Application of a VMI spectrometer to near-threshold photoionization with synchrotron radiation

P. O’Keeffe¹, P. Bolognesi¹, A. Mihelic², R. Richter³, A. Moise³, E. Ovcharenko¹,⁴, G.C. King ⁵ and L. Avaldi¹,*

¹ CNR Istituto di Metodologie Inorganiche e dei Plasmi, Area della Ricerca di Roma 1, CP10,00016 Monterotondo Scalo, Italy
² Jožef Stefan Institute, Jamova cesta 39, SI-1000 Ljubljana, Slovenia
³ Sincrotrone Trieste, Area Science Park, I-34149 Basovizza (Trieste), Italy
⁴ Institute of Electron Physics, Uzghorod, Ukraine
⁵ Dept. of Physics and Astronomy, University of Manchester, Manchester, England

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

Abstract. A new developed velocity map imaging spectrometer has been used to study the photoionization of atoms near threshold. The application of the spectrometer to the measurement of the angular distributions of the photoelectrons emitted in the photoionization of the Ne 2p 3/2 state between the 2p spin orbit thresholds and of polarised Ne atoms are presented.

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 characterize 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 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 facilities, 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].

The near threshold photoionization offers the opportunity to study different interesting processes, which are illustrated in the case of Ne in figure 1. In case (a) the ionisation occurs in the region between the two spin-orbit thresholds. This region is populated by the 2p 5(2P1/2) nl Rydberg states that can decay to the Ne 2p 3/2 continuum and therefore affect the cross section and angular distribution of the photoelectrons.

---

*To whom any correspondence should be addressed.
In case (b) synchrotron radiation (SR) is used to excite the neutral atoms and then an IR laser ionizes the polarised atom. In this work a novel VMI spectrometer specialized to detect low energy electrons has been used to investigate these two processes which characterize the near threshold photoionization of Ne.

Figure 1. Scheme of the Ne energy levels near the 2p thresholds and of the ionizing processes that can be achieved combining VUV-SR and IR photon sources.

2. Experiment and data analysis
The experiments have been performed at the Gas phase photoemission beamline at the Elettra storage ring (Trieste, Italy). The layout, characteristics and performances of the beamline have been described previously [5] and will not be repeated here. Recently a branch line of the GasPhase beamline has been equipped with a mode-locked Ti:Sapphire oscillator (Tsunami, Spectra Physics) [6] modified to allow operation at a frequency of 83.3MHz, which corresponds to exactly 1/6 of the storage ring frequency. The laser is 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).

The present VMI spectrometer design (see figure 2) is based on a classical three element system (20 mm aperture, 15 mm spacing) and a 190 mm time of flight tube, at the end of which a set of two MCPs is placed. The spectrometer is equipped with a position sensitive detector [7] developed by the Instrumentation and Detector Laboratory at Elettra. The UHV section of the detector consists of two 40 mm MCPs mounted in a Chevron configuration, and a cross delay line detector for X,Y position identification. 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 two ends of each delay line of the detector are immediately amplified at the air side of the UHV flange. The amplified pulses are sent to constant fraction discriminators and then fed into time-to-digital converters (TDCs). The TDCs are controlled by a mother board 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 atoms or molecules under investigation are introduced into the chamber via a continuous supersonic beam formed by expanding 1-2 bars of gas through a 50 μm nozzle. This nozzle is mounted on an XYZ-manipulator in order to allow the nozzle to be centered on a 0.5 mm skimmer, the tip of which is placed at a distance of about 12 cm from the interaction zone. In the two colour experiments
the synchrotron and laser beams are focussed and overlapped (both spatially and temporally) at the
center of the chamber in a counter propagating geometry. Optimization of the overlap of the two light
beams with the supersonic jet was achieved by monitoring a double resonant two-colour signal and
adjusting the position of the laser beam and of the entire experimental chamber along all three axes.

Figure 2. Schematic representation of the VMI spectrometer where REP, EXT and GRD are the
repeller, extractor and ground electrodes of the set-up, respectively. TOF represents the field-free time
of flight region and PSD is the position sensitive detector (figure not on scale). The directions of the
polarizations of the light sources are also shown.

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
6% when the detector is used in the high resolution mode [8]. The detector can be operated also in a
coincidence mode to improve signal to noise in pump-probe experiments either by using a gate to
count electrons only when the laser is present (down to a 27 ps gate) or by recording coincidences with
the ion formed in the ionization process [8]. 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 technique works by projecting the 3D distribution of electrons released in the ionization
process onto the 2D position sensitive detector. It is then possible to recover the PAD and kinetic
energy distribution (KED) by performing an inverse Abel transformation or other inversion methods
[9,10,11]. The data analysis in this work was performed using the pBasex method introduced by
Garcia et al. [11] combined with a new Windows type graphical user interface which has extensive
image manipulation features [12].

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.
[11]). 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

\[
\frac{d^2\sigma(E,\theta)}{dEd\Omega} = \frac{\sigma_0}{4\pi}[1 + \beta P_2(\cos\theta)]
\]  

(1)
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, \( R_{l\pm1} \), and their relative phase, \( \delta_{l-1} - \delta_{l+1} \), where \( l \pm 1 \) are the final state partial waves of the free photoelectron in the continuum. The interference between the \( l \pm 1 \) partial waves determines the variation of \( \beta \) with energy in its allowed range (-1,2).

In the two-photon ionisation when the two photon beams have parallel polarization, the angular distributions are of the form

\[
\frac{d^2\sigma(E,\theta)}{dEd\Omega} = \frac{\sigma_0}{4\pi} [1 + \beta_2 P_2(\cos \theta) + \beta_4 P_4(\cos \theta)]
\]

where both the \( \beta_2 \) and \( \beta_4 \) anisotropy parameters are combinations of \( R_{l\pm1} \), and \( \delta_{l-1} - \delta_{l+1} \). 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 \( \chi = R_{l+1}(j)/R_{l-1}(j) \) of the matrix elements and their relative phase.

**Figure 3.** The photoelectron electron yield (a) and the \( \beta_2 \) anisotropy parameter (b) of Ne 2p3/2. The full line in (a) is a fit to the experimental data, while in (b) is the theoretical prediction by [16]. In the inset of figure (a) the experimental spectrum is compared with the theoretical results of ref. [16] convoluted with the experimental resolution.

### 3.1 The photoionization of Ne 2p3/2 between the 2p spin orbit thresholds

The high members of the nd' and ns' Rydberg series converging to the 2P1/2 ionic states have been studied in several photoabsorption and photoionization experiments [13]. The small energy splitting
between the two fine structure components (97 meV) has made photoelectron investigation difficult and only Caldwell and Krause [14] reported a measurement of the photoelectron spectra and angular distribution over a region of about 30 meV, which includes the 12-14d' and 14-15s' resonances. In figure 3 the results of the present measurements are reported. The overall energy resolution and efficiency of the present experiment allow to distinguish clearly the two Rydberg series up to the 18s' and 17d'. From there on, the two series merge up to the ionization continuum. As for the asymmetry parameter we observe that the autoionizing resonances produce sharp variations superimposed on a $\beta$ value which is slowly decreasing towards a value of about -0.7 near the $^2P_{1/2}$ ionic threshold. The behaviour of the asymmetry parameter is consistent with the measurements by Southworth et al [15] who observed a minimum value of -0.6 at about 22.5 eV and a rise towards threshold. Caldwell and Krause [13] quoted a value of -0.17±0.15 in the region between the 13d' and 15s' resonances, which is higher of the ones measured here. The resonances result in $\beta$ values less negative at the position of the ns' peaks, while the opposite occurs at the nd' peaks. Radjević and Talman [16] calculated the photoionisation parameter in the region up to 21.95eV using the relativistic random phase approximation together with the relativistic multichannel quantum defect theory. Their spectrum convoluted with the present experimental resolution is compared with the experiments in the inset of figure 3a, while the calculated asymmetry parameters are compared with the experiments in figure 3b. A good agreement in the relative position and intensity of the peaks in the absorption spectrum is observed; the calculated asymmetry parameters agree in shape but not in absolute value, the theoretical parameters being more positive than the experimental ones.

### 3.2 The photoionization of the polarized Ne atoms

In this experiment the synchrotron radiation was set to 20.04 eV, in order to excite the Ne 2p$^6$ (1S$_0$)$\rightarrow$2p$^5$(2P$^{3/2}$)3d[3/2], transition, which is characterized by a quite large oscillator strength (1.86(±0.09)x10$^{-2}$ [17]), and then three laser wavelengths between 775 and 805 nm have been chosen to ionize the excited state. Thus all the measurements are within 90 meV from the Ne$^+$ 2p$^4$ ($^2P_{1/2}$) ionization threshold, i.e. below the Ne$^+$ 2p$^4$ ($^2P_{3/2}$) ionization threshold. The photon energies were chosen not to lie close to or on-resonance with the resonances in the autoionization region. The measured $\beta_2$ and $\beta_4$ values are reported in Table 1 and figure 4.

| Photoelectron kinetic energy (meV) | $\beta_2$       | $\beta_4$       |
|-----------------------------------|-----------------|-----------------|
|                                   | 0.84 ± 0.06     | 0.42 ± 0.02     |
| 45                                | 0.87 ± 0.03     | 0.40 ± 0.02     |
| 70                                | 0.93 ± 0.08     | 0.39 ± 0.04     |

The $\beta_2$ values slowly increase for photon energies moving away from threshold, while $\beta_4$ stays almost constant in the region investigated. Despite the small variation of the asymmetry parameters both the observed images and the 3D angular distributions reconstructed from the asymmetry parameters display clear differences, as shown in figure 4. 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 [18] for Ne 2p$^5$3p while no data exists for the Ne2p$^4$nd states. Thus we have calculated the angular distributions using a single-channel quantum defect theory [19]. In this method the interaction between the channels with different angular momenta of the atomic core is neglected. The exact energies of the ground and 2p$^5$nl (l=p, f) excited states converging to the ionization threshold have been taken from the NIST database [20]. In addition, bound-bound dipole matrix elements for the transitions to the aforementioned 2p$^5$nl states have been calculated with GRASP Dirac-Fock codes [21]. The oscillator strength distribution has been extrapolated from the discrete part of the spectrum across the threshold.
and the values of the transition matrix elements have been determined from the extrapolated values. The resonances in the autoionization region have been treated as purely bound in the extrapolation procedure. A good agreement between calculations and experiment is found in the region investigated.

Figure 4. The $\beta_2$ and $\beta_4$ anisotropy parameters for the photoionization of the Ne $2p^53d \, [3/2]_1$ excited state. The full line are the prediction of a single channel calculation (see text). On the top of the figure the maps of the angular distribution are represented. The upper part of each map contains the raw image, while the lower part shows the pBasex inverted image. The angular distributions are depicted graphically as surfaces in the insets where the distance from the origin to the surface is proportional to the probability that the electron is emitted in that direction.

4. Conclusions
A novel experimental set-up using a VMI spectrometer in conjunction with a VUV synchrotron radiation and IR laser source has been used to measure the photoelectron angular distribution in near threshold photoionization of Ne. In the case of the direct photoionization of the Ne $2p_{3/2}$ state between the two spin orbit thresholds the efficiency and energy resolution of the spectrometer has allowed to extend the investigation of autoionisation processes to higher member of the Rydberg series. The velocity map imaging detection scheme used for the measurement of the photoelectron angular distributions in the pump-probe experiments allowed the extraction of $\beta_2$ and $\beta_4$ and therefore provides more information on the ionization process than geometries in which fixed 1D-detectors are used and only the polarization of the ionizing light is changed [23]. The good agreement between the experiment and the calculations indicate that a single channel quantum defect model which accounts for the dependence of the transition matrix elements on the channel quantum numbers of the continuum wavefunction is accurate enough to describe the two-colour Ne $2p_{3/2}$ photoionization near threshold.
5. Acknowledgments
This research was partly supported by a Marie Curie Reintegration Grant within the 7th European Community Framework Programme. E. Ovcharenko acknowledges the support of the Elettra-ICTP Program for supporting his participation to the measurements at Elettra.

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] Blyth RR et al 1999 J. Electron Spectrosc. Relat. Phenom. 101-103 959
[6] Moise A, Alagia M, Banchi L, Ferianis M, Prince KC and Richter R 2008 Nucl. Instr. Meth. A 588 502
[7] Cautero G, Sergio R, Stebel L, Lacovig P, Pittana P, Predonzani M and Carrato S 2008 Nucl. Instr. Meth. A 595 447
[8] O’Keeffe P. et al 2010 Rev. Sci. Instrum. in preparation
[9] Vrakking MJJ 2001 Rev. Sci. Instrum. 72 4084
[10] Dribinski V, Ossadtchi A, Mandelstam VA, and Reisler H 2002 Rev. Sci. Instrum. 73 2634
[11] Garcia GA, Nahon L and Powis I 2004 Rev. Sci. Instrum. 75 4989
[12] Program available from the authors on request.
[13] Radler K and Berkowitz J 1979 J. Chem. Phys. 70 216; Baing MA and Connerade JP 1984 J. Phys. B: At. Mol. Opt. Phys. 17 1785; Ito K, Ueda K, Namioka T, Yoshino K and Morioka Y 1988 J. Opt. Soc. Am. B 5 2006
[14] Caldwell D and Krause M O 1990 J. Phys. B: At. Mol. Opt. Phys. 23 2233
[15] Soutworth SH, Parr AC, Hardis JE, Dehmer JL and Holland DMP 1986 Nucl. Instr. Meth. A 246 782
[16] Radović V and Talman JD 1990 J. Phys. B: At. Mol. Opt. Phys. 23 2241
[17] Chan WF, Cooper G, Guo X and Brion CE 1992 Phys. Rev. A 45 1420
[18] Chang TN and Kim YS 1982 Phys. Rev. A 26 2728
[19] O’Keeffe P et al. 2010 Phys. Rev. A submitted
[20] NIST Atomic Spectra Database, URL http://www.nist.gov/physlab/data/asd.cfm.
[21] Dyall KG, Grant L, Johnson CT, Parpia FA and Plummer EP 1989 Comput. Phys. Commun. 55 425
[22] Fano U and Cooper JW 1968 Rev. Mod. Phys. 40 441
[23] Mitsuke K., Hikosaka Y, and Iwasa K 2000 J. Phys. B: At. Mol. Opt. Phys. 33 391