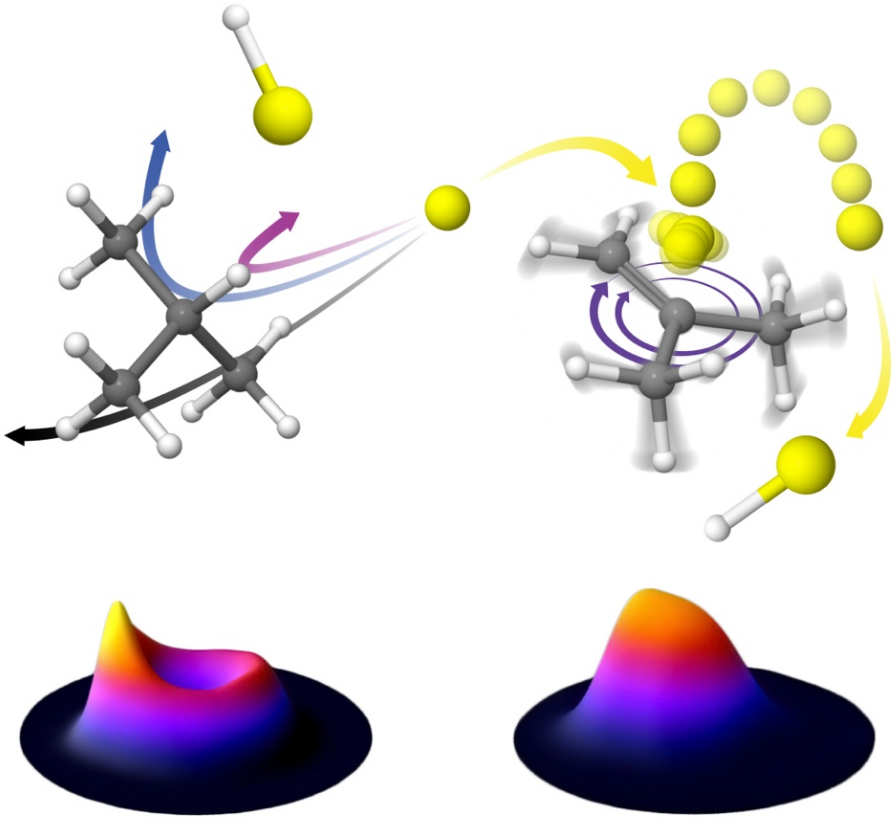
# Crossed-Beam Slice Imaging of Cl Reaction Dynamics with Butene Isomers

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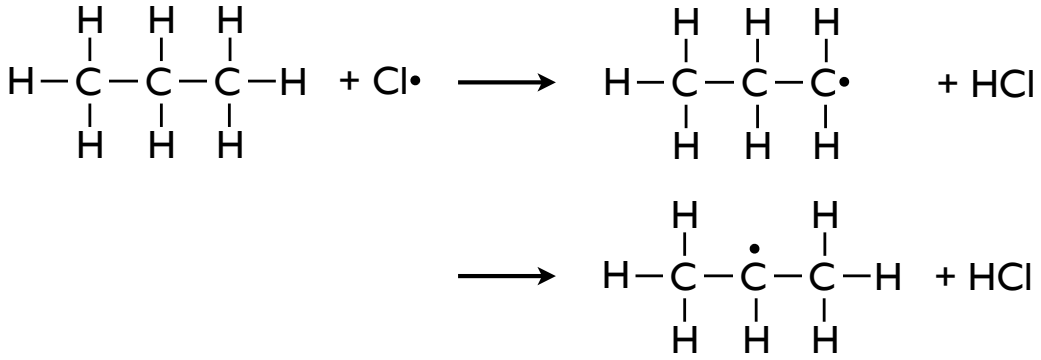
Yuanyuan Shi[1], Nitin Patel[1], Richard Van Camp[1], Alexander M. Mebel[2], Arthur G. Suits[1]

# Crossed-beam and Imaging

## Measuring differential cross sections: the case of the Cl+propane reaction




primary abstraction

-2 kcal/mol

secondary abstraction

-6 kcal/mol

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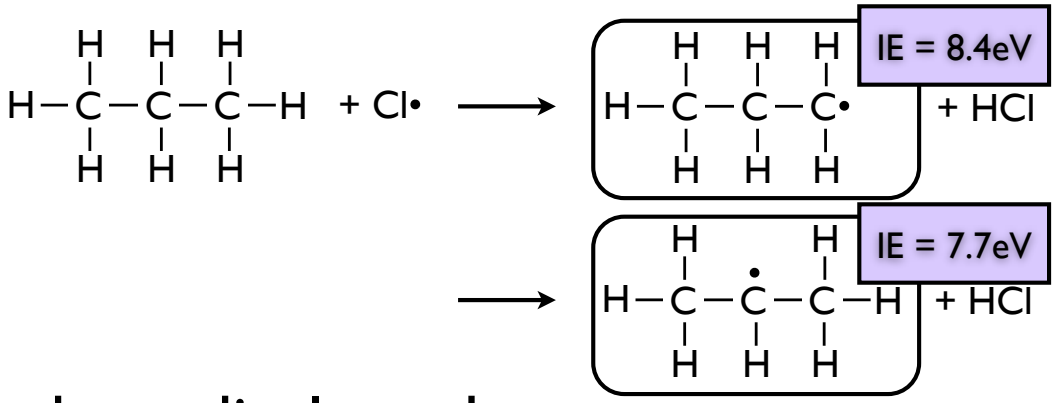


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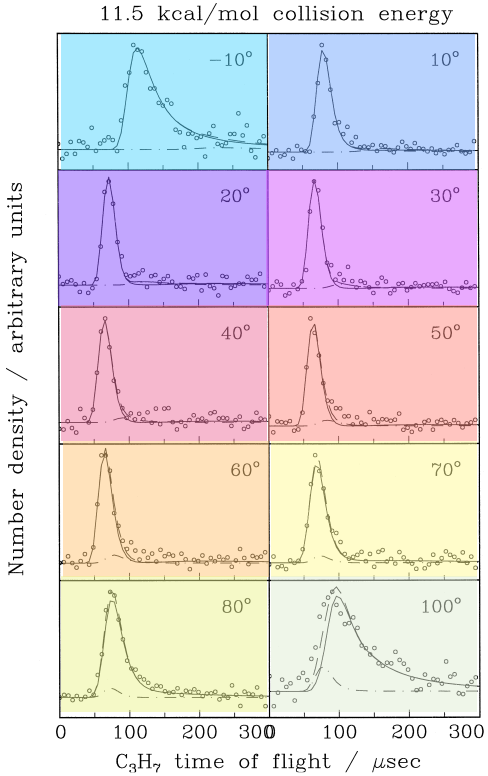
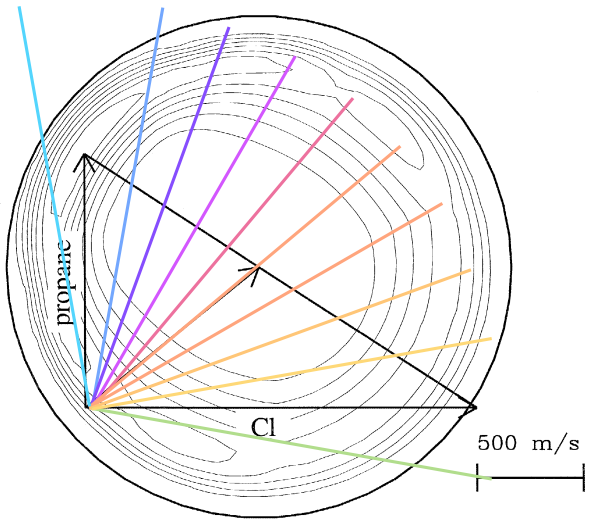
## Probing the radical product




DCSs = convolution fits from laboratory measurements

Probe: hν = 9.5eV

II

V

No disentanglement between competing abstraction sites

Blank et al., Chem. Phys., 1998

# Crossed-beam and Imaging

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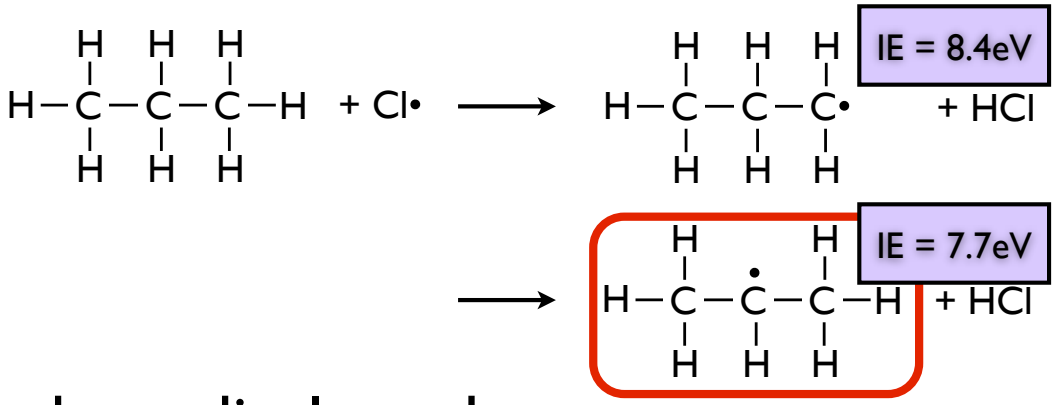


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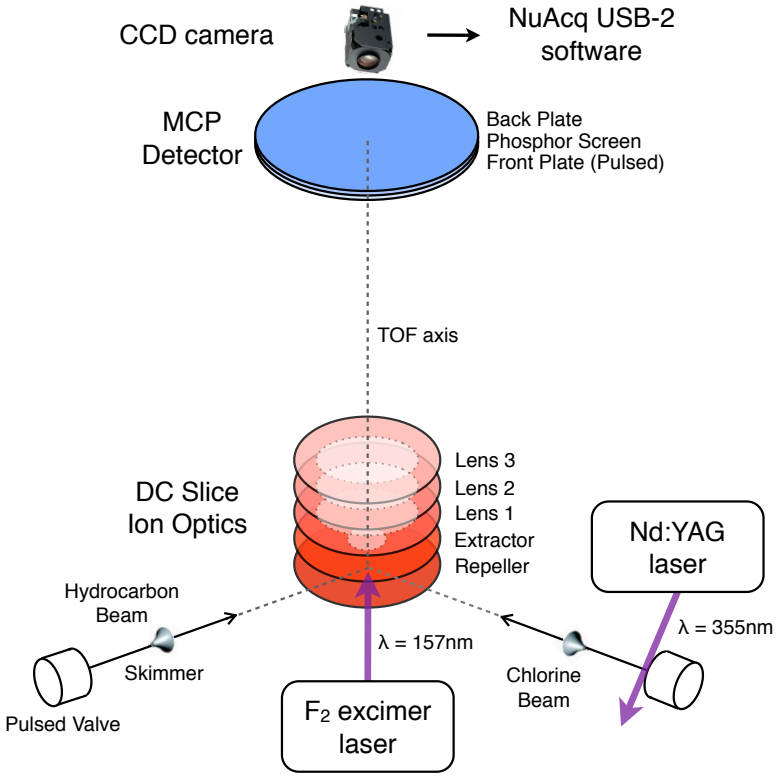
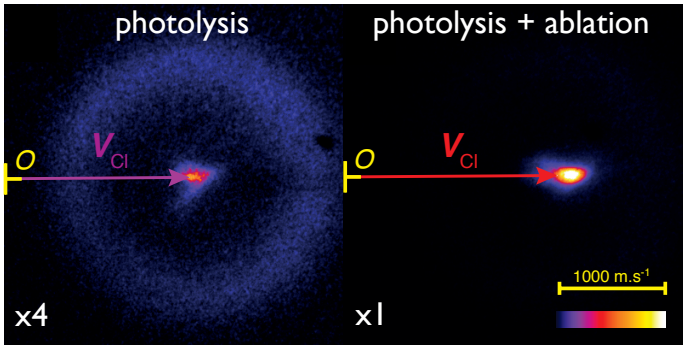
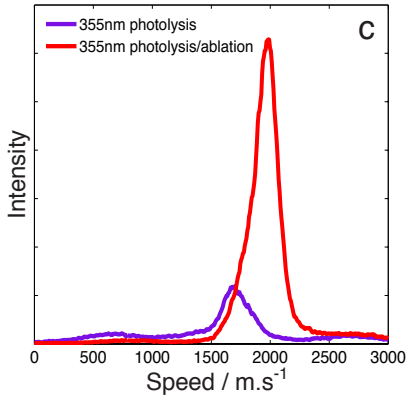



### Chlorine atom source: 355nm photolysis + ablation



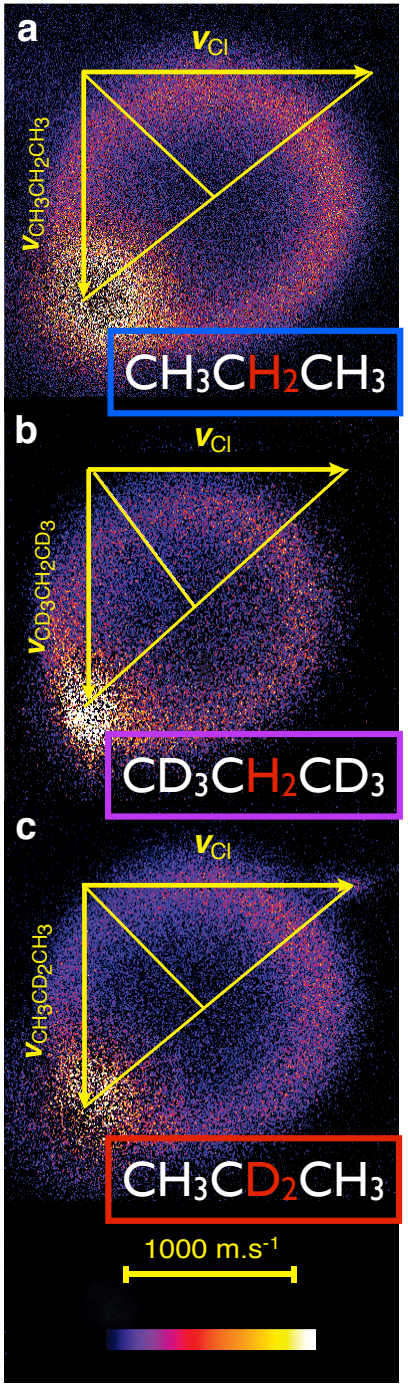




Probe: hν = 7.9eV & Unfocused

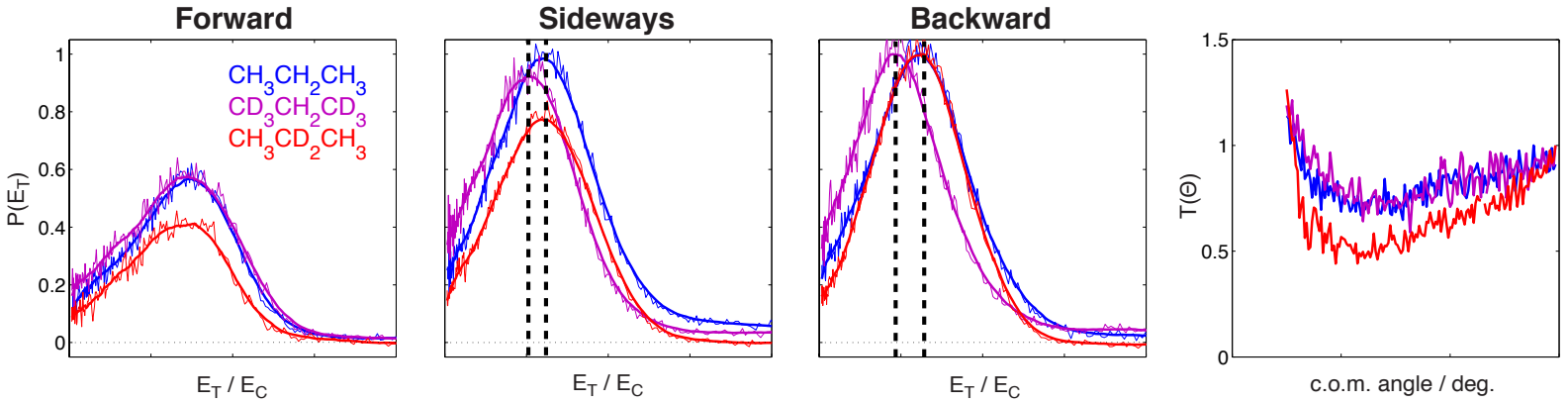
=> No multiple photon ionization

=> Product selectivity

# Cl + propane




differential cross sections for H/D secondary abstractions at 12 kcal/mol



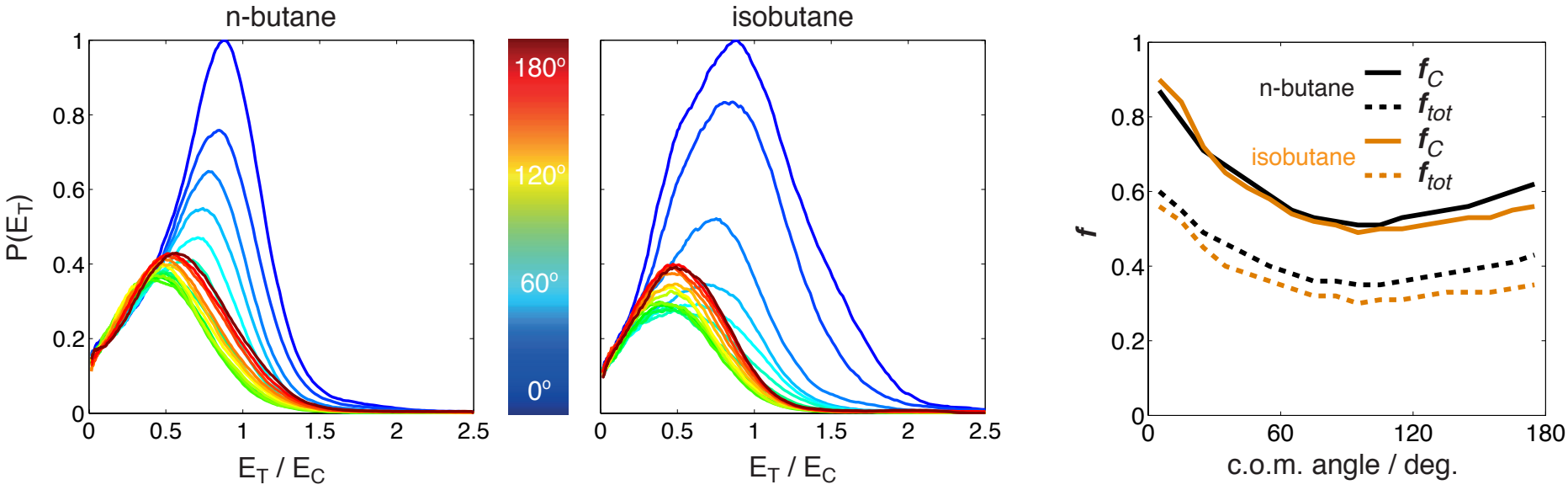

$P(E_T)$ in BW/SW directions of $CD_3CH_2CD_3$:
=> a more effective energy disposal into the propyl product
=> vibrational excitation ≠ impulsive model

Different T(Θ) for H and D abstractions:
=> a kinematic effect

# Cl + butane isomers

secondary abstraction

tertiary abstraction




Isobutane in the FW direction:

- Broad $E_T$ distribution
- Sharp angular distribution => HCl(v'=1) or steric hindrance effect?

# Cl + butane isomers

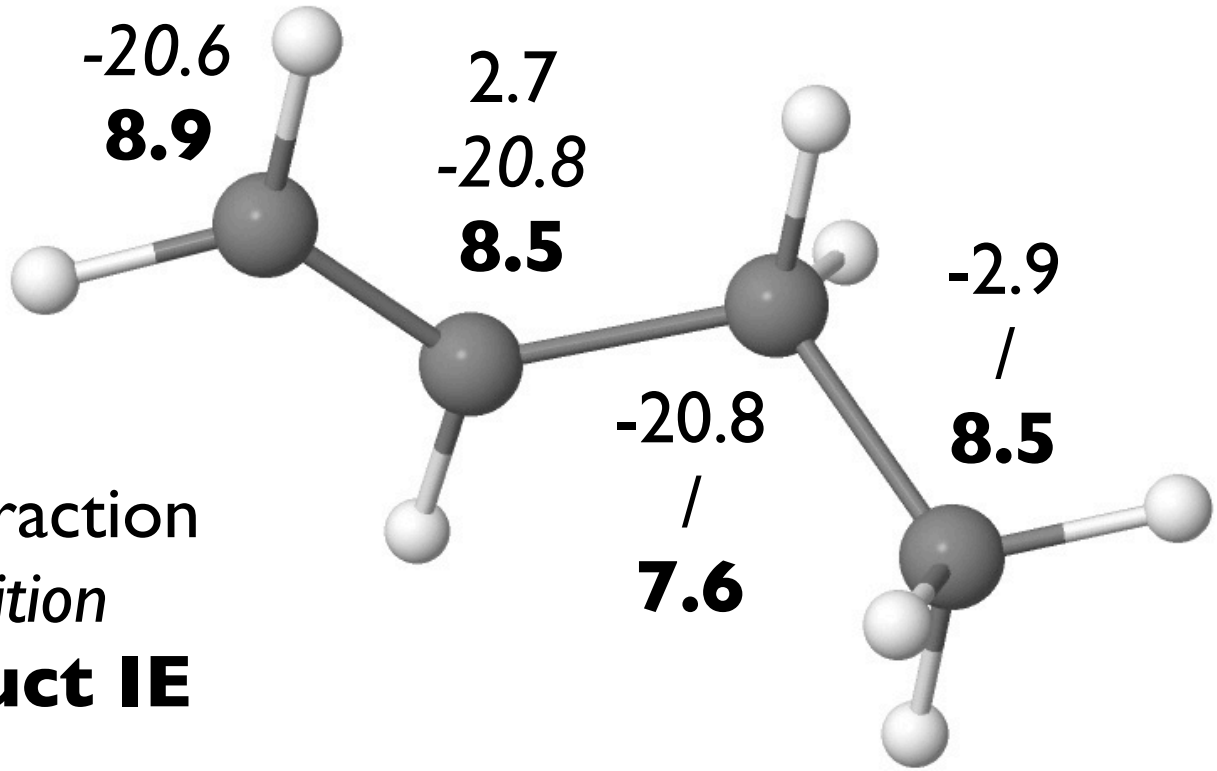
Direct abstraction

$$C_4H_8 + Cl\bullet \longrightarrow C_4H_7\bullet + HCl$$

Addition/Elimination

$$C_4H_8 + Cl\bullet \longrightarrow [C_4H_8Cl]^* \longrightarrow C_4H_7\bullet + HCl$$

# energetics

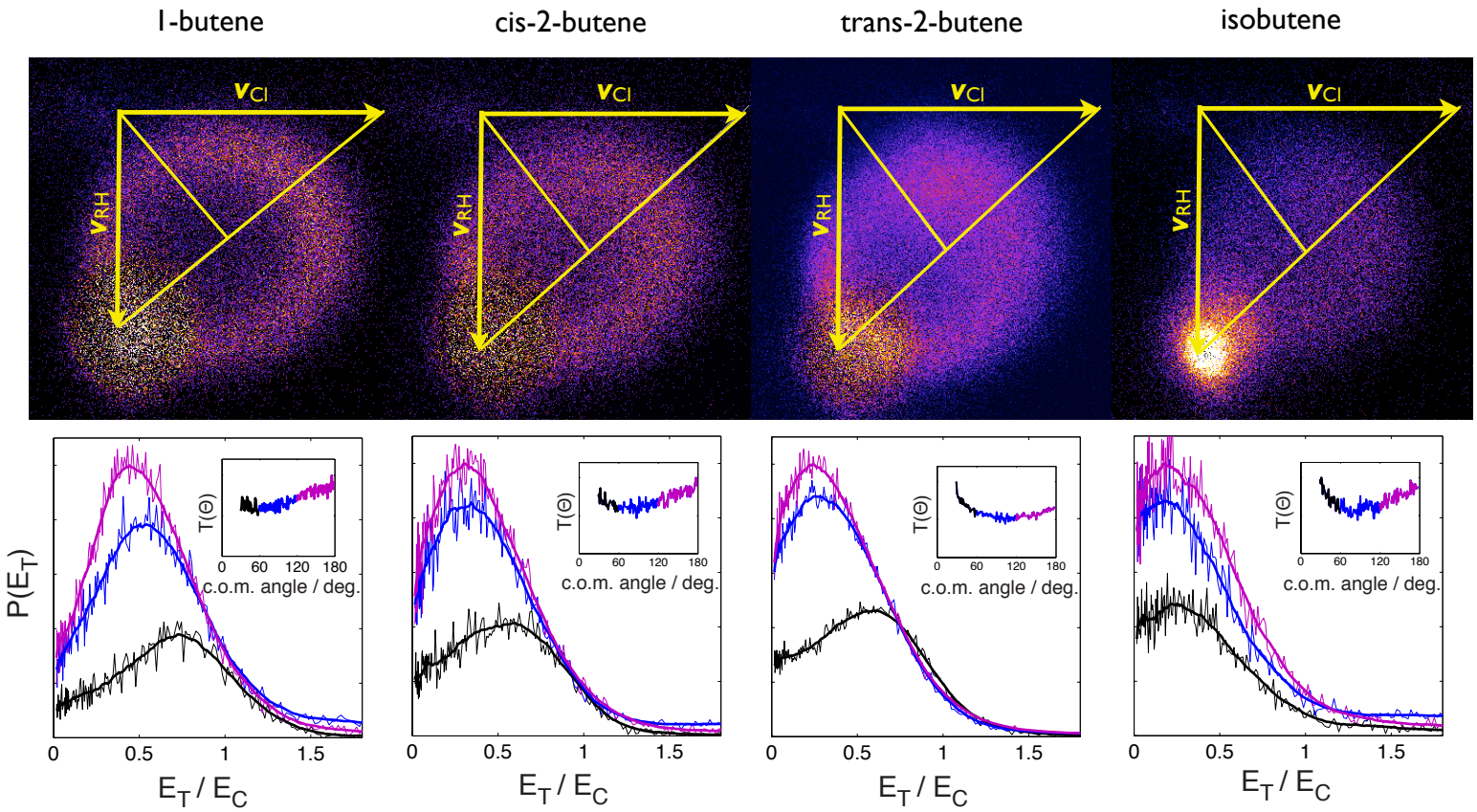



H abstraction
*Addition*
**product IE**

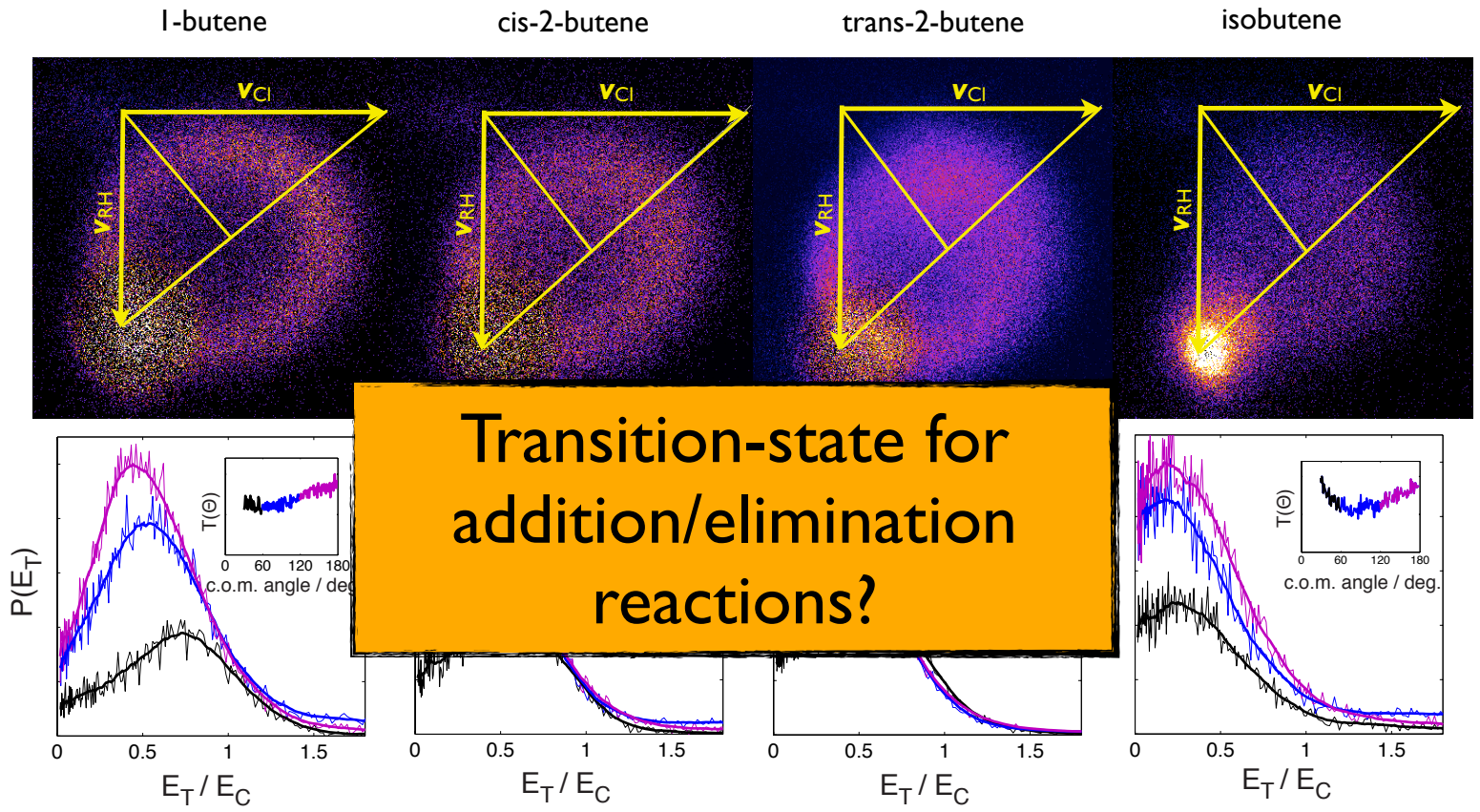
*gauche*-1-butene

CBS-QB3 level of theory

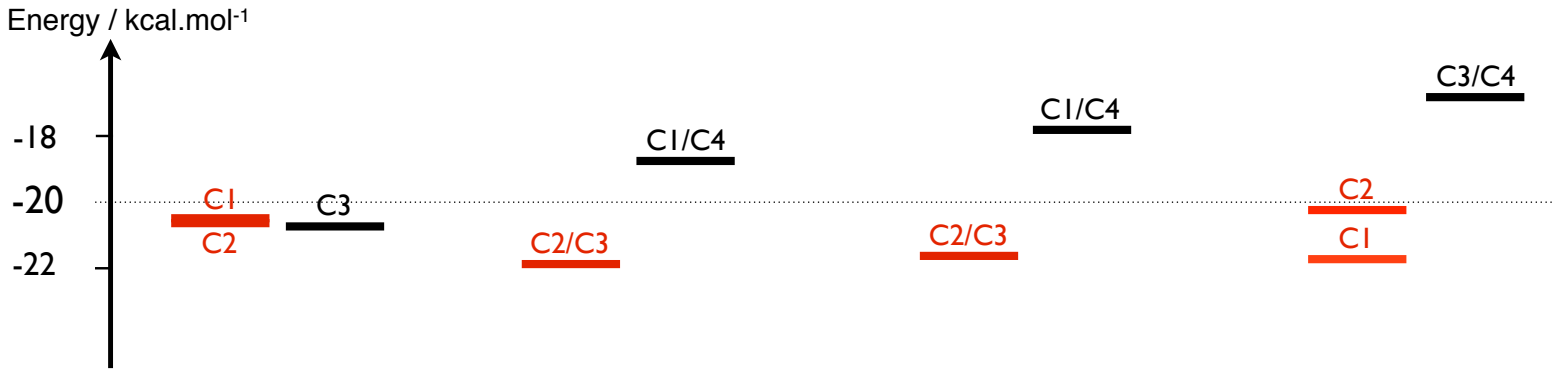
# Cl + butene isomers



# Cl + butene isomers

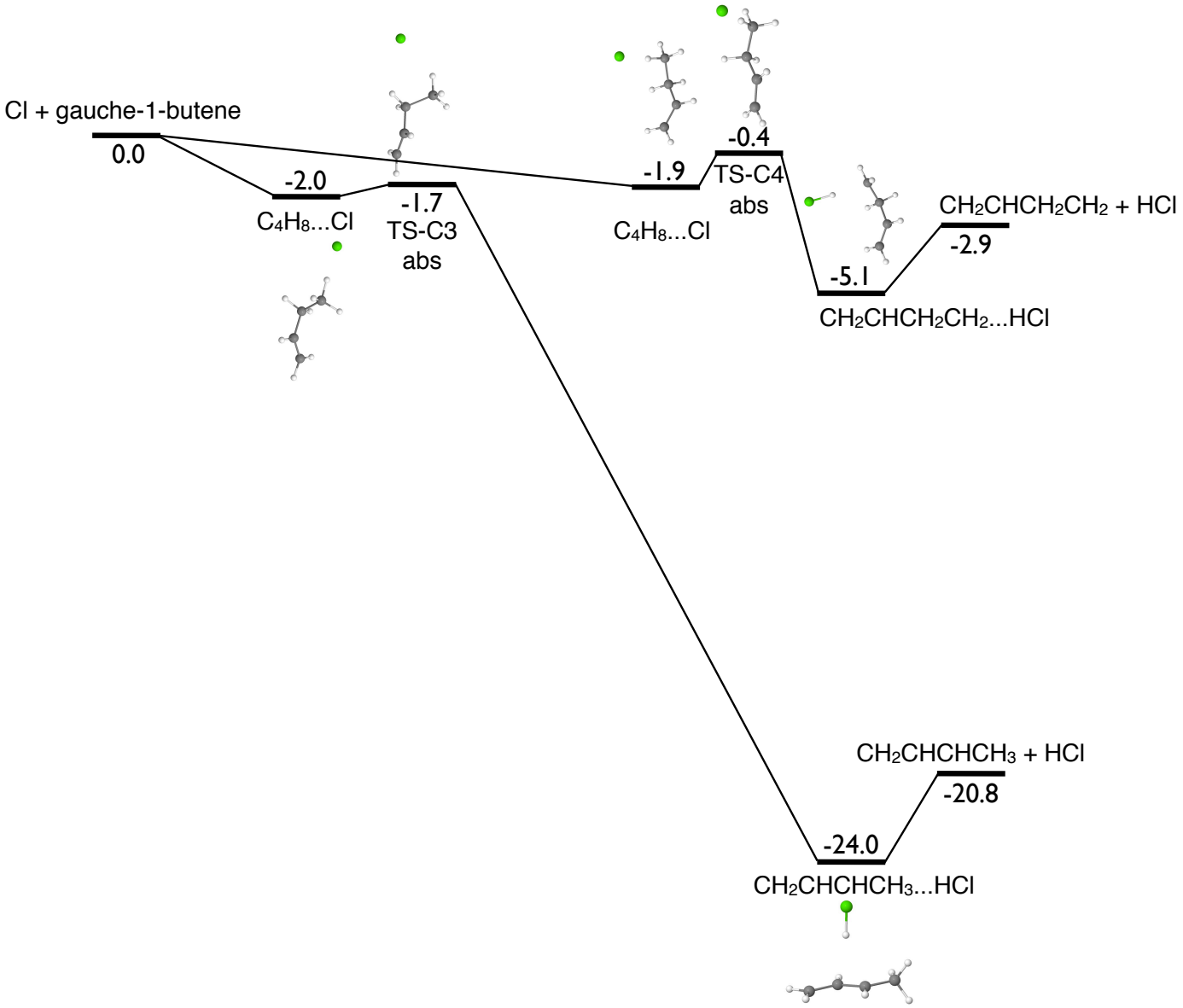



**Transition-state for addition/elimination reactions?**




Cl addition vs. H abstraction

# Cl + butene isomers




CBS-QB3, Energies in kcal/mol
Prof. Alexander Mebel

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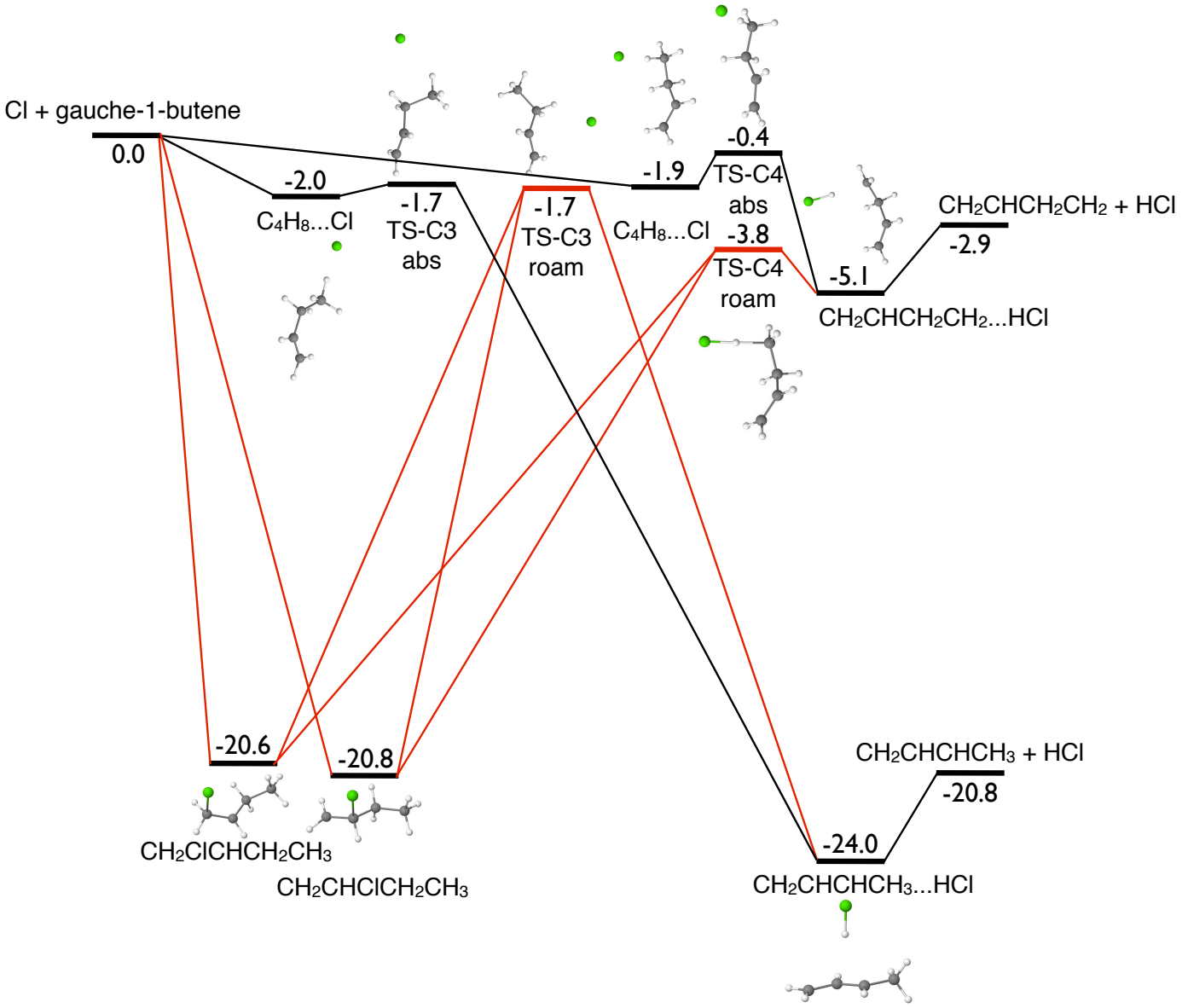


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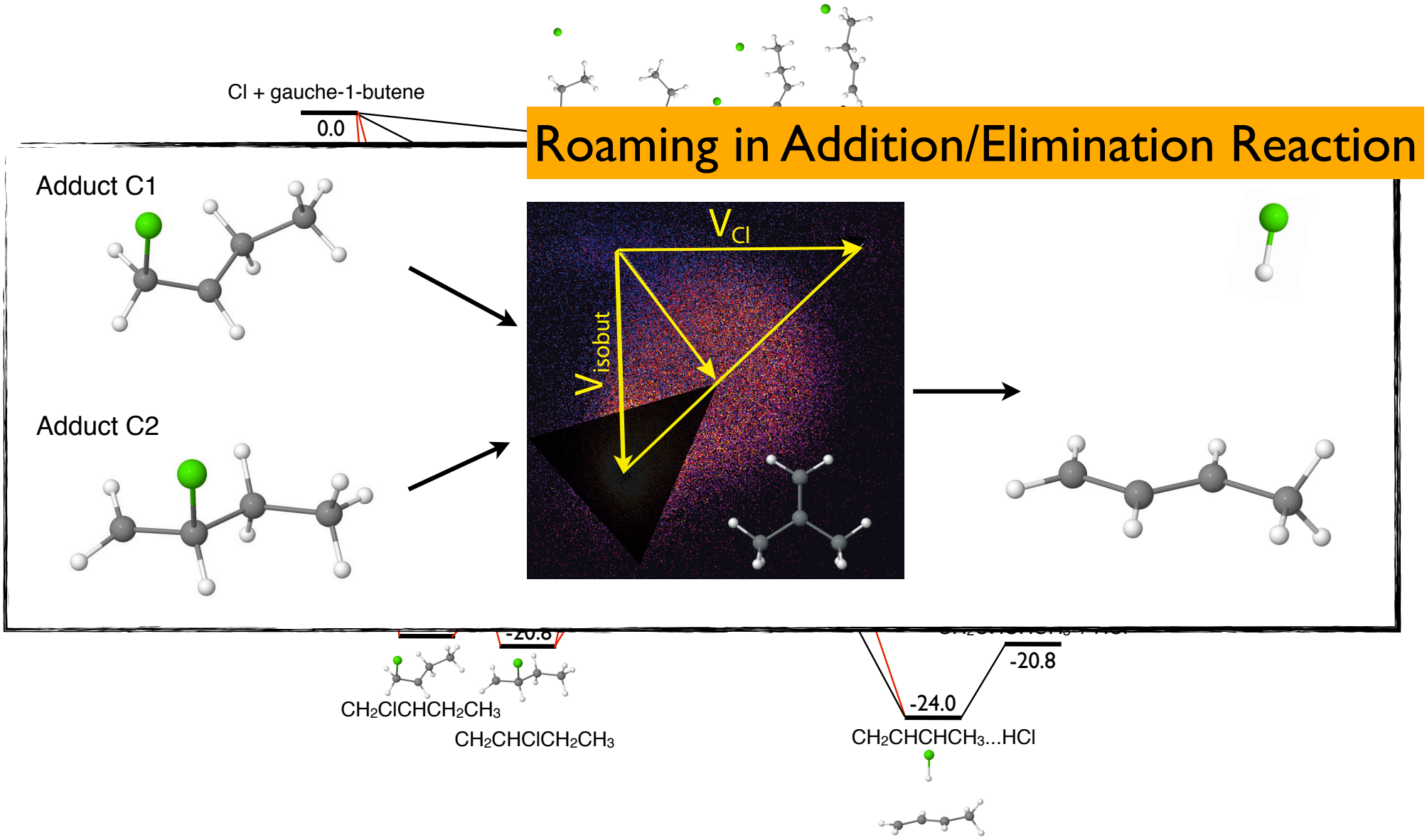


CBS-QB3, Energies in kcal/mol
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# Conclusion/Perspectives

## Cl + propane/butane

- Selective measurements of secondary and tertiary abstractions

- C3/C4 hydrocarbons = the last step before convergence to large system energy recoil

- the role of vibrational density-of-state

## Cl + butene isomers

- Distinct dynamical behaviors reflecting the competition between direct abstraction and addition/elimination

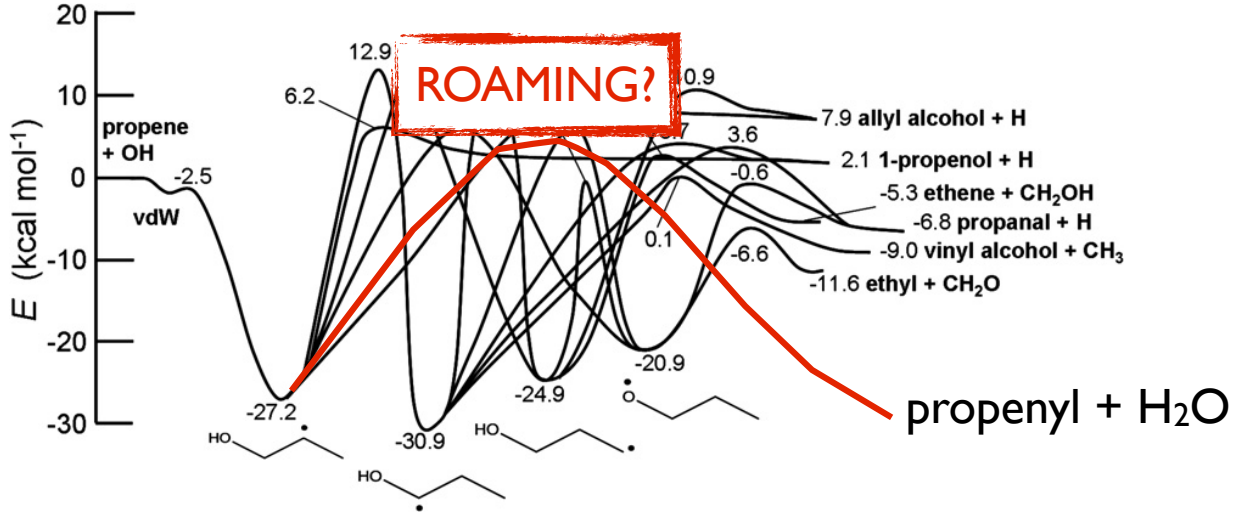
- ROAMING in addition/elimination

What about Kinetic Isotope Effect?

addition step = an inverse KIE

roaming-abstraction step = normal KIE

## Food for thought:
## Dynamics of OH + Alkene Reactions



# Acknowledgments


Prof. Arthur G. Suits
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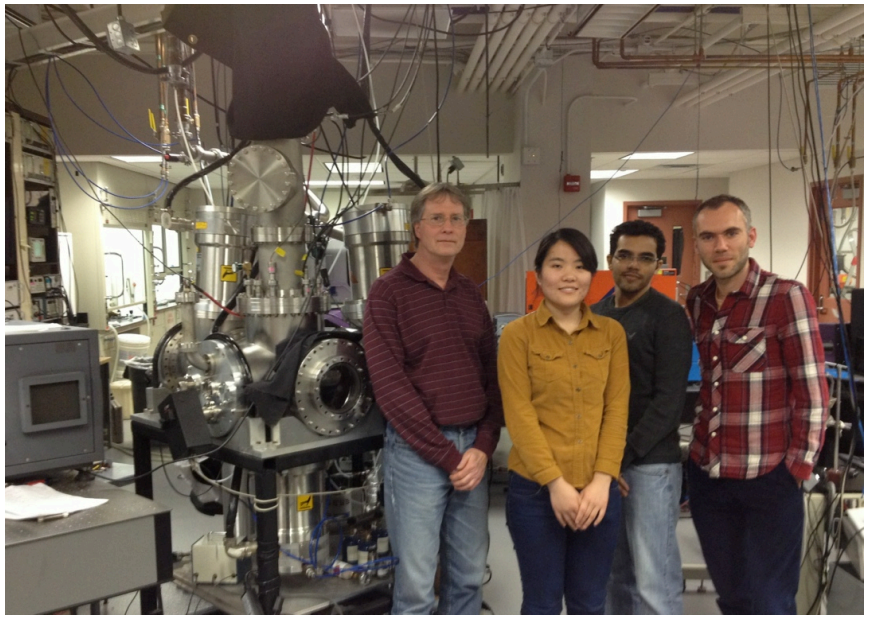

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Rick, Yuanyuan, Nitin


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