# Further analysis of the dynamically averaged vibrational spectrum for the "magic" protonated 21-water cluster

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In a recent publication,[1] the structure, dynamics, and rovibrational spectrum of the hydrated proton in the "magic" 21-water cluster[2–5] ($H^+(H_2O)_{21}$) was studied. It was found that dynamical effects were critical in determining the vibrational properties of such clusters. This result was gathered from an analysis of the vibrational density of states including (a) the Fourier transform of the nuclear velocity-velocity autocorrelation (FT-VAC) function, (b) the Fourier transform of the dipole-dipole autocorrelation (FT-DAC) function, and (c) harmonic frequencies from the isomeric structures sampled in atom-centered density matrix propagation (ADMP). The spectra obtained in (a) and (b) were directly computed from *ab initio* ADMP (Refs. 6–11) and the spectra in (c) were obtained through optimization and frequency calculations. Furthermore, the spectrum obtained from the FT-VAC was in good agreement with previous experiment[2,3] through the reproduction of the sharp free OH stretch peak at $\approx 3700$ $cm^{-1}$ and the almost complete lack of intensity in the 2000–3000 $cm^{-1}$ region. The latter was perhaps most puzzling since the harmonic spectra do reveal sharp peaks with large intensities in this region (Fig. 4 in Refs. [1,2]), resulting from the OH stretch of the protonated (Eigen-like) species. Based on the agreement of our dynamical results with experiment[2] we concluded the importance of dynamics.

The experiments in Ref. 2 were not conducted using the argon-tag method, but the exact temperature of the experimental system is uncertain. However, from previous theoretical results[13] it could be concluded that the experimental system may be cooler than the simulated 250 K in Ref. 1 and closer to 150 K. Hence, we simulate the system for a range of temperatures that are substantially lower than in the previous study.[1] (See Table I for details.) On the outset we state that while our general conclusions remain the same as in Ref. 1, we find that there exist additional features in our dynamically averaged spectrum at lower frequencies that provide information on the spectroscopic structure of the excess proton. Internal temperature is defined here (as in Ref. 1) in terms of the total classical kinetic energy of the nuclei. This may relate to the frequency of the incident photon in an action spectrum experiment.[14,15]

Firstly, there is very little intensity in the FT-VAC spectrum [Fig. 1(a)] in the region of 2000–3000 $cm^{-1}$, in good agreement with experiment.[2] However, Fig. 1(a) does not contain the dipole selection rules required for IR spectroscopy. The FT-DAC in Fig. 1(b) does contain this information and even here the intensities in the 2000–3000 $cm^{-1}$ are reduced and "averaged out" as a result of dynamical and temperature effects based on the sampling of the (anharmonic) potential energy surface during dynamics. These results are consistent with previous studies,[1] although the low temperature dynamics calculations here do not display proton hopping unlike the previous higher temperature calculations.[1] It is important to note that while the FT-VAC intensities in the 2000–3000 $cm^{-1}$ are very small, the FT-DAC intensities in this same region are substantially larger although still negligible as compared to the other peaks in the FT-DAC. This is because the vibrations in the 2000–3000 $cm^{-1}$ are those that belong to the excess proton; even small excursions here (characterized by small intensities in the FT-VAC) give rise to a sizable effect on the polarizable surrounding of the excess, thus affecting the dipole moment.

The question remains: Is there a peak in our dynamical FT-VAC that corresponds to the excess proton? We address this by assigning all peaks in the FT-VAC by decomposing it in terms of constituent nuclear velocities. Analyzing the Fourier transform of the velocities of each component leads to the conclusion that the features at $\approx 1050$ and $\approx 1350$ $cm^{-1}$ in Fig. 1(c) are obtained from the coupled stretch and bending motion of the protonated species. Importantly, these peaks remain in the harmonic frequency results [bottom panel of Fig. 1(c) and in Fig. 4 in Ref. 1], but get "spread out" in the 250 K simulation on account of the larger kinetic energy available in the higher temperature simulation. In addition, one of these features is blueshifted by $\approx 300$ $cm^{-1}$ with respect to the experimentally observed Zundel cation peak[16] because the modes here are coupled Zundel-bending-

TABLE I. Summary of *ab initio* molecular dynamics (AIMD) simulations performed.

| Temperature (K) | Simulation time ($T$) (ps) | $1/(2T)$[a] ($cm^{-1}$) |
|---|---|---|
| 250[b] | 7.5 | 4.5 |
| 167 | 6.0 | 5.5 |
| 162 | 3.0 | 11 |
| 153 | 3.0 | 11 |
| 133 | 2.5 | 13 |
| 123 | 3.5 | 9.5 |

[a]Based on Shannon sampling theorem, (Ref. 12), we estimate here the uncertainty in frequency, when the dynamics is utilized to compute vibrational spectra.
[b]This row contains results from Ref. 1.

 

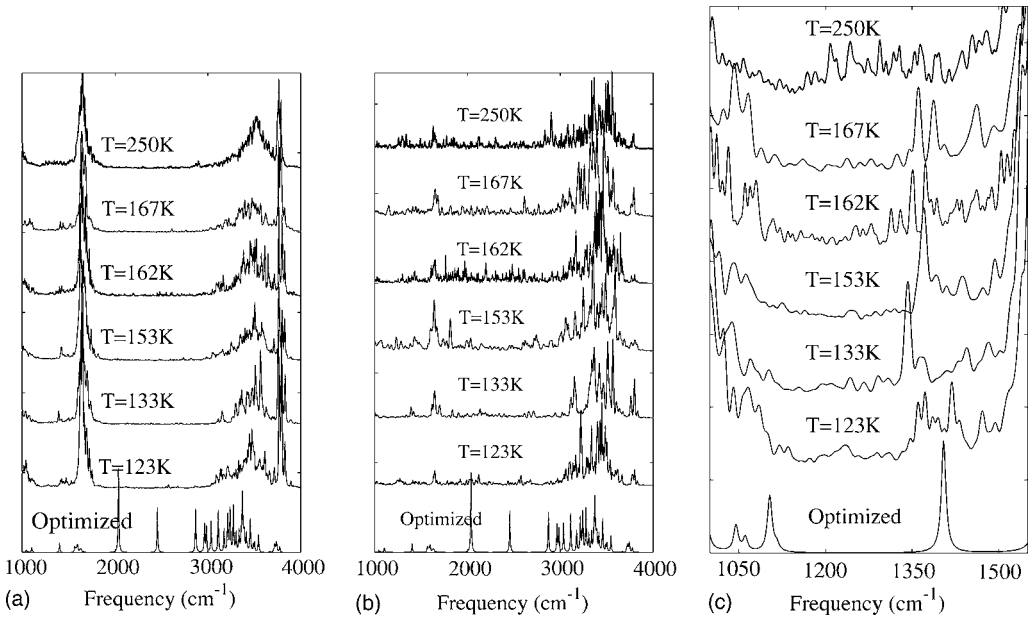


FIG. 1. Fourier transform of the nuclear velocity-velocity autocorrelation function (a) and dipole-dipole autocorrelation function (b) obtained using ADMP simulations for a range of temperatures. Bottom panels in both (a) and (b) represent harmonic frequencies computed at the B3LYP/6-31+G** level starting from a snapshot obtained from low temperature ADMP simulation. This shows intensity in the 2000–3000 $cm^{-1}$ region, which gets averaged out as a result of dynamical sampling of the anharmonic potential surface in the FT-VAC and FT-DAC. A scaling factor of 0.962 is used for the geometry optimized spectrum, while no scaling factor is necessary for the ADMP spectrum since it already contains contributions from anharmonicity. The region to the left of the 1500 $cm^{-1}$ peak is expanded in (c) to show the vibrational properties for the three hydrogen atoms connected to the oxygen that is on average most protonated during the 123 K simulation.

Eigen-like modes due to time-averaged sampling of both Zundel and Eigen geometries.

We conclude that the vibrational spectrum for $H^+(H_2O)_{21}$ has a striking free OH stretch peak, but the hydronium stretch in the 2000–3000 $cm^{-1}$ region gets spread out during the finite temperature dynamical simulations conducted here. While standard electronic structure calculations only account for vibrations in a local minimum, nuclear quantum effects will allow the spreading of contributions from conformational space due to zero point effects. At finite temperatures the number of conformations that contribute to the spectrum may grow exponentially as a result of the soft (anharmonic) modes that are present in systems such as those treated here and *ab initio* molecular dynamics provides an alternate formalism to sample these soft modes efficiently.

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