

**THE BOWERS GROUP**

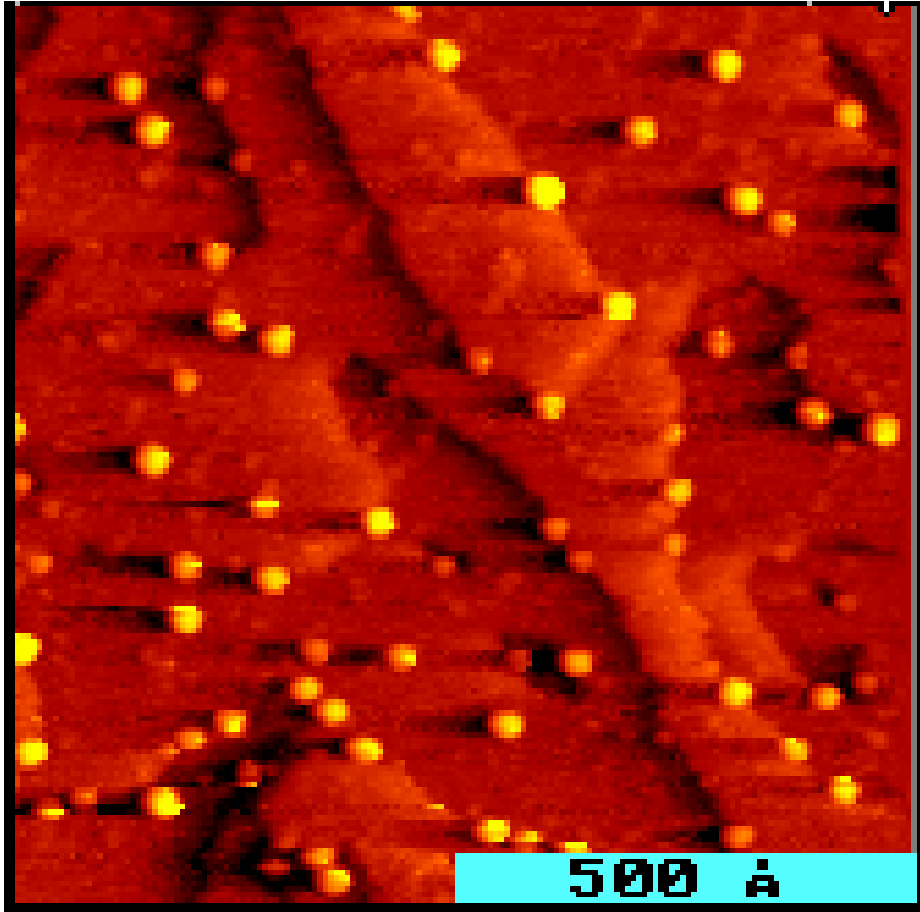
DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY AT UCSB



# **Binding Interactions and Dissociation Reactions of Mono and Diatomic Silver Cations with Small Alkenes**

Manuel J. Manard, Paul R. Kemper, Catherine J. Carpenter,  
and Michael T. Bowers

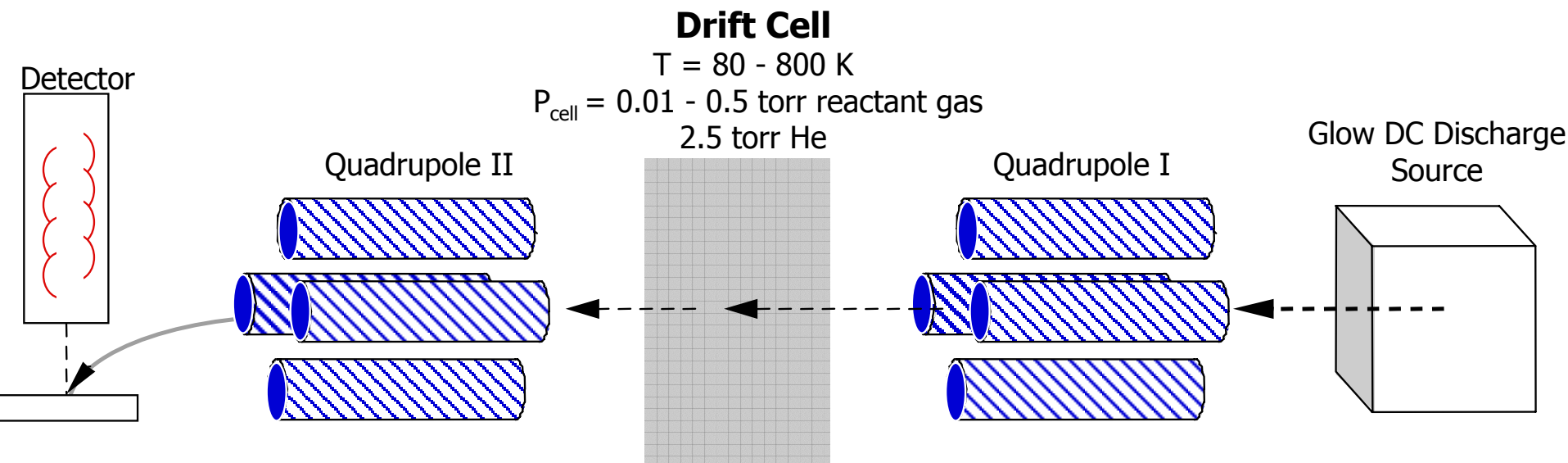
# Motivations



- A new instrument has been developed to study size-selected metal cluster deposited on metal-oxide surfaces at UCSB.
- Interactions of metal clusters on surfaces with ligands such as  $H_2$ ,  $O_2$ , and small alkenes are of particular interest due to the catalytic activity of the metal clusters.
- Gas Phase investigation into the binding interactions of these cluster provides information that is essential for the elucidation of the origin of their catalytic properties.

Size-Selected Ag clusters on (110)  $TiO_2$

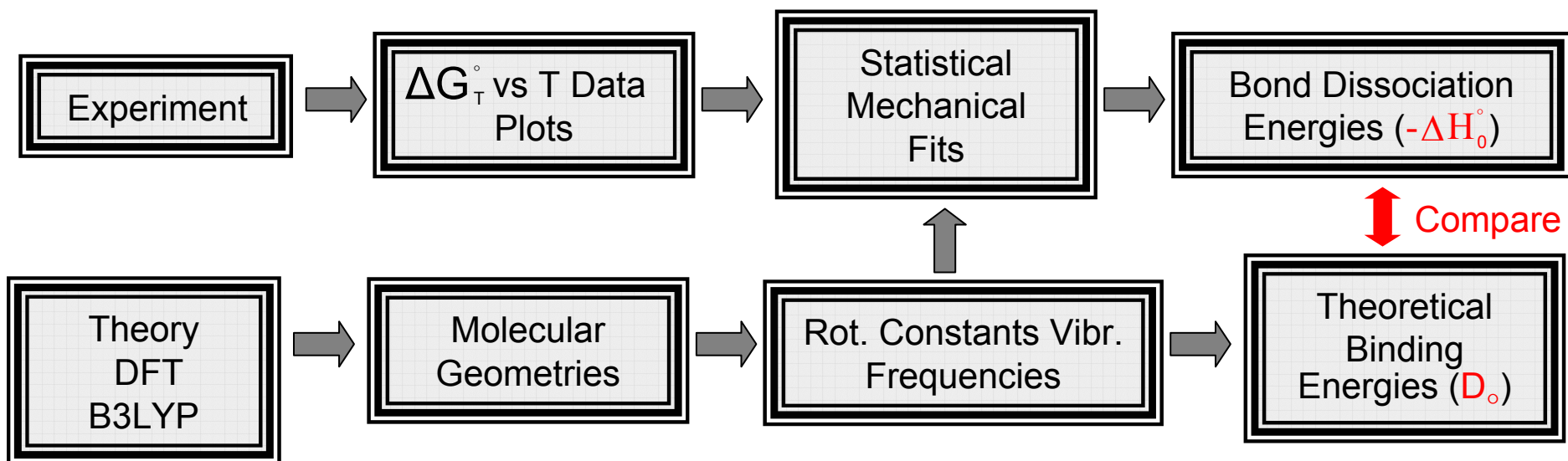
# The Instrument

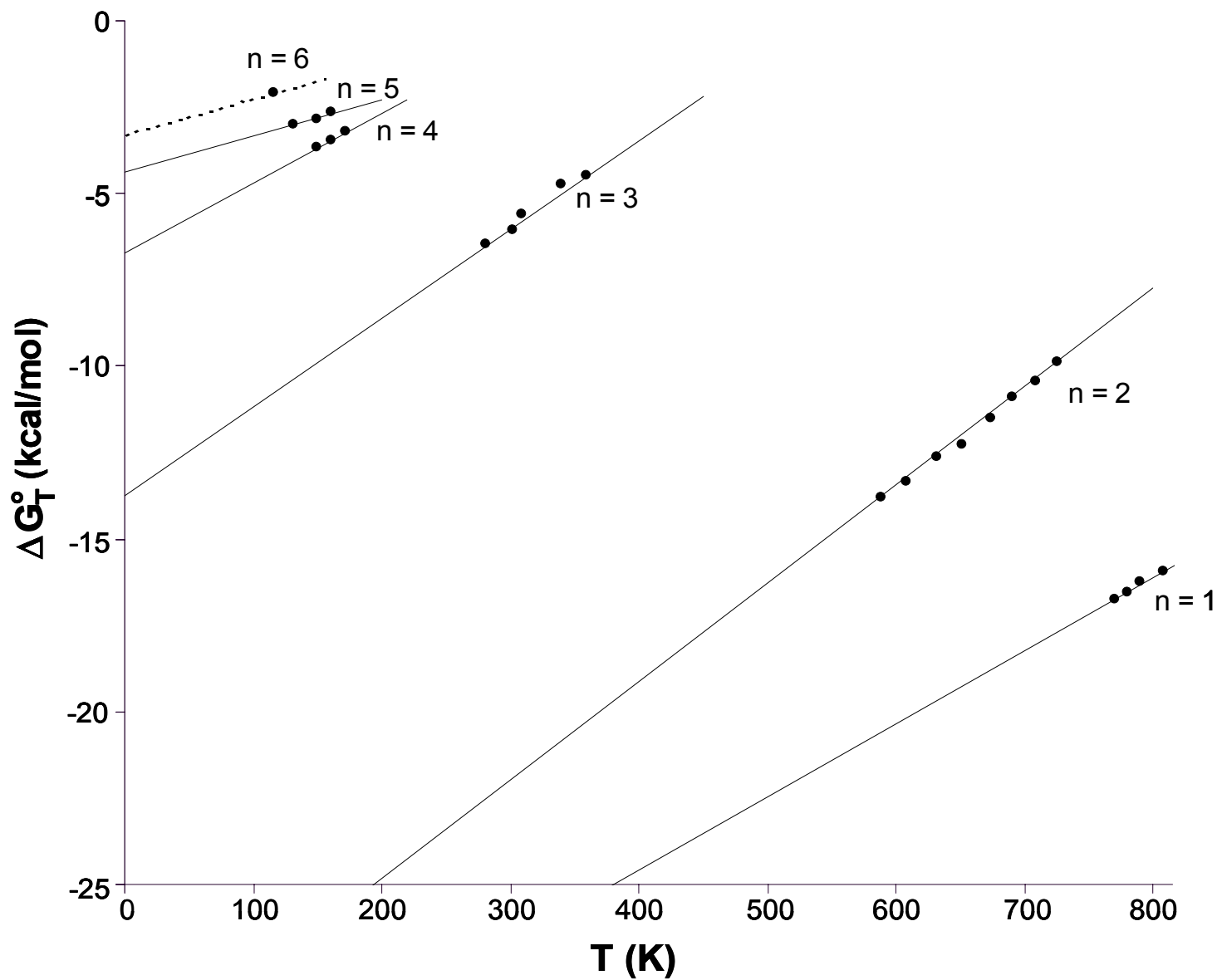
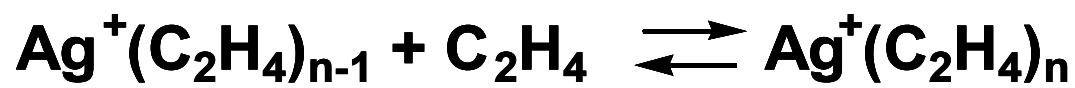


# Binding Interactions

$$K_P^\circ = \frac{Ag^+(L)_n}{Ag^+(L)_{n-1}} * \frac{760}{P_L} \quad \Delta G_T^\circ = -RT \ln[K_P^\circ] \quad \Delta G_T^\circ = \Delta H_T^\circ - T \Delta S_T^\circ$$

The equilibrium constants can then be used to calculate the standard Gibbs free energy of the reaction, and the values obtained for  $\Delta G_T^\circ$  plotted versus the temperature, to obtain  $\Delta H_T^\circ$  and  $\Delta S_T^\circ$ .



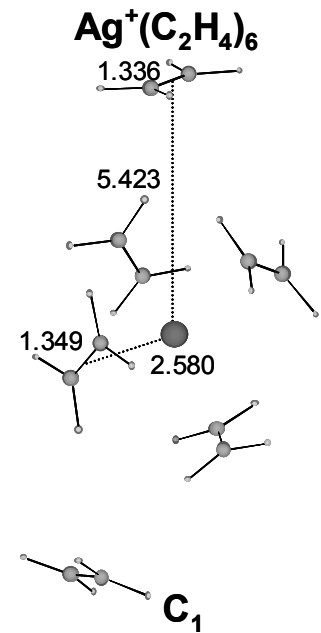
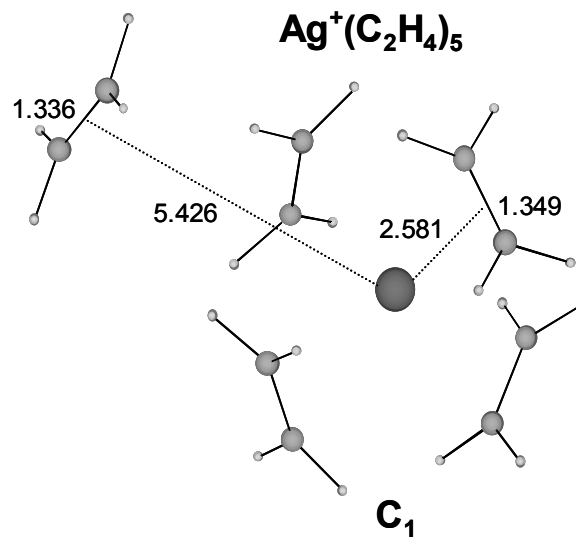
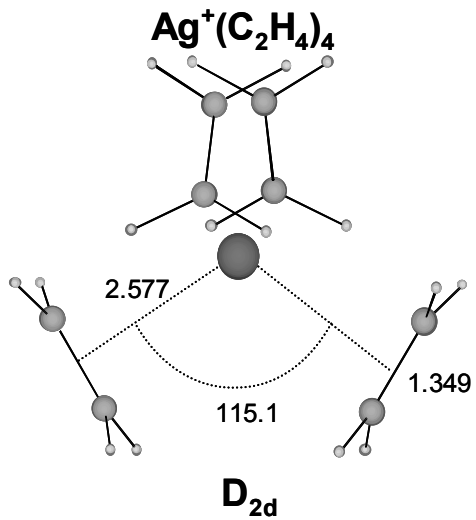
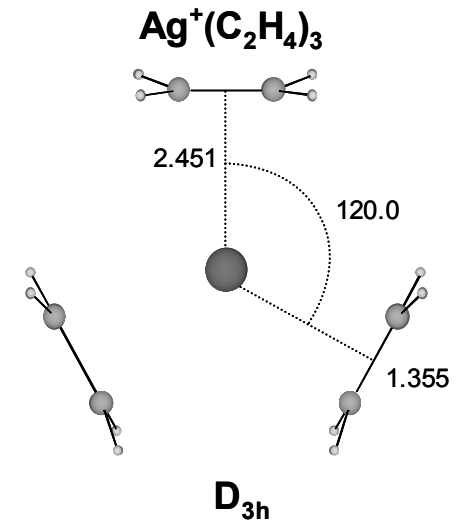
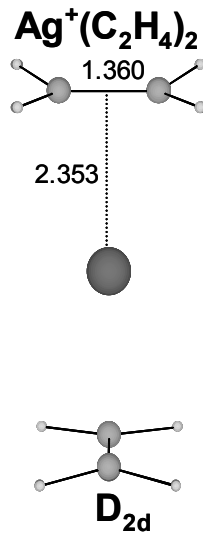
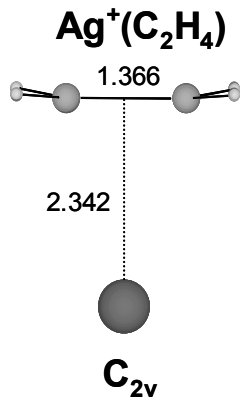


# Data Summary for $\text{Ag}^+(\text{C}_2\text{H}_4)_{n-1} + \text{C}_2\text{H}_4 \rightleftharpoons \text{Ag}^+(\text{C}_2\text{H}_4)_n$

n	Experiment			Theory		
	$-\Delta H_T^\circ{}^a$	$-\Delta S_T^\circ{}^b$	$-\Delta H_0^\circ{}^a$	$T^d$	$D_e{}^a$	$D_o{}^a$
1	$32.9 \pm 0.7$	$21.0 \pm 2$	$32.6 \pm 1.0$	770 - 800	32.53	<b>31.24</b>
2	$30.7 \pm 0.5$	$28.6 \pm 1$	$30.5 \pm 0.8$	590 - 725	27.59	<b>26.10</b>
3	$14.0 \pm 0.6$	$26.7 \pm 2$	$13.6 \pm 0.8$	280 - 360	10.42	<b>9.10</b>
4	$6.8 \pm 0.4$	$21.0 \pm 1$	$6.6 \pm 0.5$	150 - 170	3.61	<b>2.85</b>
5	$4.5 \pm 0.5$	$11.3 \pm 3$	$4.4 \pm 0.6$	130 - 160		
6			$\sim 3.3^e$	115		

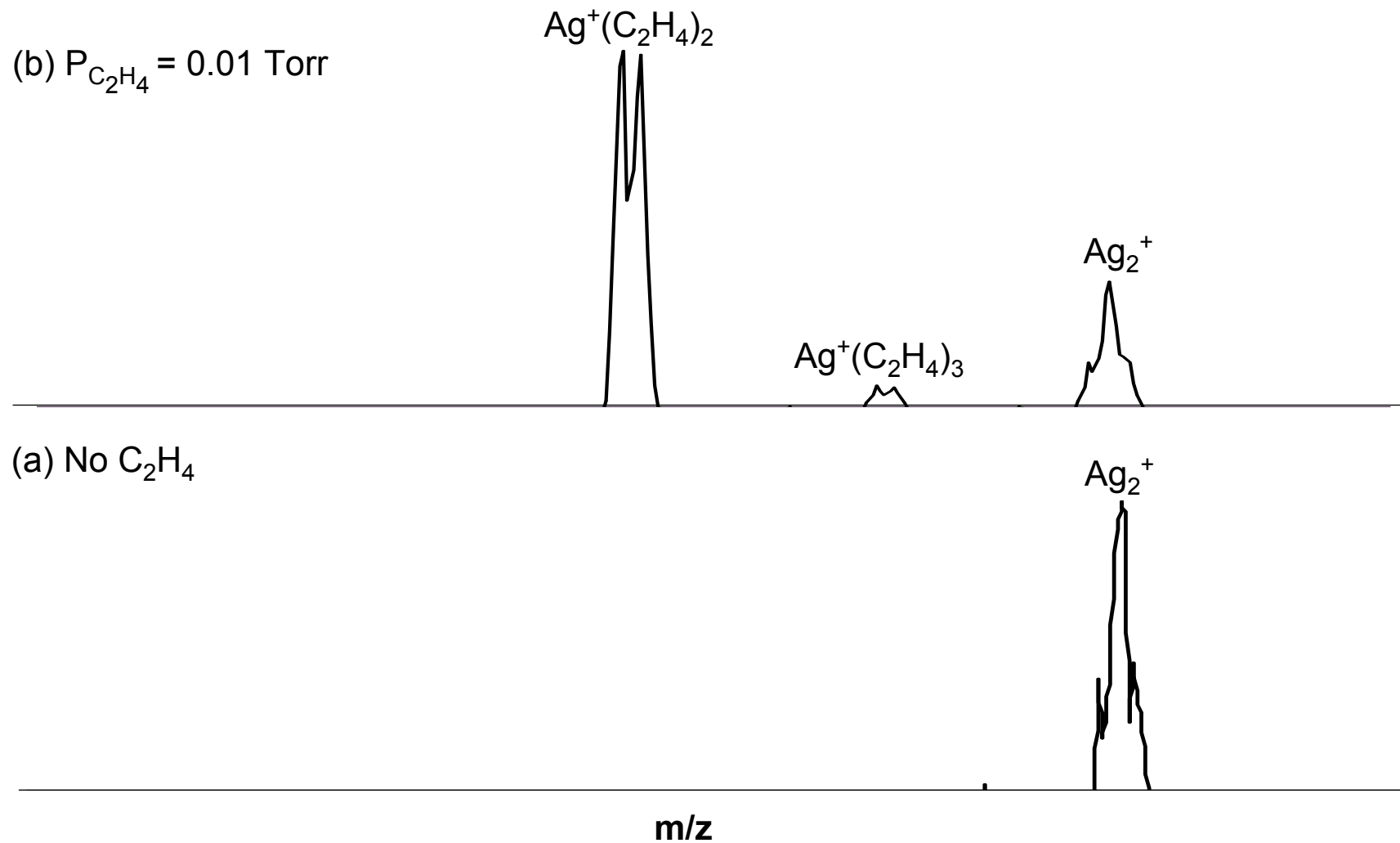
<sup>a</sup> In units of kcal/mol. <sup>b</sup> In units of cal/mol K. <sup>c</sup> Value from fitting data with theoretical vibrational frequencies, rotational constants and geometries, in units of kcal/mol. <sup>d</sup> Temperature range over which equilibrium data was acquired, in Kelvin. <sup>e</sup> Estimate, fit by correspondence with fifth cluster.

# Ag<sup>+</sup>(C<sub>2</sub>H<sub>4</sub>)<sub>n</sub> Clusters (DFT)



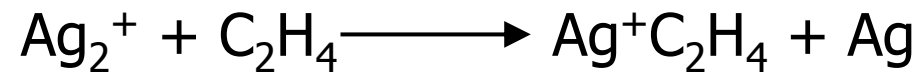
# Dissociation Reactions

Spectra acquired at 300 K

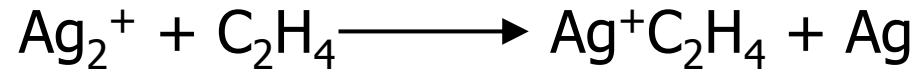




# Dissociation Reactions



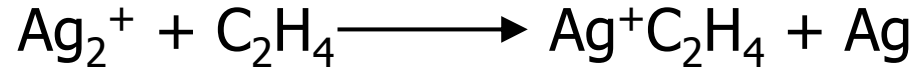
# Dissociation Reactions



Pseudo first-order, bimolecular reaction

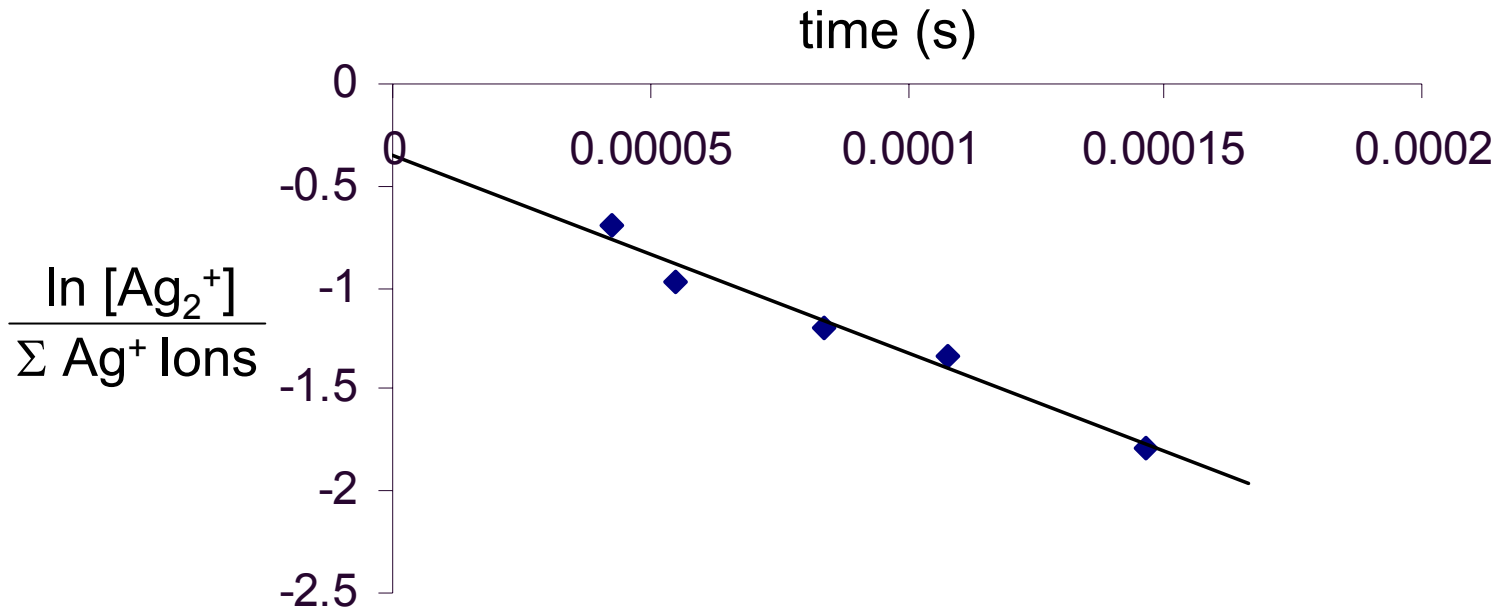
$$\text{Rate Law} \longrightarrow \ln[A(t)] = \ln[A_0(t)] - k_d t$$

# Dissociation Reactions



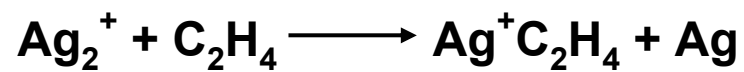
Pseudo first-order, bimolecular reaction

$$\text{Rate Law} \longrightarrow \ln[A(t)] = \ln[A_0(t)] - k_d t$$



$$k_d = \frac{\text{Slope}}{\rho_n(P, T)}$$

# Dissociation Reactions



$\text{Ag}_2^+$



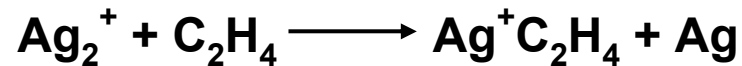
$4d^{20} \sigma(5s)^1$

$\text{C}_2\text{H}_4$



$\pi(2p_x)^2$

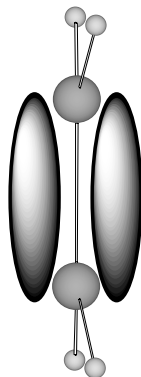
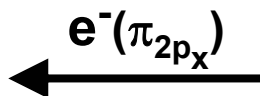
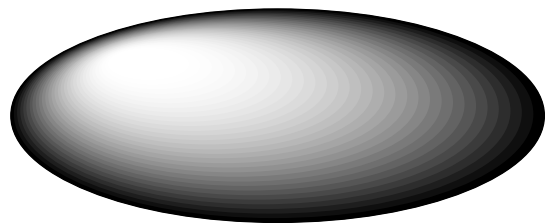
# Dissociation Reactions



$\text{Ag}_2^+$

+

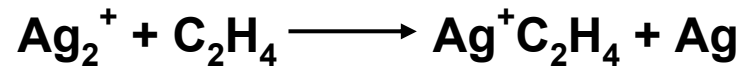
$\text{C}_2\text{H}_4$



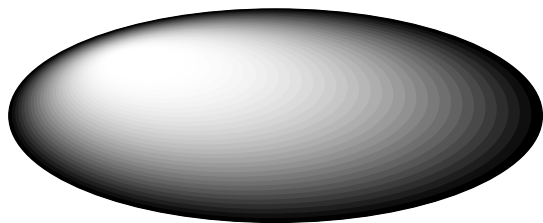
$4d^{20} \sigma(5s)^1$

$\pi(2p_x)^2$

# Dissociation Reactions



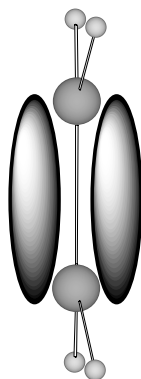
$\text{Ag}_2^+$



$4d^{20} \sigma(5s)^1$

+

$\text{C}_2\text{H}_4$



$\pi(2p_x)^2$

→

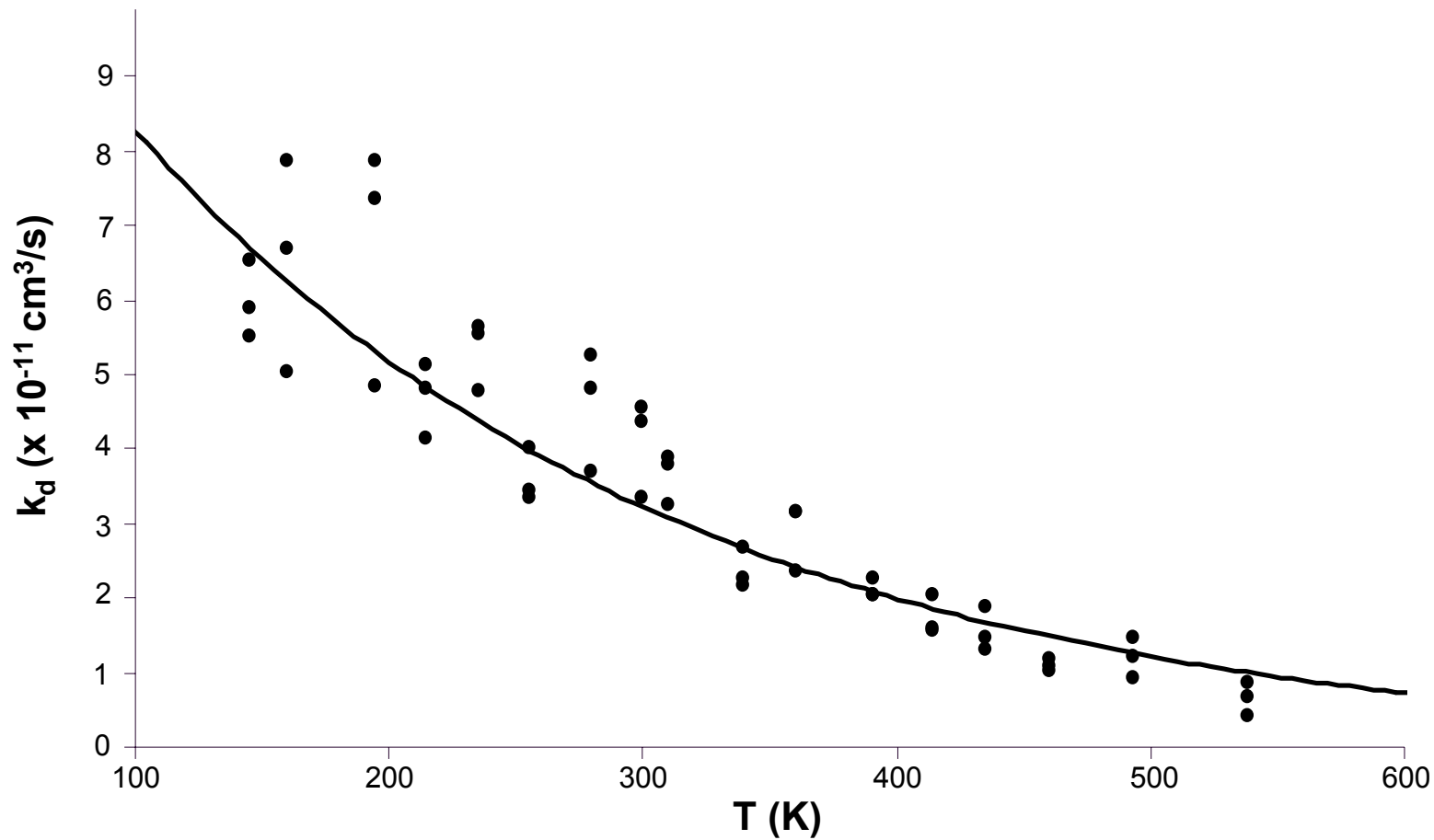
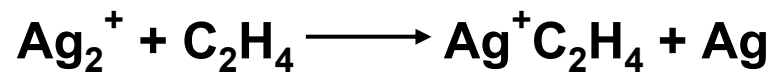
$\text{Ag} + \text{Ag}^+(\text{C}_2\text{H}_4)$



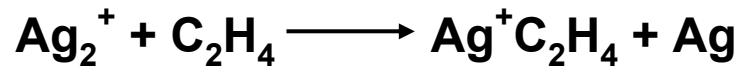
+



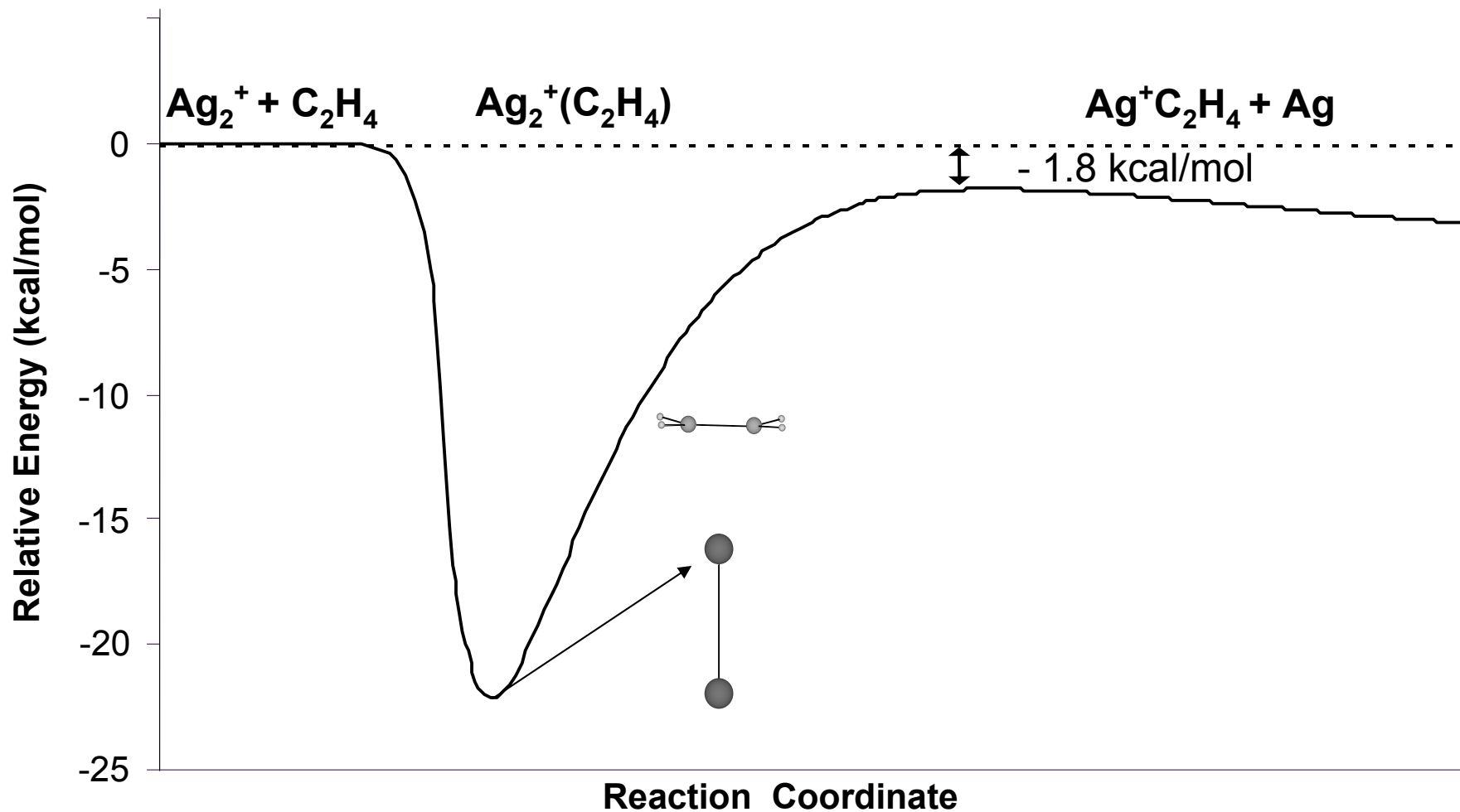
# Dissociation Reactions



# Dissociation Reactions

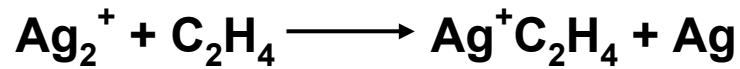


DFT Potential Energy Surface

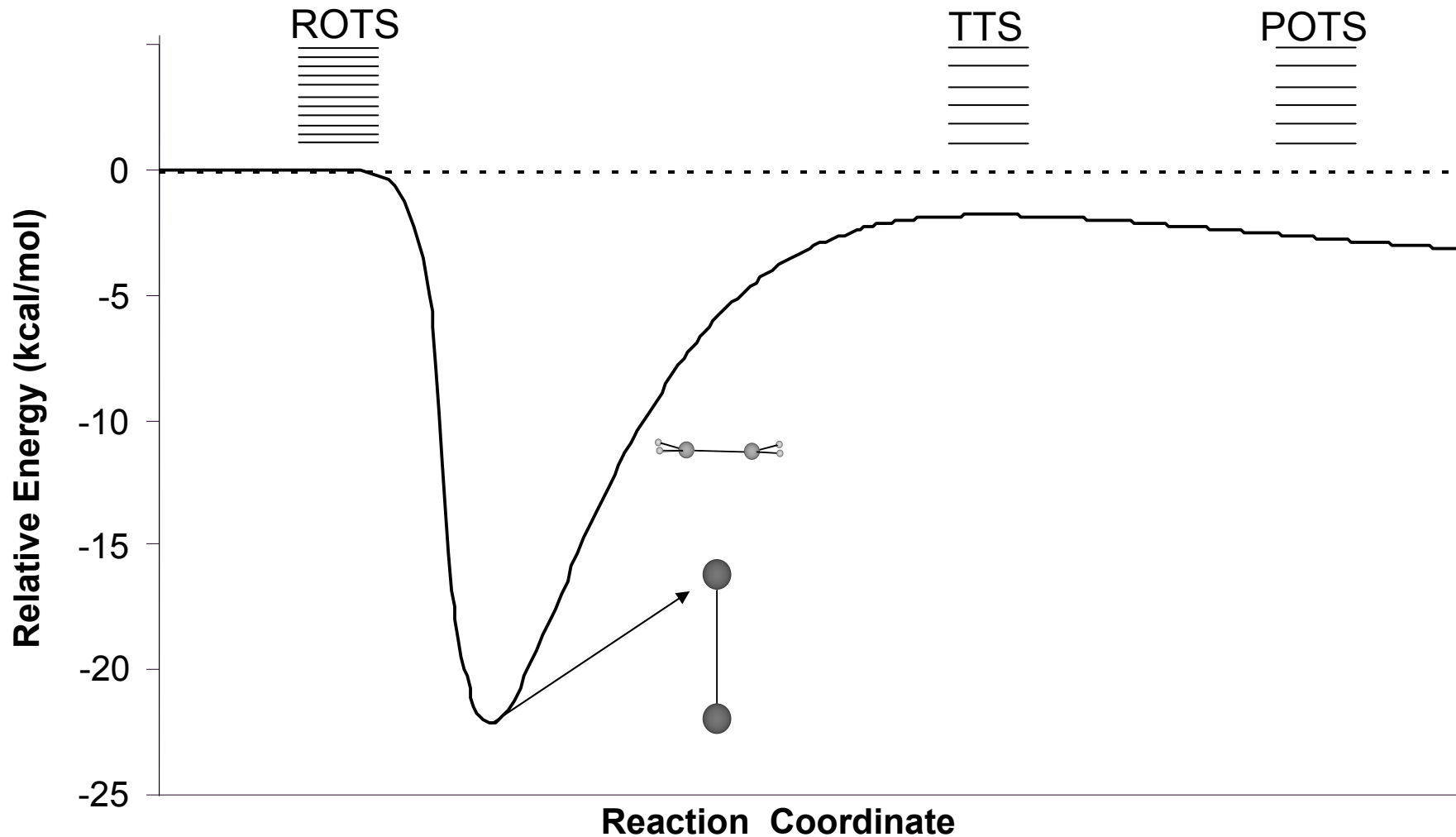




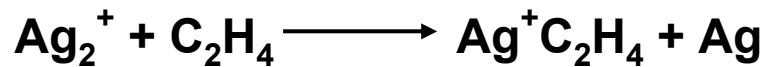
# Dissociation Reactions



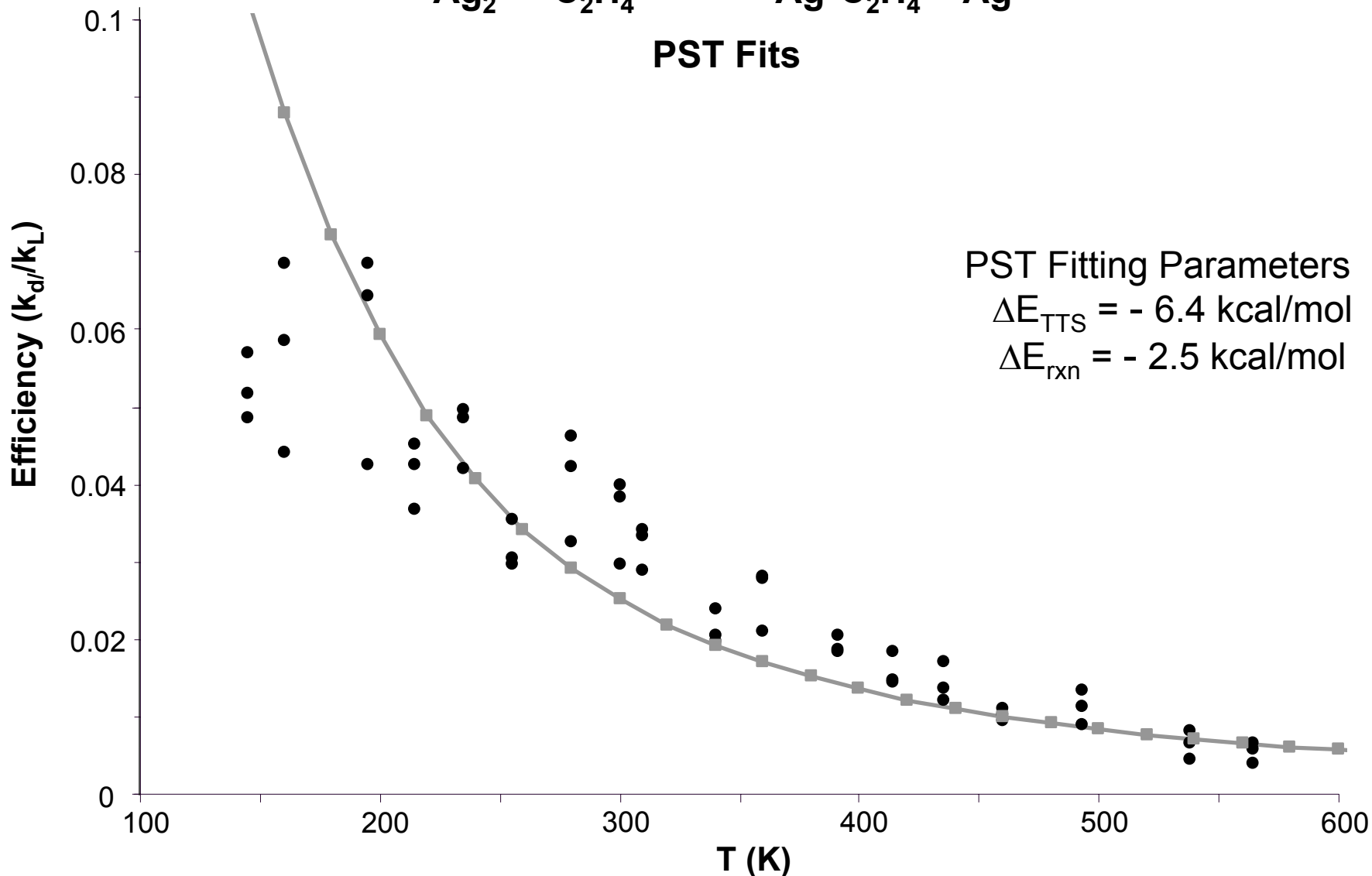
Phase Space Theory (PST)



# Dissociation Reactions

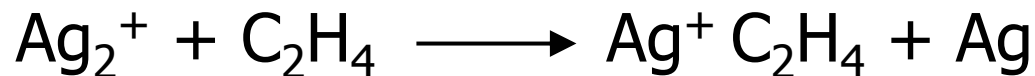


PST Fits



# Conclusions

- Bond dissociation energies and association entropies were determined for  $\text{Ag}^+(\text{C}_2\text{H}_4)_{1-6}$ .
- Density functional theory calculations (B3LYP) were performed to obtain theoretical BDE's, geometries, rotational constants, and vibrational frequencies.
- The primary bonding interaction of the clusters was determined.
- Rate Constants for the dissociation reaction ...



were measured and were found to be in good agreement with theoretical efficiencies calculated using Phase Space Theory.