HIGH RESOLUTION ELECTRONIC SPECTROSCOPY OF P-VINYLPHENOL IN THE GAS PHASE [a]

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Recently, a controversy has developed over the proper assignment of the electronic spectrum of trans-p-coumaric acid (*tP*CA), the chromophore in photoactive yellow protein. Ryan *et al.*[b] claim that two closely spaced peaks near 33,200 cm^{-1} are the $S_1 \leftarrow S_0$ origin bands of *tP*CA, whereas de Groot and Buma[c] argue (based on REMPI results) that the spectrum should be contributed to the decomposition product *p*-vinylphenol (*p*VP). We have addressed this issue by recording the fully resolved spectra of these two bands. The derived values of the rotational constants show unambiguously that the carrier of these bands is *p*VP; the two conformers are due to the two possible orientations of the -OH group with respect to the vinyl group. With the aid of theoretical calculations, the origin at 33,207.3 cm^{-1} has been assigned to *trans-p*VP and the origin at 33,211.8 cm^{-1} to *cis-p*VP. These results confirm the thermal decarboxylation of *tP*CA.

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[b]W. L. Ryan, D. J. Gordon, and D. H. Levy, *J. Am. Chem. Soc.* **124**, 6194 (2002).

[c]M. de Groot and W. J. Buma, *J. Phys. Chem. A* **109**, 6135 (2005).