Supporting Information: Vibronic Spectroscopy of Methyl Anthranilate and its Water Complex: Hydrogen Atom Dislocation in the Excited State

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Table of Contents

1. Mass-Resolved Two-Color Resonant Two-Photon Ionization Spectra (2C-R2PI) of MA and MA-H\textsubscript{2}O p. 3

2. Rotamers of MA p. 4

3. NH\textsubscript{2} Inversion Potential of MA p. 5

4. Molecular Orbitals Involved in Electronic Transitions of MA p. 5-6

5. Fluorescence Decay Traces of MA and MA-H\textsubscript{2}O p. 7


7. Dispersed Fluorescence Spectra of Vibronic Bands with Increasing Energy in MA p. 8

8. Fermi Resonance Analysis p. 9-11

9. Low-Energy Water Complex Conformers p. 11-12

10. Molecular Orbitals Involved in Electronic Transitions of MA-H\textsubscript{2}O p. 12-14
11. Normal Modes, and Reduced Duschinsky Matrix, of MA-H₂O
   p. 14

12. Aniline S₀ and S₁ Calculated Geometries and Molecular Orbitals involved in the Transition
   p. 15

13. Methyl Benzoate S₀ and S₂ Calculated Geometries and Molecular Orbitals Involved in Electronic Transitions
   p. 16-17

14. Comparison of the Anthranilates
   p. 17-18

15. Franck-Condon Analysis
   p. 19-20

16. Transition Dipole Moment Vectors of Methyl Anthranilate, Aniline, and Methyl Benzoate
   p. 21
1. Mass-Resolved Two-Color Resonant Two-Photon Ionization Spectra (2C-R2PI) of MA and MA-H$_2$O

The identity of MA and MA-H$_2$O were confirmed with mass-resolved 2C-R2PI spectra. In this scheme, two temporally overlapped, counter-propagating UV lasers, $\lambda_{\text{scan}}$ and $\lambda_{\text{ionize}}$, interact at a 90° angle with the skimmed molecular beam in the extraction region of the Time of Flight (TOF) mass-spectrometer. The ionization potential of MA and MA-H$_2$O are such that two photons at the absorbing 0$^0_0$ region ($\lambda_{\text{scan}}$) do not possess sufficient energy to ionize either species. A second, higher energy photon ($\lambda_{\text{ionize}}$) ensures that molecules that have undergone absorption of $\lambda_{\text{scan}}$ are promoted to the ionization continuum. Care is taken to ensure that no ion signal is generated from either $\lambda_{\text{scan}}$ or $\lambda_{\text{ionize}}$ individually.

The 2C-R2PI spectra of MA and MA-H$_2$O are shown in Figure S1(a) and S1(b), respectively. These spectra were recorded by monitoring ion current in the 151 and 169 amu mass channels, respectively, as a function of $\lambda_{\text{scan}}$. The same region that was recorded using LIF spectroscopy was recorded using 2C-R2PI for MA. For MA-H$_2$O, only the first ~250 cm$^{-1}$ region was recorded. The peak positions, in both cases, verify the identity of the species.

**Figure S1:** 2C-R2PI spectra of MA (a) and MA-H$_2$O (b).
2. Rotamers of MA

![Figure S2](image)

*Figure S2*: The two low-energy rotamers of MA. Zero-point corrected energies calculated at the DFT B3LYP-D3BJ/def2TZVP level of theory.

3. NH$_2$ Inversion Potential of MA

![Figure S3](image)

*Figure S3*: Relaxed potential energy scans about the improper CNHH dihedral defining the NH$_2$ inversion in MA, in the $S_0$ (bottom) and $S_1$ (top) electronic states.
4. Molecular Orbitals Involved in Electronic Transitions of MA

**Figure S4:** Molecular orbitals involved in the $S_0 - S_1$ electronic transition of MA, along with the coefficients, calculated vertical excitation wavelength, and oscillator strength. Calculations performed at the DFT B3LYP-D3BJ/def2TZVP level of theory.

**Figure S5:** Molecular orbitals involved in the $S_0 - T_1$ electronic transition of MA, along with the coefficients, calculated vertical excitation wavelength, and oscillator strength. Calculations performed at the DFT B3LYP-D3BJ/def2TZVP level of theory.
**Figure S6:** Molecular orbitals involved in the $S_0 - S_2$ electronic transition of MA, along with the coefficients, calculated vertical excitation wavelength, and oscillator strength. Calculations performed at the DFT B3LYP-D3BJ/def2TZVP level of theory.

**Figure S7:** Molecular orbitals involved in the $S_0 - S_3$ electronic transition of MA, along with the coefficients, calculated vertical excitation wavelength, and oscillator strength. Calculations performed at the DFT B3LYP-D3BJ/def2TZVP level of theory.
5. Fluorescence Decay Traces of MA and MA-H$_2$O

![Fluorescence Decay Traces](image)

**Figure S8:** Fluorescence decay traces of (a) MA and (b) MA-H$_2$O. Lifetimes were obtained by fitting each trace to a single exponential decay and extracting the time constant, $\tau$ (lifetime). The lifetime is measured to be 27 ns for MA and 23 ns for MA-H$_2$O.

6. Rotational Band Contour of the Electronic Origin of MA

![Rotational Band Contour](image)

**Figure S9:** Rotational band contour (RBC) scan of the electronic origin transition (top trace), taken at a UV laser resolution of 0.15 cm$^{-1}$. The bottom trace is the computed fit using the calculated transition dipole moment ($a:b:c = 77:23:0$) components and rotational constants from calculated ground and excited states. This fit was computed using the JB95 spectral fitting program.$^1$
7. Dispersed Fluorescence Spectra of Vibronic Bands with Increasing Energy in MA

**Figure S10:** DFL spectra taken at increasing energies from the origin transition in MA.
8. Fermi Resonance Analysis

As described in the main text, two pairs of peaks in the LIF spectrum were identified as Fermi-Resonance pairs (see Figure S11). These pairs are assigned to the $50^{1}0_{52}^{1}$ combination and Franck-Condon allowed $35^{1}0$ fundamental transition, and the $50^{1}0_{51}^{1}$ combination and Franck-Condon allowed $34^{1}0$ fundamental transition. The DFL spectra collected from each member of the second pair of Fermi-mixed transitions is shown in Figure S12. The $\Delta v=0$ emission to both the $50_{51}^{1}$ and $34_{1}$ ground state levels enables a quantitative analysis of the Fermi resonance mixing coefficients, $\alpha$ and $\beta$, to which we now turn.

Figure S11: The portion of the LIF spectrum containing the two pairs of Fermi-mixed vibronic levels, marked with asterisks.

Figure S12: DFL spectra collected from each member of the Fermi-mixed $50^{1}0_{51}^{1}$ combination and Franck-Condon allowed $34^{1}0$ fundamental transitions.
In the $S_1$ electronic state, the Fermi-mixed wavefunctions may be expressed, using bra-ket notation, as a linear combination of the unmixed wavefunctions,

$$|\psi_{366}\rangle = \alpha|a'\rangle + \beta|2a''\rangle$$

$$|\psi_{360}\rangle = \beta|a'\rangle - \alpha|2a''\rangle$$

Where $|a'\rangle$ is the $S_1$ 341 wavefunction, $|2a''\rangle$ is the $S_1$ 501511 wavefunction, $\alpha$ and $\beta$ are the mixing coefficients. Solving for the Franck-Condon factor (FCF) from the $S_0$ zero-point level, $<0|$, to each of these $S_1$ vibrational levels, and assuming that the wavefunction overlap $<0|2a''\rangle$ is negligible, we obtain

$$\text{FCF}_{0,366} = |<0|\psi_{366}\rangle|^2 = \alpha^2 |<0|a'\rangle|^2$$

and

$$\text{FCF}_{0,360} = |<0|\psi_{360}\rangle|^2 = \beta^2 |<0|a'\rangle|^2$$

Taking the ratio

$$\frac{\text{FCF}_{0,366}}{\text{FCF}_{0,360}} = \frac{\alpha^2}{\beta^2}$$

gives the relative intensities of the vibronic bands in the LIF spectrum. Integrating these experimental bands, we obtain

$$\frac{\alpha^2}{\beta^2} = 1.80$$

Solving the FCF integrals for the projection of each Fermi-mixed $S_1$ level onto the individual $S_0$ components, $<a'|(341)$ and $<a''|(501511)$, we obtain

$$|<a'|\psi_{366}\rangle|^2/|<2a''|\psi_{366}\rangle|^2 = (\alpha^2|<a'|a'>|^2)/(\beta^2|<2a''|2a''|^2) = \alpha^2/\beta^2 = 1.80$$

and

$$|<a'|\psi_{360}\rangle|^2/|<2a''|\psi_{360}\rangle|^2 = (\beta^2|<a'|a'>|^2)/(\alpha^2|<2a''|2a''|^2) = \beta^2/\alpha^2 = 0.55$$

where we have assumed a 1:1 correspondence between analogous $S_0$ and $S_1$ normal modes (i.e., no Duschinsky mixing). From the experimental DFL spectra, we measure the relative integrated intensities to be

$$|<a'|\psi_{366}\rangle|^2/|<2a''|\psi_{366}\rangle|^2 = 1.70$$
and

\[ |<a'|\psi_{360}>|^2/|<2a'|\psi_{360}>|^2 = 0.52 \]

The good agreement between calculated and measured peak intensities allows us to express the normalized S\(_1\) Fermi-mixed wavefunctions as

\[ |\psi_{366} > = 0.802|a'> + 0.597|2a'' > \]

\[ |\psi_{360} > = 0.597|a'> - 0.802|2a'' > \]

As anticipated, the excited state level +366 cm\(^{-1}\) above the S\(_1\) ZPL is about 64% 34\(^{1}\) and 36% 50\(^{1}\)51\(^{1}\), while the one at 360 cm\(^{-1}\) is the reverse; that is, 36% 34\(^{1}\) and 64% 50\(^{1}\)51\(^{1}\) (see Figure S11).

### 9. Low-Energy Water Complex Conformers

In addition to the assigned MA-H\(_2\)O water complex, several other low-energy conformational minima were found. These conformers, along with their basis-set superposition error (BSSE) corrected and/or zero-point (ZPE) corrected energies are presented in Table S1 and Figure S13.

**Table S1:** Relative zero-point corrected potential energies, BSSE and zero-point corrected potential energies, adiabatic and vertical excitation energies of the water complex conformers calculated to lie within 10 kJ/mol of the global minimum. Calculations performed at the DFT B3LYP-D3BJ/def2TZVP level of theory.

<table>
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<tr>
<th>Complex</th>
<th>ZPE corr. Electronic energy (kJ/mol)</th>
<th>BSSE and ZPE corr. Electronic energy (kJ/mol)</th>
<th>TD-DFT Adiabatic S(_0)-S(_1) Excitation Energy (cm(^{-1}))</th>
<th>TD-DFT Vertical S(_0)-S(_1) Excitation Energy (cm(^{-1}))</th>
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<td>0</td>
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<tr>
<td>MAw9</td>
<td>4.6812665</td>
<td>5.352848133</td>
<td>27,220</td>
<td>32,995</td>
</tr>
</tbody>
</table>
10. Molecular Orbitals Involved in Electronic Transitions of MA-H₂O

**Figure S13:** All MA-H₂O conformers, with their BSSE/ZPE-corrected energies, calculated to lie within 10 kJ/mol of the global minimum.

**Figure S14:** Molecular orbitals involved in the $S_0 - S_1$ electronic transition of MA-H₂O, along with the coefficients, calculated vertical excitation wavelength, and oscillator strength. Calculations performed at the DFT B3LYP-D3BJ/def2TZVP level of theory.
Figure S15: Molecular orbitals involved in the $S_0$ - $T_4$ electronic transition of MA-H$_2$O, along with the coefficients, calculated vertical excitation wavelength, and oscillator strength. Calculations performed at the DFT B3LYP-D3BJ/def2TZVP level of theory.

Figure S16: Molecular orbitals involved in the $S_0$ - $S_2$ electronic transition of MA-H$_2$O, along with the coefficients, calculated vertical excitation wavelength, and oscillator strength. Calculations performed at the DFT B3LYP-D3BJ/def2TZVP level of theory.
14

Figure S17: Molecular orbitals involved in the $S_0 - S_3$ electronic transition of MA-H$_2$O, along with the coefficients, calculated vertical excitation wavelength, and oscillator strength. Calculations performed at the DFT B3LYP-D3BJ/def2TZVP level of theory.

11. Normal Modes, and Reduced Duschinsky Matrix, of MA-H$_2$O

Figure S18: Reduced Duschinsky rotation matrix, and vector displacement representation of the Franck-Condon active normal modes of MA-H$_2$O. Values in parentheses are those corresponding values in the MA monomer. Calculations performed at the DFT B3LYP-D3BJ/def2TZVP level of theory.
12. Aniline $S_0$ and $S_1$ Calculated Geometries and Molecular Orbital Transitions

$S_0 \rightarrow S_1 (\pi\pi^*) \quad \lambda = 261.30 \text{ nm} \quad f = 0.0359$

**Figure S19:** The (a) molecular orbitals, transition coefficients, oscillator strength, (b) bond distance, and (c) bond angle parameters associated with the $S_0 - S_1$ transition of aniline. Calculations performed at the DFT B3LYP-D3BJ/def2TZVP level of theory.
13. Methyl Benzoate $S_0$ and $S_1$ Calculated Geometries and Molecular Orbital Transitions

Figure S20: The (a) bond distance, and (b) bond angle parameters associated with the $S_0 - S_2$ transition of methyl benzoate. Calculations performed at the DFT B3LYP-D3BJ/def2TZVP level of theory.

Figure S21: Molecular orbitals involved in the $S_0 - S_2$ electronic transition of methyl benzoate, along with the coefficients, calculated vertical excitation wavelength, and oscillator strength. Calculations performed at the DFT B3LYP-D3BJ/def2TZVP level of theory.
Figure S22: Molecular orbitals involved in the $S_0 \rightarrow T_3$ electronic transition of methyl benzoate, along with the coefficients, calculated vertical excitation wavelength, and oscillator strength. Calculations performed at the DFT B3LYP-D3BJ/def2TZVP level of theory.

14. Comparison of the Anthranilates

The results presented herein allow us to compare similar systems to one another. We begin with MA and MA-H$_2$O. As we saw in section III, the LIF excitation and 0$_0^0$ DFL spectra of MA and MA-H$_2$O are quite similar to one another, with analogous modes dominating the spectra of both. Aside from breaking the C$_s$ symmetry of the monomer unit, the effect of water binding on molecular structure, and therefore, vibrational frequencies, seems to have little effect. This is evident by the small shift in analogous Franck-Condon active frequencies between hydrated and non-hydrated MA, shown in Table 2 of the main text. The MA-H$_2$O 0$^0_0$ transition is 278 cm$^{-1}$ lower energy than that of MA. In a simple estimation, this shift may be explained by the polarization of molecular orbitals involved in the electronic transition by the water interaction.

The structural changes that occur in MA upon UV excitation also occur in MA-H$_2$O, to a degree that is modulated by the water interaction. Upon excitation in MA-H$_2$O the aromatic ring flattens, the amine group tilts toward the methoxycarbonyl group, closing the C6 ring formed by
the NH···O=C hydrogen bond. The N-H$_{\text{donor}}$ bond increases in length by 0.022 Å, the O=C bond increases in length by 0.034 Å, resulting in a decrease of the H···O hydrogen bonding distance by 0.180 Å (going from 1.935 to 1.755 Å). **Table 3** in the main text lists the $S_0$, $S_1$, and difference in structural parameters for MA and MA-H$_2$O. The water molecule rotates and moves out of plane (see **Figure 11** in the main text). This has the effect of decreasing the OH···O=C hydrogen bonding distance by 0.080 Å and increasing the H$_2$O···CH$_3$ distance by 0.220 Å. We see, then, that the structural change of MA-H$_2$O upon electronic excitation proceeds along the same hydrogen dislocation coordinate as that of MA, to a degree determined by the H$_2$O interaction.

Time dependent density functional theory results indicate that the electronic $S_0$-$S_1$ transition in both MA and MA-H$_2$O may be described by two single-electron transitions from one molecular orbital to another. The molecular orbitals responsible for these transitions in MA and MA-H$_2$O are shown in **Figure S4** and **S14**. The orbitals, and coefficients, involved in the electronic transition in each case are nearly identical to one another and may be described as a textbook example of conjugated $\pi$ bonding orbitals moving electron density onto conjugated $\pi^*$ anti-bonding orbitals.

The nature of the structural change upon electronic excitation between MA and AA are very similar to one another. Hydrogen atom dislocation occurs in each case.\(^2\) The LIF excitation spectrum of each species also has progressions in the same normal modes, designated as modes $v_{36}$ and $v_{33}$ in MA. The single water complexes of MA and AA are also quite similar to one another.\(^3\) In each case, a water hydrogen bonds with the monomer C=O. In AA-H$_2$O, an additional hydrogen bond is formed between the water oxygen and monomer acid H-O group, which MA lacks. The absence of water hydrogen bonding with the NH$_2$ in each case is perhaps not surprising, given the extremely strong hydrogen bond in which the amine group is already participating.
15. Franck-Condon Analysis

To further quantify the difference between excited and ground electronic states of MA, we carried out one-dimensional Franck-Condon analyses of nearly all vibronically active normal modes. Harmonic Franck-Condon overlap integrals were calculated as a function of the parameters $D$ and $\delta$, which represent normal coordinate displacement upon excitation and square root of the ratio between ground and excited state vibrational frequencies, respectively. $D$ is varied to find the best fit between calculated and experimental excitation and DFL spectra of the members of the progression under consideration. Figures S23 and S24 show the calculated fits to the members of the 421 and 179 cm$^{-1}$ progressions, respectively. The best fit displacement value for these modes is 1.27 and 0.97, respectively. We find that, while the over-all fits are reasonably good, the spectral fits do not quantitatively emulate the DFL and LIF excitation spectra simultaneously, in that the best fits to the series of DFL spectra require larger Franck-Condon activity in excitation than is observed experimentally. Since the UV-D spectra shows no non-radiative turn on over the wavelength region we are probing, this is an indication that a one-dimensional analysis is not sufficient for the vibronic spectra of MA, which is further evidence of Duschinsky mixing in MA between the ground and excited state normal coordinates.
Figure S23: Franck-Condon factor fits of the members of the mode 33 progression. The best fit displacement for this mode is 1.27.

Figure S24: Franck-Condon factor fits of the members of the mode 36 progression. The best fit displacement for this mode is 0.97.
16. Transition Dipole Moment Vectors of Methyl Anthranilate, Aniline, and Methyl Benzoate

Figure S25: Transition dipole moment vectors for the lowest energy ‘bright’ $S_0 - S_n$ electronic transition of (a) aniline ($S_0 - S_1$), (b) methyl benzoate ($S_0 - S_2$), and (c) methyl anthranilate ($S_0 - S_1$).
References