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Supporting Information to

Isolated 2-Hydroxypyrene and its Dimer: A Frequency- and Time-Resolved Spectroscopic Study

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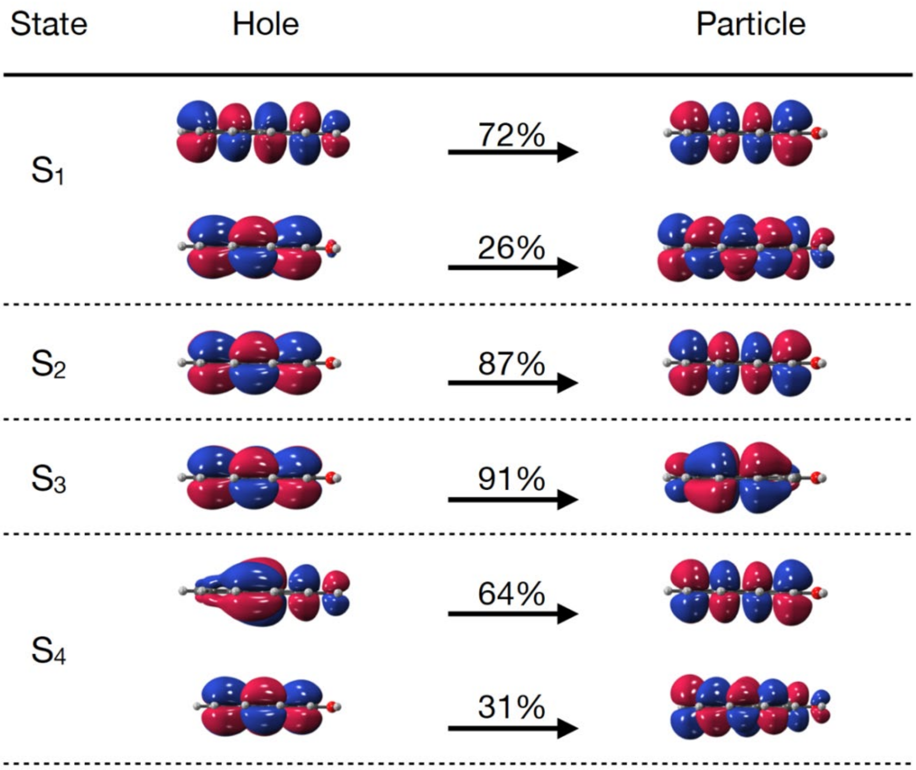

Figure S1. Natural transition orbitals of the first four excited states of 2-hydroxypyrene at the TDDFT (wB97XD/def2-TZVP) level. Only contributions that are 20% or larger shown.

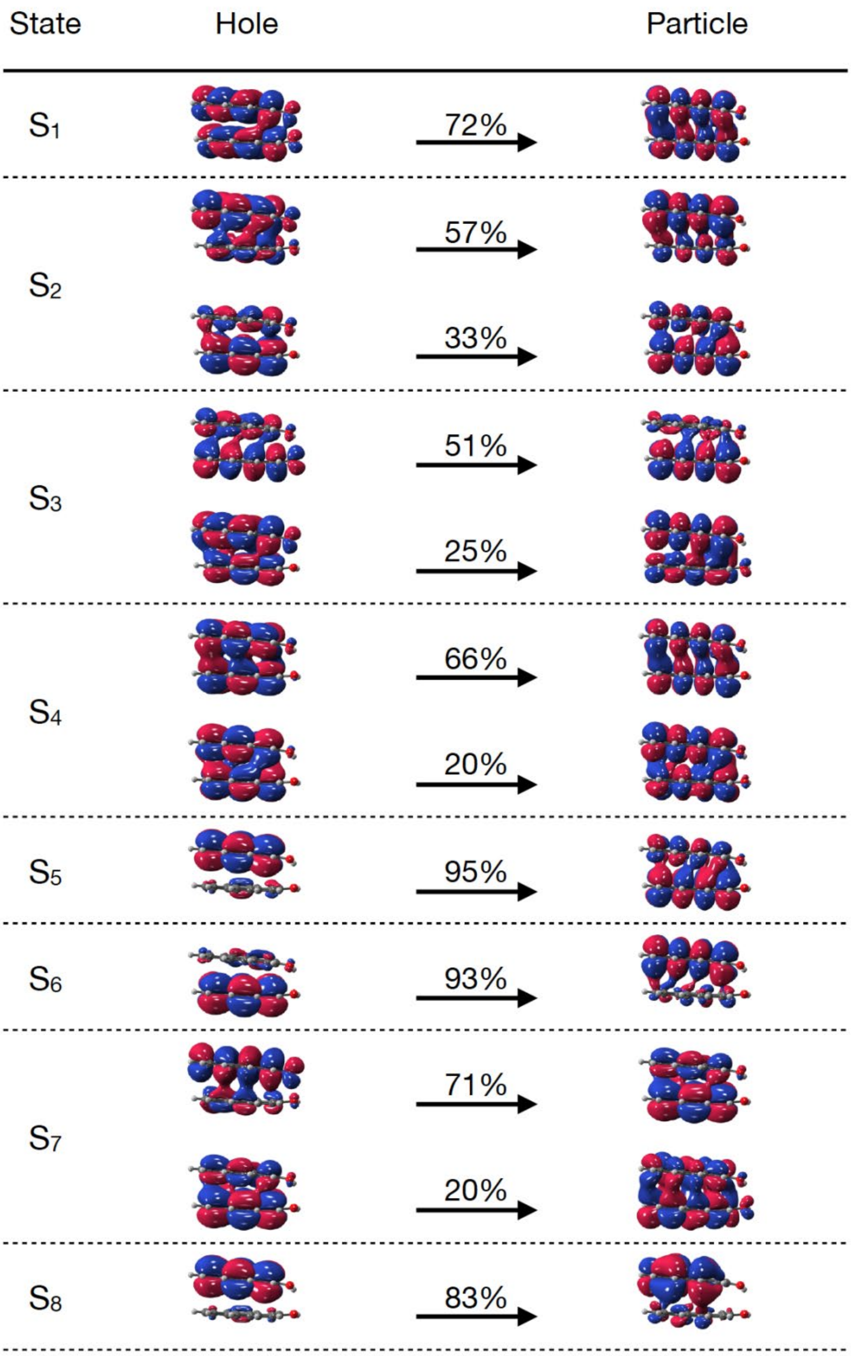

Figure S2. Natural transition orbitals of the first eight excited states of the 2-hydroxypyrene dimer at the TDDFT (wB97XD/def2-TZVP) level. Only contributions that are 20% or larger shown.

Fragmentation in cluster experiments

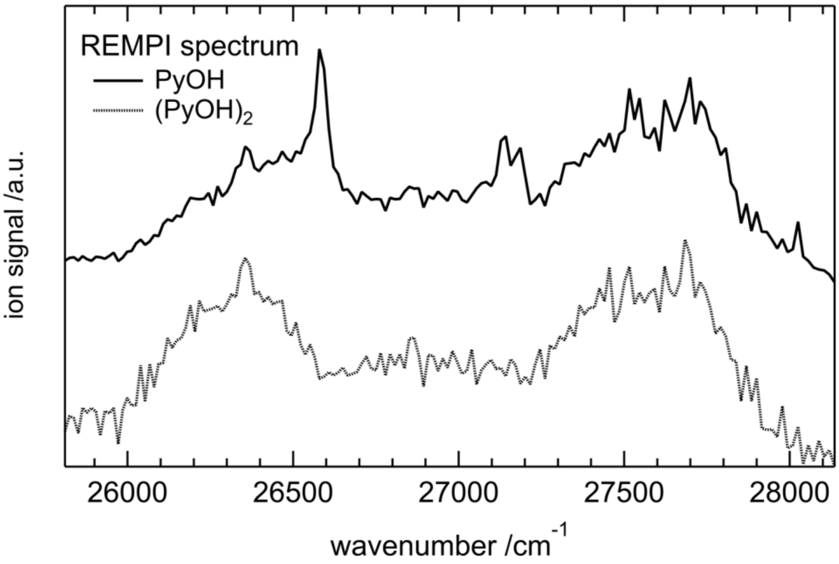

Figure S3. Under suitable expansion conditions, PyOH dimers are formed through three-body collisions (see Figure 2 of the main manuscript). These dimers can fragment and superimpose the monomer ion signal. The Figure compares the ion signal in the monomer and dimer mass channels in the presence of clusters. The features of the dimer absorption spectrum are present in the monomer mass channel.

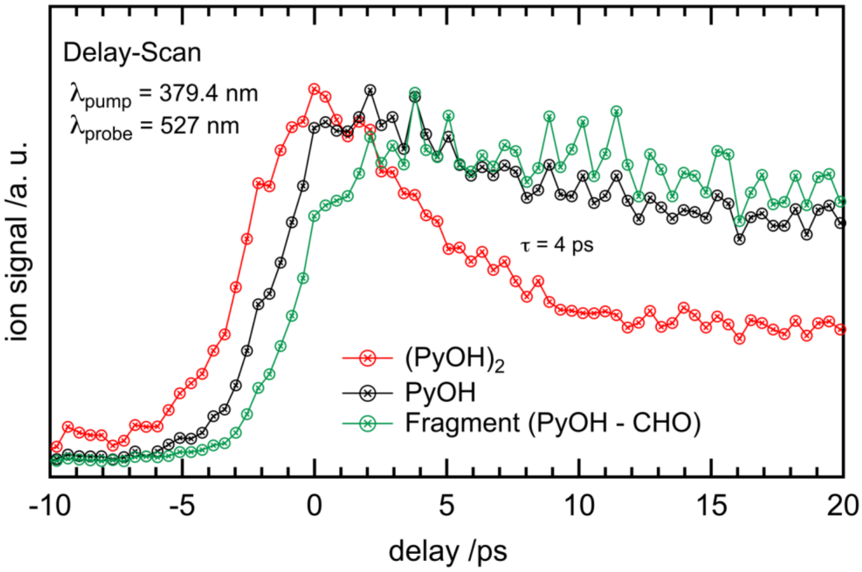

Figure S4. After excitation of the origin band of the 2-hydroxypyrene dimer, fragment signals appear slightly shifted in time ($\Delta t \approx 2$ps). We assume that the initially excited S_4 state deactivates in a multi-step process via lower-lying singlet states. In one of them, branching seems to occur between further IC to a long-lived S_1 state of the dimer and fragmentation. These steps are too fast to be fully time-resolved with our setup.

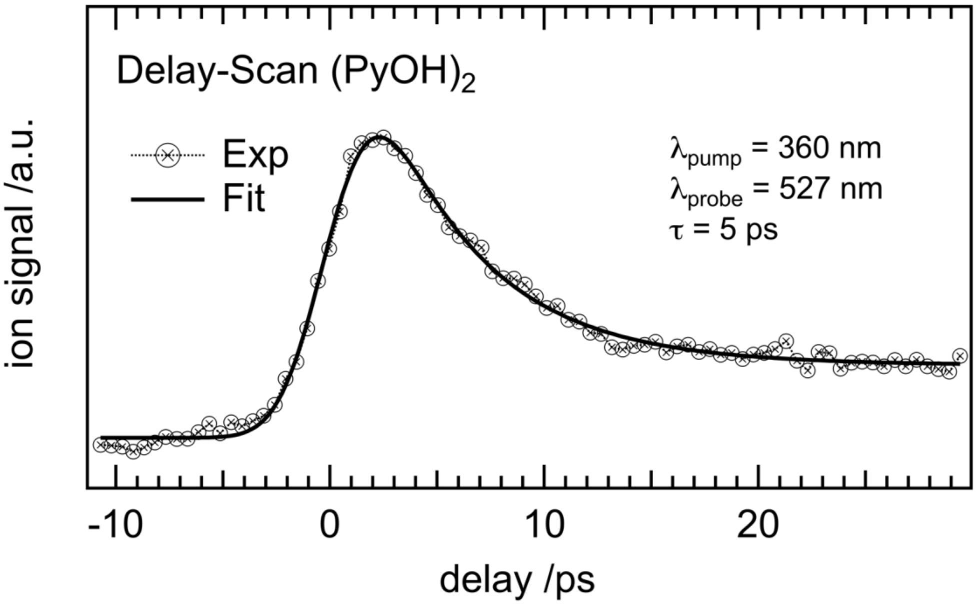

Figure S5. Time delay scan of the 27690 cm^{-1} band of the 2-hydroxypyrene dimer. As is the case for the origin band, the signal decays to an offset at longer delay times. It can again be fitted by a time constant of 5 ps

Table S1. Comparison of the experimental and calculated wavenumbers for the vibrational bands of the S_1 state of 2-hydroxypyrene. In addition, the experimental band positions for the $S_1 \leftarrow S_0$ transition in pyrene are given. [a](wB97xD, def2-TZVP, unscaled), [b]Hoche et al.[1], [c]Baba et al.[2]

2-hydroxypyrene		pyrene
rel. wavenumber /cm^{-1} (exp.)	wavenumber /cm^{-1} (calc. [a])	wavenumber /cm^{-1} (exp.)
26590 (origin)	29699	27218 (origin)
+410	+367	+376[b]
+550	+568	+559[b]
+590	+620	
+750	+764	
+770	+808	+777[b]
+950	+979	+919[b]
+1030	+1006	+1014[b]
+1040	+1096	
+1120	+1127	+1094[b]
+1150	+1140	+1144[c]
+1210	+1214	+1246[c]
+1270	+1276	+1282[c]
+1340	+1374	+1331[c]
+1380	+1384	+1397[c]
+1430	+1423	
+1480	+1480	+1467[c]
+1500	+1496	+1520[c]

Table S2. Comparison of the experimental and calculated wavenumbers for the vibrational bands of the S_2 state of 2-hydroxypyrene. In addition, the experimental band positions for the $S_2 \leftarrow S_0$ transition in pyrene are given. [a](wB97xD, def2-TZVP, unscaled), [b]Hoche et al.[1]

2-hydroxypyrene		pyrene
rel. wavenumber /cm^{-1} (exp.)	wavenumber /cm^{-1} (calc. [a])	wavenumber /cm^{-1} (exp.[b])
30940 (origin)	31364	31191 (origin)
+360	+363	+414
+610	+620	+595
+710	+762	+696
+850	+983	+809
+1110	+1159	+1119
+1240	+1276	+1224
+1390	+1392	+1414
+1540	+1454	
+1730	+ 1688	+1617
+1890	+1818	+1834
+2110	+2074	+2010

References

1. J. Hoche, H.-C. Schmitt, A. Humeniuk, I. Fischer, R. Mitrić and M. I. S. Röhr, *Phys. Chem. Chem. Phys.*, 2017, **19**, 25002-25015.
2. M. Baba, M. Saitoh, Y. Kowaka, K. Taguma, K. Yoshida, Y. Semba, S. Kasahara, T. Yamanaka, Y. Ohshima, Y.-C. Hsu and S. H. Lin, *J. Phys. Chem.*, 2009, **131**, 224318.