Resonant Dissociative Attachment, Vibrational Excitation and Recombination of Molecules and Molecular Ions

Ann E. Orel

Department of Applied Science

University of California, Davis

Work supported by the US DOE Office of Basic Energy Science, Division of Chemical Sciences and by the National Science Foundation


Collaborators
S. Chourou
V. Ngassam
T. Rescigno
J. Royal
C. Trevisan

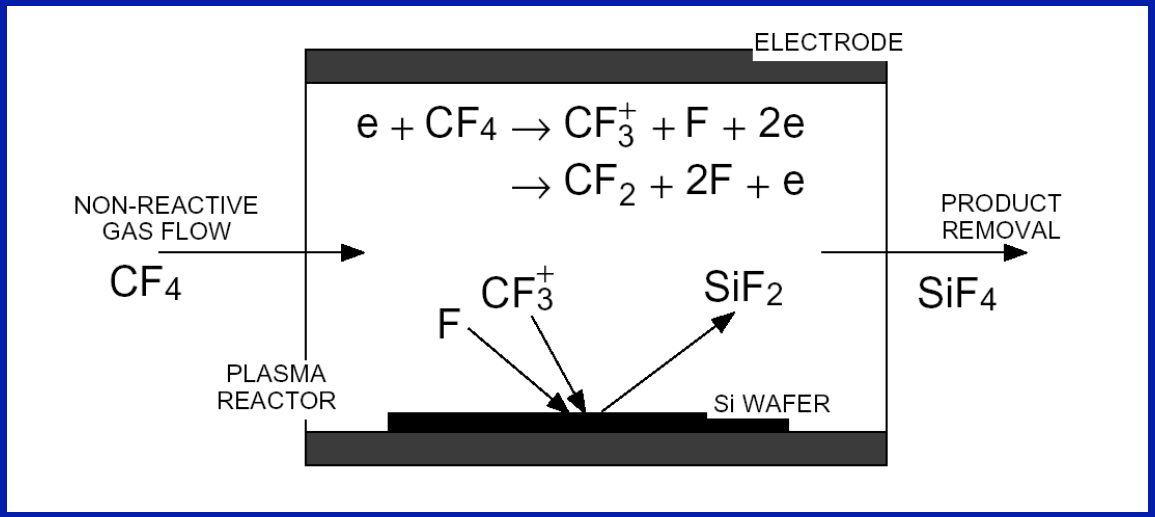
OUTLINE

- Why is low-energy electron scattering important?
- How do we address the problem?
- Examples
  - Dissociative Recombination of Rare Gas Ions
  - Dissociative Attachment of Formic Acid
  - Dissociative Attachment of C_2H_2

Electron-Driven Chemistry Plays a Crucial Role in a Multitude of Applications

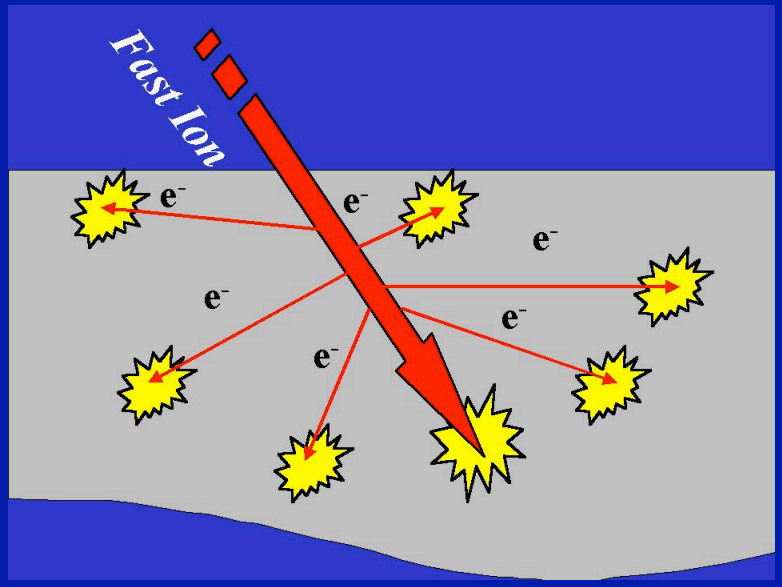
High Intensity Plasma Arc Lamp (OSRAM-Sylvania)

Plasma Flat Panel Display (Fujitsu)

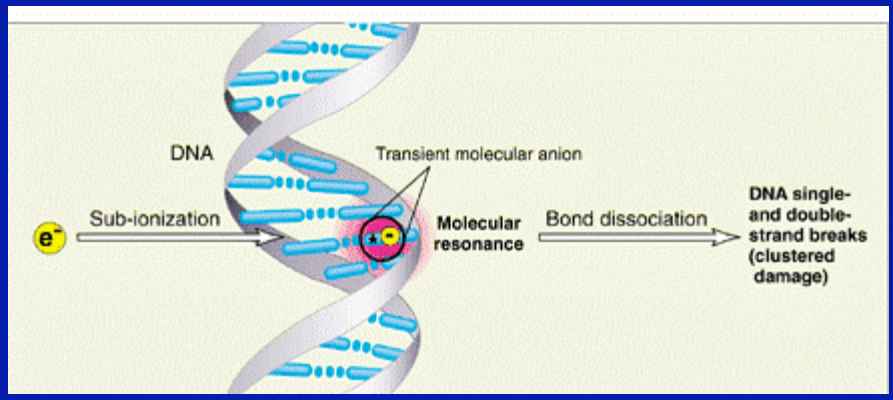


Plasma vapor deposition and plasma etching – no chemistry without electrons.

Electron-Driven Chemistry Associated with Ionizing Radiation



Cascades of secondary electrons from ionizing radiation



Most energy deposited in cells by ionizing radiation is channeled into secondary electrons between 1eV and 20eV (Research group of L. Sanche)

Resonant vs Non-Resonant Collisions

- Electronic energy must be transferred into nuclear motion to produce vibrational excitation
- Non-resonant Collisions
  - 1800 times difference in mass
  - Electron collision time scale different from molecular vibration time scale
  - Inefficient transfer
- Resonant Collisions
  - Electron collision time commensurate with molecular vibration
  - Electron collision drives dissociation and vibration

Method of Attack

Split the problem into two parts:

Electron scattering at fixed nuclear geometries

- Calculate position and lifetime of the shape or Feshbach resonances

Nuclear dynamics during the resonant collision

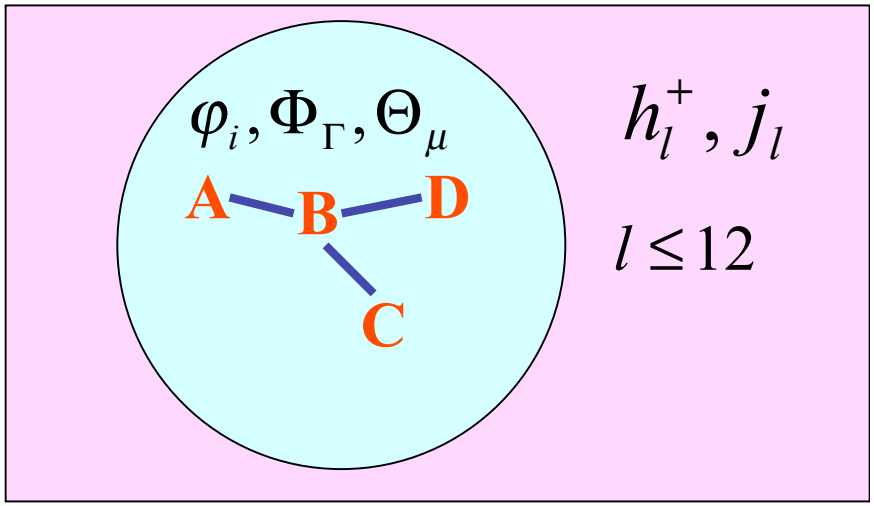
- Calculate the quantum molecular dynamics leading to vibrational excitation or dissociative attachment/recombination

Complex Kohn Variational Method

Variational Functional for the T-Matrix (scattering amplitude)

$$[T^{\Gamma\Gamma_0}] = T^{\Gamma\Gamma_0} - 2\int \Psi_\Gamma (H-E)\Psi_{\Gamma_0}$$

$$\delta[T] = 0$$



Trial wave function for the N+1 electron system

$$\Psi_{\Gamma_0} = \sum_\Gamma A\{\Phi_\Gamma(\mathbf{r}_1 \cdots \mathbf{r}_N) F_{\Gamma\Gamma_0}(\mathbf{r}_{N+1})\} + \sum_\mu d_\mu^{\Gamma_0} \Theta_\mu(\mathbf{r}_1 \cdots \mathbf{r}_{N+1})$$

exchange target continuum Correlation and Polarization

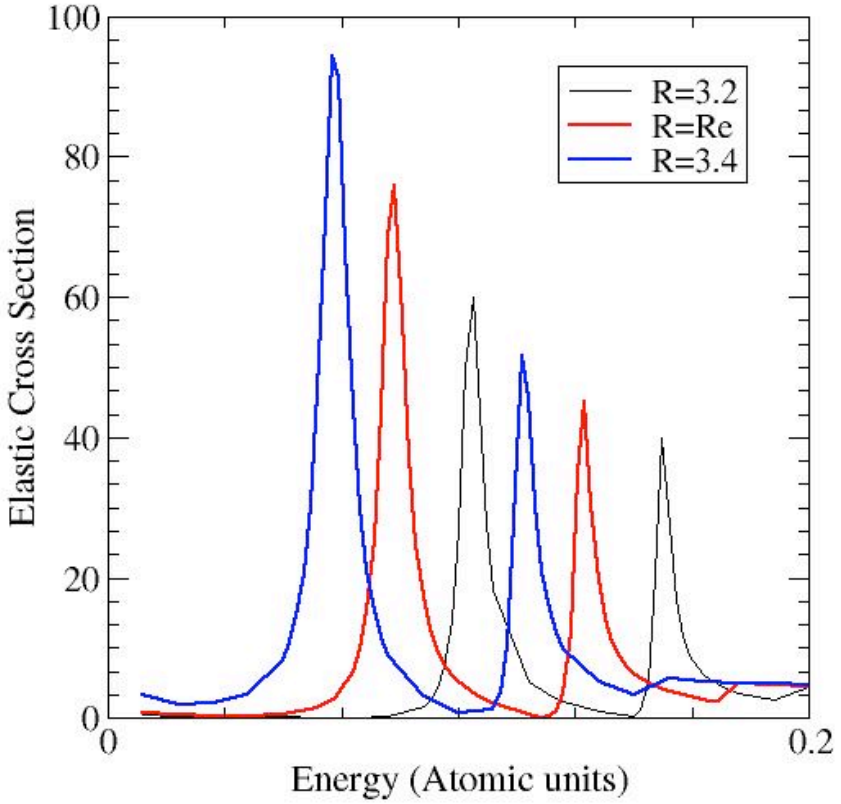
Continuum functions are further expanded in combined basis of Gaussians and continuum functions

$$F_{\Gamma\Gamma_0}(\mathbf{r}) = \sum_i c_i^{\Gamma\Gamma_0} \varphi_i(\mathbf{r}) + [j_l(k_\Gamma r)\delta_{ll_0}\delta_{mm_0} + T_{ll_0mm_0}^{\Gamma\Gamma_0} h_l^+(k_\Gamma r)] Y_{l,m}(\hat{\mathbf{r}})/r$$

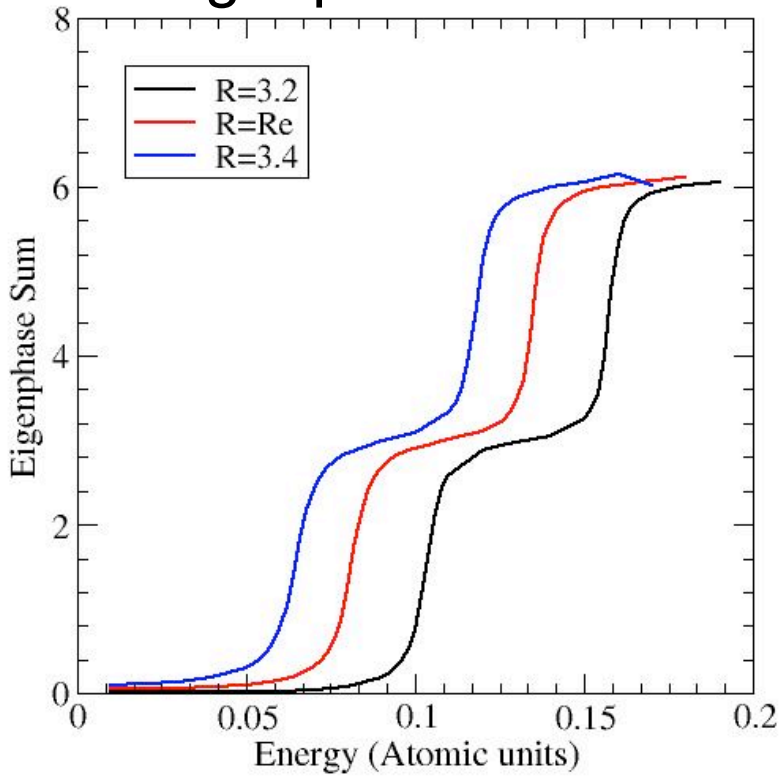
Position and Autoionization Width are determined by Breit-Wigner fit of the Eigenphase sum

Ne_2^+ Π_u Symmetry

Elastic Cross Section



Eigenphase Sum



Resonance peak gives a position and width: A complex energy for the resonance $E(R) = E_r - i\Gamma/2$ which can be understood qualitatively as:

$$\left|\Psi(r,t)\right|^2 = \left|\Psi(r)e^{-iEt}\right|^2 = \left|\Psi(r)\right|^2 e^{-\Gamma t}$$

Some working equations…

$$(E - K_R - V_{res})\xi_\nu = \left(\frac{\Gamma(R)}{2\pi}\right)^{1/2} \eta_\nu(R)$$

$$\frac{k^2(R)}{2} = E_{res} - E_{tar}$$

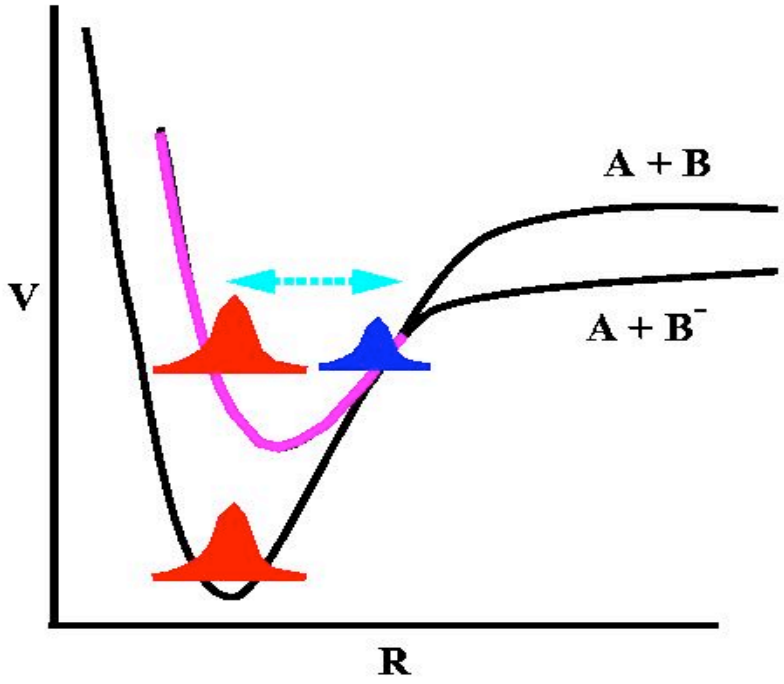
$$V_{res}(R) = E_{res}(R) - i\frac{\Gamma(R)}{2}$$ ← ***Local complex potential or "Boomerang" model***

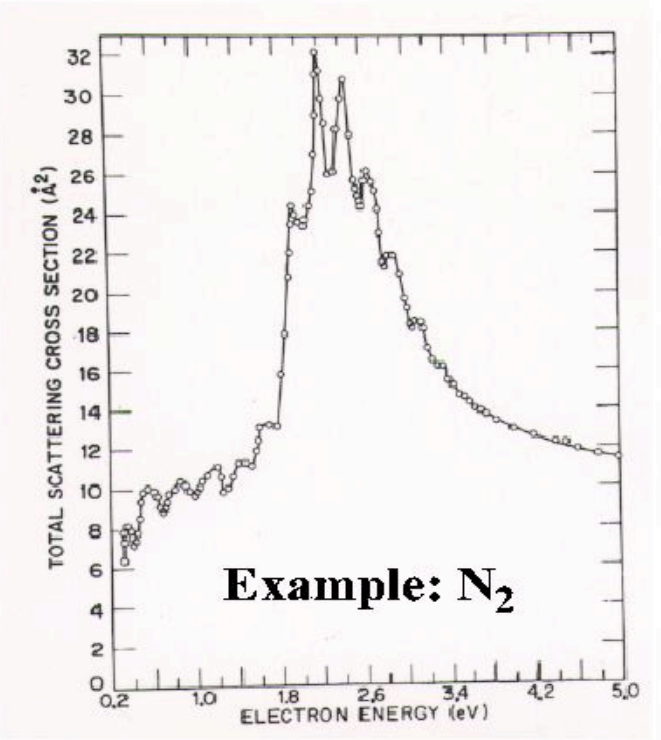
Nonlocal potential model

$$V_{res}(R,R') = E_{res}(R)\delta(R-R') - i\pi\sum_{\nu}^{open} U_\nu(k_\nu,R)U_\nu(k_\nu,R')$$

$$U_\nu(k_\nu,R) = \left(\frac{\Gamma(R)}{2\pi}\right)^{1/2} \eta_\nu(R)$$

Local Complex Potential or "Boomerang" model for Resonant Vibrational Excitation in 1D (diatomics)





Time-dependent formulation $\Phi_{initial}(R) = \left(\frac{\Gamma(R)}{2\pi}\right)^{1/2} \chi_i(R)$

$$T_{f,i}(E) = -i\int_0^\infty e^{iEt}\langle\Phi_{final}|\Psi_t\rangle dt$$

with

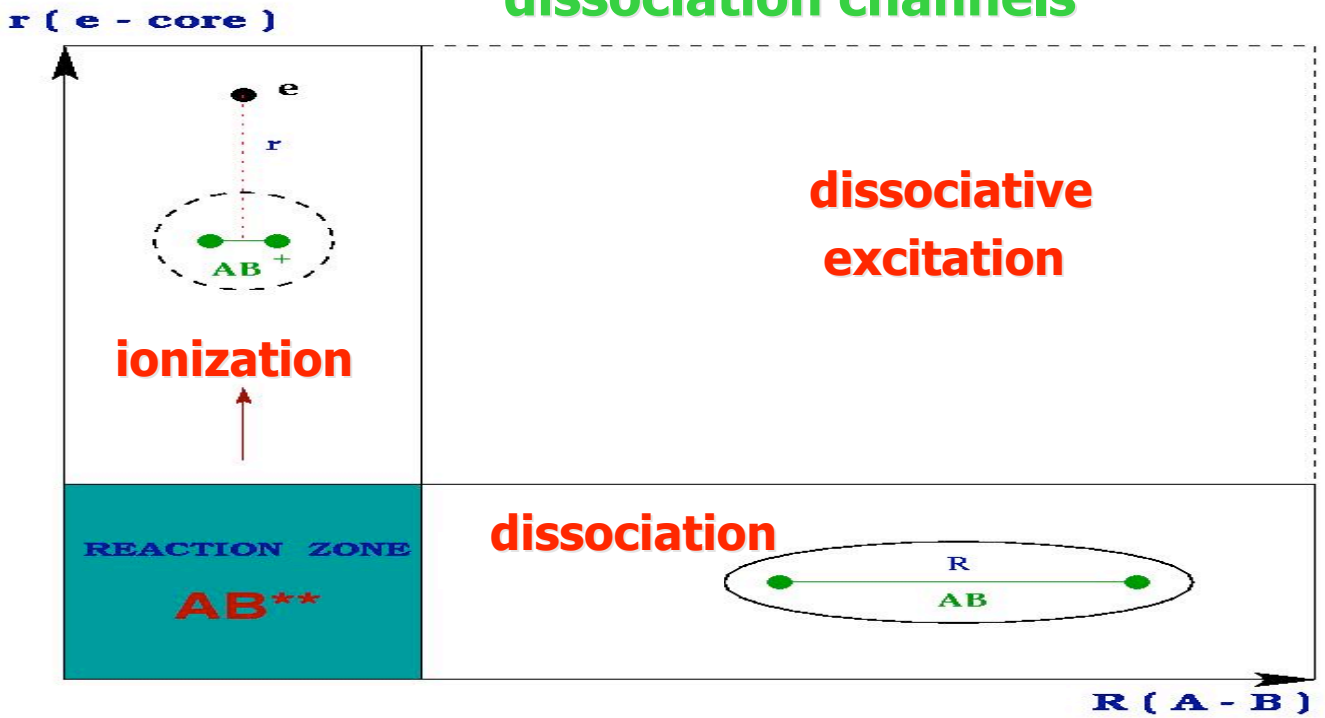
$$\Psi_t = e^{-iH_{anion}t}|\Phi_{initial}\rangle$$

MQDT

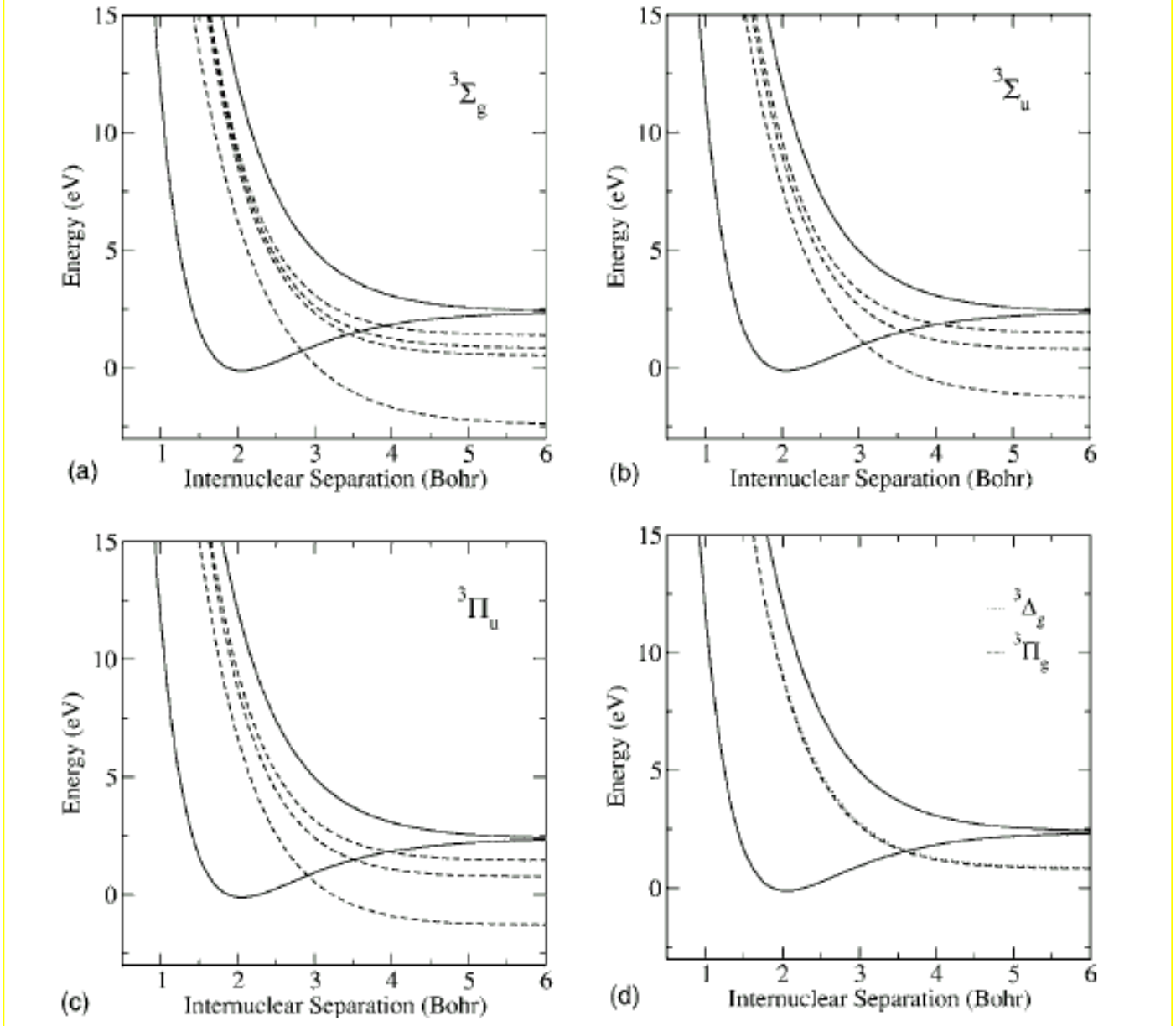
reactive scattering:

ionization channels

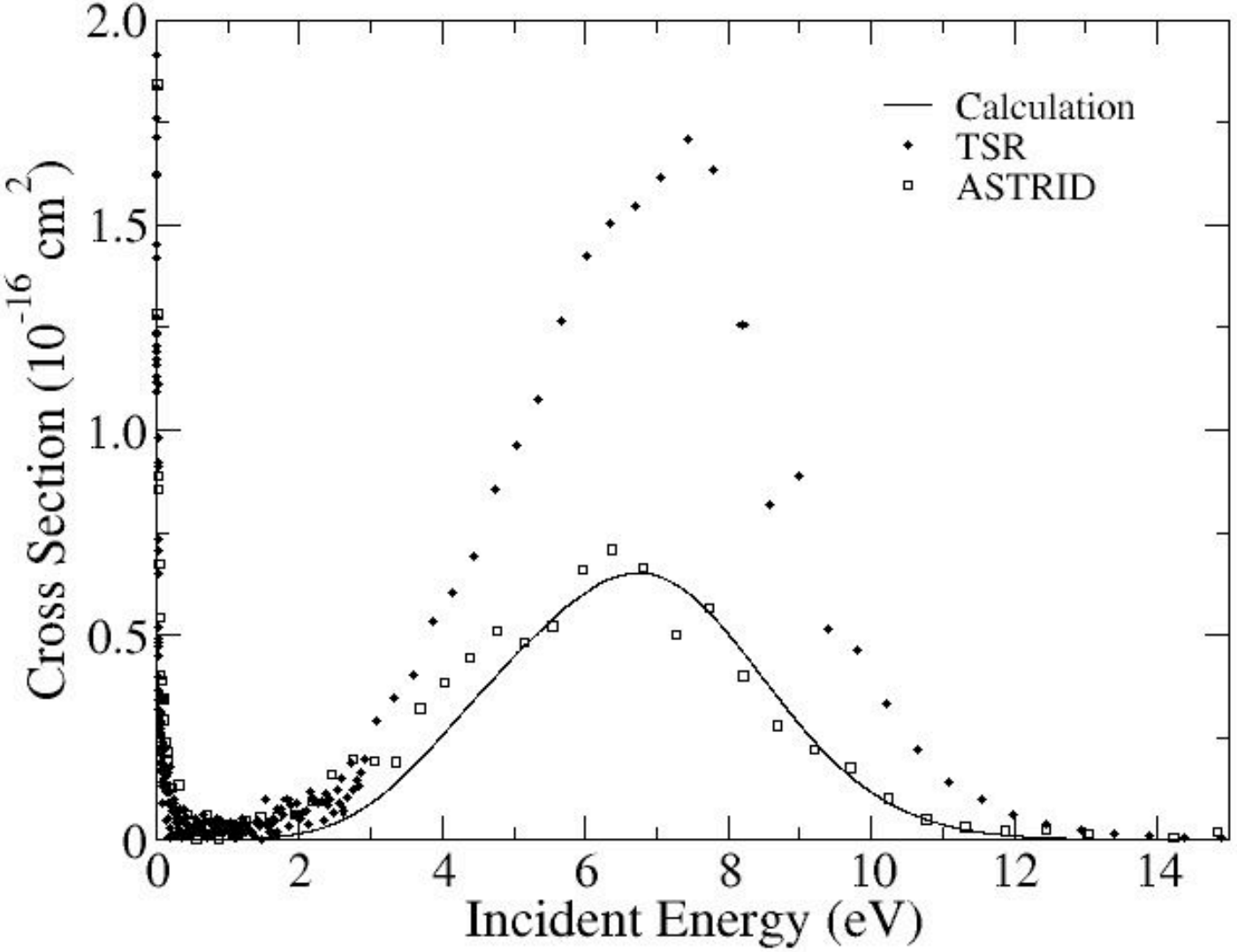
dissociation channels



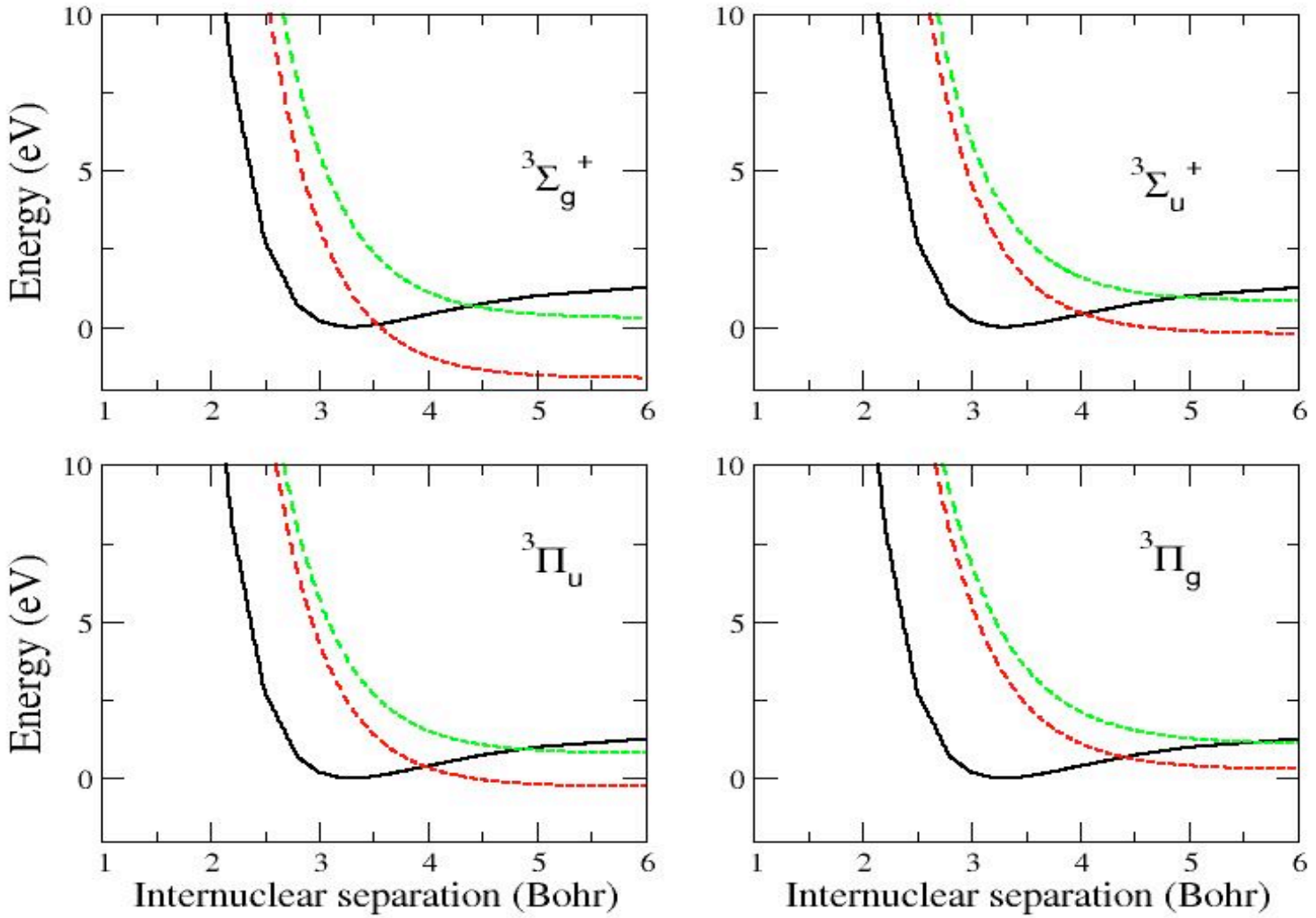
Resonance Curves – He_2^+



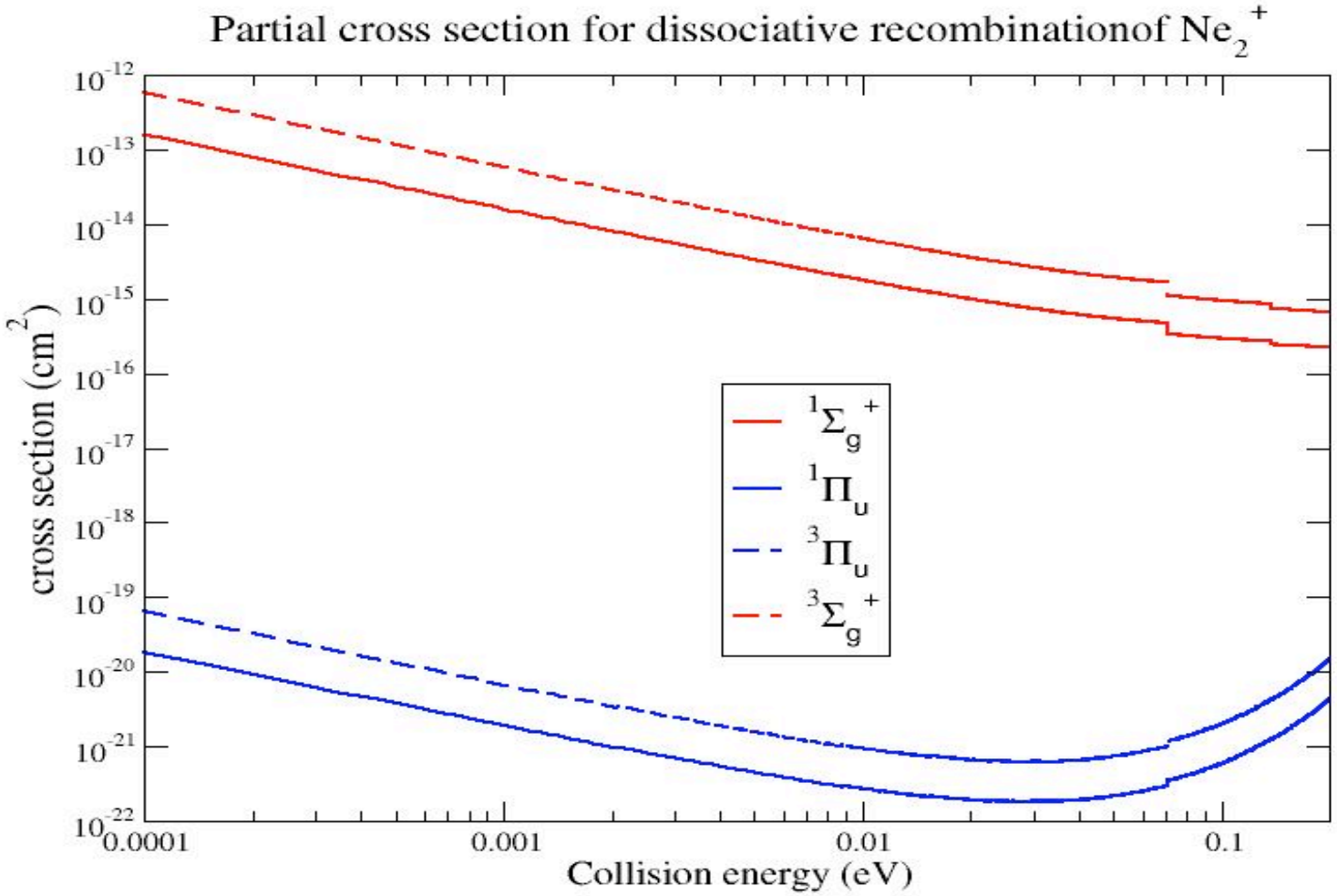
He_2^+ Comparison to Experiment



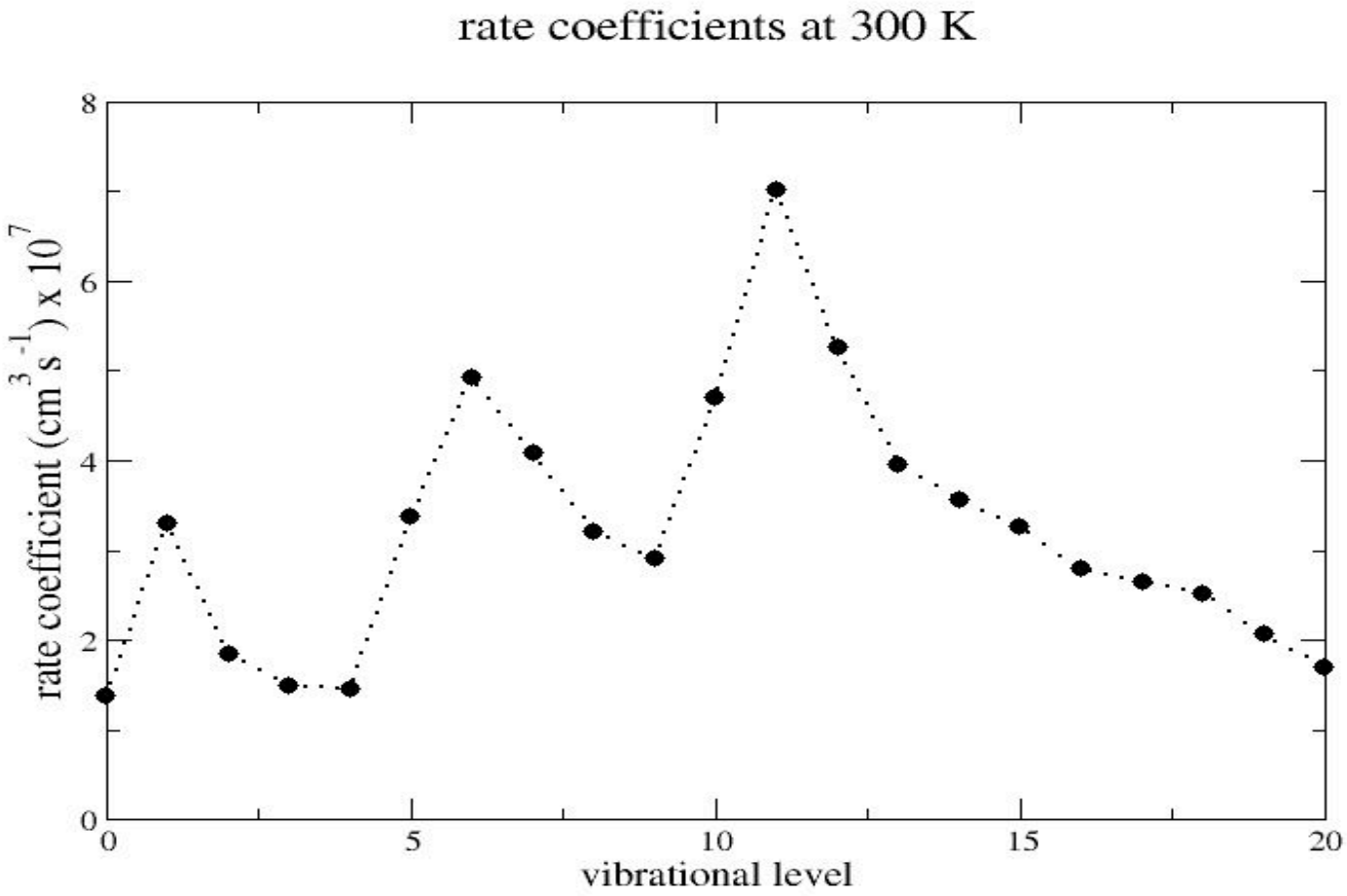
Potential curves of Ne_2^+ and Ne_2



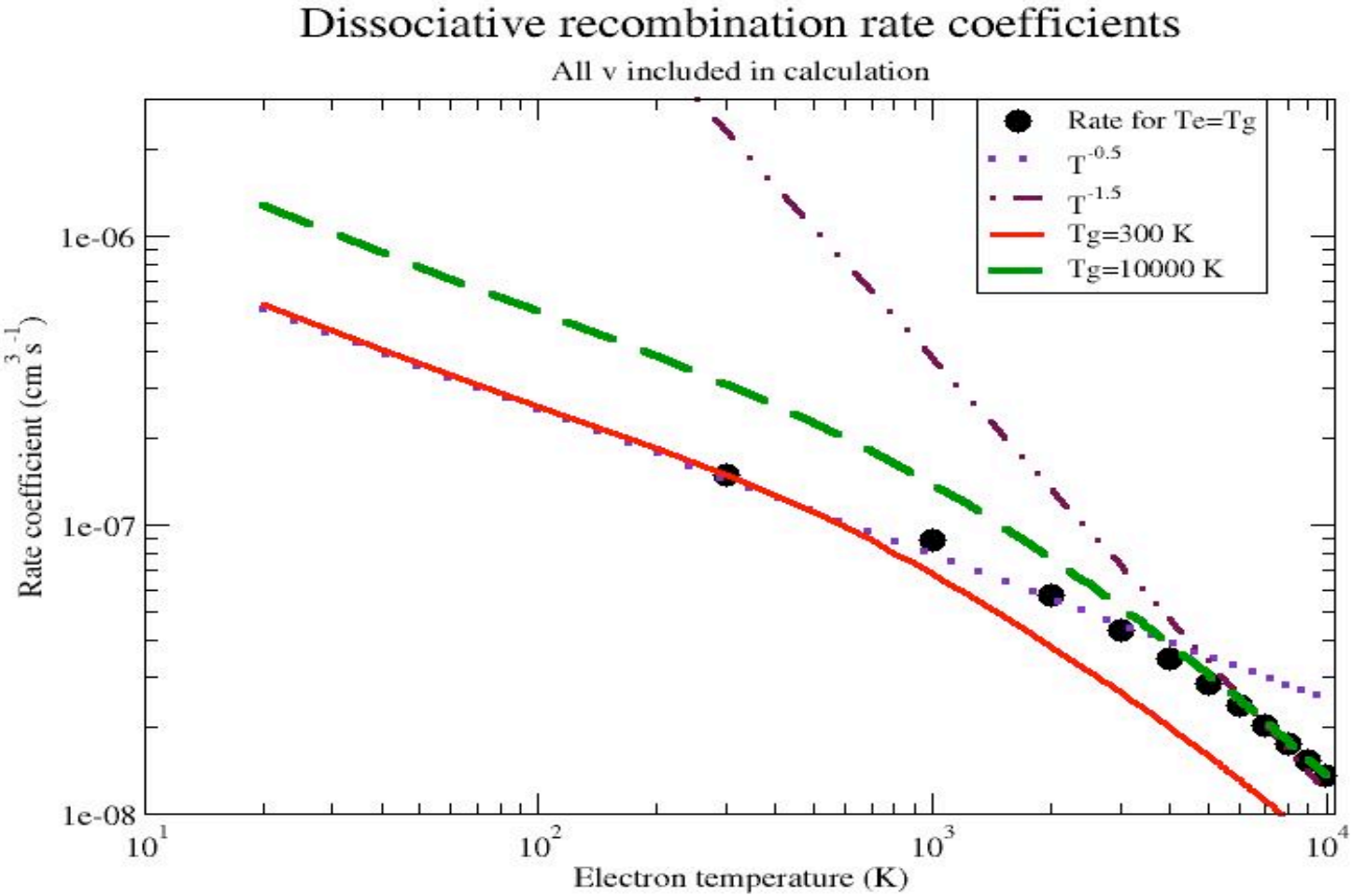
Cross Section



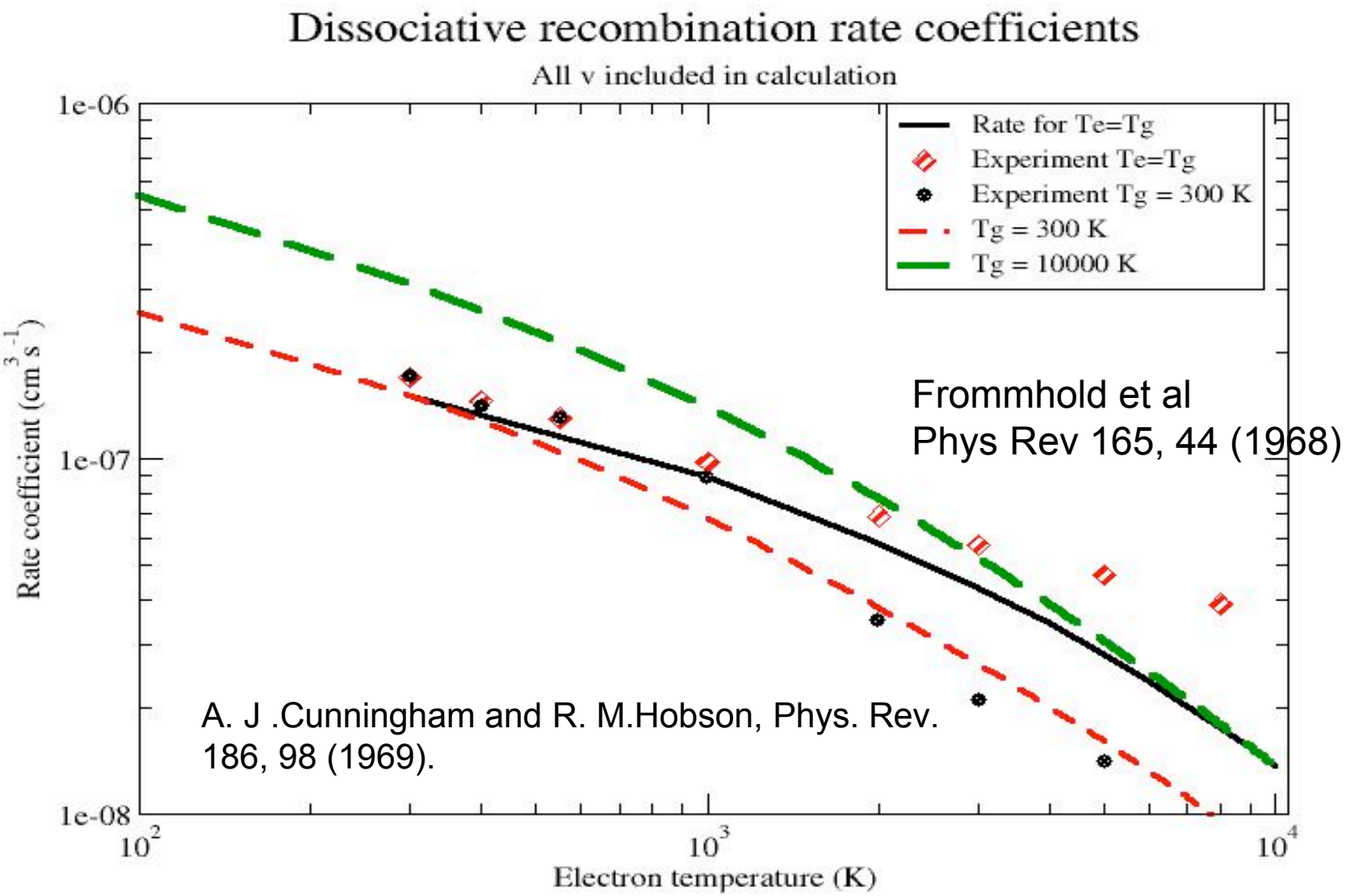
Mechanism


rate coefficients at 300 K
rate coefficient (cm^3 s^{-1}) x 10^7
vibrational level
0
2
4
6
8
0
5
10
15
20

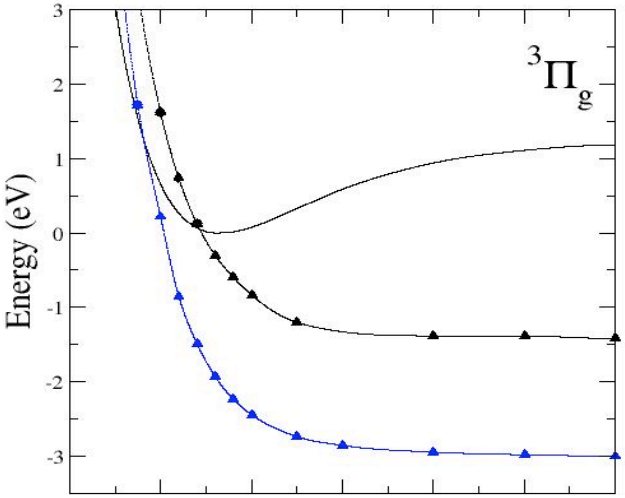
DYNAMICS

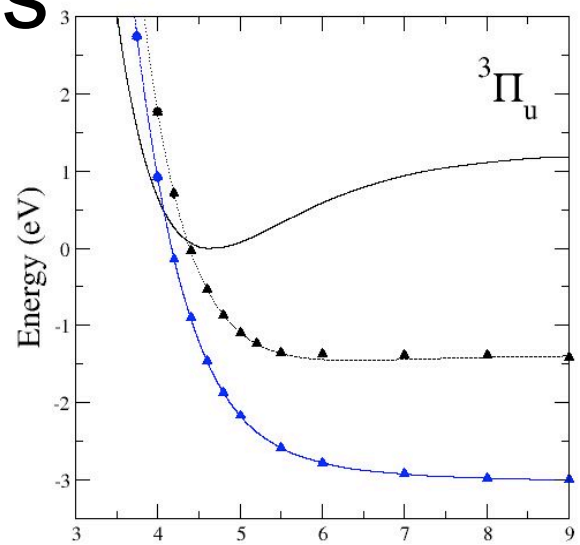

Dissociative recombination rate coefficients
All v included in calculation
Rate for Te=Tg
T^-0.5
T^-1.5
Tg=300 K
Tg=10000 K
Rate coefficient (cm^3 s^-1)
1e-06
1e-07
1e-08
10^1
10^2
10^3
10^4
Electron temperature (K)

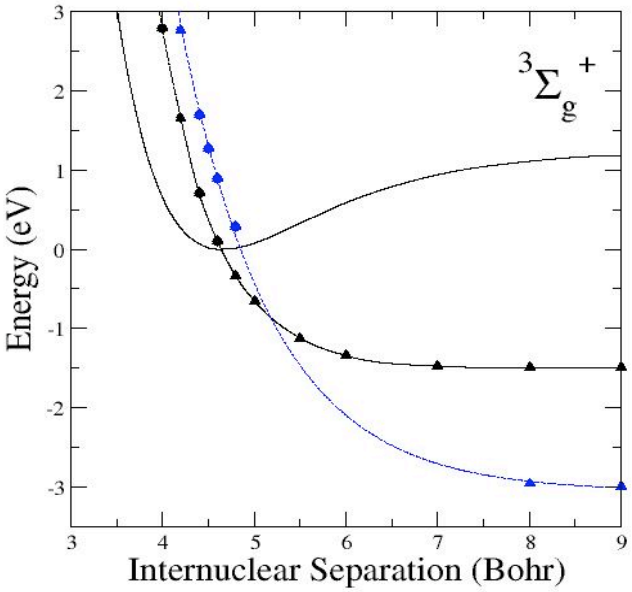
Comparison with experiments

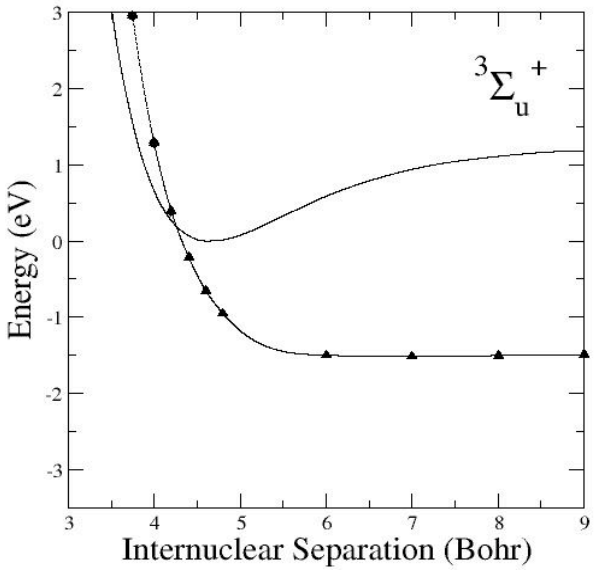


Ar_2^+ and Ar_2 Potential Energy Curves

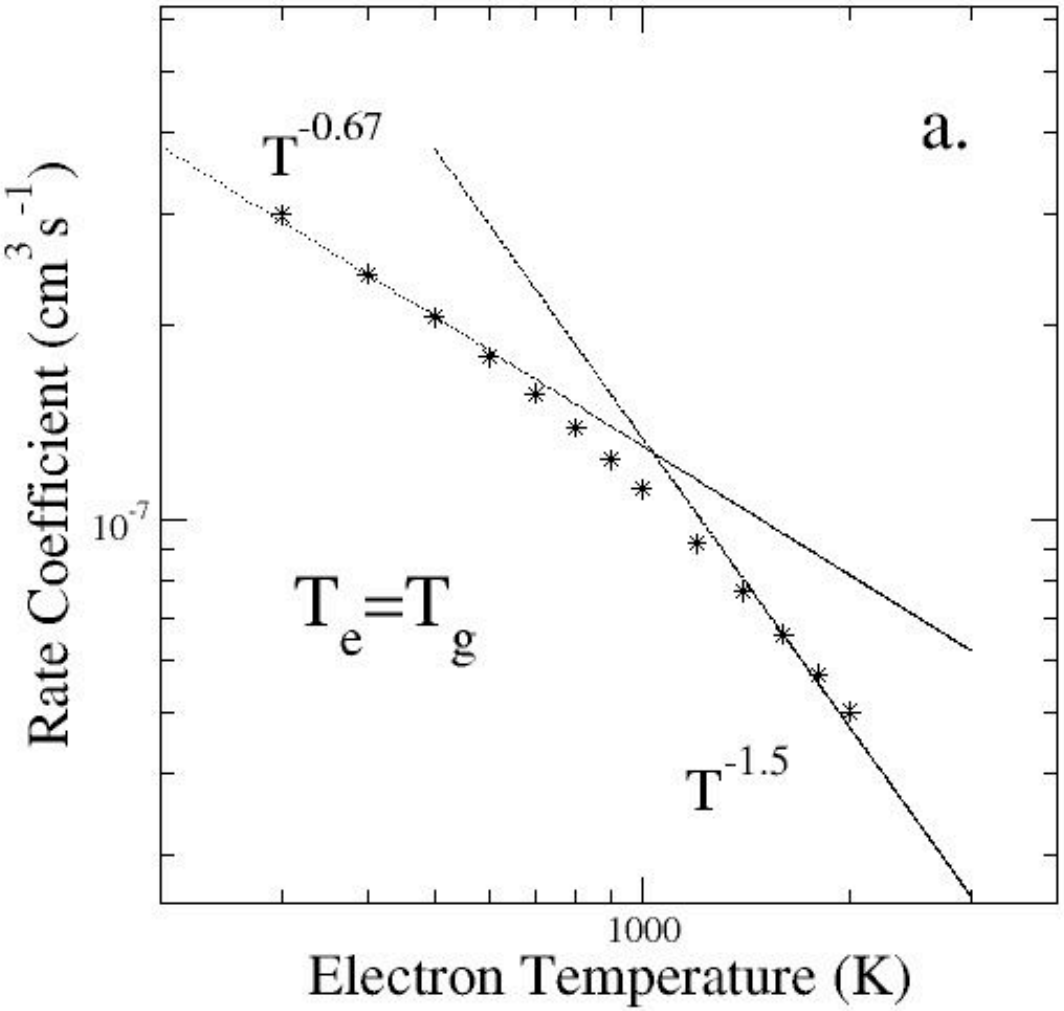




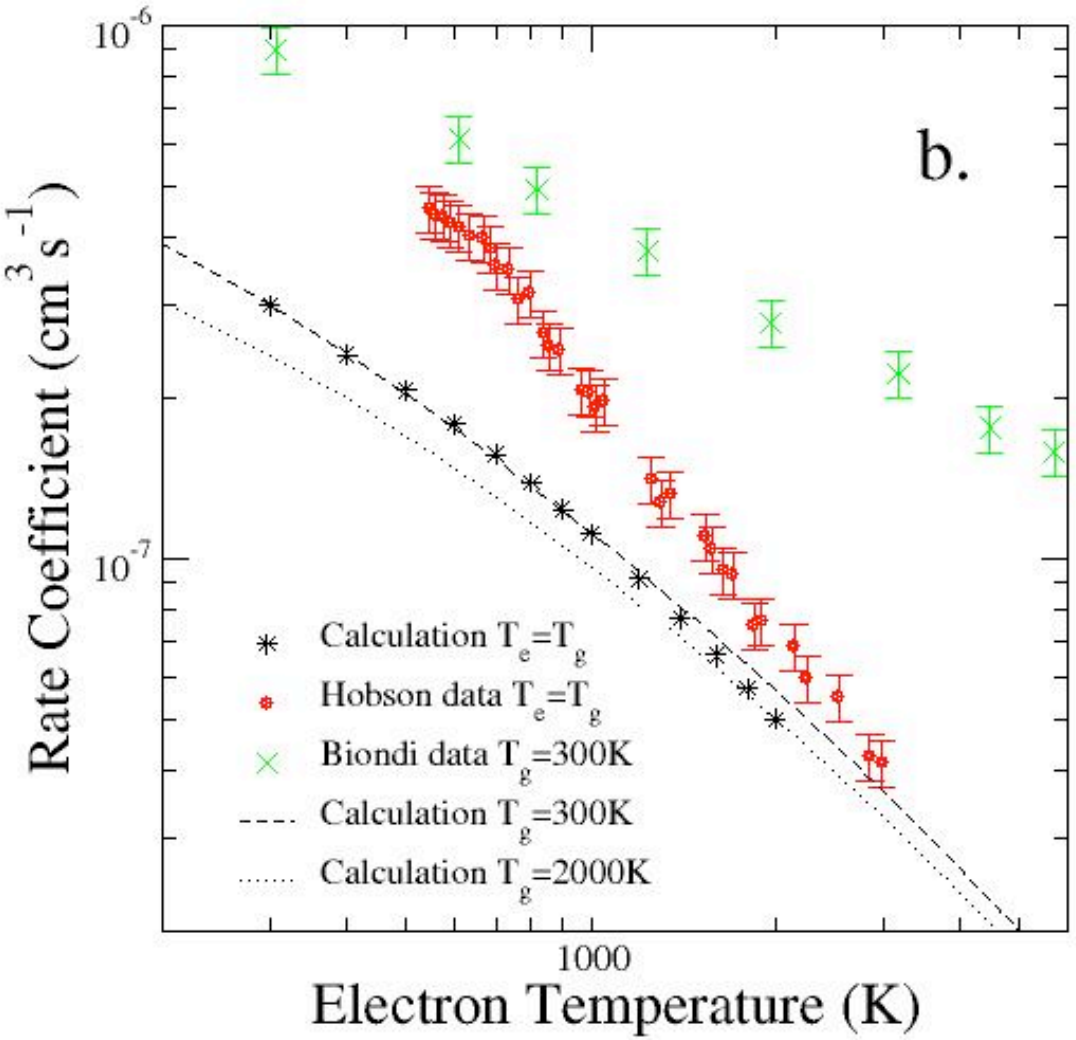




Dissociative Recombination Rate



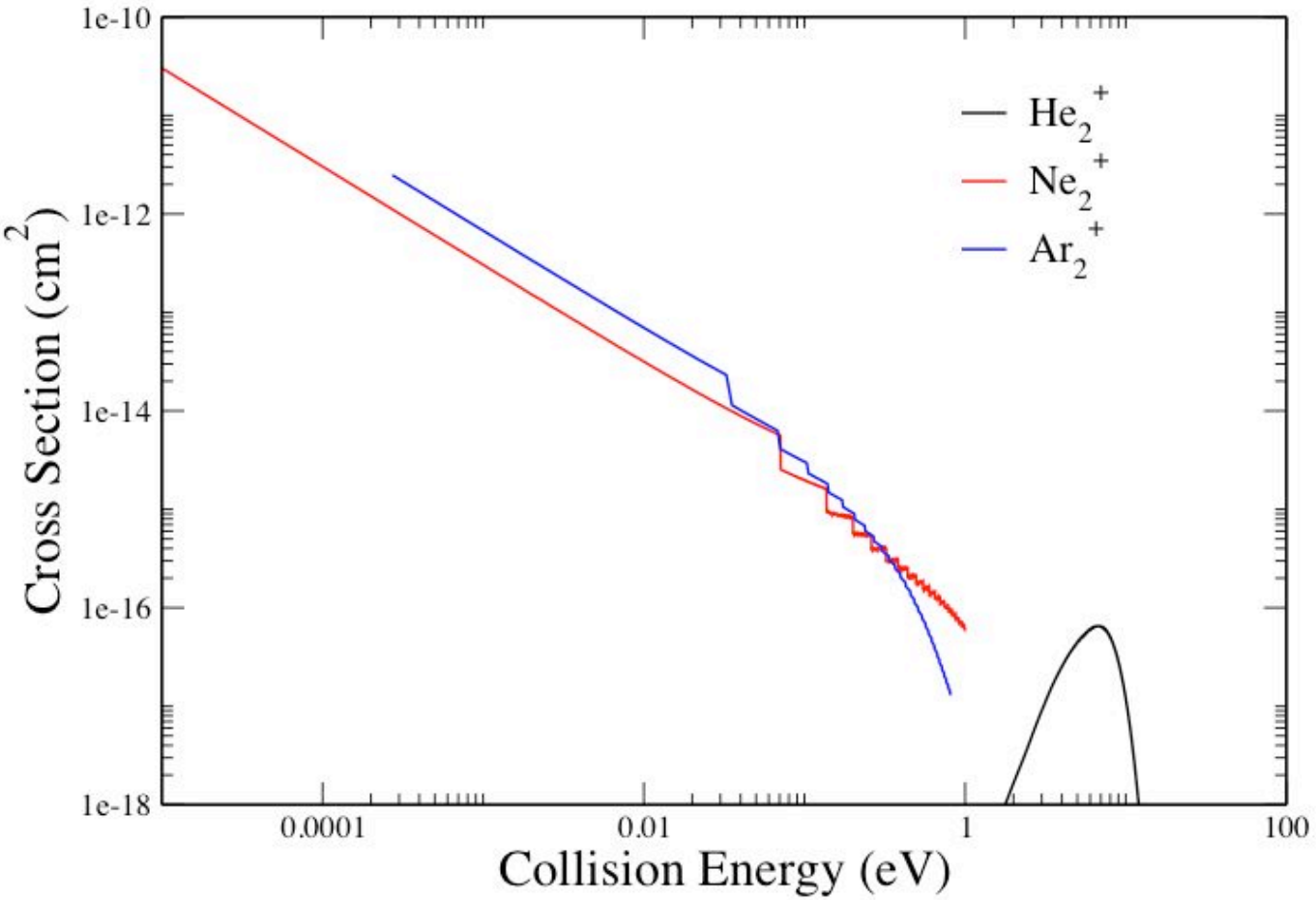
Comparison with Experiment



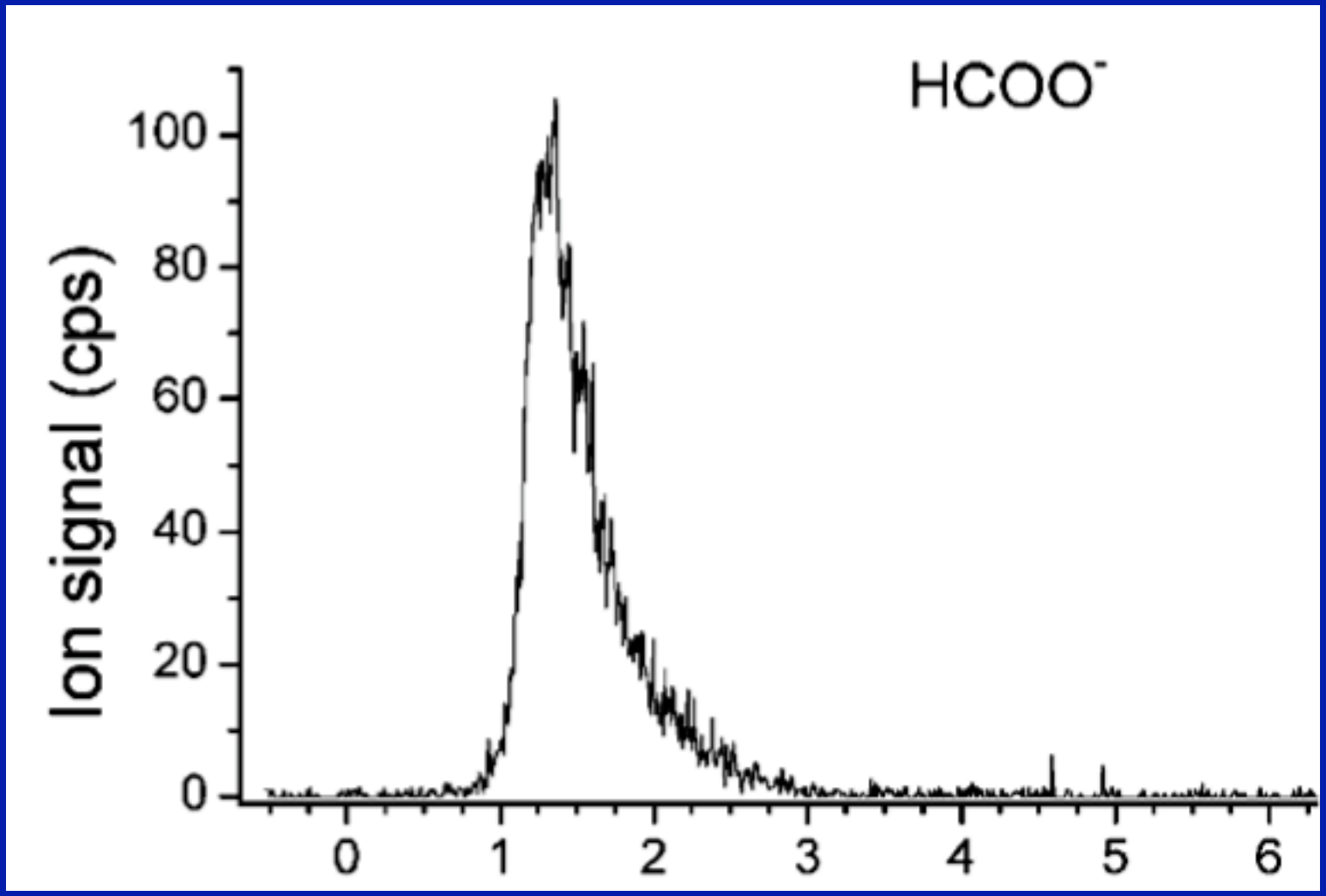
Y. J. Shiu and M. A. Biondi PRA, 17, 858 (1978).

A. J .Cunningham and R. M. Hobson, Phys. Rev. 186, 98 (1969).

Comparison Rare Gas Ions



Dissociative Electron Attachment to Formic Acid

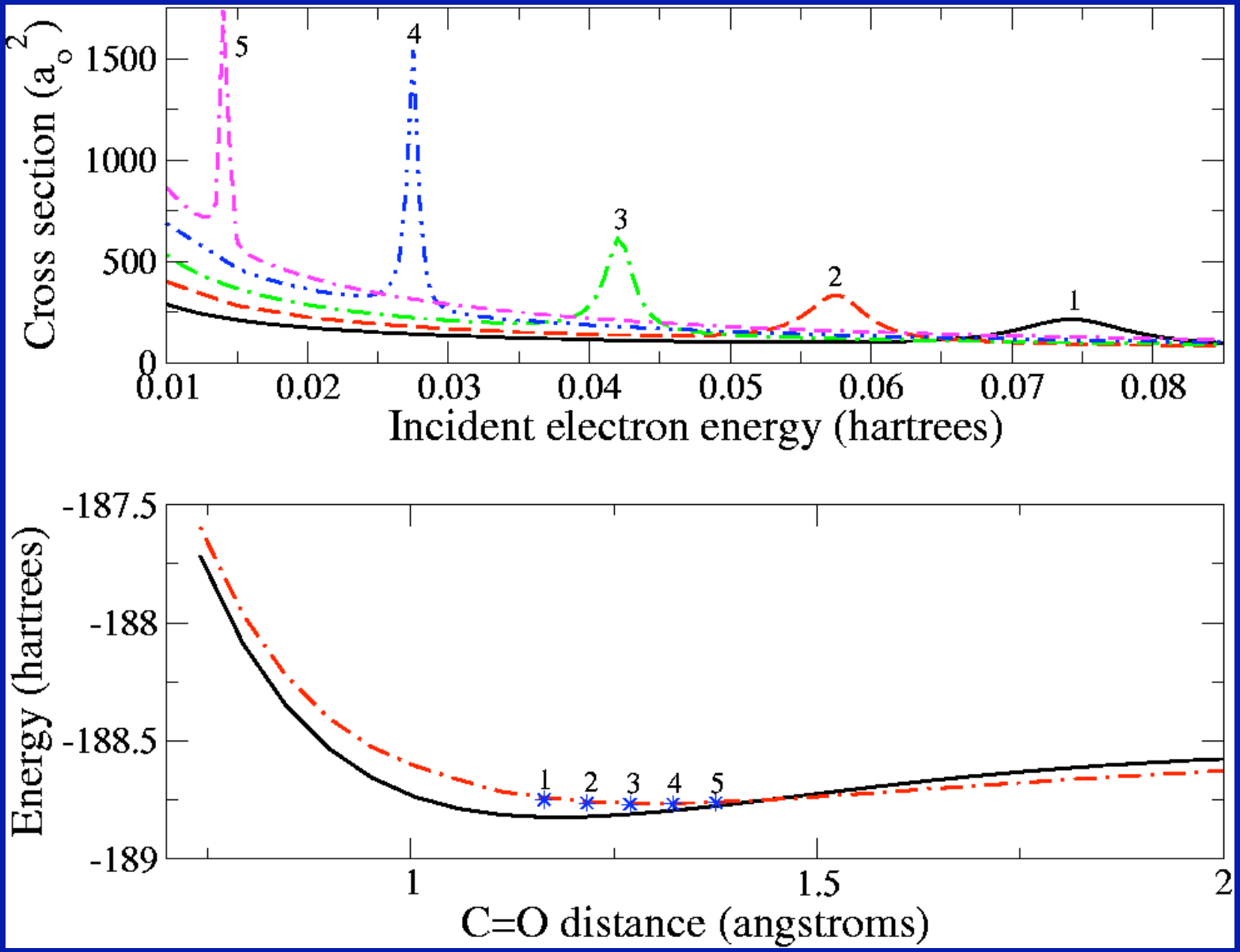


From Pelc et al., Chem. Phys. Lett. 361, 277 (2002)

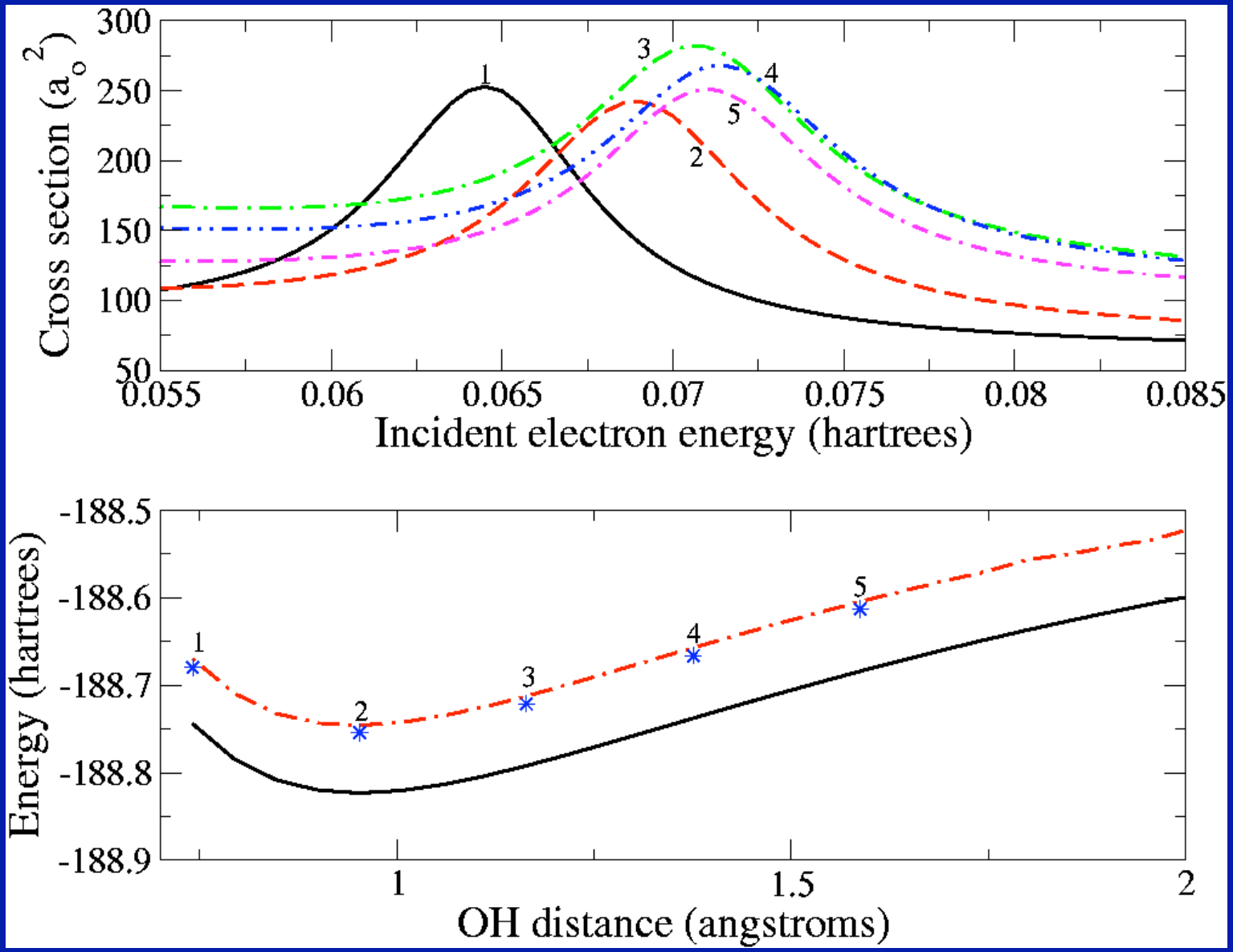
An Interesting Symmetry Puzzle

- **Formic acid is a closed-shell, planar (A') molecule**
- **Formate and H also have A' symmetry**
- **So how does a π^* $HCOOH^-$ anion, which has a nodal plane (ie has A" symmetry), dissociate to produce A' fragments?**

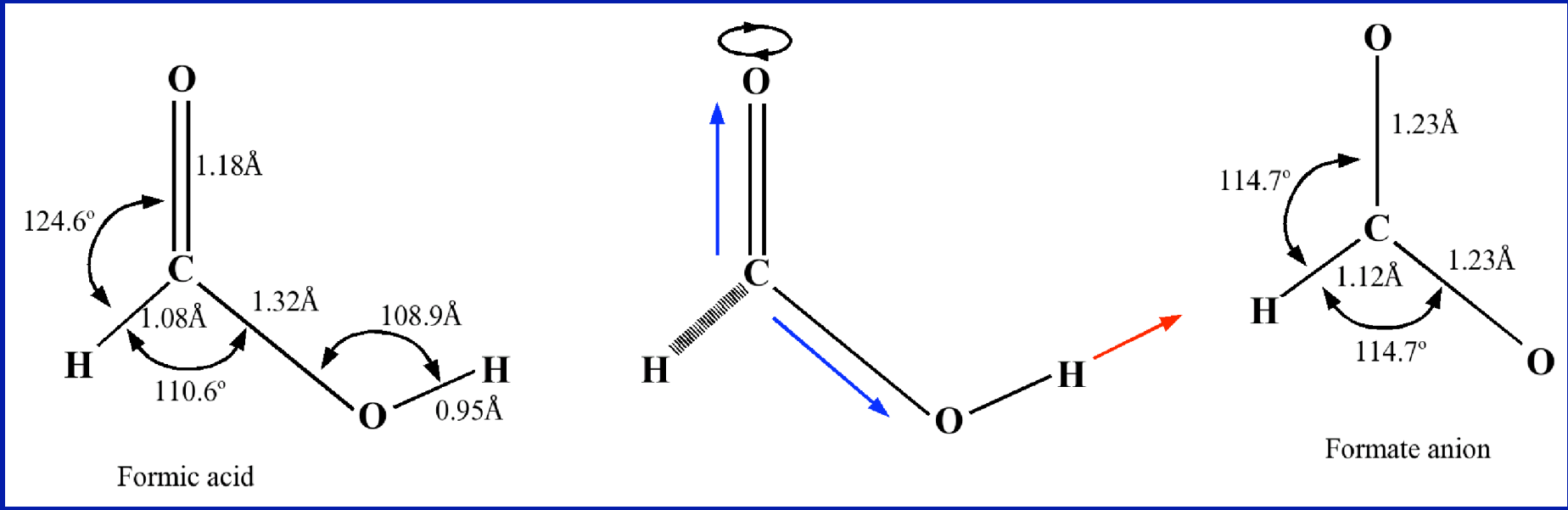
Effect of C=O Stretch



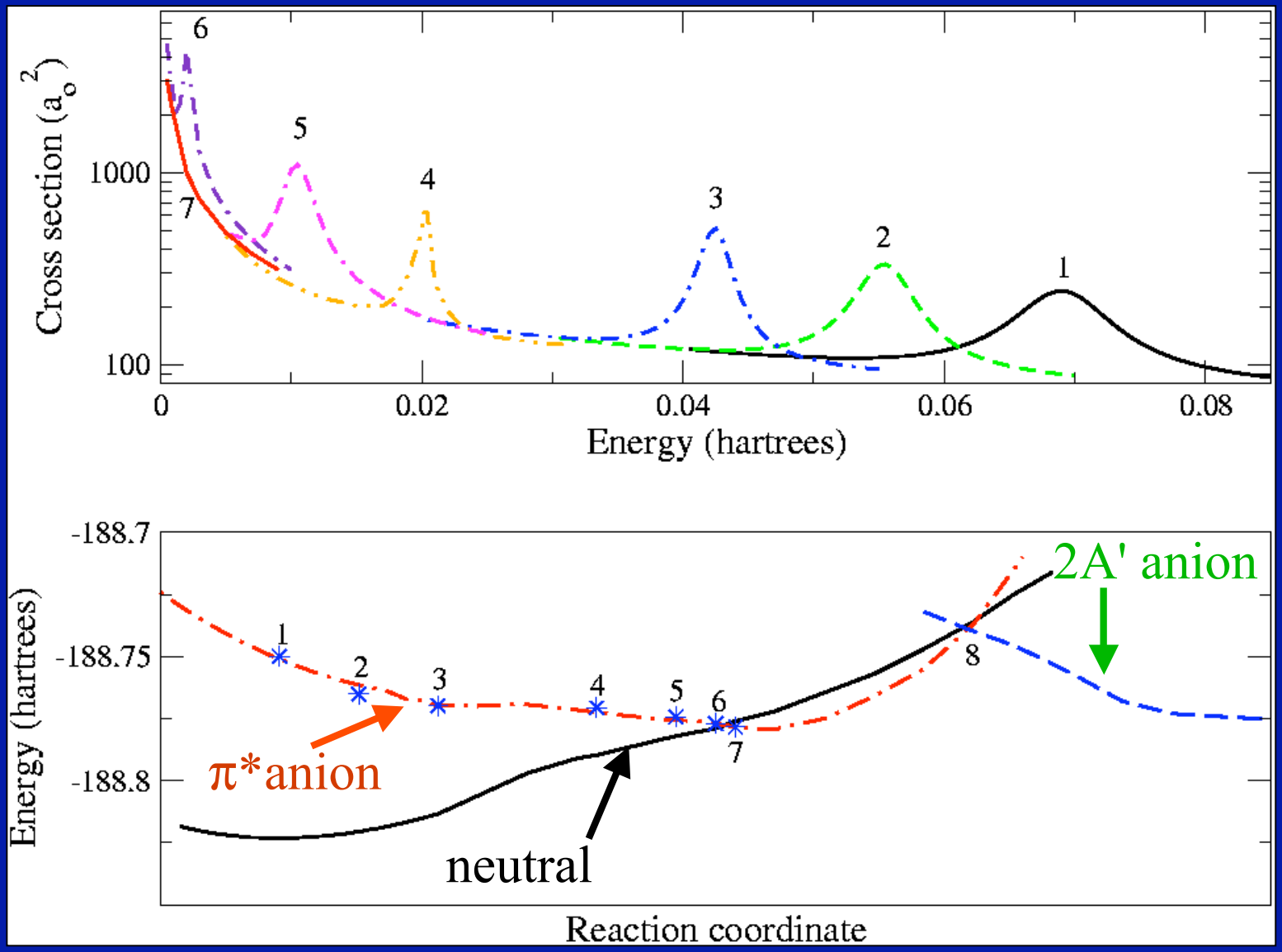
Effect of OH Stretch

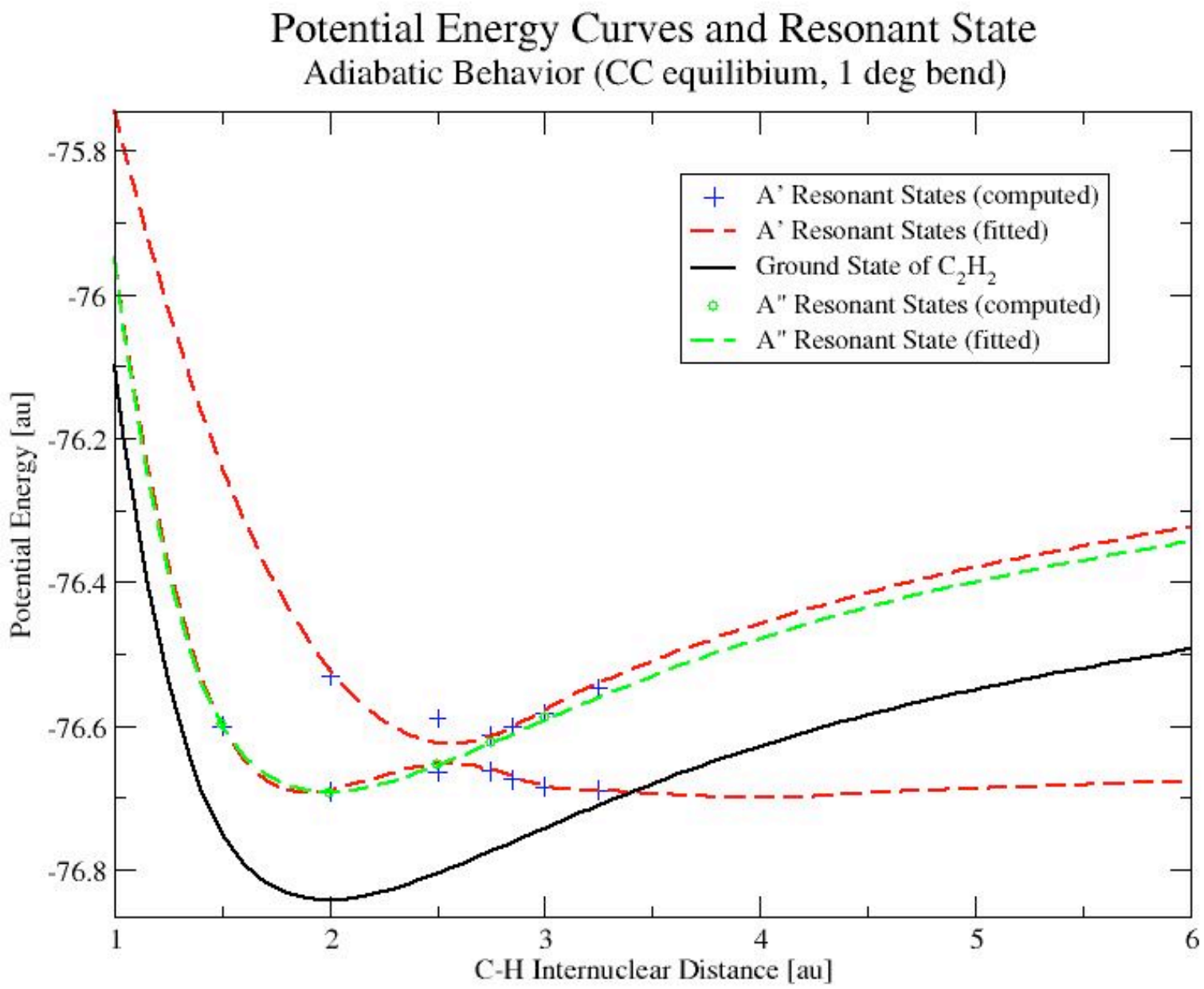


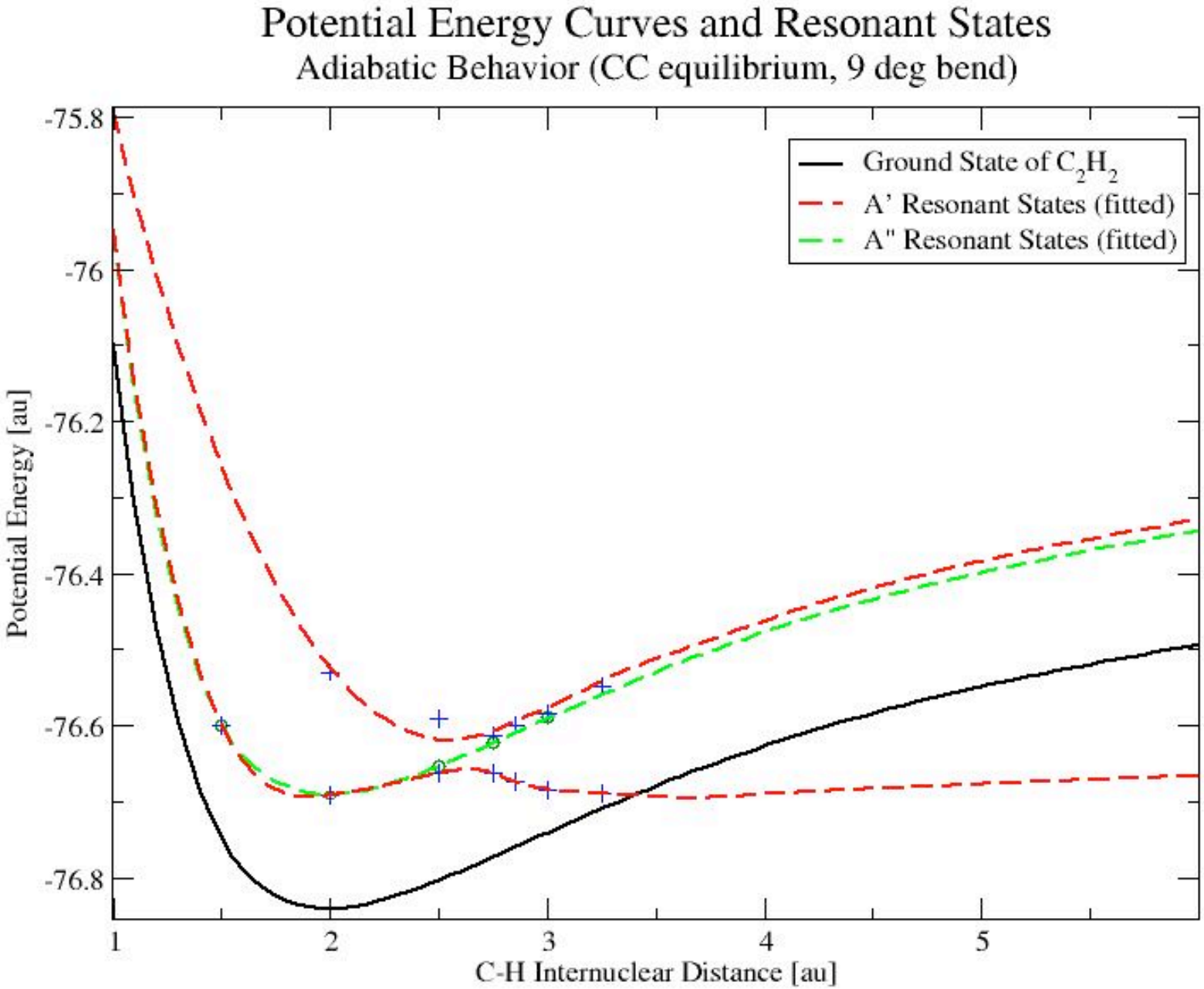
Reaction Path for DEA Leading to Formate Anion

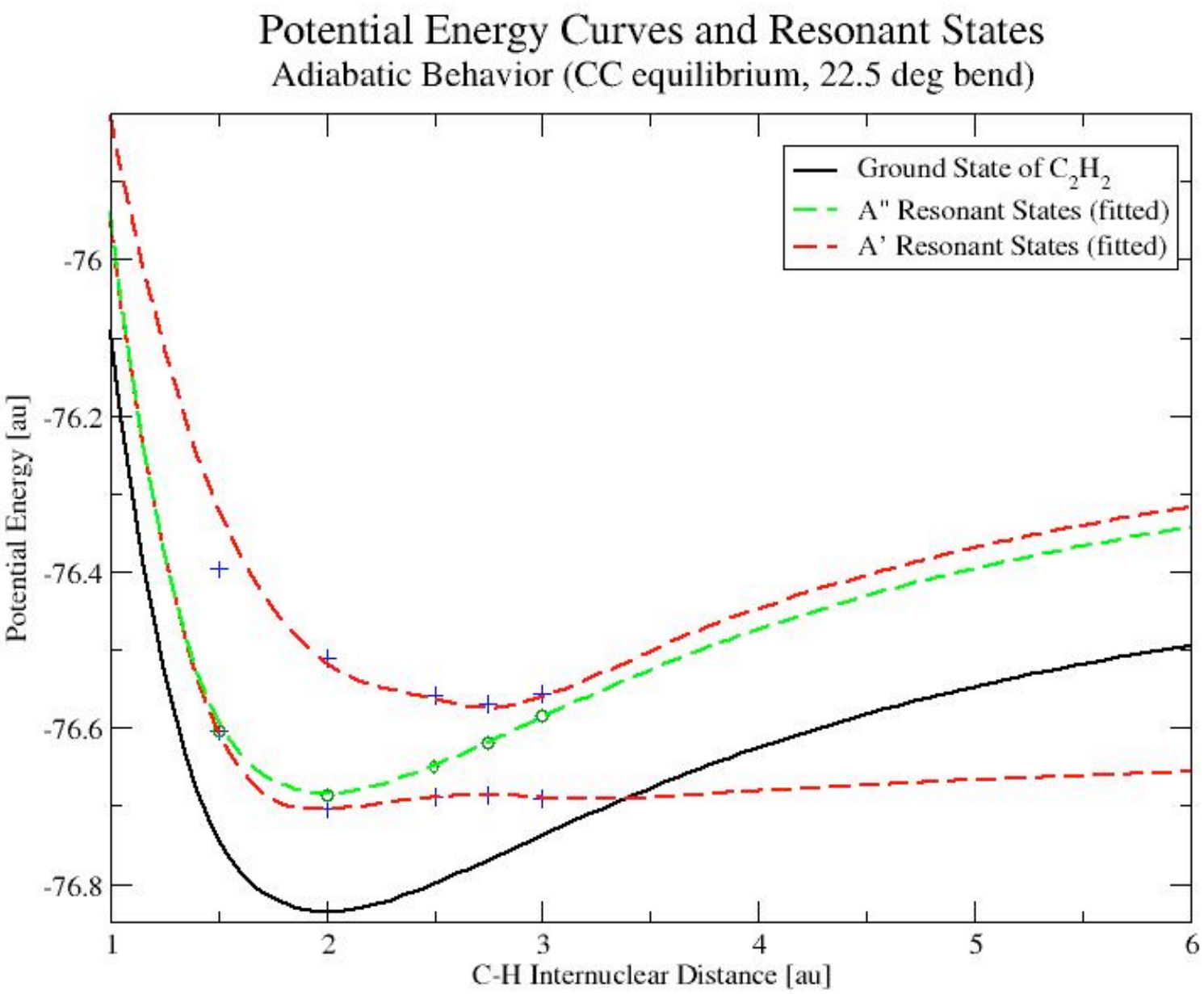


HCOOH Cross Section Along the "Reaction Path"




Potential Energy Curves and Resonant State
Adiabatic Behavior (CC equilibium, 1 deg bend)
A' Resonant States (computed)
A' Resonant States (fitted)
Ground State of C2H2
A" Resonant States (computed)
A" Resonant State (fitted)
Potential Energy [au]
-75.8
-76
-76.2
-76.4
-76.6
-76.8
1
2
3
4
5
6
C-H Internuclear Distance [au]


Potential Energy Curves and Resonant States
Adiabatic Behavior (CC equilibrium, 9 deg bend)
Ground State of C_2H_2
A' Resonant States (fitted)
A" Resonant States (fitted)
Potential Energy [au]
-75.8
-76
-76.2
-76.4
-76.6
-76.8
1
2
3
4
5
C-H Internuclear Distance [au]


Potential Energy Curves and Resonant States
Adiabatic Behavior (CC equilibrium, 22.5 deg bend)
Ground State of C_2H_2
A" Resonant States (fitted)
A' Resonant States (fitted)
Potential Energy [au]
-76
-76.2
-76.4
-76.6
-76.8
1
2
3
4
5
6
C-H Internuclear Distance [au]

CONCLUSIONS

- Electron resonances are ubiquitous in low-energy scattering from molecules
- These resonances provide an efficient path for channeling energy into nuclear motion
- Vibrational excitation and dissociative attachment/recombination proceed predominately through resonant excitation
- Multiple resonances complicate the temperature dependence of dissociative recombination rate constants
- The temperature dependence is dependent both on ion (vibrational) and electron (collision) temperature
- Ab initio theory requires both an accurate treatment of electronic scattering and nuclear dynamics