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.[b] 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 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.

Acknowledgments: We gratefully acknowledge G. V. Lopez for his contributions to some of the experimental masurements. Work at Brookhaven National Laboratory was carried out under Contract No. DE-AC02-98CH10886 with the U.S. Department of Energy and supported by its Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences.

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