National Aeronautics and Space Administration



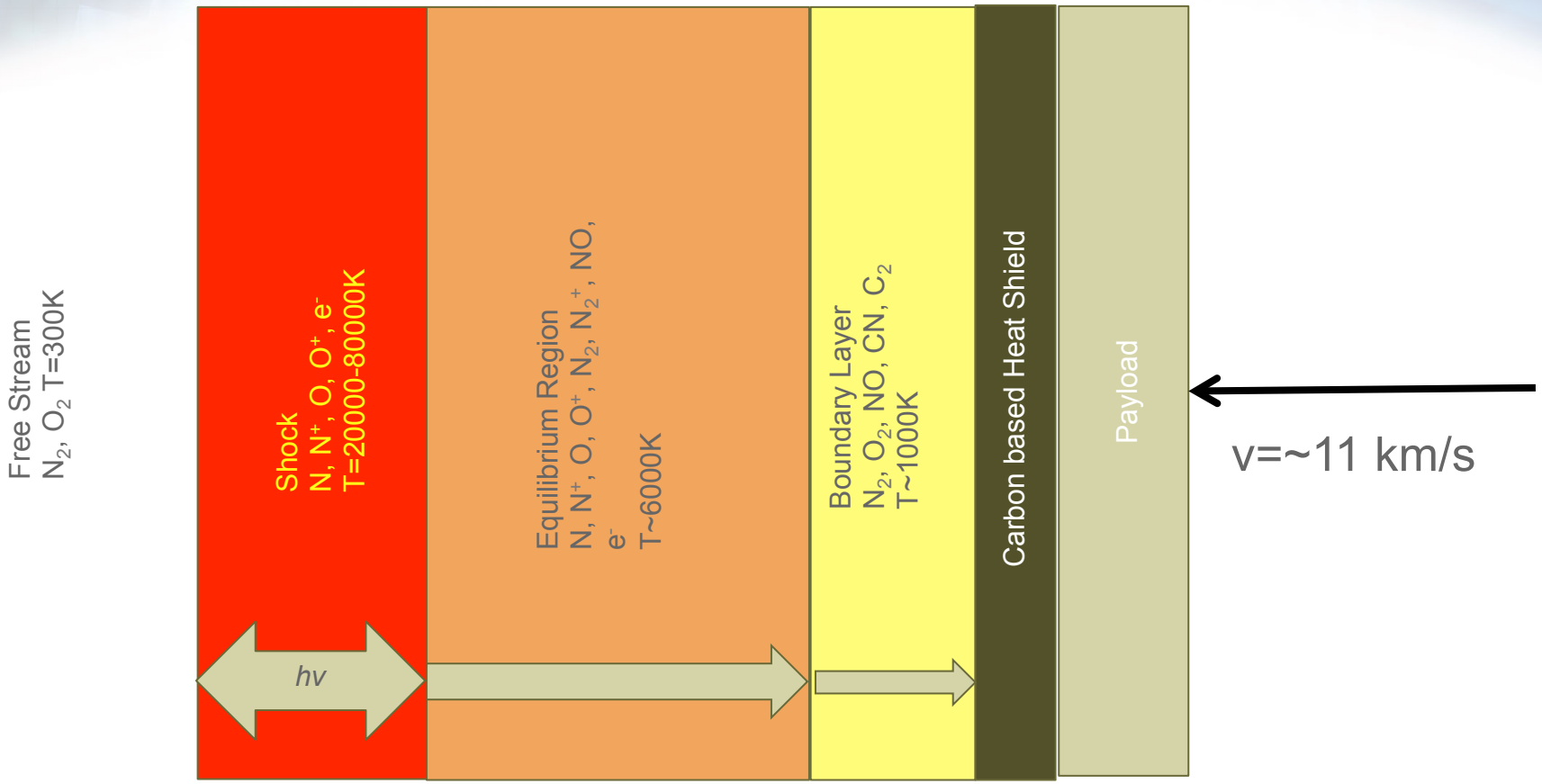
To ∞ and beyond: diatomic molecules above the dissociation limit

David W. Schwenke
NASA Ames Research Center

Applied Modeling & Simulation Seminar Series
July 29, 2014

Re-entry is Hot!!!




Free Stream
N_2, O_2 T=300K
Shock
N, N^+, O, O^+, e^-
T=20000-80000K
hv
Equilibrium Region
N, N^+, O, O^+, N_2, N_2^+, NO, e^-
T~6000K
Boundary Layer
N_2, O_2, NO, CN, C_2
T~1000K
Carbon based Heat Shield
Payload
v=~11 km/s

HyperRad Development team



Alan Wray

Yen Liu

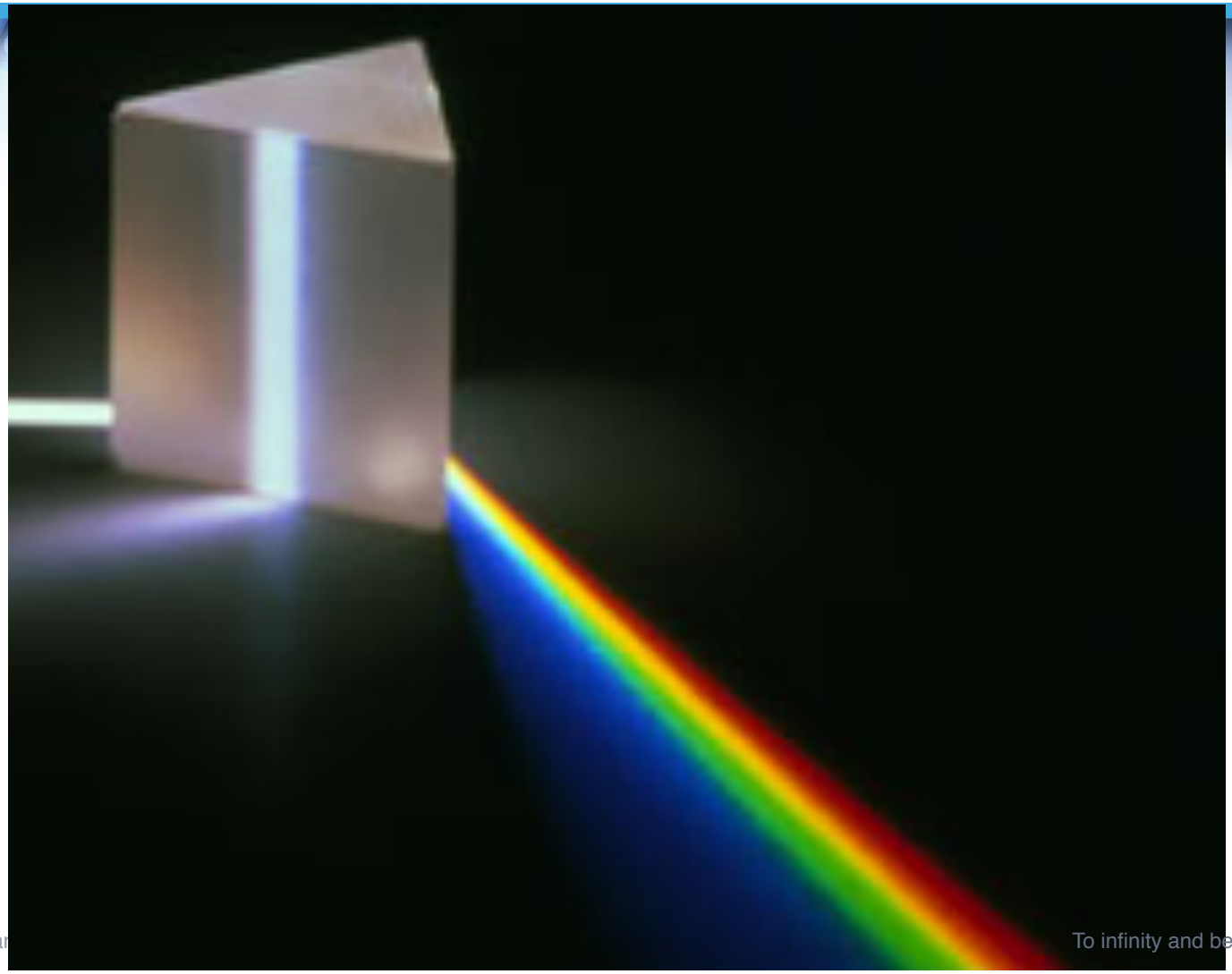
Duane Carbon

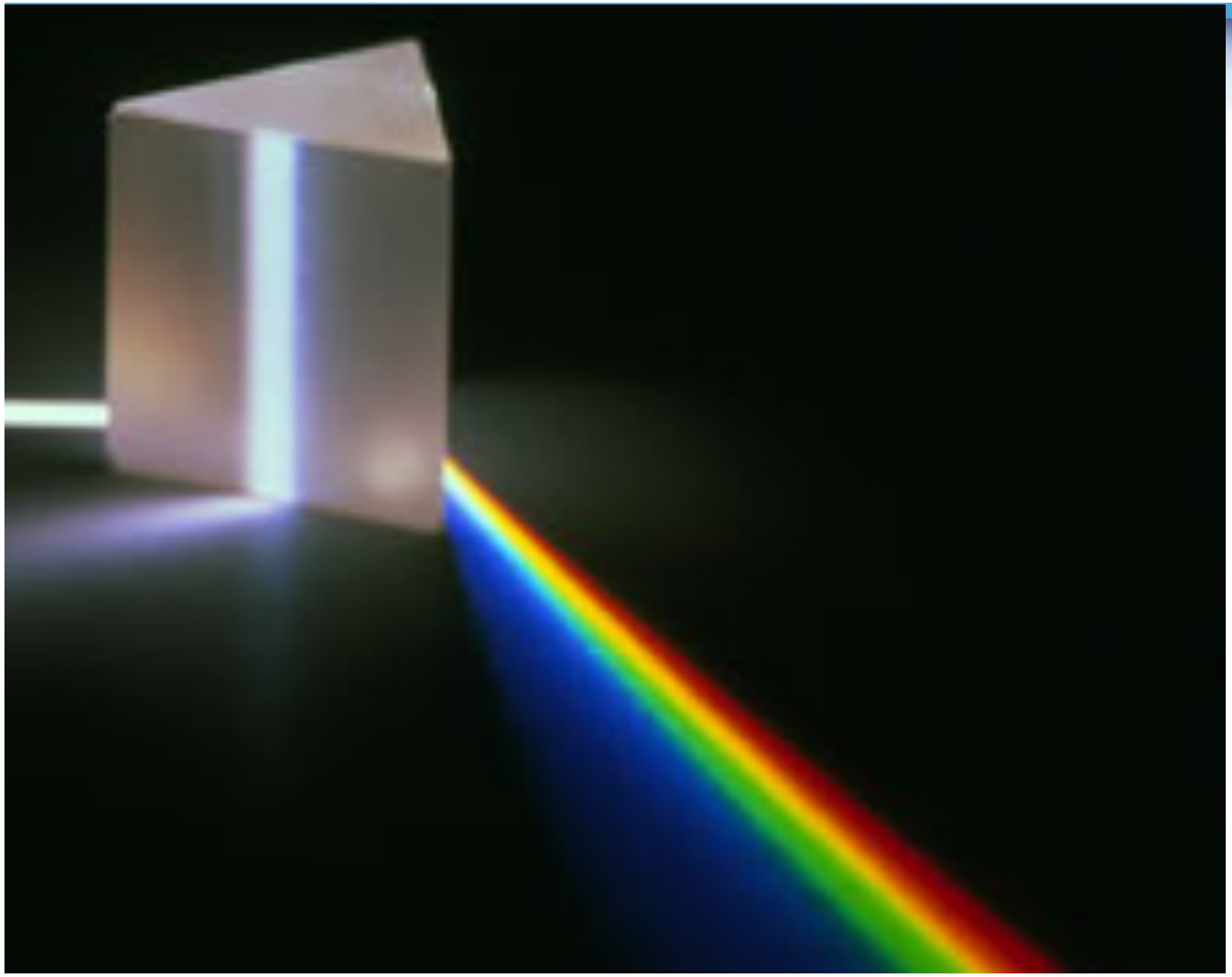
Winifred Huo

Galina Chaban

Richard Jaffe

David Schwenke



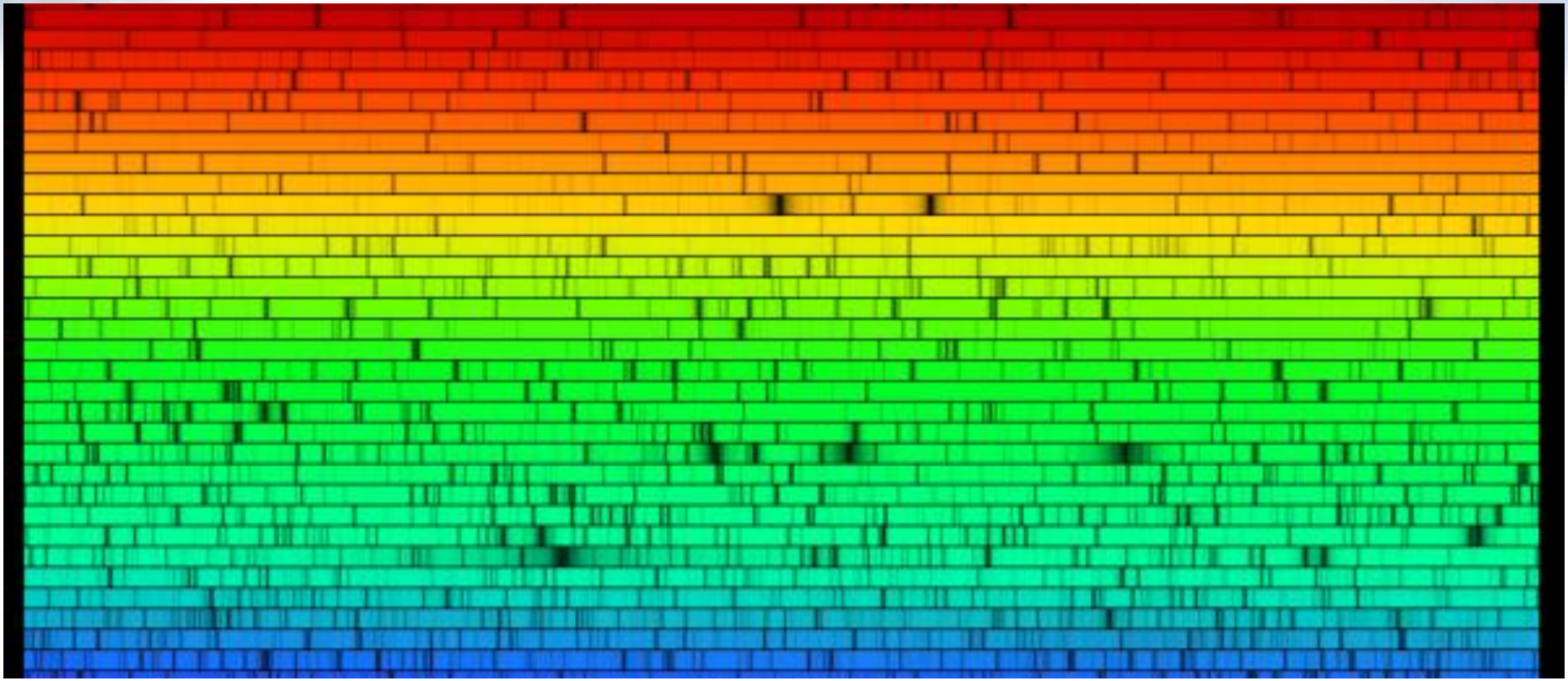


+



=

Solar spectrum



Spectrum for each compound is unique ➔ remote detection

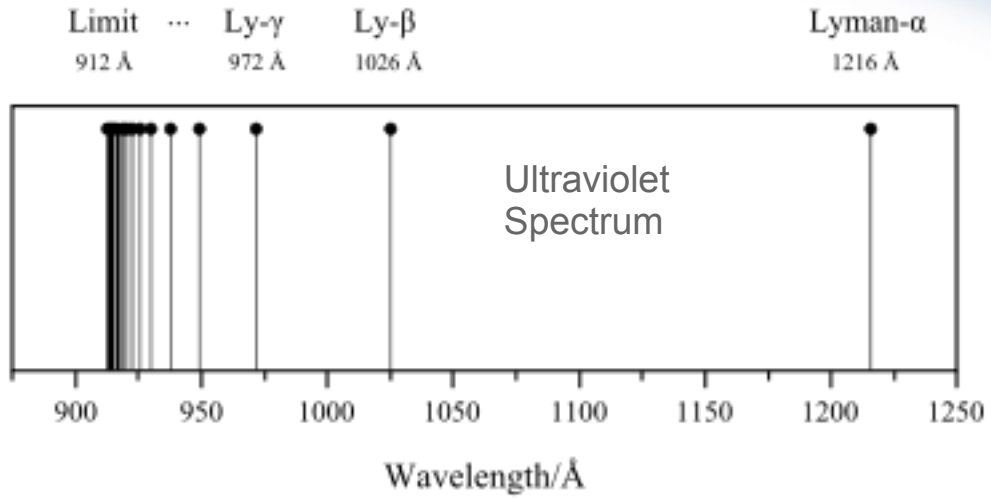
Helium: solar in 1868, terrestrial in 1895

What causes the spectrum?

Newton didn't know

Simplest spectrum: Hydrogen Atom

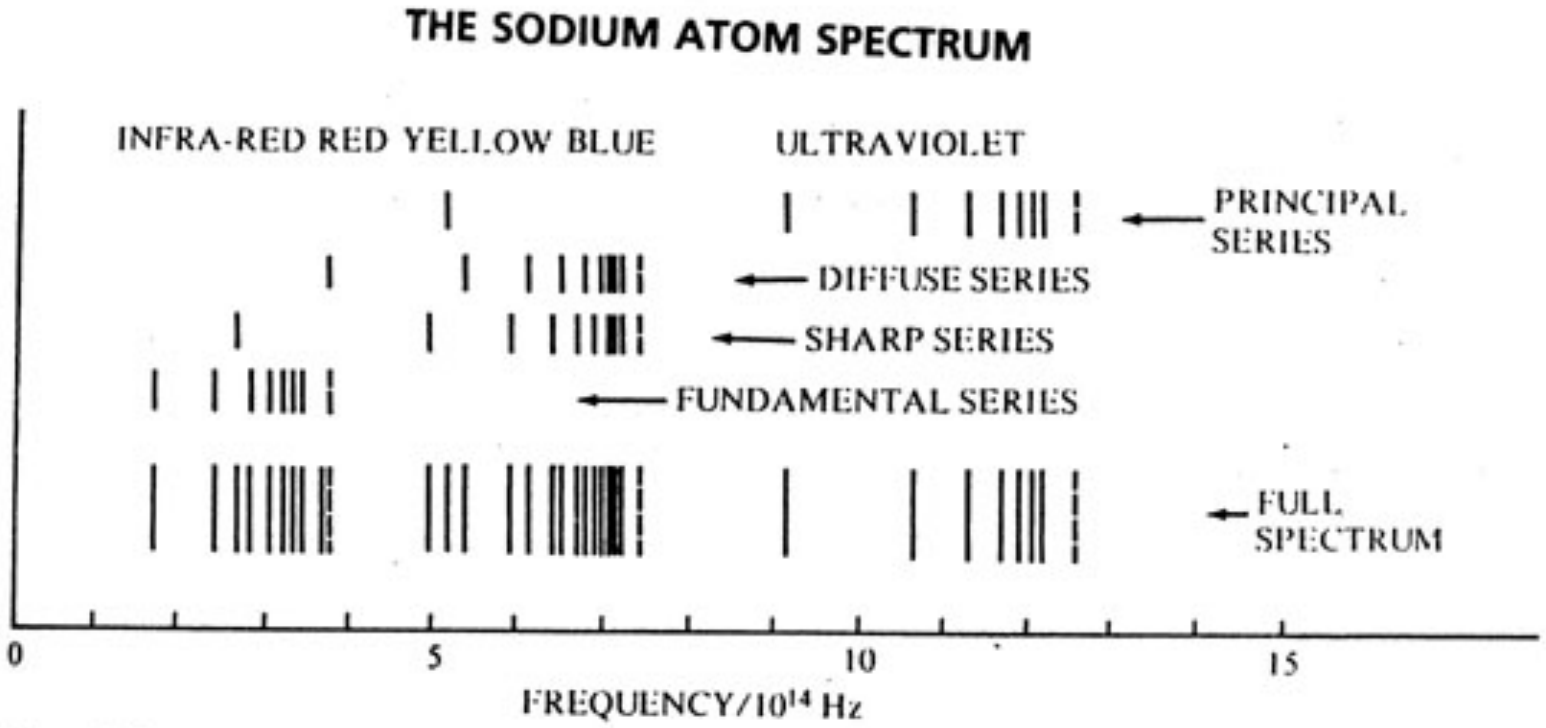
1880s:
$1/\lambda = R[(1/n'')^2 - (1/n')^2]$



Visible Spectrum



More complicated: Na



Quantum Mechanics

$$i\hbar \frac{\partial}{\partial t} \Psi_\alpha(x,t) = \left[-\tfrac{1}{2} \nabla_x^2 + V(x) \right] \Psi_\alpha(x,t) \equiv H(x) \Psi_\alpha(x,t)$$

$$\Psi_\alpha(x,t) = e^{-iE_\alpha t/\hbar} \psi_\alpha(x)$$

$$H(x) \psi_\alpha(x) = E_\alpha \psi_\alpha(x)$$

$$c = \lambda \nu$$

$$h\nu_{\beta\alpha} = E_\beta - E_\alpha$$

$$\left| \int \psi_\beta^*(x) M(x) \psi_\alpha(x) dx \right|^2$$



Quantum numbers

n: principle quantum number

1,2,3,4,…

l: electronic angular momentum quantum number

0 (S for sharp), 1 (P for principle), 2 (D for diffuse), 3 (F), 4 (G), …

Λ: electronic angular momentum along diatomic axis

0 ($\Sigma^{\pm}$), ±1 (Π), ±2 (Δ), ±3 (Φ), …

S: electron spin angular momentum quantum number

0,1/2, 1, 3/2, …

Spin multiplicity: 2S+1

1 (S=0, singlets), 2 (S=1/2, doublets), 3 (S=1, triplets), …

Interchange symmetry: g,u

Divide and Conquer



1: Freeze nuclei, solve for electron wave functions

high dimensionality, low density of states

2: Allow nuclei to move under forces of electron wave functions

low dimensionality, high density of states

Born and Oppenheimer 1927

$H=H^{elec}+H^{nuc}+H^{cross}$

Divide and Conquer

1: Freeze nuclei, solve for electron wave functions

high dimensionality, low density of states

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$H=H^{elec}+H^{nuc}+$ 

Divide and Conquer

1: Freeze nuclei, solve for electron wave functions

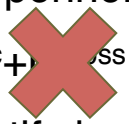
high dimensionality, low density of states

2: Allow nuclei to move under forces of electron wave functions

low dimensionality, high density of states

Born and Oppenheimer 1927

$H=H^{elec}+H^{nuc}+$ ...ss



justify by low density of states, $m_N/m_e >>1$

Solving for electron motion

Integral-differential equation with homogenous boundary conditions at infinity

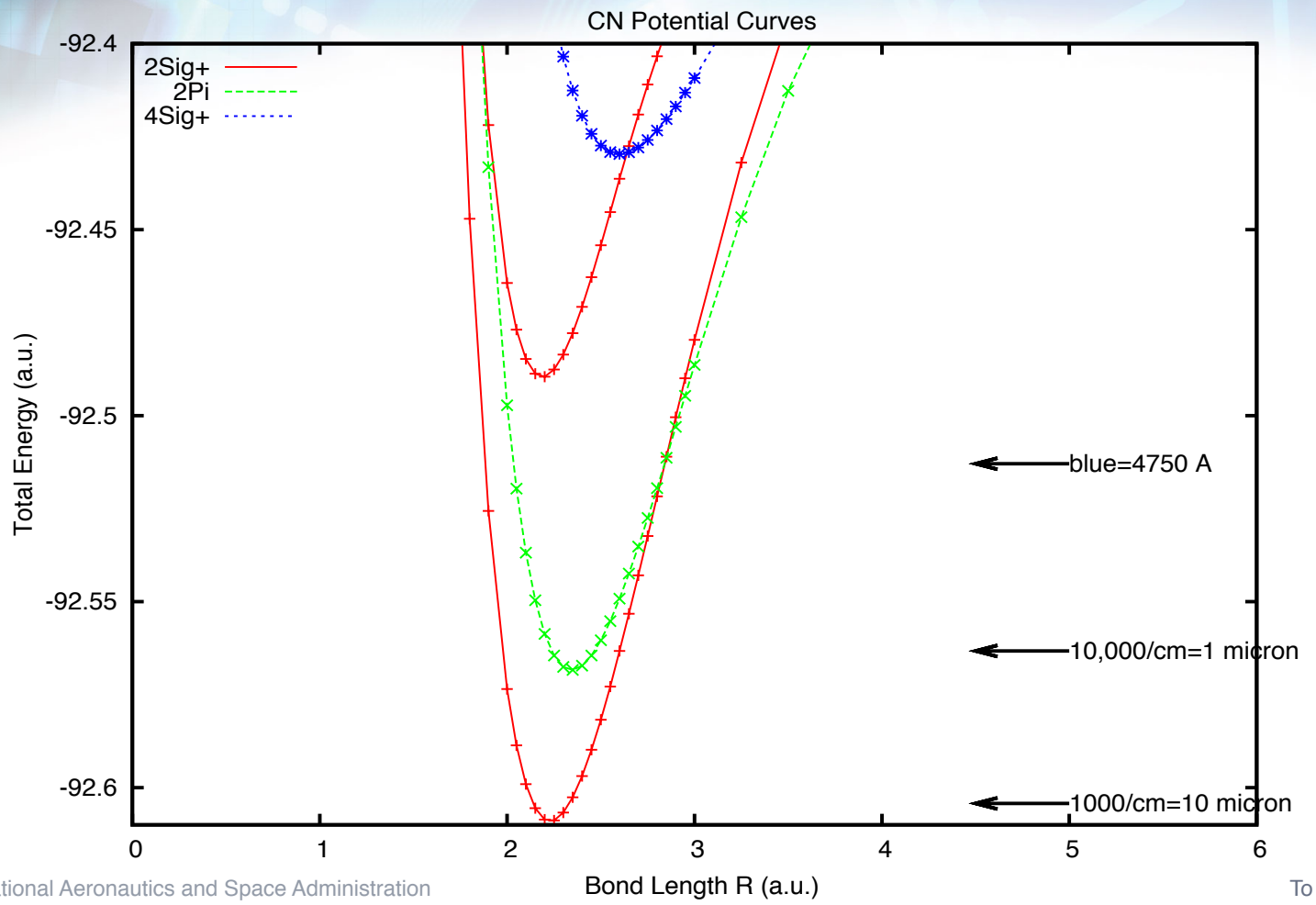
➔expand in terms of analytic basis functions

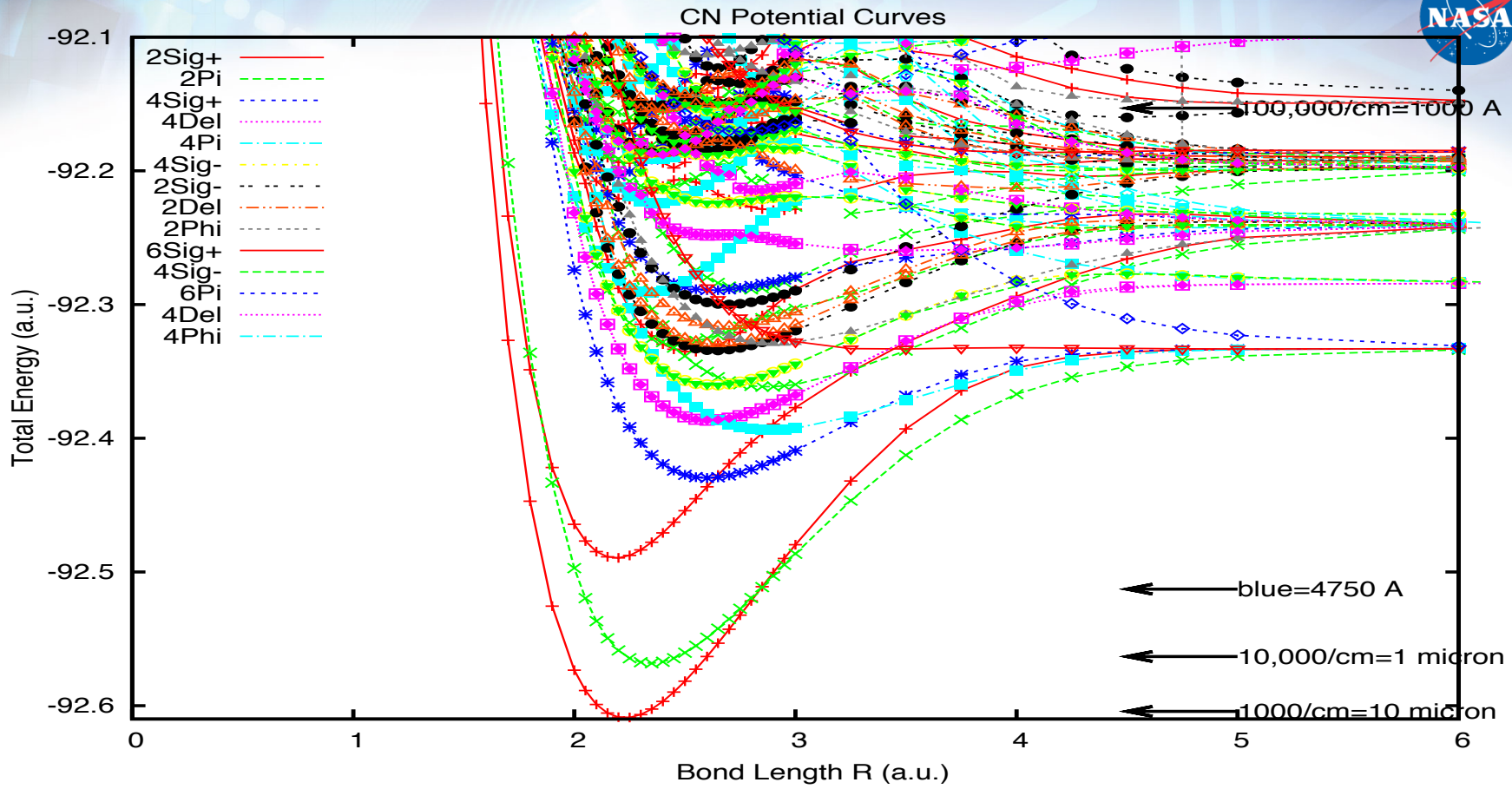
- Assign electrons to basis functions in all possible ways & diagonalize:

  full configuration interaction (FCI)

  For 10 e^-, 92 basis functions, $\binom{92}{5}^2 \approx 2.5 \times 10^{15}$

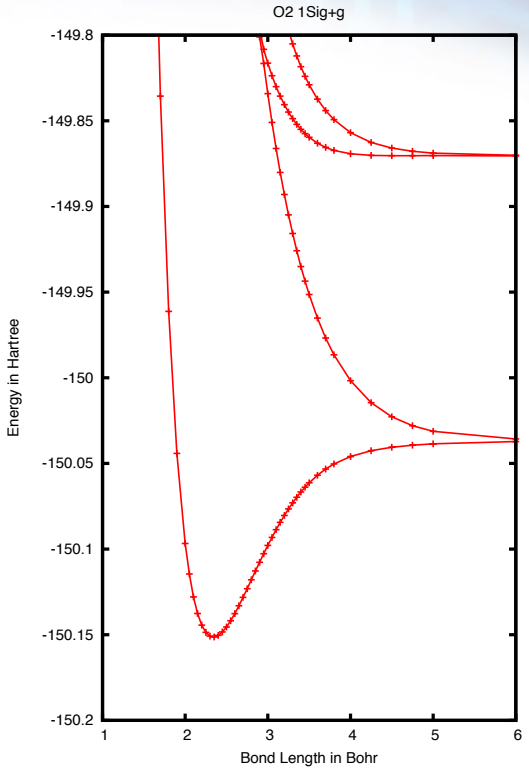
- Or
  - Optimize molecular orbitals with small FCI: 536 variables
  - Allow 0, 1, or 2 e^- outside of small FCI space: 1,729,808 functions
  - Contract pair excitations: 47,375


CN Potential Curves
2Sig+
2Pi
4Sig+
-92.4
-92.45
-92.5
-92.55
-92.6
Total Energy (a.u.)
0
1
2
3
4
5
6
Bond Length R (a.u.)
blue=4750 A
10,000/cm=1 micron
1000/cm=10 micron


CN Potential Curves
Total Energy (a.u.)
Bond Length R (a.u.)
-92.1
-92.2
-92.3
-92.4
-92.5
-92.6
0
1
2
3
4
5
6
2Sig+
2Pi
4Sig+
4Del
4Pi
4Sig-
2Sig-
2Del
2Phi
6Sig+
4Sig-
6Pi
4Del
4Phi
100,000/cm=1000 A
blue=4750 A
10,000/cm=1 micron
1000/cm=10 micron

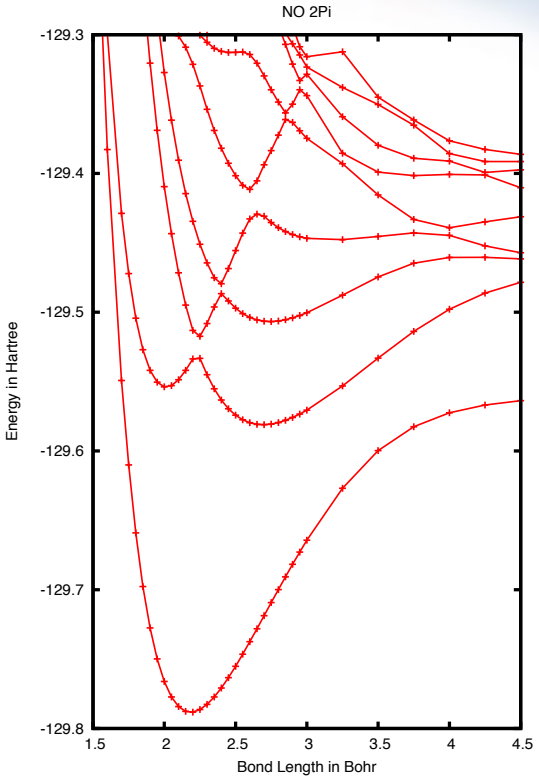
Advances in potential energy curve calculation

A) Dynamic weighting for valence MO determination
   A) Adjust weighting by value of energy
B) Rydberg Orbital Calculation
   A) First compute valence MOs: inward
   B) Freeze valence MOs, compute Rydberg MOs: outward
C) Diabatic States
   A) H^{cross} remains small
   B) Phase factors!
   C) Splitting
   D) Easier to interpolate
   E) Easier to adjust



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Adiabatic vs. Diabatic states

Thermodynamics: without gain or loss of heat

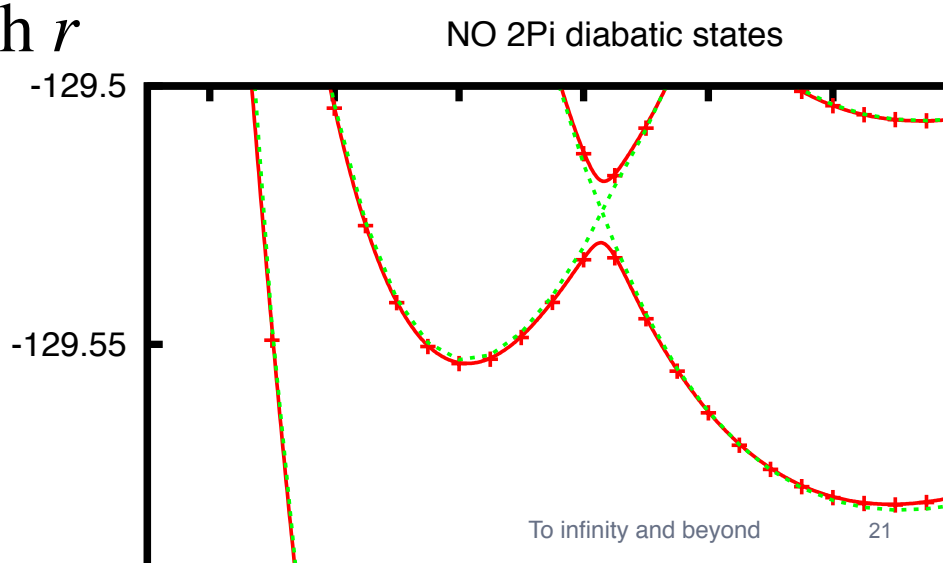
Adiabatic from the Greek “incapable of being crossed”

Nuclei are stationary, solve for electron motion: $H(r)\psi_\alpha^a = E_\alpha(r)\psi_\alpha^a$

Diabatic – not adiabatic

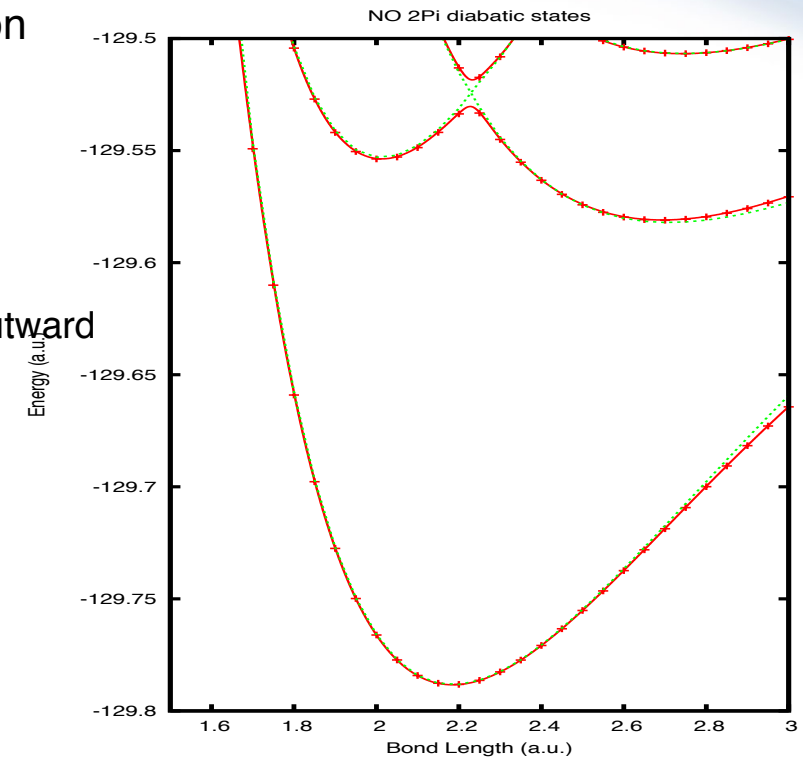
ψ_α^d does not "change" with r

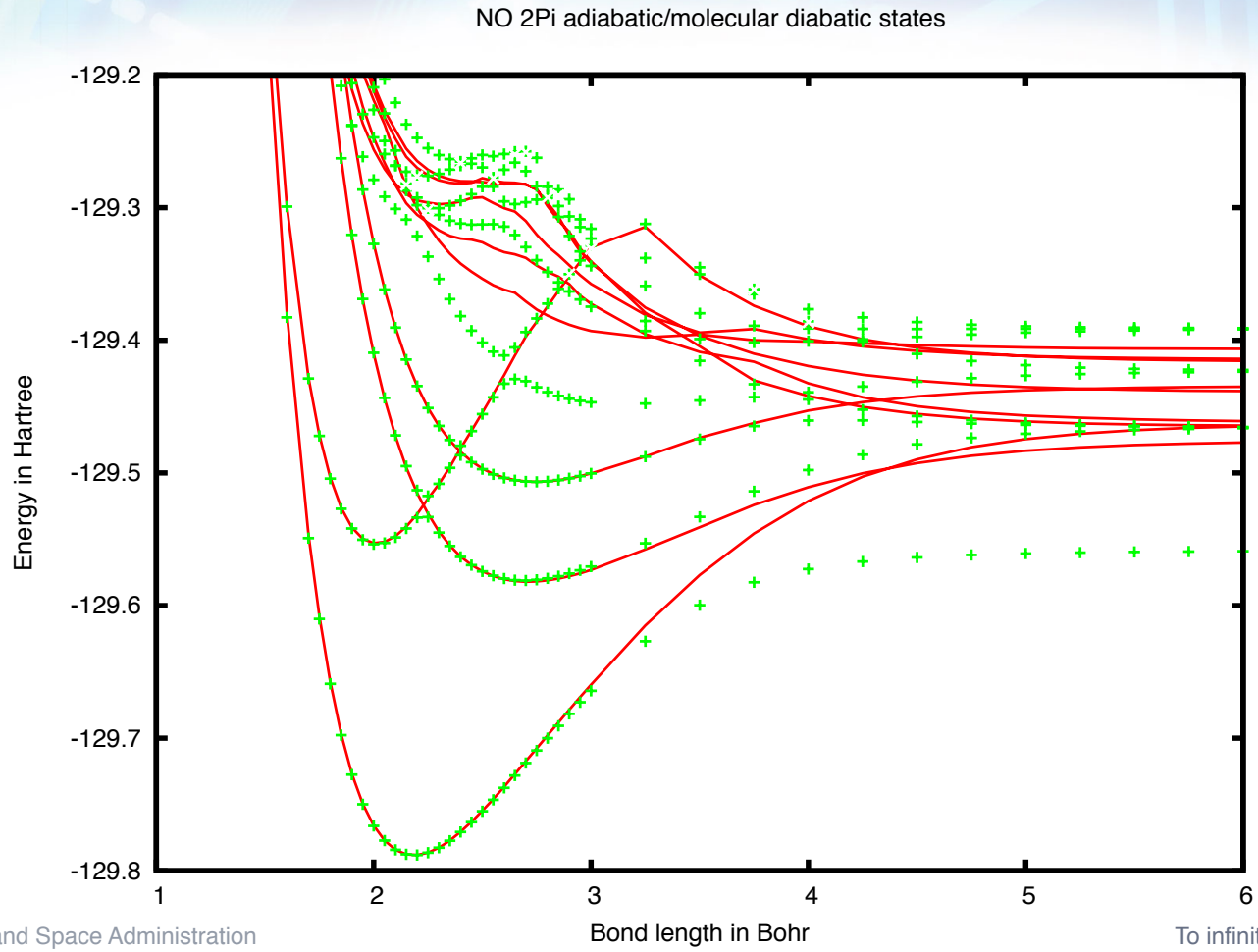
$$\begin{matrix} E_1 & 0 \\ 0 & E_2 \end{matrix} = U^T \begin{matrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{matrix} U$$

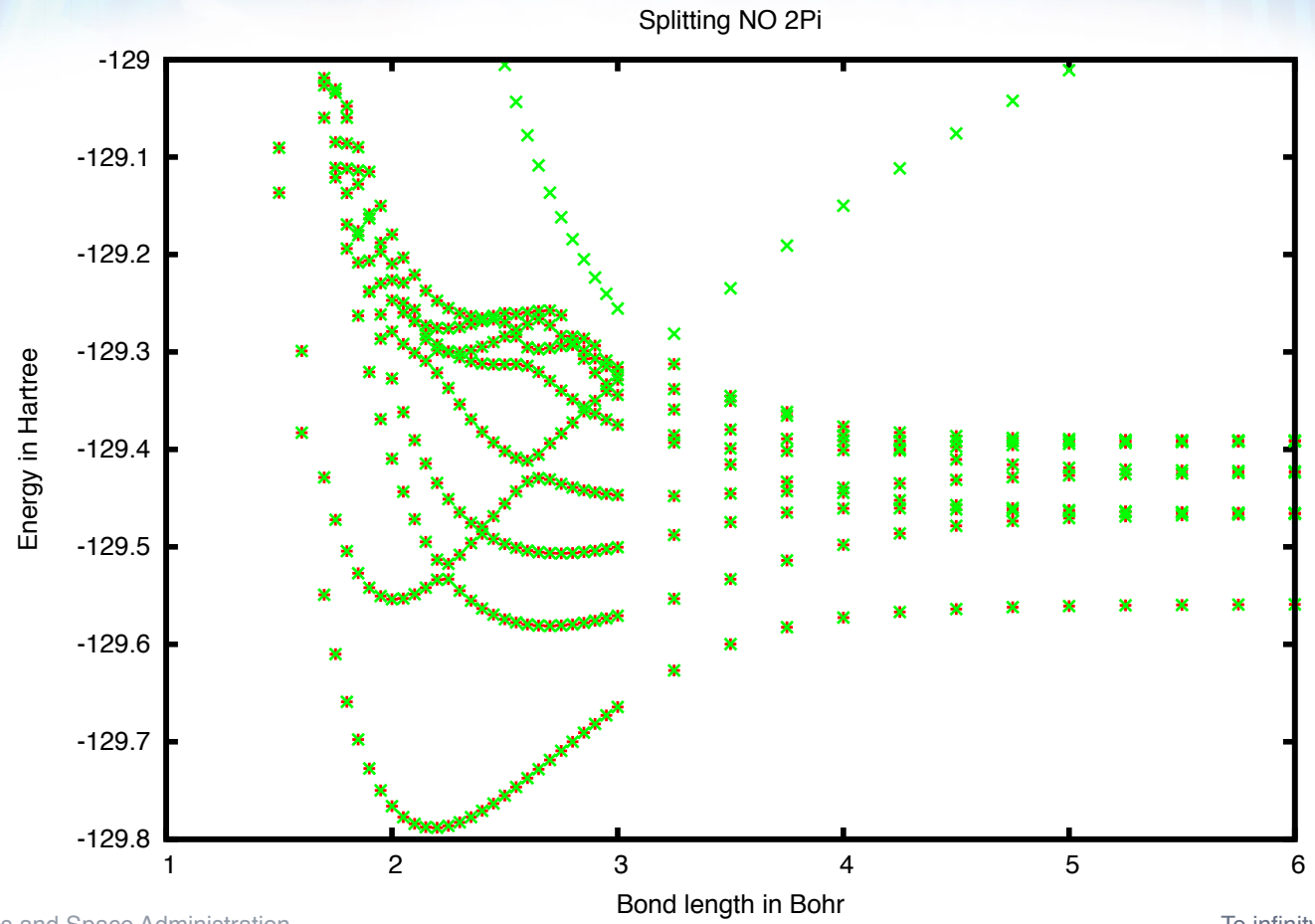


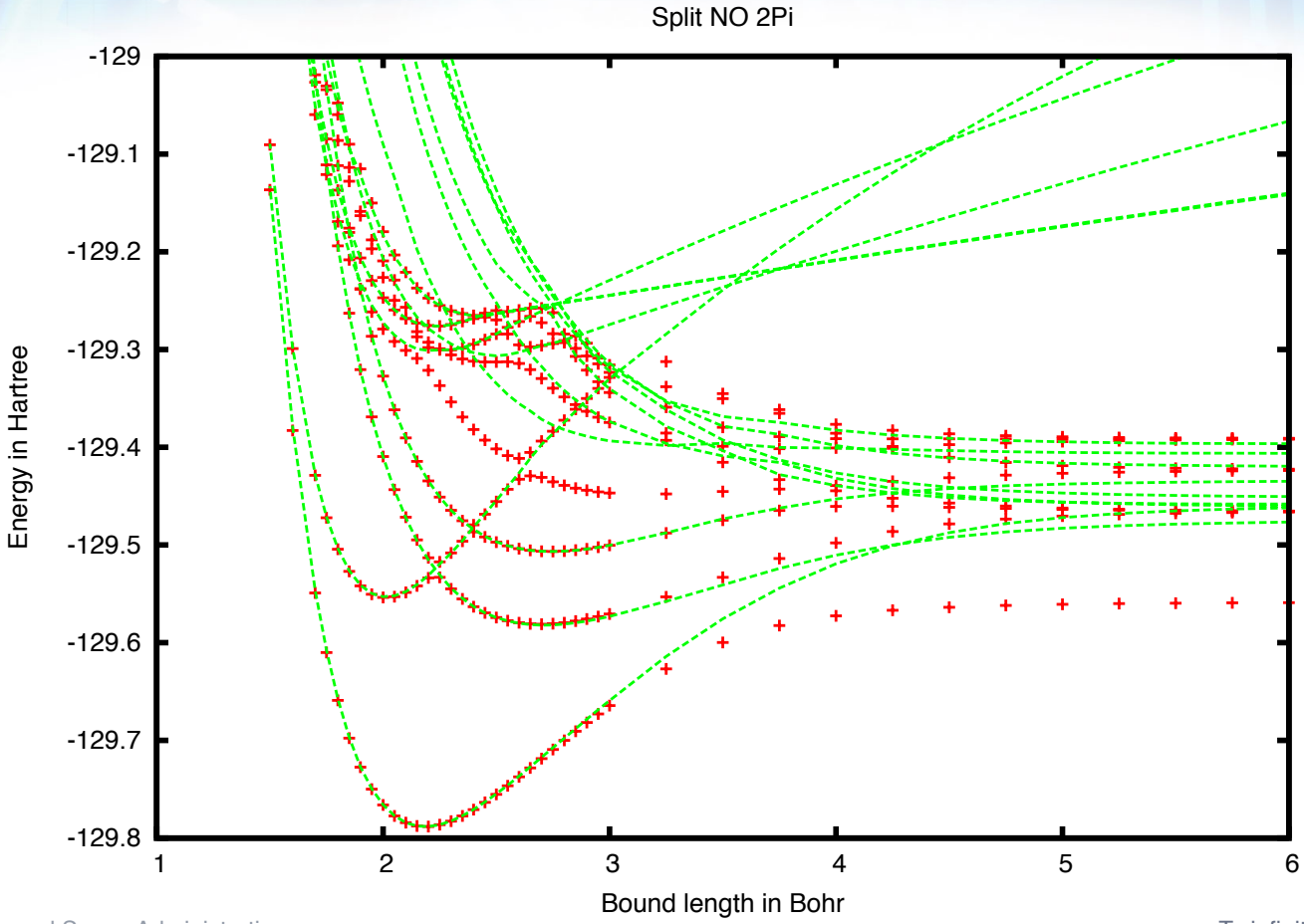
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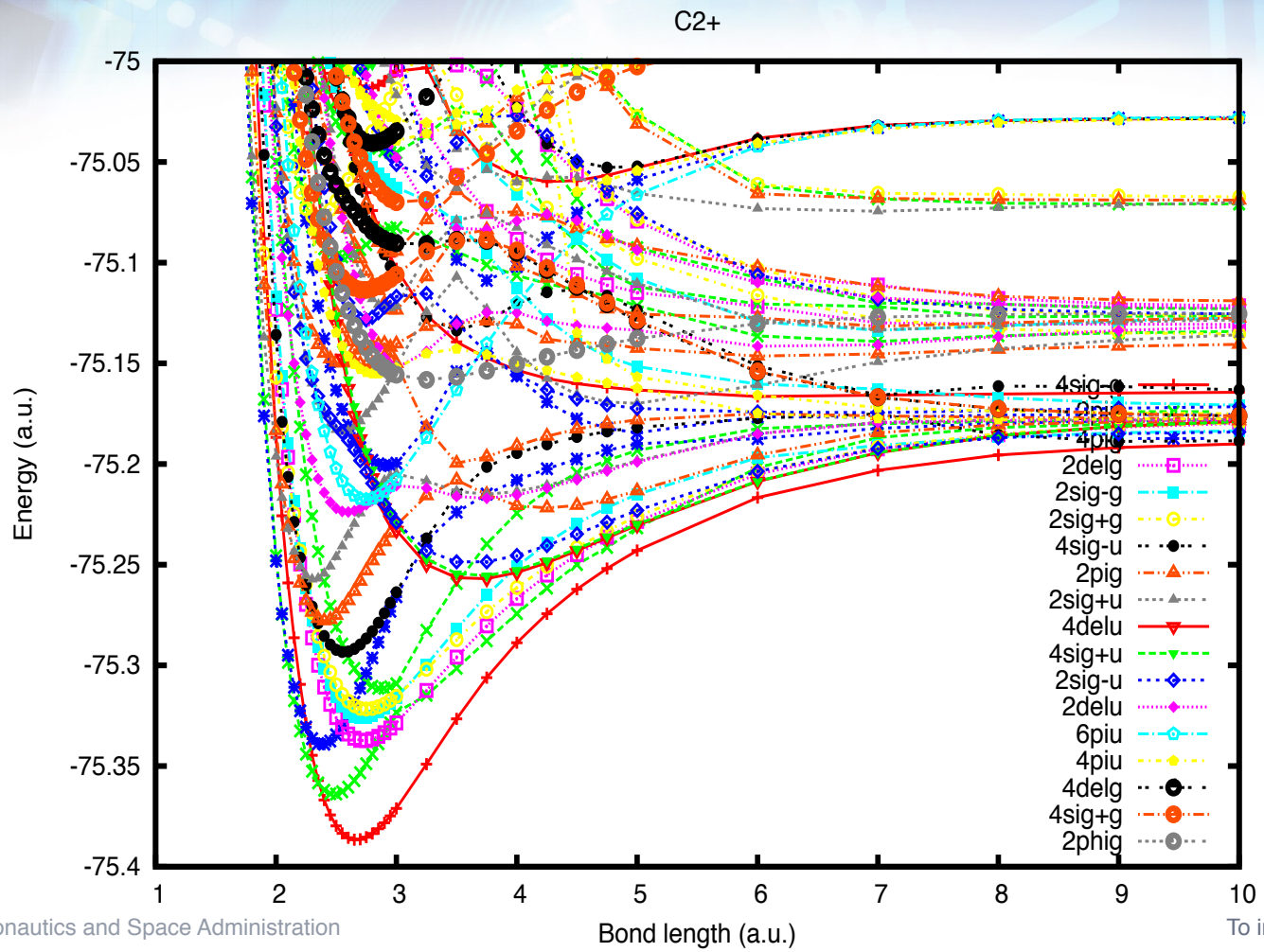
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C) Diabatic States
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   D) Easier to adjust
   E) Splitting

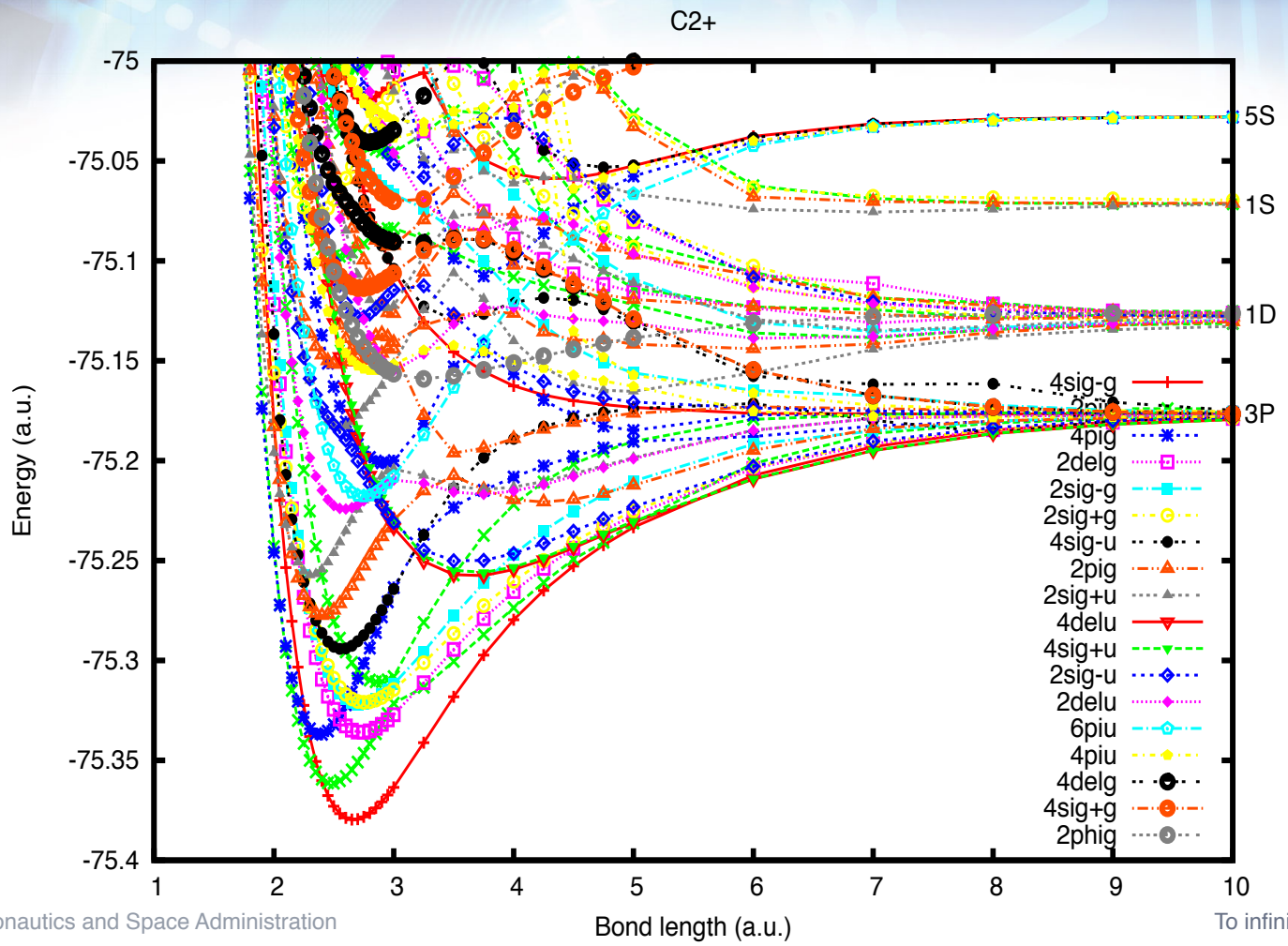



NO 2Pi adiabatic/molecular diabatic states
Energy in Hartree
-129.2
-129.3
-129.4
-129.5
-129.6
-129.7
-129.8
1
2
3
4
5
6
Bond length in Bohr

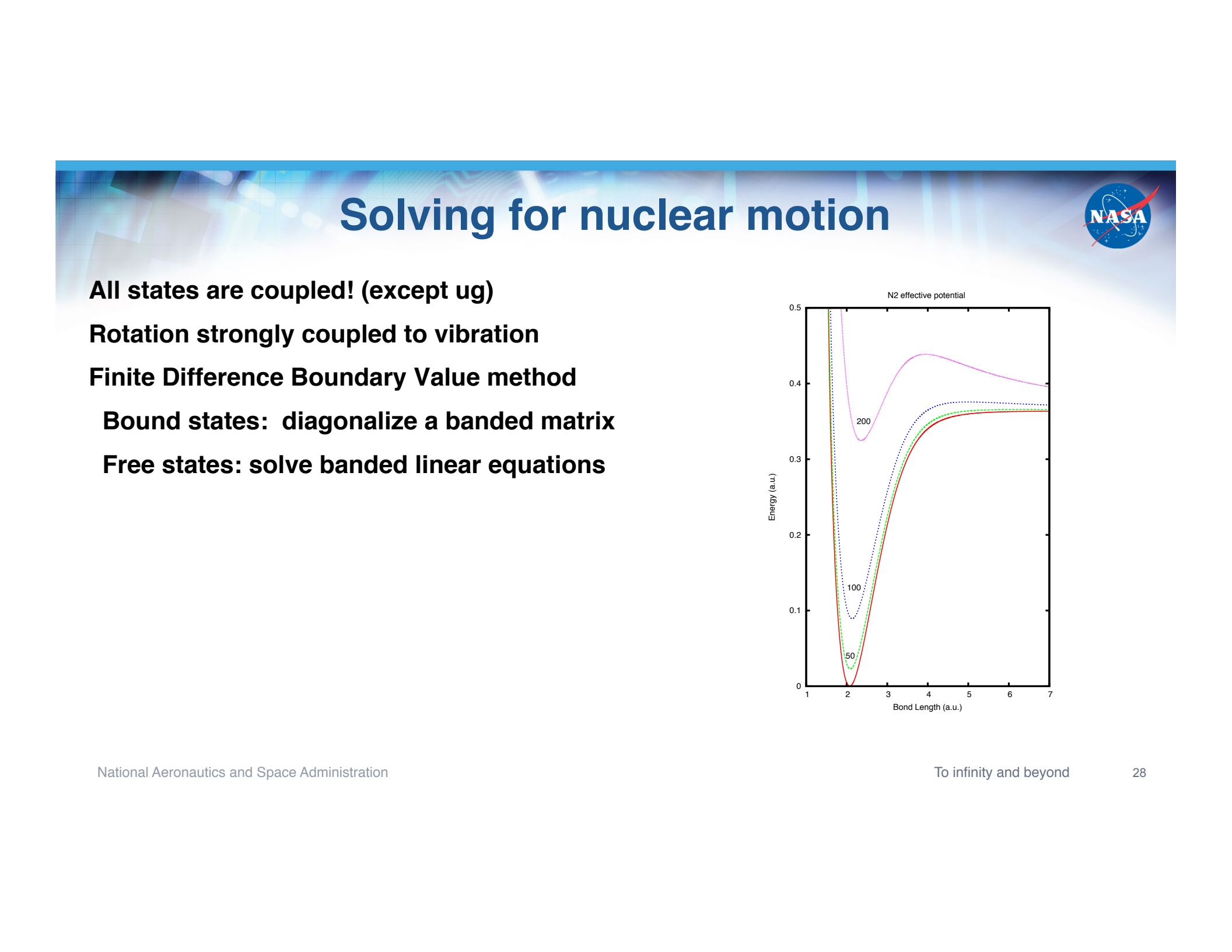

Splitting NO 2Pi
Energy in Hartree
-129
-129.1
-129.2
-129.3
-129.4
-129.5
-129.6
-129.7
-129.8
1
2
3
4
5
6
Bond length in Bohr


Split NO 2Pi
Energy in Hartree
-129
-129.1
-129.2
-129.3
-129.4
-129.5
-129.6
-129.7
-129.8
1
2
3
4
5
6
Bound length in Bohr


C2+
Energy (a.u.)
Bond length (a.u.)
-75
-75.05
-75.1
-75.15
-75.2
-75.25
-75.3
-75.35
-75.4
1
2
3
4
5
6
7
8
9
10
4sig-g
2pig
4pig
2delg
2sig-g
2sig+g
4sig-u
2pig
2sig+u
4delu
4sig+u
2sig-u
2delu
6piu
4piu
4delg
4sig+g
2phig


C2+
Energy (a.u.)
Bond length (a.u.)
-75
-75.05
-75.1
-75.15
-75.2
-75.25
-75.3
-75.35
-75.4
1
2
3
4
5
6
7
8
9
10
5S
1S
1D
3P
4sig-g
4pig
2delg
2sig-g
2sig+g
4sig-u
2pig
2sig+u
4delu
4sig+u
2sig-u
2delu
6piu
4piu
4delg
4sig+g
2phig

Solving for nuclear motion



All states are coupled! (except ug)

Rotation strongly coupled to vibration

Finite Difference Boundary Value method

- **Bound states: diagonalize a banded matrix**
- **Free states: solve banded linear equations**

How to find energies

$$H\psi_\alpha = E_\alpha \psi_\alpha, \qquad \psi_\alpha = \sum_\eta |\eta\rangle F_\eta^\alpha(r)$$

$$H = -\frac{\hbar^2}{2\mu}\sum_\eta |\eta\rangle \frac{\partial^2}{\partial r^2}\langle\eta| + \sum_{\eta\eta'} |\eta\rangle V_{\eta\eta'}(r)\langle\eta'|$$

Bound state:

$$\lim_{r\to 0} F_\eta^\alpha(r) = 0 \text{ and } \lim_{r\to\infty} F_\eta^\alpha(r) = 0$$

b.c. determine energy

Free state:

$$\lim_{r\to 0} F_{\eta'}^{\eta E}(r) = 0$$

$$\lim_{r\to\infty} F_{\eta'}^{\eta E}(r) = k_{\eta'}^{-\frac{1}{2}}\left[\exp\left(-ik_{\eta'}r\right)\delta_{\eta\eta'} - \exp\left(ik_{\eta'}r\right)S_{\eta\eta'}(E)\right]$$

complex

$$k_\eta^2 = 2\mu\left(E - e_\eta\right)$$

incoming outgoing

energy determines b.c.

How to find energies

$$H\psi_\alpha = E_\alpha \psi_\alpha, \qquad \psi_\alpha = \sum_\eta |\eta\rangle F_\eta^\alpha(r)$$

$$H = -\frac{\hbar^2}{2\mu}\sum_\eta |\eta\rangle \frac{\partial^2}{\partial r^2}\langle\eta| + \sum_{\eta\eta'} |\eta\rangle V_{\eta\eta'}(r)\langle\eta'|$$

Bound state:

$$\lim_{r\to 0} F_\eta^\alpha(r) = 0 \text{ and } \lim_{r\to\infty} F_\eta^\alpha(r) = 0$$

b.c. determine energy

acoustics:
echoes,
whisper rooms, …

Free state:

complex

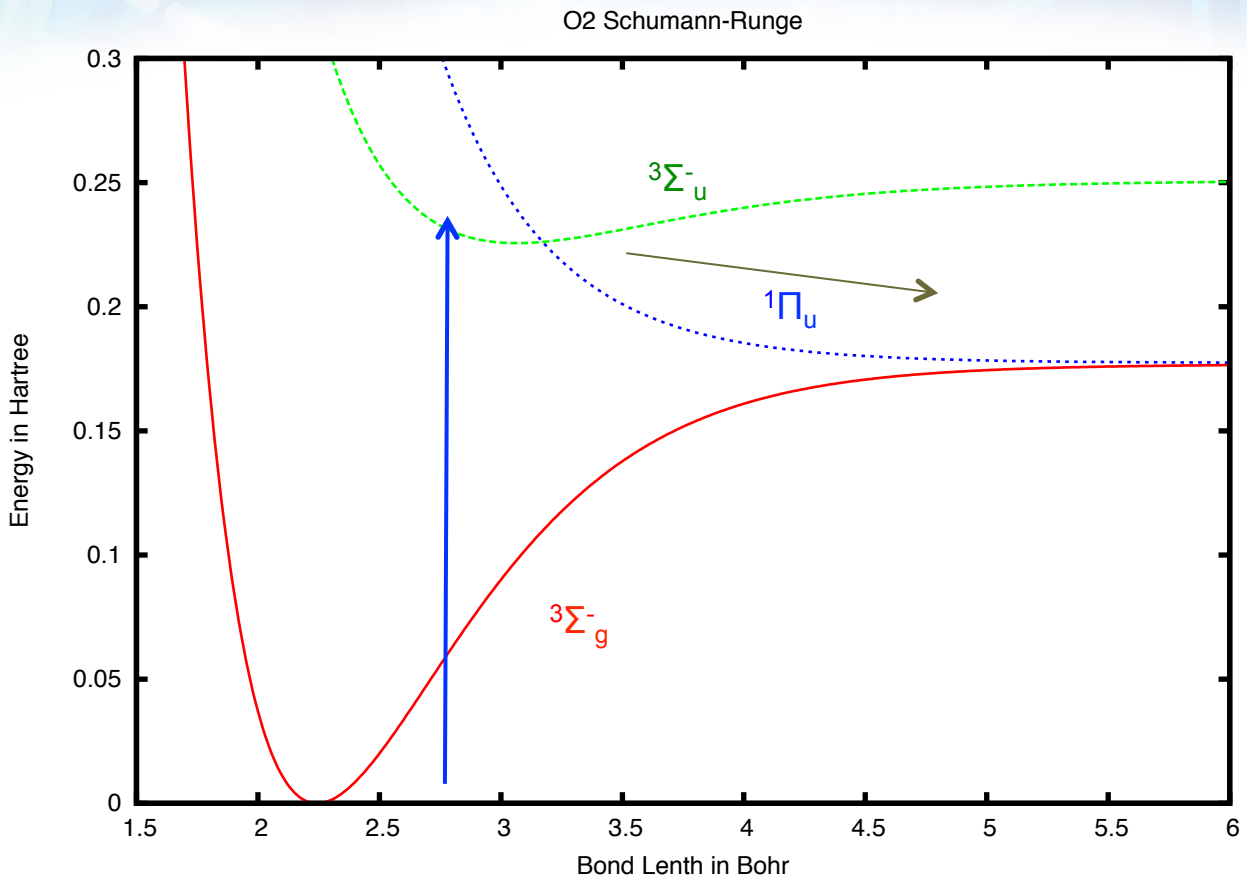
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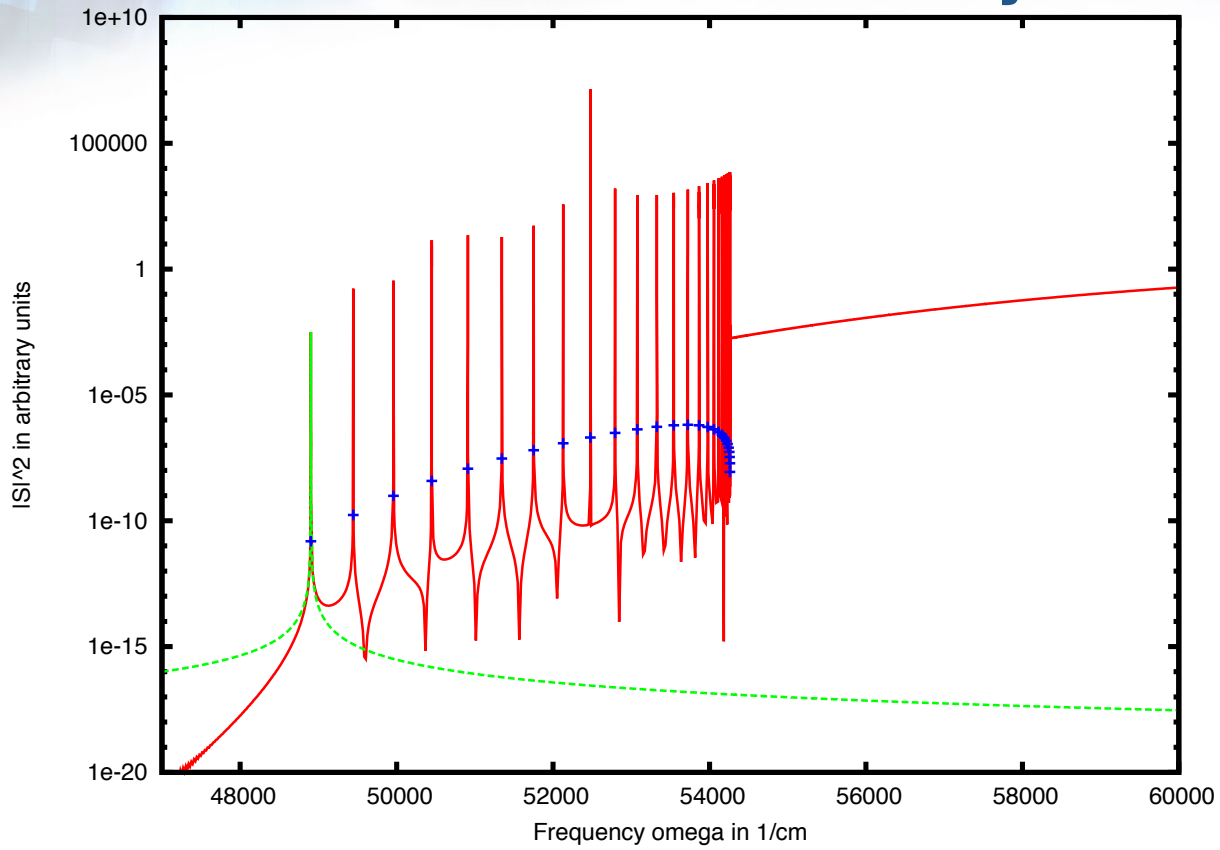
incoming outgoing

$$k_\eta^2 = 2\mu(E - e_\eta)$$

energy determines b.c.

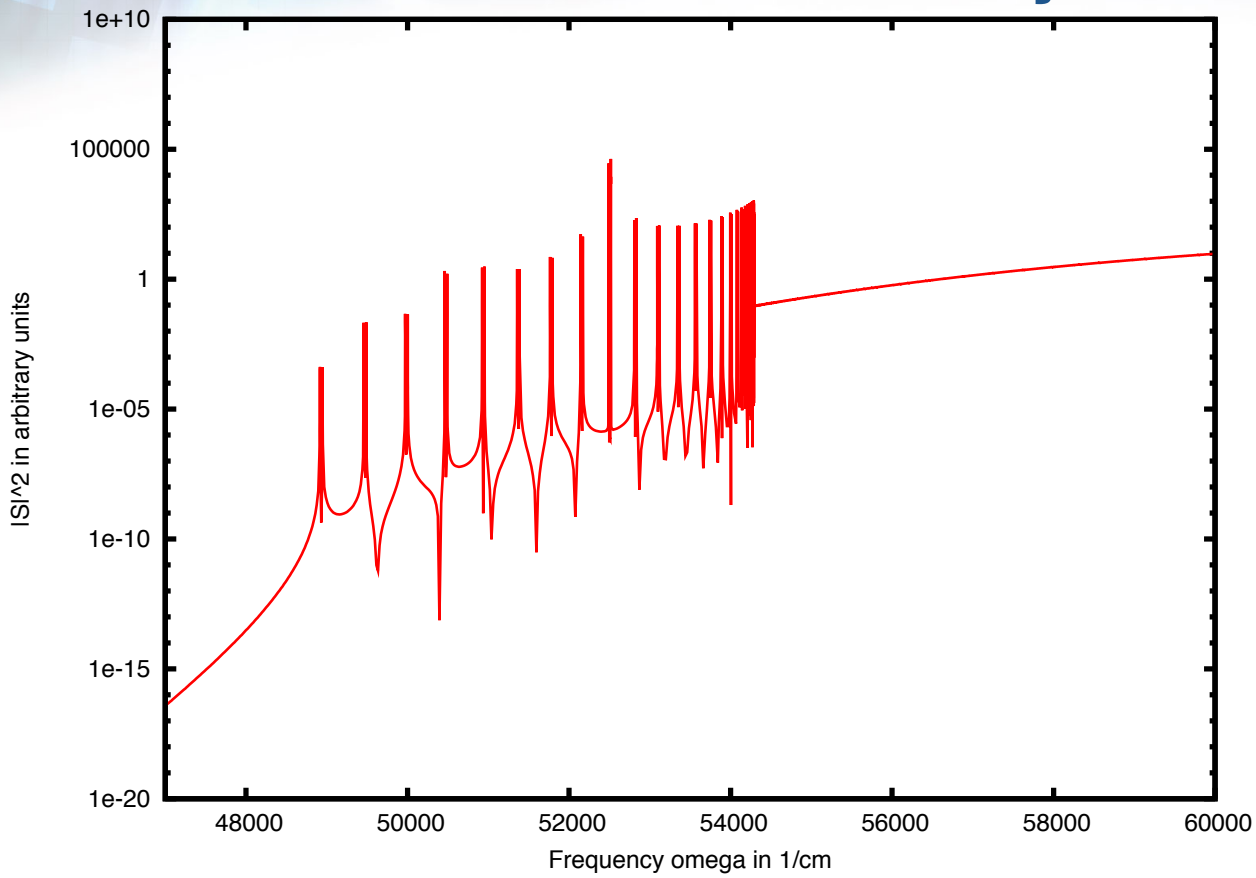

O2 Schumann-Runge
Energy in Hartree
Bond Lenth in Bohr
0.3
0.25
0.2
0.15
0.1
0.05
0
1.5
2
2.5
3
3.5
4
4.5
5
5.5
6
$^3\Sigma^-_u$
$^1\Pi_u$
$^3\Sigma^-_g$

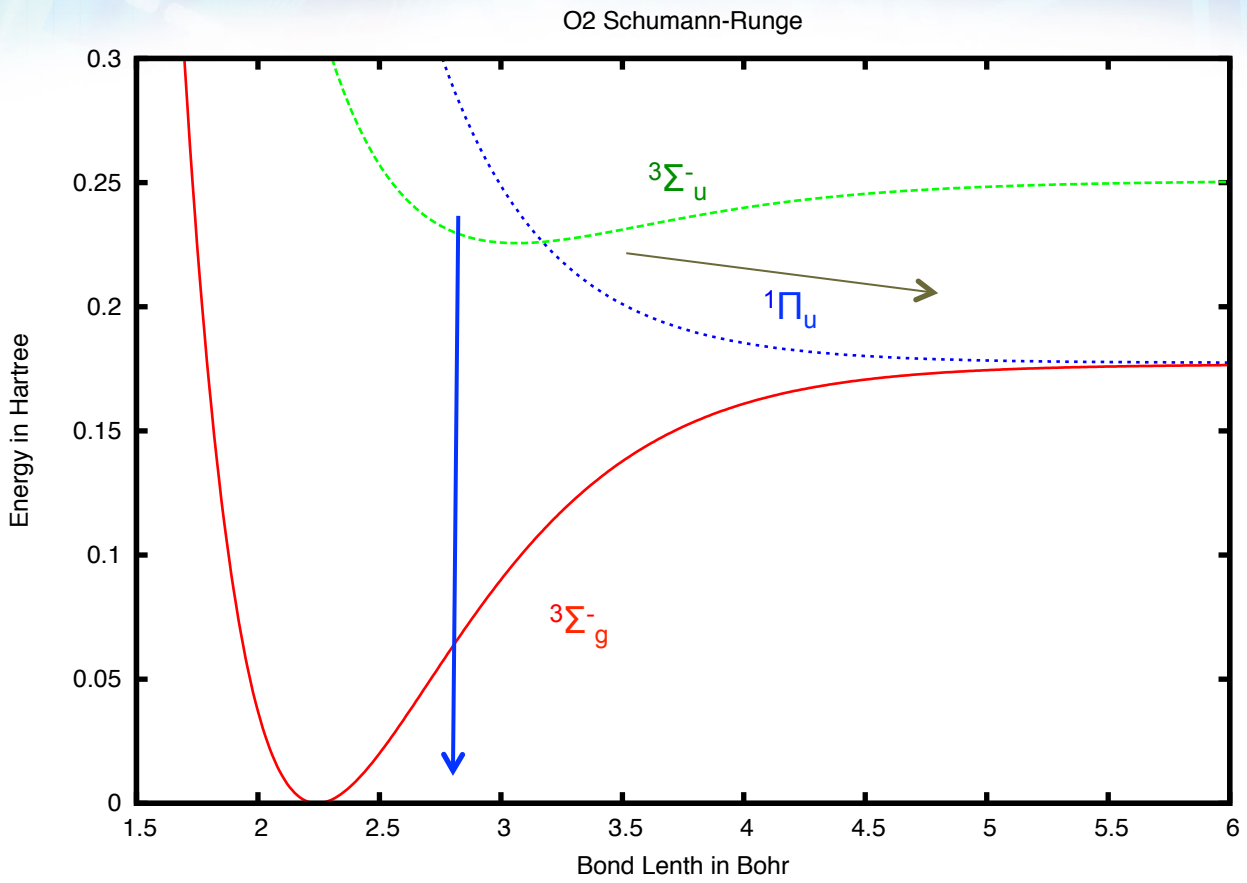
Odd Parity

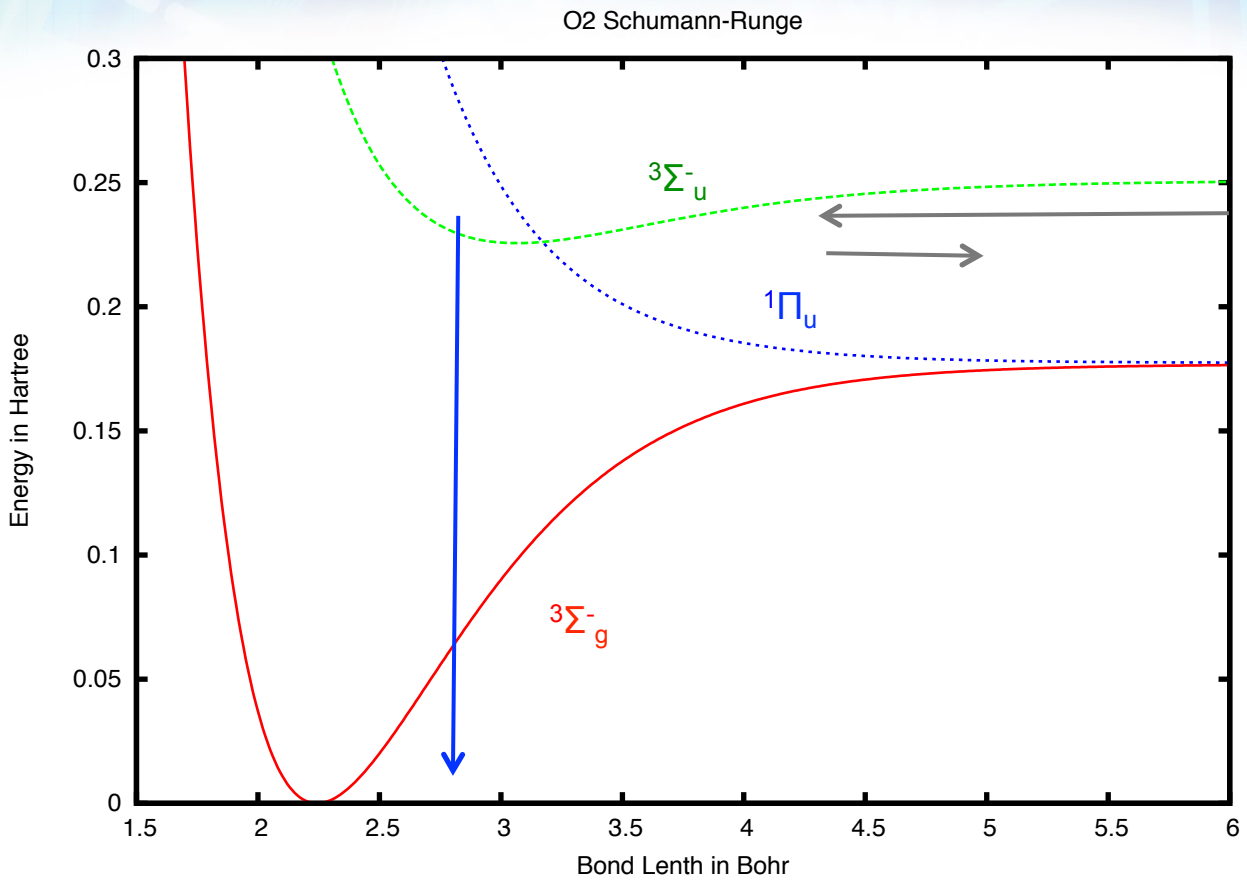


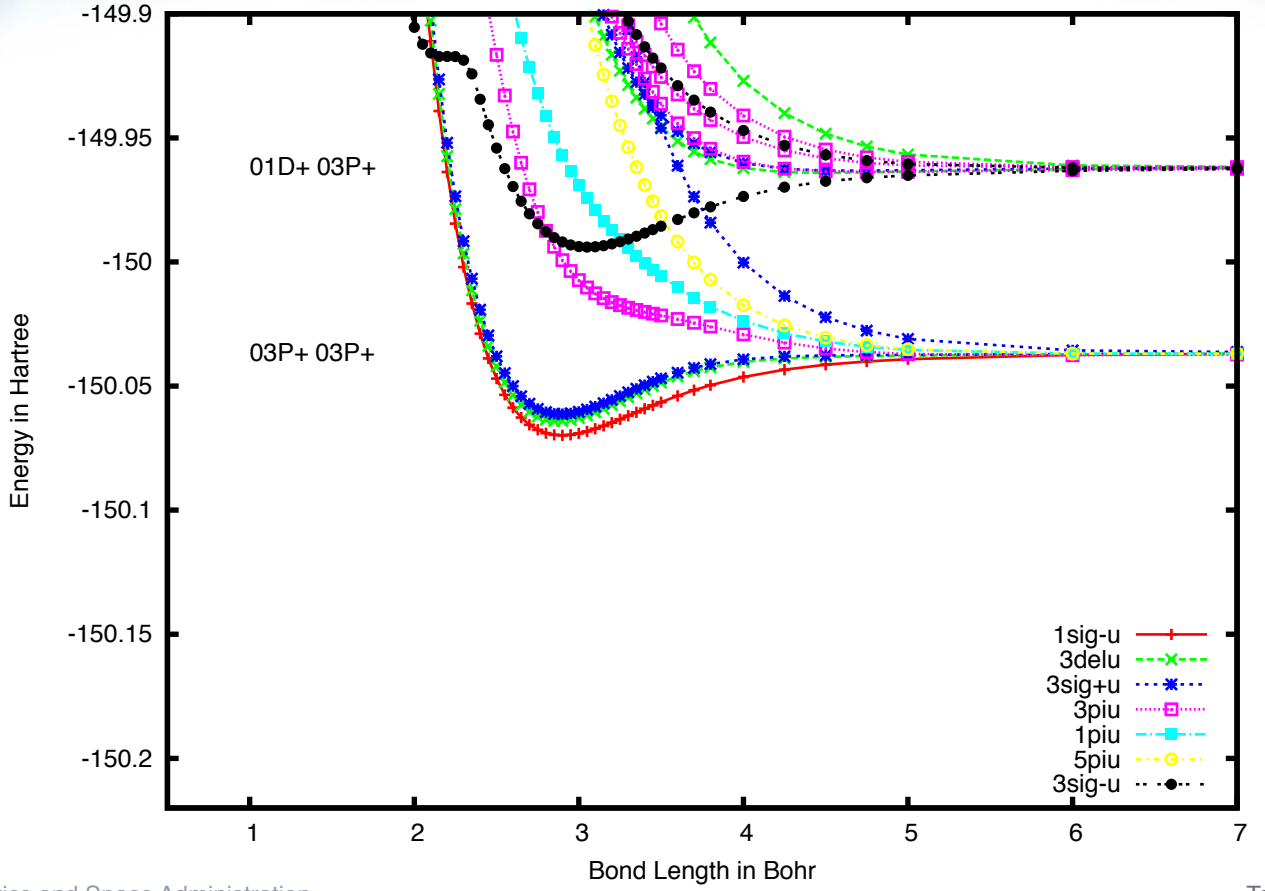
$$\frac{\Gamma_\alpha / 2}{\left(E - E_\alpha\right)^2 + \Gamma_\alpha^2 / 4}$$

Even Parity


1e+10
100000
1
1e-05
1e-10
1e-15
1e-20
|S|^2 in arbitrary units
48000
50000
52000
54000
56000
58000
60000
Frequency omega in 1/cm


O2 Schumann-Runge
Energy in Hartree
Bond Lenth in Bohr
0.3
0.25
0.2
0.15
0.1
0.05
0
1.5
2
2.5
3
3.5
4
4.5
5
5.5
6
$^3\Sigma^-_u$
$^1\Pi_u$
$^3\Sigma^-_g$


O2 Schumann-Runge
Energy in Hartree
Bond Lenth in Bohr
0.3
0.25
0.2
0.15
0.1
0.05
0
1.5
2
2.5
3
3.5
4
4.5
5
5.5
6
$^3\Sigma^-_u$
$^1\Pi_u$
$^3\Sigma^-_g$


-149.9
-149.95
-150
-150.05
-150.1
-150.15
-150.2
Energy in Hartree
01D+ 03P+
03P+ 03P+
1
2
3
4
5
6
7
Bond Length in Bohr
1sig-u
3delu
3sig+u
3piu
1piu
5piu
3sig-u

Line shapes…

Bound-bound

Voigt profile is Gold-Standard

$$L(\nu) = A(\nu_0)\int_0^{\infty} \exp\left[-\frac{(\nu-\nu')^2}{2\sigma^2}\right]\frac{\gamma/2}{(\nu'-\nu_0)^2+\gamma^2/4}\,d\nu'$$

Bound-free

$$L(\nu) \overset{?}{=} A(\nu_0)\int_0^{\infty} \exp\left[-\frac{(\nu-\nu')^2}{2\sigma^2}\right]\frac{\gamma'/2}{(\nu'-\nu_0)^2+\gamma'^2/4}\,d\nu',$$

$$\gamma' = \gamma + \Gamma$$

Line shapes…

Bound-bound

Voigt profile is Gold-Standard

$$L(\nu) = A(\nu_0)\int_0^\infty \exp\left[-\frac{(\nu-\nu')^2}{2\sigma^2}\right]\frac{\gamma/2}{(\nu'-\nu_0)^2+\gamma^2/4}\,d\nu'$$

Bound-free

$$L(\nu) \overset{?}{=} A(\nu_0)\int_0^\infty \exp\left[-\frac{(\nu-\nu')^2}{2\sigma^2}\right]\frac{\gamma'/2}{(\nu'-\nu_0)^2+\gamma'^2/4}\,d\nu',$$

$$\gamma' = \gamma + \Gamma$$

$$\sigma = \frac{\nu'}{c}\sqrt{\frac{kT}{m}}$$

$$A(\nu_0) = \frac{4\nu_0^3}{3gc^3\hbar}|\mu|^3$$

Review

- Hypersonic Re-entry
- Spectroscopy
- Quantum Mechanics
- Born-Oppenheimer Approximation
- Electronic Structure Calculations
- Diabatic States
- Bound vs. Free states
- Line shapes



