

VALENCE ELECTRONIC STRUCTURE OF 2,6-STELLADIONE: EXPERIMENTAL AND COMPUTATIONAL STUDIES

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2,6-Stelladione (or tricyclo[3.3.0.0^{3,7}] octan-2,6-dione) has been investigated for the first time using experimental High Resolution Electron Momentum Spectroscopy (HREMS) [1]. EMS produces the probability density map of the electrons in the target. This is a fundamental observable of the electronic structure and provides a comprehensive test for theoretical models. This technique is particularly sensitive to the low momentum region of the wavefunction which correspond to the outer (valence) orbitals of the molecule.

Details of our HREMS spectrometer and measurement techniques can be found elsewhere [1]. For the present study the binding energy range of interest was 7-16 eV, while the target momenta probed was in the range 0.03-2.5 a.u. The total energy was 1500 eV.

The ground state of 2,6-Stelladione has also been studied using *ab-initio* and density functional theory (DFT) calculations. Theoretical momentum distributions (MDs) for the outer valence molecular orbitals were simulated using DFT calculations and the plane wave impulse approximation (PWIA).

In this poster we show a selection of our binding energy spectra and our theoretical and experimental MD results for some of the outer valence orbitals of 2,6-stelladione. A comparison between the experimental and theoretical MDs is also made.

Previous HREMS studies of complex organic molecules [1,2] have been used to evaluate the quality of different basis sets and also the relative success of local density approximation (LDA) exchange correlation (XC) functionals compared with generalized gradient approximation (GGA)

XC functionals. However, for the first time, in our present study the experimental results are of high enough quality to evaluate the accuracy of various XC functionals within the GGA method (see Figure 1). In addition, we confirm the earlier photoelectron spectra result for strong through-bond interactions in this molecule.

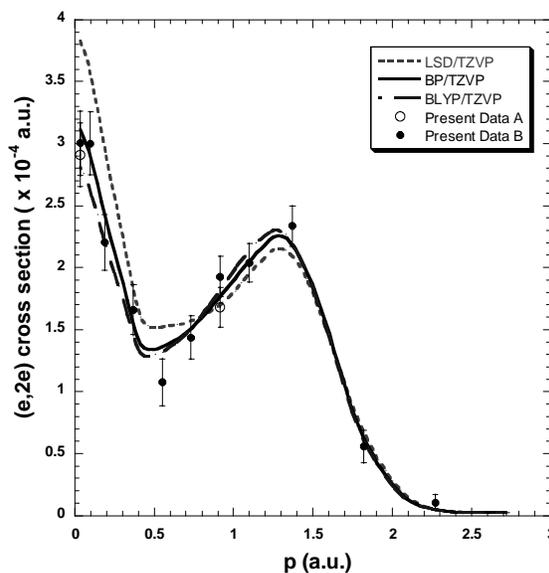


Figure 1: The 1500 eV symmetric non-coplanar MD for the 7a orbital. Experimental data from run A (°) and B (·), are compared with theoretical results from LDA (· · ·), BLYP (- - -) and BP (-) XC functionals.

References

- [1] MJ Brunger, W Adcock, *J Chem. Soc., Perkin Trans. 2* (2002) 1.
- [2] H Mackenzie-Ross *et al.*, *J. Phys. Chem. A*, (2002), **106**(41), 9573-9581.