PUMP-PROBE DELAYED IONIZATION STUDY OF PHENYLACETYLENE

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Pump-probe photoionization experiments on the origin of the $S_1 \leftarrow S_0$ transition of phenylacetylene (PA) have revealed the production of long lived ($\gg$ 100 μsec lifetime) species with low ionization potential where short lifetimes ($nsec$ lifetime) are expected if simple intersystem crossing takes place.[a] The pump-probe delay photoionization decay curve for the band origin, previously presented by Hofstein et al.,[a] and four other assigned strong bands in the $S_1 \leftarrow S_0$ transition of PA have been obtained in recent experiments. Following $S_1 \leftarrow S_0$ excitation, the decay consists of a prompt short-lived component matching the measured singlet fluorescence lifetime and a second, very long-lived, component. The ratios between the singlet channel signal to that of the long-lived species for these bands are not the same: 3.03±0.38, 1.48±0.33, 1.75±0.19, 3.11±0.36 and 2.77±0.35 for the origin, ν_{15}, ν_{6a}, β_{cc} and ν_1, respectively. The fact that the ν_{15} and ν_{6a} modes have low ratios suggests that the normal coordinates of these modes could lie near the reaction path for the formation of the long lived species. Thus, these results combined with theoretical calculations may potentially give an indication of the identity of the long-lived species.
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[a] J. Hofstein, H. Xu, T. J. Sears and P. M. Johnson, J. Phys. Chem. A **112**, 1195-1201 (1999)