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In the Classroom

Visualization of Using Hyperfine Structure To Calculate Nuclear Spin: A Spectroscopy Exercise

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…high-resolution optical spectrum is utilized in an exercise for upper-level chemistry students

An example and two exercises are presented that use hyperfine structure (HFS) to calculate the nuclear spin (**I**). The example uses the visible spectrum of a ^{187}rhenium(I) atomic emission at 527.7 nm. The spectrum of the rhenium(I) ($^8P_{5/2} \rightarrow {}^6S_{5/2}$) transition was recorded with a Fourier-Transform spectrometer with 0.026 cm^{-1} resolution. This exercise for upper-level chemistry majors serves as an introduction to the coupling of the quantum momenta associated with the total electronic angular momentum (**J**) and **I**.

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Introduction

In teaching freshman chemistry, the quantum numbers n, l, m_l, and m_s associated with electrons are introduced along with relevant concepts such as the Pauli exclusion principle and Hund's rule. In organic chemistry, the concept of nuclear spin is discussed in relation to NMR experiments. In physical chemistry, term symbols for electrons in atomic orbitals, and in some cases molecular orbitals, are introduced. Also in physical chemistry nuclear spin is discussed in greater depth. The interaction of unpaired electrons with the nucleus is introduced in many upper-level organic and instrumental analysis courses by demonstrating the effects paramagnetic shift reagents (PMRs) have on NMR spectra; however, models that explain this interaction at the undergraduate level are rarely presented.

In this exercise the hyperfine structure (HFS) observed in a rhenium(I) emission spectrum, as recorded by a high-resolution Fourier-transform spectrometer, is used to illustrate the interaction between the electrons and nucleus of an atom. HFS, which is the result of the coupling of the nuclear spin (**I**) with the total electronic angular momentum (**J**) of an atom, illustrates the reverse interaction of paramagnetic shift reagents (Figure 1). The included high-resolution optical spectrum is utilized in an exercise for upper-level chemistry students seeking additional insight into quantum mechanics. Before performing this exercise, the student should be familiar with the quantum numbers: n, l, m_l, m_s, J, L, S, and I; with deriving term symbols for atoms; and with the scientific terms "degenerate" and "undegenerate" as they apply to the spectra of atomic transitions.

Experimental Considerations

The Los Alamos Fourier-transform spectrometer (LAFTS) recorded a visible emission spectrum from a rhenium hollow-cathode lamp [1–3]. The LAFTS was operated at 0.026 cm^{-1} resolution with 2 scans. Compared to dispersive systems, a high-resolution Fourier-transform spectrometer has the advantages of high resolution, wavenumber precision and accuracy, intensity precision, the multiplex advantage, and the throughput advantage. High-resolution FT-UV/vis systems are more difficult to build than FTIR instruments because the shorter wavelengths require much higher optical tolerances in mirror flatness and mechanical tolerances in mirror movement. The spectrum used for this exercise is shown in Figure 2. It is presented as part of the

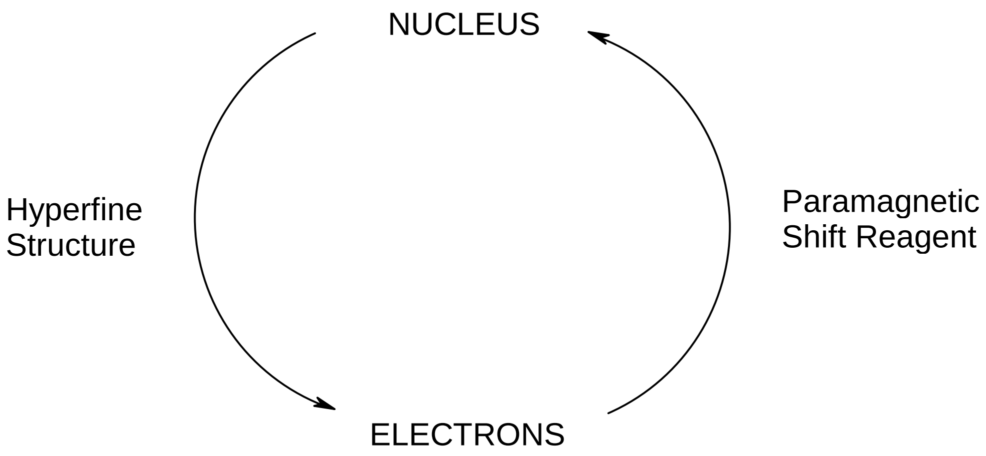

FIGURE 1. PARAMAGNETIC SHIFT REAGENTS (PMRS) DEMONSTRATE THE EFFECTS OF ELECTRONS ON THE NUCLEUS WHILE HYPERFINE STRUCTURE (HFS) DEMONSTRATES THE EFFECTS OF THE NUCLEUS ON ELECTRONS.

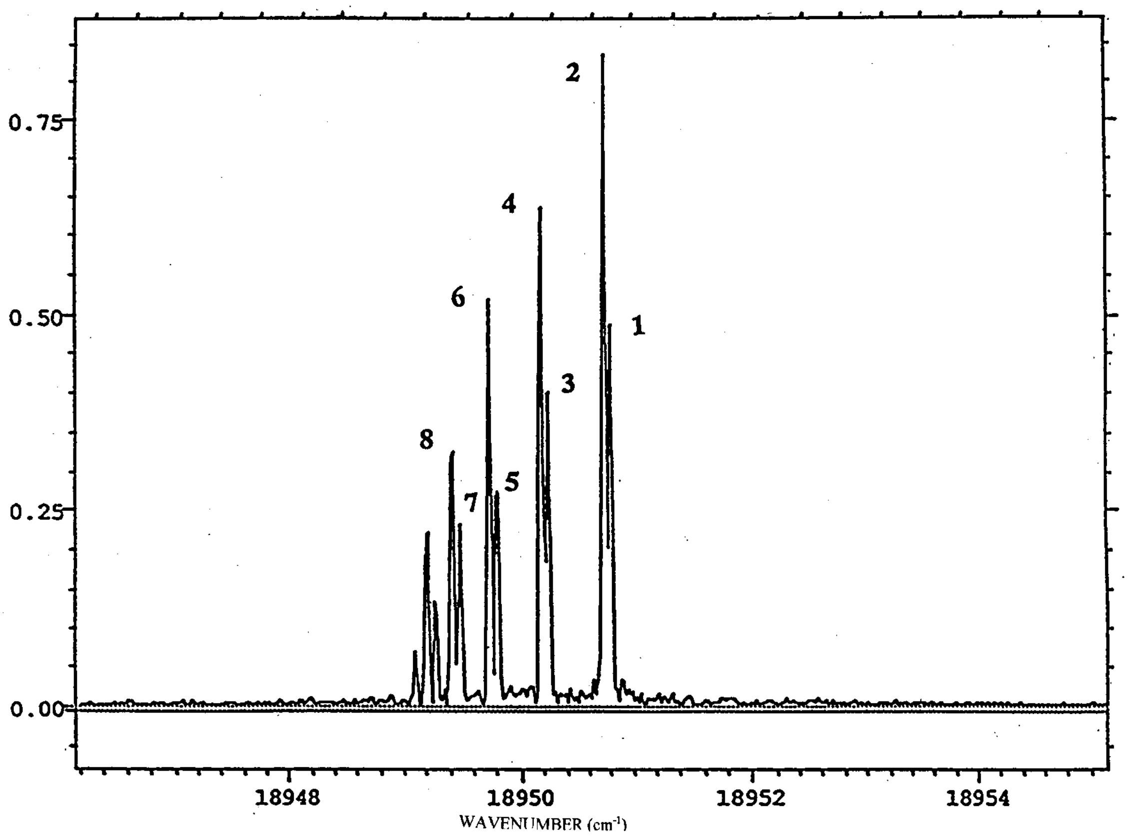

FIGURE 2. HIGH RESOLUTION HFS SPECTRUM OF A RHENIUM(I) TRANSITION RECORDED WITH THE LOS ALAMOS FOURIER-TRANSFORM SPECTROMETER.

exercise because the LAFTS instrument that was used to obtain the spectrum is not routinely available.

Discussion

The HFS for a single transition is often a complex spectrum that occurs when an atom has an I of 1/2 such that I causes splitting of a J energy level into F sublevels. The total atomic angular momentum (**F**) is the result of the coupling between **J** and **I** [4, 5]. Equation 1 is used to determine the maximum quantum value of **F** for a given value of **J** and **I**:

$$\mathbf{F}_{\mathbf{max}} = \mathbf{J} + \mathbf{I} \tag{1}$$

Figure 3 illustrates the relationship between **F**, **J** (**J** = **L** + **S**), and **I**. Electronic transitions between F energy levels for split J energy levels occur in accord with the selection rule for F (equation 2)

$$F = \pm 1, 0; \text{ (except } F = 0 \text{ to } F = 0 \text{ not allowed)} \tag{2}$$

Additional rules exist for calculating the number of energy levels and assigning the F values to each level. In the case that $I > J$, there are $(2J+1)$ F energy levels that are assigned sequential values from $(I - J)$ to $(I + J)$ in increments of 1. In the case that $I < J$, there are $(2I+1)$ F energy levels that are assigned sequential values from $(J - I)$ to $(J + I)$ in increments of 1. All cases assume that $I = 1/2$.

> *Exercise*: You are given the following information about an atomic emission spectrum exhibiting HFS. The ground state is undegenerate with $J = 3/2$ and the excited state is degenerate with $J = 3/2$. There are four lines in the spectrum. Is it possible to calculate I and assign each line in the spectrum an F value from this information?
>
> *Answer:* Since there are $2J+1$ energy levels, we know that $I > J$ in the excited energy level. Because one energy level is undegenerate and the other is degenerate, it is possible to outline their positions and assign the following F values to the undegenerate energy levels (see Figure 4). It is not possible, however, to assign the actual F values to spectral lines, or to calculate I from the given data. More information is needed to calculate I.

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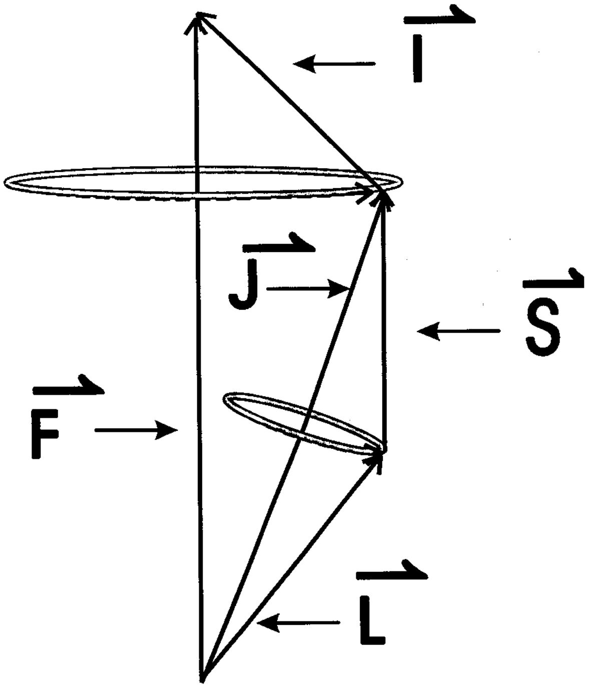

FIGURE 3. *F* RESULTS FROM INTERACTIONS BETWEEN ELECTRONS (*J*, *L*, *S*) AND NUCLEAR SPIN *I*.

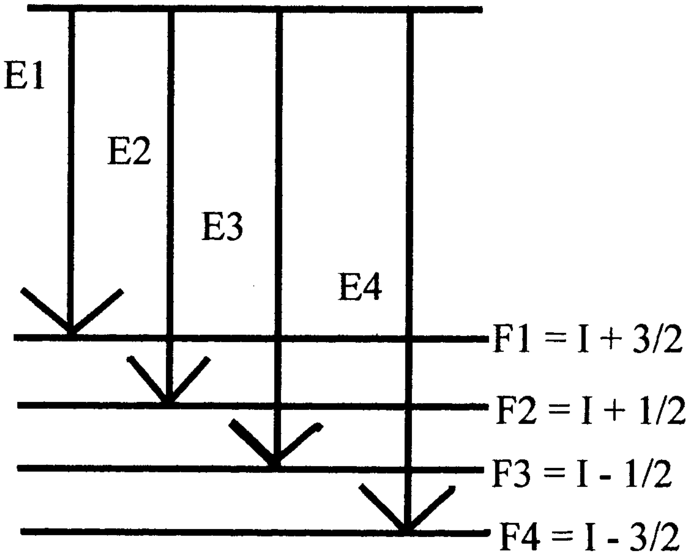

FIGURE-4. THE EXCITED STATE FOR THIS TRANSITION IS DEGENERATE AND THE GROUND STATE IS UNDEGENERATE; THEREFORE, THE ENERGY VALUES E_1, E_2, ..., WHICH ARE THE RESULT OF ELECTRONIC TRANSITIONS, ARE RELATED TO THE *F* VALUES FOR THE UNDEGENERATE ENERGY LEVELS

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The relative energy (E) of each F value can be calculated from the relationship:

$$E = 2\,\mathrm{a}\,F\,(F + 1) \tag{3}$$

where a is the hyperfine splitting constant discussed below.

First, a brief review of the spectral data relevant to the emission spectra shown in Figure 1 will be given. The review is followed by an outline of how to use the data to calculate I.

Rhenium(I)

Re has two naturally occurring isotopes: 185 (37.07%) and 187 (62.93%). The relative abundance of the isotopes (185:187) is demonstrated in Figure 2 by the relative intensities of lines 1 and 2, or any other sequential odd/even pair. The single-electron splitting constants for the $6s6p_z\,{}^8\mathrm{P}_{5/2}$ and $6s^2\mathrm{a}\,{}^6\mathrm{S}_{5/2}$ energy levels are $\mathrm{a}_{6\mathrm{p}} = 0.032\ \mathrm{cm}^{-1}$ and $\mathrm{a}_{6\mathrm{s}} = 0.735\ \mathrm{cm}^{-1}$ respectively [6, 7]. The small splitting constant for the $6s6p_z\,{}^8\mathrm{P}_{9/2}$ energy level ($\mathrm{a}_{6\mathrm{p}} = 0.032\ \mathrm{cm}^{-1}$) relative to the much larger splitting constant for the $6s^2\mathrm{a}\,{}^6\mathrm{S}_{5/2}$ energy level ($\mathrm{a}_{6\mathrm{s}} = 0.735\ \mathrm{cm}^{-1}$) indicates that the $6s6p_z\,{}^8\mathrm{P}_{5/2}$ F energy levels are essentially degenerate relative to the $6s^2\mathrm{a}\,{}^6\mathrm{S}_{5/2}$ F energy levels, which are undegenerate. Figure 5a illustrates the theoretical F splitting that would be observed for the ${}^8\mathrm{P}_{5/2} \rightarrow {}^6\mathrm{S}_{5/2}$ transition if the splitting constants are not considered, and Figure 5b illustrates the observed splitting that occurs for the ${}^8\mathrm{P}_{5/2} \rightarrow {}^6\mathrm{S}_{5/2}$ transition because the a value for the ${}^6\mathrm{S}_{5/2}$ energy level is relatively large compared to the a value for the ${}^8\mathrm{P}_{9/2}$ energy level. The Rhenium(I) transition was selected because of its clarity, simplicity, and symmetry.

Method to Calculate I

This method is based on principles outlined by the interval rule and uses the intervals between the spectral lines of a specific Re isotope (see Table 1) [4]. The splitting or interval in cm^{-1} involving four different energy levels that are the result of four consecutive F values can be used to calculate I if J is known. In this case, the excited state of the transition is degenerate, and the ground state is undegenerate. First, using data from the HFS spectrum we set the energy (in cm^{-1}) of consecutive peaks equal to E_1, E_2, E_3, and E_4.

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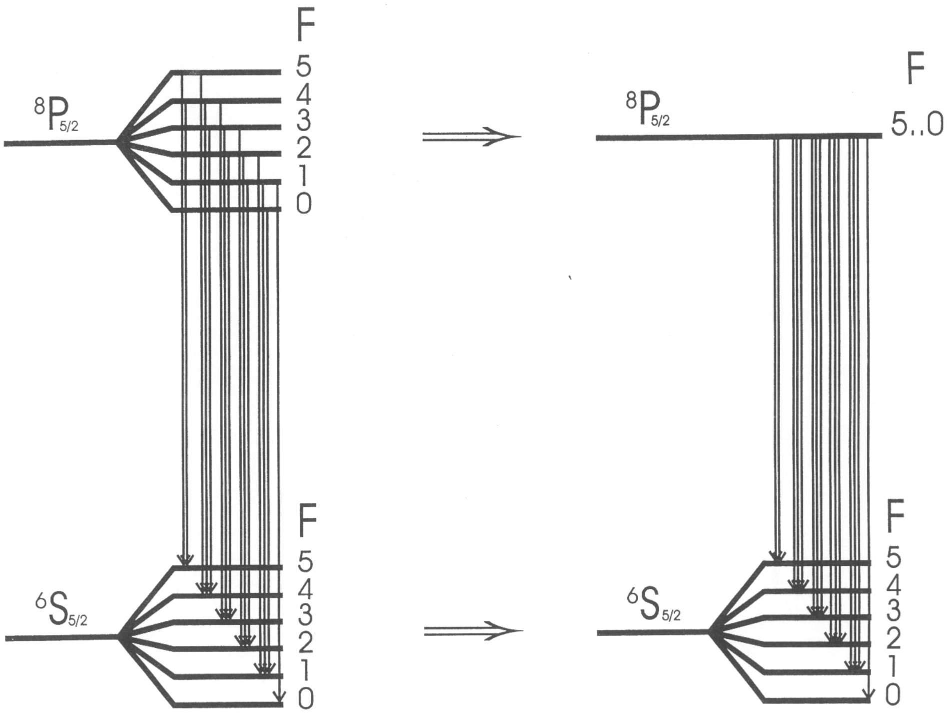

FIGURE 5. (A, LEFT) THE THEORETICALLY ALLOWED *F* TRANSITIONS THAT WOULD OCCUR IF THE SPLITTING CONSTANT IS NOT CONSIDERED; (B, RIGHT) THE OBSERVABLE *F* TRANSITIONS IF THE SPLITTING CONSTANTS ARE CONSIDERED.

The energy difference between two consecutive spectral peaks is proportional to the F splitting of the undegenerate energy level; therefore, the ratio of two energy differences that is the result of three consecutive spectral peaks, starting from the most intense peak, is equal to $F_x/F_{x\text{-}1}$ where x is equal to an integer multiple of 1/2. Refer to Table 1 and use the wavenumbers that correspond to peaks 2, 4, 6, and 8 for E_1, E_2, E_3, and E_4, respectively. We can calculate the ratio of F_1/F_2 =1.30 by using equation 4 and the ratio of F_2/F_3 = 1.37 by using equation 5.

$$\frac{E_1 - E_2}{E_2 - E_3} = \frac{F_1}{F_2} \tag{4}$$

$$\frac{E_2 - E_3}{E_3 - E_4} = \frac{F_2}{F_3} \tag{5}$$

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TABLE 1. Corrected wavenumbers (cm^{-1}), wavelengths (nm), isotope, and line number labels for Figure 2.

Wavenumber	Wavelength	Isotope	Line Number
18950.8035	527.6821	185	1
18950.7438	527.6838	187	2
18950.2397	527.6978	185	3
18950.1756	527.6996	187	4
18949.8044	527.7099	185	5
18949.7384	527.7118	187	6
18949.4877	527.7187	185	7
18949.4189	527.7206	187	8

These values are close to 5/4 (1.25) and 4/3 (1.33) respectively. This indicates that the maximum value for F is 5. Because $F_{max} = J + I$ and $J = 5/2$ (J is given), I is equal to 5/2 for ^{187}Re.

There is a small discrepancy between experimental and theoretical values for the predicted ratio's F_1/F_2 and F_2/F_3.

This can be accounted for when both experimental and physical affects are considered. Experimentally, discrepancies can be attributed to small errors in measuring wavenumber positions and identifying the exact peak of a spectral profile. Physical interactions would include the Stark effect (electric field, electron impact) and its impact on energy levels positions.

Conclusion

Most examples illustrating the coupling of **J** and **I** employ a spectrum that is difficult for an undergraduate to interpret. This particular example gives a "best possible scenario" in which one energy level is undegenerate and the other is degenerate. Listed below are two additional problems for students to solve.

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Problem 1: For the ^{185}Re isotope in Figure 2 and Table 1, the excited state has $J = 5/2$ and a = 0.03 cm^{-1} and the ground state has $J = 5/2$ and a =0.78 cm^{-1}, calculate the nuclear spin of the ^{185}Re isotope. (*Answer*: I = 5/2)

Problem 2: A high resolution spectrum (0.015 cm^{-1}) was recorded over a portion of the ultraviolet/visible region (300–600 nm) using a hollow cathode lamp as a spectral source. The following line positions are from the atomic emission spectra of some element M. The transition clearly exhibits HFS and the energy levels have the values:

23,301.583 cm^{-1}
23,301.379 cm^{-1}
23,301.209 cm^{-1}
23,301.073 cm^{-1}
23,300.971 cm^{-1}
23,300.903 cm^{-1}

The excited state has $J = 5$ and a splitting constant (a) of 0.0071 cm^{-1}. The ground state has $J = 5$ and a splitting constant (a) of 0.872 cm^{-1}. Illustrate the energy level diagram for the transition and calculate the nuclear spin of this element. (Answer: $I = 1$)

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