

# Electronic Structure



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PAPER

## Sample degradation and beam-induced damage in (synchrotron-based) electronic structure experiments

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E-mail: [antje.vollmer@helmholtz-berlin.de](mailto:antje.vollmer@helmholtz-berlin.de)**Keywords:** synchrotron, sample degradation, photoemission, work function

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### Abstract

Synchrotron radiation-based methods, in particular photoemission spectroscopy, are very powerful tools for studying the electronic, chemical, and structural properties of materials and combinations of materials. Numerous experimental studies have been performed in the last decades using synchrotron radiation in physics, chemistry, material science, biology, medicine, and more. However, the advantage of high photon flux from synchrotron storage rings, which is beneficial or even crucial for many experiments, may impose new problems when sensitive samples are investigated, such as organic systems. They are prone to chemical changes when exposed to high photon fluxes. Here, we demonstrate how to identify beam-induced sample degradation and provide the best practice rules for reliable investigations and control experiments.

### 1. Introduction

Synchrotron radiation facilities provide state-of-the-art instrumentation and methods to understand the fundamental properties of materials in almost all fields of natural sciences. Various spectroscopies, diffraction and scattering, imaging, microscopy, and tomography are the main methods available at synchrotron light sources around the globe. More than 50 light sources serve several ten-thousands of users. In Europe alone, roughly 30 000 scientists [1] produce more than 10 000 publications per year encompassing results from synchrotron-based experiments [2].

Spectral continuity, an almost free choice of wavelength, adjustable to the experimental need as well as photon-energy scanning options are advantages of synchrotron radiation; others are the beam temporal structure of picoseconds (at free electron lasers and in particular cases at synchrotrons also femtoseconds [3]) and the flexibility in polarisation of the light.

The most important advantage of synchrotron radiation over laboratory x-ray sources, however, lies in its brilliance, defined as  $\text{photons} \cdot \text{s}^{-1} \text{ mm}^{-2} \text{ mrad}^{-2}/0.1\% \text{BW}$  (photons per time, space, energy definition), which is larger than  $10^{18} \text{ photons s}^{-1} \text{ mm}^{-2} \text{ mrad}^{-2}/0.1\% \text{BW}$  for 3rd generation synchrotrons. Flux is a measure of number of photons per unit time and flux density is defined as flux per unit area [4]. Table 1 provides a short overview of the main characteristics of several light sources, for comparison purposes. For sample degradation, the most important parameter is the flux density, which depends not only on individual beamline designs, but also on the position of the sample with respect to the beamline focus.

Although the growth of brilliance has generally enabled more sophisticated experiments [6, 7], the advantage of high photon flux from synchrotron storage rings, however, may impose new experimental problems when delicate samples are investigated, such as organic systems or other irradiation-sensitive specimens [8].

### 2. Sample degradation during photoemission and photoabsorption experiments

Photoemission is a powerful tool in material science. Numerous tutorial and review papers describe the application and best practices [9–11].

**Table 1.** Comparisons of light sources.

Source	Brilliance	Photonenergy tunability	Variable polarisation	Time resolution
Candle	$10^5$	No	No	No
Lightbulb	$10^6$	No	No	No
X-ray tube/rotating anode	$10^8\text{--}10^{10}$	Limited	No	No
Sun	$10^{10}$	Yes	No	No
Synchrotron 3rd generation bending magnet	$10^{15}$	Yes	Yes (to some extend)	Yes
Synchrotron 3rd generation undulator	$10^{20}$	Yes	Yes	Yes
Ultimate storage rings [5]	$10^{24}$	Yes	Yes	Yes
FEL	$10^{34}$	Yes	Yes	Yes

However, giving recipes to detect and avoid sample degradation is the scope of this tutorial paper. Chemical alteration of a sample when exposed to high brilliance beams, degradation, or even complete destruction of a sample's integrity can eviscerate whole investigation campaigns.

These alterations comprise chemical changes due to bond breaking, radical formation, polymerisation, loss of conjugation as well as morphological and phase changes, all leading to modifications in electronic structure. Already in the earlier days of synchrotron radiation-based research, concerns were expressed regarding the integrity of samples under irradiation [12–14].

Therefore, care must be taken when measuring with high photon flux densities and a variety of references and control experiments are indispensable. Occasionally, however, it may be difficult to judge whether sample degradation occurs, especially when degradation happens on the same timescale or even much faster than the data acquisition time.

Positive charging near the surface—due to the photoemission process—creates free charge carriers potentially leading to chemical reactions and alterations of the specimen. Besides charging free charge carriers can cause electric fields that distort or mask a meaningful photoemission spectrum. Even without charging, photoelectrons and their secondaries with a kinetic energy of several eV can break intra-molecular bonds and result in chemical changes of the sample, for example via bond-breaking, cross-linking and polymerization [15, 16]. This is particularly important since there are usually more secondary than primary electrons as can be estimated using the Tougaard background [17].

Particularly in systems where conjugation facilitates the conductivity of the sample, irradiation damage of the conjugation leads to chemical changes of the specimen and consequently to sample charging due to the loss of efficient conductivity. A clear indication of this effect is a reduction in the sample current, i.e. carriers (from ground) compensating the loss of electrons by the photoelectric effect during measurement.

Illuminating the sample with visible light, which can be absorbed by the specimen surface (due to its optical band gap) charging can be compensated through the generation of free charge carriers. The mechanisms here are internal photoemission [18] or the formation of singlet excitons, which dissociate in quasi-free charge carriers, increasing the conductivity and removing charging efficiently [19].

The effect of sample degradation through charging is more pronounced with increasing thickness of the sample and when samples are (or become) less conductive. For example, investigations of organic single crystals remained a field of challenge for a long time and up to 2010 there were no reports of angle-resolved photoemission spectroscopy to determine a full bandstructure of organic single crystals [20].

In general, these problems may be solved or at least partially overcome by executing measurements with considerably reduced the photon flux, which—in turn requires novel high-performance detectors [21] as revealed by an example of the investigation of an organic single crystal using an extremely attenuated photon beam [22].

## 2.1. How to detect ‘beam damage’

### 2.1.1. Visible beam damage

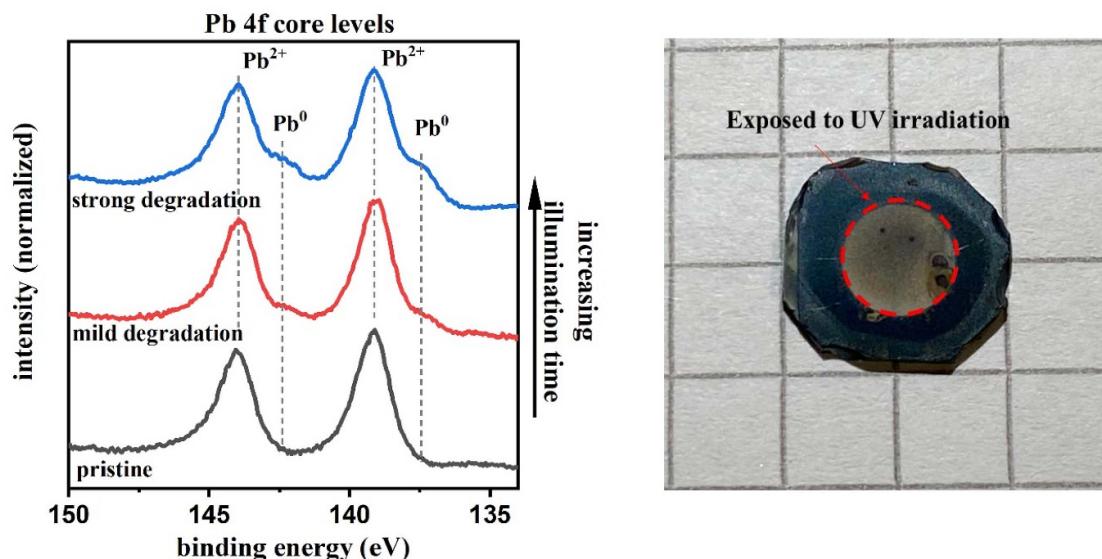
In some cases, beam damage is not only obvious, but even visible to the eye after the measurement, when a clear scar from the beam spot appears on the sample. An example is shown in figure 1, where a drop casted organic polymer film on a transparent conducting substrate is shown after exposure to soft x-rays at a dipole beamline. While the pristine polymer showed a blue colour, the spot exposed to synchrotron light is clearly visible as an orange square, indicating severe change of electronic structure, e.g. the optical band gap. Here a rectangular shaped pin-hole was used to control the size of the beam.

### 2.1.2. Spectral broadening and additional signals

A clear indication of changes in the structure or chemistry of a given specimen is the arising of additional signals in XPS spectra with exposure time to x-ray radiation, as shown for the methylammonium lead



**Figure 1.** Visible beam damage (orange square) of a blue polymer film after exposure to synchrotron radiation at the dipole beamline IISS at BESSY II.



**Figure 2.** Left: Pb 4f core level spectra of methylammonium lead triiodide perovskite. Degradation, i.e. the reduction of  $\text{Pb}^{2+}$  to metallic Pb upon illumination. Details see [23], right:  $\text{MAPbI}_3$  film after 4 h UV irradiation (focused beam).

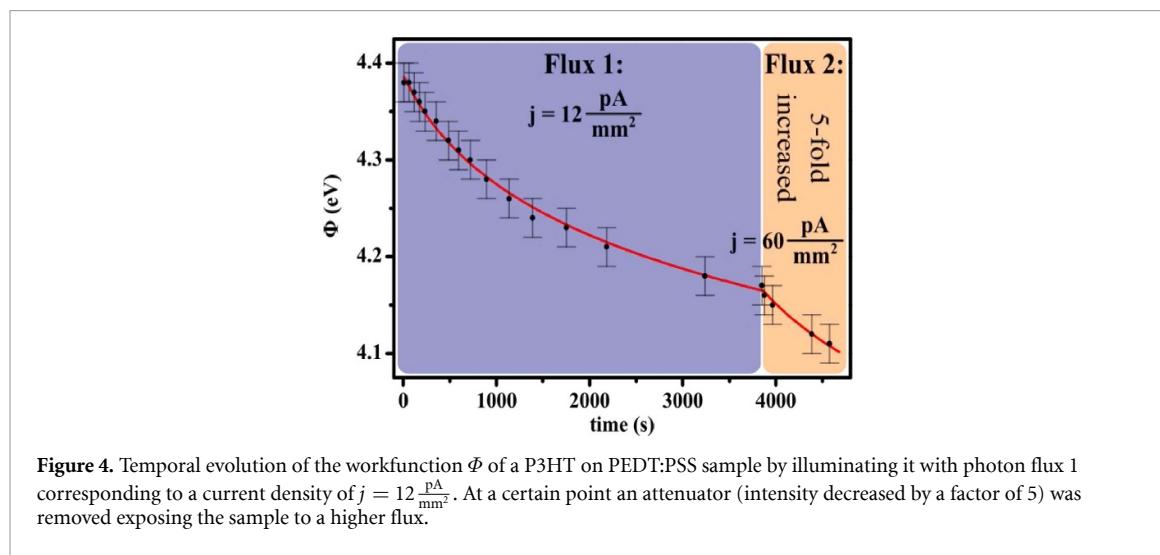
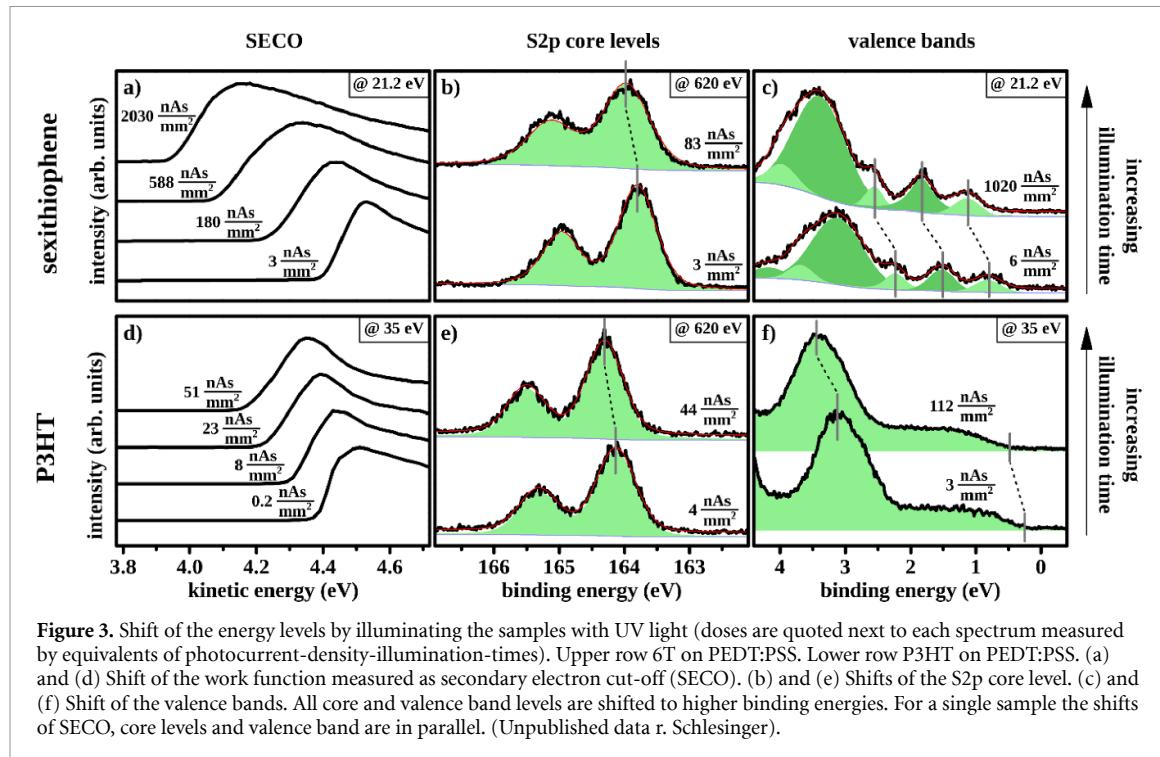
triiodide perovskite ( $\text{CH}_3\text{CH}_3\text{PbI}_3$ ) Pb4f core levels in figure 2. The decomposition of the material leads to additional signals due to the existence of several species with different chemical shifts, which arise in the spectra at different binding energies. In this example, irradiation in UHV leads to the decomposition of  $\text{CH}_3\text{CH}_3\text{PbI}_3$  perovskite into  $\text{PbI}_2$ ,  $\text{CH}_3\text{NH}_3^+$  and  $\text{I}^-$ , where  $\text{PbI}_2$  further decomposes into metallic Pb and  $\text{I}_2$  via photolysis reaction. An extensive study of the photodecomposition of methylammonium lead triiodide perovskite is given in [23] (note here: data take with a laboratory x-ray source).

### 2.1.3. Peak shifts, energy level alignment and work function changes

Changes in the electronic structure and therewith shifts in the work function  $\Phi$ , in the core level signals as well as in the valence bands can become apparent in the XPS and UPS data. The two examples in figure 3 shows the development of spectral changes upon illumination with synchrotron radiation of sexithiophene (6T) on the conducting polymer PEDT:PSS (poly-3,4-ethylendioxythiophene) and of polythiophene poly(3-hexylthiophen-2,5-diyl) (P3HT) also on PEDT:PSS. Exposure to VUV and x-ray light is given as a dose, calculated as the product of the photocurrent density and time

$$\text{Flux : } j_{\text{ph}}^{35\text{ eV}} = 5 \times 10^9 \frac{\text{phot}}{\text{s mm}^2} \leftrightarrow j_{\text{e}}^{\text{Au}} = 1.5 \frac{\text{pA}}{\text{mm}^2}. \quad (1)$$

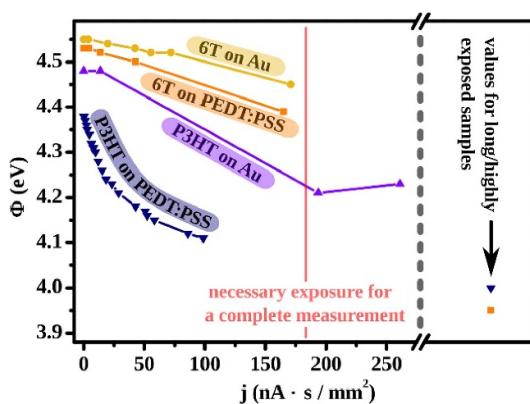
Equation (1):  $j_{\text{ph}}$ : photon flux, superscript: photon energy; this corresponds to  $j_{\text{e}}$ : electron flux measured at a gold reference (superscript Au) measured via the sample current in pA.



For both materials P3HT and 6 T all levels (secondary electron cut-off, core levels and valence band) shift in parallel to higher binding energy. Several tests were undertaken to exclude that this is due to sample charging. The sample was illuminated with visible light to increase the sample conductivity due to the internal photo effect. Secondly, the impinging photon flux was varied by a factor of  $10^4$  in consecutive analogue measurements. Both measures did neither set back nor stop the energy level shifts. If the effect was due to reversible charging, energy level would shift back.

As the work function is severely influenced by material changes at the surface, surface morphology, surface roughness, or impurities, the value of work function  $\varphi$  is highly sensitive to the integrity of the sample. Determined by the onset of secondary electrons, a shift of this onset during measurements is a clear indication of beam damage.

Figure 4 shows the evolution of the work function upon irradiation time for P3HT on PEDT:PSS. A sample of P3HT on PEDT:PSS was illuminated with a given photon flux 1; after roughly one hour a beam attenuator was removed and the photon flux was increased by a factor of five leading to an increased speed of the work function shift. Here one can see that the speed of the alteration of the work function scales with the impinging photon flux density.



**Figure 5.** Comparison of the different degradation speeds for all four investigated systems. The red line indicates the estimated exposure necessary to do a UPS measurement with typical equipment. The points after the break are the energy levels of P3HT and 6 T on PEDT:PSS, when they were highly exposed to UV illumination.

Figure 5 shows equivalent temporal evolutions of the work function  $\Phi$  upon beam exposure for two different materials on two different substrates. Also, for these systems valence band and core levels shift in parallel (not show here). A characteristic exposure necessary for measuring a complete set of data including valence band and core levels spectra as well as work function is indicated as a red line in figure 5. As one can see, the energy levels are already highly altered before completing the measurement campaign. Therefore, these alterations could only be uncovered by performing very short measurements of the secondary electron cut-off. For comparison reasons, all data used in figures 3–5 were recorded at the same experimental infrastructure (SurICat no longer in operation, dipol beamline PM4 at BESSY II) [24].

### 3. Recipes—how to avoid sample degradation

The main effort to avoid sample degradation is to minimize the effect of secondary electrons, and with this charging and chemical changes of the sample. Two main paths should be followed: reduction of the number of secondary electrons (flux reduction) and their removal as fast as possible (thin samples, good conduction, illumination).

#### 3.1. Reduction of the photon flux

Whenever possible beam intensity should be minimized. Attenuators in the beam, such as thin metal foils can help to reduce the flux and are sometimes even beneficial in suppressing higher order beam arising from grating monochromators in synchrotron beamlines. The reduction of unwanted higher order light from the monochromator significantly reduces the overall flux at the sample, while this unwanted light does not contribute to the signal, but increases the background. Attenuators work very well particularly for measurements in the valence band region, however attenuators of different thicknesses or materials might be required to cover higher photon energy ranges. The effect of attenuator foils is not only a matter of their thickness, but also depends strongly on the absorption edge of the material. For photon energies above the respective edges the absorption is of course much stronger resulting in a much higher impact of the attenuator foil.

#### 3.2. Choice of photon energy

The choice of photon energy for the experiment depends on the scientific question in the first place. While core level spectroscopies require higher energies than valence band measurements, for the individual methods parameters like cross-section, information depth, surface sensitivity also guide the choice of photon energy. Nonetheless within the available range one should take care to make an appropriate choice of photon energy to minimise secondary electron formation, e.g. by choosing an energy below instead of directly above an absorption edge of a present element.

#### 3.3. Sample positioning

Another highly recommended method is not to work in the focal position of a beamline, but move the sample out of focus to dilute the photon density at the sample. An illuminated area corresponding to the acceptance area of the respective detector, usually  $1 \text{ mm}^2$ , does not decrease the overall signal, however one must keep in mind, that the signal averages over this area. If degradation takes place in reasonable time scales

(minutes) the measurements position can be continuously changed during the measurement to avoid measuring degraded areas.

### 3.4. Experimental infrastructure

As described, beam damage can be reduced or avoided by considerably reducing the photon flux and the exposure time, which—on the other hand requires high-performance detectors. An example is given in [16] where band structures of organic single crystals were measured at a 10 000 times attenuated flux compared to the optimized flux at the beamline using an angle resolved time of flight spectrometer (Scienta ARTOF 10k). Despite the low photon flux, data were obtained about significantly faster (minutes) than with conventional electron energy analysers (hours). This was achieved by 300 times higher electron transmission of the ARTOF than hemispherical analysers, angle-resolved measurements of a full 30° cone within one measurement, and data acquisition in the MHz range.

### 3.5. Sample illumination and conductivity

Illumination with visible light (a green laser, class 3 is recommended) can help to avoid sample charging. The area of the visible laser illumination should fully overlap with the synchrotron spot. Measurements with visible light on and off allow to assess the effect of illumination.

Bad sample conductivity in general and poor connection to ground in particular increase the unwanted effects of charging. It is necessary to ensure that the sample is properly connected and grounded and the sample current should be monitored throughout the entire experiment. A decreasing sample current indicates an increasing damage of the sample. To quantify this problem and exclude effects from the light source, a metallic, clean reference sample should be measured regularly. A freshly prepared gold film or gold crystal mounted next to the sample is highly recommended. Monitoring pressure changes during measurements is recommended, too, since sample damage induces sometimes outgassing of the sample.

### 3.6. Spectroscopic measures

Sample work function must be checked regularly, but definitely in the beginning and end of the experiment. Use alternative, non-light-based methods such as Kelvin-probe measurements to verify the experiments. The sample current must be monitored during the entire measurement. A decreasing sample current is a clear indication of less conductivity of the sample and therefore of possible beam damage braking for example conjugated bonds.

Zoomed-in scans of core-levels are used to discover new species via the chemical shift. Monitoring selected peak(s) over the time allows for detecting changes in the sample integrity. Not only change of shape but also rigid shift can indicate sample degradation. The degradation processes can happen very fast and consequently changes are visible only within the first two sweeps of the measurements or less. In addition, an increasing background signal (in particular in VB region) or modified shape of the background can indicate degradation.

### 3.7. ‘Visible inspection’

Last but not least: Check your sample through an eye inspection and by using microscopical methods such as optical microscopes, atomic force microscopy or scanning tunnel microscopy.

## 4. Summary

To summarize, beam-induced sample degradation presents a non-negligible problem in synchrotron-based experiments. It can manifest itself in a variety of phenomena, like change in chemical structure due to bond braking, morphological changes and others. All of those can affect electronic and chemical properties. A particular challenge is to detect beam damage when it happens in or faster than the time range of the measurement. Commonly beam damage can be identified by a variety of spectroscopic as well as microscopic measures and by varying the photon flux in subsequent experiments of the same sample at different positions. Organic samples in particular are highly sensitive. While sample degradation can be reduced by several measures specified in the ‘recipe section’, care must be taken during the experiment and when evaluating data. Although there are means to minimize beam damage, it is not avoidable in all cases and must be considered.

## Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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## Conflict of interest

The authors declare that they have no affiliations with or involvement in any organization or entity with any financial interest in the subject matter or materials discussed in this manuscript.

## Ethical Compliance

no experiment involved human participants, human tissues, human data or animals

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