

Vibrations as a probe of reaction mechanisms

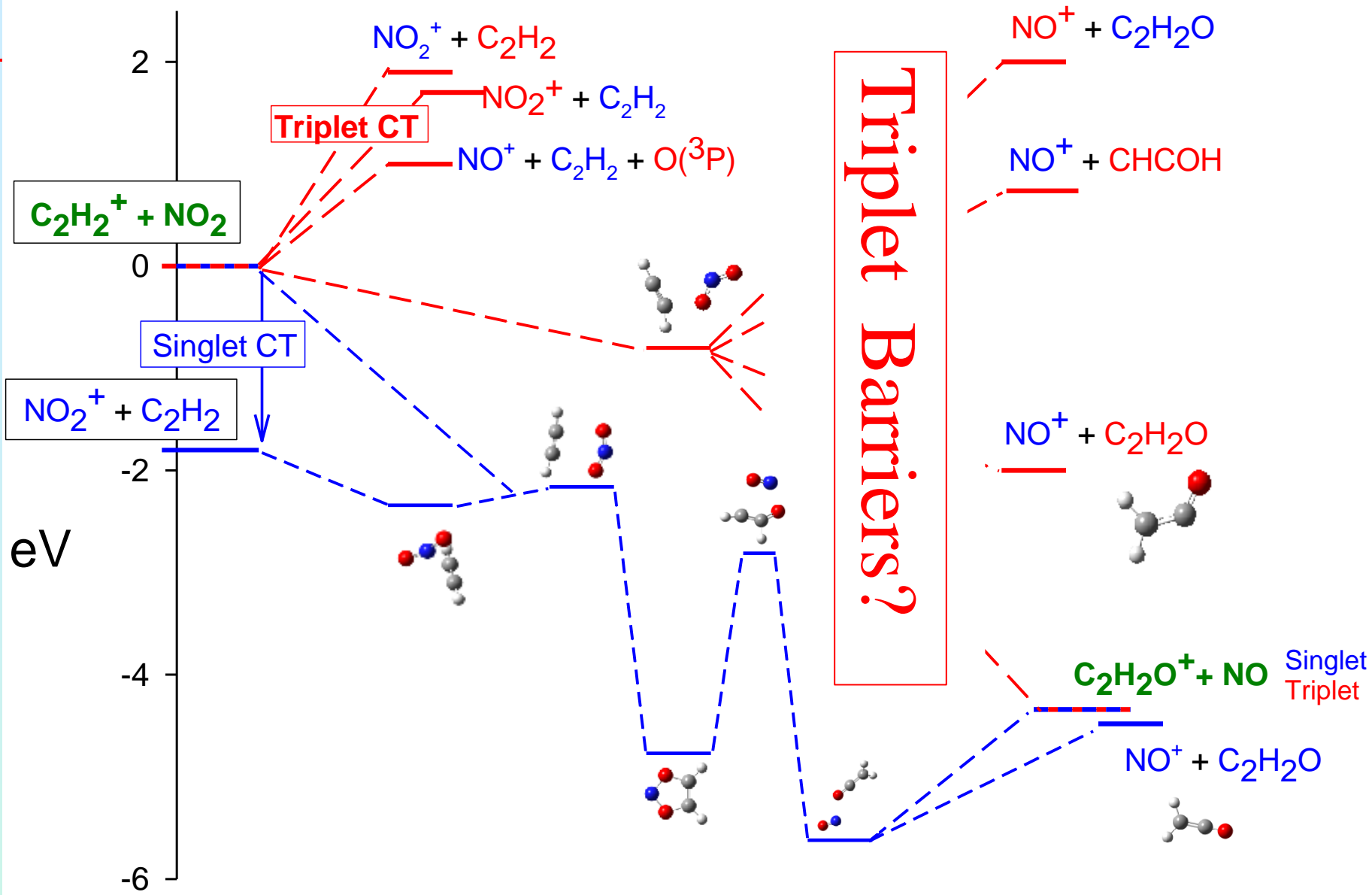
Jason Boyle, Dave Bell, Jianbo Liu

Funding:

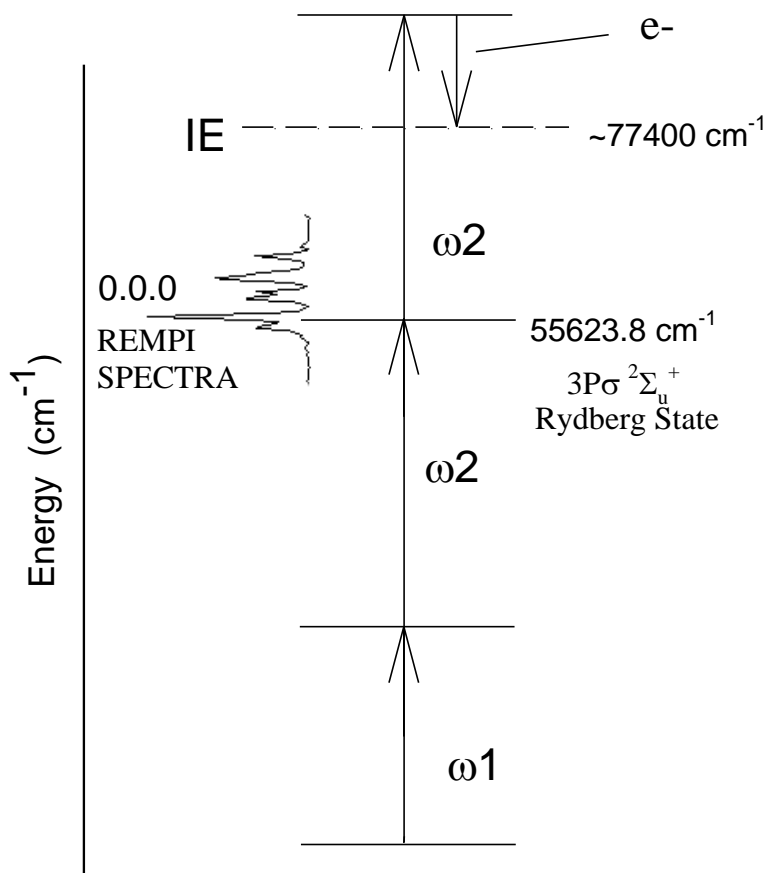
NSF



THE SYSTEM – [C₂H₂-NO₂]⁺

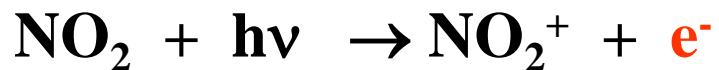


REMPI State Selection



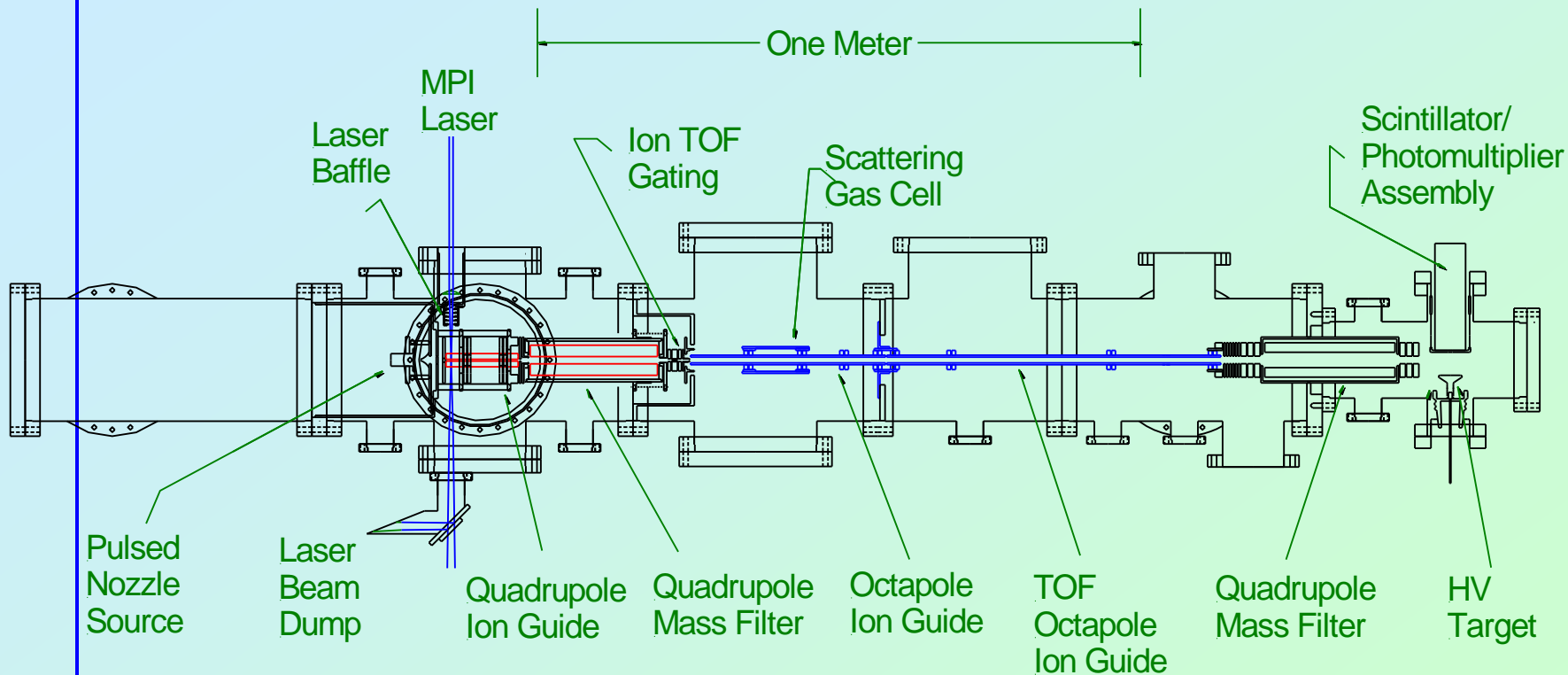
Selectable States:

- (000) = Ground state
- (100) = Sym Stretch (170 meV)
- (010) = Bend (78 meV)
- (02⁰⁰) = Bend overtone (153 meV)
- (02²⁰) = Bend overtone (155 meV)
- (001) = Asym Stretch (290 meV)



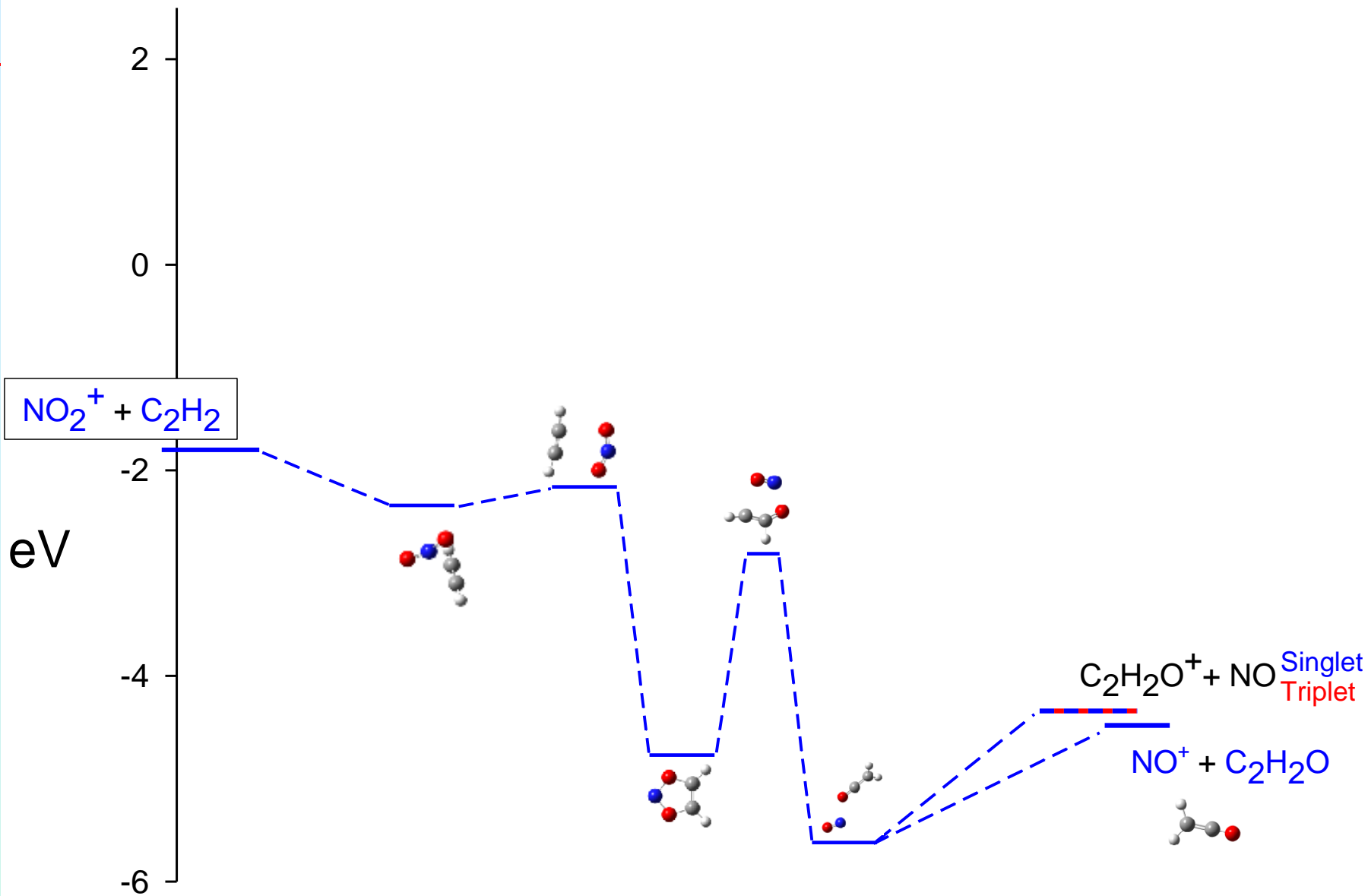
$$E_{\text{int}}(\text{ion}) = n \times h\nu - \text{I.P.} - \text{KE}_{\text{electron}}$$

The Instrument



J. Liu, B. van Devener, and S. L. Anderson, *J Chem Phys* 116, 5530 (2002)

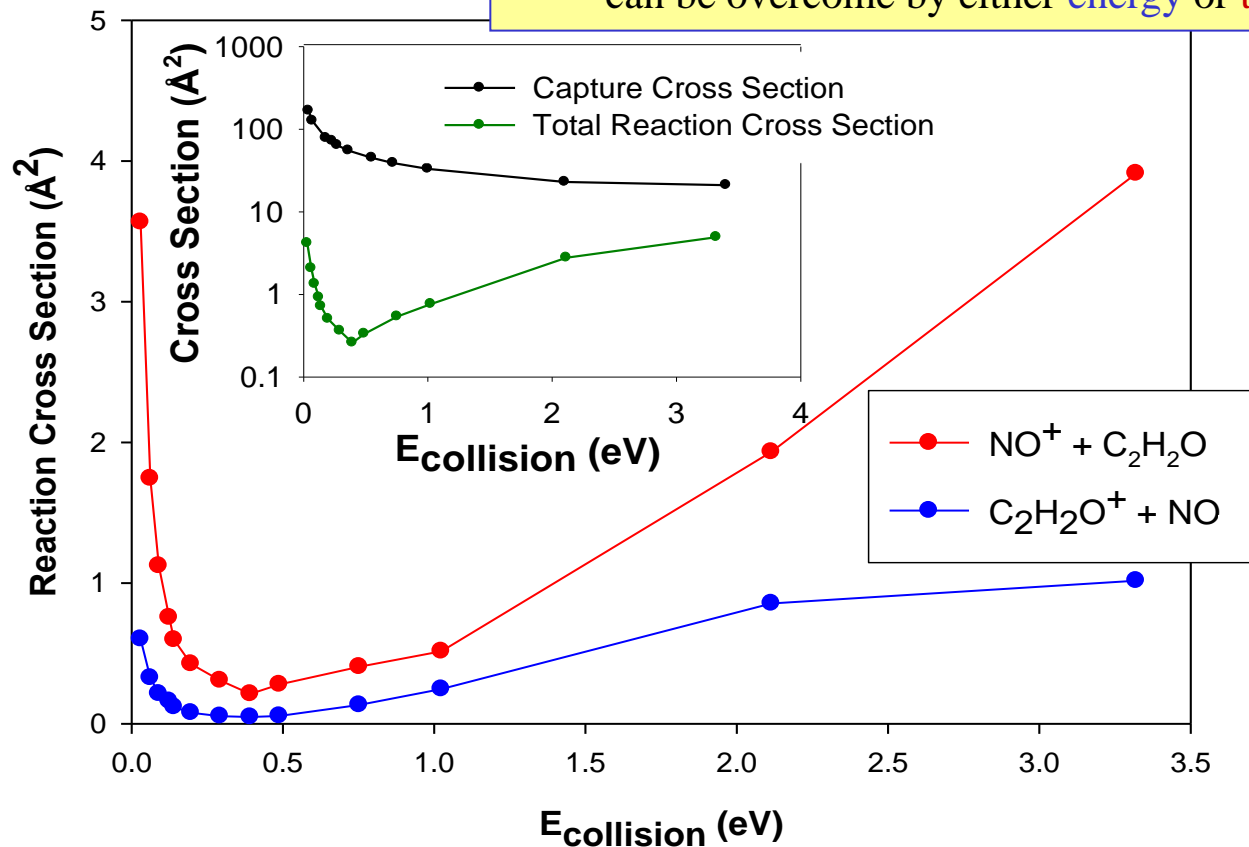
THE REACTION – $\text{NO}_2^+ + \text{C}_2\text{H}_2$



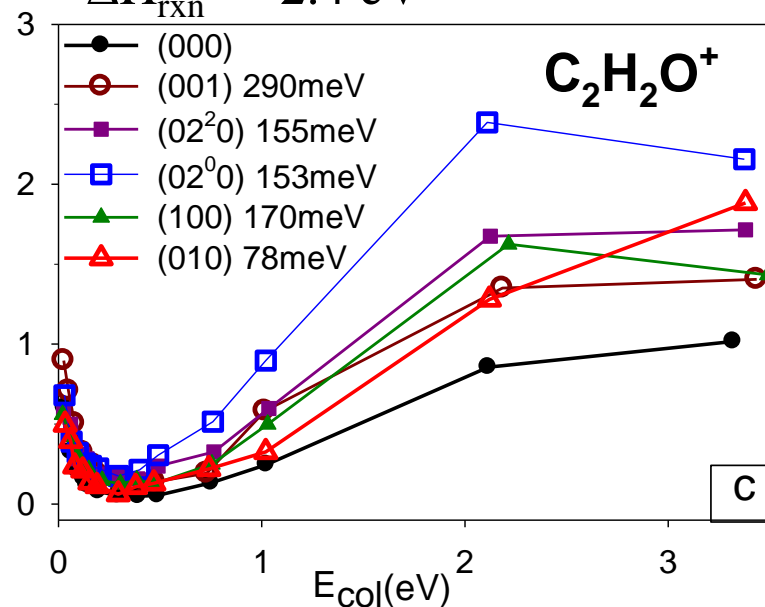
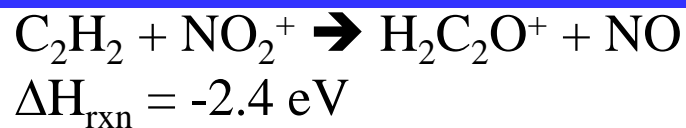
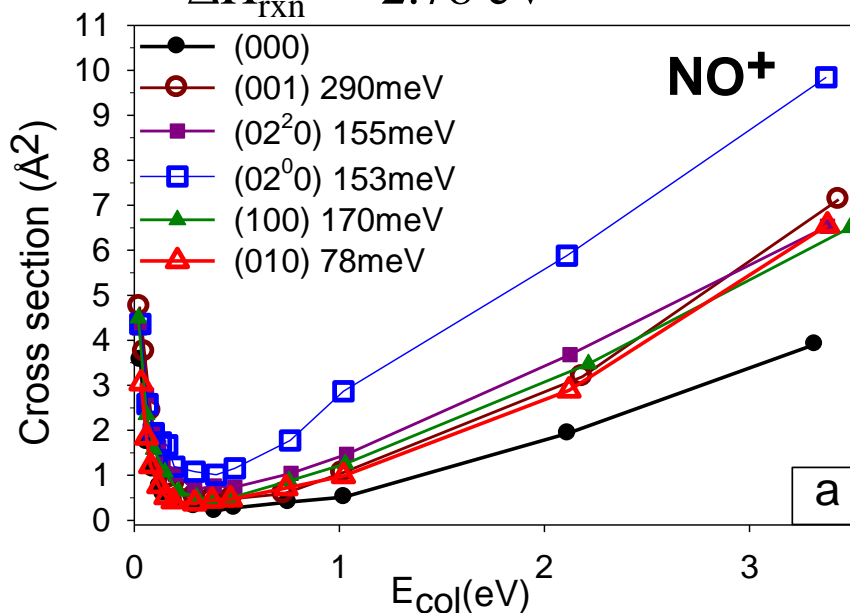
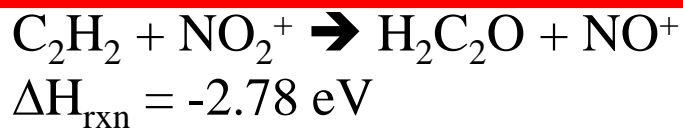
Ground State Cross Sections



1. NO^+ and $\text{C}_2\text{H}_2\text{O}^+$ similar
2. Reactivity peaking at low E_{col} implies no energetic barriers
3. Reaction efficiency $< 1\%$ suggests a severe bottleneck that can be overcome by either **energy** or **time**



Integral Cross Sections



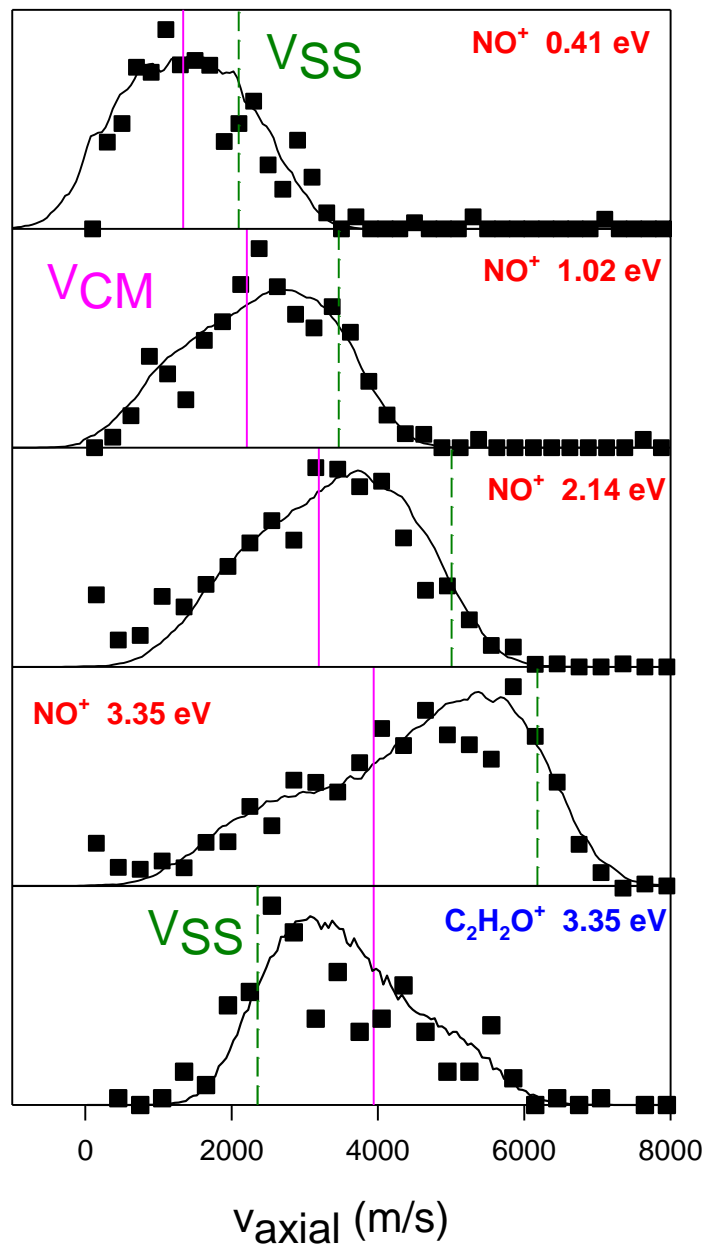
E_{col} and E_{vib} dependence nearly identical for the two charge states

→ Mode effects show dynamics at rate-limiting step

→ Must occur early, while NO_2^+ “remembers” the initial state

→ Product branching is determined late in collision

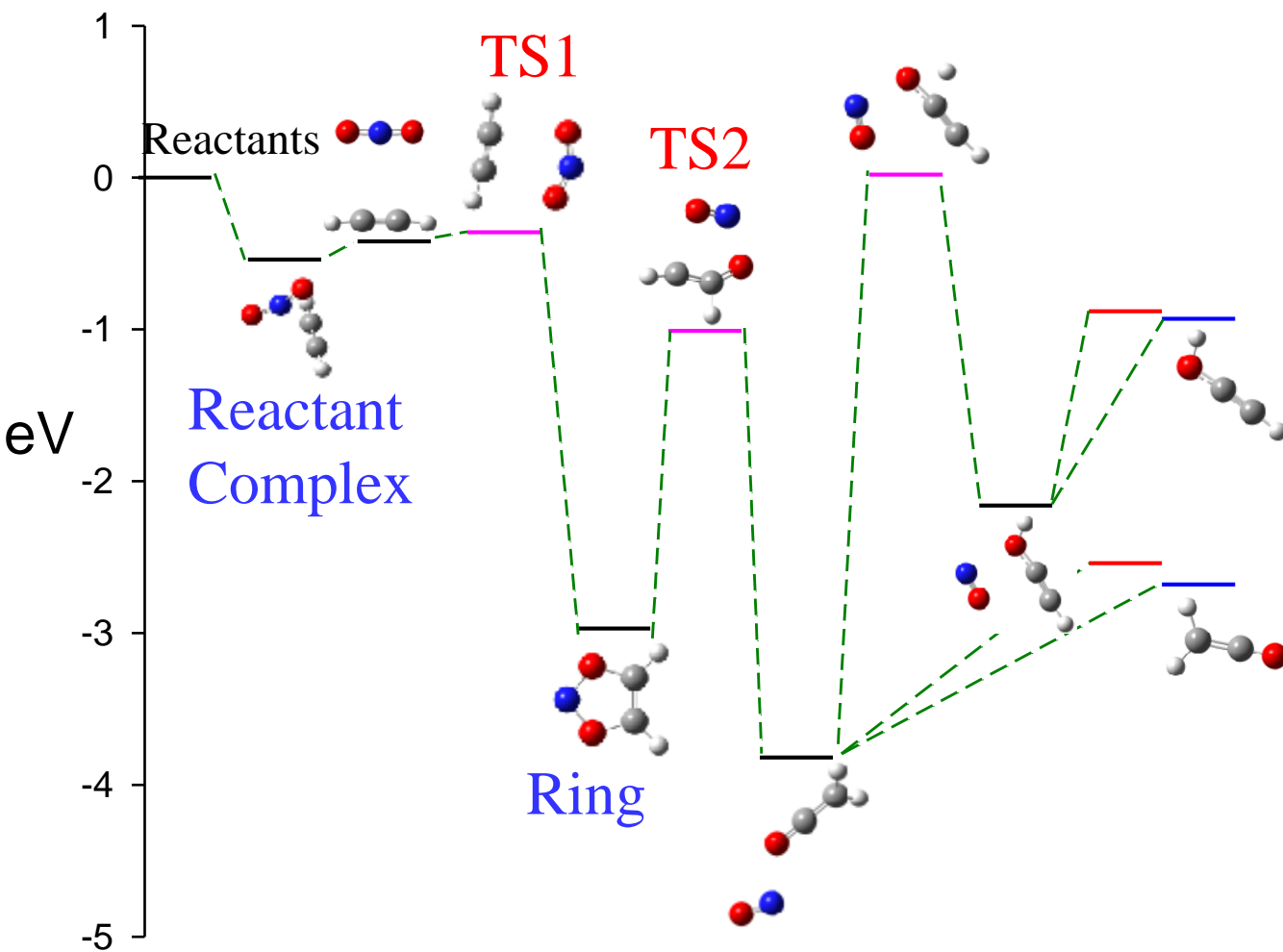
Velocity distributions



1. Distributions for $\text{C}_2\text{H}_2\text{O}^+$ and NO^+ are fit by the same dynamical parameters
2. **Branching between channels determined late in the collision – after the rate-limiting step**
3. Complex mediated at low E_{col} ?
4. Direct at high E_{col}

Focus on the NO^+ channel

$\text{NO}_2^+ + \text{Acetylene}$ Reaction Coordinate



What is responsible for the bottleneck?

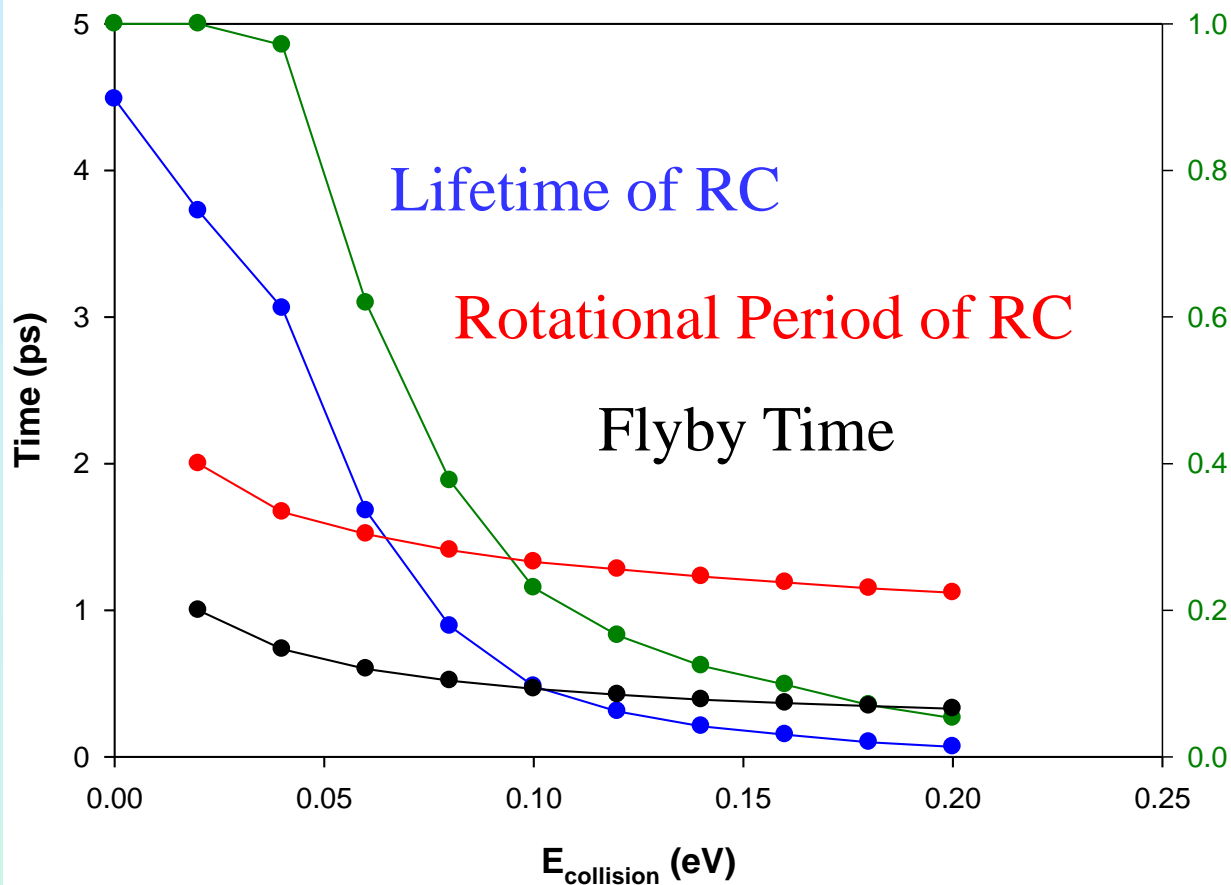
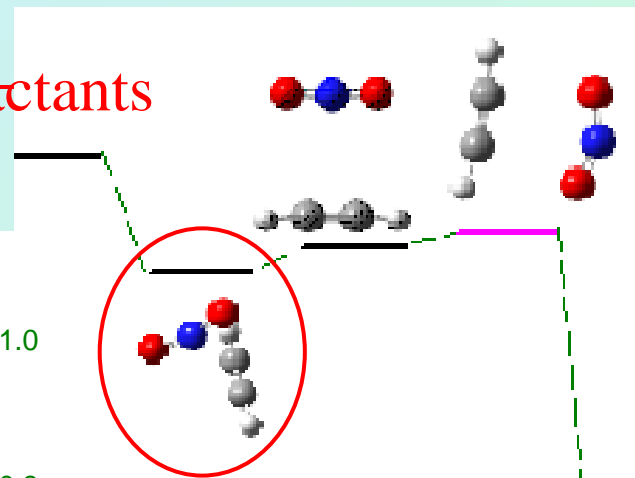
Why does σ shoot up at low E_{col} ?

Why is v_{axial} F-B symmetric up to ~ 1 eV?

RRKM Results for Reactant Complex

Reactants

TS1



Forward Branching Ratio

Precursor complex explains low energy spike in reactivity

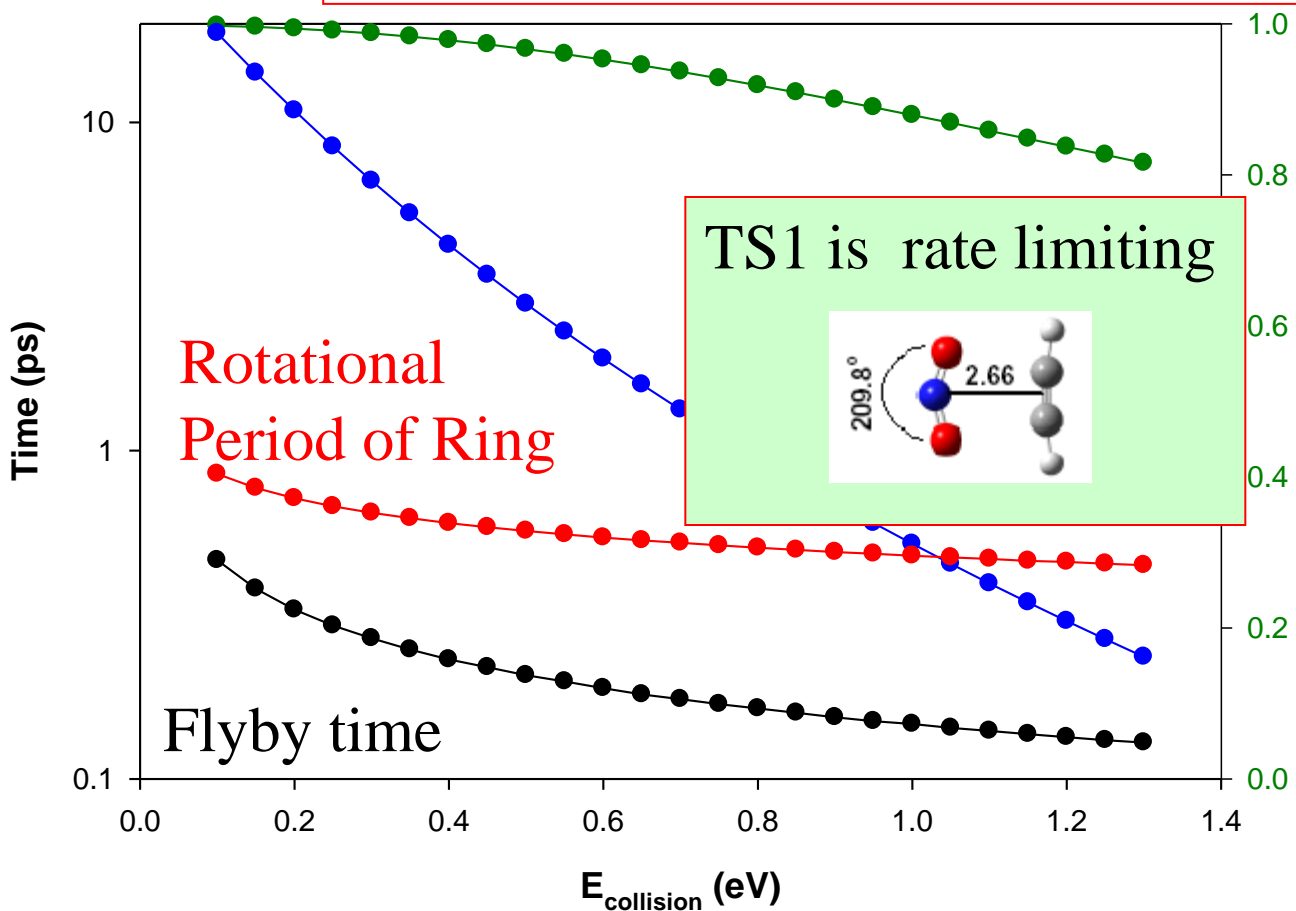
Vibration does not scramble in this complex

Cannot account for forward backward symmetry at higher collision energies!

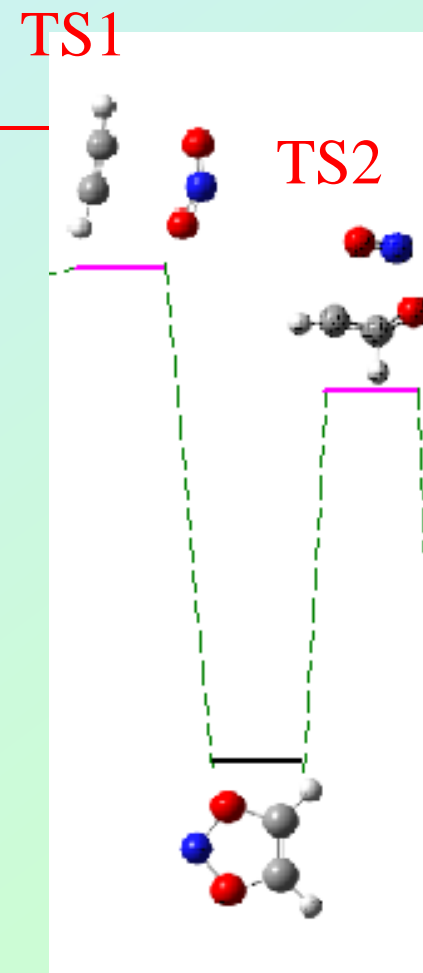
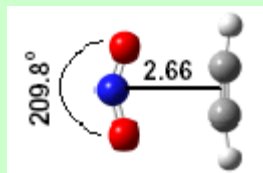
RRKM Results for Ring Complex

Ring complex occurs after rate limiting step – no effect on reactivity

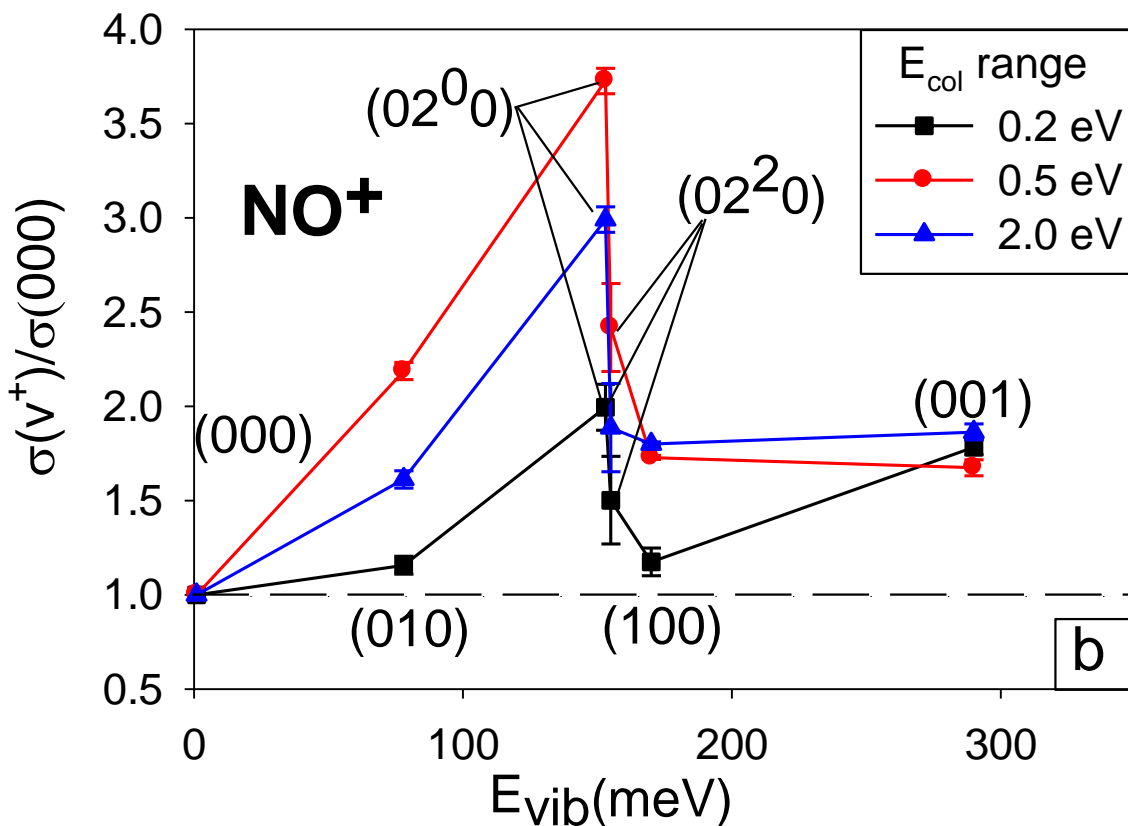
But it does account for F-B symmetry to 1 eV



TS1 is rate limiting



Vibrational Effects on σ



Enhancement linear with bend quantum number

(100) and (001) rather ineffective

Enhancement killed by bending angular momentum

$L_{\text{orb}} > 100, \gg 2$

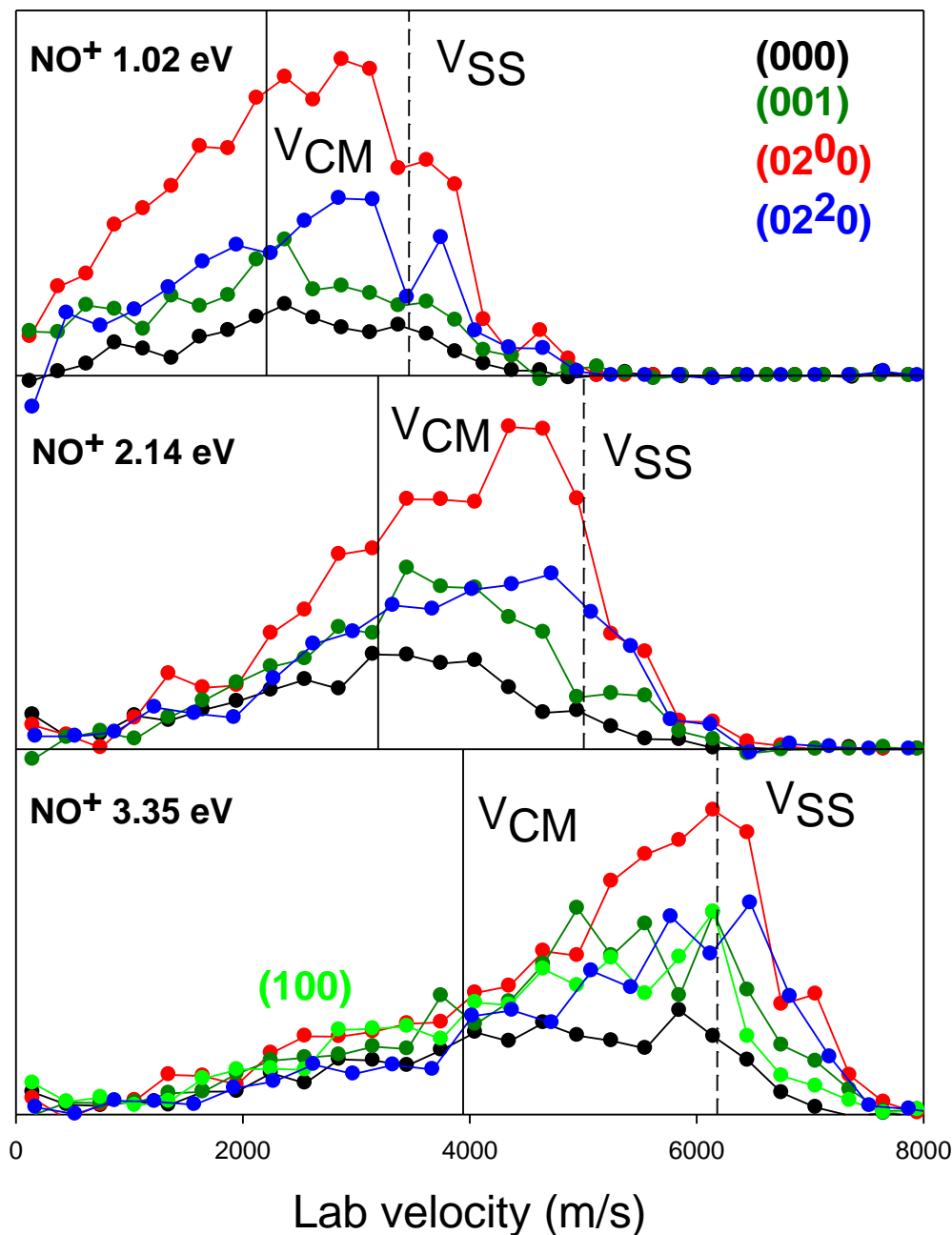
$\Delta E(02^20 - 02^00) \sim 2 \text{ meV}$

Vibrational Effects on v_{axial}

(02⁰0) excitation increases stripping, with little effect on back-scattering

- **Bending vibration increases $P(b)$ at large b only (NO?)**

Similar but smaller effects from (100) and (001)



Direct Dynamics Simulation

- ❑ *Quasi-classical trajectories*
 - *Classical dynamics*
 - *Semiclassical approx. to initial states*
 - *Born-Oppenheimer surfaces*
 - *Forces calculated “on the fly”*
 - *Schegel-Millam-Hase updating Hessian*

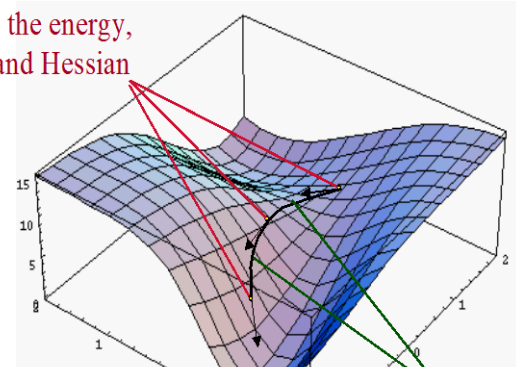
❑ *Trajectory initial conditions (VENUS - Hase)*

❑ *Recovering bend effects requires good forces*

- | | | | |
|--------------------|-----------|----------------------------|-----------------|
| - MP2/6-31g* | ~8 hours | x 300 x 6 (b) x 5 (states) | = ~8 cpu years |
| - B3LYP/6-31g* | ~10 hours | | = ~10 cpu years |
| - PBE1PBE/6-311g** | ~22 hours | | = ~22 cpu years |

Ab Initio Classical Trajectory on the Born-Oppenheimer Surface Using a Hessian-based Predictor-Corrector Method

Calculate the energy, gradient and Hessian

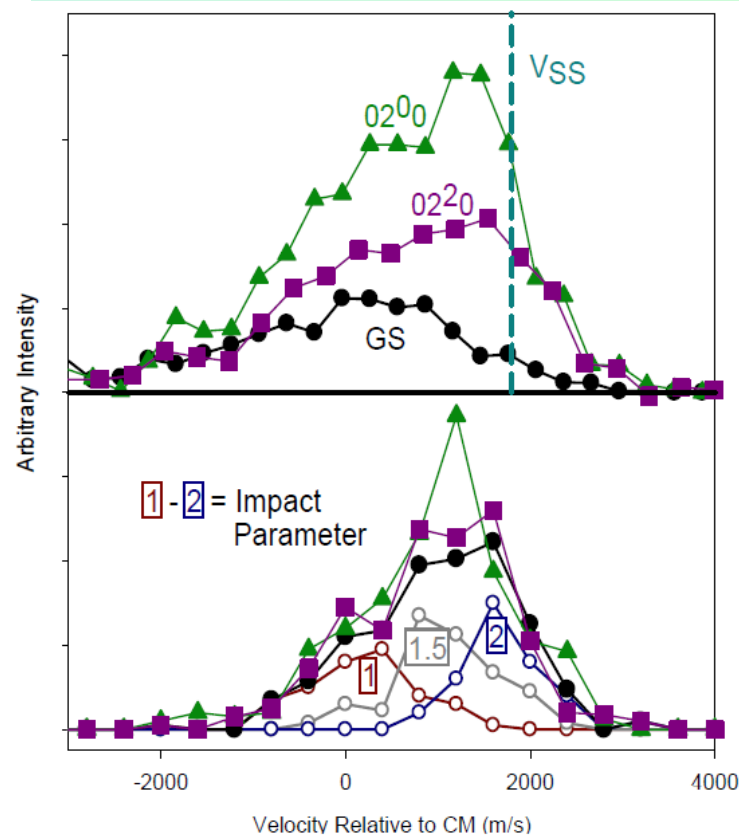


NOTE: Single reference BO dynamics work here because the rate-limiting step is early – before charge state separation

Trajectory – Expt'l agreement?

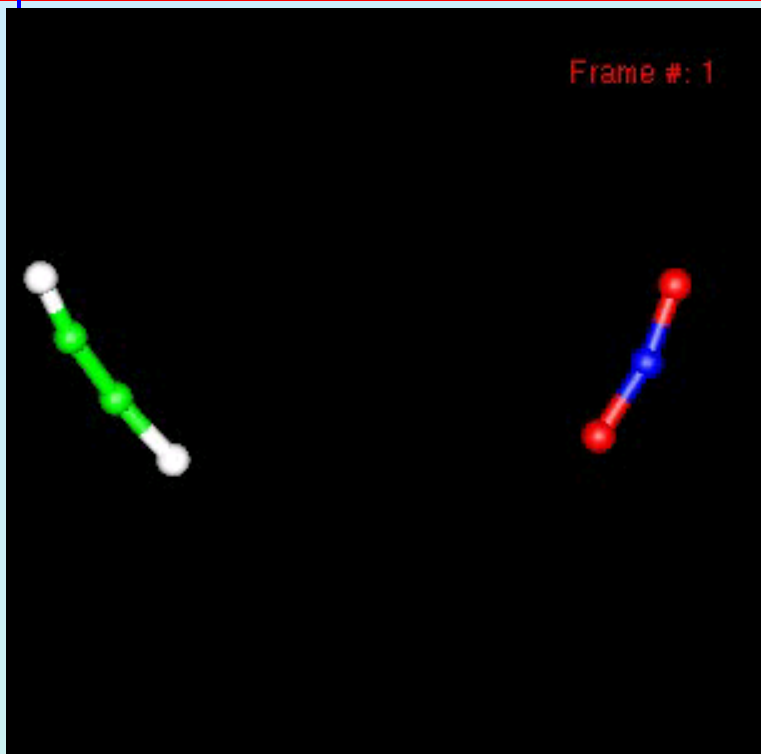
Impact Parameter	Reactant State		
	GS	02 ⁰⁰	02 ²⁰
b (Å)			
1.0	0.328	0.397	0.331
1.5	0.265	0.347	0.281
2.0	0.140	0.140	0.140
2.5	0.000	0.000	0.000
$\sigma(\text{Å}^2)$ trajectory	3.16 ± 0.35	3.76 ± 0.36	3.25 ± 0.38
$\sigma(\text{Å}^2)$ expt.	2.79	5.36	4.13

NOTE: trajectories show P(b) increases in mid range of b, not near stripping limit

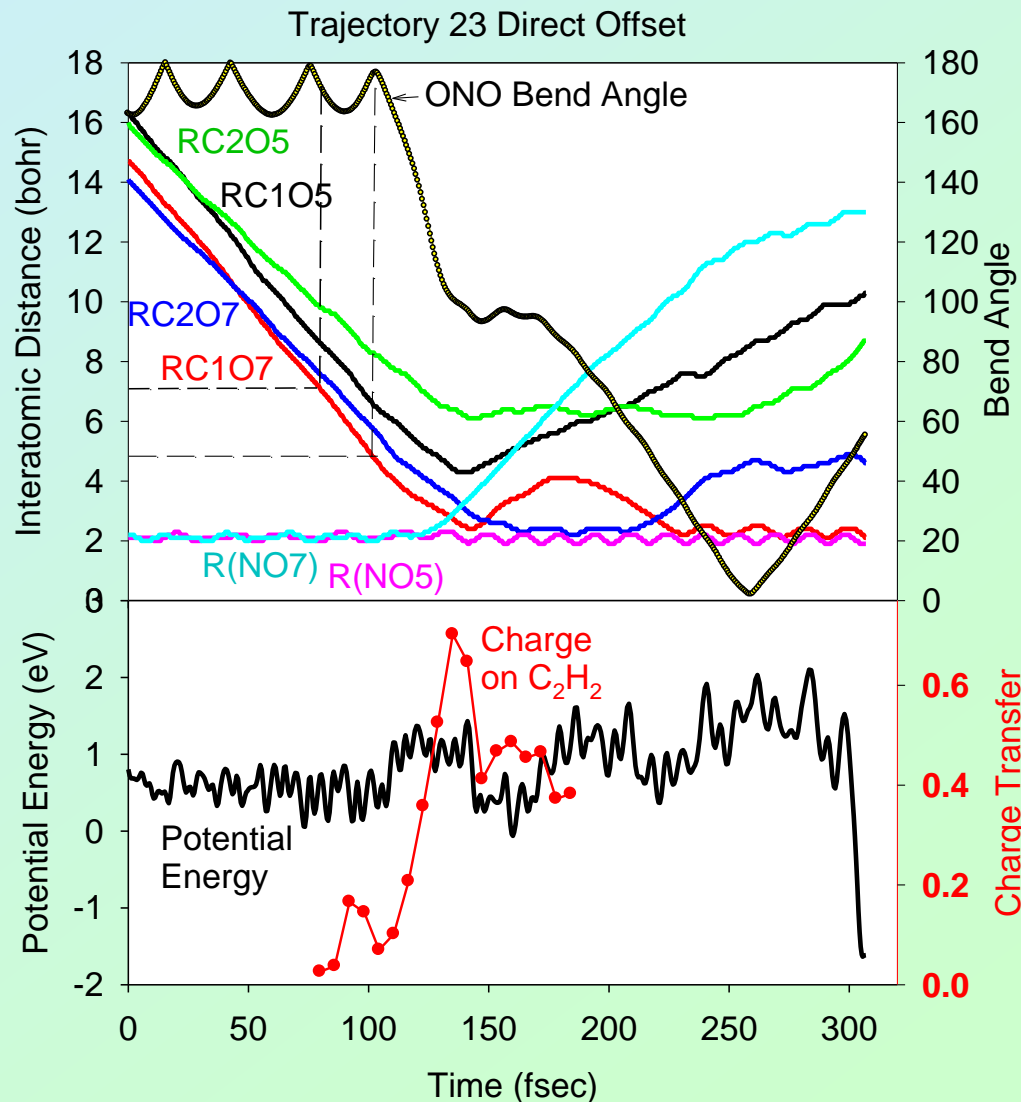


Absolute magnitude good
Vib effects qualitative

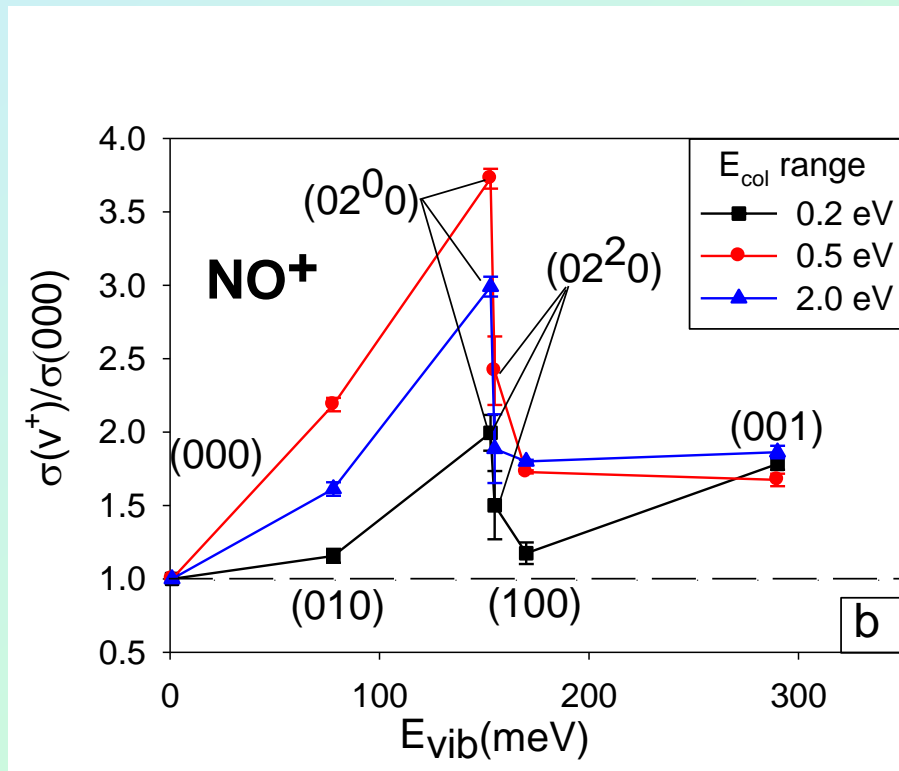
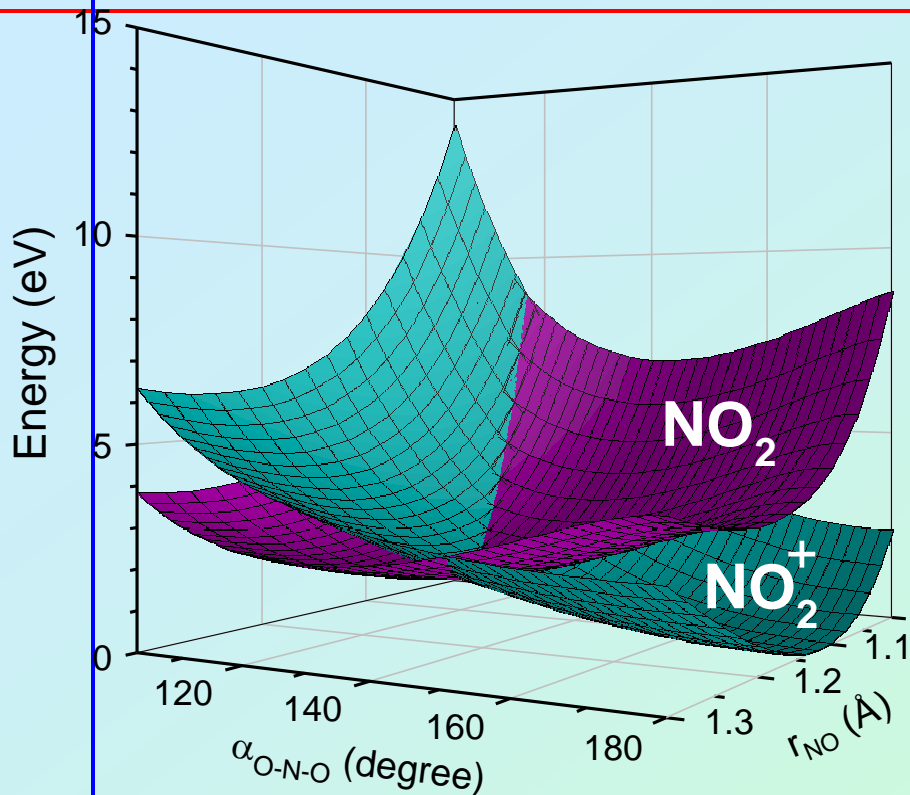
A typical reactive collision



Note: strong NO_2 bending just before O transfer



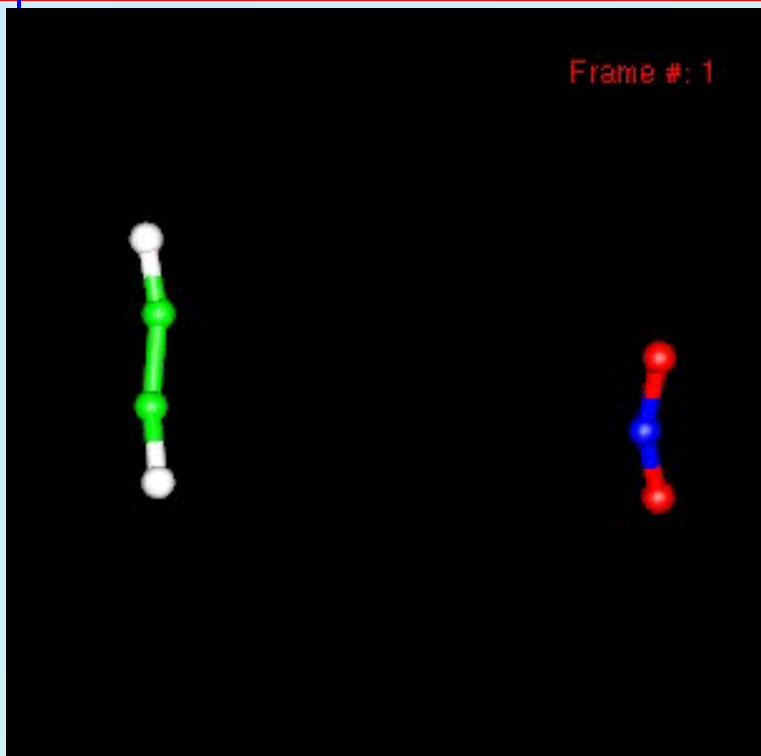
Charge Transfer Switching Causes Reaction?



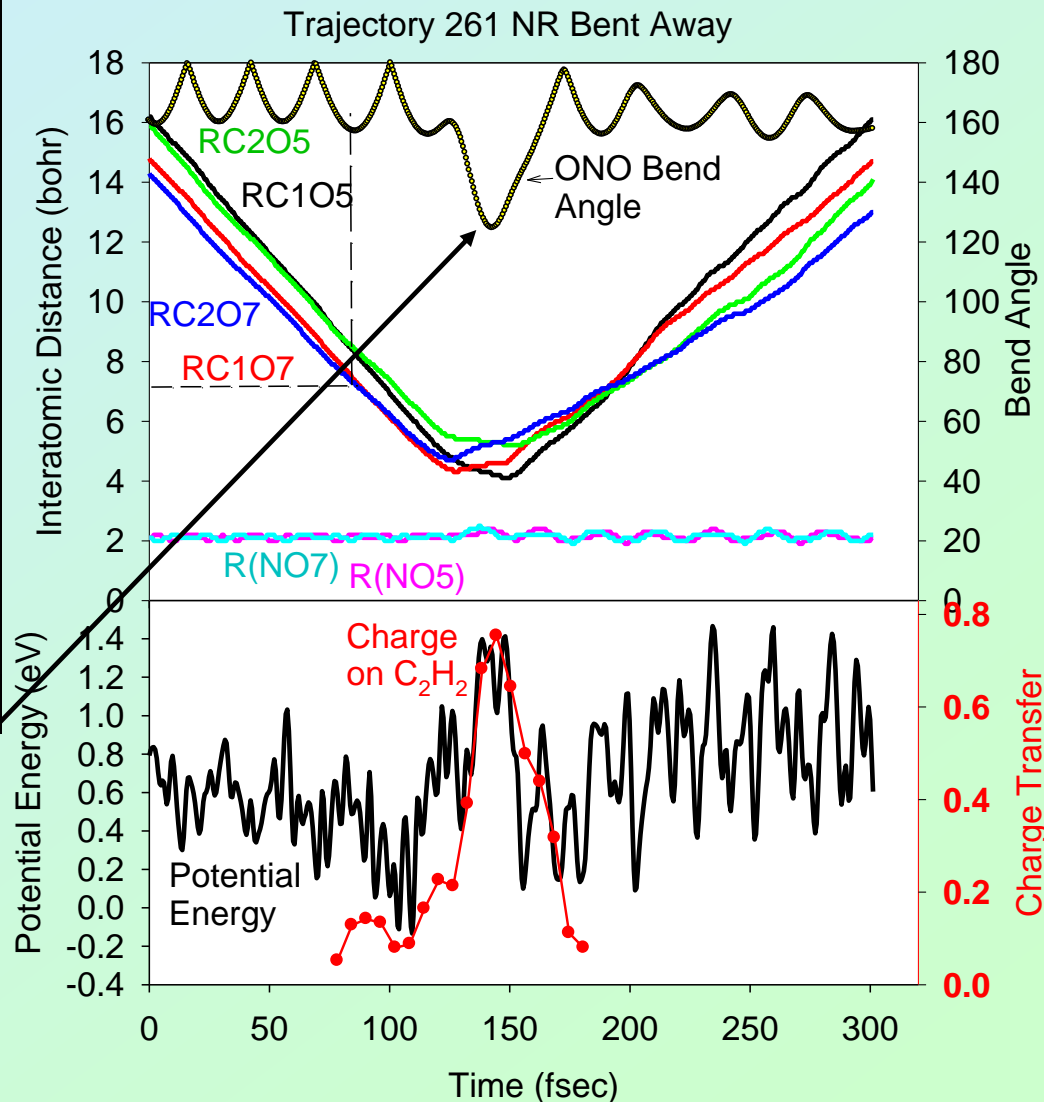
$NO_2^+ + C_2H_2$ is singlet-singlet – non reactive?

$NO_2 + C_2H_2^+$ is doublet-doublet – reactive?

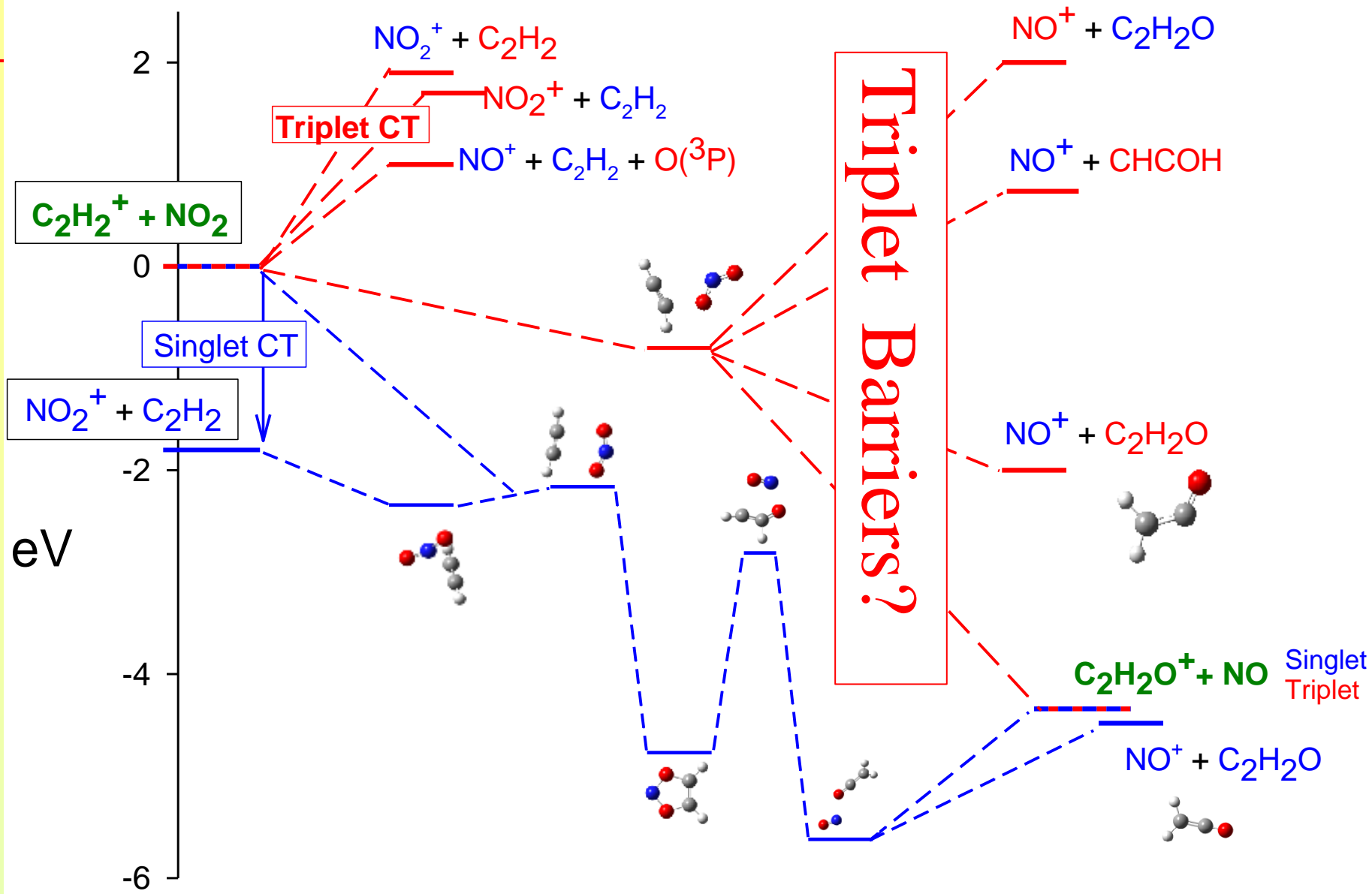
Bending is not enough Orientation also critical



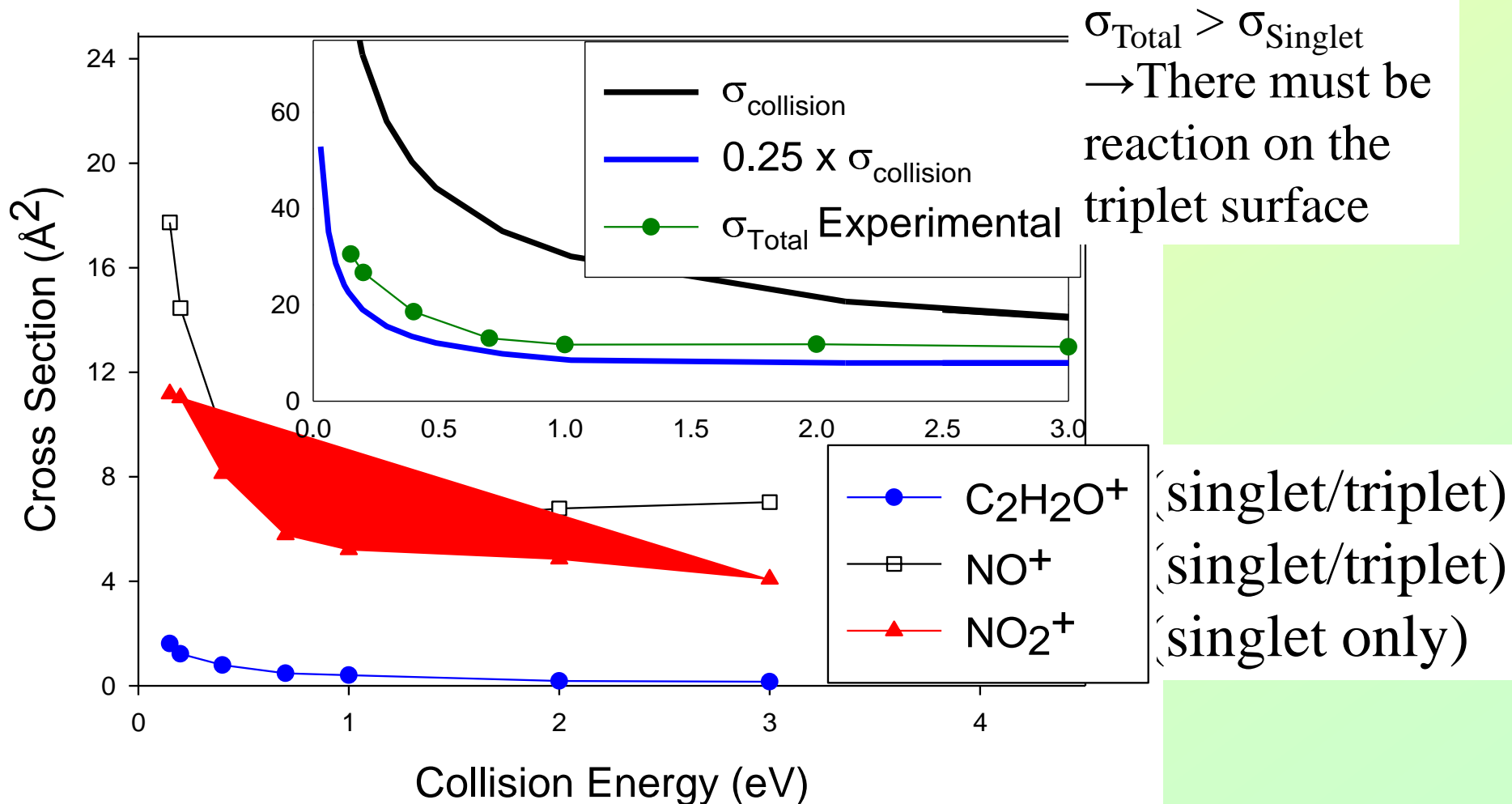
Bend goes to 126°
CT > 0.65



What about $C_2H_2^+ + NO_2$



Ground State Cross Sections



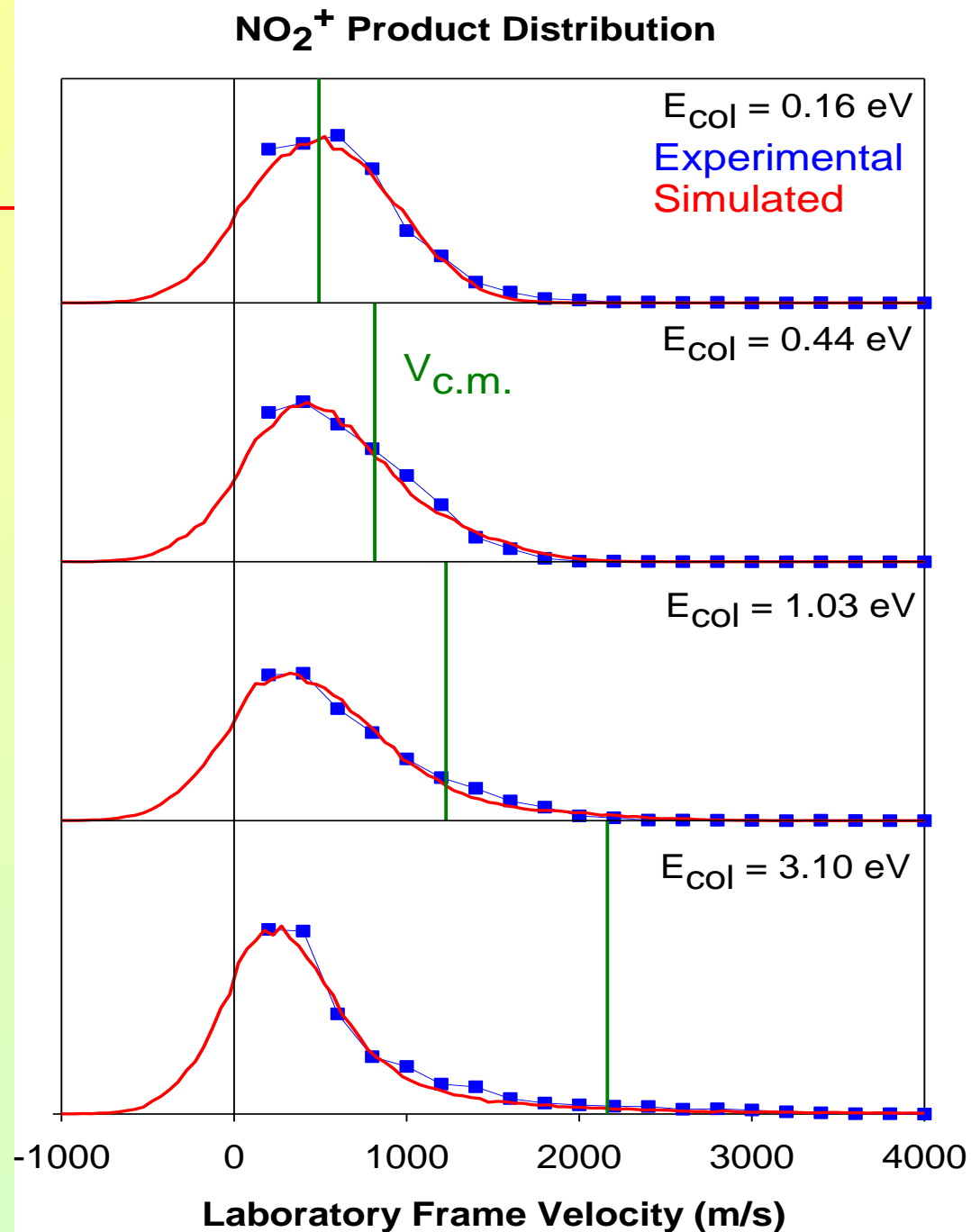
Recoil dynamics: Charge Transfer

Only possible on singlet surface

Low E_{col} – forward-backward symmetric:
Complex or just lots of momentum transfer

Shifts to back-scattered with increasing E_{col} : long-range electron transfer

E resonance and Good FC factors to high v_{bend} levels of NO_2^+



Recoil dynamics: $C_2H_2O^+ + NO$

Could form on either singlet or triplet surface

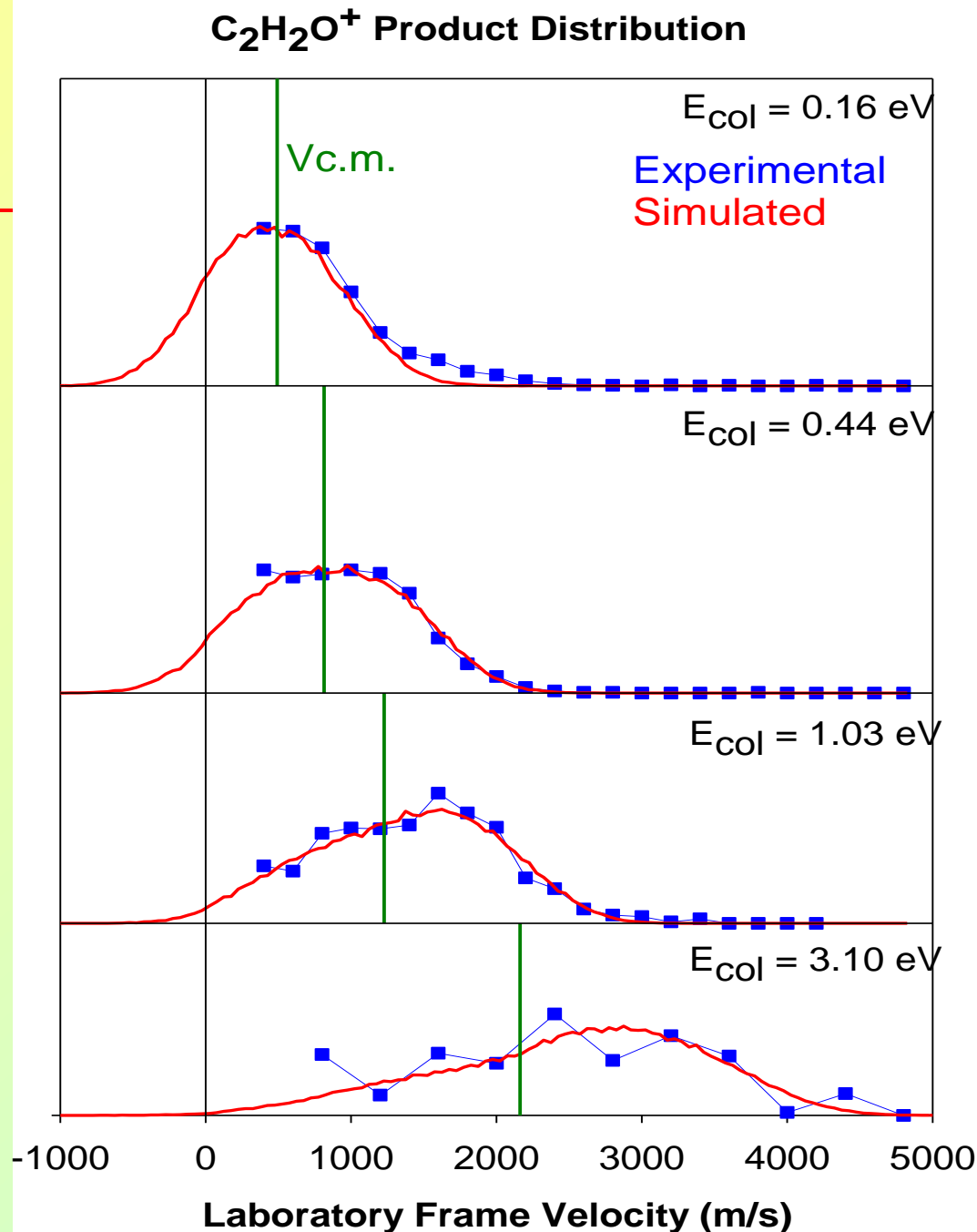
Low E_{col} – forward-backward symmetric.

Accessing deep wells found only on singlet surface?

Why no $C_2H_2O^+ + NO$ on triplet surface

Why so inefficient?

$\sigma_{Ketene} \rightarrow 0$ at high E_{col}



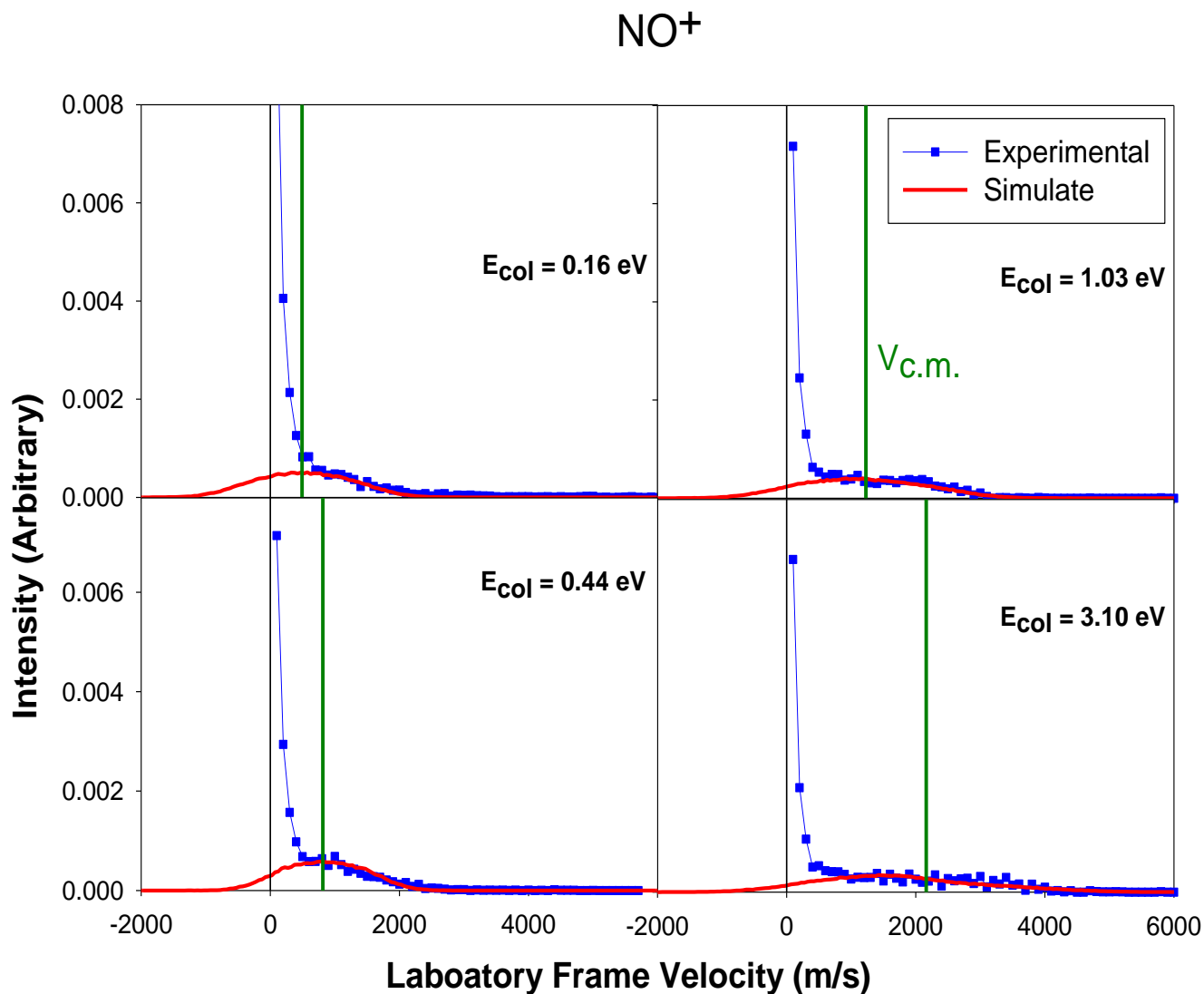
Recoil dynamics: NO⁺ formation

Two components at all E_{col} :

Very broad component centered on V_{CM}

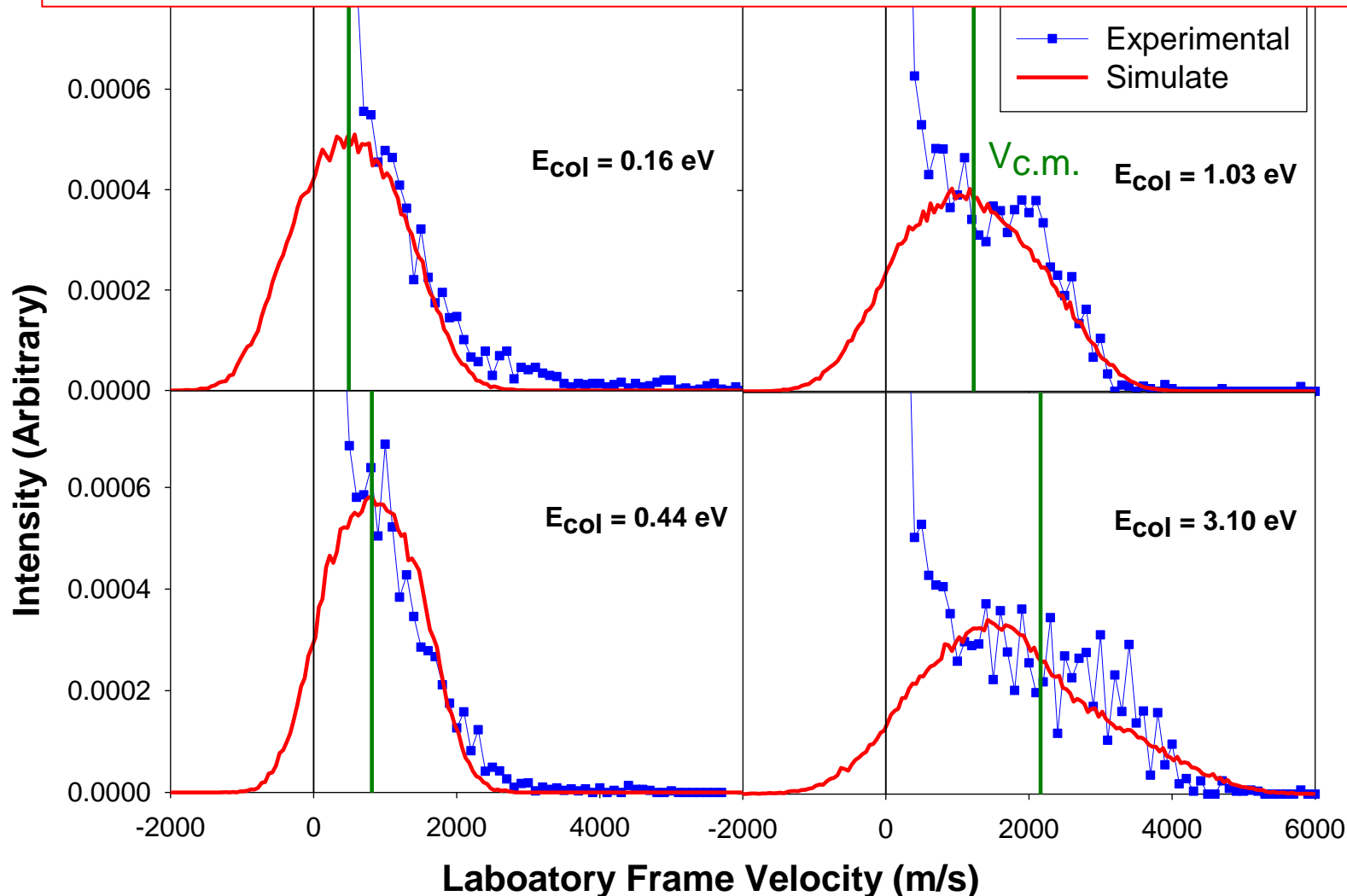
Backscattered component – piles up at zero lab velocity

Could this be from reaction on singlet and triplet surface?

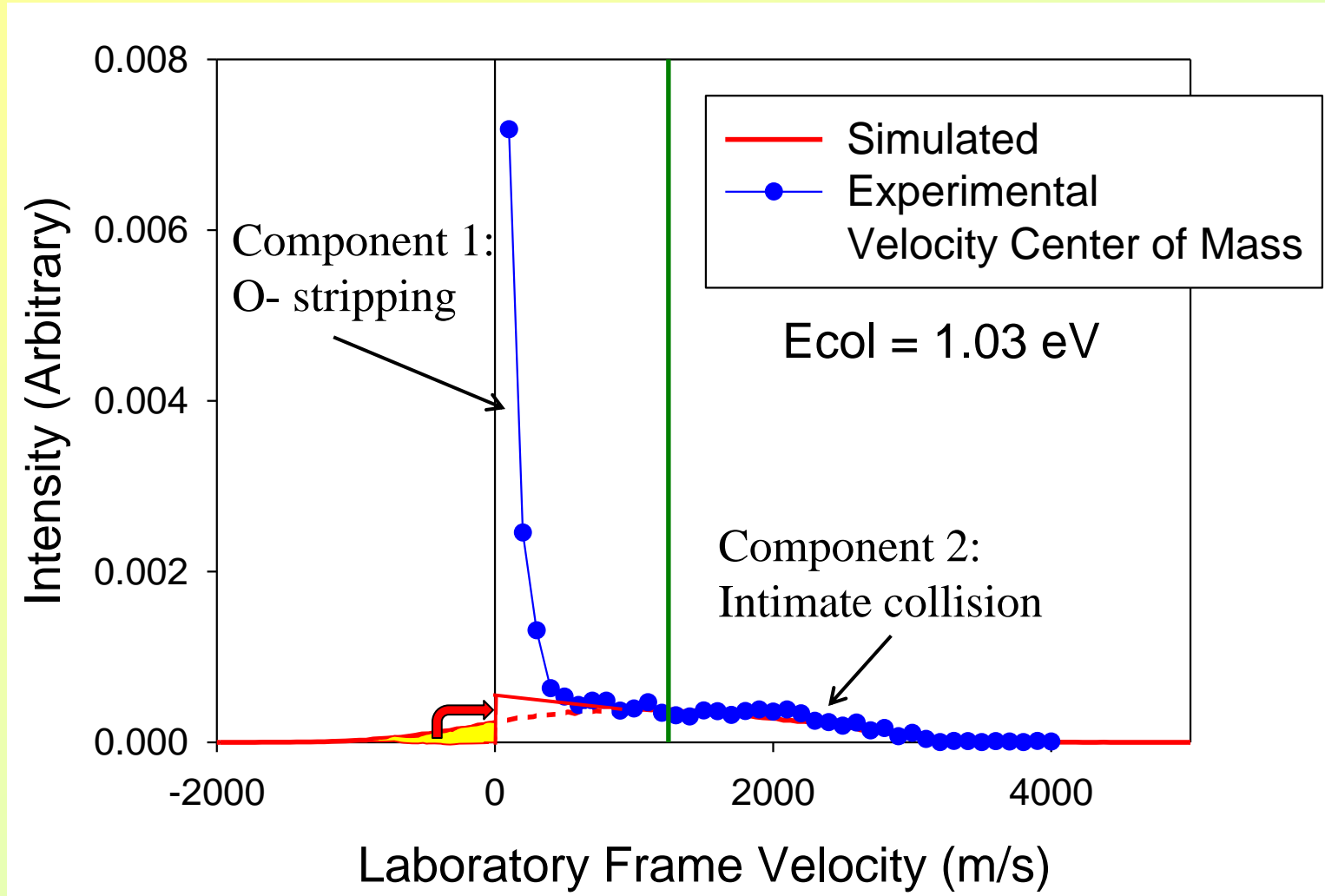


What are the two components?

Broad component *fit to same parameters* as $C_2H_2O^+$ - accessing well on singlet surface?

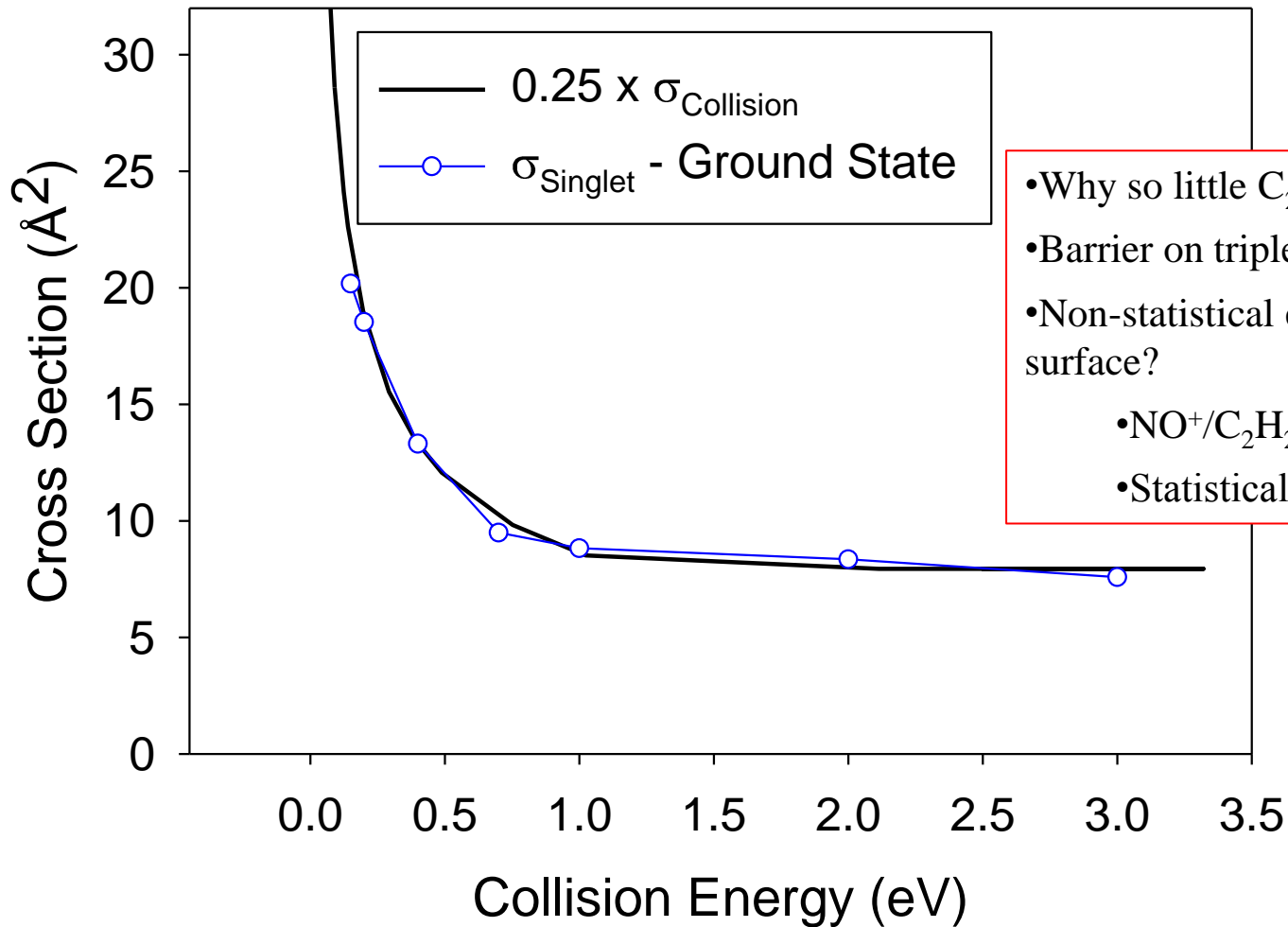


Looks like two components – separate them using the v_{axial} information



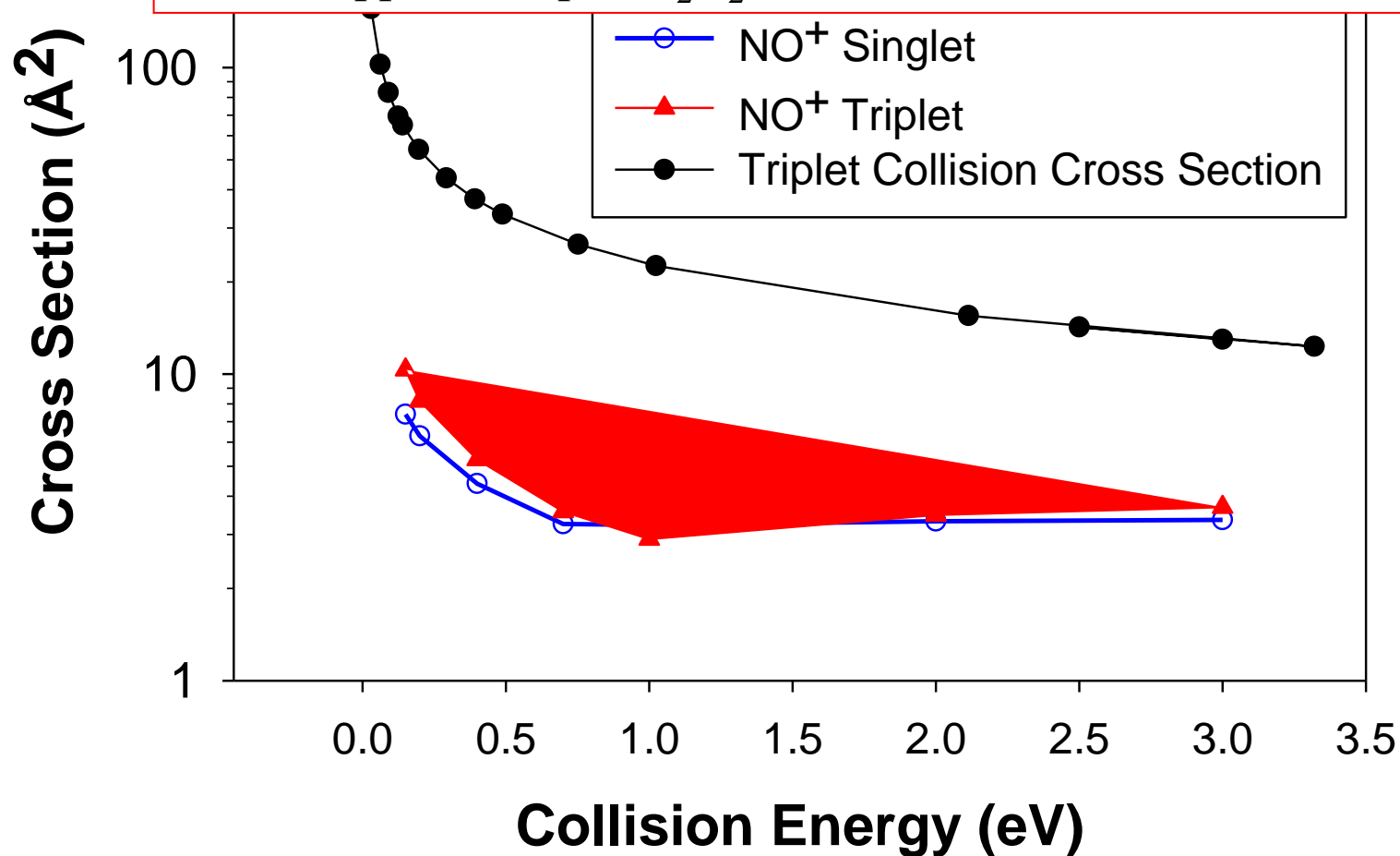
Total Singlet Reaction Cross Section

$$\sigma_{\text{Singlet}} = \sigma(\text{CT} + \text{C}_2\text{H}_2\text{O}^+ + \text{NO}^+_{\text{broad}})$$



Breakdown of NO^+ signal into Singlet and Triplet contributions

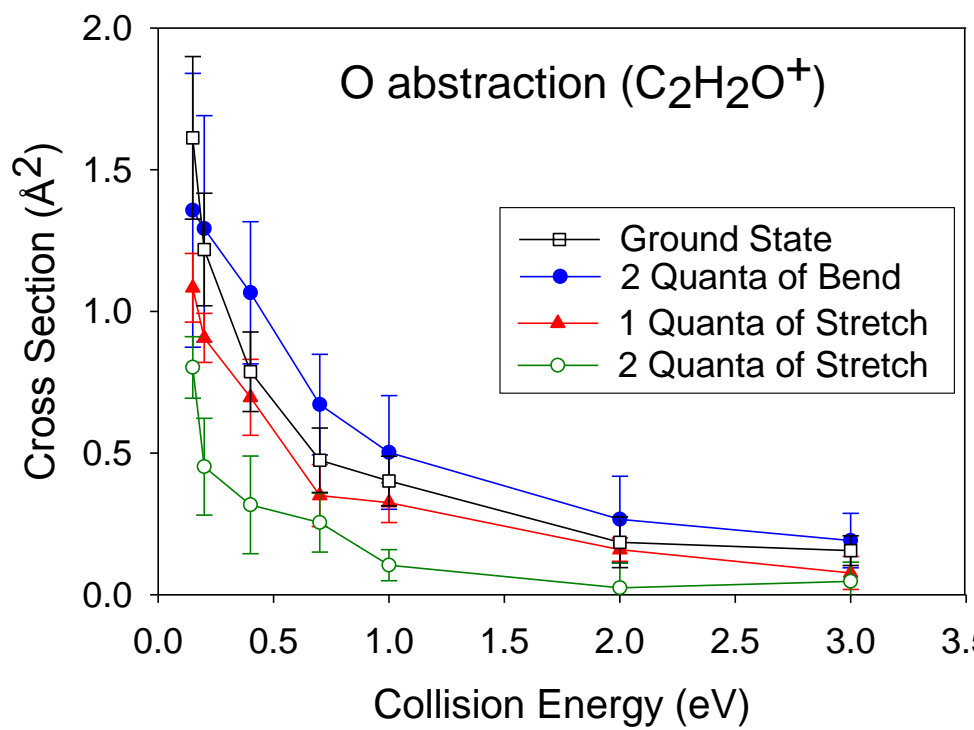
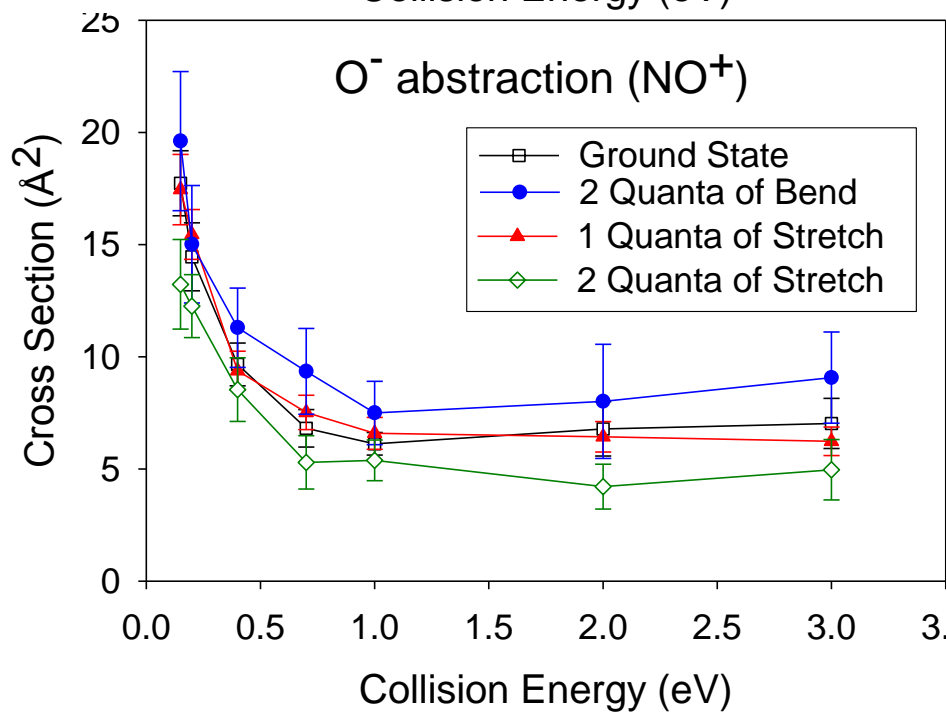
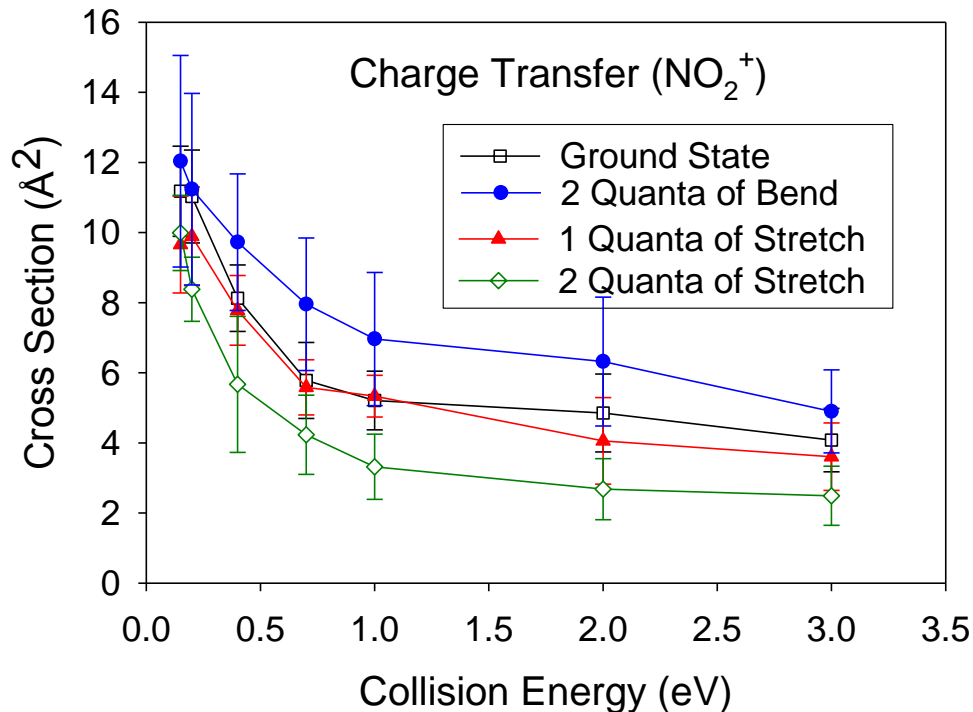
Reaction on triplet surface is quite inefficient
O⁻-stripping with little momentum transfer
No apparent triplet $\text{C}_2\text{H}_2\text{O}^+ + \text{NO}$

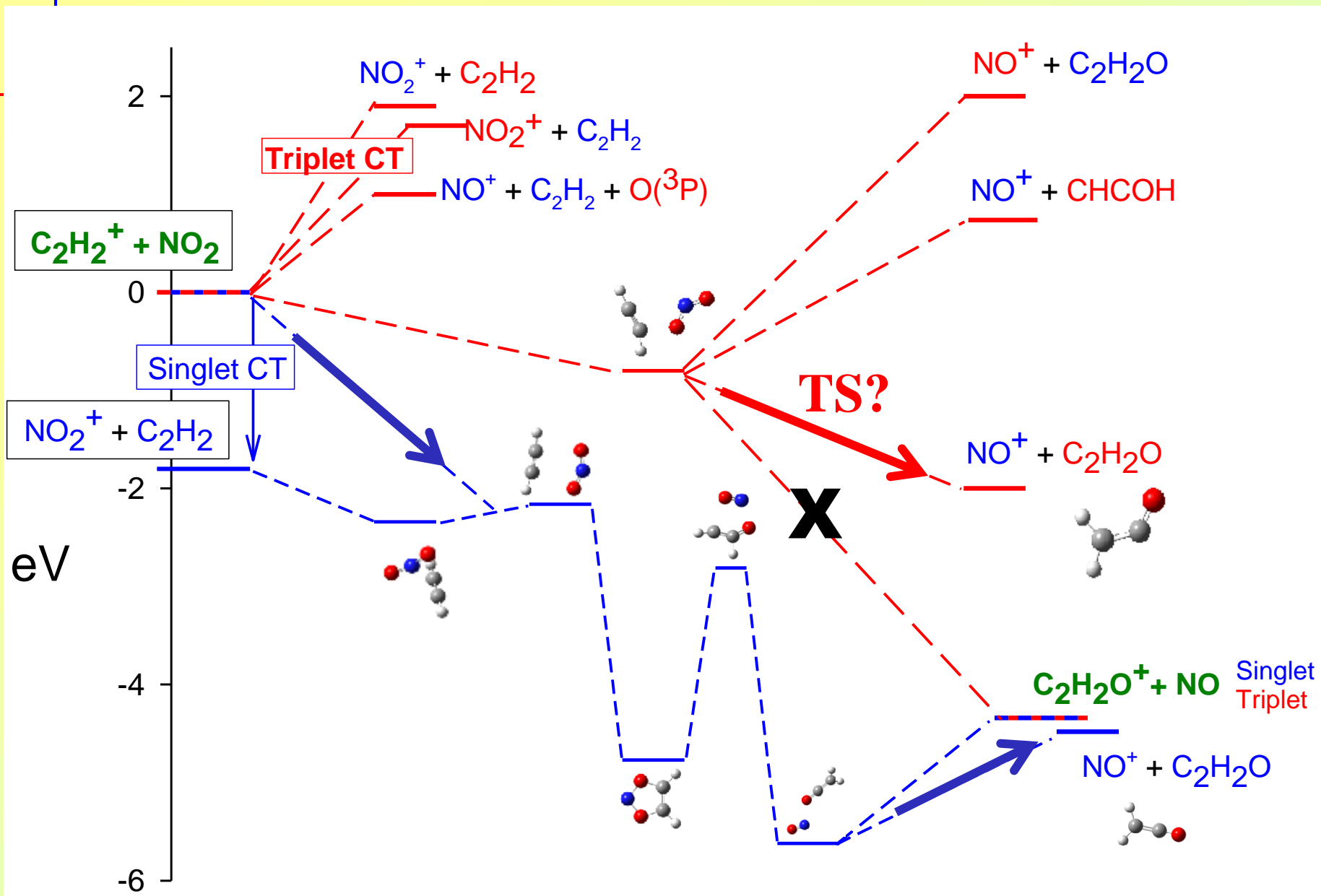


Vibrational effects:

- All channels enhanced by C_2H_2^+ cis-bend excitation
- All channels inhibited by CC-stretch excitation

WHY?

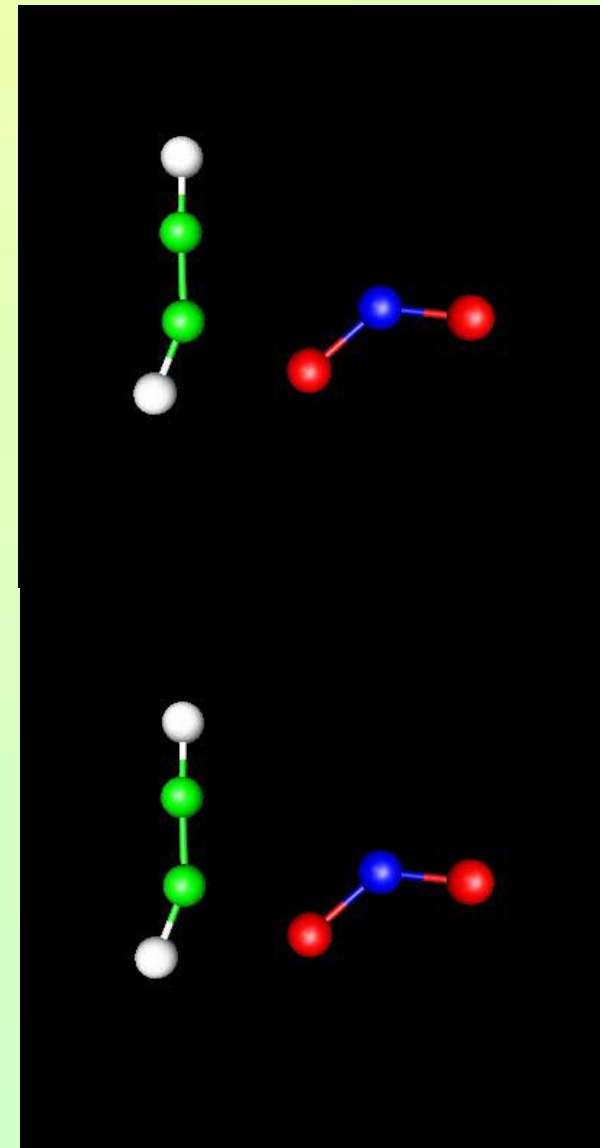
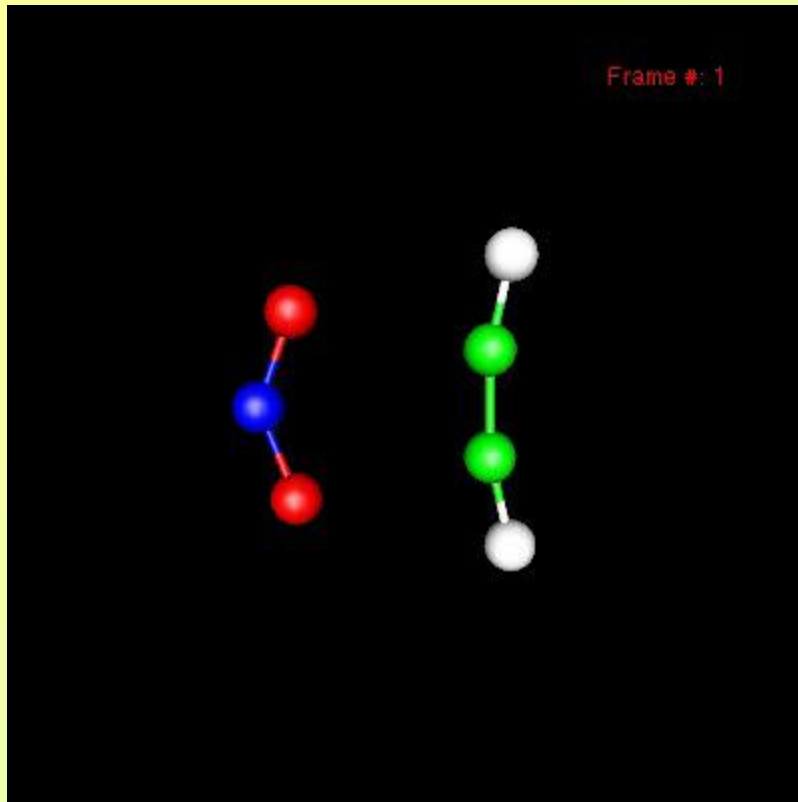




Vibrations

Triplet Complex

TS to Singlet Complex



Summary

- Pretty well understand the dynamics on both the singlet and triplet surfaces, starting from both $\text{NO}_2^+ + \text{C}_2\text{H}_2$ and $\text{C}_2\text{H}_2^+ + \text{NO}_2$
- The $\text{C}_2\text{H}_2^+ + \text{NO}_2$ charge state is more reactive, but only when singlet coupled (triplet < 10%)
- For $\text{NO}_2^+ + \text{C}_2\text{H}_2$, NO_2^+ vibration mainly helps push the system into the more reactive charge state
- For $\text{C}_2\text{H}_2^+ + \text{NO}_2$, vibrational effects appear related to type of distortions needed to drive reaction, except what about CT?

Jason Boyle, Dave Bell. NSF support

