

PHYSICS 320 LABORATORY
The diatomic Sulfur anion (S_2^-) modeled as a
Quantum Harmonic Oscillator

OBJECTIVE:

In this lab, you will study the energy levels of the diatomic sulfur anion (S_2^-) contained within a mineral. Fluorescence emission spectra will be taken at room temperature and at 77 K. The spectra will be analyzed to determine differences in energy among the vibrational energy states of the ground state potential well, the shape of the ground state well and other defining parameters of this system.

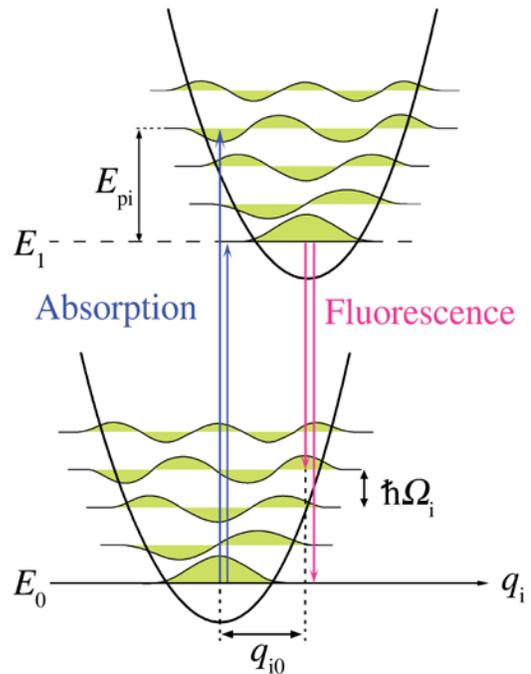
BACKGROUND:

Minerals are formed in the high temperature, high pressure environment within Earth's core and work their way to the surface through a variety of geophysical processes. Depending on the local mix of elements, different minerals can form simple to quite complex structures. Minerals can contain a fluorescence activator that, when the mineral is exposed to ultraviolet light, will glow brightly and colorfully. Nature's Rainbow (www.naturesrainbows.com) is a fluorescent mineral supersite! At the website Online Database of Luminescent Minerals (www.fluomin.org/uk/), information about minerals including names, colors and activators, can be searched. In minerals such as wernerite (Ontario), emerald sodalite (Greenland), tugtupite (Greenland), among others, the activator is the diatomic sulfur anion (S_2^-). This anion is not part of the regular arrangement of ions that make up the mineral structure but is located within the vacant spaces of the mineral matrix.

A diatomic molecule can be modeled to a first approximation as a quantum simple harmonic oscillator. Classically, the two sulfur atoms, plus another electron, are bound by a linear restoring force. The motion of the two atoms can be reduced to that of a single mass oscillating about an equilibrium position in a quadratic potential. The solution to the time-independent Schrödinger equation for a quadratic potential yields energy levels that are equally-spaced and energy eigenstates (wave functions) based on the Hermite polynomials. In addition to there being discrete electronic transitions between electronic eigenstates, the diatomic anion can make transitions between vibrational eigenstates. The figure below is a diagram showing two electronic eigenstates of energy E_0 and E_1 and their associated vibrational levels. The axes of the two wells are offset in the coordinate q_i because the excited anion has a different shape than the anion in the ground state.

A laser emitting photons of sufficient energy will raise some of the $(S_2)^-$ anions to an excited electronic state through the absorption process. Then the $(S_2)^-$ ion will relax to the lowest-energy vibrational state within the excited electronic state through a non-radiative process. From this lowest excited energy level, the electrons will fall back to the ground state, emitting photons (“fluorescing”) as they do so.

As the electrons return to their ground state, some vibrational energies will be more favored than others – those ground vibrational levels with wave functions that overlap substantially with the excited state vibrational levels will be more favored, while those with less overlap will be less favored. Because the electronic transitions originate from the same energy level, the spacing of peaks within the spectrum will then be the spacing of the vibrational energy levels of the $(S_2)^-$ anion ($\hbar\Omega_i$ in the diagram).

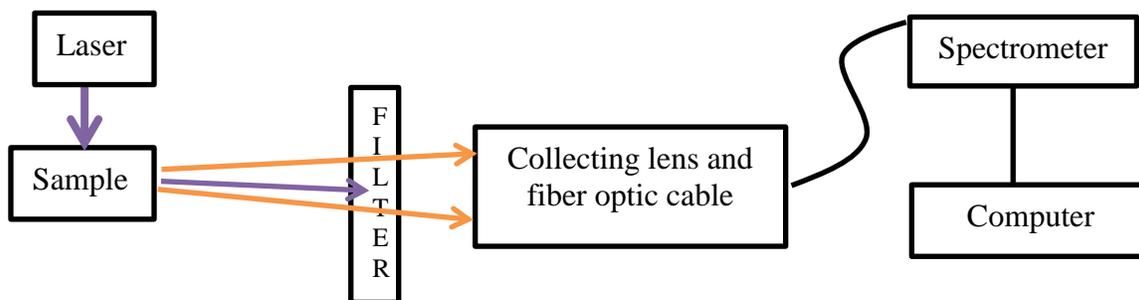


In Procedure I, we will begin our analysis by assuming a quadratic form of for the ground state well, so the equation of this well will be $V = \frac{1}{2}m\Omega_i^2x^2$. This would give a spacing between energy levels of $\hbar\Omega_i$. In reality, however, the quadratic approximation may not be entirely accurate, which would affect the shape of the ground state well and thus the spacing of the energy levels. In Procedure II, you will take a low temperature spectrum to determine a more accurate shape of the ground state well. Procedure III will add more precision by zooming in on the weaker peaks at the high and low energy transitions.

INITIAL QUESTIONS for your write-up.

1. Look up the mineral families called *Scapolite* and write a few sentences about the mineral family (chemical composition, crystal shape, history, locations found, etc.) What are the end members of this family called? What is the difference between *sodalite* and *scapolite*?
2. Your instructor will provide you the name of the mineral and its place of origin that you will be studying. From this information, determine what you can about the chemical formula and unit cell dimensions for the mineral.

PROCEDURE I: Determining the Spring Constant of (S₂)⁻



1. Set up the optical equipment as shown above. The laser should hit the sample directly, and the filter and collecting lens should be aligned as straight as possible to maximize fluorescent light entering the fiber optic cable. Tighten all mechanical adjustments once the optical elements are properly aligned.
2. Open the spectrometer software and choose the scope mode.
3. Set the integration time so that the spectrum graph is not saturated (no wavelengths have the maximum signal) and set the acquisition to average several scans to reduce the effects of optical noise.
4. Turn off the laser and take a dark spectrum. Determine that the spectrometer software automatically subtracts the dark spectrum from subsequent spectra.
5. Turn on the laser and measure the fluorescence spectrum of the sample. Save the spectrum and open it in Excel. You may need to turn the Text to Columns. Plot the spectrum in Excel. Print the Excel graph for your report.
6. In Excel, determine the energies at which peaks occur, and from this data determine the average energy difference between peaks.
7. From this average, determine the vibrational constant k , the spring constant for the coupled S atoms. $\Omega_i = \sqrt{\frac{k}{\mu}}$, where $\mu = \frac{m_S}{2}$, and m_S is the mass of a sulfur atom.

PROCEDURE II: The Shape of the Ground State Well

1. Fill the dewar 3/4 full with liquid nitrogen, then clamp the dewar in place.
2. Lower the sample into the liquid nitrogen. The LiN₂ will boil quickly at first, but by the time you are taking data, the boiling rate will have slowed so as not to be a problem.
3. Adjust the optical elements as necessary to bring everything back into alignment.
4. Take a fluorescence spectrum as before, adjusting the integration time as necessary. If you change the integration time, take a new dark spectrum. Once you have obtained a clear spectrum, save the spectrum and plot it in Excel. Print the Excel graph for your report.

5. Record the peak wavelengths and convert them to the units of energy, wavenumbers [cm^{-1}].
6. Create a plot of the difference in energy between consecutive peaks (in wavenumbers [cm^{-1}]) vs. Energy level (each peak corresponds to a transition to a separate energy level; be sure that the transitions to lowest energy levels are on the left side of your plot). Find the linear best-fit for this data, then print the plot.
7. Based on the slope of the plot you just created, determine whether the ground state energy well is, in fact, parabolic, or whether it is steeper or shallower than a parabola at high energies (this change in shape is due to higher-order terms in the potential energy that we ignore with our initial approximation). Draw a qualitative sketch of this ground state energy well.
8. We say that an oscillator *softens* if the spring constant decreases and *hardens* if the spring constant increases. Does this well harden or soften with increasing energy?

PROCEDURE III: Examining the Highest and Lowest Energy Transitions

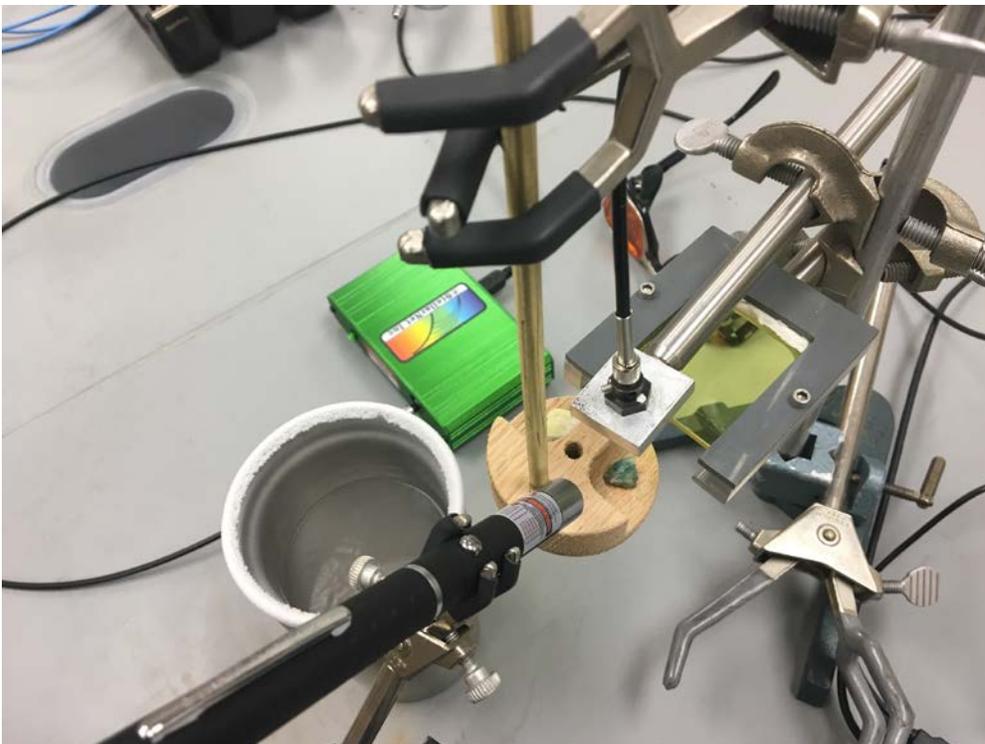
1. With the same setup as in Procedure II, take one more spectrum at 77 K, this time increasing the integration time so that the spectrometer is saturated in the mid-range, allowing us to see the less intense peaks on either side more clearly. As usual, plot in Excel, and print this graph for your report.
2. Use this spectrum to obtain more precise values for the peaks representing the higher and lower energy peaks.
3. With these new values, redo the plot of the difference in energy between consecutive peaks vs. energy level.
4. Print this plot, and comment on any observed changes from the plot obtained in Procedure II.

Image Citation: <https://commons.wikimedia.org/wiki/File:Phonon-energy-diagram.png> The image file is licensed under the Creative Commons Attribution-Share Alike 2.5 Generic license.

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We thank Mark Cole for his generous supply of some of the mineral samples.

Images of Experimental Setup

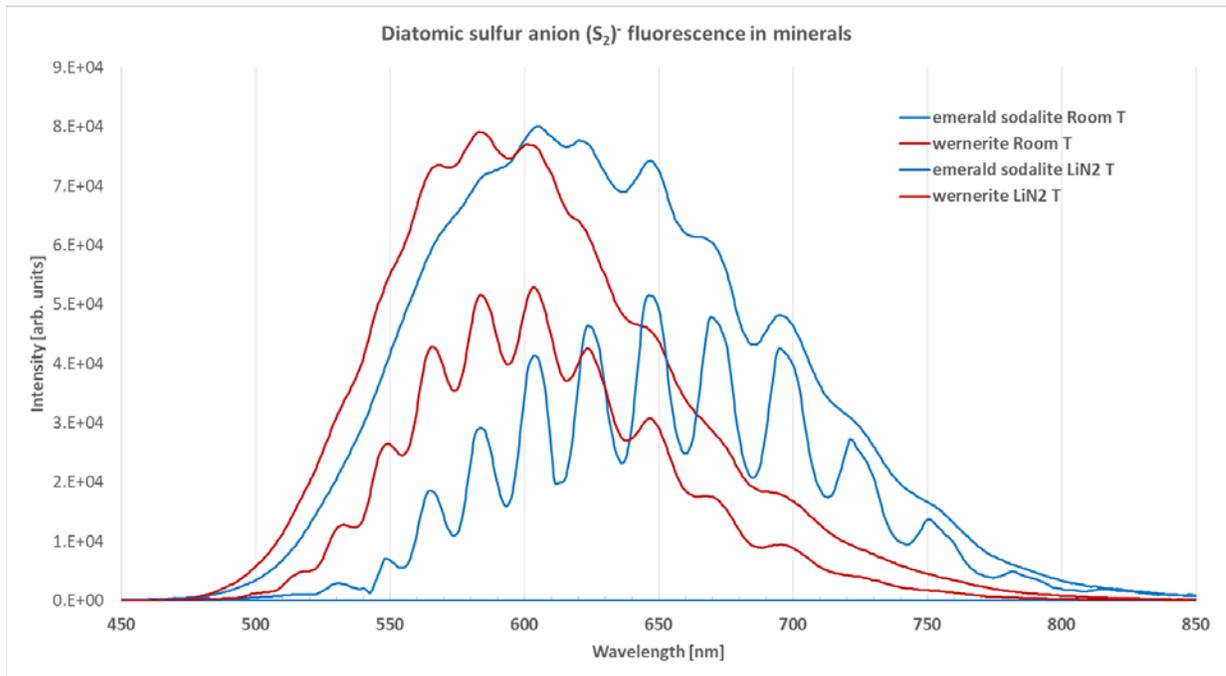


Photos by Dan Boye, Physics Dept. Davidson College, Davidson, NC 28035

Equipment List

USB Spectrometer	Shown is StellarNet GREEN Wave (350-1150nm range with 50 μ m slit) with 400 μ m fiber optic cable and collecting lens with holder (www.stellarnet.us)
Colored filter	Schott GG455nm longpass filter, 2 in. square with filter holder (also Thorlabs FGL455)
Sample holder	In-house design for two samples, made of oak
Samples	Miner Shop (www.minershop.com) Ward's Science (www.wardsci.com)
Laser pointer	405nm, 20-25mW
Laser safety goggles	190-532nm & 900-1700nm OD4+ (www.certified-laseryewear.com)
Dewar	Shown is double-wall aluminum vacuum insulation coffee mug Can use doubled Styrofoam cups Can use silvered or unsilvered dewars (Pope Scientific Lab Grade) (www.popedewars.com/labgrade.html)
Assorted rods, clamps and stands	

Sample spectra



S_2^- Activator minerals

Search of luminescent mineral by activator

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Quick search by fluorescent mineral name:

Search by activator

Search made on: S_2^-

UV type selected: *All UV Types*

Number of results: **15**

Click on the name to open the complete information page of the mineral.

AFGHANITE	
ANHYDRITE	
BARYTE	
DELHAYELITE	
hackmanite	See: SODALITE
HAUYNE	
LAZURITE	
MARIALITE	
MEIONITE	
scapolite	See: MEIONITE / (Group: MEIONITE, MARIALITE)
SODALITE	
tetranatrolite	See: GONNARDITE
tugtupite	See: TUGTUPITE
TUGTUPIITE	
wernerite	See: MEIONITE / (voir aussi/see also MARIALITE)

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