Resonances in Chemical Reactions : Theory and Experiment

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What is Chemical Reaction ?

Collision process between molecules (atoms) containing rearrangement of chemical bonding

Theoretically · · · ·

Nuclear dynamics on the potential energy surface

PES: Interaction potential energy between and atoms molecules

PES is determined by quantized electron motions (within Born-Oppenheimer approximation)

Determination of accurate potential energy surfaces (PESs) of chemical reactions

Solving electronic structure problems for given a nuclear configuration

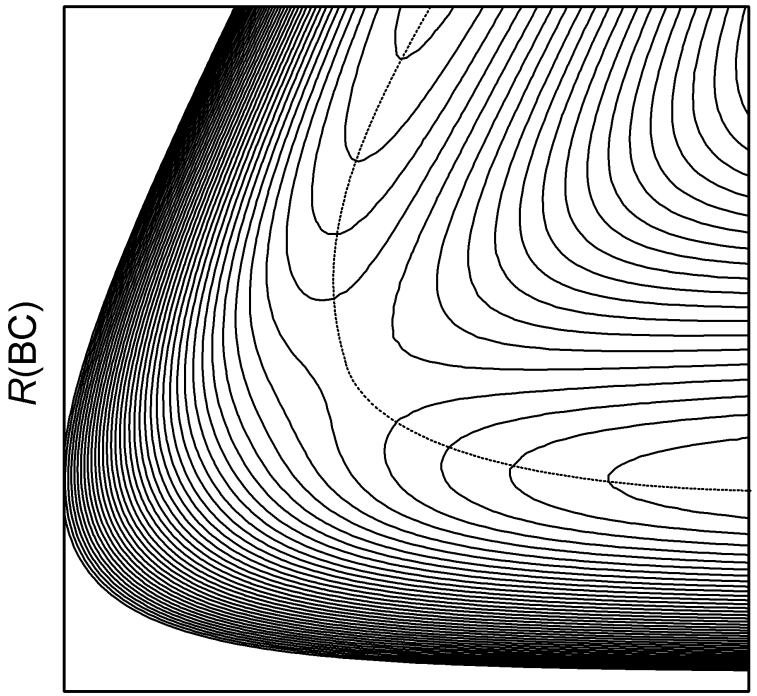
ab initio quantum chemistry calculations in chemistry field

First-principles calc. in physics

Many package programs: Gaussian, Molpro, Molcas etc.

Very accurate calculations can now be possible for very small chemical systems

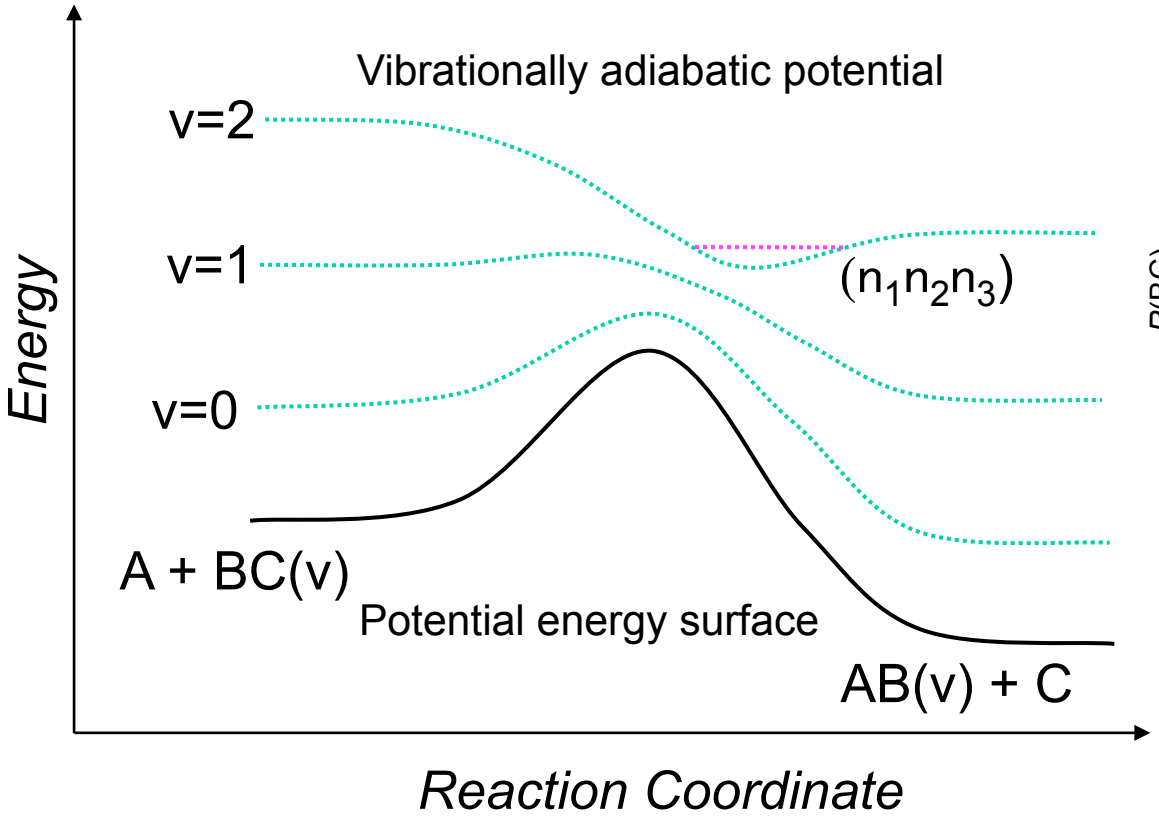
PES for A + BC → AB + C (potential energy function of nuclear configurations)

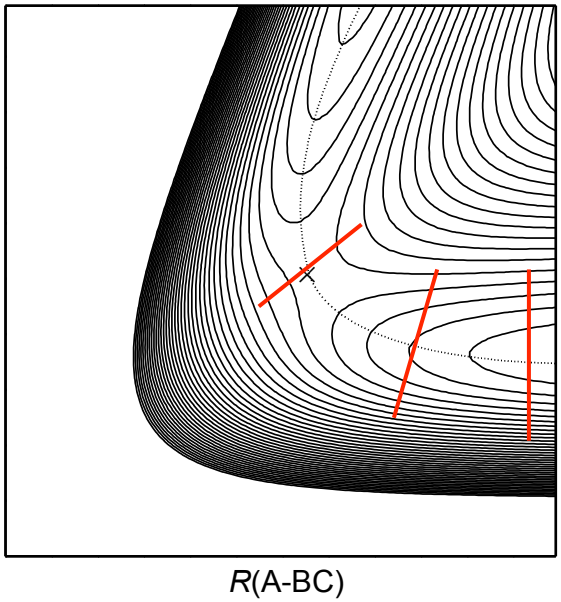


Outline of this talk

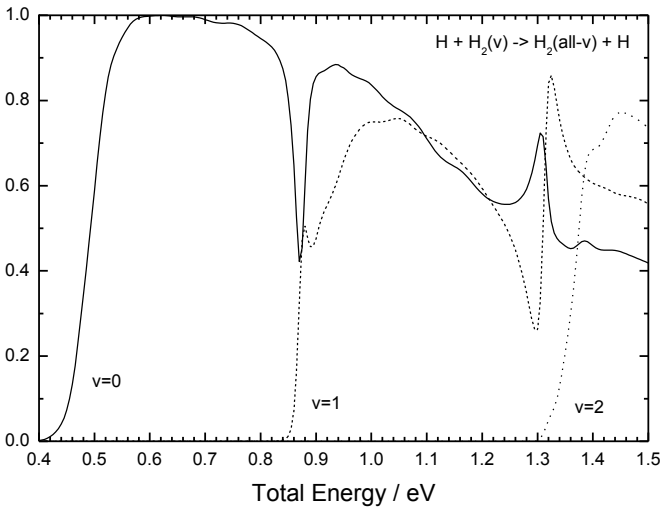
- Feshbach resonances in chemical reactions
  - $F + H_2$ → $HF + H$ and $F + HD$ → $HF/DF + D/H$
  - Vibrational adiabaticity and tunneling
- van der Waals resonances in chemical reactions
  - Long-range attractive interaction
  - Very sharp resonances
  - Low-temperature behavior of reaction rate
    - Interstellar chemistry, Cold reactions
- Resonances in atmospheric chemistry ?
  - Anomalous isotopic ratio of atmospheric ozone
  - (also in interstellar chemistry : H/D ratio)
- Resonances in roaming reactions : $Mg + H_2$ → $MgH + H$
- Resonances in DNA radiation damage (electron collision)

Feshbach Resonances in Chemical Reactions





Reaction Probabilities from 2D calc.

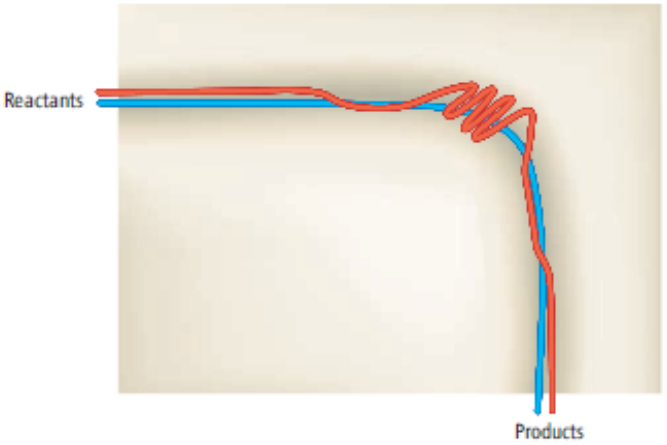


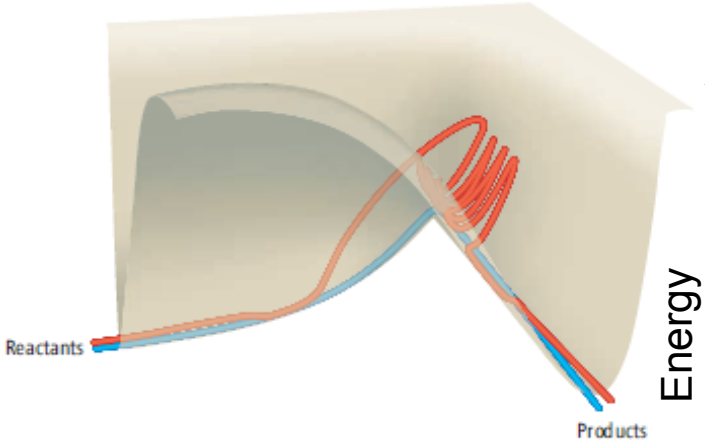
Difficulty for predicting reactive resonances from topological features of potential surfaces

Importance of dynamics calculations

something happens at threshold energy

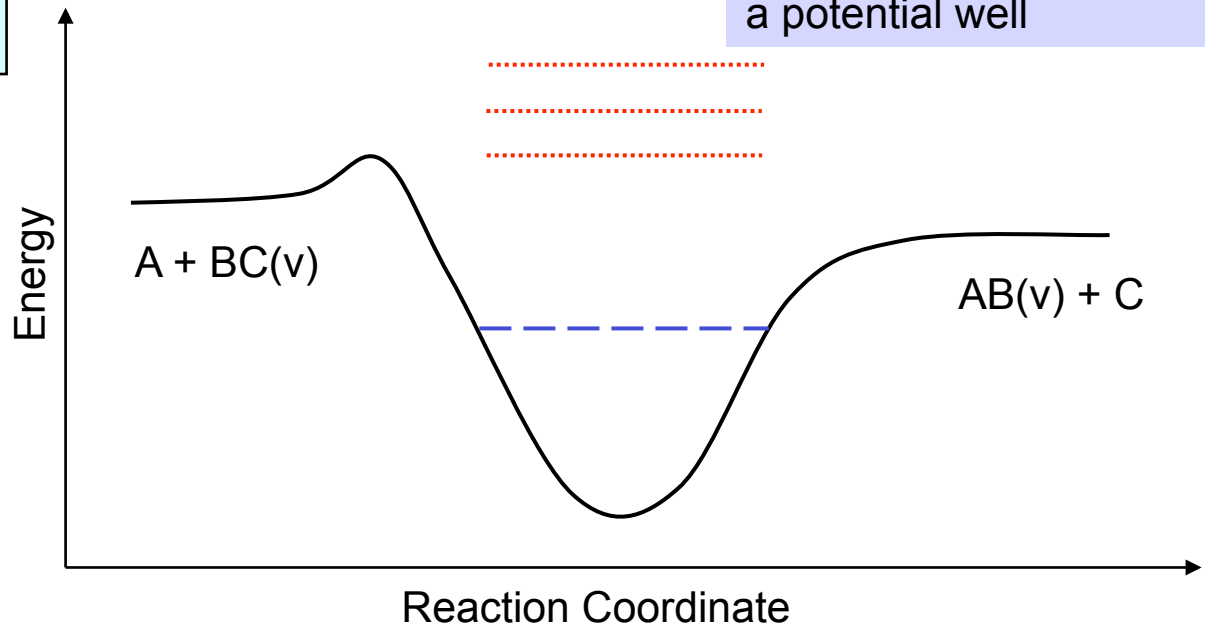
Resonance trajectory (classical picture)



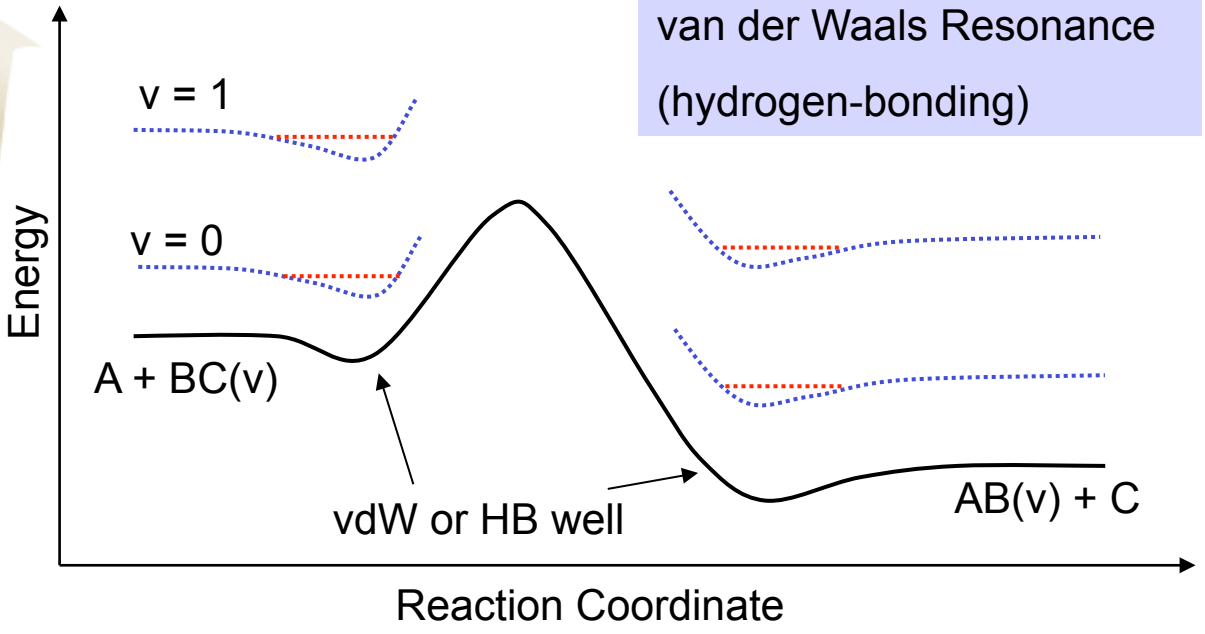


Other mechanisms

Quasi-bound states in a potential well



van der Waals Resonance (hydrogen-bonding)



How to observe resonances in chemical reactions ?

Collision energy dependence of cross sections

Nuclear Reaction for n + ^{235}U

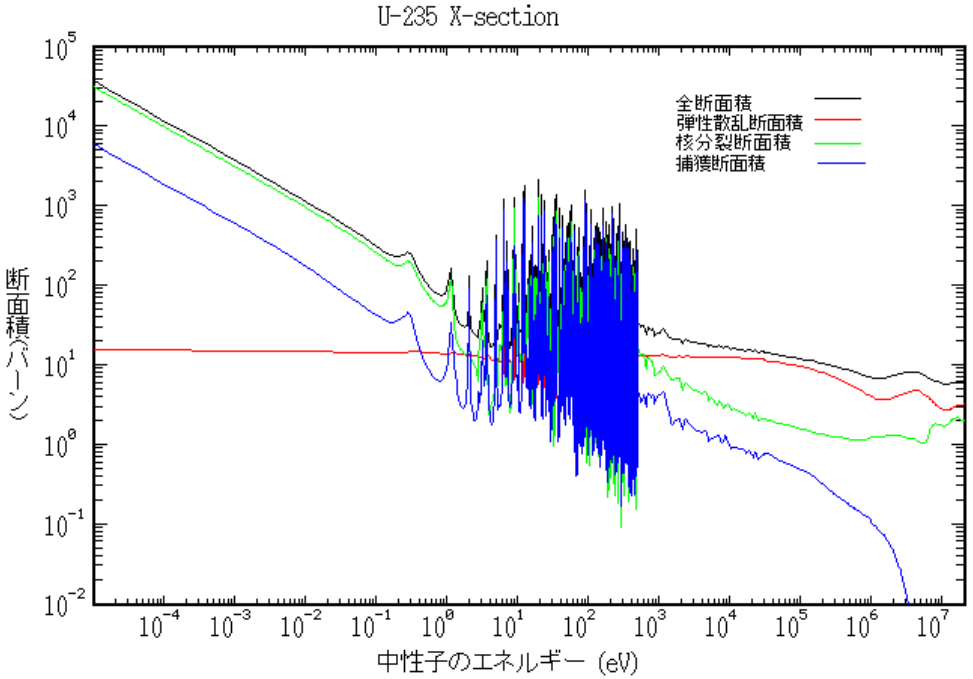


図8　ウラン235の断面積の図

Electron Collision, e + N_2

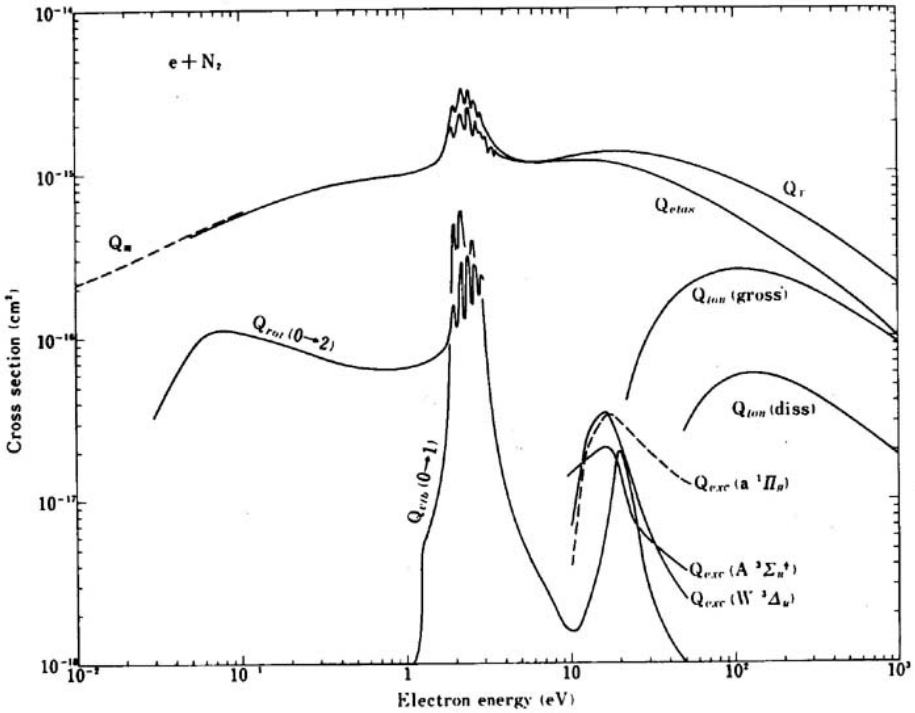


FIG. 10.1. Summary of the cross sections for the electron collision with N_2.

- High-resolution molecular beam experiment (~ 0.01 eV)

  State-to-state differential cross sections

- Electron photodetachment measurement of anions

Collision energy dependence of cross sections

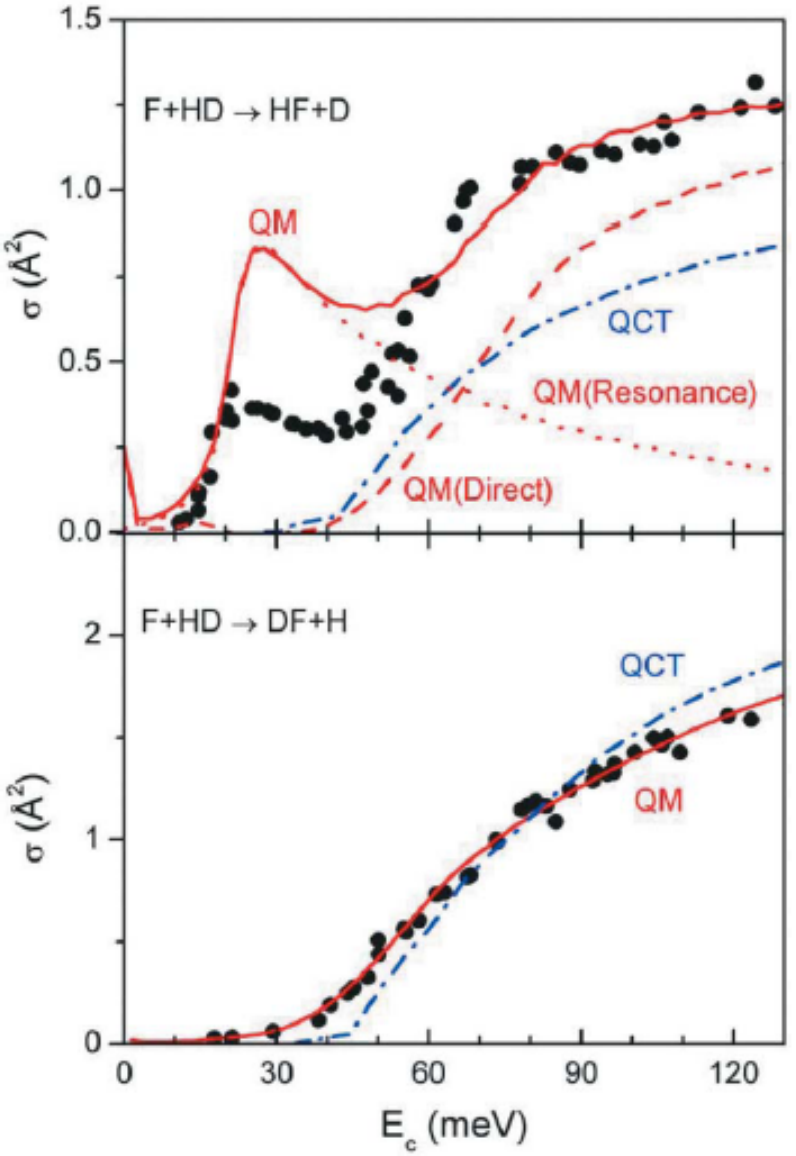
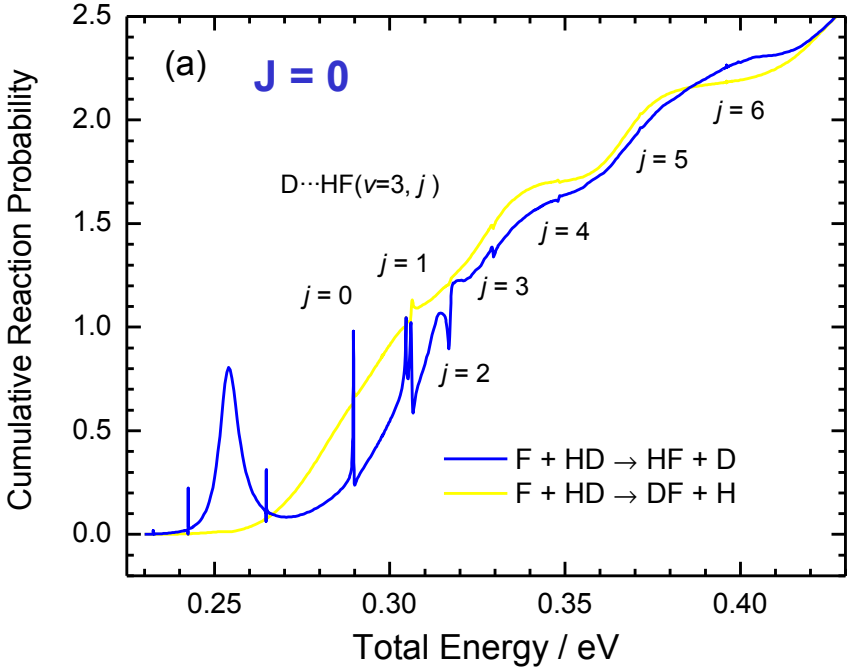
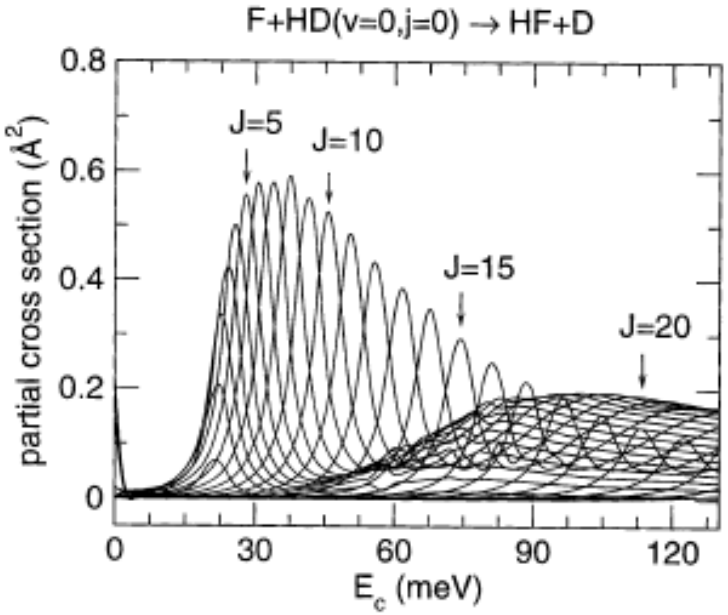


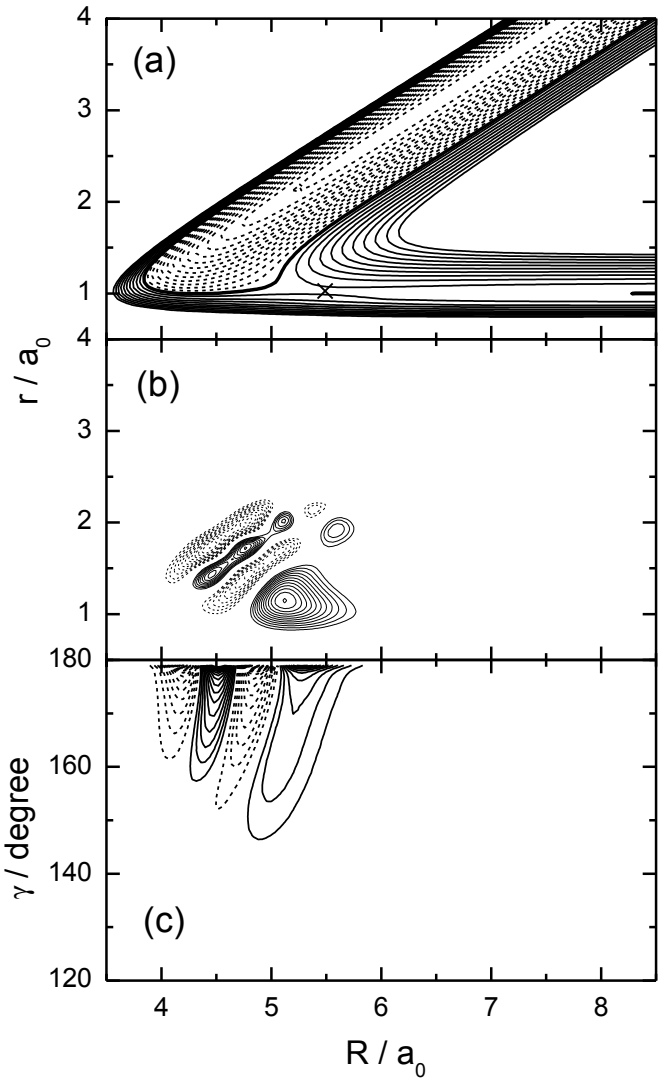
Fig. 1 Normalized excitation functions of the two isotopic product channels in the F + HD(v = 0; 80%j = 0 + 20%j = 1) reaction. The black dots are the experimental results, which have been normalized to the QM curves using a single scaling factor for both channels (modified from ref. 13.)

Quantum results on Stark-Werner-PES



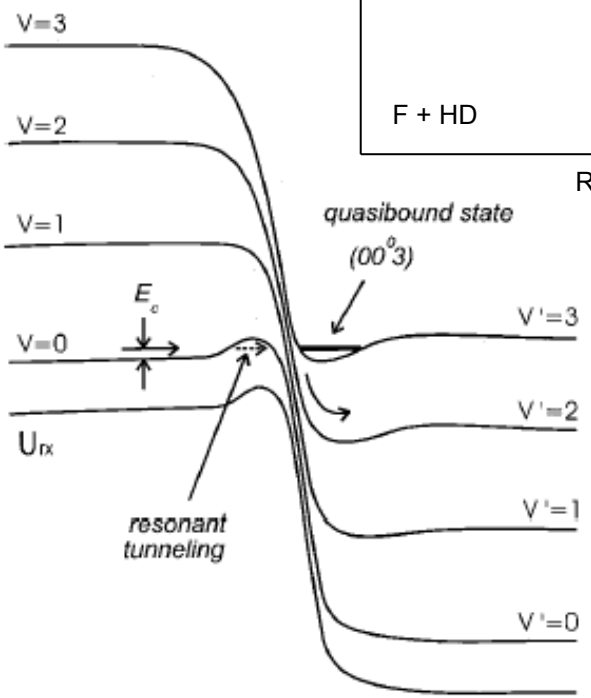


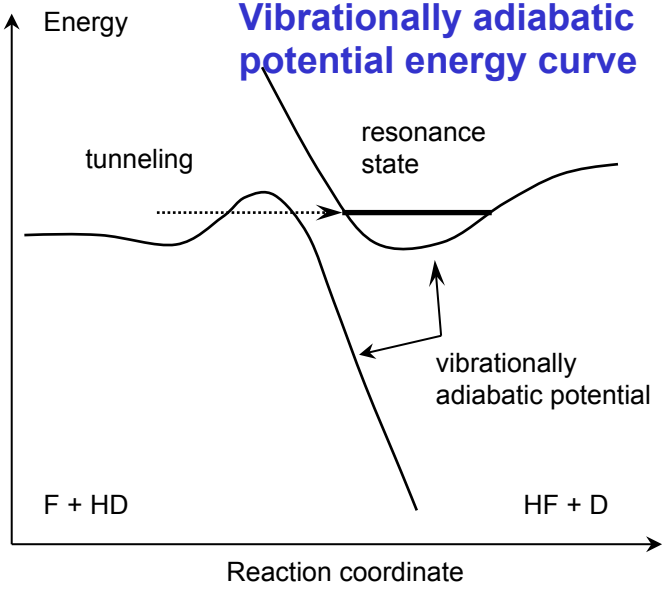
Wave function of reactive resonance in F + HD

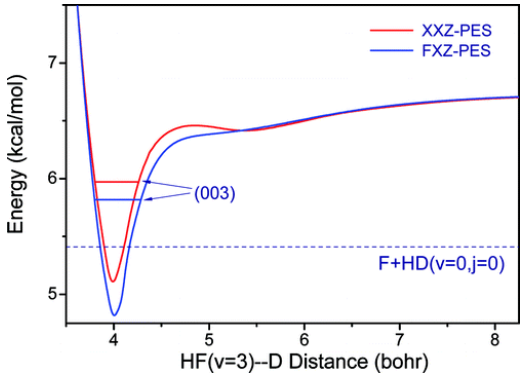


F•••H•••D(003)

(transient) Vibrationally excited state of linear triatomic molecule





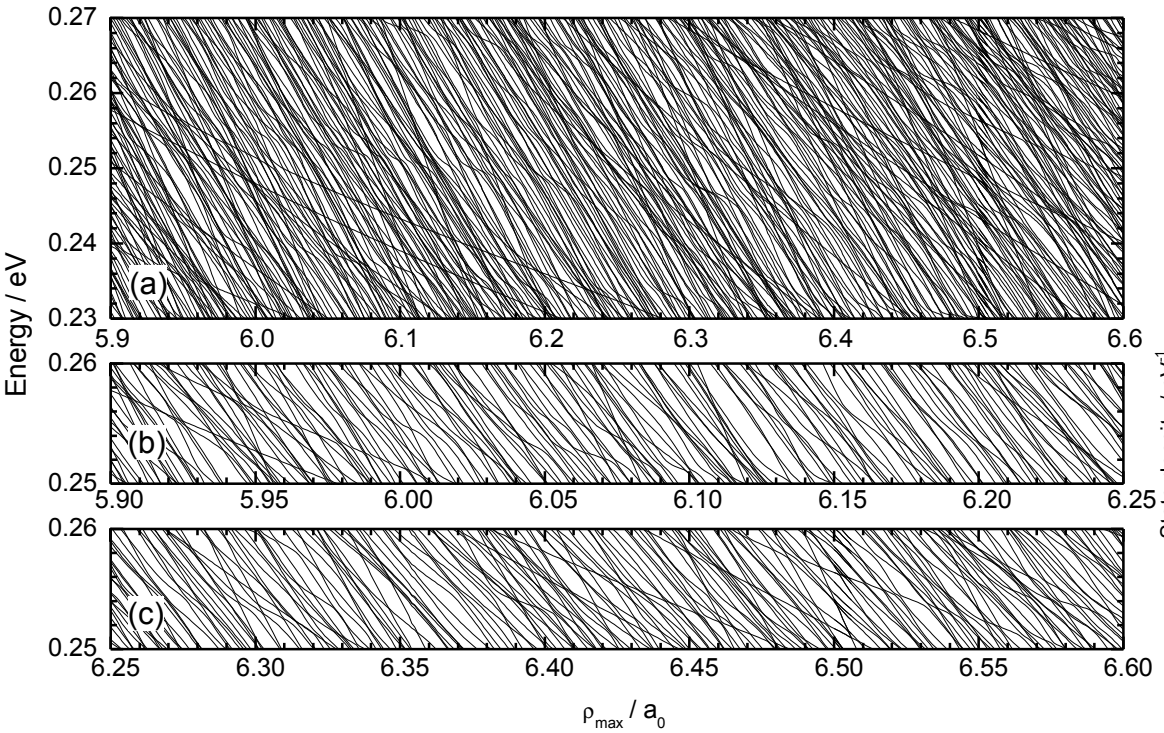


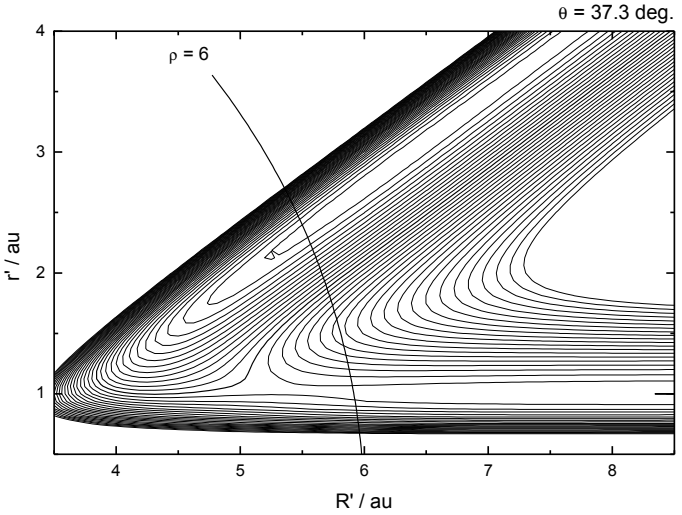
$F + HD(v) \rightarrow F \overset{H}{\diagdown} D \rightarrow F-H-D \rightarrow FH(v') + D$

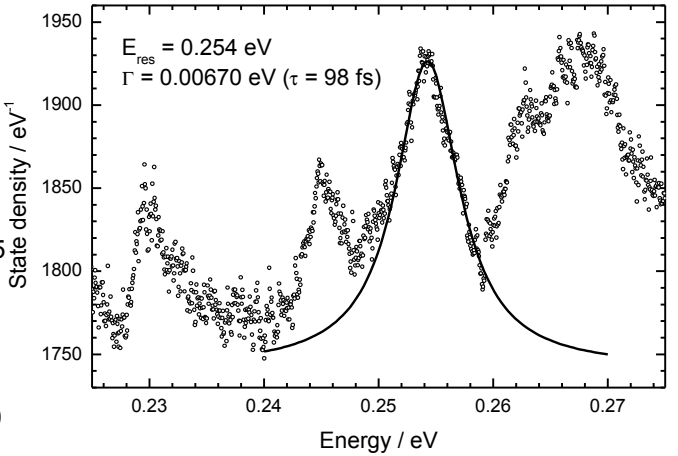
Stabilization Diagram & State Density

Extraction of resonance wave function

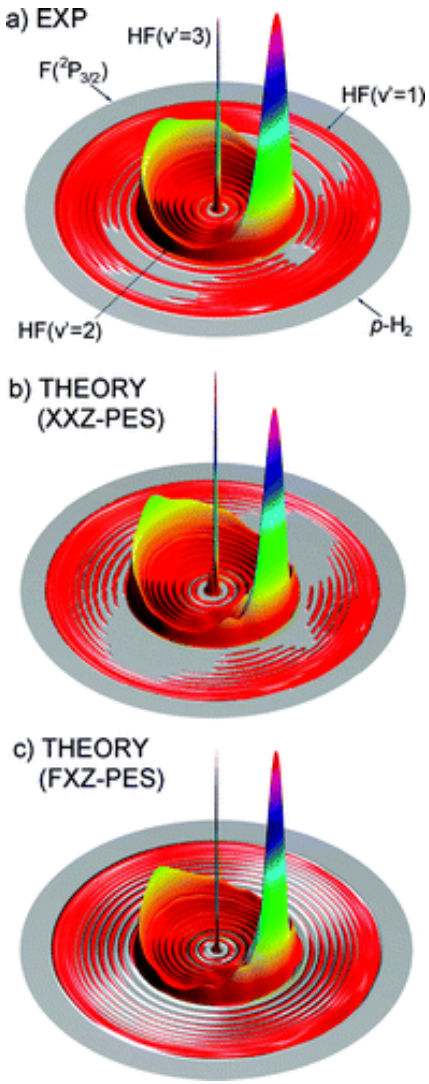
Solving 3D eigenvalue problems using DVR representation in hyperspherical coordinates (r,q,f) DVR Grid points ~ (50,100,200)



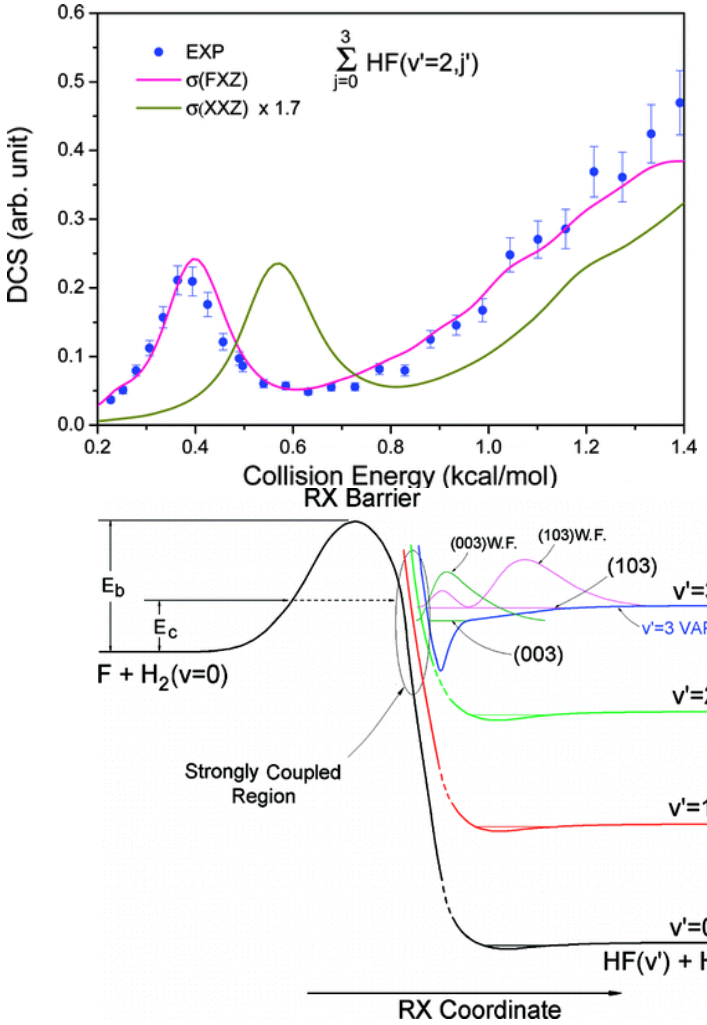




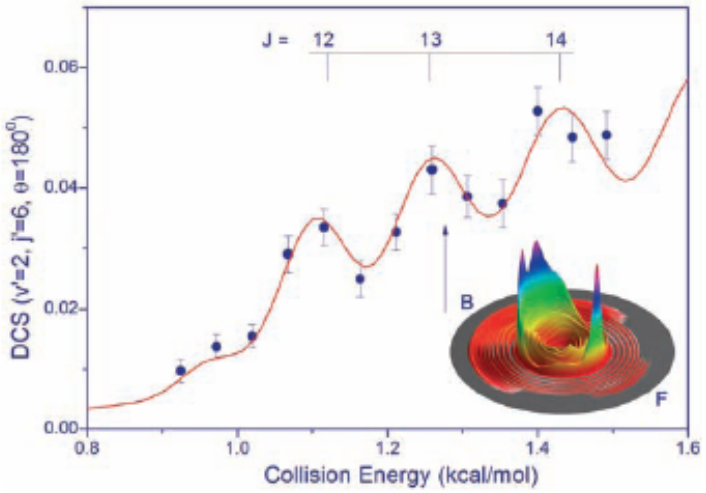
State-to-state differential cross section measurements for F + H_2, HD

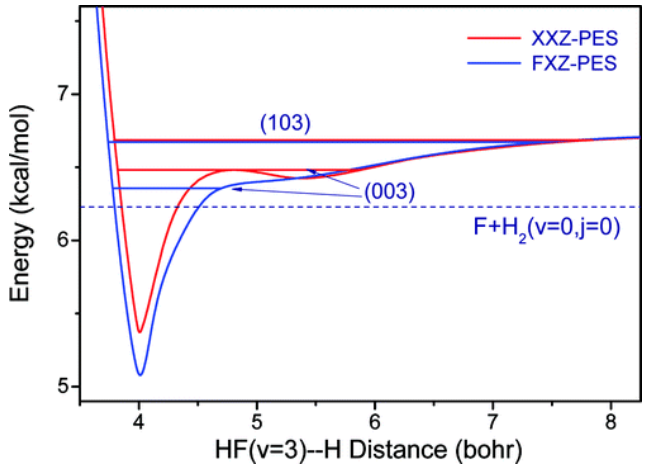


HF(v = 2, j)



HF(v = 2, j = 6)





Science 311 (2006) 1440.

Differential cross sections

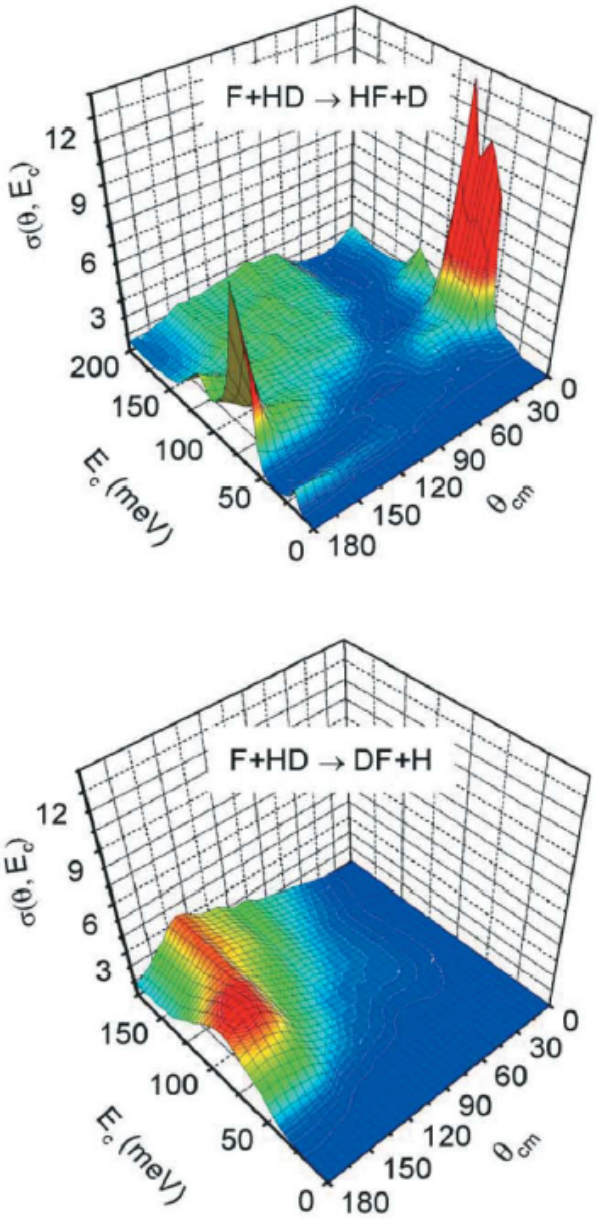


Fig. 5 Experimental total differential cross sections of the two isotopic product channels over an extended range of collision energies (adapted from ref. 14.)

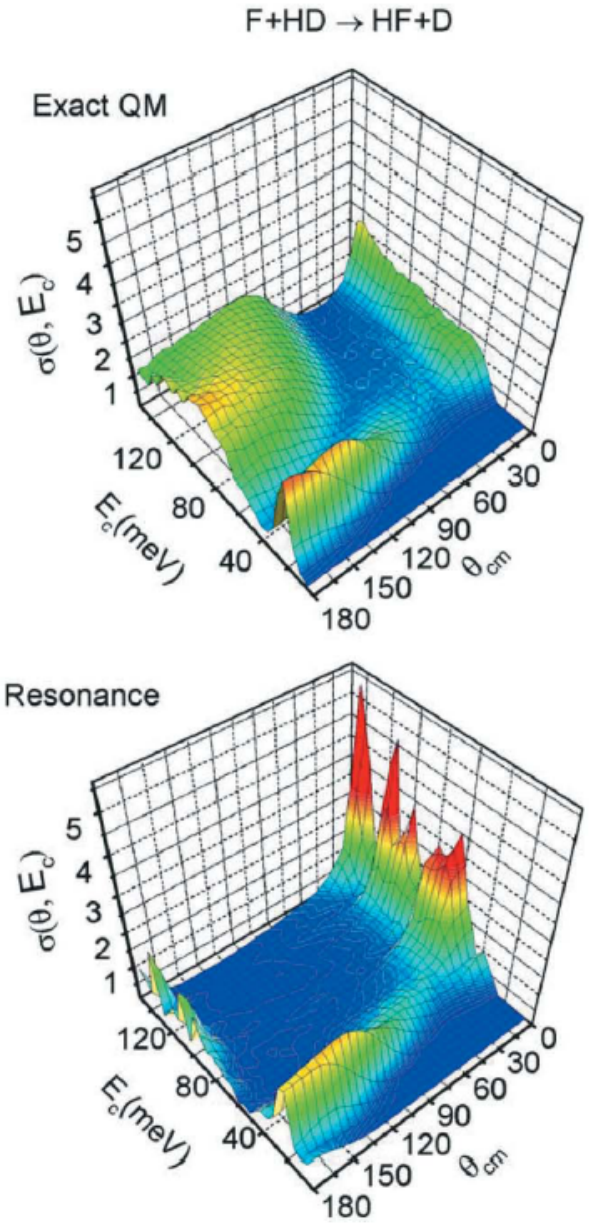


Fig. 6 Computed differential cross sections for F + HD → HF + D, over the same extended energy range as in Fig. 5. The upper panel is the result of the QM calculation, while the lower panel shows the resonance contribution (adapted from ref. 14.)

Vibrationally resolved cross sections

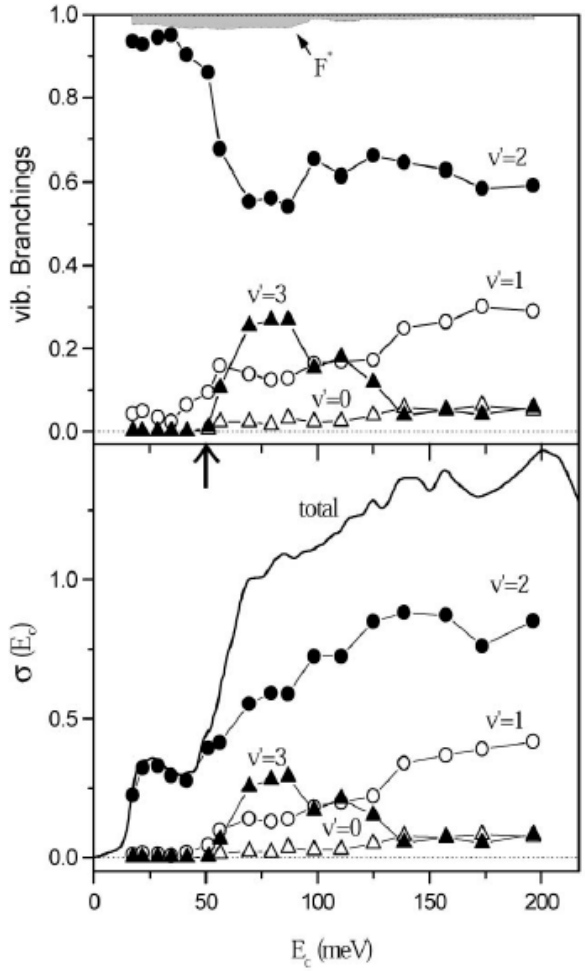


Fig. 3 Collision energy dependence of the HF product vibrational branching ratio (upper panel) and the vibration-specific excitation function for F + HD → HF(v') + D (lower panel). The arrow marks the threshold for the production of HF(v' = 3) + D (adapted from ref. 15.)

Differential cross sections

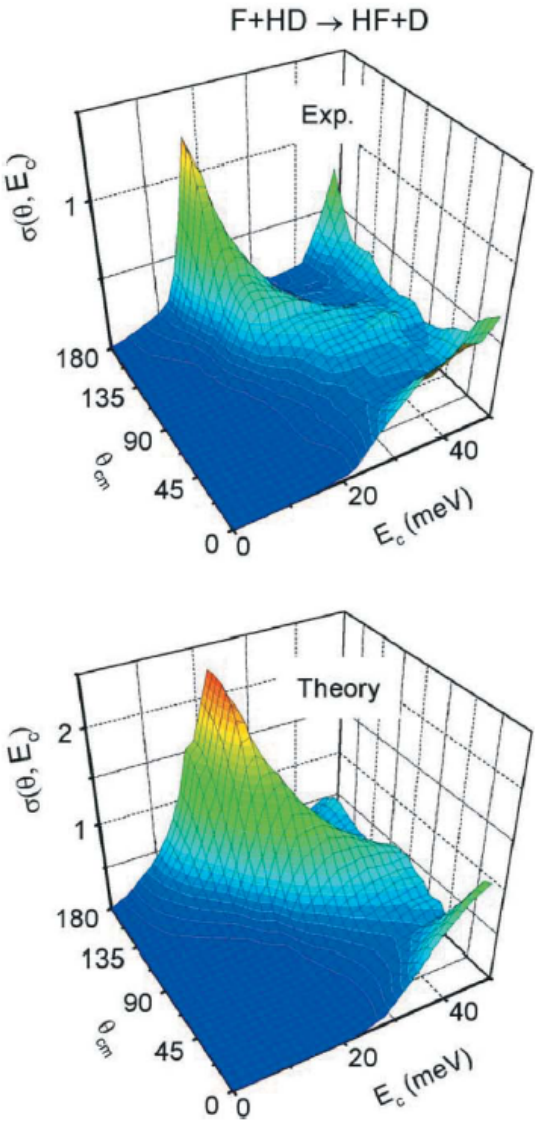
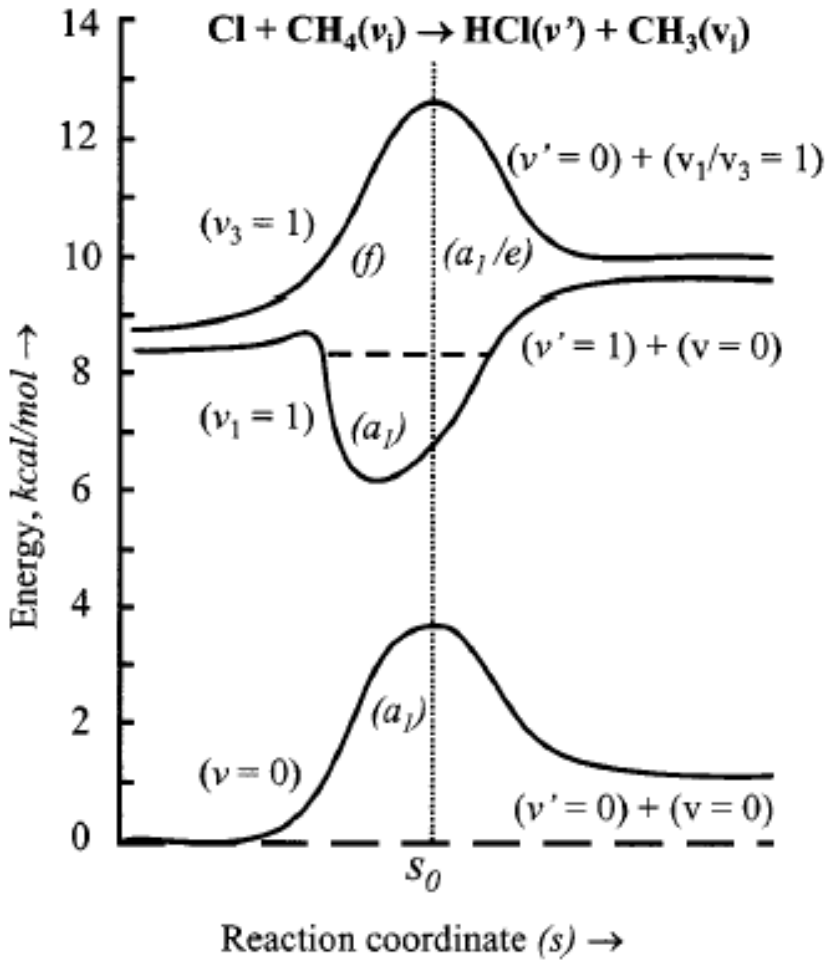
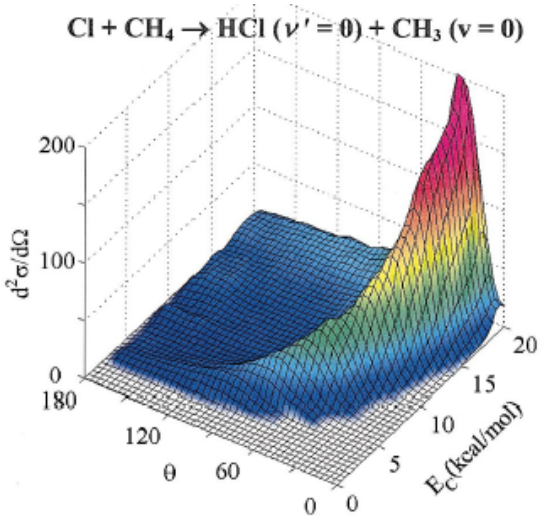


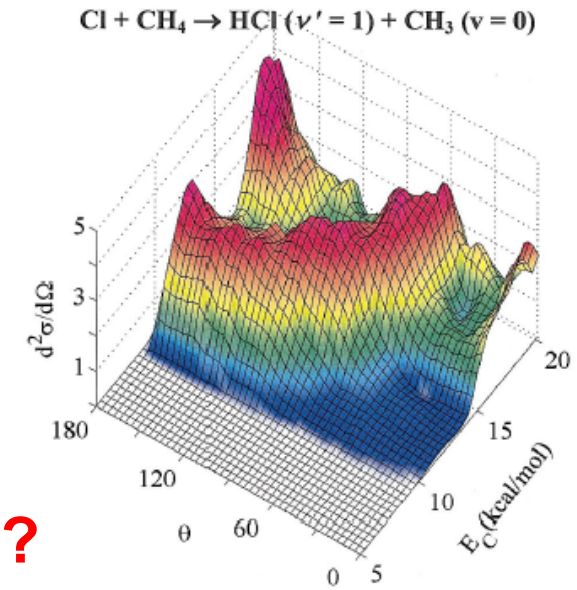
Fig. 4 Comparison of experimental and theoretical F + HD($v = 0, j = 0$ and 1) → HF + D differential cross sections in the low energy regime (adapted from ref. 14.)

HF($v' = 3$). However, there is of course an additional direct scattering component for $E_c > 45$ meV, and its interference with the resonant scattering may also play a role.

Resonances in complex chemical reactions ?
Cl + CH_4 ⇄ HCl + CH_3 case



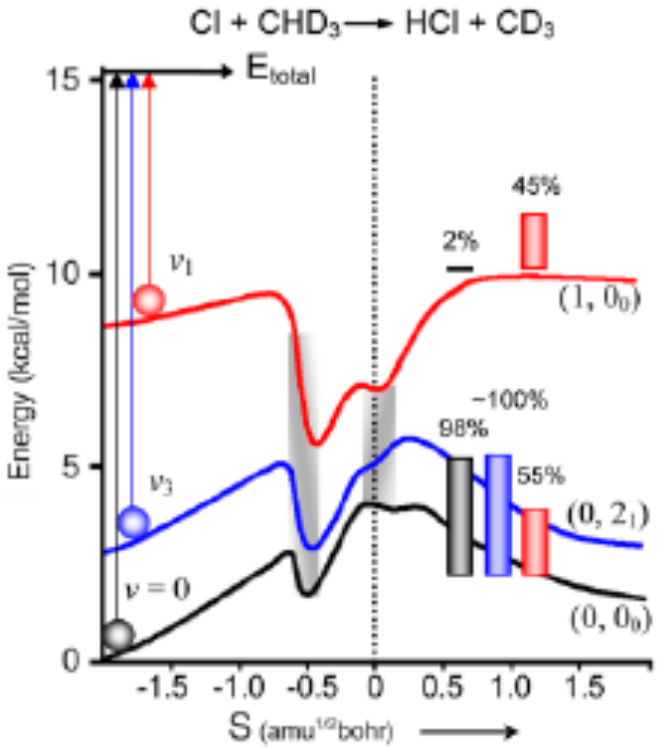


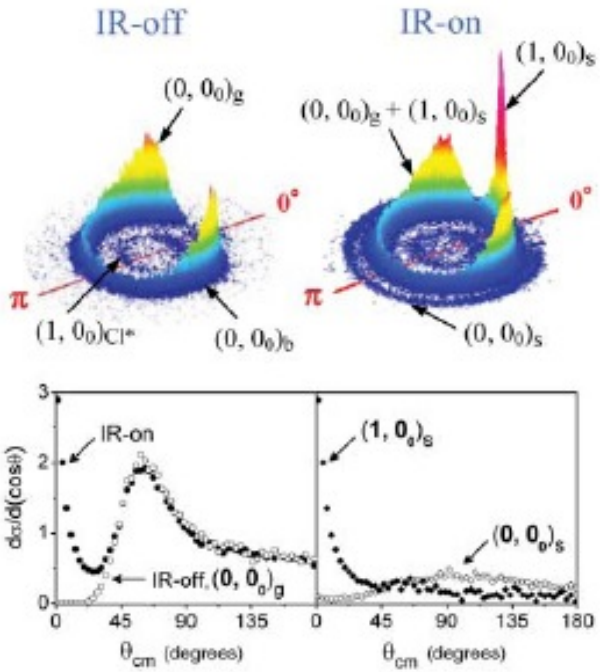


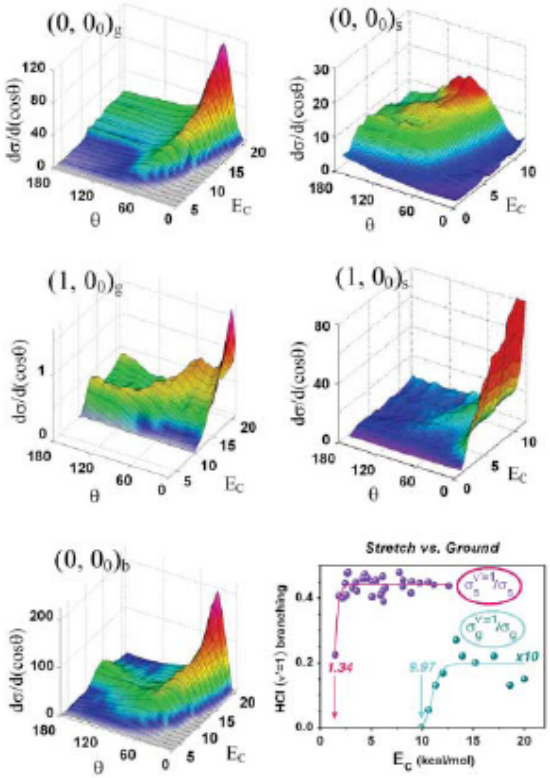
Vibrational mode dependence ?

Resonances in Cl + CHD_3 ⇄ HCl + CD_3 ?

Do Vibrational Excitations of CHD3 Preferentially Promote Reactivity Toward the Chlorine Atom?
Shannon Yan, *et al.*
Science **316**, 1723 (2007);



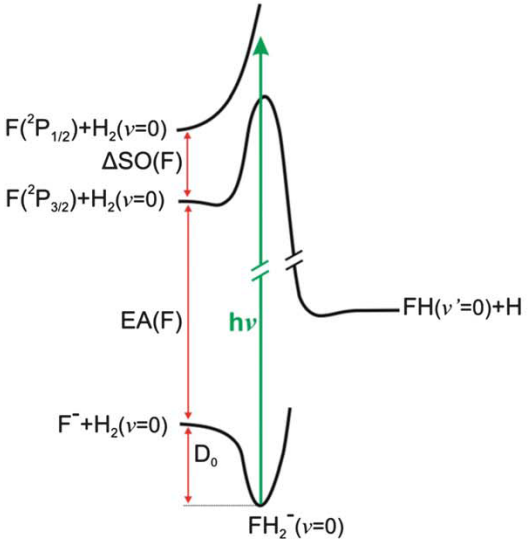


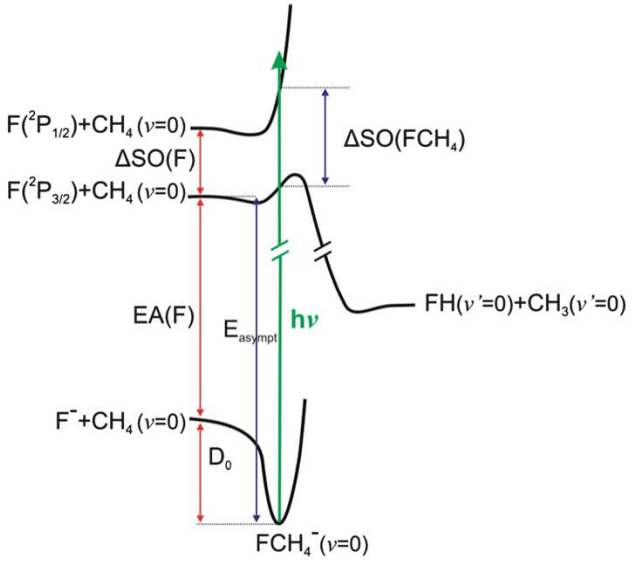


The effect of vibrational excitation.

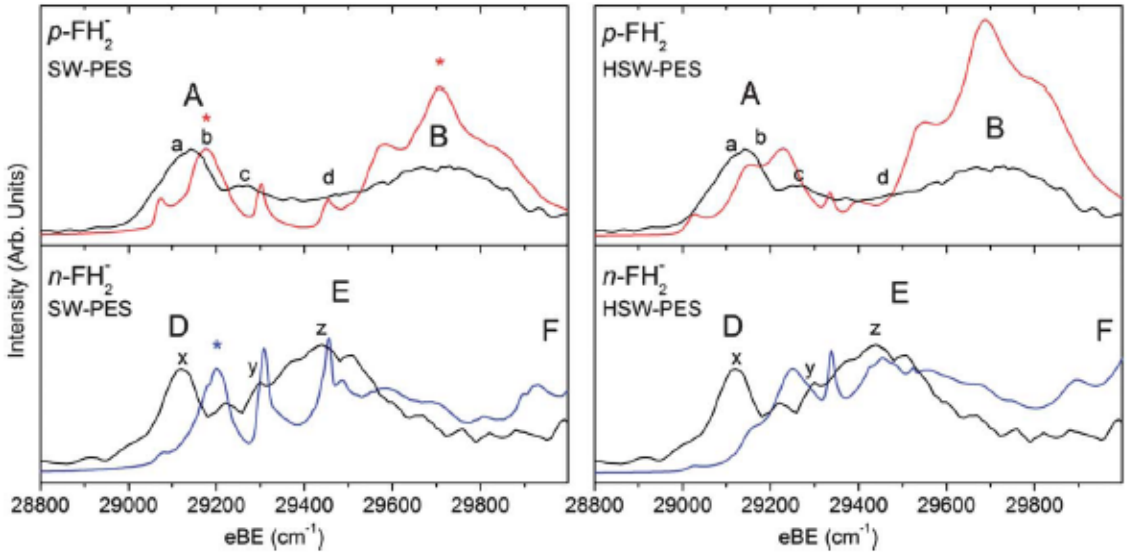
The answer is not clear. Further studies are needed.

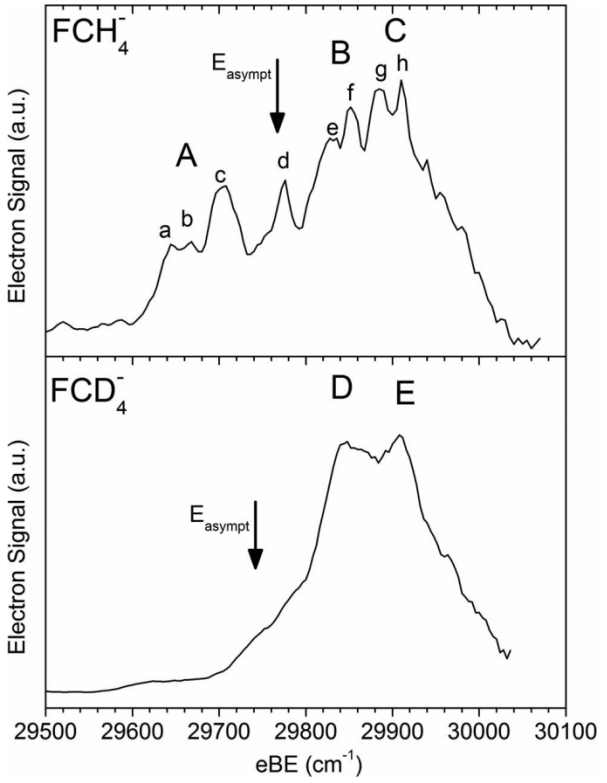
Electron photodetachment spectra of molecular anions

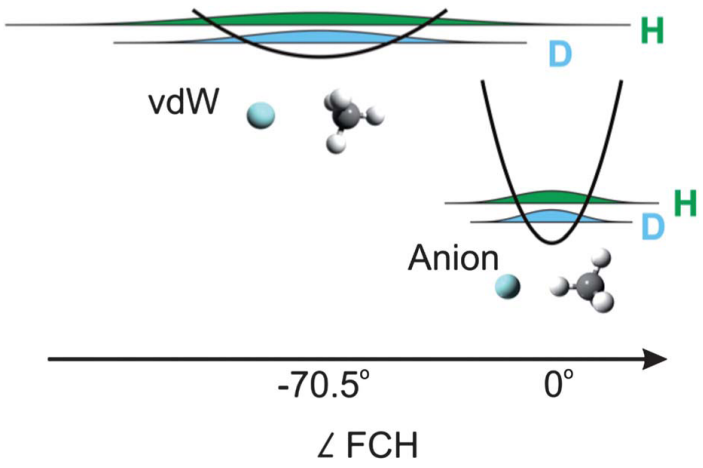




Information of transition-states, resonances







Resonances in Cl + CD_4 ⇄ DCl + CD_3

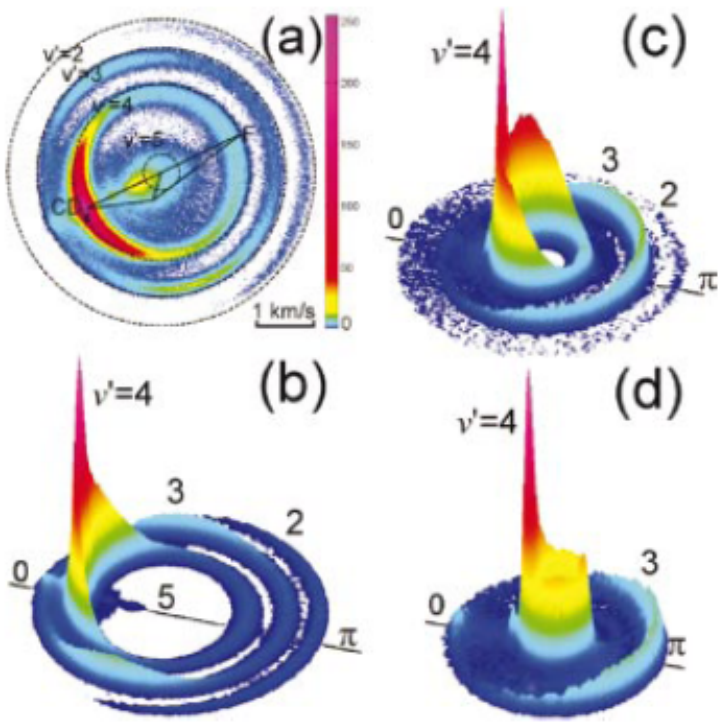


FIG. 1. (Color) (a) Raw image of the state-selected CD_3 products from the $F+CD_4 \rightarrow DF+CD_3$ reaction at $E_c = 8.36$ kcal/mol. The successive ring features correspond to the labeled vibrational states of the coincident DF product. (b) CD_3 product state-resolved flux-velocity contour maps derived from (a). The density-to-flux correction has been made. The intensity has been weighted by u^2 in accordance with conventional representation of the doubly differential cross section $[d^2\sigma/du\, d(\cos\theta)]$. (c) and (d), as (b) but for $E_c = 2.77$ and 1.48 kcal/mol, respectively.

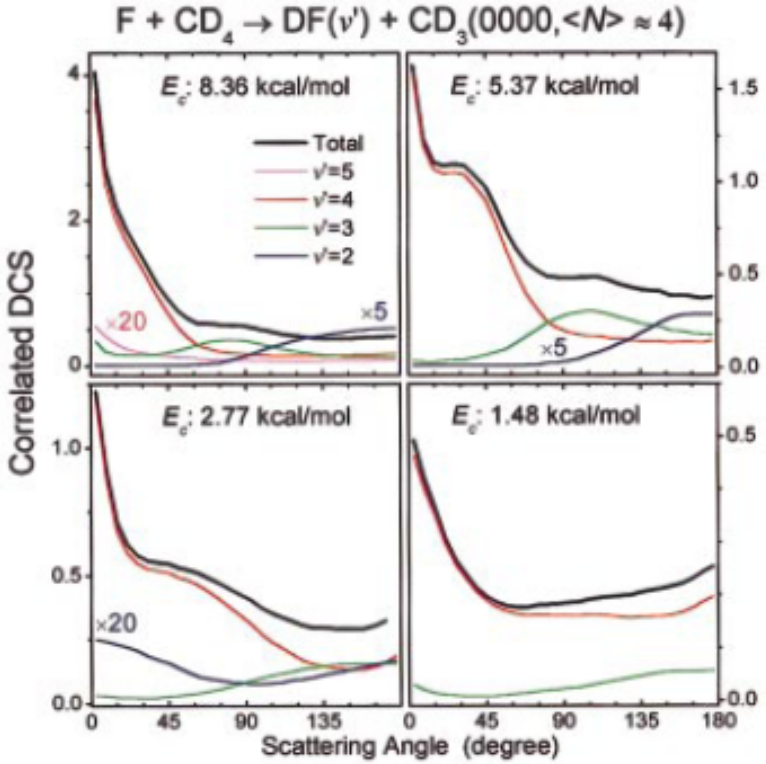
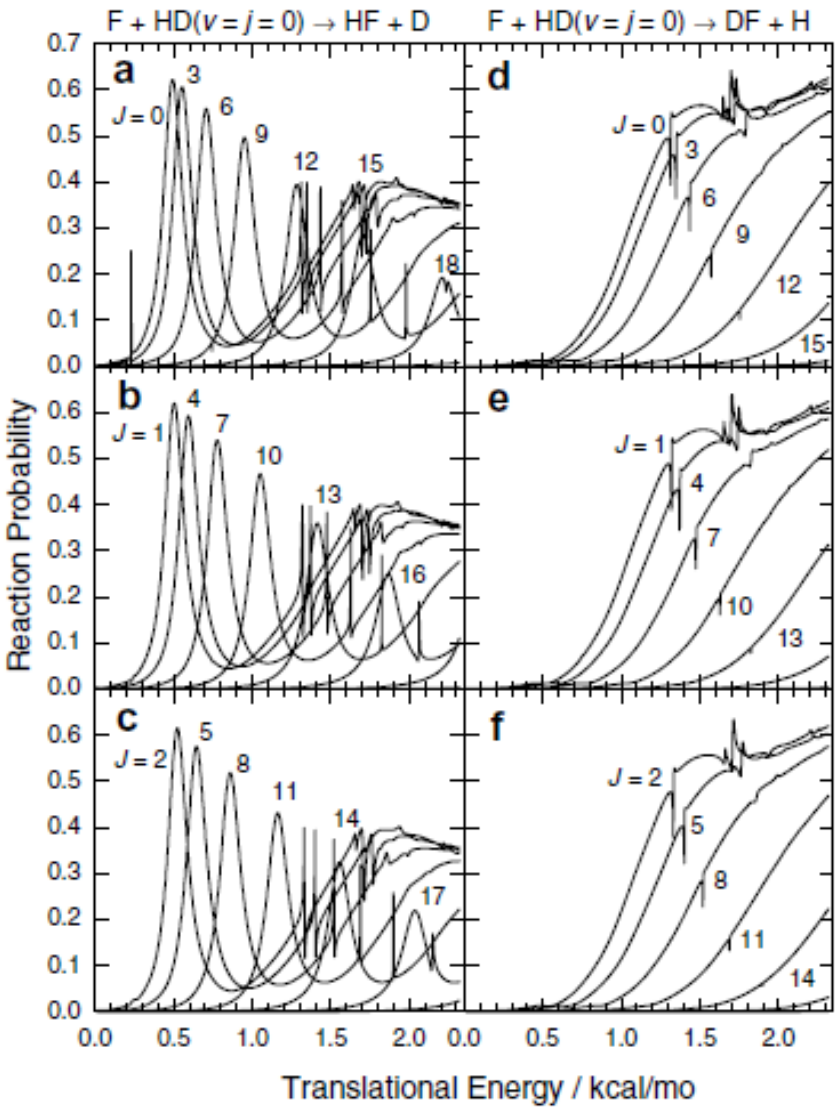
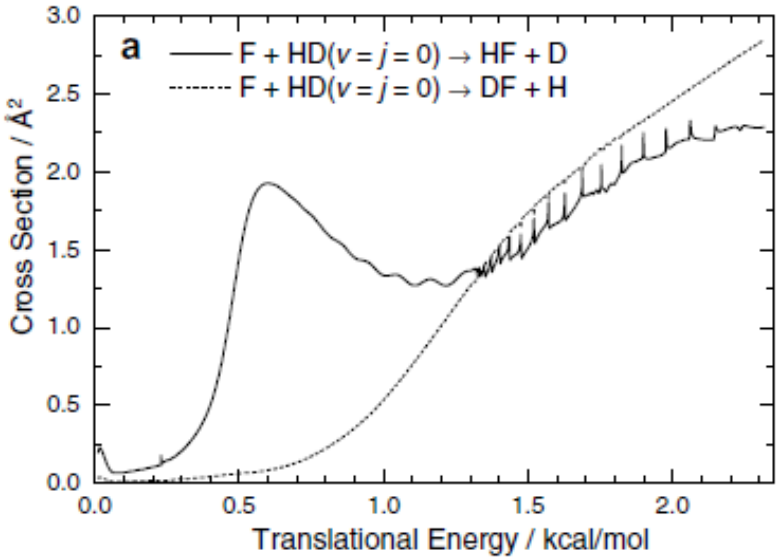


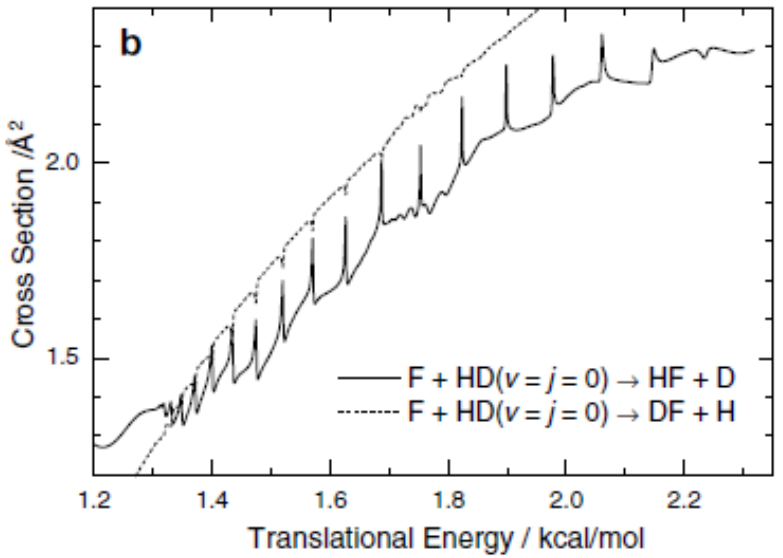
FIG. 2. (Color) Summary of the state-resolved, pair-correlated angular distribution (CDCS). The result for $E_c = 5.37$ kcal/mol (from Ref. 11) is included for comparisons. The scales of the four panels are normalized according to the excitation function for $CD_3(0000)$ shown in Ref. 15. The black lines represent the vibration-resolved angular distribution of CD_3 products.

Van der Waals resonances
Cross Sections for the F + HD reaction (fine grid)

Reaction Probabilities for each *J*



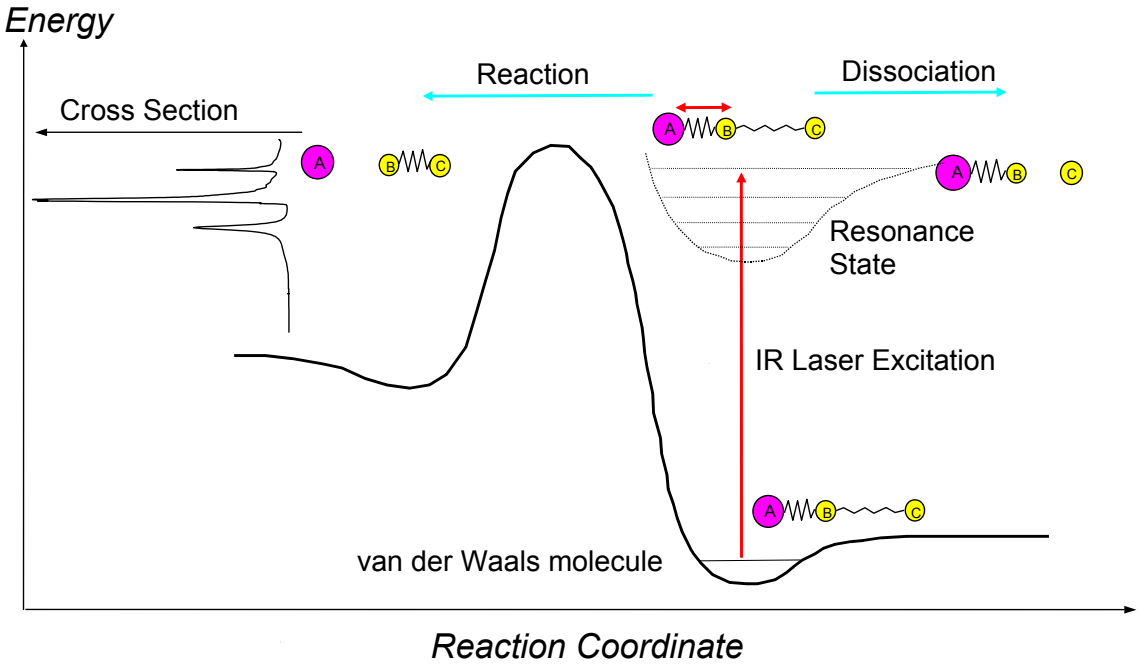




Takayanagi, *Chem. Phys. Lett*. 433 (2006) 15.

Reaction induced by photoexcitation via vdW resonances

Prereaction Process

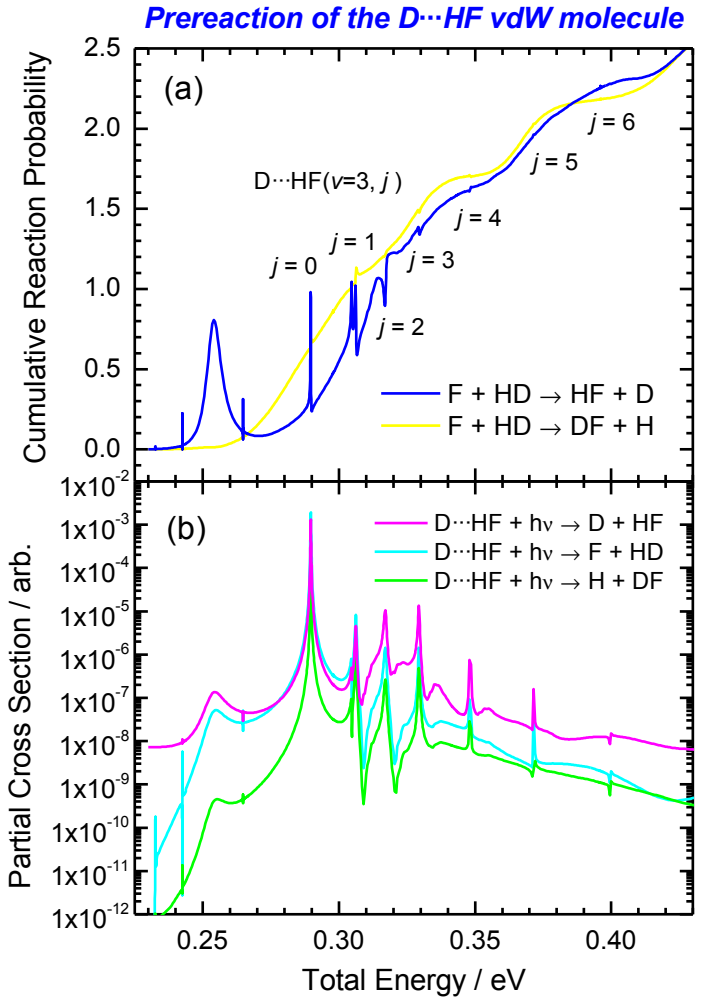


Formation of van der Waals complexes (Cl•••HF, Br•••HF, I•••HF etc) in low temperature helium nanodroplets

Takayanagi, *Phys*. Chem. *Chem. Phys*. 1 (1999) 1099.

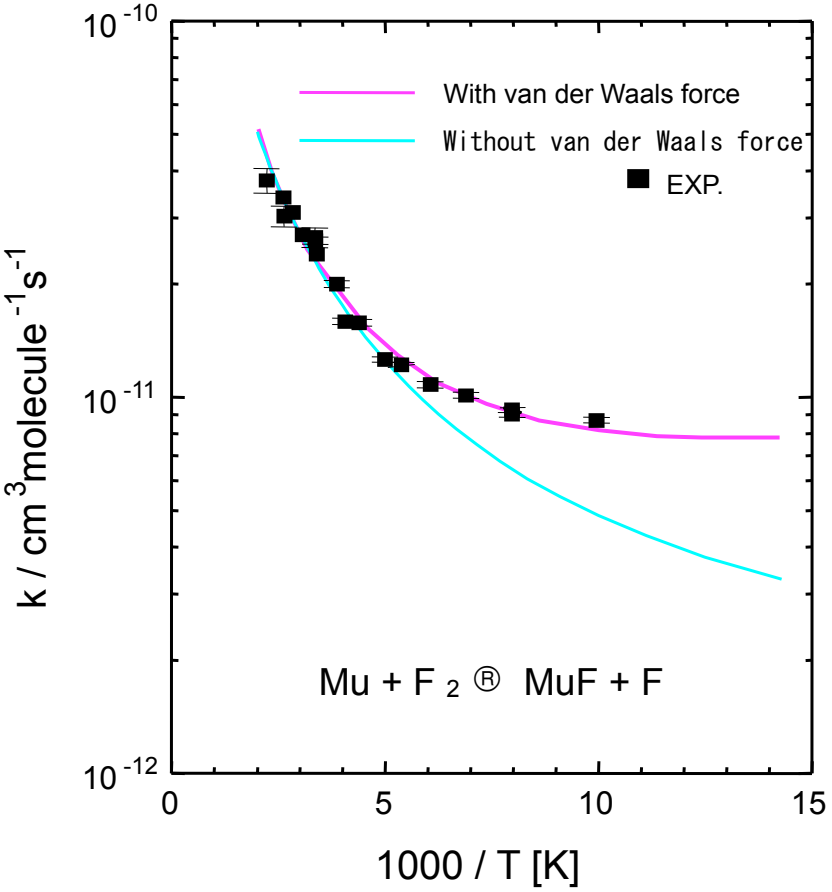
Takayanagi, *Chem. Phys*. *Lett*. 338 (2001) 195.

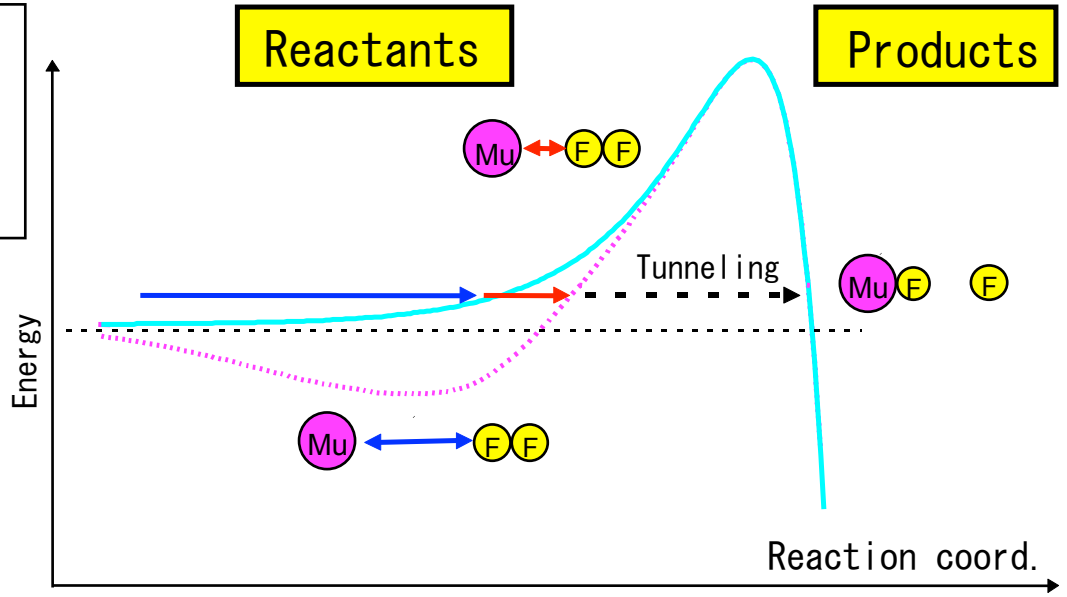
Computational results for prereaction processes for H•••HF, H•••DF, D•••HF van der Waals complexes



van der Waals effects in Mu + F_2

Results of reduced dimensionality quantum reactive scattering calculations on model potential energy surfaces (with vdW vs. without vdW interaction)





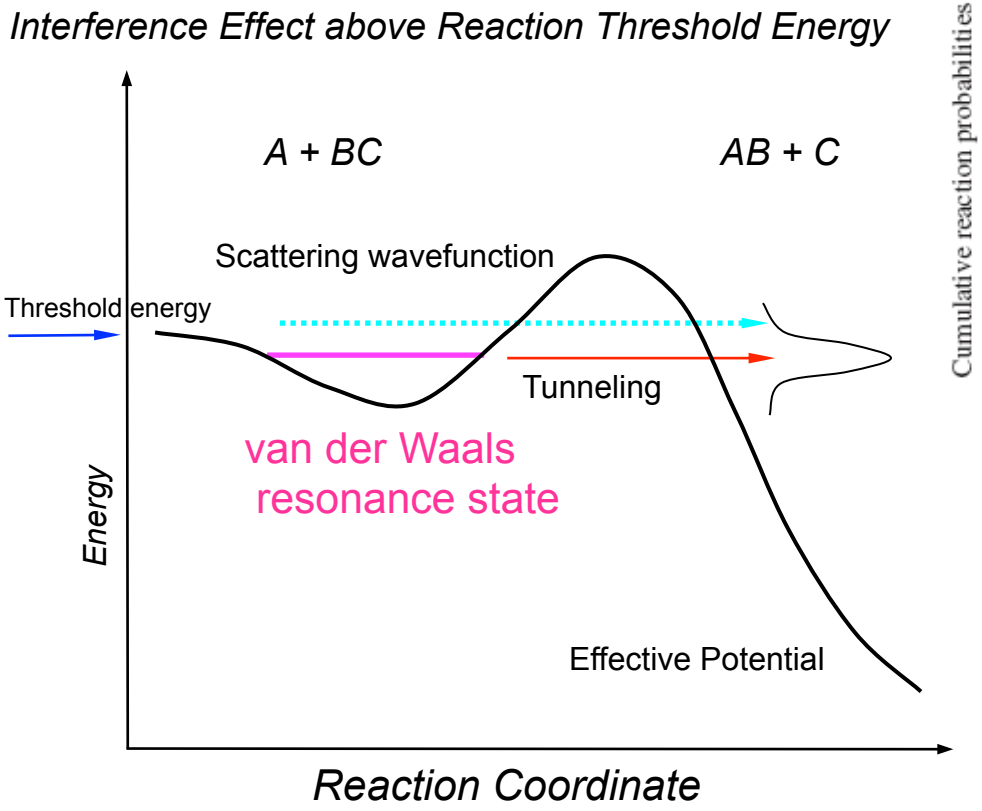
Repulsive force vs. vdW attractive force

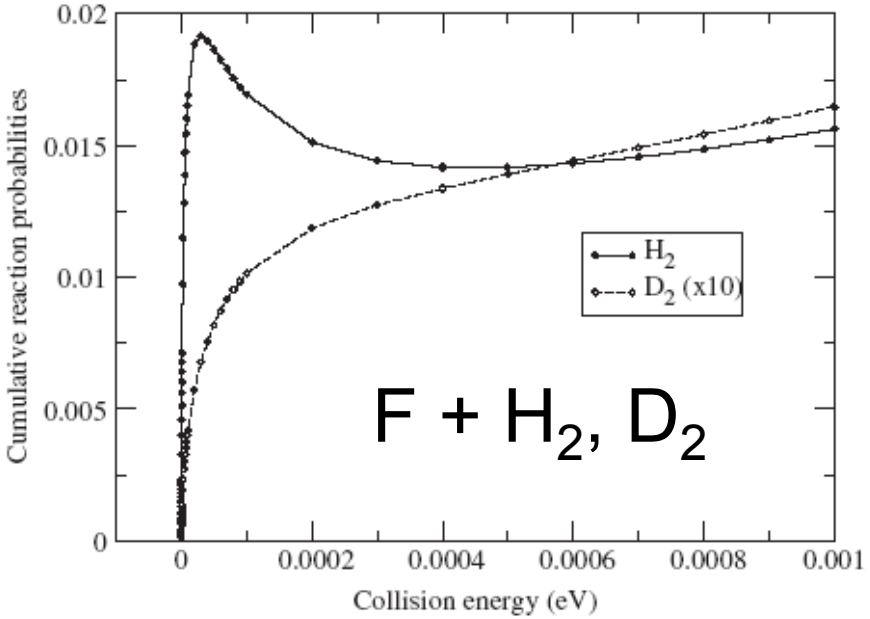
Tunneling distance is short
→ Large tunneling probability

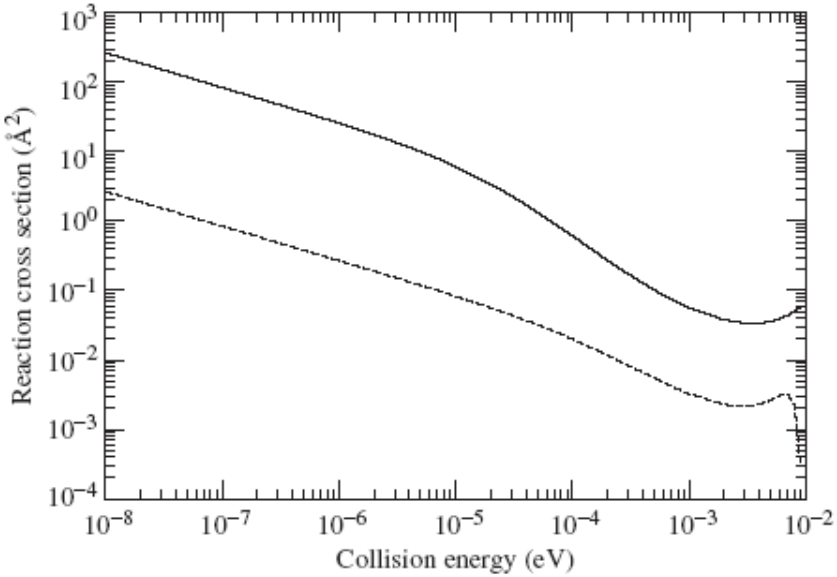
van der Waals interaction plays an important role in rate constants at low temperatures

Takayanagi et al, *J. Phys*. Chem. *A* 101 (1997) 7098.

van der Waals effects in low-energy collisions



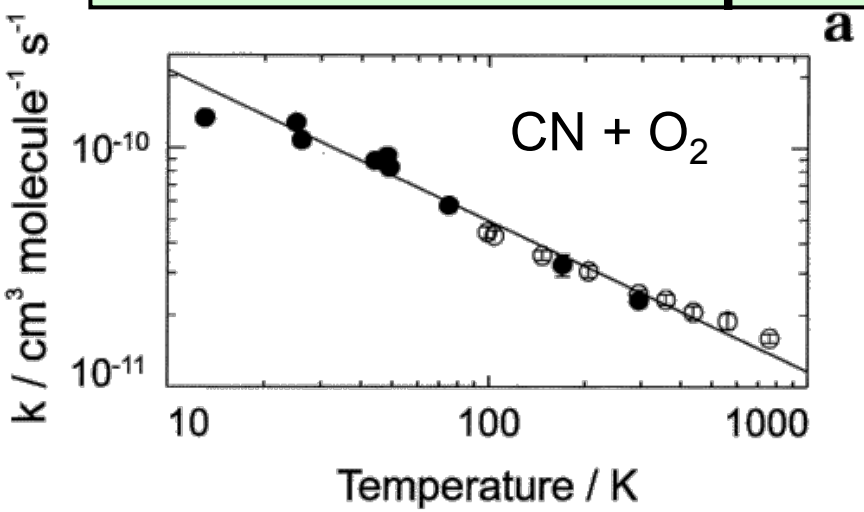


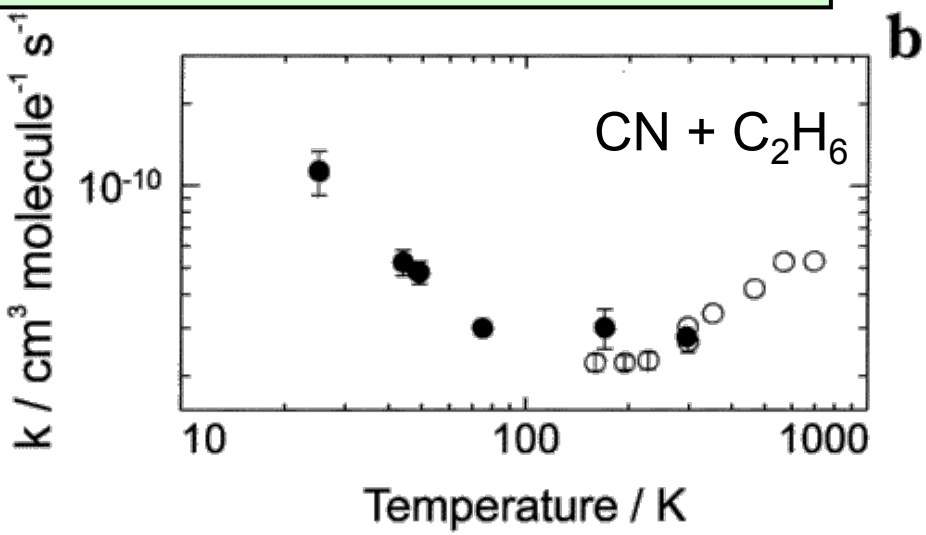


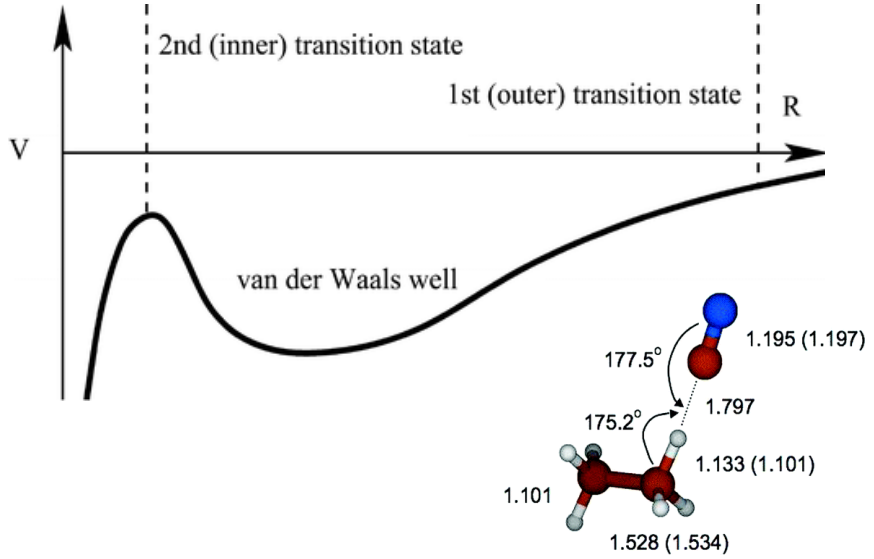
"Importance of long-range interactions in chemical reactions at cold and ultracold temperatures"

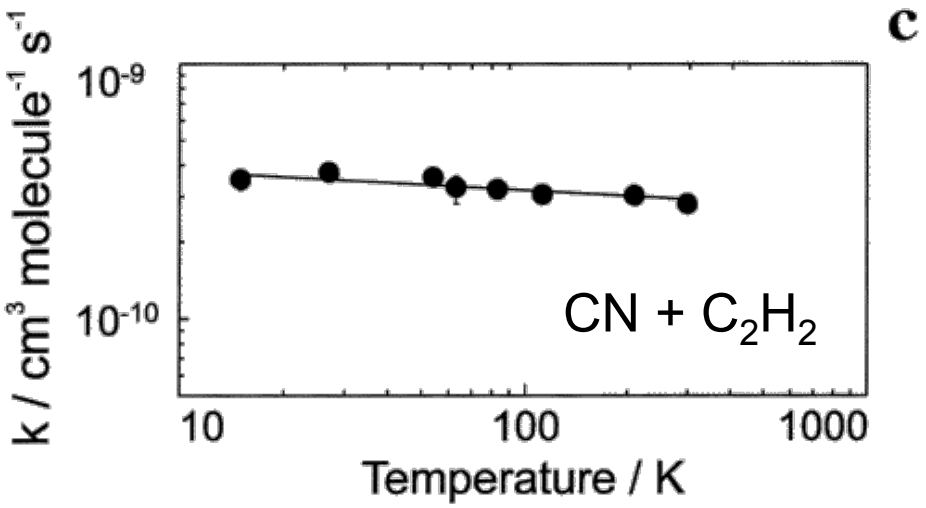
Weck and Balakrishnan, *Int. Rev. Phys. Chem.* 25 (2006) 283-311

Interstellar Chemistry : Low-temperature reactions









Georgievskii, *J. Phys.* Chem. *A* 111 (2007) 3802.

I.W.M. Smith, *Acc. Chem. Res.* 33 (2000) 261.

Cold and Ultracold Molecules

Faraday Discussion Vol. 142

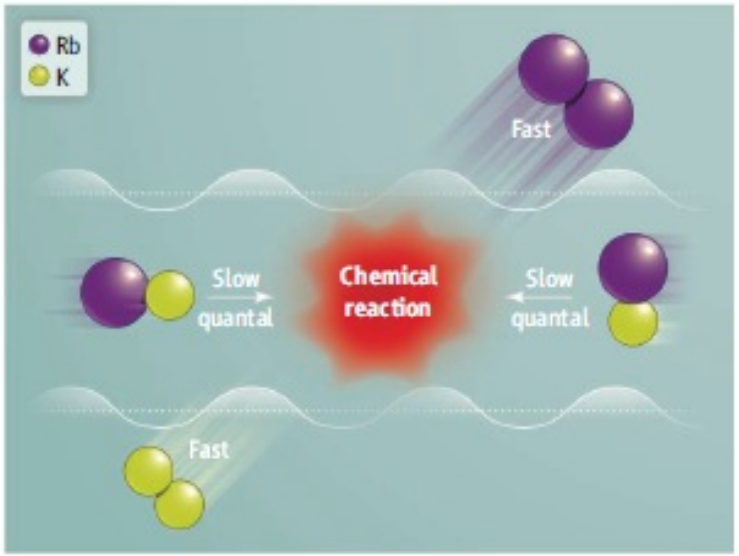
"**Molecular collisions, from warm to ultracold**"

D. Herschbach, Faraday Discuss. 142 (2009) 9-23.

Quantum-State Controlled Chemical Reactions of Ultracold Potassium-Rubidium Molecules

S. Ospelkaus,[1*] K.-K. Ni,[1*] D. Wang,[1] M. H. G. de Miranda,[1] B. Neyenhuis,[1] G. Quéméner,[1] P. S. Julienne,[2] J. L. Bohn,[1] D. S. Jin,[1†] J. Ye[1†]

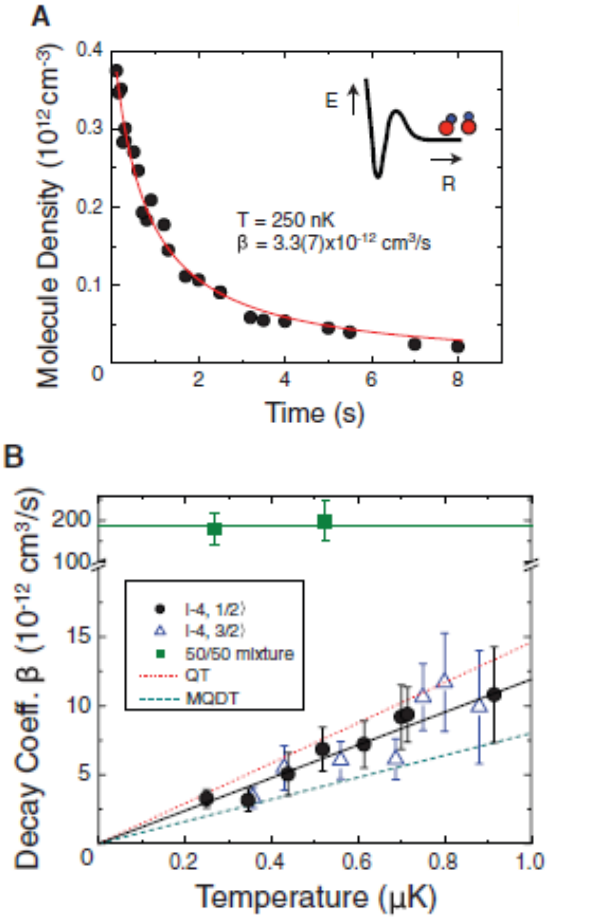
SCIENCE VOL 327 12 FEBRUARY 2010 853



Ultracold Chemistry

Jeremy M. Hutson

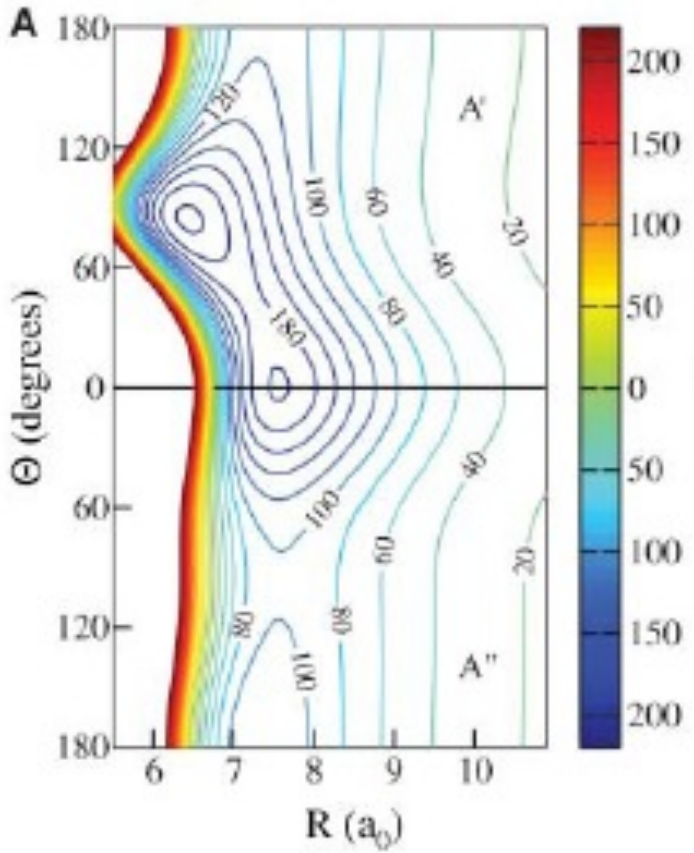
12 FEBRUARY 2010 VOL 327 SCIENCE www.sciencemag.org



Cold and Ultracold Molecules

Near-Threshold Inelastic Collisions Using Molecular Beams with a Tunable Velocity
Joop J. Gilijamse, *et al.*
Science **313**, 1617 (2006);
DOI: 10.1126/science.1131867

Xe + OH collision



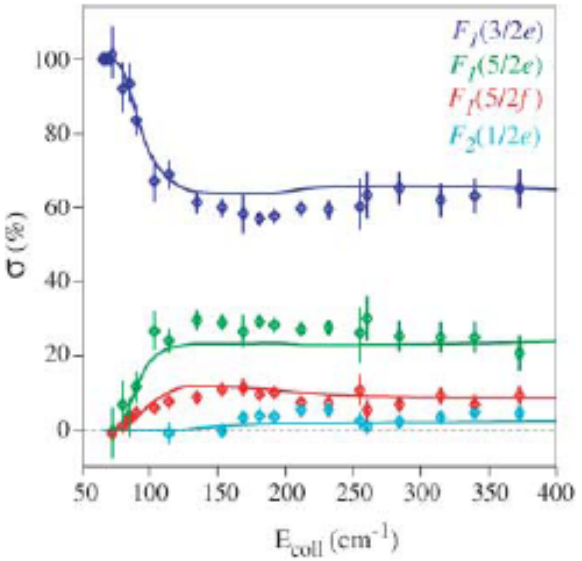


Fig. 4. Comparison of the collision energy dependence of the measured (data points with error bars) and calculated (solid curves) relative cross-sections—i.e., the fractional scattering of OH radicals into one of the $F_1(3/2e)$, $F_1(5/2e)$, $F_1(5/2f)$, or $F_2(1/2e)$ channels.

Low-energy collision : CO + H_2

PRL 109, 023201 (2012) PHYSICAL REVIEW LETTERS week ending 13 JULY 2012

Appearance of Low Energy Resonances in CO–*Para*-H_2 Inelastic Collisions

Simon Chefdeville,[1,2] Thierry Stoecklin,[1,2] Astrid Bergeat,[1,2] Kevin M. Hickson,[1,2] Christian Naulin,[1,2] and Michel Costes[1,2,*]

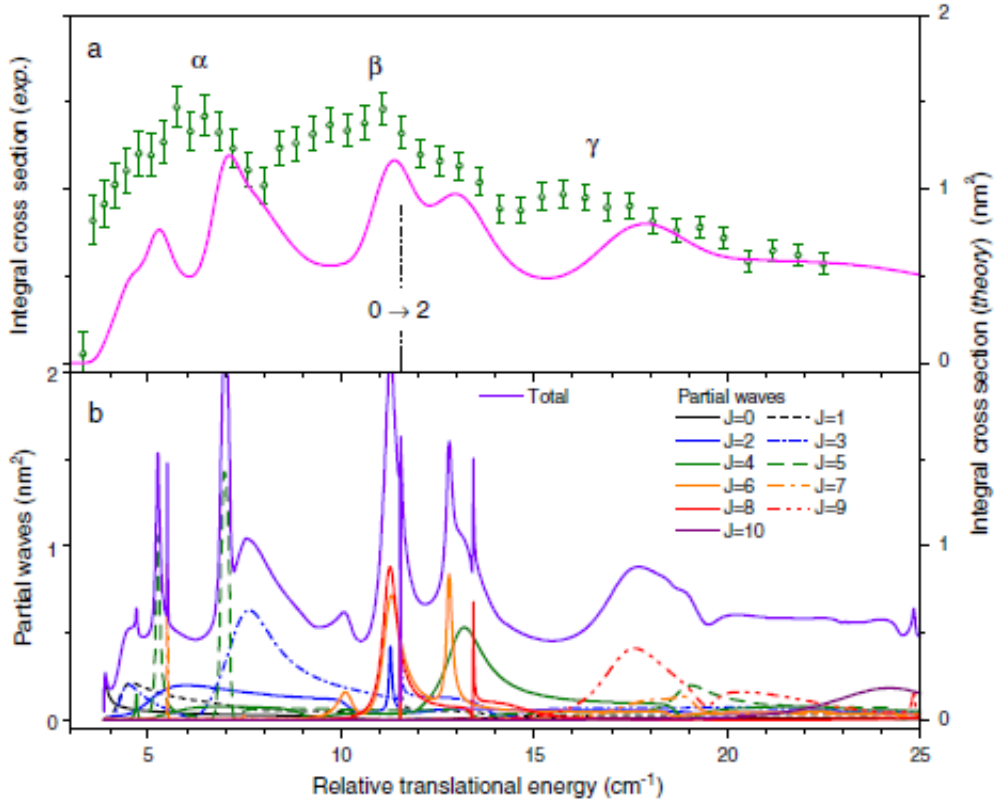


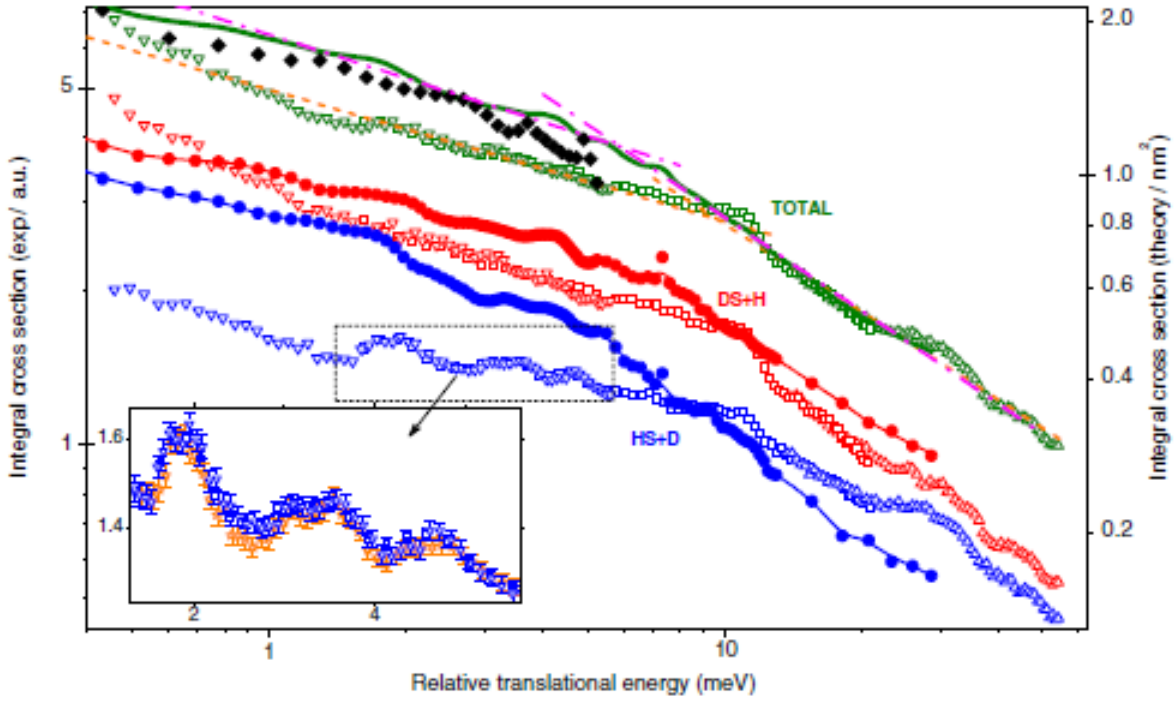
FIG. 2 (color online). (a) Experimental integral cross sections in arbitrary units (open circles with vertical error bars at a 95% confidence interval) and theoretical integral cross sections (solid curve) convoluted over the energy spread. (b) Partial wave cross sections and resulting theoretical integral cross sections from QM calculations performed with the PES of Jankowski and Szalewicz [27].

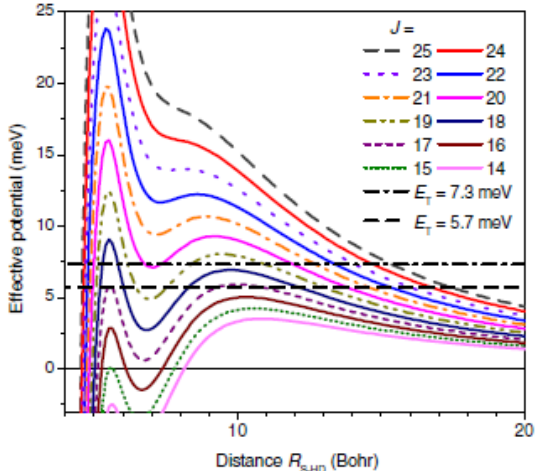
Cold reaction of S(^{1}D) + HD

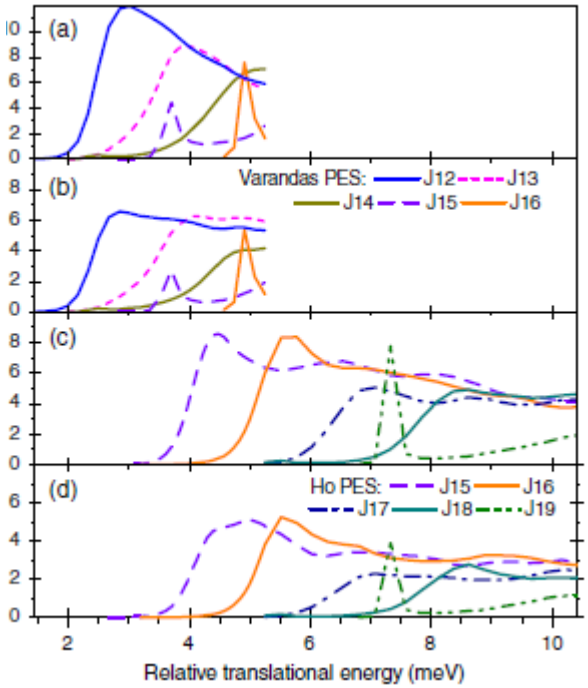
PRL 109, 133201 (2012) PHYSICAL REVIEW LETTERS week ending 28 SEPTEMBER 2012

Dynamics of the S($^1D_2$) + HD($j = 0$) Reaction at Collision Energies Approaching the Cold Regime: A Stringent Test for Theory

Manuel Lara,[1] Simon Chefdeville,[2,3] Kevin M. Hickson,[2,3] Astrid Bergeat,[2,3] Christian Naulin,[2,3] Jean-Michel Launay,[4] and Michel Costes[2,3,*]







Recombination Mechanism

Collision-Induced Dissociation ⇌ Recombination

AB + M ⇌ A + B + M (A, B: atom or molecule, M: third-body)

Two important mechanisms

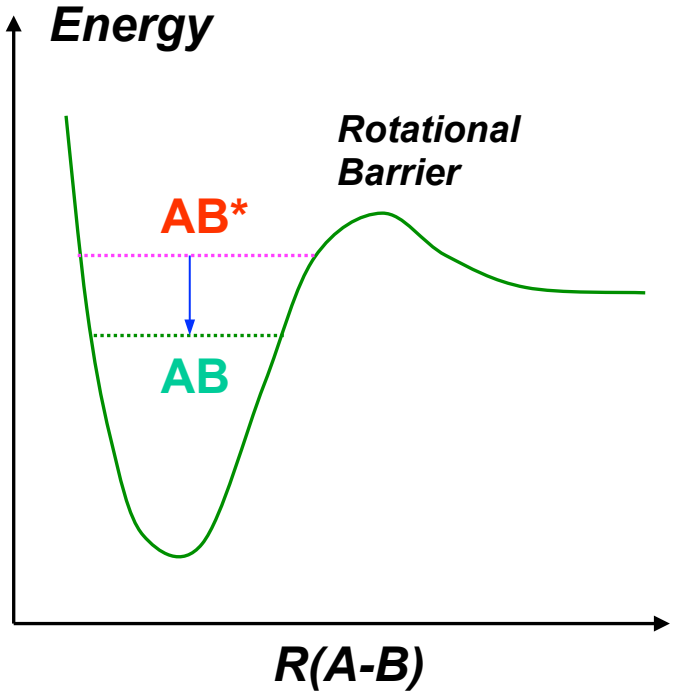
1) Sequential two-body mechanism

A + B ⇌ AB* (AB*: resonance state)

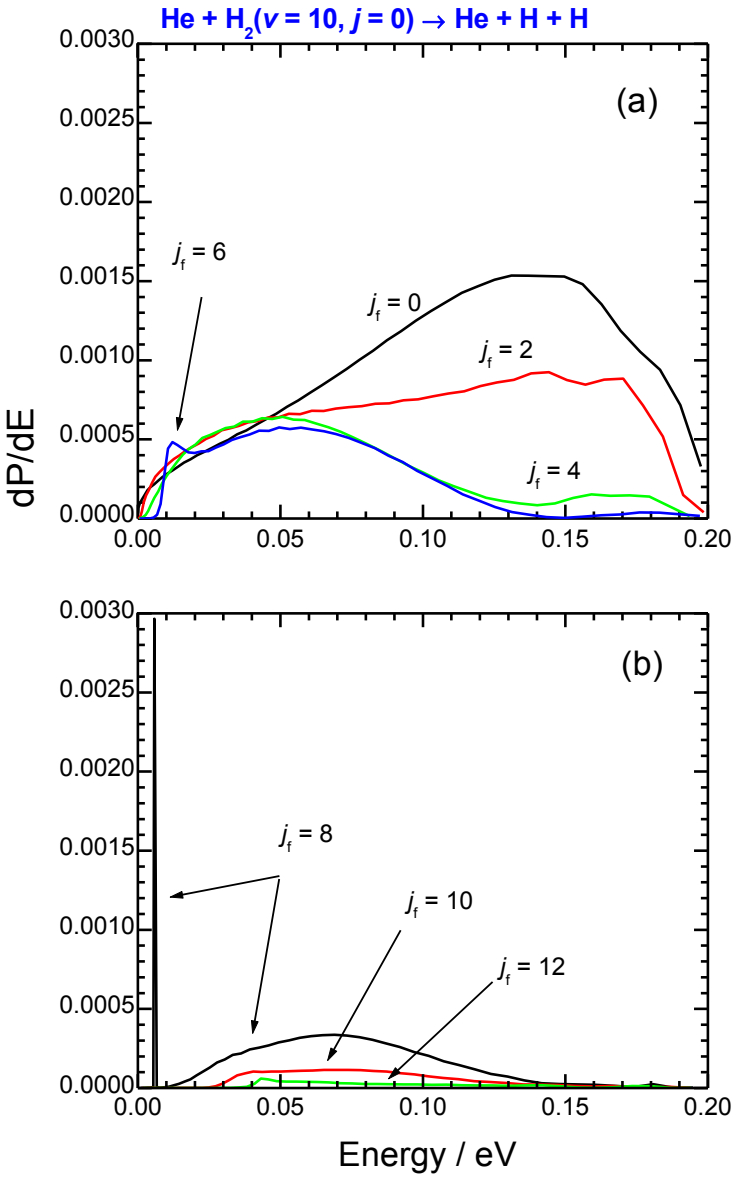
AB* + M → AB + M

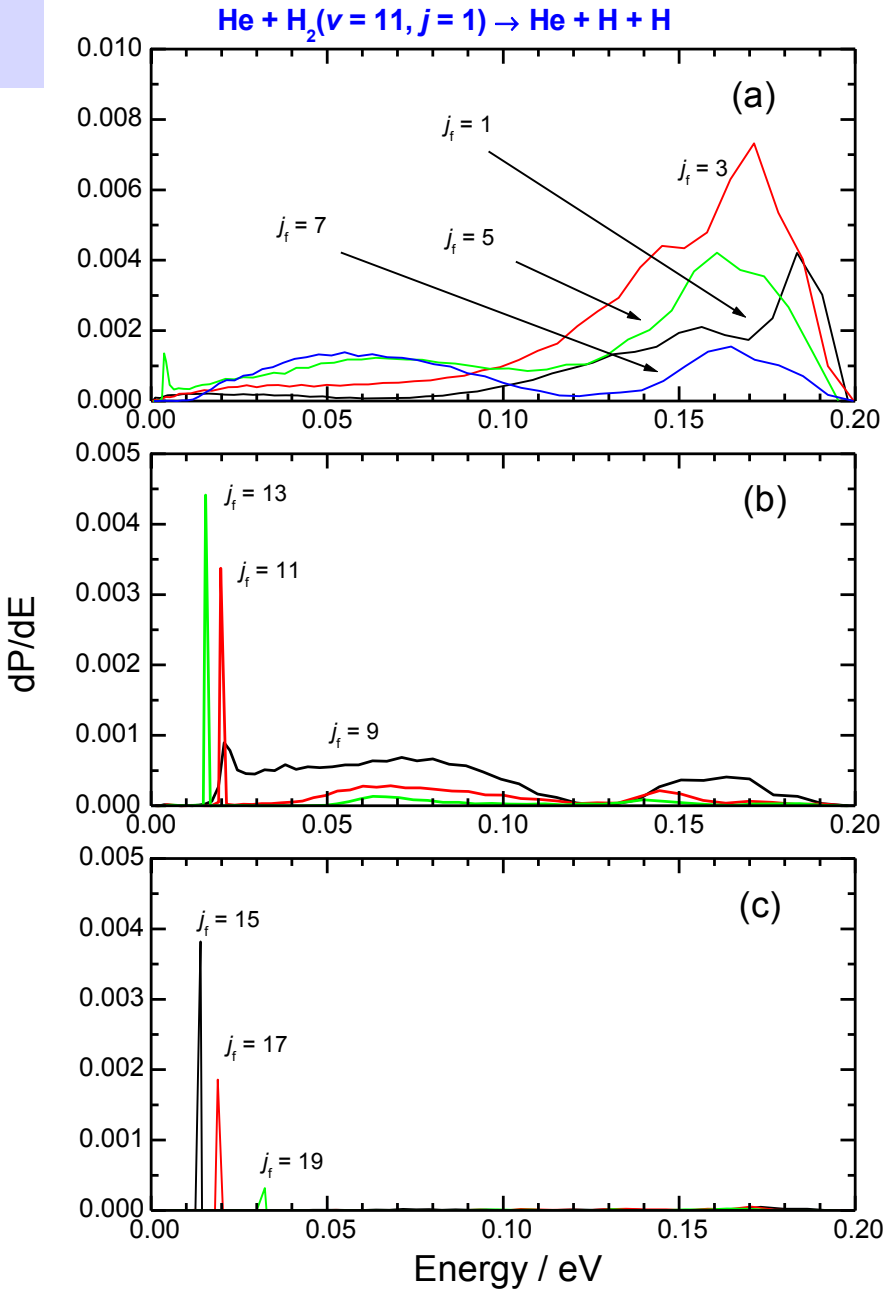
2) Direct three-body mechanism

A + B + M → AB + M



H+H translation energy distributions from close-coupling calculations

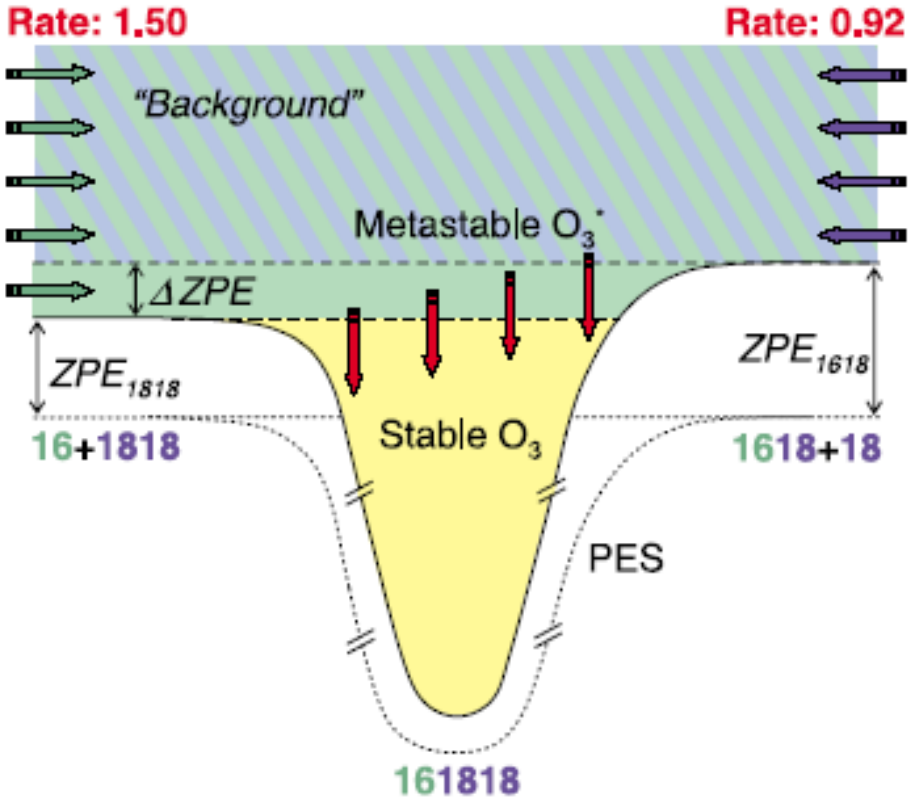


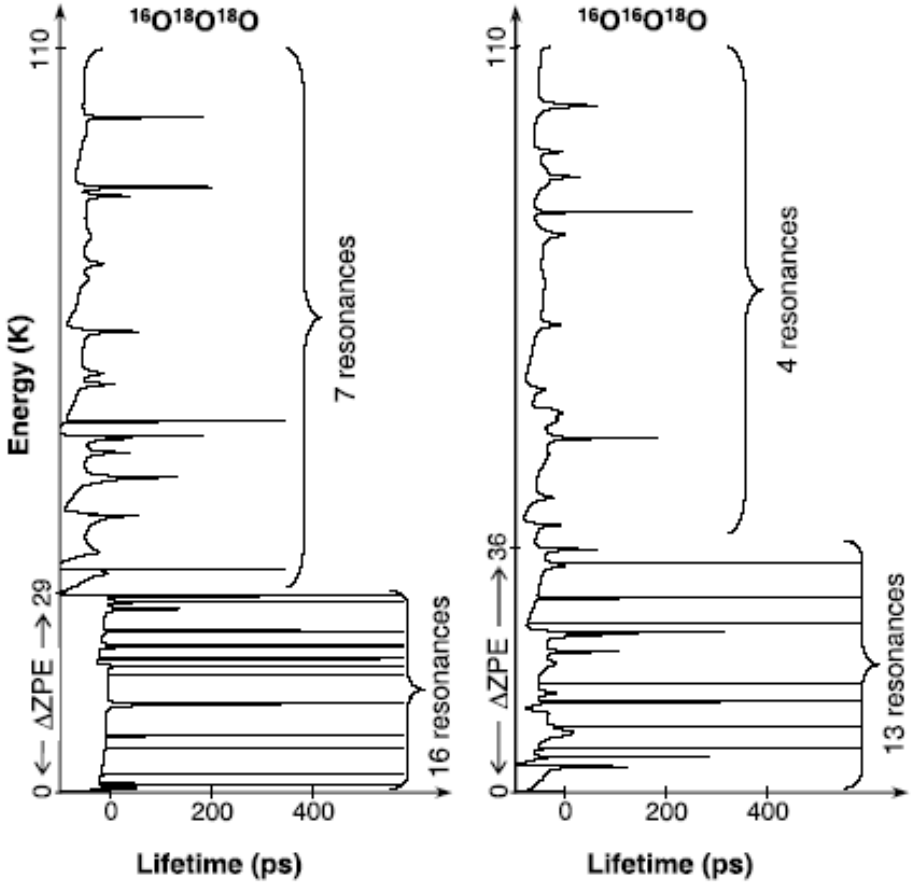


Anomalous isotope effects in ozone formation reactive resonances ?

$^{16}O^{16}O^{16}O$, $^{16}O^{18}O^{16}O$, $^{18}O^{16}O^{18}O$ etc

$O + O_2 + M(N_2) \rightleftharpoons O_3 + M(N_2)$

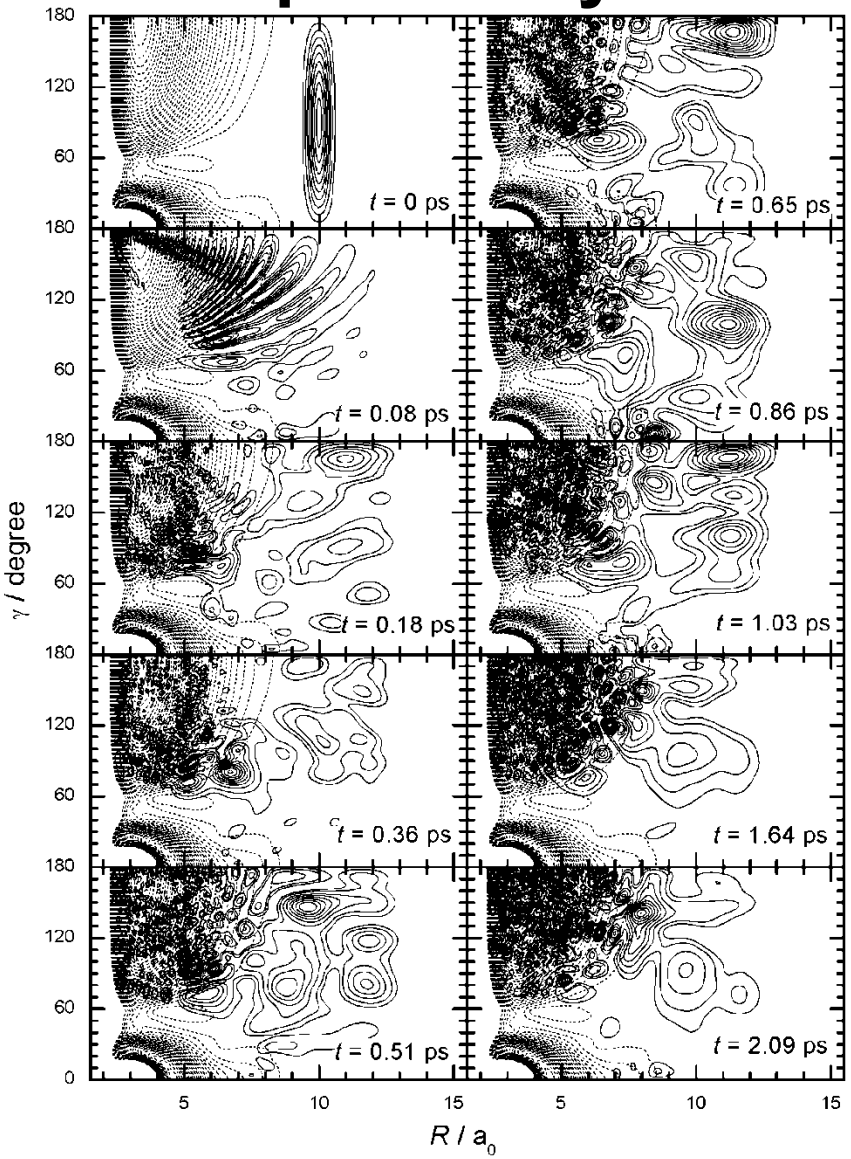


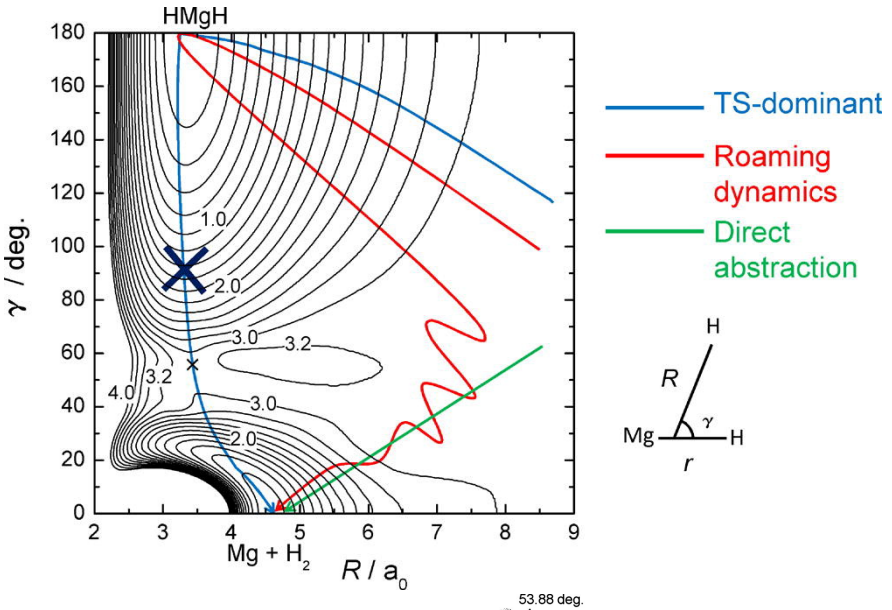


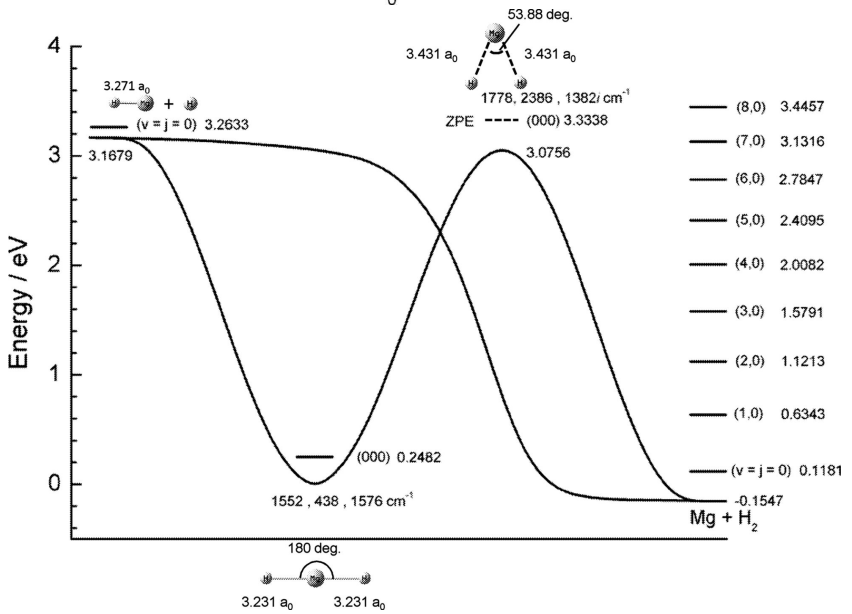
Babikov et al, *Chem. Phys. Lett.* 372 (2003) 686-691.

Roaming dynamics in **Mg + H_2 ⇄ MgH + H**

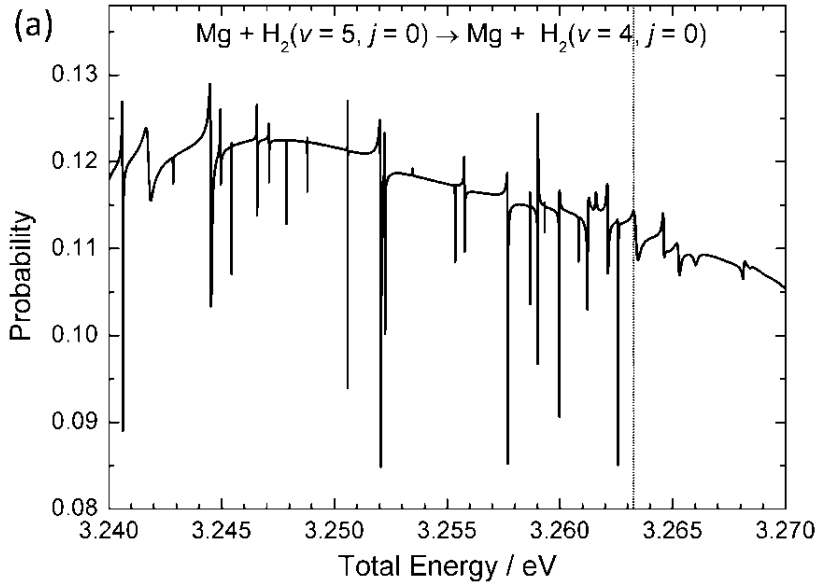
Wave packet dynamics

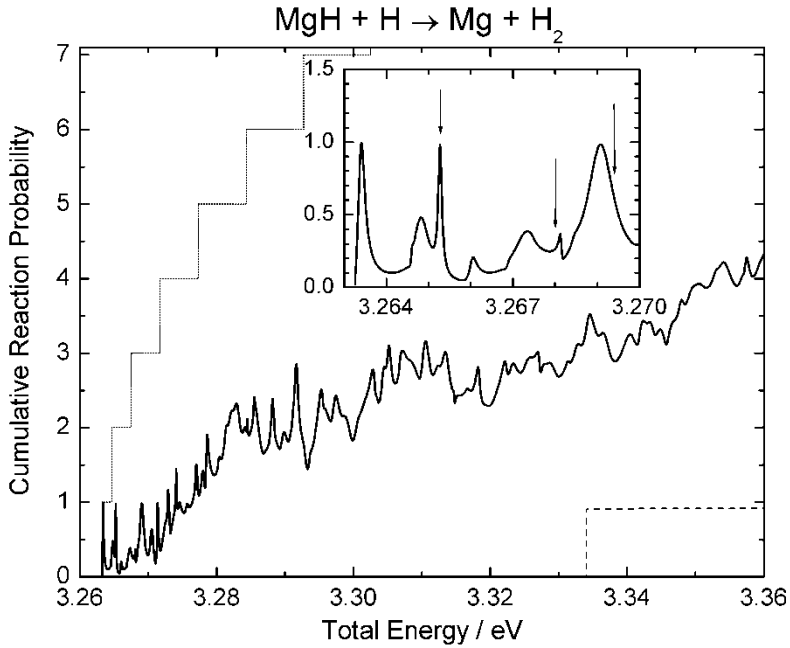


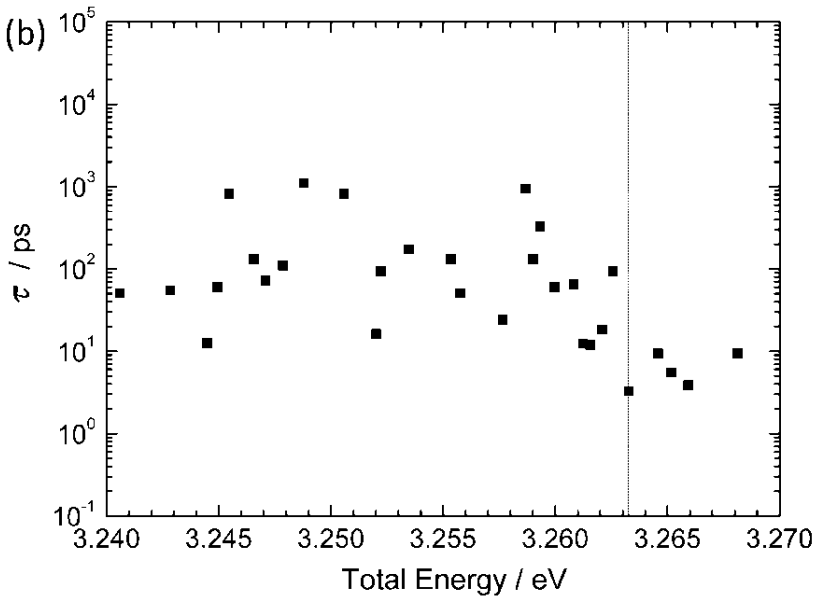




Roaming dynamics in chemical reactions







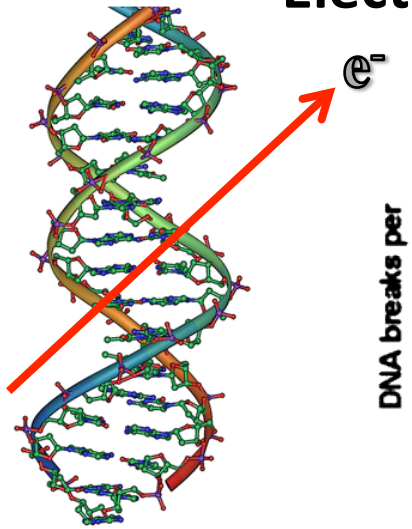
Roaming dynamics should be strongly correlated with resonances (above threshold energy)

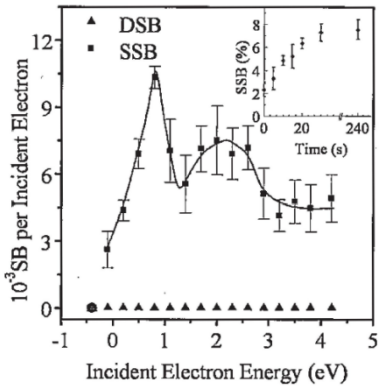
Radical-radical reactions (atmospheric chemistry)

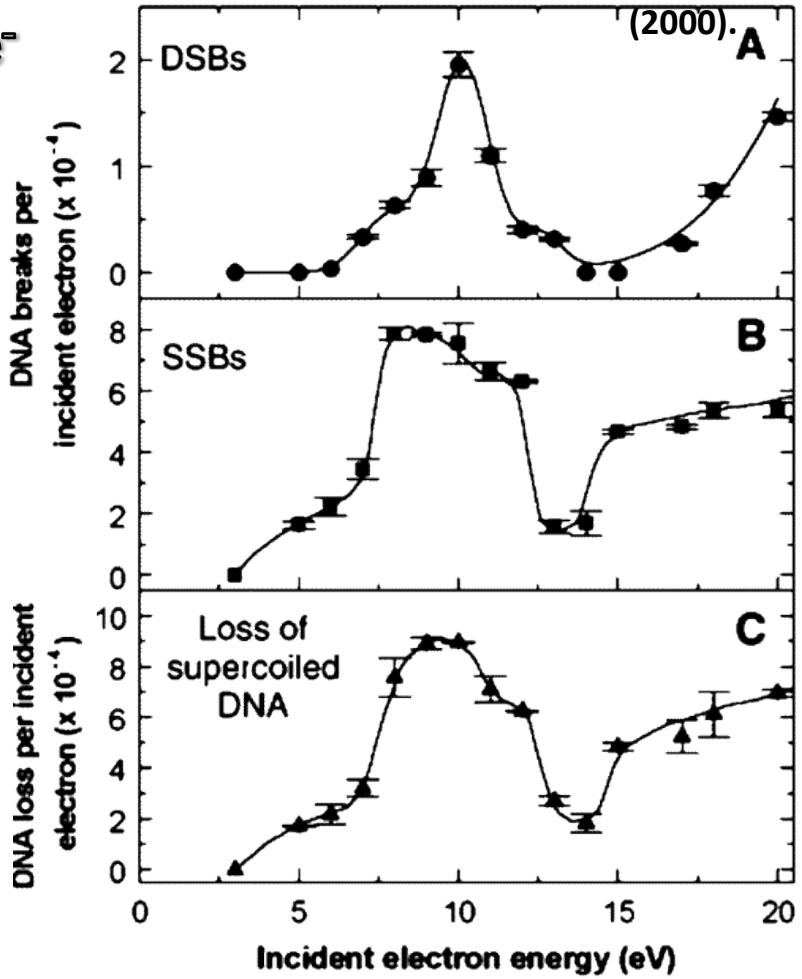
DNA damage by low-energy electrons

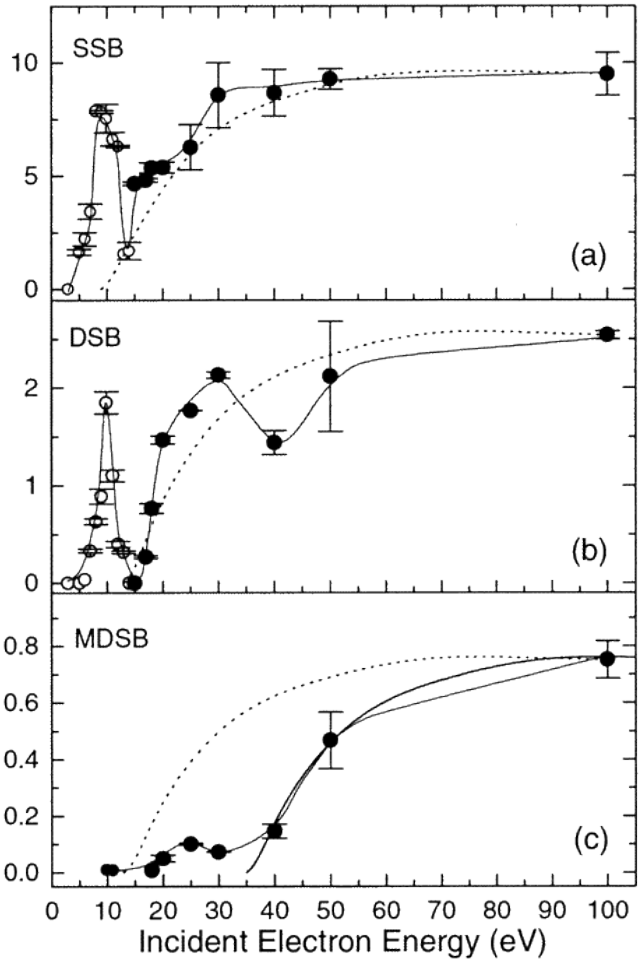
Electron irradiation to Plasmid DNA

Boudaïffa et al., *Science*, 287, 1658 (2000).



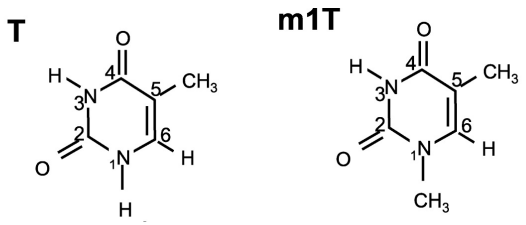


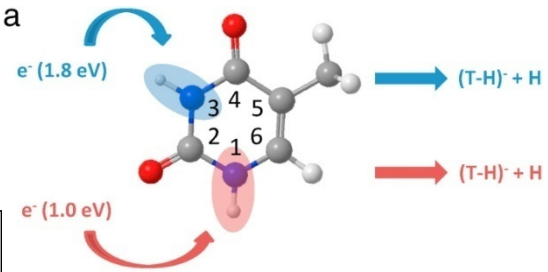




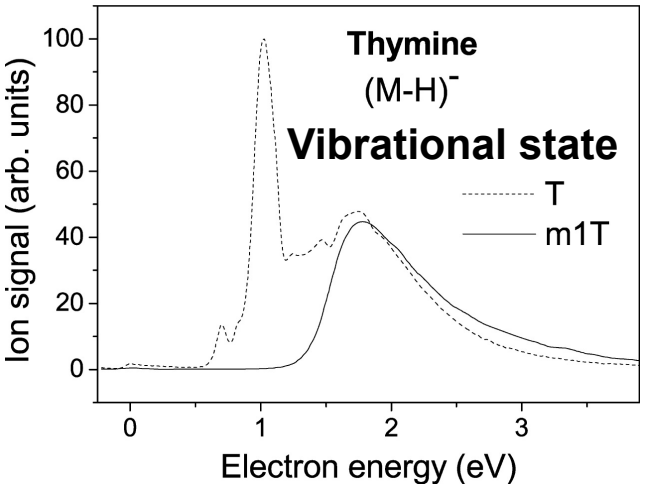
DNA/RNA damage occurs via resonances !

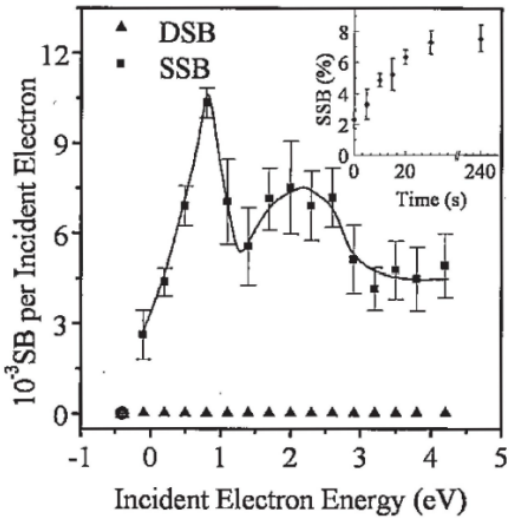
DNA damage by low-energy electrons

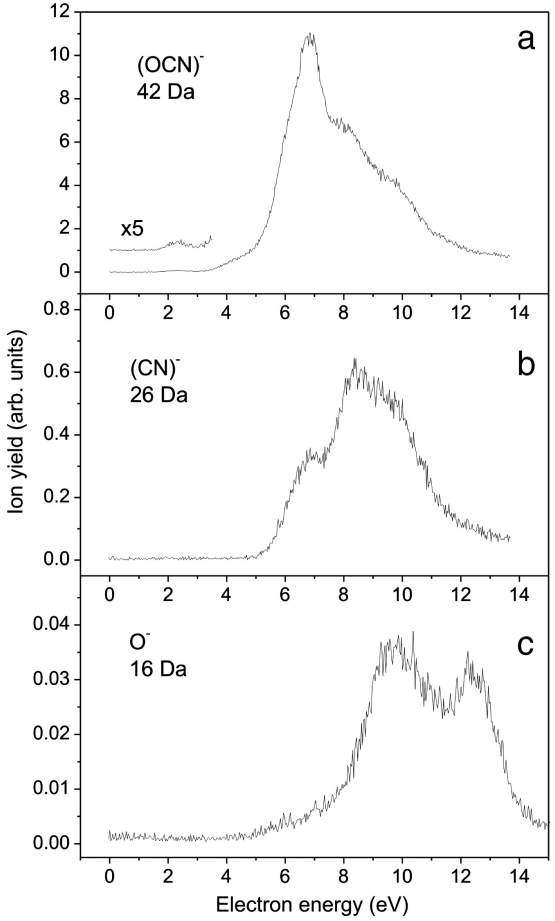


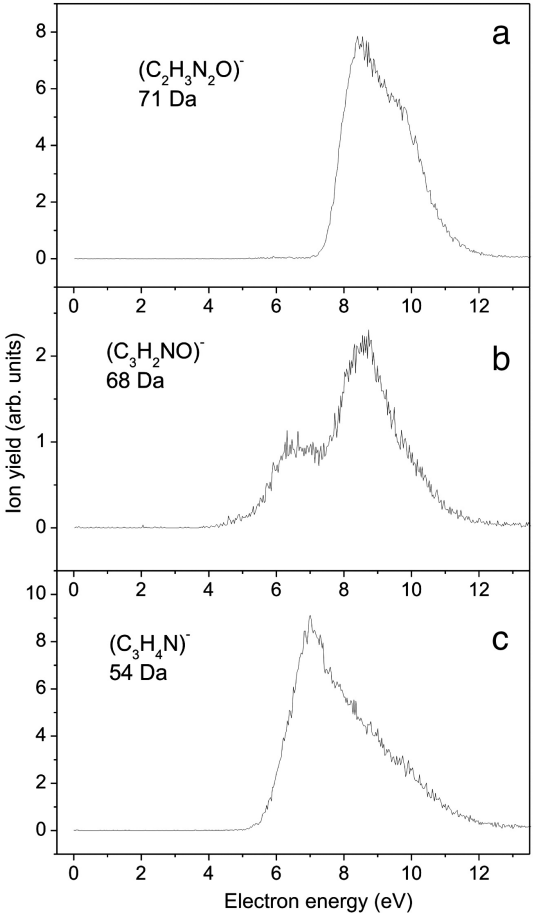


Other dissociation channels can be seen at high energy

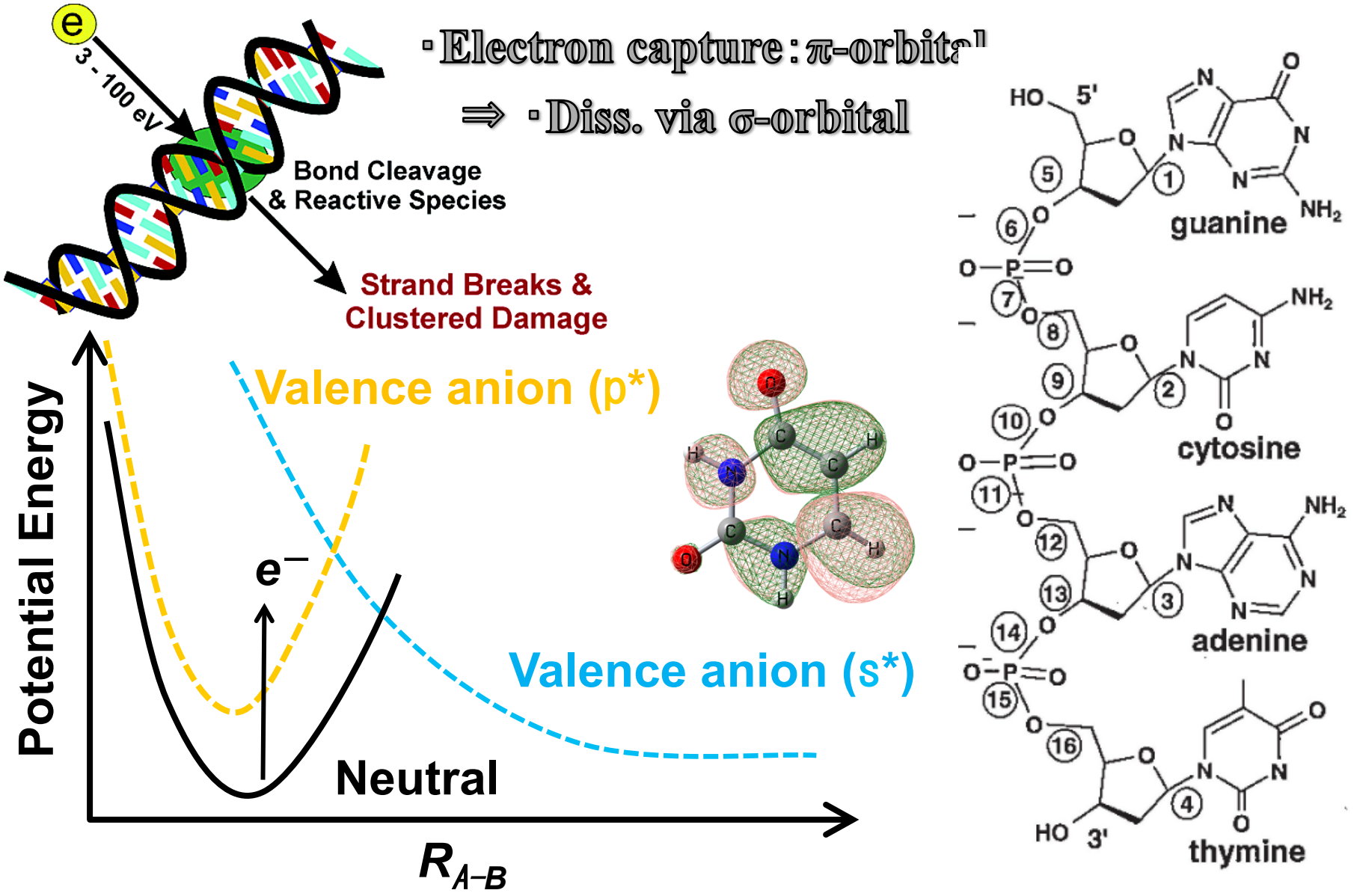








Mechanism of DNA damage



Conclusions

- Resonances in chemical reactions have been experimentally observed in several systems due to advances in sophisticated experimental techniques.
- Resonances in chemical reactions may be very important in various fields !?
  - Atmospheric and interstellar chemistry
  - Anomalous isotope ratios
  - More cold chemistry experiments in the future
- Resonances in DNA radiation damage (electron collision)