The Role of Perturbations in the B-X UV Spectrum of $S_2$ in a Temperature Dependent Mechanism for S-MIF

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Sulfur isotope ratios in rocks follow simple mathematical relationships...

• Stable Sulfur Isotopes: $^{32}$S (94.99%) $^{34}$S (4.25%) $^{33}$S (0.75%) $^{36}$S (0.01%)

\[ \delta^x = \frac{\left( \frac{[xS]}{[32S]} \right)_{\text{sample}} - \left( \frac{[xS]}{[32S]} \right)_{\text{ref}}}{\left( \frac{[xS]}{[32S]} \right)_{\text{ref}}} \]

• Kinetics and thermodynamics tell us that:
  • $\delta^{33} = 0.515 \delta^{34}$
  • $\delta^{36} = 1.90 \delta^{34}$

• Following these rules = Mass Dependent Fractionation (MDF)
...But not always

\[ \Delta^{33} = (\delta^{33} - 0.515 \delta^{34}) \times 1000 \]

Mass Independent Fractionation (S - MIF)

Oxygenated Atmosphere

Anoxic Atmosphere

Best guess: \( pO_2 < 10^{-6} \text{ atm} \)
(Pavlov and Kasting, 2002)

Johnston, 2011
Sulfur in Modern Atmosphere

Volcanism:
- $H_2S$ → $HS$ → $SO_2$ → $SO_3$ → aerosol
- Oxidized Pathway: $SO_2$ → O$_3$, NO$_2$ → HSO$_3$ → OH → O$_2$, O
- Reduced Pathway: $HS$ → $H_2S$ → $HCO$ → $H_2S$ → $H_2S$ aerosol

Ocean:
- Troposphere
- Sediment:
  - FeS$_2$

Sediment:
- $BaSO_4$

Adapted from: Pavlov and Kasting (2002) and Lyons (2009)
B-X UV Transition in $S_2$

Green and Western (1997)

Green and Western (1996)

Avg. lifetime: ~30 ns

$S(3P_2) + S(3P_1)$

Avg. lifetime: ~4 μs

$$H = B[J^2 - L^2 - J_z^2 - L_z^2 - S_z^2]$$
$$+ A(L_z S_z - B[(J_z L_+ + J_+ L_z) + (J_z S_- + J_- S_z)])$$
$$+ (0.5A + B)(L_+ S_- + L_- S_+) - DR^4$$
$$- 2/3\lambda(3S_z^2 - S^2) + \gamma NS + 1/2\lambda_D[2/3(3S_z^2 - S^2),N^2]$$
Hypothesis:

- Isotope shifts change location where the B and B” curves intersect.
- Perturbations (randomly) occur at J’s with significant ground state population for one isotopologue, but not the other.
- Collisions with inert gases can move population to states with even longer lifetimes (chemistry).
- Temperature dependent effect.
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Some Organization:

• My program calculates ~200,000 transitions.
• Each transition is characterized by its upper state.
  
  • \( |\Psi >_{upper} = \alpha |\psi_B > + \beta |\psi_B" > \)

• Each transition is sorted by the \( |\beta| ^2 \) of its upper state eigenvector

• For bins \( 0.9 < |\beta| ^2 < 1.0 \), \( 0.8 < |\beta| ^2 < 0.9 \), etc...
  
  • calculate \( \sum_i \sigma_{i,3232} - \sum_i \sigma_{i,3234} \), \( i \in \) all transitions in a given bin
Total Intensity 3232 – 3234 /arb. units

200 K

Bin ($|\beta|^2$)

Lifetime (ns)

More 3232 intensity

More 3234 Intensity
Total Intensity 3232 – 3234 /arb. units

Bin ($|\beta|^2$) | Lifetime (ns) | 200 K
--- | --- | ---
0.1 | 32 | 32
0.1-0.2 | 35 | 39
0.2-0.3 | 39 | 45
0.3-0.4 | 45 | 54
0.4-0.5 | 54 | 66
0.5-0.6 | 66 | 84
0.6-0.7 | 84 | 117
0.7-0.8 | 117 | 191
0.8-0.9 | 191 | 525
0.9-1 | More 3232 intensity

More 3234 Intensity
Potential Fractionation!

~3% of total intensity

Total Intensity 3232 – 3234 /arb. units

Bin (|\beta|^2)

Lifetime (ns)

200 K

[Graph showing intensity distribution across different bins and lifetimes, with an ellipse highlighting the 0.6-0.7 and 0.7-0.8 bins.]

32, 35, 39, 45, 54, 66, 84, 117, 191, 525
\[ B \text{ state } v = 9 \]

\[ B^{''} v = 18 \Omega = 1 \ 3232 \]

\[ B^{''} v = 18 \Omega = 1 \ 3234 \]

\[ B^{''} v = 18 \Omega = 0 \ 3232 \]

\[ B^{''} v = 18 \Omega = 0 \ 3232 \]
B state $v = 8$

$\Omega = 0\ 3232$

$\Omega = 1\ 3234$

$J(J+1)$

$E(\text{dark}) - E(\text{bright})$

Ground State Population Maximum

$B'' v=15\ \Omega=1\ 3232$

$B'' v=15\ \Omega=1\ 3234$

$B'' v=15\ \Omega=0\ 3232$

$B'' v=15\ \Omega=0\ 3234$
For these relative energy plots, a few things are consistent:

1) The dark state energies decrease in energy, relative to bright states, with increasing $J$
   - (Crossings can only occur from above)

2) The 3232 dark states are shifted higher in energy, relative to 3234 dark states

Patterns!
• **Conclusions**
  - Pattern of greater absorption to long lived states for 3232 relative to 3234
  - We’ve identified a potential mechanism for Sulfur Mass Independent Fractionation
  - “Random” perturbations aren’t entirely random, so this kind of analysis could be applied to other species.

• **Next Steps**
  - Self-Shielding
  - Master Equation Modeling (absorption, collisional transfer, chemistry, etc.)
  - Experiments
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Rocks showing S-MIF

FeS$_2$
Reduced Pathway

BaSO$_4$
Oxidized Pathway

Pavlov and Kasting (2002)