Electron and positron scattering from biomolecules

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Abstract. We review recent results from experimental studies of electron and positron collisions with the important biomolecules 3-hydroxy-tetrahydrofuran, formic acid and methanol and ethanol. Where possible, comparison to corresponding results from theoretical calculations is made. Finally, some possible future directions for this research area will be explored.

1. Introduction

Since the pioneering paper of Boudaiffa et al. [1], which questioned the belief that ballistic impacts were responsible for the majority of cell and tissue damage when ionising radiation enters the body, it is now widely accepted that this initial high-energy ionising radiation liberates many low-energy secondary electrons which can in turn attach to the various components of DNA (i.e. the bases, sugars and water). Through the process of dissociative attachment this leads to single or double DNA strand breaks, or the formation of free radicals which through chemical reactions with DNA can also lead to strand breaking [1]. It is therefore not surprising that significant recent work has been devoted to understanding the interaction of charged particles and photons with biomolecules.

In this review we focus our discussion on the interactions of electrons and positrons with the fundamental biomolecules formic acid, 3-hydroxy-tetrahydrofuran and methanol and ethanol. In particular we will consider for each species the results from recent cross section measurements, with a comparison of these data to theory, where possible, also being made. We stress at this time that the mechanisms leading to biological damage are quantitatively different for positrons and electrons. In fact, while positron and electron total cross sections merge at energies above a few keV, they are quite different below a few tens of eV [2]. Qualitatively, the presence of the positronium formation channel makes an even larger difference for positron scattering, as in diagnostic and real treatment situations the first fate of the positrons is to be annihilated inside the organic tissue, which adds the ionising effects of the annihilation gamma rays. No attempt is made here to describe relevant dissociative attachment results for electrons, rather we refer the interested reader to a selection of articles in the special issue of the International Journal of Mass Spectrometry [3] in honour of one of the pioneers of that field, namely Professor Eugen Illenberger.

In the next section we sequentially consider the species formic acid, 3-hydroxy-tetrahydrofuran and methanol and ethanol. Thereafter some conclusions from those studies
are drawn, and possible future research directions canvassed.

2. Results and discussion

2.1. Formic acid (HCOOH)

Formic acid, the simplest organic acid, is considered to play an important role in the formation of the larger biomolecules such as glycine and acetic acid. Furthermore, the formate group (–COOH) is a key component of more complex biomolecules including the amino acids. It is therefore not surprising that there has been significant recent interest in this species, with the papers of Vizcaino et al. [4], Allan [5] and Zecca et al. [6] being particularly relevant to this article.

In figure 1 we show a series of absolute elastic differential cross sections (DCSs), for electron scattering from HCOOH [4] in the energy range 1.8–50 eV. Also shown in this figure are corresponding calculations from Gianturco and Lucchese [7] and Trevisan et al. [8], for the predominant trans-HCOOH conformer. At room temperature, formic acid consists of a mixture of monomer and dimer [9] forms, so that Vizcaino et al. [4] performed the measurements illustrated in figure 1 at an elevated temperature (∼130 °C) to ensure >98% monomer composition. Note that Vizcaino et al. [4] also derived elastic integral and momentum transfer cross sections from their DCS data, although we do not discuss them further here.

It is clear from figure 1 that the overall level of agreement between experiment [4] and theory [7, 8] is quite good, in spite of the very different theoretical approaches applied in each case. Trevisan et al. performed fixed-nuclei (FN) calculations at the equilibrium geometry using the complex Kohn variational method [8], with the equilibrium nuclei positions being optimised at the Hartree-Fock (HF) level. They determined the small ℓ-components of the T-matrix variationally, although, due to the polar nature of formic acid, higher-order partial wave components were included through a Born correction. Gianturco and Lucchese [7], on the other hand, used a density functional approach within a FN-approximation and included short-range correlation through the addition of a local energy-independent potential. This potential was then corrected to agree with the known form of the long-range polarisation effects. So while the complex-Kohn approach, which is fully ab initio, is the more exact, the computationally “cheaper” approach of Gianturco and Lucchese nonetheless provides results at a level of accuracy that would be sufficient for e.g. modelling charged-particle tracks of electrons through a formic acid medium. In all cases, both experiment and theory, we finally note the important role played by the formic acid dipole moment (∼1.41 D) and dipole polarisability (∼22.5 a.u.) in the scattering process (see figure 1).

Resonance effects in electron–formic acid scattering, for incident electron energies between threshold and 5 eV, were studied in detail by Allan [5]. In this work absolute excitation functions, for elastic scattering and a range of vibrational processes, were measured at the scattered electron angle of 135°. Significant resonance effects (see figures 4–6 in Allan [5]) were observed, particularly in the vibrational channels where, in addition to the expected threshold structure, other structures due to the well-known π* shape-resonance at around 1.8 eV were prevalent. In addition, however, Allan also noted other features in some of the excitation functions, which he speculated might be due to contributions from a higher-lying O–H stretch σ* shape resonance.

The only published investigation into positron scattering from HCOOH is the recent study by Zecca et al. [6]. That work included experimental grand total cross sections (TCSs) and theoretical elastic integral cross sections (ICSs), as calculated using a Schwinger Multichannel (SMC) approach. The TCSs were measured in the positron energy range 0.3–50.2 eV, while the SMC results were computed for energies up to 30 eV and at the static, static plus polarisation and static plus polarisation plus Born-closure levels. A summary of the results of Zecca et al. [6]
Figure 1. Absolute DCS ($10^{-16}$ cm$^2$/sr) for elastic scattering from formic acid at: (a) 1.8 eV, (b) 5 eV, (c) 10 eV, (d) 15 eV, (e) 30 eV and (f) 50 eV. The data from Vizcaino et al. [4] (●) and the calculations from Gianturco and Lucchese [7] (green —) and Trevisan et al. [8] (blue —) are shown where possible.

is given in figure 2, where we find that the most accurate SMC elastic ICS calculation (i.e. that which includes the static, polarisation and Born-closure (dipole) effects) significantly overestimates the magnitude of the experimental GTS at most energies. This is of course unphysical. Zecca et al. addressed this issue by noting the observed discrepancy might be caused by the experimental GTS not having been corrected for forward angle scattering effects, the existence of dimers in the experiment whereas the calculations were for the monomer
only, the calculations being restricted to scattering from an initial $j = 0$ state whereas in the measurements there will be scattering from a Boltzmann distribution of initial $j$-states, and finally that it is well-known [10] that the Born-closure approach overestimates elastic ICS at lower energies. In any event, figure 2 clearly illustrates, consistent with the electron-scattering results, the importance of both the dipole-polarisability and dipole moment of HCOOH in the positron scattering process. It also nicely showcases the importance of the positronium formation channel (threshold = $4.6 \pm 0.2$ eV) on the TCS, contributing significantly to the magnitude of the TCS above its threshold. Finally we plot some very recent, preliminary, TCS data from the Australian National University group. In the common energy regime agreement between it and that of Zecca et al. [6] is very good.

![Figure 2](image.png)

**Figure 2.** The experimental (•) total cross sections and theoretical elastic integral cross sections (both in $10^{-16}$ cm$^2$) for positron scattering from HCOOH [6]. The static level (———), static plus Born-dipole correction (—–), static plus polarisation (—–) and static plus polarisation plus Born dipole correction (—) results from [6] are shown. Preliminary results (○) from the ANU are also given [J. Sullivan, private communication (2009)].

2.2. 3-hydroxy-tetrahydrofuran ($C_4H_8O_2$)

Molecules such as 3-hydroxy-tetrahydrofuran (3-h-THF) and tetrahydrofuran (THF) [11, 12, 13], at least in part due to the practical difficulties in producing a molecular beam or target cell of DNA, are of real interest to the ATMOP community. This is because of their similarity to the nucleotide ring systems, so that they might be considered as prototypical building blocks for living matter. This reductionist philosophy whereby the physical, chemical and biological properties of a system stem from the fundamental properties of the constituent molecules and their interactions, appears to have been embraced by our field [10, 14]. Note that we fully appreciate that gas-phase cross sections, such as those discussed here, are only a first-order approximation to those for the true in vivo situation. Nonetheless they are a good starting point for simulations devoted to the development of energy deposition models at the molecular level [15].

In figure 3 we show the experimental and Schwinger Multichannel (SMC) theoretical elastic differential cross sections [16] for electrons scattering from 3-h-THF. The energy range of this work was 6.5–20 eV, and to the best of our knowledge it remains the only such study for electron scattering from 3-h-THF that is available in the literature. Note that elastic ICS and elastic momentum transfer cross sections were also reported in that study [16]. Further note that,
where possible, corresponding elastic DCS results for electron scattering from THF [12] are also shown.

Figure 3. Absolute DCS ($10^{-16}$ cm$^2$/sr) for elastic electron scattering from 3-h-THF [16] at: (a) 6.5 eV, (b) 8 eV, (c) 10 eV, (d) 15 eV and (e) 20 eV are shown. The full circles (•) are for 3-h-THF, the open circles (○) are for THF [12], while the Schwinger results have a solid line (---) for 3-h-THF and a dashed line (---) for THF.

There are several features we can glean by considering figure 3 in more detail. Firstly, the experimental DCS and corresponding SMC variational calculation results for 3-h-THF are in fair agreement with one another at each of the energies studied. Although not shown, this statement also applies to the elastic ICS and momentum transfer cross sections for 3-h-THF. Secondly, the results from Vizcaino et al. [16] indicate that there are no real major differences between the elastic electron scattering cross sections for THF and 3-h-THF. However, the measured cross sections for 3-h-THF are consistently a little lower in magnitude compared to those for THF whereas the calculations show the opposite trend. On this basis, Vizcaino et al. [16] noted that further studies would be appropriate and we reiterate that view here. Finally, the angular distributions of both the measured and calculated data are consistent with what one might anticipate given both the strong permanent dipole moment and significant dipole polarisability of 3-h-THF [17]. This latter point is similar to the effect discussed previously in regard to formic acid.

With respect to positron scattering from 3-h-THF, we know of no theory being available in the literature for any of the possible scattering processes. The situation in relation to experimental work is only marginally better, with the recent total cross sections data from Zecca et al. [17] being available. That data, along with earlier work from the same group for THF [2], are
The main feature of the 3-h-THF data was that the magnitude of the TCS increased dramatically as they went to lower incident positron energies (note the log scale). This observation again reflected both the strong permanent dipole moment and important dipole polarisability of 3-h-THF. Note that the effect for the opening of the positronium channel at 3 eV, on the TCS, is also apparent in figure 4. Given that the molecular geometries (bond lengths, bond angles) of both 3-h-THF and THF are very similar, suggesting that the molecular diameters of both species are similar, and given that the dipole moments and dipole polarisabilities of THF and the global minimum conformer of 3-h-THF are almost identical [17], Zecca et al. argued that below the positronium threshold the energy dependence and magnitude of the TCSs of THF and 3-h-THF should be similar. Indeed, this is precisely what they observed for positron energies in the range $1.6 \lesssim E < 3.1$ eV. Thereafter, however, as they went to even lower energies, the TCSs in 3-h-THF became significantly stronger in magnitude than those for THF. This effect was postulated by Zecca et al. [17] to reflect the existence in their 3-h-THF sample of the next most stable conformer of 3-h-THF, which has a significantly larger dipole moment compared to both that of the global minimum conformer and THF. Hence they concluded that their data indicated the important role that will be played by conformers when observing scattering behaviour. Such an effect is not really that surprising, however, as the effect of conformers on molecular structure and activity has been appreciated in the physical chemistry community for quite some time [18].

### 2.3. Methanol and ethanol

An extensive series of measurements and calculations for low energy (1–100 eV) elastic electron scattering from methanol (CH$_3$OH) and ethanol (C$_2$H$_5$OH) was recently reported by Khakoo et al [19]. Both differential and integral elastic cross sections were provided, as was a very detailed summary of the available electron scattering data for both these targets.

It was clear from this work, which experimentally applied the relative flow technique with helium as the standard gas (to set the absolute scale) and a thin aperture as the collimating target gas source, that except at the lowest incident electron energies there was good agreement between the data and both implementations of the Schwinger Multichannel method, at both the differential and integral cross section levels, and for both target species. Indeed, particularly at the lower energies, the role of the molecular dipole moments and dipole polarisabilities of CH$_3$OH and C$_2$H$_5$OH, on the elastic electron scattering process, was manifest.
An important point from this work, that was not addressed in the original paper [19], was that the experimental elastic $e^- + \text{CH}_3\text{OH}$ integral cross sections were $\sim 2$ times larger in magnitude at 1 eV and 2 eV, than the grand total cross section data of Szmytkowski and Krzysztofowicz [20] at those same energies. Of course, as we noted earlier in this paper, it is unphysical for an elastic integral cross section to be greater in magnitude than the grand total cross section, so that there is a clear inconsistency between the measurements at 1 and 2 eV [19, 20]. As the accurate SMC theory supports the experimental elastic ICS results from Khakoo et al. [19], it might be prudent to revisit the low energy grand total cross section data in this case.

With respect to positron scattering from these molecules, the only measurements available are total cross sections from Kimura et al. [21] and Zecca et al. [22] for $e^+ - \text{CH}_3\text{OH}$ scattering, and Zecca et al. [22] for $e^+ - \text{C}_2\text{H}_5\text{OH}$ scattering. All this available TCS data is summarised in figure 5, where it is also clear that there are currently no available theories against which the measurements might be compared.

![Figure 5. The total cross sections ($10^{-16}$ cm$^2$) for positron scattering from methanol (•) and ethanol (△) from Zecca et al. [22]. Also shown is the methanol TCS (Ω) from Kimura et al. [21].](image)

It is apparent from figure 5 that the $e^+ - \text{ethanol}$ data of Zecca et al. [22] are in general larger in magnitude than their corresponding $e^+ - \text{methanol}$ TCS results [22]. Some of this behaviour might be due to ethanol being a larger molecule than methanol, but more likely we believe this reflects the higher dipole polarisability of ethanol ($\alpha \sim 5.26 \times 10^{-24}$ cm$^2$) compared to that of methanol ($\alpha \sim 3.28 \times 10^{-24}$ cm$^2$) particularly since their respective dipole moments are almost identical. The methanol TCS of Kimura et al. [21] is in good agreement with the Trento data [22] for positron energies greater than about 15 eV, but as we go to progressively lower energies this level of accord gets much worse. This is a common feature we find when we are able to compare positron TCS measurements from Trento with those made at Yamaguchi University. Finally, the effect of the opening of the positronium channel was apparent for both ethanol and methanol, the monotonic decrease in the TCS with increasing energy being seen in figure 5 to change significantly at $E_{Ps} \sim 4$ eV.

3. Conclusions and future directions

We have reviewed results from recent experimental studies of electron and positron collisions with the biomolecules 3-hydroxy-tetrahydrofuran, formic acid and methanol and ethanol. In all cases, irrespective of whether the incident projectile was an electron or a positron, the effect of the target molecular dipole moment and molecular dipole polarisability on the scattering process,
particularly at lower incident energies, was apparent. This is not to say that the scattering process is identical for incident electrons and positrons, indeed while positronium formation can only occur when positrons are the incident projectiles exchange can only occur when electrons are incident on the target species. Hence there is a richness of different physics to be probed and understood when either electrons or positrons are incident on different targets.

As to the future, many larger biomolecules are solid at room temperature with little or no volatility. To enable access to those species for scattering experiments, Surdutovich et al. [23] recently devised a technique for measuring total cross sections for positron scattering from uracil which serves as a template for studying the DNA bases and proteins at that level. In terms of elastic electron scattering experiments, an elevated-temperature relative flow technique apparatus is currently being trialed at the Australian National University [24]. Therefore we believe the future of this field is very bright, with many new systems to be investigated both theoretically and experimentally in the near future.

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