

## THE CHARACTER OF THE LONG-LIVED STATE FORMED FROM $S_1$ OF PHENYLACETYLENE

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Compared to other small aromatic molecules, phenylacetylene (PA) and benzonitrile exhibit strikingly anomalous photophysics on excitation to the  $S_1$  state. Firstly, products are formed on  $S_1$  excitation of a beam-cooled sample that seem to live indefinitely (as defined by the flight time through the apparatus), while action spectra of their formation mirror the rotationally-resolved absorption spectrum of the monomer. Secondly, the long lived products appear immediately during the nsec. laser pulse rather than build up during the lifetime of the singlet level, as is seen in benzene, for example.<sup>b</sup> The question has therefore arisen: is the long lived product of the  $S_1$  excitation the triplet state, as is assumed in all previous work on other molecules, or is it an isomer of some sort? New pump-probe ionization mass spectroscopy experiments have been performed to study the distribution of fragments and metastable ions produced by PA cation derived from the neutral  $S_1$  state, and from the long-lived species. These combined with other experimental results showing weak long-lived components in both the  $S_1$  fluorescence and pump-probe photoelectron spectra that we interpret as recurrence behavior, definitively show the long-lived state is a triplet state of PA, not an isomer. PA with a singlet-triplet gap of  $10000\text{ cm}^{-1}$  is acting like intermediate case molecules with much smaller singlet-triplet gaps such as pyrazine and pyrimidine. Calculations point to the existence of four triplet states of PA at or below the energy of  $S_1$  providing a very large density of vibronic states in which to distribute the energy from singlet-triplet crossing. PA  $T_1$  is calculated to be non-planar, in contrast to what is found in benzene, possibly helping to explain the different photophysics.

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