

## **Supporting Information: The Missing NH Stretch Fundamental in S<sub>1</sub> Methyl Anthranilate: IR-UV Double Resonance Experiments and Local Mode Theory**

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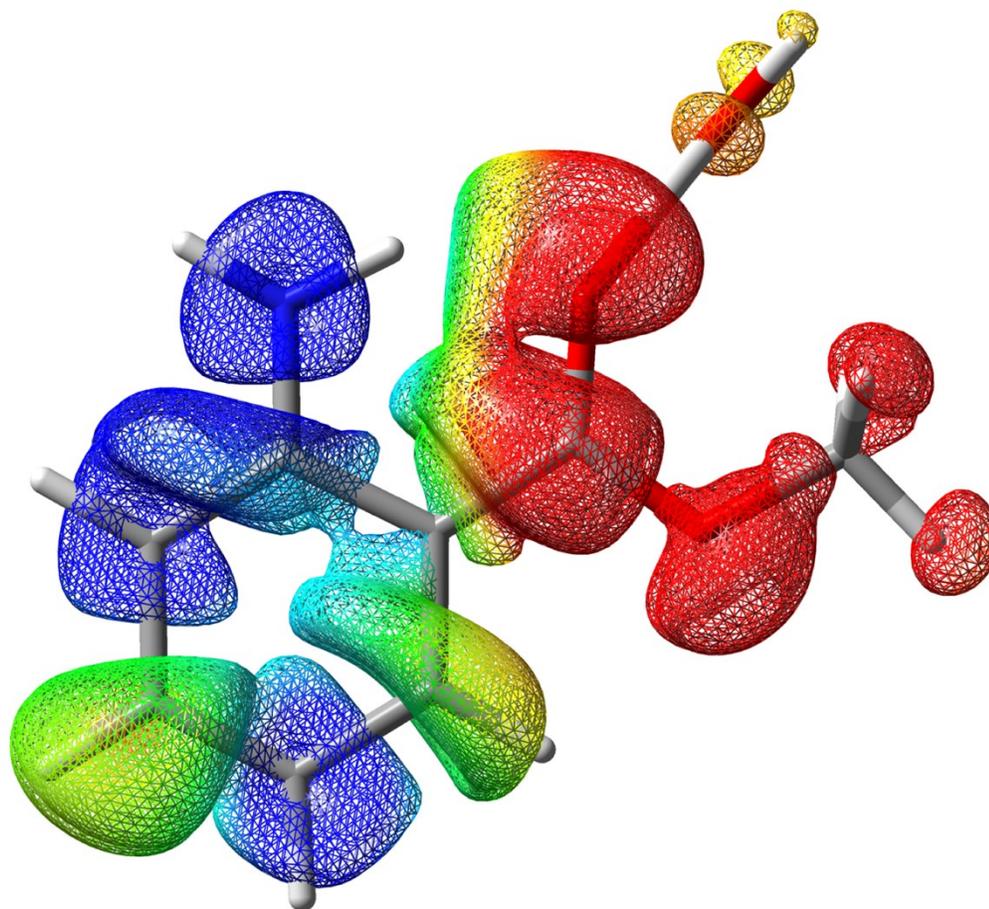
## 1. Electronic States in MA and MA-H<sub>2</sub>O

**Table S1:** Electronic States in MA and MA-H<sub>2</sub>O<sup>a</sup>. Adapted from *Phys. Chem. Chem. Phys.*, 2019, 21, 21355 with permission of the PCCP Owner Societies.

Methyl Anthranilate			Methyl Anthranilate-H <sub>2</sub> O		
State	Energy (eV)	$f_{0n}$	State	Energy (eV)	$f_{0n}$
$^3\pi\pi^*$	3.03	0.0000	$^3\pi\pi^*$	2.95	0.0000
$^3\pi\pi^*$	3.56	0.0000	$^3\pi\pi^*$	3.50	0.0000
$^1\pi\pi^*$	3.92	0.1036	$^1\pi\pi^*$	3.84	0.1077
$^3\pi\pi^*$	4.17	0.0000	$^3\pi\pi^*$	4.12	0.0000
$^3n\pi^*$	4.69	0.0000	$^3n\pi^*$	4.81	0.0000
$^1n\pi^*$	5.08	0.0002	$^1n\pi^*/\pi\pi^*$	5.15	0.0530
$^1\pi\pi^*$	5.23	0.0481	$^1n\pi^*/\pi\pi^*$	5.18	0.0117

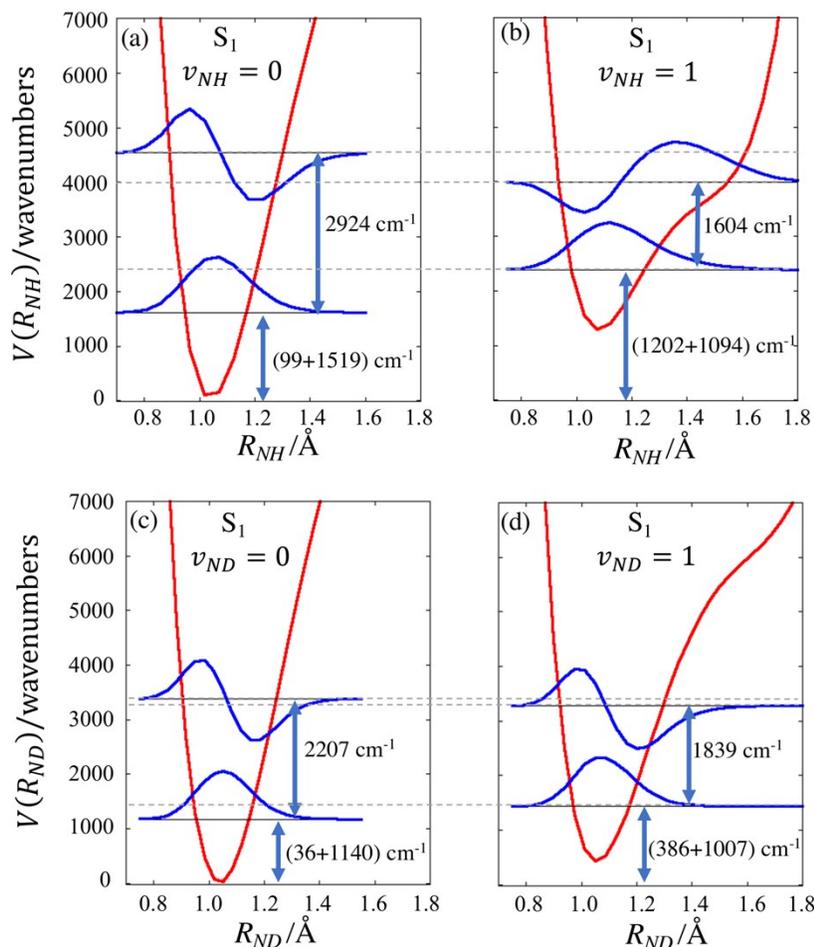
<sup>a</sup>Values calculated at the DFT B3LYP-D3BJ/def2TZVP level of theory

## 2. Change in Electrostatic Potential Mapped onto Increasing Electron Density Surface in MA-H<sub>2</sub>O



**Figure S1:** The change in electrostatic potential mapped onto the surface of increasing electron density in going from  $S_0 - S_1$  in MA-H<sub>2</sub>O. Calculated at the TD-DFT B3LYP-D3BJ/def2TZVP level of theory. The appearance of a covalent bond between the C=O and water OH groups is an artifact of the calculation.

### 3. NH and ND Stretch Eigenfunctions and Corresponding Potentials in S<sub>1</sub>



**Figure S2:** (a) and (b) show the two lowest energy NH stretch eigenfunctions and corresponding potentials in S<sub>1</sub> plotted as a function of bond length. The zero of energy is the true calculated potential minimum of the excited state. Remaining coordinates values were chosen to minimize  $E(v=0)$  in (a) and  $E(v=1)$  in (b). In (a) there is 99  $cm^{-1}$  of energy at the bottom of the well; in (b) there is 1202  $cm^{-1}$  of energy. In (a)  $E(v=0)$  is 1618  $cm^{-1}$  and  $E(v=1)$  is 4542  $cm^{-1}$ . In (b)  $E(v=0)$  is 2296  $cm^{-1}$  and  $E(v=1)$  is 3900  $cm^{-1}$ . The energy difference between 4542 and 3900  $cm^{-1}$  will get deposited into the remaining degrees of freedom. Results are for excited states using TD/B3LYP/6-311++(d,p) level of theory with dispersion. (c) and (d) displays analogous results for the S<sub>1</sub> state of the ND stretch. The difference between vertical and minimum energies for the  $v_{ND} = 1$  state is  $\Delta E_s = 151$   $cm^{-1}$  compared to the analogous 642  $cm^{-1}$  value found for the NH stretch.