Development of a Reduced C$_3$ NEQAIR radiation model based on ab-initio calculations

Marat Kulakhmetov
Ph.D. Candidate at Purdue University

NASA Mentors:
Aaron Brandis
Brett Cruden

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Outline

• Motivation
• Introduction
  - Radiation
  - NEQAIR
  - Ab-initio Calculations
• Reduced Radiation Model
  - Selection of Strong Lines
  - Fitting Weak Lines
  - SpectraRedux/ NEQAIR Implementation
• Results and Discussion
  - 2-cell test case
  - 16 km/s test case
  - Absorption Cross Sections
• Conclusions
Motivation

- Atmospheric entry spans a wide range of chemical physical regimes:
  - Laminar-Turbulent Transition
  - Thermo-Chemical Excitation
  - Continuum-Rarefied Transition
  - Nonequilibrium
  - Radiative transport

Introduction

Radiation

- Molecules may transition between internal energy levels by:
  - Spontaneous emissions
  - Stimulated Emissions
  - Stimulated Absorption
  - Collisions
- Radiance is a function of:
  - Transition wavelength
  - Einstein Coefficients
  - Population of levels \( f(g,N,T,E) \)
  - Broadening \( f(P,T) \)
- A full spectra is generated by considering:
  - All energy levels
  - Allowed state to state transitions

\[ \Delta E = h\nu \]

\[ \frac{dI}{dx} \sim E \sim \frac{hc}{4} A_{ul} \]
Introduction

Radiation

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  - Population of levels \( \rightarrow f(g,N,T,E) \)
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\[
E \sim \frac{hc}{4} A_{ul} \left[ g_u N \exp\left( \frac{E_u}{kT} \right) / Q(T) \right] \left[ f(P,T) \right]
\]
Introduction

Radiation

- Molecules may transition between internal energy levels by:
  - Spontaneous emissions
  - Stimulated Emissions
  - Stimulated Absorption
  - Collisions

- Radiance is affected by
  - Transition wavelength
  - Einstein Coefficients
  - Population of levels -> f(g,N,T,E)
  - Broadening -> f(P,T)

- A full spectra is generated by considering
  - All energy levels
  - Allowed state to state transitions

\[ E \sim \frac{Nh\nu c}{4Q(T)} \sum_{u} \sum_{\ell} A_{u\ell}g_{u} \exp\left(\frac{E_{u}}{kT}\right) (P,T) \]
Introduction

NEQAIR

• Line-by-line line-of-sight code
• Calculates emission/absorption from a fluid media under thermo-chemical non-equilibrium conditions
• NASA Software of the Year?
• Is currently able to model emissions from:

<table>
<thead>
<tr>
<th>Molecular Bands</th>
<th>Atomic Lines</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2</td>
<td>N</td>
</tr>
<tr>
<td>NO</td>
<td>O</td>
</tr>
<tr>
<td>O2</td>
<td>C</td>
</tr>
<tr>
<td>CN</td>
<td>H</td>
</tr>
<tr>
<td>CO</td>
<td>C3</td>
</tr>
<tr>
<td>C3</td>
<td>Ar</td>
</tr>
<tr>
<td>OH</td>
<td>H2</td>
</tr>
<tr>
<td>NH</td>
<td>CH</td>
</tr>
<tr>
<td>CO2</td>
<td>C3</td>
</tr>
</tbody>
</table>

$$\frac{dI}{dx} = E^{\text{Spon.Emis}} + \left(E^{\text{Stim.Emis}} \ E^{\text{Stim.Abs}} \right) I$$
Introduction

What is C₃?

- Formed during vaporization of graphite/carbonaceous ablating heat shield
- Is able to absorb in the 140-220 nm band
  - NO, Nitrogen and Oxygen atomic and molecular lines
  - ~60% of radiative heating in VUV

<table>
<thead>
<tr>
<th>Case</th>
<th>Dominant Boundary-Layer Species</th>
<th>Reference</th>
</tr>
</thead>
</table>

Introduction

Ab-initio Calculations

• C$_3$ potential surfaces have been calculated by R. Jaffe, G. Chaban and D. Schwenke using:
  - Complete Active Self-Consistent Field method (CASSCF) within the MOLPRO electronic structure package
  - Only available C$_3$ dataset

• Einstein coefficients can be calculated from a transition dipole moment,

\[ M_{ul} = \int \mu^* \mu \, dl \]

• As

\[ A_{ul} = \frac{16 \, \nu^3}{3 \, \hbar c^3} M_{ul}^3 \]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of electronic levels</td>
<td>19</td>
</tr>
<tr>
<td>Number of rovibronic levels</td>
<td>~745,000</td>
</tr>
<tr>
<td>Number of lines</td>
<td>~1.8 billion</td>
</tr>
<tr>
<td>Data size</td>
<td>&gt;200 gigs</td>
</tr>
</tbody>
</table>

Selection of Strong Lines

- 1.8 billion lines need to be modeled efficiently within NEQAIR
- A complete set of lines are used to calculate an emission spectra, which depends on:
  - Strong lines
  - Density of weak lines
- Strong lines are selected by comparing to the local base of the spectra
Reduced Radiation Model

Fitting Weak Lines

• High density of weak lines can contribute significantly toward radiation.

• Combined emissivity and absorptivity of weak lines within $\lambda + \Delta \lambda$ can be calculated as:

\[
\begin{align*}
\frac{hc}{4} \frac{N}{Q(T)} \sum_{u \in u} \sum_{E_u} A_{ul} g_u \exp\left(\frac{E_u}{kT}\right) \\
= \frac{4}{8} \frac{N}{c Q(T)} \sum_{l \in l} \sum_{E_l} A_{ul} g_u \exp\left(\frac{E_l}{kT}\right) \frac{5}{2hc^2}
\end{align*}
\]

• These are fit to an exponential expansion to ensure better than 1% convergence in the 300-6,000 K temperature range

\[
\begin{align*}
\sum_{u \in u} \sum_{E_u} A_{ul} g_u \exp\left(\frac{E_u}{kT}\right) &= \sum_i A_i \exp\left(\frac{B_i}{T}\right) \\
\sum_{l \in l} \sum_{E_l} A_{ul} g_u \exp\left(\frac{E_l}{kT}\right) &= \sum_j C_j \exp\left(\frac{D_j}{T}\right)
\end{align*}
\]
Reduced Radiation Model

SpectraRedux

- A MATLAB program was created to produce Redux files for arbitrary ab-initio data that can be used by NEQAIR
  - User has to specify structure of the ab-initio output file
- The program is capable of producing 2-temperature models and can be extended to 4 temperature models
- C3 database reduction takes ~ 1 day on TSA cluster (in serial)
- NEQAIR 14.0 and 14.1 have been modified to accept C3 Redux files. – MPI compatible
  - Will be released as a feature in 14.1
Results and Discussion

2-Cell Test Case

- C\textsubscript{3} Off, Q = 31.93 W/cm\textsuperscript{2}
- Tol: 0.5, Q = 19.10 W/cm\textsuperscript{2}
- Tol: 0.1, Q = 19.14 W/cm\textsuperscript{2}
- Tol: 0.01, Q = 19.14 W/cm\textsuperscript{2}

- T = 10,000 K
- O\textsubscript{2} = 1E15/cm\textsuperscript{3}
- E\textsuperscript{-} = 1E11/cm\textsuperscript{3}
- T = 4,000 K
- C3 = 1E18/cm\textsuperscript{3}

2-Cell test case is used for convergence studies:
- C\textsubscript{3} results in a 40% drop in heat flux
- Spectra is insensitive:
  - fit block width,
  - insensitive to Linecut tolerance parameter,

Aug, 2015

Partnering ab-initio quantum chemistry with engineering problems
Johnston Test Case

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tbody>
<tr>
<td>Earth Entry</td>
<td>16 km/s</td>
</tr>
<tr>
<td>Ablator:</td>
<td>Carbon Phenolic</td>
</tr>
<tr>
<td>Nose Radius</td>
<td>1 m</td>
</tr>
<tr>
<td>Density</td>
<td>1e-3 kg/m^3</td>
</tr>
</tbody>
</table>


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Results and Discussion

Johnston Test Case

- Radiative heat transfer was calculated for Johnston’s 16km/s flowfield

- Originally ablation resulted in 26.7% drop in heat flux

- Addition of C3 dropped heat flux by an additional 14.7%
  - weak lines absorb ~10% of radiation
  - Strong lines absorb ~5% of radiation

- C3 absorbs strongly in:
  - 140 nm - 180 nm
  - 240 nm – 320 nm

Johnston predicted:
- Non-Ablating: 1.60e4 W/cm²
- Ablating: 8.30e3 W/cm² (23% diff)
## Results and Discussion

- Original file had:
  - 1,830,044,539 emission lines
  - 224 gigs of data
- Reduced C3 model
  - Kept: ½ - 2 million lines
  - ~ 1 - 30 % increase in computation time

<table>
<thead>
<tr>
<th>Case</th>
<th>Heat Flux (W/cm^2)</th>
<th>% Change</th>
<th># Lines</th>
<th>Size (MB)</th>
<th>Redux frac</th>
<th>Calc Time (s)</th>
<th>% Change</th>
</tr>
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<tbody>
<tr>
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<td>17,280.68</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>323</td>
<td>N/A</td>
</tr>
<tr>
<td>No C3 Radiation</td>
<td>12,655.42</td>
<td>0.00%</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>495</td>
<td>0.00%</td>
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<td>552,203</td>
<td>27</td>
<td>8296</td>
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<td>-1.0 %</td>
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<td>1,919,729</td>
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<td>2383</td>
<td>654</td>
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<td>10,867.76</td>
<td>14.1 %</td>
<td>1,866,664</td>
<td>91</td>
<td>2462</td>
<td>539*</td>
<td>8.89%</td>
</tr>
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<td>LineCut: 0.01,</td>
<td>10,867.91</td>
<td>14.1 %</td>
<td>6,738,581</td>
<td>328</td>
<td>683</td>
<td>786</td>
<td>58.8%</td>
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</tr>
</tbody>
</table>
Results and Discussion

Absorption Cross Section

- Ab-initio calculated absorption cross sections are up to 1 order of magnitude lower than predicted by Shinn
  - Thermochemical equilibrium assumed
  - Thermodynamic data required for data reduction not accurately known
  - Possible contribution of other absorbing species
- C_3 emissions in HARA (NASA Langley) are modeled using a polynomial fit of absorption cross sections based on data by Shinn
- Ab-initio data has been smoothed and fit with polynomial splines for implementation in HARA

Conclusions

• $\text{C}_3$ has been identified as an important absorber in ablating boundary layers
• Energy levels and Einstein coefficients for $\text{C}_3$ have been calculated by Jaffe, Chaban and Schwenke
• Ab-initio database for $\text{C}_3$ has been reduced and implemented in NEQAIR v14.0 and v14.1
• For a 16km/s test case, $\text{C}_3$ is able to absorb up to 14% of radiant energy reaching the surface.
• Calculated absorption cross sections are up to 1 order of magnitude lower than those previously measured by Shinn

• Deliverables
  - SpectraRedux code is able to reduce arbitrary ab-initio datasets
  - SpectraRedux manual
  - NEQAIR v14.0 and v14.1 is updated to accept the reduced $\text{C}_3$ model
    ▪ Can be simply extended to other arbitrary molecules
Questions?
National Aeronautics and Space Administration

Ames Research Center
Entry Systems and Technology Division