

## Sample Modulation in Core Level Spectroscopies

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Core level spectroscopies are relevant for an extremely wide range of research areas, comprising systems spanning all levels of complexity from fundamental atomic models to practical systems of economic relevance. Sample modulation by local radiative heating can play a role for micro- and nanostructured samples where heat transfer may be slow, but the more common mode of sample modulation are reactions induced by low-energy secondary electrons. I will give examples of unwanted radiative modulations in organic materials during X-ray photoelectron and absorption spectroscopies, including X-ray Raman scattering. Correlations between known rates of thermal degradation and radiation damage have been observed for libraries of saccharides. I will show how for a liquid system the kinetics of the photodegradation are so rapid as to prohibit collection of a core level spectrum even under constant sample renewal by flow. High intensity radiation can in fact be used as a preparative technique for photochemical synthesis, leading to products otherwise not accessible by conventional chemistry. If the kinetics of radiative degradation are sufficiently slow then snapshot scanning can permit the collection of meaningful spectra by differential measurements. Crucial for predictive modelling the rates of sample modulation effects is an understanding of electron transport in matter, especially their ranges, elastic scattering and inelastic losses. These are required because secondary electron generation stems mostly from pair formation events induced by energetic electrons associated with the decay of the primary core holes (i.e. Auger and fluorescence-excited photoelectrons). At energies above 10 keV electron ranges can be modelled with standard Bethe theory. I will show how modified Bethe laws permit such calculations also for lower photon energies. A desired effect of pair formation by Auger electrons is the use of the gas over a sample as a charge neutraliser, both in X-ray photoelectron and electron-yield X-ray absorption spectroscopies.