# Long-lived states of hydrogen molecular anion

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1. Molecular anions and their role
2. Hydrogen molecular anion
3. Experimental search before 2004
4. AMS experiment, etc.
5. Theoretical explanation by NRM
6. Conclusion

# Molecular anions

Molecular anions play an important role in many area of physics. For example they mediate a series of reactions:

1. Vibrational excitation by electron impact

$$e + M(v_i) \rightarrow (M^-)^* \rightarrow e + M(v_f)$$

2. Dissociative electron attachment

$$e + AB \rightarrow (AB^-)^* \rightarrow A + B^-$$

3. Associative detachment

$$A + B^- \rightarrow (AB^-)^* \rightarrow AB(J,v) + e$$

# Why these processes are important?

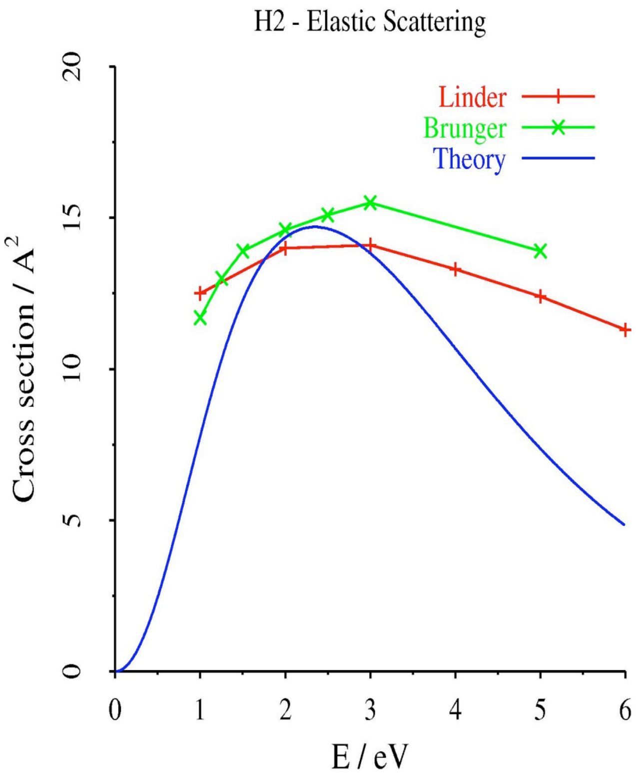
- Many applications from basic science to technology
- Production of negative ions DA $e+H_2 \rightarrow H+H^-$
- Early stages of the Universe AD $e+H_2 \leftarrow H+H^-$
- Planetary atmospheres
- Plasma physics
- Chemical lasers
- Molecular switches, etc.
- Biology – radiation damage

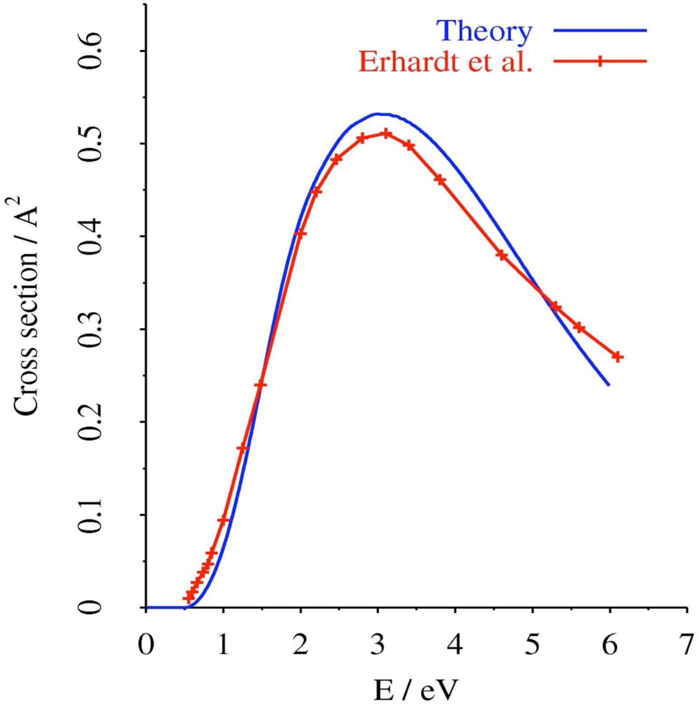
# Hydrogen molecular anion

Molecules do not always form stable anions, but usually many short-lived states exist.

Theory predicts the life time of the lowest state of molecular hydrogen anion in the $\Sigma_u$ state to be of the order of $10^{-14}$ s. This life time is extremely short and is of the order of vibrational period of the molecule. The shortness of the lifetime is confirmed by many experiments.

# Elastic scattering and vibrational excitaton 0 →1 of $H_2$





# Molecular hydrogen anion puzzle

The existence of short-lived states of molecular hydrogen anion is firmly established both theoretically and experimentally. However, states with the lifetime of microseconds (longer by 9 orders) seemed to be observed in some experiments but strongly ruled out by other experimental work.

Do these states really exist and if yes what is their nature and what is their lifetime? Why they were seen in some experiments and not in others?

# Experimental search for $H_2^-$

1. Khvostenko and Dukelskii, (1958)
   (recharging method). Antimonium needed

2. Hurley et al. Nucl.Inst.Meth. 118(1974)307
   (discharge ion source)
   $H_2^-$ observed 5.5 times more abundant than $H^-$

3. Aberth et al. PRL34(1975)1600
   (duoplasmon source)
   $D_2^-$ observed with the lifetime $>10^{-5}$ s,
   but no $H_2^-$ !

# Experimental search for $H_2^-$

4. Barnett, Oak Ridge Natl. Lab. Report No. ORNL/TM-8693, (1983) (unpublished) simultaneous two-electron capture collisions of $H^+$ in $H_2$ and Xe gasses. His careful studies gave completely negative results!

5. Bae et al. PRA29(1984)2888 (two step electron capture in Cs) No $H_2^-$, no $D_2^-$ with the life time > $10^{-10}$ s!

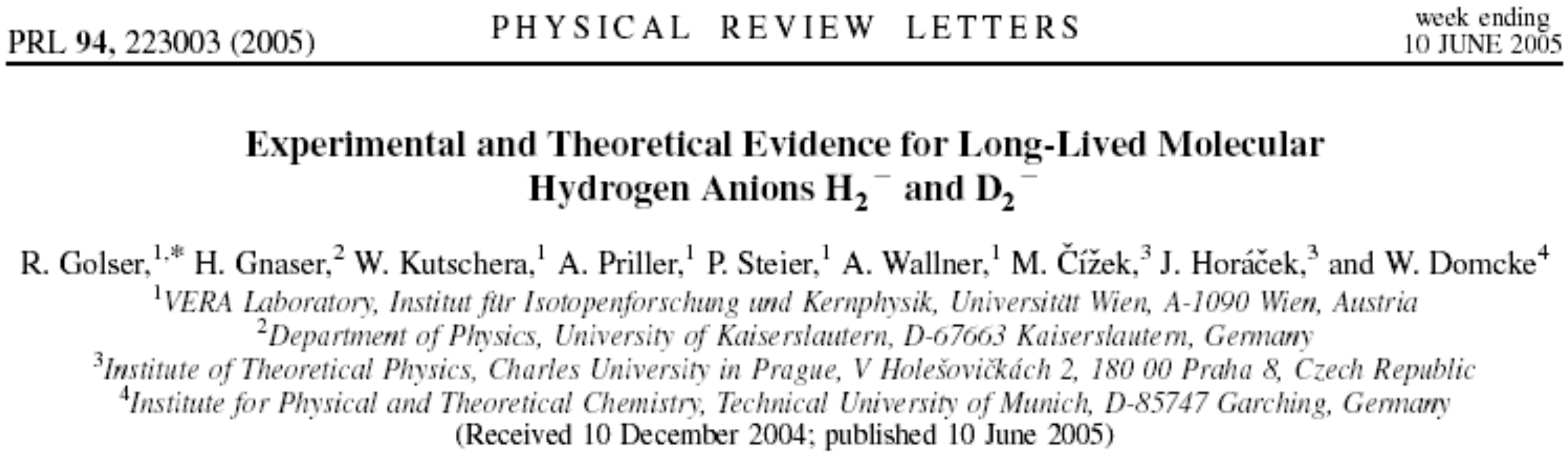
6. Wang et al. Chem. Phys. Lett. 377, 512 (2003) dielectric-barrier discharge plasma. No explicit identification of $H^-_2$!

# Experimental search for $H_2^-$

7. The $H_2^-$ ion was probably observed without any effort to form the ion by people studying interplanetary dust and the H/D ratios for meteors, see e.g.: E. Zinner, K. D. McKeegan, and R. M. Walker, Nature **305**, 119-121 (1983).

# Search for $H^-_2$ by AMS

VERA, the Vienna Environmental
Research Accelerator.



PRL 94, 223003 (2005) PHYSICAL REVIEW LETTERS week ending
10 JUNE 2005

## Experimental and Theoretical Evidence for Long-Lived Molecular Hydrogen Anions $H_2^-$ and $D_2^-$

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# Accelerator mass spectrometry AMS

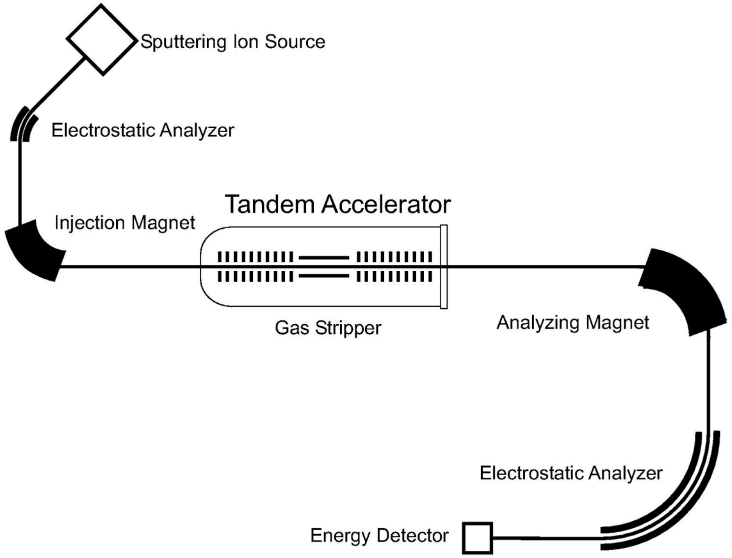
An ultrasensitive technique to detect individual ions.

Used primarily to count carbon-14 in arecheological and geologic samples for dating purposes.

AMS can seek out one carbon-14 isotope from among a quadrillion other carbon atoms.

# How AMS works for hydrogen anion

1. Sputtering: mostly singly charged particles with energy about 70 keV.
2. Electrostatic analyzer E/Q
3. Magnetic analyzer M/Q
   M/Q=2 $H_2^-$ or $D^-$
4. Acceleration by tandem accelerator 1.5 Mev, ions gain energy of about 1.57 MeV.
5. Stripper: $O_2$ gas. Ions lose electrons molecules break up
   $D^- \rightarrow D^+$ E=1.57 MeV
   $H_2^- \rightarrow H^+ + H^+$, E= 0.785 MeV
6. Second acceleration by 1.5 MeV
   $D^+$ E=3.07 MeV
   $H^+$ E=2.285 MeV, $2H^+$ E=4.570 MeV
7. Again M/Q and E/Q and energy E measured (TOF).



# 1. Conclusion-experiment

These experiments demonstrate conclusively that both $H_2^-$ and $D^-_2$ are formed in the sputtering process; from the respective flight times from the ion source to the tandem terminal stripper, we infer lifetimes of at least 3 µs and 4 µs, respectively.

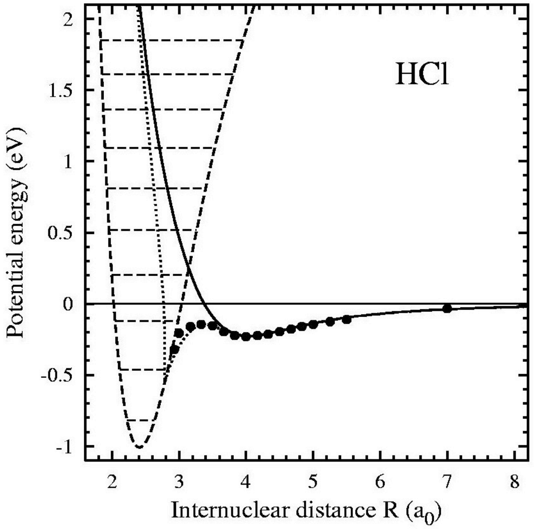
# 2. Theory: Nonlocal Resonance Model

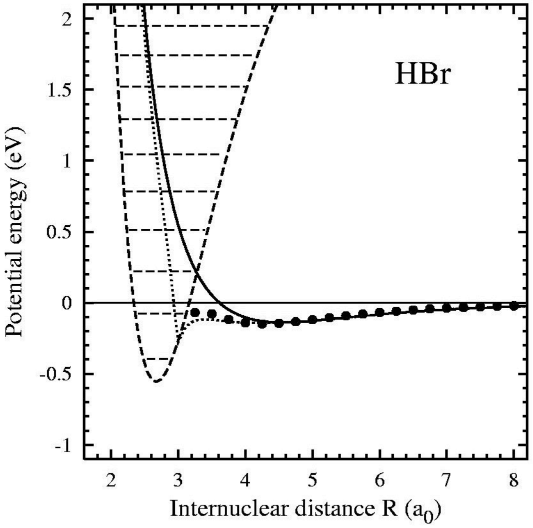
Review: W. Domcke, Phys.Rep.208(1991)97

Recent application to hydrogen:

1. Čížek, Horáček and Domcke: J.Phys.B. 31 (1998)2571
2. Horáček, Čížek, Houfek, Kolorenč and Domcke, Phys.Rev. A70(2004)052712
3. Horáček, Čížek, Houfek, Kolorenč and Domcke, Phys.Rev. A73, 022701 (2006)

# Nonlocal resonance model





Coupling of the resonance state with the orthogonal continuum.

$\Phi_d(R, r_i)$ discrete state

$<\Phi_d | \Phi_d> = 1$

$V_d(R) = <\Phi_d | H_{el} | \Phi_d>$

$\Psi(k,R)$ orthogonal continuum

$<\Phi_d | \Psi_k> = 0$

$V_{dc}(k,R) = <\Phi_d | H_{el} | \Psi_k>$

Nonlocality follows from breakdown of the BO approximation.

# HBr/DBr vibrational excitation

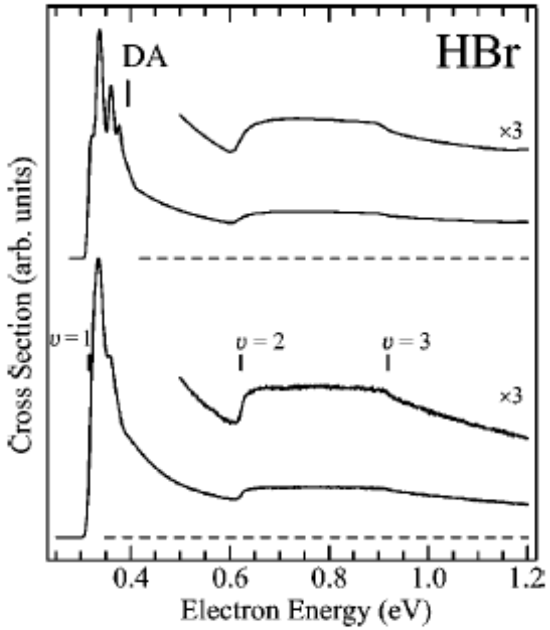


FIG. 10. Experimental (lower part) and theoretical (upper part) cross sections for the $v=0\rightarrow1$ transition in HBr. (See also explanations in the caption of Fig. 8.)

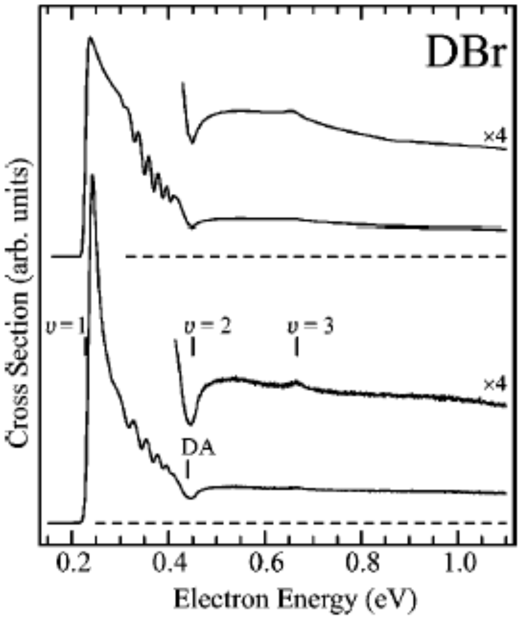


FIG. 11. Experimental (lower part) and theoretical (upper part) cross sections for the $v=0\rightarrow1$ transition in DBr. (See also explanations in the caption of Fig. 8.)

# HBr/DBr elastic scattering

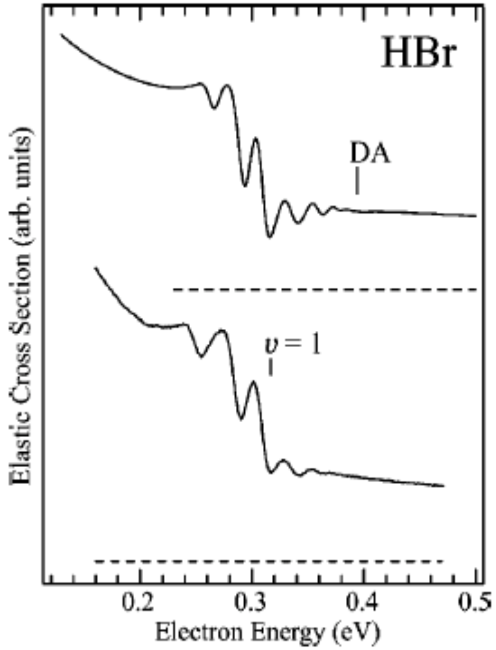


FIG. 8. Vibrationally elastic cross section of HBr. Bottom trace shows the cross section recorded at 90° using the hemispherical analyzer spectrometer. Top trace shows the results of the nonlocal resonance theory, including the broadening caused by thermal rotational excitation of the target at 100 K and convoluted with a Gaussian (5 meV FWHM) to simulate, in part, the finite experimental resolution. The dissociative attachment threshold and the threshold for vibrational excitation are marked.

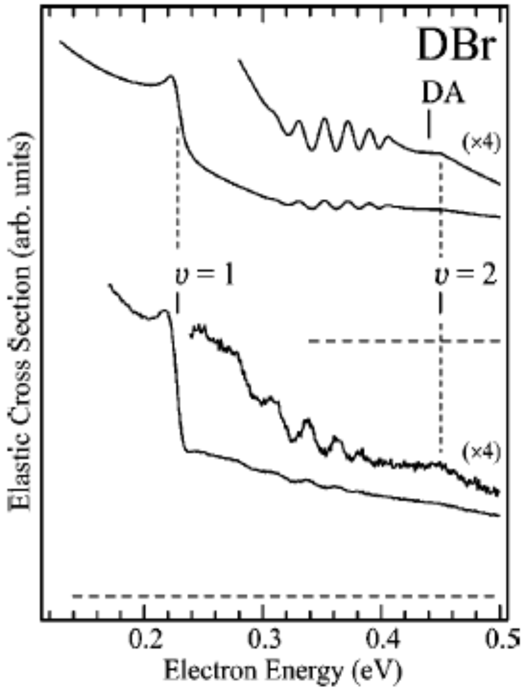


FIG. 9. Experimental (lower part) and theoretical (upper part) vibrationally elastic cross section of DBr. Parts of the curves are shown vertically expanded and offset (the slope of the expanded part of the experimental spectrum is also slightly reduced) to improve the visibility of the structure. (See also explanations in the caption of Fig. 8.)

# Dissociative electron attachment

# $e + AB \rightarrow A + B^-$

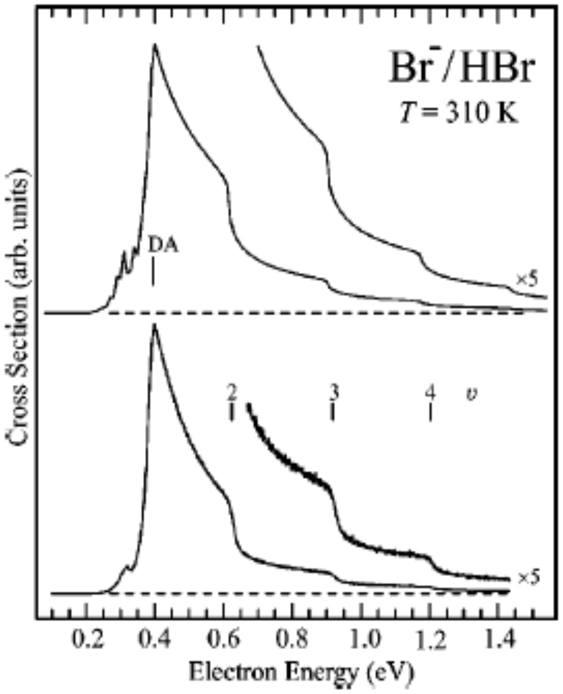


FIG. 12. Experimental (lower part) and theoretical (upper part) dissociative attachment cross sections in HBr at 310 K. The thresholds for dissociative attachment and vibrational excitation are marked. The theoretical spectrum is not convoluted with a simulated instrumental profile.

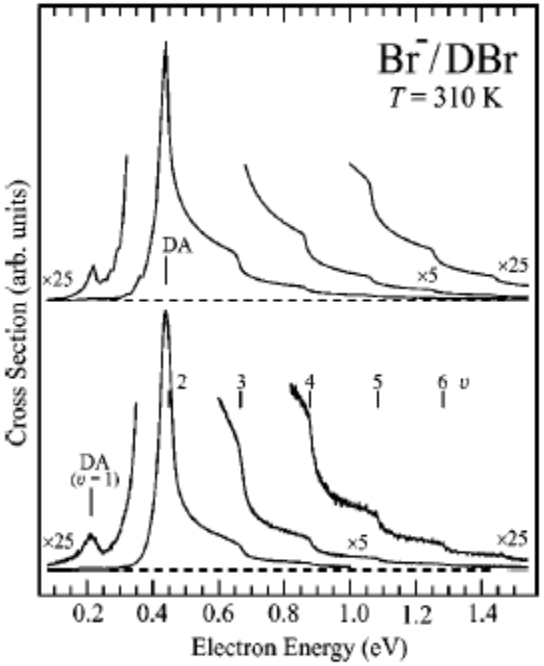


FIG. 13. Experimental (lower part) and theoretical (upper part) dissociative attachment cross sections in DBr at 310 K. The thresholds for vibrational excitation, dissociative attachment, and dissociative attachment to HBr in the $\upsilon = 1$ state are marked. The theoretical spectrum is not convoluted with a simulated instrumental profile.

# High rotational excitation in AD

Čížek, Horáček and Domcke:
J.Phys.B. 31 (1998)2571

2578 *M Čížek et al*

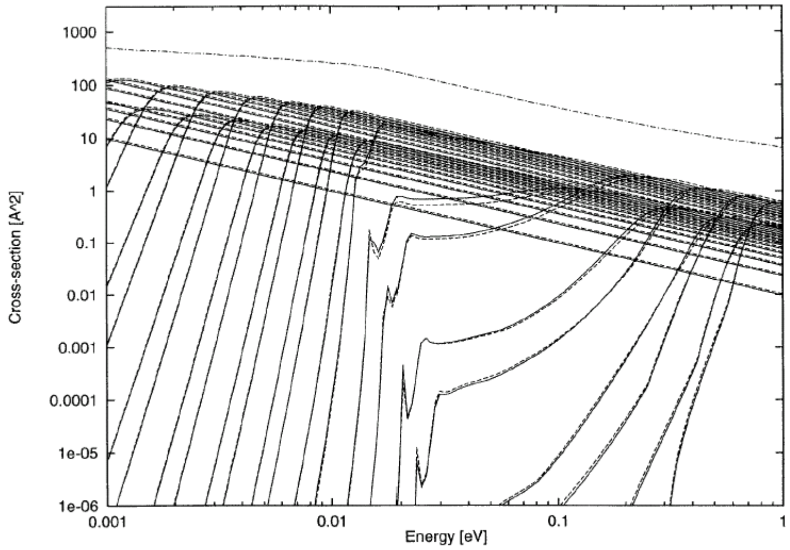


**Figure 2.** The total H + $H^-$ associative-detachment cross section (chain curve) and its partial-wave components (full curves), $l = 30, 29, \ldots$ (from the right). Results of the local approximation are given by broken curves.

2580 *M Čížek et al*

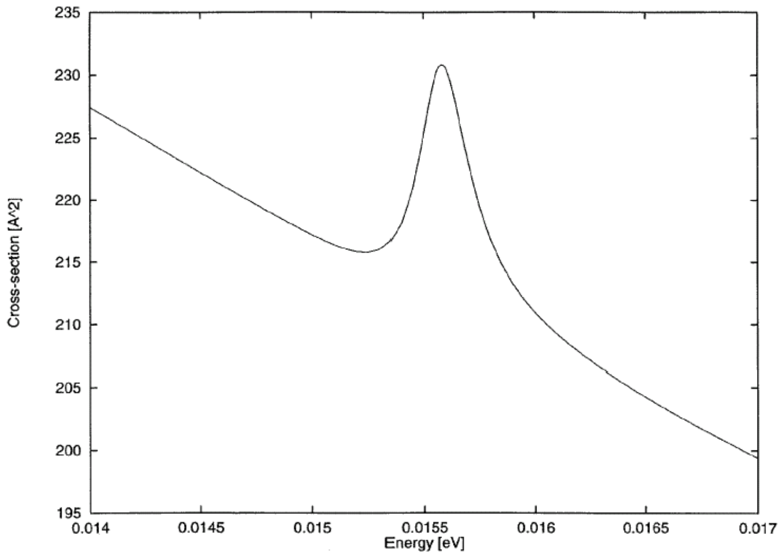
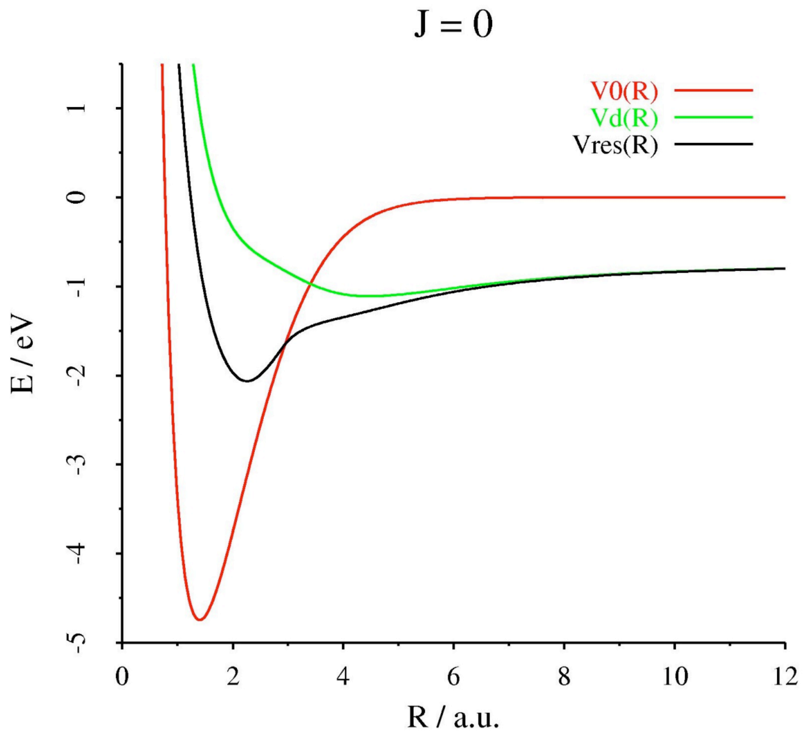
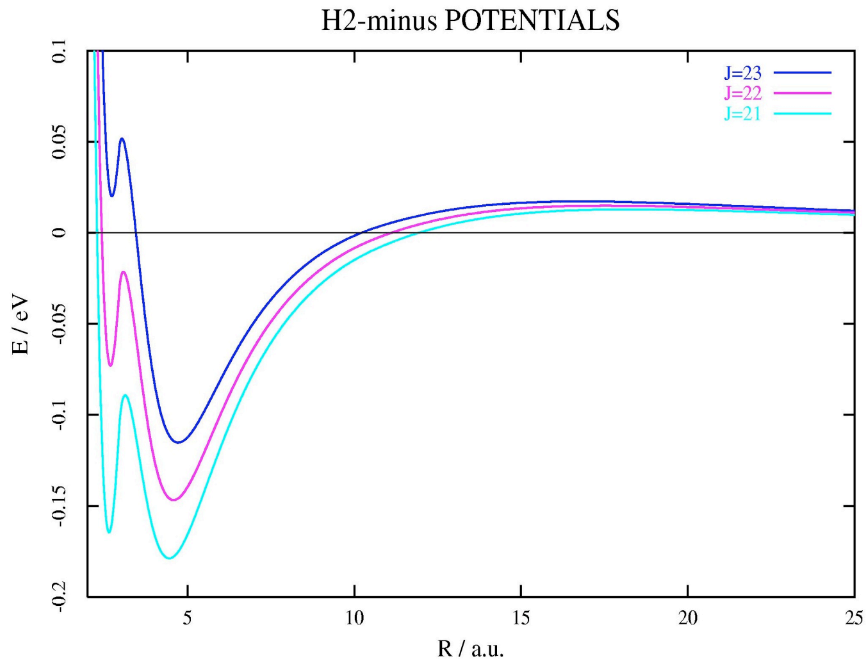


**Figure 4.** Detailed view of a resonance in the total cross section for the associative detachment of $D^-$ in the collision with D. The partial wave $l = 32$ is responsible for this resonance.

# Role of the rotational excitation of the target

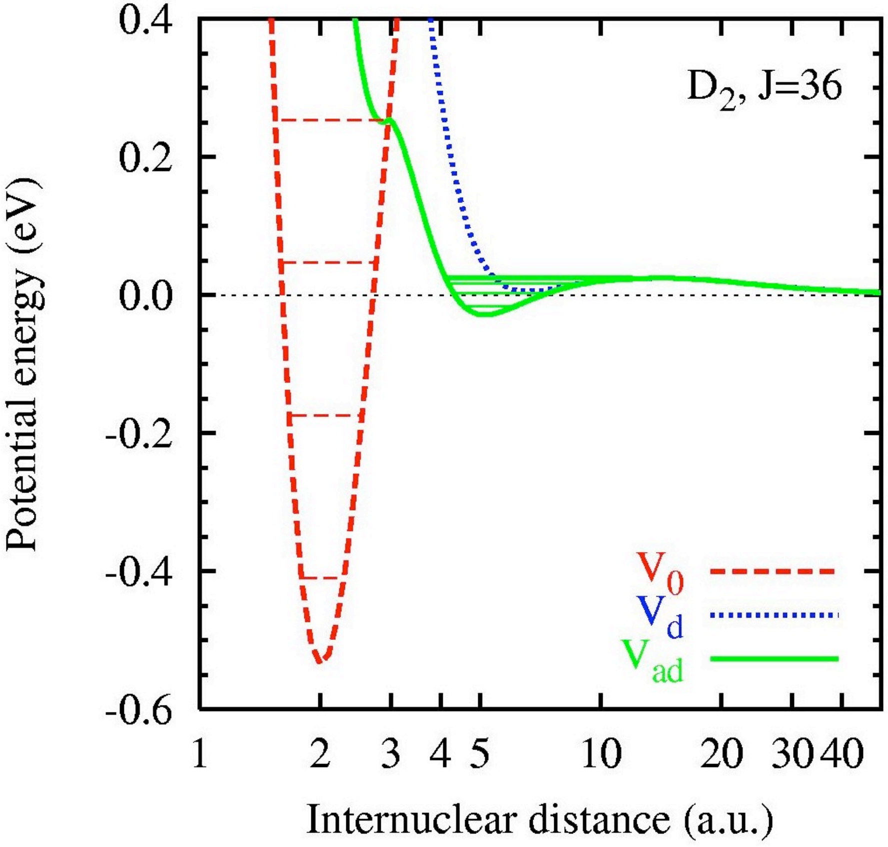
$$V(R) \Rightarrow V(R) + J(J+1)/R^2$$



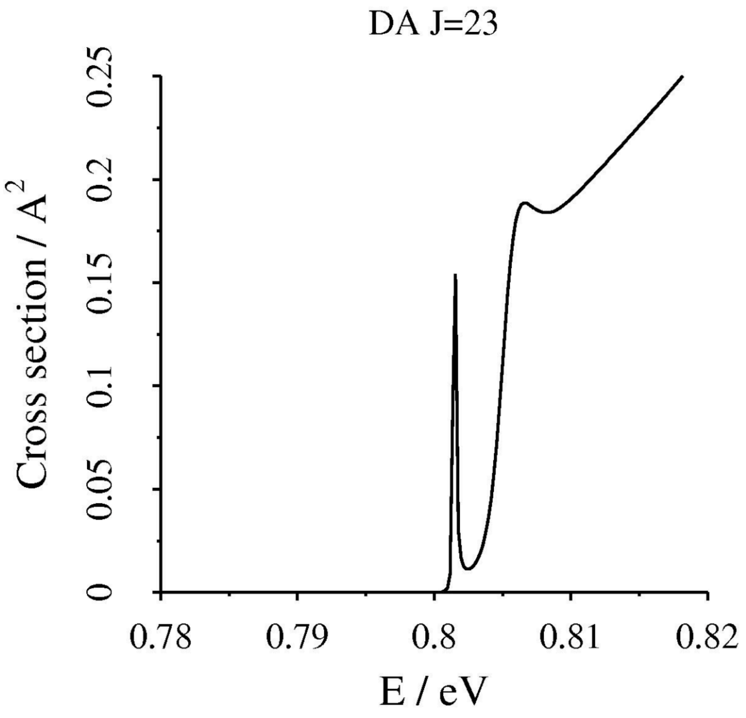


# Role of the rotational excitation of the target (deuterium)

$$V(R) \Rightarrow V(R) + J(J+1)/R^2$$



# High J DA resonances


DA J=23

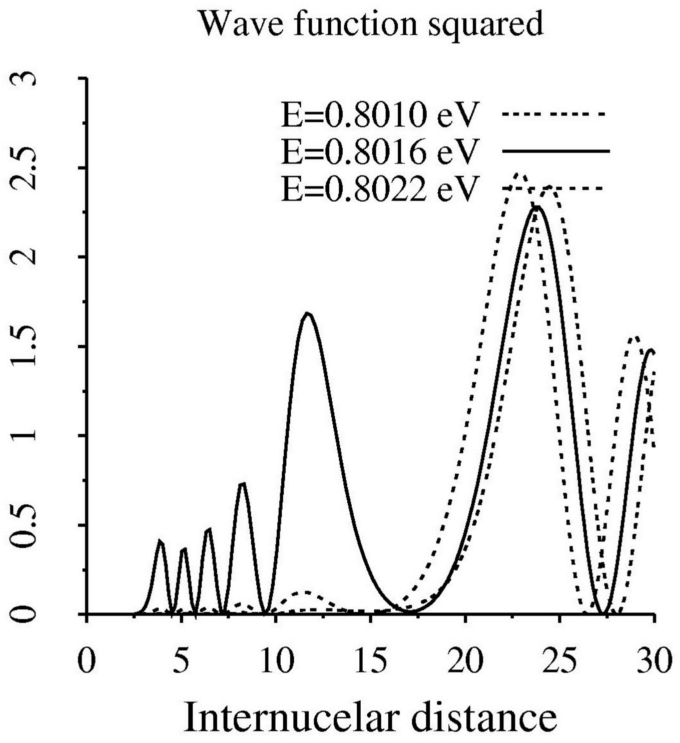

Wave function squared

**Table I:** Parameters of $H_2^-$ states

| $J$ | $E_{res}$ (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** | **0.25 μs** |
| 27 | 28 meV | 2 ns |

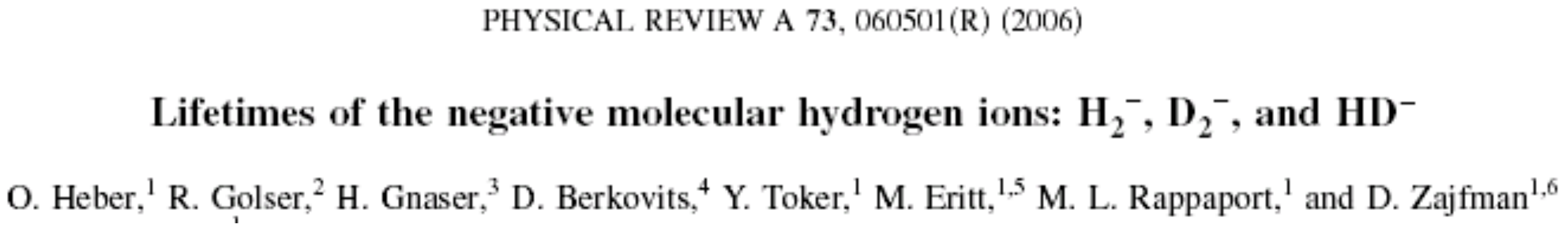
**Table II:** Parameters of $D_2^-$ states

| $J$ | $E_{res}$(relative to DA) | $\tau$ |
|---|---|---|
| 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** |
| **37** | **18 meV** | **16 µs** |
| **37** | **2 meV** | **61 µs** |
| **38** | **19 meV** | **2108 µs** |

# Conclusions Theory

- 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 **2108 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.

# Measured and calculated lifetimes



PHYSICAL REVIEW A 73, 060501(R) (2006)

### Lifetimes of the negative molecular hydrogen ions: $H_2^-$, $D_2^-$, and $HD^-$

O. Heber,[1] R. Golser,[2] H. Gnaser,[3] D. Berkovits,[4] Y. Toker,[1] M. Eritt,[1,5] M. L. Rappaport,[1] and D. Zajfman[1,6]

| Species | J | Expt. (μs) | Theory(μs) |
|---|---|---|---|
| $H_2^-$ | 26 | 8.2±1.5 | 0.25 |
| HD | 31 | 50.7±1.0 | 23 |
| $D_2^-$ | 37 | 23±3 | 16 |
| $D_2^-$ | 37 | 84±3 | 61 |
| $D_2^-$ | 37 | 1890±80 | 2108 |

# Final conclusions

The existence of long-lived states of molecular hydrogen anion with the lifetime of the order of μs were confirmed by various experiments.

The theory based on the use of the nonlocal resonance model predicted their existence and explains them as states of high rotational excitations.

# Coworkers

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