

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 ¹ Paul Scherrer Institute, Forschungsstrasse 111, 5232 Villigen, Switzerland

Fulvenone and 2-carbonyl cyclohexadienone, as elusive and ketene intermediates, are not only responsible for the branching of the reaction pathways in reactions, but also escape from conventional detection, such as GC/MS and NMR. Thanks to sensitive photoelectron photoion coincidence techniques, we can catch both ketene species on reactions.

In this contribution, we produced both species via salicylamide pyrolysis on py-PEPICO endstation, and discussed the potential energy surface (PES). Moreover, the vibration of 2-carbonyl cyclohexadienone on photoion massselected threshold photoelectron spectra (ms-TPES) is assigned that helps its identification in reactions. Eventually, absolute photoionization cross section (PICS) of both species were precisely measured, which are unreplaceable quantitative parameters for understanding the kinetic/mechanistic results in reactions.



identified by ms-TPES.

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internal energies were calculated using G4 composite methods. can ring-close to the almost isoenergetic 6 subsequently forming 5 by CO_2 loss.

ms-TPES of 6-carbonyl-2,4-cyclohexadien-1-one



Fig. 4 | Energy diagram of the three frontier orbitals Fig. 3 | ms-TPES (black trace) and PI spectrum (grey trace) of 6carbonyl-2,4-cyclohexadien-1-one together with Franck-Condon (FC) of 6-carbonyl-2,4-cyclohexadien-1-one calculated at simulations for the $\widetilde{\mathbf{X}}^+ {}^2\mathsf{A}^" \leftarrow \widetilde{\mathbf{X}} {}^1\mathsf{A}'$ (red trace) and $\widetilde{\mathsf{A}}^+ {}^2\mathsf{A}' \leftarrow \widetilde{\mathsf{X}} {}^1\mathsf{A}'$ (green the B3LYP/6-311+G(d,p) level of theory. trace) transitions. The harmonic frequencies and geometries of neutral and ion are calculated at B3LYP/6-311+G(d,p) level of theory.



Fig. 5 | The ionization cross section of fulvenone shown with a Fig. 6 | The lumped photoionization cross section (red curve) of 20% range of uncertainty. NH₃ was used as calibrant for the m/z 120 species 2-carbonyl cyclohexadienone 2 and fulvenone PICS and the NH₃ PICS was replied on the benzpropiolactone 6 along with the fulvenone fragment (blue determination of XIA et al. The same method was applied to Fig. curve). Effective PICS of the ketoketene 2 is depicted in black. We assume a conservative error bar of 40%.

Reference

1. Z. Pan et al., Chemical Science, 2021, 12, 3161-3169. Interestingly, 2 not only can lose CO producing fulvenone but also 2. T. J. Xia et al., J. Quant. Spectrosc. Radiat. Transfer, 1991, 45, 77-91. 3. H.-F. H. Grützmacher, Justus Liebig's Annalen der Chemie, 1971, 748, 152 -162.



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