

# Electronic Supplementary Information

## for “Ultrafast decay dynamics of electronically excited 2-ethylpyrrole”

Wenpeng Yuan,<sup>†ab</sup> Dongyuan Yang,<sup>†b</sup> Baihui Feng,<sup>bc</sup> Yanjun Min,<sup>bc</sup> Zhichao Chen,<sup>b</sup>  
Shengrui Yu,<sup>\*a</sup> Guorong Wu<sup>\*b</sup> and Xueming Yang<sup>b</sup>

<sup>a</sup> *Hangzhou Institute of Advanced Studies, Zhejiang Normal University, 1108 Gengwen Road, Hangzhou, Zhejiang 311231, China. E-mail: sryu@zjnu.cn*

<sup>b</sup> *State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian, Liaoning 116023, China. Email: wugr@dicp.ac.cn*

<sup>c</sup> *University of Chinese Academy of Sciences, Beijing 100049, China*

<sup>†</sup> These authors made equal contributions.

<sup>\*</sup> Authors to whom correspondence should be addressed.

E-mails: sryu@zjnu.cn; wugr@dicp.ac.cn.

## The analysis of the 1.88 eV feature at pump wavelengths of 248.3 and 246.1 nm

A closer examination of the TRPES spectra at pump wavelengths of 248.3 and 246.1 nm also finds the existence, although very weak, of the 1.88 eV feature appearing at 237.4 nm (Fig. 3 in the main text), as shown in Fig. S1 (a-b). The transient of the 1.88 eV feature is analysed in a same way as that for 1.36 eV feature at 254.8 nm (see the main text), and lifetimes of  $690 \pm 60$  and  $840 \pm 170$  fs are derived at 246.1 and 248.3 nm pump wavelengths, respectively (Fig. S1 (c-d)). The error bars represent one standard deviation.

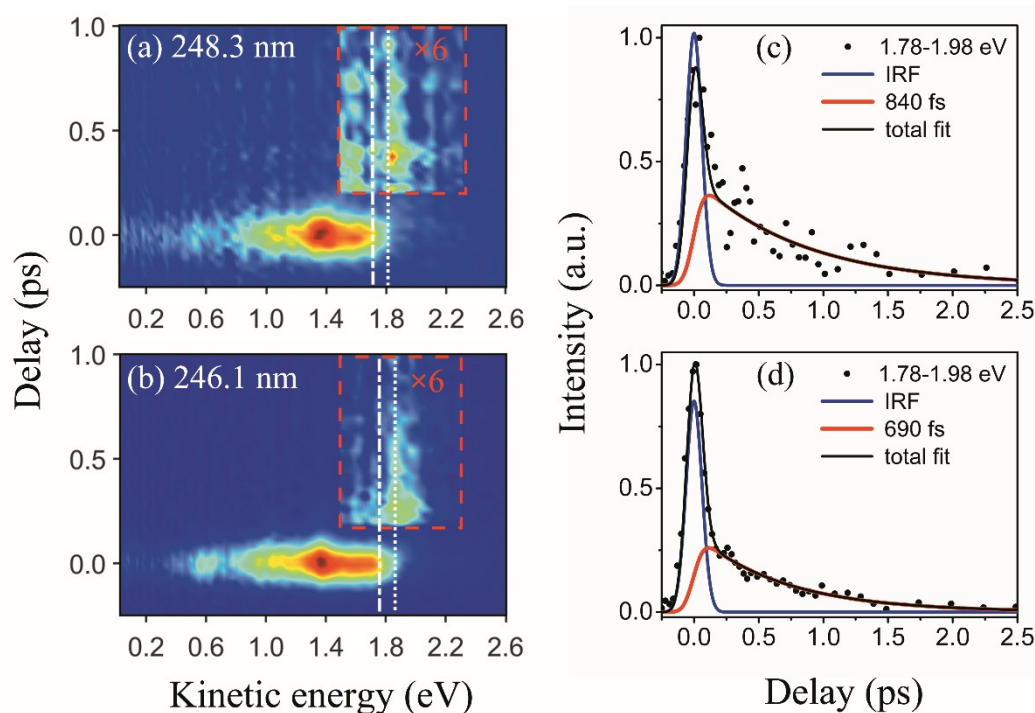


Fig. S1 (a-b) TRPES spectra at pump wavelengths of 248.3 and 246.1 nm, respectively, after subtracting the background photoelectrons generated from single-color multiphoton ionization. The 1.88 eV feature is scaled up by a factor of 6 for a better presentation. The energetic limits for ionization to the ground state ( $D_0$ ) of the 2-EP cation, are indicated by the write dash-dot lines and dot lines, calculated using an ionization potential derived in the current work (7.70 eV) and a recent calculation (7.59 eV, ref. 36 in the main text), respectively. (c-d) Normalized photoelectron transients derived by summing up the TRPES spectra in (a) and (b), respectively, over a kinetic energy range of 1.78-1.98 eV. The solid circles show the experimental data, while black, blue and red lines show the total fit, the contributions from non-resonant photoionization and photoionization from the excited state, respectively.