



# METASTABLE MOLECULAR HYDROGEN ANION

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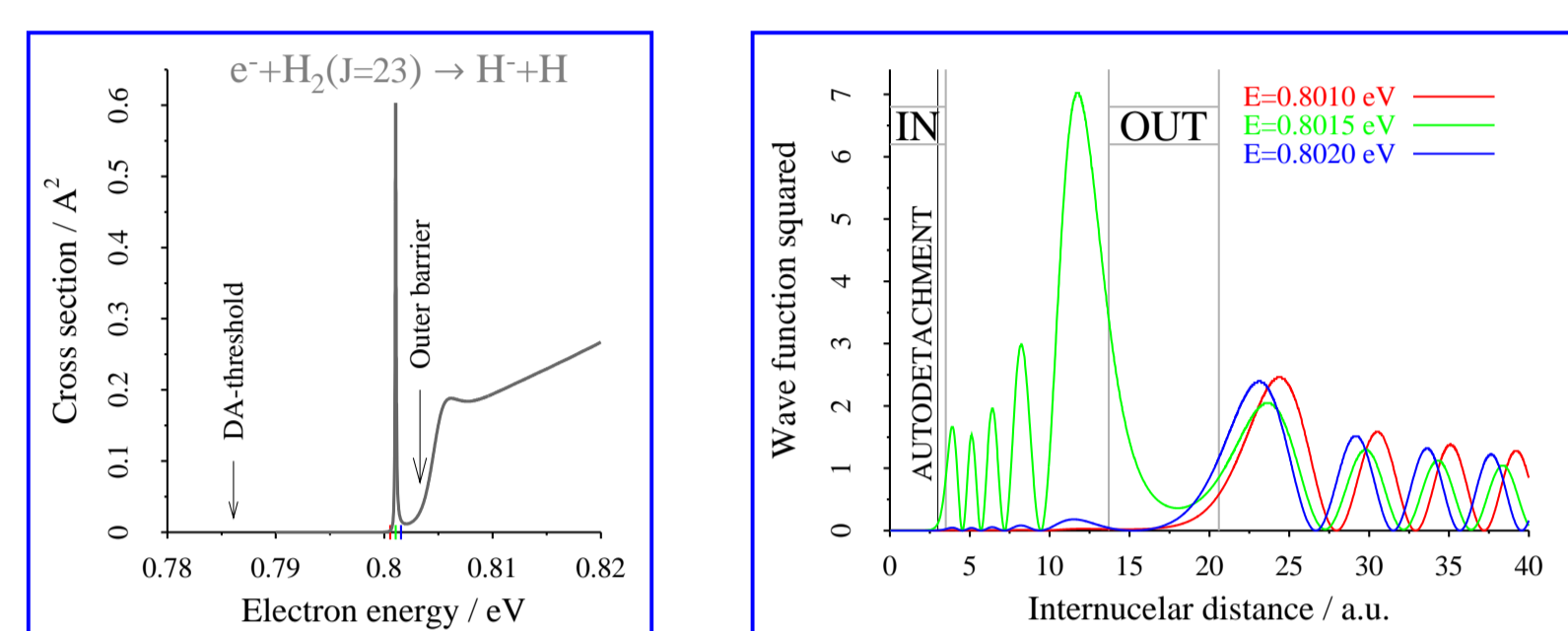
## I. Motivation

### 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 ( $\tau < 2 \times 10^{-11} s$ ).
- Wang *et al.* 2003 – observed signature of  $H_2^-$  in signal from discharge plasma.

### Theoretical motivation

- $H_2^-$  is unstable for internuclear separations  $R$  close to the equilibrium distance of  $H_2$  ( $1.4 a_0$ ) and decays within few fs.  $H+H^-$  is stable electronically for  $R > 3a_0$  but the nuclei can move freely in an attractive polarization force towards smaller internuclear separations  $R$ .
- Signatures of narrow resonances are seen in calculated  $H+H^-$  cross sections for nonzero angular momentum  $J$  (see the figures below).



Wave functions indicate the existence of four lower lying resonances with possibly much higher lifetime. Such resonances are known to exist in electron scattering from the HCl molecule for  $J=0$  and were confirmed in experiments of Allan 2000.

**GOAL:** To find the resonances and their lifetimes for various  $J$  and for both  $H_2^-$ ,  $D_2^-$

## II. Theory

### Basic equations

Nonlocal resonance theory (see Domcke 1991) is employed, with the model described by Čížek *et al.* 1998. The theory is based on selection of the discrete electronic state  $\phi_d$  describing the diabatic transition of the bound  $H+H^-$  state into the resonance in  $H_2+e^-$  electronic continuum  $\phi_e$ . The electronic hamiltonian  $H_{el}$  is then completely described by its components within this basis

$$\langle \phi_d | H_{el} | \phi_d \rangle = V_d(R), \quad \langle \phi_d | H_{el} | \phi_e \rangle = V_{de}(R), \quad \langle \phi_e | H_{el} | \phi_e \rangle = V_e(R) + \epsilon.$$

The vibrational dynamics is then solved for the projection  $\psi_d$  of the complete wave function  $\psi$  of the system on the discrete state  $\phi_d$

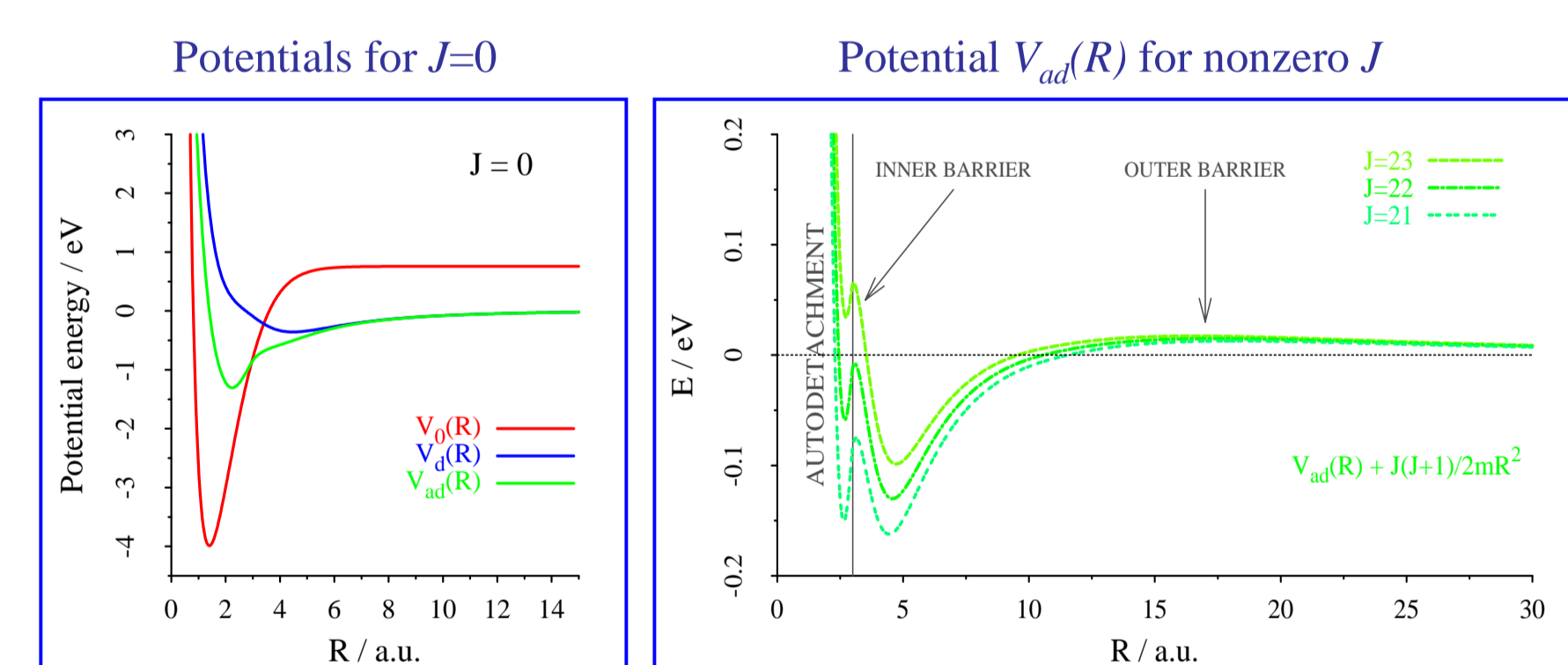
$$\psi_d(R) = \int \phi_d^*(R, r) \psi(r, R) dr,$$

where  $r$  stands for all electronic coordinates. The function  $\psi_d$  is the unique solution of the time-independent Schrödinger (Lippmann-Schwinger) equation with the effective hamiltonian

$$T_N + V_d(R) + [V_{de}(R)(E - \epsilon - T_N - V_e + i0)^{-1} V_{de}^*(R)] \psi_d(R) = E \psi_d(R).$$

Nonzero angular momentum  $J$  is taken into account by adding the centrifugal term  $J(J+1)/2\mu R^2$  both to  $V_d(R)$  and  $V_e(R)$ . It is also useful to know the adiabatic potential  $V_{ad}(R)$  within the model, given implicitly by

$$V_{ad}(R) = V_d(R) + v.p. \int \frac{|V_{de}(R)|^2}{V_{ad}(R) - V_e(R) - \epsilon} d\epsilon.$$



### Determination of resonance parameters

The position and the width of a narrow resonance can reliably be obtained from a cross section shape fitting the *Fano formula*

$$\sigma(E) = \sigma_a \frac{(q + \epsilon)^2}{1 + \epsilon^2} + \sigma_b, \quad \epsilon \equiv \frac{E - E_{res}}{\frac{1}{2} \Gamma_{res}}.$$

Many resonances studied here are *too narrow* to be obtained in this way. Since the resonances can well be understood as metastable states trapped in the outer well, a simple method can be used to obtain the position and width directly. First we calculate nuclear wave functions  $\psi_{res}(R)$  and the corresponding energies  $E_{res}$  for the adiabatic bound states in the potential  $V_{ad}(R)$ . The results for  $J=23$  are collected in the following table

v	LCP: $E_{res}$	Fano: $E_{res}$	LCP: $\Gamma_{res}$	Fano: $\Gamma_{res}$
0	-0.075362	-0.075294	$1.662 \times 10^{-5}$	$6.020 \times 10^{-6}$
1	-0.037674	-0.037587	$9.168 \times 10^{-5}$	$3.912 \times 10^{-5}$
2	-0.011331	-0.011244	$2.174 \times 10^{-4}$	$9.611 \times 10^{-5}$
3	0.005578	0.005701	$2.861 \times 10^{-4}$	$1.227 \times 10^{-4}$
4	0.015078	0.015055	$2.414 \times 10^{-4}$	$1.007 \times 10^{-4}$

The energies obtained from this procedure compare very well with the ones obtained from the Fano fit to cross sections. Also shown in the table is the estimate of the width from the local complex potential approximation (LCP)

$$\Gamma_{res}^{(LCP)} = \langle \psi_{res} | 2\pi | V_{de}(R) |^2 | \psi_{res} \rangle_{R=V_d^{-1}(E_{res})}$$

The results are not very good compared to the Fano fit. The Born-Oppenheimer approximation breaks down at small  $R$ . It is well known that the LCP can't describe accurately the dynamics of anions at small  $R$  which is the region responsible for the decay of the resonances.

The accurate estimates of  $\Gamma_{res}$  for very narrow resonances were obtained from the imaginary part of the projection of the complete Green's function at energy  $E_{res}$  on the adiabatic state  $\psi_{res}(R)$ .

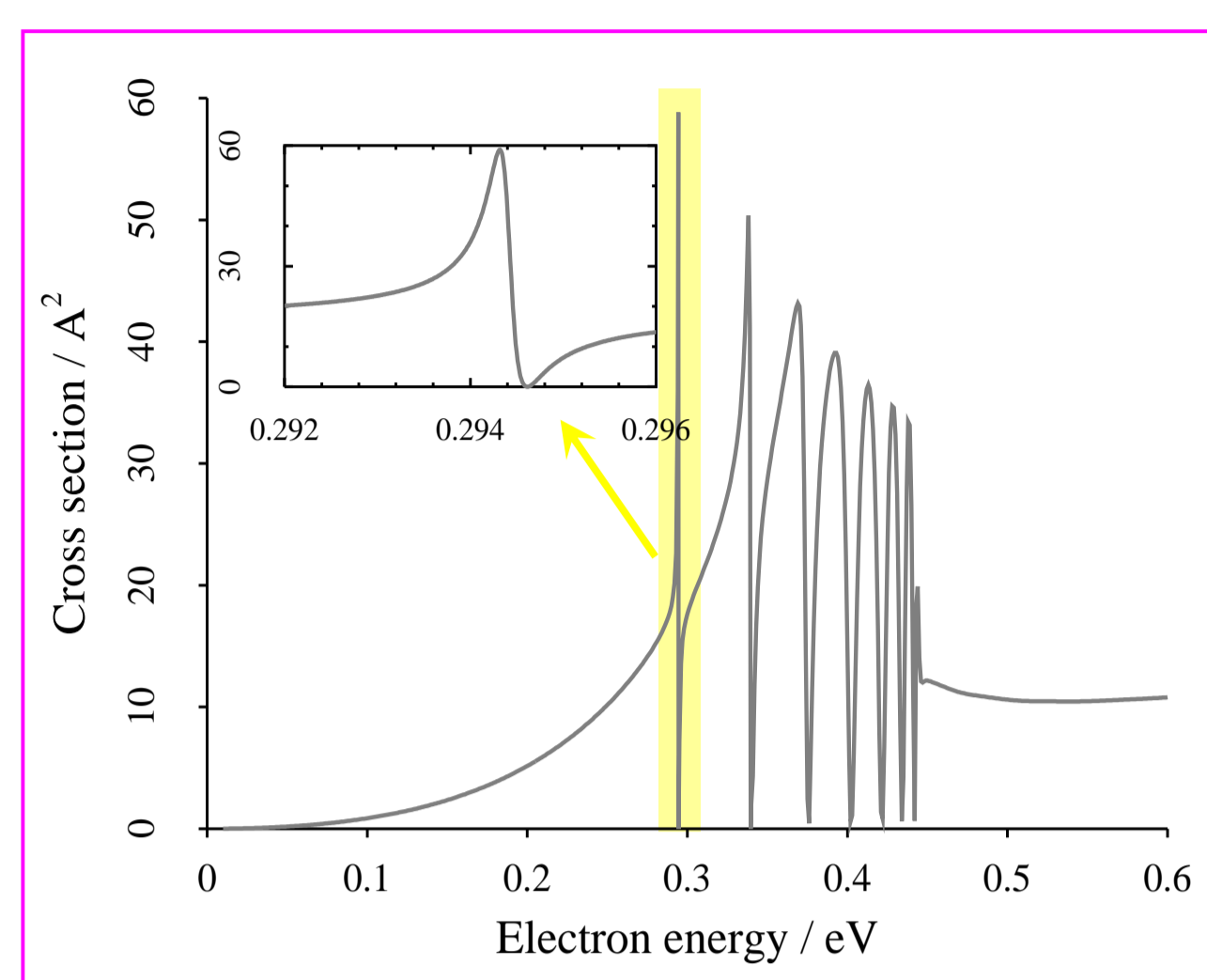
## III. VE cross sections

and

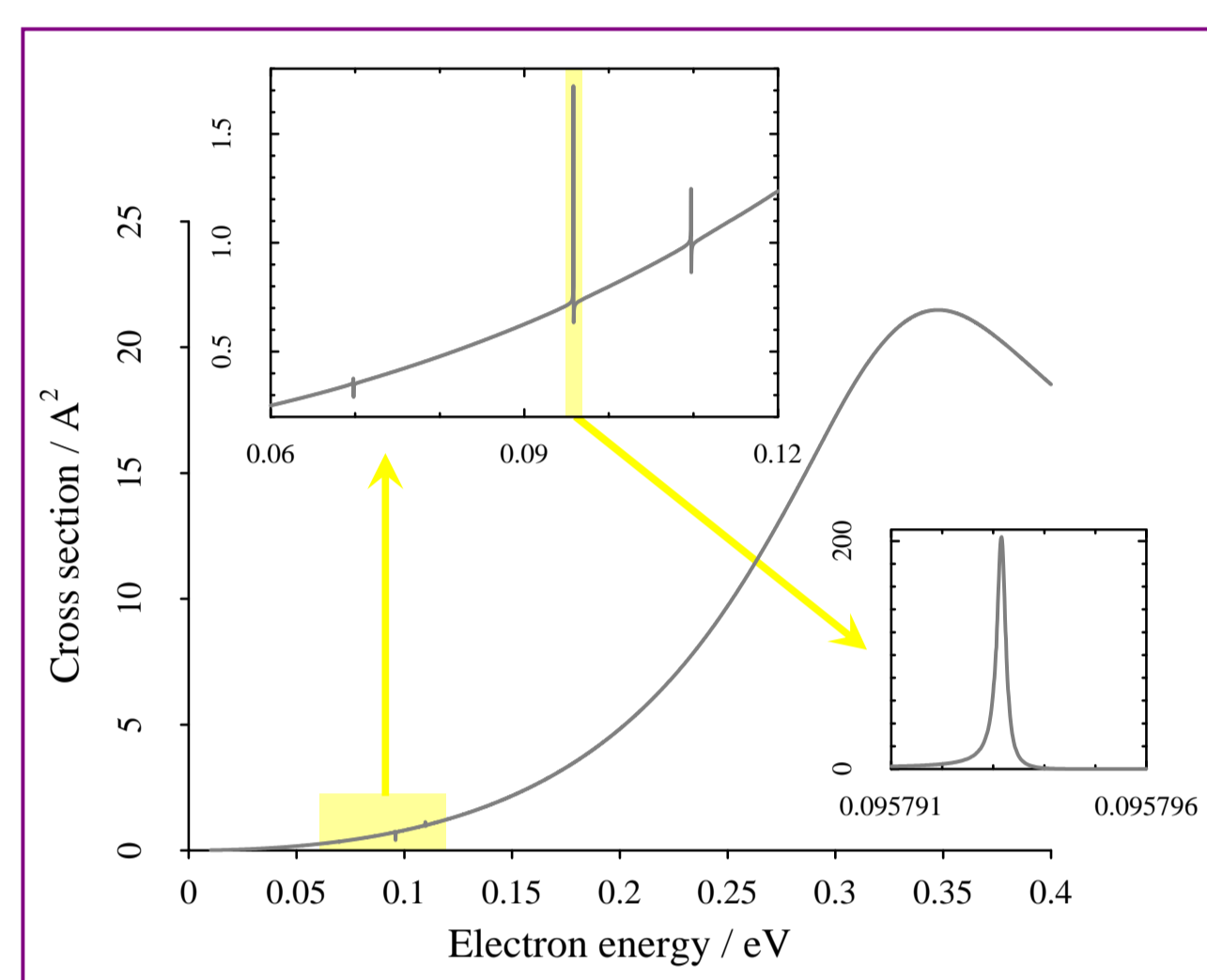
## Interpretation

### Two representative examples of cross sections:

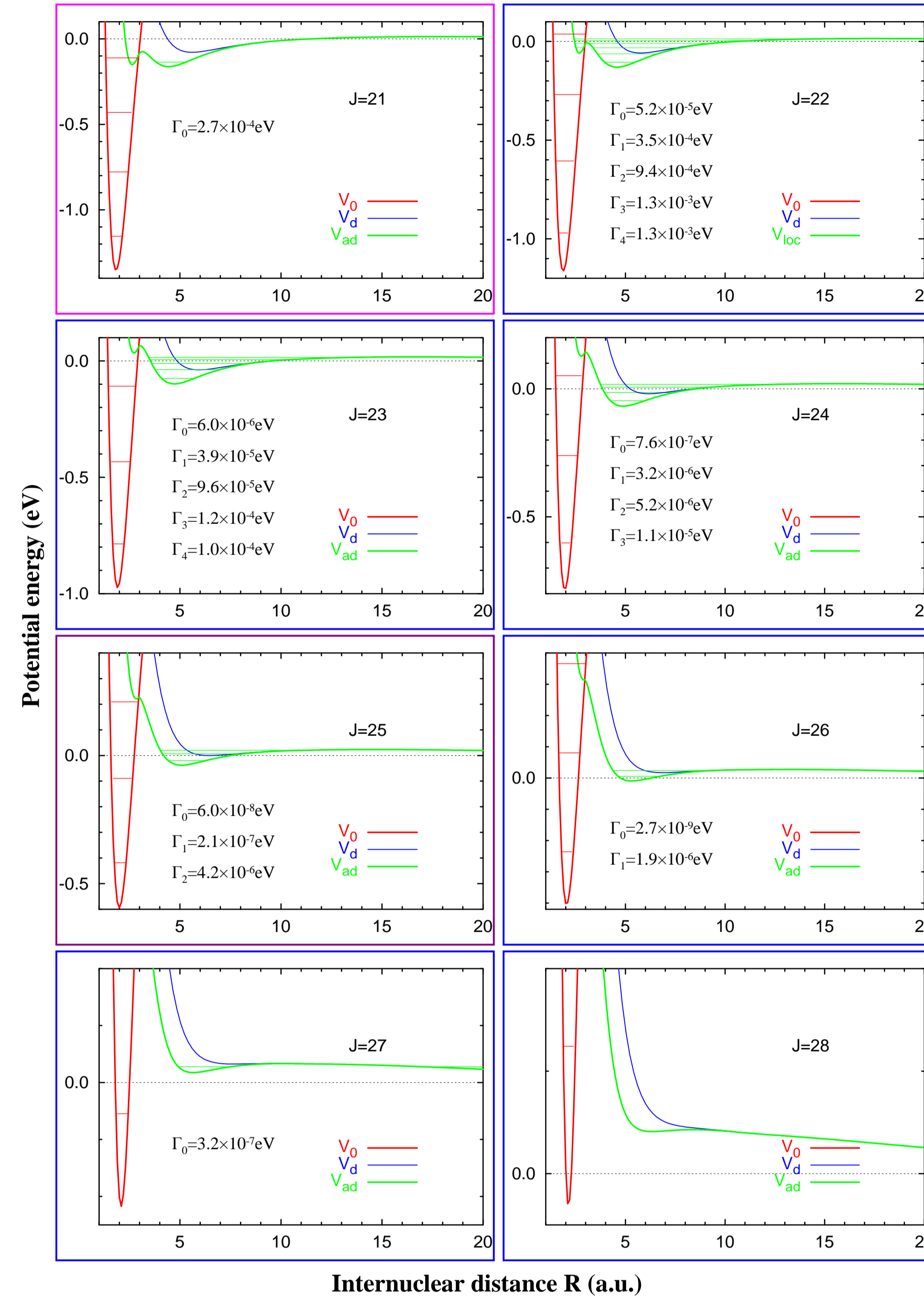
- Elastic  $e^- + H_2 (J=21, v=2)$  – boomerang oscillations turn into narrow resonances



- Elastic  $e^- + H_2 (J=25, v=1)$  – only narrow resonances present



For each  $J$  we fit the cross section in 100 points in the vicinity of resonances to a Fano profile. Resulting positions and width of resonances are shown together with potentials in right part of this panel.



## IV. Summary

### Metastable molecular hydrogen anion

The lowest states (i.e. the ones with longest life-time) are collected in the table below. The same values were found both from Fano fit and from the projection of the full Green's function on adiabatic state in the outer well.

$J$	$E_{res}$ (relative to DA)	$\tau$
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 $\mu s$
27	28 meV	2 ns

### Metastable molecular deuterium anion

All the parameters below were calculated from the projection of the full Green's function on the adiabatic state in the outer well

$J$	$E_{res}$ (relative to DA)	$\tau$
31	-118 eV	0.13 ns
32	-97 eV	0.70 ns
33	-76 eV	6 ns
34	-55 eV	39 ns
35	-35 eV	0.51 $\mu s$
36	-16 eV	5.7 $\mu s$
37	2 eV	14 $\mu s$
38	19 eV	7.2 $\mu s$
39	34 eV	41 ps

### References:

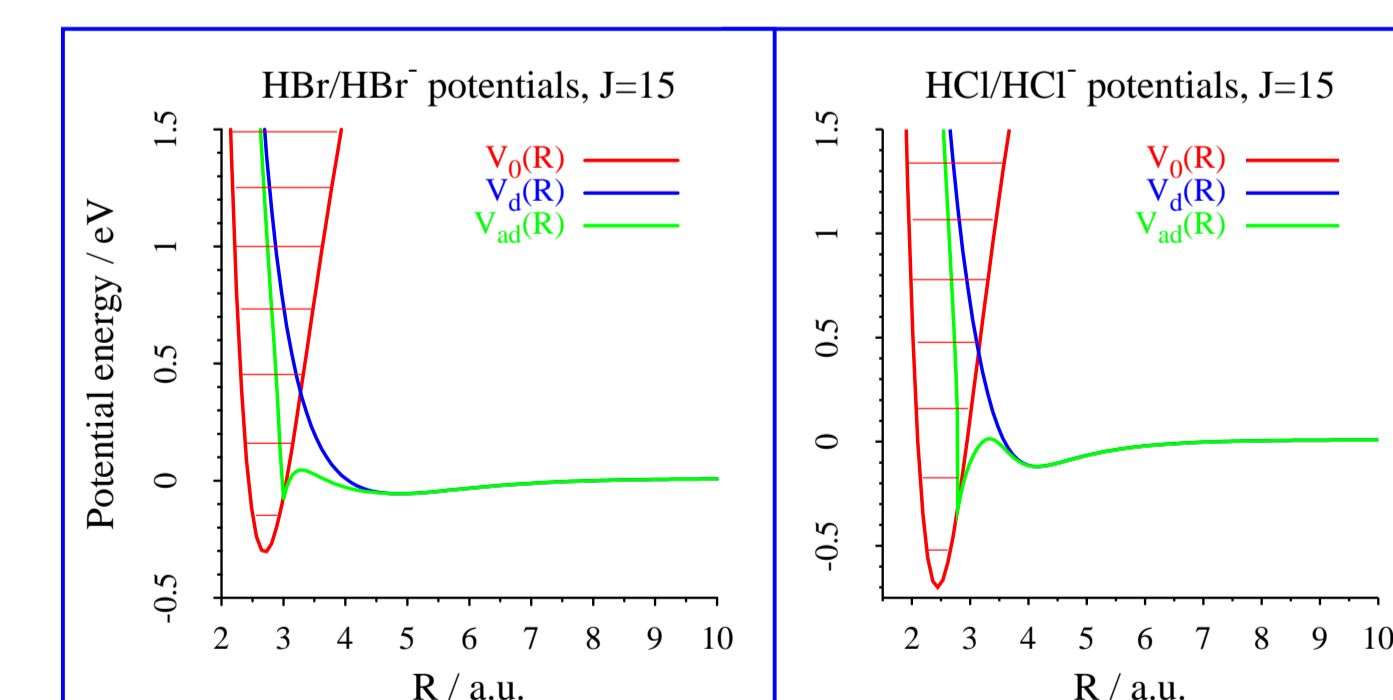
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## V. Conclusions

- 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  $\mu s$**  and **14  $\mu s$**  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).

### Acknowledgement:

I would like to thank prof. Xuefeng Yang for drawing my attention to the problem of long-lived anionic states of hydrogen molecule and to experimental evidence for their existence.  
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