

Asymmetry of Peaks in the XPS of Polymers

When a photon is absorbed by a material, the energy transferred may cause the excitation of both the electronic and atomic structure of the compounds on the surface. Thus, an electron ejected from the surface following the absorption of a photon of a given energy, appears with kinetic energy dependent on more than simply the initial core level state of the electron. A proportion of the photon energy may contribute to atomic oscillations associated with the bonds within a molecule and is not available to the photoelectron as kinetic energy. The consequence of these alternative energy transfer mechanisms is that the XPS peaks exhibit asymmetry.

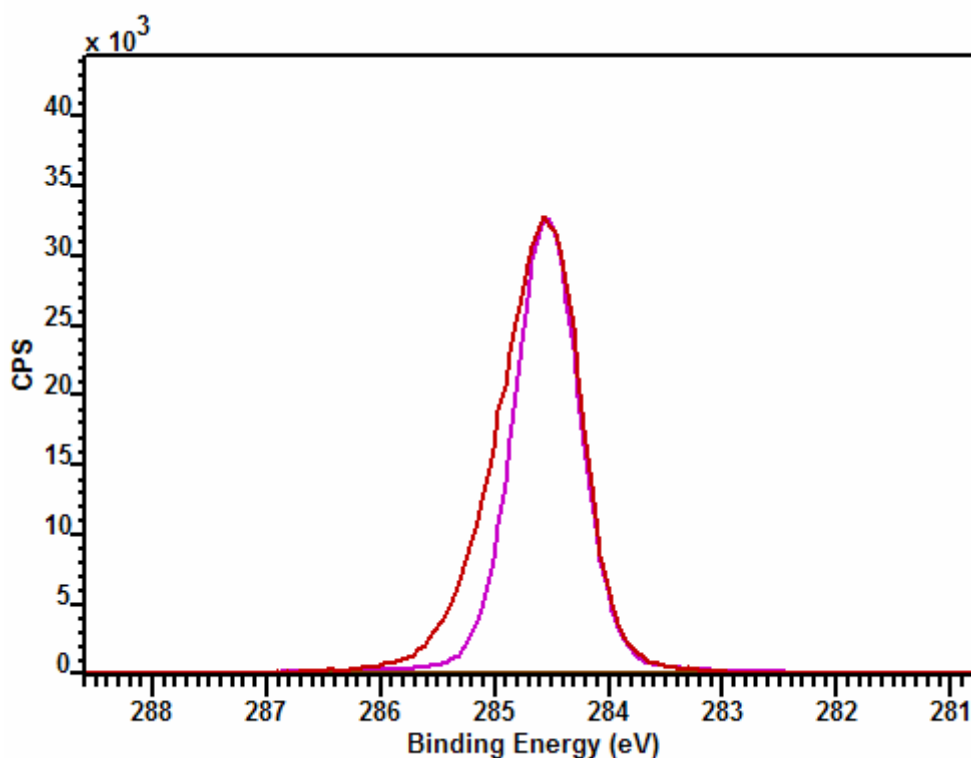


Figure 1: High density poly(ethylene) C 1s peak illustrating asymmetry in the observed data.

While atoms bonded together to form a molecule have many modes of oscillations (stretches, bends, etc), the modes of interest to XPS are those for which the energy absorbed is of the order of the FWHM of the underlying electronic transition. The most energetic absorption modes are *stretch* type oscillations along the directions of the bonds. Within a molecule the bonds between the atoms vibrate, which to a first order approximation, can be modelled using the theory governing harmonic motion. If k is a constant characteristic of the force bonding to atoms of mass m_1 and m_2 , then applying Hooke's law, the classical frequency of the oscillations is given by

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\frac{m_1 m_2}{m_1 + m_2}}} = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

The story is however incomplete without introducing a quantum mechanically description of the atomic oscillations. The Schrödinger equation for a particle of reduced mass m performing harmonic motion is:

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} \left(E - \frac{1}{2} kx^2 \right) \psi = 0.$$

The solutions of the Schrödinger equation require the energy of the oscillations to be quantized:

$$E_n = \left(n + \frac{1}{2} \right) h\nu \text{ for } n = 0, 1, 2, \dots$$

Thus, so far as the potential energy between two atoms can be described by the harmonic oscillatory potential of $\frac{1}{2}kx^2$, the atoms within a bond may vibrate with energies which are equally spaced. Therefore, energy loss events associated with the ejection of an electron by the absorption of a photon result in a sequence of XPS peaks offset in energy by the allowed vibrational energy levels in the atomic bonds.

Infrared spectroscopy is based on the absorption of photons by molecular bonds with frequencies from the infrared region of the electromagnetic spectrum. Absorption peaks occur at frequencies corresponding to the quantized vibrational energy level of these bonds; therefore IR spectra provide a measure of the expected peak separations contributing to the asymmetry in the XPS C 1s data. The IR spectra from even the simplest materials are complicated by the numerous vibrational modes, so any assumption that the observed XPS spectra are a simple sequence of symmetric peaks is only an approximation to the reality of the processes responsible for the XPS data. Nevertheless, an idea of the energies involved in the vibrational splitting of a XPS peak can be estimated.

The peaks in IR spectra are typically plotted using wave number in units of cm^{-1} . The energy in eV can be computed from the wave number, which is the reciprocal of the wave length λ is given by (h is Planks constant and c is the speed of light) :

$$E(\text{eV}) = 6.242 \times 10^{18} (\text{eVJ}^{-1}) h(\text{Js}) c(\text{ms}^{-1}) \left(\frac{1}{\lambda} \right) (\text{cm}^{-1}) 100 = 1.239841 \times 10^{-4} \left(\frac{1}{\lambda} \right)$$

The wave number for a C-H bond absorption peak is typically 3100cm^{-1} , therefore the energy is 0.384 eV. As a result, the energy transitions in the stretch vibrational states of C-H molecular bond in high density poly(ethylene) are in the region of 0.384 eV and therefore small compared to the binding energy of a 1s electron in a carbon atom, but are significant compared to the FWHM of the C 1s peak measured using high resolution XPS (~ 1 eV). These shifted C 1s peaks account for the asymmetry apparent in the data envelope for HDPE in Figure 1.

When constructing a peak model for vibrational states in XPS data there are at least two strategies for fitting peaks to the asymmetric data:

1. Introduce a set of symmetric Gaussian-Lorentzian peaks where the position constraint for each of the peak-set are defined in terms of equally spaced offsets from the principal peak. Typically the FWHM constrains can be established so that each of the peaks representing the vibrational states are of identical width.
2. Construct a line-shape using the VS(E,A1,A2,A3,A4)GL(n) or VS(E,A1,A2,A3)GL(n) strings. The resulting line-shape is a sequence of Gaussian-Lorentzian peaks separated by the value of the E parameter, where the amplitude of each peak is defined relative to the first peak and specified using the parameters A1, A2, A3 and A4. The advantage of modelling the data using the VS(,,,)GL() or VS(,,,)SGL() line-shapes over other asymmetric line-shapes is that the resulting profiles are asymmetric in a physically understandable way and also have the localised nature of the SGL/GL profiles.

Figure 2 is an example of the VS(SGL()) line-shape where the separation of the peaks are large compared to the FWHM of the underlying SGL definition. The same sequence of peaks used to construct a more appropriate line-shape for the C 1s peak is illustrated in Figure 3, where the step size between the peaks in the VS model is 0.633.

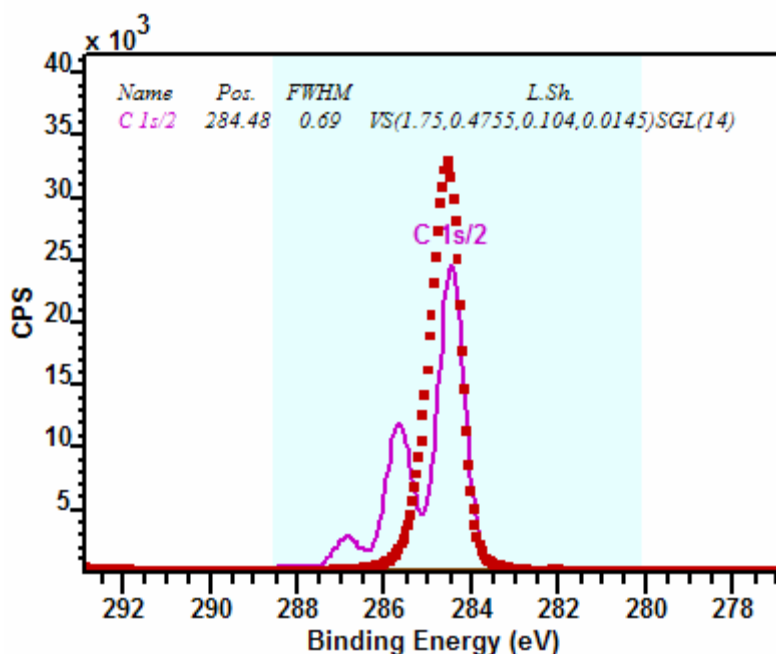


Figure 2: VS(SGL()) line-shape where the energy step is too large for the FWHM. The essential structure of the VS peaks can be seen clearly.

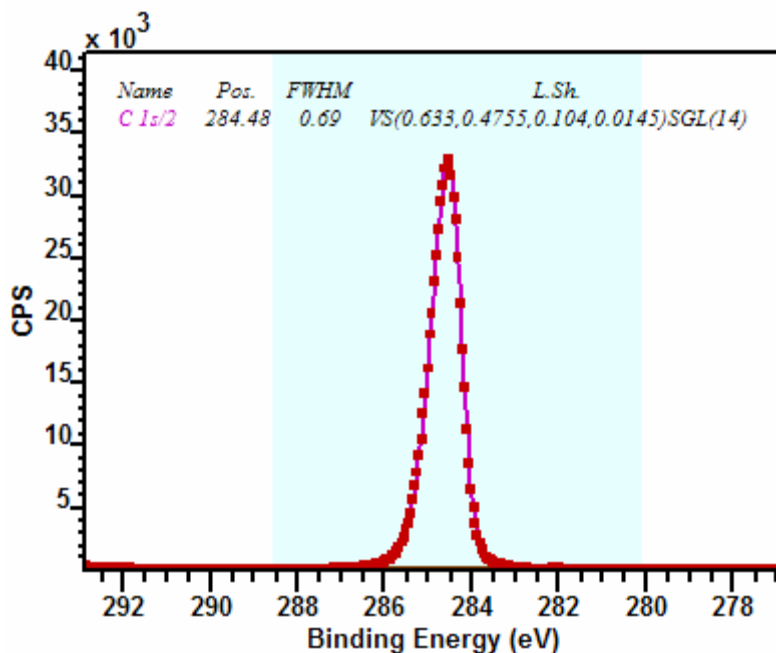


Figure 3: Correctly adjusted energy offset parameter in the VS(SGL) line-shape appropriate for the data.

The relative height of the component peaks in the VS line-shape can be deduced by an analysis on the data using strategy 1 above. That is, the C 1s peak in Figure 1 can be fitted using constrained peaks as shown in Figure 4. The position and FWHM constraints were established before fitting to the C 1s data, while the area constraints were set follow fitting as a means to illustrate the relative areas of the constituent peaks. Since the FWHM are all the same, the relative amplitudes of the peaks are also in the same proportion. These amplitude ratios were used to determine the parameters for the VS(SGL) line-shape. Note, the offset is not directly transferable from strategy 1 to strategy 2. This is because the line-shape is constructed using peaks of unit FWHM rather than physically meaningful parameters and the resulting line-shape is mapped onto the data in units of the physically meaningful FWHM. That is to say, the E parameter is scaled by the FWHM of the fitted line-shape.

The environment of an electron ejected from a core level of carbon in a C=O bond may differ from a similar core level from a C-H bond, therefore the separation of the vibrational states change and as a result the degree of asymmetry in an XPS peak may also change. Figure 5 is an example of a fit to PMMA in which varying degrees of asymmetry are used to model the data. Again, the significance of the energy offset used in the VS line-shape is limited to the objective of obtaining a fit to the data. It is the ability of the VS line-shape to recreate the types of shapes observed in the data that is important rather than attempting to construct the exact structure underlying the electronic plus vibrational states.

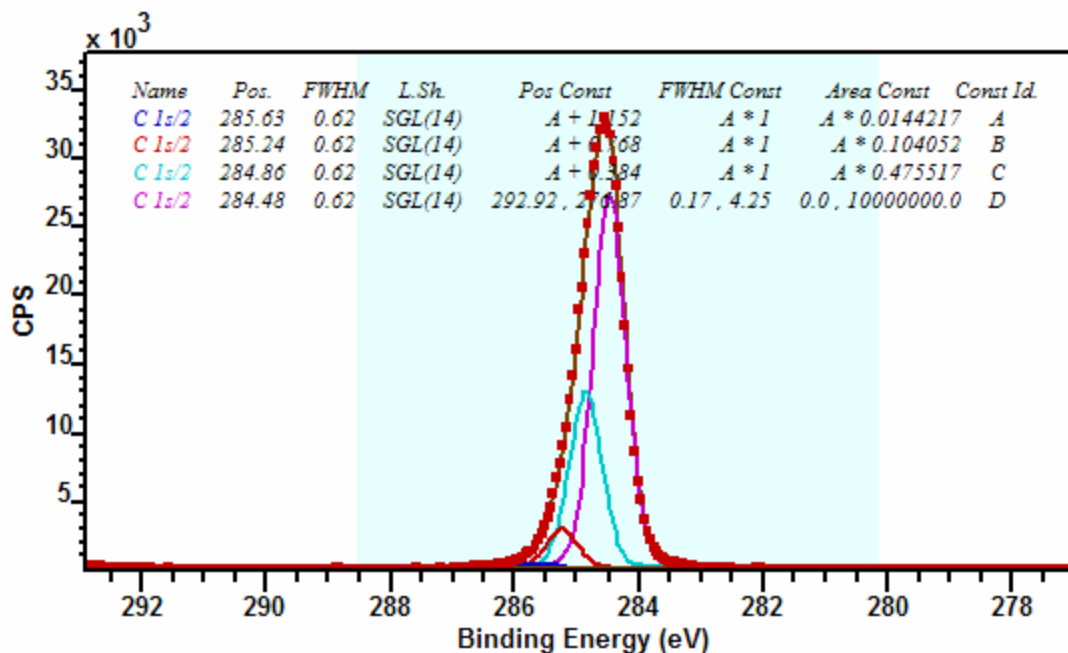


Figure 4: Constrained peaks modeling the asymmetry in the HDPE C 1s spectrum.

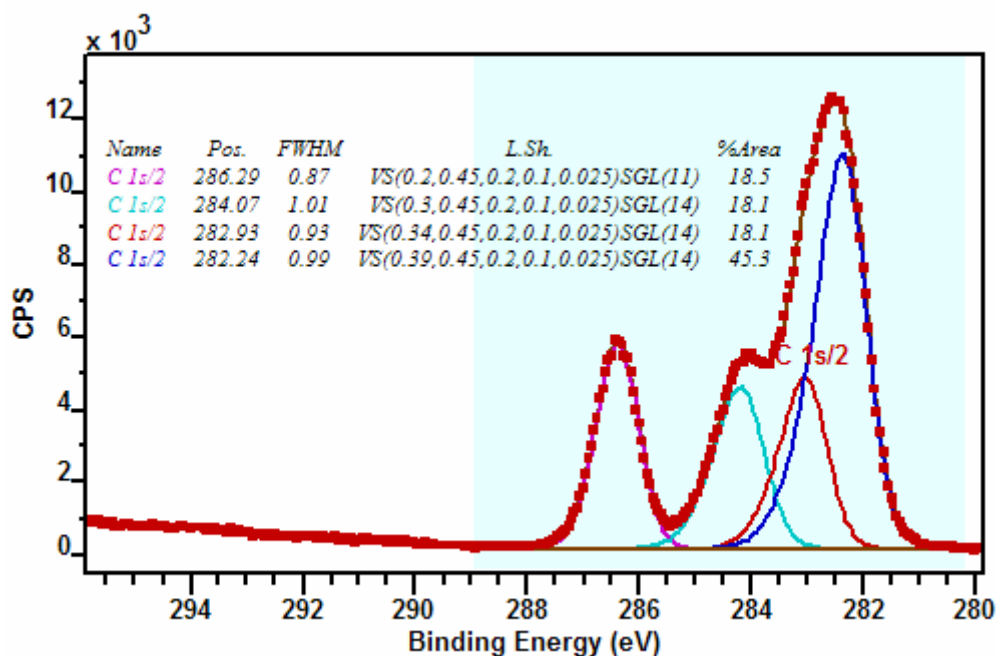


Figure 5: Poly(methyl methacrylate) PMMA fitted using a variety of VS(SGL) parameters.