Ab initio potential surfaces, vibrational and reaction dynamics of H_5^+ and CH_5^+ (and isotopomers)

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National Science Foundation,
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Issues in Astrophysics

- Deuterium fraction
- Spectroscopy
- Thermochemistry
- Reaction rates

Challenges for Theoretical Chemistry

- Potential energy surfaces
- Spectroscopy
- Thermochemistry/ZPE
- Dynamics

Triatomics, are a "solved" problem,

ab intio PES for HCN/HNC done in 1993

Dynamics and Reaction Rates

$$HD + H_3^+ \rightarrow H_2^+ + H_2D^+$$

$$k(T) = < vQ_i >$$

Q_i is Reaction Cross section for initial state i ,v is relative speed

$$Q_i = 2\pi \int_0^\infty d(\frac{b^2}{2}) P(b, E_{col}) \approx \pi b_{max}^2$$

$$Q_i = \frac{\pi}{2\mu E_{col}} \sum_{J=0}^{\infty} (2J+1) | S_i^J (E_{col}) |^2$$

Spectroscopy and Thermochemistry

$$HD + H_3^+ \rightarrow [H_4D^+] \rightarrow H_2 + H_2D^+$$

Thermochemistry - get the ZPEs accurately. HO?

Spectroscopy - detect reactant and products and maybe stabilized H_4D^+

Potential Energy Surface

$$HD + H_3^+ \rightarrow [H_4D^+] \rightarrow H_2 + H_2D^+$$

$$HD + CH_3^+ \rightarrow [CH_4D^+] \rightarrow H_2 + CH_2D^+$$

- Calculate ca 50 000 *ab initio* energies
- Fit to a flexible functional form
- Describe dissociation
- Build in permutational symmetry (need this to describe 5! equivalent minima, etc.)

A word about fitting

The Potential Energy Surface must be symmetric with respect to any permutation of the H atoms. In the field, this has been an open problem.

One solution is to replicate *ab initio* data and fit to the large replicated data set. Not very useful for larger molecules.

Example H_5^+ - 5! = 120 equivalent minima, etc.

A word about fitting

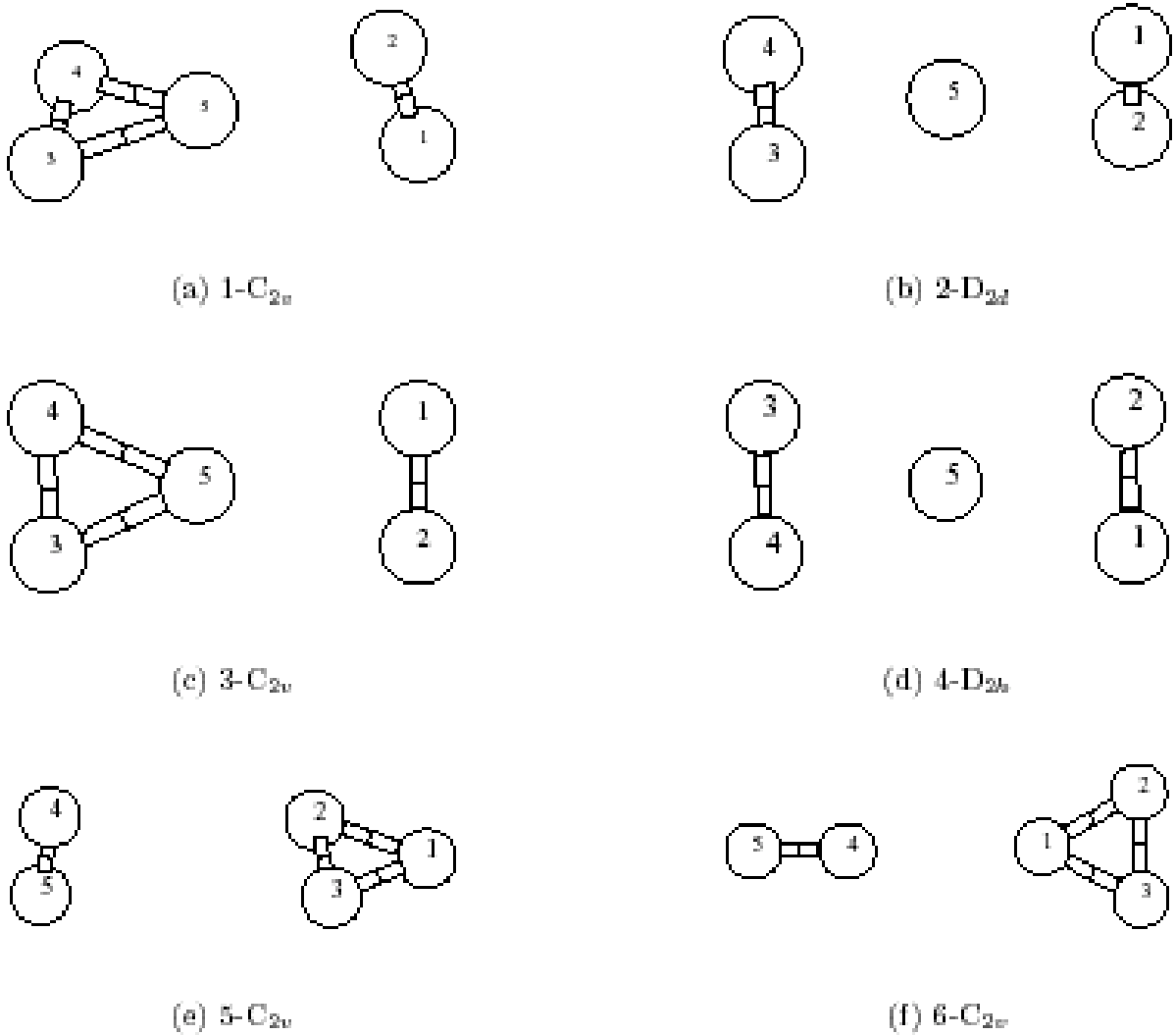
- Use all internuclear distances r_i (or $x_i(r_i)$)
- Use basis functions that are Perm. Invariant
- Linear parameters determined via least squares

$$V(x_1,\cdots x_d)=\sum_{i_1\cdots i_d} C_{i_1\cdots i_d} S\{x_1^{i_1}\cdots x_d^{i_d}\}$$

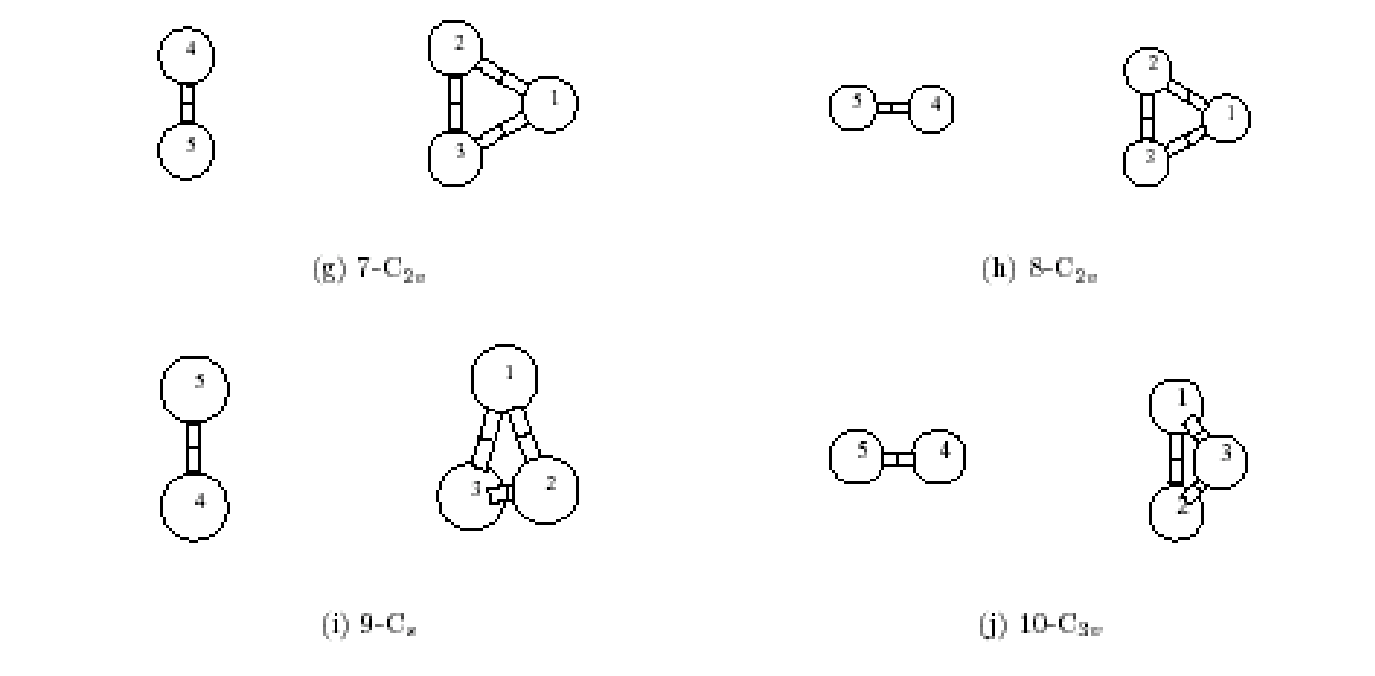
S is symmetrization operator, e.g., $(x_1+x_2+\ldots+x_N)$

Ab initio data required only at one minimum and surrounding saddle points.

H_5^+ Potential Landscape Stationary Points

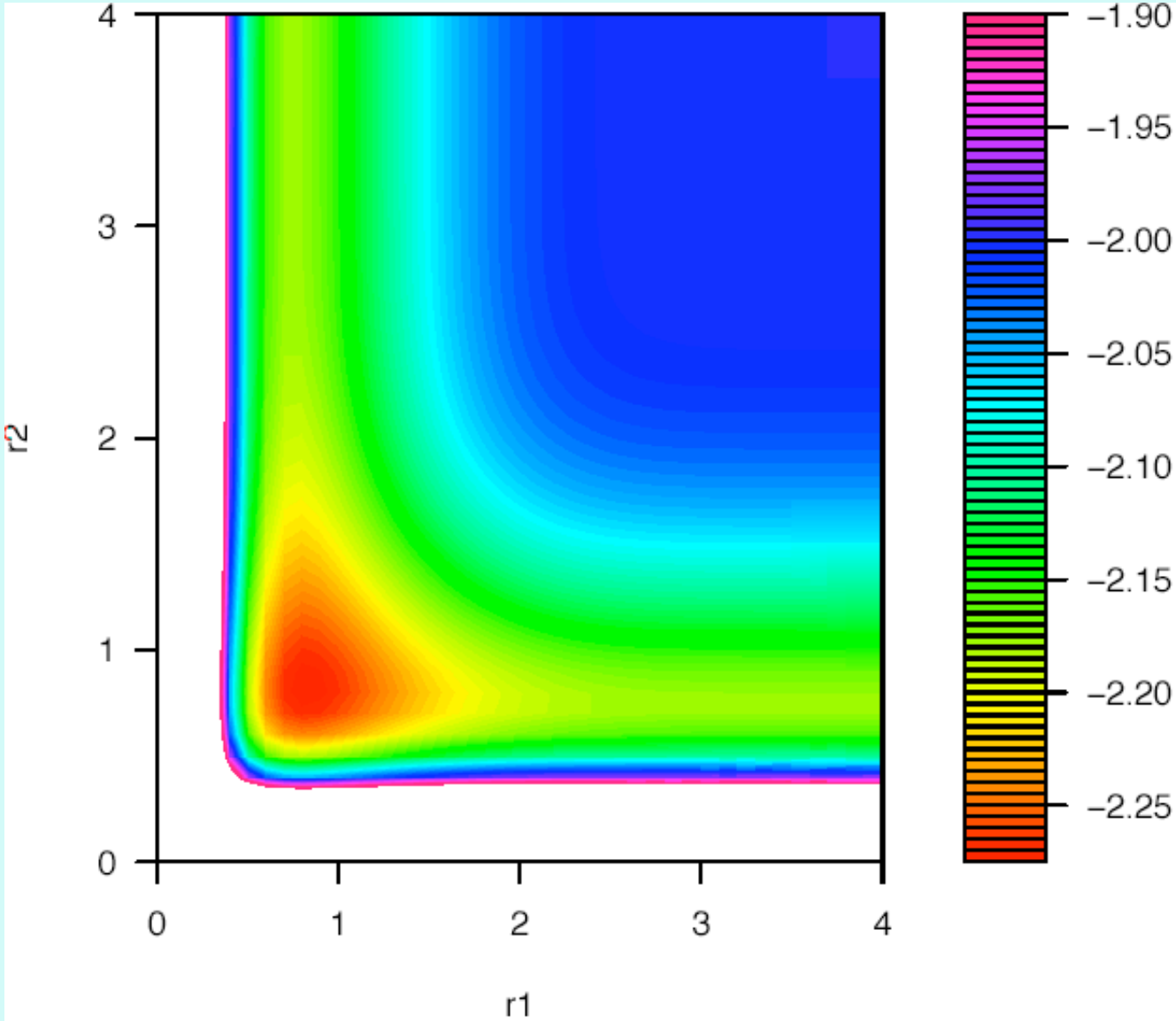


H_5^+ Potential Landscape Stationary Points

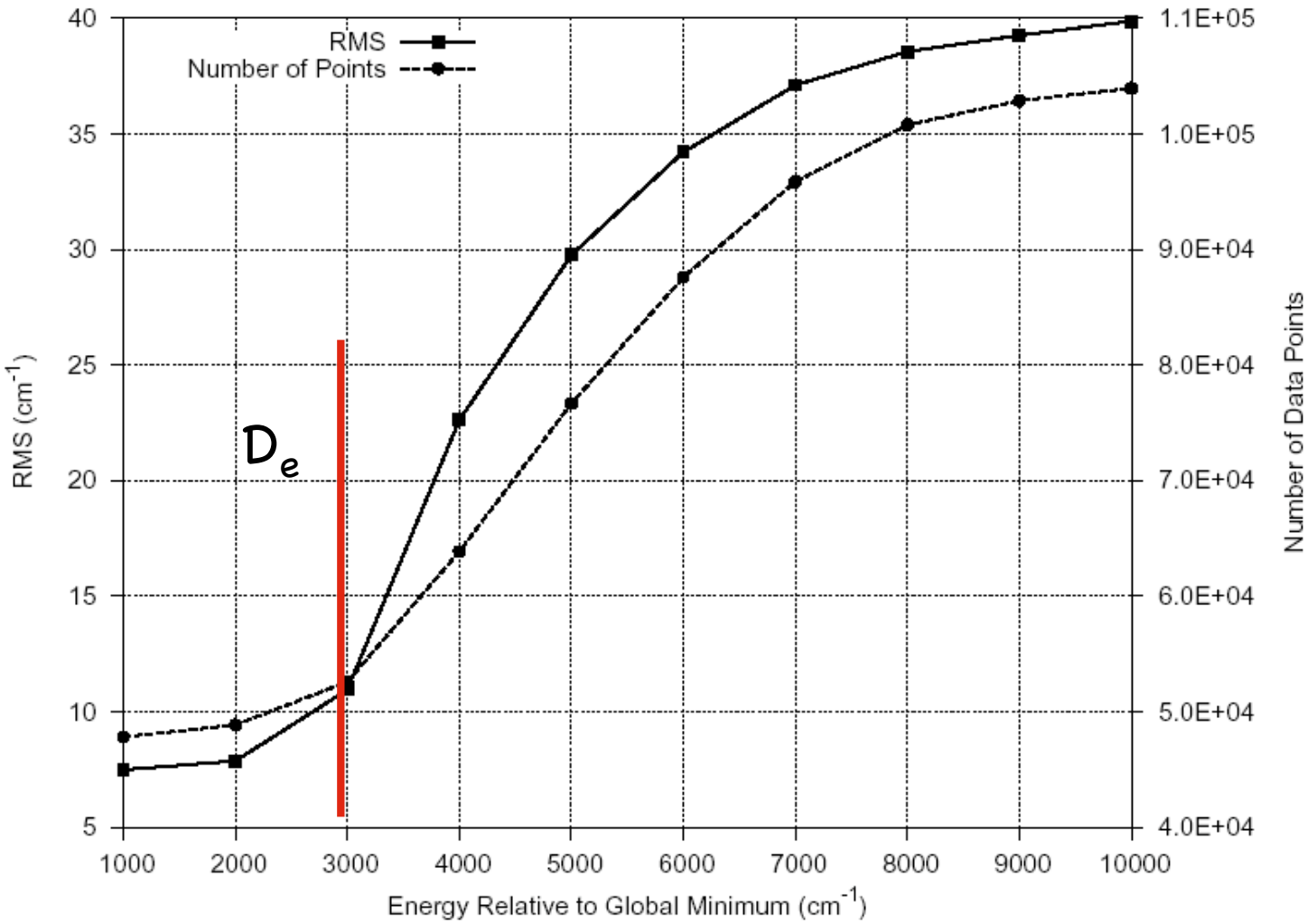


Roughly 110 000 *ab initio* energies [CCSD(T)/aug-cc-pVTZ] fit with a special basis of multinomials and n-body representation which includes separate fits to the fragments H_3^+ and H_2.

H_3^+ Fragment



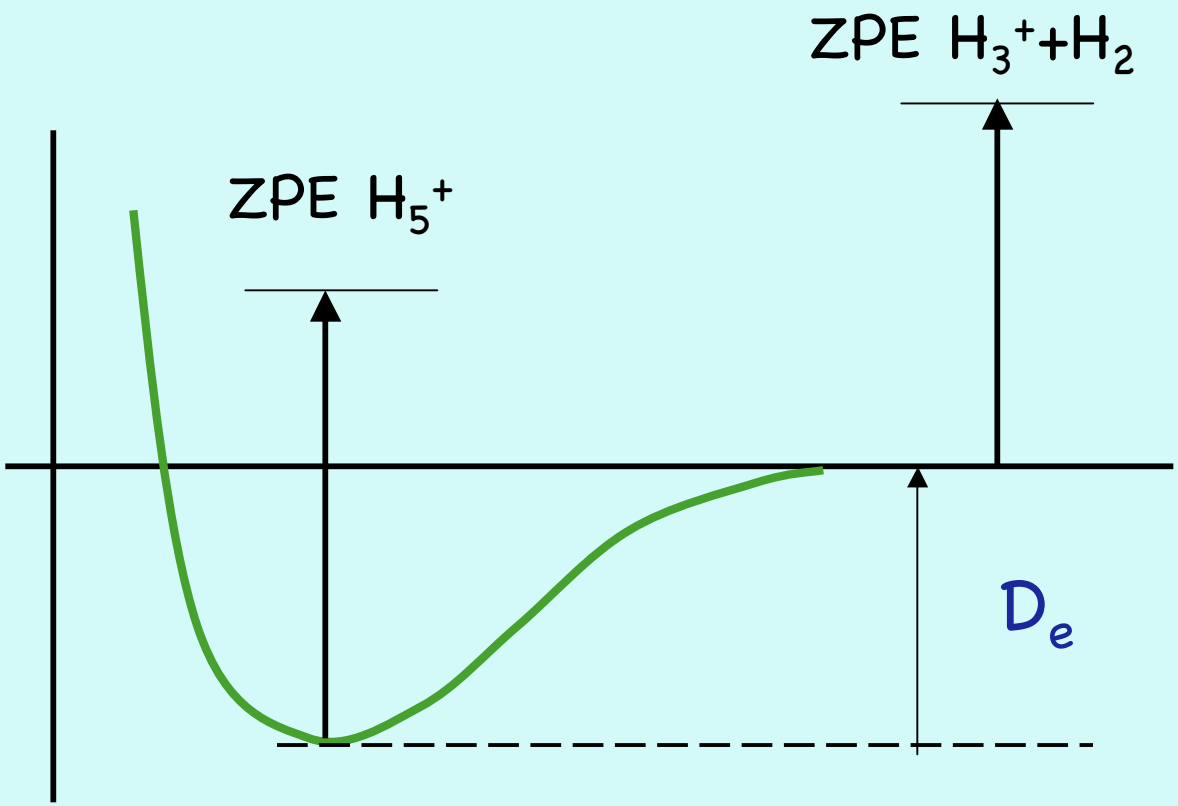
RMS Fitting Error



Thermochemistry

$H_5^+ \longrightarrow H_3^+ + H_2$, $D_0(\text{exp}) = 6.8 \pm 0.3$ kcal/mol

Recall $D_0 = D_e + \Delta ZPE$



Thermochemistry

$H_5^+ \longrightarrow H_3^+ + H_2$, D_0 = 6.8±0.3 kcal/mol

- The most accurate D_e = 8.58 kcal/mol
- The present PES D_e = 8.30 kcal/mol
- Using HO ZPEs PES gets D_0 = 5.57 kcal/mol

(Not in good agreement with experiment)

Quantum Diffusion Monte Carlo ZPEs

Solution to the TDSE

$$\Psi(t) = \sum_{n=0} \langle \chi_n | \Psi(0) \rangle \chi_n e^{-i(E_n - E_0)t}; \quad H\chi_n = E_n \chi_n$$

E_0 is the exact ZPE

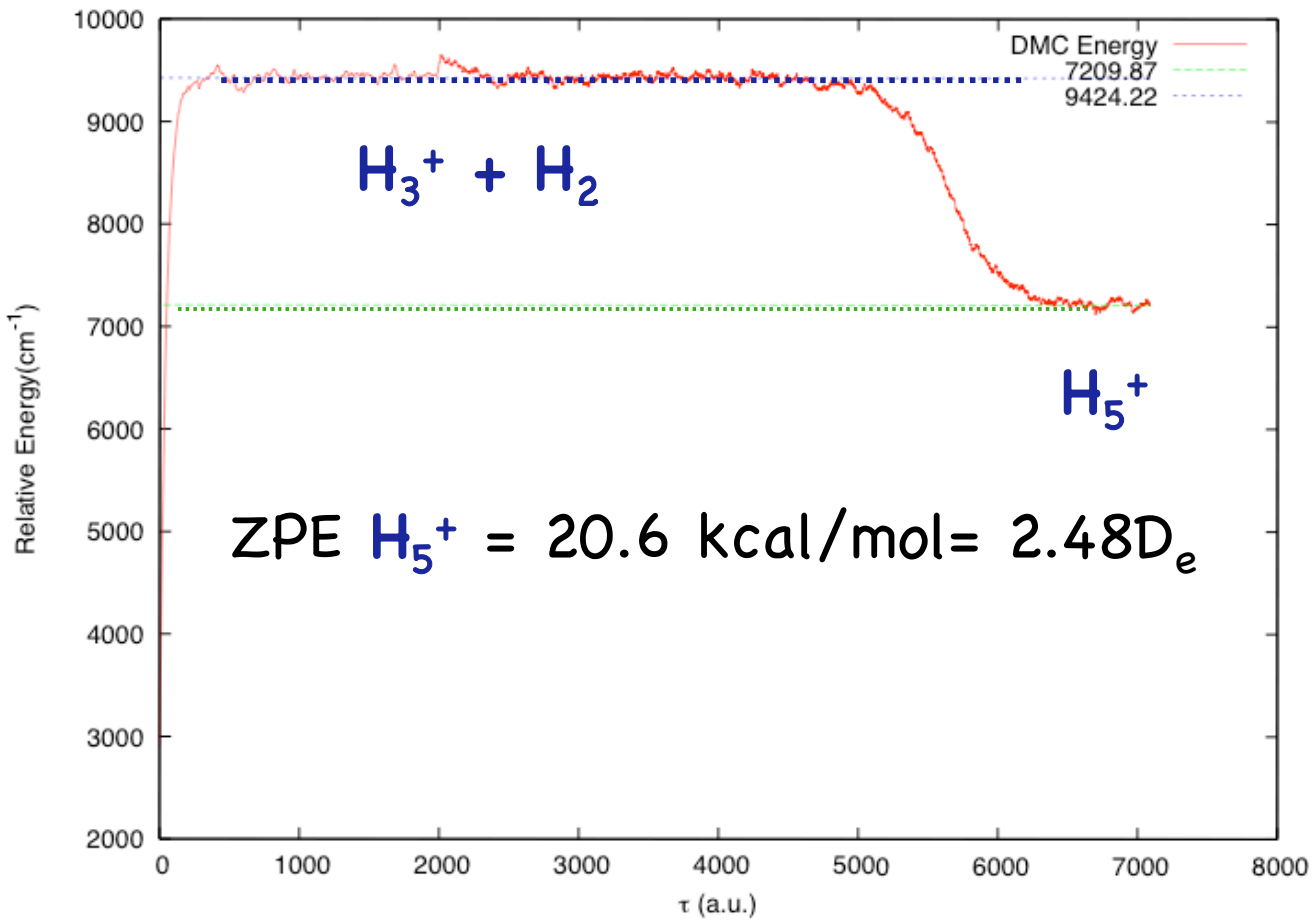
Let $\tau = it$

$$\Psi(\tau) = \sum_{n=0} \langle \chi_n | \Psi(0) \rangle \chi_n e^{-(E_n - E_0)\tau}$$

$$\xrightarrow[\tau \to \infty]{} \langle \chi_0 | \Psi(0) \rangle \chi_0$$

$$\frac{\langle \Psi(\tau) | H | \Psi(\tau) \rangle}{\langle \Psi(\tau) | \Psi(\tau) \rangle} \xrightarrow[\tau \to \infty]{} E_0$$

$H_5^+ \rightarrow H_3^+ + H_2$



(Application of DMC requires a global PES)

$$H_5^+ \longrightarrow H_3^+ + H_2$$

From the DMC ZPEs we get D_0 = 6.33±.03 kcal/mol

Exp* = 6.8±0.3 (HO = 5.57)

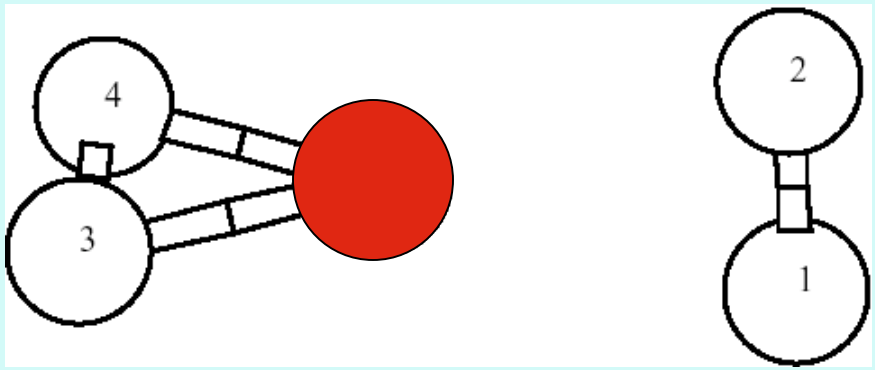
*Exp1 = 6.6 ±0.3, Exp2 = 7.0 ±0.1

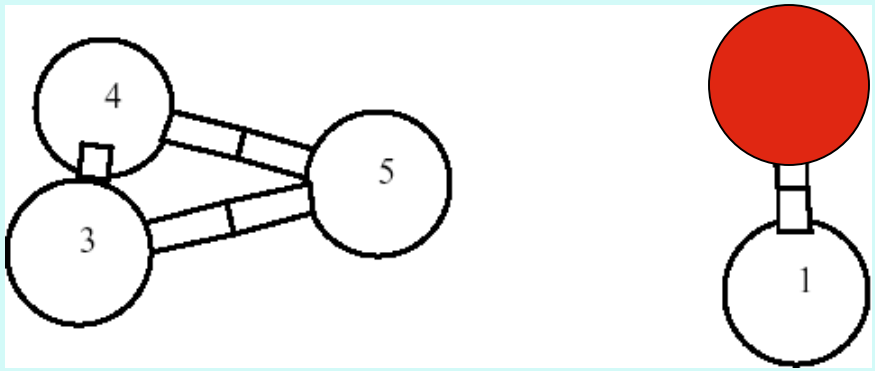
Present D_e is low by 0.28 compared to most accurate *ab intio* value

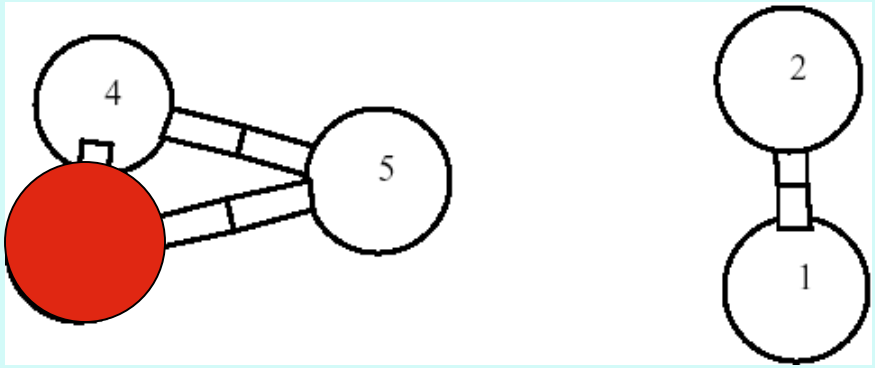
So, our estimate would be 6.6 kcal/mol

$$HD + H_3^+ \leftrightarrow H_4D^+ \rightarrow H_2^+ + H_2D^+$$

Structure of the Global Minimum



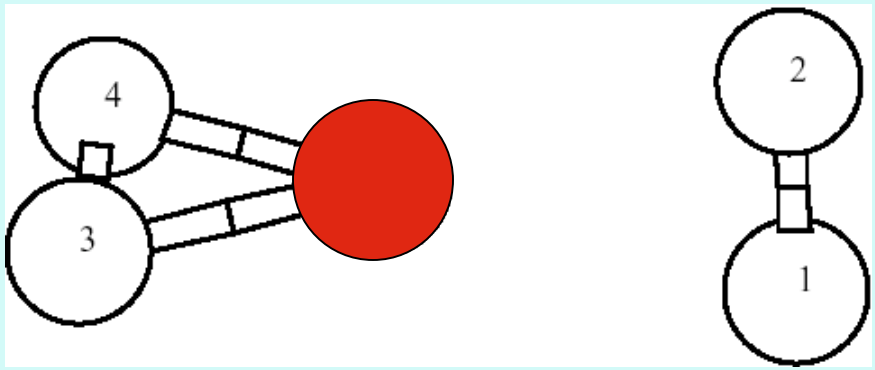


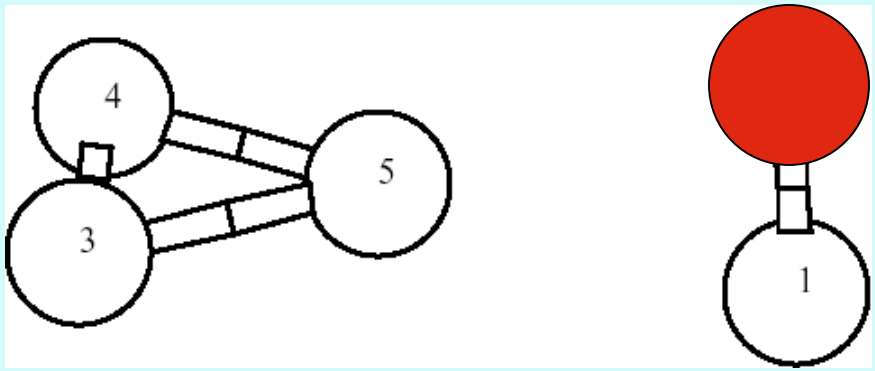


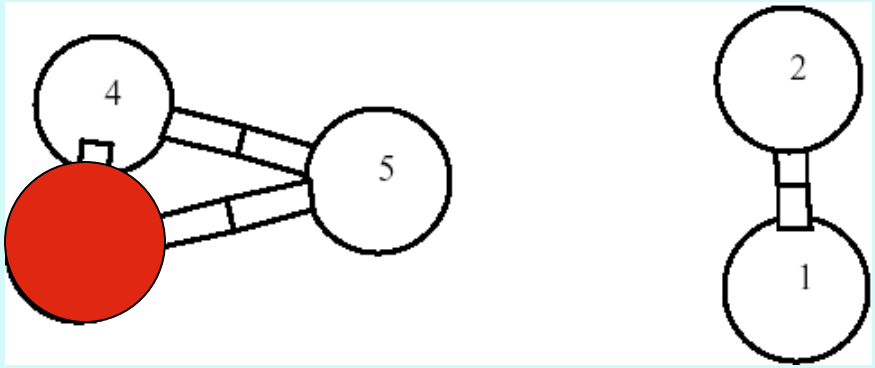
Three distinct localized locations for D

$$HD + H_3^+ \leftrightarrow H_4D^+ \rightarrow H_2 + H_2D^+$$

Structure of the Global Minimum







Three distinct localized locations for D

$$HD + H_3^+ \leftrightarrow H_4D^+ \rightarrow H_2^+ + H_2D^+$$

Classical MD starting at the 3 distinct locations with a total energy 28 kcal/mol (statistical expectation: 40% HD, 60% H_2)

TABLE VII: Classical branching ratio of products H_4D^+ indicated to initial configuration

Reaction Channel			Ratio
$H_3^+ \cdots HD$	$\rightarrow$	$HD+H_3^+$	0.549
	$\rightsquigarrow^a$	$H_2+H_2D^+$	0.451
$DHH^+ \cdots H_2$	$\rightsquigarrow$	$HD+H_3^+$	0.379
	$\rightarrow$	$H_2+H_2D^+$	0.621
$HHD^+ \cdots H_2$	$\rightsquigarrow$	$HD+H_3^+$	0.067
	$\rightarrow$	$H_2+H_2D^+$	0.933

[a] the squiggle arrow indicates a non-least motion path

$$HD + H_3^+ \leftrightarrow H_4D^+ \rightarrow H_2 + H_2D^+$$

Results are not statistical and not too surprising*

* • Distinct and quite "different" minima

• Dynamics is not "chaotic"

Caveats: The results are from classical MD.
the HO treatment of ZPE supports distinct minima
but the rigorous DMC results are more equivocal.

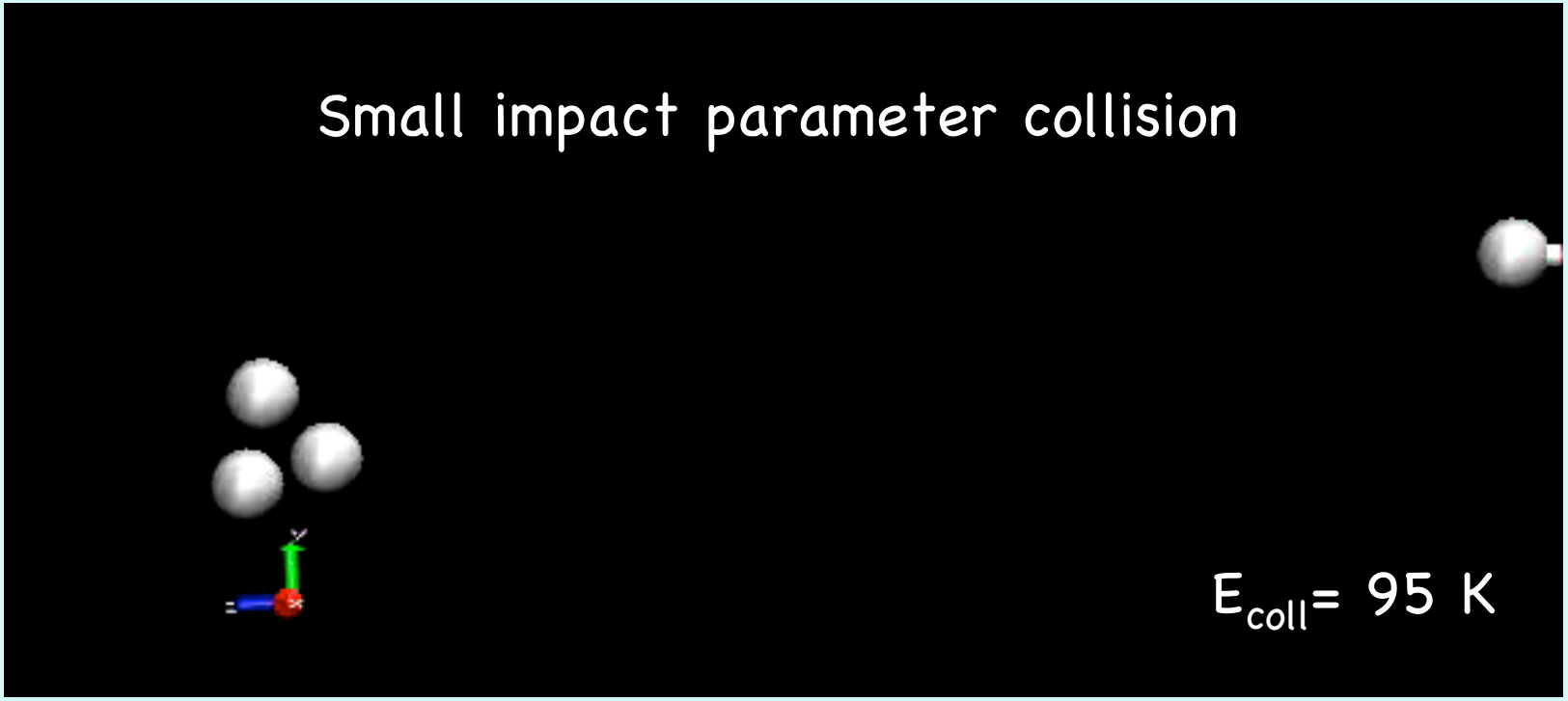
$HD + H_3^+ \rightarrow H_2^+ + H_2D^+$

The long range interaction

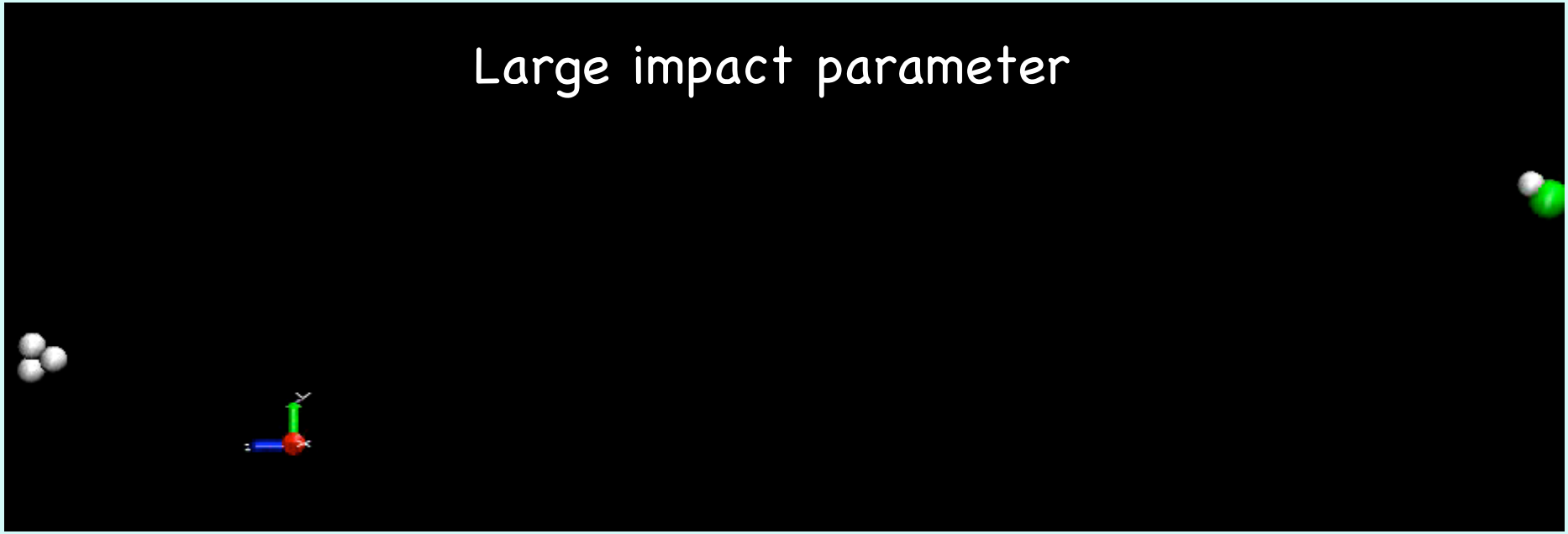
has been added to the PES

$$U_4 = -\left[\frac{1}{2}\alpha + \frac{1}{3}(\alpha_{\parallel} - \alpha_{\perp})P_2(\cos\theta)\right]/R^4$$

$$U_3 = Q_{H_2}P_2(\cos\theta)/R^3,$$



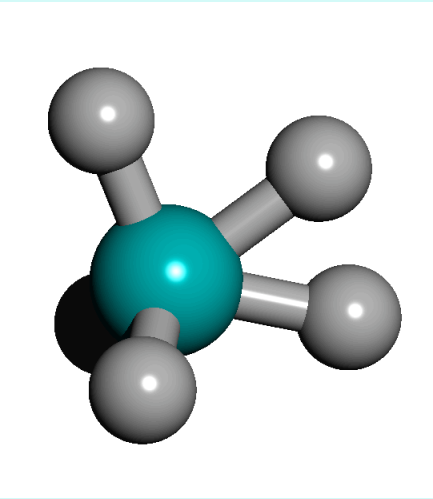
$$HD + H_3^+ \rightarrow H_2^+ + H_2D^+$$



To be continued…

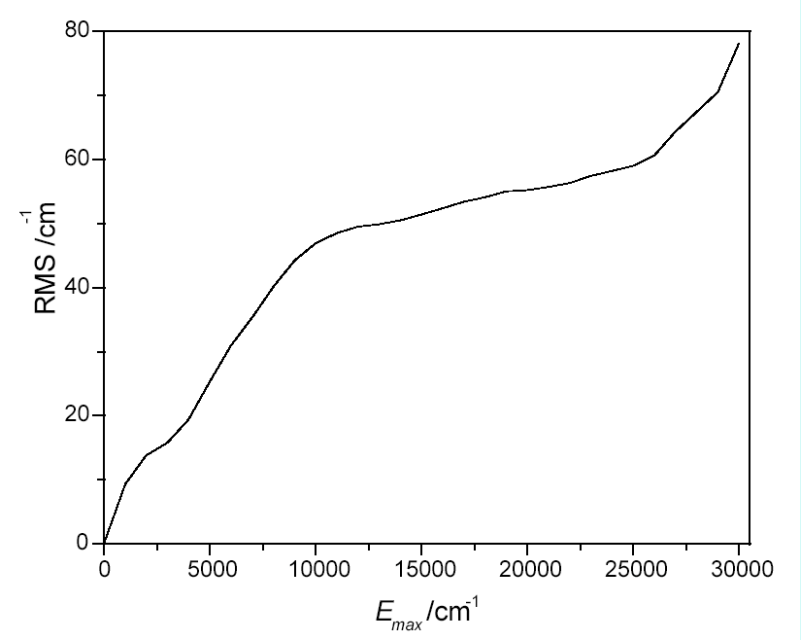
$$CH_5^+ \rightarrow CH_3^+ + H_2$$

CH_5^+



Like H_5^+ there are 5! equivalent Minima, saddle points.

Fit to 36173 CCSD(T)/aug-cc-pVTZ



Does CH_5^+ have a structure?

- Oka's unassigned spectrum
- Marx and Parinello
- Schaefer, Scheiner, Schlyer Klopper and Kutzelnigg

Submitted to PCCP 22.11.2004

Probing the structure of CH_5^+ ions and deuterated variants via collisions

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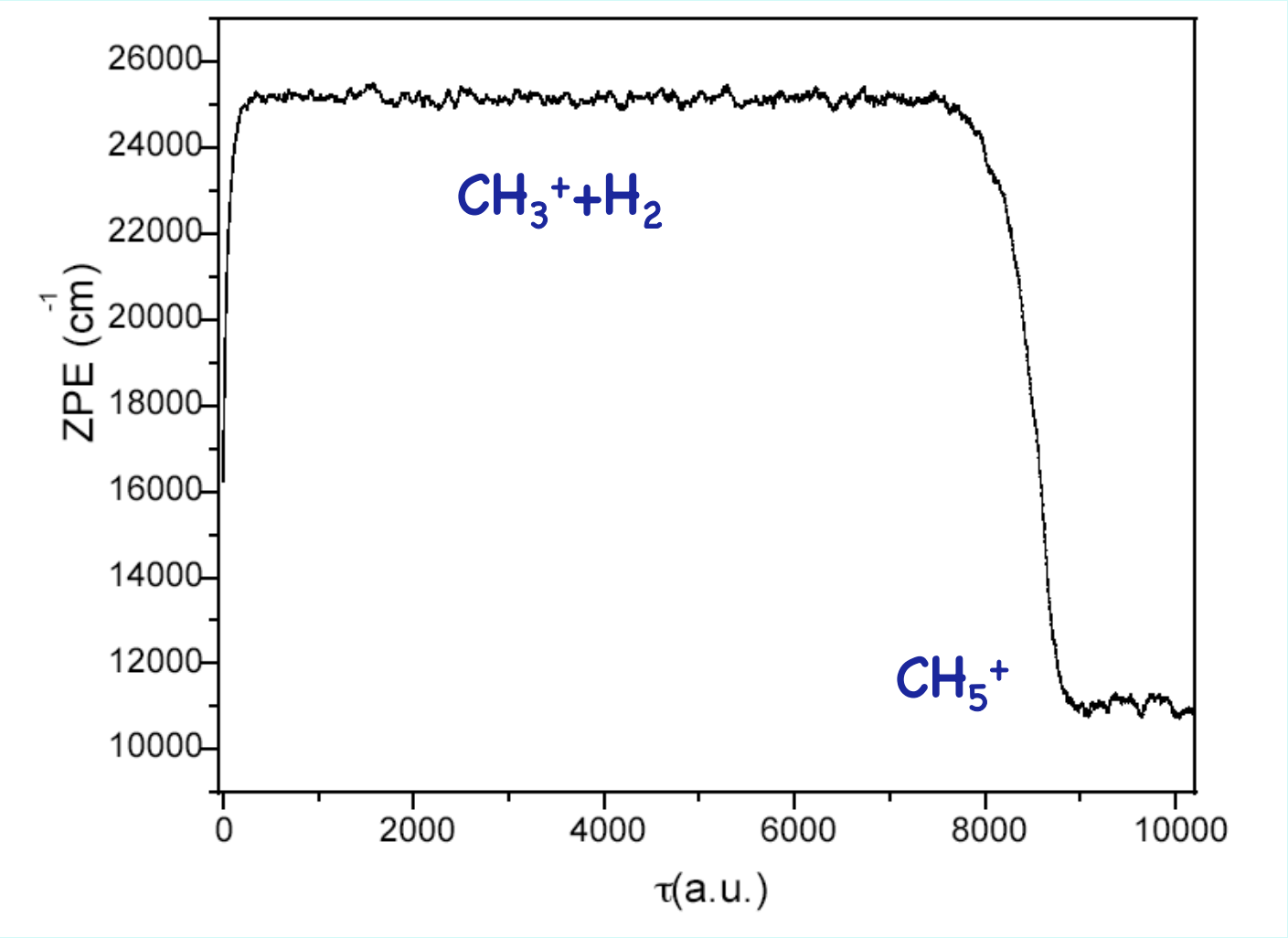
A. Brown, B. J. Braams, K. Christoffel, Z. Jin,
and J. M. Bowman, *J. Chem. Phys.*, 2003, **119**, 8790. - fit and MD spectrum

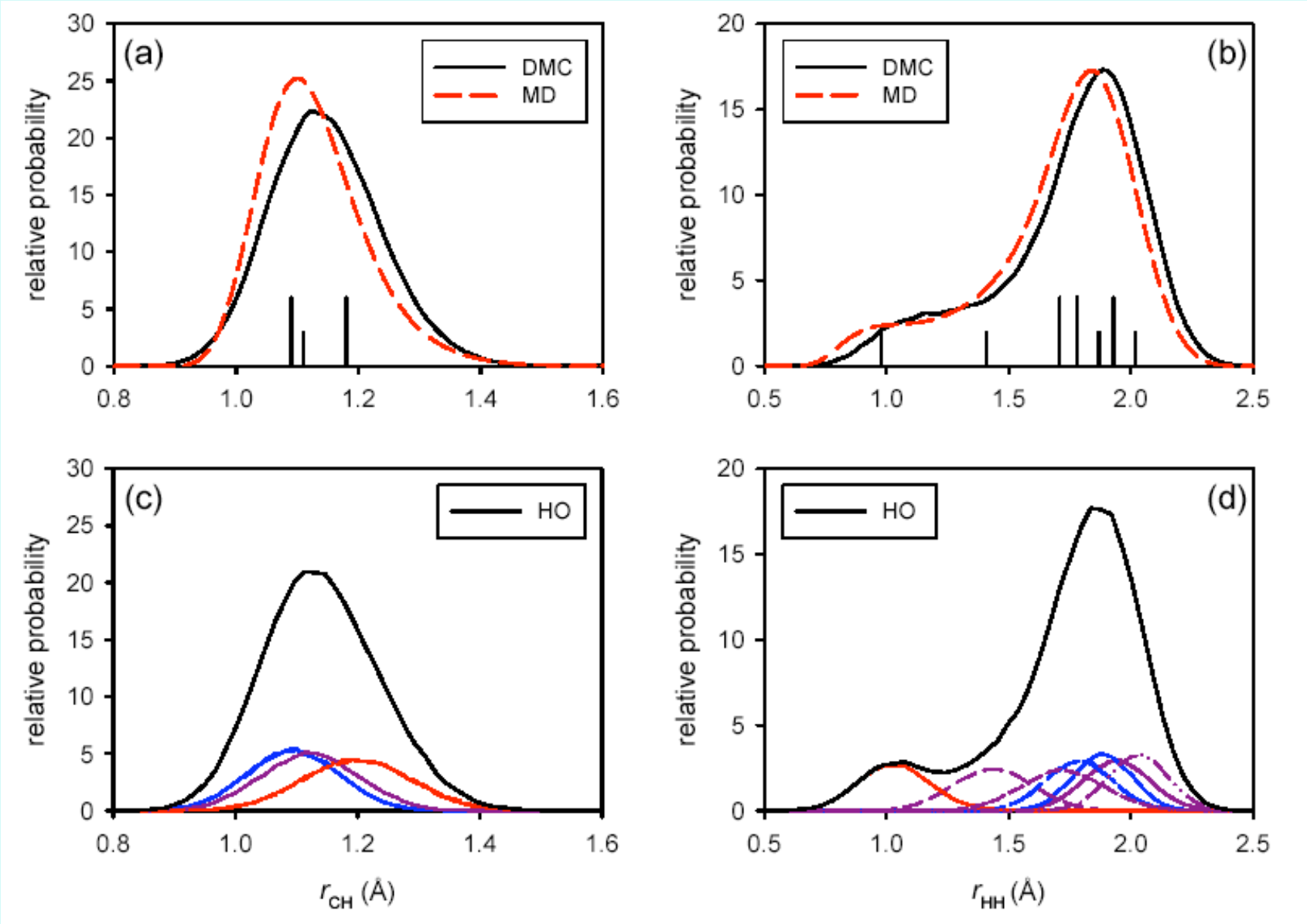
A. Brown, A. B. McCoy, B. J. Braams, Z. Jin,
and J. M. Bowman, *J. Chem. Phys.*, 2004, **121**, 4105. - fit and DMC

A.B. McCoy, B .J. Braams, A. Brown
et al., *J. Phys. Chem. A*, 2004, **108**, 4991. - DMC isotopmers

DMC Calculation of the ZPEs



Bond length distributions



$$CH_4D^+ \rightarrow CH_3^+ + HD,\ CH_2D^+ + H_2$$

Table IV Product ratio in the simulation of CH_4D^+ dissociation

Position of D	$HD + CH_3^+$ (%)	$H_2 + CH_2D^+$ (%)
2	33.2	66.8
3	37.1	62.9
4	35.5	64.5
5	34.0	66.0
6	35.4	64.6
Average	35.1	64.9

Close to statistical and independent of initial geometry

Summary and to do...

- *Ab initio* calculation of potential energy surfaces
- Fitting to global, P.I. forms
- Applications to two relevant but very challenging systems

  H_5^+ and CH_5^+
- Reviewed thermochemistry - need for accurate ZPE
- Reaction dynamics underway
- Cross sections, rate constants to very low T.
- Quantum effects in scattering?

Interest in $(H^+)(H_2O)_n$ and $(OH^-)(H_2O)_n$?