

# Low-energy resonant reactions of free electrons and glycine oligomers

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## Overview

### Purpose:

To study low-energy resonance reactions of the simplest peptides with free electrons at precisely determined interaction energies

### Method:

Resonant electron capture mass spectrometry performed on an orthogonal acceleration reflectron time-of-flight mass spectrometer with a trochoidal electron monochromator and a gas chromatograph

### Results:

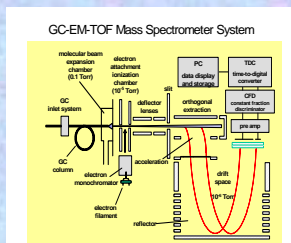
Resonant reactions of the simplest peptides with free electrons were conducted at precisely determined interaction energies for the first time

## Introduction

Energy-controlled low-energy reactions of free electrons with peptides must be studied in order to understand charge-transfer processes that occur in living cells. Different types of mass spectrometric ionization techniques applied with and without collision induced dissociation in general showed  $[M-H]^-$  and  $\gamma$ -type negative ions (NIs) as the major fragmentation processes occurring in NIs of underivatized peptides. This is in contrast to electron capture dissociation (ECD) of multiply-charged peptide positive ions, where  $z$ - and  $c$ -type ions have been observed as the most abundant ion peaks in the mass spectra. To gain more insight into the discrepancy posed, elementary resonant reactions of low-energy free electrons and the simplest peptides of the glycine (Gly) base have been studied under well controlled conditions.

## Methods

A custom-made gas chromatograph/resonant electron capture-TOF mass spectrometer incorporating a trochoidal electron monochromator (70-200 meV, FWHM, energy from 0 to 12 eV) was used for the study of energy-controlled resonant electron-peptide (Sigma/Aldrich) reactions.  $CCl_4$  and low pressure ( $< 10^{-7}$  Torr)  $SF_6$  gas were used for calibration of energy and mass scales. The purity of the samples was checked on the base of a Thermo-Finnegan-LCQ-classic mass spectrometer. Accurate mass measurements made using a two-sector JEOL JMS-600H mass spectrometer. PFK was used to calibrate the mass scale. Electronic and geometric structures of all molecular and fragment negative ions from Gly oligomers were interpreted using semi-empirical (PM3 level) and density-functional (B3LYP/6-31++G\*\* basis set) quantum chemical calculations.



## Results

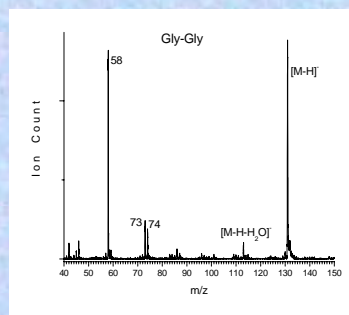


Fig.1. Negative ion mass spectrum of glycine-dimer integrated over resonance energy range from ca. zero to 12 eV.

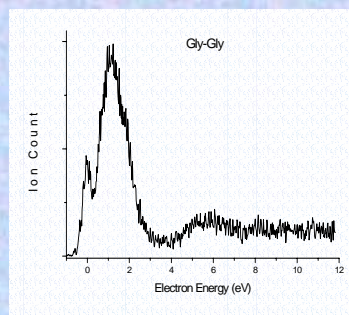


Fig.2. Total dissociative electron capture cross-section of glycine-dimer for the negative ions displayed in Fig. 1.

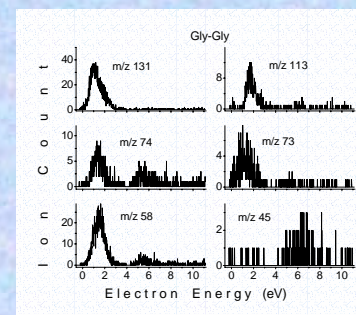


Fig.3. Effective yield curves of selected negative ions ( $m/z$  are shown) from dimer of glycine as functions of electron energies.

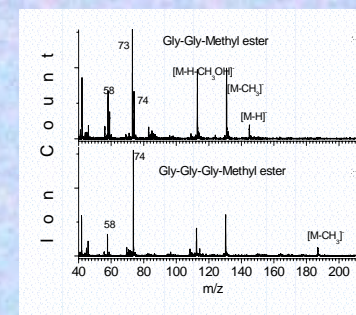


Fig.4. Negative ion mass spectra of methylated glycine-dimer (A) and methylated glycine-trimer integrated over resonance energy range from ca. zero to 12 eV.

## Conclusions

- Relative electron attachment cross sections as functions of interaction energy for the simplest peptides Gly-Gly, Gly-Gly-Gly and their methyl esters have been measured for the first time
- It was established that the loss of a hydrogen atom occurs in the energy range 1-1.5 eV and was found to be a very efficient dissociation process in reactions of underivatized peptides. The relative cross-section of the process has been found however to decrease gradually with increasing size of the oligomers from the Gly monomer to the dimer and trimer
- According to quantum chemical calculations, this behavior is associated with changes in the character of the electron capturing center. In the monomer, the electron capturing center is primarily localized at the carboxylate group, and in the dimer and trimer it is shared with the other carbonyl groups in the peptide backbone
- Other fragmentation channels have been found to associate with generation of  $b$ ,  $\gamma$  and  $c$  and  $z$  negative ions occurring at low (1-2 eV) and high energy range ( $> 4$  eV)

## Acknowledgements

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