

Transformation of intensity scale from arbitrary units to absorption coefficient (cm^{-1})

It may be noted here that the incident photon flux has energy dependence arising due to the non-uniform absorption by the beamline optics (monochromator, grating, mirror etc.). Therefore in order to take into account the energy dependence of the incident photon flux, the sample drain current ($I_{\text{sample}}(\hbar\omega)$) requires to be normalized to the drain current from the clean gold sample ($I_{\text{Au}}(\hbar\omega)$) featuring an unstructured absorption cross section in the energy range of interest.

The drain current from the sample (I_{sample}) can be expressed as,

$$I_{\text{sample}}(\hbar\omega, t) = V_{\text{sample}} C_{\text{sample}}(\hbar\omega) \sigma_{\text{sample}}(\hbar\omega) N_{\text{sample}} \Phi(\hbar\omega, t) \quad (1)$$

where V_{sample} is the excitation volume of the sample, $C_{\text{sample}}(\hbar\omega)$ is the electron-per-photon conversion function for the sample, σ_{sample} is the optical absorption cross-section of the sample, N_{sample} is the number of absorbing atoms per unit volume and $\Phi(\hbar\omega, t)$ is the incident photon intensity. The mesh drain current which is monitored simultaneously and is a measure of the incident photon intensity can be expressed as,

$$I_{\text{mesh}}(\hbar\omega, t) = M(\hbar\omega, t) \Phi(\hbar\omega, t) \quad (2)$$

where $M(\hbar\omega, t)$ is the overall photon conversion function of the mesh. Similar expressions can be written for the gold reference sample as

$$I_{\text{Au}}(\hbar\omega, t') = V_{\text{Au}} C_{\text{Au}}(\hbar\omega) \sigma_{\text{Au}}(\hbar\omega) N_{\text{Au}} \Phi(\hbar\omega, t') \quad (3)$$

and

$$I_{\text{mesh}}(\hbar\omega, t') = M(\hbar\omega, t') \Phi(\hbar\omega, t') \quad (4)$$

Here t and t' represent the different times when the sample and the clean gold were measured respectively. Combining the above equations the absorption coefficient of the sample can be expressed as follows,

$$\begin{aligned} \sigma_{\text{sample}} N_{\text{sample}} &= \left(\frac{I_{\text{sample}}(\hbar\omega, t) I_{\text{mesh}}(\hbar\omega, t')}{I_{\text{Au}}(\hbar\omega, t') I_{\text{mesh}}(\hbar\omega, t)} \right) \left(\frac{V_{\text{Au}}(\hbar\omega) C_{\text{Au}}(\hbar\omega)}{V_{\text{sample}}(\hbar\omega) C_{\text{sample}}(\hbar\omega)} \right) \sigma_{\text{Au}} N_{\text{Au}} \\ &= R(\hbar\omega) \left(\frac{V_{\text{Au}}(\hbar\omega) C_{\text{Au}}(\hbar\omega)}{V_{\text{sample}}(\hbar\omega) C_{\text{sample}}(\hbar\omega)} \right) \sigma_{\text{Au}} N_{\text{Au}} \end{aligned} \quad (5)$$

In the above expression the number density N can be calculated from the expression, $N = \frac{\rho N_A}{A}$, where ρ is the density of the material, N_A is the Avogadro number and A is the atomic weight of the material. The first quantity on the right-hand side of equation (5) can be obtained directly from the drain current measurements. The σ_{sample} and σ_{Au} can be obtained from known atomic σ values [<http://ulisse.elettra.trieste.it/services/elements/WebElements.html>] as will be described later in this document.

The first quantity on the right hand side of equation (5),

$$R(\hbar\omega) = \frac{I_{\text{sample}}(\hbar\omega, t)}{I_{\text{mesh}}(\hbar\omega, t)} \times \frac{I_{\text{mesh}}(\hbar\omega, t')}{I_{\text{Au}}(\hbar\omega, t')} \quad (6)$$

gives a normalized data which takes into account the photon energy dependence of the incident flux.

It is important to note that at this stage after application of the energy shifts to four datasets viz., $I_{\text{sample}}(\hbar\omega, t)$, $I_{\text{mesh}}(\hbar\omega, t)$, $I_{\text{Au}}(\hbar\omega, t')$ and $I_{\text{mesh}}(\hbar\omega, t')$ their X-axis values are not identical anymore and before applying any mathematical operation we first require to perform interpolate the four sets of data within a suitable range eg. for the C K-edge the energy range of 280-320 eV is good enough.

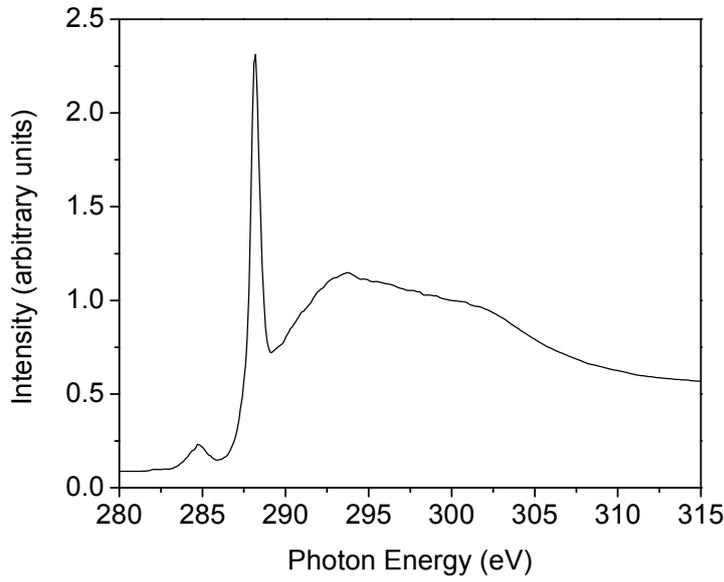


Fig. 1: Spectrum obtained after performing normalization to remove the energy dependence of the incident photon flux.

However, the intensity of the spectrum at this stage is still in arbitrary unit and therefore quantitative analysis is not possible.

Now in terms of the optical absorption coefficient $\alpha(\hbar\omega)$ equation (5) can be written as,

$$R(\hbar\omega) = F(\hbar\omega) \frac{\alpha_{\text{sample}}(\hbar\omega)}{N_{\text{Au}} \sigma_{\text{Au}}(\hbar\omega)} \quad (7)$$

where $F(\hbar\omega) = \frac{V_{\text{sample}}(\hbar\omega)C_{\text{sample}}(\hbar\omega)}{V_{\text{Au}}(\hbar\omega)C_{\text{Au}}(\hbar\omega)}$ can be calculated from equation (7) with the help of the approximation that far from absorption edge $\alpha_{\text{sample}}(\hbar\omega)$ can be represented as $\sum_k N_k \sigma_k(\hbar\omega)$, where

N_k is the atomic density and $\sigma_k(\hbar\omega)$ the atomic absorption cross section (can be found tabulated) for chemical species k .

In the present tutorial the energy value of 280 eV is chosen for the calculation of the $\alpha_{\text{sample}}(\hbar\omega)$ at the C K-edge. For the purpose of data analysis a linear background $L(\hbar\omega)$ was subtracted from $\alpha_{\text{sample}}(\hbar\omega)$ which approximates the removal of the atomic contribution in the spectral range. Finally the NEXAFS data will be given as, $\Delta\alpha(\hbar\omega) = \alpha(\hbar\omega) - L(\hbar\omega)$, which actually represents the molecular contribution to the optical absorption coefficient over the atomic background. The above method is illustrated below using our example.

Calculation of N :

Using the values $\rho = 1.3 \text{ gm/cm}^3$ and $A=71$ (molecular weight of the monomer $\text{C}_3\text{H}_5\text{NO}$) for PAM, $N_{\text{sample}} = 0.018 \times N_A = 1.08 \times 10^{22}$ monomer units/cm³. Similarly for the gold reference sample the $N_{\text{Au}} = 0.1 \times N_A = 5.9 \times 10^{22}$ atoms/cm³.

At our chosen energy (280 eV) $R = 0.09$ (approximated value) (obtained from datasheet)

From atomic data table [<http://ulisse.elettra.trieste.it/services/elements/WebElements.html>] total c.s. of C, N and O atoms at 280 eV are

$$\sigma_{\text{C}}|_{280 \text{ eV}} = 0.05 \text{ Mbarn}; \quad \sigma_{\text{N}}|_{280 \text{ eV}} = 0.09 \text{ Mbarn}; \quad \sigma_{\text{O}}|_{280 \text{ eV}} = 0.16 \text{ Mbarn}$$

Therefore for the PAM unit

$\sigma_{\text{PAM}} = 0.05 \times 3 + 0.16 \times 1 + 0.09 \times 1 = 0.41 \text{ barns} = 0.41 \times 10^{-18} \text{ cm}^2$, as we have 3 C, 1 N and 1 O in each PAM unit. Here we have neglected H as the c.s. at these energies is negligible.

For gold

$$\sigma_{\text{Au}} = 5.47 \times 10^{-18} \text{ cm}^2$$

Therefore,

$$\begin{aligned} \alpha_{\text{PAM}} &= \sigma_{\text{PAM}} N_{\text{PAM}} \\ &= 0.41 \times 10^{-18} \times 1.08 \times 10^{22} \text{ cm}^{-1} \\ &= 4.43 \times 10^3 \text{ cm}^{-1} \end{aligned}$$

Therefore the normalization constant for the C K-edge spectrum is, $\alpha / R = 4.43 \times 10^3 / 0.09 = 4.92 \times 10^4$. Multiplying the whole dataset (y-values) by this number will result in the Y-axis getting transformed to "Absorption coefficient (α) (cm⁻¹)". The final normalized spectrum is shown in figure 2.

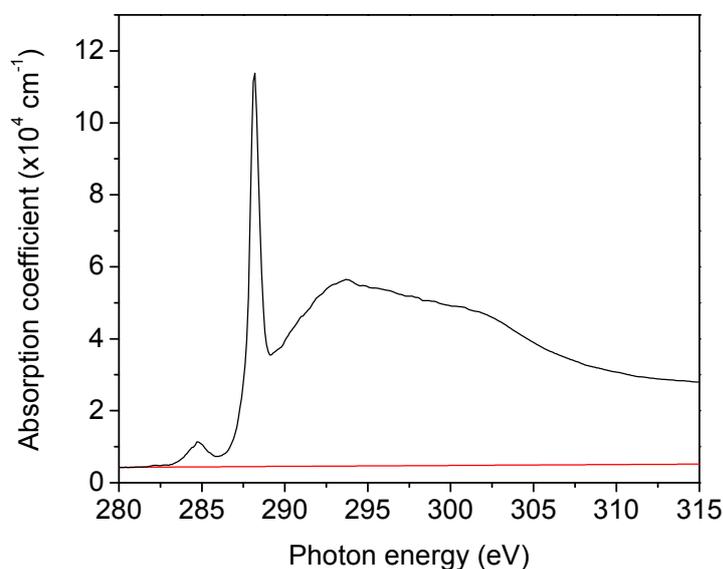


Fig. 2: The normalized C K-edge spectrum in terms of the absorption coefficient (α) and fitted with a linear background to remove the atomic contribution.

Using the above value for $\alpha_{\text{PAM}}(\hbar\omega)$ we can calculate the ratio $F(\hbar\omega)$. The latter can then be used to calculate $\alpha(\hbar\omega)$ for a similar unknown sample. For example, in our manuscript¹ which involves a detailed NEXAFS study of PAM and the products formed due to controlled thermal degradation the $\alpha(\hbar\omega)$ values of the degradation products were calculated based on the assumption that the quantity $F(\hbar\omega)$ for the degradation products should be approximately same as that of the pure polymer.

Using equation (7) we obtain

$$\begin{aligned}
 F(\hbar\omega) &= R(\hbar\omega) \frac{N_{\text{Au}} \sigma_{\text{Au}}(\hbar\omega)}{\alpha_{\text{sample}}(\hbar\omega)} \\
 &= \frac{0.09 \times 5.87 \times 10^{22} \times 5.47 \times 10^{-18}}{4.43 \times 10^3} \\
 &= 6.52
 \end{aligned}$$

It is important to note here that all the above calculated (α and F) are energy dependent. Therefore calculating the same at a different energy (say, N K-edge or O K-edge) would yield different values.

¹ *Onset Kinetics of Thermal Degradation of Ultrathin Polyacrylamide Films*, S. Mukherjee, M. H. Mondal, M. Mukherjee, B. P. Doyle and S. Nannarone, *Macromolecules* 42, 7889 (2009).

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