RECENT STUDIES OF ELECTRON MOLECULE SCATTERING WITH THE R-MATRIX METHOD

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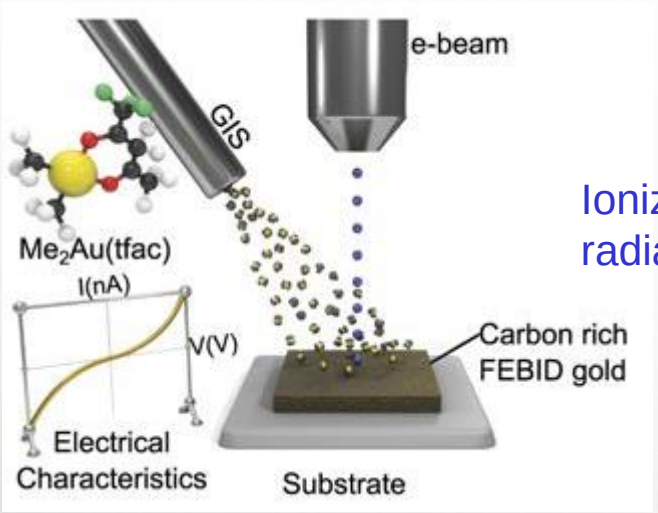
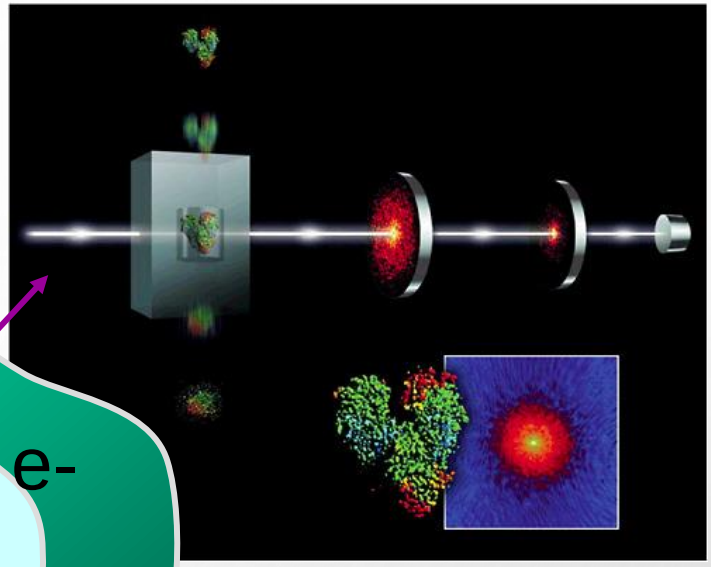
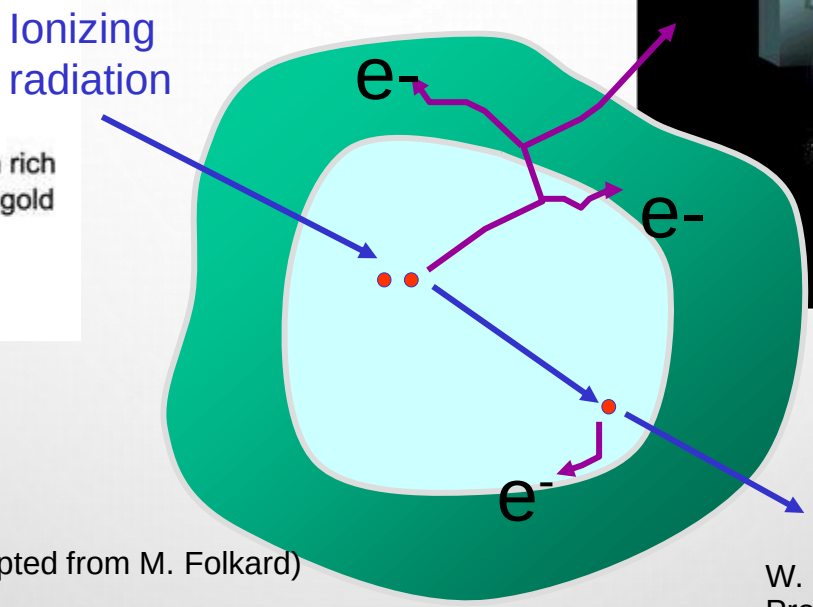
Electron-molecule collisions

Scientific Reports **6** (2016) 34003



Chapman, Lawrence Livermore National Laboratory

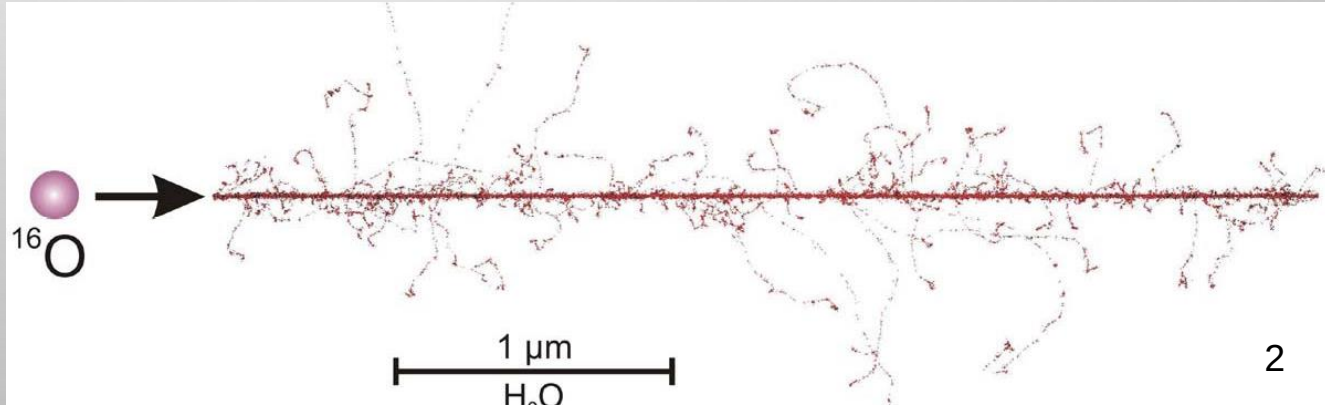




(Adapted from M. Folkard)

Osaka University

W. Friedland, GSF-Insitute of Radiation Protection . PARTRAC, MC simulation



Low energy electron-molecule collisions

Elastic scattering

$$AB + e \longrightarrow AB + e$$

Rotational excitation

$$AB(N'') + e \longrightarrow AB(N') + e$$

Vibrational excitation

$$AB(v''=0) + e \longrightarrow AB(v') + e$$

Electronic excitation

$$AB + e \longrightarrow AB^* + e$$

Dissociative electron attachment

$$AB + e \longrightarrow A + B^-$$

Dissociative excitation*

$$AB + e \longrightarrow A + B + e$$

Ionization

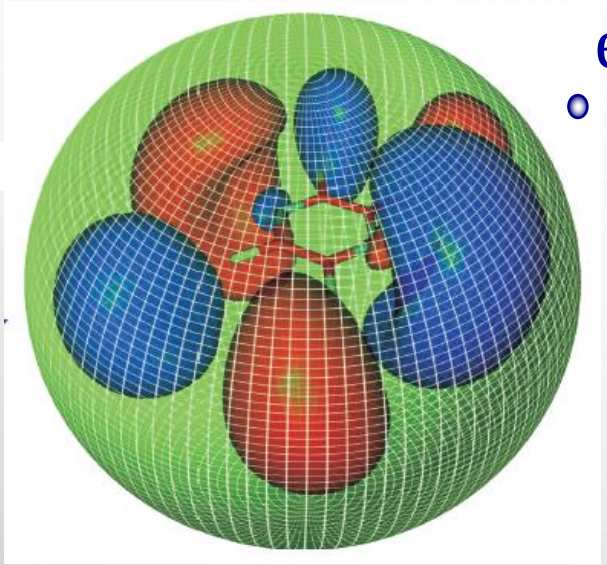
$$AB + e \longrightarrow AB^+ + e + e$$

Energy

* Impact dissociation

R-matrix method for e-molecule collisions

Fixed-Nuclei approximation: neglect of nuclear motion



R-matrix sphere of radius *a*

P. G. Burke, *R-Matrix Theory of Atomic Collisions: Application to Atomic, Molecular and Optical Processes* (Springer) 2011.

Inner region:

- exchange and correlation important
- explicitly multielectronic
- basis set methods
- multicentre expansion

Outer region:

- exchange negligible and 'correlation' very simple
- one explicit electron
- long-range multipolar interactions
- single centre expansion

R-matrix method for e-molecule collisions

Inner region: calculation of Ψ_k^{N+1} from diagonalization of $\mathbf{H}^{N+1}$

$$\Psi_k^{N+1} = \mathcal{A} \sum_{i,j} a_{i,j,k} \phi_i^N \eta_{i,j} + \sum_j b_{j,k} \phi_j^{N+1}$$

- Good description of electronic molecular states ϕ_i^N: SA-CASSCF method

$$\phi_i^N = \sum_{i,j} c_{i,j} \zeta_j^N \qquad \zeta_j^N = \| \varphi_1 \varphi_2 \varphi_3 \ldots \varphi_N \|$$

  Limited by methodology, size of calculation and size of R-matrix sphere

- Good description of correlation/polarization effects: choice of L^2 functions
- Good description of continuum using continuum orbitals $\eta_{i,j}$: use of GTOs, BTOs or both

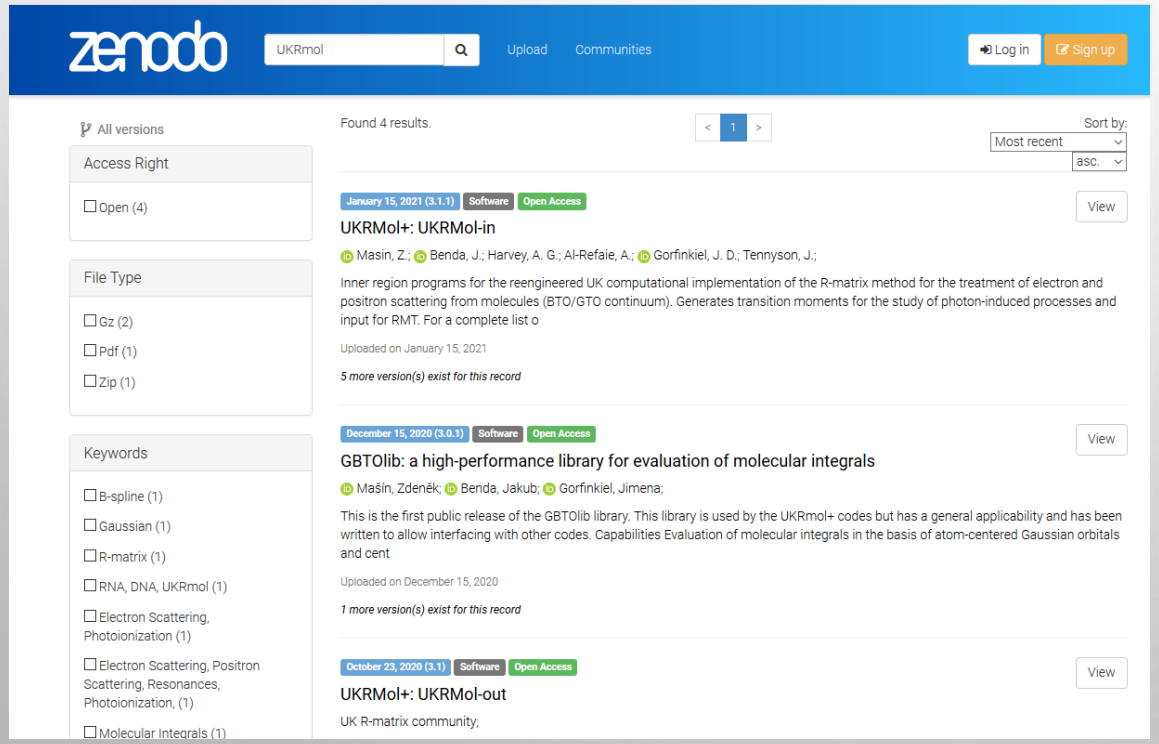
R-matrix software

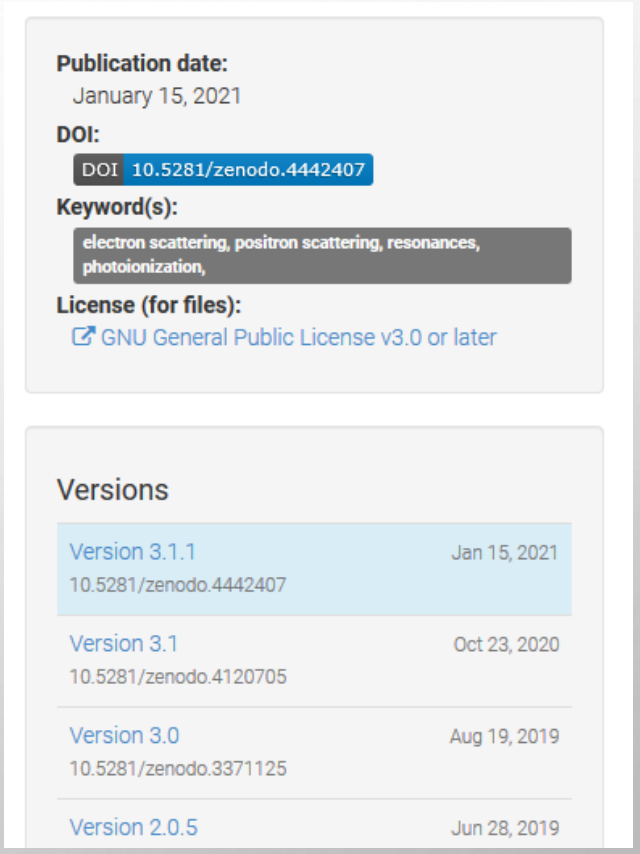
UKRmol+ suite

Mašin et al, CPC, **249**, 107092 (2020)
https://doi.org/10.1016/j.cpc.2019.107092

arxiv.org/abs/1908.03018

Time-independent approach to low-energy electron/positron scattering and photoionization

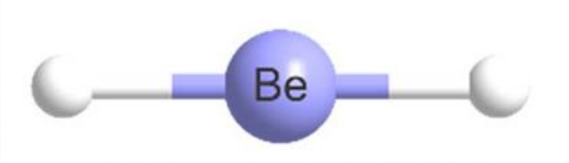




https://zenodo.org/

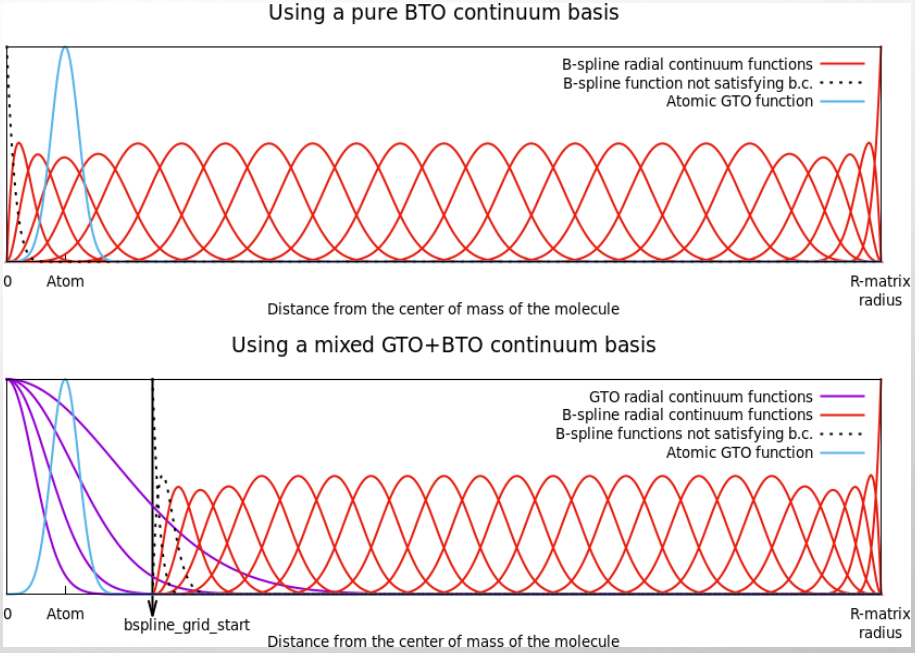
BeH_2: inelastic cross section and DCS

Present in plasma in divertors of thermonuclear fusion reactors (e.g. ITER)



Small enough (and 6 e^-) to use our best models:

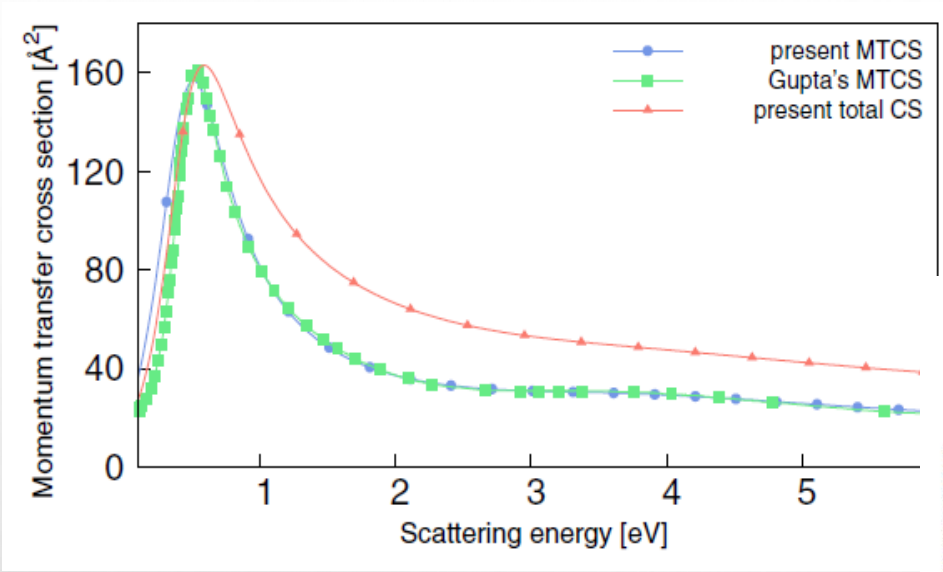
- cc-pVDZ basis set (aug had little effect)
- CASSCF (4,14)
- 40 target states
- R-matrix radius = 15 a_0
- BTO-only continuum
- Max. partial wave l=8



GBTOlib

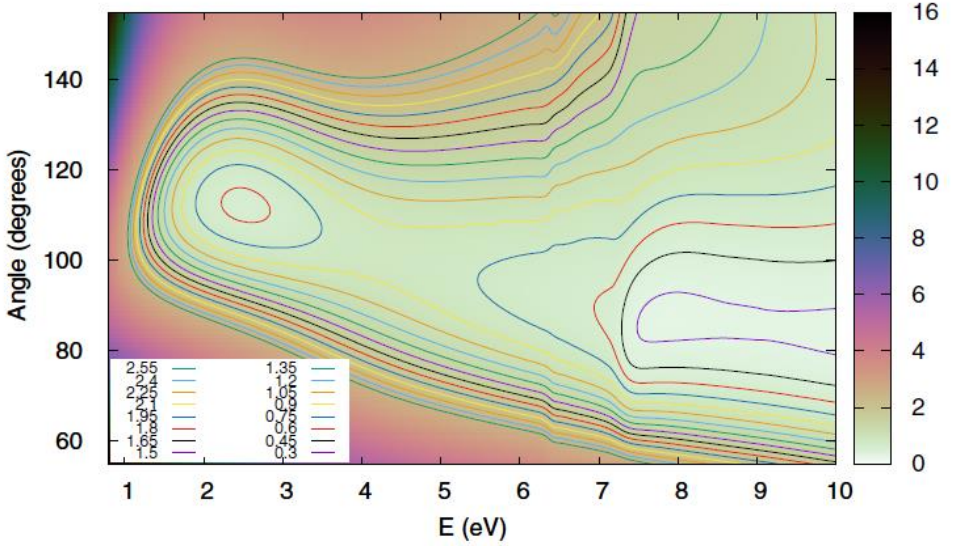
Sukuba and Gorfinkiel, PRA (2020) **101**, 052709

BeH_2: cross sections

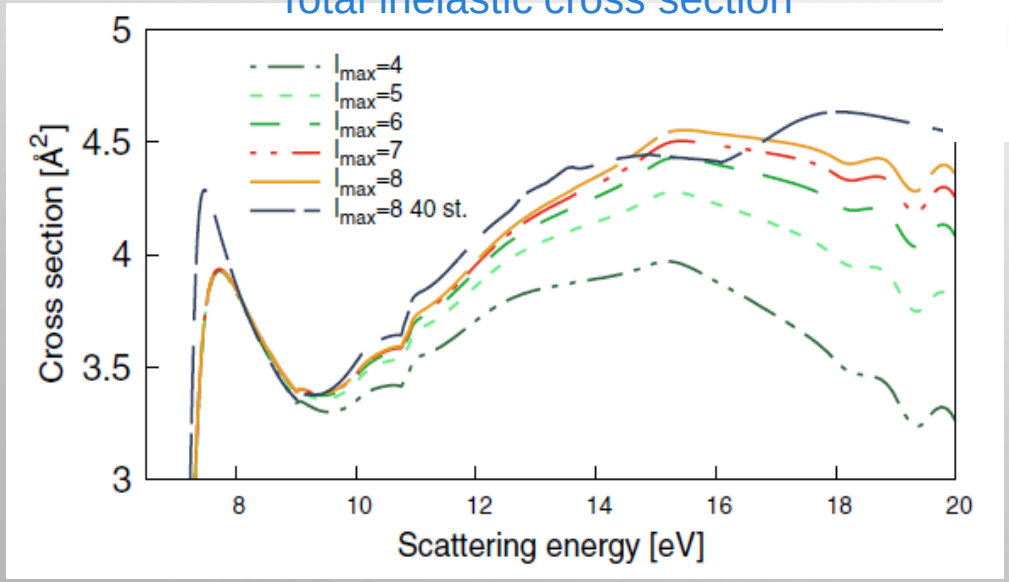


Total and momentum transfer cross section

Elastic DCS



Total inelastic cross section



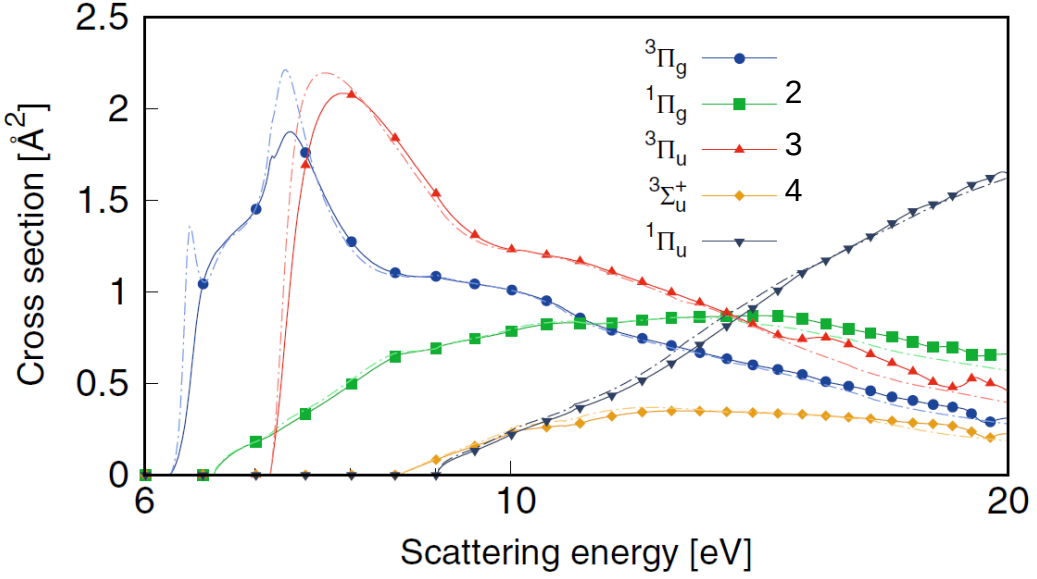
Effect of improved continuum and polarization description

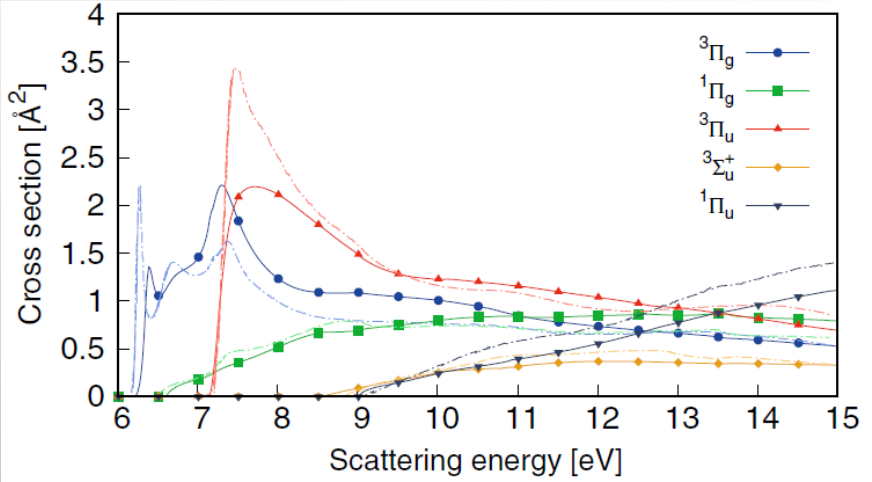
Sukuba and Gorfinkiel, PRA 2020, **101**, 052709

BeH_2: inelastic cross section and DCS

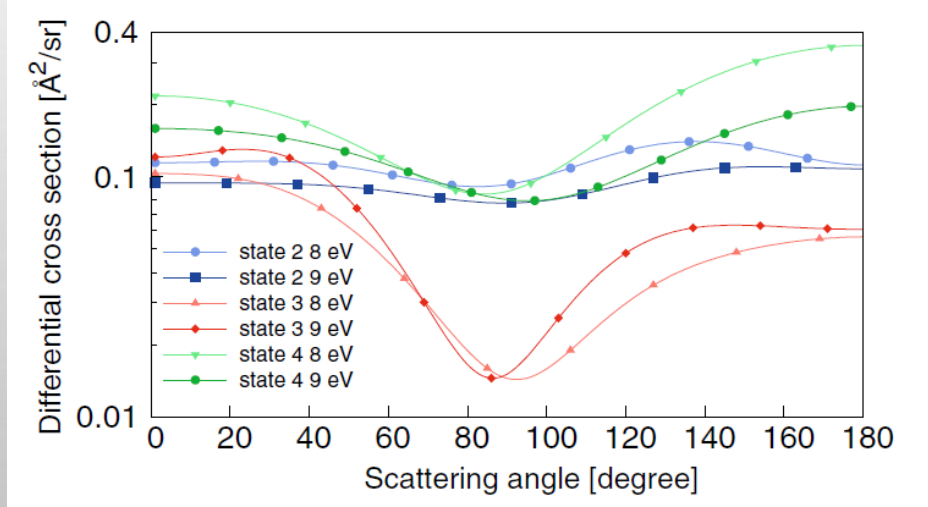
State-to-state integral cross sections: 14 (solid) vs. 40 (dashed) target states

Comparison with earlier (dashed) results





State-to-state DCS: expected behaviour for singlets and triplet states



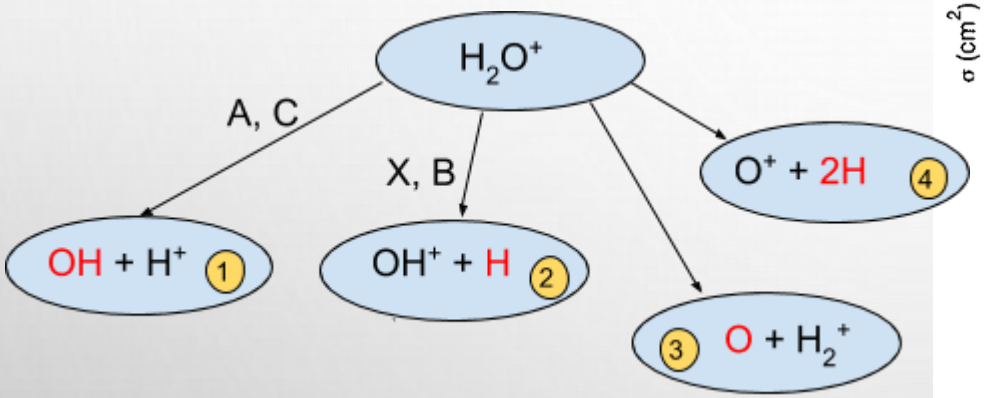
Sukuba and Gorfinkiel, PRA (2020) **101**, 052709

H_2O^+: dissociative excitation

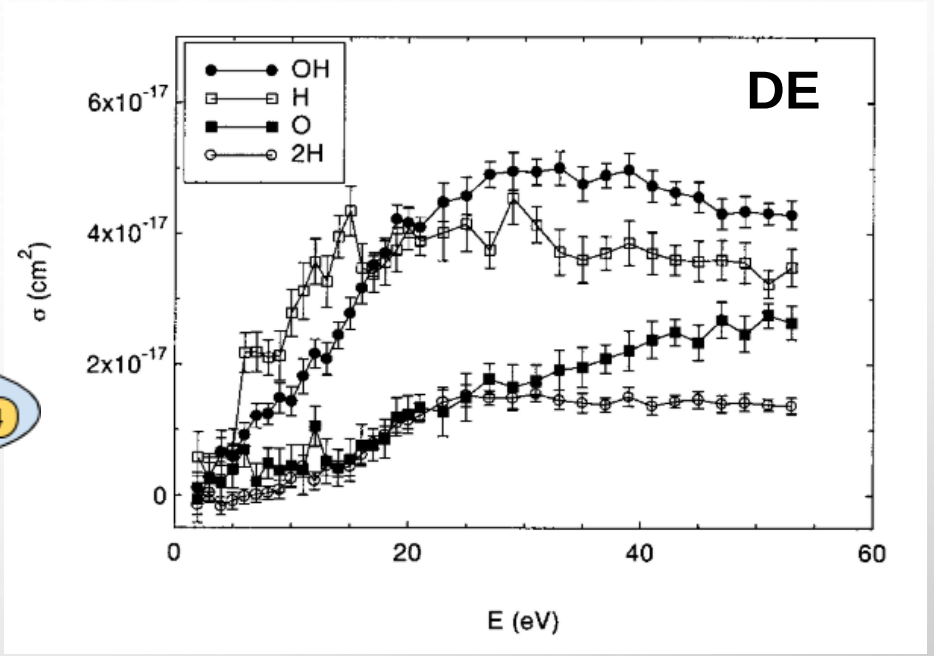
Dissociative excitation

$$AB^+ + e \longrightarrow A^+ + B + e$$

$$\longrightarrow A + B^+ + e$$



Storage ring measurements of DE and DR



Jensen et al, PRA **60** (1999) 2970

Dissociative recombination

$$AB^+ + e \longrightarrow A + B + e$$

Complexity similar to DR

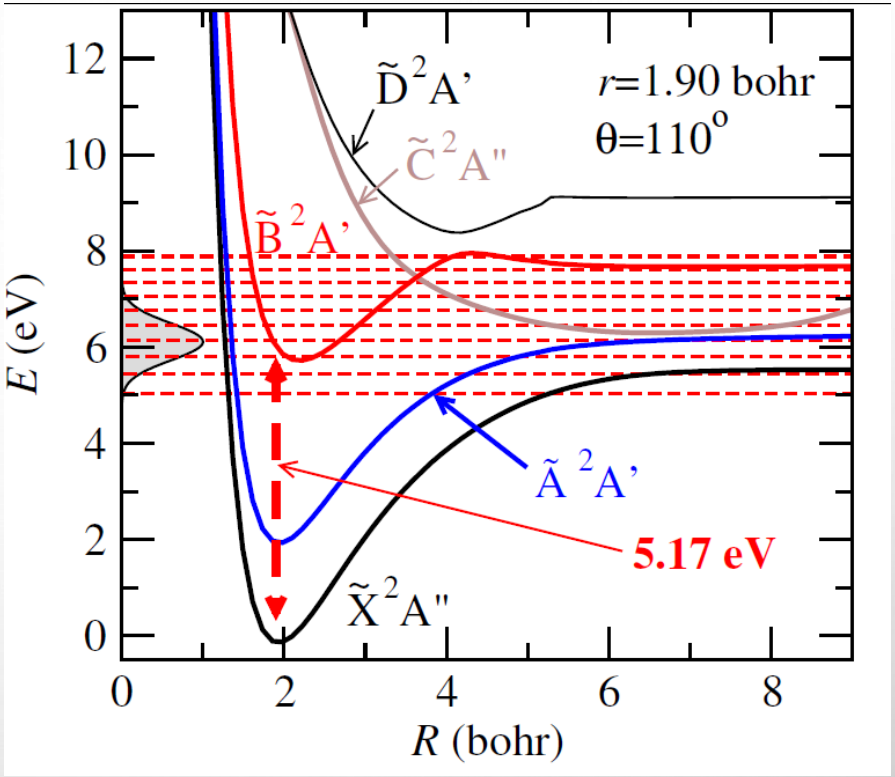
Rabadan and Gorfinkiel, PRA **103** (2021) 012808

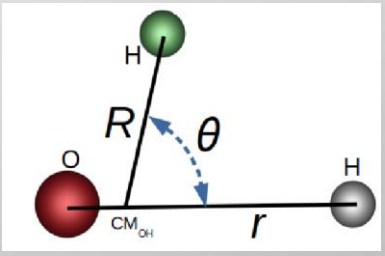
H_2O^+: dissociative excitation (DE)

Possible ‘routes’:

a) Excitation into electronic (pre)dissociative state
b) Excitation into vibrational continuum of bound electronic state
c) Coupling between electronic states
d) Excitation into resonant state that decays into a dissociative state
e) Excitation into dissociative resonant state (followed by detachment)

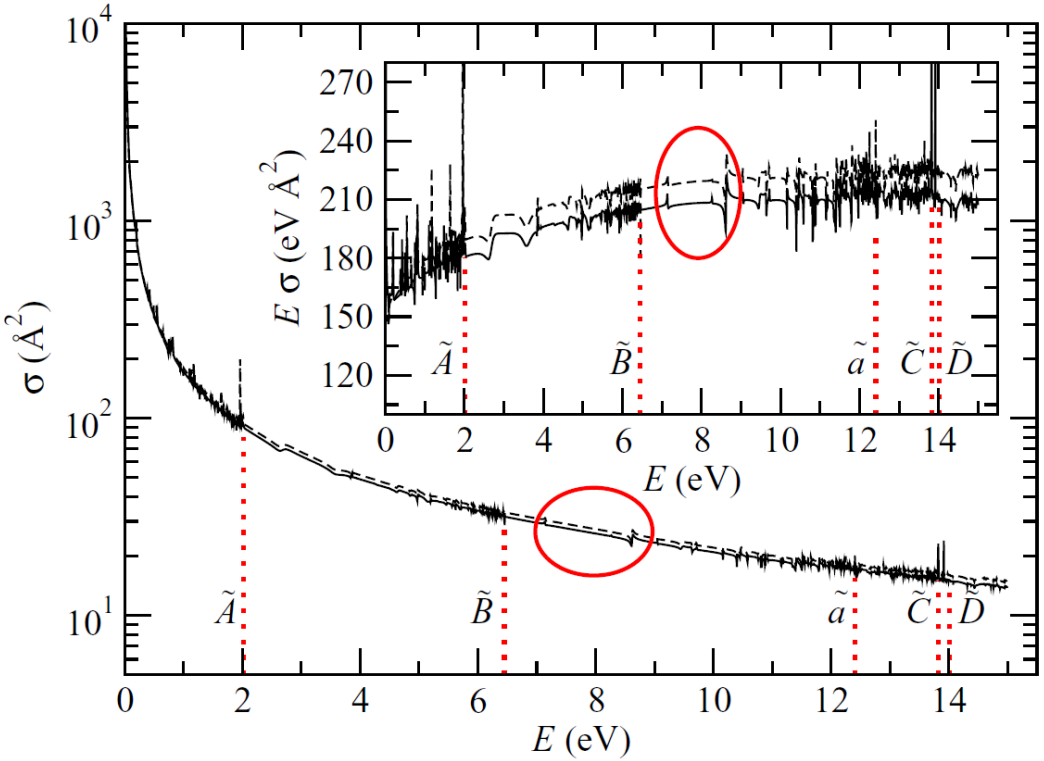
d and e normally compete and outcome (DE/DR) depends on resonance lifetime among other things.





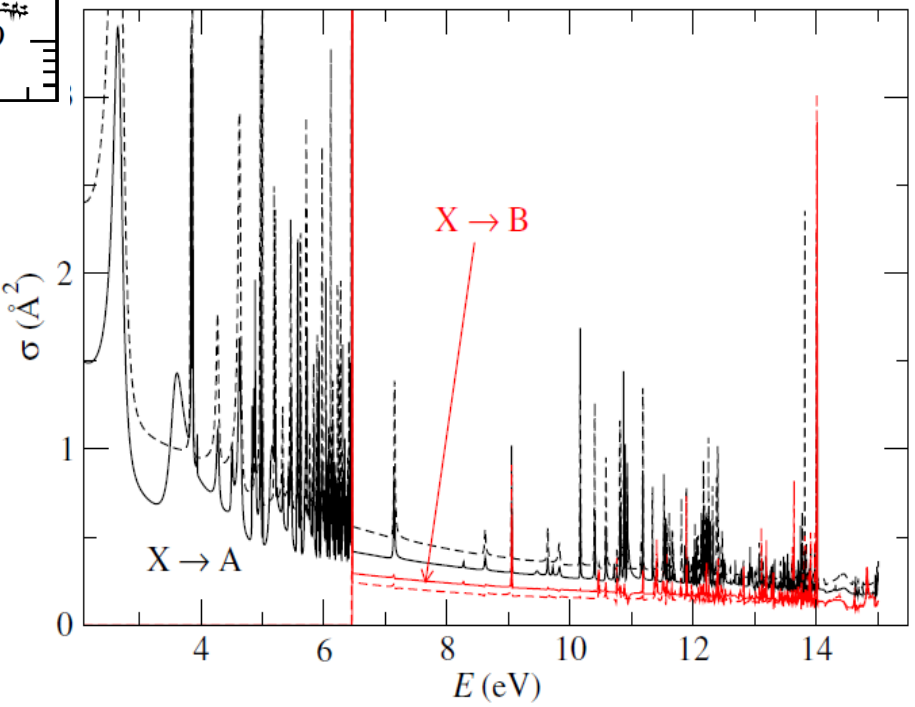
Rabadan and Gorfinkiel, PRA **103** (2021) 012808

H_2O^+: elastic and inelastic scattering



Elastic cross section

Excitation into the first and second electronic states

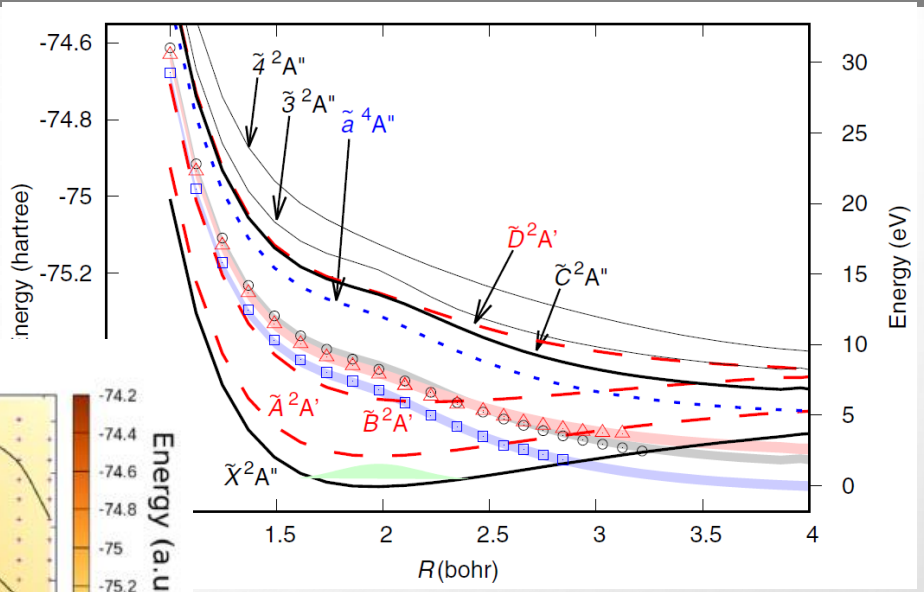


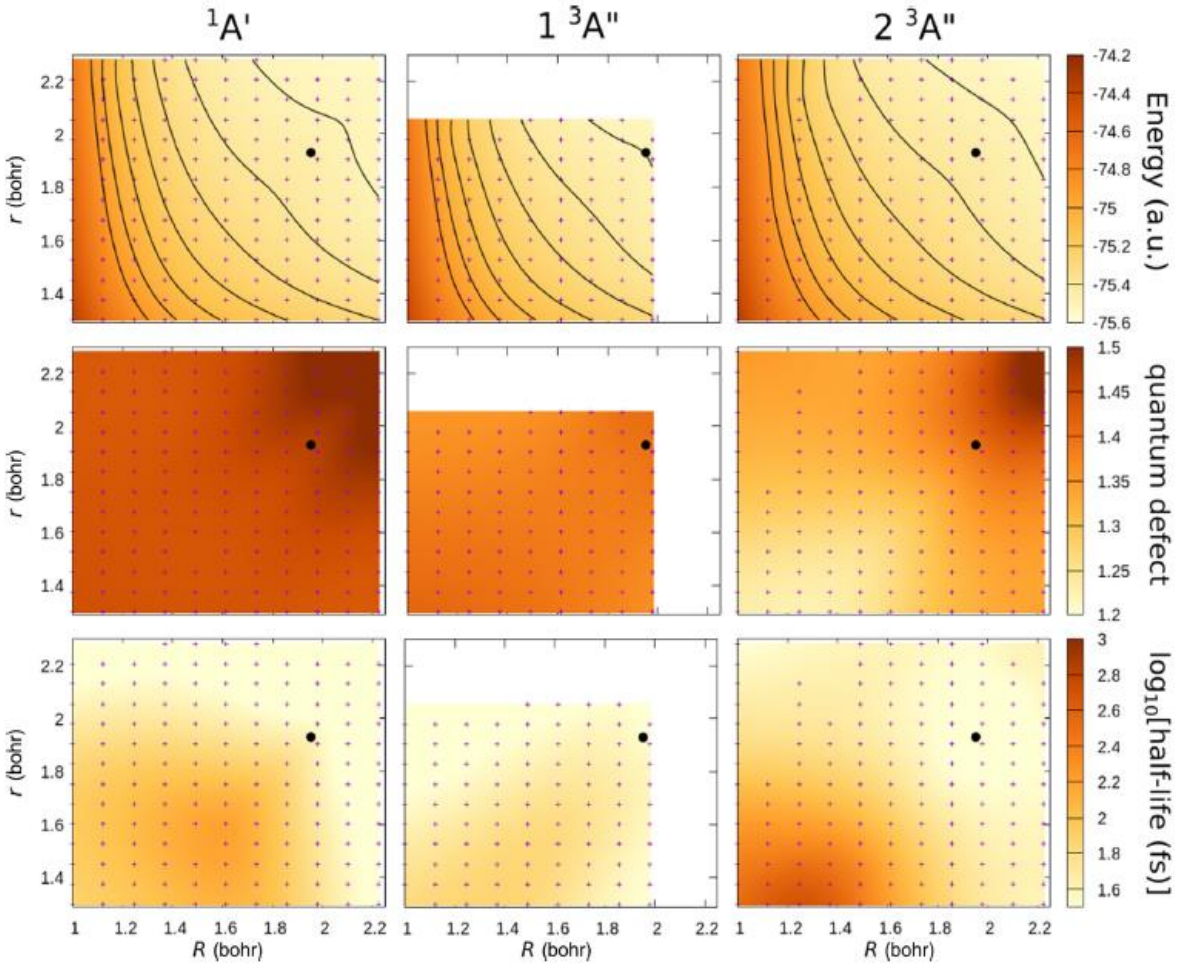
H_2O^+ present in biomedical plasmas, Saturn's inner plasma disk, other astrophysical environments, etc.

Rabadan and Gorfinkiel, PRA **103** (2021) 012808

H_2O^+: towards DE

Large number of resonances decaying to B state: effect on DE?
Study of 3 ‘dissociative’ resonances.





Investigated survival probability resonances above B state: resonance lifetimes vs. ‘ 1D dissociation time’ for DR seem to indicate DR is more likely than DE…

Interatomic Coulombic electron capture

Environment enabled process

$e + Ne^+ \rightarrow Ne^+ + e$ elastic/inelastic scattering

$e + Ne^+@He_n \rightarrow Ne@He^+_n + e$ **capture**

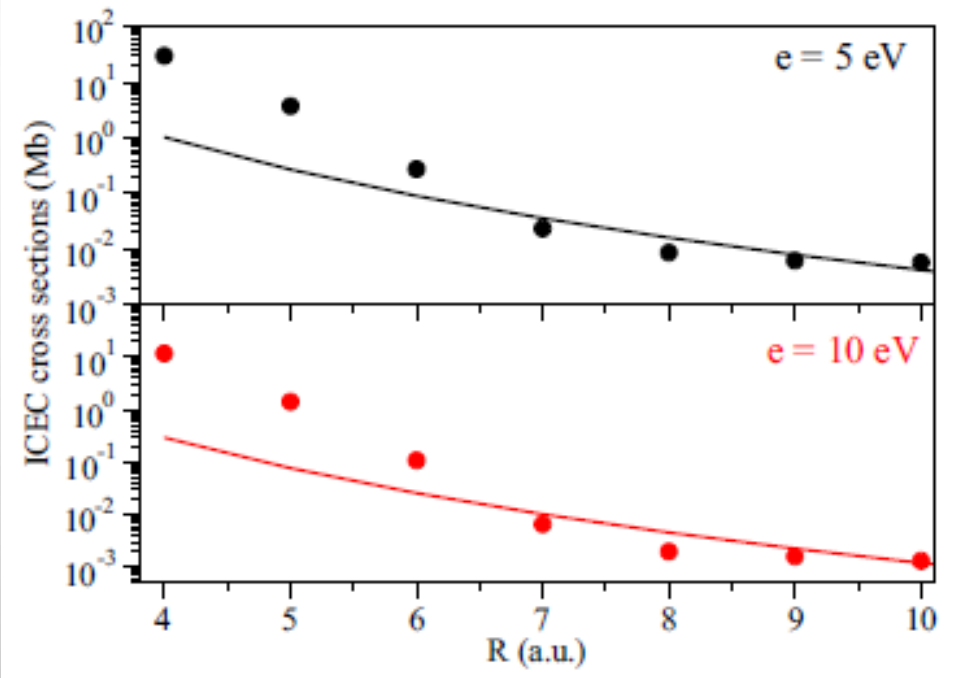
IP Ne: 21.56 eV < IP He: 24.59 eV → no 'spontaneous' electron transfer

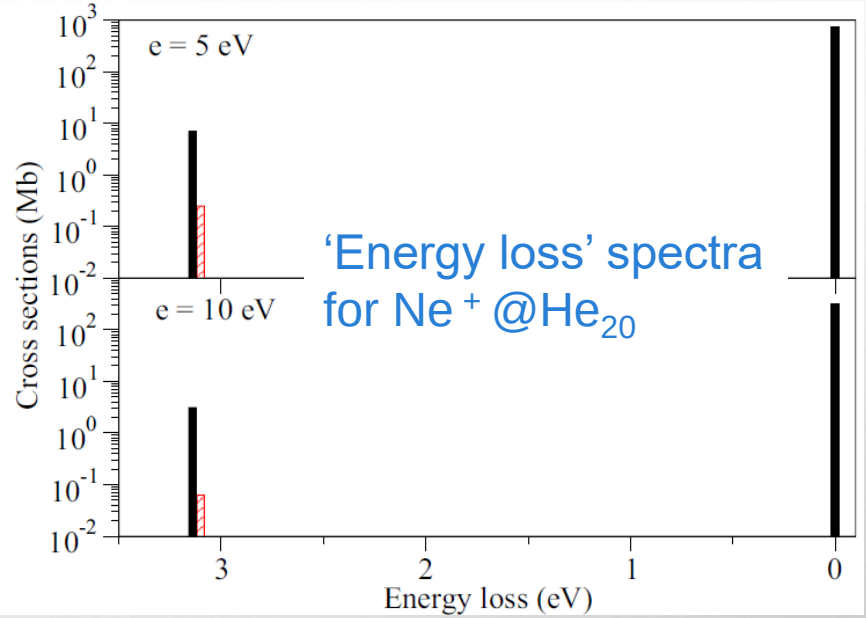
If KE of projectile > ~ 3 eV → ionization of He is possible

K. Gokhberg and L. S.Cederbaum, JPB **42** (2009) 231001, PRA **82** (2010) 052707

Interatomic Coulombic electron capture

$e + Ne^+ He \rightarrow Ne\ He^+ + e$ $\qquad$ $e + Ne^+@He_n \rightarrow Ne@He^+_n + e$





R: Ne-He distance (circles, calculated; lines, predicted)

$Ne^+@He_{20}$: 2000 geometries obtained from a MonteCarlo approach and then a sum over all Ne^+-He pairs for each

ICEC/elastic cross section ratio $\approx 10^{-2}$

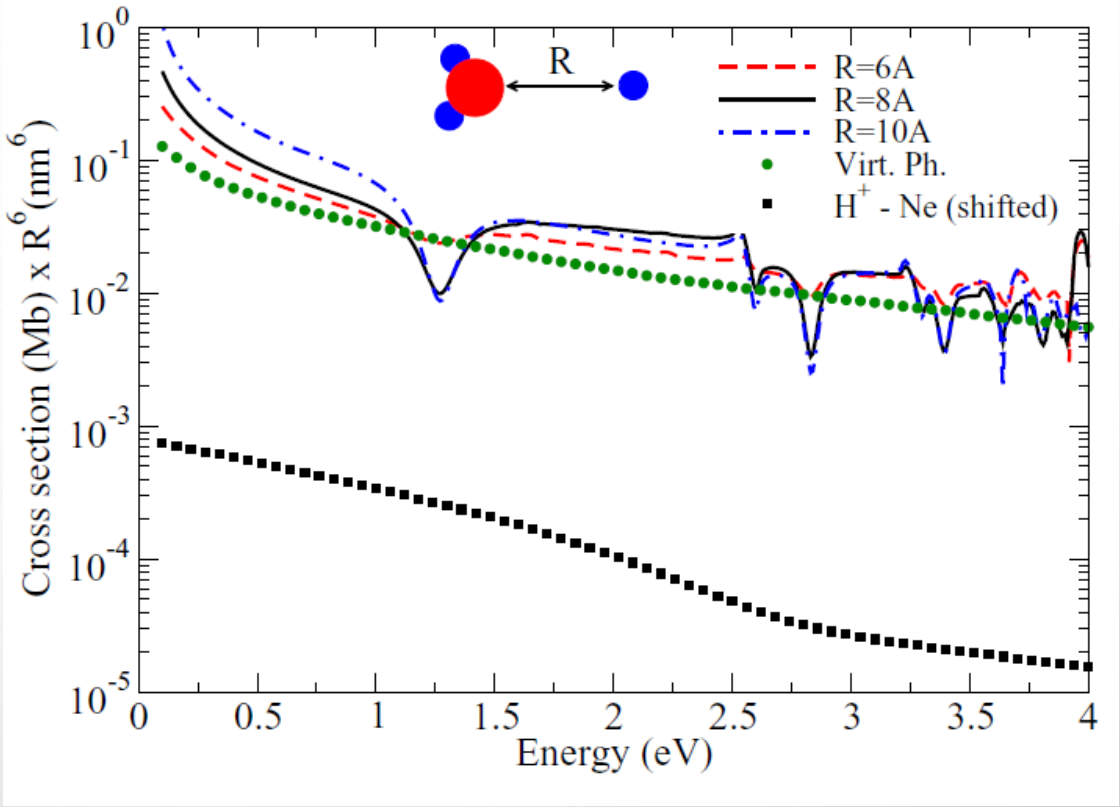
Inelastic/elastic cross section ratio, measured by EELS $\approx 2\ 10^{-2}$ (e.g. pyrimidine)

Sisourat *et al* PRA **98**, 020701(R) (2018)

Interatomic Coulombic electron capture

$$e + H^+ H_2O \rightarrow H\, H_2O^+ + e$$

Spin	Sym.	E (eV)	State
Singlet	B_1	0.0	$H(1s)\text{-}H_2O^+(1b_1^{-1})$
Triplet	B_1	0.0	$H(1s)\text{-}H_2O^+(1b_1^{-1})$
Singlet	A_1	2.29	$H(1s)\text{-}H_2O^+(3a_1^{-1})$
Triplet	A_1	2.29	$H(1s)\text{-}H_2O^+(3a_1^{-1})$
Singlet	A_1	2.50	$H^+\text{-}H_2O(\tilde{X})$
Singlet	B_2	6.66	$H(1s)\text{-}H_2O^+(1b_2^{-1})$
Triplet	B_2	6.66	$H(1s)\text{-}H_2O^+(1b_2^{-1})$
Triplet	$\boldsymbol{B_1}$	**9.29**	$\mathbf{H^+\text{-}H_2O^*(^3B_1)}$
Singlet	$\boldsymbol{B_1}$	**9.95**	$\mathbf{H^+\text{-}H_2O^*(^1B_1)}$
Triplet	$\boldsymbol{A_1}$	**11.93**	$\mathbf{H^+\text{-}H_2O^*(^3A_1)}$
Singlet	$\boldsymbol{A_1}$	**12.85**	$\mathbf{H^+\text{-}H_2O^*(^1A_1)}$
Triplet	B_1	14.70	$H(1s)\text{-}H_2O^+(^4B_1)$
Triplet	$\boldsymbol{B_2}$	**15.49**	$\mathbf{H^+\text{-}H_2O^*(^3B_2)}$
Triplet	$\boldsymbol{B_1}$	**15.74**	$\mathbf{H^+\text{-}H_2O^*(^3B_1)}$
Singlet	$\boldsymbol{B_1}$	**15.74**	$\mathbf{H^+\text{-}H_2O^*(^1B_1)}$
Singlet	$\boldsymbol{A_1}$	**15.87**	$\mathbf{H^+\text{-}H_2O^*(^1A_1)}$
Triplet	$\boldsymbol{A_1}$	**15.87**	$\mathbf{H^+\text{-}H_2O^*(^3A_1)}$
Singlet	$\boldsymbol{B_2}$	**16.69**	$\mathbf{H^+\text{-}H_2O^*(^1B_2)}$



ICEC cross section enhanced/supressed due to the presence of resonant neutral states

The presence of a cation near the molecules substantially changes the scattering processes

Molle *et al* PRA **103** (2021) 012808

Conclusions

- Electronically elastic and inelastic integral and differential cross sections can be calculated *ab initio* for:
  - small and mid-size molecules.
  - lower excited states
  - up to ~15-20 eV
- Break-up (dissociative excitation) harder to model: **work in progress.**
- 'Novel' process like ICEC have hardly been explored but could be significant.

Collaborators

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Ismanuel Rabadan, Madrid, Spain

Nicolas Sisourat et al., Paris, France

Software development: UCL, Charles University Prague, STFC, MBI, etc.

CoSeC
Computational Science Centre for Research Communities

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E L E V A T E