

University of Louisville
Department of Chemistry
Waliul Islam Khan
Literature Seminar

When: May 4, 2023

Time: **12:00 p.m.**

Location: CBL-16

Protonated Hydrates and Their Application in H⁺ Ion Transport

Abstract:

The H⁺ ion (proton) is often represented as an acid source in chemical reactions and neglects the presence and interactions with water molecules in both aqueous and non-aqueous solutions. In aqueous solution the H⁺ in water is better represented as the hydronium ion, H₃O⁺, which contains three strongly hydrogen bonded water molecules in the first solvation sphere. This ion is known as the Eigen cation (H₉O₄⁺). Another hydrated H⁺ is the Zundel cation (H₅O₂⁺), which contains four additional strongly hydrogen bonded water molecules and is known as the Reed cation (H₁₃O₆⁺)¹. In non-aqueous solvents, such as acetonitrile, the hydrated H⁺ is best represented as the H₇O₃⁺ ion². The structures of H₃O⁺, H₅O₂⁺ and H₁₃O₆⁺ have been confirmed by x-ray crystallography and are thought to play an integral role in proton mobility in different media and under different environmental conditions. For example, in the membrane bound protein gramicidin A, H⁺ migration is proposed to occur along water wires via the DeGrotthuss mechanism involving the hydronium ion during proton shuttling. In bulk water, however, the Eigen and Zundel ions participate in the translocation of H⁺ through the medium⁴.

This seminar will provide recent insight into the structure and electronic properties of hydrated forms of H⁺. One study examines the nature of the first hydration sphere of the hydronium ion in acetonitrile using Infrared Spectroscopy (IR), X-ray absorption spectroscopy (XAS) and provides spectroscopic evidence for the H₇O₃⁺ ion². While a second study examines the structure of D₂O in the presence of different D⁺ concentrations on various M(111) surfaces, where M=Pt, Au and Cu. This study employs Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM) to image the hydrated H⁺ species and uses the AFM tip to force the interconversion between the Zundel and Eigen cations on both Pt and Au surfaces⁵. These results provide useful insight into the nature of the hydrated H⁺ species involved in the hydrogen evolution reaction (HER) catalyzed by these metals in acidic media. Low Zundel concentration can favor hydrogen production by Heyrovsky mechanism, while high Zundel concentration favors hydrogen production by Tafel mechanism⁶.

References:

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6. Zhu, J., Hu, L., Zhao, P., Lee, L. Y. S., & Wong, K. Y. (2019). *Chemical reviews*, 120(2), 851-918.