Photoinduced water splitting in pyridine water clusters

SUPPLEMENTARY INFORMATION

Table SI-1: Calculated vertical transition energies for PyH[•] in C_{2v} symmetry using the RI-CC2 method with the aug-cc-pVDZ basis set: first column: symmetry of the excited state; second column: calculated energy of the electronic state in eV; third column: oscillator strength; fourth column: energy of the electronic state in nm.

vertical excitation of PyH^{\bullet} in $C_{2v}symmetry$			
	E (eV)	Osc. Str.	nm
1^2A_1	3.58	4*10 ⁻⁰³	346.8
$2^2 A_1$	4.45	$9*10^{-05}$	278.5
3^2A_1	4.77	$2*10^{-02}$	259.9
$1^2 A_2$	2.81	0	440.8
2^2A_2	3.43	0	361.3
3^2A_2	4.78	0	259.5
$1^{2}B_{1}$	1.64	1*10 ⁻⁰³	265.0
$2^{2}B_{1}$	4.68	$4*10^{-02}$	265.0
$3^{2}B_{1}$	5.35	$4*10^{-02}$	231.6
$1^2 B_2$	1.98	$8*10^{-04}$	625.9
2^2B_2	2.74	$4*10^{-05}$	451.8
3^2B_2	3.32	$1*10^{-02}$	373.3
4^2 B ₂	3.78	$2.7*10^{-03}$	327.7
5^2B_2	4.28	1.3*10 ⁻⁰⁴	289.8

FIGURE SI-1: Action spectra of $Py-H_2O$: the pump laser is scanned and the detection is set on the $Py-H_2O^+$ mass (lower trace), or on the PyH^+ mass with the probe laser at 225 nm (upper trace). The spectra are similar but not identical. This suggests that part of the PyH^\bullet products are coming from clusters larger than the $Py-H_2O$ complex.



FIGURE SI-2: Mass spectra obtained for pyridine without water through a one-color two-photon excitation/ionization scheme. Upper panel: at low backing pressure only the pyridine monomer is present. Lower panel: at higher backing pressure the pyridine dimer grows together with PyH^+ product coming from a reaction in the ionic pyridine dimer.



FIGURE SI-3: Comparison between mass spectra obtained in presence (A) or in absence (B) of water clusters. A (same as Fig. 3): Upper trace: pump laser at 255 nm alone: thePy- $(H_2O)_n$ clusters are excited and thePyH⁺ion is obtained through one-color two-photon absorption. Middle trace: probe laser at 225 nm alone: nearly no ion signal sincePy and Py- $(H_2O)_n$ clusters absorb very weakly at this wavelength. The time t=0 for the ion time of flight is triggered by the pump laser, and the probe laser is delayed by 600 ns so that thePy⁺signal coming from the probe laser is 600 ns later than thePy⁺ion signal coming from the pump laser. Lower trace: pump (255 nm) and probe (225 nm) lasers delayed by 600 ns: the most intense peak is thePyH⁺ion produced by excitation of the clusters and ionization of thePyH[•]radical via a one-photon process.

B: Upper panel: pump laser only, the PyH^+ signal comes from a ionic reaction in pyridine clusters (see fig. SI-2). Middle panel: probe laser only, the delay between the pump and the probe lasers is 600 ns. The weakness of the Py^+ signal indicates that pyridine absorbs only weakly at 225 nm. Lower panel: the PyH^+ signal coming from the pump and probe lasers (in the green circle) is very weak as compared to what it is when water clusters are present (A lower panel). The peak marked with x is an electronic ringing of the MCP due to the intense Py^+ signal.



Figure SI-4: Excitation/actionspectra of the species in the jet. For the homodimer, the $Py-H_2O$ and the Py channels, the spectra correspond to a one-color two-photon excitation / ionization process. For the PyH^{\bullet} and $dPyD^{\bullet}$ channels, the action spectra correspond to excitation of the $Py-(H_2O)_n$ clusters (or $dPy-(D_2O)_n$) and ionization of the reaction product at 225 nm. The band observed at 262 nm is observed in dPyD/PyH and in the water complex. One can see also that the product spectrum is quite different from the homodimer spectrum. In the Py channel, the weak absorption in the 255-265 nm regions is most probably due to the evaporation of water molecules from $Py-(H_2O)_n$ ionic clusters.

