Supporting Information

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

Jürgen Bernard¹, Roland. G. Huber², Klaus R. Liedl², Hinrich Grothe³,* and Thomas Loerting¹,*

¹Institute of Physical Chemistry, University of Innsbruck, A-6020 Innsbruck, Austria
²Institute of General, Inorganic and Theoretical Chemistry, University Innsbruck, A-6020 Innsbruck, Austria
³Institute of Materials Chemistry, Vienna University of Technology, A-1060 Vienna, Austria

*e-mail: grothe@tuwien.ac.at, thomas.loerting@uibk.ac.at

Band assignment

CO stretching mode

This region is discussed in the main text of the manuscript.

OH and OD stretching modes

Between 3630 – 3590 cm⁻¹ six bands arise in the case of H₂CO₃ isolated in Ar (as marked in Figure 3b), two of which we assign to the 2ν₂ + ν₃ combination band of CO₂ (lit. 3603 and 3597 cm⁻¹) S¹, and the other four to the ν(O-H) stretching modes in carbonic acid. In the case of D₂CO₃ (Figure 3c) these two combination bands are also seen, and two bands now appear in the region between 2670 – 2640 cm⁻¹ at 2661 and 2658 cm⁻¹, which correspond to ν(O-D) stretching modes. In the spectrum of H₂¹³CO₃ (Figure 3a) we find the 2ν₂ + ν₃ of ¹³CO₂ (lit. 3627 and 3619 cm⁻¹) at 3627 cm⁻¹ and 3619 cm⁻¹ S¹. Obviously, the bands at 2661 and 2658 cm⁻¹ belong to the νₐ(OD) of the most abundant monomer, namely C₂v, for D₂CO₃ and appear as two bands because of matrix splitting. The assignment to νₐ(OH) of the C₂v monomer for H₂CO₃ and H₂¹³CO₃ is more complicated. We interpret the bands at 3611 and 3607 cm⁻¹ (matrix splitting) to the νₐ(OH) of the C₂v monomer of H₂CO₃, and the band at 3610 cm⁻¹ to νₐ(OH) of the C₂v monomer of H₂¹³CO₃. Due to the small amount of the less abundant C₆ monomer in the matrix the search for the respective ν(OH) is rather difficult. However, the ν(OH) of the cis OH-group should shift to higher wavenumbers compared to the νₐ(OH) of C₂v symmetry. In Figure 3b two weak bands appear at 3617 and 3614 cm⁻¹, which we assign to the C₆ monomer.

C-(OH) asymmetric and symmetric stretching and in-plane deformation modes

In the spectral region 1000 – 1500 cm⁻¹ three fundamental modes, namely asymmetric and symmetric C-(OH) stretching and in-plane deformation modes exist. The asymmetric C-(OH) stretching mode has a predicted red shift between C₂v and C₆ of 58 cm⁻¹ and is predicted at
1467 cm$^{-1}$ for the C$_{2v}$ and at 1409 cm$^{-1}$ for the C$_{s}$ (see Table 1). The experiment shows a doublet at 1446/1438 cm$^{-1}$ (assigned to C$_{2v}$) and at 1392/1385 cm$^{-1}$ (assigned to C$_{s}$) in Ar. In Kr the bands are at 1443 and 1390 cm$^{-1}$ (Figure S2a). The experimental shift of 54/53 cm$^{-1}$ in Ar and 53 cm$^{-1}$ in Kr correlates excellently with the theory. In case of H$_2^{13}$CO$_3$ (Figure 3a) a doublet at 1415/1408 cm$^{-1}$ (assigned to C$_{2v}$) and at 1367/1362 cm$^{-1}$ (assigned to C$_{s}$) are observed. The predicted shifts between $^{12}$C and $^{13}$C of 34 cm$^{-1}$ for C$_{2v}$ and 27 cm$^{-1}$ for the C$_{s}$ monomer again agree excellently with the observations of of 31/30 cm$^{-1}$ and 25/23 cm$^{-1}$, respectively. In the spectrum of D$_2$CO$_3$/Ar (Figure 3c) bands at 1428/1414/1399 cm$^{-1}$ marked with asterisk can be assigned to the $\nu_3$ bend of HDO monomer and dimer $^{S2,S3}$. The doublet at 1374/1365 cm$^{-1}$ has a red shift of 72/73 cm$^{-1}$ relative to the doublet in H$_2$CO$_3$. The predicted shift of the asymmetric C-(OH) stretching mode of 68 cm$^{-1}$ between C$_{2v}$ of H$_2$CO$_3$ and D$_2$CO$_3$ again compares very well with the observed shift of 72/73 cm$^{-1}$.

The in-plane mode is weakly IR active and cannot be observed in all spectra. The predicted position of the $\delta_{ip}$(COH) for the C$_{2v}$ monomer is at 1289 cm$^{-1}$ and for the C$_{s}$ monomer at 1270 cm$^{-1}$. The spectrum of H$_2$CO$_3$/Ar (Figure 4b) shows two peaks with a shift of 27 cm$^{-1}$ at 1255 cm$^{-1}$ and 1228 cm$^{-1}$. The agreement in position and shift leads to the assignment of 1255 cm$^{-1}$ to $\delta_{ip}$(COH) of C$_{2v}$ and 1228 cm$^{-1}$ to C$_{s}$. The spectrum of D$_2$CO$_3$/Ar shows a doublet at 1066/1062 cm$^{-1}$ (not shown in Figure 3c), which is not there in case of the $^{12}$C and $^{13}$C spectra. The predicted position at 1077 cm$^{-1}$ for $\delta_{ip}$(COD) in the C$_{2v}$ monomer of D$_2$CO$_3$ shows a red shift of 212 cm$^{-1}$ to $\delta_{ip}$(COH) of H$_2$CO$_3$. The experiment is very close with a shift of 189 cm$^{-1}$ and supports the interpretation.

The symmetric C-(OH) stretching is the second most intensive absorption in the predicted spectrum of H$_2$CO$_3$. The predicted peak at 1166 cm$^{-1}$ for C$_{2v}$ of H$_2$CO$_3$ shifts to 1160 cm$^{-1}$ (red shift of 6 cm$^{-1}$) for C$_{2v}$ of H$_2^{13}$CO$_3$ and to 962 cm$^{-1}$ (red shift 204 cm$^{-1}$) for C$_{2v}$ of D$_2$CO$_3$. In the region 1160 – 1100 cm$^{-1}$ the spectra in Figure 3 show a band located at 1136 cm$^{-1}$ in the H$_2$CO$_3$/Ar spectrum (Figure 3b). This peak shifts to lower wavenumbers in the case of H$_2^{13}$CO$_3$/Ar (Figure 3a) and a quartet of bands at 1130/1129/1128/1127 cm$^{-1}$ arise. The spectrum of D$_2$CO$_3$/Ar does not show an absorbance in this region (Figure 3c), but a band at 947 cm$^{-1}$, which is not present in the spectra of the other isotopologues. A shift of 189 cm$^{-1}$ between 1136 cm$^{-1}$ (H$_2$CO$_3$) and 947 cm$^{-1}$ (D$_2$CO$_3$) correlates with the predicted shift of 204 cm$^{-1}$. An assignment of the bands to the symmetric stretching $\nu$(O-C-O) is obvious.

**CO$_3$ out of plane deformation mode**

The region at 800 – 750 cm$^{-1}$ shows the out of plane deformation of carbonic acid, in which a more intensive band at 792 and a less intensive one at 782 cm$^{-1}$ are observed in the spectrum. The predicted $\delta_{oop}$(CO$_3$) of the C$_{2v}$ monomer is located at 802 cm$^{-1}$ and for the C$_{s}$ monomer at 790 cm$^{-1}$ (red shift 12 cm$^{-1}$). The observed shift and position suggests the assignment of 792 cm$^{-1}$ to $\delta_{oop}$(CO$_3$) of the C$_{2v}$ monomer and 782 cm$^{-1}$ to the C$_{s}$ monomer. Confirmation of the assignment is provided by the spectra of the other isotopologues. In D$_2$CO$_3$/Ar (Figure 3c) the $\delta_{oop}$(CO$_3$) of the C$_{2v}$ monomer appears at 791 cm$^{-1}$. In H$_2^{13}$CO$_3$/Ar (Figure 3a) $\delta_{oop}$(CO$_3$) of the C$_{2v}$ monomer shifts to lower wavenumber at 768 cm$^{-1}$. The predicted shift of about 25 cm$^{-1}$ between C$_{2v}$ of $^{12}$C and $^{13}$C correlates with the observed shift of 24 cm$^{-1}$ (Table 1). In the spectrum of H$_2^{13}$CO$_3$ not only the C$_{2v}$ monomer is isolated but also the C$_{s}$ monomer. The very weak band at 758 cm$^{-1}$ we assign to $\delta_{oop}$(CO$_3$) of the C$_{s}$ monomer.

All the predicted and observed band positions, isotope shifts and assignments are summarized in Table 1.
Comparing the band positions assigned here to the two conformers of carbonic acid monomers (symmetries $C_{2v}$ and $C_s$) isolated from crystalline $\beta$-$\text{H}_2\text{CO}_3$ and crystalline $\alpha$-$\text{H}_2\text{CO}_3$ a slight disagreement occurs (see Figure S4). The spectra show a small blue shift between the monomers isolated above the $\beta$-polymorph compared to the monomers isolated above the $\alpha$-polymorph. For instance, the $\nu(C=O)$ stretch vibration of the $C_{2v}$ monomer in this work is found in Ar matrix at 1792/1788 cm$^{-1}$ and is blue shifted by about 13 cm$^{-1}$ compared with the isolation product from the crystalline $\alpha$-$\text{H}_2\text{CO}_3$.$^{54}$ The $\nu(C=O)$ stretching mode of the $C_s$ monomer shifts by $2/3$ cm$^{-1}$ from 1830/1826 cm$^{-1}$ ($\alpha$-$\text{H}_2\text{CO}_3$) to 1832/1829 cm$^{-1}$ ($\beta$-$\text{H}_2\text{CO}_3$). Additionally, the matrix splitting in Ar exhibits different intensity patterns, i.e., 1:4 for $\alpha$-$\text{H}_2\text{CO}_3$ and 5:4 for $\beta$-$\text{H}_2\text{CO}_3$ sublimation products, even though the matrix deposition procedure was exactly the same, with the exception of the different sublimation temperatures. These shifts and splittings in the $\nu(C=O)$ signify clues due to different surroundings, or slightly different geometries of the trapped gas-phase molecules. This might be a result of the lower partial pressure that was isolated from above the $\beta$-polymorph. Also differences in the vibrational density of states as a result of the different sublimation temperature might be at the origin of these small shifts of monomer frequencies. We do not fully understand the reason for these shifts presently. Additional experiments on the dependence of the band positions on the sublimation temperature and partial pressure might shed light on this issue in the future.
Figure S1: IR spectra of vapour phase isolated in solid Ar matrix after sublimation of crystalline a) β-H$_2^{13}$CO$_3$, b) β-H$_2$CO$_3$, c) β-D$_2$CO$_3$ at 230 – 260 K. Spectra are shifted for clarity. The assignment of trapped species, namely undecomposed carbonic acid isotopologues (H$_2$CO$_3$) and decomposition products CO$_2$ and H$_2$O are indicated. Please note the break in the ordinate.
Figure S2: Influence of the matrix material on the bands assigned to carbonic acid. Spectra recorded at 6 K in a) Krypton (Kr), b) Argon (Ar). Spectra are shifted for clarity.
Figure S3: Difference spectrum in the C=O stretching region before and after irradiation of the matrix with UV light. Bands pointing upwards indicate an appearing species and bands pointing downwards a disappearing species. a) H$_2$CO$_3$/Ar and b) H$_2$$^{13}$CO$_3$/Ar
Figure S4: Comparison of the $\nu$(C=O) region of carbonic acid vapour isolated in argon after sublimation of a) $\beta$-H$_2$CO$_3$ and b) $\alpha$-H$_2$CO$_3$.

References:


