Spectral Analysis of a New Electronic Transition of Platinum Fluoride, PtF

Carol Welch
caw8b9@umsystem.edu

Follow this and additional works at: https://irl.umsl.edu/urs

Part of the Analytical Chemistry Commons, and the Physical Chemistry Commons

Recommended Citation

Available at: https://irl.umsl.edu/urs/79

This Presentation is brought to you for free and open access by the UMSL Undergraduate Works at IRL @ UMSL. It has been accepted for inclusion in Undergraduate Research Symposium by an authorized administrator of IRL @ UMSL. For more information, please contact marvinh@umsl.edu.
Spectral Analysis of a New Electronic Transition of Platinum Fluoride, PtF

Carol Welch
Mentors: Jim & Leah O’Brien
University of Missouri – Saint Louis

Chemistry Seminar
Zoom Meeting
April 21, 2021
Measuring Absorption by Intracavity Laser Spectroscopy

- Highly sensitive technique
- Equivalent to a multi-pass cell with thousands of passes
  - Typical experimental settings yield effective pathlength of 1-2 km
Motivation

• Understanding the electronic structure of small molecules
• Compare experiment work with theoretical predictions
• 20+ years of NSF funding – an indication of impact

• Specific interests:
  • Understand interactions between electronic states [there are several]
  • Pt has a lot of angular momentum, lots of 5d electrons (5d⁹), calculations with large number of valence electrons are challenging
(0,0) band of the $[15.3]\Omega=3/2 - X \ ^2 \Pi_{3/2}$ transition of PtF

(0,1) band of the $[15.8+x]\Omega=5/2 - B \ ^2 \Delta_{5/2}$ transition*

*Harms et al., *J. Mol. Spectrosc.* 2019
Spectral Analysis Part 1

- Identified branches
- Measured line positions
- Input data into Excel
- Create column of line positions
  - Graph P vs. J
- Calculate differences in P
  - Graph ‘P diff’ vs. J
  - Confirm no mistakes are in the data by identifying outliers
(0,0) band of the $[15.3] \Omega = 3/2 - X^2 \Pi_{3/2}$ transition of PtF

(0,1) band of the $[15.8+x] \Omega = 5/2 - B^2 \Delta_{5/2}$ transition*

*Harms et al., *J. Mol. Spectrosc.* 2019
(0,0) band of the [15.3]Ω=3/2 - X ²Π₃/₂ transition of PtF

\( J'' = \begin{array}{c}
25.5 \\
49.5 \\
\end{array} \)

\( J'' = \begin{array}{c}
24.5 \\
48.5 \\
47.5 \\
46.5 \\
\end{array} \)
Isotopologue Pattern of $^{194}$PtF, $^{195}$PtF, $^{196}$PtF, and $^{198}$PtF

Pt Relative Abundance

- $^{194}$Pt, 32.9%
- $^{195}$Pt, 33.8%
- $^{196}$Pt, 25.2%
- $^{198}$Pt, 7.4%

$R_f(47.5)$
$P_f(23.5)$
$P_e(23.5)$
$R_e(47.5)$
Isotope Relationships & Vibrational Frequency

• Harmonic Oscillator Model
  • Eigenvalues, \( E_v = \hbar \nu \left( v + \frac{1}{2} \right) \)
  • \( v = 0, 1, 2, 3 \ldots \)
  • \( \hbar \nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \)

• Born Oppenheimer Approximation
  • Neutrons do not affect the motion of electrons
  • All isotopologues have the same potential energy curve
  • All isotopologues have the same \( k \)
  • \( \hbar \nu \) is inversely proportional to \( \mu^{-1/2} \), \( \hbar \nu \propto \frac{1}{\sqrt{\mu}} \)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( \hbar \nu'' \text{ value (cm}^{-1}) )</th>
<th>( \hbar \nu' \text{ value (cm}^{-1}) )</th>
<th>Isotope Shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>194PtF</td>
<td>600.138</td>
<td>500.115</td>
<td>-0.023</td>
</tr>
<tr>
<td>195PtF</td>
<td>600.000</td>
<td>500.000</td>
<td></td>
</tr>
<tr>
<td>196PtF</td>
<td>599.864</td>
<td>499.887</td>
<td>0.023</td>
</tr>
<tr>
<td>198PtF</td>
<td>599.596</td>
<td>499.663</td>
<td>0.067</td>
</tr>
</tbody>
</table>
Isotopologue Pattern of $^{194}$PtF, $^{195}$PtF, $^{196}$PtF, and $^{198}$PtF

- $^{194}$Pt, 32.9%
- $^{195}$Pt, 33.8%
- $^{196}$Pt, 25.2%
- $^{198}$Pt, 7.4%

$P_t(23.5)$

$P_e(23.5)$

$R_t(47.5)$

$R_e(47.5)$

Pt Relative Abundance

PtF Spectrum

$^{194}$PtF Simulation

$^{195}$PtF Simulation

$^{196}$PtF Simulation

$^{198}$PtF Simulation
Isotope Relationships & Rotational Constants

• Rigid Rotor Model
  • Eigenvalues, \( E_J = B(J+1) \)
  • \( J = 0, 1, 2, 3... \)
  • \( B = \frac{\hbar^2}{2\mu r_e^2} \)

• Born Oppenheimer Approximation
  • Neutrons do not affect the motion of electrons
  • All isotopologues have the same potential energy curve
  • All isotopologues have the same \( r_e \)
  • \( B \) is inversely proportional to \( \mu \), \( B \propto \frac{1}{\mu} \)
  • Example of \( B \) values for excited state

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( B' ) value (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>194PtF</td>
<td>0.277065300</td>
</tr>
<tr>
<td>195PtF</td>
<td>0.276938255</td>
</tr>
<tr>
<td>196PtF</td>
<td>0.276812752</td>
</tr>
<tr>
<td>198PtF</td>
<td>0.276565231</td>
</tr>
</tbody>
</table>

Spectral Analysis Part 2

• Used PGOPHER, a spectral simulation software program
  • Developed the model in PGOPHER, the # of unpaired electrons, orbital angular momentum in each electronic state, and the reduced mass of each isotope, includes isotope relationships for the B, D, and H values
  • Prepared an input file includes the molecular species, rotational assignments, line positions, and estimated uncertainty in the line position
  • 430 total observed line positions for all four isotopologues

<table>
<thead>
<tr>
<th>#</th>
<th>Molecule</th>
<th>M'</th>
<th>J'</th>
<th>S'</th>
<th>#''</th>
<th>M''</th>
<th>J''</th>
<th>S''</th>
<th>#''</th>
<th>Position</th>
<th>Std Dev</th>
</tr>
</thead>
<tbody>
<tr>
<td>27</td>
<td>194PtF</td>
<td>T15t3</td>
<td>3.5</td>
<td>e</td>
<td>1</td>
<td>X2Pi_1.5</td>
<td>4.5</td>
<td>e</td>
<td>1</td>
<td>15245.6852</td>
<td>0.02</td>
</tr>
<tr>
<td>28</td>
<td>194PtF</td>
<td>T15t3</td>
<td>4.5</td>
<td>e</td>
<td>1</td>
<td>X2Pi_1.5</td>
<td>5.5</td>
<td>e</td>
<td>1</td>
<td>15244.9392</td>
<td>0.02</td>
</tr>
<tr>
<td>29</td>
<td>194PtF</td>
<td>T15t3</td>
<td>5.5</td>
<td>e</td>
<td>1</td>
<td>X2Pi_1.5</td>
<td>6.5</td>
<td>e</td>
<td>1</td>
<td>15244.1529</td>
<td>0.02</td>
</tr>
<tr>
<td>30</td>
<td>194PtF</td>
<td>T15t3</td>
<td>6.5</td>
<td>e</td>
<td>1</td>
<td>X2Pi_1.5</td>
<td>7.5</td>
<td>e</td>
<td>1</td>
<td>15243.3174</td>
<td>0.02</td>
</tr>
<tr>
<td>31</td>
<td>194PtF</td>
<td>T15t3</td>
<td>7.5</td>
<td>e</td>
<td>1</td>
<td>X2Pi_1.5</td>
<td>8.5</td>
<td>e</td>
<td>1</td>
<td>15242.4437</td>
<td>0.02</td>
</tr>
</tbody>
</table>
Spectral Analysis Part 3

• Also in the input file, we programmed PGOPHER to use isotope relationships to determine excited state B values
  • Constrained B values to obey that relationship
  • Rotational constants (B, D, and H values) are related by the reduced masses of each molecule

• PGOPHER uses the input file to determine the molecular constants for the two states involved in the electronic transition
  • Held the ground state constants fixed

• PGOPHER used to determine optimized molecular constants and prepare a spectral simulation based on those constants for comparison
(0,0) band of the $[15.3]\Omega=1.5 - X^2\Pi_{1.5}$
# Table 2. Molecular Constants for the [15.3]Ω=3/2 state of PtF (in cm⁻¹).

<table>
<thead>
<tr>
<th>Origin</th>
<th>B₀</th>
<th>D₀ x 10⁷</th>
<th>H₀ x 10¹²</th>
</tr>
</thead>
<tbody>
<tr>
<td>¹⁹⁴PtF</td>
<td>15248.49868(67)</td>
<td>0.2560820(13)</td>
<td>2.46080(772)</td>
</tr>
<tr>
<td>¹⁹⁵PtF</td>
<td>15248.52802(69)</td>
<td>0.2559645(13)</td>
<td>2.45854(772)</td>
</tr>
<tr>
<td>¹⁹⁶PtF</td>
<td>15248.55747(71)</td>
<td>0.2558485(13)</td>
<td>2.45631(772)</td>
</tr>
<tr>
<td>¹⁹⁸PtF</td>
<td>15248.61660(75)</td>
<td>0.2556198(13)</td>
<td>2.45192(772)</td>
</tr>
</tbody>
</table>

*B₀, D₀, and H₀ values constrained to isotopic relationship based on ¹⁹⁵PtF.*

\[
B = \frac{h^2}{8\pi^2\mu r^2} \\
r_0 = 1.9505 \, \text{Å}
\]
Based on experimental B values, our [15.3] $\Omega=3/2$ state correlates to the 5(3/2) state of Zou and Suo.
Synergy of Experimental & Computational Studies

1. Handler et al, 2011; observed the first electronic transition of PtF by ILS
2. Zou and Suo, 2016; high level of initial calculations to determine electronic states and spectroscopic constants
3. Ng et al., 2016; observed for electronic transitions including two of the three low lying states
4. Harms et al, 2019; identified the (0,0) band of \([15.8+x] \Omega - 5/2 - B^2 \Delta_{5/2}\) transition

This Work: (0,0) band of the \([15.3] \Omega=3/2 - X^2 \Pi_{3/2}\) of PtF
Dipole moment for this transition is very small
- 1 is a strong dipole moment
- Used the $S\Lambda$ configuration to study electron configurations
Based on the calculations, a $^4\Pi$ and $^4\Delta$ states are the primary parents of the $[15.3]\Omega=3/2$ state.

The $^4\Pi$ and $^4\Delta$ states come from the second $^4\text{F}$ state of Pt$^+$. We used Charlotte Moore’s tables, which list electronic configurations and atomic terms.

The $2^{\text{nd}}^4\text{F}$ state has a configuration of $\delta^3\sigma^2\pi^3$.

Thus the blue arrow indicates a transition that is consistent with these states.

However, a $\delta \rightarrow \sigma$ electronic transition is not allowed, which explains why the transition dipole moment is so weak.
• Small transition dipole moment due to the minor $^2\Delta$ and $^2\Pi$ components
• Also explains why we did not observe Lambda doubling in the excited state due to large $^2,^4\Delta$ configurations
Conclusions

• We see isotopologue structure and Lambda doubling in the spectrum
• Isotope relationships constrained for the excited state B value
• Excellent reproduction of spectral features considering blob like nature of the spectrum
• Doppler width determined to be approx. $0.05 \text{ cm}^{-1}$ consistent with dispersion of 2 meter spectrometer
• Presenting experimental findings at International Symposium on Molecular Spectroscopy in June
• Have completed a first draft of a manuscript we intend to submit later this summer
• We hope to record the same transition with enhanced resolution with our ILS-FTS system to confirm our analysis
• Quantum mechanics carried us through the analysis using isotope relations, known ground state molecular constants, and molecular constraints in PGOPHER
Acknowledgments

- Funding (NSF)
- Data collected by Jack Harms
- Appreciate the encouragement from PhD student Kristin Bales
- Undergraduate Research Day at the Capitol 2021 (URDC)
  - Kate Votaw
- Jim & Leah O’Brien