

Supplementary Information

Photoinduced water oxidation in pyrimidine-water clusters:

A combined experimental and theoretical study

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1. Additional Computational Data

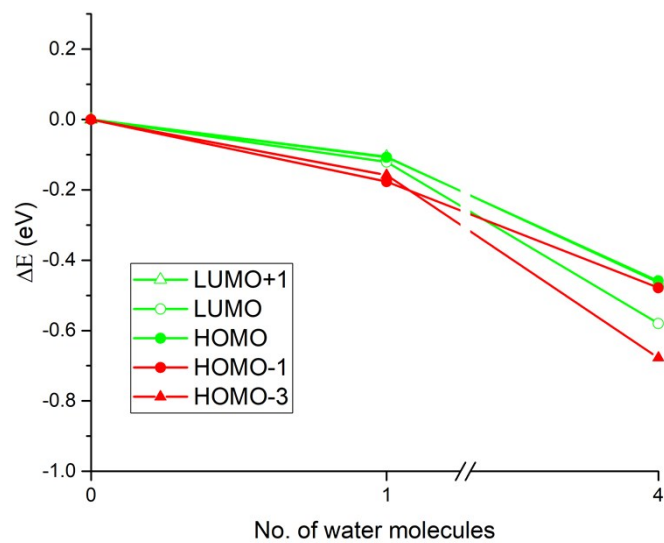


Figure SI.1. Variation of the energy of Hartree-Fock molecular orbitals of Pm in $\text{Pm}-(\text{H}_2\text{O})_n$ clusters with the cluster size. The energies of π orbitals of Pm are shown in green, the energies of σ orbitals of Pm in red.

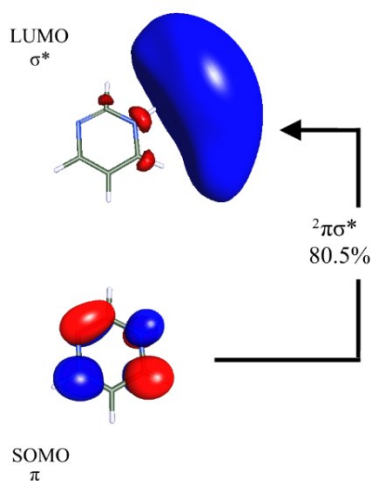


Figure SI.2. Frontier molecular orbitals involved in the main configuration of the D_2 ($2\pi\sigma^*$) state of the $\text{PmH}\cdot$ radical.

2. Additional Experimental Data

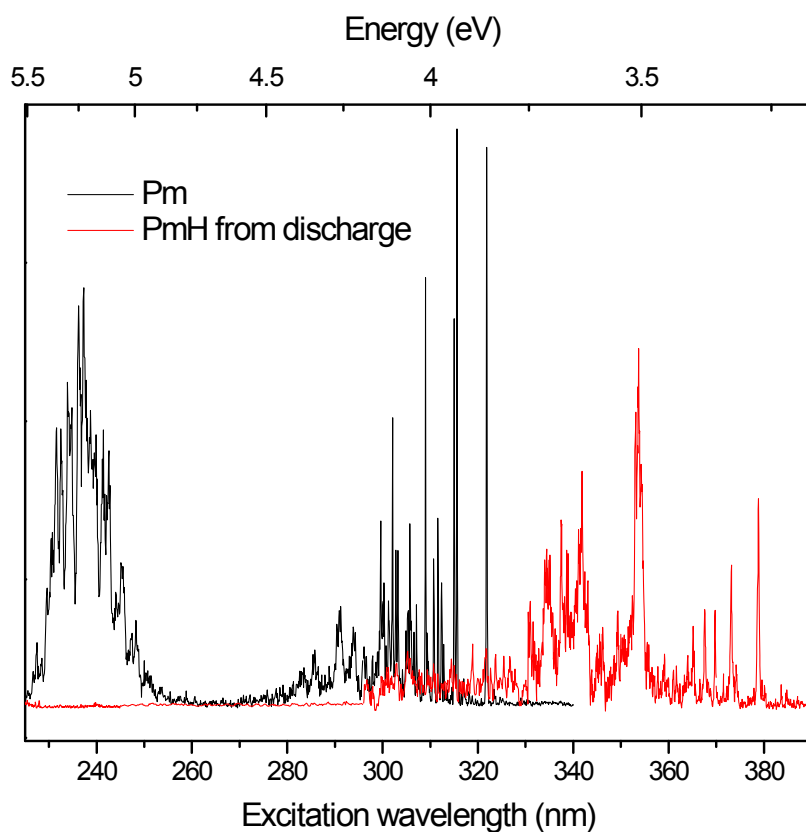


Figure SI.3. Comparison between REMPI spectra of pyrimidine (Pm, black) and the PmH• radical (red). For Pm, there are two absorption regions: one between 322 and 280 nm, and a second centered around 240 nm, with no absorption bands at wavelengths above 322 nm. The PmH• radical produced in the discharge source and cooled down in the supersonic expansion can be excited in the 330-380 nm spectral region, where pyrimidine does not absorb. Conversely, pyrimidine can be selectively excited at around 240 nm, where the PmH• radical does not absorb.

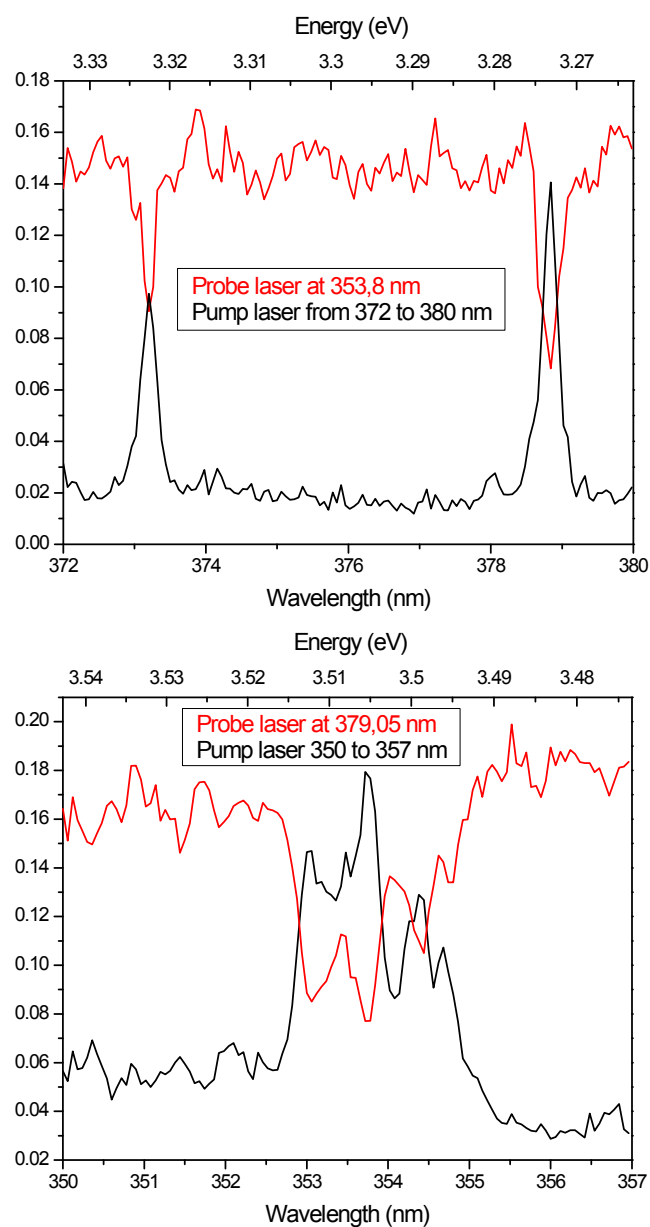


Figure SI.4. UV-UV Hole Burning spectra (red traces) obtained either by fixing the probe laser to the first band of the lower-energy PmH• system at 379.05 nm and scanning the pump laser through the broad band at higher energy between 350 and 357 nm (lower panel), or by fixing the probe laser on the broad band at 353.8 nm and scanning the pump laser across the low energy part of the spectrum between 372 and 380 nm (upper panel). In both cases, dips in the signal of the probed species (red trace) are observed compared to the PmH• spectrum obtained with the pump laser only (black trace), which implies that the two electronic transitions (379 and 353.8 nm) correspond to the same ground state species.

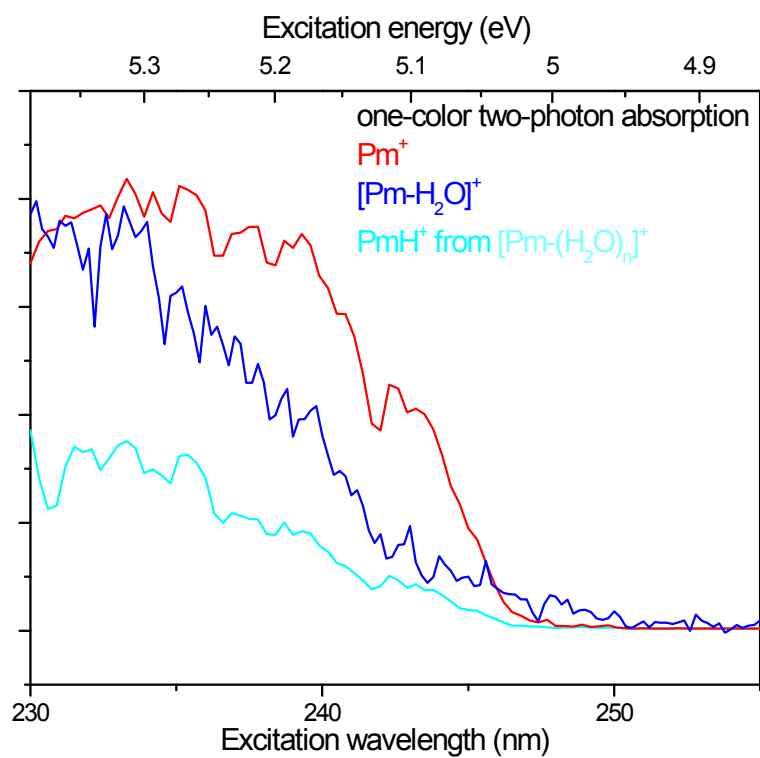


Figure SI.5. Pm^+ , PmH^+ and $\text{Pm}-(\text{H}_2\text{O})^+$ signals obtained from one-color two-photon ionization of Pm and $\text{Pm}-(\text{H}_2\text{O})_n$. Since $\text{PmH}\cdot$ does not absorb in this spectral region, in this experiment the PmH^+ comes from ionic reactions in $\text{Pm}-(\text{H}_2\text{O})_n^+$ clusters.