# Técnicas com Luz Síncrotron Monograph: Resonant photoemission spectroscopy (RPES)

Nataly Z. Herrera R.

#### July, 9 2018

Resonant photoemission spectroscopy (RPES) is a technique based on the process of chemically selective photoemission enhanced by the phenomenon of resonance. In the resonant conditions, the photonemission peaks have greater intensity due to the fact that the excitation energy is close to the absorption threshold of a core level. Hence, this experimental technique is typically used to investigated the electronic contribution of an specific element to the valence band structure. To carried out RPES experiments, the energy of the photon close to the absorption threshold of a core level must be determined previously by X-ray Absorption Spectroscopy (XAS). To be able to chose the excitation energy according to the resonant energy of a given core level, it is necessary to use a tunable phonon energy source such as synchrotron radiation.

Below we present a brief theoretical review of the technique that includes some quantitative foundations that justify the intensity increase of the RPES peaks and some examples that illustrate the use of the technique. Then we have the application section, here we discuss about three articles published in the last 10 years where RPES was employed to solve relevant scientific problems.

#### 1 Theoretical Background

Resonant photoemission spectroscopy (RPES) is the photoelectron emission process that occurs in the vicinity of a X-ray absorption threshold, that is with a photon energy around the binding energy of a core-level. Here we are focus on resonant photoemission from **valence** states. In the photoemission process a photon is absorbed whereby one electron is excited from a valence state into the continuum and is detected at some energy  $E_k$ . The process may be written as

$$|\Psi_g\rangle + \hbar\omega \stackrel{rad}{\to} |\Psi_f(\underline{v})\rangle \tag{1}$$

where  $|\Psi_g\rangle$  is the N-electron ground state with energy  $E_g$ ,  $|\Psi_f(\underline{v})\rangle$  a N-1-electron final state with a valence hole ( $\underline{v}$ ) and energy  $E_f$ , and  $\stackrel{rad}{\rightarrow}$  denotes a radiative absorption process. From energy conservation we have  $E_k = \hbar \omega - E_f + E_g$  and the spectral intensity is given by

$$I(E_k,\omega) = \sum_f |\langle \Psi_g | T(\omega) | \Psi_f(\underline{v}) \rangle|^2 \delta(\hbar\omega - E_k - E_f + E_g)$$
(2)

In off-resonant photoemission, there is only the direct process where the transition operator  $T(\omega)$  corresponds the interaction of the electrons with the photon filed  $V_{rad} = \frac{-e}{mc} \overrightarrow{A} \cdot \overrightarrow{p}$  where  $\overrightarrow{A}$  is the vector potential of the light and  $\overrightarrow{p}$  is the electron momentum.

For photon energies around and above an absorption threshold, a new transition channel opens up, namely the photoabsorption from a core-level followed by the decay of the coreexcited (intermediate) state through auto-ionization. In the latter process the excited electron and one valence electron scatter by Coulomb interaction such that one electron fills the core-hole and the other one is ejected as the photoelectron. In resonant photoemission the core-excitation and auto-ionization have to be considered as a coherent process which leads to the same final state as the direct photoemission process. The resonant process is

$$|\Psi_g\rangle + \hbar\omega \stackrel{rad}{\to} |\Psi_m(\underline{c})\rangle \stackrel{AI}{\to} |\Psi_f(\underline{v})\rangle \tag{3}$$

where  $|\Psi_m(\underline{c})\rangle$  denote a N-electron intermediate state with one core-hole ( $\underline{c}$ ) and one electron in an excited state, and  $\stackrel{AI}{\rightarrow}$  is the auto-ionization process. When the resonant process is included, the transition operation becomes, to lowest order

$$T(\omega) = V_{rad} + V_{AI} \sum_{m} \frac{|\Psi_m\rangle \Psi_m\langle|}{\hbar\omega + E_g - E_m + i\Gamma_m/2} V_{rad}$$
(4)

In this equation,  $V_{AI} = \frac{e^2}{r_{12}}$  is the electron-electron Coulomb interaction which is responsible for the auto-ionization process and  $E_m$  and  $\Gamma_m$  are the energy and width of the intermediate state. The resonant denominator  $\hbar\omega + E_g - E_m + i\Gamma_m/2$  gives rise to a fast variations of the intensity around threshold. Since the direct and resonant processes are added on the level of transition matrix elements (rather that intensities) they interfere which leads to the characteristic Fano profile as a function of the photon [O. Tjernberg and Karlsson, 1996].

It is worthwhile to show the article published in 1994 by [Tanaka and Jo, 1994], where is calculated 3d, 3p and 3s resonant photoemission spectra in some transition compounds at 2p core threshold. They are among the first to propose a transition operator like that of equation 4 and show theoretical results based on this model. Here, we want to show the gigantic theoretical difference in intensity (number of counts) of the spectra of the valence band off-resonance and on-resonance for the 3d level for the (*CuO*) (see figure 1.). The photon energies corresponding to various multiplets of 2p XAS were used to do the calculations.

Another interesting example can be taken from the work of [H. Magnan and Morgante, 2010], where the resonant photoelectron across the  $Fe L_3$  edge of  $Fe_3O_4$  was investigated.



Figure 1: The calculated 3d RPES spectra of CuO for photon energies corresponding to multiplet of 2p XAS, the off-resonance spectrum in also shown [Tanaka and Jo, 1994].

The experiments were performed at the ALOISA beamline of the Elettra Synchrotron Light Source in Trieste, Italy. The authors present resonant spectra of the valence band at the  $L_3$ edge  $(Fe_2p)$  using photon with linear polarization. In an atomic picture, it is caused by the final-state interference between direct photoemission from the 3d levels  $(3d^n \rightarrow 3d^{n-1} + e)$ and auto-ionization processes  $(2p^63d^n \rightarrow 2p^53d^{n+1} \rightarrow 2p^63d^{n-1} + e)$  following the  $2p \rightarrow 3d$ core excitation. The case of  $L_3$  edge is particularly interesting since the  $Fe_3O_4$  crystallizes in the cubic inverse spinel structure, in which the Fe cations are located either on tetrahedral sites (A sites) or on octahedral sites (B sites), at room temperature, one third of Fe atoms are located on A site as  $Fe^{3+}$ , while the remaining two thirds of the Fe ions (with a formal valence  $Fe^{2,5+}$ ) reside in B sites  $(B - Fe^{2+} \text{ and } B - Fe^{3+})$ , so the excitation of  $B - Fe^{2+}$ ,  $A - Fe^{3+}$ , and  $B - Fe^{3+}$  are well separated in the absorption spectra, which allows to clearly associate each contribution of the photoemission spectra. Figure 2.(a) shows the different spectra taken in the region near the Fermi edge. The excitation energies used were 707.5eV, 708.9eV and 709.6eV, these values were obtained from the deconvolution of the X-ray absorption spectrum ( $FeL_3$  XAS) which correspond to different values of oxidation of Fe located in specific positions.

An interesting representation of the results is found in the figure 2.(b), where the spectra are plotted as a function of the binding energy (horizontal scale) and for the different photon energies across the  $FeL_3$  edge (vertical scale). The color scale gives the photoemission intensity at each point of this two-dimensional (2D) map.

It is important to mention that part of the conclusion proposed by the authors states that is observed that the valence band strongly resonates at the  $FeL_3$  edge. Indeed, the global intensity is enhanced by a factor of twenty. Moreover, the different structures in the VB resonate at different photon energies.

From this study we can affirm that the remaining resonant process is element selective, since it involves x-ray absorption from a core-level. Therefore, a resonant photoemission spectra is approximately proportional to an element-projected density of states, rather than the total density of states. This property of resonant photoemission is routinely used to decompose the valence band spectrum of a compound into its element contribution. On the other hand, the technique needs to be done with synchrotron radiation since the experiment is carried out a tunable photon source is necessary.



Figure 2: (a)Valence band recorded at different photon energies 707.5eV (black line), 708.9eV (red open circles), and 709.6eV (green squares). Inset: absorption curve at the  $FeL_3$  edge. Dashed vertical lines indicate the position of 707.5, 708.9, and 709.6eV photon energy. Vertical lines indicate the positions in binding energy where relevant features are located. (b) (left)Experimental absorption spectrum at  $FeL_3$  edge recorded, (right) 2D plot of the resonant valence-band spectra recorded on  $Fe_3O_4$ . The spectra are plotted as a function of the binding energy (horizontal scale) and for the different photon energies across the Fe L3 edge (vertical scale) with the same scale than in (left), the colors indicating the photoemission intensity as a function of these two variables [H. Magnan and Morgante, 2010].

## 2 Applications

In order to discuss some recent applications of the technique, below is a brief review of the article:

**Resonant PhotoEmission Spectroscopy investigation of**  $Fe_2O_3 - TiO_2$ **heterojunctions for solar water splitting** by [M. Rioult and Magnan, 2016] (to read the abstract of the article see figure 3.).



Figure 3: Abstract of the article: Resonant PhotoEmission Spectroscopy investigation of  $Fe_2O_3 - TiO_2$  heterojunctions for solar water splitting by [M. Rioult and Magnan, 2016]

The focus of this article is to understand the electronic structure of the valence band of the  $TiO_2/Ti$  -doped  $Fe_2O_3$  heterojunctiones using RPES, since these materials have potential possibilities of being used in solar splitting water processes (production of hydrogen from water using solar light, therefore, a process free of greenhouse gas emissions). The authors studied several samples of  $TiO_1/Ti_1$  depend  $FaO_2$  with different thicknesses of

The authors studied several samples of  $TiO_2/Ti$ -doped  $Fe_2O_3$  with different thicknesses of each film. Before RPES measures were taken X-ray spectra Photoelectron Spectroscopy (XPS) using  $AlK_{\alpha}$  radiation (1486.7eV). RPES experiments were carried out on the CASSIOPEE beamline at synchrotron SOLEIL (Saint-Aubin, FRANCE). Prior to taking the photon emission spectra, it was necessary to determine the incident radiation (close to the absorption threshold of a core level) by X-ray Absorption Spectroscopy (XAS), which provides (in a simple picture) chemically selective photoemission. The authors determined, based on the literature, that excitation energy used should be around the  $L_3$  absorption edge for Fe and/or Ti. In figure 4. is illustrated valence band photoemission paths for RPES at the  $L_3$  edge.

As we discussed in the theoretical background, by choosing the energy of the appropriate photon, one can expect an increase of the photoemission signal coming from the atoms for which the excitation energy matches the  $L_3$  absorption edge, thanks to the coherent interferences phenomena.



Figure 4: Valence band photoemission paths for RPES at the L3 edge: (a) photoemission from the valence band, (b) Auger relaxation (auto-ionization process) [M. Rioult and Magnan, 2016].

In figure 5. is showed the X-ray absorption spectra (XAS) and the corresponding resonant photoemission maps of the valence band obtained with photons energies around the  $FeL_3$ absorption edge for the samples. The authors report that the quantitative analysis of  $FeL_3$ XAS allows to distinguish electronic configurations of Fe in different oxidation environments, therefore the presence of Fe2+ (resp. Fe3+) is identified, which is associated to the peak  $L_{3A}$  (resp.  $L_{3B}$ ). It is observed how the intensity and shape of these two contributions to the XAS spectrum vary with the thickness of the films that make up the samples. Concerning the VB resonant photoemission maps for heterojunctions (Figure 5.e and 5.f), it is noticed an increase of intensity for binding energies below 2eV. This zone, which accounts for electronic states within the band gap, widens and intensifies when the  $TiO_2$  upper layer thickness increases and is visible only at photons energies matching the  $FeL_{3A}$  XAS contribution. Since these states resonate at the photons energy corresponding to Fe2+ like in  $Fe_3O_4$ , the authors conclude that they correspond to Fe2+ species which are favored by the presence of a  $TiO_2$  upper layer. This result confirms the XAS results and highlights a major advantage of RPES, which is its sensitivity to buried species.



Figure 5: RPES at the Fe L3 edge. (Left panel) Fe L3 XAS. (Right panel) Corresponding valence band (VB) photoemission maps, the color scale is given at the figure bottom. [M. Rioult and Magnan, 2016]



Figure 6: RPES at the Ti L3 edge. (Left panel) Ti L3 XAS. (Right panel) Corresponding valence band (VB) photoemission maps, the color scale is given at the figure bottom. [M. Rioult and Magnan, 2016]

In figure 6. is showed the X-ray absorption spectra (XAS) and the corresponding resonant photoemission maps of the valence band obtained with photons energies around the  $TiL_3$ absorption edge for the samples. From the analysis of XAS it was determined that the structure of  $TiO_2$  depends on the substrate, when it is deposited on hematite it seems to be mainly in the rutile crystallographic structure although the  $TiL_3$  edge of the (a) sample resembles more anatase. Since for all the samples, the results of the RHEED experiments, carried out by the authors to characterize the structure of the films, demonstrated a longrange rutile structure, hence they conclude that these differences in the XAS data are more likely due to different distortions of the  $TiO_6$ . VB maps have areas of greater intensity within the band gap, as in the case of the FeL3 edge. Possibly it is due to species of Ti3+ present in the material. Since seen in the figure, Ti3+ is detected in all the samples and its quantity increases when the thickness of the  $TiO_2$  layer increases. It is important to note that the species Ti3+ was not detected using conventional XPS, which indicates greater sensitivity of the RPES technique.

In order to continue the literature review that allows us to exemplify recent applications RPES, we are going to analyze the following article:

Hydrogen spillover monitored by resonant photoemission spectroscopy by [T. Wakita, 2012] (to read the abstract of the article see figure 7.).

As mentioned in the abstract of the article, they use resonant photoemission spectroscopy to study the hydrogen spillover phenomenon in the sample  $Pt/CeO_2(111)/Cu(111)$ , where Ptis in nanoparticle form. The resonance experiments were carried out at the Materials Science Beamline at the Elettra synchrotron facility in Trieste, Italy. Prior to characterization with synchrotron radiation, it was used a conventional spectrometer ( $AlK_{\alpha}(1486.6eV)$ ) to take high-resolution scans of the core levels of O1s, Ce3d, and  $Cu2p_{3/2}$ , in order to determine the thickness of each of the deposited materials.

RPES is based on measuring the valence band photoemission spectra at photon energies corresponding to the  $4d \rightarrow 4f$  resonance either in the Ce3+ or in the Ce4+ ions. The Ce3+resonance at a photon energy of 121.4eV is caused by a Super-Coster-Kronig decay involving electron emission from Ce4f states located about 1.4eV below the Fermi edge. The Ce4+resonance at a photon energy of 124.8eV involves emission of O2p electrons (hybridized with Ce states) from the valence band around 4.0eV. Additionally, the valence band spectrum at a photon energy of 115eV is measured corresponding to the off-resonance conditions. Typical valence band spectra acquired at the Ce3+ and Ce4+ resonances, as well as off-resonance. The resonant enhancements for Ce3+ (denoted as D(Ce3+)) and for Ce4+ (D(Ce4+)) are quantified by calculating the intensity difference between the corresponding features in- and off-resonance. The resonant enhancement ratio (RER), calculated as D(Ce3+))/(D(Ce4+), is the direct measure of the change of the cerium oxidation state. (see figure 8. (a))

The evolution of the RER was also investigated during stepwise annealing of  $CeO_2/Cu(111)$ and  $Pt/CeO_2/Cu(111)$  preexposed to 50L of hydrogen at 150K. As shown in the figure 8(b), the  $CeO_2/Cu(111)$  are not detected significant variations in the temperature range studied,



Figure 7: Abstract of the article: Hydrogen spillover monitored by resonant photoemission spectroscopy by [T. Wakita, 2012]

which indicates that the sample does not absorb molecular hydrogen. On the other hand, for  $Pt/CeO_2/Cu(111)$ , substantial changes were detected in the monitored temperature range. For a detailed analysis of these changes caused by the increase in temperature, the authors separated the result into three particular regions of temperature. In the first region below 180K, the RER remains largely unaffected. This is attributed to the fact that hydrogen dissociatively adsorbs on the Pt nanoparticles, but remains confined to the surface of the Pt particles. At temperatures exceeding 180K, we observe a sharp increase in RER, followed by a plateau between 220 and 260K. This change, according to the authors, can be assigned to the transfer of dissociated hydrogen to the support. Electron transfer from atomic hydrogen to the oxide causes reduction of Ce4+ to Ce3+ and, simultaneously, produces OH species on the  $CeO_2$  surface. Finally, in the temperature region from 260K to 310K, the RER decreases reaching the low-temperature value again, this is due to desorption of  $H_2$ .

These results allow the authors to conclude that the hydrogen spillover and reverse spillover are processes with an activation barrier sufficiently low to be overcome even below room temperature.

To end our literature review, we will briefly review and discussion of results of the following article:

Ce4f electronic state of  $Ce_{(1-x)}F_xBiS_2$  studied by soft x-ray photoemission spectroscopy [Y. Lykhach and Libuda, 2017] (to read the abstract of the article see figure 9.)



Figure 8: (a) Typical valence band spectra obtained on  $Pt/CeO_2/Cu(111)$  sample containing Ce4+ and Ce3+ ions at  $\hbar\omega = 115eV$  (off-resonance mode, black line), 121.4eV (Ce3+ resonance, red line), and 124.8eV (Ce4+ resonance, green line). Resonant enhancement ratios (RERs), D(Ce3+) and D(Ce4+), are determined as intensity differences between the valence bands measured in- and off-resonance. (b) Development of the RER during stepwise annealing of the  $Pt/CeO_2/Cu(111)$  sample exposed to 50L of hydrogen at 150K. The inset drawings represent the situation on the surface while switching between the temperature regions. [T. Wakita, 2012]



Figure 9: Abstract of the article: Ce4f electronic state of  $Ce_{(1-x)}F_xBiS_2$  studied by soft x-ray photoemission spectroscopy by [Y. Lykhach and Libuda, 2017]

The article highlights that  $Ce_{(1-x)}F_xBiS_2$  is one of the newly discovered superconductors  $Ln_{(1-x)}F_xBiS_2$  (Ln = La, Ce, Pr, Nd, Yb) where the  $Ce_{(1-x)}F_x$  and the  $BiS_2$  layers are stacked alternatively. The latter layer has no metallic d band and it is a narrow-gap semiconductor. Also, the compound exhibits not only superconductivity but also ferromagnetic-like behaviors. The authors with the objective of deepening the compression of this compound used photoemission spectroscopy in the region of soft x-rays, and in this way clarify the nature of Ce4f states. The article focuses on the study of the Ce 4f states since many of the properties exhibited by the Ce (magnetic ordering, heavy fermion, Kondo insulator, mixed valence, and so on) compounds can be explained in terms of the hybridization strength between Ce4f and conduction electrons, which is formulated by single-impurity or periodic-impurity Anderson models. When the hybridization is negligible, Ce4f electrons are localized on the atomic sites and the electronic states of the system can be described with one 4f electron state and conduction band. Besides, Ce3d - 4f resonant PES can provide Ce4f partial density of states and therefore directly reveal the relation of Ce4f states with conducting properties.

The measures were taken in the Photon Factory (PF), KEK in Japan. The total energy resolution was set to be 0.2 - 0.4eV (0.02eV) for PES measurements using photon energies of 870 - 1200eV (70eV). The binding energies were referenced to  $E_F$  of gold. Figure 10(a) shows Ce3d PES spectra of single-crystal samples, x = 0.3 (light green) and 0.7 (dark green), measured with a photon energy of 1200eV. The x = 0.3 spectrum is composed of several peaks that are attributed to the transitions to the three different 4f final states ( $f^0$ ,  $f^1$ , and  $f^2$ ) for each spin-orbit splitting ( $3d_{3/2}$  and  $3d_{5/2}$ ). It is important to mention the  $f^1$  and  $f^2$  final states have relatively close energies, which results in relatively strong hybridization between them, in contrast with the  $f^0$  state, which generally has a clearly defined position. Figure 10(b)-(c) the authors show off- and on-resonance spectra of the x = 0.7 single-crystal and polycrystalline samples measured at two photon energies, 870eV(A) and 881.7eV(B) in XAS spectra near the  $CeM_5$  edge shown in the inset. Each spectrum is magnified by the scale factor denoted on the right side of the figure.

We can see the off-resonance spectrum shows some features with very low intensities in the region near the Fermi level. The contribution of Ce4f is almost imperceptible. The major intensity distributions indicate the partial density of states (pDOS) of O2p and S3pmultiplied photoemission cross sections. In the other hand, for the on-resonance spectrum in the single crystal the intensity around 1.4eV shows a drastic increase while the intensity just near the  $E_F$  region stays lower. The polycrystalline sample exhibits the same spectral shape as the one, indicating that the on-resonance spectrum for the single crystal can be regarded as the f pDOS, though normally it reflects the f-derived electronic structure which is integrated only for a limited region in the Brillouin zone (BZ). Another important observation that can be made about the spectrum is that the absence of the strong enhancement just below the  $E_F$  region for both samples indicates that the hybridization of Ce4f electrons and



Figure 10: (a) Ce3d PES spectra of  $CeO_{1-x}F_xBiS_2$  single-crystal samples, x = 0.3 (light green) and 0.7 (dark green), measured with photon energy of 1200eV. The inset shows the magnified spectra of the  $f^1$  and  $f^2$  components for  $3d_{5/2}$  where the spectra are normalized to the integrated intensities and the spectrum for x = 0.7 is shifted by -0.3eV to match the peak positions with the ones for x = 0.3. (b)-(c) Ce3d - 4f RPES spectra of polycrystalline and single-crystal  $CeO_{1-x}F_xBiS_2$ . Off- and on-resonance spectra (thin and thick curves, respectively) are measured at two photon energies 870eV (A) and 881.7eV (B) in x-ray absorption spectra near the  $CeM_5$  edge shown in the inset, respectively. Each spectrum is magnified by the scale factor denoted on the right side of the figure [Y. Lykhach and Libuda, 2017].

the non-f valence states near the EF is negligible. This suggests a transcendent conclusion: Ce4f electrons hardly contribute to the states near the  $E_F$  and therefore give a negligible contribution to the superconductivity. This result is, furthermore, consistent with the recent resonant photoemission result for single-crystal  $CeO_{0.5}F_{0.5}BiS_2$  using 4d-4f resonant photoemission reporting by other authors.

In this way we can perceive the advantages of the technique, due to both the selectivity in chemical states and the clear improvement in the intensity of the spectrum in the valence band (greater number of counts).

### References

- S. Soderholm O. Tjernberg and U.O. Karlsson. Resonant photoelectron spectrosocpy on *nio*. *Phyisical review B*, 53(15), 1996.
- A. Tanaka and T. Jo. Resonant 3d, 3p and 32 photoemission in transition metal oxides predicted at 2p threshold. Journal of the Pysical Society of Japan, 63(7), 1994. doi: 10.1143/JPSJ.63.2788.
- D. Chandesris P. Kruger S. Bourgeois B. Domenichini A. Verdini L. Floreano H. Magnan, P. Le Fevre and A. Morgante. Resonant photoelectron spectrosocpy on *nio. Physical review B*, 81, 2010. doi: 10.1103/PhysRevB.81.085121.
- P. Le Fevre A. Barbier M. Rioult, D. Stanescu and H. Magnan. Resonant photoemission spectroscopy investigation of  $fe_2o_3 tio_2$  heterojunctions for solar water splitting. *Physics Proceedia*, 85, 2016. doi: 10.1016/j.phpro.2016.11.074.
- T. Hamada H. Fujiwara M. Minohara M. Kobayashi K. Horiba H. Kumigashira G. Kutluk M. Nagao S. Watauchi I. Tanaka S. Demura H. Okazaki Y. Takano Y. Mizuguchi O. Miura K. Okada Y. Muraoka T. Wakita, K. Terashima. ce4f electronic state of  $ce_{(1-x)}f_xbis_2$  studied by soft x-ray photoemission spectroscopy. Journal of catalysis, 285, 2012. doi: 10.1016/j.jcat.2011.09.002.
- M. Vorokhta T. Skála V. Johánek K. C. Prince V. Matolín Y. Lykhach, T. Staudt and J. Libuda. Hydrogen spillover monitored by resonant photoemission spectroscopy. *Physical review B*, 95, 2017. doi: 10.1103/PhysRevB.95.085109.