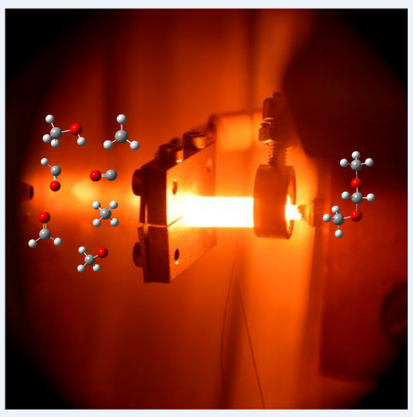
Pyrolysis of Methylal Revealed by Imaging Photoelectron Photoion Coincidence Spectroscopy

Tongpo Yu , Patrick Hemberger, Xiaoguo Zhou* , Shilin Liu*, Andras Bodi*

1.National Synchrotron Radiation Laboratory(NSRL), Hefei, Anhui 230026, China

2.Laboratory for Femtochemistry and Synchrotron Radiation, Paul Scherrer Institute, Villigen 5232, Switzerland.

Introduction



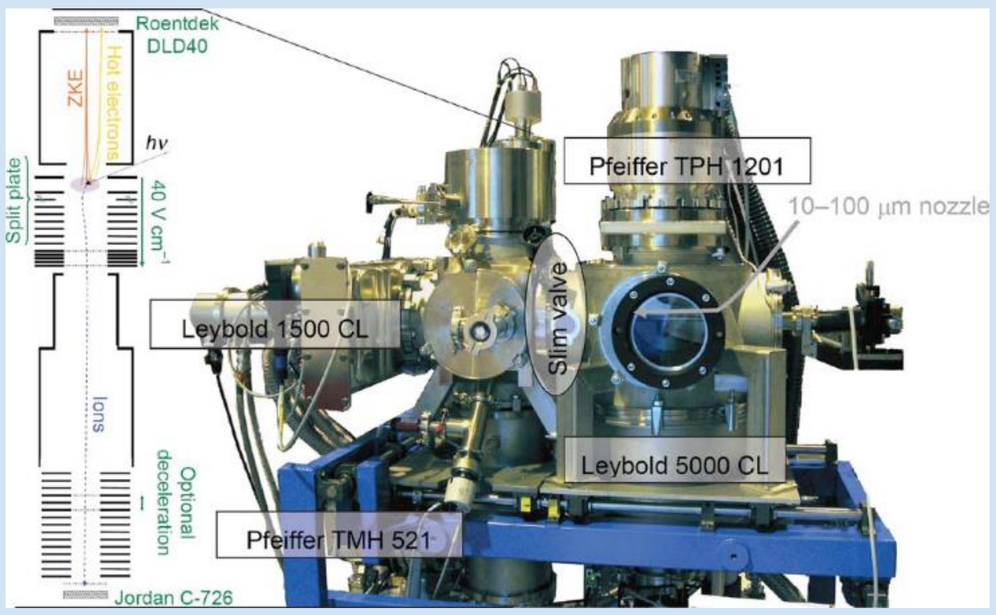
Methylal($CH_3OCH_2OCH_3$) participate in the chemical process of combustion

Many fundamental questions remain open:

•Pyrolysis mechanisms?

•Dissociation channels under different conditions?

Experimental Method



imaging photoelectron photoion coincidence spectrometer, iPEPICO

The spectra of Methylal

TOF MS spectrum of Methylal under different conditions

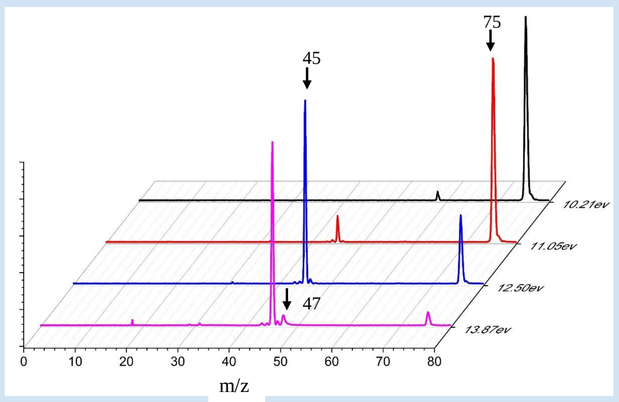


Figure 1. Illustrative threshold photoionization mass spectra of methylal recorded at five photon energies.

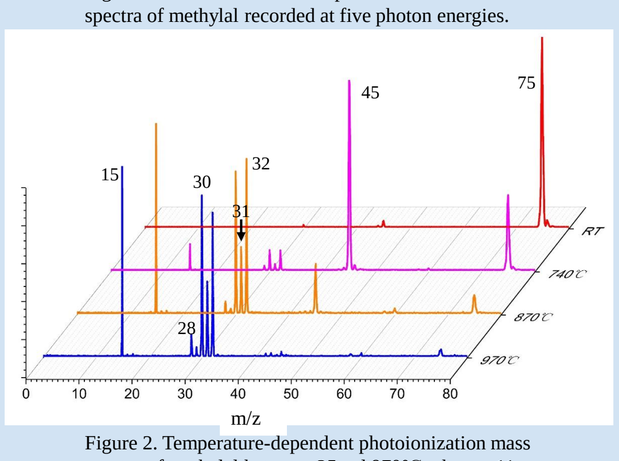


Figure 2. Temperature-dependent photoionization mass spectra of methylal between 25and 970°C,taken at 11ev.

The unimolecular rate constant of each dissociation pathway, $k(E)$, is obtained as:

$$k(E) = \frac{\sigma N^{\ddagger}(E - E0)}{h\rho(E)},$$

where σ is the reaction symmetry, $N^{\ddagger}(E - E0)$ is the sum of states of the transition state from 0 to $E - E0$, h is Planck's constant, and $\rho(E)$ is the density of states of the parent ion at energy E.

Results & Discussion

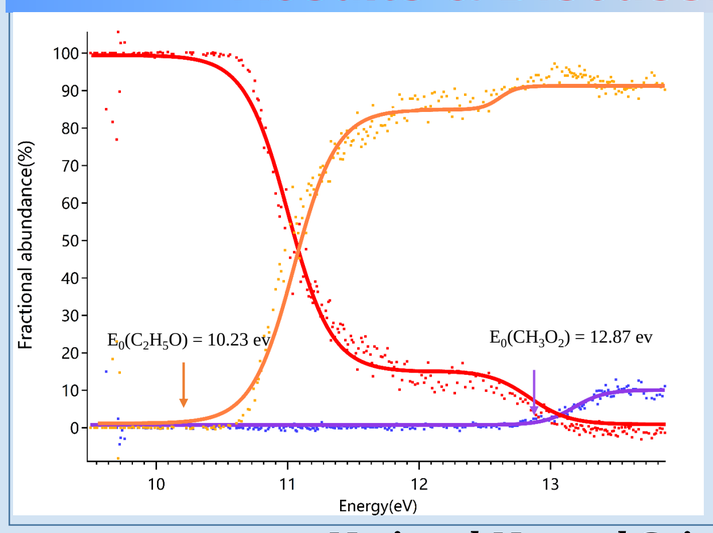


Figure 3. Modeling of the breakdown curves of DMM. Markers show the experimental fractional ion abundances, whereas the solid lines show the modeled results. The fitted 0 K appearance energy are $E_0(C_2H_5O)$ = 10.23 ev, $E_0(CH_3O_2)$ = 12.87 ev.

The pathway of formatin of m/z=45、 m/z=31、 m/z=30 m/z=32、 m/z=28 、m/z=15 and m/z=16.

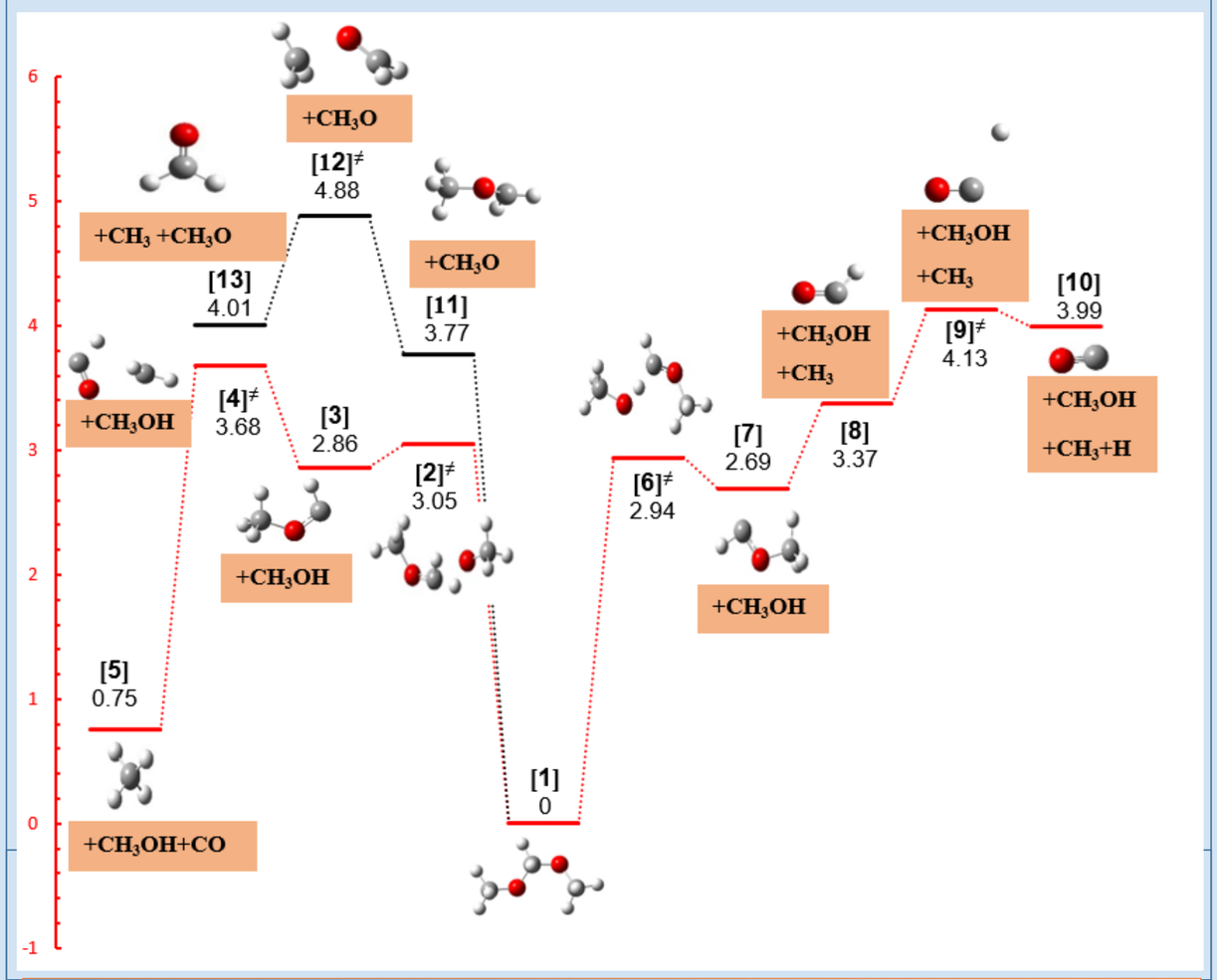


Figure 4. Fragmentation pathways and potential energy surface of the adipic acid ion at the CBS-QB3 level of theory. The energies are given in electronvolts and are relative to the neutral methylal. red lines show minor reaction channels

Conclutions

- The 0 K appearance energy of m/z=45 and m/z=45 was determined to be $E_0(C_2H_5O)$ = 10.23 ± 0.010 eV and $E_0(CH_3O_2)$ = 12.87 eV.
- The low-energy breakdown diagram could only be reproduced well when a second process was included for the formation of the cation of m/z=75, namely a parall dissociation from the $CH_3OCHOCH_3^+$ intermediate by C_2H_4-loss.
- Finally, the CH_3^+ fragment ion can be formed by two processes: either as a simple dissociation of the methylal cation parent ion [**1**] by a CH_3 loss from $CH_3OCH_2OCH_3$ or as sequential decomposition of the CH_3OCH^+ respectively.

references

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