I. Overview

- The nature of solvation structures of hydroxide (OH\textsuperscript{−}) and hydronium (H\textsubscript{3}O\textsuperscript{+}) is of fundamental importance.
- Required to understand the proton transfer (PT) process in water.
- Current photoemission spectroscopy (PES) experiments are able to measure the ionization potentials (IPs) of both hydrated OH\textsuperscript{−} and H\textsubscript{3}O\textsuperscript{+}.
- Critical need to connect IP distributions to the solvation structures.
- Previous work calculated PES spectra using DFT with ab initio molecular trajectories.
- Strongly underestimates the IP distributions.
- Current work uses Hedin's GW self-energy approximation with ab initio molecular trajectories.

III. Quasiparticle Density of States and IP distributions:

- Theoretical PES spectra (red line) for the (a) OH\textsuperscript{−} and (b) H\textsubscript{3}O\textsuperscript{+} ion solutions.
- IP distributions (shaded blue area) for hydrated (a) OH\textsuperscript{−} and (b) H\textsubscript{3}O\textsuperscript{+}.
- Averaged over 100 configurations.
- Accurate reproduction of experimental peak positions (see table).

<table>
<thead>
<tr>
<th>Peaks (eV)</th>
<th>Current theory</th>
<th>Exp.</th>
<th>DFT</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH\textsuperscript{−}</td>
<td>9.99</td>
<td>9.2</td>
<td>5</td>
</tr>
<tr>
<td>H\textsubscript{3}O\textsuperscript{+}</td>
<td>19.01</td>
<td>20</td>
<td>12</td>
</tr>
</tbody>
</table>

V. Effect of PT on IP distributions

- IP distributions for hydrated (a) OH\textsuperscript{−} and (b) H\textsubscript{3}O\textsuperscript{+}.
- Blue shaded areas indicates PT, red shaded area indicates no PT.
- PT shifts main IP peak into region of bulk water.
  - (a) OH\textsuperscript{−} blue shift toward 1b\textsubscript{1} region of bulk water.
  - (b) H\textsubscript{3}O\textsuperscript{+} red shift toward 3a\textsubscript{1} region of bulk water.
- Relative fraction of PT configurations percentages, OH\textsuperscript{−} \approx 10\% and H\textsubscript{3}O\textsuperscript{+} \approx 16\%.

VI. Quasiparticle (de)localization:

- IP main feature states, (b) OH\textsuperscript{−} 1b\textsubscript{1} and (c) H\textsubscript{3}O\textsuperscript{+} 1b\textsubscript{2}.
- Delocalized 3a\textsubscript{1} regions, (a) OH\textsuperscript{−} (d) H\textsubscript{3}O\textsuperscript{+}.
- Strongly hybridized with surrounding water.

VIII. Acknowledgments /Support:

- Supported by Department of Energy Scidac Grant No. DE-SC0008726.
- Computational support provided by National Energy Research Scientific Computing Center (NERSC).

Contact info: charles.swartz@temple.edu