Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Formation of water-chlorophyll clusters in dilute samples of chlorophyll-a in ether at low temperature

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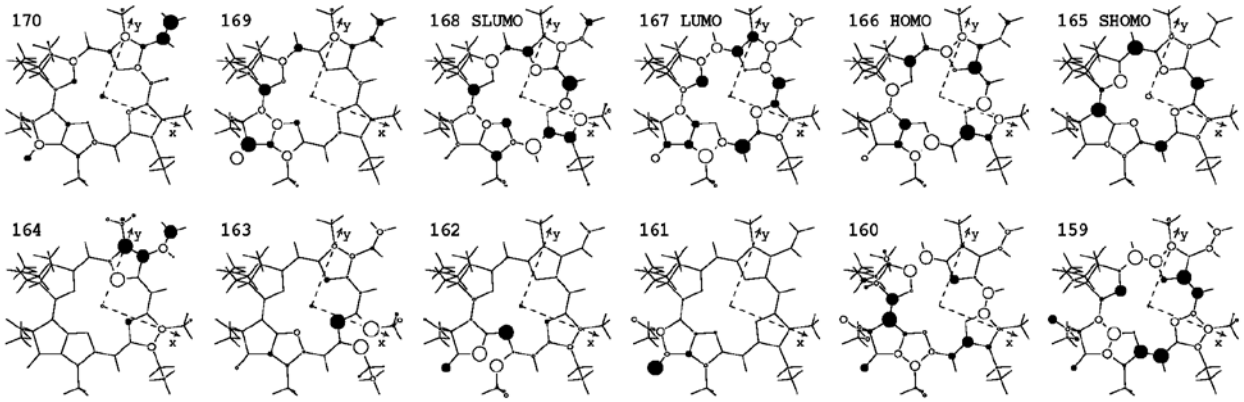
Electronic Supporting Information

S1. Origin of the ligand dependence of the Q_x-Q_y band gap.

The following figure shows the CAM-B3LYP/6-31G* orbital diagrams for chlorophyll a from ref. 27.

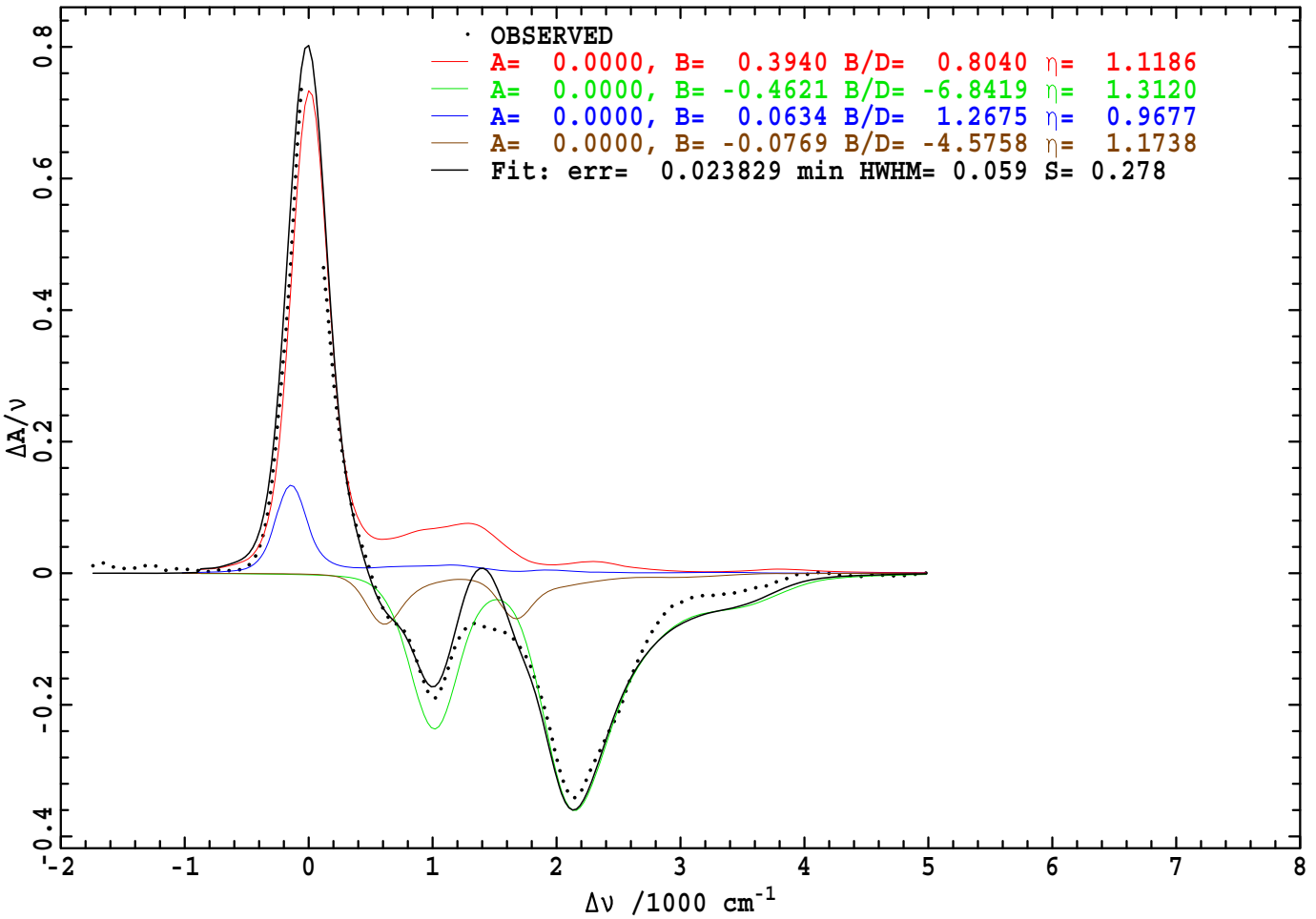


The CAM-B3LYP calculations indicate that the Q_y transition is composed of wavefunction excitations 0.24 165→168 + 0.66 166→167 while Q_x is composed of 0.57 165→167 – 0.39 166→168. Orbital 165, the second-highest-occupied (SHOMO) molecular orbital is therefore important to the Q_x transition whilst orbital 166, the HOMO is important for Q_y. The SHOMO involves a large interaction with the magnesium whilst the HOMO involves very little interaction. Hence ligands which are good Lewis bases destabilize the Q_x excited state much more than they do Q_y, leading to a decrease in the Q_x-Q_y band gap.

S2. Fitted ABS and MCD spectra for Chl-a in ether with contaminant water.

The following figures, one per page, show using dots the observed MCD (top) and ABS (bottom) spectra and their fit to sums of spectral components: black- total fit, colours- each individual component. The pages are, in order, for Fig. 1a-k. The spectra of the 5CO and 6CO mixture components are shown.

Fig. 1a: Chl-a wet ether 186 K



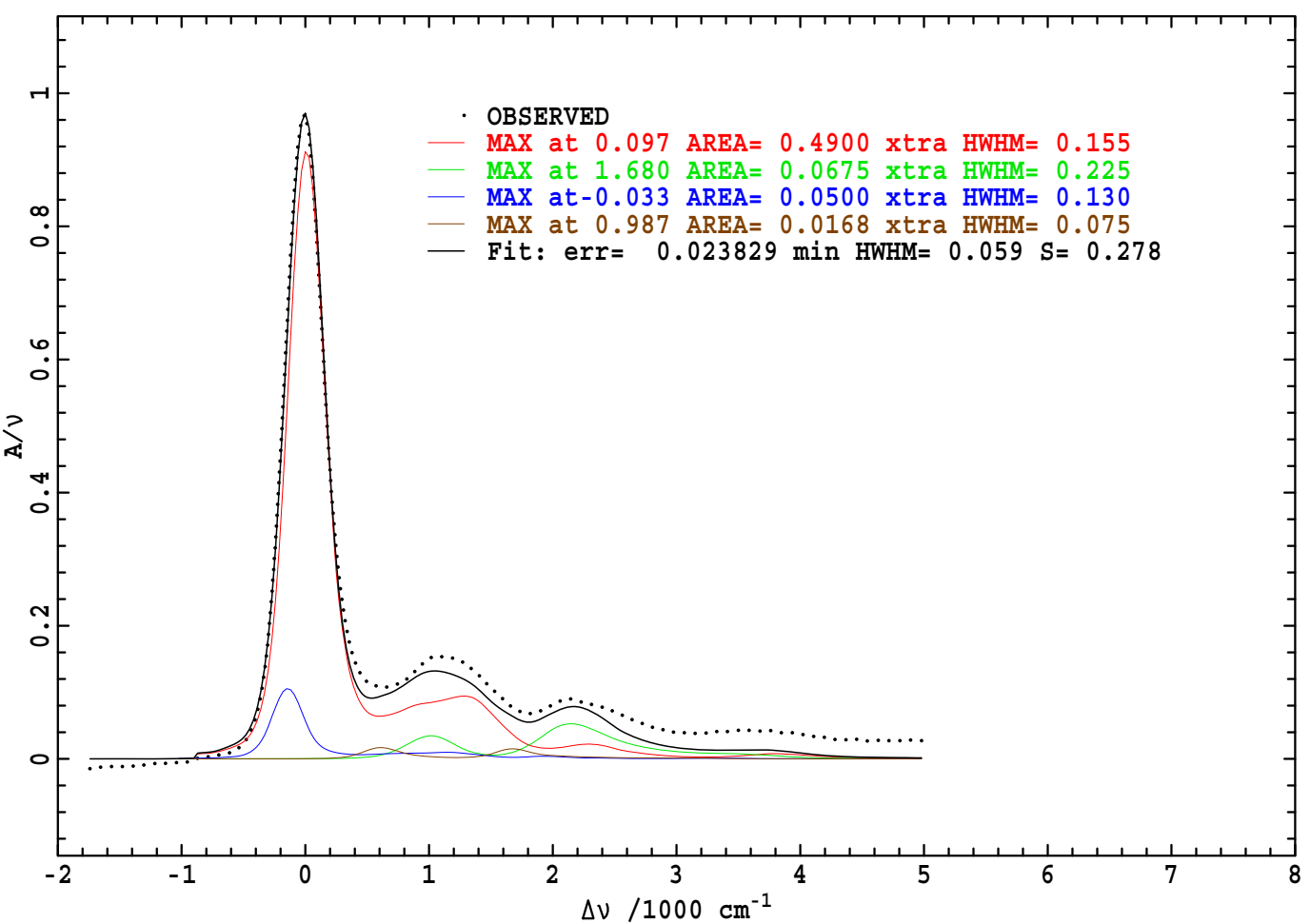
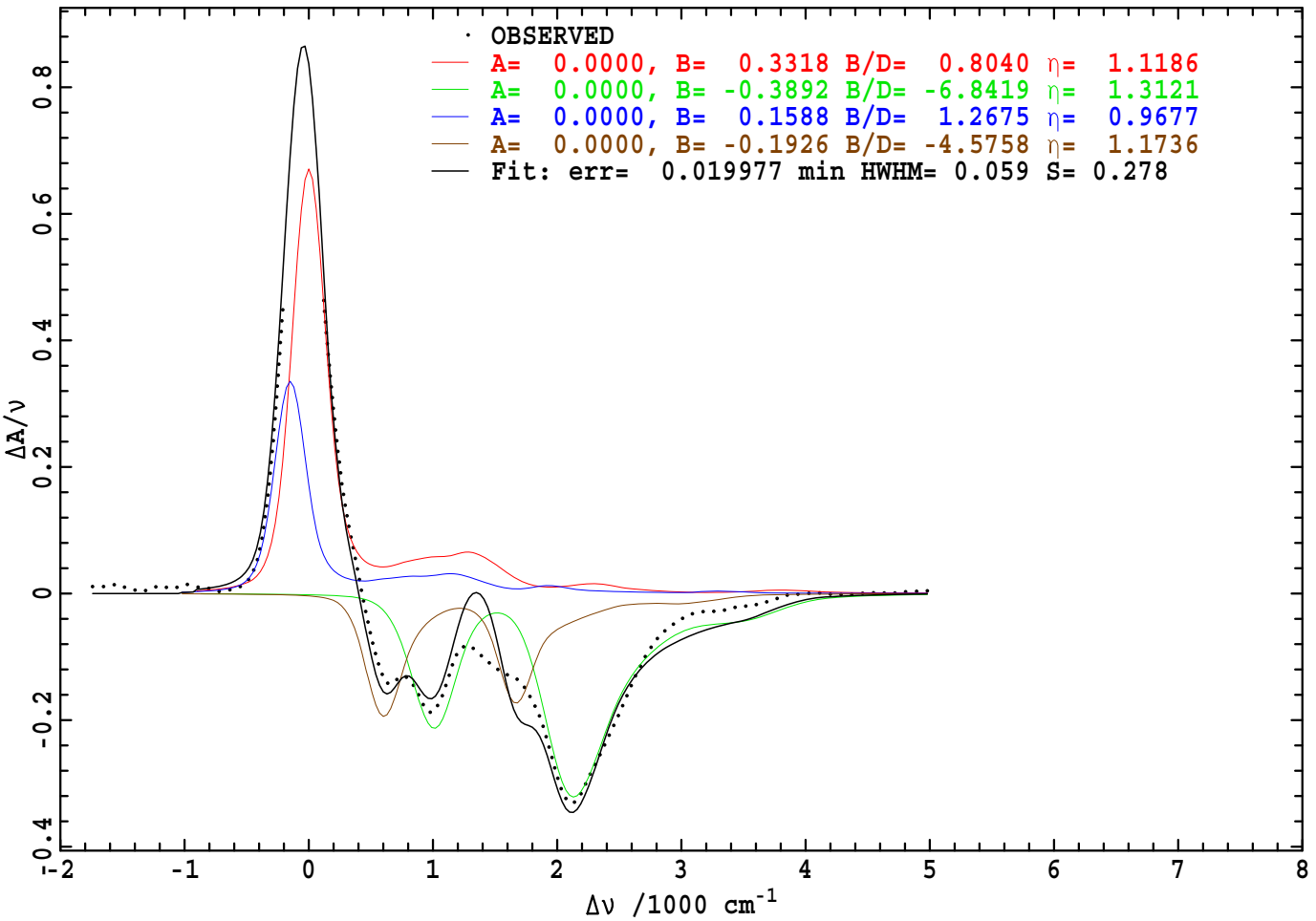


Fig. 1b: Chl-a wet ether 168 K



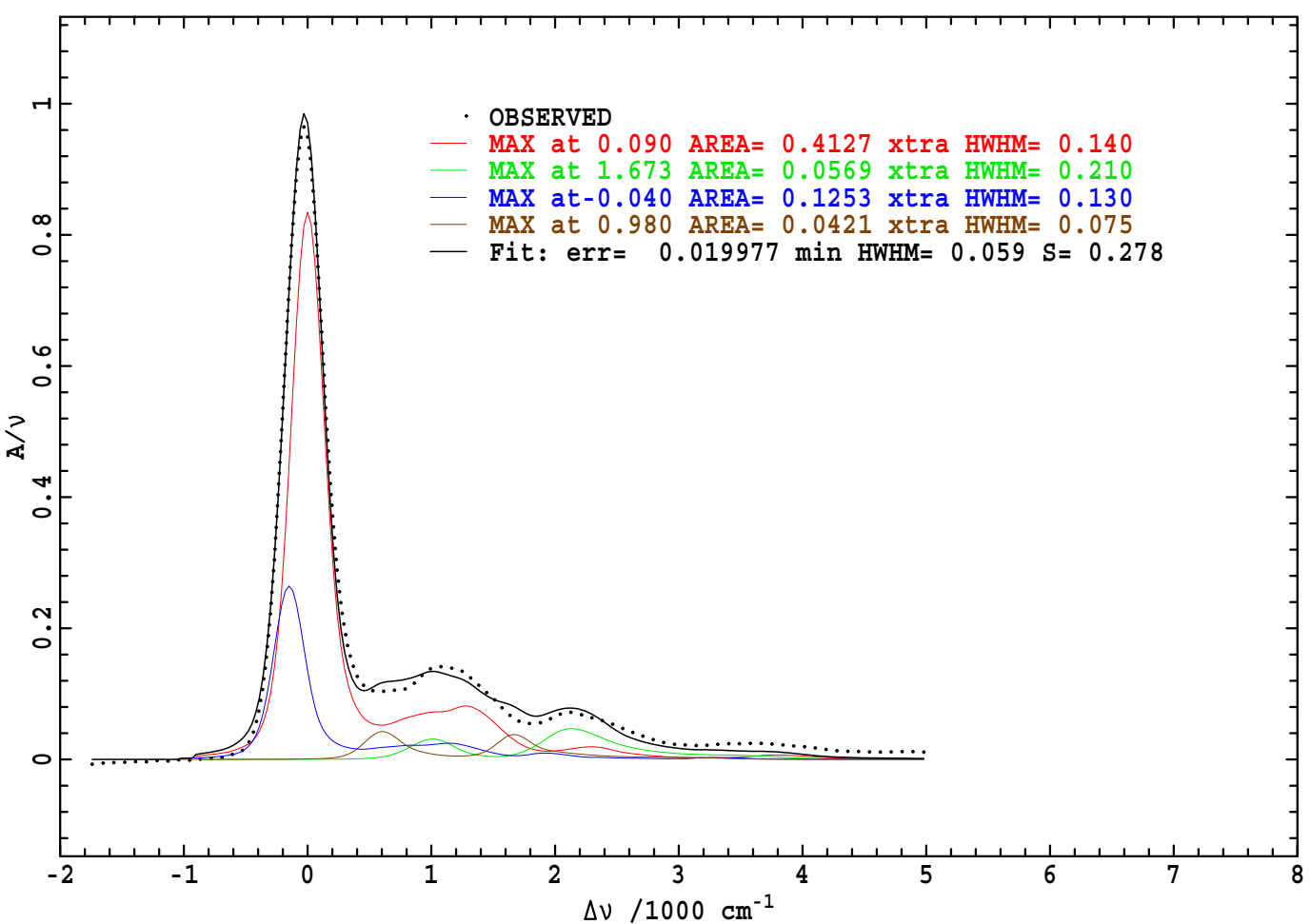
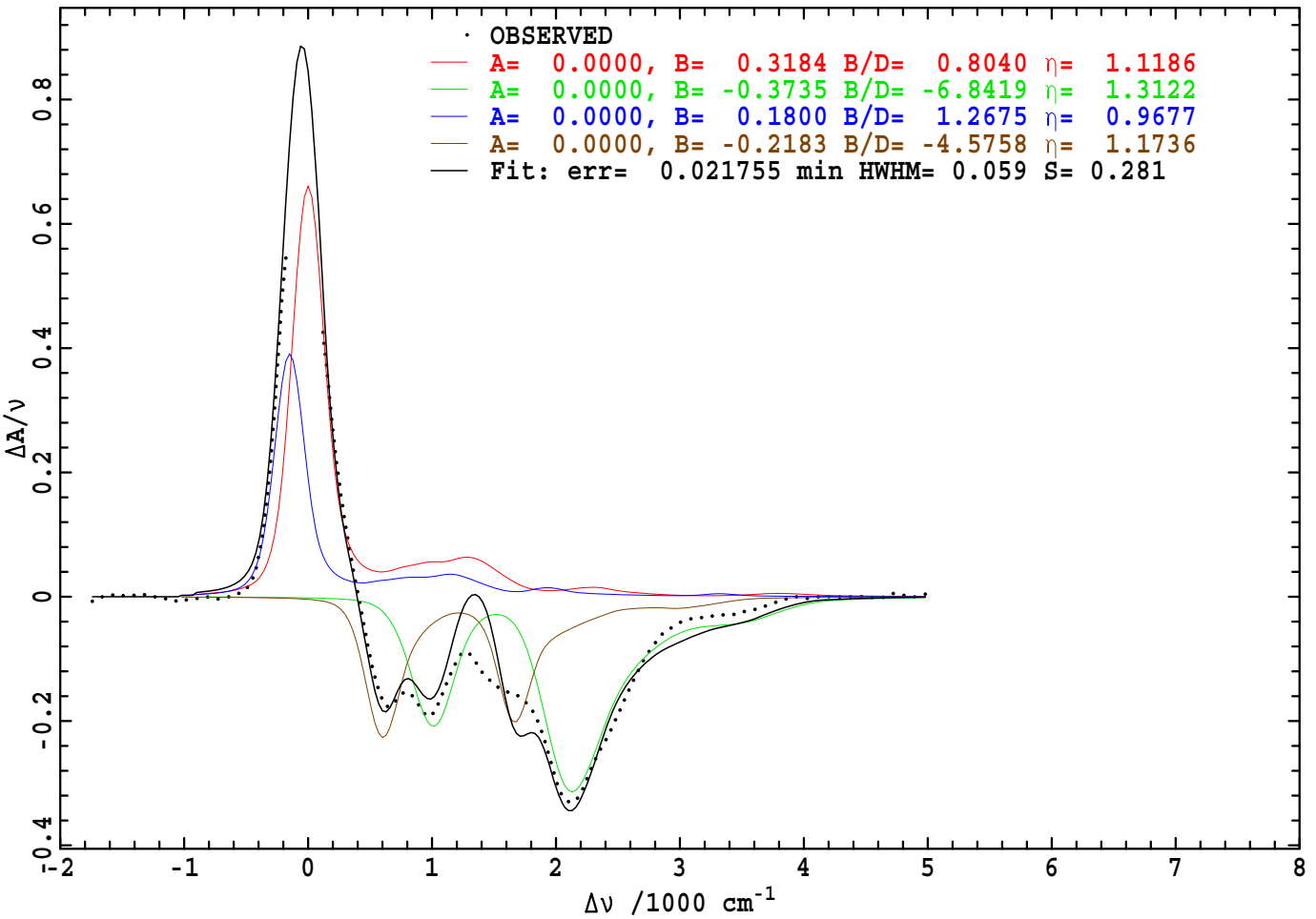


Fig. 1c: Chl-a wet ether 163 K



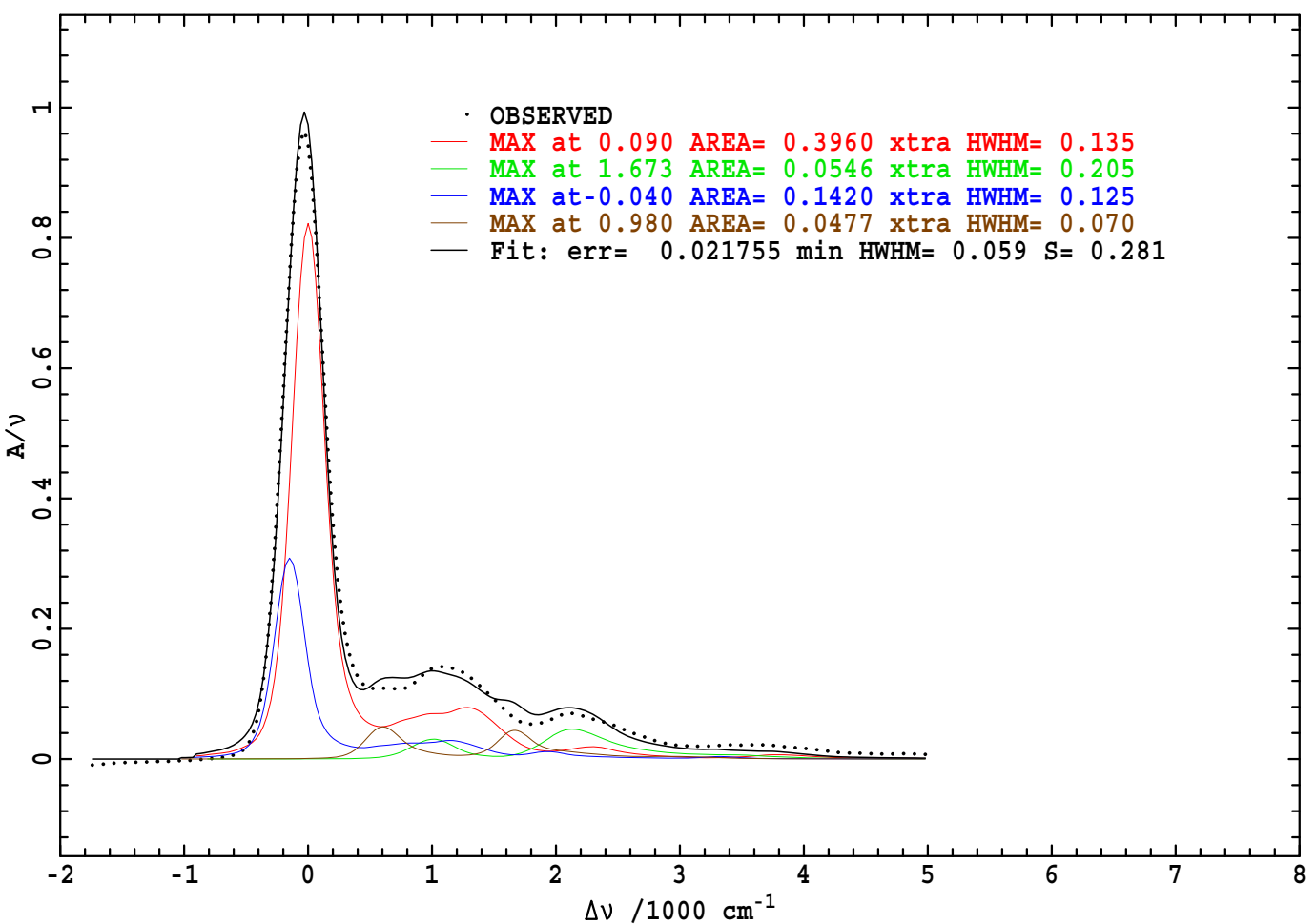
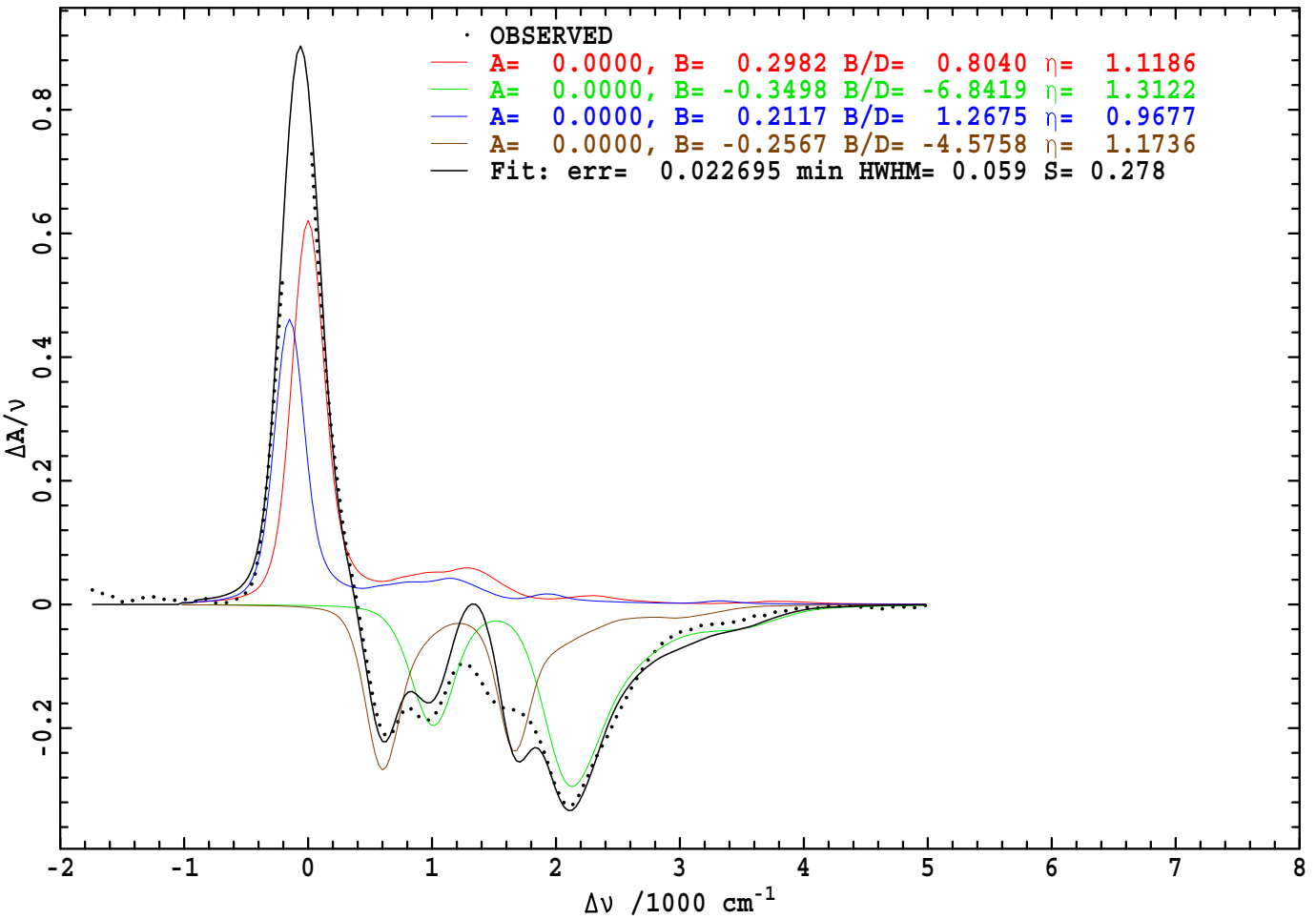


Fig. 1d: Chl-a wet ether 156 K



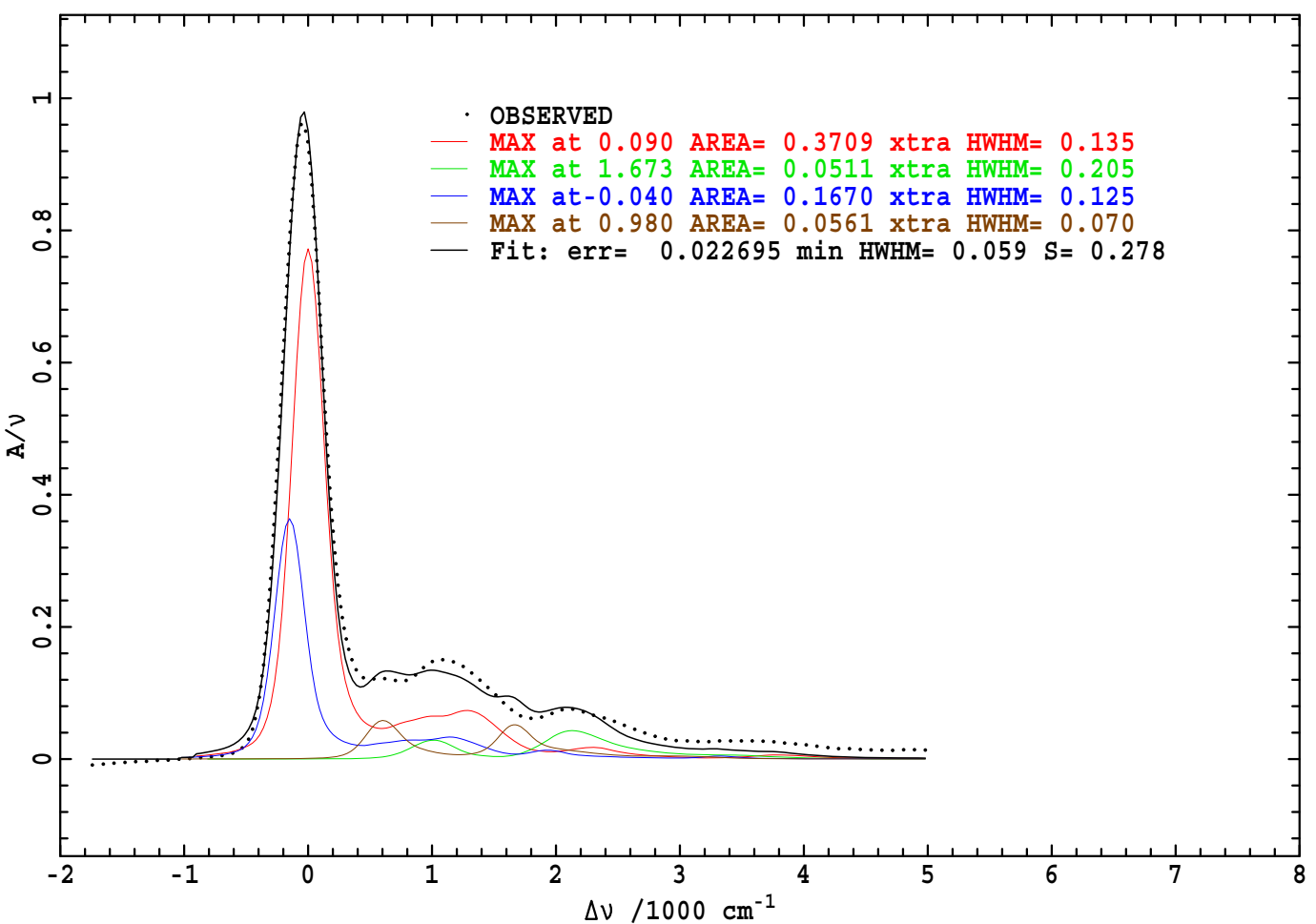


Fig. 1e: Chl-a ether 295 K

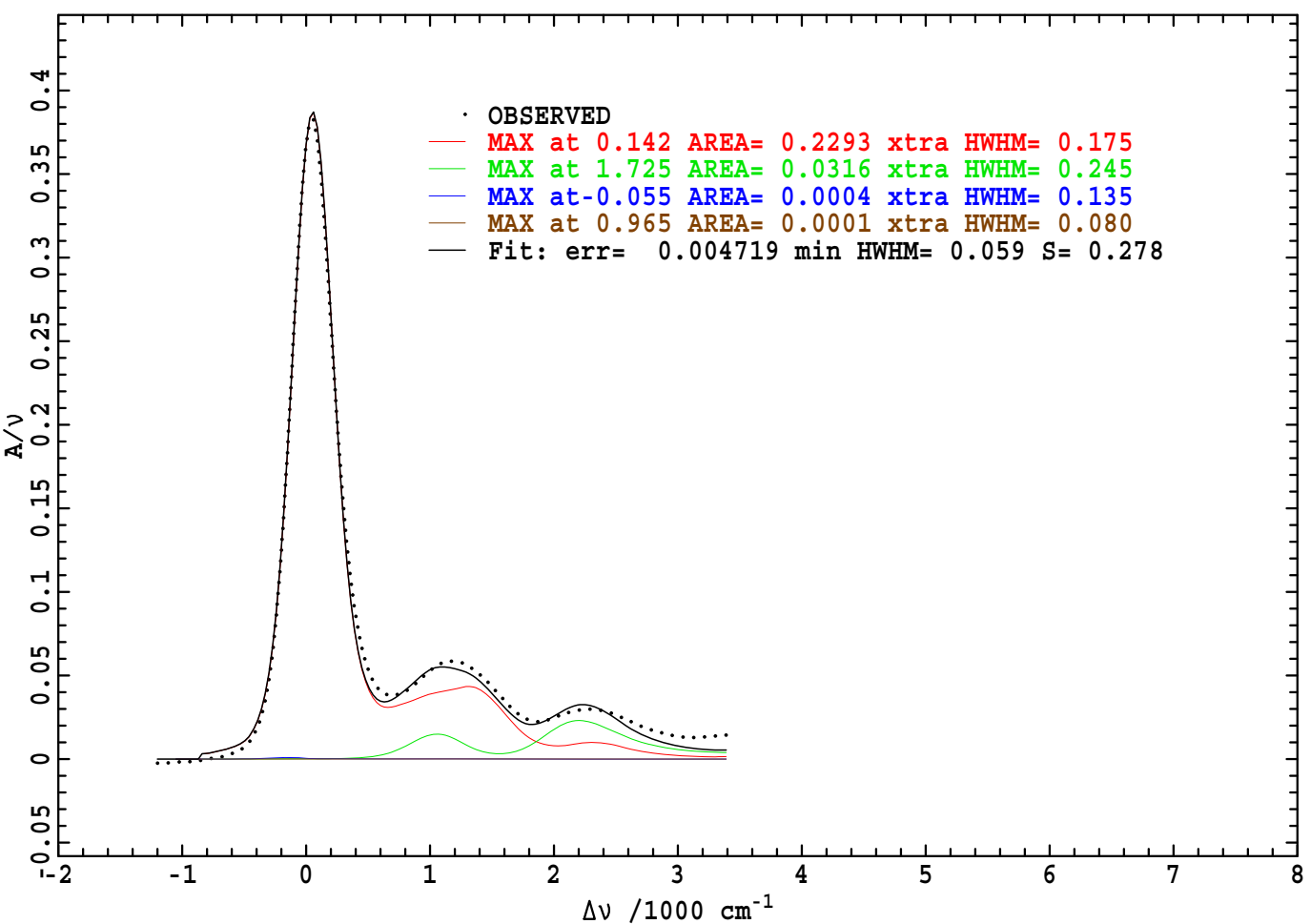


Fig. 1f: Chl-a ether 180 K

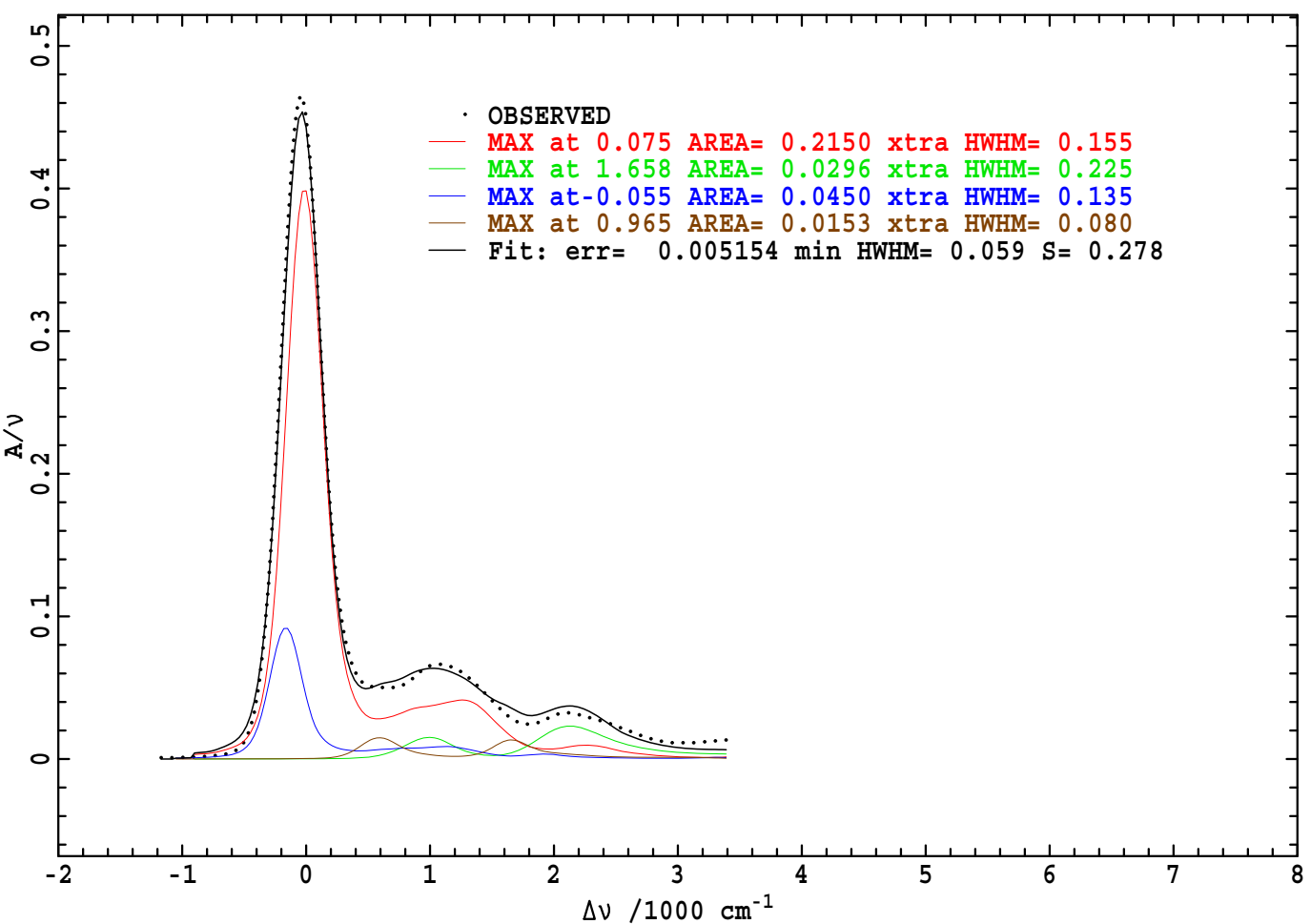


Fig. 1g: Chl-a ether 155 K

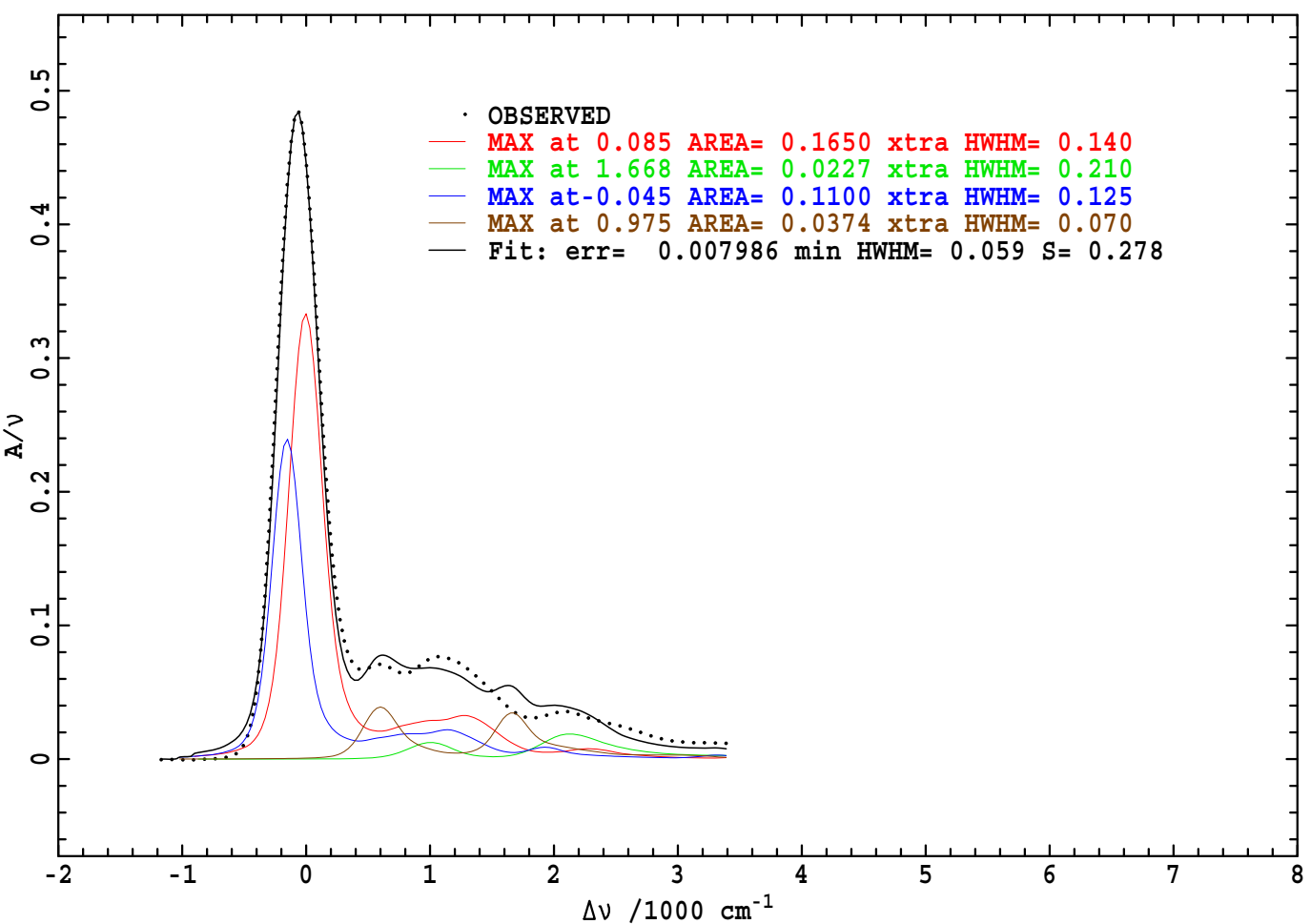


Fig. 1h: Chl-a ether 120 K

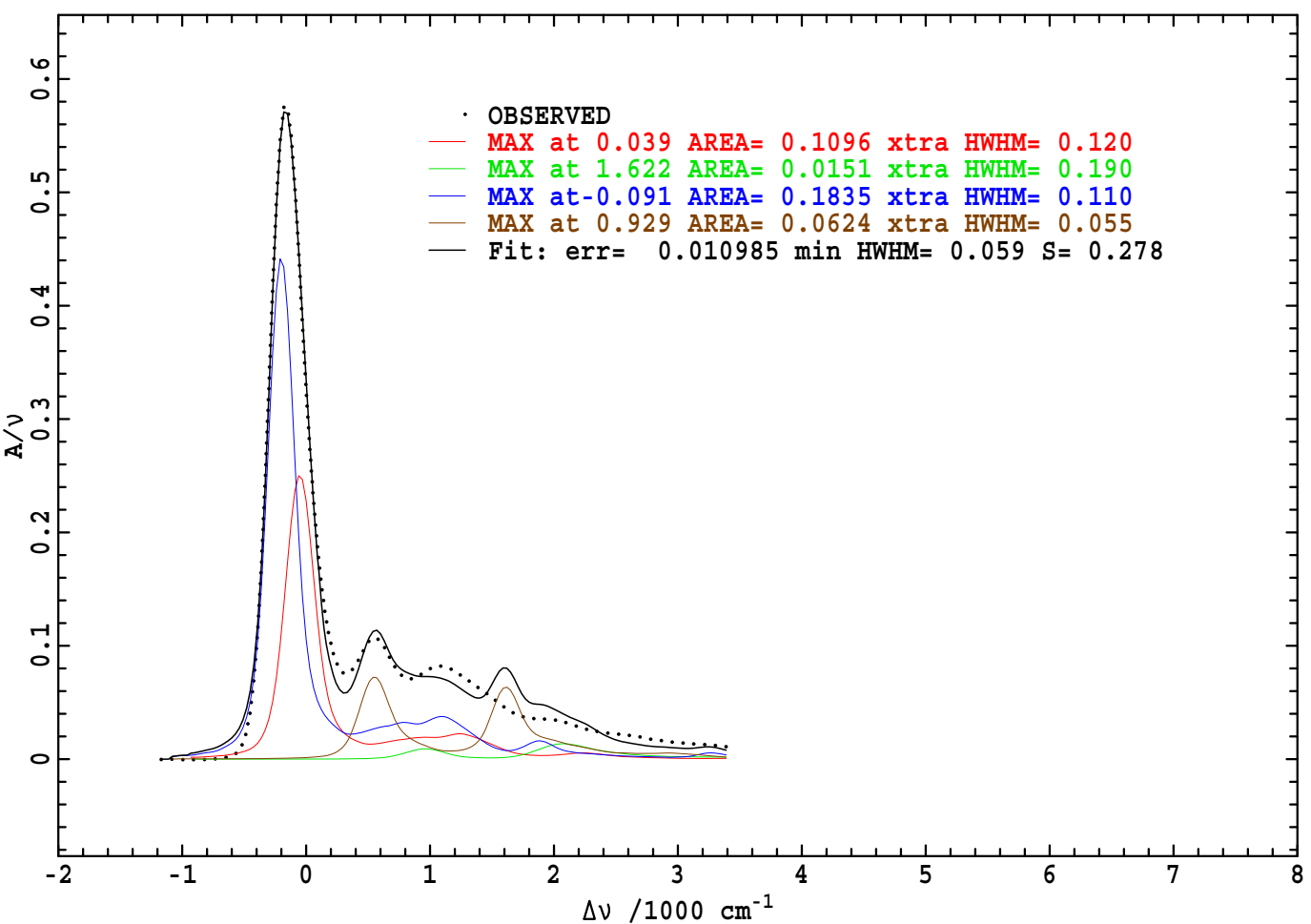
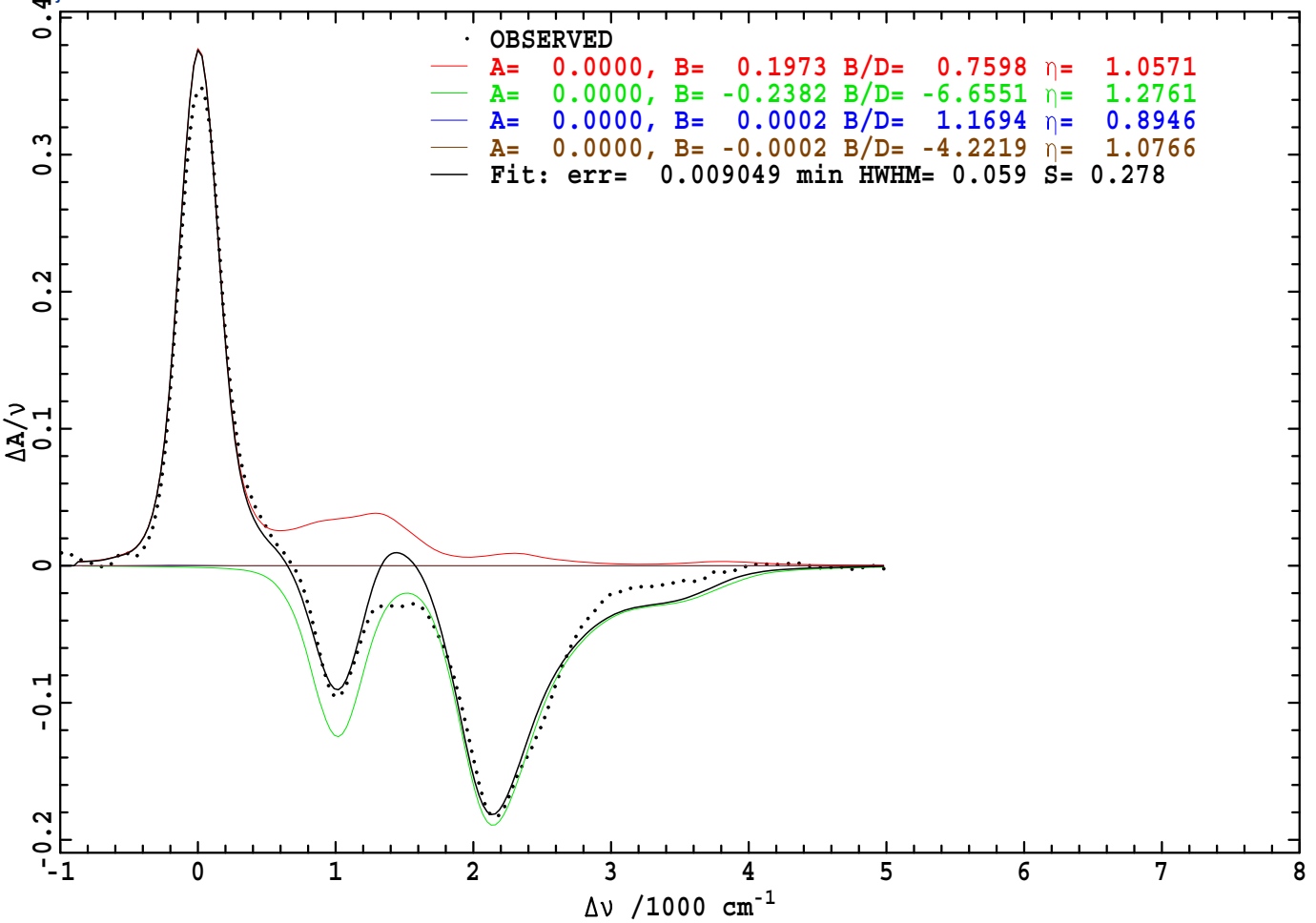


Fig. 11: Chl-a dry ether 180 K



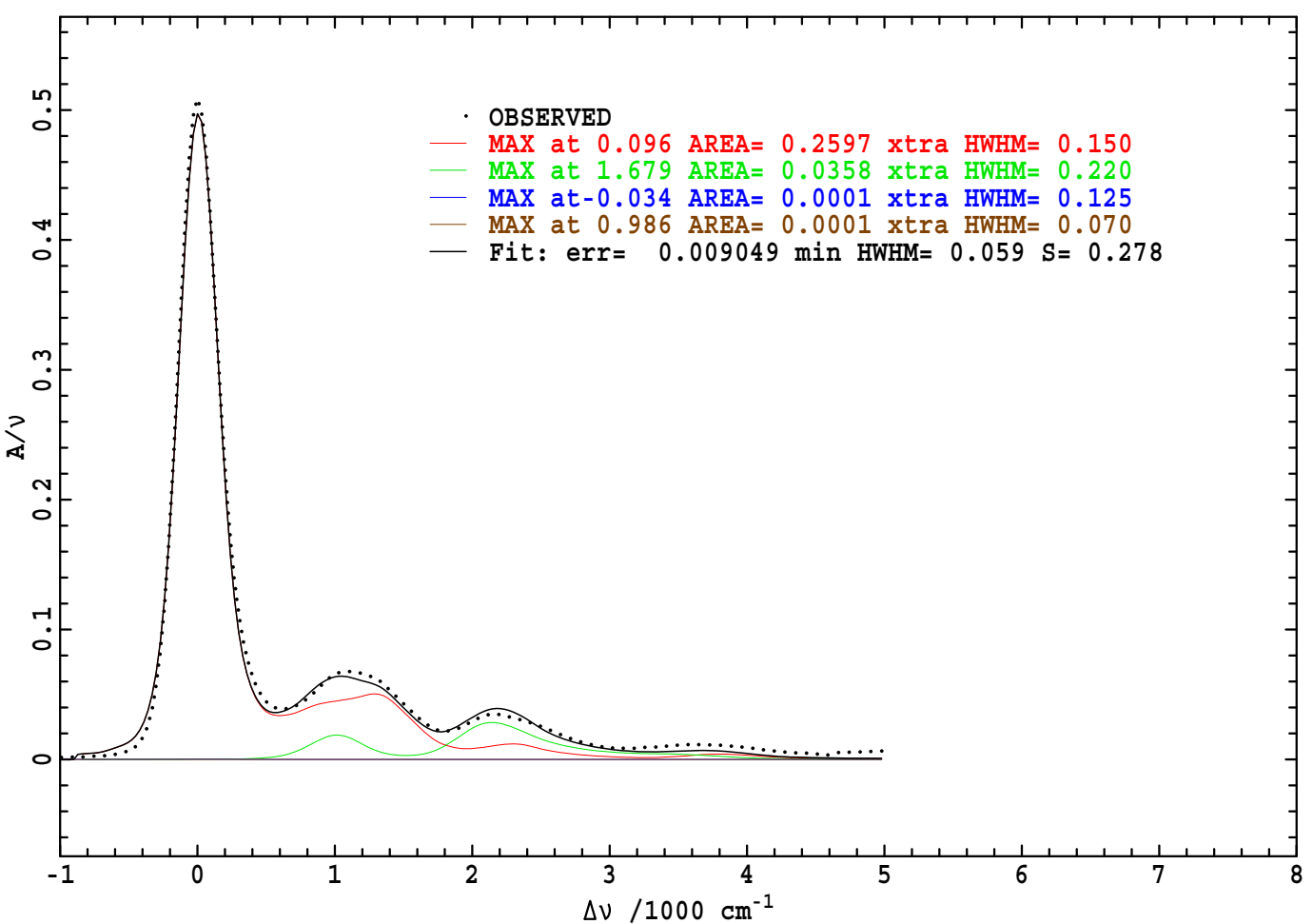
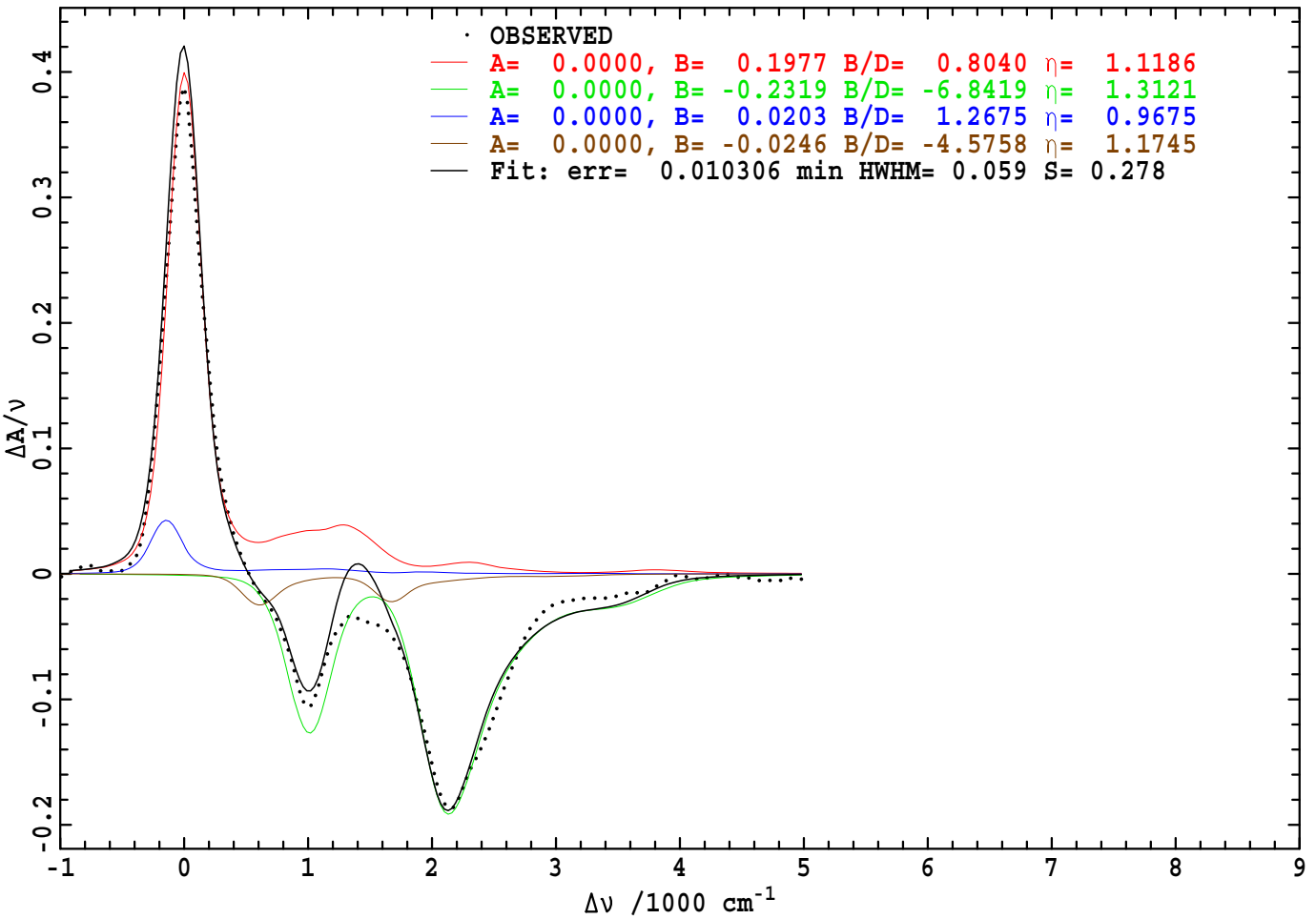


Fig. 1j: Chl-a dry ether 160 K



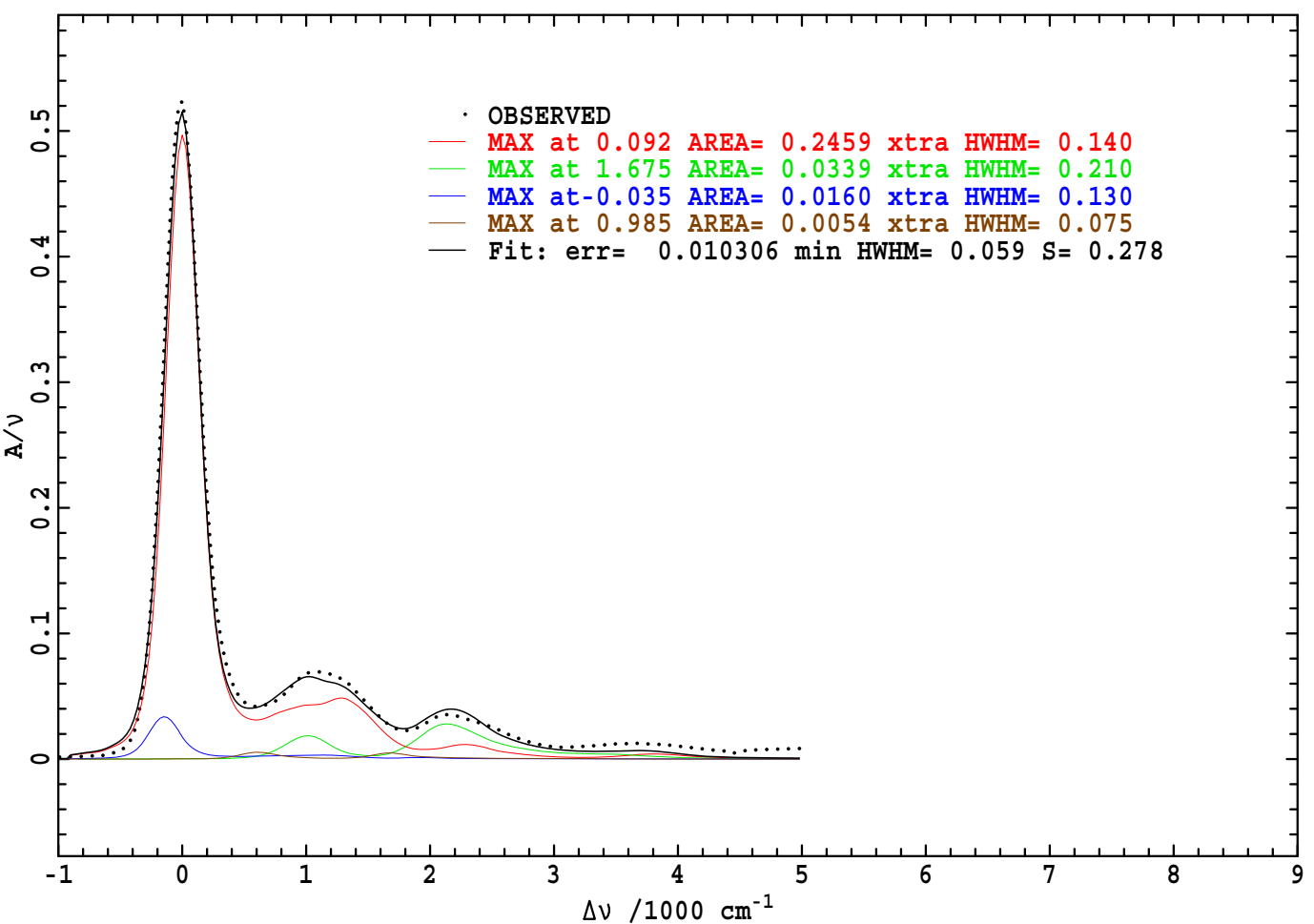


Fig. 1k: Chl-a dry ether 150 K