Electron interaction with deoxyribose analogue molecules in gaseous phase

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Abstract. We present recent results on elastic and inelastic low/medium energy electron interaction with tetrahydrofuran, C₄H₈O; tetrahydrofurfuryl alcohol, C₅H₁₀O₂ and 3-hydroxytetrahydrofuran, C₄H₈O₂ molecules in gaseous phase. A comparative study of both absolute differential cross sections for elastic electron scattering and electron energy loss spectra, in a wide incident electron energy range from 50 to 300 eV, has been given. The measurements of the cross sections were performed both as a function of scattering angle and incident electron energy and normalized to the absolute scale according to relative flow measurements and reliable calculations. The experimental elastic DCSs are compared with the most recent theoretical results. Both for elastic and inelastic scattering a special attention has been paid to investigate potential differences in electron scattering processes upon substitution of one of the H-atom in tetrahydrofuran by the OH group (in 3-hydroxytetrahydrofuran) or CH₂OH group (in tetrahydrofurfuryl alcohol).

1. Introduction
The investigation of electron interaction with the furanose-structured molecules: tetrahydrofuran (THF), C₄H₈O; 3-hydroxytetrahydrofuran (3HTHF), C₄H₈O₂ and tetrahydrofurfuryl alcohol (THFA), C₅H₁₀O₂ has been dominantly motivated in recent years by the research of radiation damage in biomolecular systems. Since a large number of secondary low-energy electrons are formed on the track of primary high-energy ionizing particles, they carry most of the energy deposited in the tissue and play a particularly important role in the final radiation damage, ascribed to the primary ionizing particle. Recently, it has been clearly established that low-energy electrons (E≤20 eV) induce damage of single- and double-strand breaks in supercoiled DNA with high efficiency [1]. This result prompted extensive investigations of low(medium)-energy electron interaction with the basic DNA components, namely, the purine and pyrimidine bases, the phosphate group, and the deoxyribose sugar including its simpler analogs of the furanose-structured molecules [2]. Here, the cross-beam experiments with the molecular targets in gaseous phase provide an opportunity to study a well defined, isolated molecular system, under well defined conditions and using already established and very efficient experimental techniques and procedures. Although the obtained results cannot be applied in a straightforward manner to real complex biological systems, they are very important as a starting point in understanding and theoretical description of electron driven processes at the molecular level and modelling the energy deposition in a living tissue.

In order to investigate an electron interaction with the deoxyribose sugar, which forms the backbone of the DNA molecule, one can perform experiments either with the deoxyribose itself or
with some model molecules like THF, THFA and 3HTHF (see figure 1). The latter approach appears to have several advantages: simpler experimental setup (because of using liquids there is no need to have an oven to produce the target beam), avoiding mixing of different isomeric forms in the target beam of deoxyribose (a six member ring being the most abundant form), a possibility to study physical processes upon substitution of one of the groups in deoxyribose by the H atom etc. Furthermore, Tonzani and Greene [3] recently pointed out that the positions of OH groups of the deoxyribose within DNA are fundamentally modified by the neighbour phosphate and base that are attached to the main furan ring, so one should either consider performing the assay with a whole nucleotide or use THF which mimics only the ring structure.

THF, THFA and 3HTHF compounds have been the focus of intense studies in recent years, especially the simplest one – THF, for which a number of published papers (both experimental and theoretical) increased by more than an order of magnitude in the last three years. The experimental investigation of electron interaction with above mentioned molecules in the gaseous or solid phase covers: VUV absorption and electron energy loss spectra [4-6], vibrational excitation [7-9], electron-stimulated desorption yields of H from thin films [10, 11], electron-induced damage of solid THF films and fragmentation of gaseous THF [12-14], total cross sections for electron(positron) scattering [15-17], absolute DCSs for elastic electron scattering [18-21], dissociative electron attachment to gas-phase THF [22-24]. The recent theoretical results cover: calculations of integral and differential elastic and ionization cross-sections (independent atom model) [19, 25] and calculations of low-energy electron interaction with THF [3, 26-28]. It should be noted, however, that existing results for THFA and 3HTHF are still rather sparse. In the present paper, we give a comparative study of these three molecules (THF, 3HTHF, THFA), regarding electronic excitations and elastic electron scattering in the incident electron energy range from 50 eV to 300 eV and scattering angle range from 20° to 120°. To the best of our knowledge, we present the first electron energy loss spectra (EELS) for 3HTHF and THFA and the first elastic differential cross sections (DCSs) for 3HTHF.

2. Experiment
A detailed description of the present crossed-beam experimental setup has been given elsewhere [29, 30]. Briefly, it consists of an electron gun producing a well-collimated electron beam, stainless steel needle producing the molecular beam and a double cylindrical mirror energy analyzer. The latter is preceded by a four-element electrostatic lens and followed by a three-element lens and a single channel electron multiplier as a detector. The gun can be rotated around the needle in the angular range from about -40° to 120°. The base pressure was about 4x10^{-7} mbar (turbo-molecular pump). The working pressure was usually about 5x10^{-6} mbar. The uncertainty of the incident energy scale was determined by observing a threshold for He^+ ions yield to be less than ±0.4 eV. The best energy resolution was about 0.5 eV (limited by thermal spread of primary electrons). The resolution was lowered (1.1.5 eV) for measurements of DCSs as a function of incident electron energy in order to reduce energy dependence of the transmission function [29]. The angular resolution was determined to be better than ±2°. The experimental procedure was checked according to benchmark DCSs for elastic electron scattering by Ar and Kr, as a function of both scattering angle and incident electron energy, which were measured directly before and after electron-molecule measurements. The anhydrous THF, 3HTHF and THFA were purchased from Merck KGaA with declared purities better than 98% and were used after several cycles of freeze-thaw under vacuum. Because of a rather low vapor pressure of 3HTHF and THFA (more than two orders of magnitude lower at 20°C than that of THF), the sample container was heated during a measurement at the temperature of about 60-70°C.

The experimental setup has been recently upgraded to perform relative flow measurements, as well. This procedure allows an independent absolute calibration of the measured relative DCSs and has been applied so far in our laboratory only for 3HTHF molecule, the first preliminary results being presented in this paper. The relative flow method [31, 32] is based on measurements of intensities for elastic scattering by an etalon atom (Ar in the present case) and the gas under study, at given incident electron energy (E_0) and scattering angle (θ), under experimental conditions where ratios can be accurately
established, so allowing determination of the absolute DCS of the gas under study according to the known elastic DCS for the etalon gas. In the present case, the pressure of 3HTHF behind the tube forming the molecular beam was maintained below 0.2 mbar. The ratio of the pressures behind the tube for argon to that of 3HTHF was adjusted to be about 1.8 according to the molecular diameters. Here the value of the diameter for 3HTHF has been taken according to the reference for the linear isomer of this molecule – ethyl acetate [33]. The flow of the gases has been measured by closing the outlet to the gas chamber and recording the increase of the absolute pressure in the gas line behind the needle as a function of time.

3. Results and discussion

3.1. Electron energy loss spectra
The comparison of electron energy loss spectra for THF, 3HTHF and THFA at the incident electron energy of 100 eV and the scattering angle of 10° is given in figure 2. The spectra are presented in the energy loss range up to about 15 eV (except for the THF molecule which was recorded up to about 11 eV). In figure 2a, the positions of the bands obtained by VUV photoabsorption measurements by Bremner et al [5], which are described as excitations to Rydberg states, are marked, as well. Recent preliminary results for VUV absorption spectroscopy of other two molecules (3HTHF and THFA) [34] are also indicated in figures 2b and 2c. It is evident that the present EELS are in a very good agreement with the high energy resolution optical data. Also, the present EELS for THF molecule compares well with the previous measurements performed with a higher resolution [4,5]. Note that present electron-molecule collision measurements have been performed at high incident electron energy (100 eV) and small scattering angle (10°), which are the conditions that favor dipole allowed transitions and almost exclusively correspond to the optical data. The structure of the shown EELS is generally similar, showing similar positions of the electronic bands (note that EELS have not been corrected to the transmission function of the analyzer). The spectra of all three molecules show broad electronic excitation bands which are thought to involve the excitation of a non-bonding electron from the oxygen heteroatom to Rydberg states.

3.2. Elastic scattering
Absolute DCSs for elastic electron scattering from THF, 3HTHF and THFA at the incident energy of 100 eV and in the scattering angle range from 20° to 115° are presented in figure 3. The DCSs for all three molecules show a very similar relative behaviour at 100 eV, which is characterised by a small shoulder at about 50° and a broad minimum close to 90°. A very similar angular dependence of DCSs for all three molecules is also confirmed at other incident energies from 50 eV to 300 eV (not shown in this paper). Generally, at higher energies the minimum disappears, while DCSs become rather independent on the scattering angle above about 80° (see [18, 19] for THF and THFA, respectively). It should be also noted a very good agreement between experimental and calculated relative DCSs in this energy range (see [19]), the latter being obtained by applying independent atom method (IAM) [25] or upgraded version of it, known as screen corrected additivity rule (SCAR) [19].

The DCSs for THF, 3HTHF and THFA also appear to be very close on the absolute scale at 100 eV (see figure 3). Here it is interesting to note that an absolute calibration for each of the molecules has been obtained in a different way: DCS for THF has been calibrated according to both relative flow measurements at lower incident electron energies performed in Liège with N₂ as a referent gas and the measurements of the energy dependence of DCS performed in Belgrade [18]; DCS for 3HTHF has been calibrated according to relative flow measurements at 100 eV with Ar as a referent gas performed in Belgrade and, finally, DCS for THFA has been calibrated according to SCAR calculations [19] at the incident energy of 150 eV and the scattering angle of 50°. The absolute DCSs slightly increase going from THF to THFA, which is to be expected considering the size of the molecules. The theoretical absolute DCSs (SCAR rule [19]) are in a good agreement with the experiment (see figure 3), although somewhat shifted to lower values and with a bit higher difference between THF and
THFA (calculations for 3HTHF are in progress [35]). However, it should be noted that an overall uncertainty for the experimental absolute DCSs (considering both experimental procedure and referent DCSs) is estimated to be between 20% and 30%.

4. Conclusion
We have investigated elastic and inelastic scattering of electrons by the furanose-structured molecules: tetrahydrofuran (THF), 3-hydroxytettrahydrofuran (3HTHF) and α-tetrahydrofurlyl alcohol (THFA), which have been considered as model compounds to investigate electron interaction with the deoxyribose molecule and further with the DNA sugar backbone. The present paper is focused on absolute differential cross sections for elastic scattering and electron energy loss spectra in the range of electronic excitations. The low-resolution EELS show similar structure for all three molecules, with similar position of the broad electronic bands which can be generally ascribed to the excitation to Rydberg states. Also, the experimental EELS are in a very good agreement with the VUV photoabsorption data. The angular dependences of our experimentally obtained DCSs are confirmed by comparison with the calculations based on the independent atom method. The DCSs for all three molecules are very similar in shape at all covered incident electron energies. At the incident electron energy of 100 eV, the DCSs for all three molecules are very close on the absolute scale, which is, again, in a good agreement with the calculations. Finally, the experimental results suggest that both low-resolution EELS and elastic DCSs do not change significantly upon substitution of one of the H atom in the simplest THF by either OH group (in 3HTHF) or CH<sub>2</sub>OH group (in THFA) in the covered energy and angular range.

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Figure captions

**Figure1.** A short chain segment of a single strand of DNA and a schematic drawing of furanose-structured molecules: β-D-ribofuranose (ribose), 2-deoxy-D-ribose (deoxyribose), tetrahydrofuran, 3-hydroxytetrahydrofuran and α-tetrahydrofurfuryl alcohol.

**Figure2.** Electron energy loss spectra of tetrahydrofuran (a), 3-hydroxytetrahydrofuran (b) and α-tetrahydrofurfuryl alcohol (c) recorded at the incident electron energy of 100 eV and the scattering angle of 10°. The vertical bars represent position of the bands according to VUV absorption measurements: Ref. [5] for (a) and Ref. [34] for (b) and (c). The inset of figure (a) shows both threshold electron energy loss (dotted line) and VUV (full line) spectrum of THF published in Ref. [5].

**Figure3.** Absolute differential cross sections for elastic electron scattering from tetrahydrofuran (THF), 3-hydroxytetrahydrofuran (3HTHF) and α-tetrahydrofurfuryl alcohol (THFA). Experiment: , THF [18]; , 3HTHF; ▽, THFA [19]. Theory [19]: full line, THF; dashed line, THFA.
Figures

Figure 1

β-D-ribofuranose (ribose)

2-deoxy-D-ribose (deoxyribose)

tetrahydrofuran (C₄H₈O)

3-hydroxytetrahydrofuran (C₄H₈O₂)

α-tetrahydrofuranyl alcohol (C₅H₁₀O₂)

Short-chain segment of DNA
Figure 2

(a) THF

(b) 3HTHF

(c) THFA

Relative intensity

Electron energy loss (eV)
Figure 3

**Absolute elastic DCSs**

100 eV

**Experiment:**
- THF ($C_4H_8O$)
- 3THF ($C_4H_6O_2$)
- THFA ($C_5H_{10}O_2$)

**Theory:**
- THF ($C_4H_8O$)
- THFA ($C_5H_{10}O_2$)