Determination of the signs and magnitudes of all heteronuclear coupling using IPAP-MODO-FESTA data.
Notebook automatically determines optimum ratio when combining IP and AP data, adjusting ratio and number of points to shift until rms difference is minimum

Automatically determines the optimum ratio when combining the IP and AP data, adjusts the ratio and numbers of points required to shift until the RMS difference is at its minimum.
Information required:
shifts={chemical shift in ppm}; (each chemical shift to be separated by a comma)
widths={width of multiplet in ppm}; (each width to be separated by a comma)
nreps=1; (number of repetitions of that data - typically 1)
filestart=12; (EXPNO in file)
filenamebase=”data/folder/nmr/filename/”; (filepath of data)
procnoIP=”1001”; (PROCNO of IP data)
procnoAP=”1002”; (PROCNO of AP data - ensure IP and AP are processed with identical parameters)

In[ ]:=
```
Clear[Evaluate[Context[] <> "*"]];
vardiff[tspip_, tspap_, ratio_?NumericQ, diff_?NumericQ] :=
  Module[{zspm, len}, len = Length[tspip];
   zspm = Join[Table[0, {i, len}], Join[tspip - ratio tspap, Table[0, {i, len}]]];
   Total[(tspip + ratio tspap - Take[RotateRight[zspm, diff], {len + 1, 2 len}])^2]
  ]; (* Calculate variance between shifted spectra obtained by IPAP processing *)

getpars[filenamebase_, procno_] :=
 Module[{filename}, filename = filenamebase <> "/pdata/" <> procno <> "/procs";
  stream = OpenRead[filename];
  offset = Read[StringToStream[Find[stream, "OFFSET= "]], {Word, Number}][[2]];
  si = Read[StringToStream[Find[stream, "SI= "]], {Word, Number}][[2]];
  Close[stream];
  filename = filenamebase <> "/acqus";
  stream = OpenRead[filename];
  sfo1 = Read[StringToStream[Find[stream, "SFO1= "]], {Word, Number}][[2]];
  swp = Read[StringToStream[Find[stream, "SW= "]], {Word, Number}][[2]];
  Close[stream];
  {offset, si, sfo1, swp}
 ]

process[filenamebaseIP_, filenamebaseAP_, shift_, width_, swp_, offset_, si_, sfo1_] :=
  Module[{diff, dip, start, end, hzpp, ncproc, spip, spap},
   filename = filenamebaseIP <> "/procs";
   stream = OpenRead[filename];
   ncproc = Read[StringToStream[Find[stream, "NC_proc= "]], {Word, Number}][[2]];
   (* Need to correct for any difference in scaling during FT etc. *)
   Close[stream];
   filename = filenamebaseIP <> "/1r";
   spip = 2.^ncproc Import[filename, "Integer32"] / 10^6;
```

```
    filename = filenamebaseAP <> "/procs";
    stream = OpenRead[filename];
    ncproc = Read[StringToStream[Find[stream, "NC_proc= "]], {Word, Number}][[2]];
    (* Need to correct for any difference in scaling during FT etc. *)
    Close[stream];
    filename = filenamebaseAP <> "/1r";
    spap = 2.^ncproc Import[filename, "Integer32"] / 10^6;

    hzpp = swp sfo1 / (si - 1);
    start = Round[sfo1 (offset - shift - width / 2) / hzpp];
    end = Round[sfo1 (offset - shift + width / 2) / hzpp ];
    tspip = Take[spip, {start, end}];
    len = Length[tspip];
    tspap = Take[spap, {start, end}];
    Print[Style["Chemical shift = ", "Subsection"],
     Style[shift, "Subsection"], Style[" ppm", "Subsection"]];
    (* Do optimistion in two stages, otherwise fails to find global minimum *)
    res1 =
     NMinimize[{vardiff[tspip, tspap, fratio, 5 fdiff], fdiff > -len / 5, fdiff < len / 5,
       fratio > 0.8, fratio < 1.2}, {fdiff ∈ Integers, fratio}, MaxIterations → 100];
    res2 = NMinimize[{vardiff[tspip, tspap, fratio, fdiff], fratio > 0.5,
       fratio < 1.2, fdiff > Round[ (5 fdiff /. res1[[2]]) ] - len / 10,
       fdiff < Round[len / 10 + 5 fdiff /. res1[[2]]]},
      {fdiff ∈ Integers, fratio}, MaxIterations → 1000];
    Print["Variance and optimised shift and ratio:"];
    Print[res2];
    ratio = fratio /. res2[[2]];
    spp = tspip + ratio tspap;
    spm = tspip - ratio tspap;
    Print[Style["Input data", "Subsection"]];
    Print[ListPlot[{spp, spm}, Joined → True, PlotRange → All]];
    len = Length[spp];
    zspm = Join[Table[0, {i, len}], Join[spm, Table[0, {i, len}]]];
    diff = Table[0, {i, 2 len + 1}];
    For[i = 1, i ≤ Length[diff], i++,
     diff[[i]] = Total[ (spp - Take[RotateRight[zspm, len - i], {len + 1, 2 len}]) ^2];
    ];
Print[Style["RMS difference vs displacement in data points", "Subsection"]];
    Print[ListPlot[diff, Joined → True, PlotRange → All]];
    min = Min[diff];
    For[i = 1, i ≤ Length[diff], i++, If[diff[[i]] == min, minpoint = i];];
    Print[Style[
      "Expansion of RMS difference vs displacement in data points, with parabolic fit",
      "Subsection"]];
    dip = Take[diff, {minpoint - 10, minpoint + 10}];
    dipfit = NonlinearModelFit[dip, a + b (x - x0) ^2, {a, b, x0}, x];
    Print[
     Show[{Plot[dipfit[x], {x, 1, Length[dip]}, PlotRange → {All, {0, 1.1 Max[dip]}}],
       ListPlot[dip, Joined → False, PlotRange → All]}]];
    Print["Interpolated frequency shift with best match is ",
     -hzpp ((x0 /. dipfit["BestFitParameters"]) + minpoint - 11 - len), " Hz"];
    -hzpp ((x0 /. dipfit["BestFitParameters"]) + minpoint - 11 - len)
   ];
```

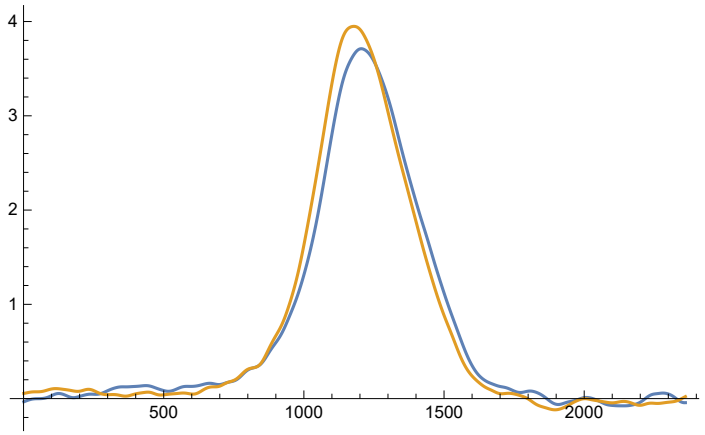
```
shifts = {6.4649, 5.4092, 2.433, 2.287, 1.786};
widths = {0.09, 0.23, 0.16, 0.13, 0.15};
njs = Length[shifts];
nreps = 2;
filestart = 13;
js = Table[0, njs, nreps];
filenamebase = "W:/CM/2022/b500b07/data/IPAP-FESTA/nmr/220128-FormFlut_CDCl3/";
procnoIP = "1001";
procnoAP = "1002";
getpars[filenamebase <> ToString[filestart], procnoIP];
starttime = AbsoluteTime[];
For[jnumber = 1, jnumber ≤ Length[shifts], jnumber++,
  For[rep = 1, rep ≤ nreps, rep++,
    filename = filenamebase <> ToString[filestart + rep - 1] <> "/pdata/";
    js[[jnumber, rep]] = process[filename <> procnoIP, filename <> procnoAP,
      shifts[[jnumber]], widths[[jnumber]], swp, offset, si, sfo1];
   ];
 ];
Print[Style["Coupling constants", "Subsection"]];
TableForm[js]
jslb1 = js;
timeused = AbsoluteTime[] - starttime;
Print["Time used = ", timeused, "seconds"];
meansdandsdmean[x_] := {Mean[x], Sqrt[Variance[x] / ((Length[x] - 1))],
   Sqrt[Variance[x] / (Length[x] (Length[x] - 1))]};
If[nreps > 1, reslb1 = Table[0, Length[shifts]];
 reslb1 = Prepend[
   Table[Flatten[{shifts[[i]], meansdandsdmean[jslb1[[i]]]}], {i, Length[shifts]}],
   {"Shift / ppm", "JHF / Hz", "std dev / Hz", "sd of mean of J / Hz"}];
 Print[TableForm[reslb1]];]
```

Chemical shift = 6.4649 ppm

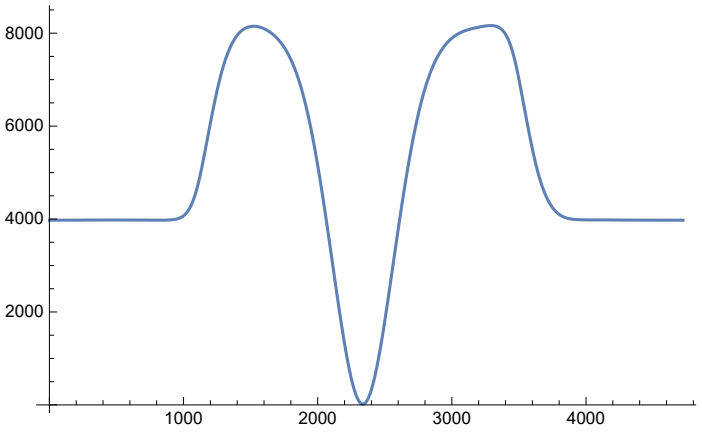
Variance and optimised shift and ratio:

$\{16.8346, \{\text{fdiff} \to 24, \text{fratio} \to 0.5\}\}$

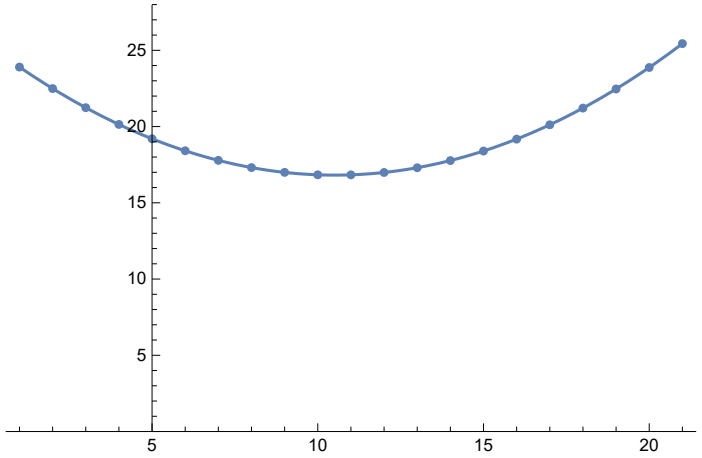
Input data



RMS difference vs displacement in data points



Expansion of RMS difference vs displacement in data points, with parabolic fit



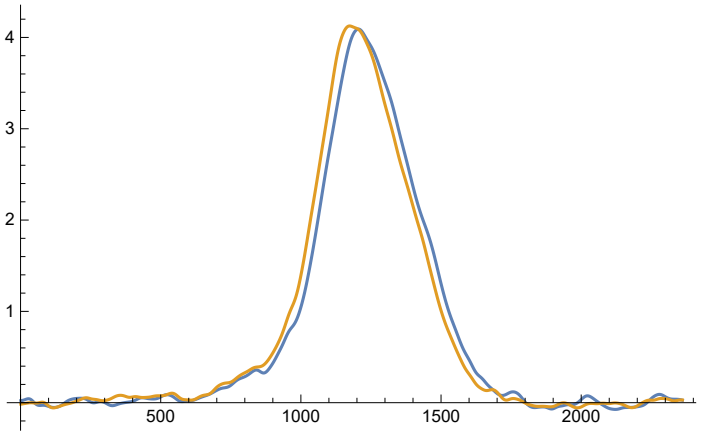

```
Interpolated frequency shift with best match is 0.467096 Hz
```

Chemical shift = 6.4649 ppm

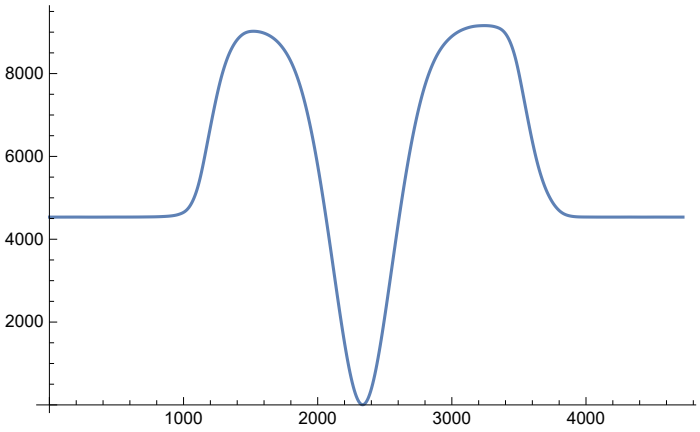
```
Variance and optimised shift and ratio:
```

$$\{4.77851, \{\text{fdiff} \to 26, \text{fratio} \to 0.5\}\}$$

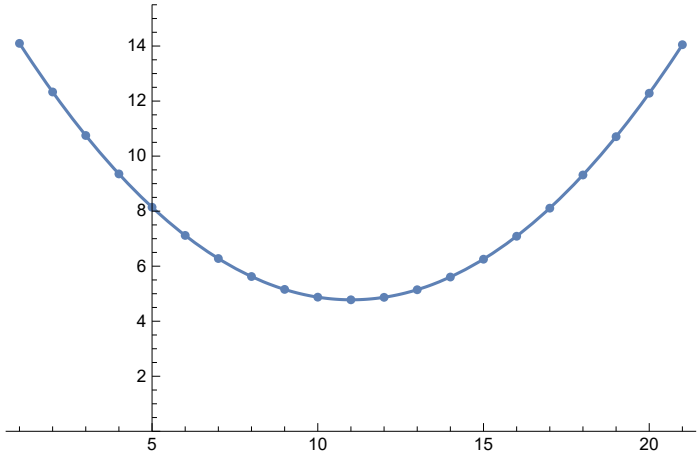
Input data



RMS difference vs displacement in data points



Expansion of RMS difference vs displacement in data points, with parabolic fit



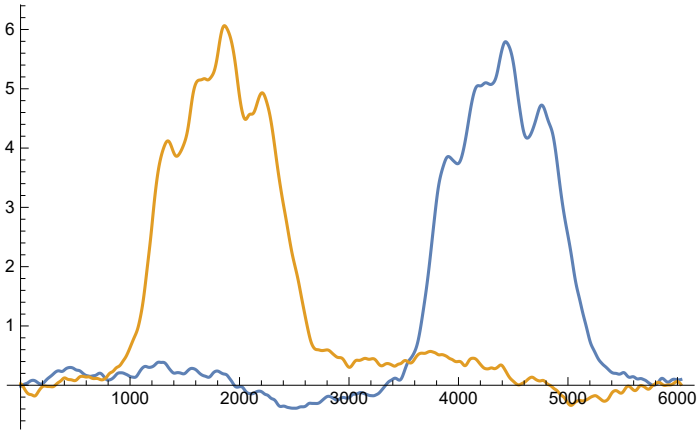

```
Interpolated frequency shift with best match is 0.495639 Hz
```

Chemical shift = 5.4092 ppm

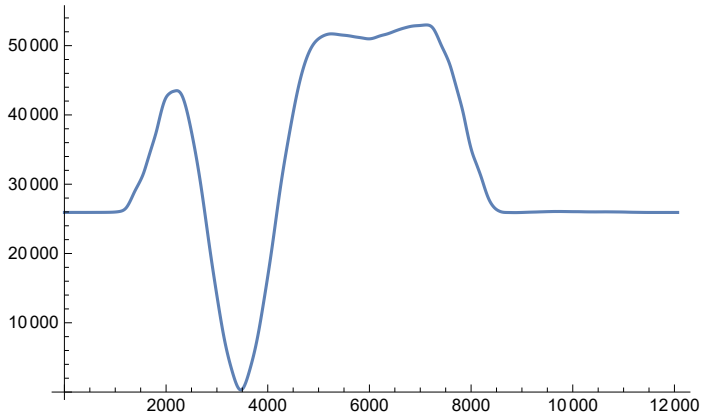
```
Variance and optimised shift and ratio:
```

```
{311.982, {fdiff → 2562, fratio → 0.991657}}
```

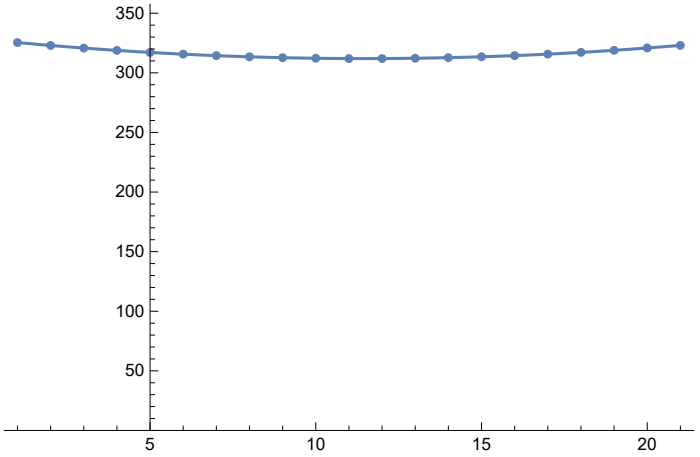
Input data



RMS difference vs displacement in data points



Expansion of RMS difference vs displacement in data points, with parabolic fit



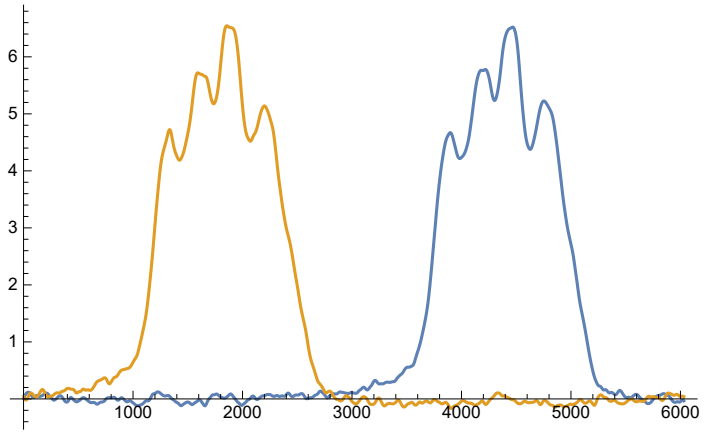

```
Interpolated frequency shift with best match is 48.8572 Hz
```

Chemical shift = 5.4092 ppm

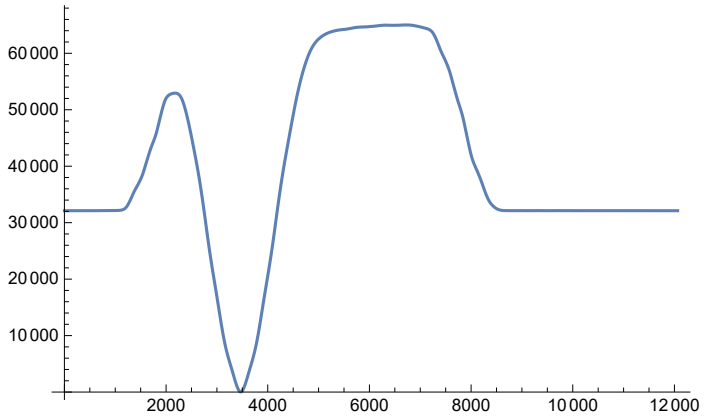
```
Variance and optimised shift and ratio:
```

$$\{32.6643, \{\text{fdiff} \to 2563, \text{fratio} \to 1.07171\}\}$$

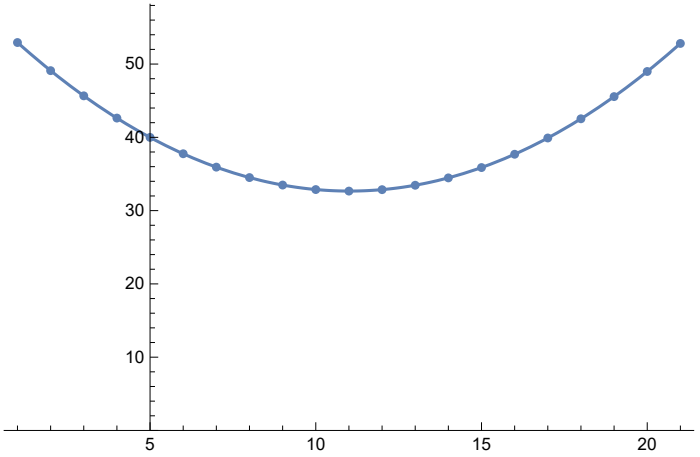
Input data



RMS difference vs displacement in data points



Expansion of RMS difference vs displacement in data points, with parabolic fit



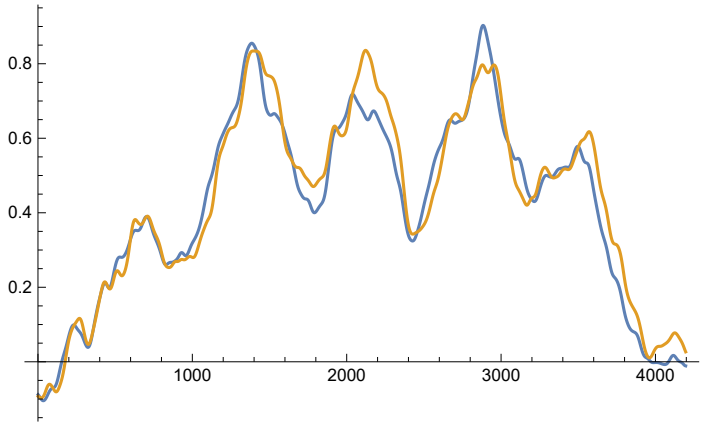

```
Interpolated frequency shift with best match is 48.8852 Hz
```

Chemical shift = 2.433 ppm

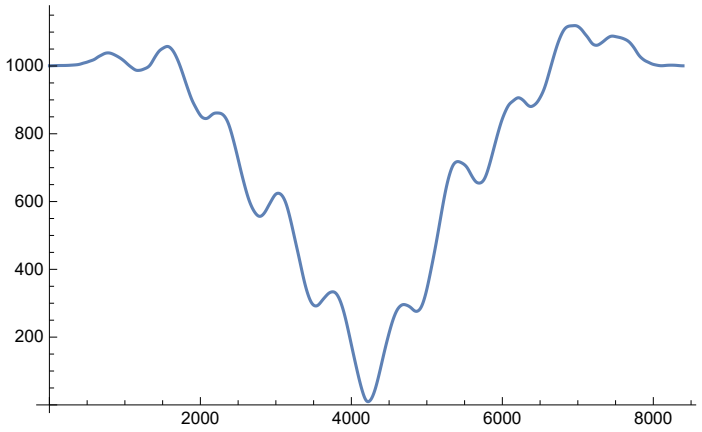
```
Variance and optimised shift and ratio:
```

$$\{9.61546, \{\text{fdiff} \to -25, \text{fratio} \to 0.5\}\}$$

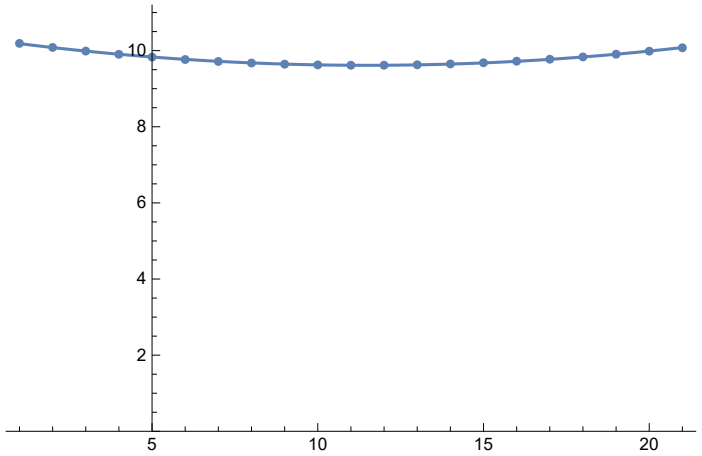
Input data



RMS difference vs displacement in data points



Expansion of RMS difference vs displacement in data points, with parabolic fit



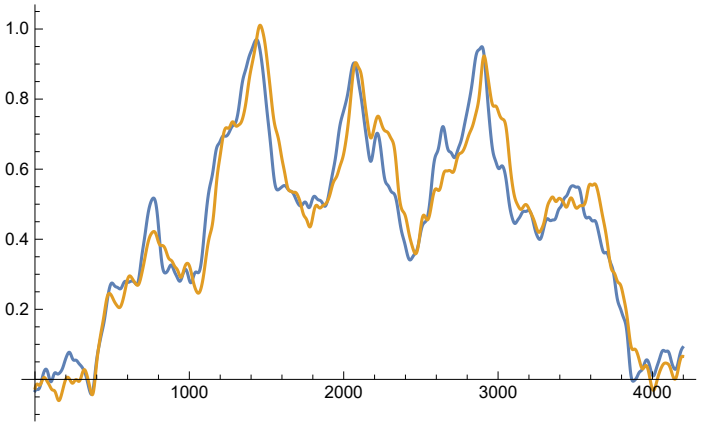

```
Interpolated frequency shift with best match is -0.486352 Hz
```

Chemical shift = 2.433 ppm

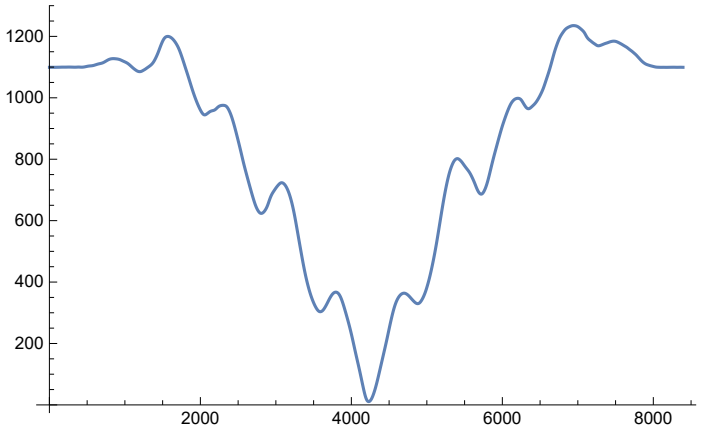
```
Variance and optimised shift and ratio:
```

```
{10.8492, {fdiff → -34, fratio → 0.5}}
```

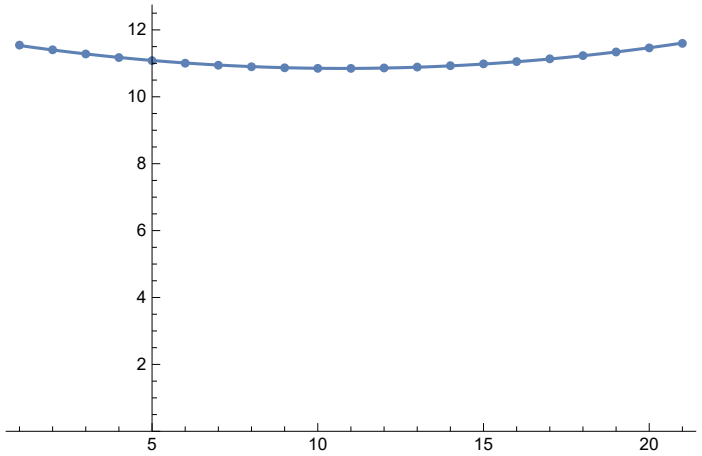
Input data



RMS difference vs displacement in data points



Expansion of RMS difference vs displacement in data points, with parabolic fit



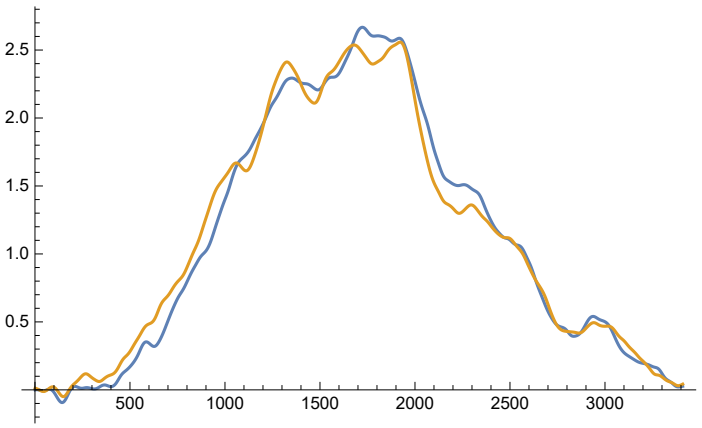

```
Interpolated frequency shift with best match is -0.643692 Hz
```

Chemical shift = 2.287 ppm

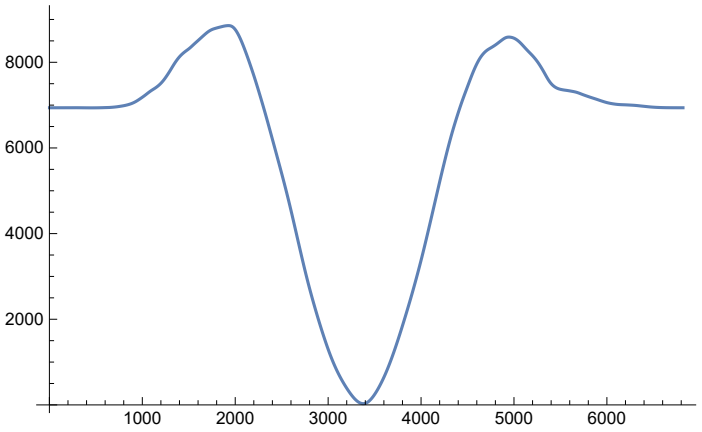
```
Variance and optimised shift and ratio:
```

```
{28.9295, {fdiff → 31, fratio → 0.5}}
```

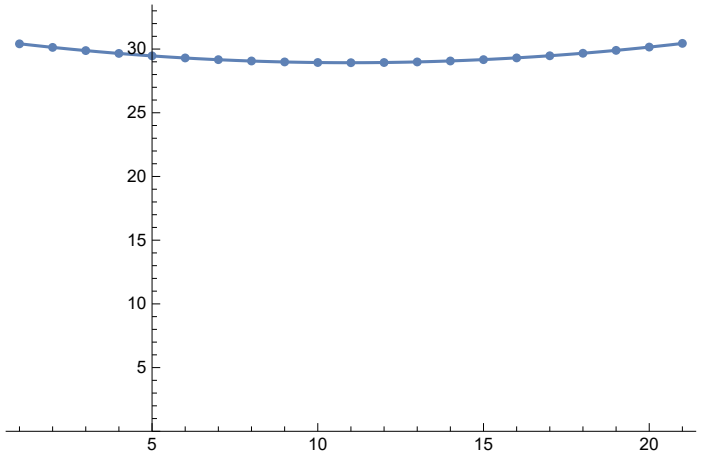
Input data



RMS difference vs displacement in data points



Expansion of RMS difference vs displacement in data points, with parabolic fit



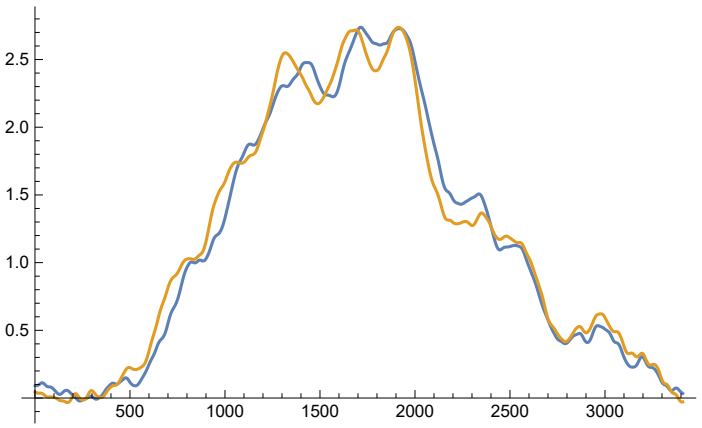

```
Interpolated frequency shift with best match is 0.592004 Hz
```

Chemical shift = 2.287 ppm

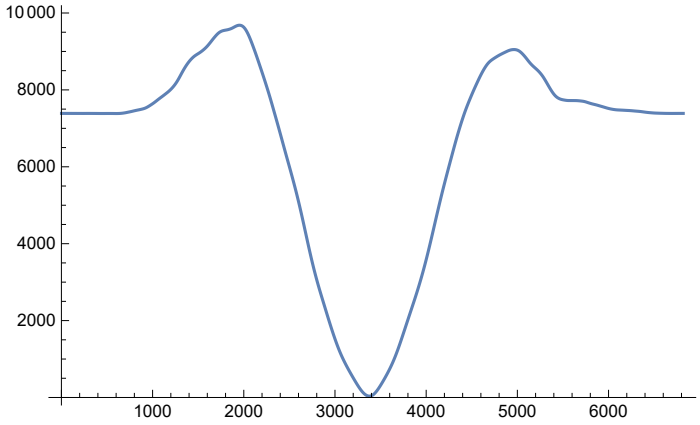
```
Variance and optimised shift and ratio:
```

$$\{35.6326, \{\text{fdiff} \to 31, \text{fratio} \to 0.5\}\}$$

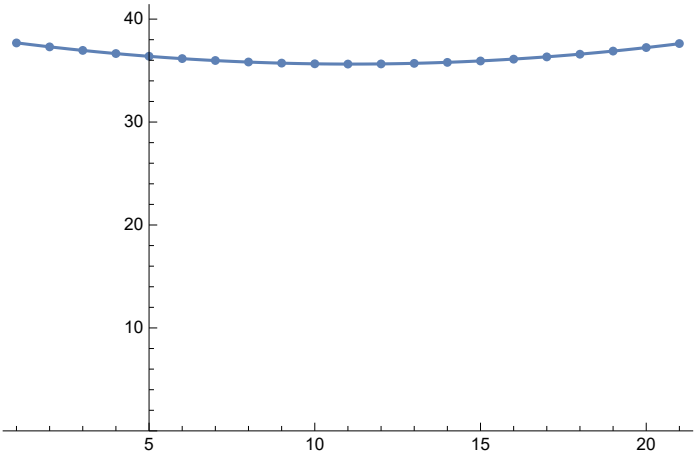
Input data



RMS difference vs displacement in data points



Expansion of RMS difference vs displacement in data points, with parabolic fit



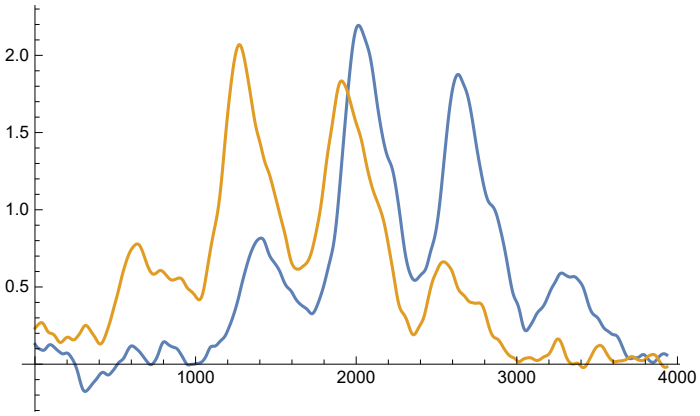

```
Interpolated frequency shift with best match is 0.589341 Hz
```

Chemical shift = 1.786 ppm

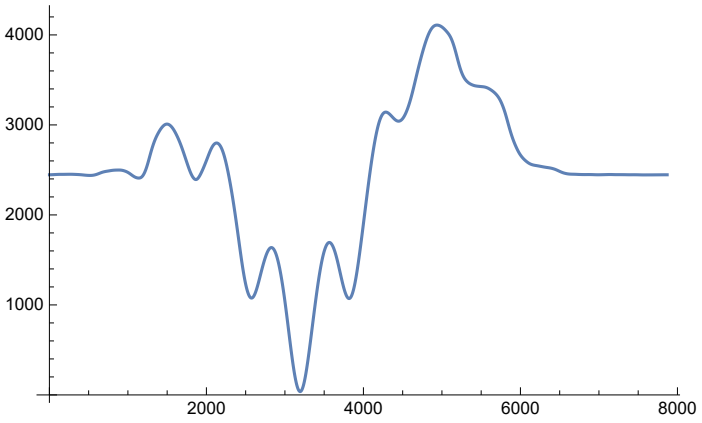
```
Variance and optimised shift and ratio:
```

$$\{37.4384, \{\text{fdiff} \to 740, \text{fratio} \to 1.07134\}\}$$

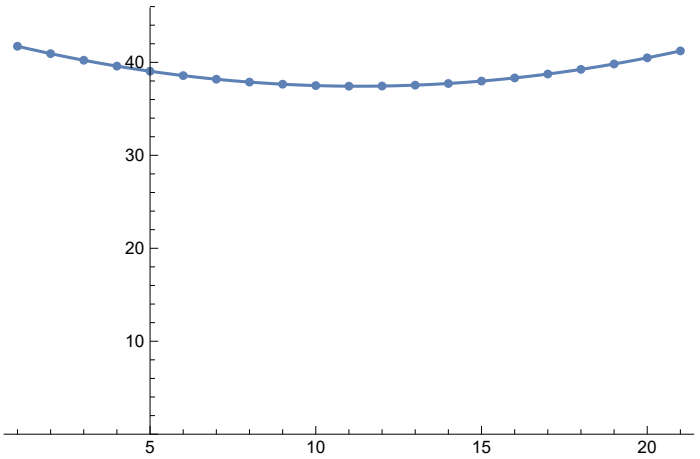
Input data



RMS difference vs displacement in data points



Expansion of RMS difference vs displacement in data points, with parabolic fit



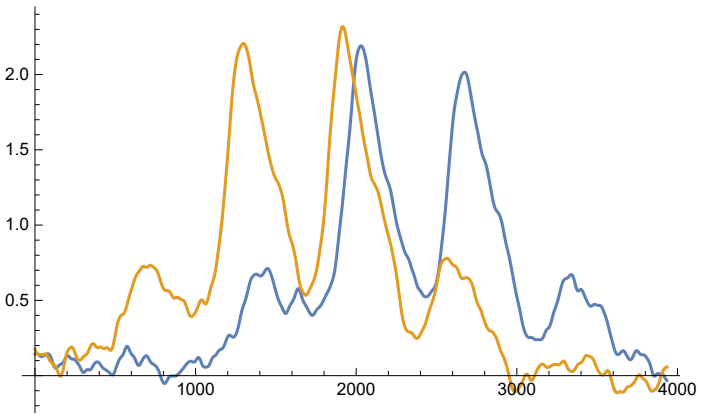

```
Interpolated frequency shift with best match is 14.1085 Hz
```

Chemical shift = 1.786 ppm

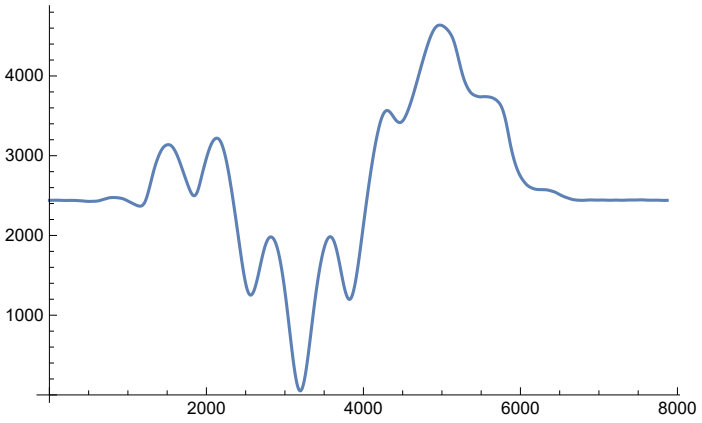
```
Variance and optimised shift and ratio:
```

$$\{51.277, \{\text{fdiff} \to 739, \text{fratio} \to 1.02879\}\}$$

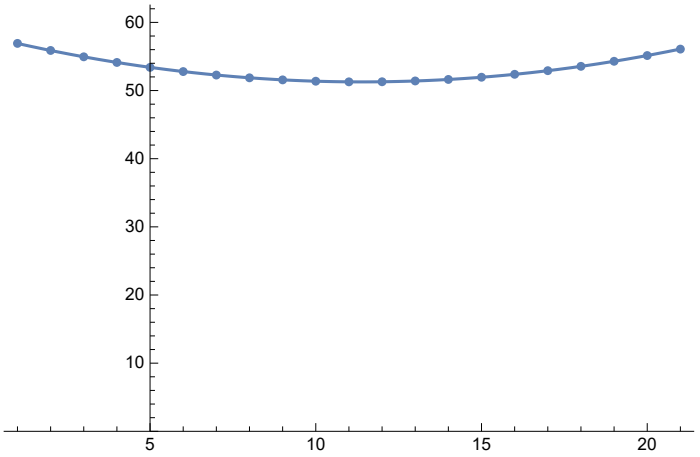
Input data



RMS difference vs displacement in data points



Expansion of RMS difference vs displacement in data points, with parabolic fit




```
Interpolated frequency shift with best match is 14.0879 Hz
```

Coupling constants

Out[ ]//TableForm=

0.467096	0.495639
48.8572	48.8852
−0.486352	−0.643692
0.592004	0.589341
14.1085	14.0879

```
Time used = 1389.2077470seconds
```

Shift / ppm	JHF / Hz	std dev / Hz	sd of mean of J / Hz
6.4649	0.481368	0.0201833	0.0142718
5.4092	48.8712	0.0197866	0.0139913
2.433	−0.565022	0.111256	0.0786699
2.287	0.590672	0.00188269	0.00133126
1.786	14.0982	0.0146129	0.0103329