Supporting Information

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

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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 H_2CO_3 isolated in Ar (as marked in Figure 3b), two of which we assign to the $2\nu_2 + \nu_3$ combination band of CO_2 (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 D_2CO_3 (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 $H_2{}^{13}CO_3$ (Figure 3a) we find the $2\nu_2 + \nu_3$ of $^{13}CO_2$ (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 ν_{as}(OD) of the most abundant monomer, namely C_{2v}, for D_2CO_3 and appear as two bands because of matrix splitting. The assignment to ν_{as}(OH) of the C_{2v} monomer for H_2CO_3 and $H_2{}^{13}CO_3$ is more complicated. We interpret the bands at 3611 and 3607 cm^{-1} (matrix splitting) to the ν_{as}(OH) of the C_{2v} monomer of H_2CO_3, and the band at 3610 cm^{-1} to ν_{as}(OH) of the C_{2v} monomer of $H_2{}^{13}CO_3$. Due to the small amount of the less abundant C_s 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 ν_{as}(OH) of C_{2v} symmetry. In Figure 3b two weak bands appear at 3617 and 3614 cm^{-1}, which we assign to the C_s 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 C_{2v} and C_s 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_2CO_3/Ar (Figure 3c) bands at 1428/1414/1399 cm^{-1} marked with asterisk can be assigned to the ν_2 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_2CO_3. The predicted shift of the asymmetric C-(OH) stretching mode of 68 cm^{-1} between C_{2v} of H_2CO_3 and D_2CO_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 δ_{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_2CO_3/Ar (Figure 4b) shows two peaks with a shift of 27cm^{-1} at 1255 cm^{-1} and 1228 cm^{-1}. The agreement in position and shift leads to the assignment of 1255 cm^{-1} to δ_{ip}(COH) of C_{2v} and 1228 cm^{-1} to C_s. The spectrum of D_2CO_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 δ_{ip}(COD) in the C_{2v} monomer of D_2CO_3 shows a red shift of 212 cm^{-1} to δ_{ip}(COH) of H_2CO_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_2CO_3. The predicted peak at 1166 cm^{-1} for C_{2v} of H_2CO_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_2CO_3. In the region 1160 – 1100 cm^{-1} the spectra in Figure3 show a band located at 1136 cm^{-1} in the H_2CO_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_2CO_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_2CO_3) and 947 cm^{-1} (D_2CO_3) correlates with the predicted shift of 204 cm^{-1}. An assignment of the bands to the symmetric stretching ν(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_2CO_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 β-H_2CO_3 and crystalline α-H_2CO_3 a slight disagreement occurs (see Figure S4). The spectra show a small blue shift between the monomers isolated above the β-polymorph compared to the monomers isolated above the α-polymorph. For instance, the ν(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 α-H_2CO_3.[S4] The ν(C=O) stretching mode of the C_s monomer shifts by 2/3 cm^{-1} from 1830/1826 cm^{-1} (α-H_2CO_3) [4] to 1832/1829 cm^{-1} (β-H_2CO_3). Additionally, the matrix splitting in Ar exhibits different intensity patterns, i.e., 1:4 for α-H_2CO_3 and 5:4 for β-H_2CO_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 ν(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 β-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.

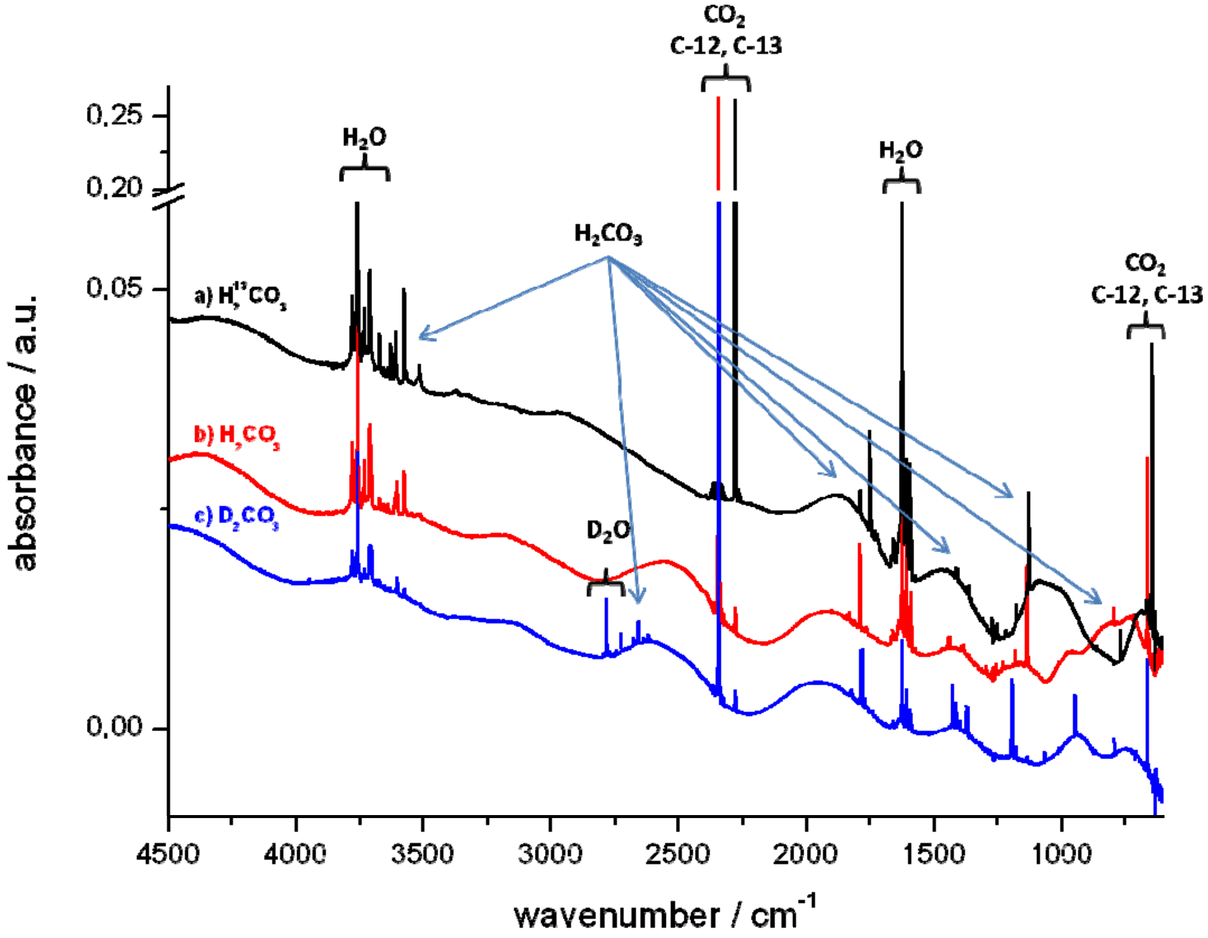

Figure S1: IR spectra of vapour phase isolated in solid Ar matrix after sublimation of crystalline a) β-$H_2{}^{13}CO_3$, b) β-H_2CO_3, c) β-D_2CO_3 at 230 – 260 K. Spectra are shifted for clarity. The assignment of trapped species, namely undecomposed carbonic acid isotopologues (H_2CO_3) and decomposition products CO_2 and H_2O are indicated. Please note the break in the ordinate.

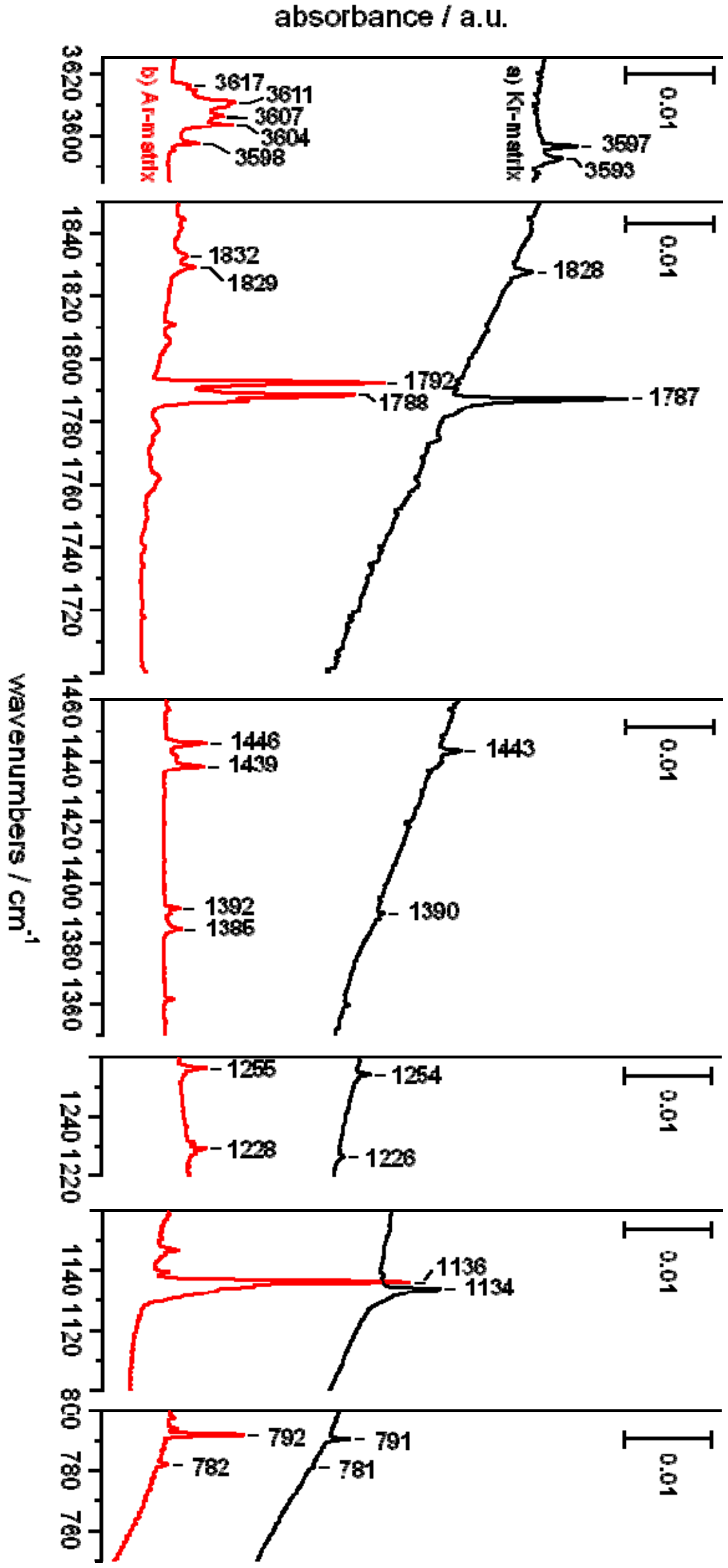

Figure S2: Influence of the matrix material on the bands assigned to carbonic acid. Spectra recorded at 6 K in a) Krypton (Kr), b) Argon (Ar).Spectra are shifted for clarity.

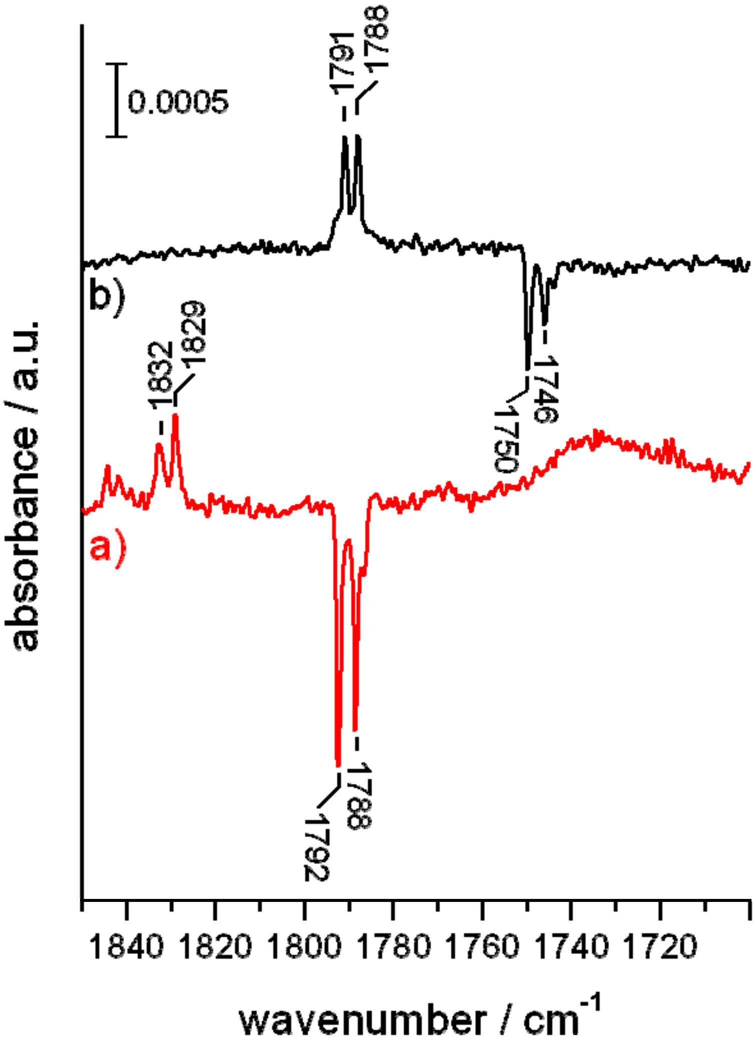

Figure S3: Difference spectrum in the C=O stretching region before and after irradiation of the matrix with UV light. Bands pointing upwards indicate an appearing species and bands pointing downwards a disappearing species. a) H_2CO_3/Ar and b) $H_2{}^{13}CO_3$/Ar

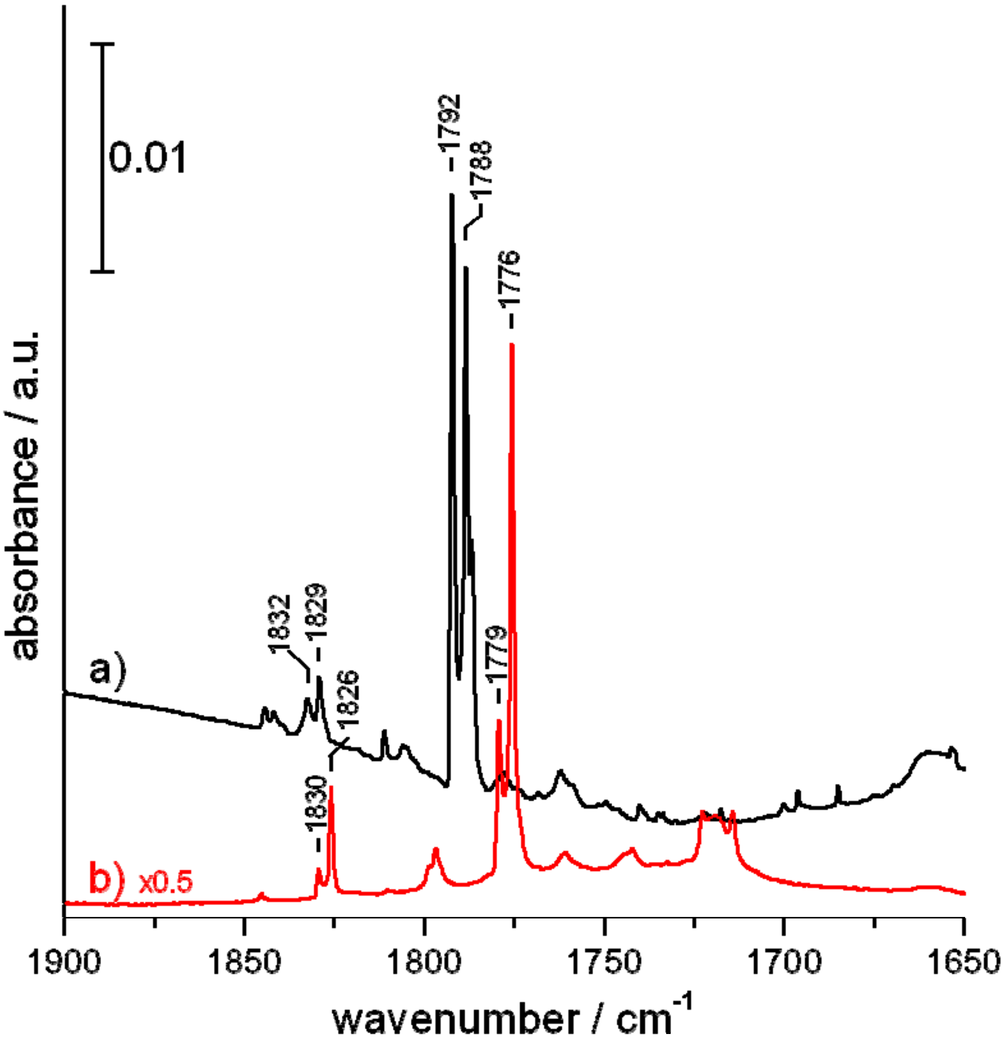

Figure S4: Comparison of the ν(C=O) region of carbonic acid vapour isolated in argon after sublimation of a) β-H_2CO_3 and b) α-H_2CO_3.

References:

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