

# Swiss Light Source

## VUV beamline, Imaging photoelectron photoion coincidence spectroscopy

A. Bodi, M. Johnson, T. Gerber\*

Paul Scherrer Institut, Molecular Dynamics,  
5232 Villigen/PSI, CH

An imaging photoelectron photoion coincidence spectrometer at the vacuum ultraviolet (VUV) beamline of the Swiss Light Source is presented and a few initial measurements are reported. Monochromatic synchrotron VUV radiation ionizes the cooled or ambient temperature gas-phase sample. Photoelectrons are velocity focused, with a resolution better than 1 meV in order to detect threshold electrons. The electron detection also starts the counter for the time-of-flight analysis of the associated ion. The ions are accelerated in a relatively low, 40 – 80 V/cm field, which enables the direct measurement of rate constants in the  $10^3 - 10^7$  Hz range. All electron and ion events are recorded in a triggerless multiple-start/multiple-stop protocol enabling coincidence measurements at 100 kHz event frequencies.

### Introduction

The VUV beamline at the Swiss Light Source had first light in fall, 2007. After the initial experiments and preliminary adjustment of the optical elements, the first experimental station has been built, brought to operation and has been used in different configurations. Since fall 2008 the VUV beamline changed its operation status normal and accepts users performing their projects [1].

The main components (Fig.1) of the experimental chamber are the vacuum system, a continuous molecular beam source, a slim “clockwork” valve, velocity map imaging electron optics, a time-of-flight analyzer for ion mass analysis, detector electronics and data acquisition software.

The vacuum system consists of four high vacuum pumps and two Alcatel ACP Roots blower oil-free forepumps in order to maintain a background pressure of  $< 5 \cdot 10^{-4}$  mbar in the molecular beam source chamber.

The molecular beam source consists of a  $10 \mu\text{m} - 100 \mu\text{m}$  diameter heatable nozzle or a compound pyrolytical source. The beam of molecules passes from the nozzle into the experimental chamber through a valve comprising six ports arranged on a disk. Different skimmers can be brought into the beam axis by turning the valve

disk to the appropriate position. The valve is very slim ( $\sim 4$  cm) and thereby minimizes the distance between the beam skimmer and the experimental interaction region.

The sample is ionized by the incident VUV radiation from the X04DB bending magnet port of the SLS. In the imaging photoelectron photoion coincidence setup (iPEPICO), the photoelectrons are energy- and the photoions are mass-analyzed, by extraction into a flight tube. Velocity map imaging of photoelectrons is achieved by imaging the electrons onto a 40 mm diameter position sensitive MCP (micro channel plate) detector. Electrons with the same absolute momentum perpendicular to the flight axis arrive on the detector in concentric circles. After a convolution the kinetic electron energy can be retrieved to study the dissociation pattern of internal energy selected ions. With the kinetic energy of electrons and the energy of the monochromatized ionizing photons, the full energy balance of a dissociation process can be established if also the ionization threshold is either known or if it can be derived from an additional measurement.

The ions are accelerated in slow fields to measure rate constants of slow reactions directly. Their mass-analysis is carried out in a two-stage linear time-of-flight tube. The electron and ion optics were designed and constructed at PSI. A new data acquisition program, basing on a correlation of electron and ion event counting [2], has been installed including a graphical user interface and scripting possibilities for automated data acquisition and analysis. The electronics and the software enable a triggerless multi-start/multi-stop setup for two-particle coincidence experiments.

The iPEPICO endstation is connected to an 8-stage differentially pumped gas filter, which acts as a “gas stream” window [3]. Despite the direct connection between the synchrotron storage ring ( $10^{-9}$  mbar ultrahigh vacuum), it is now possible to have up to 40 mbar sample pressure in the experimental chamber without any danger of contamination of

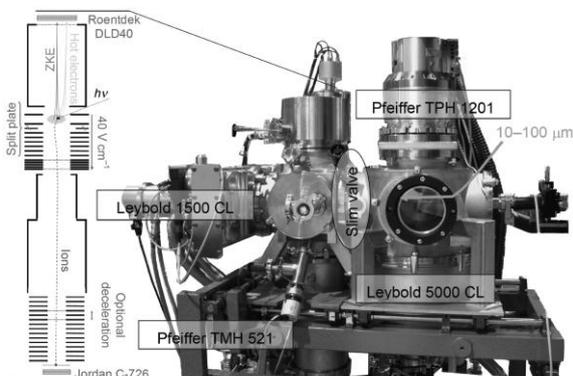


Fig. 1: Experimental setup

\* Corresponding author: thomas.gerber@psi.ch  
Towards Clean Diesel Engines, TCDE 2009

vacuum parts. Absorption and VUV fluorescence measurements are thus readily possible with little or no system modification.

## Results

The iPEPICO setup was tested on methane molecule that dissociates rapidly on the time scale of the ion TOF. Both effusive and molecular beam sample sources were used. The room temperature breakdown diagram, which is a plot of the fractional abundance of the parent and fragment ion signals as a function of the photon energy, is shown in Fig. 1. The solid line through the points is the expected breakdown diagram assuming all three rotational degrees of freedom of methane are available for the dissociation process. The derived 0 K onset, which corresponds to the photon energy when the complete methane thermal energy distribution is above the methane ion dissociation limit, was found to be  $14.319 \pm 0.003$  eV. A similar experiment with a cooled  $\text{CH}_4$  yielded an onset of  $14.321 \pm 0.001$  eV. This is slightly below the value

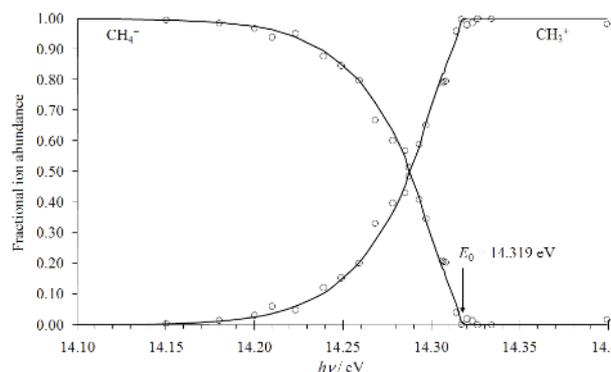


Fig. 2. Breakdown diagram of thermal methane. Empty circles correspond to measured ion abundances, the continuous curves are modeled taking into account the thermal energy distribution at 298 K and that all methane ions above the barrier lose a H-atom instantaneously.

reported by Weitzel *et al.* of  $14.323 \pm 0.001$  eV [4]. The slowly descending parent ion signal and the corresponding ascending methyl ion signal is a result of the thermal rotational distribution of the sample at 298 K.

Stevens *et al.* [5] measured and modeled the dissociation rates of halogen atom loss from halo-benzenes over a wide internal energy range. We used 2%  $\text{C}_6\text{H}_5\text{Cl}$  seeded in 1 bar Ar with a 100  $\mu\text{m}$  nozzle in the molecular beam source to reproduce their results and measure the temperature of the sample in the molecular beam [1]. The optimized breakdown diagram, assuming a sample temperature of 100 K and yielding a best fit RRKM barrier of 3.235 eV, is shown in Fig. 3. The breakdown diagram and the TOF distributions of daughter ions were fit using the reported  $k(E)$  function. Only the internal temperature of chlorobenzene in the molecular beam and the barrier to dissociation were

varied. As shown in the insert of Fig. 3, the statistical goodness of fitting the measured TOF distributions did not vary with the assumed tempera-

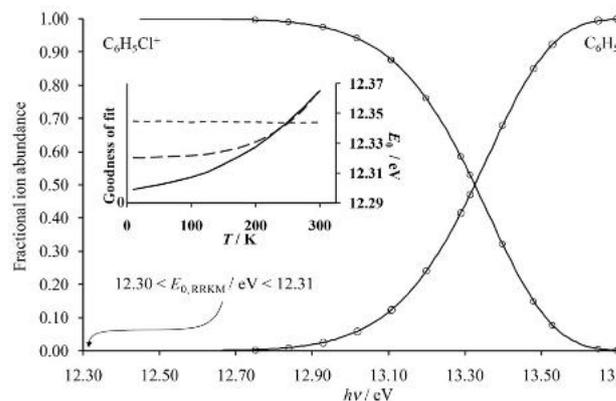


Fig. 3. Breakdown diagram of chlorobenzene in a molecular beam. The insert shows that the goodness of the fit to the measured TOF signal is independent of the assumed temperature (short dash). But, both the goodness of the breakdown diagram (long dashed) and the barrier height (solid line) gets worse with increasing temperature (indicated by increasing departure from zero). Based on the goodness of the breakdown diagram fit, 125 K is an upper limit to the temperature, resulting to a  $1 \text{ kJ mol}^{-1}$  uncertainty in the barrier height.

ture. However, the fit to the breakdown diagram gets worse at temperatures above 125 K. This suggests that the sample temperature is below 125 K, a temperature at which the sample contains only 2.1 kJ/mol (22 meV) of rovibrational energy, compared to a room temperature average energy of 104 meV. The insensitivity of the breakdown diagram to temperature below 125 K is because the major broadening of the breakdown diagram is a result of the slow dissociation rates. In view of previously published studies on the cooling of vibrations in continuous molecular beams [6], a temperature around 100 K is not unreasonable, and the total 0–125 K temperature range only trans-

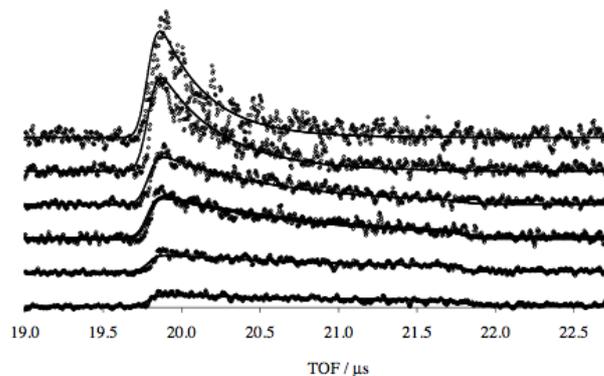


Fig. 4. Measured ( $\circ$ ) and modeled ( $\text{—}$ ) daughter ion TOF distributions at  $h\nu = 13.313, 13.399, 13.480, 13.529, 13.649$  and  $13.698$  eV (from bottom to top) for chlorobenzene.

lates into 1 kJ/mol uncertainty in the barrier height. The measured and calculated TOF distributions (see Fig.4) agree very well, which corroborates the reported  $k(E)$  [5] curve as well as our ability to measure slow dissociation rates.

The imaging PEPICO, originally proposed by Sztáray and Baer [7] in 2003 has been designed and built at the Paul Scherrer Institut and is now operational at the VUV beamline of the Swiss Light Source. The main benefits of the experiment in comparison with the one described in [7] include a 1 meV electron kinetic energy resolution in a continuous experiment, simultaneous electron kinetic energy analysis in the 0–800 meV range, the use of tunable synchrotron radiation up to 30 eV photon energy, and a large throughput pump system to allow for a continuous supersonic molecular beam. Successful applications of the iPEPICO setup could be demonstrated with the determination of accurate appearance energies H atom loss from methane, and with the measurement of slow photodissociation rate constants in the context of dissociative photoionization of chlorobenzene.

## References

1. Bodi A., J.M., Gerber T., Gengeliczki Z., Sztaray B., Baer T., Imaging photoelectron photoion coincidence spectroscopy with velocity focusing electron optics. *Review of Scientific Instruments*, 2009. 80(3): p. 034101.
2. Andras Bodi, B.S., Tomas Baer, Melanie Johnson and Thomas Gerber, Data acquisition schemes for continuous two-particle time-of-flight coincidence experiments. *Rev. of Sci. Instrum.*, 2007. 78(8): p. 084102.
3. Johnson, M., A. Bodi, L. Schulz, and T. Gerber, New vacuum ultraviolet beamline at the Swiss Light Source for chemical dynamics studies. in preparation, 2009.
4. Weitzel, K.-M., M. Malow, G.K. Jarvis, T. Baer, Y. Song, and C.Y. Ng, High-resolution pulsed field ionization photoelectron--photoion coincidence study of  $\text{CH}_4$ : Accurate 0 K dissociation threshold for  $\text{CH}_3^+$ . *The Journal of Chemical Physics*, 1999. 111(18): p. 8267-8270.
5. Stevens, W., B. Sztaray, N. Shuman, T. Baer, and J. Troe, Specific Rate Constants  $k(E)$  of the Dissociation of the Halobenzene Ions: Analysis by Statistical Unimolecular Rate Theories. *The Journal of Physical Chemistry A*, 2009. 113(3): p. 573-582.
6. Mayer, P.M. and T. Baer, A photoionization study of vibrational cooling in molecular beams. *International Journal of Mass Spectrometry and Ion Processes*, 1996. 156(3): p. 133-139.
7. Sztaray, B. and T. Baer, Suppression of hot electrons in threshold photoelectron photoion coincidence spectroscopy using velocity focusing optics. *Review of Scientific Instruments*, 2003. 74(8): p. 3763-3768.