

Ultrafast photoelectron spectroscopy of photoisomerization reaction of ethylene

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1. Introduction

The ultrafast internal conversion of ethylene from the $1\pi\pi^*$ state is the paradigm for *cis-trans* photoisomerization of olefines.

However,

The isomerization dynamics have not been observed entirely from the Franck-Condon region in the $1\pi\pi^*$ state up to ground state products.

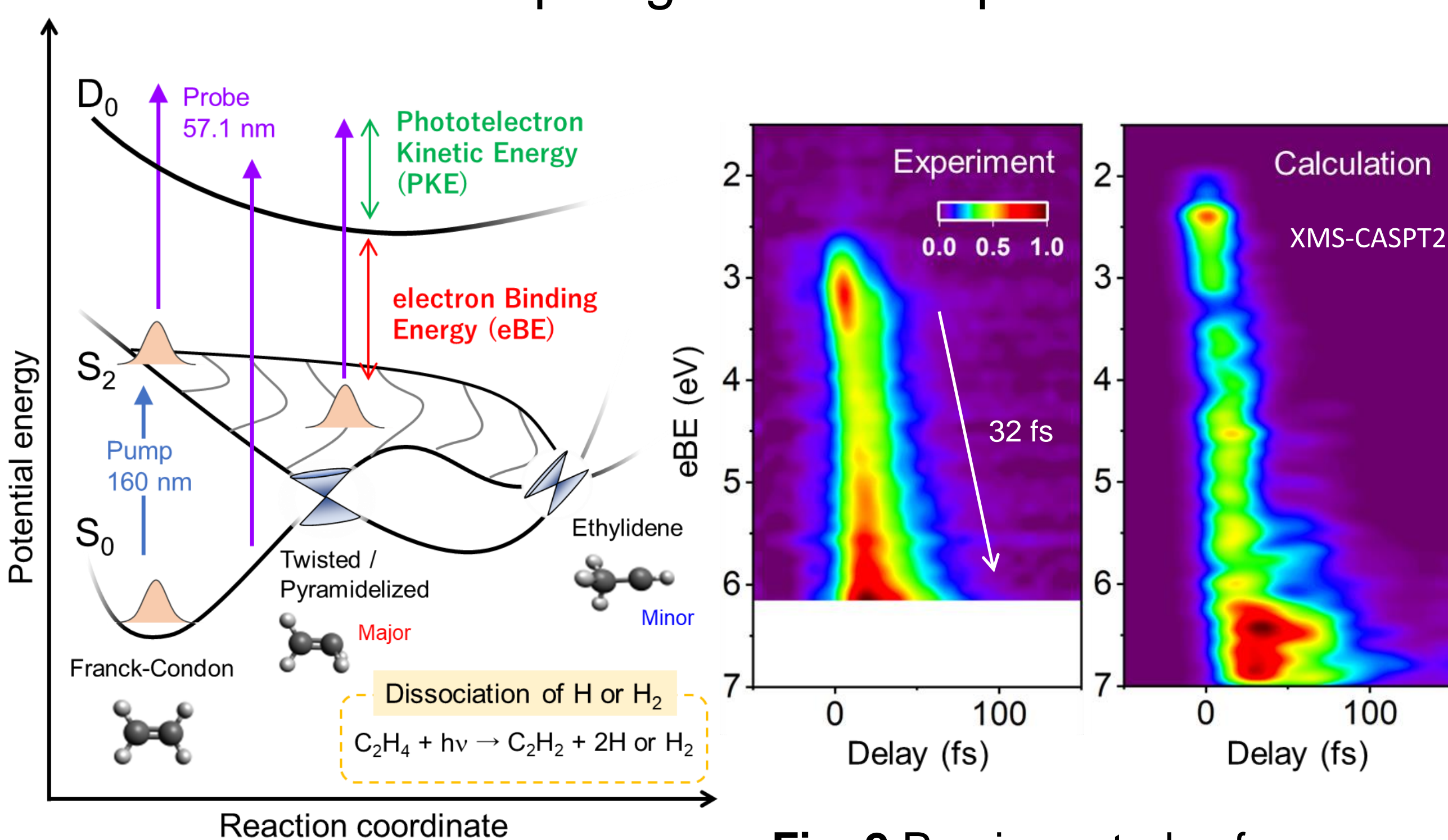


Fig. 1 Relaxation scheme

Fig. 2 Previous study of photoelectron spectroscopy [1], [2]

We performed time-resolved photoelectron spectroscopy using extreme UV pulses (21.7 eV), and real-time observations of the entire relaxation process.

2. Experiment

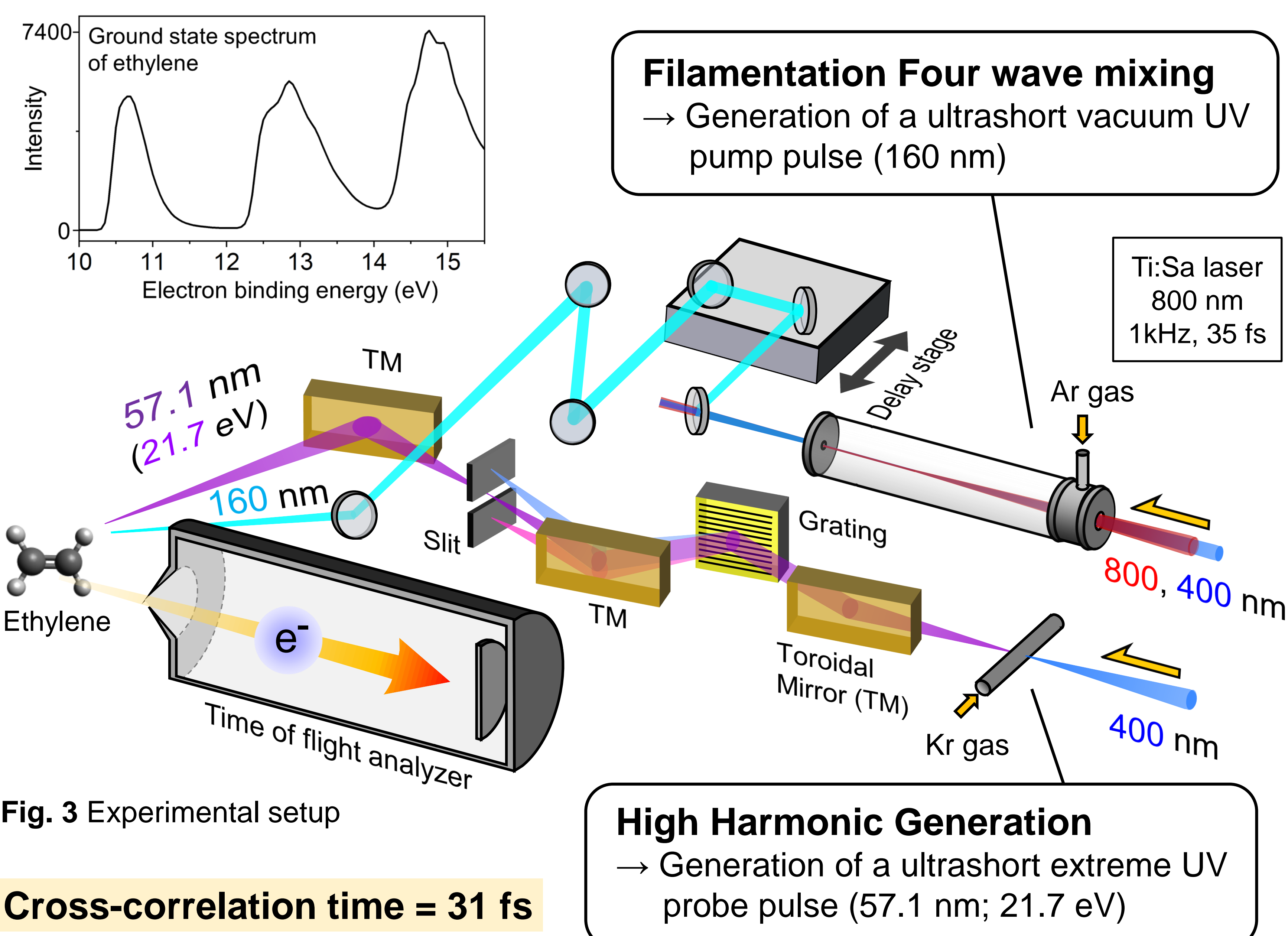
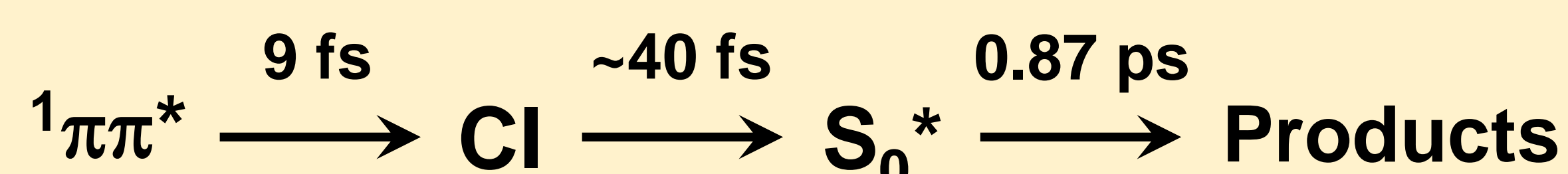


Fig. 3 Experimental setup

Cross-correlation time = 31 fs

3. Results and Discussion

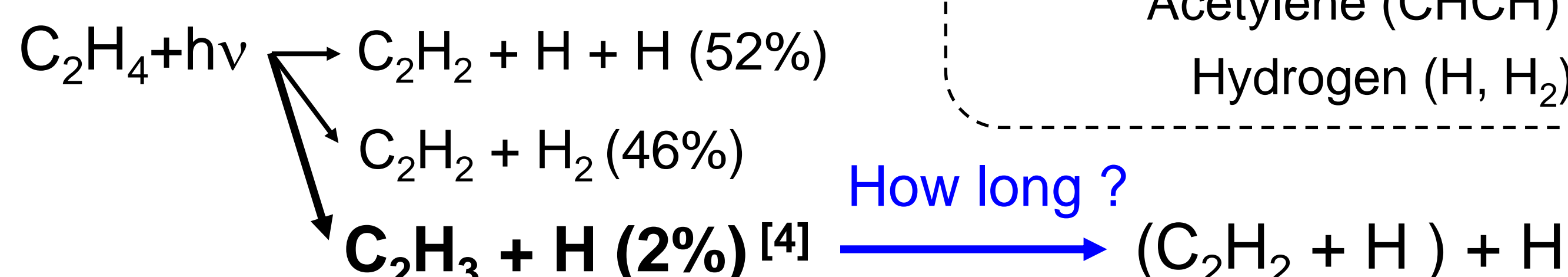
- ✓ The photoelectron signal of the $1\pi\pi^*$ state appears from 3 eV and exhibits a very rapid energy shift. → Due to the C=C motion
- ✓ The photoelectron intensity increases around 6.5 eV. → Sing of conical intersection (CI)
- ✓ Vibrationally hot ground state spectra appear between 8 and 10 eV after a little delay time of ca. 50 fs.



- ✓ The photoelectron spectra of ground state (GS) products measured at 2 and 7 ps exhibit a hump at 9 eV.

What is the long-lived component ?

Ethylidene (CH_3CH) ... I.E. = ~ 9 eV [3]
Vinyl radical (CH_2CH) ... I.E. = > 8.3 eV
 Acetylene (CHCH) ... I.E. = 11.4 eV
 Hydrogen (H, H_2) ... I.E. = 13.6, 15.4 eV



Clear observations of the formation of reaction products (C_2H_2 , H and H_2) and ground-state bleach recovery are desired in future experiments.

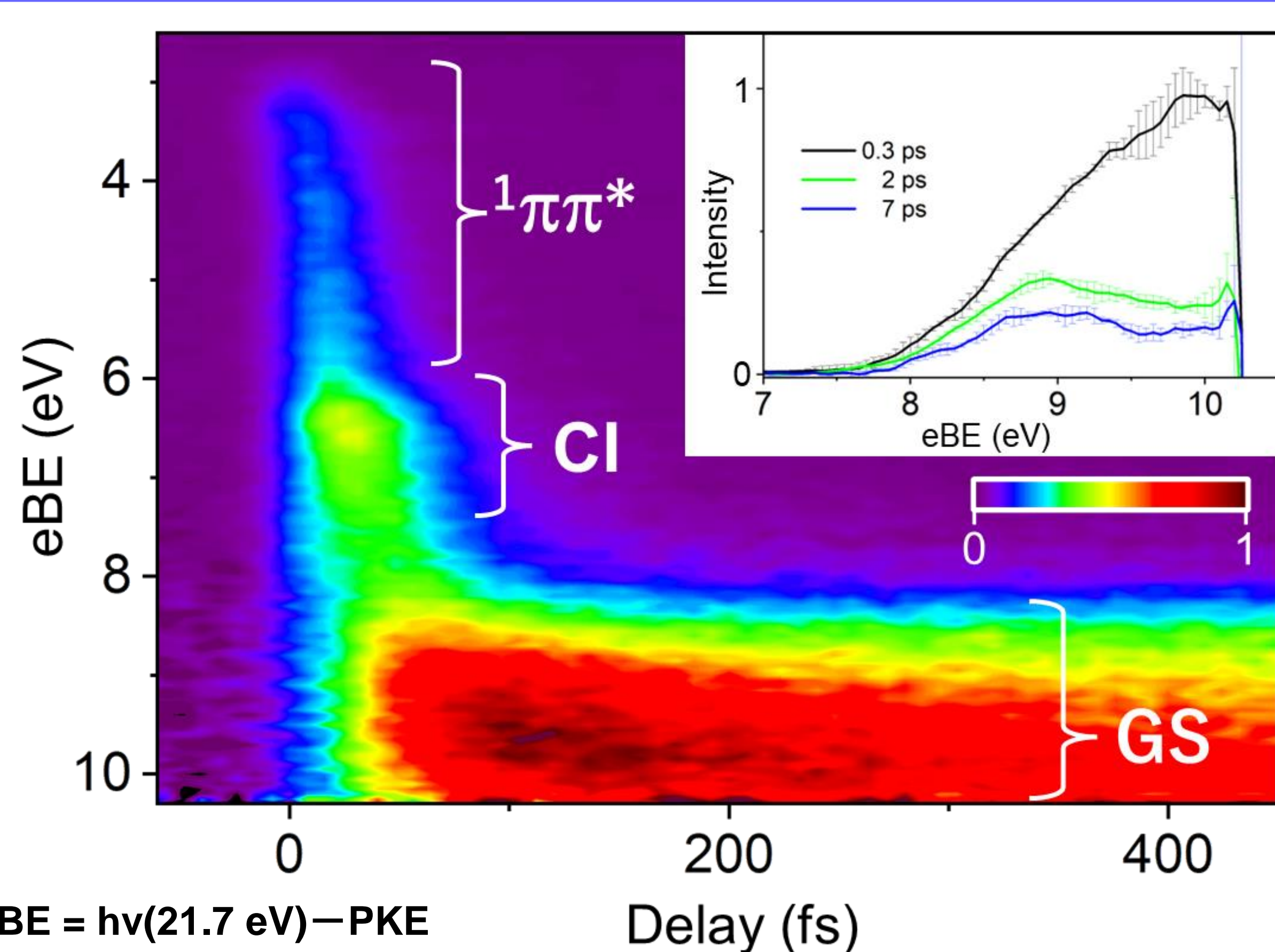


Fig. 4 Experimental results of photoelectron spectra. The inset shows photoelectron spectra measured at 0.3, 2 and 7 ps.

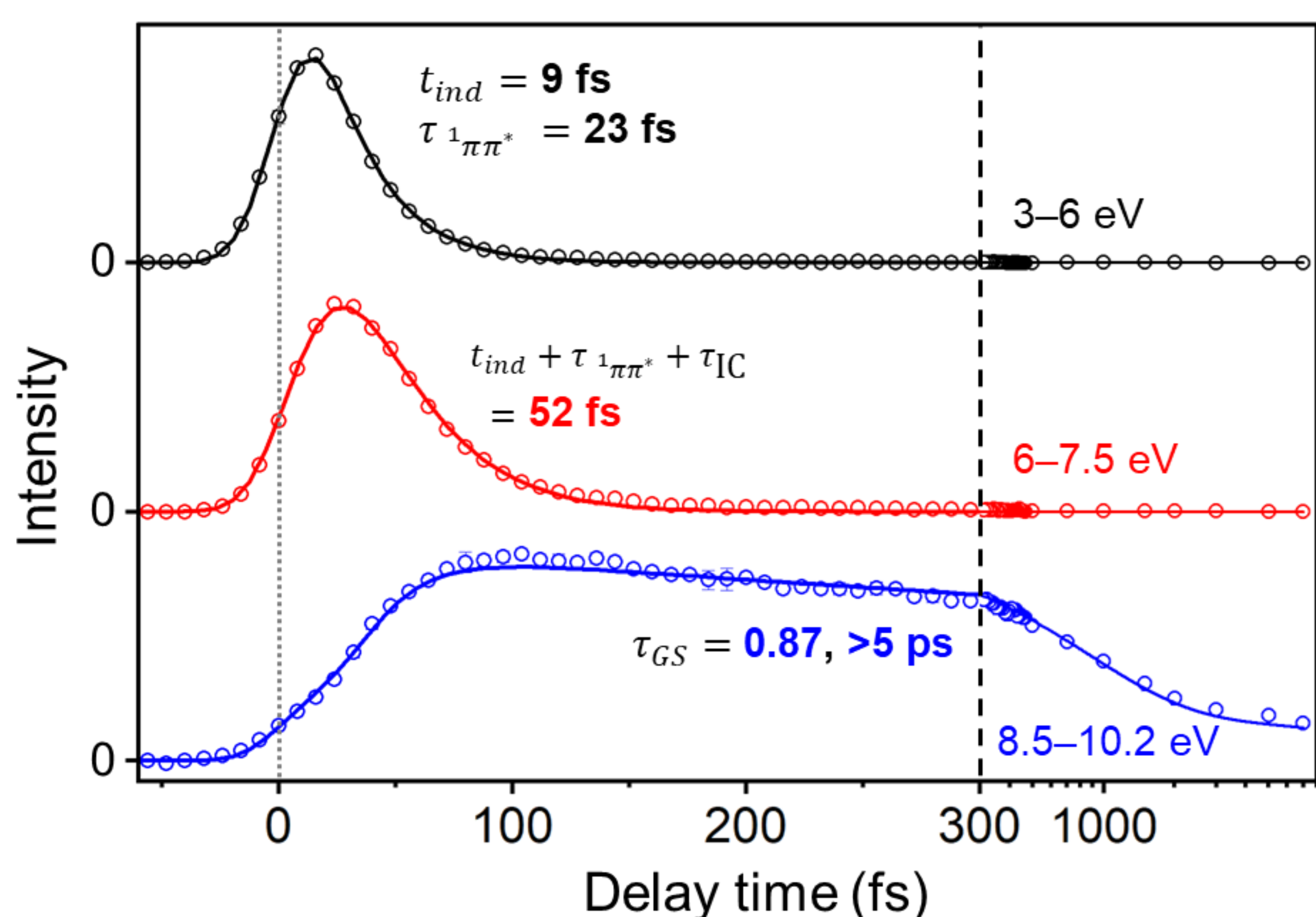


Fig. 5 Time profiles of photoelectron intensity integrated over eBE ranges of 3–6, 6–7.5 and 8.5–10.2 eV. Open symbols show experimental data and solid lines are best-fit curves.

4. Conclusion

- We have succeeded in the clear real-time observation of the entire reaction dynamics from the Franck-Condon region in $1\pi\pi^*$ to S_0 .
- The nuclear wave packet accesses the conical intersections within 10 fs, and the population transfer from the excited to the ground state occurs in ca. 50 fs.
- Short-lived products are ascribed to vibrationally excited ethylene and possibly a small amount of ethylidene, and a long-lived products are presumably of metastable ethylene and vinyl radical.

Reference:

- [1] T. Kobayashi, et al. *J. Phys. Chem. A*, **119**, 9518 (2015), [2] T. Mori, et al. *J. Phys. Chem. A*, **116**, 2808 (2012)
 [3] X. K. Wu, et al. *Phys. Chem. Chem. Phys.* **21**, 22238 (2019), [4] S. H. Lee, et al. *J. Chem. Phys.* **120**, 10983 (2004)