

# Vibrational Relaxation of CH<sub>2</sub>ClI in Cold Argon



Amber Jain

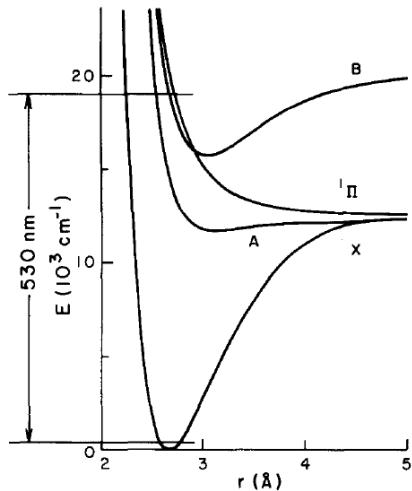
Sibert Group

# Introduction

## Interpreting spectra of relaxing molecules using theory

Slow vibrational relaxation in picosecond iodine recombination in liquids

Nesbitt, Hynes, J. Chem. Phys. **77**, 2130



- ❖ Time scale of 100 ps observed spectroscopically
- ❖ Theory reveals mechanism of energy transfer:
  - ❖ Diffusive relative motion
  - ❖ Vibrational-translation relaxation followed by vibrational-vibrational relaxation

# Introduction

## Interpreting spectra of relaxing molecules using theory

Slow vibrational relaxation in picosecond iodine recombination in liquids

Nesbitt, Hynes, J. Chem. Phys. **77**, 2130

A molecular dynamics simulation of NBr trapping in an argon matrix

Fraenkel, Haas, Chem. Phys. Lett. **220**, 77

A femtosecond study of the infrared-driven cis-trans isomerization of nitrous acid

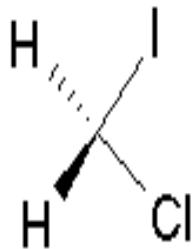
Schanz, Botan, Hamm, JCP **122**, 44509

The dynamical role of solvent on the ICN photodissociation reaction: connecting experimental observables directly with molecular dynamics simulations

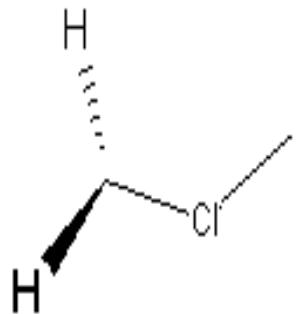
Rivera *et al.* Phys. Chem. Chem. Phys. **13**, 8269

# Chloroiodomethane and Its Isomer

- ❖ Features halogen halogen bond.
- ❖ Low vibrational frequencies leads to better coupling with bath.
- ❖ Large amplitude motions leads to rearrangement of bath molecules.

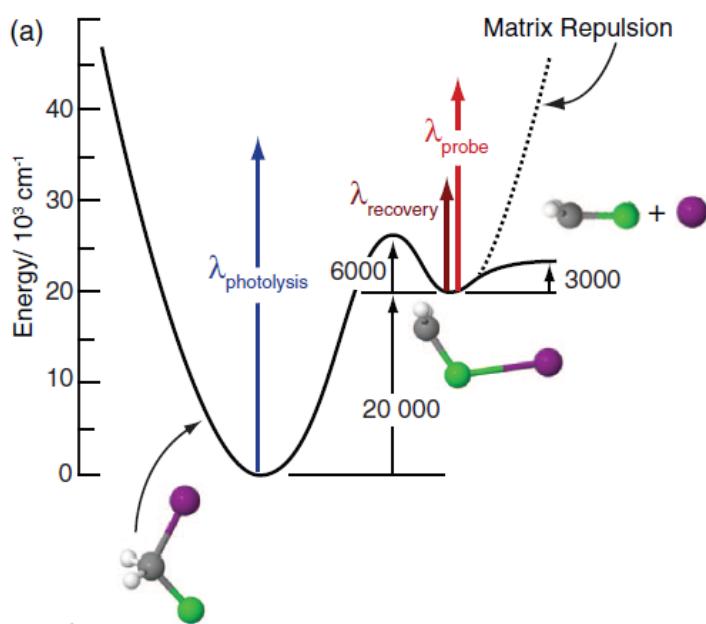
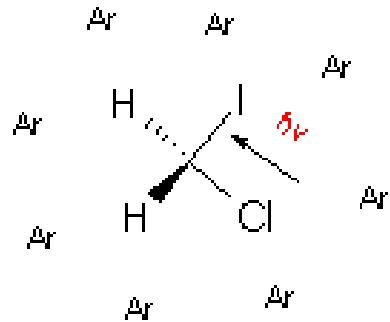


Parent Molecule



Isomer Molecule

# The Experiment



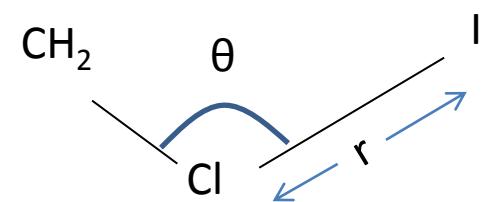
Probe at 435 nm and 485 nm

Decay rates :  $0.45 \text{ ps}^{-1}$   
 $0.07 \text{ ps}^{-1}$

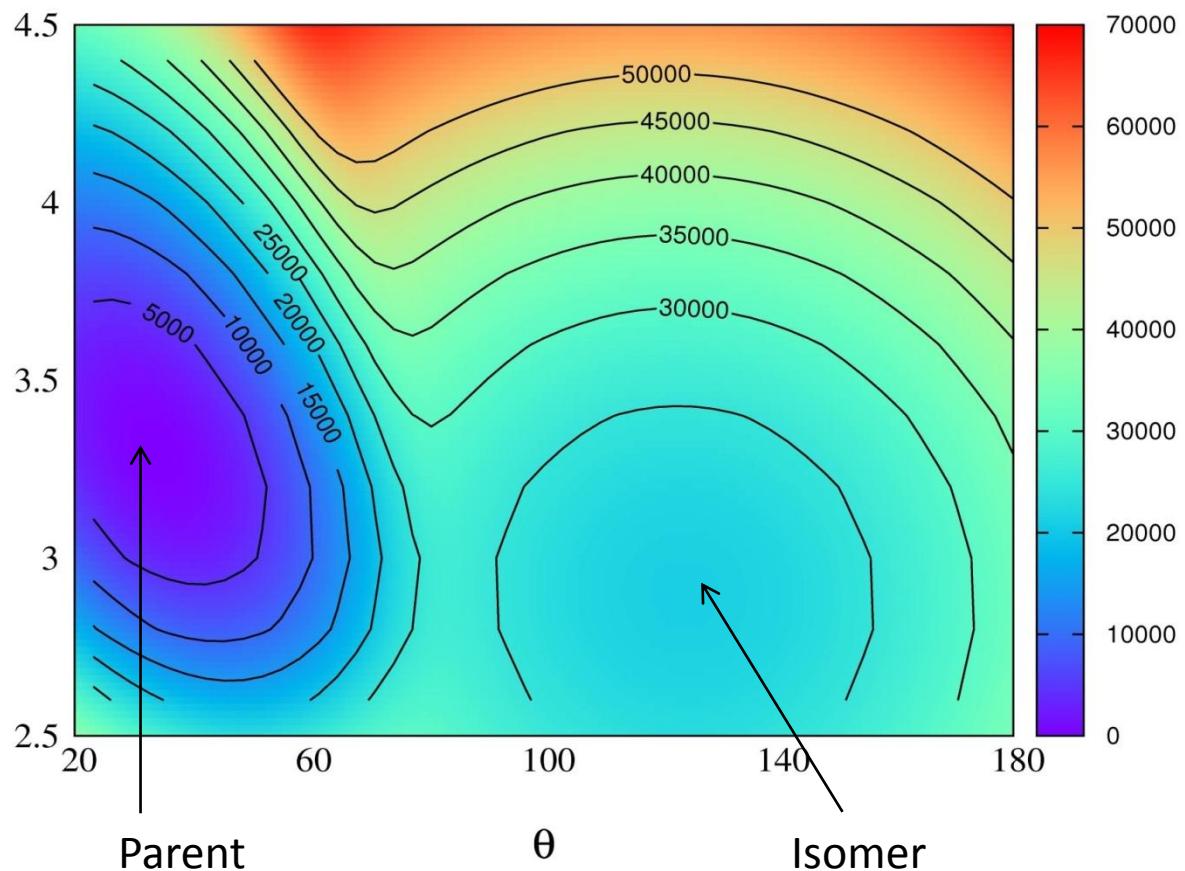
\* T. J. Preston *et al.*, J. Chem. Phys. 135,  
114503 (2011)

# Model

- ❖ Excited mode being C-I stretch ( $577\text{ cm}^{-1}$ ), only lowest 2 modes included :
  - C-Cl-I bend ( $\theta$ ) ( $159\text{ cm}^{-1}$ )
  - Cl-I stretch ( $r$ ) ( $235\text{ cm}^{-1}$ )
- ❖  $\text{CH}_2$  treated as a point mass.
- ❖ C-Cl bond frozen



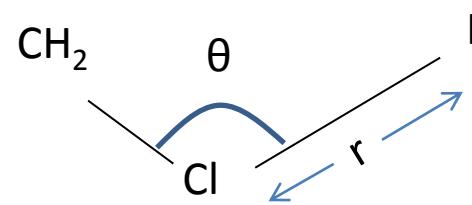
# Potential Energy Surface



Basis : H,C,Cl : 6-31++G\*\*

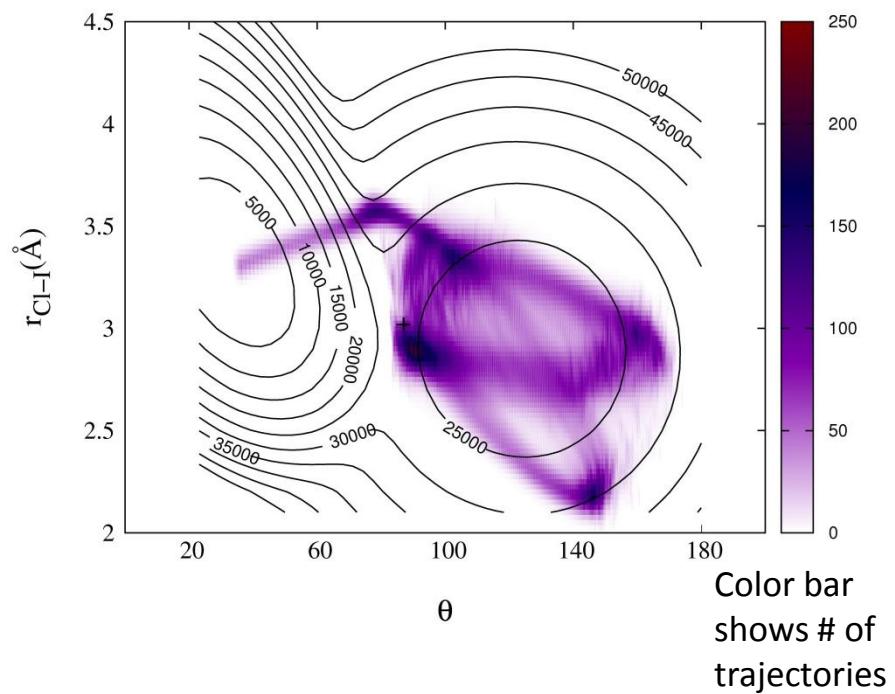
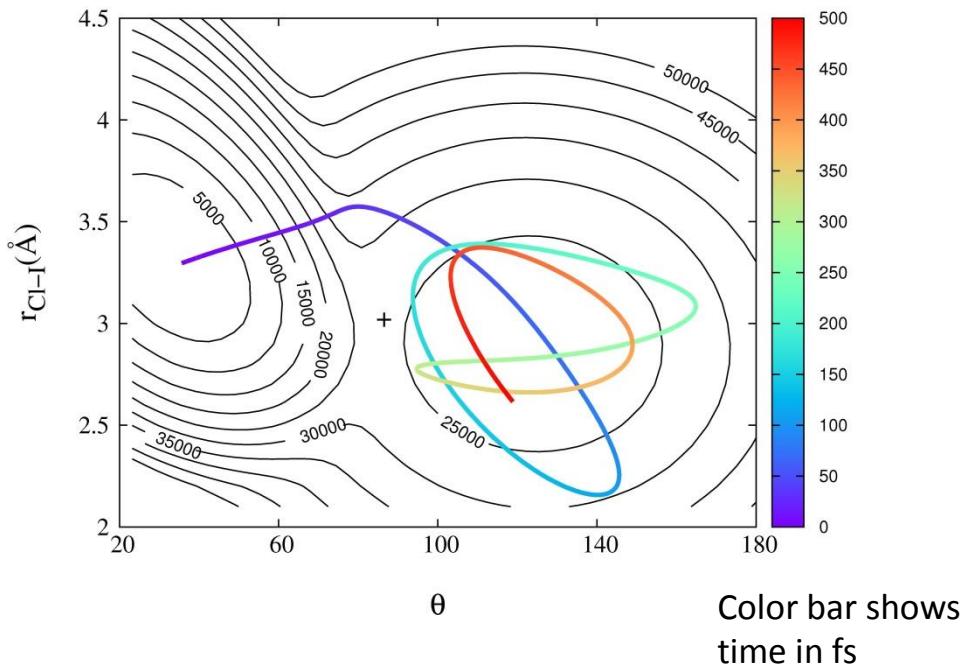
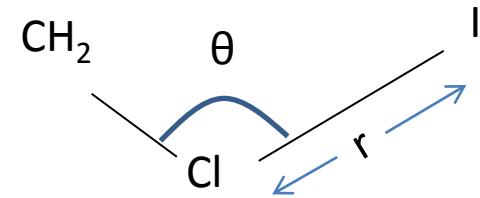
I : MidiX

Theory : MP2

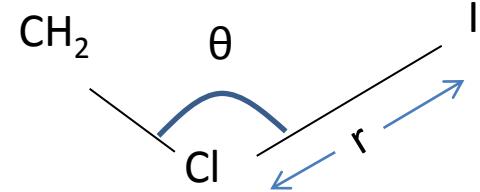


\* Chang; Miller, J. Phys. Chem. 94, 5884  
(1990)

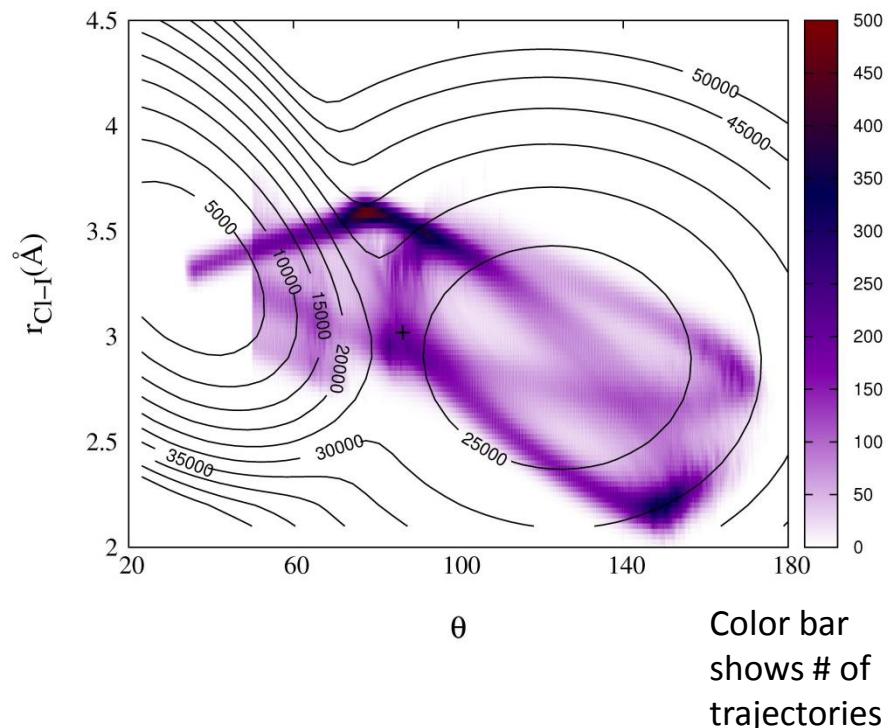
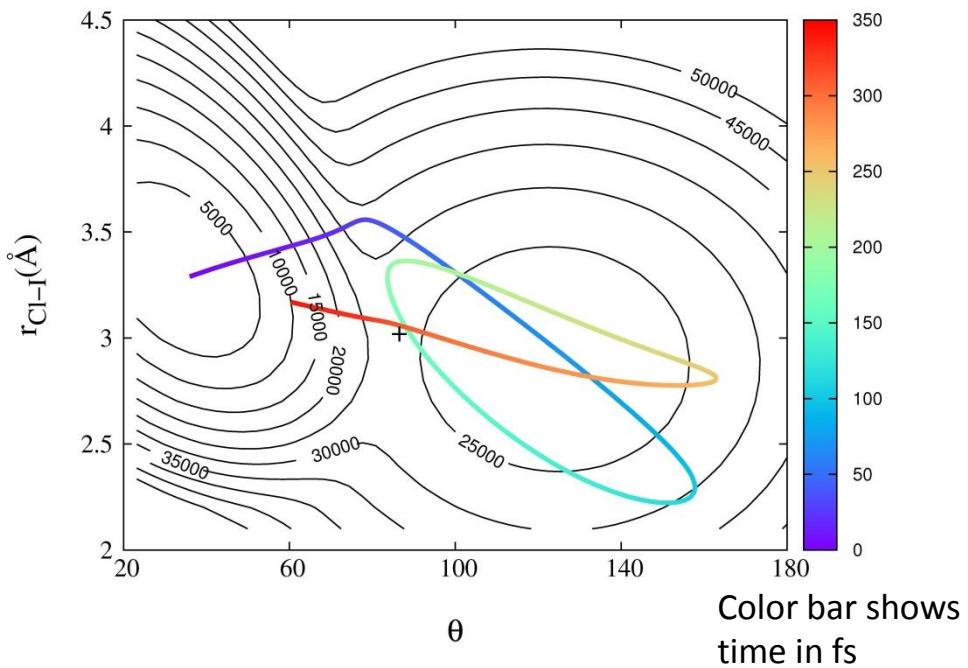
# Trajectories



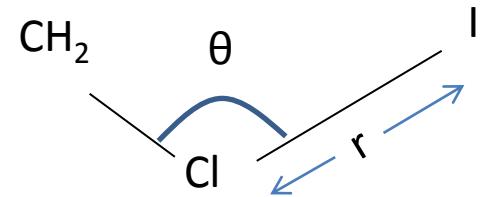
Reactive trajectory  
Statistics : 334/1500



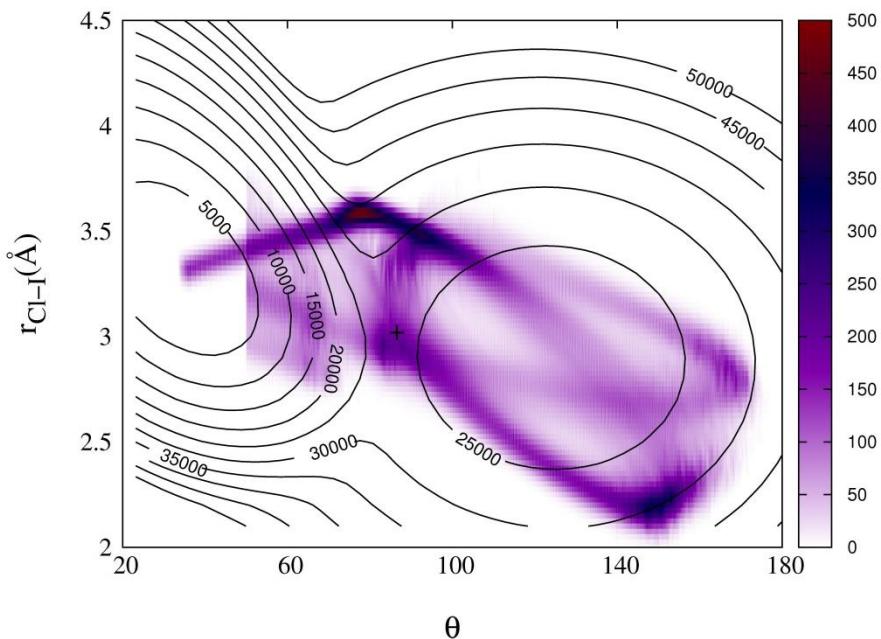
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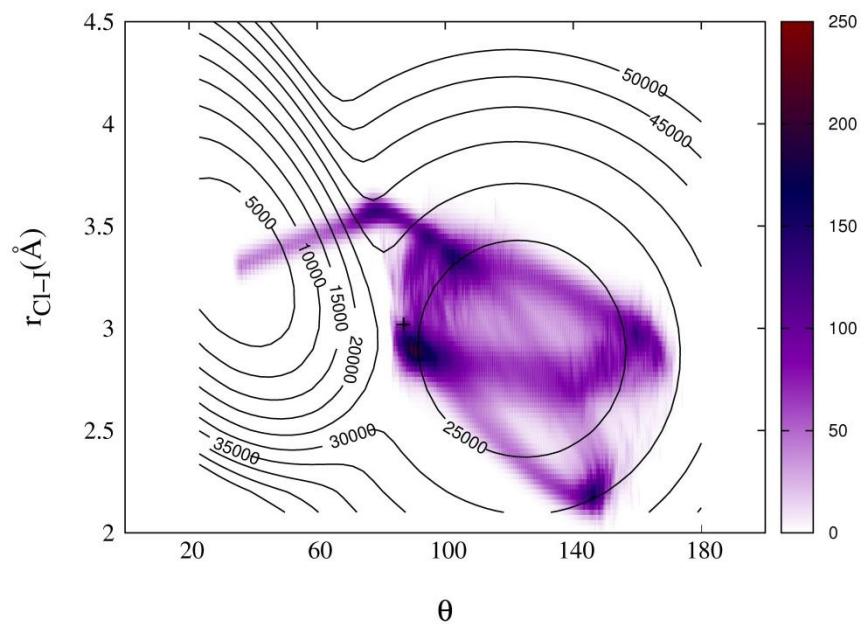
Non reactive trajectory  
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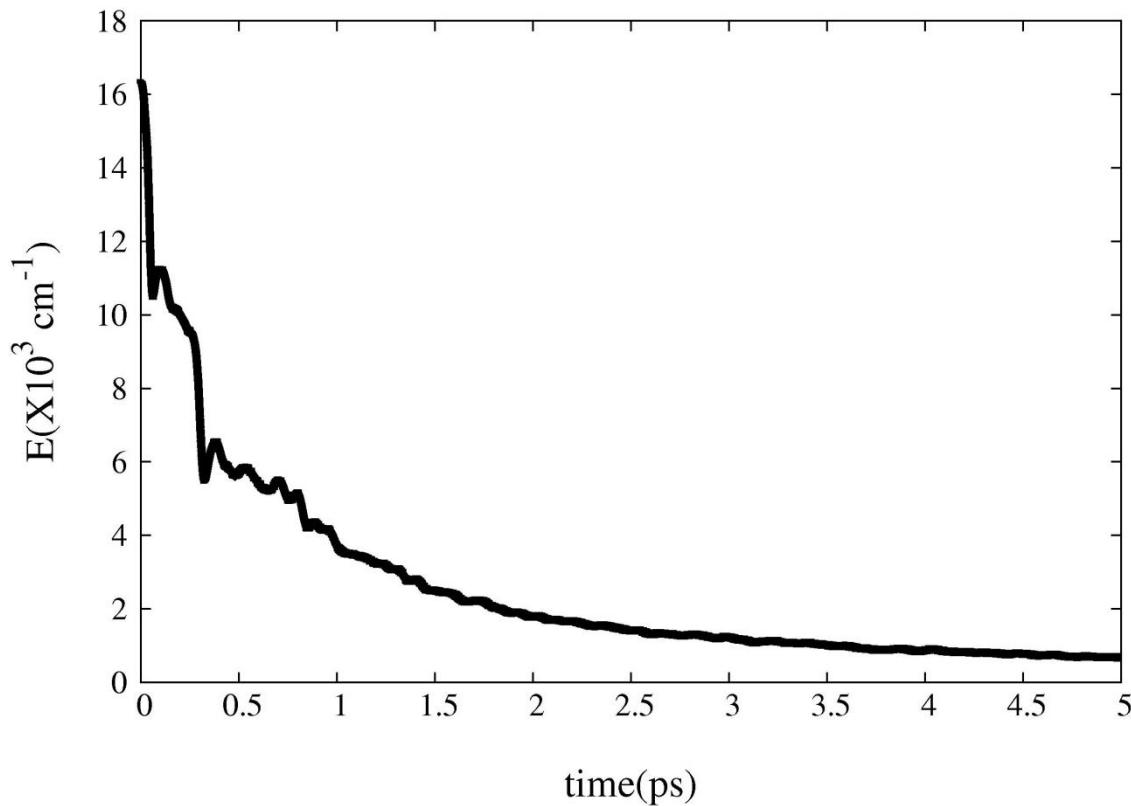


Non reactive trajectory  
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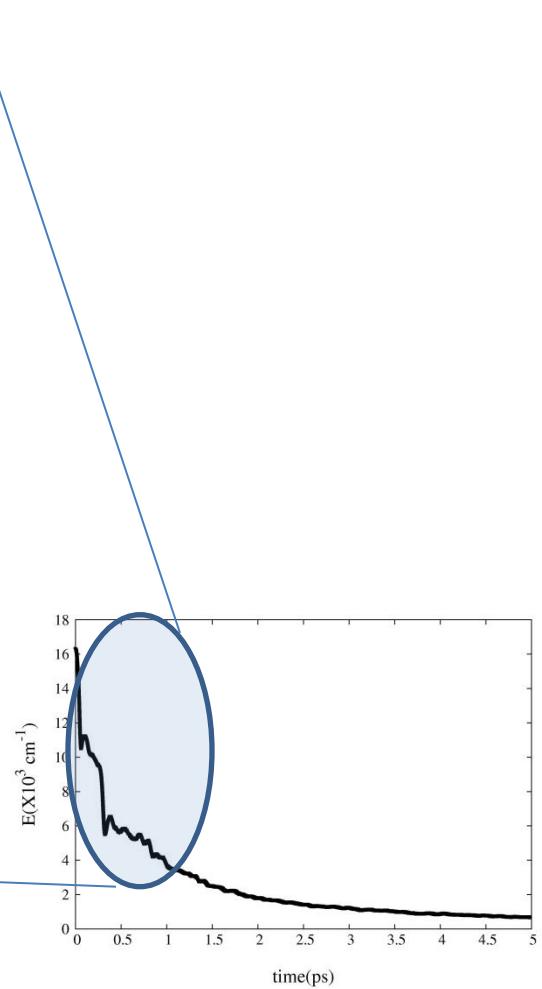
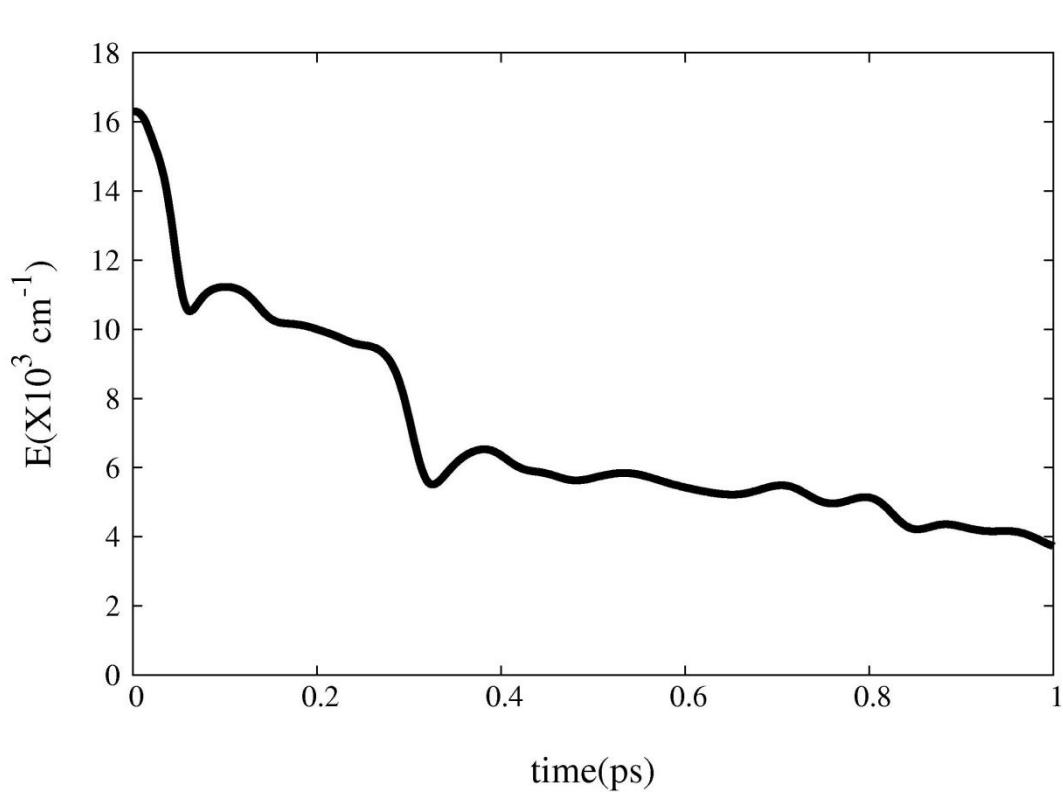


Reactive trajectory  
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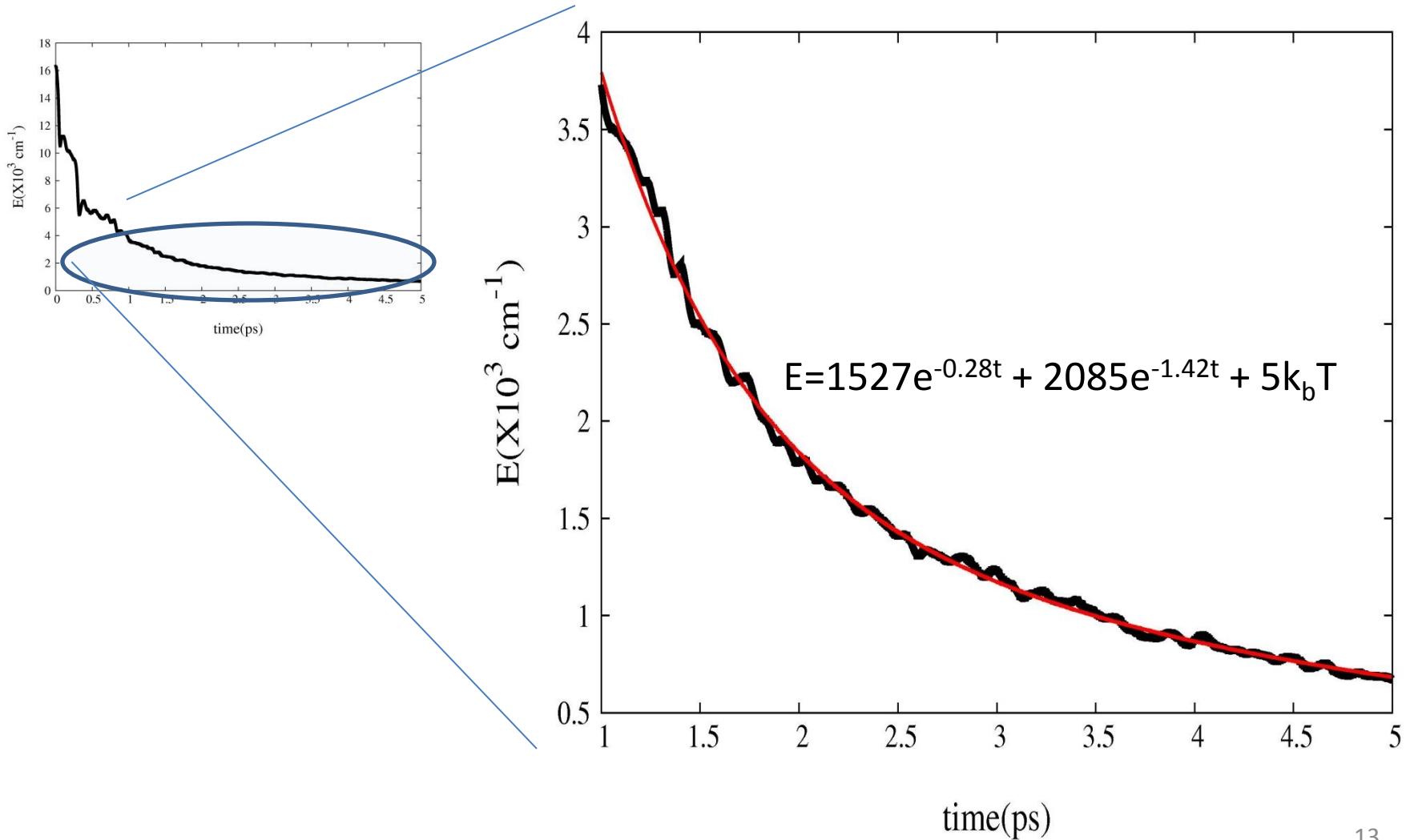
# Energy Decay



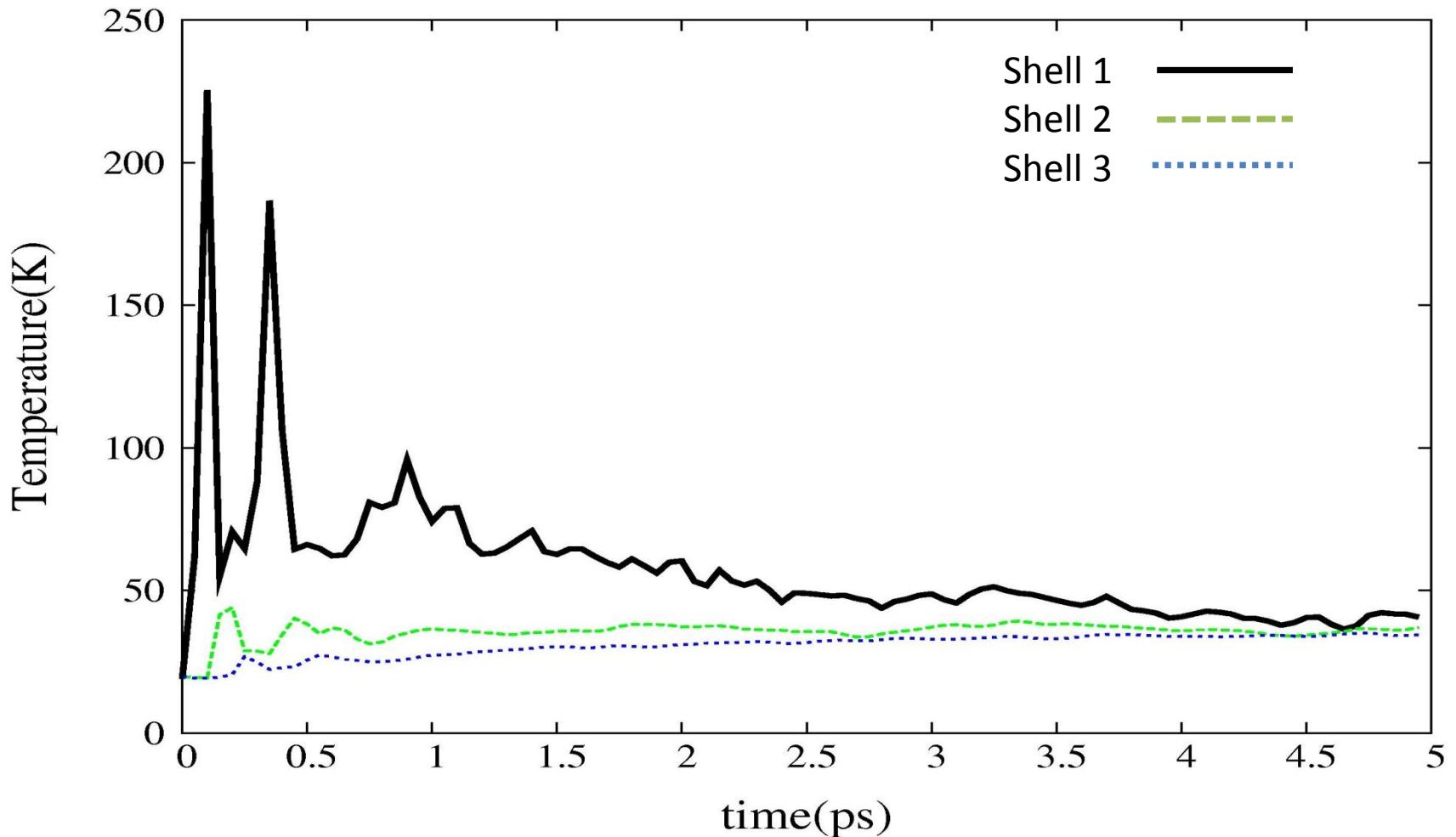
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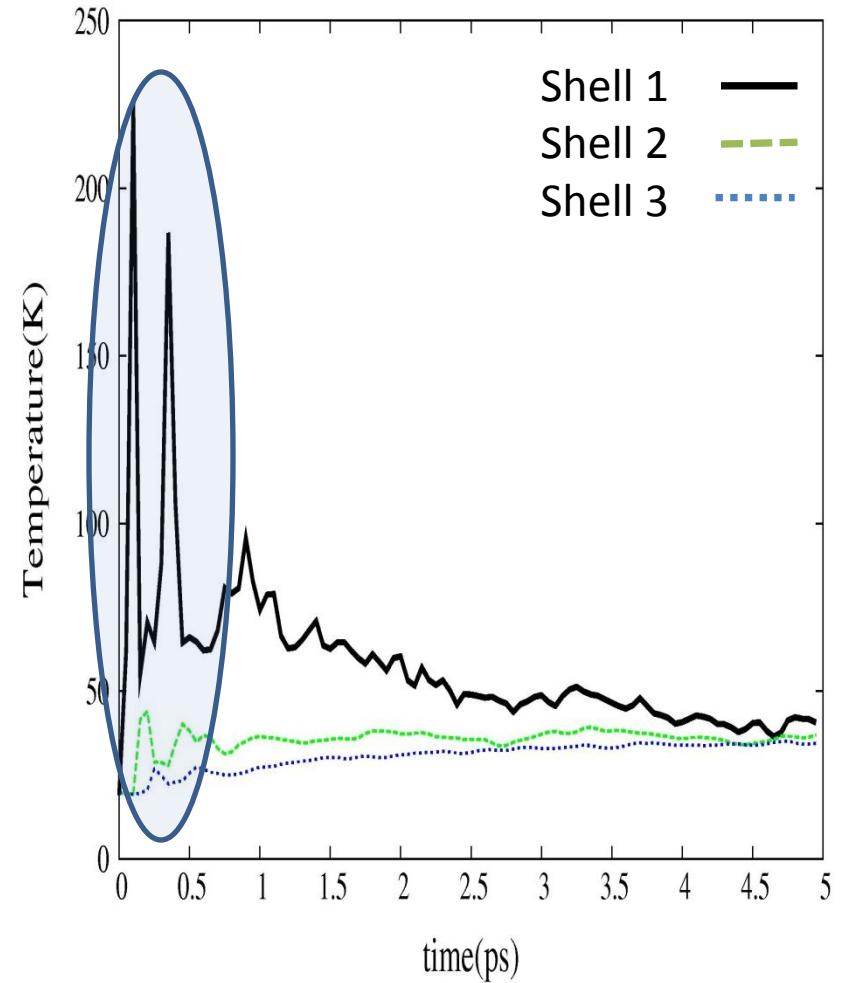
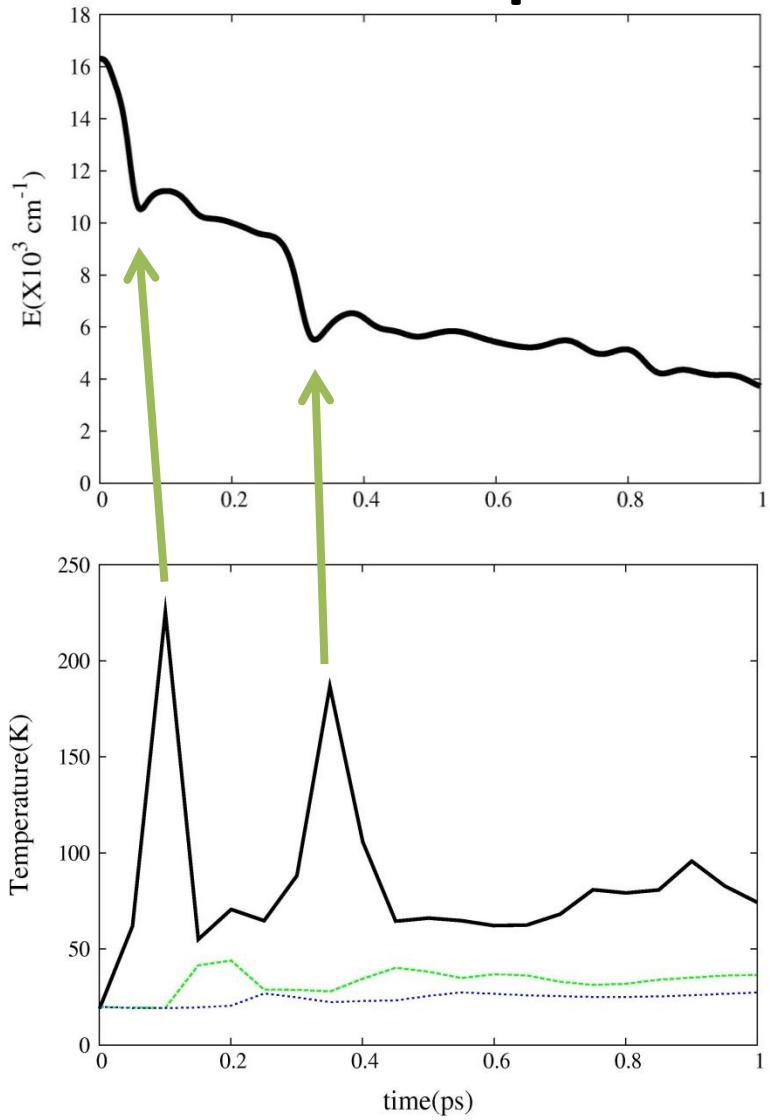
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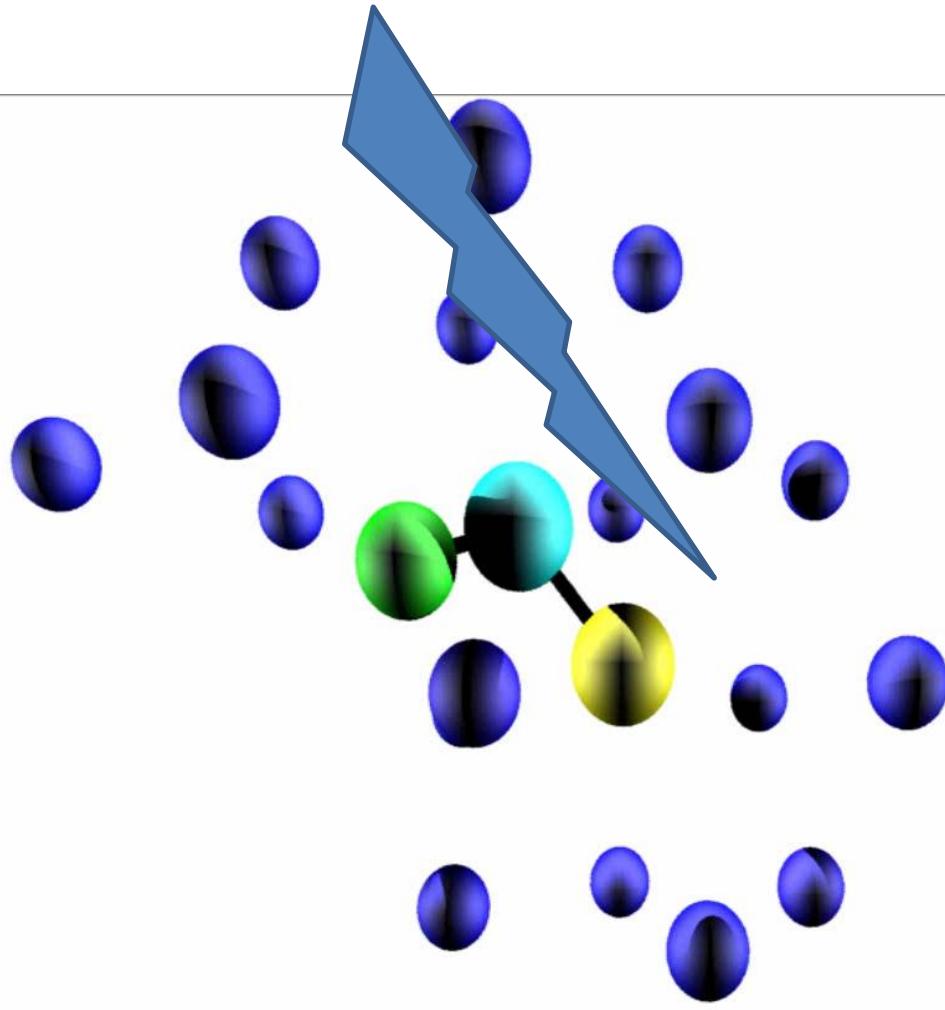


# Temperature of Bath



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CAST

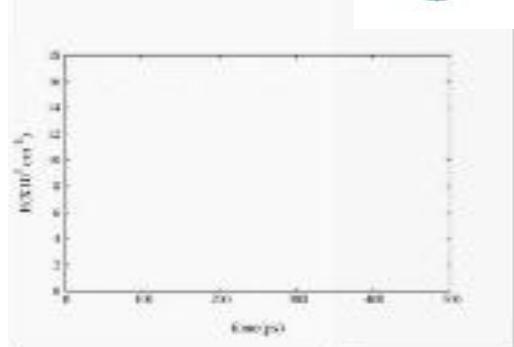
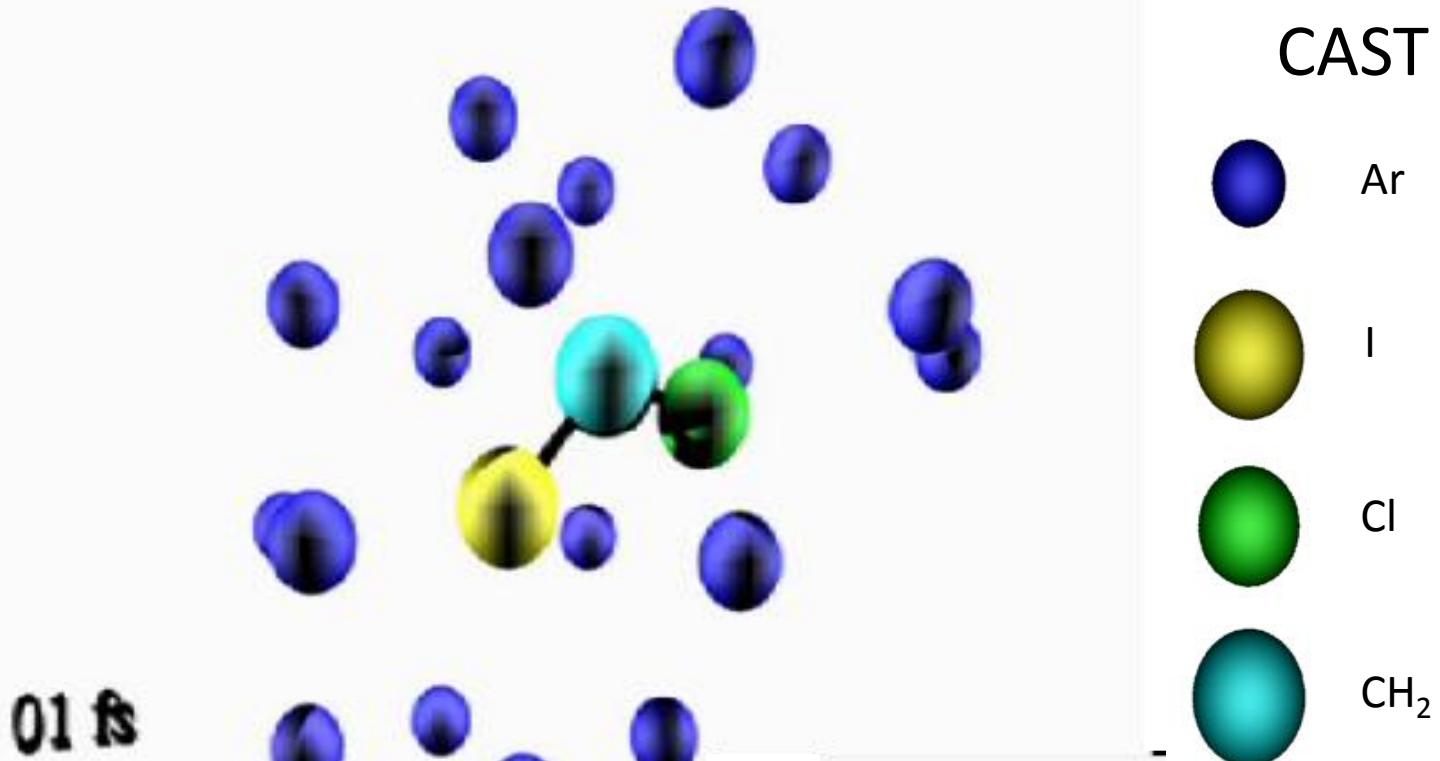
Ar

I

Cl

$\text{CH}_2$

CAST



# Effect of Initial Conditions

- ❖ Temperature of bath
- ❖ Initial energy deposited in the molecule
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T(K)	Slow Decay Rate (ps <sup>-1</sup> )	Fast Decay Rate (ps <sup>-1</sup> )
4	$0.267 \pm 0.005$	$1.31 \pm 0.03$
20	$0.28 \pm 0.03$	$1.4 \pm 0.1$
40	$0.34 \pm .02$	$1.7 \pm 0.2$
60	$0.28 \pm 0.03$	$1.5 \pm 0.3$

Initial Energy (cm <sup>-1</sup> )	Slow Decay Rate (ps <sup>-1</sup> )	Fast Decay Rate (ps <sup>-1</sup> )	% of Isomerizing Trajectories
37500	$0.28 \pm 0.03$	$1.4 \pm 0.1$	22.3%
42500	$0.33 \pm .02$	$1.81 \pm 0.02$	25.6%
47500	$0.39 \pm 0.03$	$1.9 \pm 0.1$	41.2%
52500	$0.40 \pm 0.01$	$2.19 \pm 0.1$	54.9%

T:300 K → 20 K

Decay rates :  $0.18 (\pm 0.01) \text{ ps}^{-1}$ , and  $1.5 (\pm 0.3) \text{ ps}^{-1}$

# Effect of Initial Conditions

- ❖ Temperature of bath
- ❖ Initial energy deposited in the molecule
- ❖ Temperature quench

**Rates are relatively constant**

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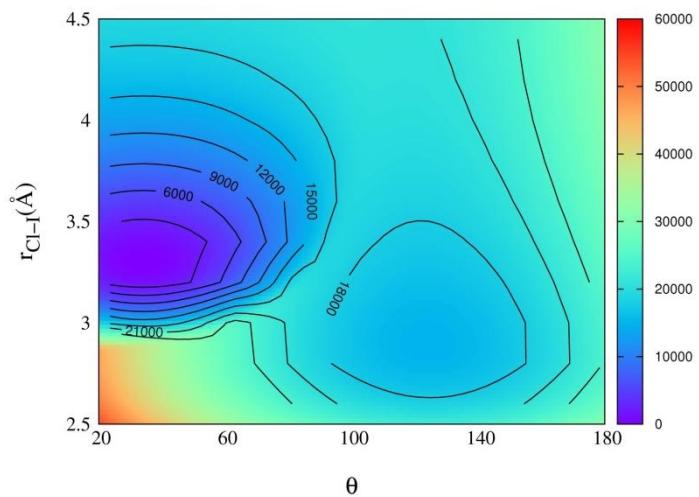
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# Comparision

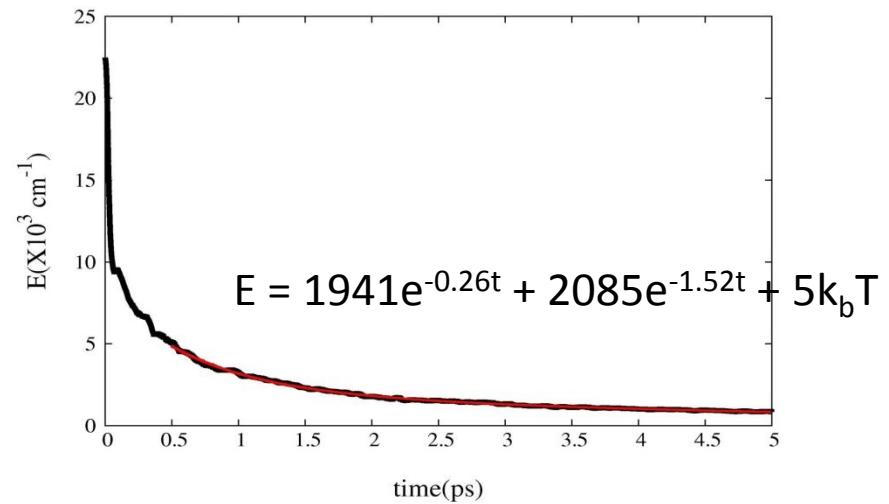
- Theoretical decay rate (20K, 37500 cm<sup>-1</sup>)  
0.28 ps<sup>-1</sup> & 1.4 ps<sup>-1</sup>
- Experimental decay rate  
0.07 ps<sup>-1</sup> & 0.45 ps<sup>-1</sup>

# Future Directions

- ❖ Surface which dissociates at large Cl-I distance required
- ❖ Excited surface for early time dynamics



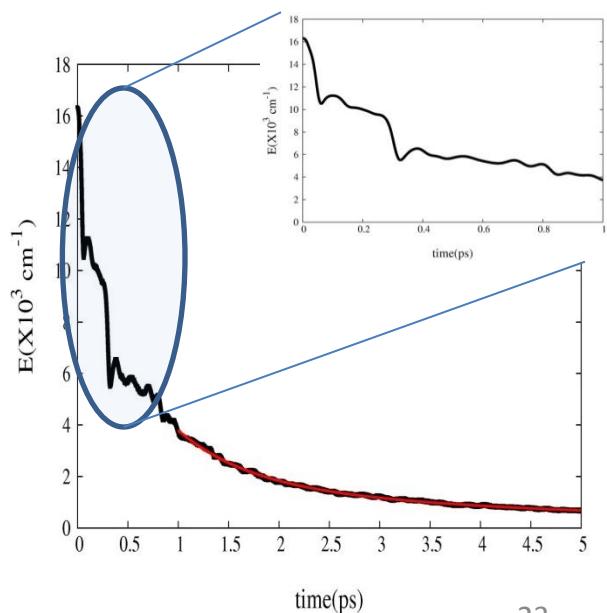
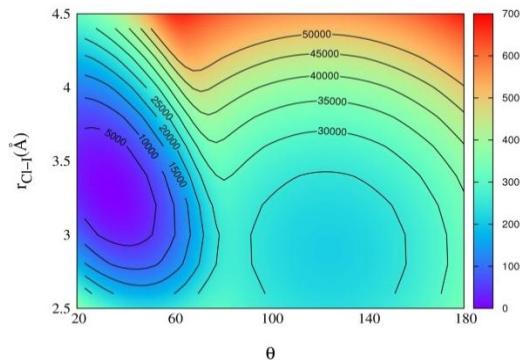
Preliminary Surface



Decay rates :  $0.22 (\pm 0.02) \text{ ps}^{-1}$  &  $1.47 (\pm 0.04) \text{ ps}^{-1}$   
(Earlier :  $0.28 (\pm 0.03) \text{ ps}^{-1}$  &  $1.4 (\pm 0.1) \text{ ps}^{-1}$ )

# Summary

- ❖ Calculated potential energy surface with respect to Cl-I distance and C-Cl-I angle
- ❖ Observed multi-step energy decay:
  - ❖ Binary collision with argon atoms, losing  $12000 \text{ cm}^{-1}$  in first 1 ps
  - ❖ Vibrational energy relaxation with decay rates of  $\sim 0.28 \text{ ps}^{-1}$  and  $1.42 \text{ ps}^{-1}$



# Acknowledgments

- Ned Sibert
- Sibert Group
- Fleming Crim and T.J. Preston
- NSF for funding



Thank You

