

# The Structural-Spectral-Energetic Correspondence for hydrogen bonded networks: Adding an Energy component to *Badger's rule* <sup>#</sup>

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Badger's rule represents a relationship between intermolecular distances and bond force constants [1]. Its application to hydrogen bonded systems since its introduction [2] has paved the path for establishing the *structural-spectral correspondence*, i.e. the correlation between molecular structure and vibrational spectra. Since the Infrared (IR) spectra of aqueous clusters in the 3,000-4,000  $\text{cm}^{-1}$  range represent a fingerprint of the underlying hydrogen bonding network, this correspondence has been previously used for the assignment of cluster structures from the experimentally measured spectra [3].

We will discuss an extension of this relationship to include an energetic component. The resulting *Structural-Spectral-Energetic Correspondence* establishes an energetic ordering between the different isomers of hydrogen bonded networks based on properties of their spectral signatures. The proposed scheme is based on the origin of the most red-shifted, infrared (IR) active, hydrogen bonded OH stretching vibrations for  $(\text{H}_2\text{O})_n$  in the cluster regime  $2 \leq n \leq 21$ . These correspond to localized vibrations of donor OH stretches that are connected to neighbors via "strong" (water dimer-like) hydrogen bonds and belong to a water molecule with a "free" OH stretch. The orientational dependence of the nearest neighbor molecules, associated with the most IR active vibrations, is the basis of a discrete model used for the fast screening of hydrogen bonded networks.

We will present the results of the application of this discrete model for the energetic screening of all 30,026 networks of the pentagonal dodecahedron  $5^{12} (\text{H}_2\text{O})_{20}$  and the  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_{20}$  clusters that arise for a fixed position of the oxygen atoms due to the Bernal-Fowler rules. In both cases, initial screening with the discrete model and subsequent quantitative refinement with a hierarchy of theoretical methods ranging from classical interaction potentials, density functional theory (DFT) and first principles electronic structure (MP2) methods leads to the identification of new global minima that were previously missed using other global minimization approaches. The implications of this scheme for the analysis of the structural patterns in liquid water in conjunction with recently measured IR spectra will be also discussed.

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<sup>#</sup> This work was supported by the Division of Chemical Sciences, Geosciences and Biosciences, Office of Science, US Department of Energy. Battelle operates the Pacific Northwest National Laboratory for the US Department of Energy.