Queens College

CITY UNIVERSITY OF NEW YORK

Toward a "Polanyi Rule" Picture of Nuclear Dynamics in Complex Polyatomic Ion-Molecule Reactions

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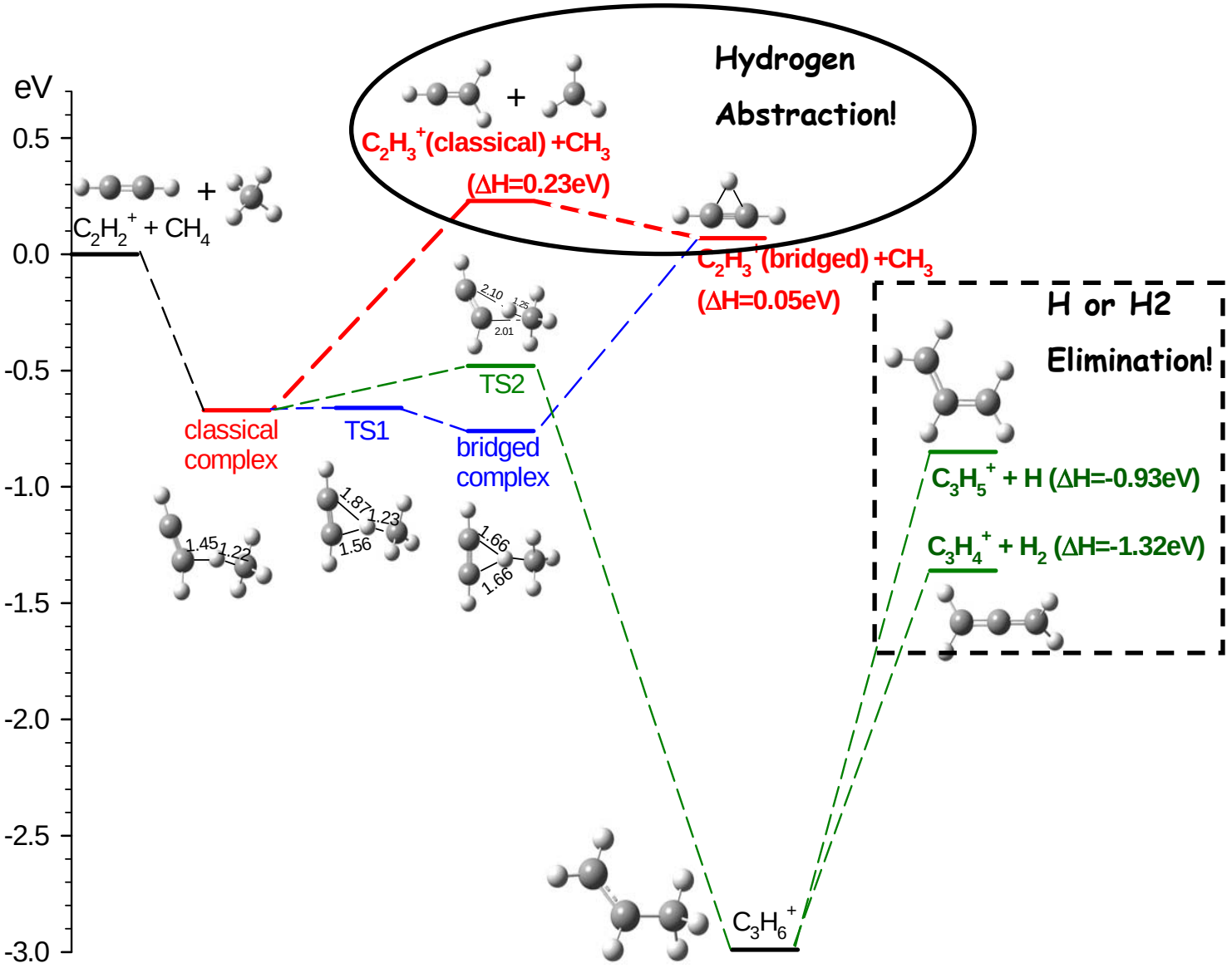
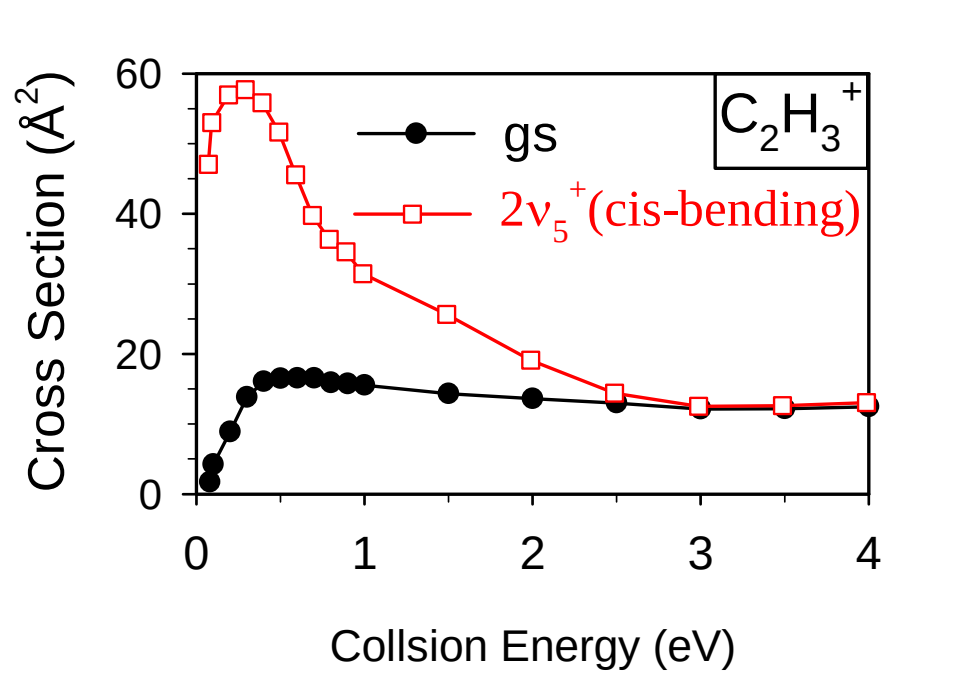
GRC on Gaseous Ions: Structures, Energetics and Reactions

Galveston, TX, March 1-6, 2009

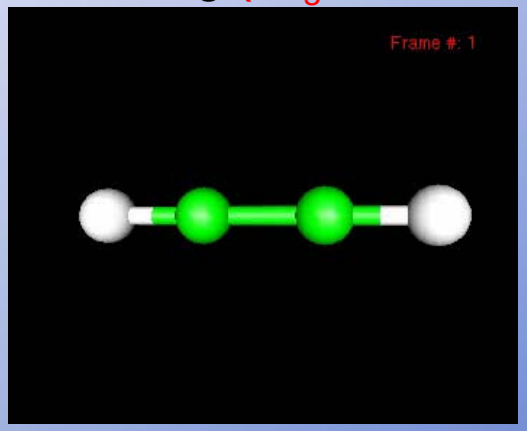
Properties of the System — Early Time Dynamics



Summary of Experimental Results



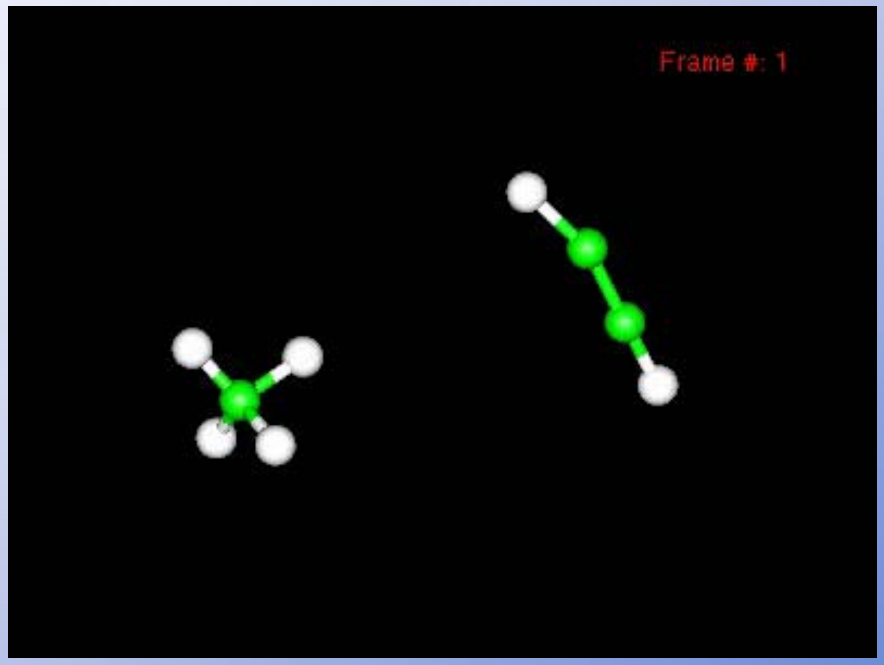
Excitation of $C_2H_2^+$ with two quanta of cis-bending ($2\nu_5^+$, 0.155 eV)

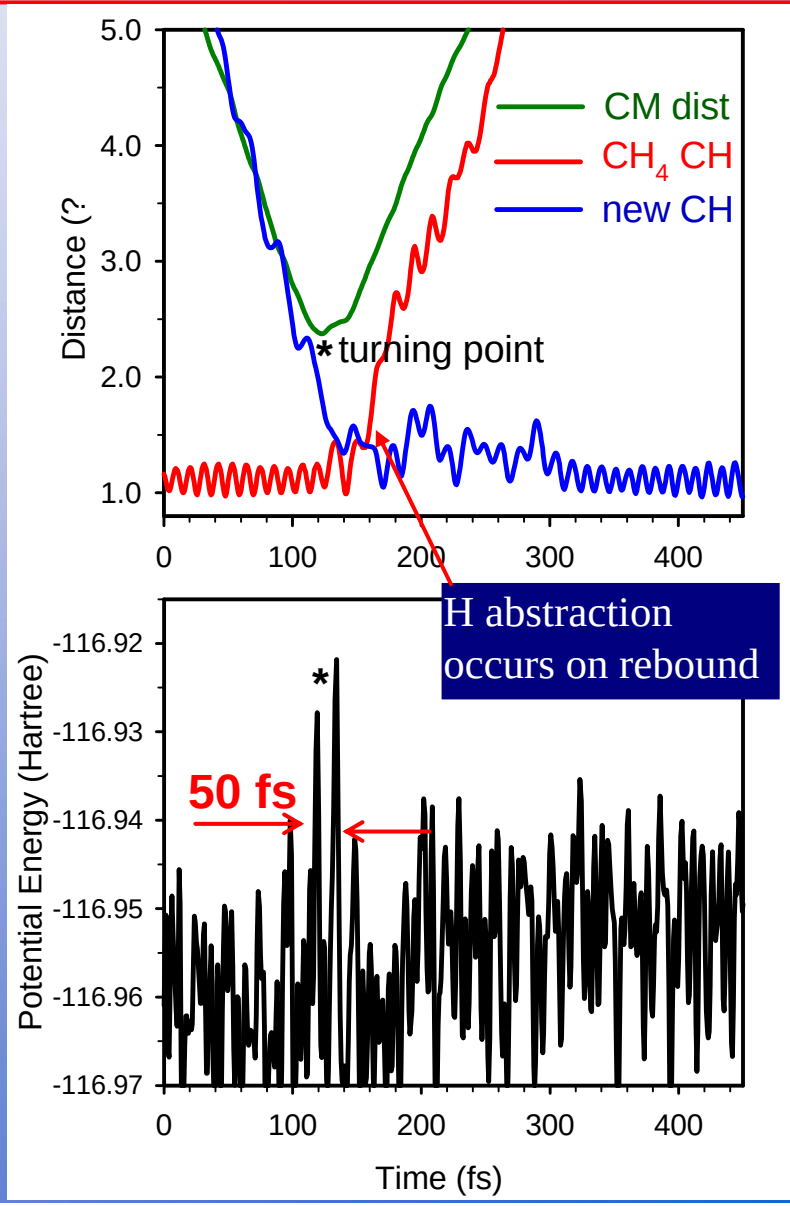


Y. Chiu, H. Fu, J. Huang, and S. L. Anderson. JCP, 102, 1199(1995)

Direct Dynamics Simulations on $C_2H_2^+ + CH_4$: Nature and Time Scale of Nuclear Motions

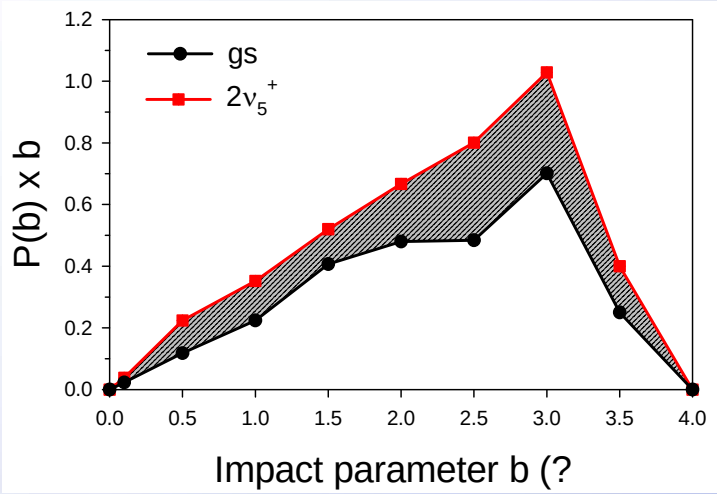
- **Set initial conditions using Hase's VENUS (represent expt. conditions)**
- E_{col} : 0.5 eV
- Vibrational states: $C_2H_2^+$(gs and $2\nu_5^+$)
- **Integrate trajectory using G03**
- MP2/6-31+G* with "SCF=XQC" option



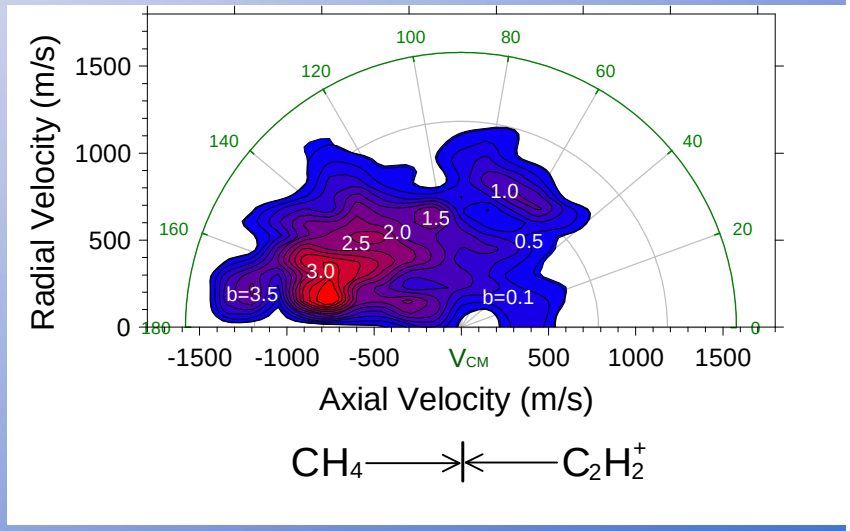


Trajectory Validation:
Cross Sections & Product Ion Angular Distribution

Opacity Functions for Hydrogen Abstraction



σ (HA)	exp	traj
Ground state	16	8.1
$2\nu_5^+$ state	42	12.6
Enhancement	**2.6**	**1.6**



Trajectories qualitatively reproduce vibrational enhancement effects and angular distribution!

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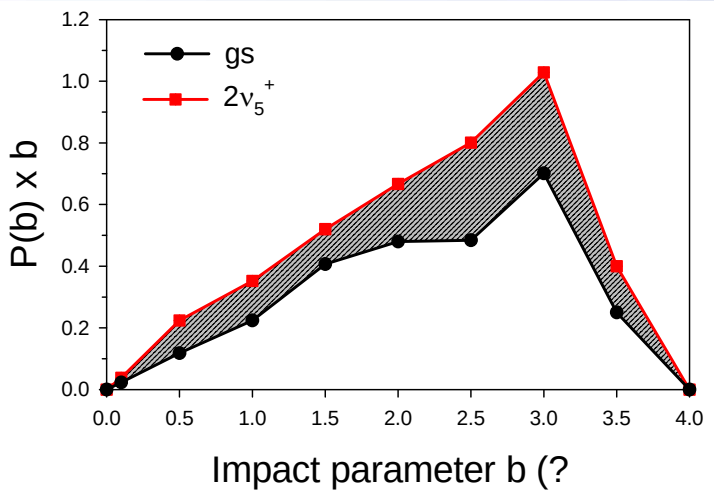

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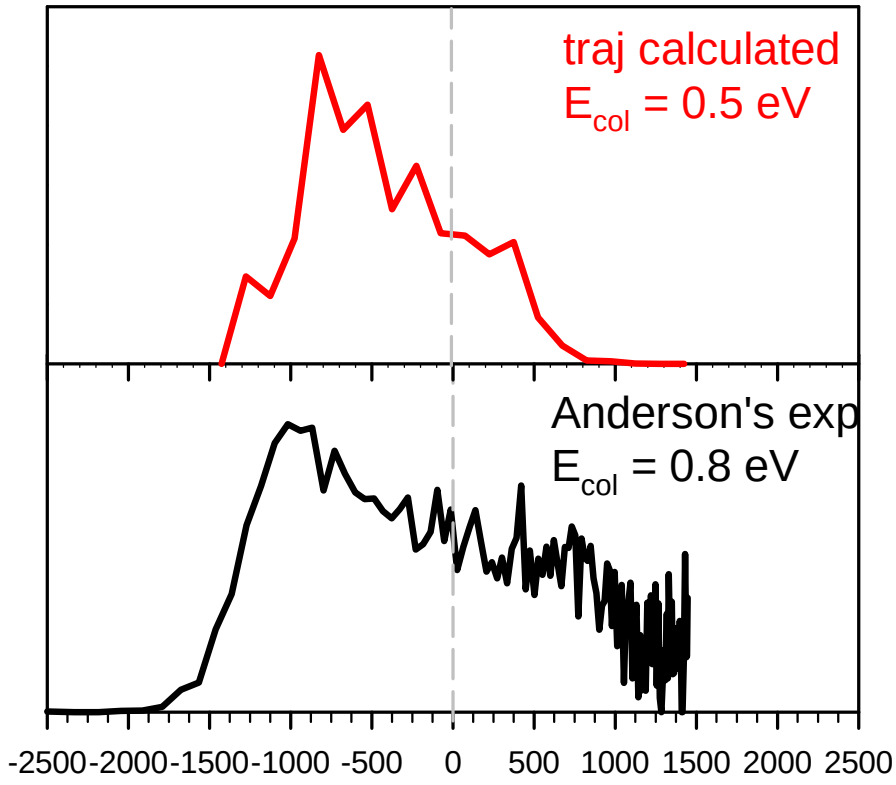
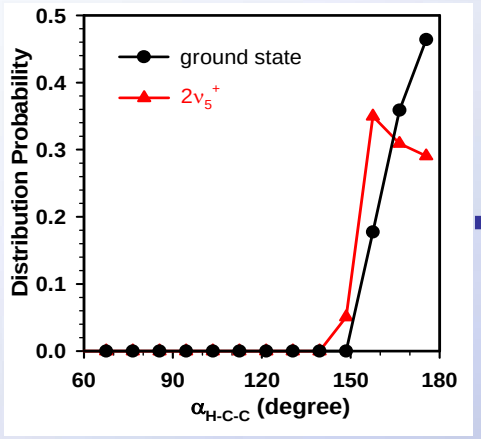


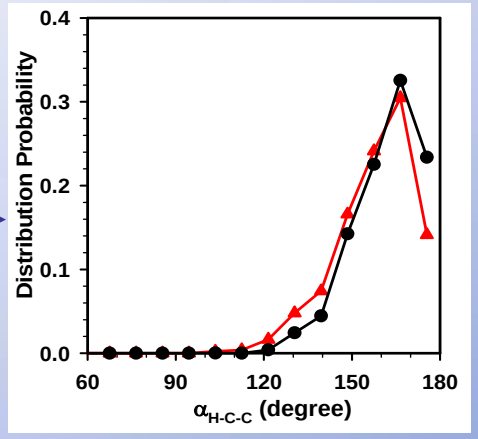
Trajectories qualitatively reproduce vibrational enhancement effects and angular distribution!

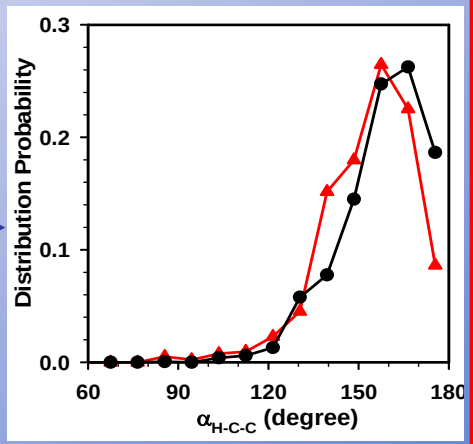
Effects of $C_2H_2^+$ bending

At beginning of trajectories | **25 fs before CM turning points** | **at CM turning points**

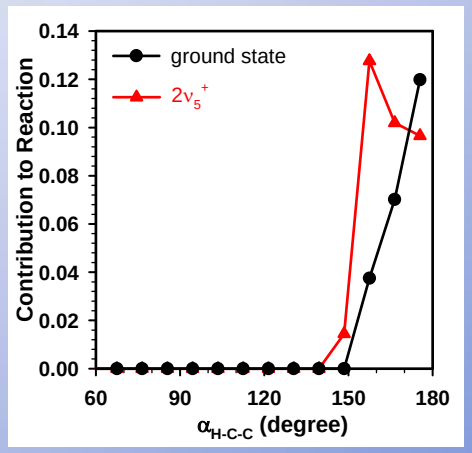
Distribution of $C_2H_2^+$ bend angle

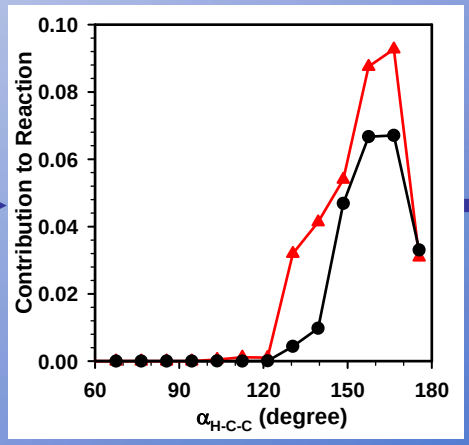


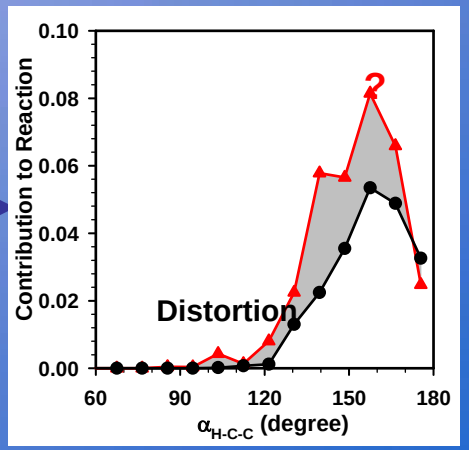




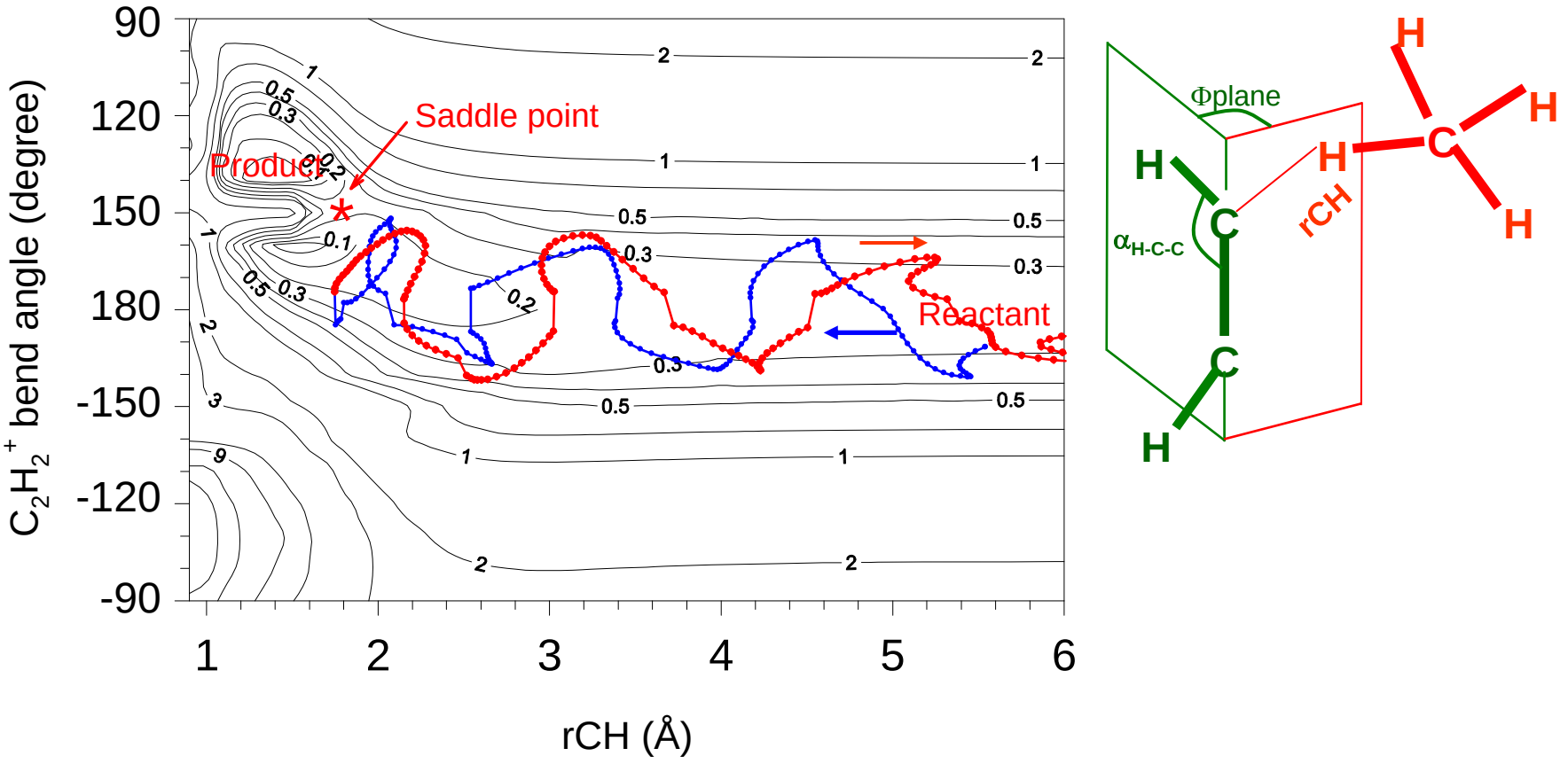
Cross section as a function Of bend angle







Toward A "*Polanyi-type" Picture for Polyatomic System*



E_{col} = 0.5 eV, and $C_2H_2^+$(gs)

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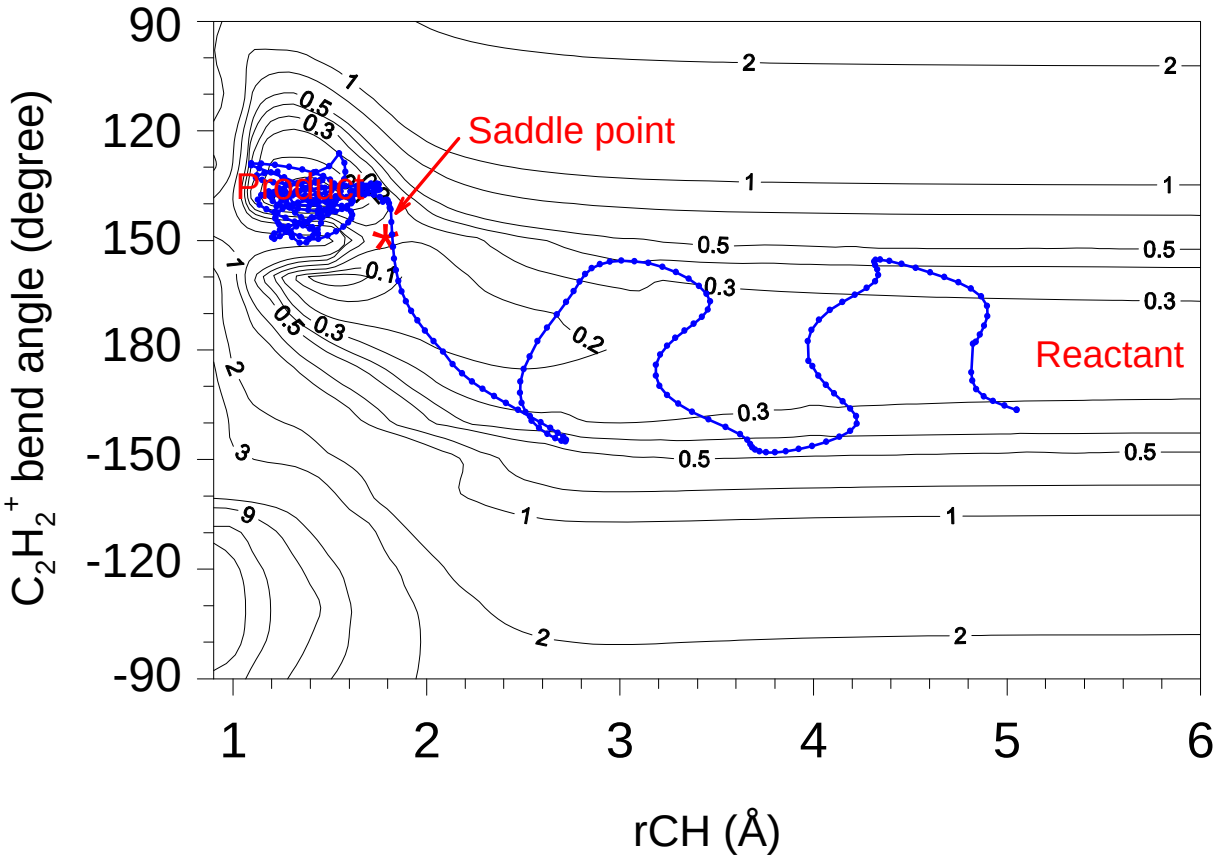

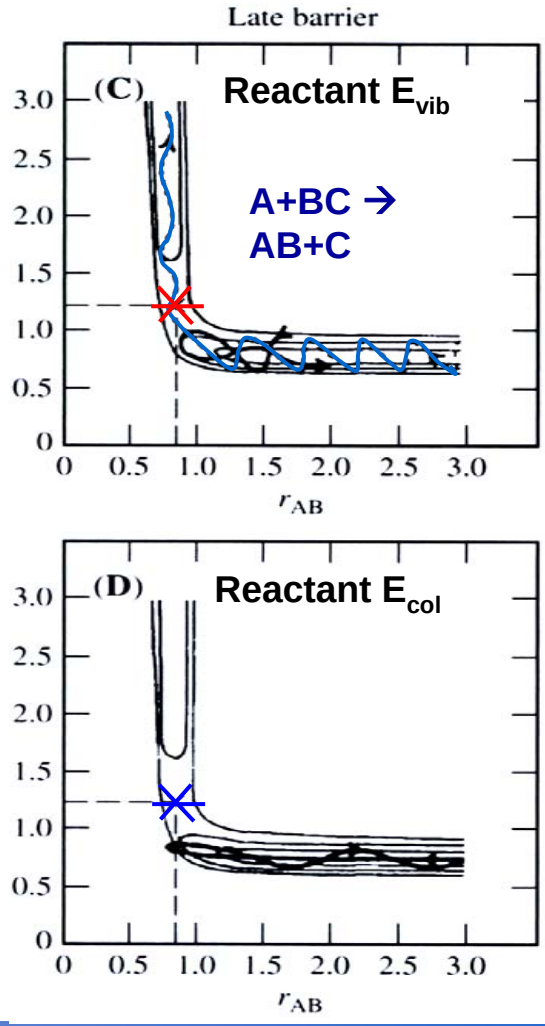

E_{col} = 0.5 eV, and $C_2H_2^+(2\nu_5^+)$ with E_{vib} = 0.15 eV

Origins of Vibrational Effects on Reactions:

Distortion *vs.* Momentum

Acknowledgements

Scott Anderson (U of Utah)

ACS-PRF Grant
CUNY Collaboration Grant

Biochemical ion-molecule reactions