High Resolution Electron Spectroscopy Using Conventional and Synchrotron Light Sources

A. Naves de Brito*, S. Aksela† and S. Svensson‡

The Finnish Synchrotron Radiation Facility at

Max-Laboratory, University of Lund, S-22100 Lund, Sweden

Received May 6, **1994;** revised manuscript received July 25, **1994**

Fundamental concepts in resonant and non-resonant Auger electron spectroscopy, core photoelectron spectroscopy will be presented. New synchrotron radiation (SR) based measurements performed using these techniques are discussed. A comparison of Auger spectra taken with different excitation sources such as AlK_α ($h\nu = 1487$ eV), synchrotron radiation, and electron beam will be made showing the complementary information that can be obtained with each of these techniques. For core photo line and core shake-up/off correlation satellites a similar discussion will be presented including the advantage of using high intensity undulator radiation as compared to bending magnet radiation at synchrotron facilities for the study of these spectral regions. A new high performance undulator beam line, BL 51 the "Finnish beam line" at MAX laboratory is discussed. The resolution test measurements from electron and ion yield spectra of noble gases are presented. The results show that very high resolution is achieved at this beam line, comparable with that of the best spherical and plane grating monochromators. Recent results obtained at this beamline are discussed. Among them, the Auger Raman effect has been observed for the first time in the VUV region. The first observation of an anomalous Auger decay from molecular field split S2p core hole states in H_2S. This observation leads to a need for re-interpretation of a number of high resolution Auger spectra presented in the literature.

I. Introduction

During the last few years a rapid progress lias occurred in electron spectroscopy utilising synchrotron radiation as an excitation source. Part of this progress is due to improvement in the manufacturing of critica1 optical elements in high resolution monochromators and part is due the appearance of very high intensity sources such as undulators[1,2]. High intensity sources permit to perform experiments with small slit size still keeping enough photons to allow for high resolution electron spectroscopy experiments even on low density samples such as gases.

The competing source to synchrotron radiation in the soft X-ray region has hitherto been the monochromatized $A1K_\alpha$ anode source based on the 1487 eV characteristic X-rays. However, the anode source does not yield a collimated beam of radiation and therefore the grazing incidence monochromator technique would give a very low intensity. The anode sources have been monochromatized using spherically bent quartz crystals. However, such a scheme also implies that the resolution is limited by the rocking curve of the crystal. In practice the energy resolution is then limited to about 300 meV. For synchrotron radiation the extreme collimation of the beam, notably at undulator sources, opens up the possibility to use the grazing incidence monochromator technique, presently giving a relative resolution in the soft X-ray regime, in the order of 10000. As an example of the improvements in resolution in photoelectron spectroscopy when comparing the two schemes one may take the narrowest core photoelectron lines from C, Si, P, S, Cl, Br and I[3–8]. The vibrational structure of these line can be readily observed

*Department *of* **Physics, University** *of Oulu*, **FIN-90570** *Oulu*, Finland

†Department *of* **Physics, Uppsala University, Box 530, S-75 121 Uppsala, Sweden**

‡**Present address: Departamento de Física, Universidade de** Brasília, **70910-900** Brasília, Brazil

with the total resolution below 100 meV at a high resolution monochromator using SR at the Finnish beam line at MAX[3,4] and also by other groups using high resolution SR[5–8], in contrast to earlier anode based XPS where structure has been resolved only in the case of the C1s photoelectron line in methane.

The opening up of a core hole is associated to decay processes. Tlie Auger process is most important for the determination of the life times of the state. In this process the core hole vacancy is filled by a valence electron anc in addition to the photoelectron a second Auger electron is emitted. In the simplest picture this process is described in two steps. First the core hole is created and tlie photoelectron leaves the system. In a second step the core hole is filled and the Auger electron escapes. In this last step one then assumes that the photoelectron is decoupled from the rest of the system. One interesting field of research using the new higli intensity beamlines is to test the applicability of this two step model. It has since long been known that the model fails near the threshold where the photoelectron is slower thaii tlie Auger electron and thus a postcollision process takes place[9]. However, one interesting finding at the Finnish beamline is that the two step model may be inaccurate also far from thresliold, showing that the photoionization process should be considered as a one step scattering phenomenon.

Another process that in practice is only observed using the tunability of the synchrotron sources is tlie resonant Auger decay. Here instead of ionising the system the core electron is promoted to an unoccupied orbital. In a similar way as for the normal Auger decay, the core hole is filled and another electron is ejected. Using the simple single particle formulation one can divide the resonant Auger process into two main different classes: the spectator Auger transition and the participator Auger transition. In the spectator process the excited electron remains in the same orbital during the resonant Auger decay. In the participator process the excited electron is ionised during the resonant Auger decay. The final state of the participator process is the same as obtained by direct photoionization of the valente orbitals while the final state of the spectator process corresponds to a correlation state in the valence spectrum. This simple picture has its limitations since the excited electron may jump to a higher or lower laying energy state during the decay (shake-up or shake down transitions). Very recently the so called resonant Auger Raman effect[10] was observed for the first time in the VUV region. This occurs when the photon band width is narrower than the life time width of the respective core hole. The resonant Auger line width then decreases with tlie plioton band widtli. This effect opens the possibility to obtain a sub natural line width in resonant Auger spectra provided that a sufficient energy resolution is achieved, both for the exciting photons and analysed electrons.

Apart from the main line in the core hole photoelectron spectrurn, one can also observe low intensity correlation satellites at the higlier binding energy side. These correlation structures have been divided in the literature in two main groups: shake-up and shake-off satellites[11,12]. In the shake-up one valence electron is promoted to an unoccupied orbital upon core ionisation. In the shake-off process two electrons are ionised in the same event. While the shake-up process gives rise to distinct structures in tlie spectrum the shake-off process appears in the spectrum as a continuum background, since tlie photon energy is divided between the two electrons in an arbitrary way. In the studies of tlie gas phase shake-up/off spectra high intensity and reasonable resolution of tlie excitation photon source are absolutely necessary. Before tlie appearance of the high intensity SR sources inost of tlie spectra for free atoms and molecules were studied by using monochromatized Al Koc radiation frorn rotating anodes[12]. The tunability of the synchrotron radiation also permits a study of tlie intensity variation of the shake-up lines with the photon energy.

II. Experimental set for measurements using AlK_α and electron beain sources

The electron beam excited experiments were recorded in a electron spectrometer developed for high resolution electron beam Auger spectroscopy and ultraviolet valence photoelectron spectroscopy[13]. This hemispherical electrostatic analyser has a mean radius of 144 mm. It contains a modern four element lens system situated between the gas cell and the instrument. The electron beam was acelerated to 1.5 KeV and a typical beam current $\leq$ 1mA was used. The X-ray excited spectra were obtained using a monochromatized AlK_α

(radiation (hv=1487 eV) source[14]. A rotating and water cooled aluminium anode was used. A four elements lens system was used for pre-retardation of the ejected electrons and a double focusing electrostatic splierical sector of 360 mm radius was used to select tlie retarded electrons according to tlieir energy.

III. Description of the Finnish beamline

High brilliance sources combined with very liigli resolution monochromators have recently been taken into operation or are planned at severa1 SR facilities. One such facility is tlie so called Finnish beamline (BL51) at MAX SR laboratory in Sweden. This beamline was designed to be used maiiily in the study of gas pliase samples as well as experiinents not directly compatible witli UHV requirements. In order to achieve tlie desired liigli brilliance in a more conventional and low energy (550 MeV) storage ring a short period undulator (λ_0=24 mm) capable of operating at very narrow magnetic gap ($MagGap_{min}$=7.7 mm) was installed in a straiglit section at MAX I, in Sweden. The undulator delivers usable radiation in the energy range 60-600 eV. The radiation is nionochromatized by a modified plane grating monocliromator SX-700 constructed by Zeiss. The clioice of tliis type of construction was based on tlie high resolution, tlie liigh flux and tlie small number of optical elements required. There is no need for a moveable exit slit and it is a rather compact construction. Tlie plioton flux il1 the experimental chamber was ineasured at different undulator gaps, Fig. 1 shows a typical undulator spectrum for a inagnetic gap of 9 mm. Tlie overall shape of tlie spectrum is partially determined by tlie monochroinator efficiency. A flux of more than 10^{12} photons per second (indicated in the figure as Giga pliotons per second), at 150 eV, was obtained using an exit slit size of 200 μm. The flux was measured by using a GaAs photo diode and the intensity was corrected for tlie anode efficiency. In tlie spectrum shown in Fig. 1 one can notice tlie small contribution of liigher order light from the plane grating. In tlie spectrum the second order peak sliows up at half the photon energy of tlie first order light. Higher order lights are responsible for tlie appearance of undesirable extra peaks in the resonant Auger spectrum (normal Auger, core plioto line, etc.). Tlie intensity of tlie second order liglit in bending magnet based beamlines are not smaller than 10 % of tlie first order. Electron yield measurements made at BL 51 in the ClS CO edge witli first and second order liglit showed a decrease of about 500 times in the yield intensity for the second order light. One can explain tlie small intensity of higher order light in part due to a stronger decrease of photon flux at liigher energy for a fixed undulator gap as compared witli bending magnet radiation.

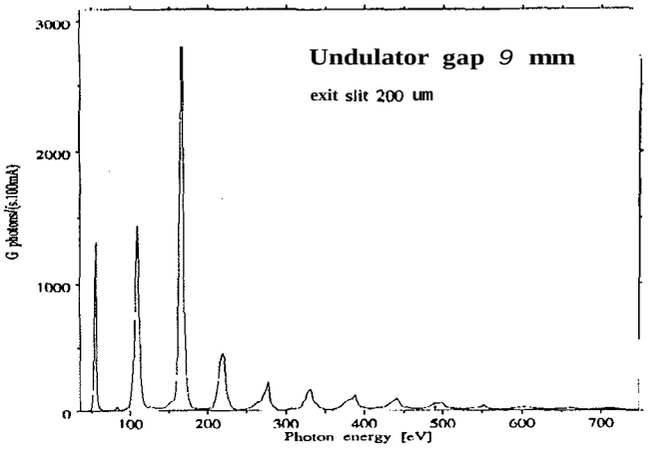

Figure 1: Measiired plioton flux spectrum of the beamline 51 undulator at MAX laboratory. Tlie exit slit of the monochromator was set to 200 μm, the undiilator magnetic gap iised was 9 mm. Tlie flux was measured using GaAsP Schottky diode as a detector.

In gas phase electron spectroscopy the need for liigh resolution monocliromators capable of liigli brilliance is much stronger as compared witli solid state physics. Small broadening of spectral lines, larger number of possible overlapping lines, absence of phonon and other solid state broadening mecliaiiisms as well as low sample density are some of the factors behind this statement. Tlierefore from the beginning we tried to find a monochromator delivering as higli as possible plioton resolution combined witli as higli as possible efficieiicy. The PGM fulfilled most of these requirements. Due to the low energy of tlie storage ring tliere was no need for cooling tlie optical elements of the monochromator. The undulator provides a photon beam witli a small spot size and divergence, the beam size at the entrance of tlie monocliromator is about 3 by 3.5 mm in tlie vertical and horizontal directions respectively. With such a colliniated beam, tliere is no need for a focusing mirror before tlie monocliromator. Such a mirror is normally needed on a bending magnet beamline.

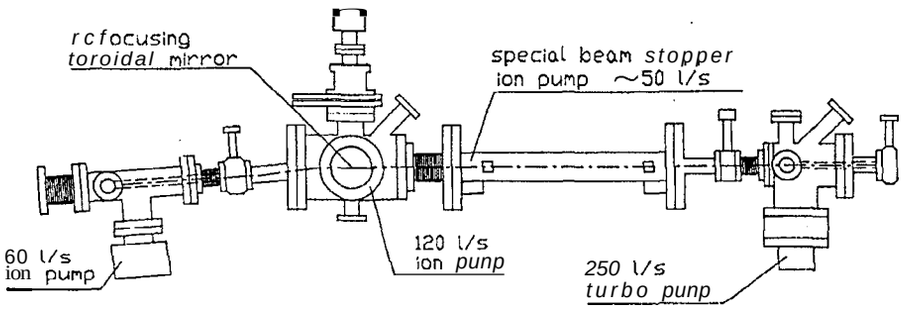

Figure 2: Permanent differential pumping and re focusing toroidal mirror set up at beamline 51.

During measurements on gas phase samples tlie spectrometer is normally kept at pressure up to 10^{-5} mbar range. The monochromator need to be kept at least in the 10^{-10} mbar range in order to avoid rapid contamination of the critical optical elements. A permanent differential pumping section was constructed for this pur ɔose. Fig. 2 shows a schematic drawing of this section In the first stage after tlie spectrometer there is a 250 l/min turbo pump taking most of tlie gas load. Tliis section is further separated from the spectrometer chamber by capillary tuhes. Next tliere is a cpecial ion pump. This long ion pump is designed so that the ionising electrons are orbiting tlirough the photon beam path, in this way the direct molecular beam coming from the spectrometer chamber is pumped efficiently, small orifices before and after the pump helps further reducing the transmittance. Next there is a toroidal refocusing mirror. This mirror further disperses the direct molecular beam and refocuses the photon beam to a spot of about one mm in diameter at the gas sample. This feature is very important for small acceptance spectrometers. Two ion pumps, one in the toroidal mirror chamber and another in the chamber next to the exit slit completes the pumping system.

The resclving power of the monochromator was tested by measuring the total ion and electron yield from noble gases Kr and Ar in tlie resonance excitation region just below the Kr $M_{4,5}$ and Ar $L_{2,3}$ ionisation thresho ds. The line widtli and shape in a yield spectrum is the convolution of two factors namely: life time broadening of tlie core levels and monochromator resolution. The life time contribution gives rise to a Lorentzian line shape while the monoclironiator contribution for the SX-700 can, in a first approximation, be considered to have a Gaussian shape. The monochromator contribution is further given by three major factors: source size, slope errors in the surface of the optical elements, and exit slit size. For an undulator it is unclear exactly what value one should take for the source size, one possible approximation would be to use the known beam size in the straight section of the insertion device. However, tlie phase space of the undulator is more coniplicated than sucli a simple source would give and a full simulation of tlie undulator is probably necessary to completely understaiid the influence of tlie source on tlie resolution.

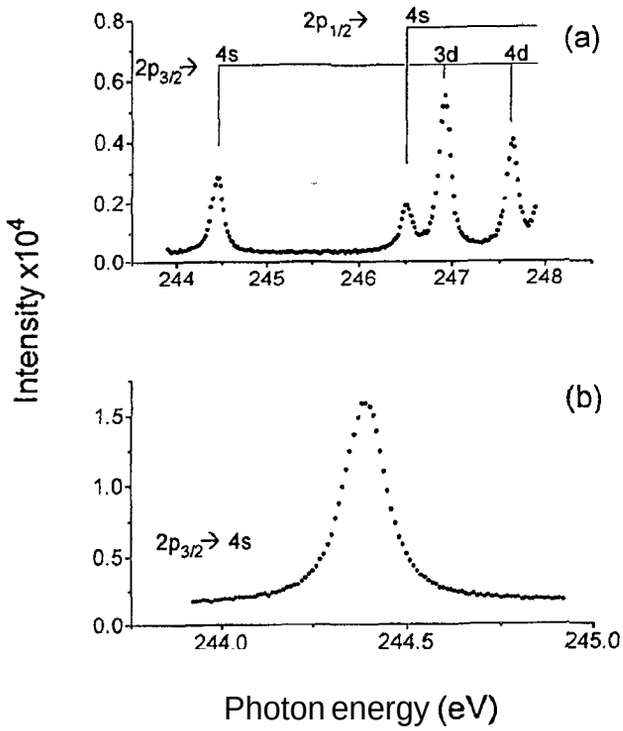

Figure 3: Total electron yield spectrum of Ar around the 2p thresholds.

Tlie monoclirornator resolution behaves like $\Delta E \alpha E^{3/2}$ [15], therefore for smaller plioton

energies the monochromator contribution decreases. In order to increase accuracy in the determination of the monochromator resolution one should therefore try to find a resonant excitation line with as small as possible life time broadening at as high as possible photon energy. The Ar $2p_{3/2} \rightarrow 4s$ resonance excitation line at 244.39 eV with a rather accurately known life time broadening, $\Gamma = 116 \pm 3$ meV [16] turned out to be the best choice. The life time contribution is dominating in the case of Kr $3d_{5/2} \rightarrow 5p$ at 91.20 V with $\Gamma = 83 \pm 4$ meV, since the monochromator contribution can be calculated to be only 12 meV compared with a calculated contribution of 51 meV at the 244.39 eV. In the present article we will only present the data corresponding to Ar absorption spectrum, more detailed information can be found in ref. [1]. The beam size in the vertical direction is calculated to be 0.2 mm, using ray tracing calculations it was found that a contribution of 30 meV (FWHM) should come from the source size contribution with a 1221-lines/mm grating. The slope errors contributions are completely dominated by the slope errors in the surface of the plane elliptical focusing mirror. A slope error given by the manufacture of ≤ 0.4 arcsec (rms.) will result in a Gaussian broadening of 40 meV. A slit width of 5 μm will give a 17 meV broadening. Convolution of all these factors give the 51 meV width mentioned above. In the first preliminary measurement for the Ar $2p_{3/2} \rightarrow 4s$ line the FWHM varied from 130 to 133 meV, when the illumination of the plane elliptical mirror was restricted, see Fig. **3** . Curve fitting with Voight functions gave typically 110 meV for the Lorentzian and 50 meV for the Gaussian width, in good agreement with the predictions. The improvement obtained by restricting the illuminated surface area of the plane elliptical mirror is not fully understood, since one could either he decreasing the slope errors (smaller illuminated area) and/or, reducing tlie effective source size. During the preliminary test we found a small misalignment of the exit slit with respect to the grating. New careful alignment was made and restricting the mirror illuminated area for a 5 μm exit slit it was possible to measure a FWHM of only 125 meV for the Ar $2p_{3/2} \rightarrow 4s$ line giving a monochromator contribution of 24 ± 2 meV, if no restriction of the mirror surface illumination was employed the total line width was about 135 meV with a resulting monochromator resolution of 51 ± 2 meV. Therefore, keeping tlie value of the life time broadening fixed, one has to conclude that the slope error and source size.contributions (as calculated in the simple approximation **as** above) are overestimated when surface mirror shadowing is used.

The electron analyser used in this beamline was an hemispherical type with radius of 144 mm [17]. The spectrometer has a four element electron Iens an it is placed in tlie pseudo-magic angle with respect to the SR polarization plane.The spectrometer is equiped with a multi channel detector system.

IV. Auger electron spectroscopy

In order to illustrate the Auger decay we show in Fig. 4 the H_2S Auger spectrum from reference [18]. Around the kinetic energy of 140 eV the lines were assigned to the a $L_{2,3}VV$ type of Auger process. The labelling in Auger spectroscopy follows tlie X-ray notation. The first label indicates where the core hole was created, the second and third the two final hole orbitals. In this way LVV corresponds to a core hole in the 2p orbital, the label VV represents the two valente orbitals involved. The excitation source for this spectrum was a 2 keV electron beam. Therefore a core hole in the 2s orbital is also created. The L_1VV Auger lines should be seen at the higher kinetic energy side of the $L_{2,3}VV$ group. In the spectrurn no structures are observed, instead the L_1LV is indicated at lower kinetic energy. This effect is called a Coster-Kronig transition. The Coster-Kronig transition corresponds to tlie situation where one of the final state holes are in the same main shell as the initial core hole. In case both final hole states are in the same main shell as the core hole state the transition is called super Coster-Kronig. In tlie Auger spectrum the Coster-Kronig transition is responsible of the appearance of the Auger lines at lower kinetic energy as one can see in Fig. 4.

When an electron is excited to unoccupied valence orbitals, the created hole is filled by the same or another electron and a valence electron is ejected, tlie process is called autoionization. Normally this process has this name when the initial hole is create by an electron

beam. In case a photon beam is used, its energy must be tuned to resonantly excited core or valence electrons to unoccupied valence orbitals. The decay process, already descr'bed in the introduction, is called resonant Auger decay and SR sources are used due to its tunability. If the photon energy is much higher than the excitation energy no excitation can take place but rather the electron is ionized and the normal Auger decay follows.

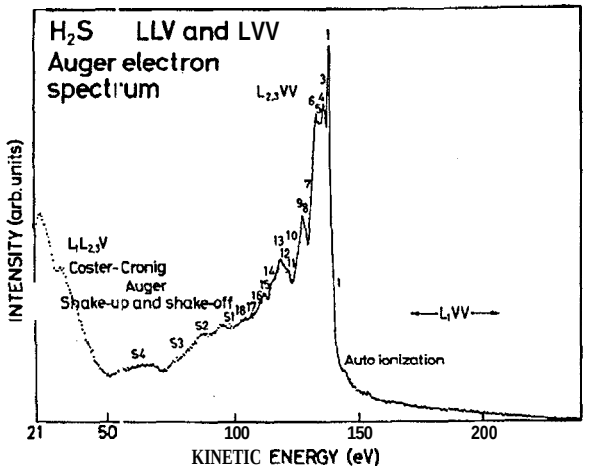

Figure 4: The LLV Coster-Kronig and $L_{2,3}VV$ Auger electron spectra of H_2S. The autoionization region and the region where the L_1VV lines should appear is also shown.

At the high kinetic energy side of the highest $L_{2,3}VV$ group in Fig. 4, another group of lines with low intensity can be observed. These lines are related with an Auger decay from an initial core shake-up state or are autoionization transitions. Fig. 5 shows two spectra taken using Al K_α and electron beam as excitation sources. According to the discussion in the last paragraph, comp trison of these two spectra gives a possibility to identify which structure correspond to an autoionization decay. X-rays witli much higher photon energy than the autoionization resonances exclude this process from the spectrum. The initial shake-up Auger decay, however, is still present. The excitation from an electron bearn is to a good approximation equivalent to the excitation using a white light source, therefore an electron excited Auger spectrum contains both processes. Furthermore if one is using an electron beam instead of monochromatic synchrotron radiation the direct valence photoelectron lines smear out. The valence photoelectron lines appear in the same region of the resonance Auger lines making the assignment of possible overlapping lines difficult. In reference [19] we have used an electron beam source to confirm and solve some questions in the interpretation of the H_2S resonant Auger spectrum studied in refs. [20,21]. In this study we used the advantages connected to the electron beam source referred above.

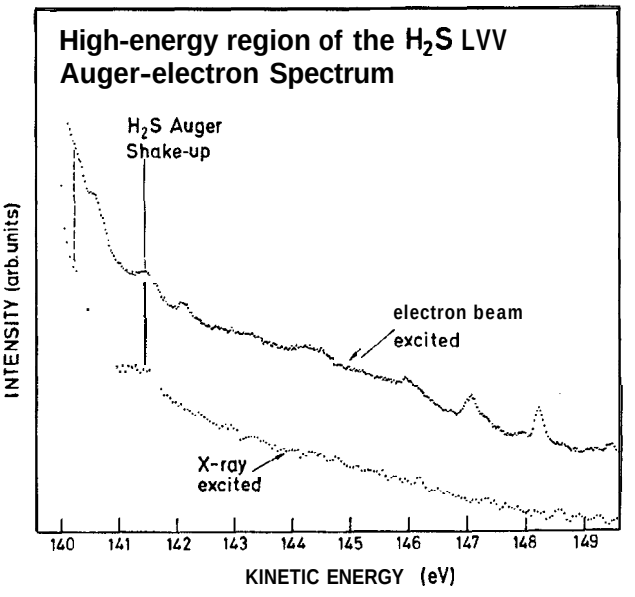

Figure 5: High energy region of the H_2S LVV Auger electron spectrum. Both, the X-ray excited (lower) and tlie electron beam excited (upper) spectra are displayed.

V. Resonant **Auger** electron spectroscopy

In molecules upon core excitation new effects may occur as compared with atoms. Apart from the appearance of vibrational bands in tlie resonant Auger spectrum, neutra1 dissociation may take place before the resonant Auger decay. The fast dissociation before the Auger decay was observed for tlie first time in HBr[22]. In Fig. 6 we show about the same kinetic energy region shown in Fig. 5 using synchrotron radiation from a bending magnet as excitation source at the Canadian Synchrotron Radiation Facility in Stoughton, Wisconsin[20]. Note that by "about the same kinetic energy region" we mean a diagram where the kinetic energy axis shows tlie same interval as the one compared to. In this case it is shown the spectrum of electrons with kinetic energy in the interval from about 140 to about 149.5 eV. The spectrometer used for this measurements has a broadening of 0.3 eV and the photon band width was about 0.5 eV. In this spectrum tlie S 2p core levels in H_2S were excited to the first two lowest

unoccupied orbitals. According to calculations[21] the $2p \rightarrow 6a_1$ state in H_2S contains a strongly dissociative channel leading to a core excited HS fragment in an $^2\Sigma^-$ state. The resonant structures in Fig. 6 labelled ill alphabetic order were assigned to tlie decay process from the $^2\Sigma^-$ state in tlie HS fragment. In order to study the enhancement of tlie resonant spectra in more detail the valence photo electron spectrum was recorded at 125 eV wliich is well below the resonance energies indicated in Fig. 6 in the upper right position. The shifted and normalised spectrum was subtracted from tlie spectra sliown in Fig. 6. In addition second and higher order diffracted light in the photon beam can also give rise to normal Auger lines whicli would appear in the left side of the resonant Auger features shown in Fig. 6. Therefore the normal Auger spectrum taken at 278 eV was also normalised and subtracted from the resonant spectrum, tlie resulting spectrum is shown in Fig.6.

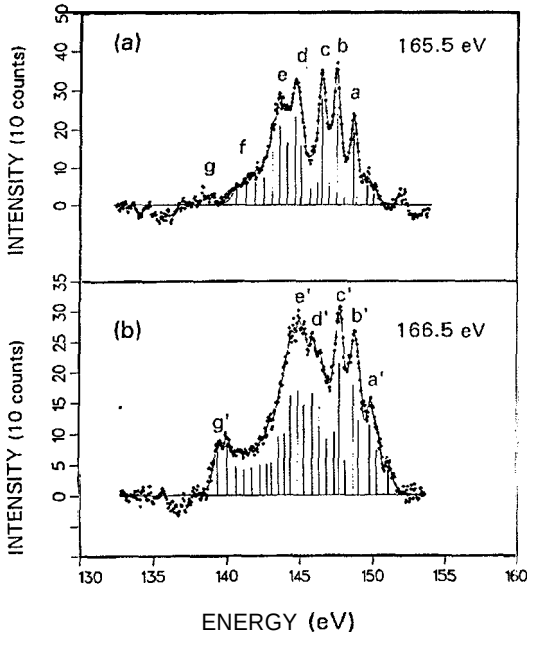

Figure 6: The resonant Auger electron spectra of H_2S taken at mean excitation energy of 165.5 and 166.5 eV.

In Fig. 6a the plioton energy is enough to predominantly excite an electron from tlie core $2p_{3/2}$ wliile in Fig. 6b the photon band widtli selects predominantly electron from the $2p_{1/2}$ spin orbit component. Peaks a-e and g, (a'-e' and g' for tlie $2p_{1/2}$ component) were assigned to the final states $5\sigma^2 2\pi^2(^3\Sigma^-)$, $5\sigma^2 2\pi^2(^1\Delta)$, $5\sigma^2 2\pi^2(^3\Sigma^+)$, $5\sigma^1 2\pi^3(^3\Pi$, $5\sigma^1 2\pi^3(^1\Pi)$ and $5\sigma^0 2\pi^4(^1\Sigma^+)$. If the electronic decay and dissociation occur in overlapping time scales a competition between these two processes may occur. In the H_2S molecule the presence of molecular lines in the resonant Auger spectrum coulcl not be eliminated or confirmed. New studies are under progress using high intensity undulator radiation combined with a liigh resolution monochromator in order to elucidate this question as well as to study the vibrational progressions in the resonant Auger spectrum of tlie fragment. In tlie next section we will describe tlie first results obtained using the so called Finnish beamline decribed above.

VI. Auger resonant Raman effect

In this and tlie following sections we will present new phenomena that are possible to observe using high resolution tuneable radiation comhined with high brilliance sources.

When tlie photon band widtli is smaller than tlie life time of the corresponding core hole, tlie associated resonant Auger spectra sliows decreasing line width with tlie photon band width. Moreover when the narrow plioton beam is scanned over the resonance, the kinetic energies of the resonant Auger lines display linear dispersion. This is the so called resonant Auger Rarnan, this effect was first observed by Brown et al[23] in the $L_3M_4M_5$ resonant Auger spectrum, which lies deep in tlie X-ray region ($\approx$ 4786 eV). We have now observed this effect for the first time for gas phase atoins in the VUV region[10]. The high resolution results show that the line width of the resonant Auger lines reflects the width of the exciting radiation if its band width is smaller tlian the corresponding core hole life time. The effect was observed in the resonant Auger spectrum corresponding to tlie Xe 4d$\rightarrow$ 6p and Kr 3d $\rightarrow$ 5p resonances at 65.11 and 81.20 eV, respectively. In Fig. 7 tlie Kr $3d_{5/2} \rightarrow$ 5p resonant Auger spectrum, measured using decreasing slit size is sliown. The 4s photo line was also included in the spectrum in order to compare with the resonant lines. The Kr 3d inherent lifetime widtli is 83 meV while the photon band widtli is 109 meV for 200 μm monochromator exit slit. The electron analyser energy resolution is about 50 meV. For 25, 50 and 200 μm slits the 4s photoelectron line and the sharpest Auger features have very accurately

the same widtli. This demonstrates that for this slits the resonant Auger line follows the width of tlie used photon band and does iiot depend upon tlie core level lifetime width. Perliaps one of tlie most important consequences of these findings is the possibility to use the Auger resonant Raman effect to increase the experimental resolution of the resonant Auger lines far below tlie inherent life time determined resolution, which allow us to resolve very fine details of the spectra. Also more reliable relative intensity comparison can be done. Finer details of the electron correlation can also be studied using this effect.

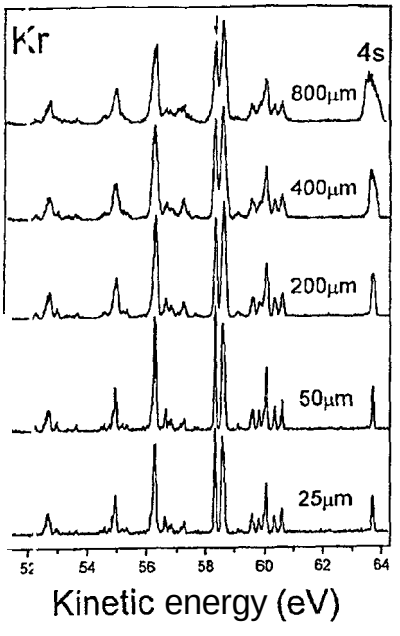

Figure 7: The Kr $3d_{5/2} \rightarrow 5p$ resonant Auger spectrum taken with 10-eV pass energy of tlie electron analyser and different exit slit widths of the monocliromator.

VII. Observation of an aiiomalous Auger decay from molecular field split S2p core liole states in H_2S

In an early report, where the excitation source was a monochromatized Al K_α ($h\nu$=1487 eV) radiation from a rotating anode, it was reported that tlie spin orbit splitting between the $S2p_{1/2}$ and S $2p_{3/2}$ in H_2S was found to be 50 meV larger than tlie shift observed between peaks maxima from the LVV Auger spectrum[24]. Two possible explanations were discussed, namely: 1) An electronic interference between tlie deexitatior channels originating in the two spin orbit components of the S2p core holes; 2) A possible splitting of the $S2p_{3/2}$ component. No firm conclusions could be made about tlie second explanation. The experimental resolution of the XPS (380 meV) did not permit an unambiguous interpretation.

By using high resolution electron spectroscopy and synchrotron radiation from BL 51, the resolution could be improved substantially by setting the excitation radiation energy to a value just slightly above the S 2p threshold ($h\nu$=186 eV). At this photon energy the monocliromator contribution is calculated to be only 37 meV, tlie spectrometer resolution is measured to be 45 meV[3]. In Figs. 8 and 9 tlie S 2p photoelectron spectrum and the $S2p^{-1} \rightarrow X^1A_1(2b_1^{-2})$ Auger electron spectra.are sliown respectively. From these two figures an unambiguous explanation could be given. Tlie S2p core electron lines were resolved in its molecular field split relativistic levels. As indicated in the spectrum, tlie "$S2p_{3/2}$" level is split into $4e_{1/2}$ and $5e_{1/2}$. The splitting was measured to be 110 (3) meV. The Auger spectrum shows an anomalous decay ratio from tlie $4e_{1/2}$ and $5e_{1/2}$ levels. Only decay from the $5e_{1/2}$ core liole is observed. This effect has been explained as originating from a new propensity rule that applies for tlie molecular field split core levels. This new finding may lead to re-interpretation of a number of high resolution Auger spectrum reported in the literature. From these higli resolution spectra the life time of the S2p levels was measured to be 70 (10) meV, substantially narrower than measured so far when the life time was erroneously measured from the split S $2P_{3/2}$ core line.

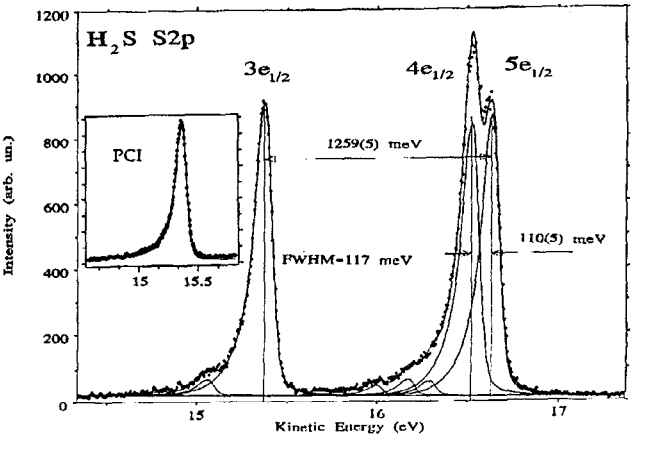

Figure 8: The S2p core photoelectron spectrum of H2S taken at a photon excitation energy of 187 eV.

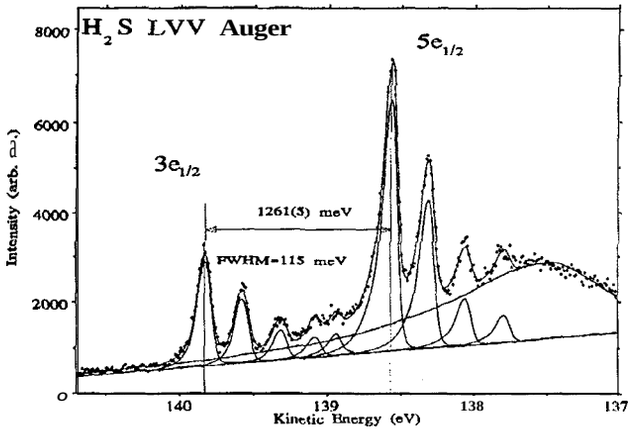

Figure *9:* The $S2p^{-1} \rightarrow X^1A_1(2b_1^{-2})$ transition of the $L_{2,3}VV$ electron Auger spectrum taken at **187** eV plioton excitation energy. The difference in energy between tlie *0-0* transition agrees with the *difference* between the $3e_{1/2}$ and $5e_{1/2}$ measured in the core photoelectron spectrum.

VIII. Xe 4d correlation satellites studied by synchrotron radiation and mnochromatized AlKoc radiation

Botli liigli resolution and intensity is needed in order to study correlation satellites in gas phase photoelectron spectra. Before the appearance of liigli intensity synchrotron radiation sources this region was mostly studied using radiation from Al K_α rotating anodes and by HeII discrete sources. The constraints of having access to a fixed wave length did not permit the study of the relative brancliing ratio as a function of the photon energy. In these studies not only a tuneable source is required but also the capability to resolve overlapping structures and still have enougli intensity in a wide photon energy range. Only recently tliese requirements start to be partially matched by the undulator beamline. In order to give an example of the great potential of this area we compare the Xe 4d satellite region measured with a more conventional source with another spectrum measured very recently at BL 51 at about 129 eV.

Fig. 10 shows an expanded view of the Xe 4d satellite region. In the notation 4d6lnl, "l" stands for p or s orbital and n=6,7 is tlie shell label. Tlie assigned value for nl is indicated in the lower part of Fig. 10. Tlie orbitals with a hole are underscored. Therefore 4d5p6p correspond to a state with a 4d core hole and an electron promoted from the 5p orbital to the 6p orbital. More detailed assignment of the shake-up peaks could not be done wliich illustrates the need for more accurate calculations in this field. Fíg. 11 shows the Xe 4d5pnp, spectrum recorded at BL 51 for an excitation plioton energy of 129.12 eV. In Fig. 10 one can easily notice an improvement in the resolution, moreover the relative intensities of the shake-up peaks are drastically modified. At around 17 eV and 19 eV shake-up energy two peaks gain intensity compared with peaks 1-6 observed in Fig. 9. This clearly shows the presence of two types of shake-up process that can be distinguished with the help of synchrotron radiation. Studies aiming to assigned tlie nature of these two processes are under progress[25]

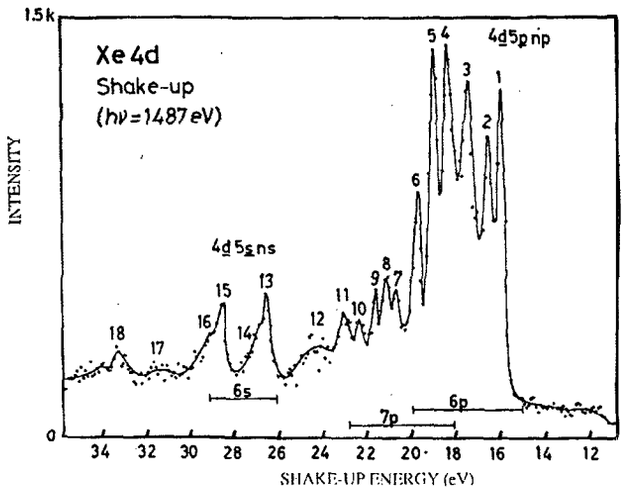

Figure *10:* The Xe 4d core shake-up/off region measured using AlK_α radiation ($h\nu = 1487$ eV).

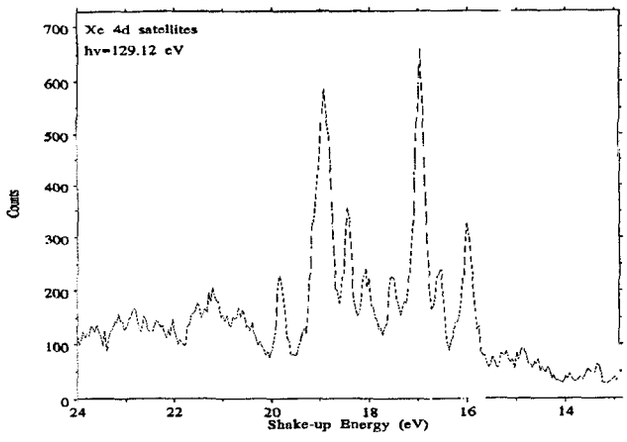

Figure 11: The Xe 4d core shake-up/off region measured using high intensity undulator radiation at BL **51** at *129.12* excitation photon energy.

IX. Concluding remarks

The aim of this report has been to show the new possibilities opened up at higli intensity undulator beamline. In particular, we have described some of tlie results obtained in the Finnish beamline (BL51) at MAX laboratory. Also we gave some examples showing how studies performed with more conventional sources can complement each other and synchrotron radiation based studies. Moreover, studies performed in "laboratory" sources are very important tools to direct synchrotron research to potentially interesting problems to be studied.

We presented a description of resonant and non-resonant Auger electron spectroscopy, core photoelectron, core shake-up/off spectroscopy. The normal LVV Auger spectrum of H_2S was discussed togetlier with the electron beam excited autoionization region. The resonant study of this region performed witli bending magnet radiation was also presented.

The new undulator beamline at MAX laboratory, dedicated mainly for higli resolution gas phase studies was discussed. Tlie resolution test measurements were analysed and from those one can predict a nuniber of potential applications in pure and applied research.

The first results obtained at this beam line such as the resonant Auger Raman effect in tlie VUV region, tlie anomalous Auger decay from molecular field split core levels in H_2S and the shake- up relative intensity variations as a function of tlie excitation photon energy in core shake-up satellites have been discussed.

Acknowledgements

The authors want to thank their collegues Drs. O.-P. Sairanen, A. Kivimaki, A. Ausmees and S. Osborne and the staff at MAX laboratory for assistance. This work has been supported by the Finnisli Academy of Science, tlie Swedish Natural Research Council (NFR). ANB would like to thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for financial suppcrt during part of this project.

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