Advanced Undergraduate Laboratory Course PHY442/542

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Originally supported by: NSF-ILI, NSF, MU College of Arts and Science, & Department of Physics and originally initiated by Dr. Marcum.
Spectroscopy of Atoms and Molecules

The spectroscopy laboratory makes a unique contribution to our curriculum. Students observe atomic and molecular spectra and are then challenged to understand how the spectra relate to the structures of the associated atoms or molecules. A common student reaction to the course is that “it makes quantum mechanics real,” a statement that indicates that our goal has been attained.

GOAL:

• Establish an understanding of the fundamental connections between atomic and molecular spectra and the underlying structures that give rise to such spectra.
• Educate and motivate the laboratory and analytical skills of the students through practice, well designed standard experiments, and encouragement of creativity and originality.
• Introduce a wide variety of spectroscopic techniques.
• Employ state-of-the-art equipment.
• Use a guided discovery approach.
• Develop the student’s ability to express and communicate coherently their scientific findings.
Creating, implementing, and sustaining an advanced optical spectroscopy laboratory course

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Department of Physics, Miami University, Oxford, Ohio 45056

(Received 15 September 2009; accepted 1 February 2010)

An upper-division laboratory course in atomic and molecular spectroscopy is described. Examples of outcomes that also benefit second-year physics laboratories and demonstrations in introductory courses are presented. The overarching goal that drove the development of the course was to assist students in understanding the fundamental connections between atomic and molecular spectra and the underlying structures. A selection of laboratory experiences supporting this goal, and the equipment and techniques necessary to provide them, are outlined. © 2010 American Association of Physics Teachers.

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III. THE COURSE

Spectroscopy of Atoms and Molecules is a one-semester, four credit course that emphasizes experimental techniques found in research. The course typically meets three times a week, with two 1-h classroom meetings and one 3-h laboratory meeting. We use Herzberg’s classic Atomic Spectra and Atomic Structure as a textbook. Texts on reserve in the department form important additional student resources, especially Haken and Wolf’s The Physics of Atoms and Quanta, Svanberg’s Atomic and Molecular Spectroscopy and Herzberg’s Molecular Spectra and Molecular Structure I: Spectra of Diatomic Molecules. Many handouts and the individual laboratory handouts have been developed over the years.

The origins of both the modern optics and laser physics laboratory, and the spectroscopy course that is the subject of this paper, was an advanced undergraduate elective on spectroscopy and physical optics, which had no laboratory-based component. The addition of a laboratory component began in 1984 when one of us taught this course using existing equipment and borrowed time on research equipment. With the addition of new faculty, collaboration on proposals to fund advanced laboratories was initiated. The two new laboratory courses on optics and spectroscopy were seminally funded by two NSF Instrumentation and Laboratory Improvement grants, with matching funds from the university totaling to $124,000. The first grant largely funded the creation of the two new courses, and the second was for enhancement of these successful efforts.

Text (optional): Atomic Spectra & Atomic Structure – G. Herzberg

Resources: Supplements will be supplied via handouts from:

- Spectra of Diatomic Molecules- G. Herzberg
- Atomic and Molecular Spectroscopy- S. Svanberg
- Optics- E. Hecht
- Introduction to Modern Optics- G.R. Fowles
- Miscellaneous handouts from a wide variety of texts, journal articles etc.
- Lab handouts will be supplied by your instructor.

Goals: Spectroscopic techniques are powerful tools for determining both structural and quantitative changes in organic and inorganic compounds. The reason spectroscopic techniques can ascertain the structure of compounds is because different structures absorb energies at specific frequencies or wavelengths. In other words, absorbed energy is quantized by having discrete energy levels and is specific to the particular structure. This intensity is a measure for determining whether the electronic, vibrational, or rotational transition is allowed. These concepts and techniques will be discussed in this course.

Outline of the goals: (i) Introduce you to a wide variety of spectroscopic tool and techniques and hands-on experience using various light sources and lasers such as continuous wave (cw) and pulsed lasers, (ii) Study selected applications of spectroscopy, (iii) Establish understanding of some of the more fundamental connections between atomic and molecular spectra and the underlying structures that give rise to such spectra, (iv) Understand the interaction of electromagnetic radiation with matter, (v) Develop professional scientific and technical writing, (vi) Improving effective professional oral presentation skills.

Grading Policy:

Quizzes: 20% (in class, take-home)
Lab write-ups: 60%
Presentation: 20%
Exams: None

Grades for this course will be based on lab write-ups, quizzes and a project presentation. Class attendance is mandatory. If you have to miss a class you should inform your instructor.

Queen's University - April 26, 2018
I encourage students to write lab reports using LaTeX, high-quality typesetting to create professional scientific and technical documents (such as thesis, journal papers, reports, etc.). Besides this course, I have been providing LaTeX workshop to many graduate & undergraduate students in the Department of Physics at Miami.
Atomic Spectra

Blackbody radiation, atomic and molecular spectra

D-H isotope shift and Balmer series of hydrogen

Fine structure splitting of alkali metals (LS Coupling)

Zeeman effect in atomic sodium or cadmium light source

Molecular Spectra

Raman scattering spectroscopy of liquid nitrogen

Vibrational structure of nitrogen molecules

Vibrational spectroscopy: Laser induced fluorescence spectrum of diatomic iodine

Rotational spectra of N$_2^+$

Other Experiments Related to Optics

Make a dye laser from the construction of laser cavity from Littman-Metcalf configuration

Resonance excitation of Na and Na$_2$ vapor

Lifetime measurement of D2 line of sodium

Beam profile to measure Electric Field

Optical rotation using wave plates
Given: atomic hydrogen is the template (Lyman, Balmer, Paschen, etc., simple series). $H$ & He spectrum comparisons show that electron screening breaks the $l$-degeneracy in $H$. Further structure due to “L-S coupling”

Alkalis: spin-orbit splitting & related topics
Vibrational structure of diatomics ($N_2$ and $I_2$)
Rotational structure of diatomic ($N_2$)

DC discharge tube that can be filled with the desired gas mixture, e.g. He-$N_2$ or Ar-$N_2$. 
Inexpensive AC capillary discharge tubes are available for H, D, Hg, the noble gases, N$_2$, O$_2$, CO$_2$, halogens (~$25 each, D is a bit more).

Very robust OSRAM lamps are available for the alkalis, Hg, Cd, He, Ar (expensive).
Atomic Spectroscopy

Spin-orbit interaction setup

Na

K

Rb

Cs

Bright source – setup is easy.
Cs principal series: orbital B vs n

<table>
<thead>
<tr>
<th>Doublet</th>
<th>D lines (nm)</th>
<th>7-6</th>
<th>8-6</th>
<th>9-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength (nm)</td>
<td>894.36</td>
<td>459.32</td>
<td>388.86</td>
<td>361.7</td>
</tr>
<tr>
<td></td>
<td>852.12</td>
<td>455.53</td>
<td>387.61</td>
<td>361.1</td>
</tr>
<tr>
<td>Energy (eV)</td>
<td>1.386</td>
<td>2.700</td>
<td>3.189</td>
<td>3.428</td>
</tr>
<tr>
<td></td>
<td>1.455</td>
<td>2.722</td>
<td>3.199</td>
<td>3.434</td>
</tr>
<tr>
<td>Difference</td>
<td>0.069</td>
<td>0.022</td>
<td>0.010</td>
<td>0.006</td>
</tr>
<tr>
<td>B (Tesla)</td>
<td>594</td>
<td>194</td>
<td>89</td>
<td>49</td>
</tr>
</tbody>
</table>
L-S coupling selection rules are obeyed, and predictions of intensity ratios within doublets (using statistical weights and the sum rule) is verified.

A.A. Radzig and B.M. Smirnov
Reference Data on Atoms, Molecules, and Ions
Springer-Verlag
• The complexity of typical molecular spectra can be quite daunting.

• My solution is to selectively excite particular electronic bands using a commercial N₂ AC capillary discharge (has some noble gas).

• Makes use of energy pooling in noble gas metastable levels as in the He-Ne laser.

• View the plasma near the cathode.
Raman Scattering Spectroscopy

Nd:YAG 532 nm Pulsed laser
Liquid nitrogen Dewar
A spectrometer+fiber+PC

Highly Visual Experiment

Frequency doubled, pulsed Nd:YAG laser scattering from liquid nitrogen yields uncommon Raman.

Examples from a student’s report:

<table>
<thead>
<tr>
<th>λ (nm)</th>
<th>Intensity</th>
<th>E (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>427.11</td>
<td>161</td>
<td>2.903233</td>
</tr>
<tr>
<td>474.14</td>
<td>638</td>
<td>2.615261</td>
</tr>
<tr>
<td>532</td>
<td>4095</td>
<td>2.330827</td>
</tr>
<tr>
<td>607.84</td>
<td>2337</td>
<td>2.040011</td>
</tr>
<tr>
<td>707.91</td>
<td>1281</td>
<td>1.751635</td>
</tr>
<tr>
<td>844.65</td>
<td>115</td>
<td>1.468064</td>
</tr>
</tbody>
</table>

Table II: Calculated values for the force constant and frequency of a simple QHO compared against literature [4]

<table>
<thead>
<tr>
<th></th>
<th>Experimental</th>
<th>Uncertainty</th>
<th>Literature</th>
<th>Error (N/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K (N/m)</td>
<td>2229.8982</td>
<td>109.8141</td>
<td>2300</td>
<td>70.10</td>
</tr>
<tr>
<td>ω (rad/s)</td>
<td>4.3789E+14</td>
<td>1.0782E+13</td>
<td>4.39E+14</td>
<td>1.1099E+1</td>
</tr>
</tbody>
</table>

Rayleigh Scattering

2'nd Anti-Stokes shifted scattering
1'st Anti-Stokes shifted scattering
Rayleigh Scattering
1'st Stokes shifted scattering
2'nd Stokes shifted scattering
3'rd Stokes shifted scattering
Electron impact excitation of the argon gas is the primary excitation mechanism. Metastable states of Ar at 11.55 eV or 11.72 eV.


Electron impact excitation of the helium gas is the primary excitation mechanism. There are other gases but the great majority of the targets for electron impact excitation collisions are predominantly helium atoms. Some direct electron impact excitation of nitrogen molecules will occur, but the frequency of such reactions will be at least an order of magnitude lower than for such electron-He atom collisions.

Helium has metastable states at 19.8 & 20.6 eV. Helium metastable states have energies that are essentially resonant with the B-state in the nitrogen molecular ion N$_2^+$. Efficient population of the B electronic level in nitrogen will proceed by the reaction,

$$\text{He}^*(M) + \text{N}_2(X, v = 0, \text{various} \ J's) \rightarrow \text{N}_2^+(B, \text{primarily} \ v' = 0, \text{various} \ J's) + \text{He} + \text{e}$$

followed by a spontaneous emission via,

$$\text{N}_2^+(B, \ v' = 0, \ J') \rightarrow \text{N}_2^+(X, \ v'' = 0, \ J'') + \text{hv}.$$
Rotational Spectra of $\text{N}_2^+$

Boltzmann Rotational Distribution

Nitrogen ion emission band

**Extractable structure information:**

<table>
<thead>
<tr>
<th>Constants</th>
<th>Students</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_{00}$ (cm$^{-1}$)</td>
<td>$25570 \pm 3$</td>
<td>$25580$ (Ref. 13); $25566$ (Ref. 25)</td>
</tr>
<tr>
<td>$B'_e$ (cm$^{-1}$)</td>
<td>$2.014 \pm 0.110$</td>
<td>$2.083$ (Ref. 13); $2.085$ (Ref. 26)</td>
</tr>
<tr>
<td>$B''_e$ (cm$^{-1}$)</td>
<td>$1.857 \pm 0.110$</td>
<td>$1.933$ (Ref. 13); $1.932$ (Ref. 26)</td>
</tr>
<tr>
<td>$I'$ (10$^{-46}$ kg m$^2$)</td>
<td>$1.39 \pm 0.08$</td>
<td>$1.34$ (Ref. 13)</td>
</tr>
<tr>
<td>$I''$ (10$^{-46}$ kg m$^2$)</td>
<td>$1.51 \pm 0.08$</td>
<td>$1.45$ (Ref. 13)</td>
</tr>
</tbody>
</table>
Vibrational Spectroscopy of I₂

Laser Induced Fluorescence in diatomic iodine

Room temperature iodine cell
Spectrometer
Fiber and PC


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Vibrational Structure of $I_2$

Laser Induced Fluorescence in diatomic iodine


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**Task 1: Spectral line assignment**

Use the Franck-Condon factors in the insert to assign each peak on the graph. Assign at least 20 of them.

**Task 2: Data tabulation in a Deslandres table for iodine**

Use once again the I$_2$ emission spectrum to fill out the table below with the following parameters for each spectral line:
- The emitted wavelength, $\lambda$ (nm). Employ the program provided to verify the values.
- The transition energy, $G_{\nu'\rightarrow \nu''}$ (cm$^{-1}$).
- The energy separation between successive levels, $\Delta G = G_{\nu'\rightarrow \nu''} - G_{\nu'\rightarrow \nu''+1}$ (cm$^{-1}$).

Then, to get a sense of the vibrational fine structure, use any pair of successive lines to estimate the energy separation with

$$G_{\nu'\rightarrow \nu''} \approx \left(10^7 \text{ nm} / \lambda \text{[nm]} \right)$$

**Task 4: Summarizing the results**

As explained in the manual, the fundamental frequency and the anharmonic term can be used to determine other parameters of the molecule. For the equilibrium state, the force constant $k_0$ of the bond, the dissociation energies $D_0$ and $D_e$, with respect to the lowest level and the equilibrium position (bottom of the potential well), and the factor $\beta$ in the Morse potential. Use the provided formulas to estimate these parameters for the ground level $X$ of the iodine molecule, and list them in the table below.

**Conversion:**
- from cm$^{-1}$ to eV: $E_{\text{[eV]}} = E_{\text{[cm}^{-1}]}/1.24 \times 10^{-4}$ cm$^{-1}$ eV
- from cm$^{-1}$ to J: $E_{\text{[J]}} = E_{\text{[cm}^{-1}]}/1.99 \times 10^{-23}$ cm$^{-1}$ J
Advanced Laboratory Physics Association (ALPhA)

Laboratory Immersions in 2012: My workshop attendee has produced an excellent spectrum with his students after returning back to his college.
1. For the following list of transitions and reactions, answer yes or no as to whether you would expect them to occur or not (e.g. dipole allowed? energetically possible?). For any case in which your answer is no, state why you say no. You may wish to refer to the $N_2$ potential curves when necessary.

(a) $N_2^+ (B^2\Sigma_u, v = 3) \rightarrow N_2^+ (B^2\Sigma_u, v = 3) + hf$

(b) $N_2^+ (B^2\Sigma_u, v = 3, J = 10) \rightarrow N_2^+ (B^2\Sigma_u, v = 3, J = 9) + hf$

(c) $N_2(A^3\Sigma_u, v = 0) \rightarrow N_2^+ (X^1\Sigma_g, v = 0) + hf$

(d) $N_2^+ (W^1\Delta_u, v = 0) \rightarrow N_2^+ (X^1\Sigma_g, v = 0) + hf$

(e) $N_2^+ (B^2\Sigma_u, v = 4) \rightarrow N_2^+ (X^2\Sigma_g, v = 0) + hf$

(f) $CO^+ (B^2\Sigma_u, v = 3, J = 10) \rightarrow CO^+ (B^2\Sigma_g, v = 2, J = 9) + hf$

(g) $Na_2(A^1\Sigma_u, v = 8, J = 49) \rightarrow Na_2 (X^1\Sigma_g, v = 0, J = 50) + hf$

Reactions:

(h) $Ne^+ + He \rightarrow He^+ + Ne$

(i) $He(2^3S) + N_2 \rightarrow N_2^+ (D^2\Pi_g, v = 0) + He + e$

(j) $He^+ + N_2 \rightarrow N_2^+ (C^2\Sigma_u, v = 0) + He$

(k) $He(2^1S) + N_2 \rightarrow N_2^+ (B^2\Sigma_u, v = 10) + He + e$

(l) $He(2^3S) + He(2^3S) \rightarrow He^+ + He + e$
The Zeeman structure is not fully resolved. Either need better resolution, or more field...
Students Gain

Experiential Learning
Critical Thinking
Scientific and Technical Writing
Oral Presentation Experience
Peer Review Experience
Advanced Spectroscopy Lab: PHY442/542

Assessment

Scientific Writing Rubric
Peer Review Rubric
Quizzes
Oral Presentation Rubric
### Peer Review Rubric

Developed by Drs. S.B. Bayram and M. Freamat for student-student peer review.

#### Table: Peer Review Rubric

<table>
<thead>
<tr>
<th>Aspect</th>
<th>Good</th>
<th>Fair</th>
<th>Poor</th>
</tr>
</thead>
<tbody>
<tr>
<td>The format of the text respects the requirements: font, margins, spacing. Or the format is different, but similar.</td>
<td>2.5</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>If required, the figures – including diagrams, graphs and tables – are numbered, inserted in text, clear and neat, with captions.</td>
<td>2.5</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>If required, the equations are numbered, well edited and organized, readable, with consistent symbols.</td>
<td>2.5</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>The terminology is competent and adapted to the vocabulary introduced in our course.</td>
<td>2.5</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>The text is free of systematic grammar and spelling errors.</td>
<td>2.5</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>The solution is stylistically fluent, clear, with complex and meaningful phrasing.</td>
<td>2.5</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>The Abstract respects the formatting, styling and content requirements described in Sections 3.1/4.1.</td>
<td>5</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>The Introduction respects the formatting, styling and content requirements described in Sections 3.1/4.1 above.</td>
<td>5</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>The Experimental-Details section respects the formatting, styling and content requirements described in Sections 3.1/4.1.</td>
<td>5</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>The Results and Discussion sections respect the formatting, styling and content requirements described in Sections 3.1/4.1.</td>
<td>5</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>The Conclusions and References sections respect the formatting, styling and content requirements described in Sections 3.1/4.1.</td>
<td>5</td>
<td>4</td>
<td>1</td>
</tr>
</tbody>
</table>

#### Table: Peer Review Rubric (continued)

<table>
<thead>
<tr>
<th>PIN on the reviewed paper:</th>
<th>Total score:</th>
<th>Percent:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
How to use active verbs in lab reports

For a powerful and energetic proposal, avoid passive verbs — was and were — that hide the agent of action. Avoid static verbs that lack movement: am, is, are, be, being, been, bad, have, has, do, did, does, could, should, would. Replace overused verbs (get, went, put) with more precise active verbs.
Techniques

- Fluorescence analysis using a photomultiplier tube (PMT)
- Fluorescence analysis using CCD
- Vibrational spectroscopy by electron impact excitation
- Vibrational spectroscopy by laser induced fluorescence
- Raman scattering spectroscopy
- Zeeman resolved polarization spectroscopy
- Laser excitation to study lifetime of Na atoms
- High and medium resolution spectrograph
- Rotational spectroscopy
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- Metallurgical Analysis
- Polymer Analysis
- Protein & Nucleic Acid Analysis
- Teaching Labs

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USB-ISS series integrated cuvette holder-light source accessories for USB2000+ and USB4000 spectrometers accommodate 1 cm path length cuvettes and are ideal for creating monolithic spectrophotometers from Ocean Optics components. The USB-ISS-UV-VIS-2 covers UV-Vis and Shortwave NIR wavelengths (200-1100 nm) and the USB-ISS-VIS covers Vis-Shortwave NIR wavelengths (390-900 nm). It uses either deuterium-tungsten or tungsten-violet LEDs. $1,970.00
Educational Experiments Available:

http://oceanoptics.com

Fluorescence of an Unknown Fluorophore

Educational Experiments from OceanOptics

http://oceanoptics.com

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- Raman
- Multispectral Sensing
- Software
- Service Plans
- Light Sources
- Sampling Accessories
- Fibers and Probes
- Education Systems
- Integrated Systems
- Chemical Sensors
- Switches, Filters & Shutters

Bringing spectroscopy to teaching labs and science classrooms is as exciting as it's ever been, with new technologies to explore and a proliferation of communication tools for engaging students. Ocean Optics has compiled the basics of spectroscopy and some sample experiments to help you develop your own curricula and course work.

Examples of Education Experiments:

- Determining Color Difference
- Fluorescence of an Unknown Fluorophore
- Radiometric Characterization of LEDs
- Characterization of Spice Extracts

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