Collisions of Low-Energy Electrons with Formamide

Márcio H. F. Bettega

Departamento de Física
Universidade Federal do Paraná

bettega@fisica.ufpr.br

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Outline

Motivation.
General,
Formamide ($\text{HCONH}_2$) and formamide dimer ($\text{HCONH}_2 \ldots \text{HCONH}_2$).

Schwinger multichannel method.

Results.

Summary.

Acknowledgments.
Motivation

- Electron collisions with molecules of biological relevance (biomolecules).

SSBs and DSBs.

- DNA damage - single- and double-strand breaking in DNA is caused by secondary low-energy (up to 20 eV) electrons generated by the ionizing radiation (X-rays, \( \beta \)-rays, \( \gamma \)-rays).
- Radiation-induced DNA damage can lead to the cell death or can initiate the development of cancer cells.
- The understanding of the fundamental mechanism of DNA damage can help in cancer treatment.
DNA molecule

- Transient negative ions (TNI) - shape, core-excited, or Feshbach resonances: dissociative electron attachment (DEA) → electron-molecule collision problem.
- Double-bonds and hydrogen bonds.
- DNA subunits, organic molecules, model (small) systems - biomolecules.
Motivation

Types of resonances

- **Shape resonance** (elastic scattering, low-energy - one particle): the continuum electron is trapped by an unoccupied molecular orbital (angular momentum barrier) - $\pi^*$ (indirect-symmetry breaking) and $\sigma^*$ (direct).
  

- **Core-excited and Feshbach resonances** (electronic excitation - two particles-one hole): the molecule is excited and the continuum electron is trapped by an unoccupied molecular orbital. 
  
  core-excited (shape) resonance: the energy of the TNI is above energy of the parent (neutral) state
  
  Feshbach resonance: the energy of the TNI is below the energy of the parent state.

\[
\begin{align*}
\text{shape resonance} & \quad \text{core–excited (shape) and Feshbach resonances} \\
\hline
E(N) & \quad E(N+1) \\
\hline
E(N) (ground state) & \quad E(N) (excited – parent – state) \\
\hline & \quad E(N+1) \\
\hline
E(N) (ground state) & \quad E(N) (ground state)
\end{align*}
\]
Structures of formamide and formamide dimer.

- Formamide: $\pi^*$ shape resonance at 2.05 eV (Seydou et al. – experiment) and at 3.77 eV (Goumans et al. – theory) (recall Josue’s talk).
- Formamide dimer: we expect 2 $\pi^*$ shape resonances.
Schwinger multichannel method

K. Takatsuka and V. McKoy, PRA 24, 2473 (1981),

- Variational approach for the scattering amplitude;
- Formulated for applications to low-energy electron-molecule collisions;
- Capable of addressing important aspects of these collisions as:
  molecular targets of general geometry;
  exchange interactions (*ab initio*);
  effects arising from the polarization of the target by the incident electron (*ab 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 [PRL 26, 4199 (1982)].
Computational Details.

Formamide.
- Group: $C_s$
- Basis set: C, N, and O: 5s5p3d; H: 4s/3s1p
- Geometry: experimental (http://cccbdb.nist.gov)
- Orbitals: improved virtual orbitals ($< 27.212$ eV)
- Singlets and triplets;
- CSFs: $A'$: 6402; $A''$: 5376.
- Dipole moment: 4.28 D (calc.) – 3.72 D (expt.) (we neglected the long range dipole interaction - no effect on the resonance’s location, only in the background scattering).

Formamide dimer.
- Group: $C_s(C_{2h})$
- Basis set: C, N, and O: 5s4p2d; H: 4s/3s1p
- Geometry: optimized (GAMESS) - MP2 aug-cc-pVDZ
- Orbitals: improved virtual orbitals ($< 20.41$ eV)
- Singlets and triplets;
- CSFs: $A''(B_g + A_u)$: 8546;
- $B_g$ and $A_u$: partial wave analysis.
Previous studies on electron interactions with formamide.

- **Seydou et al.**: electron attachment to isolated formamide and to formamide clusters by measuring the derivative of the electronic current. In the case of the isolated formamide they found a resonance at 2.05 eV.

- **Goumans et al.**: DEA to formamide (possible mechanisms of DEA upon stretching the C–H, N–H and C–N bonds). $\pi^*$ ($A''$ symmetry) located at 3.77 eV, and a $\sigma^*$ ($A'$ symmetry) located at 14.9 eV.

- **Dissociation**: HCO + NH$_2$ (breakage of the C–N bond). The $\pi^*$ resonance initiate the dissociation mechanism (as in formic acid).

- **Mechanism**: coupling between $\pi^*$ and $\sigma^*$ anions (symmetry breaking, as in formic acid).
Indirect mechanism for formamide.

The electron is captured by a $\pi^*$ resonance on the C=O double bond. The C–N bond is stretched, and at a given value of $R$ the symmetry is broken (pyramidalization of the $\text{NH}_2$). The $\pi^*$ anion crosses a $\sigma^*$ anion, leading to the C–N bond breakage.
Cross sections for formamide.

Cross sections.

- \(\pi^*\) shape resonance in the \(A''\) symmetry at 4.5 eV (SE) and at 2.5 eV (SEP). \(\sigma^*\) resonance at \(\sim 15\) eV (SE).
**Results**

LUMO, LUMO+1, LUMO+2

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**Minimal basis set calculations.**

- Minimal basis set (6-31G(d)) calculations at the MP2 (geometry optimization) and at the Hartree-Fock (energy) levels with GAMESS.

- We computed the Fock operator’s eigenvalues ($\varepsilon$) to the LUMO ($\pi^*_{a''}$), LUMO+1 ($\sigma^*_{a'}$), LUMO+2 ($\sigma^*_{a'}$), and LUMO+5 ($\sigma^*_{a'}$) orbitals.

- Koopmans’ Theorem: electron affinity = $E_N - E_{N+1} = -\varepsilon$.

- Vertical electron attachment energy (VAE) = - vertical electron affinity.

- Empirical scaling formula: $\text{VAE} = a + b \varepsilon_{\text{computed}}$


- After the scaling: LUMO = 2.10 eV, LUMO+5 = 8.0 eV.
Cross sections for formamide dimer.

Cross sections (preliminary results).

- $\pi^*$ shape resonance in the $B_g$ symmetry at 3.7 eV (SE) and at 2.0 eV (SEP) and in the $A_u$ symmetry at 4.2 eV (SE) and at 2.6 eV (SEP).
Results

LUMO and LUMO+1

Minimal basis set calculations.

- Minimal basis set (6-31G(d)) calculations at the MP2 (geometry optimization) and at the Hartree-Fock (energy) levels with GAMESS.

- We computed the Fock operator’s eigenvalues ($\varepsilon$) to the LUMO ($\pi^*$) and LUMO+1 ($\pi^*$) orbitals.

- After scaling: LUMO ($a_u$) = 1.99 eV, LUMO+1 ($b_g$) = 2.12 eV.
Summary

- $\pi^*$ resonance at 2.5 eV, in agreement with the experimental value of 2.05 eV and with the computed LUMO of 2.10 eV (after scaling). This resonance is suggested to initiate the dissociation mechanism of formamide along the C–N bond.

- The LUMO+1, LUMO+2, and LUMO+5 plots indicate the possibility of breakage of the N–H, C–H, and C–N bonds.

- Formamide dimer: two $\pi^*$ shape resonances at 2.0 eV ($B_g$) and at 2.6 eV ($A_u$). LUMO ($a_u$) = 1.99 eV, LUMO+1 ($b_g$) = 2.12 eV (after scaling). Polarization?
  
Poster 141 by Freitas, Varella, Sanchez, and Bettega – formic acid dimer.

- Future work: look at the $\pi^*$ and $\sigma^*$ resonances upon stretching the N–H, C–H, and C–N bonds.
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viiwfme@fisica.ufpr.br
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