

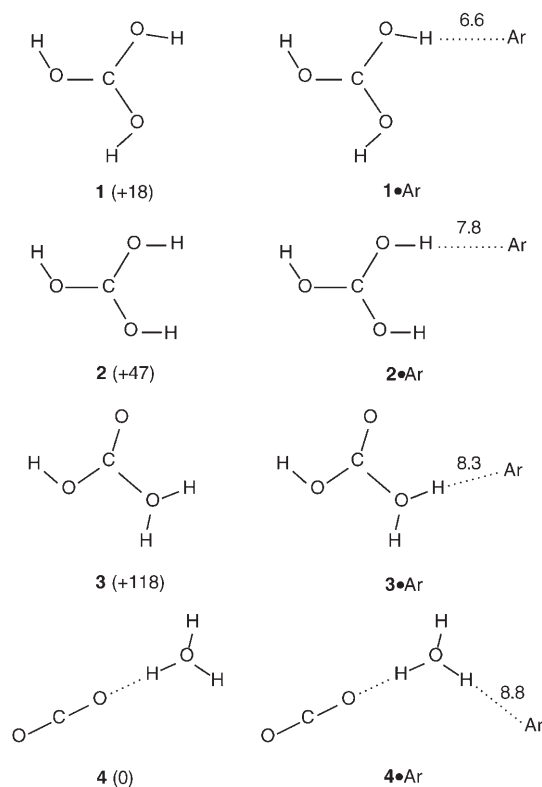
# IR Spectra of Protonated Carbonic Acid and Its Isomeric $\text{H}_3\text{O}^+\cdot\text{CO}_2$ Complex\*\*

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Carbonic acid,  $\text{H}_2\text{CO}_3$ , and its isomeric weakly bound  $\text{H}_2\text{O}\cdot\text{CO}_2$  complex are short-lived intermediates in the hydrolysis of  $\text{CO}_2$ , a process of fundamental importance in geochemistry and biology.<sup>[1–5]</sup> Whereas  $\text{H}_2\text{O}\cdot\text{CO}_2$  has been characterized by spectroscopy,<sup>[6,7]</sup> there is only indirect experimental evidence for the existence of  $\text{H}_2\text{CO}_3$  in the gas phase.<sup>[1,3]</sup> Theoretical calculations predict that isolated  $\text{H}_2\text{CO}_3$  should be stable but that it decomposes into  $\text{H}_2\text{O}$  and  $\text{CO}_2$  in the presence of water.<sup>[2,8–11]</sup> There have been several unsuccessful attempts to generate and characterize gas-phase  $\text{H}_2\text{CO}_3$  by heating solid  $\text{H}_2\text{CO}_3$ <sup>[3]</sup> or  $\text{NH}_4\text{HCO}_3$ .<sup>[12]</sup> Herein we describe the properties of gas-phase protonated  $\text{H}_2\text{CO}_3$  and report the first spectroscopic identification of the fundamental  $\text{C}(\text{OH})_3^+$  carbocation and its  $\text{H}_3\text{O}^+\cdot\text{CO}_2$  isomer by argon-tagging photodissociation spectroscopy.

Quantum chemical calculations demonstrate that there are several isomers on the  $[\text{C}_3\text{H}_3\text{O}_3]^+$  potential-energy surface (**1–4**, Figure 1).<sup>[13,14]</sup> The most stable structure corresponds to the hydrogen-bonded  $\text{H}_3\text{O}^+\cdot\text{CO}_2$  complex (**4**,  $E_{\text{rel}} = 0$ ). The attraction is dominated by charge-induced dipole and charge–quadrupole interaction leading to nearly linear hydrogen bonding.<sup>[15,16]</sup> The predicted dissociation energy of  $62 \text{ kJ mol}^{-1}$  is in good agreement with the binding enthalpy of  $64 \text{ kJ mol}^{-1}$  measured by high-pressure mass spectrometry.<sup>[17]</sup>

Protonation of  $\text{H}_2\text{CO}_3$  at the carbonyl group results in two planar isomers of the trihydroxycarbenium ion, *anti*- and *syn*- $\text{C}(\text{OH})_3^+$ . The *anti* structure (**1**,  $C_{3h}$ ,  $E_{\text{rel}} = 18 \text{ kJ mol}^{-1}$ ) is separated by a barrier of  $50 \text{ kJ mol}^{-1}$  from the less stable *syn* structure (**2**,  $C_s$ ,  $E_{\text{rel}} = 47 \text{ kJ mol}^{-1}$ ). Conversion between the  $\text{C}(\text{OH})_3^+$  isomers and **4** is suppressed by a high isomerization barrier ( $214 \text{ kJ mol}^{-1}$ ). In the NMR, IR, Raman, and X-ray crystallography spectra of  $\text{C}(\text{OH})_3^+$  in superacid solutions or corresponding salts only the *anti* isomer was observed.<sup>[18,19]</sup> Finally, a fourth nonplanar  $[\text{C}_3\text{H}_3\text{O}_3]^+$  isomer can be generated by protonation of  $\text{H}_2\text{CO}_3$  at a hydroxyl group (**3**,  $C_1$ ,



**Figure 1.** Structures, relative energies (left, in  $\text{kJ mol}^{-1}$ ), and intermolecular binding energies (right, in  $\text{kJ mol}^{-1}$ ) of various isomers of  $[\text{C}_3\text{H}_3\text{O}_3]^+$  and  $[\text{C}_3\text{H}_3\text{O}_3]^+\cdot\text{Ar}$  calculated at the B3LYP/6-311G\*\* level. The positive charge has been omitted in each structure for clarity.

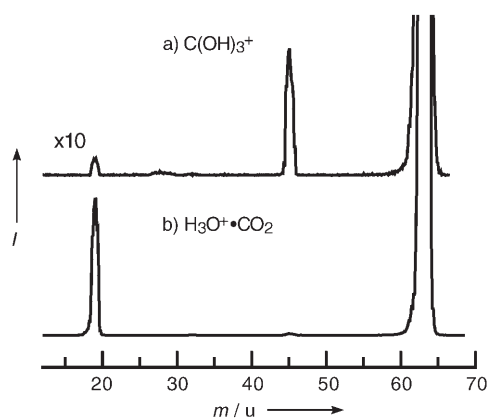
$E_{\text{rel}} = 118 \text{ kJ mol}^{-1}$ ), leading to a hitherto undetected complex of  $\text{H}_2\text{O}$  and  $\text{OCOH}^+$ <sup>[14]</sup> with a binding energy of  $105 \text{ kJ mol}^{-1}$ .

Electron ionization (EI) of diethyl carbonate is known to selectively produce  $\text{C}(\text{OH})_3^+$  ions through consecutive elimination of a vinyl radical and ethene.<sup>[13,14]</sup> They could be distinguished from  $\text{H}_3\text{O}^+\cdot\text{CO}_2$  complexes made by EI of a  $\text{H}_2\text{O}/\text{CO}_2$  mixture by their different fragmentation patterns in metastable decay (MD) and high-energy (8 keV) collision-induced dissociation (CID).<sup>[13,14]</sup> This work takes advantage of low-energy (8 eV) CID spectra for the assignments of isomers. Specifically, the major collision fragments of  $\text{C}(\text{OH})_3^+$  and  $\text{H}_3\text{O}^+\cdot\text{CO}_2$  correspond to  $\text{OCOH}^+$  and  $\text{H}_3\text{O}^+$ , respectively (Figure 2). Experimental conditions can be optimized to favor exclusive production of either  $\text{C}(\text{OH})_3^+$  or  $\text{H}_3\text{O}^+\cdot\text{CO}_2$  isomers.

Although mass spectrometry experiments can distinguish between different isomers, they do not provide direct structural information. Therefore, the highly sensitive

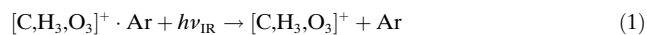
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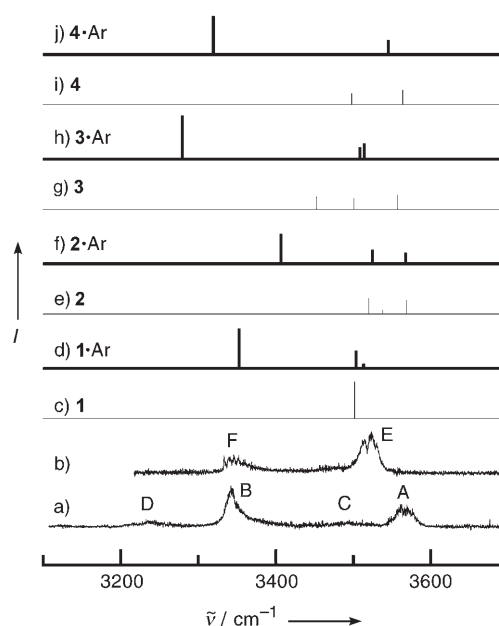
**Figure 2.** CID spectra of mass-selected  $[\text{C},\text{H}_3,\text{O}_3]^+$  ions (63 u) prepared by EI of diethyl carbonate (a) and by EI of a  $\text{H}_2\text{O}/\text{CO}_2$  mixture (b). Major fragment ions correspond to  $\text{H}_3\text{O}^+$  (19 u) and  $\text{OCOH}^+$  (45 u). Both spectra are normalized with respect to the parent-ion intensity. Spectrum (a) is vertically expanded by a factor of 10.

method of single-photon IR photodissociation (IRPD) spectroscopy of mass-selected ions<sup>[15]</sup> was employed here to determine the structures of the  $[\text{C},\text{H}_3,\text{O}_3]^+$  ions and to directly probe the acidities of their O–H bonds. IRPD spectra of cold ions can be recorded with this approach only if the IR photon energy ( $E = 42 \text{ kJ mol}^{-1}$  for  $\nu_{\text{IR}} = 3500 \text{ cm}^{-1}$ ) surpasses the lowest dissociation energy of the ion. As the calculated dissociation energies of all four  $[\text{C},\text{H}_3,\text{O}_3]^+$  isomers exceed typical IR photon energies, Ar atoms are attached to the ions to facilitate resonant single-photon fragmentation [Eq. (1); Ar tagging].<sup>[20,21]</sup>



To investigate the effect of Ar on the spectroscopic properties of  $[\text{C},\text{H}_3,\text{O}_3]^+$ , the minimum-energy structures and IR spectra of the relevant  $[\text{C},\text{H}_3,\text{O}_3]^+ \cdot \text{Ar}$  isomers were calculated. For all of them, Ar forms a nearly linear hydrogen bond to one of the available acidic OH protons (Figure 1) with comparable binding energies (6.6–8.8  $\text{kJ mol}^{-1}$ ). The major effects of the complexation on the  $[\text{C},\text{H}_3,\text{O}_3]^+$  ions are an elongation of the O–H donor bond, a reduction in the wavenumber and an enhancement in the IR intensity of the corresponding OH stretch vibration, and shifts and splittings arising from reducing the symmetry. Figure 3 compares computed IR spectra of **1–4** with those of their Ar complexes in the OH stretch range. The IR spectra of **1–4** show pronounced differences in the positions and intensities of the OH stretch bands, and these differences are amplified by Ar complexation, thus making IRPD spectroscopy a suitable tool for identifying the  $[\text{C},\text{H}_3,\text{O}_3]^+$  isomers through their Ar complexes.

The IRPD spectrum of  $[\text{C},\text{H}_3,\text{O}_3]^+ \cdot \text{Ar}$  generated by EI of the  $\text{H}_2\text{O}/\text{CO}_2/\text{Ar}$  mixture is shown in Figure 3a. Comparison with the calculated stick spectra of the  $[\text{C},\text{H}_3,\text{O}_3]^+ \cdot \text{Ar}$  isomers immediately suggests that **4**·Ar is the dominant carrier for these bands. Bands A and B observed at 3566 and 3343  $\text{cm}^{-1}$  can be assigned to the free and Ar-bound OH stretch vibrations predicted at 3545 and 3319  $\text{cm}^{-1}$ , respectively.



**Figure 3.** IR absorption stick spectra of  $[\text{C},\text{H}_3,\text{O}_3]^+$  and  $[\text{C},\text{H}_3,\text{O}_3]^+ \cdot \text{Ar}$  isomers calculated at the B3LYP/6-311G\*\* level (c–j; scaling factor of 0.95) compared to experimental IRPD spectra of  $[\text{C},\text{H}_3,\text{O}_3]^+ \cdot \text{Ar}$  complexes prepared from the Ar/ $\text{H}_2\text{O}/\text{CO}_2$  mixture (a) and the Ar/diethyl carbonate mixture (b).

The nearly symmetric shape of band A and blue shading of band B are consistent with the assignments to free and hydrogen-bonded OH stretch modes.<sup>[15]</sup> The  $\text{CO}_2$ -bonded OH stretch mode of **4**·Ar is predicted to occur outside the scanned range (at 2869  $\text{cm}^{-1}$ ). The two much weaker bands D and C near 3237 and 3493  $\text{cm}^{-1}$  in the IRPD spectrum may tentatively be attributed to the Ar-bound and free OH stretch modes of **3**·Ar, which are predicted to be near 3279 and 3511  $\text{cm}^{-1}$ , respectively. It is conceivable that a small amount of **3** may be produced in the ion source, because both  $\text{H}_2\text{O}$  and  $\text{OCOH}^+$  are present in the  $\text{H}_2\text{O}/\text{CO}_2/\text{Ar}$  ion-source plasma.

Comparison of the IRPD spectrum of  $[\text{C},\text{H}_3,\text{O}_3]^+ \cdot \text{Ar}$  generated by EI of the diethyl carbonate/Ar mixture shown in Figure 3b with the simulated spectra clearly demonstrates that **1**·Ar is the primary absorber. The bands F and E at 3343 and 3519  $\text{cm}^{-1}$  are attributed to the Ar-bound and free OH stretch modes of **1**·Ar, which are predicted to be at 3352 and 3508  $\text{cm}^{-1}$ , respectively. The spectrum lacks any noticeable contributions from other  $[\text{C},\text{H}_3,\text{O}_3]^+ \cdot \text{Ar}$  isomers, in particular from **2**·Ar. On the basis of the similar Ar binding energies and calculated IR intensities, **2** must be less abundant than **1** by at least one order of magnitude, in agreement with the predicted lower stability of the *syn* versus the *anti* structure of  $\text{C}(\text{OH})_3^+$ . No features attributable to **3**·Ar were observed in the experimental spectra, in agreement with the much higher energy of isomer **3**.

The  $\nu_{\text{OH}}$  wavenumber in isolated *anti*- $\text{C}(\text{OH})_3^+$  can be estimated from the **1**·Ar spectrum to be about 3520  $\text{cm}^{-1}$  (band E, 3519  $\text{cm}^{-1}$ ) because the shifts and splittings induced by Ar complexation are predicted to be small for the free OH modes. In contrast, the  $\nu_{\text{OH}}$  absorptions of **1** in its salts with  $[\text{SbF}_6]^-$  (3457 and 3390  $\text{cm}^{-1}$ ) or  $[\text{AsF}_6]^-$  (3409  $\text{cm}^{-1}$ )<sup>[13]</sup> are

strongly red-shifted, reflective of the large impact of the counterions on the O–H bonds. The  $\nu_{\text{OH}}$  wavenumber and its complexation shifts provide an indirect measure of the OH bond strength and the acidity of the OH protons, respectively. Comparison of the  $\nu_{\text{OH}}$  value of **1** (ca. 3520  $\text{cm}^{-1}$ ) with the  $\nu_{\text{OH}}$  value of  $\text{H}_3\text{O}^+$  (av. 3499  $\text{cm}^{-1}$ )<sup>[22]</sup> demonstrates that the O–H bonds in **1** are slightly stronger and shorter than those in  $\text{H}_3\text{O}^+$  ( $d(\text{O–H}) = 0.9757$  vs. 0.9797 Å). On the other hand, the O–H bonds in  $\text{H}_3\text{O}^+$  are significantly more acidic than those in **1**, leading to stronger and shorter hydrogen bonds with Ar ( $D_0 = 13.2$  vs. 6.6  $\text{kJ mol}^{-1}$ ,  $d(\text{H–Ar}) = 2.086$  vs. 2.275 Å) and correspondingly larger  $\nu_{\text{OH}}$  red shifts upon complexation. The latter observation is consistent with a proton affinity value for  $\text{H}_2\text{CO}_3$  (predicted as 769  $\text{kJ mol}^{-1}$ )<sup>[14]</sup> that is larger than that for  $\text{H}_2\text{O}$  (691  $\text{kJ mol}^{-1}$ )<sup>[23]</sup>. As expected, the O–H bonds in the cation **1** are much weaker than those in the isoelectronic neutral compound  $\text{B}(\text{OH})_3$  ( $\nu_{\text{OH}} \approx 3520$  vs. 3705  $\text{cm}^{-1}$ )<sup>[24]</sup>.

It is instructive to contrast the binding of Ar to **1** and to the simplest carbenium ion,  $\text{CH}_3^+$ . IR spectra and calculations demonstrate that the positive charge in the  $\text{CH}_3^+$  ion is localized on the C atom, and as a result, Ar binds to the vacant electrophilic  $2p_z$  orbital of  $\text{CH}_3^+$ , leading to a  $C_{3v}$ -symmetrical structure of  $\text{CH}_3^+\cdot\text{Ar}$  with a strong charge-transfer bond (binding energy 56.8  $\text{kJ mol}^{-1}$ )<sup>[25–28]</sup>. The hydrogen-bonded  $\text{CH}_3^+\cdot\text{Ar}$  structure has a far lower binding energy (3.6  $\text{kJ mol}^{-1}$ ). In contrast, the IR spectra and calculations for  $\text{C}(\text{OH})_3^+\cdot\text{Ar}$  confirm previous conclusions<sup>[18,19]</sup> that the charge in  $\text{C}(\text{OH})_3^+$  is largely delocalized, and as a result, the hydrogen-bonded complex is more stable (6.6  $\text{kJ mol}^{-1}$ ) than the C-bound one (0.8  $\text{kJ mol}^{-1}$ ).

The results presented herein characterize isomers of protonated carbonic acid and provide a glimpse of the properties of carbonic acid itself. Future research in this area will focus on studying protonated carbonic acid with variable degrees of solvation by Ar,  $\text{CO}_2$ ,  $\text{N}_2$ , and most importantly,  $\text{H}_2\text{O}$ . Characterization of protonated carbonic acid with different degrees of solvation will improve our understanding of processes occurring during  $\text{CO}_2$  hydrolysis and chemical reactions involving simple carbocations.

### Experimental and Theoretical Methods

IRPD spectra of  $[\text{C}_2\text{H}_3\text{O}_3]^+\cdot\text{Ar}$  complexes were recorded in a tandem quadrupole mass spectrometer (QMS1 + 2) coupled to an ion source and an octopole ion trap.<sup>[25]</sup> The ion source combines a pulsed supersonic beam expansion with EI. For Ar complexes of  $\text{C}(\text{OH})_3^+$ , the gas mixture was obtained by passing Ar at a pressure of  $p = 7$  bar through a reservoir filled with diethyl carbonate ( $T = 300$  K). For Ar complexes of  $\text{H}_3\text{O}^+\cdot\text{CO}_2$ , the gas mixture was Ar and  $\text{CO}_2$  (ratio > 20:1) at  $p = 3$  bar passing over ice ( $T = 260$  K). The  $[\text{C}_2\text{H}_3\text{O}_3]^+\cdot\text{Ar}$  ions were mass selected by QMS1 and irradiated in the octopole ion guide with a tunable IR laser pulse ( $\nu_{\text{IR}}$ ) generated by an optical parametric oscillator laser. Vibrational excitation led to the loss of Ar from  $[\text{C}_2\text{H}_3\text{O}_3]^+\cdot\text{Ar}$  [Eq. (1)]. The resulting  $[\text{C}_2\text{H}_3\text{O}_3]^+$  fragment ions were selected by QMS2 and monitored as a function of  $\nu_{\text{IR}}$  to obtain

the IRPD spectrum. CID spectra of mass-selected  $[\text{C}_2\text{H}_3\text{O}_3]^+$  ions with a laboratory kinetic energy of 8 eV were obtained by introducing air into the octopole region ( $p = 10^{-5}$  mbar). Quantum chemical calculations were carried out at the B3LYP/6-311G\*\* level of theory. Minima were located on the potential-energy surface corrected for basis-set superposition error. Harmonic vibrational wavenumbers were scaled by a factor of 0.95 and all energies were corrected for harmonic zero-point energies.

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