Evaluation of State-Resolved Reaction Probabilities applied in Collisional Radiative Models for H, H_2 and He

D. Wünderlich and U. Fantz

Atomic and molecular data in CR models:
Principle of CR models

Population models

- Predict population densities in dependence of plasma parameters (T_e, n_e, ground state densities)
- Main field of application: plasma diagnostics
- Low temperature, low pressure plasmas
  ⇒ collisional radiative models

Collisional radiative models

- Several excited states of the considered atom/molecule
- Balance all relevant exciting and de-exciting reactions

⇒ Needed: extensive data base with reaction probabilities

⇒ Drastically increased complexity for molecules
(electronic, vibrational and rotational excitation)

Error bar of model results directly correlates with the quality of the used input data → Critical evaluation of the available data using the flexible solver `Yacora`

Atomic and Molecular Data in CR Models:
Outline of the talk

- CR models for light atoms (He and H)
- CR model for H_2 and the used input data

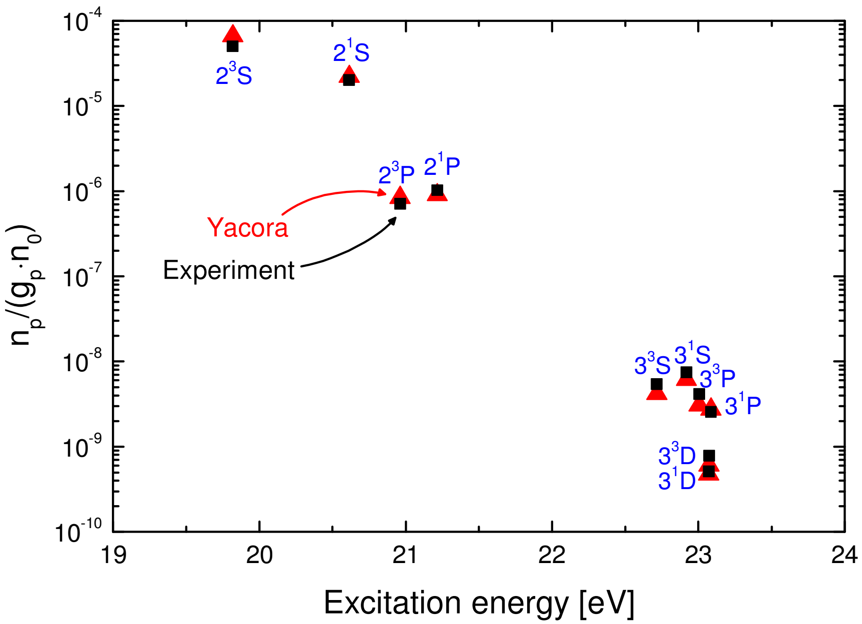
CR model for helium:
Input and main results

CR model for excited states up to n=4

- Cross sections from Ralchenko
- Optical thickness

Experimental benchmark

- Microwave driven ECR plasma experiment
- T_e and n_e from Langmuir probe
- Measured population densities:
  - $n_{n=2}$: white light absorption spectroscopy
  - $n_{n=3}$: optical emission spectroscopy

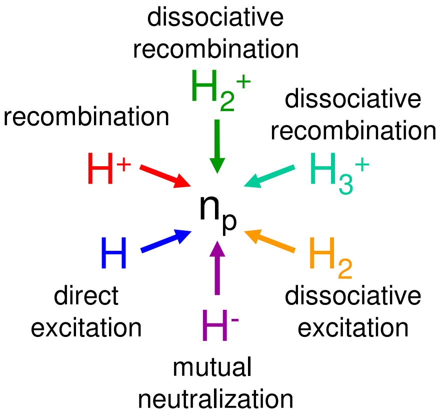


Excellent agreement of CR model results with measured population densities

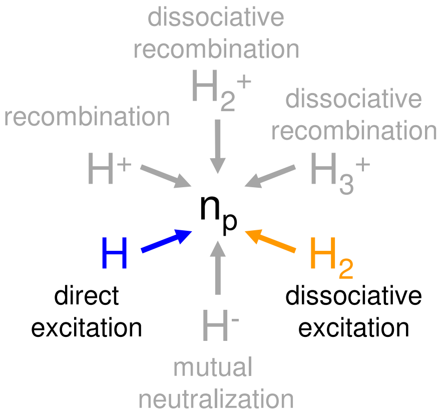
Y. Ralchenko et al, ADNDT 94, 2008, 603

CR model for atomic hydrogen:
Different excitation channels

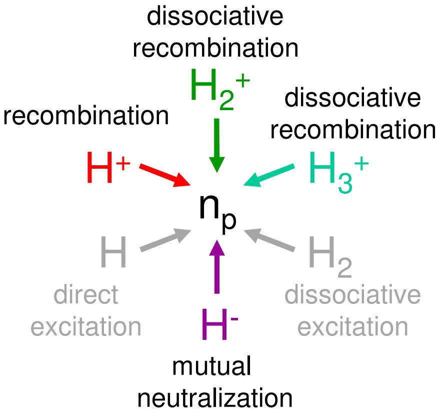
Excitation of atomic hydrogen…



…in ionizing…



…and recombining plasmas



Huge number of free parameters

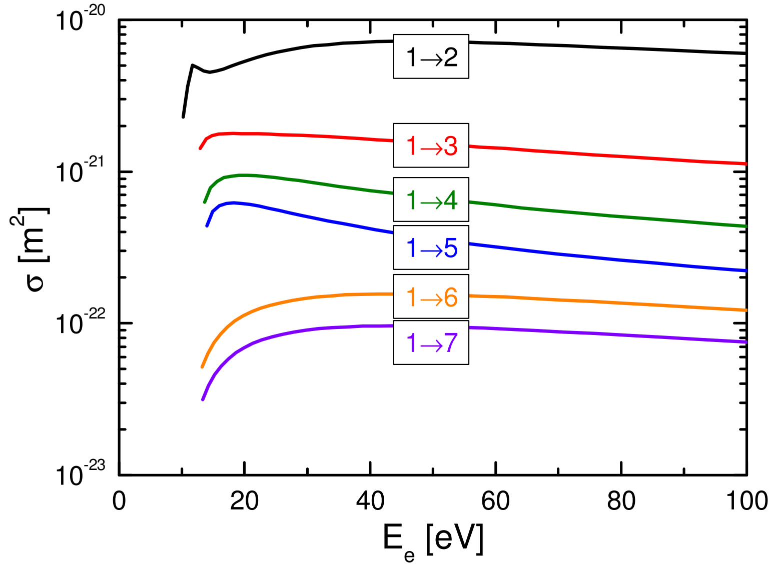
⇒ Evaluation needs a lot of time and experience

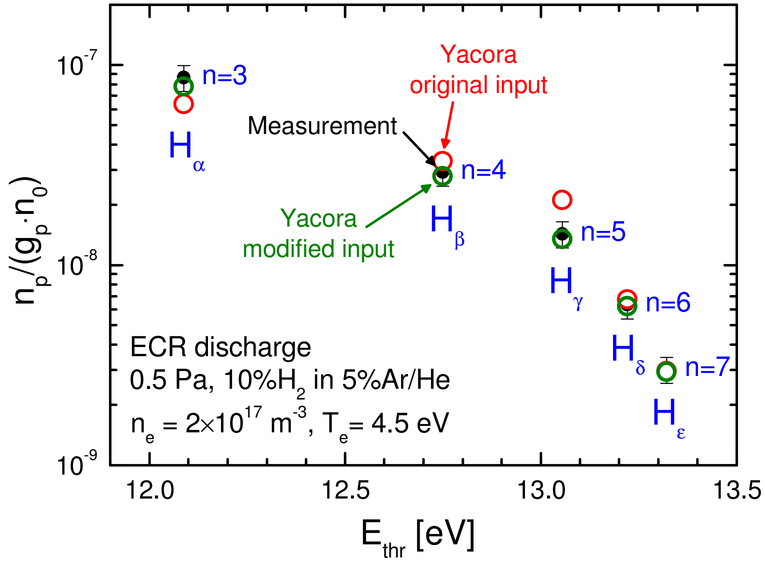
CR model for atomic hydrogen: Cross sections for direct excitation

Data from Janev report

- Compilation of recent calculations and measurements
- Low energies (E_e<40 eV): discontinuity between cross sections for 1→5 and 1→6
  - Reason: different primary data sources (R-Matrix, semi empirical modification of Born-Bethe)
  - Solution: fit of rate coefficients
  - Result: excellent agreement of measurement and model for ionizing plasma with known T_e and n_e ✓

Benchmarked set of rate coefficients for direct excitation



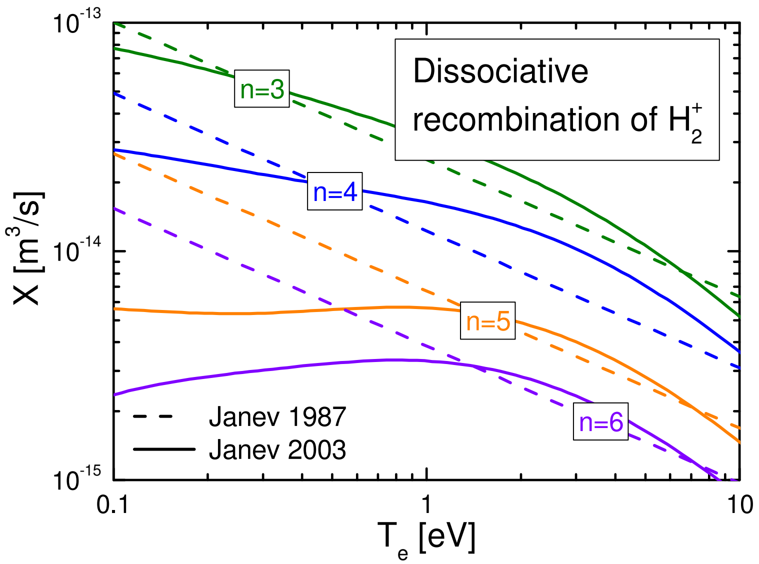


R. Janev et al, JÜL-4105, Forschungszentrum Jülich, 2003
D. Wünderlich et al, JQSRT 110, 2009, 62

CR model for atomic hydrogen: Dissociative recombination of molecular ions

Dissociative recombination of H_2^+

- Total cross section and branching ratio: Janev
- Extrapolation performed
  - For low (E_e<0.5 eV) and high electron energies (E_e>10 eV)
  - For high (v>5) vibrational excitation in H_2^+



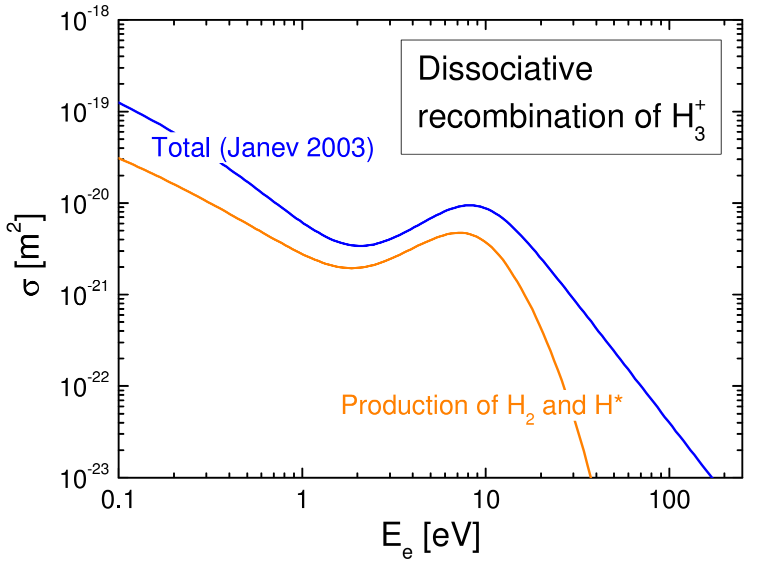
Dissociative recombination of H_3^+

- Total cross section: Janev
- Two reaction channels:

$$H_3^+(v) + e^- \rightarrow \mathrm{H{+}H{+}H}$$

$$H_3^+(v) + e^- \rightarrow H_2 + H^*$$

- Branching ratio: Storage ring (Datz)
- 2nd channel: quantum state distribution?
  Kulander et al: only n=1 and n=2 for low E_e



R. Janev et al, JÜL-4105, Forschungszentrum Jülich, 2003

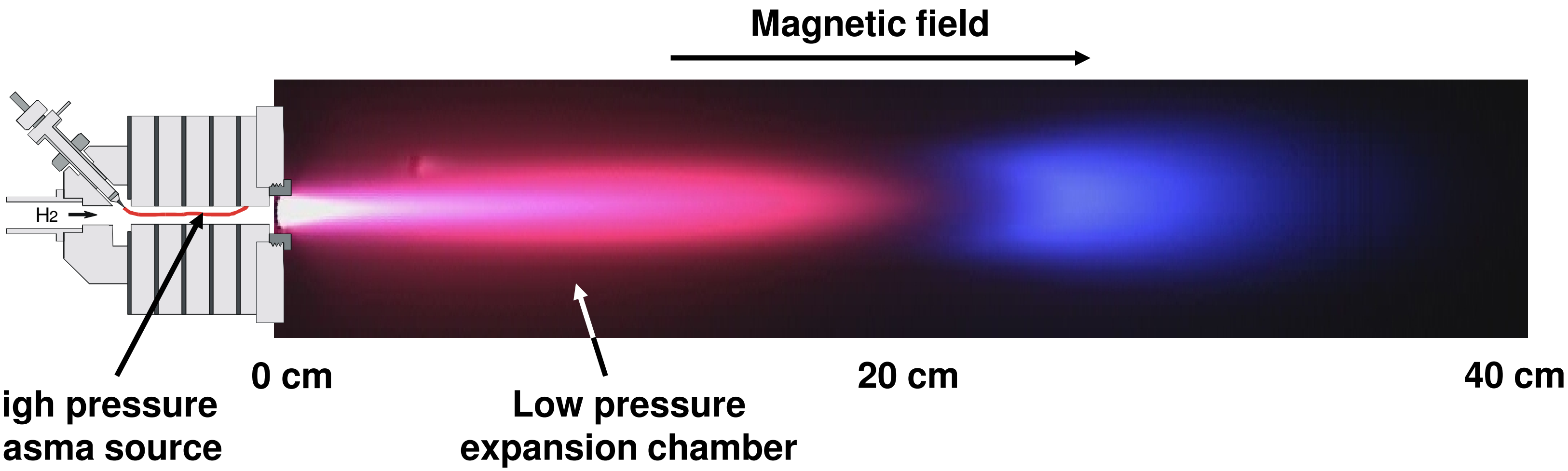
CR model for atomic hydrogen: Benchmark at a magnetized plasma expansion

Magnetized plasma expansion at TU/e:

- Cascaded arc, P_{input}=6.8 kW
- Axial magnetic field (14 mT, generated by Helmholtz coils)
- $P_{source}=10^4$ Pa, $P_{vessel}\approx 8$ Pa ⇒ supersonic plasma expansion
- Pressure of plasma jet approaches background pressure after ≈20 cm

⇒ Shock front and transition red plasma → blue plasma

Investigate red and blue plasma
using `Yacora` for H based on most recent cross sections



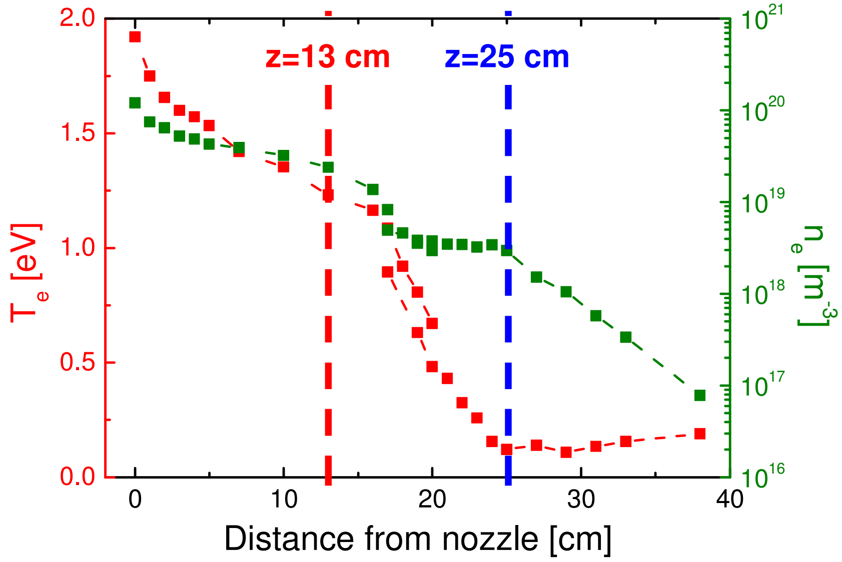
CR model for atomic hydrogen: Benchmark at a magnetized plasma expansion

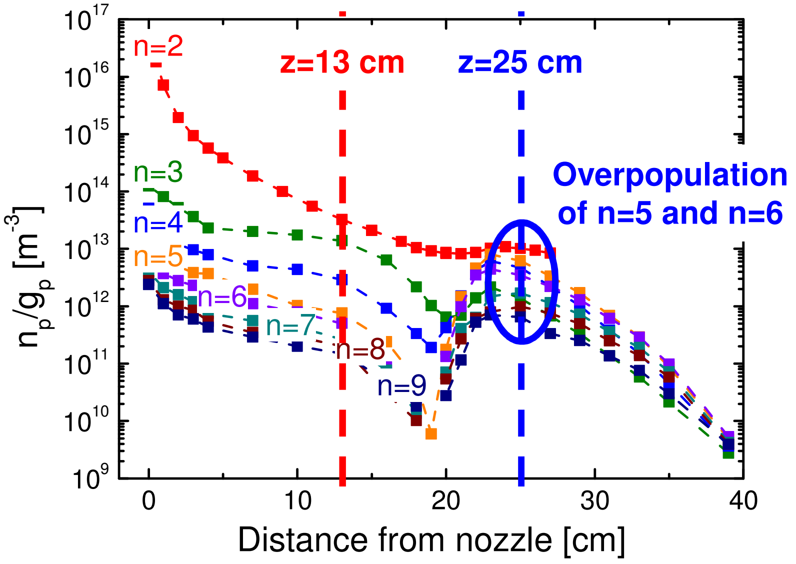
Input: population densities and plasma parameters

- $n_{n=1}$: TALIF
- $n_{n=2}$: absorption spectroscopy (TDLAS)
- $n_{n\geq3}$: emission spectroscopy
- Electron temperature:
  - Fulcher emission (red plasma)
  - Langmuir double probe (blue plasma)
- Electron density:
  - Saha equation (red plasma)
  - Langmuir double probe (blue plasma)

Application of Abel inversion ⇒

Locally resolved plasma parameters





CR model for atomic hydrogen: Benchmark at a magnetized plasma expansion

Compare experiment with model for red and blue plasma

- Excellent agreement
- Correct prediction of overpopulation of n=4,5 and 6

Mutual Neutralization of H_2^+ and H^-:

- Two reaction channels:

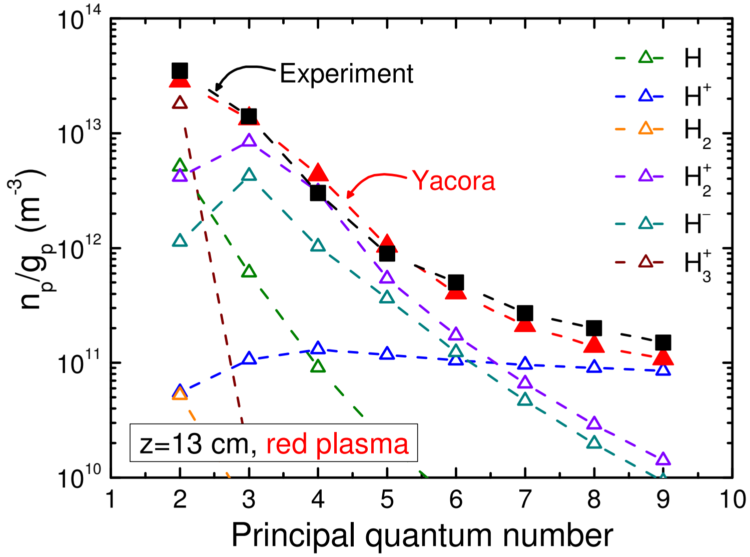
$$H_2^+(v) + H^- \rightarrow H_2^* + H$$

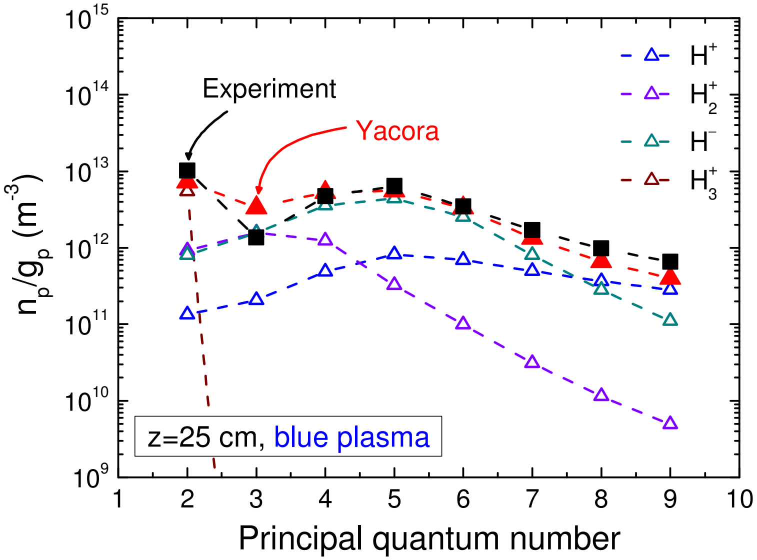
$$H_2^+(v) + H^- \rightarrow H_2 + H^*$$

Cross sections from Janev and Eerden, respectively.
CR model ⇒ Mixture of both channels

Influence of H_3^+

- Needs to be considered in order to fulfill quasi neutrality

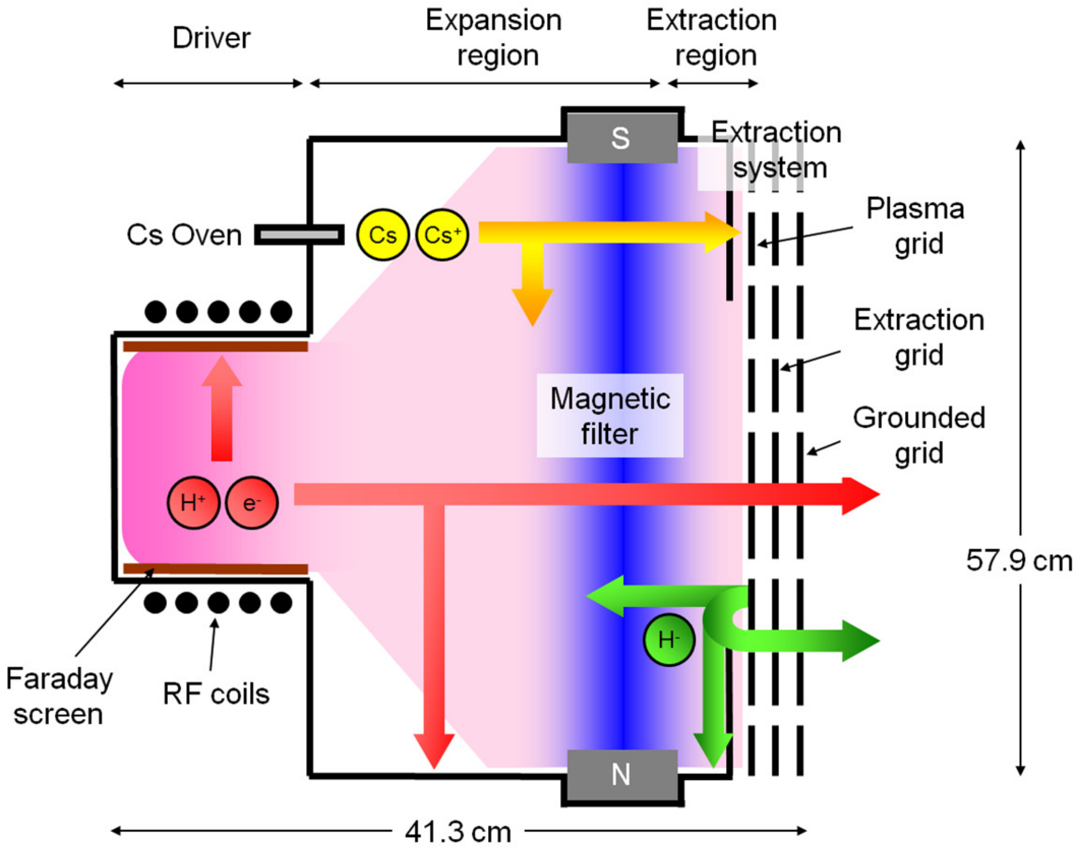




CR model for atomic hydrogen: Benchmark at a tandem type negative hydrogen ion source

Negative ion source prototype for ITER NBI at IPP Garching

- Plasma generation in driver (P_{RF}≤100 kW per driver)
- Reduce T_e: magnetic filter field
- Reduce co-extracted electrons: bias voltage (plasma grid against source walls and bias plate)
- Conversion of atoms and positive ions at caesiated surface of plasma grid



Investigate ionizing and recombining plasma using `Yacora` for H

CR model for atomic hydrogen: Benchmark at a tandem type negative hydrogen ion source

Ionizing plasma in the Driver

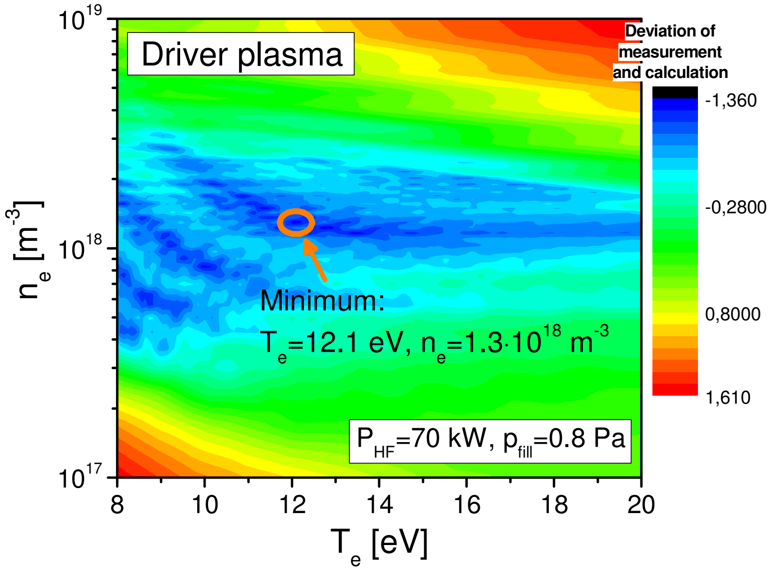
- Good agreement of model with OES ✓
- T_e and n_e agree reasonably well with Langmuir probe results
- Relevant excitation channels: Direct excitation and dissociative excitation

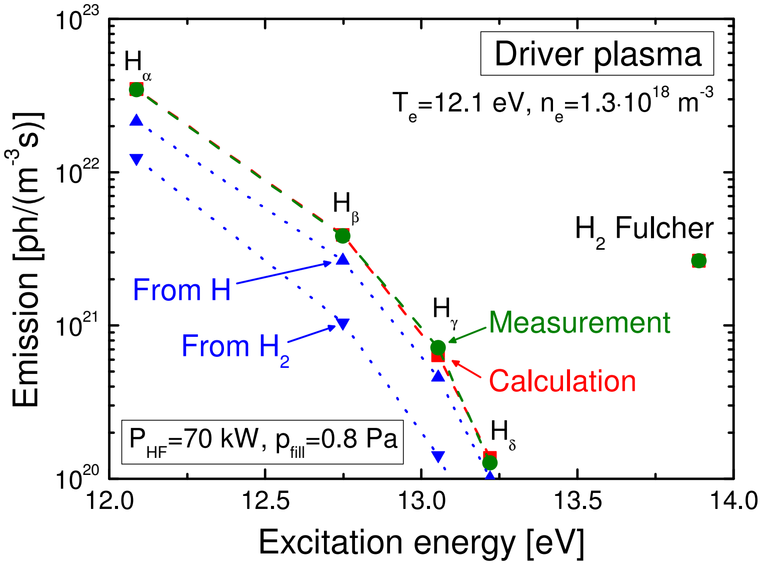
Recombining plasma in the expansion region

- In some cases no fit of model to measurements possible at all

Influence of gradients in the plasma parameters (caused by magnetic filter?)

New IPP test facility ELISE: combine OES with tomography for obtaining locally resolved emission

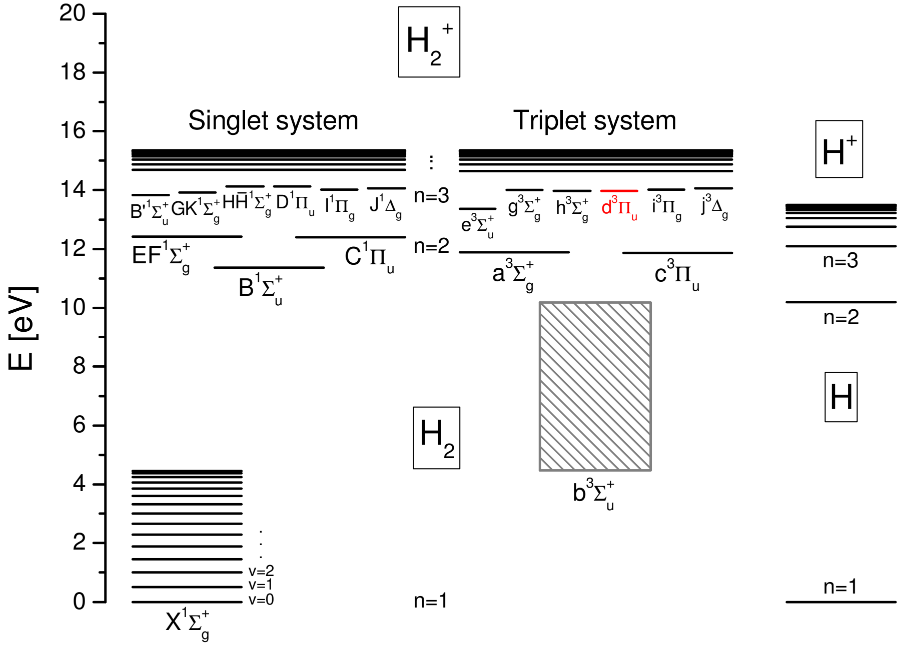




Atomic and Molecular Data in CR Models: Outline of the talk

- CR models for light atoms (He and H)
- CR model for H_2 and the used input data

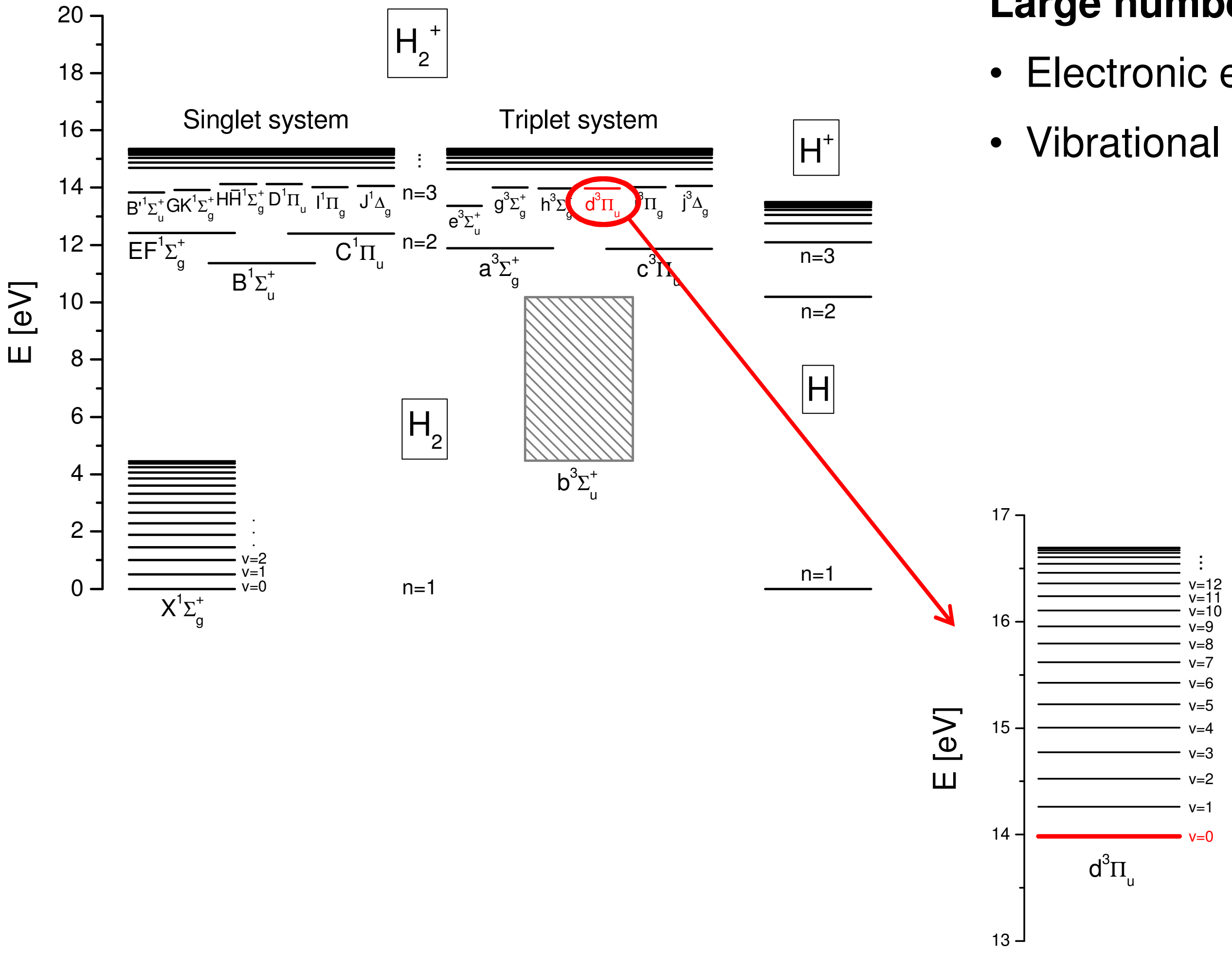
Reaction probabilities for molecular hydrogen: CR model for H_2



Large number of excited states

- Electronic excitation

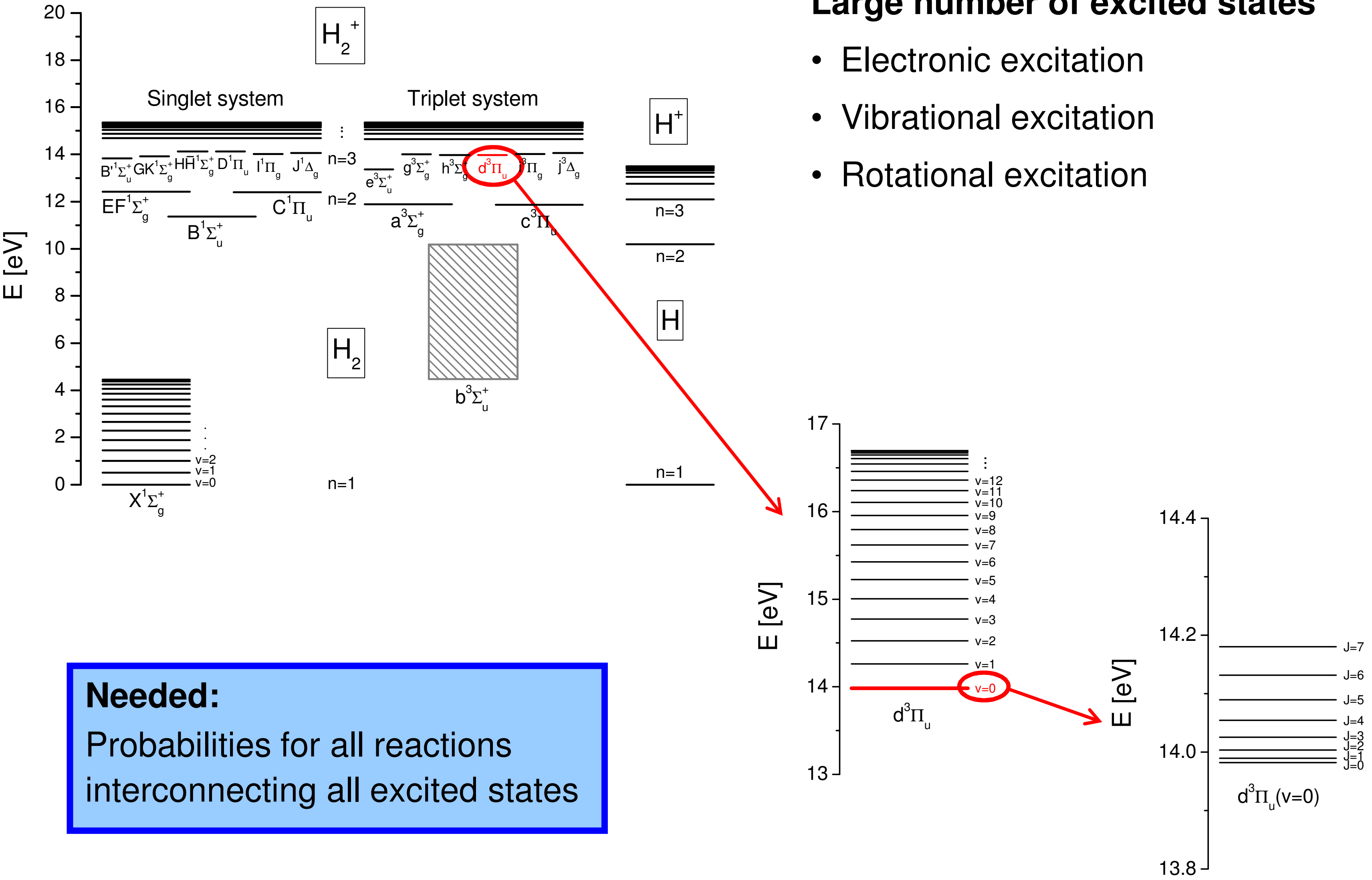
Reaction probabilities for molecular hydrogen: CR model for H_2



Large number of excited states

- Electronic excitation
- Vibrational excitation

Reaction probabilities for molecular hydrogen: CR model for H_2



Large number of excited states

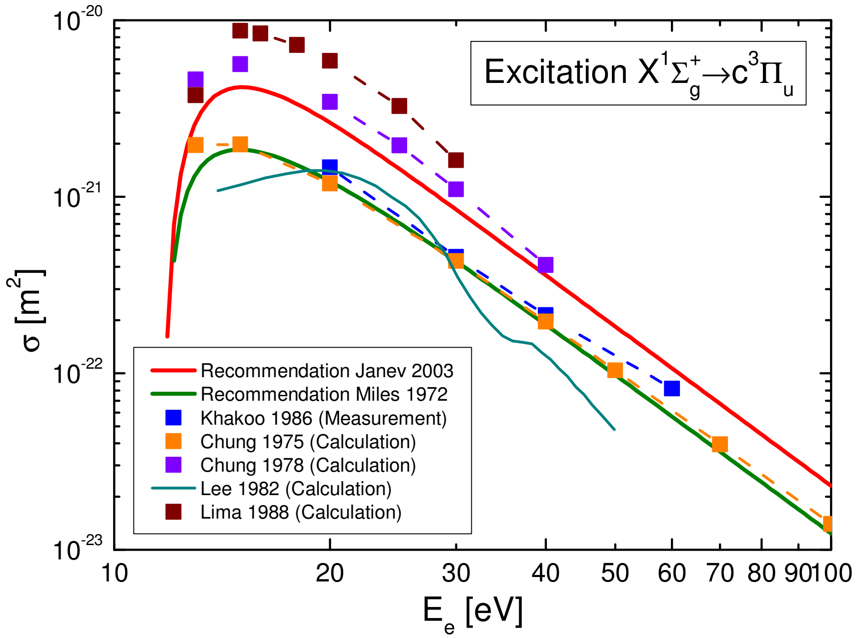
- Electronic excitation
- Vibrational excitation
- Rotational excitation

Needed:
Probabilities for all reactions interconnecting all excited states

Reaction probabilities for molecular hydrogen: Cross sections for electron collision excitation

Literature:

- Only few vibrationally or rotationally resolved data
- Excitation from the ground state:
  - Contradictions between cross sections from different data sources
  - Most excited states of n=2 and n=3: too few reliable data
  - States of n>3: no reliable data
- Excitation between excited states:
  - Almost no reliable data
- Two „data sets“ up to n=3
  - Miles (1972, semi empiric)
  - Janev (2003, summary of recent measurements and calculations)

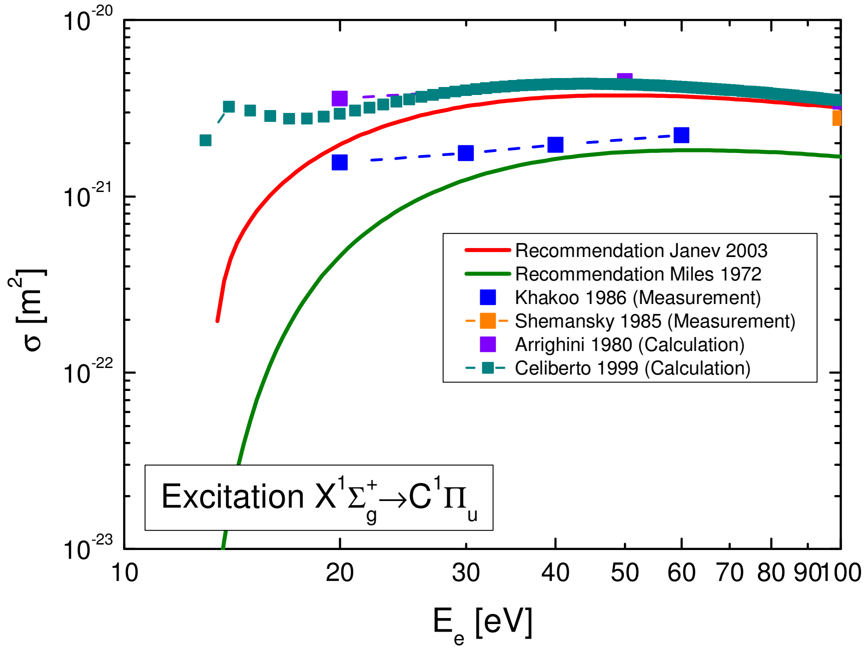


More reliable data for optically allowed transitions (e.g. impact parameter method) than for forbidden transitions

Reaction probabilities for molecular hydrogen: Cross sections for electron collision excitation

Literature:

- Only few vibrationally or rotationally resolved data
- Excitation from the ground state:
  - Contradictions between cross sections from different data sources
  - Most excited states of n=2 and n=3: too few reliable data
  - States of n>3: no reliable data
- Excitation between excited states:
  - Almost no reliable data
- Two „data sets“ up to n=3
  - Miles (1972, semi empiric)
  - Janev (2003, summary of recent measurements and calculations)

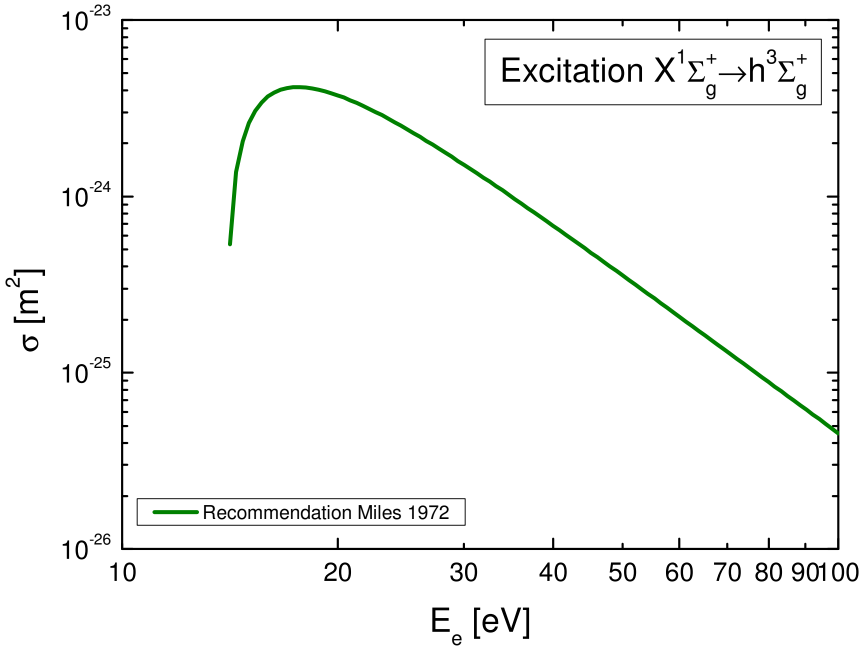


More reliable data for optically allowed transitions (e.g. impact parameter method) than for forbidden transitions

Reaction probabilities for molecular hydrogen: Cross sections for electron collision excitation

Literature:

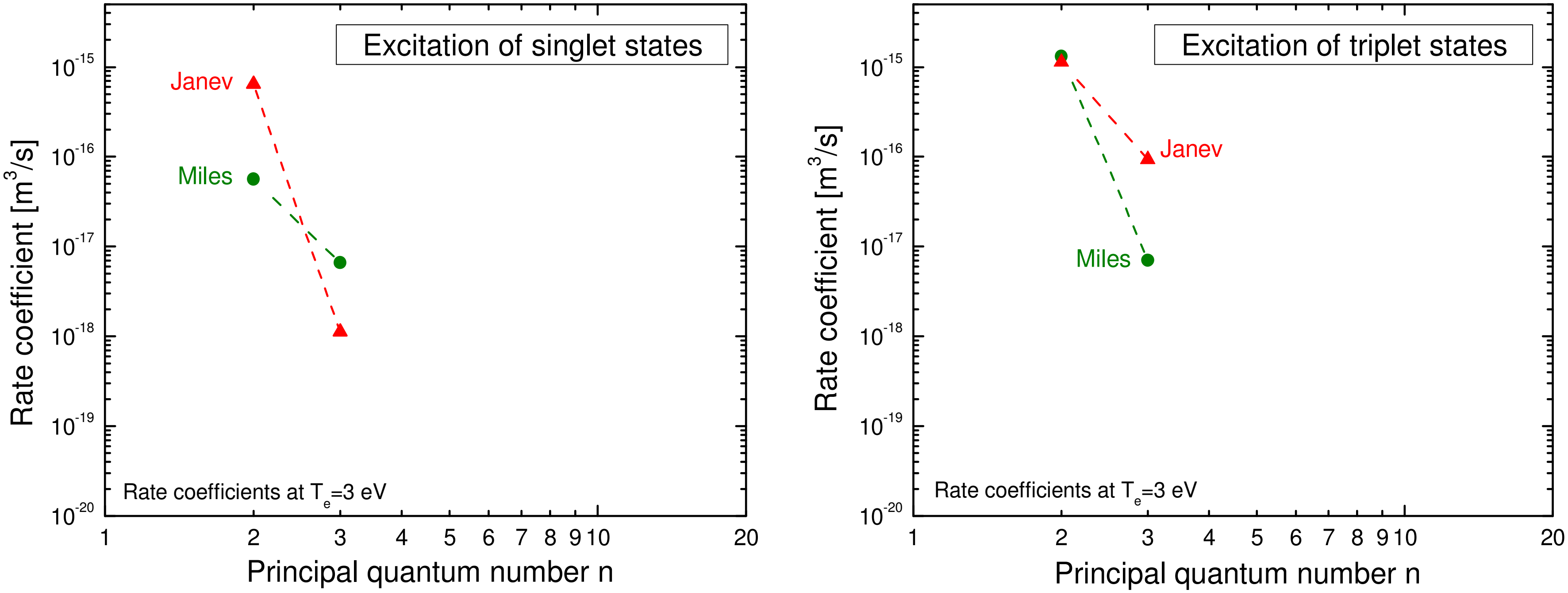
- Only few vibrationally or rotationally resolved data
- Excitation from the ground state:
    - Contradictions between cross sections from different data sources
    - Most excited states of n=2 and n=3: too few reliable data
    - States of n>3: no reliable data
- Excitation between excited states:
    - Almost no reliable data
- Two „data sets“ up to n=3
    - Miles (1972, semi empiric)
    - Janev (2003, summary of recent measurements and calculations)



More reliable data for optically allowed transitions (e.g. impact parameter method) than for forbidden transitions

Reaction probabilities for molecular hydrogen: Compare available cross sections

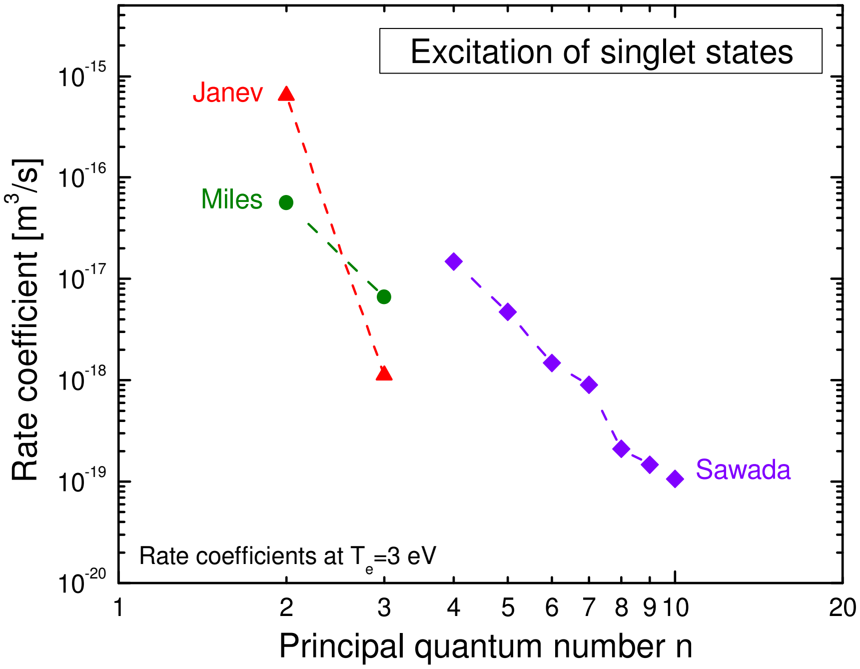
Use Janev or Miles. Excitation to states with n>3?

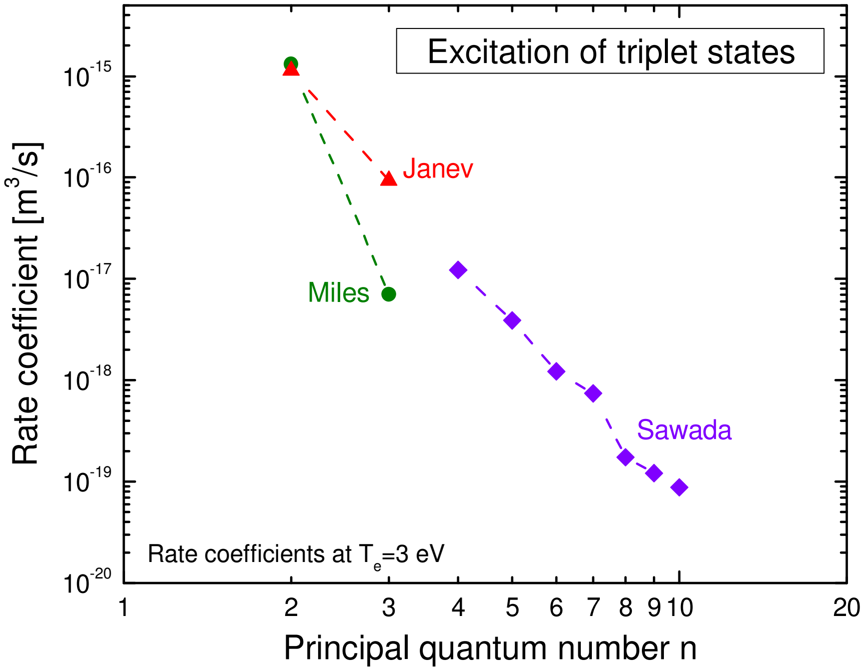


Reaction probabilities for molecular hydrogen: Compare available cross sections

Use Janev or Miles. Excitation to states with n>3?

- Scaling used in the Sawada CR model (based on H-like He)

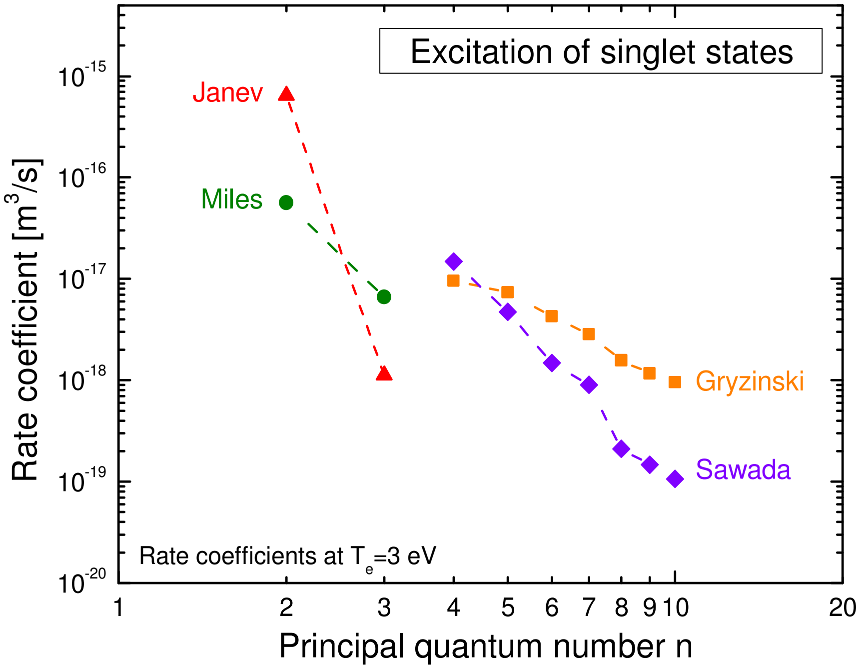


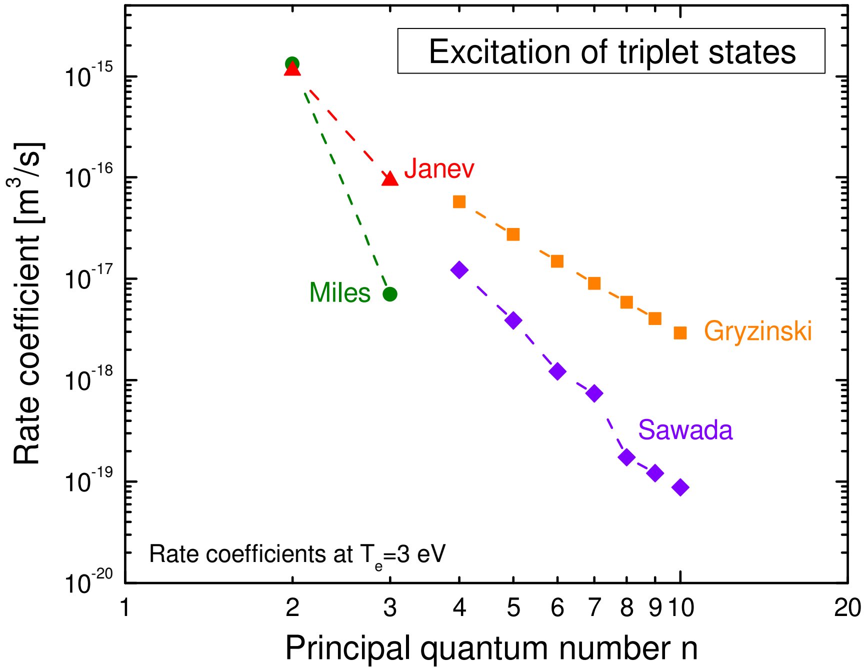


Reaction probabilities for molecular hydrogen: Compare available cross sections

Use Janev or Miles. Excitation to states with n>3?

- Scaling used in the Sawada CR model (based on H-like He)
- Gryzinski method



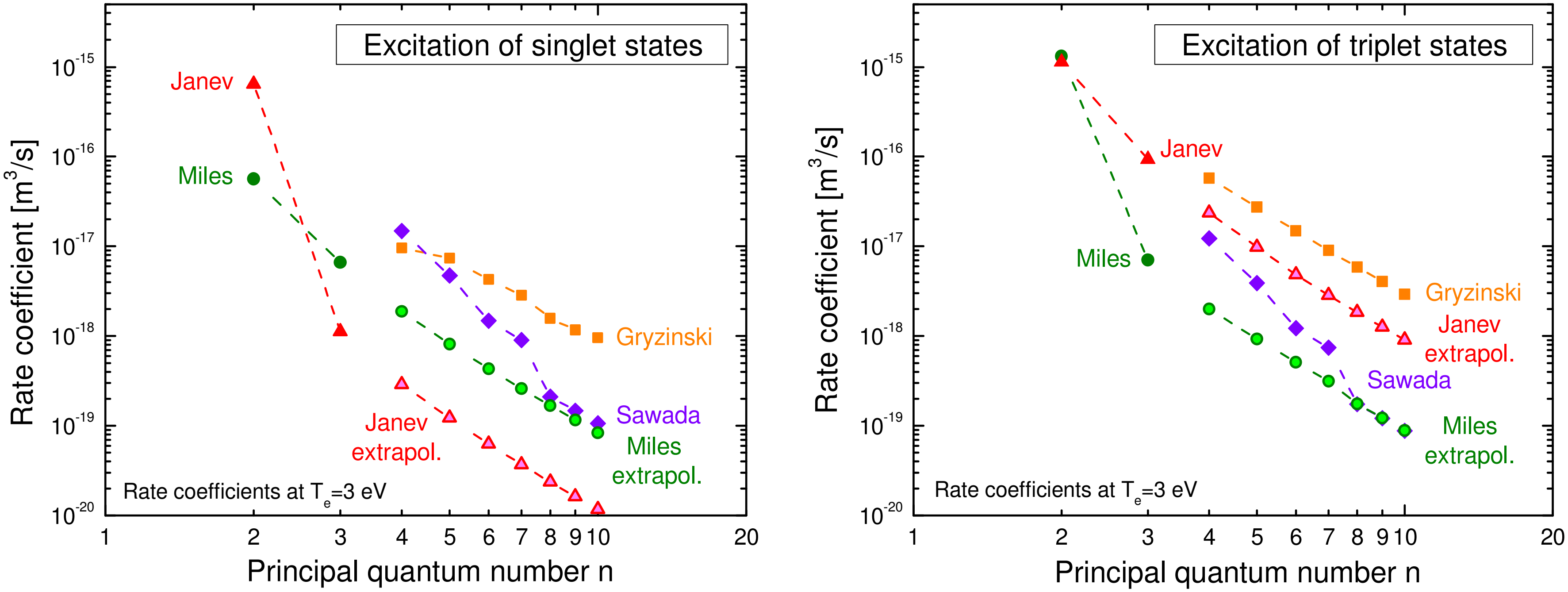


Reaction probabilities for molecular hydrogen: Compare available cross sections

Use Janev or Miles. Excitation to states with n>3?

- Scaling used in the Sawada CR model (based on H-like He)
- Gryzinski method
- Extrapolation based on formulae suggested by Janev[2]:

$$\sigma(X^1 \to N\Lambda_u) = \left(\frac{N_0}{N}\right)^3 \left(\frac{\Delta E_{N_0}}{\Delta E_N}\right) \cdot \sigma(X^1 \to N_0\Lambda_u) \qquad \sigma(X^1 \to N\Lambda_g) = \left(\frac{N_0}{N}\right)^6 \left(\frac{\Delta E_{N_0}}{\Delta E_N}\right) \cdot \sigma(X^1 \to N_0\Lambda_g)$$

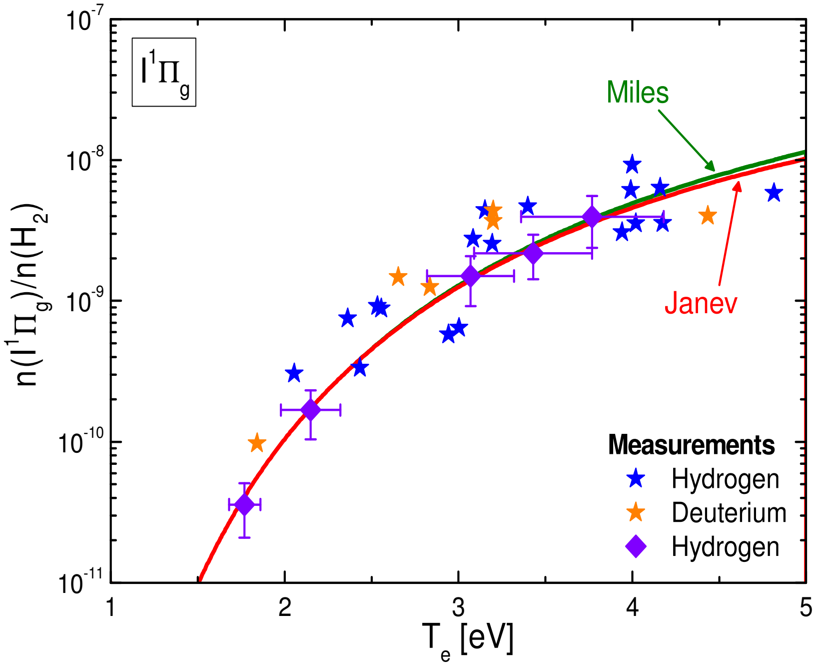


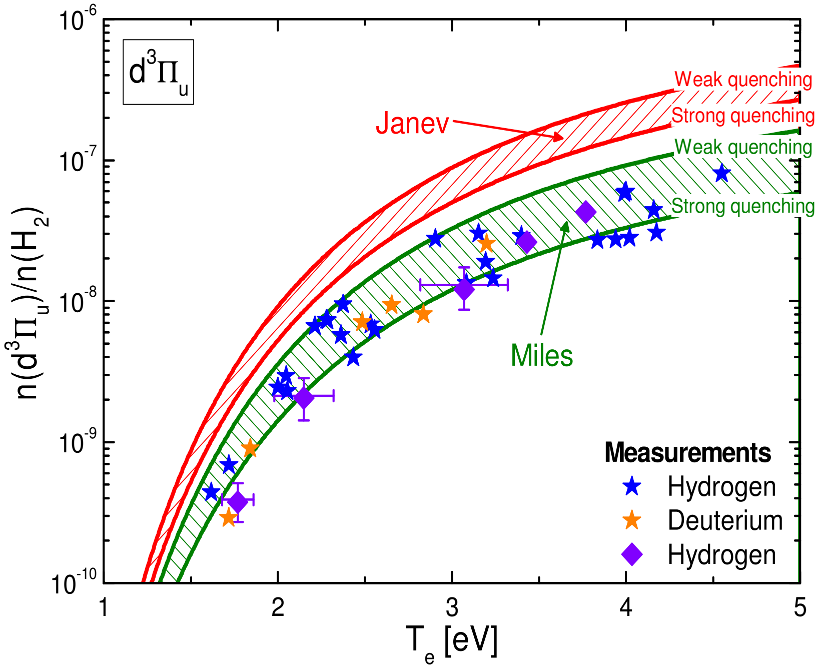
Reaction probabilities for molecular hydrogen: Benchmark available cross sections

Compare CR model results with experiment

- Calculations based on Miles or Sawada
- Higher excited states (n>3): Janev scaling

Better agreement between model and experiment for the (outdated and semiempiric) Miles data



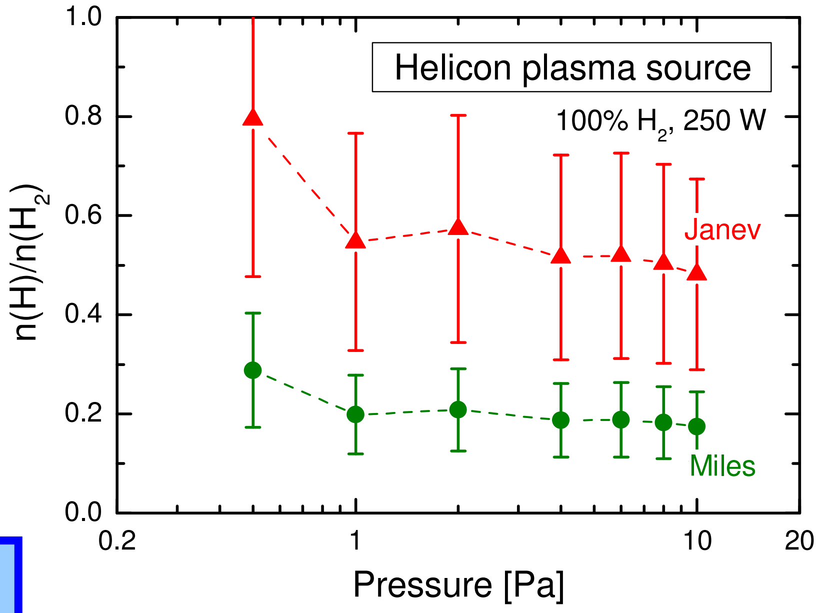


Reaction probabilities for molecular hydrogen: Benchmark available cross sections

CR models on Miles and Janev data

- Differences in population densities directly mapped onto diagnostics results

⇒ Model almost not usable for diagnostics in its current status



Needed:

New or extended cross section data base for H_2:

- Complete
- Consistent
- Including vibrational (and rotational) levels

Perform – as far as possible – calculations on the missing reaction probabilities

Reaction probabilities for molecular hydrogen: Franck Condon factors and Einstein coefficients

Prepare extension of cross section database

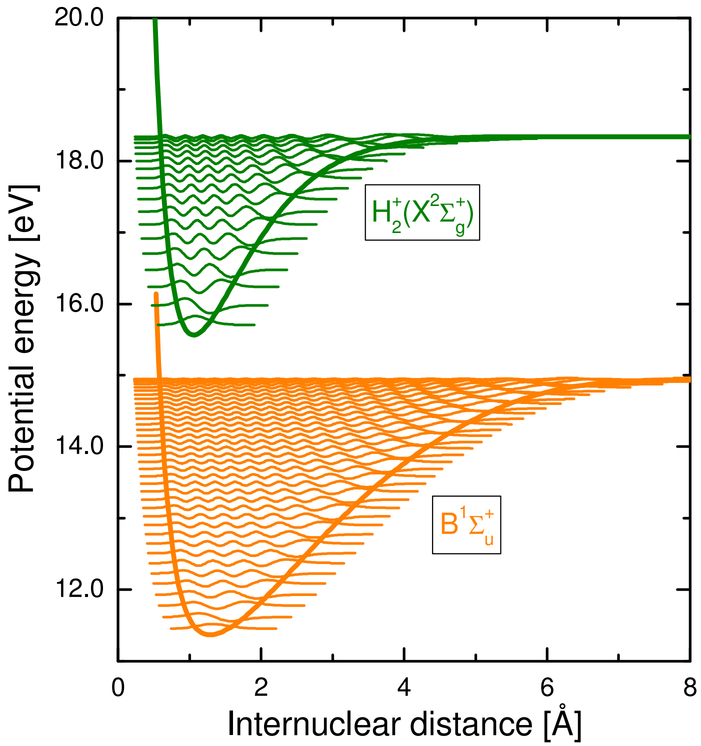
Collect and prepare eigenvalues of electronic wave functions (=potential energy curves)

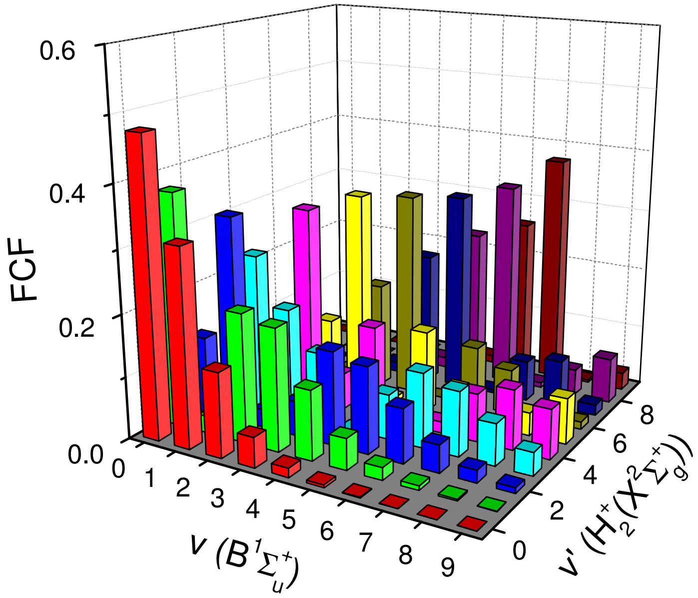
⇒ Vibrational eigenvalues

⇒ Vibrational wave functions

⇒ Franck Condon Factors

… for H_2 and H_2^+ (and its isotopomeres)





v

v'

q	0	1	2	3	4
0	4.76E-01	3.17E-01	1.36E-01	4.82E-02	1.54E-02
1	3.75E-01	2.73E-02	2.07E-01	1.96E-01	1.12E-01
2	1.26E-01	3.32E-01	2.93E-02	5.59E-02	1.51E-01
3	2.10E-02	2.53E-01	1.75E-01	1.15E-01	6.82E-04
4	1.56E-03	6.44E-02	3.22E-01	5.91E-02	1.49E-01
…					

Reaction probabilities for molecular hydrogen: Franck Condon factors and Einstein coefficients

Prepare extension of cross section database

Collect and prepare eigenvalues of electronic wave functions (=potential energy curves)

⇒ Vibrational eigenvalues

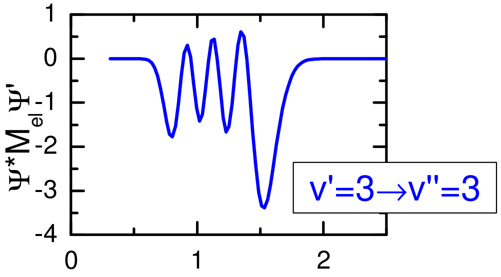
⇒ Vibrational wave functions

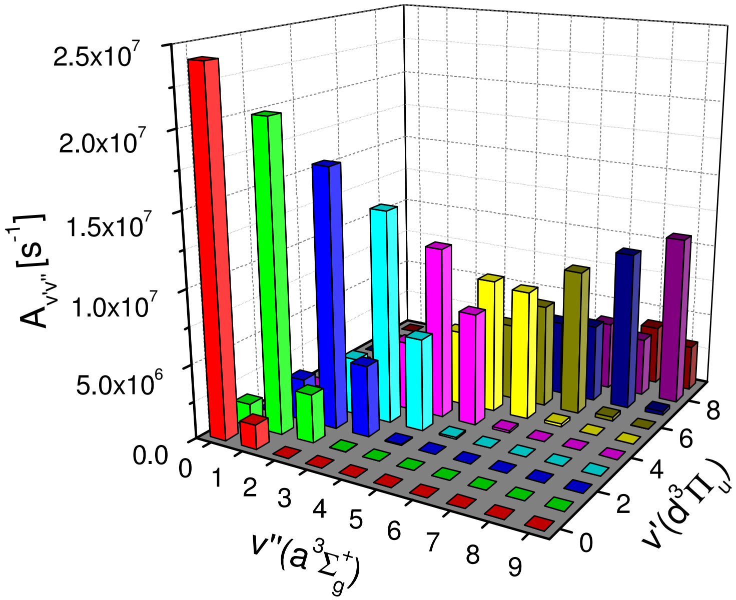
⇒ Franck Condon Factors

… for H_2 and H_2^+ (and its isotopomeres)

Collect and prepare dipole transition matrix elements

⇒ Einstein coefficients





v''

v'

q	0	1	2	3	4
0	2.41E+07	1.66E+06	9.27E+03	7.75E-02	5.62E-02
1	1.53E+06	2.07E+07	3.26E+06	2.97E+04	2.82E+00
2	1.07E+05	2.84E+06	1.74E+07	4.80E+06	6.23E+04
3	8.40E+03	3.19E+05	3.89E+06	1.43E+07	6.24E+06
4	5.87E+02	3.64E+04	6.22E+05	4.64E+06	1.15E+07
…					

U. Fantz, ADNDT 92, 2006, 853
D. Wünderlich, ADNDT 97, 2011, 152

Reaction probabilities for molecular hydrogen: New cross sections for ionization

Literature: virtually no data for ionization of excited states in H_2

Test case for cross section calculations based on the Gryzinski method. Two possible reaction channels:

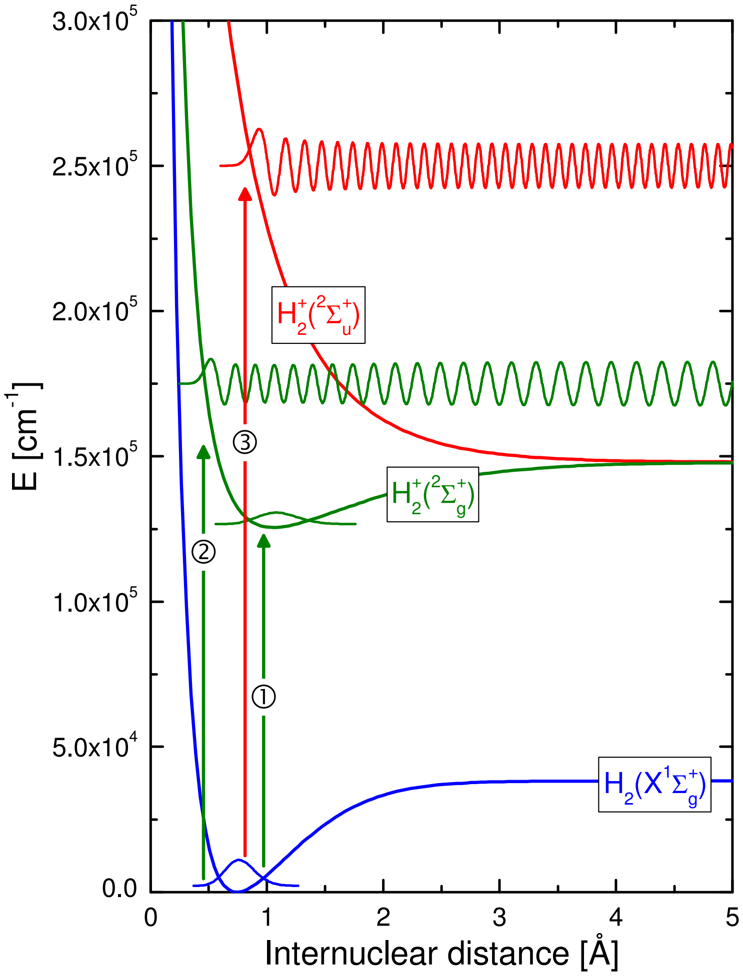
Non-dissociative

$$\mathrm{H}_2(p',v') + e^- \rightarrow \mathrm{H}_2^+\left({}^2\Sigma_\mathrm{g}^+, v''\right) + 2e^-$$

Dissociative

$$\mathrm{H}_2(p',v') + e^- \rightarrow \mathrm{H}_2^+\left({}^2\Sigma_\mathrm{g}^+, E''\right) + 2e^- \rightarrow \mathrm{H} + \mathrm{H}^+ + 2e^-$$

$$\mathrm{H}_2(p',v') + e^- \rightarrow \mathrm{H}_2^+\left({}^2\Sigma_\mathrm{u}^+, E''\right) + 2e^- \rightarrow \mathrm{H} + \mathrm{H}^+ + 2e^-$$



Needed for calculation of cross sections:

Franck Condon factors $q_{v'v''}^{p'p''}$ and…

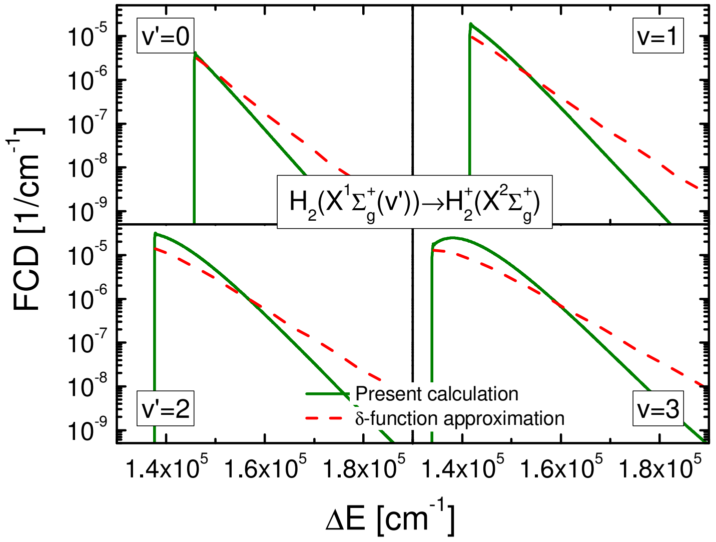
D. Wünderlich, Chem. Phys. 390, 2011, 75

Reaction probabilities for molecular hydrogen: New cross sections for ionization

Franck Condon densities $Q^{p'p''}_{v'E''}$ for transitions $H_2 \leftrightarrow H_2^+$

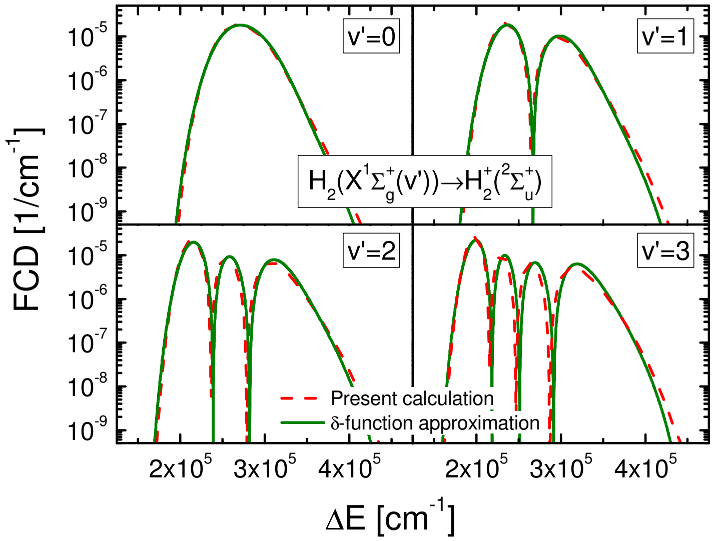
Most publications: δ-function-approximation:

$$Q^{p'p''}_{v'E''}\,\mathrm{d}E'' = \left|\left(\frac{\mathrm{d}U^{p''}(r)}{\mathrm{d}r}\right)^{-1}_{r=r^{p''}_{\mathrm{tp}}(E'')} \left|\psi^{p'}_{v'}\right|^{2}_{r=r^{p''}_{\mathrm{tp}}(E'')}\right| \mathrm{d}E''$$



More appropriate calculation based on wave functions from `TraDiMo`:

$$Q^{p'p''}_{v'E''}\,\mathrm{d}E'' = \frac{2}{h}\sqrt{\frac{2\mu}{(E''-E''_{\mathrm{diss}})}}\left|\psi^{p'}_{v'}(r)\psi^{p''}_{v''}(r)\mathrm{d}r\right|^{2} \mathrm{d}E''$$



Full set of FCD for H_2 and H_2^+

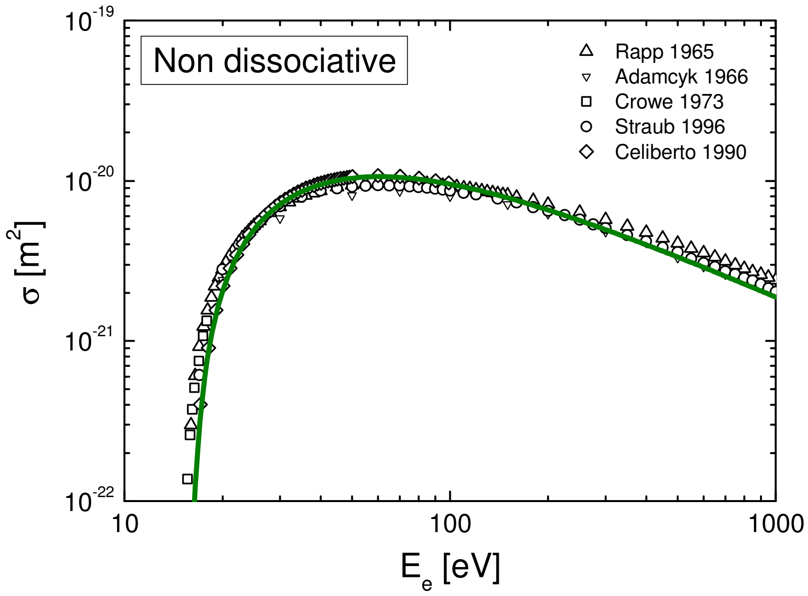
D. Wünderlich, Chem. Phys. 390, 2011, 75

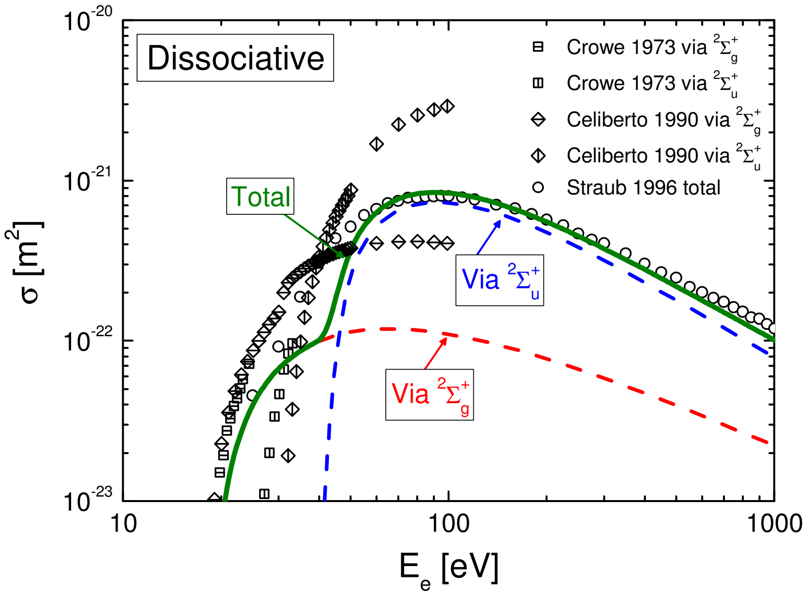
Reaction probabilities for molecular hydrogen: New cross sections for ionization

D. Wünderlich, Chem. Phys. 390, 2011, 75

$H_2(X^1)$: Comparison with existing data (experimental and theoretical)

- Perfect agreement for non dissociative process ✓
- Dissociative ionization:
  - Very good agreement with experiment ✓
  - Previous calculations:
    simplified theoretical framework

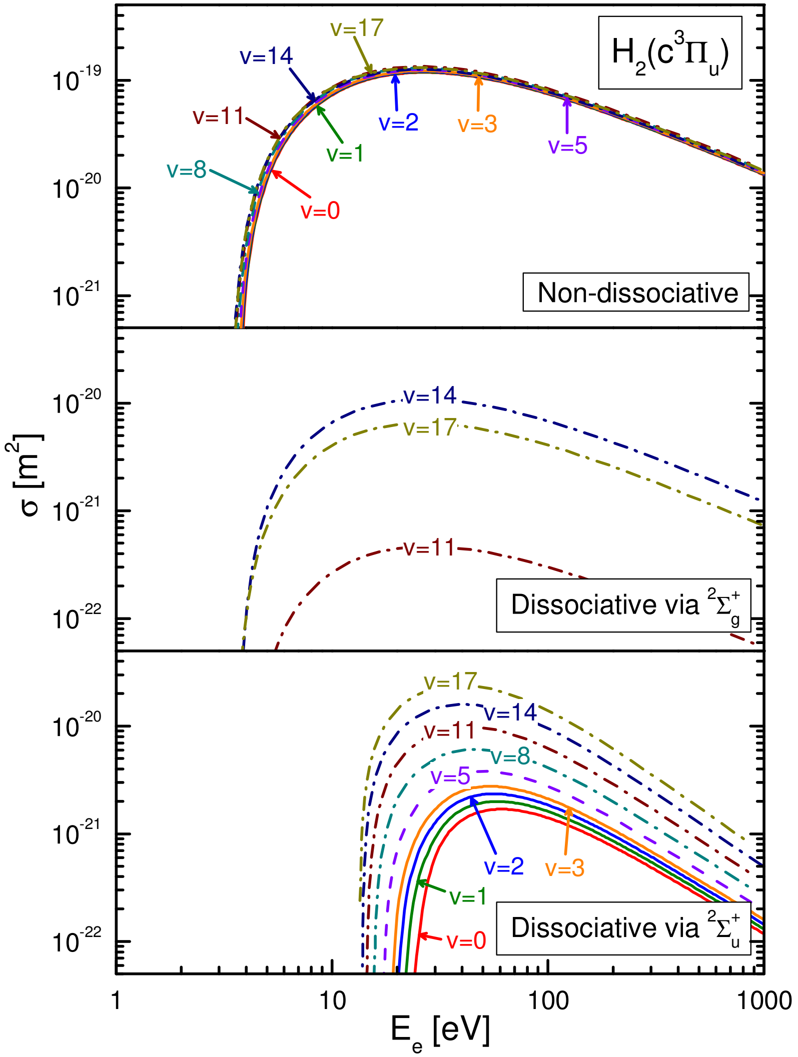




Reaction probabilities for molecular hydrogen: New cross sections for ionization

Construct set of ionization cross sections for H_2

- First five non repulsive electronic states:
  - Vibrational sublevels considered
  - All dissociative and non-dissociative channels

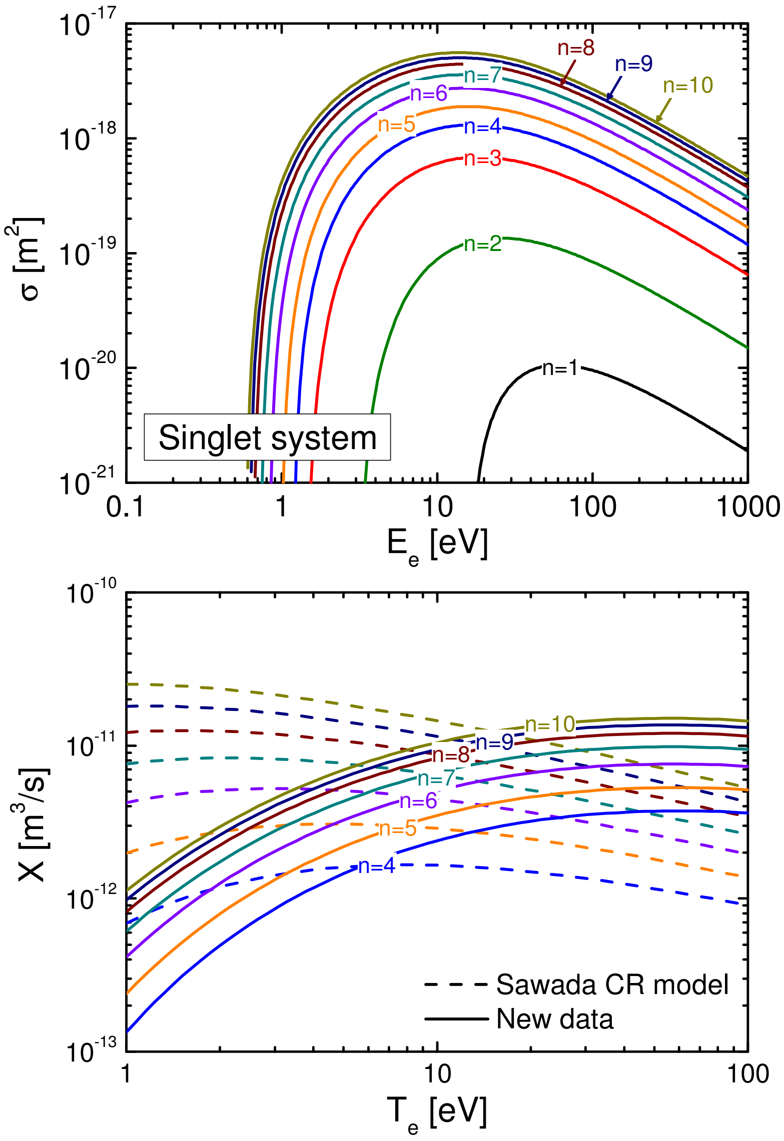


Reaction probabilities for molecular hydrogen: New cross sections for ionization

Construct set of ionization cross sections for H_2

- First five non repulsive electronic states:
  - Vibrational sublevels considered
  - All dissociative and non-dissociative channels
- Electronically excited states with n>2:
  - Gryzinski formula
  - Vibrational sublevels neglected
  - Disagreement with data previously used in models

Most accurate existing set of theoretical ionization cross sections for H_2



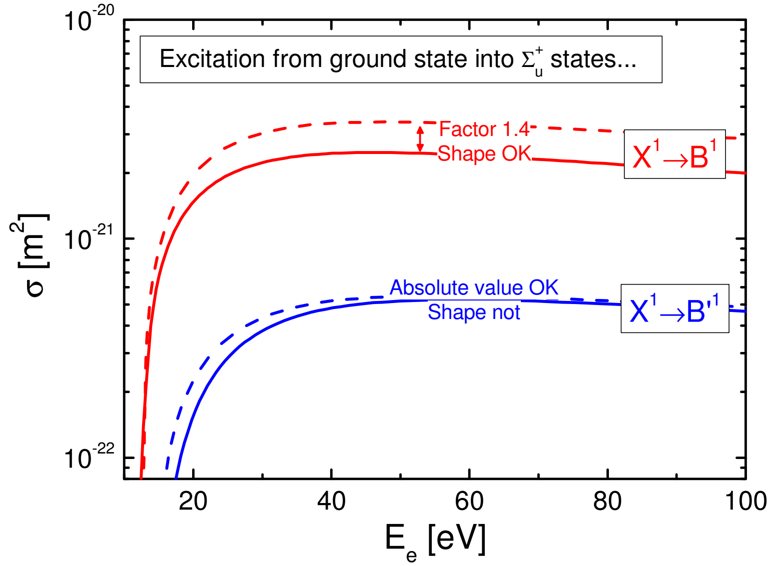
Reaction probabilities for molecular hydrogen: Apply Gryzinski method for collisional excitation?

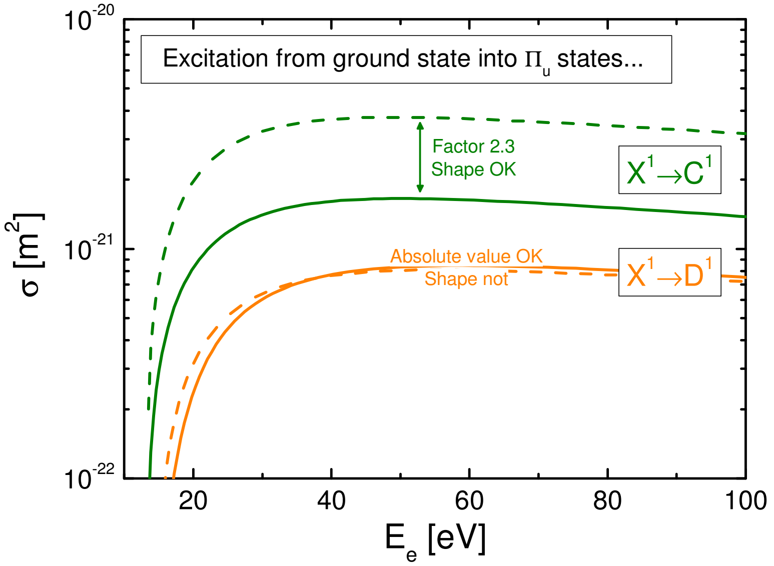
Gryzinski calculations for excitation of H_2

- Original Gryzinski integral
  (not the simplified GBB formulation)
- Benchmark by comparison with σ suggested by Janev
  - Highly variable agreement
  - Situation worse for forbidden transitions
    (e.g. excitation into triplet system)
  - Allowed transitions:
    impact parameter as alternative.
    But: high relevance of triplet levels (OES)

Semiempiric methods not appropriate for molecular excitation.

Needed: new, complete and comprehensive set of quantum mechanical calculations



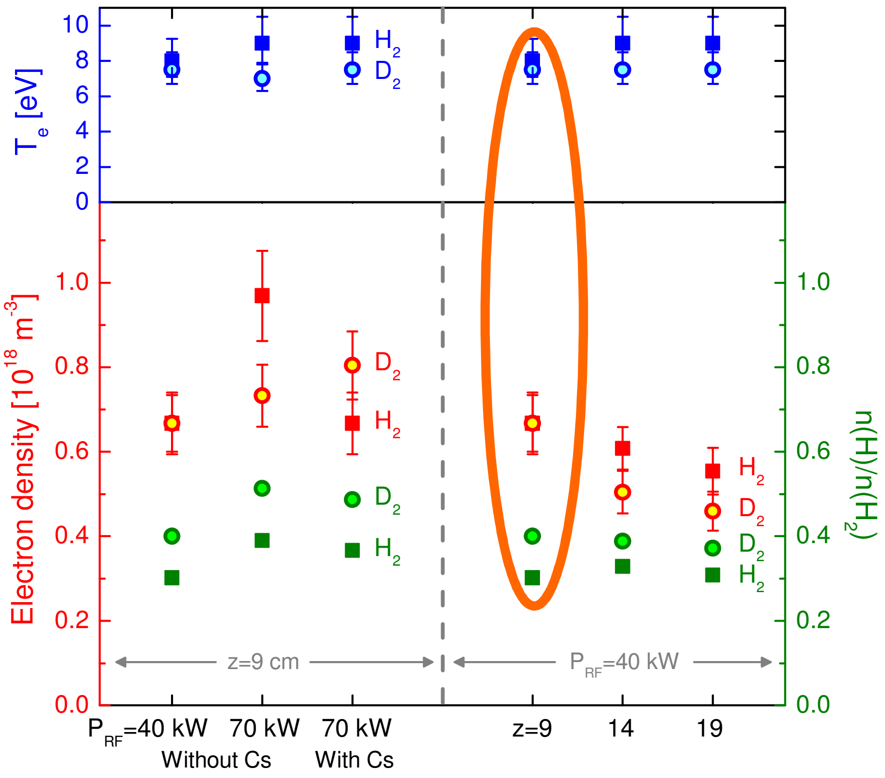


Reaction probabilities for molecular hydrogen: Extension of the model to deuterium

Evaluation of available data

- Only few vibrationally resolved data available for H_2 and D_2
  (main exception:
  impact parameter calculations for optically allowed transitions)
- CR model for D_2 urgently needed
  (example: isotope effect in dissociation and electron extraction in negative ion sources)
- Interim solution:
  vibrational splitting of data by Janev
  (or Miles?) by means of Gryzinski method
- Long-term solution:

Comprehensive set of cross sections for both isotopes



Atomic and molecular data in CR models: Conclusions and outlook

State resolved reaction probabilities for CR models

- Flexible solver `Yacora`: models for H, H_2, He, …
- Error bar of results is correlated with the quality of the used input data:
  - He: excellent quality of input data for models ✓
  - H: very good results of model possible ✓
    Negative ion source for ITER NBI: observed issues explainable by gradients of plasma parameters?
  - H_2: Existing data basis not sufficient
    First steps towards an improved data set have been done

> More efforts needed, especially based on sophisticated quantum mechanical calculations

Outlook

- Increased modeling efforts for Deuterium
- Rotational excitation (neglected up to now)