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COMMENTS

Comment on “Gas-Phase Photochemistry of the Photoactive Yellow Protein Chromophore *trans-p*-Coumaric Acid”

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Model compounds of the photoactive yellow protein (PYP) chromophore *trans-p*-coumaric acid (*trans*-pCA) and some of its derivatives have been studied extensively in recent years.[1−17] A recurring theme in a large number of these papers is the gas-phase work on pCA of Ryan et al.[1] This study reported the first vibrationally resolved laser-induced fluorescence excitation and emission spectra of this chromophore and had quite some impact because of the conclusion that a wavelength-dependent excited state *cis*−*trans* isomerization could be inferred from the data. Furthermore, the authors assigned the S_1 and S_2 states as being of $\pi\pi^*$ and $n\pi^*$ nature, respectively.

Both the isomerization and the state assignment are somewhat controversial. Studies of model chromophores in solution show no evidence for full *cis*−*trans* isomerization.[2−4] The simulations of Yamada et al.[5] suggest that the protein plays an essential role driving the photoisomerization of the chromophore. Two theoretical studies[6,7] report a different state ordering and two more experimental studies[8,9] show features in the absorption spectra of model chromophores that cannot easily be rationalized on the basis of the proposed $n\pi^*$ character of the S_2 state. Very recently, Li and Fang have published an ab initio CASPT2 study[6] that comes to the conclusion that the photoisomerization dynamics of *trans*-pCA should be reinvestigated, because of the controversy over the character of the excited electronic states.

In the present Comment, all of these controversies are resolved unambiguously. It is based on the preliminary results of gas-phase studies on various PYP model chromophores that we have recently started. During these studies we tried to remeasure the (fluorescence detected) excitation spectrum of *trans*-pCA reported by Ryan et al. with mass-resolved resonance enhanced two-photon ionization spectroscopy (MR-RE2PI). *trans*-pCA purchased from Aldrich was heated to 160 °C in a glass container and seeded into a helium supersonic jet. Figure 1 shows the time-of-flight mass spectrum of *trans*-pCA excited at 33 210 cm^{-1}, the 0−0 transition to the S_1 state reported by Ryan et al. The small signal at 80 amu derives from pyrazine, which was used to calibrate the mass spectrum.

Most importantly, the spectrum does not give any evidence for ions with a molecular weight of 164 amu, the weight of pCA. The largest signal comes from a species with a molecular weight of 120 amu, which we attribute to the decarboxylation product of *trans*-pCA, *p*-vinylphenol (pVP). The question whether decarboxylation occurs *thermally* in the oven before excitation or *photochemically* after excitation of *trans*-pCA was resolved by measuring the MR-RE2PI excitation spectrum of pVP, which was purchased from Apin Chemicals Ltd. This spectrum, shown in Figure 2, is identical to the spectrum reported by Ryan et al. for *p*-CA.

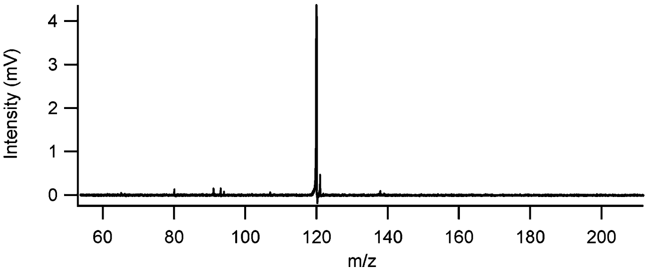

Figure 1. Time-of-flight mass spectrum of trans-pCA excited at 33 210 cm^{-1}.

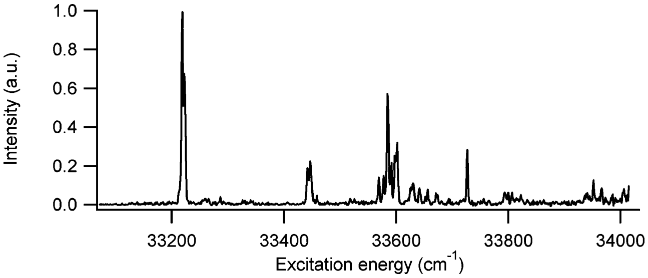

Figure 2. MR-RE2PI excitation spectrum of *p*-vinylphenol.

We thus conclude that the fluorescence excitation and dispersed emission spectra reported by Ryan et al. must be attributed to pVP and not to pCA. Under the conditions used to generate a supersonic jet of pCA the compound decarboxylates to form pVP and we have not been able to find conditions under which this process could be prevented. One possible way to circumvent thermal decarboxylation is to employ laser desorption.[18] Apart from working on the full interpretation of the spectrum of pVP, we will therefore shortly also start MR-RE2PI experiments on *trans*-pCA seeded into supersonic expansions by laser desorption.

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