

## Supporting Information

### **Pronounced Changes in Atomistic Mechanisms for the $\text{Cl}^- + \text{CH}_3\text{I}$ $\text{S}_{\text{N}}2$ Reaction with Increasing Collision Energy**

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**Table 1.** Numbers of Trajectories for Different Indirect Mechanisms<sup>a</sup>

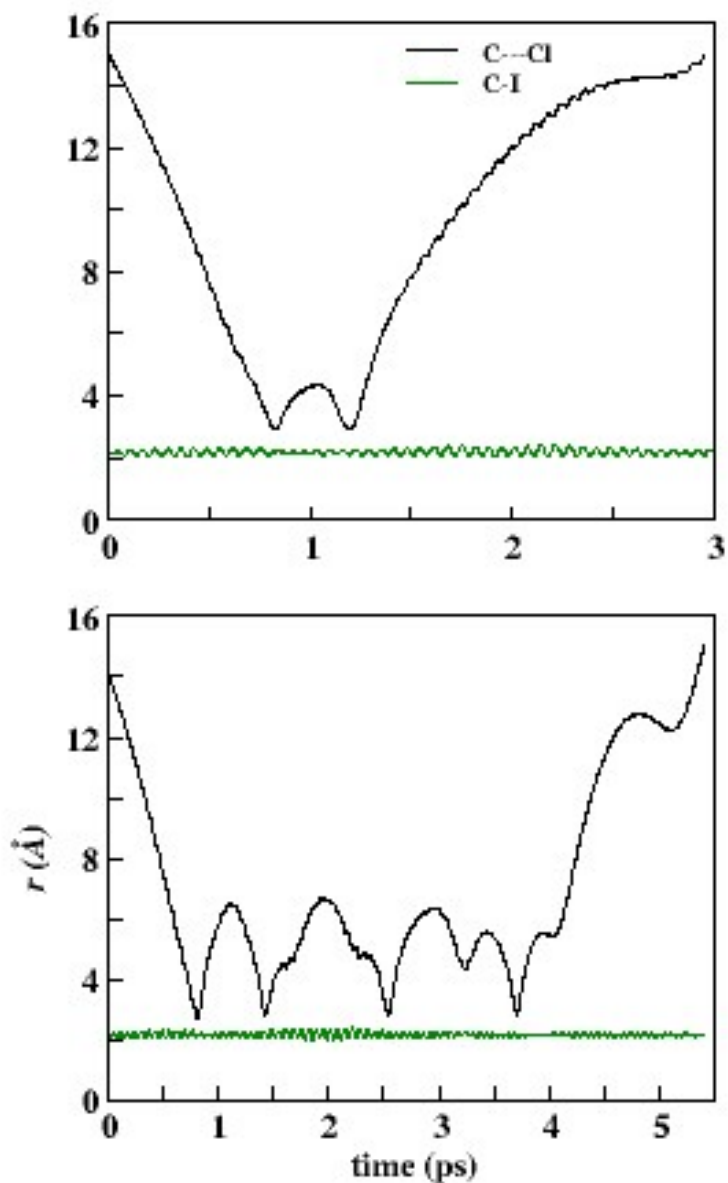
Erel	A	B	A+B	Ra	br	A+B+br	Ra+A	Ra+B	Ra+A+B	Ra+A+br	Ra+B+br	Ra+A+B+br	Ra+br	Ra+B+Ra'
<b>b = 0 Å</b>														
0.15	7	1	6	1, 2			11, 15		2, 3	- , 2				
0.20	5			2, 4	1	1	1, 4	1, -	- , 1					2
0.25	3			3, 5		2	6, 3		- , 5				1, -	
0.30	2		1	3, 3	1		1, 1		1, 1	- , 1		1, -		
0.35				2, -			1, 3							1
0.40	3		1	- , 4			- , 1	- , 1						1
<b>b = 1 Å</b>														
0.15	11		7	1, 6	1	1	3, 15		2, 2	1, -	- , 1	- , 1		
0.20	5			2, 4		1	1, 6		- , 2	1, -			- , 1	
0.25	1		1	3, 2			2, 5		1, 1	1, 2				
0.30	4	2		1, -			5, 2						- , 1	
0.35	4			1, -			3, 6			- , 1				
0.40			1	2, 1			- , 2	1, -					- , 1	
<b>b = 2 Å</b>														
0.25	8	1	5	2, 1	1		2, 7		1, -					
0.30	5		5	- , 1		1	1, 1		- , 1					
0.35	3		3	- , 1			2, -							

a. Mechanisms are defined in Table 1 of the manuscript. Total numbers of trajectories are given in Table 2 of the manuscript.

b. Collision energy in eV.

c. The first number is for Ra(1) and the second for Ra(n)

d. Ra' is roundabout motion of CH<sub>3</sub> moiety around the I<sup>-</sup> after formation of the post-reaction complex.



**Figure 1:** Sample representation of two typical non-reactive trajectories with complexation.

Top panel: A short lived pre-reaction complex formation followed by reverse reaction.

Bottom panel: A comparatively long-lived pre-reaction complex formation with multiple rotation of -CH<sub>3</sub> moiety around I, followed by reaction.

[Animations of these types of non-reactive trajectories are provided on [hase-group.ttu.edu/group/animations/ch3i.html](http://hase-group.ttu.edu/group/animations/ch3i.html)]