

## IONIZATION ENERGIES AND SINGLE VIBRONIC LEVEL EMISSION (SVLE) SPECTROSCOPY OF CIS- AND TRANS-1-VINYLPROPARGYL RADICALS

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The resonance-stabilized 1-vinylpropargyl radical (1vpr), which can adopt *cis*- and *trans*- conformations, is held to be a significant intermediate in hydrocarbon pyrolysis and has also been observed in the crossed-beam reaction of C<sub>2</sub> with propyne. We have cleanly generated 1vpr in a discharge of pent-1-ene-4-yne and measured the adiabatic ionization energy (AIE) of each conformer by two-colour ion-yield spectroscopy. Our work takes advantage of an earlier report by one of us of the 1vpr electronic origin bands near 460 nm and 470 nm. Extrapolation to zero-field yields AIEs of 7.823(1) eV and 7.894(1) eV for the *trans*- and *cis*- forms respectively, in superb agreement with a QCISD(T) calculation (Hansen *et al.*, J. Phys. Chem. A 2006, 110, 4376-4388), and further supporting the identification of 1vpr in flames. As part of on-going work, we have also secured vibrational assignments for a number of levels in the ground and first excited states of both conformers, first by decomposing the mass-resolved electronic spectrum (as much as possible) into *cis*- and *trans*- contributions using hole-burning spectroscopy, and then by measuring SVLE spectra for sufficiently well-resolved bands. The apparent projection of a low-frequency excited state mode onto both *a'* and *a''* levels in the ground state is taken as evidence of a Duschinsky rotation that mixes *a'* and *a''* modes, and perhaps, therefore, of some reduction in planarity in the excited state, particularly for the *cis* isomer. The extent to which this interpretation is reflected by B3LYP and CASSCF calculations will be discussed.