# Spektri-Sim 1.0

# User's Guide

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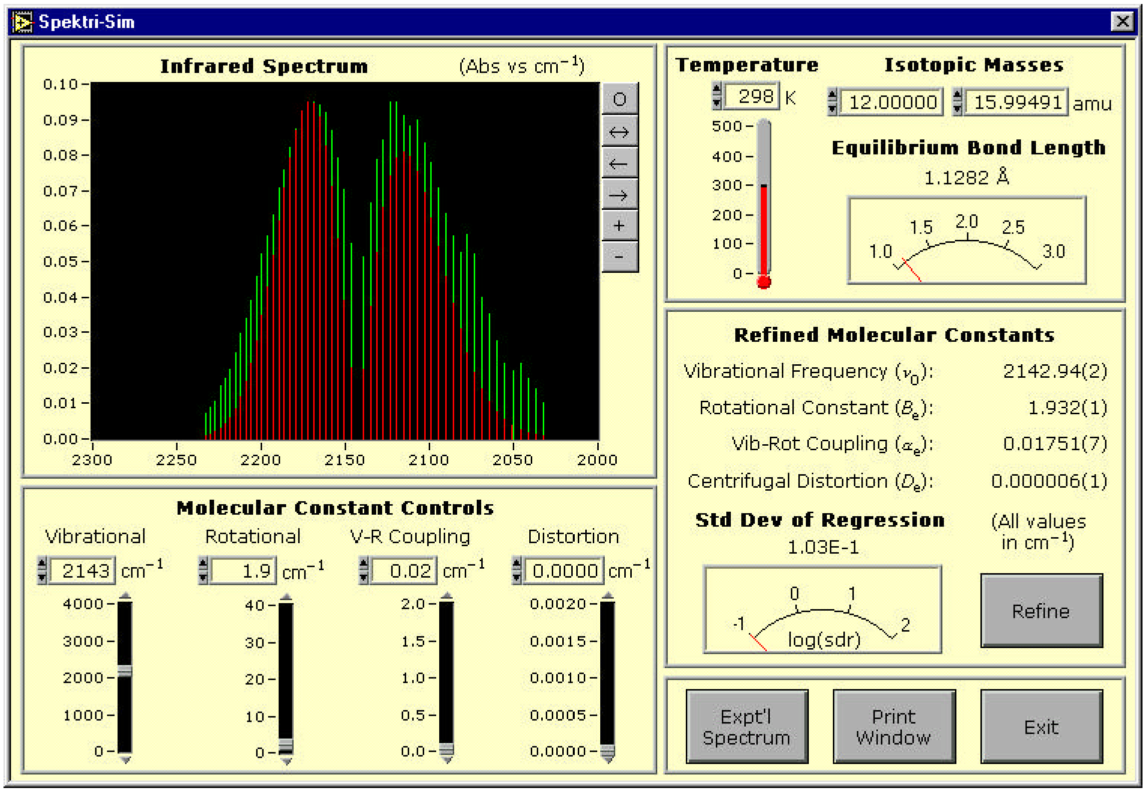
# Contents

# 1. Introduction

Spektri-Sim is a Windows-based software application for simulating and analyzing infrared absorption spectra of diatomic molecules. It offers an appealing alternative to the usual spreadsheet-based methods of analysis encountered by students in the physical chemistry laboratory. The application features a unique, visual approach for evaluating molecular constants in which the student interactively seeks the optimal fit of a simulated spectrum to the experimental spectrum. Using Spektri-Sim forces students to consider the influence that the molecular constants and temperature have on the features of the infrared spectrum.

Below is an example of the main Spektri-Sim interface, showing the data for the CO molecule after successful completion of the analysis. Two spectra appear in the graphical display, the experimental spectrum in green and a simulated spectrum (based on the molecular constant control values and a temperature of 298 K) in red. The equilibrium bond length of CO is reported and the best-fit molecular constants are listed along with their uncertainties.

Section 3 of this guide (*The HBr Spectrum: A Tutorial*) will lead you through a sample Spektri-Sim session for the analysis of the HBr molecule.



**Temperature** 298 K

**Isotopic Masses** 12.00000 15.99491 amu

**Equilibrium Bond Length** 1.1282 Å

**Refined Molecular Constants**

Vibrational Frequency ($\nu_0$): 2142.94(2)
Rotational Constant ($B_e$): 1.932(1)
Vib-Rot Coupling ($\alpha_e$): 0.01751(7)
Centrifugal Distortion ($D_e$): 0.000006(1)

**Std Dev of Regression** 1.03E-1

(All values in cm$^{-1}$)

**Molecular Constant Controls**

Vibrational 2143 cm$^{-1}$
Rotational 1.9 cm$^{-1}$
V-R Coupling 0.02 cm$^{-1}$
Distortion 0.0000 cm$^{-1}$

## 2. Infrared Spectra of Diatomic Molecules

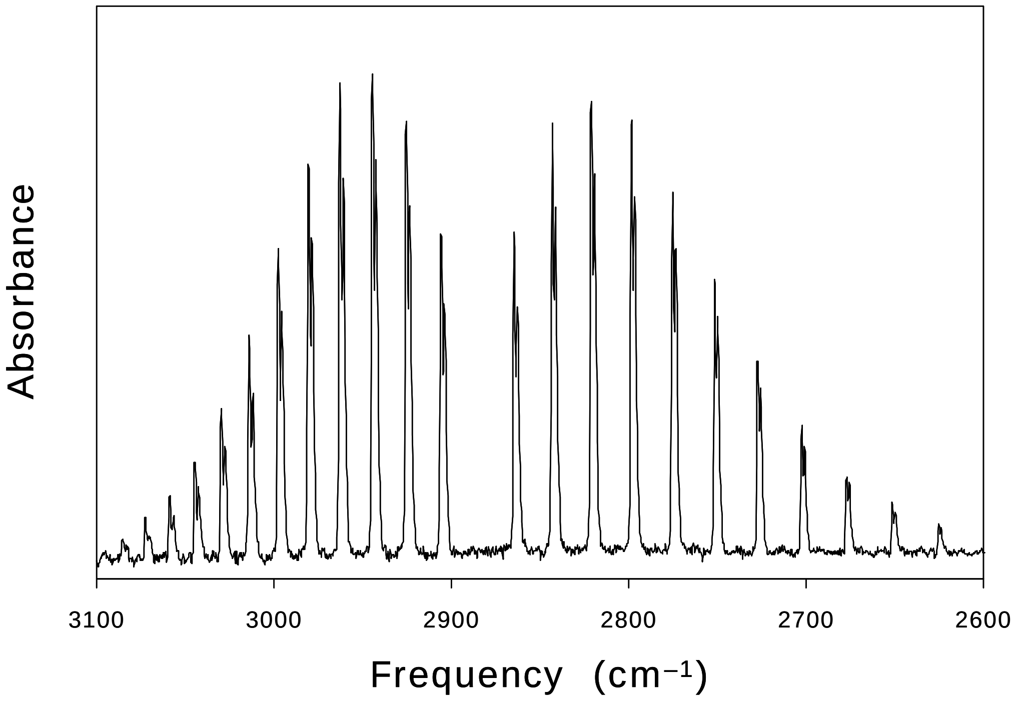
This section briefly presents theoretical background on infrared (rovibrational) transitions for diatomic molecules. In particular, we focus on those aspects that relate directly to the application of Spektri-Sim. More complete discussions of the theory of infrared spectra for diatomics can be found elsewhere.[1]

### *Infrared Absorption Spectra*

Figure 1 shows a representative IR absorption spectrum of a diatomic molecule, in this case the fundamental band of HCl. The lines in this band arise from transitions between various rovibrational states of the molecule. Rovibrational states are typically indexed by their vibrational and rotational quantum numbers, $v$ and $J$, respectively. Absorption arises from the transition from a lower-energy state, designated ($v''$, $J''$), to a higher-energy state, ($v'$, $J'$).

While there is an unlimited number of rovibrational states for a diatomic molecule, only a handful of these states must be considered in the analysis of the fundamental absorption band. First, by definition, a fundamental absorption arises from a transition from the $v''=0$ state to the $v'=1$ state. Overtone transitions are also possible (*e.g.* a transition from $v''=0$ to $v'=2$), but such transitions require

**Figure 1.** The infrared spectrum of HCl.



higher-energy light, typically outside the infrared region of the spectrum. Second, selection rules indicate that transitions are allowed only when $J$ changes by one unit ($\Delta J = \pm 1$). All other transitions are formally forbidden and, therefore, are not generally observed in the spectrum.

There are 23 clearly resolved lines appearing in the fundamental band of Figure 1. The eleven lines on the right-hand side arise from $\Delta J = -1$ transitions. These are referred to as *P* branch transitions. The twelve lines on the left-hand side correspond to $\Delta J = +1$ and are referred to as *R* branch transitions. Interestingly, the spectrum appears to be missing a line at the center of the band. The “missing” line corresponds to $\Delta J = 0$ (*Q* branch) transitions, which are forbidden.

On closer inspection, one sees that each line in Figure 1 is, in fact, a pair of lines. The dominant line of a pair arises from the transition for the more abundant isotope, $H^{35}Cl$. The weaker line arises from transitions for $H^{37}Cl$.

Absorption spectra for other diatomics are qualitatively similar to that shown in Figure 1. *Q* branch transitions are rarely observed. Lines to the low-frequency side of the spectrum are the *P* branch transitions while those on the high-frequency side are the *R* branch.

## *Rovibrational States and Absorption Frequencies*

The energy (in $cm^{-1}$) of a rovibrational state ($v$, $J$) is generally written in the following form,

$$\begin{aligned}\tilde{E}(v,J) &= n_e(v+½) - n_e x_e(v+½)^2 + B_e J(J+1) \\ &\quad - a_e(v+½)J(J+1) - D_e J^2(J+1)^2 \qquad (1)\end{aligned}$$

where $n_e$ is the harmonic vibrational frequency, $n_e x_e$ is the anharmonicity constant, $B_e$ is the rotational constant, $a_e$ is the vibrational-rotation coupling constant, and $D_e$ is the centrifugal distortion constant (all expressed in $cm^{-1}$ units).

The frequency (in $cm^{-1}$) of a rovibrational transition between states ($v''$, $J''$) and ($v'$,$J'$) is given by

$$\tilde{n} = \tilde{E}(v',J') - \tilde{E}(v'',J''). \qquad (2)$$

Substituting eq (1) into eq (2) and considering only the fundamental vibrational transition ($v''=0$, $v'=1$) and allowed rotational transitions

$\Delta J = \pm 1$, one obtains the expressions for the frequencies of the *R* and *P* branch transitions as a function of the lower-state rotational quantum number *J*",

$$\tilde{n}_R(J'') = n_0 + 2B_e(J''+1) - a_e(J''+3)(J''+1) - 4D_e(J''+1)^3 \qquad (3a)$$

$$\tilde{n}_P(J'') = n_0 - 2B_eJ'' - a_eJ''(J''-2) + 4D_eJ''^3 . \qquad (3b)$$

The fundamental vibrational frequency, $n_0$, in eqs (3) is given by

$$n_0 = n_e - 2n_ex_e \ . \qquad (4)$$

If one now defines an index variable *m* such that $m = J''+1$ for *R* branch transitions and $m = -J''$ for *P* branch transitions, the eqs (3) reduce to a single expression,

$$\tilde{n}_m = n_0 + 2(B_e - a_e)m - a_em^2 - 4D_em^3 . \qquad (5)$$

Eq (5) relates the molecular constants $n_0$, $B_e$, $a_e$, and $D_e$ to the absorption frequencies of the infrared spectrum.

## *Equilibrium Bond Length and Absorption Intensities*

The equilibrium bond length of a diatomic molecule can be determined from its rotational constant, $B_e$, viz.

$$R_e = \left( \frac{h}{8p^2 cmB_e} \right)^{1/2} \qquad (6)$$

where *h* is Planck’s constant, *c* is the speed of light, and *m* is the reduced mass. The latter, $m = m_1m_2/(m_1+m_2)$, is evaluated from the isotopic masses ($m_1$, $m_2$) of the two atoms.

The intensity distribution of the *R* and *P* branch transitions is approximated by the expressions

$$I_R \propto \tilde{n}_R(J''+1) \exp\left[ \frac{-J''(J''+1)hcB_e}{kT} \right] \qquad (7a)$$

$$I_P \propto \tilde{n}_P J'' \exp\left[ \frac{-J''(J''+1)hcB_e}{kT} \right] \qquad (7b)$$

where *k* is the Boltzmann constant and *T* is the absolute temperature.

## *Implementation in Spektri-Sim*

The Spektri-Sim user interface (window) includes five principal controls, one for each of the molecular constants ($n_0$, $B_e$, $a_e$, $D_e$) and one for the temperature. Based on the values set by these controls, Spektri-Sim uses eqs (5) and (7) to calculate a simulated absorption spectrum (intensity vs frequency). This spectrum is plotted together with a stick representation of the experimental spectrum on a graphical display in the Spektri-Sim window. By interactively manipulating the controls, you can refine the molecular constants, visually seeking the optimal overlap of the simulated and experimental spectra.

A quantitative measure of the quality of the fitted spectrum is provided by the standard deviation of regression (SDR). The SDR (in $\text{cm}^{-1}$) for a four-parameter fit is defined by

$$\mathrm{SDR} = \left( \frac{\sum_m \left( \tilde{n}_m^e - \tilde{n}_m \right)^2}{N - 4} \right)^{1/2} \qquad (8)$$

where $\tilde{n}_m^e$ are the frequencies of the experimental spectrum and $\tilde{n}_m$ are the frequencies of eq (5). The magnitude of the SDR can be considered a measure of the average error in fitting a simulated line of the spectrum relative to its corresponding experimental line. Digital and analog displays of the SDR appear in the Spektri-Sim window to help you refine the molecular constants.

You can use Spektri-Sim to perform a final numerical refinement after the molecular constants have been optimized “by hand” to give an SDR value less than 3 $\text{cm}^{-1}$. Spektri-Sim’s numerical optimization routine is based on the Levenberg-Marquardt algorithm. Standard deviations for each of the refined molecular constants are reported.

Spektri-Sim calculates the equilibrium bond length using eq (6). This bond length appears on both digital and analog displays.

## 3. The HBr Spectrum: A Tutorial

This section guides you through the Spektri-Sim analysis of the IR absorption spectrum of the HBr molecule. The section is divided into two parts. Part A introduces you to the main Spektri-Sim window and the manipulation of the molecular constant and temperature controls to influence the features of a simulated IR spectrum. Part B focuses on entering the experimental assignments for the HBr spectrum and optimizing the molecular constants.

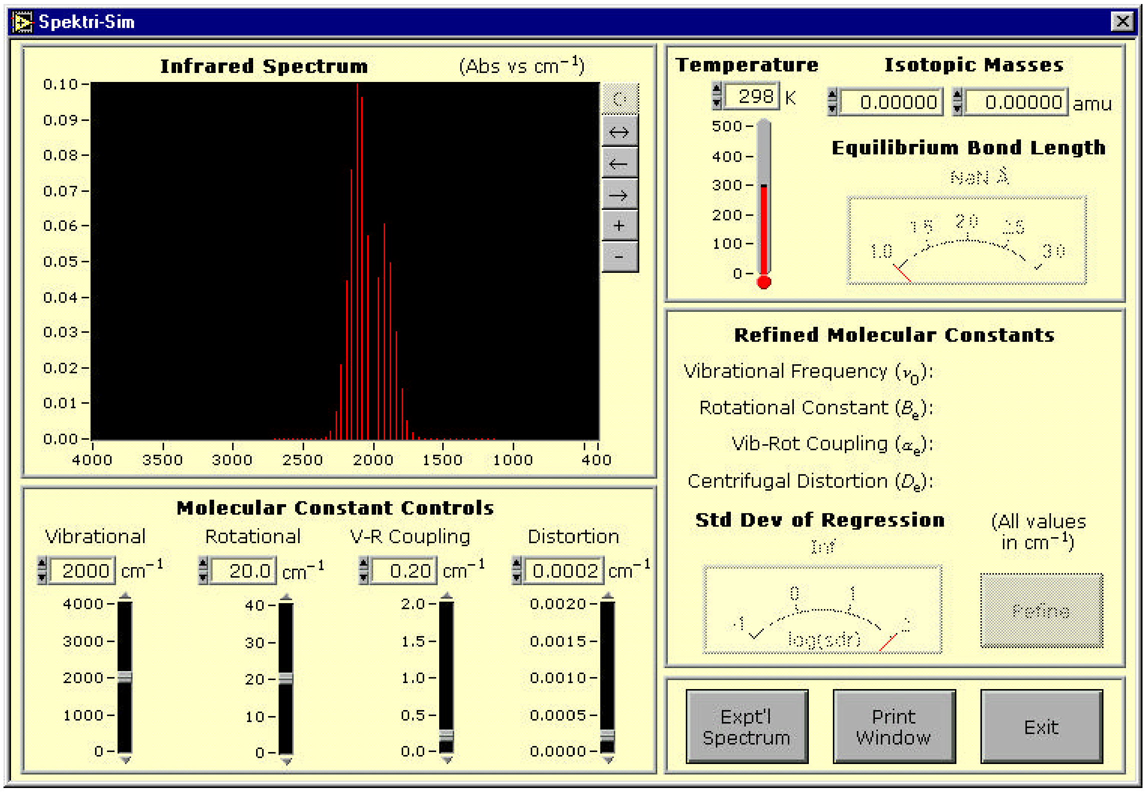
### *A: Spektri-Sim Controls and the Simulated IR Spectrum*

1. Start Spektri-Sim.

   If installed correctly, a shortcut to Spektri-Sim can be found on the Start menu (**Start > Programs > Spektri-Sim**). If you still need to install the distribution, see the instructions in Section 4 (*Installing Spektri-Sim*).

   The *Spektri-Sim* window opens. The window should appear as shown below.

   The *Spektri-Sim* window consists five principal panels. The upper left-hand panel shows a graphical display for IR spectra. The



Temperature 298 K

Isotopic Masses 0.00000 0.00000 amu

Equilibrium Bond Length NaN Å

Std Dev of Regression Inf

Vibrational 2000 cm$^{-1}$

Rotational 20.0 cm$^{-1}$

V-R Coupling 0.20 cm$^{-1}$

Distortion 0.0002 cm$^{-1}$

simulated spectrum is shown in red (the experimental spectrum will eventually appear in green). This panel can also display regression and residual plots for judging the quality of the optimized molecular constants.

The lower left-hand panel contains controls for adjusting the four molecular constants. Each control consists of a vertical slider coupled to a digital display.

The upper right-hand panel has controls for the setting temperature and isotopic masses. Displays (both digital and analog) for the equilibrium bond length are also shown.

The middle panel on the right-hand side is used to refine the molecular constants. Included here are digital and analog displays of the standard deviation of regression (SDR) and the **Refine** button that initiates the numerical optimization of the constants.

The lower right-hand panel includes buttons for entering the assignments of the experimental spectrum, printing an image of the Spektri-Sim window, and exiting the application.

Notice that several of the controls and displays appearing on the Spektri-Sim window are disabled (“grayed-out”) when the application starts. These include the indicators for the equilibrium bond length and SDR, the **Refine** button, and one of the viewport buttons adjacent to the graphical display. These features of the Spektri-Sim window remain disabled until you provide additional information to the program, such as isotopic masses for the bond length display and an experimental spectrum for the SDR.

The graphical display shows a simulated spectrum based on the current (default) values of the molecular constants ($n_0$=2000, $B_e$=20.0, $a_e$=0.20, $D_e$=0.0002 cm$^{-1}$). The intensity of each line in this spectrum is calculated from thermally equilibrated populations for the $v$=0 rotational states at the temperature shown on the thermometer (default: $T$=298 K).

2. Increase the fundamental frequency ($n_0$) to 3000 cm$^{-1}$ using the **Vibrational** control.

   You can make gross adjustments to this control (and others like it) by clicking the gray slider and dragging it to the desired value. Try this and observe the response of the simulated spectrum.

Make fine adjustments to the control by clicking the up or down arrows at the top and bottom of the slider or to the left of the digital display. The control value increases or decreases by a small, fixed increment (±1 $cm^{-1}$ for the vibrational frequency).

Alternatively, you can enter the value of a control directly into the digital display. First, select the text in the digital display (click and drag to highlight), and then enter the desired value on the keypad (hit the keypad Enter key to complete the entry).

3. Similarly, use the **Rotational** control to decrease the rotational constant ($B_e$) to 10.0 $cm^{-1}$.

   How does the simulated spectrum respond to changes in the rotational constant?

4. Adjust the **V-R Coupling** (vibration-rotation coupling constant, $a_e$) and **Distortion** (centrifugal distortion constant, $D_e$) controls to arbitrary values.

   The influence of these controls on the simulated spectrum should be more subtle than those of the **Vibrational** and **Rotational** controls.

5. Adjust the **Temperature** control.

   You can make gross temperature changes by clicking the “mercury meniscus” of the thermometer and dragging up or down.

   How does the temperature affect the appearance of the spectrum?

6. Set the isotopic masses to appropriate values for $H^{79}Br$.

   Notice that the digital display and meter for the equilibrium bond length are disabled until the isotopic masses are defined.

   Enter isotopic masses of 1.007825 and 78.9183 amu for H and $^{79}Br$, respectively.

7. Now, adjust each of the molecular constant and temperature controls while watching the equilibrium bond length meter.

   Which control(s) influence the equilibrium bond length?

8. Reset the molecular constant and temperature controls to their default values.

   Right-click on either the digital displays or the sliders for these controls. A control window will appear. Select **Reinitialize to Default**.

9. Adjust the graphical display viewport.

   Use the five active buttons to the right of the spectrum display to change the apperance of the spectrum. Clicking these buttons results in the following actions:

   ↔ : adjust horizontal scale to fit the full spectrum
   ← : shift the viewport to the left (spectrum to right)
   → : shift the viewport to the right (spectrum to left)
   + : zoom in by 50%
   − : zoom out by 50%

   Experiment with each of these buttons to determine how the viewport responds.

## *B: Fitting Molecular Constants to Experimental Data*

1. Click the **Expt'l Spectrum** button.

   The *Experimental Spectrum* window will appear, similar to the figure shown below but without the data.

   The experimental spectrum—that is, the assigned *R* (*N*>0) and *P* (*N*<0) branch transitions—can be read from an external, tab-delimited text file by clicking the **Open** button. The assignments will appear in the table.

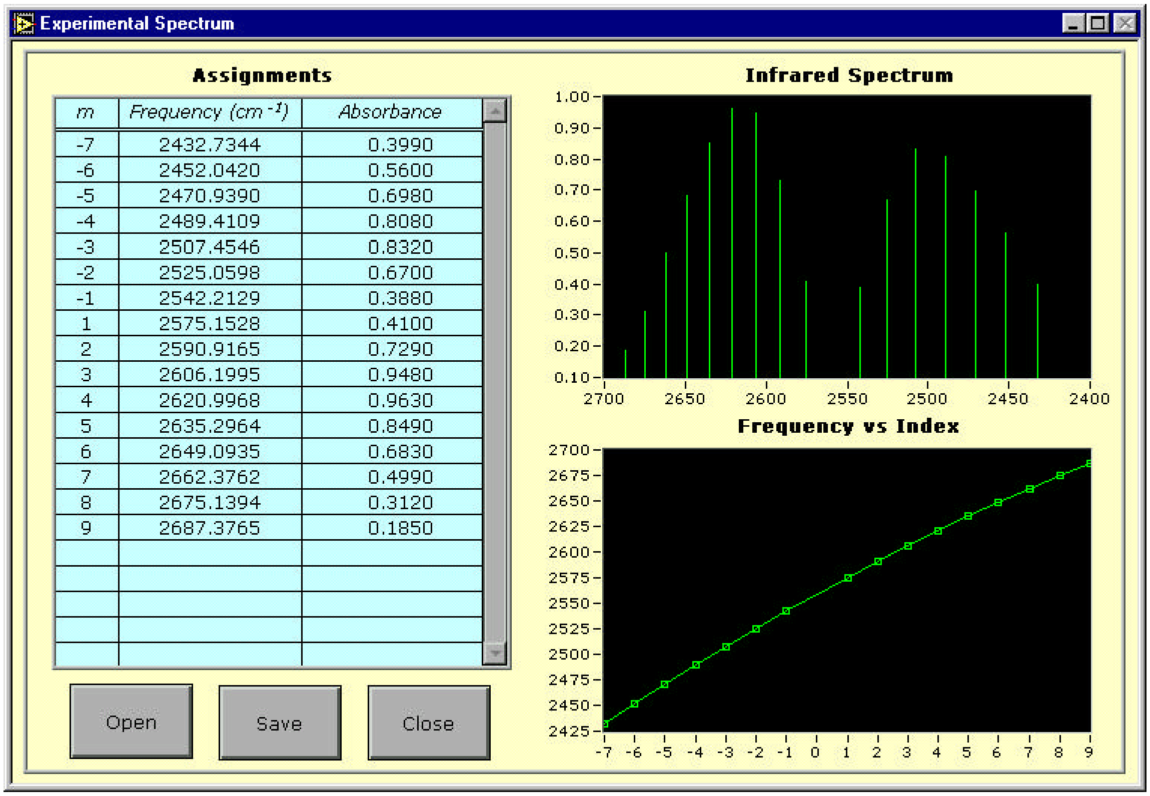
   Alternatively, you can enter the spectrum "by hand" into the table. Click the **Save** button to save the data in the assignments table to an external file for later use.

   Now, we will read the spectrum from external file.

2. Click the **Open** button.

3. Open HBr-79.txt in the folder C:\Program Files\Spektri-Sim.[2]

   The spectral assignments appear in the table, as shown below.



**Assignments**

| *m* | *Frequency (cm⁻¹)* | *Absorbance* |
|---|---|---|
| -7 | 2432.7344 | 0.3990 |
| -6 | 2452.0420 | 0.5600 |
| -5 | 2470.9390 | 0.6980 |
| -4 | 2489.4109 | 0.8080 |
| -3 | 2507.4546 | 0.8320 |
| -2 | 2525.0598 | 0.6700 |
| -1 | 2542.2129 | 0.3880 |
| 1 | 2575.1528 | 0.4100 |
| 2 | 2590.9165 | 0.7290 |
| 3 | 2606.1995 | 0.9480 |
| 4 | 2620.9968 | 0.9630 |
| 5 | 2635.2964 | 0.8490 |
| 6 | 2649.0935 | 0.6830 |
| 7 | 2662.3762 | 0.4990 |
| 8 | 2675.1394 | 0.3120 |
| 9 | 2687.3765 | 0.1850 |

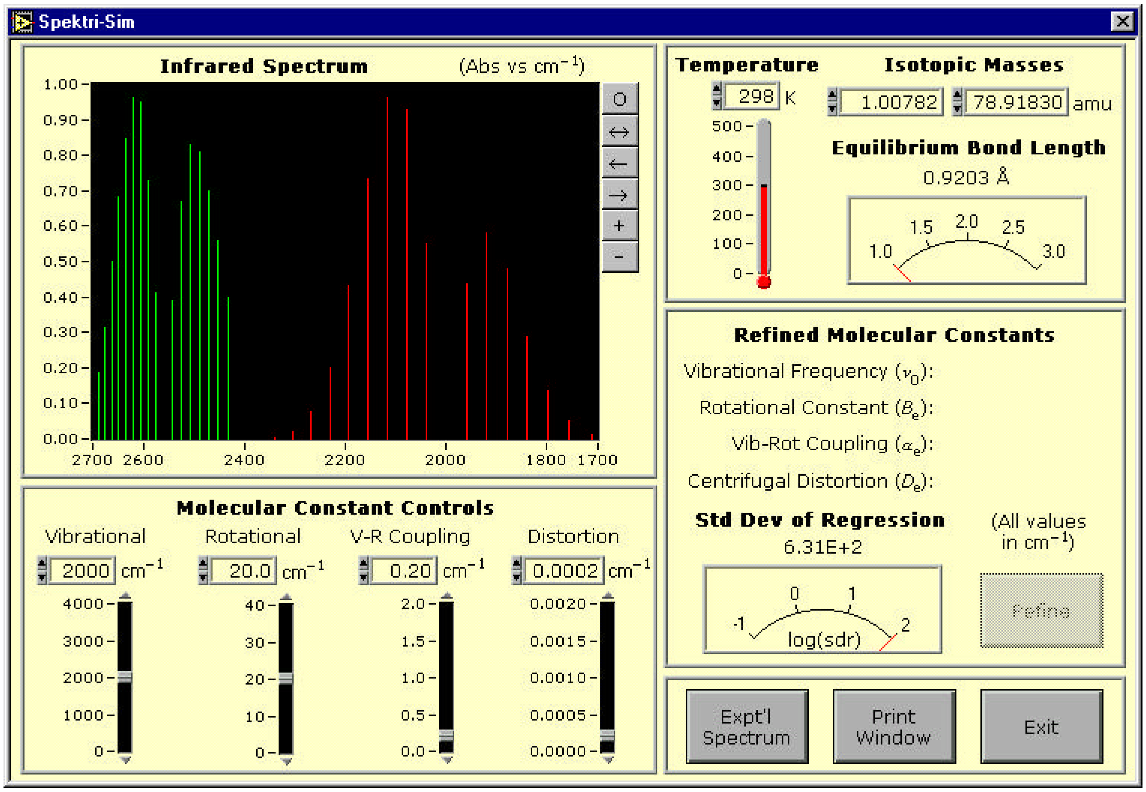
Note that you can use the two plots on the right-hand side of the *Experimental Spectrum* window to visually judge whether the data entered are reasonable. The upper plot shows a stick representation of the experimental IR spectrum. The lower plot shows the variation in frequency as a function of index *m*. It is the latter plot that will eventually be used to numerically fit the molecular constants.

4. **Close** the *Experimental Spectrum* window.

As shown below, the experimental spectrum now appears in green on the graphical display, together with the simulated spectrum, which is still in red.

The **Std Dev of Regression** displays (both digital and analog) are now enabled. The SDR (631 cm$^{-1}$) is a measure of the goodness-of-fit of the simulated spectrum to the experimental one. You will eventually optimize the molecular constants by minimizing the SDR value.

Also, notice that the **O** viewport button on the right-hand side of the spectrum display is enabled. Clicking this button cycles through three separate representations of the experimental and simulated data.



Temperature: 298 K

Isotopic Masses: 1.00782 78.91830 amu

Equilibrium Bond Length: 0.9203 Å

Vibrational: 2000 cm$^{-1}$

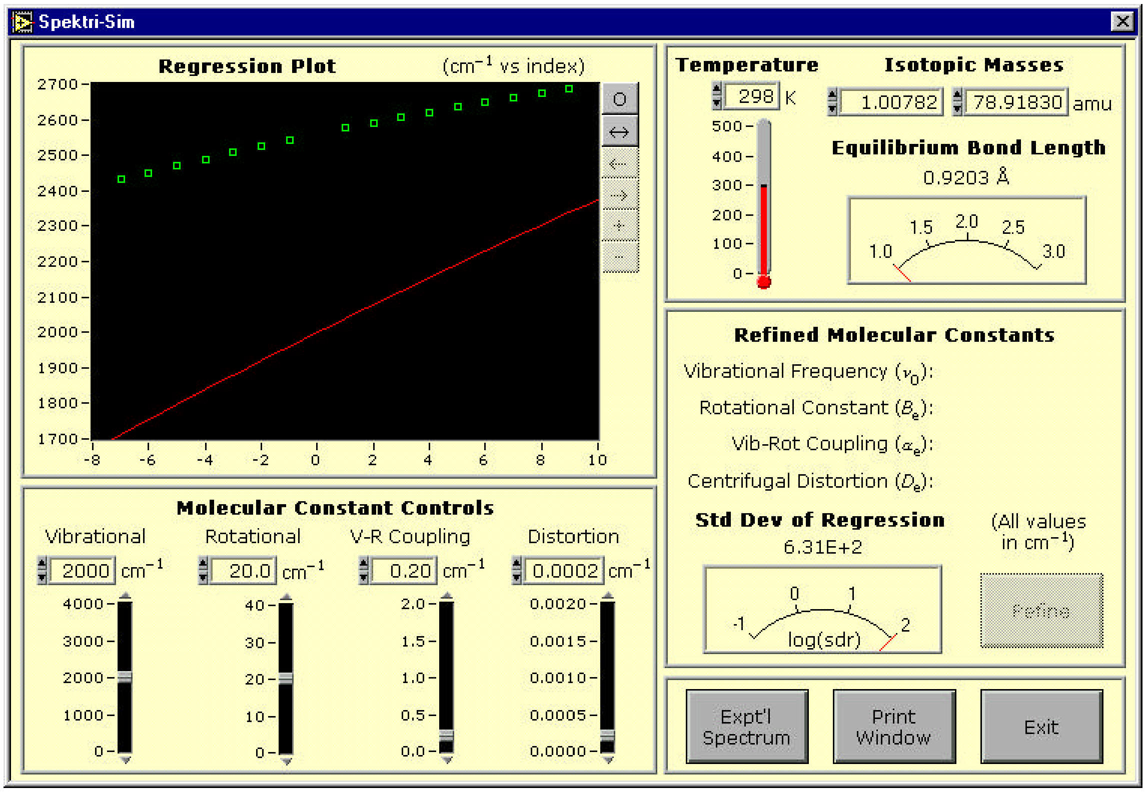
Rotational: 20.0 cm$^{-1}$

V-R Coupling: 0.20 cm$^{-1}$

Distortion: 0.0002 cm$^{-1}$

Std Dev of Regression: 6.31E+2

(All values in cm$^{-1}$)



Temperature: 298 K

Isotopic Masses: 1.00782 78.91830 amu

**Equilibrium Bond Length**

0.9203 Å

Vibrational: 2000 $cm^{-1}$

Rotational: 20.0 $cm^{-1}$

V-R Coupling: 0.20 $cm^{-1}$

Distortion: 0.0002 $cm^{-1}$

Vibrational Frequency ($\nu_0$):

Rotational Constant ($B_e$):

Vib-Rot Coupling ($\alpha_e$):

Centrifugal Distortion ($D_e$):

**Std Dev of Regression**

6.31E+2

(All values in $cm^{-1}$)

5. Click the **O** button.

   As shown above, the graphical display switches to a regression plot of frequency vs index [cf eq (5)] similar to that which we just saw in the *Experimental Spectrum* window. The green squares represent the experimental frequencies. The red curve shows how well the current values of the molecular constants fit the experimental data.

6. Click the **O** button again.

   The regression plot now switches to a residuals plot that shows the difference between the experimental and simulated frequencies, the latter based on the current set of molecular constants.

7. Click the **O** button one more time.

   The display returns to the infrared spectrum.

8. Adjust the molecular constants to visually maximize the overlap of the simulated and experimental spectra.

You might find it convenient to periodically rescale or shift your view of the spectra using the viewport buttons.

In addition, you can use the SDR display to help optimize the fit. Increasing the overlap of the experimental and simulated spectra corresponds to decreasing the SDR.

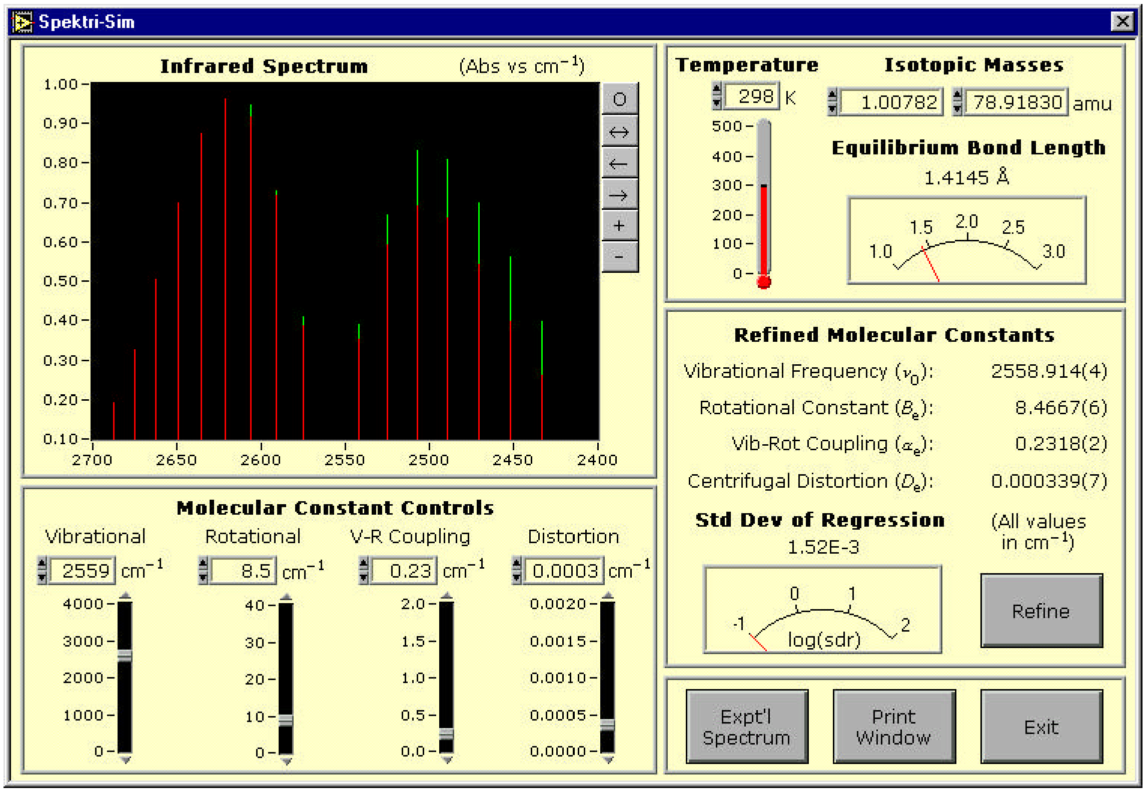
9. Continue adjusting the molecular constant controls until the SDR decreases to a value less than 3 $cm^{-1}$.

   The **Refine** button in the Spektri-Sim window is now enabled and you can use Spektri-Sim's numerical optimizer to complete the final refinement of the molecular constants.

10. Click **Refine**.

    The Spektri-Sim window should appear as shown below. The SDR has decreased to $1.52x10^{-3}$ $cm^{-1}$.

    Spektri-Sim reports the refined molecular constants together with their standard deviations (the values in parentheses represent one standard deviation in the last digit displayed). Table 1 lists the molecular constants for $H^{79}Br$ determined by Spektri-Sim along with literature values.



Temperature: 298 K

Isotopic Masses: 1.00782 78.91830 amu

Equilibrium Bond Length: 1.4145 Å

Molecular Constant Controls

Vibrational: 2559 $cm^{-1}$

Rotational: 8.5 $cm^{-1}$

V-R Coupling: 0.23 $cm^{-1}$

Distortion: 0.0003 $cm^{-1}$

Refined Molecular Constants

| | |
|---|---|
| Vibrational Frequency ($\nu_0$): | 2558.914(4) |
| Rotational Constant ($B_e$): | 8.4667(6) |
| Vib-Rot Coupling ($\alpha_e$): | 0.2318(2) |
| Centrifugal Distortion ($D_e$): | 0.000339(7) |

Std Dev of Regression: 1.52E-3

(All values in $cm^{-1}$)

After numerical refinement, all features (molecular constant controls, equilibrium bond length, regression and residual plots) are updated using the best-fit molecular constants.

11. Click **Print Window**.

    An image of the Spektri-Sim window is sent to your default Windows printer.

12. **Exit** the application.

**Table 1.** Molecular Constants (in $cm^{-1}$) and the Equilibrium Bond Length (in Å) of $H^{79}Br$ ($X\ ^1\Sigma^+$).

| | Spektri-Sim | Literature[3] |
|---|---|---|
| $n_0$ | 2558.914(4) | 2558.541 |
| $B_e$ | 8.4667(6) | 8.46488 |
| $a_e$ | 0.2318(2) | 0.23328 |
| $D_e$ | $3.39(7)\text{x}10^{-4}$ | $3.457\text{x}10^{-4}$ |
| $R_e$ | 1.4145 | 1.41443 |

Value in parentheses represent one standard deviation uncertainties in the last displayed digit.

## 4. Installing Spektri-Sim

Spektri-Sim is a Windows-based application. It has been installed and tested under Windows 95 and 98. We recommend a 133 MHz Pentium or faster processor with at least 16 MB of memory. The installation requires only a few megabytes of disk space. Video display resolution should be set to 800x600 pixels or higher.

Spektri-Sim was developed using LabVIEW 5.1 from National Instruments. The application is distributed as a standalone program on four diskettes. Two of these diskettes (the Spektri-Sim Installation Disks) include the main setup program for Spektri-Sim. The other two diskettes (the Run-Time Engine Disks) contain LabVIEW support libraries.

For information on obtaining the Spektri-Sim distribution, see Section 5 (*Spektri-Sim Distribution*).

**To install Spektri-Sim:**

1. Insert the Spektri-Sim Installation Disk 1 into the A: drive.

2. Click on **Start** on the Windows taskbar and select **Run**.

   A Run dialog box opens.

3. Enter the command **a:setup**, and click **OK**.

   By default, the setup program installs Spektri-Sim in the folder C:\Program Files\Spektri-Sim. You are given to option to select an alternate folder.

   During installation you will be prompted to insert the second Spektri-Sim disk and the two LabVIEW Run-Time Engine disks.

4. When the installation completes, restart your computer.

A shortcut to Spektri-Sim should be available on the Start menu. Use **Start > Programs > Spektri-Sim** to start the application.

The Spektri-Sim distribution includes documentation (in PDF format) and four sample data files (HCl-35.txt, HCl-37.txt, HBr-79.txt, HBr-81.txt and CO.txt). The latter each contain an experimental IR spectrum in Spektri-Sim format. These files are located in the folder C:\Program Files\Spektri-Sim.

There is an uninstaller in the folder C:\Program Files\Spektri-Sim, should you decide to remove the application from your computer.

## 5. Spektri-Sim Distribution

Spektri-Sim is available, free-of-charge, either by contacting the authors, or preferably by downloading compressed copies of the installation diskettes from http://carbon.indstate.edu/spektri-sim. The distribution includes the LabVIEW 5.1 Run-Time Engine, documentation (with a tutorial) in PDF format, and sample data for HCl, HBr, and CO.

## 6. Credits

Eric Glendening is an assistant professor of chemistry at Indiana State University. He can be contacted for bug fixes and upgrades at the following address:

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Terre Haute, IN 47809
e-mail: ericg@carbon.indstate.edu

Jarno Kansanaho completed a significant portion of the code development during the 1998-99 academic year as a foreign exchange student at Indiana State University. His current address is:

Department of Chemistry
University of Jyväskylä
Jyväskylä, Finland
e-mail: jmkansan@st.jyu.fi

A description of Spektri-Sim has been submitted to the *Journal of Chemical Education* for publication.

Both authors wish to acknowledge Arthur Halpern for his encouragement and constructive comments regarding the development and testing of Spektri-Sim.

## 7. References

1. See, for example, Experiment 37 of A. M. Halpern, *Experimental Physical Chemistry*, Prentice-Hall, 1997.

2. Data in HBr-79.txt is taken from: (a) D. H. Rank, U. Fink, and T. A. Wiggins, *J. Mol. Spect.*, *18*, 170 (1965). (b) B. S. Rao, *J. Phys. B, 4*, 791 (1971).

3. K. P. Huber and G. Herzberg (data prepared by J.W. Gallagher and R.D. Johnson, III), "Constants of Diatomic Molecules," in *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, Eds. W.G. Mallard and P.J. Linstrom, February 2000, National Institute of Standards and Technology, Gaithersburg MD, 20899 (http://webbook.nist.gov).