

Resonant Ion Pair formation (RIP) and associative ionization (AI): their possible connections

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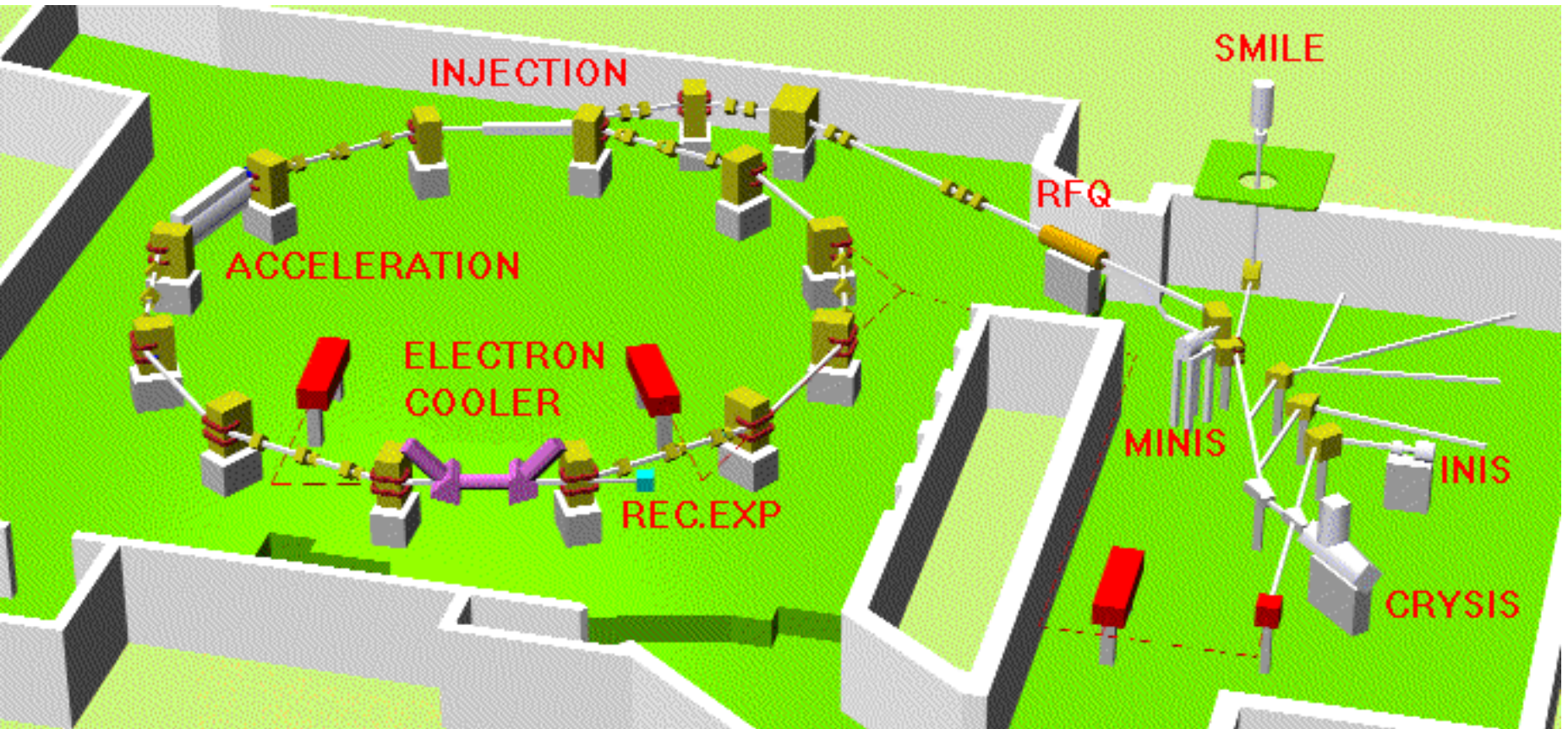
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Outline

- Introduction
- Resonant Ion Pair Formation (Sweden)
 - Experimental setup : CRYRING
 - Results : HD^+ and HF^+
- Associative Ionization (Belgium)
 - Experimental setup : MB2
 - Results : $\text{H}^+ + \text{H}^-$ and $\text{C}^+ + \text{O}^-$
- Conclusions

CRYRING Sweden



Circumference : 51.6m
Interaction region : 0.85 m

Analysis procedure

Important points

- **Electron cooling** (Reduction of the phase space of the ion beam by momentum transfer between the “cold” electrons and the “hotter” ion beam).
 - ⇒lengthening of the lifetime
 - ⇒cooling of the internal degree of freedom of a molecule with a sizeable dipole moment
- **Detuning energy** $E_d = \mu v_d^2/2$
 - ⇒excellent energy resolution in the cm frame (1meV) - Use of the adiabatic decompression of an electron beam in a gradient magnetic field
 - ⇒limitation due to the transverse motion of the electrons
 - ⇒space charge correction on the centre-of-mass energies has to be achieved
 - ⇒special caution concerning the drag force

– Measured parameter : rate coefficient

$$R(E_{\text{cm}}) = \langle \sigma(E_{\text{cm}}) v_{\text{cm}} \rangle$$

⇒ True signal to be extracted from background coming from the molecular ions - rest gas interactions

⇒ possible complications due to the “trapping effect” ?

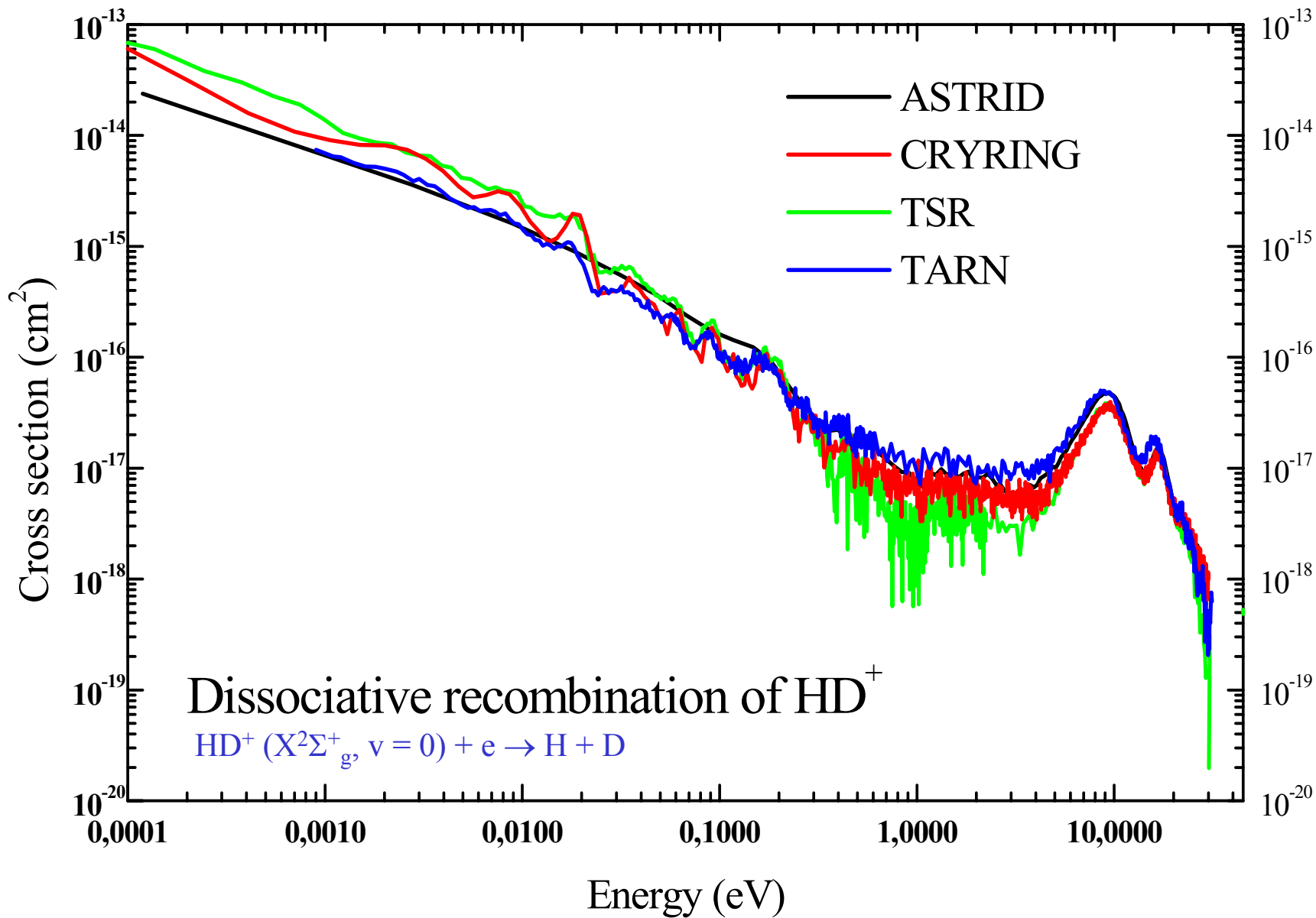
DISSOCIATIVE RECOMBINATION



RESONANT ION PAIR FORMATION



⇒ In a storage ring, the target molecular ion can be prepared in its electronic and vibrational ground states



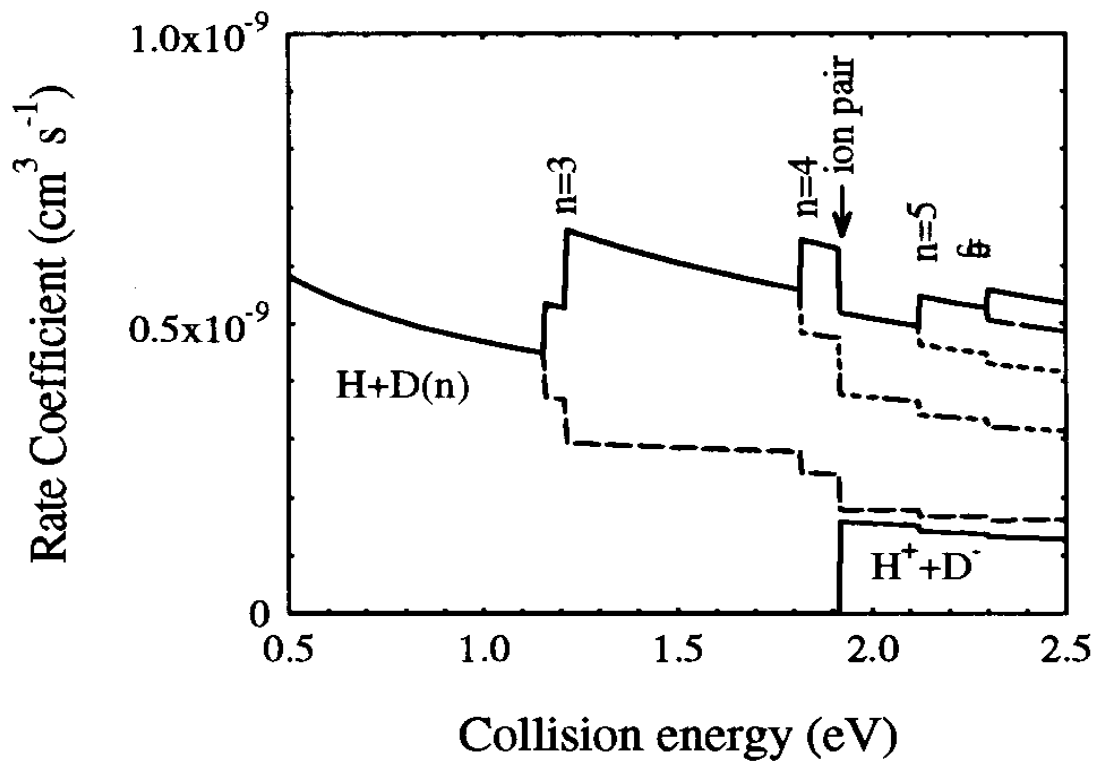


Figure 4. Total and partial rate coefficients obtained with the MSCC model. The absolute scale is given by the direct cross section of Schneider *et al.*²¹

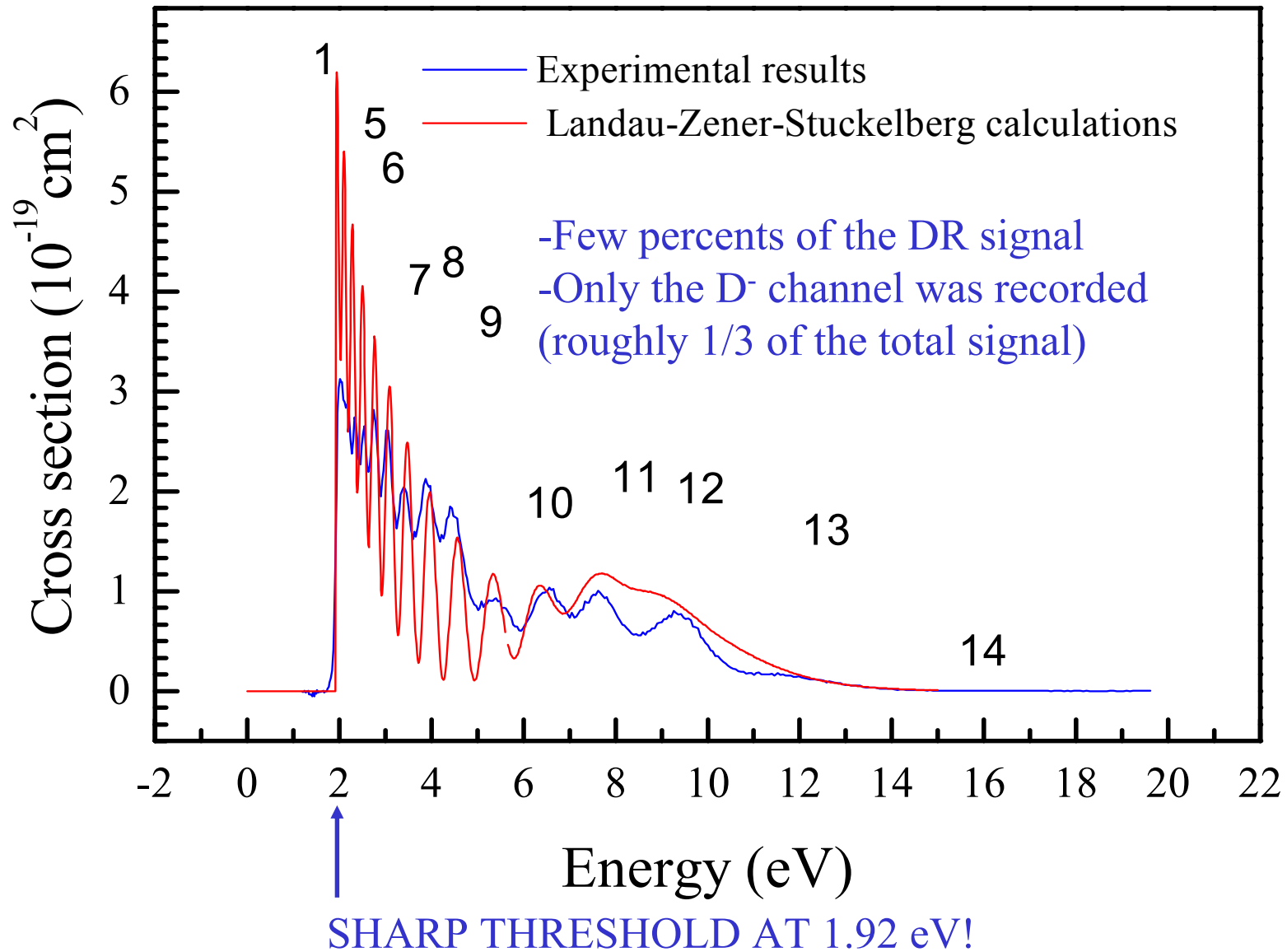


TABLE I. Energies from Fig. 1 at which the HD^+ RIP cross section shows peaks for both the observed and modeled cases, the observed spacings between adjacent peaks, and energy regions Δ_i relating to text discussion.

#	Observed peak energies (eV)	Landau-Zener-Stückelberg theory (eV)	Region	Observed energy splitting to previous peak (eV)
1	1.99	2.00		...
2	2.17	2.15		0.18
3	2.36	2.32	Δ_1	0.19
4	2.53	2.54		0.17
5	2.76	2.79		0.23
6	3.04	3.10		0.28
7	3.40	3.49	Δ_2	0.36
8	3.87	3.97		0.47
9	4.44	4.58		0.57
10	5.34	5.37		0.90
11	6.50	6.39		1.16
12	7.61	7.77	Δ_3	1.11
13	9.28	9.66		1.67
14	11.31	12.38		2.03

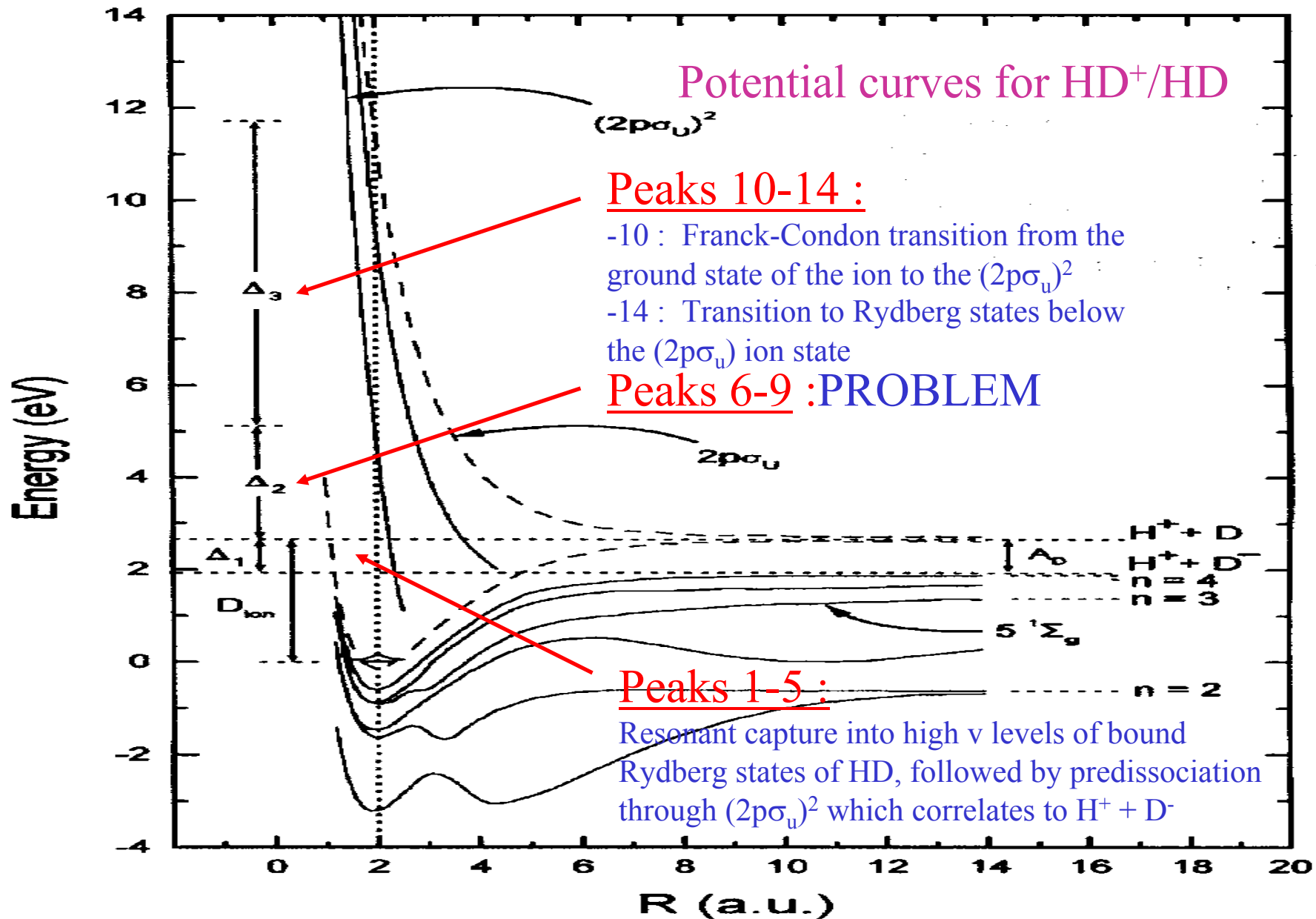


FIG. 2. Potential curves adapted from Ref. [12]. Dashed curves are potential curves for HD⁺; solid curves are exemplary for neutral HD. Δ_i indicates energy regions relevant to the text discussion. Asymptotic limits are indicated on right.

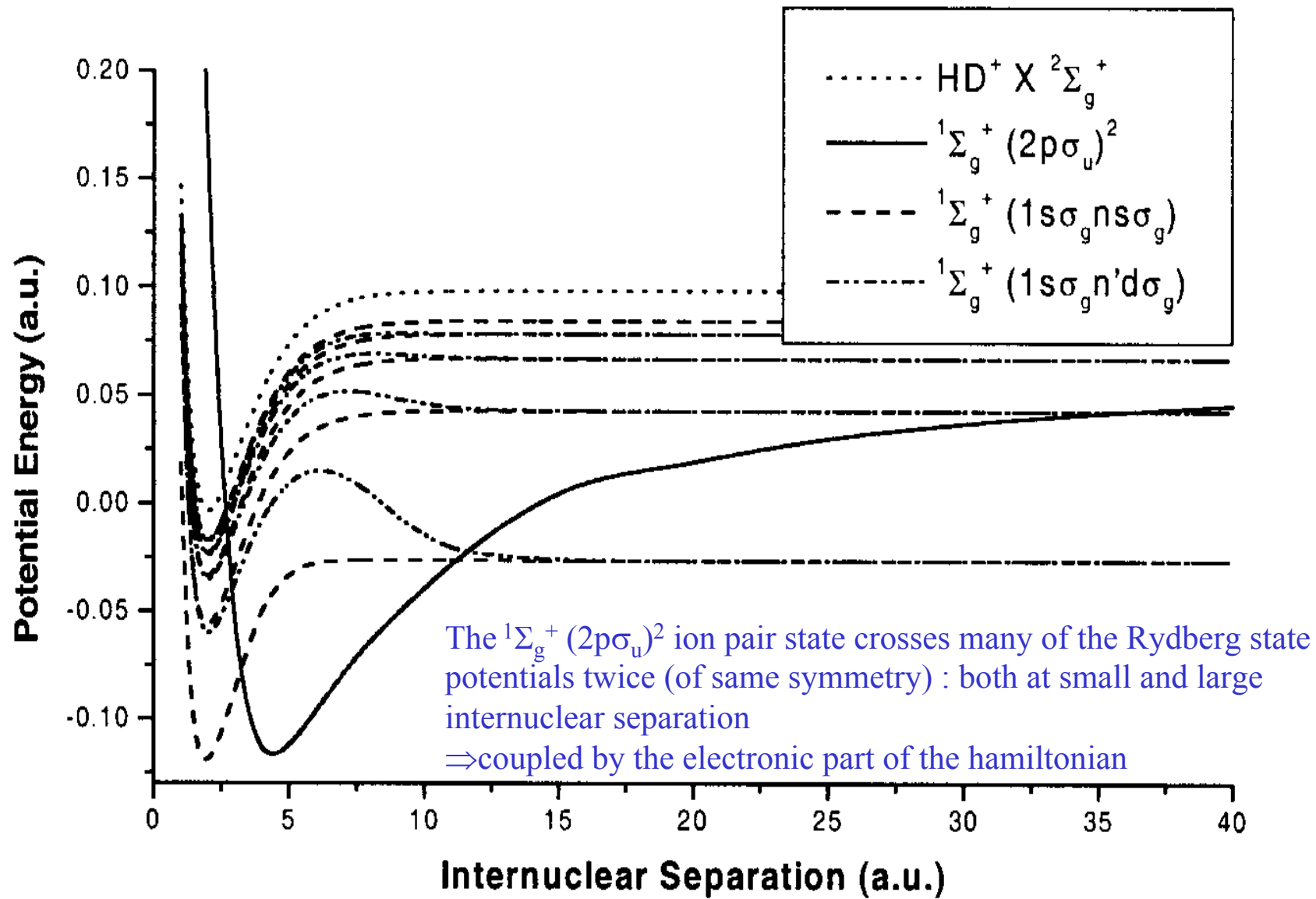


Figure 1. Diabatic potential energy curves of HD⁺ and HD.

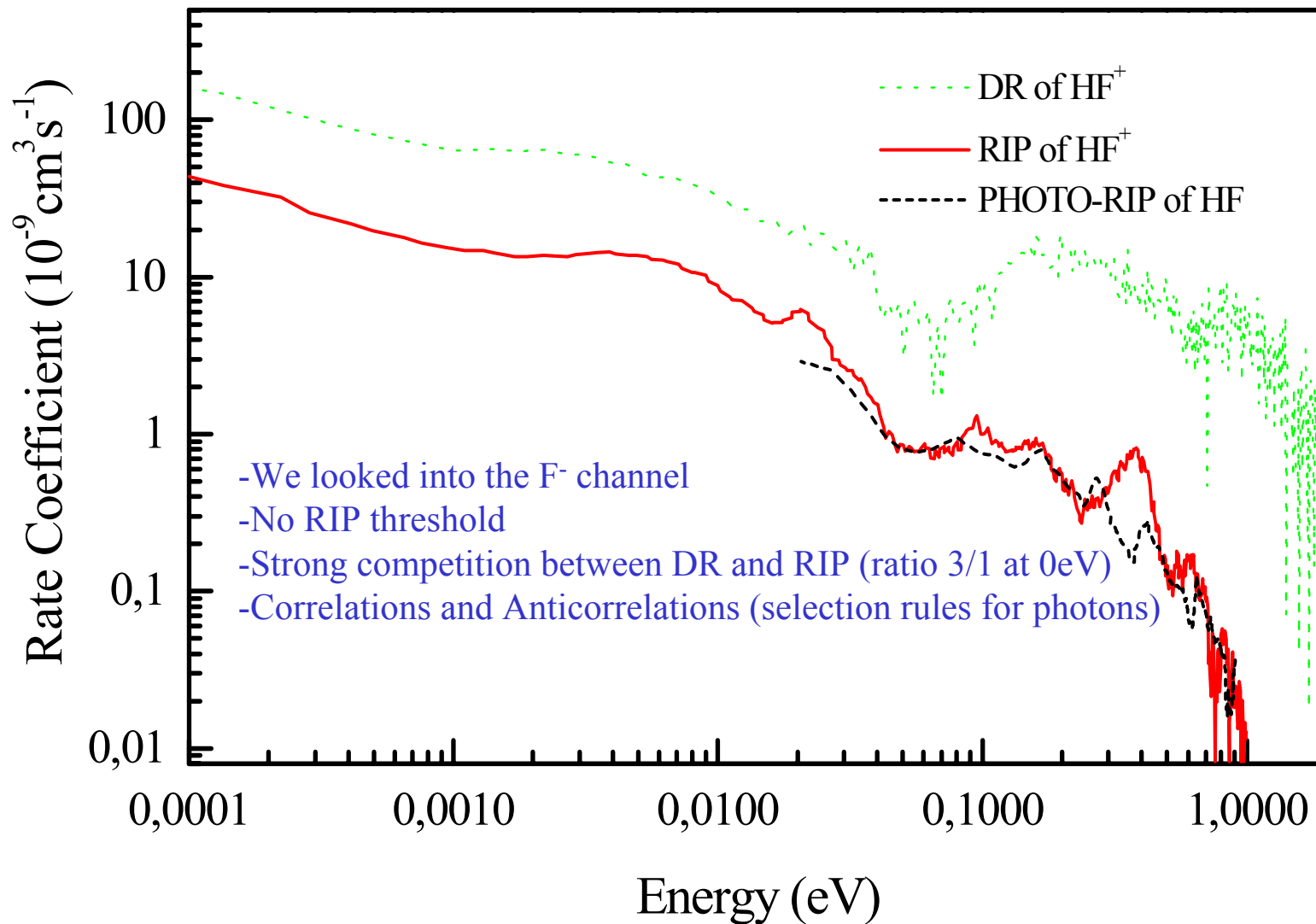
Landau - Zener - Stuckelberg calculations

The energy-dependent (semi-classical) phases accumulated along the different pathways have to be taken into account :

$$\varphi_i(E) = \int_{R_E}^{R_2} k_i(R) dR = \int_{R_E}^{R_2} \sqrt{2\mu(E - V_i(R))} dR .$$

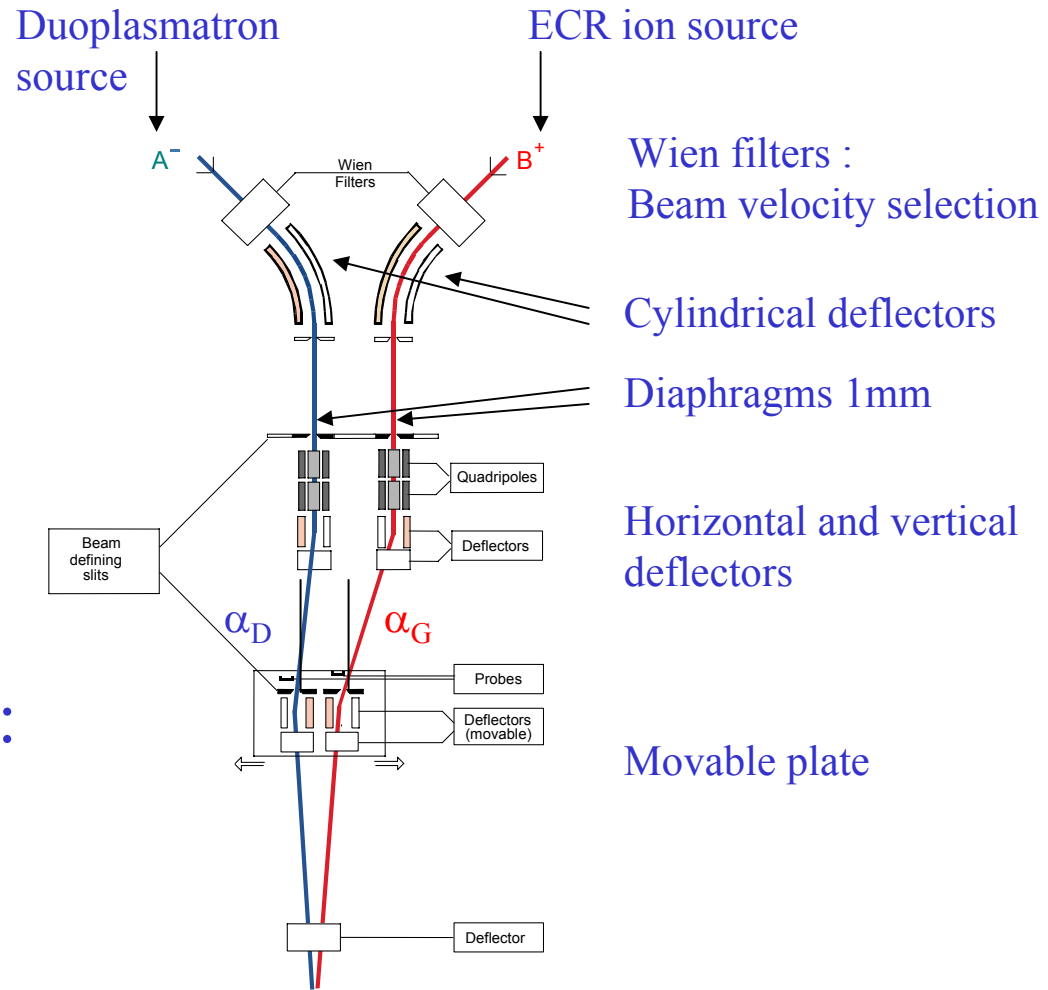
The transition amplitudes at the curve crossings are treated by the L-Z method and the product amplitudes are added coherently. The autoionization is included by a complex term of the dissociative potential and the capture probability is estimated by assuming a delta nuclear wave function of the dissociative state. Thus, the cross section for the ion- pair formation becomes :

$$\sigma_{ip}(E) = \frac{2\pi^2}{E} \Gamma(R_E) |\chi_0(R_E)|^2 \left| \frac{\mu\omega}{2V'} \right|^2 \left| A_1(E)e^{i\varphi_1(E)} + A_2(E)e^{i\varphi_2(E)} + \dots + A_4(E)e^{i\varphi_4(E)} \right|^2$$



MB2 machine UCL Belgium

Merging conditions :
 $\alpha_G / \alpha_D = A_D / A_G$



CINEMATICS OF THE EXPERIMENT

Center-of-mass energy in the interaction region (for beams merging at 0 angle) :

$$E_{CM} = \mu \left[\sqrt{\frac{q_2 (A_2 - V_0)}{m_2}} - \sqrt{\frac{q_1 (A_1 - V_0)}{m_1}} \right]^2$$

With :

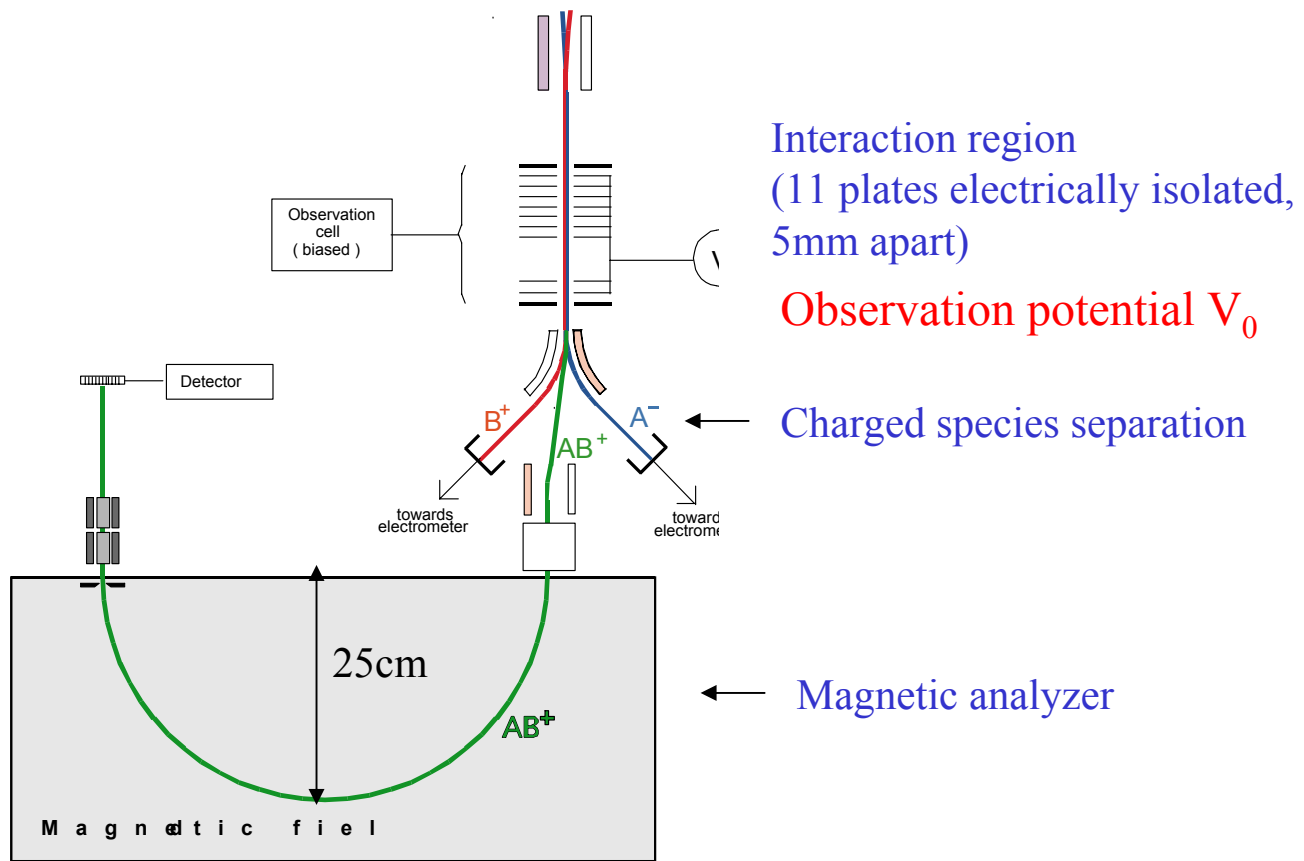
$$\begin{array}{lll} q_1 = q_G = 1 & m_1 = m_G & A_1 = A_G \\ q_2 = q_D = -1 & m_2 = m_D & A_2 = A_D \end{array}$$

Beams assumed to be monoenergetic and with velocities close from each other in the lab frame !

and :

Observation potential V_0

ENERGY RESOLUTION : 2meV at $E_{cm} = 10\text{meV}$!!!!!!!!!!!!!!!



DETERMINATION OF THE CROSS SECTION

$$\sigma = q_1 \cdot q_2 \frac{V_1 \cdot V_2}{V_r} \frac{1}{\int_0^T I_1(t) \cdot I_2(t) \cdot dt} \frac{N(T)}{F}$$

Total number of events

Current integral

With :

$$q_1 = q_G = 1$$

$$v_1 = v_G$$

$$I_1 = I_G$$

$$q_2 = q_D = -1$$

$$v_2 = v_D$$

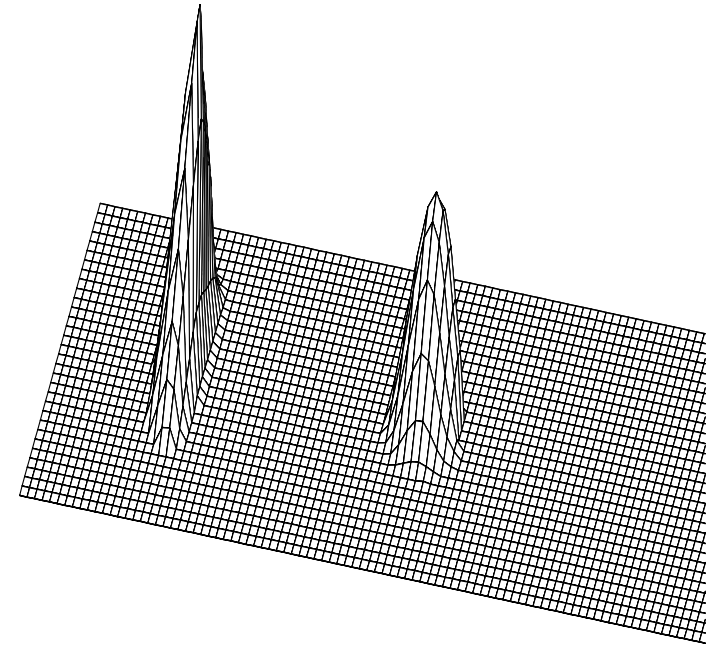
$$I_2 = I_D$$

and :

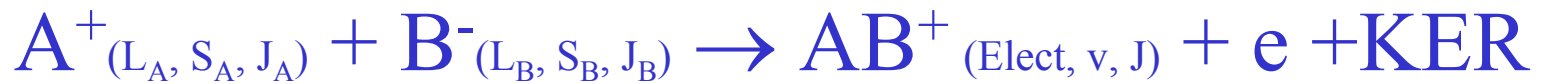
Relative velocity v_r

Form factor F

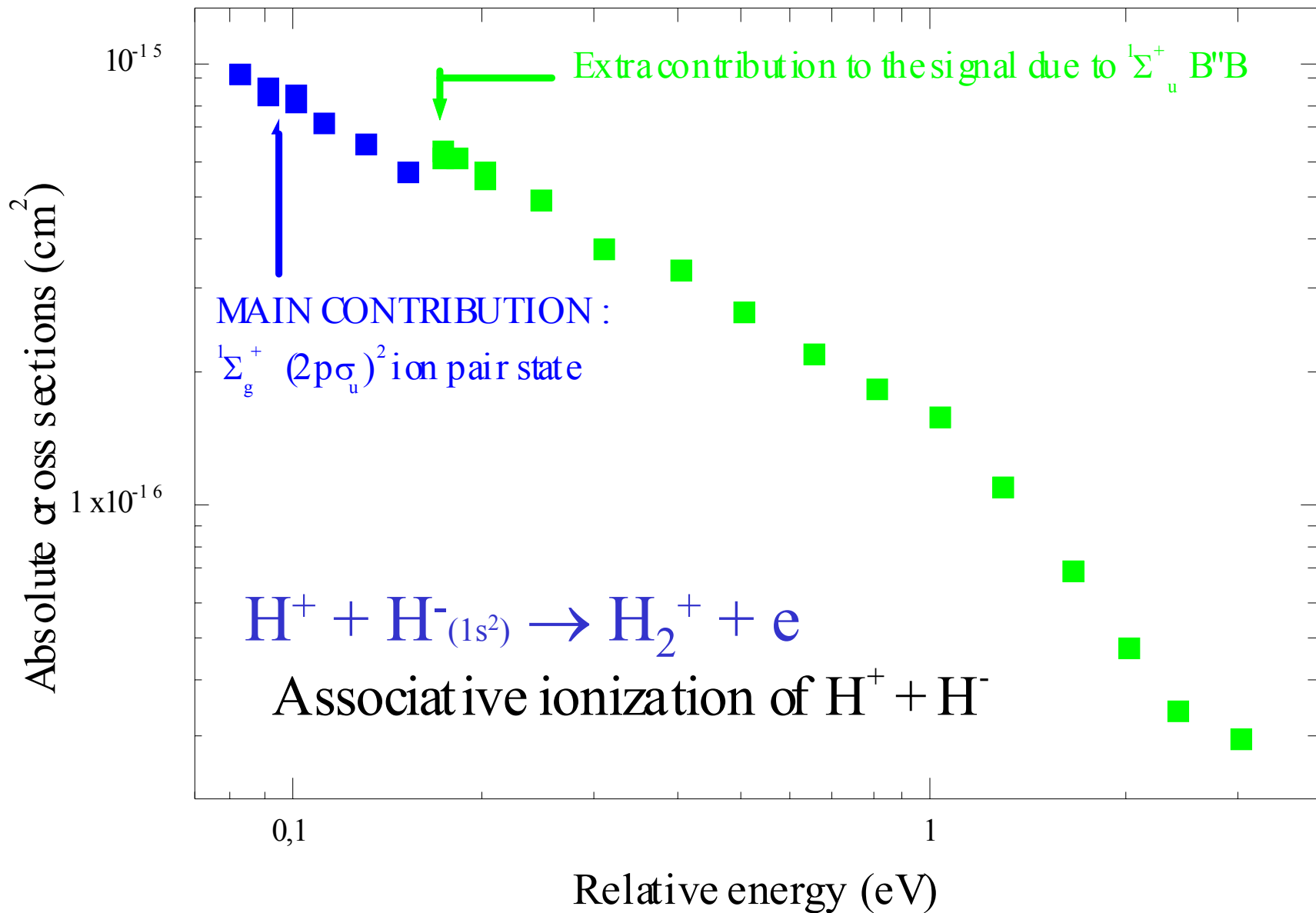
$$F(z) = \frac{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} j_1(x, y, z) \cdot j_2(x, y, z, t) \cdot dx dy}{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} j_1(x, y) \cdot dx dy \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} j_2(x, y) \cdot dx dy}$$

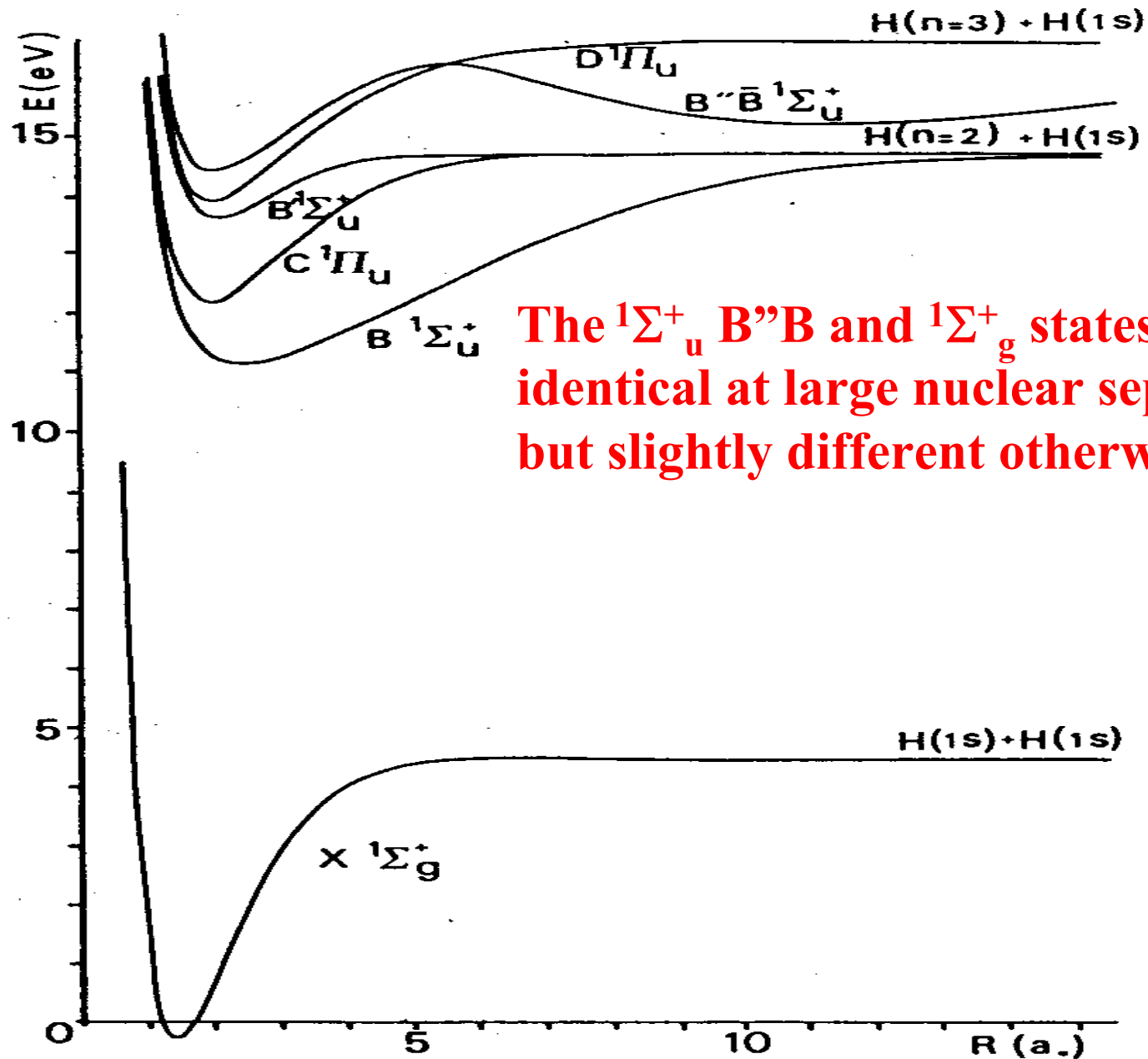


ASSOCIATIVE IONIZATION



- Efficient process when the time spent by the nuclei in the binding part of the potential is in the same order than the vibrating period.
- The product molecular ion is formed in different electronic, vibrational and rotational states !
- When the dissociation energy of the molecular ion is overcome, the Penning ionization is competing.
- To have more infos concerning the v , N distributions, means to record the energy spectrum of the electrons ; NOT POSSIBLE with this setup!





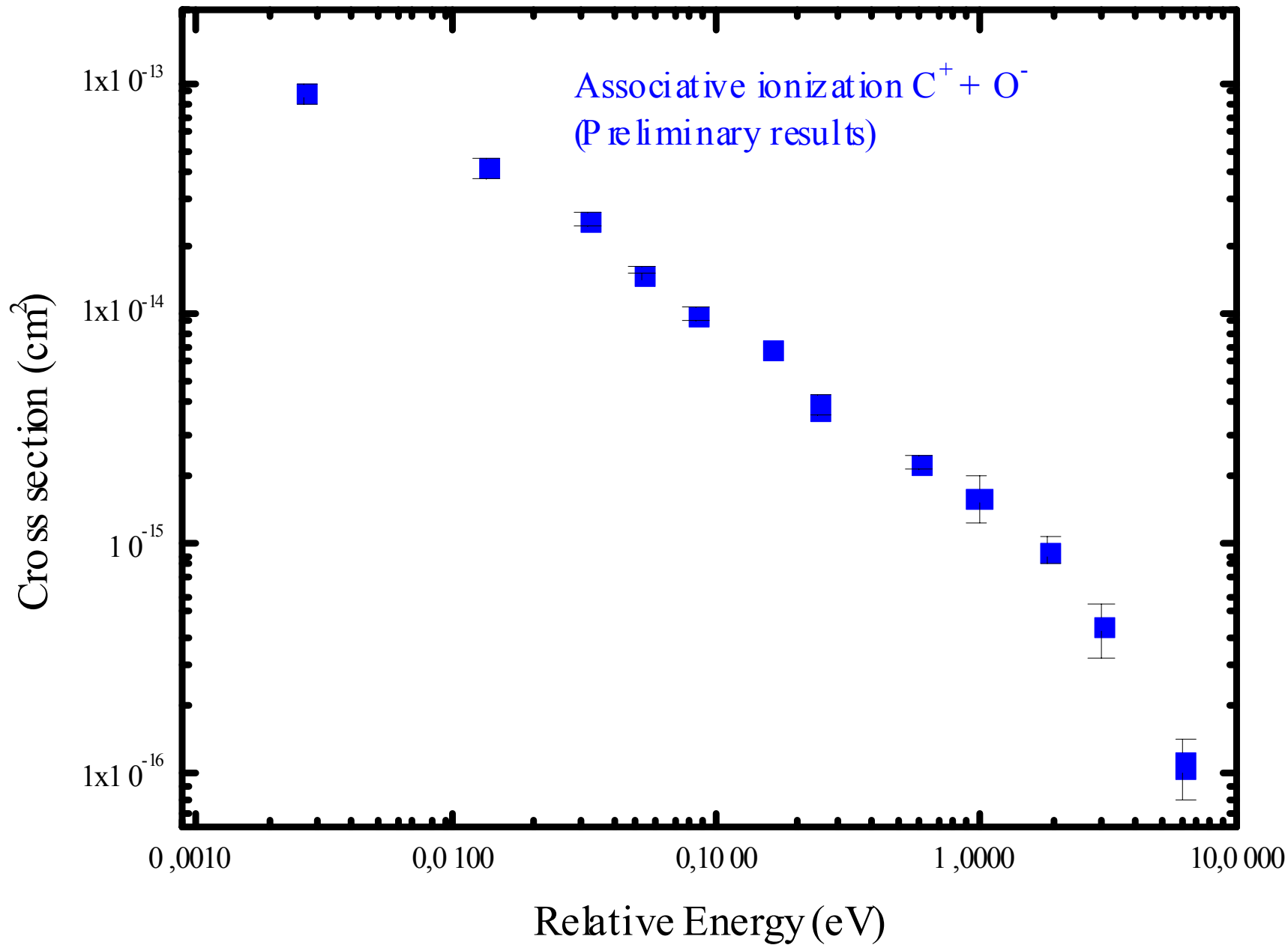
The $1\Sigma_u^+$ B''B and $1\Sigma_g^+$ states are identical at large nuclear separations but slightly different otherwise !

FIG. 1. Relevant potential energy curves for the lowest singlet states of H_2 from Refs. 1-4.

-There is only one H_2^+ electronic state which can be populated from $\text{H}^+ + \text{H}^-$ at low energy.

⇒this might have some influence on the magnitude of the cross section ($1 \cdot 10^{-15} \text{ cm}^2$ at 0.08eV).

-Sharp cutoff at 3eV (competition with the Penning ionization).



- -Very large cross sections !

$$\sigma = 6 \cdot 10^{-14} \text{ cm}^2 \text{ at } 10 \text{ meV}$$

Possible reasons : number of exothermic channels !

- Different electronic states for CO^+ ($X^2\Sigma^+$, $A^2\Pi$, $B^2\Sigma^+$, $C^2\Delta$, $D^2\Pi$).
- Possible rovibronic excitation of the molecular ion.
- Many potential curves to drive the process : the correlation rules for the ionic states give
 - 2x Σ^+
 - 1x Σ^-
 - 2x Π
 - 1x Δ

Both singlet and triplet states !!

- -Cutoff at 6 eV (Penning Ionization)

Links between RIP and AI

- Theoretical cross sections (Development in partial waves) :

$$\sigma_{\text{RIP}}^{(v,N)}(E_{\text{cm}}) = \Pi/k_{\text{cm}}^2 \left| S^{v,N} \right|^2$$

$$\sigma_{\text{AI}}^{(v,N)}(E'_{\text{cm}}) = \Pi/k'_{\text{cm}}^2 \sum_N \sum_v \left| S^{v,N} \right|^2 (2N+1)$$

The matrix elements are given by :

$$S = (1+iK)/(1-iK) \text{ with } iK \approx -\Pi V \text{ and } V \approx \left\langle \left| 1/r_{12} \right| \right\rangle$$

Conclusion and perspectives

- Results concerning the RIP process
 - Rosenthal oscillations for HD^+ .
 - Data for HF^+ for which DR and RIP present the same trend.
- Results concerning the AI process
 - $\text{H}^+ + \text{H}^-$: interplay between gerade and ungerade states.
 - $\text{C}^+ + \text{O}^-$: large cross sections due to the manifold of possible exit channels.

Acknowledgments

- Stockholm
 - M Larsson
 - W Zong
 - GH Dunn
 - N Djuric
 - A Larson
 - The other members of the Molecular Physics Group
- LLN
 - F Brouillard
 - S Szucs
 - X Urbain
 - E Naji
 - T Nzeyimana