

Abstract Submitted
for the MAR15 Meeting of
The American Physical Society

Electric Field: Maker *and* Breaker of Molecular co-operativity: the paradigm of $(\text{CH}_3\text{OH})-(\text{H}_2\text{O})_n$ [$n = 1-4$] hetero-clusters¹ RAJEEV PATHAK, Department of Physics, University of Pune — Hydrogen-bonded hetero-clusters of methanol and water: $(\text{CH}_3\text{OH})-(\text{H}_2\text{O})_n$ [$n = 1-4$], when subjected to an externally applied dipolar electrostatic field, exhibit remarkable stability up to their characteristic maximal threshold field strengths. Moderate fields below the threshold endow a given cluster with enhanced stability against dissociation, whereas beyond the threshold its HOMO-LUMO gap abruptly closes down, resulting into structural breakdown. The electric field thus plays a dual role of a maker *and* breaker of molecular co-operativity in a hydrogen-bonding scenario. *Ab initio* investigations on these clusters employing M06-2X hybrid functional with a 6-311++G(2d, 2p) basis set reveal the structural evolution of the conformers with increasing electric field strengths: structural deformations, enhancement in their dipole moments with concomitant decrease in their HOMO-LUMO gaps interspersed with abrupt changes in these attributes when the clusters “open out.” Energetics quantify the stability of the clusters in field, while the IR vibrational spectra bring out shifts in the normal modes with marked emergence of exotic low-frequency O-H stretches as precursors of breakdown at the threshold field strengths.

¹We thank the Center for Development of Advanced Computing, Pune for computational time.

Rajeev Pathak
Department of Physics, University of Pune

Date submitted: 09 Oct 2014

Electronic form version 1.4