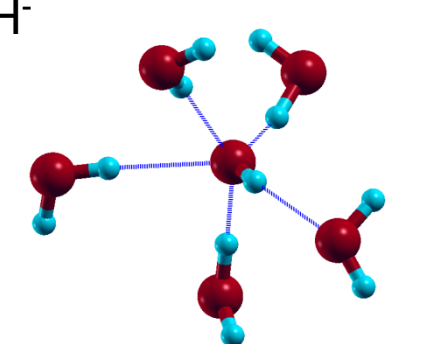
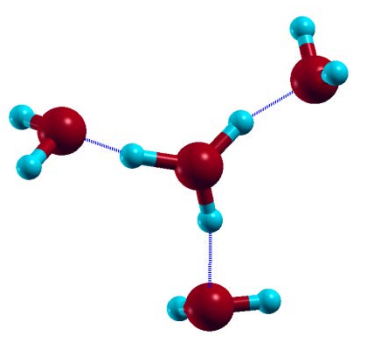


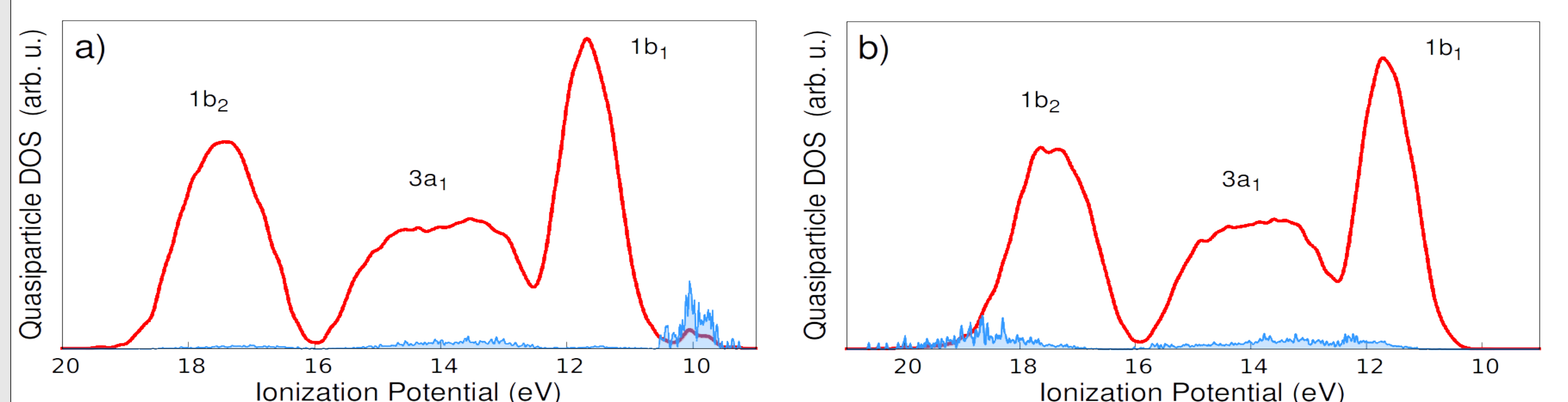
I. Overview

- The nature of solvation structures of hydroxide (OH^-) and hydronium (H_3O^+) is of fundamental importance
 - Required to understand the proton transfer process (PT) in water
- Current photoemission spectroscopy (PES) experiments are able to measure the ionization potentials (IPs) of both hydrated OH^- and H_3O^+
 - 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

II. Calculation Details:

- Ab initio* molecular trajectories
 - Car-Parrinello dynamics
 - 63 water molecules with either an OH^- or H_3O^+ ion (25ps)
 - Cubic supercell, corresponding to experimental ambient density
 - Canonical ensemble, $T = 330\text{K}$
 - PBE functional, $E_k = 71.0\text{ Ry}$
 - Dominant solvation complexes:

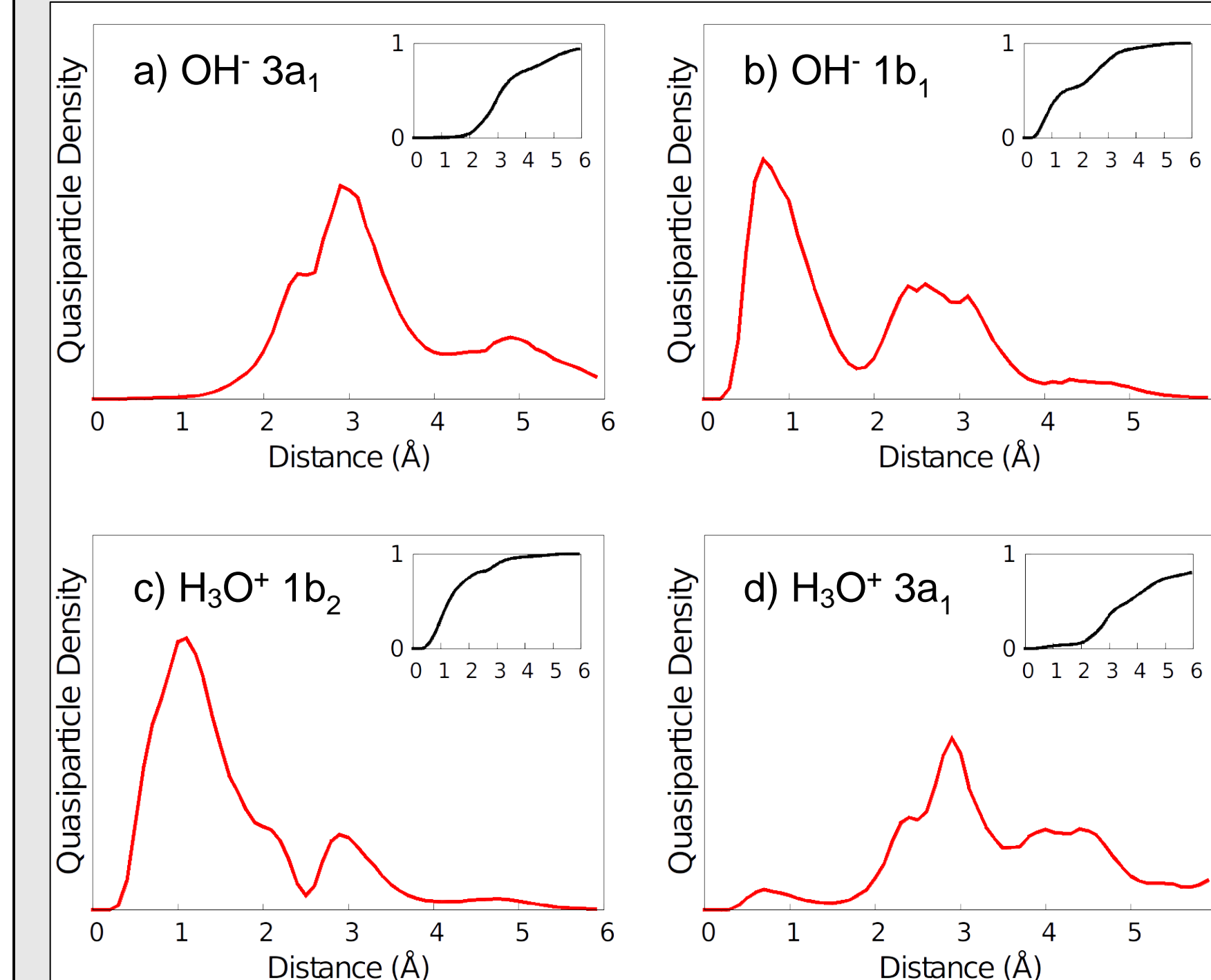


- Electron excitations
 - GW quasiparticle theory
 - Maximally localized Wannier functions, for increased efficiency
 - Static Coulomb hole and screened exchange (COHSEX)
 - Inhomogeneous electronic screening of the medium, Hybertsen-Louie ansatz
- Ionization Potentials (IP)
 - Real space projection of quasiparticle density of states onto solvated ion complexes



III. Quasiparticle Density of States and IP distributions:

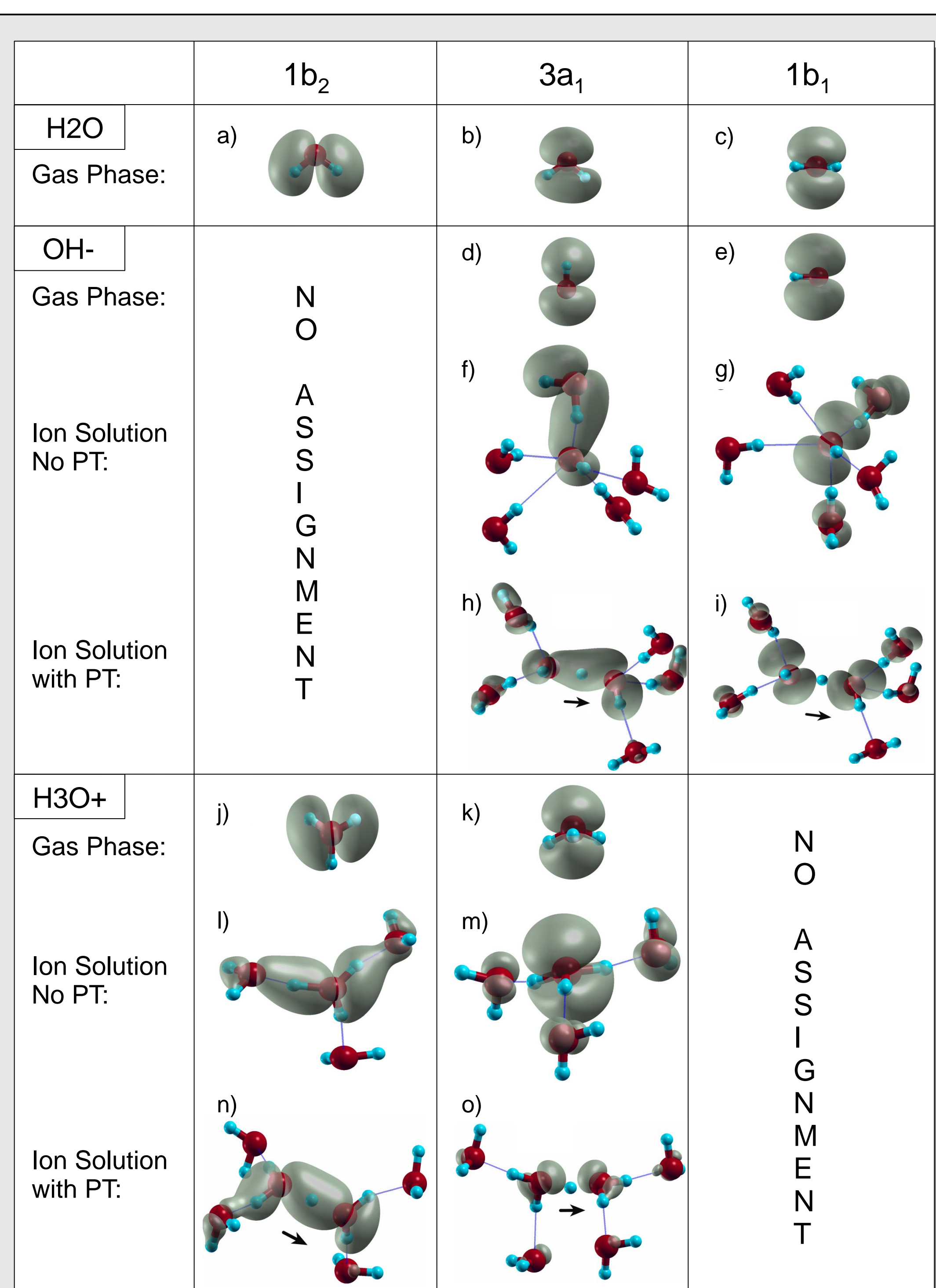
- Theoretical PES spectra (red line) for the (a) OH^- and (b) H_3O^+ ion solutions
- IP distributions (shaded blue area) for hydrated (a) OH^- and (b) H_3O^+
 - Averaged over 100 configurations
- Accurate reproduction of experimental peak positions (see table)
 - J. Am. Chem. Soc. **128**, 3864 (2006)

Peaks (eV)	Current theory	Exp.	DFT
OH^-	9.99	9.2	~5
H_3O^+	19.01	20	~12

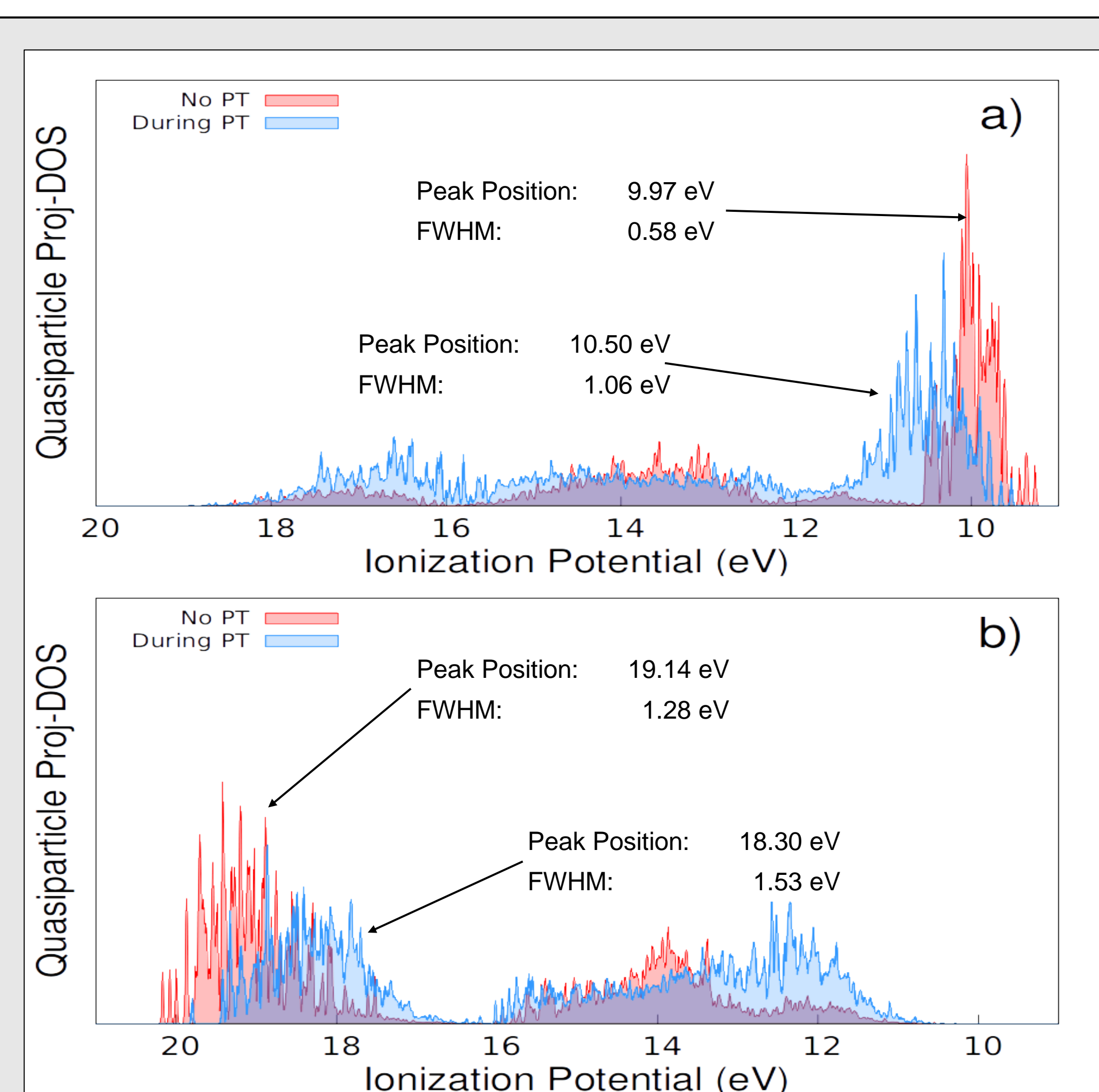


VI. Quasiparticle (de)localization:

- IP main feature states, (b) OH^- $1b_1$ and (c) H_3O^+ $1b_2$, strongly localized
- Delocalized $3a_1$ regions, (a) OH^- (d) H_3O^+
 - Strongly hybridized with surrounding water



IV. Molecular excitation IP assignment



V. Effect of PT on IP distributions

- IP distributions for hydrated (a) OH^- and (b) H_3O^+
- Blue shaded areas indicates PT, red shaded area indicates no PT
- PT shifts main IP peak into region of bulk water
 - (a) OH^- blue shift toward $1b_1$ region of bulk water
 - (b) H_3O^+ red shift toward $3a_1$ region of bulk water
- Relative fraction of PT configurations percentages, OH^- ~10% and H_3O^+ ~16%

VII. Conclusions

- IP distributions of hydrated ions studied accurately by quasiparticle theory
- Excitations of solvated ions can be assigned to molecular excitations
 - Strongly perturbed by solvation structure
- Main features of IP distributions are determined by stable solvation complexes
- PT introduces a change in position and broadening
 - Suggest detection with isotope effect in future PES experiments
- Theory improvements
 - More accurate AIMD solvation structures
 - Frequency dependence, beyond static GW

VIII. Acknowledgments /Support:

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