Ultrafast photoelectron spectroscopy of photoisomerization reaction of ethylene

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1. Introduction

The ultrafast internal conversion of ethylene from the $\pi\pi^*$ 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 $\pi\pi^*$ state up to ground state products.

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

2. Experiment

![Experimental setup](Image)

- Filamentation Four wave mixing
  - Generation of a ultrashort vacuum UV pump pulse (160 nm)
- High Harmonic Generation
  - Generation of a ultrashort extreme UV probe pulse (57.1 nm; 21.7 eV)

Cross-correlation time = 31 fs

3. Results and Discussion

- The photoelectron signal of the $\pi\pi^*$ 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.

9 fs

3-6 eV

6-7.5 eV

8.5-10.2 eV

C2H4 + hv → C2H2 + H + H (52%) 

C2H2 + H + H (52%) 

C2H4 + hv → C2H3 + H (2%) [4]

How long?

Ethylidene (CH2=CH) ... I.E. = ~ 9 eV

Vinyl radical (CH=CH) ... I.E. = > 8.3 eV

Acetylene (CHCH) ... I.E. = 11.4 eV

Hydrogen (H, H2) ... I.E. = 13.6, 15.4 eV

Clear observations of the formation of reaction products (C2H2, H and H2) and ground-state bleach recovery are desired in future experiments.

4. Conclusion

- We have succeeded in the clear real-time observation of the entire reaction dynamics from the Franck-Condon region in $\pi\pi^*$ 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: