Simulating the infrared spectra of small protonated water clusters

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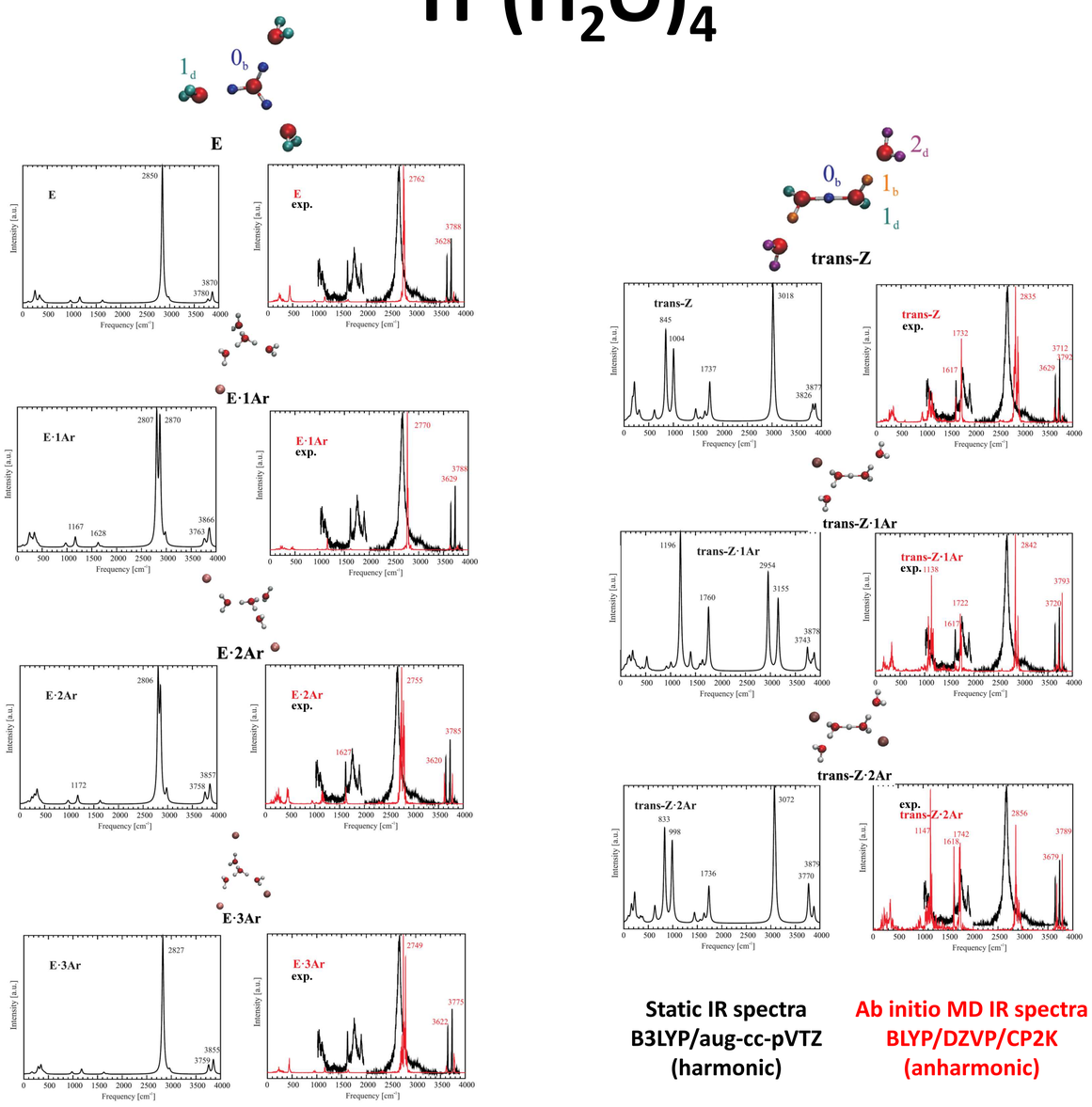
Is the Eigen cation dominant in the protonated water tetramer and pentamer as widely believed?

$H^+(H_2O)_4$



Static IR spectra B3LYP/aug-cc-pVTZ (harmonic)

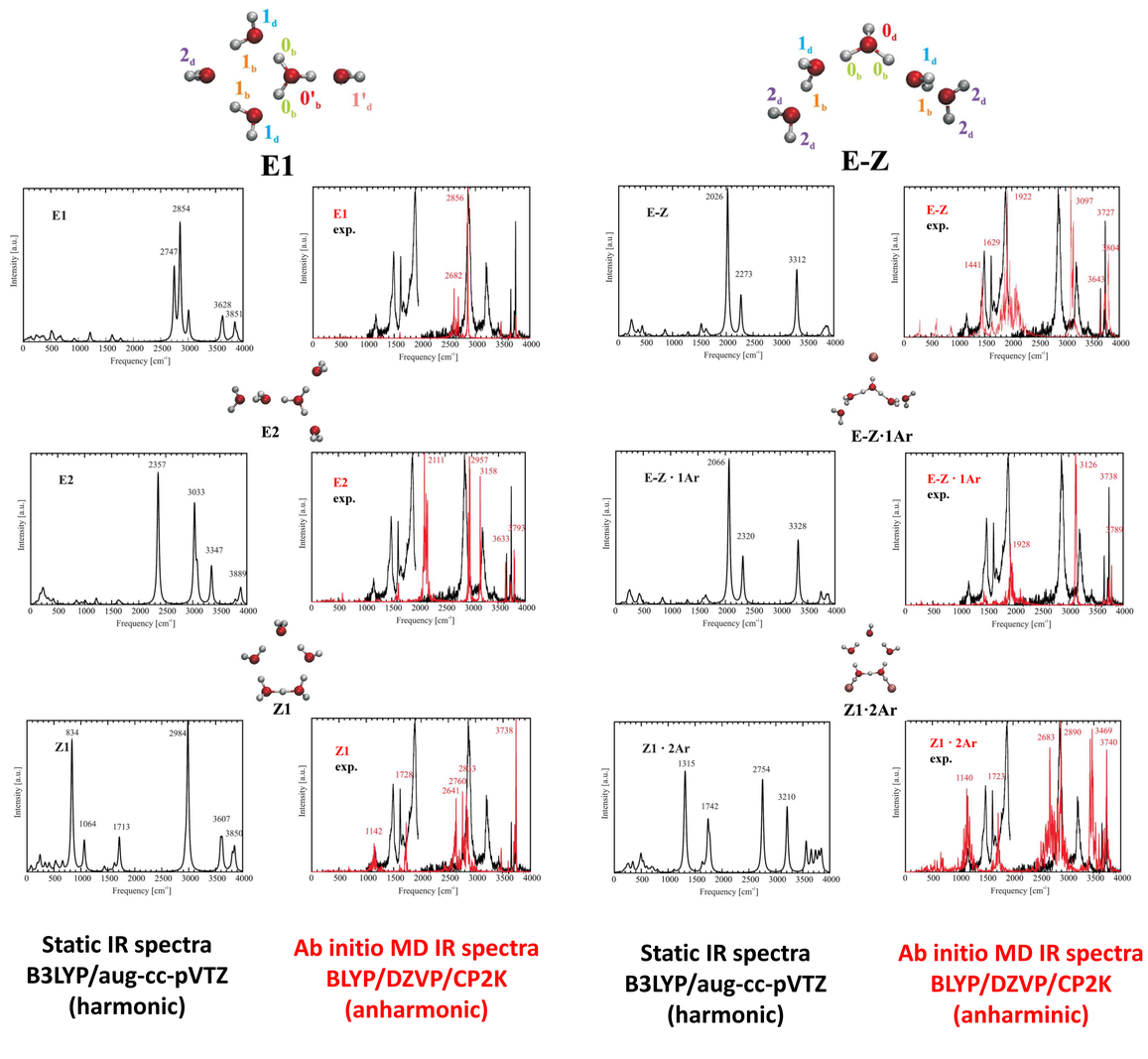
Ab initio MD IR spectra BLYP/DZVP/CP2K (anharmonic)

exp. – J. M. Headrick, et al. Science 308 (2005) 1765

E – Eigen isomer

Z – Zundel isomer

$H^+(H_2O)_5$



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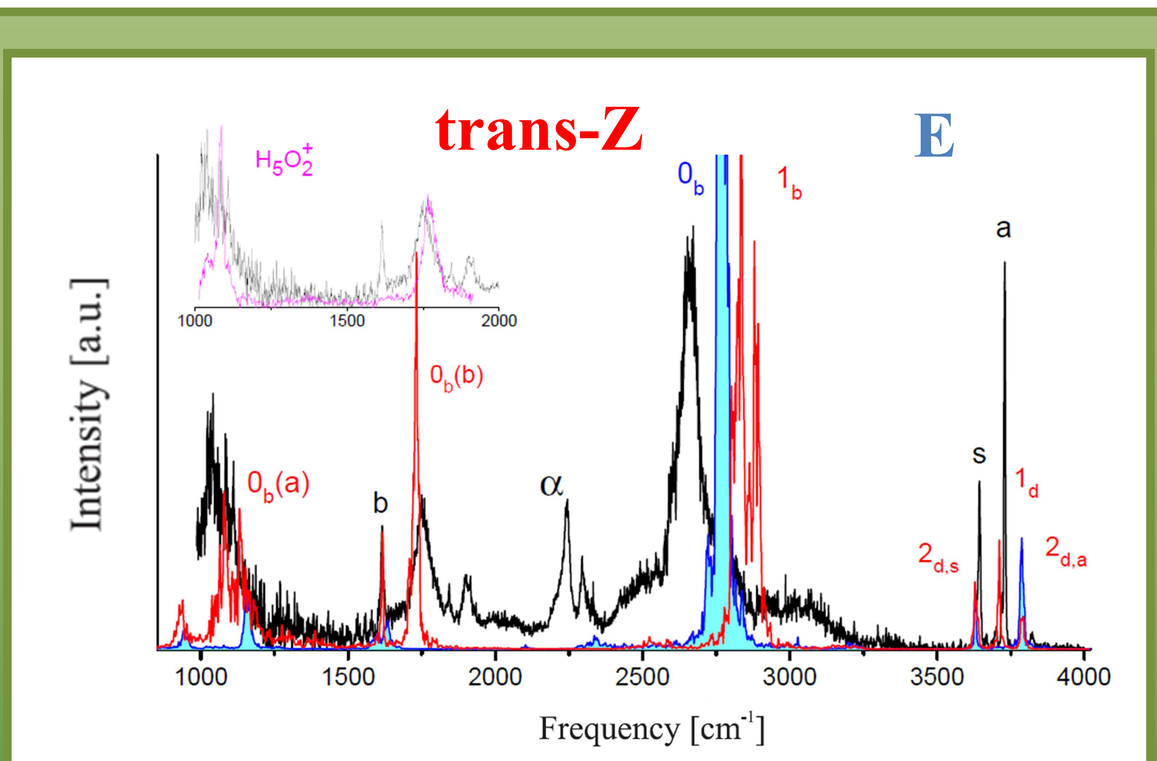
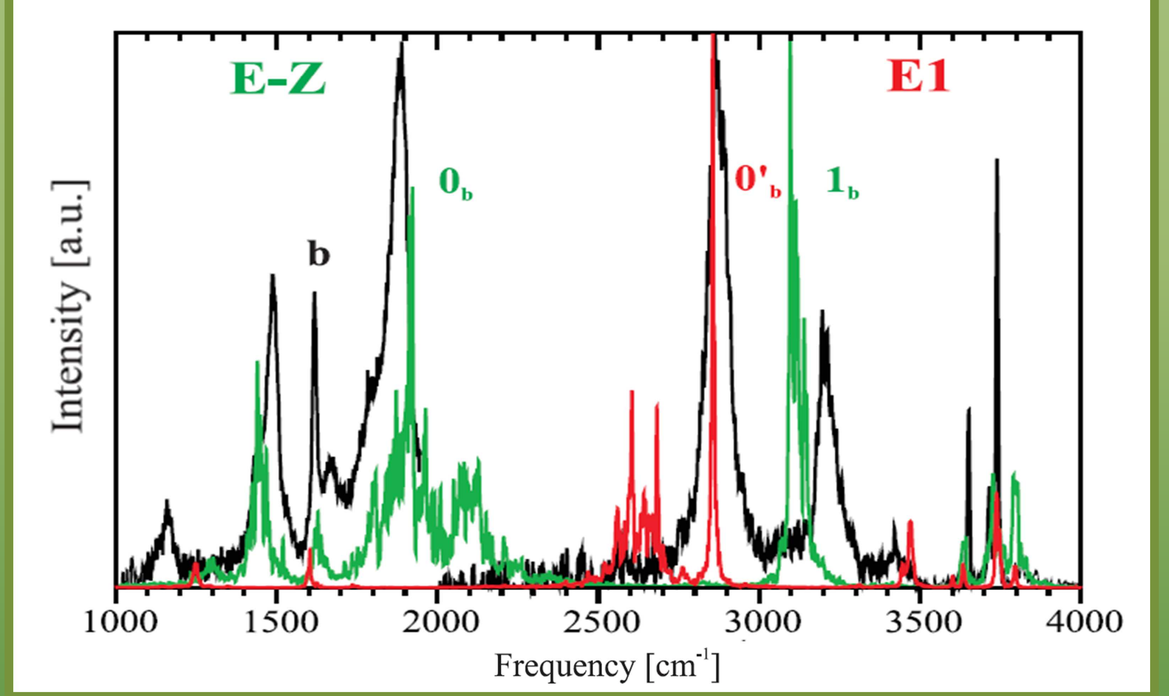
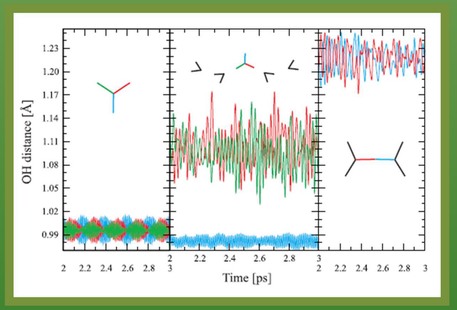




Conclusions:

The conventional interpretation of the IR spectra of small protonated water clusters based on a branched Eigen isomer is inadequate, and a higher energy linear isomer must also be contributing. Its core is either a Zundel core (for $H^+(H_2O)_4$) or an Eigen-Zundel hybrid (for $H^+(H_2O)_5$).



W. Kulig and N. Agmon, *J. Phys. Chem. B* 118 (2014) 278

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