

Chapter 2

Experimental Setup

We will in this chapter describe the experimental setup for conducting time-resolved photoionization experiments such as time-resolved mass spectrometry (TRMS) and photoelectron spectroscopy (TRPES) on gaseous samples. The main setup consists of a laser system capable of producing laser pulses of a femtosecond time duration, a means of preparing a cold gaseous sample, and a detection apparatus for charged particles. We will in the following sections describe these components.

2.1 The Laser System and Optical Setup

The laser system and optical setup used in the experiments is schematically illustrated in Fig. 2.1. The laser system consists of a Ti:Sapphire oscillator (Spectra Physics Tsunami, 80 MHz, 800 nm, 80 fs, 700 mW) which is pumped by a Nd:YLF continuous wave (CW) laser (Spectra Physics Millennia Pro Vs, 532 nm, 5 W). The oscillator seeds a regenerative Ti:Sapphire amplifier (Spectra Physics SpitFire, 1 kHz, 800 nm, 100 fs, 1.1 W) which is pumped by a Q-switched Nd:YVO₄ laser (Spectra Physics Empower-15, 1 kHz, 527 nm, 100 ns, 6.7 W). The output of the amplifier is split and used to pump an optical parametric amplifier (Light Conversion TOPAS-C, 240–2600 nm) and a harmonic generation setup which can generate the second (2ω), third (3ω), and fourth harmonic (4ω) of the fundamental. In addition to the laser system, the setup also consists of a retro-reflector mounted on a computer-controlled translatable stage on the harmonic generation arm of the optical setup. The stage allows for changes to the path length of the harmonic generation arm and can thereby be used to change the time-delay between pulses from the two arms. The beams from the two arms are combined using a dichroic mirror, and the collinear beams are focused into the vacuum chamber using a concave aluminium mirror. Pulses from either arm can act as the pump pulses in the experiments, and pulses from the other arm will act as the probes.

fundamental and third harmonic. The third harmonic can easily be extracted from the setup by removing the beam splitter and the first 267 nm HR whereas the second harmonic can be extracted if the second BBO crystal is also removed.

2.2 Time-of-Flight Spectrometers

The vacuum chamber incorporating the time-of-flight (TOF) spectrometers as well as the molecular beam generation is illustrated in Fig. 2.3. The setup can handle both gaseous, liquid, and solid samples. In the case of liquid samples, the inert helium carrier gas is bubbled through the sample at a backing pressure of 0.3 bar, and a mixture of helium and sample molecules are let into the chamber through a stainless steel inlet tube. Solid samples can be placed in a small heatable chamber at the end of the inlet tube and sublimed into the helium carrier gas.

In the first chamber, the gas mixture continuously expands through a conical nozzle ($\varnothing = 100 \mu\text{m}$) at the end of the inlet tube. In the course of the expansion, the sample molecules are first accelerated to the velocity of the carrier gas whereafter they start transferring energy to the carrier gas molecules through two-body interactions thereby cooling their rotational and vibrational degrees of freedom [1–3]. Rotational temperatures down to $\sim 2 \text{ K}$ can be obtained with continuous inlet systems such as the one in our setup whereas high-pressure pulsed valve systems can obtain temperatures down to $\sim 0.4 \text{ K}$ [3, 4]. The expansion beam is termed a supersonic molecular beam as the speed of the carrier molecules ($\sim 1750 \text{ m/s}$ for He at room temperature [3]) can exceed that of sound. The expansion of the mixture leads to a low-density sample thereby eliminating intermolecular interactions providing an ensemble of molecules in one or a few well-defined quantum states [5]. Approximately one centimeter from the nozzle of the inlet tube, a skimmer ($\varnothing = 200 \mu\text{m}$) ensures the formation of a turbulence free molecular beam in the next chamber. From the middle chamber, the beam passes through a pinhole ($\varnothing = 1 \text{ mm}$) into the main interaction chamber where it is intersected at a right angle by the laser beams.

The interaction between the laser pulses and the beam molecules leads to photoionization forming cations and photoelectrons. These charged particles can be extracted and detected at the top or bottom of the chamber by the respective detector. Thus, the apparatus operates as either a TOF mass or photoelectron spectrometer but cannot be operated in coincidence. The mass spectrometer can also be operated as a reflectron TOF mass spectrometer although this mode of operation was not employed in this work.

When operated as a mass spectrometer, the apparatus uses a two-field Wiley-McLaren configuration [6]. The voltage difference $V_E = V_{A1} - V_{A2}$ creates a uniform field $\mathcal{E}_E = -V_E/l_E$ as shown in the inset of Fig. 2.3. This field extracts the cations generated by the laser-molecule interaction. The voltage difference $V_A = V_{A2} - V_L$ creates another uniform field $\mathcal{E}_A = -V_A/l_A$ which accelerates the cations into the field free flight tube above the accelerator grid. At the top of the flight tube, the cations are incident upon the ion detector consisting of a set of chevron-stacked

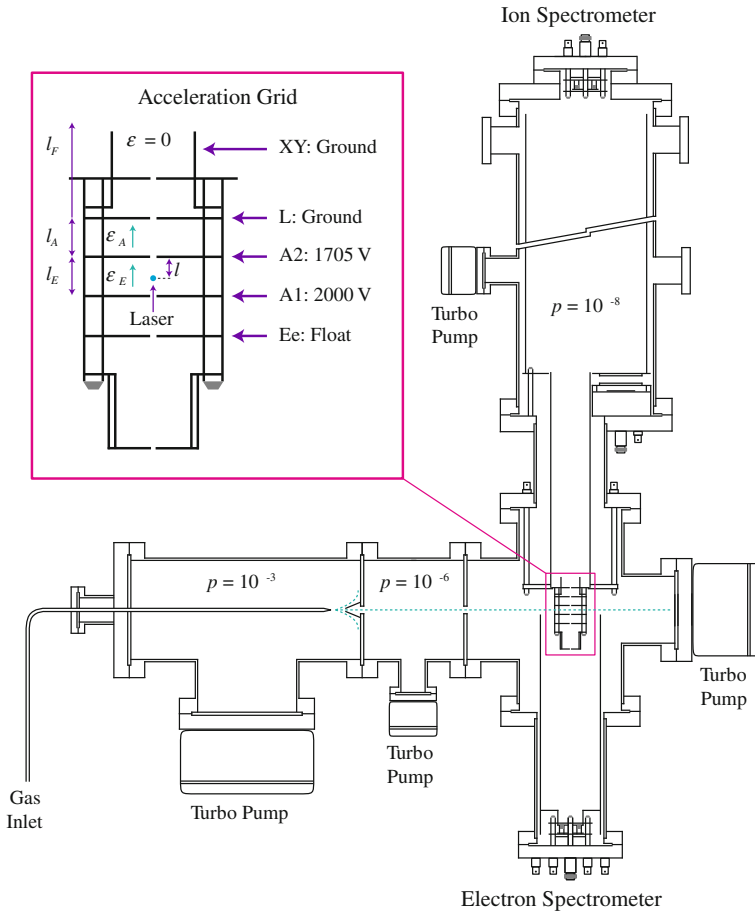


Fig. 2.3 Schematic overview of the vacuum chamber, molecular beam generation, and TOF spectrometers. The inset shows a close-up of the acceleration grid with typical voltages employed when the apparatus is operated in ion mode. Measurements run in electron mode are field free, and all grid connections are grounded. The typical pressures in the chambers (mbar) are indicated showing the differential pumping. Dimensions are not to scale

micro-channel plates (MCP) operated at negative potential. A small DC voltage (~ 70 mV) is generated in an anode on the backside of the MCP stack when an ion impinges on the detector. This voltage signal is subsequently sent to a time digitizer card (FAST ComTec P7888-2(E)) in a computer. As the card also receives a trigger signal from the laser system, the computer can register the TOF for the impinging cations. The total TOF of the cations is given by the sum of the times spent in the extraction, acceleration, and free flight regions which are given by [7]

$$t_E = \sqrt{\frac{m}{z}} \sqrt{\frac{2l_E l}{V_E}} \quad (2.1)$$

$$t_A = l_A \sqrt{\frac{m}{z}} \left[\sqrt{\frac{2}{V_A} \left(1 + \frac{V_E l}{V_A l_E} \right)} - \sqrt{\frac{2}{V_A} \frac{V_E l}{V_A l_E}} \right] \quad (2.2)$$

$$t_F = l_F \sqrt{\frac{m}{z}} \sqrt{\frac{1}{2V_A + 2V_E l/l_E}} \quad (2.3)$$

It is assumed that all photoionization events occur at the same distance l from the acceleration region, and that the initial velocity along the flight tube axis is zero. The total TOF is dependent on the mass to charge ratio m/z , and the cations are therefore separated into bunches when they reach the detector with the lightest first followed by successively heavier masses (assuming identical charges). Taking into account that the digitizer card records the TOF with respect to the laser trigger signal, which is not identical to the time of photoionization, the masses of the recorded signal are given by

$$m/z = K_{\text{ion}} (t_{\text{ion}}^{\text{TOF}} - t_0)^2 \quad (2.4)$$

where all the spectrometer dependent parameters are collected into a single constant K_{ion} , and t_0 measures the difference between the laser trigger and the time of photoionization. The mass spectrometer is calibrated by measuring samples with known mass spectra usually acetone, N , N -dimethylisopropylamine (DMIPA), and xenon.

When operated as a photoelectron spectrometer, all connections on the acceleration grid are grounded. A tube of μ -metal shields the inside of the downward flight tube from magnetic fields, and the experiments are (ideally) run field free. Furthermore, the surfaces of the accelerator are made from oxidized molybdenum which has a high work function such as to reduce background photoelectrons. Nonetheless, scattered photons can contribute to the background signal, and, therefore, an iris is placed in the vacuum chamber before the interaction region, and a laser-grade CaF_2 entrance window is used (CVI PW-1009-CFUV). The part of the photoelectrons generated by the laser-molecule interaction with a primarily downward pointing velocity vector will be incident upon the electron detector. This detector consists of another set of chevron-stacked MCPs operated at a positive potential. The anode is also operated at a high positive potential, and the signal from the electrons is thus at a high DC potential. The timing electronics are protected by a capacitive decoupling of the anode. The decoupled, negative DC voltage signal (~ 10 mV) is passed through a pre-amplifier (Phillips Scientific 6954B 100), and the amplified signal (~ 500 mV) is sent to the time digitizer card. Similar to the case of ions, the TOF is measured which in this case is given by

$$t_e^{\text{TOF}} = l_F \sqrt{\frac{1}{2(E_k + E_0)}} \quad (2.5)$$

where E_k is the kinetic energy gained by the photoelectrons in the ionization process. E_0 is a correction term resulting from deviations from field free operation due to e.g. contact potential terms leading to acceleration/deceleration of the photoelectrons. The latter term is usually on the order of meV. l_F is here the length of the downward free flight path of the photoelectrons. Inverting the expression in Eq. 2.5 yields the kinetic energy as a function of the TOF

$$E_k = \frac{K_e}{(t_e^{\text{TOF}} - t_0)^2} + E_0 \quad (2.6)$$

We have again collected parameters and constants into a single coefficient K_e , and the time difference between trigger and photoionization is taken into account via t_0 . Equation 2.6 provides the position of the spectral peaks, however, to determine the full photoelectron spectrum, the Jacobian has to be taken into account to establish the correct relative spectral intensities

$$\sigma(E_k) = \sigma(E_k(t_e^{\text{TOF}})) \left| \frac{dt_e^{\text{TOF}}}{dE_k} \right| = \sigma(E_k(t_e^{\text{TOF}})) \frac{(t_e^{\text{TOF}})^3}{2K_e} \quad (2.7)$$

When determining the mass spectrum, it is not necessary to take the Jacobian into account as the cationic signals are only spread over a few TOF bins, i.e. the spectrum consists of almost discrete peaks. Similarly to the case for ions, the parameters K_e , E_0 and t_0 are determined from TOF spectra with sharp peaks of known energy usually xenon and DMIPA.

The above procedures describe how to obtain mass and photoelectron spectra $\sigma(m/z)$ and $\sigma(E_k)$ from the appropriate TOF spectra $\sigma(t_{\text{ion}}^{\text{TOF}})$ and $\sigma(t_e^{\text{TOF}})$. A Lab-View program records the data from the time digitizer card and furthermore controls the retroreflector stage. By repeating the above procedures for a given set of pump-probe time-delays by moving the stage, time-resolved spectra $\sigma(t_{\text{ion}}^{\text{TOF}}, \Delta t)$ and $\sigma(t_e^{\text{TOF}}, \Delta t)$ can automatically be recorded by the program from which the spectra $\sigma(m/z, \Delta t)$ and $\sigma(E_k, \Delta t)$ can be determined.

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