A Density Functional Theory for Studying Ionization Processes in Water Clusters

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ABSTRACT: A generalized Kohn–Sham (GKS) approach to density functional theory (DFT), based on the Baer–Neuhauser–Livshits range-separated hybrid, combined with ab initio motivated range-parameter tuning is used to study properties of water dimer and pentamer cations. The water dimer is first used as a benchmark system to check the approach. The present brand of DFT localizes the positive charge (hole), stabilizing the proton transferred geometry in agreement with recent coupled-cluster calculations. Relative energies of various conformers of the water dimer cation compare well with previously published coupled cluster results. The GKS orbital energies are good approximations to the experimental ionization potentials of the system. Low-lying excitation energies calculated from time-dependent DFT based on the present method compare well with recently published high-level “equation of motion-coupled-cluster” calculations. The harmonic frequencies of the water dimer cation are in good agreement with experimental and wave function calculations where available. The method is applied to study the water pentamer cation. Three conformers are identified: two are Eigen type and one is a Zundel type. The structure and harmonic vibrational structure are analyzed. The ionization dynamics of a pentamer water cluster at 0 K shows a fast <50 fs transient for transferring a proton from one of the water molecules, releasing a hydroxyl radical and creating a protonated tetramer carrying the excess hole.

I. INTRODUCTION

Absorption of ionizing radiation by aqueous systems has considerable implications for a broad variety of fields, such as chemistry of the ionosphere, waste remediation, environmental clean-up, radiation processing, nuclear reactions, and medical diagnosis and therapy. Various processes of water ionization have been studied experimentally, finding a high abundance of protonated water clusters. Molecular beam experiments confirmed this finding and determined the preferred protonated “magic number” clusters sizes. Unprotonated cation clusters were found in Ar-seeded beams, where excess energy can be released as kinetic energy of emitted Ar atoms.

A large number of experimental and theoretical studies have been published concerning the electronic structure and ionization dynamics of water clusters as well as the vibrational properties of both protonated and unprotonated products. Additional detailed experimental results including at the attosecond and femtosecond time scales are becoming available concerning the electronic structure and ionization potentials and dynamics in water.

Gaining a detailed understanding of these ionization processes has so far been hampered by the complexities involved in developing a sound theoretical approach for describing them. Impressive algorithmic developments and increased computational speed have allowed high level ab initio studies shedding light on the ionization dynamics in clusters of the water dimer. However, these methods are limited to small clusters due to the steep increase in algorithmic complexity as the number of electrons and atoms grows. What is needed is a method that can deliver useful accuracy at moderate algorithmic complexities. Such approaches are often found within the density functional theory (DFT) which for many systems delivers a favorable blend of accuracy and applicability. The strengths and weaknesses of DFT for studying dynamical aqueous processes as well as other electronic properties are subjects of considerable theoretical interest.

In this paper, a new DFT approach, recently developed for treating symmetric radical cations, is assessed for the water dimer ionization, using experimental and high-level ab initio benchmark data available for the water dimer cation. The DFT method we use can be viewed as an approximation to the “in principle exact” generalized Kohn–Sham approach to DFT which uses orbital functionals, in addition to pure density

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The remaining correlation energy in GKS/BNL is not known exactly but can be approximated as $E_{\text{corr}} = E_{\text{LYP}} - w \Delta E_{\text{LYP}}$, where the first term is the LYP correlation energy and the second involves subtraction of a small (10%) amount of the short-range exchange energy. The BNL functional is described in greater detail in ref 37.

Two theoretical benefits are obtained by this GKS approach: (1) the long-range part of the self-interaction energy, that due to the Hartree self-repulsion, is greatly reduced, and (2) a large part of the KS derivative discontinuity is absorbed in the orbital functional reducing the necessity for finding noncontinuous density functionals. While most applications of the RSH approach use a “universal” range-parameter $\gamma$, we find that for good quantitative results this parameter must be adapted to each system separately. Theoretical reasons are given in ref 39, and for systems involving symmetric radical cations this was shown explicitly in ref 32. In the past we have checked in our group two relevant ways to determine the range-parameter value in a first principles manner (i.e., without reference to specific empirical data). One way is motivated by the ionization potential theorem (IPT), which states that the negative highest occupied (HO) molecular orbital (MO) energy $-E_g$ is equal to the ionization potential (IP). This method gave good charge-transfer excitation energies, ionization potentials of and Rydberg excitations in many systems. The second method is based on the physical principle of energy degeneracy between two charged states of the well-separated dimer ($H_2O \cdot H_2O$), namely, the energies of the localized charge state (when the hole is localized on a monomer) and the symmetric delocalized state (when the hole is symmetrically delocalized between the fragments). This latter tuning method enabled quantitative description of symmetric cations such as $H_2^+$, $He_2^+$, and $Ne_2^+$. In the present study we found that the two ab initio motivated methods for determining $\gamma$, the IP theorem applied to $H_2O$ and the energy degeneracy criterion applied to ($H_2O$)$_2^-$, yield almost identical values for $\gamma$, namely, 0.56 and 0.58 $a_0^{-1}$, respectively. This near identity has been seen in other systems and explained elsewhere. It is related to the fact that in RSHs the GKS energy changes almost linearly as a function of HO occupation number, due to small self-repulsion.

The BNL functional has been coded into widely available codes (QCHEM 3.2, Quantum Espresso, and NWChem). In the present paper, all electronic structure calculations were done using the QCHEM implementation. Following ref 7 we use the 6-311++G** basis set; the inclusion of diffuse functions is important for decreasing basis set superposition errors. Below we test the degree of convergence by comparing some results to those obtained by using a larger basis set, namely, aug-cc-pVQZ (see Table 2).

### A. Assessment of Orbital Energies as IPs

We address not only water molecules, dimers, and their cations but also products of the proton transfer reaction ($H_2O$)$_2^- \rightarrow H_2O^- + OH$. For both OH and $H_2O^-$ the IP theorem method yields identical values $\gamma = 0.63a_0^{-1}$, somewhat different from the optimal parameters of the water molecule, $\gamma = 0.56, 0.58a_0^{-1}$. Consequently, there are several different values of $\gamma$ relevant for the system we are studying. However, these values of the range parameters do not vary by much, so selecting $\gamma = 0.6a_0^{-1}$ seems a reasonable compromise. Indeed, this choice makes only a small deviance from the IPT for the water molecule: with $\gamma = 0.56a_0^{-1}$ the IP ($\Delta$SCF) and $\gamma = 0.6a_0^{-1}$ the IP ($\Delta$SCF) and IP of $H_2O$ have the identical value of 12.7 eV while for $\gamma = 0.6a_0^{-1}$ the $\Delta$SCF IP is 12.6 eV while the HOMO
energy is 12.8 eV. These values compare well with the experimental vertical ionization potential of water 12.6 eV. We show in Table 1 a comparison of the GKS orbital energies from the bound state (metastable as well as transition state) estimated by wave function calculations and ab initio calculations and recent experiments. BLYP, as a range separated hybrid, does not suffer from long-range self-repulsion; furthermore, its range parameter is tuned to balance the description of the ionization levels. We should mention that this result is not particular to the present systems and has recently been demonstrated to have a broader scope of applicability.

### B. Assessment of the BNL* Energetics

In Table 2 energy differences of various configurations (metastable as well as transition state) estimated by wave function calculations and several density functional methods including BNL*. It is seen that BNL* results are similar to the high-level ab initio wave function methods, with discrepancies of ≤2 kcal/mol. BNL* avoids the erroneous prediction of the generalized gradients approximation (BLYP) and hybrid (B3LYP) functionals. BLYP predicts that the h-bonded (HB) configuration of the (H₂O)₂⁺ cation is more stable than the proton transferred (PT) configuration, in contrast to a wealth of post-HF ab initio calculations and recent experiments. B3LYP, as well as other local KS approximations, destabilizes the PT complex where the positive hole is localized (on the H₂O⁻ fragment), while it stabilizes the HB complex for which charge is delocalized between the two monomers. This can be attributed to the spurious self-repulsion in these approximations. Hybrid GKS functionals, such as B3LYP, partially correct for the long-range self-repulsion, although they still exhibit a significant amount of overestabilization of the charge delocalized state in symmetric radical cations. BNL*, being a range separated hybrid, does not suffer from long-range self-repulsion; furthermore, its range parameter is tuned to balance the energies of the localized and delocalized charge states and it is thus able to deliver a good overall description of the relative energies involved. This latter issue is explained in more detail in refs 32 and 39. BNL* predicts almost zero energy difference for the reaction \((\text{H}_2\text{O})_2^+ (\text{N}) \rightarrow \text{OH} + \text{H}_2\text{O}^+\) (the symbol (N) is the stable configuration of the neutral water dimer). This is close to the ab initio result, predicting that the reaction is slightly exothermic (by less than 1 kcal/mol). Using a new saddle location method located we located the transition state and estimated the energy barrier for the isomerization reaction from the HB to the PT configuration. The barrier found by BNL* is higher by 2 kcal/mol than the CCSD(T) prediction. While this deviance of HF is small, it is an important one since the probability of hydroxyl radical release due to ionization is critically dependent on this energy. There is no clear experimental indication as to the energetics of hydroxyl radical release from water dimers upon ionization.

### C. Assessment of Electronic Excitations

To further test GKS/BNL* as an electronic structure method for the water dimer cation, we benchmarked the electronic excitations at C₃ proton-transferred geometry. In Table 3 we compare predictions of different methods. All excitations considered here involve transfer of electron to the half-filled orbital. The excitations can be classified as transition within the OH fragment and electron transfer transitions from H₂O⁻ to OH. The first excitation involves very low frequencies as it describes two internal transitions within the OH radical, between the filled 1σ or 2σ orbitals to the half-filled 2π HOMO. When compared to equation of motion estimates of excitation energies, these two local excitations are reasonably described by the TDDFT methods, although the 2σ → 2π transition is lower by 0.5 eV in the BNL*. However, when the nonlocal charge-transfer excitations are considered, B3LYP considerably underestimates the excitation energies when compared with the EOM results (by 2.5–3 eV) while BNL* excitations are 0.7 eV higher than the EOM-IP results but only 0.3 eV higher than the EOM-EE result. Regarding the oscillator strengths, there is considerable misfit in this quantity between the EOM and the BNL* (in two cases out of three). In charge transfer excitations oscillator strengths are sensitive to the overlap between exponential tails of the excited and ground state wave functions.

Summarizing this section, we described the BNL* functional, the method of tuning its range-parameter, and presented several tests, showing it gives a good account of the cation water dimer electronic structure. In the next sections we apply our BNL* method to the ionization of dimer and pentamer clusters.

### III. RESULTS

In this section we apply the BNL* functional to study the water dimer and pentamer cation IR spectra and the associated ionization dynamics.

#### A. Structure of the Water Dimer Cation

The structure of the water dimer cation, predicted by BNL* shown in the top part of Figure 1 is that of a Zundel type, where a hydrogen is “shared” by a hydroxyl (OH) radical and a water (H₂O) molecule. The OH bond lengths in the H₂O molecule and in the hydroxyl radical are almost identical, equal on the average to 0.989 Å. This should be
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The calculated IR absorption spectrum involves an estimation of the thermal average of the dipole–dipole correlation functions

\[ C(t) = \frac{1}{3} \sum_i \langle M_i M_i(t) \rangle \]  
(3.1)

where \( M_i \) is the dipole moment in direction \( i \), \( i = x, y, z \) of \((H_2O)_2^{+}\). (Comment: even though the dipole of a charged system is arbitrarily dependent on the position of the coordinate origin, the AC part of the spectrum is well-defined since \( \langle M_i(t) \rangle \) is time-independent). Thermal averaging is attained by sampling an Andersen thermostat\(^6\) stochastic dynamics trajectory of \((H_2O)_2^{+}\) at temperature \( T \) (30 and 300 K). The first 0.5 ps of the trajectory were discarded and subsequently \( M = 10 \) configurations at intervals of 100 fs were used to produce, via a microcanonical AIMD simulation dipole moment signals \( M_i(t) \) \( (i = x, y, z) \) as a function of time \( t \) (at 10 au intervals). The trajectory average

\[ \overline{C_d}(t) = \frac{1}{3} \sum_{i=x,y,z} M_i M_i(t) \]  
(3.2)

Table 2. Energy Differences (kcal/mol; No Vibrational Energy Corrections) Computed by BNL (0.6) with 6-311++G** Basis Compared to Results of Various Methods

<table>
<thead>
<tr>
<th>A(config)</th>
<th>B(config)</th>
<th>DZV</th>
<th>BLYP</th>
<th>BSLYP</th>
<th>HF</th>
<th>EOM-IP-CCSD</th>
<th>EOM-IP-CC(2,3)</th>
<th>CCSD(T)**</th>
<th>BNL* (0.6)</th>
<th>CCSD(T)**</th>
<th>BNL* (0.6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((H_2O)_2^{+})</td>
<td>(N) OH + H_3O^+</td>
<td>-18.1</td>
<td>-10.6</td>
<td>-10.5</td>
<td>-14.6</td>
<td>-20.0</td>
<td>-21.8</td>
<td>-23.6</td>
<td>-23.3</td>
<td>-21.5</td>
<td></td>
</tr>
<tr>
<td>((H_2O)_2^{+})</td>
<td>(PT) ( (H_2O)_2^{+} )</td>
<td>-6.5</td>
<td>-16.5</td>
<td>-23.7</td>
<td>-20.0</td>
<td>-20.0</td>
<td>-21.8</td>
<td>-21.6</td>
<td>-23.6</td>
<td>-21.5</td>
<td></td>
</tr>
<tr>
<td>((H_2O)_2^{+})</td>
<td>(HB) ( (H_2O)_2^{+} )</td>
<td>-9.3</td>
<td>-1.8</td>
<td>27.1</td>
<td>5.3</td>
<td>7.4</td>
<td>8.2</td>
<td>9.7</td>
<td>7.1</td>
<td>9.5</td>
<td></td>
</tr>
<tr>
<td>((H_2O)_2^{+})</td>
<td>(TS) ( (H_2O)_2^{+} )</td>
<td>-24.6</td>
<td>-24.2</td>
<td>-18.9</td>
<td>-24.6</td>
<td>-23.6</td>
<td>-22.3</td>
<td>-25.1</td>
<td>-25.1</td>
<td>-25.1</td>
<td></td>
</tr>
</tbody>
</table>

*BNL results change by less than 2% when compared to the aug-cc-pVQZ basis. Nuclear geometries of \((H_2O)_2^{+} \) (N) = the neutral configuration of \((H_2O)_2 \), (PT) = stable proton transferred configuration of \((H_2O)_2 \) (structure 1 of ref 17), (HB) = hemibonded metastable configuration of \((H_2O)_2 \) (structure 7 in ref 17), (TS) is the saddle configuration for the \( \text{HB} \rightarrow \text{PT} \) transition (structure 10 of ref 17).

Table 3. Vertical Excitation Energies (eV) and Oscillator Strengths \((10^{-4})\) of in \((H_2O)_2^{+}\) at Proton-Transferred Geometry: Comparison between TDDFT and EOM CCSD Methods at the 6-311++G** Basis Set Level

<table>
<thead>
<tr>
<th>orbital</th>
<th>EOM-IP-CCSD</th>
<th>EOM-EE-CCSD</th>
<th>BLYP</th>
<th>BNL* ((\phi = 0.6))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( h \nu )</td>
<td>( f )</td>
<td>( h \nu )</td>
<td>( f )</td>
</tr>
<tr>
<td>OH_{1x}</td>
<td>0.5</td>
<td>0</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>OH_{2x}</td>
<td>4.5</td>
<td>15</td>
<td>4.5</td>
<td>14</td>
</tr>
<tr>
<td>((H_2O)_2^{+})</td>
<td>8.4</td>
<td>29</td>
<td>8.9</td>
<td>21</td>
</tr>
<tr>
<td>((H_2O)_2^{+})</td>
<td>13.1</td>
<td>6</td>
<td>10.5</td>
<td>13.7</td>
</tr>
<tr>
<td>((H_2O)_2^{+})</td>
<td>14.3</td>
<td>8</td>
<td>11.0</td>
<td>15.0</td>
</tr>
</tbody>
</table>

*All excitations are to the half-filled HOMO which is the \( 2\pi \) orbital on OH.
was used to estimate the IR spectrum using the formula
\[
\bar{n}(\omega)\alpha(\omega) \approx (\bar{\beta} \omega^2/2)C_\text{ff}(\omega), \quad \text{where } C_\text{ff}(\omega) = \int_0^\infty \bar{C}_\text{ff}(t) e^{-i\omega t} dt.
\]
The spectrum obtained in this way is shown in Figure 1 for 30 and 300 K. The peaks are compared to calculated harmonic frequencies based on CCSD(T)\cite{17} and to anharmonic variational CI frequencies based on EOM-IP-CCSD PESs\cite{9} and to experimental vibrational predissociation spectra for Ar\cdot(H_2O)\cite{12}. The 30 K peaks correspond closely to the shown harmonic BNL lines. The latter are in reasonable agreement with the CCSD(T) harmonic spectrum. The water bend frequencies of the present calculations are red-shifted relative to the CCSD(T) harmonic frequencies by 50 cm\(^{-1}\) but are in closer agreement with experiment and EOM-IP-CC/VCI results.

The high end of the spectrum dominated by the OH vibrations shows similar trends: BNL\cite{9} harmonic frequencies are red-shifted by 50–100 cm\(^{-1}\) relative to the CCSD(T) harmonic results but agree more closely to experiment. On comparison to the EOM-IP-CC/VCI spectrum (which includes quantum anharmonic effects), the harmonic spectra are similar with one noticeable deviation: the harmonic \(v_{\text{OH}}\) peak at 2370 cm\(^{-1}\) is considerably red-shifted (by about 400 cm\(^{-1}\)) in the anharmonic spectrum. This was attributed to anharmonic mixing of the hydrogen vibration with that of O–O vibrational mode.\cite{9,17} As the lines involve hydrogen vibration, our classical calculation at 30 K does not significantly sample the anharmonic structure of the potential. The 300 K spectrum on the other hand does exhibit many anharmonic effects, and a considerably larger number of lines are seen. The lines at 2370 cm\(^{-1}\) are shifted to the red by about 100 cm\(^{-1}\), and a considerable vibrational activity is seen at 1550 cm\(^{-1}\) in accordance with the experimental lines and VCI spectra.

C. Ionization Dynamics of the Water Dimer. We now apply the method for studying molecular dynamics (MD) of a small ionized water cluster, in a special ionized water dimer cluster and water pentamer cluster. The calculations were done using ab initio (Born–Oppenheimer) molecular dynamics (AIMD) implemented in Q-Chem 3.2\cite{12} software. The dynamics corresponds to a Franck–Condon approximation, where the ionization is immediate so the initial nuclear configuration is that of stable water dimer, but the electronic wave function is that of the ground state cation.

The two water molecules in the neutral dimer are bound by a hydrogen bond (HB). We find that upon ionization the initial hole forms on the HB donor (HBD), a fact seen also in HF and EOM-CC calculations.\cite{15} Formation of a hole on the HB acceptor (HBA) is higher in energy by about 1.5 eV. In Figure 2 (top panel) we plot the distance of the transferred proton from the two oxygen nuclei. Initially the proton is transferred from Od to Oa within about 18 fs. At the same time the heavier O nuclei start moving toward each other, albeit on a slower time scale, reaching a minimal distance of 2.4 Å at \(t = 35\) fs. The proton bounces back and forth twice between the two O nuclei during the process. Finally, the latter start receding at \(t = 45\) fs. When the O atoms move to a distance larger than 2.6 Å, the proton localizes on Oa. However, the Oa–Od vibration brings these atoms to closer proximity again at \(t = 140\) fs. Once close, the proton again delocalizes and oscillates between them. This happens at \(t = 250\) fs. The trajectory stops at 320 fs because of failure of SCF to converge (the proximity of the excited state, situated on the OH radical, plagues the SCF convergence throughout the calculation). The dynamics seen in the present calculation is different from that described using a Hartree–Fock (HF) electronic structure.\cite{12} In HF, the initial proton transfer is slower, taking 30 fs, then the proton oscillates 3 times between Od and Oa and at 50 fs localizes on Od for 60 fs.

Figure 2. AIMD trajectory for the photoionization of the water dimer at 0 K: (top) selected atom–atom distances vs time \(t\) since photoionization of the water dimer. Od (Oa) is the donor (acceptor) oxygen while H is the transferred proton. (bottom) Potential energy changes vs \(t\).

Only then does the proton move to Oa and stays localized on it for at least 150 fs. Furthermore, the maximal O–O distance in the HF calculation reaches 3.25 Å while in the present calculation it is only 3.0 Å. This larger amplitude is due to the weaker hydroxyl radical–protonated water cation bond predicted by the HF calculation. Indeed dissociation of the hydroxyl radical leaving hydronium behind is energetically possible according to Hartree–Fock (exothermic by 3.8 kcal/mol, see Table 2) but forbidden in the present DFT calculation (exothermicity is 0 kcal/mol, see Table 2). The present full dimensional dynamics can be compared with the reduced dimension wave packet quantum dynamics in ref 9 where only the O–O and H–Oa are considered. The similarity in the calculation is that a similar trend is observed, where the O–O distance is initially reduced while the O–H distance vibrates several times. However, the quantum dynamics is ended after 50 fs and thus cannot see the O–O receding and vibrating. This brief time is also not sufficient to determine just how close the two oxygen atoms approach each other. In our calculation the closest distance is 2.35 Å while the quantum calculation is stopped when the O–O distance is significantly larger. Obviously, in our calculation the O–O vibration is significantly faster.

The changes in the potential energy (negative changes in kinetic energy) in the dimer as a function of time since photoionization are shown in Figure 2 (bottom). The average energy change is 12 kcal/mol with strong and rapid oscillations of amplitude between \(-9\) and \(+7\) kcal/mol. In the Hartree–Fock calculation the average potential energy is similar but the oscillations have larger amplitude (\(-11\) to \(+11\) kcal/mol) and the rate of oscillations is different.
D. Structures of Water Pentamer Cation. We now consider the water pentamer cation and ionization process. The three conformers of the water pentamer cation are shown in Figure 3b–d. The first structure considered (Figure 3b) involves a ringlike conformation, where the hydroxyl radical OH is bound from both sides to a bent-linear protonated tetramer (H⁺O⁻H⁻). The bent tetramer involves a proton in a Zundel type O-O bond connecting two water dimers. This Zundel conformer is 0.05 eV higher in energy than the lowest Eigen conformer considered next. The structure of this conformer is similar to the lowest energy geometry of water pentamer (see the t = 0 panel of Figure 5) and thus relevant for low-temperature IR spectra taken from pentamer cations formed by photoionization of the pentamer in an Ar seeded beam. The positive charge of the tetramer is located on the Zundel proton and the two water molecules connected to it.

In the lowest energy structure is an Eigen structure (Figure 3c) where the central hydronium (H₃O⁺) binds three water molecules and the hydroxyl radical is attached to one of the end water molecules. Eighty percent of the cation charge is localized on this hydronium. A second Eigen structure, almost identical in energy to the first (higher by 0.02 eV) is shown in Figure 3d where it is the OH radical which is bonded to the hydronium and the third water molecule binds to the hydroxyl. The closeness of energies between these two isomers indicates that they can coexist in an ensemble at room temperature. As in the first Eigen conformer, here too 80% of the charge is located on the hydronium, with the hydroxyl carrying the rest of the charge.

E. IR Spectra of Water Pentamer Cations. Calculated harmonic frequencies related to hydrogen vibrations of the water pentamer cation conformers are shown in Table 4. Only strong absorption lines are shown (for a complete list of harmonic data, including the frequencies and normal modes. The Zundel structure is unique in that the shared proton has a low vibrational...
The HOH bending modes have frequencies in the range 1600–1750 cm\(^{-1}\). The Zundel structure does not exhibit strong vibrational lines in the frequency region 1750–3000 cm\(^{-1}\), and in the region 3000–4000 cm\(^{-1}\) it displays strong absorption lines due to hydrogen stretching vibrational modes. Both Eigen structures exhibit significant activity in the region 2500–3100 cm\(^{-1}\). These vibrations are due to hydrogen vibrational motion in the hydronium. The OH stretching models of the outer water molecules and the OH radical form the highest features in the spectrum, 3600–3900 cm\(^{-1}\).

The calculated anharmonic IR spectra at 300 K of the pentamer cation was produced using classical molecular dynamics in basically the same way as described for the dimer cation. We used 9 1ps AIMD trajectories for averaging the correlation function, taking their initial configuration and velocities from a 300 K Andersen thermostat trajectory. The spectrum reveals a great wealth of vibrational lines, which are due to a combination of anharmonic effects and the Boltzmann statistical coexistence of the Zundel (10%), Eigen1 (60%), and Eigen2 (30%) clusters. The low-frequency bands (at around 200–400 cm\(^{-1}\)) involve significant O–O vibrations in the normal modes while most of the stronger bands at higher frequencies can be related to the above values of harmonic frequencies for the various cluster configurations (see Table 4). The strong peaks at 2000 cm\(^{-1}\) where there are no harmonic frequencies, are a result of the strong anharmonicities in the underlying potential surface.

F. Ionization Dynamics of the Water Pentamer. The ionization dynamics is studied using the Franck–Condon approximation, assuming that the initial geometry of the cluster is that of the ground state pentamer. Several snapshots at the

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**Table 4. Calculated Harmonic Frequencies (cm\(^{-1}\)) and Vibrational Modes Related to Hydrogen Motion in the Water Pentamer Conformers**

<table>
<thead>
<tr>
<th>Conformer</th>
<th>Frequency (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zundel</td>
<td>880, 1710, 3060, 3740, 3860</td>
</tr>
<tr>
<td>Eigen 1</td>
<td>1580, 2610, 3000, 3610, 3880</td>
</tr>
<tr>
<td>Eigen 2</td>
<td>1580, 2870, 2890, 3170, 3880</td>
</tr>
</tbody>
</table>

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**Figure 4.** The anharmonic spectrum of the pentamer cation at 300 K, computed from the windowed Fourier transform of the dipole–dipole correlation function averaged AIMD trajectories.

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**Figure 6.** The total charge on each water molecule in the tetramer (depicted by its oxygen atom) as a function of time.
O4, with occasional visits to O2. One can time average the trajectory and reveal the “average” structure of the complex. We find it is that of a Zundel-type protonated cluster with a middle proton connecting two water dimers. This result correlates with experimental and computational studies of protonated water clusters $\text{H}^+ (\text{H}_2\text{O})_n (n = 2−5$ (ref 62) and $n = 27$ (ref 63)).

IV. SUMMARY AND DISCUSSION

The failures of local and semilocal density functionals for studying the ionized symmetric cation radicals, such as $\text{H}_2^+$, $\text{He}_2^+$, $\text{Ne}_2^+$, etc., and the water dimer cation ($\text{H}_2\text{O})^+_2$ has motivated the development of a new approach, which is the subject of this paper. Our method, BNL*, is based on the generalized Kohn–Sham approach to DFT, employing a RSH orbital functional with a tuned range parameter. The tuning is performed in first principles ways, discussed in several former publications. 32,36,37,45,46,54,64 The first part of the paper assessed the quality of the method for the water–cation dimer and related systems, by comparing to high level wave function methods and experiments, where possible. We found that our “tuned” BNL* functional is appropriate for describing the electronic structure and the underlying potential surface, including internal barriers, ionization energies, excited state energies, and vibrational spectrum of the water dimer cation.

Using our method we studied the vibrational and ionization dynamics of the water dimer and pentamer cations. In the pentamer, we found that the time scale for the initial proton transfer (from O1 to O2) is performed very fast, within about 10−20 fs; O1 is the oxygen of the hydroxyl. The proton subsequently moves (within 20−30 fs) to O3 and then spends most of its time on the O3–O4 dimer (see Figure 6). Future studies should address yet larger clusters, striving to reach near aqueous conditions as done, for example, in ref 10 using the Hartree–Fock approach.

The present work shows that by addressing the issue of self-repulsion and using the tuning procedure it is possible to improve considerably the range of applications of DFT for systems such as the present, where charge localization is a dominant feature. Using the suggested approach, larger water systems may be accessible for study using DFT approaches. The value of the range parameter found most suitable for the problem studied here is 0.6 $a_0^{-1}$ corresponding to a separation distance of 0.9 Å. This is extremely short, well below the bond length between first row heavy atoms (C, N, O). The results for the properties considered, geometry, ionization, and excitation and binding energies of the water molecule and water dimer cation ion, are however impressive. However, switching to full exact exchange at such short-range could have some drawbacks, especially the disturbance of the delicate cancellation of long-range exchange and long-range (static) correlation which is part of the success of local/semilocal functionals. This issue of the complementarily between static correlation and delocalization errors is currently at the forefront of current research in density functionals. 38,65

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