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## Reversed interfacial fractionation of carbonate and bicarbonate evidenced by X-ray photoemission spectroscopy and theory

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The fractionation of ions at liquid interfaces and its effects on the interfacial structure are of vital importance in many scientific fields. Of particular interest is the aqueous carbonate system, which governs both the terrestrial carbon cycle and physiological respiration systems. We have investigated the relative fractionation of carbonate, bicarbonate, and carbonic acid at the liquid/vapor interface finding that both carbonate ( $\text{CO}_3^{2-}$ ) and carbonic acid ( $\text{H}_2\text{CO}_3$ ) are present in higher concentrations than bicarbonate ( $\text{HCO}_3^-$ ) in the interfacial region. While the interfacial enhancement of a neutral acid relative to a charged ion is expected, the enhancement of doubly charged, strongly hydrated carbonate anion over the singly charged, less strongly hydrated bicarbonate ion is surprising. As vibrational sum frequency generation experiments have concluded that both carbonate and bicarbonate anions are largely excluded from the air/water interface, the present results suggest that there exists a significant accumulation of carbonate below the depletion region outside of the area probed by sum frequency generation. These observations are confirmed by first principles XPS simulations, and free energy simulations reveal a second minima in the interfacial region for the bicarbonate anion that is not present in either carbonate or carbonic acid. This suggests a new theory of aqueous carbonate solvation based on a competition between electrostatic screening and entropic, solvent dynamical effects.

<sup>1</sup>Royce K. Lam, Jacob W. Smith, Anthony M. Rizzuto, Osman Karshog, Hendrik Bluhm, and Richard J. Saykally, *J. Chem. Phys.* **146**, 094703 (2017).

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