CN Spectroscopy from the IR (microns) to the VUV (1000 Å)

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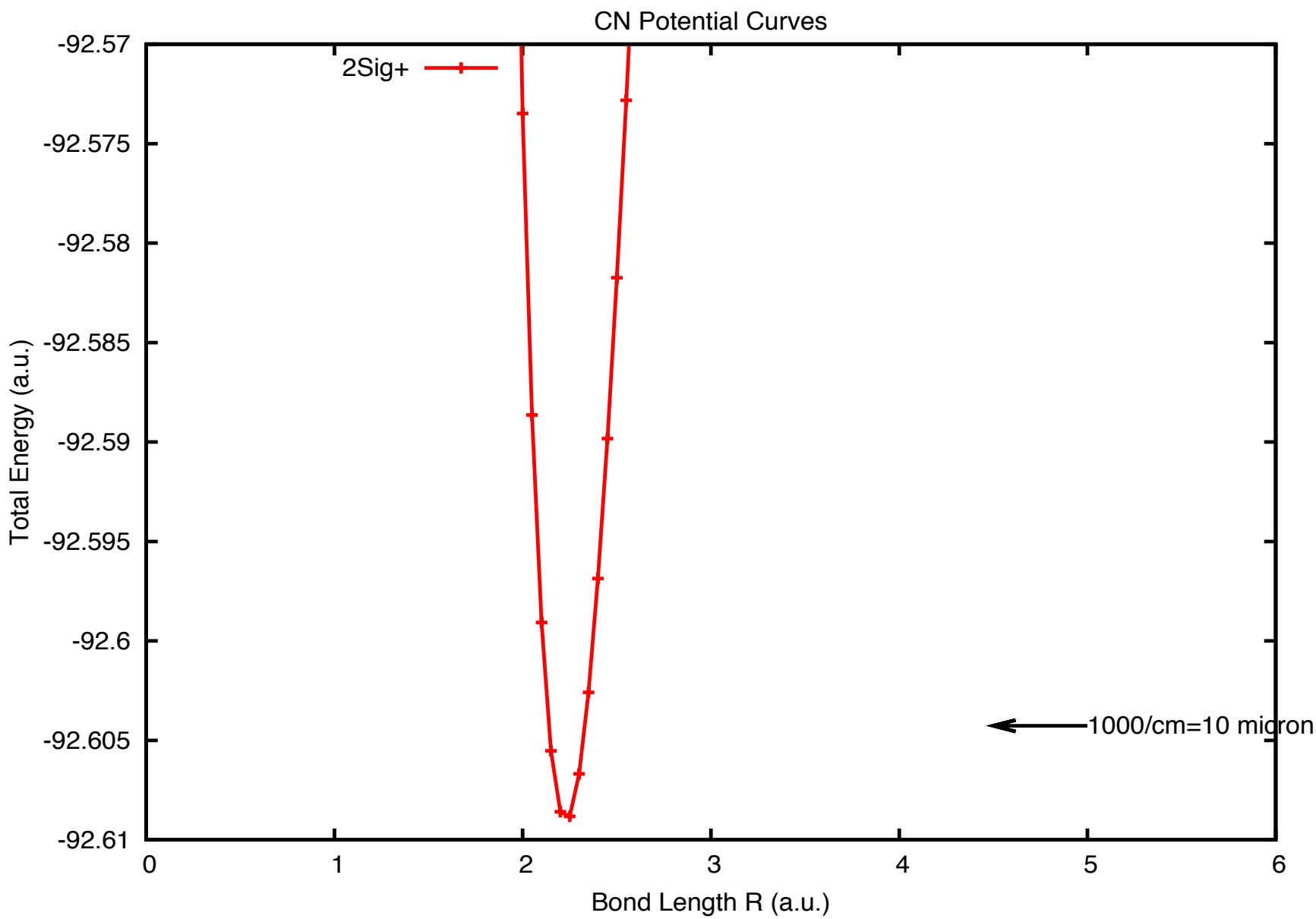
Hypersonics Entry Descent and Landing Project
HyperRad

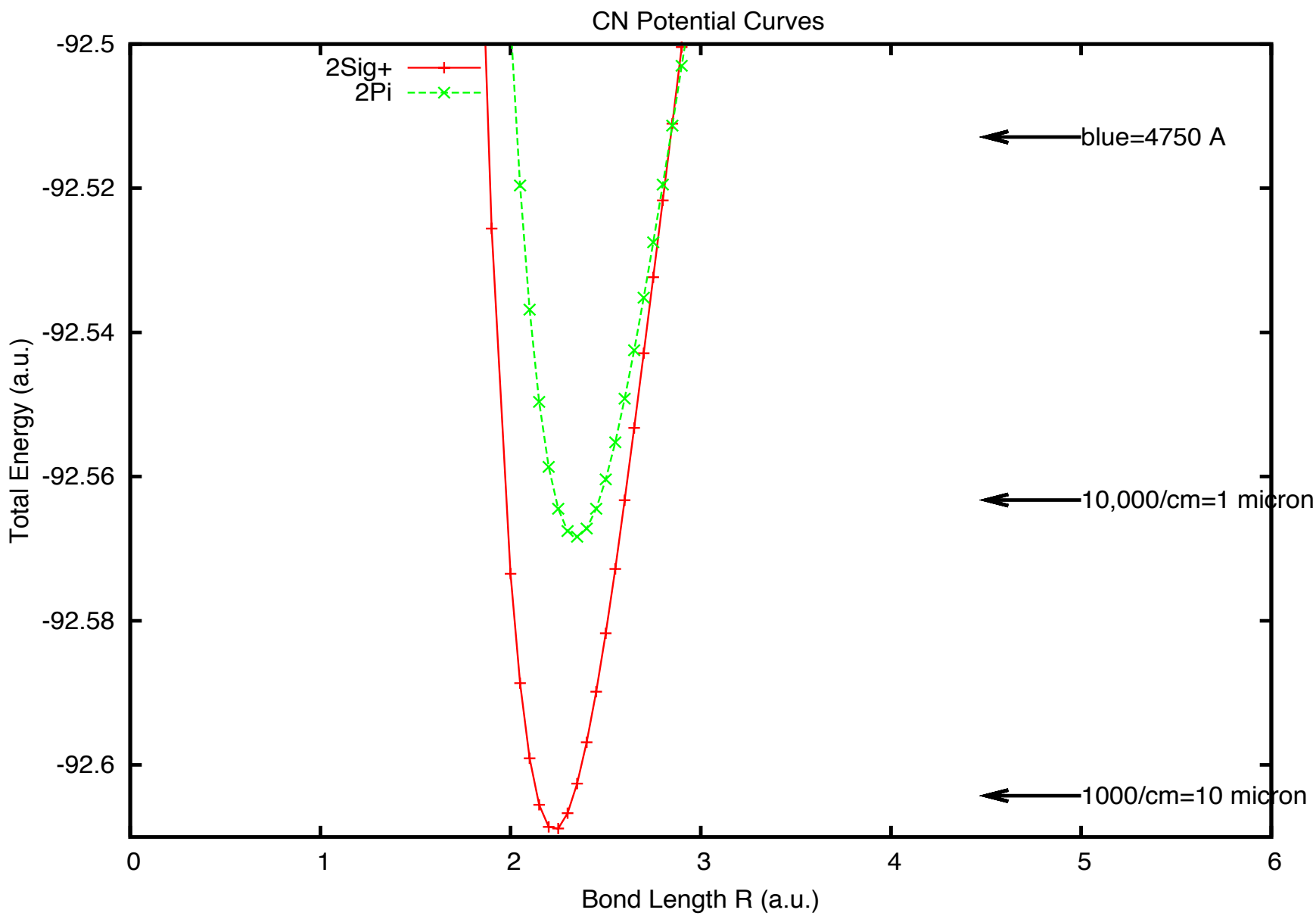
Details of Calculations

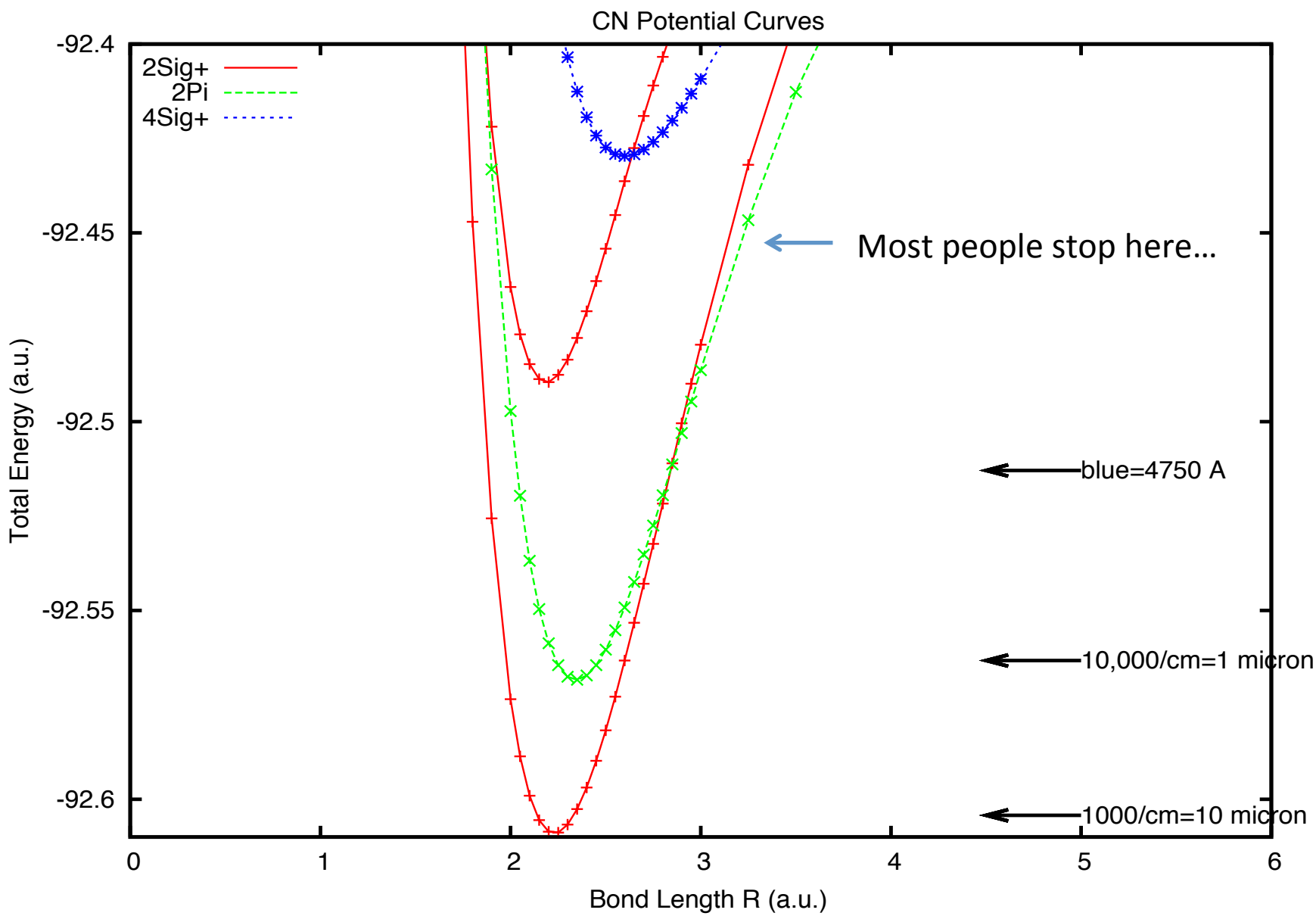
- Electronic structure
  - MOLPRO
    - t-aug-ccPVTZ
    - DK, valence orbs from inward dynamically weighted multi-state MCHF, 4 Rydberg orbs from outward MCHF
    - Projected state icMRCI

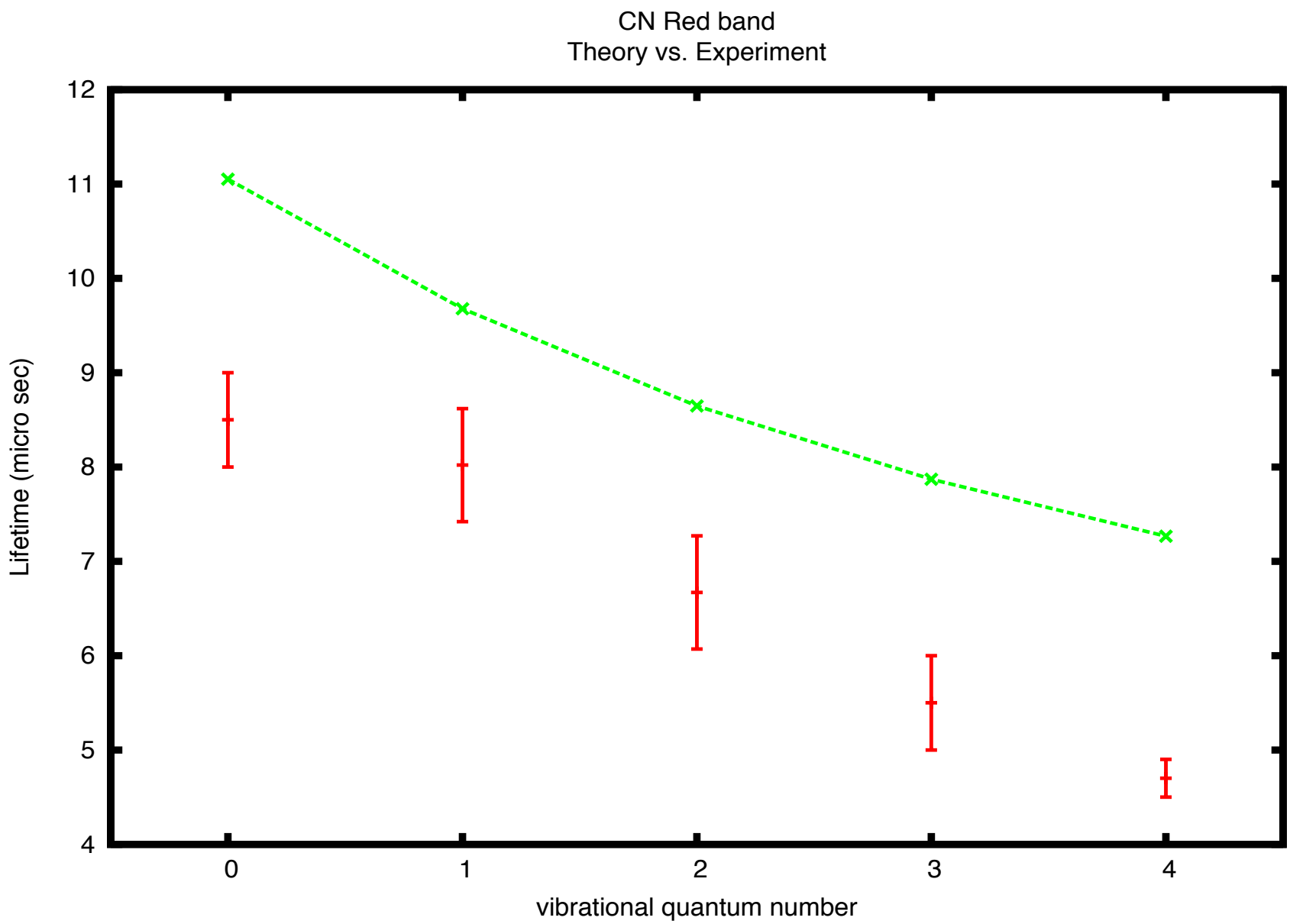
$$H_{nn'}, S_{nn'}, \vec{d}_{nn'}, \vec{\vec{q}}_{nn'}, \vec{l}_{nn'}, \vec{M}^{SO}_{nn'}$$

- Nuclear dynamics
  - ODIE
    - Openshell Diatomic Intensity and Energy
    - Full coupling, F.D.B.V.M.


CN Potential Curves
2Sig+
Total Energy (a.u.)
-92.57
-92.575
-92.58
-92.585
-92.59
-92.595
-92.6
-92.605
-92.61
0
1
2
3
4
5
6
Bond Length R (a.u.)
1000/cm=10 micron


CN Potential Curves
2Sig+
2Pi
blue=4750 A
10,000/cm=1 micron
1000/cm=10 micron
Total Energy (a.u.)
Bond Length R (a.u.)
-92.5
-92.52
-92.54
-92.56
-92.58
-92.6
0
1
2
3
4
5
6

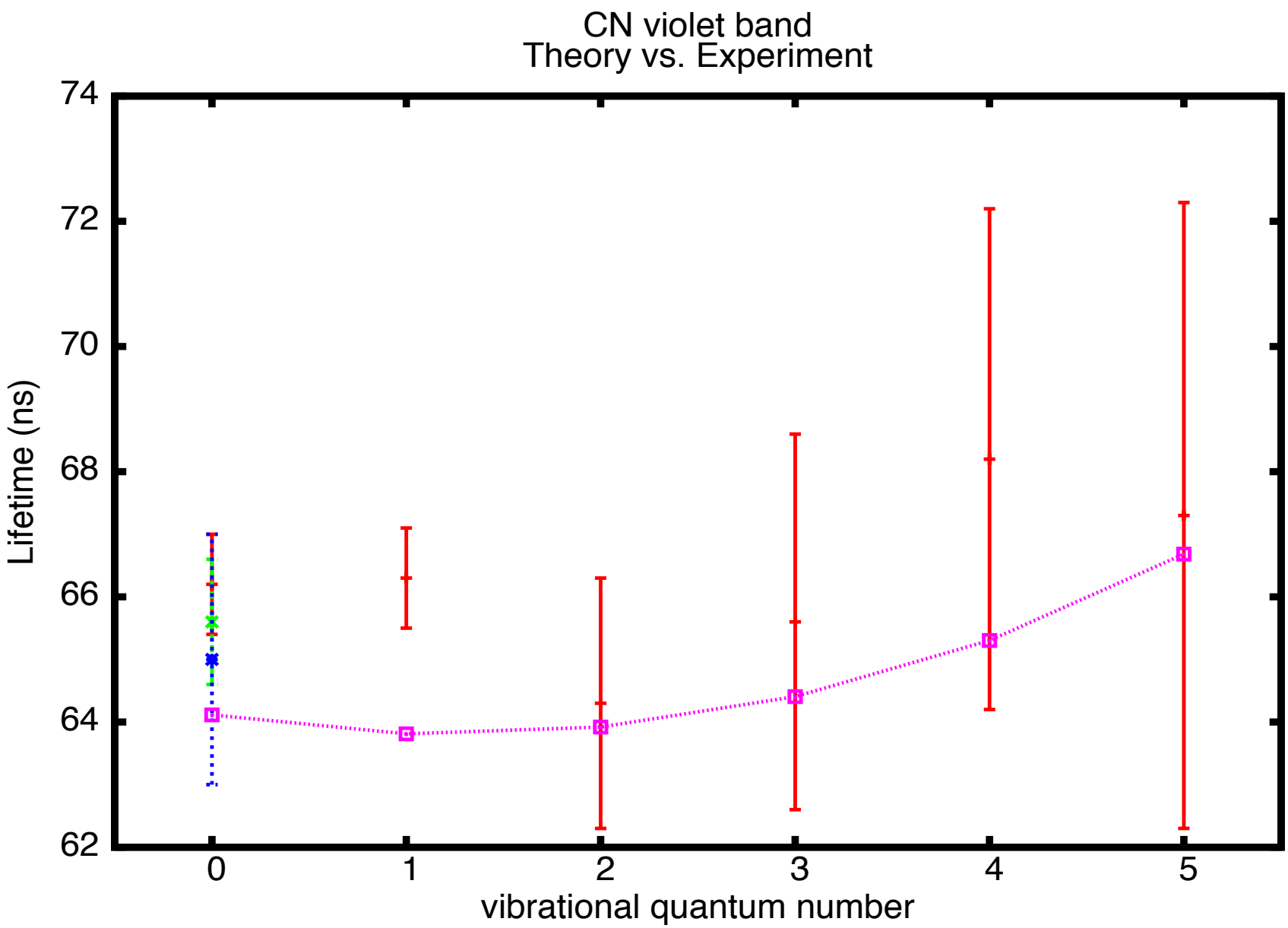

CN Potential Curves
2Sig+
2Pi
4Sig+
Most people stop here...
blue=4750 A
10,000/cm=1 micron
1000/cm=10 micron
Total Energy (a.u.)
Bond Length R (a.u.)
-92.4
-92.45
-92.5
-92.55
-92.6
0
1
2
3
4
5
6

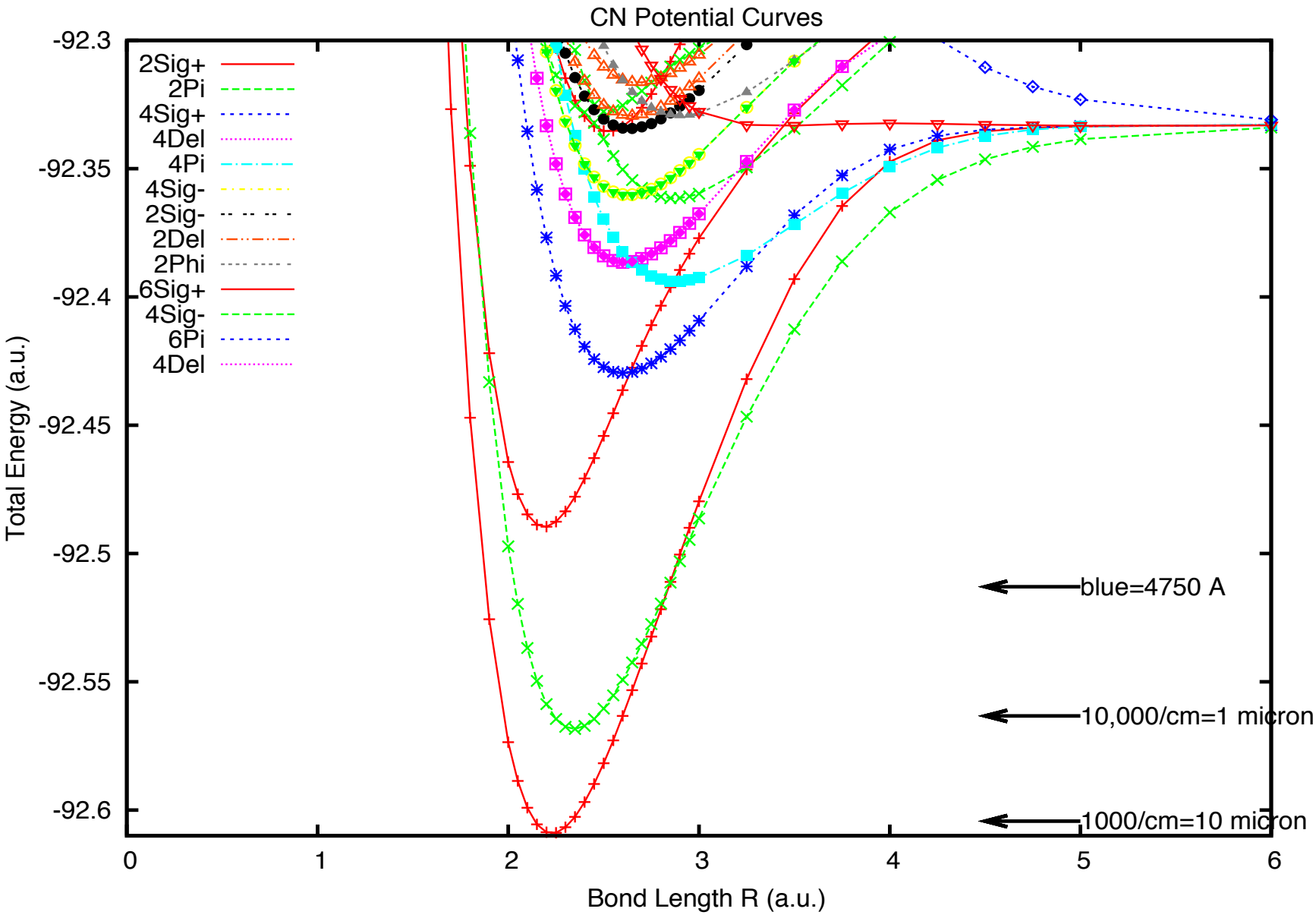

CN Red band
Theory vs. Experiment
Lifetime (micro sec)
12
11
10
9
8
7
6
5
4
0
1
2
3
4
vibrational quantum number

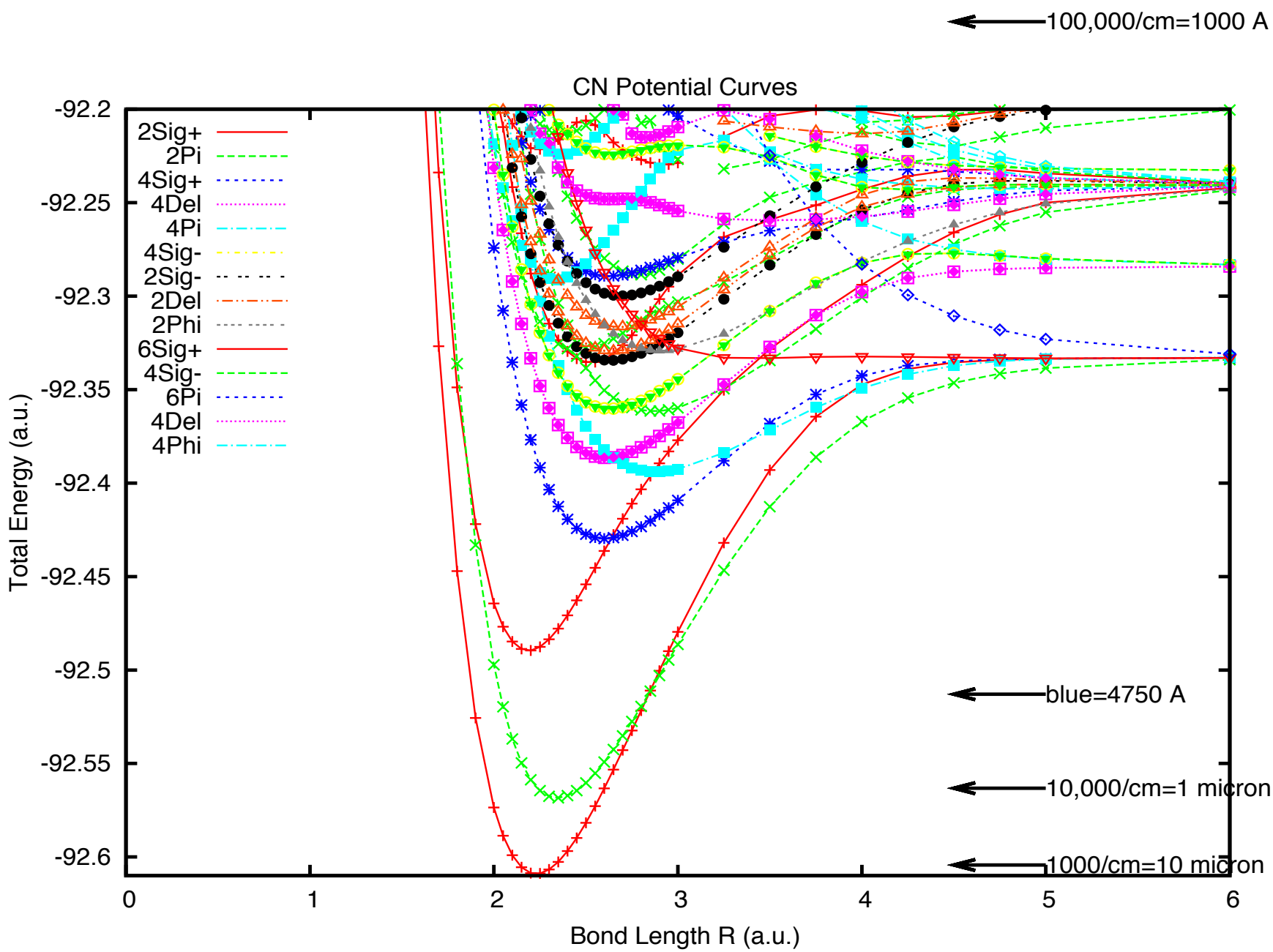
Experimental issues

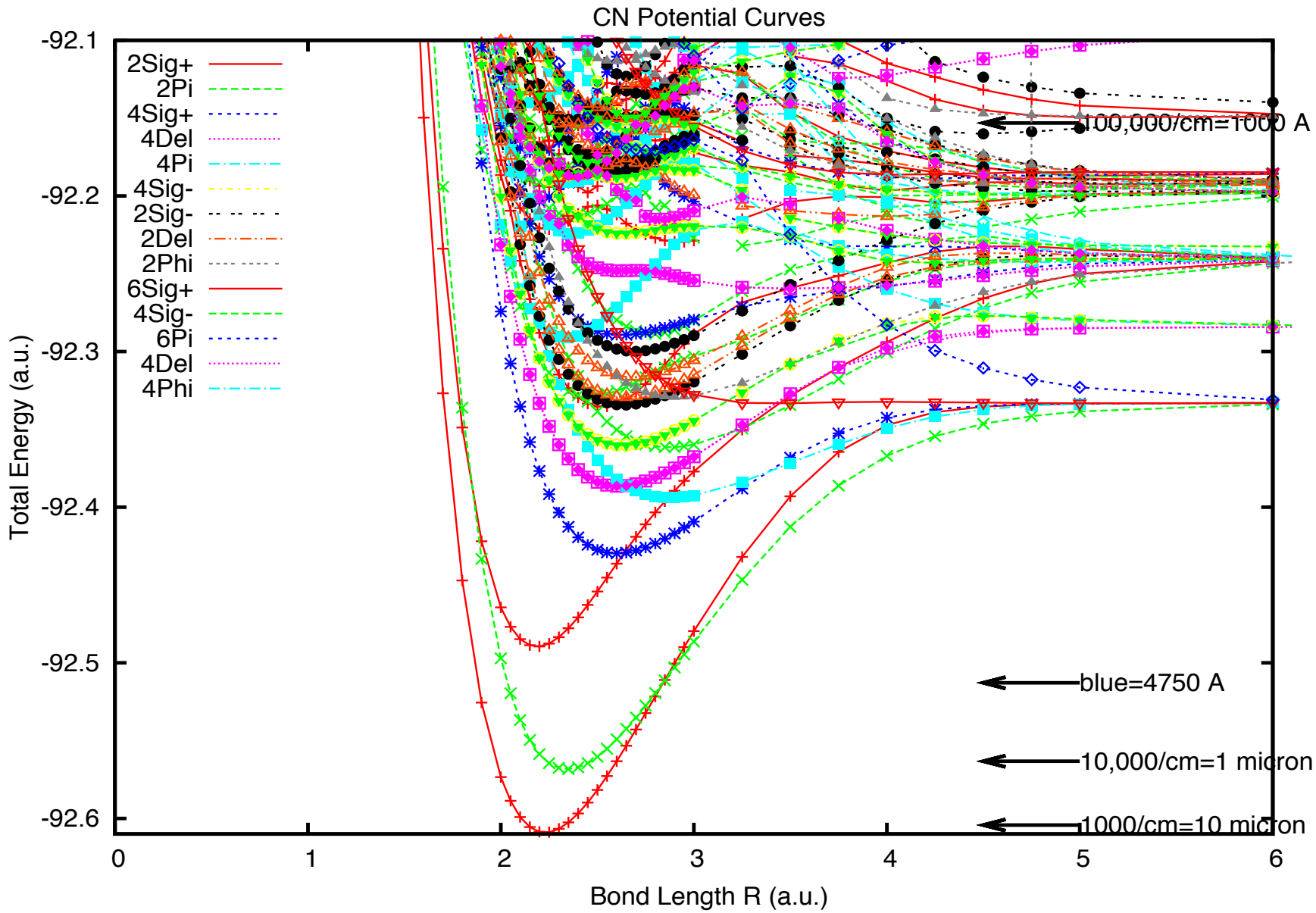
Taherian and Slanger, J. Chem. Phys. **81**, 3814 (1984)

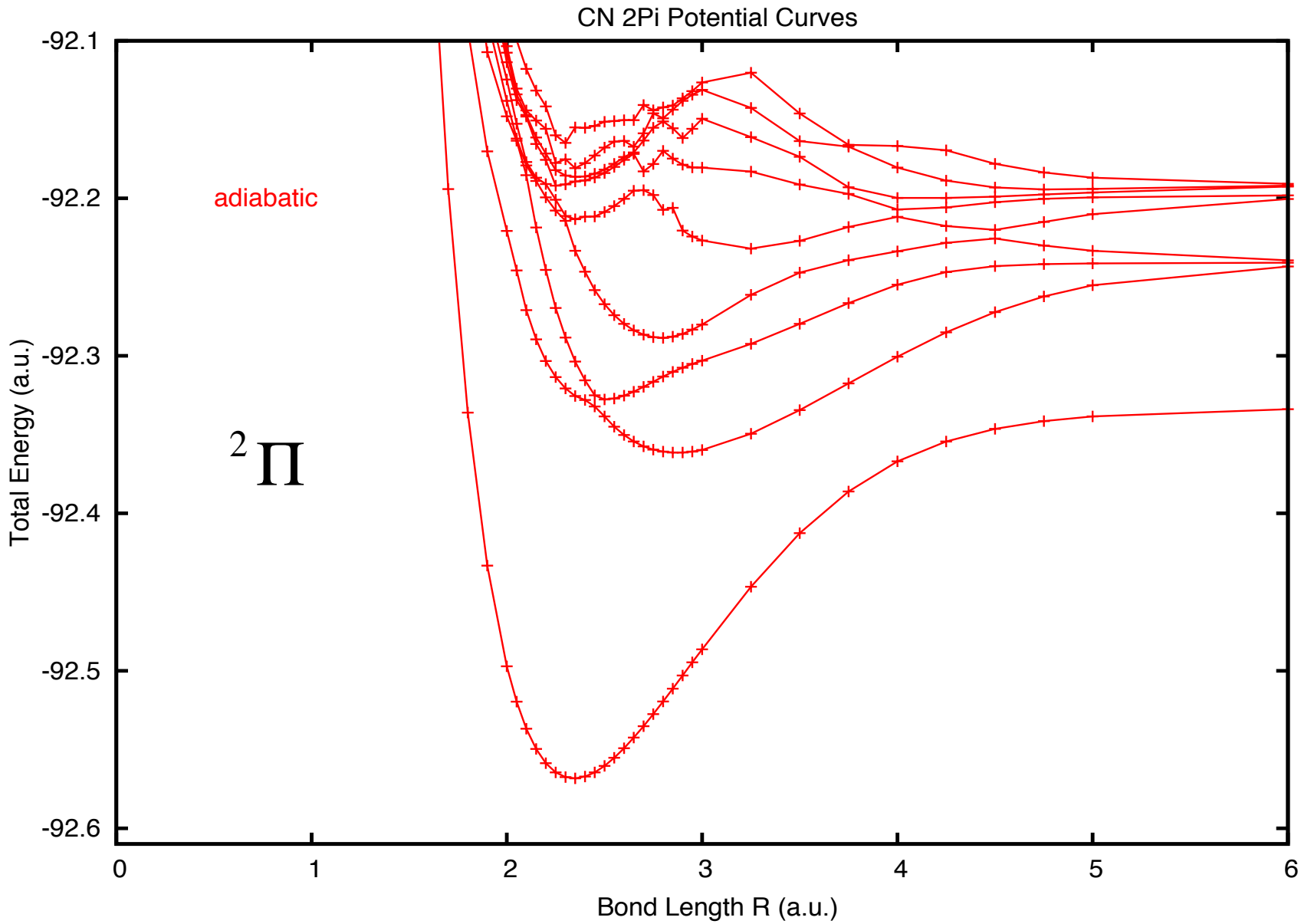
- Error bars are from decay rate fit to pressure
- Diffusion was not considered
- Results were in good agreement with best available *ab initio* calculations… circa 1983

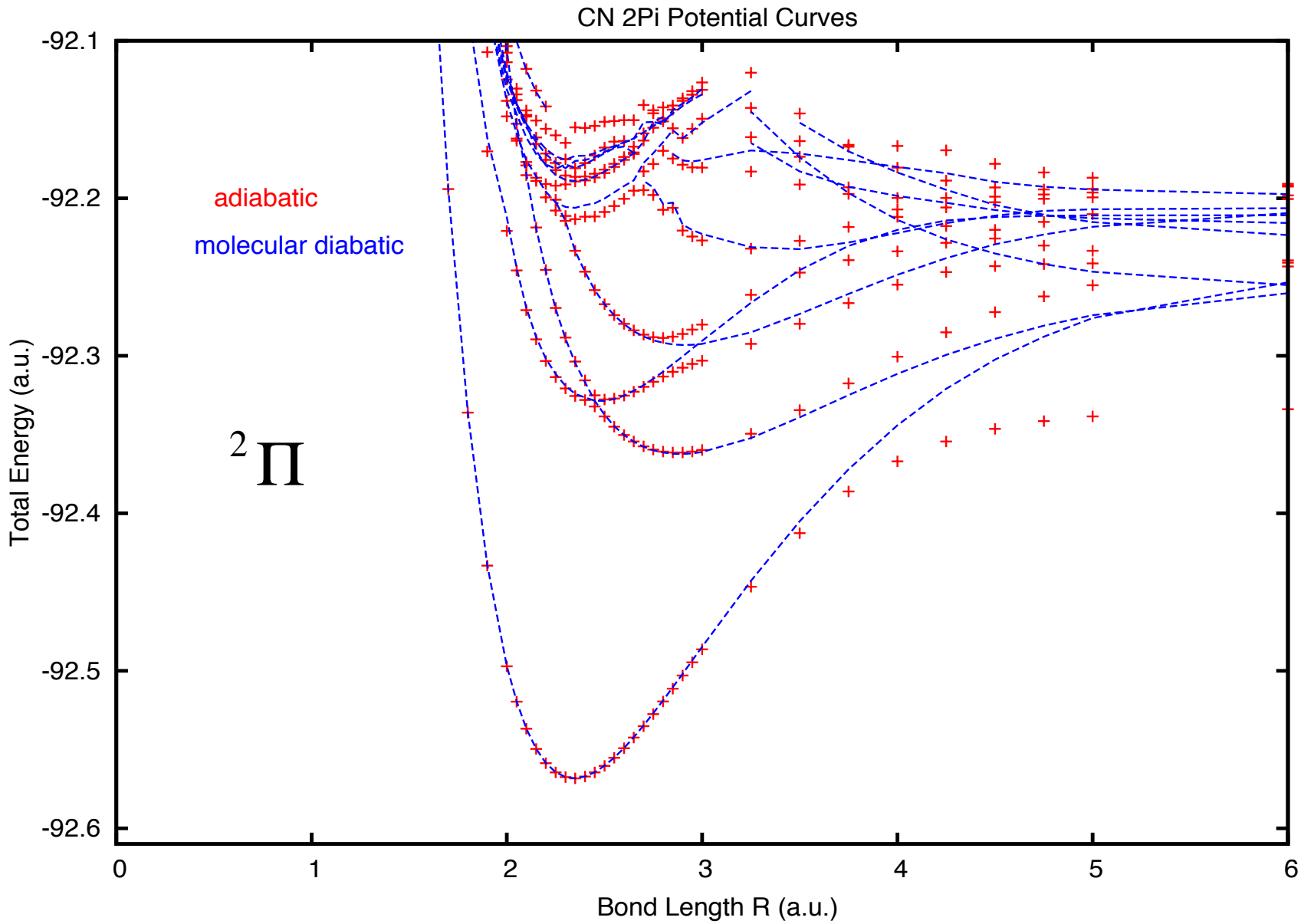

CN violet band
Theory vs. Experiment
Lifetime (ns)
74
72
70
68
66
64
62
0
1
2
3
4
5
vibrational quantum number

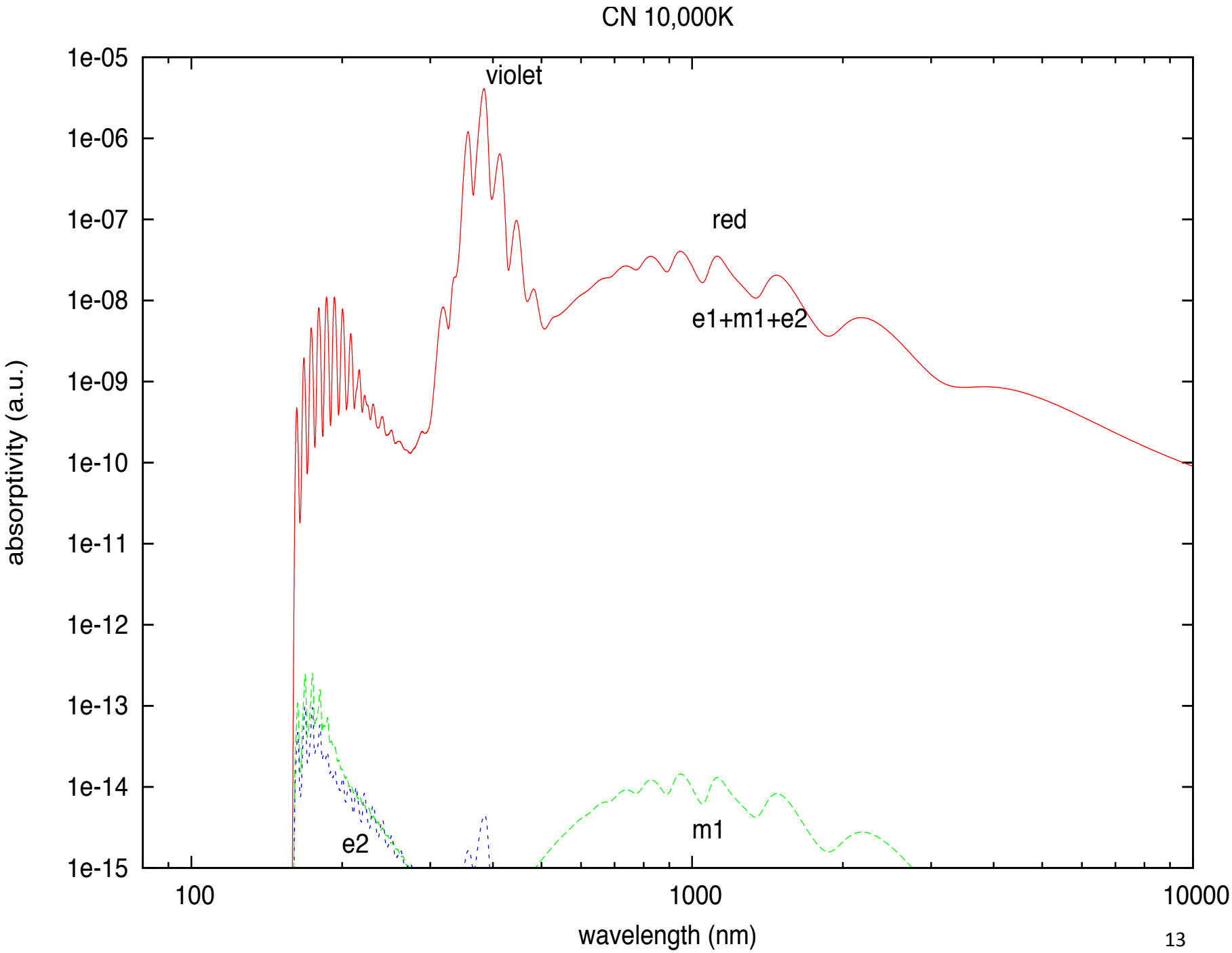

CN Potential Curves
Total Energy (a.u.)
Bond Length R (a.u.)
-92.3
-92.35
-92.4
-92.45
-92.5
-92.55
-92.6
0
1
2
3
4
5
6
2Sig+
2Pi
4Sig+
4Del
4Pi
4Sig-
2Sig-
2Del
2Phi
6Sig+
4Sig-
6Pi
4Del
blue=4750 A
10,000/cm=1 micron
1000/cm=10 micron


100,000/cm=1000 A
CN Potential Curves
2Sig+
2Pi
4Sig+
4Del
4Pi
4Sig-
2Sig-
2Del
2Phi
6Sig+
4Sig-
6Pi
4Del
4Phi
blue=4750 A
10,000/cm=1 micron
1000/cm=10 micron
Total Energy (a.u.)
Bond Length R (a.u.)
-92.2
-92.25
-92.3
-92.35
-92.4
-92.45
-92.5
-92.55
-92.6
0
1
2
3
4
5
6

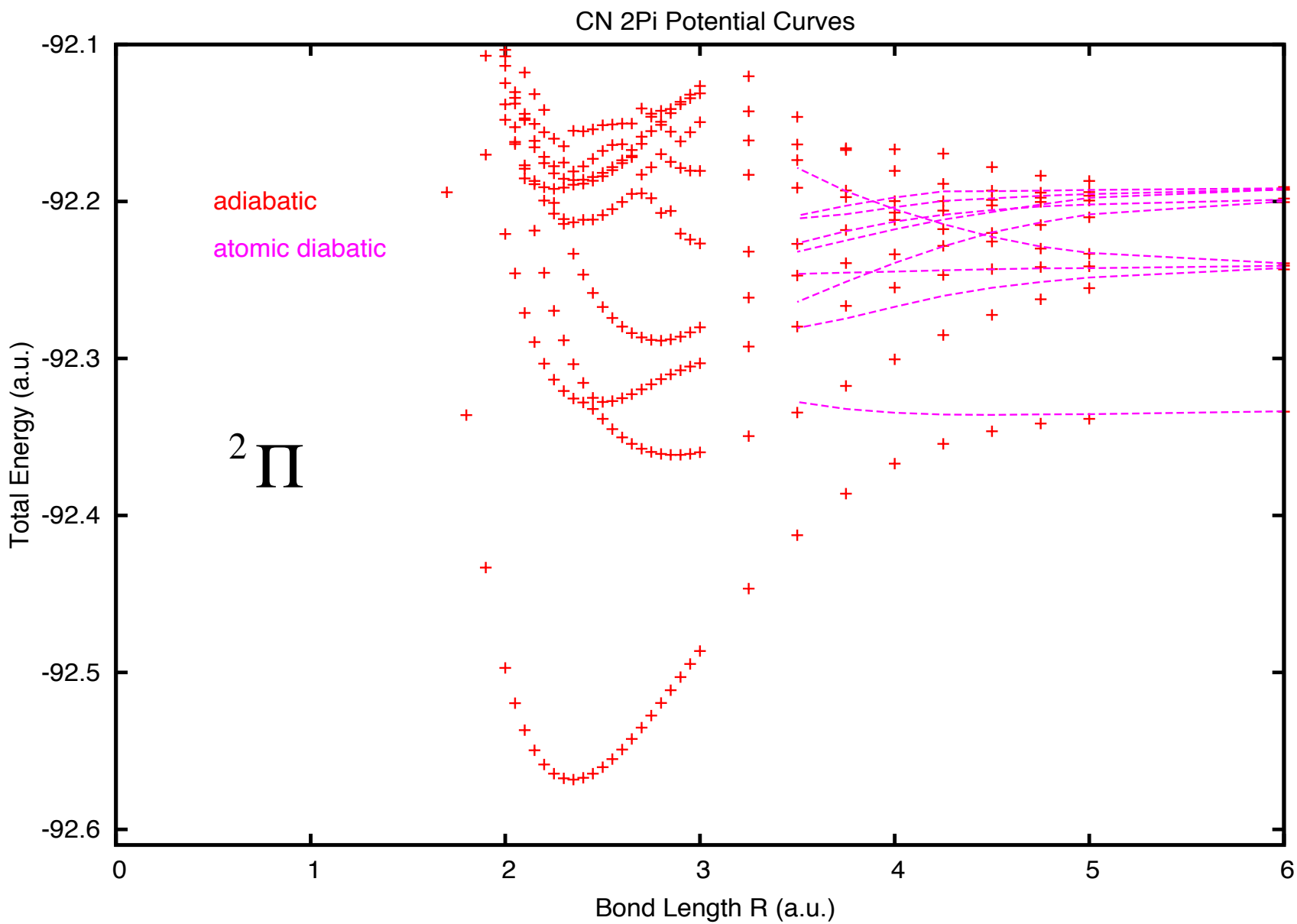

CN Potential Curves
Total Energy (a.u.)
Bond Length R (a.u.)
-92.1
-92.2
-92.3
-92.4
-92.5
-92.6
0
1
2
3
4
5
6
2Sig+
2Pi
4Sig+
4Del
4Pi
4Sig-
2Sig-
2Del
2Phi
6Sig+
4Sig-
6Pi
4Del
4Phi
100,000/cm=1000 A
blue=4750 A
10,000/cm=1 micron
1000/cm=10 micron


CN 2Pi Potential Curves
adiabatic
$^2\Pi$
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


CN 2Pi Potential Curves
adiabatic
molecular diabatic
$^2\Pi$
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


CN 10,000K
violet
red
e1+m1+e2
e2
m1
absorptivity (a.u.)
wavelength (nm)
1e-05
1e-06
1e-07
1e-08
1e-09
1e-10
1e-11
1e-12
1e-13
1e-14
1e-15
100
1000
10000

- Below dissociation limit eigenvalue problem
  - Spontaneous emission: $\mathrm{CN}(n) \rightarrow \mathrm{CN}(n') + h\nu$
    - Einstein A (units inverse time)
  - Stimulated emission
  - Absorption: $\mathrm{CN}(n) + h\nu \rightarrow \mathrm{CN}(n')$
- Above dissociation limit boundary value problem
  - All of the above
  - And Inverse Pre-dissociation: $\mathrm{C}(n) + \mathrm{N}(n'') \rightarrow \mathrm{CN}(n') + h\nu$
    - cross section (units area)


CN 2Pi Potential Curves
adiabatic
atomic diabatic
$^2\Pi$
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

Conclusions and Future Work

- CN Red experimental lifetimes wrong
- Molecular diabatic states critical for high states
- Line list for all bound-bound transitions
  - Only e1 important
  - 69 Million lines
- Clean up adiabatic states
- Merge higher level calculations
- Lineshapes