

# Electron-Initiated Photochemistry

Karl K. Irikura

*Chemical Sciences Division, National Institute of Standards and Technology,  
Gaithersburg, Maryland, USA*

[www.nist.gov](http://www.nist.gov)

# Overview

- Importance of photochemistry
- “Photochemistry” generalized
- Examples
  - Gamma radiolysis
  - Proton beam therapy
  - Electron impact
  - Gas-phase catalysis

# Photochemistry is important

- Cosmochemistry ( $t = 380,000$  yr)
- Supports life on Earth (photosynthesis)
- Basis of vision (rhodopsin)
- Spectroscopy and analytical chemistry
- Photography and photolithography
- Photodegradation (weathering; skin cancer)
- Cleaner source of energy for civilization (photovoltaics; plants)
- Fluorescence, phosphorescence, chemiluminescence
- Synthetic chemistry

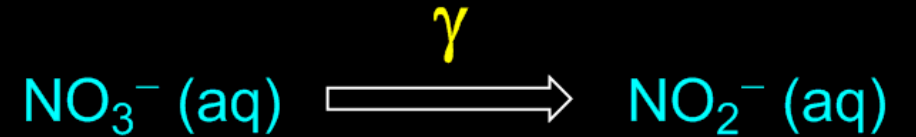
# “Photochemistry” generalized

- **Goal: inject lots of energy non-thermally** (without incineration)
  - Non-adiabatic dynamics
- “Photochemistry” usually means visible/UV light
  - Sunlight is abundant and free
  - Enough energy for electronic excitation
- Shorter wavelengths of light
  - Gamma radiolysis
- Charged particles (alpha, beta “rays”)
  - Proton-beam cancer therapy
  - Electron-ionization mass spectrometry
- Lightning bolts, plasmas (both particles and radiation)

# Gamma radiolysis

- High-energy photon
  - Everything is a “chromophore”
- “Pulse radiolysis” uses high-energy electrons (several MeV)
- Mostly ionize solvent, not solute
  - Oxidative DNA damage
  - Radiation damage of materials
- Example: reduction of aqueous nitrate (nuclear reactors)
  - Compare with municipal wastewater treatment by photocatalytic reduction

Tugaoen, H. O.; Garcia-Segura, S.; Hristovski, K.; Westerhoff, P. Challenges in photocatalytic reduction of nitrate as a water treatment technology. *Sci. Total Environ.* **2017**, 599, 1524.

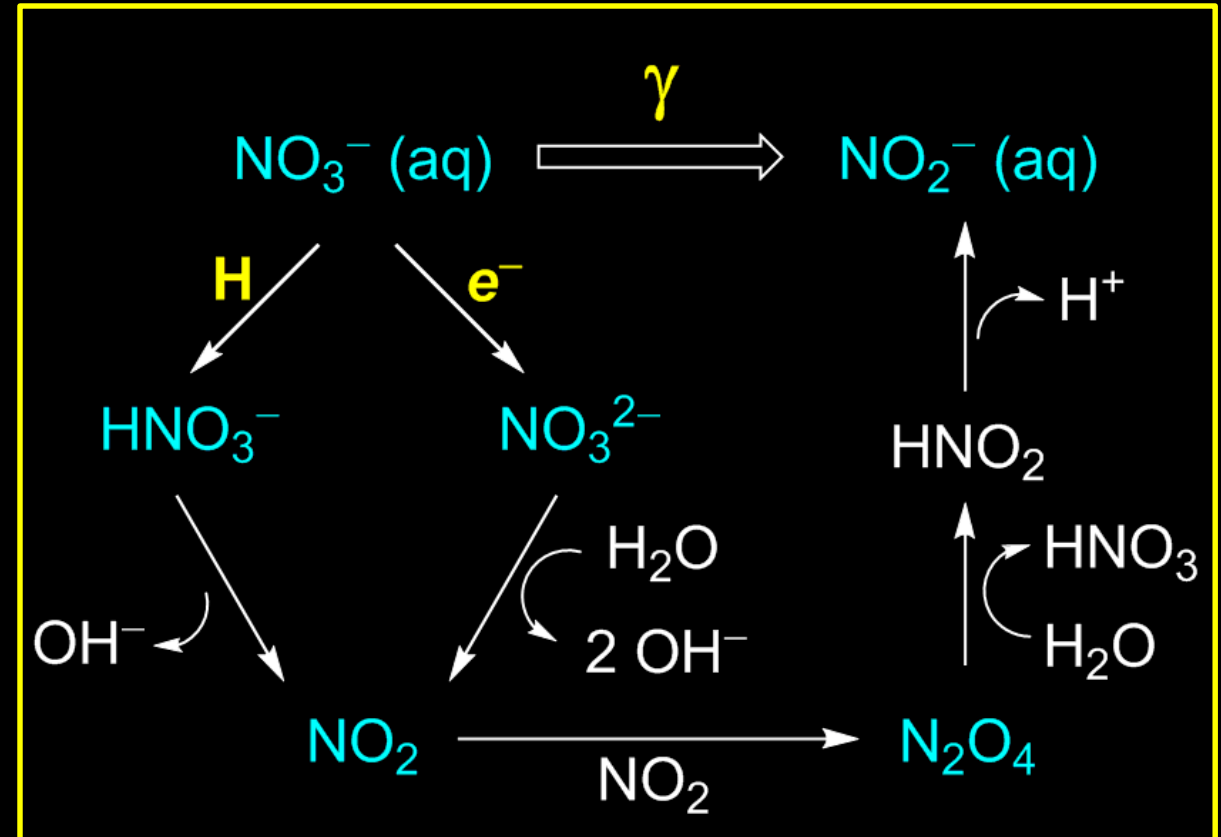


Horne, G. P.; Donoclift, T. A.; Sims, H. E.; Orr, R. M.; Pimblott, S. M. Multi-Scale Modeling of the Gamma Radiolysis of Nitrate Solutions. *J. Phys. Chem. B* **2016**, 120, 11781.

# Gamma radiolysis

- High-energy photon
  - Everything is a “chromophore”
- “Pulse radiolysis” uses high-energy electrons (several MeV)
- Mostly ionize solvent, not solute
  - Oxidative DNA damage
  - Radiation damage of materials
- Example: reduction of aqueous nitrate (nuclear reactors)
  - Compare with municipal wastewater treatment by photocatalytic reduction

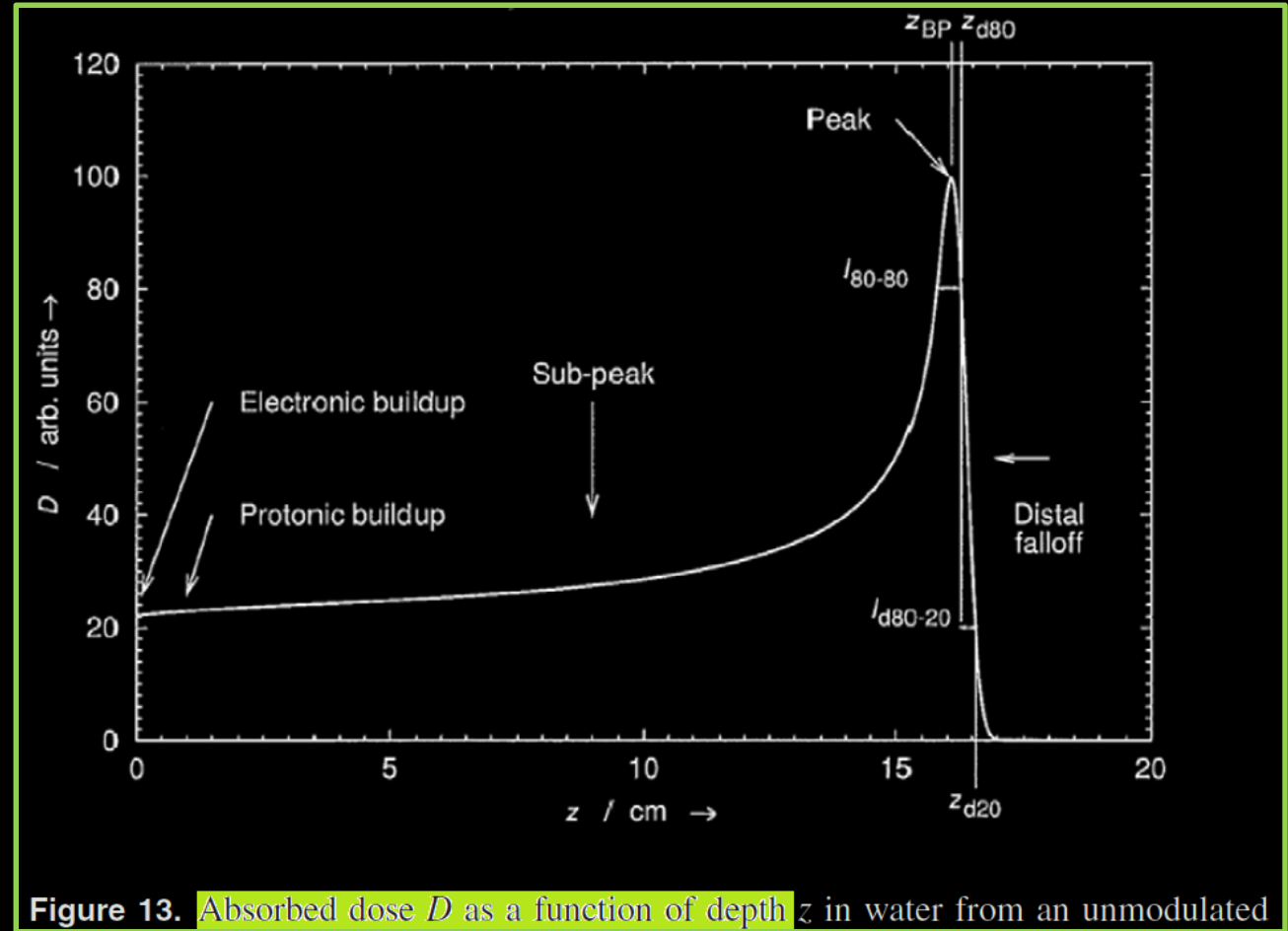
Tugaoen, H. O.; Garcia-Segura, S.; Hristovski, K.; Westerhoff, P. Challenges in photocatalytic reduction of nitrate as a water treatment technology. *Sci. Total Environ.* **2017**, 599, 1524.



Horne, G. P.; Donoclift, T. A.; Sims, H. E.; Orr, R. M.; Pimblott, S. M. Multi-Scale Modeling of the Gamma Radiolysis of Nitrate Solutions. *J. Phys. Chem. B* **2016**, 120, 11781.

# Proton beam therapy

- For treating cancer
- Dosage is better targeted than radiation therapy
  - No exit dose
  - Less damage to healthy tissue
- High-energy  $H^+$  slows down
  - By scattering electrons
- Slow  $H^+$  has big cross section
  - Radiolysis chemistry (DNA damage)



# Proton ionization cross sections

- Cross section ( $\sigma$ ) is the extinction coefficient per particle (units of area)

$$\ln(I/I_0) = -\sigma \cdot (\text{density}) \cdot (\text{path length})$$

- The slower the  $H^+$  gets, the more it slows down

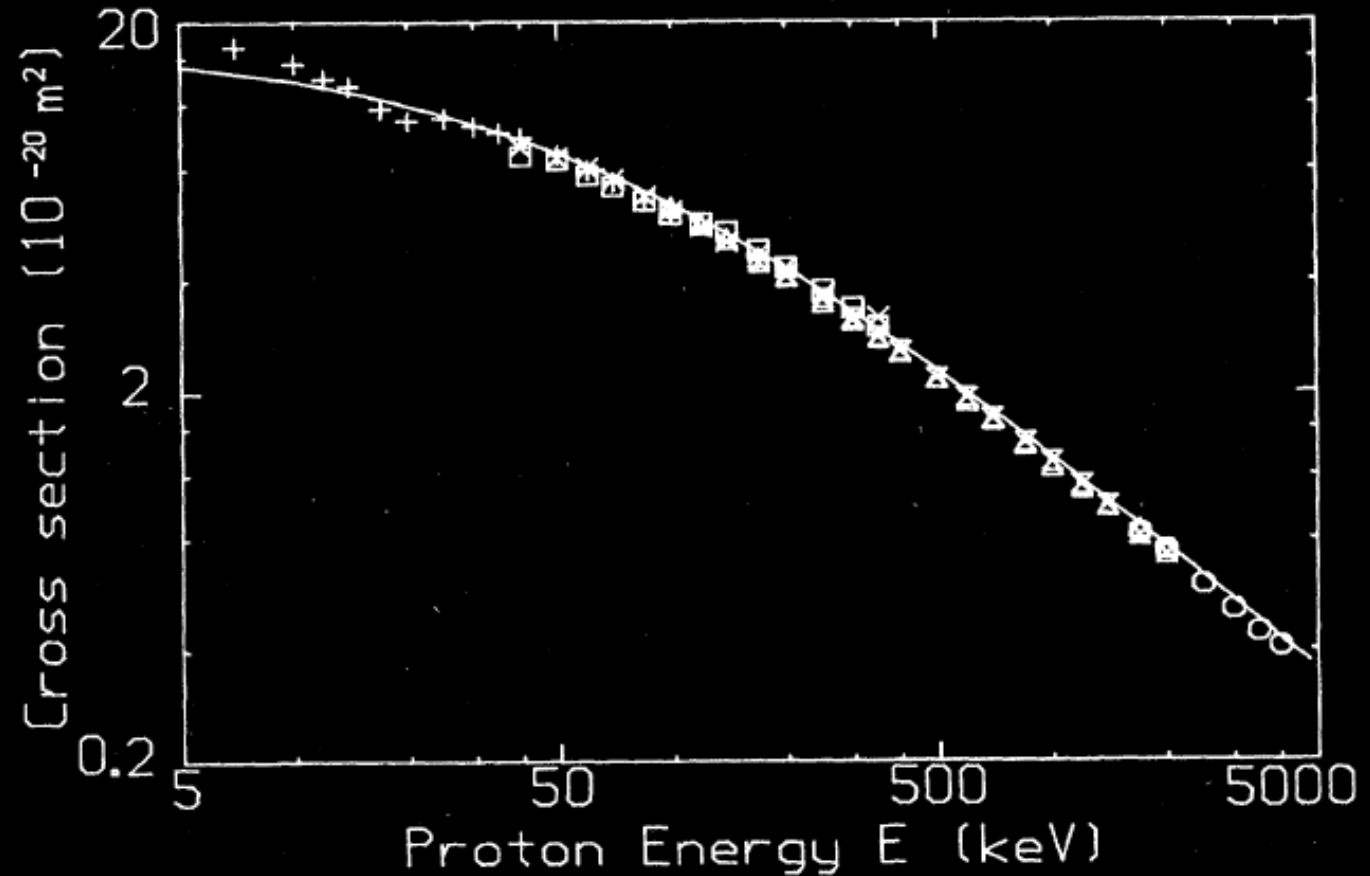
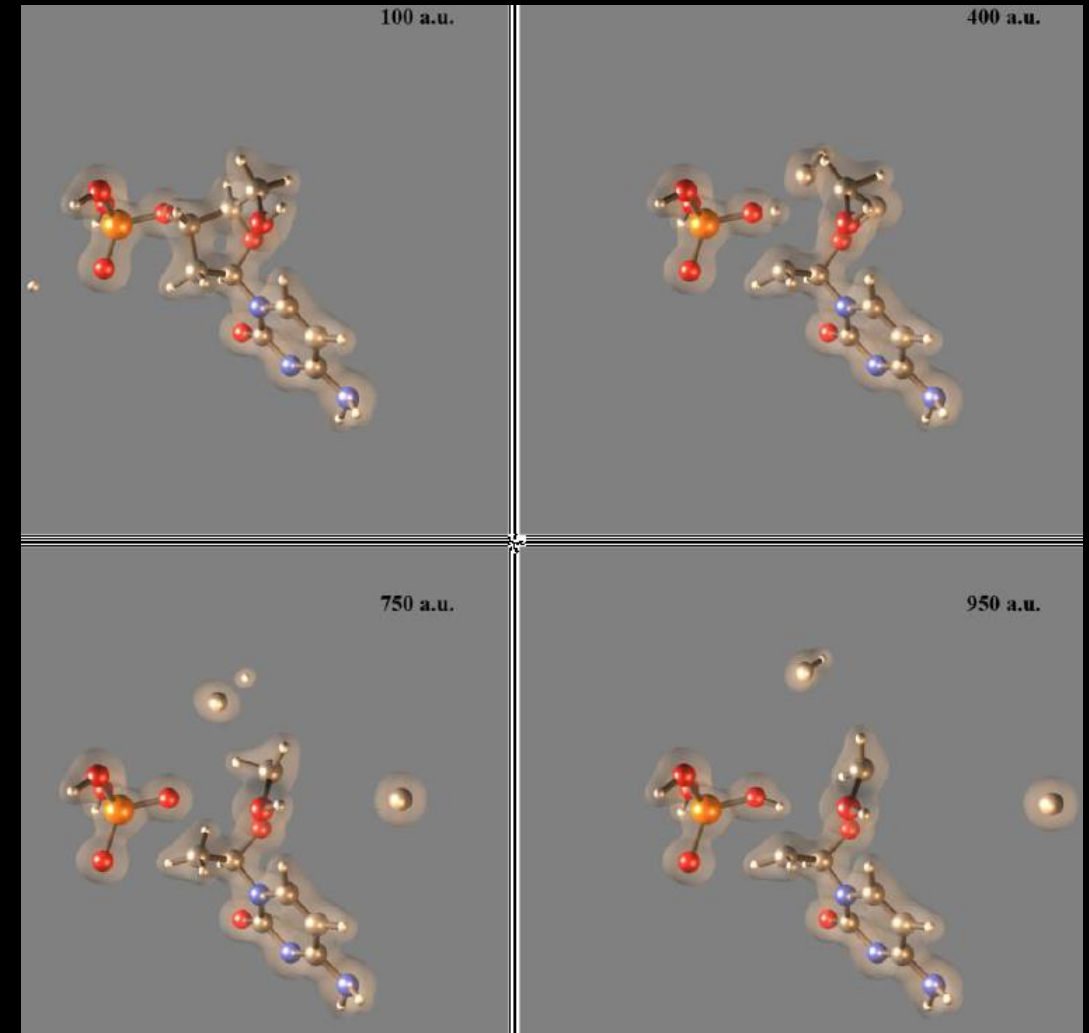


FIG. 3. Cross sections  $\sigma_+$  after adjustment of data. Solid line is the fit using Eqs. (1) and (4). Symbols as in Fig. 1.



# Proton beams: non-adiabatic dynamics

- High-energy (10s of keV) radiolysis of water
  - Free radicals (H, OH)
  - Secondary ions ( $\text{H}^+$ ,  $\text{OH}^-$ ,  $e^-$ )
  - Excited states
  - Reactive molecules ( $\text{HOOH}$ )
- Some direct  $\text{H}^+$  collisions with DNA
  - Snapshots at right
    - Time shown  $\approx 23$  fs

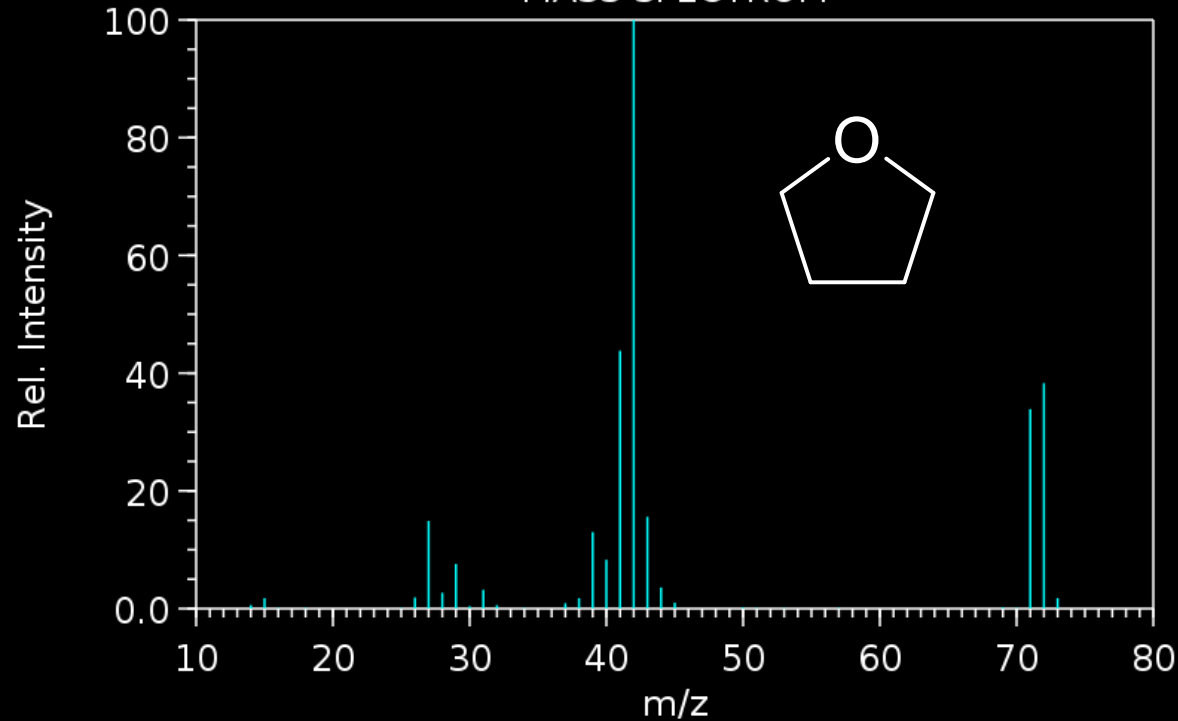


# Electron beams on molecules

- Electronic excitation ( $M^*$ )
  - Like photo-excitation, but **can change spin by  $\pm 1$**
- **Ionization ( $M^+$ )**
  - Produces many different fragment ions
  - Basis of electron-ionization mass spectrometry (EIMS)
- Attachment ( $M^-$ )
  - Low-energy electrons
- Processes that are chemically boring but relevant in plasmas
  - Vibrational/rotational excitation
  - Elastic scattering

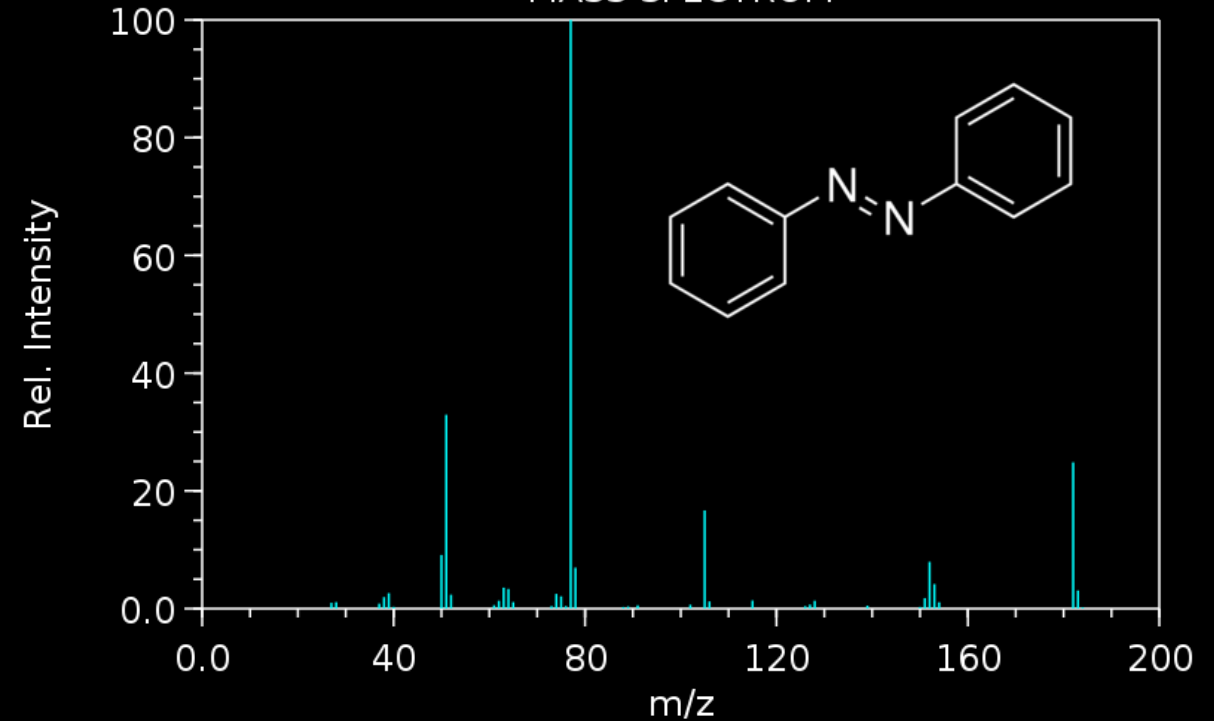
# EIMS examples

Tetrahydrofuran  
MASS SPECTRUM



NIST Chemistry WebBook (<https://webbook.nist.gov/chemistry>)

Azobenzene  
MASS SPECTRUM



NIST Chemistry WebBook (<https://webbook.nist.gov/chemistry>)

**No reliable, predictive theory!**

# First-Principles modeling of EIMS?

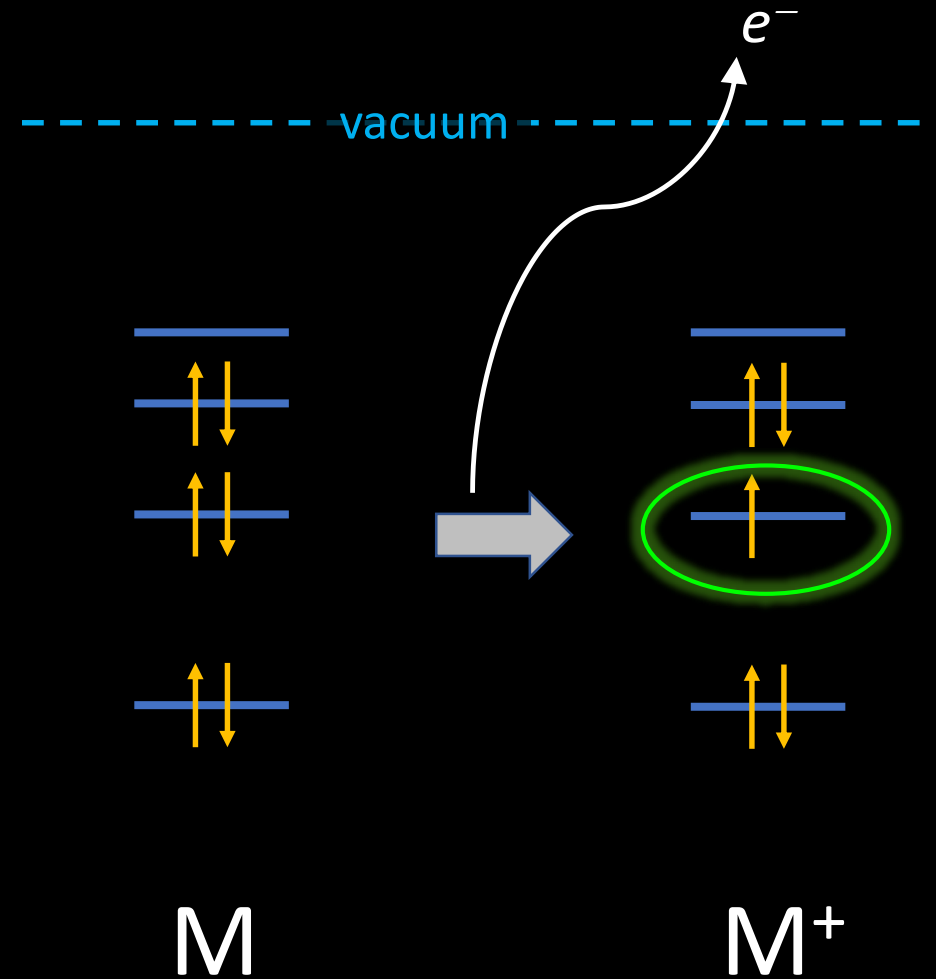
- Distribution of internal energies
  - Can be computed ab initio 😊
- Chemical fate (branching fractions of reaction products)
  - Adiabatic (on ground state potential-energy surface) 😐
  - Diabatic (on excited-state surface) 😞
  - Non-adiabatic (with electronic transitions) 😱
- Smaller effects that partly cancel 😞
  - Thermal energy of neutral target gas
  - Instrumental detection bias

# First-Principles modeling of EIMS?

- Distribution of internal energies
  - Can be computed ab initio 😊
- Chemical fate (branching fractions of reaction products)
  - Adiabatic (on ground state potential-energy surface) 😐
  - Diabatic (on excited-state surface) 😞
  - Non-adiabatic (with electronic transitions) 😱
- Smaller effects that partly cancel 😞
  - Thermal energy of neutral target gas
  - Instrumental detection bias

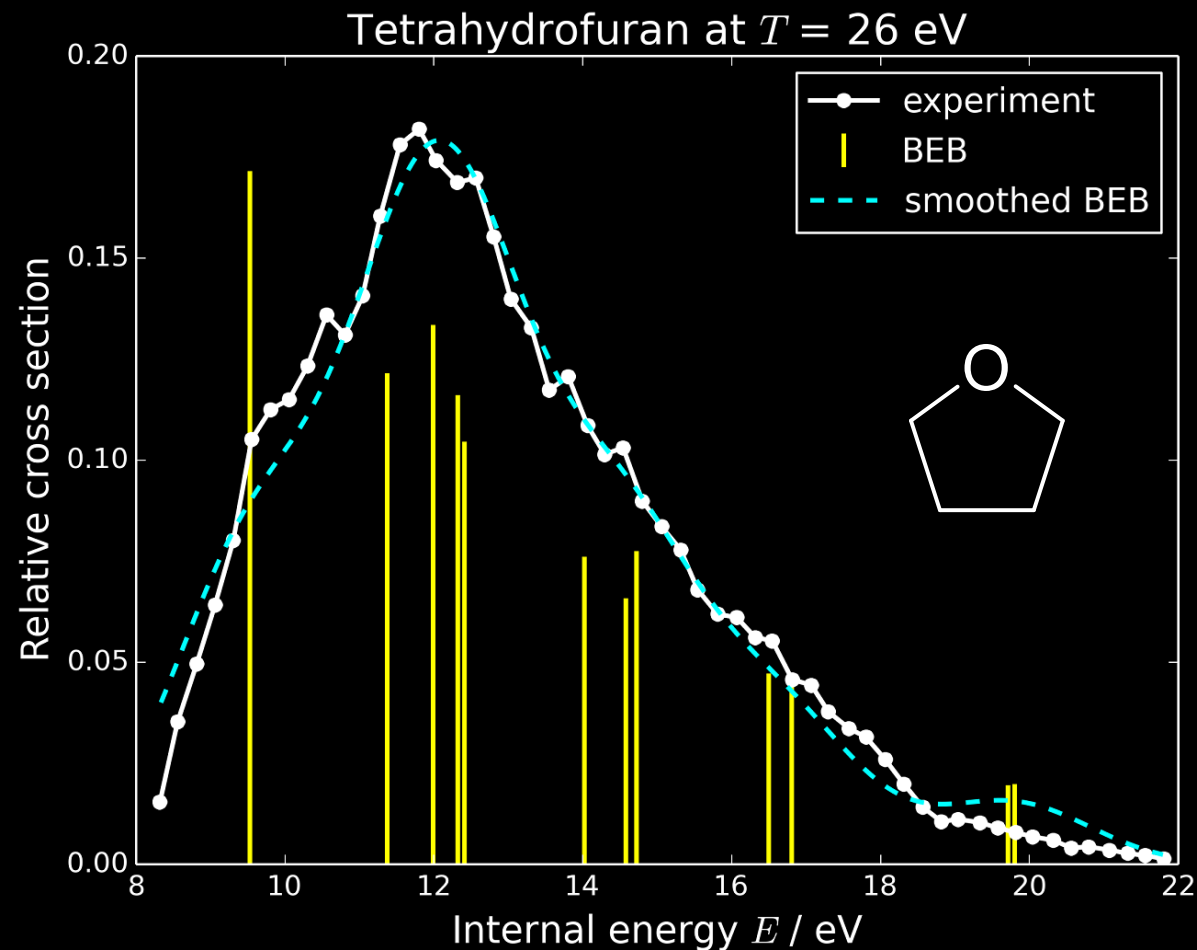
# Ions are created by removing electrons

- Just delete 1 electron
  - Creates a hole-state cation
  - Often an excited state
- **Excited-state chemistry**
  - Energy may be high
    - High density of electronic states
  - Probably non-adiabatic



# Internal energy distribution

- From Kim's BEB (Binary-encounter Bethe) theory
  - Yields **ionization cross section for each molecular orbital (MO)**
  - <https://github.com/kkinist/BEB>
- Agrees with all experimental measurements!
  - But there are only two



Irikura, K. K. Ab Initio Computation of Energy Deposition During Electron Ionization of Molecules. *J. Phys. Chem. A* **2017**, *121*, 7751.

Ren, X.; Pflüger, T.; Weyland, M.; Baek, W. Y.; Rabus, H.; Ullrich, J.; Dorn, A. An ( $e$ ,  $2e$ -ion) study of low-energy electron-impact ionization and fragmentation of tetrahydrofuran with high mass and energy resolutions. *J. Chem. Phys.* **2014**, *141*, 134314.

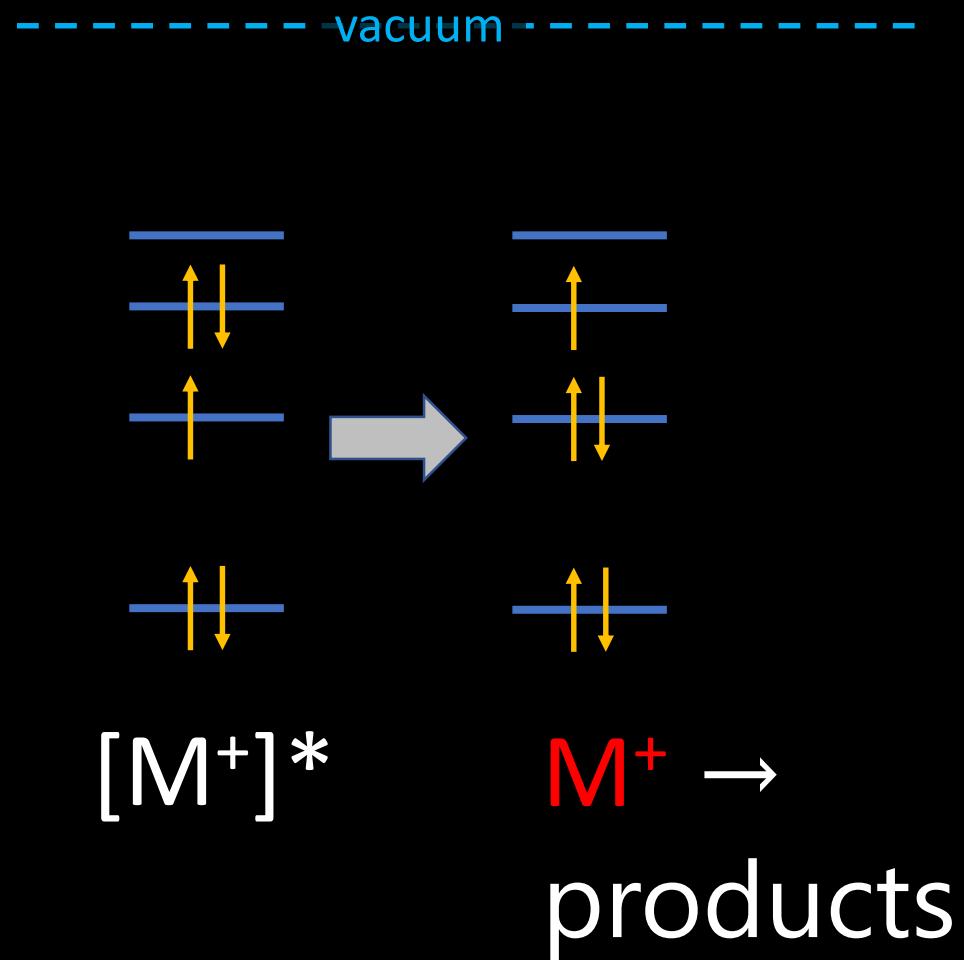
# First-Principles modeling of EIMS?

- Distribution of internal energies
  - Can be computed ab initio 😊
- Chemical fate (branching fractions of reaction products)
  - **Adiabatic** (on ground state potential-energy surface) 😐
  - Diabatic (on excited-state surface) 😞
  - Non-adiabatic (with electronic transitions) 😱
- Smaller effects that partly cancel 😞
  - Thermal energy of neutral target gas
  - Instrumental detection bias



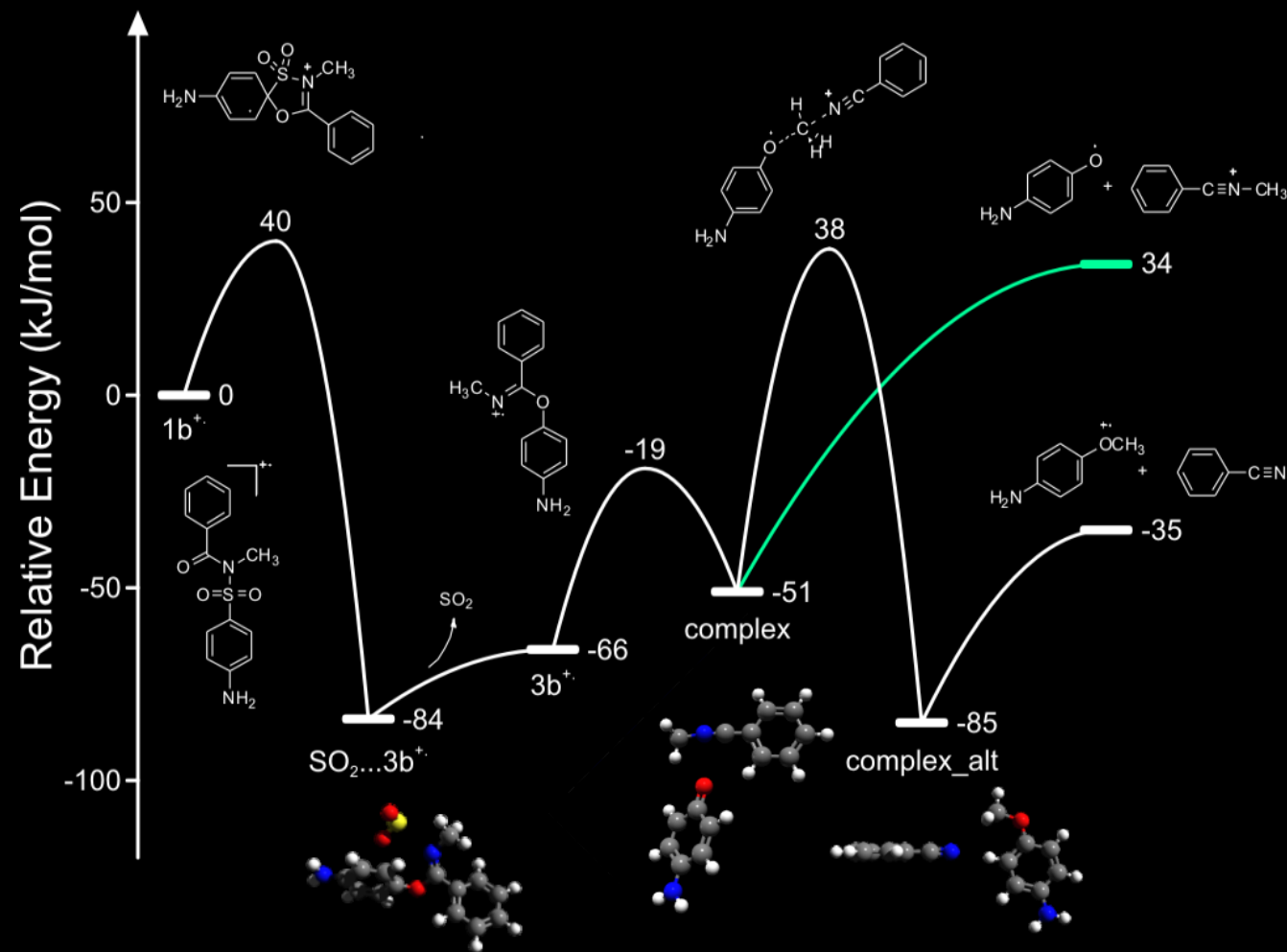
# Some reactions are in ground state

- Some ions are born in the ground state
  - Low internal energy
- Many ions are born in hole states
  - Relaxation to ground state transfers energy to vibrations
  - Hot ions can dissociate
- Molecular dynamics *and/or* RRKM theory for kinetics



# Predicting ground-state reactivity

- Useful across chemistry!
- Feasible but laborious
- Automation is a current research topic
  - Some software is becoming available publicly
    - <http://forge.cesga.es/wiki/g/tsscds>
- Often we can predict accurately



Irikura, K. K.; Todua, N. G. Facile Smiles-type rearrangement in radical cations of N-acyl arylsulfonamides and analogs. *Rapid Commun. Mass Spectrom.* **2014**, 28, 829.

# First-Principles modeling of EIMS?

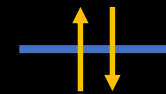
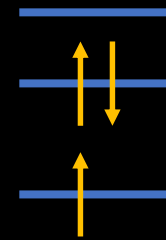
- Distribution of internal energies
  - Can be computed ab initio 😊
- Chemical fate (branching fractions of reaction products)
  - Adiabatic (on ground state potential-energy surface) 😐
  - **Diabatic** (on excited-state surface) 😞
  - Non-adiabatic (with electronic transitions) 😱
- Smaller effects that partly cancel 😞
  - Thermal energy of neutral target gas
  - Instrumental detection bias

# Predicting excited-state reactivity

- Dissociative (broken-bond) states are easy
  - Follow the forces to products
- But many excited states are bound
  - Must explore the excited-state surface
  - How to stay on the “same” excited state across intersections?
- Sometimes we can predict accurately



-----vacuum-----

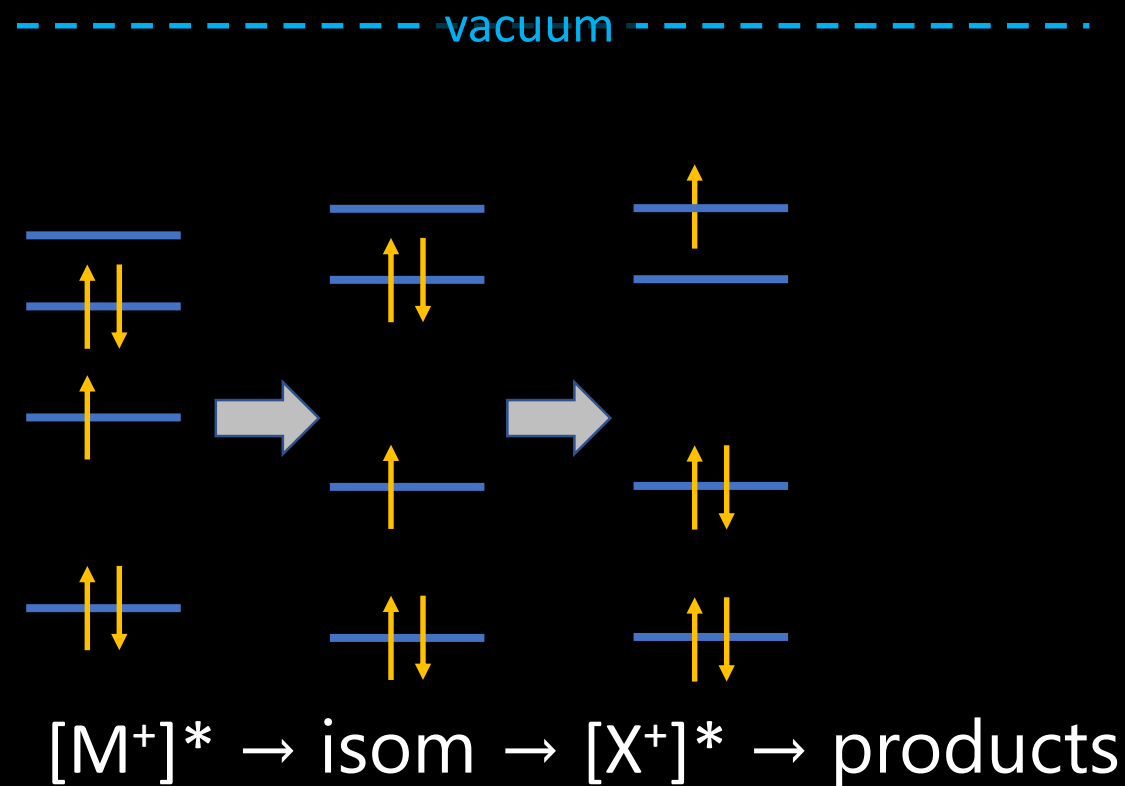


# First-Principles modeling of EIMS?

- Distribution of internal energies
  - Can be computed ab initio 😊
- Chemical fate (branching fractions of reaction products)
  - Adiabatic (on ground state potential-energy surface) 😐
  - Diabatic (on excited-state surface) 😞
  - **Non-adiabatic** (with electronic transitions) 😱
- Smaller effects that partly cancel 😞
  - Thermal energy of neutral target gas
  - Instrumental detection bias

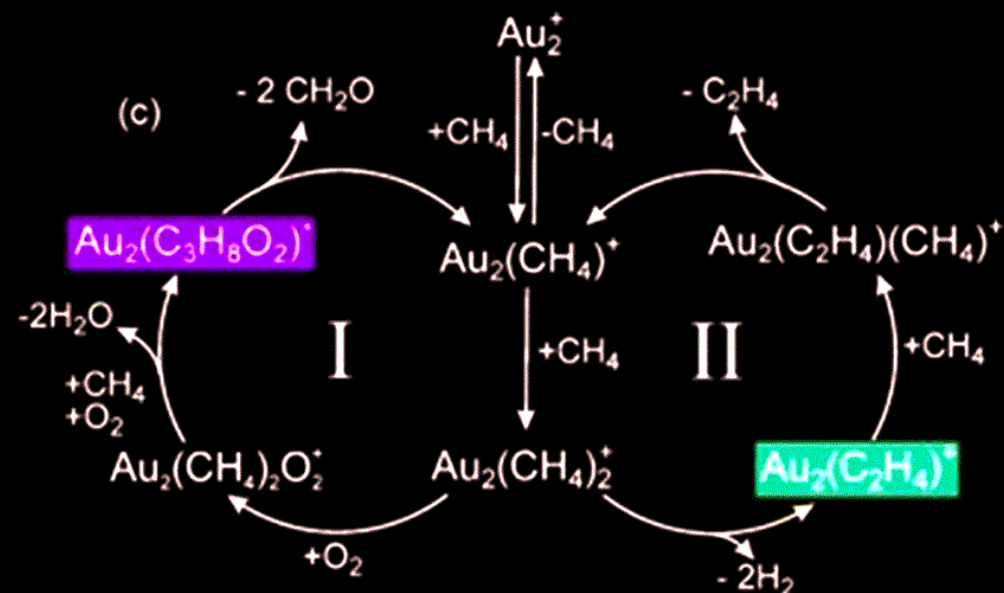
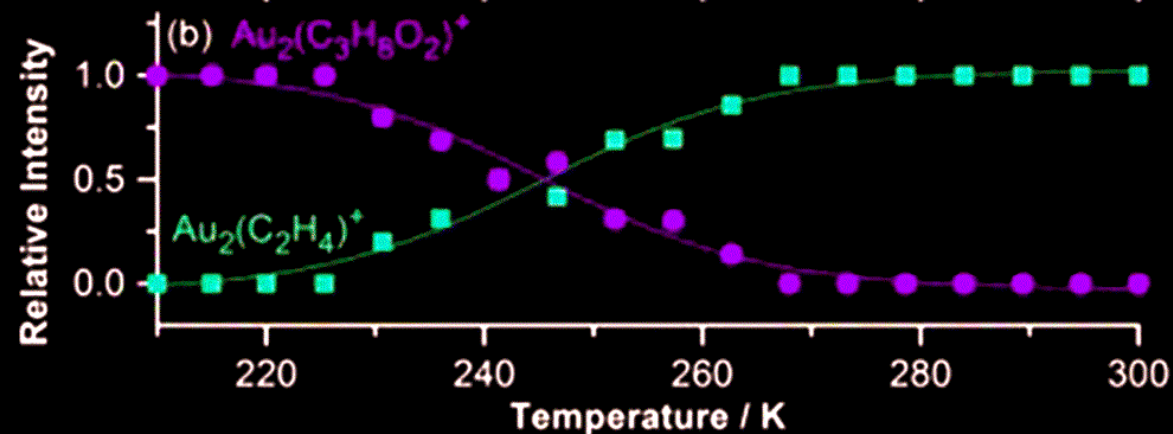
# Predicting non-adiabatic reactivity

- Electron dynamics coupled to nuclear dynamics
  - A challenging research topic
- Many theoretical strategies
  - None validated?
- Can anyone predict accurately??



# Catalysis by gas-phase ions

- CH<sub>4</sub> conversion by Au<sub>2</sub><sup>+</sup> (shown)
  - In presence of O<sub>2</sub>, selectivity is controlled by temperature
  - C<sub>2</sub>H<sub>4</sub> for  $T > 260$  K
  - CH<sub>2</sub>O for  $T < 230$  K
- Olefin dehydroaromatization (not shown)
  - Catalyzed by Fe<sub>4</sub><sup>+</sup> and by some atomic ions

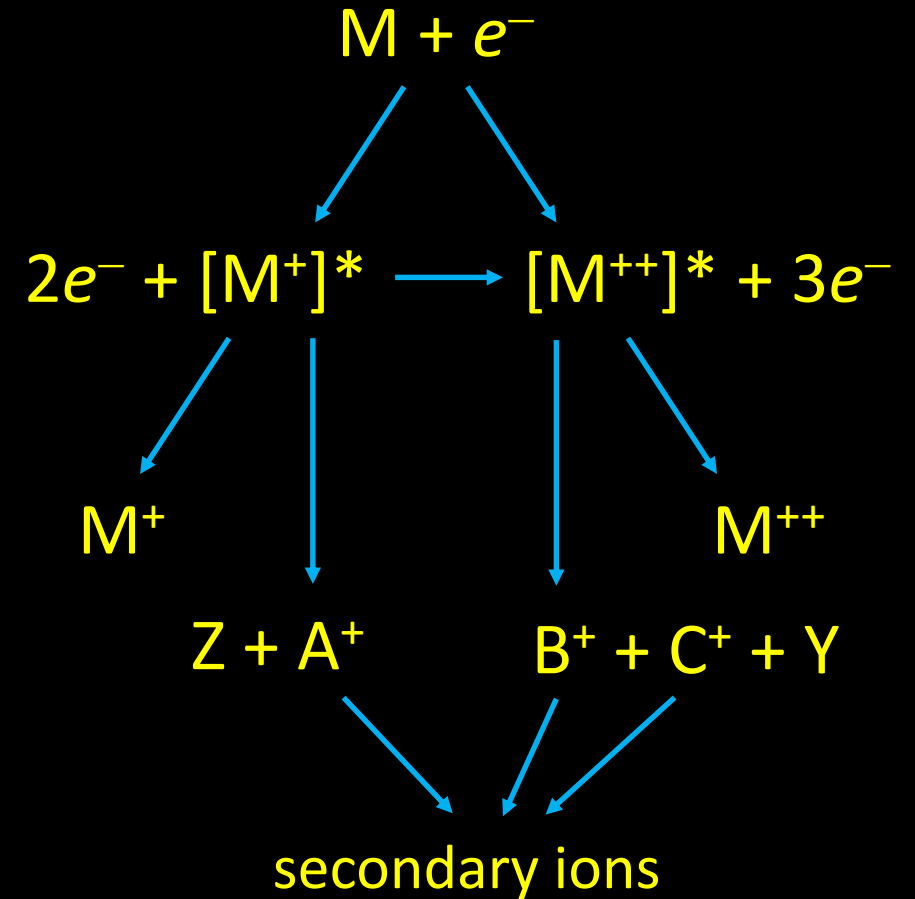


Questions or  
comments?



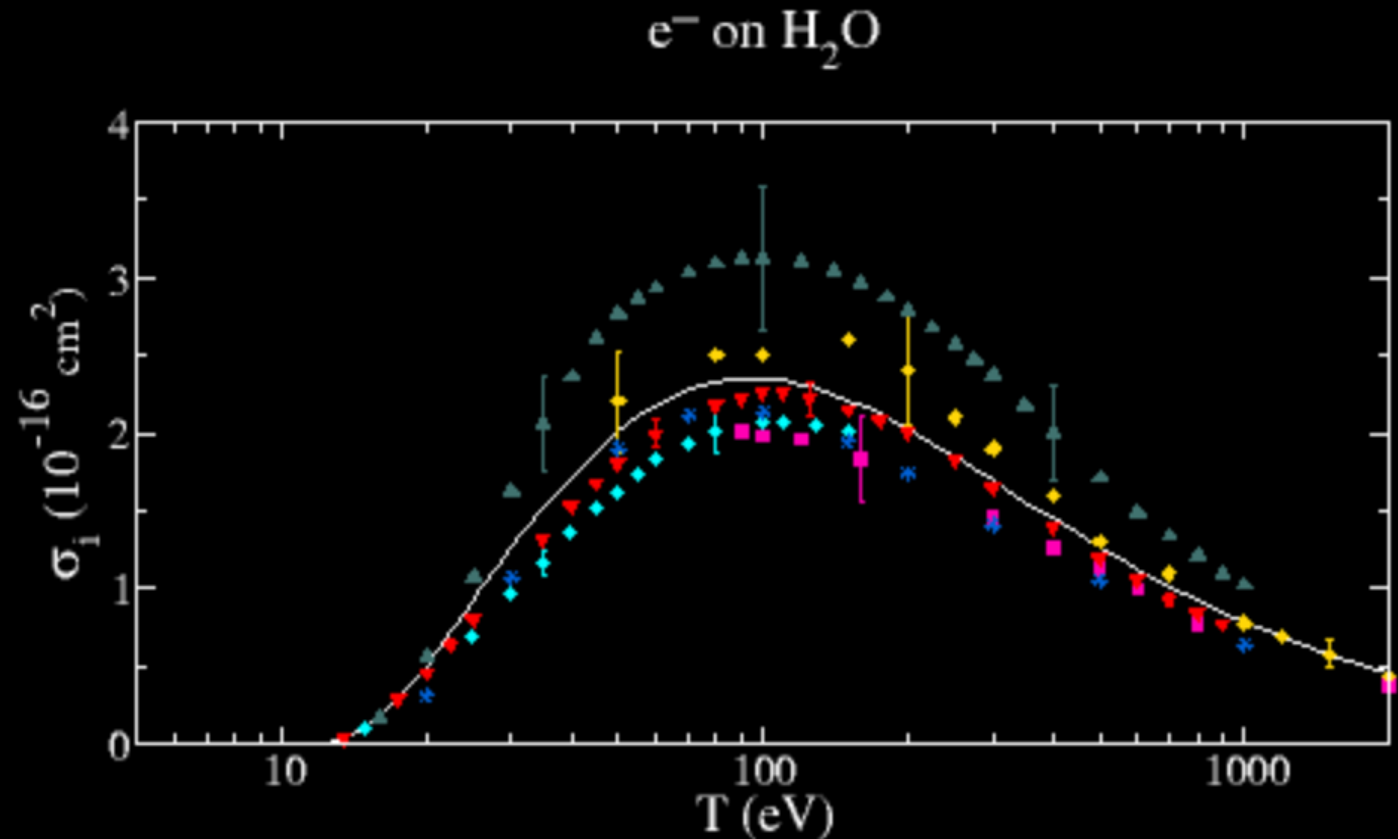
# Electron ionization mass spectrometry (EIMS)

- Molecular ions ( $M^+$ ) are created with a wide range of internal energies
- Many break into fragments
  - Characteristic spectrum of fragment masses
  - Important for analytical chemistry
- 70 eV is typical in analytical work
  - Strong signal
  - Stable fragmentation pattern



# Total ionization cross sections (TICS) from BEB

- Sum over all MO's = molecular cross section
- TICS typically within 15% of experiments
- BEB is the most popular theory for computing TICS
  - <https://github.com/kkinist/BEB>



<http://physics.nist.gov/ionxsec>

Kim, Y.-K.; Rudd, M. E. Binary-Encounter-Dipole Model for Electron-Impact Ionization. *Phys. Rev. A* **1994**, *50*, 3954.

# Binary-encounter Bethe (BEB) theory

- Yields **total ionization cross section** for one molecular orbital (MO)
  - Sum over occupied MOs
- Input quantities are obtained from routine ab initio calculations
  - $T$  = kinetic energy of incident electron
  - $U$  = MO kinetic energy
  - $B$  = MO binding energy

$$\sigma_{\text{MO}}(T; n) = \frac{S}{t + (u + 1)/n} \left[ \frac{\ln t}{2} \left( 1 - \frac{1}{t^2} \right) + 1 - \frac{1}{t} - \frac{\ln t}{t + 1} \right]$$

- $t = T/B$ ;  $u = U/B$ ;  $n$  is a parameter usually = 1

# Proton ionization cross sections

- Cross section ( $\sigma$ ) is the extinction coefficient per particle (units: area)

$$\ln(I/I_0) = -\sigma \cdot (\text{density}) \cdot (\text{path length})$$

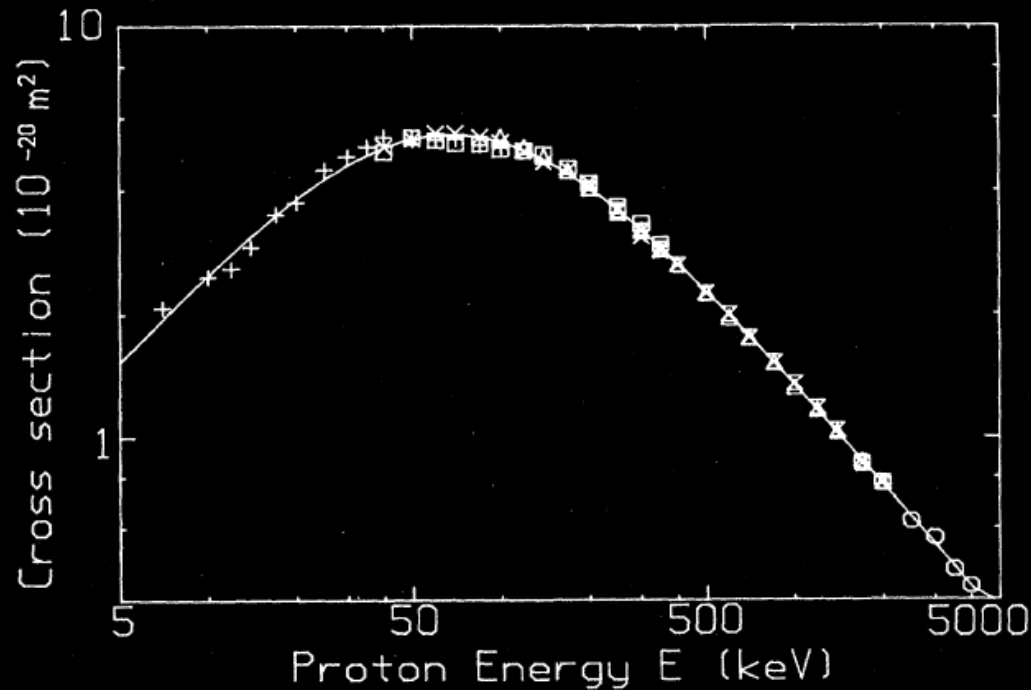


FIG. 2. Cross sections  $\sigma_-$  after adjustment of data (see text). Solid line is the fit using Eq. (1). Symbols as in Fig. 1.

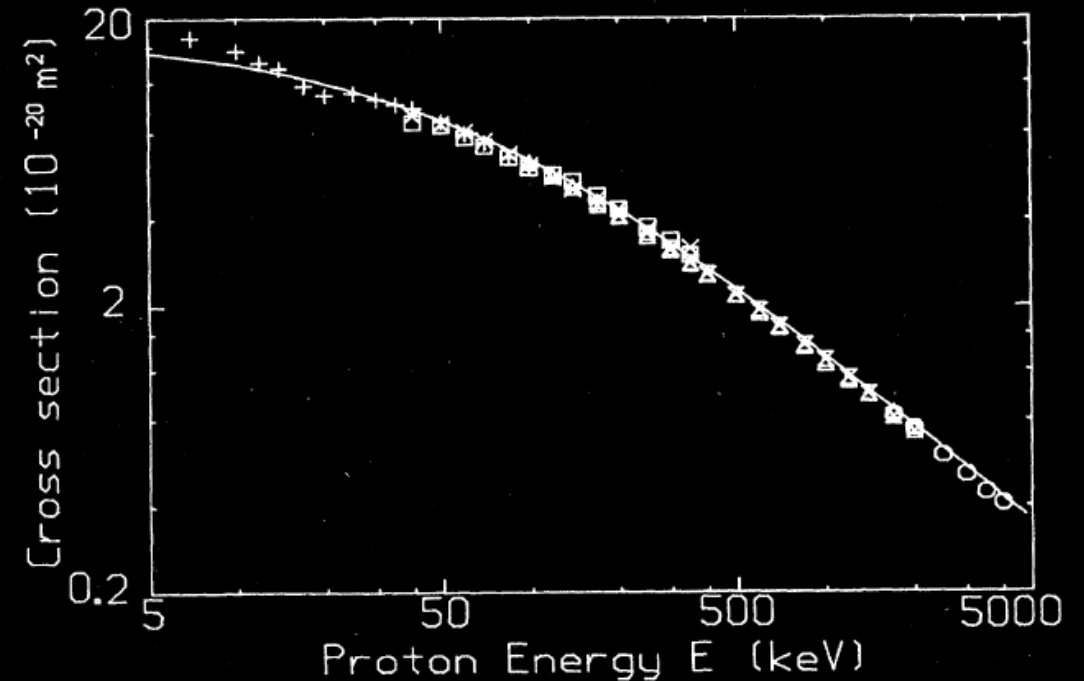


FIG. 3. Cross sections  $\sigma_+$  after adjustment of data. Solid line is the fit using Eqs. (1) and (4). Symbols as in Fig. 1.