MULTISPECTRUM ANALYSIS OF THE OXYGEN A-BAND

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OCO-2 MISSION USES HIGH RESOLUTION SPECTROSCOPY

• 3-band grating spectrometer in orbit with other Earth observing satellites
• Measure Carbon Dioxide concentration globally
• Determine details of carbon cycle: sources, sinks, seasonal effects
AT HIGH PRESSURE MANY LINESHAPE ISSUES ARISE

• Doppler (‘Dicke’) narrowing
  • Narrows Gaussian at low pressures

• Pressure (‘Lorentz’) broadening
  • Convoluted with Gaussian to get Voigt profile

• Speed Dependence
  • Modifies Lorentz component for deviations from symmetric velocity distribution

• Line Mixing
  • Collisions that change quanta during absorption

• Collision induced absorption
  • Absorption of the collision pair
CAVITY RINGDOWN DATA (NIST CA. 2008)

Pros:
- High Optical Depth
- Low and high pressures
- Stable frequency axis
- Calibrated
- No background

Cons:
- Segmented
- Single Temperature
- Missing line cores

FOURIER TRANSFORM SPECTRA (JPL 2012, 2015)

Pros:
- Low and high pressures
- Low Temperatures
- Entire spectrum
- Line cores

Cons:
- Low Optical Depth
- Frequency axis jitter
- Instrument function
- Background
LABFIT
MULTISPECTRUM
ANALYSIS - DATA

• CRDS data previously published and pre-calibrated
• FTS data from two different cells, three pathlengths and four temperature ranges,
• FTS frequency calibration in LABFIT

\[ \sigma_{cal} = (1 + d_1) \times \sigma_{meas} + d_2 \]

a. New K absorption model essential to calibration
b. these intensity calibrated spectra are scaled to this pathlength
c. Optical Path difference (OPD) is \(1/(2 \times \text{resolution})\)
d. Calibration factor, \(d_1\) is defined in Eqn. 2
LABFIT

- Multispectral fitting software
  - Ideal for band spectra at high pressures
  - Lineshapes include Speed Dependence Rautian
  - Instrument functions include sinc, jitter, time constant

- Determines systematic errors
  - Pressures, temperatures
  - Zero offsets, calibration factors
  - Mixing ratios & isotope ratios
LABFIT – OXYGEN ABSORPTION MODEL

- **Line Positions**
  \[ \sigma_0(J', E'') = E'(J') - E'' \]
  \[ E'(J') = G_0 + B_0 J' (J' + 1) - D_0 J'^2 (J' + 1)^2 + H_0 J'^3 (J' + 1)^3 \]

- **Line Intensities**
  \[ I(J, m, T) = G_{ev} \sigma_0 S_{HL}(J) \mu_{SO}^2 (1 + c_1 m + c_2 m^2) e^{-E''/kT} \]
  \[ G_{ev} = \frac{8 \pi^3 \mu_{SO}^2}{3 \hbar c Q_{e, sr}} \]

- **Line Widths**
  \[ y = \left( p \left[ X_f \gamma_f (T_{ref}/T)^{n_f} + X_s \gamma_s (T_{ref}/T)^{n_s} \right] \right) / \gamma_D \]

- **Line Shifts**
  \[ x = \left( \sigma - \sigma_0 - p \left[ X_f (\delta_f + (T - T_{ref}) \delta'_f) + X_s (\delta_s + (T - T_{ref}) \delta'_s) \right] \right) / \gamma_D \]

- **Line Narrowing**
  \[ F(x, y, S) = \frac{2}{\pi} \int_{-\infty}^{+\infty} ve^{-v^2} \arctan \left( \frac{x + v}{y(1 + S(v^2 - \frac{3}{2}))} \right) dv \]

- **Line Mixing**
  \[ F'(x, y, S) = \frac{1}{\pi} \int_{-\infty}^{+\infty} ve^{-v^2} \ln \left( 1 + \frac{x + v}{y(1 + S(v^2 - \frac{3}{2}))} \right) dv \]
  \[ Y_k(T) = \text{imag} \left[ \sum_{j=1}^{N'} X_j T^A + \rho X A^{-1} \right] \]
  \[ X_j = \sqrt{I_j / \rho_j} \]
  \[ \rho_j(T) = e^{-E_j''/kT} \]
  \[ A = \text{diag}(G) \]
  \[ G(\sigma) = \sigma - \sigma_0 - iW \]

- **Resonant absorption**
  \[ \kappa_i = \sum_{k=1}^{N'} \left[ F_k(x_i, y, S) + Y_k(p, T) F'_k(x_i, y, S) \right] I_k(J, m, T) \]

- **Collision Induced Absorption**
  \[ B'(\sigma) = B(\sigma) e^{-\alpha(\sigma)L} \]
  \[ \alpha(\sigma) = \varrho_{O_2} \varrho_{N_2} \alpha(\sigma)_{O_2N_2} + \varrho_{O_2} \varrho_{O_2} \alpha(\sigma)_{O_4} \]

- a. Lower state energies significantly improved; b. Honl-London factor issue from early work resolved; c. new feature in software
GOALS AND DATA RANGE

• Many spectroscopic parameters are already determined well enough to predict the O2 A-band with accuracy and precision, e.g. line position $\sigma_{0k}$, line intensity $I_k$, room temperature lineshape $\gamma_{kf}$, $\delta_{kf}$, $\gamma_{ks}$, $\delta_{ks}$.

• Sensitivity testing has shown that sources of $n$, $\alpha$ & $W$ are limiting accuracy of OCO-2 retrievals
  
  • Improve accuracy of temperature dependence of pressure broadening (15% → 5%)
    • FTS data from 170 - 300 K can achieve 1.5%
  
  • Improve CIA model (5% → 1%)
    • CRDS data in P-branch gives <0.5% at STP
  
  • Test/vet LM theory (5% → ?)
    • Highest density/path FTS and CRDS data sensitive, but at 50% level
TEMPERATURE DEPENDENCE OF LINESHAPE IMPROVED

Red circles are multi-spectrum fitted values from NIST CRDS (295 K only) and JPL FTS data (175-295 K)
Black squares are Brown & Plymate JMS 199, 166-179 (2000), (210-296 K, low temp at short path only)
these values are used in HITRAN for the Temperature dependence of the air-broadened width

Taking absolute differences and dividing by B&P values gives a spread of 0-26%
B&P O₂ values are clearly worse, so take binary air differences, now spread is 3-14%
Average of these air differences is 8% Values for m = 8 (strongest lines) are 5%, 6%, 12%, 13%
Brian Connor’s sensitivity analysis suggests this will (un)bias the XCO₂ by almost a ppm
Data was sensitive enough to identify scale factor of ½ needed to input theoretical W into LABFIT
However, the full RMF still produced issues at origin and bandhead (central residual trace and 2nd Tran paper)
Tran et al suggested ad hoc ‘triangle’ function that significantly reduces all LM at high J
Removal of odd ΔJ matrix values provides acceptable solution (lower residual trace)
Tran, Boulet & Hartmann revised the algorithm (but not the matrix) for calculating LM and introduced a J-dependent scale factor. Used in conjunction with their CIA this fit the atmosphere well. The large differences in LM at $m = -5$ to $-15$ could not be reconciled in LABFIT without modifying the matrix. Removing the odd elements (connecting even J with odd J removes this issue and smooths out the Y coefficients. This is consistent with Y-values derived directly from data at room temperature.
EXTRACTION OF CIA FROM ATMOSPHERIC DATA

• Until sensitive laboratory data is available in R-branch region, utilize well characterized atmospheric data from TCCON site, co-located with DOE-ARM site at Lamont, OK
  • Microwave instrument provide precipitable water vapor (PWV)
  • NIMFR provides Aerosol Optical Depth (AOD)
  • TCCON provides full A-band

• Data selection
  • Cloud free
  • PWV variability < 10%
  • AOD variability < 10%
  • Large range of airmass, based on solar zenith angle

• Convert LABFIT output to CIA free ABSCO table
• Determine optical depths (ODs) throughout A-band from table
• Difference TCCON and ODs to obtain CIA
LABFIT CIA MODEL

The $I_j$ and $\sigma_0$ are from the 67 strongest $O_2$ lines in A-band (HITRAN units)

$f, w, l$ are tuned to fit P-branch CRDS data
And TCCON derived air data

\[ \alpha(\sigma) = \xi_{O_2} \xi_{N_2} \alpha(\sigma)O_2N_2 + \xi_{O_2} \xi_{O_2} \alpha(\sigma)O_4 \]

\[ \alpha(\sigma) = \sum_{j=1}^{N} \frac{f \omega I_j}{(\sigma - \sigma_0)^2 + \omega^2} \]

ABSCO CIA MODEL

The $\alpha(\sigma)$ are from the table
Determined from TCCON data
And resonant model from LABFIT

\[ This\ work \]
\[ This\ work\ (smooth) \]
\[ Tran\ et\ al. \]
\[ Long\ et\ al. \]
\[ Sperling\ et\ al. \]
SUMMARY OF CHANGES

• Prior database (ABSCO 4.2) based on Tran, Boulet & Hartmann LM, CIA and Long et al.’s positions, intensities, widths, shifts and Brown and Plymate’s temperature dependence of widths, fits atmospheric data to about 1%, with known bias on surface pressure and air mass

• FTS and CRDS data are mutually compatible at <1% level in multi-spectrum fitting program, optimization of model parameters and empirical CIA fits air spectra to noise level and pure O2 spectra to <1%

• New database (ABSCO 5.0) utilizes LBL and LM from self-consistent Labfit with approximate CIA based on self-consistent TCCON analysis

• Comparison to atmosphere reveals problem with Line mixing near bandhead
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LINE BY LINE PARAMETERS II

Temperature dependence

O$_2$ broadening
- Present Study
- HITRAN 2012

O$_2$ shift
- Present Study
- Long et al.

$n_S$ Coefficient
- Present Study
- Brown and Plymate

N$_2$ shift
- Temperature dependence

O$_2$ shift
- Temperature dependence

$n_S$ Coefficient
- Speed dependence
FINAL TCCON COMPARISON
LINE MIXING

• Incompatibility with CRDS data and subroutine testing for sensitivity to LM was resolved to enable fitting of LM in CRDS+FTS multispectrum analysis

• Determined values trended similar to TBH theory, but much noisier

• Bandhead LM not well defined with TBH or with fitted values
PRIOR STUDIES WITH CRDS

Oxygen spectra are recorded using a Fourier Transform Spectrometer (FTS, JPLs IFS-125HR pictured below) that modulates broadband radiation in a Michelson interferometer (left). The apparatus is entirely under vacuum and the source radiation is passed through a potassium cell in series with the temperature controlled long path Oxygen cell for wavelength calibration.

- Designed/developed for CIA study by Ed Wishnow (Loaned from UBC, Canada for free of charge)
- Wishnow et al. RSI 70, 23-32, 1999
- Moazzen-Ahmadi et al. JQSRT, 123-132, 2015
- Mirror: Pyrex, gold-coated on chromium
- Variable pathlength (up to 60 m)
- Pressure holding (up to ~2.5 atm)
- Temperature (down to 25 K)
- ~2 K control currently
- Upgrade coming in July
OXYGEN IS A WEAK ABSORBER

- Radiative interaction is spin-forbidden between triplet and singlet states
- Spin Orbit coupling gives $^1\Sigma_g^+$ state a few percent triplet character and allows a magnetic transition dipole of $0.026\mu_b$
- Atmosphere has enough $O_2$ to see ‘delta’ band, magnetic vibrational band, quadrupole bands and collision-induced absorption bands
- Existing database (ABSCO 4.2) based on Tran, Boulet & Hartmann LM, CIA and Long et al.’s positions, intensities, widths, shifts and Brown and Plymate’s temperature dependence of widths, fits atmospheric data to about 1%, with known bias on surface pressure and air mass