אוניברסיטת בן-גוריון בנגב
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Real time generation and observation of carbonic acid

Carbonic acid is formed when carbon dioxide comes into contact with water. This fundamental aqueous species has been observed for the first time by scientists of the Max Born Institute for Nonlinear Optics and Short Pulse Spectroscopy in Berlin, Germany. In a collaboration with a research group of the Ben Gurion University of the Negev (Beersheva, Israel), they succeeded in protonating bicarbonate ions to generate carbonic acid which was then detected by ultrafast spectroscopy. In contrast to what is often suggested in chemistry textbooks, carbonic acid is stable on sufficiently long time scales to allow for its detection. From their studies, they also determined the acidity constant of carbonic acid with higher accuracy than what was previously available. These results, published in Science Express, will prove of importance in fields where the aqueous chemistry of carbon dioxide plays a major role such as in the blood physiology of living animals, the acidification of the oceans, chemical weathering of rock formations, and carbon dioxide sequestration schemes using sediment layers.

Carbon dioxide (CO_2) can be hydrated to form carbonic acid (H_2CO_3). However, carbonic acid is not a stable molecule in aqueous solution as it readily re-dissociates. Additionally, carbonic acid may release a proton to water yielding a bicarbonate ion. „Before the advent of ultrafast spectroscopy, the protonation reaction of bicarbonate giving carbonic acid was inaccessible because of limited time resolution“, says Dr. Erik T.J. Nibbering. That is why, even though this formation reaction has been postulated by scientists for more than a century, no reports on the detection of carbonic acid as an intact species in water exist until now. Indeed, even the isolated molecule in the gas phase (e.g. in interstellar clouds) or in frozen ice matrices (e.g. in the polar ice cap of mars or at asteroid surfaces), was detected for the first time only about twenty years ago.

Using femtosecond laser pulses, the scientists investigated the formation dynamics of carbonic acid from the protonation of bicarbonate ion. They used a photoacid in order to generate protons since photoacids are chemical compounds that are converted from very weak acids to strong acids by a light pulse. „These photoacids are ideal for dynamical studies, because they release a proton at a precisely determined instant in time: when the light pulse arrives“, says Katrin Adamczyk, one of the Ph.D. students involved in this work.

The researchers sent ultrashort light pulses (“pump pulses”) through a solution containing bicarbonate and the photoacid. Upon excitation the photoacids release a proton which is captured by bicarbonate and thus converted into carbonic acid. With a second light pulse (“probe pulse”) the researchers measured molecular vibrations characteristic of all the species in solution. In such a way, they can determine how much carbonic acid has been generated at a particular time. The reaction time is given by the delay between the pump and probe pulse. By measuring spectra for many such delays, one obtains snapshots at different reaction times. These delay times are on femtosecond time scales. A femtosecond is a millionth of a billionth of a second (10^{-15} second). They were able to determine that the protonation of bicarbonate yielding carbonic acid occurs in 6 picoseconds, i.e. 6000 femtoseconds. They also found that carbonic acid persists for at least one nanosecond with no dehydration into carbon dioxide occurring on this timescale.

Because carbonic acid only dissociates on time scales much longer than nanoseconds, but definitely shorter than milliseconds, and its equilibrium concentration is so low, chemists could only roughly determine the acidity constant (pK_a-value) to be 3.6 ± 0.3. „The standard chemical experiment to determine the acidity of molecules – by a titration – leads to a much higher value for the acidity: 6.35; the reason for this is that the additional dissociation of carbonic acid into carbon dioxide and water influences strongly the outcome of the titration experiment.“ says Ph.D. student Mirabelle Prémont-Schwarz, who also contributed to this work. In the ultrafast protonation experiment, and using mathematical models describing the diffusion influenced bimolecular reaction between the photoacid and bicarbonate, the much slower dissociation of carbonic acid into carbon dioxide and water does not affect the outcome of the experiment. As a result the true acidity constant for carbonic acid has been derived to be 3.45 ± 0.15. From this one can conclude that carbonic acid is a moderate acid, with an acid strength between formic acid and chloroacetic acid.

„The relative long lifetime of carbonic acid and its moderate acidity should be taken into account in studies which involve the aqueous chemistry of carbon dioxide,“ argues Nibbering. The reason for this is that carbonic acid is not just a short lived intermediate when carbon dioxide is transformed into bicarbonate and protons. Carbonic acid has a distinct identity of its own which could play a role for example in the reaction of carbonic acid at interfaces between the aqueous phase and sediment layers, e.g. at the bottom of the oceans or in subsurface injection reservoirs used in carbon dioxide sequestration schemes.

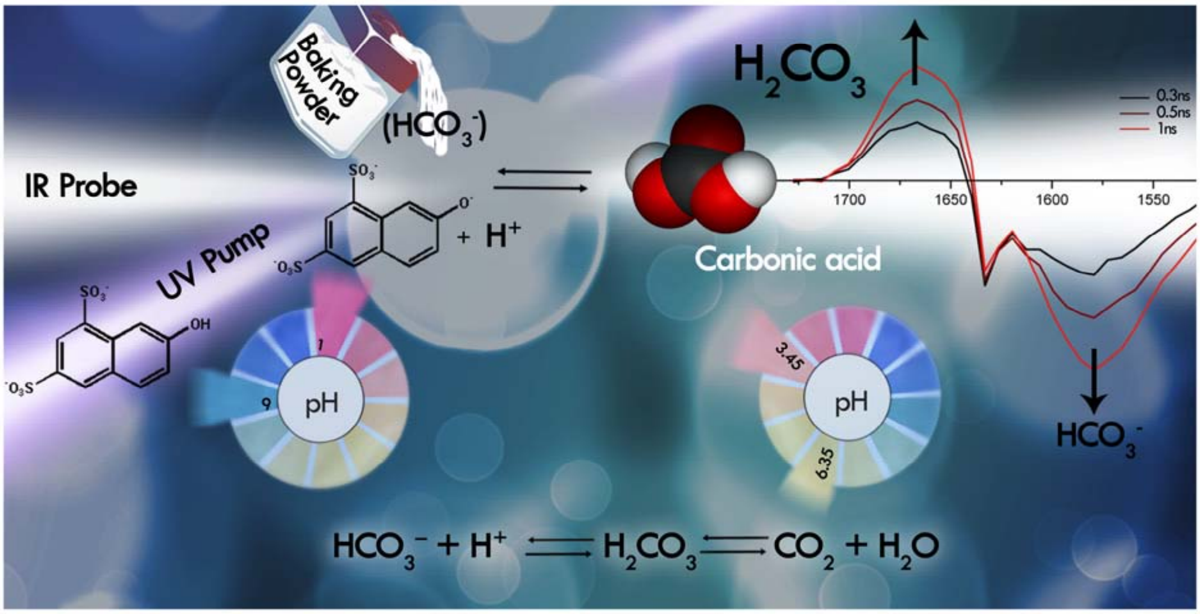

Figure: Ultrafast protonation of bicarbonate using UV-photoexcited naphthol photoacid generates carbonic acid, H_2CO_3, in aqueous solution as followed by infrared-active marker modes

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