Reactive collisions of electrons with molecular cations

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Research topics

- partial differential equation methods in quantum mechanics

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Exact solution to the Schrödinger's equation with pseudo-Gaussian potential

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Felix Iacob[1, a)] *and* Marina Lute[2, b)]

Research topics

- differential geometric methods in physics

ELSEVIER

Physics Letters A

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On the geometric quantization of the ro-vibrational motion of homonuclear diatomic molecules

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Research topics

- collision theory of electrons on molecular cations

Study of bound and resonant states of NS molecule in the R-matrix approach

submitted
to

Journal of Physics B: Atomic, Molecular and Optical Physics

D_2^+, BeD^+, BeT^+, H_2^+, HD^+, ArH^+,
SH^+

Outline

1) Scattering technique in electron-ion collision
2) Research method
3) Applications, NS^+
4) MQDT mechanism on CH^+ cation,
   and how the cross-section undergoes changes by introducing different excited cores

Scattering technique in electron-ion collision

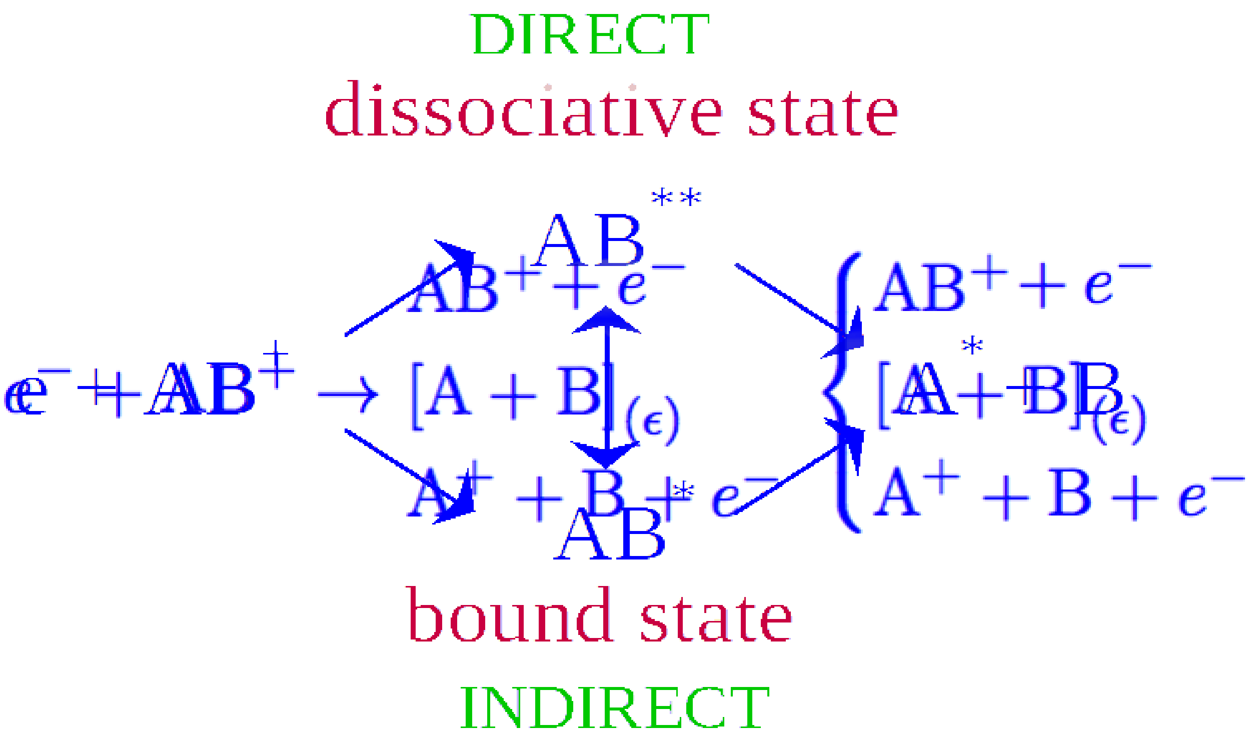
Fundamental processes:

$e^- (l) + AB^+(N_i^+, v_i^+) \rightarrow$	$AB^+ (N_f^+, v_f^+) + e^- (l')$	Ro-Vibrational (de)Excitation: VE(VdE)	
	$A + B$	Dissociative Recombination: DR	Rearrangement or Resonance scattering
	$A + B^+ + e^-$	Dissociative Excitation: DE	

Consider:

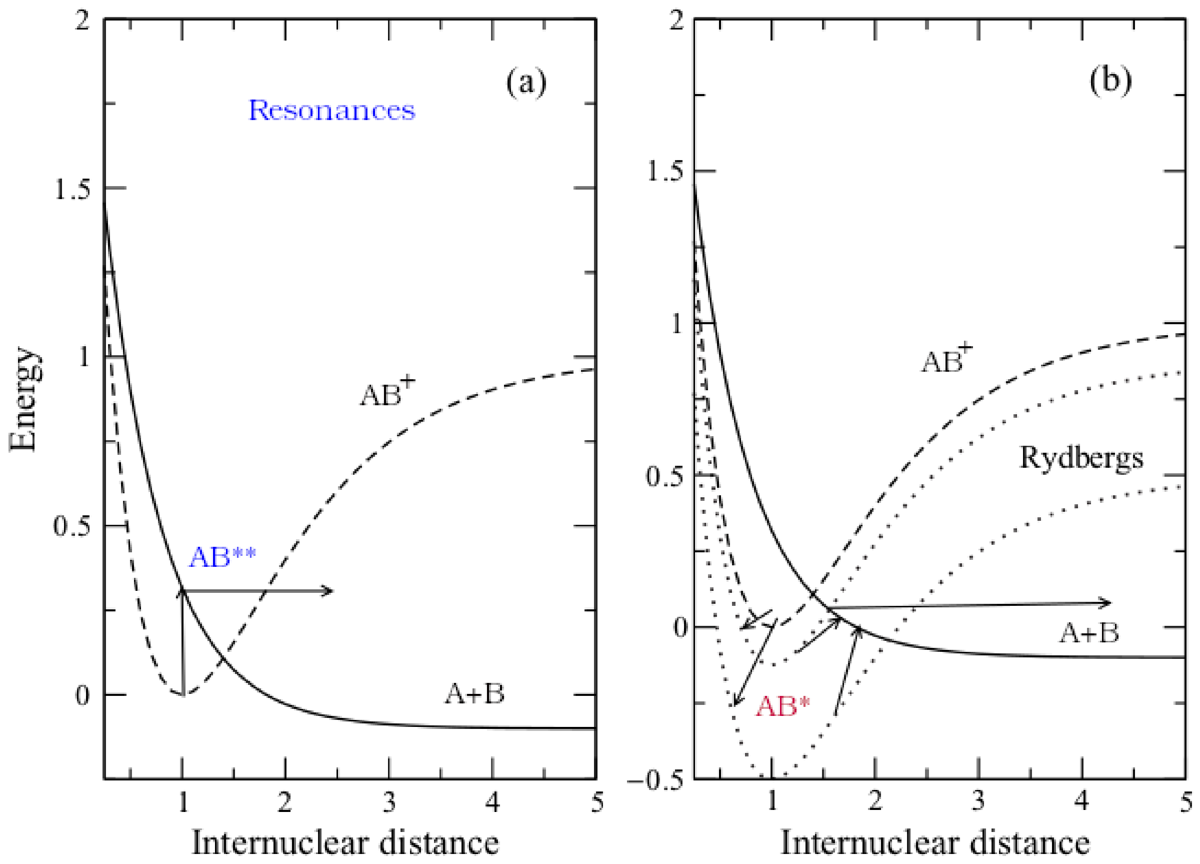
- partial wave of projectile, l
- internal structure of target, N_{pi}, v_i

Scattering technique in electron-ion collision



chemical reaction

Scattering technique in electron-ion collision

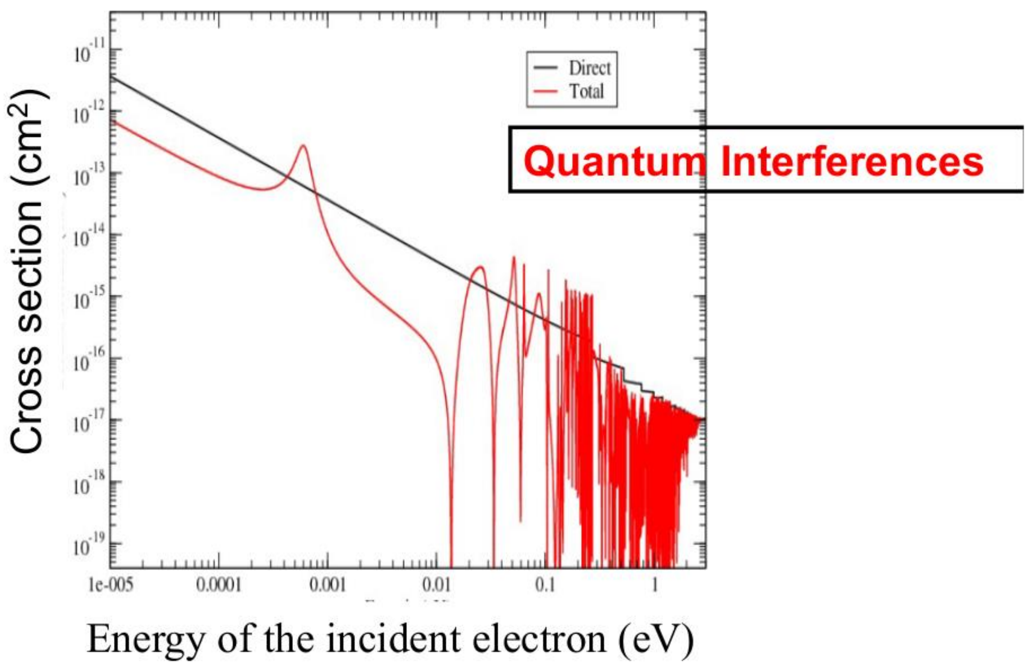


Born-Oppenheimer

Scattering technique in electron-ion collision

H_2^+: DR

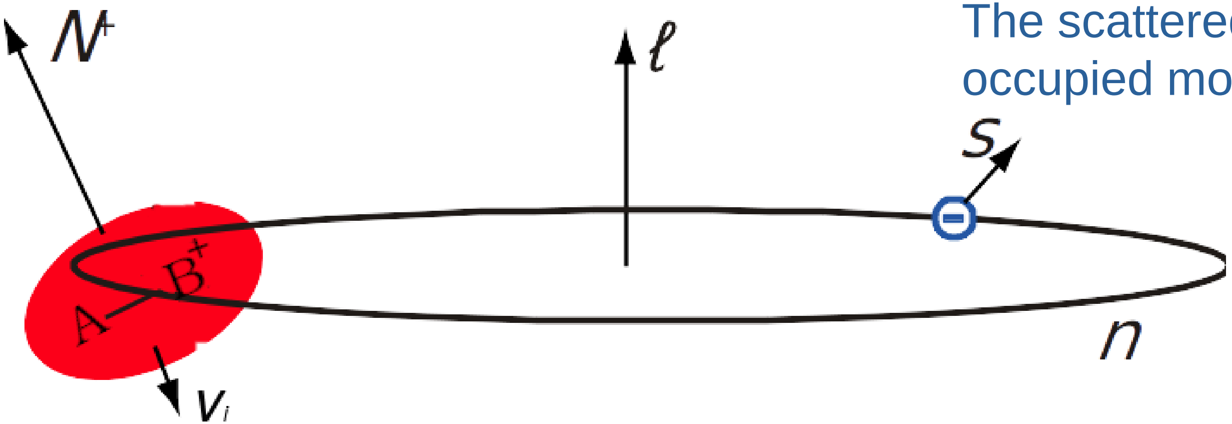
Total (direct & indirect) vs **direct** mechanisms



Super-excited molecular states

Electronic excitation emerges when:

- **intense** radiation arising from sources such as lasers, swift ions, or high-flux X-ray or electron pulses, interact with molecules.
- **low** electron collision with molecules, especially molecular cations



The scattered electron is viewed in the outermost occupied molecular orbital, called virtual orbital

Research method

I. Ab-Initio calculation involving multireference electronic structure configurations

Deliverables:

- Feshbach resonances
- bound mono-excited Rydberg states
- autoionization widths
- quantum defects

II. Multichannel Quantum Defect Theory

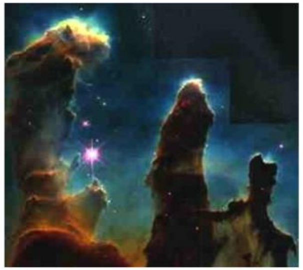
Deliverables:

- cross-sections
- thermal rate coefficients

Result applies to molecular dynamics

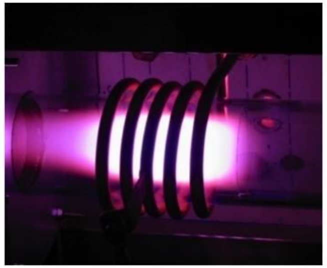
incorporating rate constants as kinetic constraints

Interstellar molecular clouds

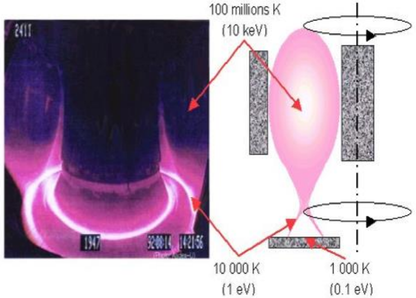


Planetary atmospheres

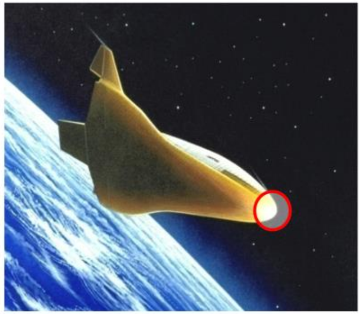
Cold laboratory plasmas



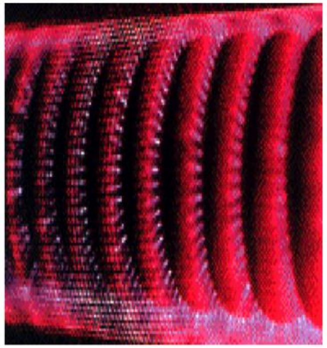
At the wall of the fusion devices (ITER) project



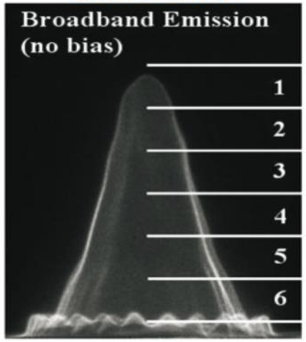
Hypersonic entry of spacecrafts



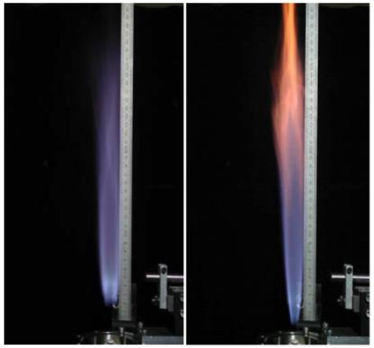
Plasma-assisted depollution



Electric-field-assisted combustion

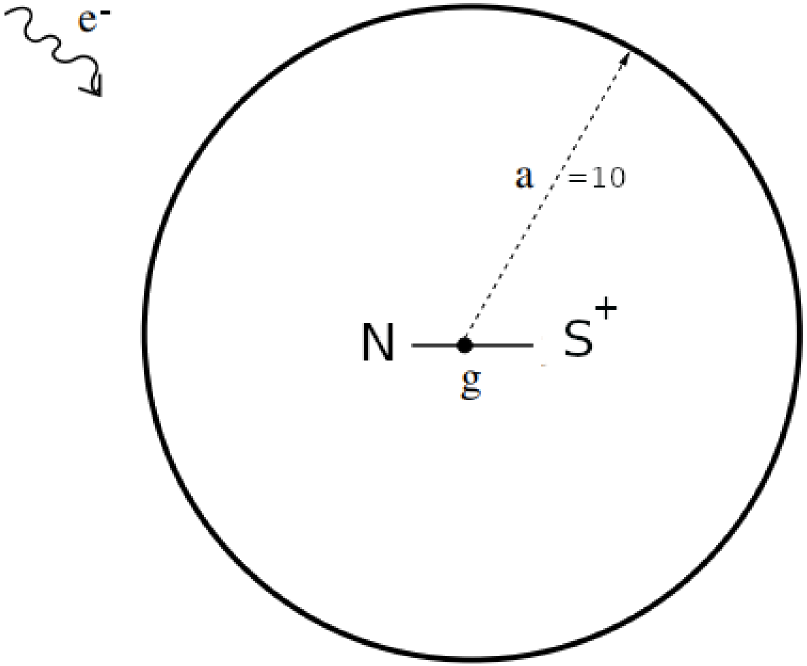


Plasma-assisted-combustion



$e^- + NS^+$ scattering, R-matrix method

- In the **inner region**, exchange and other short range, possibly non-local, interactions are important
- In the **outer region** it is assumed that only long range potentials will affect the scattering



Asymptotic channel i is a state
1) of target with energy E_i^N
2) and of the scattering electron of energy E with partial wave , (l_i, m_i) .

The wavenumber of the scattering electron associated with this channel $k_i^2 = 2(E - E_i^N)$.
A channel is said to be **open** if $k_i^2 \geq 0$
The wave function of the outer region solutions:

$$F_{ij} \sim \frac{1}{\sqrt{k_i}} (\sin \theta_i \delta_{ij} + \cos \theta_i K_{ij})$$

$$\mathbf{S} = \frac{(\mathbf{1} + \mathrm{i}\mathbf{K})}{(\mathbf{1} - \mathrm{i}\mathbf{K})}$$

$$\delta(E) = \sum_i \arctan(K_{ii}^D).$$

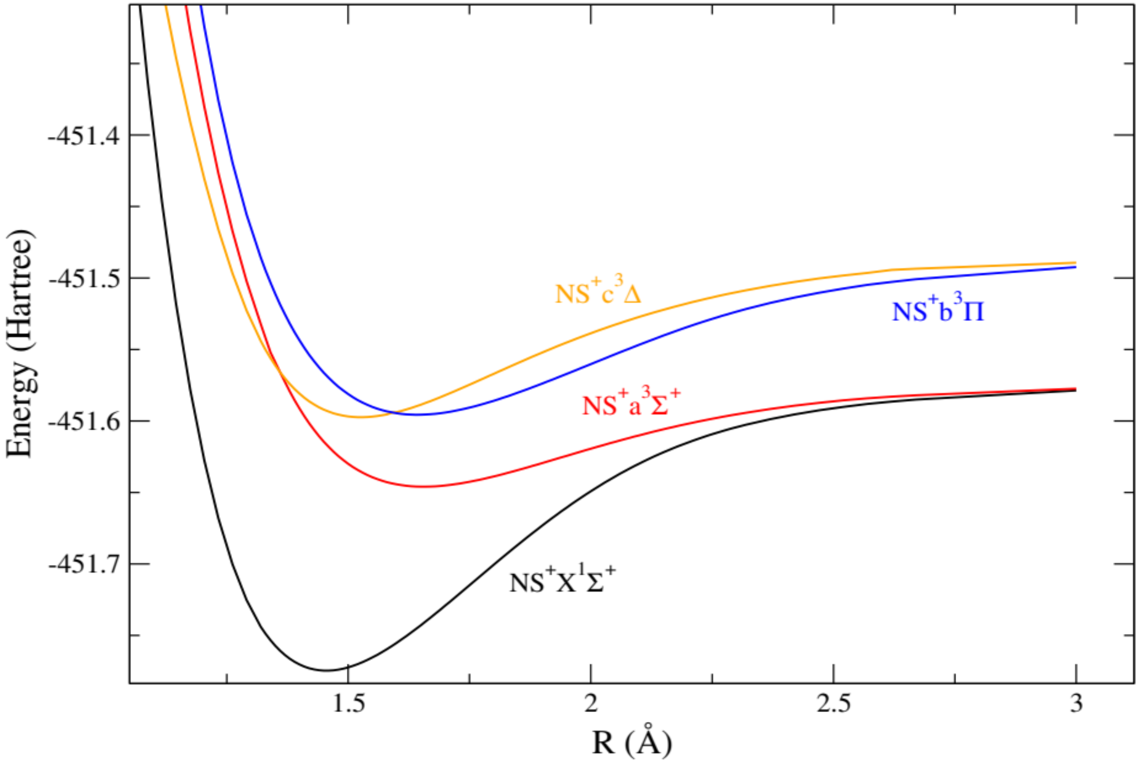
NS^+ target

Multi-Configuration, Self-Consistent-Field approach
Complete Active Space - CASSCF
C_{2v} point group
code symmetry
Ordering:

A_1 B_1 B_2 A_2
FRO(4,1,1,0)
CAS(4,2,2,0)

OCC(8,3,3,0)
VIR(2,1,1,1)

TOT(10,4,4,1)



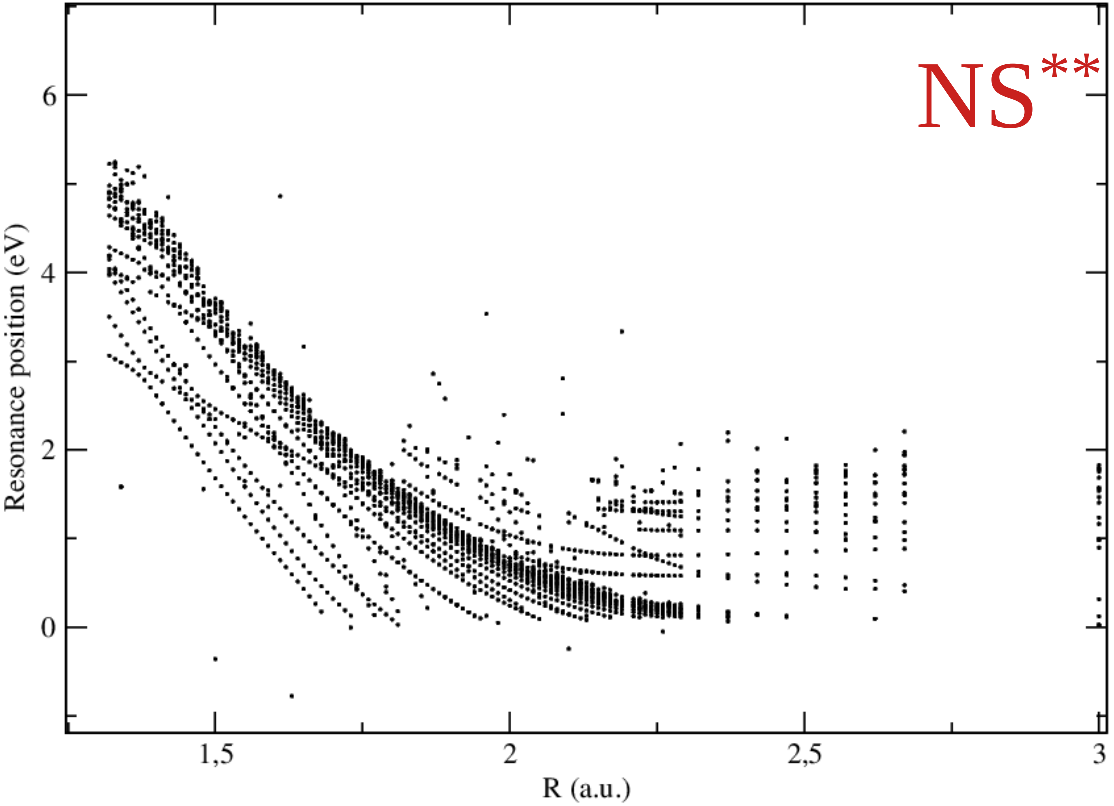
e^- + NS^+ scattering, R-matrix method

Feshbach resonances:

temporary trapping of an electron to form a quasibound or short-lived state of neutral in continuum of ion.

-
-

energy of ion is zero reference

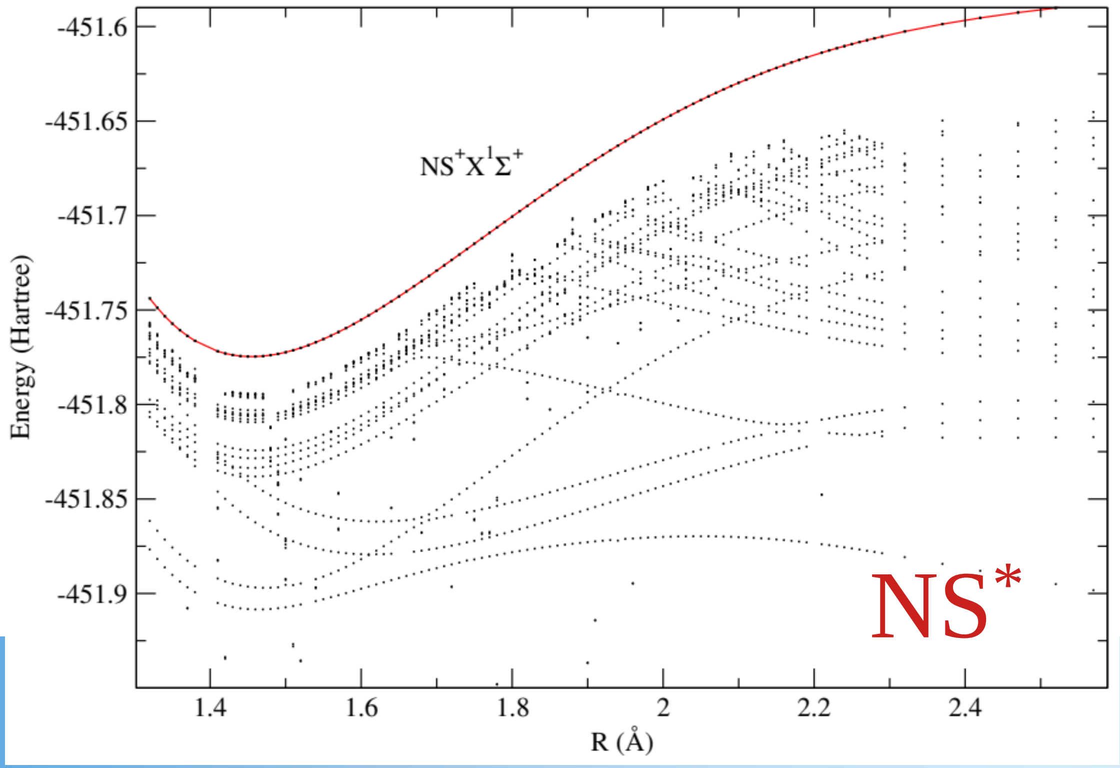


$e^- + NS^+$ scattering, R-matrix method

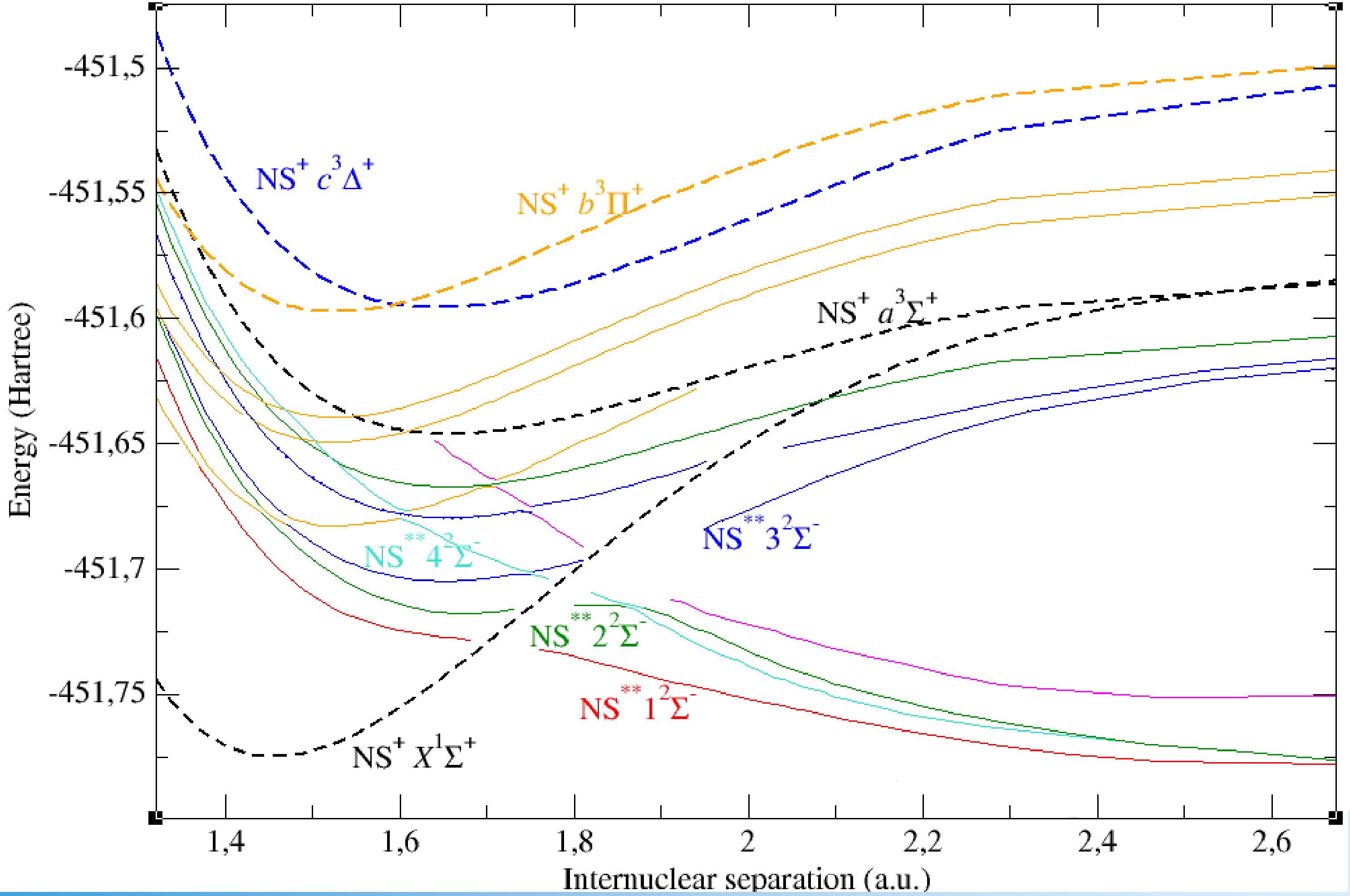
Bound states

temporary trapping of an electron to form a quasibound or short-lived state of neutral,

are found by performing the scattering calculations at negative energy.



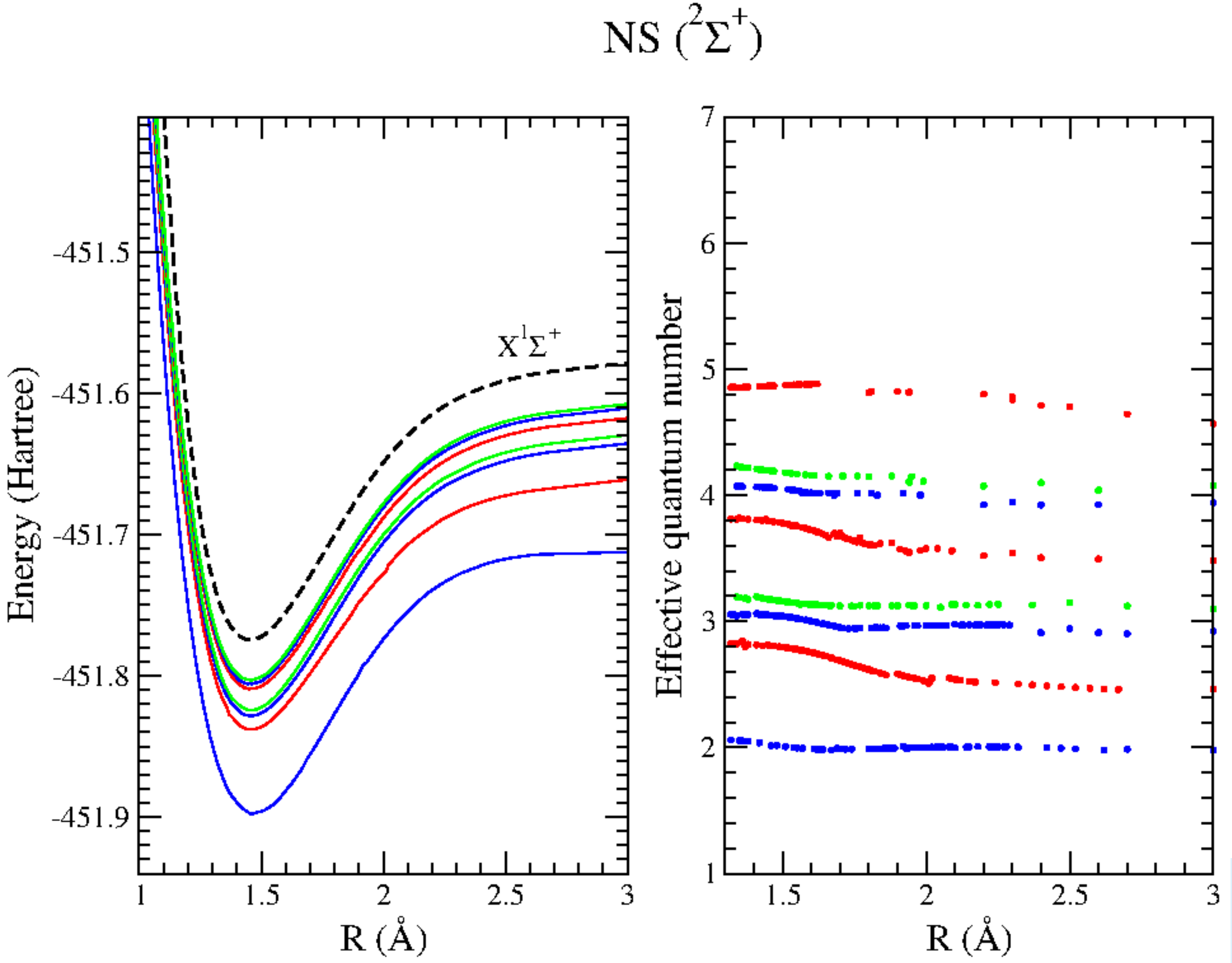
Diabatization: PEC of NS*,NS**



Diabatization: PEC of NS*

partial wave characterizing the incoming electron:

- blue s-state,
- red p-state,
- green d-state



Multichannel Quantum Defect Theory

The minimum set of **input data** for an MQDT:

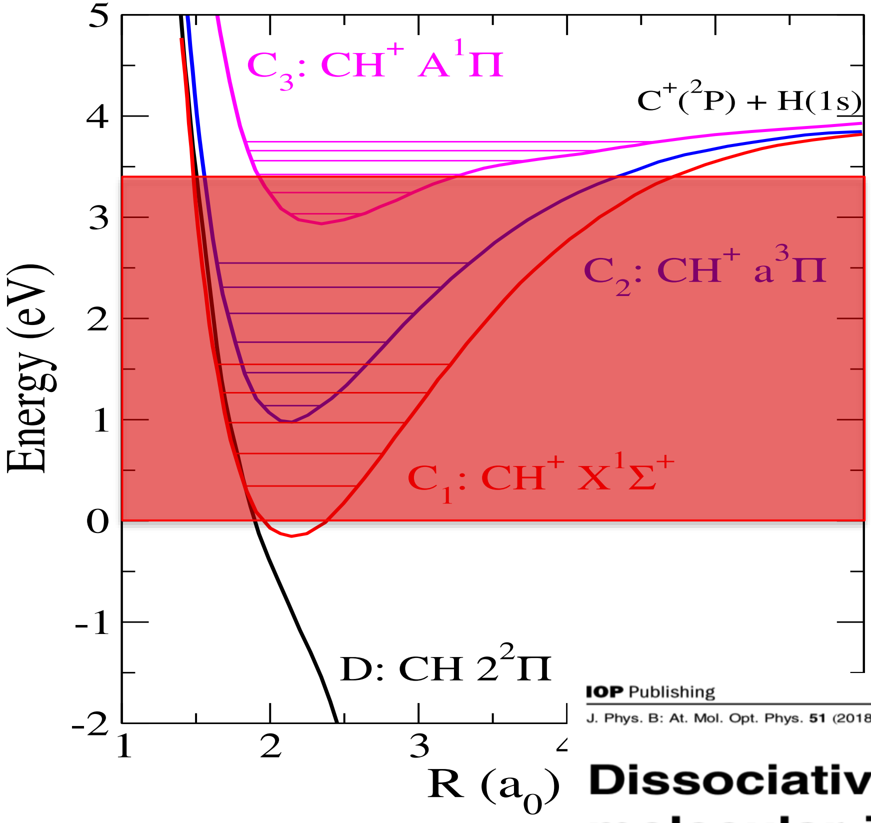
- PEC of the ground state of the molecular ion,
- PEC of the dissociative states of the neutral,
- Widths, electronic couplings of the dissociative states with the ionization continuum of the ground state of ion,
- Quantum defects of the each Rydberg series converging to the ground state of the ion.

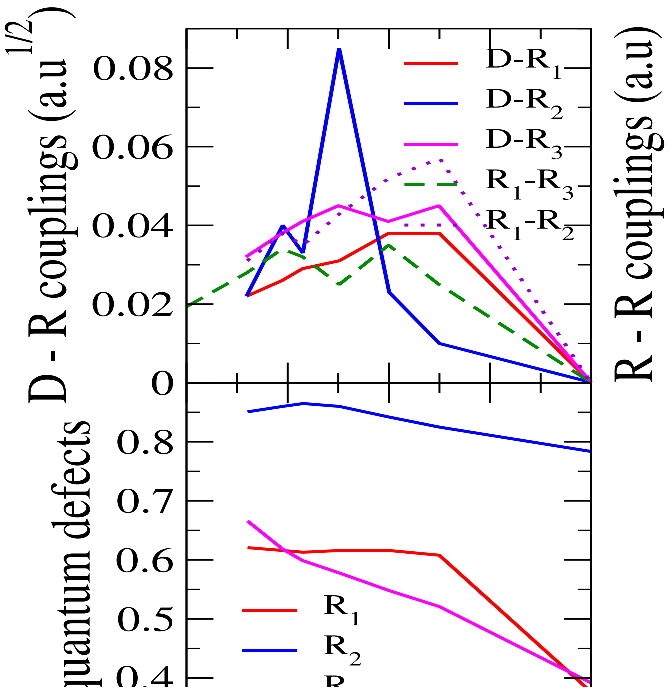
MQDT $\longrightarrow$ cross-sections,

thermal rate coefficients

CH^+: molecular data

MQDT mechanism





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Dissociative recombination of the CH^+ molecular ion at low energy

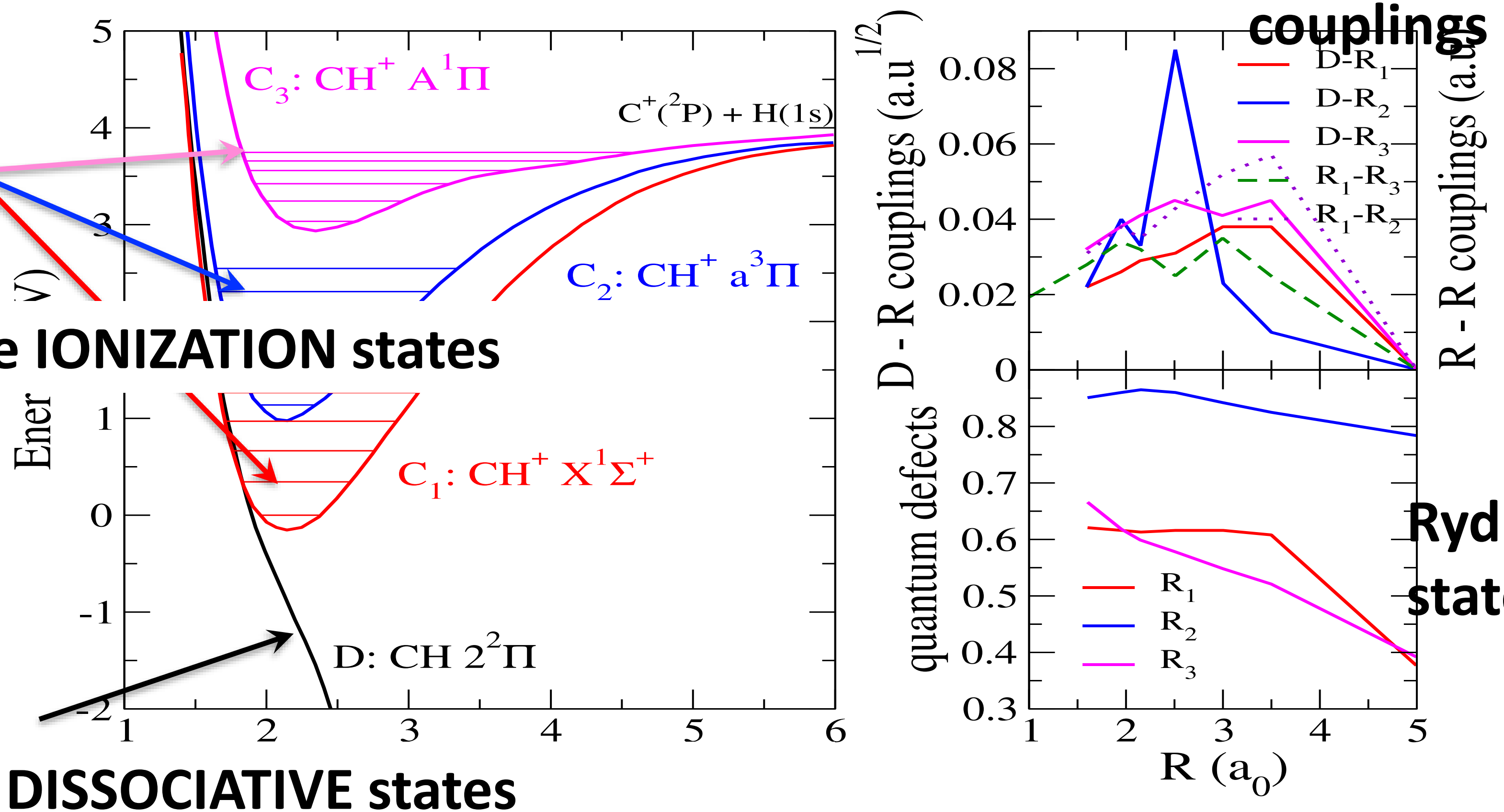
K Chakrabarti[1,2], J Zs Mezei[1,3,4], O Motapon[5], A Faure[6], O Dulieu[7], K Hassouni[3] and I F Schneider[1,7]

CH^+: molecular data

Valence-Rydberg couplings

ION

Valence IONIZATION states



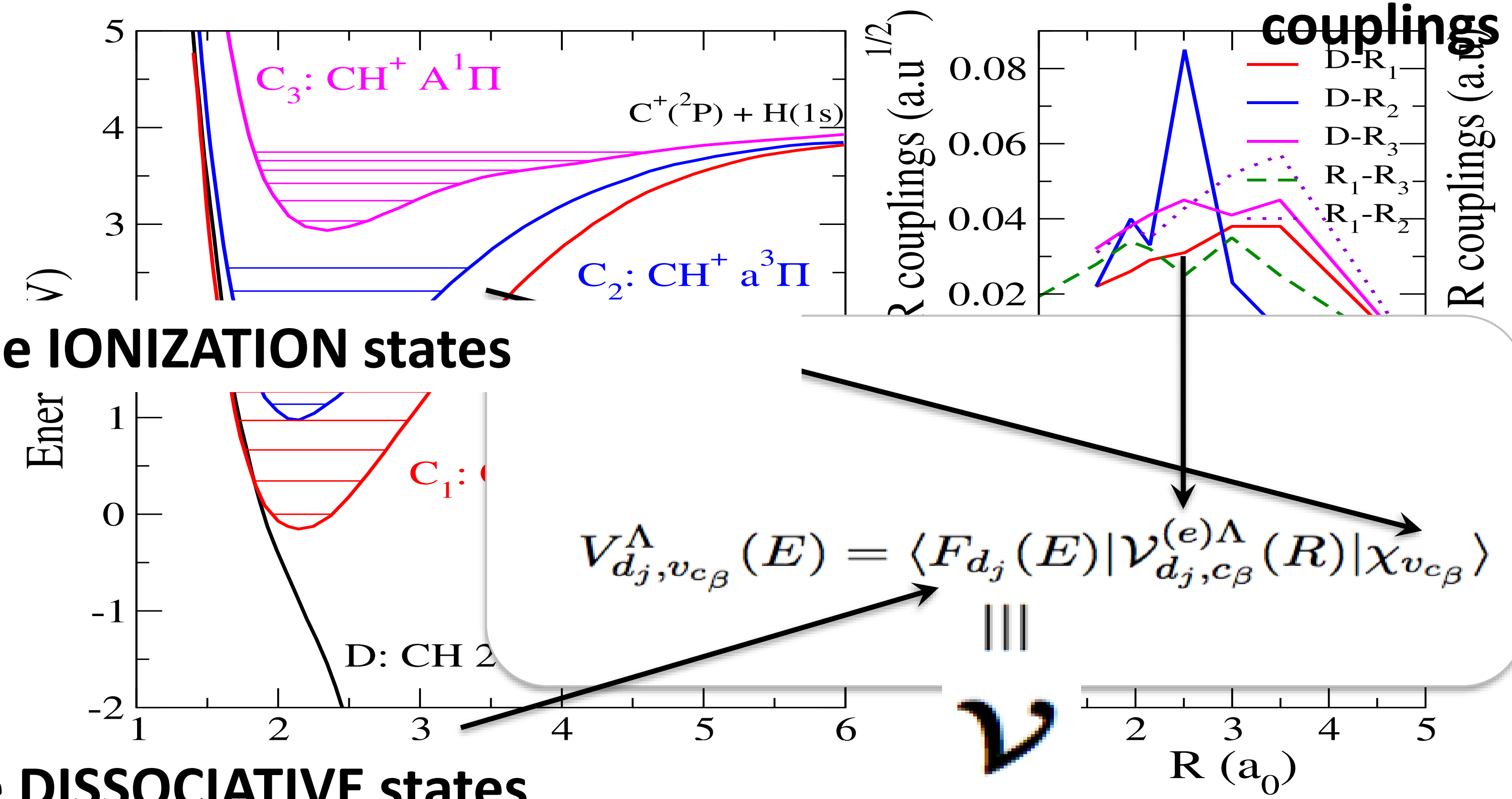
Rydberg states

Valence DISSOCIATIVE states

CH^+: molecular data

Valence-Rydberg couplings

ION



Valence IONIZATION states

berg

es

$$V^{\Lambda}_{d_j,v_{c_\beta}}(E) = \langle F_{d_j}(E) | \mathcal{V}^{(e)\Lambda}_{d_j,c_\beta}(R) | \chi_{v_{c_\beta}} \rangle$$

$$|||$$

$$\mathcal{V}$$

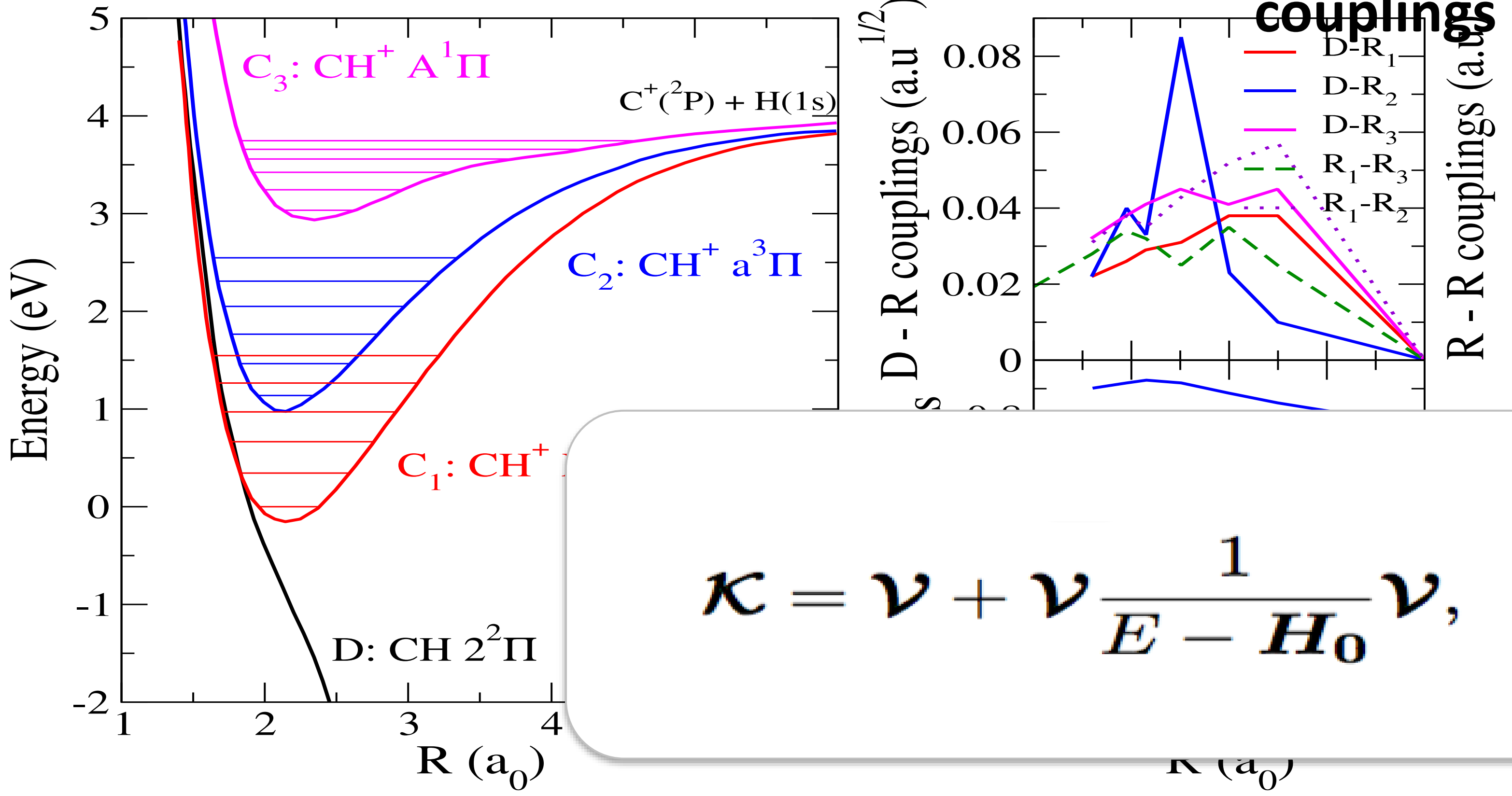
Valence DISSOCIATIVE states

1.) Vibronic interaction matrix

CH^+: molecular data

Valence-Rydberg couplings

ION



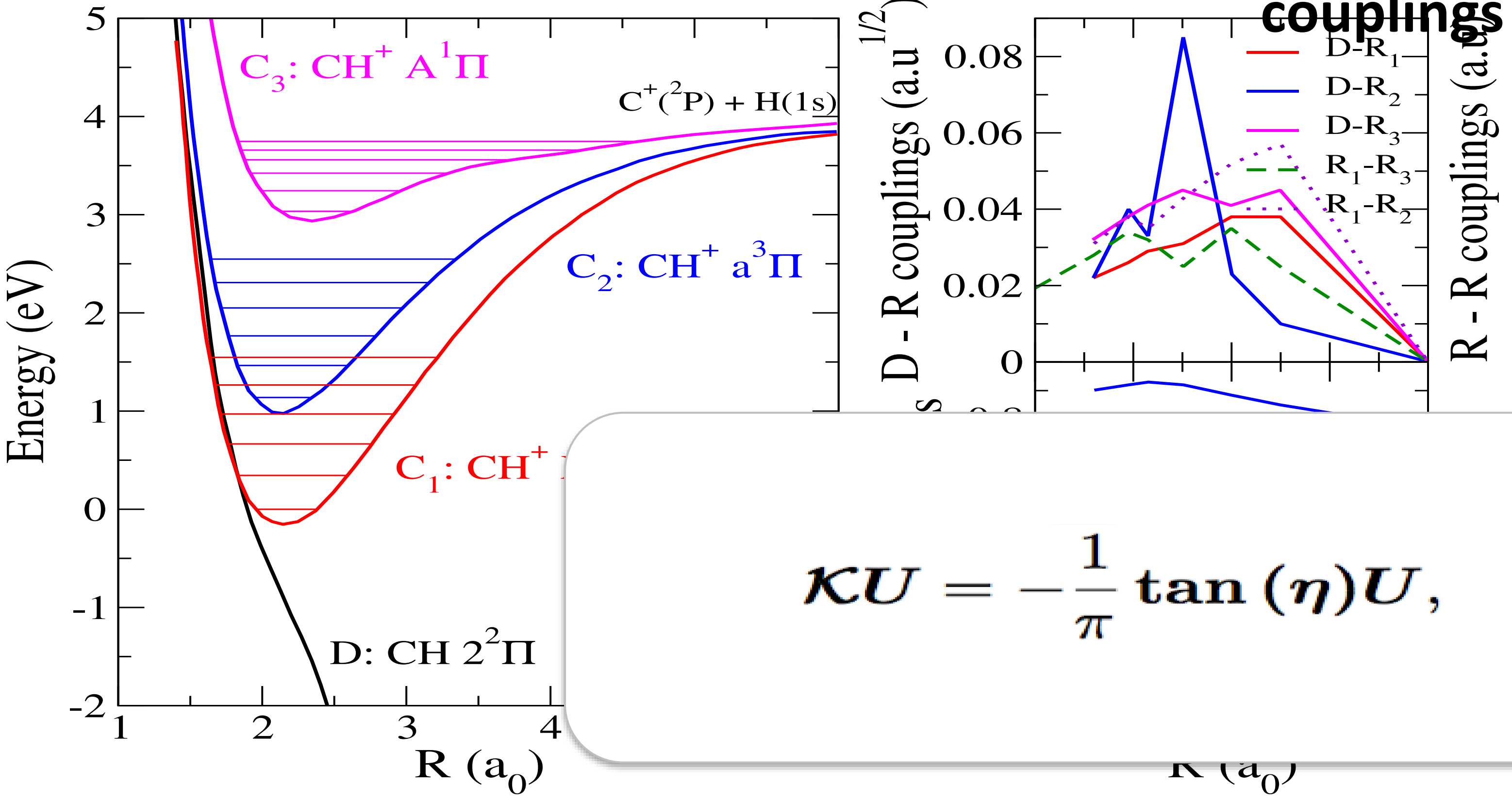
$$\mathcal{K} = \mathcal{V} + \mathcal{V}\frac{1}{E - H_0}\mathcal{V},$$

2.) Lippmann-Schwinger equation: K-matrix

CH^+: molecular data

Valence-Rydberg couplings

ION



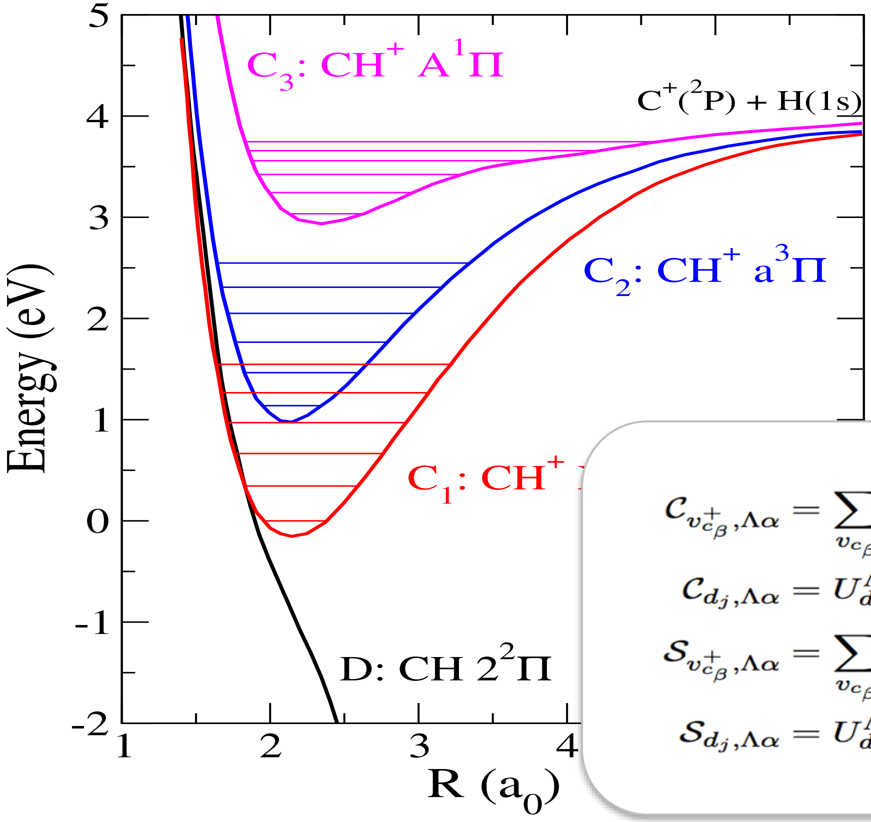
$$\boldsymbol{\mathcal{K}U} = -\frac{1}{\pi}\tan(\boldsymbol{\eta})\boldsymbol{U},$$

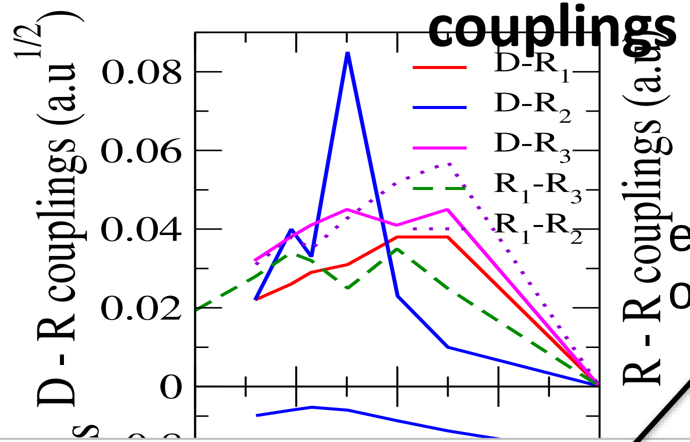
3.) Diagonalization of the K-matrix

CH^+: molecular data

ION

Valence-Rydberg couplings





$$\mathcal{C}_{v^+_{c_\beta},\Lambda\alpha} = \sum_{v_{c_\beta}} U^{\Lambda}_{v_{c_\beta},\alpha} \left\langle \chi_{v^+_{c_\beta}}(R) \left| \cos\left(\pi\mu^{\Lambda}_{c_\beta}(R) + \eta^{\Lambda}_{\alpha}\right) \right| \chi_{v_{c_\beta}}(R) \right\rangle$$

$$\mathcal{C}_{d_j,\Lambda\alpha} = U^{\Lambda}_{d_j,\alpha} \cos \eta^{\Lambda}_{\alpha}$$

$$\mathcal{S}_{v^+_{c_\beta},\Lambda\alpha} = \sum_{v_{c_\beta}} U^{\Lambda}_{v_{c_\beta},\alpha} \left\langle \chi_{v^+_{c_\beta}}(R) \left| \sin\left(\pi\mu^{\Lambda}_{c_\beta}(R) + \eta^{\Lambda}_{\alpha}\right) \right| \chi_{v_{c_\beta}}(R) \right\rangle$$

$$\mathcal{S}_{d_j,\Lambda\alpha} = U^{\Lambda}_{d_j,\alpha} \sin \eta^{\Lambda}_{\alpha},$$

eigenvalues of K matrix

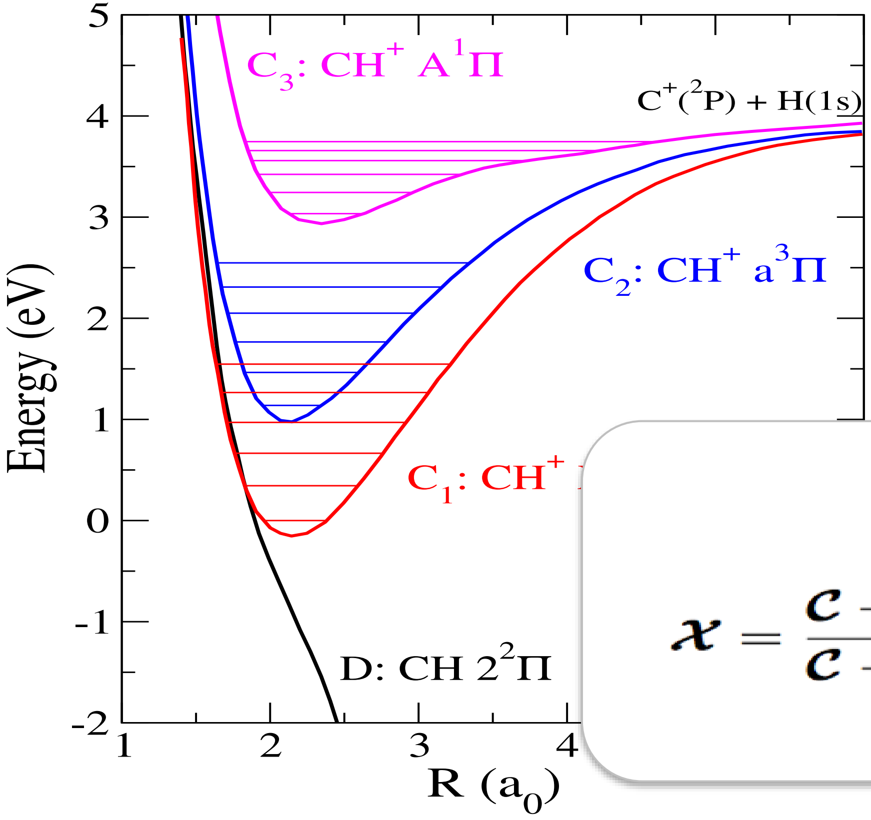
Quantum defect

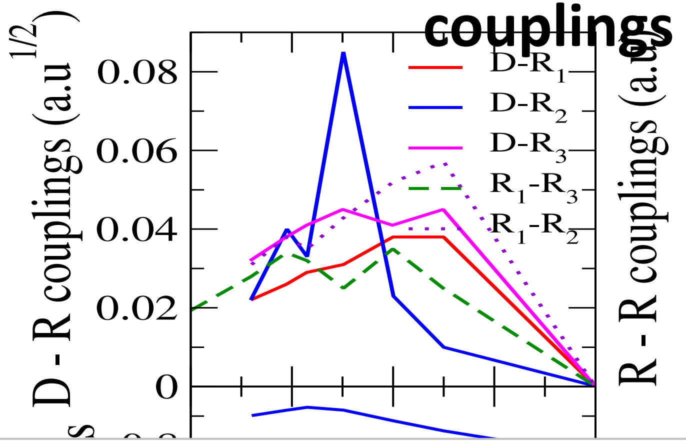
4.) Frame transformation

CH^+: molecular data

Valence-Rydberg couplings

ION





"o" : open channels

$$\mathcal{X} = \frac{\mathcal{C} + i\mathcal{S}}{\mathcal{C} - i\mathcal{S}} \qquad \mathcal{X} = \begin{pmatrix} X_{oo} & X_{oc} \\ X_{co} & X_{cc} \end{pmatrix}$$

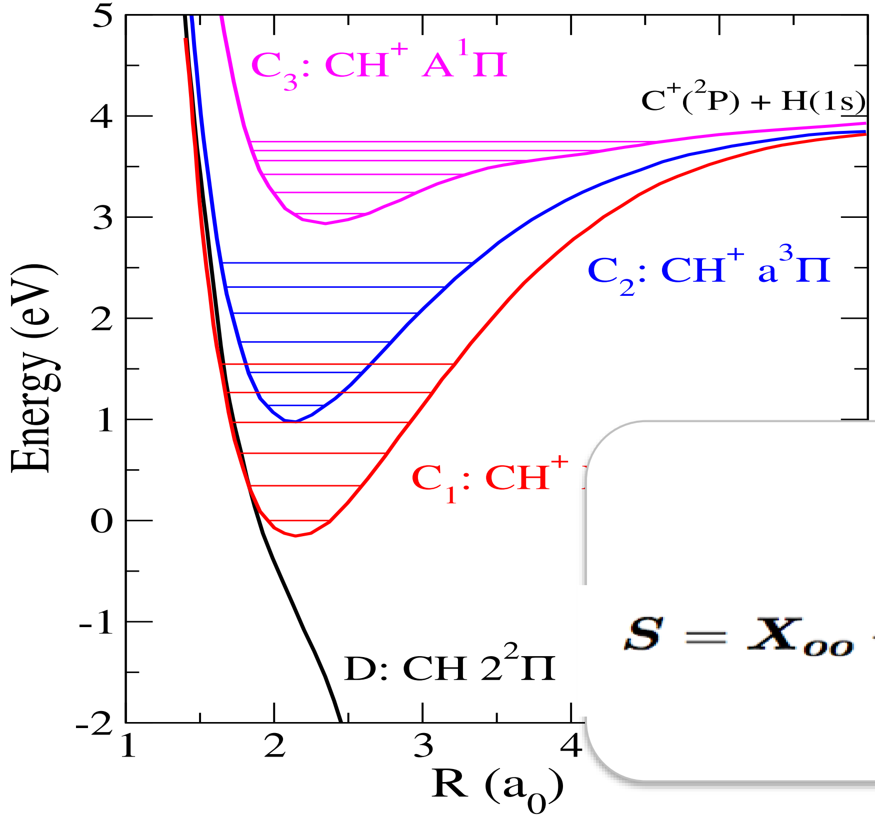
"c" : closed channels

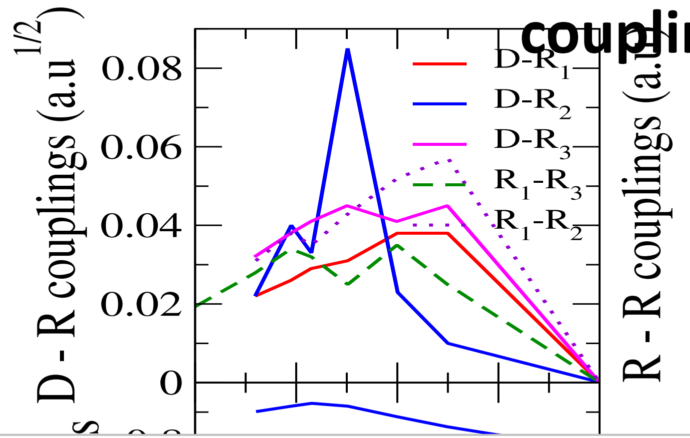
5.) Cayley transform

CH^+: molecular data

Valence-Rydberg couplings

ION





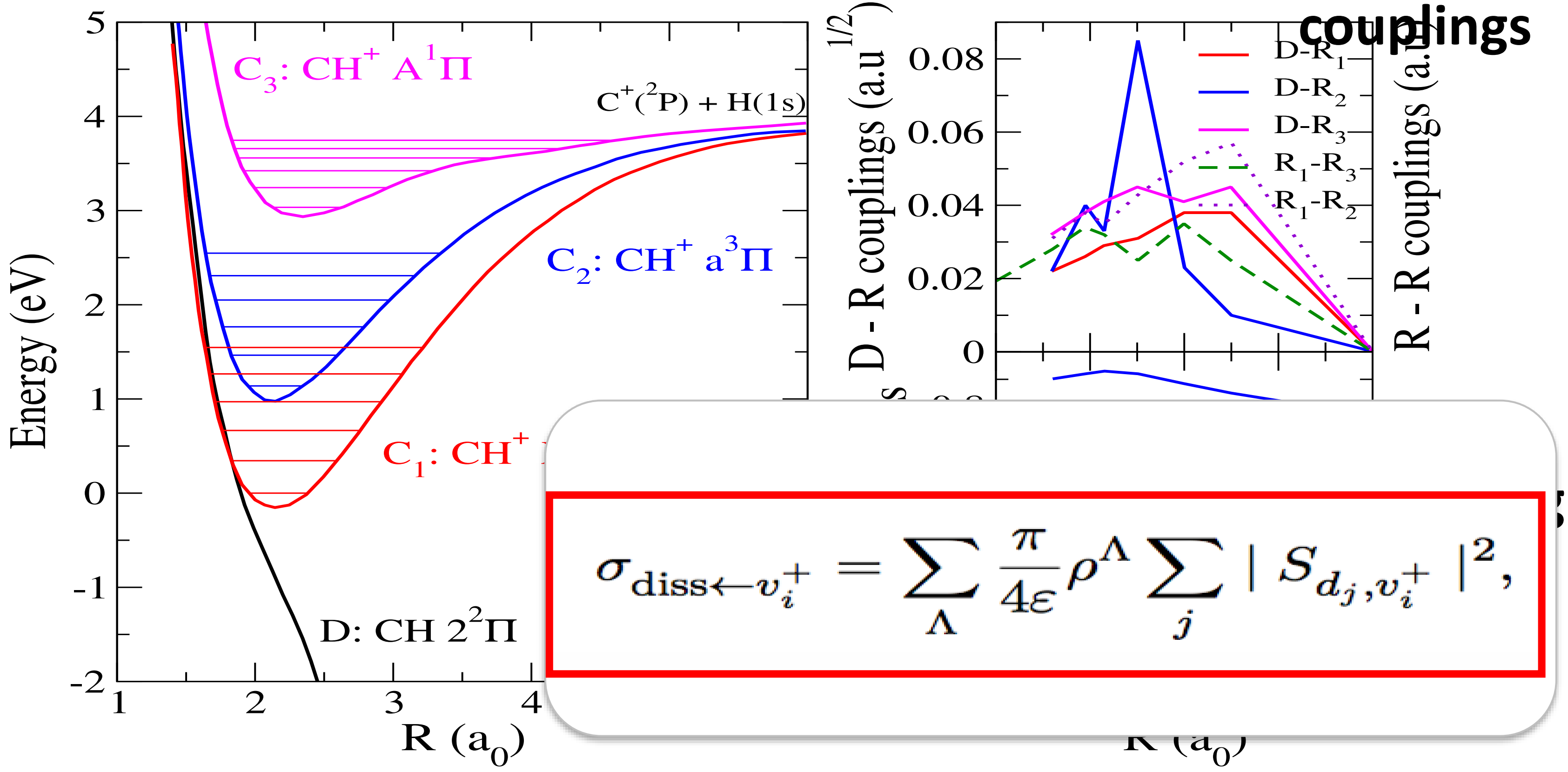
$$\boldsymbol{S} = \boldsymbol{X}_{oo} - \boldsymbol{X}_{oc}\frac{1}{X_{cc} - \exp(-i2\pi\boldsymbol{\nu})}\boldsymbol{X}_{co}.$$

6.) Scattering matrix: elimination of closed channels

CH^+: molecular data

Valence-Rydberg couplings

ION

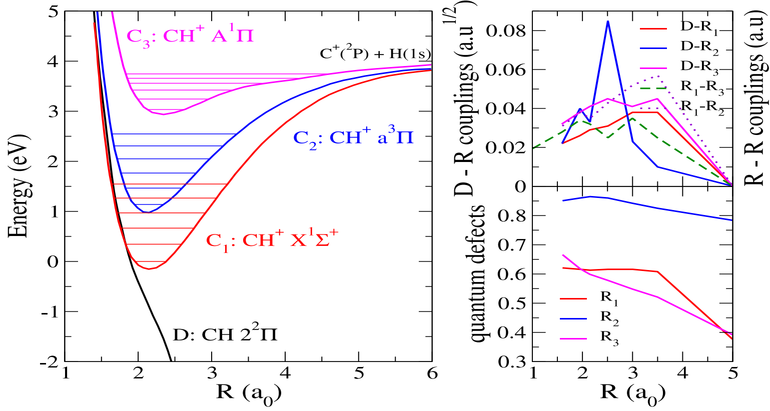


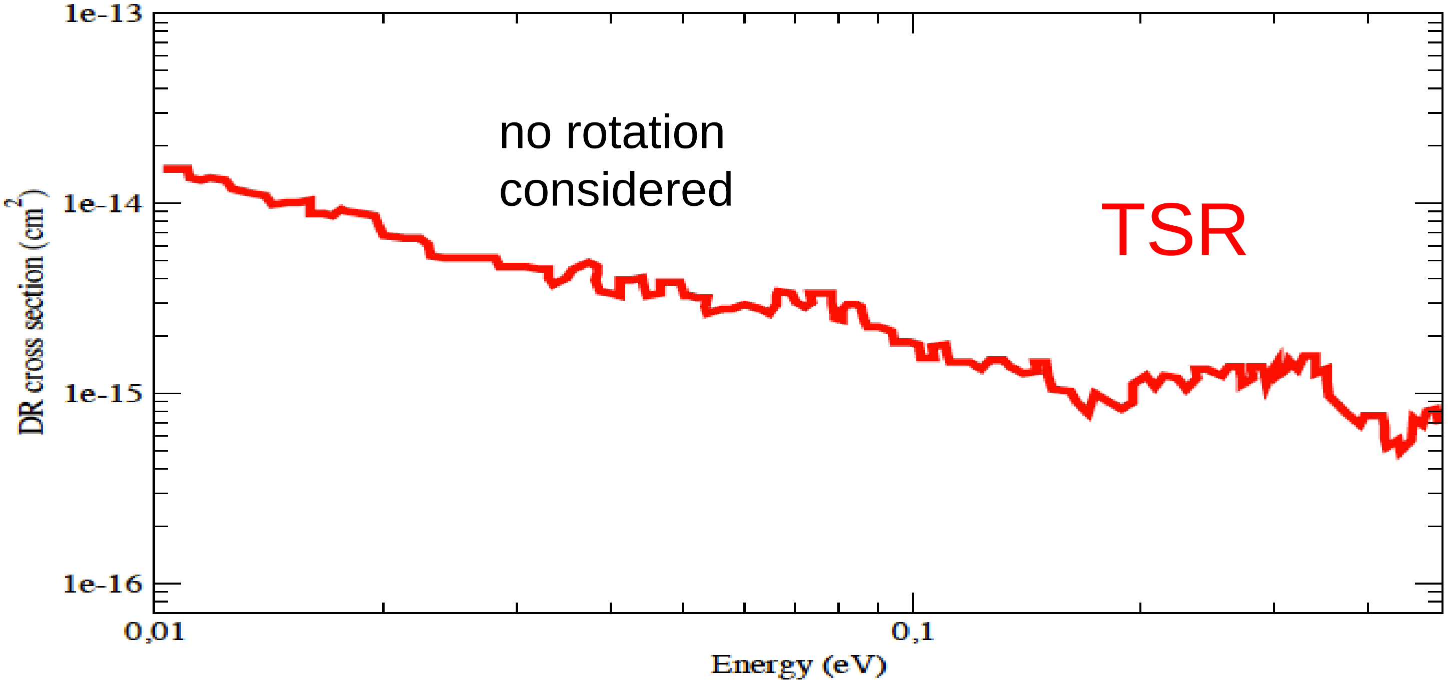
$$\sigma_{diss \leftarrow v_i^+} = \sum_{\Lambda} \frac{\pi}{4\varepsilon} \rho^{\Lambda} \sum_{j} \mid S_{d_j, v_i^+} \mid^2,$$

7.) Cross section

CH^+: DR cross section

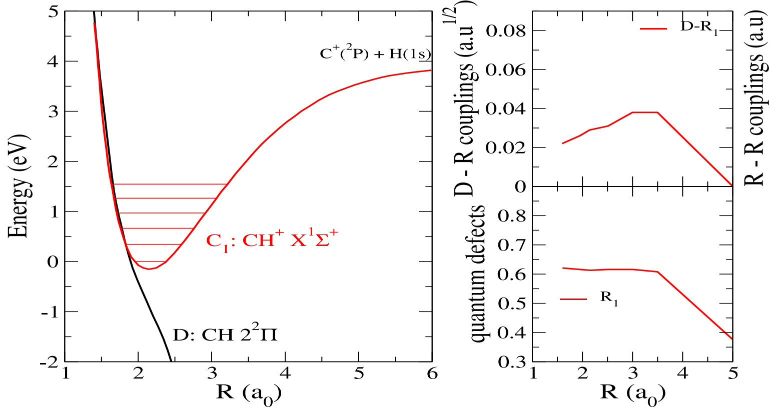
Test Storage Ring experiment

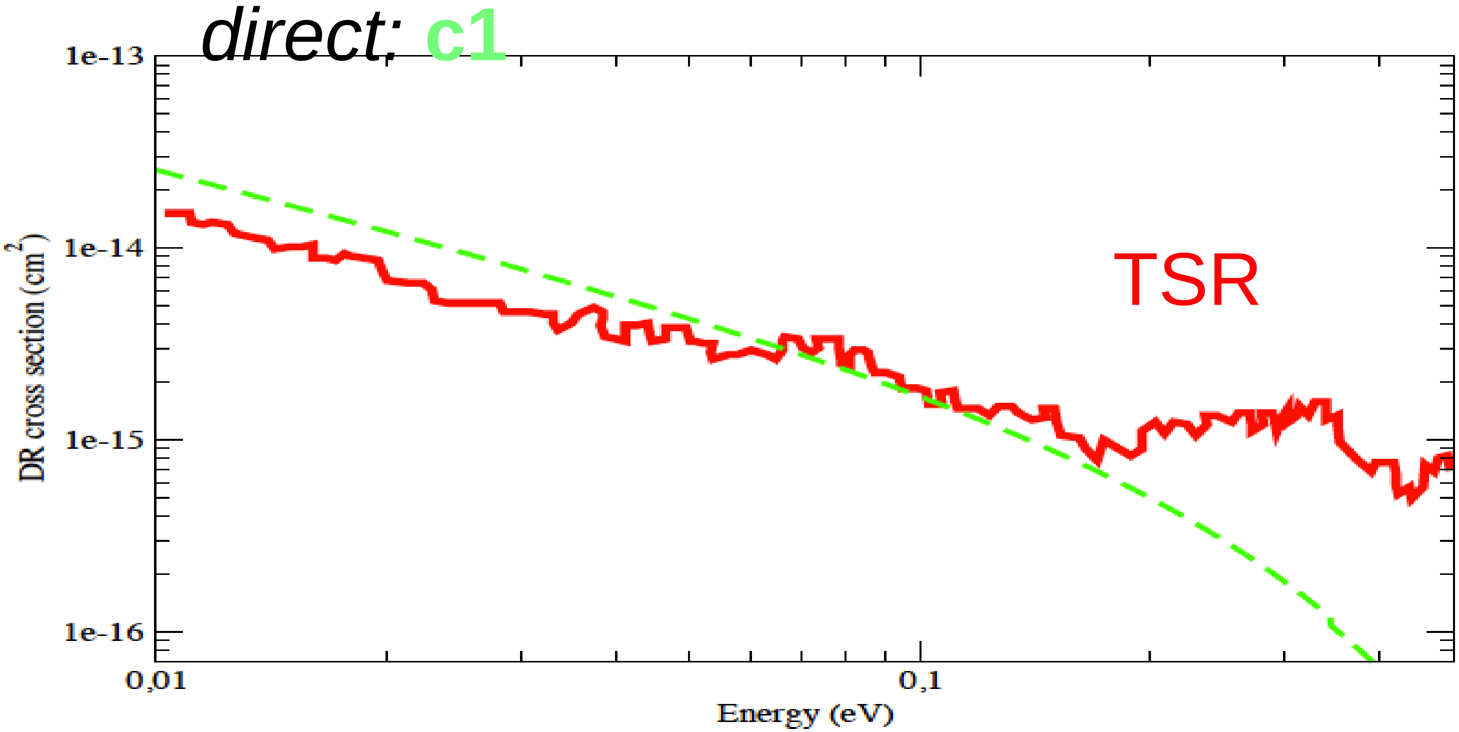




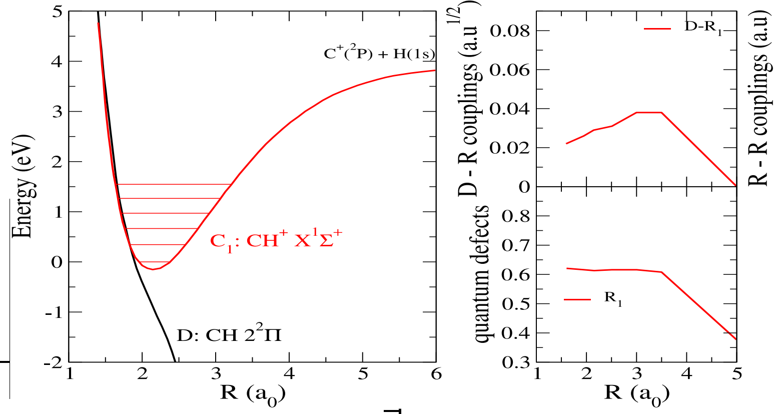
CH⁺: DR cross section

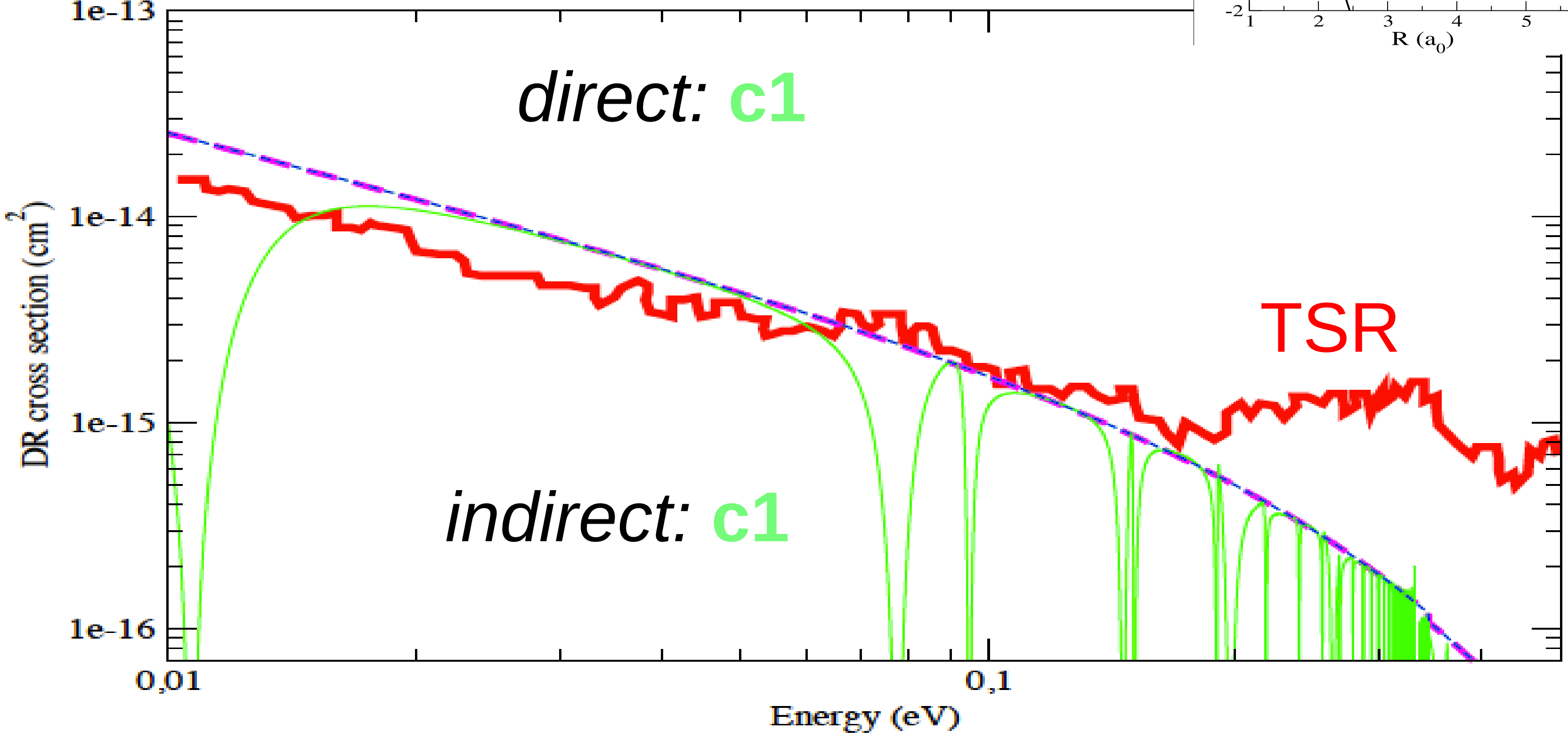
no rotation considered



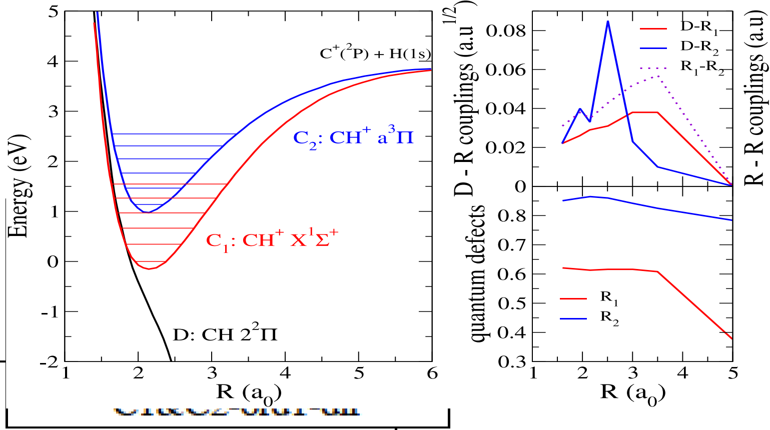


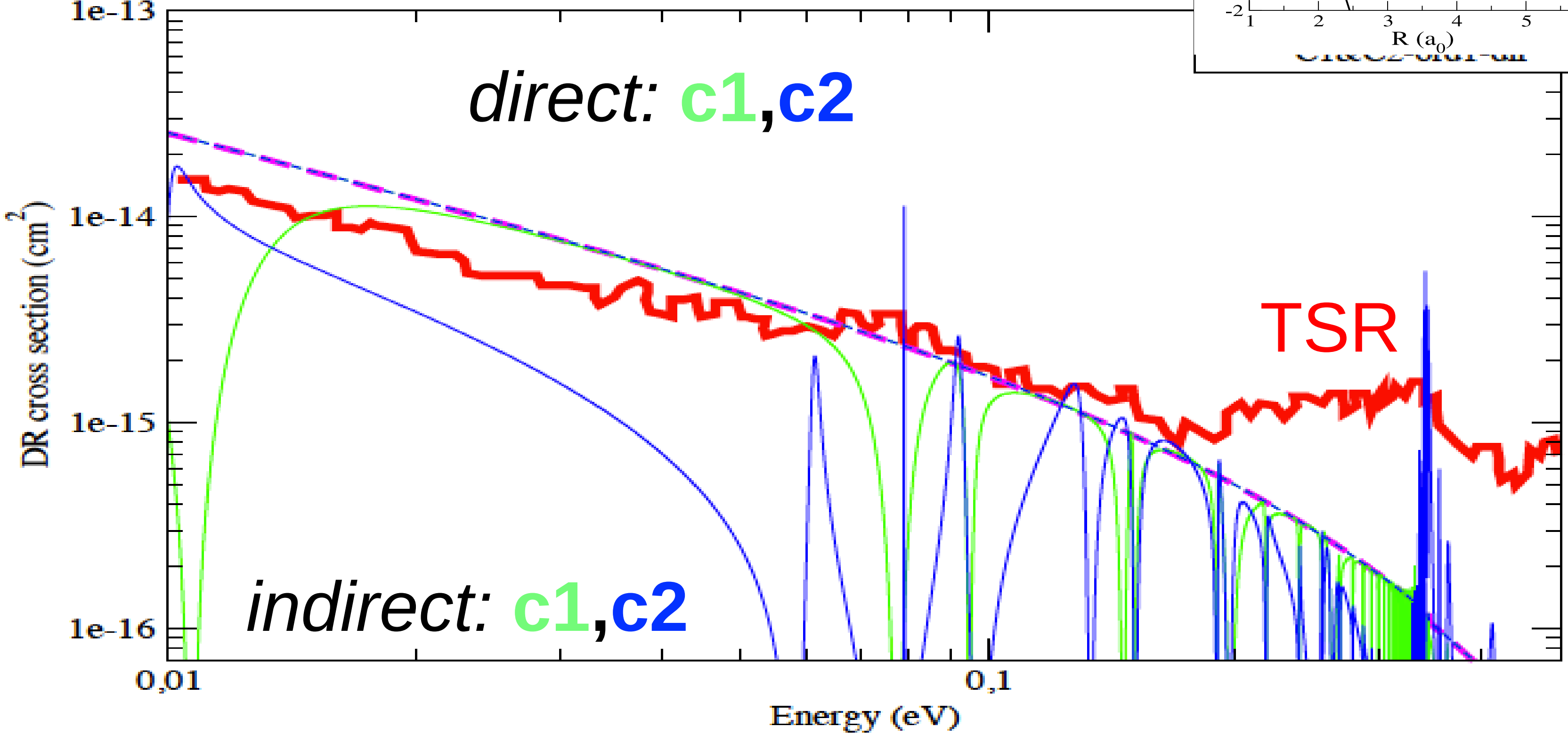
CH^+: DR cross section



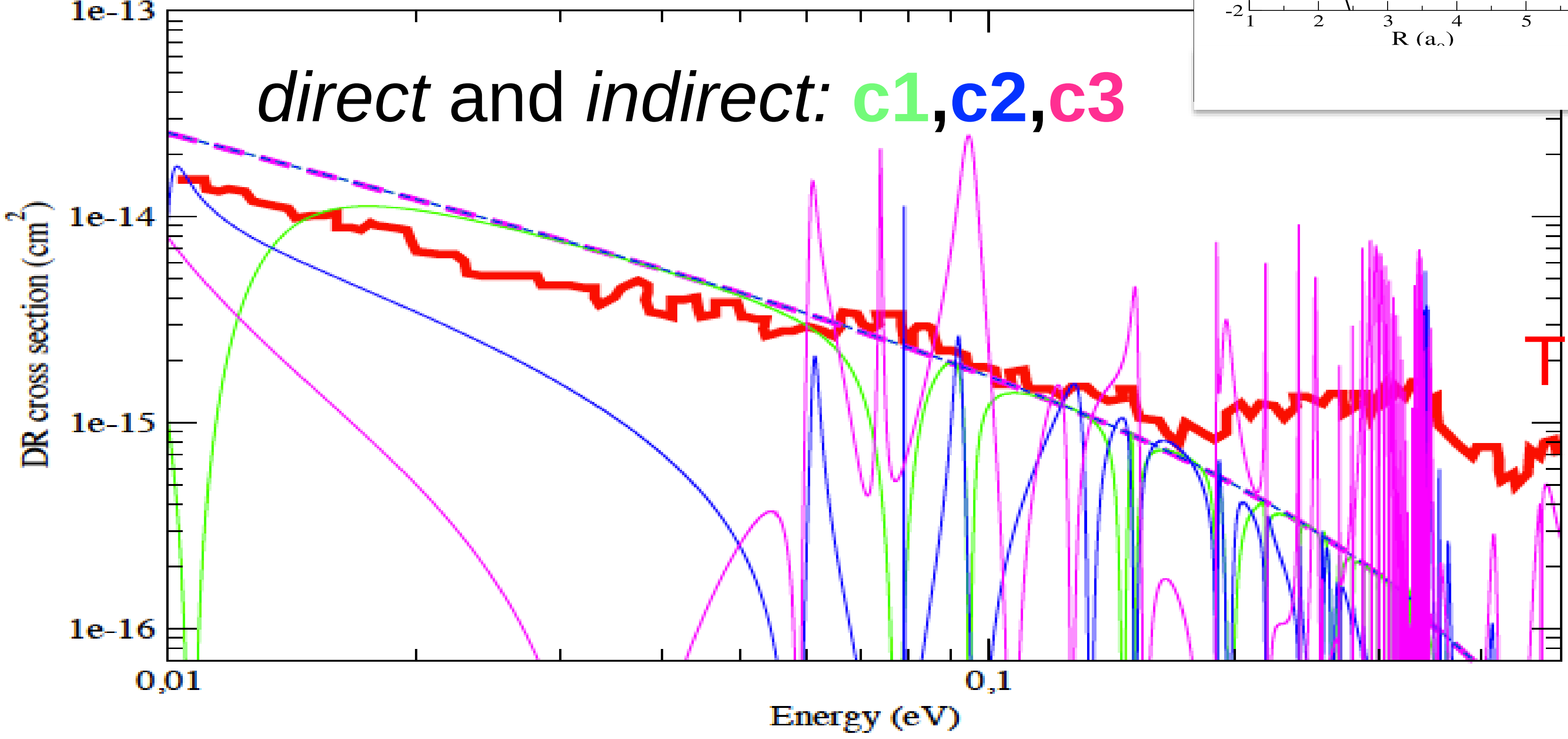


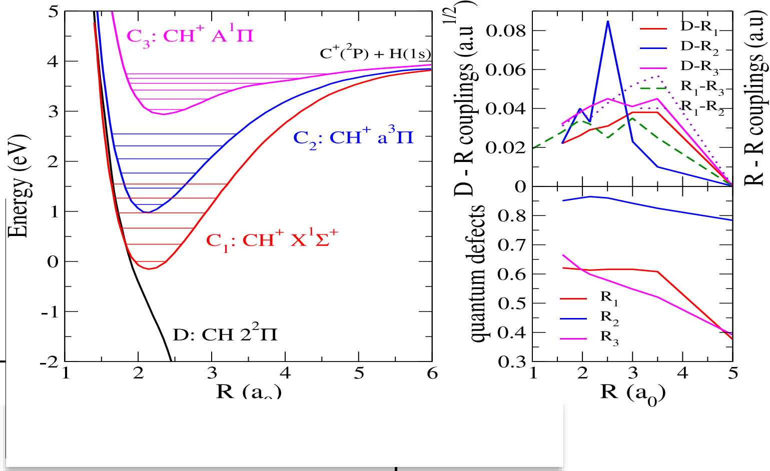
CH^+: DR cross section





CH^+: DR cross section





TSR

Thermal rates coefficients

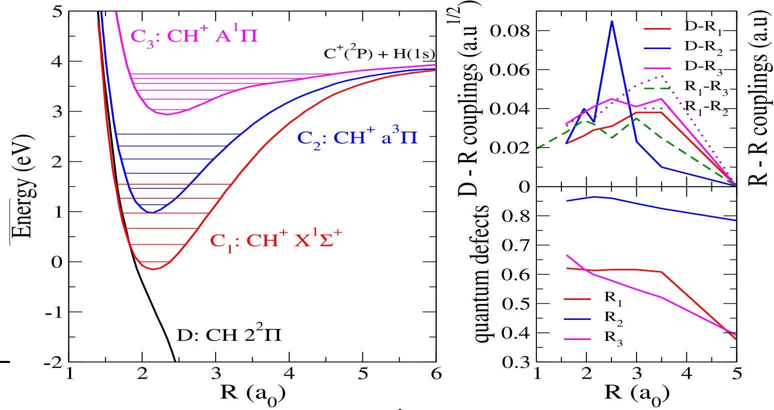
Convoluted: experimental conditions

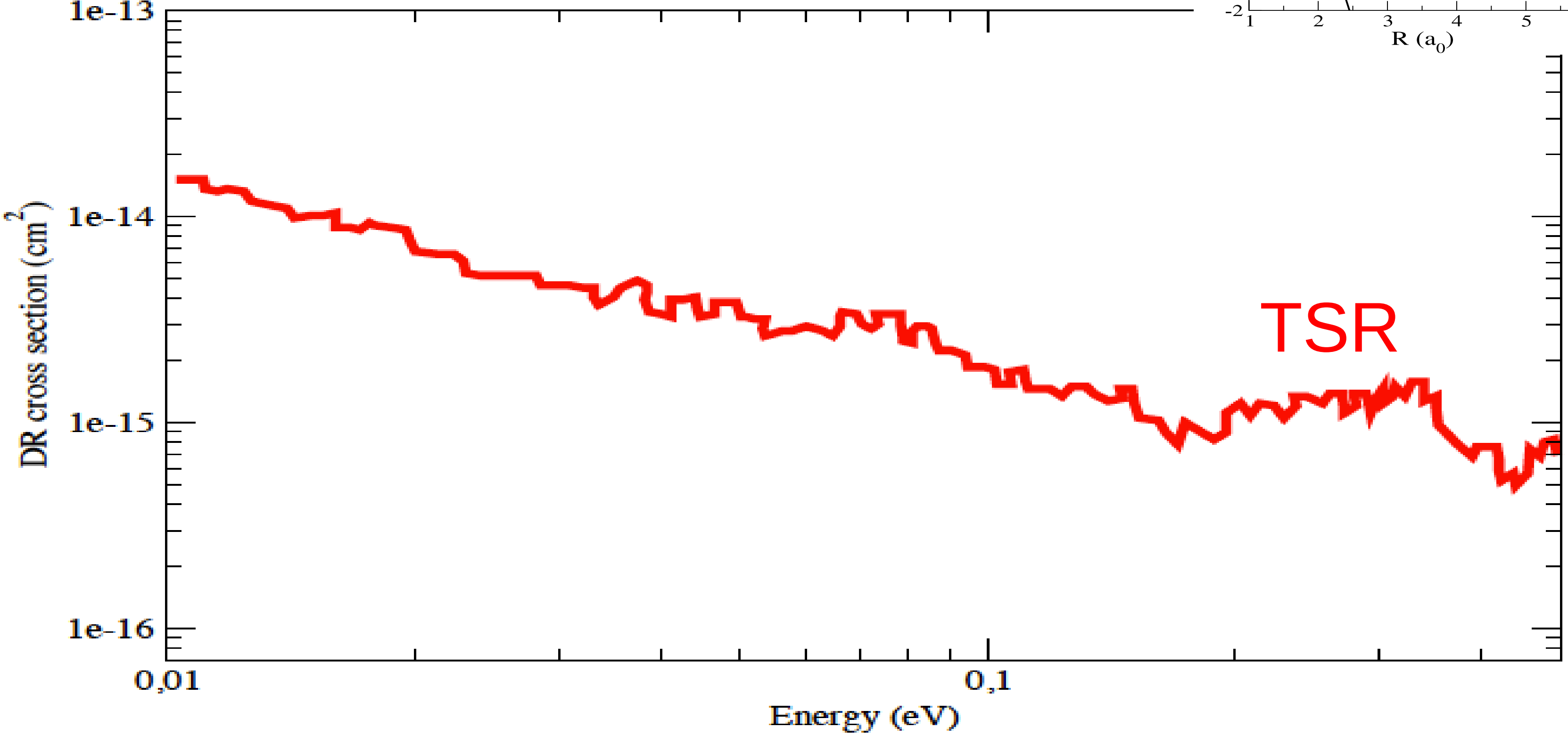
$$\alpha = < \mathrm{v}\sigma > = \int\int\int \sigma(\mathrm{v})\mathrm{v} f(\mathrm{v}_d, \mathbf{v}) d\mathbf{v}$$

$$f(\mathrm{v}_d, \mathbf{v}) = \frac{m}{2\pi k T_{e\perp}} exp(-\frac{m\mathrm{v}_\perp^2}{2kT_{e\perp}}) \sqrt{\frac{m}{2\pi k T_{e\|}}} exp(-\frac{m(\mathrm{v}_\| - \mathrm{v}_d)^2}{2kT_{e\|}})$$

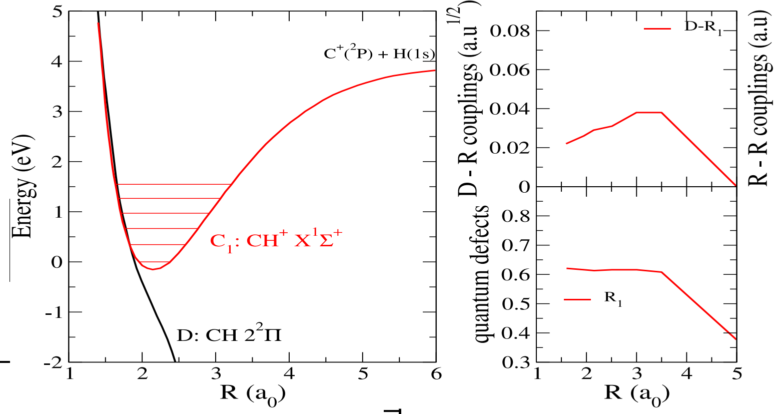
$T_{e\perp}$=17 meV $T_{e\|}$ =1 meV

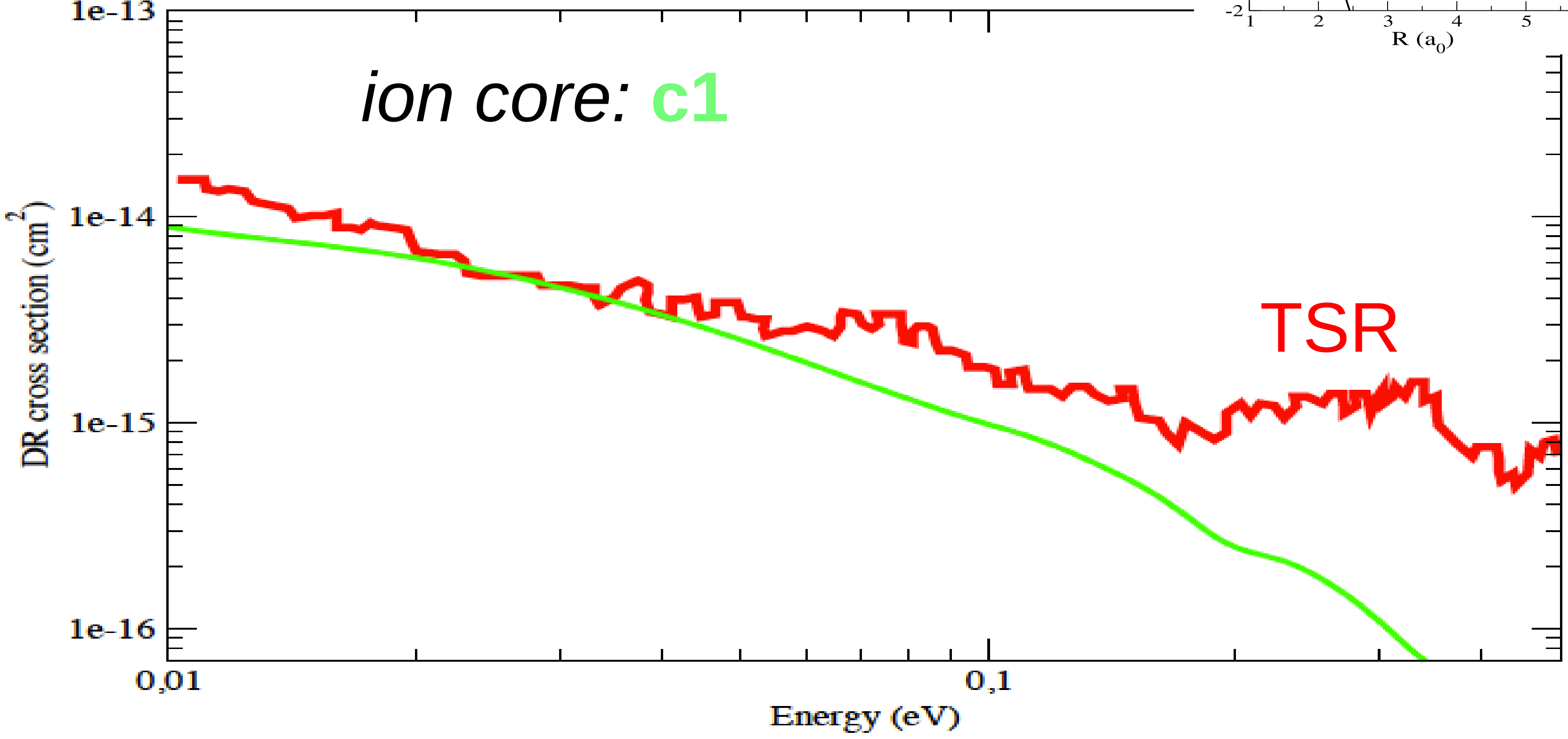
CH^+: DR cross section



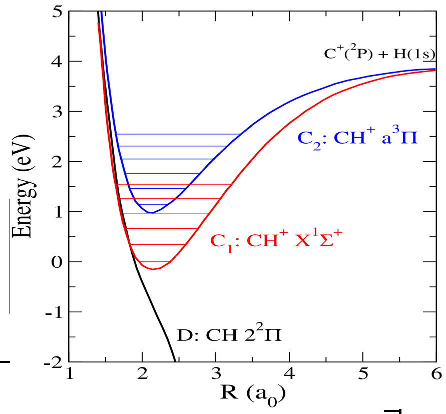


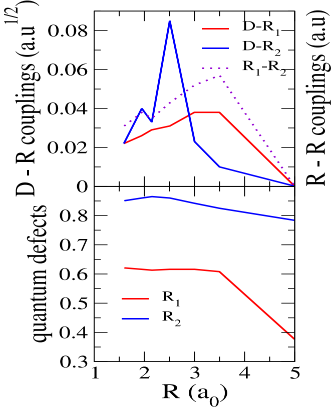
CH^+: DR cross section

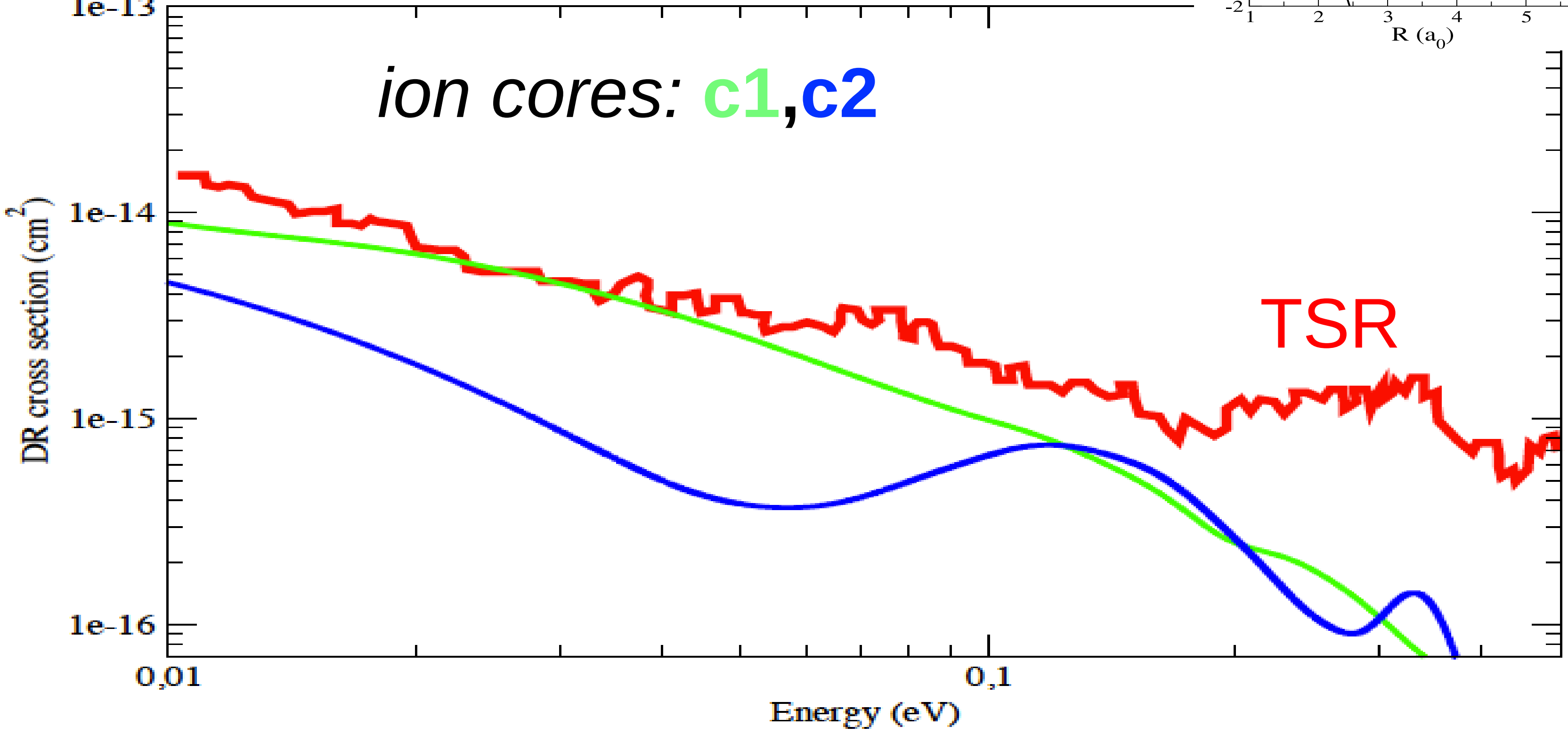




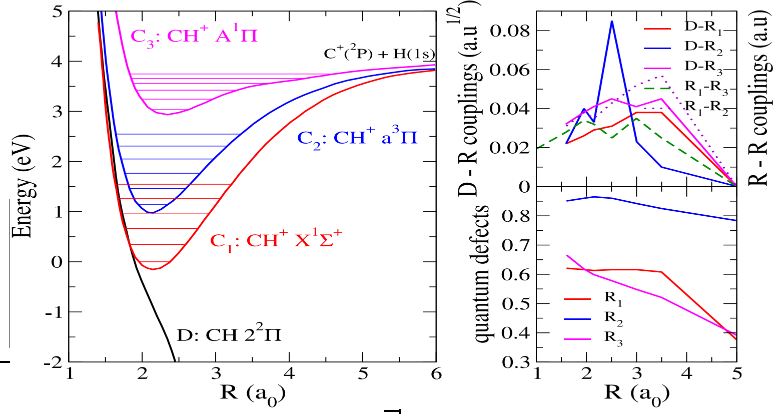
CH^+: DR cross section

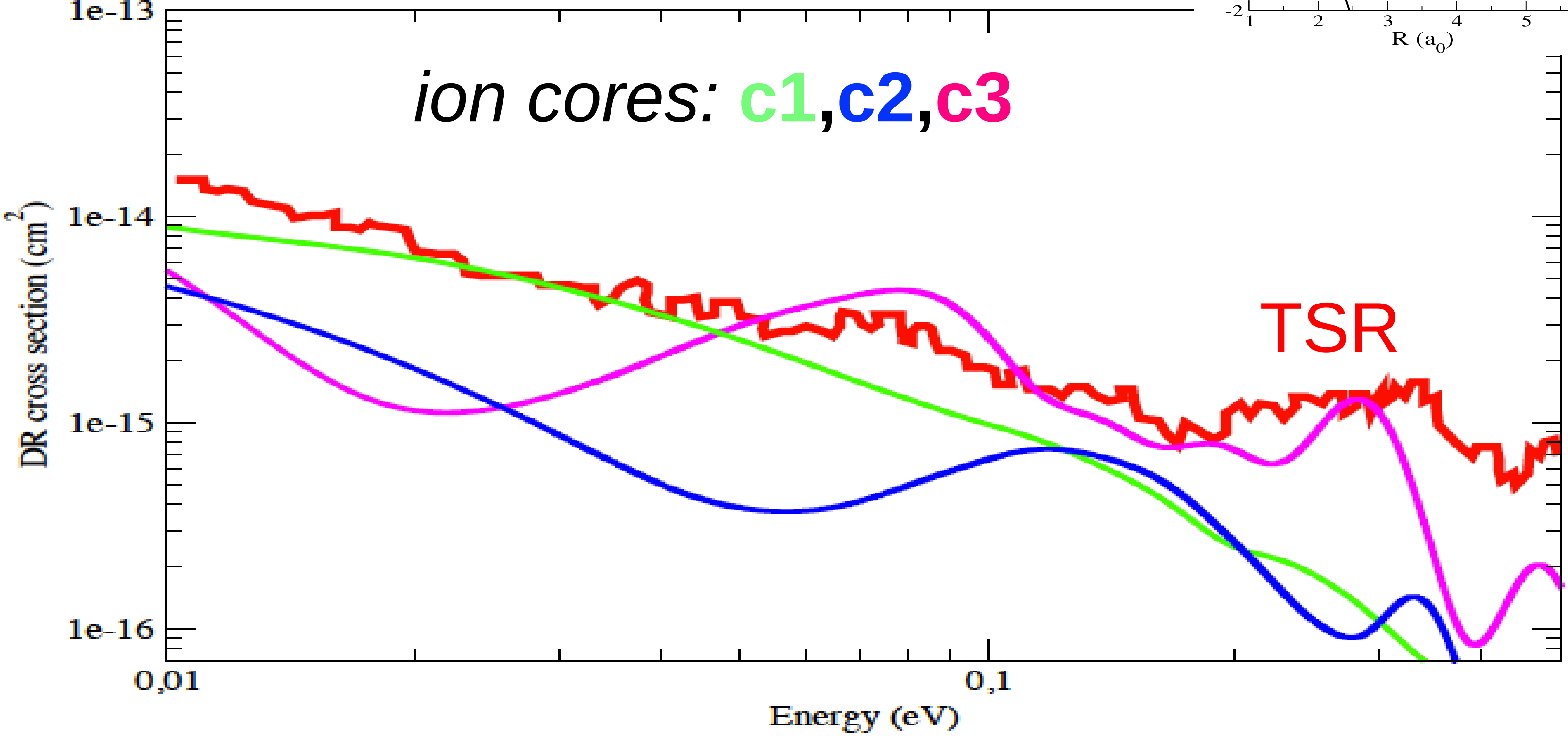






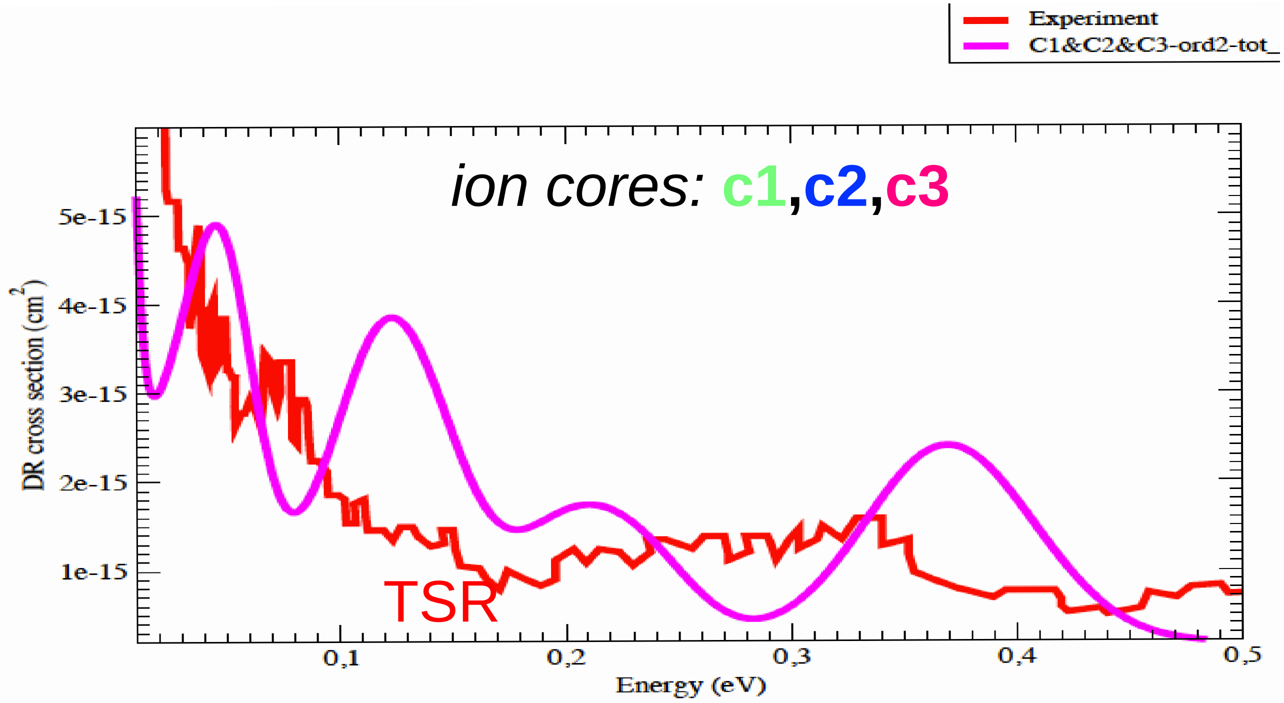
CH^+: DR cross section

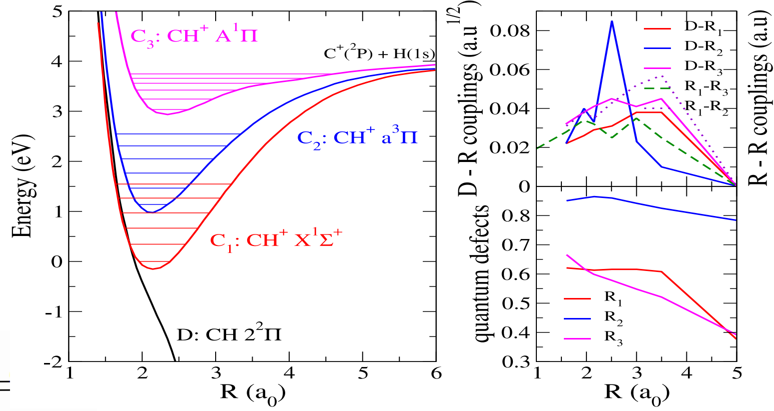




CH^+: DR cross section

Range up to 0.5 eV





the difference at low energy is due to the lack of spin, and at higher energy is due to the lack of next dissociative curves

Thank you for your attention

acknowledge
West University of Timisoara for support