Electron-molecule collisions: The influence of microsolvation on the shape resonance spectra and in the differential cross sections

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Population: 1,851,215 people
(IBGE/2009)

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Outline:

✓ Motivation.

✓ Schwinger multichannel (SMC) method.

✓ Applications:
CH$_2$O...H$_2$O,
HCOOH... (H$_2$O)$_n$ ($n=1,2$)
C$_5$H$_6$OH... (H$_2$O)$_n$ ($n=1,2$)

✓ Conclusions.

✓Acknowledgements.
Motivation:

Resonant Formation of DNA Strand Breaks by Low-Energy (3 to 20 eV) Electrons

Badia Boudaïffa, Pierre Cloutier, Darel Hunting, Michael A. Huels,* Léon Sanche

DNA damage - single- and double-strand breaks in DNA are caused by secondary low-energy (up to 20 eV) electrons generated by the ionizing radiation (X-rays, γ-rays, β-rays).
The formation of H\(^-\), O\(^-\) and OH\(^-\) is attributed to dissociative electron attachment (DEA).

"This result further indicates that the measured yields results from a local interaction (e.g., DEA to a basic constituent) not related to the long range geometrical properties of DNA."
Motivation:

- The $\pi^*$ shape resonances initiate the DEA to DNA.

- Results obtained in gas-phase can help in the understanding of processes that occur in condensed phase.

Model using resonances locations
Computed in gas-phase.

Gas-phase.
Motivation:

- **DEA to DNA** initiates with the formation of a transient negative ion (shape, core-excited, or Feshbach resonances) electron-molecule collision problem (gas phase).

- **Solvation**: systems with water.

- **Gas phase** condensed phase: systems with hydrogen bonds.
The SMC method:


- Extension of the Schwinger variational principle for the scattering amplitude for applications to low-energy electron-molecule collisions;

- Capable of addressing important aspects of these collisions as:
  - exchange interactions \((ab \text{ initio})\);
  - effects arising from the polarization of the target by the incident electron \((ab \text{ initio})\);
  - electronic excitation (multichannel coupling).

- In the present implementation of the SMC method, to represent the core electrons we employ the local-density norm-conserving pseudopotentials of Bachelet, Hamann and Schlüter [PRB 26, 4199 (1982)].
CH$_2$O...H$_2$O complex:

CH$_2$O: $\pi^*$ shape resonance at around 1 eV ($B_1$).
Rescigno et al. PRL 63, 248 (1989); Kaur and Baluja, JPB 38, 3917 (2005).

A, B, C, and D: 1W proton donor.
K. Coutinho and S. Canuto,
CH$_2$O...H$_2$O complex:

Simulation: the lowest unoccupied orbitals ($\pi^*$) are mostly localized on the solute.
HCOOH...H₂O complex:

HCOOH: π* shape resonance at around 1.9 eV (A´´).
HCOOH...(H₂O)ₙ complex (n=1,2):

Electron collisions with the HCOOH⋯(H₂O)ₙ complexes (n = 1, 2) in liquid phase: The influence of microsolvation on the π* resonance of formic acid

T. C. Freitas,¹,² K. Coutinho,³ M. T. do N. Varella,² M. A. P. Lima,⁴ S. Canuto,³ and M. H. F. Bettega²,³

A to F: 1W proton donor.
A to C: trans; D to F: cis
HCOOH...$(\text{H}_2\text{O})_n$ complex ($n=1,2$):

G to J: 1W proton acceptor.
G and H: trans; I and J: cis
HCOOH...H$_2$O complex:

K to P: 2W proton donor/acceptor.
A to C: *trans*; D to F: *cis*
HCOOH...H₂O complex:

Simulation: the lowest unoccupied orbitals ($\pi^*$) are mostly localized on the solute.
**TABLE IV.** Dipole moment, $\mu$ (in D), vertical attachment energy, VAE (in units of eV), dipole moment of the formic acid in aqueous solution, $\mu$\textsubscript{aq}(HCOOH), induce dipole moment due to the aqueous solution, $\Delta\mu$, the net charge sign, $q\textsubscript{net}$, and the energy of the resonance peak using the SEP approximation, $E_r$. In brackets the experimental values are presented for the dipole moment\textsuperscript{46} and the energy of the resonance.\textsuperscript{14–24}

<table>
<thead>
<tr>
<th></th>
<th>$\mu$</th>
<th>VAE</th>
<th>$\mu$\textsubscript{aq}(HCOOH)</th>
<th>$\Delta\mu$</th>
<th>$q\textsubscript{net}$</th>
<th>$E_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>1.81 [1.85]</td>
<td>5.26</td>
<td></td>
<td></td>
<td></td>
<td>[10.0] ($\sigma^*$)</td>
</tr>
<tr>
<td>trans-HCOOH</td>
<td>1.42 [1.41]</td>
<td>3.59</td>
<td></td>
<td></td>
<td>1.9 [1.9] ($\pi^*$)</td>
<td></td>
</tr>
<tr>
<td>cis-HCOOH</td>
<td>3.89</td>
<td>3.59</td>
<td></td>
<td></td>
<td>1.3 ($\pi^*$)</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>1.85</td>
<td>3.18</td>
<td>1.94</td>
<td>0.53 (36%)</td>
<td>+</td>
<td>1.2 ($\pi^*$)</td>
</tr>
<tr>
<td>B</td>
<td>1.49</td>
<td>3.29</td>
<td>1.93</td>
<td>0.52 (36%)</td>
<td>+</td>
<td>1.2 ($\pi^*$)</td>
</tr>
<tr>
<td>C</td>
<td>1.73</td>
<td>3.32</td>
<td>1.94</td>
<td>0.53 (36%)</td>
<td>+</td>
<td>1.2 ($\pi^*$)</td>
</tr>
<tr>
<td>D</td>
<td>6.29</td>
<td>2.75</td>
<td>5.45</td>
<td>1.56 (40%)</td>
<td>+</td>
<td>1.2 ($\pi^*$)</td>
</tr>
<tr>
<td>E</td>
<td>5.92</td>
<td>3.08</td>
<td>5.28</td>
<td>1.39 (36%)</td>
<td>+</td>
<td>1.1 ($\pi^*$)</td>
</tr>
<tr>
<td>F</td>
<td>6.06</td>
<td>2.99</td>
<td>5.25</td>
<td>1.36 (35%)</td>
<td>+</td>
<td>1.3 ($\pi^*$)</td>
</tr>
<tr>
<td>G</td>
<td>3.05</td>
<td>4.19</td>
<td>1.95</td>
<td>0.53 (37%)</td>
<td>–</td>
<td>2.1 ($\pi^*$)</td>
</tr>
<tr>
<td>H</td>
<td>2.65</td>
<td>4.18</td>
<td>1.96</td>
<td>0.54 (38%)</td>
<td>–</td>
<td>2.2 ($\pi^*$)</td>
</tr>
<tr>
<td>I</td>
<td>6.52</td>
<td>3.80</td>
<td>5.33</td>
<td>1.44 (37%)</td>
<td>–</td>
<td>3.5 ($\pi^*$)</td>
</tr>
<tr>
<td>J</td>
<td>6.78</td>
<td>3.85</td>
<td>5.33</td>
<td>1.44 (37%)</td>
<td>–</td>
<td>3.7 ($\pi^*$)</td>
</tr>
<tr>
<td>K</td>
<td>4.43</td>
<td>2.74</td>
<td>2.07</td>
<td>0.65 (46%)</td>
<td>+</td>
<td>1.7 ($\pi^*$)</td>
</tr>
<tr>
<td>L</td>
<td>3.08</td>
<td>2.37</td>
<td>2.00</td>
<td>0.58 (41%)</td>
<td>+</td>
<td>1.6 ($\pi^*$)</td>
</tr>
<tr>
<td>M</td>
<td>4.40</td>
<td>2.09</td>
<td>1.95</td>
<td>0.53 (37%)</td>
<td>+</td>
<td>1.5 ($\pi^*$)</td>
</tr>
<tr>
<td>N</td>
<td>8.00</td>
<td>3.70</td>
<td>5.37</td>
<td>1.48 (38%)</td>
<td>–</td>
<td>2.2 ($\pi^*$)</td>
</tr>
<tr>
<td>O</td>
<td>9.25</td>
<td>3.84</td>
<td>5.31</td>
<td>1.41 (36%)</td>
<td>–</td>
<td>2.3 ($\pi^*$)</td>
</tr>
<tr>
<td>P</td>
<td>9.35</td>
<td>3.61</td>
<td>5.41</td>
<td>1.52 (39%)</td>
<td>–</td>
<td>2.1 ($\pi^*$)</td>
</tr>
</tbody>
</table>
**C₆H₅OH...H₂Oₙ complex (n=1,2):**

**Communication:** Transient anion states of phenol...H₂Oₙ (n = 1, 2) complexes: Search for microsolvation signatures

Eliane M. de Oliveira,¹ Thiago C. Freitas,² Kaline Coutinho,³ Márcio T. do N. Varella,³ Sylvio Canuto,³ Marco A. P. Lima,¹ and Márcio H. F. Bettega⁴,ᵃ

Geometry optimization
\[ C_6H_5OH\ldots(H_2O)_n \text{ complex (} n=1,2) : \]

**TABLE 1.** \( \pi^* \) resonance positions \( E_{\text{res}} \) and widths \( \Gamma \), in units of eV, for phenol and the phenol...\( (H_2O)_n \) complexes, with \( n = 1, 2 \), shown in Fig. 1. The resonance parameters were obtained from fits to the SE-level eigenphase sums.\(^{18}\)

<table>
<thead>
<tr>
<th>System</th>
<th>( E_{\text{res}}(\pi_1^*) )</th>
<th>( \Gamma(\pi_1^*) )</th>
<th>( E_{\text{res}}(\pi_2^*) )</th>
<th>( \Gamma(\pi_2^*) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>2.81</td>
<td>0.47</td>
<td>3.43</td>
<td>0.60</td>
</tr>
<tr>
<td>Complex A</td>
<td>3.20</td>
<td>0.51</td>
<td>3.83</td>
<td>0.64</td>
</tr>
<tr>
<td>Complex B</td>
<td>2.74</td>
<td>0.41</td>
<td>3.30</td>
<td>0.60</td>
</tr>
<tr>
<td>Complex C</td>
<td>2.81</td>
<td>0.38</td>
<td>3.35</td>
<td>0.58</td>
</tr>
<tr>
<td>Complex D</td>
<td>2.82</td>
<td>0.47</td>
<td>3.41</td>
<td>0.64</td>
</tr>
</tbody>
</table>
$\text{C}_6\text{H}_5\text{OH}...(\text{H}_2\text{O})_n$ complex $(n=1,2)$:
### CH$_2$O...H$_2$O complex:

Simulation

Lowest unoccupied orbitals ($\pi^*$).

#### Virtual orbital energies (eV)

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>Opt.</th>
<th>CH$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.38</td>
<td>1.99</td>
<td>2.21</td>
<td>2.14</td>
<td>2.54</td>
<td>2.85</td>
</tr>
</tbody>
</table>

Geometry optimization

Electron-induced hydrogen loss in uracil in a water cluster environment

M. Smyth,1 J. Kohanoff,1 and I. I. Fabrikant2,a)

FIG. 2. Illustration of molecular structure of a fully optimized cluster, consisting of one thymine surrounded by five water molecules. The grey balls show hydrogen bonds within the structure.

TABLE 1. Vertical attachment energies for gas phase thymine, three thymine-single water structures (A, B, and C), and the fully solvated cluster are also given (T+5H2O). Energies are calculated using PBE0 and 6-311++G** basis set, and are given in eV.

<table>
<thead>
<tr>
<th>U/T</th>
<th>1A</th>
<th>1B</th>
<th>1C</th>
<th>5H2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.435</td>
<td>0.299</td>
<td>0.163</td>
<td>0.218</td>
<td>0.109</td>
</tr>
</tbody>
</table>

FIG. 3. Optimized structure of each individual water molecule attached to a thymine nucleobase, in configurations A, B, and C, from left to right.

FIG. 6. Dissociative attachment cross section for isolated U/T (black solid curve) and for U/T embedded in the (H2O)5 cluster calculated for three values of the VAE shift ΔE: dashed blue, ΔE = 0.04 eV; dotted red, ΔE = 0; dashed-dotted green, ΔE = −0.04 eV.
Conclusions:

- The presence of water stabilizes (donor)/destabilizes (acceptor) the shape resonance of with respect to the corresponding values in the gas phase (net charge in the solute).

- The DCSs of a gas of the complexes and of a gas of the independent molecules differ at around 60° suggesting a solvation signature.

- Geometry optimization: stabilizes (donor)/destabilizes (acceptor) the resonance.
Dr. Carlos de Carvalho for computational support at DFis-UFPR and at LCPAD-UFPR.