

Dynamically averaged vibrational spectroscopy of protonated and hydroxide water clusters: Insights from *ab initio* molecular dynamics

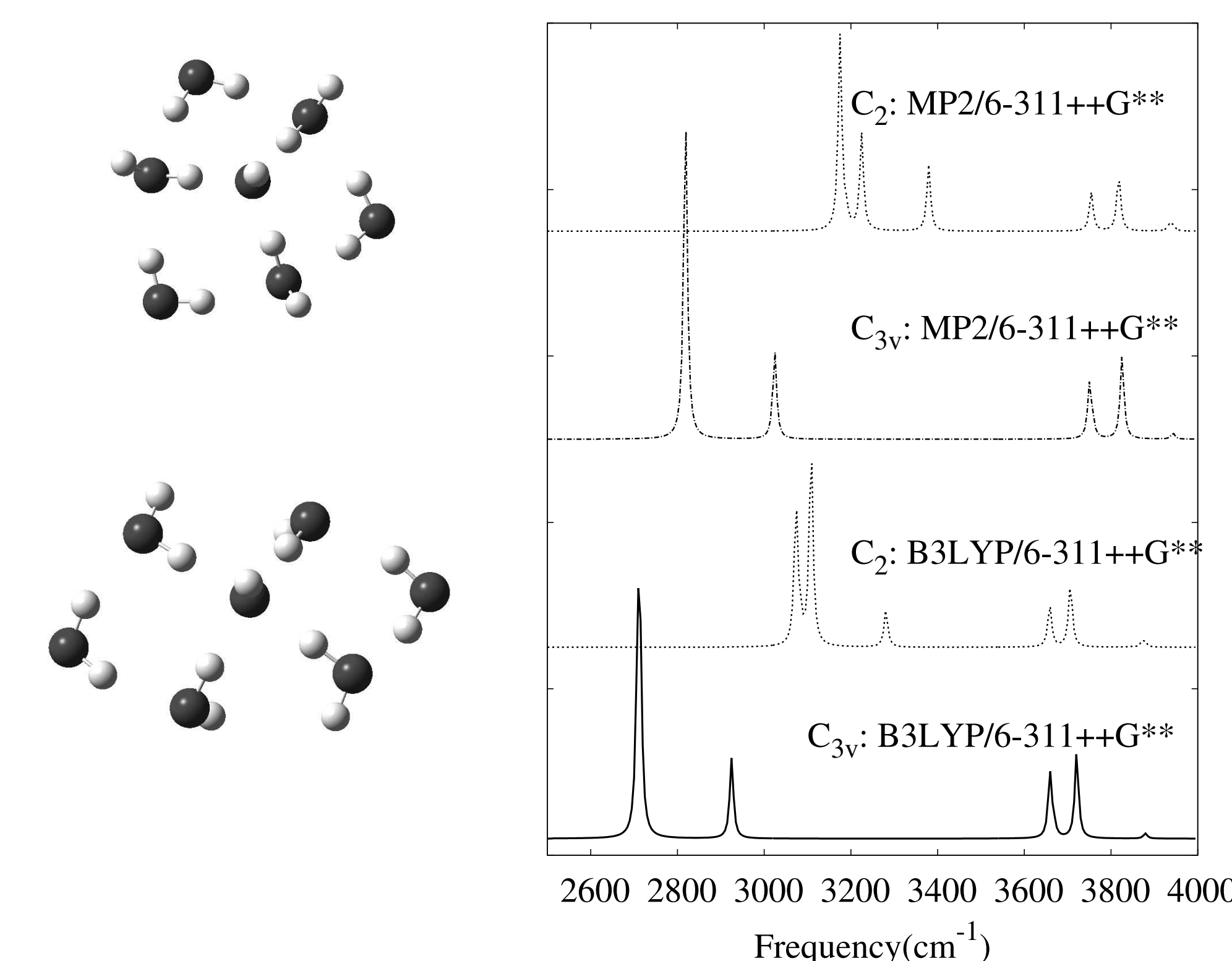
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This poster considers a detailed study of the vibrational spectroscopy in the protonated and hydroxide water clusters using *ab initio* molecular dynamics, inclusive of nuclear quantum effects.

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

Structure, dynamics and spectroscopy of protonated, un-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.

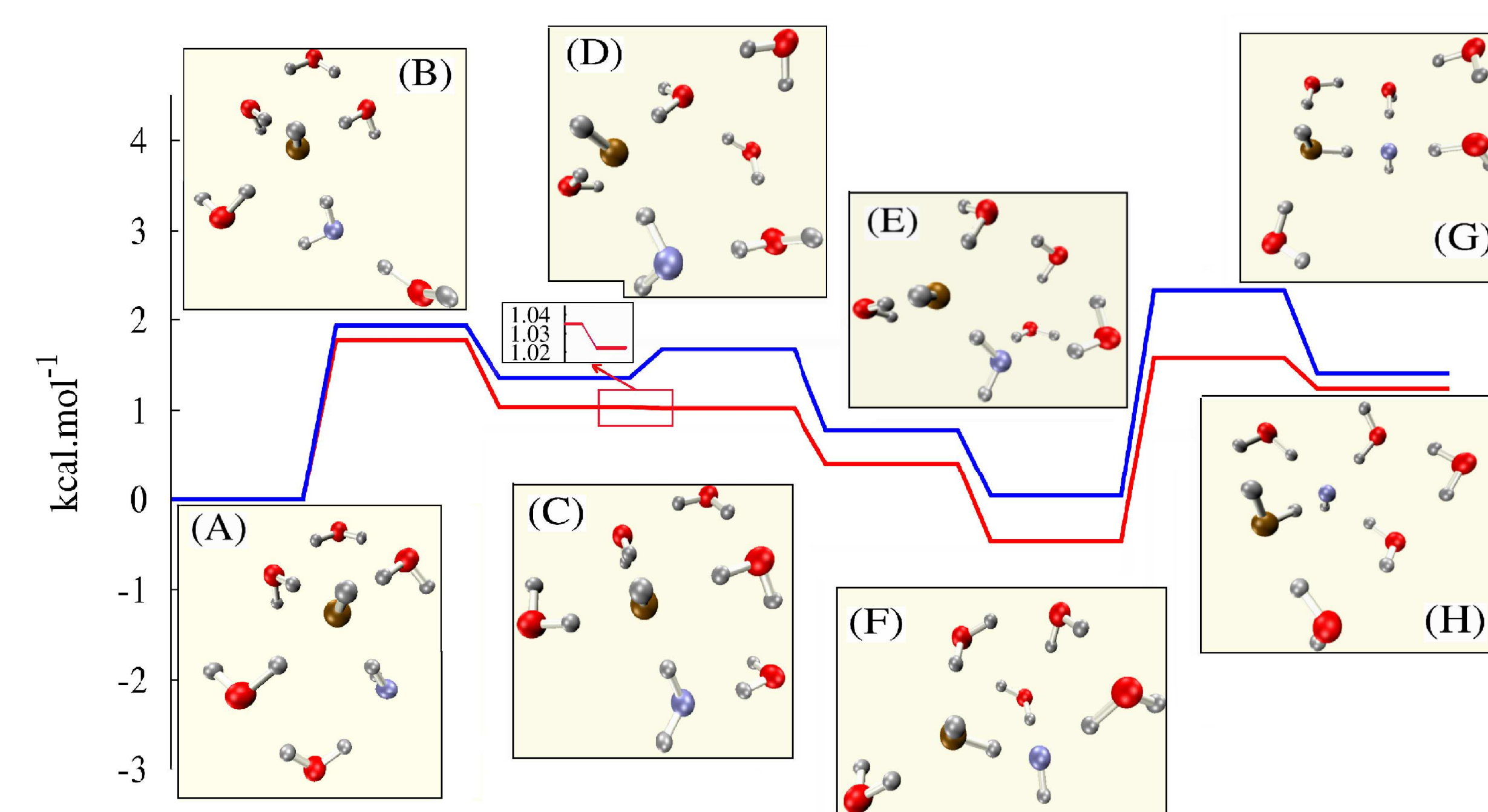
Here[1], we construct the smallest hydroxide water cluster, $\text{OH}^-(\text{H}_2\text{O})_6$, in gas phase that (a) could support a stable hydroxide ion with a four-coordinated hydroxide oxygen and (b) display hydroxide ion migration. We study the energetic stability and dynamical evolution of the 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* atom-centered density matrix propagation (ADMP)), 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 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.



The four-coordinated structure is lower in energy by 1 kcal/mol (MP2) and is spectroscopically distinct as seen above. Would the difference in these fundamental stretch frequencies be useful in detecting a four-coordinated oxygen spectroscopically?

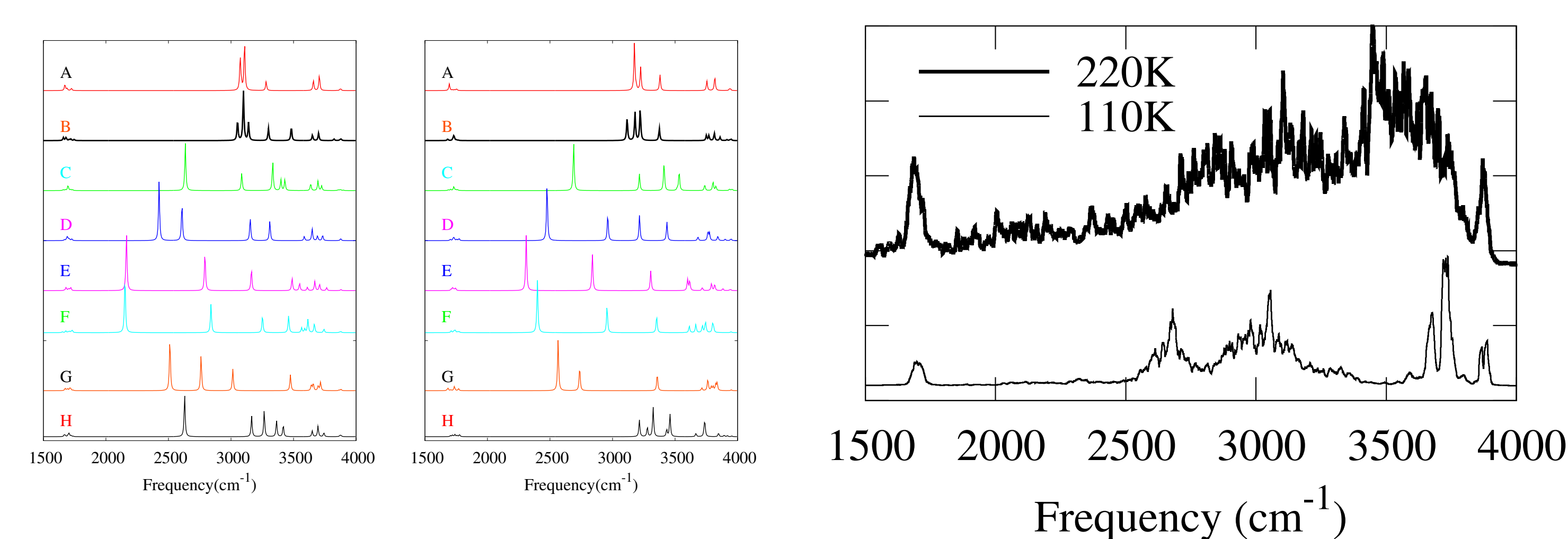
Dynamical pathways for hydroxide transfer

To understand if the spectral features above will remain in vibrational action spectrum experiments, we simulate the finite temperature behavior of these clusters using AIMD. The structural evolution of the system inclusive of the various isomers (or inherent structures) sampled during the AIMD dynamics at 220K is shown below. Starting from the four-coordinated structure (A), the system evolves through accessible intermediates (B and C) into five-membered ring structures D and E that facilitate a proton hop and a resultant hydroxide migration eventually leading into another four-coordinated central hydroxide (H). The five-membered ring that supports the hydroxide through three water molecules donating hydrogen bonds (similar to the three-coordinated structure) seems central to this hydroxide transfer process. The Figure below also illustrates a family of four-coordinated (A,B,C,H) and three-coordinated structures (D,E,F).



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 these isomers are very different as highlighted in the two figures on the left (below). There is a great deal of fluctuation in the 2000-3500 cm^{-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 such 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. The signature peaks for the three- and four-coordinated geometries (2710 cm^{-1} and 3100 cm^{-1}) are substantially weakened and broadened as a result of dynamical averaging at 220K. At lower temperatures (110K spectrum shown above) the dynamics does indeed preserve features representing the four-coordinated central oxygen, thus leading to a temperature dependence of the vibrational spectrum. The reason for this temperature dependence in the spectrum is because the energy domains and regions of the potential surface sampled are different at different temperatures. The lower temperature dynamics, on average, samples structures that are 5-10 kcal/mol above structure A while the 220K dynamics samples structures that are on average about 15 kcal/mol above the energy of structure A.

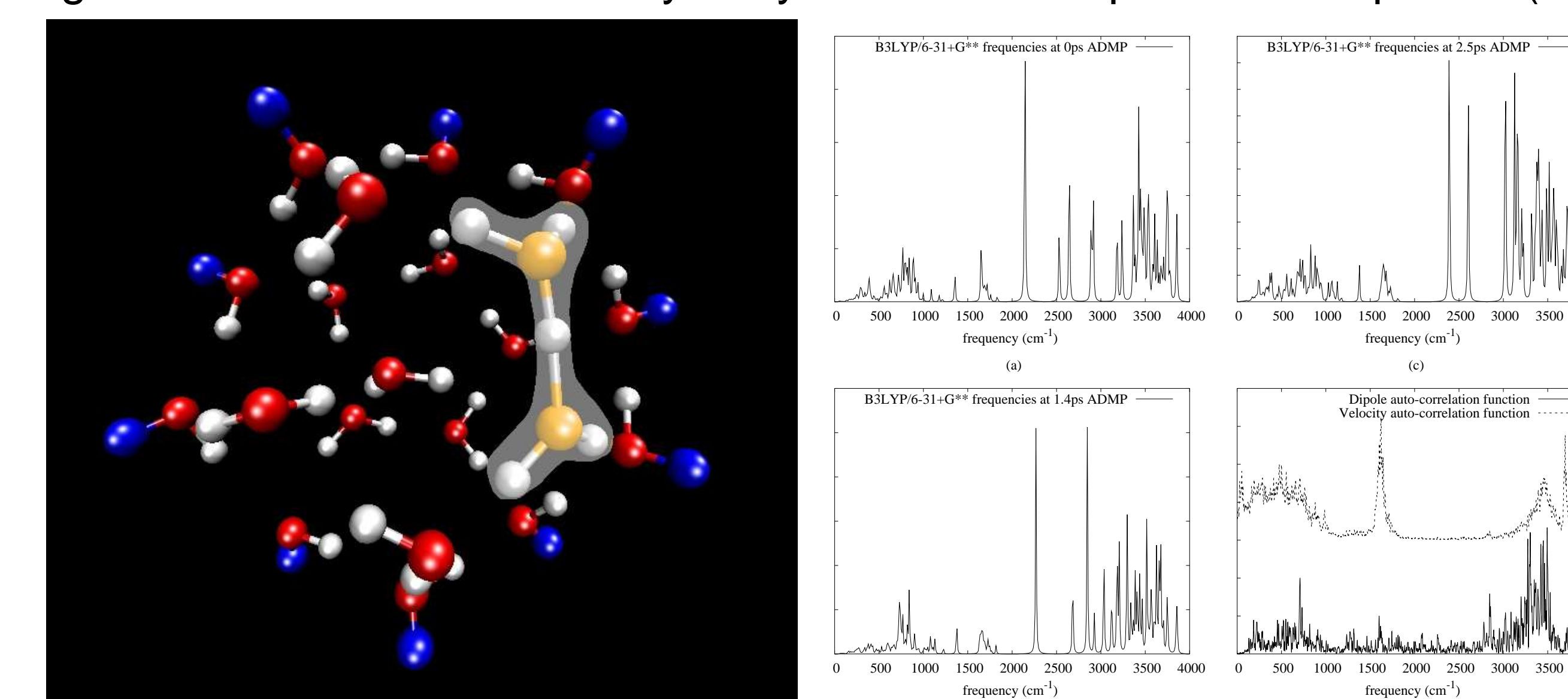
II. Dynamical averaging in protonated water clusters

Protonated water clusters have been the subject of a rich experimental and theoretical literature. Early mass spectrometric studies [4] on protonated clusters revealed $\text{H}^+(\text{H}_2\text{O})_{21}$ and $\text{H}^+(\text{H}_2\text{O})_{31}$ to have greater stability as compared to clusters of similar sizes. Due to this fact, the well-studied $\text{H}^+(\text{H}_2\text{O})_{21}$ 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 $\text{H}^+(\text{H}_2\text{O})_{21}$. The authors show that the spectral features observed for the

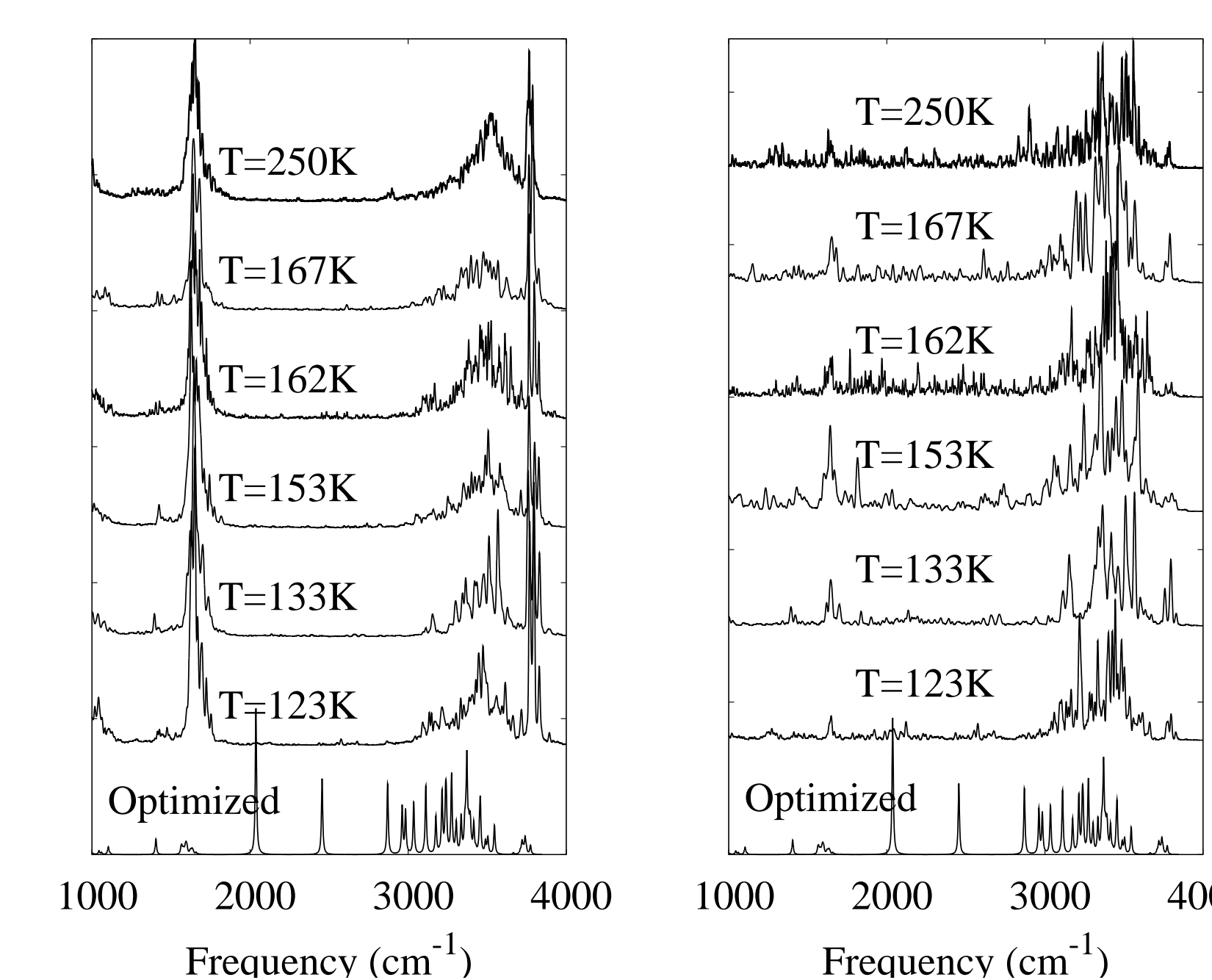
dangling hydroxyl bond stretch collapse into a single feature for 21 and 22 molecule clusters then re-emerge as a multiplet for 23 molecule and larger clusters.

Harmonic spectra differ from experimental results

However, the experimental and theoretical IR spectral in Ref. [5] studies were not in agreement concerning the modes accessible for hydroxyl stretch in the protonated species (see below).



Here[6, 7], we examine the behavior of the "magic number" 21-water protonated cluster at many different temperatures using *ab initio* Atom-centered Density Matrix Propagation (ADMP). The experimental frequencies are in good agreement with the vibrational spectra obtained directly from ADMP simulation data at finite temperature.



Thus dynamical effects are critical in determining the vibrational properties of such clusters since the spectra (on the left) are in good agreement with previous experiment [5, 8] through the reproduction of the sharp free OH stretch peak at $\approx 3700\text{cm}^{-1}$ and the almost complete lack of intensity in the 2000-3000 cm^{-1} region.

Acknowledgments

The Arnold and Mabel Beckman Foundation and the ACS-PRF are gratefully acknowledged.

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