Characterization of CO Thermochemistry in Incident Shockwaves

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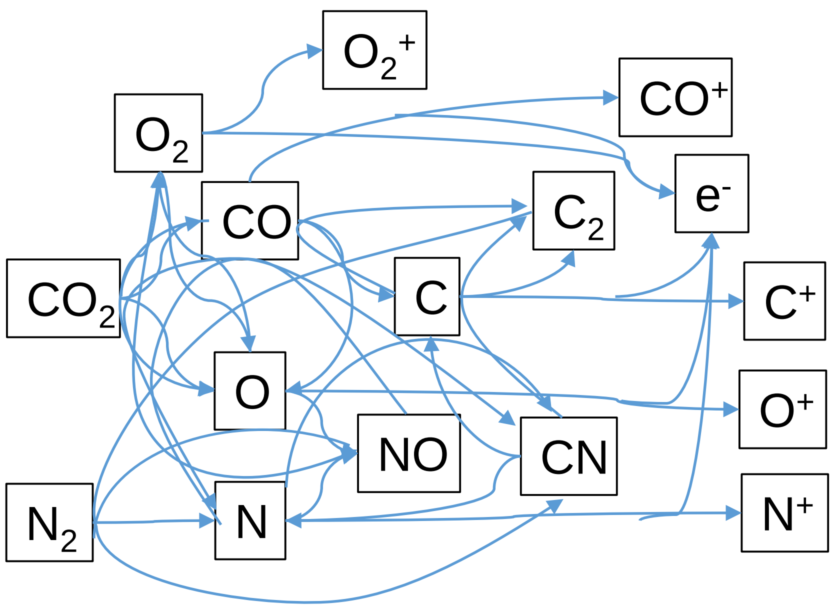
Outline

- Motivation
- Features of CO Shocks
- Temperature vs Position from shock
  - Determination of CO Dissociation Rate
- C_2 Swan Band Radiation
  - Influence of C_2 reaction rates
- CO VUV and IR Radiation
- Summary

Motivation

- Spacecraft to Mars typically enter the atmosphere at 5-7 km/s
- Mars Atmosphere is 96% CO2, 1.9% N_2, 1.9% Ar
- Radiative and Convective Heating Depend Upon Reactions in Shock Layer
- Most rates in use based upon old (60s-70s) shock tube studies
- Recent updates (i.e. Johnston 2014) based on data in mixture

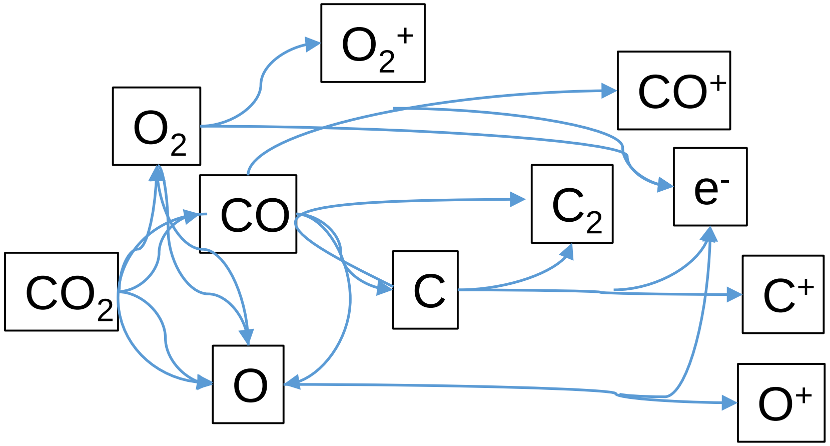


Simplified Chemistries

- Extensive validation work has been performed on full chemistry set
- Model revisions* have also been based on measurements of full chemistry
- Studies of simplified chemistry sets may result in better informed modeling choices

- ~~Mars~~

  CO_2



Eliminate N_2

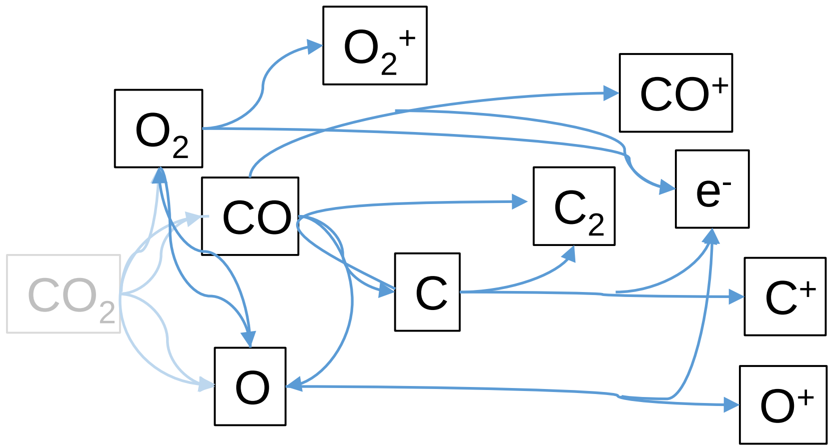
* Johnston, C. O., and Brandis, A. M., "Modeling of nonequilibrium CO Fourth-Positive and CN Violet emission in CO2–N2 gases," *Journal of Quantitative Spectroscopy and Radiative Transfer*, Vol. 149, 2014, pp. 303-317

Simplified Chemistries

- Substituting CO for CO_2 minimizes the influence of CO_2 reactivity on results

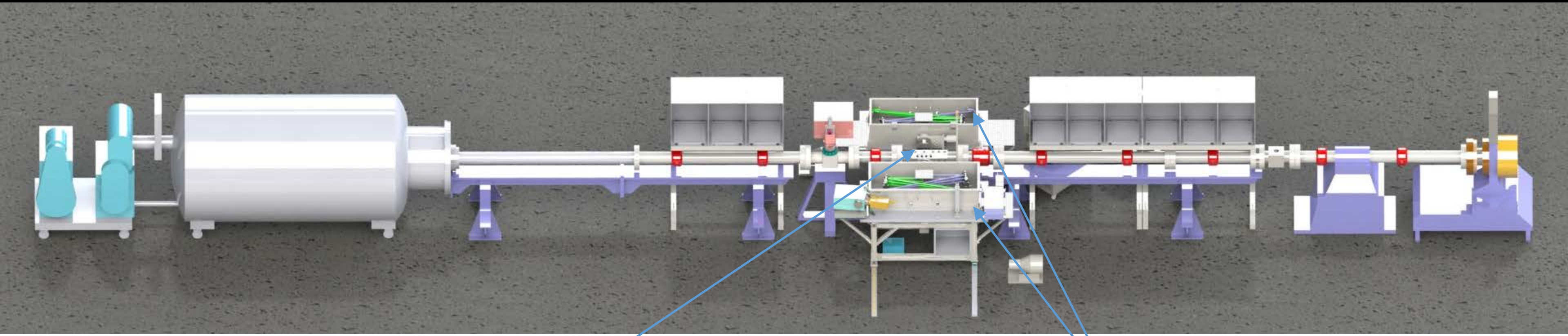
- ~~Mars~~

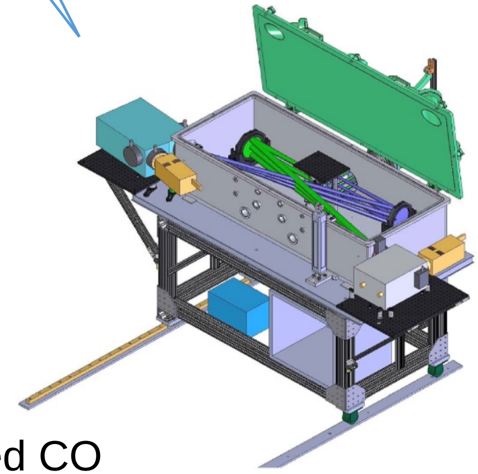
  CO



Start with CO

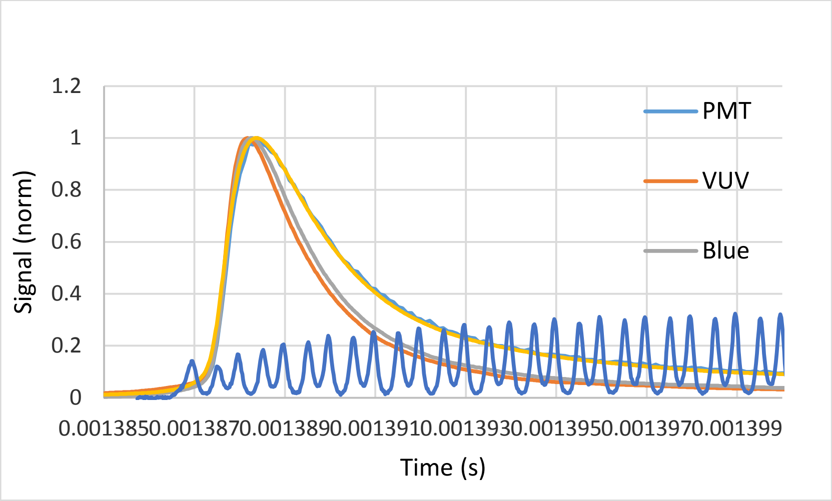
Electric Arc Shock Tube (EAST)

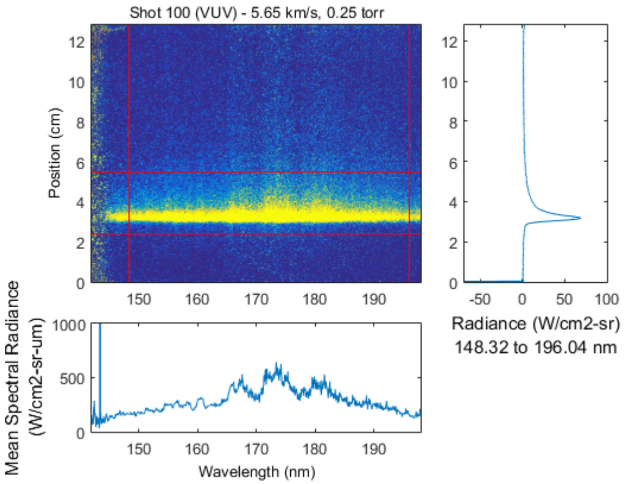




- Experiments Conducted in EAST Facility to study shock-heated CO
- 4" Aluminum Tube, 7.9 m from primary diaphragm to test section
- Initial condition of 0.1 and 0.25 Torr CO, shock velocities from 3-9 km/s
- Diagnostics
  - Tunable Diode Laser Spectroscopy (Mid-Wave Infrared)
  - Imaging Emission Spectroscopy (4 spectrometers covering VUV through mid-Infrared)

Analysis of CO Data



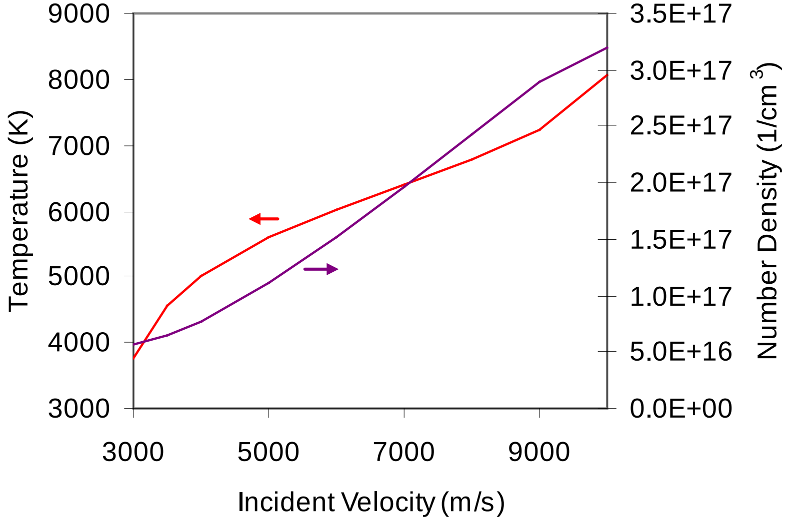


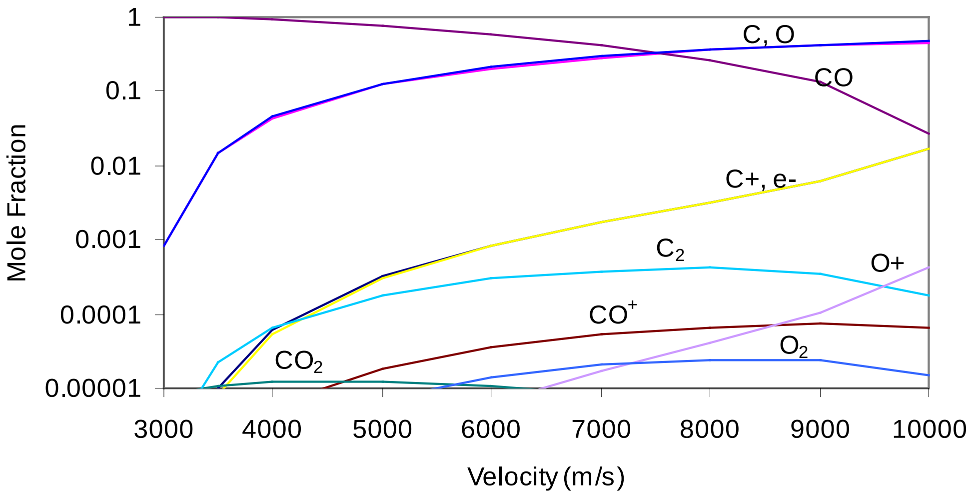
- TDLAS data*:
  - Measures one molecular line vs. time
  - Obtain translational temperature, CO number density
- Emission spectroscopy
  - Measure radiance versus position and wavelength over broad spectral range:
    - VUV (145-195nm, CO A-X transition), UV (190-330 nm), Visible (480-890 nm, C_2 Swan Bands), mid-Infrared (4000-5500 nm, CO vibrational)
  - Radiant Power depends on temperature, (excited) species number densities

* Macdonald, et al., 2:30 pm Thur.

Characteristics of CO Shocks

Equilibrium CO Shocks





- Temperatures from 4000-8000K
- Major species CO, C and O
- C_2 at 10-200 ppm, starting at 3.5 km/s
- C^+ ion at 100 ppm at 4 km/s, 0.1% at 6 km/s, 1% at 10 km/s
- CO_2, CO^+, O^+ and O_2 are more minor species
- Mole fractions, temperatures not strong function of pressure from 0.1-0.25 Torr

Primary Reaction Set

- CO Dissociation

$$CO + M \rightarrow C + O + M$$

- CO Exchange

$$CO + O \rightarrow C + O_2$$

$$CO + C \rightarrow C_2 + O$$

- O_2/C_2 Dissociation

$$O_2 + M \rightarrow O + O + M$$

$$C_2 + M \rightarrow C + C + M$$

- Ionization kicks in at higher velocity
- 5 sp, 5 rxn

Space of Valid Solutions

- 1D Shock must satisfy conservation equations:

Atom conservation: $$n_{CO} + n_C + 2n_{C_2} = \frac{\rho_0 v_0}{M_{CO} v}$$

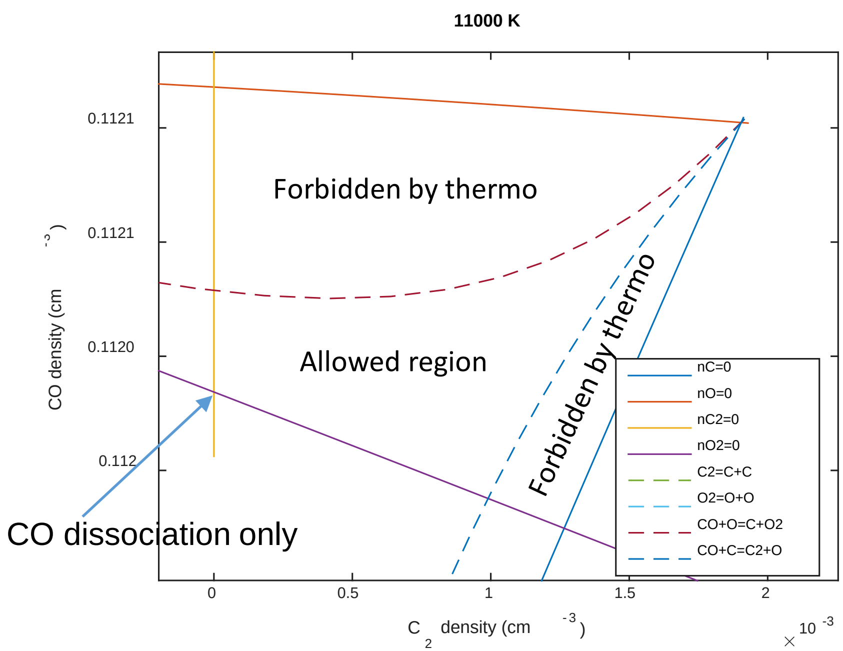
Stoichiometry: $$n_C + 2n_{C_2} = n_O + 2n_{O_2}$$

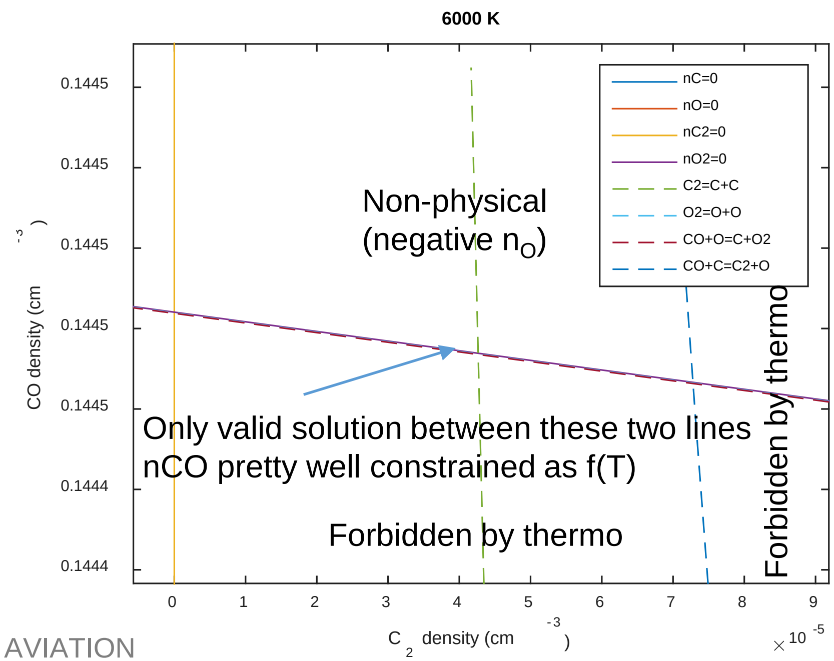
(Atom + Stoichiometry conservation enforces Conservation of Mass)

Momentum: $$\sum n_i (RT + M_i v^2) = p_0 + \rho_0 {v_0}^2$$

Energy: $$\sum n_i \left(h_i(T) + M_i \left(\tfrac{1}{2} v^2 - h_0 - \tfrac{1}{2} {v_0}^2 \right) \right) = 0$$

- 4 equations, 7 unknowns (v, T, 5 n_i's) – 3 DOF

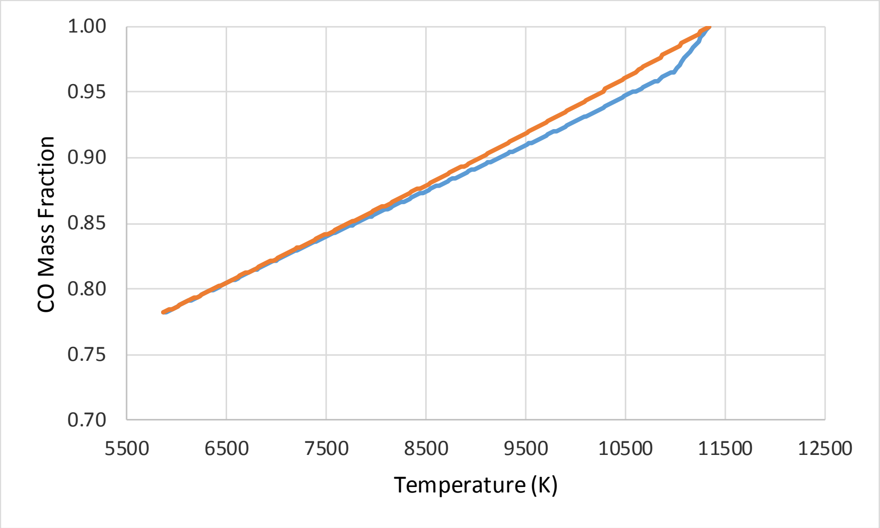


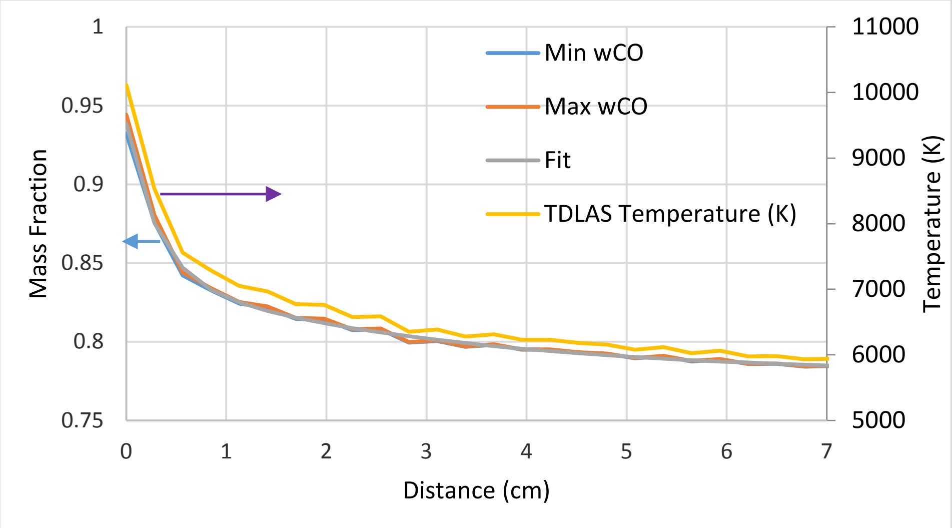


Reaction Rate Analysis

CO Reaction Rates

- Reaction Rate may be inferred from T vs. x:





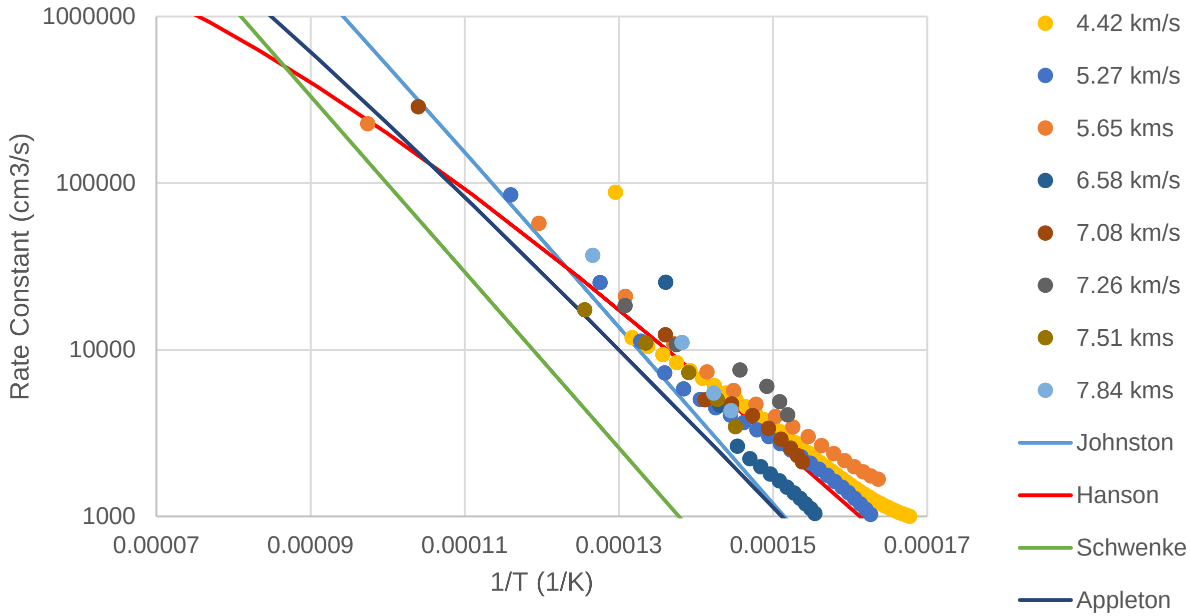
- $\omega = f(T)$
- $\frac{d\omega_{CO}}{dx} = \frac{M_{CO} r_{CO}}{\rho_0 v_0}$
- $\frac{r_{CO}}{n_{CO} n_M} \approx k_{diss}$

Mass fraction is a (narrowly bounded) function of Temperature, per conservation equations

Derivative of mass fraction proportional to reaction rate

Reaction rate dominated by CO dissociation by heavy particle collision

CO Dissociation Rate



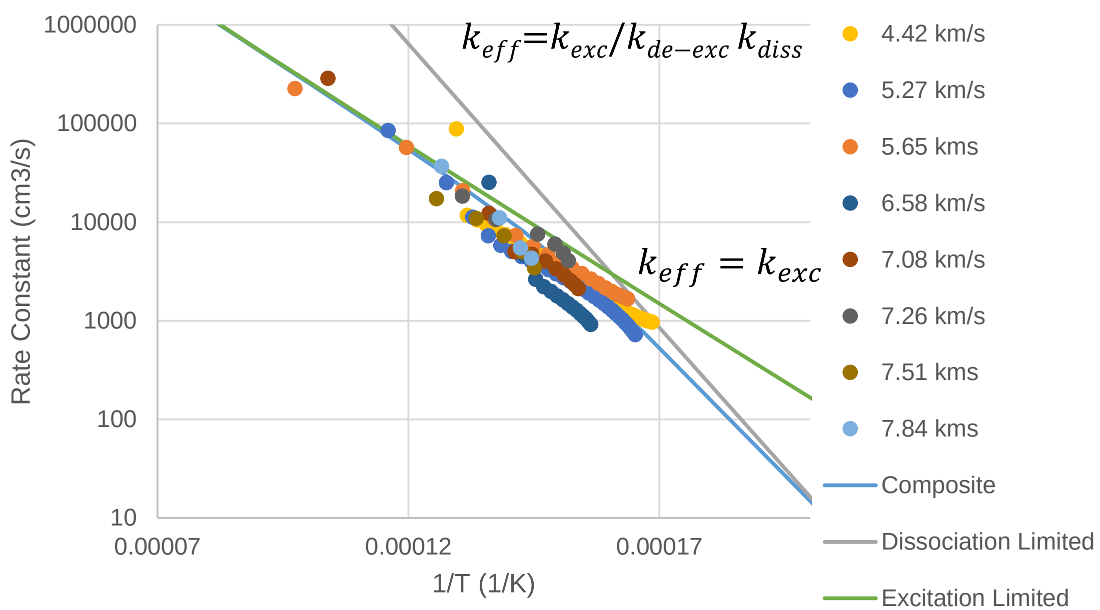
- Reaction rate measured over many tests cluster around the rate curve reported by Hanson
  - Note that reaction at high Temperature is faster than the time scale of TDLAS : fit is less reliable/more scattered
  - Rate has large Arrhenius ($T^{-5.5}$) coefficient : suggests compound mechanism

Compound Mechanism for CO dissociation

$$CO(X) + M \leftrightarrow CO^* + M$$
$$CO^* + M \rightarrow C + O + M$$

$$k_{eff} = \frac{k_{diss} k_{exc}}{k_{de-exc} + k_{diss}}$$

$$= \frac{k_{diss} k_{exc}}{\left(\frac{n_{CO^*}}{n_{CO(X)}}\right)_{eq} k_{exc} + k_{diss}}$$

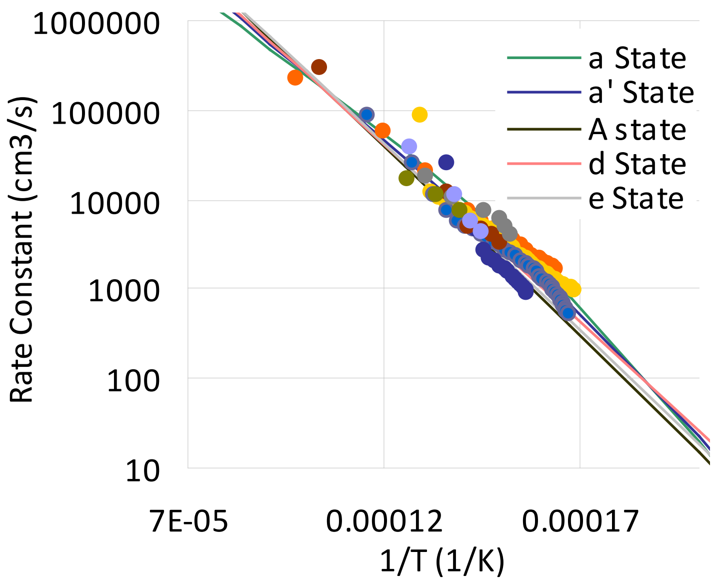


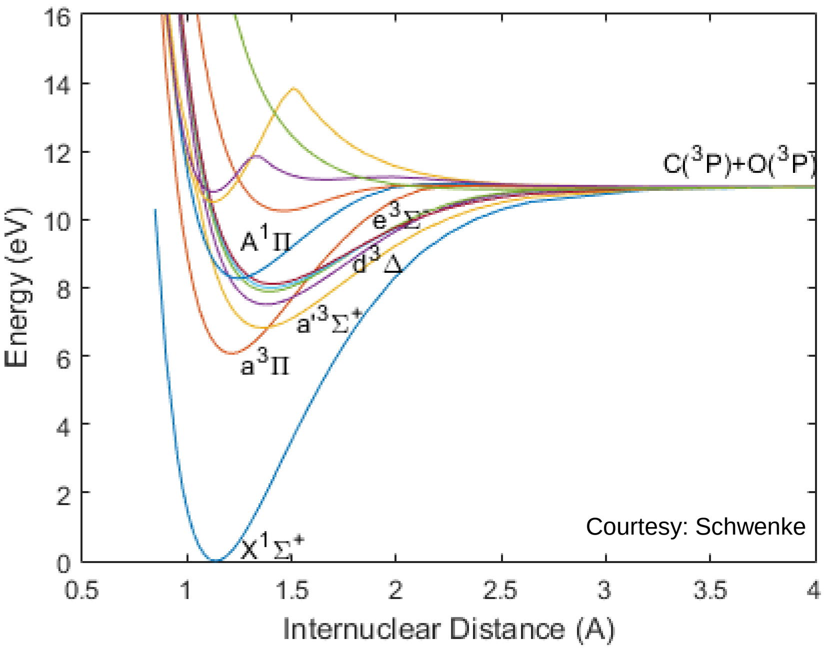
- Compound mechanism involves excitation to an excited state that then dissociates
  - At high temperature, excitation is rate limiting step, excited state is populated *below* equilibrium
  - At low temperature, dissociation is rate limiting, excited state is equilibrated
- What is the excited state?
  - Some literature has suggested M not inert and could be intermediate such as CO_2, C_2, O_2
  - An obvious choice may be the CO metastable, CO(a)

Intermediate States

- Evaluation of rate using a, a', A, d, e states of CO all can plausibly explain data

$$k_{exc} = A_{exc} T^{1/2} \exp\left(-\frac{E^*}{T}\right) \qquad k_{diss} = A_{diss} T^{1/2} \exp\left(-\frac{E - E^*}{T}\right)$$



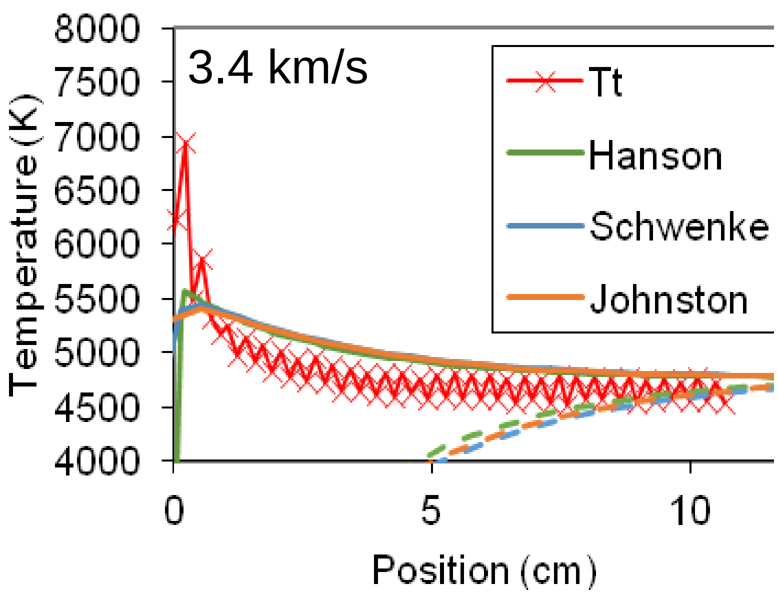


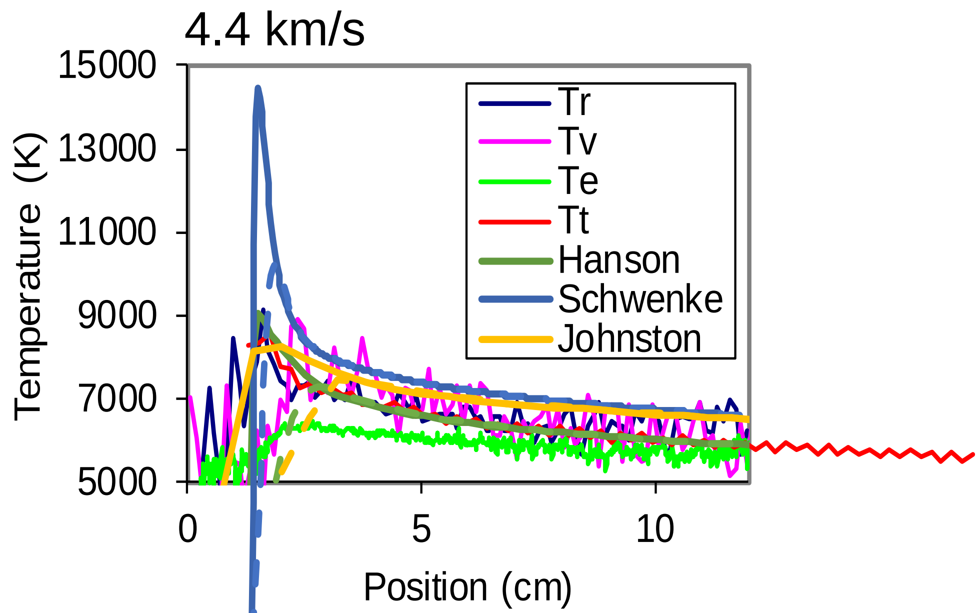
- Dissociation rates derived from a, a' are within an order of magnitude of estimates from Park
- De-excitation rates are somewhat lower than rates measured at 300K
- Likely a combination of the above

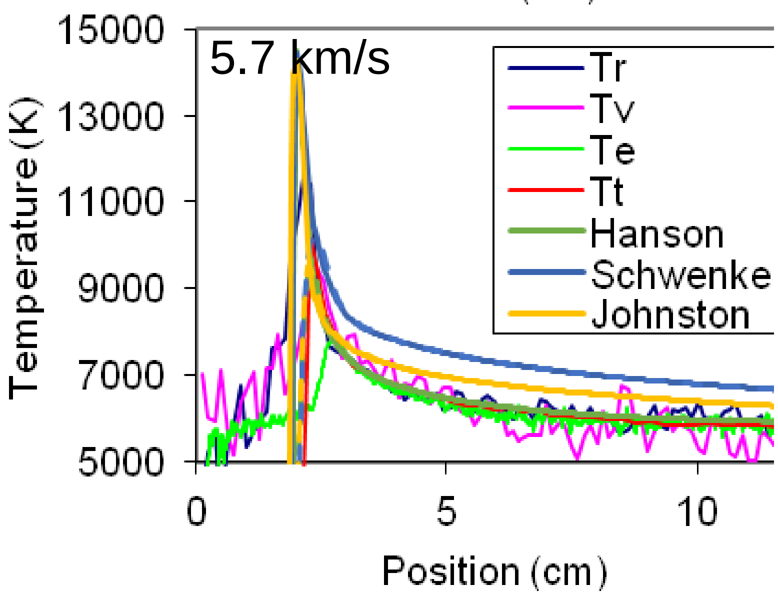
Data Comparisons

Temperature

Temperature Predictions 3-6 km/s



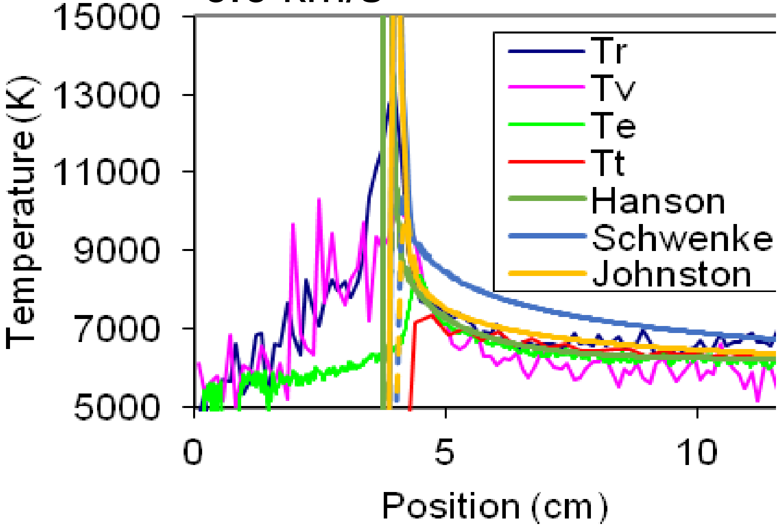




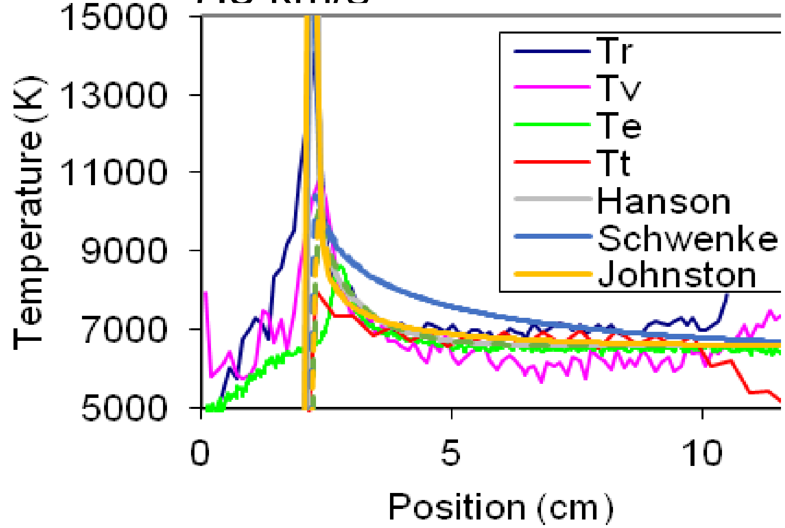
- At 3.4 km/s – No dissociation, trend driven by T-Tv relaxation
- At 4.4 km/s and 5.7 km/s
  - Schwenke and Johnston Rate too slow
  - Hanson rate matches data
  - T_v trend looks ok

Temperature Predictions 6-9 km/s

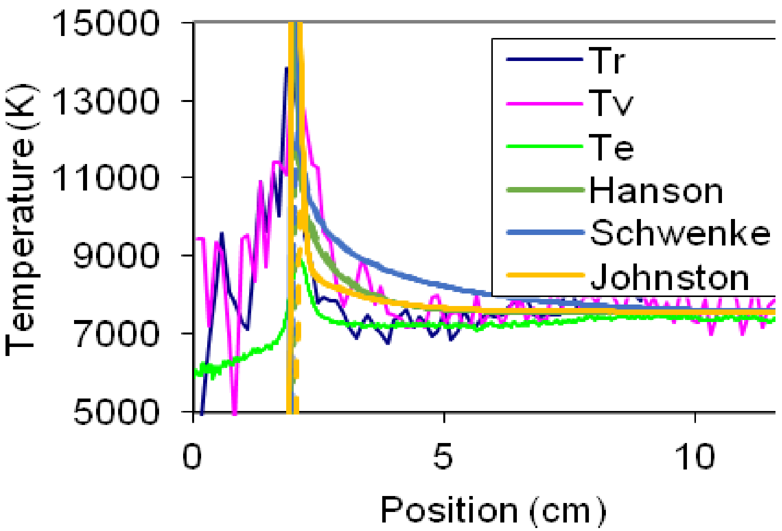
6.6 km/s



7.5 km/s



8.6 km/s



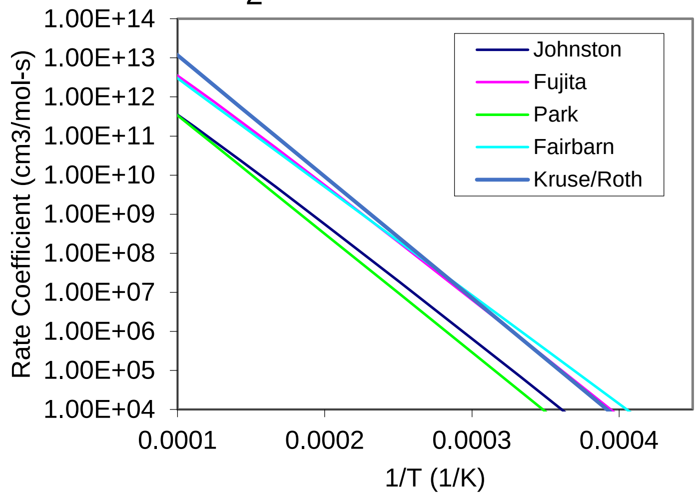
- Schwenke Rate too slow
- At 6.6-7.5 km/s
  - Johnston and Hanson rates similarly match data
- At 8.6 km/s
  - Data relaxes faster than any rate predicts

C_2 Thermochemistry

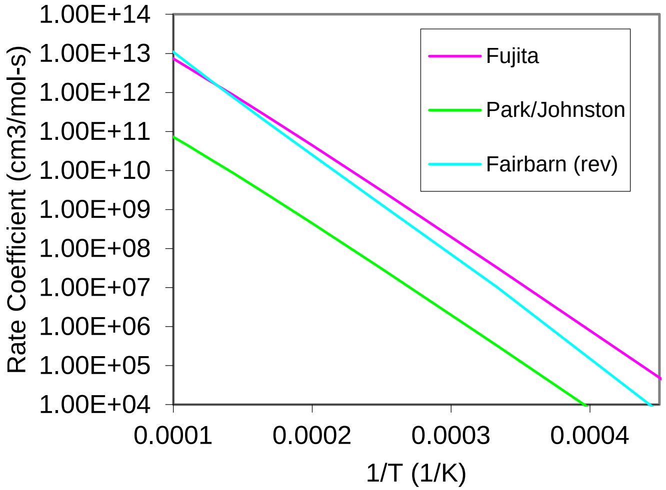
C_2 Rates

- There are two rates that matter for C_2 radiation : Dissociation and Exchange

$C_2 + M \rightarrow C + C + M$



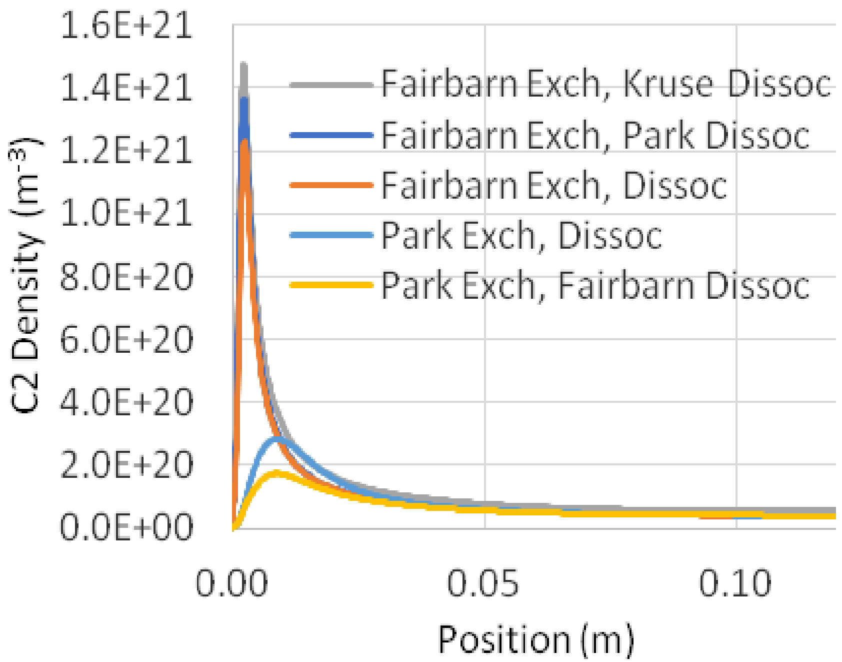
$CO + C \rightarrow C_2 + O$

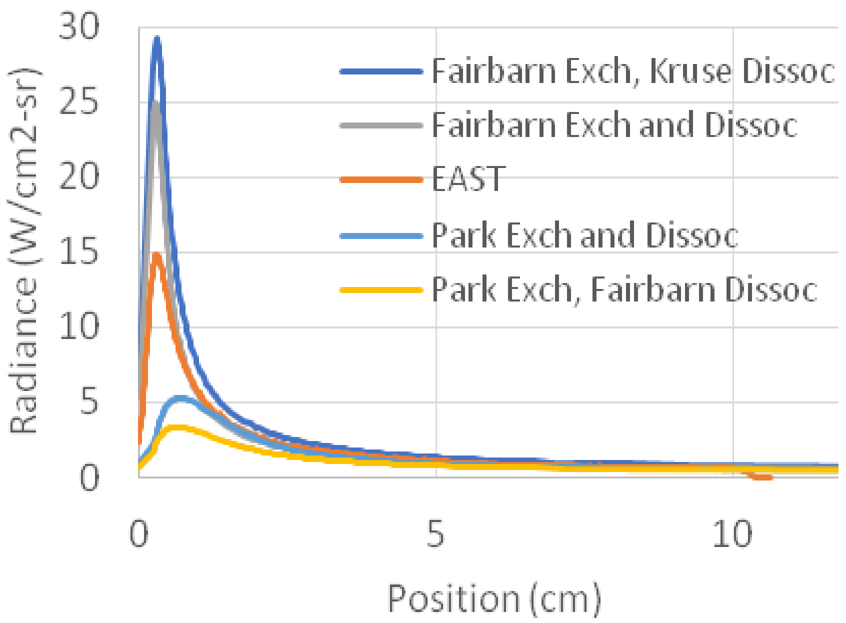


- There is about 1 OOM difference between Park and literature for dissociation rate
- Up to 2 OOM difference between Park and literature for exchange rate

C_2 Rate Sensitivity

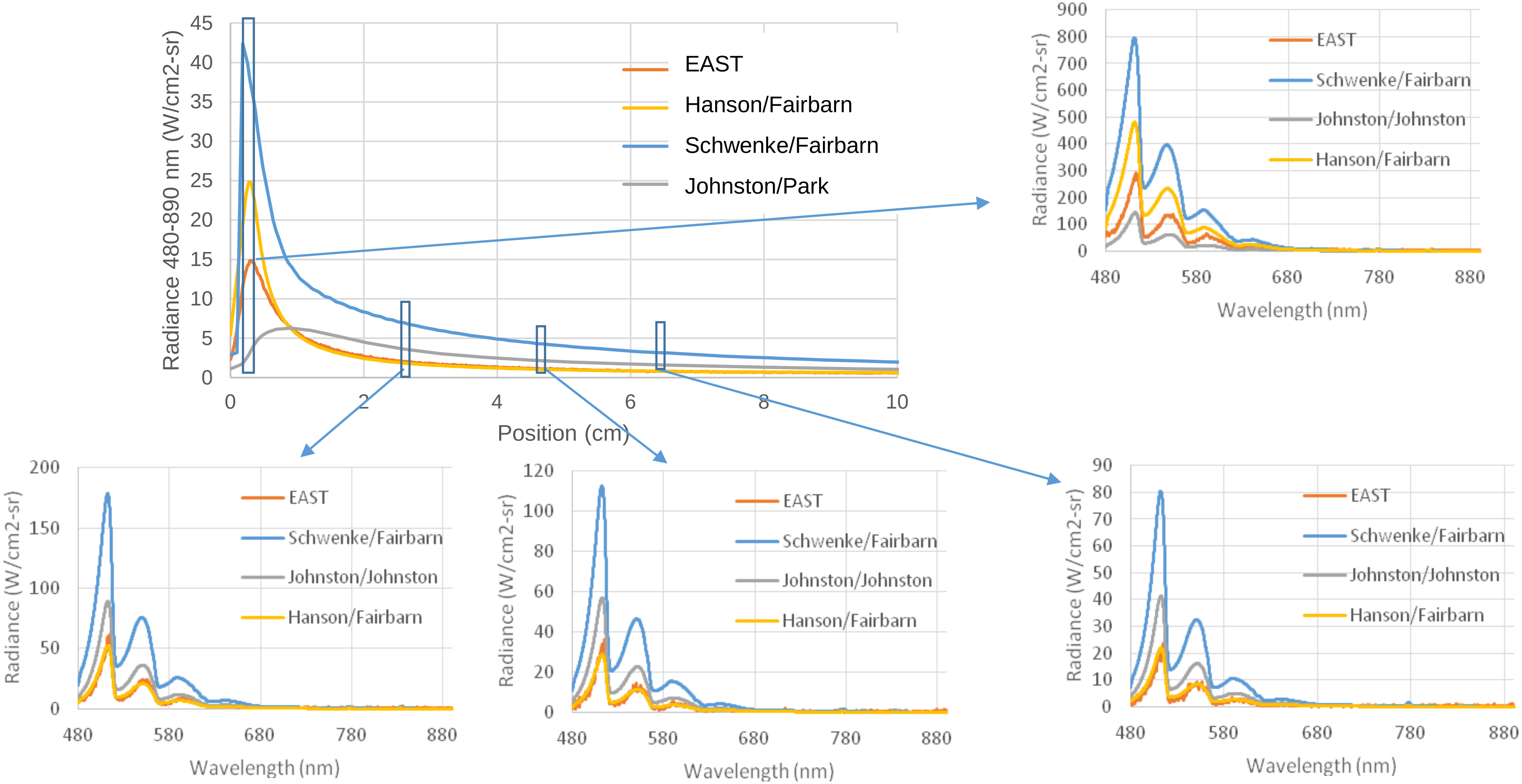
5.6 km/s





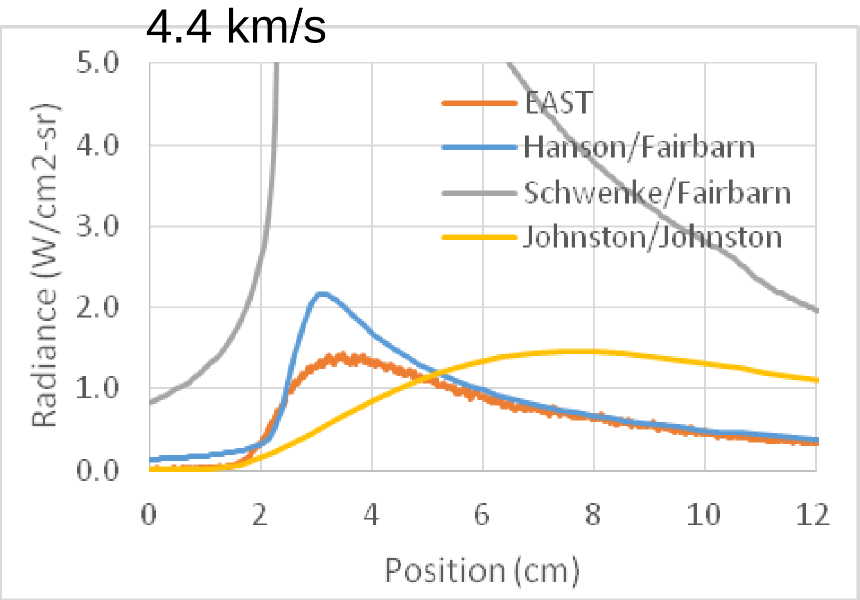
- Radiation shows significant sensitivity to exchange
  - Park's exchange puts peak at wrong location, makes it wider
- Result is less sensitive to dissociation rate
  - Discrepancy at the peak may be due to Boltzmann model
  - If not, rate would need to be even faster
- Fairbarn's rates appear more consistent with data

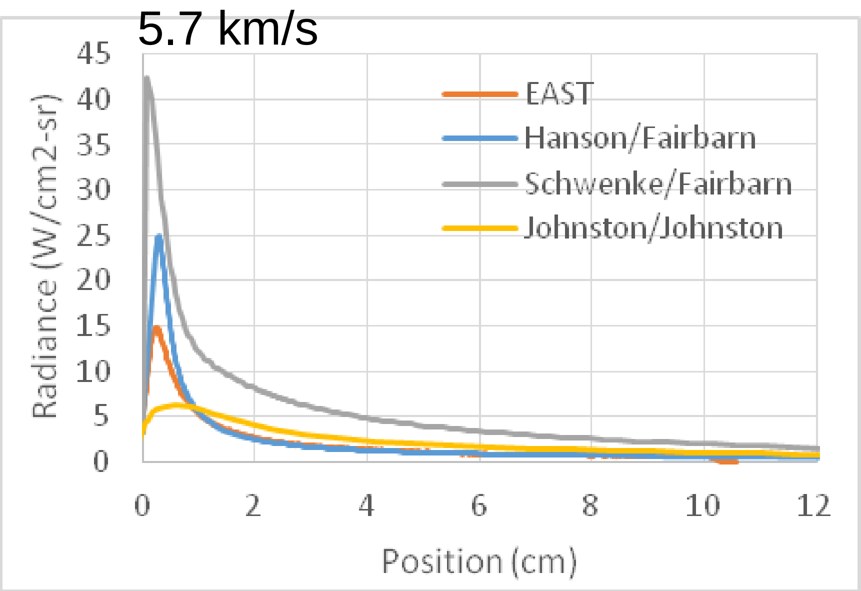
C_2 Radiance Predictions

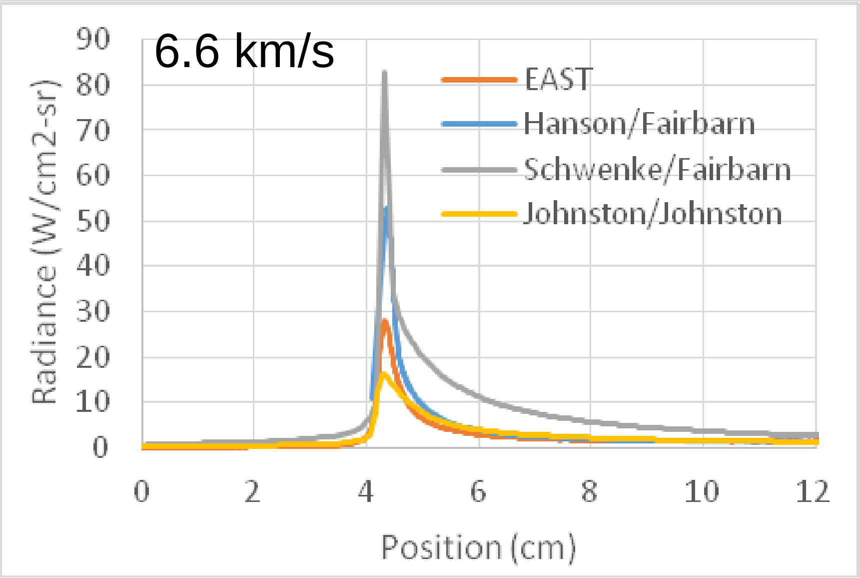


- Except for peak, agreement is very good
- C_2 reaction rates from Fairbarn agree better than those of Park
- Further improvement would be construction of a non-Boltzmann model

C$_2$ Radiance – 4-7 km/s

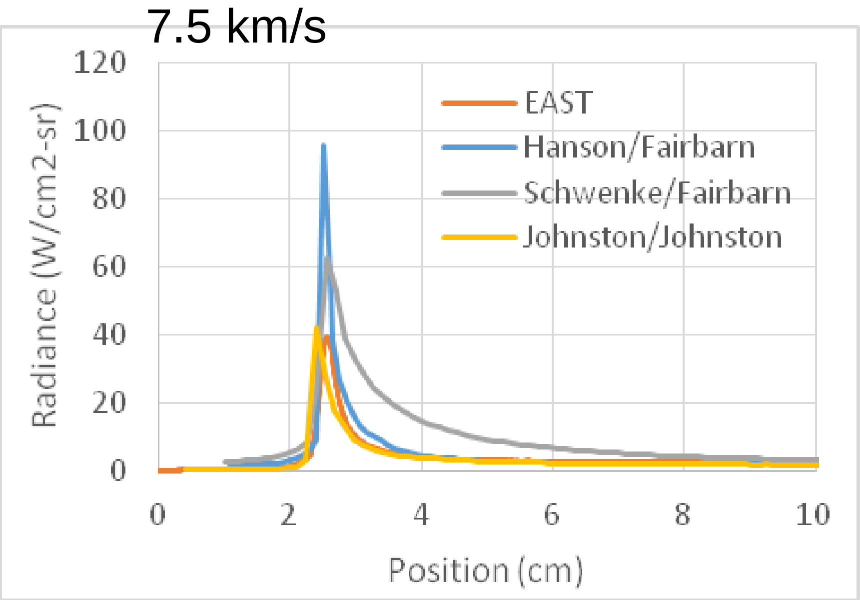


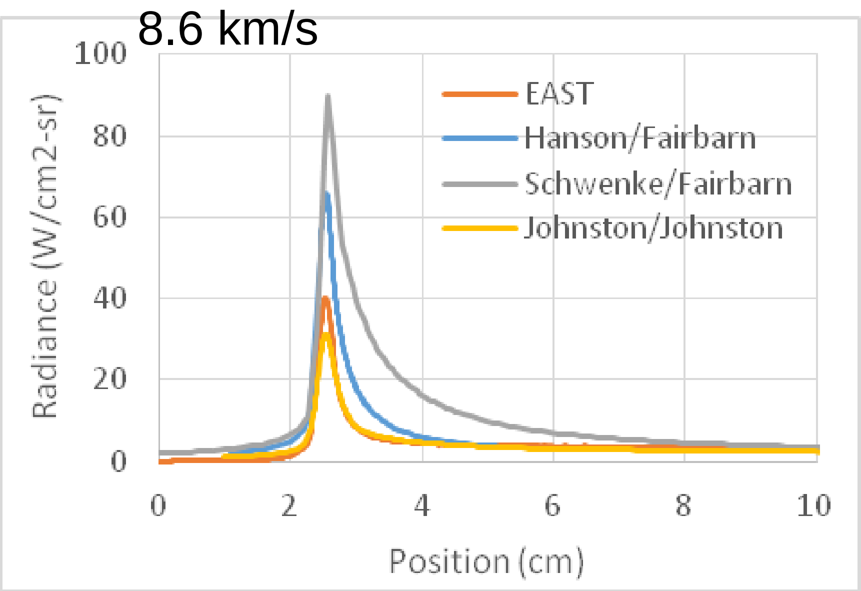


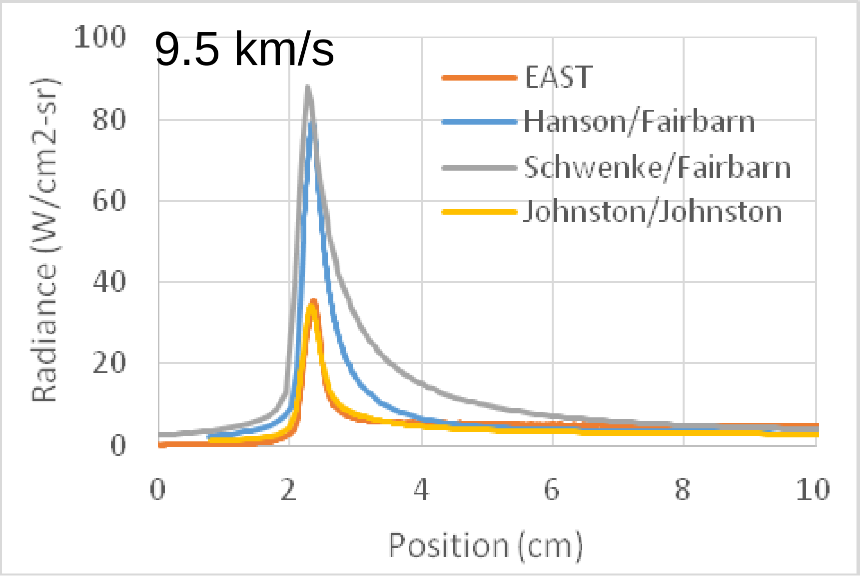


- 4.4 and 5.7 km/s
  - Schwenke overpredicts (T too high)
  - Hanson+Fairbarn overpredicts peak, good elsewhere
  - Johnston (Park) gets trend wrong
- 6.6 km/s
  - Similar observations, Johnston showing better agreement

C_2 Radiance – 7-9 km/s





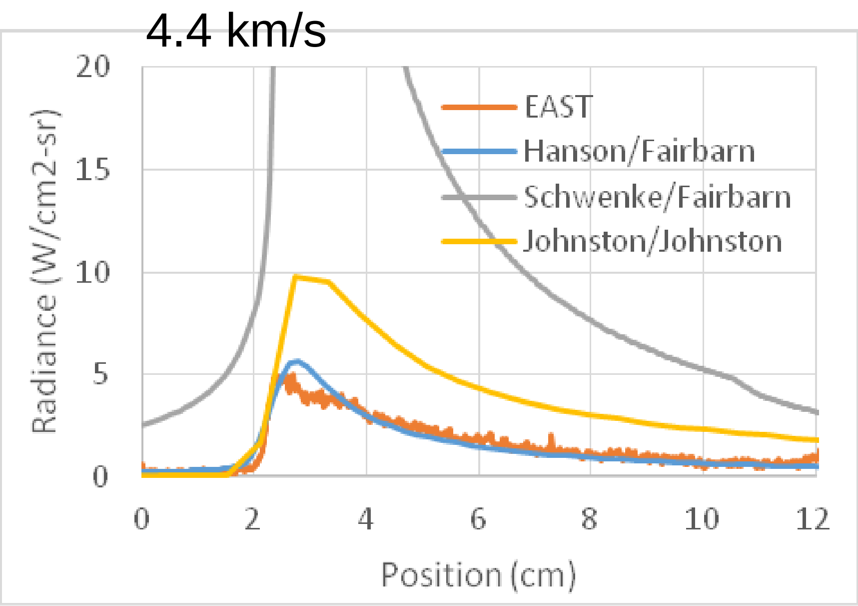


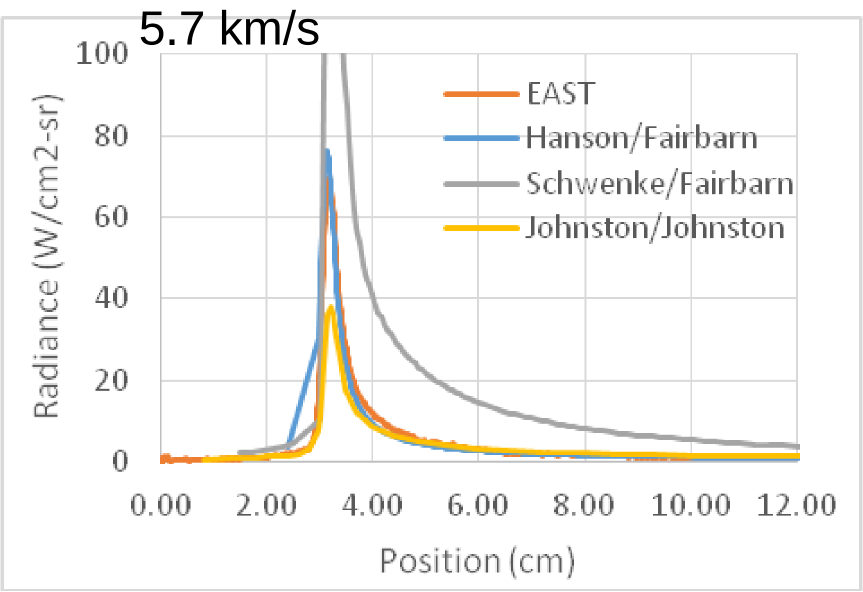
- Johnston agrees well with data at these velocities
  - Boltzmann model for C_2
- Hanson/Fairbarn relaxation trend is no longer matched at 8.6 and 9.5 km/s

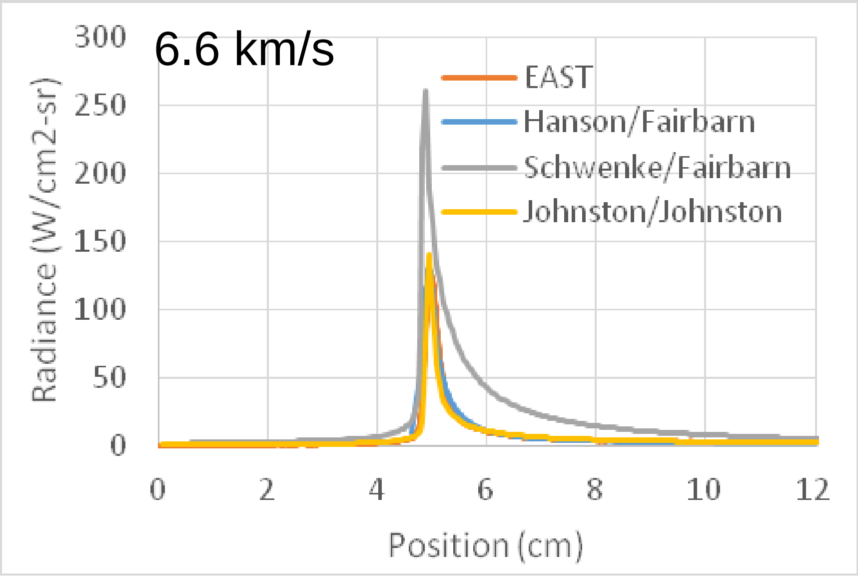
CO Radiation Analysis

VUV and mid-IR

CO VUV Radiance – 4-7 km/s

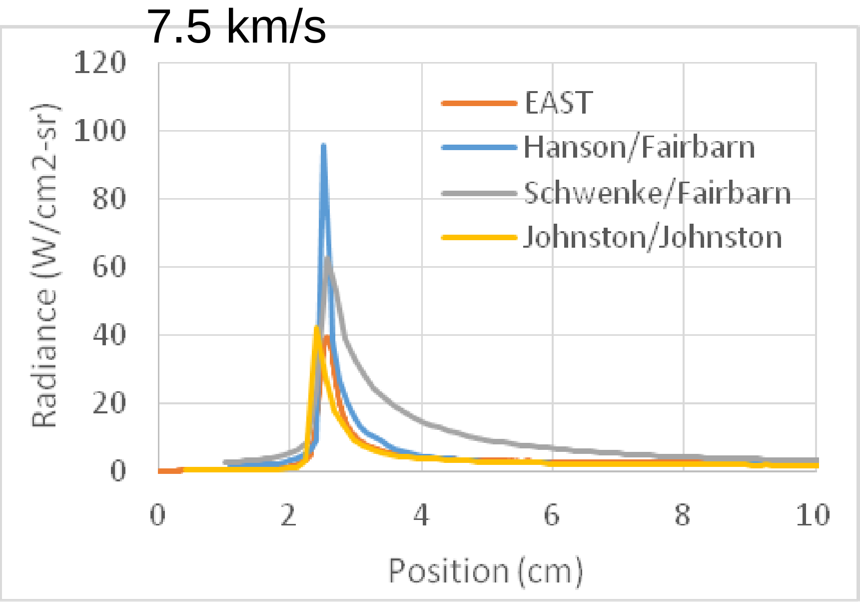


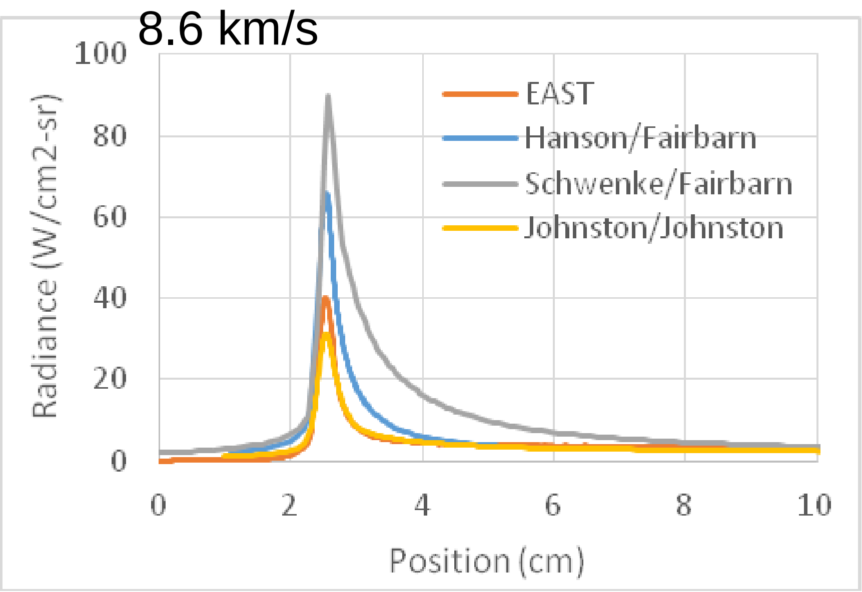


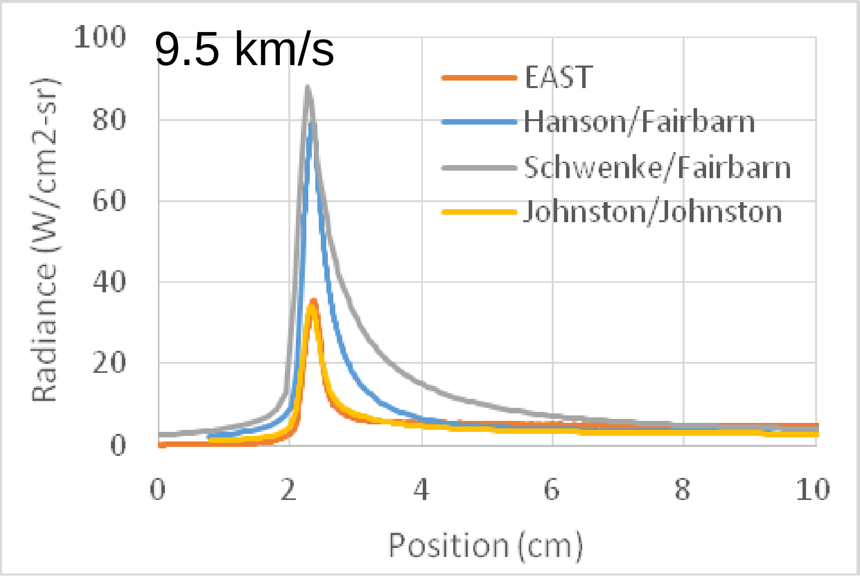


- 4.4 and 5.7 km/s
  - Schwenke overpredicts (T too high)
  - Hanson+Fairbarn matches data
  - Johnston over/under
- 6.6 km/s
  - Hanson and Johnston same result

CO VUV Radiance – 7-9 km/s

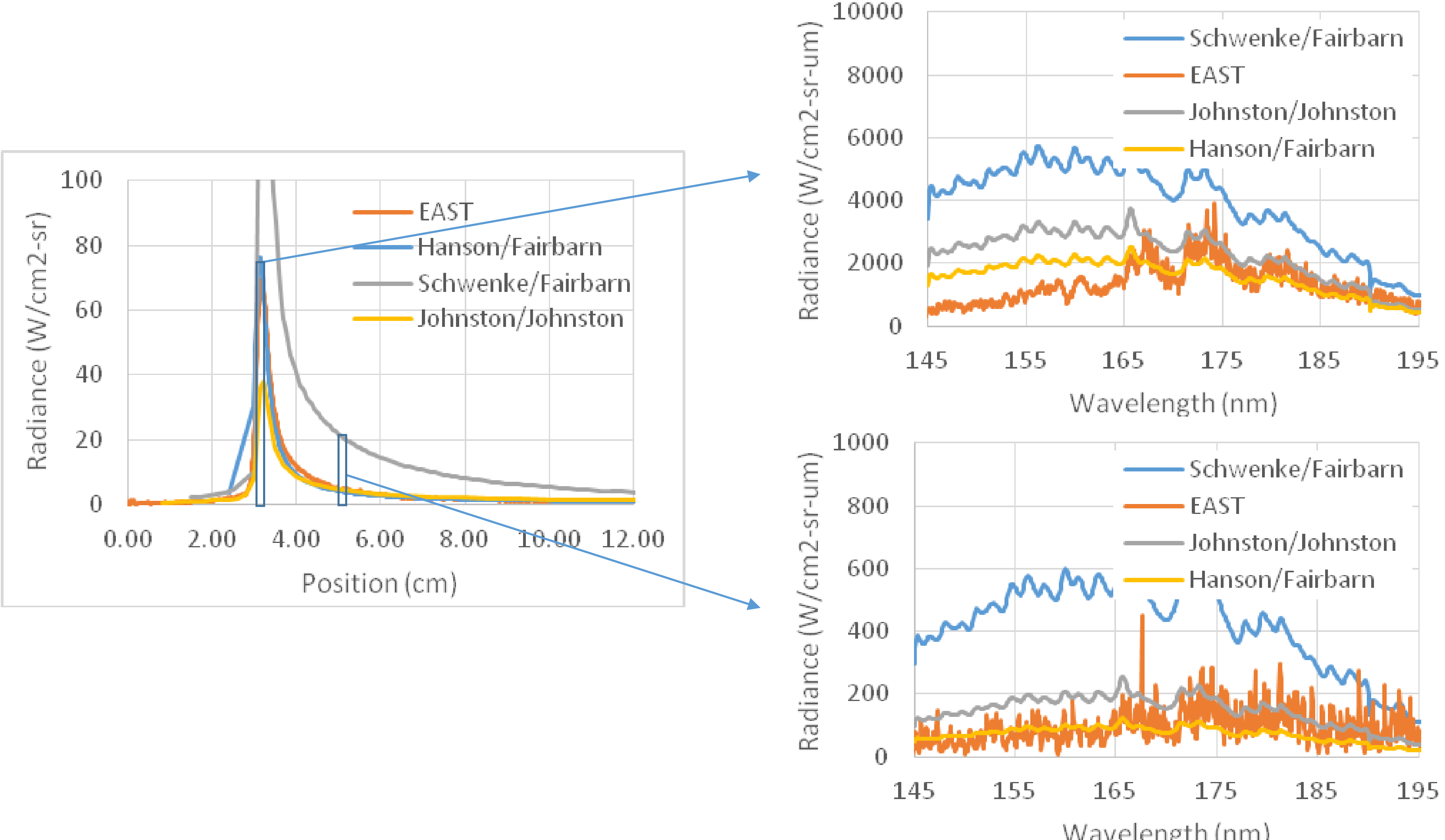






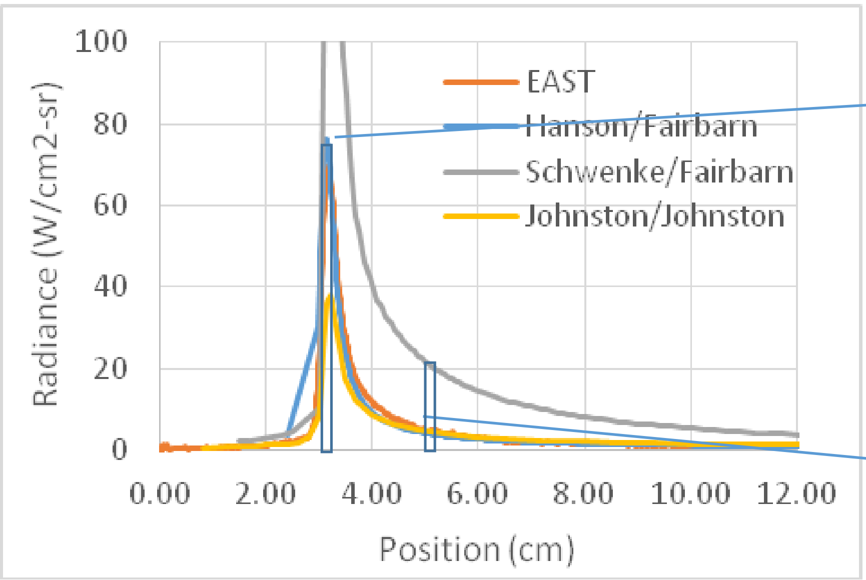
- Johnston agrees well with data at these velocities
- Hanson overprediction becomes worse as velocity increases

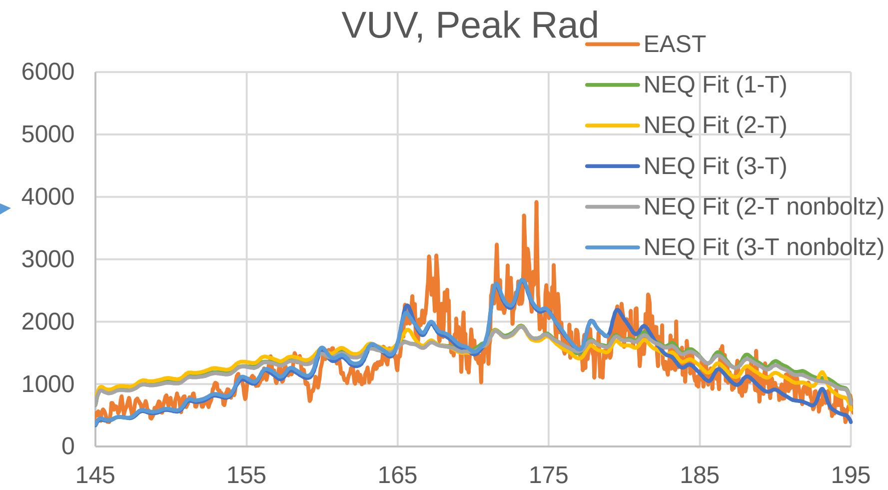
VUV Spectral Comparison (5.7 km/s)

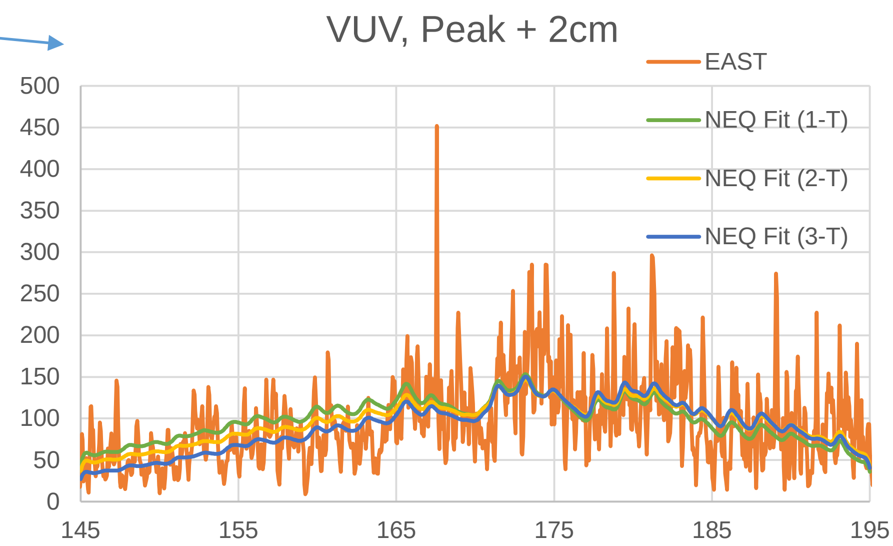


- VUV Prediction does not simultaneously match low and high wavelength region

Fitting of CO VUV Bands

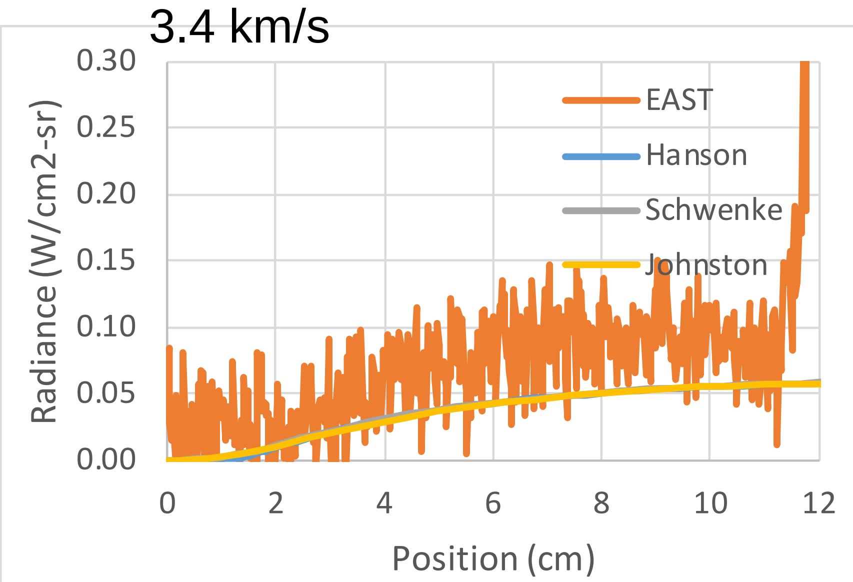


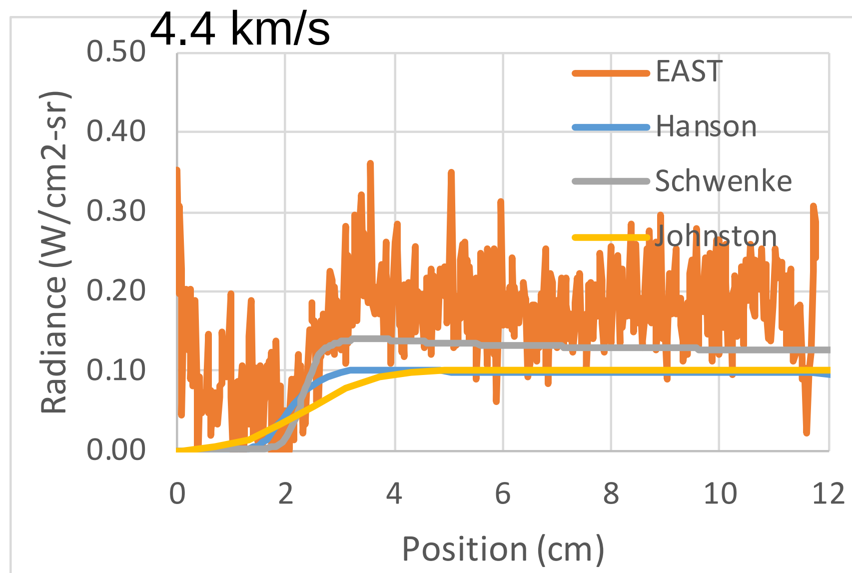


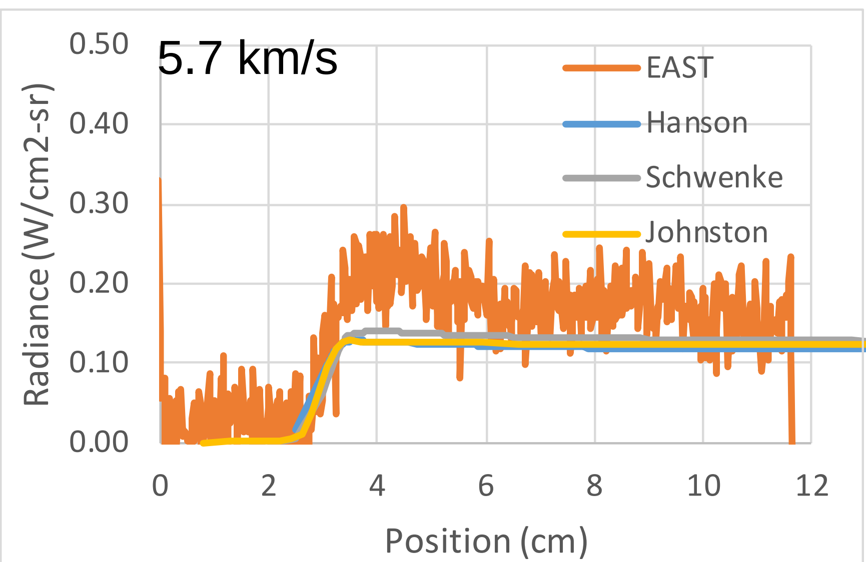


- Fits of the VUV spectrum:
  - Requires 3 Temperatures in Non-equilibrium
  - Result in elevated CO density (compared to what conservation allows)

CO MWIR Radiance – 3-6 km/s

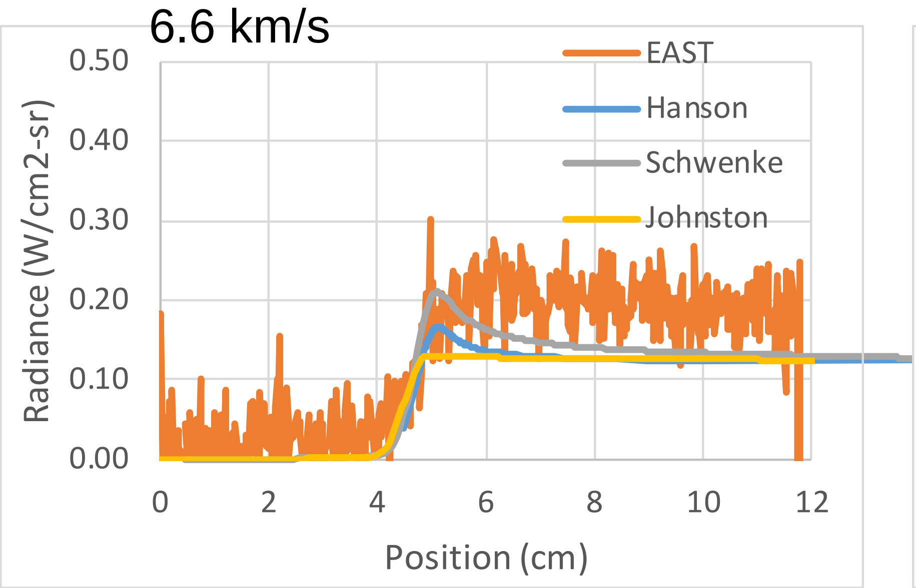


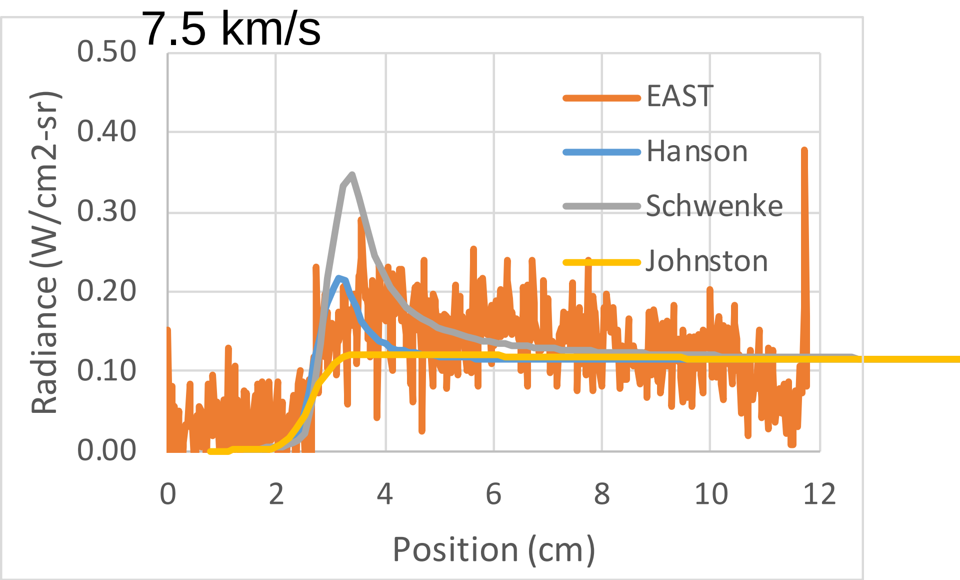


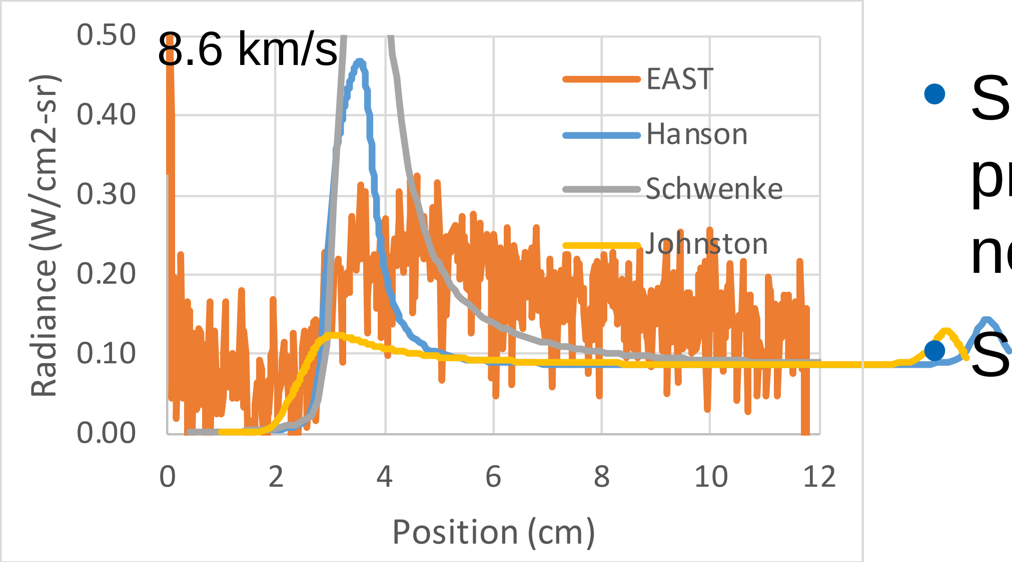


- CO IR radiance not very sensitive to reaction rates in this velocity regime
- Always underpredicted

CO MWIR Radiance – 6-9 km/s

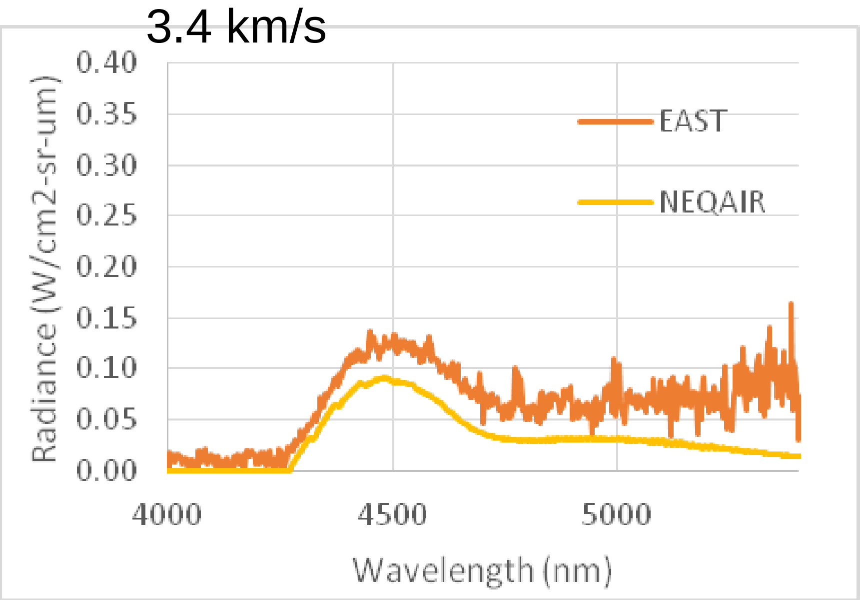


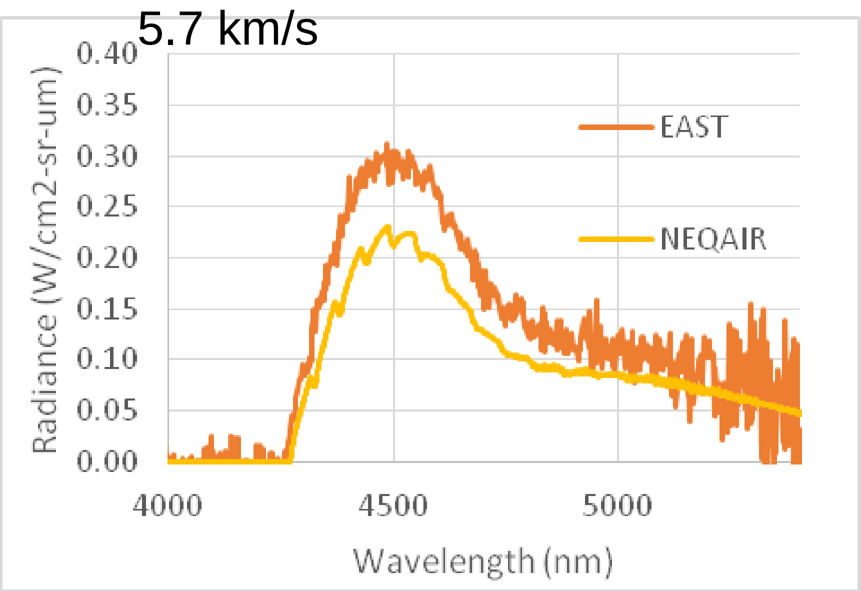


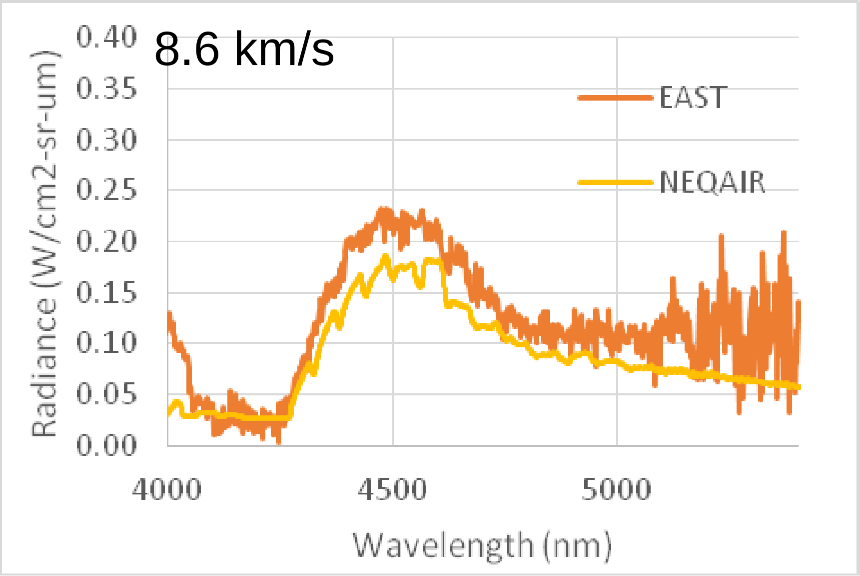


- Slower reaction rates predict overshoots that are not observed in experiment
- Still underpredicted

IR Underprediction

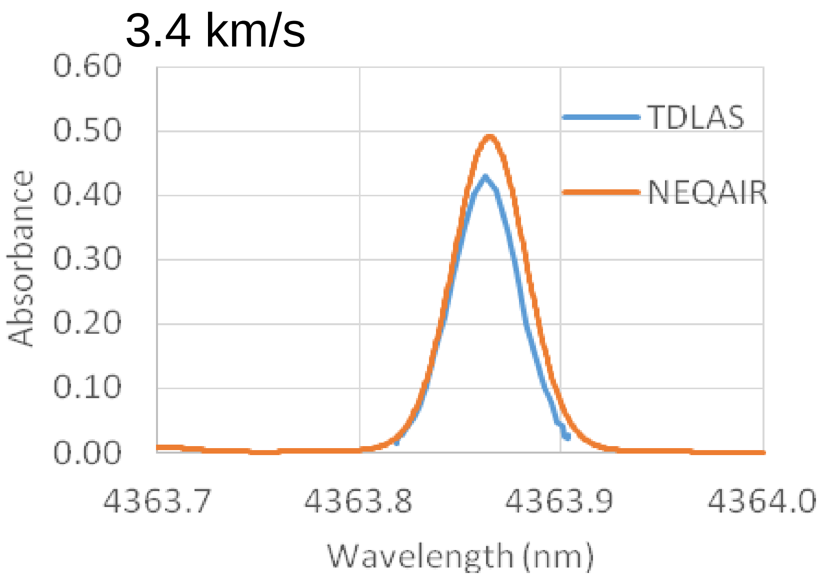


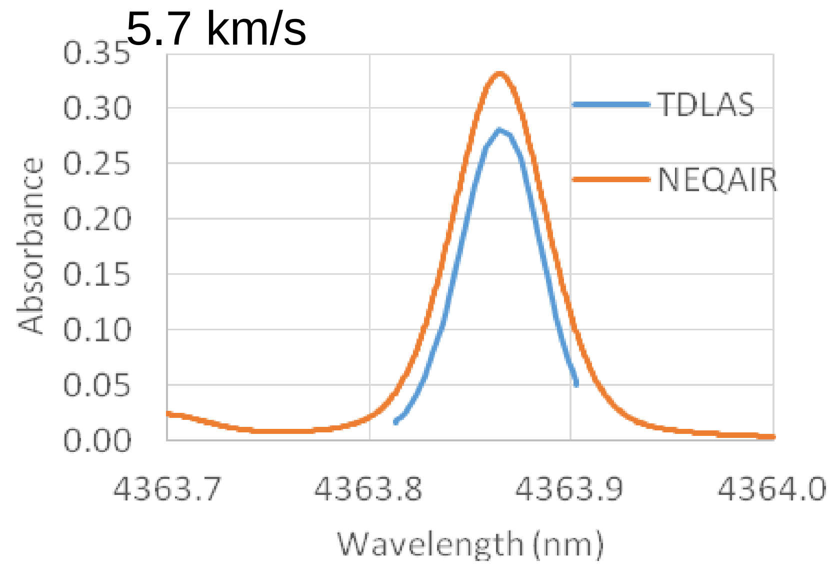


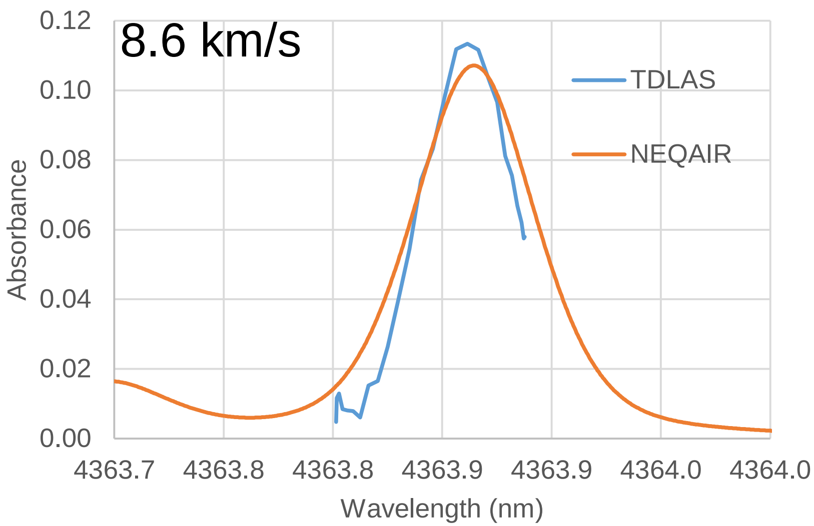


- Underprediction nearly constant with wavelength
- Correction required would be ~1.3x

Absorbance is Overpredicted

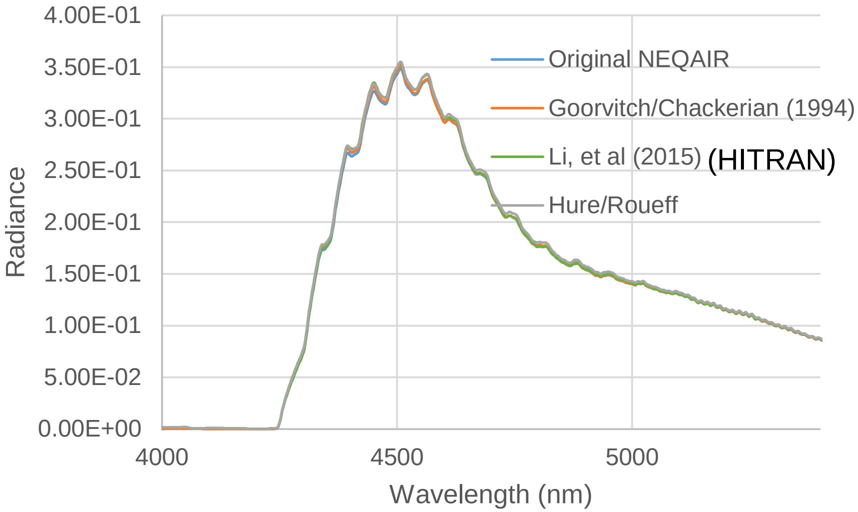


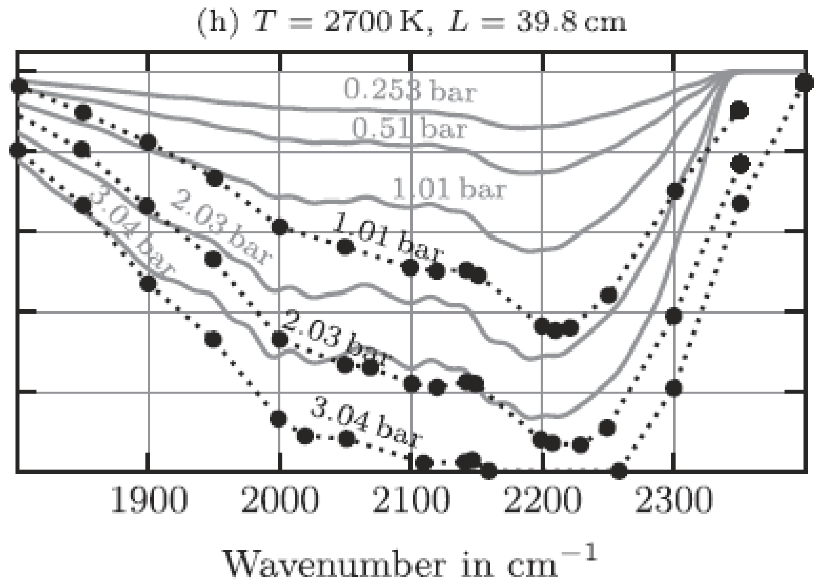




- Absorbance overpredicted by ~25%
  - Opposite to trend in Emission, cannot be error in linestrength or CO number density
- At 8.6 km/s, temperature prediction does not match

CO MWIR Predictions





- Different linelists have been tested in NEQAIR and all produce substantially the same result
- Alberti, et al. (2017) showed that HITRAN underpredicts experimental data above ~1200K at pressures up to 3 bar
  - Consistent with emission trend
- To underpredict the band but overpredict a line indicates there are additional contributors to the band
  - Additional excited states of CO not accounted for?
  - May have implications for CO partition function and thermodynamics

Conclusions

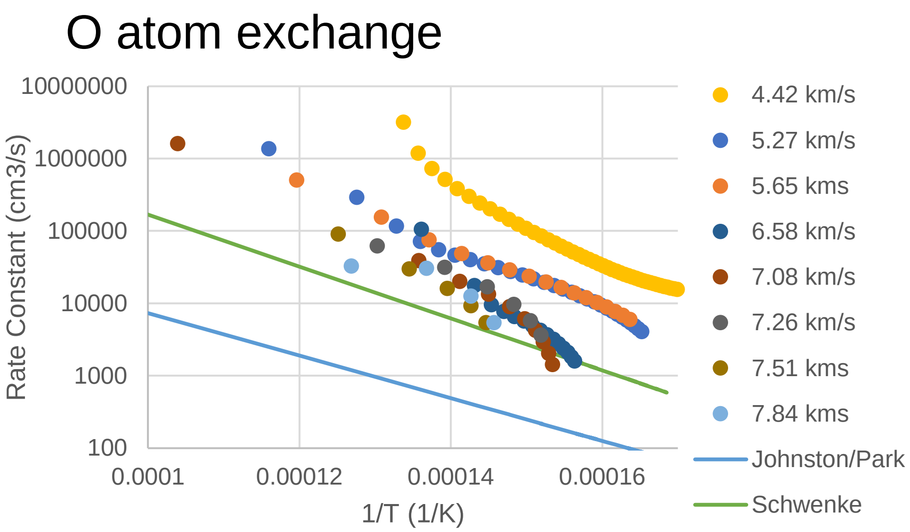
- Analysis of Temperature Relaxation Finds CO dissociation rate in agreement with that of Hanson
  - It is suggested this is a compound reaction that proceeds through CO metastable levels
  - Excited states must be considered in QCT calculations!
    - CO Metastable is at about half of the dissociation energy
- Emission trends are consistent with CO rate of Hanson below ~7 km/s, and Johnston above 7 km/s
- C_2 Emission more consistent with rates of Fairbarn than Park

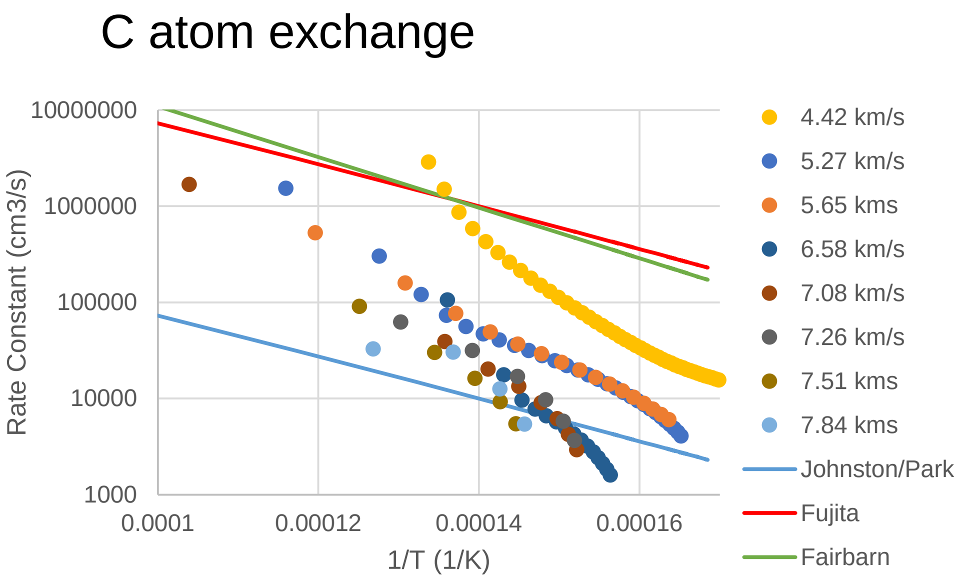
Open Questions

- Deviation of Data at High Velocity
  - Role of electron impact dissociation of CO?
  - Need for merged Johnston/Hanson reaction rate?
- Overprediction of C_2 Swan band at shock front
  - Non-Boltzmann modeling of C_2
- Inconsistencies in CO radiance
  - Absorption and emission disagree with predictions in opposite direction
    - HITRAN database shown not to match high temperature CO data
    - Possible errors in CO Partition function and energy levels?
  - Predicted shape of CO 4^{th} Positive radiation
    - Dipole moments and potential energy surfaces for CO

Backup

Rate Extracted – Assuming exchange





- Rates fail to collapse – not correlated with O or C atom fraction
- Rates inconsistent with predicted rates
- Suggests exchange does not drive dissociation