

Developing spectroscopic representations on the web.

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Abstract

In 1997, we began collaboration with MDL Information Systems Ltd and incorporated our spectroscopy (JCAMP-DX) viewer code into MDL Chime. By 2005, when the contract ended, MDL had had over 2 million downloads of the free version of the browser plug-in.

In 2006, we followed up with the release of JSpecView (<http://jspecview.sourceforge.net>), a JAVA based spectroscopy viewer, which can be run as an applet from a web page or as a standalone application. There are several expected uses of JSpecView, and in this presentation I will demonstrate examples where the applet can be used in a teaching environment for the interpretation of IR, MS and NMR spectra, delivery of spectral unknowns and in a laboratory setting in combination with Jmol and another JAVA applet for characterisation of visible spectra with Tanabe-Sugano diagrams.

Introduction.

In 1997, a group at UWI began collaboration with MDL Information Systems Ltd and incorporated our spectroscopy (JCAMP-DX) viewer code into MDL Chime. By 2005, when the contract ended, MDL had clocked up over 2 million downloads of the free version of the browser plug-in. MDL have stated that they will continue to maintain Chime for at least another year but no further updates to the spectroscopy viewer code are envisaged.

In March 2006, we followed up with the release of JSpecView (<http://jspecview.sourceforge.net>), an Open Source JAVA based spectroscopy viewer, which can be run as an applet from a web page or as a standalone application to display spectra encoded as JCAMP-DX or AnIML files.

There are several expected uses of JSpecView, and in this presentation I will demonstrate examples where the applet can be used in a teaching environment for the interpretation of IR, MS and NMR spectra, delivery of spectral unknowns and in a laboratory setting in combination with Jmol and another JAVA applet for characterisation of visible spectra with Tanabe-Sugano diagrams.

Some background to JCAMP-DX and AnIML

The [Joint Committee on Atomic and Molecular Physical Data](#) (JCAMP) published their first data exchange protocol in the 1980's. Since then the protocols for a range of techniques have been developed and from 1995 IUPAC took over the responsibility through the Committee for Printed and Electronic Publications (CPEP). The types of spectra that are commonly represented by JCAMP-DX file formats

include: IR, UV/Vis, MS (including GC/MS), NMR (with pulse sequence schemes), IMS and EMR. By following these protocols it is possible to generate files from other spectral techniques not already covered, thereby extending this range.

The XML in Chemistry initiative within IUPAC started with a one day meeting at the IUPAC General Assembly held in Brisbane in 2001. This was followed up by a consultation exercise to all Divisions and then an open meeting in Cambridge 2002 for all those who had expressed an interest.

The image shows a side-by-side comparison of an XML file and its visualization. On the left is the raw XML code, and on the right is a screenshot of a web browser displaying the visualization.

```
<?xml version="1.0" encoding="UTF-8"?>
<AnIML xmlns:xsi="http://www.w3.org/2001/XMLSchema-instance" xmlns:ds="http://www.w3.org/2000/09/xmldsig#" xsi:noNamespaceSchemaLocation="http://www.w3.org/2000/09/xmldsig#" >
  <SampleSet>
    <Sample sampleID="sample" derived="false">
      <ParameterCategorySet>
        <ParameterCategory name="SampleDescription">
          <ParameterSet>
            <Parameter name="SampleName">
              <string>p methoxybenzoic acid</string>
            </Parameter>
            <Parameter name="SampleOwner">
              <string>public domain</string>
            </Parameter>
          </ParameterSet>
        </ParameterCategory>
      </ParameterCategorySet>
    </Sample>
  </SampleSet>
  <Sample sampleID="solvent" derived="false">
    <ParameterCategorySet>
      <ParameterCategory name="SampleDescription">
        <ParameterSet>
          <Parameter name="SampleName">
            <String>CDCl3</String>
          </Parameter>
          <Parameter name="SampleState">
            <String>Liquid</String>
          </Parameter>
        </ParameterSet>
      </ParameterCategory>
    </ParameterCategorySet>
  </Sample>
  <MeasurementData>
    <ExperimentStep name="NMR SPECTRUM">
      <Author type="software">
        <Name>Department of Chemistry, UWI, Mona, JAMA</Name>
        <Location>public domain</Location>
      </Author>
      <Timestamp>2006/04/08 13:48:32.0718 -0500</Timestamp>
      <SamplesUsed>
        <SampleRef sampleID="sample" role="SampleMeasurement" purpose="consumed"/>
        <SampleRef sampleID="solvent" role="Solvent" purpose="consumed"/>
      </SamplesUsed>
      <Technique name="NMR" uri="http://animl.sf.net/schema/techniques/NMR%20base%20instance%20document.atid"/>
      <PageSet>
        <Page name="spectrum">
          <VectorSet length="8318">

```

The browser window on the right shows the visualization of the NMR spectrum. The title is "Demonstration of JSpecView applet". The plot shows intensity versus chemical shift (ppm) for p-methoxybenzoic acid. The x-axis ranges from 10.5 to -1.5 ppm, and the y-axis ranges from -15000 to 135000. There are several sharp peaks, with the most prominent ones around 7.5 ppm and 3.8 ppm. Below the plot, there are checkboxes for "Reverse plot" and "Toggle Grid", and a "Load IR spectrum" button. Text below the plot explains that the H NMR of p-methoxybenzoic acid is shown and that clicking on the spectrum will produce a dialog pop-up box.

The [Analytical Information Markup Language](#) (AnIML) is a standardization effort of ASTM (formerly the American Society for Testing and Materials) Subcommittee E13.15 on Analytical Data, in conjunction with a number of other groups including IUPAC.

AnIML provides an XML-based format for analytical data and is designed specifically for spectroscopic and chromatographic data, but once again is suitable for use with many different analytical measurement techniques.

JSpecView - an Open Source project

The JSpecView Project provides an applet and application for the display of JCAMP-DX and AnIML spectral files. For this presentation I will be solely concentrating on the use of the JAVA applet for web-

based displays and leave discussion of the application to another session!

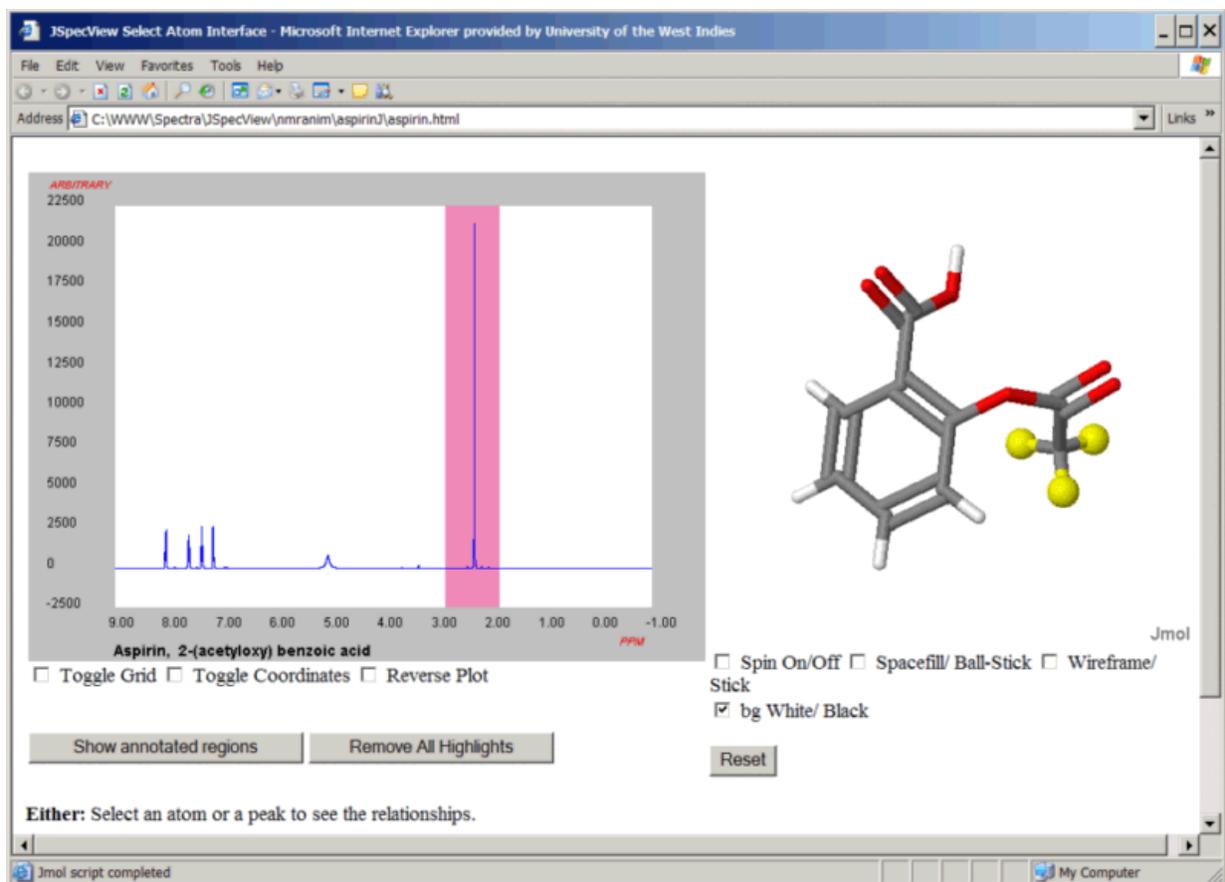
The impetus for much of this has been that the web site I maintain at the [Department of Chemistry, UWI, Mona](#) has relied heavily on MDL Chime and has hundreds of spectroscopic data files linked through its thousands of pages that feature not only our coursework but the Chemistry of "Things Jamaican" like our bauxite, rum, coffee and spices.

To get a feel for aspects of the site, check out the following pages that are used in the interpretation and display of spectra. In creating each of these, the method employed was to establish a template such that the necessary infrastructure to display one set of information could be reused for the next set without major recoding of HTML. This was achieved by storing filenames and links etc. as small JavaScript files.

To be able to view the following pages requires that you have a recent version of the [Sun JRE](#) installed (1.5 at least)

- [IR of hexane](#)
- [H NMR spectrum of aspirin](#)
- [MS of dodecane](#) $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$
- [IR, HNMR and CNMR of acetophenone](#)
- [GC/MS of pimento \(allspice\)](#)

In the first example, the major peaks in the IR spectrum of hexane are linked to animations of the vibrational modes which are displayed using Jmol. Similar displays have been designed for using Marvin and Chime.



In the display of the ^1H NMR of aspirin, links are possible in either direction. That is, it is possible to click on a peak in the spectrum to highlight the H atom(s) or click on an H atom and highlight the peak in the NMR.

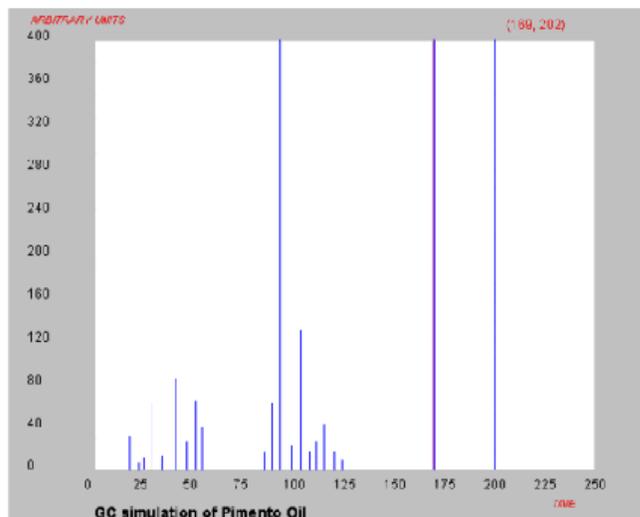
For the Mass Spectrum example, the display initially shows the molecule and the MS of dodecane. Using routines designed by Professor Hanson, it is possible to predict a fragmentation list from likely bond cleavages. Clicking on any of these links then highlights the molecule in green and red to show the position of bond cleavage and highlights that molecular ion in the spectrum. Again this is bi-directional since clicking on a peak in the MS will show the red/green molecular display as well.

The next example shows acetophenone as either an FTIR, ^1H NMR or ^{13}C NMR spectrum. Initially the JCAMP-DX BLOCK file containing the 3 spectra is loaded and the different spectra are selected using a radio button. With each display feedback to and from the Jmol display is possible.

methyleugenol

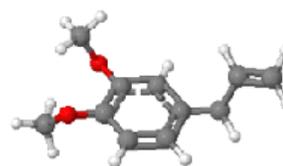
Interpretation of the GC from pimento oil

Click on a peak in the GC trace below.



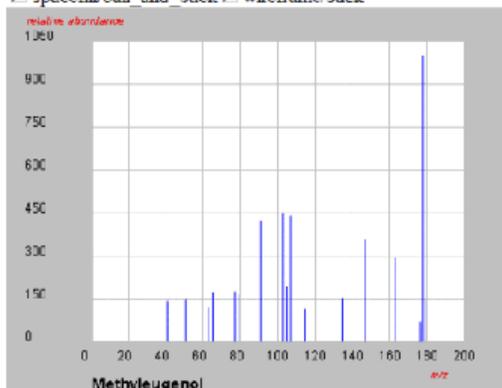
The pimento component corresponding to this GC peak is:

methyleugenol



Jmol

spin On/Off bg white/black
 spacefill/ball_and_stick wireframe/stick

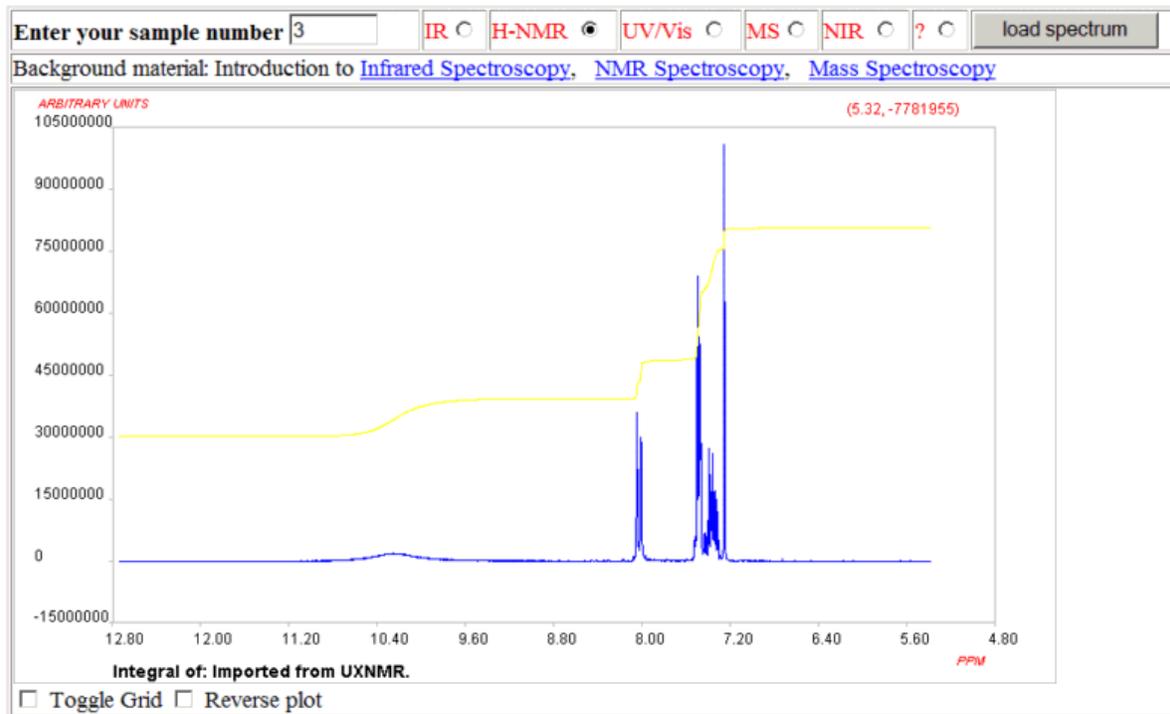


The MS for that component.

The last of these examples shows a simulated GC trace of pimento oil (allspice). This has been an area of study in the Department for many years and two of our Postgraduates have shown their entrepreneurial skills by establishing a production facility in the country for the export of pimento oil and eugenol. Clicking on a peak in the GC shows the molecular graphic for that component along with its MS.

Delivery of spectra for Organic unknowns

Traditionally, advanced organic laboratory programmes will have a session where students are presented with unknown materials and are asked to prepare derivatives and collect spectra to identify the materials. In our course each student is issued with a solid and a liquid and in the past were given a hard copy printout of an IR and NMR spectra.



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With time we have been able to build up a database of 150-200 IR, UV/Vis, H NMR, C NMR, MS as well as some NIR spectra. For a couple of years we used a web page form to deliver spectra using MDL Chime, but due to problems with printing and the lack of an Integration option for the NMR spectra the staff opted to return to hard copies last year. I am determined to show that with JSpecView incorporating functions for Integration and printing that the on-line method provides advantages to the students who can then access the information outside of laboratory hours so that it will return to an on-line system in the near future.

Inorganic Laboratory experiment on Cr(III) complexes

In a previous Conf. Chem. series (1999b) I presented a paper on the use of Tanabe-Sugano diagrams for the interpretation of visible spectra of transition metal complexes.

Choose a Chromium complex. Potassium Chrome Alum

In the visible spectrum displayed, select the lowest energy peak then the higher energy peak and the ratio will be calculated automatically for you.

○ peak 1 cm^{-1} ● peak 2 cm^{-1} . The ratio of the energies is

Now find where this ratio falls on the Tanabe-Sugano diagram and to get the predicted value of B' and the energies of the transitions.

B' , v1, v2, v3, f1, f2, f3, f4, f5, f6, f7, f8

Thanks to C. Muir and D.-A.P. Facey for help with the Applet and L. Muir-Green for preparing some of the Cr(III) complexes.

spin forbidden transitions:
 ${}^2T_{2g}(D) \leftarrow {}^4A_{2g}$ Purple (E)
 ${}^2T_{2g}(G) \leftarrow {}^4A_{2g}$ Dk green (F)
 ${}^2E_g(G) \leftarrow {}^4A_{2g}$ Copper (G)
 ${}^2T_{2g}(E) \leftarrow {}^4A_{2g}$ Lt green (H)
 ${}^2A_{1g}(G) \leftarrow {}^4A_{2g}$ Grey (I)
 ${}^2T_{2g}(G) \leftarrow {}^4A_{2g}$ Brown (J)
 ${}^2T_{1g}(G) \leftarrow {}^4A_{2g}$ Orange (K)
 ${}^2E_g(G) \leftarrow {}^4A_{2g}$ Teal (L)

Since then I have further developed the series of JAVA applets for the display of TS diagrams and created a web page that combines the d^3 diagram appropriate for octahedral Cr(III) complexes with the visible spectrum displayed in JSpecView.

By selecting the peaks in the visible region the ratio of the energies of these peaks is calculated and can then be used as input to the TS diagram which returns the predicted position of all the spin-allowed and forbidden transitions as well as the Racah parameter, B.

[spectra of Cr\(III\) complexes.](#)

Conclusion

With a little effort it is possible to create web pages that can display a wide range of spectral types and design teaching material to support discussion of spectral interpretation.

In a laboratory setting, the ability to deliver live spectra that can be manipulated, expanded, peaks highlighted etc. and printed adds considerable value compared to hard copies.

Combining laboratory time with computer laboratory time allows spectra to be recorded in one lab and interpreted in the other. The overall impact, based on many favourable student responses is that topics that are considered difficult can be simplified by personal involvement rather than just trying to read and hear about it.

Useful Electronic Resources

[Confchem presentation by Scott van Bramer](#) on tools for processing and interpreting spectral data.

[SDBS: Integrated Spectral Data Base System](#) (bitmaps - not live data)

[Polymer Science Learning Center with 200+ spectra](#)

[WebBook from NIST](#) a source for IR and MS JCAMP-DX files.

[Jmol](#) an Open Source JAVA molecular graphics viewer.

[Marvin from Chemaxon](#) another molecular graphics viewer (free for academic use)

[MDL Chime](#) browser plugin for spectra and molecular graphics (free for academic use)

[xvibs](#) for generation of vibrational mode xyz files

[Babel](#) converter between molecular graphics formats

[WebMO](#) front end for computational chemistry packages

[MOPAC](#) general-purpose semi-empirical molecular orbital package

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