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## Dynamical (e, 2e) studies using tetrahydrofuran as a DNA analogue

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**Abstract.** We present dynamical (e, 2e) measurements for the electron impact ionization of formic acid and tetrahydrofuran molecules performed under similar kinematics. The experiments have been performed in the coplanar asymmetric geometry for a range of momentum transfers, at an incident electron energy of 250 eV and with an ejected electron energy of 10eV. The experimental results are compared with theoretical calculations carried out using the molecular 3-body distorted wave (M3DW) model.

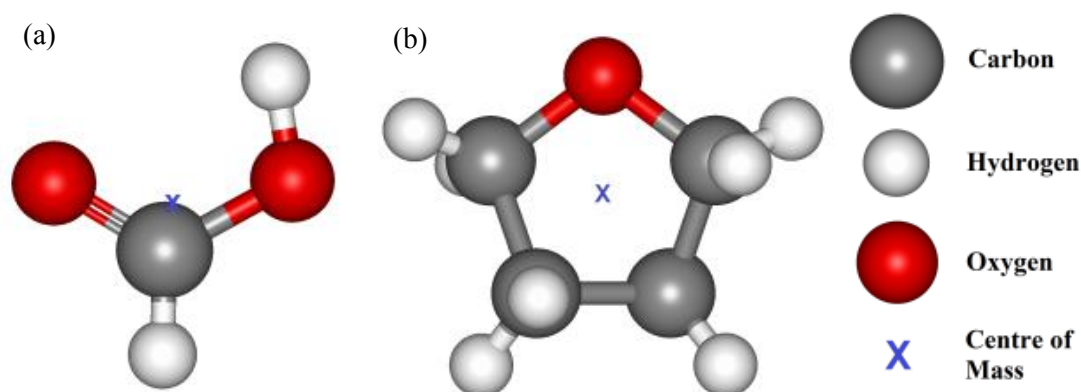
### 1. Introduction

While numerous dynamical (e, 2e) studies exist for atomic targets (see Lahmam-Bennani [1] and Coplan *et al.* [2]) and an impressive number of electron momentum spectroscopy (EMS) measurements exist for molecular systems (see McCarthy and Weigold [3] and Takahashi [4]), (e, 2e) studies dedicated to the dynamics of molecular systems are quite limited. Triply differential cross sections (TDCSs) for molecular targets can be used to elucidate the molecular effects responsible for structures in the cross section. Such structures in the TDCS may be influenced by the non-spherical shape of the molecular target as well as contributions from rotationally and vibrationally excited ground states left after a direct single ionizing collision [5].

Experimental difficulties associated with TDCS measurements for molecular targets arise from the inability of the experiment to resolve different molecular electronic states. Molecular orbitals can, depending on the molecular configuration of the target, be quite closely spaced and contributions from the vibrational and rotational states only add to the challenge. Many of the molecules for which experimental dynamical (e, 2e) studies have been undertaken are summarized in ref. [6]. In addition,

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**Figure 1.** (Colour online) Molecular structures of (a) formic acid and (b) tetrahydrofuran with the centre of mass of each molecule denoted with a (X).

theory has had to deal with modelling polyatomic target species, with many of the approximations that work for the atomic case breaking down due to the polycentric nature of these molecules. Madison and Al-Hagan [7] have reviewed the recent theoretical work that has been performed for some of these molecules.

Ionizing radiation is used widely in medicine as a probe in radio-diagnostic examinations, as a treatment method for many forms of cancer and in industrial production as a means of quantifying internal defects. Traditionally, damage to biological systems by incident high energy radiation was thought to be caused by high-energy ballistic impacts of the incident particle. As the radiation travels through the medium, its energy is redistributed via elastic and inelastic collisions, and produces an abundance of secondary species. In recent years, theoretical and experimental studies have indicated that secondary species generated by the primary ionizing particle also play a significant role in radiation damage to biological media [8]. In the study of Boudaiffa *et al.* [9] it was observed that electrons in the energy range 3-20 eV can cause significant damage to DNA through the process of dissociative attachment, which can occur even at energies well below ionization thresholds. Triple differential cross sections for electron impact ionization of water have been used as an input for a simulation to determine the charged particle track structure of an electron through a biological medium [10]. The challenge is to extend this modelling to other biomolecules, and hence obtain a complete picture for real biological material.

To improve our understanding of the interaction of electrons with biological matter we are investigating this electronic interaction using smaller biomolecules such as formic acid and tetrahydrofuran (THF) as a model for the components of larger biological systems. Formic acid is the simplest organic acid and is thought to play a key role in the formation of larger biologically relevant molecules such as acetic acid and glycine. THF can be regarded as a structural unit in a number of biological molecules including the sugar moiety in the sugar-phosphate backbone of DNA and RNA. This backbone structure can be represented as a series of THF molecules bonded to phosphate units and DNA Bases. Figure 1 shows the structure of (a) formic acid and (b) THF molecules. Also indicated on each figure is the location of the molecules' centre of mass.

Here we describe our recent progress in investigating the electron-impact ionization of formic acid and THF molecules. Our recently published TDCS measurements for the formic acid monomer [6] are directly compared with new measurements for THF under the same kinematics. We also compare the experimental results with distorted wave calculations of the TDCS.

## 2. Experiment

This study has been performed using a conventional (e, 2e) spectrometer, operating in the coplanar asymmetric geometry. The experimental apparatus has been described in detail in [11]. Briefly, the spectrometer consists of an electron gun and two hemispherical electron energy analysers, all mounted in-plane and perpendicular to the target gas jet. Electrons produced by thermionic emission from a thoriated tungsten filament in the electron gun are collimated and transported to the interaction region where the incident electron beam crosses a molecular target beam, formed by effusion of the target through a 0.7 mm internal diameter stainless steel capillary.

(e, 2e) events are identified by the relative arrival times of electrons at the two detectors and background events are subtracted using standard statistical methods. The two electron energy analysers are mounted on independent turntables concentric with the interaction region. The higher energy (scattered) electron is detected at a fixed small angle with respect to the incident electron beam direction. Electron angular distributions are measured by scanning the lower energy (ejected) electron energy analyser and detecting electrons at a number of different angles within the scattering plane. The coincidence energy resolution of the system is approximately 1.2 eV full width half maximum (FWHM).

Formic acid and THF are both liquids at room temperature and a vapour target is obtained from the liquid sample held in a glass vial which has been purified prior to use via several freeze-pump-thaw cycles. In the case of formic acid, the vapour is a mixture of monomers and dimers whose ratio is a function of temperature and driving pressure. At higher temperatures, the extra kinetic energy serves to break up most of the dimers into monomers. It was demonstrated in ref. [12] that at temperatures in excess of 120°C, the target is composed of greater than 99% monomers. As a result, the beam-forming needle is held at approximately 135°C, while the associated gas handling system and vacuum chamber are heated to approximately 75°C and 50°C, respectively, to prevent condensation. Similarly for THF the gas handling system and chamber are heated to prevent condensation and to further inhibit THF being deposited on the electron optics and other elements within the vacuum chamber, a liquid nitrogen filled cold finger located directly above the interaction volume was used to trap THF.

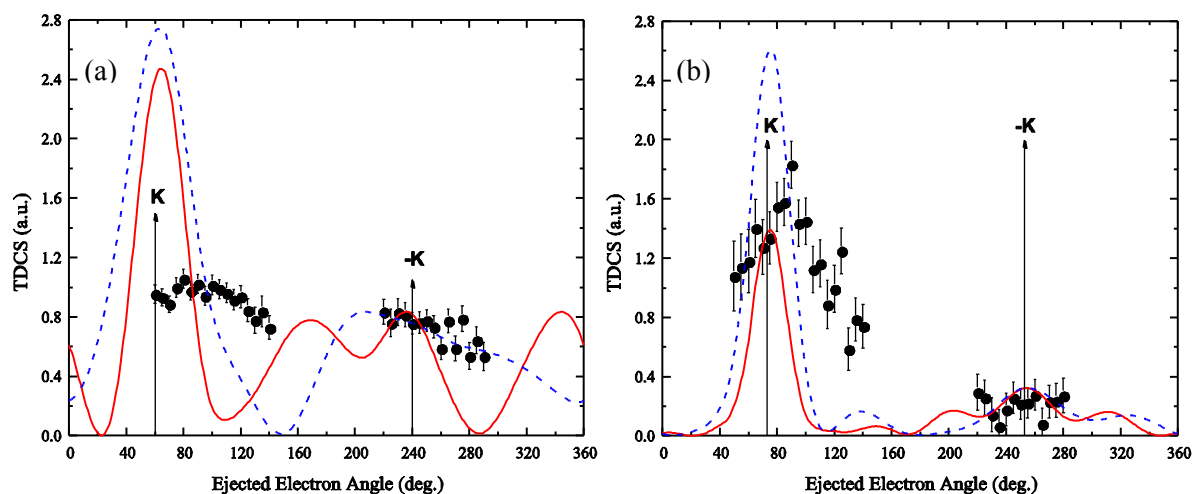
## 3. Results and Discussion

### 3.1. Triple differential cross sections for formic acid

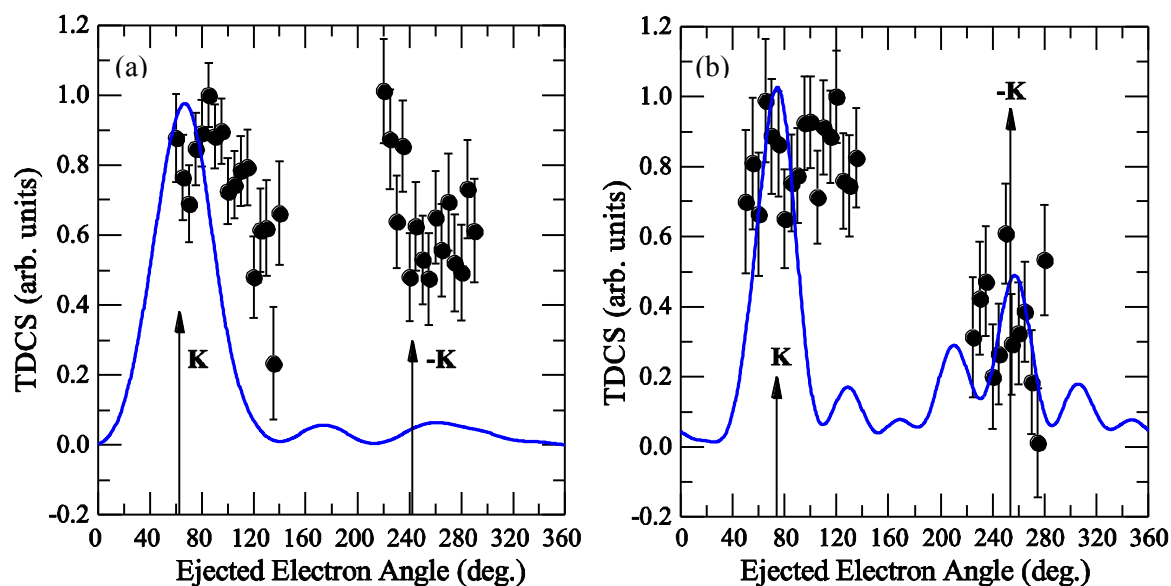
As discussed previously, closely spaced molecular orbitals are difficult to resolve and with the limited coincident energy resolution of our spectrometer we were unable to fully resolve contributions from the outermost  $10a'$  and  $2a''$  valence orbitals of formic acid. Figure 2 shows our recent TDCS data for formic acid which was presented in ref [6]. The experimental data are for electron impact ionization of the summed ( $10a' + 2a''$ ) outermost valence orbitals. The energy of the incident electrons ( $E_0$ ) is 250 eV and the energy of the ejected electrons ( $E_b$ ) is 10 eV. Results are shown for scattering angles of (a)  $-5^\circ$  and (b)  $-15^\circ$ . Also shown on the figure are molecular 3-body distorted wave (M3DW) [7] and M3DW-CPE calculations for the  $10a'$  orbital. While experimental results are shown for the sum of the  $10a'$  and  $2a''$  valence orbitals, we are able to calculate results for the  $10a'$  orbital only. The orientation averaged molecular orbital (OAMO) approximation used in the calculations for formic acid is not valid for the  $2a''$  orbital since the average is zero for this symmetry, see ref [6] for details. The M3DW-CPE calculations include correlation-polarization-exchange terms in the M3DW model [6].

The angular distributions can be divided into two regions. The first is the binary region which ranges from  $0^\circ$  to  $180^\circ$ . Structure here arises from single binary collisions and depending upon the kinematics it may contain strong signatures of the orbital structure [13]. The second, which extends from  $180^\circ$  to  $360^\circ$ , is referred to as the recoil region. It is aptly named as it contains structure arising from processes in which the ejected electron produced by an initial binary collision undergoes recoil scattering from the target nucleus.

As the scattered electron angle is changed from  $-5^\circ$  to  $-15^\circ$  the magnitude of the recoil peak relative to the binary peak decreases significantly. The M3DW predicts the shape of the recoil peak quite well,



**Figure 2.** (Colour online) Experimental triple differential cross sections for the summed  $10a'$  and  $2a''$  valence orbitals of formic acid (solid circles), with  $E_0 = 250$  eV and  $E_b = 10$  eV, plotted against the M3DW-CPE (solid line) and M3DW (dashed line) calculations for the  $10a'$  orbital only. The scattered electron detection angles and corresponding momentum transfers are (a)  $-5^\circ$ ,  $|K| = 0.42$  au and (b)  $-15^\circ$ ,  $|K| = 1.11$  au (Adapted from Colyer *et al.* [6].).



**Figure 3.** (Colour online) Plot of the triple differential cross sections for ionization of the combined  $9b+12a'$  valence orbital of tetrahydrofuran, with  $E_0 = 250$  eV and  $E_b = 10$  eV. The scattered electron detection angles and corresponding momentum transfers are (a)  $-5^\circ$ ,  $|K| = 0.40$  au and (b)  $-15^\circ$ ,  $|K| = 1.11$  au. The points are the experimental data and the solid line is the M3DW calculation. The positions of the momentum transfer vector,  $\mathbf{K}$ , and  $-\mathbf{K}$  are indicated by the arrows. in both cases.

however, the relative size of the binary and recoil peaks is better predicted by the M3DW-CPE, which successfully predicts the correct relative magnitudes of the binary peak and the recoil peak at  $-15^\circ$ . The experimental data exhibits a broader binary peak when compared to the theory, which is due to contributions from the  $2a''$  state that are not included in the M3DW calculations.

### 3.2. Triple differential cross sections for tetrahydrofuran

At room temperature THF exists in two conformers in approximately equal proportions [14] and we are unable to separate the individual contributions from each of these. The two conformers are of  $C_2$  and  $C_s$  point group symmetry and their outermost orbitals are assigned as  $9b$  and  $12a'$ , respectively [14]. Figure 3 shows the TDCS for electron impact ionization of THF, again with 250 eV incident electrons and measured for 10 eV ejected electrons. A M3DW calculation for the combined  $9b + 12a'$  orbital is also shown on the figure. The contribution of the outermost orbital for each conformer in the calculation is 50%. In the binary region, it appears that the experiment has a double peak structure whilst the theory only predicts a single peak which is centred about the momentum transfer direction. It is expected that the second peak is lost in the averaging process used to calculate the molecular wave function.

As is the case for formic acid the magnitude of the recoil peak relative to that of the binary peak is less for  $-15^\circ$  (figure 3(b)) than for the  $-5^\circ$  scattering angle (figure 3(a)). This is in contrast to our earlier TDCS measurements for  $H_2O$  under the same kinematics [15]. Following from arguments presented in ref. [16], it is postulated that a lack of nuclear charge at the molecules' centre of mass results in reduced recoil scattering.

The experimental TDCS's for both formic acid and THF molecules exhibit a very broad binary peak with a minimum centred close to the momentum transfer direction. A similar very broad binary peak has also been observed for ionization of the outer valence orbital of methane [17]. At the  $-5^\circ$  scattering angle the intensity of the binary peak is close to that of the recoil peak, as is observed for the formic acid monomer. At  $-15^\circ$  the shape of the formic acid binary peak appears sharper than at  $-5^\circ$  and closer to the M3DW calculation whereas the THF binary peak is still very broad at this scattering angle. Further THF results and a more detailed analysis will appear in a future publication [18].

## 4. Conclusions

(e, 2e) TDCSs for the THF molecule, which is a model compound to investigate electron interactions with the deoxyribose molecule, are reported and compared to our recent measurements on the formic acid monomer. Similar to the formic acid monomer, the TDCSs at all scattered electron angles investigated show a broad binary peak. The ratio between the recoil peak magnitude and binary peak magnitude for both formic acid and THF is much smaller than that observed for ionization of water under the same kinematics.

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