Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

On the Absolute Photoionization Cross Section and Dissociative Photoionization of Cyclopropenylidene

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1. Mass Discrimination Factor

The mass discrimination factor can be attributed preliminarily to the flow conditions of the sample molecules in the molecular beam.[1, 2] While the velocity along the beam axis is the same for all masses, the velocity perpendicular to the beam axis scales with $m^{-1/2}$.[1] The transverse velocity will consequently be higher for lighter species, which leads to an enrichment of heavier molecules in the centre line of the molecular beam. The ionization probability is therefore higher for heavier molecules and this effect must thus be considered in the determination of the absolute photoionization cross section by introducing the mass discrimination factor.

Binary mixtures of two components with exactly defined concentrations and known absolute photoionization cross sections are used to determine the mass discrimination factor.[2-5] Propene often serves as a reference due to its intermediate *m/z* and well determined cross section.[6] The mass discrimination factor is then expressed as the ratio of the analyte's spectrometer response F_A to propene's one F_P.

$$\frac{F_A}{F_P} = \frac{S_A}{S_P} \cdot \frac{P_P}{P_A} \cdot \frac{\sigma_i^P(E)}{\sigma_i^A(E)} \qquad (1)$$

Here, S_A and S_P are the detected ion signals, P_A and P_P are the partial pressures of the two components in the gas mixture, and σ_i^A and σ_i^P are the photoionization cross sections of the analyte and propene, respectively.

We measured the mass discrimination factors for five different mixtures of 1 % analyte (NO, acetone, benzene, cyclohexane, ethyl bromide) and 1 % propene in argon under the same conditions (pressure, pyrolysis, spectrometer settings) as in the cyclopropenylidene experiment. The results are depicted in Fig. S1. Note that the mass of propene (42) is close to the one of cyclopropenylidene.

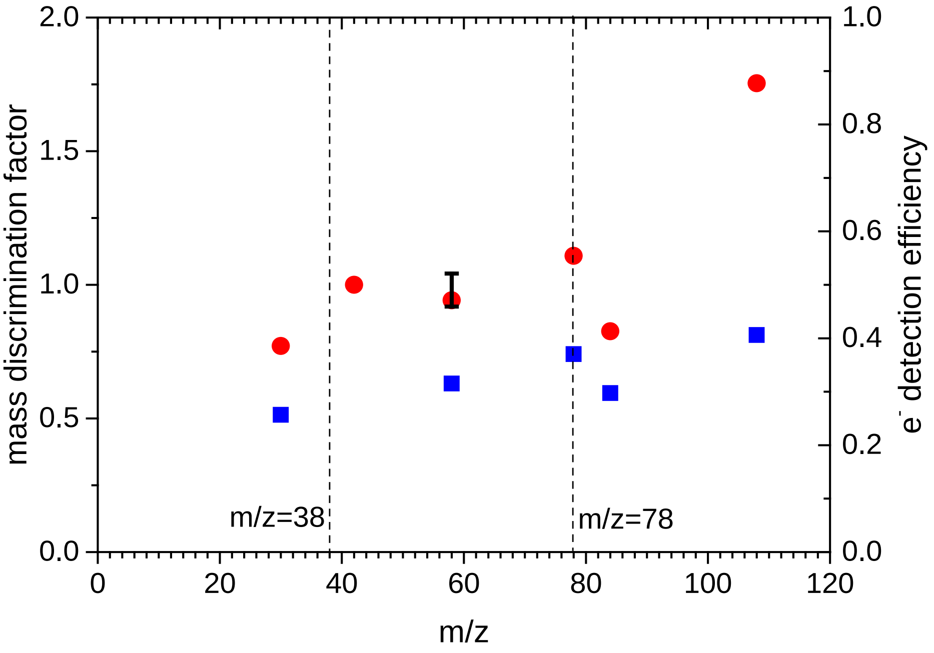

Fig. S1 Mass discrimination factors (red dots) for five analyte molecules relative to propene (*m/z* = 42). The black bar shows the range of dispersion for the mass discrimination factor of acetone for different pyrolysis conditions. As the mass discrimination factors do not follow the expected curve, but follow the same trend as the electron detection efficiencies, it is concluded that the former can be in good approximation assumed as equal over the mass range relevant for the experiment, indicated by the dashed lines. The blue squares show the mass dependence of the electron signal.

The mass discrimination factors would have been expected to follow a monotonically increasing growth function, which is 1 for *m/z* = 42. As visible in Fig. S1, the mass discrimination factors seem to stray randomly around 1 in the mass range of interest. Interestingly, the mass discrimination factors show the same trend as the electron collection efficiency η_e, which is the coincidence count rate N_c over the ion count rate N_i, depicted as blue squares.

$$\eta_e = \frac{N_c}{N_i} \qquad (2)$$

The electron collection efficiency η_e is independent from the mass discrimination factor because it only takes into account detected particles and thus does not relate to any concentration effects in a molecular beam. So the reduced mass discrimination factor of m/z = 82 is considered as an outlier. Mass discrimination factors of acetone were recorded for different pyrolysis conditions (pyrolysis off, pyrolysis at various T), which should alter significantly the molecular beam properties[7] and therefore the mass discrimination factors. However, the mass discrimination factor, which also includes the uncertainties of the pressure gauges utilized for the preparation of the binary mixtures, deviate by a maximum of 8 % only, which is small compared to the error in the literature photoionization cross sections of the analytes and propene (20 %)[3, 6, 8, 9]. Mass discrimination effects under the employed experimental conditions are consequently assumed to be negligibly small.

The Franck-Condon simulations of the threshold photoelectron spectra of cyclopropenylidene (see main paper) and benzene, for which vibrational temperatures of 740 K have been employed, indicate that no supersonic molecular beam forms under the chosen experimental conditions, but rather an effusive one, because no vibrational cooling is observed. This is in good agreement with computational fluid dynamics simulations by Guan *et al.* of a similar micro-reactor, in which sonic conditions were reached only at the end of the reactor tube at a flow rate of 100 sccm.[7] The flow rate in the cyclopropenylidene experiment is estimated to be significantly lower (25-50 sccm) and an effusive molecular beam is consequently assumed to form, for which no mass discrimination effects are expected. This is in good agreement with our experimental findings and the mass discrimination factor was consequently disregarded in the derivation of the absolute photoionization cross section of cyclopropenylidene.

3. Influence of the Temperature

While our experiments were conducted at an effusive beam temperature of 720K, the benzene cross sections by Cool et al have been studied at lower temperature. To evaluate the influence of the temperature on the absolute photoionization cross section we recorded PIE spectra of benzene at different temperatures, depicted in Figure S2. As visible in the figure, the cross sections of benzene do not differ appreciably above the IE.

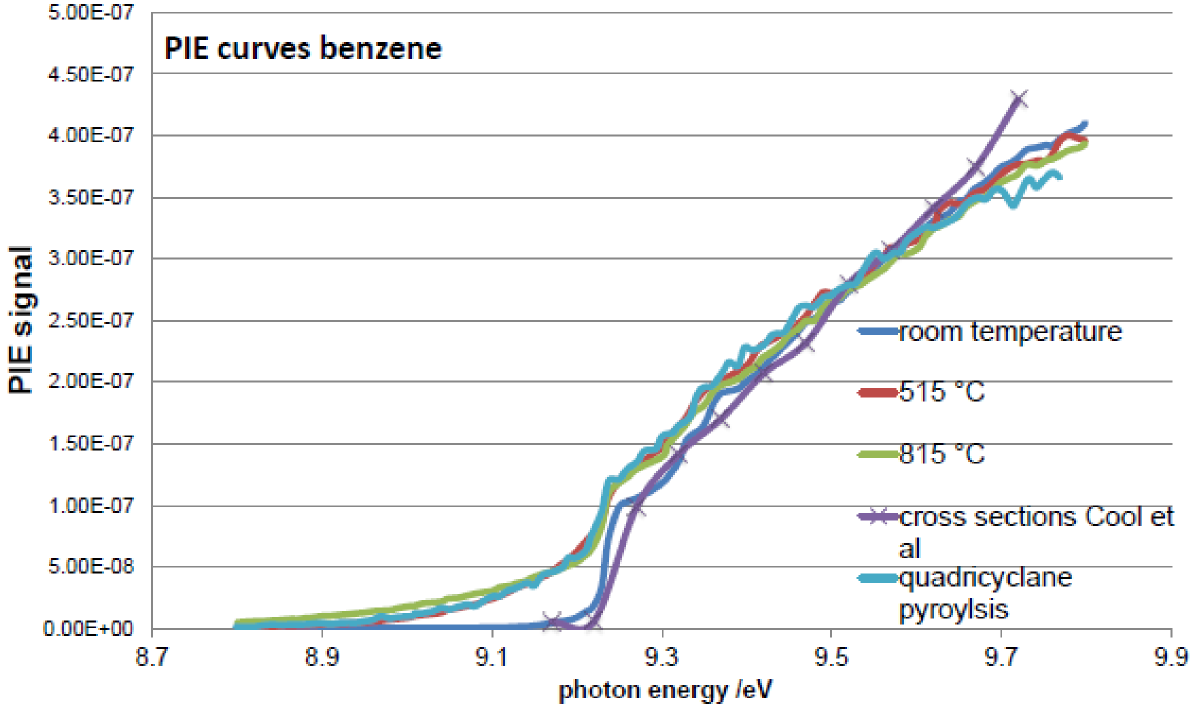

Fig. S2: Photoionization efficiency curves of benzene recorded at different temperatures.

3. Absolute Photoionization Cross Section of Cyclopropenylidene

$h\nu$ /eV	σ_i /Mb
8.80	0.0
8.81	0.0
8.82	0.0
8.83	0.0
8.84	0.0
8.85	0.0
8.86	0.0
8.87	0.1
8.88	0.0
8.89	0.0
8.90	0.0
8.91	0.1
8.92	0.0
8.93	0.1
8.94	0.1
8.95	0.1
8.96	0.1
8.97	0.1
8.98	0.1
8.99	0.1
9.01	0.1
9.01	0.1
9.02	0.1
9.03	0.1
9.04	0.2
9.05	0.2
9.06	0.2
9.07	0.2
9.08	0.2
9.09	0.2
9.10	0.2
9.11	0.3
9.12	0.3
9.13	0.3
9.14	0.3
9.15	0.4
9.16	0.6
9.17	0.8
9.18	0.8
9.19	0.9
9.20	0.9
9.21	1.0
9.22	1.0
9.23	1.1
9.24	1.0
9.25	1.1
9.26	1.1
9.27	1.1
9.28	1.2
9.29	1.4
9.30	1.8
9.31	1.8
9.32	2.0
9.33	2.2
9.34	2.3
9.35	2.3
9.36	2.5
9.37	2.8
9.38	2.8
9.39	2.9
9.40	2.8
9.41	3.0
9.42	3.2
9.43	3.2
9.44	3.4
9.45	3.5
9.46	3.8
9.47	3.8
9.48	4.1
9.49	4.4
9.50	4.5
9.51	4.7
9.52	5.0
9.53	5.0
9.54	5.1
9.55	5.2
9.56	5.4
9.57	5.4
9.58	5.7
9.59	6.2
9.60	6.0
9.61	6.6
9.62	6.6
9.63	6.6
9.64	6.9
9.65	7.0
9.66	7.2
9.67	7.5
9.68	7.7
9.69	7.7
9.70	8.0
9.71	8.1
9.72	8.1
9.73	8.7
9.74	8.5
9.75	9.1
9.76	9.0
9.77	9.1

4. TOF Distributions for the DPI of Cyclopropenylidene

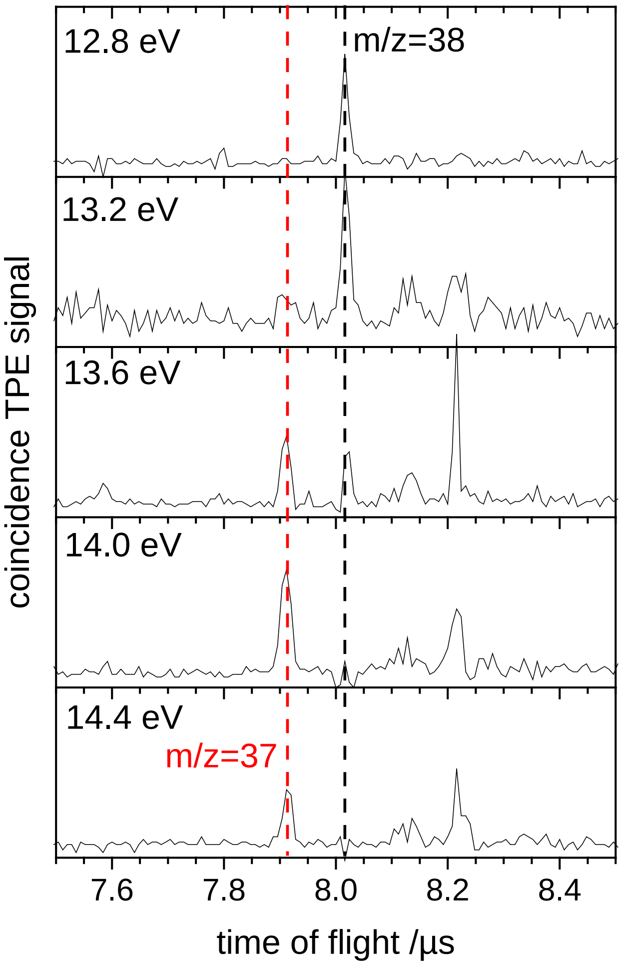

Fig. S3 TOF distributions of ions detected in coincidence with threshold photoelectrons for the dissociative photoionization of cyclopropenylidene (*m/z* = 38). As there is no asymmetry observed in the daughter ion peak (*m/z* = 37), the rate constant for the dissociation must be fast on the timescale of the iPEPICO experiment. The peak at 8.2 µs originates most likely from a contamination of a previous experiment.

5. Franck-Condon Simulation of the C_3H_2 TPES at a Vibrational Temperature of 1200 K

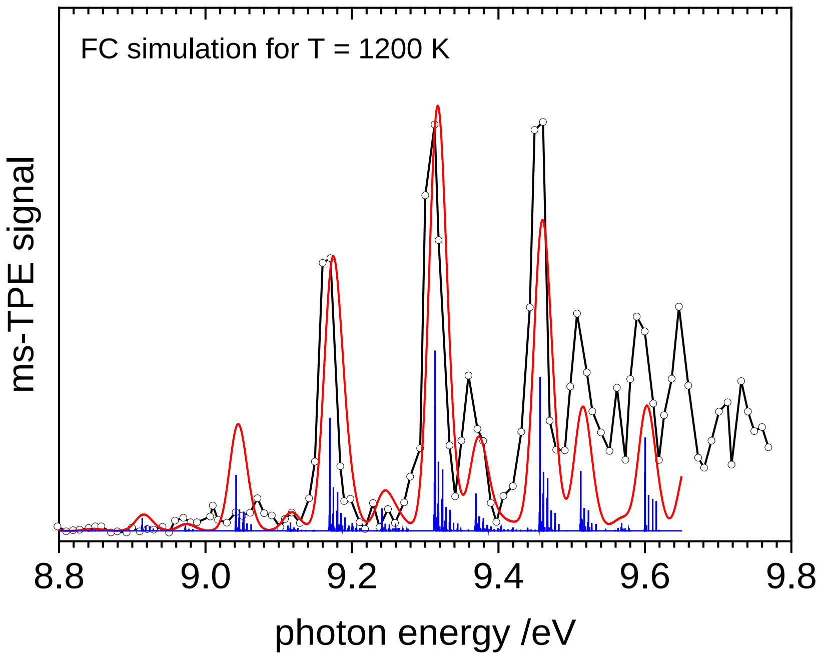

Fig. S4: The Franck-Condon simulation for a vibrational temperature of 1200 K predicts intense contributions of hot and sequence bands, which are not observed in the experimental spectrum.

Notes and References

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