The Mystery of the Electronic Spectrum of Ruthenium Monophosphide

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UNB
NSERC CRSGN
Motivation - Previous Work on Ruthenium Diatomics

  - $^1\Sigma^+$ from $\sigma^2\delta^4\pi^4$ configuration
  - $^5\Delta_i$ from $\delta^3\sigma^1\pi^2$ configuration
  - $^2\Sigma^+$ from $\pi^4\delta^4\sigma^1$ configuration
  - $^4\Phi_i$ from $\delta^3\sigma^1\pi^3$ configuration
  - $^3\Delta_3$ from $\pi^4\delta^3\sigma^1$ configuration
  - $^2\Delta_i$ from $\sigma^2\pi^4\delta^3$ configuration
  - $^4\Sigma^-$ from $\sigma^1\delta^2\pi^4$ configuration ➔ theoretical prediction
- **RuP**: no experiments/no theoretical predictions
Motivation – Catalysis, Drug Design
Apparatus

Timing Scheme (repetition rate of 10Hz):
A = T₀
B = T₀ + 500µs
C ≈ T₀ + 100µs

Gas Mixture: 1% PH₃ in He(g) held at 40 psi
Low Resolution Spectrum of RuP

From DFs:
\[ \omega \approx 515 \text{ cm}^{-1} \]

- 576.5 nm
- 591.8 nm
Theoretical $^2\Sigma - ^2\Sigma$ Transition

RuN (RuP)
$^2\Sigma^+$ from $\pi^4\delta^4\sigma^1$ configuration

PGOPHER, Colin Western, http://pgopher.chm.bris.ac.uk
High Resolution Spectrum of RuP
The “Head” Region of the 576.5 nm Band

- $^{104}\text{Ru} - 18.62\%$
- $^{102}\text{Ru} - 31.55\%$
- $^{101}\text{Ru} - 17.06\%$
- $^{100}\text{Ru} - 12.60\%$
- $^{99}\text{Ru} - 12.76\%$
- $^{98}\text{Ru} - 1.87\%$
- $^{96}\text{Ru} - 5.54\%$
Loomis-Wood Plot for some branches of RuP
Combination Differences

\[ \Delta_2 F^" = R(N-1) - P(N+1) = 4B^"(N+0.5) \]

\[ \Delta_2 F^' = R(N) - P(N) = 4B^'(N+0.5) \]
Theoretical $^2\Pi - ^2\Sigma$ Transition

PGOPHER, Colin Western, http://pgopher.chm.bris.ac.uk
Low Resolution Spectrum of RuP

From DFs:
\[ \omega \approx 515 \text{ cm}^{-1} \]

576.5 nm
591.8 nm
Combination Differences (part ii)

\[ \Delta_1 F'' = R(N) - Q(N+1) = 2B''(N+1) \]

\[ \Delta_1 F'' = Q(N) - P(N+1) = 2B''(N+1) \]
Low Resolution Spectrum of RuP
Low Resolution Spectrum of RuP
Dispersed Fluorescence

DF Spectrum of 512 nm band

\[ \varepsilon' \]

\[ \varepsilon'' = 0 \]

Intensity

Relative wavenumber / cm\(^{-1}\)

511.7 nm
523.0 nm
536.0 nm
549.4 nm
550.8 nm
563.3 nm
577.0 nm
Dispersed Fluorescence

DF Spectra of Several Bands

Assignments are for low-lying electronic state.

\[ \varepsilon' = 0 \]

\[ \varepsilon'' = 0 \]

Intensities at different wavenumbers:

- 511.7 nm
- 523.0 nm
- 536.0 nm
- 549.4 nm
- 550.8 nm
- 563.3 nm
- 577.0 nm

Relative wavenumber / cm\(^{-1}\)

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# Dispersed Fluorescence Results

<table>
<thead>
<tr>
<th>Ground State</th>
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<th></th>
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</thead>
<tbody>
<tr>
<td><strong>Fitted Parameter</strong></td>
<td><strong>Value</strong></td>
<td><strong>Standard Deviation</strong></td>
</tr>
<tr>
<td>$\omega_e$ (cm$^{-1}$)</td>
<td>513</td>
<td>1</td>
</tr>
<tr>
<td>$\omega_e x_e$ (cm$^{-1}$)</td>
<td>2.17</td>
<td>0.19</td>
</tr>
<tr>
<td>$\overline{T}_0$ (cm$^{-1}$)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Low-lying Electronic State</th>
<th></th>
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<tbody>
<tr>
<td><strong>Fitted Parameter</strong></td>
<td><strong>Value</strong></td>
<td><strong>Standard Deviation</strong></td>
</tr>
<tr>
<td>$\omega_e$ (cm$^{-1}$)</td>
<td>525</td>
<td>2</td>
</tr>
<tr>
<td>$\omega_e x_e$ (cm$^{-1}$)</td>
<td>3.48</td>
<td>0.61</td>
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<tr>
<td>$\overline{T}_0$ (cm$^{-1}$)</td>
<td>2034</td>
<td>1</td>
</tr>
</tbody>
</table>

$G_v - G_0 = (\omega_e - \omega_e x_e)v - \omega_e x_e v^2$
Q-head region of 1-0 Band

- $^{102}\text{RuP}$
- $^{101}\text{RuP}$
- $^{100}\text{RuP}$
- $^{99}\text{RuP}$
- $^{98}\text{RuP}$
- $^{96}\text{RuP}$
## Ground State Rotational Constants

<table>
<thead>
<tr>
<th>Fitted Parameter</th>
<th>Value</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_{102} \text{ (cm}^{-1}\text{)}$</td>
<td>0.346057</td>
<td>$2.6 \times 10^{-5}$</td>
</tr>
<tr>
<td>$D_{102} \text{ (cm}^{-1}\text{)}$</td>
<td>$1.51 \times 10^{-7}$</td>
<td>$3.1 \times 10^{-8}$</td>
</tr>
<tr>
<td>$B_{96} \text{ (cm}^{-1}\text{)}$</td>
<td>0.351063</td>
<td>$3.5 \times 10^{-5}$</td>
</tr>
<tr>
<td>$D_{96} \text{ (cm}^{-1}\text{)}$</td>
<td>$1.67 \times 10^{-7}$</td>
<td>$5.8 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

\[ \Delta_{1F''} = 2B''(N+1) - 4D''(N+1)^3 \]

\[ R_0 = 1.432\text{Å} \]
Perturbation in the $^{102}\text{RuP}$ 1-0 Band
Hyperfine Broadening in the Odd Isotopologues

\[ {^{100}\text{RuP}} P(3) \]
\[ {^{102}\text{RuP}} Q(20) \]

\[ {^{99}\text{RuP}} P(4) \]
Problems!

- The excited state is perturbed.
  - Loomis-Wood plots
  - Irregular isotopologue spacing in the Q-heads
  - Missing R-branches

- Upper state combination differences give half-integer quantum numbers but the effective B value is not constant.

- Lowest transitions identified conclusively are Q(3) and P(3).
  - Would expect transitions of lower N for a $^2\Pi - ^2\Sigma$ transition
  - Lowest transitions currently indicate $\Omega´=5/2$ and a $^2\Pi$ state has $\Omega´=1/2, 3/2$

- The ion laser has been dead since mid-January ... unable to access the green system! (repaired June 3, 2016 😊)
• DF analysis of RuP has been performed.
• $\Delta_1 F$ ground state combination differences for give integer quantum numbers consistent with a $\Sigma$ electronic state – rotational parameters have been obtained.
• Upper state is currently unknown.

Future Work

• Take high resolution spectra of the 536 nm system to determine if the ground state is indeed $^2\Sigma^+$.
• Solve the mystery of the excited state of RuP.

Acknowledgements

• Joyce MacGregor