

**Lectures - Wednesday, June 18****L11****X-RAY IMAGING USING SYNCHROTRON RADIATION****R. Mokso***SL, Paul Scherrer Institut, Villigen, Switzerland*

X-ray imaging is a relatively new technique. A considerable part of knowledge in this field follows from the work made in visible optics or electron microscopy. An overview of the principles and methodology of X-ray image acquisition 0D, 1D, 2D, and 3D will be given with the emphasis on the specificities of synchrotron radiation.

One possible way to look at the current trends in X-ray imaging with synchrotron radiation is to say that the development is carried out in two distinct directions which necessarily meet once in a while but still both require a separate research. The two directions can be identified as the improvement of temporal and spatial. What are the motivations and where are the real limitations in these two directions? The aim of the tutorial is to be able to give some answers to this question.

Principles of synchrotron based X-ray imaging

It follows from the relativistic electrons properties that the divergence of the X-ray beam emerging from a synchrotron source is extremely low. As a consequence we speak about parallel beam imaging in contrast to laboratory X-ray experiments where by the nature of its generation the fan- or cone-beam geometry is usually the case. The parallel beam has many advantages for tomography, such as easy and artifact free reconstruction. The high brilliance of the source also results in a much higher number of useful photons at the level of the detector. The beam angular divergence is typically $0.1 - 1$ rad demonstrating the important difference in this value when looking at a usual laboratory source divergence which emits over half space.

The unique properties of the X-rays emerging from an instrument such as one of the numerous operational and planned 3rd generation synchrotrons allow to develop and implement state-of-art instruments, a tool for applications that can hardly be addressed elsewhere with the same resolution (in many senses of the word).

The spatial resolution with laboratory X-ray sources has achieved remarkable results in the last decade. Commercially available systems routinely offer spatial resolutions close to a few micrometers. Very recently even sub-micrometer resolution laboratory systems are reported.

The image quality is however often poor when imaging real materials. In this work we also address sub-micrometer resolution in tomography with 3rd generation synchrotron radiation X-ray beams that do offer additional possibilities to those used in laboratory setups.

Using laboratory sources, the acquisition time for a complete tomographic set at a resolution of few micrometers is of the order of hours. At synchrotron sources the sit-

uation is far better because of the available high flux of X-ray photons.

When an X-ray beam impinges on a sample, part of it can be absorbed (mainly photoelectric effect), scattered or reflected.

The attenuation of the X-rays of the initial intensity I_0 in a material of thickness z is expressed by the Beer-Lambert law with boundary condition $I(z=0) = I_0$

$$I(z) = I_0 \exp(-\mu z) \quad (1)$$

μ is referred to as the linear attenuation coefficient. The complex refractive index can be expressed as:

$$n = 1 - \delta - i\beta \quad (2)$$

When instead of the intensity we regard the wave function in the media traveling a distance z , where $k = 2\pi/\lambda$ is the wave vector, we can write $\exp(i(1-\delta)kz) \exp(-\beta kz)$, where $\delta = \delta/(2k)$, it becomes clear that δ is responsible for the phase shift $(2\pi/\lambda) dz$ and β for the amplitude attenuation. Both factors will be present in imaging, but one important advantage of synchrotron sources is the possibility to use both factors selectively. How and why to do this selection will also be discussed in detail.

Tomography

It is a big step from radiography (2D imaging) to tomography (3D imaging). Tomographic techniques are nowadays employed using several complementary probes including X-rays. The first ever tomographic images were obtained in 1957 by Bartolomew and Casagrande [1]. Cormack and Hounsfield [4] got a Nobel price in medicine in 1979 for their work with computed axial tomography.

We can say that the utilization of X-rays was in the 20th century the most important trigger of the developments in tomography. This fact is due to the property of X-rays to go through the studied sample without being completely absorbed or scattered. It allows to obtain an image of the cross section of a sample from projection data. The projections consist in this case of line integrals of the complex refractive index $n(x,y,z)$.

Imaging with a partially coherent source

Perhaps the most spectacular difference in imaging performed with a synchrotron beam compared to laboratory sources is the interference effects resulting from the spatial coherence properties of the x-ray radiation. Coherent radiation comes from a point source, which is not the case in



practice, since the dimension of the source is not infinitely small. We say therefore that the radiation is partially coherent.

The *coherence* is the property of a signal or data set in which the phase of the constituents is measurable and plays a significant role in the way in which several signals or data combine. This term is also used to characterize radiation in two distinct respects. The first is the *longitudinal (temporal) coherence* which is related to the monochromaticity of the source.

The *transverse coherence* is related to the source size and its distance. Depending on the source of radiation that is used in a given imaging system we can consider two limiting cases: the spatially coherent and the incoherent case. One way of defining our system is to say that it is incoherent if the transverse coherence length is much smaller than the resolution of the images we acquire. Changing from coherent to incoherent illumination changes the blurring process substantially. A coherent imaging system has an abrupt cut-off in the frequency domain, which results in "ringing" around edges. Incoherent illumination produces a smooth drop-off in the frequency domain which blurs edges gradually.

The inverse problem in phase contrast imaging consists in finding the phase and the amplitude of the object from the available information which is the measured intensity. This is not a trivial problem. Several alternatives to retrieve the information from phase contrast images are to be reviewed.

If the imaging system is designed to record the Fresnel diffraction pattern on the detector, then there are various approaches to approximate the forward problem in order to be able to retrieve the phase. They are generally either based on the *Transport of intensity equation* [3] or the *Contrast transfer function* [2]. If the diffraction pattern is in the Fraunhofer regime, the iterative methods are the most performant, as reviewed in [7].

Special imaging techniques

Changing the parallel geometry of a synchrotron beam in order to take advantage of both the geometric magnification and high monochromatic flux appears to be a very promising direction towards nano-imaging. Using Fresnel zone plates as objective lens and keeping the X-ray energy below 7 keV has brought resolutions approximately 100 nm [6, 9]. One step forward is to combine X-ray microscopy with tomography to access the bulk properties of materials at similar precision using highly penetrating hard X-ray radiation [5, 8].

Numerous other techniques are merging today. We will shortly look at these 3D techniques: coherent diffraction imaging, analyzer based imaging, fluorescence tomography, laminography, diffraction contrast tomography.

Applications

Two principal applications will be selected to demonstrate the two aspects of imaging as stated in the introduction. The first is the liquid foams; a system that requires fast image acquisition eventually real time imaging.

Scientists know a great deal about the individual bubbles in foams and how they "talk" to one another through simple friction. But when many bubbles clump together to form a foam, the resulting material exhibits a host of unexpected properties and behaviors. Liquid foams, for instance, are composed of roughly 95 percent gas and 5 percent liquid, yet they tend to be far more rigid than their components. This is due to a phenomenon called jamming. Because the bubbles are so tightly packed, when a foam is pressed down, the bubbles can't hop around one another. The more the bubbles are jammed together, the greater the pressure inside them grows and, consequently, the more they take on the characteristics of a solid.

The biggest challenge facing scientists is to create predictive models of foam rheology, or just simply coarsening that is, the way it flows or evolves over time. As foams age, gravity drains their liquid downward, and smaller bubbles are absorbed by larger ones, a process called coarsening. But until quite recently our understanding of this process has been limited to 2D foams by the inherent difficulties of studying such an ephemeral material in three dimensions.

The spatial distribution and shape of particles in Near nano-structured or ultrafine-grain materials is the second selected application demonstrating the need for submicrometer spatial resolution. These materials are defined as materials having grain sizes whose linear dimensions are in the range of 100 nm to 1 μ m. The physical properties of these materials are potentially superior to those of their coarse-grained counterparts. This potential superiority results from the reduced size or dimensionality of the near nanometer-sized grains as well as from the numerous interfaces between adjacent grains resulting in large volume fraction of grain boundaries. It is of high technological importance to study the bulk of these materials in different conditions.

Further examples in the field of biology, medicine, paleontology and other fields will be shortly mentioned.

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CHEMISTRY IN THE GAS PHASE USING THE VUV RADIATION

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Introduction

The investigation of model ionic systems in the gas phase brings often deep insight into the intrinsic properties of complex systems. For example, we have shown that as small system as $\text{Ag}_2\text{O}^+/\text{C}_2\text{H}_4$ is capable to reproduce all reaction steps in the oxidation of ethylene on a silver catalyst [1]. The small models allow not only detailed investigations of kinetics and reaction mechanisms using mass spectrometry, but also ask for a concerted theoretical study. The isolated systems in the gas phase permit the application of high level quantum chemical calculations and direct correlations between the molecular structure and the investigated properties (e.g. ionization energies or proton affinities) or reactivity. On the other hand, lack of solvation leads often to observation of larger reactivity of the ions than it is expected in the condensed phase, which has to be considered in the translation of the results obtained for a model to a real system. Among the biggest disadvantages of the gas-phase experiments is the fact that the internal energy of the generated ions is often not well defined. The state-of-art method for the ionization is usage of the synchrotron radiation. Photons from synchrotron have very well defined energy and the radiation is moreover smoothly tunable. Therefore the conditions for ionization can be precisely defined and the internal energy of the generated ions can be controlled. The tutorial will be devoted to a demonstration of the power of synchrotron experiments for benchmark studies in chemistry and for the reactivity investigations in dependence of internal energy of ions.

Main objectives of the tutorial

Ionization energies

The simplest application of the power of synchrotron radiation is the determination of ionization energies. Ionization energies can be determined from the dependence of the ion yield on the photon energy. The precision of the obtained value can be very high (± 10 meV) and the limits are usually not set by the energy resolution of the synchrotron radiation, but rather by the properties of the studied molecules, sensitivity of the detection and by the method used for the evaluation of the collected data. Thus, measurements using synchrotron radiation provide us with highly accurate energies, which relates thermodynamic of the charged systems with neutral precursors.

$$\sigma^+(E - E_0) = \sigma_0^+ (E - E_0)^m \quad (1)$$

The dependence of the ion yield on the energy of the ionizing photons is described by so-called Wannier law (Equation (1)), σ^+ is cross section and E_0 is ionization en-

ergy) [2, 3]. For the cross section of singly charged ions is m equal to zero, which means that the onset of the yield of the monocations should appear as a step function. Due to an inevitable imprecision of the experiment caused by thermal broadening and Franck – Condon effects, the onset appears not as a pure step function, but rather as a linear increase of the ionic yield. The threshold is therefore determined as a linear extrapolation of the onset to the baseline (Figure 1). For generation of doubly charged cations, m is equal to one, which means that the ionic yield at the onset is a linear function of the excess of photon energy over the ionization energy. This dependence makes determination of the second ionization energy much more difficult, because the ion yield at E_0 is zero and a linear extrapolation of the onset leads to large errors (Figure 2). We have proposed to convert the measured ionization curve to its first derivative and consequently evaluate the derived curve in an analogous manner as it is done for single ionization (Figure 2) [4].

Internal energies

The reactivity of ions is drastically influenced by their internal energy. Conventional ionization of neutral molecules can lead to highly vibrationally excited ions or can even yield electronically excited species. The observed reactivity can be thus due to vaguely defined excited states of the reactants. Synchrotron radiation is a unique tool for the preparation of reactant ions with defined internal energy and for the investigation the reactivity in dependence of the internal energy.

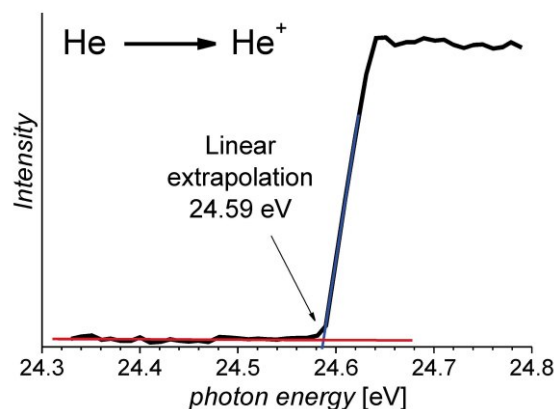


Figure 1. Yield of monocations generated from helium as a function of photon energy. Linear extrapolation of the ion yield leads to a value of 24.59 ± 0.01 eV. Note that the ion yield shows almost perfect step behavior as it is expected for atomic monocations (measured at ELETTRA).

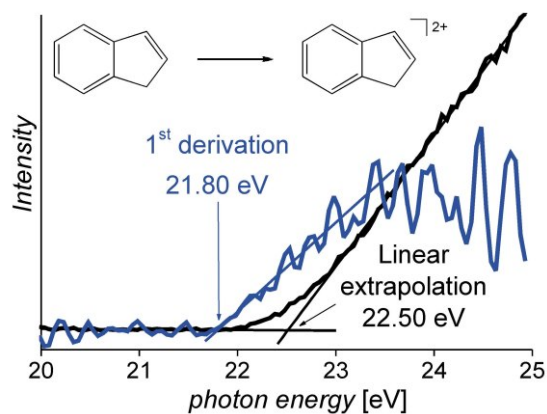


Figure 2. Yield of dication generated from indene as a function of photon energy. Linear extrapolation of the ion yield leads to a value of 22.50 ± 0.10 eV, whereas an analogous evaluation of the derived curve leads to a value of 21.80 ± 0.10 eV (measured at ELETTRA).

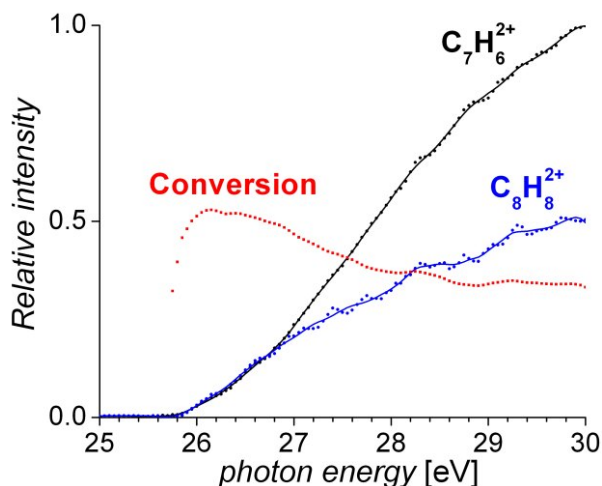
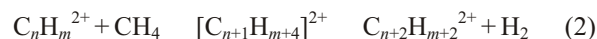


Figure 3. Yield of the doubly charged product $C_8H_8^{2+}$ from the reaction of $C_7H_6^{2+}$ and CH_4 as a function of photon energy used for generation of $C_7H_6^{2+}$ from toluene. Note that the conversion decreases with increasing internal energy of the $C_7H_6^{2+}$ reactant (measured at SOLEIL).

The effect of the internal energy of reactants on their reactivity will be shown on an example of a reaction of the $C_7H_6^{2+}$ dication with methane. It has been shown that medium sized dications easily undergo a coupling reaction with methane to yield larger hydrocarbons (Equation (2)) [5]. This reaction can be of high relevance for the explanation of the hydrocarbon growth in extreme environments as interstellar medium of planetary atmospheres. To this end, it is particularly important to exclude the possibility that observed reactivity is caused by internally excited ions. The first results from the beamline DESIRS of SOLEIL demonstrate that indeed the internally cold ions react fastest (Figure 3).



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APLIKÁCIA SYNCHROTRÓNNEHO ŽIARENIA PRI ŠTÚDIU IONOSFÉRY PLANET

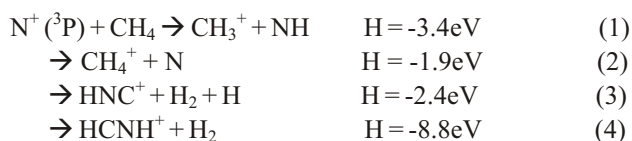
Jan Žabka

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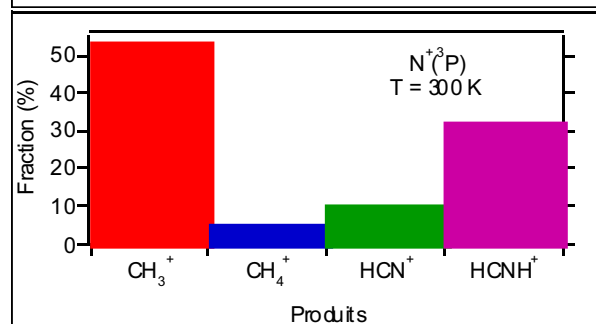
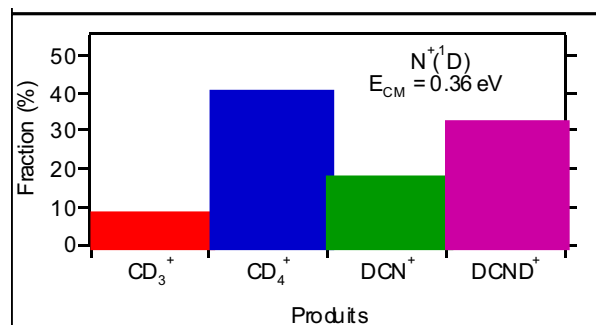
Oblas aplikácie synchrotrónneho žiarenia sa týka experimentálneho výskumu chémie iónov v plynnej fáze v súvislosti s atmosférou Titánu a iných objektov slnečnej sústavy. Výzkum sa koncentruje na sledovanie kinetiky a dynamiky elementárnych reakcií iónov s molekulami, ktorých produkty boli identifikované sondami predovšetkým v iónosfére Titánu a Marsu. Cieľom je poskytnúť potrebné data (identifikácia procesov, ich reakčné prierezy a mechanizmy) pre planetológov, ktorí sa zaoberajú modelovaním iónosféry príslušných objektov.

Použitím synchrotrónu ako zdroja fotónov s regulovateľnou energiou a techniky PEPICO (photoelectron photoion coincidence) je možné pripraviť iónové reaktanty s vybranou vnútornou energiou a následne sledovať ich reaktivitu s neutrálnym reaktantom. Túto metódu sme použili pri sledovaní reakcie $N^+(^3P)$, $N^+(^1D)$ s metánom :



Táto reakcia hrá dôležitú úlohu v chémii Titánu a je silne závislá na excitácii primárneho atómového reaktantu. Pre túto reakciu produkty DCN^+ a $DCND^+$, pochádzajúce z rozpadu dlho žijúceho komplexu prekvapivo nie sú veľmi citlivé na N^+ excitáciu. Oproti tomu pre N^+ v základnom stave je hlavný produkt disociatívny prenos náboja, vedúci k CD_3^+ (1), v prípade N^+ v 1D stave je hlavný kanál nedisociatívny prenos náboja vedúci k CD_4^+ (2). Metastabilný stav N^+ vďaka svojej dlhej dobe života a špecifickej reaktivite musí byť zahrnutý v modeloch popisujúcich planetárnu iónosférickú chémiu.

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