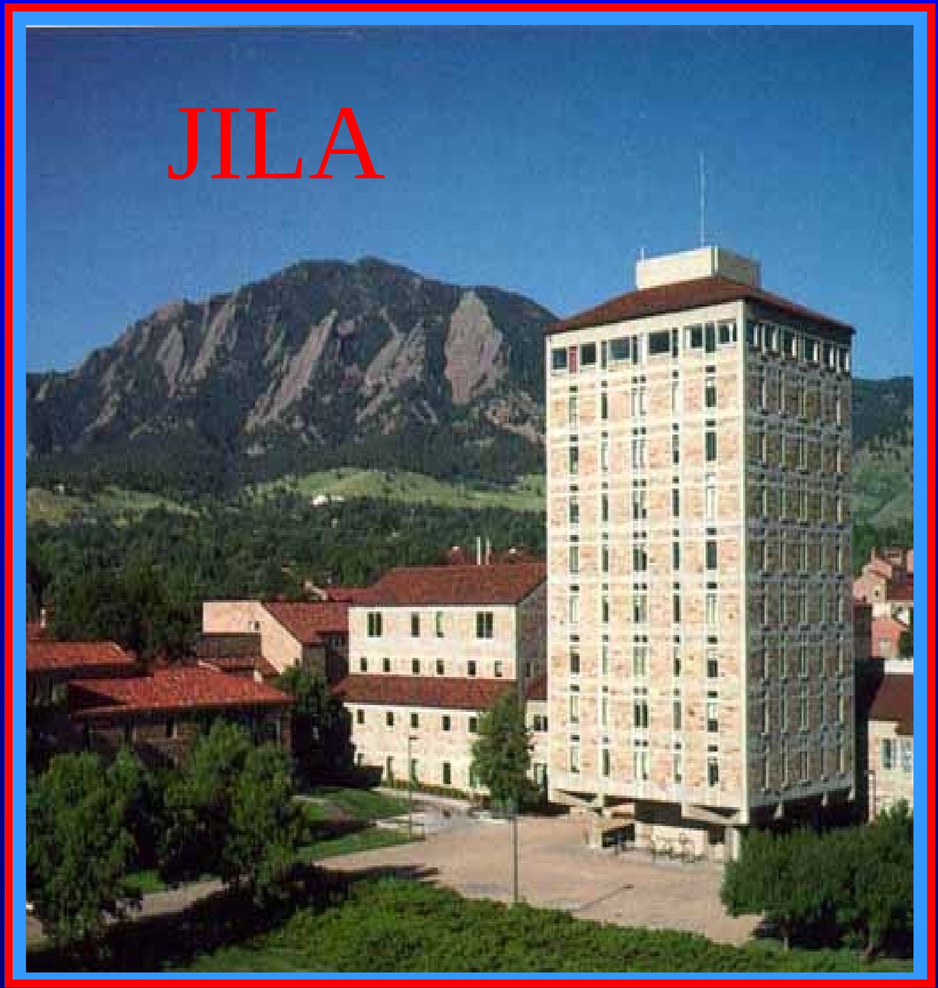
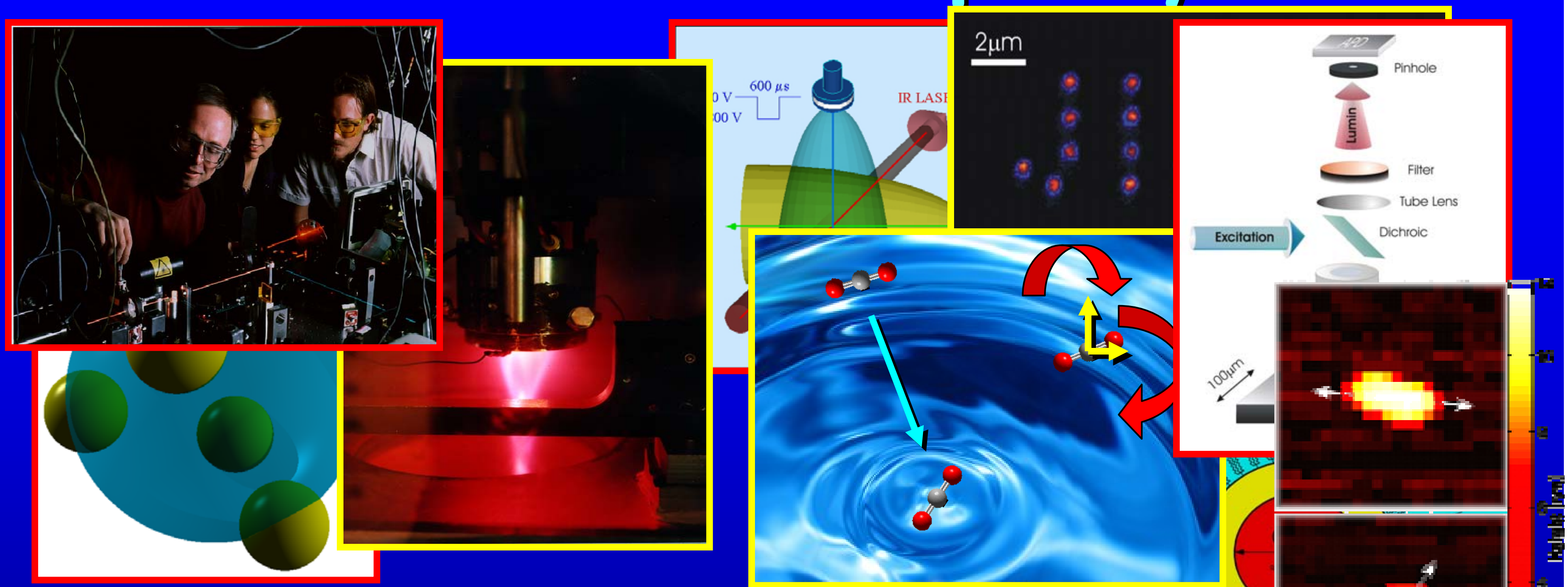
State-to-State Dynamics in Ultracold Collisions: Insights From High Resolution Spectroscopy of Weakly Bound Molecular Complexes?



Conference on New Physics with Ultracold Molecules
Kavli Institute for Theoretical Physics
March 11 – 15, 2013

Work done at
JILA/Department of Chemistry and Biochemistry
National Institute for Standards and Technology
University of Colorado
Boulder, CO

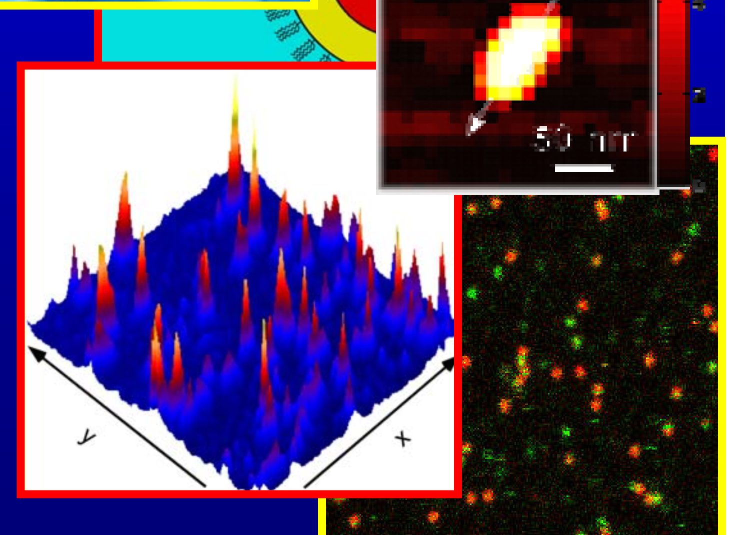
In Search of Simplicity…



- High Resolution Laser Spectroscopy/ Dynamics (jet cooled radicals, clusters, molecular ions)

- Chemical Reaction Dynamics (state-to-state reactive scattering, stereochemistry, inelastic/reactive collision dynamics at gas-liquid interfaces)

- Single Molecule Microscopy/Kinetics (RNA folding, quantum dot blinking, SERS nanocrystals, photoelectron imaging microscopy)



Establishing a Common Lexicon

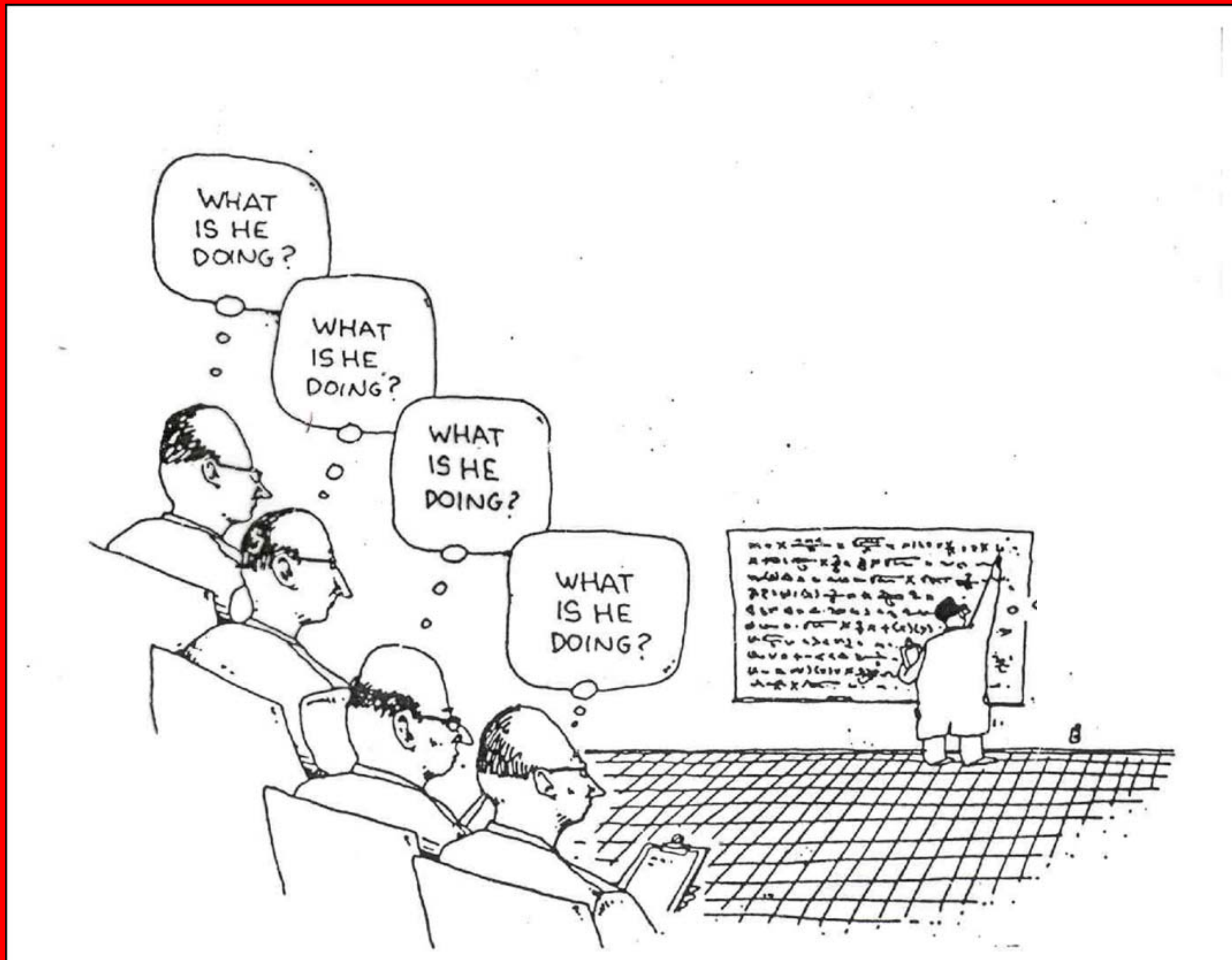
1 eV…

= 8065.73 cm^{-1}
= 241,804 GHz
= 11,605 K
= 0.003675 au
= 96.552 kJ/mol
= 23.061 kcal/mol

Take Home Messages

- Half collision dynamics in van der Waals complexes as models for Feshbach *resonance scattering phenomena* in ultracold collisions
- Potential for catastrophic failure (by up to factors of 10^{12}) of statistical theories for systems with small (3-4) numbers of atoms
- Importance of probing not just *loss of reactant* but *appearance of final quantum state distributions* in ultracold collision chemistry

Definitely Not a Take Home Message…



(i.e. questions welcome!)

Outline

I. Experimental background

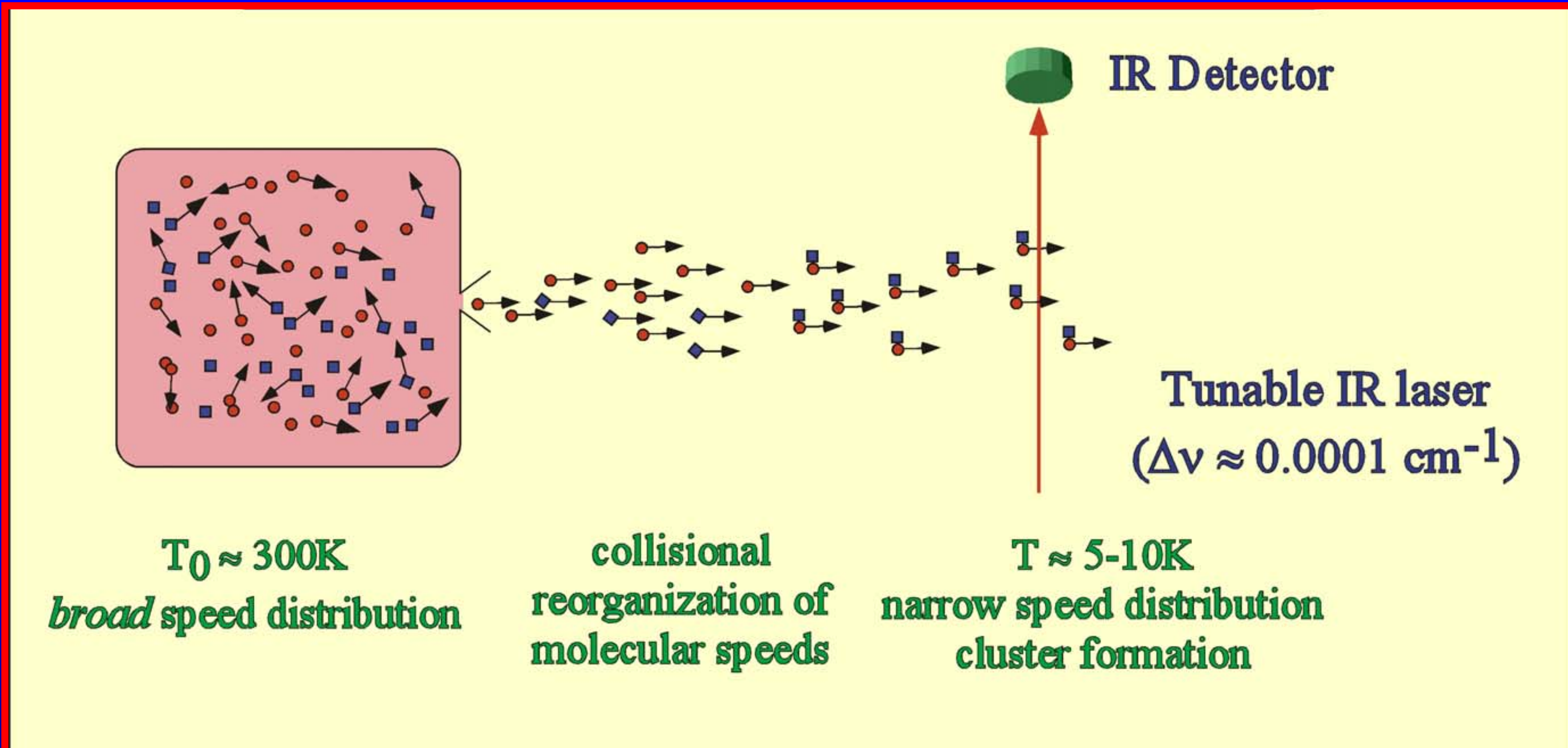
II. High resolution vdWs spectroscopy "recast" as ultracold *Feshbach (vibrational and rotational) and shape resonance dynamics*

III. Final quantum state product distributions from vdWs Feshbach vibrational resonance dynamics

IV. Quo vadis? Product quantum states from ultracold chemistry (intuitions and predictions)

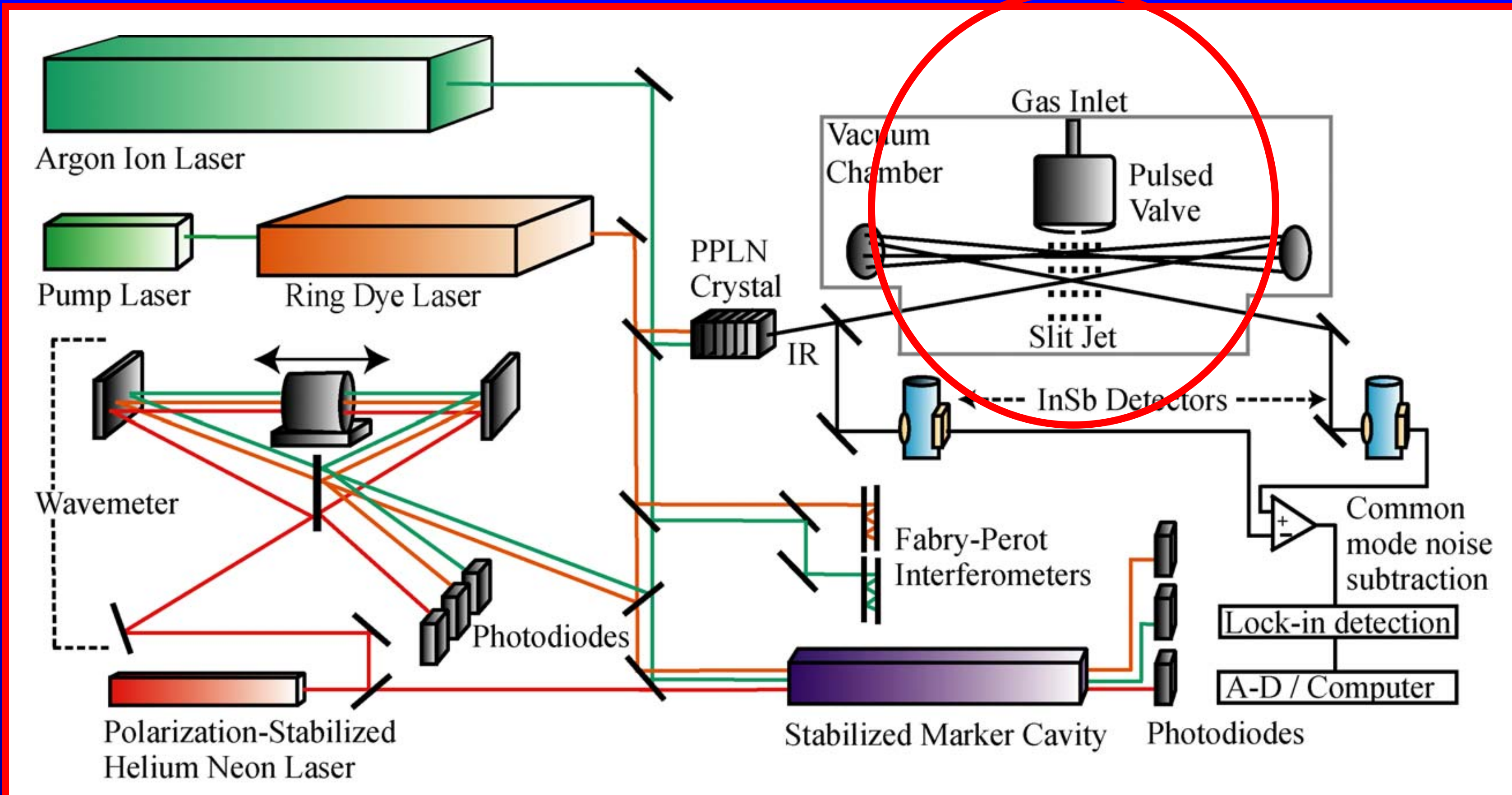
V. Summary

I. Making vdWs Complexes



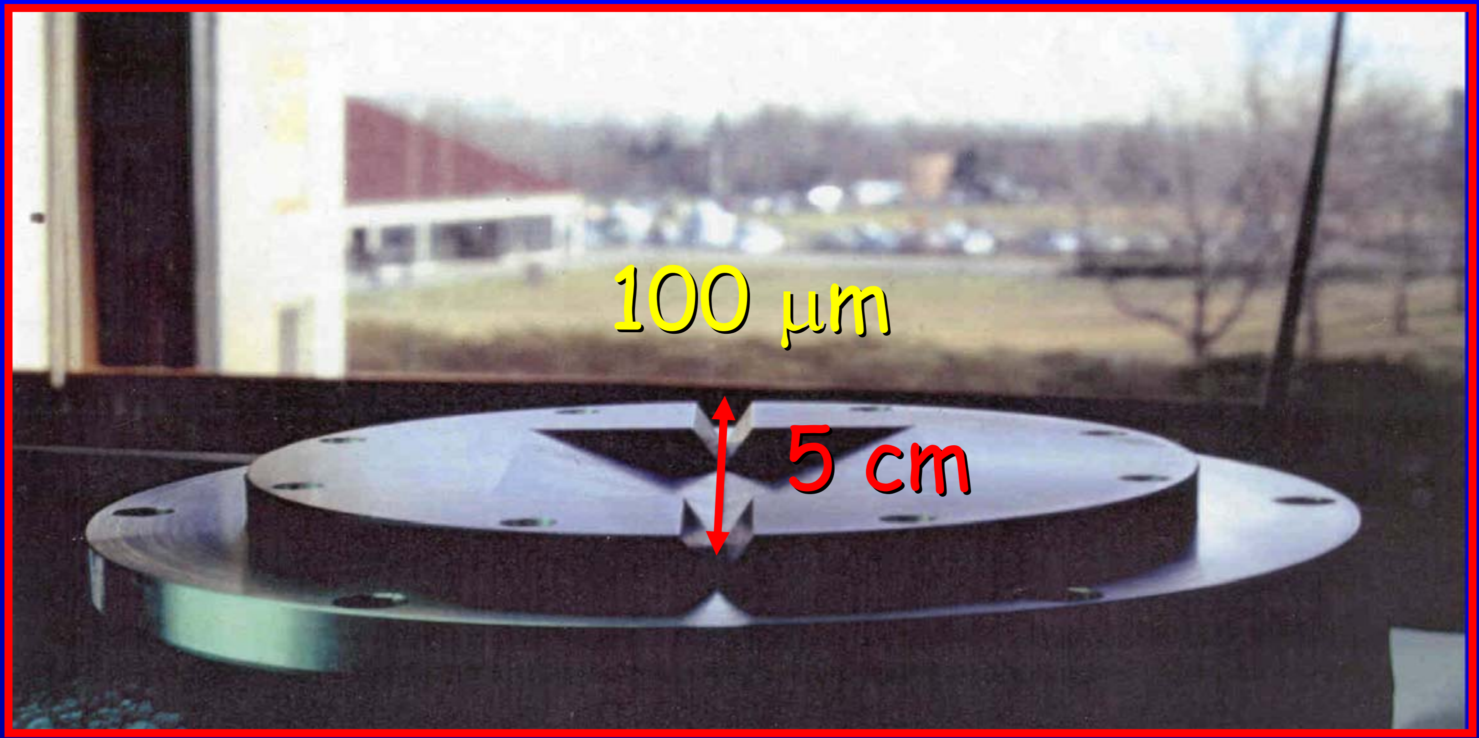
- Beer's Law detection (i.e., $A = N\sigma l$) …
- …but with full v,J quantum resolution ($\Delta\nu \approx 0.0001$ cm^{-1})
- …at the fundamental "shot noise" limit ($\approx 10^{-6}$ /Hz$^{1/2}$)
- Universal, state-selective and surprisingly sensitive!

Experimental Strategy



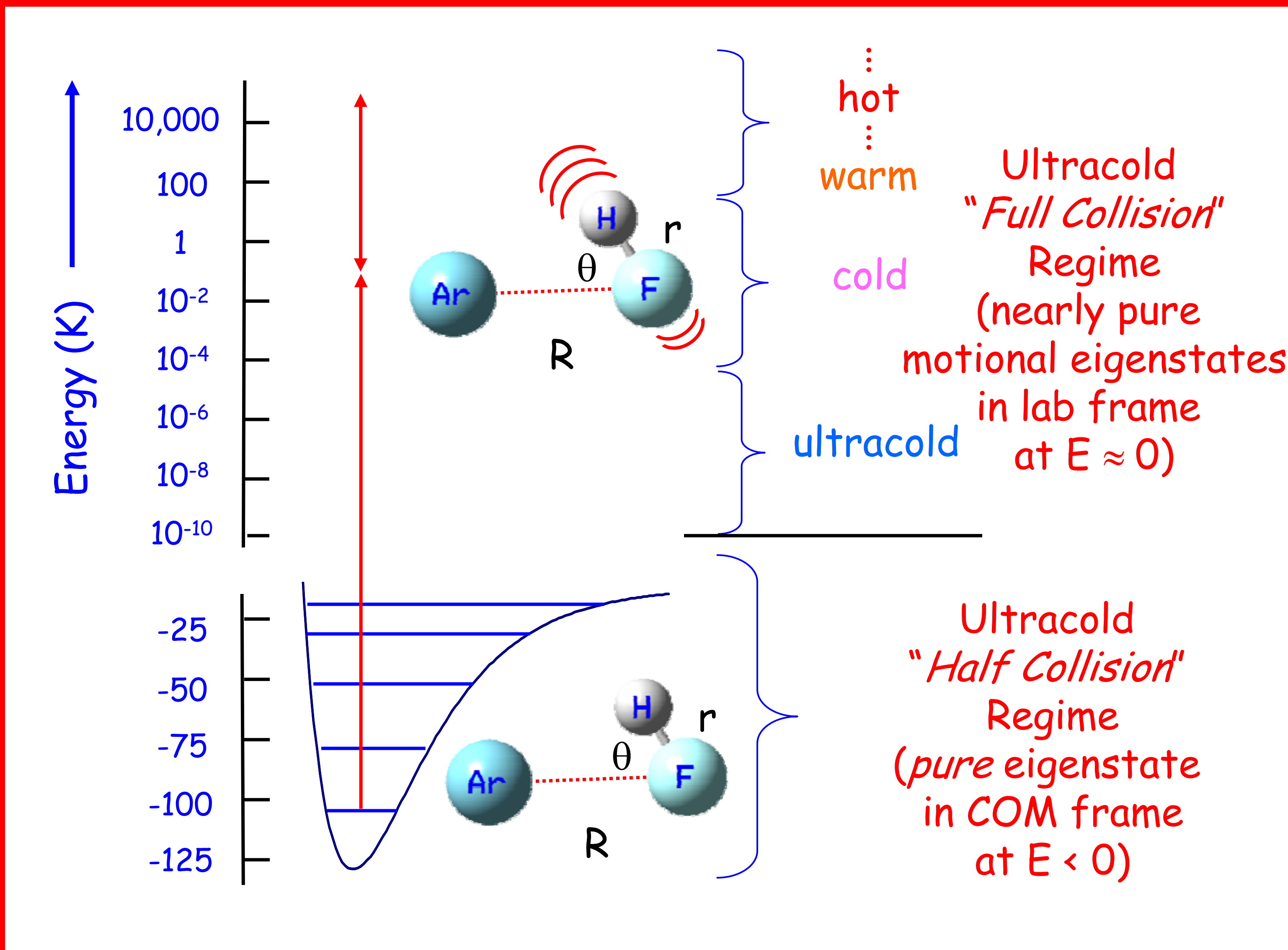
- Sub-Doppler molecular linewidths (≈ 40 MHz in Ne expansion)
- Stabilized optical transfer cavities for frequency precision
- Quantum shot noise limited sensitivity: $A_{min} \approx 1.5 \times 10^{-5}$

"Slit Jets 101"
(Beer's Law at 10^{-9} Torr)

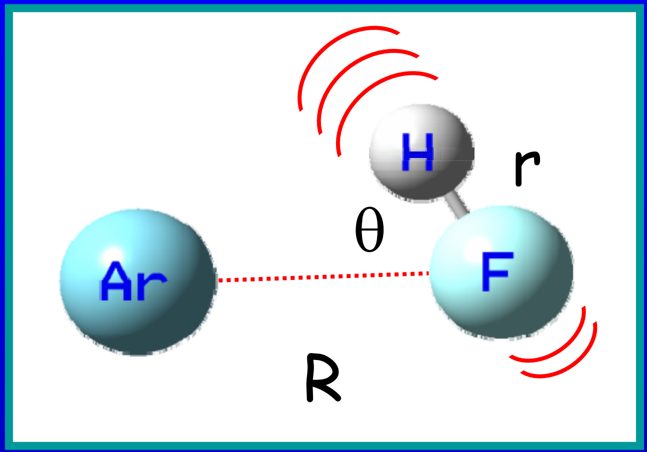


- "Absorbance = density (ρ) x cross section (σ) x path length"
- Optical multipass (x 100 enhancement in l)
- Slow density drop off in slit: $1/r$ vs $1/r^2$ (x 100 enhancement in ρ)
- Sub-Doppler velocity collimation (x 10 enhancement in σ)
- Laser noise subtraction down to "shot noise" limit (< .005% in 10 KHz)
- $\Rightarrow N_{min} \approx 10^7$ #/cm^3/q.s. for *vib'l* transitions

II. vdWs Spectroscopy as Probe of Ultracold Collision Dynamics

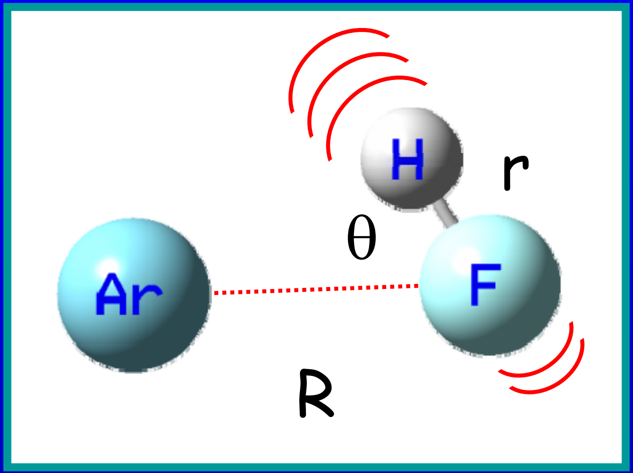


Vibrational Predissociation Lifetime Predictions (#1)?



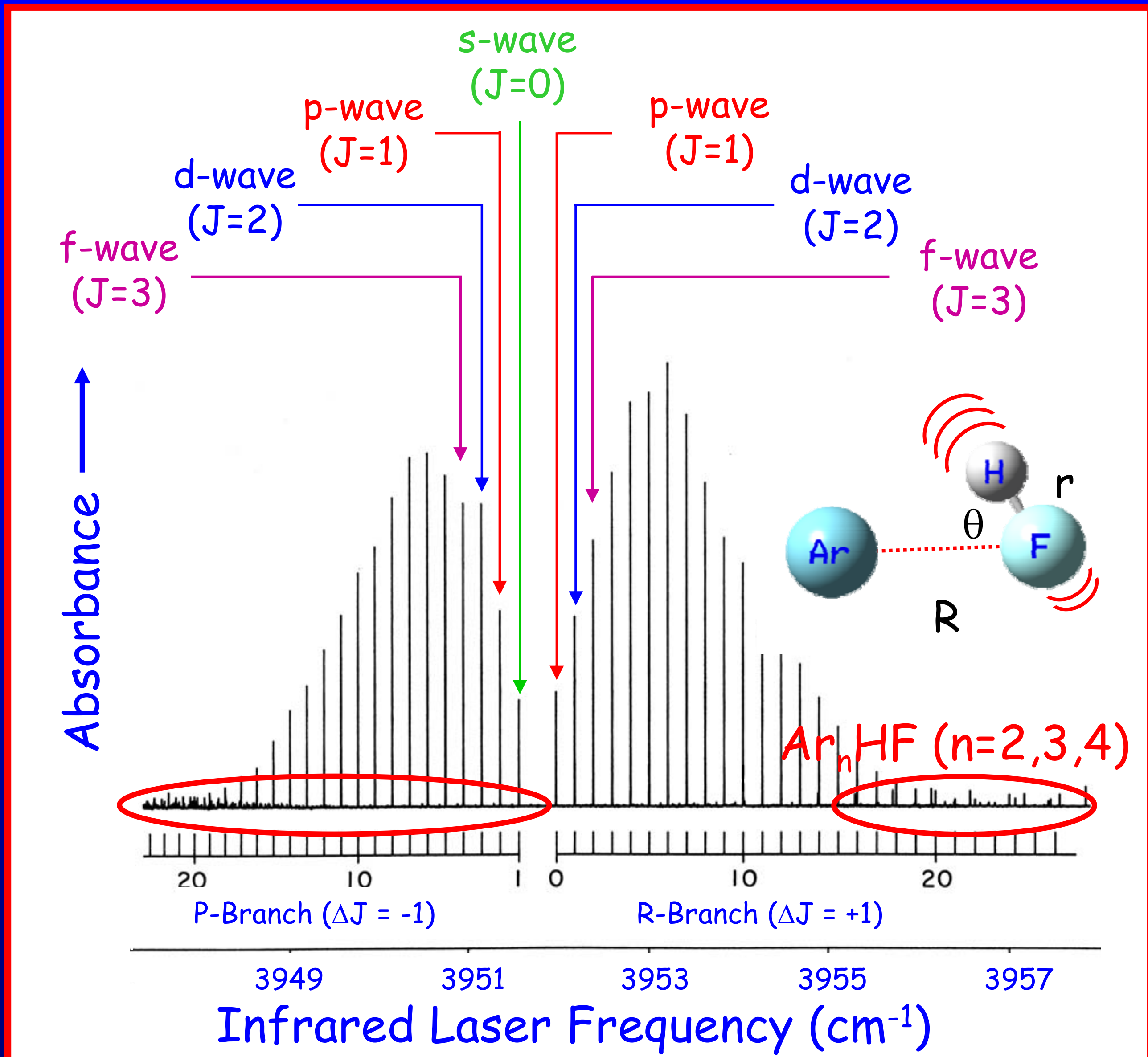
- $E(v=1,J) - D_0$ (Ar-HF) ≈ 3950 cm^{-1} – 120 cm^{-1} ≈ 3830 cm^{-1} >> 0
- Near linear Ar-H-F equilibrium geometry (i.e., good for momentum transfer into weak vdW bond)
- Statistical phase space, RRKM theories predict *extremely rapid* vib'l predissociation ($\tau_{prediss}$ ≈ single HF oscillation ≈ 8 fs)

Vibrational Predissociation Lifetime Predictions (#2)?



- Dissociation coordinate ($\omega_{vdW} \approx 40$ cm^{-1}) 100-fold *non-resonant* with HF vibration ($\omega_{HF} \approx 4000$ cm^{-1})
- Requires high order multiquantum vibrational energy transfer
- Must deposit $E_{vdW} \approx 3830$ cm^{-1} into HF rotation (very widely spaced levels) and/or relative translation of Ar + HF(v',J')
- $\Rightarrow$ *Extremely slow* vib'l prediss

Ultracold *Vibrational* Feshbach Resonances



- Sharp, "stick" like Ar-HF(v=1,J) rovibrational lines…
- …with instrument limited line widths ($\Delta\nu_{Lor}$ < 1 MHz)
- $\Rightarrow$ Extremely long lived *vibrational Feshbach* resonances…
- …each from *single partial wave* states (J = 0, 1, 2, 3…)

How Long?

- $\Delta\nu_{Lor} < 1$ MHz
- $\tau_{prediss} > 1/2\pi\,\Delta\nu_{Lor} > 160$ ns…
- … > 20,000,000 Ar-HF(v=1) vibrations

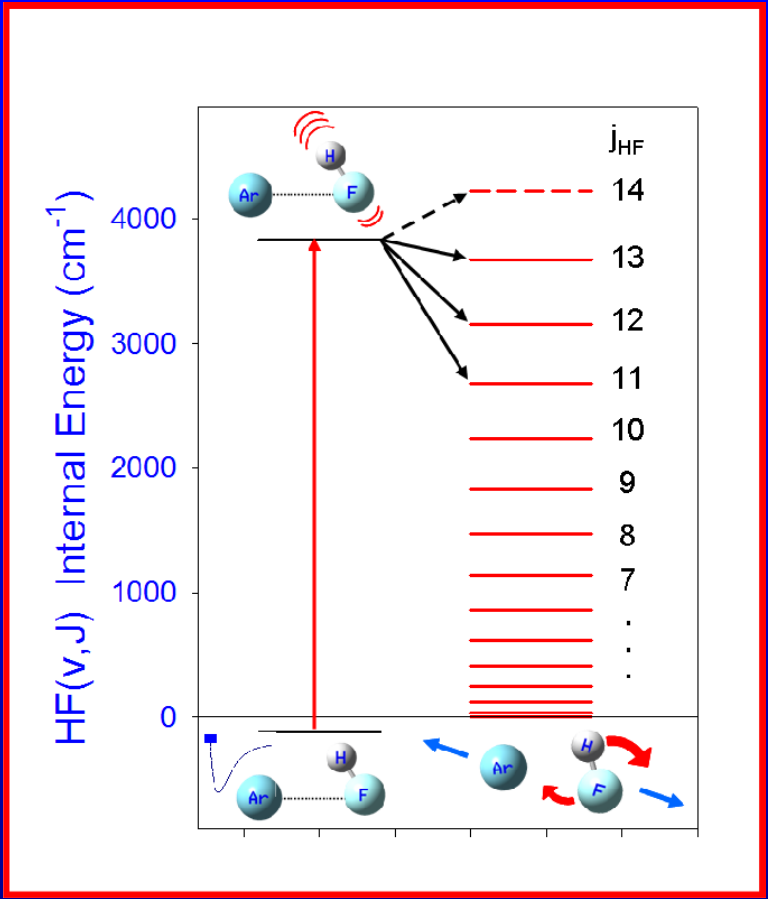
- Molecular beam depletion studies by Miller and coworkers…
- …$\tau_{prediss} > 300\ \mu s$
- $\Rightarrow$ in excess of 36,000,000,000 Ar-HF(v=1) vibrations!

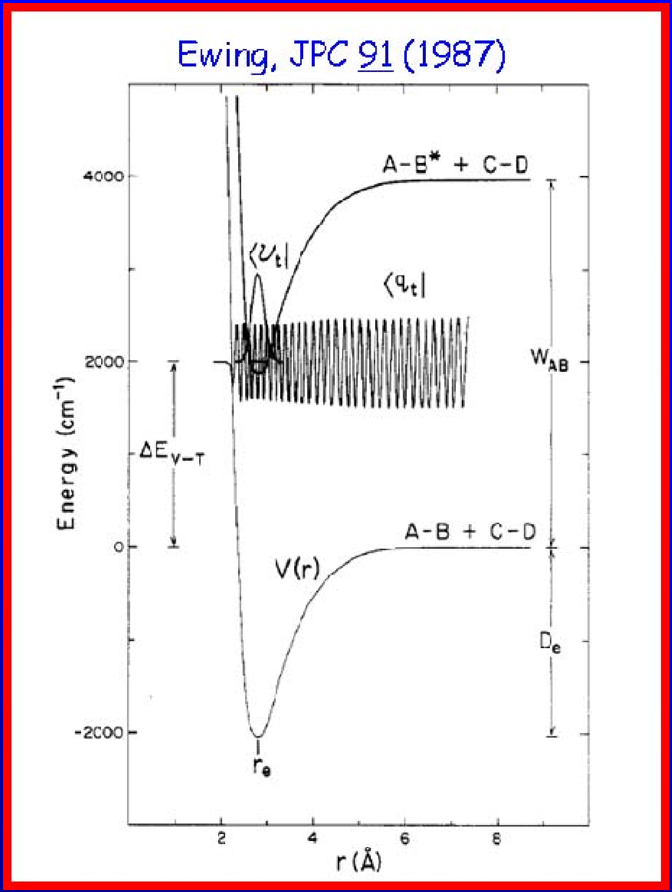
- Consistent with Ewing predictions based on exponential "quantum number gap law", $\nu_{prediss} \approx \nu_{HF}\,\exp(-\Delta N) < 1/$(minutes to hours)

- Likely *radiatively limited* by HF(v=1→0) emission ($\tau_{rad} \approx 10$ ms) with *non-radiative*, pure predissociation lifetimes >> 10 ms

- Failure of statistical RRKM theory in small complexes by 12 orders of magnitude! (8 fs vs. >> 10 ms)

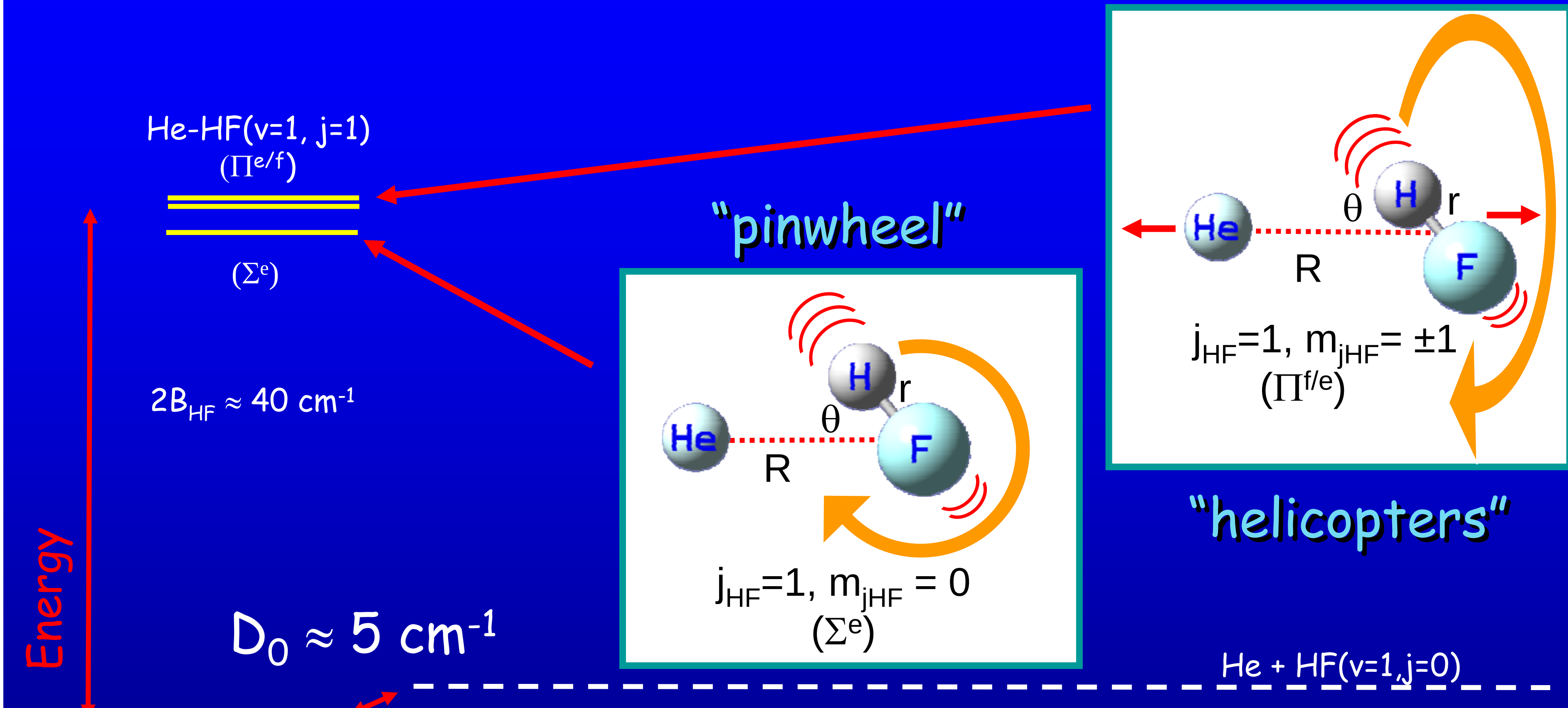
Mind the (Excess Recoil Energy) Gap?

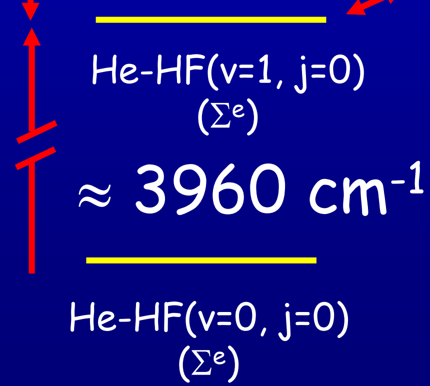




- Probability as overlap matrix element $|\langle\Psi recoil|\Psi vdw\ stretch\rangle|^2$
- *Exponentially* dependent on ratio of $\lambda_{de\ broglie}$ for bound and continuum states…
- …strong propensity for minimizing translational recoil energy!

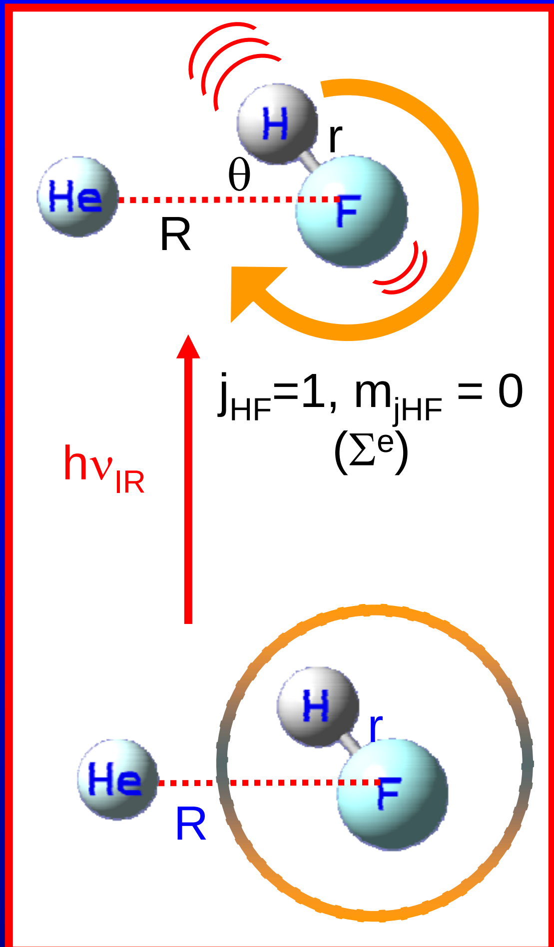
He-HF: "Molecular Baseball"

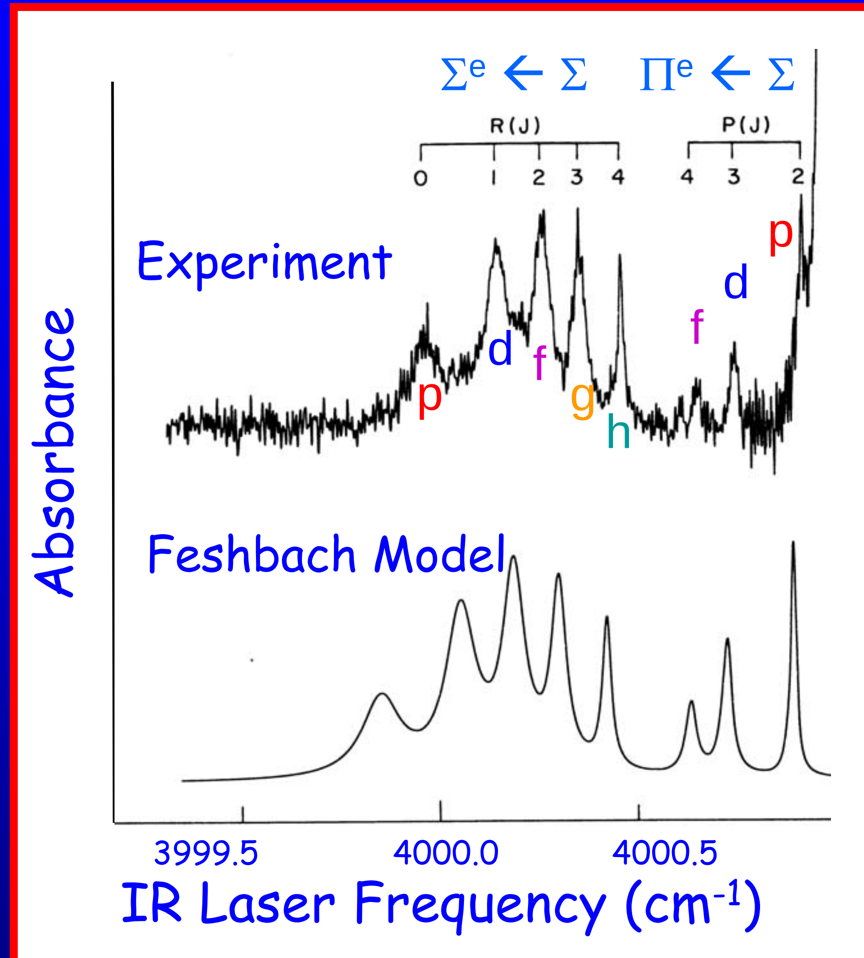




- 2j+1 = 3 (j=1) internal rotor states …
- … each above dissociation limit to form He + HF(v=1,j=0)
- Predict faster predissociation lifetimes for pinwheel vs. helicopter "swings" of the bat

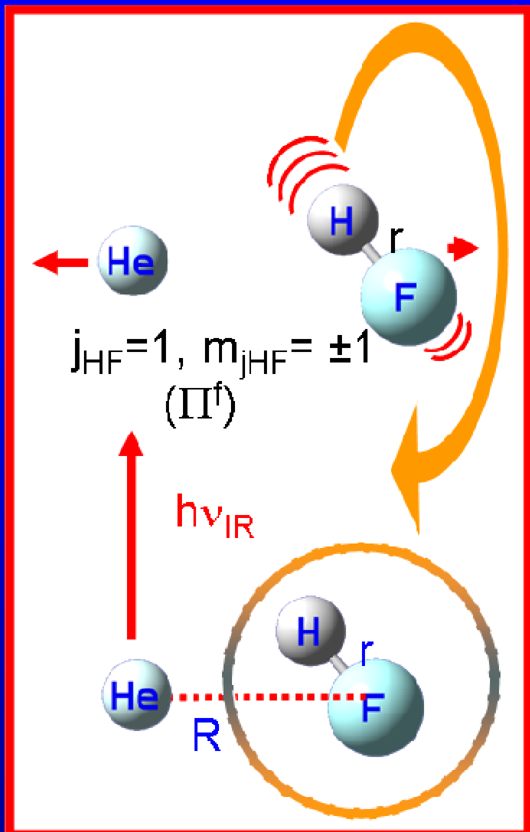
Ultracold *Internal Rotor* Feshbach Resonances
He---HF(v_{HF}=1, j_{HF}=1, Σ^e) "p,d,f,g,h-partial waves"

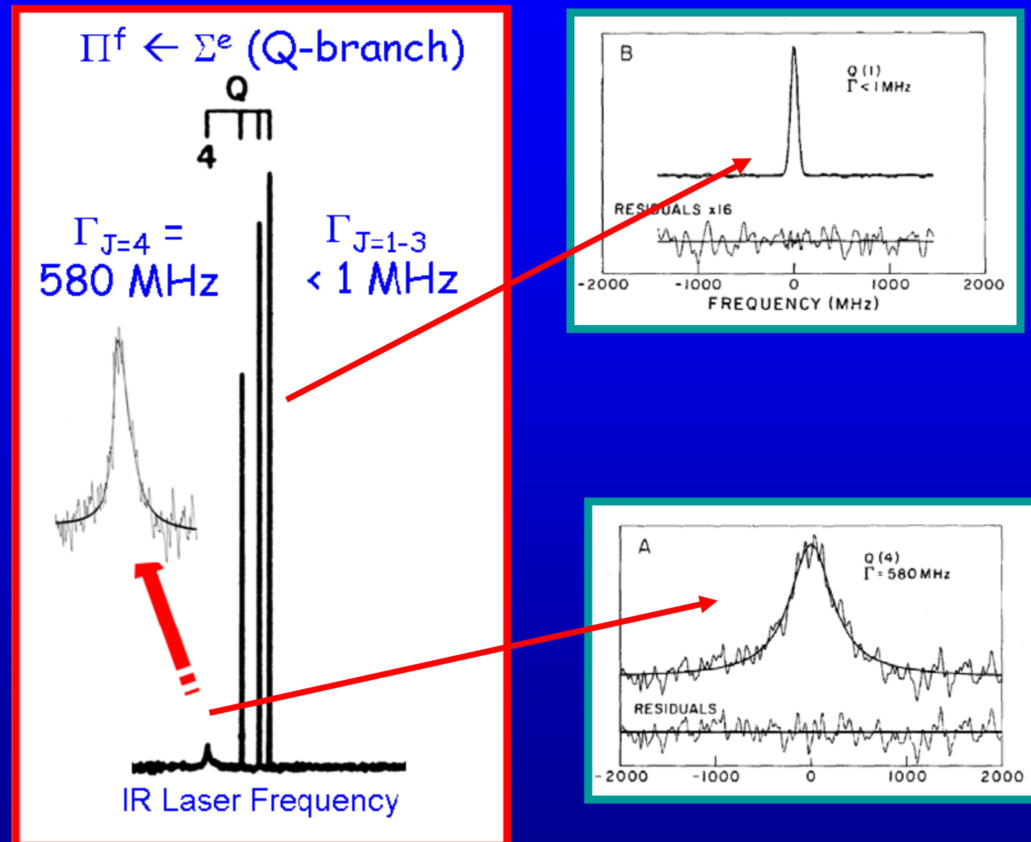




- Clear lifetime broadening (partial wave J-dependent)
- 30-300 ps "R→T" lifetimes, even for optimal Σ^e orientation of "swing"
- Q = 400-4000 (i.e., "batting average" ≈ 1/400-1/4000)

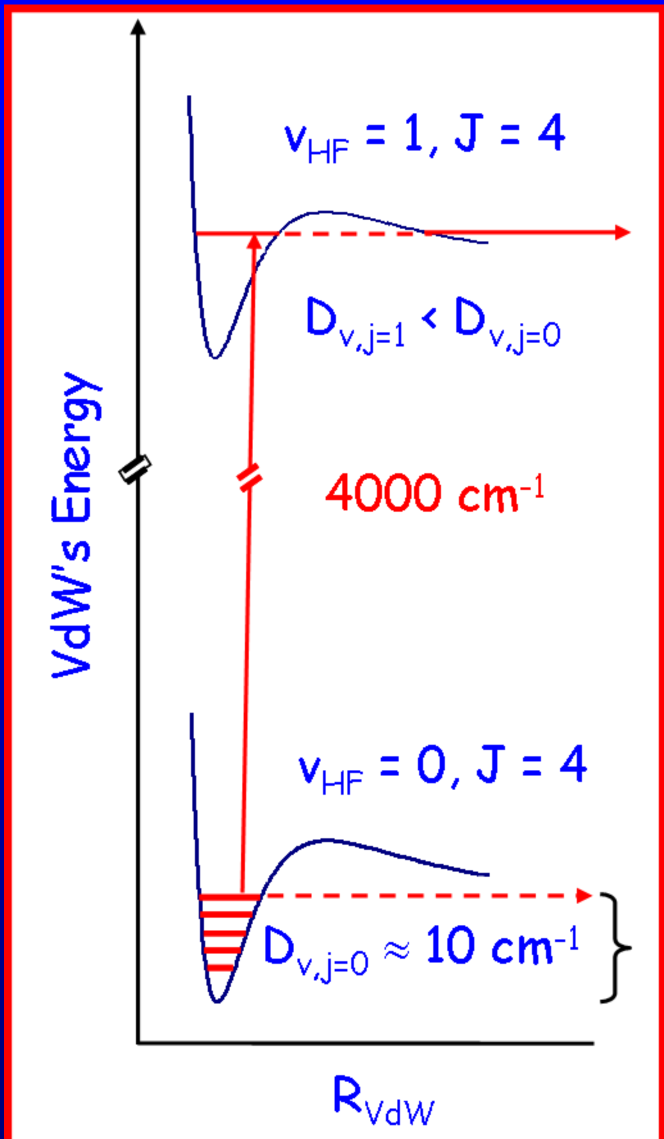
Ultracold *Internal Rotor* *Shape* Resonance
He--HF(v_{HF}=1, j_{HF}=1, Π^f) "g-wave"

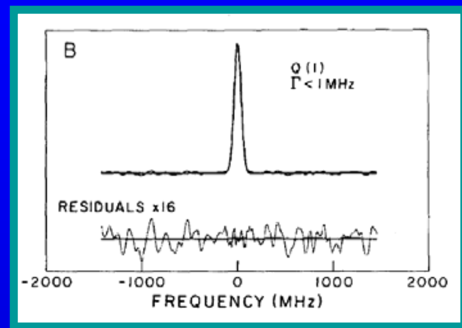


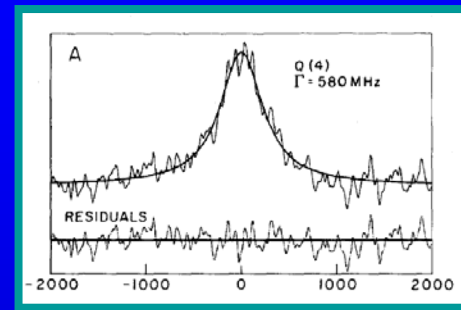


- Sudden onset of broadening at J = 4
- "Shape resonance" tunneling through the angular momentum barrier
- Single partial wave ("g-wave", J=4) half collision

Shape Resonance Dynamics



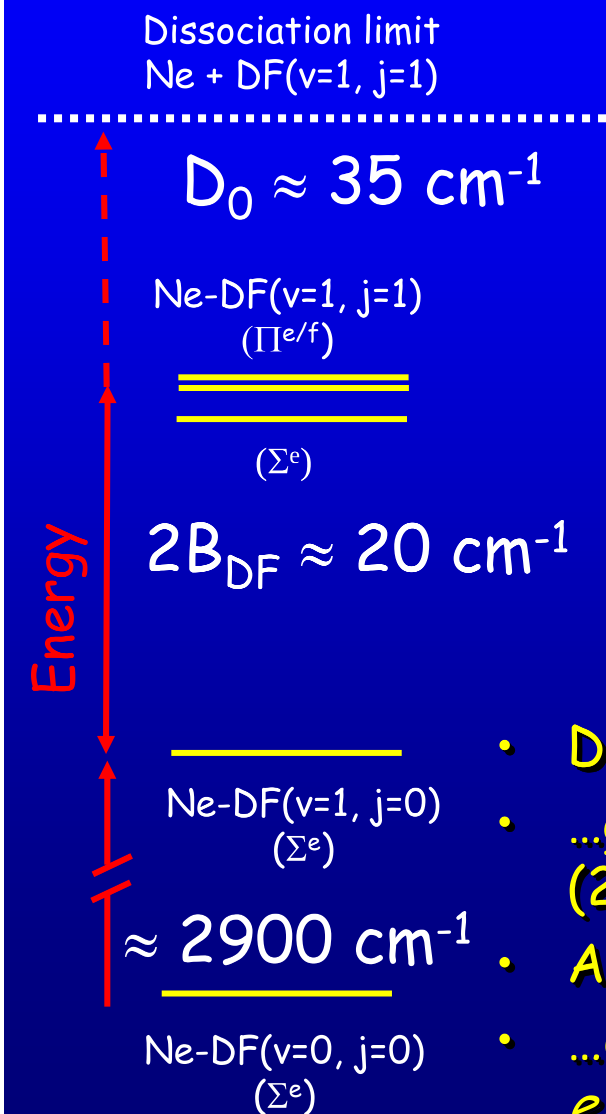


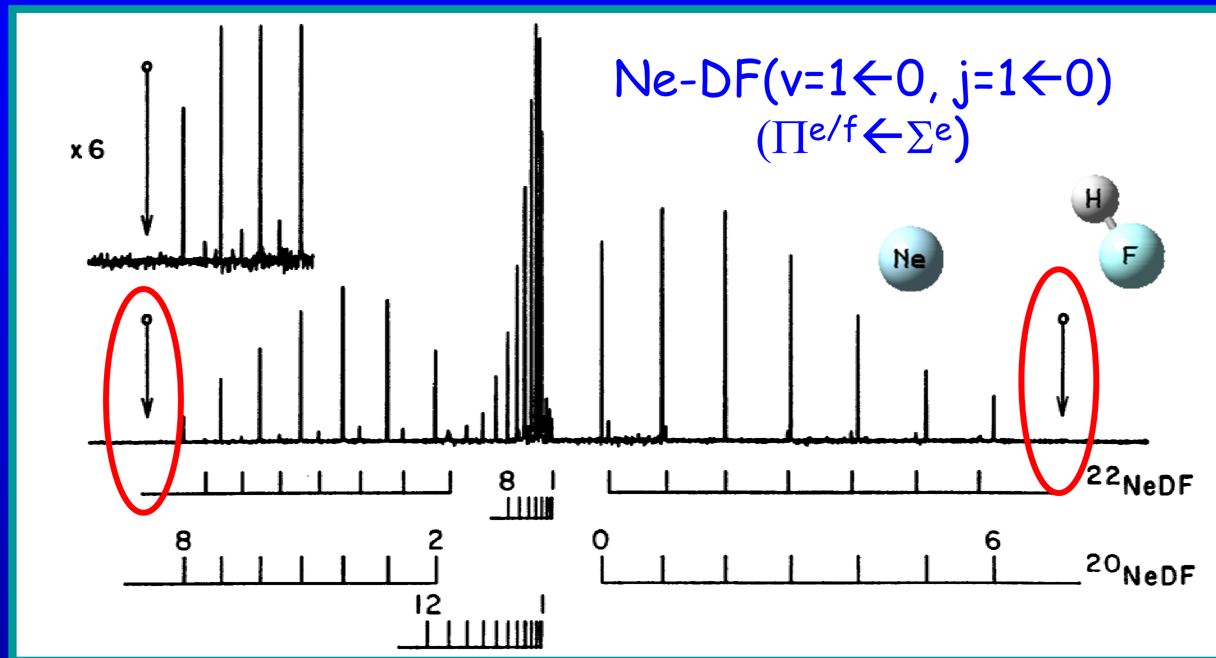


- J = 0-4 *bound* (E < 0) in He-HF(v=0,j=0) lower state…
- …but well depth decreases for j=1 "helicopter" states (HF dipole points *away* from He)

- He-HF(v=1,j=1) upper state still energetically stable for J =0-3…
- …but now E > 0 for J = 4
- …trapped behind the J = 4 angular momentum barrier and tunnels to He + HF(v=1,j=1)

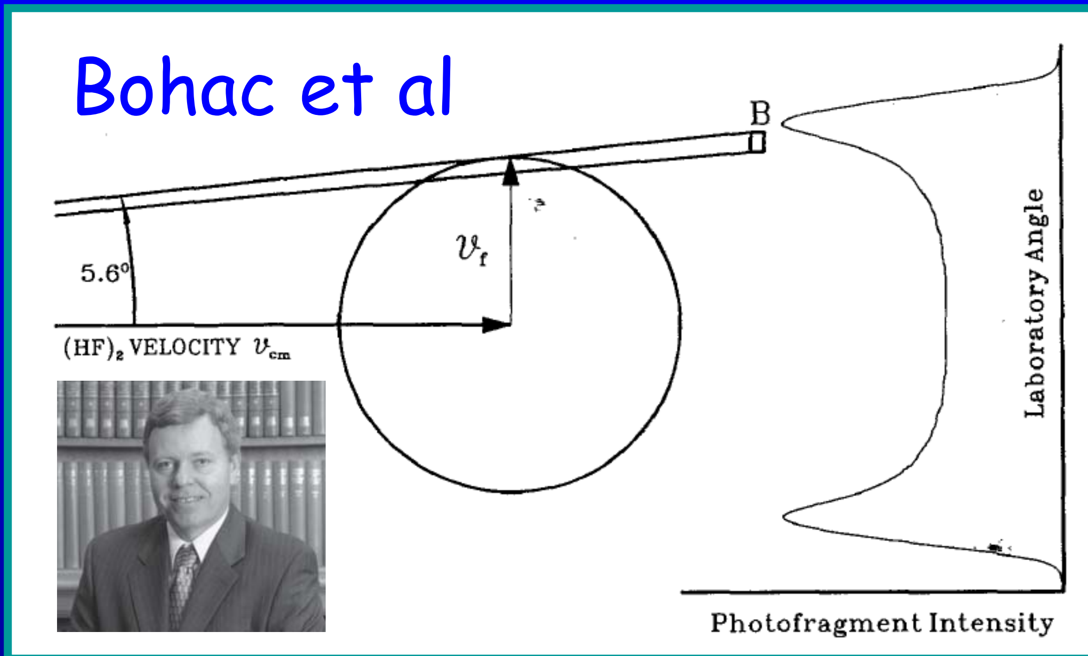
"Centrifugal Bond Breaking"

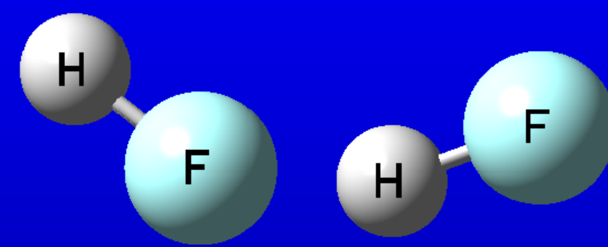




- D_0 (Ne-DF) ≈ 35 cm^{-1} …
- …greater than Ne-DF (j=1) internal rotation ($2B_{DF} \approx 20\ cm^{-1}$)
- Abrupt termination of spectrum at J = 8…
- …due to centrifugal + internal rotor energy *exceeding* D_0 (*shape resonance* in *lower* state)

III. Product State Distributions From vdWs Feshbach Resonances

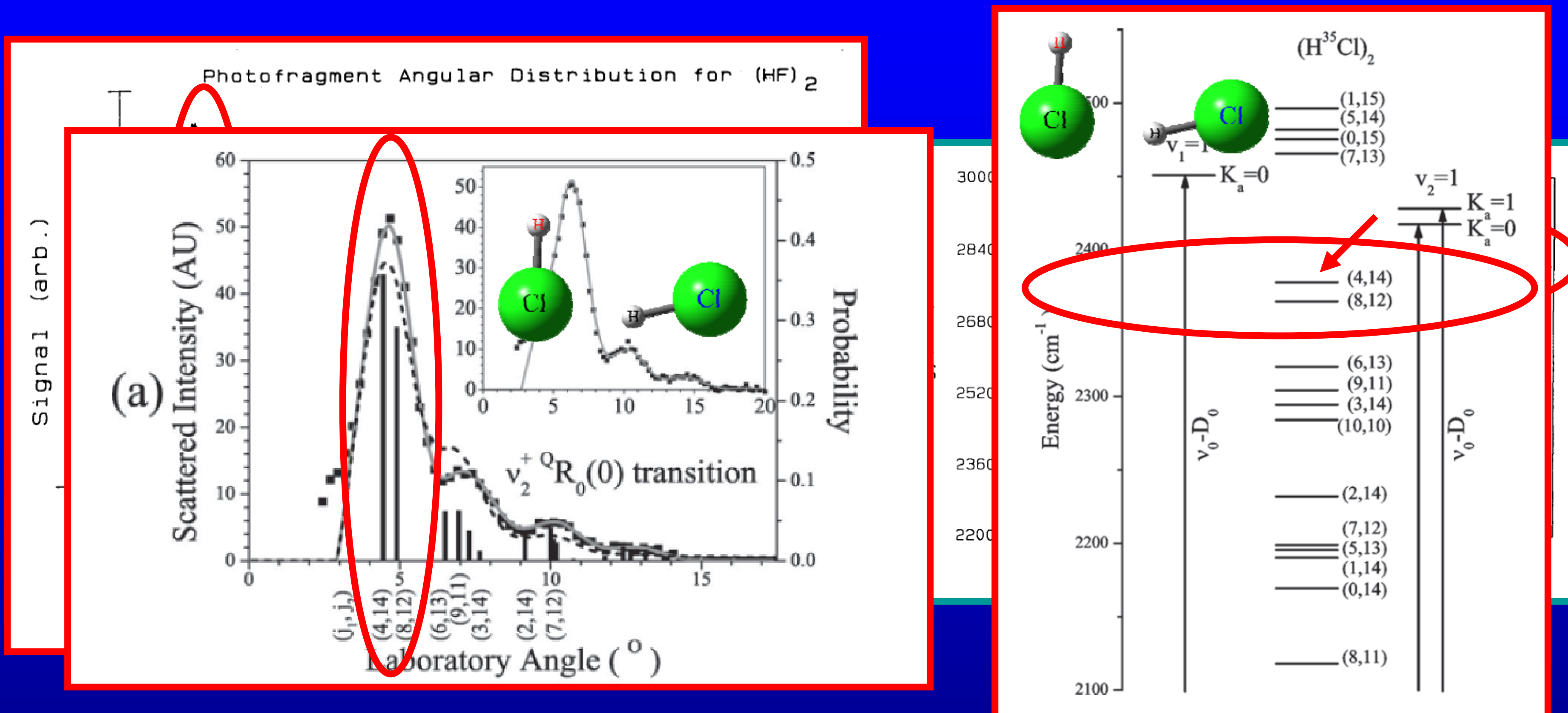




D_0 = 1062(1) cm^{-1}

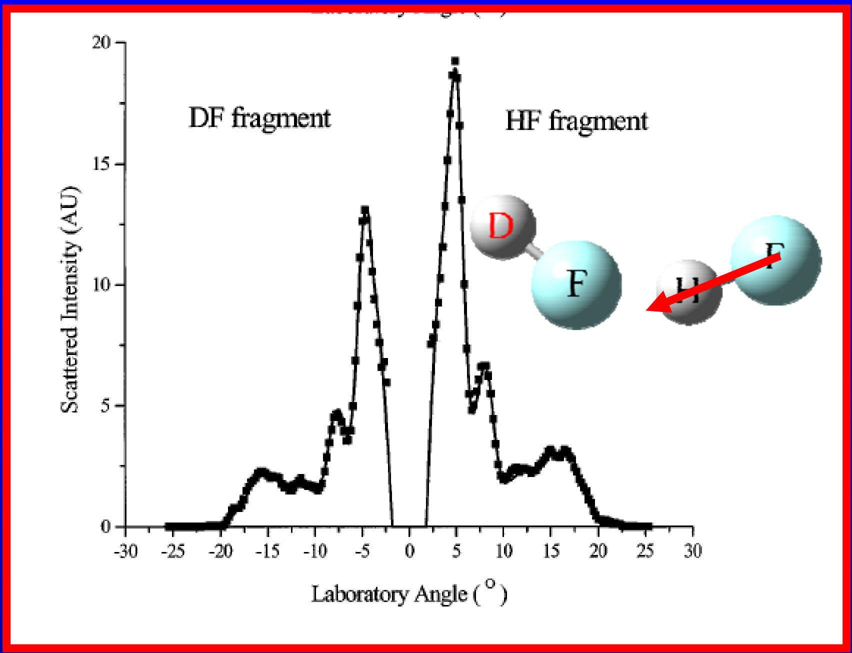
- Molecular beam IR laser photofragmentation studies (R.E. Miller and coworkers)
- Angular deflection, beam velocity, momentum/energy conservation…
- …yields correlated state-to-state product quantum distributions for pure initial vdWs "Feshbach resonances"

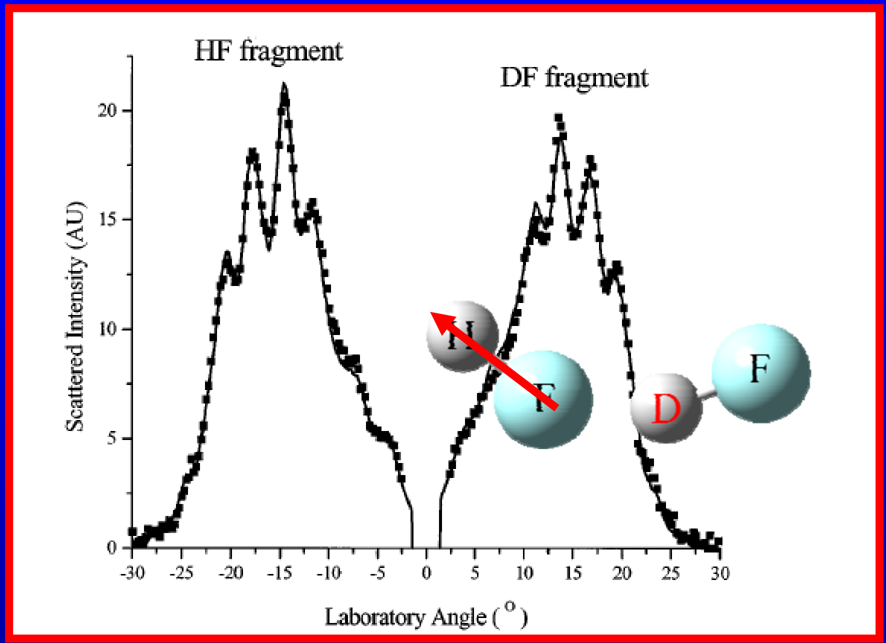
Minimize Recoil Energy!



- Deeply H-bonded well (1062 cm^{-1})
- $h\nu - D_0$ = 2800 cm^{-1} to distribute into (j_1, j_2)
- …dominated by *near resonant* channel (2,11)

Non-statistical Product States



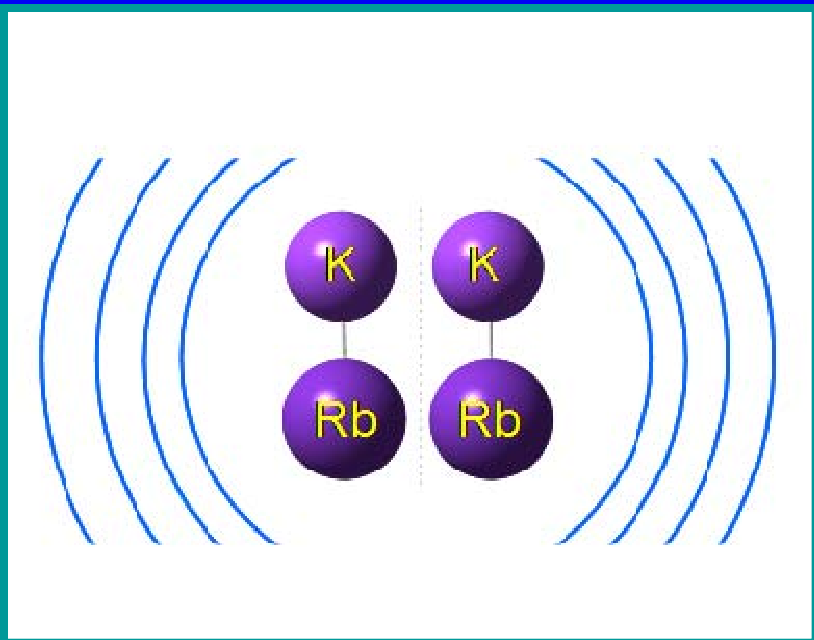


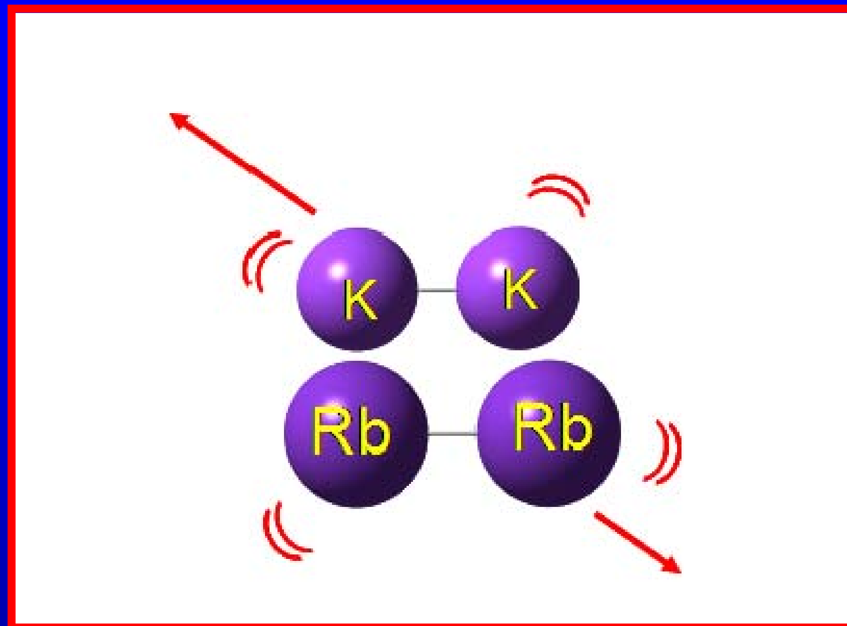
- Final quantum state distributions non-statistical…
- …exquisitely sensitive to i) potential energy surface and ii) initial quantum state

IV. Quo Vadis?

- KRb + KRb → K_2 + Rb_2 ultracold reaction kinetics (measured by loss of reactant states) experimentally at "unitary" limit
- Fantastic success!...
- ...but also a little disappointing - requires knowledge only of the *long range* potential energy surface
- Where is the "fingerprint" of the short range potential energy surface in ultracold reactions…?
- … in the final product quantum state distributions (e.g., Rb + Rb + Rb → Rb + Rb_2 , Denschlag and coworkers)!

Product State Distributions



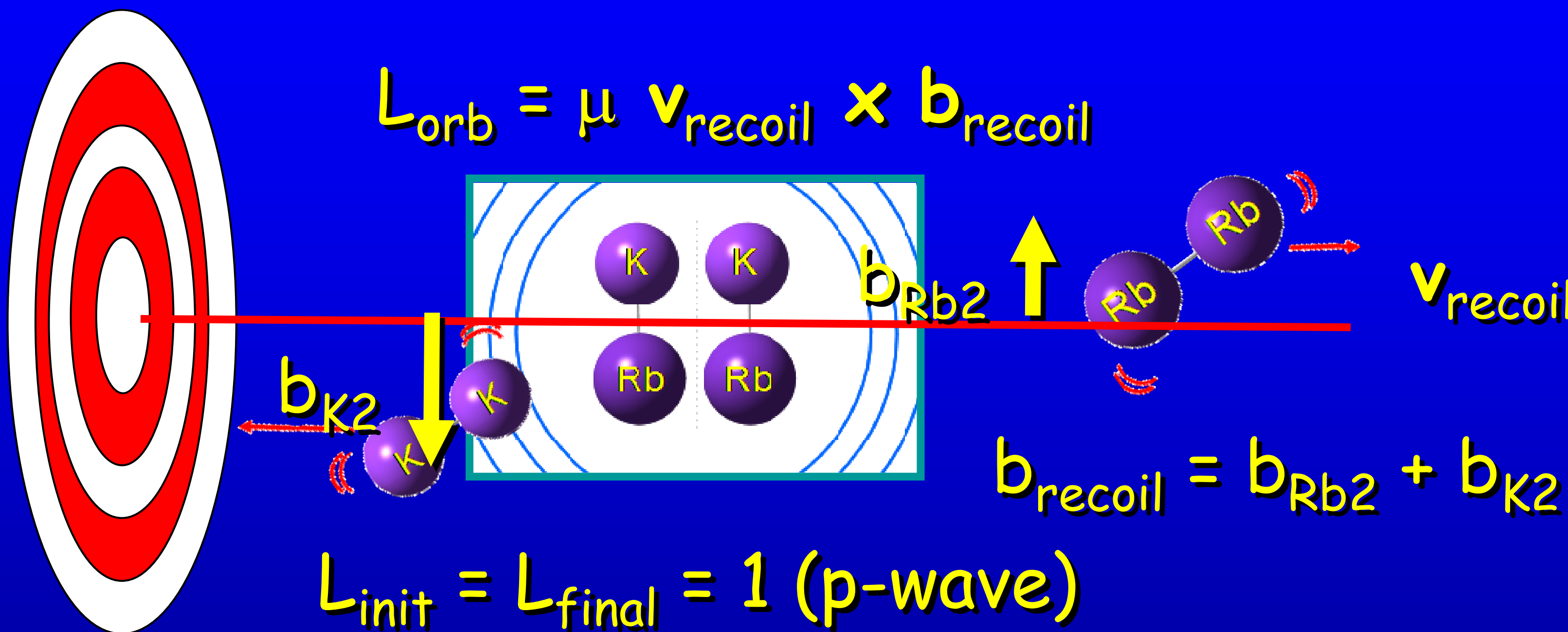


- $T \approx 200$ nK collisions in dipolar $^{40}K^{87}Rb$
- Single p-partial wave
- Control of all nuclear spin states

- "Hot" $^{40}K_2$, $^{87}Rb_2$ products ($\approx$ 10 cm^{-1} exothermic)
- Nearly classical $\mathbf{L}_{orb} = \mu\, \mathbf{v} \times \mathbf{b}$
- $\mathbf{j}_{K2} + \mathbf{j}_{RB2} + \mathbf{L}_{orb} = \mathbf{L}_{init} = \mathbf{L}_{final}$

Simple Dynamical Constraints

$L_{orb} = \mu\, \mathbf{v}_{recoil} \times \mathbf{b}_{recoil}$



$b_{recoil} = b_{Rb2} + b_{K2}$

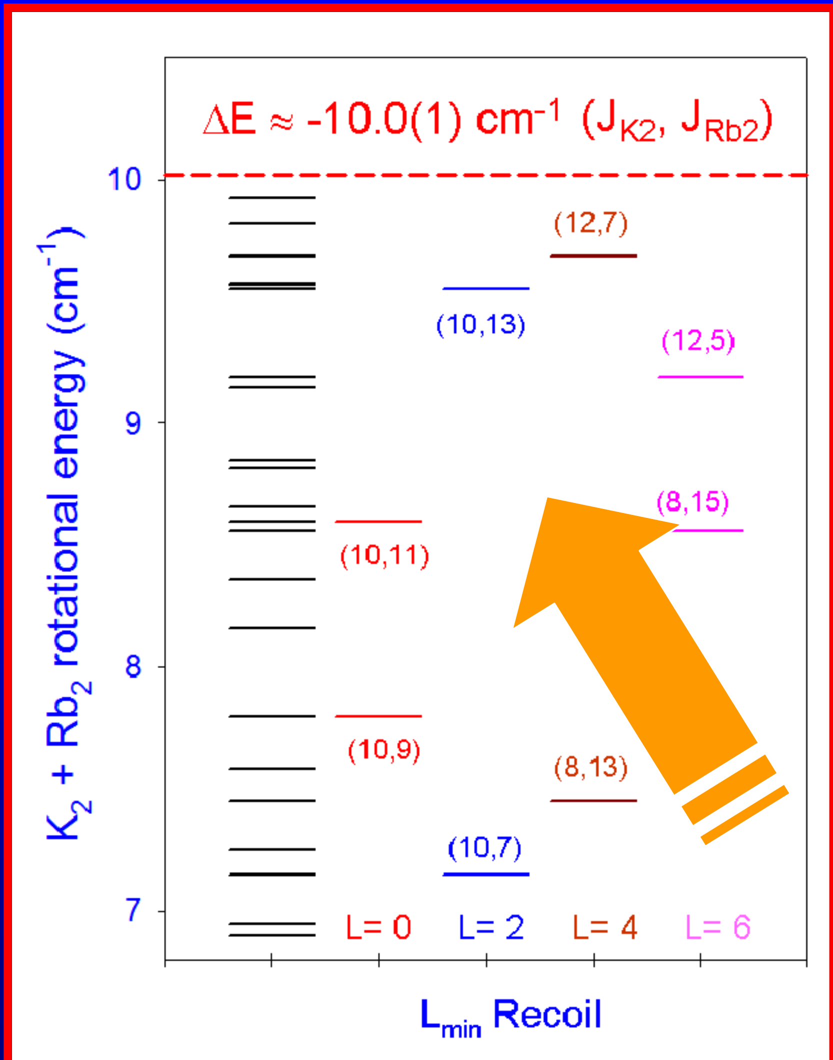
$L_{init} = L_{final} = 1$ (p-wave)

i) $L_{orb} + j_{K2} + j_{RB2} = 1$ (plus nuclear spin statistics)

ii) Physically reasonable b_{recoil} for reverse reaction opacity ($L_{orb} \approx |j_{K2} - j_{Rb2}| \approx$ small)

iii) Minimized energy in translational recoil

Simpl(istic) 1st Order Picture



- *Non-statistical* product states
- *Strongly correlated* j_{K2}, j_{Rb2} (*upper left* corner)
- Clear area for further theoretical and experimental efforts!

Summary

- High resolution vdWs spectroscopy as model for ultracold (COM frame) rovibrational Feshbach resonances with single partial wave resolution
- Failure of statistical RRKM theory for predicting predissociation lifetimes in 3-4 atom systems
- Highly non-statistical, correlated product state distributions – sensitive to short range PES, initial quantum state and excess recoil energy
- Critical information on dynamics and the PES at short range imprinted on the ultracold chemistry product state distributions – much work to be done to understand how!

Acknowledgment

Thanks!

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