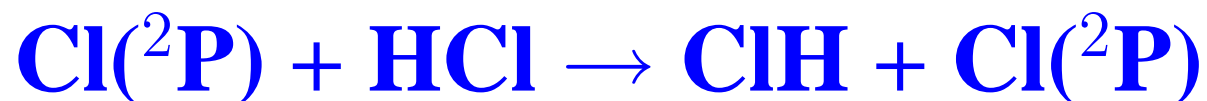


# Initiating the hydrogen exchange reaction



by vibrational excitation of the molecule

Gé W. M. Vissers and Anne B. McCoy



# Cl + HCl

- Only three atoms, yet still computationally challenging due to open-shell character
- Prototype system for reactions involving open-shell species
- Potential energy surfaces show Van der Waals well in reaction channels, which has been shown to have a large effect on reaction rates in similar systems [1]

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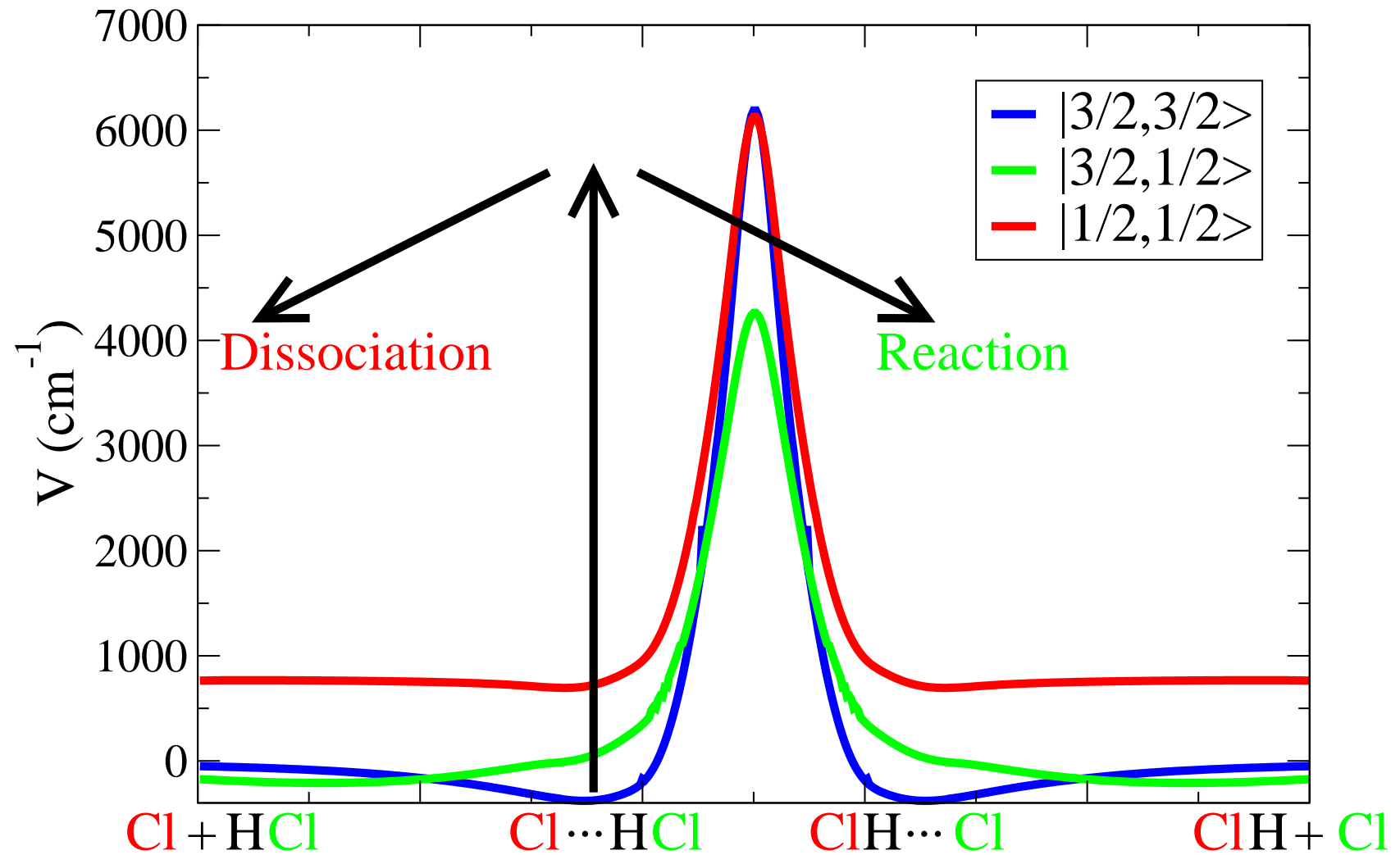
Can we initiate the hydrogen exchange reaction by vibrationally exciting the HCl molecule?

If yes, what are the spectroscopic signatures of this reaction?

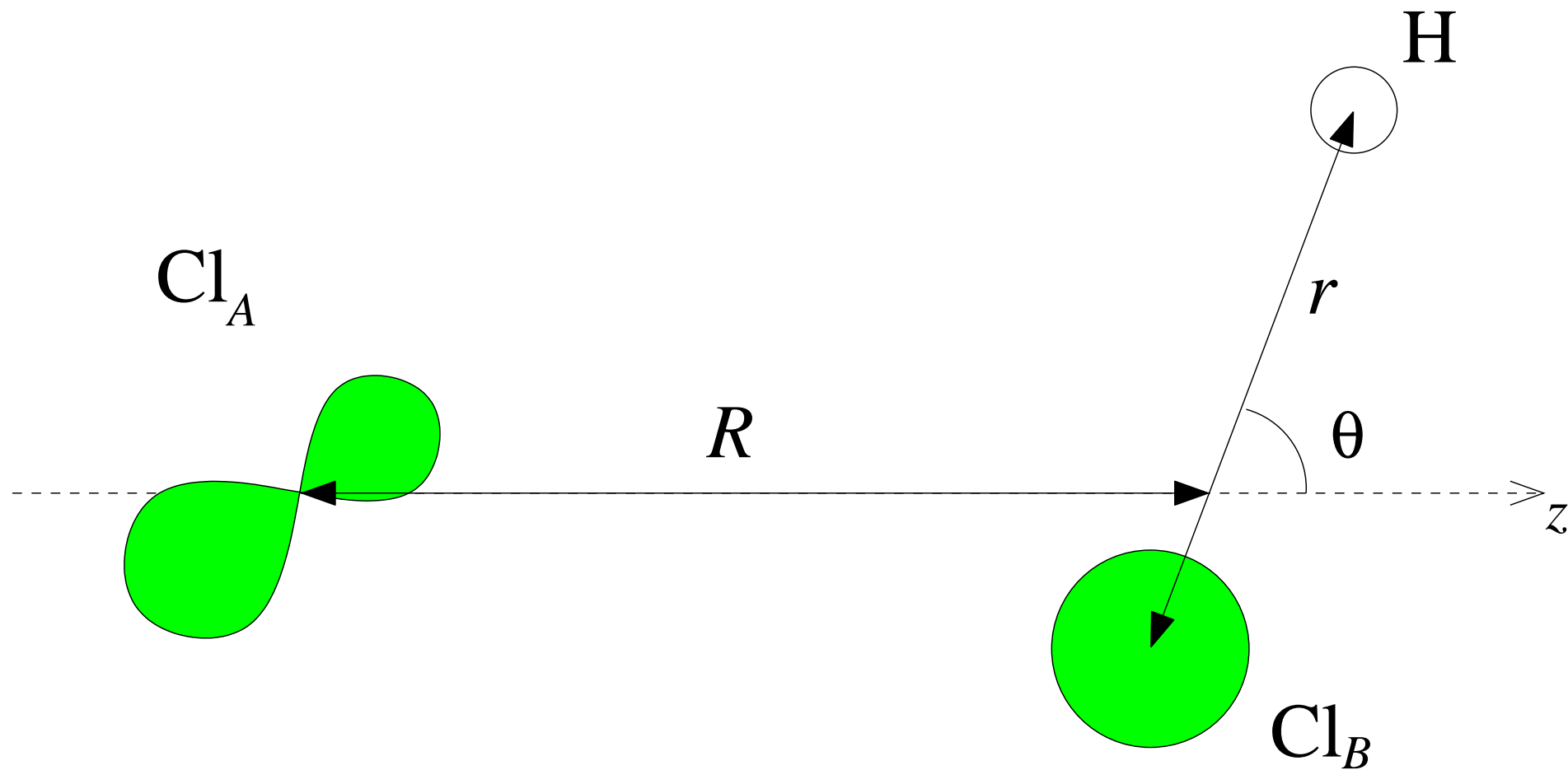
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1: D. Skouteris *et al.*, Science 286, 1713 (1999)

# The process



# The system



# Calculations

- Potential energy surface taken from literature [1,2]
- Initial state is lowest state with  $v_{\text{HCl}} = 2$  or 1
- Propagated wave packet up to 4.8 ns
- Started with different isotopologues:  $^{35}\text{Cl-H}^{35}\text{Cl}$ ,  $^{37}\text{Cl-H}^{35}\text{Cl}$ , and  $^{35}\text{Cl-H}^{37}\text{Cl}$
- Calculations done for  $J = 1/2$ , and both  $e$  and  $f$  parity

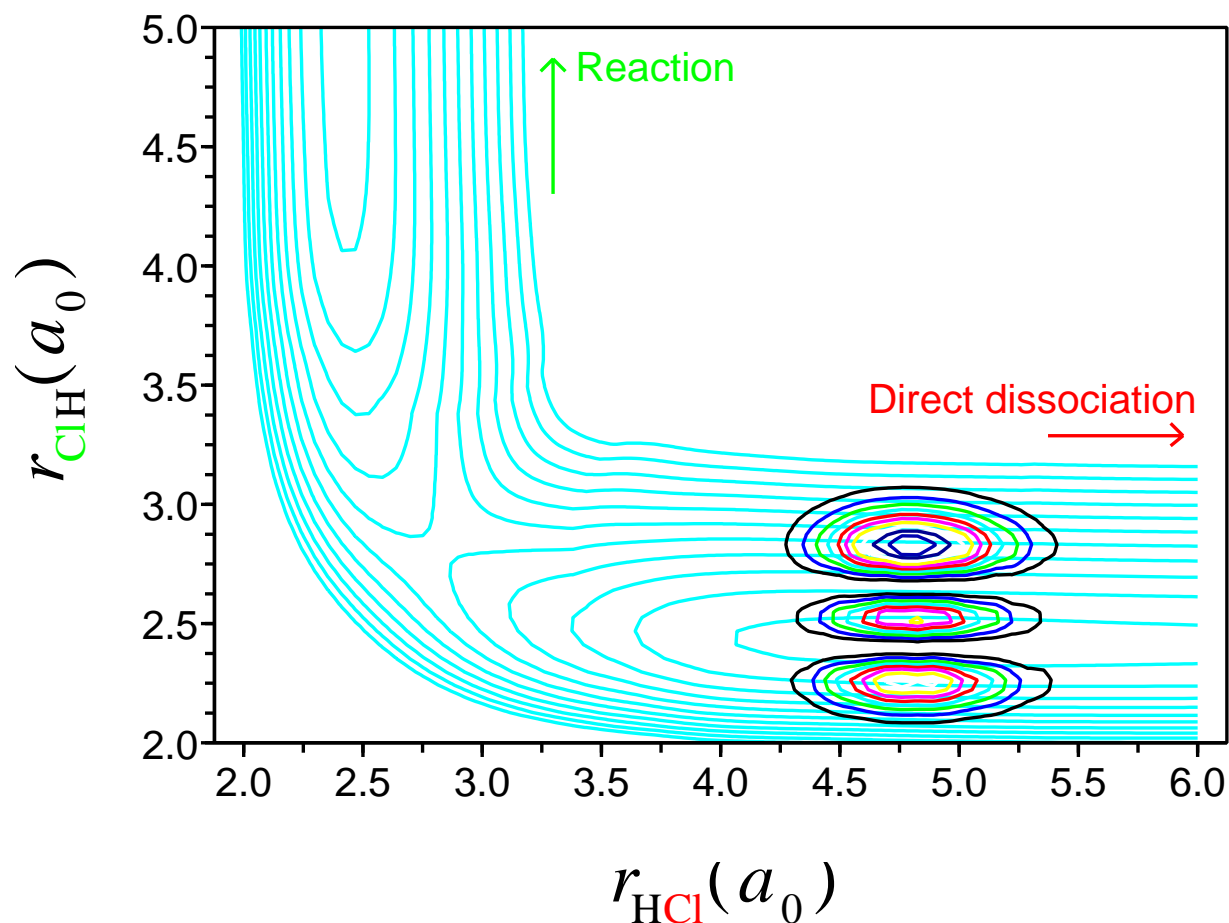
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1: Whiteley *et al*, Phys. Chem. Chem. Phys. 2, 549 (1999)

2: Dubernet and Hutson, J. Phys. Chem. A 98, 5844 (1994)

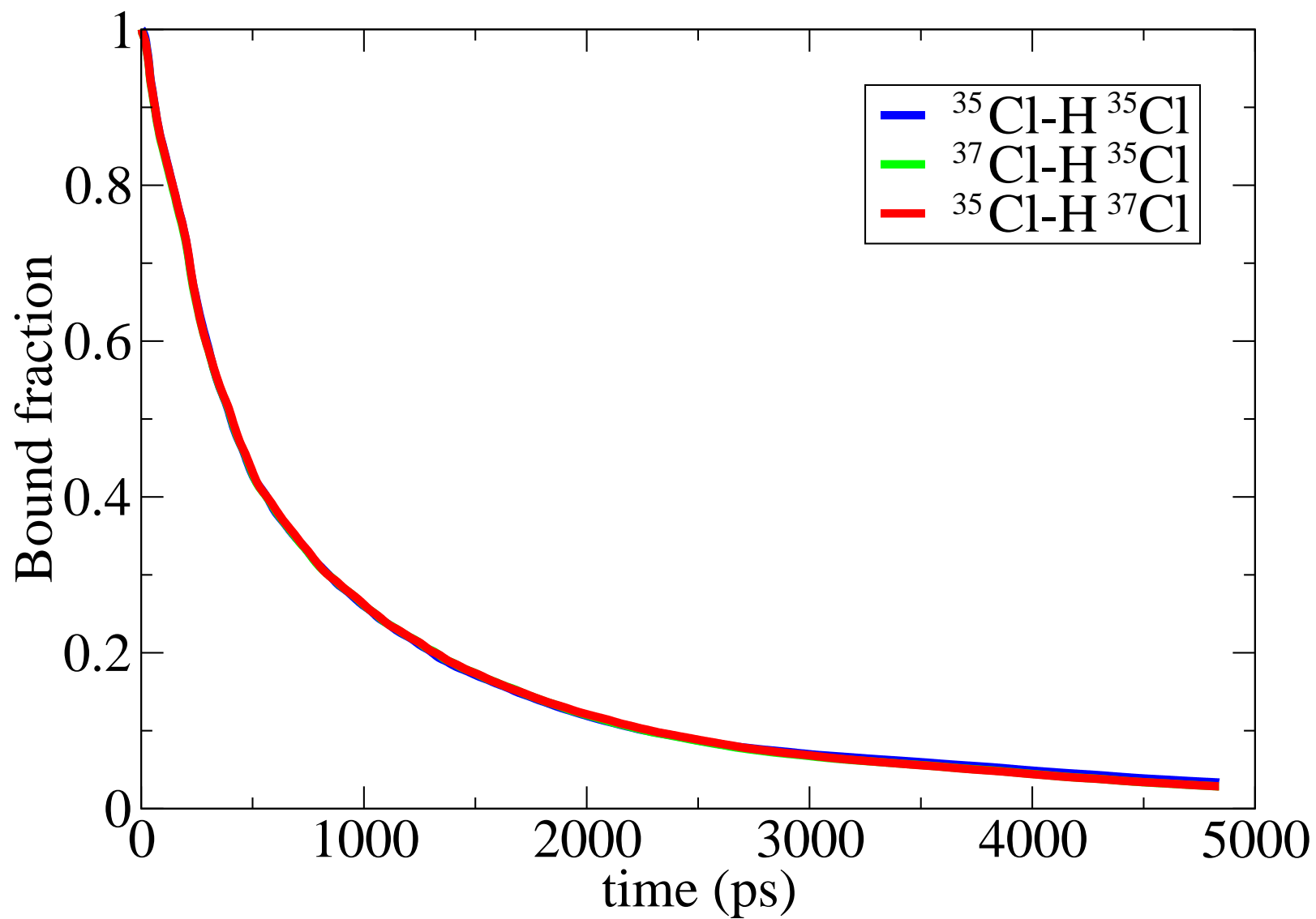
# Initial state

The initial state for the reaction is computed as a quasi-bound state in the Van der Waals well

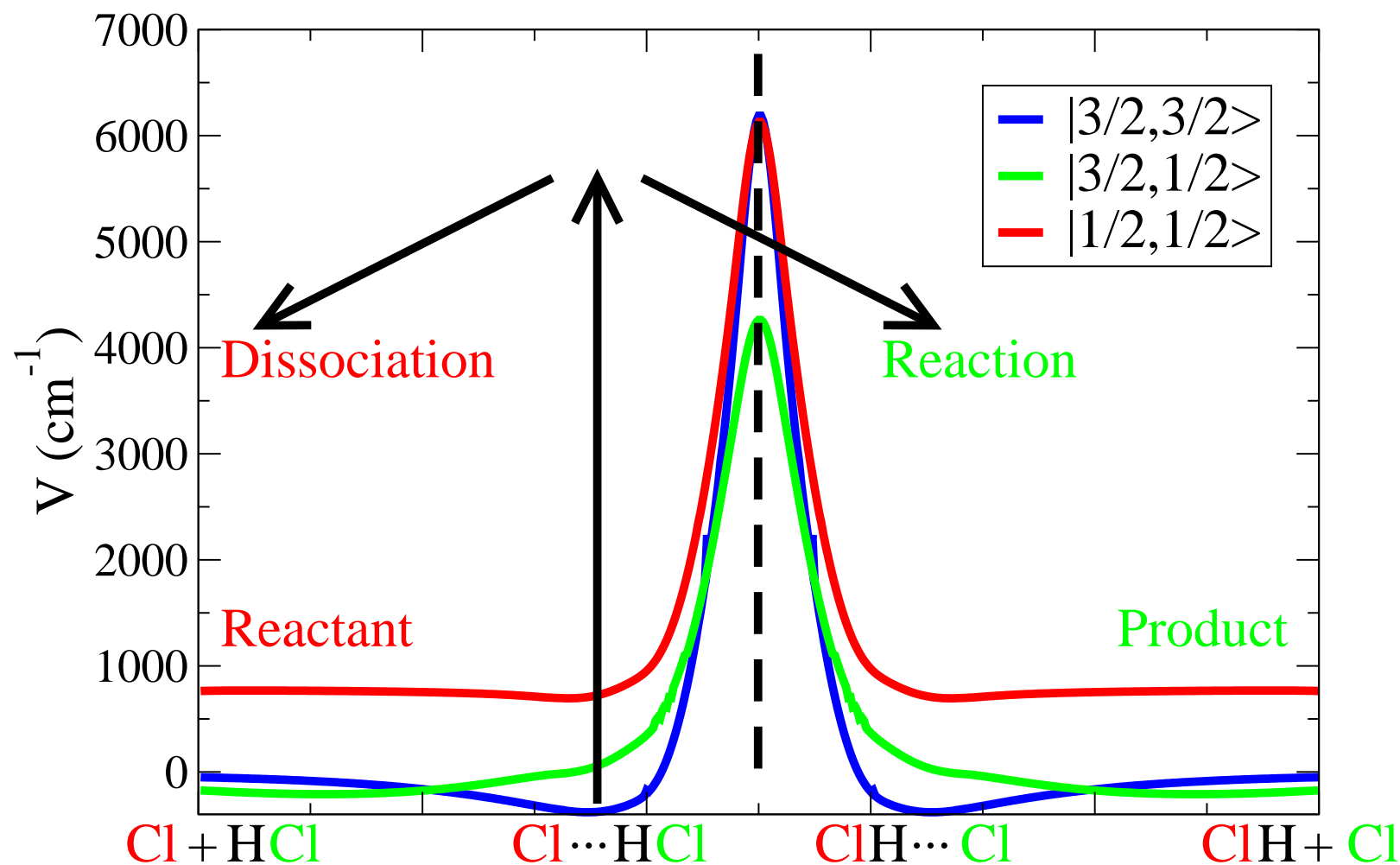




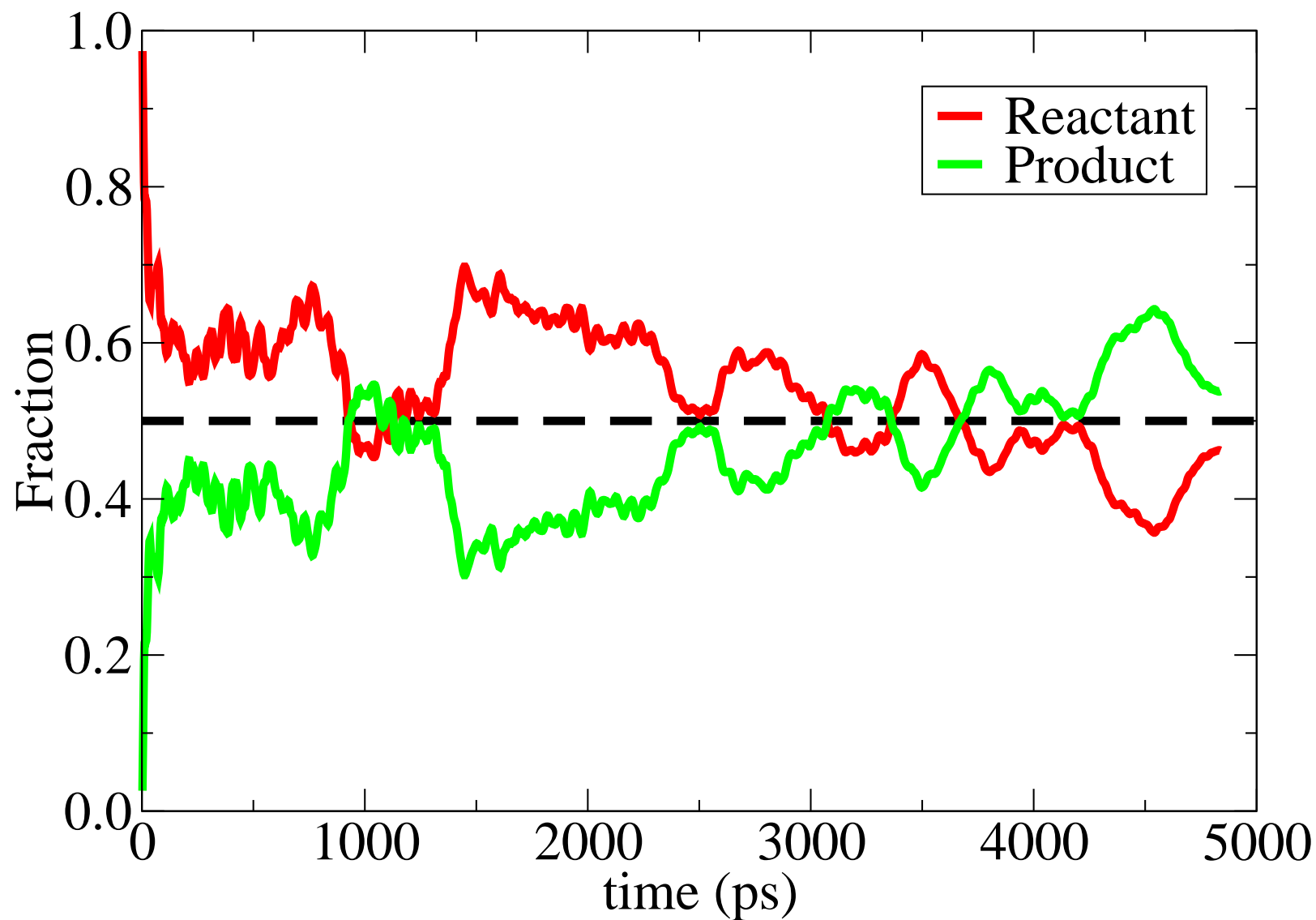
# Wave packet decay



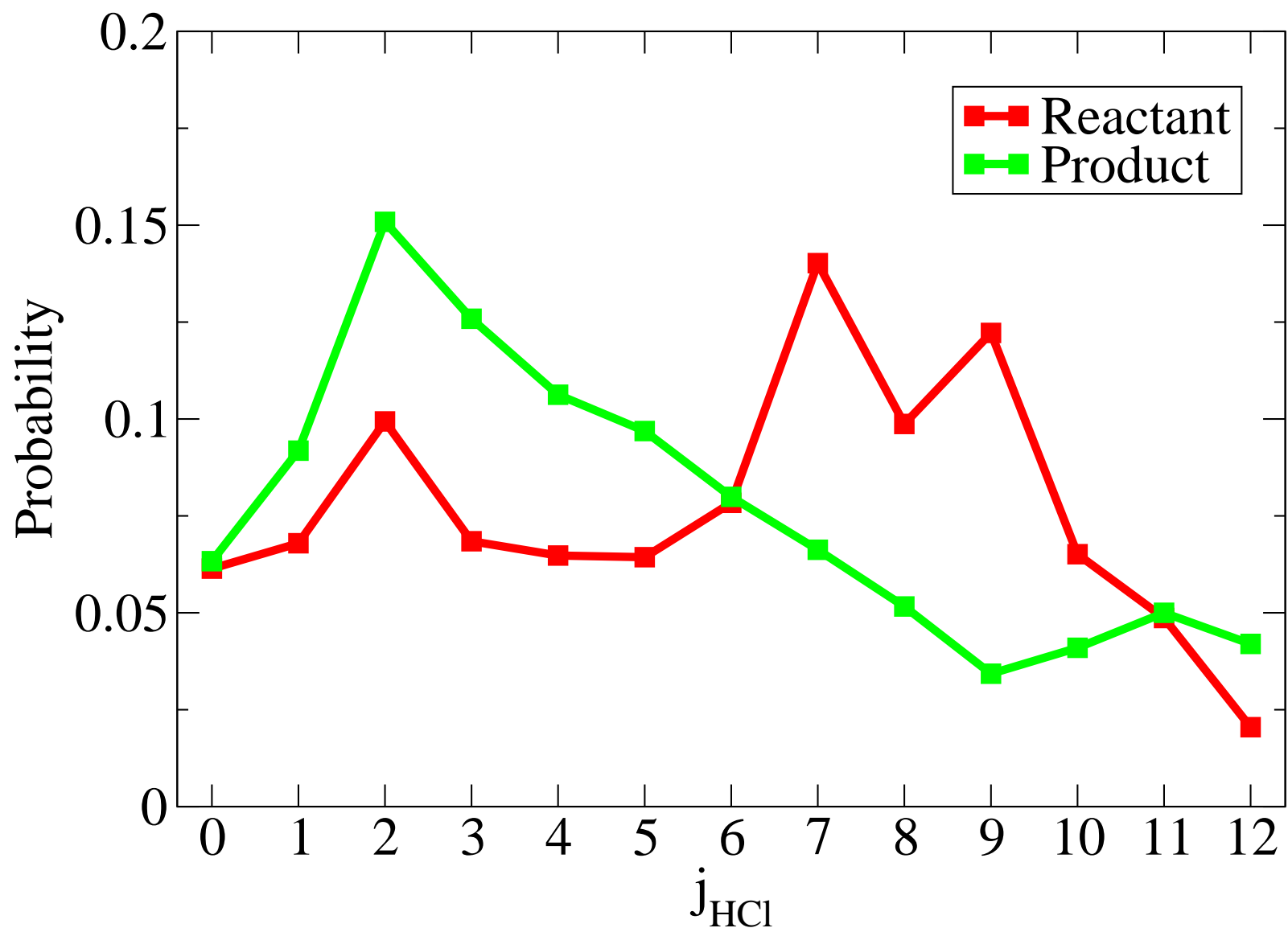
# Distribution over channels



# Distribution over channels

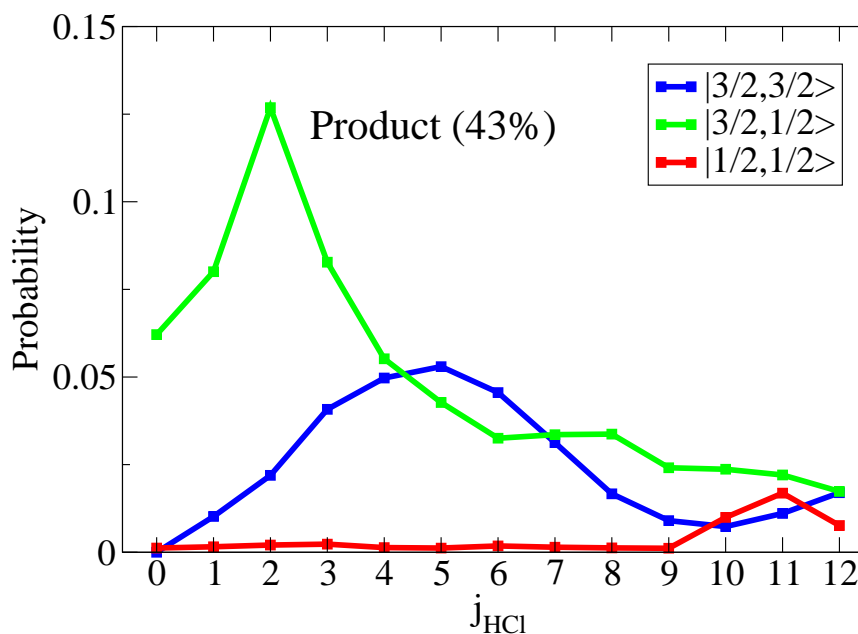
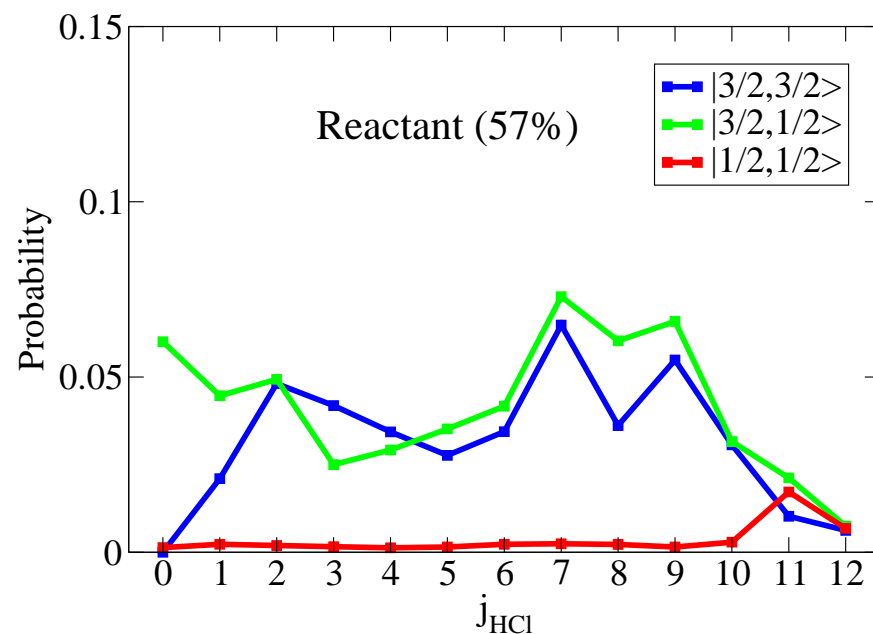


# Rotational state distributions

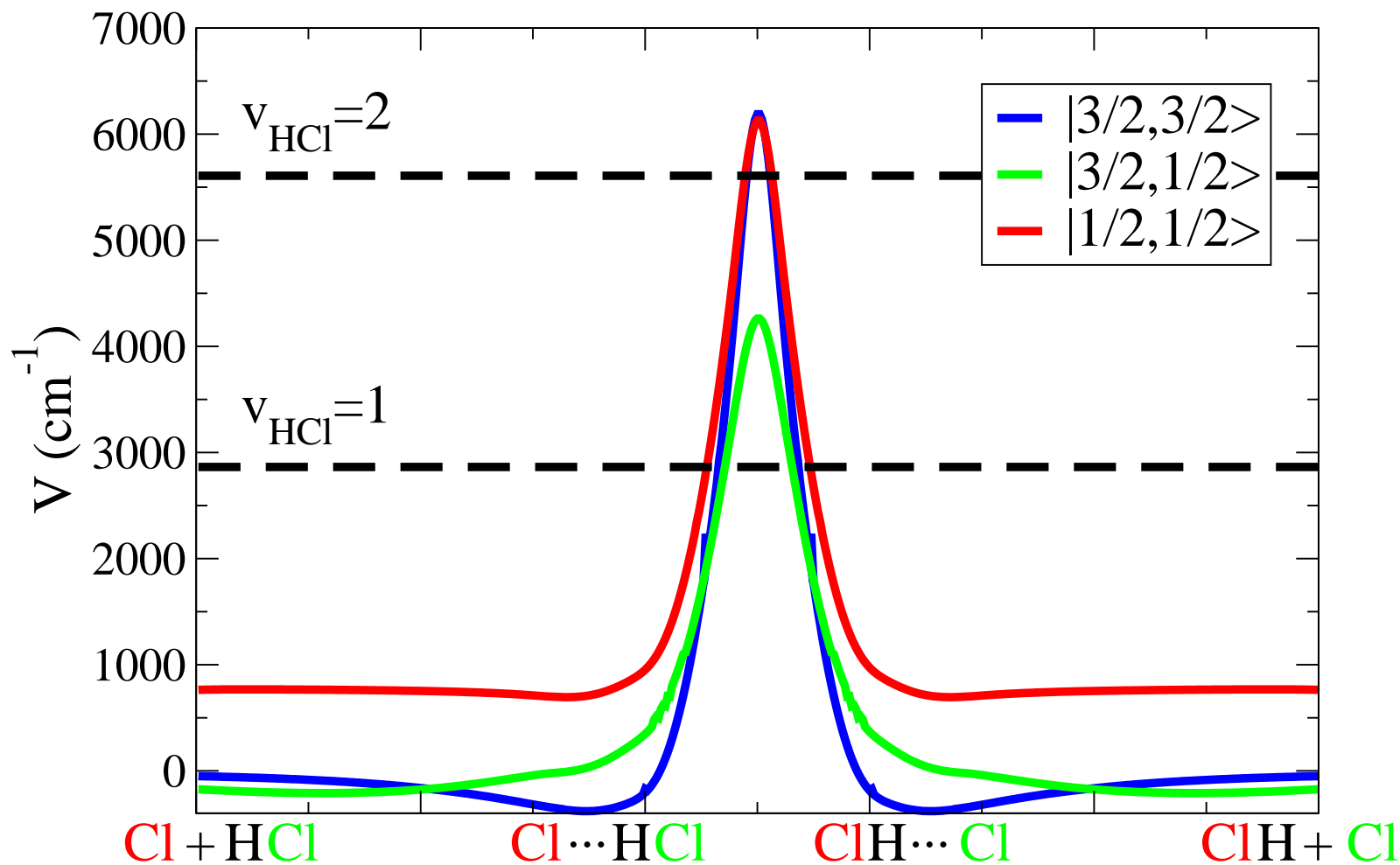


# Rotational state distributions

Look at contributions to rotational distributions from different electronic surfaces

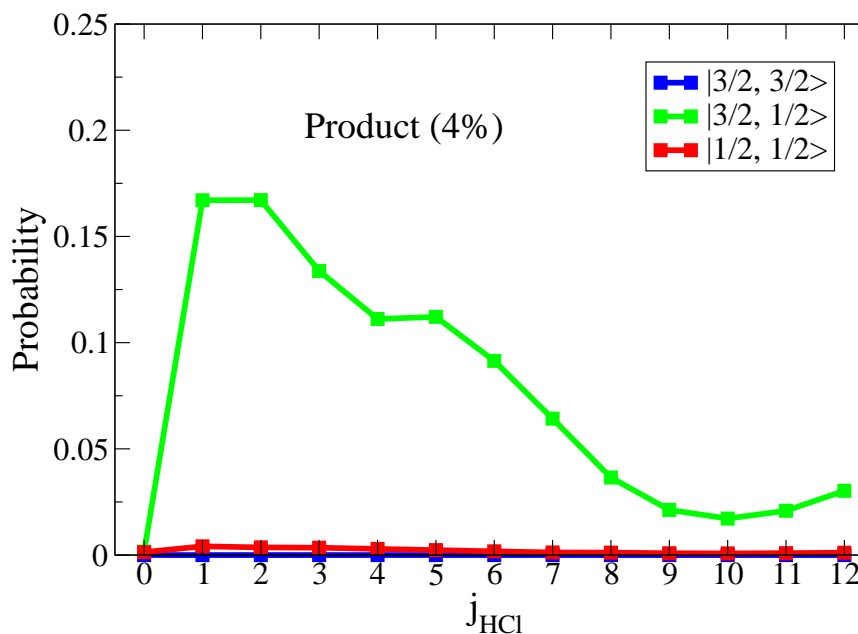
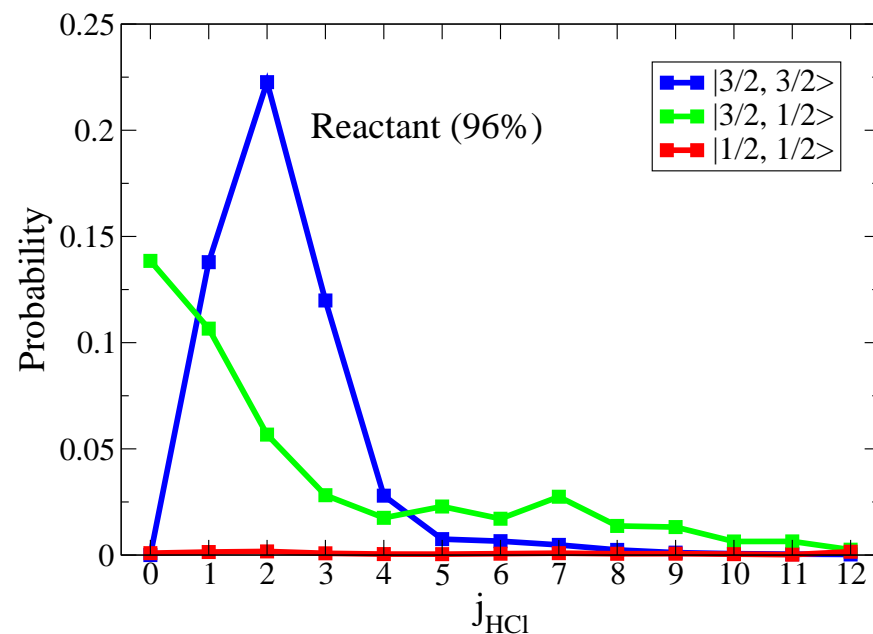


# Rotational state distributions



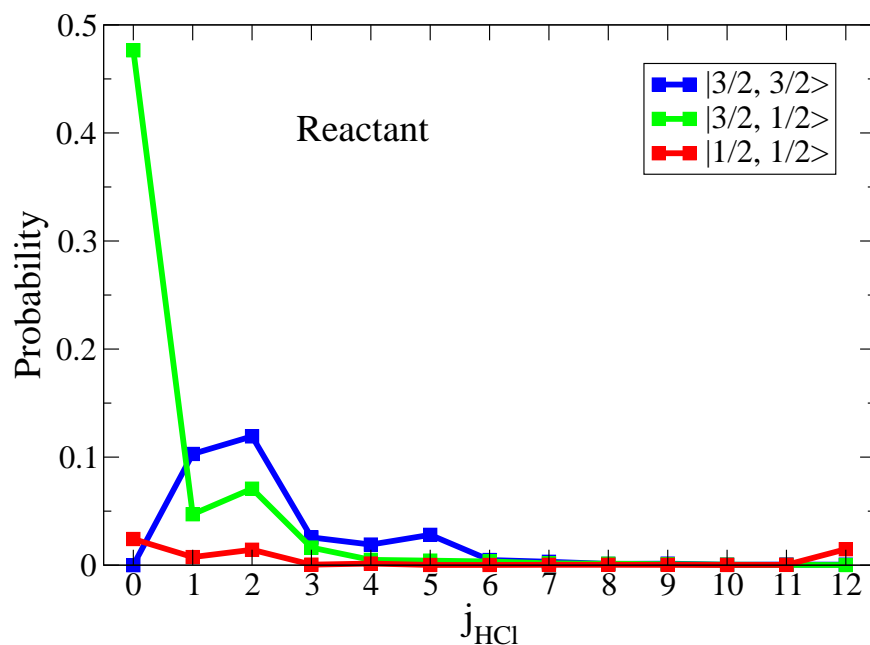
# Rotational state distributions

Turn off all couplings between different potential energy surfaces



# Rotational state distributions

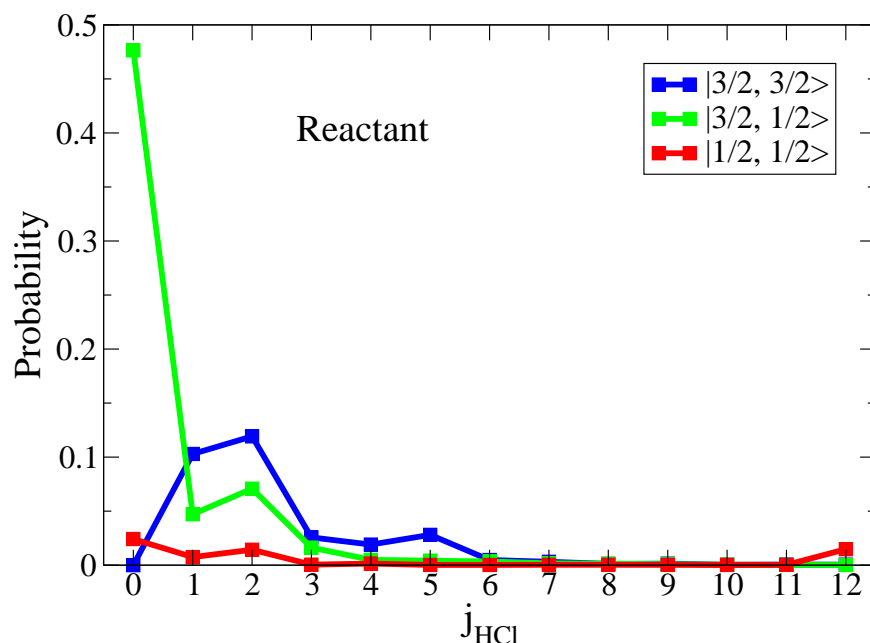
Don't allow the wave packet to cross the reaction barrier:  
start from  $v_{\text{HCl}} = 1$





# Rotational state distributions

Don't allow the wave packet to cross the reaction barrier:  
start from  $v_{\text{HCl}} = 1$



Motion of the wave packet crossing and recrossing the reaction barrier is responsible for the broad rotational distribution in the reactant channel when starting from  $v_{\text{HCl}} = 2$

# Conclusions

- **YES!** The system reacts after exciting the HCl stretch vibration
- Very little dependence on Cl isotope: reaction from “asymmetric”  $^{37}\text{Cl}-\text{H}^{35}\text{Cl}$  as fast as for “symmetric”  $^{35}\text{Cl}-\text{H}^{35}\text{Cl}$
- Rotational state distributions are affected by wave packet sloshing back and forth between reactant and product channels
- No effect of parity on overall decay times, but small effect on electronic state distributions

# Acknowledgments

- The McCoy group:
  - Anne McCoy
  - Sara Ray
  - Lindsay Johnson
  - Samantha Horvath
  - Charlotte Hinkle
  - Eric Egnot
- NSF



# Electronic distributions

	<i>e</i> parity		<i>f</i> parity	
	reactant	product	reactant	product
$ \frac{3}{2}, \frac{3}{2}\rangle$	41.0	31.3	38.5	29.2
$ \frac{3}{2}, \frac{1}{2}\rangle$	54.4	63.6	51.8	60.4
$ \frac{1}{2}, \frac{1}{2}\rangle$	4.5	5.0	9.6	10.4