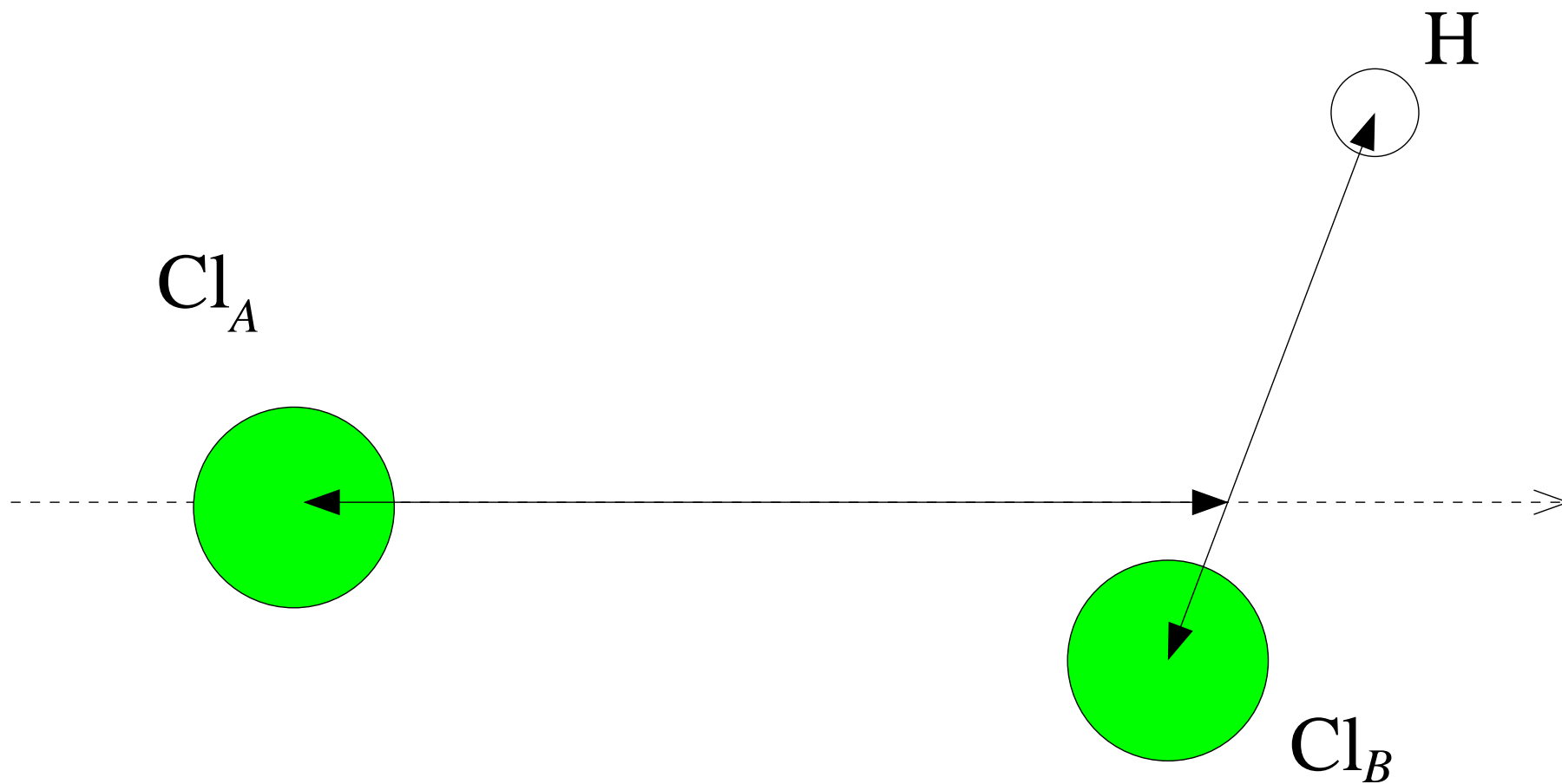
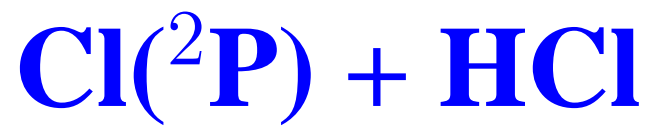


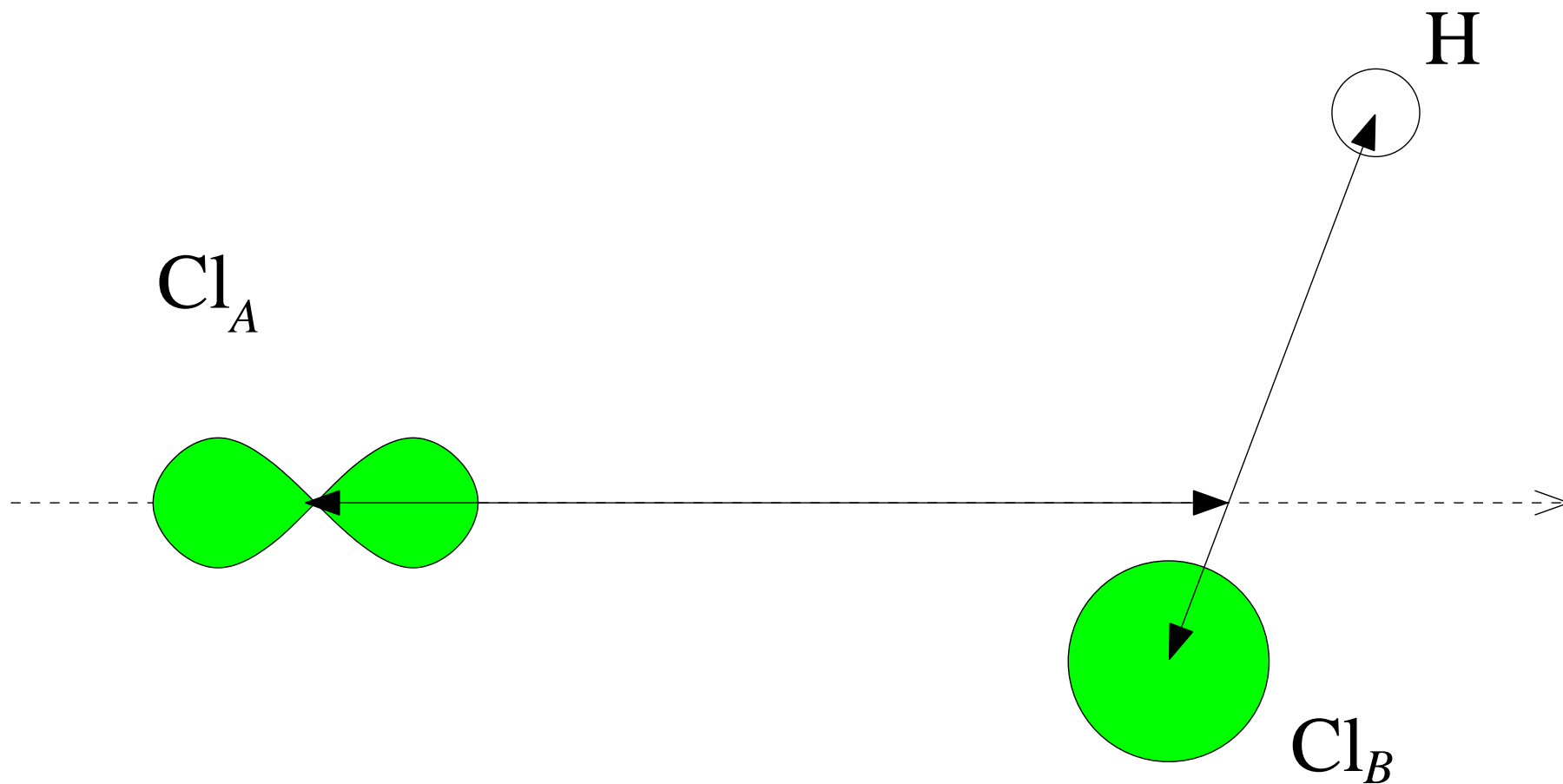
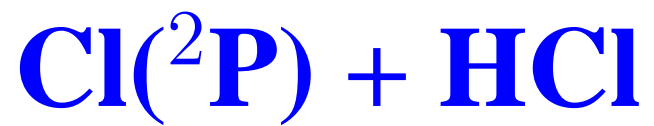
Computational studies of the $\text{Cl}(^2\text{P}) + \text{HCl} \rightarrow \text{ClH} + \text{Cl}(^2\text{P})$ hydrogen exchange reaction

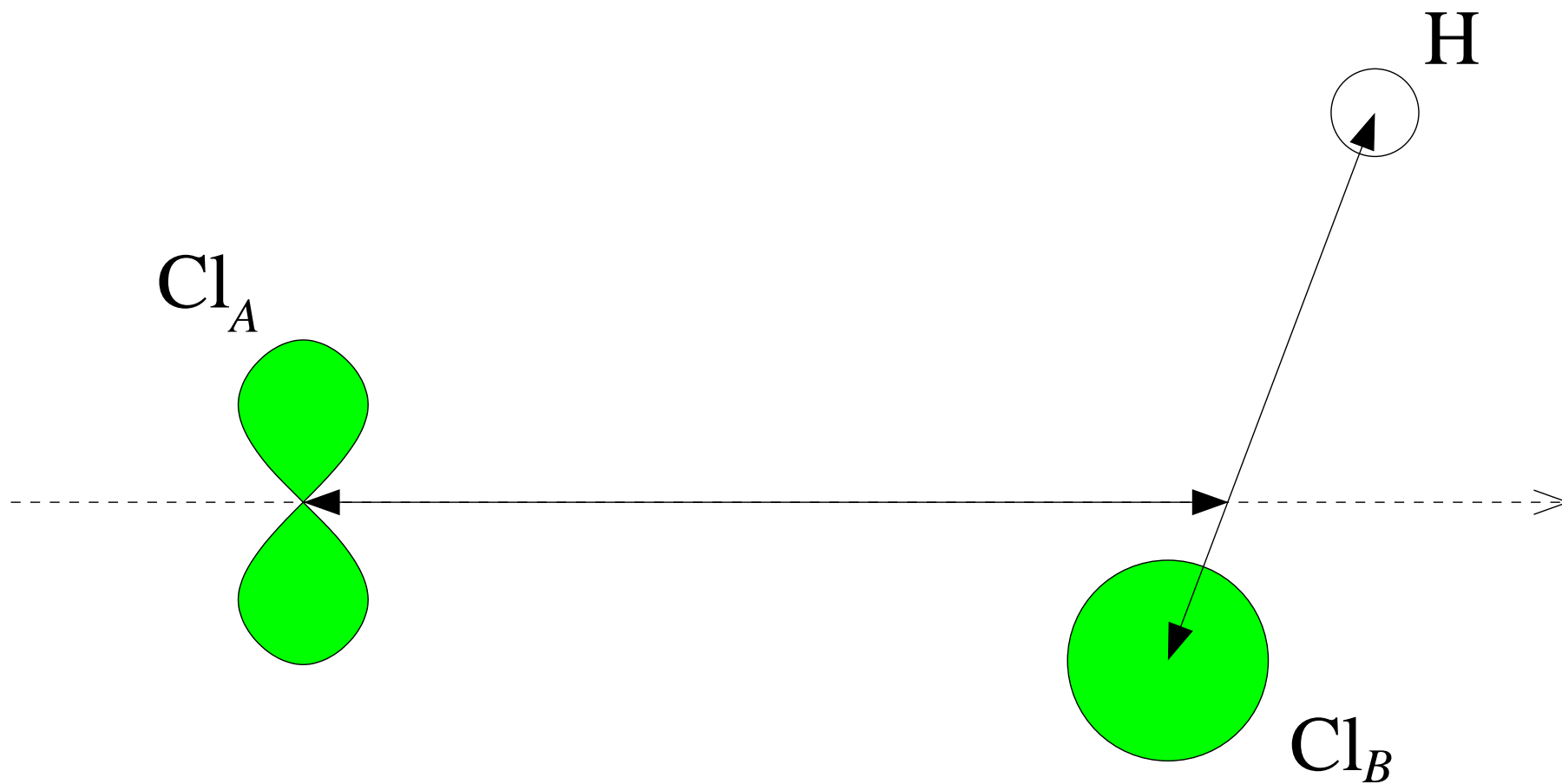
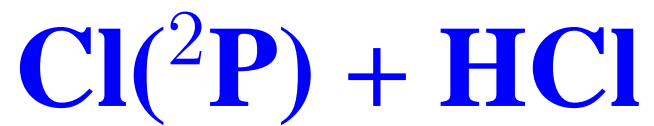
Gé W.M. Vissers and Anne B. McCoy

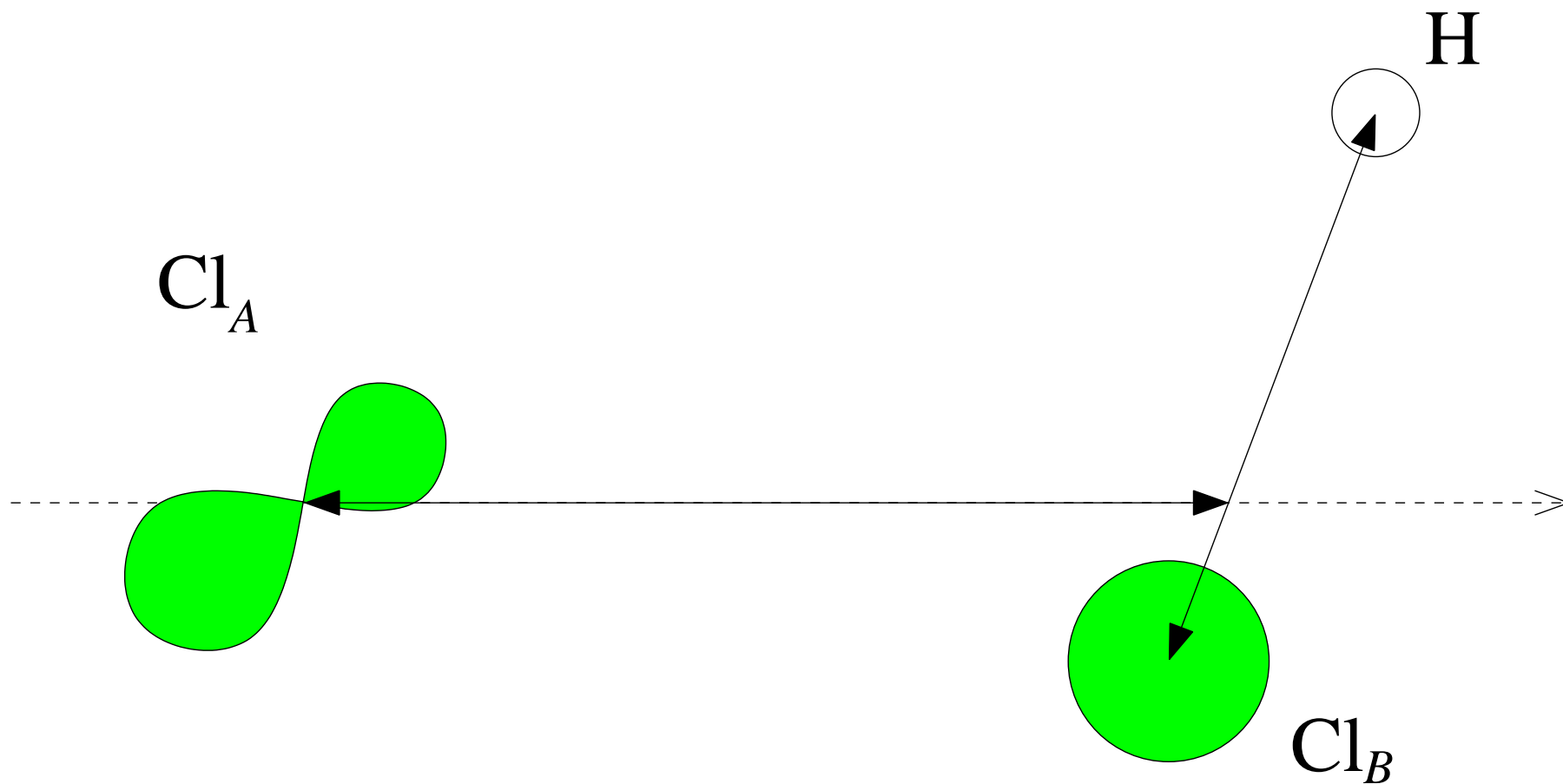
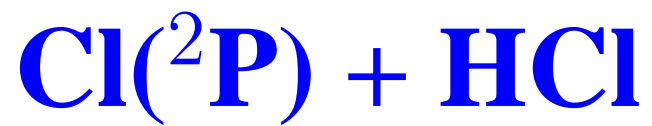
Department of Chemistry, Columbus

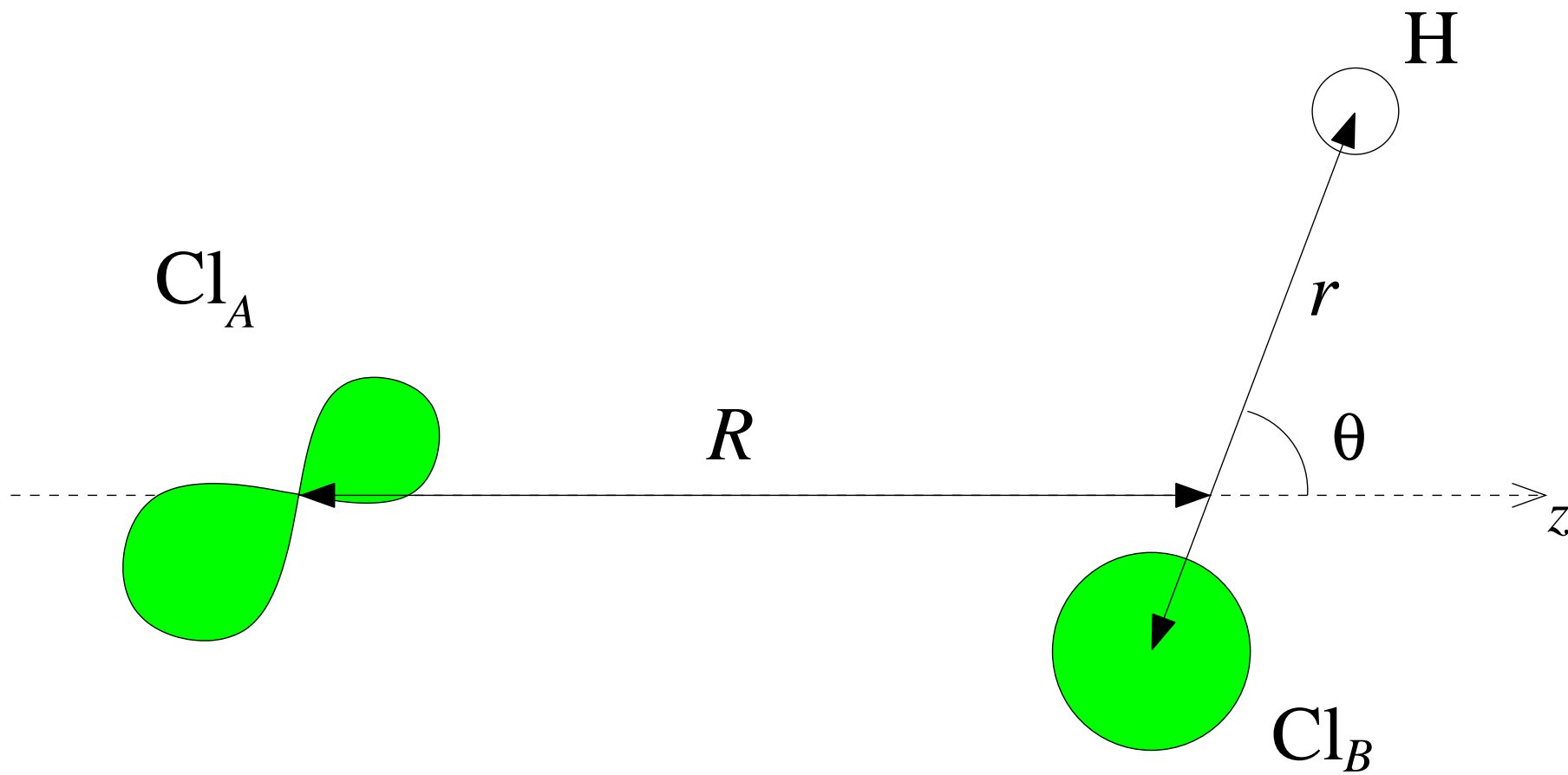
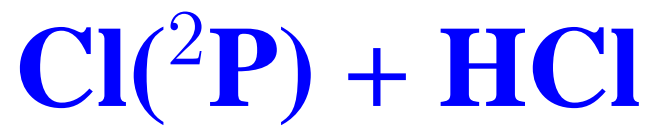












Hydrogen exchange reaction

Question: can we initiate the hydrogen exchange reaction by vibrationally exciting the HCl molecule?

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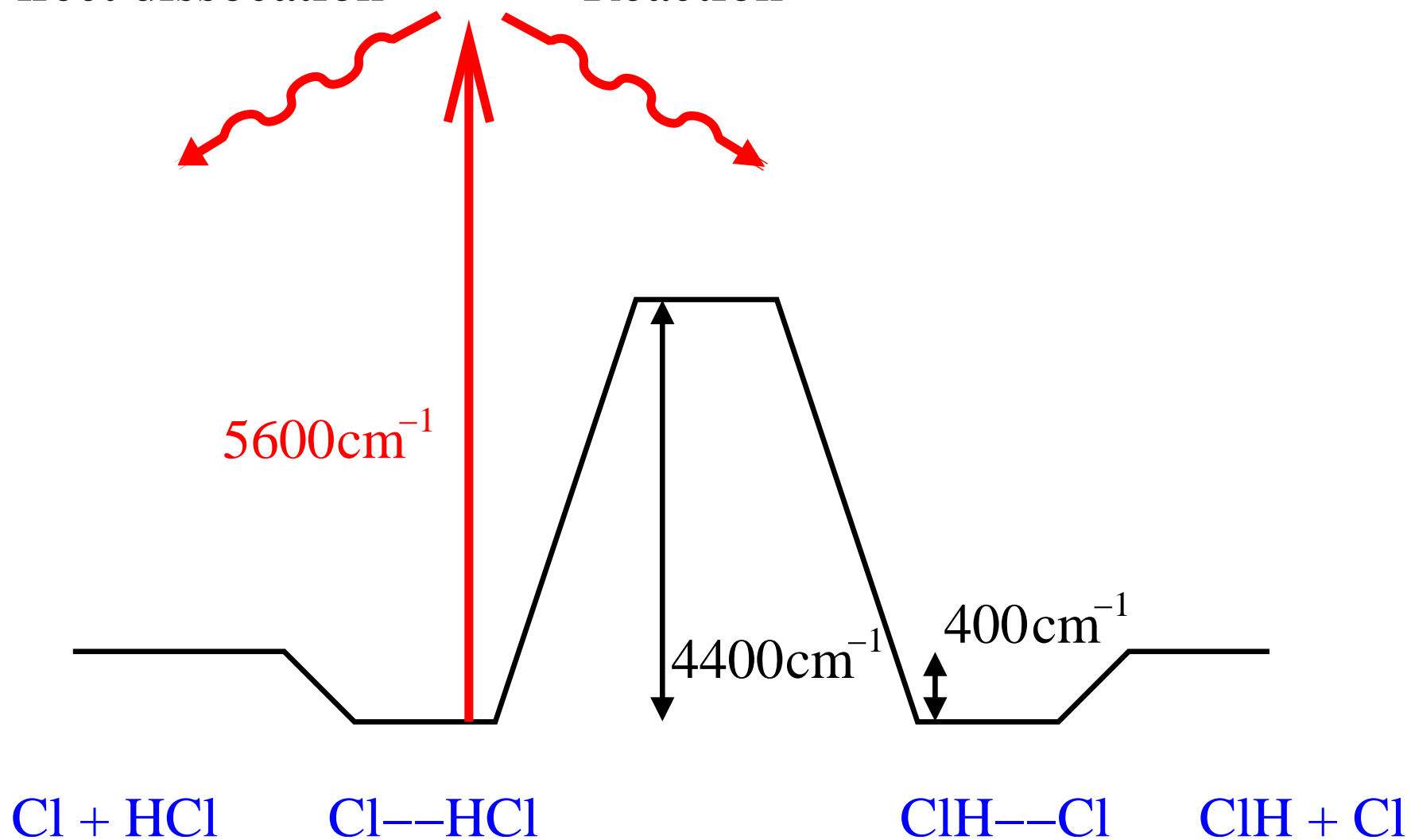
Question: can we initiate the hydrogen exchange reaction by vibrationally exciting the HCl molecule?

- Time dependent wave packet calculations
- Start with wave packet in vibrationally excited state
- Include all three potential energy surfaces and couplings
- How important is the electronic angular momentum?
- What is the influence of the Van der Waals well?

The process

Direct dissociation

Reaction



(Quasi-)Bound states (1)

Initial state is approximated by a quasi-bound state in the Van der Waals well.

Hamiltonian:

$$\hat{H} = -\frac{1}{2\mu R} \frac{\partial^2}{\partial R^2} R + \frac{1}{2\mu R^2} [\hat{J}^2 + (\hat{j}_A + \hat{j}_B)^2 - 2(\hat{j}_A + \hat{j}_B) \cdot \hat{J}] \\ - \frac{1}{2\mu_{\text{HCl}} r} \frac{\partial^2}{\partial r^2} r + \frac{1}{2\mu_{\text{HCl}} r^2} \hat{j}_B^2 + A \hat{\lambda} \cdot \hat{S} + \hat{V}$$

Potential operator

$$\hat{V} = \sum_{\mu\mu'} V_{\mu'\mu} |\lambda\mu'\rangle \langle \lambda\mu|$$

is expanded in spherical harmonics

$$V_{\mu'\mu}(R, r, \theta) = \sum_{l_B} C_{l_B, \mu-\mu'}(\theta, \phi) v_{l_B}^{\mu'\mu}(R, r)$$

(Quasi-)Bound states (2)

- Potential surfaces are taken from literature [1,2,3]
- Radial basis functions are calculated using DVR, uncoupled angular basis
- Bound states calculated for $J = 1/2, \dots, 7/2$, both e and f parity
- Very good agreement with earlier studies [3,4] is found for the bound states

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

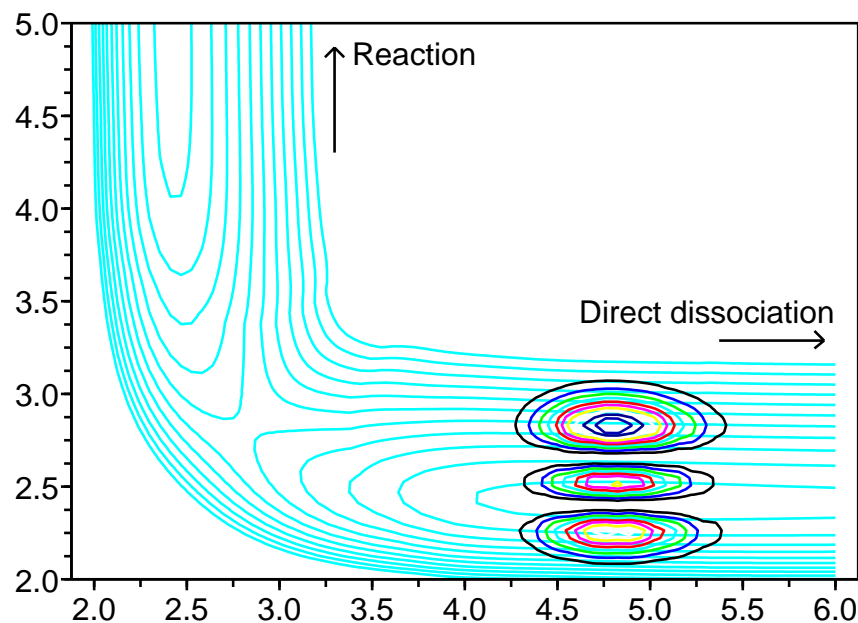
2: Kłos *et al*, J. Chem. Phys. 115, 3085 (2001)

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

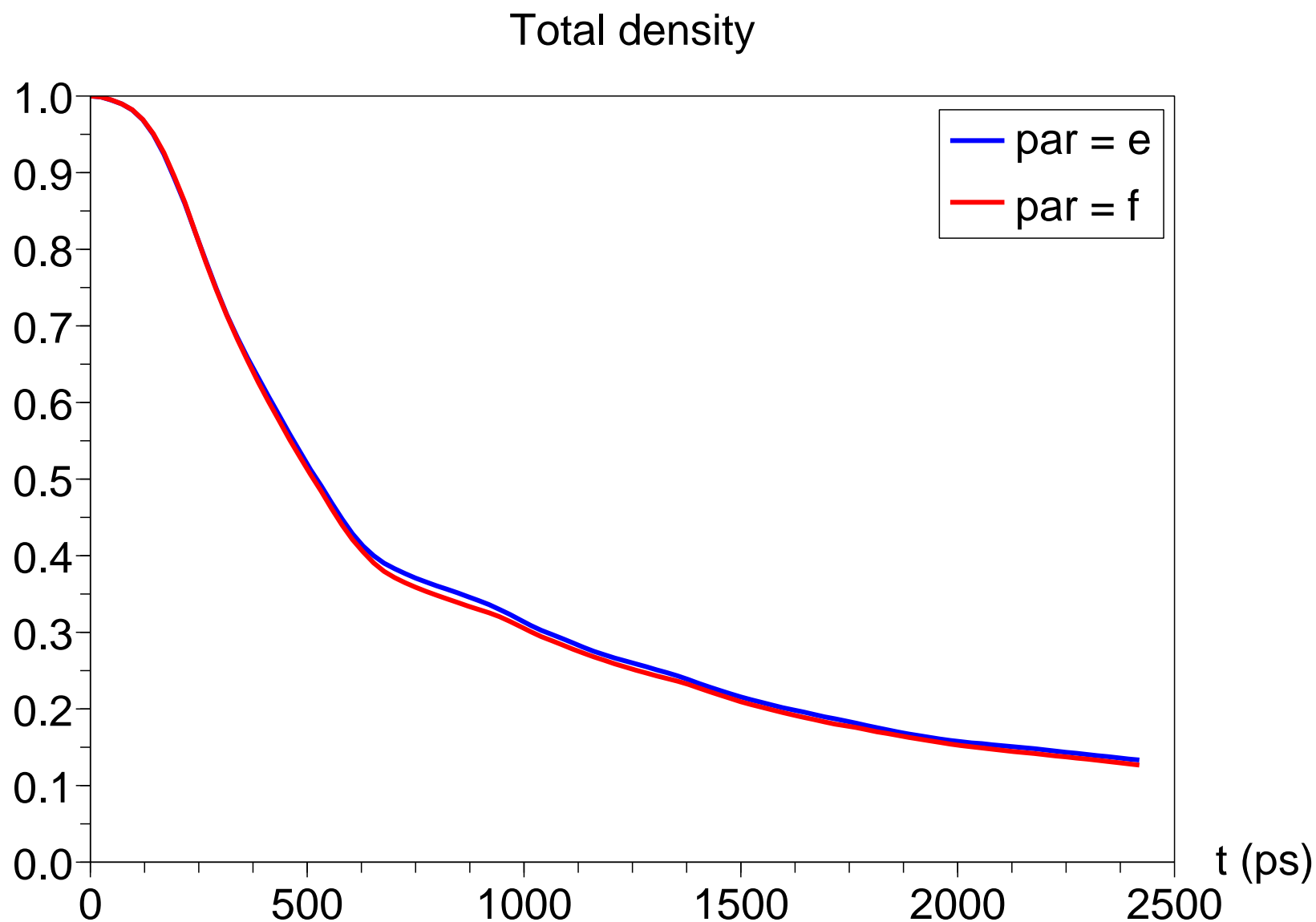
4: Zeimen *et al*, J. Phys. Chem. A 107, 5110 (2003)

Wave packet calculations

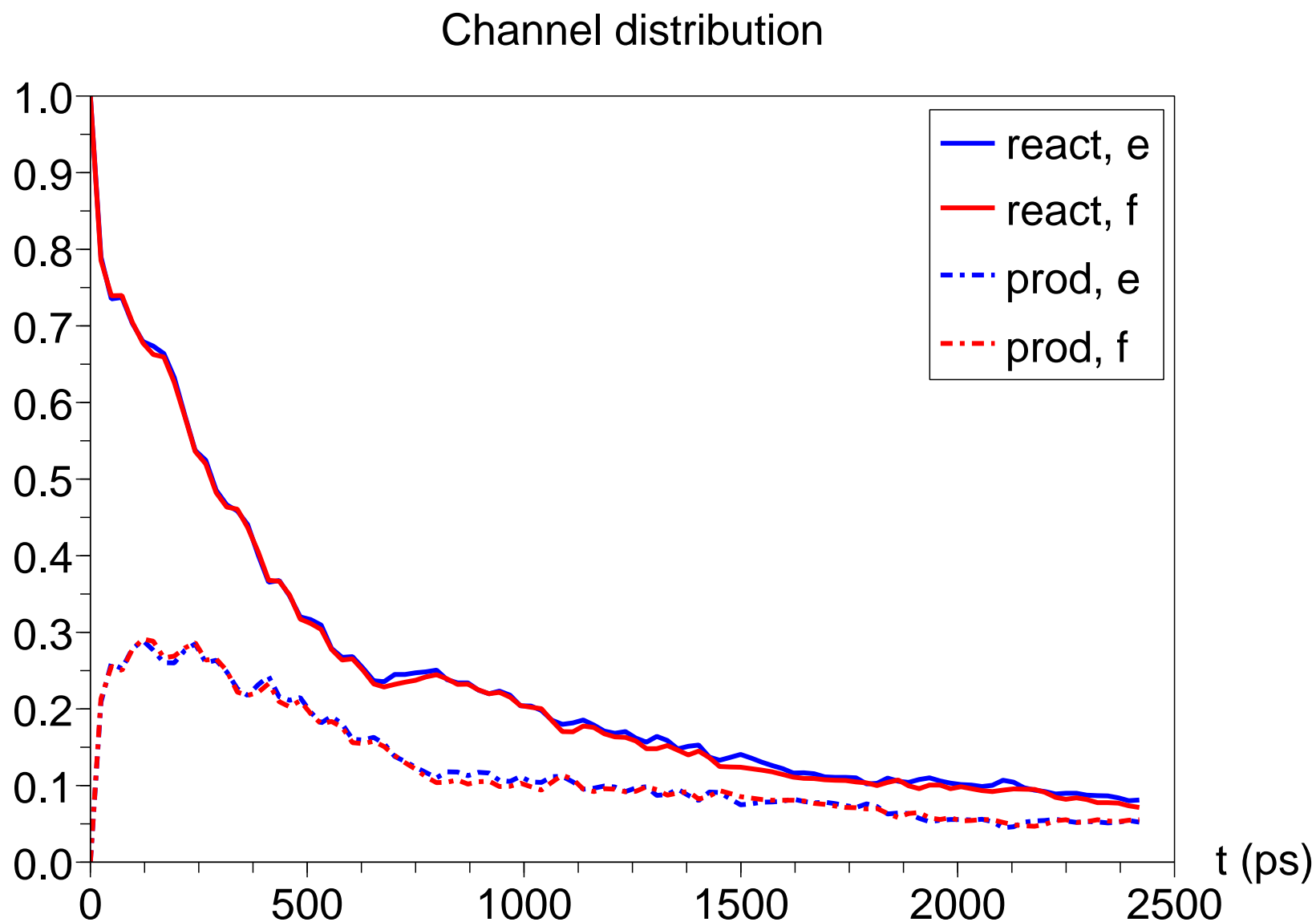
- Start from lowest $v_{\text{HCl}} = 2$ state
- Propagation up to ≈ 2.4 ns, using Chebyshev propagator
- Dissociated wave packet is captured by Gaussian damping for $R, R' > 9 a_0$
- Calculation so far $J = 1/2$ and both e and f parity



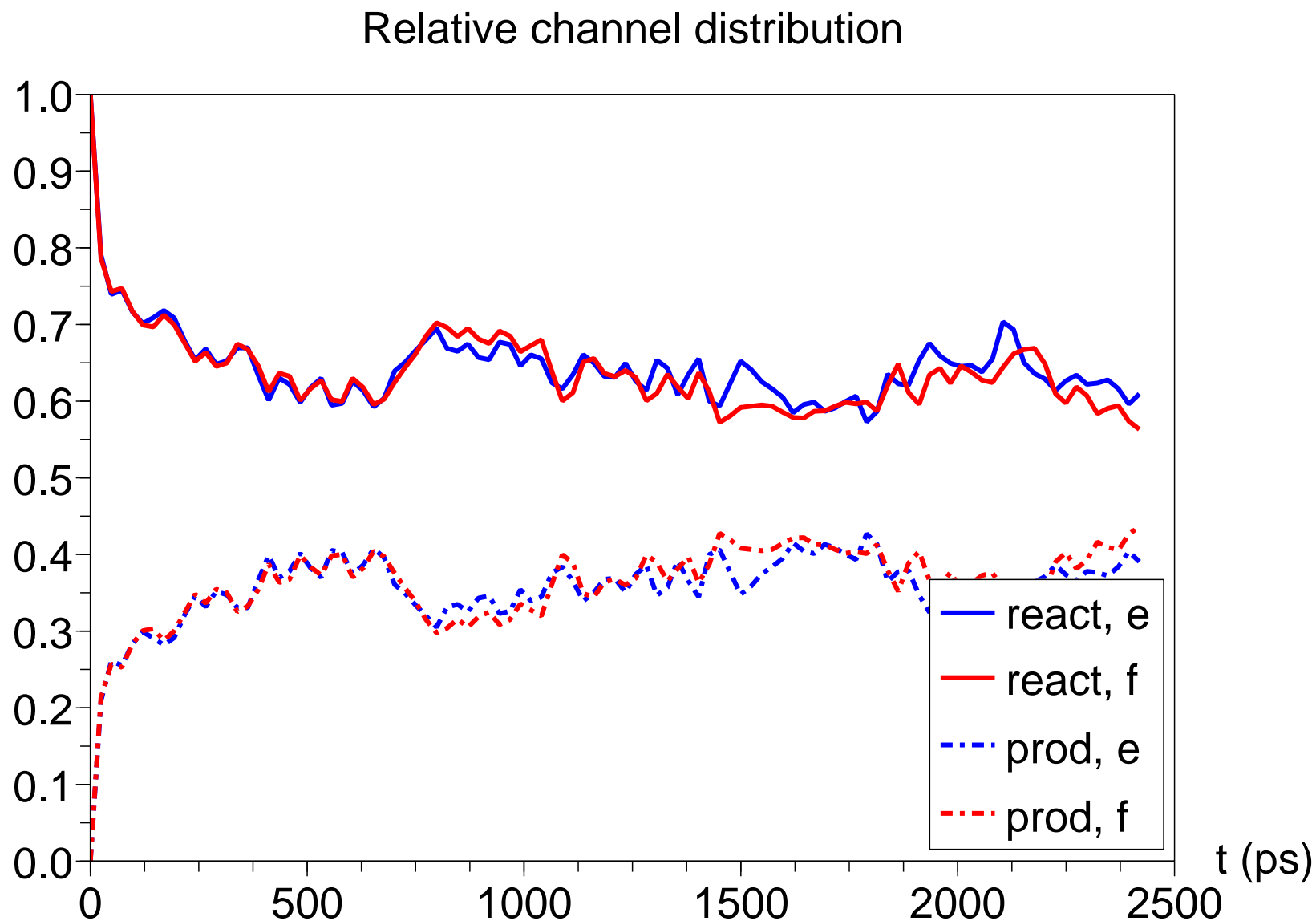
Dissociation of the wave packet



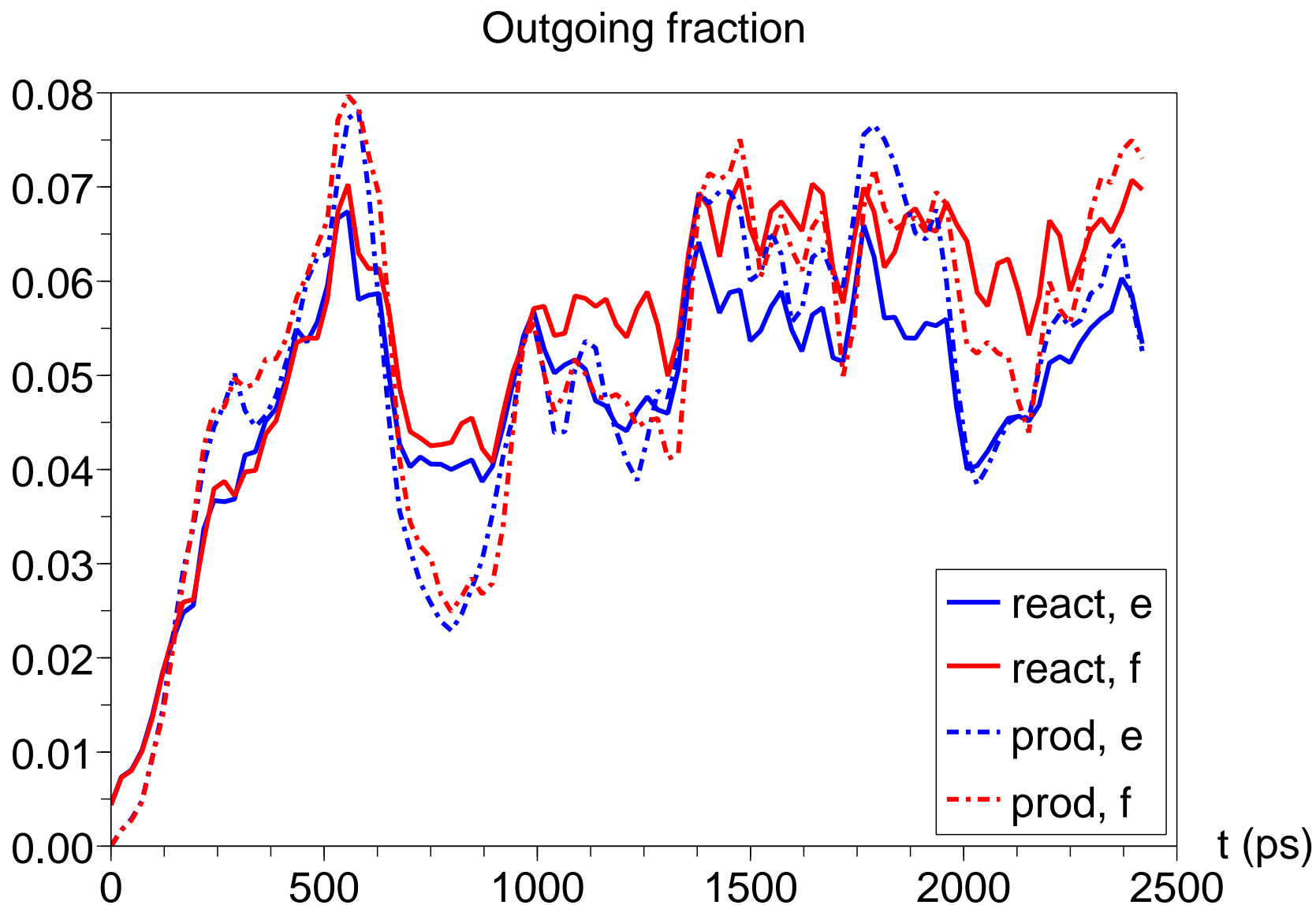
Distribution over channels



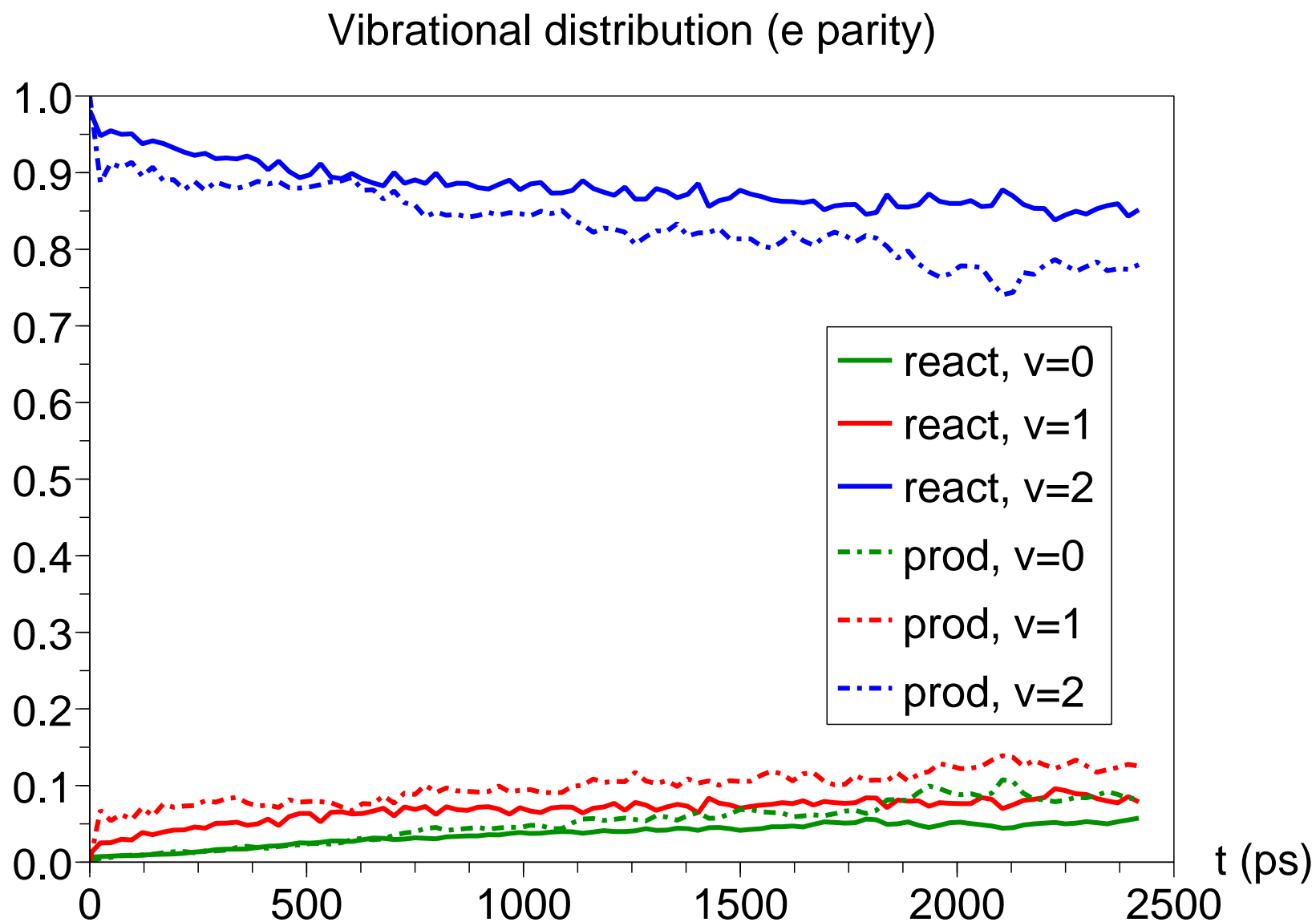
Relative distribution over channels



Dissociating fraction

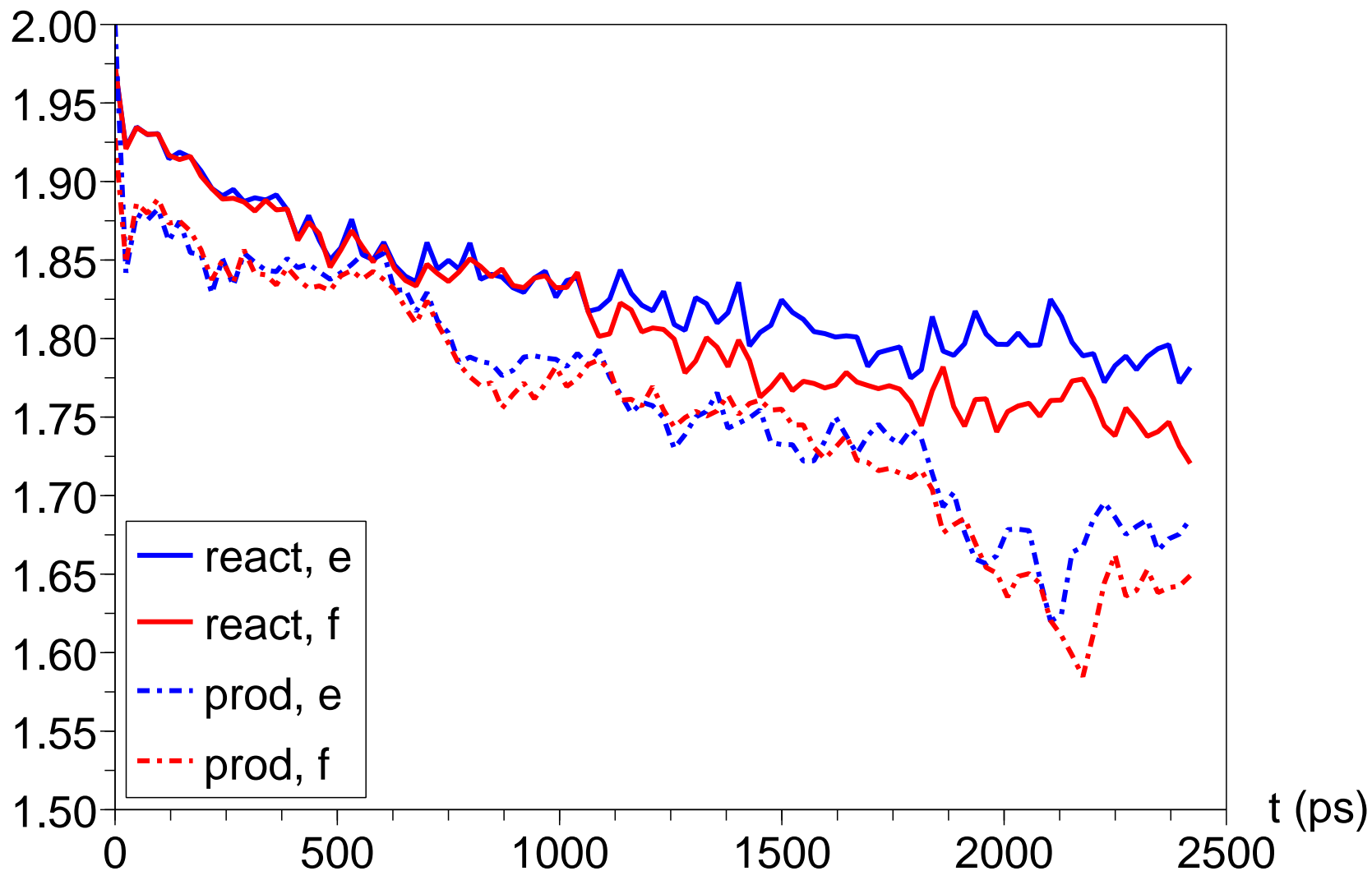


Vibrational distribution



Vibrational distribution

Average vibrational quantum number



Conclusions

- The hydrogen exchange reaction can be initiated by vibrationally exciting the initial HCl molecule
- Vibrational predissociation life time for $v_{\text{HCl}}=2$ is ≈ 500 ps
- Dissociation proceeds faster in the product channel than in the reactant channel, due to energy transfer from monomer vibration to dissociative motion
- Difference between e and f parity is minor for $J=1/2$
- More extensive calculations are currently in progress

Acknowledgements

● NSF

Acknowledgements

- NSF
- McCoy Group:

