Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information for: "Structure of the aqueous electron"

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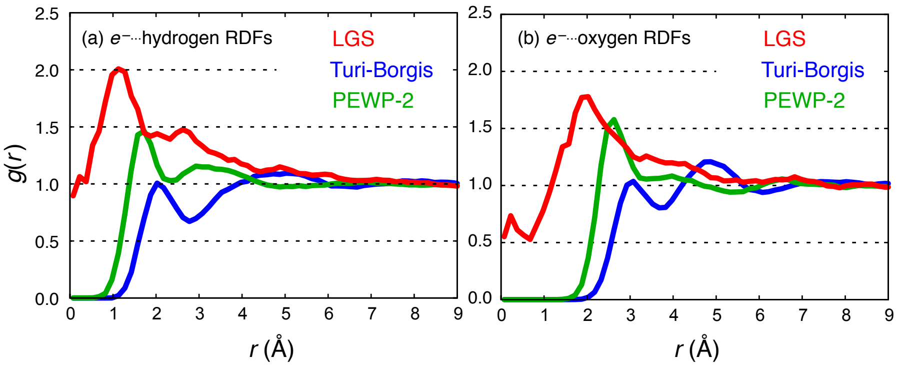

Figure S1: Radial distribution functions (RDFs), $g(r)$, for the Larsen-Glover-Schwartz (LGS),[1] Turi-Borgis (TB),[2,3] and Jacobson-Herbert[4] (PEWP-2) pseudopotential models of e^{-}(aq). Panel (a) shows the $e^{-}\cdots$hydrogen RDF and (b) shows the $e^{-}\cdots$oxygen RDF, where the electron coordinate (e^{-}) is the centroid of the one-electron wave function. These plots were constructed using simulation data originally reported in Ref. 5.

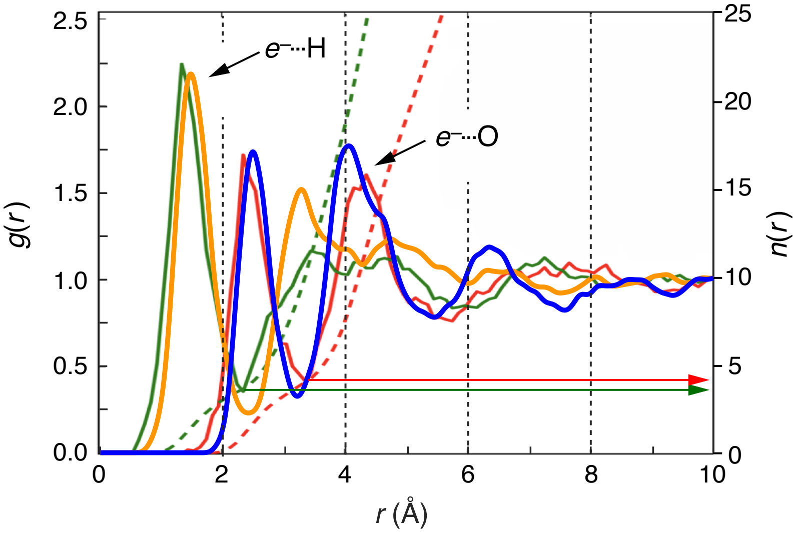

Figure S2: Overlay of the RDFs from Fig. 7, representing $g(r)$ data from from two different QM/MM simulations of e^{-}(aq), one at the BLYP(SIC)+D3 level (from Ref. 6) and the other at the HF+D3 level (from Ref. 7). The RDFs for the $e^{-}\cdots$H coordinate are shown in green [BLYP(SIC)+D3] and in orange (HF+D3), while those for the $e^{-}\cdots$O coordinate are shown in red [BLYP(SIC)+D3] and in blue (HF+D3). Dashed curves are the integrated coordination numbers $n(r)$ from the BLYP(SIC)+D3 simulation and should be read from the axis on the right. The green and red arrows that point to the axis on the right suggest coordination numbers obtained by integrating Eq. (4) that defines $n(r)$, up to the first local minimum in either RDF.

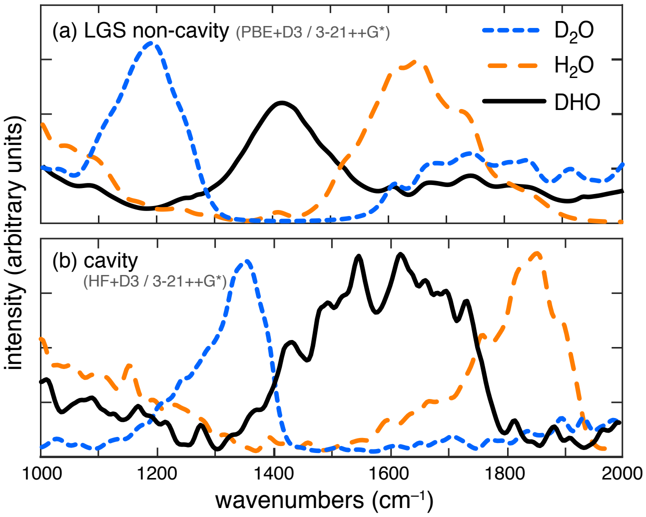

Figure S3: Resonance Raman (RR) spectra of e^-(aq) computed within the instantaneous normal modes (INM) approach, using the excited-state gradient approximation of Eq. (6).[8] (a) INM-RR spectrum computed at non-cavity liquid geometries obtained from a simulation using the LGS model. (b) INM-RR spectrum computed from a QM/MM trajectory at the HF+D3/3-21++G* level, which supports a stable cavity. These spectra represent ensemble averages of harmonic stick spectra computed for QM/MM snapshots and then broadening with 20 cm^{-1} Lorentzian functions, with RR intensity enhancements computed according to Eq. (6). The INM-RR spectra in Figs. 8 and 9 were computed in the same way but use Lorentzian broadening of 45 cm^{-1}. Adapted from Ref. 8; copyright 2019 American Chemical Society.

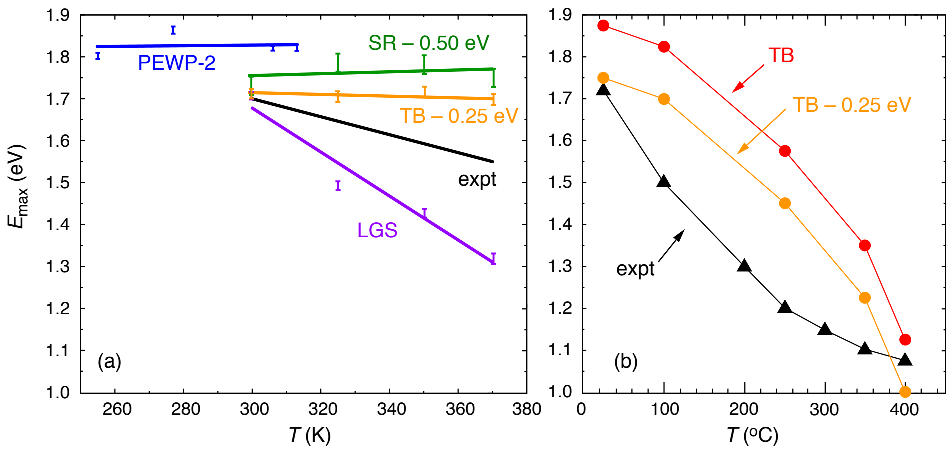

Figure S4: Temperature dependence of the aqueous electron's absorption maximum, $E_{\max}(T)$. (a) Comparison of predictions from the TB, SR, LGS, and PEWP-2 pseudopotential models. All simulation data are from Ref. 9 except for the PEWP-2 data, which are new.[10] All simulations were carried out at a fixed water density of 0.997 g/cm^3. The SR and TB values of $E_{\max}$ are shifted by −0.50 eV and −0.25 eV, respectively, as indicated. Experimental data are from Ref. 11. (b) Predictions from the TB model using variable densities, where the density used in the simulation corresponds to the experimental density of neat liquid water at the indicated temperature. Results plotted are from simulations reported in Ref. 12 and experiments reported in Ref. 13. Note that the energy (vertical) scale is the same in both panels but that the data in (b) span a much broader range of temperatures, including supercritical data.

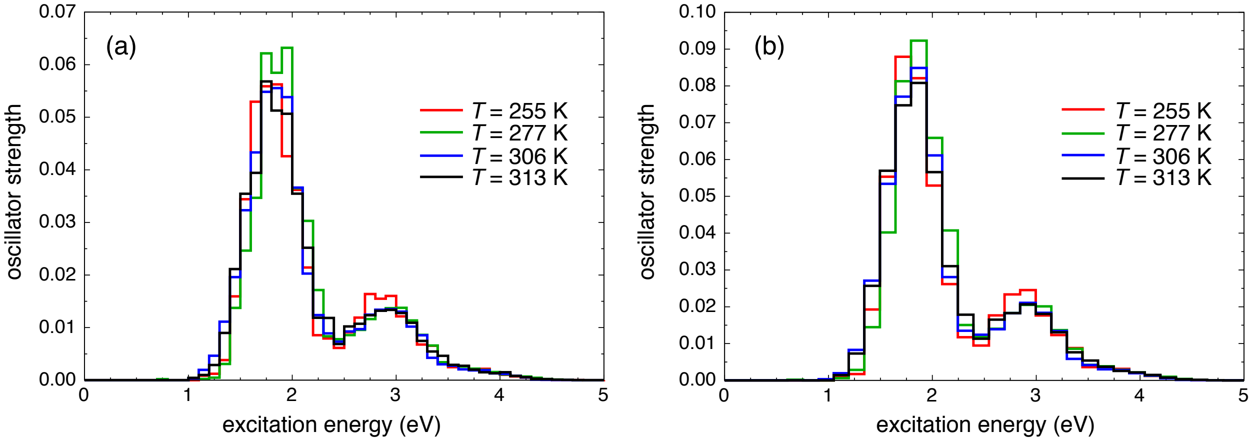

Figure S5: Absorption spectra computed using the Jacobson-Herbert (PEWP-2) pseudopotential model at several different temperatures, using bin widths of (a) 0.10 eV and (b) 0.15 eV. Excitation energy data up to 2.5 eV were fit to a Gaussian envelope, with $E_{\max}$ as one fitting parameter. This value of $E_{\max}$ is then used to plot the T-dependent absorption maximum for the PEWP-2 model in Fig. S4.

References

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[10] The PEWP-2 simulations were performed with 200 molecules in a periodic simulation cell of dimensions $L \times L \times L$, where $L = 18.1671$ Å corresponding to a water density of 0.997 g/cm^3. The same water density is used at each temperature, with temperature conservation (NVT ensemble) enforced by means of a Nosé-Hoover thermostat. Other simulation details follow the calculations reported in Ref. 4.

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