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IR Spectroscopy

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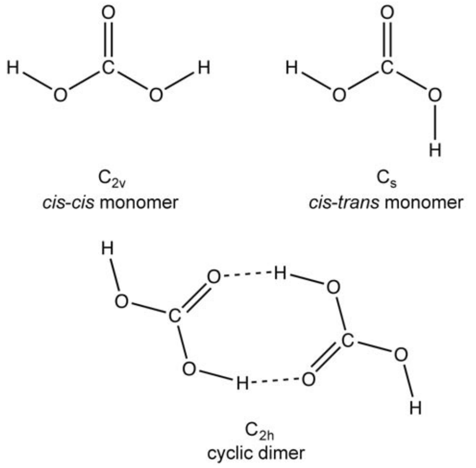
Spectroscopic Observation of Matrix-Isolated Carbonic Acid Trapped from the Gas Phase**

Jürgen Bernard, Markus Seidl, Ingrid Kohl, Klaus R. Liedl, Erwin Mayer, Óscar Gálvez, Hinrich Grothe, and Thomas Loerting**

Carbonic acid (H_2CO_3) is of fundamental importance, for example, for regulation of blood pH, in the acidification of the oceans, and in the dissolution of carbonates. This six-atom molecule commonly found in carbonated drinks in submicromolar concentrations has so far eluded most attempts at isolation and direct detection. Despite the widespread belief that it is a highly instable molecule, the pure solid could be prepared previously,[1–5] and it is thought that solid carbonic acid exists in cirrus clouds on Earth and in astrophysical environments.[6–11] Gas-phase carbonic acid was long thought to immediately decompose to water and carbon dioxide, and therefore to be nonexistent or detectable only as a trace component.[12]

We show herein that gas-phase carbonic acid is stable at temperatures above 200 K and describe the trapping of carbonic acid vapor in an inert matrix at 6 K. Spectroscopic analysis of this matrix reveals that carbonic acid vapor is composed of at least three species (Scheme 1): two monomeric conformers and the cyclic dimer $(H_2CO_3)_2$; carbon dioxide and water are minor components. The molar ratio of the two monomers suggests that the *cis-cis* monomer is the most stable one, and the *cis-trans* monomer is less stable by about 4 kJ mol^{-1}, in accordance with theoretical predictions.[13,14] The stability of gas-phase carbonic acid at temperatures above 200 K suggests that carbonic acid may sublime in astrophysical environments without decomposition, for example, on the poles of Mars or in the coma of comets such as Hale-Bopp, and, therefore, our infrared spectra represent a benchmark for possible identification of naturally occurring carbonic acid vapor.



Scheme 1. Carbonic acid species identified in the current study.

Carbonic acid easily decomposes to carbon dioxide and water at ambient conditions, and even more so in the presence of water.[15] In aqueous solution detection of its formation and/or decomposition is feasible only by use of fast[16] or ultrafast spectroscopic techniques.[17] However, at the temperature of many extraterrestrial environments, its decomposition is hindered. Formation of solid carbonic acid was achieved in laboratory experiments by acid–base chemistry at low temperatures[2] and also under conditions akin to those encountered in space. For example, solid carbonic acid is formed from 1:1 mixtures of solid CO_2 and H_2O ice by proton irradiation[1,3,4] or UV photolyis[4] from the reaction of CO with OH radicals,[11] and in the absence of water from solid CO_2 ice by H implantation.[3,5] It has thus been suggested that solid carbonic acid may be found on the Martian surface, on interstellar grains, on comets, especially in the Oort cloud, and on Jupiter's icy satellites Europa, Ganymede, and Callisto.[6–10]

The α polymorph (spectrum shown in Figure 1 a) is stable up to at least 200 K. Above this temperature it sublimes slowly in vacuo, and it was believed to decompose upon sublimation. Even more thrilling, though, carbonic acid vapor can be recondensed on cold substrates.[8] Hudson recently

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[*] Prof. Dr. H. Grothe
Institut für Materialchemie, Technische Universität Wien
Getreidemarkt 9/BC/01, 1060 Wien (Austria)
Fax: (+43) 1-58801-165122
E-mail: grothe@tuwien.ac.at
Homepage: http://www.imc.tuwien.ac.at
J. Bernard, M. Seidl, Prof. Dr. T. Loerting
Institut für Physikalische Chemie, Universität Innsbruck
Innrain 52a, 6020 Innsbruck (Austria)
Fax: (+43) 512-507-2925
E-mail: thomas.loerting@uibk.ac.at
Homepage: http://homepage.uibk.ac.at/~c724117/
J. Bernard, Dr. I. Kohl, Prof. Dr. K. R. Liedl, Prof. Dr. E. Mayer
Institut für Allgemeine, Anorganische und Theoretische Chemie
Universität Innsbruck (Austria)
Dr. Ó. Gálvez
Instituto de Estructura de la Materia, CSIC Madrid (Spain)

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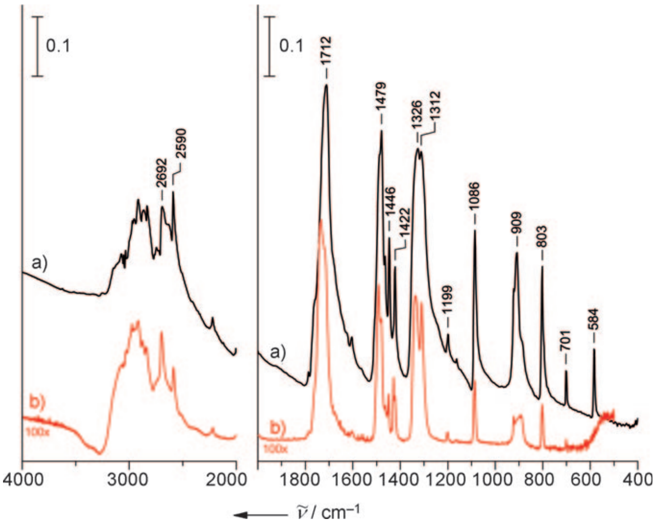

Figure 1. a) IR spectrum of a thin film of crystalline α-H_2CO_3 as prepared by protonation of $KHCO_3$ with HCl in methanolic solution at cryogenic temperatures (80–210 K) and removal of solvent in vacuum. b) IR spectrum of crystalline α-H_2CO_3 obtained after sublimation of the thin film of crystalline α-H_2CO_3 at 210 K, isolation of carbonic acid vapor in an argon matrix at 6 K, and removal of argon in vacuum by heating to 180 K. The good match of the two spectra proves first that carbonic acid has sublimed without decomposition to carbon dioxide at 210 K, and second that the same crystalline polymorph crystallizes from a supercooled methanolic solution and from solid argon. Spectra are shifted vertically for clarity.

emphasized that “this gives cause to hope that gas-phase interstellar H_2CO_3 may one day be detected, adding this elusive species to the other interstellar molecules” and that this exciting challenge is “awaiting the next generation of scientists”.[18]

In order to bear this challenge it is necessary to measure laboratory spectra of gaseous carbonic acid. This task has proven to be so difficult that no one has succeeded so far. The only pieces of evidence that gaseous carbonic acid even exists were provided by Terlouw et al.,[12] who obtained a weak mass spectrometric signal at *m*/*z* 62, by Mori et al., who obtained microwave spectra of *cis-trans* carbonic acid,[14] and by Hage et al., who recondensed solid H_2CO_3 from the gas phase.[8] The extremely low sublimation rates of $10^{-8}\,g\,cm^{-2}\,s^{-1}$ at 200 K estimated by Hage et al.[8] and the vapor pressure of 10^{-7} mbar at 250 K estimated by Moore et al.[19] are quite discouraging for the prospect of measuring laboratory spectra of gaseous carbonic acid. For comparison, typical matrix-isolation experiments of gas-phase species are done with volatile liquids, which have vapor pressures on the order of mbar at room temperature. Defying these odds, we here report infrared spectra of gaseous carbonic acid trapped in a solid matrix of either argon or neon.

Selected regions of the spectra of the matrix-isolated material on a gold mirror recorded at 6 K are depicted in Figure 2. The spectra contain bands assignable to water monomers, dimers, and trimers,[24] carbon dioxide,[25] and traces of methanol trapped in argon;[26] however, water adducts of CO_2 and CH_3OH are absent.[27] These matrix-trapped species can be assigned unequivocally because the band positions typically agree with literature data to within $\pm 0.1\,cm^{-1}$.

The most intense bands depicted in Figure 2, however, cannot be explained by any of the known matrix-isolated species. We argue below that these bands arise from two conformers of the matrix-isolated carbonic acid monomer and the cyclic $(H_2CO_3)_2$ dimer (C_{2h} point group symmetry). The assignments of the bands have been confirmed by selective changes of the experimental conditions: a) $^{12}C/^{13}C$ and H/D isotope shifts, b) changes of the matrix/absorber ratio for identification of dimer bands, c) photolysis of the matrix with UV/Vis light, and d) annealing of the matrix at 20 K and 30 K for monitoring transitions between different conformers. Every trapped species exhibits bands having constant relative intensities, which allows identification in successive experiments. In addition the assignments of monomer versus dimer bands were double-checked by comparison to the spectra of trapped monocarboxylic acid monomers and dimers. Finally, the experimental assignment was validated by comparing the experimental isotope shifts with calculated isotope shifts.

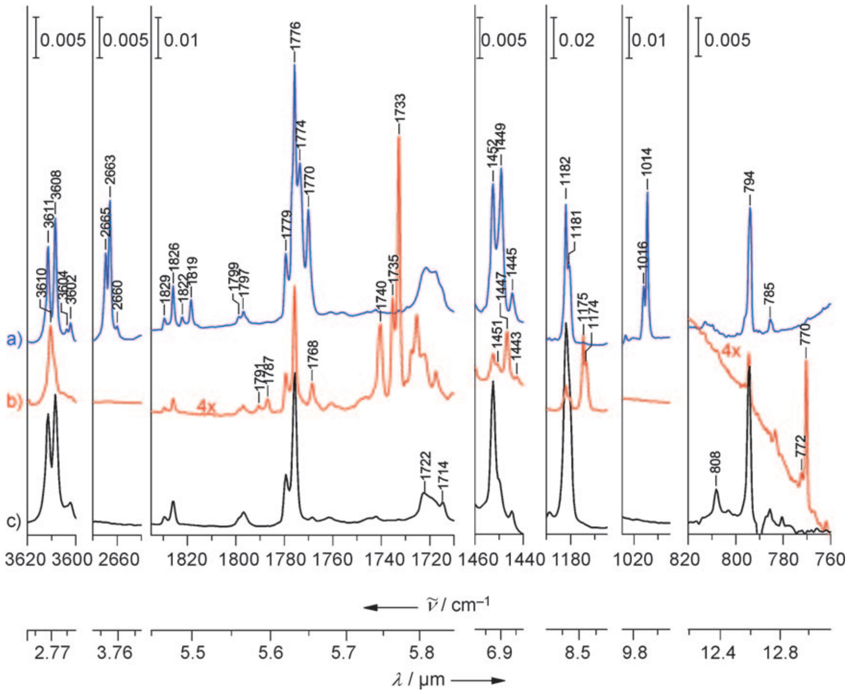

Figure 2. IR spectra of carbonic acid vapor and isotopologues after sublimation of crystalline α-H_2CO_3 at 210 K and isolation in argon matrix at 6 K. The matrix to absorber ratio is estimated to be approximately 1000:1, which is in coincidence with the half-bandwidth of similar isolated molecules. a) D_2CO_3 (50%), b) $H_2{}^{13}CO_3$ (65%), c) H_2CO_3. Spectra are shifted for clarity. Assignment of bands is given in Table 1.

Table 1: Assignment of bands (all values in cm^{-1}; weak bands are denoted with a "w"). For more details see the Experimental Section.

	$H_2{}^{12}CO_3$		$H_2{}^{13}CO_3$	$^{12}C/^{13}C$ shift		$D_2{}^{12}CO_3$	H/D shift		Normal	Assign.	Molec.
in Ne	in Ar	theor.	in Ar	expt.	theor.	in Ar	expt.	theor.	mode		symmetry
3634	3611	3790	3610	1	0.2	2665	946	1031	$\nu(A_1)/\nu(A')$	$\nu_s(OH)$	C_{2v}/C_s
3630	3608	3788	3607	1	0.1	2663	945	1033	$\nu(B_2)$	$\nu_{as}(OH)$	C_{2v}
3628	3604w	3785	3603w	1	0.2	2660w	944	1030	$\nu(A')$	$\nu_{as}(OH)$	C_s
3623	3602w	3783	3601w	1	0.2	2660w	942	1030	$\nu(A_g)/\nu(B_u)$	$\nu(OH)$	C_{2h}
1836	1829/1826	1860	1791/1787	38/39	47	1822/1819	7	14	$\nu(A')$	$\nu(C{=}O)$	C_s
1799	1799/1797	1780	1768/1740	31/57	45				$\nu(B_u)$	$\nu(C{=}O)$	C_{2h}
1727	1722/1714	1716							$\nu(A_g)$	$\nu(C{=}O)$	C_{2h}
1783	1779/1776	1815	1735/1733	44/43	46	1774/1770	6/5	13	$\nu(A_1)$	$\nu(C{=}O)$	C_{2v}
1565		1554							$\nu(A_g)$	$\nu_{as}(C(OH)_2)$	C_{2h}
1515		1520							$\nu(B_u)$	$\nu_{as}(C(OH)_2)$	C_{2h}
1456	1452/1451	1453			32			75	$\nu(B_2)$	$\nu_{as}(C(OH)_2)$	C_{2v}
1427		1401							$\nu(A')$	$\nu_{as}(C(OH)_2)$	C_s
1274w	ca. 1270w	1234							$\nu(B_u)$	$\delta_{ip}(COH)$	C_{2h}
1184w	ca. 1175w	1155							$\nu(A')$	$\delta_{ip}(COH)$	C_s
1187	1182/1181	1166	1175/1174	7	8	1016	167/166	203	$\nu(B_2)$	$\delta_{ip}(COH)$	C_{2v}
811	808	801/800	784 sh	24	25/25			−5/−1	$\nu(A_u)/\nu(B_g)$	$\delta_{oop}(CO_3)$	C_{2h}
798	794	789	772/770	24	25	794	0	1	$\nu(B_1)$	$\delta_{oop}(CO_3)$	C_{2v}
784	785	777	762	23	24	785	0	1	$\nu(A'')$	$\delta_{oop}(CO_3)$	C_s

Ab initio calculations of the band positions of H_2CO_3, D_2CO_3, and $H_2CO_3{\cdot}H_2O$ have been reported before.[13] Since a comparison with the experimental data of the isotopically substituted compounds reported in Figure 2 necessitates also availability of data on $H_2{}^{13}CO_3$ and on other monomer conformers, we repeated the geometry optimization and frequency calculations at the MP2/aug-cc-pVDZ level of theory. The relevant frequencies and isotope shifts are reported in Table 1. According to ab initio calculations three conformations of monomeric carbonic acid are possible,[13] which can be interconverted by rotating around the two OCO–H dihedral angles. The three rotamers representing local potential minima are called *cis-cis* (C_{2v} symmetry), *cis-trans* (C_s symmetry), and *trans-trans*. The C_{2v} monomer is predicted to be the dominant gas-phase species since it is the most stable (because of two weak internal hydrogen bonds). The C_s monomer is predicted to be less stable by about 4–8 kJ mol^{-1} and to be a possible gas-phase species, whereas the *trans-trans* conformation is less stable by more than ≈ 40 kJ mol^{-1} and is not expected to appear in experiments.[13,14] The cyclic dimer $(H_2CO_3)_2$ is stabilized by two strong hydrogen bonds, and the enthalpy of decomposition to carbon dioxide and water is astonishingly close to zero.[28] By contrast, the monomers show a negative enthalpy of decomposition; in other words, they are kinetically stable, but thermodynamically they should decompose. For this reason, an appreciable fraction of the cyclic dimer $(H_2CO_3)_2$ possibly forms and persists in the gas phase. Higher oligomers such as $(H_2CO_3)_3$ are thermodynamically even more stable in the gas phase,[29] but are not thought to occur because an encounter of three or more carbonic acid molecules in the gas phase is extremely unlikely.

In the OH-stretching region there is a triplet at 3611/3608/3602 cm^{-1}, which shows an intensity ratio of 8:10:1, that is, two intense bands and one weak band. A carbonic acid sample, in which roughly 50 % of all H atoms have been replaced by D atoms, shows a similar triplet with a similar intensity ratio at 2665/2663/2660 cm^{-1} in the OD-stretching region. In some spectra, the weak band is resolved as two weak bands of roughly the same intensity. In the calculations it is predicted that a mixture of the C_{2v} monomer, C_s monomer, and C_{2h} dimer shows four bands at 3790/3788/3785/3783 cm^{-1}, which show an H/D isotope shift of roughly 1000 cm^{-1}, but no $^{12}C/^{13}C$ isotope shift, which is in agreement with the experimental data. The two weak bands can be attributed to the C_{2h} dimer and C_s monomer, whereas the most intense band can be attributed to the C_{2v} monomer according to the calculations.

Assuming identical cross-sections, the intensity pattern suggests an abundance ratio of 10:1:1; in other words, the C_{2v} monomer is indeed the most abundant molecule in the matrix. A ratio of 10:1 translates in thermodynamic equilibrium at 210 K to a difference in Gibbs energies $\Delta G(C_{2v}{\rightarrow}C_s)$ of 4.0 kJ mol^{-1}, which is in excellent agreement with the calculations.[13,14] While we observe mainly the C_{2v} monomer, Mori et al. observed exclusively the less stable C_s monomer.[14] We believe this is so because an isomerization to the thermodynamically less stable takes place under the influence of the high voltages applied by Mori et al.[14] Similarly, we observe an isomerization from C_{2v} to C_s under the influence of UV/Vis radiation (see Figure 2 in the Supporting Information).

This picture of almost 90 % C_{2v} monomers and the presence of some C_s monomers and C_{2h} dimers is corroborated also in the other spectral regions shown in Figure 2. In the C=O stretching region at ca. 1700–1850 cm^{-1} the most intense band is located at 1776 cm^{-1} and shows a matrix splitting of 3 cm^{-1}. These bands are attributed to the C_{2v}

monomer. The intense ν(C=O) is observed at very similar positions in small argon-isolated monocarboxylic acids such as formic acid (1767 cm^{-1}), acetic acid (1779 cm^{-1}), and propionic acid (1777 cm^{-1}).[30] Bands at 1826 cm^{-1}, 1797 cm^{-1}, and 1714 cm^{-1} show an intensity of about one-tenth of the most intense band at 1776 cm^{-1}. A predicted shift between the C_{2v} and C_s modes of +45 cm^{-1} compared to the observed +50 cm^{-1} suggests an assignment of the 1826 cm^{-1} band as ν(C=O) of the C_s monomer. In acetic acid the most stable cyclic dimer shows a band at 1720 cm^{-1},[31] very close to the band at 1722 cm^{-1}, which we have assigned to the cyclic carbonic acid dimer in Table 1. After assignment of the species C_{2h}, C_s, and C_{2v} some very weak features (< 1 % of the intensity of the C_{2v} absorptions) remain unexplained; they may, for example, arise from traces of an open dimer[32] or an $H_2CO_3 \cdot H_2O$ adduct. Such species were also observed in matrix-isolated mixtures of water and carboxylic acids.[30,31] The spectral region at 1000–1500 cm^{-1} is the most difficult to interpret since in this region three fundamental modes, namely asymmetric and symmetric C−(OH) stretching and in-plane deformation modes, overlap, and since some of these modes are only weakly IR active. In the spectral region at roughly 750–820 cm^{-1} again this intensity ratio of 1:10:1 is observed for the bands at 808/794/785 cm^{-1}, which are assigned to the out-of-plane deformation of carbonic acid in the $C_{2h}/C_{2v}/C_s$ conformations, respectively. This represents, to the best of our knowledge, the first experimental proof for the existence of dimeric carbonic acid in the gas phase, and also for the existence of more than one monomer conformation.

An important piece of evidence for the success of the isolation of carbonic acid from the gas phase is provided by checking what remains on the gold mirror after removal of the matrix. Heating matrix-isolated carbonic acid to 180 K results in desorption of argon, and to some extent carbonic acid is dragged away from the surface along with argon. However, some carbonic acid molecules remain on the surface even after removal of argon. The spectrum of the sample remaining after evaporation of the matrix is shown in Figure 1 b. This spectrum exhibits a remarkable similarity to the spectrum of the as-produced thin film of carbonic acid shown in Figure 1 a. There is only one band missing in Figure 1 b (at 584 cm^{-1}), which is explained by the fact that the available detector in Vienna had no sensitivity below 600 cm^{-1}. This spectrum can be clearly attributed to crystalline carbonic acid. That is, the isolated carbonic acid molecules form larger aggregates upon removal of argon and finally arrange themselves to produce the same polymorph produced also after removal of the solvent methanol from dissolved carbonic acid.[2,22,23] The main difference between the two spectra is that the absorbance is roughly a factor 100 lower in Figure 1 b, which corresponds to the reduced thickness of the film. The morphology and the texture of the respective crystallites and clusters are in turn responsible for the additional differences in the two spectra.

The matrix data allow firm assignment of the gas-phase bands at (3608 ± 30) cm^{-1} [(2.77 ± 0.02) μm], (1776 ± 7) cm^{-1} [(5.63 ± 0.03) μm], (1452 ± 4) cm^{-1} [(6.89 ± 0.02) μm], (1182 ± 5) cm^{-1} [(8.46 ± 0.03) μm], and (794 ± 4) cm^{-1} [(12.59 ± 0.06) μm] to the C_{2v} monomer. The band positions for the C_s monomer and the C_{2h} dimer are found in Table 1. These appear at a fraction of roughly 10 % here, but may be the main components under different conditions in nature. These are the positions to be employed for the search of carbonic acid in astrophysical environments.

We emphasize that our spectra do not show the rotational transitions observable in high-resolution infrared spectra recorded in astrophysical environments, for instance, by the Infrared Space Observatory (ISO), because rotation is prevented in the matrix cages. Nevertheless, the spectra indicate the exact position of the Q branch and the respective center of the zero gap. Unidentified bands may be attributable to carbonic acid fundamentals on the basis of our data. We, thus, suggest including our data in spectroscopy databases for molecules of astrophysical or atmospheric interest, for example, the Cologne Database for Molecular Spectroscopy (CDMS).[33] In many astrophysical environments solid carbonic acid may form from CO_2 and H_2O upon irradiation and then undergo many sublimation and recondensation cycles without decomposition. We expect gaseous carbonic acid to be present, for example, in the atmosphere of Mars or Venus and in cometary comae or tails once the comet reaches a position sufficiently close to the sun, where the temperature rises beyond 200 K. In principle, one or the other of these four modes may also be caused by other species; the C=O stretching mode of monocarboxylic acids such as formic acid, for instance, is also found at 5.6 μm.[34] However, these do not show any intense bands in the vicinity of 6.9 μm, 8.6 μm, and 12.7 μm, and so the presence of carbonic acid can be distinguished from the presence of monocarboxylic acids by employing the set of four monomer marker bands in high-resolution IR spectra.

Experimental Section

Matrix-isolation spectroscopy is a technique aimed at obtaining pure vibrational spectra of nonrotating molecules by trapping them in an inert and transparent matrix of argon or neon. In the ideal case there is no interaction between the matrix material and the trapped species. In reality, there is a weak interaction resulting in a slight blueshift of individual absorptions. In addition, there may be different geometrical types of cages, resulting in matrix-induced band splittings. These shifts are typically on the order of a few wavenumbers compared to the gas-phase spectrum. Spectra obtained in neon matrices are considered to most closely resemble gas-phase spectra. Similarly, the probably most common matrix material, argon, is known to result in only a small deviation from gas-phase spectra. Comparison between argon and neon matrix reveals the particular impact of the matrix and explains the respective splitting of some bands. Our matrix-isolation study was done in the ultrahigh-vacuum chamber in Vienna (see Figure 1 in the Supporting Information), which was previously employed for successfully isolating reactive species such as halogen oxides.[20,21] Solid carbonic acid was produced for the purpose of matrix isolation as a micrometer-thin film on IR-transparent windows, typically CsI, in Innsbruck using the low-temperature technique developed in the 1990s in this laboratory.[2,22,23] The IR spectrum depicted in Figure 1 a was recorded on the carbonic acid sample after production and coincides with the literature spectrum,[2,22,23] which implies that the thin film is crystalline. The sample was then transported immersed in liquid nitrogen to Vienna, and the matrix-isolation procedure was performed as described in the Supporting Information by subliming solid carbonic acid at 210 K. Gaseous carbonic acid together with argon was deposited at a gold mirror placed a distance of six centimeters from the sample window.

The experimental data in Table 1 ("expt.") are taken from Figure 2 for the argon matrix and from Figure 3 in the Supporting Information for neon matrix. Calculated data ("theor.") were obtained at the MP2/aug-cc-pVDZ level of theory from harmonic frequency calculations of optimized geometries. Three carbonic acid species are considered, namely the *cis-cis* monomer (C_{2v}), the *cis-trans* monomer (C_s), and the cyclic dimer (C_{2h}). Please note that frequencies calculated using MP2 ab initio methods are known to deviate from experimentally observed gas-phase results typically by factors between 0.95 and 1.05. These scaling factors differ for low-frequency and high-frequency modes.[35] Deviations of up to 50 cm^{-1} for modes at <2000 cm^{-1} and up to 200 cm^{-1} for OH-stretching modes are to be expected. Thus, agreement of absolute frequencies is not the basis for assignment of vibrational modes, but rather the shift incurred upon isotopic substitution.

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Keywords: carbonic acid · IR spectroscopy · matrix isolation

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