Dissociation Dynamics of the Low-lying Rydberg States of H_3 and its Isotopomers

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Motivation

H_3 - simplest neutral triatomic molecule

3 protons, 3 electrons

- *Amenable to high level theoretical treatments*
- *Predissociating Rydberg states with D_{3h} symmetry*
- *Exhibits Jahn-Teller effect*
- *Important for understanding interstellar and hydrogen plasma chemistry*

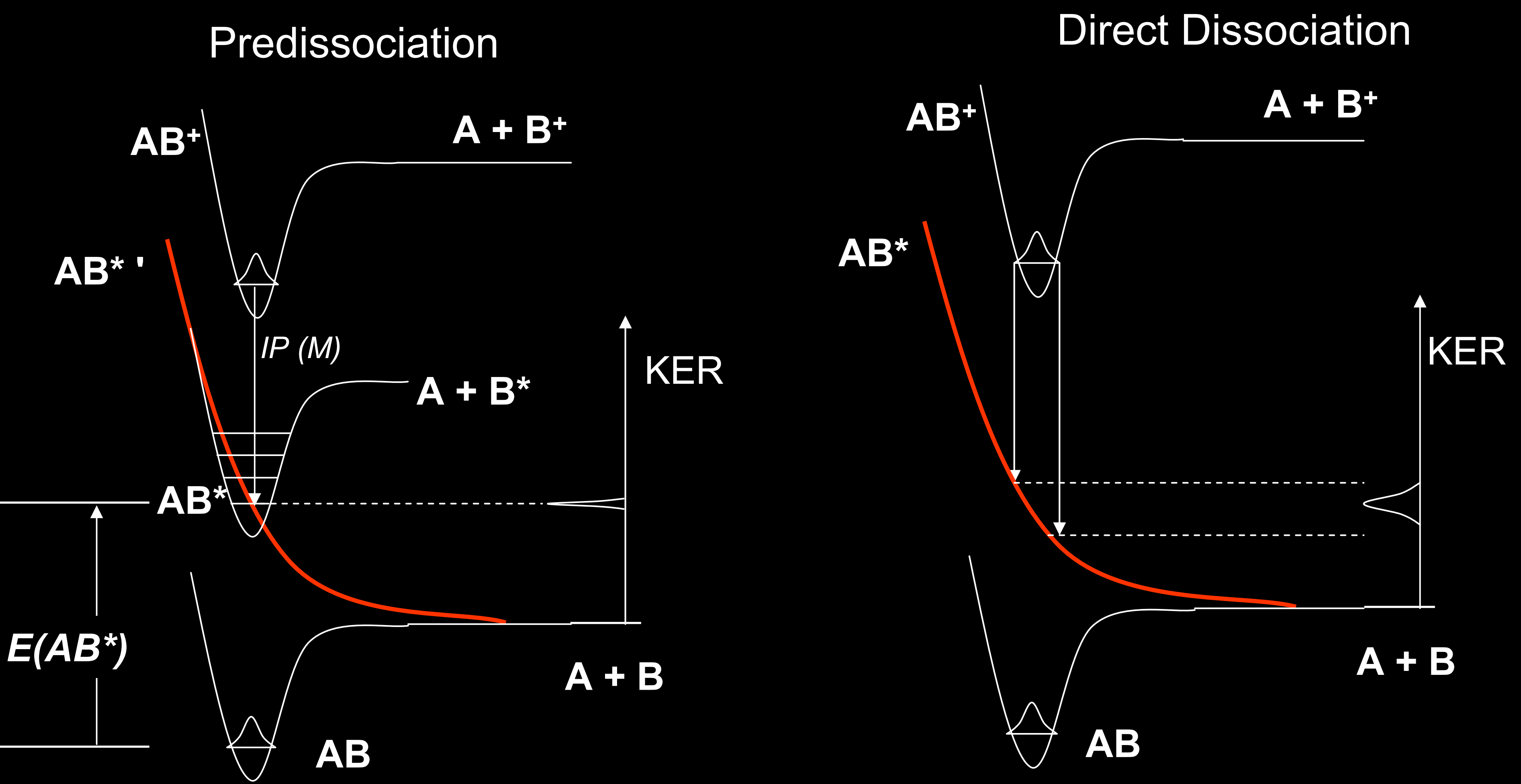
Dissociative Charge Exchange

$AB^{+} + M \quad\quad AB^{*} + M^{+} \quad\quad A + B + M^{+} + KER$

- *Prototypical elementary charge-transfer reactions*
- *Source of energetic neutral atoms in planetary atmospheres*
- *Produce excited neutral states below the ionization potential of AB*
- *Insights into intermediate steps in DR to ground state neutral products*

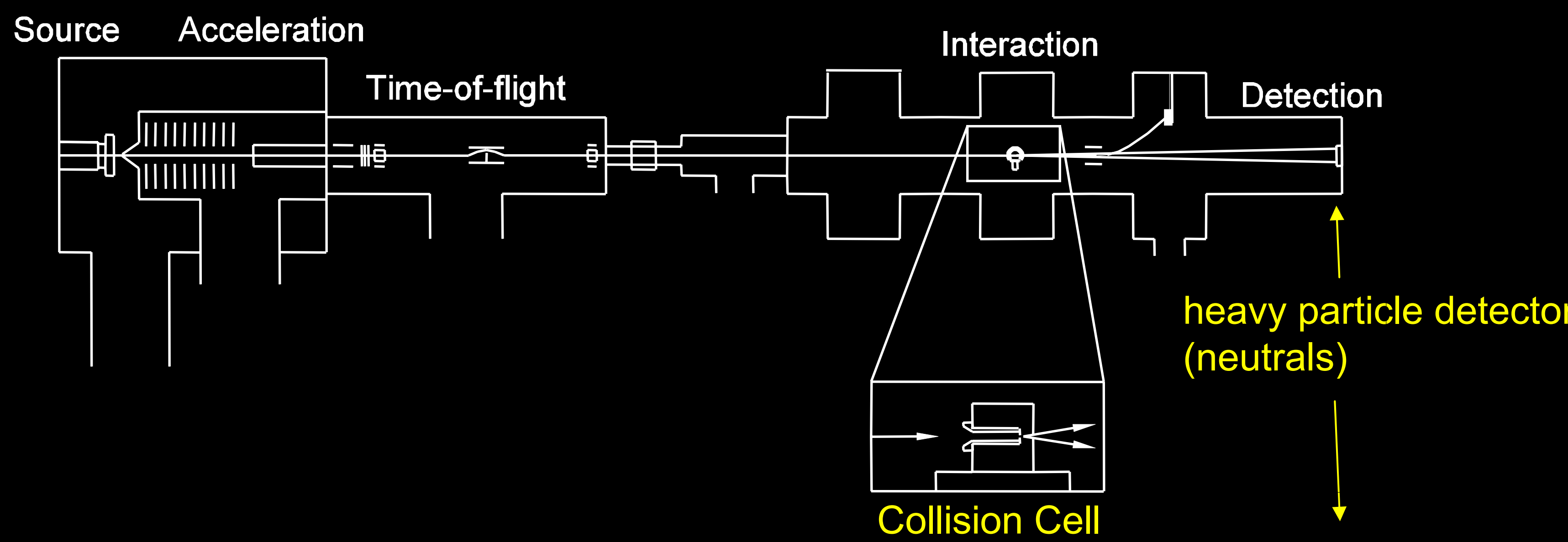
Charge Exchange Energetics and Dynamics

$$AB^+ + M \longrightarrow A + B + M^+ + KER$$



$$KER = E(AB^*) - \Delta D_0(A\text{-}B) - E_{int}(A) - E_{int}(B)$$

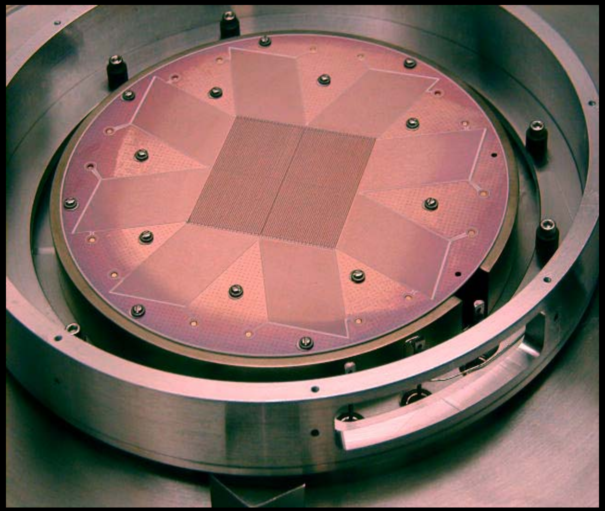
Multiparticle Translational Spectrometer
Charge Exchange / Dissociative Recombination



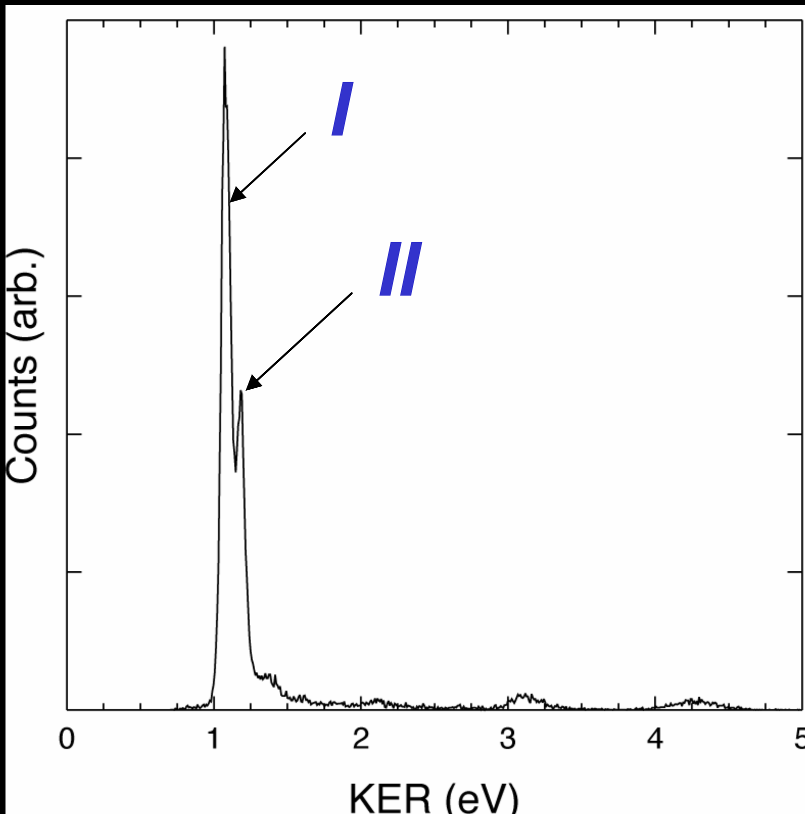
Pulsed Discharge Supersonic Expansion Ion Source (O_2, n-H_2 , D_2, n,i-C_3H_7Br)

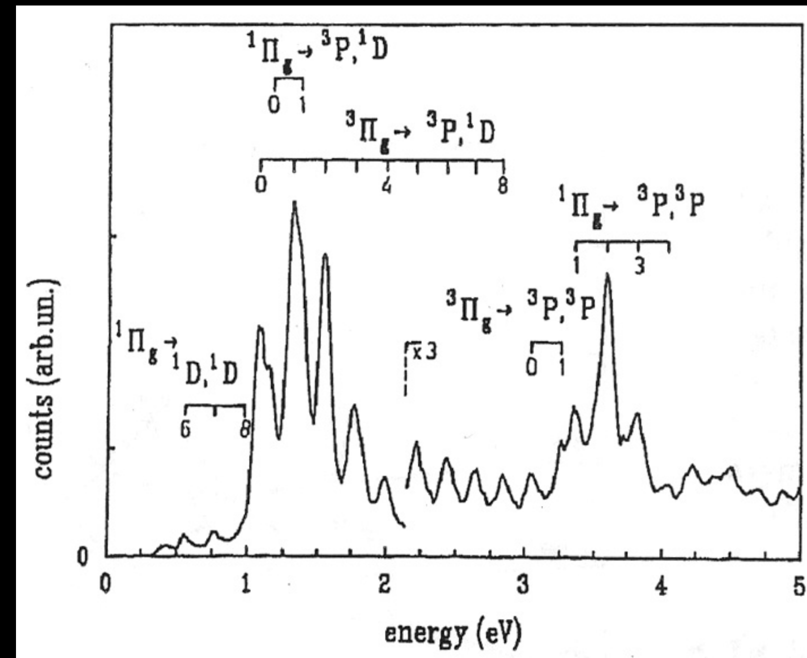
Collision Cell: 10^{-4} torr Cs
1 mm path length

Measure product momenta with multiparticle time- and position-sensitive detector



$O_2^+ + Cs \longrightarrow O + O + Cs^+$



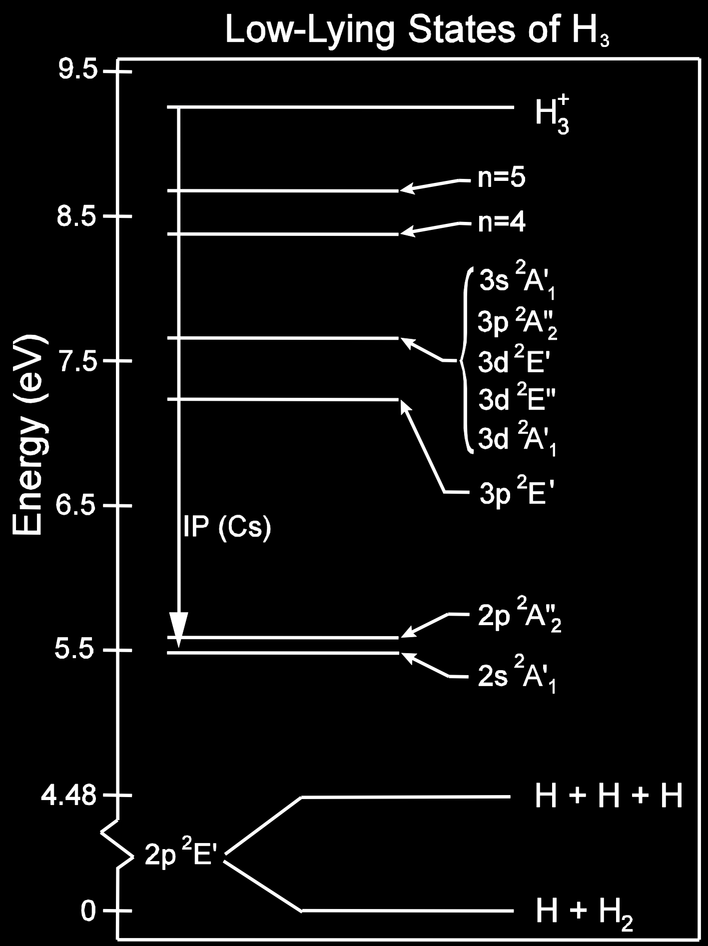


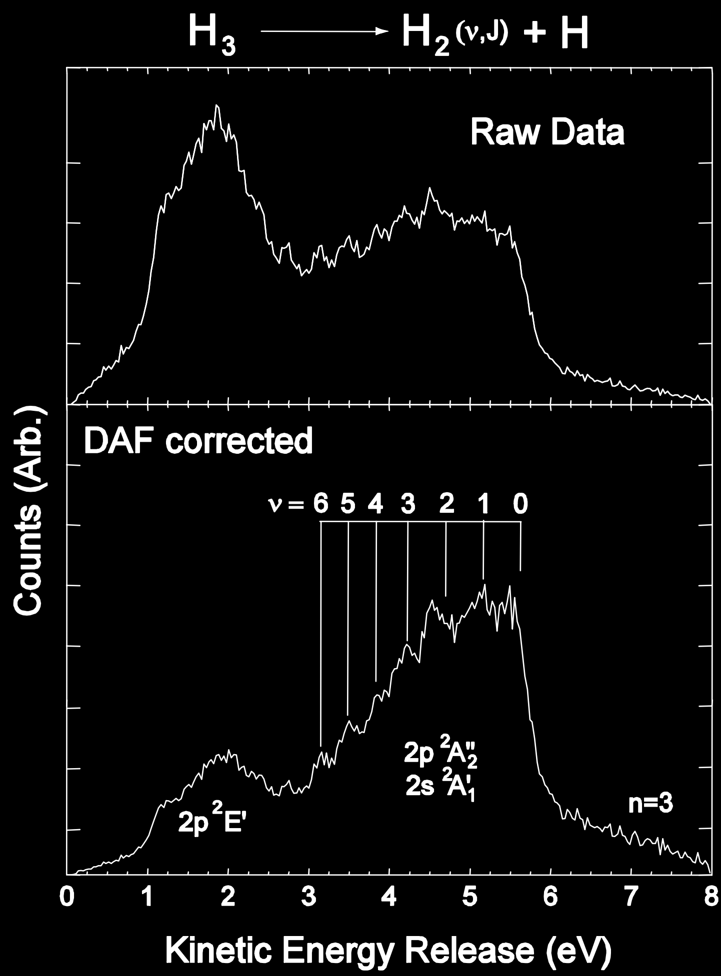
I ,II: $O_2^+(X\ ^2\ \ _g)$ + Cs $O_2\,(^{1,3}\ \ _g)$ $O(^3P) + O(^1D)$

We produce vibrationally and rotationally cold cations

DCE – probe of O_2^+ vibrational distribution

$H_3^+ + Cs \longrightarrow H_2 + H + Cs^+$





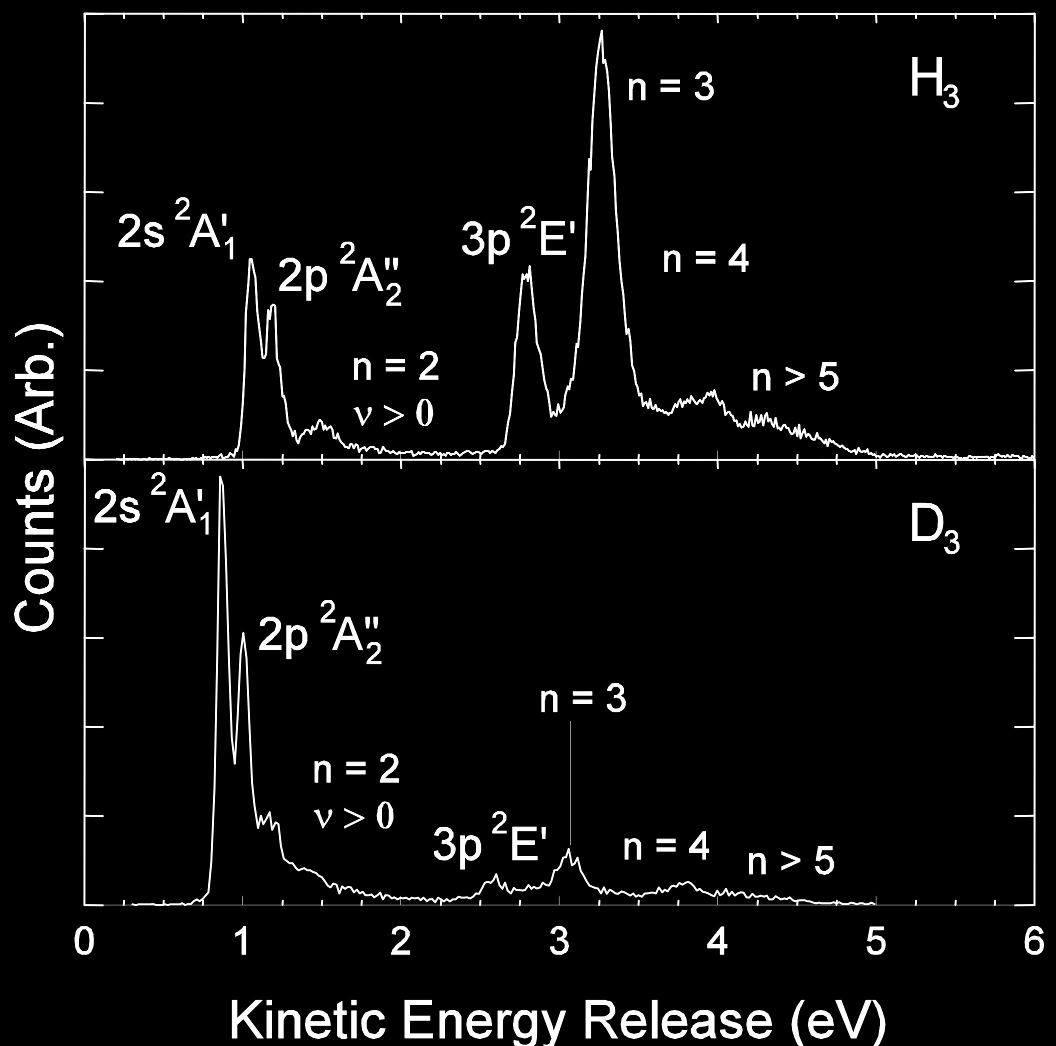
$H_3^+ + Cs \longrightarrow H_3^* \longrightarrow H_2 + H(^2S)$

H_2 rovibrational excitation prevents resolution of specific intermediate H_3 Rydberg states

Kinetic Energy Release for 3-Body DCE: H_3^* 3 H

$^2A_1'$, $^2A_2''$, $^2E'$ Rydberg states resolved

Evidence for some vibrational excitation

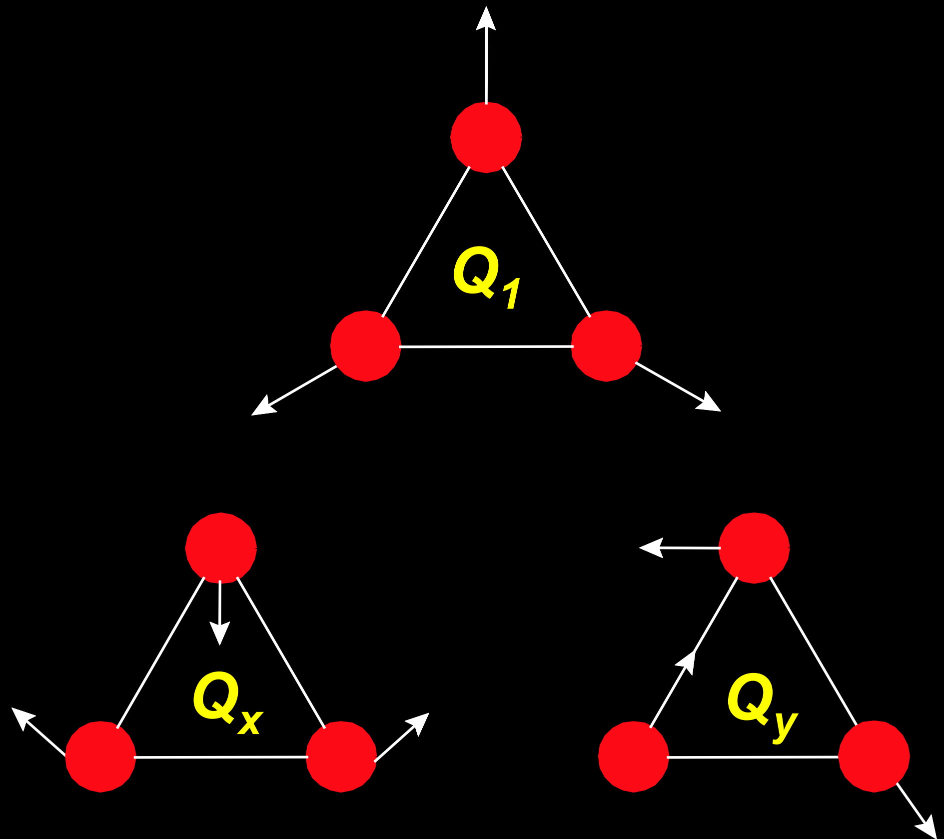


Production of n=3 levels reduced in D_3 (less non-resonant charge exchange)

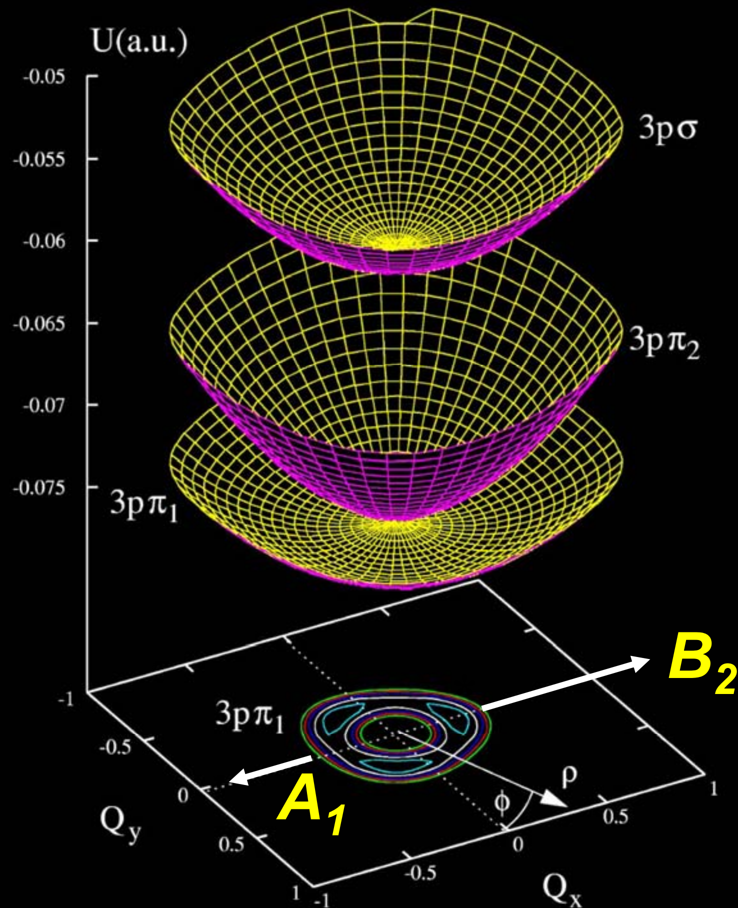
Physical Review Letters (2004)

Vibronic Structure of Rydberg States of H_3

Normal modes of H_3^+/H_3



PES for degenerate 3p $^2E'$ state as $f(Q_x,Q_y)$

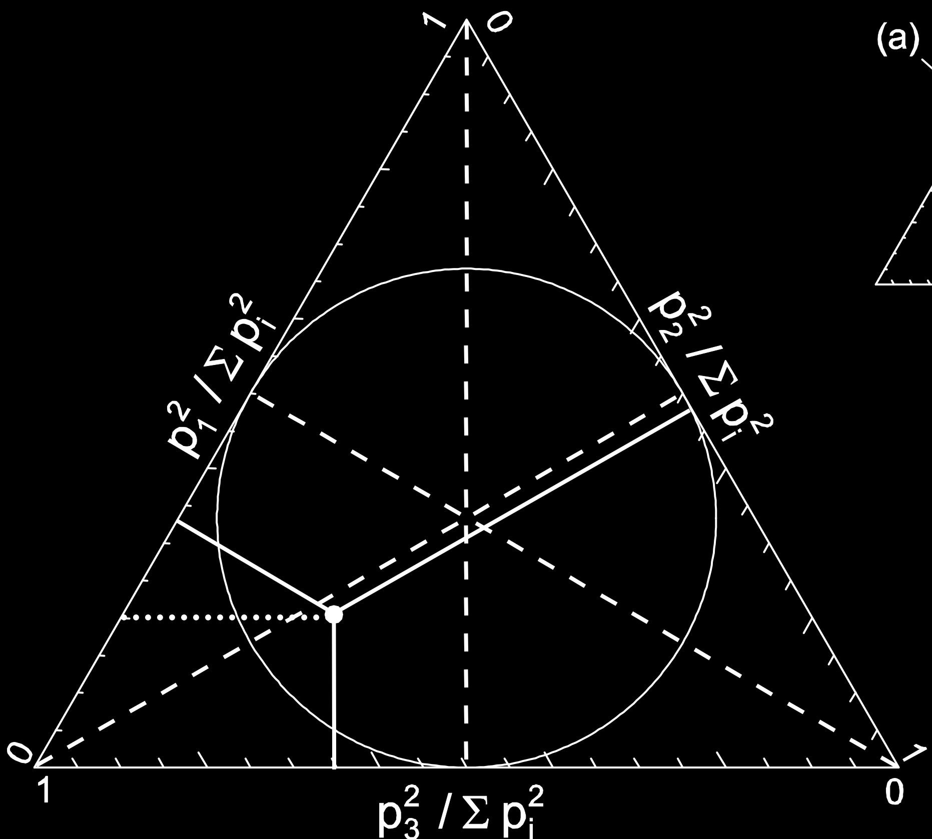


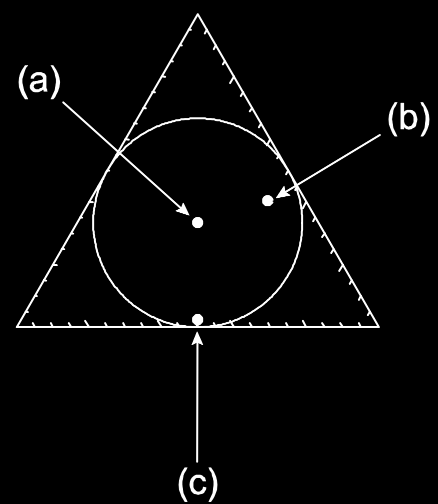
* Figure from V. Kokoouline, C. H. Greene, *Phys. Rev. A 68, 012703 (2003)*

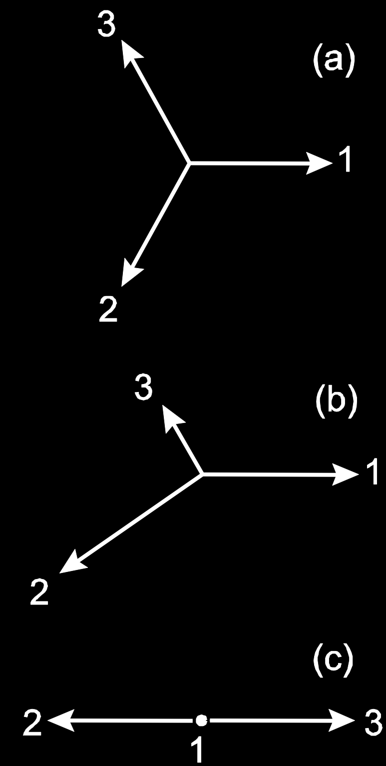
Dalitz Plot – Partitioning of Product Momenta

- *Plot fractional square of momentum as distance from edge of the triangle*
- *Triangle: Energy Conservation*
- *Circle: Three-Body Momentum Conservation*

$$f(p_n) = \frac{p_n^2}{\sum p_i^2}$$

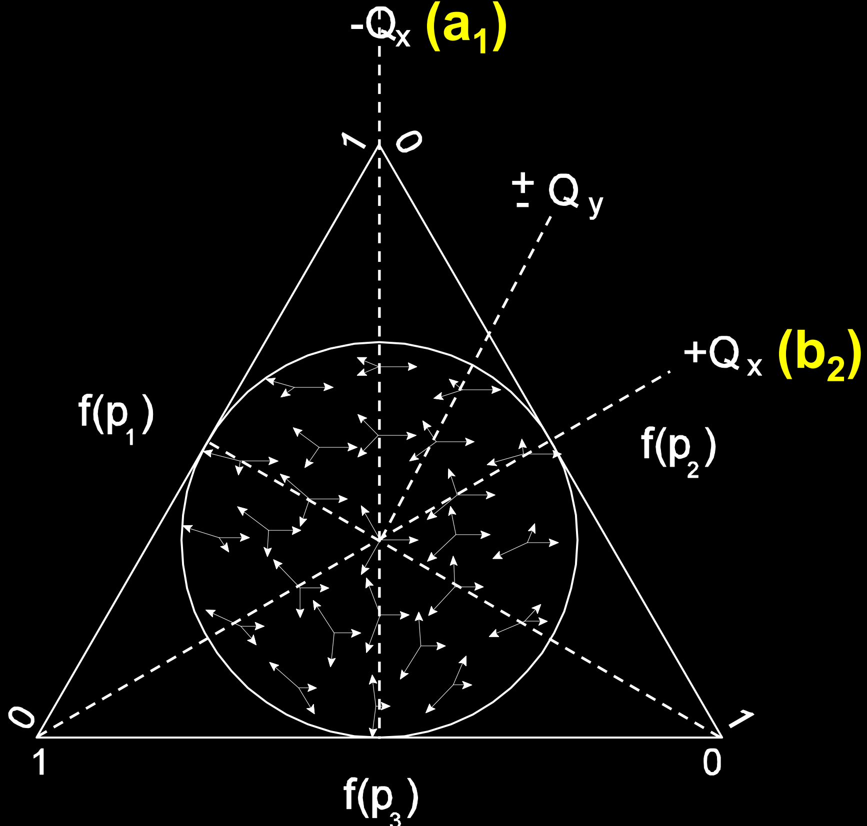




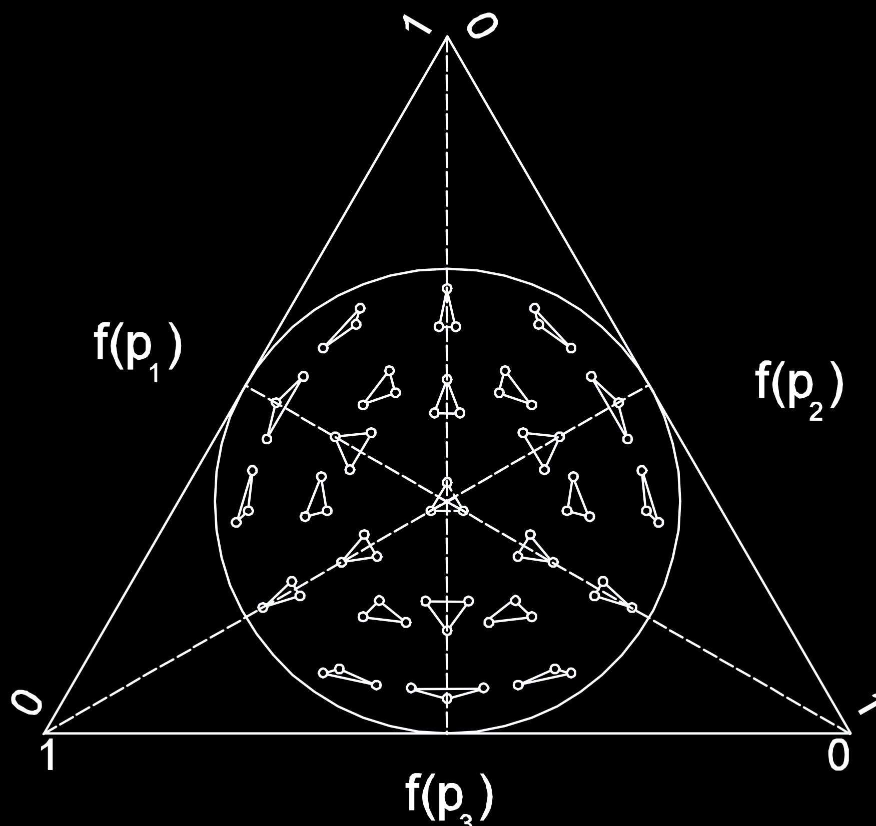


R.H. Dalitz (1953)

Product Momenta, Molecular Configurations and Dalitz Plots



A measure of the molecular configuration at crossing to 3-body continuum, assuming minimal exit-channel interactions

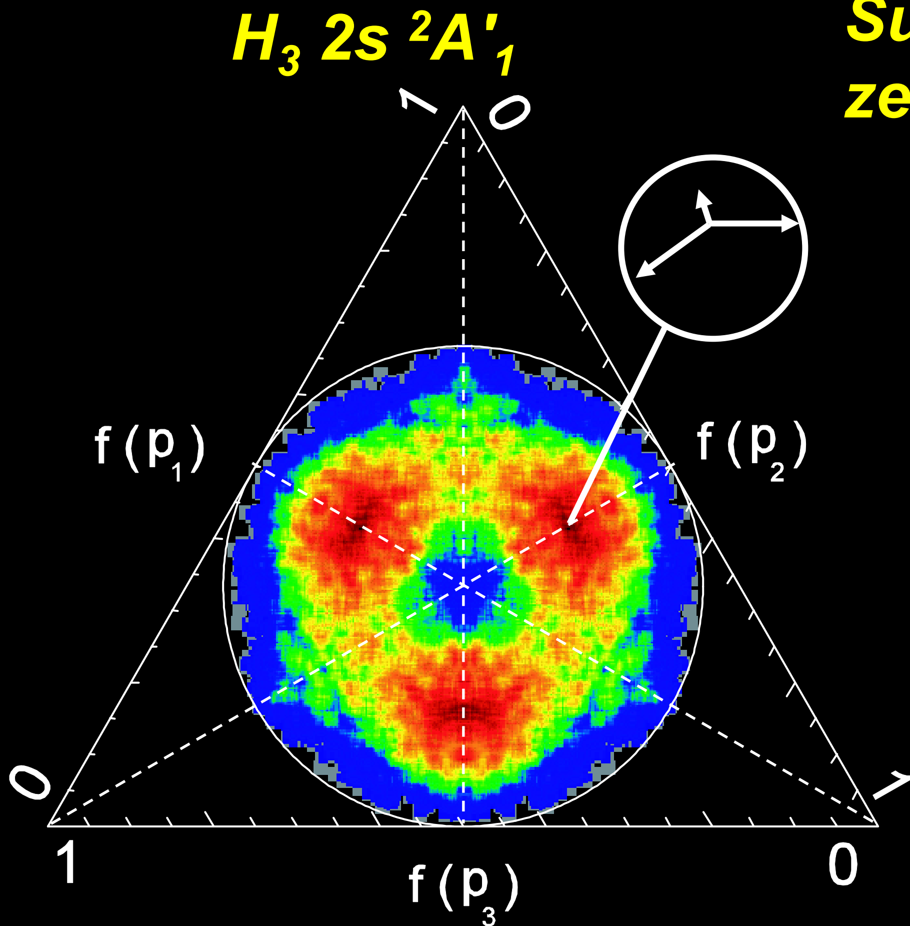


Momentum partitioning correlates with molecular configurations for distortions near D_{3h} configuration

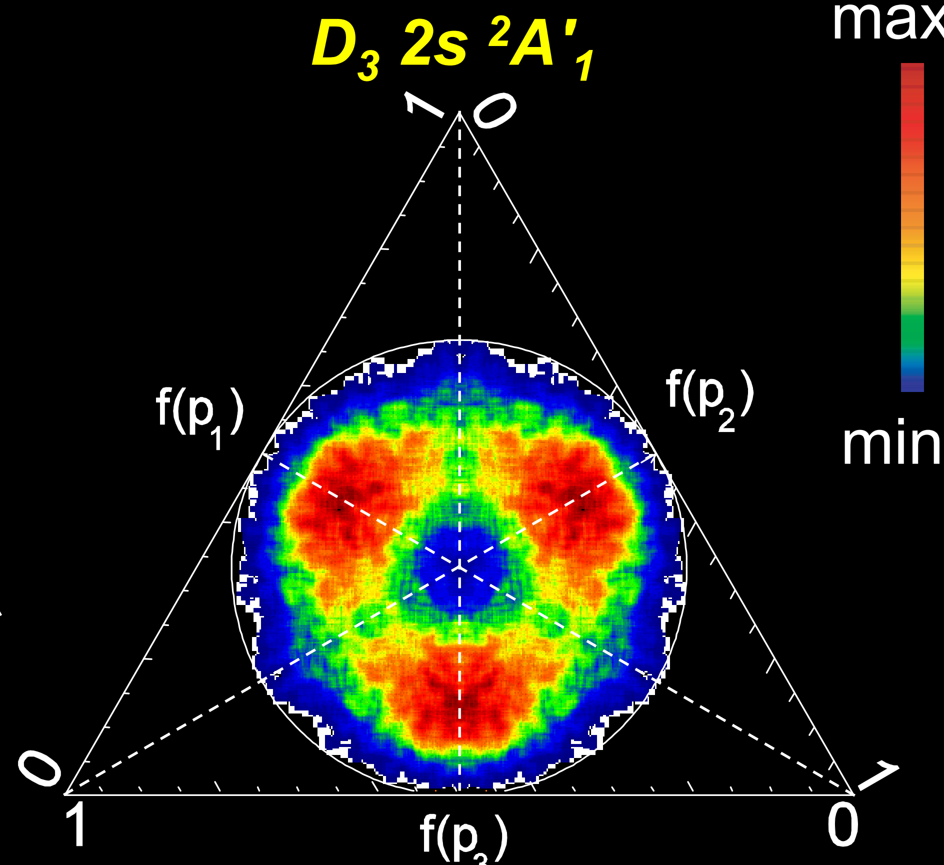
$$f(p_n) = \frac{p_n^2}{\sum p_i^2}$$

R.H. Dalitz (1953)

The 2s $^2A_1'$ state – H_3 and D_3



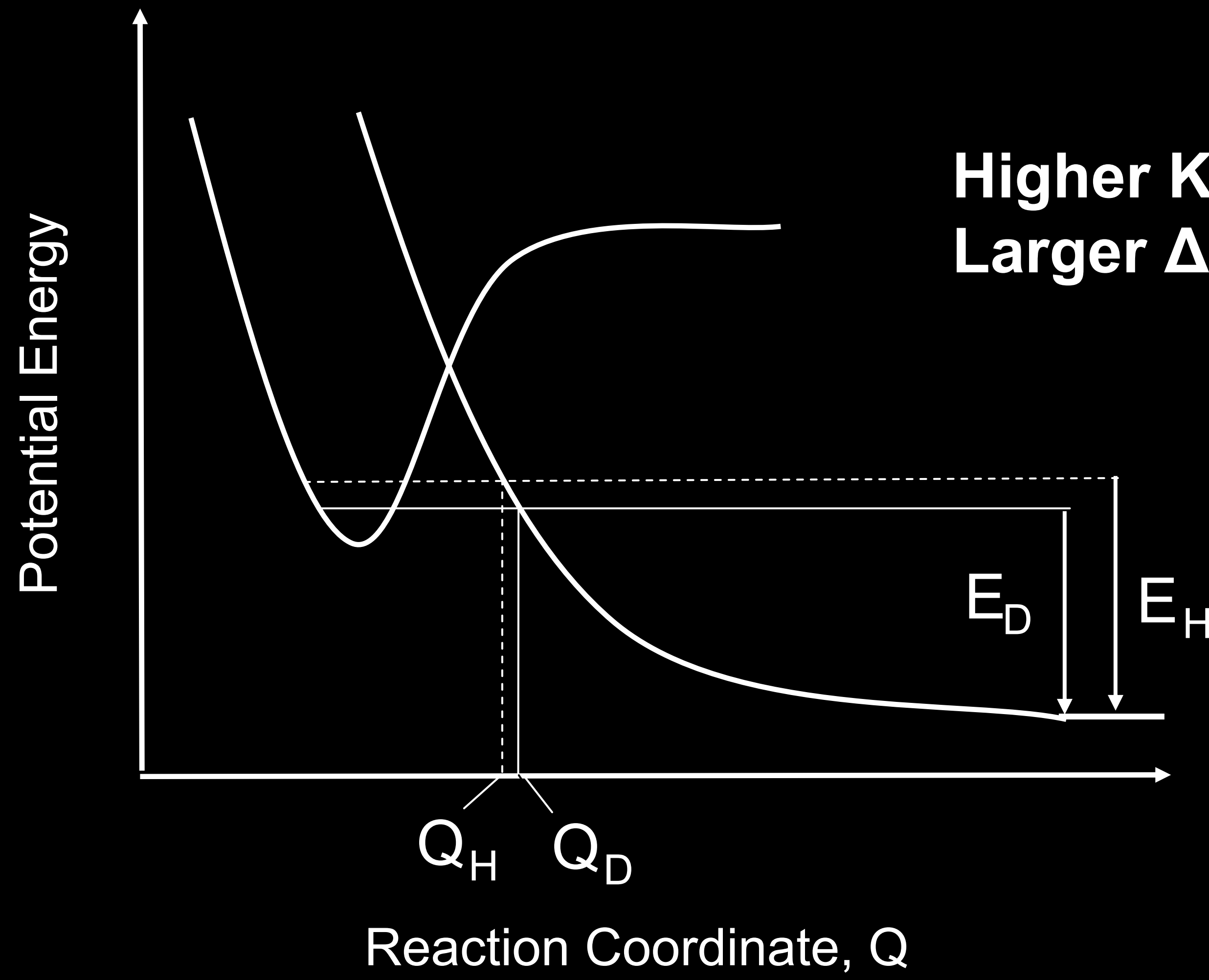
Subtle differences – different zero-point wavefunctions



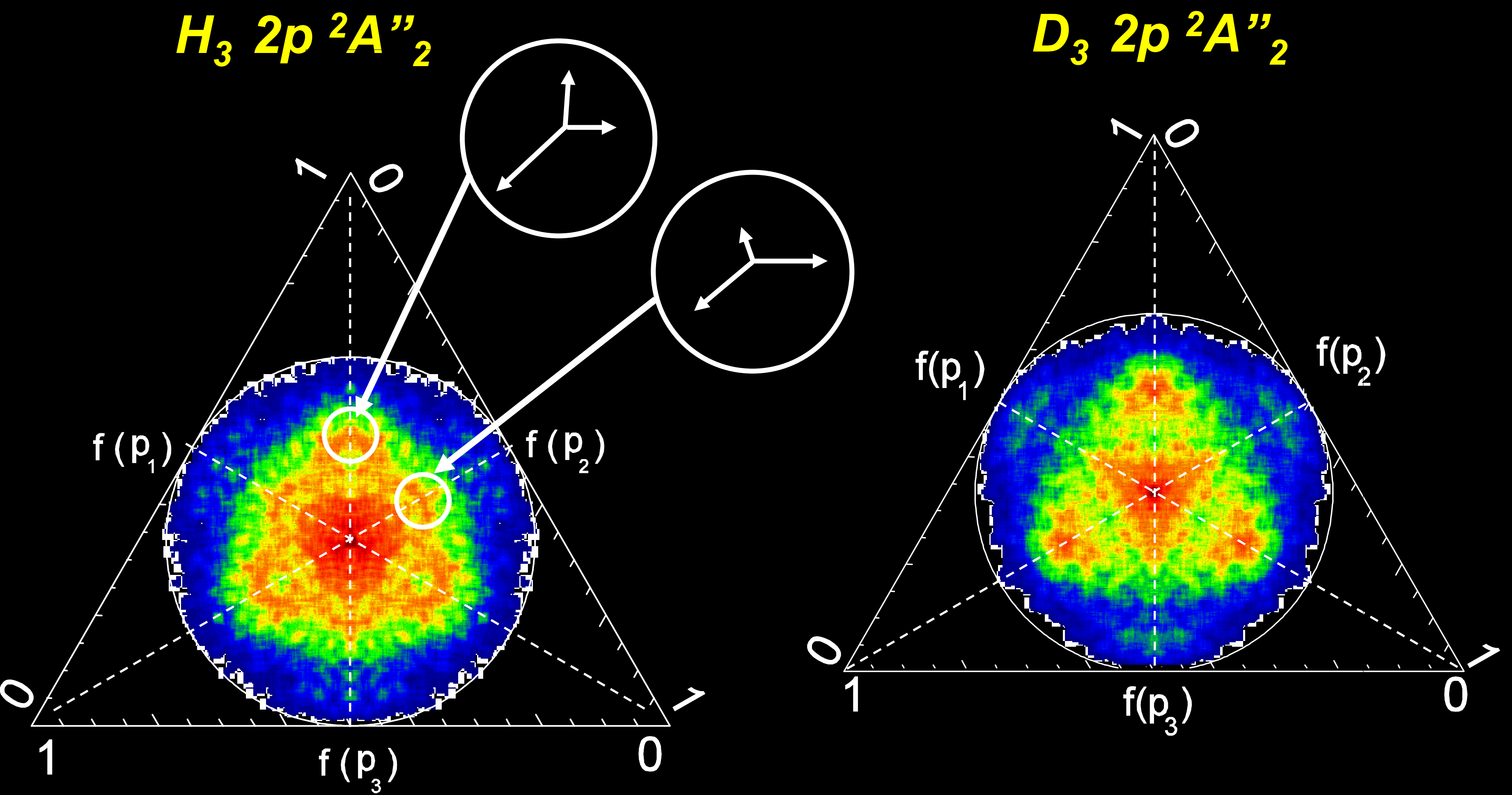
Dissociation via a C_{2v} distortion towards a linear geometry
Coupling to the 2p $^2E'$ dissociative state via bend zero pt.

Isotope Effects: Partitioning of Product Momenta

Consider tunneling along a hypothetical reaction coordinate:

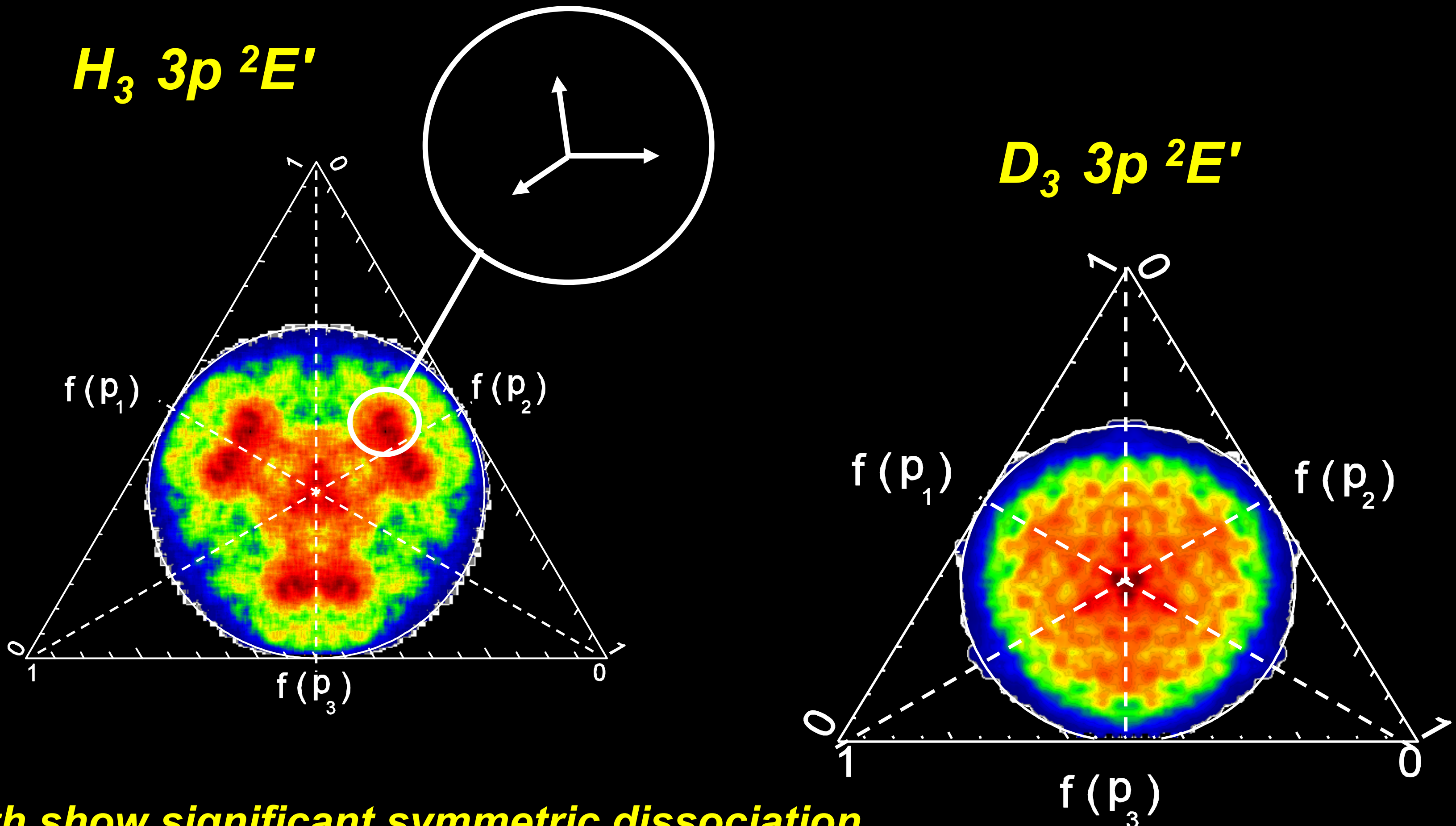


The 2p $^2A_2$'' state – H_3 and D_3



Dominated by symmetric dissociation accompanied by C_{2v} distortions
Coriolis coupling to 2p $^2E'$ dissociative state

The degenerate 3p $^2E'$ state – H_3 and D_3



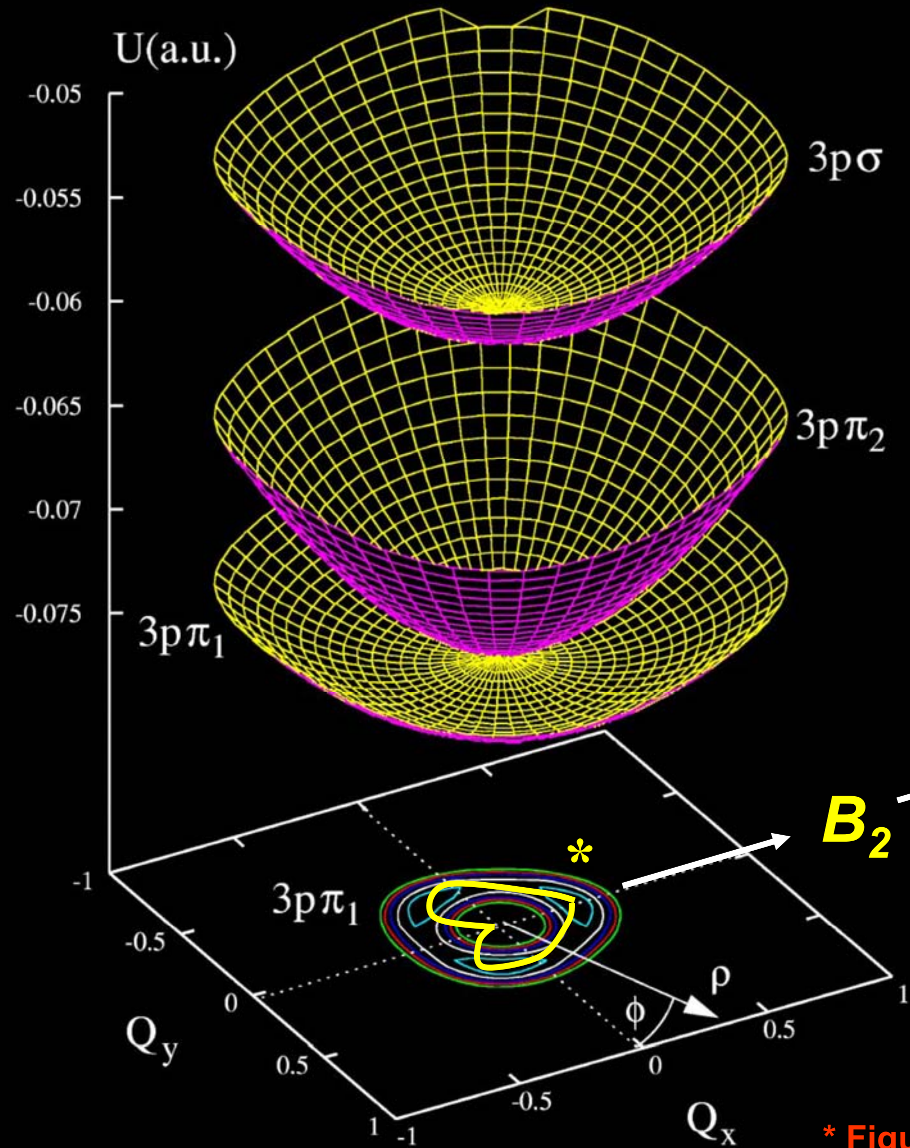
Both show significant symmetric dissociation

H_3 – pathway to a C_s symmetry Jahn-Teller distorted configuration

D_3 — broad distribution of momentum partitioning

Differences: Time-scale for nuclear motion, zero-point , rotational symmetries, nuclear spin statistics, …. Geometric phase?

Dissociation of the degenerate 3p 2E’ Rydberg State



Is the symmetric feature for H_3 from the ‘inner’ cone?

Is the asymmetric feature a result of evolution on the lower surface?

B_2 → ***D** h* **(linear)**

*** Figure from V. Kokoouline, C. H. Greene, *Phys. Rev. A 68, 012703 (2003)***

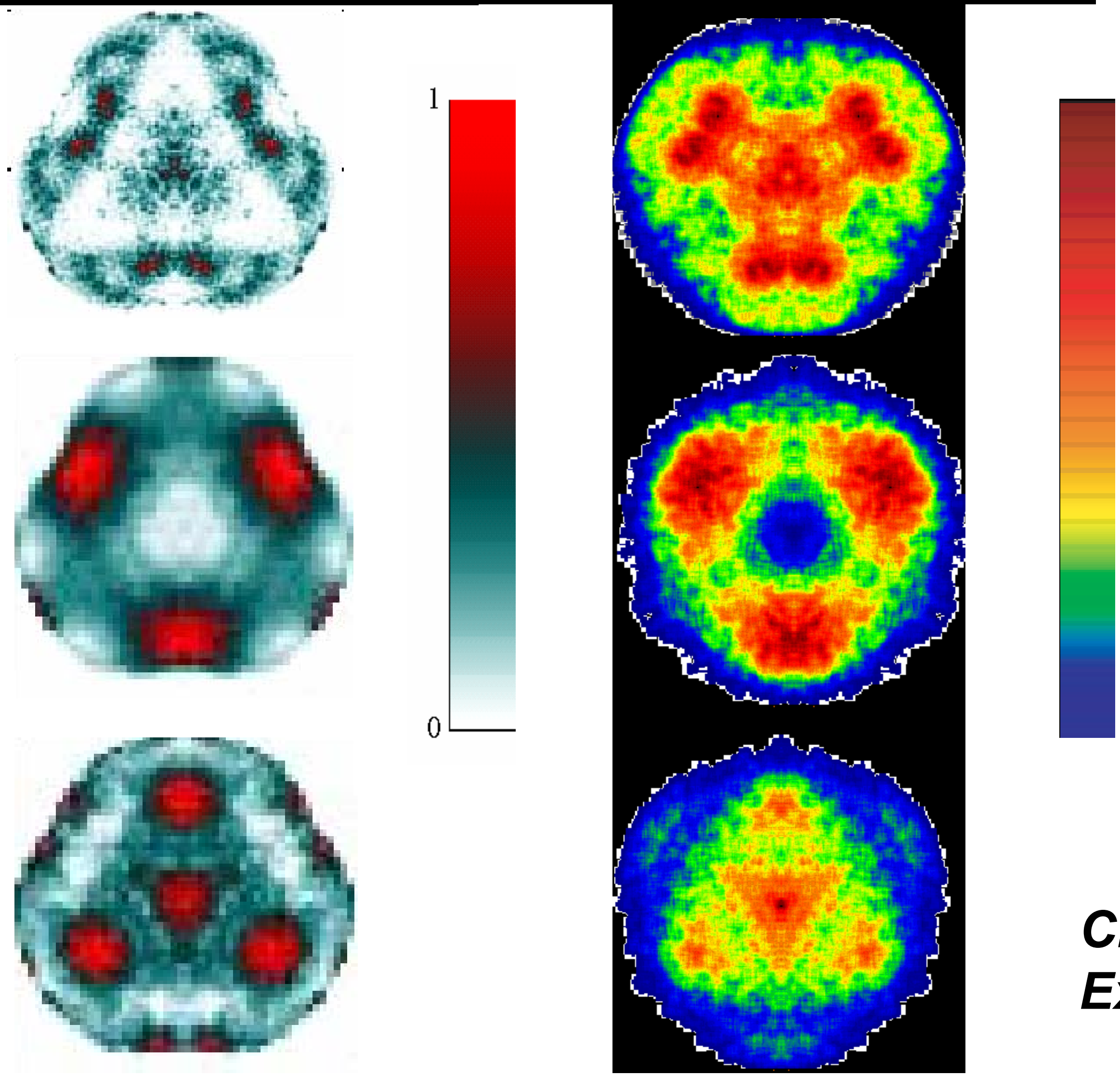
Comparison to Results from Helm's Group (Freiburg)

DAF Corrected Data | **Raw Data**

$H_3\,3pE'$

$D_3\,2sA_1'$

$D_3\,2pA_2''$



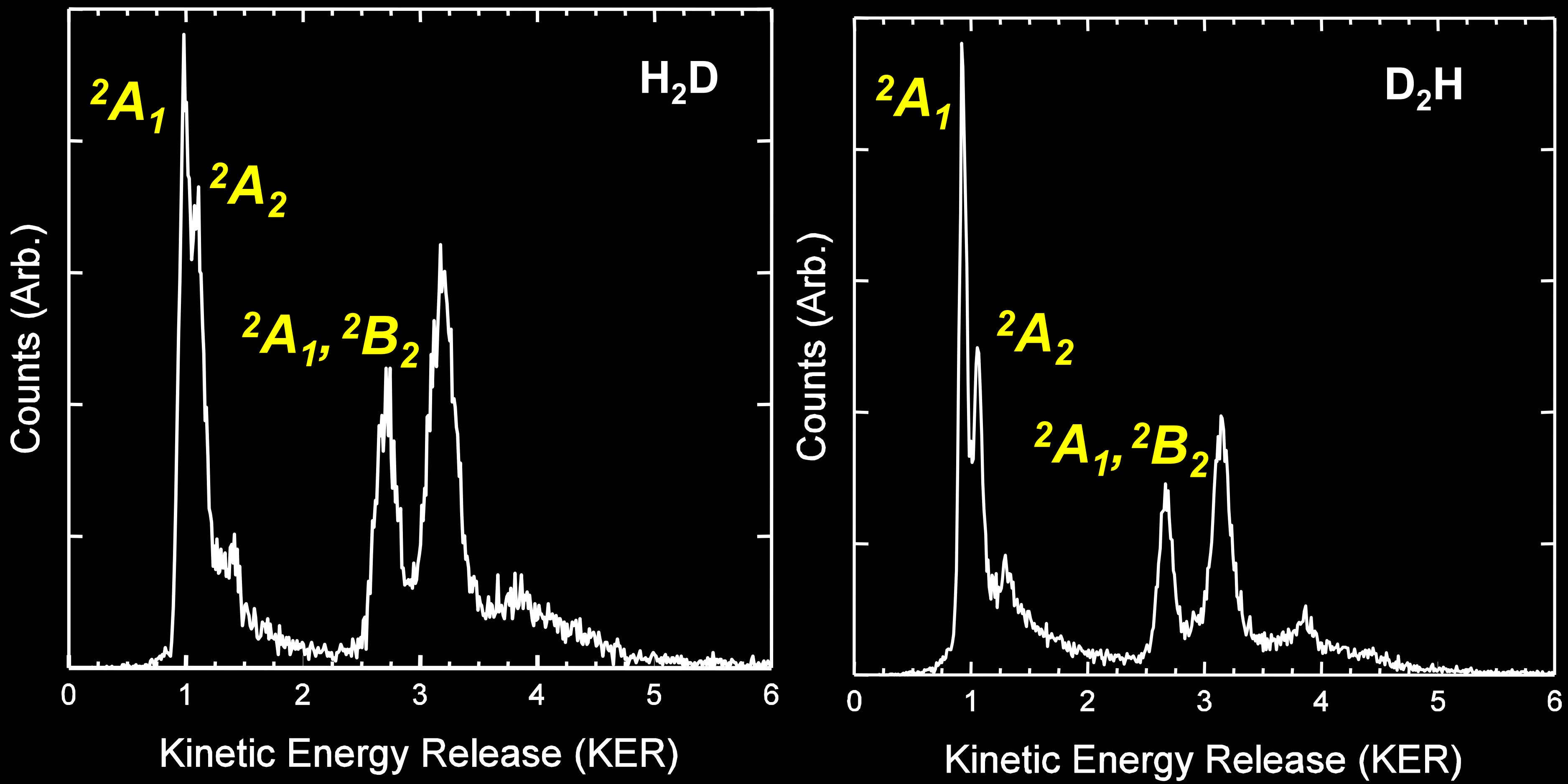
Radiative Preparation

Charge Exchange

FREIBURG | *SAN DIEGO*

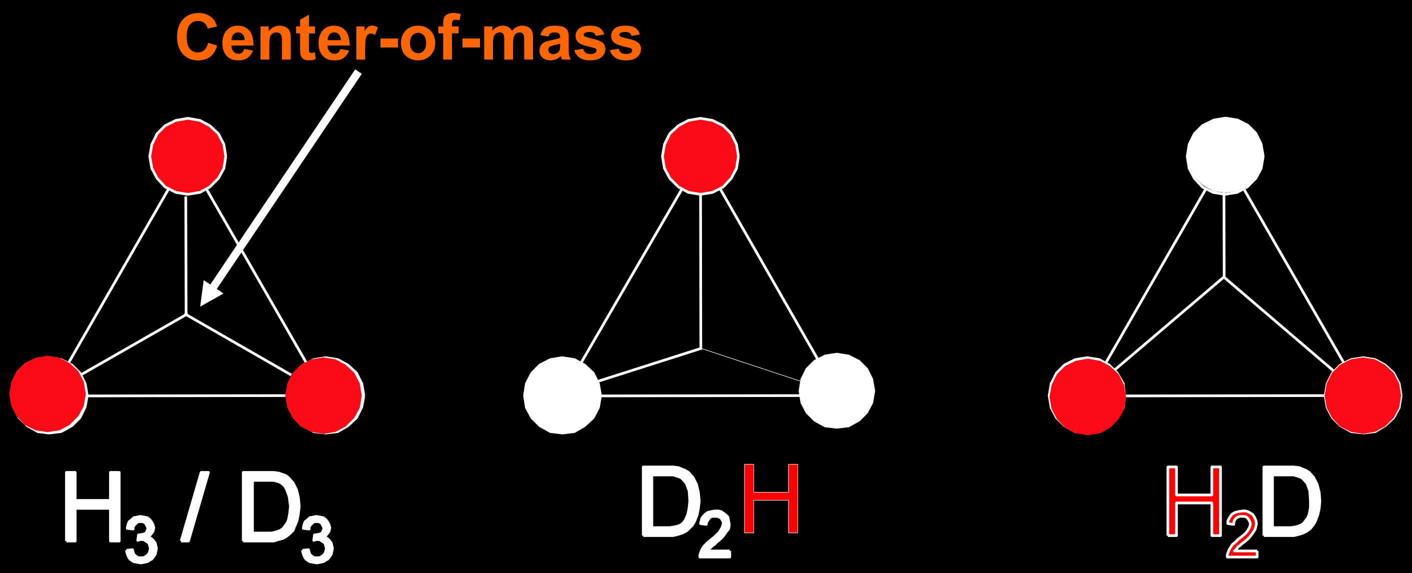
Mixed Isotopomers: H_2D and D_2H

12 keV/Cs



Heavier, slower D_2H exhibits reduced non-resonant charge transfer (as expected!)

Kinematic Effects in Mixed Isotopomers

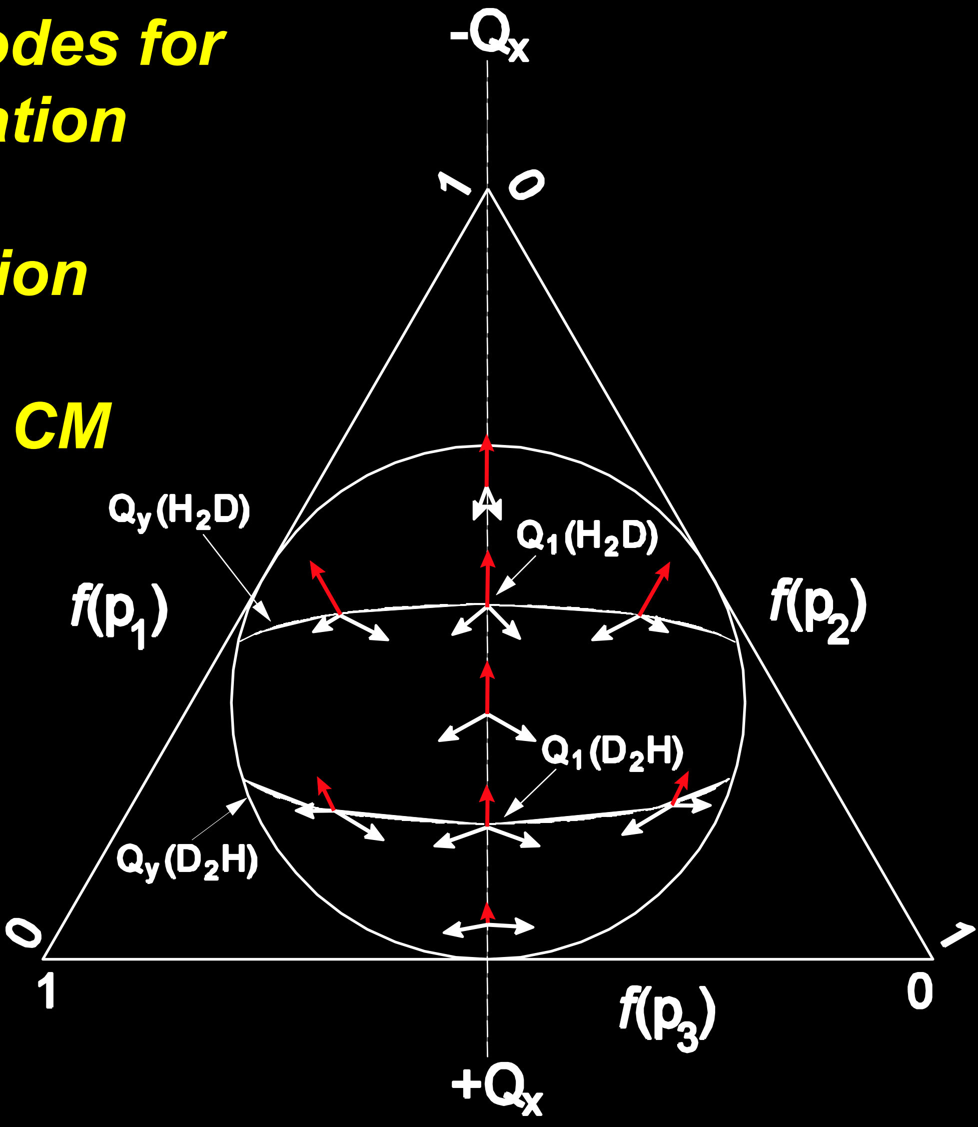


Dalitz Map: H_2D vs. D_2H

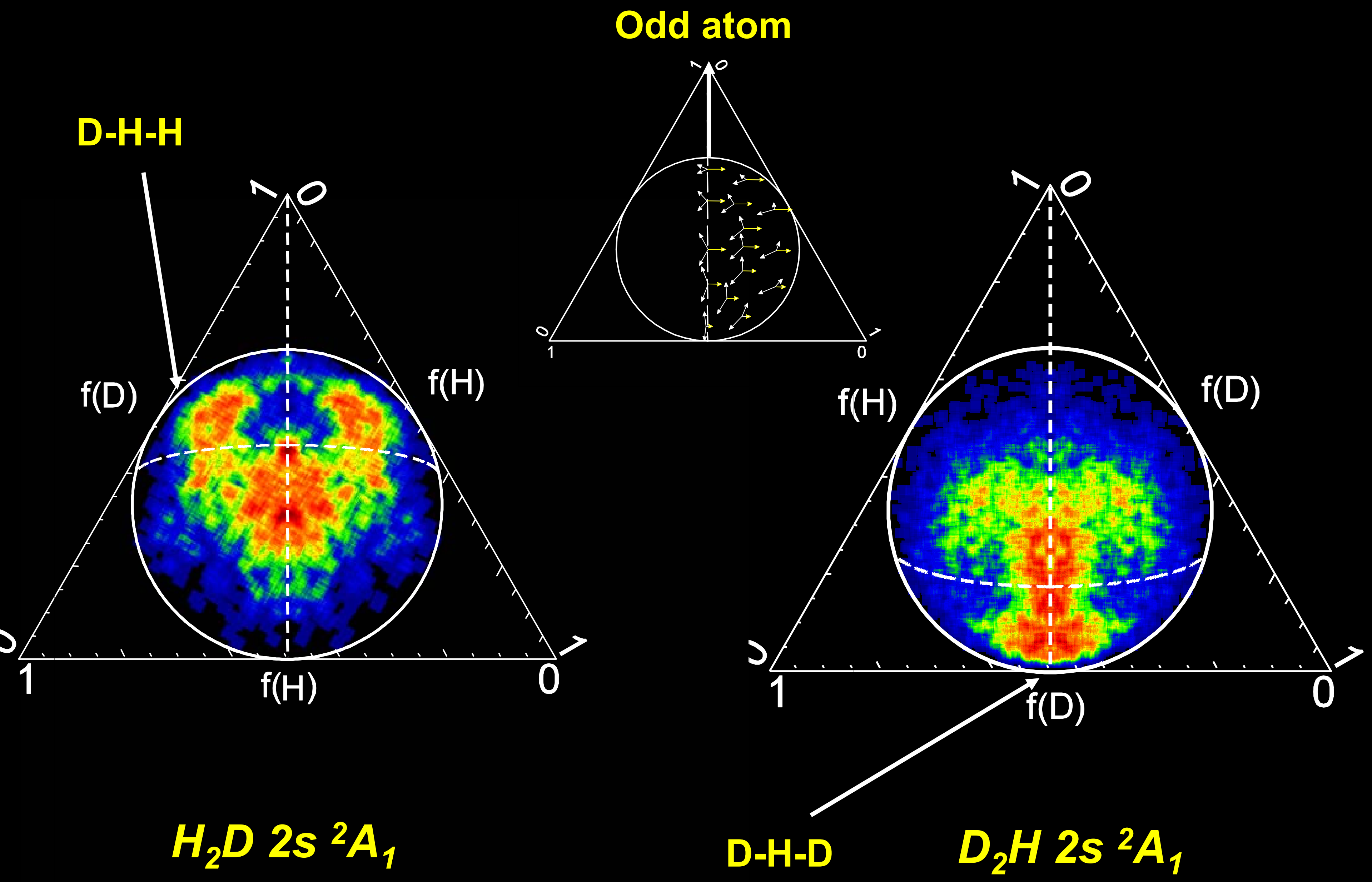
Mapping of Normal Modes for Synchronous Dissociation

Momentum Conservation

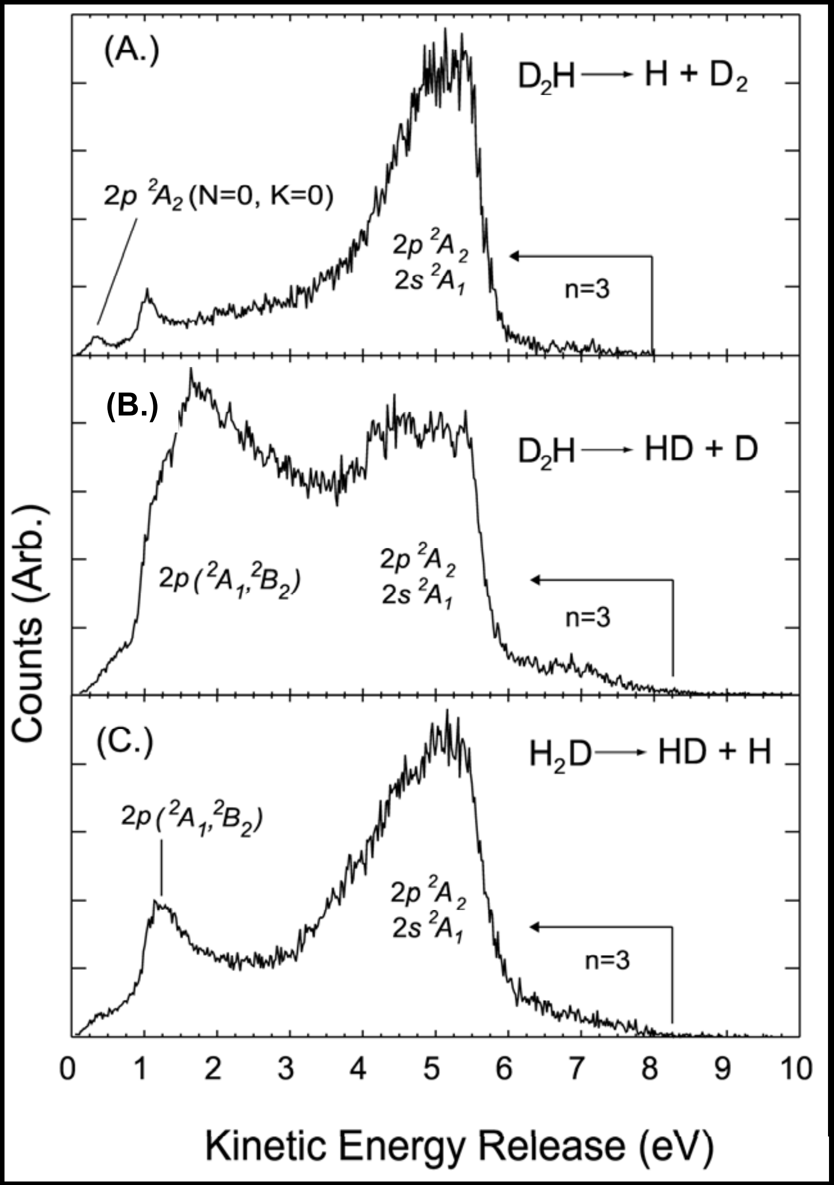
Forces operative from CM



Isotope Effects – H_2D vs. D_2H



Isotope Effects – 2-Body Dissociation of D_2H



Significant 2-Body Dissociation Isotope Effect in D_2H

H_2D^+ Beam Contaminated by D_2^+

(no problem for three-body breakup or dissociation to HD + H)

Branching Ratios To Be Determined

H_2D / D_2H Preliminary Conclusions and Questions

H_2D: D atom elimination in 3-body dissociation
favors acute isosceles configuration
(D atom 'elimination' C_{2v} distortion)
some evidence for D-H-H configuration

D_2H: Prefers D-H-D in C_{2v} distortion towards linear
Large isotope effect in 2-body HD/D_2 channel

Vibrational motion, nuclear spin statistics affected by isotopic substitution – probe different nuclear configurations

Potential Practical impact:
- source for higher energy D atoms in interstellar space
- effect on isotope enrichment processes

Dissociative Charge Exchange of H_3 / Isotopomers

- Resolved KER spectra for three lowest Rydberg states

- Momentum partitioning - measure of 3-body dissociation configuration

- The H_3 3p $^2E'$ state – system undergoing Jahn-Teller distortion
    - Evidence for inner-cone state?

- Momentum distributions - profound challenge for theoretical predictions of non-adiabatic couplings and 3-body dissociation dynamics

- Significant isotope effects in D_3, D_2H and H_2D

- Future: DR? Experiments with p-H_2?