

Electron-Initiated Photochemistry

Karl K. Irikura

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

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

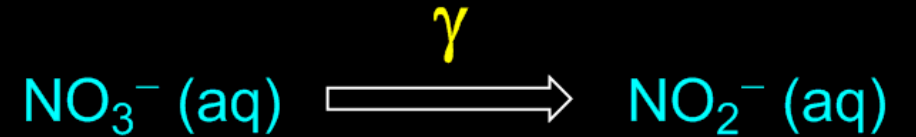
“Photochemistry” generalized

- **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.

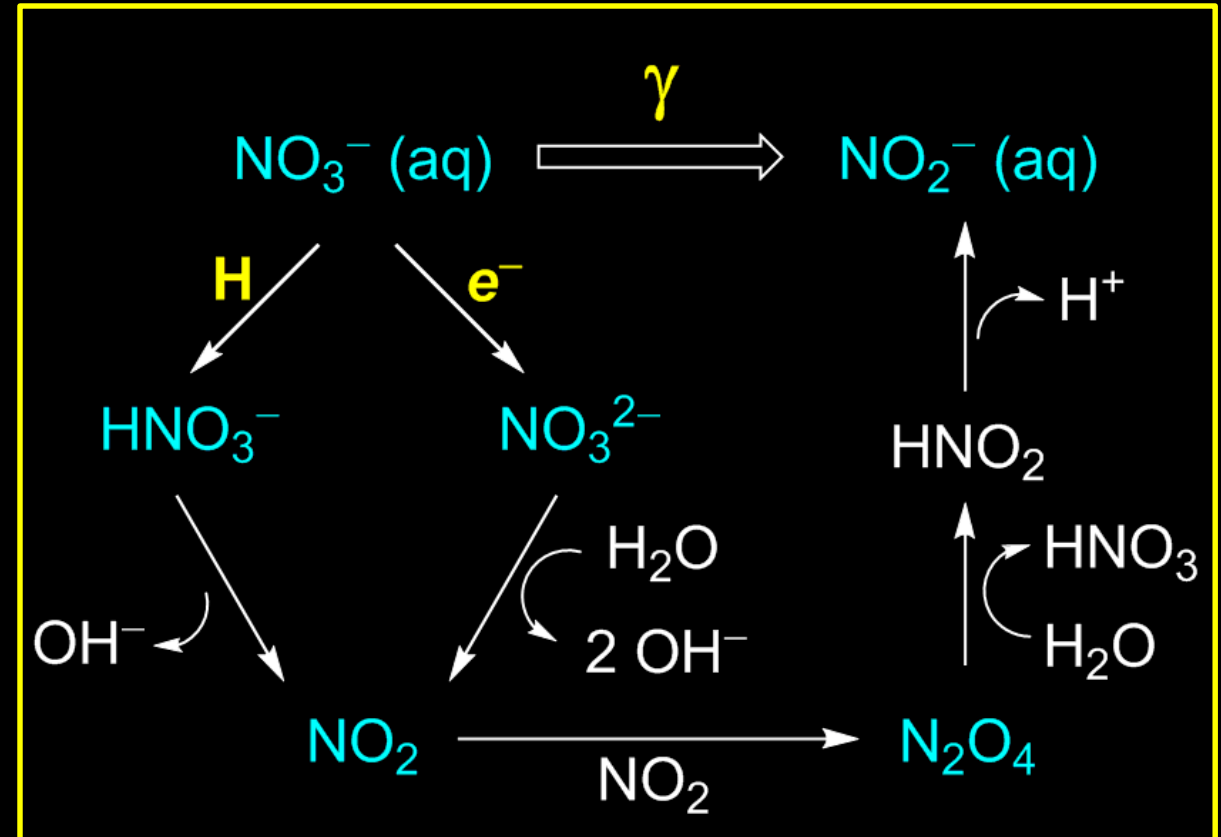


Horne, G. P.; Donoclift, T. A.; Sims, H. E.; Orr, R. M.; Pimblott, S. M. Multi-Scale Modeling of the Gamma Radiolysis of Nitrate Solutions. *J. Phys. Chem. B* **2016**, 120, 11781.

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

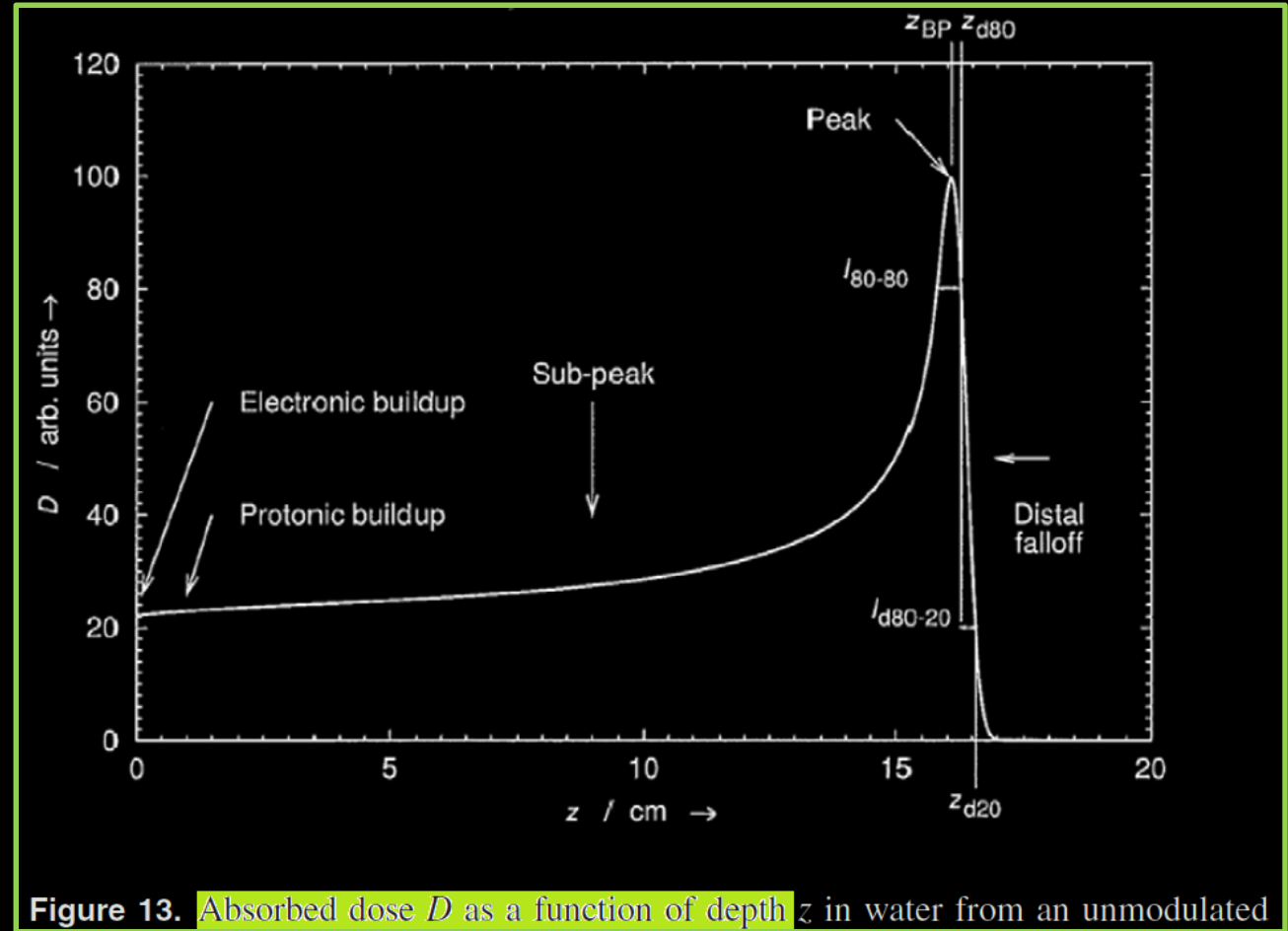
Tugaoen, H. O.; Garcia-Segura, S.; Hristovski, K.; Westerhoff, P. Challenges in photocatalytic reduction of nitrate as a water treatment technology. *Sci. Total Environ.* **2017**, 599, 1524.



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 (σ) 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

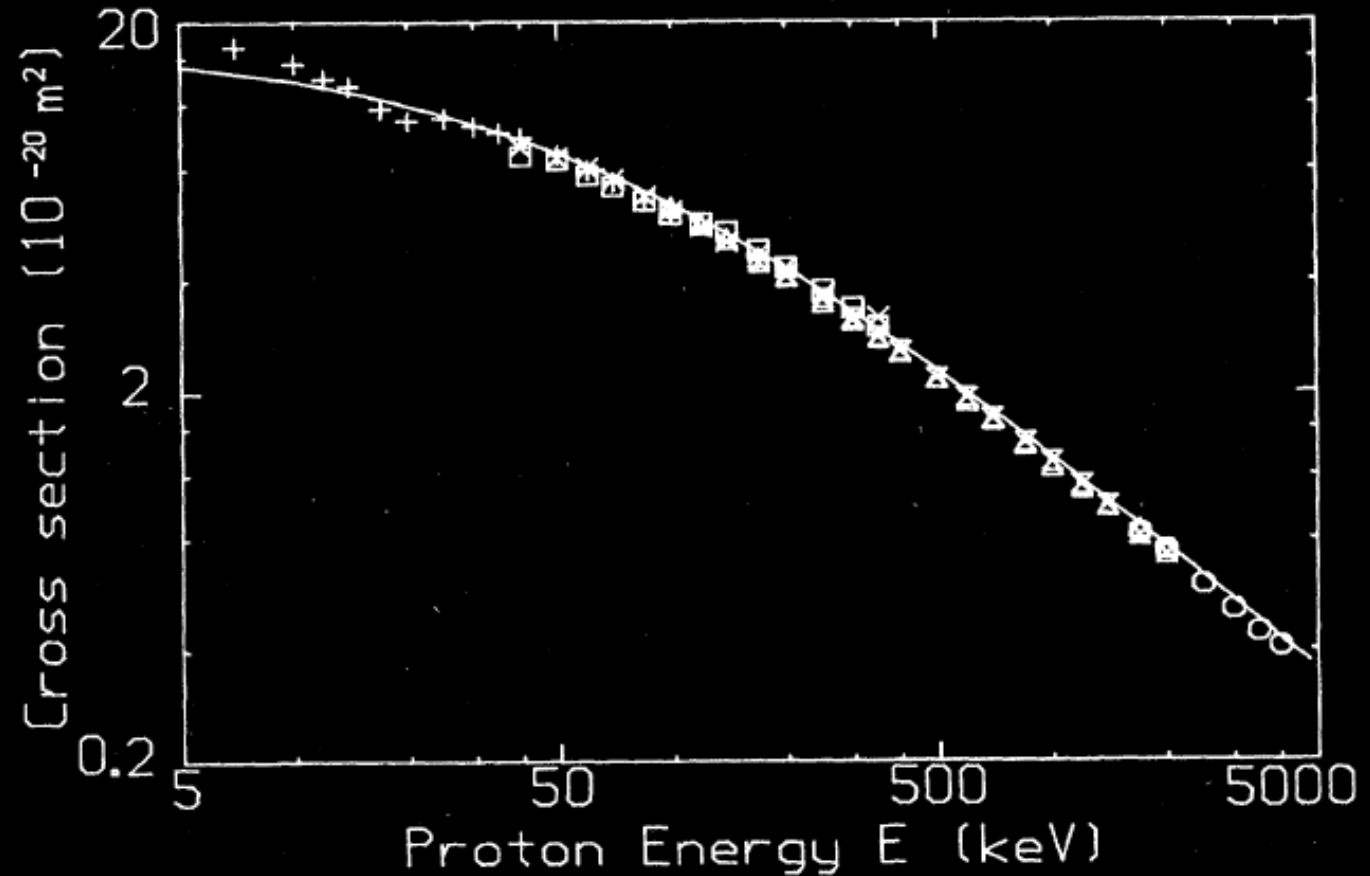
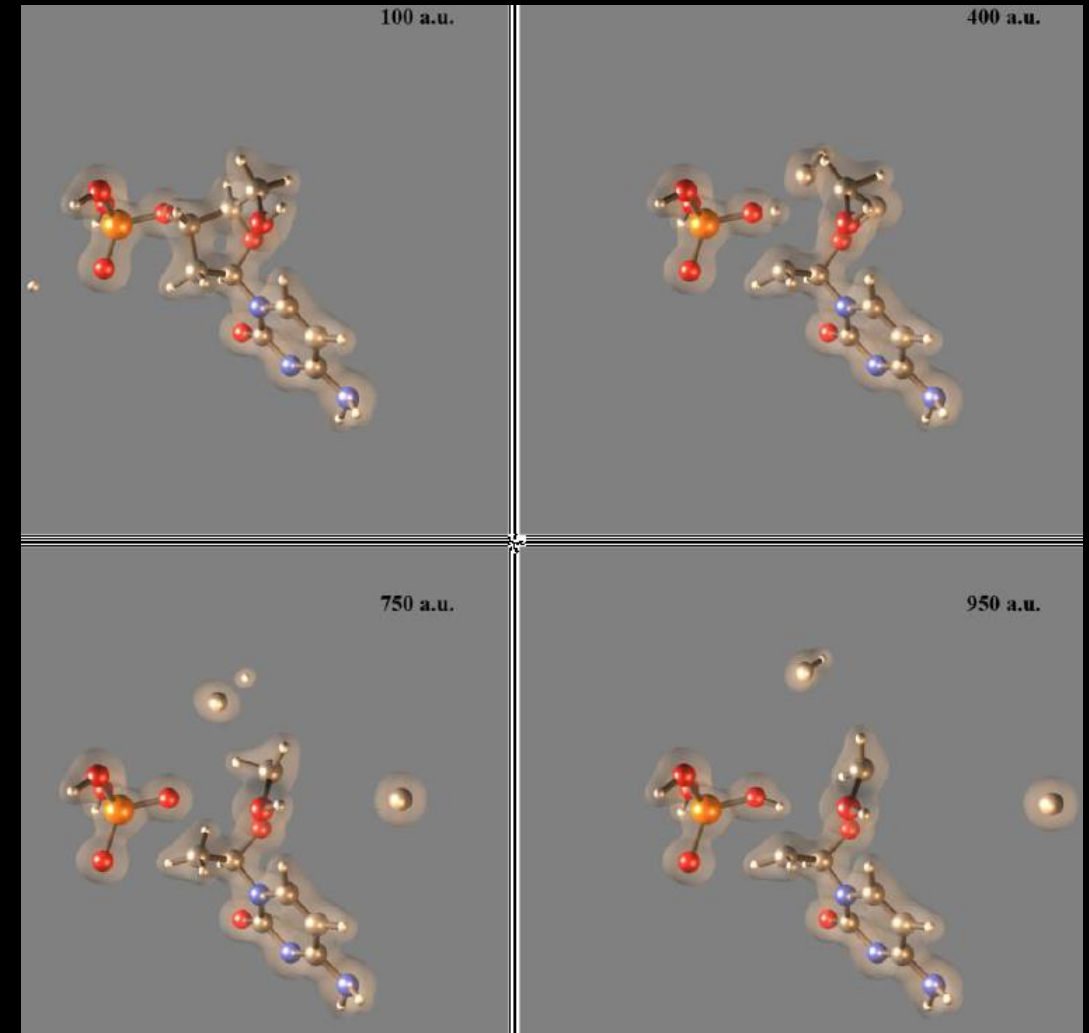


FIG. 3. Cross sections σ_+ after adjustment of data. Solid line is the fit using Eqs. (1) and (4). Symbols as in Fig. 1.

Proton beams: non-adiabatic dynamics

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

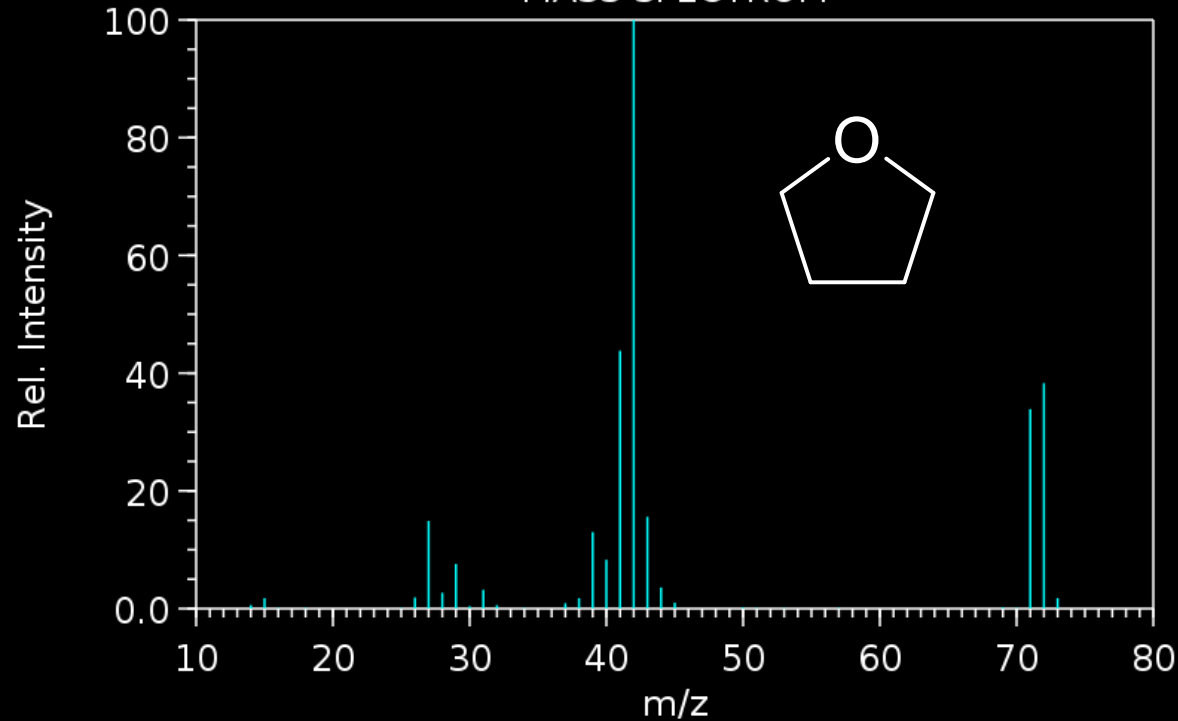


Electron beams on molecules

- Electronic excitation (M^*)
 - Like photo-excitation, but **can change spin by ± 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

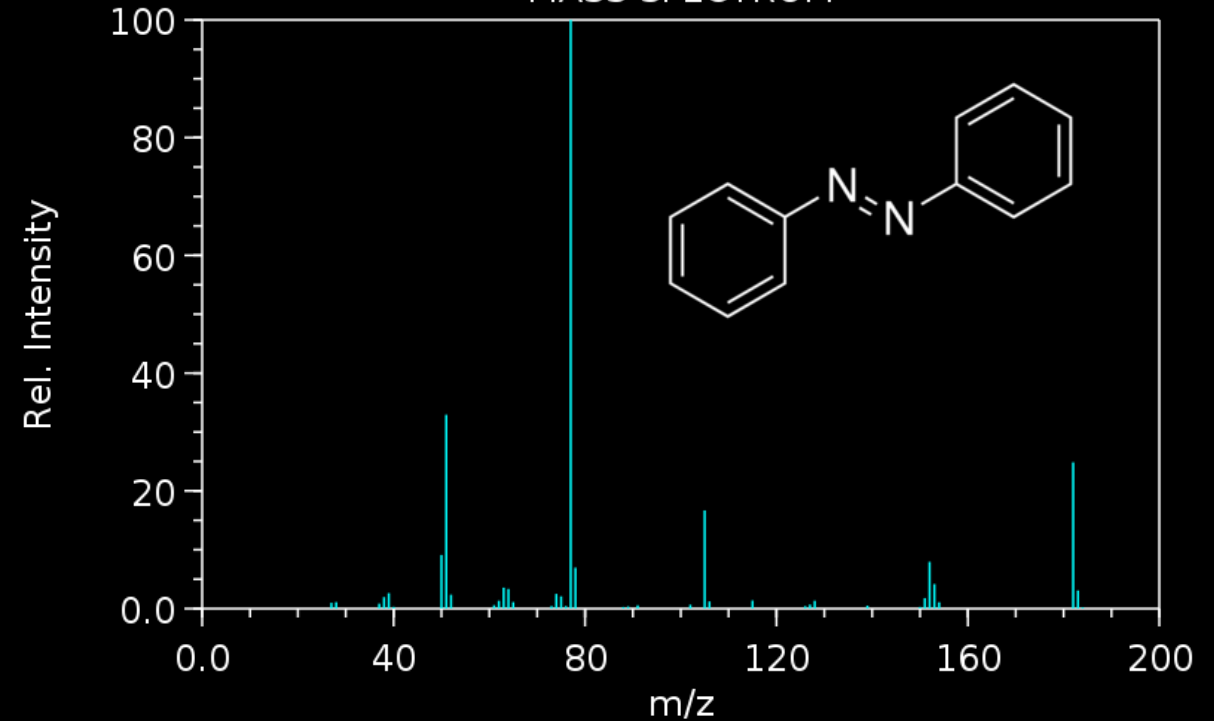
EIMS examples

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?

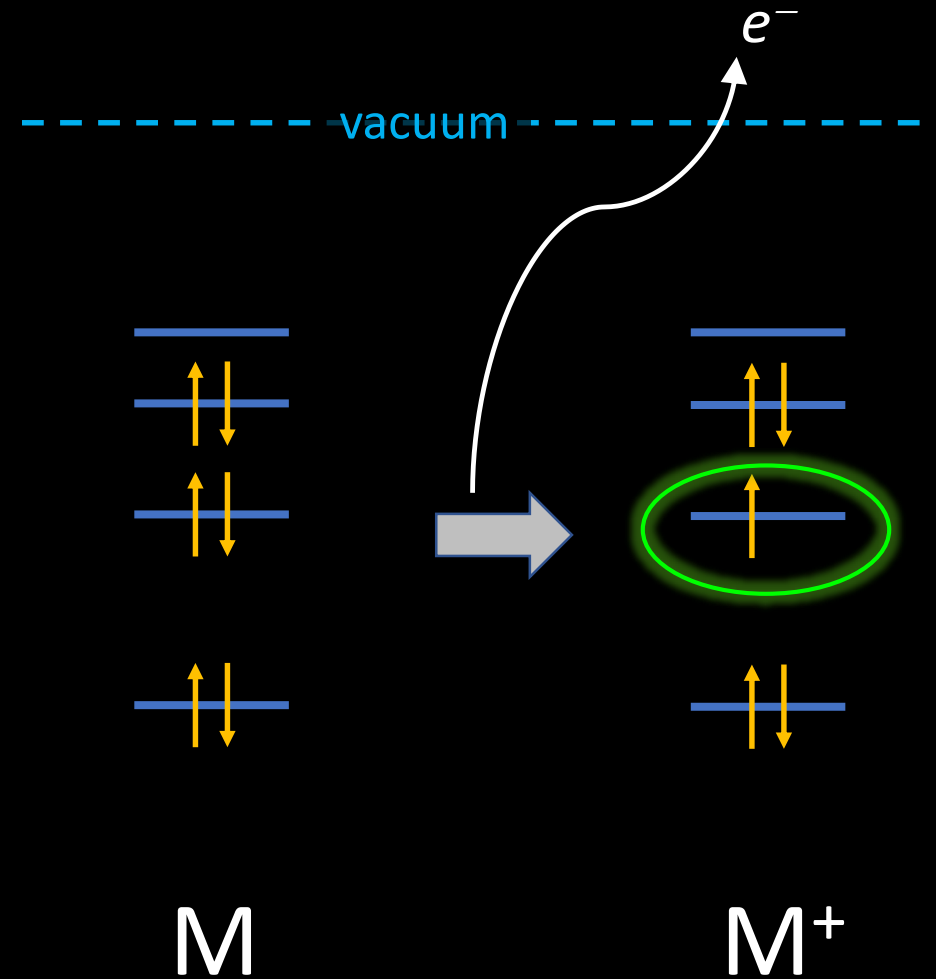
- Distribution of internal energies
 - Can be computed ab initio 😊
- Chemical fate (branching fractions of reaction products)
 - Adiabatic (on ground state potential-energy surface) 😐
 - Diabatic (on excited-state surface) 😞
 - Non-adiabatic (with electronic transitions) 😱
- Smaller effects that partly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

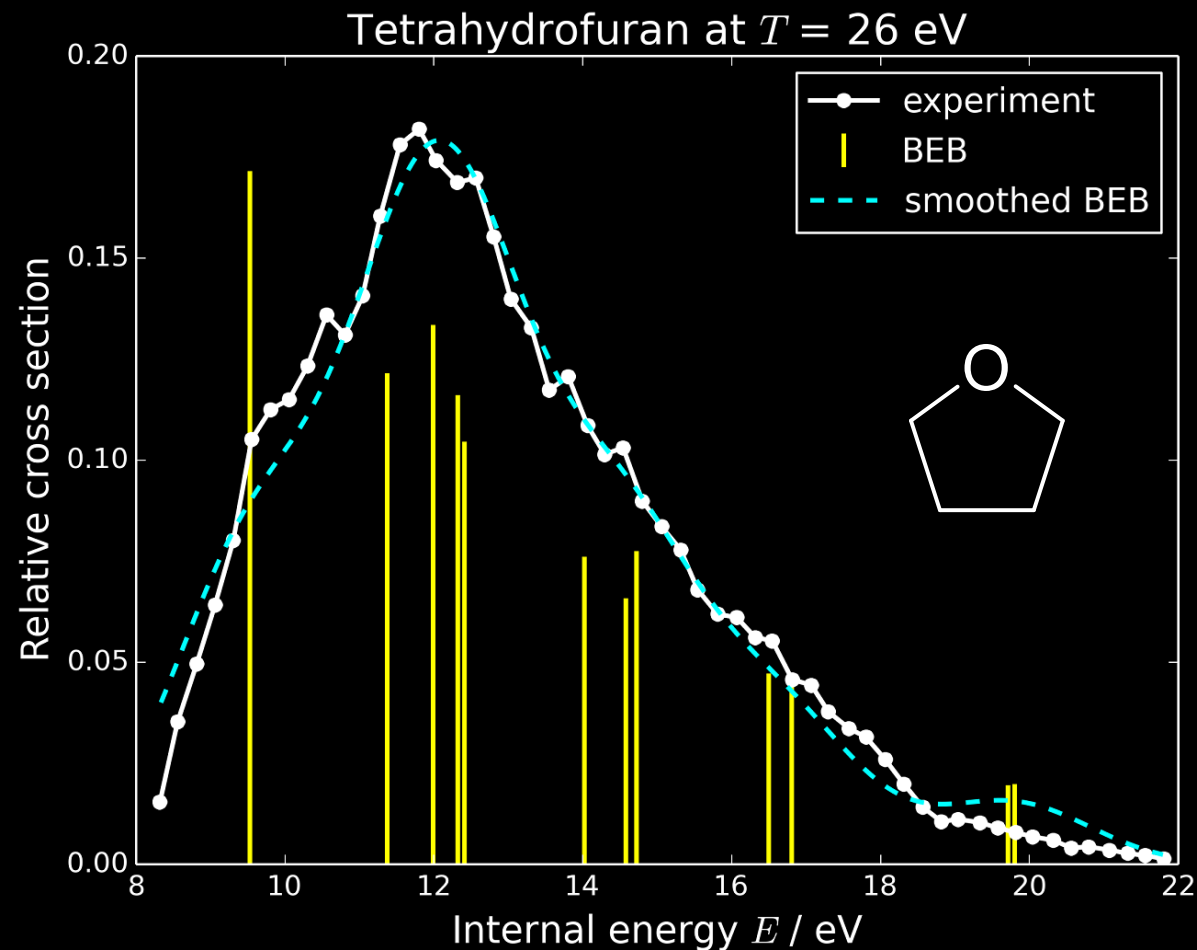
Ions are created by removing electrons

- 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.

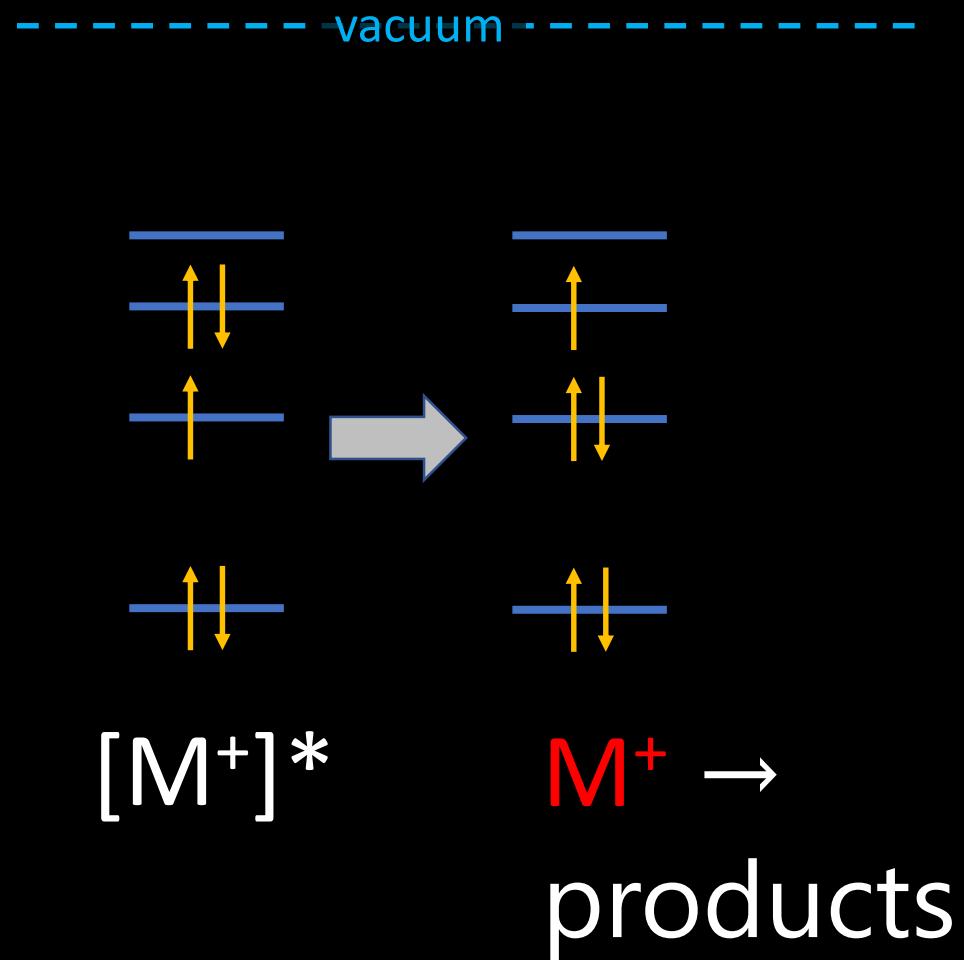
Ren, X.; Pflüger, T.; Weyland, M.; Baek, W. Y.; Rabus, H.; Ullrich, J.; Dorn, A. An (e , $2e$ -ion) study of low-energy electron-impact ionization and fragmentation of tetrahydrofuran with high mass and energy resolutions. *J. Chem. Phys.* **2014**, *141*, 134314.

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

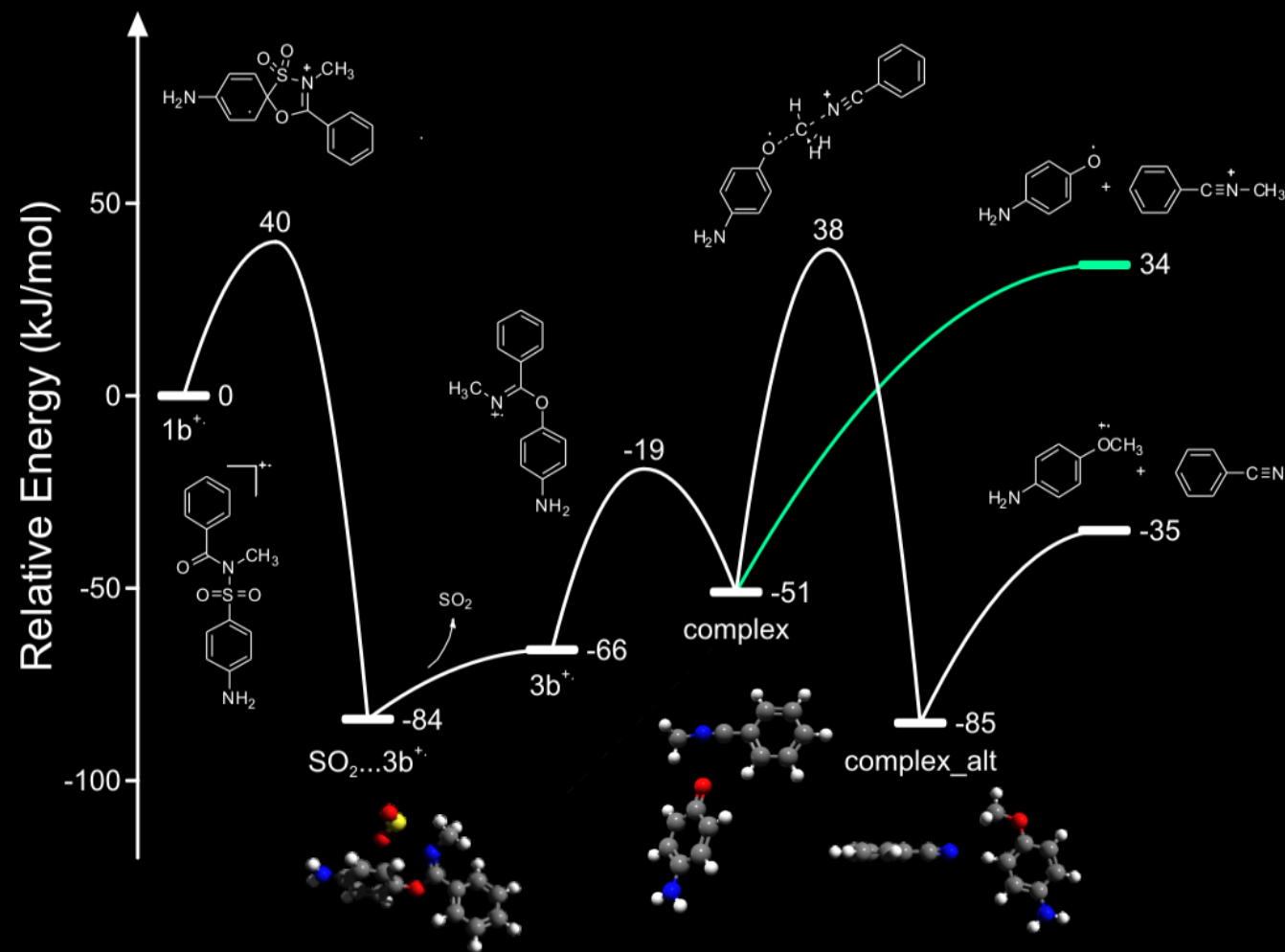
Some reactions are in ground state

- 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?

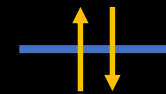
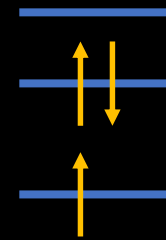
- Distribution of internal energies
 - Can be computed ab initio 😊
- Chemical fate (branching fractions of reaction products)
 - Adiabatic (on ground state potential-energy surface) 😐
 - **Diabatic** (on excited-state surface) 😞
 - Non-adiabatic (with electronic transitions) 😱
- Smaller effects that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

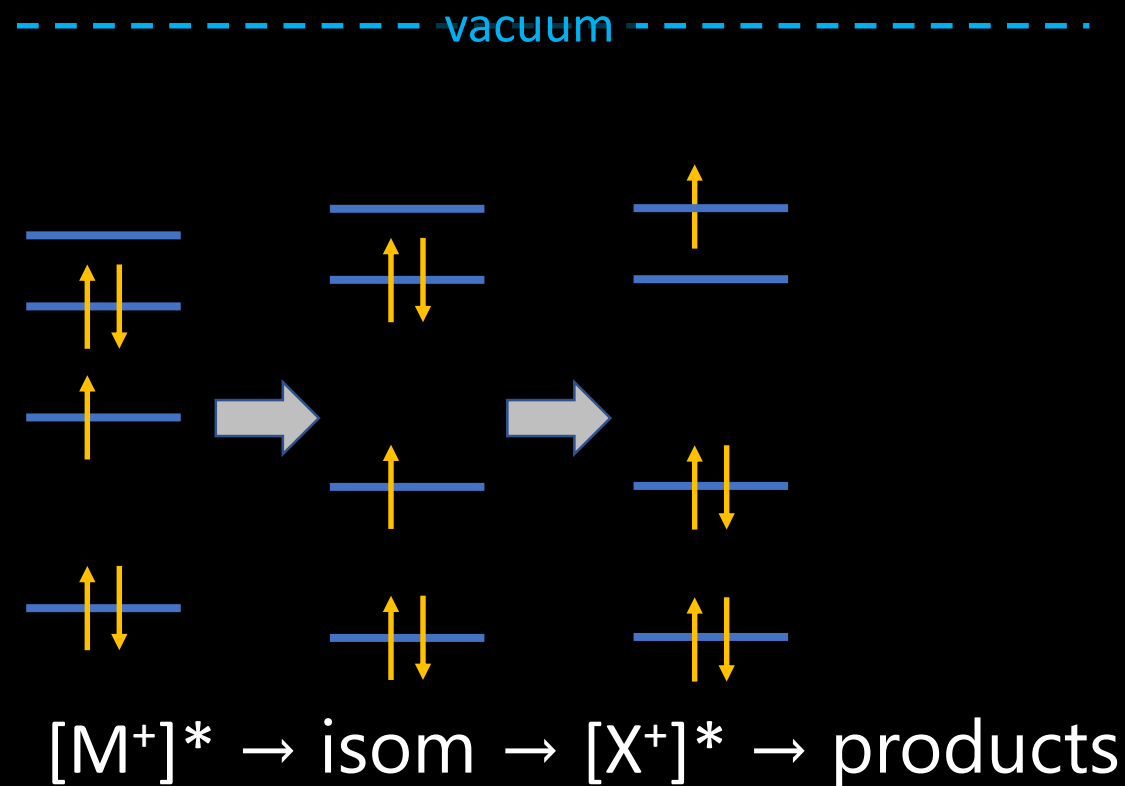


First-Principles modeling of EIMS?

- 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

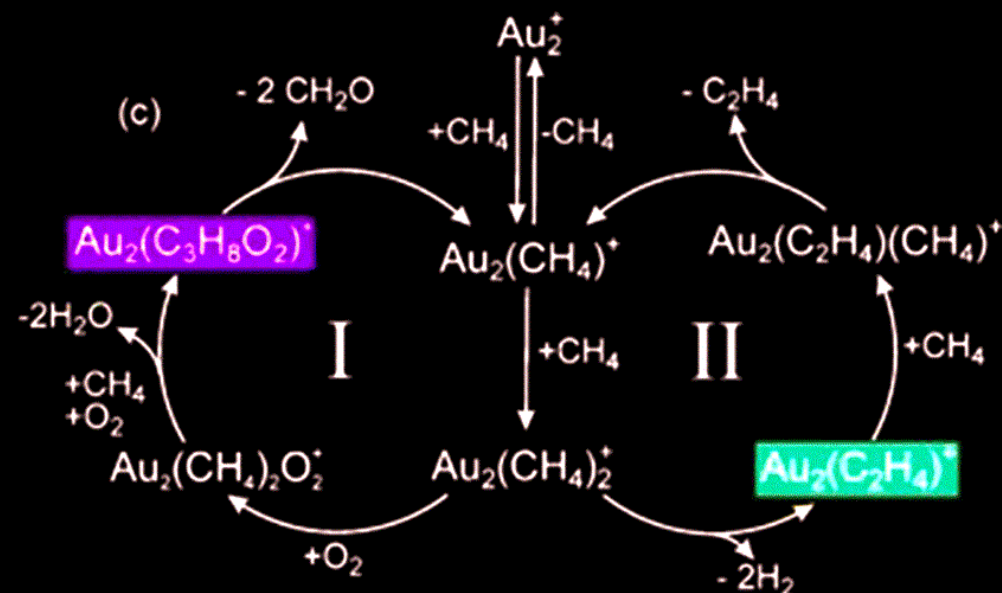
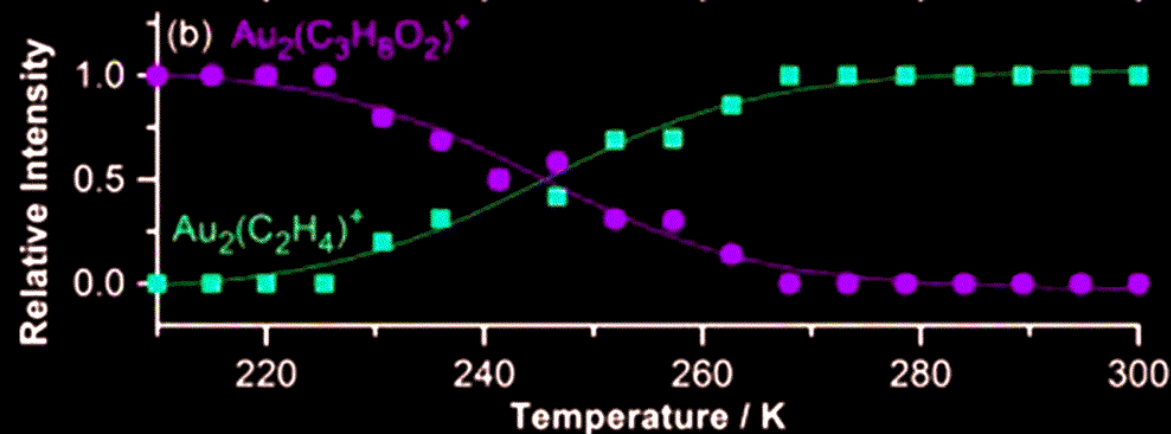
Predicting non-adiabatic reactivity

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



Catalysis by gas-phase ions

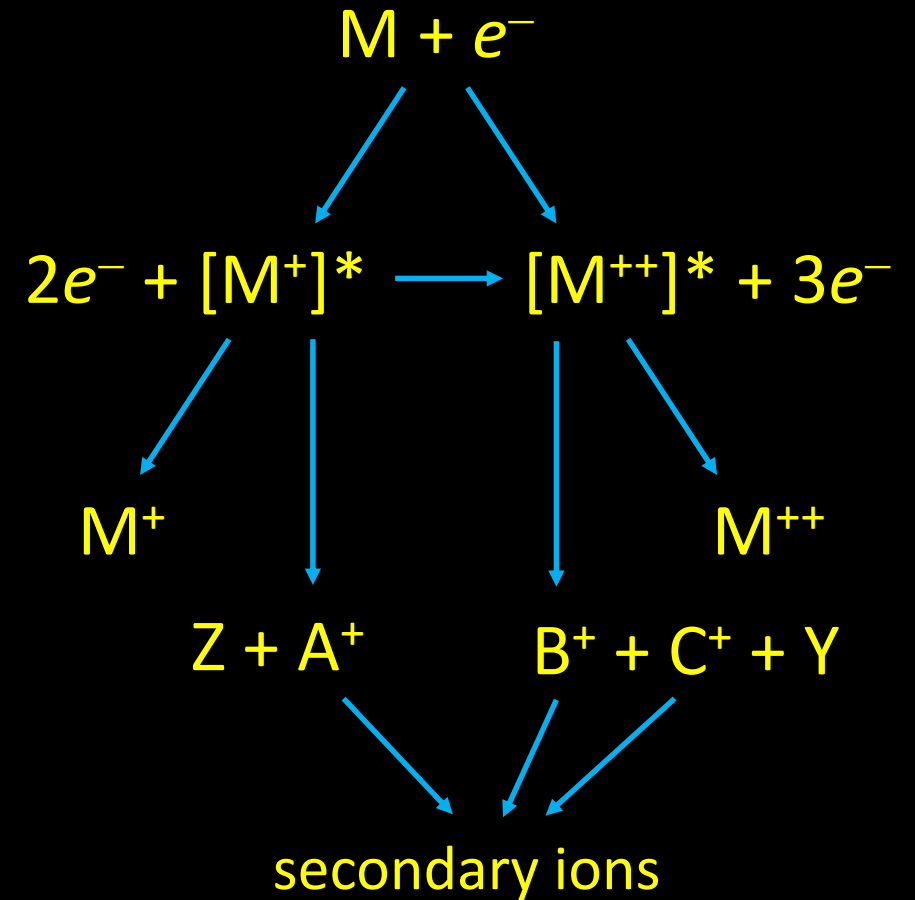
- CH₄ conversion by Au₂⁺ (shown)
 - In presence of O₂, selectivity is controlled by temperature
 - C₂H₄ for $T > 260$ K
 - CH₂O for $T < 230$ K
- Olefin dehydroaromatization (not shown)
 - Catalyzed by Fe₄⁺ and by some atomic ions



Questions or
comments?

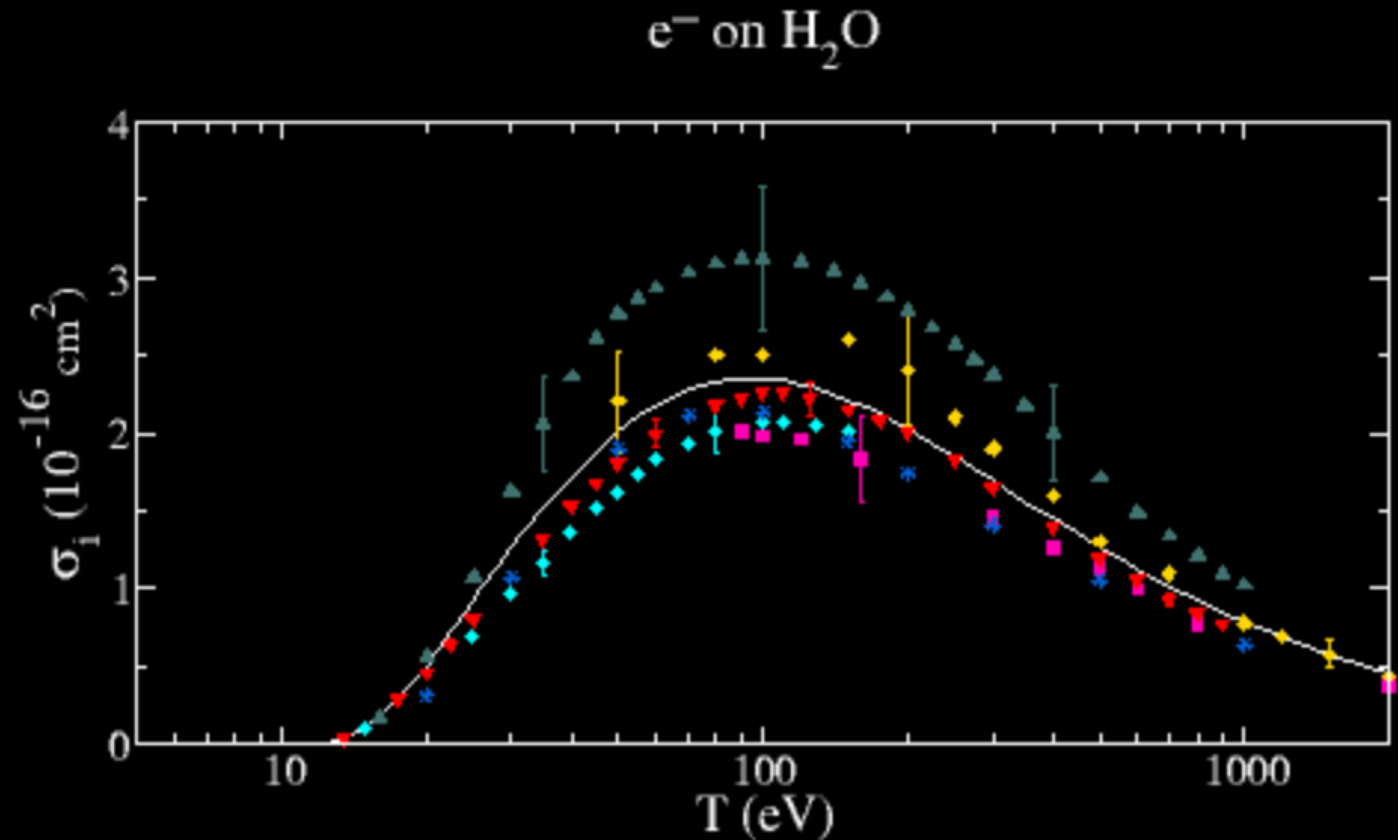
Electron ionization mass spectrometry (EIMS)

- 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 (σ) is the extinction coefficient per particle (units: area)

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

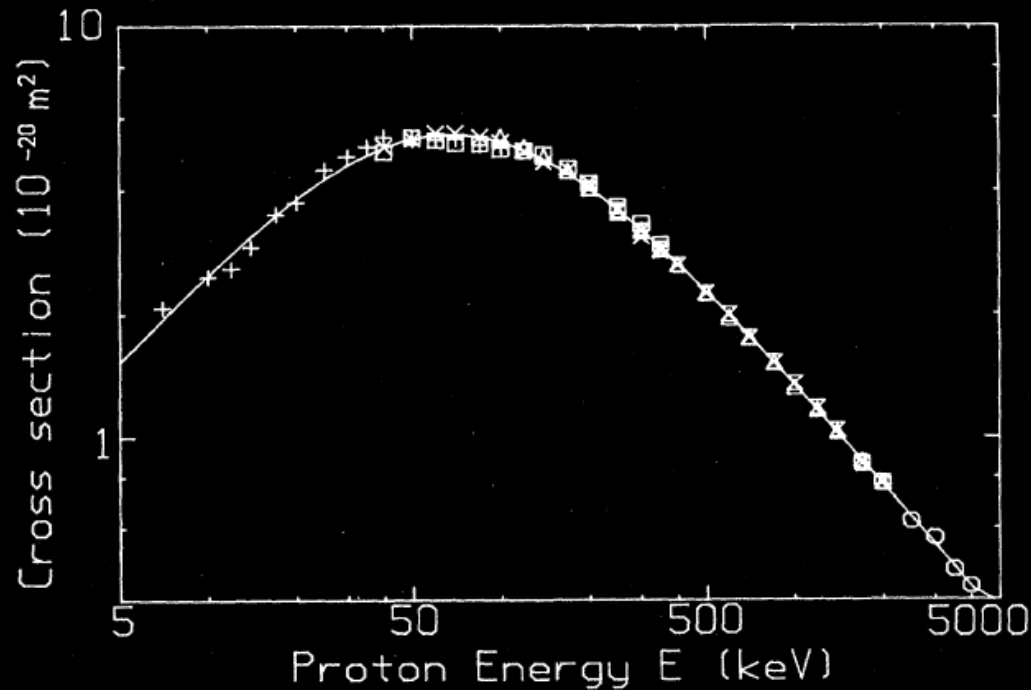


FIG. 2. Cross sections σ_- after adjustment of data (see text). Solid line is the fit using Eq. (1). Symbols as in Fig. 1.

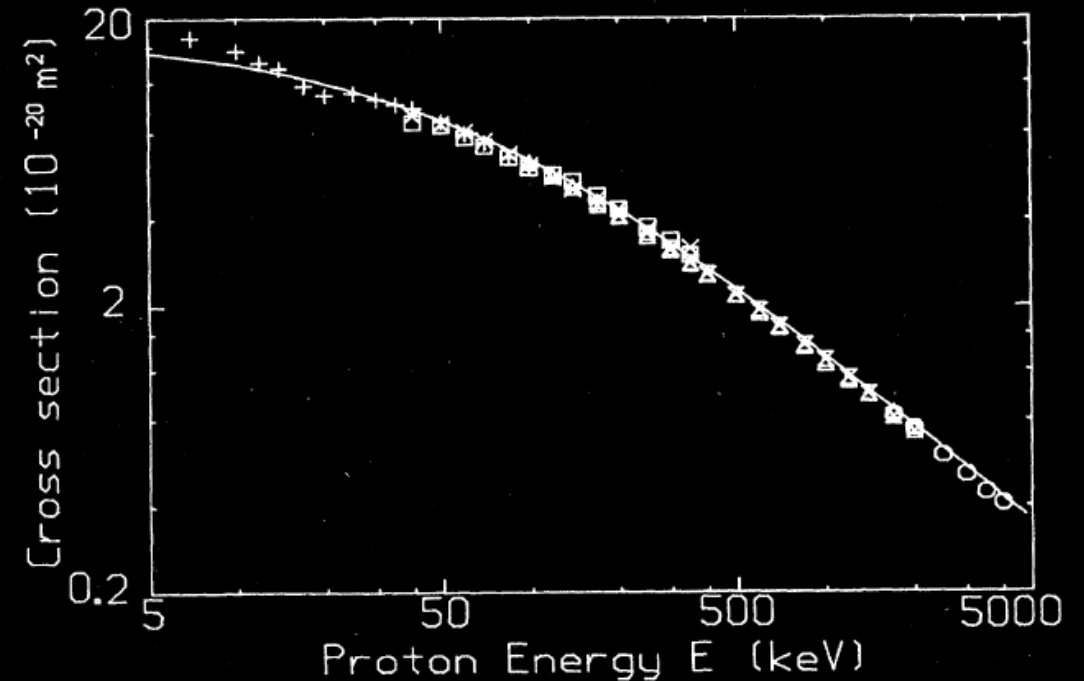


FIG. 3. Cross sections σ_+ after adjustment of data. Solid line is the fit using Eqs. (1) and (4). Symbols as in Fig. 1.