

HREMS AND DFT STUDY INTO THE VALENCE ELECTRONIC STRUCTURE OF THE CHEMICALLY SIMILAR MOLECULES C₇H₈, C₇H₁₀ AND C₇H₁₂

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We report on results from our High-Resolution Electron Momentum Spectroscopy (HREMS) and Density Functional Theory (DFT) calculations into the complete valence electronic structures of the chemically similar molecules; norbornadiene (C₇H₈), norbornene (C₇H₁₀) and norbornane (C₇H₁₂). In particular, the effect on the respective valence electronic structures as their π -like double bonds are progressively saturated is highlighted.

The symmetric non-coplanar HREMS spectrometer used in the present measurements is described elsewhere [1]. Briefly, however, a beam of 1500 eV + binding energy (ϵ_f) electrons ionises the target of interest and the resulting scattered and ejected electrons are detected in coincidence. As this is a kinematically complete process, the binding energy of the target electron (ϵ_f) and its momentum (p) at the instant of ionisation can be determined. From the number of true coincidences as a function of ϵ_f and p , the HREMS binding energy spectra and momentum distributions (MDs) can be ascertained. For each of the molecules we studied the ϵ_f range was $\epsilon_f \sim 6$ -33 eV and $p \sim 0.03$ -2.8 a.u. The overall coincidence resolution was ~ 0.5 -0.6 eV (FWHM).

Corresponding theoretical MDs were also calculated within a plane-wave impulse, Born-Oppenheimer and target Kohn-Sham approximation framework [2]. The basis sets used in our computations were all calculated within density functional theory, and they also employed a range of exchange correlation (XC) functional levels.

Representative examples of our measured and calculated orbital momentum densities (see

figure 1) for each of the molecules are presented and systematically discussed. In addition, some of their important physico-chemical properties (particularly their respective structures), as derived from our studies, are also presented. These latter results are compared against corresponding values from independent measurements and calculations.

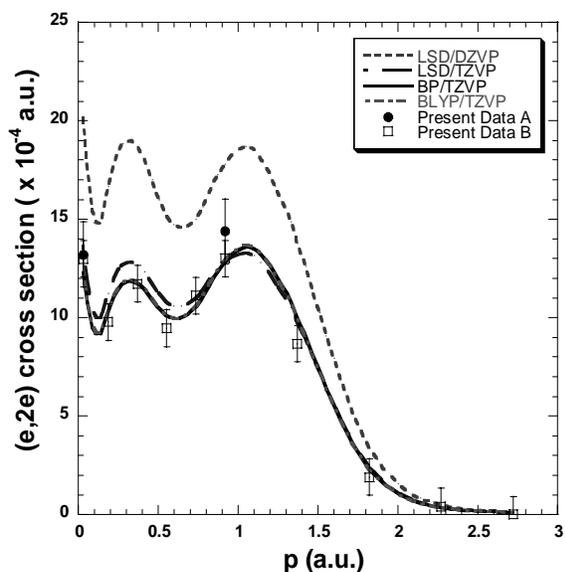


Figure1: The 1500 eV symmetric non-coplanar MD for the 6a''+11a'+10a'+9a'+5a'' orbitals of norbornene.

References

- [1] MJ Brunger, W Adcock, *J Chem. Soc., Perkin Trans. 2* (2002) 1.
- [2] E Wiegold and IE McCarthy, *Electron Momentum Spectroscopy*, (Klewer Academic/Plenum Publishers: New York: 1999).