

Matrix Isolation Studies of Carbonic Acid—The Vapor Phase above the β -Polymorph

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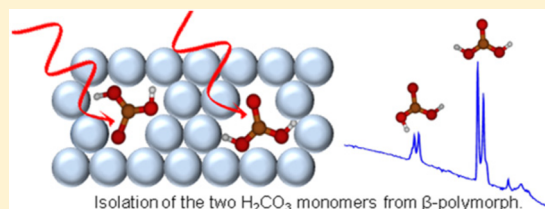
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Supporting Information

ABSTRACT: Twenty years ago two different polymorphs of carbonic acid, α - and β - H_2CO_3 , were isolated as thin, crystalline films. They were characterized by infrared and, of late, by Raman spectroscopy. Determination of the crystal structure of these two polymorphs, using cryopowder and thin film X-ray diffraction techniques, has failed so far. Recently, we succeeded in sublimating α - H_2CO_3 and trapping the vapor 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 - H_2CO_3 , β - H_2CO_3 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 - H_2CO_3 adds a new aspect to the chemistry of carbonic acid in astrophysical environments, especially because there is a direct way of β - H_2CO_3 formation in space, but none for α - H_2CO_3 . Assignments of the FTIR spectra of the isolated molecules unambiguously reveal two different carbonic acid monomer conformers (C_{2v} and C_s). In contrast to the earlier study on α - H_2CO_3 , we do not find evidence for centrosymmetric (C_{2h}) carbonic acid dimers here. This suggests that two monomers are entropically favored at the sublimation temperature of 250 K for β - H_2CO_3 , whereas they are not at the sublimation temperature of 210 K for α - H_2CO_3 .



INTRODUCTION

Carbonic acid, H_2CO_3 , plays an important role in many fields¹ of chemistry and physics, including astrophysics,^{2–6} and 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 under ambient conditions and even more so in the presence of water.⁷ In aqueous solution, detection of its formation and/or decomposition is only feasible by use of fast⁸ or ultrafast spectroscopic techniques.⁹ 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 cryotemperatures.¹⁰ β - H_2CO_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 irradiation,¹² or UV-photolysis.^{11,13} In the absence of water it may form from solid 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 cryotechniques were recently employed by us to observe two amorphous forms of carbonic acid, which then crystallize to the two polymorphs.²⁰ 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 β - H_2CO_3 suggests a centrosymmetric building block, whereas mutual exclusion and a local inversion center were not found for α - H_2CO_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 vapor phase produced after ammonium bicarbonate (NH_4HCO_3) thermolysis.²¹ Later, two 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 studied the vapor phase above α - H_2CO_3 by slowly sublimating the crystalline thin film at 210 K in vacuo.

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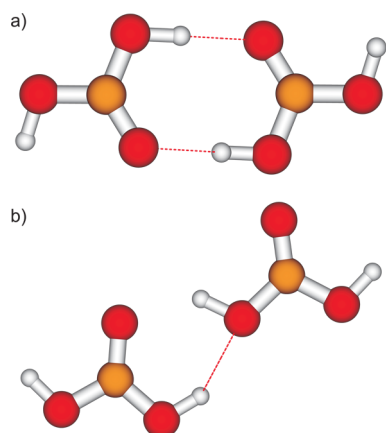


Figure 1. Possible basic building blocks in the solid state for (a) β - H_2CO_3 , which is studied in this work, and (b) α - H_2CO_3 , which was studied in our previous work.²⁴ The local symmetries of these polymorphs were inferred by testing the validity of the mutual exclusion principle from Raman and IR spectroscopic data.¹⁹ 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 - H_2CO_3 , but not in the gas phase above β - H_2CO_3 . We attribute this to the lower temperature of the gas-phase above α - H_2CO_3 (210 K vs 250 K), which favors dimerization in the gas phase.

Thrillingly, the vapor phase above α - H_2CO_3 can be recondensed as α - H_2CO_3 on cold substrates at a different location,¹⁷ which demonstrates that carbonic acid sublimates at least partly without decomposition to carbon dioxide and water. Previously, we succeeded in isolating the vapor phase above α - H_2CO_3 in a range of noble gas matrices and analyzed these matrices by infrared spectroscopy.²⁴ We have interpreted these infrared spectra in terms of the presence of the C_{2v} and C_s monomers at a ratio of 10:1, a small fraction of centrosymmetric (C_{2h}) carbonic acid dimers, and some carbon dioxide and water mono- and oligomers. After removal of the matrix, the isolated gas-phase molecules rebuild a hydrogen-bonded network and condense to a crystalline polymorph. Interestingly, it is again the α -polymorph that is observed after sublimation of the α -polymorph, matrix isolation, and removal of the matrix.

In the present paper, we show the isolation of the β -polymorph in a solid rare gas matrix. The vapor phase above the β -polymorph is harder to isolate because the vapor pressure and sublimation rate of this polymorph are even lower than for the α -polymorph, so higher sublimation temperatures are required.¹⁷ Calculation of the vapor pressure for α - H_2CO_3 at 200 K by Hage et al. shows the saturation vapor pressure (p_s) of 4×10^{-7} mbar for the H_2CO_3 monomer and 3×10^{-7} mbar for the dimer in the gas phase.¹⁷ Peeters et al. measure the vapor pressure of β - H_2CO_3 of about $(0.29\text{--}2.33) \times 10^{-9}$ mbar at 240–255 K.⁶

EXPERIMENTAL SECTION

Matrix isolation spectroscopy is a technique aimed at obtaining pure vibrational spectra at low temperatures that isolates nonrotating single molecules by trapping them in a solid matrix of, for example, neon, argon, or krypton, which are optically transparent in the mid infrared and are chemically inert. Our matrix isolation study was done in the ultrahigh-vacuum chamber in Vienna (see Supp.-Figure 1 in ref 24), which was previously employed for successfully isolating reactive species such as halogen oxides²⁵ or the sublimation product of the α -

polymorph of H_2CO_3 .²⁴ The preparation of the starting material (β - H_2CO_3) was done in Innsbruck as described in refs 5, 10, and 26 by layer-by-layer spray deposition of glassy aqueous solutions of acid (2 M HBr) and base (1 M KHCO_3) on optical windows kept at 80 K. Subsequently, this acid–base “sandwich” is heated slowly to 180 K in order to trigger translational diffusion and acid–base chemistry. Finally, ice is removed in the high-vacuum chamber by heating to 210 K, which results in the formation of first an amorphous thin film of carbonic acid, which finally crystallizes to β - H_2CO_3 . The preparation process of the thin film of carbonic acid is monitored in situ by FTIR spectra recorded on the Varian Excalibur spectrometer in Innsbruck. Figure 2a shows the typical FTIR spectrum (recorded at 80 K) of a

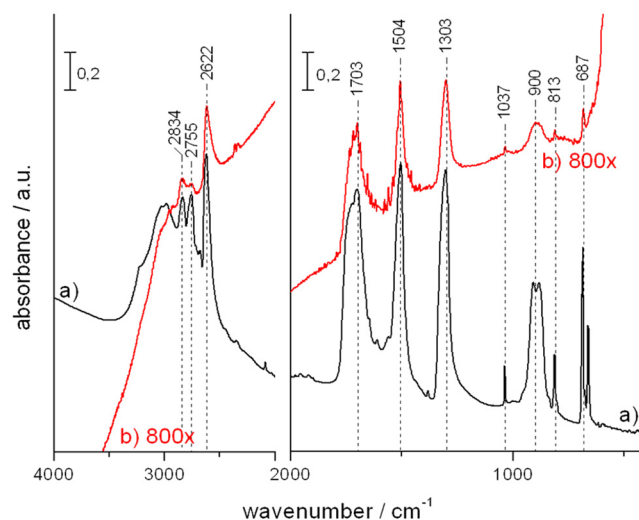


Figure 2. (a) IR spectrum of a thin film of crystalline β - H_2CO_3 at 80 K, as prepared by protonation of KHCO_3 with HBr in aqueous solution and removal of the solvent in vacuum at 230 K. (b) IR spectrum of crystalline β - H_2CO_3 that re-forms after removal of the argon matrix containing trapped carbonic acid molecules. Only a small fraction of carbonic acid re-forms, so the intensity of this spectrum has to be multiplied by 800 to obtain comparable intensities. Spectra are shifted vertically for clarity.

thin film of crystalline β - H_2CO_3 prepared using this procedure on a Si window. The vertical lines indicate the position of the absorption bands of crystalline β - H_2CO_3 .²⁶ These thin films on the optical windows were then stored in liquid nitrogen and transferred to the matrix isolation chamber in Vienna. In this chamber the ice that has condensed during the transfer of the window at 77 K from ambient air was first removed and then the thin film was sublimated. The vapor above the thin film was then mixed with noble gas (argon or krypton) and recondensed on a cold mirror as a solid mixture of sublimation products and noble gas, typically at a ratio of 1:1000. The details of the matrix isolation procedure can be found in ref 24. FTIR spectra of the matrix were recorded by a Vertex 80v (Bruker Optic GmbH, Karlsruhe, Germany) equipped with a liquid N_2 cooled narrow band MCT detector applying a spectral resolution of 0.5 cm^{-1} , adding 512 scans, and using a Ge-coated KBr beamsplitter. The optical path of the spectrometer was evacuated down to 2 mbar, which minimizes interferences from CO_2 and H_2O absorptions of the ambient atmosphere. Such a sensitive setup is particularly important when measuring a substance like carbonic acid, which is a very weak absorber in especially these spectral regions.

Ab initio quantum mechanical calculations of carbonic acid in various isotope configurations were performed to obtain reference frequencies for annotating measured spectra. All calculations were performed using the Gaussian 09 package.²⁷ Both the C_{2v} and C_s conformations were employed for geometry optimization, where the former is the energetically most favorable conformation.^{28,29} Calculations were performed using second-order Møller–Plesset

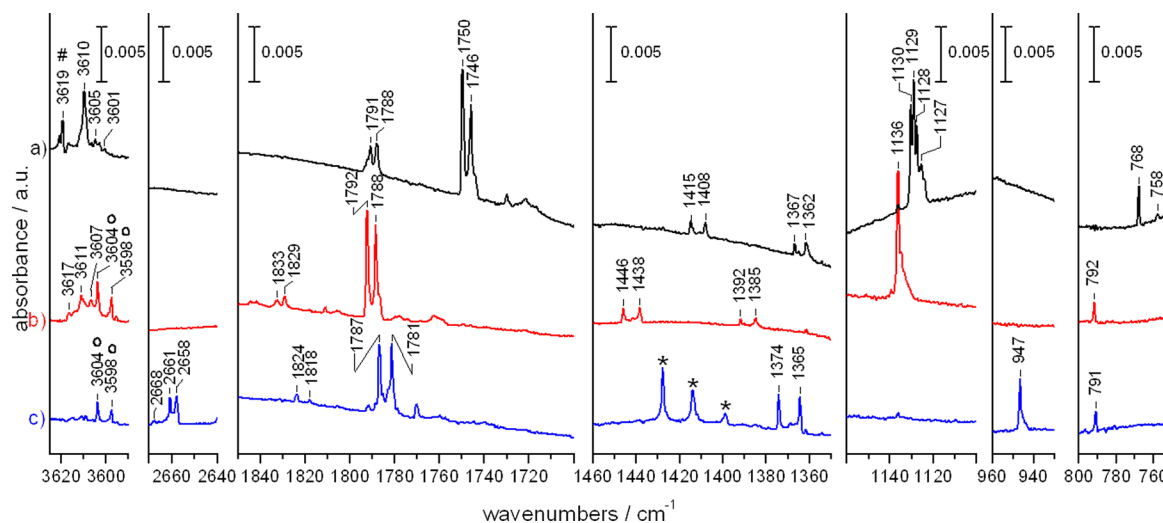


Figure 3. Selected regions of the IR spectra of carbonic acid vapor and isotopologues after sublimation of crystalline β - H_2CO_3 at 230–260 K and isolation in solid argon at 6 K: (a) $\text{H}_2^{13}\text{CO}_3$, (b) H_2CO_3 , (c) D_2CO_3 . Spectra are shifted for clarity. Bands marked by \star arise 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})^a

$\text{H}_2^{12}\text{CO}_3$			$^{12}\text{C}/^{13}\text{C}$ 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	950/949	1037	$\nu(\text{B}_2)$	$\nu_{as}(\text{OH})$	C_{2v}
1833/1829	1828	1880	42/41	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

^aData taken from Figure 2 and Figure S2 (Supporting Information). Values in columns labeled “theor” are calculated at the MP2/aug-cc-pVTZ level of theory. Normal modes are assigned on the basis of 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.

perturbation theory (MP2) with the augmented correlation consistent basis sets of Dunning and co-workers.^{30–32} Initial optimization was done at the MP2/aug-cc-pVDZ level of theory requiring “very tight” convergence on displacement and forces. Starting from the resulting geometry, further optimization at the MP2/aug-cc-pVTZ level of theory using very tight convergence criteria yielded an energy minimum for frequency calculations. Subsequently, IR modes were determined at this minimum geometry using MP2/aug-cc-pVTZ. Isotope shifts were calculated by performing frequency calculations at the same minimum for either all ^2H - or ^{13}C -labeled carbonic acid. Calculated frequencies and isotope shifts were then used to identify the various signals observed in the experimentally obtained spectra.

RESULTS

For β - H_2CO_3 , the same procedure of sublimation and trapping in solid matrices (Ar or Kr) was applied as for α - H_2CO_3 , 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, Supporting Information). 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 nonrotation mode of H_2O monomer and dimer,^{33,34} and the bands near 1600 cm^{-1} with the bending mode of H_2O monomer and dimer.^{33,34} The most intensive bands near 2300 cm^{-1} and the band around 680 cm^{-1} appertain to CO_2 (with ^{12}C or ^{13}C) molecules.³⁵

During the transfer of the Si window from the liquid N_2 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 H_2CO_3 is shown in the spectrum of matrix isolated D_2CO_3 (Figure S1c, Supporting Information). The band system at 2783, 2771, 2746, 2724, and 2678 cm^{-1} belongs to the absorption bands of the D_2O monomer and polymer.^{33,36} Unambiguously, this band can only result from the decomposition of D_2CO_3 . In the spectrum of $\text{H}_2^{13}\text{CO}_3$ (Figure S1a, Supporting Information), the decomposition is clearly evident in the strong $^{13}\text{CO}_2$ bands at 2280, 2275, and 2274 cm^{-1} .³⁵ These bands are unequivocally assigned

because the band positions typically agree with literature data to within $\pm 0.5 \text{ cm}^{-1}$.

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 $\nu(\text{C}=\text{O})$ mode in carbonic acid amounts to about 10% of the intensity of the most intense $\nu(\text{O}-\text{H})$ 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 $\beta\text{-H}_2\text{CO}_3$ sublimates with decomposition, whereas another part does not decompose.

Figure 3 shows the spectral regions that cannot be explained using CO_2 or H_2O mono- or oligomers, which we assign to H_2CO_3 and its isotopologues after sublimation of crystalline $\beta\text{-H}_2\text{CO}_3$ 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) on the basis of selective changes of the experimental conditions: (a) $^{12}\text{C}/^{13}\text{C}$ and H/D isotope shifts, (b) UV radiation of the matrix, and (c) change of the matrix material (Ar or Kr). Also theoretical prediction concerning band positions and shifts between the symmetry of the isotopologues support our interpretation.

Our band assignment is exemplarily explained here on the CO-stretching region at $1850\text{--}1700 \text{ cm}^{-1}$, which contains two doublets (see Figure 3b). They appear as doublets because of a splitting induced by different Ar matrix cages. By contrast, in Kr matrix two single bands appear at a similar position (see Figure S2, Supporting Information). This immediately suggests the presence of two distinct gas-phase carbonic acid species. These doublets are red-shifted by $5\text{--}11 \text{ cm}^{-1}$ for $\text{D}_2\text{CO}_3/\text{Ar}$ (Figure 3c) and by 42 cm^{-1} for $\text{H}_2^{13}\text{CO}_3/\text{Ar}$. These isotope shifts are in excellent agreement with the theoretical prediction of isotope shifts for $\nu_s(\text{C}=\text{O})$ of the H_2CO_3 monomers (see Table 1). The assignment of the two carbonic acid species is immediately evident when looking at the calculated separation of the $\nu_s(\text{C}=\text{O})$ between the cis–cis monomer of C_{2v} symmetry and the cis–trans monomer of C_s symmetry. This amounts to 46 cm^{-1} at the MP2/aug-cc-pVTZ level of theory (1880 vs 1834 cm^{-1} ; see column labeled 'theor' in Table 1) employed here and is almost the same also at other levels of theory.^{37–39} In the matrix spectrum the two bands are separated by 41 cm^{-1} (1828 vs 1787 cm^{-1} ; see Table 1), which is an excellent match and allows an unambiguous assignment of the bands.

Upon UV irradiation of the $\text{H}_2\text{CO}_3/\text{Ar}$ matrix one of the two doublets increases with time at the cost of the other doublet (see difference spectra in Figure S3, Supporting Information). According to the assignment this implies that the C_s isomer grows at the expense of the C_{2v} isomer. That is, the isomer that is calculated to be slightly energetically disfavored is formed from the favored one upon UV irradiation. Most likely this shift of the equilibrium takes place by a rotation of one H-atom around the C–O bond from the cis-position to the trans-position. The ratio of the intensities of C_{2v} and C_s bands before UV irradiation varies between 5:1 (Figure 3a) and 10:1 (Figure 3c), which is in accordance with the theoretical predictions of the higher stability of the C_{2v} monomer. The presence of the two weak internal hydrogen bonds in the C_{2v} monomer compared to the single internal hydrogen bond in the C_s monomer results in an increased stability of about $4\text{--}8 \text{ kJ/mol}$.^{22,28,29,38–41} This interpretation of the presence of these two monomers at these ratios can also be deduced from all

other spectral ranges shown in Figure 3 and is demonstrated in the Supporting Information.

After having assigned these bands, all the bands observed in the whole spectral range are explained. Other possible species, such as complexes of water with carbonic acid or carbonic acid dimers, trimers, or higher oligomers, are not present or are at most trace components producing bands near the noise level of the spectrum.

In order to hedge our assignments, we have evaporated the solid noble gas matrices at the end of the spectroscopic characterization by carefully heating the matrix and checking for the component remaining on the sample holder. The spectrum after sublimation of $\beta\text{-H}_2\text{CO}_3$, matrix isolation of gas-phase carbonic acid in argon at 6 K, and removal of the argon matrix by heating to 220 K is shown in Figure 2b. This spectrum is highly similar to the spectrum of $\beta\text{-H}_2\text{CO}_3$ before sublimation, albeit with intensities that are about a factor of 1000 lower. That is, the isolated carbonic acid monomers start to hydrogen bond upon removal of the argon and finally produce crystalline $\beta\text{-H}_2\text{CO}_3$. For comparison, after isolation of the gas-phase above $\alpha\text{-H}_2\text{CO}_3$ in argon and removal of argon, $\alpha\text{-H}_2\text{CO}_3$ is finally observed.²⁴

CONCLUSIONS AND IMPLICATIONS FOR CARBONIC ACID DETECTION

In the past we were successful in the isolation of the α -polymorph of carbonic acid ($\alpha\text{-H}_2\text{CO}_3$) in a solid matrix.²⁴ Now we show the isolation of the β -polymorph ($\beta\text{-H}_2\text{CO}_3$) in a solid noble gas matrix and present our band assignment. The β -polymorph has a lower vapor pressure and lower sublimation rates than the α -polymorph at the same temperature. In order to reach a significant vapor pressure above the β -polymorph, it is necessary to sublime the β -polymorph at 230–260 K, as compared to 210 K for the α -polymorph. Similar to our former experiment, we also find the C_{2v} monomer to be the dominating species in the gas phase. The ratio between C_{2v} and C_s of the β -polymorph at 230–260 K is similar to that of the α -polymorph at 210 K²⁴ and to the calculations of Schwerdtfeger et al.⁴² Both polymorphs show the C_s monomer as the minor species, which occurs at a ratio from about 1:5 to 1:10. In contrast to our earlier matrix isolation study, we now do not find evidence for the presence of a centrosymmetric dimer. We attribute this difference to the higher sublimation temperature, which favors two monomers over the dimer because of the entropy term. That is, the results suggest that the enthalpy gain incurred because of hydrogen bond formation in the dimer is sufficient for the observation of the dimer at a sublimation temperature of 210 K,²⁴ but not at sublimation temperatures of 230–260 K used here. There is furthermore no indication for the presence of a linear oligomer⁴³ in the gas phase. As a consequence of this difference in the composition of the gas phase, also the polymorph that crystallizes upon removal of the matrix is different: $\alpha\text{-H}_2\text{CO}_3$ crystallizes from sublimed $\alpha\text{-H}_2\text{CO}_3$, and $\beta\text{-H}_2\text{CO}_3$ crystallizes from sublimed $\beta\text{-H}_2\text{CO}_3$.

The finding here that not only $\alpha\text{-H}_2\text{CO}_3$ can sublime and recondense as $\alpha\text{-H}_2\text{CO}_3$ but also $\beta\text{-H}_2\text{CO}_3$ can sublime and recondense as $\beta\text{-H}_2\text{CO}_3$ is novel and of atmospheric and astrophysical relevance, especially because it was previously thought that $\beta\text{-H}_2\text{CO}_3$ decomposes entirely upon sublimation.^{2,6,11,12,14–16}

In our atmosphere some solid-state carbonic acid may be present in cirrus clouds or on mineral dust. This possibility was

conjectured 15 years ago,¹⁷ but only very recently it could be shown that indeed β -H₂CO₃ may form as a bulk species on mineral dust in the presence of acids and remain stable in the troposphere even in the presence of high relative humidities up to 260 K.⁴⁴ Huber et al.³⁹ have emphasized that the sublimation temperature of α -H₂CO₃ of 210 K^{17,24} is too low for a possible existence of gas-phase carbonic acid in Earth's atmosphere. This is because such low temperatures are only found in the stratosphere, where cirrus clouds cannot be observed. However, the sublimation temperature of β -H₂CO₃ of up to 260 K reported in this work is of relevance in the troposphere, where β -H₂CO₃ is presumed to exist and may sublime and recondense without decomposition. That is, some gas-phase carbonic acid may indeed be present in the troposphere, albeit at very low mixing ratios: the vapor pressure of β -H₂CO₃ at 260 K is on the order of 10⁻⁸–10⁻⁹ mbar, and the atmospheric pressure is about 200–400 mbar at the relevant altitudes of 5–10 km. These low mixing ratios will make it very challenging to detect gas-phase carbonic acid in Earth's troposphere.

Our findings presented here increase the chance for detection of gas-phase carbonic acid in astrophysical environments. First, direct routes for the formation of β -H₂CO₃ in astrophysical environments are known,^{2,3,11,12} whereas no direct route for the formation of α -H₂CO₃ is known. Typically, β -H₂CO₃ is considered in environments containing both H₂O and CO₂ ices, which are exposed to radiation, e.g., solar photons or cosmic rays. This is the case for the icy satellites of Jupiter and Saturn and also for the polar caps of Mars. The stability of gas-phase carbonic acid up to 260 K presented here might then result in a release and accumulation of carbonic acid in these thin atmospheres. For example, on the Mars surface it is known that the temperatures may change between 140 and 300 K, so carbonic acid may experience sublimation and recondensation cycles and reach a steady-state concentration near the icy caps. However, even with next-generation telescopes, the remote detection of carbonic acid in the thin atmospheres of such bodies seems very challenging, as explained by Huber et al.³⁹ Because of the high angular resolution required we might need to wait for the European Extremely Large Telescope (E-ELT), which is planned to be operative in the early 2020s.³⁹ It might, therefore, be useful to investigate the gas phase there in the future using microwave^{22,23} or infrared absorption spectroscopy, e.g., by the METIS instrument on the E-ELT. Judging from the present and our earlier work,²⁴ the most intense and characteristic bands suitable for detection of the most abundant C_{2v} carbonic acid monomers are the bands at 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 (12.6 μm). A distinction between C_{2v} C_s monomers and C_{2h} dimers will always be very hard. However, the ν(C=O) band seems most promising for this purpose, because it has the best separation (see Figure S4, Supporting Information): 1830 ± 5 cm⁻¹ (5.46 μm, C_s), 1780 ± 10 cm⁻¹ (5.62 μm, C_{2v}), and 1720 ± 10 cm⁻¹ (5.81 μm, C_{2h}).²⁴

In addition to remote detection, the possibility of on-site detection might be feasible in the future: for instance, a mid-infrared spectrometer on a Mars lander might provide the possibility to locate carbonic acid, both in the solid state on icy soil and also in the atmosphere. In this context, the detection of (bi)carbonate anions in soil excavated near the Martian pole in the Wet Chemistry Laboratory on the Phoenix Mars Lander seems very promising for the future endeavor of carbonic acid detection.^{45,46} Also lander missions to other bodies, such as the

attempt of Philae to land on the comet 67P/Churyumov–Gerasimenko at the end of 2014 (ESA's Rosetta mission) or the plan of an ESA spacecraft visiting the icy Jovian moons ("Jupiter Icy Moon Explorer"), hold promise for the detection of carbonic acid.

■ ASSOCIATED CONTENT

Supporting Information

Additional spectra and more details about band assignments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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