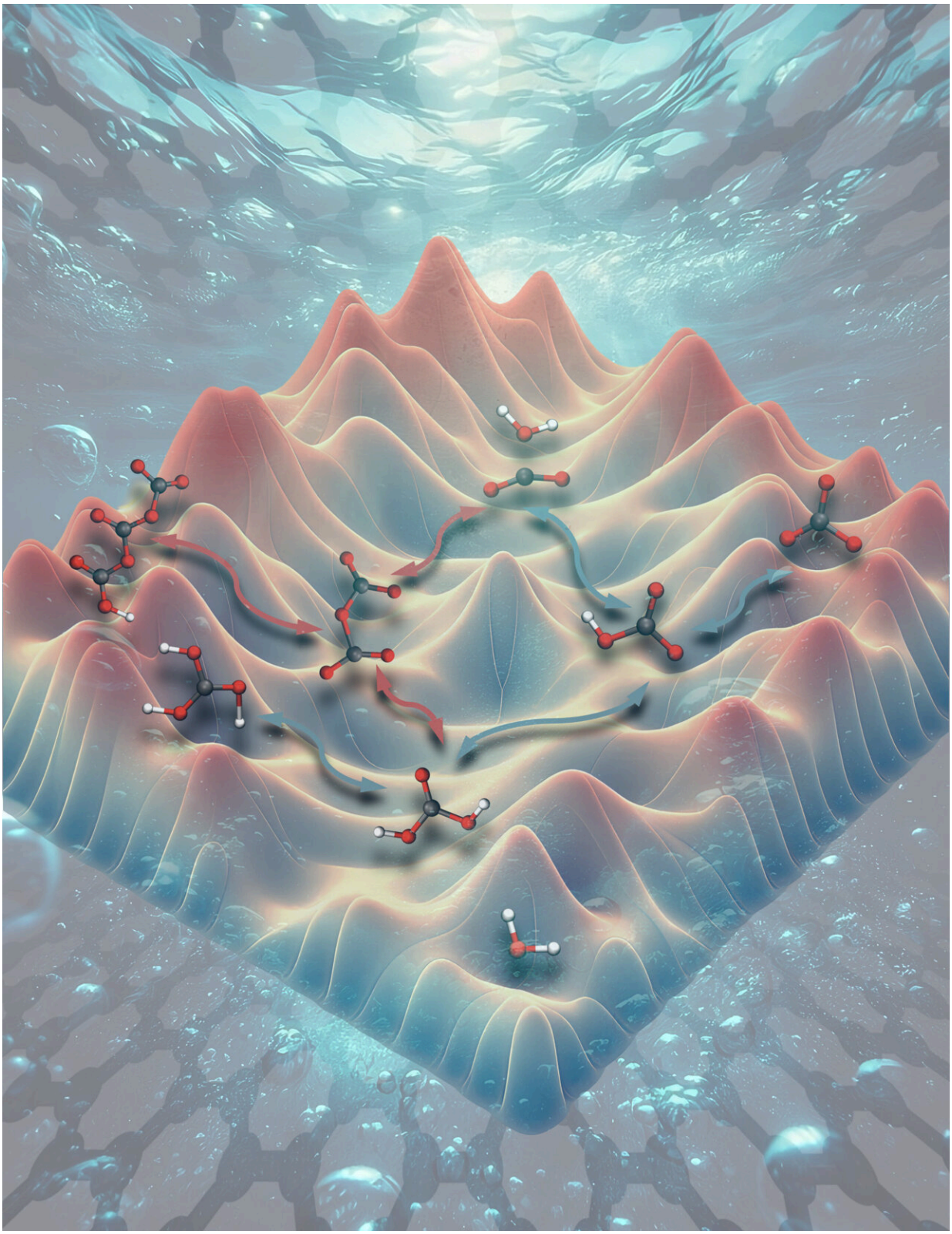
Reaction pathways of carbon dioxide in supercritical water revealed

January 24 2025



The first-principles Markov state models elucidate the complex reaction kinetics

of CO_2 in supercritical water. Credit: Prof. Chu Li, Jie Shu, Prof. Ding Pan

A research team has made significant discoveries regarding the complex reaction mechanisms of carbon dioxide (CO_2) in supercritical water. These findings are crucial for understanding the molecular mechanisms of CO_2 mineralization and sequestration in nature and engineering, as well as the deep carbon cycle within the Earth's interior. This understanding will help pave the way for new directions in future carbon sequestration technologies. The study was published in the *Proceedings of the National Academy of Sciences*.

The dissolution of CO_2 in water and its subsequent hydrolysis reactions are key processes for effective carbon capture and mineralization storage, playing a significant role in carbon sequestration to mitigate global warming. Prof. Pan's team developed and applied first-principles Markov models to reveal the reaction mechanisms of CO_2 with supercritical water in both bulk and nanoconfined environments.

They discovered that pyrocarbonate ($C_2O_5^{2-}$) is a stable and important reaction intermediate in nanoconfined environments, which had been previously overlooked because pyrocarbonate is highly unstable and decomposes rapidly in aqueous solutions. The unexpected appearance of pyrocarbonate is related to the superionic behavior of the confined solutions.

Additionally, they found that carbonation reactions involve collective proton transfer along transient water chains, which exhibits concerted behavior in bulk solutions but proceeds stepwise under nanoconfinement. This study demonstrates the great potential of first-principle Markov models in elucidating complex reaction kinetics in aqueous solutions.

"Our innovative approach has enabled us to discover a new pathway for CO_2 dissolution involving pyrocarbonate ions," said Prof. Chu Li, Research Assistant Professor from the Department of Physics.

"Our efficient computational method does not rely on prior knowledge and can automatically identify reaction pathways without human bias, revealing unknown reaction mechanisms based on the first principles of physics."

Prof. Ding Pan added, "Our method employs unsupervised learning techniques to reveal the importance of large oxocarbons in aqueous reactions under extreme conditions, while also demonstrating that nanoconfinement can be an effective strategy for regulating chemical processes. These findings are expected to provide new directions for future carbon sequestration technologies."

The study was led by Associate Professor Pan from the Department of Physics and the Department of Chemistry at the Hong Kong University of Science and Technology (HKUST), in collaboration with Prof. Yuan Yao from the Department of Mathematics.

More information: Chu Li et al, Unveiling hidden reaction kinetics of carbon dioxide in supercritical aqueous solutions, *Proceedings of the National Academy of Sciences* (2024). DOI: 10.1073/pnas.2406356121

Provided by Hong Kong University of Science and Technology