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Electronic Supplementary Information for

The gas-phase infrared spectra of the 2-methylallyl radical and its high-temperature reaction products

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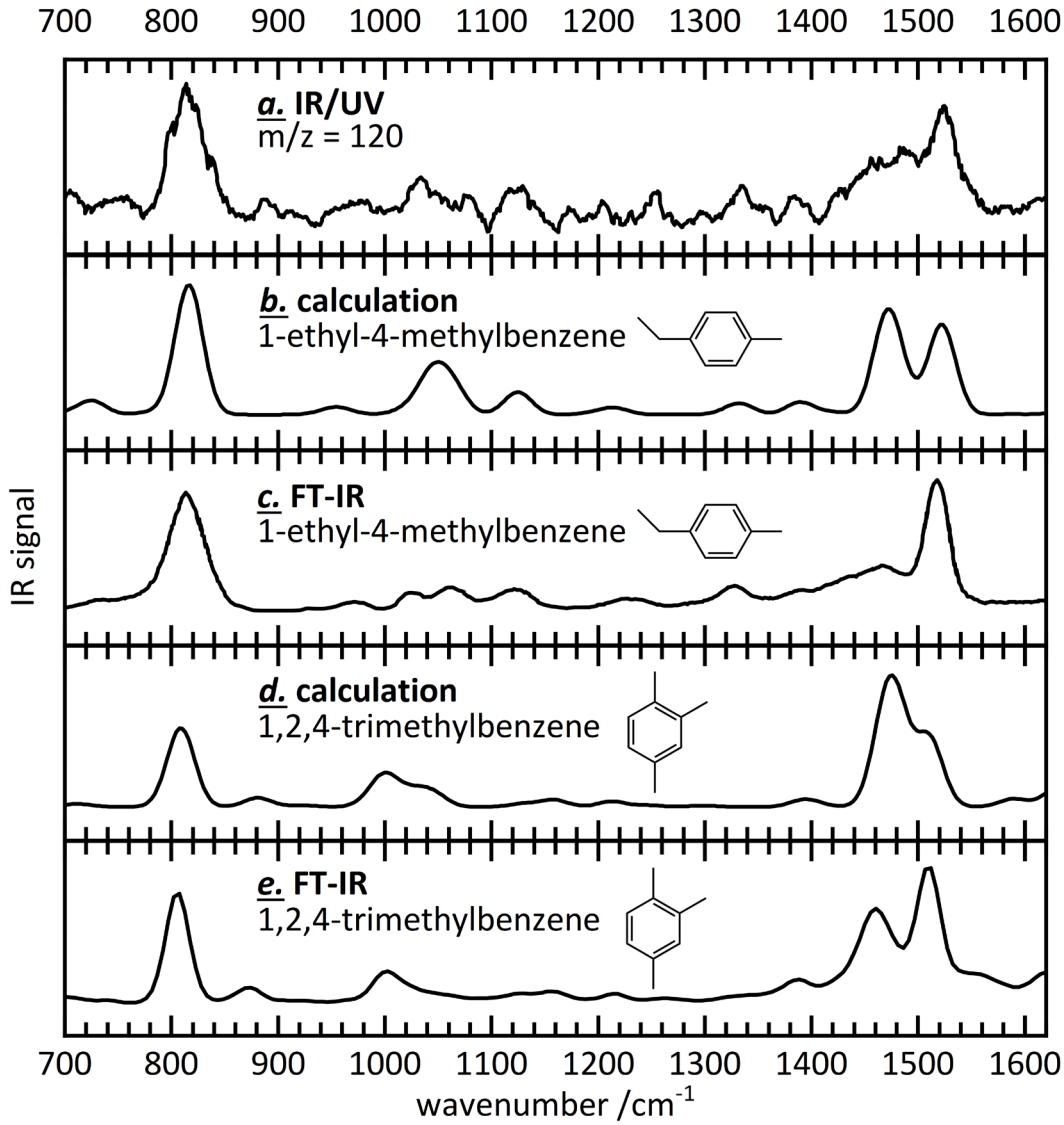

Fig. S.1 IR/UV spectrum of *m/z*=120 (trace a.) in comparison to computed IR spectra of 1-ethyl-4-methylbenzene (b.) and 1,2,4-trimethylbenzene (d.). Both computations overestimate the intensities of the bands at around 1470 cm^{-1}. To substantiate the assignments, gas-phase FT-IR spectra were recorded, and excellent agreement is observed between the IR/UV data and the FT-IR spectrum of 1-ethyl-4-methylbenzene (c.).

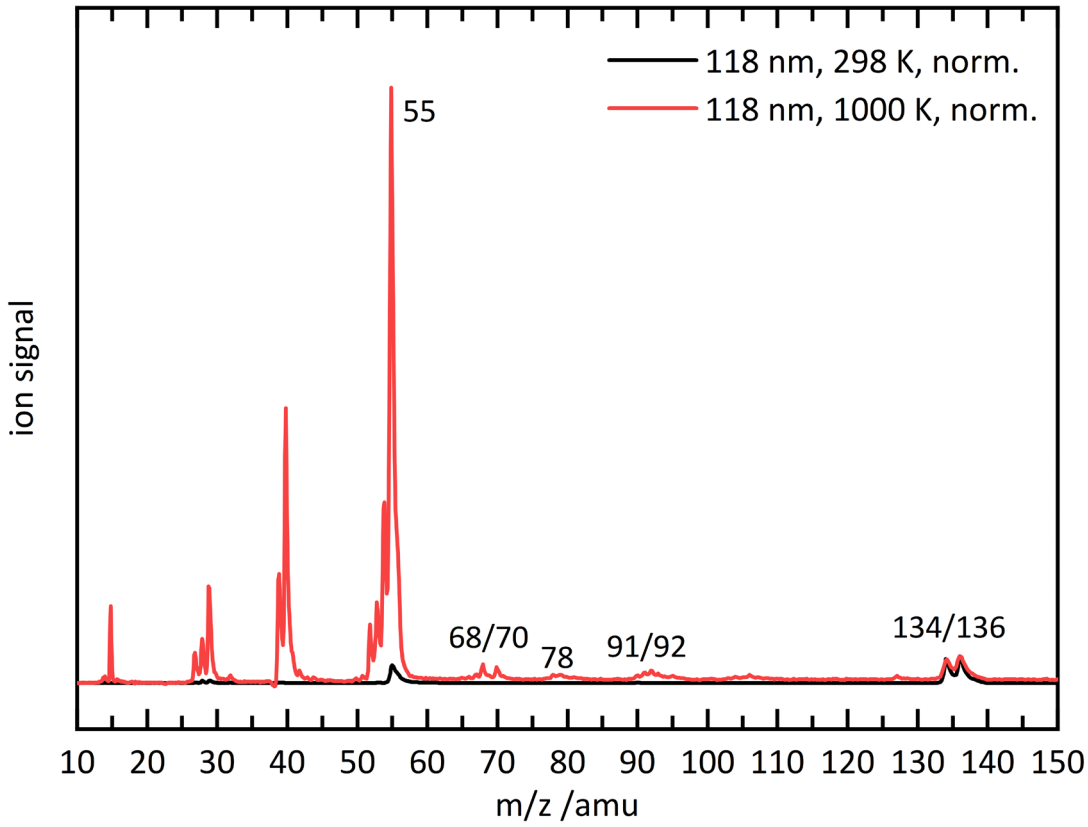

Fig. S. 2 118 nm TOF mass spectra recorded with (1000 K) and without (298 K) pyrolysis showing only small contributions of dissociative photoionization.

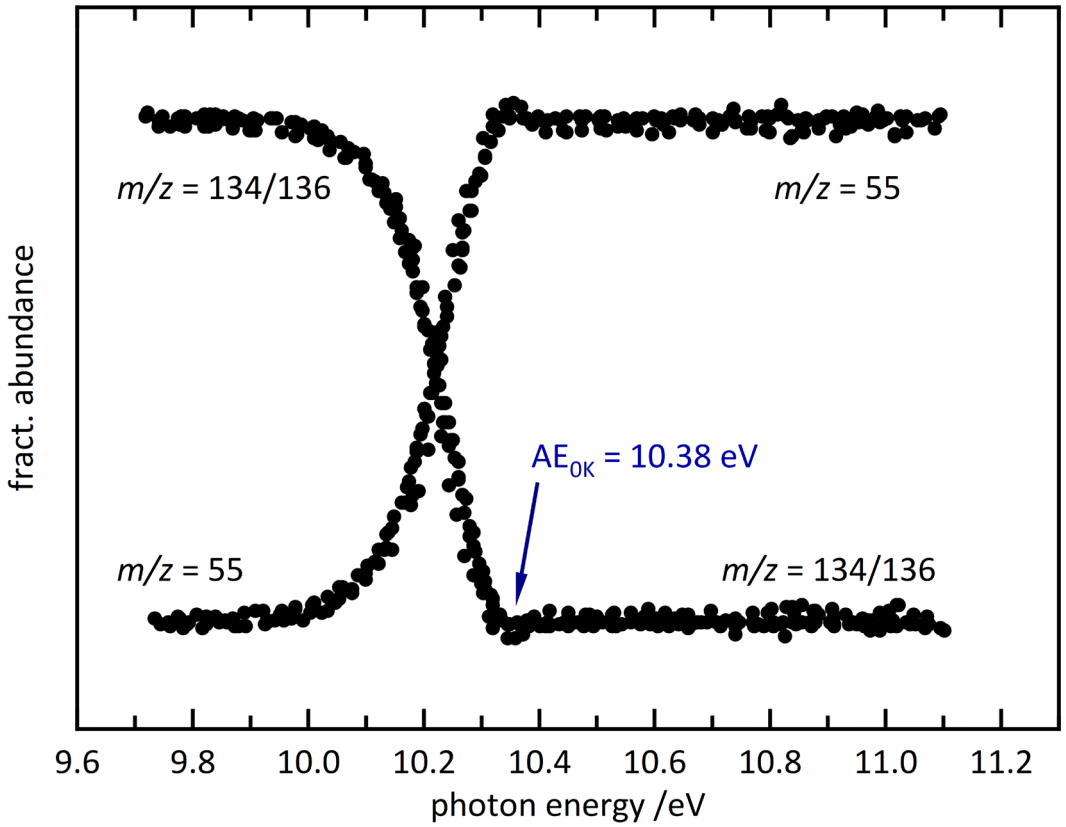

Fig. S. 3 Breakdown diagram of 3-bromo-2-methylpropene, taken from Ref. 1 yielding an $AE_{0K}(C_4H_7Br, C_4H_7^+)$=10.38 eV.

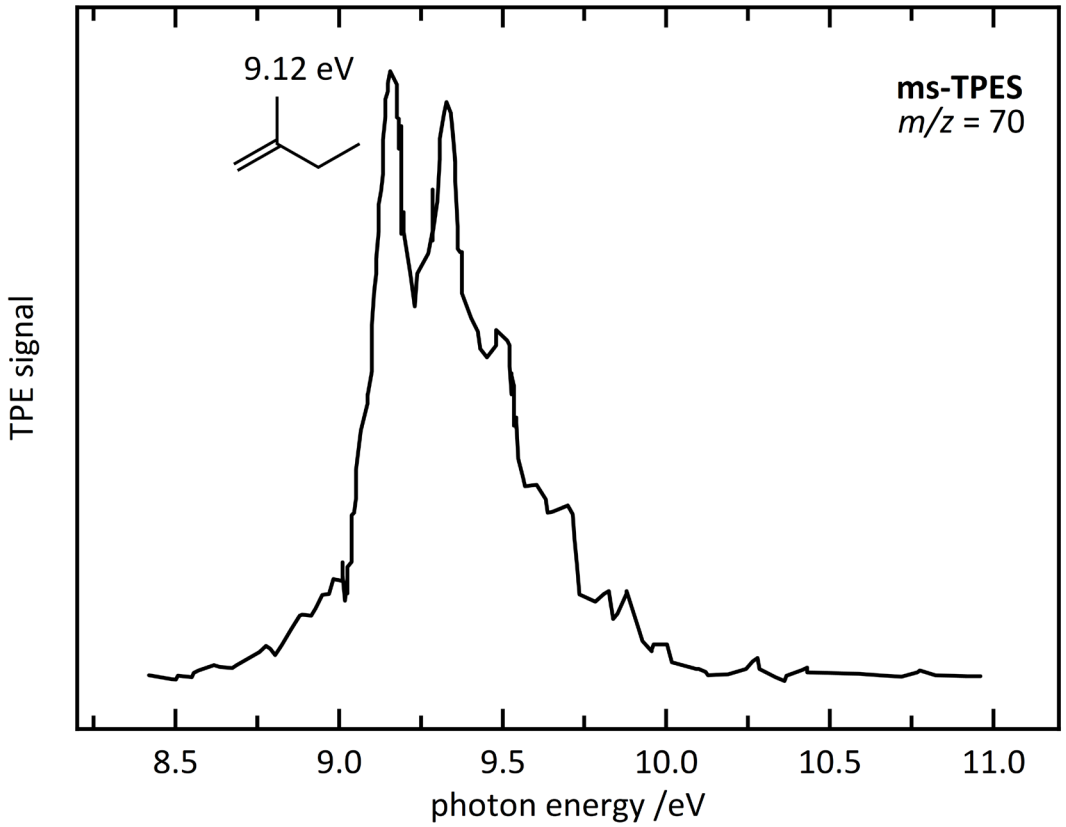

Fig. S. 4 Mass-selected threshold photoelectron spectrum (TPES) of *m/z*=70 recorded under comparable experimental conditions in the pyrolysis of 3-bromo-2-methylpropene.[1] 2-Methyl-1-butene is identified based on a comparison with a literature spectrum.[2]

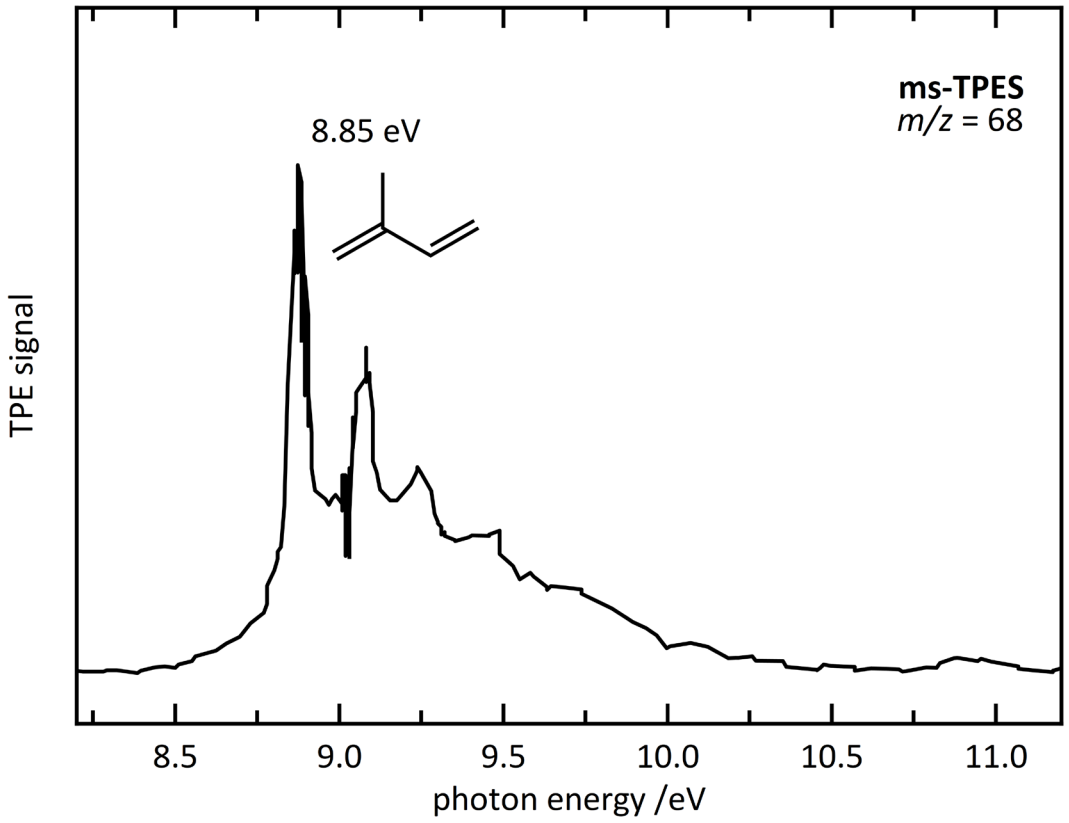

Fig. S. 5 Mass-selected threshold photoelectron spectrum (TPES) of m/z=68 recorded under comparable experimental conditions in the pyrolysis of 3-bromo-2-methylpropene.[1] 2-Methyl-1,3-butadiene (isoprene) is identified by comparison with a published photoelectron spectrum.[3]

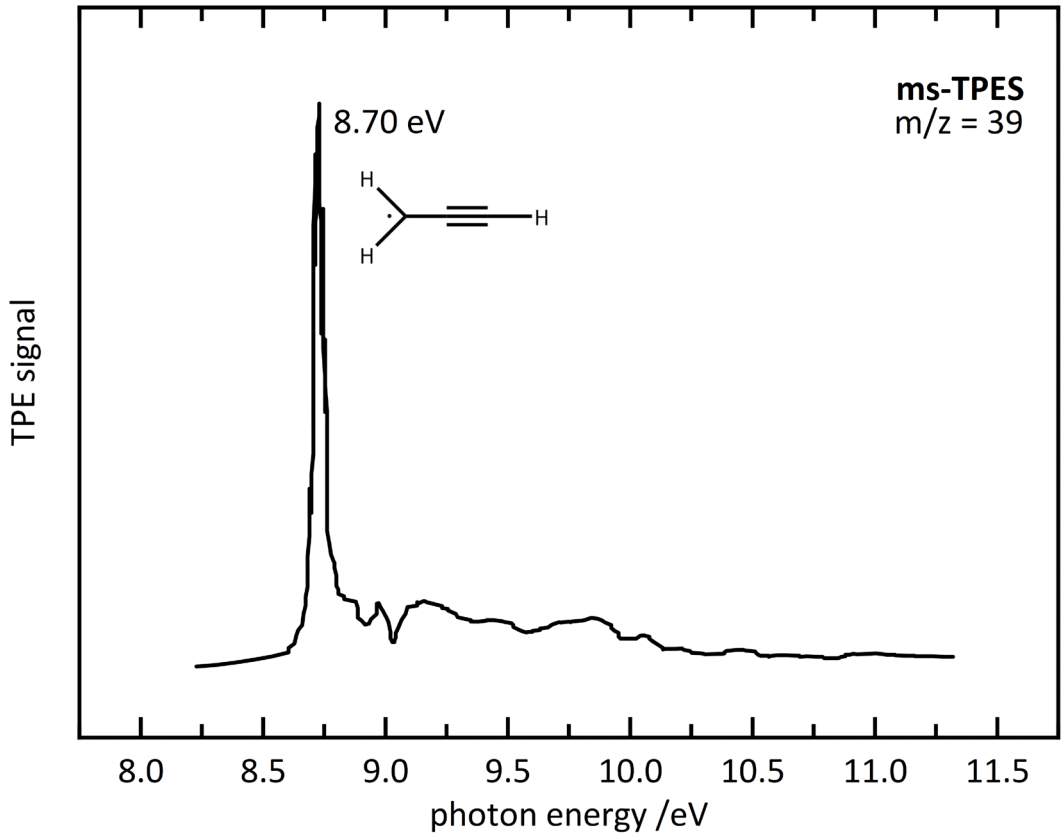

Fig. S. 6 Mass-selected threshold photoelectron spectrum of m/z=39 recorded under comparable experimental conditions of the pyrolysis of 3-bromo-2-methylpropene.[1] Propargyl is identified based on the comparison with a previous TPES.[4]

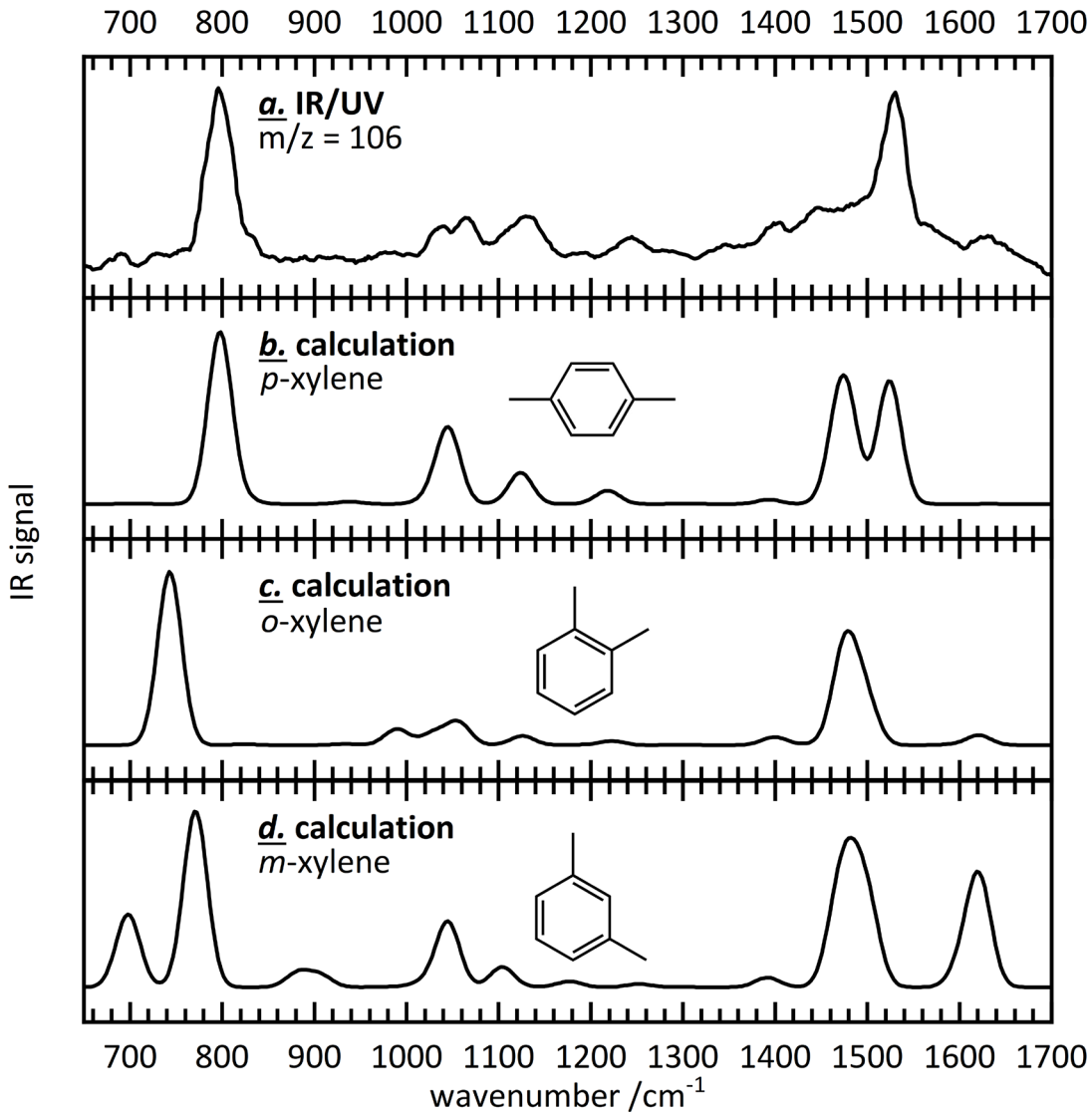

Fig. S. 7 The IR/UV spectrum of m/z=106 (trace a.) in comparison with computed IR spectra of para-, ortho- and meta-xylene (traces b.-d.). The carrier of the experimental spectrum is unambiguously identified as para-xylene. All computations predict the band positions well but overestimate the intensities of a few bands. To substantiate the assignment, a gas-phase FT-IR spectra was recorded (see Fig. 3.b.), and excellent agreement is observed.

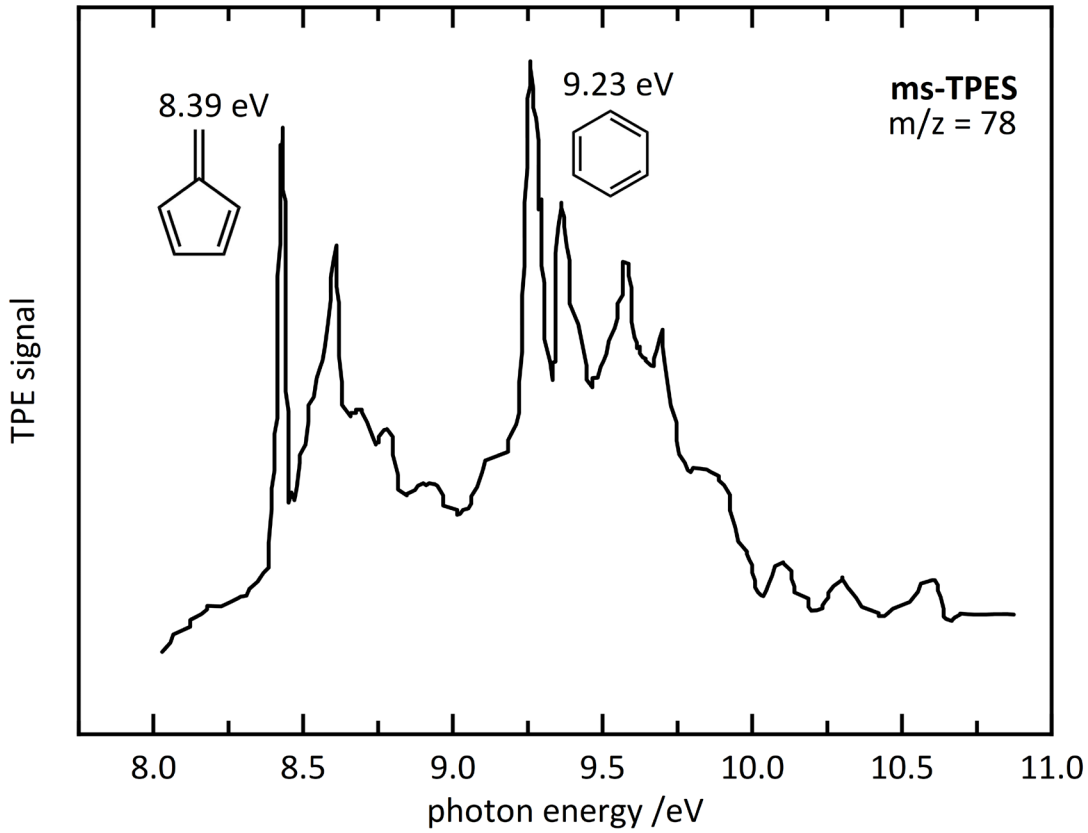

Fig. S.8 Mass-selected threshold photoelectron spectrum (TPES) of *m/z*=78 recorded under comparable experimental conditions in the pyrolysis of 3-bromo-2-methylpropene.[1] The two isomers fulvene and benzene are identified based on their ionization energies[5] as well as a previous TPES.[6]

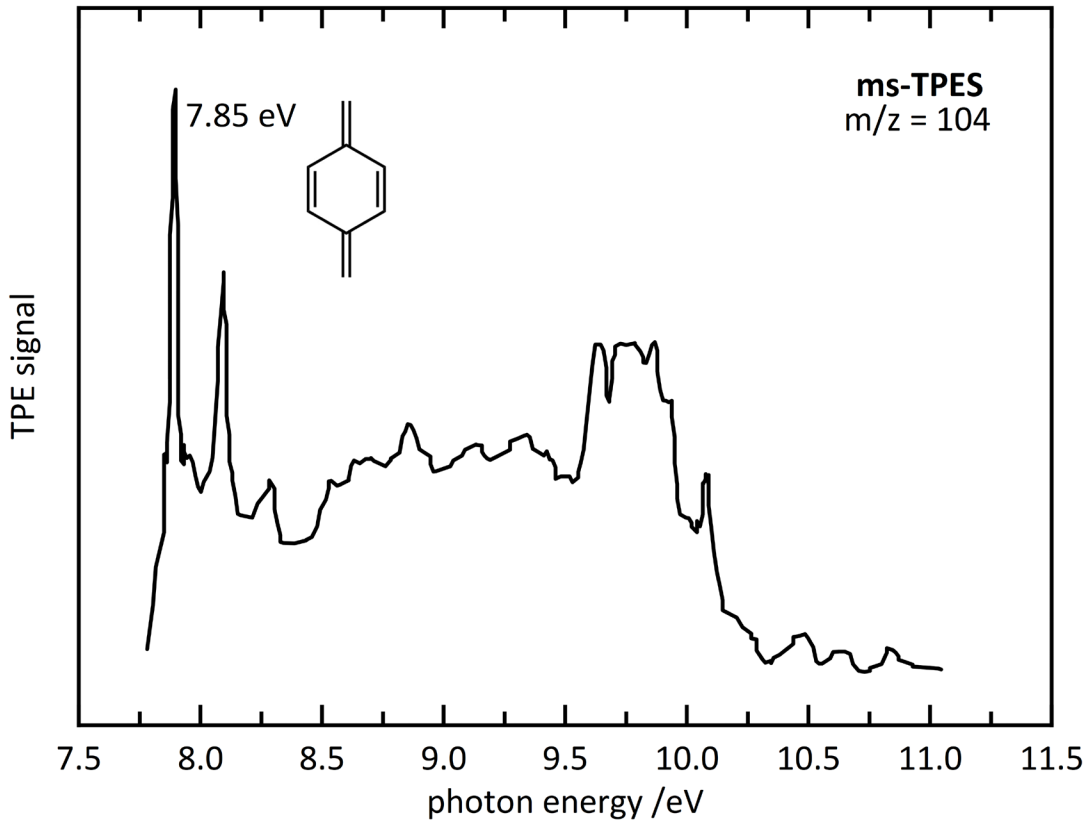

Fig. S.9 Mass-selected threshold photoelectron spectrum of *m/z*=104 recorded under comparable experimental conditions in the pyrolysis of 3-bromo-2-methylpropene.[1] *Para*-xylylene is identified based on its ionization potential and a Franck-Condon simulation.[7]

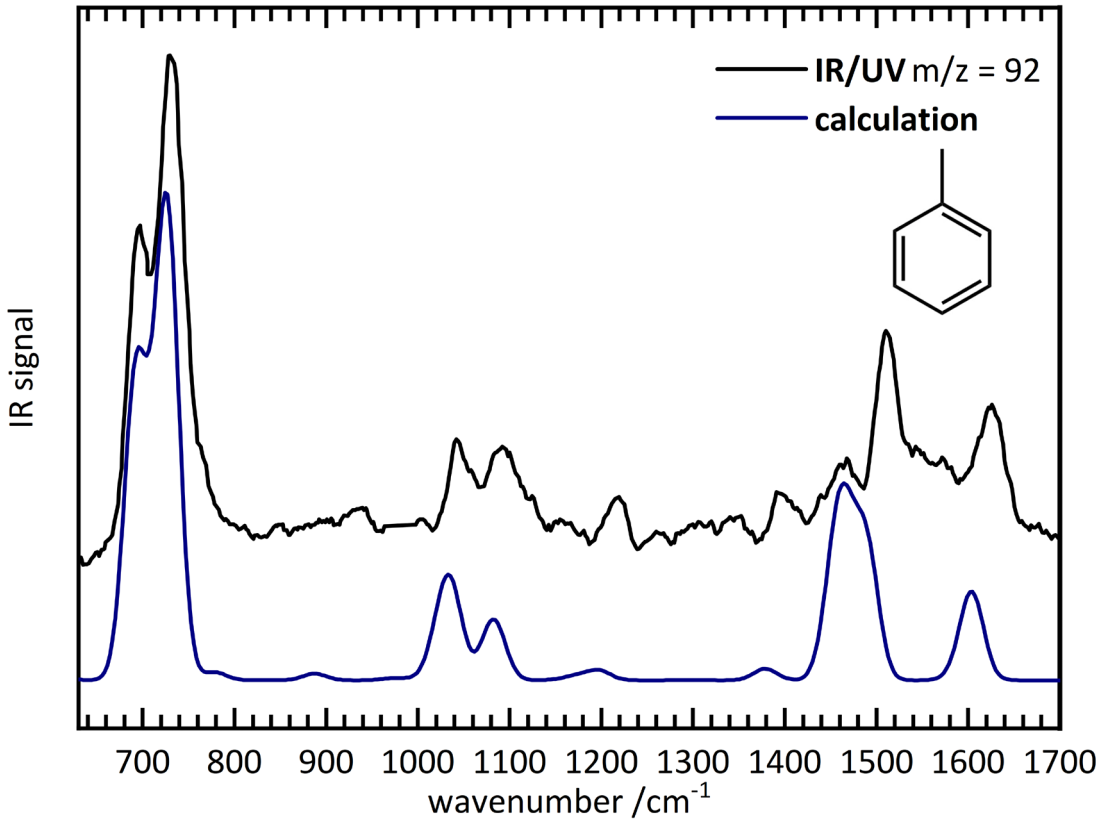

Fig. S.10 The carrier of the mass signal at *m/z*=92 is unambiguously identified as toluene by comparison with a computed IR spectrum.

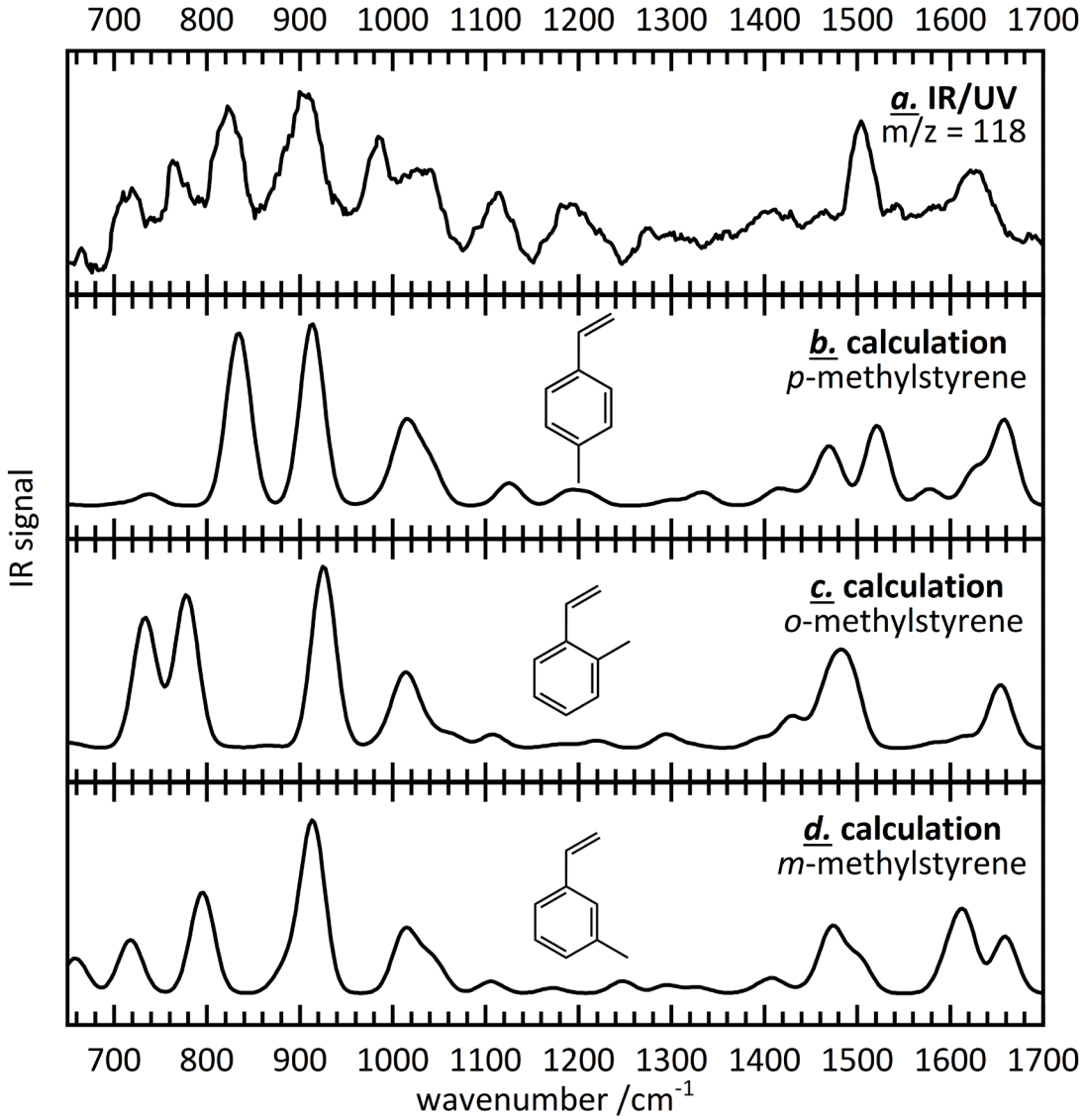

Fig. S.11 The IR/UV spectrum of *m/z*=118 (trace a.) in comparison with computed IR spectra of methylated styrene isomers. The formation of *para*- and *ortho*-methylstyrene (traces b. and c.) is confirmed by the experimental data, while signals of the *meta* isomer cannot be identified (d.).

Literature

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