Photoelectron imaging in pump-probe experiments combining synchrotron and laser radiation

P. O’Keeffe¹, P. Bolognesi¹, R. Richter², A. Moise², E. Ovcharenko¹, L. Pravica⁴, R. Sergo², L. Stebel², G. Cautero² and L. Avaldi¹,*

¹ CNR Istituto di Metodologie Inorganiche e dei Plasmi, Area della Ricerca di Roma 1, CP10,00016 Monterotondo Scalo, Italy
² Sincrotrone Trieste, Area Science Park, I-34149 Basovizza (Trieste), Italy
³ Institute of Electron Physics, Uzghorod, Ukraine
⁴ ARC Centre for Antimatter-Matter Studies, Physics Department, The University of Western Australia, Perth 6009, Australia

E-mail: Lorenzo.Avaldi@imip.cnr.it

Abstract. A new photoelectron imaging spectrometer has been used to measure the photoelectron angular distributions in pump-probe experiments where the VUV radiation of the synchrotron is used to prepare an aligned state of the target and the radiation of a Ti:sapphire laser ionizes it. The new set-up and its use to study the photoionization of the He 1s3p (¹P₁) and Ne 2p⁵nd (¹P₁) states are described.

1. Introduction
Measurements of the photoelectron angular distributions (PADs) in the photoionization of atoms and molecules have long been known as a valuable tool to characterise the structure of the continuum and bound electronic states, to provide information on photoionization dynamics and to test theoretical models. Since the early experiments in the 1930s [1], PADs have been used to perform complete photoionization experiments, to observe effects due to site specific emission and alignment of fixed-in-space molecules, and to probe chirality and time-dependent dynamics [2 and references therein]. Renewed interest in the measurement of the PADs has been triggered by the development of new highly efficient imaging detectors [3] and the availability of new sources, such as third generation synchrotron radiation beamlines, fast and intense lasers for multi-photon ionisation and, more recently, by the possibility to combine these two photon sources to tackle processes previously not accessible [4]. In particular, the two-photon photoemission, where the electron ejection proceeds via the excitation and subsequent ionisation of an intermediate state, is an efficient tool for various applications such as i) the study of intermediate, neutral excited states [5], ii) the measurement of molecular alignment [6], iii) the achievement of complete experiments where the phase differences and the dipole matrix elements are determined [7] and iv) the investigation of time-resolved photoelectron angular distributions (TRPADs) of intermediate states [8]. However, most of the early studies employed
exclusively laser sources and were confined to targets with suitable intermediate states, matching the available laser wavelengths. We have undertaken a program at the Gasphase photoemission beamline of Elettra to combine the synchrotron radiation with the radiation of a Ti:Sapphire oscillator laser in order to investigate the valence and inner shell states of a broad range of targets via PAD measurements. The use of the synchrotron radiation has several advantages. It is widely and continuously tunable giving access not only to valence but also to core-excited and Rydberg states with energy of tens and even hundreds of eV. Moreover in comparison with the fs pulses of high harmonic generation (HHG) sources it is characterized by a narrower excitation band. The disadvantage is that the duration of the synchrotron bunches limits time-resolved experiments to, at best, a time scale of tens of ps. Within this framework a new velocity map imaging (VMI) spectrometer has been built. Here we present the first results of this new set-up used to investigate the near threshold photoionization of the He 1s3p (1P1) and Ne 2p3d (1P1) states.

2. Experiment and data analysis
The experiments have been performed at the Gasphase photoemission beamline at the Elettra storage ring (Trieste, Italy). The lay-out, characteristics and performances of the beamline have been described previously [9] and will be not repeated here. Recently a branch line of the GasPhase beamline has been equipped with a mode-locked Ti:Sapphire oscillator (Tsunami, Spectra Physics) [10] modified to allow operation at a frequency 83.3MHz, which corresponds to exactly 1/6 of the storage ring frequency. By switching off the mode-locking option, the laser can also be used in CW mode. The laser was operated in the picosecond configuration with a measured pulse width of 15 ps, in order to achieve a better temporal overlap with the synchrotron pulses (about 60 ps). In these experiments the polarizations of both radiations have been chosen to be parallel to the detector and perpendicular to the counterpropagating photon beams. The photoelectron yields are very sensitive to the configuration of the electric fields of the exciting and ionizing radiations and Mitsuke et al. [11] showed that the photoionization yield has a maximum in a parallel configuration for the transitions they probed.

![Diagram of the VMI spectrometer](image)

**Fig.1:** Schematic representation of the VMI spectrometer where REP, EXT and GRD are the repeller, extractor and ground electrodes of the set-up, TOF represents the field-free time of flight region and PSD is the position sensitive detector. The directions of the polarizations of the light sources are also shown.
The present VMI spectrometer design (see figure 1) is based on a classical three element system (20 mm aperture, 15 mm spacing) and a 360 mm time of flight tube, ended by a 95% transparency grid placed in front a set of two MCPs to avoid field penetration effects. The axis of the VMI is perpendicular to the plane containing both the counterpropagating photon beams and their polarization axes. The target gas is let into the experimental chamber via a 0.25 mm inner diameter needle. An x-y-z manipulator allows the precise positioning of the needle near the interaction region. In the operating conditions, the voltages of the extractor and repeller electrodes are both negative, with a fixed ratio of 71% and the needle potential set close to the mean value of the two. A fine tuning of the needle potential was essential to recreate the ‘ideal’ working conditions of the VMI.

The spatial overlap of the two light beams at the interaction region is very critical for two-color experiments and, because of the nature of the VUV synchrotron radiation, it had to be optimized and monitored under vacuum. To this purpose a specifically designed alignment “tool” with a set of 1.5, 1.0 and 0.5 mm holes has been mounted on the x-y-z manipulator of the gas inlet and moved to the interaction region to check the overlap of the two beams. The spot size of the laser beam has not been measured. The beam was focused to the center of the chamber using a 50 cm focal length lens. Thus, the size of the focus can be estimated to have a diameter of 0.25 mm, which is of the same order of magnitude as the synchrotron beam size. The estimated power density of the laser is 1 MW/cm² (when mode-locked).

The spectrometer is equipped with a position sensitive detector [12] developed by the Instrumentation and Detector Laboratory at Elettra. The UHV section of the detector consists of two 50 mm MCP mounted in chevron configuration, a high voltage decoupling system based on a resistive sheet and a cross delay line detector. The spatial resolution is about 100 μm in one direction and 150 μm in the other. The X,Y start and stop signals from the detectors are immediately amplified at the UHV flange. The amplified pulses are sent to constant fraction discriminators and then fed to a time-to-digital converter (TDC). An ACAM TDC-GPX has been chosen because, according to the selected operation mode, up to 10 ps time resolution with a broad time window and high count rate (deadtime of the TDC is less than 10 nsec when operating in multihit mode) can be achieved. Two TDCs, one for each detector dimension, are used. The TDCs are controlled by a mother board hosting a field programmable gate array (FPGA), which handles the flux of events, controls their logical consistency, correlates them with “time stamps” and transfers the digitized data. The motherboard is connected via an external SCSI cable to a PCI Interface board inside a PC. Finally a Labview code manages the data acquisition, analysis and on-line graphical presentation.

The chamber is lined with a 2mm thick μ-metal shield. This allows the measurement of the angular distribution of photoelectrons with kinetic energy as low as 13 meV with a typical energy resolution of 5%. Under normal working conditions, a gas pressure of about 3x10⁻⁷ mbar was used, with synchrotron photon beam current of about 10¹¹ photons/s. This setting was used to avoid saturation of the MCP, due to the high efficiency of the 4π collection of the spectrometer. Typical acquisition times of an image were of the order of 5 minutes for one photon and 40 minutes for singly resonant two-photon ionisation processes.

The VMI spectrometer works by projecting the 3D distribution of electrons released in the ionization process onto the detector. It is then possible to recover the PAD and kinetic energy distribution (KED) by performing an inverse Abel transformation or other inversion methods such as the onion-peeling [13], Basex [14], or pBasex [15] methods. The data analysis in this work was performed using the pBasex method introduced by Garcia et al. [15] in which the original 3D image is reconstructed as a linear combination of basis set functions adapted to the cylindrical symmetry of the photoionization process. Furthermore, we have ported the code of Garcia et al. [15] into a new Windows type graphical user interface which has extensive image manipulation features.

The reported anisotropy parameters are determined using a weighted average of all points contained within the full width half maximum of the peak in the kinetic energy distribution (as suggested in ref. [15]). The errors are then determined based on the spread of the anisotropy parameters extracted by varying the centre point of the image and other parameters related to the image processing.
3. Results

In one-photon ionisation of randomly oriented targets by fully linearly polarized radiation the photoelectron angular distribution is represented by the double differential cross section

\[
\frac{d^2\sigma(E,\theta)}{dEd\Omega} = \frac{\sigma_0}{4\pi}[1 + \beta_2(\cos \theta)]
\]

where \(\sigma_0\) is the total photoionization cross section, \(\theta\) the angle of the photoelectron with respect to the polarization direction of the incident radiation, \(P_2(\cos \theta)\) is the second order Legendre polynomial and \(\beta\) the asymmetry parameter. The \(\beta\) parameter holds information on the photoionization dynamics, because it depends on the radial matrix elements, \(R_{\ell \pm 1}\), and their relative phase, \(\delta_{\ell+1} - \delta_{\ell-1}\), where \(\ell \pm 1\) are the final state partial waves of the free photoelectron in the continuum. The interference between the \(\ell \pm 1\) partial waves determines the variation of \(\beta\) with energy in its allowed range (-1,2). However, despite the fact that \(\beta\) contains the full information on the photoionization matrix elements and their relative phase, its determination alone does not allow this information to be extracted.

In two-photon ionisation when both photon beams have parallel polarization, the angular distributions are of the form [5]:

\[
\frac{d^2\sigma(E,\theta)}{dEd\Omega} = \frac{\sigma_0}{4\pi}[1 + \beta_2(\cos \theta) + \beta_4(\cos \theta)]
\]

where both the \(\beta_2\) and \(\beta_4\) anisotropy parameters are combinations of \(R_{\ell \pm 1}\), and \(\delta_{\ell+1} - \delta_{\ell-1}\). Thus an experimental determination of \(\beta_2\) and \(\beta_4\) allows the extraction of at least two (even though not all) independent quantities governing the photoionization, i.e. the ratio \(\chi = R_{\ell+1}(j)/R_{\ell-1}(j)\) of the matrix elements and their relative phase.

3.1 The photoionization of He 1s3p(1P1) state

In this measurement the He 1s2 (1S0) → 1s3p (1P1) transition at 23.09 eV was resonantly excited by synchrotron radiation and then ionised by a synchronised laser pulse of 750 nm, producing a photoelectron of 160 meV kinetic energy. The long lifetime (1.7 ns [16]) of the state guarantees a large population of the excited state during the probing with the IR laser. The raw and reconstructed images of the two-photon photoelectron angular distribution are shown on the right side of fig.2, panels b and d respectively. The comparison to the ‘equivalent’ one-photon distributions, i.e. at the same photoelectron kinetic energy, (fig. 2a and c) shows clear differences between the two cases, with a much sharper angular distribution in the two-photon case. Indeed, in the one-photon ionization the photoelectron is constrained to a \(p\) partial wave resulting in a dipolar, \(\beta=2\), angular distribution. In the two-photon ionization case, the angular distribution is described by the \(\beta_2\) and \(\beta_4\) anisotropy parameters (see formula 2), each one resulting from the energy dependent interference of both the \(s\) and \(d\) photoelectron partial waves providing a more complex picture. The extracted anisotropy parameter for the one-photon distribution is \(\beta=1.98\pm0.02\). This value confirms the reliability of the VMI set-up, the inversion and analysis procedures and gives a hint of the accuracy of the measured

| Photoelectron kinetic energy (eV) | \(\beta_2\) | \(\beta_4\) |
|----------------------------------|----------|----------|
| 0.04                            | 2.88±0.06\textsuperscript{a} | 1.93±0.07\textsuperscript{a} |
| 0.16                            | 2.86±0.07\textsuperscript{b} | 2.17±0.13\textsuperscript{b} |
| 1.6                             | 2.81±0.05\textsuperscript{a} | 1.88±0.13\textsuperscript{a} |
| 3.14                            | 2.55±0.17\textsuperscript{a} | 1.78±0.2\textsuperscript{a} |

\textsuperscript{a} values reported in ref.[17]; \textsuperscript{b} present work
Fig. 2: Left hand side: the raw photoelectron image (a) and its pBasex reconstruction (c) following He one-photon ionization. Right hand side: the raw photoelectron image (b) and its pBasex reconstruction (d) following two-photon ionization of He via the 1s3p intermediate state. In both cases the kinetic energy of the photoelectron is 160 meV.

anisotropy parameter. The extracted values of the anisotropy parameters for the two-photon distribution are $\beta_2=2.86\pm0.07$ and $\beta_4=2.17\pm0.13$.

Recently Haber et al. [17] measured the two-photon ionization of He via the same intermediate state using high-order harmonics for the excitation of the target and a laser at three different wavelengths (800, 400 and 267 nm) for the final ionization. Their results are reported in table 1 and figure 3, where they are compared with the present determination and the calculated values [17,18]. Good agreement between the two set of measurements is observed in the $\beta_2$ case, while a slightly higher value of $\beta_4$ has been measured in the present work. In two-photon processes the values of the anisotropy parameters are not limited to the (-1,2) range and indeed in the range studied the $\beta_2$ value is always larger than 2. The calculations show an increase of $\beta_2$ for photoelectron energies smaller than 0.3 eV and then a monotonic decrease. A similar behaviour, but for values smaller than 2 is observed for $\beta_4$. 

International Workshop on Electronic Spectroscopy for Gas-phase Molecules and Solid Surfaces  
Journal of Physics: Conference Series 235 (2010) 012006  
doi:10.1088/1742-6596/235/1/012006
Fig. 3: The $\beta_2$ and $\beta_4$ anisotropy parameters for the photoionization of the He 1s3p ($^1P_1$) excited state. The present values (full dots) are compared with previous experimental results (open circles) and calculations [17].

3.2 The photoionization of Ne 2p3d $[3/2]_1$ in the threshold region

In the Ne case the synchrotron radiation was set to 20.04 eV, in order to excite the Ne 2p$^6$ ($^1S_0$)$\rightarrow$2p$^5$(2P$^{1/2}$)3d$[3/2]_1$ transition, which is characterized by a quite large oscillator strength (1.86(±0.09)$\times$10$^{-2}$ [19]), and then several laser wavelengths between 775 and 805 nm have been chosen to ionize the excited state. Thus all the measurements are within 100 meV from the Ne$^+$ 2p$^1$(2P$^{3/2}$) ionization threshold, i.e. below the Ne$^+$ 2p$^1$(2P$^{1/2}$) ionization threshold. In this way only one continuum is open and the anisotropy parameters are not affected by the multiple interactions between the Rydberg electron and the other electrons, which can lead to a change of the angular momentum of the ion core. The measured $\beta_2$ and $\beta_4$ values are reported in Table 2 and figure 4.

Table 2. The $\beta_2$ and $\beta_4$ anisotropy parameters for the photoionization of Ne 2p3d $[3/2]_1$ intermediate state.

| Photoelectron kinetic energy (meV) | $\beta_2$     | $\beta_4$     |
|-----------------------------------|---------------|---------------|
| 20                                | 0.84 ± 0.06   | 0.42 ± 0.02   |
| 50                                | 0.87 ± 0.03   | 0.40 ± 0.02   |
| 70                                | 0.93 ± 0.08   | 0.39 ± 0.04   |

To our best knowledge the only calculation of the anisotropy parameters for the photoionization of a Ne excited state is the one due to Chang et al [20] for Ne 2p$^5$3p while no data exists for the Ne2p$^5$nd states. The values of the anisotropy parameters $\beta_2$ and $\beta_4$ are smaller than those observed and calculated for the excited state of He because here different partial waves ($p$ and $f$) are involved. The $\beta_2$ values increase for photon energies away from threshold, while $\beta_4$ stays almost constant in the region investigated.
Fig.4: The $\beta_2$ and $\beta_4$ anisotropy parameters for the photoionization of the Ne 2p$^5$3d $[3/2]$ excited state. The dashed lines through the experimental points serve only to guide the eyes.

4. Conclusions
A novel experimental set-up using a VMI spectrometer in conjunction with a VUV synchrotron radiation + IR laser source has been used to measure the photoelectron angular distribution in two-photon - two-colour ionization experiments. The photoelectron angular distribution from the excited Ne 2p$^5$(2P$^0_{3/2}$)3d state has been studied in the first 100 meV above threshold, a region rarely studied in previous photoionization studies with synchrotron radiation. The independent-particle models, often used to describe photoionization of atoms [22] are expected to break down near threshold and in the case of non negligible many-electron interaction. Thus the present measurements on Ne may be used to extend the successful test of theoretical predictions done in He [17] to a more challenging situation.

The high efficiency and the capability of handling very low energy electrons make the VMI technique a suitable tool to investigate the dynamics of molecular dissociation via time resolved photoelectron angular distribution and pump-probe experiments where ps time delays are introduced between the synchrotron excitation of the target and its probe with the IR laser.

5. Acknowledgments
LP acknowledges the support of the CNR-Short Term Mobility Program and the Australian Academy of Science for an Australia-Italy Award

References
[1] Lawrence EO and Chaffee MA 1930 Phys. Rev. 36 1099
[2] Reid KL 2003 Annu. Rev. Phys. Chem. 54 397
[3] Eppink AT and Parker JB 1997 Rev. Sci. Instrum. 68 3477
[4] Meyer M et al 1987 Phys. Rev. Lett. 59 2963
[5] Hansen JC et al 1980 Phys Rev. A 21 222; Eldestein S et al 1974 Phys. Rev. A 9 2459; Kaminski H et al 1980 Phys. Rev. Lett. 45 1161
[6] Appling JR, White MG, Orlando TM and Anderson SL 1986 J. Chem. Phys. 85 6803
[7] Strand MP, Hansen J, Chien R L and Berry RS 1978 Chem. Phys. Lett. 9 205
[8] Davies JA, Continetti RE, Chandler DW and Hayden CC 2000 Phys. Rev. Lett. 84 5983
[9] Blyth RR et al 1999 J. Electron Spectrosc. Relat. Phenom. 101-103 959
[10] Moise A, Alagia M, Banchi L, Ferianis M, Prince KC and Richter R 2008 Nucl. Instr. Meth. A 588 502
[11] Mitsuke K, Hikosaka Y and Iwasaki K 2000 J. Phys. B: At. Mol. Opt. Phys. 33 391
[12] Cautero G, Sergio R, Stebel L, Lacovig P, Pittana P, Predonzani M and Carrato S 2008 Nucl. Instr. Meth. A 595 447
[13] Vrakking MJJ 2001 Rev. Sci. Instrum. 72 4084
[14] Dribinski V, Ossadtchi A, Mandelstam VA, and Reisler H 2002 Rev. Sci. Instrum. 73 2634
[15] Garcia GA, Nahon L and Powis I 2004 Rev. Sci. Instrum. 75 4989 (2004)
[16] Johansson A et al 2003 Eur. Phys. J. D 22 3
[17] Haber LH, Doughty B and Leone SR 2009 Phys. Rev. A 79 031401(R)
[18] Chang TN and Fang TK 1995 Phys. Rev. A 52 2638
[19] Chan WF, Cooper G, Guo X and Brion CE 1992 Phys. Rev. A 45 1420
[20] Chang TN and Kim YS 1982 Phys. Rev. A 26 2728
[21] Czasch A et al 2005 Phys. Rev. Lett. 95 243003
[22] Cooper J and Zare RN 1968 J. Chem. Phys. 48 942