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)

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Charles University Prague
History of this project

1997 with Wolfgang Domcke (Duesseldorf)

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

\( X=H: \quad J. \text{Phys. B} \ 31 \ (1998) \ 2571, \)
\( X=Cl: \quad \text{Phys. Rev. A} \ 60 \ (1999) \ 2873, \)
\( X=Br: \quad \text{Phys. Rev. A} \ 63 \ (2001) \ 062710. \)

1999 with Hartmut Hotop (Kaiserslautern)

simulation of electron spectra

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

\( J. \text{Phys. B} \ 34 \ (2001) \ 983. \)
History of this project

2001 - Michael Allan (Fribourg)

Svetlana Živanov:

\[ \text{H} + \text{X}^- \leftrightarrow \text{HX} + \text{e}^- , \]

\[ \text{X} = \text{Cl}, \text{Br} \]

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

\[ V_0(R) + \varepsilon \]

\[ V_\delta(R) \]

\[ V_\delta\varepsilon(R) \]

\[ V_{ad}(R) \]
Associative detachment \[ \text{X}^- + \text{H} \rightarrow \text{HX} + \text{e}^- \]
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

\[ \langle \phi_d | H_{el} | \phi_\varepsilon \rangle = V_{de} (R) \]

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

Hamiltonian in the basis:
\[ H = T_N + \langle \phi_d | V_d | \phi_d \rangle + \int \left( \langle \phi_\varepsilon | (V_0 + \varepsilon) | \phi_\varepsilon \rangle + \langle \phi_d | V_{de} | \phi_\varepsilon \rangle + \langle \phi_\varepsilon | V_{\varepsilon d}^* | \phi_d \rangle \right) d\varepsilon \]

\[ = H_0 + V = \begin{pmatrix} T_N + V_d (R) & \cdots & 0 & \cdots \\ \vdots & \ddots & 0 & \vdots \\ 0 & \cdots & V_0 (R) + T_N + \varepsilon & \vdots \\ \vdots & \ddots & 0 & \vdots \end{pmatrix} + \begin{pmatrix} 0 & \cdots & V_{de} (R) & \cdots \\ \vdots & \ddots & 0 & \vdots \\ V_{\varepsilon d}^* (R) & \cdots & 0 & \vdots \\ \vdots & \ddots & 0 & \ddots \end{pmatrix} \]
Equation of motion for nuclei

\[
\left[-\frac{1}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{J(J+1)}{2\mu R^2} + V_d(R) - E\right] \psi_d(R) + \\
+ \sum \chi^J_v(R) \int dR' f\left(E - E^*_v, R, R'\right) \chi^J_v(R') \psi_d(R') = 0
\]

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 : \(0 < \alpha < \frac{1}{2}\)

s - wave scattering : \(\alpha = \frac{1}{2}\)

p - wave scattering : \(\alpha = \frac{3}{2}\)
Calculation of electron spectra

AD cross section:

\[
\sigma^J_v (E) = \frac{2\pi^2}{E} (2J + 1) \left| \left\langle \psi_d \left| V_{d\varepsilon^J_v} \right| \chi^J_v \right\rangle \right|^2
\]

Electron spectrum (ideal conditions):

\[
\frac{d\sigma}{d\varepsilon} (\varepsilon, E) = \sum_{J,v} \sigma^J_v (E) \delta(\varepsilon - E + E^J_v)
\]

Experimental electron rate:

\[
\frac{dk}{d\varepsilon} (\varepsilon) = \int \frac{d\sigma}{d\varepsilon} (\varepsilon, E = \frac{1}{2} mu^2) f(u) ud\varepsilon = \sum_{J,v} \sigma^J_v (E) f\left(\sqrt{2m(\varepsilon + E^J_v)}\right)
\]
$\text{H} + \text{Cl}^- \rightarrow \text{HCl}(J,v) + e^-$

$J=0$ contribution to AD cross section in HCl

Cross section $[\text{A}^2]$ vs. Collisonal energy [eV]
AD cross section – final states at fixed collision energy

![Graph showing AD cross section with final states at fixed collision energy. The graph includes points for different energy levels (v=0, v=1, v=2) and two labels: Nonlocal and Local. The energy of released electron is measured in eV. The label J=13 indicates a particular energy level or parameter.](Image)
Count rate (arb. uni.)

Electron energy (eV)

- $v=0$
- $v=1$
- $v=2$

$S_1$

$S_0$
H+Cl^-, E_{Cl} = 0.5\text{eV}, Electron resolution = 30\text{meV}
$H+Cl^-, E_{Cl}=4eV, \text{ Electron resolution = 30meV}$
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 cannot simply be explained by energy distribution function. Cross section increases faster with vibrational state in experiment than in theory.
Figure 5. Final-state distribution in $\text{H}+\text{H}^-$ associative detachment at 0.01 eV collision energy. Relative probabilities for the different final states of $\text{H}_2$ 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 $\text{H}_2$ state on the $y$-axis, and the cross section $\sigma_l^0$ (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.
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.
The Origin of the Resonances

Potentials for $J=0$

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

Potential energy / eV

$V_d(R)$

$V_{ad}(R)$

$V_0(R)$

$J=0$

$J=23$

$J=22$

$J=21$

$V_{ad}(R) + J(J+1)/2mR^2$
Resonant tunneling wave function

Cross section

AUTODETACHMET

E=0.8000
**Experimental motivation**

- Hurley 1974 – observation of $\text{H}_2^-$ from low-energy arc source.
- Aberth *et al.* 1975 – observation of $\text{HD}^-$, $\text{D}_2^-$ from ($\tau > 10\mu\text{s}$).
- Bae *et al.* 1984 – existence of $\text{D}_2^-$ not confirmed in two-step experiment designed to produce metastable quartet state ($\tau < 2\times10^{-11}\text{s}$).
- Wang *et al.* 2003 – observed signature of $\text{H}_2^-$ in signal from discharge plasma.
Elastic cross section for $e^- + \text{H}_2$ ($J=21$, $\nu=2$)
\( \Gamma_0 = 2.7 \times 10^{-4} \text{eV} \)
Elastic cross section for $e^- + H_2 (J=25, \nu=1)$
$\Gamma_0 = 2.7 \times 10^{-9} \text{eV}$

$\Gamma_1 = 1.9 \times 10^{-6} \text{eV}$
<table>
<thead>
<tr>
<th>$J$</th>
<th>$E_{res}$ (relative to DA)</th>
<th>$\tau$</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>-136 meV</td>
<td>2.4 ps</td>
</tr>
<tr>
<td>22</td>
<td>-105 meV</td>
<td>12 ps</td>
</tr>
<tr>
<td>23</td>
<td>-75 meV</td>
<td>0.11 ns</td>
</tr>
<tr>
<td>24</td>
<td>-47 meV</td>
<td>0.9 ns</td>
</tr>
<tr>
<td>25</td>
<td>-20 meV</td>
<td>12 ns</td>
</tr>
<tr>
<td><strong>26</strong></td>
<td><strong>5 meV</strong></td>
<td><strong>0.52 µs</strong></td>
</tr>
<tr>
<td>27</td>
<td>28 meV</td>
<td>2 ns</td>
</tr>
</tbody>
</table>
### Table II: Parameters of $D_2^-$ states

<table>
<thead>
<tr>
<th>$J$</th>
<th>$E_{\text{res}}$(relative to DA)</th>
<th>$\tau$</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>-118 meV</td>
<td>0.13 ns</td>
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<tr>
<td>32</td>
<td>-97 meV</td>
<td>0.70 ns</td>
</tr>
<tr>
<td>33</td>
<td>-76 meV</td>
<td>6 ns</td>
</tr>
<tr>
<td>34</td>
<td>-55 meV</td>
<td>39 ns</td>
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<tr>
<td>35</td>
<td>-35 meV</td>
<td>0.51 $\mu$s</td>
</tr>
<tr>
<td>36</td>
<td>-16 meV</td>
<td>5.7 $\mu$s</td>
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<tr>
<td>37</td>
<td>2 meV</td>
<td>14 $\mu$s</td>
</tr>
<tr>
<td>38</td>
<td>19 meV</td>
<td>7.2 $\mu$s</td>
</tr>
<tr>
<td>39</td>
<td>34 meV</td>
<td>41 ps</td>
</tr>
</tbody>
</table>
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⁻ + H₂ autoionisation region by inner barrier and separated from dissociation into H + H⁻ by an outer centrifugal barrier.

• The decay into the e⁻ + H₂ 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 H₂⁻ and D₂⁻ respectively. Even larger values can be expected for T₂⁻.

• 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 H₂ 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 H₂. It is probably much easier to create the states in *H⁻ + H₂ collisions*. The cross sections are unknown, however (to be the subject of further study).
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