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Matrix isolation studies of carbonic acid – the vapour phase above the β -polymorph

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Abstract

Twenty years ago two different polymorphs of carbonic acid, α - and β -H₂CO₃, were isolated as thin, crystalline films. They were characterized by infrared and, lately, by Raman spectroscopy. Determination of the crystal structure of these two polymorphs, using cryo-powder and thin film X-ray diffraction techniques, has failed so far. Recently, we succeeded in sublimating α -H₂CO₃ and trapping the vapour phase in a noble gas matrix, which was analyzed by infrared spectroscopy. In the same way we have now investigated the β -polymorph. Unlike α -H₂CO₃, β -H₂CO₃ was regarded to decompose upon sublimation. Still, we have succeeded in isolation of undecomposed carbonic acid in the matrix and recondensation after removal of the matrix here. This possibility of sublimation and recondensation cycles of β -H₂CO₃ adds a new aspect to the chemistry of carbonic acid in astrophysical environments, especially because there is a direct way of β -H₂CO₃ formation in space, but none for α -H₂CO₃. Assignments of the FTIR spectra of the isolated molecules unambiguously reveal two different carbonic acid monomer conformers (C_{2v} and C_s). By contrast to the earlier study on α -H₂CO₃ we do not find evidence for centrosymmetric (C_{2h}) carbonic acid dimers here. This suggests that two monomers are entropically favoured at the sublimation temperature of 250 K for β -H₂CO₃, whereas they are not at the sublimation temperature of 210 K for α -H₂CO₃.

Introduction

Carbonic acid, H_2CO_3 , plays an important role in many fields¹ of chemistry and physics including astrophysics²⁻⁶, biological and geochemical carbonate containing systems. This six-atom molecule commonly found in carbonated drinks at submicromolar concentration has so far eluded most attempts of isolation in its pure form and direct detection. This is mainly because it easily decomposes to carbon dioxide and water at ambient conditions, and even more so in the presence of water⁷. In aqueous solution detection of its formation and/or decomposition is only feasible by use of fast⁸ or ultrafast spectroscopic techniques⁹. However, at the temperature of many extraterrestrial environments, its decomposition is hindered. Formation of two distinct solid carbonic acid polymorphs, α and β , was achieved in laboratory experiments by acid-base chemistry at cryo-temperatures¹⁰. $\beta\text{-H}_2\text{CO}_3$ is also formed under conditions akin to those encountered in space. For example, it is formed from 1:1 mixtures of solid carbon dioxide CO_2 and water H_2O ice by proton-irradiation^{2,3,11}, electron irradiation¹² or UV-photolysis^{11,13}. In the absence of water it may form from solid carbon dioxide CO_2 ice by H-implantation^{3,14} or from carbon monoxide CO by reaction with hydroxyl radicals $\text{OH}\cdot$ ¹⁵. It has thus been suggested that β -carbonic acid may be found on the Martian surface, on interstellar grains, on comets, especially in the Oort cloud, or on Jupiter's icy satellites Europa, Ganymede and Callisto^{4,16-19}.

The crystal structures of both carbonic acid polymorphs still remain unsolved. Powder X-ray diffraction cryo-techniques were recently employed by us to observe two amorphous forms of carbonic acid, which then crystallize to the two polymorphs²⁰. So far our attempts of indexing and refining the Bragg reflections after crystallization were unsuccessful, though. For this reason, FTIR and Raman studies of the solid polymorphs remain to date the only available data providing clues about symmetry and short-range order. The mutual exclusion of Raman and IR bands in the case of $\beta\text{-H}_2\text{CO}_3$ suggests a centrosymmetric building block, whereas mutual exclusion and a local inversion centre were not found for $\alpha\text{-H}_2\text{CO}_3$ ^{19,20}. Examples for possible building blocks of the two polymorphs are depicted in Figure 1, which can merely be regarded as working hypotheses in lieu of refined crystal structures.

First indications for the possible existence of carbonic acid in the gas phase were provided by mass-spectrometric observation of the vapour phase produced after ammonium bicarbonate NH_4HCO_3 thermolysis²¹. Later, two carbonic acid H_2CO_3 conformers with symmetry C_{2v} (denoted cis-cis, see Figure 1) and C_s (denoted cis-trans) were produced by using a pulsed supersonic jet discharge nozzle and studied using microwave spectroscopy^{22,23}. We have

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3 studied the vapour phase above α -H₂CO₃ by slowly sublimating the crystalline thin film at
4 210 K *in vacuo*. Thrillingly, the vapour phase above α -H₂CO₃ can be recondensed as α -
5 H₂CO₃ on cold substrates at different location ¹⁷, which demonstrates that carbonic acid
6 sublimates at least partly without decomposition to carbon dioxide and water. Previously, we
7 succeeded in isolating the vapour phase above α -H₂CO₃ in a range of noble gas matrices and
8 analysed these matrices by infrared spectroscopy ²⁴. We have interpreted these infrared
9 spectra in terms of the presence of the C_{2v} and C_s monomers at a ratio of 10:1, a small fraction
10 of centrosymmetric (C_{2h}) carbonic acid dimers and some carbon dioxide and water mono- and
11 oligomers. After removal of the matrix the isolated gas-phase molecules rebuild a hydrogen
12 bonded network and condense to a crystalline polymorph. Interestingly, it is again the α -
13 polymorph that is observed after sublimation of the α -polymorph, matrix isolation and
14 removal of the matrix.
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24 In the present paper we show the isolation of the β -polymorph in a solid rare gas matrix. The
25 vapour phase above the β -polymorph is harder to isolate because the vapour pressure and
26 sublimation rate of this polymorph are even lower than for the α -polymorph, and so higher
27 sublimation temperatures are required ¹⁷. Calculation of the vapour pressure for α -H₂CO₃ at
28 200 K by Hage et al. shows the saturation vapour pressure (p_s) of $4 \cdot 10^{-7}$ mbar for the H₂CO₃
29 monomer and $3 \cdot 10^{-7}$ mbar for the dimer in the gas phase. ¹⁷ Peeters et al. measure the vapour
30 pressure of β -H₂CO₃ of about $(0.29-2.33) \cdot 10^{-9}$ mbar at 240–255 K ⁶.
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37 Experiment

38 Matrix isolation spectroscopy is a technique aimed to obtaining pure vibrational spectra at low
39 temperatures isolating non-rotating single molecules by trapping them in a solid matrix of,
40 e.g., neon, argon, or krypton, which are optically transparent in the mid infrared and are
41 chemically inert. Our matrix isolation study was done in the ultrahigh-vacuum chamber in
42 Vienna (see Supp.-Fig. 1 in ref. 24), which was previously employed for successfully
43 isolating reactive species such as halogen oxides ²⁵ or the sublimation product of the α -
44 polymorph of H₂CO₃ ²⁴. The preparation of the starting material (β -H₂CO₃) was done in
45 Innsbruck as described in refs. 5,10,26 by layer-by-layer spray-deposition of glassy aqueous
46 solutions of acid (2 M HBr) and base (1M KHCO₃) on optical windows kept at 80 K.
47 Subsequently this acid-base “sandwich” is heated slowly to 180 K in order to trigger
48 translational diffusion and acid-base chemistry. Finally, ice is removed in the high-vacuum
49 chamber by heating to 210 K, which results in the formation of first an amorphous thin film of
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3 carbonic acid, which finally crystallizes to β -H₂CO₃. The preparation process of the thin film
4 of carbonic acid is monitored *in situ* by FTIR spectra recorded on the Varian Excalibur
5 spectrometer in Innsbruck. Figure 2a shows the typical FTIR spectrum (recorded at 80 K) of a
6 thin film of crystalline β -H₂CO₃ prepared using this procedure on a Si window. The vertical
7 lines indicate the position of the absorption bands of crystalline β -H₂CO₃²⁶. These thin films
8 on the optical windows were then stored in liquid nitrogen and transferred to the matrix
9 isolation chamber in Vienna. In this chamber the ice that has condensed during the transfer of
10 the window at 77 K from ambient air was first removed and then the thin film was
11 sublimated. The vapour above the thin film was then mixed with noble gas (Argon or
12 Krypton) and recondensed on a cold mirror as a solid mixture of sublimation products and
13 noble gas, typically at a ratio of 1:1000. The details of the matrix isolation procedure can be
14 found in ref. 24. FTIR spectra of the matrix were recorded by a Vertex 80v (Bruker Optic
15 GmbH, Karlsruhe, Germany) equipped with a liquid N₂ cooled narrow band MCT detector
16 applying a spectral resolution of 0.5 cm⁻¹, adding 512 scans, and using a Ge-coated KBr
17 beamsplitter. The optical path of the spectrometer was evacuated down to 2 mbar, which
18 minimizes interferences from CO₂ and H₂O absorptions of the ambient atmosphere. Such a
19 sensitive set-up is particularly important when measuring a substance like carbonic acid,
20 which is a very weak absorber in especially these spectral regions.
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34 *Ab-initio* quantum mechanical calculations of carbonic acid in various isotope configurations
35 were performed to obtain reference frequencies for annotating measured spectra. All
36 calculations were performed using the Gaussian 09 package²⁷. Both the C_{2v} and C_s
37 conformations were employed for geometry optimization, where the former is the
38 energetically most favorable conformation^{28,29}. Calculations were performed using second-
39 order Møller-Plesset perturbation theory (MP2) with the augmented correlation consistent
40 basis sets of Dunning and co-workers³⁰⁻³². Initial optimization was done at the MP2/aug-cc-
41 pVDZ level of theory requiring ‘verytight’ convergence on displacement and forces. Starting
42 from the resulting geometry, further optimization at the MP2/aug-cc-pVTZ level of theory
43 using ‘verytight’ convergence criteria yielded an energy minimum for frequency calculations.
44 Subsequently, IR modes were determined at this minimum geometry using MP2/aug-cc-
45 pVTZ. Isotope shifts were calculated by performing frequency calculations at the same
46 minimum for either all ²H or ¹³C-labeled carbonic acid. Calculated frequencies and isotope
47 shifts were then used to identify the various signals observed in the experimentally obtained
48 spectra.
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Results

For β -H₂CO₃ the same procedure of sublimation and trapping in solid matrices (Ar or Kr) was applied as for α -H₂CO₃, with the exception that higher sublimation temperatures are required. The β -polymorph (spectrum shown in Figure 2a) is stable up to at least 230 K. Above this temperature it sublimates slowly in vacuum. So far it was believed to decompose under such conditions. Indeed, we do observe the decomposition products carbon dioxide and water in the spectra (see Figure S1). Besides carbon dioxide and the water monomer also higher water oligomers are found in the matrix. The bands near 3750 cm⁻¹ correlate with the rotation and non-rotation mode of H₂O monomer and dimer^{33,34}, and the bands near 1600 cm⁻¹ with the bending mode of H₂O monomer and dimer^{33,34}. The most intensive bands near 2300 cm⁻¹ and the band around 680 cm⁻¹ appertain to CO₂ (with ¹²C or ¹³C) molecules³⁵.

During the transfer of the Si window from the liquid N₂ to the high vacuum chamber some air moisture condenses on the window, which we tried to remove before the matrix isolation by pumping it off in the vacuum at 210 – 220 K. During the matrix production some ambient water can also be isolated. A differentiation between water molecules stemming from moisture or from the decomposition of H₂CO₃ is shown in the spectrum of matrix isolated D₂CO₃ (Figure S1c). The band system at 2783, 2771, 2746, 2724 and 2678 cm⁻¹ belongs to the absorption bands of the D₂O monomer and polymer^{33,36}. Unambiguously, this band can only result from the decomposition of D₂CO₃. In the spectrum of H₂¹³CO₃ (Figure S1a) the decomposition is clearly evident in the strong ¹³CO₂ bands at 2280, 2275 and 2274 cm⁻¹³⁵. These assignments are unequivocally because the band positions typically agree with literature data to within ± 0.5 cm⁻¹.

However, additional bands that cannot be assigned to carbon dioxide or water are apparent in the spectrum, which we assign to carbonic acid as outlined below. The intensity of the ν (C=O) mode in carbonic acid amounts to about 10% of the intensity of the most intense ν (O-H) mode in the water monomer and to about 5% of asymmetric stretching mode ν_3 in carbon dioxide. Thus, above 230 K a part of β -H₂CO₃ sublimates with decomposition, whereas another part does not decompose.

Figure 3 shows the spectral regions that cannot be explained using CO₂ or H₂O mono- or oligomers, which we assign to H₂CO₃ and its isotopologues after sublimation of crystalline β -H₂CO₃ at 230 – 260 K and isolation in solid argon at 6 K. We assign all these bands to two conformers of the carbonic acid monomer (symmetries C_{2v} and C_s; see Scheme 1 in ref. 24)

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3 based on selective changes of the experimental conditions: a) $^{12}\text{C}/^{13}\text{C}$ and H/D isotope shifts,
4 b) UV radiation of the matrix, and c) change of the matrix material (Ar or Kr). Also
5 theoretical prediction concerning band positions and shifts between the symmetry of the
6 isotopologues support our interpretation.
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10 Our band assignment is exemplarily explained here on the CO-stretching region at 1850 –
11 1700 cm^{-1} , which contains two doublets (see Figure 3b). They appear as doublets because of a
12 splitting induced by different Ar matrix cages. By contrast, in Kr matrix two single bands
13 appear at similar position (see Figure S2). This immediately suggests the presence of two
14 distinct gas-phase carbonic acid species. These doublets are red-shifted by 5–11 cm^{-1} for
15 $\text{D}_2\text{CO}_3/\text{Ar}$ (Figure 3c), and by 42 cm^{-1} for $\text{H}_2^{13}\text{CO}_3/\text{Ar}$. These isotope shifts are in excellent
16 agreement with the theoretical prediction of isotope shifts for $\nu_s(\text{C}=\text{O})$ of the H_2CO_3
17 monomers (see Table 1). The assignment of the two carbonic acid species is immediately
18 evident when looking at the calculated separation of the $\nu_s(\text{C}=\text{O})$ between the cis-cis
19 monomer of C_{2v} symmetry and the cis-trans monomer of C_s symmetry. This amounts to 46
20 cm^{-1} at the MP2/aug-cc-pVTZ level of theory (1880 vs. 1834 cm^{-1} , see values in parentheses
21 in Table 1) employed here and is almost the same also at other levels of theory³⁷⁻³⁹. In the
22 matrix spectrum the two bands are separated by 41 cm^{-1} (1828 vs. 1787 cm^{-1} , see Table 1),
23 which is an excellent match and allows an unambiguous assignment of the bands.
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34 Upon UV irradiation of the $\text{H}_2\text{CO}_3/\text{Ar}$ matrix one of the two doublets increases with time at
35 the cost of the other doublet (see difference spectra in Figure S3). According to the
36 assignment this implies that the C_s isomer grows at the expense of the C_{2v} isomer. That is, the
37 isomer that is calculated to be slightly energetically disfavoured is formed from the favoured
38 one upon UV irradiation. Most likely this shift of the equilibrium takes place by a rotation of
39 one H-atom around the C-O bond from the trans-position to the cis-position. The ratio of the
40 intensities of C_{2v} and C_s bands before UV irradiation varies between 5:1 (Figure 3a) and 10:1
41 (Figure 3c), which is in accordance with the theoretical predictions of the higher stability of
42 the C_{2v} monomer. The presence of the two weak internal hydrogen bonds in the C_{2v} monomer
43 compared to the single internal hydrogen bond in the C_s monomer results in an increased
44 stability of about 4–8 kJ/mol ^{22,28,29,38-41}. This interpretation of the presence of these two
45 monomers at these ratios can also be deduced from all other spectral ranges shown in Figure 3
46 and is demonstrated in the Supplementary Information.
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56 After having assigned these bands all the bands observed in the whole spectral range are
57 explained. Other possible species such as complexes of water with carbonic acid or carbonic
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3 acid dimers, trimers or higher oligomers are not present or at most as trace components
4 producing bands near the noise level of the spectrum.
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7 In order to hedge our assignments, we have evaporated the solid noble gas matrices at the end
8 of the spectroscopic characterization by carefully heating the matrix and checking for the
9 component remaining on the sample holder. The spectrum after sublimation of β -H₂CO₃,
10 matrix isolation of gas-phase carbonic acid in argon at 6 K and removal of the argon matrix
11 by heating to 220 K is shown in Figure 2b. This spectrum is highly similar to the spectrum of
12 β -H₂CO₃ before sublimation, albeit with intensities that are about a factor of 1000 lower. That
13 is, the isolated carbonic acid monomers start to hydrogen-bond upon removal of the argon and
14 finally produce crystalline β -H₂CO₃. For comparison, after isolation of the gas-phase above α -
15 H₂CO₃ in argon and removal of argon, α -H₂CO₃ is finally observed²⁴.
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24 **Conclusions and Implications for Carbonic Acid Detection**

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26 In the past we were successful in the isolation of the α -polymorph of carbonic acid (α -H₂CO₃)
27 in a solid matrix²⁴. Now we show the isolation of the β -polymorph (β -H₂CO₃) in a solid noble
28 gas matrix and present our band assignment. The β -polymorph has a lower vapour pressure
29 and lower sublimation rates than the α -polymorph at the same temperature. In order to reach a
30 significant vapour pressure above the β -polymorph it is necessary to sublime the β -polymorph
31 at 230 – 260 K, as compared to 210 K for the α -polymorph. Similar to our former experiment,
32 we also find the C_{2v} monomer to be the dominating species in the gas-phase. The ratio
33 between C_{2v} and C_s of the β -polymorph at 230 – 260 K is similar to that of the α -polymorph at
34 210K²⁴ and to the calculations of Schwerdtfeger et al. 2011⁴². Both polymorphs show the C_s
35 monomer as the minor species, which occurs at a ratio of about 1:5 – 1:10. By contrast to our
36 earlier matrix isolation study we now do not find evidence for the presence of a
37 centrosymmetric dimer. We attribute this difference to the higher sublimation temperature,
38 which favours two monomers over the dimer because of the entropy term. That is, the results
39 suggest that the enthalpy gain incurred because of hydrogen bond formation in the dimer is
40 sufficient for the observation of the dimer at a sublimation temperature of 210 K²⁴, but not at
41 sublimation temperatures of 230–260 K used here. There is furthermore no indication for the
42 presence of a linear oligomer⁴³ to be present in the gas phase. As a consequence of this
43 difference in the composition of the gas-phase also the polymorph that crystallizes upon
44 removal of the matrix is different: α -H₂CO₃ crystallizes from sublimed α -H₂CO₃ and β -H₂CO₃
45 crystallizes from sublimed β -H₂CO₃.
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3 The finding here that not only α -H₂CO₃ can sublime and recondense as α -H₂CO₃, but also β -
4 H₂CO₃ can sublime and recondense as β -H₂CO₃ is novel and of atmospheric and astrophysical
5 relevance, especially because it was previously thought that β -H₂CO₃ decomposes entirely
6 upon sublimation^{2,6,11,12,14-16}.
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10 In our atmosphere some solid-state carbonic acid may be present in cirrus clouds or on
11 mineral dust. This possibility was conjectured 15 years ago¹⁷, but only very recently it could
12 be shown that indeed β -H₂CO₃ may form as a bulk species on mineral dust in the presence of
13 acids and remain stable in the troposphere even in the presence of high relative humidities up
14 to 260 K⁴⁴. Huber et al.³⁹ have emphasized that the sublimation temperature of α -H₂CO₃ of
15 210 K^{17,24} is too low for a possible existence of gas-phase carbonic acid in Earth's
16 atmosphere. This is because such low temperatures are only found in the stratosphere, where
17 cirrus clouds can not be observed. However, the sublimation temperature of β -H₂CO₃ of up to
18 260 K reported in this work is of relevance in the troposphere, where β -H₂CO₃ is presumed to
19 exist and may sublime and recondense without decomposition. That is, some gas-phase
20 carbonic acid may indeed be present in the troposphere, albeit at very low mixing ratios: the
21 vapour pressure of β -H₂CO₃ at 260 K is on the order of 10⁻⁸–10⁻⁹ mbar, and the atmospheric
22 pressure is about 200–400 mbar at the relevant altitudes of 5–10 km. These low mixing ratios
23 will make it very challenging to detect gas-phase carbonic acid in Earth's troposphere.
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34 Our findings presented here increase the chance for detection of gas-phase carbonic acid in
35 astrophysical environments. First, direct routes for the formation of β -H₂CO₃ in astrophysical
36 environments are known^{2,3,11,12}, whereas no direct route for the formation of α -H₂CO₃ is
37 known. Typically, β -H₂CO₃ is considered in environments containing both H₂O and CO₂ ices,
38 which are exposed to radiation, e.g., solar photons or cosmic rays. This is the case for the icy
39 satellites of Jupiter and Saturn and also for the polar caps of Mars. The stability of gas-phase
40 carbonic acid up to 260 K presented here might then result in a release and accumulation of
41 carbonic acid in these thin atmospheres. E.g., on the Mars surface it is known that the
42 temperatures may change between 140 K and 300 K, and so carbonic acid may experience
43 sublimation and recondensation cycles and reach a steady-state concentration near the icy
44 caps. However, even with next-generation telescopes the remote detection of carbonic acid in
45 the thin atmospheres of such bodies seems very challenging as explained by Huber et al.³⁹.
46 Because of the high angular resolution required we might need to wait for the European
47 Extremely Large Telescope (E-ELT), which is planned to be operative in the early 2020s³⁹. It
48 might, therefore, be useful to investigate the gas-phase there in the future using microwave
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3 ^{20,21} or infrared absorption spectroscopy, e.g., by the METIS instrument on the E-ELT.
4 Judging from the present and our earlier work ²⁴, the most intense and characteristic bands
5 suitable for detection of the most abundant C_{2v} carbonic acid monomers are the bands at
6 3608±30 cm⁻¹ (2.77 μm), 1780±10 cm⁻¹ (5.62 μm), 1445±10 cm⁻¹ (6.92 μm) and 794±4 cm⁻¹
7 (12.6 μm). A distinction between C_{2v}, C_s monomers and C_{2h} dimers will always be very hard.
8 However, the ν(C=O) band seems most promising for this purpose, because of the best
9 separation (see Figure S4): 1830±5 cm⁻¹ (5.46 μm, C_s), 1780±10 cm⁻¹ (5.62 μm, C_{2v}), and
10 1720±10 cm⁻¹ (5.81 μm, C_{2h}) ²⁴.
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17 In addition to remote detection the possibility of on-site detection might be feasible in the
18 future: for instance a mid-infrared spectrometer on a Mars lander might provide the possibility
19 to locate carbonic acid, both in the solid state on icy soil and also in the atmosphere. In this
20 context, the detection of (bi)carbonate anions in soil excavated near the Martian pole in the
21 Wet Chemistry Laboratory on the Phoenix Mars Lander seems very promising for the future
22 endeavour of carbonic acid detection ^{45,46}. Also lander missions to other bodies, such as the
23 attempt of Philae to land on the comet 67P/Churyumov–Gerasimenko end of 2014 (ESA’s
24 Rosetta mission) or the plan of an ESA spacecraft visiting the icy Jovian moons (“Jupiter Icy
25 Moon Explorer”) hold promise for the detection of carbonic acid.
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32 33 **Associated Content**

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35 Supporting Information: Additional spectra and more detail about band assignment are
36 available free of charge via the Internet at <http://pubs.acs.org>.
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39 40 **Acknowledgement**

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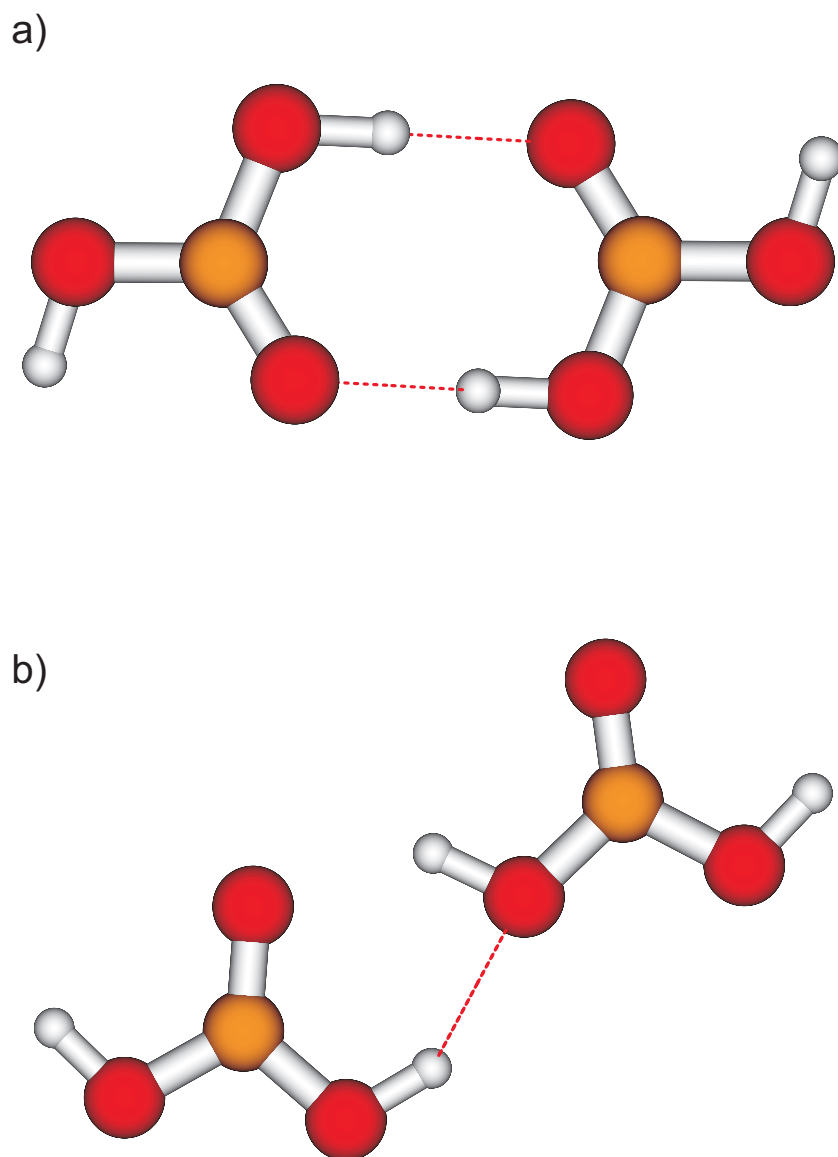


Figure 1: Possible basic building blocks *in the solid state* for a) β -H₂CO₃, which is studied in this work, and b) α -H₂CO₃, which was studied in our previous work²⁴. The local symmetries of these polymorphs were inferred by testing the validity of the mutual exclusion principle from Raman- and IR-spectroscopic data^{17,43}. The monomers are arbitrarily depicted in the cis-cis conformation (C_{2v}). In the crystal-field of each of the two polymorphs also the cis-trans conformation (C_s) could be the more stable one. Counterintuitively, the centrosymmetric dimer can only be detected in *the gas phase* above α -H₂CO₃, but not in the gas phase above β -H₂CO₃. We attribute this to the lower temperature of the gas-phase above α -H₂CO₃ (210 K vs. 250 K), which favours dimerization in the gas-phase.

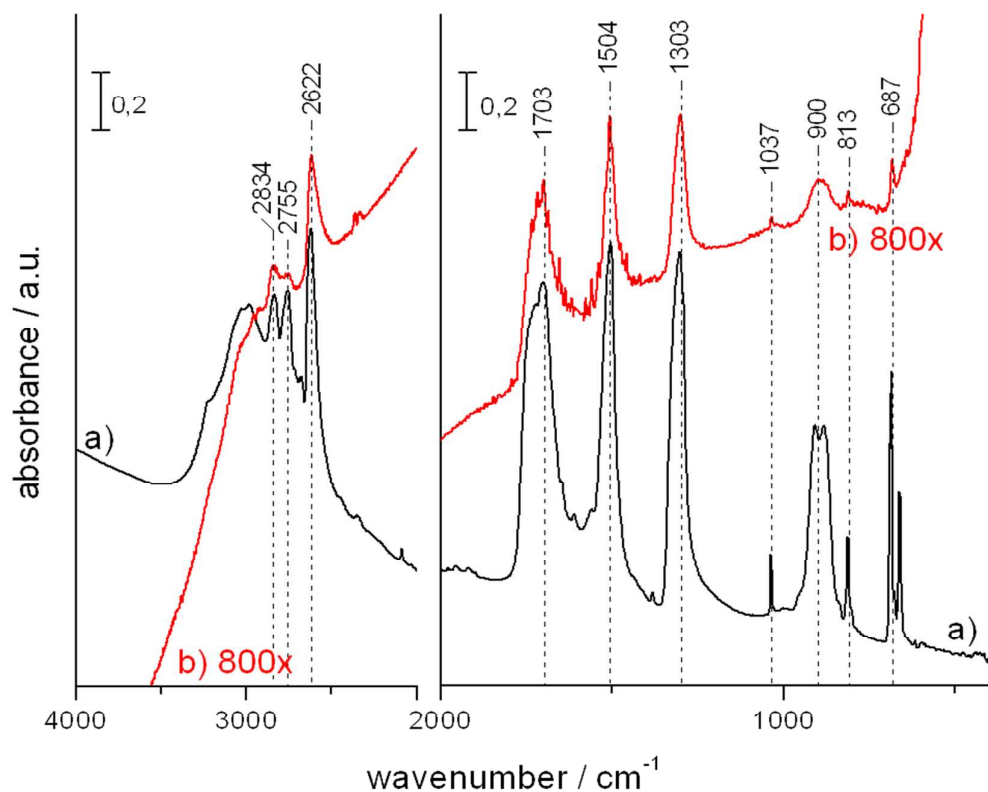


Figure 2 a) IR spectrum of a thin film of crystalline β -H₂CO₃ at 80 K, as prepared by protonation of KHCO₃ with HBr in aqueous solution and removal of the solvent in vacuum at 230 K. b) IR spectrum of crystalline β -H₂CO₃ that reforms after removal of the argon matrix containing trapped carbonic acid molecules. Only a small fraction of carbonic acid reforms, and so the intensity of this spectrum has to be multiplied by 800 to obtain comparable intensities. Spectra are shifted vertically for clarity.

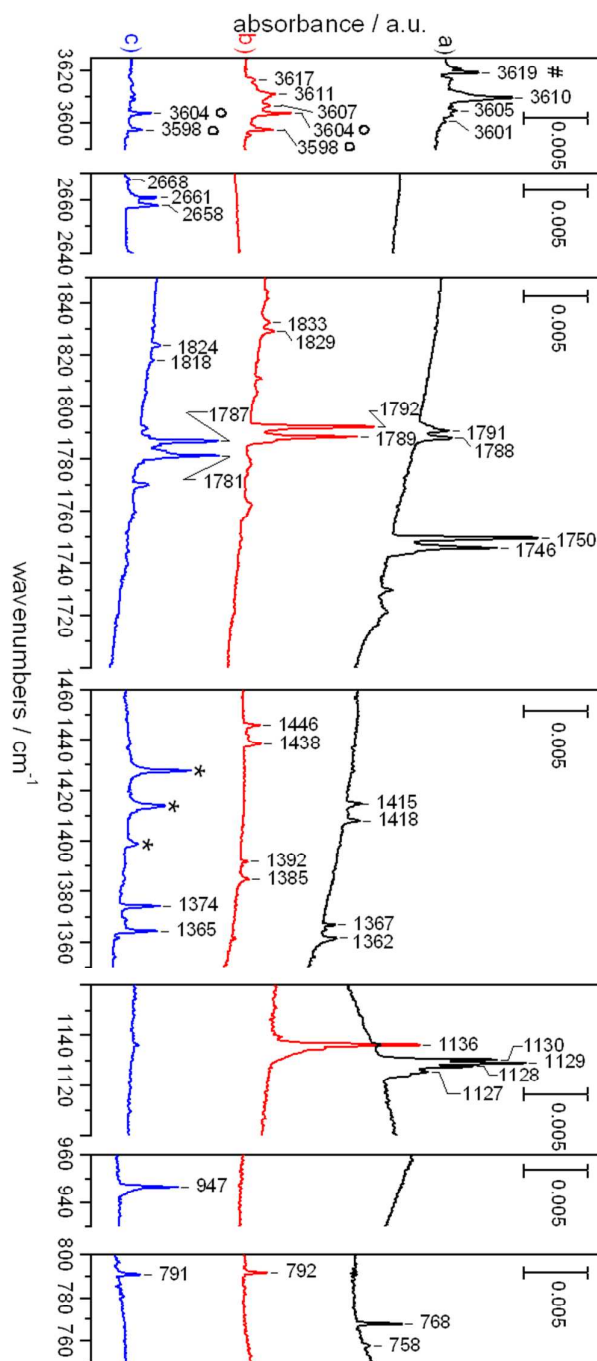


Figure 3 Selected regions of the IR spectra of carbonic acid vapour and isotopologues after sublimation of crystalline β - H_2CO_3 at 230–260 K and isolation in solid argon at 6 K. a) $\text{H}_2^{13}\text{CO}_3$, b) H_2CO_3 , c) D_2CO_3 . Spectra are shifted for clarity. Bands marked by * arise from the ν_2 bend of the HDO monomer and dimer, by # from combination bands of $^{13}\text{CO}_2$ and by o from combination band of CO_2 .

Table 1: Band positions assigned to carbonic acid monomers and isotope shifts [both in cm^{-1}]. Data taken from Figure 2 and Figure S2. Values in parentheses are calculated at the MP2/aug-cc-pVTZ level of theory. Normal modes are assigned based on these calculations. Two distinct monomer geometries, namely in the cis-cis (C_{2v} point group symmetry) and the cis-trans conformation (C_s point group symmetry) are necessary to explain the spectra.

$\text{H}_2^{12}\text{CO}_3$			$^{12}\text{C}/^{13}\text{C}$ – shift		H/D – shift		Norm. mode	Assign.	Molec. sym.
Ar	Kr	(theor.)	Ar	(theor.)	Ar	(theor.)			
3617/3614		(3805)					$\nu(\text{A}')$	$\nu_s(\text{OH})$	C_s
3611/3607		(3801)	1/-3	(0)	950/94	(1037)	$\nu(\text{B}_2)$	$\nu_{as}(\text{OH})$	C_{2v}
					9				
1833/1829	1828	(1880)	44/41	(48)	9/11	(13)	$\nu(\text{A}')$	$\nu(\text{C}=\text{O})$	C_s
1792/1788	1787	(1834)	42	(46)	5/7	(12)	$\nu(\text{A}_1)$	$\nu(\text{C}=\text{O})$	C_{2v}
1446/1438	1443	(1467)	31/30	(34)	72/73	(68)	$\nu(\text{B}_2)$	$\nu_{as}(\text{C}(\text{OH})_2)$	C_{2v}
1392/1385	1390	(1409)	25/23	(27)			$\nu(\text{A}')$	$\nu_{as}(\text{C}(\text{OH})_2)$	C_s
1255	1254	(1289)			189	(212)	$\nu(\text{A}_1)$	$\delta_{ip}(\text{COH})$	C_{2v}
1228	1226	(1270)					$\nu(\text{A}')$	$\delta_{ip}(\text{COH})$	C_s
1136	1134	(1166)	6	(6)	189	(204)	$\nu(\text{B}_2)$	$\delta_{ip}(\text{COH})$	C_{2v}
792	791	(802)	24	(25)	1	(1)	$\nu(\text{B}_1)$	$\delta_{oop}(\text{CO}_3)$	C_{2v}
782	781	(790)	24	(23)			$\nu(\text{A}'')$	$\delta_{oop}(\text{CO}_3)$	C_s

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