

Dynamics of the excited electronic states of pyrene in the deep UV

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We investigated pyrene using electronic two-dimensional, heterodyne transient grating, and transient absorption spectroscopies in a 250-300 nm spectral range. We resolved several cross-peaks and oscillations providing an insight to the S_3 vibronic excited state. Our findings are corroborated by theoretical simulations resulting in multiple oscillating diagonal and off-diagonal peaks.

Pyrene is a dye which has a rich structure in the allowed electronic transitions due to well-resolved vibronic states. We obtained a wealth of novel information on the dynamics of the S_3 excited state using femtosecond heterodyne-detected transient grating (HTG), transient absorption (TA), and two-dimensional photon-echo spectroscopy (2DPE) with the recently developed setup [1] for the broadband UV spectroscopy in a range of 250-300 nm which fully covers the absorption spectrum of the S_3 state. In this study we present an analysis of the Raman frequencies detected in the experiments. Our theoretical approach utilizes a single trajectory as input in combination with state-of-the-art electronic structure computations that describe the contributions to the 2DPE signals due to coherent nuclear motion, and explicitly correlates the fluctuations of the higher lying excited states to the dynamics in S_3 [2].

By comparing the absorption spectrum with the 2D spectra we assigned the main peaks and a series of cross peaks based on the couplings between the different vibrational bands (Fig. 1). Furthermore, the transient absorption contributions from the higher lying electronic states are clearly resolved. The experimentally detected HTG and TA spectra show a series of oscillations whose frequencies are well-resolved in the Fourier spectrum (Fig. 1 c, d); furthermore, these oscillations are also present in the 2D spectra (Fig. 1 b). They match known Raman frequencies, yet some of them originate from the fluctuations of the higher-lying electronic states as confirmed by our computations.

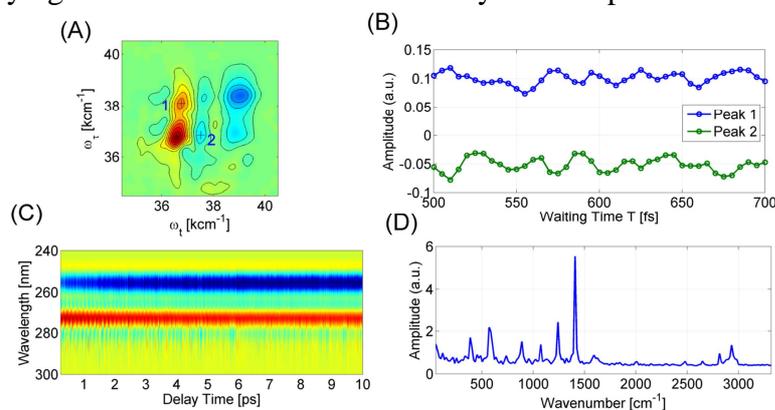


Fig. 1 (A) 2D-spectrum of pyrene in ethanol at 500-fs waiting time; (B) oscillations retrieved from the 2D spectra at labeled positions; (C) pump-probe spectra in a range of 100 fs - 10 ps showing the long-lasting oscillations, and their Fourier spectrum (D).

[1] V. I. Prokhorenko, A. Picchiotti, S. Maneshi, and R. J. D. Miller, Springer Proc. Phys. **162**, 432(2015).

[2] A. Nenov, A. Giussani, B. P. Fingerhut, I. Rivalta, E. Dumont, S. Mukamel, and M. Garavelli, PCCP **17**, 30925 (2015).