# Isotopically invariant Dunham fit for the $X\,^3\Sigma_g^-$, $a\,^1\Delta_g$, and $b^1\Sigma_g^+$ states of oxygen

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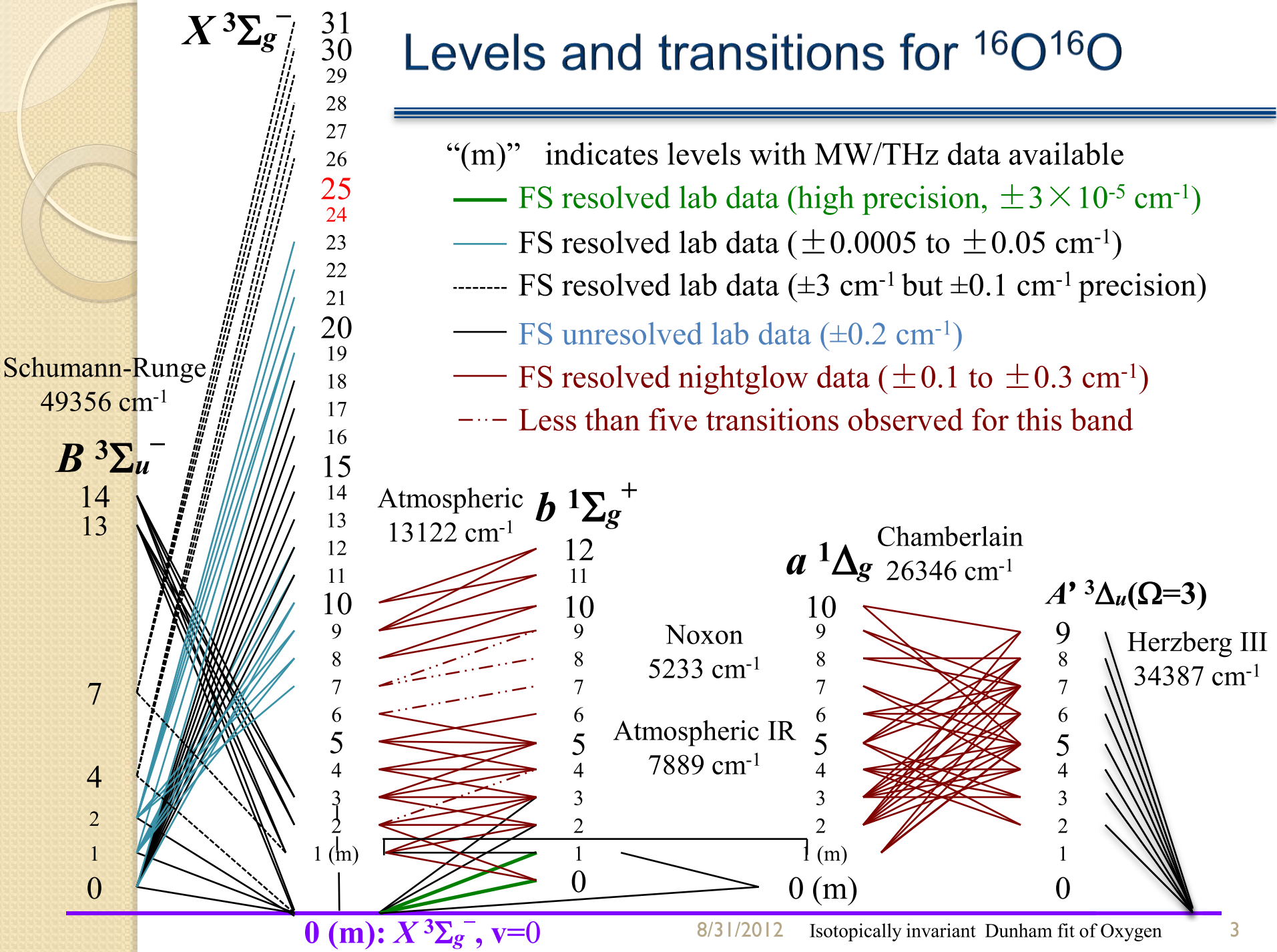
# Project goals

- Simultaneously fit MW, THz, infrared, visible and UV transitions of $^{16}O^{16}O$, $^{16}O^{17}O$, $^{16}O^{18}O$, $^{17}O^{17}O$, $^{17}O^{18}O$, $^{18}O^{18}O$
- Treat all six $O_2$ isotopologues as the same molecule using well-known reduced mass relationships
- Leverage experimental information from one isotopologue to accurately predict the spectra of any other isotopologue
- Use analysis to determine precision and accuracy of line positions and to identify issues and holes in the data sets
- Make new measurements to verify and improve model

# Levels and transitions for $^{16}O^{16}O$

"(m)" indicates levels with MW/THz data available

- FS resolved lab data (high precision, $\pm 3\times10^{-5}$ cm$^{-1}$)
- FS resolved lab data ($\pm$0.0005 to $\pm$0.05 cm$^{-1}$)
- FS resolved lab data ($\pm$3 cm$^{-1}$ but $\pm$0.1 cm$^{-1}$ precision)
- FS unresolved lab data ($\pm$0.2 cm$^{-1}$)
- FS resolved nightglow data ($\pm$0.1 to $\pm$0.3 cm$^{-1}$)
- Less than five transitions observed for this band



# Hamiltonian

- For $X^3\Sigma_g^-$, $b^1\Sigma_g^+$ and $B^3\Sigma_u^-$

$$\mathbf{H} = T_e + G_v + B_v\mathbf{N}^2 + D_v(\mathbf{N}^2)^2 + H_v(\mathbf{N}^2)^3 + [\lambda_v + \lambda_{Dv}\mathbf{N}^2 + \lambda_{Hv}(\mathbf{N}^2)^2]\tfrac{2}{3}(3S_z^2 - \mathbf{S}^2) + [\gamma_v + \gamma_{Dv}\mathbf{N}^2 + \gamma_{Hv}(\mathbf{N}^2)^2]\mathbf{N}\cdot\mathbf{S} + b_{Fv}\mathbf{I}\cdot\mathbf{S} + c_v\left(I_zS_z - \tfrac{1}{3}\mathbf{I}\cdot\mathbf{S}\right) + eQq_v\frac{(3I_z^2 - \mathbf{I}^2)}{4I(2I-1)} + C_{Iv}\mathbf{I}\cdot\mathbf{N}$$

- For $a^1\Delta_g$ and $A'^3\Delta_u$ ($\Omega$=3)

$$\mathbf{H} = T_e + G_v + B_v(\mathbf{N}^2 - \mathbf{L}^2) + D_v(\mathbf{N}^2 - \mathbf{L}^2)^2 + H_v(\mathbf{N}^2 - \mathbf{L}^2)^3 + a_vI_zL_z + eQq_v\frac{(3I_z^2 - \mathbf{I}^2)}{4I(2I-1)} + C_{Iv}\mathbf{I}\cdot\mathbf{N}$$

# Dunham-type expansions for *X*, *a* and *b* states

$$G_v = \sum_{l=1} Y_{l,0}\left(v+\tfrac{1}{2}\right)^l = \sum_{l=1}\left(U_{l,0}\left(\frac{1}{\mu}\right)^{\frac{l}{2}+(m=0)} + U_{l,0}\Delta^{O}_{l,0} m_e \left(\frac{1}{\mu}\right)^{1+\frac{l}{2}+(m=0)}\right)\left(v+\tfrac{1}{2}\right)^l$$

$$B_v = \sum_{l=0} Y_{l,1}\left(v+\tfrac{1}{2}\right)^l = \sum_{l=0}\left(U_{l,1}\left(\frac{1}{\mu}\right)^{\frac{l}{2}+(m=1)} + U_{l,1}\Delta^{O}_{l,1} m_e \left(\frac{1}{\mu}\right)^{1+\frac{l}{2}+(m=1)}\right)\left(v+\tfrac{1}{2}\right)^l$$

For $X = \lambda, a, b_F, c, eQq$:

$$X_v = \sum_{l=0} X_{l,0}\left(v+\tfrac{1}{2}\right)^l = \sum_{l=0}\left(U^{X}_{l,0}\left(\frac{1}{\mu}\right)^{\frac{l}{2}+(m=0)} + U^{X}_{l,0}\Delta^{X,O}_{l,0} m_e \left(\frac{1}{\mu}\right)^{1+\frac{l}{2}+(m=0)}\right)\left(v+\tfrac{1}{2}\right)^l$$

$$X_{Dv} = \sum_{l=0} X_{l,1}\left(v+\tfrac{1}{2}\right)^l = \sum_{l=0}\left(U^{X}_{l,1}\left(\frac{1}{\mu}\right)^{\frac{l}{2}+(m=1)} + U^{X}_{l,1}\Delta^{X,O}_{l,1} m_e \left(\frac{1}{\mu}\right)^{1+\frac{l}{2}+(m=1)}\right)\left(v+\tfrac{1}{2}\right)^l$$

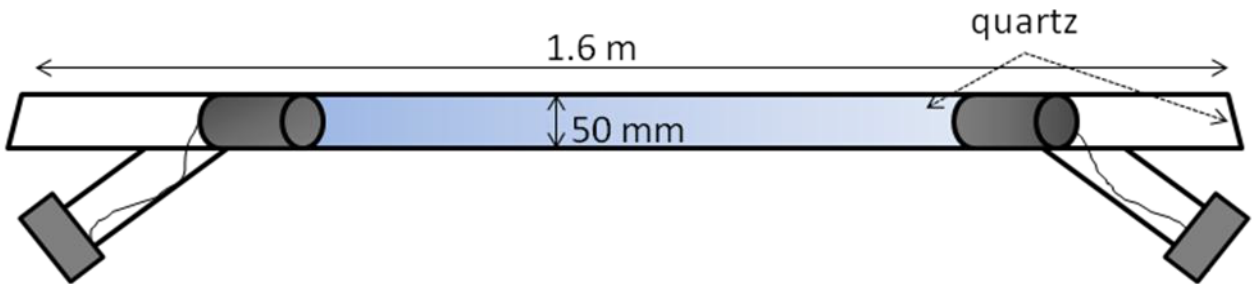
For $X = \gamma, C_I$:

$$X_v = \sum_{l=0} X_{l,0}\left(v+\tfrac{1}{2}\right)^l = \sum_{l=0}\left(U^{X}_{l,0}\left(\frac{1}{\mu}\right)^{1+\frac{l}{2}+(m=0)} + U^{X}_{l,0}\Delta^{X,O}_{l,0} m_e \left(\frac{1}{\mu}\right)^{2+\frac{l}{2}+(m=0)}\right)\left(v+\tfrac{1}{2}\right)^l$$

# Issues

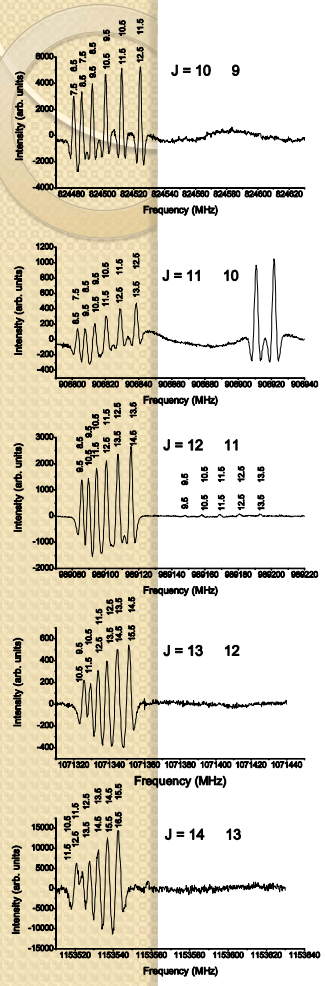
- Higher electronic states have perturbations
- No pure rotational data for $^1\Delta$ 17O isotopologues
- Raman data for 17-18 does not fit
- Many levels in $^3\Sigma$, $^1\Delta$ & $^1\Sigma$ states only connected by atmospheric nightglow measurements

# Static Dicharge Cell

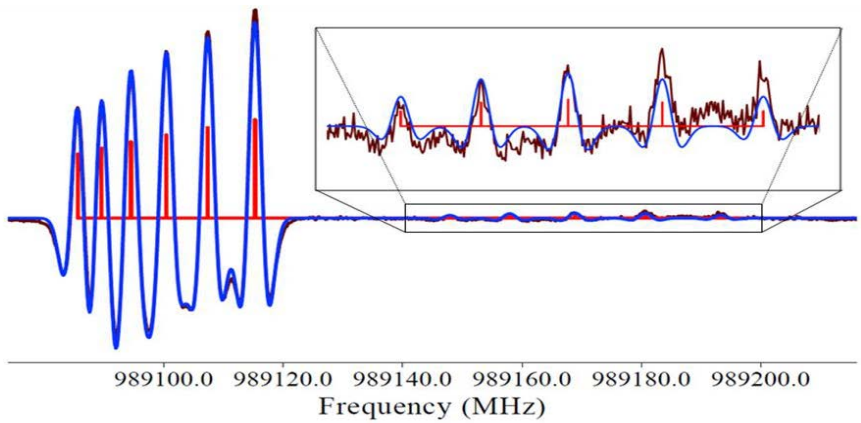



- Gas is introduced through a con-flat metal valve that is also ground electrode
- Two con-flat / quartz transitions on either end of cell
- Hot electrode is externally connected to power supply and shielded with Teflon
- THz radiation is passed through angled quartz windows
- Amorphous quartz attenuates 20% of 500 GHz, 50% of 1000 GHz, 100% 1600 GHz
- After conditioning, gas pressure stays close to ignition pressure for days

# New Data for $^1\Delta$ - $^{16}O^{17}O$




- Despite better throughput at < 500 GHz, best SNR was near 1000 GHz
- Observed by mixing 90% $^{17}O_2$ with natural sample 50/50
- Discharge Voltage 2kV, 40 mA
- Hyperfine Pattern from I = 5/2 $^{17}O$ nucleus
- spin-orbit coupling dominates




- Boltzmann peak for rotational distribution near 1200 GHz
- Integration time unlimited
- Cell contamination and harmonic purity are issues
- (Blue) prediction from Yu et al. JCP 2012

# Dunham Analysis

TABLE V. Comparison of Dunham model parameters for $O_2$ ($a^1\Delta_g$). All parameter values, and the fit rms, are reported in MHz, while the number of lines and reduced rms ($\sigma_{red}$) are dimensionless.[a]

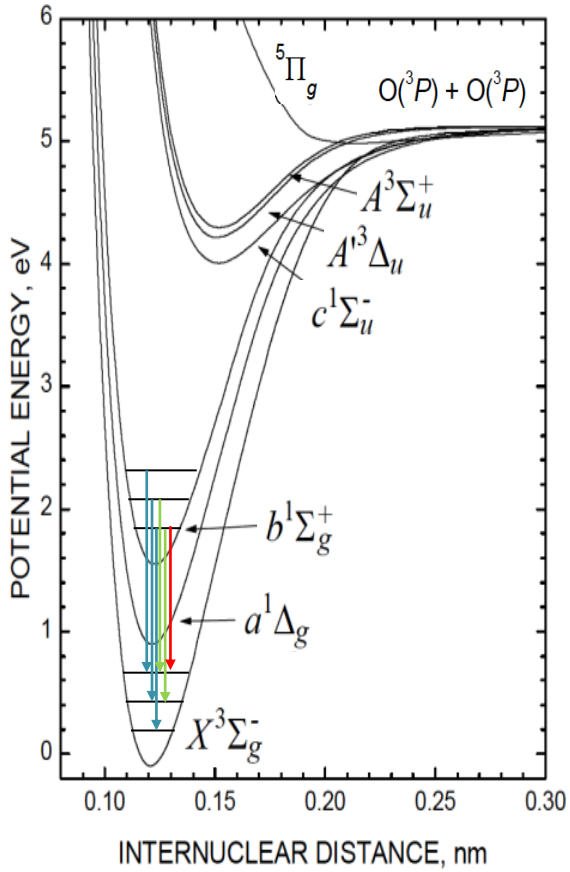
| Parameter (MHz) | Cohen *et al.* [6] | Global Model [1] | This Work |
|---|---|---|---|
| $U_{01}/\mu$ | 42766.5220(172) | 42766.1712(193) | 42766.4797(111) |
| $\delta_{01}^{O}$ | −5.4586(184) | −5.6031(157) | −5.5286(59) |
| $\frac{1}{2}Y_{11}$ | −256.5435(32) | −255.8792(280) | −256.3936(163) |
| $\frac{1}{4}Y_{21}$[b] | – | −0.1663(70) | −0.0382(41) |
| $Y_{02}$ (x$10^3$) | −152.616(92) | −152.6378(15) | −152.7176(38) |
| $\frac{1}{2}Y_{12}$ (x$10^3$) | −0.330(88) | −0.3314(139) | −0.24269(300) |
| $Y_{03}$ (x$10^9$) | −63.7 | – | −71.15(133) |
| $a$ | – | −212.53(51) | −211.9329(283) |
| $1.5eQq$ | – | – | −12.390(282) |
| $U_{00}^{C_I}/\mu$ (x$10^3$) | – | – | −20.70(141) |
| # lines | 16 | –[c] | 344(201)[d] |
| $\sigma_{red}$ | 0.74 | –[c] | 0.94 |

New!


1) S. Yu, *et al.*, J. Chem. Phys. 2012 – [This Work] Drouin *et al.* J. Chem. Phys 2012

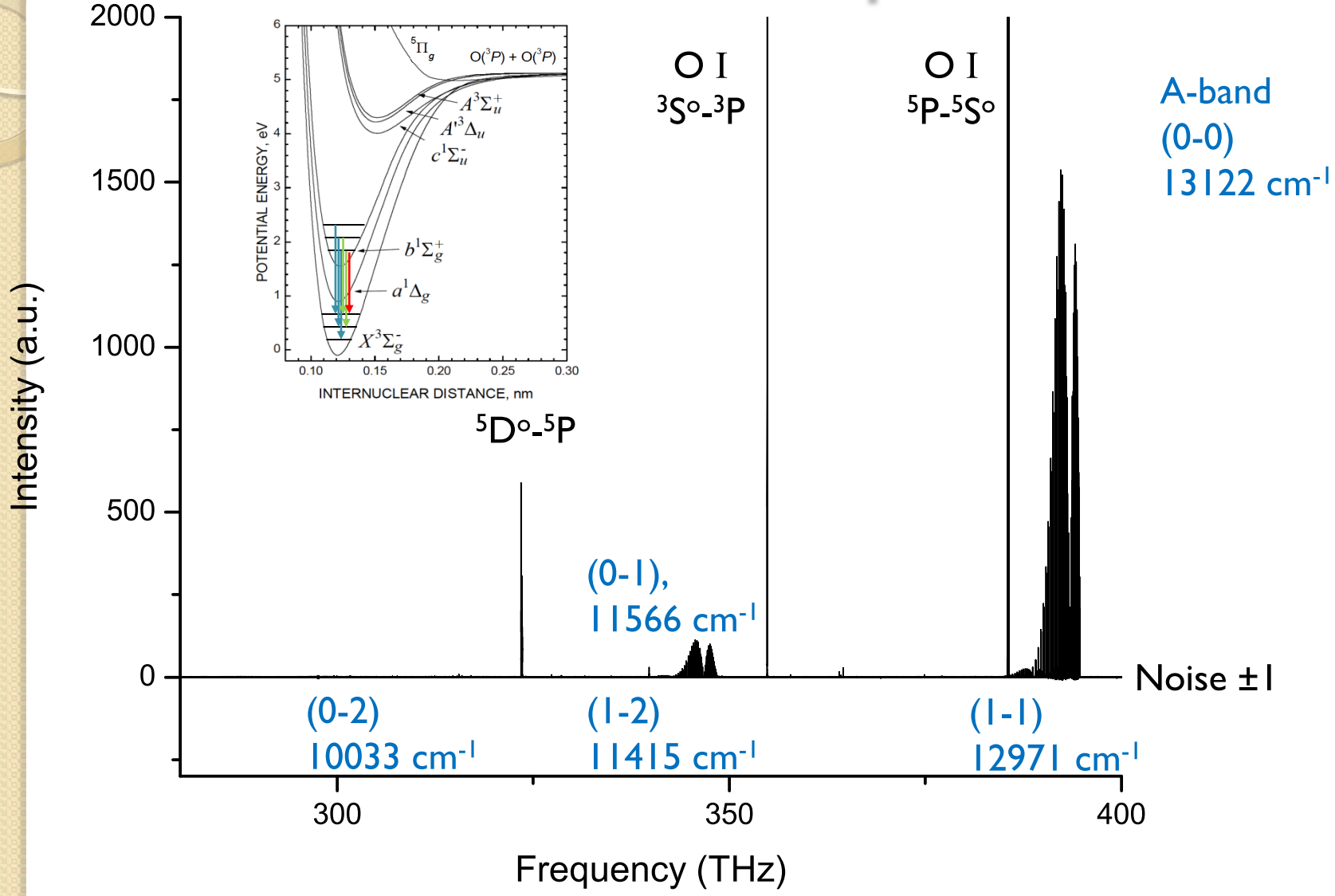
6) E.A. Cohen, *et al.*, J. Mol. Spectrosc. **352/353, 283-287 (1995).**

# Emission spectroscopy



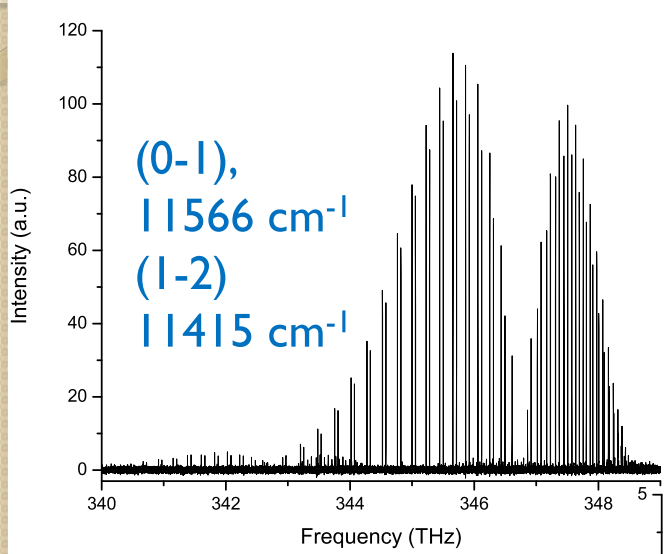
Visible light is atomic emission, optimal molecular emission was achieved at pressures that minimized atomic emission and visible light (0.4-1.1 Torr, 0.9 Torr optimal)

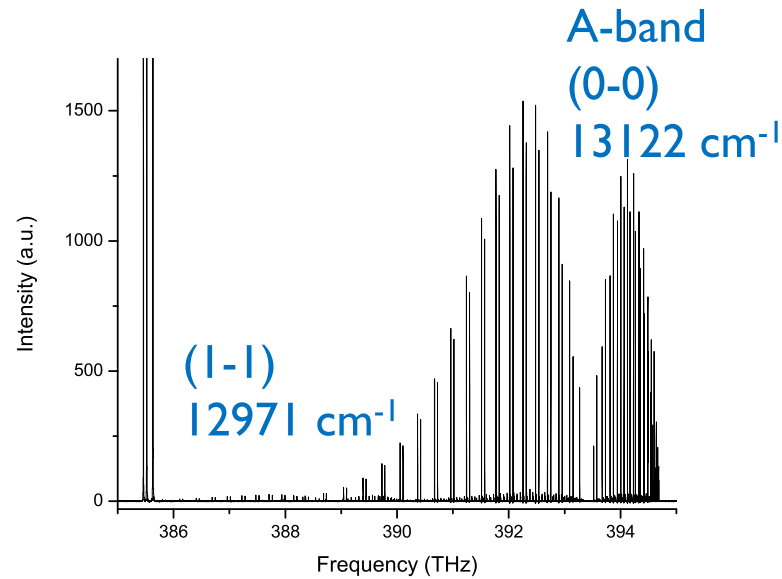
# New FTS emission spectra



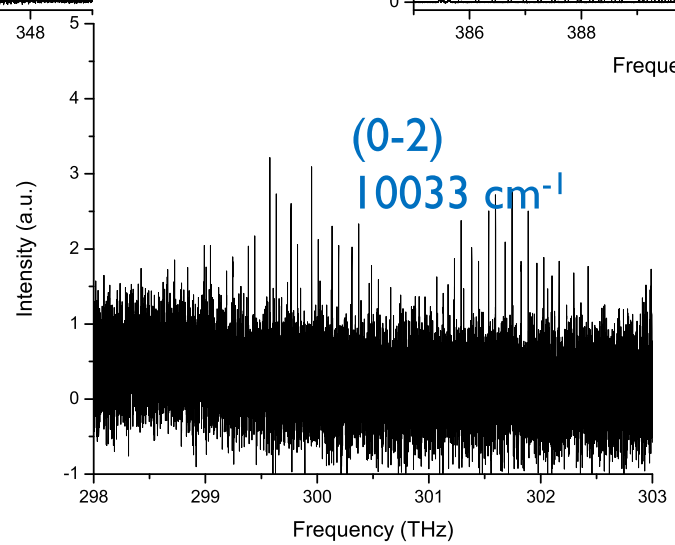
# Band Details

5.5 days integration

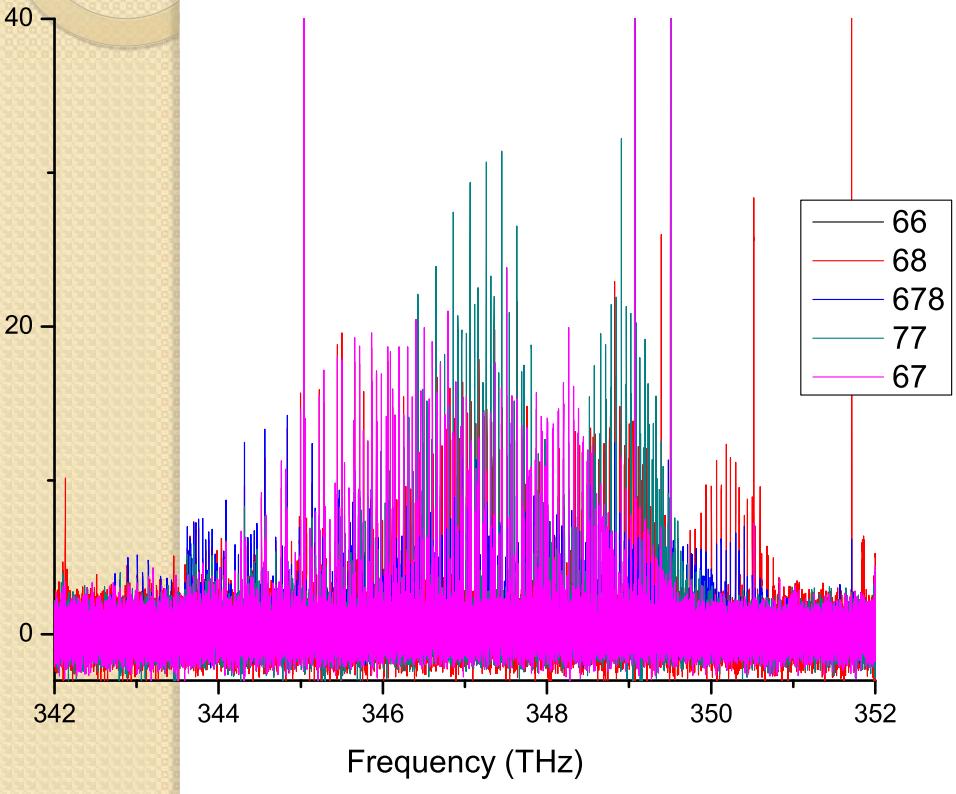


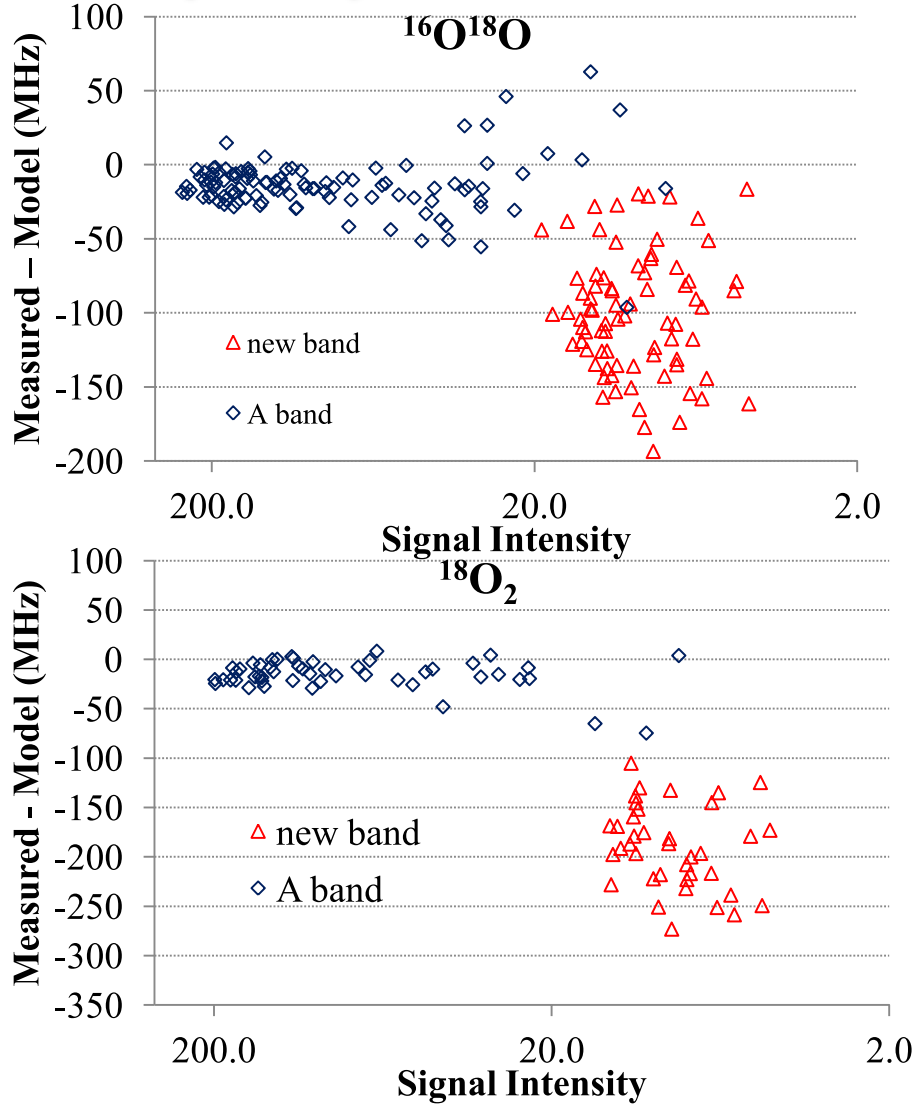




All of these bands were Predicted to higher Precision than the Measurement (9-150 MHz, 0.0003 – 0.05 $cm^{-1}$)



# Isotopic Data for (0-1)




The isotopic (0-1) bands were systematically shifted

100 MHz = 0.0033 $cm^{-1}$

# The Raman Data

- Edwards *et al.* J. Ram. Spec. 10, 1980
  - Raman data for

18-18, 17-18, 17-17 & 16-16

- Model
  - 0.18 $cm^{-1}$ discrepancy for 17-18
- This work
  - Experimental confirmation of 17-18 discrepancy

| | | | | NIR Emission | | Edwards | | |
|---|---|---|---|---|---|---|---|---|
| N' | v' | N" | v" | Frequency ($cm^{-1}$) | Unc. ($cm^{-1}$) | Frequency ($cm^{-1}$) | Unc. ($cm^{-1}$) | Diff (cm-1) |
| 6 | 0 | 7 | 1 | 11637.7858 | 0.0016 | 18-18 | | |
| 6 | 0 | 5 | 0 | 13138.7128 | 0.0005 | | | |
| 7 | 1 | 5 | 0 | 1500.9271 | 0.0020 | 1500.9180 | 0.0040 | 0.0091 |
| 8 | 0 | 9 | 1 | 11631.8932 | 0.0014 | 18-18 | | |
| 8 | 0 | 7 | 0 | 13142.5834 | 0.0004 | | | |
| 9 | 1 | 7 | 0 | 1510.6902 | 0.0018 | 1510.6790 | 0.0040 | 0.0112 |
| 10 | 0 | 11 | 1 | 11625.7820 | 0.0012 | 18-18 | | |
| 10 | 0 | 9 | 0 | 13146.1191 | 0.0004 | | | |
| 11 | 1 | 9 | 0 | 1520.3371 | 0.0017 | 1520.3300 | 0.0040 | 0.0071 |
| 4 | 0 | 5 | 1 | 11620.9353 | 0.0018 | 17-18 | | |
| 4 | 0 | 3 | 0 | 13133.7786 | 0.0005 | | | |
| 5 | 1 | 3 | 0 | 1512.8433 | 0.0023 | 1513.0170 | 0.0040 | -0.1737 |
| 10 | 0 | 11 | 1 | 11602.7557 | 0.0013 | 17-18 | | |
| 10 | 0 | 9 | 0 | 13145.7264 | 0.0004 | | | |
| 11 | 1 | 9 | 0 | 1542.9707 | 0.0017 | 1543.1370 | 0.0040 | -0.1663 |
| 12 | 0 | 13 | 1 | 11596.2454 | 0.0017 | 17-18 | | |
| 12 | 0 | 11 | 0 | 13149.0196 | 0.0004 | | | |
| 13 | 1 | 11 | 0 | 1552.7742 | 0.0021 | 1552.9480 | 0.0040 | -0.1738 |

# Model Changes ($T_e$ and $G_v$)

Although the SNR of the $^{16}O_2$ data was best, the model was unaffected by addition of those measurements.
The only significant model parameter value changes occurred upon introduction of the isotopic (0,1) measurements

| | | $X^3\Sigma_g^-$ | | $b^1\Sigma_g^+$ | |
|---|---|---|---|---|---|
| $T_e$ | $U^{T_e} \times \mu^{-0.0}$ | | | 395594904(149) | 395596144(95) |
| | $U^{T_e}\Delta^{T_e,O} m_e \times \mu^{-1.0}$ | | | 25556(149) | 24288(92) |
| $G_v$ | $U_{1,0} \times \mu^{-0.5}/2$ | 23683150(166) | 23683967(21) | 21473929( 68) | 21473493( 99) |
| | $U_{1,0}\Delta^O_{1,0} m_e \times \mu^{-1.5}/2$ | 2009(165) | 1157(19) | 1590( 60) | 2032( 93) |
| | $U_{2,0} \times \mu^{-1.0}/4$ | -89298.8( 67) | -89287.5( 63) | -104798.0( 75) | -104800.1( 75) |
| | $U_{3,0} \times \mu^{-1.5}/8$ | 137.94( 99) | 136.79( 96) | 25.09( 81) | 25.31( 81) |
| | $U_{4,0} \times \mu^{-2.0}/16$ | -1.591( 56) | -1.539( 55) | -4.5355(226) | -4.5413(226) |
| | $U_{5,0} \times \mu^{-2.5}/32$ | 6.31(134)E-03 | 5.24(132)E-03 | | |
| | $U_{6,0} \times \mu^{-3.0}/64$ | -0.2165(114) E-03 | -0.2083(112) E-03 | | |

Sums of U and Δ are unchanged

# Summary

- Isotope independent model for $^3\Sigma$, $^1\Delta$ & $^1\Sigma$
  - S. Yu *et al.*, J. Chem. Phys. 136, 2012.
- Hyperfine resolved rotational $^1\Delta$
  - B.J.Drouin *et al.*, J. Chem. Phys. 136, 2012.
- Laboratory Nightglow
  - Analysis complete, manuscript in preparation

# Acknowledgements

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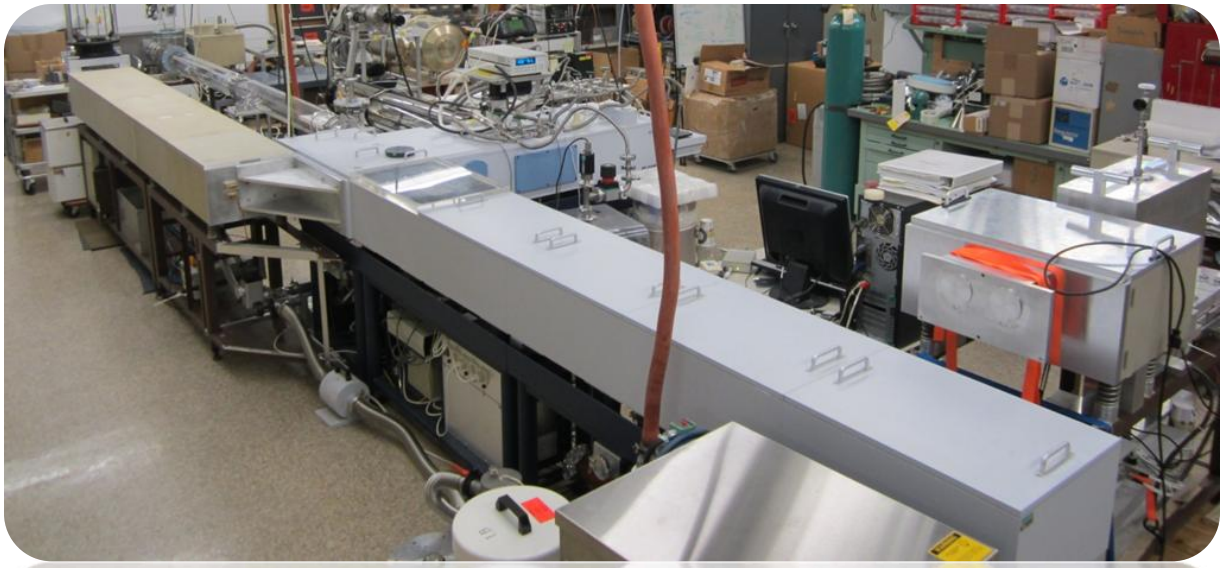

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