DUSCHINSKY MIXING BETWEEN FOUR NON-TOTALLY SYMMETRIC NORMAL COORDINATES IN THE S_1–S_0 VIBRONIC STRUCTURE OF PHENYLVINYLACETYLENE: A QUANTITATIVE ANALYSIS

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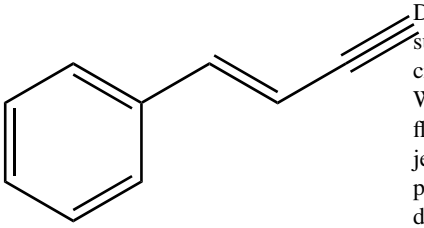
Phenylvinylacetylene is one of the $C_{10}H_8$ isomers that is a likely initial adduct formed by radical-molecule reactions of importance in combustion processes[1].



Due to its longer conjugated side chain compared to that of its parent styrene, PVA can support Duschinsky mixing among several low-frequency out-of-plane coordinates, increasing the complexity of this mixing relative to that of styrene.

We have studied the fluorescence excitation spectrum and several single vibronic level fluorescence (SVLF) spectra of the $S_1 \leftarrow S_0$ transition of PVA cooled in a supersonic jet. Visual inspection of four hot-band SVLF spectra and seven normal SVLF spectra provided evidence for mixing between the lowest non-totally symmetric vibrational coordinates (ν_{45}, ν_{46}, ν_{47}, and ν_{48}). The intensities of nearly 280 overtone and combination transitions of these normal modes in the eleven SVLF spectra and the fluorescence excitation spectrum were quantitatively analyzed in order to determine the amount of Duschinsky mixing between the four vibrational coordinates. Four-dimensional Franck-Condon overlap integrals were calculated based on recursion relations between harmonic oscillator wavefunctions derived using the standard generating function approach[2]. The calculated intensities were fit to experimental intensities in an automated fitting procedure in which an unweighted least-squares sum was minimized using a patternsearch algorithm to find the optimized Duschinsky rotation angles.

The results of the Duschinsky analysis will be discussed in light of the π–π^* transition involved in the electronic excitation.

(1) A. G. Robinson, P. R. Winter and T. S. Zwier, *J. Phys. Chem. A*, **2002**, *106*, 5789.
(2) P. T. Ruhoff, *Chem. Phys.*, **1994**, *186*, 355.