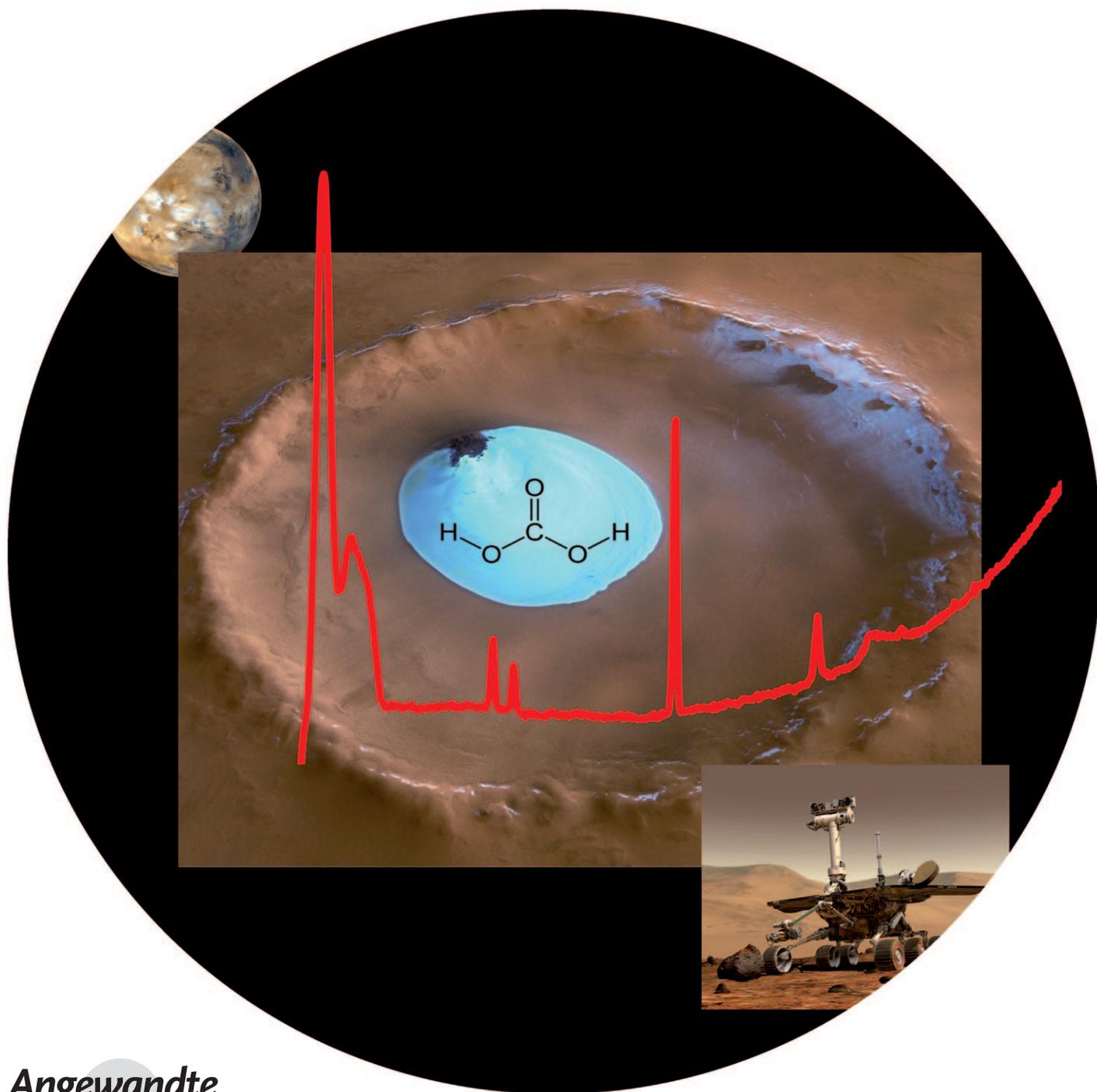


Raman Spectroscopic Study of the Phase Transition of Amorphous to Crystalline β -Carbonic Acid**

Ingrid Kohl, Katrin Winkel, Marion Bauer, Klaus R. Liedl, Thomas Loerting,* and Erwin Mayer



Carbonic acid (H_2CO_3), the short-lived intermediate in CO_2 - $\text{HCO}_3^-/\text{CO}_3^{2-}$ proton-transfer reactions,^[1-9] has been synthesized at low temperatures by two fundamentally different routes: 1) by high-energy irradiation of cryogenic $\text{CO}_2/\text{H}_2\text{O}$ mixtures^[10-17] and proton irradiation of pure solid CO_2 ,^[13] and 2) by protonation of hydrogencarbonate or carbonate in a new cryogenic technique developed by our group.^[18-24] Fourier transform infrared (FTIR) spectroscopic studies led to characterization of two polymorphs. One ($\beta\text{-H}_2\text{CO}_3$) is formed by high-energy irradiation^[10-17] or by protonation in freeze-concentrated aqueous solution.^[19,20,22,24] The other ($\alpha\text{-H}_2\text{CO}_3$) is formed by protonation in methanolic solution;^[18,19,21-24] $\beta\text{-H}_2\text{CO}_3$ is transformed into $\alpha\text{-H}_2\text{CO}_3$ on treatment with methanol/HCl.^[19] So far these polymorphs have been characterized only by IR spectroscopy. High-level molecular quantum mechanical calculations further show that in the gas phase water-free H_2CO_3 is kinetically very stable, with a half-life of about 180000 years at ambient temperature.^[25] It was also found that up to three water molecules are required to approach the experimental decomposition rate.^[26]

Since H_2O and CO_2 coexist in various astrophysical environments such as in icy grain mantles in the interstellar medium, the formation of solid or gaseous carbonic acid by high-energy irradiation and its astrophysical significance is of interest.^[8,12,13,16,17,19,20,23,27-31] In particular, a comparison of the IR spectrum of $\beta\text{-H}_2\text{CO}_3$ with spectra of Mars suggests $\beta\text{-H}_2\text{CO}_3$ to be present on the surface.^[28]

Herein we report Raman spectra of amorphous H_2CO_3 and of $\beta\text{-H}_2\text{CO}_3$ formed on phase transition induced by heating. These spectra are essential in the search for carbonic acid on Mars by "in situ planetary Raman spectroscopy".^[32] Raman spectroscopic detection of minerals and of water-containing and organic phases is being planned, and laboratory Raman spectra are required for comparison. The Mars Microbeam Raman Spectrometer^[33] is being developed in anticipation of a Mars landing in 2009 (Ref. [32]).

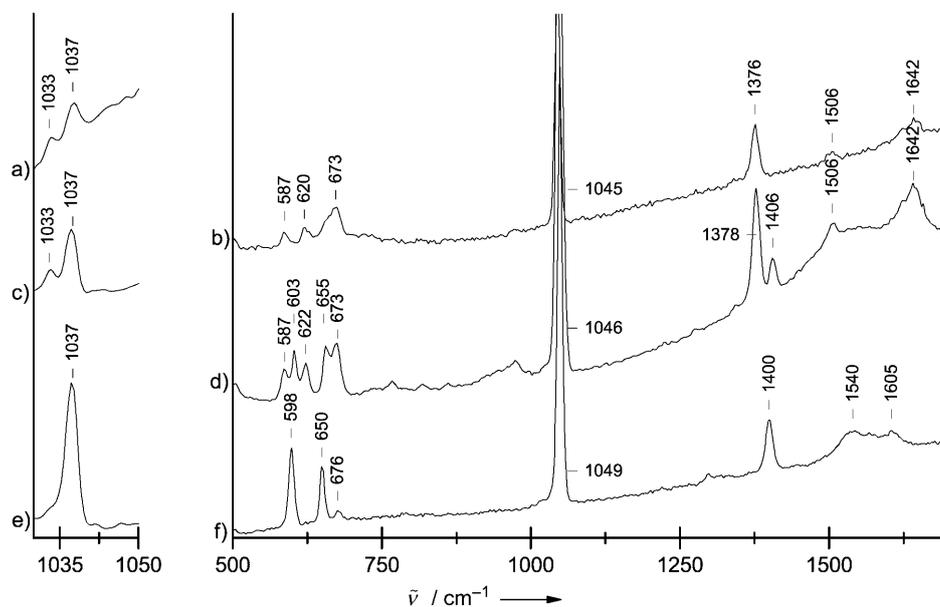


Figure 1. Characterization of the phase transition of amorphous to $\beta\text{-H}_2\text{CO}_3$ by IR and Raman spectra of a film made by reaction of aqueous solutions of KHCO_3 and HBr at $T < 180$ K and recorded at 80 K. a) IR spectrum after heating in vacuo at 180 K for 10 h and at 190 K for 3 h; b) Raman spectrum of the same film, recorded after transfer of the film and ZnSe window under liquid nitrogen from the high-vacuum apparatus used for IR measurements, to the Raman microstat. For (c) the film and ZnSe window were transferred back under liquid nitrogen to the high-vacuum apparatus and heated at 200 K for 3 h before the IR spectrum was recorded; the corresponding Raman spectrum is shown in (d). For (e) the film was heated at 210 K for 7 h before the IR spectrum was recorded; the corresponding Raman spectrum is shown in (f). The intense band centered at (1047 ± 2) cm^{-1} has been cut off in order to show the weak bands at sufficient intensity. The three IR spectra are shown on the same scale. Raman spectra were scaled to show similar intensity of the band at 1376 cm^{-1} in (b) and at 1400 cm^{-1} in (f).

In Figure 1 we show how the Raman spectrum of amorphous H_2CO_3 transforms into that of $\beta\text{-H}_2\text{CO}_3$ on heating from 190 to 200 and 210 K. In the IR spectrum (Figure 1 in Ref. [24]) the best indicator for formation of $\beta\text{-H}_2\text{CO}_3$ is growth of the sharp band centered at 1037 cm^{-1} (assigned to the $\nu_s\text{C}(\text{OH})_2$ vibration in Refs. [10,12,18]). This IR band is weak after heating to 190 K and becomes much more intense on subsequent heating to 200 K and 210 K (Figure 1 a,c,e). The Raman spectra (Figure 1 b,d,f) recorded after each IR spectrum show how the species present after heating to 190 K transforms on further heating to 200 K and 210 K into another species. For example, the band centered at 1376 cm^{-1} (Figure 1 b) shifts to 1400 cm^{-1} (Figure 1 f), and the three-band system with peaks at 587, 620, and 673 cm^{-1} (Figure 1 b) develops into a two-band system at 598 and 650 cm^{-1} . At 200 K (Figure 1 d) the spectrum consists of a mixture of both species. In accordance with our IR spectral

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[**] This work was supported by a grant from the Austrian Science Fund FWF (P18187) and by the European Research Council ERC (SULIWA). We thank Prof. Sarah L. Price for constructive comments.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.200805300>.

study,^[24] we assign the Raman spectral features recorded after heating the sample to 190 K to amorphous H_2CO_3 , after heating to 200 K to a mixture of amorphous and $\beta\text{-H}_2\text{CO}_3$, and after heating to 210 K to $\beta\text{-H}_2\text{CO}_3$. The latter still contains a minor amount of amorphous H_2CO_3 , as indicated by the weak band at 676 cm^{-1} .

In Figure 2 we compare the IR spectrum of a film of $\beta\text{-H}_2\text{CO}_3$ (Figure 2a) with the Raman spectrum of the same film at low (Figure 2b) and high (Figure 2c) resolution. The IR spectrum is analogous to that of $\beta\text{-H}_2\text{CO}_3$ reported in Refs. [10–17, 19, 20, 22, 24]. The corresponding Raman spectrum is shown for an extended region, and it shows bands in addition to the bands in Figure 1f at lower and higher wavenumbers. We find that on the whole, Raman bands have no counterpart in the IR spectrum and vice versa. This condition is called “the rule of mutual exclusion”, and it holds for any molecule with a center of symmetry.^[34, 35] The only coincidence seems to be the Raman band centered at 657 cm^{-1} (Figure 2c), which has a counterpart in the IR spectrum at 658 cm^{-1} (or at 664 cm^{-1} , see Table 1 in Ref. [20]). Such a coincidence can be accidental, and Ref. [36] contains several examples of the accidental coincidence of Raman and IR bands in cyclic dimers of carboxylic acids in the solid state. We note that the Raman spectrum of $\alpha\text{-H}_2\text{CO}_3$ contains several Raman bands coincidental with those in the IR spectrum,^[18, 19, 21–24] and that therefore $\alpha\text{-H}_2\text{CO}_3$ cannot have a center of symmetry (these results will be reported separately).

The total number of bands in the Raman spectrum of $\beta\text{-H}_2\text{CO}_3$ is low, which points toward a structural unit of high symmetry for the crystal. We conclude that $\beta\text{-H}_2\text{CO}_3$ very likely has a local center of symmetry (*i*). Raman transitions must be symmetric with respect to *i*, whereas IR transitions must be antisymmetric with respect to *i*. In crystals, IR and Raman activity is determined by the symmetry of the primitive (or Wigner–Seitz) unit cell.^[37] As a dicarboxylic acid, crystalline carbonic acid can form intermolecular hydrogen bonds between the OH proton-donating group and the C=O proton-accepting group, resulting in either dimers or catemers.^[38] The most simple way of obtaining a local center of symmetry is to consider the cyclic dimer, which has C_{2h} symmetry, rather than the monomer. Our quantum mechanical calculations of gaseous $(\text{H}_2\text{CO}_3)_2$ made from two anti-anti monomers indicate that this dimer is remarkably stable, and that the energy difference between the dimer and the constituents H_2O and CO_2 is, after correction for zero-point energy differences, “astonishingly close to zero”.^[23, 39] Thus, the dimer and larger clusters of H_2CO_3 ^[40, 41] should be considered as building blocks in the crystal structures of α - and $\beta\text{-H}_2\text{CO}_3$.

In order to test the hypothesis of a dimer building block we have carried out a quantum mechanical geometry optimization and harmonic frequency calculation (including IR and Raman intensities) at the MP2/aug-cc-pVDZ level^[42, 43] for the gas-phase cyclic dimer. Furthermore, we

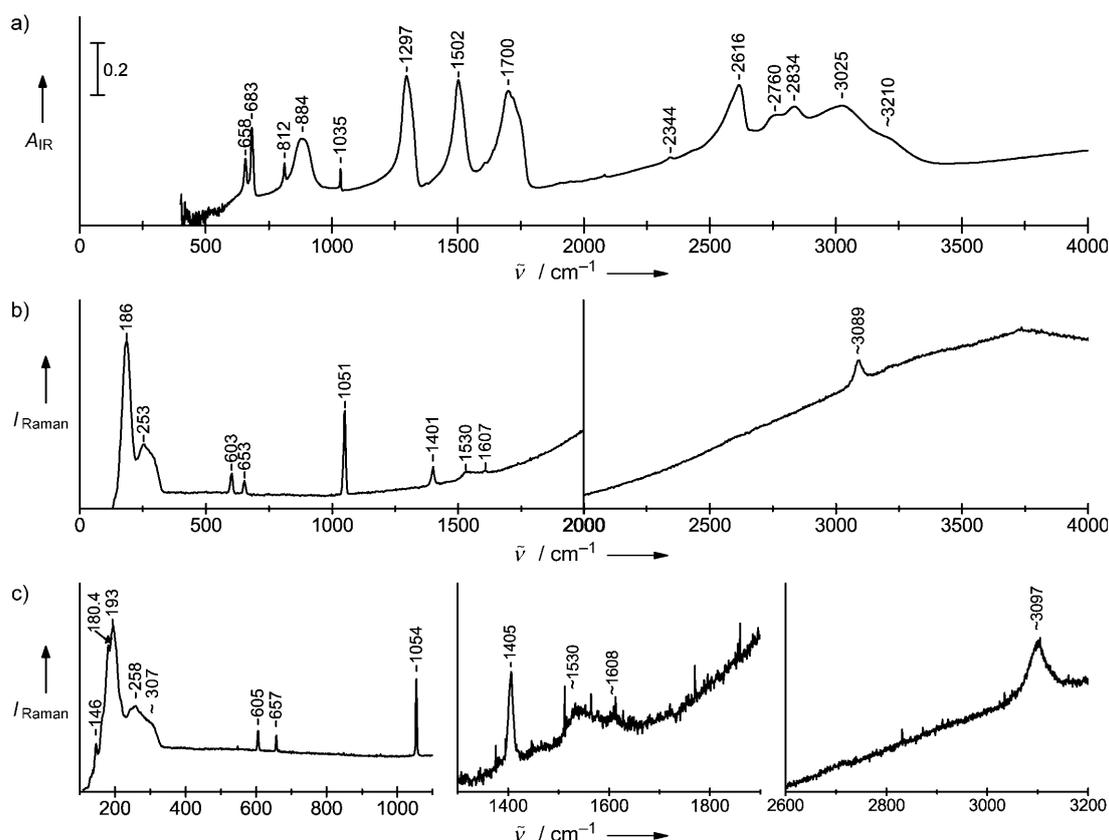


Figure 2. Comparison of IR and Raman spectra of $\beta\text{-H}_2\text{CO}_3$ prepared as described in Figure 1 and recorded at 80 K, and then after heating in vacuo at 240 K for 30 min. a) IR spectrum, b) Raman spectrum obtained with a grating of 600 lines per mm, and c) Raman spectrum obtained with a grating of 1800 lines per mm. The sharp band centered at 180.4 cm^{-1} is a He–Ne plasma line.

tethered the two free hydrogen atoms by assigning an arbitrarily high mass of 1000 amu (so that all oscillations involving these atoms are shifted to $< 200 \text{ cm}^{-1}$). In Table 1

Table 1: Raman and IR peak positions (from Figure 2 a and Figure 2 c; in cm^{-1}) of $\beta\text{-H}_2\text{CO}_3$. For comparison harmonic frequencies calculated at the MP2/aug-cc-pVDZ level of theory in cyclic $(\text{H}_2\text{CO}_3)_2$ of C_{2h} symmetry are listed. The assignment is made on the basis of a local center of symmetry (see also the Supporting Information).^[a]

$\tilde{\nu}_{\text{Raman}} [\text{cm}^{-1}]$	$\tilde{\nu}_{\text{Raman,calcd}} [\text{cm}^{-1}]$	$\tilde{\nu}_{\text{IR}} [\text{cm}^{-1}]$	$\tilde{\nu}_{\text{IR,calcd}} [\text{cm}^{-1}]$	Assignment
		ca. 3500–2500	3241 (3240)	$\nu_{\text{as}}(\text{O-H})$
	3134 (3134)			$\nu_{\text{s}}(\text{O-H})$
ca. 1608 vw	1705 (1715)	1700	1762 (1780)	$\nu_{\text{as}}(\text{C=O})$
ca. 1530 w	1536 (1553)			$\nu_{\text{s}}(\text{C=O})$
				$\delta_{\text{ip}}(\text{COH})$ and $\nu(\text{C-O})$
1405 m	1359 (1381)	1502	1509 (1520)	$\nu_{\text{as}}(\text{C(OH)}_2)$ $\delta_{\text{ip}}(\text{COH})$ and $\nu(\text{C-O})$
				$\delta_{\text{ip}}(\text{COH})$
1054 s	1092 (1015)	1297	1368 (1385)	$\nu_{\text{s}}(\text{C-O})$ and $\nu_{\text{s}}(\text{C=O})$
		1035	1085 (1006)	$\nu_{\text{as}}(\text{C-O})$ and $\nu_{\text{as}}(\text{C=O})$
	936 (938)			$\delta_{\text{oop}}(\text{COH})$
	800 (800)	884		$\delta_{\text{oop}}(\text{COH})$ $\delta_{\text{oop}}(\text{CO}_3)$
		812	800 (801)	$\delta_{\text{oop}}(\text{CO}_3)$
		683	683 (643)	$\delta_{\text{ip}}(\text{COO})$
		658		
657 m	662 (630)			$\delta_{\text{ip}}(\text{COO})$
605 m				skeletal bending lattice modes?
307 sh				
258 s				
193 vs				

[a] Calculated values for the tethered dimer are not in brackets, those for the free cyclic dimer are in brackets.

we compare the peak positions in Figure 2 with the calculated frequencies for the tethered (free) cyclic dimer. Those calculated frequencies, which are barely affected by the tethering, match the measured frequencies on the whole very well, and so we suggest the cyclic dimer (or higher oligomers of C_{2h} symmetry such as the tetramer) to be the building block for $\beta\text{-H}_2\text{CO}_3$. The qualitative assignment of bands in Table 1 is explained in the Supporting Information, where in-plane normal modes are also depicted schematically.

On Mars, CO_2 ice is the dominant constituent of the polar caps and of ice particles in the atmosphere, in intimate mixture with or segregated from lower amounts of water ice.^[44,45] The existence of water ice on Mars has been confirmed recently by NASA. Thus it seems likely that H_2CO_3 may form as a high-energy radiation product. Recent studies by Moore et al.^[16] have shown that the yield of $\beta\text{-H}_2\text{CO}_3$ is independent of the energy source; that is, the yield in UV-photolyzed and ion-bombarded H_2O and CO_2 ices is about the same. For identification of H_2CO_3 by its Raman spectrum with the Mars Microbeam Raman Spectrometer^[32,33] two spectral regions, one from 200 to 1700 cm^{-1} and

the other from 2500 to 4000 cm^{-1} at a spectral resolution of about 4 cm^{-1} are available.^[32] The obvious band to use in the search for solid H_2CO_3 is the intense Raman band of $\beta\text{-H}_2\text{CO}_3$ centered at 1054 cm^{-1} (Table 1). The position of this Raman band in amorphous H_2CO_3 is only slightly lower, and thus this Raman band alone cannot be used to differentiate between amorphous and $\beta\text{-H}_2\text{CO}_3$. This is possible, however, when a second, weaker, Raman band can be identified, for example, the band centered at 1376 cm^{-1} in amorphous H_2CO_3 , which shifts to 1400 cm^{-1} in $\beta\text{-H}_2\text{CO}_3$ (Figure 1). For Raman detection of carbonate and sulfate minerals on Mars, laboratory spectra of fine-grained powders have been recorded and collected in Ref. [32]. It is fortunate that none of these mineral spectra show Raman bands in the two spectral regions pointed out above where amorphous and/or $\beta\text{-H}_2\text{CO}_3$ can be detected.

Received: October 29, 2008

Published online: February 11, 2009

Keywords: amorphous materials · carboxylic acids · molecules in outer space · Raman spectroscopy · solid-state structures

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