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Non-Commercial Software for the Analysis and Interpretation of High Resolution Molecular Spectra

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Infrared spectroscopy is a powerful method of analysis with a rich chemical history. Indeed, the application of this technique to identify functional groups in complex organic molecules by their characteristic infrared absorption band features is well known (Silverstein etal., 1981). Moreover, if the absorption intensities can be accurately measured, a quantitative analysis for the material absorbing the radiation can be performed (Bernath, 1995; Miller, 2000). For the most part, low resolution commercial FTIR instruments are well suited for this type of analytical measurement. However, in the gas phase, using an infrared spectrometer with sufficient resolution, spectroscopists can not only obtain accurate vibrational frequencies for the molecular systems under investigation, they can also quantitatively measure the rotational energy spacing within a vibrational state. The measurement and subsequent analysis of such data provides a wealth of fundamental information about the chemical and physical bonding interactions in the molecule. Details concerning molecular structure, the strength of chemical bonds, and the shape of molecular potential energy surfaces can all be extracted from the high resolution spectra (Nesbitt, 1988). Although there are a number of methods which have been developed to extract this detailed molecular information (Hollas, 1996), assignment of the individual spectral features (to include rotational quantum number assignments) is necessarily required. Assigning spectral features for a previously unknown or unreported molecular spectrum can be a tedious, time consuming task, particularly if the species under investigation is a symmetric top possessing perpendicular vibrational bands or an asymmetric top molecule (Herzberg, 1950; Hollas, 1998). One commonly used method for assigning the individual transitions in a complex spectrum involves calculating a stick spectrum (to include relative intensities), overlaying the stick spectrum on the observed spectrum, and translating the calculated spectrum until a set of likely features in the observed spectrum can be identified. As the stick spectrum is initially generated using molecular constants obtained from *ab initio* predictions or extrapolated from ground vibrational state values, an iterative process in which the input constants are varied slightly for each iteration is often required to obtain a consistent set of assignments. Over the past year, we have developed the necessary Visual Basic code to allow this proven systematic procedure for assigning complex rotationally resolved spectra to be implemented in a spreadsheet type environment. Here we describe the software and provide one example of its utility.

In Fig. 1 we show the rotationally resolved vibrational
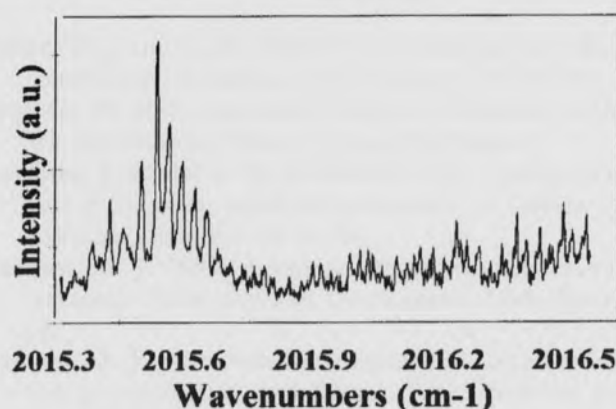
Fig. 1. Rotationally resolved infrared spectrum for the ν_{10} band of jet cooled iron pentacarbonyl.

spectrum for the jet cooled iron pentacarbonyl molecule. This particular spectrum corresponds to the ν_{10} perpendicular vibrational band of iron pentacarbonyl (Ford, 2001). Perpendicular bands of symmetric tops typically possess a number of sub-bands, due to rotation about the symmetry axis of the molecule, which are offset slightly from one another (Herzberg, 1950; Hollas 1998). A calculated stick spectrum for several different sub-bands of the iron pentacarbonyl ν_{10} band is shown in Fig. 2 (Ford, 2001). Based on the data in these figures, assignment of the individual spectral features in this spectra could potentially be a formidable task.

Chem Spec II, the software program we developed to

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Fig. 2. Predicted stick spectrum for several sub-bands or K-states and the complete ν_{10} band of iron pentacarbonyl. Note, the individual sub-bands are slightly offset from one another.

aid in the analysis and interpretation of such complex molecular spectra, is quite user friendly. In fact, we have attempted to 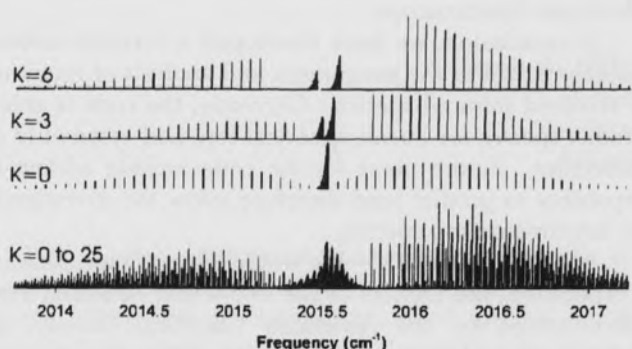make it emulate spreadsheet programs such as Excel or Quattro Pro as much as possible. In Fig. 3 the graphical user interface (GUI) for Chem Spec II is shown. Note the similarity between the GUI in Fig. 3 and an Excel
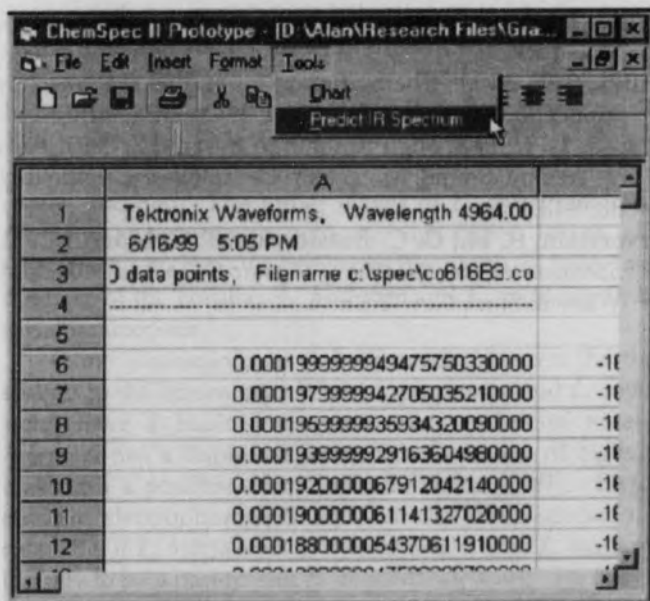
Fig. 3. The graphical user interface for Chem Spec II.

spreadsheet. To access the infrared spectral prediction portion of the program, one needs simply to select the PREDICT IR SPECTRUM option under the TOOLS pull-down menu. Upon selection of the PREDICT IR SPECTRUM option, a dialog box appears which contains the

Predict IR Spectrum Wizard (see Fig. 4). Within the Wizard dialog box, the spectroscopist must set all parameters rele-
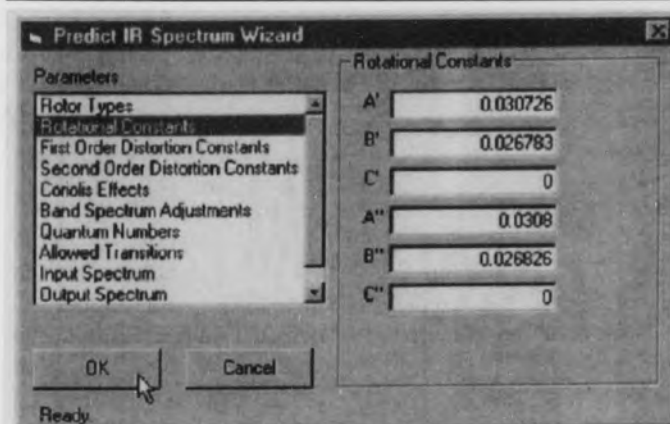
Fig. 4. The Predict IR Spectrum Wizard. Here the rotational constants for the ground and excited states of a prolate symmetric top are being entered.

vant to the problem under consideration including the Rotor Type for the molecule (e.g., symmetric top), entering values for the Rotational Constants, indicating the Allowed Transitions, and inputing the Quantum Numbers for the transitions to be plotted. This last feature is particularly useful if the operator is interested in examining a single sub-band. Chem Spec II also has the capability to include other effects that are often observed in rotationally resolved spectra such as coriolis coupling and centrifugal distortion. Once the necessary parameters have been input, the predicted spectrum must be output to the spreadsheet by selecting an appropriate output range. The output range is determined in a manner similar to that in Excel or Quattro Pro (see Fig. 5). The predicted spectrum can then be displayed and/or over-layed on the observed spectrum. Figure

Fig. 5. Selecting the output range for the calculated stick spectrum in the Chem Spec II spreadsheet.

6 provides an example of such a plot. If a likely set of spectral features cannot be identified, changes in rotational con-

Fig. 6. Plot of the calculated stick spectrum overlayed on the observed infrared spectrum.

stants can be input and a new stick spectrum can be calculated and plotted through the prediction wizard with a few mouse clicks. Once a likely progression is identified, the actual quantum number assignment is obtained by clicking on each stick in the calculated spectrum. Selection of any feature in the stick spectrum causes a dialog box to appear which contains the rotational quantum number information as shown in Fig. 7. Using this software package, we have assigned the entire v_{10} perpendicular band of jet cooled iron pentacarbonyl. A detailed analysis of these assignments will
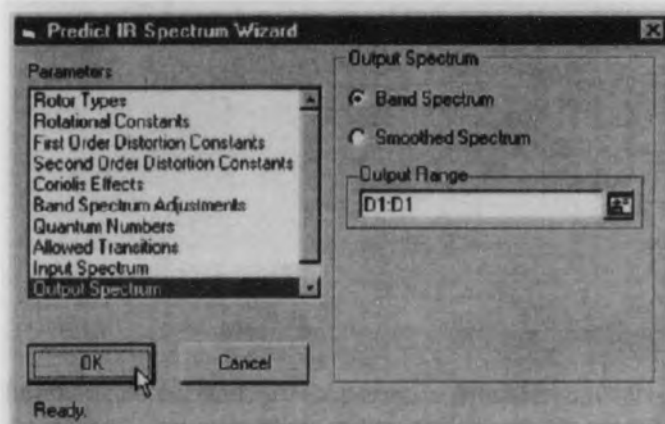

Fig. 7. Once a likely progression is identified in the observed spectrum, the quantum number assignment for a given spectral feature is obtained by clicking on the appropriate stick.

appear in a manuscript being prepared for the Journal of Molecular Spectroscopy.

In conclusion, we have developed a versatile software package to aid in the assignment and analysis of rotationally resolved infrared spectra. Currently, the code is able to predict spectra for linear, spherical top, and symmetric top molecules. Future plans for the code include adding the capability to predict (and therefore allow the investigation of) asymmetric top spectra.

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