

Spectroscopic Interrogation of Aromatic Fuel Combustion: Decomposition of the Benzyl Radical
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Significant progress has been made concerning the detection of intermediates in C_7H_7 decomposition, isomerization, and formation relevant to combustion and pyrolysis. First, we have uncovered a previously unobserved, resonance-stabilized isomer of C_7H_7 . While many C_7H_7 species have been implicated in hydrocarbon combustion, only two (the benzyl and tropylium radicals) have been characterized spectroscopically. The new isomer was detected by a synergy of mass-resolved resonant two-colour ionization and laser-induced fluorescence spectroscopies (Fig. 1). Optical-optical hole-burning spectroscopy was used to establish that the spectrum arises from a single isomer, and the ionization potential (Fig. 2) was measured to help identify the spectral carrier. From quantum chemical calculations on a range of plausible structures, we contend that the newly observed species is the 1,2,5,6-heptatetraen-4-yl radical, a substituted allylic radical which can adopt several stable, but “floppy” conformations. Anharmonic frequency calculations for the lowest-energy conformers are being undertaken to aid interpretation of single-vibronic level emission spectra, with a view to yielding a conformer-specific identification.

In computational modeling of benzyl pyrolysis, the 1,2,5,6-heptatetraen-4-yl radical has indeed been suggested to be an important intermediate on the C_7H_7 surface, predicted to result from ring-opening of a substituted cyclopentadienyl radical¹. We first detected the radical in a toluene discharge, and find that it coexists with benzyl radical in discharges that begin with a range of precursors, implying that facile rearrangement between the two structures may occur under combustion/pyrolysis conditions. It is likely that related C_7H_7 isomers can be generated and detected by similar means, including the vinylcyclopentadienyl radical, which has recently been implicated as an important molecular progenitor of polycyclic aromatic hydrocarbons in combustion.²

Second, motivated by several recent studies of C_5H_5 radicals of interest to fossil fuel combustion, we have also been investigating the electronic spectroscopy of the *cis*- and *trans*-1-vinylpropargyl radicals (1vp). Cyclopentadienyl radical (*c*- C_5H_5) is the global minimum on the C_5H_5 surface, and is typically the only C_5H_5 isomer included in chemical kinetic models of combustion. However, *l*- C_5H_5 (perhaps multiple isomers thereof) has been detected in significant quantities in flames³, as well as crossed-beam experiments of interest to astrochemistry⁴, and is a conspicuous product in the sequential addition of acetylene to propargyl (C_3H_3) radical⁵, a process that generates benzyl and tropylium radicals. We have generated copious *cis*- and *trans*-1vp under jet-cooled conditions from pent-1-ene-4-yne, and measured LIF and mass-resolved spectra, as well as high-resolution single-vibronic-level (SVL) emission spectra, to yield excited state vibronic assignments and accurate ground state vibrational frequencies. Presently, we are measuring the isomer-resolved adiabatic ionization energies of both forms to better guide flame studies, and exploring dynamics in low-frequency modes connected to the predicted *c*- C_5H_5 isomerization pathway.⁶

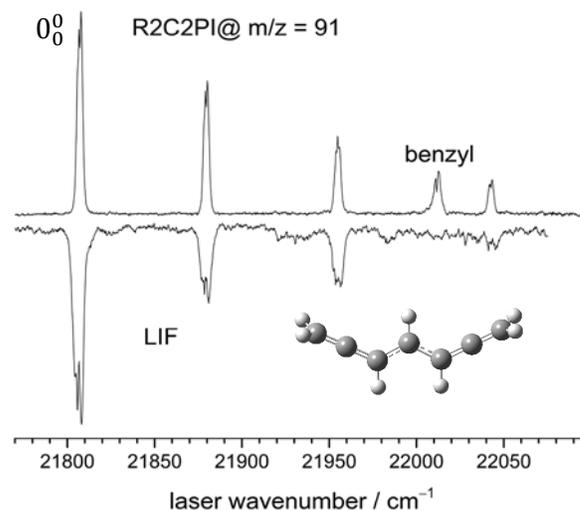


Fig. 1. Upper trace: Mass-resolved electronic spectrum of a new isomer of C_7H_7 , observed in coexistence with the benzyl radical in a heptadiyne discharge. Reflected trace: matching fluorescence spectrum. The most plausible structure for the carrier is 1,2,5,6-heptatetraen-4-yl radical, one conformer of which is indicated.

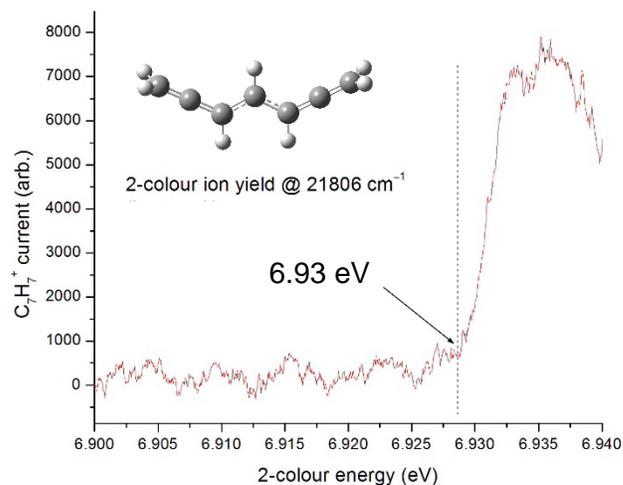


Fig. 2. 2-colour ion yield spectrum of the new C_7H_7 isomer, recorded with the first photon tuned to the origin band of the electronic transition. The arrow indicates an upper limit to the adiabatic ionization energy, which agrees to within 0.02 eV with predictions for the structure indicated, using the CBS-QB3 composite model chemistry.

Finally, an unexpected but serendipitous result has been the detection of the styrene-hydroxyl adduct. During searches for the electronic spectrum of α -styryl radical in a jet-cooled discharge containing styrene, a conspicuous fluorophore was observed near 456 nm (Fig. 3). A matching mass-resolved spectrum was measured at $m/z = 121$ amu, and increased considerably in intensity when the backing gas was doped with water. Observation of a similar spectrum at $m/z = 122$ with added D_2O suggests strongly that the radical is formed by addition of OH/OD to the terminal carbon of styrene, yielding a benzylic radical. Styrene is one of the most-emitted chemicals in the United States, and its primary initial fate upon release to the atmosphere is attack by hydroxyl radical. Multiple conformers of the adduct can exist as a result of hindered rotation of both the OH and CH_2OH groups, but we have shown by hole-burning spectroscopy that only one conformer gives rise to the observed spectrum. Coupling of the OH/ CH_2OH internal rotations produces complex vibronic structure at low energy, which we are attempting to unravel through SVL spectroscopy and deuteration studies. The remarkable facility with which this species is detected in our molecular beam (S/N ratio ~ 1000 with less than 2 seconds of integration time) suggests that hydroxyl adducts of other alkenes released to the atmosphere, both anthropogenically and biogenically, might be optically detectable. Having a spectroscopic probe of such adducts enables direct measurement of their rates of reaction, rather than by inference from depletion of their reaction partners. A highly compelling target from this point of view is the isoprene-OH adduct - a substituted allyl radical which might be expected, by analogy with allyl itself, to exhibit detectable absorption at wavelengths near 400nm.

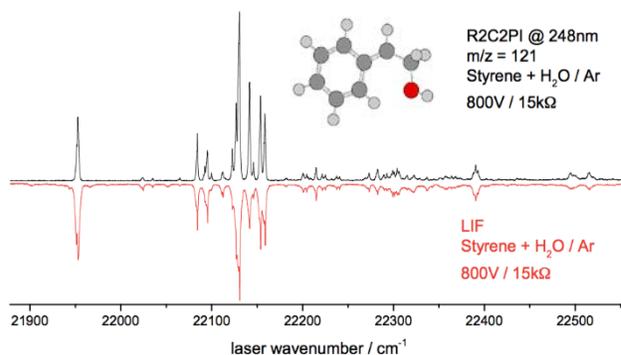


Fig. 3. Mass-resolved (upper trace) and fluorescence (reflected) electronic spectrum C_8H_9O , which we identify as the styrene-hydroxyl adduct, on the basis of chemical tests, ionization potential measurements, and quantum chemical calculations. The adduct is formed with great facility in a discharge doped with water (the hydroxyl source), suggesting that radicals of interest to atmospheric oxidation (e.g., isoprene-OH) can be generated in a similar way.

The PRF award has had a substantial positive impact on the PI's career and on student development. Early results on the styrene-OH system served as a seed for a proposal to the National Science Foundation's Chemical Structure, Dynamics, and Mechanisms program, which was awarded in 2018. In addition, they inspired a successful application for an NSF Graduate Research Fellowship, awarded in 2018 to one of the PI's three PhD students. Another student was invited to attend the 2018 ACS Summer School on Green Chemistry & Sustainable Energy, where they presented work on the C_7H_7 system. The detection of the new C_7H_7 isomer was also reported by the PI at the 2018 International Symposium on Molecular Spectroscopy in Urbana-Champaign, and at the July 2018 Molecular Interactions and Dynamics Gordon Research Conference as a "hot topic". Two of the PI's students have received research assistantships from the PRF award, which has allowed them to pursue their studies with vigour. With close oversight from the PI, all students have received training with vacuum systems, lasers, instrument interfacing, spectroscopic analysis, electronic structure calculations, and proposal preparation.

References

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