

SCIENTIFIC REPORT

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Title: Low energy electron attachment to molecules in the gas phase

Purpose of the visit

The purpose of the visit in the group of Prof. E. Illenberger at the Freie University in Berlin was to investigate interactions of the low energy electrons with the biologically relevant molecules in the gas phase.

Description of the work carried out

The experiments were performed with a crossed electron-molecular beam apparatus and mass spectrometric detection of the fragment anions. The apparatus consists of an electron source, an oven, a quadrupole mass analyzer and a detection system. An electron beam of the defined energy generated from a trochoidal electron monochromator crossed perpendicularly with a molecular beam. The generated negative ions are extracted by a weak electric field and accelerated by a series of parallel electrodes onto the entrance hole of the quadrupole mass analyzer and detected by a single pulse counting technique as a function of incident electron energy. The energy scale was calibrated using the well known resonance in SF₆ near 0 eV generating metastable SF₆⁻.

Description of the main results obtained

I was involved in the gas phase studies of the dissociative electron attachment to amides namely acetamide (CH₃CONH₂), glycolamide (CH₂OHCONH₂) and trifluoroacetamide (CF₃CONH₂) in the energy range 0-12 eV. Such small amides having linkages which in biochemical context are called peptide linkages (-CO-NH-) might be assumed to mimic interactions for the localized electron in the polypeptide media.

Low energy electron attachment to amide derivatives is a very effective and complex process involving appreciable rearrangement in the transitory anion (TNI) resulting in multiple bond cleavages and the formation of the new molecules.

Each of the three compounds acetamide ($\text{CH}_3\text{C}(\text{O})\text{NH}_2$), glycolamide ($\text{CH}_2\text{OHC}(\text{O})\text{NH}_2$) and trifluoroacetamide (CF_3CONH_2) appears within a resonant structure associated with the neutral hydrogen abstraction generating $(\text{M}-\text{H})^-$. In addition to that all of the molecules show a resonance located near 2 eV and leading to the formation of CN^- (Fig.1). CN^- formation represents an excision of the unit from the amide group and requires substantial rearrangement associated with multiple bond cleavages. From glycolamide CN^- ion also appears from an additional resonance at 6,2 eV.

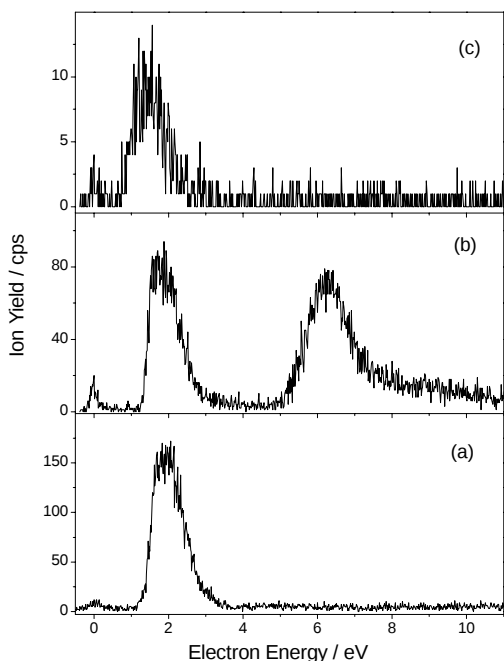


Fig. 1 Anion yield of CN^- following DEA to acetamide (a), glycolamide (b) and trifluoroacetamide (c).

In acetamide and glycolamide the formation of OCN^- is an operative process (Fig. 2). In trifluoroacetamide

the situation changes as now OCN^- appears within the weak signals at around 0 and 2 eV (Fig. 2) and the formation of the complementary anion $(\text{M}-\text{OCN})^-$ is much more operative (Fig. 3).

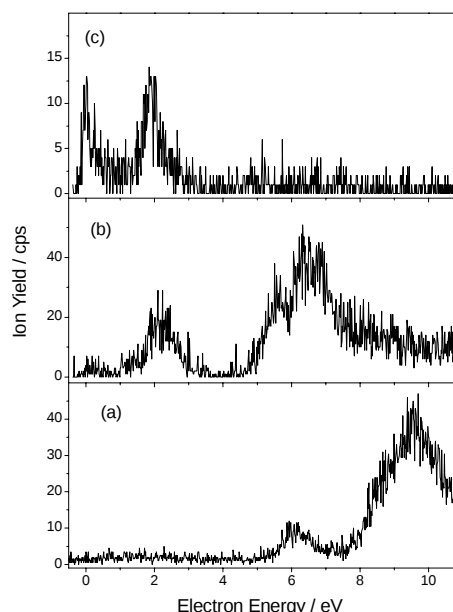


Fig. 2 Anion yield of OCN^- following DEA to acetamide (a), glycolamide (b) and trifluoroacetamide (c).

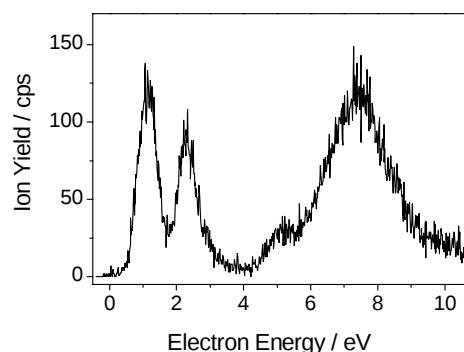


Fig. 3 Anion yield of $(\text{M}-\text{OCN})^-$ following DEA to trifluoroacetamide.

From glycolamide and trifluoroacetamide a reaction pathway resulting in the loss of water is operative (Fig. 4). The loss of a water unit in glycolamide is apparently possible via rearrangement at one carbon site. The most likely position for the loss of H₂O from CH₂OHC(O)NH₂ is the glycol site which would require cleavage of two bonds (C-OH and C-H) while loss of H₂O from CF₃CONH₂ is only possible from the amide group and require cleavage of three bonds, among them one is a double bond.

Besides, from trifluoroacetamide such fragment anions as (M-CF₂)⁻, (M-HF)⁻, CF₂⁻ and F⁻ were observed. These fragments were formed via a resonance with an intensity maximum in the low energy region 1-2 eV. In addition to that anions as (M-CF₂)⁻ and F⁻ were observed within signal at around 7,5 eV.

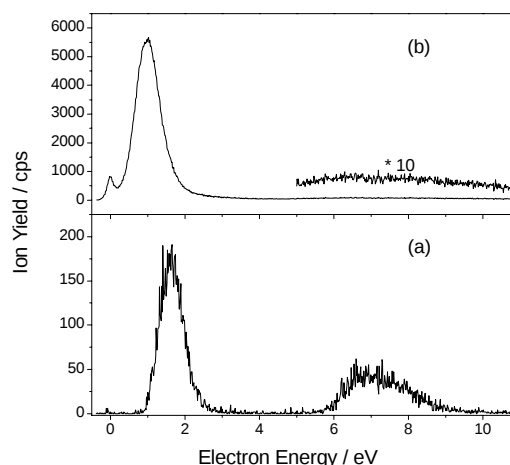


Fig. 4 Anion yield of (M-H₂O)⁻ following DEA to glycolamide (a) and trifluoroacetamide (b).

Additionally, the studies of electron attachment to thymine were performed. The aim of this project was to determine a cross section for DEA reaction. The cross section was obtained by measuring the negative ion production ((T-H)⁻) and comparison with a known cross section for Cl⁻/CHCl₃ [1]. An estimated cross section at 1 eV for ((T-H)⁻) is equal to $3,0 \cdot 10^{-17} \text{ cm}^2$.

[1] J. Kopyra, I. Szamrej, K. Graupner, L. M. Graham, T. A. Field, P. Sulzer, S. Denifl, T. D. Märk, P. Scheier, I. I. Fabrikant, M. Braun, M.-W. Ruf, and H. Hotop, Low-energy electron attachment to chloroform (CHCl₃) molecules: a joint experimental and theoretical study, *Int. J. Mass Spectrom.*, 2008 (accepted).

Future collaboration with host institution

Projected publications resulting from the grant

The publications of presented results are under preparation.