Dynamics of associative detachment

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$$\mathrm{H} + X^- \to (\mathrm{H}X)^- \to \mathrm{H}X + e^-,$$
$$X = \mathrm{H},\ \mathbf{F},\ \mathbf{Cl},\ \mathbf{Br},\ \mathrm{I}$$

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- Frank Thiel
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- Michael Allan

Potential energy surfaces for HX and HX^-

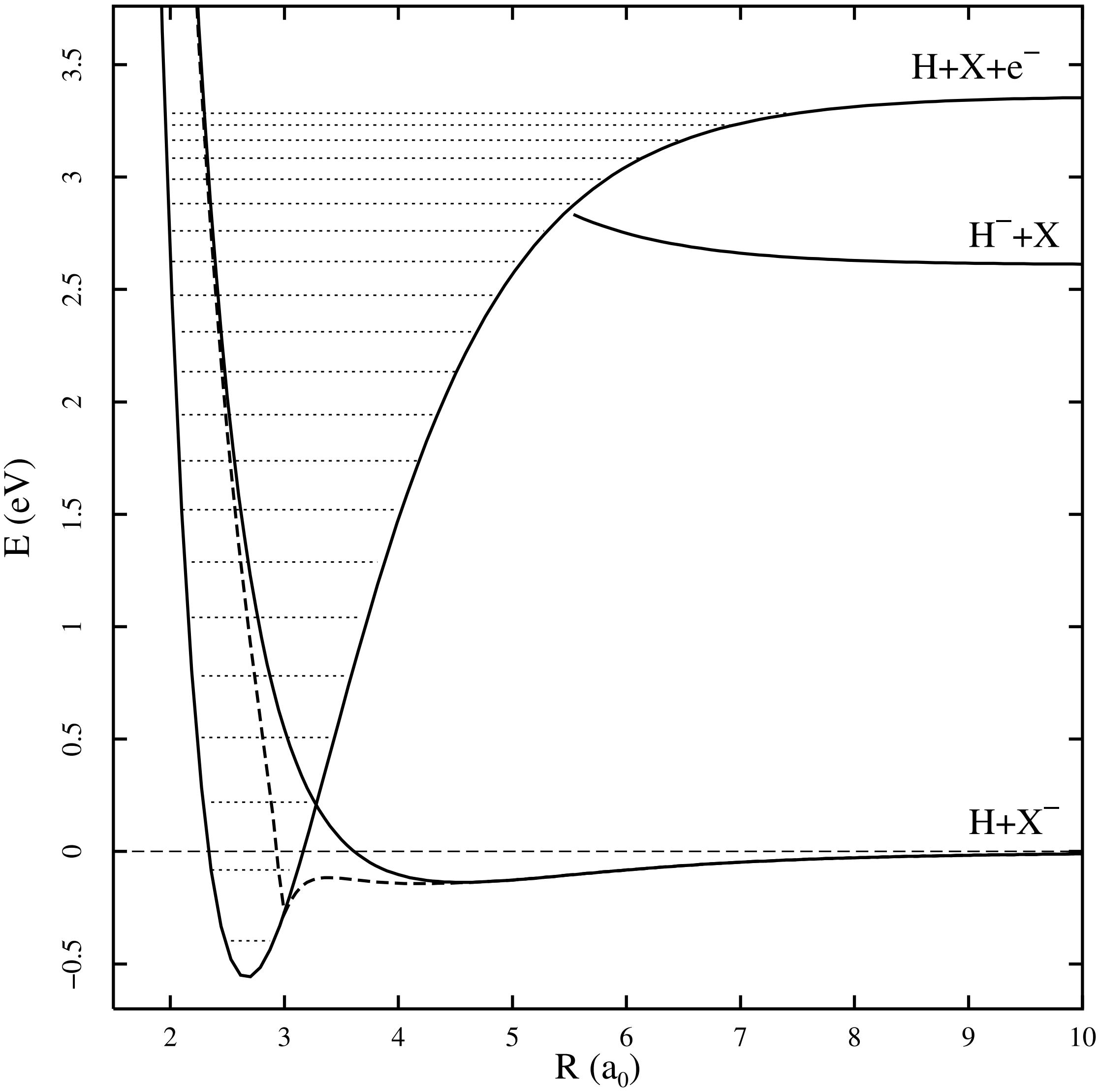


Table: values of parameters

	H_2	**HF**	**HCl**	**HBr**	HI
Electron affinity of X (eV)	0.75	3.40	3.61	3.36	3.06
Charge transfer threshold (eV)	0	2.65	2.86	2.61	2.31
Dissociation energy of HX (eV)	4.48	5.87	4.43	3.76	3.05
Number of states below H+X^-	10	6	3	2	0
Equilibrium distance of HX (a_0)	1.40	1.73	2.41	2.67	3.05

Goals of this talk:

- How are the threshold structures manifested in the associative detachment cross sections?
- What can be learned about the dynamics of the process from experiments?
- What is the difference between the local and nonlocal theory in predictions for experiment.
- How do the main features of dynamics evolve in the sequence: HF, HCl, HBr, and HI.

Theoretical description (outline)

Nonadiabatic resonance theory (review - Domcke 1991)

Diabatic states: $(\langle\phi_\epsilon|T_\mathrm{N}|\phi_{\epsilon'}\rangle \simeq 0 \simeq \langle\phi_\epsilon|T_\mathrm{N}|\phi_\mathrm{d}\rangle)$

$|\phi_\mathrm{d}\rangle$ ... HX^- resonance
$|\phi_\epsilon\rangle$ ... e^-+HX scattering states $(\langle\phi_\epsilon|\phi_\mathrm{d}\rangle = 0)$

$$H = \left(\begin{array}{c|ccc} V_\mathrm{d}+T_\mathrm{N} & & V_{\mathrm{d}\epsilon} & \\ \hline & \ddots & & 0 \\ V_{\mathrm{d}\epsilon}^* & & V_0+\epsilon+T_\mathrm{N} & \\ & 0 & & \ddots \end{array}\right)$$

Dynamics of nuclei:

$$\Psi(R,r) = \psi(R)\phi_\mathrm{d}(R,r) + \int \mathrm{d}\vec{\epsilon}\,\psi_\epsilon(R)\phi_\epsilon(R,r)$$

Elimination of ψ_ϵ from Schrödinger (Lippmann-Schwinger) equation yields equation for $\psi(R)$ with

$$H_\mathrm{eff} = T_\mathrm{N} + V_\mathrm{d}(R) + \int \mathrm{d}\vec{\epsilon}\, V_{\mathrm{d}\epsilon}(R) G_0(E-\epsilon, R, R') V_{\mathrm{d}\epsilon}^*(R')$$

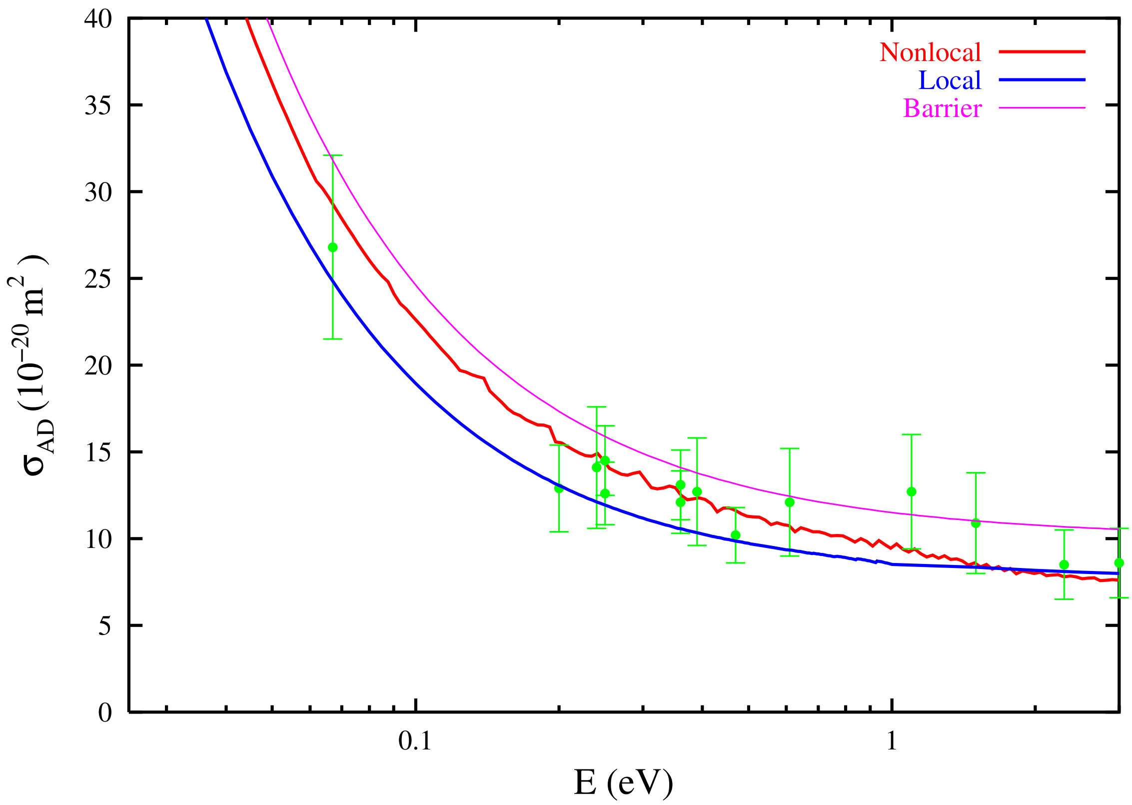
where

$$G_0(E,R,R') = \sum_v \frac{\chi_v(R)\chi_v(R')}{E - E_v + i\varepsilon}$$

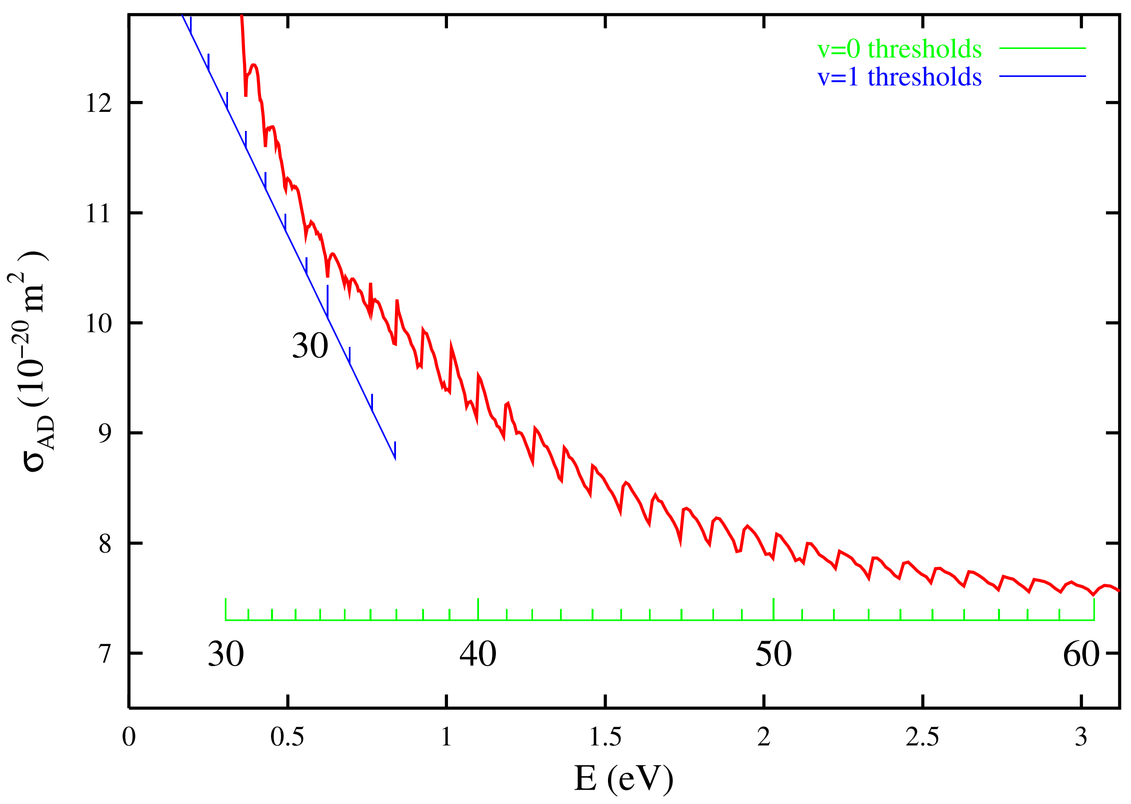
T-matrix and cross section for Associative Detachment (AD)

$$\begin{aligned} T_\mathrm{AD} &= \langle\chi_n|V_{\mathrm{d}\epsilon_n}|\psi\rangle \\ \sigma_\mathrm{AD}(v,J) &= \frac{2\pi^2}{E}(2J+1)|T_\mathrm{AD}|^2 \end{aligned}$$

Total cross section for $H + Cl^- \to HCl + e^-$

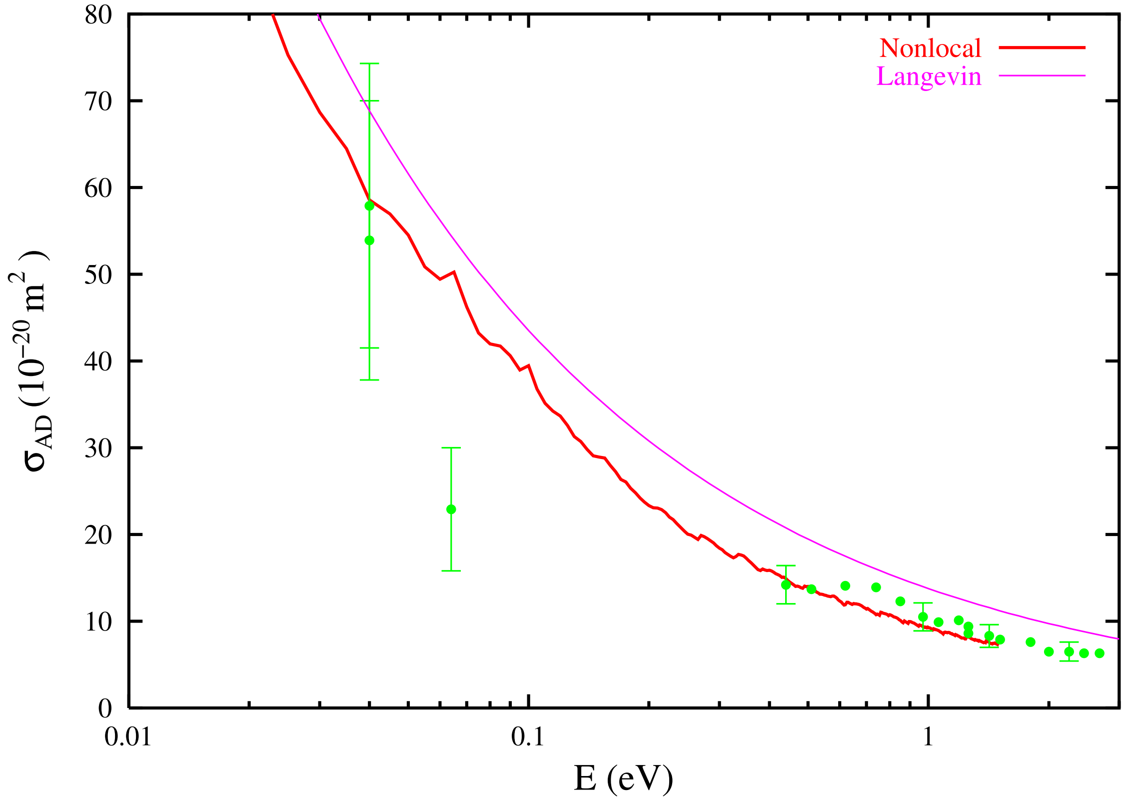


Threshold structures in total detachment cross section

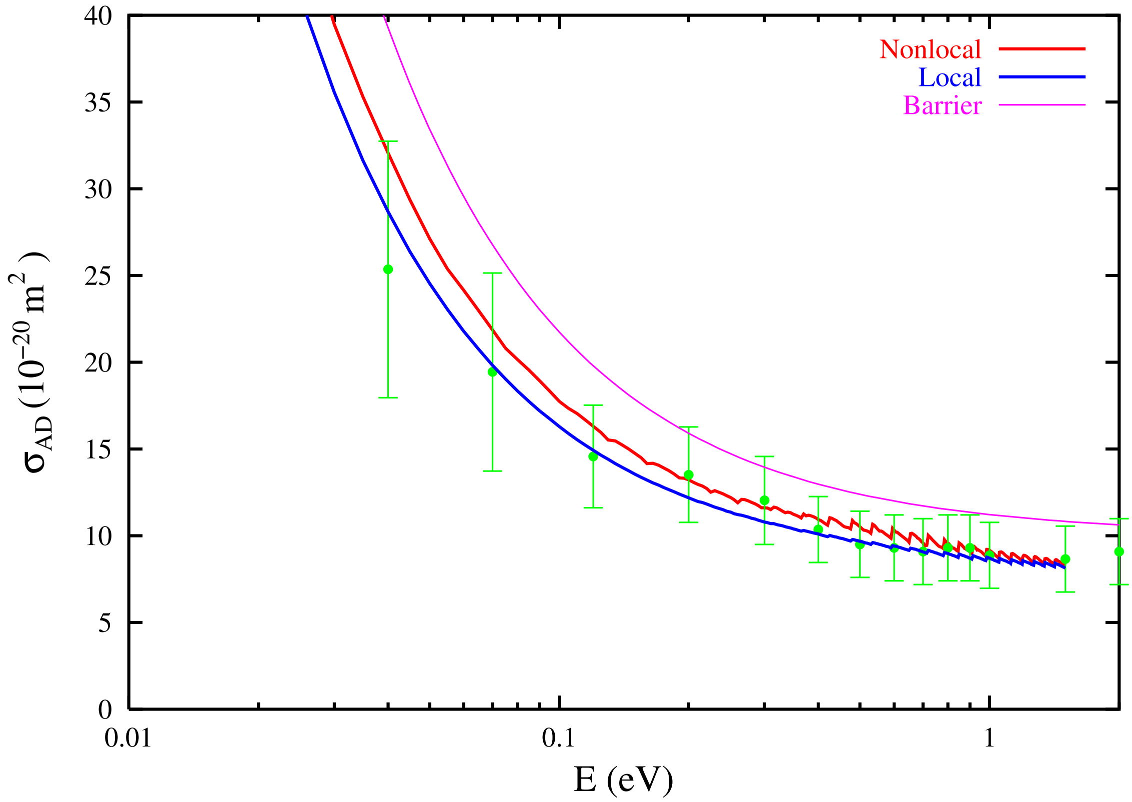


Experiment: Huels *et al.* 1994, PRA **49**,255

Total cross section for $H + F^- \to HF + e^-$



Total cross section for $H + Br^- \to HBr + e^-$

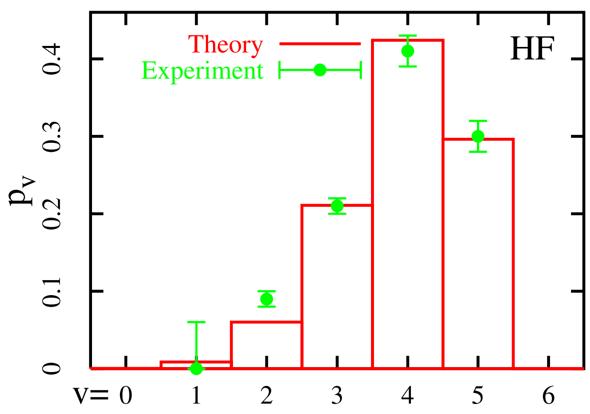


Experiment: Huels *et al.* 1994, PRA **49**,255

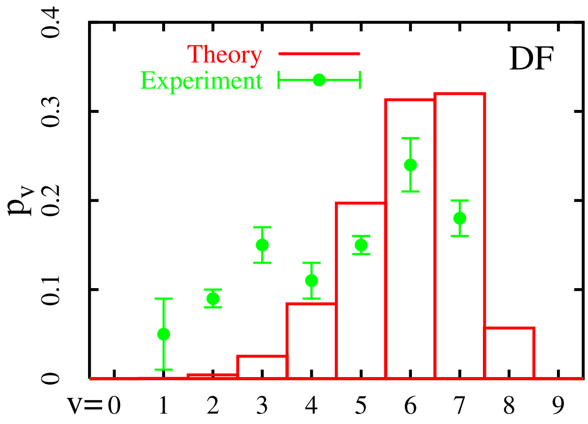
Measurements of final state distribution

Comparison is made for rotationally relaxed final vibrational state distribution. Probability p_v for the given vibrational state v is obtained from sum over J of final state specific reaction rates for room temperature (normalised to unit sum).

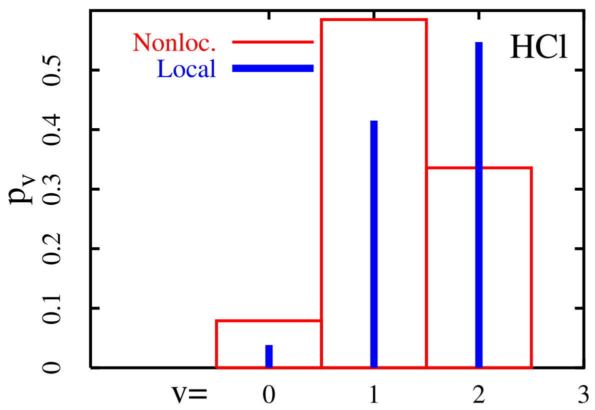
$H + F^- \rightarrow HF(v, J) + e^-$ [1]



$D + F^- \rightarrow DF(v, J) + e^-$



$H + Cl^- \rightarrow HCl(v, J) + e^-$ [2]



Experiment:
$p_2/p_1 = 0.60 \pm 0.03$

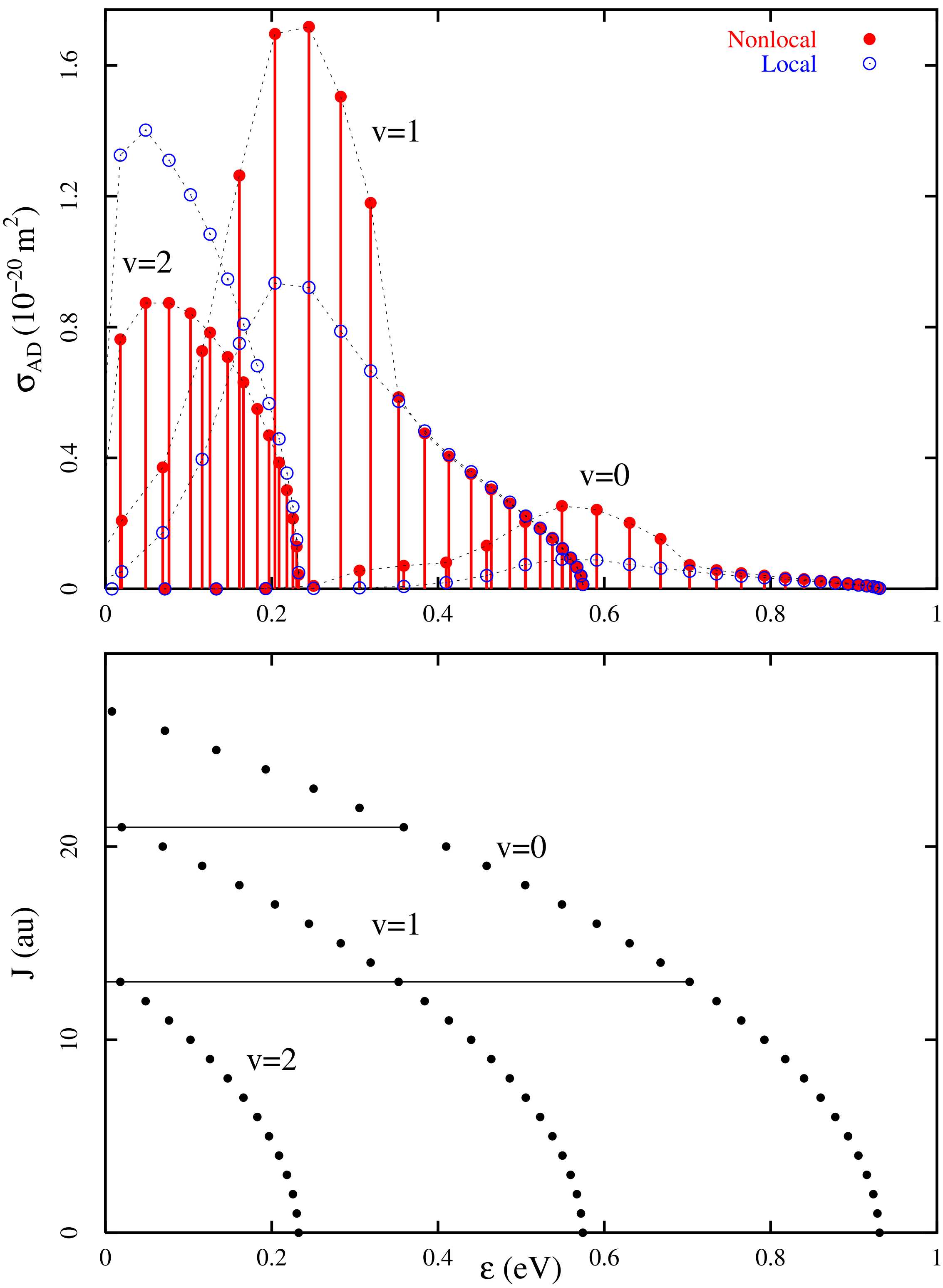
Theory: $p_2/p_1 = 0.57$
LCP Theory: $p_2/p_1 = 1.32$

$H + Br^- \rightarrow HBr(v, J) + e^-$

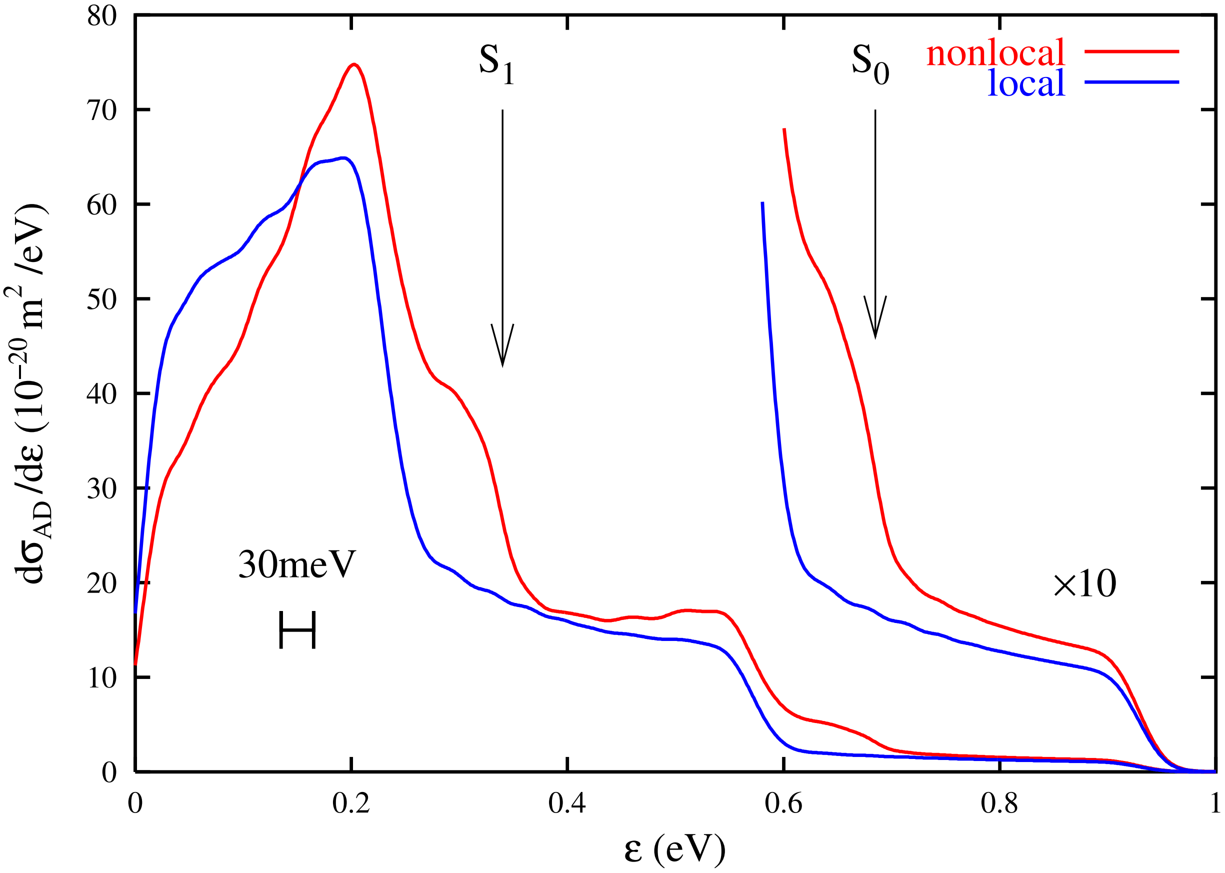
Nonlocal theory: $p_0 = 0.59$ $p_1 = 0.41$
LCP theory: $p_0 = 0.43$ $p_1 = 0.57$

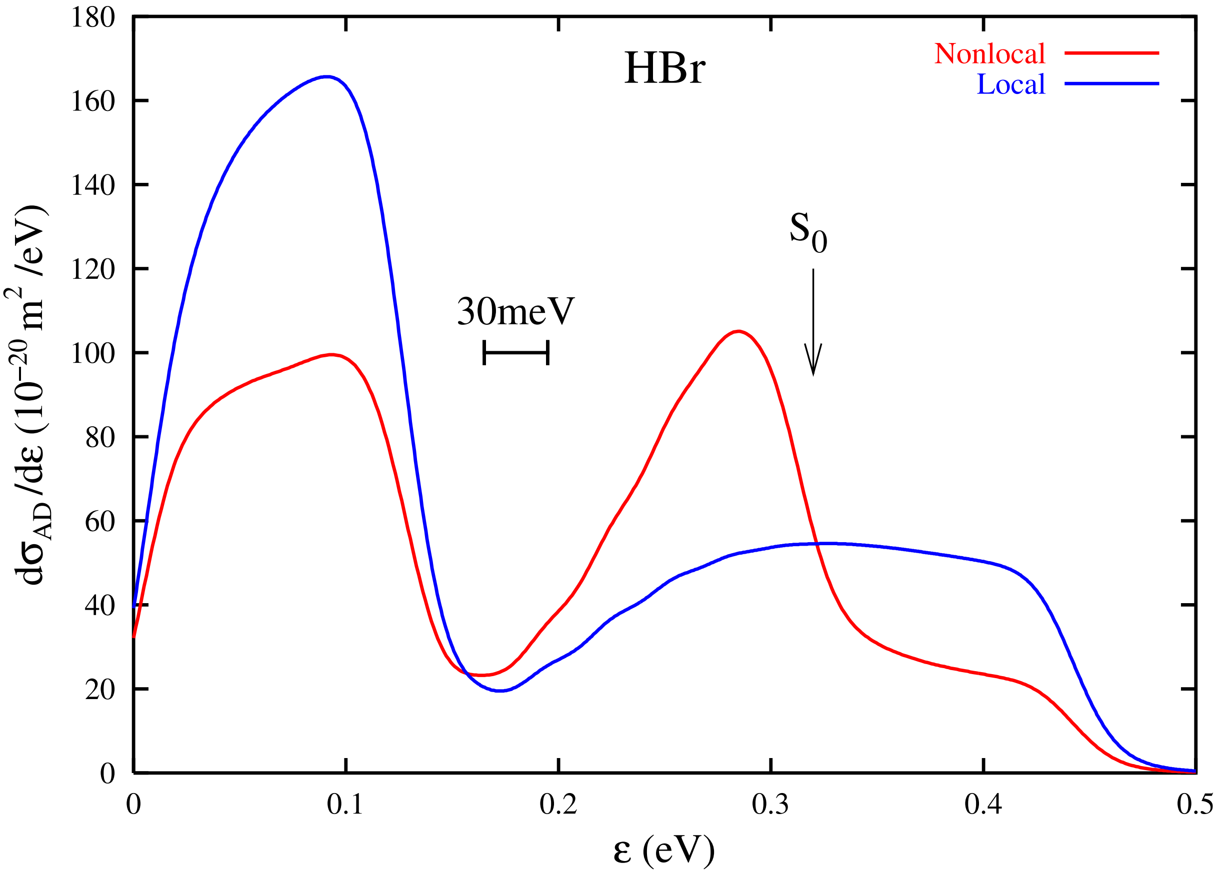
[1]Experiment HF, DF: Smith, Leone 1983, JChP **78**, 1325
[2]Experiment HCl: Zwier *et al.* 1980, PRL **44**,1050

Final state-specific cross sections for HCl at E=110eV



Simulated electron spectra in crossed-beam experiment





Conclusions

- AD cross sections exhibit cusps, which are closely related to Wigner cusps in dissociative attachment cross section. These cusps can be recognised both in energy and angular momentum dependence of the final state specific cross sections.
- The cusps are too weak to be resolved in the total detachment cross sections. Nevertheless, they produce pronounced effects in electron spectra. These cusps can not be reproduced by calculations using the local complex potential approximation.
- The positions of the cusps are insensitive to the total collision energy. They can be resolved in crossed beam experiment with rather moderate requirements for the resolution .

Future prospects:

- Interpretation of experiments which are being built in group of Michael Allan.
- Inclusion of HI system.
- Inclusion of the angular momentum transfer to released electron in the theoretical description.