

Proton Transfer in 3-amino-2-naphthol Paige Brown, Class of 2019

Proton transfer (PT) is an essential process in photosynthesis and artificial photosynthesis¹. In order to optimize these systems, it is necessary to understand PT and be able to model it. In the Takematsu lab, aminonaphthols are used to model PT. Aminonaphthols are photoacids, which means that they become significantly more acidic upon excitation. Therefore, it is possible to use light to trigger PT and to access different protonation states.

For this project, the molecule of interest was on 3-amino-2-naphthol (3N2OH). This molecule has a similar structure as 2-naphthol, a well characterized²⁻³ photoacid. In 3N2OH there is an added amine ($\text{NH}_2/\text{NH}_3^+$) group on the carbon adjacent to the alcohol (OH) group. This allows us to study how the proximity of the amine functional group affects PT. PT can occur either between the two functional groups as intramolecular PT or between each functional group and the solvent as intermolecular PT. In the ground state, there are three possible protonation states, the cation, neutral, and anion (Figure 1). The protonation state of the molecule depends on the pH of the system and the pK_a of each functional group. In the ground state, the pK_a of the NH_2 group is 3.9 ± 0.1 and the pK_a of the OH group is 9.1 ± 0.1 .

In the excited state, 3N2OH undergoes electron redistribution³, changing the acidity of the molecule, and thus the pK_a s. To study the kinetics of this system, Time-Resolved Single Photon Counting (TCSPC) was used. TCSPC allowed us to determine the lifetime of each species and to determine if it decays biexponentially or monoexponentially. Both the anion and the neutral had monoexponential decays. This indicates that these species are not in equilibrium with any other species in the excited state. When the cation was excited it had a biexponential decay, indicating that it was in equilibrium with another species in the excited state, the zwitterion (Figure 1). Thus, the zwitterion is only accessible in the excited state.

Since the zwitterion is not present in the ground state, it is formed in equilibrium with another species in the excited state (Figure 2). Previous works claimed that the zwitterion was forming from the neutral, providing strong evidence that intramolecular PT was occurring⁴. However, we have found that the zwitterion is in equilibrium with the cation, indicating that the molecule undergoes intermolecular PT. With this knowledge, it was possible to fit this system to the Laws-Brand Two State model⁵ and determine the pK_a^* of the OH group. When the amine group is protonated (NH_3^+), the $\text{pK}_a^* = 0.61 \pm 0.1$. When the amine group is deprotonated (NH_2), the $\text{pK}_a^* = 9.1 \pm 0.1$. Thus, the protonation state of the amine group determines the pK_a^* of the OH group. It acts as a switch, dictating whether or not 3N2OH is photoacidic.

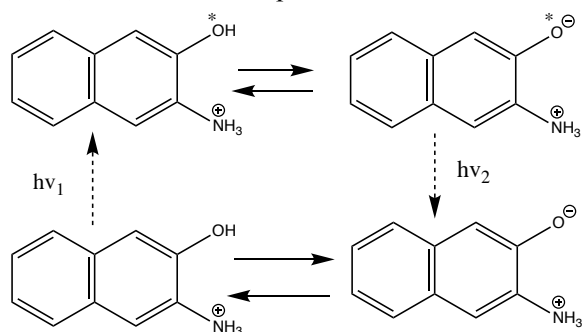


Figure 2. Excited State equilibrium between the cation and zwitterion

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Funded by the: Maine Space Grant Consortium Fellowship

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