FLUORESCENCE SPECTROSCOPY OF JET-COOLED 1-PHENYL-1-BUTEN-3-YNE IN ITS GROUND AND FIRST EXCITED STATES

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In seeking to understand the thermal and photochemical pathways that lead to naphthalene, it is important to consider the $C_{10}H_8$ potential energy surface as a whole, since facile routes could involve formation of a $C_{10}H_8$ isomer followed by isomerization to naphthalene. 1-phenyl-1-buten-3-yne is a structural isomer of naphthalene, which is known to isomerize to naphthalene when heated. It is a likely product of phenyl radical reaction with vinylacetylene, and has been identified as one of the $C_{10}H_8$ products formed from ultraviolet photochemistry of diacetylene with styrene. We have studied the fluorescence excitation (FE) and the single vibronic level dispersed fluorescence (SVLF) spectra for the $S_0 - S_1$ transition of 1-phenyl-1-buten-3-yne cooled in a supersonic expansion. The $S_0 - S_1$ origin occurs at 33585.0 cm^{-1}, with vibronic structure extending out to about 1400 cm^{-1} above the origin. SVLF spectra have been recorded for more than fifteen vibronic bands in the FE spectrum. The spectra display low frequency vibronic structure reminiscent of that in styrene, attributable to out-of-plane torsion and bend of the vinylacetylene group. The vibrational assignments are assisted by ab initio calculations and the results are compared with the analogous motions in styrene. The three lowest frequency out-of-plane modes (ν_{46}, ν_{47}, and ν_{48}) show strong Duschinsky mixing. A short vinyl torsion vibrational progression in S_0 is fitted to a torsional potential. The spectroscopy provides a foundation for pump-probe experiments designed to study the photochemical transformation of E-1-phenyl-1-buten-3-yne into its Z isomer and on to naphthalene.