Supporting information for "Optical Spectroscopy of the Bulk and Interfacial Hydrated Electron from *Ab Initio* Calculations"

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Supporting Information contains additional spectral calculations (Figures S1- S3), addtional radial profiles of the excited states (Figures S4- S11), dissection of excited state spin densities of the interfacially solvated electron into individual contributions (Table S1), and averaged distances of the centers of ground and excited state spin densities (Table 2).

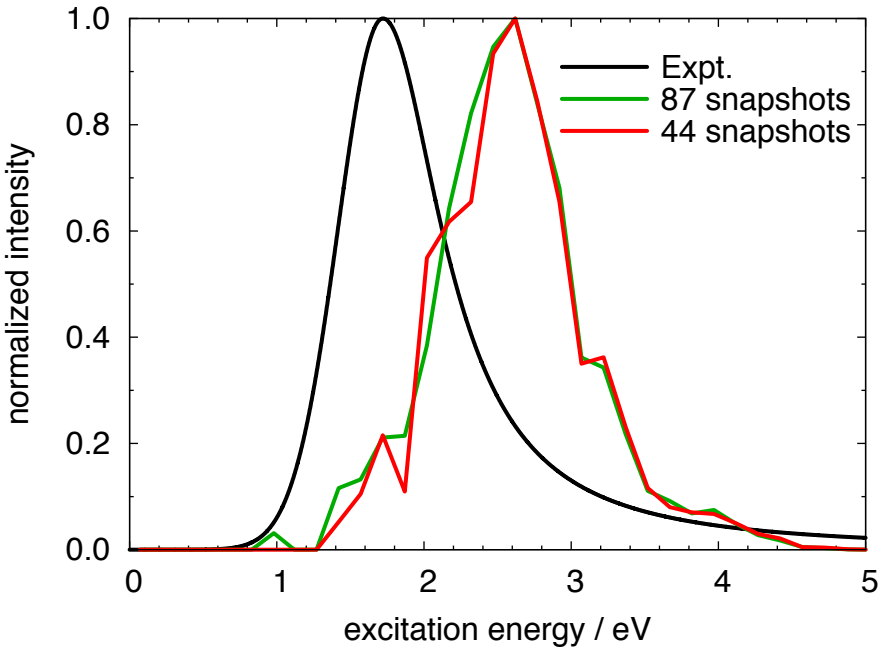

Figure S1: LRC-μBOP/6-31++G* spectra of the bulk hydrated electron, using $\mu = 0.37\ a_0^{-1}$ and a 7.5 Å QM region, demonstrating that a factor of two reduction in the number of snapshots does not adversely affect the TD-DFT spectrum.

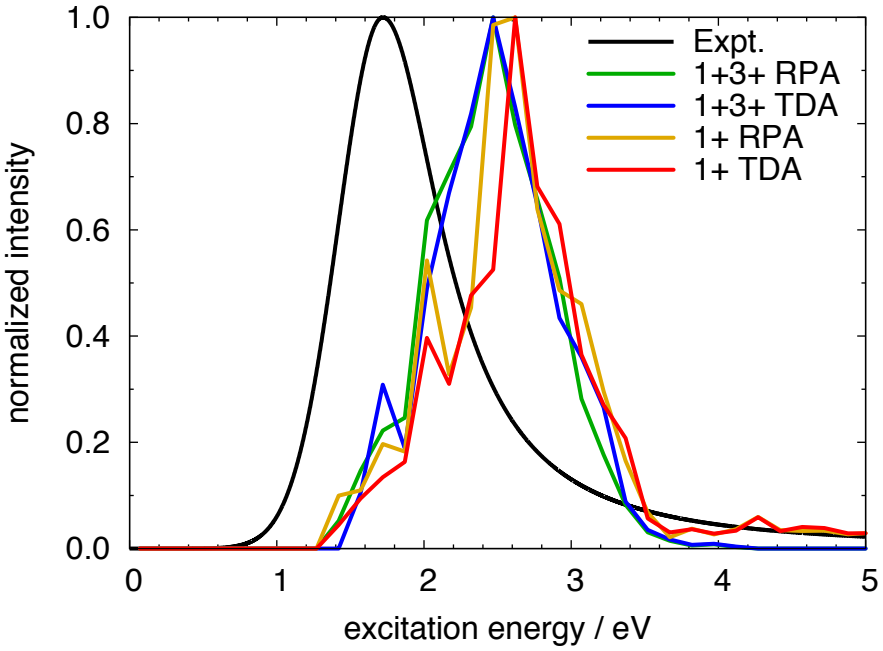

Figure S2: LRC-μBOP spectra of the bulk hydrated electron, using $\mu = 0.37\ a_0^{-1}$ and a 5.5 Å QM region, for two different basis sets: 6-31++G* and 6-31(1+,3+)G*. The figure also compares spectra computed in the Tamm-Dancoff approximation (TDA) versus "full" TD-DFT calculations (labeled "RPA" here). These spectra were computed using only half as many snapshots as the production spectra in the paper.

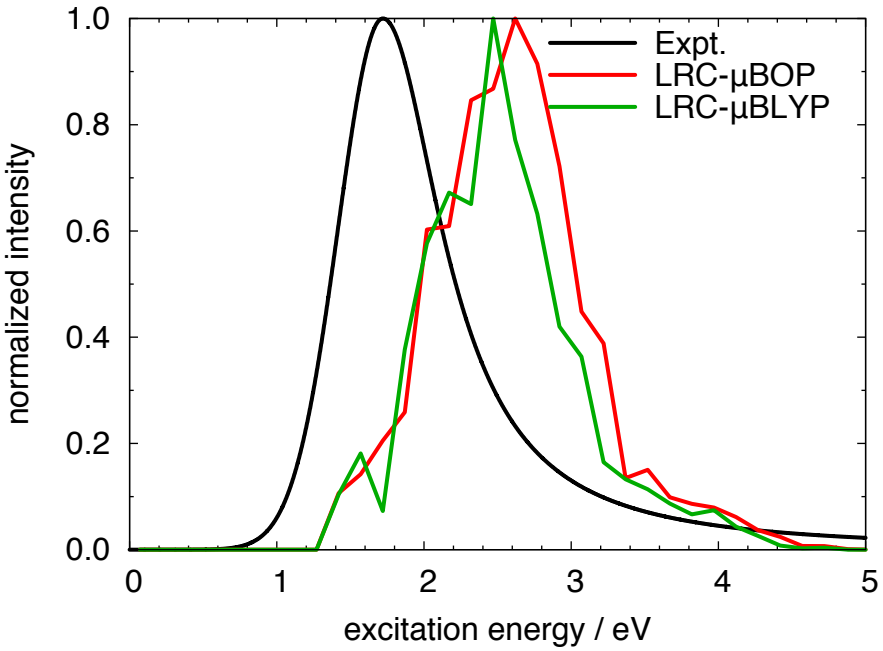

Figure S3: TD-LRC-DFT/6-31++G* spectra of the bulk hydrated electron, using $\mu = 0.37\ a_0^{-1}$ and a 7.0 Å QM region, for two different LRC functionals. These spectra were computed using only half as many snapshots as the production spectra in the paper.

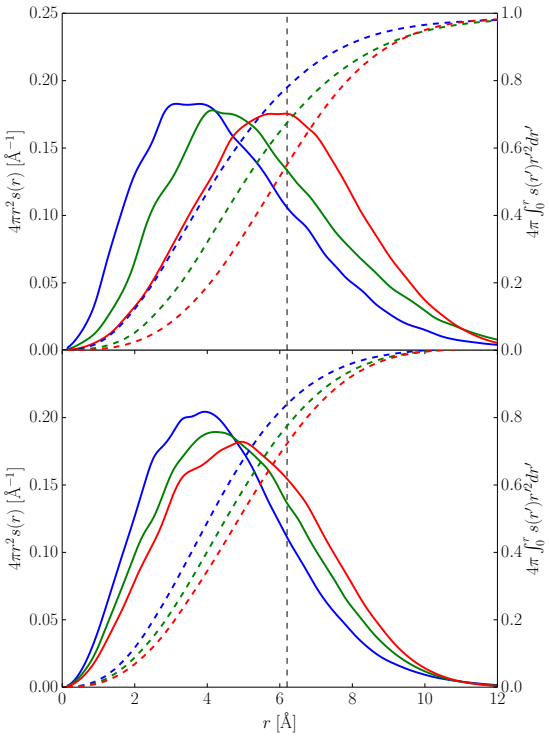

Figure S4: Radial profiles of excited state spin densities in first three excited states with B3LYP (upper panel) and LRC-μBLYP (lower panel) in TD-DFT/MM calculations of a bulk-hydrated electron. Solid curves (read from the scale at left) denote the radial spin density profiles $4\pi r^2 s(r)$, where $r = 0$ represents the centroid of the excited-state spin density. Broken curves (read from the scale at right) depict the cumulative radial integral of this quantity density profile. Dashed vertical lines indicate the average value of r_{g} of the QM subsystem.

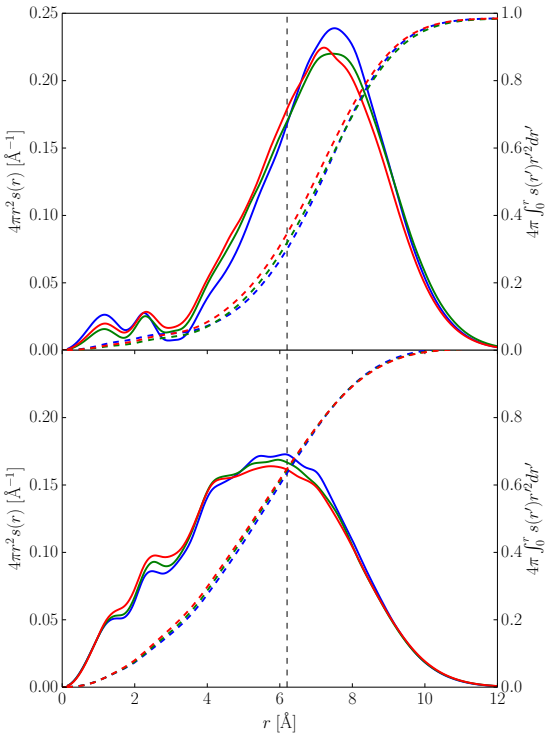

Figure S5: Radial profiles of excited state spin densities in first three excited states with B3LYP (upper panel) and LRC-μBLYP (lower panel) in TD-DFT/MM calculations of a bulk-hydrated electron. Solid curves (read from the scale at left) denote the radial spin density profiles $4\pi r^2 s(r)$, where $r = 0$ represents the centroid of the ground-state spin density. Broken curves (read from the scale at right) depict the cumulative radial integral of this quantity density profile. Dashed vertical lines indicate the average value of r_{g} of the QM subsystem.

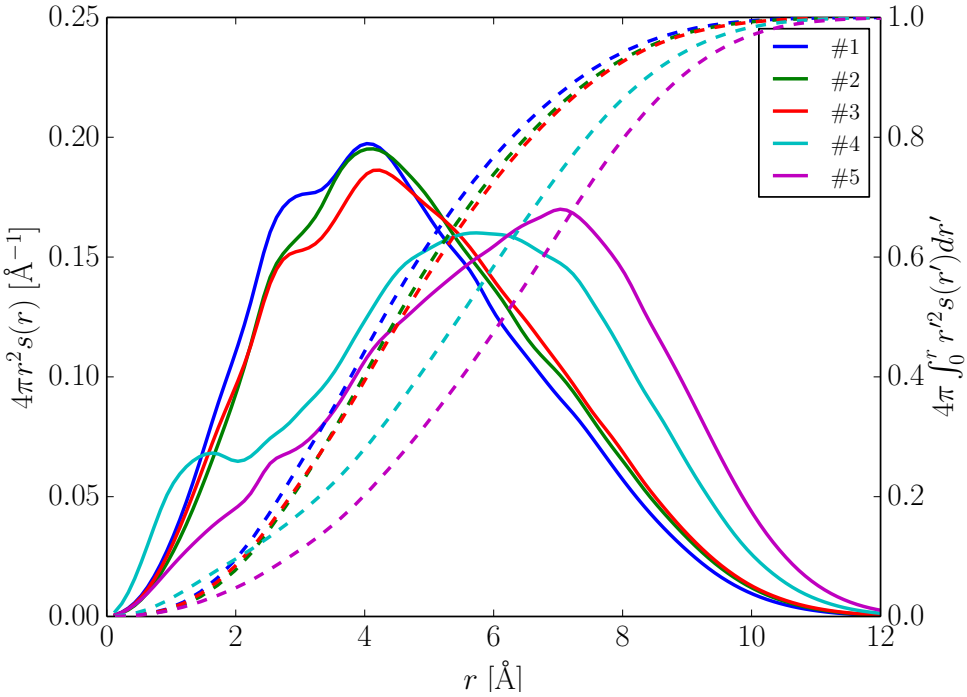

Figure S6: Average radial profiles of the first five excited state of the interface-hydrated electron.

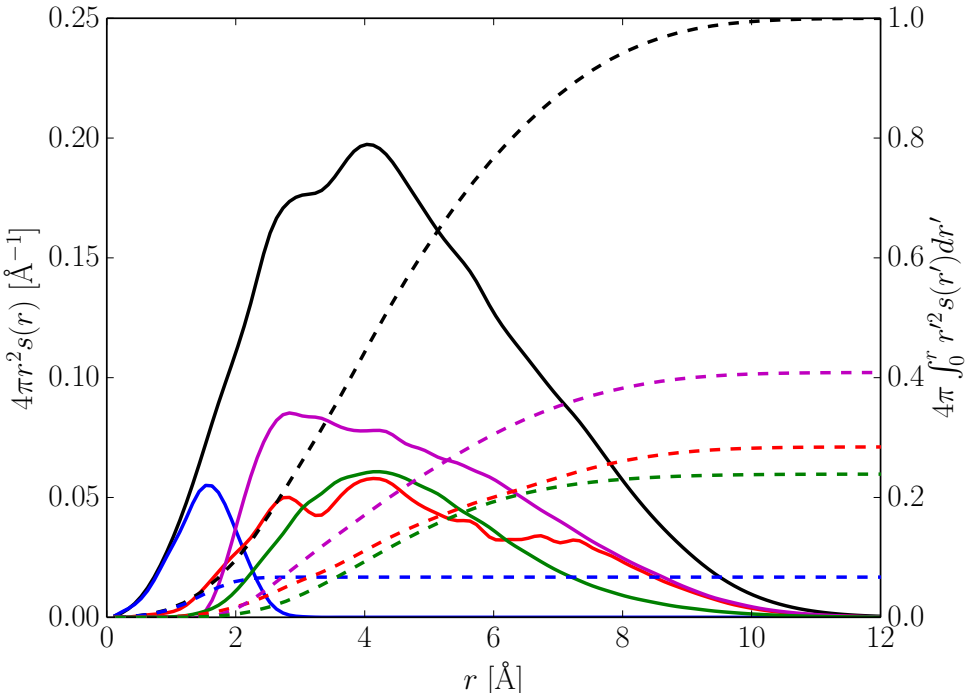

Figure S7: Average total radial profile of first excited state of interface-hydrated electron (black) and average radial profiles of individual contributions from parts of the spin density in a cavity (blue), on water (red), in the interstitial regions between water molecules (magenta) and parts of the spin density protruding into the water-vapor phase.

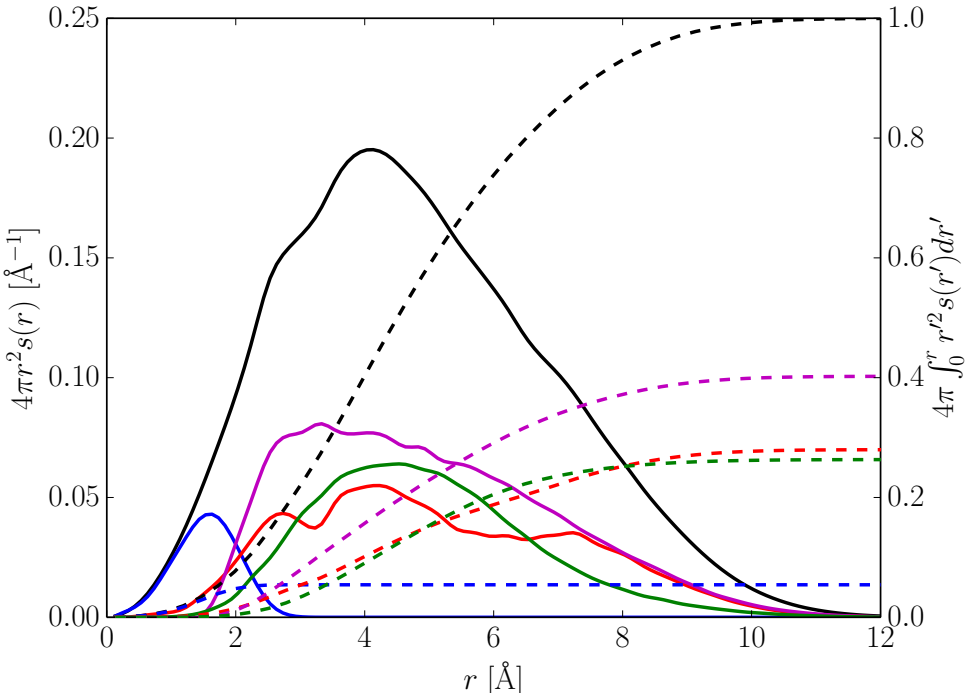

Figure S8: Average total radial profile of second excited state of interface-hydrated electron (black) and average radial profiles of individual contributions from parts of the spin density in a cavity (blue), on water (red), in the interstitial regions between water molecules (magenta) and parts of the spin density protruding into the water-vapor phase.

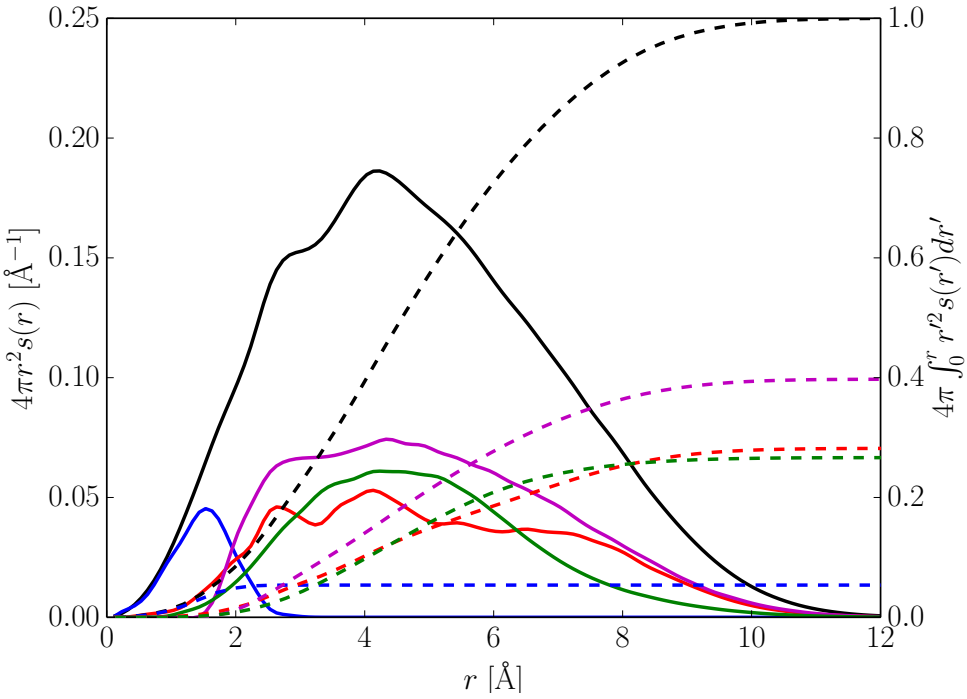

Figure S9: Average total radial profile of third excited state of interface-hydrated electron (black) and average radial profiles of individual contributions from parts of the spin density in a cavity (blue), on water (red), in the interstitial regions between water molecules (magenta) and parts of the spin density protruding into the water-vapor phase.

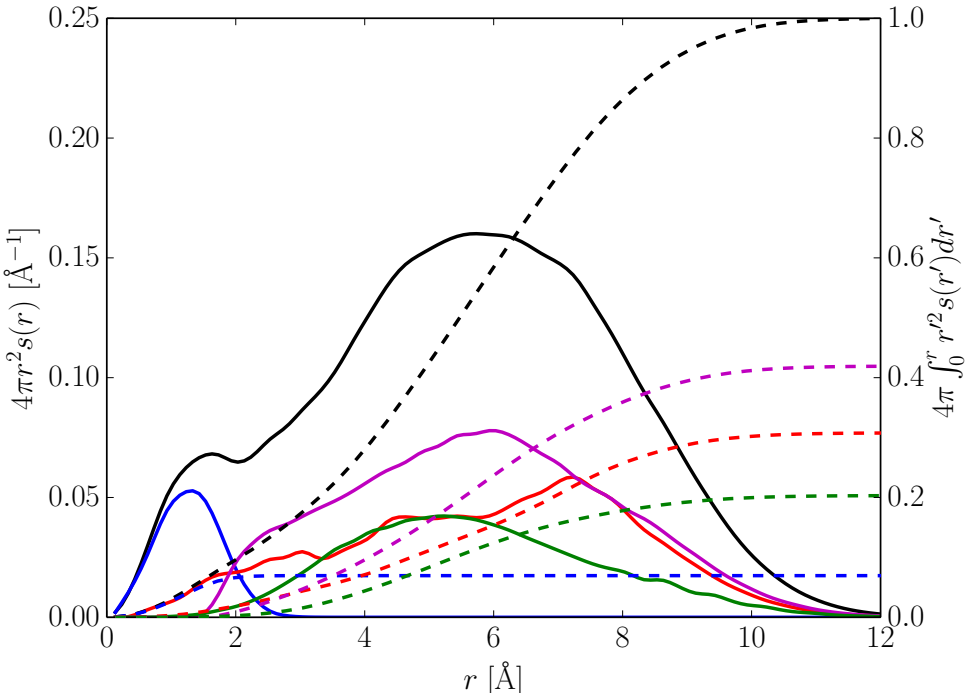

Figure S10: Average total radial profile of fourth excited state of interface-hydrated electron (black) and average radial profiles of individual contributions from parts of the spin density in a cavity (blue), on water (red), in the interstitial regions between water molecules (magenta) and parts of the spin density protruding into the water-vapor phase.

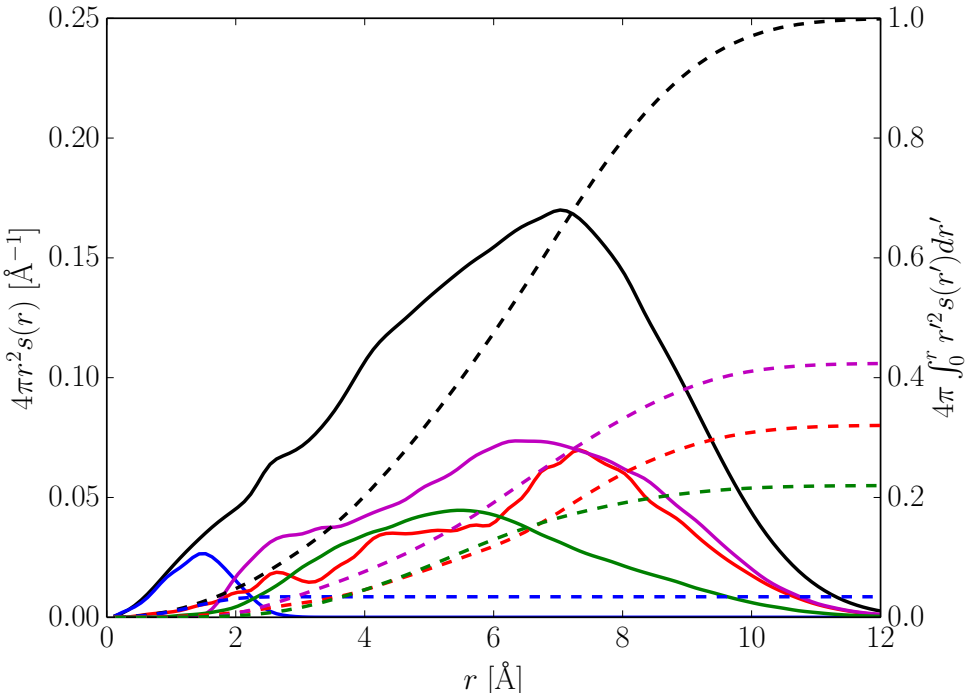

Figure S11: Average total radial profile of fifth excited state of interface-hydrated electron (black) and average radial profiles of individual contributions from parts of the spin density in a cavity (blue), on water (red), in the interstitial regions between water molecules (magenta) and parts of the spin density protruding into the water-vapor phase.

Table S1: Average integrated dissection of the excited state spin density of an electron hydrated at the water-vapor interface.

excitation	in cavity	on water	as diffuse	on surface
1	7	28	41	24
2	5	28	40	26
3	5	28	40	27
4	7	31	42	20
5	3	32	42	22

Table S2: Average distance of center of the ground state spin density to excited state spin density in Å.

excitation	distance
1	1.95
2	1.69
3	1.60
4	1.42
5	2.34