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

Supporting Information for: Unraveling the hydration-induced ground-state change of AtO^+ with relativistic and multiconfigurational wave-function-based methods

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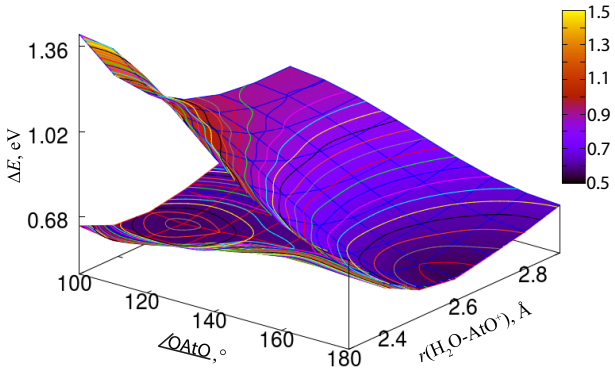

Figure S1 Evolution of the energies of the $S_0(^1\Delta)$ and $S_1(^1\Delta)$ electronic states of the $AtO^+(H_2O)$ system computed at the NEVPT2/AVTZ level of theory as a function of the H_2O–AtO^+ bond distance and of the ∠OAtO bond angle.

Equation S1 c-SOCI compositions of the five lowest spin-orbit coupled states at the equilibrium spin-restricted-singlet $AtO^+(H_2O)_n$ (n=3–5) geometries.

$$
n=3\begin{cases}
|\Psi_0\rangle = & 73\%\left|\mathrm{S}_0(^1\Delta)\right\rangle + ... \\
|\Psi_1\rangle = & 24\%\left|\mathrm{T}_0(^3\Sigma^-)\right\rangle_{M_S=+1} + 24\%\left|\mathrm{T}_0(^3\Sigma^-)\right\rangle_{M_S=-1} + 26\%\left|\mathrm{T}_0(^3\Sigma^-)\right\rangle_{M_S=0} + ... \\
|\Psi_2\rangle = & 18\%\left|\mathrm{T}_0(^3\Sigma^-)\right\rangle_{M_S=+1} + 18\%\left|\mathrm{T}_0(^3\Sigma^-)\right\rangle_{M_S=-1} + 33\%\left|\mathrm{T}_0(^3\Sigma^-)\right\rangle_{M_S=0} + ... \\
|\Psi_3\rangle = & 44\%\left|\mathrm{T}_0(^3\Sigma^-)\right\rangle_{M_S=+1} + 44\%\left|\mathrm{T}_0(^3\Sigma^-)\right\rangle_{M_S=-1} + ... \\
|\Psi_4\rangle = & 76\%\left|\mathrm{S}_1(^1\Delta)\right\rangle + ...
\end{cases}
$$

$$
n=4\begin{cases}
|\Psi_0\rangle = & 82\%\left|\mathrm{S}_0(^1\Delta)\right\rangle + ... \\
|\Psi_1\rangle = & 36\%\left|\mathrm{T}_0(^3\Sigma^-)\right\rangle_{M_S=+1} + 36\%\left|\mathrm{T}_0(^3\Sigma^-)\right\rangle_{M_S=-1} + 25\%\left|\mathrm{T}_1(^3\Pi)\right\rangle_{M_S=0} + ... \\
|\Psi_2\rangle = & 43\%\left|\mathrm{T}_0(^3\Sigma^-)\right\rangle_{M_S=+1} + 43\%\left|\mathrm{T}_0(^3\Sigma^-)\right\rangle_{M_S=-1} + ... \\
|\Psi_3\rangle = & 11\%\left|\mathrm{T}_1(^3\Pi)\right\rangle_{M_S=+1} + 11\%\left|\mathrm{T}_1(^3\Pi)\right\rangle_{M_S=-1} + 58\%\left|\mathrm{T}_0(^3\Sigma^-)\right\rangle_{M_S=0} + ... \\
|\Psi_4\rangle = & 55\%\left|\mathrm{S}_1(^1\Delta)\right\rangle + 21\%\left|\mathrm{T}_1(^3\Pi)\right\rangle_{M_S=+1} + 21\%\left|\mathrm{T}_1(^3\Pi)\right\rangle_{M_S=-1} + ...
\end{cases}
$$

$$
n=5\begin{cases}
|\Psi_0\rangle = & 83\%\left|\mathrm{S}_0(^1\Delta)\right\rangle + ... \\
|\Psi_1\rangle = & 32\%\left|\mathrm{T}_0(^3\Sigma^-)\right\rangle_{M_S=+1} + 32\%\left|\mathrm{T}_0(^3\Sigma^-)\right\rangle_{M_S=-1} + 33\%\left|\mathrm{T}_1(^3\Pi)\right\rangle_{M_S=0} + ... \\
|\Psi_2\rangle = & 41\%\left|\mathrm{T}_0(^3\Sigma^-)\right\rangle_{M_S=+1} + 41\%\left|\mathrm{T}_0(^3\Sigma^-)\right\rangle_{M_S=-1} + ... \\
|\Psi_3\rangle = & 16\%\left|\mathrm{T}_1(^3\Pi)\right\rangle_{M_S=+1} + 16\%\left|\mathrm{T}_1(^3\Pi)\right\rangle_{M_S=-1} + 50\%\left|\mathrm{T}_0(^3\Sigma^-)\right\rangle_{M_S=0} + ... \\
|\Psi_4\rangle = & 44\%\left|\mathrm{S}_1(^1\Delta)\right\rangle + 26\%\left|\mathrm{T}_1(^3\Pi)\right\rangle_{M_S=+1} + 26\%\left|\mathrm{T}_1(^3\Pi)\right\rangle_{M_S=-1} ...
\end{cases}
$$