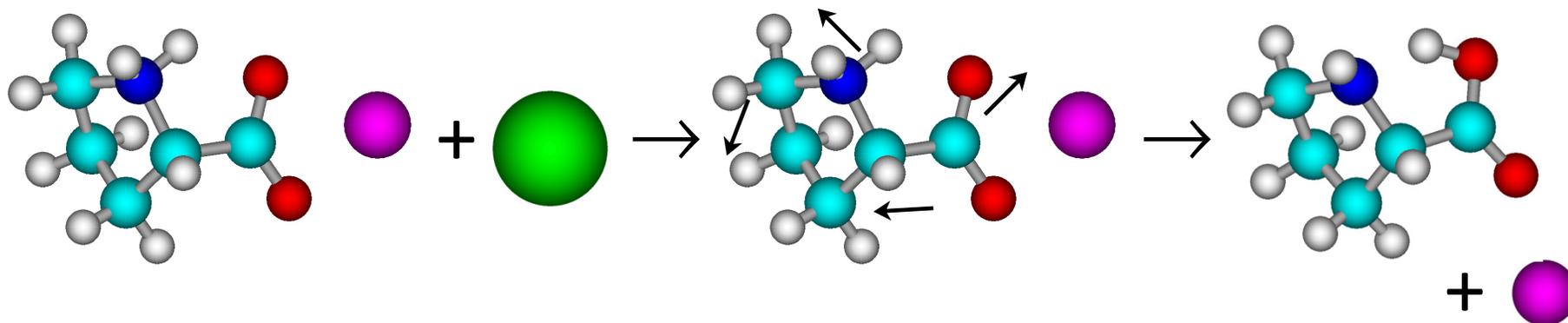


Collision-induced dissociation:

How does it really work and
what it can (or can't) tell you



Peter B. Armentrout

Department of Chemistry,

University of Utah, Salt Lake City, UT

National Science Foundation & Dept. of Energy

What is CID?

From IUPAC Compendium on Analytical Nomenclature (**Orange book**)

Collision-induced Dissociation –

An ion/neutral species interaction wherein the projectile ion is dissociated as a result of interaction with a target neutral species. This is brought about by conversion of part of the translational energy of the ion to internal energy in the ion during collision.

What is CID?

Collision-induced Dissociation - an ion/neutral collision induces kinetic to internal energy transfer that leads to dissociation of the ion

How does it really work?

Three critical terms

Collisions

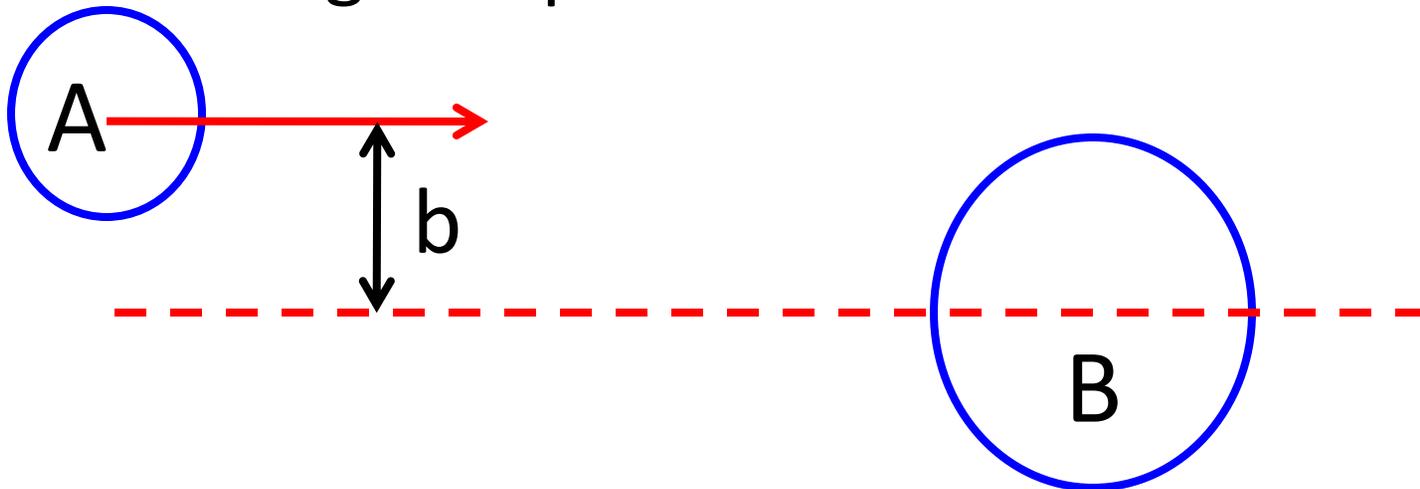
Energy transfer

Dissociation

Collisions – impact parameter

What is a collision?

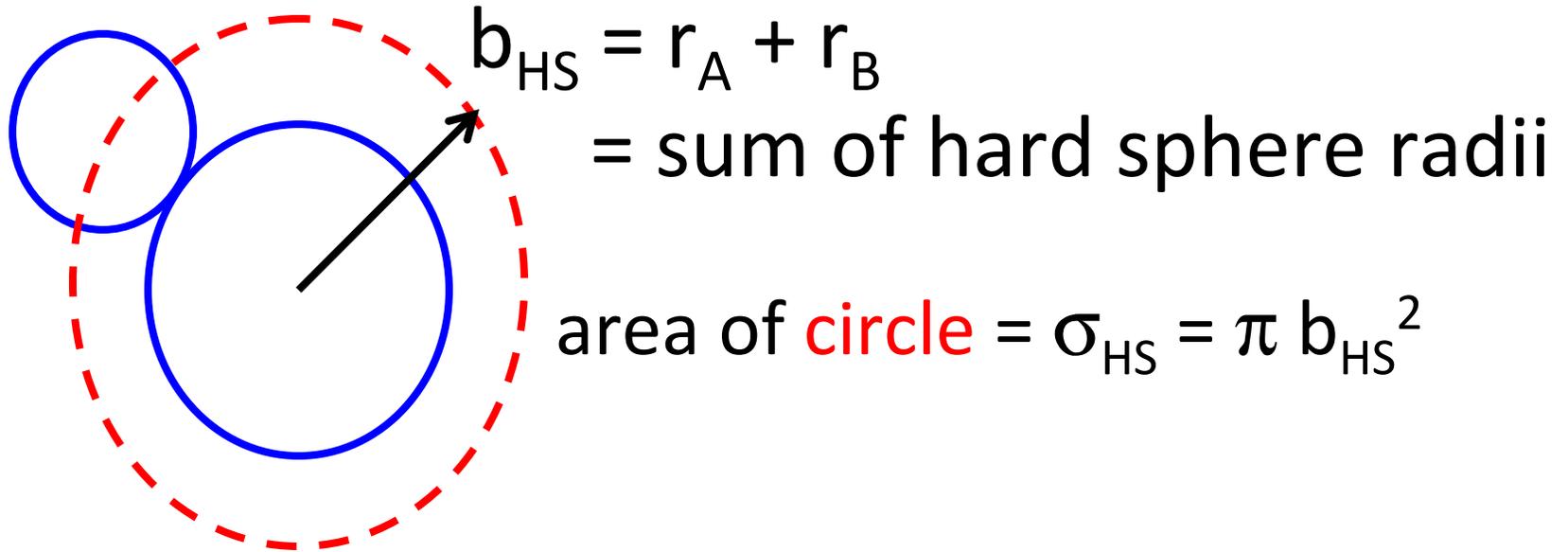
A collision can be defined in terms of the impact parameter (b) – the distance of closest approach of two particles (A and B) if they had continued in their original direction of motion at their original speed.



Collisions – cross section

What is a collision?

If $b < b_{\text{HS}}$, then a collision occurs.

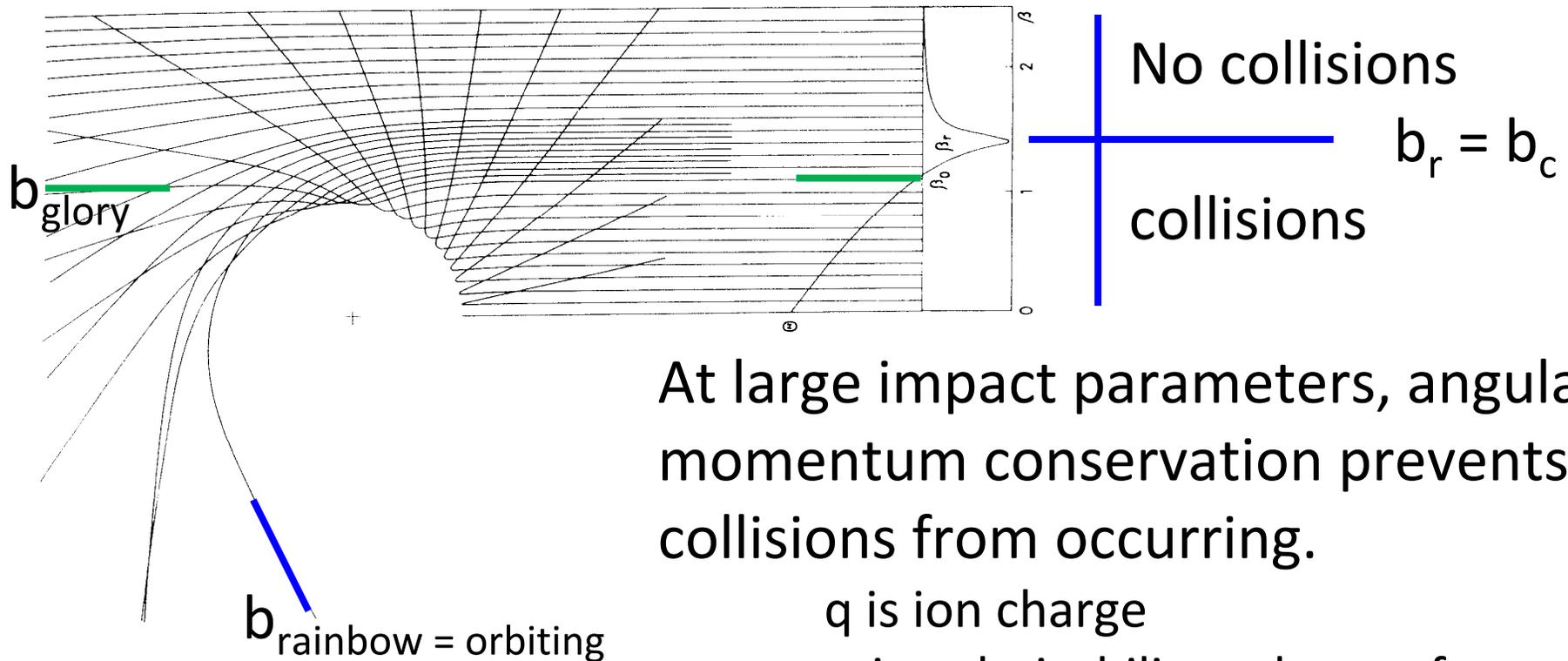


σ_{HS} = Collision cross section for **hard spheres**
(no energy dependence)

Collisions – ion/neutral

What is the cross section for ion/neutral collisions?

The long-range attractive ion-induced dipole potential ($V = -q^2 \alpha / 8\pi\epsilon_0 R^4$) pulls the colliding partners together.



At large impact parameters, angular momentum conservation prevents collisions from occurring.

q is ion charge

α is polarizability volume of neutral

R is distance between particles

Pauly, *Atom-Molecule Collision Theory*,
Bernstein, Ed., Plenum, New York, 1979, 127

Collisions – centrifugal barrier

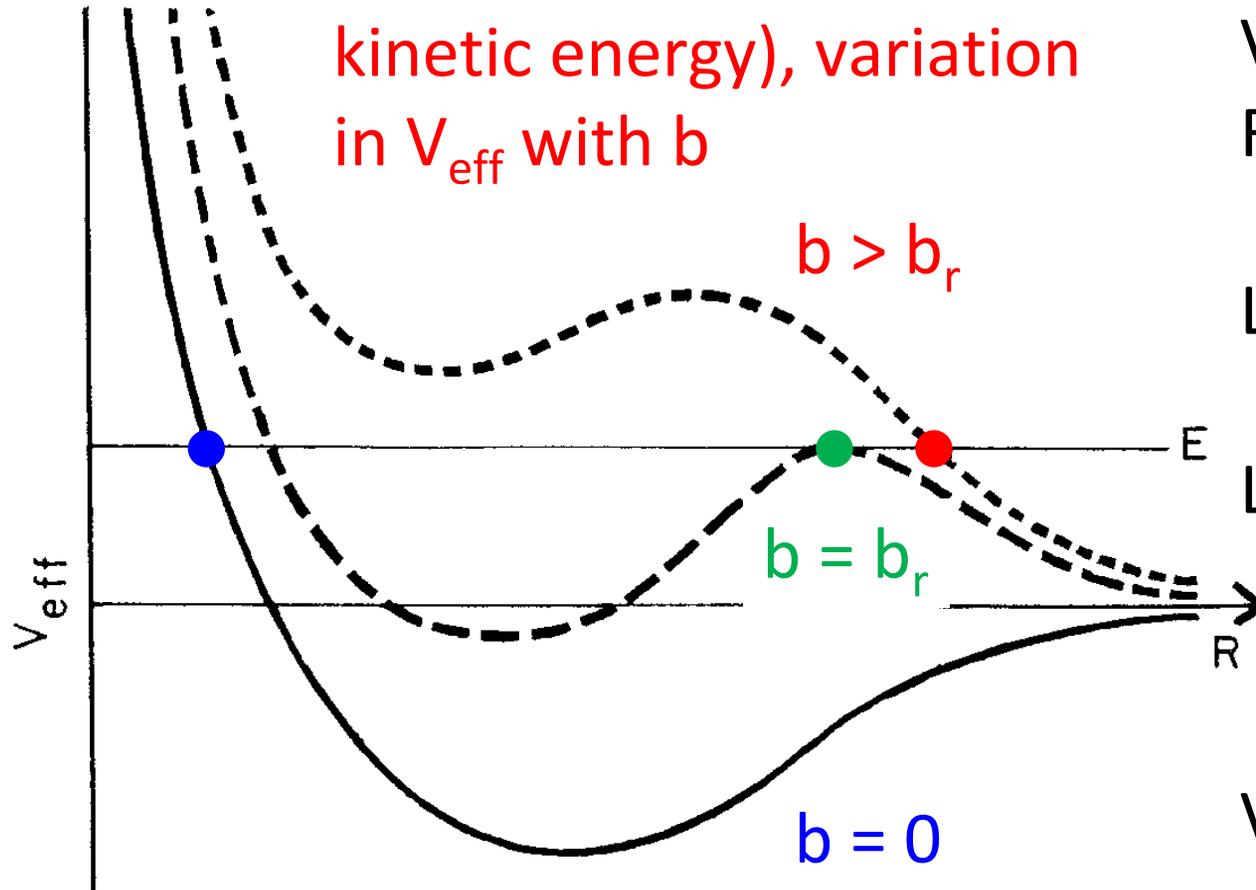
At a fixed E (relative kinetic energy), variation in V_{eff} with b

$$V_{\text{eff}} = -\frac{q^2 \alpha}{8\pi\epsilon_0 R^4} + \frac{L^2}{2\mu R^2}$$

L = angular momentum

$$\frac{L^2}{2\mu R^2} = \frac{Eb^2}{R^2}$$

$$V_{\text{eff}} = E \text{ at } b = b_r$$



Collisions – ion/neutral cross section

What the cross section for ion/neutral collisions?

Langevin-Gioumouisis-Stevenson cross section

$$\sigma_{\text{LGS}} = \pi b_r^2 = \pi q (\alpha/2\pi\epsilon_0 E)^{1/2}$$

Depends on polarizability of neutral.

Neutrals with dipole moments need additional terms (orientation dependent). **ADO theory**

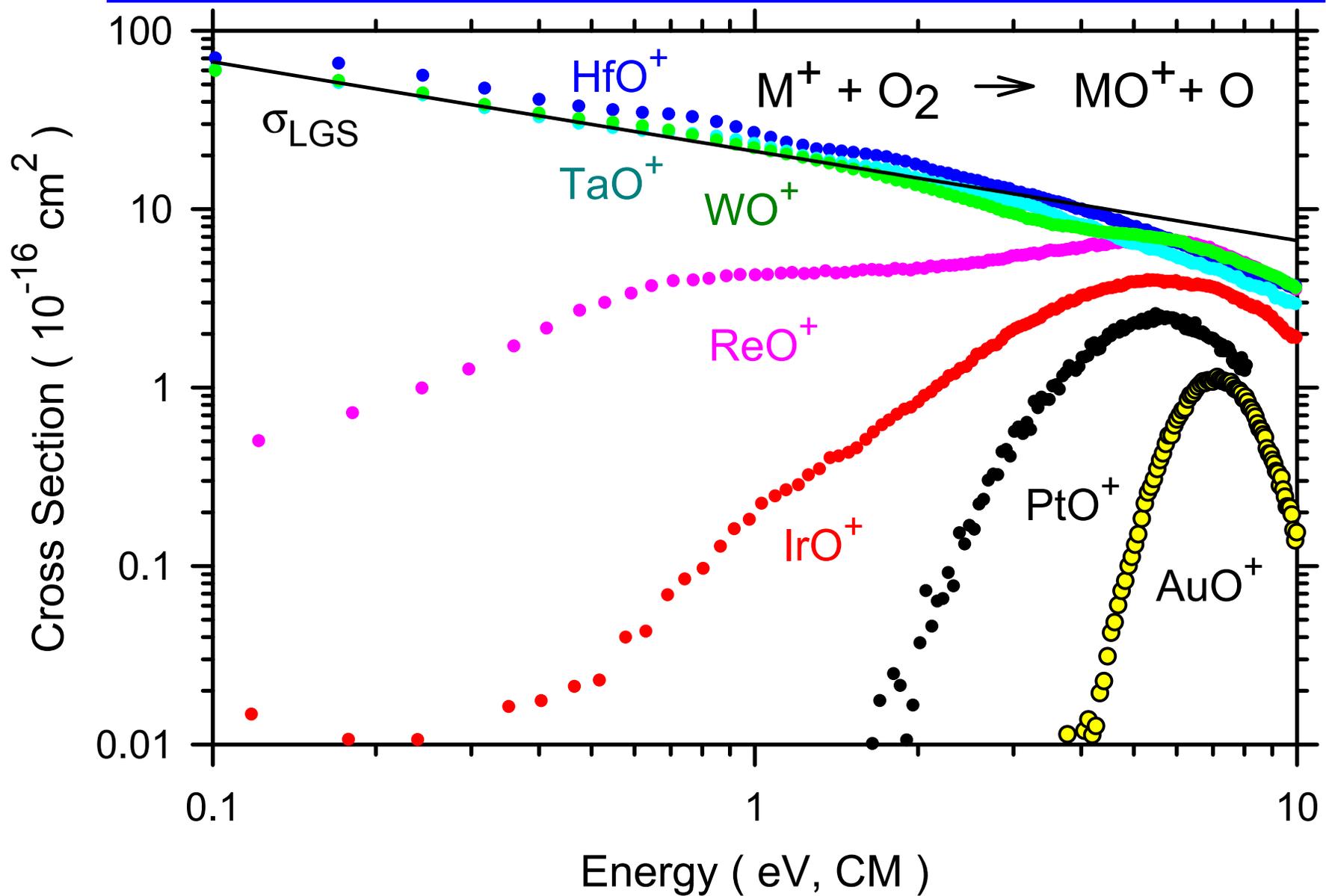
Su & Bowers, Gas Phase Ion Chemistry, Bowers, Ed.; Academic, New York, 1979

At low energies ($< \sim 1$ eV), $\sigma_{\text{LGS}} > \sigma_{\text{HS}}$

At high energies, $\sigma_{\text{LGS}} < \sigma_{\text{HS}}$

Can't easily show LGS cross section for CID reactions because these are intrinsically endothermic.

Collisions – LGS cross section



Collisions - probability

What is the probability of a collision?

Beer's law formula

$$I_p = I_0 [1 - \exp(-P\sigma\ell/RT)]$$

I_p = intensity of ions undergoing 1 or more collisions

I_0 = incoming intensity of ions

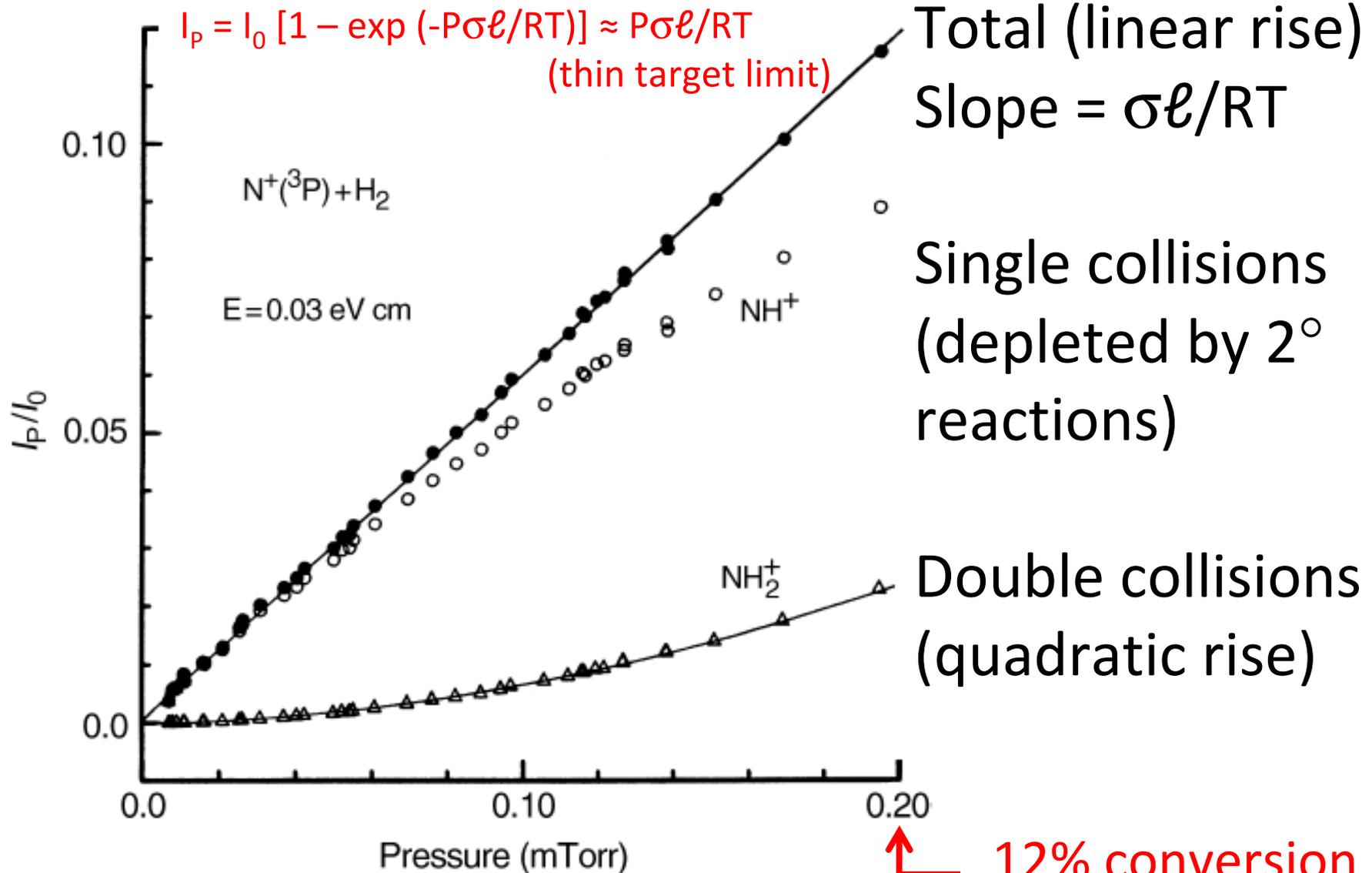
P = pressure of neutral (**easily varied**)

T = temperature of neutral

ℓ = interaction length \sim gas cell length (**instrument dependent**)

σ = cross section (**system dependent**)

Collisions – P dependence



Energy transfer

How much energy is transferred from translation to internal energy during a collision?

Maximum amount of energy transfer is rigorously limited by linear momentum conservation.

For a stationary target gas, the available energy (Center-of-mass energy or relative energy) is

$$E(\text{CM}) = q V m_N / (m_N + m_I)$$

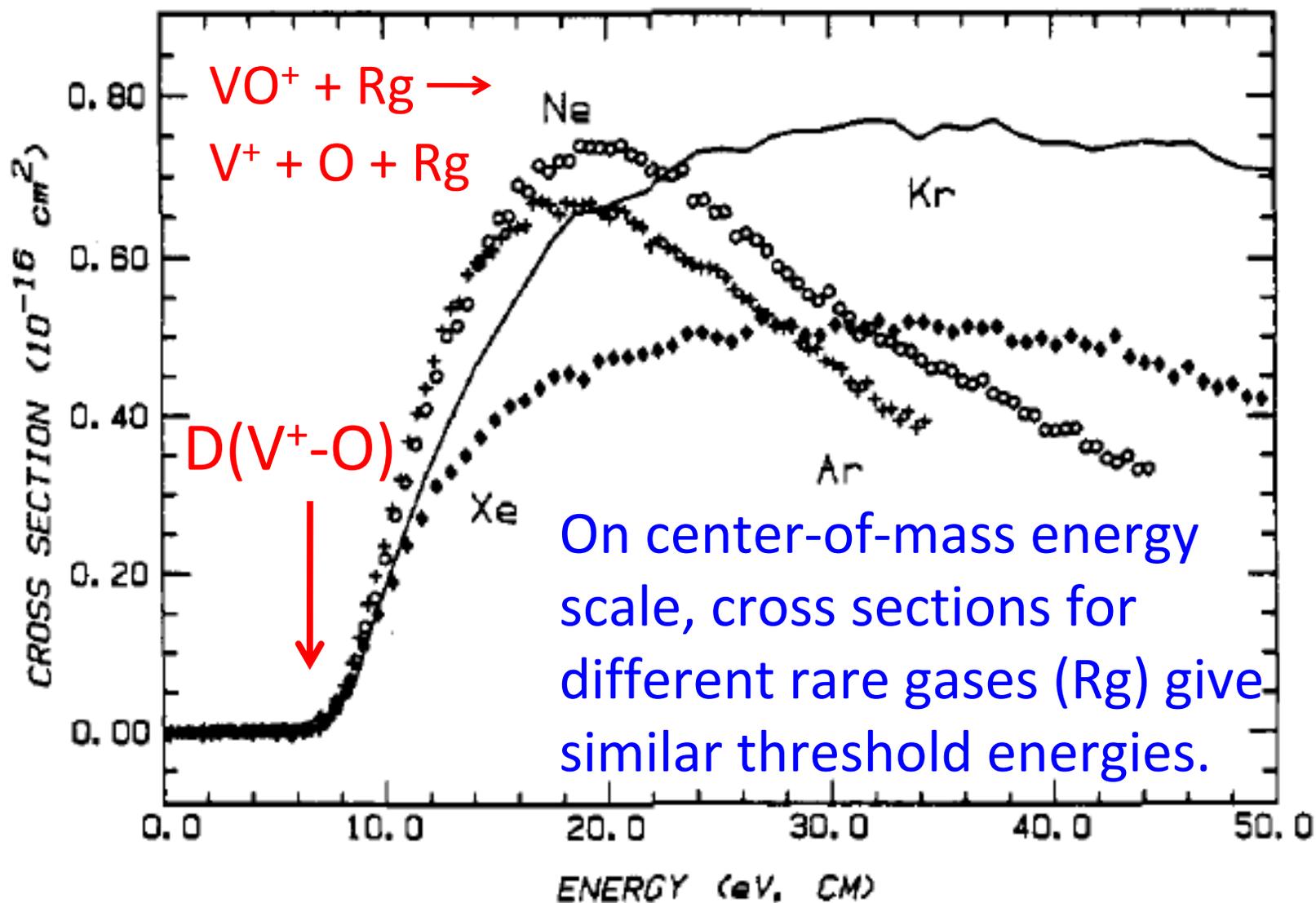
q = charge of ion

V = acceleration voltage of ion

m = masses of neutral (N) and ion (I)

Energy of ion in laboratory frame = $E(\text{lab}) = q V$

Energy transfer – center-of-mass

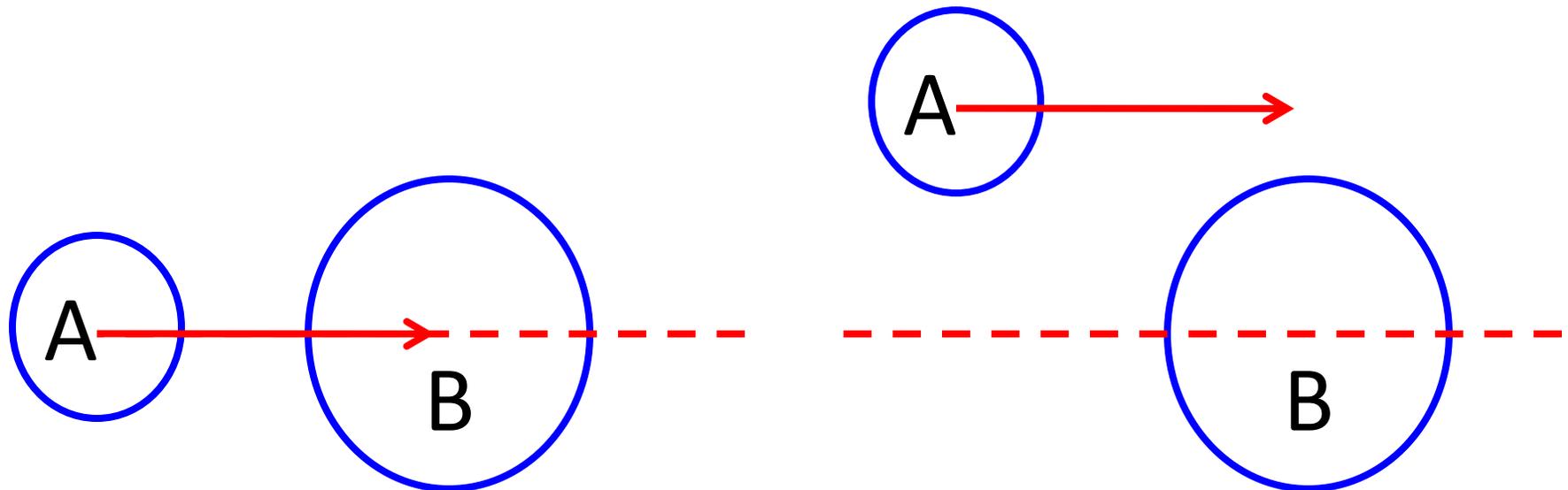


Aristov, Armentrout, *J. Phys. Chem.* **1986**, *90*, 5135

Energy transfer – impact parameter

How much energy is transferred from translation to internal energy during a collision?

Energy transfer is limited by **angular** momentum conservation.



$b = 0$, all of relative energy is available

grazing collision
little energy between spheres

Energy transfer – angular momentum

angular momentum conservation (hard spheres)

L = angular momentum

$$E_{\text{rot}} = L^2/2\mu R^2 = Eb^2/R^2$$

when $b = 0$, $E_{\text{rot}} = 0$

when $b = b_{\text{HS}}$, $E_{\text{rot}} = E$

$$E_{\text{available}} = E$$

$$E_{\text{available}} = 0$$

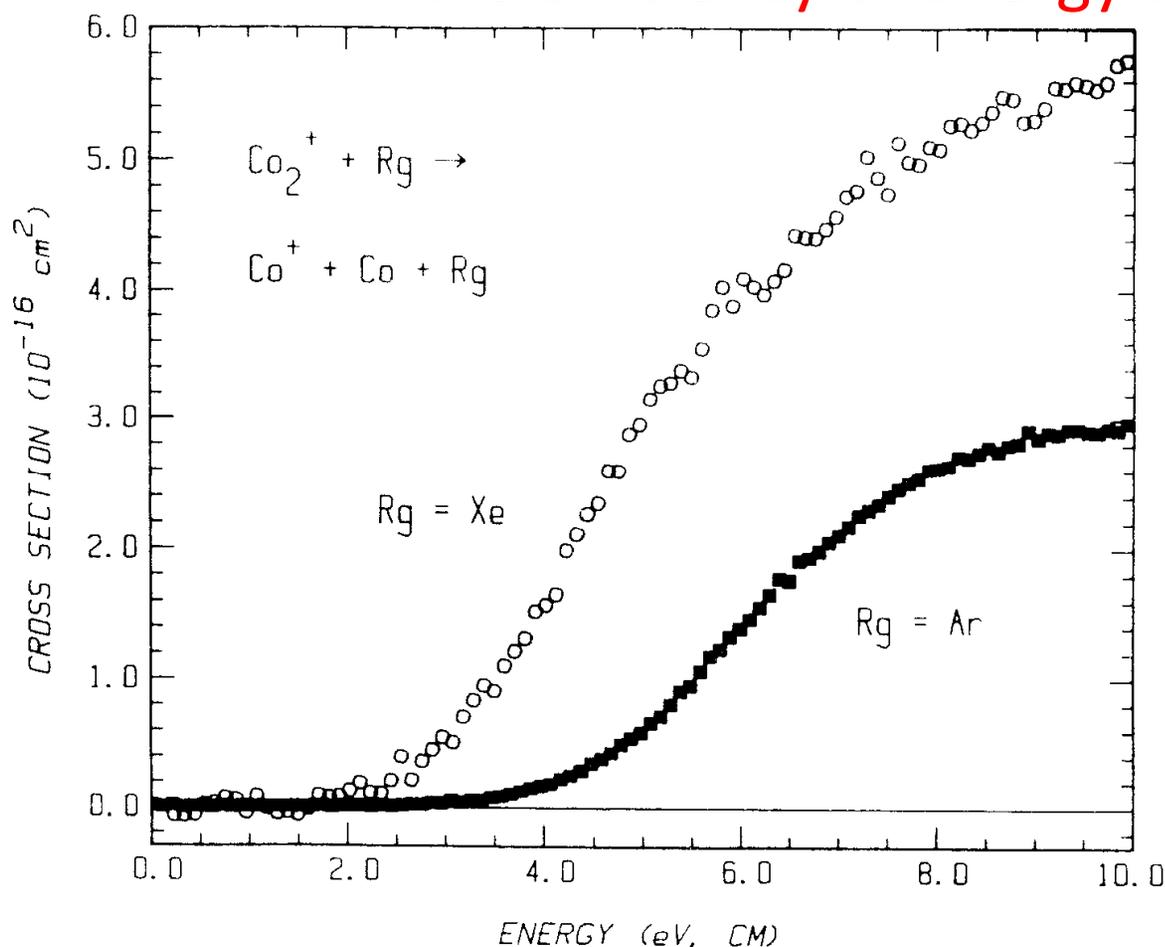
This explains why there is a correlation between
the extent of CID and scattering

small angle scattering (grazing) = less dissociation

large angle scattering = more dissociation

Energy transfer - collision partner

The identity of the collision partner affects the efficiency of energy transfer



Rg = He exhibited **NO** dissociation

Xe more efficient than Ar

Why?

The more polarizable neutral has a stickier (longer lived) collision allowing more complete energy transfer.

Sticky collisions shown by the observation of

Energy transfer

The identity of the collision partner affects the efficiency of energy transfer

Of course, there are even stickier gases (molecules) but now energy can be lost to internal degrees of freedom of the neutral.

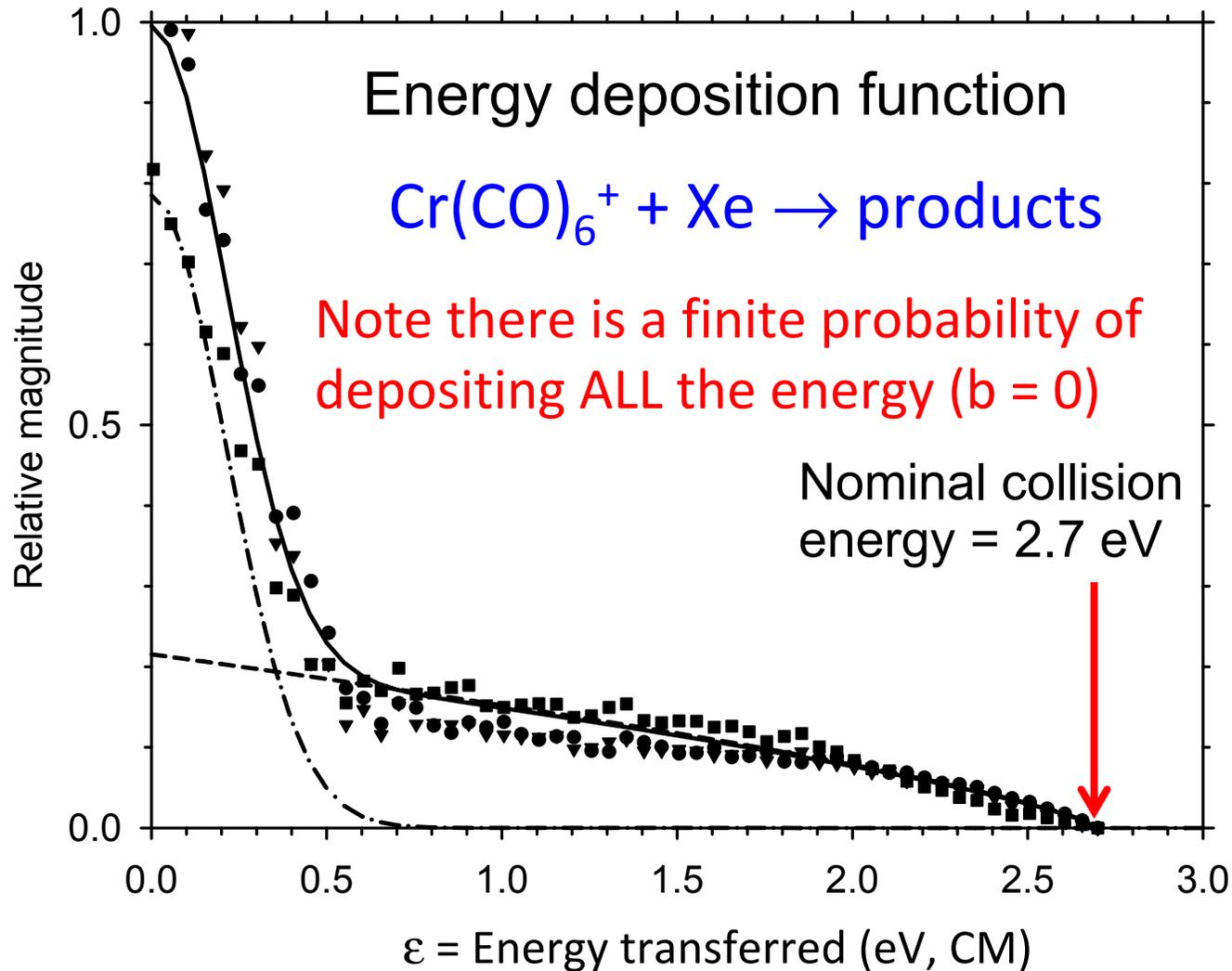
He is often a preferred collision gas at very high collision energies (keV).

He may induce “electronic” versus “rovibronic” excitation.

He is less likely to strongly scatter the ions (conservation of linear momentum).

At keV energies, grazing collisions can deposit sufficient energy for decomposition.

Energy transfer – deposition function



$$P(\varepsilon) \sim$$

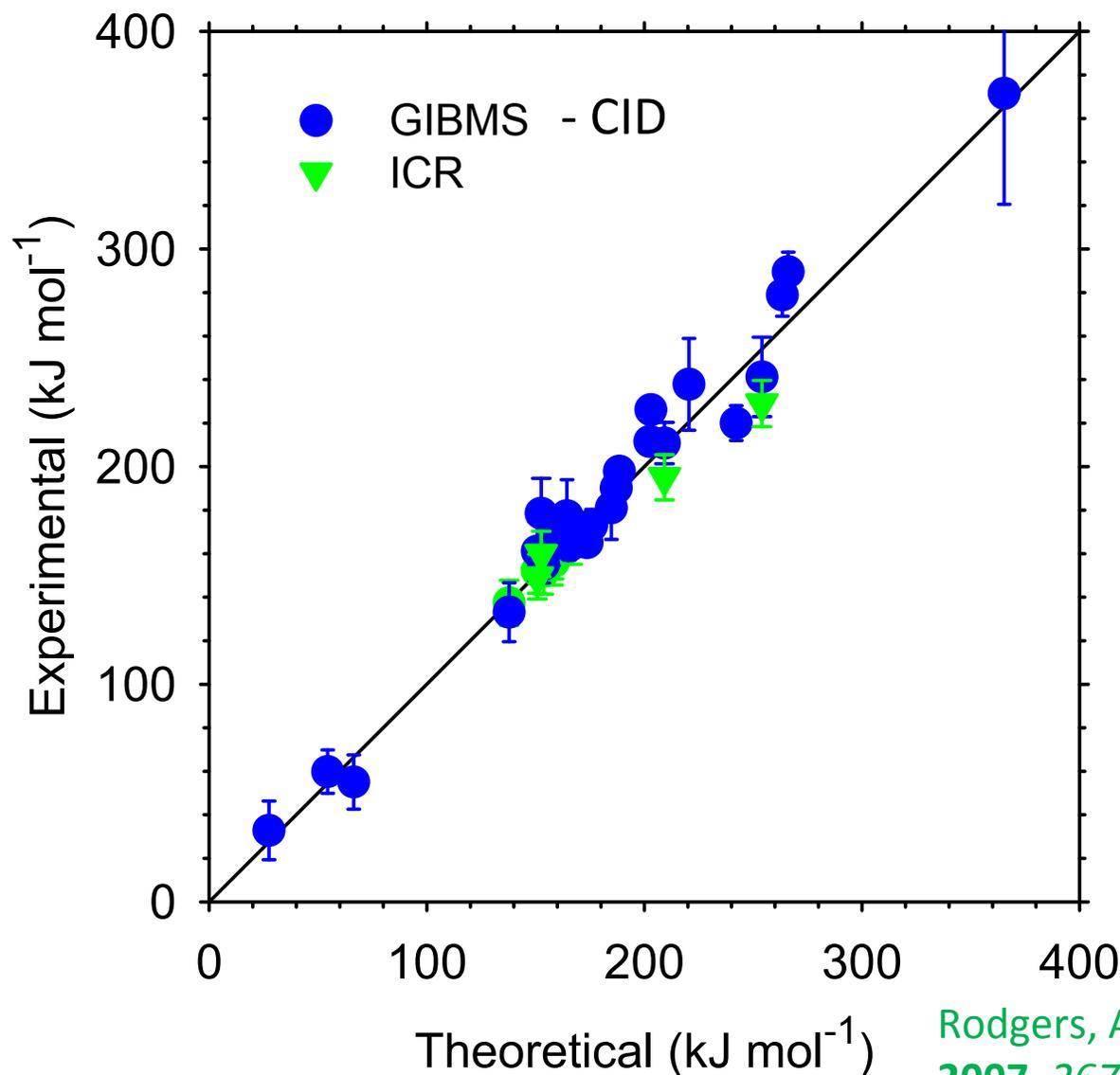
$$(E - \varepsilon)^{n-1}/E$$

ε = energy transferred

n = controls shape
= 1 for hard spheres

At low ε , grazing collisions lead to large peak

Energy transfer – deposition function



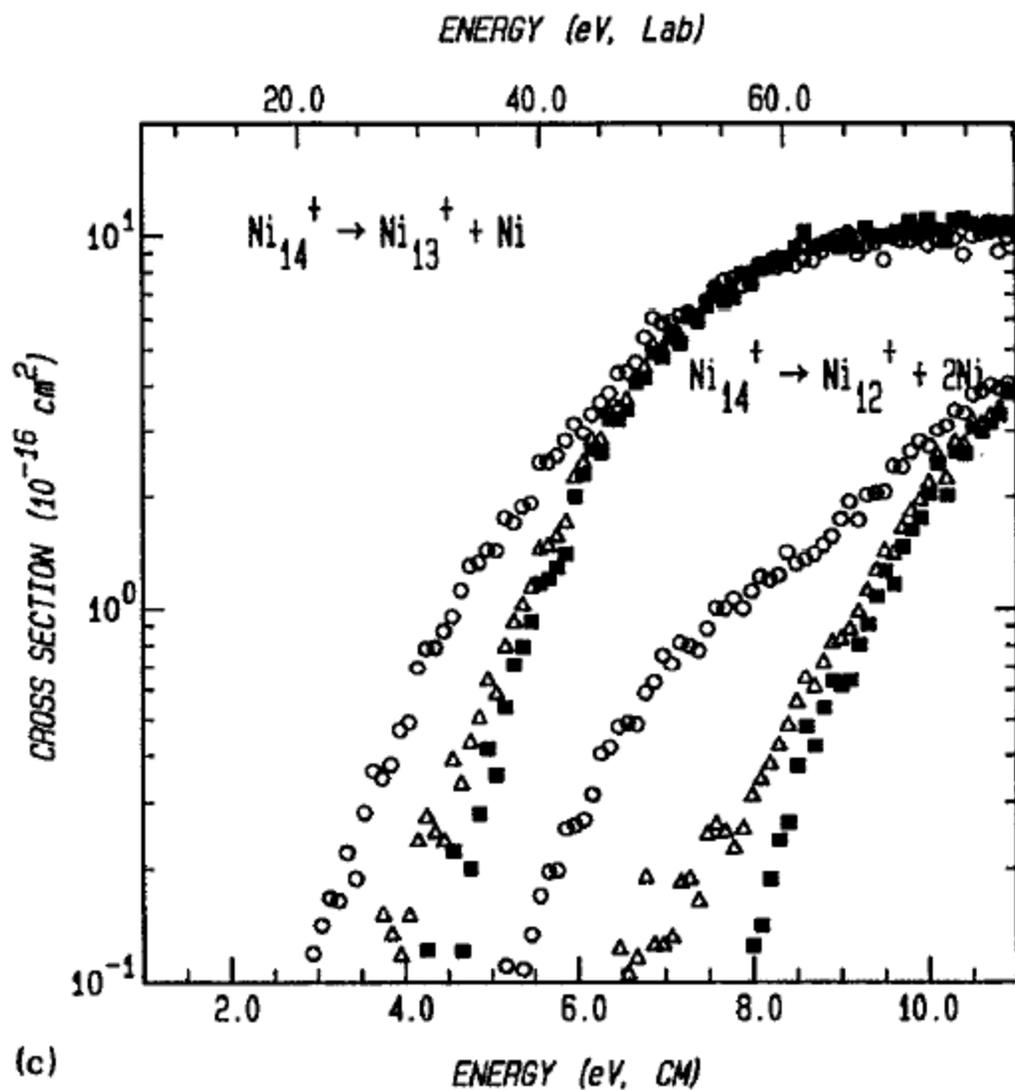
The binding energies of Li⁺ to 25 molecules of varying complexity agree well with high-level theory.

Comparable agreement has been found for many other systems.

If only a fraction of the collision energy were transferred, then threshold energies would not correspond to thermodynamic values.

Rodgers, Armentrout, *Int. J. Mass Spectrom.*, **2007**, *267*, 167.

Energy transfer – multiple collisions



$P(\text{Xe})/\text{mTorr}$ (1 coll./2)

○ 0.3 (8% / <1%)

△ 0.05 (1.5%)

■ 0.0

- Multiple collisions add more energy to ion & lower threshold.
- Higher threshold process shows greater shift.
- Energy of extra collisions not well known and gets smaller as ion slows.

Dissociation

When does dissociation occur and how rapidly?

$$P_D(E) = [1 - e^{-k_{tot}(E^*)\tau}]$$

Probability of dissociation of the energized ion will occur with a rate that can usually be described by **statistical unimolecular rate theory**

(RRKM, variational transition state, phase space)

$k_{tot}(E^*)$ = total rate constant for dissociation at E^*

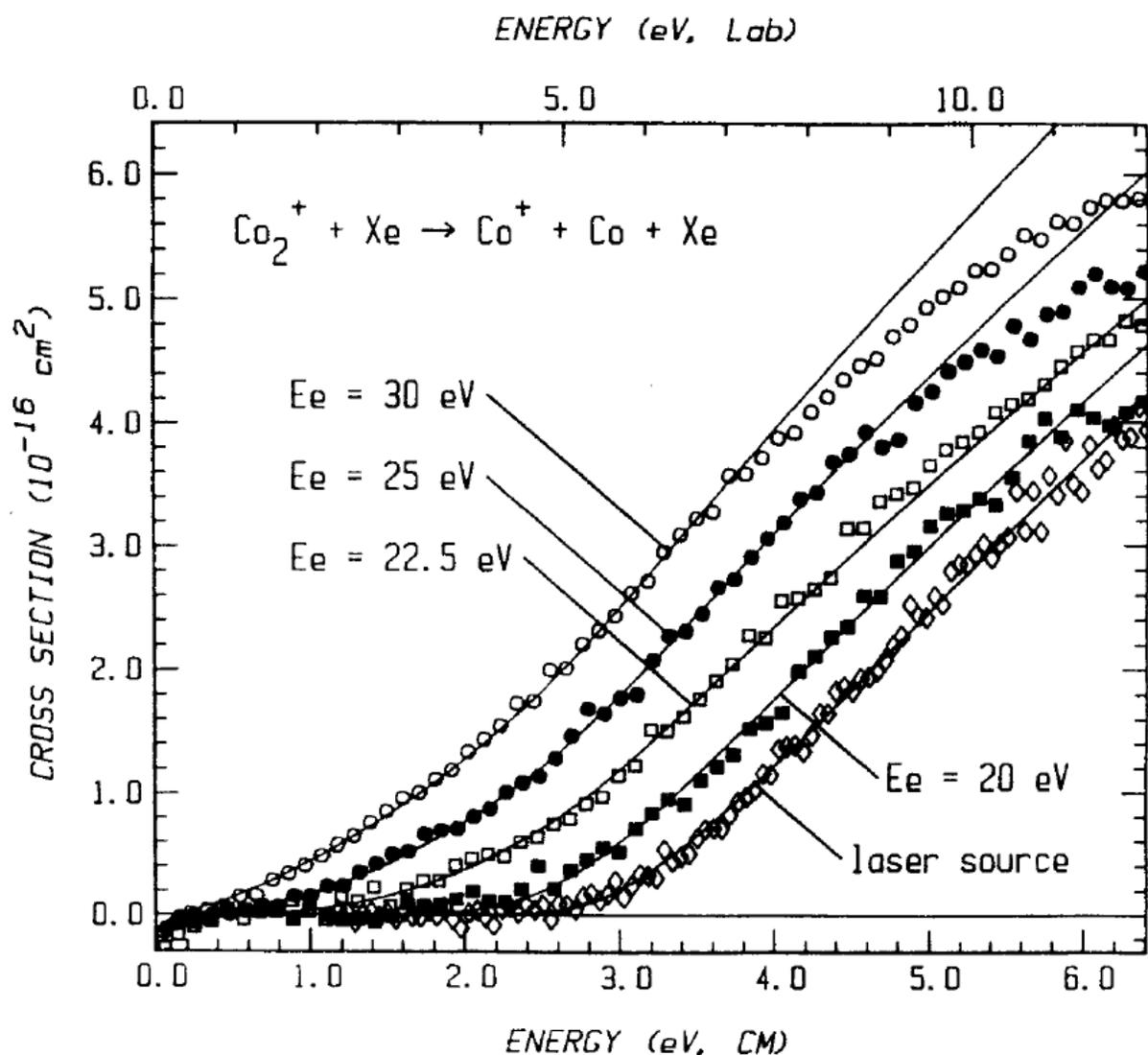
$E^* = \varepsilon + E_i$ = energy available

ε = energy deposited by collision (see above)

E_i = internal energy of reactant ion

τ = time available for dissociation (**instrument dependent**)

Dissociation – internal energy of ion



Co_2^+ formed either by laser ablation/
supersonic expansion (thermal) or
electron ionization of $\text{Co}_2(\text{CO})_8$ at variable
electron energy (E_e)

Hot dimers ($E_i > 0$)
formed by electron
ionization need less
collision energy (ϵ) to
dissociate

Dissociation - rate

Rate of unimolecular dissociation

$$k(E^*) = dN_{vr}^\ddagger(E^* - E_0) / h\rho_{vr}(E^*)$$

d = degeneracy of reaction path

$N_{vr}^\ddagger(E^* - E_0)$ = number of states at transition state

$\rho_{vr}(E^*)$ = density of states of energized ion

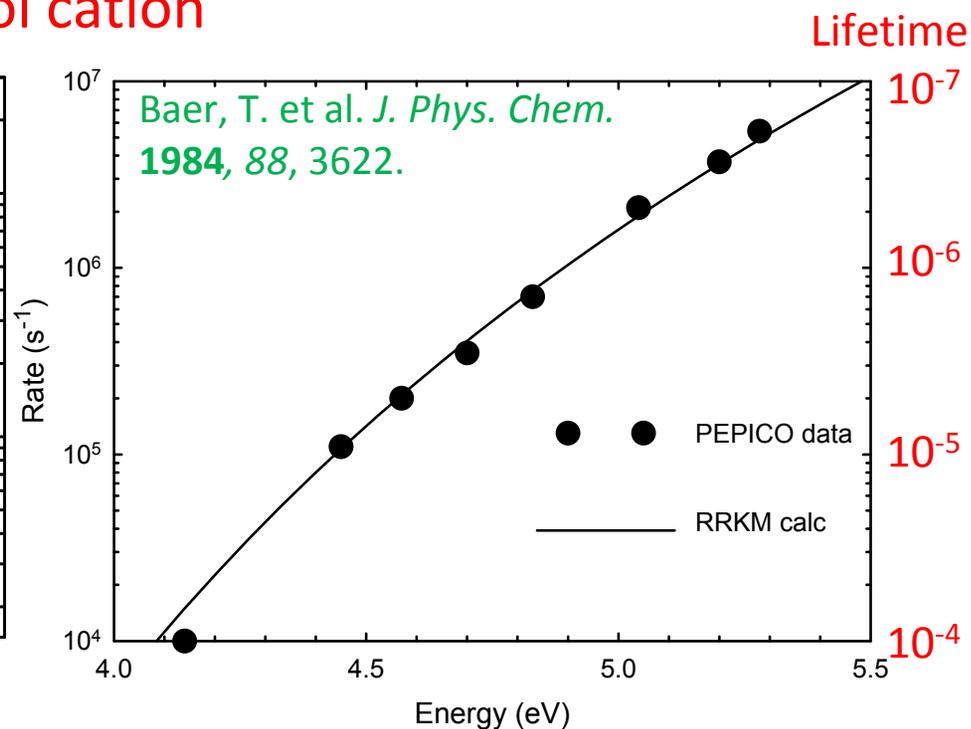
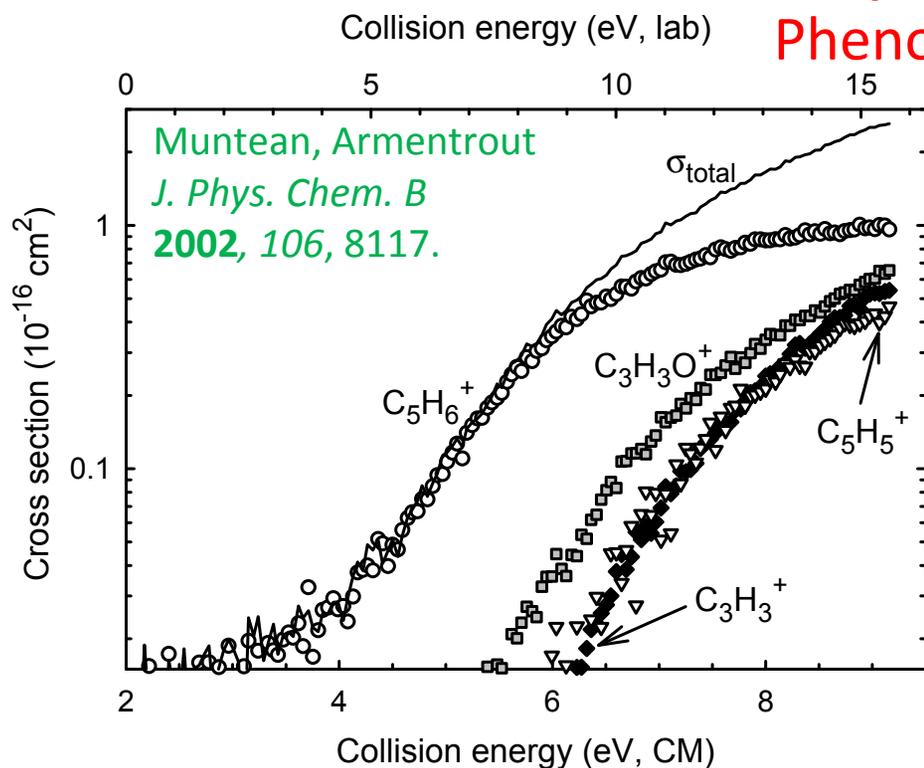
E_0 = threshold energy for dissociation

Calculation requires the vibrational and rotational constants of the ion and the transition state for the dissociation pathway

Dissociation - rate



Phenol cation



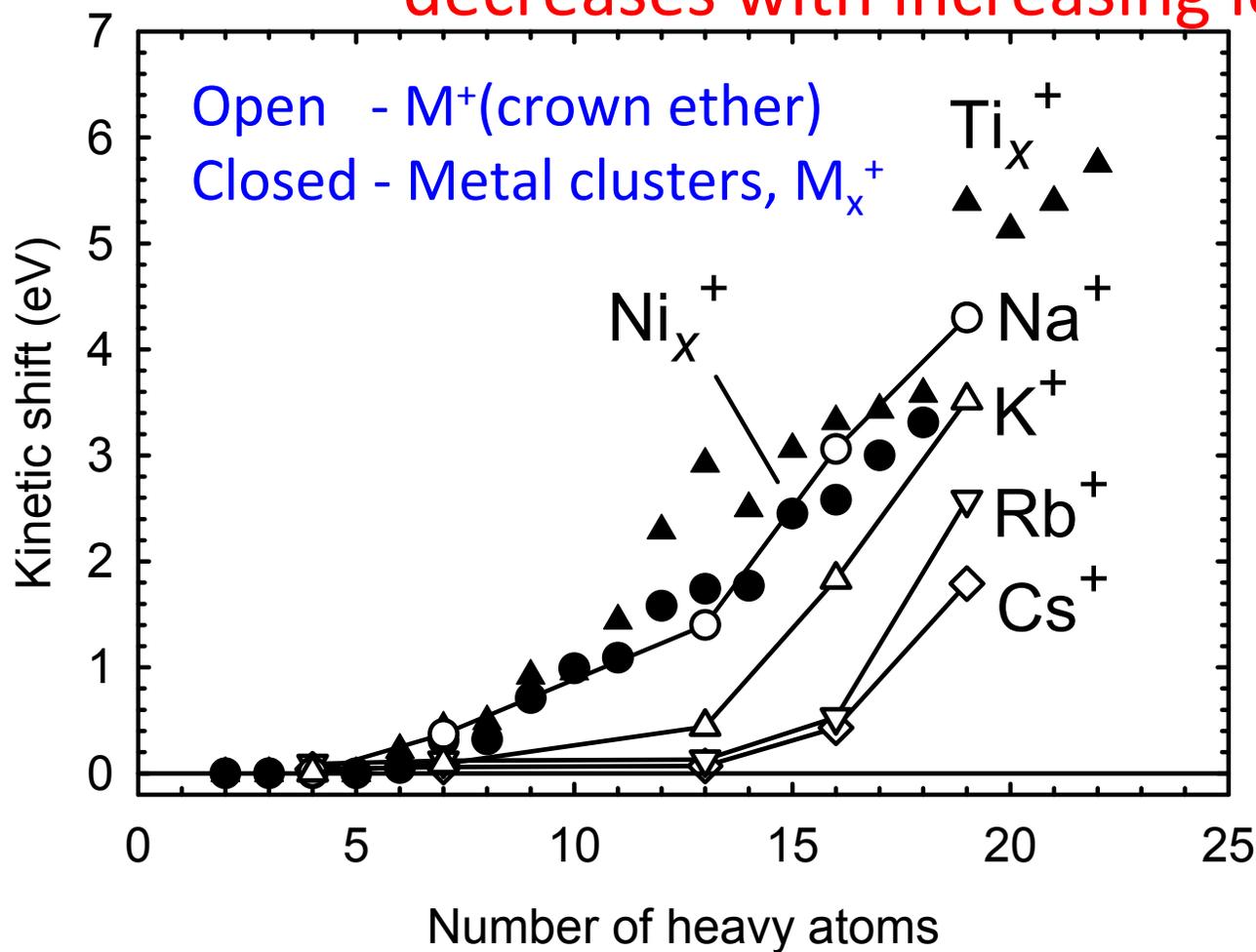
Rate of dissociation must match the time scale available to the instrumentation used.

On left, $\tau = 10^{-4} \text{ s}$.

$E_0 = 3.03 \pm 0.14 \text{ eV}$

Dissociation – ion size

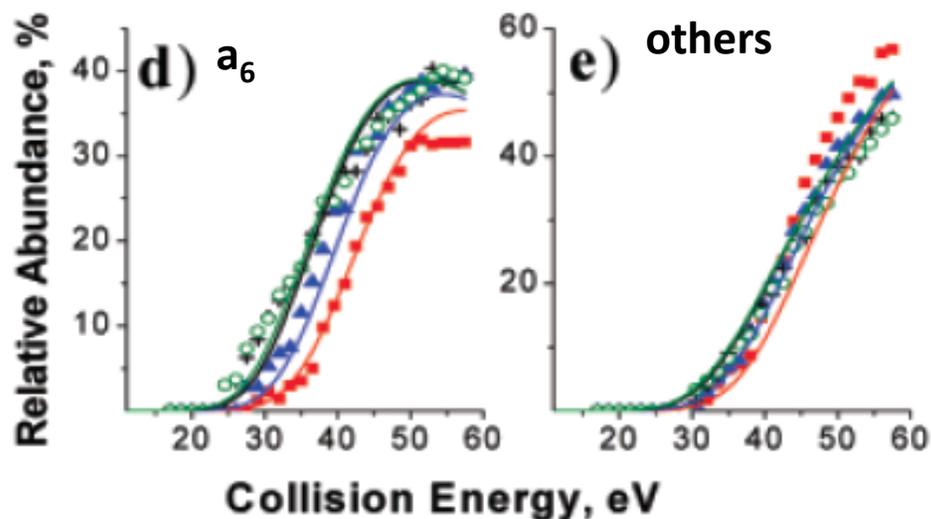
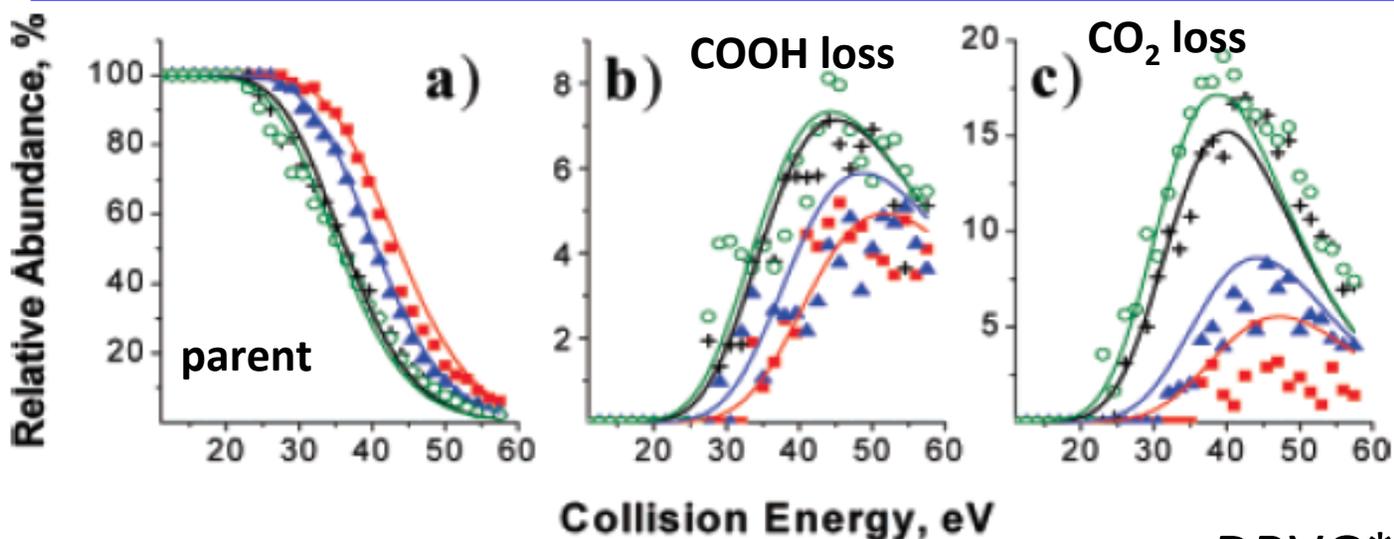
The rate of unimolecular dissociation decreases with increasing ion size



because the density of states of the ion at a particular energy increases.

This leads to a kinetic shift in the appearance energy of dissociation.

Dissociation – time (kinetic shift)

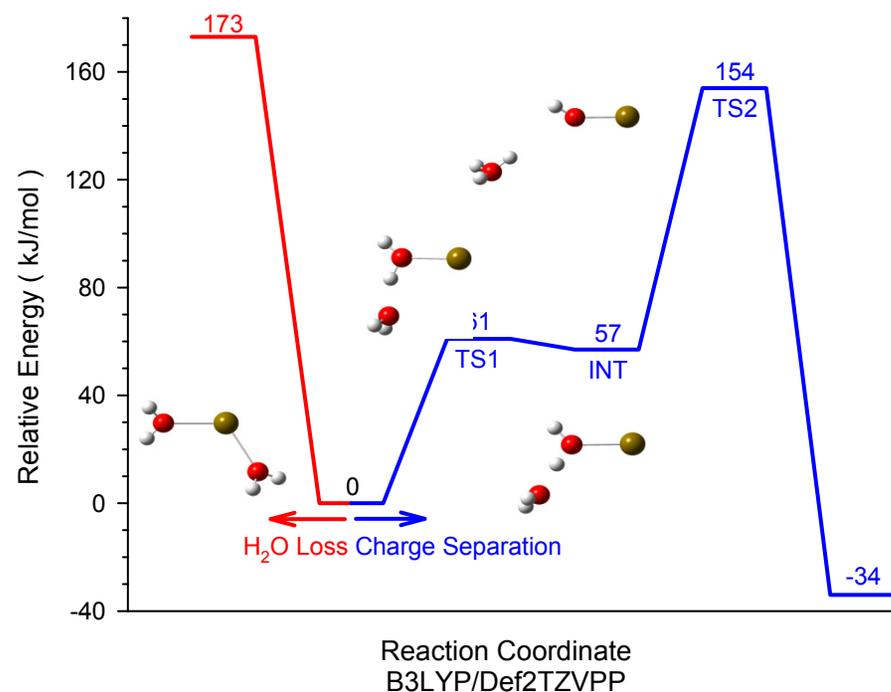
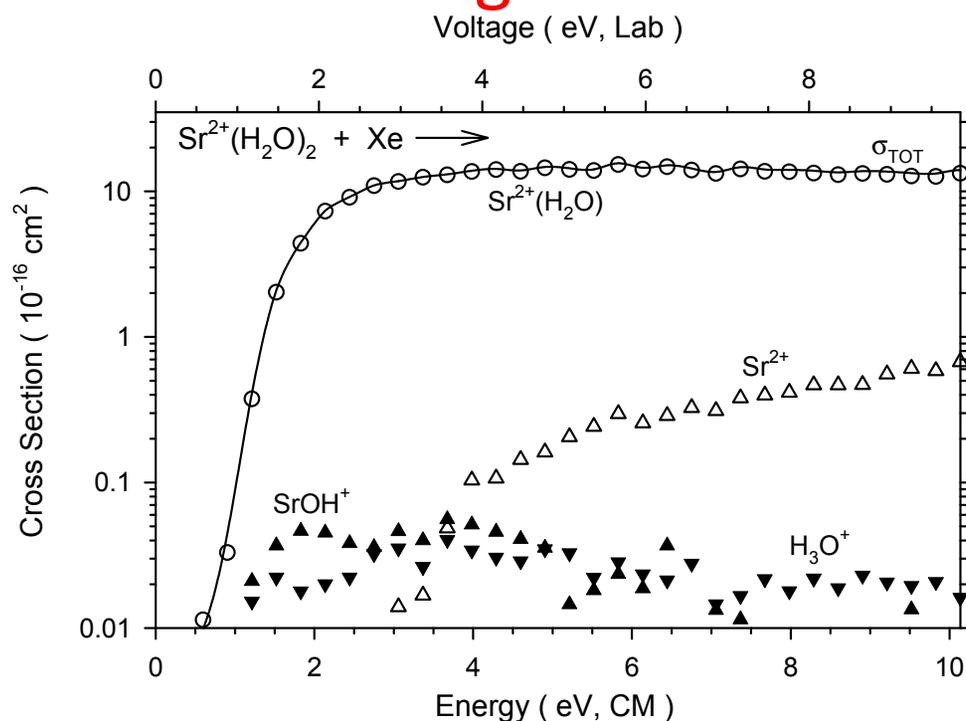


DRVG*IHPF⁺
SID in FTICR

Reaction delays
1 ms (red)
5 ms (blue)
50 ms (black)
1 s (green)

Dissociation – transition states

Rate of unimolecular dissociation is influenced by tight versus loose transition states

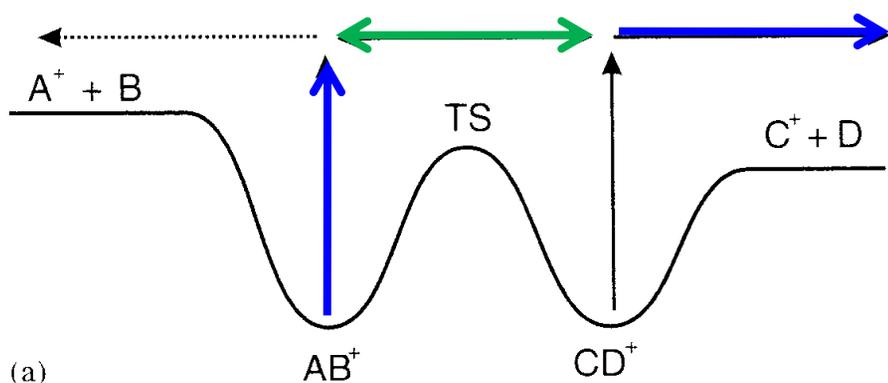


The **tight TS** for charge separation (favored energetically) greatly limits the number of states compared to the **loose TS** for water loss, which therefore dominates the products.

Carl, Chatterjee, Armentrout, *J. Chem. Phys.* **2010**, *132*, 044303

Dissociation vs. isomerization

High excitation energies are more likely to yield structurally specific information

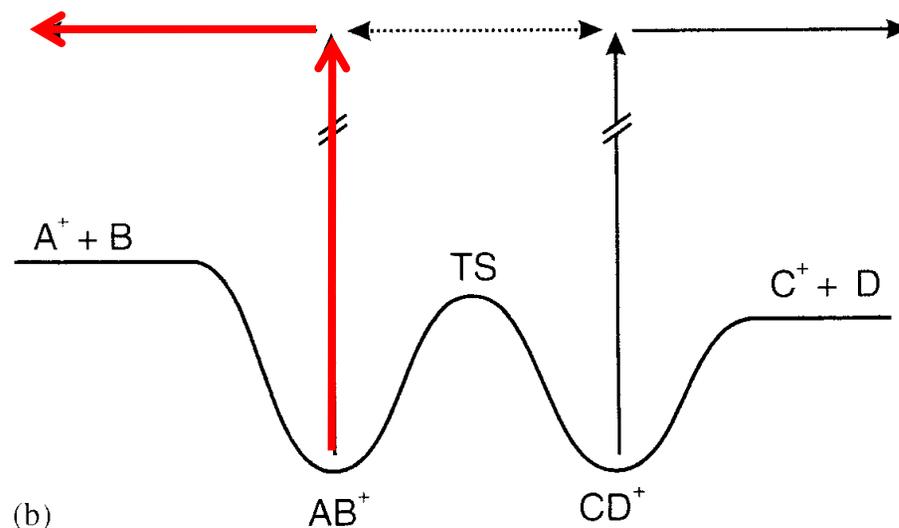


(a)

Low excitation energies.

Isomerization competes with dissociation.

Observed – lowest energy dissociation channel



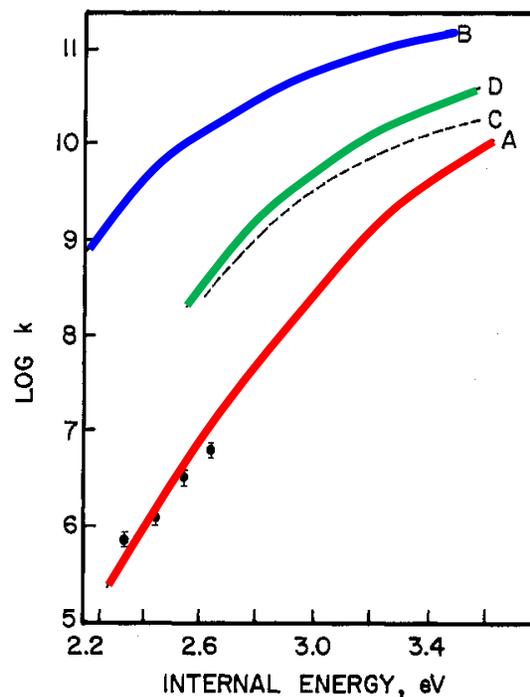
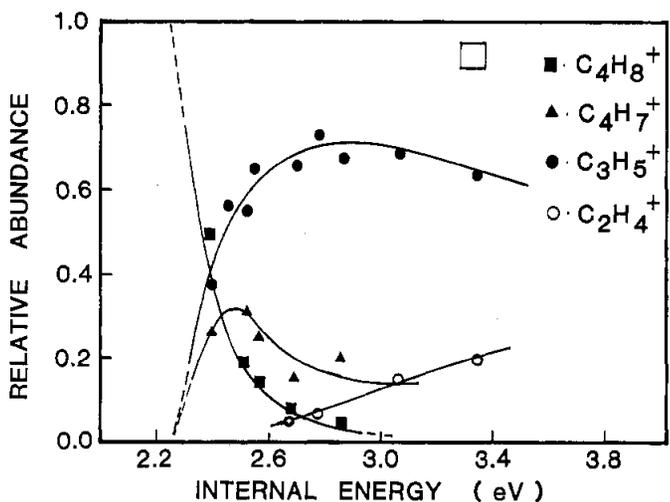
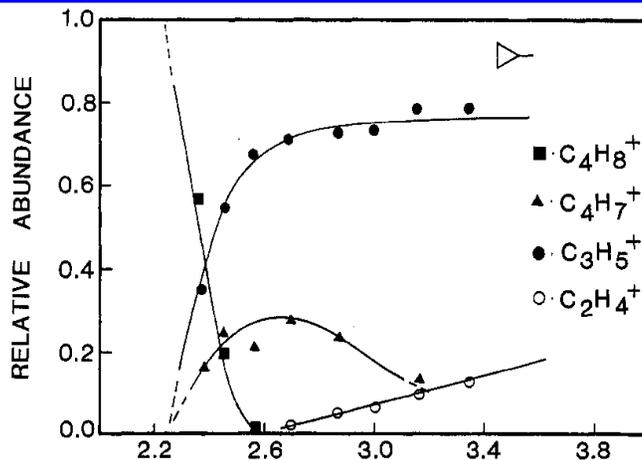
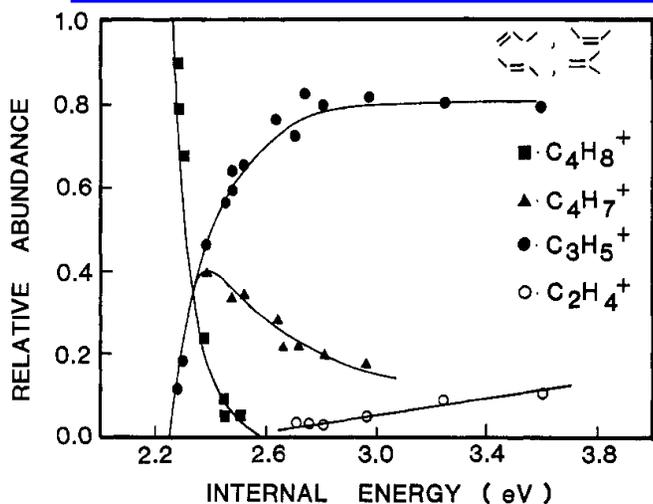
(b)

High excitation energies.

Isomerization is slow relative to dissociation.

Observed - entropically favored dissociation channel

Dissociation vs. isomerization



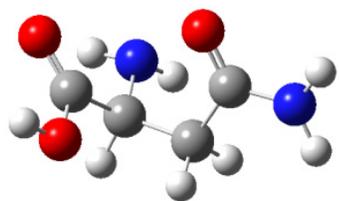
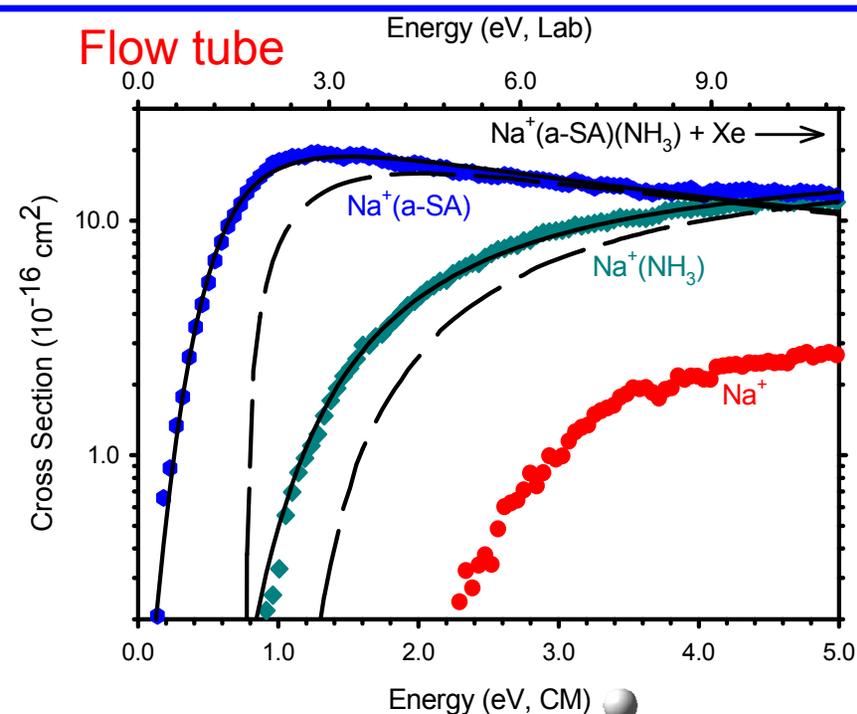
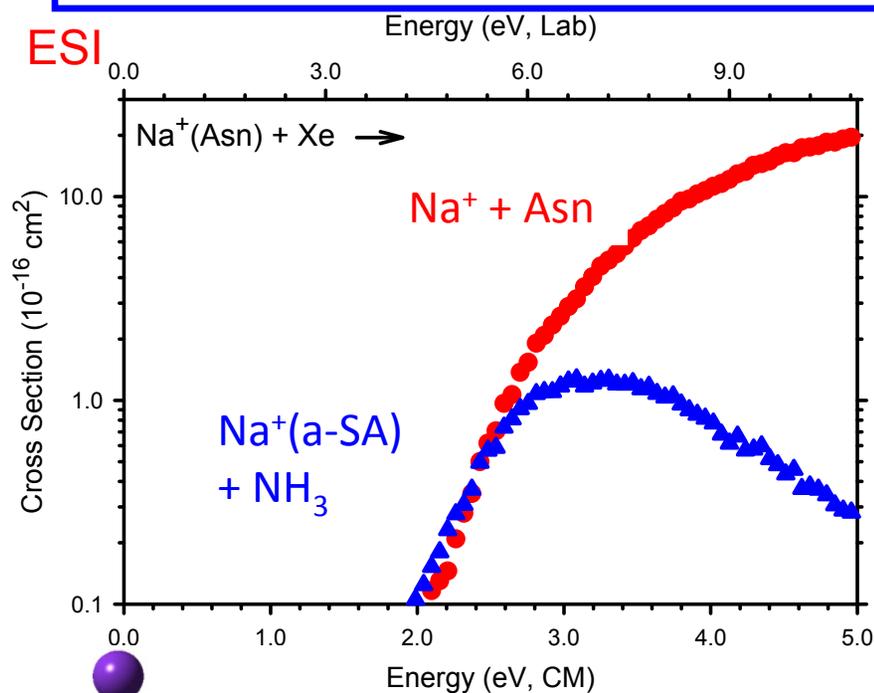
Six $C_4H_8^+$ ions dissociate with nearly identical patterns. Cyclo isomers shown slight differences at high energy.

Rate of
Isomerization



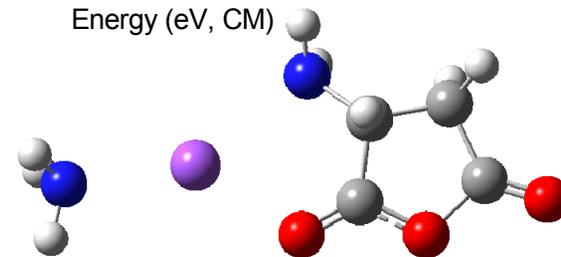
Hsieh, Gilman, Welss, Meisels,
J. Phys. Chem. **1981**, *85*, 2722.

Dissociation vs. isomerization



Na⁺(Asn)

This rearranges to this
at low energies



Na⁺(a-SA)(NH₃)

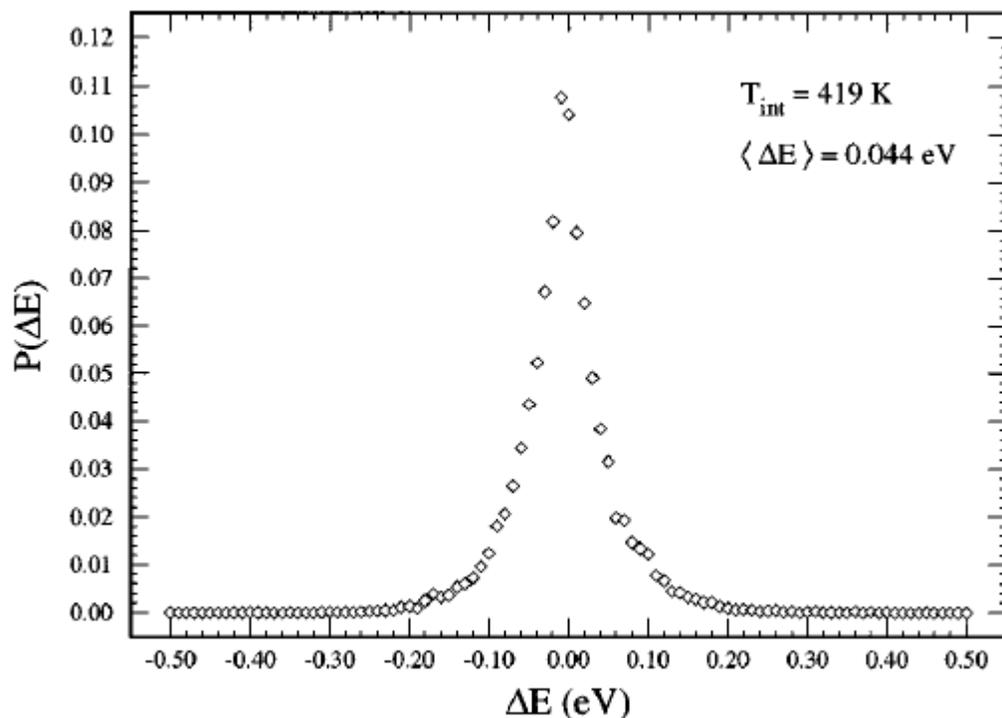
Under multiple collision conditions (low collision energies), both species would be expected to yield only Na⁺(a-SA) + NH₃.

Heaton, Armentrout, *J. Am. Chem. Soc.* **2008**, *130*, 10227

Dissociation vs. thermalization

As the number of collisions increases, the system can reach **equilibrium** such that further collisions are just as likely to remove

($-\Delta E$) energy from the ion as to add ($+\Delta E$) to it.



IR emission can also cool ions on timescales of ms – s.

Simulation of **ion-trap** excitation of *n*-butylbenzene cations in He.

Goeringer, McLuckey, *J. Chem. Phys.* 1996, 104, 2214.

Dissociation – multiple pathways

Probability of dissociation

$$P_D(E) = [1 - e^{-k_{tot}(E^*)\tau}]$$

Energy (Lab, eV)

$$k_{tot}(E^*) = \sum k_j(E^*)$$

= sum of rates
for all pathways

(j)

$$P_j = (k_j/k_{tot}) P_D$$

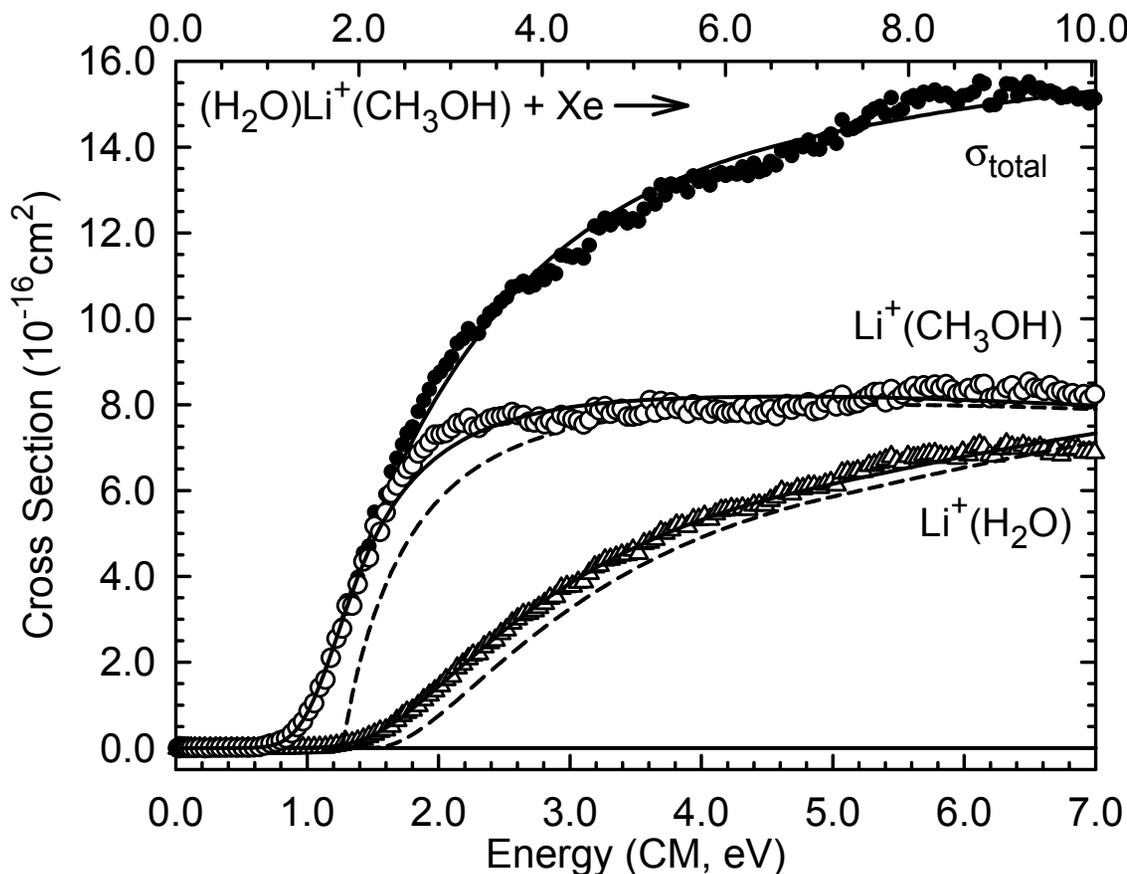
(H₂O)Li⁺(CH₃OH)

Both TSs are loose.

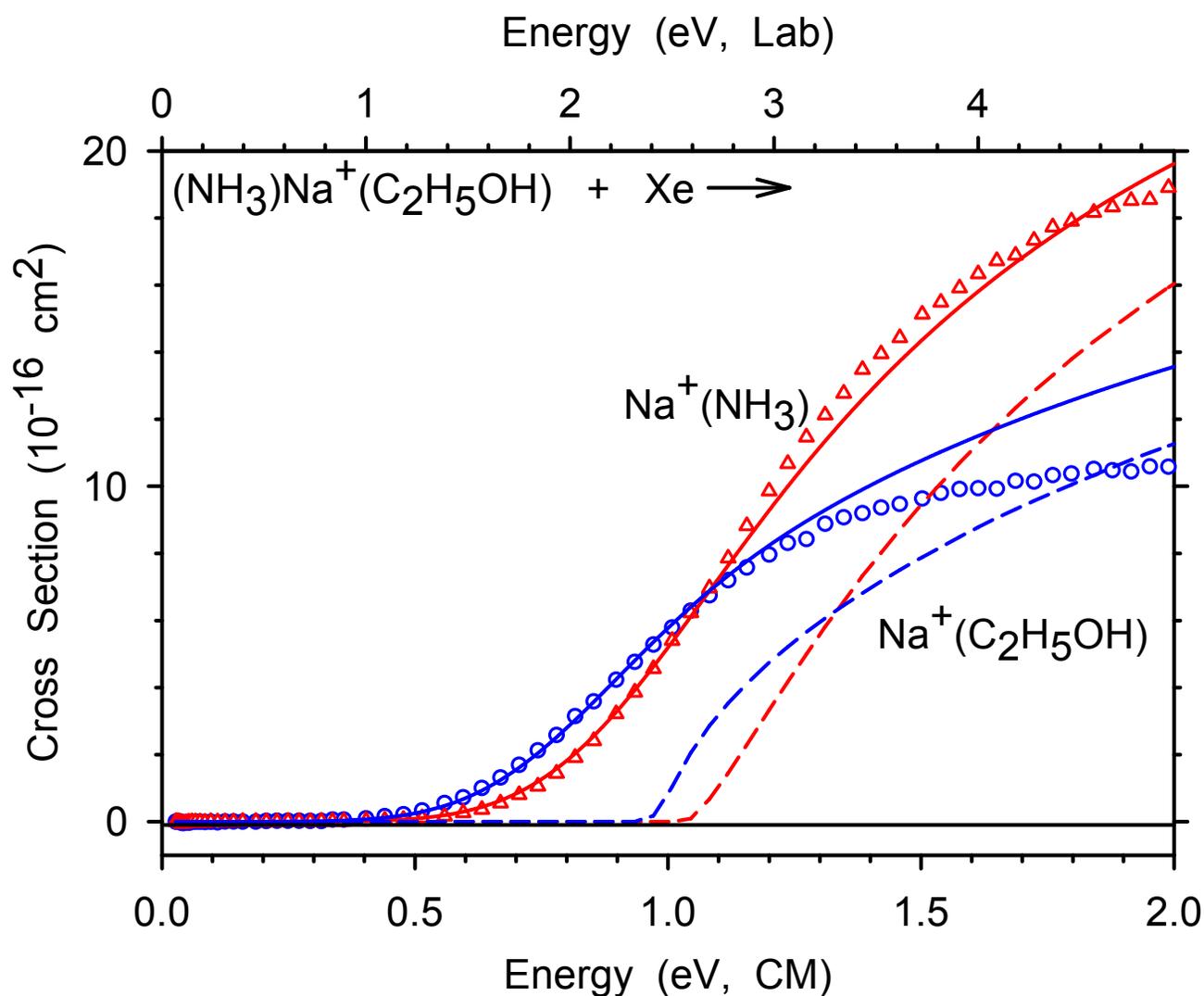
Competitive shift for

Li⁺(H₂O) + CH₃OH

Rodgers, Armentrout, *J. Phys. Chem. A* **1997**, *101*, 2614



Dissociation – entropic effects

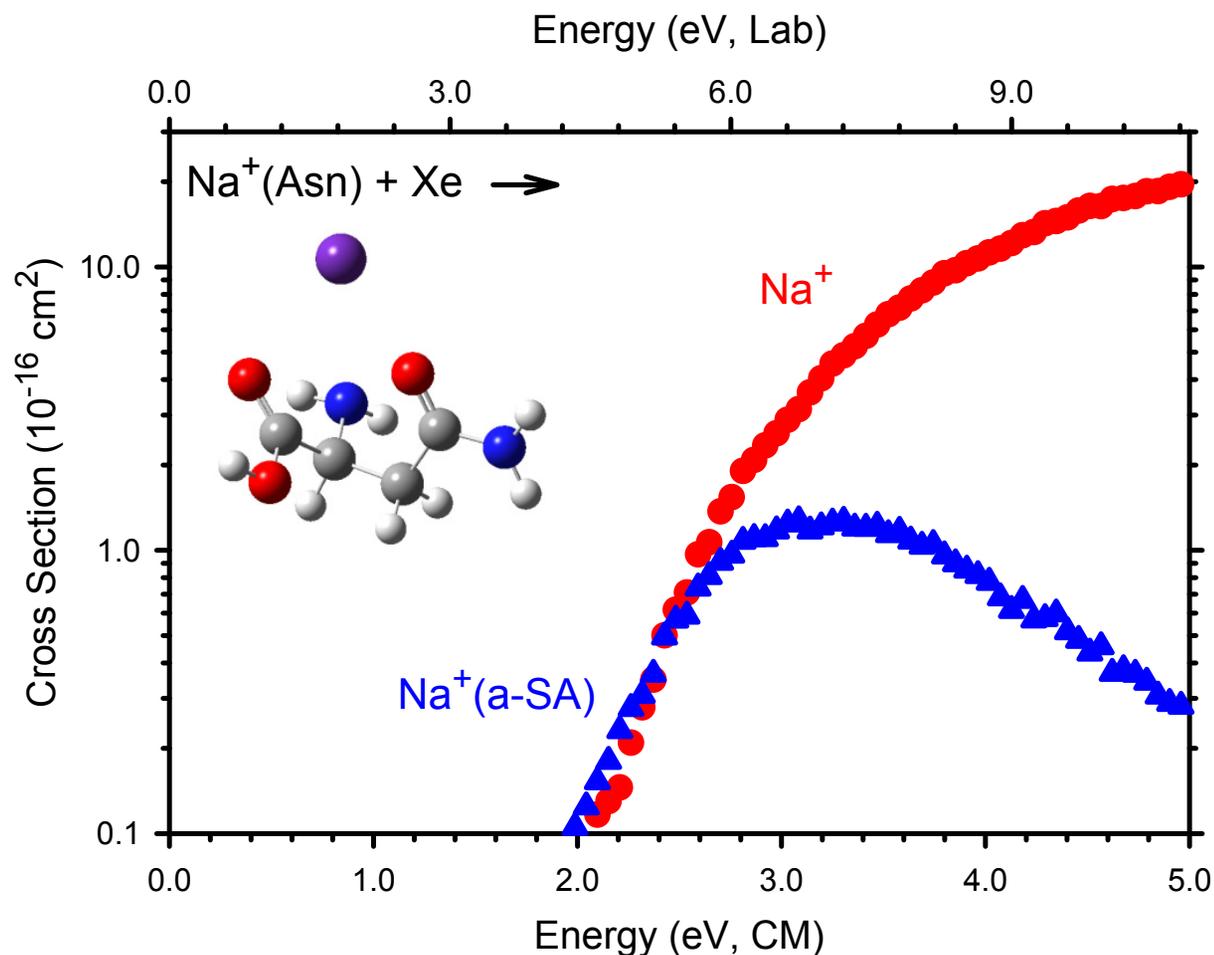


Both TSs are loose.

$\text{Na}^+(\text{C}_2\text{H}_5\text{OH})$ is favored at low energy because ethanol binds Na^+ more tightly.

$\text{Na}^+(\text{NH}_3)$ is favored at high energy because the 3-fold internal rotor of ethanol is available.

Dissociation – tight vs. loose TS



$\text{Na}^+(\text{a-SA}) + \text{NH}_3$ is favored at low energy but involves a **tight TS**.

$\text{Na}^+ + \text{Asn}$ is favored at high energy because it involves a **loose TS** (entropically favored).

Collision-induced dissociation:

How does it really work and
what it can (or can't) tell you

At this point, we begin to understand
how CID “really” works.

How does this translate to what it
can and can't tell you?

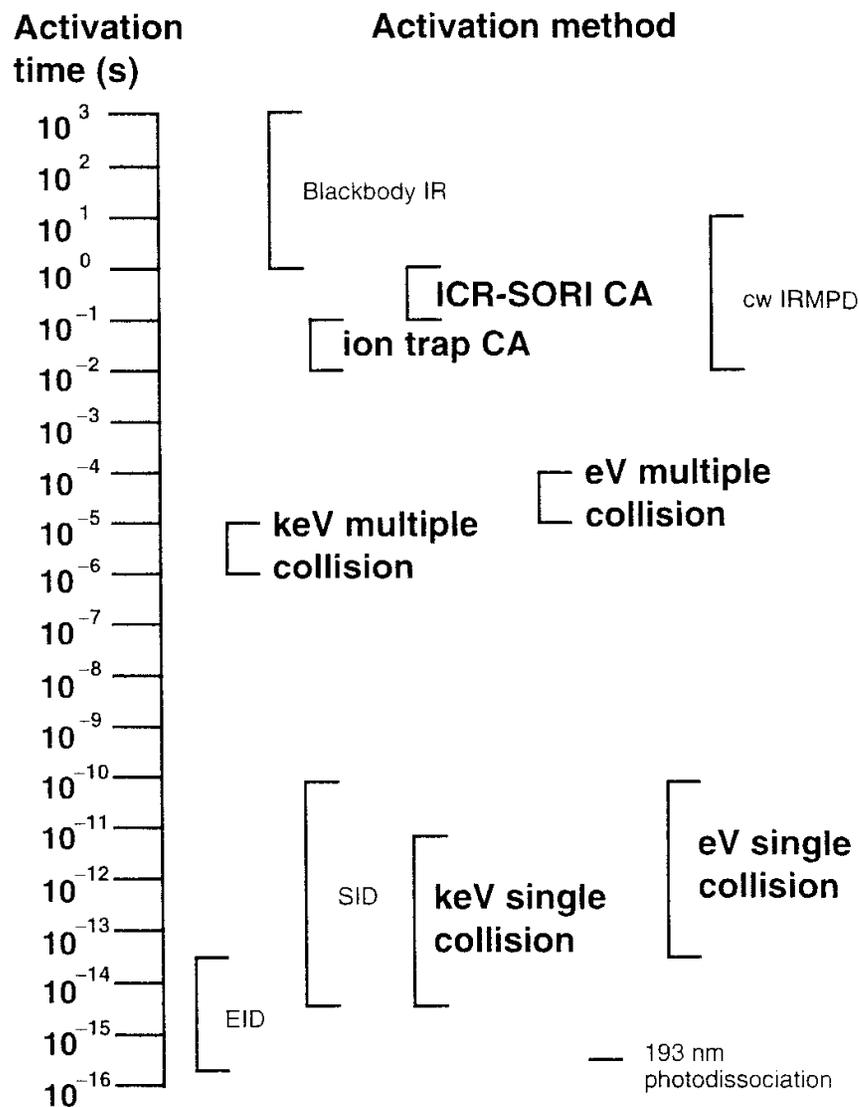
Figures of Merit for CID

Wells & McLuckey, In *The Encyclopedia of Mass Spectrometry*.
Volume 1: Theory and Ion Chemistry, Armentrout, P. B., Ed.;
Elsevier: Amsterdam, **2003**, 441.

Figures of merit for CID

- 1) the efficiency of the CID process, in terms of cross section or rate constant – (**collisions, time, & energy**)
- 2) the magnitude of **energy** that can be transferred during a collision
- 3) the distribution of the transferred **energy**
- 4) the variability of the **energy** distribution (**E dependence**)
- 5) the mechanism of **excitation** (electronic vs. rovibronic)
- 6) the **time**-frame in which activation occurs relative to the time for unimolecular dissociation or rearrangement and the time for possible deactivation processes
- 7) the **time**-scale of the instrument used (the kinetic window within which dissociation reactions must occur in order to be observed)

Timescale – activation & dissociation



Low energies

Slow dissociation

+ isomerization

Long time window

0.1 – 10 s

Higher energies

Fast dissociation

Short time window

1 μ s – 1 ms

Collision-induced dissociation

What can it tell you?

- **Structural information.**

An understanding of energy and time requirements of the system and instrument are needed. Competition with isomerization can complicate the interpretation.

- **Energetic information.**

Absolute bond energies. Relative energetics for competing pathways. Accurate, quantitative analysis requires molecular information and modeling.

- **Kinetic information.**

Relative time scales for competing pathways.

Collision-induced dissociation

Resources

- *The Encyclopedia of Mass Spectrometry. Volume 1: Theory and Ion Chemistry*, Armentrout, P. B., Ed.; Elsevier: Amsterdam, **2003**, 441. articles by McLuckey, Armentrout, Scheier, Schröder, Morton, Cooks
- Armentrout, Ervin, Rodgers, *J. Phys. Chem. A*, **2008**, *112*, 10071
- Holbrook, Pilling, Robertson, *Unimolecular Reactions*, 2nd Ed., Wiley
- Levine, Bernstein, *Molecular Reaction Dynamics*, or *Molecular Reaction Dynamics & Chemical Reactivity*, Oxford