Positive Probability Ltd

Note P2: Peak Modelling – ESI MS

Introduction

Following a deconvolution, the quantified errors are dependent on the quality of the data and the quality of the model. Errors are smallest when all the peaks have the same width and shape, the model fits the peak profiles within the noise and the S/N is high. These conditions are rare because there is usually some variation in peak width and shape and any designed model is therefore a compromise. Very often the S/N is poor and this increases the errors because there is less certainty about the peak positions and intensities. Errors also increase with increasing peak overlap, again reflecting the increased uncertainty of positions and intensities for overlapped peaks. In such situations, the smallest errors are only obtained when care is taken over model design.

Data

The data described here are a small part of the ESI spectrum of a digest showing a Z5 isotope cluster of overlapped peaks. The half height peak width is approximately 9 sampling intervals and this was used as the input for the ***Nadir***™ baseline correction program. The baseline corrected data are shown in Figure 1 below.

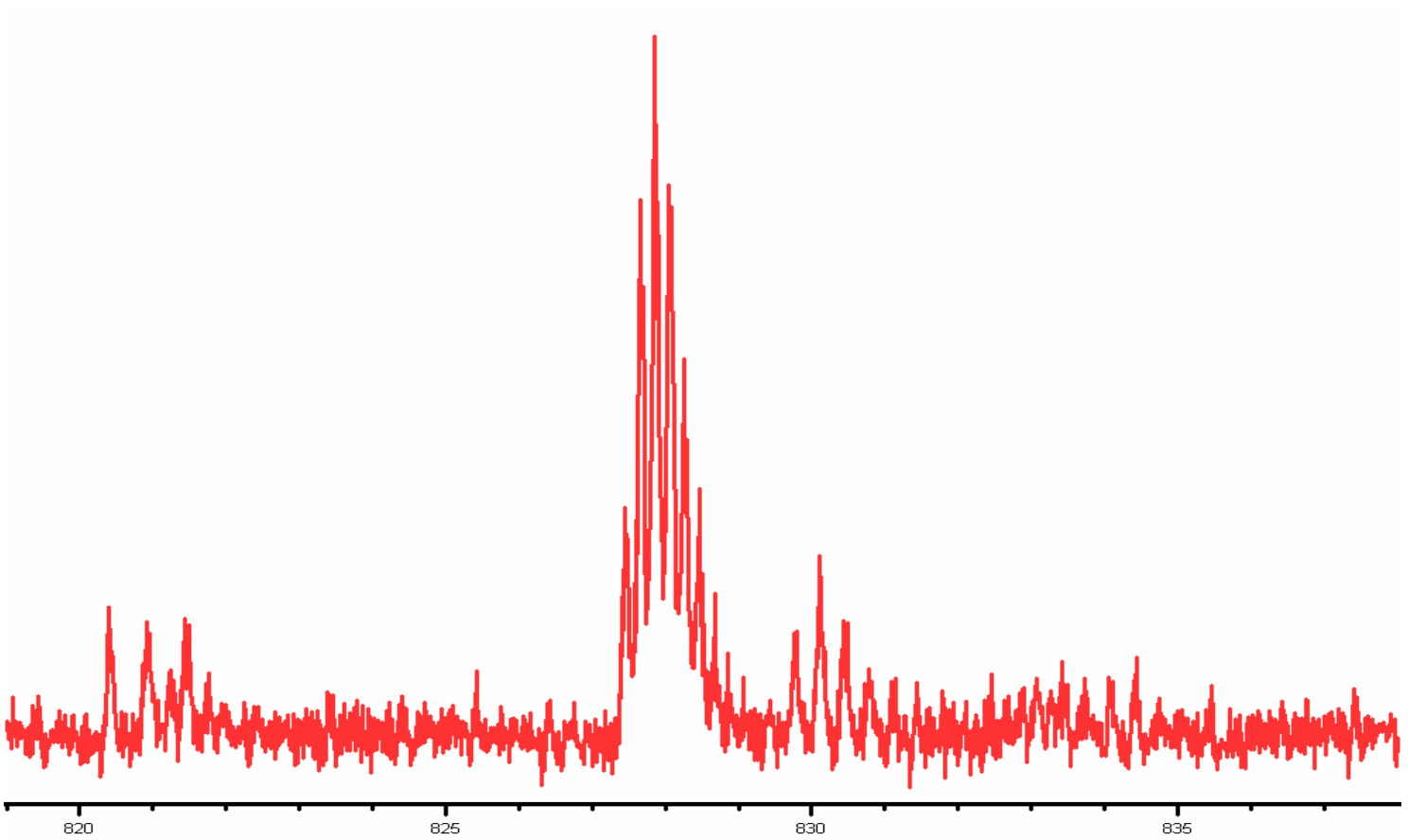

Figure 1. Baseline corrected data.

Model Design

For data where peaks are at least partially resolved, models are obtained using the automatic option provided in the ***Profile***™ modelling program. Single peaks or clusters of peaks may be modeled. The program presents the user with a box that is positioned around the peak(s) to be modeled as illustrated in Figure 2.

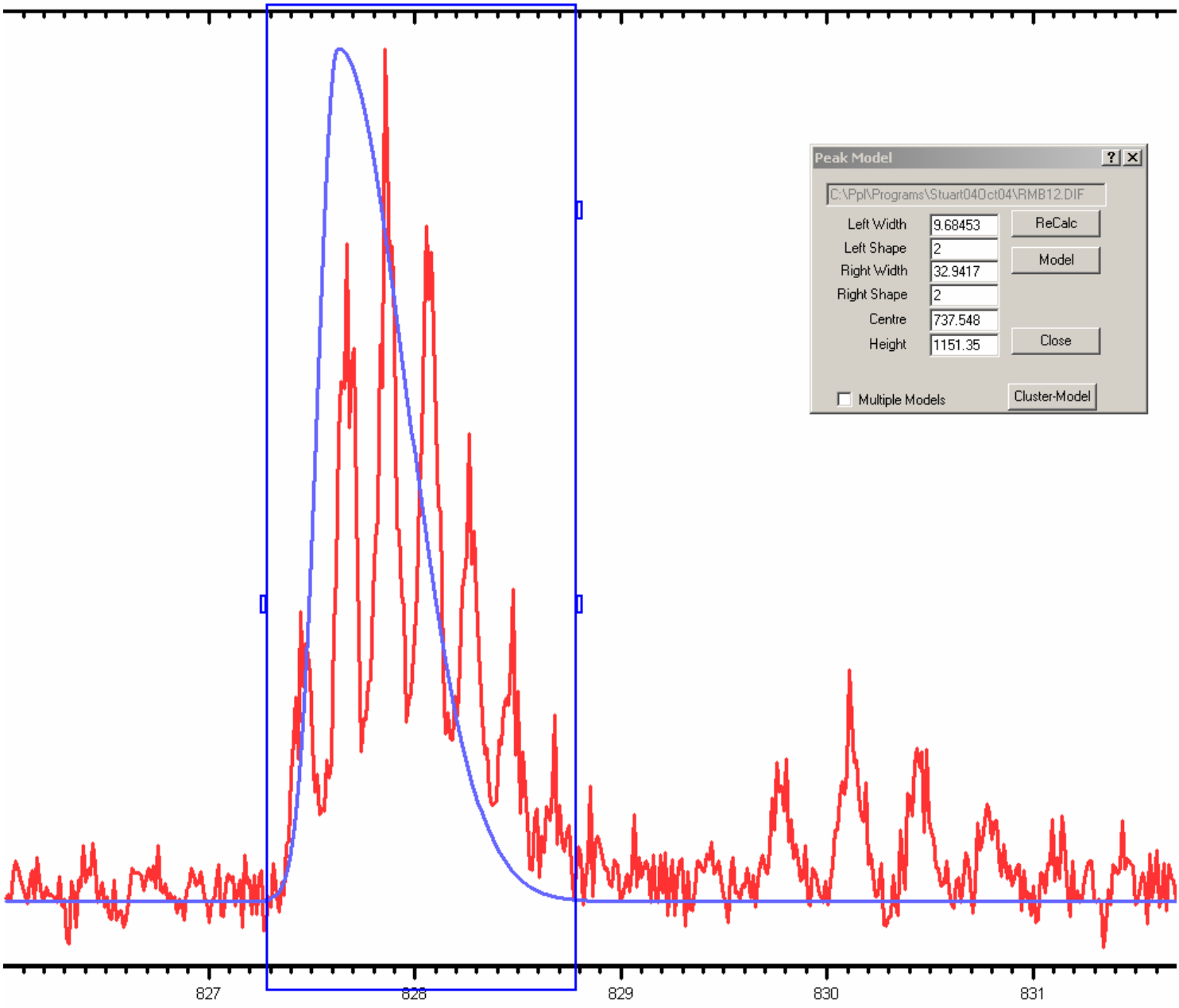

Figure 2. Modelling box.

Selecting the “cluster model” option for these data initiates the automatic fitting. The method is iterative and fits a left and right width (to accommodate any peak width asymmetry) and a left and right shape to the contents of the modelling box to provide a single model that best fits the data. The result is shown in Figure 3.

The user may manually refine the model if required but this may only be necessary in exceptional circumstances when a single peak of a cluster of overlapped peaks is modelled.

The result is shown below in Figure 3.

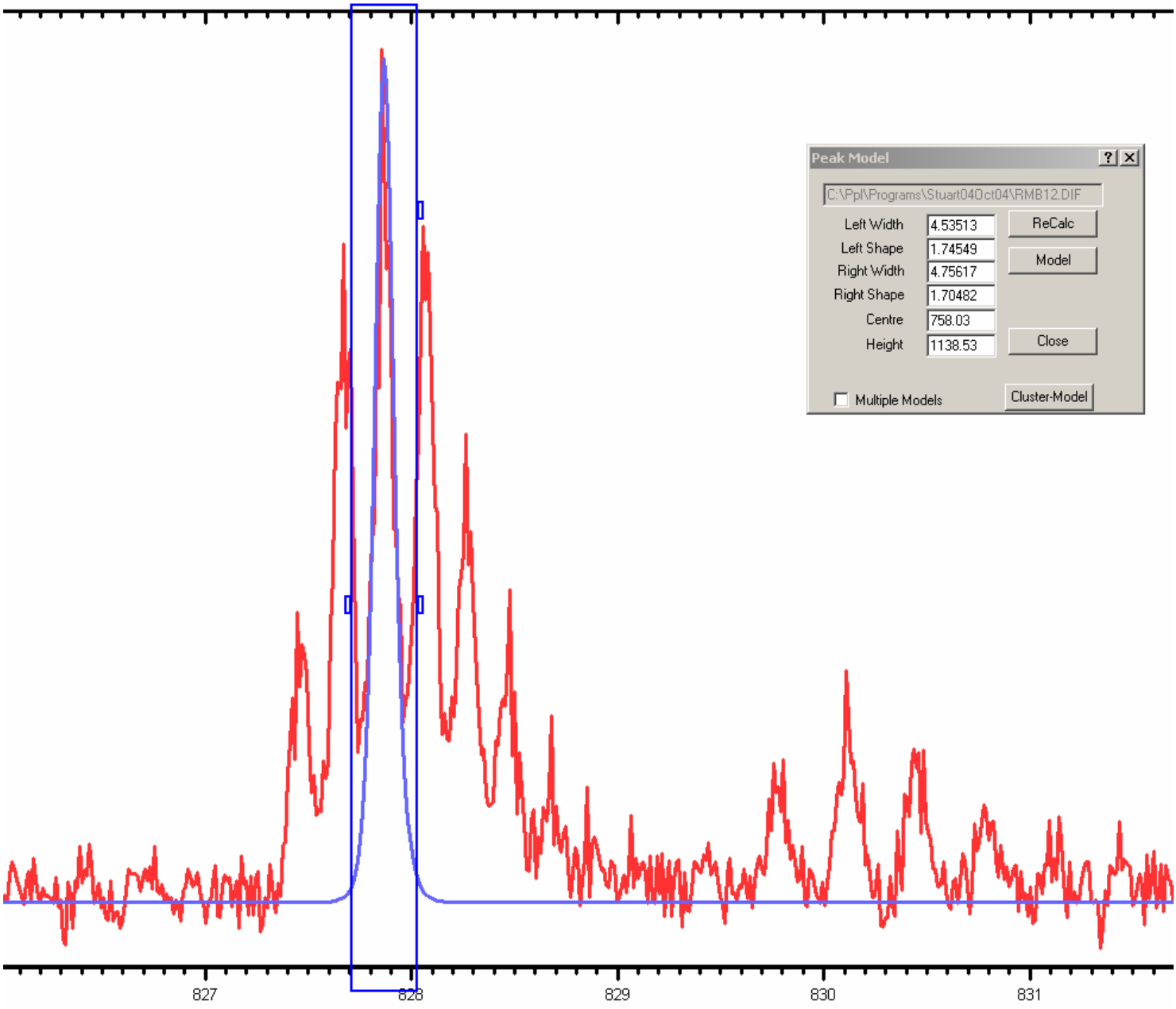

Figure 3. Computed model.

To illustrate the quality of the computed model, Figure 4 shows the computed model overlaid with each data peak.

Note that for data of reasonable S/N where the peak width in sampling intervals is reasonably constant, the modelling box may be set to cover all the data. Other options are available to deal with modelling data in which the peak width varies systematically.

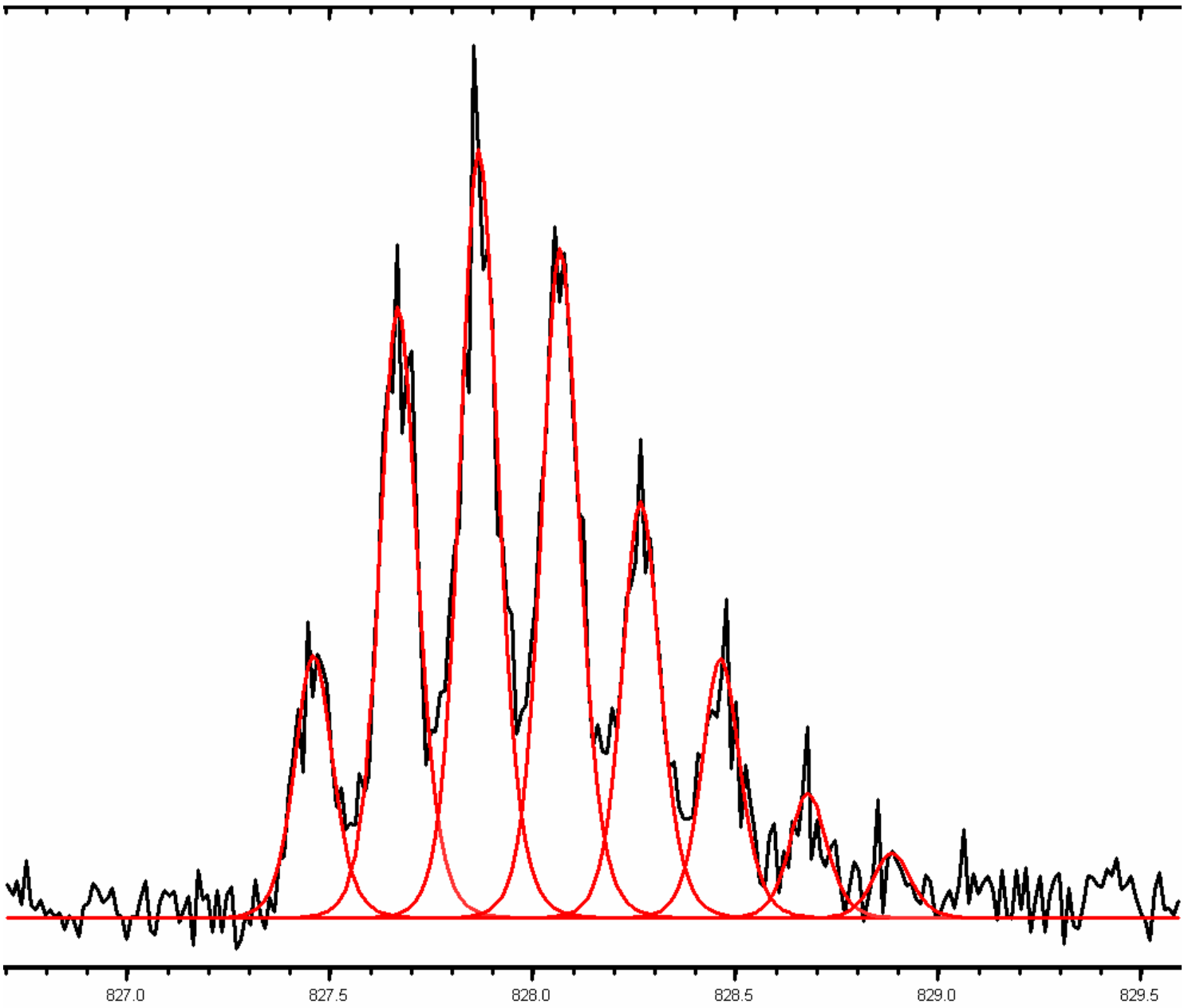

Figure 4. Computed model overlaid on each peak.