distinct crystal structures can have cohesive energies within a few kcal mol^{-1}, thus making it difficult for computations to discriminate between them. One can of course, employ physical intuition and available empirical evidence to come up with model structures and evaluate their stabilization energies, based either on classical interatomic potentials or using Kohn–Sham density functional theory.[28,29] We proceed to summarize one such approach adopted by us below.

It should be possible to construct building blocks (say, oligomers of CA), and calculate their vibrational spectra in gas phase. Such motifs, possessing hydrogen bonds, can work as models to capture the intermolecular interactions in the crystal. Vibrational spectra of such blocks can be calculated for a comparison to experiment. Tossell had undertaken such an exercise.[30] He calculated the vibrational spectrum of the anti–anti dimer at CCSD/6-311+G(2d,p)//B3LYP/CBSB7 level of theory.[31] Calculated features for bands related to the carbonyl and hydroxyl groups were found to closely correspond with experimental spectra. Our own quantum chemical calculations, which included anharmonic corrections, for oligomers up to an octamer have shown that the hydrogen bonded one-dimensional oligomer chain motif reproduces the vibrational spectra of β-carbonic acid rather well.[26] Fig. 2 compares the calculated
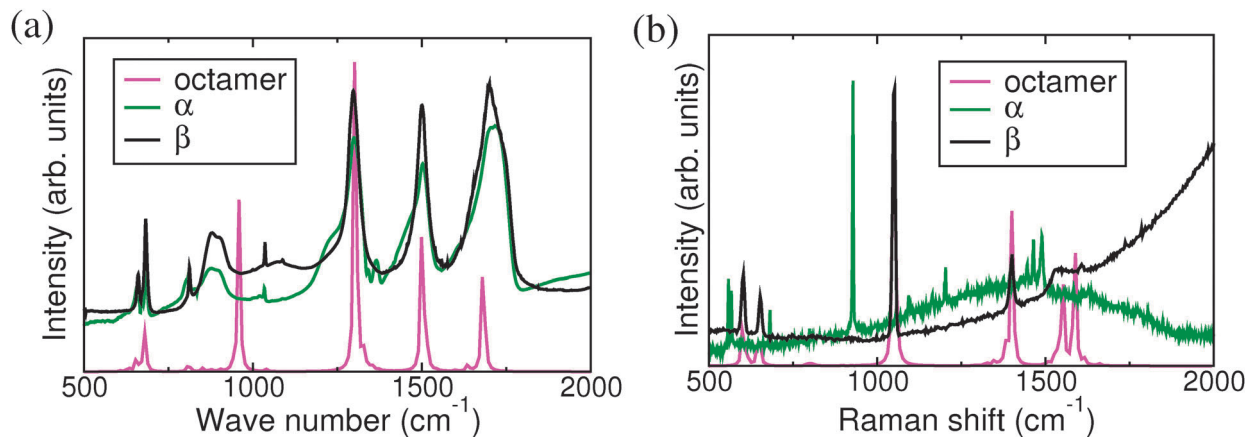
Fig. 2 Calculated (a) infrared and (b) Raman spectra of a linear octamer of carbonic acid compared against those of α- and β-carbonic acid. Experimental data of the polymorphs are from ref. 19, 24 and 25. Features related to modes involving terminal atoms of the octamer are not shown.[26] Reprinted with permission from J. Phys. Chem. A, 2012, 116, 1638. Copyright (2012) American Chemical Society.

IR and Raman spectra of the octamer with the experimental spectra of α- and β-carbonic acid respectively.[26] The calculated spectra match those for β-carbonic acid suggesting that this polymorph could be constituted by linear oligomers composed of *anti–anti* conformers. Such chains can interact with each other *via* van der Waals interactions in the solid state.

4.2 Condensed phase calculations

Predicting the crystal structure of CA is lot more difficult than identifying the building block. In one early attempt to understand the polymorphism exhibited by CA, a computational study was undertaken to generate low energy crystal structures.[19] The molecular interactions were described through distributed multipoles. Among the many structures generated, a frequent motif within the highly stable ones was the cyclic dimer made of two *anti–syn* conformers. An observation from these calculations was that crystals with two-dimensional, sheet-like hydrogen bonding topologies were more stable than those with linearly hydrogen bonded chains. Our specific focus has been on the β-polymorph

and the work involved using quantum chemical methods, Kohn–Sham density functional theory based zero Kelvin, periodic calculations and finite temperature *ab initio* MD simulations as well.[28,29]

Using a multi-tiered approach, we have been able to come up with a reasonable candidate structure for β-carbonic acid (Fig. 3).[27] The first step was to carry out high quality quantum chemical calculations of oligomers of CA. The geometry, relative energies between oligomers and the monomer, and that between different conformers were used as benchmarks in refining an existing force field for the molecule. Subsequently, the rigid molecule in its *anti–anti* conformation was packed in various space groups and these structures were ranked based on their 0 K energies evaluated using the force field. The assumption of rigidity of the molecule is a reasonable one as the barrier for conformational change is around 9 kcal mol^{-1} (see Fig. 1). Few structures among them were selected on the basis of interesting hydrogen bonding topologies and their stability. These were further studied using Kohn–Sham density functional theory.[28,29]
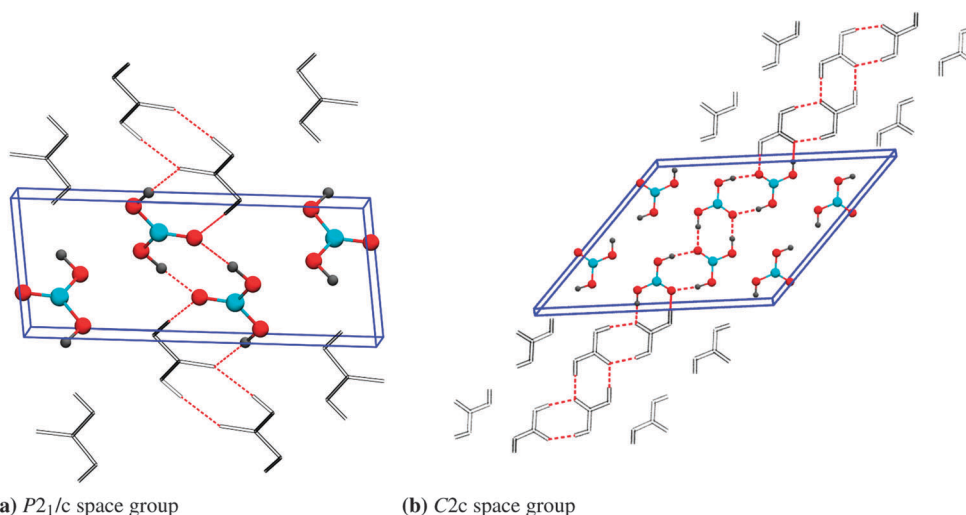

(a) *P*2$_1$/c space group   **(b)** *C*2c space group

Fig. 3 Possible crystal structures for β-carbonic acid obtained using a multi-tiered approach.[27] Hydrogen bonds are shown as red dotted lines.

It was found that crystals with one-dimensional hydrogen bonded topologies were more stable than those with sheet-like topologies, which is not in agreement with the conclusions of ref. 19. The difference is likely to be due to the different computational methods adopted.

Finite temperature (200 K) DFT based MD simulations of these crystals were carried out for periods of tens of picoseconds. The infrared spectrum was calculated as the Fourier transform of the total dipole moment–dipole moment time correlation function. The Raman activity tensor of modes in the wavenumber range 900–1200 cm^{-1} was also calculated. The stretching mode of C–O and C=O bonds was observed at 978 cm^{-1} in agreement with experiment.[27] The far-infrared region of the IR spectrum for sheet-like topologies contained two features, one at 250 cm^{-1} and another at 150 cm^{-1}. However, crystals with chain-like motifs exhibited IR absorption at 250 cm^{-1} alone. This feature can be assigned to the rocking mode of CA molecules in the crystal. The 150 cm^{-1} band is likely to arise from intermolecular modes and is absent/weak in crystals with chain-like topologies. We propose that this distinction can be exploited to experimentally identify possible structural motifs of β-CA. Apart from vibrational spectroscopy, inelastic neutron scattering in this frequency range could also be employed to distinguish between the two polymorphs. However, neutron scattering, in general, requires larger amounts of sample than that for X-ray scattering.

Among the structures with one-dimensional hydrogen bonding motifs, two candidates exhibit significantly high cohesive energies. These are present in $P2_1/c$ and $C2/c$ space groups with mass densities of 1.67 and 1.49 g cc^{-1} respectively (Fig. 3). The latter is less dense than the former structure due to twisting of the hydrogen bonded chains. Further, the hydrogen bond length in the $C2/c$ crystal is 1.58 Å when compared to the value of 1.62 Å in the $P2_1/c$ structure. Thus, the former is more stable on grounds of absolute energy; however, the chains are closer to each other in the $P2_1/c$ crystal making it denser and more favoured in terms of energy density. Details can be found in our article.[27] Either of these can be a suitable choice for β-carbonic acid,[27] although our cohesive energy density calculations favour the latter structure.

4.3 Crystal stability

The free energy of the $C2/c$ crystal was obtained as a function of temperature with contributions from internal energy, translational and vibrational contributions. The latter was obtained from a harmonic approximation to the potential energy surface (*via* a Hessian and normal mode calculation). The free energies of the *anti–anti* monomer in gas phase were calculated in a similar manner. The crossover temperature (*i.e.*, the temperature at which the free energy of the crystal exceeds that of the monomer) was obtained at many pressures. Regions of stability of the phases were delineated as shown in Fig. 4. It suggests that under dry conditions, the carbonic acid crystal is stable relative to its gas phase up to 359 K at 1 atm – a remarkable estimate and one that needs to be verified experimentally. At a pressure of 10^{-5} Pa, the calculated sublimation temperature is 212 K compared to the experimental result of 230 K. Although this agreement could be fortuitous, the fact that no empirical information
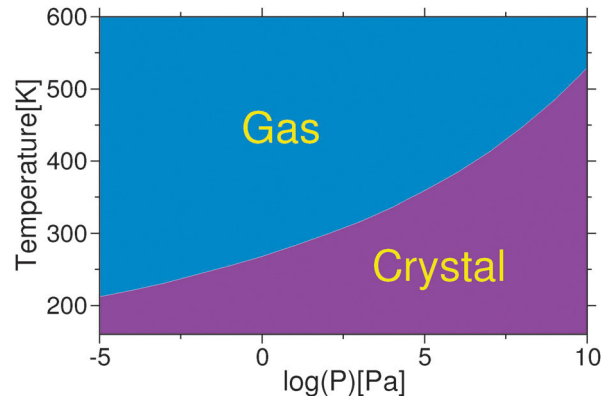

Fig. 4 Predicted solid–gas equilibrium of carbonic acid obtained from *ab initio* simulations. The shaded regions show the stability of perdeuterated β-carbonic acid crystal (violet) and gas composed of monomers (blue) respectively. Reprinted with permission from ref. 27. Copyright 2011, American Institute of Physics.

was built into the computational exercise makes this result quite significant. As there exists no model for liquid carbonic acid, it could not be included in the phase diagram shown in Fig. 4.

A note is in order regarding intermolecular proton transfer occurring in the crystalline state, a possibility that has not been taken into account in the discussion above. Crystals of other carboxylic acids such as formic acid, acetic acid or benzoic acid are constituted by discrete hydrogen bonded dimeric or catemeric units. Intermolecular proton transfer in such crystals can lead to conformational change of the molecule which has been studied using path integral Car–Parrinello molecular dynamics simulations.[32–34] Carbonic acid, however is a dicarboxylic acid and is capable of forming two strong hydrogen bonds per molecule. The $P2_1/c$ or $C2/c$ structures of carbonic acid described herein are thus constituted by infinite chains of hydrogen bonded CA molecules. Our calculations, at B3LYP/aug-cc-pVTZ level of theory, show that the barrier for concerted proton transfer in the gas phase *anti–anti* carbonic acid dimer is around 6.2 kcal mol^{-1}. In the CA dimer, the proton transfer event is accompanied by conformational change to the *anti–syn* conformer which is higher in energy than the *anti–anti* one. Further, such an event will disrupt the chain beyond the proton transfer site. Thus, proton transfer in the solid state is likely to be disfavoured on enthalpic grounds due to the replacement of strong hydrogen bonds by weaker ones.

5 Gas phase detection and kinetic stability

5.1 Gas phase

Schwarz and coworkers had first reported gaseous CA upon the thermal decomposition of NH_4HCO_3 using mass spectroscopy.[36] Employing microwave spectroscopy, Mori *et al.* have observed the *anti–anti* and *anti–syn* conformer of CA, generated by passing CO_2 gas through a water reservoir followed by the application of high, pulsed electrical potential.[12,37] Recently, Bernard *et al.* were able to isolate several species of CA from gas phase onto an

inert argon matrix.[38–40] The molecule in gas phase was generated by the sublimation of α-carbonic acid at 210 K, and was later trapped in a cold argon matrix and characterized using high-resolution infrared spectroscopy. They showed that α-carbonic acid can be sublimed at 210 K and trapped as monomers and dimers in the argon matrix at 6 K and can be recrystallized back to the same polymorph by evaporating the matrix at 180 K. This observation demonstrates that the CA molecule is intact in gas phase and does not dissociate into water and carbon dioxide, proving its kinetic stability. Interestingly, Bernard et al. observed a gas phase composition of 1 : 10 : 1 for the mixture of anti–syn monomer, anti–anti monomer and anti–anti hydrogen bonded dimer respectively.[38] Boltzmann inversion of this population ratio indicates the free energy difference between anti–syn and anti–anti monomers in gas phase to be about 0.9 kcal mol^{-1} at 210 K, compared to the value of 1.1 kcal mol^{-1} obtained using CBS-QB3 level of theory. These estimates are not inconsistent with the internal energy difference of 1.53 kcal mol^{-1} between these species estimated from quantum chemical calculations (see Fig. 1).

It was believed earlier that β-carbonic acid decomposes upon sublimation.[23,41–44] However, very recently, the vapour phase of β-carbonic acid at 230–260 K was collected in argon matrix without decomposition by Loerting and coworkers.[40] Temperatures higher than that required to sublime the α-form were found to be necessary due to the lower sublimation rates and lower vapour pressure of β-carbonic acid. Unlike the case of the α-polymorph, the anti–anti hydrogen bonded dimer was not observed in the gas phase of β-CA.[40] The absence of the dimer in gas phase is likely due to the higher sublimation temperature employed which entropically disfavours dimers over monomers. Thus, the few anti–anti CA dimers observed over α-CA at 210 K must have been formed in gas phase through double hydrogen bonding of monomers. The ratio of populations of anti–anti to anti–syn conformers in the vapour phase of β-CA was estimated to be between 5 to 10.[40] Upon UV irradiation, the number of anti–syn conformers increased at the cost of anti–anti conformers. The change in conformational state potentially occurs by a rotation of one of the bonds (H–O–C=O) instead of proton tunnelling as the latter is facile only in the presence of water. This needs to be verified. Remarkably and similar to the case of α-carbonic acid, monomers of CA present in the vapour recrystallize to β-carbonic acid, on recondensation.

5.2 Stability

Wight and Boldyrev suggested a pathway for the conversion of H_2CO_3 to CO_2 and H_2O by internal dihedral rotation followed by an intramolecular proton transfer in gas phase.[45] Later, to investigate how water molecules affect the stability of carbonic acid, Liedl et al. performed ab initio calculations of a molecule of H_2CO_3 interacting with either one, two or three water molecules.[20,21] The reaction pathway leading to the formation of carbon dioxide was explored. Under dry conditions, the equilibrium favors the dissociated (product) state, i.e., CO_2 + H_2O over the carbonic acid molecule (reactant). However, the reaction path involves a high barrier transition state with respect to CA and CO_2–H_2O states respectively.[20] Thus, the CA

molecule, once formed, can be kinetically stable for millions of years. However, the scenario changes in the presence of water.

Liedl and coworkers found the barrier for the dissociation of the CA molecule to decrease systematically with an increase in the number of water molecules interacting with it.[20] This observation is consistent with the rapid dissociation of CA in aqueous solution. Further, the energy of the anti–anti CA dimer was nearly the same as or even lower than its dissociated molecular components, viz. two molecules each of carbon dioxide and water.

Nguyen et al. carried out a complete gas phase and implicit solvation study of neutral hydration of CO_2 with different numbers of water molecules. They examined the role of water on the transition state for the dissociation of carbonic acid.[7] Their results on the energetics, geometries of transition, reactant and product states with increasing number of water molecules from zero to three are depicted in Fig. 5. Water plays a catalytic role and is directly involved in the transition state by forming cyclic structures with CA. Each transition state involves proton transfers from water oxygen to the oxygen of CO_2 as shown in Fig. 5. Also, three water molecules were found to be sufficient to achieve the experimental rate constants observed in the bulk solution.[7,46]

6 Aqueous solution

6.1 Structure around CA

Molecular dynamics simulations over an electronic energy surface described by Kohn–Sham density functional theory is an important tool in understanding the intermolecular structure of aqueous carbonic acid solutions.[28,29] Herein, we present new results from such a study. We have carried out Born–Oppenheimer molecular dynamics simulations of one molecule of CA present in either the anti–anti or anti–syn conformation solvated in a bath of water (63 water molecules) at ambient conditions. The simulations using the BLYP functional augmented with empirical van der Waals corrections were carried out through the CP2K code.[47–49] Trajectories were generated for 40 ps out of which the last 30 ps was used for analyses. Water is found to interact strongly with the hydroxyl group of CA rather than the carbonyl group (Fig. 6) in agreement with the results of Kumar et al.[50] The pair correlation function between the hydrogen of CA and oxygen of water is identical in the first coordination shell for both anti–anti and anti–syn conformers. However, the second coordination shell around the anti–syn conformer is relatively more structured. The g(r) between carbonyl oxygen and water hydrogen (Fig. 6a) exhibits significant difference for the two conformers of CA. The anti–syn conformer is a better acceptor of hydrogen bond than the anti–anti one. The number of water molecules around the anti–syn conformer too is marginally higher than that around the anti–anti one. Thus, the additional stabilization from the solvent could reduce the (free) energy difference between these two conformers, relative to that in gas phase.

6.2 Reaction equilibrium

In water, carbonic acid is in equilibrium with dissolved CO_2 and bicarbonate and this reaction is represented as

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \quad (1)$$
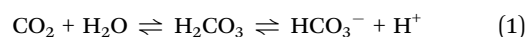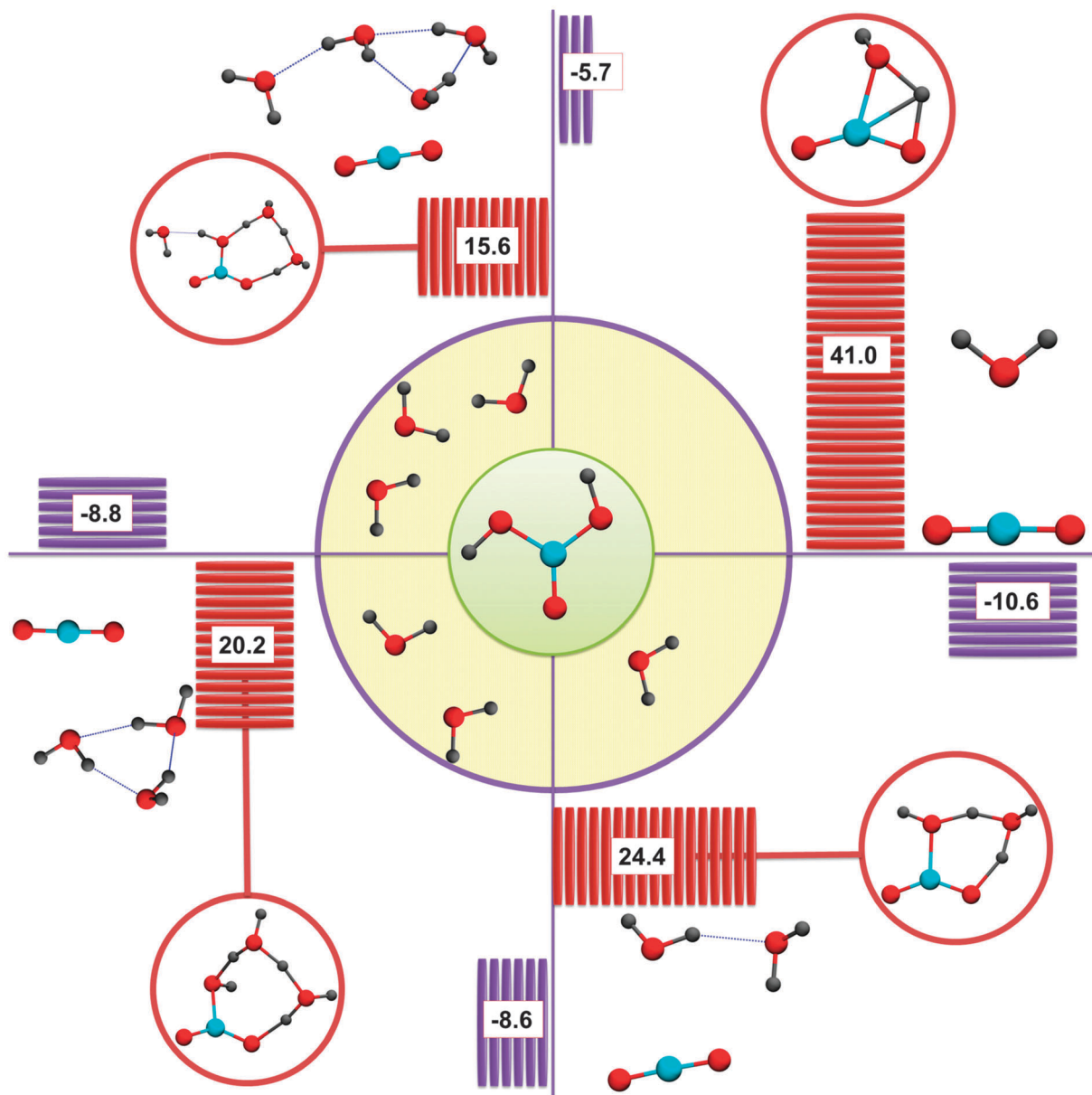
Fig. 5 Schematic representation of results from quantum chemical calculations performed by Nguyen *et al.* for carbonic acid reacting with either zero, one, two or three water molecules.[7] Red and blue pillars denote transition and product states and their respective energies. The energy values (in kcal mol⁻¹) are relative to the corresponding carbonic acid and water system (reactant state). For carbonic acid reacting with three water molecules, the experimental value of activation energy determined for the bulk solution[35] is used.

Since the concentration of H_2CO_3 is much less than that of dissolved CO_2, the overall reaction is assumed to be a single step *i.e.*, by skipping the intermediate step of the formation of carbonic acid. Thus, the dissociation constant, called as an apparent dissociation constant (K_1), for this reaction is defined as

$$K_1 = \frac{[H^+][HCO_3^-]}{[CO_2] + [H_2CO_3]} \quad (2)$$

Here, the reactants are CO_2 and trace amounts of H_2CO_3. But, the true dissociation constant (K_a) of H_2CO_3 is independent of

the CO_2 hydration reaction (1) and is defined as,

$$K_a = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \quad (3)$$

Dividing (3) by (2) gives,

$$K_a = K_1 \left[1 + \frac{[CO_2]}{[H_2CO_3]} \right] \quad (4)$$

Eqn (4) gives the relation between the true and apparent dissociation constants. The direct measurement of $[CO_2]/[H_2CO_3]$ is difficult due to the low concentration of the latter. Thus, the value of K_a needs to be obtained indirectly from the
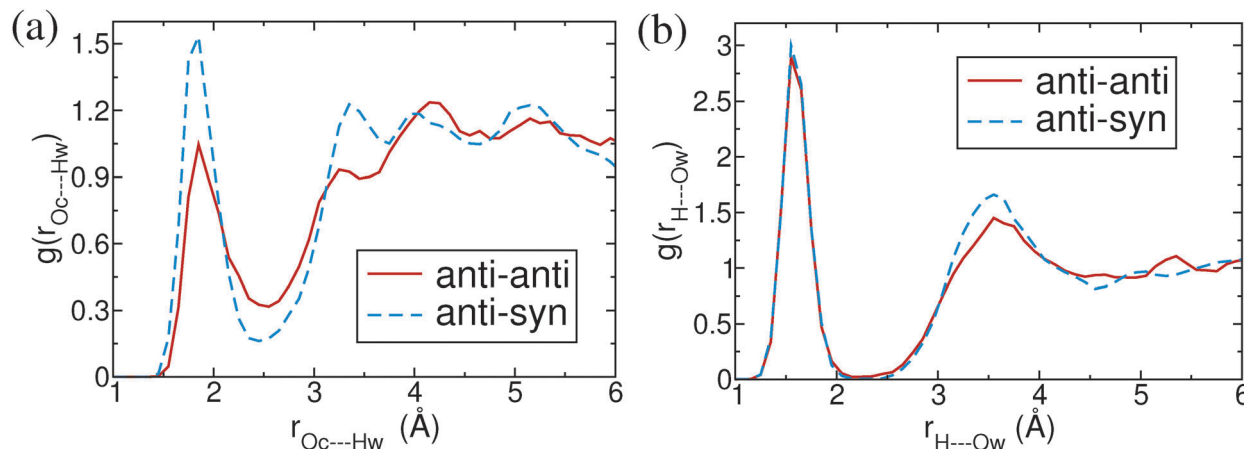
Fig. 6 Intermolecular structure in a system of carbonic acid dissolved in liquid water at ambient conditions. Pair correlation functions between (a) carbonyl oxygen of CA and water hydrogen and (b) hydroxyl hydrogen of CA and water oxygen. Legends display the conformation of the CA molecule.

ratio of rate constants of deprotonation and protonation of H_2CO_3, using methods such as carbamino quenching, rapid flow and manometric methods, isotopic exchange, and the stopped flow method. Incidentally, none of them could determine the rate constants accurately due to the very short life time of CA in water.[51] Further, since the concentration ratio of CO_2 to H_2CO_3 in eqn (4) is equal to the ratio of the rate constants for the first reversible reaction in eqn (1), rate measurements of these reactions too can be used to provide an estimate of K_a. However, K_a values obtained with the above methods do not agree well with each other and a range of values between 3.35–3.80 have been reported.[51] Taking into account the concentration of dissolved CO_2 and CA (the precise determination of which posed difficulties), eqn (4) leads to an estimate of pK_a to be around 4 or so. What is the pK_a of CA?

6.3 pK_a

Carbonic acid in aqueous solution was first detected by measuring the Raman spectrum of a $NaHCO_3$ sample rapidly acidified by HCl in a continuous flow apparatus.[52] The experiment utilized the fact that the dehydration of carbonic acid is a slower process than the protonation (rather, deuteration, see later) of bicarbonate. To determine the acid dissociation constant of carbonic acid, Nibbering and coworkers used ultrafast spectroscopy through the real-time deuteration of DCO_3^- to form carbonic acid.[53] They used a photo acid to deuterate DCO_3^- in deuterated aqueous solution. The formation of carbonic acid was detected by monitoring the infrared active $C{=}O$ stretching mode using time-resolved infrared spectroscopy. The advantage of focussing on this mode alone is that it can be used to identify all the three different species: carbonic acid, bicarbonate and carbonate. They report the rate for the deuteron transfer from the photo acid to bicarbonate to be 1.7×10^{11} s^{-1} and calculate the pK_a of H_2CO_3 to be 3.45 ± 0.15. It is thus conclusively established that carbonic acid is more acidic than what was once thought[51] and its acidity is comparable to that of formic acid.[54]

Further, CA was estimated to have a lifetime of 300 ns in water before it releases deuterium.[53] This short lifetime had effectively prohibited its detection in aqueous phase for a long time. Theoretical calculations have shown that the difference in pK_a between the *anti–anti* and *anti–syn* conformers is small and lies within the range of experimental error.[55,56]

The corrected pK_a value of carbonic acid can now be used to estimate the concentrations of different carbonate species present in aqueous solution. For evaluating these, one must consider the equilibria between CO_2 and the other three carbonates species (H_2CO_3, HCO_3^- and CO_3^{2-}). At ambient conditions, the concentration of CO_2 in aqueous solution ($CO_2(aq)$) is obtained from Henry's law which can be written as,

$$[CO_2(aq)] = K_{CO_2}P_{CO_2}(gas) \qquad (5)$$

where K_{CO_2} is equal to 3.38×10^{-2} (mol L^{-1}) atm^{-1} and P_{CO_2} is the partial pressure of CO_2 gas in the atmosphere.[57] The overall equilibrium between CO_2 and the carbonate species present in aqueous solution can be written as,

$$CO_2(aq) \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \rightleftharpoons CO_3^{2-} + H^+ \qquad (6)$$
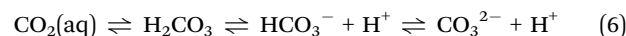
The equilibrium constants[51,53] governing the equilibrium between the species can be used to calculate the concentration of H_2CO_3, HCO_3^- and CO_3^{2-} in water. The concentrations thus calculated are displayed in Fig. 7 along with the corresponding free energies. At ambient conditions, the concentration of hydrated CO_2 is higher than those of other species. The concentration of carbonic acid is about three orders of magnitude less than that of CO_2 and comparable to that of the bicarbonate ion. The concentration of CO_3^{2-} species is negligible.

By employing free energy sampling methods in combination with *ab initio* MD simulations, Liu *et al.*[58] have calculated the pK_a for each hydrogen to be 3.11 in the *anti–anti* conformer and 2.60 and 3.75 in the *anti–syn* conformer, in agreement with value obtained for deuterated carbonic acid using femtosecond infrared spectroscopy.[53]

In a pioneering work, Eigen *et al.* had first proposed the reaction scheme between aqueous solutions of CO_2, H_2CO_3 and
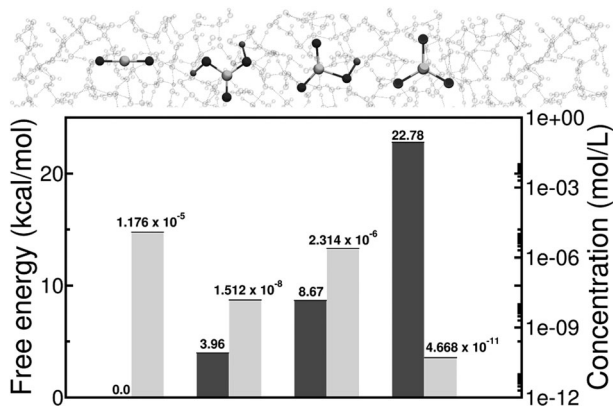
Fig. 7 Free energy difference (black) and concentration (grey) of CO_2, H_2CO_3, HCO_3^- and CO_3^{2-} species in aqueous solution at 298 K. Energies are with respect to dissolved CO_2. Values are calculated assuming the hydration of CO_2 to be first order.

HCO_3^-.[59] Later, through molecular dynamics simulations, Stirling and Pápai have demonstrated that in aqueous solution, unlike in gas phase, the conversion of CO_2 to H_2CO_3 proceeds *via* two steps: (i) formation of HCO_3^-, followed by (ii) its combination with the proton to form H_2CO_3.[60] The rate-determining step of this reaction is the formation of HCO_3^-. Using the metadynamics technique,[61] they calculated the free energy barrier for CO_2 hydration to HCO_3^- or CA to be 18.8 kcal mol^{-1}, close to the experimental value of 21.8 kcal mol^{-1}. Similar calculations have been carried out by Galib and Hanna,[62] whose focus was on determining the dissociation mechanism of H_2CO_3 to HCO_3^- and CO_2. In gas phase, the *anti–anti* and *syn–syn* conformers of CA transform to the *anti–syn* conformer through a dihedral angle change, prior to decomposition. However, in liquid water, it is facilitated by proton transfer from CA to a water molecule and an abstraction of a proton from water (possibly another water molecule) to CA, through water chains. In fact, conformational change in the solution would require dislodging water molecules and hence will involve a larger barrier than in gas phase. Further, the dissociation in aqueous phase is shown to proceed *via* the formation of a bicarbonate species.

6.4 High temperature

High-temperature water (HTW), defined as a water in the temperature range 423–623 K is regarded as a good solvent for carrying out acid-catalyzed organic chemical reactions that can proceed without the addition of a catalyst. Its characteristics such as low dielectric constant, increased acidity and high isothermal compressibility are conducive for the dissolution of many small organic molecules. Since the ionic product of water increases thousand-fold on increasing the temperature from 300 K to 573 K,[63] acid-catalyzed reactions can be carried out in HTW relatively more easily than in room temperature water. Pressurized CO_2 pumped into HTW has been shown to further increase the reaction rates of acid-catalyzed reactions.[64] Herein, a fraction of CO_2 molecules combine with water to form carbonic

acid, which in turn dissociates into bicarbonate ions and protons. The reduction in the pH of CO_2-enriched HTW increases reaction rates and product yield. This methodology bears an advantage over the addition of an acid catalyst in that it does not require a neutralization step; after the completion of the reaction, the CO_2 can be pumped off easily by depressurization. By using this procedure, Hunter and Savage reported the increase of reaction rates and product yield of the dehydration of cyclohexanol and the alkylation of *p*-cresol with *tert*-butyl alcohol.[64] Instead of using any additive catalyst or sulfuric acid, sorbitol has been converted to isosorbide and anhydrosorbitol by using HTW and pressurized CO_2 as a solvent.[65] The conditions employed are 523–573 K and around 10 MPa. Although the maximum yield obtained in this procedure is less compared to that in sulfuric acid, it has several advantages such as avoiding the usage of catalysts, increased reaction rates, avoiding additives for neutralization, easy separation and purification.[65] Despite these many advantages and growth in the use of carbonated high temperature water as a reaction medium, much work remains to be done to understand the equilibrium between carbonate, bicarbonate, carbonic acid, protons and hydroxyl ions in such a solution. The kinetics of species transformation too has not been explored much.

7 Surface adsorbed species

Heterogeneous reactions between dust aerosols formed with minerals such as calcium carbonate and atmospheric gases are important in the troposphere as they can alter the species equilibrium. The calcium carbonate surface, in general, is terminated with one or two layers of water at environmentally relevant conditions. Water, in turn modifies the surface so as to terminate it as $Ca(OH)(CO_3H)$ and OH functional groups. As discussed earlier, since carbonic acid is highly unstable in the presence of water, it was not expected to be present under ambient conditions. Grassian and coworkers have shown that carbonic acid is an important intermediate formed when acidic gases such as nitric acid, sulphur dioxide, formic acid and acetic acid react with calcium carbonate surface.[66] Interestingly, the acidic gas need not possess a proton itself and yet was shown to induce the formation of carbonic acid on the calcium carbonate surface. Since the IR absorption frequency of the C=O bond stretch in CA is different from that in CO_3^{2-} or HCO_3^-, they utilized this band position as a probe to detect its existence among carbonate species using infrared spectroscopy. When the calcite surface is exposed to acidic gas, carbonic acid is formed on the surface possibly by the following reaction,[67]

$$Ca(OH)(CO_3)H + SO_2(g) \rightarrow CaSO_3(s) + H_2CO_3(a) \qquad (7)$$
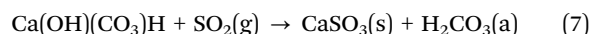
Here SO_2 is taken as an example that forms calcium sulfite and carbonic acid. The CA thus formed is referred to as surface adsorbed carbonic acid. The formation of carbonic acid is confirmed by the appearance of a new feature at 1685 cm^{-1} that correlates well with the value of 1705 cm^{-1} for the C=O stretch frequency found in crystalline CA. They also demonstrated

the adsorbed carbonic acid to be stable for a long time under dry conditions. The adsorbed carbonic acid was stable up to 350 K without decomposition.[67] On heating above this temperature, the peak at 1685 cm^{-1} decreased and simultaneously, a peak appeared at 2342 cm^{-1} which is the characteristic frequency of asymmetric stretching mode of CO_2 gas. Expectedly, when the surface is exposed to water vapour at ambient temperature, carbonic acid was found to dissociate into water and carbon dioxide leaving the surface $Ca(OH)(CO_3H)$ unaffected. Isotopic substitution (with deuterium) confirmed these conclusions.

An alternate mechanism was proposed for the surface reactions with HNO_3 that could also generate carbonic acid as an intermediate.[68] HNO_3 may react with $CaCO_3$ aerosol to form carbonic acid and calcium nitrate which is hygroscopic in nature. Calcium nitrate absorbs water vapour from the atmosphere and facilitates decomposition of carbonic acid into CO_2 and H_2O. Upon this dissociation, the original calcite dust (solid aerosol) is effectively turned into a liquid aerosol which alters the composition and properties of clouds.[68] These studies demonstrate that carbonic acid is stable at ambient conditions at room temperature under dry conditions. Although it decomposes under exposure to water vapour, it can be stable at sub-room temperatures due to favourable enthalpy. To investigate this aspect, Loerting et al. have recently used FTIR spectroscopy to study bulk carbonic acid formation under conditions more relevant to the troposphere.[69] Firstly, $CaCO_3$ dust particles were protonated using HCl at a temperature above 200 K under a humid environment. The formation of carbonic acid was detected by comparing the infrared bands with that of β-carbonic acid. On heating it further to 250 K at 60–100% relative humidity, carbonic acid was found to be surprisingly stable for long periods without decomposition. At 260 K, it started decomposing and disappeared in about an hour. This provides a tantalising possibility for the existence of carbonic acid in the troposphere.

8 Summary and outlook

The importance of carbonic acid in fields ranging from atmospheric, surface and geochemistry cannot be stressed adequately. Despite its compositional and structural simplicity, it is still not considered a "mainstream molecule" and thus has not received attention from researchers commensurate to its role in the acid–base chemistry of carbonated aqueous solutions. In this article, we have attempted to summarize the current understanding of carbonic acid in various conditions and forms – as a molecule in gas phase, in aqueous solutions, in its crystalline state, and as an adsorbate on inorganic surfaces.

The equilibrium constants for the two deprotonation events of CA have been determined experimentally. Under ambient conditions, carbonic acid is estimated to have a lifetime of about 300 ns in water and several million years in dry environment.[53] The barrier for deprotonation decreases drastically upon the addition of few water molecules to CA.[7] The stability of CA under dry conditions is kinetic; the equilibrium of course, favors CO_2 + H_2O rather than a CA molecule. Recent ultrafast

infrared spectroscopic measurements[53] have yielded the true acid dissociation constant (pK_a) of carbonic acid to be 3.45, a value which has been confirmed by computer simulations.[58,60,62] Its determination should dispel notions of carbonic acid being rather weak; the acidity of CA is comparable to that of formic acid.

Quantum chemical calculations carried out in gas phase, and density functional theory based molecular dynamics simulations carried out on aqueous solutions have provided a microscopic picture of the molecular processes involved in the dissociation of CA in water. They have been remarkably in close agreement with experiments on equilibrium and rate constants. In particular, they have shown that CA is formed through a stepwise mechanism with bicarbonate as an intermediate.[60]

In the gas phase, the anti–anti monomer is the predominant species as determined using matrix isolation techniques, while the anti–syn monomer and a dimer of carbonic acid are the other two species identified.[12,37,38] These recent studies mark the first detection of the carbonic acid molecule in gas phase. Interestingly, the centrosymmetric anti–anti dimer of CA is observed only in the vapour above the α polymorph at 210 K while it is absent in that above the β polymorph at 250 K.[40] This is counterintuitive as the latter crystal has been demonstrated to be composed of centrosymmetric units, based upon the mutual exclusion of IR and Raman active modes. Thus, although the vapour just sublimed from the solid may be composed of monomers, such molecules could hydrogen bond at 210 K to form dimers (10% of the gas at 210 K observed to be dimeric) and not at 250 K due to entropic factors.

Interesting possibilities for the formation and adsorption of carbonic acid on the surface of calcium carbonate particles, under cold laboratory conditions have emerged over the past decade.[66,69] Dust aerosols in the troposphere constituted with mineral particles can react with acidic gases to generate carbonic acid molecules as surface species.

Crystalline carbonic acid, in contrast, has been studied more extensively. The synthesis of thin films of two polymorphs of carbonic acid under equilibrium conditions have been pioneered by the group at Innsbruck.[18] In particular, one of the polymorphs, β, has been shown to possess a centre of inversion symmetry due to mutual exclusion of IR and Raman active modes. Various computer modelling efforts have been carried out to come up with possible crystal structures, particularly for β-carbonic acid.[19,30,45,70] Using a range of computational techniques, our work points to two crystalline models with one-dimensional hydrogen bonded chain based structures to be highly stable with mass density around 1.49 to 1.67 g cc^{-1}. The structures not only reproduce the experimentally observed infrared and Raman spectra of β-carbonic acid but also are consistent with experimentally determined sublimation temperatures.

The presence of carbonic acid in various astrophysical environments is envisioned based on (i) favourable conditions for its formation and (ii) a comparison of infrared spectra measured in the laboratory with those collected in such conditions. On Mars, both solid and gaseous carbonic acid have been

expected to be observed.[38,40,71] Until now, no direct evidence has been presented for the presence of carbonic acid in outer space using any spectroscopic technique.[71] A crucial component in the detection of CA would be high resolution infrared spectroscopy. Huber *et al.*[71] have recently carried out DFT calculations of the monomer and dimer of CA to determine its vibrational signatures, including anharmonic effects. They have offered interesting possibilities in the spectroscopic identification of CA in extraterrestrial environments.

This field of research is poised for many new observations. The precise determination of the crystal structures would be facilitated by the synthesis of single crystals or by higher quality powder diffraction, supported by structure refinement and modelling. Further, FTIR measurements in the far-infrared region can also aid in the discrimination of model structures for β-CA. The development of an accurate, transferable force field for carbonic acid can spur efforts to model its aqueous solution as well as its amorphous solid form. The barrier for intramolecular proton transfer in gas phase needs to be determined as it can provide an additional pathway for the conformational change of the CA molecule. The populations of CA conformers and oligomers in gas phase as a function of temperature can also be a subject of theory and computer modelling. This will aid in furthering the understanding of the compositional differences in the vapour sublimed from the two polymorphs. Despite its importance in environmentally benign industrial practices, the properties of carbonated aqueous solutions have not been understood. The increase in rates of acid catalyzed reactions in such an environment points to increased acidity of the medium. Molecular modelling needs to be employed to estimate the acidity of the solution and the characterization of the species present under such extreme conditions.

Are there energy efficient routes to sequester carbon dioxide as crystalline carbonic acid? Can carbonic acid be stabilized in solvents other than water? These and many other questions require large scale, sustained efforts. It is hoped that this feature article will motivate more researchers to participate in these directions.

Acknowledgements

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