PST Modeling - Project Overview

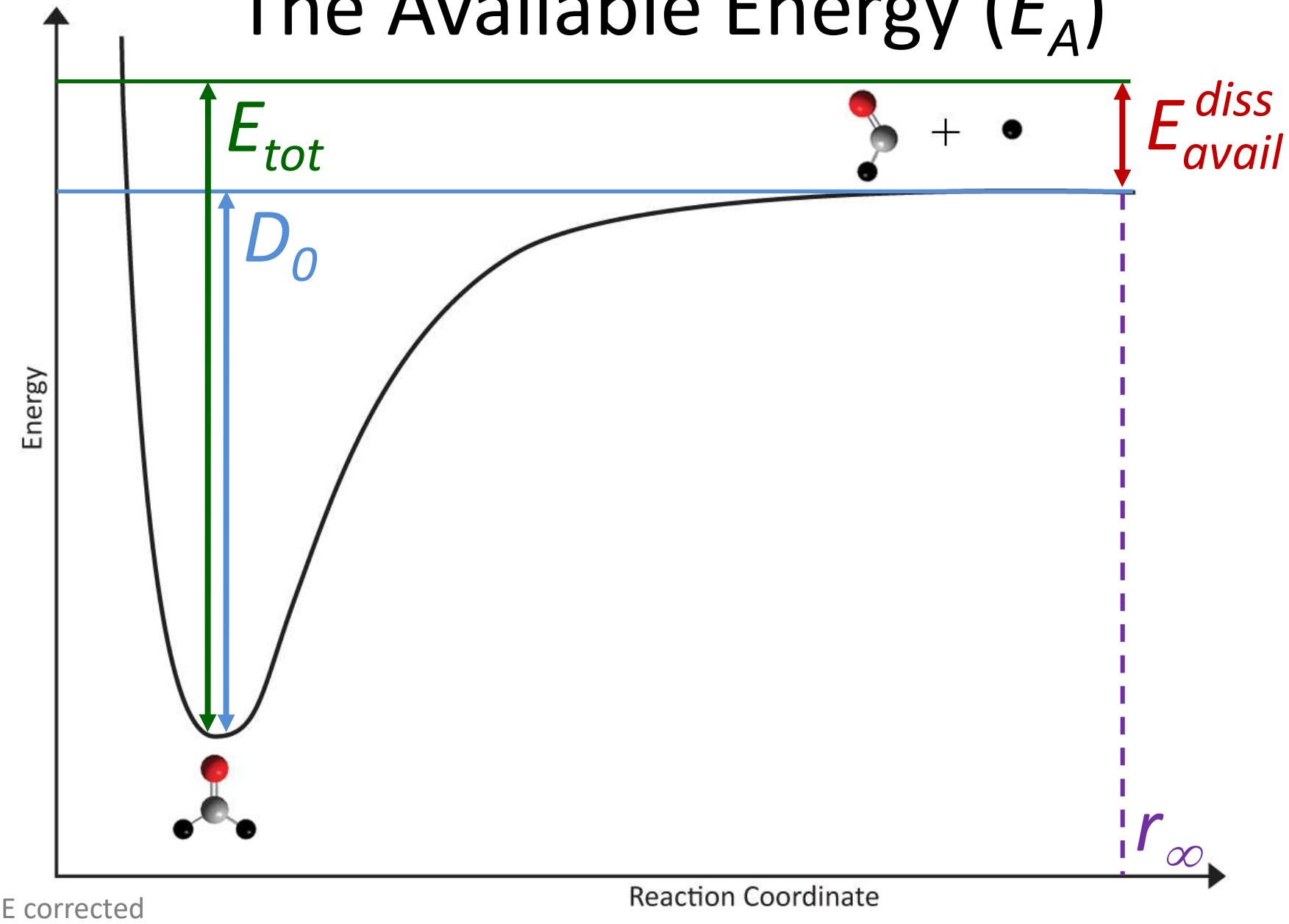
- Modeling Roaming
- Modeling Triple Fragmentation

What Is PST

- $\omega_{tot}(v_1, v_2, J_1, J_2, X_1, X_2; J_{parent}, E_A)=$

- A statistical method for calculating the sum of rovibrational states at a given available energy (E_A), while conserving energy and angular momentum

The Available Energy (E_A)



ZPE corrected

How We Implement PST

$$\omega_{tot}(v_1, v_2, J_1, J_2, X_1, X_2; J_{parent}, E_A)=$$

How We Implement PST

$$\omega_{tot}(v_1, v_2, J_1, J_2, X_1, X_2; J_{parent}, E_A) =$$

$$\sum_{v_1=0}^{v_1^{max}(E_A)} \sum_{J_1=0}^{J_1^{max}(E_A, v_1)} \sum_{K_1=0}^{J_1} \sum_{X_1=0}^{X_1^{max}(E_A, v_1, J_1, K_1)}$$

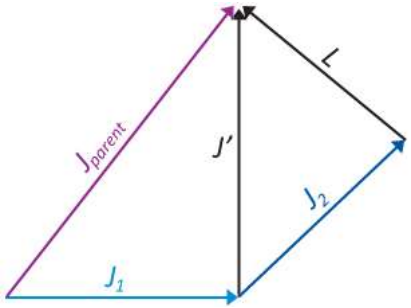
$$\sum_{v_2=0}^{v_2^{max}(E_A, v_1, J_1, K_1, X_1)} \sum_{J_2=0}^{J_2^{max}(E_A, v_1, v_2, J_1, K_1, X_1)} \sum_{K_2=0}^{J_2} \sum_{X_2=0}^{X_1^{max}(E_A, v_1, v_2, J_1, J_2, K_1, X_1)}$$

How We Implement PST

$$\omega_{tot}(v_1, v_2, J_1, J_2, X_1, X_2; J_{parent}, E_A) =$$

$$\sum_{v_1=0}^{v_1^{max}(E_A)} \quad \sum_{J_1=0}^{J_1^{max}(E_A, v_1)} \quad \sum_{K_1=0}^{J_1} \sum_{X_1=0}^{X_1^{max}(E_A, v_1, J_1, K_1)}$$

$$\sum_{v_2=0}^{v_2^{max}(E_A, v_1, J_1, K_1, X_1)} \quad \sum_{J_2=0}^{J_2^{max}(E_A, v_1, v_2, J_1, K_1, X_1)} \quad \sum_{K_2=0}^{J_2} \sum_{X_2=0}^{X_1^{max}(E_A, v_1, v_2, J_1, J_2, K_1, X_1)}$$



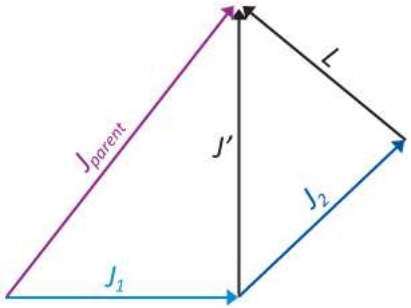
$$\sum_{J'=|J_{parent}-J_1|}^{J_{parent}+J_1} \quad \sum_{L=|J'-J_2|}^{L \le J'+J_2}$$

How We Implement PST

$$\omega_{tot}(v_1, v_2, J_1, J_2, X_1, X_2; J_{parent}, E_A) =$$

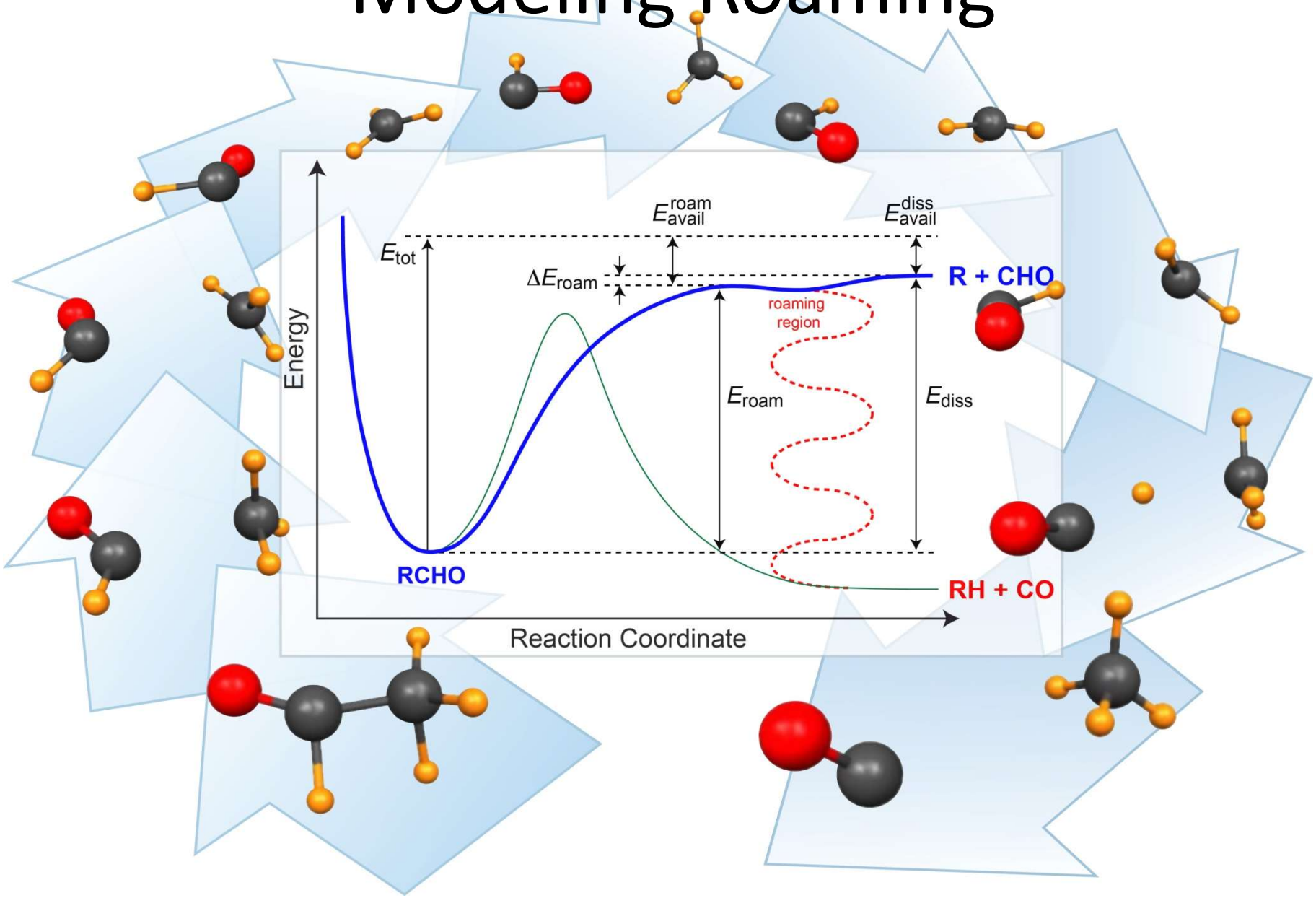
$$\sum_{v_1=0}^{v_1^{max}(E_A)} \quad \sum_{J_1=0}^{J_1^{max}(E_A, v_1)} \quad \sum_{K_1=0}^{J_1} \sum_{X_1=0}^{X_1^{max}(E_A, v_1, J_1, K_1)}$$

$$\sum_{v_2=0}^{v_2^{max}(E_A, v_1, J_1, K_1, X_1)} \quad \sum_{J_2=0}^{J_2^{max}(E_A, v_1, v_2, J_1, K_1, X_1)} \quad \sum_{K_2=0}^{J_2} \sum_{X_2=0}^{X_1^{max}(E_A, v_1, v_2, J_1, J_2, K_1, X_1)}$$

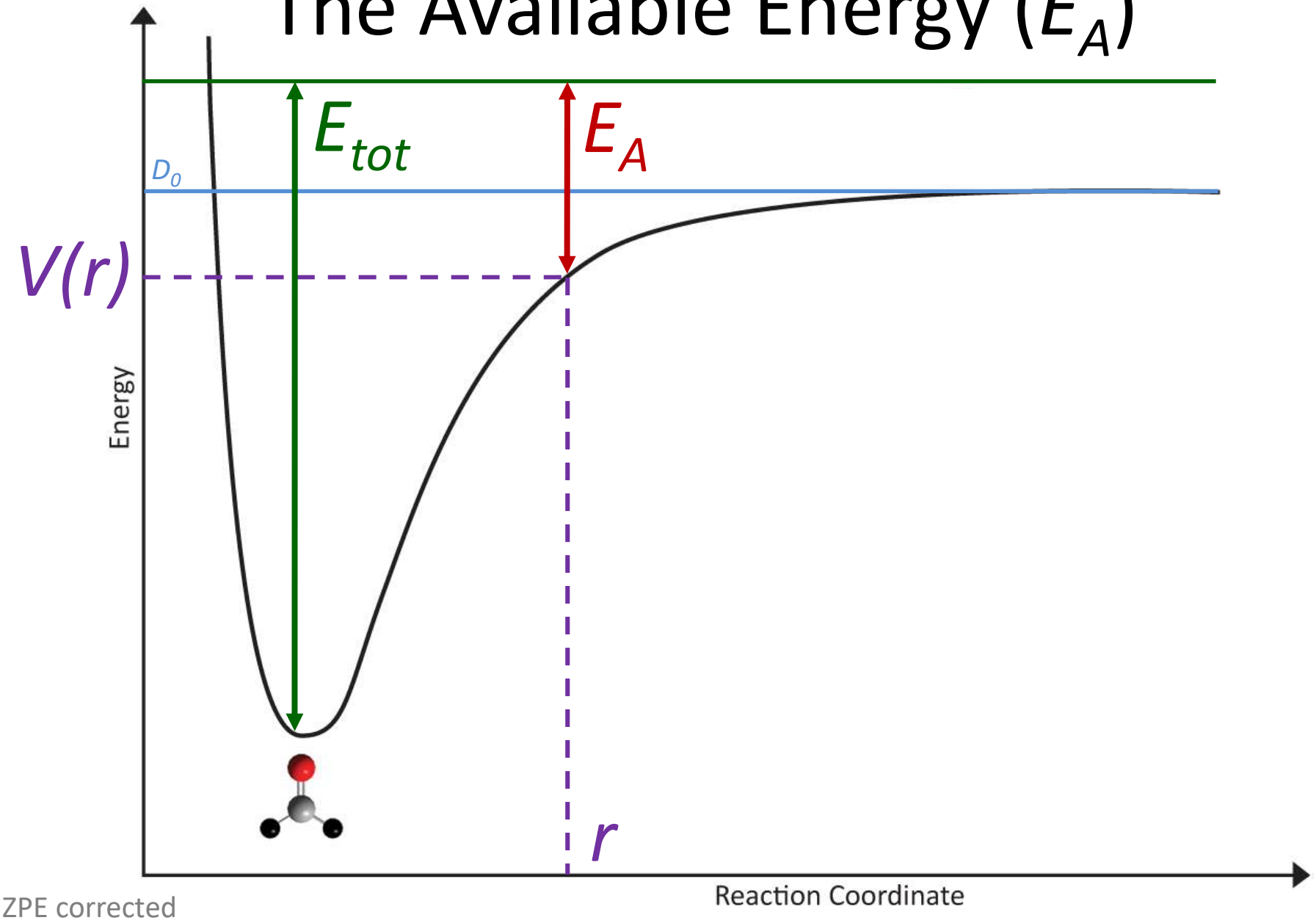


$$\sum_{J'=|J_{parent}-J_1|}^{J_{parent}+J_1} \quad \sum_{L=|J'-J_2|}^{L \le J'+J_2} \quad \prod_{i=1}^{2} d_i^{soc} d_i^{rot} d_i^{vib}$$

Modeling Roaming

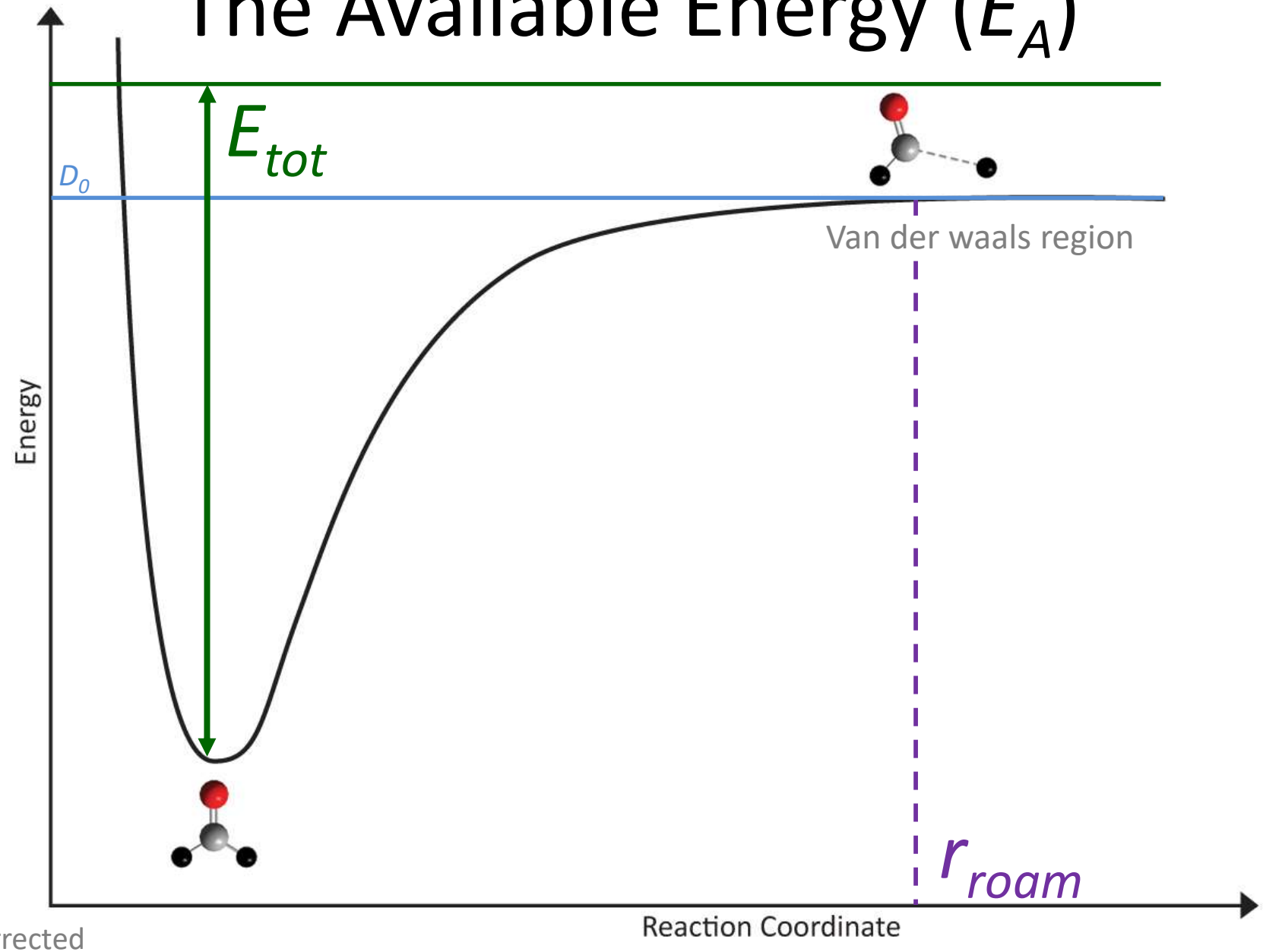


The Available Energy (E_A)



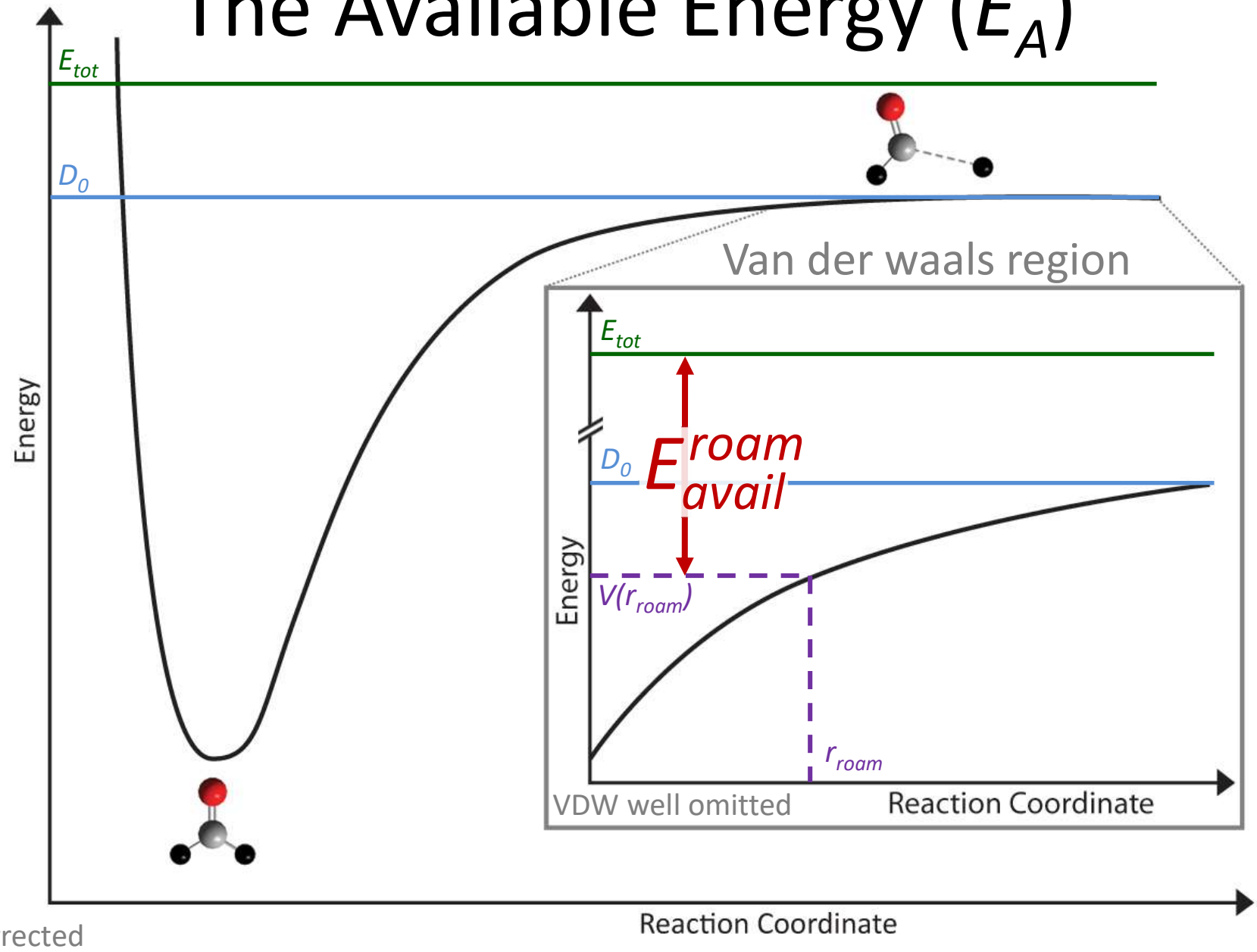
ZPE corrected

The Available Energy (E_A)



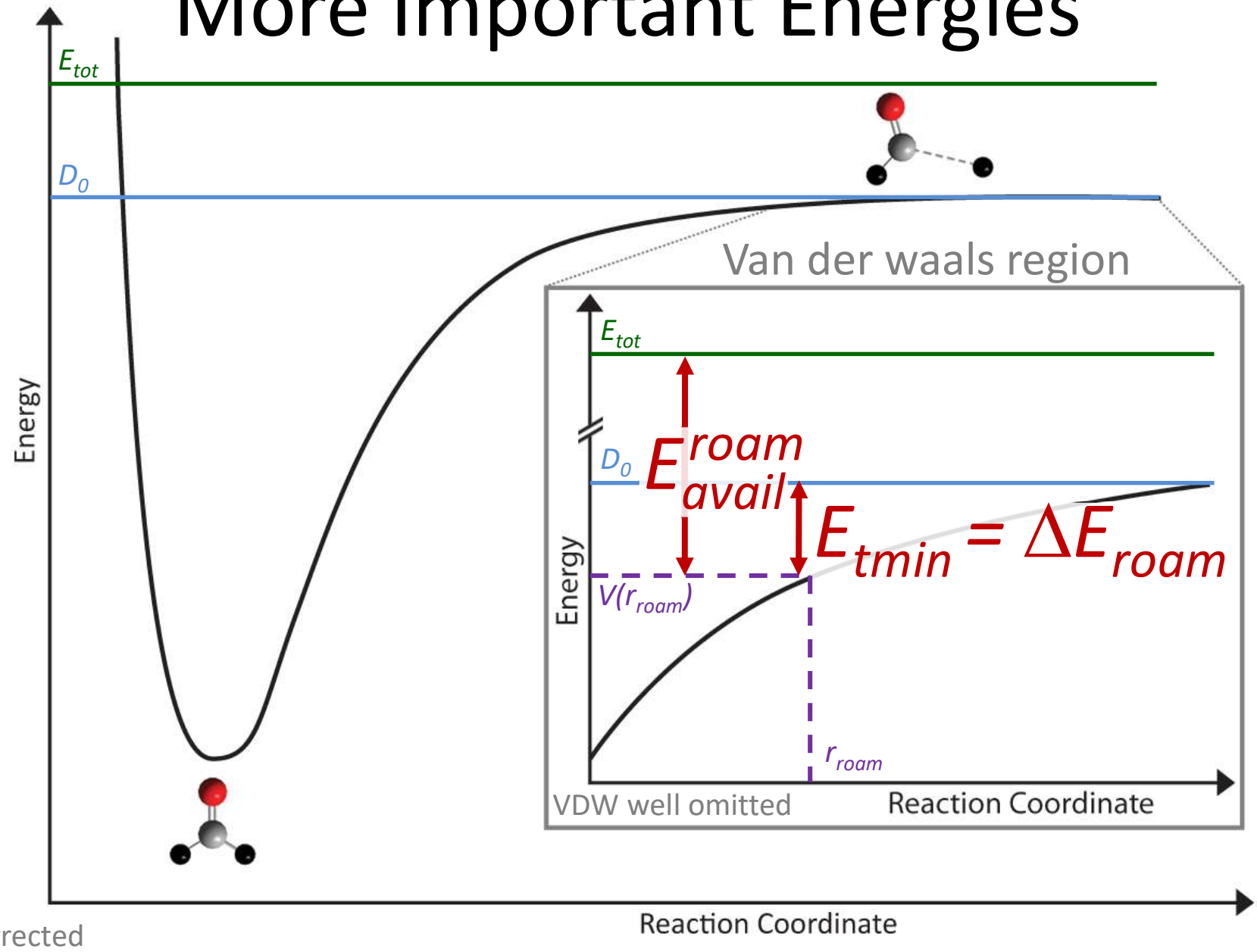
ZPE corrected

The Available Energy (E_A)



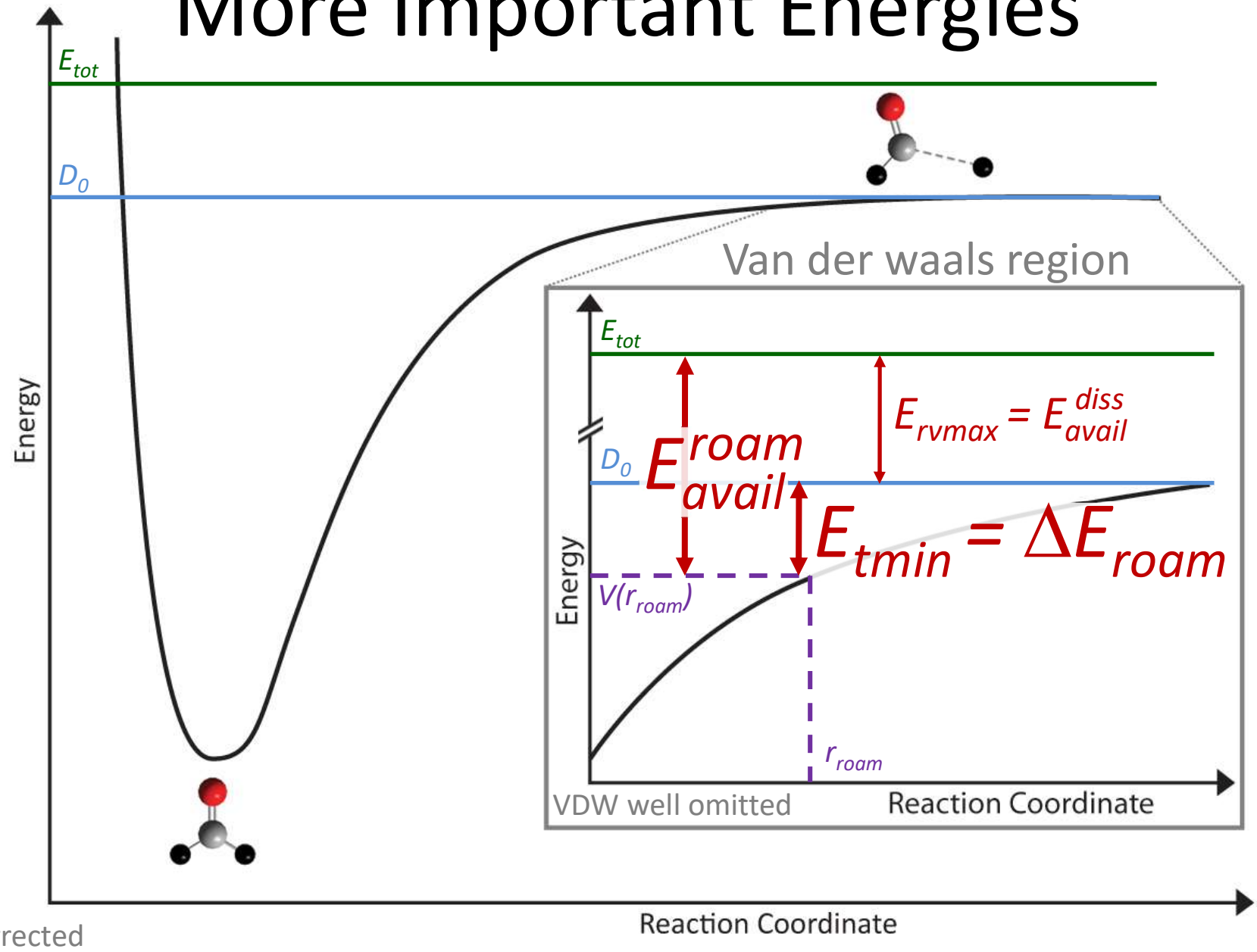
ZPE corrected

More Important Energies



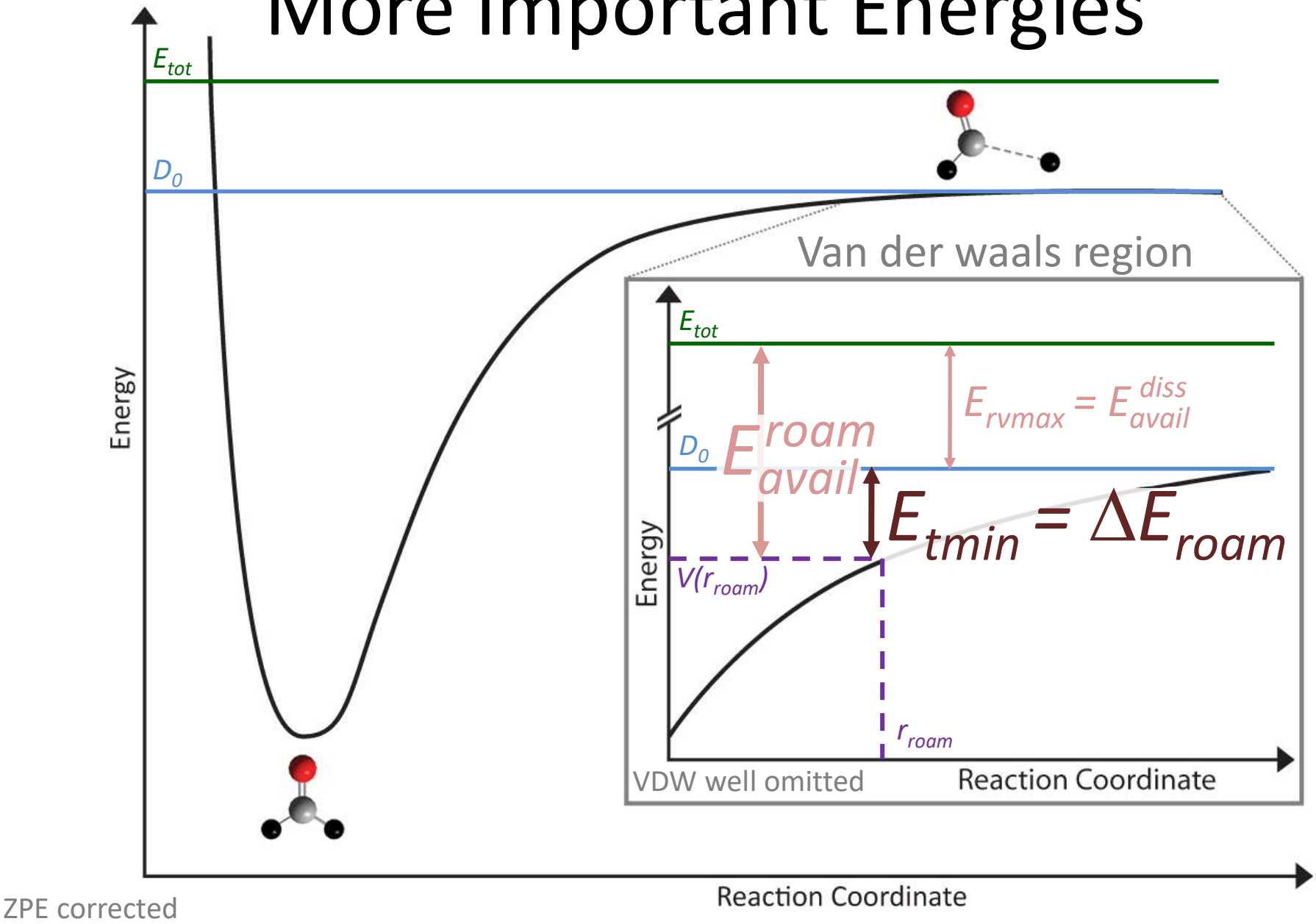
ZPE corrected

More Important Energies



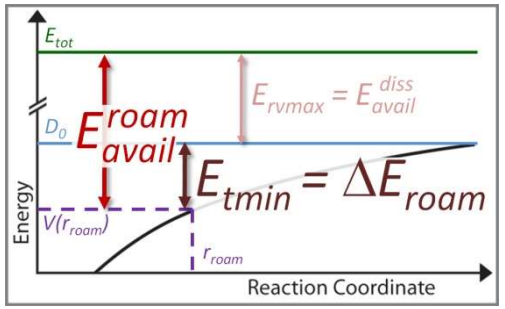
ZPE corrected

More Important Energies



ZPE corrected

Branching Fractions



$$E^{roam}_{avail}$$

$$E^{roam}_{avail} = E_{tot} - D_0 + \Delta E_{roam}$$

$$= E^{diss}_{avail} + \Delta E_{roam}$$

Percent

ΔE_{roam}

E^{diss}_{avail}

May Roam

Will Form Radicals

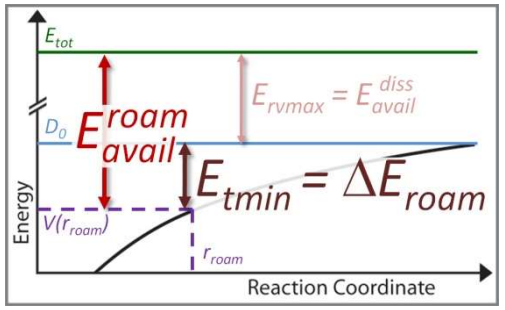
0

E_{tmin}

Relative Translational Energy

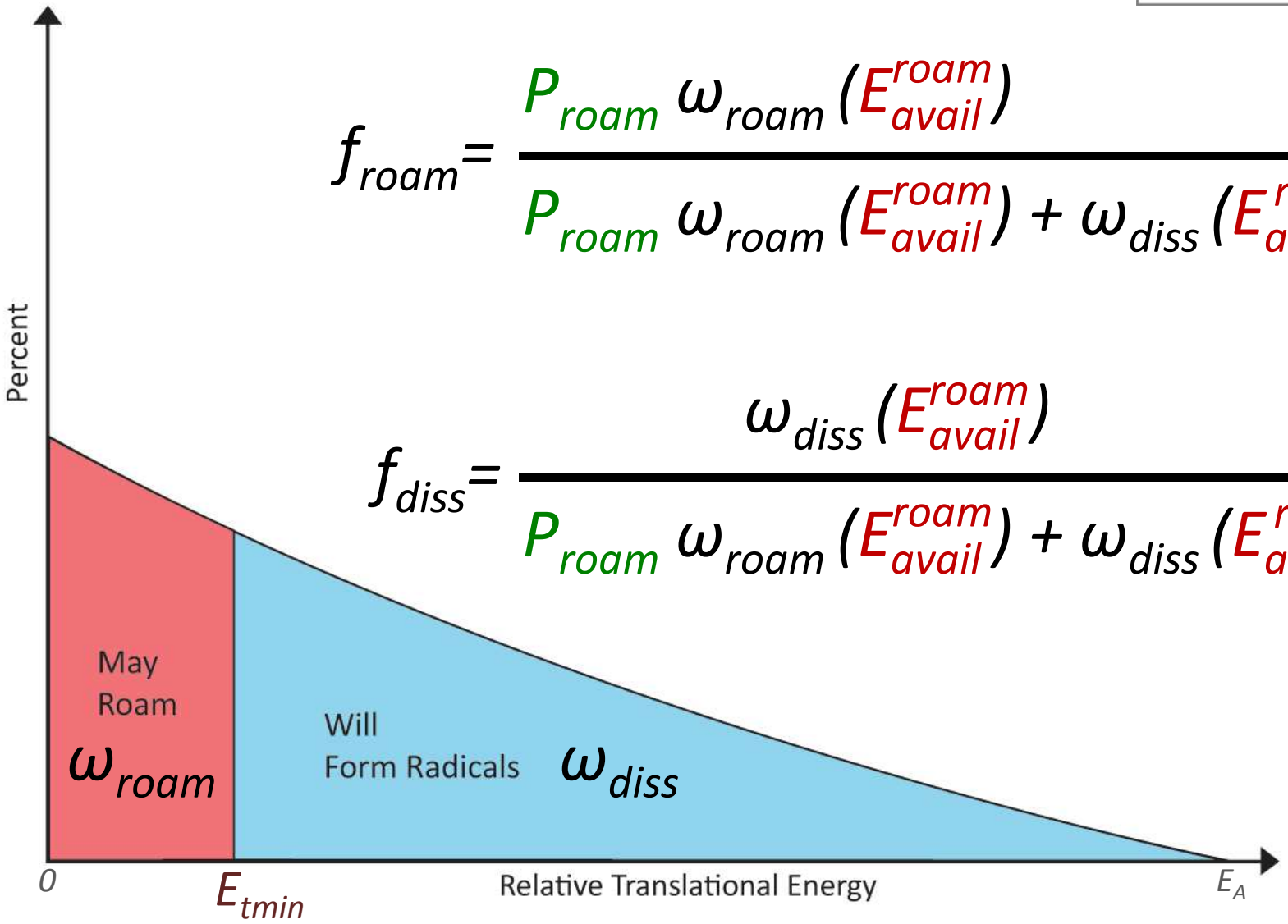
E_A

Branching Fractions

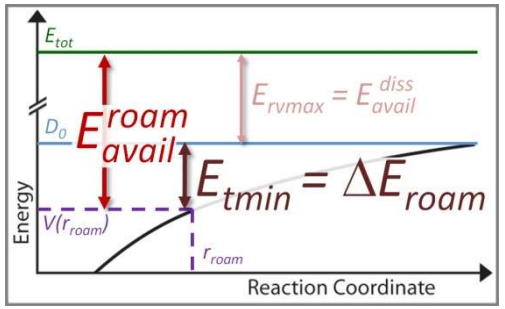


$$f_{roam} = \frac{P_{roam}\,\omega_{roam}(E^{roam}_{avail})}{P_{roam}\,\omega_{roam}(E^{roam}_{avail}) + \omega_{diss}(E^{roam}_{avail})}$$

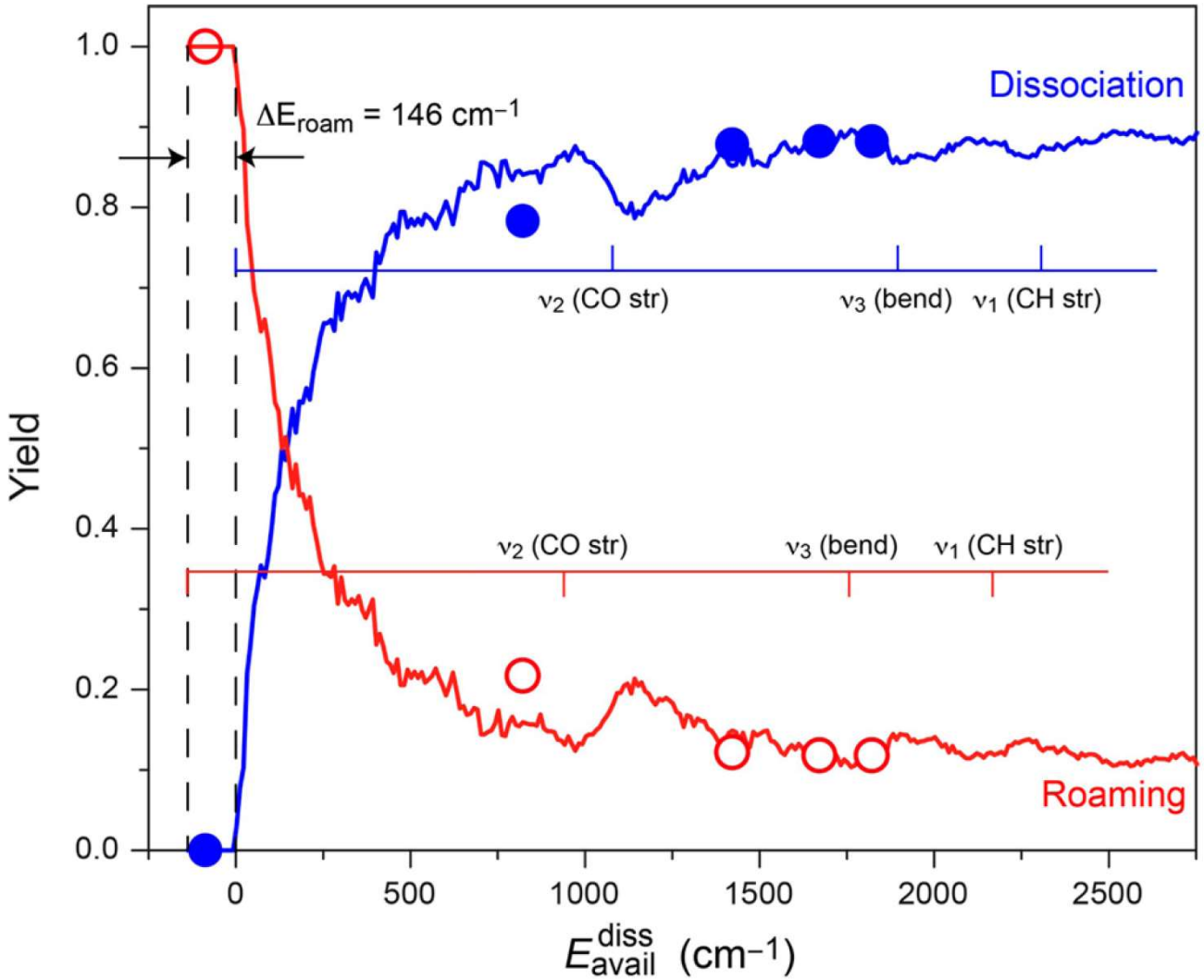
$$f_{diss} = \frac{\omega_{diss}(E^{roam}_{avail})}{P_{roam}\,\omega_{roam}(E^{roam}_{avail}) + \omega_{diss}(E^{roam}_{avail})}$$



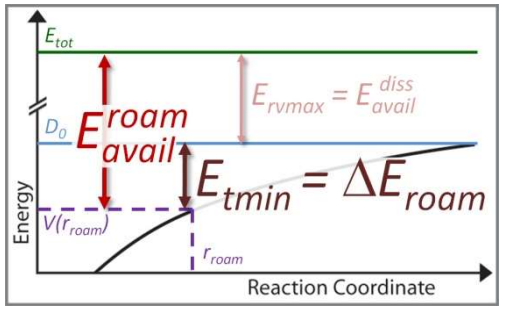
Formaldehyde Results



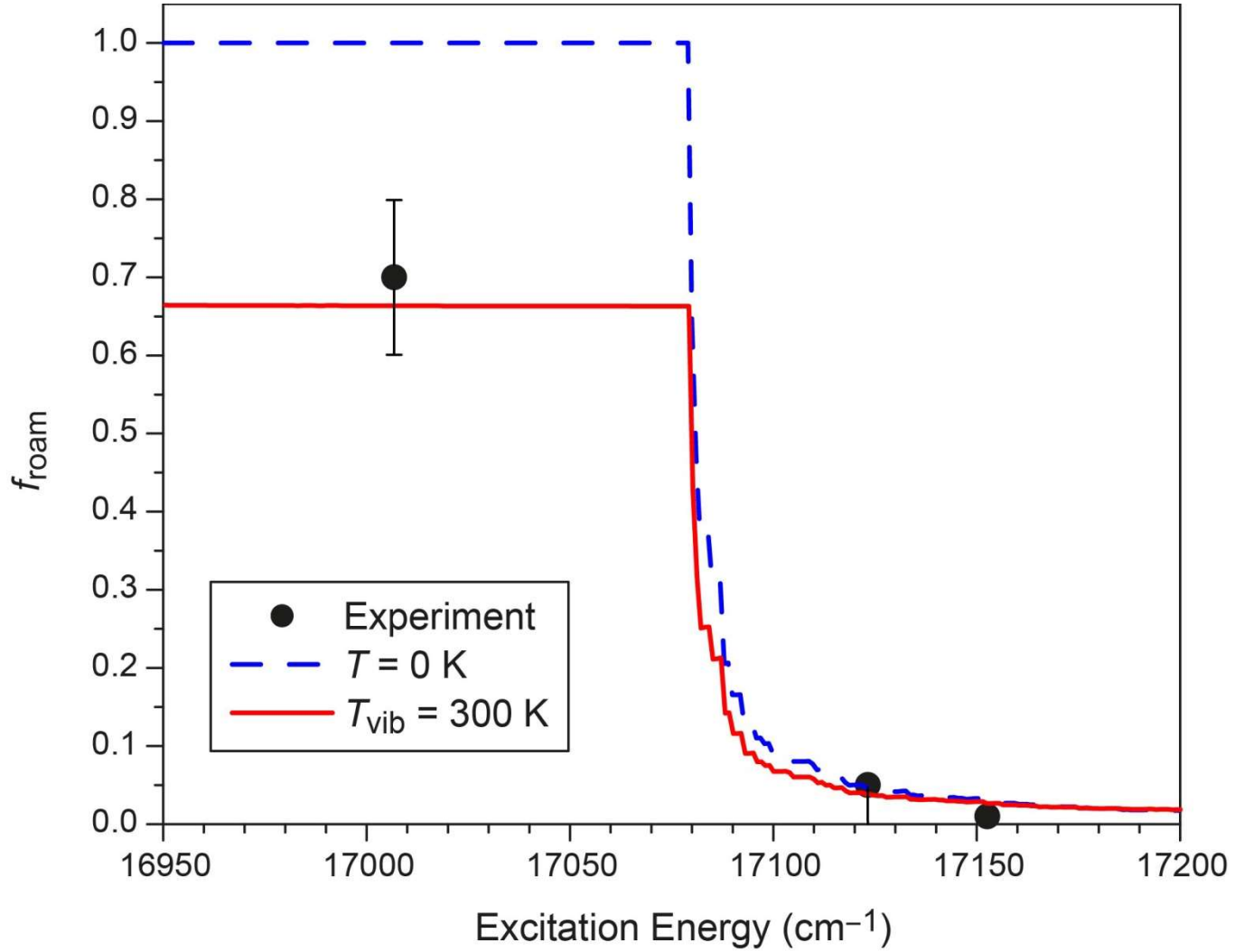
Single parameter fit: ΔE_{roam} = 146 cm^{-1} (P_{roam} set to 0)



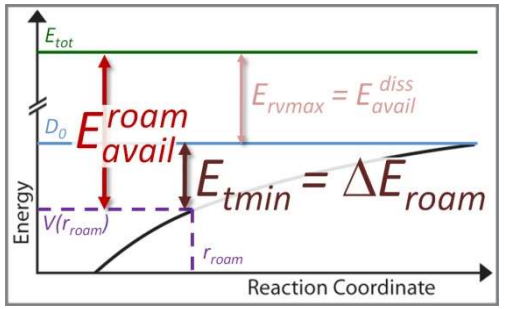
NO_3 Results

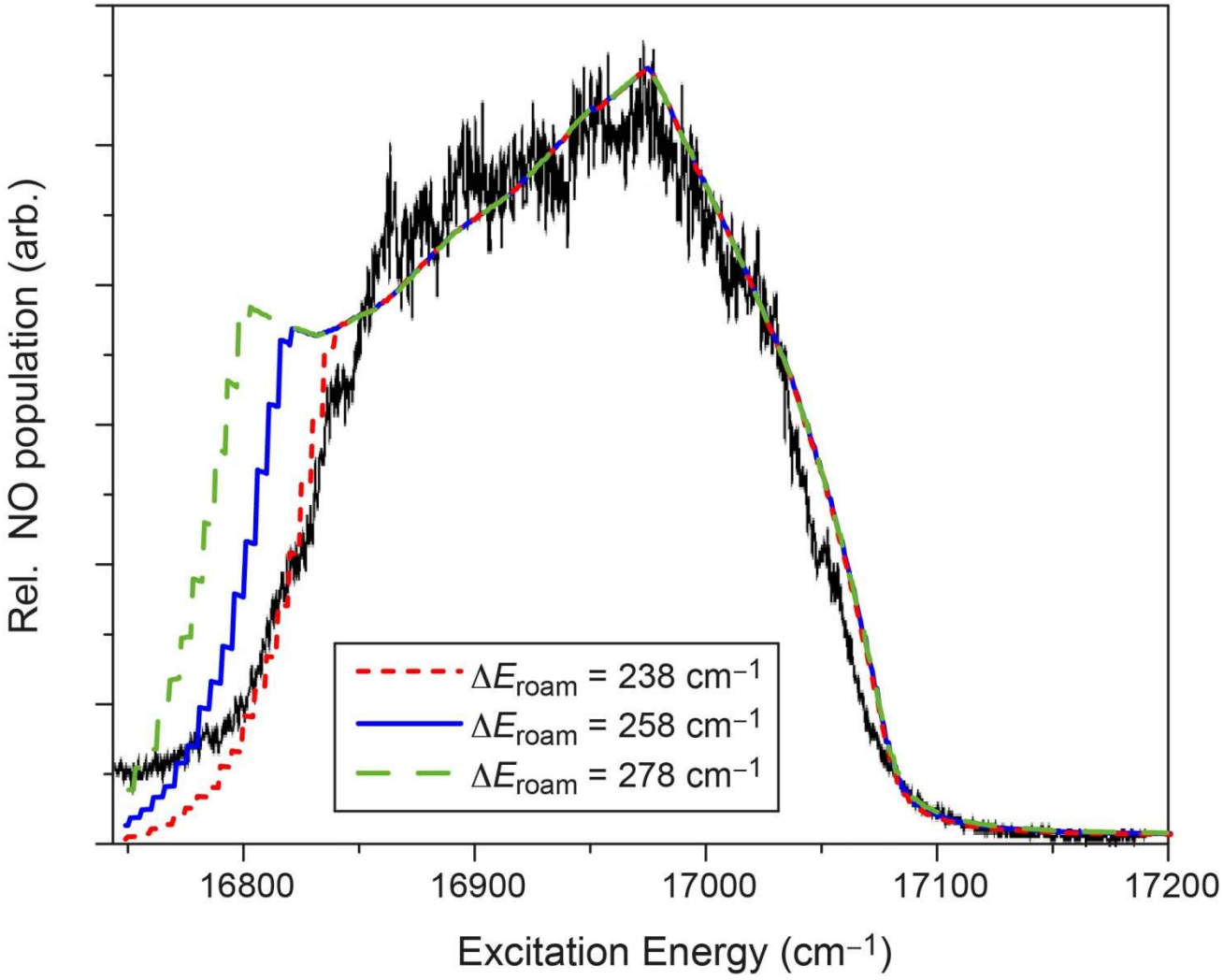


Single parameter fit: P_{roam} = 0.0075 (ΔE_{roam} set to 258 cm^{-1})

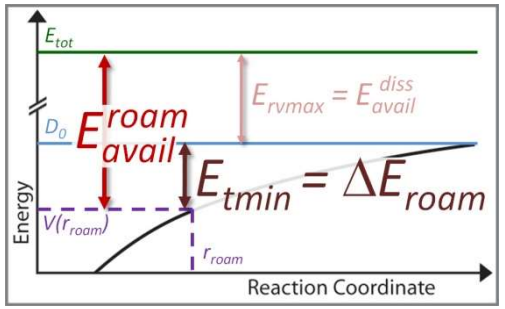


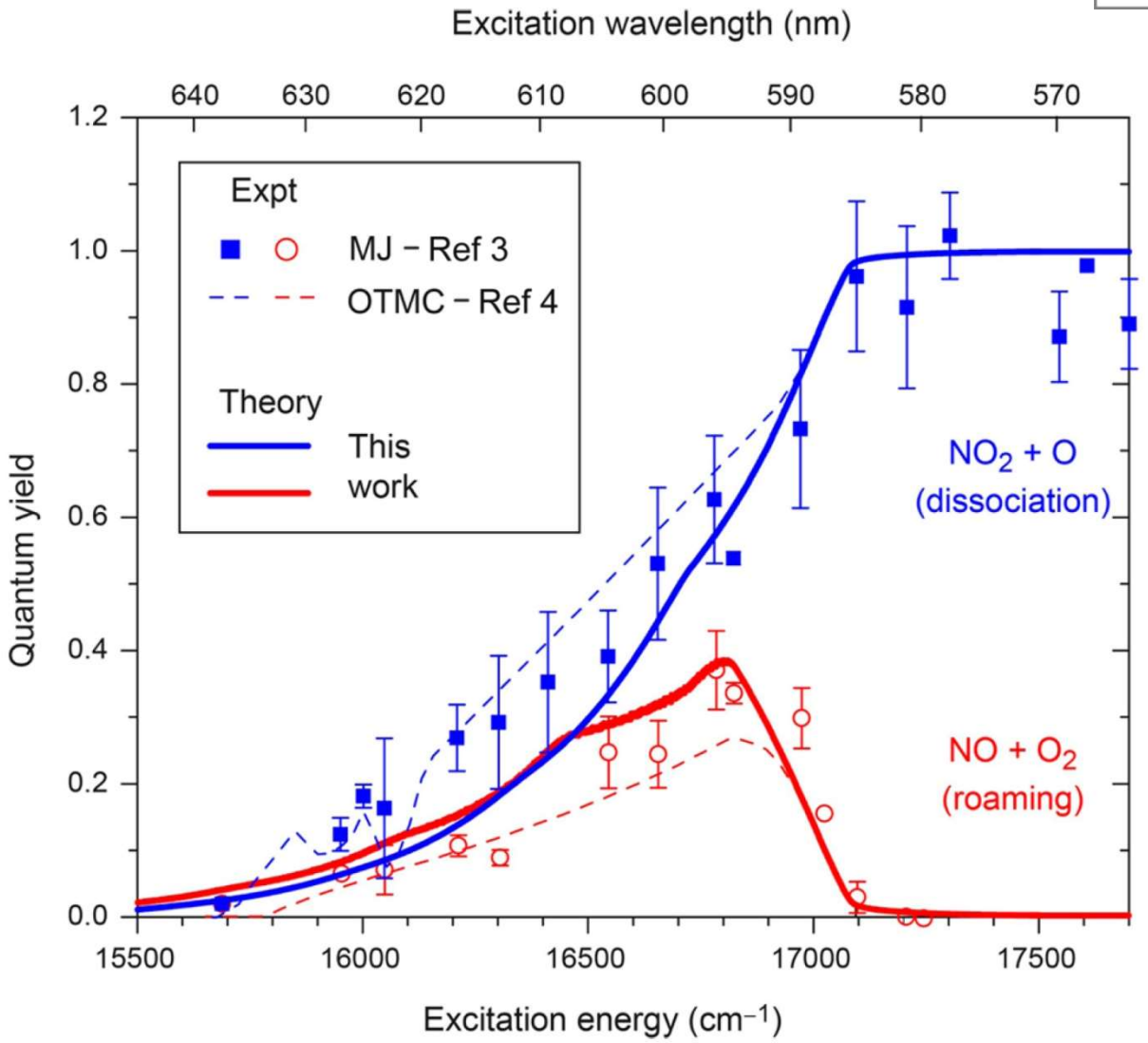
NO_3 Results


E_{tot}
$E_{rvmax} = E_{avail}^{diss}$
D_0
E_{avail}^{roam}
$E_{tmin} = \Delta E_{roam}$
Energy
$V(r_{roam})$
r_{roam}
Reaction Coordinate

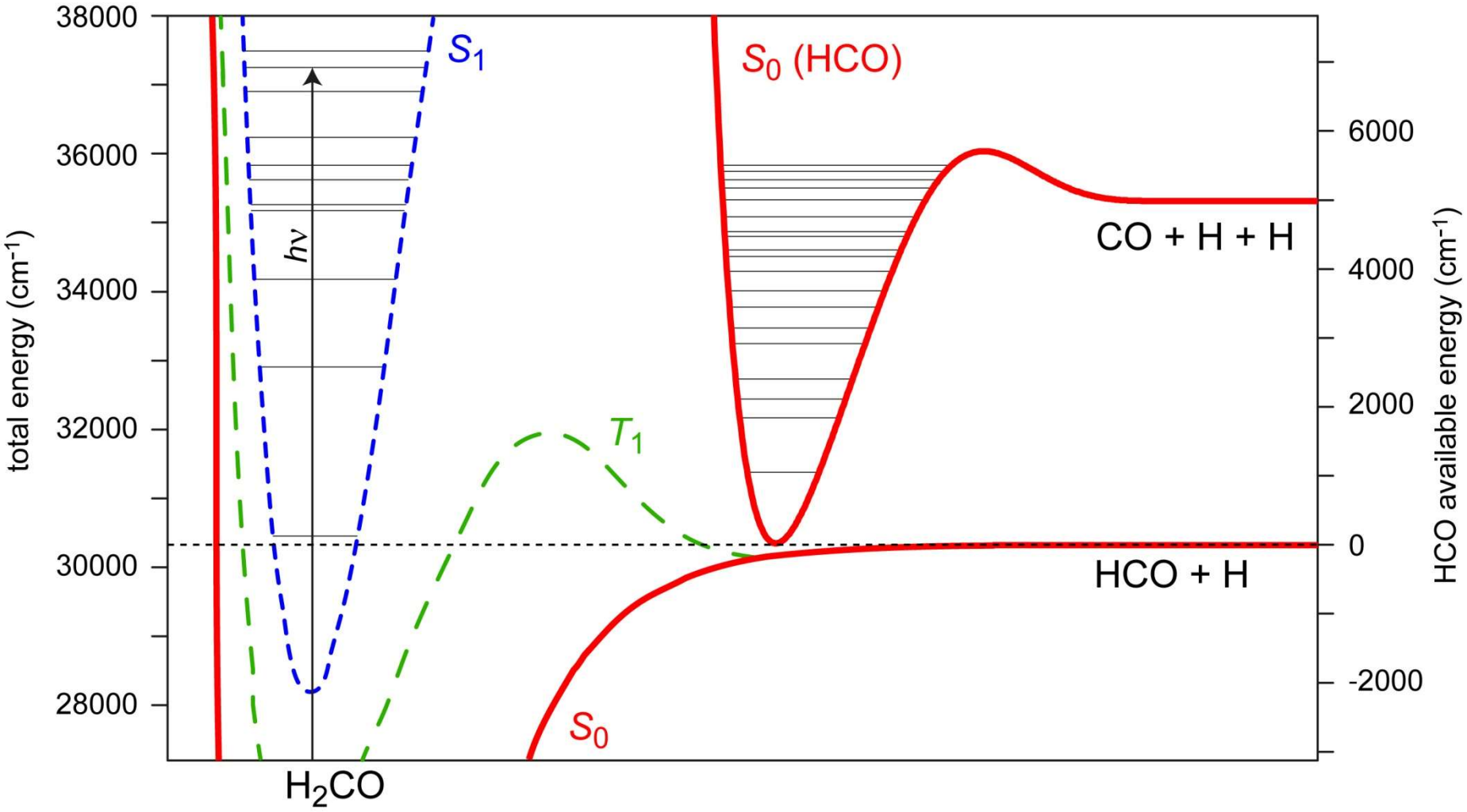

Rel. NO population (arb.)
ΔE_{roam} = 238 cm^{-1}
ΔE_{roam} = 258 cm^{-1}
ΔE_{roam} = 278 cm^{-1}
16800
16900
17000
17100
17200
Excitation Energy (cm^{-1})

NO_3 Results

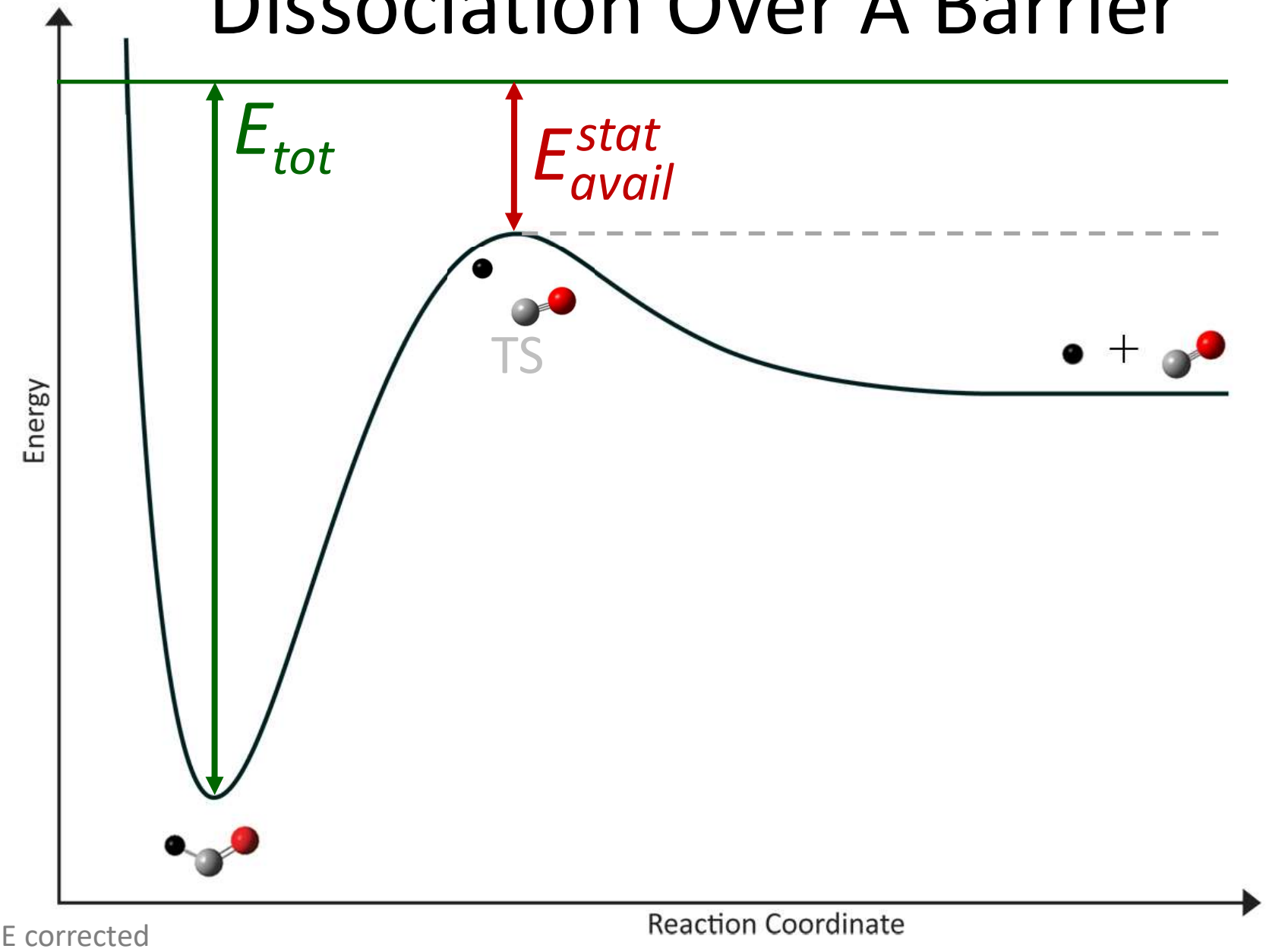

E_{tot}
$E_{rvmax} = E^{diss}_{avail}$
D_0
E^{roam}_{avail}
$E_{tmin} = \Delta E_{roam}$
Energy
$V(r_{roam})$
r_{roam}
Reaction Coordinate


Excitation wavelength (nm)
640
630
620
610
600
590
580
570
Quantum yield
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Expt
MJ – Ref 3
OTMC – Ref 4
Theory
This work
NO_2 + O (dissociation)
NO + O_2 (roaming)
15500
16000
16500
17000
17500
Excitation energy (cm^{-1})

Triple Fragmentation

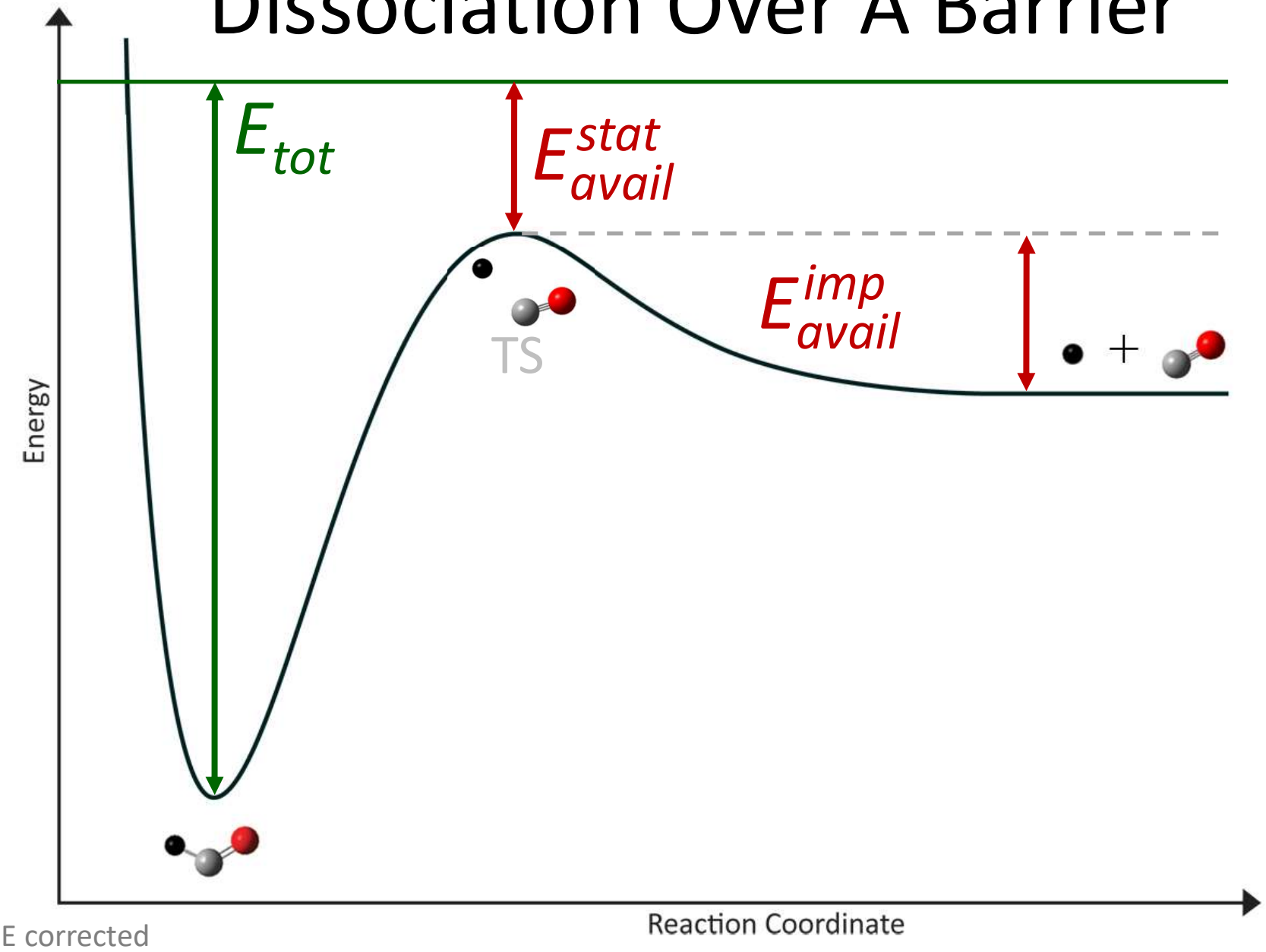


Dissociation Over A Barrier



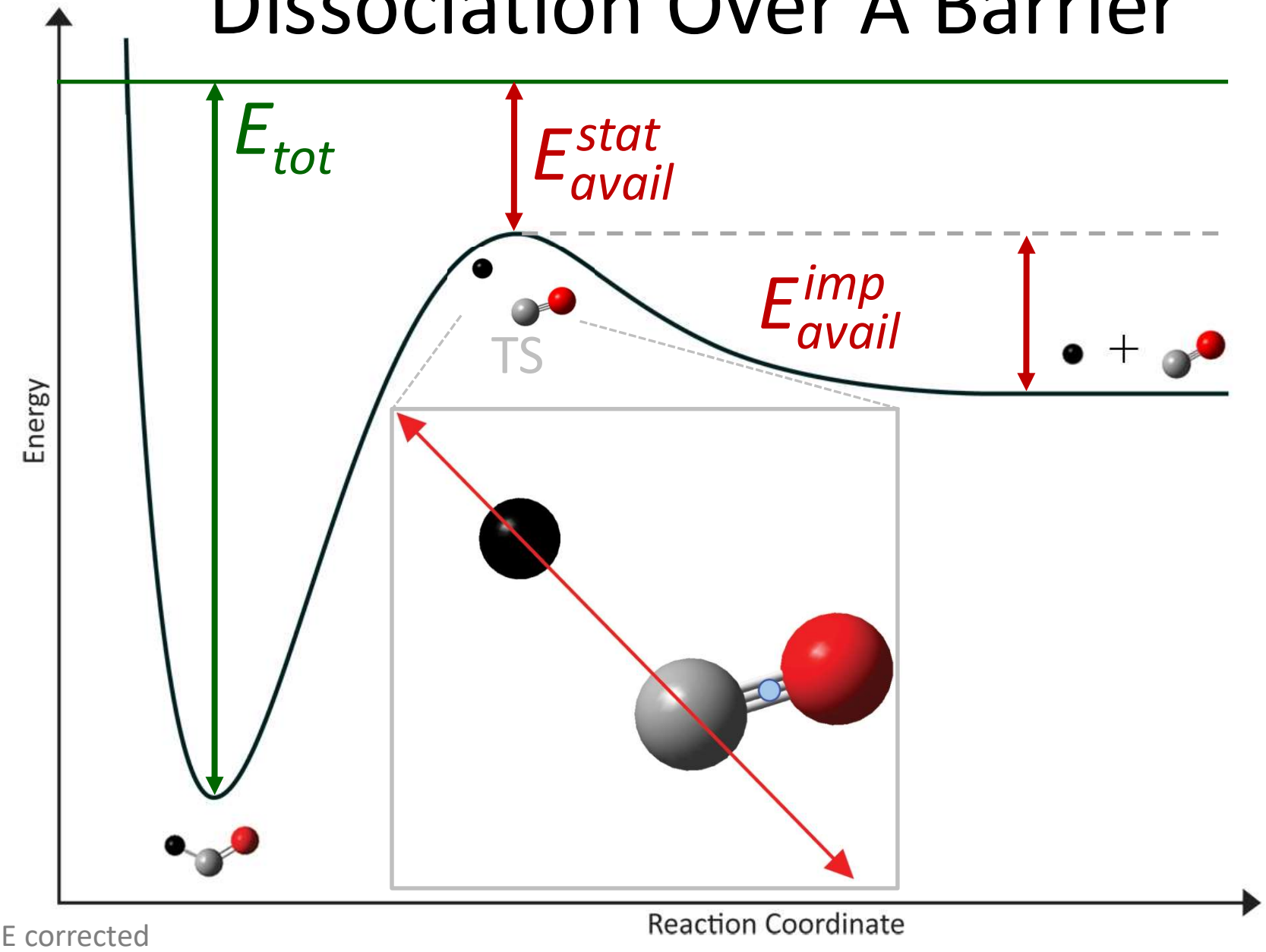
ZPE corrected

Dissociation Over A Barrier



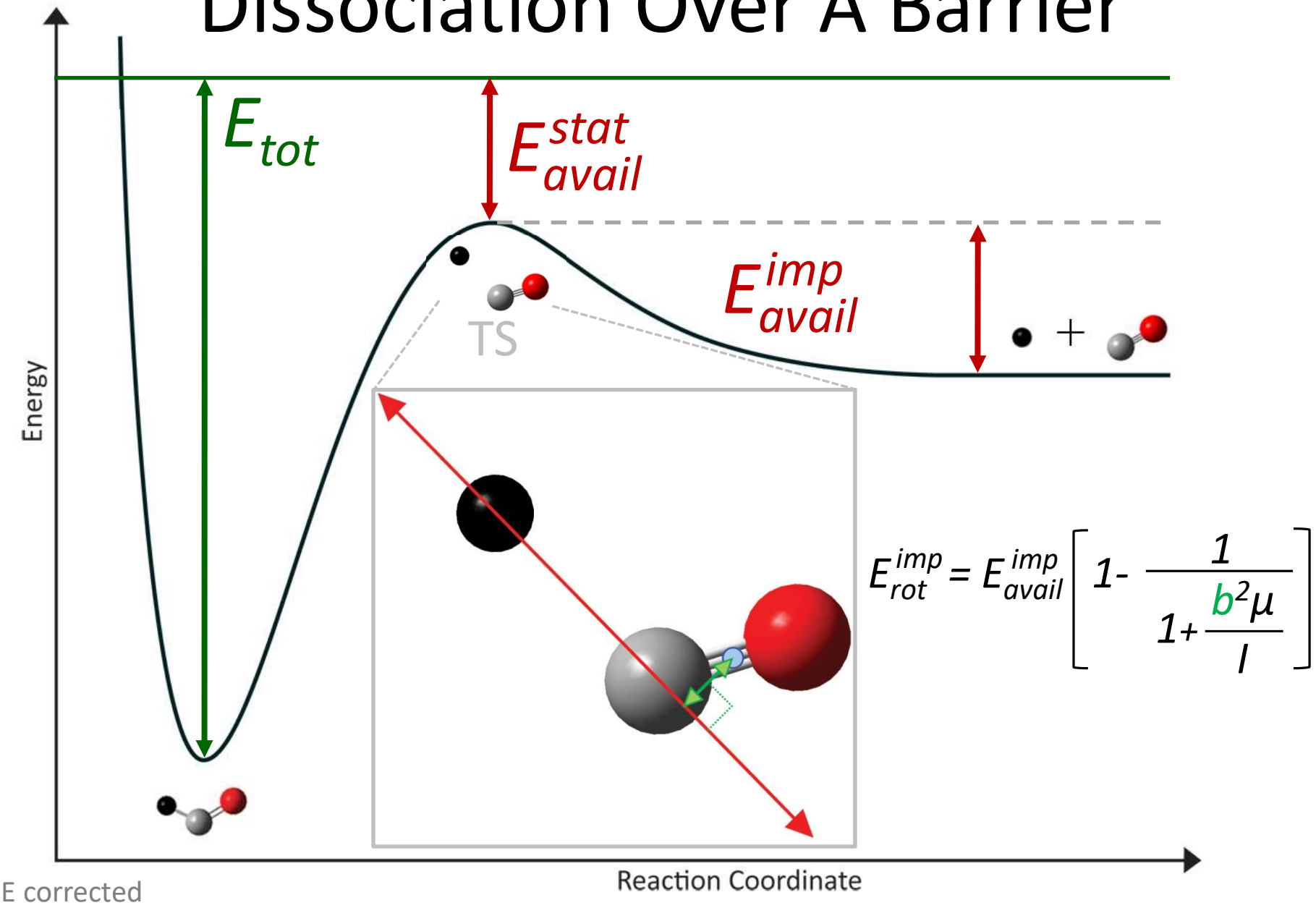
ZPE corrected

Dissociation Over A Barrier



ZPE corrected

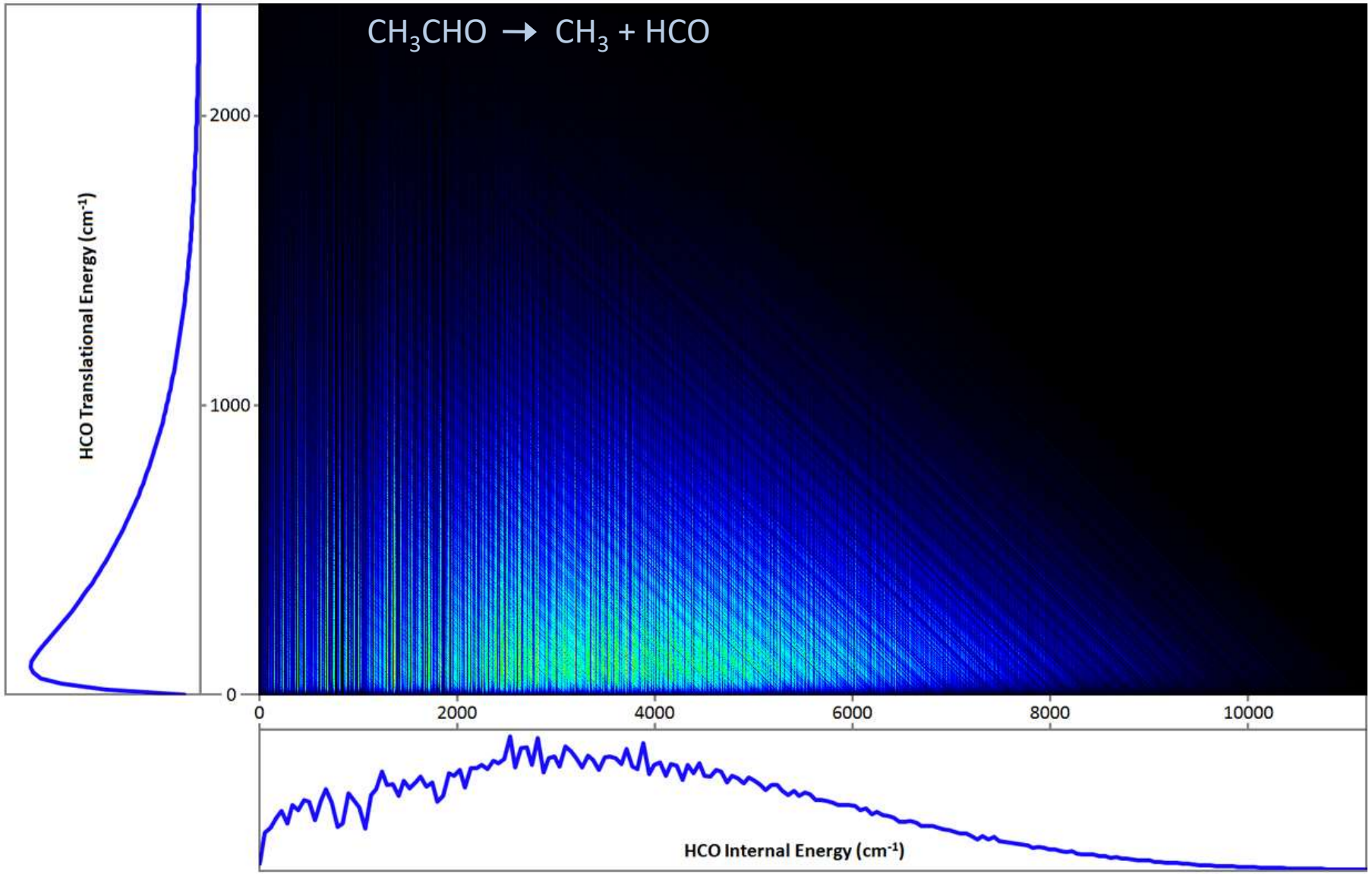
Dissociation Over A Barrier



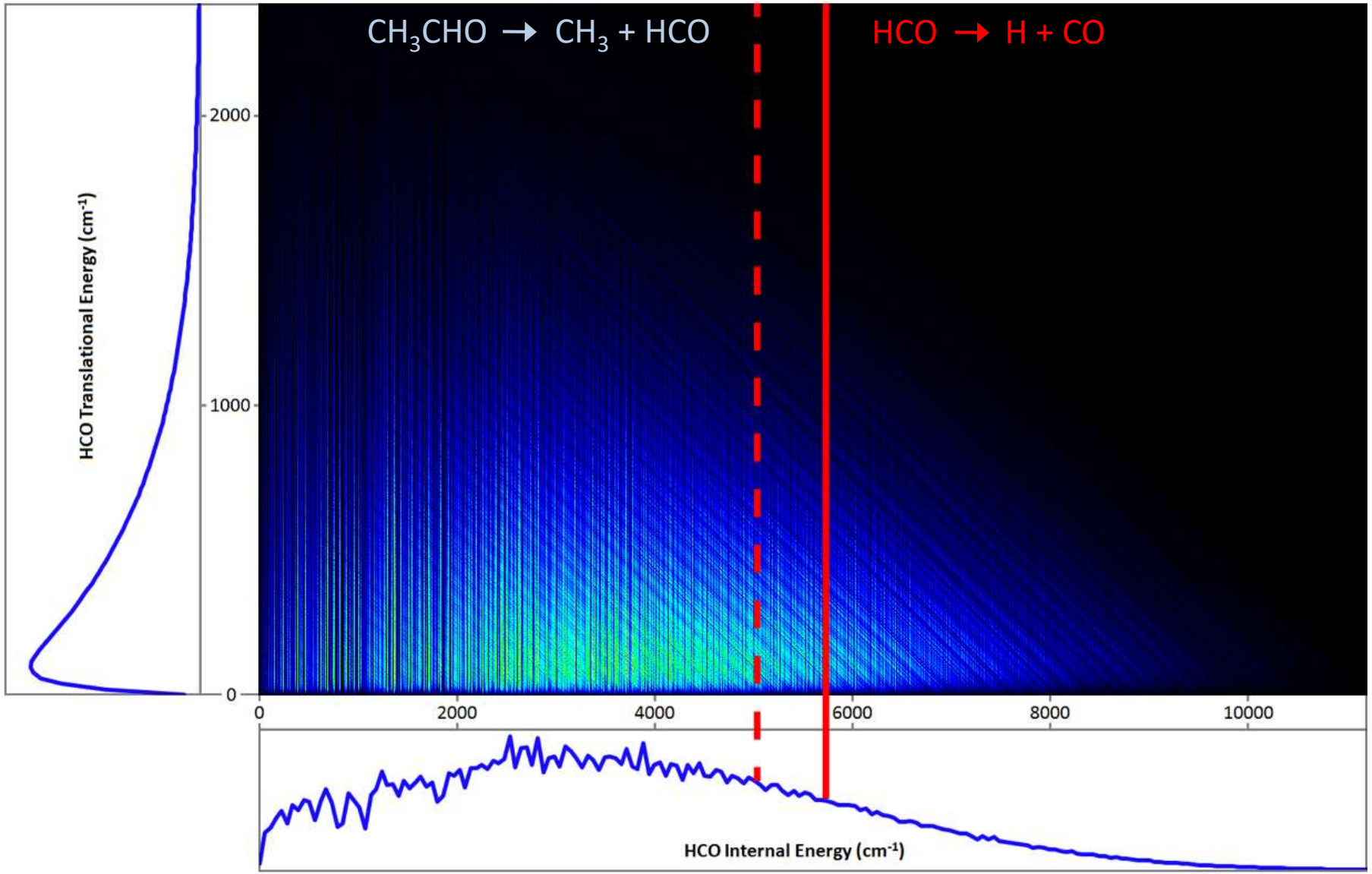
$$E^{imp}_{rot} = E^{imp}_{avail}\left[1 - \frac{1}{1 + \frac{b^2\mu}{I}}\right]$$

ZPE corrected

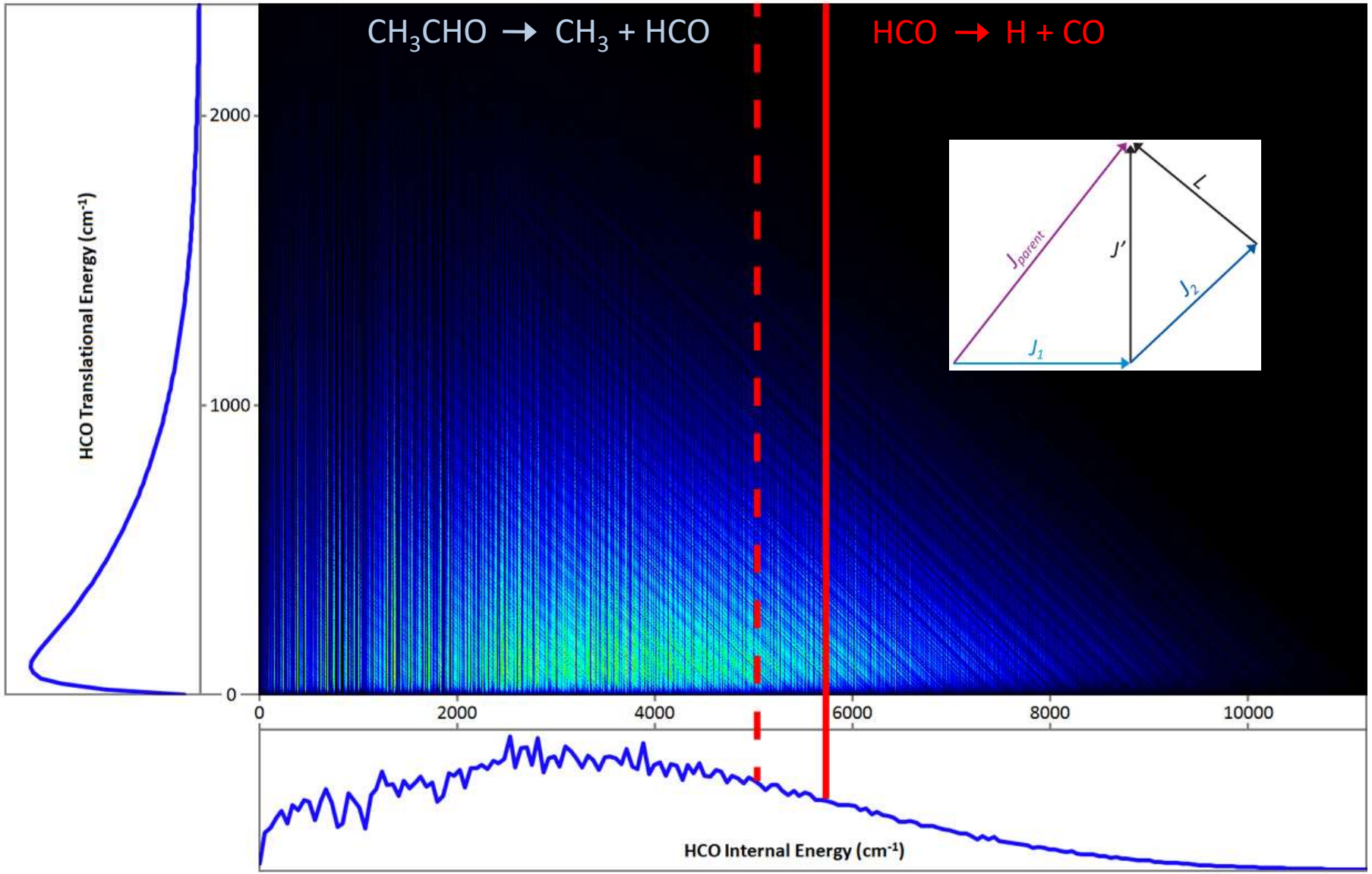
The Primary Fragmentation



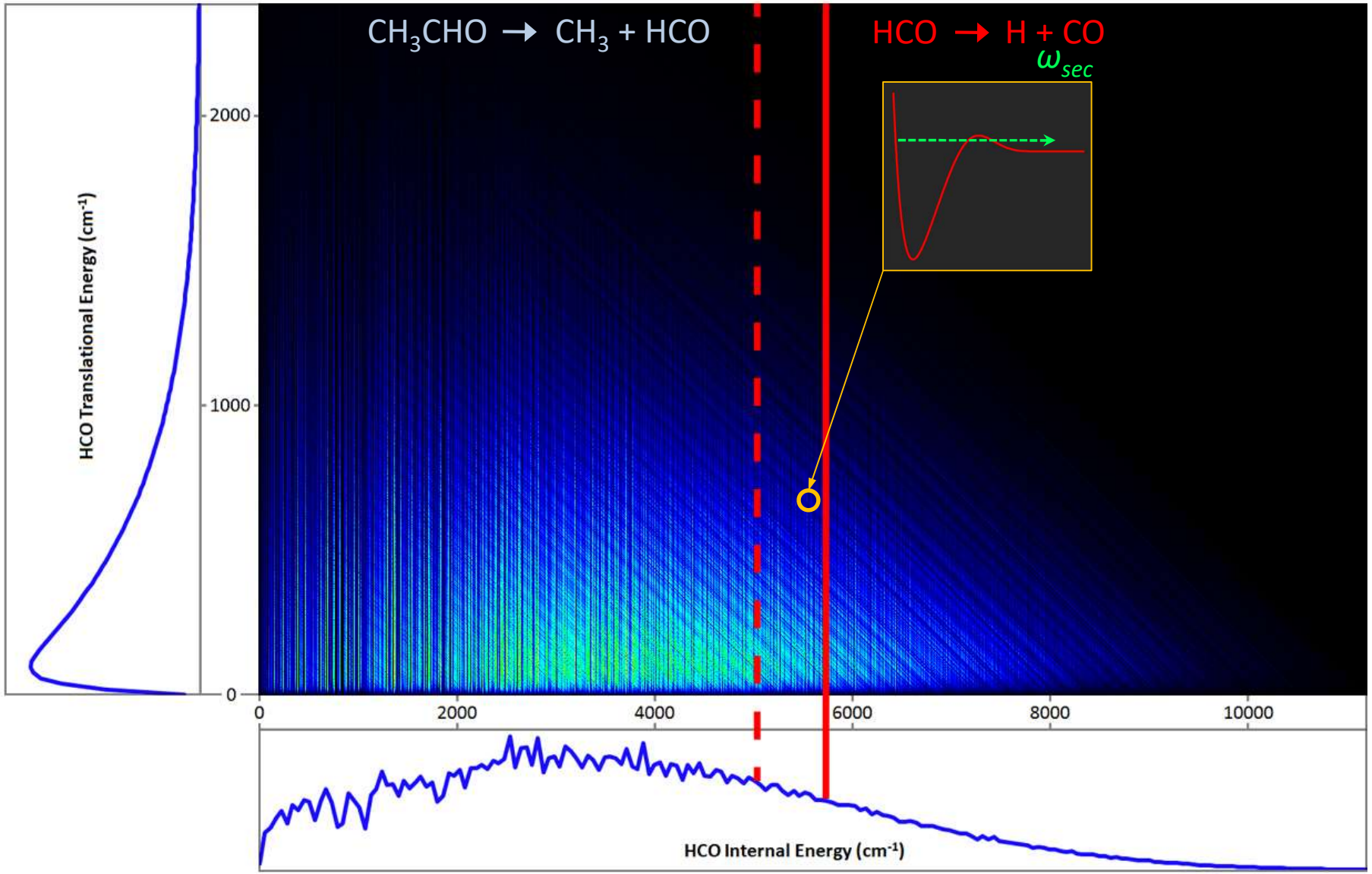
Many Secondary Fragmentations



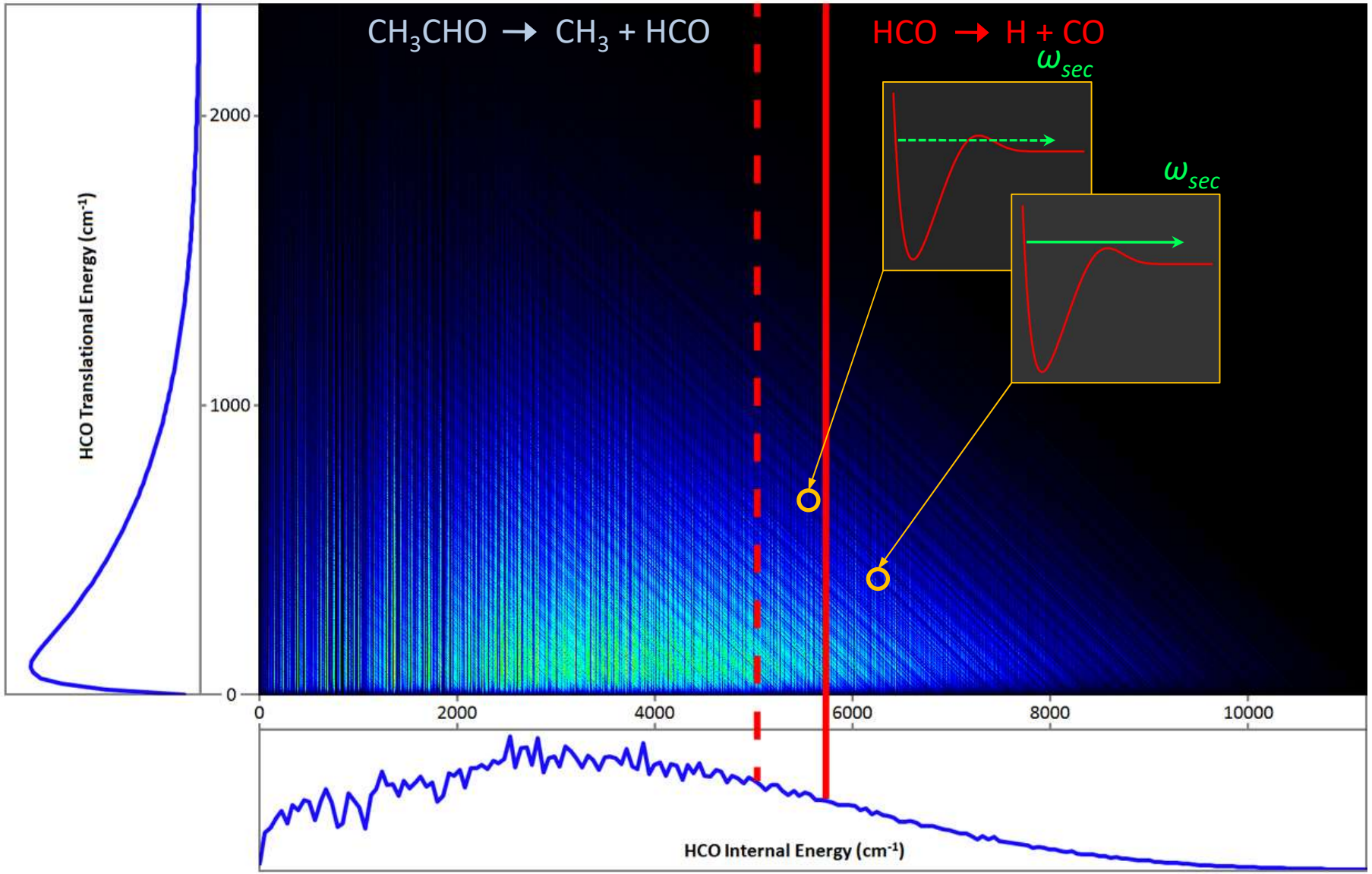
Many Secondary Fragmentations



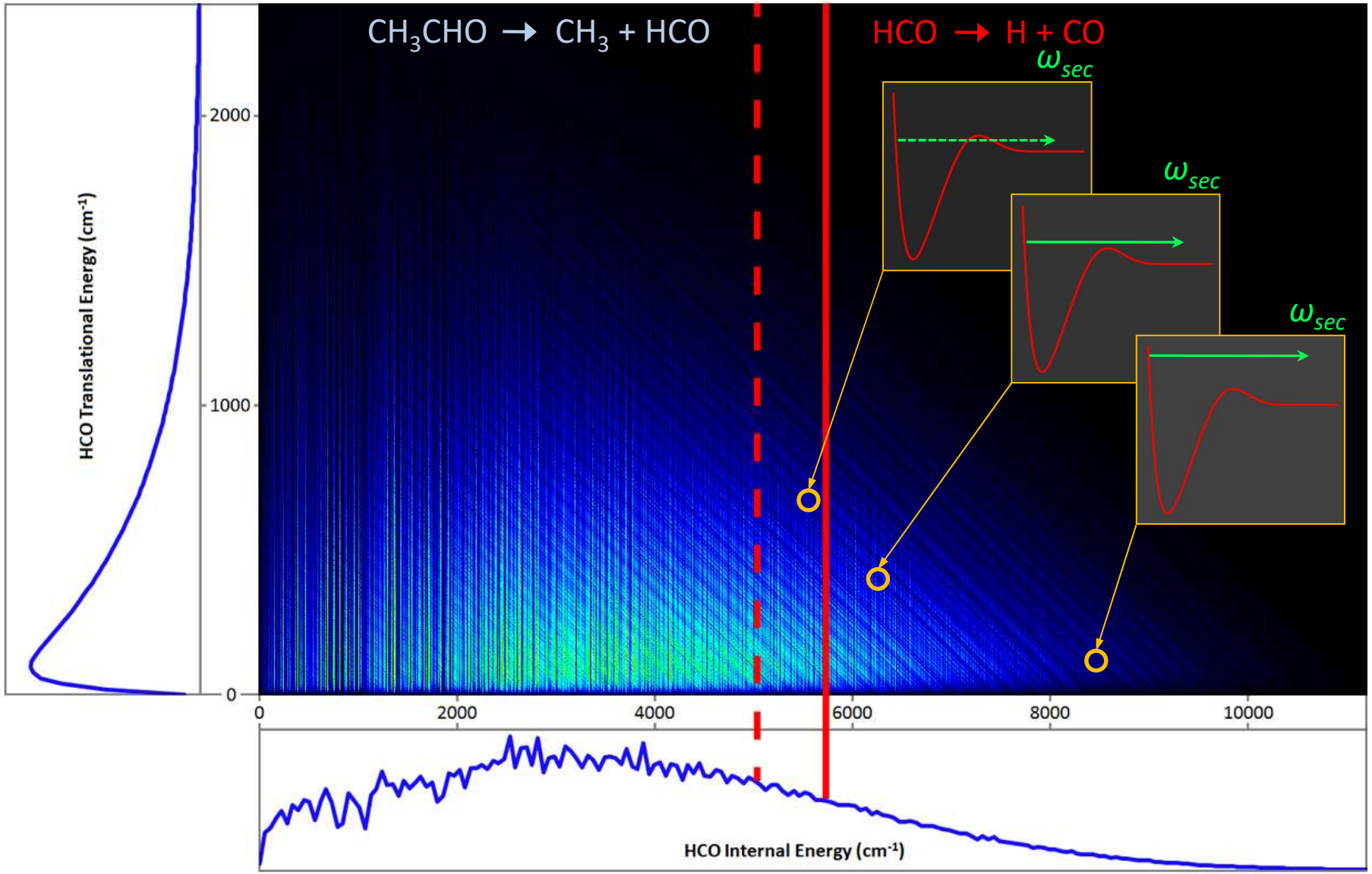
Many Secondary Fragmentations



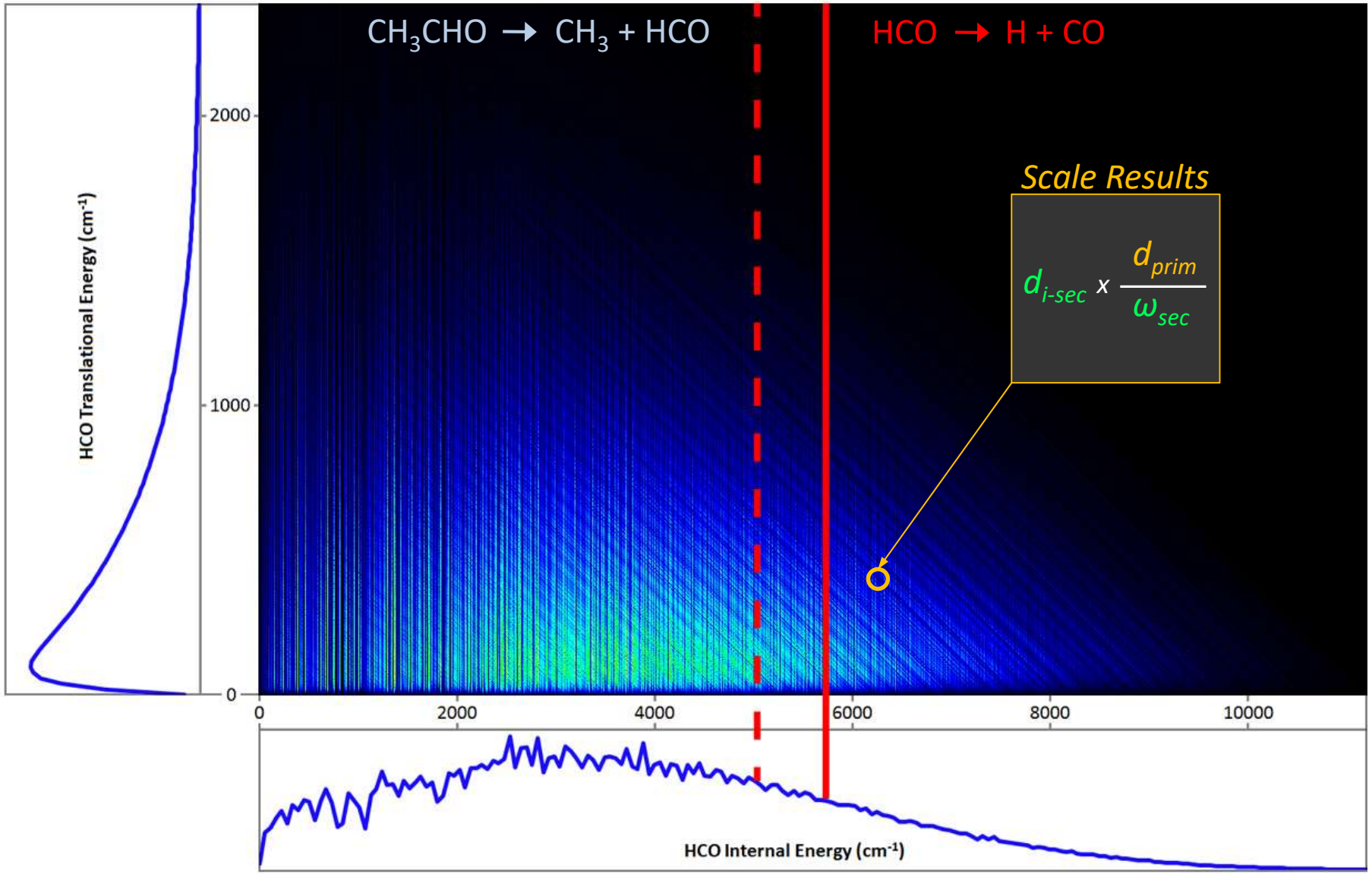
Many Secondary Fragmentations



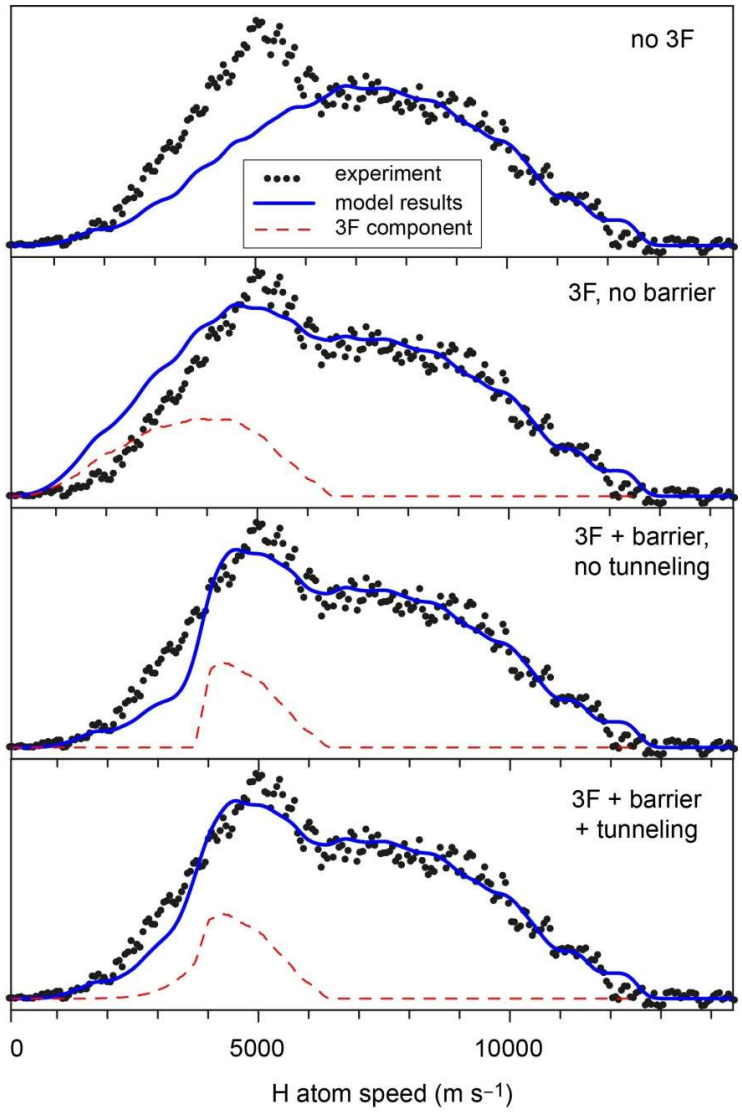
Many Secondary Fragmentations



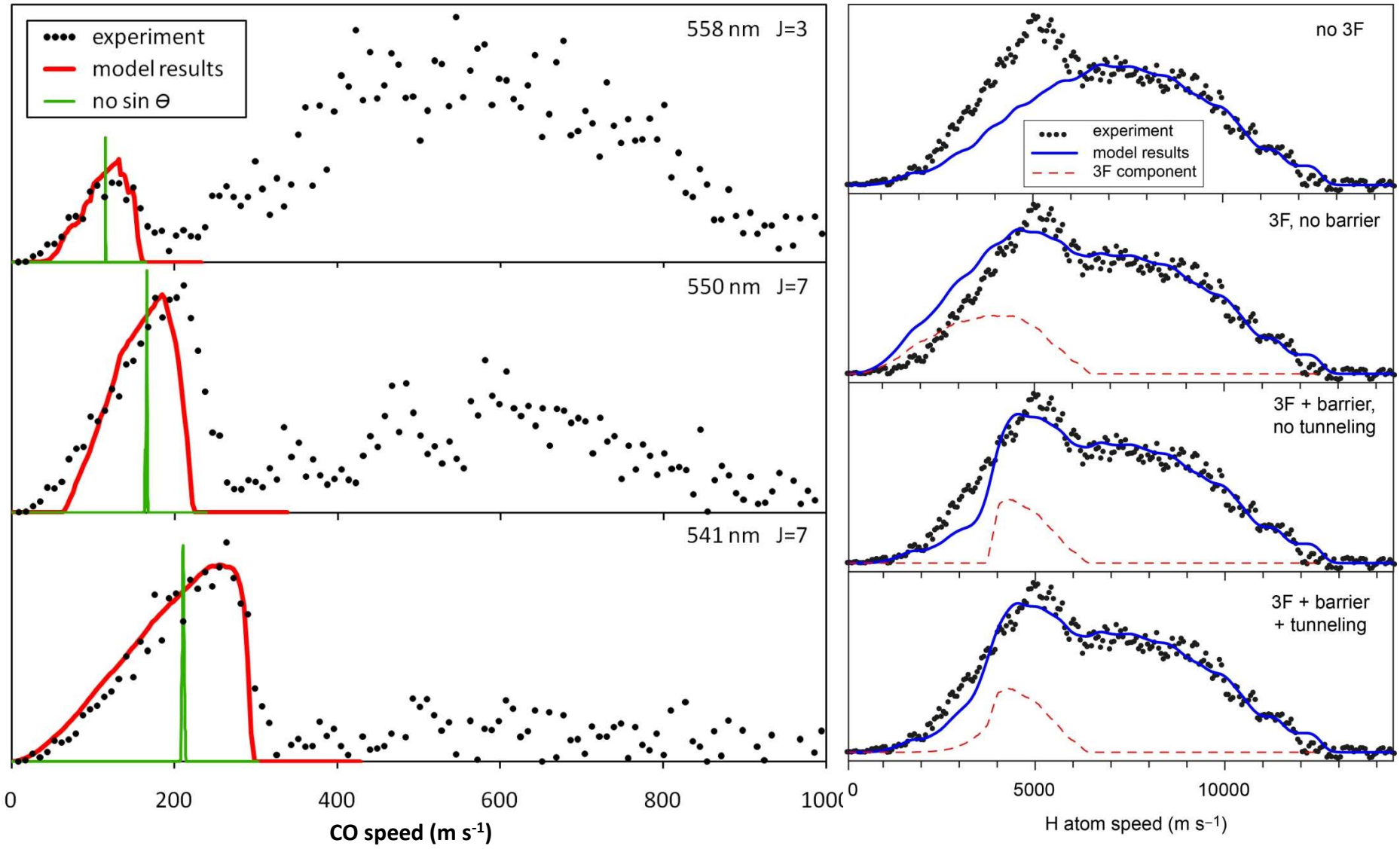
Many Secondary Fragmentations



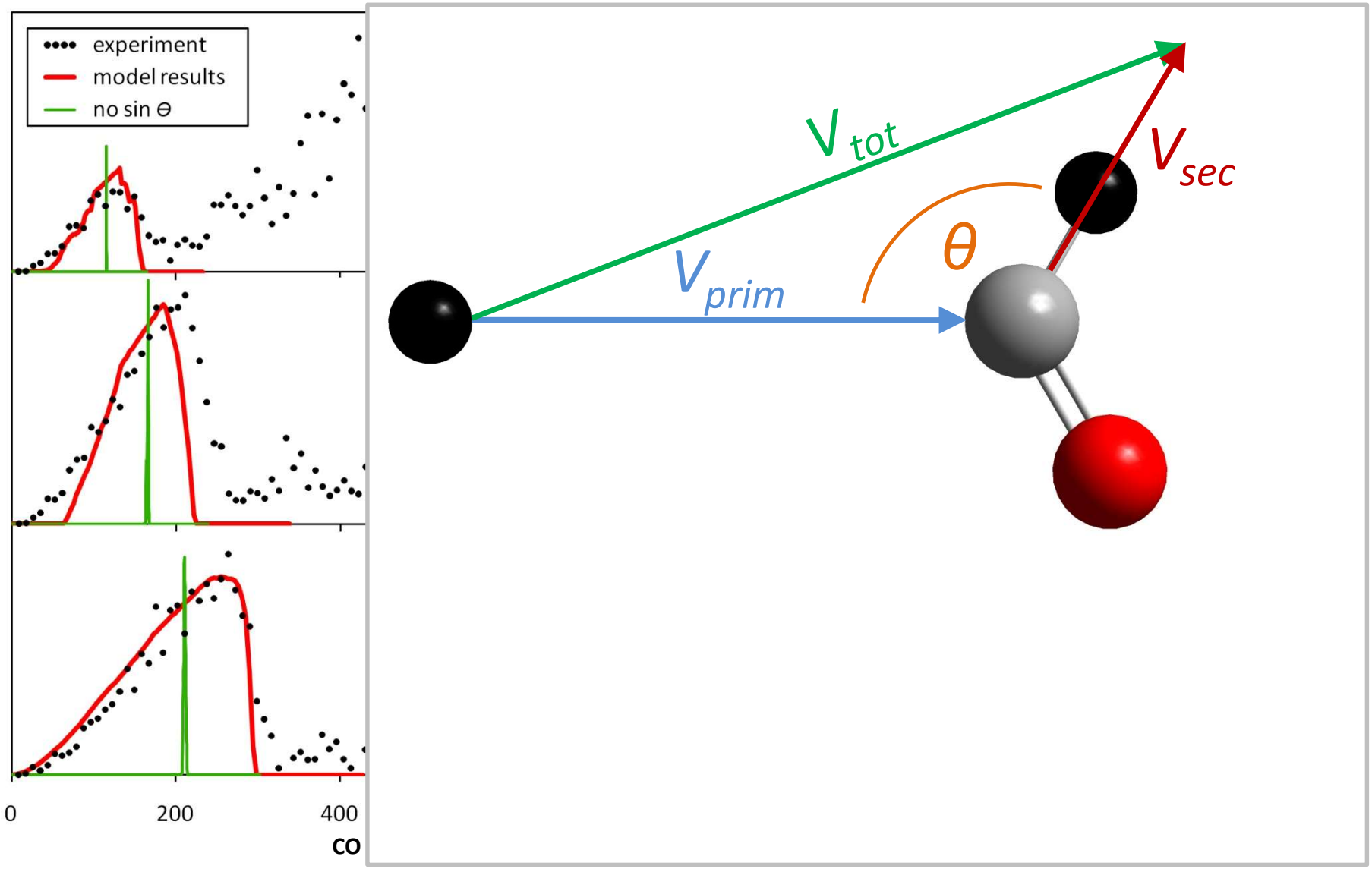
Formaldehyde Results



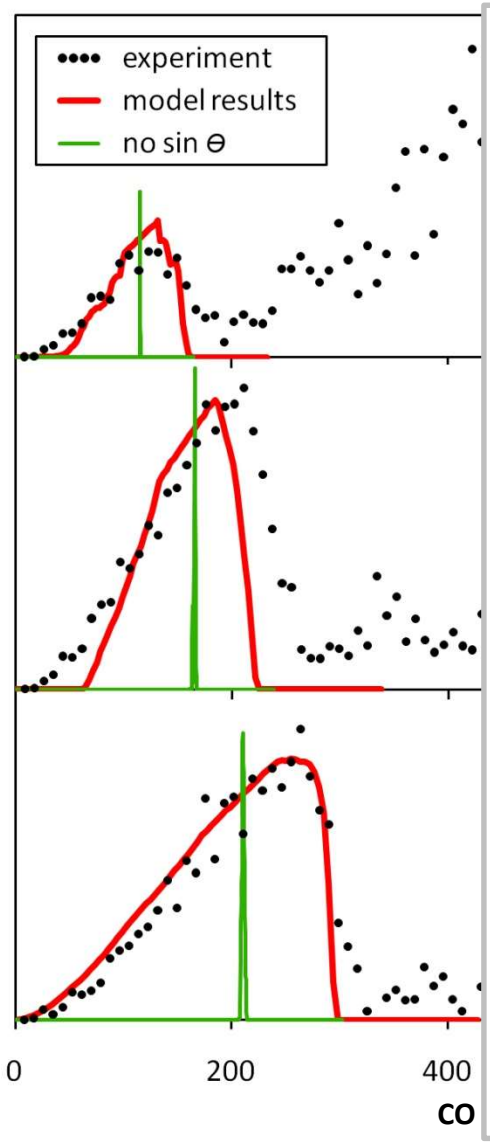
Formaldehyde Results

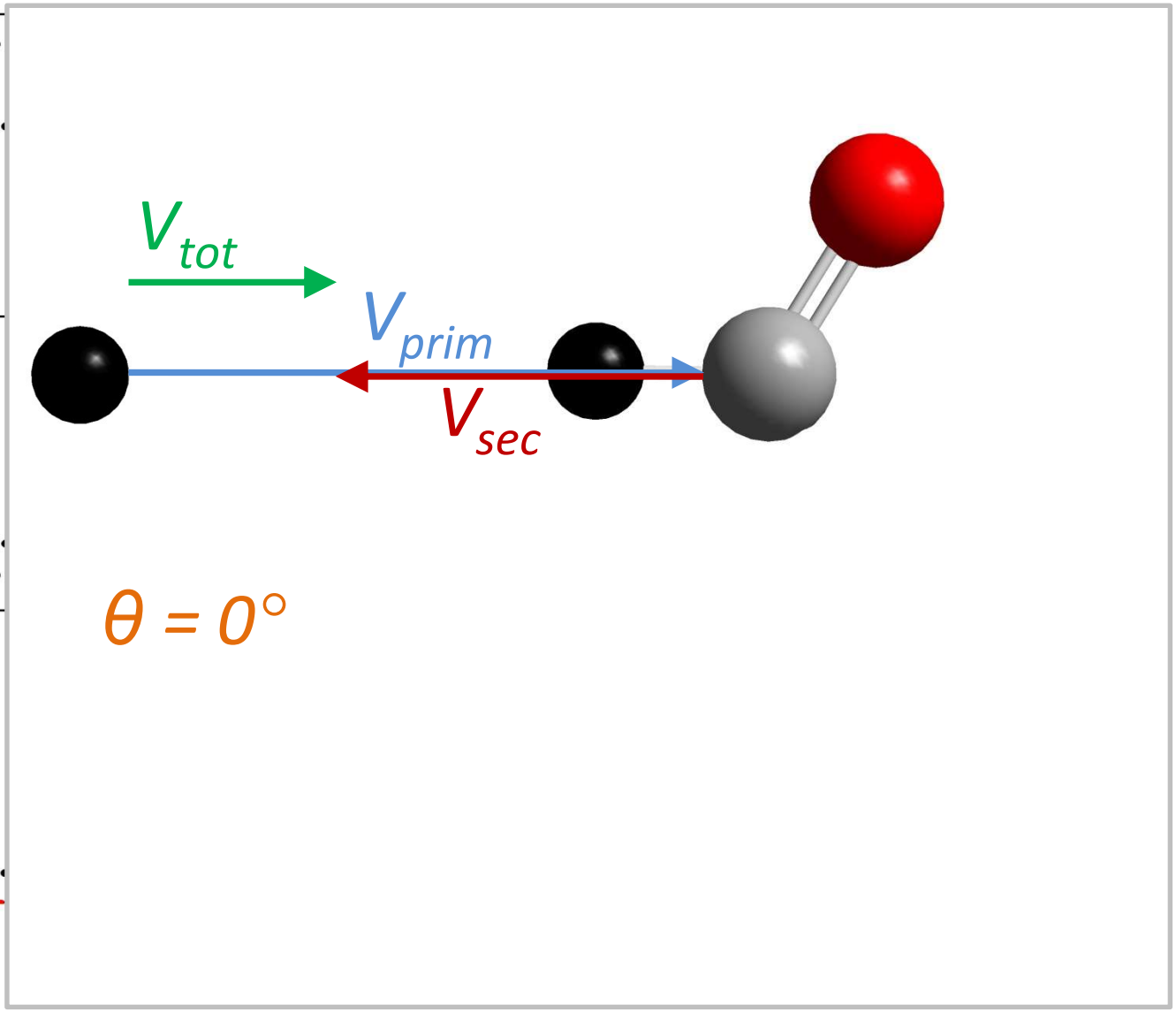


Adding Velocities

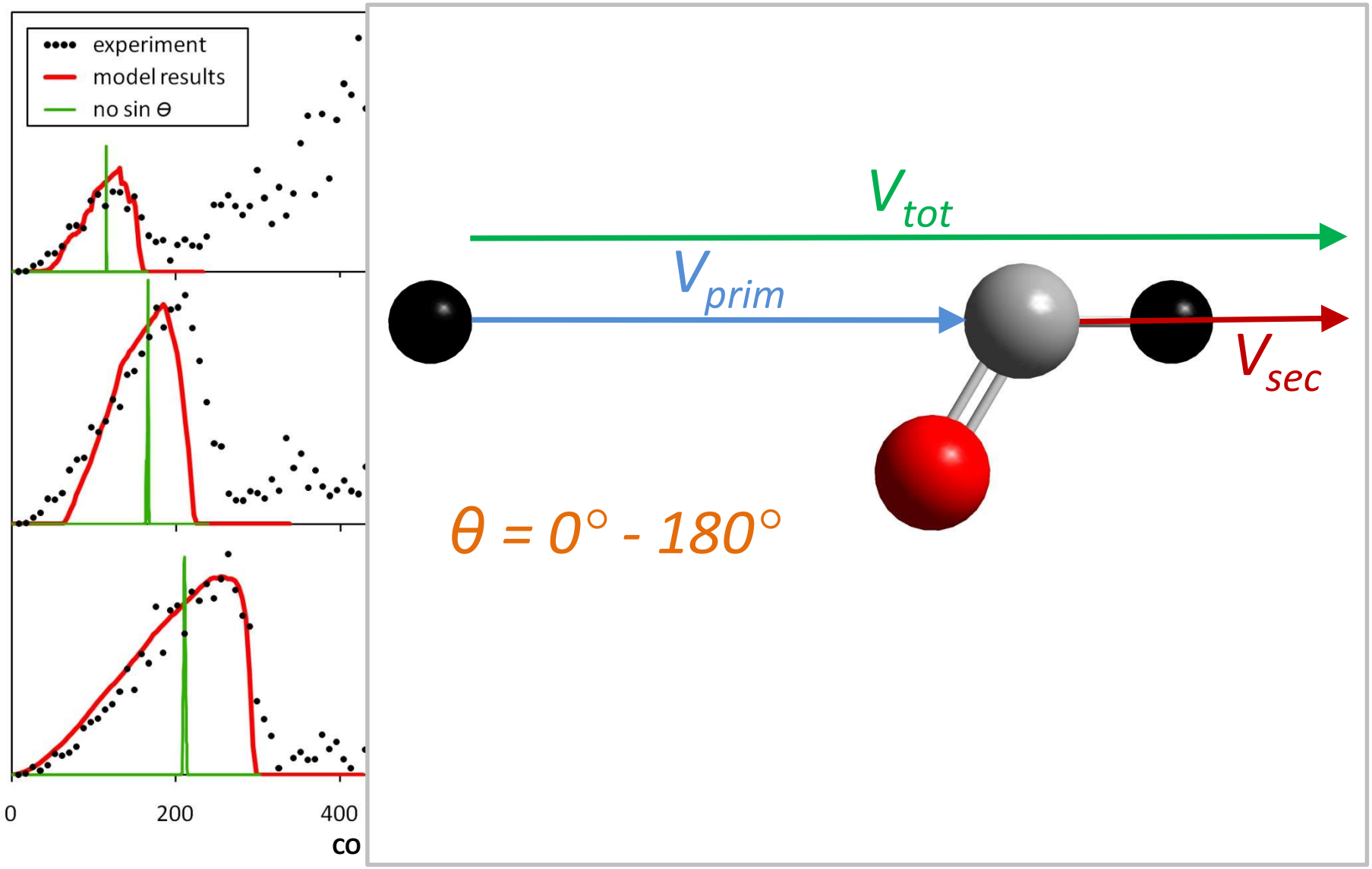


Adding Velocities

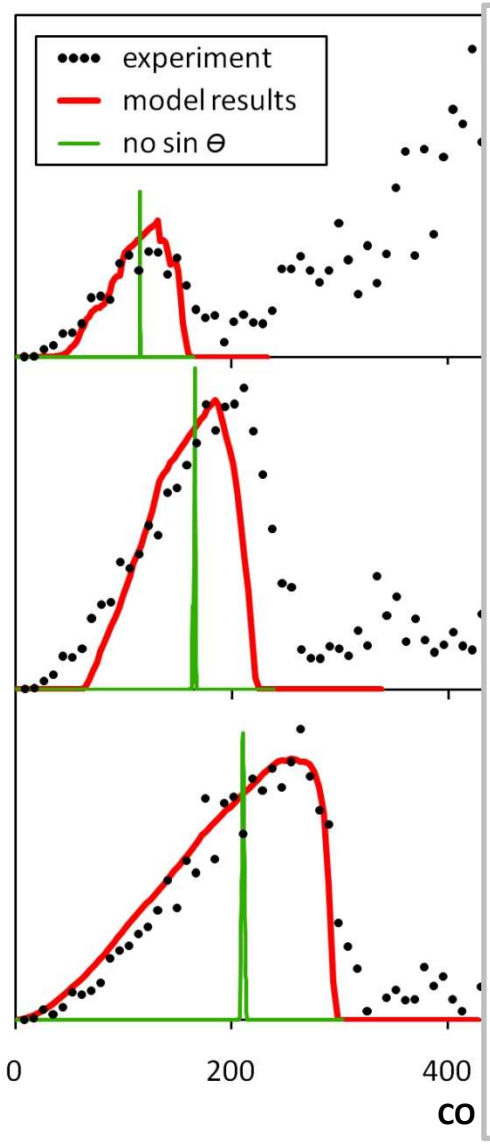


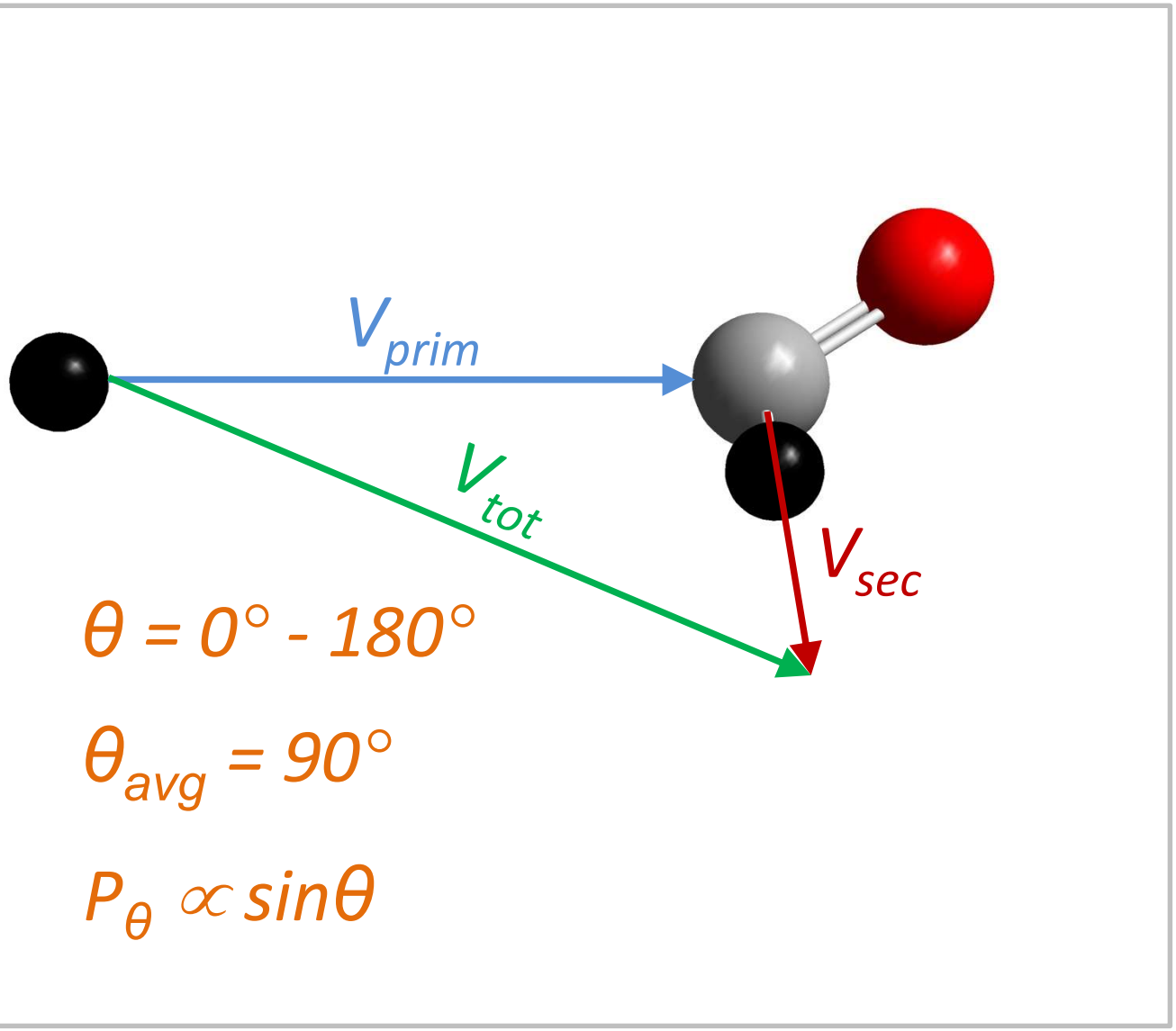


Adding Velocities

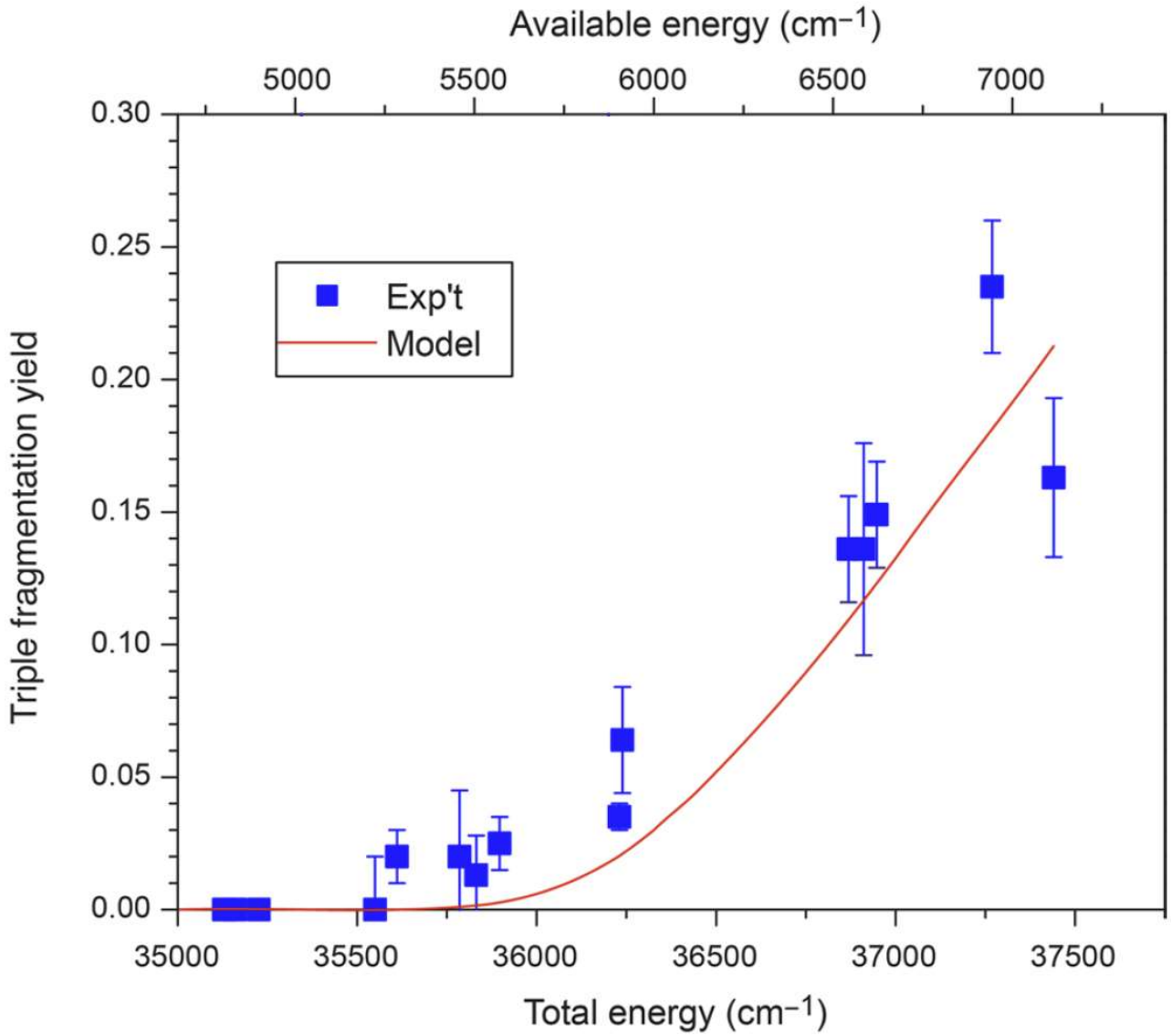


Adding Velocities

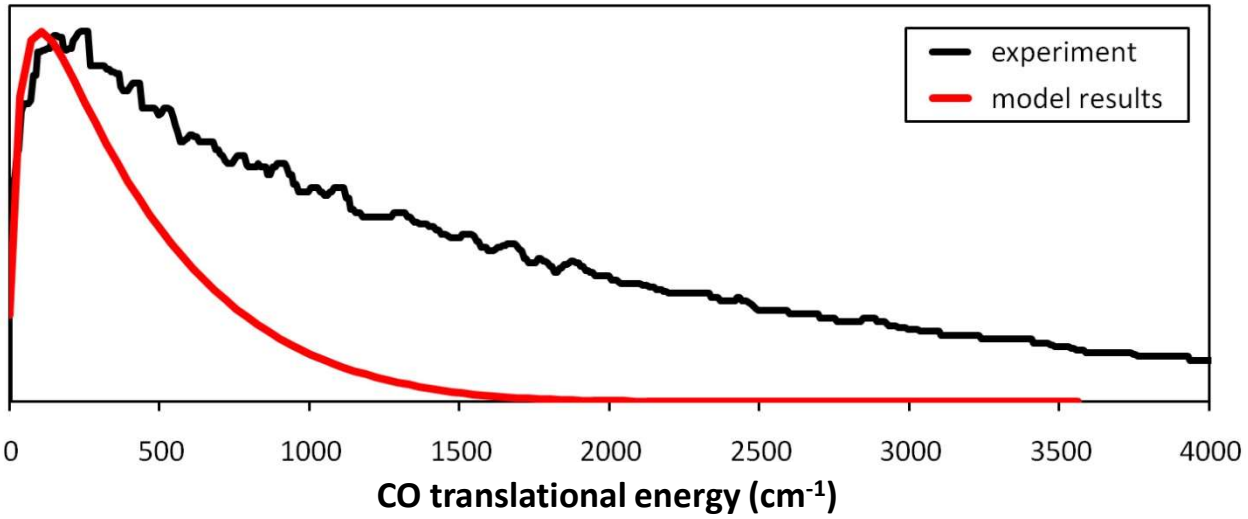


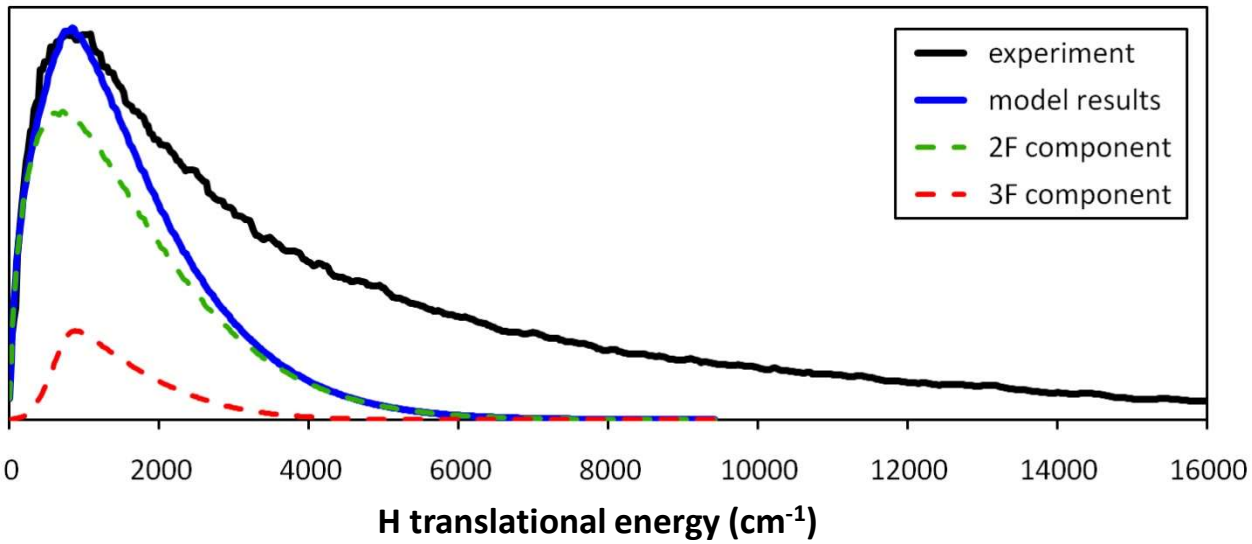


Formaldehyde Results



Acetaldehyde Results





Methyl Formate Results