Electron spectra from associative detachment of negative ions

(and metastable molecular anions)

- **Electron spectra for $H + X^- \rightarrow HX + e^-$**
  (short review of theory and experiments)
- **Long-lived metastable states HX^-**
  (theoretical predictions)

Martin Čížek

Charles University Prague

History of this project

1997 with **Wolfgang Domcke** (Duesseldorf)

numerical methods for $H + X^- \leftrightarrow HX + e^-$

X=H: *J. Phys.* B **31** (1998) 2571,

X=Cl: *Phys. Rev.* A **60** (1999) 2873,

X=Br: *Phys. Rev.* A **63** (2001) 062710.

1999 with **Hartmut Hotop** (Kaiserslautern)

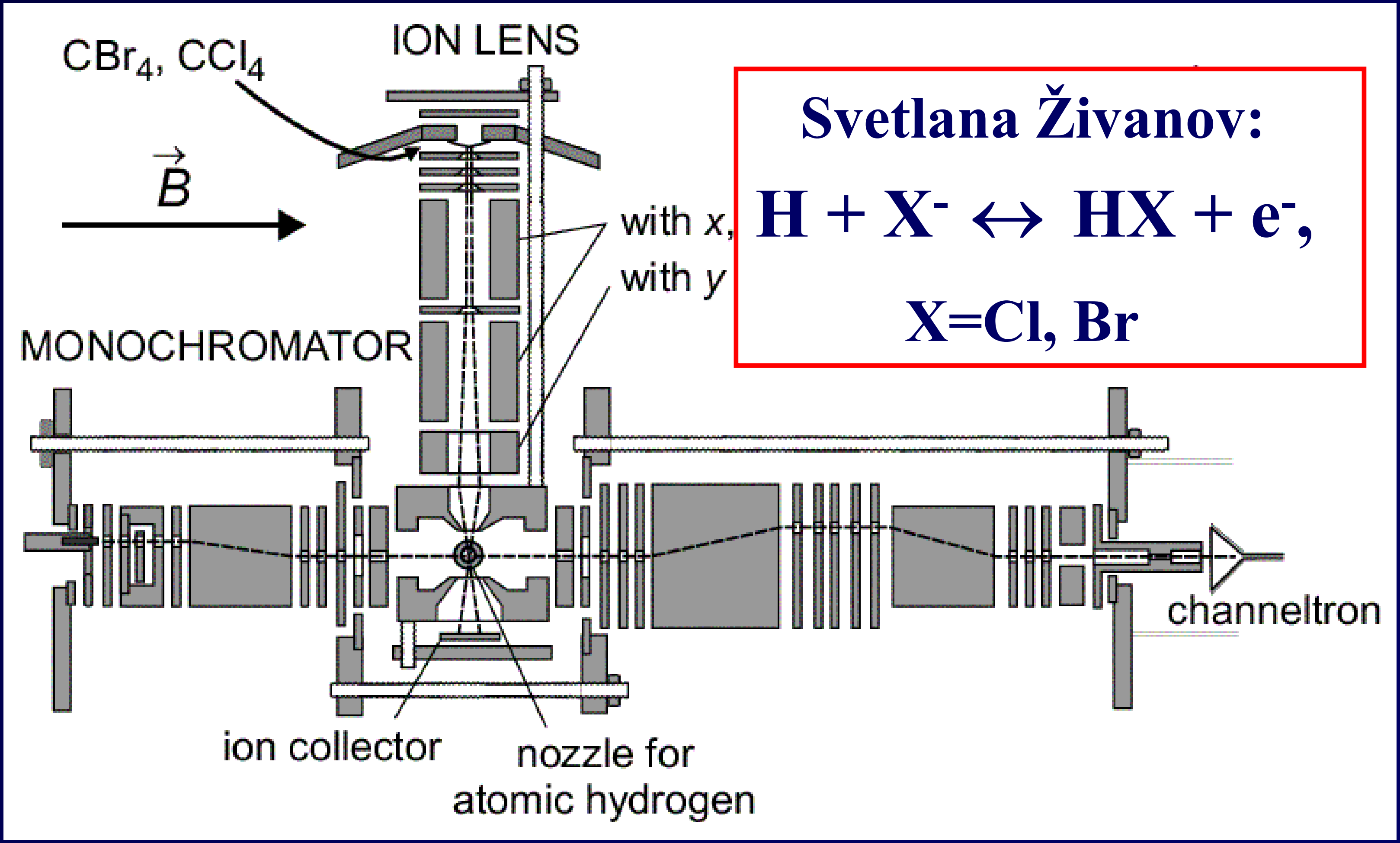
simulation of electron spectra

$$H + X^- \rightarrow HX + e^-, \quad X=F, Cl, Br$$

J. Phys. B **34** (2001) 983.

History of this project

2001 - Michael Allan (Fribourg)



Svetlana Živanov:

$$\mathrm{H} + \mathrm{X}^- \leftrightarrow \mathrm{HX} + e^-,$$

X=Cl, Br

Phys. Rev. Lett. **89** (2002) 073201, *J. Phys.* B **36** (2003) 3513.

History of this project

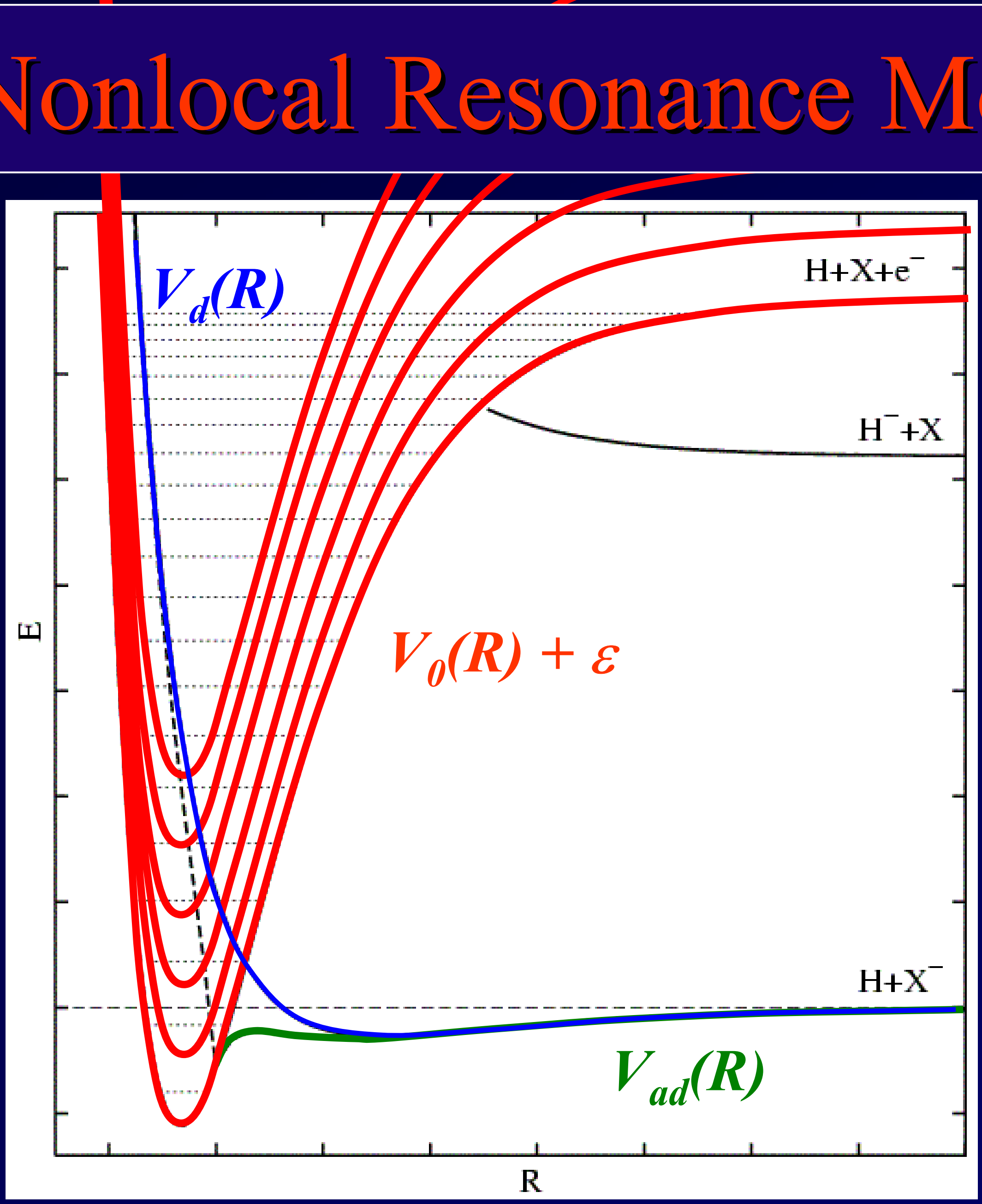
2004 question from **Xuefeng Yang**

? Existence of long-lived ($\tau \sim \mu s$) states H_2^- ?

YES! Highly rotating states (orbiting $H + H^-$)

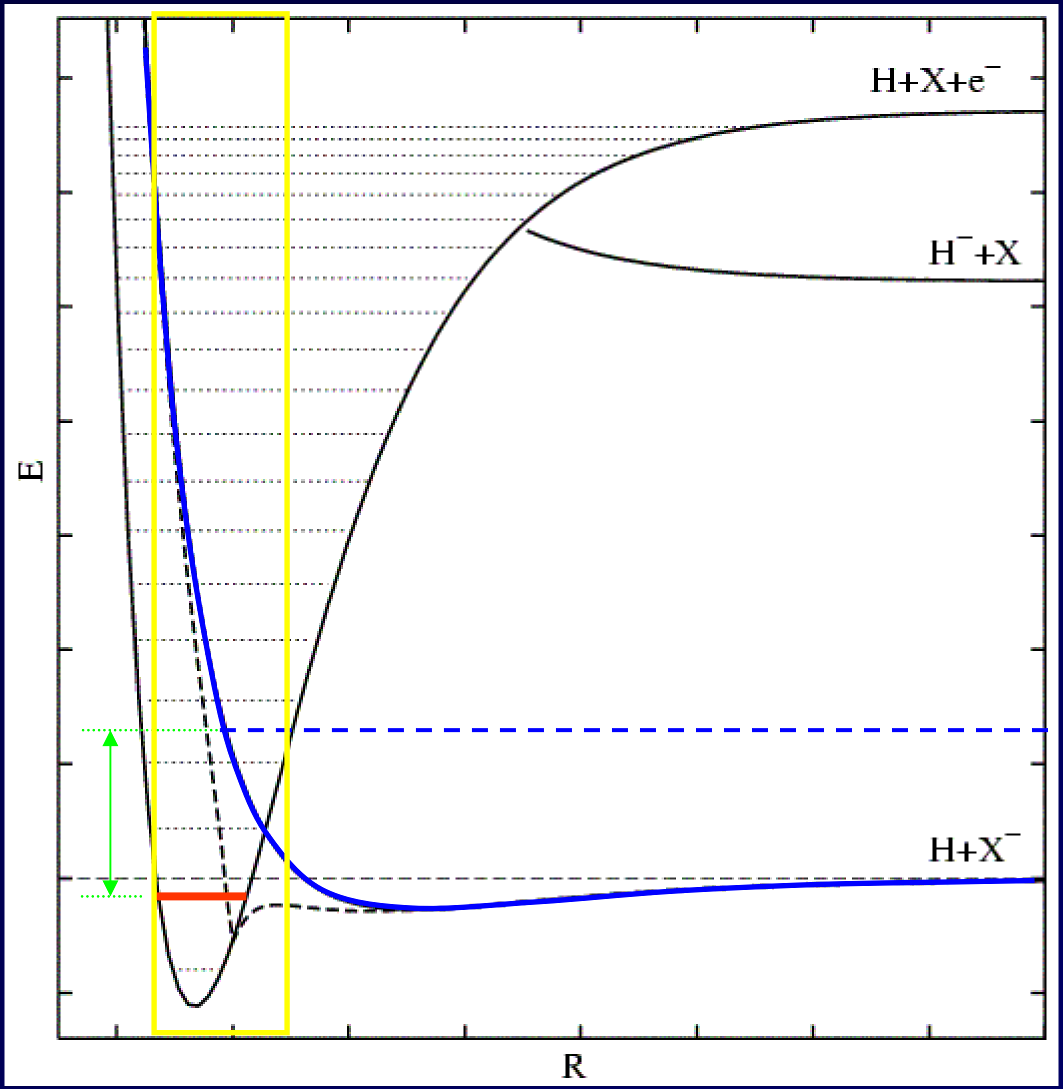
Similar states for other systems?

Nonlocal Resonance Model



$V_{d\varepsilon}(R)$

Associative detachment $X^- + H \rightarrow HX + e^-$



Final diabatic basis set

Discrete state $\phi_d(R,r)$ … $\langle \phi_d | H_{el} | \phi_d \rangle = V_d(R)$

Continuum $\phi_\varepsilon(R,r)$ … $\langle \phi_\varepsilon | H_{el} | \phi_{\varepsilon'} \rangle = (V_0(R) + \varepsilon)\delta(\varepsilon - \varepsilon')$

Coupling $\langle \phi_d | H_{el} | \phi_\varepsilon \rangle = V_{d\varepsilon}(R)$

Diabaticity of the basis: $\frac{\partial}{\partial R}\phi_d(R,r) \cong 0, \quad \frac{\partial}{\partial R}\phi_\varepsilon(R,r) \cong 0$

Hamiltonian in the basis:

$$H = T_N + |\phi_d\rangle V_d \langle \phi_d| + \int \left(|\phi_\varepsilon\rangle (V_0 + \varepsilon) \langle \phi_\varepsilon| + |\phi_d\rangle V_{d\varepsilon} \langle \phi_\varepsilon| + |\phi_\varepsilon\rangle V_{d\varepsilon}^* \langle \phi_d| \right) d\varepsilon$$

$$= H_0 + V = \left(\begin{array}{c|ccc} T_N + V_d(R) & \cdots & 0 & \cdots \\ \hline \vdots & \ddots & & 0 \\ 0 & & V_0(R) + T_N + \varepsilon & \\ \vdots & 0 & & \ddots \end{array} \right) + \left(\begin{array}{c|ccc} 0 & \cdots & V_{d\varepsilon}(R) & \cdots \\ \hline \vdots & \ddots & & 0 \\ V_{d\varepsilon}^*(R) & & 0 & \\ \vdots & 0 & & \ddots \end{array} \right)$$

Equation of motion for nuclei

$$\left[-\frac{1}{2\mu}\frac{\partial^2}{\partial R^2}+\frac{J(J+1)}{2\mu R^2}+V_d(R)-E\right]\psi_d(R)+$$

$$+\sum_v \chi_v^J(R)\int dR' f\left(E-E_v^J, R, R'\right)\chi_v^J(R')\psi_d(R')=0$$

where

$$f(\varepsilon,R,R')=\int d\varepsilon'(\varepsilon-\varepsilon'+i0)^{-1}V_{d\varepsilon'}(R)V^*_{d\varepsilon'}(R')$$

Threshold behavior

$$V_{d\varepsilon}(R)\sim\theta(\varepsilon)\varepsilon^{\alpha}$$

dipole scattering : $0<\alpha<1/2$

s - wave scattering : $\alpha=1/2$

p - wave scattering : $\alpha=3/2$

Calculation of electron spectra

AD cross section:

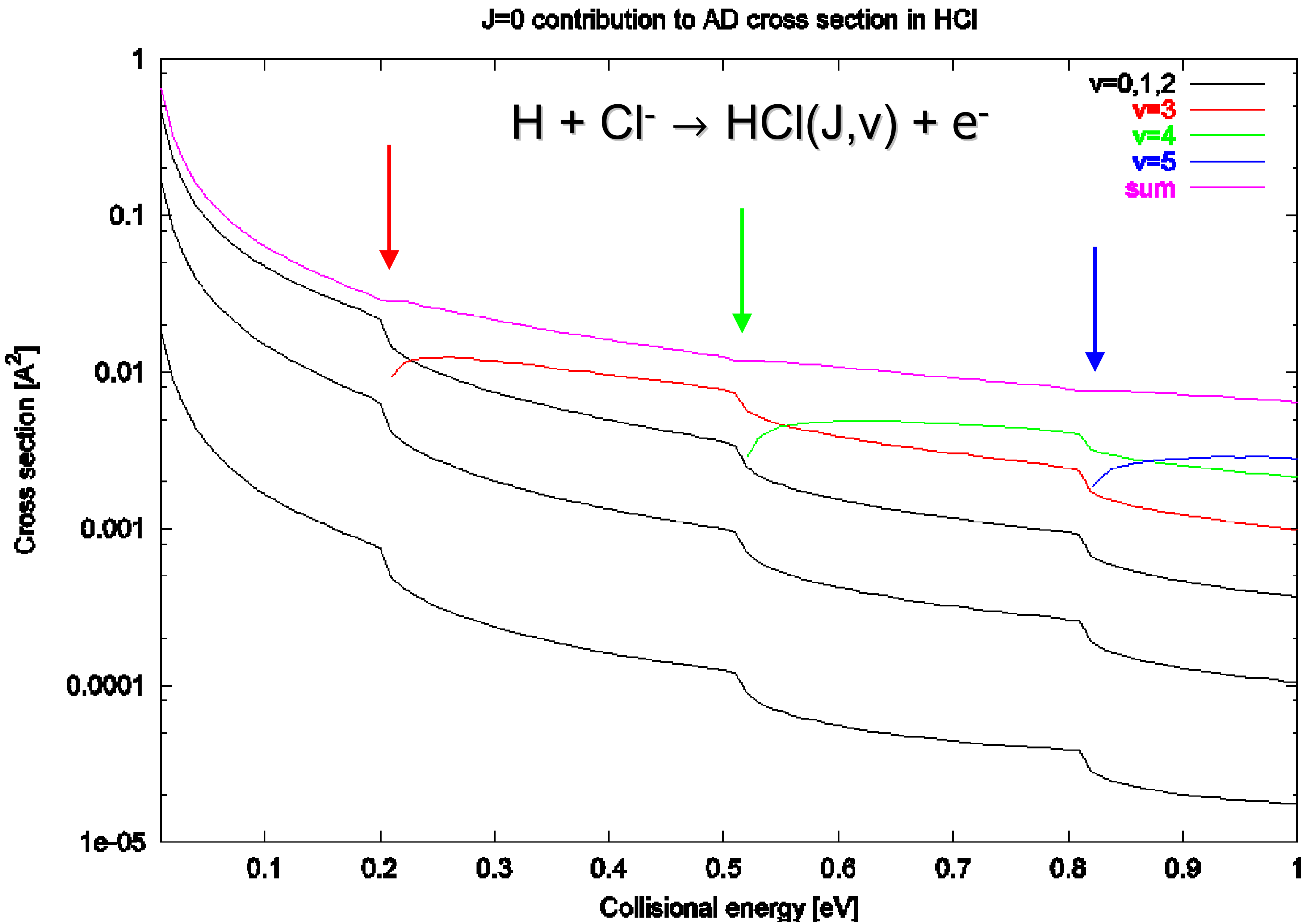
$$\sigma_v^J(E) = \frac{2\pi^2}{E}(2J+1)\left|\left\langle \psi_d \middle| V_{d\varepsilon_v^J} \middle| \chi_v^J \right\rangle\right|^2$$

Electron spectrum (ideal conditions):

$$\frac{d\sigma}{d\varepsilon}(\varepsilon, E) = \sum_{J,v} \sigma_v^J(E)\delta(\varepsilon - E + E_v^J)$$

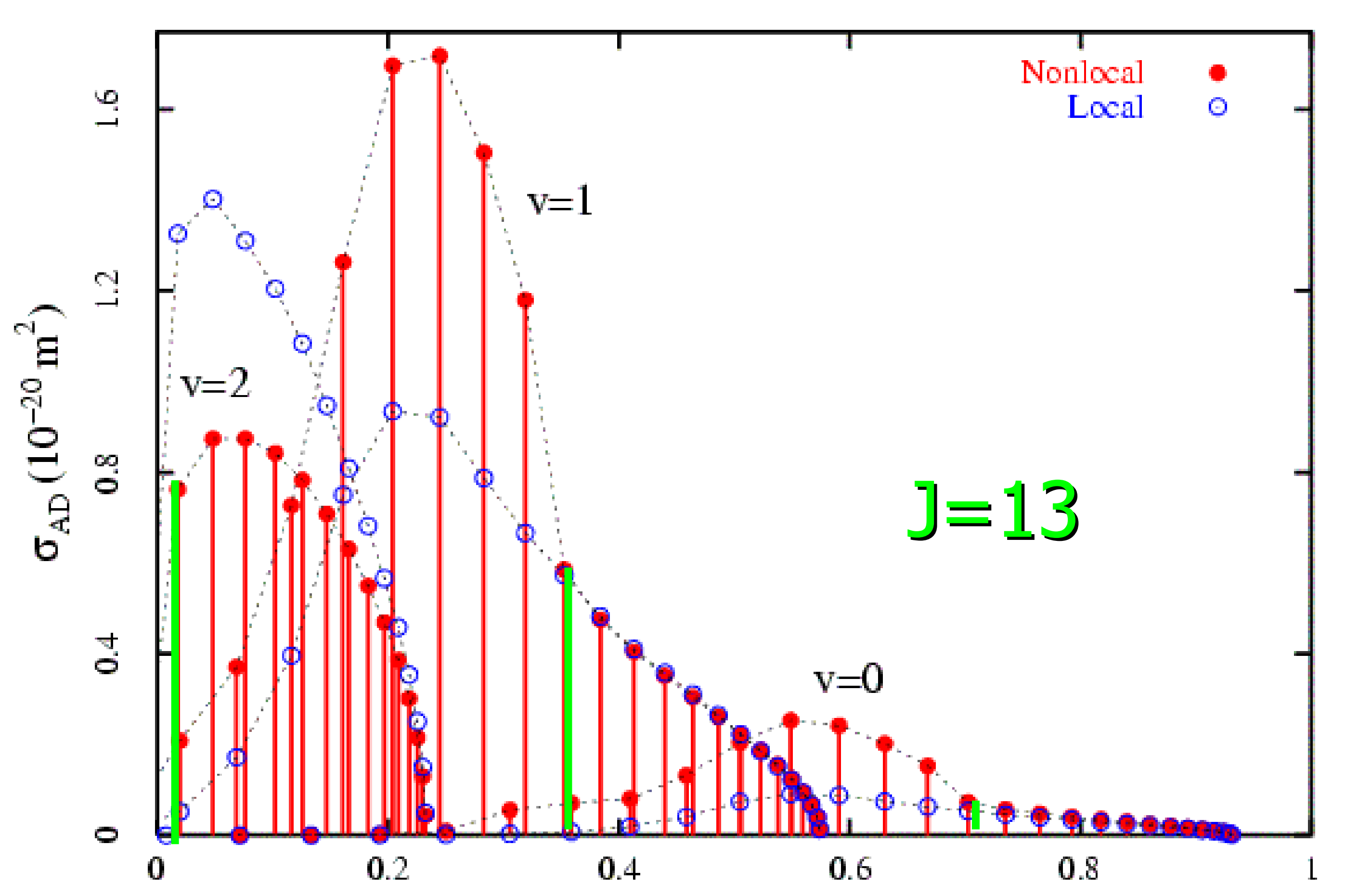
Experimental electron rate:

$$\frac{\mathrm{d}k}{\mathrm{d}\varepsilon}(\varepsilon) = \int \frac{\mathrm{d}\sigma}{\mathrm{d}\varepsilon}\left(\varepsilon, E = \tfrac{1}{2}mu^2\right) f(u)u\mathrm{d}u = \sum_{J,v} \sigma_v^J(E) f\left(\sqrt{2m(\varepsilon + E_v^J)}\right)$$

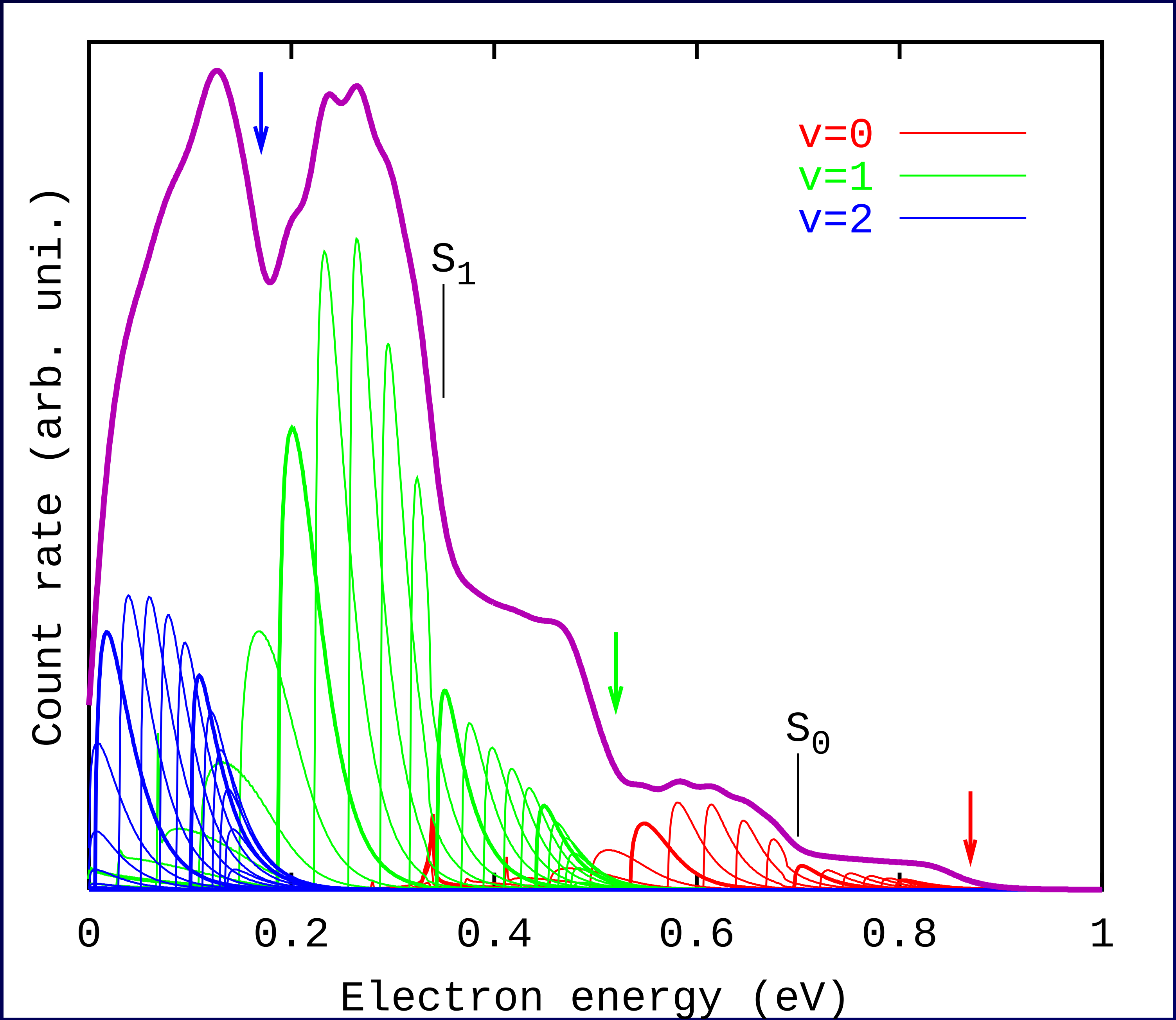


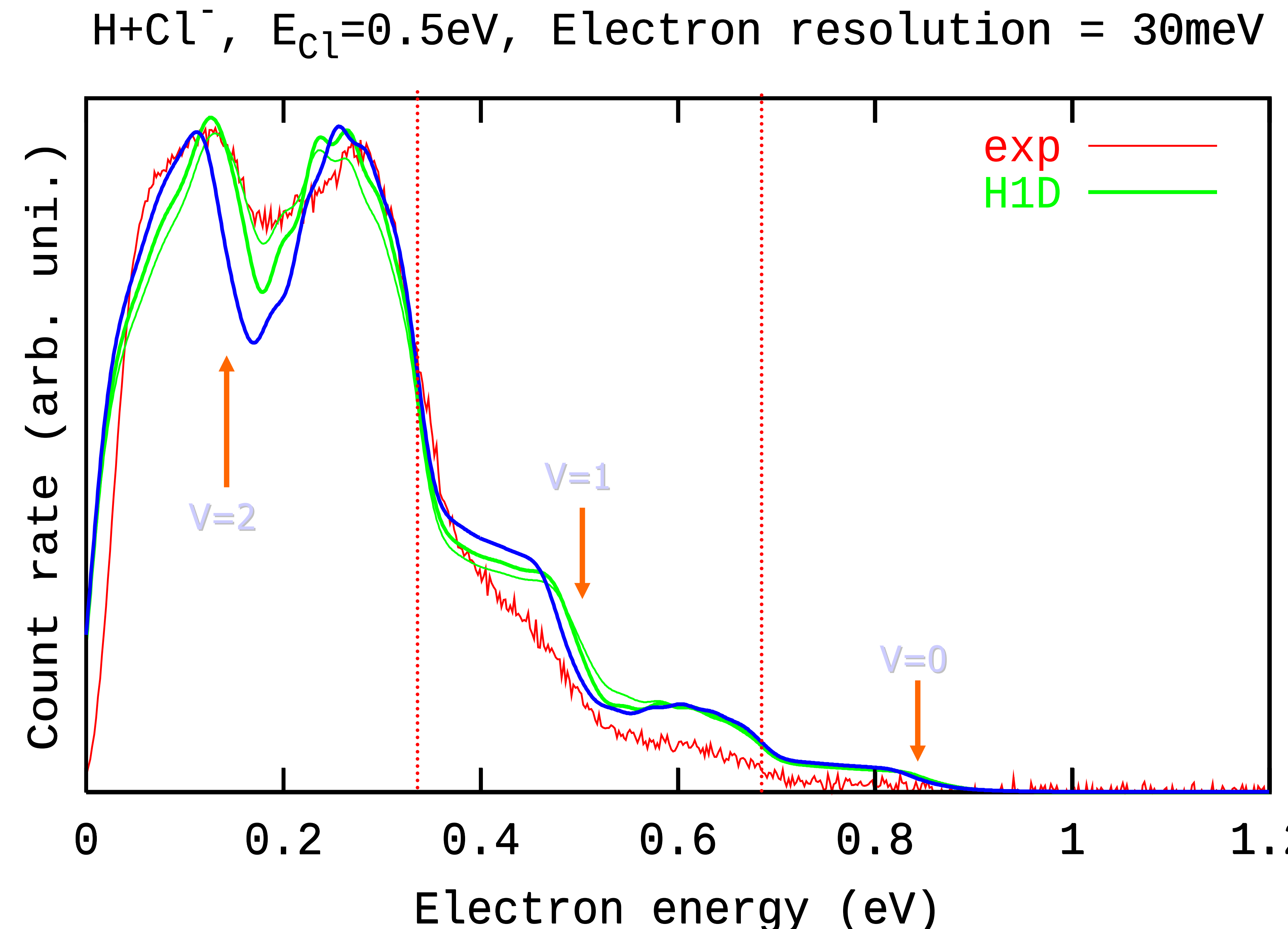
J=0 contribution to AD cross section in HCl
H + Cl⁻ → HCl(J,v) + e⁻
v=0,1,2
v=3
v=4
v=5
sum
Cross section [A²]
Collisional energy [eV]
1
0.1
0.01
0.001
0.0001
1e-05
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1

AD cross section – final states at fixed collision enegy

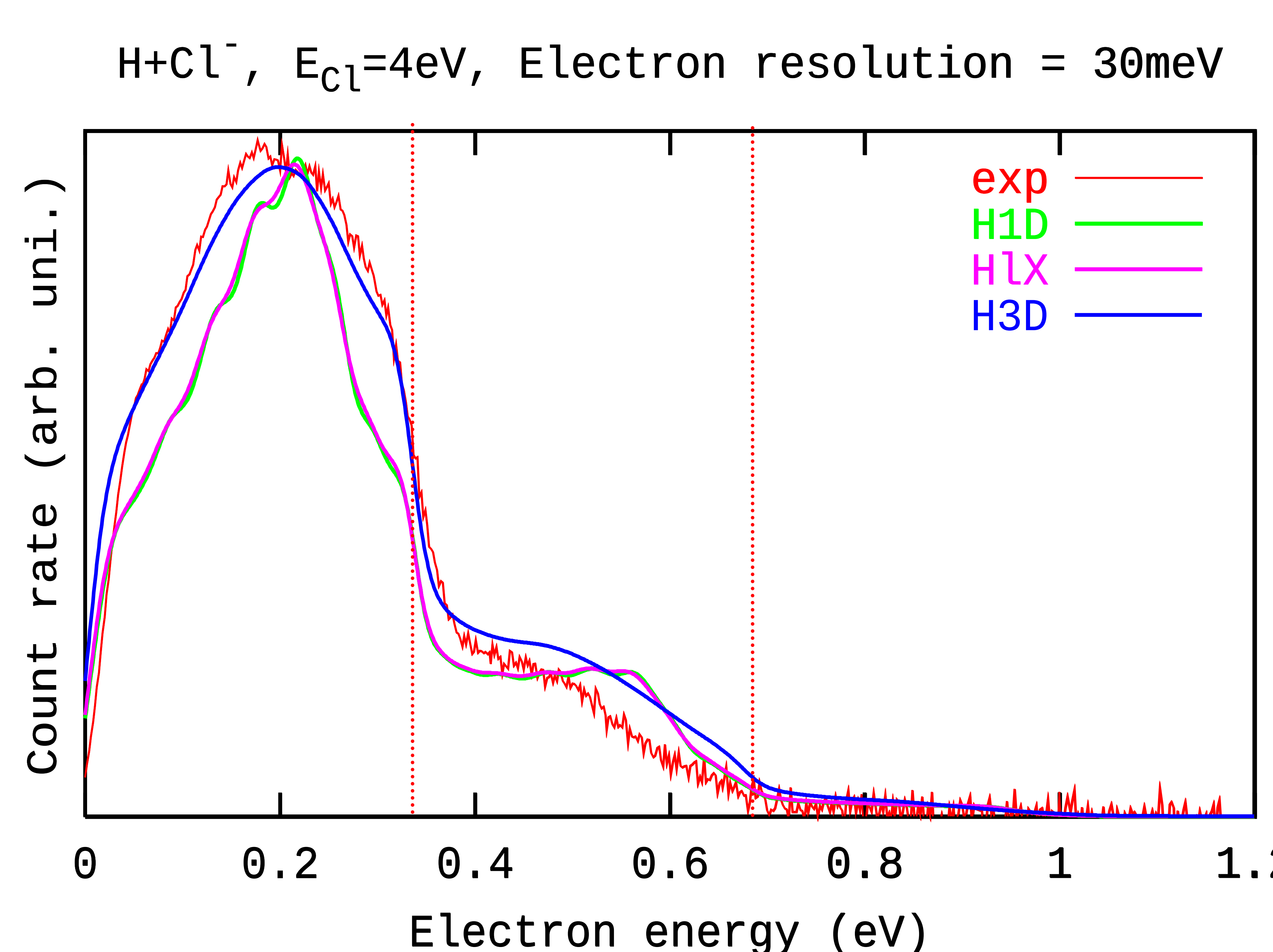


Energy of Released electron (eV)


v=0
v=1
v=2
S1
S0
Count rate (arb. uni.)
0
0.2
0.4
0.6
0.8
1
Electron energy (eV)



H+Cl⁻, E_Cl=0.5eV, Electron resolution = 30meV
exp
H1D
V=2
V=1
V=0
Count rate (arb. uni.)
Electron energy (eV)
0
0.2
0.4
0.6
0.8
1


H+Cl⁻, E_Cl=4eV, Electron resolution = 30meV
exp
H1D
HlX
H3D
Count rate (arb. uni.)
0
0.2
0.4
0.6
0.8
1
Electron energy (eV)

Conclusions

- Electron spectra for AD reaction were predicted for collisions of halogen anions with atomic hydrogen (deuterium) using nonlocal resonance theory
- The steps in the spectrum were confirmed by experiment and good agreement of data was obtained. Remaining discrepancy in shape can not simply be explained by energy distribution function. Cross section increases faster with vibrational state in experiment then in theory.

M. Čížek, J. Horáček, W. Domcke, *J. Phys.* B **31** (1998) 2571

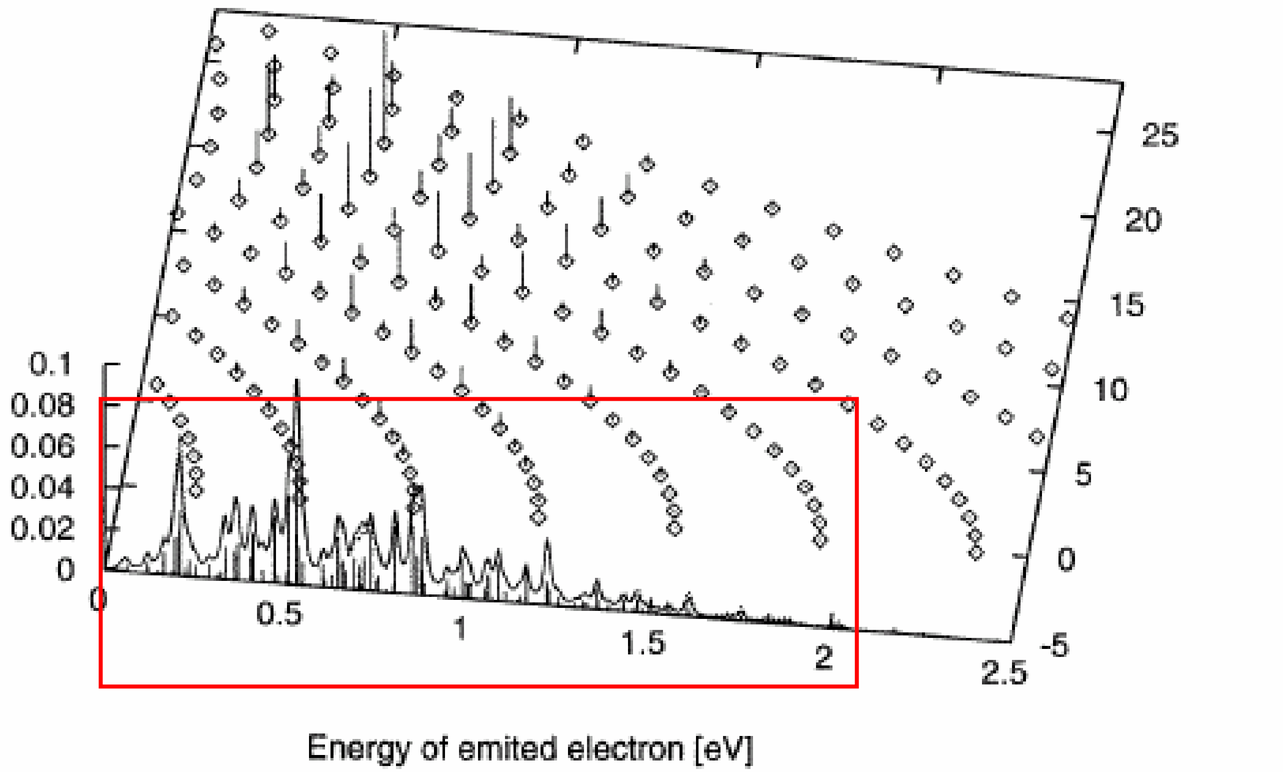


Figure 5. Final-state distribution in $H + H^-$ associative detachment at 0.01 eV collision energy. Relative probabilities for the different final states of H_2 and the energy spectrum of the released electron are shown. The energy of the emitted electron is plotted on the x-axis, the angular momentum l of the final H_2 state on the y-axis, and the cross section σ_l^{ν} (arbitrary units) on the z-axis. The calculated electron spectrum of the nonlocal model is given by the full curve; the dotted curve gives the electron spectrum obtained in the local approximation.

M. Čížek, J. Horáček, W. Domcke, *J. Phys.* B **31** (1998) 2571

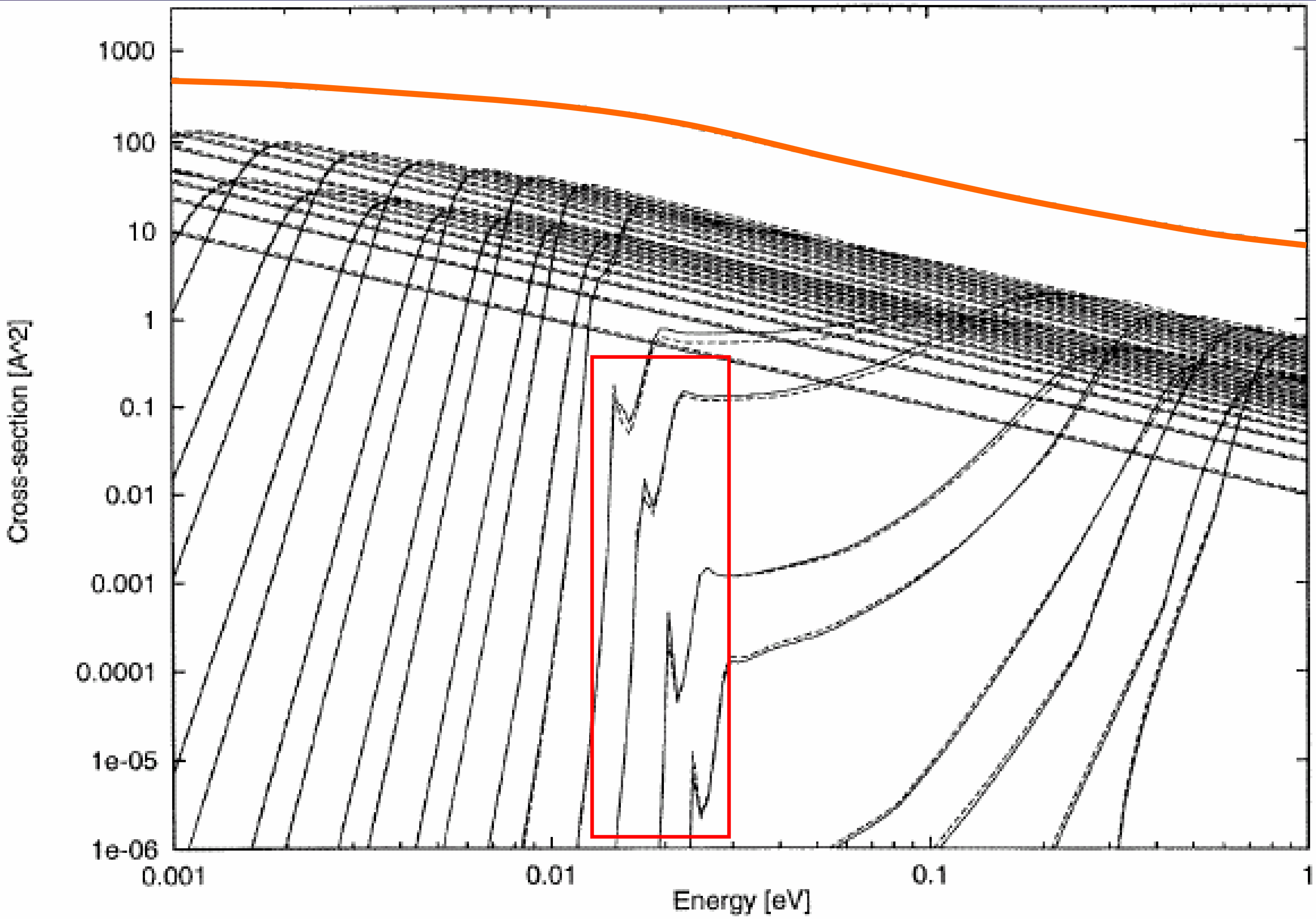
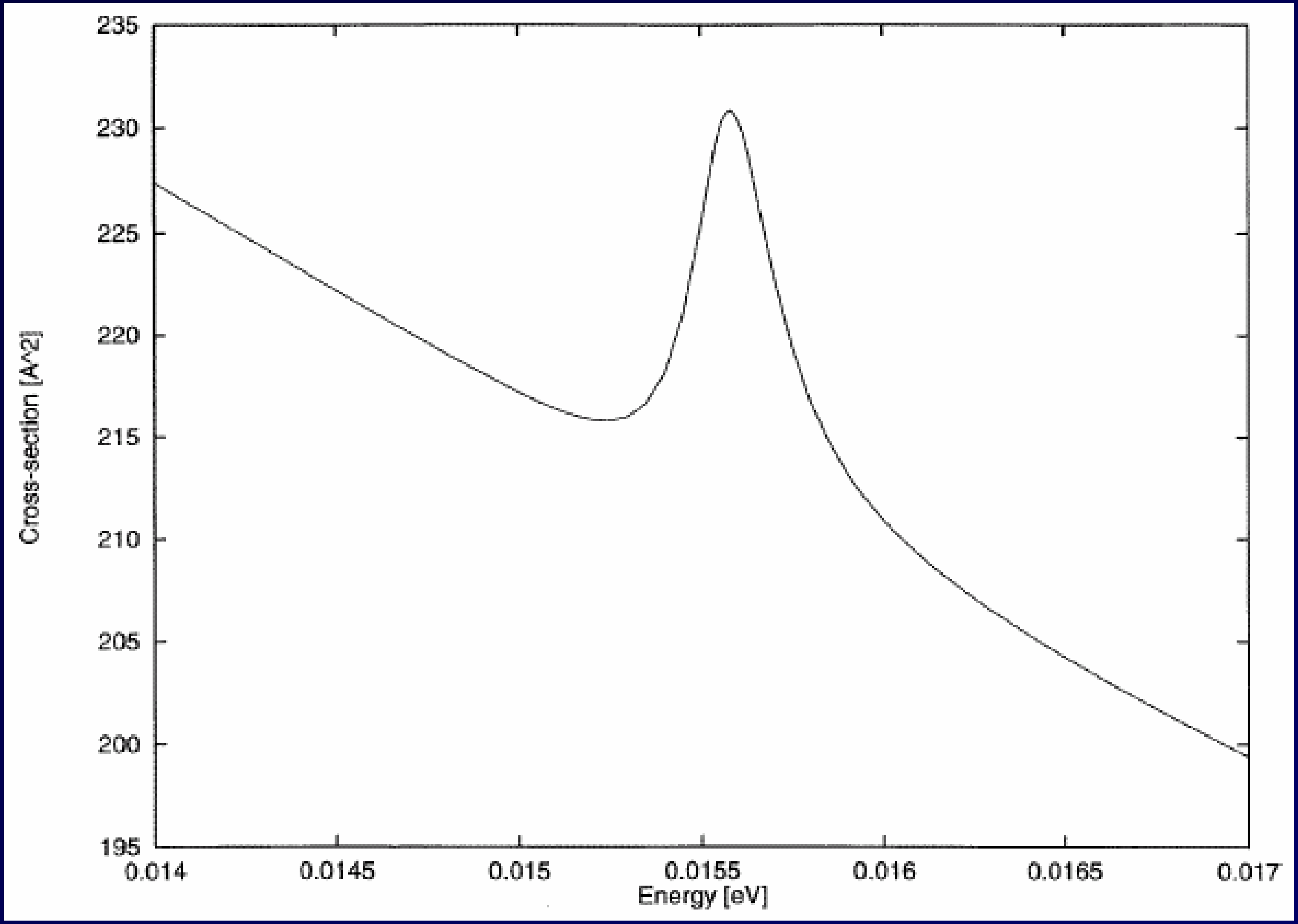


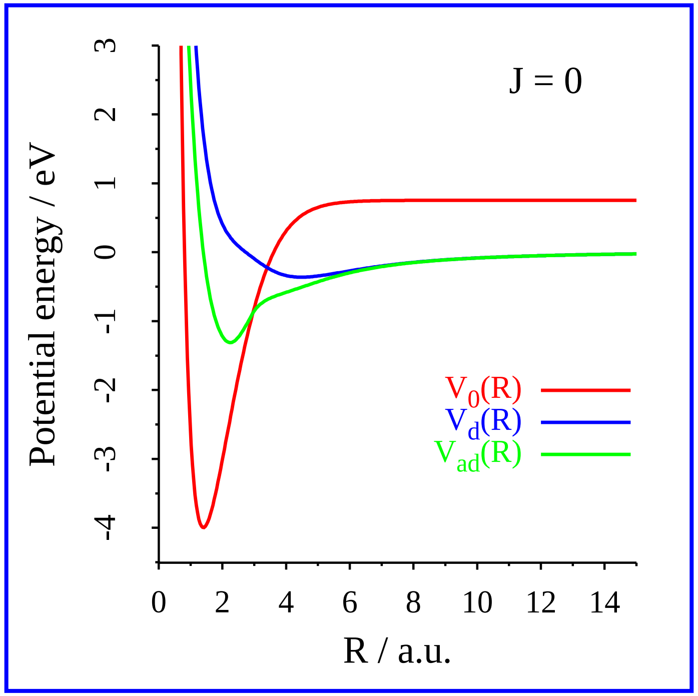
Figure 2. The total H + H^- associative-detachment cross section (chain curve) and its partial-wave components (full curves), $l = 30, 29, \ldots$ (from the right). Results of the local approximation are given by broken curves.

M. Čížek, J. Horáček, W. Domcke, *J. Phys.* B **31** (1998) 2571

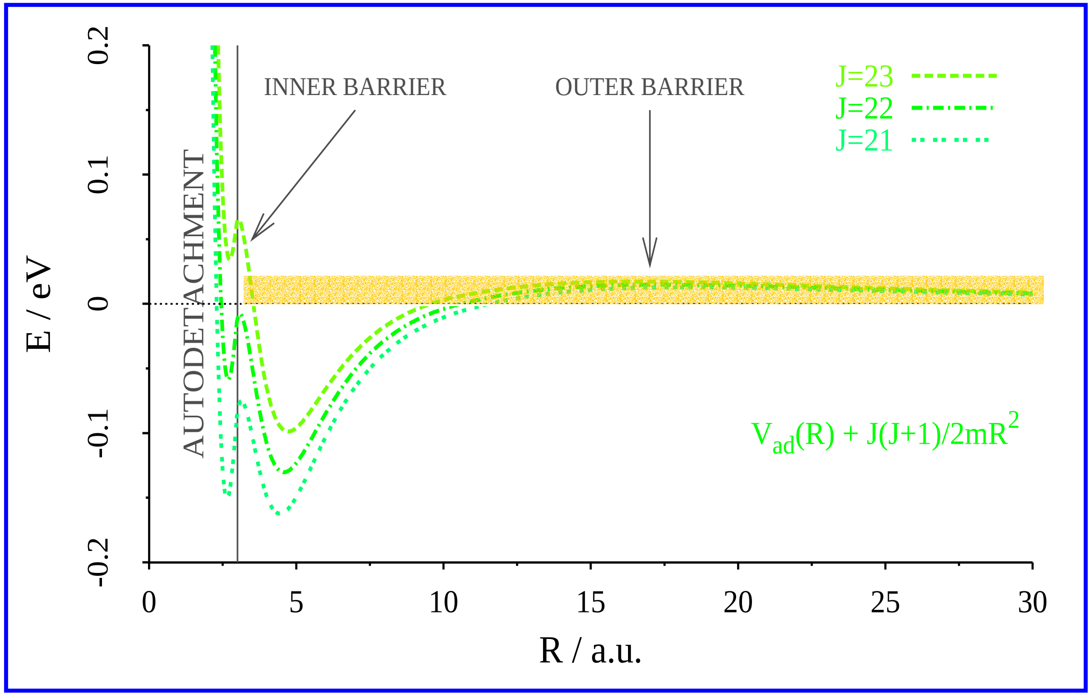


The Origin of the Resonances

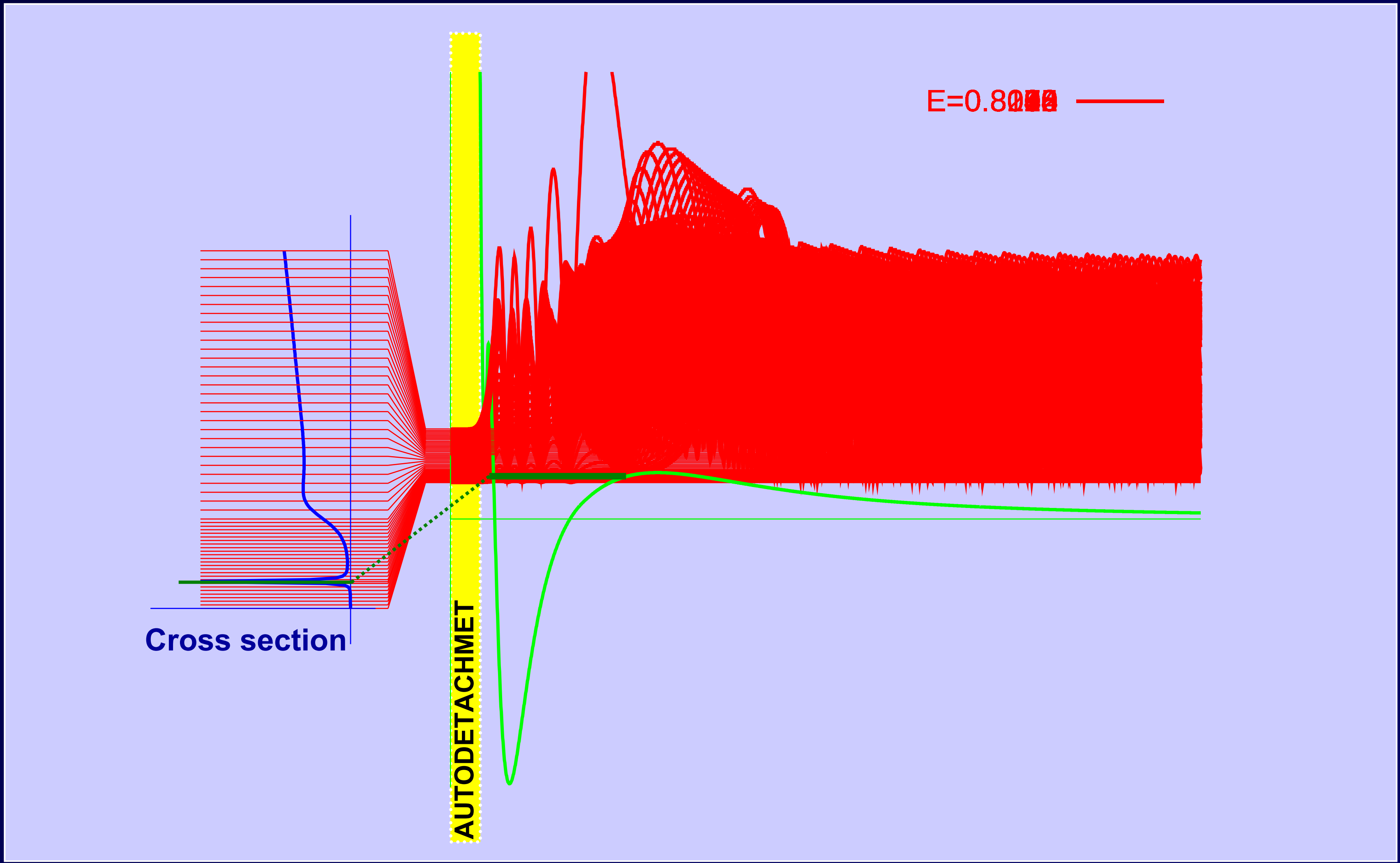
Potentials for $J=0$



Potential $V_{ad}(R)$ for nonzero J



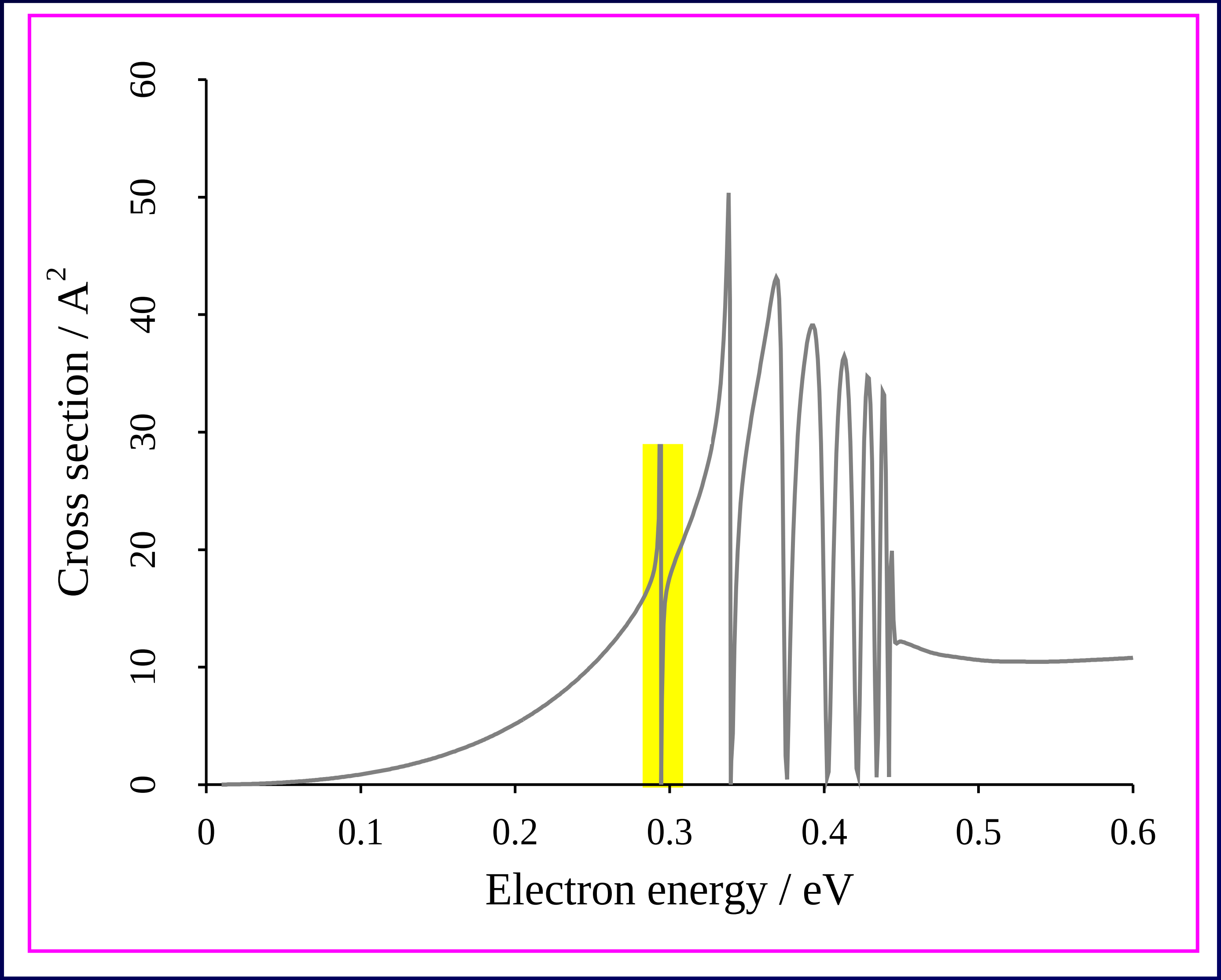
Resonant tunneling wave function

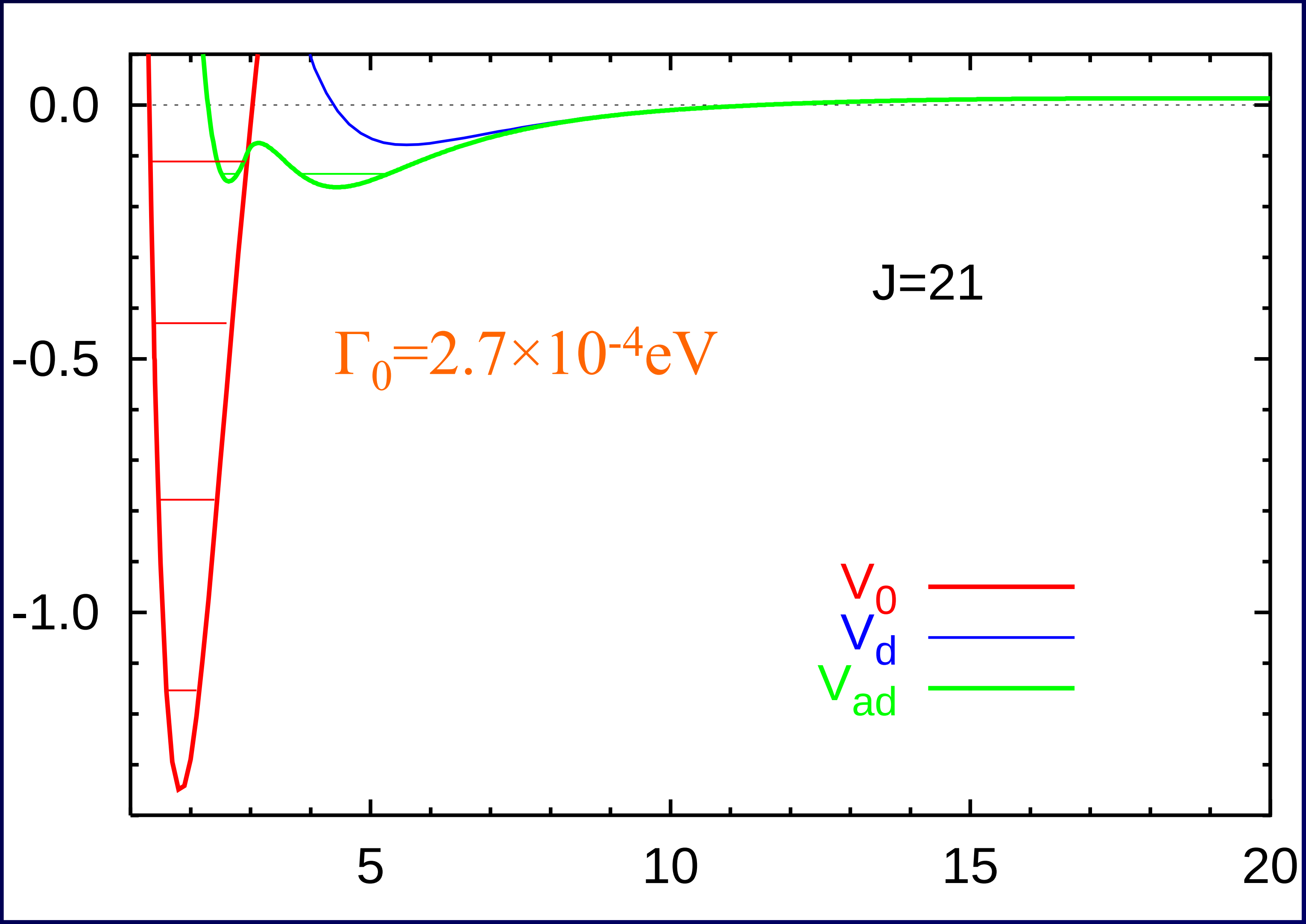


Experimental motivation

- Hurley 1974 – observation of H_2^- from low-energy arc source.
- Aberth *et al.* 1975 – observation of HD^-, D_2^- from ($\tau > 10\mu s$).
- Bae *et al.* 1984 – existence of D_2^- not confirmed in two-step experiment designed to produce metastable quartet state ($\tau < 2\times10^{-11}$s).
- Wang et al. 2003 – observed signature of H_2^- in signal from discharge plasma.

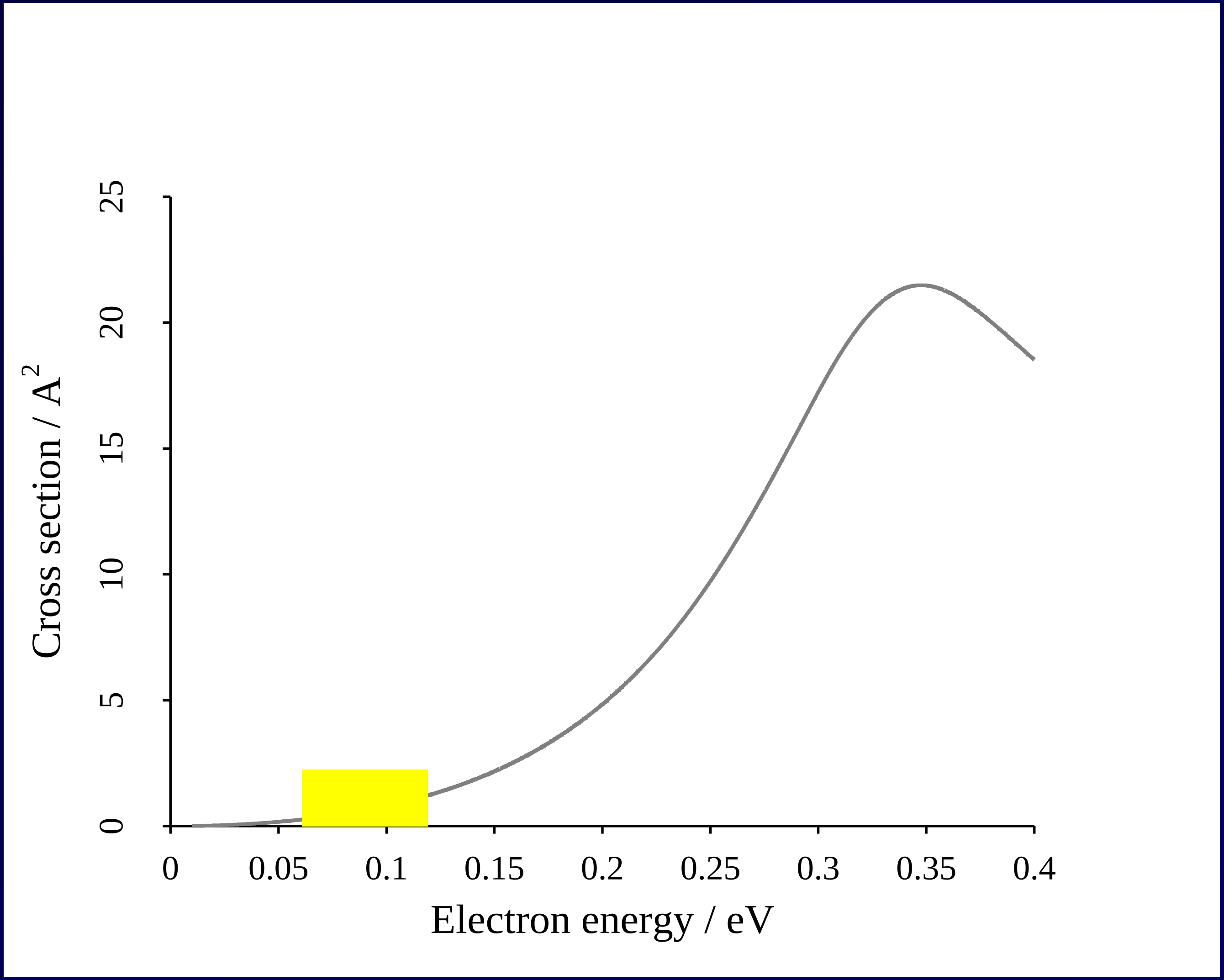
Elastic cross section for e$^-$ + H_2 (***J*=21**, *v*=2)

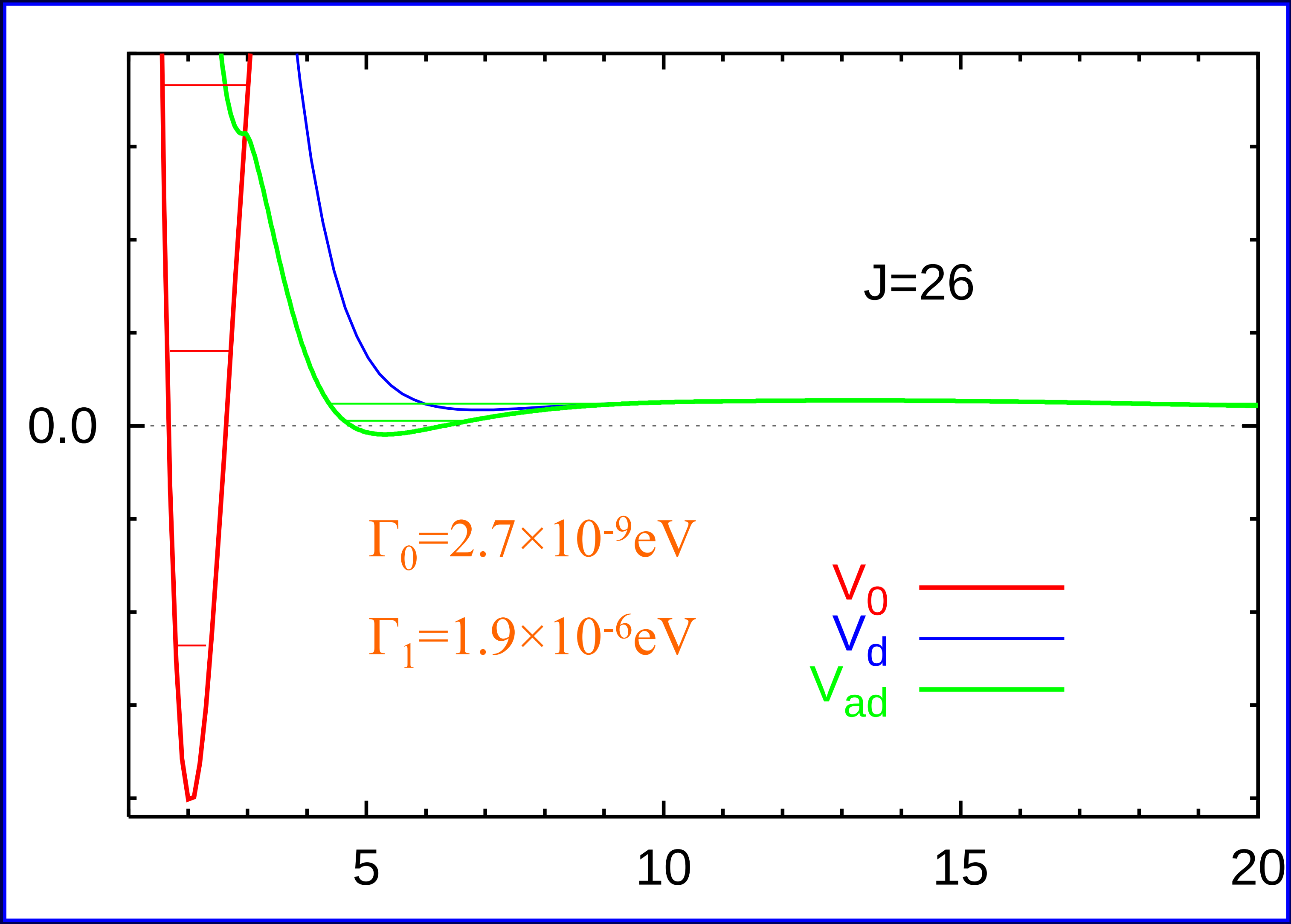




0.0
-0.5
-1.0
5
10
15
20
J=21
Γ0=2.7×10-4eV
V0
Vd
Vad

Elastic cross section for e$^-$ + H_2 (***J*=25**, v=1)





J=26
0.0
Γ_0=2.7×10^{-9}eV
Γ_1=1.9×10^{-6}eV
V_0
V_d
V_{ad}
5
10
15
20

Table I: Parameters of H_2^- states

J	E_{res} (relative to DA)	τ
21	-136 meV	2.4 ps
22	-105 meV	12 ps
23	-75 meV	0.11 ns
24	-47 meV	0.9 ns
25	-20 meV	12 ns
26	**5 meV**	**0.52 µs**
27	28 meV	2 ns

Table II: Parameters of D_2^- states

J	E_{res}(relative to DA)	τ
31	-118 meV	0.13 ns
32	-97 meV	0.70 ns
33	-76 meV	6 ns
34	-55 meV	39 ns
35	**-35 meV**	**0.51 μs**
36	**-16 meV**	**5.7 μs**
37	**2 meV**	**14 μs**
38	**19 meV**	**7.2 μs**
39	34 meV	41 ps

Conclusions

• Narrow *resonances were found in both VE and DA cross sections* with lifetimes by many orders of magnitude larger than for previously known resonances.

• The resonances can well be understood as *adiabatic states trapped in an outer well* separated from the $e^- + H_2$ autoionisation region by inner barrier and separated from dissociation into $H + H^-$ by an outer centrifugal barrier.

• The decay into the $e^- + H_2$ channel is controlled by *nonlocal dynamics* and estimates from adiabatic (local complex) potential give an order of magnitude estimate at best.

• The *lifetimes* of the states reach the values of **0.5 μs** and **14 μs** for H_2^- and D_2^- respectively. Even larger values can be expected for T_2^-.

• Our interpretation of the states *explains the lack of a molecular-anion signal* in the experiments of Bae *et al.* 1984.

Open questions - theory

- The *stability of the states with respect to collisions* with other H atoms or H_2 molecules is unknown.
- *State to state rates* for creation/destructions of ions are needed for modeling of equilibrium plasma densities.
- Highly rotating anions in *other systems* ?

Suggestions - experiment

- The existence and interpretation of the anions should be confirmed in new experiments – best with *measurement of energies and lifetimes*.
- It is very difficult to create the anions in electron attachment to H_2. It is probably much easier to create the states in $H^- + H_2$ collisions. The cross sections are unknown, however (to be the subject of further study).

Acknowledgements

Coauthors:

Jiří Horáček

Wolfgang Domcke

Experiments:

Michael Allan

Svetlana Živanov

Special thanks:

Hartmut Hotop

Frank Thiel

Xuefeng Yang