

Absolute differential cross sections for elastic electron scattering from small biomolecules

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Abstract. The results of an experimental investigation of electrons colliding with a set of biomolecules that are assumed to be analogues of the building blocks of DNA (furan, 3-hydroxytetrahydrofuran and pyrimidine) and proteins (formamide, N-methylformamide) are presented. Absolute differential cross sections at medium incident electron energies 40 eV–300 eV are presented and compared for these different targets. The experimental results are also compared with available calculations, based on the corrected form of independent atom model and show good agreement over the energy range studied.

1. Introduction

The role of low energy secondary electrons in providing a route to damage of DNA and other biomolecules during irradiation of cellular systems has only recently been recognised [1] This has led to the need to understand how electrons interact with such large macromolecules however there are both experimental and theoretical limitations in undertaking such studies (for example DNA and most membrane compounds cannot be studied in the gas phase. Accordingly it is proposed to model DNA by considering it as an ensemble of smaller molecules which are themselves analogues of the constituent biomolecules (e.g. the nuclear bases) such as Tetrahydrofuran (THF) and tetrahydrofurfuryl alcohol (THFA). This approach has resulted in an extensive investigation of electron interaction with such ‘analogue’ molecules [2-21]. Although secondary electrons are rather low energy, Scifoni et al [22] has shown that in the tail of the secondary electron distribution many electrons have energies of circa 100 eV. Therefore in the present studies we have explored 50 to 300 eV electron interactions with several biomolecular analogues including; furan (C_4H_4O) [8], 3-hydroxytetrahydrofuran (3HTHF, $C_4H_8O_2$) [4], which are analogues to deoxyribose in DNA (Figure 1.) pyrimidine (Py, $C_4H_4N_2$) [5] which is an analogue of pyrimidine bases (Figure 1.) and formamide and N-methylformamide [6,7] the smallest molecules that contain peptide bond (Figure 1.).

Several of these analogue molecules have been explored previously. VUV absorption spectra and electron energy loss spectra of Py have been reported by [9], as have electron induced vibrational and electron excitations of a Py condensate on thin film [10]. Tetrahydrofuran (THF) and tetrahydrofurfuryl alcohol have been investigated extensively [11, 12], since at standard temperature and pressure they are in a liquid state but with sufficient vapour pressure to make measurements in ‘conventional’ electron scattering apparatus. For furan very recently Khakoo and coauthors have published differential cross sections for elastic electron scattering on furan, from 1-50 eV [13]. While



Smytkowski and coauthors have published absolute total cross sections from 0.6 -400eV and ionizing and integral cross sections up to 4keV [14]. Integral and differential cross sections for electron scattering from furan have also been calculated by Bettega and Lima [15] and energy loss spectra have been reported by Guliani and coauthors with high energy resolution [16]. Electron interactions with the 3HTHF molecule has been studied by Viscaino et al [17] and differential cross sections for low energy electrons have been published.

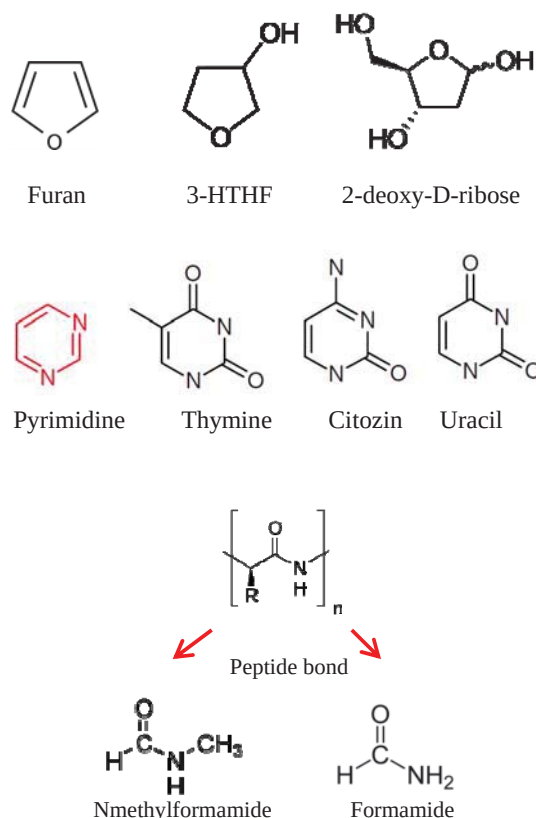


Figure 1. Schematic drawing of: furan, 3HTHF, deoxyribose, pyrimidine, pyrimidine bases, formamide, NMF and peptide bond.

Formamide (CH_3NO) and N-methylformamide (NMF, $\text{C}_2\text{H}_5\text{NO}$) (Figure 1) are interesting as they are the simplest models of the peptide bond $\text{NH}-\text{C}=\text{O}$. Bettega has published [18] theoretical cross sections for low energy electron scattering (1-12eV) from formamide. Recently photoionisation spectra of formamide and N-methylformamide have been studied because of their discovery in the interstellar medium [19] while the NMF molecule has received increased attention since it has been shown to have an important role in antitumor activity [20,21].

2. Experimental methodology

The present experimental results have been obtained using the cross beam electron spectrometer UGRA [23] within the Institute of Physics in Belgrade. The main components of the spectrometer are an electron gun, a double cylindrical mirror analyzer (DCMA) and a channeltron as detector. Primary electrons, produced by thermionic emission from a hairpin cathode, are extracted and focused by a system of cylindrical electrodes to cross, perpendicularly, a beam of target molecules exiting from a

stainless steel needle. The scattered electrons are retarded and focused with a 4-element lens into the DCMA and then focused using a 3-element lens into the channeltron. The electron gun can be rotated around the target gas beam from -30° to 110° . The whole experiment is conducted within a vacuum chamber pumped by a turbomolecular pump. A base pressure was around 4×10^{-7} mbar and the working pressure was around 2×10^{-6} mbar. The electron energy resolution was 0.5 eV determined by the thermal spread of the primary electrons. The angular resolution was about $\pm 2^\circ$ and was obtained by comparing our measured experimental results with previously published ones for noble gases [24] at the incident electron energies where DCS minima are most pronounced, for example for Ar at 40 eV and 50 eV.

2.1. Absolute differential cross sections

The measured relative differential cross sections are placed on an absolute scale using the relative flow method [25]. In this method the intensity of elastically scattered electrons from the target molecules and from a reference gas are compared, at fixed scattering angle and incident energy, under the same experimental conditions. Therefore, in the experiment the same beam profiles for both targets need to be achieved. Nickel and coauthors [25] have showed that the same beam profiles will be obtained if mean free paths for both gases are the same. According to the gas kinetic theory, the connection between the mean free path, the pressure and the squared gas kinetic diameter is:

$$\lambda = \frac{RT}{\pi D^2 N_A P \sqrt{2}} \quad (1)$$

Where λ is the mean free path, R the gas constant, T the gas temperature, D^2 the squared gas kinetic diameter, N_A is Avogadro's number and P the gas pressure. This means that in order to have the same mean free paths, one needs to adjust the pressures behind the needle according to the ratio of the squared gas kinetic diameters: $P_x : P_{ref} = D_{ref}^2 : D_x^2$. If these conditions are achieved absolute DCSs can be obtained by using the formula:

$$DCS_x(E, \theta) = DCS_{ref}(E, \theta) \frac{N_x F_{ref}}{N_{ref} F_x} \sqrt{\frac{M_{ref}}{M_x}} \quad (2)$$

$DCS_x(E_0, \theta)$ and $DCS_{ref}(E_0, \theta)$ are the absolute differential cross sections for elastic electron scattering on target molecules and reference gas, respectively. N_x and N_{ref} are measured intensities of scattered electrons, F_x and F_{ref} are the gas flow rates, M_x and M_{ref} are the molecular masses of the target and the reference gas, respectively.

Beside the intensities of the elastically scattered electrons, N_x and N_{ref} , a quantity that must be measured in the experiment is the flow rate of the target molecule and the reference gas (F_x and F_{ref}). In the experiment the target molecule (and the reference gas) is introduced into a constant volume and the pressure rise is measured using a baratron. According to gas kinetic theory, if the volume (V_0) and the temperature (T_0) are constant, the pressure rise in time can be connected to the flow, in a region of the linear dependence:

$$\frac{dP}{dt} = \frac{kT_0}{V_0} \frac{dn}{dt} = cF \quad (4)$$

Practically, a home-made LabView program has been used for measuring the pressure dependence as a function of time. It should be noted that biomolecules can adsorb on the walls of the gas line and this can influence the measured flow rates and thus, according to (2), the absolute DCSs. These effects have been investigated by Homem et al [26] and they conclude that adsorption was stronger when the method of the pressure increase was used, which is far from equilibrium, therefore the absorption and desorption cannot compensate each other. In order to reduce this effect in the present work, all

elements of the experimental setup were heated (sample, pipes, valves). The obtained experimental DCSs have been compared with the theoretical results obtained by the group in Madrid [27,28].

3. Results

Absolute differential cross sections for elastic electron scattering from formamide and N-methylformamide at 100 eV, 150 eV and 300 eV are compared in Figure 2. Absolute DCSs for formamide and NMF show very similar angular dependences – both DCS curves show broad minima at 90°. The cross sections for NMF are slightly higher than formamide, which is to be expected considering the relative size of the molecules. It is interesting to note that the measured difference between the absolute DCSs match very nicely with the absolute DCS for methane [7] suggesting that in this energy range the 'building blocks' approach can be used to estimate the elastic DCS of larger. Theoretical and experimental results for both molecules are in very good agreement both in shape and on the absolute scale. The theory is based on the Independent Atom Model (IAM) [27, 28], where the problem of collisions of electrons with molecules is reduced to the collision of electrons with individual atoms, assuming that scattering from each atom is independent. This technique gives good results for middle and high incident electron energies, but for low energy electrons the effects of screening need to be evaluated. Screening coefficients are introduced in the present Screen Corrected Additivity Rule (SCAR) method, resulting in a corrected cross section, at a given incident energy, calculated from the atomic cross sections. Relatively small differences between experimental results and SCAR theory for formamide and NMF can be seen at small scattering angles, which may be consequence of higher background contributions and less accurate volume corrections in the experiment and high contributions from interference terms at small scattering angles in the SCAR approximation [29, 30]. Therefore both, experiment and theory need improvement to adequately represent forward elastic scattering.

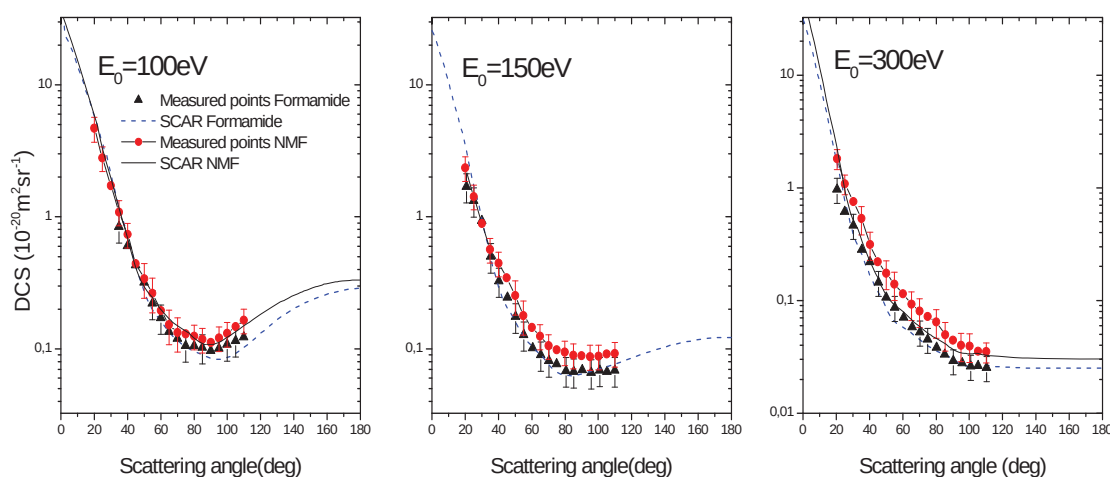


Figure 2. Comparison of absolute DCSs for formamide [6] and NMF [7]

Absolute experimental and theoretical DCSs for elastic electron scattering from Py, Furan and 3HTHF are presented in Figure 3. The experimental results are compared at 50 eV, 100 eV and 300 eV incident electron energies, for scattering angles between 8° and 110° for 3HTHF, between 20° and 110° for furan and from 30° to 110° for pyrimidine. The DCSs are very close on the absolute scale, showing similar redistribution of elastically scattered electrons from all targets. At 50 eV the absolute DCSs for 3HTHF are higher than for furan at small scattering angles, and this discrepancy decreases with increasing incident electron energy. Beside experimental imperfections at smaller scattering

angles, this effect can be also explained [27, 28] by very different dipole moments between furan and 3HTHF, 0.71D and 1.67D, respectively. A higher dipole moment induces more intensive inelastic rotational excitations, which contribute to the measured “elastic” absolute DCSs, due to the limited energy resolution. Formamide and NMF DCS curves at lower incident energies (50 eV and 100 eV) show a broad minima at 90°, since both are analogues of DNA this may suggest a similar angular distribution in electron scattering from DNA. Once again there is good agreement between experiment and theory both in shape and in absolute cross section, suggesting that the SCAR calculations can be used as a reliable estimation of the DCSs for elastically scattered electrons from these molecules over the present angular and energy ranges.

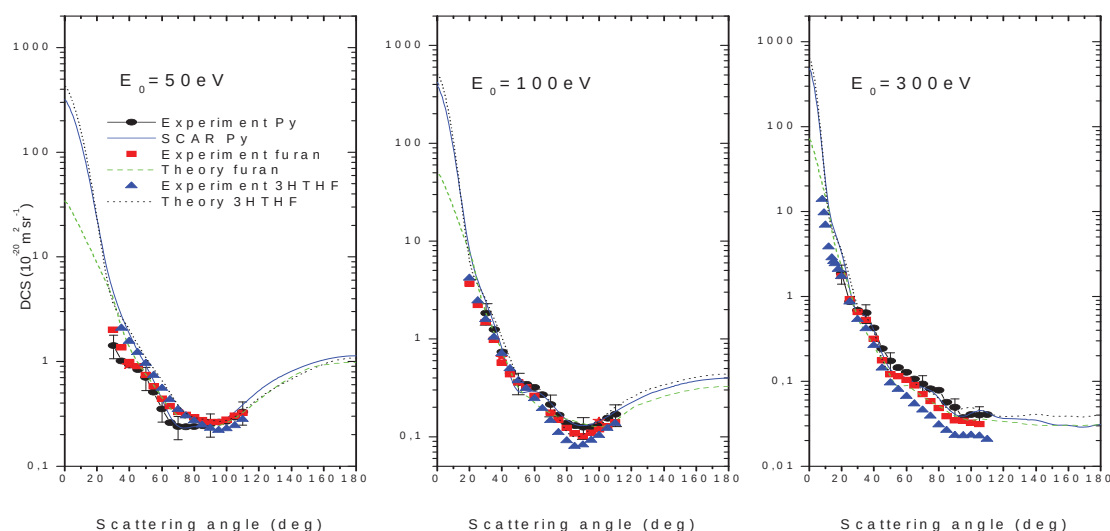


Figure 3. Comparison of absolute DCSs for pyrimidine [5], furan [8] and 3HTHF [4].

4. Conclusion

In summary, the experimental technique used to measure absolute DCSs for electron scattering from different molecules that are considered suitable analogues for some components of DNA or peptides has been reviewed. The recently published absolute DCSs for different molecules: formamide and NMF (analogues for a peptide bond) and furan, 3HTHF and Py (analogues of the building blocks of DNA) have been compared both on the absolute scale and in shape. Finally, the experimental results are compared with SCAR calculations and results are in very good agreement both in shape and magnitude.

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