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Dynamical (e,2e) Studies of Bio-Molecules

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Submitted in fulfillment for the requirements
of the degree of Masters of Science

March 2013

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A careful analysis of the process of observation in atomic physics has shown that the subatomic particles have no meaning as isolated entities, but can only be understood as interconnections between the preparation of an experiment and the subsequent measurement.

$\sim$ Erwin Schrödinger (1887-1961)

7 Conclusions

7.1 Summary of Results

The experimental TDCS results presented within this thesis examine the dynamical (e,2e) nature of the biomolecules pyrimidine and α-tetrahydrofurfuryl alcohol (THFA), as well as the cyclic ethers tetrahydrofuran (THF), tetrahydropyran (THP) and 1,4-dioxane. All measurements were performed using 250eV incident electrons and detecting 20eV ejected electrons. A complete overview of the apparatus and techniques used, along with the underlying theory behind the (e,2e) process, can be found in Chapters 3 and 2, respectively.

The prospective importance of these measurements cannot be understated. As described in Chapter 1, TDCS measurements on molecules of biological significance can help improve the current generation of charged-particle track simulations, which currently rely on the assumption that the biological medium entirely consists of H_2O. Additionally, those simulations currently only allow for the ionised secondary electrons initially moving off along the momentum transfer direction $+\vec{\kappa}$. The results in the present thesis clearly demonstrate that significant recoil intensity around $-\vec{\kappa}$ should also be considered.

In Chapter 4 the findings from a series of TDCS measurements were reported on the $10a_1$ and $7b_2$ (HOMO) orbitals of pyrimidine. The $10a_1$ orbital measurements were taken at the scattered electron angles of $-5°$, $-10°$ and $-15°$, while the $7b_2$ (HOMO) orbital measurement was taken at the scattered electron angle of $-5°$. All the TDCSs reported for pyrimidine showed a narrow binary peak, with the exception of the $10a_1$ orbital at $-5°$ which also displayed a relatively large recoil peak. We speculated that this difference in behaviour was possibly being due to contributions from the adjacent $1b_1$ orbital or due to PCI effects.

Several Molecular 3-body Distorted Wave (M3DW) calculations were performed by Madison *et al.*, and compared to the corresponding TDCS measurements for pyrimidine. Overall the agreement between the experimental and theoretical results was typically fair, although the M3DW calculations did exhibit some problems in correctly predicting the magnitude of the recoil peaks. As can be seen in the other TDCSs presented throughout this thesis, this seemed to be a recurring issue with the M3DW model. However, developments in that technique have been put forward which have shown some initial promise in terms of addressing those discrepancies [78].

Chapter 5 reported the results of a series of TDCS measurements on the $28a$ orbital of THFA. Those measurements were again taken at the scattered electron angles of $-5°$, $-10°$ and $-15°$. Across all scattered electron angles a broad binary peak was observed in this case, with only a hint of a double-lobed structure that would be expected for a 'p-type' orbital, for $\theta_{sc} = -10°$. A relatively small recoil peak was observed for the scattered electron detection angles of $-10°$ and $-15°$, although as with pyrimidine $\theta_{sc} = -5°$ seemed to be an exception to this trend. The TDCSs of THFA were also compared to the output from two theoretical models; specifically the M3DW and Distorted Wave Born Approximation (DWBA) models. Both the M3DW and DWBA calculations predicted broad binary peaks for $\theta_{sc} = -5°$ and $-10°$, but also predicted a narrow binary peak for $-15°$ which was not supported by the experimental results. Curiously the differences in the TDCSs between the M3DW and DWBA results were small, which suggests that PCI had a minimal effect in the case of the $28a$ orbital. However, as the observed binary peaks exhibited a shift in position away from the momentum transfer vector, $\vec{\kappa}$, our suggestion was that the PCI was playing a more significant role than predicted by the M3DW calculations.

Finally, in Chapter 6, the TDCSs of three seperate cyclic ethers were reported and compared. The HOMO for each of the three cyclic ethers was studied, which equated to the $9b + 12a'$ orbitals for THF, the $15a'$ orbital for THP and the $8a_g$ orbital for 1,4-dioxane. In each case the TDCS were measured at $\theta_{sc} = -5°$. All three cyclic ethers displayed a relatively broad binary peak, as well as a recoil peak that had a relatively large magnitude when compared to the binary peak. Additionally, all three experimental TDCSs were normalised to the results of M3DW calculations at $\theta_{ej} = 65°$ although the normalisation point was not significant to the behaviour we observed.

In the case of the cyclic ethers, and at the kinematic conditions of study, the

M3DW calculations generally did not reproduce the measured TDCS very well. However, it did show some promise in predicting the shape of the 1,4-dioxane binary peak. Nonetheless, these further results reinforced the view that further refinements to the M3DW were required before quantitative agreement with experiment might be achieved.

7.2 Future Directions

One of the main limitations highlighted by the current study is the angular limitations imposed upon the measured TDCSs, entirely due to the mechanical restrictions of our (e,2e) spectrometer. This limitation is clearly visible in all the TDCSs, covering both binary and recoil peaks, in terms of the ejected electron angles we could not actually measure. However, there does exist an experimental approach that is capable of allowing the otherwise inaccessible regions to be measured. This device is called a Magnetic Angle Changer (MAC) and was initially described in a publication by Read and Channing [147]. The MAC works by utilising two pairs of concentric solenoids, that are arranged to generate a magnetic field that is localised at the interaction region, to deflect the incident and outgoing scattered and ejected electrons as they emerge from the interaction region [147]. The MAC has already been successfully employed to measure the TDCS of argon, in an (e,2e) spectrometer similar in design to the one described in this thesis [148]. Incorporating a MAC device into the current (e,2e) spectrometer thus allows, in principle, a way to improve the angular range of our spectrometer.

Another limitation of the current (e,2e) spectrometer is the relative nature of the TDCS data measured by the apparatus. Indeed our present TDCSs are given an absolute magnitude only by comparing the results with a theoretical model. However if the TDCS data was itself absolute, it would provide a more comprehensive test for the validity of the theory and allow us to compare the relative probabilities of ionisation events occurring between different molecular targets; information which is particularly important to Charged Particle Track Structure Analysis (CPTSA) and thus modelling the effects of radiation damage. Quite recently a method by which to provide absolute TDCS measurements was proposed by Hargreaves *et al.* [149]. This method involves mixing the target molecule and a standard gas, specifically helium, and relying on the TDCS for He, under the kinematics being studied, being known. However, for biomolecules which are often 'sticky' or solids at room temperature, the application of that approach might be a little problematic. Nonetheless, such a development remains desirable.

Finally, in order to provide a more complete picture for CPTSA, quite a number of additional biomolecules need to undergo dynamical (e,2e) spectroscopic analysis. Previous work in this field has produced results for formic acid [15, 35], tetrahydrofuran [15, 36] and thymine [15], which represent a simple building block in biological systems, an analogue for the DNA backbone and a nucleobase respectively. With the addition of the current results on pyrimidine, α-tetrahydrofurfuryl alcohol, tetrahydrofuran, tetrahydropyran and 1,4-dioxane, this situation has clearly improved. However, there still exists quite a large number of other relevant biomolecules for which TDCS data would be useful. Some of the more important of these relevant biomolecules are: the remaining four nucleobases (adenine, cytosine, guanine and uracil), purine (which represents the basis upon which adenine and guanine are built), 3-hydroxytetrahydrofuran and phosphoric acid (the latter two representing core molecular elements of the sugar-phosphate backbone of DNA and RNA [150]). Additionally, it might also be worth measuring a more complete set of scattered electron angles for tetrahydropyran and 1,4-dioxane in order to provide more data for them to benchmark against.