

On the Absolute Photoionization Cross Section of two Reactive Ketenes: Fulvenone and 2-Carbonyl Cyclohexadienone

Zeyou Pan^{1,2}, Andras Bodi¹, Jeroen A. van Bokhoven^{1,2} and Patrick Hemberger¹

¹Photon Science Division, Paul Scherrer Institute, Switzerland

²Department of Chemistry and Applied Biosciences, ETH Zürich, Switzerland

zeyou.pan@psi.ch

Fulvenone and 2-carbonyl cyclohexadienone are elusive ketene intermediates during different reactions including lignin catalytic pyrolysis [1]. Due to their high reactivity, these species easily escape from conventional detection methods such as GC/MS and NMR. Thanks to sensitive photoelectron photoion coincidence (PEPICO) techniques, both can be captured [2]. For deeper mechanistic understanding and reliable kinetic models, however, quantitative analysis is much-needed. The absolute photoionization cross section (PICS) is widely applied for quantification, especially in flame chemistry [3] and relates the signal in a mass spectrum to the mole fraction during a chemical reaction.

Here we investigated salicylamide pyrolysis at different conditions and observed ketene intermediates, 2-carbonyl cyclohexadienone and its decarbonylation product fulvenone. The former was characterized by photoion mass-selected threshold photoelectron spectroscopy (ms-TPES) where vibrational transitions could be assigned. At higher pyrolysis temperatures, 2-carbonyl cyclohexadienone could be almost fully converted into fulvenone. By optimizing all parameters, photoionization spectra of both were recorded and finally the PICS as function of the photon energy was determined for both species, using NH₃ as a reference, as shown in Figure 1.

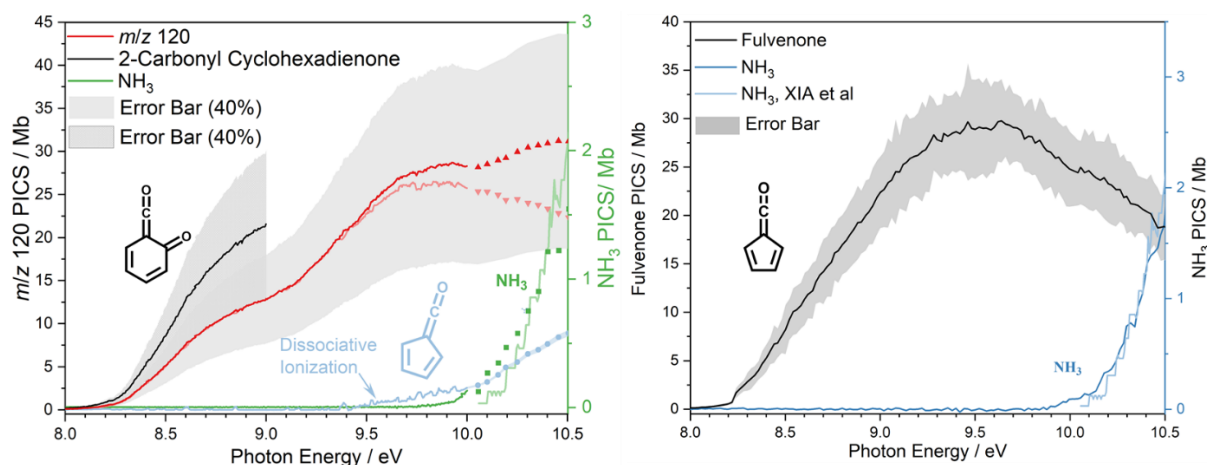


Figure 1. The photoionization cross section of 2-carbonyl cyclohexadienone (left) and fulvenone (right)

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