

*Experimental studies of non-adiabatic coupling
in dissociation of excited H₃ molecules.*

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☀ Mechanism for predissociation

(Schneider & Orel, Tashiro & Kato)

☀ New Surfaces of H₃ (M. Jungen)

☀ Momentum Correlation in H+H+H (Freiburg)

London, January 2006

Accurate Nonadiabatic Couplings for H₃ Application to predissociation of H₃ Rydberg states

Ioan F. Schneider and Ann E. Orel JCP **111** 5873 (1999)

Predict the lifetimes of $2s A_1'$, $3s A_1'$, and $3p E'$ states,
based on *ab initio* calculations of the nonadiabatic coupling

Nuclear motion of H₃ restricted to C_{2v}

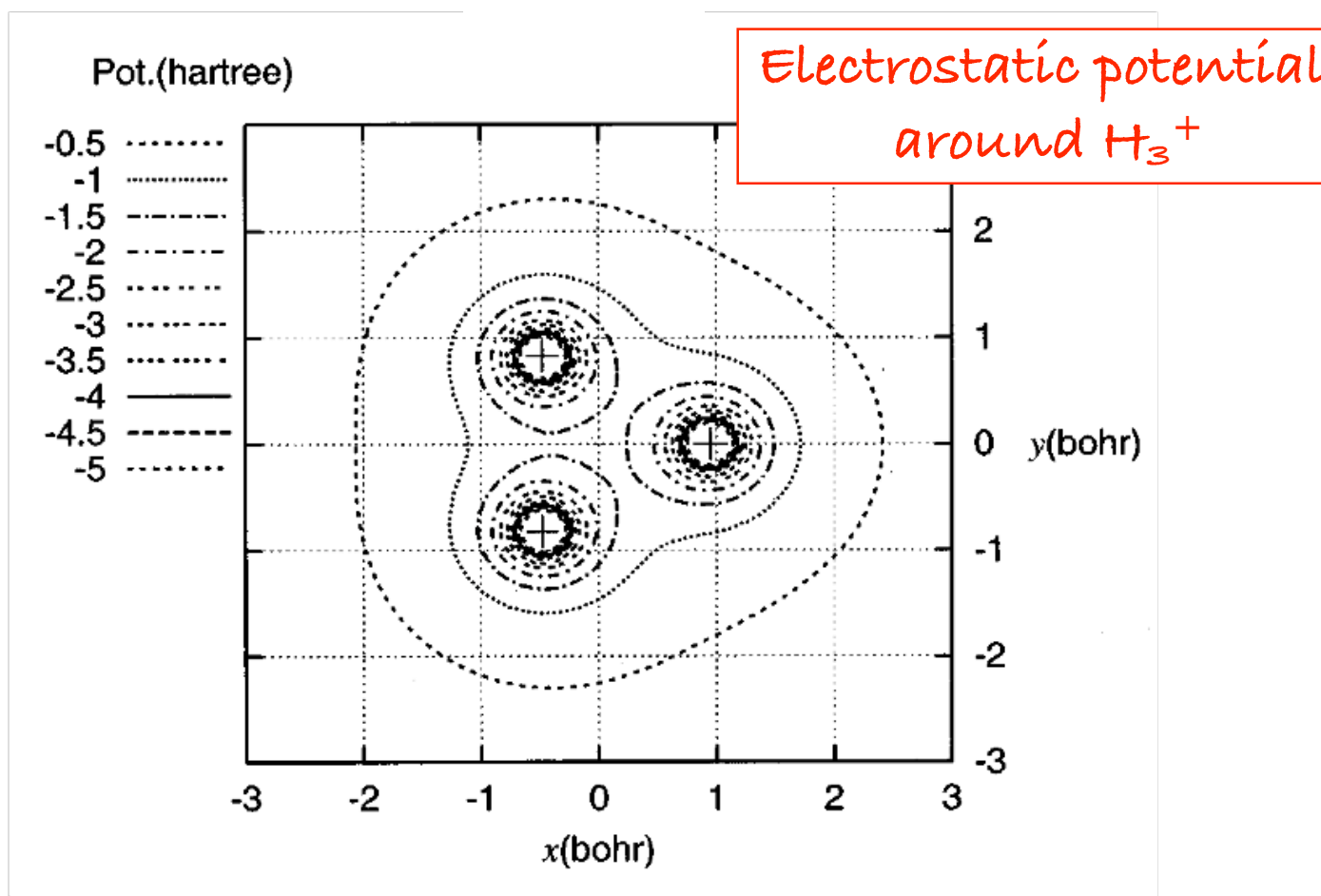
Direct coupling between $2p E'$ and excited Rydberg states

Also correctly predict the H₂(v)+H distributions

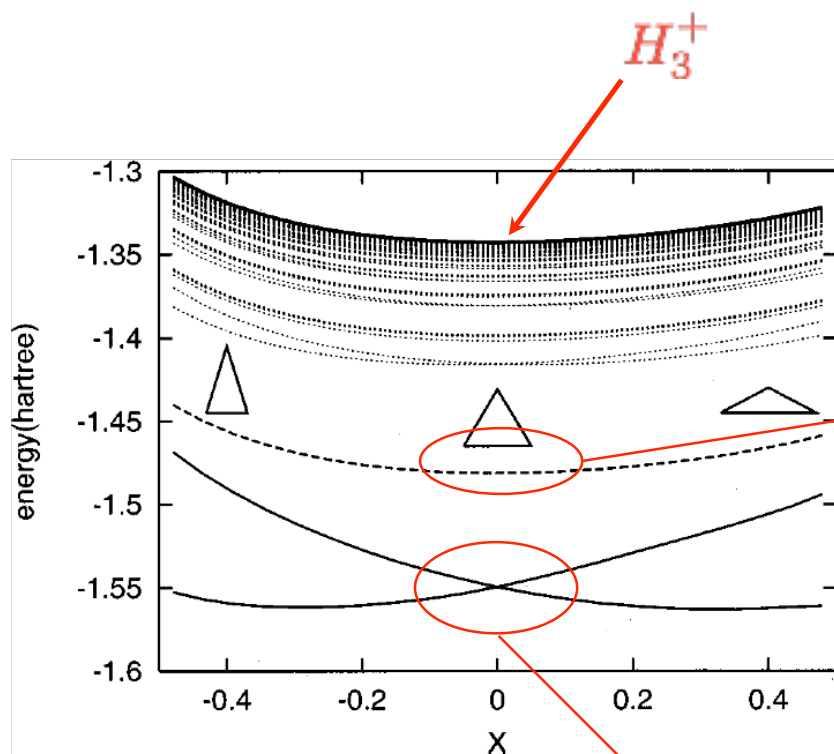
$\Gamma (s^{-1})$	theory	experiment
$2sA_1'$	5.7×10^{12}	6.6×10^{12}
$3sA_1'$	1.2×10^8	$\approx 1.0 \times 10^9$
$3pE'$	2.6×10^{10}	$< 1.5 \times 10^{10}$

Quantum dynamics study on predissociation of H_3 Rydberg states: Importance of indirect mechanism

Motomichi Tashiro and Shigeki Kato JCP **117** 2053 (2002)



Electronic States of H_3



~~$2pA_2''$~~

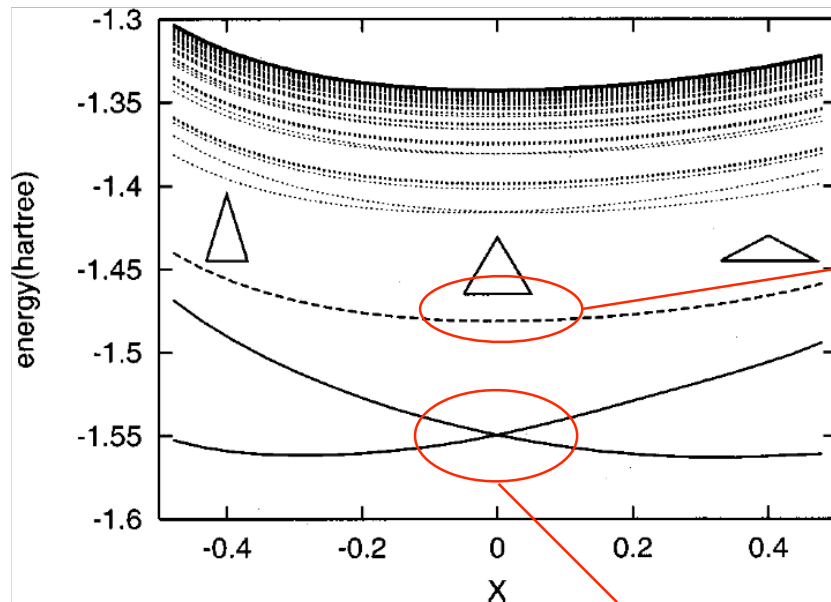
- isolated state
- rapid predissociation (170 fs, Herzberg)

$2sA_1'$

$H+H+H$

$2pE'$

NA-Coupling of $2s A_1'$ with $2p E'$

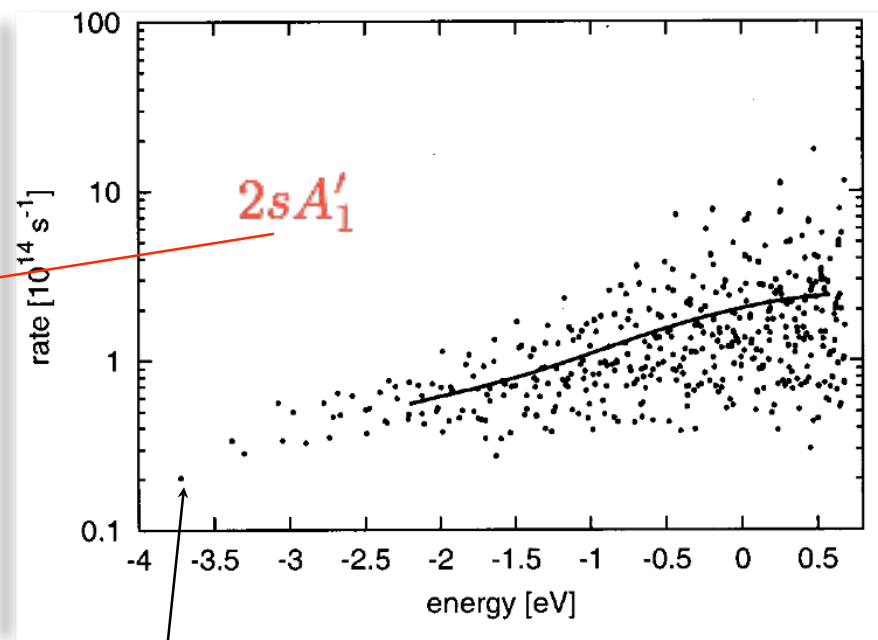
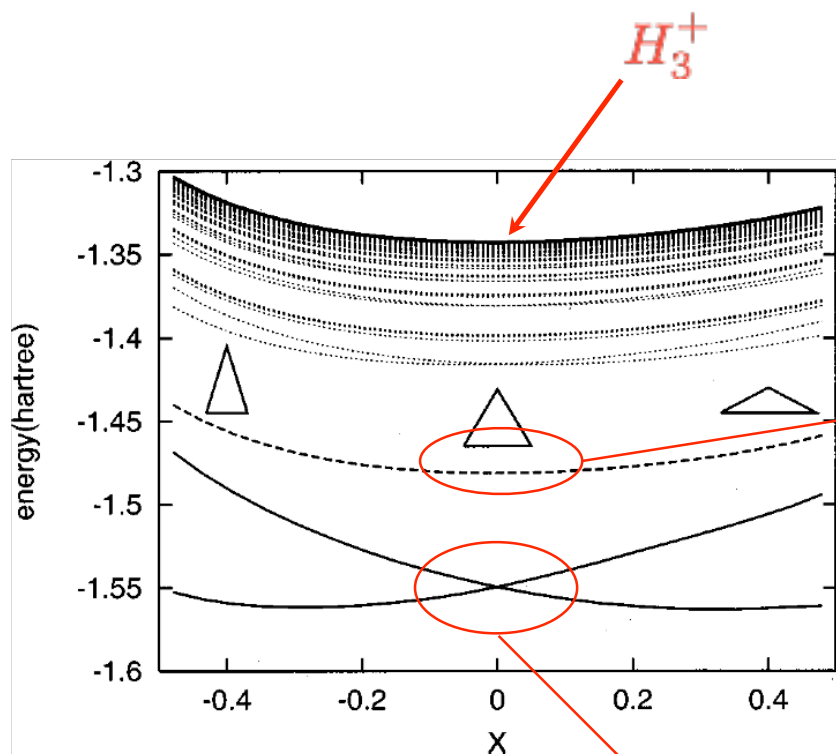


$2s A_1'$

$$\hat{V} = -\frac{\hbar^2}{2\mu} \left[2 \langle \psi_d | \frac{\partial}{\partial \rho} | \psi_{2s} \rangle \frac{\partial}{\partial \rho} + \frac{32}{\rho^2} \langle \psi_d | \frac{\partial}{\partial \theta} | \psi_{2s} \rangle \frac{\partial}{\partial \theta} \right. \\ \left. + \frac{16 \cos \theta}{\rho^2 \sin \theta} \langle \psi_d | \frac{\partial}{\partial \theta} | \psi_{2s} \rangle \right. \\ \left. + \frac{8}{\rho^2 \sin^2(\theta/2)} \langle \psi_d | \frac{\partial}{\partial \phi} | \psi_{2s} \rangle \frac{\partial}{\partial \phi} \right].$$

$2p E'$

Predissociation of $2s A_1'$ (v_1, v_2)

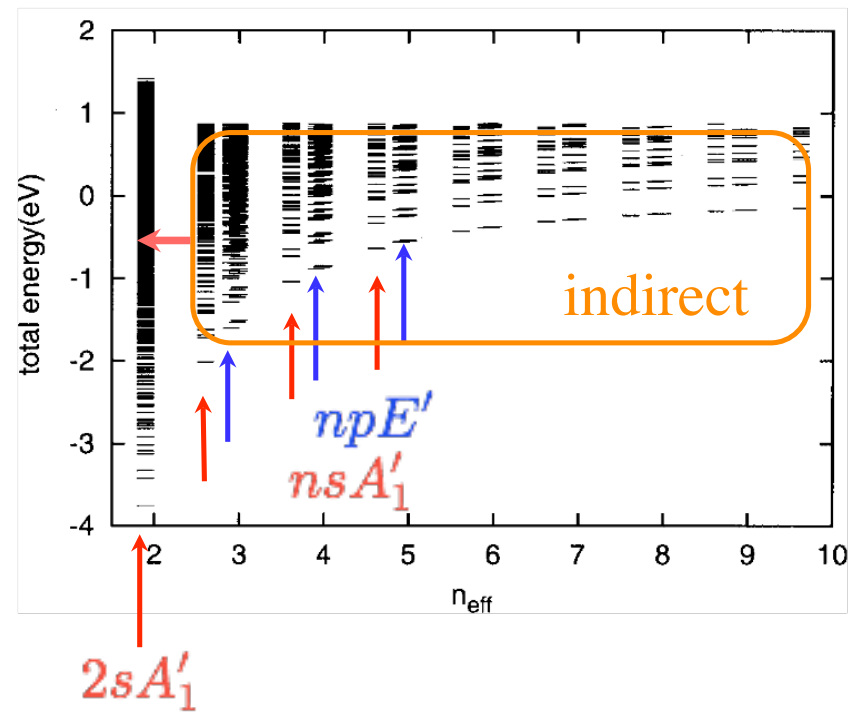
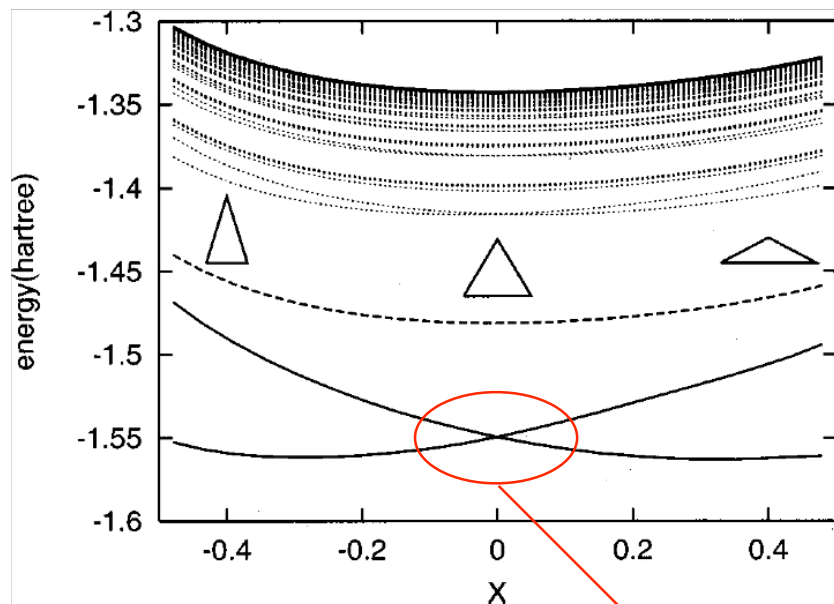


$2pE'$

50 fs

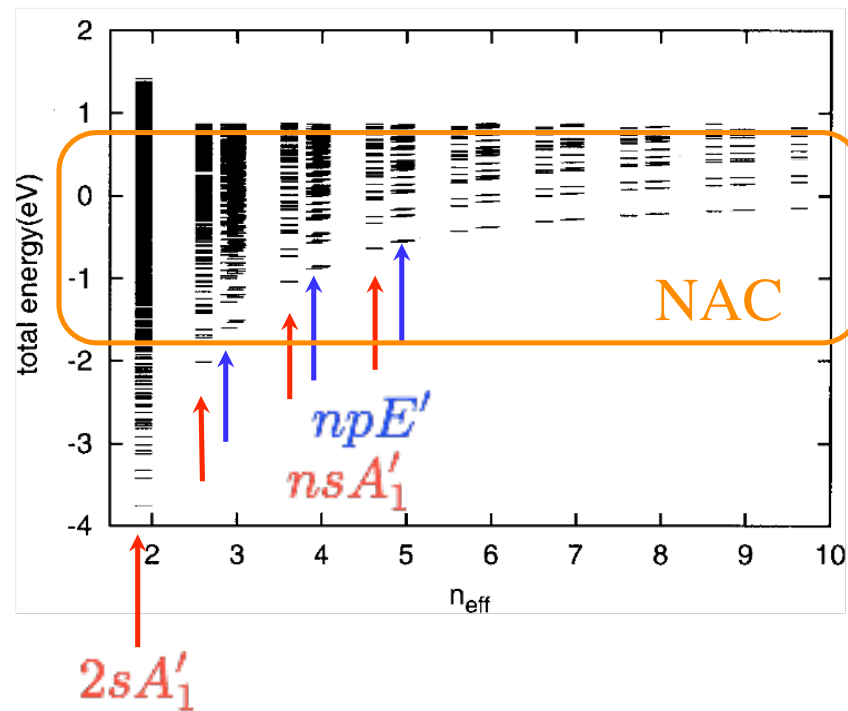
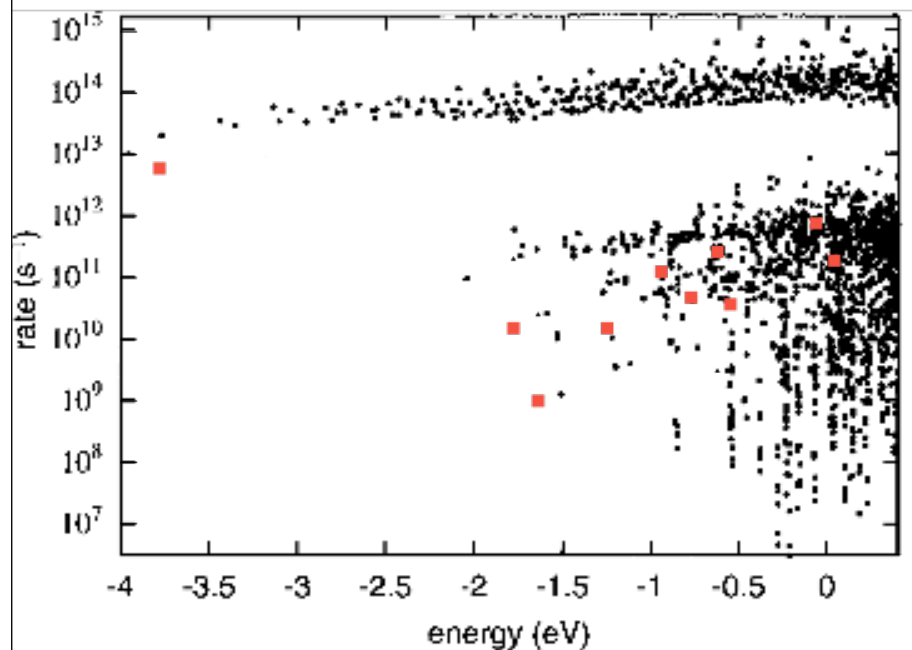
Exp: 190 fs

Bound vibrational levels (v_1, v_2)



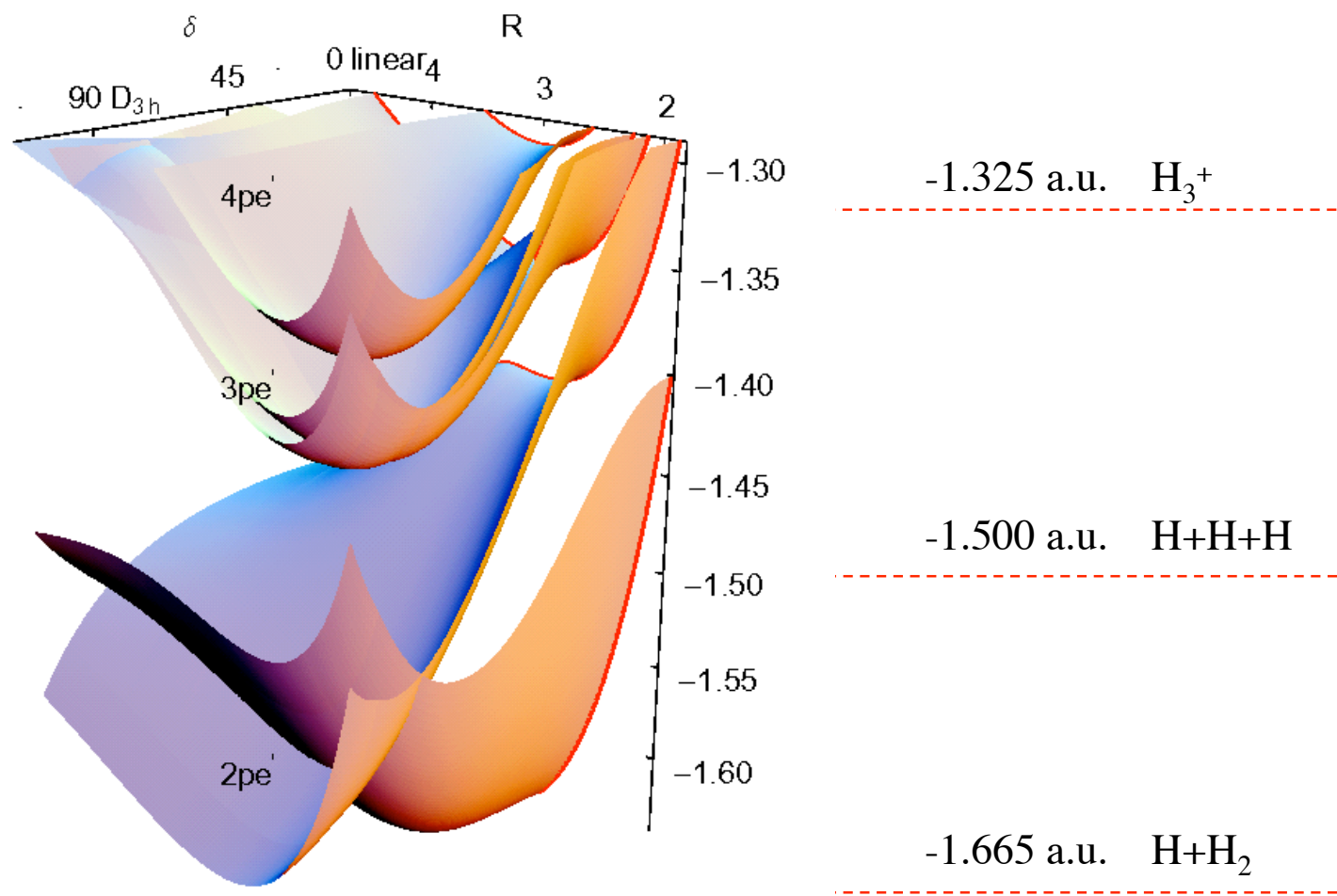
Decay of Bound vibrational levels

- theoretical
- experimental



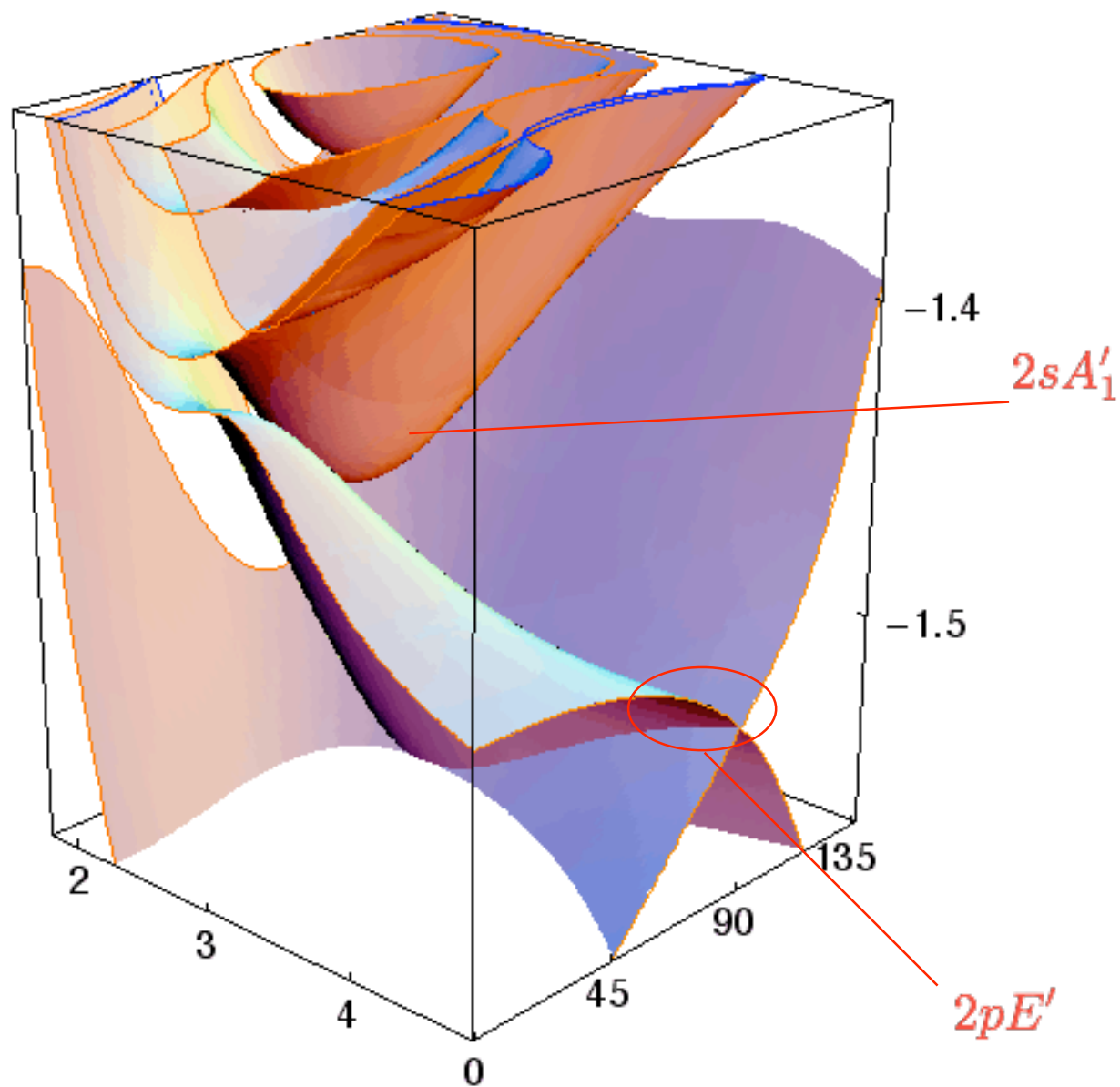
Quantum-chemical studies on the three-particle fragmentation of H_3

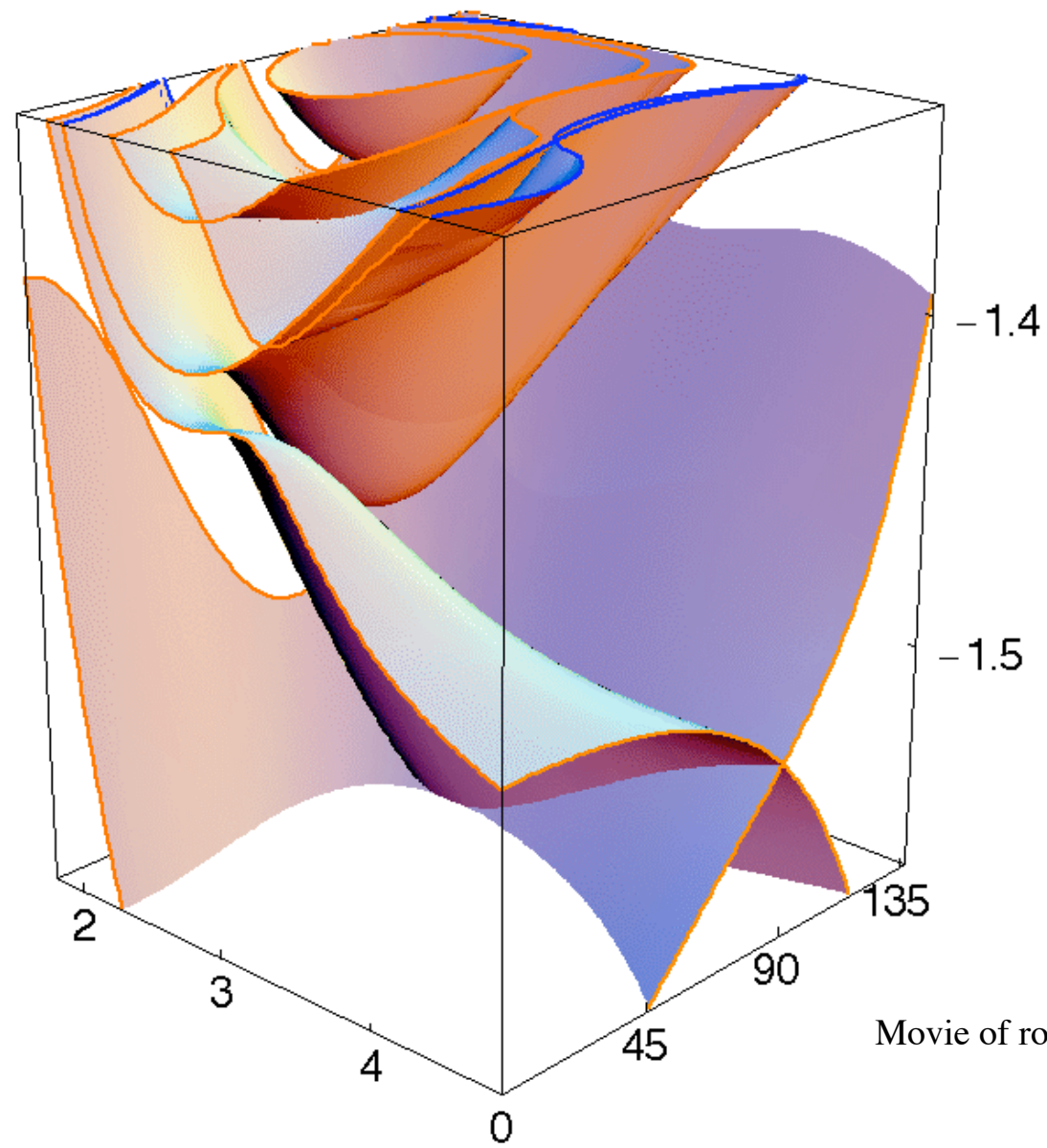
M. Jungen PRA 72 062506 2005



linear

D_{3h}





Movie of rotating cube

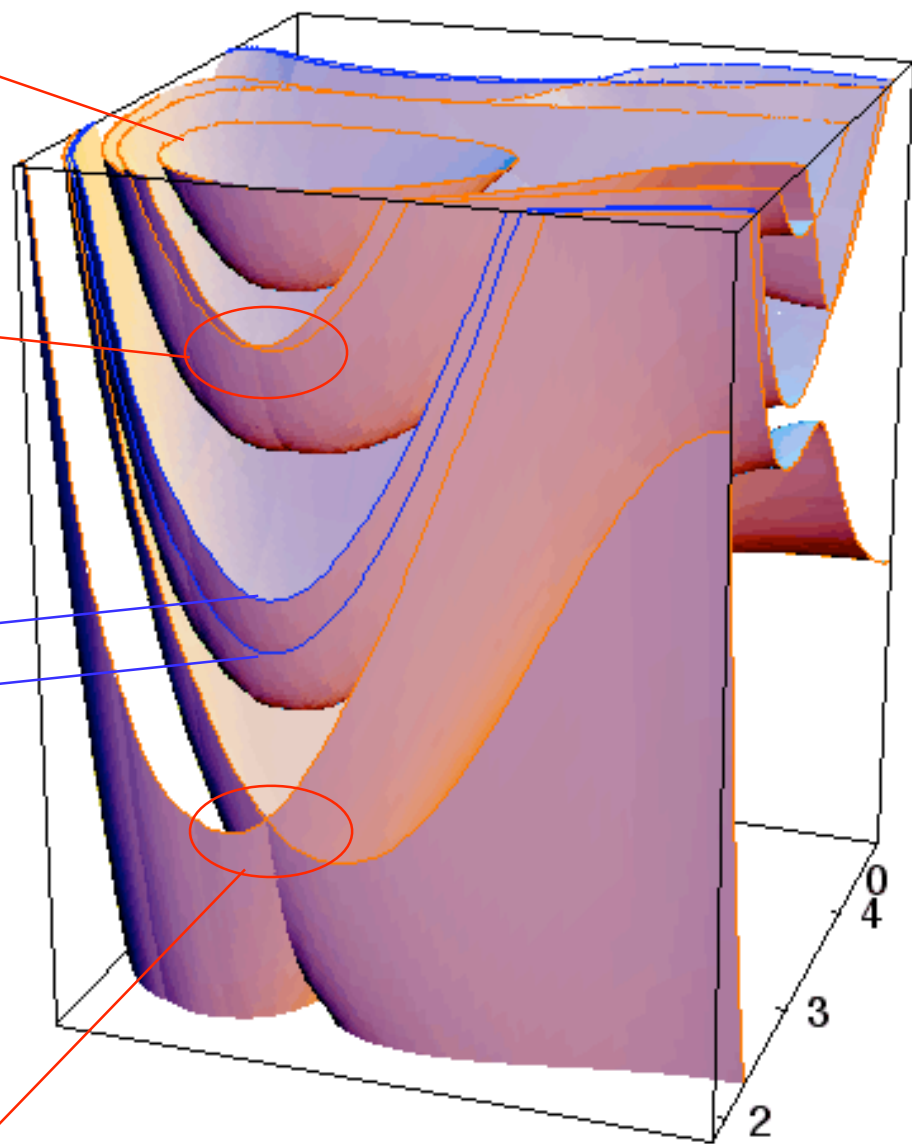
$4pE'$

$3pE'$

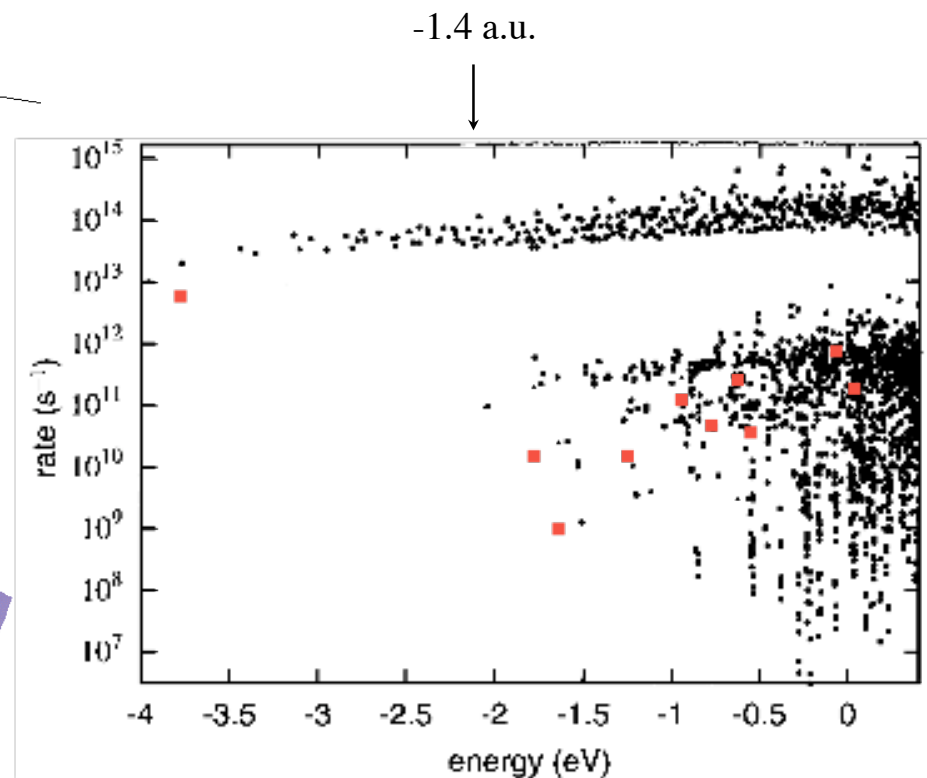
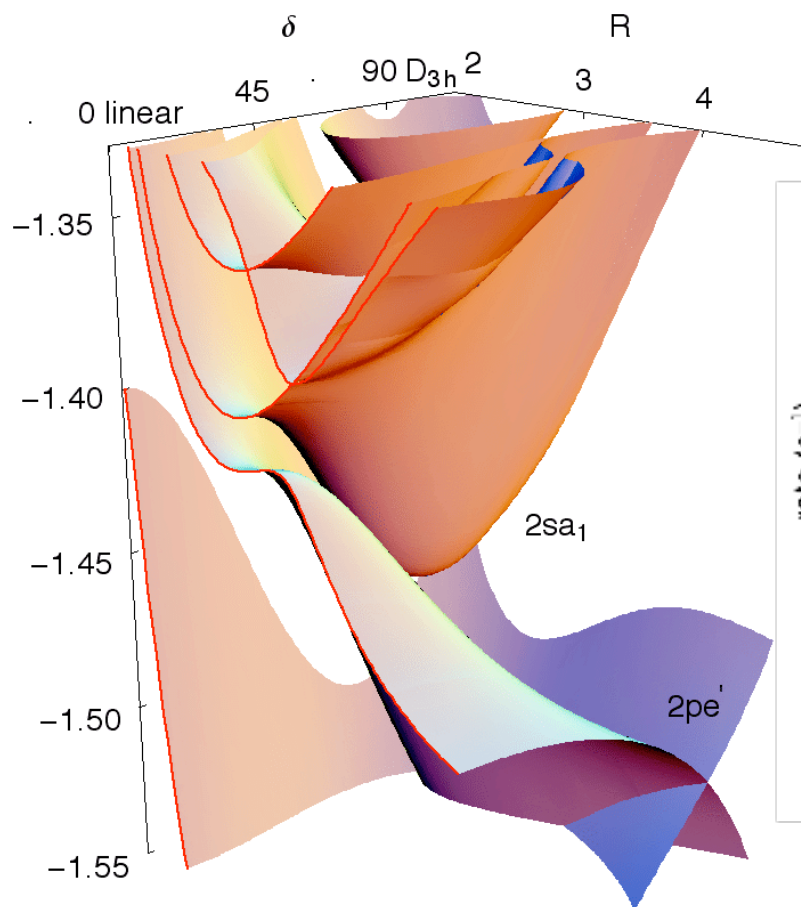
$2pA_2''$

$2sA_1'$

$2pE'$

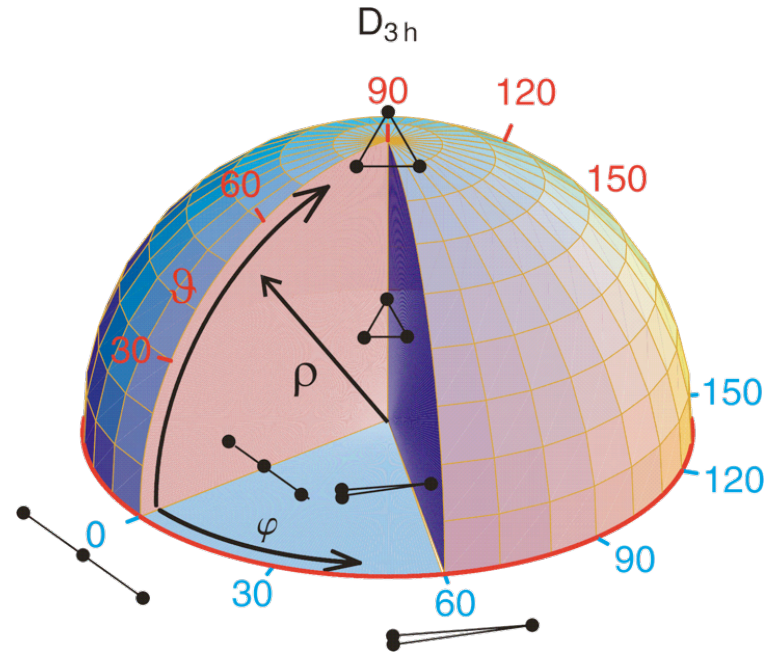
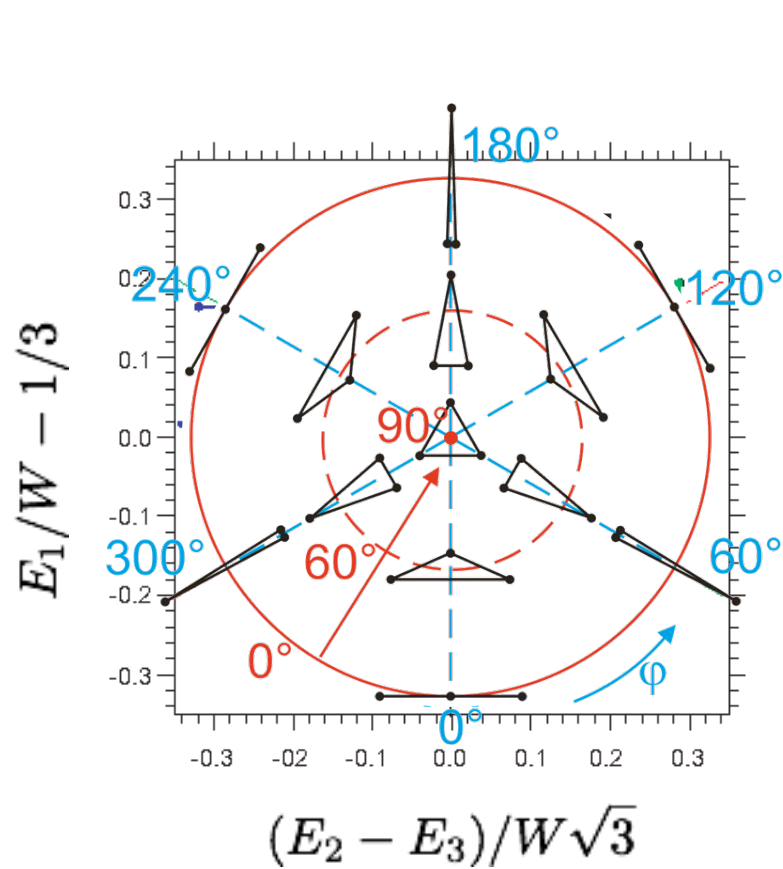


Decay of vibrational states of $2sA_1'$



Tashiro & Kato J. Chem. Phys. **117** 2002

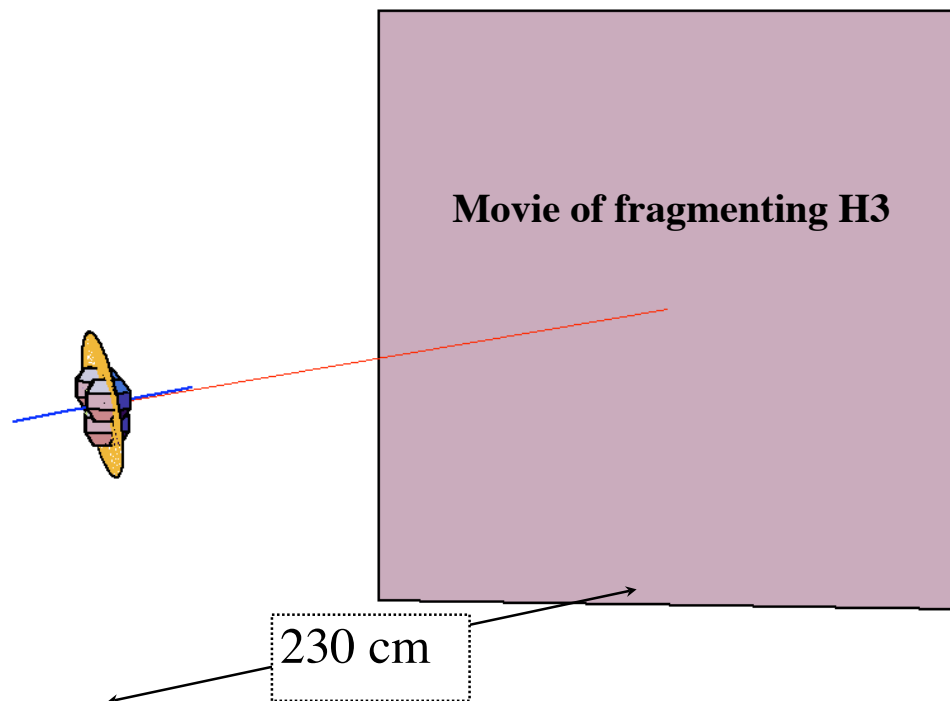
Hyperspherical Coordinates



$$W = E_1 + E_2 + E_3$$

Single Molecule Dissociation

- Fragments separate up to 10 cm
- Arrival time differences up to 300 ns



$$\Delta x, \Delta y < 100 \mu\text{m}$$

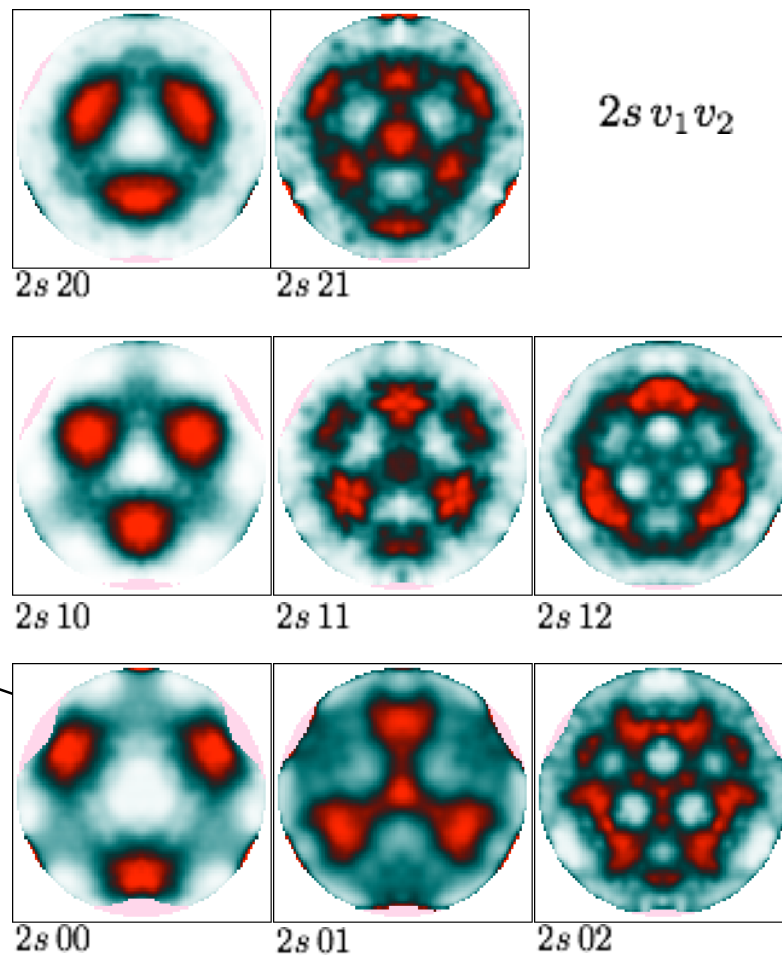
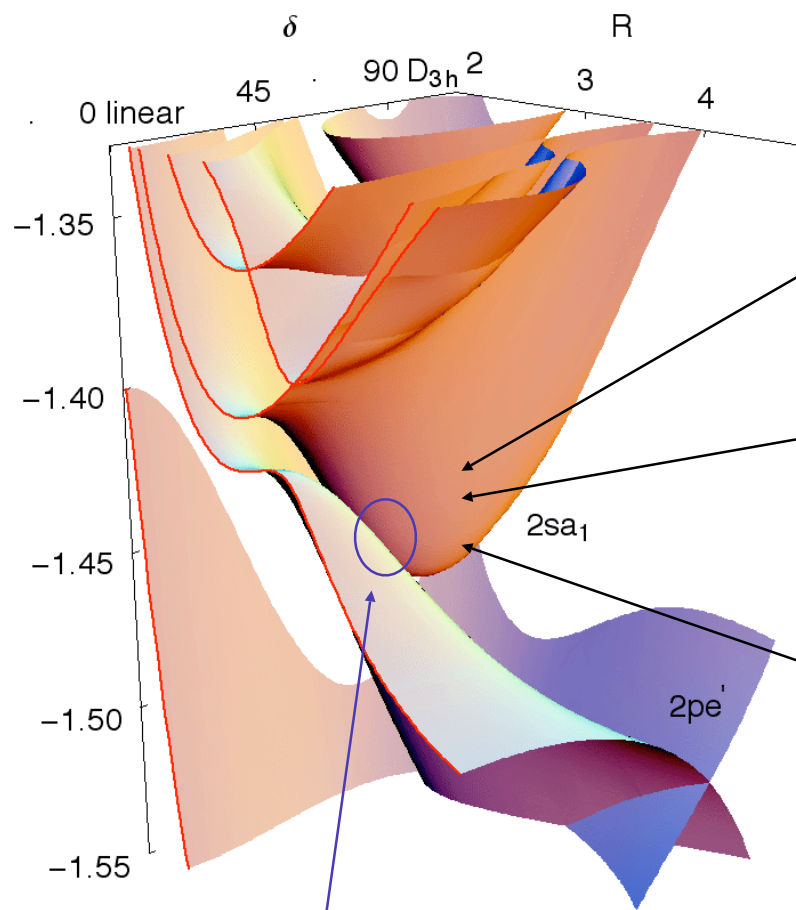
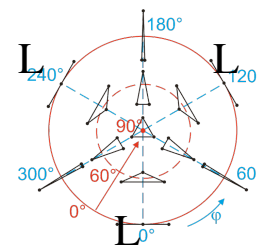
$$\Delta t < 100 \text{ ps}$$

U. Galster et al.

PRA **72** 062506 (2005)

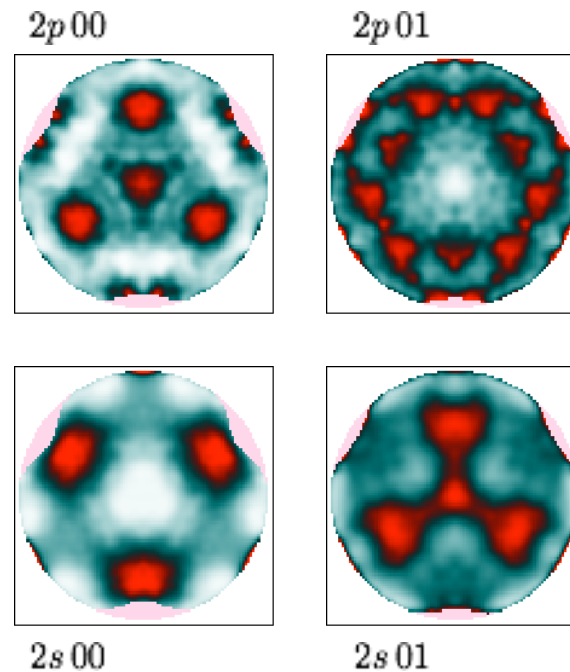
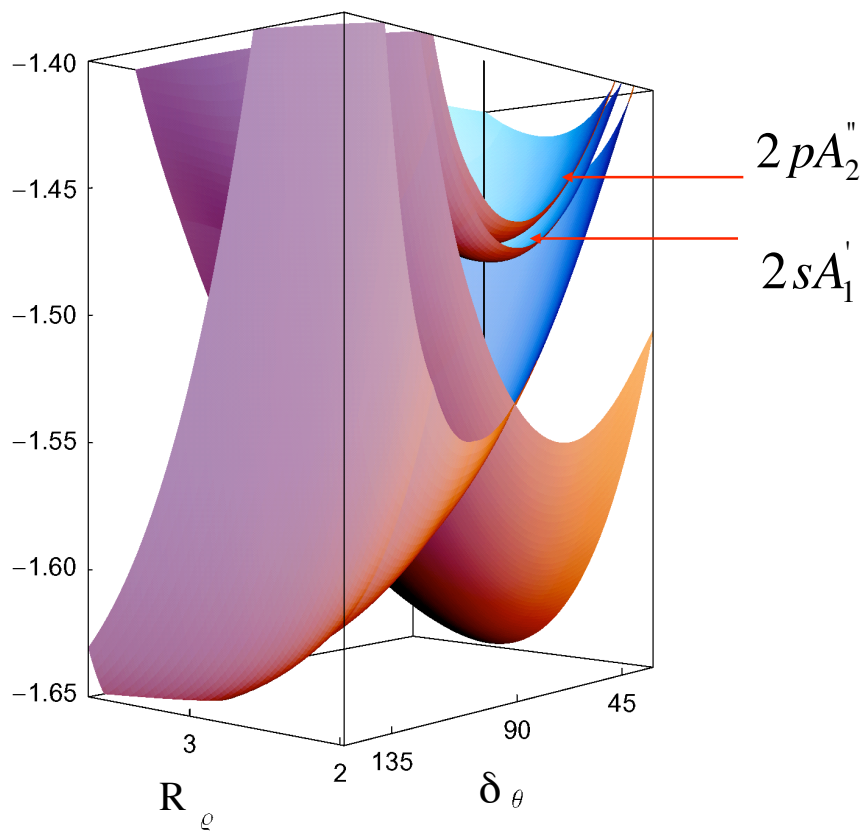
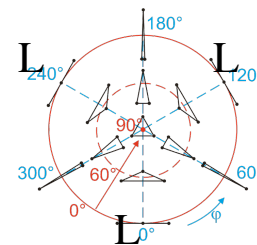
U. Müller et al. PRL 83, 2718 (1999)

Dissociation of $2sA_1'$ states



closest approach

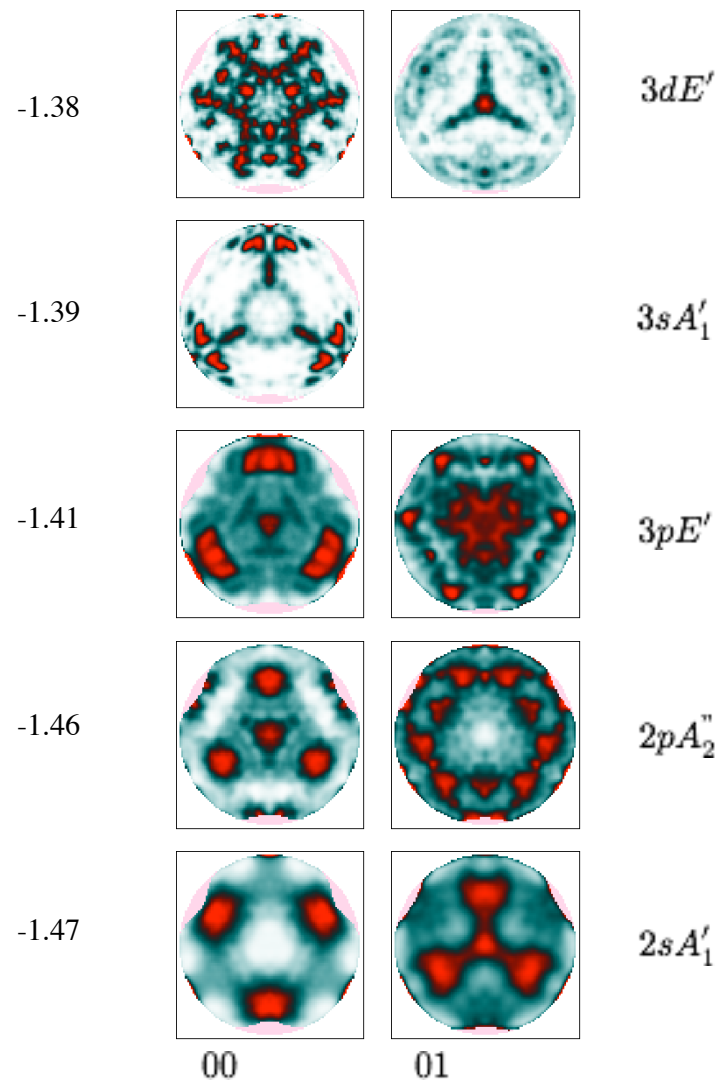
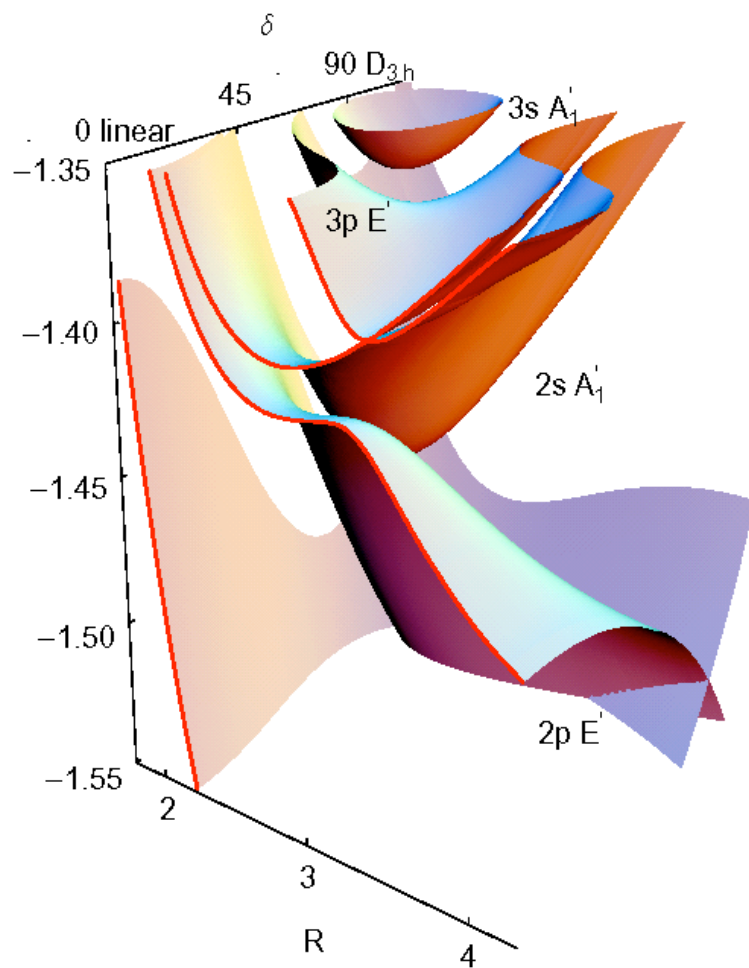
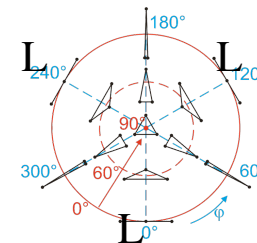
Compare $2sA_1$ and $2pA_2$ states



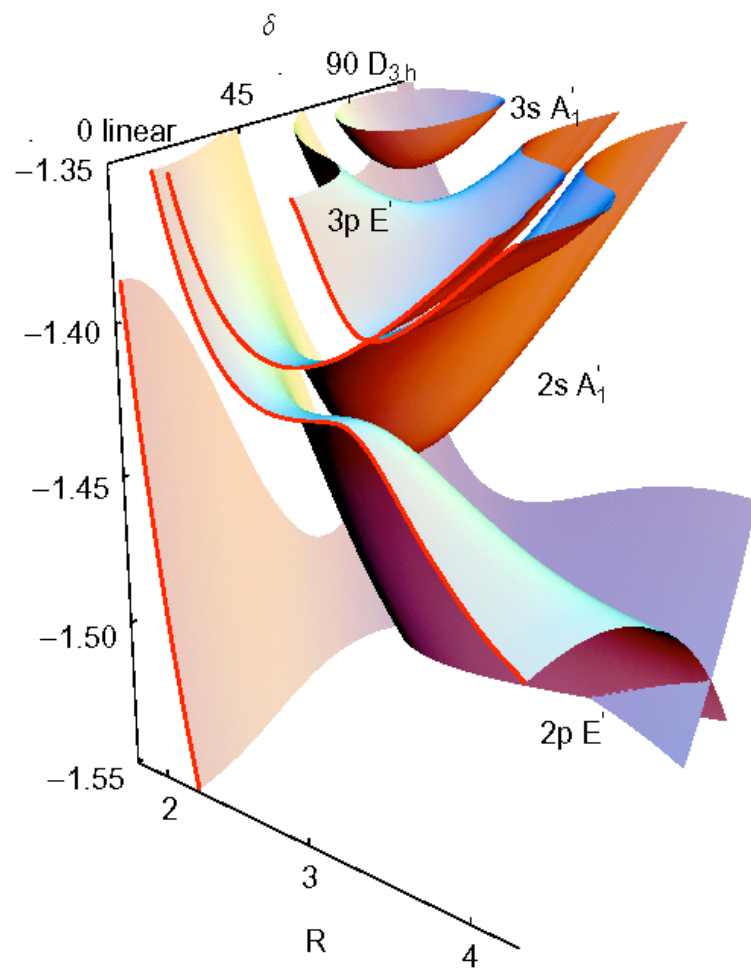
$2pA_2$: rotational coupling

$2sA_1$: vibronic coupling

Compare electronic excitation

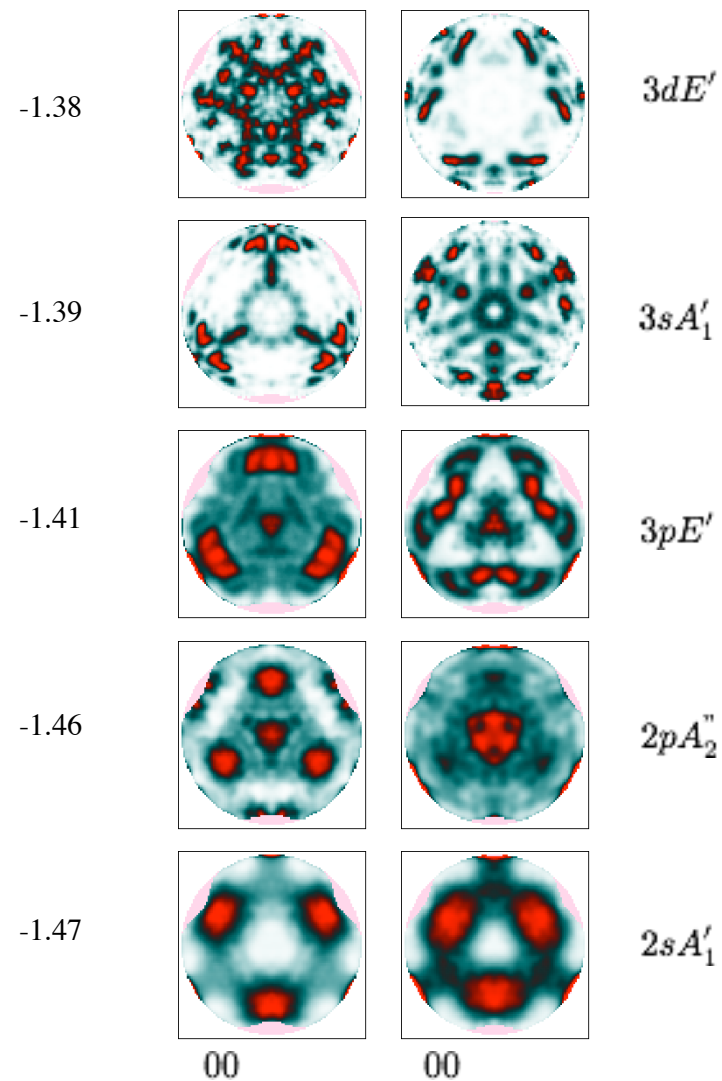


Compare isotopes

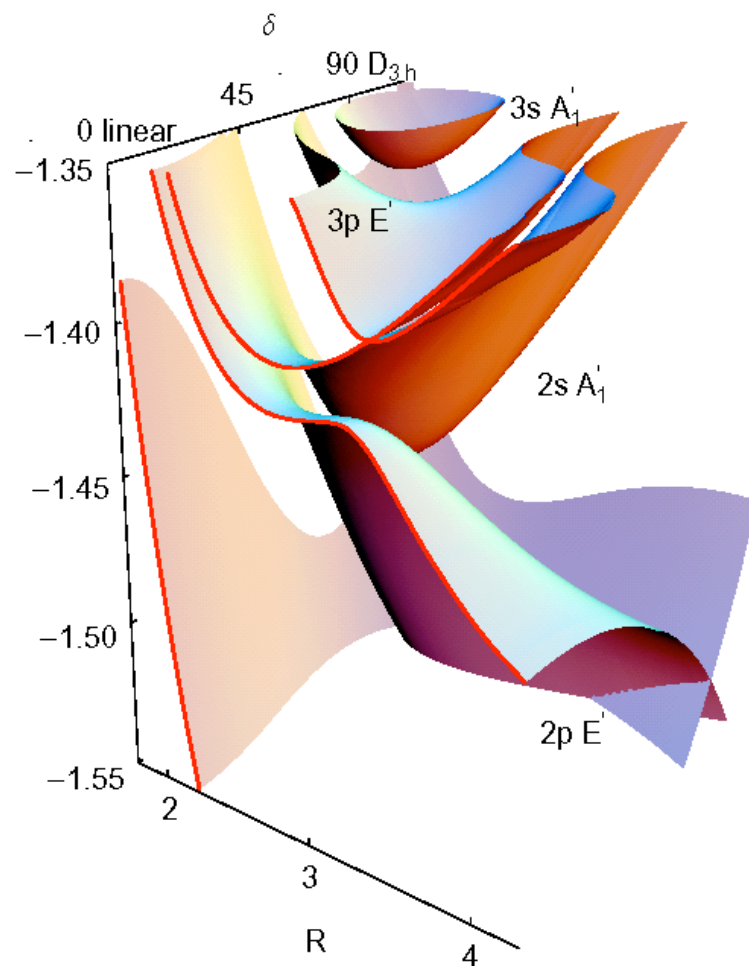


D_3

H_3



Dissociation paths from D_{3h} to linear geometry



Indirect mechanism

Jahn Teller coupling

Conclusion:
we still lack a good description
of the dynamics in the
bound region of $e + H_3^+$