I. Can the four-coordinated, penta-valent oxygen in protonated water clusters be detected through experimental vibrational spectroscopy?

Structure, dynamical and spectroscopic properties of protonated and hydroxide water clusters have remained an important challenge with fundamental implications. While proton transfer is widely accepted to follow the "Grotthuss" mechanism, the "hole hopping" hydroxide transfer process has been challenged and the existence and role of a four-coordinated (pentavalent) hydroxide oxygen as an intermediate in hydroxide transport in aqueous phase is debated. If a four-coordinated oxygen intermediate exists and can be detected experimentally, this would provide valuable insight into the hydroxide migration mechanism. Furthermore, this would be of fundamental chemical interest on account of the presence of five groups (the four non-bonded water molecules and the hydroxyl hydrogen) around a central oxygen.

Here[1], we construct the smallest hydroxide water cluster, OH$^+$ (H$_2$O)$_6$, in gas phase that (a) could support a stable hydroxide ion with a four-coordinated hydroxide oxygen and (b) display hydroxide ion migration. We study the energetic stability and dynamical evolution of the system at different internal temperatures, and analyze the corresponding "dynamically averaged" vibrational density of states inclusive of nuclear quantum effects. We find that dynamical effects and conformational averaging play an important role on the vibrational spectrum of hydroxide water clusters. Our tool includes ab initio molecular dynamics (Born Oppenheimer dynamics and ab initio atomistic molecular dynamics (AIMD)), and single point optimization and harmonic frequency calculations using DFT and post-Hartree Fock methods. Our aim is to use the dynamically averaged vibrational signatures to provide a spectroscopic probe for the existence of a four-coordinated, pentavalent central oxygen. Since the clusters of the size described in this study, are accessible to vibrational action spectrum experiments [2, 3], our predictions of the hydroxide transfer pathways and dynamically averaged vibrational spectra can be tested.

II. Dynamical averaging in protonated water clusters

Protonated water clusters have been the subject of a rich experimental and theoretical literature. Early mass spectrometric studies [4] on protonated clusters revealed H$_3$(H$_2$O)$_n$ and H$_4$(H$_2$O)$_n$ species to have greater stability as compared to clusters of similar sizes. Due to this fact, the well-studied H$_4$(H$_2$O)$_n$ species has often been referred to as a "magic number" cluster and its additional stability has been proposed as the reason for its greater abundance in the earth's stratosphere. Shin et al.[5] reported detailed infrared data and theoretical studies for small clusters including H$_4$(H$_2$O)$_n$. The authors show that the spectral features observed for the dangling hydroxyl bond stretch collapse into a single feature for 21 and 22 molecule clusters then re-emerge as a multiplet for 23 molecule and larger clusters.

 Harmonic frequencies and dynamically averaged spectra

As is to be expected based on our dynamical analysis, no single structure presented above completely dominates the vibrational spectrum at temperatures accessible to action spectrum experiments (100K-250K) due to the small energy differences between the accessible isomers. The harmonic vibrational spectral features in the isomers are very different as highlighted in the two figures on the left (below). There is a great deal of fluctuation in the 2000-3500cm$^{-1}$ and all peaks responsible for this fluctuation come from the internal hydrogen bonds in the cluster between hydroxide oxygen and neighboring water molecules.

To proceed further we first note that an experimental measurement would yield an ensemble average of the spectroscopic features seen from all the isomers. We use ab initio dynamics to construct an ensemble average. To construct the temperature dependent, dynamically averaged, vibrational spectrum we consider the Fourier transform of the dipole correlation function inclusive of nuclear quantum effects within the harmonic approximation. The dipole correlation function is constructed from the AIMD simulation results.

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References