Ben-Gurion University of the Negev

אוניברסיטת בן גוריון בנגב

Departmental Seminar

Department of Chemistry

Monday, May 22, 2023

Time: 14:30

Bldg. 43 Room 015

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Interchanging configurations of the hydrated proton based on the solvation structure of protonated water in acetonitrile

The fierce debate on the structure of the core solvation motif of the proton in water is finally approaching a closure based on recent experimental and theoretical studies by several research groups. Our contribution to relaxing the on-going debate between the $H_5^+O_2$ Zundel-like and the $H_3^+O/H_9^+O_4$ Eigen-like proton solvation perspective has been to provide strong theoretical and experimental evidence [1-4] - supporting the hybrid Eigen/Zundel $H_7^+O_3$ protonated water trimer motif as being the solvation core of the proton in water. A key observation in this recent advance is the 3-fold hierarchy in hydrogen bonds which exists in both the chain-like arrangement and the star-like arrangement of the protonated water tetramer $H_9^+O_4$ in water which encompass both the so-called deformed Zundel and deformed Eigen features within the 1st and 2nd solvation shells of the aqueous proton [1-4].

We have advanced the study of protonated water using NMR, IR and XAS spectroscopies to include large, protonated water clusters in acetonitrile. Our experimental and theoretical studies indicate that the reversibly fluctuating (back-and-forth) trimeric structure solvating the proton persists without translocating the proton on a time scale of 1 ps before an irreversible proton transport occur by the so-called Grotthuss mechanism which involves irreversible rearrangements in the 2nd solvation shell of the proton. We argue that NMR spectroscopy is sensitive to the fluctuating geometries of the hydrated proton while accurately sampling the average geometry of countless transient proton-water arrangements. We further show that IR absorption spectroscopy of protonated water allows to separate between the absorption of the shared proton sub-unit and the 3rd water molecule sub-unit of the protonated trimer. Combining the 3 spectroscopic methods enable to capture the solvation structure of the hydrated proton and its transport in water.

References

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[2] E. Kozari, M. Sigalov, D. Pines, B. P. Fingerhut, E. Pines, ChemPhysChem, 22, 716 (2021).

[3] M. Ekimova, C. Kleine, J. Ludwig, M. Ochmann, T. E. G. Agrenius, E. Kozari, D. Pines, E. Pines, N. Huse, P. Wernet, M. Odelius, E.T. J. Nibbering, Angew. Chem. Int. Ed. 61(46):e202211066 (2022).

[4] E. Kozari, D. Pines, M. Sigalov, B. P. Fingerhut, E. Pines, Trimeric core structure of large protonated water solvates in acetonitrile. Paper in preparation