Forward Modeling for Far-Infrared Remote Sensing:
Spectroscopic Issues and Line-by-Line Modeling

Tony Clough
Clough Radiation Associates, LLC

and a host of colleagues
Contribution of the atmosphere to the outgoing spectral radiance

MLS Summer

Color scale x 10^{-7} is in units of W (cm^2 sr cm^{-1})^{-1}. 

S.A. Clough, M.J. Iacono, J.-L. Moncet, JGR, 1992
Atmospheric and Environmental Research, Inc.
Formalism for the Spectral Calculation of Absorption I

- Validity from Microwave through Solar UV
- Detail Balance across entire extent of the line
  - Radiance = Planck_Fn * [ 1 - Transmittance ]

A Bit of History: With a nod to the heroes of the profession!

Problem: Incoherent understanding of line shape associated with binary collisions
  (~1972)
  What is the validity of the impact line shape?
  What is the line shape far from line center that satisfies the physical constraints?

Harvard
Van Vleck
  - Phillip Anderson thesis (student of Van Vleck) (ATC) (1950)
  - Huber and Van Vleck I (1966)
  - Huber and Van Vleck II (1972)
  - J.H. Van Vleck (Rev Mod Phys; 1978)

MIT
Weisskopf
  - M.W.P. Strandberg
Formalism for the Calculation of Spectral Absorption Coefficients II

\[ k(\ ) = \frac{1}{1+e^{hc/kT}} \left\{ e^{hc/kT} \right\}^n \quad \text{Im} < ( )+ ( )> \]

\[ k(\ ) = \tanh(hc/2kT) \quad \text{Im} < ( )+ ( )> \]

---

radiation field \text{\leftrightarrow} \text{molecular system} \leftrightarrow \text{radiation interaction}

(line shape)

<symmetrized spectral density function>

- Radiation balance is satisfied over the full extent of the spectral line irrespective of accuracy of \( ( ) \)!
- F-sum rule rigorously satisfied: integral over \( \nu \) value of the band strength
- Led to the development of the CKD continuum model

Impact Result:

\[ k(\ ) \quad \quad \quad \quad \quad <\tilde{S}_i(T) - \frac{1}{1+e^{hc/kT}} \left\{ e^{hc/kT} \right\}^n \quad \text{Im} < ( )+ ( )> \]

Microwave:

\[ <\tilde{S}_i(T) - \frac{1}{1+e^{hc/kT}} \left\{ e^{hc/kT} \right\}^n \quad \text{Im} < ( )+ ( )> \]

Infrared:

\[ <\tilde{S}_i(T) - \frac{1}{1+e^{hc/kT}} \left\{ e^{hc/kT} \right\}^n \quad \text{Im} < ( )+ ( )> \]

Van Vleck - Weisskopf  
\text{e.g.} Gross, etc.  \text{xxx}

Lorentz
Line Shape Issues

Line Shape including widths, shifts and line coupling coefficients is the dominant source of error in current radiance calculations

• Doppler
  Gaussian

• Collisional
  Lorentzian
  frequency of collision: \((P/T)\)

• Voigt
  Convolution of Gaussian with Lorentzian

• Duration of collision
  Impact approximation is just that:
  line wings must decay exponentially

• Speed Dependent Voigt
  Doppler and Collisional processes are not independent

• Line Coupling
  Collisional relaxation matrix between lines required
Water Vapor Spectroscopic Parameters

- **Line Strengths**
  - Laurent Coudert
    - Strong Lines (mid IR): Intensities increased by ~ 5%
    - Not an issue for Far Infrared (Pure Rotational region) ???

- **Line Widths and Shifts / Temperature Dependence**
  - Bob Gamache & HITRAN
  - Present Results

- **Line Coupling**
  - Linda Brown (two line resonances)
  - Revised relaxation rates
  - First Order
  - Present Result (400 cm^-1)

- **Continuum**
  - Inextricably linked to the width
  - Scaled in selected regions of the water bands
Two Closure Studies in the Far Infrared:

1) **AERI_ex at ARM NSA Site**

A far-infrared radiative closure study in the Arctic: Application to water vapor

Radiance Data:
- Linear scaling of radiance in low wavenumber region
- Removal of linearly increasing sinusoid in low wavenumber region
- Average of 5 cases
- Atmosphere: Sondes

2) **REFIR-PAD at Cerro Tocco (Chile) & Pagosa Springs (Colorado) RHUBC II**

Laboratory characterisation of the Radiation Explorer in the Far-Infrared Breadboard (REFIR/BB) for the atmospheric emission measurement in the 100-1100 cm\(^{-1}\) spectral range
Luca Palchetti\(^{(1)}\), Giovanni Bianchini\(^{(1)}\), Carmine Serio\(^{(2)}\), Francesco Esposito\(^{(2)}\),
Rolando Rizzi\(^{(3)}\), Vincenzo Cuomo\(^{(4)}\)

Data:
- Average of five spectra
- Linear scaling of radiance in low wavenumber region
- Atmosphere: Retrieved; \textit{a priori}: sondes
AERI Downwelling Radiances I

ARM NSA Site  PWV: 1.866 mm
AERI Downwelling Radiances II

ARM NSA Site

Line Coupling
Residual at 400cm-1

Line Coupling to Resolve the Residual

*This Work*

<table>
<thead>
<tr>
<th>Transition Frequency</th>
<th>Strength</th>
<th>Gamache % change</th>
<th>CRA</th>
<th>Self</th>
<th>In cpl</th>
</tr>
</thead>
<tbody>
<tr>
<td>398.976493</td>
<td>9 7 2 8 6 3</td>
<td>5.556D-20</td>
<td>0.0414</td>
<td>-13.0</td>
<td>0.0360</td>
</tr>
<tr>
<td>400.221796</td>
<td>10 4 6 9 3 7</td>
<td>1.070D-20</td>
<td>0.0791</td>
<td>0.0</td>
<td>0.0791</td>
</tr>
<tr>
<td>400.481057</td>
<td>10 6 4 9 5 5</td>
<td>1.071D-20</td>
<td>0.0510</td>
<td>0.0</td>
<td>0.0510</td>
</tr>
</tbody>
</table>

Half Width Adjustments to Resolve the Residual

*Delamere et al.*

<table>
<thead>
<tr>
<th>Transition Frequency</th>
<th>Strength</th>
<th>Gamache Width % Change</th>
<th>&quot;Clough Width&quot; Self Width</th>
</tr>
</thead>
<tbody>
<tr>
<td>396.432560</td>
<td>8 2 6 7 1 7</td>
<td>2.396E-20</td>
<td>0.0807</td>
</tr>
<tr>
<td>397.318923</td>
<td>9 3 6 8 2 7</td>
<td>5.811E-20</td>
<td>0.0804</td>
</tr>
<tr>
<td>397.675624</td>
<td>10 6 5 9 5 4</td>
<td>3.104E-20</td>
<td>0.0565</td>
</tr>
<tr>
<td>398.941390</td>
<td>9 7 3 8 6 2</td>
<td>1.825E-20</td>
<td>0.0415</td>
</tr>
<tr>
<td>398.976486</td>
<td>9 7 2 8 6 3</td>
<td>5.476E-20</td>
<td>0.0414</td>
</tr>
<tr>
<td>400.221819</td>
<td>10 4 6 9 3 7</td>
<td>1.053E-20</td>
<td>0.0791</td>
</tr>
<tr>
<td>400.481040</td>
<td>10 6 4 9 5 5</td>
<td>1.051E-20</td>
<td>0.0510</td>
</tr>
</tbody>
</table>
REFIR_PAD 20090425  Pagosa Springs, CO  RHUBC II

Retrieved atmosphere a priori: sonde

<table>
<thead>
<tr>
<th>L</th>
<th>PATH (km)</th>
<th>PBAR</th>
<th>TBAR</th>
<th>P_h2o (mb)</th>
<th>T_h2o(K)</th>
<th>PWV (cm)</th>
<th>O3 (du)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>2.33-18.00</td>
<td>414.86</td>
<td>251.72</td>
<td>606.20</td>
<td>268.86</td>
<td>0.6441</td>
<td>124.27</td>
</tr>
</tbody>
</table>
REFIR_PAD 20090425    Pagosa Springs, CO    RHUBC II

Retrieved atmosphere    a priori: sonde

<table>
<thead>
<tr>
<th>L</th>
<th>PATH (km)</th>
<th>PBAR</th>
<th>TBAR</th>
<th>P_h2o (mb)</th>
<th>T_h2o(K)</th>
<th>PWV (cm)</th>
<th>O3 (du)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>2.33-18.00</td>
<td>414.86</td>
<td>251.72</td>
<td>606.20</td>
<td>268.86</td>
<td>0.6441</td>
<td>124.27</td>
</tr>
</tbody>
</table>

![Graph showing radiance and radiance residuals over wavenumber range](image)

Clough Radiation Associates

Far-Infrared Workshop, 8 Nov 2011
REFIR_PAD 20090919    CERRO TOCO (5383M)    RHUBC II

Retrieved atmosphere a priori: sonde
Retrieved atmosphere a priori: sonde

<table>
<thead>
<tr>
<th>L</th>
<th>PATH (km)</th>
<th>PBAR</th>
<th>TBAR</th>
<th>P_h2o (mb)</th>
<th>T_h2o(K)</th>
<th>PWV (cm)</th>
<th>O3 (du)</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>5.383-18.000</td>
<td>305.70</td>
<td>234.85</td>
<td>388.01</td>
<td>249.24</td>
<td>0.0247</td>
<td>28.1</td>
</tr>
</tbody>
</table>

Graph showing radiance (RU e-03) vs. wavenumber (cm⁻¹) with labels for different curves: `lblrtn`, `refir_adj`, and `continuum`.
REFIR_PAD 20090919  CERRO TOCO (5383M)  RHUBC II
Continuum

REFIR_PAD 20090919  CERRO TOCO (5383M)  RHUBC II
CKD Continuum (1980)
- Direct consequence Van Vleck’s paper
- Line at 100 cm\(^{-1}\) is greatest contributor to continuum at 1000 cm\(^{-1}\)
- Detail balance satisfied
- Exponential decay of far wings
- Works remarkably well
- Line shape \textit{engineering}
  - 6 parameters
- Inter-molecular Potential \textit{engineering}
  - Ma and Tipping
- Super Lorentzian line shape to obtain observed ‘extra absorption’

MT_CKD Continuum
- Super Lorentzian line shape is untenable
- Collision Induced Model introduced to attain ‘extra absorption
- Direct consequence of the our work on Oxygen at 7900 cm\(^{-1}\)
Oxygen Continuum

Figure 1. (a) Solar radiances measured with the Absolute Solar Transmittance Interferometer (ASTI), (b) radiances calculated by the line-by-line radiative transfer model (LBLRTM), (c) differences between the ASTI measured radiances and the LBLRTM calculated radiances before formulation of the O₂ continuum, and (d) differences between the ASTI measured radiances and the LBLRTM calculated radiances after formulation of the O₂ continuum for the spectral range 7300–8300 cm⁻¹ and a zenith angle of 71.5°.
CKD Continuum
Continuum
the window around 2500 cm⁻¹ (see inset) the continuum plots look quite smooth. Note, however, that there is a distinct feature around 3200 cm⁻¹. Recently this has been observed also by Paynter et al. [17, 18]. Their continuum data at 351 K in the range between 3025 cm⁻¹ and 3400 cm⁻¹ are in good agreement with ours. The intensity of the feature at 3200 cm⁻¹ appears to decrease as the temperature grows and, presumably, it belongs to the overtone of the O-H-O bending mode of the water dimer at 3215 cm⁻¹, which has been predicted in theoretical calculations by Schofield and Kjaergaard [23]. Much weaker structures in the regions 1925 cm⁻¹ to 2025 cm⁻¹ and 3300 cm⁻¹ to 3500 cm⁻¹ are still not understood as are similar weak structures in the 10 μm region [11].
“Extra Absorption” Incorporated in the Continuum

**Collision Induced Model** (MT_CKD)
- Binary Collisions
- Monomer Transitions
- Agreement with Reliable DATA with minimal parameters is compelling
- Line Widths result from Duration of Collision Time
- Genesis from the CIA in the Oxygen Band at 7900 cm⁻¹
- **Collision Induced Absorption in CO has recently been observed**

**Dimer (Bound) Model**
- Not consistent with Binary Collisions
- How is the population sustained?
- No compelling spectral evidence (that I’ve seen)
  - Not that there couldn’t be if done properly

**CAVIAR**
- Avenging the mistakes of King George III ??? (facetious of course)
- Analyses have simply been inadequate
- Recent articulation: the spectra are due to monomer transitions in a loosely bound dimer
Summary

• Energetically the Far Infrared is Crucial
• Formalism for Calculations of Radiance from the Microwave to UV is well Established
• The Measurements from AERI_ex and REFIR_PAD are just beautiful
• Bravo to NSA and RHUBC II Campaigns
• Major Spectroscopic Issue: Line Widths
• Line Strengths: Strong Lines generally good; Weak Lines in need of improvement
• Spectroscopy in Absorption Windows is Extremely Important
  ▪ Continuum Value Interlinked with Widths
  ▪ Not presently being done properly!!!
  ▪ Higher Resolution is Critical for future improvement
• In my view, Collision Induced Absorption is the most Reasonable Explanation of Extra Absorption
• CAVIAR Initiative is Highly Disappointing (Distressing)

King George III Effect
Water Vapor Band Center: 1530 - 1630 cm⁻¹

Line Coupling 1540 cm⁻¹

Widths and Continuum modified

- Ave: -0.047 K
- Std: 0.267 K
- Ave: 0.007 K
- Std: 0.219 K

Clough Radiation Associates

Far-Infrared Workshop, 8 Nov 2011
the window around 2500 cm\(^{-1}\) (see inset) the continuum plots look quite smooth. Note, however, that there is a distinct feature around 3200 cm\(^{-1}\). Recently this has been observed also by Paynter et al. [17, 18]. Their continuum data at 351 K in the range between 3025 cm\(^{-1}\) and 3400 cm\(^{-1}\) are in good agreement with ours. The intensity of the feature at 3200 cm\(^{-1}\) appears to decrease as the temperature grows and, presumably, it belongs to the overtone of the O-H-O bending mode of the water dimer at 3215 cm\(^{-1}\), which has been predicted in theoretical calculations by Schofield and Kjaergaard [23]. Much weaker structures in the regions 1925 cm\(^{-1}\) to 2025 cm\(^{-1}\) and 3300 cm\(^{-1}\) to 3500 cm\(^{-1}\) are still not understood as are similar weak structures in the 10 μm region [11].
Line Coupling:      Accidental Line Resonances

<table>
<thead>
<tr>
<th></th>
<th>400 cm⁻¹</th>
<th>1540 cm⁻¹</th>
<th>1630 cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tony Clough</td>
<td>Linda Brown</td>
<td>Linda Brown</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>398.976493</td>
<td>1539.060760</td>
<td>1539.060760</td>
</tr>
<tr>
<td></td>
<td>5.556D-20</td>
<td>2.255D-19</td>
<td>2.255D-19</td>
</tr>
<tr>
<td></td>
<td>2.283E+01.0360.3283</td>
<td>1.153E+01.1053.4643</td>
<td>1.153E+01.1053.4643</td>
</tr>
<tr>
<td></td>
<td>1411.61150.29-.000910</td>
<td>79.49640.79-.004100</td>
<td>79.49640.79-.004100</td>
</tr>
<tr>
<td></td>
<td>1 1 9 7 2 8 6 3</td>
<td>2 1 0 1 2 1 2</td>
<td>2 1 0 1 2 1 2</td>
</tr>
<tr>
<td></td>
<td>5552433 5</td>
<td>3555433-1</td>
<td>3555433-1</td>
</tr>
<tr>
<td>1</td>
<td>1.456529E-01</td>
<td>1.098843E-02</td>
<td>1.098843E-02</td>
</tr>
<tr>
<td></td>
<td>1.365260E-01</td>
<td>1.048538E-02</td>
<td>1.048538E-02</td>
</tr>
<tr>
<td></td>
<td>1.300000E-01</td>
<td>1.012000E-02</td>
<td>1.012000E-02</td>
</tr>
<tr>
<td></td>
<td>1.248789E-01</td>
<td>9.829722E-03</td>
<td>9.829722E-03</td>
</tr>
<tr>
<td>11</td>
<td>400.221796</td>
<td>1540.299806</td>
<td>1540.299806</td>
</tr>
<tr>
<td></td>
<td>1.070D-20</td>
<td>1.767D-19</td>
<td>1.767D-19</td>
</tr>
<tr>
<td></td>
<td>4.643E+00.0791.3009</td>
<td>7.175E+00.0971.5173</td>
<td>7.175E+00.0971.5173</td>
</tr>
<tr>
<td></td>
<td>1216.23130.710.004940</td>
<td>136.76170.790.000020</td>
<td>136.76170.790.000020</td>
</tr>
<tr>
<td></td>
<td>1 110 4 6 9 3 7</td>
<td>1 110 6 4 9 5 5</td>
<td>1 110 6 4 9 5 5</td>
</tr>
<tr>
<td></td>
<td>5552433-1</td>
<td>5552433-1</td>
<td>5552433-1</td>
</tr>
<tr>
<td>1-1</td>
<td>2.671053E-01</td>
<td>1-1.604015E-02</td>
<td>1-1.604015E-02</td>
</tr>
<tr>
<td></td>
<td>-1.725650E-01</td>
<td>-1.409560E-02</td>
<td>-1.409560E-02</td>
</tr>
<tr>
<td></td>
<td>-1.303796E-01</td>
<td>-1.292537E-02</td>
<td>-1.292537E-02</td>
</tr>
<tr>
<td></td>
<td>-1.064366E-01</td>
<td>-1.211058E-02</td>
<td>-1.211058E-02</td>
</tr>
</tbody>
</table>

Y: 200K 250K 296K 340K
**MT_CKD Water Vapor Continuum Model**

- Definition: Continuum is that absorption with slow spectral dependence which, when added to the line by line absorption, provides agreement with measurement.

- Scaling: Dependence on pressure, temperature and mixing ratio must be correct

- The model is based on contributions from two sources:
  1. **Allowed line contribution**
     - Line wing formalism constrained by the known physics with relevant parameters (~2) determined from laboratory and atmospheric Measurements
     - Same line shape is used for every line from the Microwave to 20,000 cm\(^{-1}\)
  2. **Collision-Induced contribution**
     - Provides the extra absorption previously provided by the ‘super Lorentzian’ chi factor
     - Based on dipole allowed transitions with widths \(\sim \) 50 cm\(^{-1}\)
     - Same line shape is used for every line from the Microwave to UV

- The model includes both self and foreign continuum

- Spectral region: 0 - 20,000 cm\(^{-1}\)
<table>
<thead>
<tr>
<th>L</th>
<th>PATH (km)</th>
<th>PBAR</th>
<th>TBAR</th>
<th>P_h2o (mb)</th>
<th>T_h2o(K)</th>
<th>PWV (cm)</th>
<th>O3 (du)</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>5.383-18.000</td>
<td>305.70</td>
<td>234.85</td>
<td>388.01</td>
<td>249.24</td>
<td><strong>0.0247</strong></td>
<td>28.1</td>
</tr>
</tbody>
</table>

![Graph showing radiances and wavenumbers with various lines and markers.](image)
AERI Downwelling Radiances II

ARM NSA Site

Line Coupling

Clough Radiation Associates
Far-Infrared Workshop, 8 Nov 2011
AERI Downwelling Radiances
ARM NSA Site

<table>
<thead>
<tr>
<th>Transition Frequency</th>
<th>Strength</th>
<th>Gamache Width</th>
<th>% Change</th>
<th>&quot;Clough Width&quot;</th>
<th>Self Width</th>
</tr>
</thead>
<tbody>
<tr>
<td>396.432560</td>
<td>8 2 6 7 1 7</td>
<td>2.396E-20</td>
<td>-7.5</td>
<td>0.0746</td>
<td>0.384</td>
</tr>
<tr>
<td>397.318923</td>
<td>9 3 6 8 2 7</td>
<td>5.811E-20</td>
<td>-7.5</td>
<td>0.0743</td>
<td>0.328</td>
</tr>
<tr>
<td>397.675624</td>
<td>10 6 5 9 5 4</td>
<td>3.104E-20</td>
<td>-7.5</td>
<td>0.0522</td>
<td>0.301</td>
</tr>
<tr>
<td>398.941390</td>
<td>9 7 3 8 6 2</td>
<td>1.825E-20</td>
<td>-20.5</td>
<td>0.0330</td>
<td>0.328</td>
</tr>
<tr>
<td>398.976486</td>
<td>9 7 2 8 6 3</td>
<td>5.476E-20</td>
<td>-20.5</td>
<td>0.0329</td>
<td>0.328</td>
</tr>
<tr>
<td>400.221819</td>
<td>10 4 6 9 3 7</td>
<td>1.053E-20</td>
<td>-25.0</td>
<td>0.0593</td>
<td>0.301</td>
</tr>
<tr>
<td>400.481040</td>
<td>10 6 4 9 5 5</td>
<td>1.051E-20</td>
<td>-25.0</td>
<td>0.0383</td>
<td>0.301</td>
</tr>
</tbody>
</table>
not JCSDA

Cerro Toco
Chilean Andes (5383 m)
(after retrieval)
Formalism for LBL Calculations III

Impact Approximation »» Duration of Collision »» \( \left( \frac{n}{n_i} \right) \) factor

\[
k(n) = \frac{1}{1 + e^{\frac{hc}{kT}}} \left[ \tilde{S}_i(T) \right] \frac{1}{\left( i + \frac{iP}{(i + 1)^2 + (iP)^2} \right) + \left( i + \frac{iP}{(i + 1)^2 + (iP)^2} \right) + \left( i + \frac{iP}{(i + 1)^2 + (iP)^2} \right) + \left( i + \frac{iP}{(i + 1)^2 + (iP)^2} \right)} >
\]

\[
\tilde{S}_i(T) = \frac{1}{i + \left( i \right)} + \frac{1}{i \left( P, T \right)} + \frac{iP}{T/T_0^i} \quad (i_i)
\]

<table>
<thead>
<tr>
<th>Strength</th>
<th>Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>Line Position</td>
<td>grade</td>
</tr>
<tr>
<td>Pressure Shift</td>
<td>C/D</td>
</tr>
<tr>
<td>Width</td>
<td>B</td>
</tr>
<tr>
<td>T Dependence</td>
<td>C</td>
</tr>
</tbody>
</table>

Clough Radiation Associates
Far-Infrared Workshop, 8 Nov 2011
AERI Downwelling Radiances III
ARM NSA Site

PWV: 1.866 mm
Water Vapor R-Branch: 1640 - 1750 cm\(^{-1}\)

Widths modified

Ave: 0.060 K
Std: 0.321 K
Ave: 0.056 K
Std: 0.329 K

Line Coupling
1653 cm\(^{-1}\)