Tutorial on Ablative TPS (Entry Heating – Radiative)

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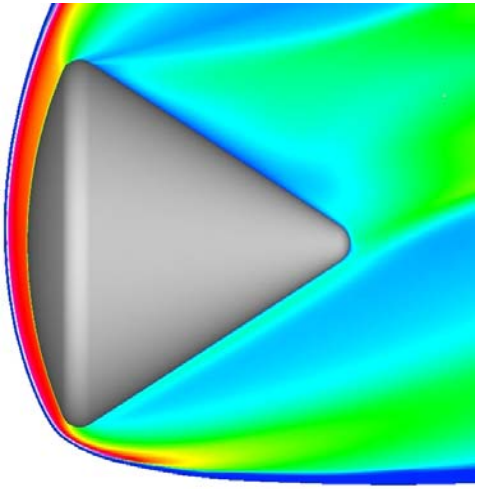
Why Study Radiation?

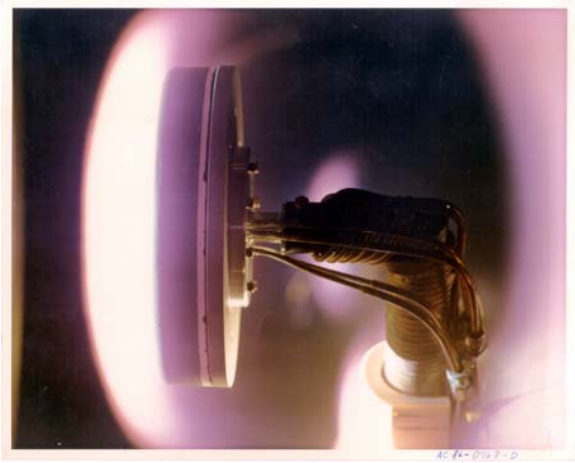
Develop predictive tool for vehicle heating

High temperatures in the shock layer [1]



Develop supplemental diagnostic tool

Ground-based facilities – arcjets & shock tubes [2]



Synergistic combination of the two aspects

Will lead to models that replicate actual flow physics with high fidelity

Preliminary Estimates for Earth Entry

General expression for stagnation point heating correlation (either convective or radiative)

$$\dot{q}_0 \propto \underbrace{(R_n)^r}_{\text{Nose radius}} \underbrace{(\rho_\infty)^m}_{\text{Freestream density}} \underbrace{(V_\infty)^n}_{\text{Flight speed}}$$

Convective Heating (Fay-Riddell correlation [3] or Tauber [4])

$$r = -0.5,\ m \approx 0.5,\ n \approx 3.15$$

- **Heating increases with increasing flight speed and density**
- **Heating <u>decreases inversely</u> with increasing nose radius**

Radiative Heating (Martin [5] or Tauber-Sutton [6])

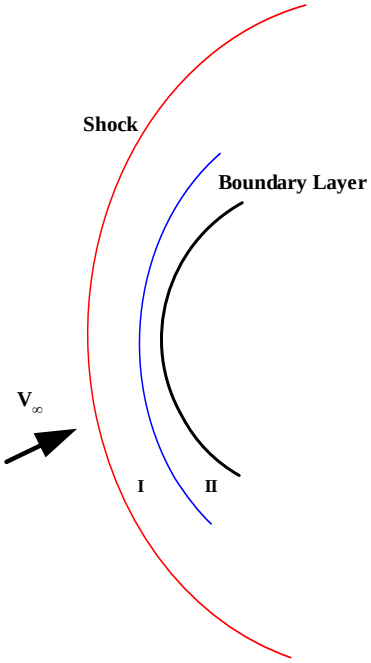
$$r = 1.0,\ m \approx 1.6,\ n \approx 8.5$$

- **Heating increases with increasing flight speed and density – faster than convective**
- **Heating <u>increases directly</u> with increasing nose radius – implications to manned missions**

Outline of this Tutorial

- Background
  - General ideas about radiation
  - Energy balance
  - Definitions
- The Macroscopic Picture
  - Assumptions and problem formulation
  - Radiative transport equation
  - Solution of the transport equation
- The Microscopic Picture
  - Transitions in two-level systems
  - Probabilities and line shapes
  - Multi-level systems
    - Atoms and spectroscopy
    - Diatomic molecules and spectroscopy
- Other Topics
- Examples
- Concluding Remarks

General Ideas about Radiation



Radiation is due to high temperatures in the shock layer (Region I)

- **Emission and absorption processes**

Aeroheated body surface radiates into Region II

The primary carrier of radiative energy is a photon, which

- **Is a massless particle traveling at the speed of light ($c \gg V$)**
- **Is governed by Bose-Einstein statistics**
- **Has a characteristic frequency ν (or wavelength λ)**
- **Has a direction of propagation**
- **Has two states of polarization**

The effects of thermal radiation are on momentum and energy [7]

- **Radiation pressure**
- **Radiation energy density**
- **Radiative heat flux**

For planetary entry vehicles we can neglect the first two [8]

Photon frequency regimes

Ref. 9

Mid-IR	2-20 μm	
Near IR	700-2000 nm	
Visible	400-700 nm	
Near UV	200-400 nm	
Vacuum UV (VUV)	100-200 nm	O_2 absorption
Extreme UV (XUV)	< 100 nm	

Spectral regions of interest in radiative heating of a probe are highlighted

Shock-Layer Energy Balance (Global)

$$\frac{\partial}{\partial t}(\rho E)+\vec{\nabla}\cdot(\rho E\vec{u})+\vec{\nabla}\cdot(p\vec{\vec{I}}\cdot\vec{u})+\vec{\nabla}\cdot(\vec{\vec{T}}\cdot\vec{u})=\vec{\nabla}\cdot(\kappa\vec{\nabla}T)-\sum_s h_s\rho_s\vec{V}_s+\vec{\nabla}\cdot\dot{\vec{q}}^R$$

Thermal equilibrium assumed in writing the above energy balance statement

- **Other energy balance equation(s) required for "internal" modes of constituent molecules, atoms** [10]

Conductive heat flux term – Fourier's Law (temperature gradient)

Diffusive heat flux term – Fick's Law (species mass gradient) or multi-component (Stefan-Maxwell)

If radiation energy density is important, we need to add it to energy balance [7,8]

If radiation pressure is important, we need to consider the momentum balance as well [7]

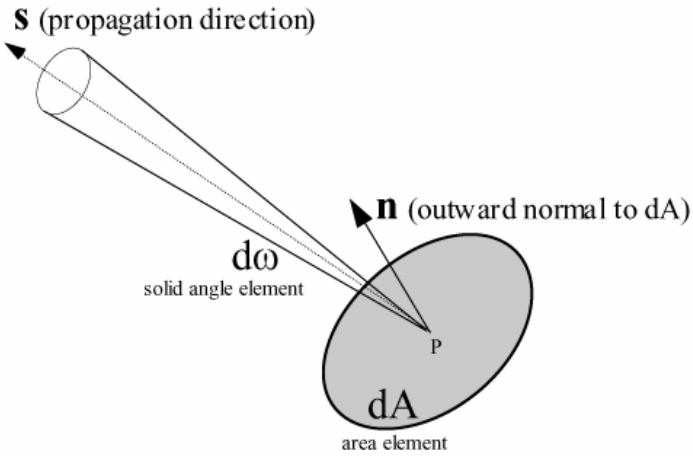
- **Add to the energy balance statement, work done by radiation pressure**

For present discussion, we only seek the divergence of the radiative heat flux vector

- **If radiation is tightly coupled to the flow, we have to solve radiation transport along with the flow equations – flow is no longer adiabatic in the inviscid region of shock layer, i.e., $h+V^2/2 \neq$ constant**
- **Usually we assume radiation is not coupled to the flow – *a posteriori* analysis of radiation transport from computed flow field quantities [temperature(s) and species mass densities]**

Definitions

Refs. 8,11-13



The energy gathered at the point P by a "pencil" of light beams enclosed in a infinitesimal solid angle $d\omega$ is of interest

s is the unit vector specifying the orientation of the light pencil and n is the unit normal of dA

We define the specific intensity (I_ν) at P as the energy per unit area (dA) per unit time (dt) per unit frequency ($d\nu$) unit solid angle ($d\omega$)

$$dE_\nu = I_\nu(\vec{r}, \hat{s}; t)(\hat{s} \cdot \hat{n}) dA d\omega d\nu dt$$

The dot product of unit vectors s and n is necessary to obtain the projected area (normal to the pencil)

A special case of specific intensity is that of a blackbody

$$B_\nu = \frac{2h\nu^3}{c^2\left[\exp(h\nu / kT) - 1\right]}$$

B_ν does not depend on direction/position

Equation of Radiative Transport, I

In the direction of traversal of the photon, we have both spontaneous emission and absorption

- **Interaction of photons with matter in motion**

We have the following statement of transport for specific intensity [13]

$$\underbrace{\frac{1}{c}\frac{\partial}{\partial t} I_\nu(\vec{r},\hat{s})}_{\text{Rate of change}} + \underbrace{\hat{s}\cdot\vec{\nabla} I_\nu(\vec{r},\hat{s})}_{\text{Streaming}} = \underbrace{j_\nu(\vec{r})}_{\text{Emission}} - \underbrace{\kappa_\nu(\vec{r},\hat{s}) I_\nu(\vec{r},\hat{s})}_{\text{Absorption}}$$

The equation of transport does not consider the following

- **Induced emission process – due to the fact that photons are bosons** [13]
- **Possibility of scattering within the volume** [11,13]
- **Polarization of the photon** [11]

The time rate of change term can be ignored for our applications

Replacing the streaming term by the directional derivative, the equation of transfer is

$$\frac{dI_\nu}{ds} = j_\nu - \kappa_\nu I_\nu$$

Equation of Radiative Transport, II

$$\frac{dI_\nu}{ds} = j_\nu - \kappa_\nu I_\nu = -\kappa_\nu \left(I_\nu - S_\nu \right)$$

I_ν has units of $W.m^{-2}.Hz^{-1}.sr^{-1}$

j_ν (the emission coefficient) has units of $W.m^{-3}.Hz^{-1}.sr^{-1}$

κ_ν (the absorption coefficient) has units of m^{-1}

κ_ν is also referred to as opacity

S_ν is referred to as the source function

The emission and absorption coefficients (j_ν and κ_ν) depend upon the microscopic states of the constituent atoms and molecules of the gas mixture [7,11-13]

- Specifically, we require knowledge of the "populations" of these microscopic states
- Populations of electrons
  - Transitions of electrons lead to radiation (either emission or absorption)

Equation of Radiative Transport, III

Refs. 12,13

The assumption of local thermodynamic equilibrium (LTE) simplifies the task of obtaining "populations" of the microscopic states of atoms and molecules in the gas mixture

- Combination of equilibrium statistical mechanics and quantum mechanics
- Boltzmann statistics provide the population distributions for atoms, molecules, and their ions
- Saha relation helps establish distribution of ionic species and electrons

LTE simply means that at any point in the shock layer there are sufficient collisions among the constituent gases to establish local equilibrium

- Knowledge of any two thermodynamic variables (e.g., p and T) is all that is required to compute the microscopic populations – hence emission and absorption coefficients
- The assumption breaks down at high altitudes, where one may not have sufficient collisions to establish local equilibrium – the LTE assumption yields higher estimates of radiative heating

For LTE, specific intensity is simply the blackbody function (B_ν) – hence,

$$\frac{dB_\nu}{ds} = 0 = j_\nu - \kappa_\nu B_\nu \quad \Rightarrow \quad j_\nu = \kappa_\nu B_\nu$$

We now have a useful relation between the emission and absorption coefficients

Equation of Radiative Transport, IV

Refs. 7, 12, 14

Our stated aim is to determine the (divergence of the) heat flux vector

Easily written as the integral over all frequencies and all solid angles of the RHS of the radiative transport equation

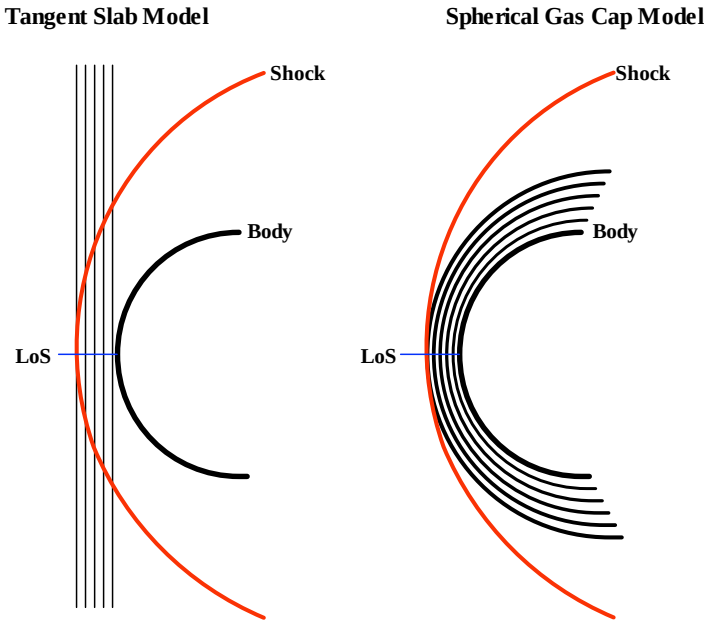
Also note that spontaneous emission is independent of the solid angle and radiates in all 4π sr of solid angle

$$\nabla \cdot \dot{\vec{q}}^{R} = 4\pi \int_{0}^{\infty} j_{\nu} d\nu - \int_{\omega} \int_{0}^{\infty} \kappa_{\nu} I_{\nu} d\nu d\omega$$

When added to the balance equation of total energy density, the resulting equation is a partial integro-differential equation

- **Quite difficult to solve without many simplifying assumptions**
- **One approach is to reduce the dimensionality of the problem to one-dimensional – confine analysis to a line of sight that coincides with the stagnation line**
- **Perform radiative transport computations after CFD computations have been completed – uncoupled approach to radiative transfer**

Solution of the Transport Equation, I



Solution of the complete three-dimensional transport equation (or the energy balance equation with radiation coupled in) is in the realm of the possible today – large supercomputers seem to make the task easier

For the purposes of this tutorial, we will tread familiar ground (i.e., the one-dimensional case and the stagnation point)

There are two possibilities [15]

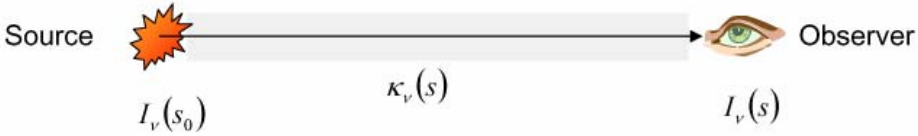
- **The shock layer in the vicinity of the line of sight is assumed to be discretized as thin slabs of infinite extent – tangent slab model**
- **The shock layer could be assumed to consist of layers that are concentric with the nose of the spacecraft – spherical gas cap model (predicted heat flux is about 20% lower than tangent slab approximation)**

Solution of the Transport Equation, II

Refs. 7, 16-18

First attempt - Integrate the transport equation in the direction of radiation propagation

- **Gas medium assumed to be both emitting and absorbing**



The solution consists of two terms

- **The first term represents attenuation of the initial intensity due to absorption along**
- **The second term represents the "summation" of pointwise emission attenuated by absorption**

$$I_\nu(s) = I_\nu(s_0)e^{-\tau_\nu(s,s_0)} + \int_{s_0}^{s} \kappa_\nu(\xi)B_\nu(\xi)e^{-\tau_\nu(s,\xi)}d\xi$$

The function τ_ν is called the optical thickness (or depth)

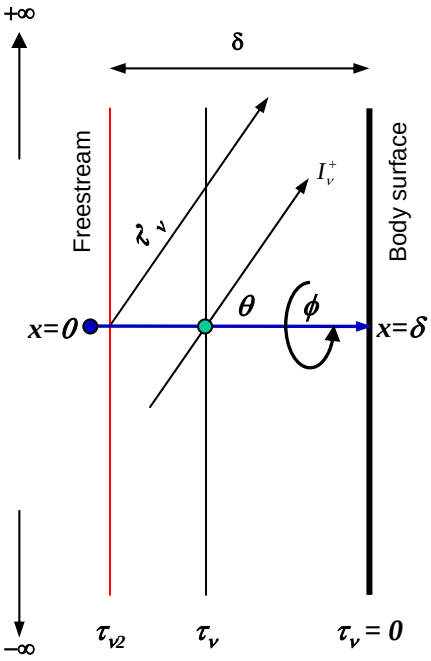
- **It is actually nondimensional (since κ_ν has units of m^{-1}) but varies from point to point**
- **Optical depth is a constant if the absorption coefficient is a constant – some simplification results**

$$\tau_\nu(s,\xi) = \int_{\xi}^{s} \kappa_\nu(\ell)d\ell$$

Solution of the Transport Equation, III

Refs. 7, 16-18

Second attempt - Integrate the transport equation for a one-dimensional slab



Shock layer is a thin slab of gas with infinite extent in the *y* and *z* directions

Only variation of properties is along the *x* axis – no variation along *y* and *z* (hence no dependence on ϕ)

We are interested in the heat flux at the stagnation point ($x=\delta$)

Uni-directional transport along slant length

$$I_\nu(\tau'_\nu) = I_\nu^{\text{freestream}} e^{-\tau'_\nu} + \int_0^{\tau'_\nu} B_\nu(\xi) e^{-(\tau'_\nu - \xi)} d\xi$$

Uni-directional transport along *x* axis

$$I_\nu^+(\tau_\nu) = I_\nu^+(\tau_{\nu_2}) e^{-\frac{(\tau_{\nu_2} - \tau_\nu)}{\cos\theta}} + \int_{\tau_\nu}^{\tau_{\nu_2}} B_\nu(\xi) e^{-\frac{(\xi - \tau_\nu)}{\cos\theta}} \frac{d\xi}{\cos\theta}$$

Integration over all frequencies and solid angle

$$\dot{q}^+ = 2\pi \int_0^{\pi/2} \int_0^\infty I_\nu^+(\tau_\nu = 0) \cos\theta \sin\theta d\theta d\nu$$

Solution of the Transport Equation, IV

Third attempt – Numerically integrate the transport equation for a one-dimensional slab – the approach taken in *NEQAIR96* [15]

The line of sight of interest is divided into as many segments as desired in the radiation propagation direction

Each segment can be viewed as a lamina(?) of infinite extent in the other two directions perpendicular to the propagation direction

In each slice or lamina, the thermochemical state is assumed constant – hence absorption coefficient is a constant

- **The properties are piecewise constant across the entire shock layer – akin to the finite-volume method in CFD**

Starting at the freestream point, the transport equation is integrated (for each value of frequency or wavelength considered) across each lamina – the emergent intensity at the end of integration across a lamina is the incident intensity for succeeding on

The final itensity distribution (over all frequencies) is then numerically integrated to obtain the heat flux

Summary of the Macroscopic Picture

Refs. 8, 16, 19

The attempt thus far has been to establish the equation of transport for radiative energy and show how it could be included in the statement of energy balance of the gas mixture

The complexity of the problem was reduced somewhat through the assumption that the flow and radiative processes were uncoupled

- **allowing for a posteriori radiative analysis-focus on solving the transport equation alone using the computed flow properties/thermochemical variables**

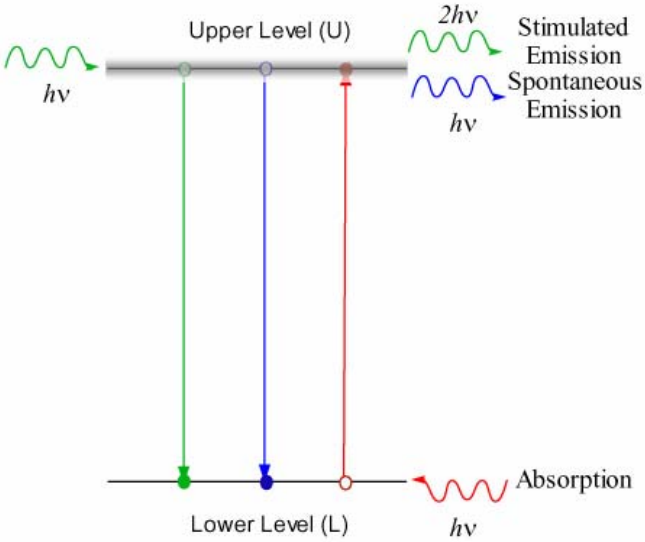
The actual three-dimensional problem was reduced to a one-dimensional problem through the tangent-slab assumption

The key to solving the one-dimensional transport equation lies in the knowledge of the absorption coefficient, which depends on the thermochemical state of the gas

The absorption coefficient also depends on the microscopic states of the constituent gas molecules – essentially how the energy is distributed amongst the various internal states

Two-Level System, I: Basic Ideas

Refs. 7, 18, 20



- Energy levels are E_U and E_L ($E_U > E_L$)
- Populations are N_U and N_L
- The energy is not known with great precision – uncertainty principle at work

There are three possible transitions

- Excitation of an electron - Absorption
- Spontaneous de-excitation of electron - Emission
- Stimulated de-excitation of electron – Emission
  - Emitted photon has same frequency and direction as the stimulating photon

Frequency of emitted (or absorbed) photon is simply the difference in the energies of the two levels

$$h\nu = \Delta E = E_U - E_L$$

The line (as recorded by film/camera) will not be sharp – there will be some width due to uncertainty in the energy difference

Two-Level System, II: Probabilities

Refs. 7, 15, 18, 20

For spontaneous emission (possible into all 4π sr)

$$j_{\nu\,\text{emission}} = \frac{1}{4\pi} N_U A_{UL} h \nu_{\text{LC}} \psi(\nu - \nu_{\text{LC}})$$

Where the line shape function y (Hz^{-1}) is defined as

$$\int \psi(\nu - \nu_{\text{LC}}) d\nu = 1$$

Combining absorption and stimulated emission (both depend on the intensity of the stimulating photon)

$$\kappa'_\nu I_\nu = \left(\kappa_{\nu\,\text{abs}} - \kappa_{\nu\,\text{st.emis}}\right) I_\nu = \left\{\left[N_L B_{LU} - N_U B_{UL}\right] h \nu_{\text{LC}} \psi(\nu - \nu_{\text{LC}})\right\} I_\nu$$

It can be shown that the "effective" absorption coefficient can be obtained from the emission coefficient and the blackbody function

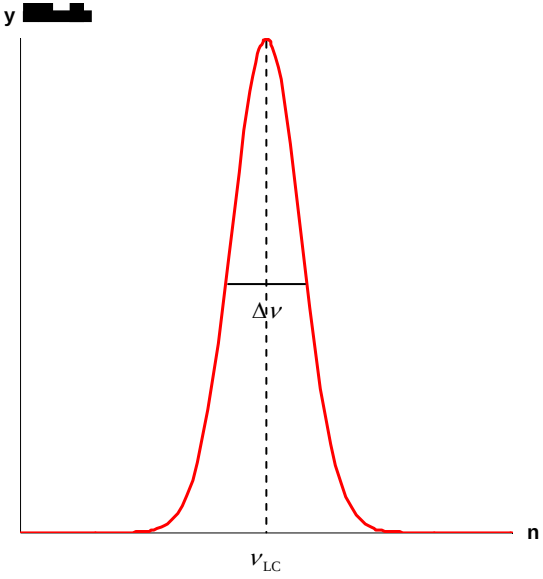
$$\kappa'_\nu = \frac{j_\nu}{B_\nu}$$

A_{UL} (Hz), B_{UL} (m^2.Hz.J^{-1}), B_{LU} (m^2.Hz.J^{-1}) are Einstein transition probability coefficients

- **These coefficients are not independent of one another – microscopic reversibility**

Two-Level System, III: Line Shapes

Refs. 15, 21



Once the intensity for the "sharp" transition is computed, the line shape function (symmetric about the line centerline) distributes the intensity over a frequency range

The line shape is based on the knowledge/computation of the line width (usually taken as the full width at half the value of the computed peak intensity)

The common line widths and shapes are

- **Natural width (due to finite radiative lifetime of the upper or excited state) – line shape is Lorentzian**
- **Doppler width (due to relative motion) – Line shape is Gaussian**
- **Pressure width (due to collisions) – Line shape is Lorentzian**

The combination of the Gaussian and Lorentzian line shapes leads to a Voigt profile

Two-Level System, II: Probabilities

Refs. 7, 15, 18, 20

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- **These coefficients are not independent of one another – microscopic reversibility**

Two-Level System, IV: Populations

Refs. 18, 22, 23

The last remaining problem is to obtain the populations of the upper and lower levels

For the particular case of LTE, the populations are easily obtained from Boltzmann statistics

$$\frac{N_i}{N} = \frac{g_i e^{-\frac{E_i}{kT}}}{\sum_j g_j e^{-\frac{E_j}{kT}}} = \frac{g_i e^{-\frac{E_i}{kT}}}{Q}$$

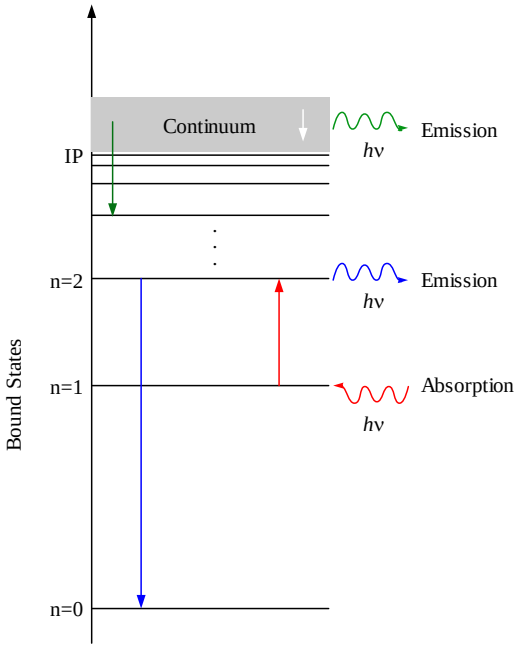
***Q* is referred to as the partition function**

For the case of non-LTE, computing the populations is quite a bit more involved

- **Energy level populations are not described by Boltzmann statistics**
- **Excitation/de-excitation of levels are now rate processes**
- **Rates depend on the colliding partners and their internal states**
- **Difficult to cover in great depth in this tutorial**

Multilevel Systems, I: Atoms

Refs. 21, 23, 24



Transitions are between electronic levels

- **Bound states are quantized – discrete energy levels**
- **"Free" states – continuous distribution**

Need four quantum numbers to describe one electron

- **Principal quantum number (n) – energy level**
  - **Takes values n = 0,1,2,…**
  - **Values correspond to shells named K, L, M,…**
- **Angular momentum (l) – shape of the orbit**
  - **Takes values l = 0,1,2,…,n-1**
  - **Values correspond to orbitals named s, p, d, f,…**
- **Magnetic quantum number (m_l) – orientation of the orbit**
  - **Takes values $m_l = -l, -l+1, -l+2, \ldots, 0, 1, \ldots, l-1, l$**
- **Spin (m_s) – intrinsic angular momentum**
  - **Has only two possible values (up/down or +/-)**

For multiple electrons conventions are little different

- **No two electrons can have the same set of q numbers – Pauli exclusion principle**

Multilevel Systems, II: Atomic Spectroscopy 1

Refs. 9, 21, 24

An orbital refers to a particular set of *n* and *l* – *l*=0,1,2,3… orbitals are labeled by s,p,d,f…

The ground configuration of an atom is obtained by filling up orbitals of increasing energy subject to the Pauli principle

- Example: Ground state of Carbon is $1s^2 2s^2 2p^2$ (K $2s^2 2p^2$)

A configuration describes electron distribution among various orbitals

A configuration can give rise to one or more terms (or states) – coupling of orbital and spin angular momenta

Angular momenta add vectorially – spin and orbital angular momenta could be coupled

- One way is to couple spin and orbital momentum of each electron and then getting the vector sum over all electrons – *jj* coupling
- Second way is couple spin angular momenta of all electrons, orbital angular momenta of all electrons, and then vectorially sum the two resultants – LS coupling (or Russell-Saunders coupling)

For LS coupling there are two cases

- Non-equivalent electrons – electrons with different values of either *n* or *l* (C example: $1s^2 2s^2 \underline{2p^1 3d^1}$)
- Equivalent electrons – electrons with the same value of *n* and *l* (C example: $1s^2 2s^2 \underline{2p^2}$)

Multilevel Systems, II: Atomic Spectroscopy 2

Refs. 9, 21, 24

An electronic configuration leads to one or more terms – Use LS coupling rules

For two non-equivalent electrons:

- $L = l_1+l_2, l_1+l_2-1,\ldots, |l_1-l_2|$ (L=0,1,2,… are labeled S,P,D,…)
  - Note: $M_L = L, L-1,\ldots, -L$
- $S = s_1+s_2, s_1+s_2-1,\ldots, |s_1-s_2|$ ($2S+1$=1,2,3,… are called singlets, doublets, triplets, …)
  - Note: $M_S = S, S-1,\ldots, -S$
- $J = L+S, L+S-1,\ldots, |L-S|$ (If $L > S$, J has $2S+1$ values, if $L < S$, J has $2L+1$ values)

A term is designated by the following symbol

Spin multiplicity

Parity

$$p=\sum_i \vec{l}_i$$

$$^{2S+1}L_J$$

Total orbital angular momentum

Total angular momentum

A term is specified by S and L – degeneracy of (2S+1)(2L+1)

A level is specified by L, S, and J – degeneracy of (2J+1)

- **A transition between two levels yields an atomic spectral line**

Multilevel Systems, III: Selection Rules 1

Refs. 9, 21

We will consider electric dipole transitions only

- **Other multipole (both electric and magnetic) transitions are usually very weak**

The change in principal quantum number (n) is unrestricted

The upper and lower states of the transition cannot have the same parity

The total spin quantum number (S) cannot change ($\Delta S = 0$)

The total angular momentum quantum number (L) can change only by -1, 0, +1 ($\Delta L = 0, \pm 1$)

- **However transition between states both having $L = 0$ is not allowed**

The total angular momentum quantum number (J) can change only by -1, 0, or +1 ($\Delta J = 0, \pm 1$)

- **As with L, transition between states both having $J = 0$ is not allowed**

For atomic transitions, the required degeneracy and Einstein transition probability coefficients for most energy levels of interest are widely available [25]

- **This knowledge is sufficient for us to compute spectra (radiative heating) from atomic transitions**

Multilevel Systems, IV: Diatomic Molecules 1

Refs. 21, 26, 27

Diatomic molecules have rotational, vibrational, and electronic internal degrees of freedom

- **Atoms only have electronic degree of freedom**

In general, the internal degrees of freedom in a molecule are coupled – increases complexity

A simplifying assumption is that these degrees of freedom are separable

- **The energy of a diatomic molecule, $E = E_{rot} + E_{vib} + E_{elec}$**
- **Each of the energy components is quantized**

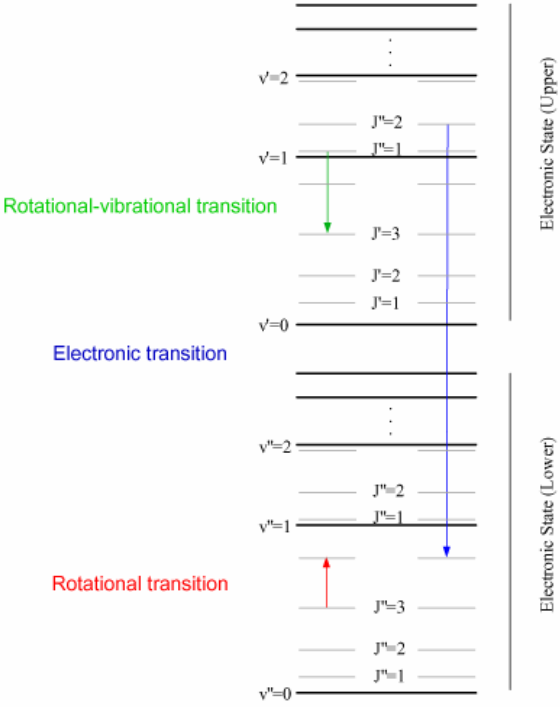
We consider transitions between the various quantized energy levels

Unlike atoms, where the energy levels are quite well known (at least for atomic systems of interest to us), experimental data for molecules are limited to a few vibrational/rotational levels, i.e., data are not complete (Note: the ground electronic states of H_2 and I_2 are exceptions)

- **This information gap, in the present day, is being closed through the use of computational quantum chemistry**
- **Another possibility is to use approximate/empirical methods of sufficient engineering accuracy to create the necessary data**

Multilevel Systems, IV: Diatomic Molecules 2

Refs. 21, 26, 27



Electronic energy levels

- Separation of motion from rotation-vibration
- Schrodinger equation solved through computational quantum chemistry
- Computed electronic energy levels/wavefunctions form the basis for solving nuclear Schrodinger equation

Rotational energy levels

- Usually computed assuming rigid rotor
- Spacing increases with J

Vibrational energy levels

- Usually computed assuming simple harmonic oscillator
- Spacing decreases with v

Upper state usually designated by ′ and the lower by ″

Multilevel Systems, V: Molecular Spectroscopy

Refs. 21, 23, 26, 27

An electronic configuration leads to one or more terms – Conceptually no different than for atomic configurations

The projection of total angular momentum along internuclear axis is the appropriate quantum number (we will still call it L for consistency with atomic levels)

- $L = l_1+l_2, l_1+l_2-1,\ldots, |l_1-l_2|$ (L=0,1,2,… are labeled Σ, Π, Δ,…)
- $S = s_1+s_2, s_1+s_2-1,\ldots, |s_1-s_2|$ (2S+1=1,2,3,… are called singlets, doublets, triplets, …)

A term is designated by the following symbol

Spin multiplicity

Letter sequence designating states of same spin multiplicity

$$(A/a)^{2S+1}L^{+/-}_{u/g}$$

Total orbital angular momentum (projected on internuclear axis)

Symmetry (to coordinate inversion)

Gerade/ungerade (homonuclear molecules only)

A term is specified by S and L – degeneracy of (2S+1)(2-$\delta_{L,0}$)

Example: Some states of the C_2 molecule – $X\,^1\Sigma_g^+$ $A\,^1\Pi_u$ $C\,^1\Pi_g$ $a\,^1\Pi_u$ $b\,^3\Sigma_g^+$ $c\,^3\Sigma_u^+$

Multilevel Systems, V: Selection Rules 2

Refs. 21, 23, 26, 27

As in the case of atoms, we will consider electric dipole transitions only

The total angular momentum (projected on internuclear axis) quantum number (L) can change only by -1, 0, +1 ($\Delta L = 0, \pm 1$)

- **However transition between states both having $L = 0$ is not allowed**

The total spin quantum number (S) cannot change ($\Delta S = 0$)

Transitions between states of different symmetries is disallowed, i.e. only + ↔ + and - ↔ -

Transitions between states ungerade and gerade states is disallowed, i.e. only g ↔ g and u ↔ u

There are additional rules on transitions between the components of multiplets

As in the case of atoms, we now have to compute the emission coefficients for the transitions

- **Despite the complexity of multiple levels, the fundamental transition is still a line – a rotational line in the case of diatomic molecules**
- **We can also exploit "patterns" (band structures) in the transitions – making bookkeeping a little easier: Electronic transitions → Vibrational bands → Rotational lines**

Multilevel Systems, VII: Molecular Spectra

Refs. 15, 23

As in the case of atoms, for any rotational line we can write the emission coefficient as

$$j_\nu = \frac{1}{4\pi} N_{n'v'J'} A_{n'v'J'-n''v''J''} \left(E_{n''v''J''} - E_{n'v'J'}\right) \psi\left(\nu - \nu_{LC}\right)$$

The Einstein transition probability is not as easily available as in the case of atoms. The general expression for a rovibronic line is

$$A_{n'v'J'-n''v''J''} \propto \nu^3 \left|R_e(\bar{r}_{v'v''})\right|^2 q_{v'v''} \frac{S_{J'J''}}{(2J'+1)}$$

Hönl-London factor

Franck-Condon factor

r-centroid

Electronic dipole transition moment

Some data exists for well-known band systems – constant literature survey/database searches are necessary to keep all the data current

Lines and Band Systems of Interest

Lines	Transitions	Notes
H, He, C, N, O	All available	H, He (Gas Giants)/C (Mars/Titan/Venus)
N_2 (1+)	$B\,^3\Pi_g \rightarrow A\,^3\Sigma_u^+$	Earth/Mars/Titan
N_2 (2+)	$C\,^3\Pi_u \rightarrow B\,^3\Pi_g$	Earth/Mars/Titan
N_2 (Lyman-Birge-Hopfield)	$a\,^1\Pi_g \rightarrow X\,^1\Sigma_g^+$	Earth/Mars/Titan
NO (β)	$B\,^2\Pi_r \rightarrow X\,^2\Pi_r$	Earth/Mars
NO (γ)	$A\,^2\Sigma^+ \rightarrow X\,^2\Pi_r$	Earth/Mars
NO (δ)	$C\,^2\Pi_r \rightarrow X\,^2\Pi_r$	Earth/Mars
NO (ε)	$D\,^2\Sigma^+ \rightarrow X\,^2\Pi_r$	Earth/Mars
O_2 (Schumann-Runge)	$B\,^3\Sigma_u^- \rightarrow A\,^3\Sigma_g^+$	Earth/?
C_2 (Swan)	$c\,^3\Sigma_u^+ \rightarrow a\,^3\Pi_u$	Mars/Titan/Venus
CO (4+)	$A\,^1\Pi \rightarrow X\,^1\Sigma^+$	Mars/Venus
CN (Red)	$A\,^2\Pi_i \rightarrow X\,^2\Sigma^+$	Mars/Titan
CN (Violet)	$B\,^2\Sigma^+ \rightarrow X\,^2\Sigma^+$	Mars/Titan

Topics Not Covered in This Tutorial

Continuum Radiation [18,29]

- **Free electrons in the flow can access an infinite number of unbound states – a continuum**
- **Some can be captured (photo de-excitation) leading to bound-free radiation**
- **Some can be decelerated (loss of energy) by positive charges leading to free-free radiation**
- **Population estimates from Saha equation – assuming LTE**

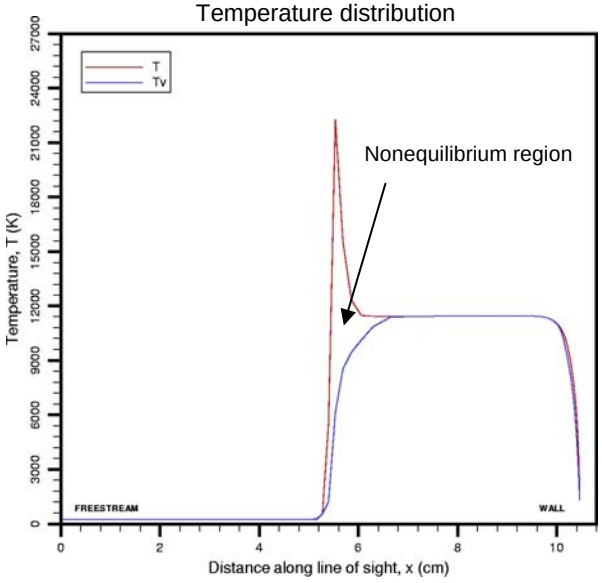
Scattering

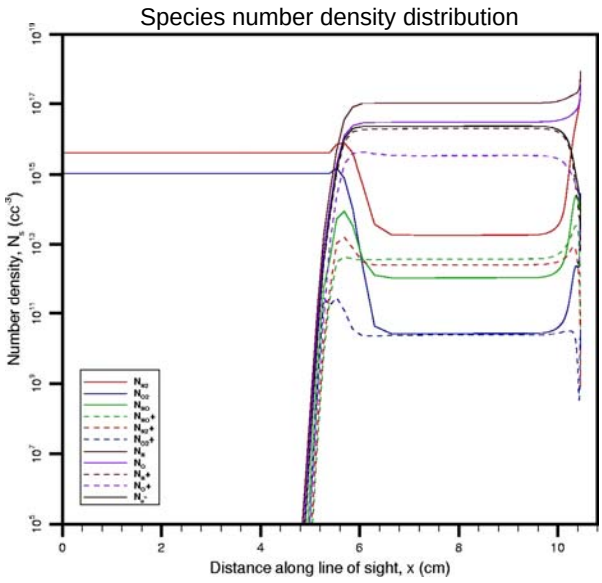
- **The radiation transport equation was based on the assumption that there was no scattering of photons in the gas medium – inclusion would lead to additional terms**
- **The additional terms require models/data of the scattering process(es)**
- **Scattering would be important in the presence of significant ionization – Thompson scattering**

Collisional-Radiative Model [22,23]

- **Population computations were based on the assumption of local thermodynamic equilibrium (Boltzmann distribution)**
- **At low densities, there are not enough collisional processes to ensure such equilibrium – models of rate processes that populate/depopulate electronic states is necessary**
  - **One such model (based on QSS) is available for the particular case of high-temperature air**
  - **Models for other gas mixtures are areas of current study**

Example: Stagnation Line of Sight (Air)





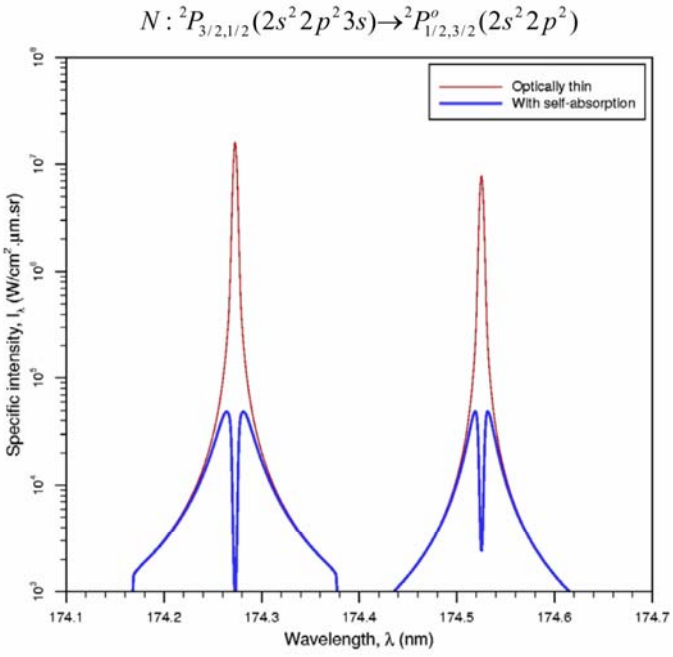
Temperature and species number density distributions along a stagnation line of sight from CFD computations

Chemical and thermal nonequilibrium

- **Two temperatures - Translational/rotational and vibrational/electronic**

Radiative heating analysis performed *a posteriori* using *NEQAIR96* code [15] **(line-by-line)**

Example: Stagnation Line of Sight (Air) 2



The specific intensity at the stagnation point is shown for a pair of atomic N lines in the VUV region

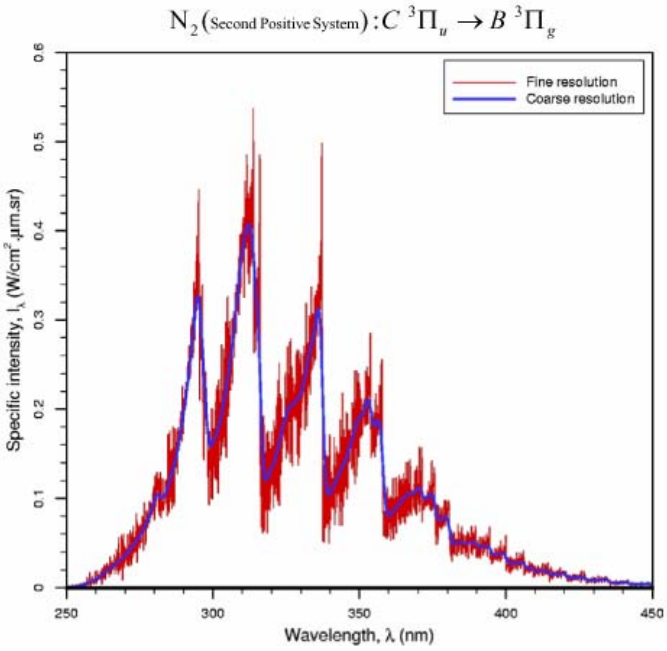
- Intensity distribution over wavelength is shown at the end of the radiation transport process starting from freestream

The heat flux at the stagnation point is the total area under the curves (integrated intensity) multiplied by the solid angle (2π sr)

The peak intensity (for the optically thin case) is completely absorbed – self absorption

- Self absorption occurs in the VUV region and is mostly associated with transitions to the ground state
- Despite absorption of the peak, considerable energy is still contained in the "wings" of the lines

Example: Stagnation Line of Sight (Air) 3



The specific intensity at the stagnation point is shown for the N_2 (second positive) band system

- As before, intensity distribution is shown at the end of the radiation transport process starting from freestream

Compared to the atomic N lines (previous slide), the intensity of the N_2 band system is weak

The spectrum shows the vibrational band structure clearly at the coarse resolution level

Higher wavelength resolutions shows rotational line structure as well

The integrated intensity (area under the curve) multiplied by the solid angle (2π sr) yields the radiative heat flux at the stagnation point

Final Remarks

Including radiative heating/transfer in the theoretical model is not conceptually difficult but is quite "messy"

The problem dimension increases significantly since we have to consider all photon frequencies

The geometry of the flow since the direction of propagation of photons is important

One way around the problem is to limit the analysis to one dimension and the stagnation point of the flow – however, the size and power of computer hardware available today makes it possible to attempt higher-dimensional approaches

The interaction between radiation and matter does require accurate knowledge of microscopic processes – to obtain gas emissivities/absorptivities

Parameters pertinent to microscopic properties (especially with respect to molecules) are best obtained through modern computational chemistry – ground-based spectroscopic experiments yield only a small part of the total information required

The present tutorial only covers a small fraction of a wide area of research – a lot remains to be done in finite-rate excitation/de-excitation of internal states, scattering, etc. – left to the enterprising student

References

1. Figure of Apollo shock layer temperature contours from recent computations of Wright *et al* (AIAA Paper 2004-2546)
2. Figure of flat-faced cylinder in arc-heated air by courtesy of John Balboni (NASA Ames Research Center)
3. Fay, J A, and Riddell, F R, "Theory of Stagnation Point Heat Transfer in Dissociated Air," *J. Aeronautical Sciences*, **25**, 1958, pp. 73-85,121.
4. Tauber, M E, "A Review of High-Speed, Convective, Heat-Transfer Computation Methods," NASA TP-2914, 1989.
5. Martin, J J, *Atmospheric Reentry: An Introduction to its Science and Engineering*. Prentice-Hall Series in Space Technology, Prentice-Hall, New Jersey, 1966
6. Tauber, M E, and Sutton, K, "Stagnation Point Radiative Heating Relations for Earth and Mars," *J. Spacecraft and Rockets*, **28**(1), 1991, pp. 40-42
7. Pai, S-I, *Radiation Gas Dynamics*. Springer-Verlag, New York, 1966.
8. Howe, J., "Hypervelocity Atmospheric Flight: Real Gas Flow Fields," NASA RP-1249, November 1990.
9. Martin, W C, and Wiese, W L, "Atomic Spectroscopy," in Chapter 10 of *Atomic, Molecular, and Optical Physics Handbook* (ed. G W F Drake), AIP Press, Woodbury, NY, 1996. Also available online at http://sed.nist.gov/Pubs/AtSpec/total.html
10. Gnoffo, P A, Gupta, R N, and Shinn, J L, "Conservation Equations and Physical Models for Hypersonic Air in Thermal and Chemical Nonequilibrium," NASA TP-2867, 1989.
11. Chandrasekhar, S, *Radiation Transfer*. Dover Publications, New York, 1960.
12. Anderson, J D, Jr., *Hypersonic and High Temperature Gas Dynamics*. McGraw-Hill, New York, 1989.
13. Pomraning, G C, "High Temperature Radiative Transfer and Hydrodynamics," in *Progress in High Temperature Physics and Chemistry* (ed C. Rouse), Vol. 4, 1971, pp.1-83.
14. Mihalas, D, and Weibel-Mihalas, B, *Foundations of Radiation Hydrodynamics*. Dover Publications, New York, 1999.
15. Whiting, E E, Park C, Liu, Y, Arnold, J O, and Paterson, J A, "NEQAIR96, Nonequilibrium and Equilibrium Radiative Transport and Spectra Program: User's Manual," NASA RP-1389, December 1996
16. Penner, S S, and Olfe, D B, *Radiation and Reentry*. Reentry Physics Series (ed J Menkes), Academic Press, New York, 1968.
17. Vincenti, W G, and Kruger, C H, Jr., *Introduction to Physical Gas Dynamics*. R E Krieger Publishing Co., Malabar, Florida, 1982.
18. Bose, T K, *High Temperature Gas Dynamics: An Introduction for Physicists and Engineers*. Springer, Berlin, 2004
19. Scala, S M, and Sampson, D H, "Heat Transfer in Hypersonic Flow with Radiation and Chemical Reaction," in *Supersonic Flow Chemical Processes and Heat Transfer* (ed. D B Olfe and V Zakkay), Pergamon Press, NY, 1964.

References

20. Cannon, C J, *The Transfer of Spectral Line Radiation*. Cambridge University Press, Cambridge, UK, 1985.
21. Hollas, J M, *Modern Spectroscopy*. 3rd Edition, John Wiley, New York, 1996
22. Park, C, *Nonequilibrium Hypersonic Aerothermodynamics*. John Wiley, New York, 1990.
23. Laux, C, “Radiation and Nonequilibrium Collisional-Radiative Models,” VKI Special Course on Physico-Chemical Models for High Enthalpy and Plasma Flows Modeling, VKI, Belgium, June 4-7, 2002Herzberg, G, *Atomic Spectra and Atomic Structure*. Dover Publications, New York, 1944.
24. NIST has an online atomic spectra database that provides both line and level data - http://physics.nist.gov/cgi-bin/AtData/main_asd
25. Herzberg, G, *The Spectra and Structure of Simple Free Radicals*. Dover Publications, New York, 1971.
26. Herzberg, G, *Molecular Spectra and Molecular Structure, I: Spectra of Diatomic Molecules*. 2nd Edition, Krieger Publishing Co., Malabar, FL, 1989
27. Huber, K P, and Herzberg, G, “Constants of Diatomic Molecules,” (data prepared by J.W. Gallagher and R.D. Johnson, III) in NIST Chemistry WebBook, NIST Standard Reference Database Number 69, Eds. P.J. Linstrom and W.G. Mallard, March 2003, National Institute of Standards and Technology, Gaithersburg MD, 20899 (http://webbook.nist.gov).
28. Zel’dovich, Ya B, and Raizer, Yu P, Physics of Shock Waves and High-Temperature Hydrodynamic Phenomena. Dover Publications, New York, 2002

Preliminary Estimates for Earth Entry

General expression for stagnation point heating correlation (either convective or radiative)

$$\dot{q}_0 \propto \underbrace{(R_n)^r}_{\text{Nose radius}} \quad \underbrace{(\rho_\infty)^m}_{\text{Freestream density}} \quad \underbrace{(V_\infty)^n}_{\text{Flight speed}}$$

Convective Heating (Fay-Riddell correlation [3] or Tauber [4])

$$r = -0.5,\ m \approx 0.5,\ n \approx 3.15$$

- **Heating increases with increasing flight speed and density**
- **Heating <u>decreases inversely</u> with increasing nose radius**

Radiative Heating (Martin [5] or Tauber-Sutton [6])

$$r = 1.0,\ m \approx 1.6,\ n \approx 8.5$$

- **Heating increases with increasing flight speed and density – faster than convective**
- **Heating <u>increases directly</u> with increasing nose radius – implications to manned missions**