

# DIRECT OBSERVATION OF $S_2-S_1$ INTERNAL CONVERSION IN PYRENE BY FEMTOSECOND TRANSIENT ABSORPTION

FREDERIK V. R. NEUWAHL<sup>a</sup> and PAOLO FOGGI<sup>b,\*</sup>

<sup>a</sup> *LENS, Largo E. Fermi 2, 50125 Florence, Italy;*

<sup>b</sup> *Dipartimento di Chimica, via G. Capponi 9, 50121 Florence, Italy*

*(Received 11 April 1997)*

UV pulses of 100 fs at 340 nm are utilised to excite pyrene to the vibrationally cold  $S_2$  state. Population and depopulation processes occurring in the  $S_2$  state are investigated by transient absorption spectroscopy with a white continuum probe. In the first 400 fs after excitation it is possible to measure the growth and disappearance of a band at 585 nm which is assigned to the  $S_{14} \leftarrow S_2$  transition. As a consequence of the internal conversion process from  $S_2$  to  $S_1$  state, the disappearance of the 585 nm band and the growth of the transient spectrum due to  $S_n \leftarrow S_1$  transitions can be observed. Kinetic measurements of the  $S_2$  decay and  $S_1$  growing signals provide an estimate of the rate of internal conversion which occurs with a time constant of  $150 \pm 50$  fs.

*Keywords:* Transient absorption; femtosecond; pyrene; internal conversion

## INTRODUCTION

In condensed phases and at room temperature the rate of the relaxation dynamics of excited molecular states is usually so fast that it prevents the observation of a population build-up in electronic states higher than the fluorescent one. In a recent paper [1] we have reported the rate of formation of the  $S_1$  state of pyrene as a function of excitation energy. With the instrumentation available at that time we

---

\*Address for correspondence: LENS, Largo E. Fermi, 2, 50125 - Florence, Italy.  
Tel.: + + 39-55-2307818; Fax: + + 39-55-224072; e-mail: foggi@lens.unifi.it

were able to give only a rough estimate of the internal conversion (IC) and vibrational relaxation (VR) rate from higher states toward  $S_1$ . Using a new femtosecond system based on an amplified Ti:Sapphire laser [2, 3] we have been able to observe the formation and decay of a transient absorption band originating from the  $S_2$  state. This observation indicates that the IC rate from  $S_2$  to  $S_1$  in pyrene in ethylene glycol is sufficiently slow, in comparison to  $S_2$  formation due to electronic dephasing, to allow some population build-up in the  $S_2$  state.

## EXPERIMENTAL

The femtosecond laser system utilised in the present experiment consists of an amplified Ti:Sapphire working at 1 KHz repetition rate [2, 3]. The amplified infrared (800 nm) pulses have an average energy of 800  $\mu$ J/pulse and a duration of 100 fs (FWHM). A three pass optical parametric generator [4] and two BBO doubling crystals are utilised to produce the tunable UV pump pulse (5  $\mu$ J/pulse, 80 fs at 340 nm), while the broad band (extending up to 250 nm) white continuum is generated by focusing 5 mW of the amplified beam into a 2.5 mm thick  $\text{CaF}_2$  plate. The cross correlation function between the pump and the probe pulse has been measured by means of stimulated Raman gain in acetonitrile and was found to be 200 fs (FWHM). Measurements were performed in a 400  $\mu$ m ethylene glycol jet at room temperature.

## RESULTS AND DISCUSSION

In Figure 1 a bidimensional time-wavelength plot is shown of the transient spectrum of pyrene following UV excitation at 340 nm, corresponding to the edge of the  $S_2 \leftarrow S_0$  transition [5]. In the spectral region around 585 nm a transient absorption band originating from  $S_2$  state is clearly distinguishable, vanishing in a time that is closely matching with the rise time of the transient spectrum originating from  $S_1$  state. This observation is directly related to the IC process from

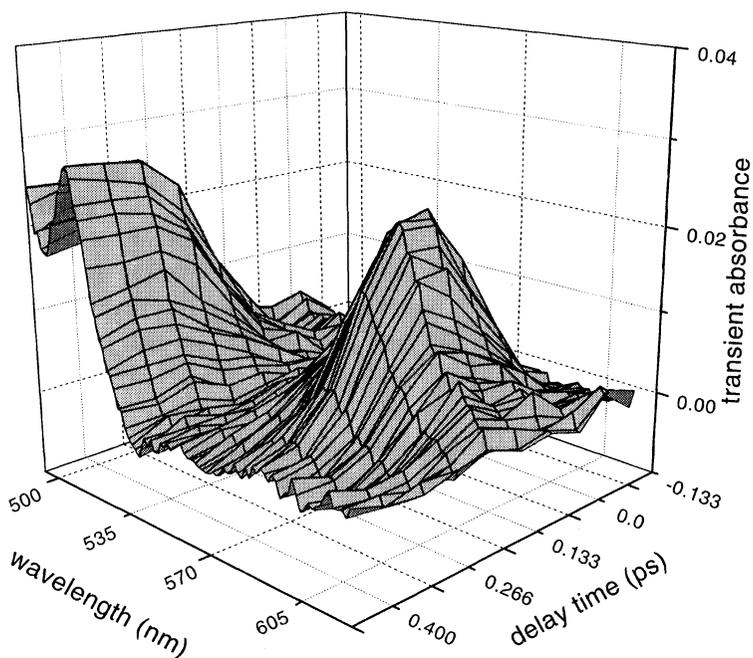


FIGURE 1 Bidimensional (time-wavelength) plot of the transient spectrum of pyrene during the first 400 fs following 340 nm excitation.

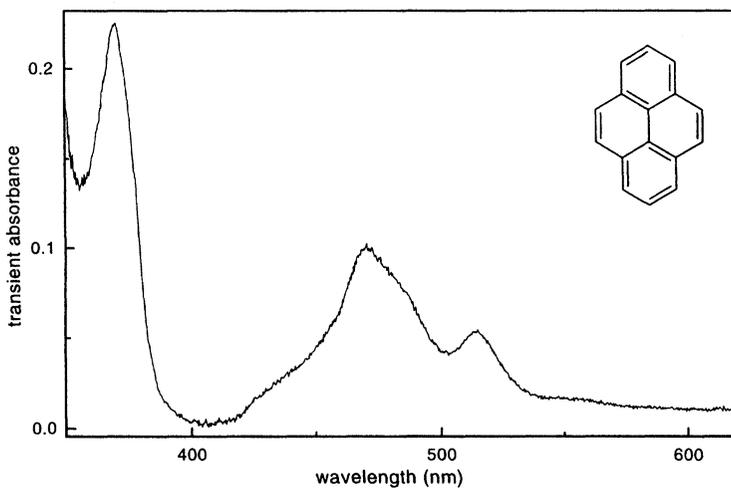


FIGURE 2 Transient spectrum of pyrene recorded 10 ps after excitation; the spectrum is attributed to the thermalised  $S_1$  state.

$S_2$  to  $S_1$  state. By convoluting the instrumental function with the following response functions

$$R_{S_2}(t) = [\exp(-t/\tau_{IC}) - \exp(-t/\tau_{deph})]$$
$$R_{S_1}(t) = [1 - \tau_{deph}/\tau_{IC} + \tau_{deph}/\tau_{IC} \exp(-t/\tau_{deph}) - \exp(-t/\tau_{IC})]$$

and adjusting the result of the simulation on the experimental data we obtained for  $\tau_{IC}$  a value of  $150 \pm 50$  fs. According to the energy level diagram reported in Ref. [1] the 585 nm band can be attributed to the  $S_{14} \leftarrow S_2$  transition, where  $S_{14}$  is a state of  $A_g$  symmetry.  $S_1$  and  $S_2$  states are separated by only  $2900 \text{ cm}^{-1}$  [5]. This implies that the population generated in the  $S_1$  state by the IC and VR processes is almost thermalised, and the spectral evolution of the transient originating from  $S_1$  can be considered completed in 10 ps [1]. In Figure 2 the transient spectrum in the 350–650 nm region recorded 10 ps after excitation is shown. The interpretation of the spectral features appearing in this region has been reported previously [1, 6]. As a consequence of solvent polarity, the transient bands are found to be about 10 nm red shifted with respect to the previous observations [1]. With the increased signal to noise ratio obtained with the new instrumentation we were able to observe new spectral details. In particular, it was possible to determine the exact peak position of the strong band appearing below 400 nm.

### *Acknowledgements*

This work has been supported by the Commission of the European Communities under the contract n.GE1\*CT920046. Authors acknowledge the contribution of R. Ballerini, M. Giuntini and M. De Pas of the LENS technical staff in setting up the transient absorption experimental apparatus.

### *References*

- [1] Foggi, P., Pettini, L., Santa, I., Righini, R. and Califano, S. (1995). *J. Phys. Chem.*, **99**, 7439.
- [2] Ciano, L., Foggi, P. and Salvi, P. R. (1997). *J. Photochem. Photobiol. A*, **105**, 129.

- [3] Danielius, R., Piskarskas, A., Di Trapani, P., Andreoni, A., Solcia, C. and Foggi, P. (1996). *Appl. Opt.*, **35**, 5336.
- [4] Bayanov, I. M., Danielius, R., Heinz, P. and Seilmeier, A. (1994). *Opt. Commun.*, **113**, 99.
- [5] Salvi, P. R., Foggi, P. and Castellucci, E. (1983). *Chem. Phys. Lett.*, **98**, 206.
- [6] Foggi, P., Corti, S., Righini, R. and Califano, S. (1996). *AIP Conf. Proc.*, **364**, 169 (Fast Elementary Processes in Chemical and Biological Systems).