Electron momentum spectroscopy studies on atom and molecules using monochromated electrons

M.J. Brunger, W. Adcock, D.A. Winkler* and M.T. Michalewicz**

Department of Physics and Chemistry, The Flinders University of South Australia, G.P.O. Box 2100, Adelaide, South Australia 5001, Australia
* CSIRO, Division of Molecular Science, Private Bag 10, Clayton South MDC, Clayton, Victoria 3169, Australia
** BoM/CSIRO, High Performance Computing and Communication Centre, 24th Floor, 150 Lonsdale Street, Melbourne, Victoria 3000, Australia

Abstract. A recently developed electron monochromator has been used in noncoplanar symmetric electron momentum spectroscopy studies on atomic argon and molecular cubane. This (e,2e) monochromator typically produces beam currents of 30μA, at better than 98% focus to the inner Faraday cup, into the interaction region. Contemporary work has concentrated on incident electron beam energies in the range 500-1800 eV. At these energies the overall coincident energy resolution is usually in the range 0.50-0.62 eV (FWHM). Binding energy spectra, at different values of recoil momenta, for both argon and cubane, highlight the performance of the spectrometer and will be presented. In addition, selected momentum distributions (MDs) for the respective valence orbitals in both argon and cubane will also be given. These MDs are compared against theory calculations made within either a distorted wave impulse approximation (argon) or plane wave impulse approximation (cubane) reaction mechanism framework. For the argon calculations Hartree-Fock orbitals were employed, while for cubane an extensive range of density functional theory basis sets were used. Some of the ramifications of the present results will be discussed.

1. INTRODUCTION

Electron momentum spectroscopy (EMS), or (e,2e) coincidence spectroscopy, is now a well developed tool for the investigation of the dynamic structure of atoms and molecules, including electron correlation effects, due to its unique ability to measure the orbital momentum profile for binding–energy–selected electrons[1]. Furthermore, within the distorted wave impulse approximation (DWIA) or plane wave impulse approximation (PWIA)[2], this measured momentum cross section may be directly compared with the calculated spherically averaged momentum distribution (MD) of a specific atomic or molecular orbital, once the appropriate angular–resolution function has been folded in. Hence EMS is also a powerful technique for evaluating the quality of theoretical wave–functions in quantum chemistry[3,4]. More recently, it has been used[3,4] to extract accurate and reliable chemical molecular property information for organic molecules and, finally, we note EMS is also a very important technique for testing the validity of the reaction mechanism description in different theoretical models.

Each of the above roles of EMS will be briefly considered in this short paper. In this particular task we have been aided by the development of an (e,2e) monochromator which has significantly improved our achievable energy resolution, thereby allowing us to unambiguously extract the MDs from the measured binding energy (ε_i) spectra. Specific examples of results for EMS studies on argon (Ar) and cubane (C_8H_8) are detailed later in Sections 4 and 5.

2. EXPERIMENTAL DETAILS

The present experiments were conducted with a noncoplanar symmetric electron–coincidence spectrometer. This spectrometer and the techniques used in the present investigation have been described at length previously[1] and so we do not go into further detail here. We note, however, that there has been three major developments to the coincidence spectrometer since the earlier description. They are, (i) the computer hardware and operating system have been upgraded, (ii) the collision region is now differentially pumped and (iii) an electron monochromator has been brought on-line[5].

The energy resolution of the present measurements was in the range 0.50-0.62 eV (FWHM), the actual value depending on the beam energy under study. The angular resolution was typically 1.2° (FWHM) and the incident beam current was around 30μA. The total energy E: $E_0 - \varepsilon_i = E_A + E_B$ was, respectively, either 500, 1000, 1500 or 1800 eV in the argon work and 1000 eV in the cubane study. The recoil momentum $\mathbf{p}$ was varied by varying the out–of–plane azimuthal angle ϕ over the angular range 0-30°. Binding–energy spectra were taken at each ϕ over the range $\varepsilon_i = 13\text{-}45$ eV for argon and $\varepsilon_i = 6\text{-}35$ eV for cubane, in each case using the binning mode[1].

The high-purity argon was commercially purchased but the cubane had to be synthesised "in–house". A sample of high–purity cubane (~ 1.3 g) was obtained by use of the procedure of Eaton *et al.*[6]. However, in order to obtain respectable yields (~ 45-50%) we found it necessary to change the reported workup procedure. These changes are detailed elsewhere[7]. The cubane we produced was found to be homogeneous with respect to vapour phase chromatographic analysis.

3. THEORY

For our argon EMS study the approximation that we used for the ionisation reaction was the DWIA, whose name implies the weak–coupling approximation for the structure amplitude[1]. The 3p and 3s Hartree-Fock orbitals of Clementi and Roetti[8] were respectively used in the argon calculations to represent each Dyson orbital. The experimental verification of the DWIA depends on the following three criteria: (i) the distorted momentum profile at a particular E must have the same shape for all the states of each orbital manifold, (ii) the cross section ratios for all the states of the manifold must be independent of E and p, and (iii) if enough states have been observed to exhaust each orbital manifold, then the spectroscopic factors (S_i^a), determined by the ratio of the experimental and calculated profiles, must sum to the same number for each manifold. The number is normalised to 1 for a chosen manifold.

In the cubane investigation the PWIA[1], within the Born–Oppenheimer and target Kohn–Sham approximations[9], was used to calculate the (e,2e) cross section. The Kohn–Sham equation of DFT may be considered as an approximate quasiparticle equation, with the potential operator approximated by the exchange–correlation potential. Typically this is known as the local density approximation (LDA). A number of DFT basis sets were used in the computations: DZ94, DZ94P, DZVP, DZVP2, TZ94, TZ94P and TZVP. Here DZ and TZ denote basis sets of double – or triple – ξ quality, while V denotes a calculation in which such a basis is used only for the valence orbitals and a minimal basis is used for the less chemically reative orbitals. The inclusion in the basis of long–range polarisation functions is denoted by P. An improvement over the LDA approach to approximating the exchange–correlation functional can be obtained by using functionals that depend upon the gradient of the charge density. Here we used two different approximations (BP or BLYP) to the exchange–correlation energy functional. The nonlocal density–gradient correction for the nonlocal models was applied self–consistently throughout the entire cubane computations.
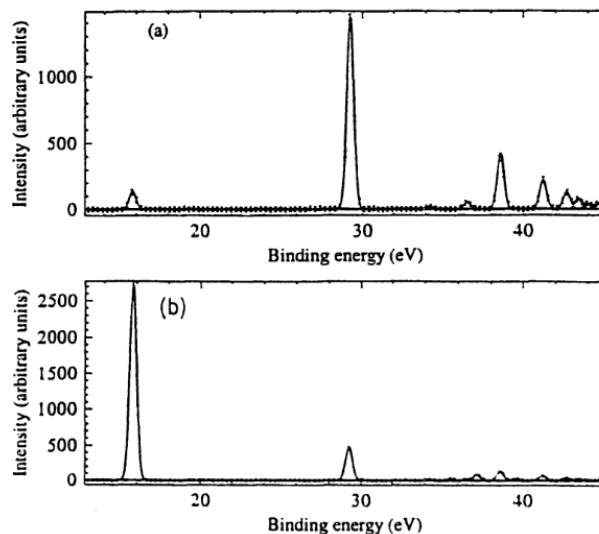
4. ARGON

Figure 1: 1000 eV noncoplanar symmetric EMS binding–energy spectra for argon at (a) $\phi = 0°$ and (b) $\phi = 10°$. The curves show the fitted spectra using the known coincident energy resolution.

The binding–energy spectrum of Ar in the region ε_i = 13-45 eV is shown above in Figure 1 for a total energy of 1000 eV and at ϕ = 0° and 10°. The spectra presented in Figure 1 are considerably better resolved than those published in earlier works[1], reflecting the higher coincidence energy resolution of this work, and thus demonstrate the good performance characteristics of the (e,2e) monochromator. In addition the statistical quality of the current investigation is also improved over that obtained in the earlier EMS work.

Thirteen Gaussian peaks were fitted to the binding–energy spectra measured in this study. Four of them (peaks 1, 4, 6 and 8) had significantly more intensity at ϕ = 10° compared to that at ϕ = 0°, and thus belong to the $^2P^\circ$ manifold. A further eight of these peaks (peaks 2, 5, 7, 9-14) had significantly more intensity at ϕ = 0° compared to that measured at ϕ = 10°, and thus belong to the $^2S^e$ manifold. The classifications for these peaks of $^2P^\circ$ and $^2S^e$ symmetry, their experimental binding energies and the derived S_i^α, at each total energy studied and ϕ = 0° and 10°, can be found in Brunger et al.[10]. At this stage we simply note that the S_i^α for each transition were independent of E and p and also that the $^2P^\circ$ and $^2S^e$ orbital manifold sums were equal to 1 in each case. These observations fulfill criteria (ii) and (iii) of Section 3. The thirteenth peak, at ε_i = 34.20 eV, doesn't correspond to a final state with $^2P^\circ$ and $^2S^e$ symmetry which must occur if, respectively a 3p or 3s electron is ionised in the target Hartree–Fock approximation. Moore[11] noted a state of $^2D^e$ symmetry at 34.20 eV in Ar$^+$, for which she assigned the configuration $3s^2$ $3p^4$ (^1D) 4s ^2D. Such a state can only be excited if there are suitable d-wave correlations in the ground state.

Binding–energy spectra similar to those shown in Figure 1 were also taken over the range of out–of–plane azimuthal angles ϕ = 0 – 30° and at each total energy. From these spectra the relevant MDs were subsequently derived. Although space restrictions prohibit us from actually showing our measured and calculated MDs, we found[10] that for all the transitions of the respective $^2P^\circ$ and $^2S^e$ manifolds and at each total energy studied, the agreement between the DWIA MDs, appropriately scaled with the relevant S_i^α, and the experimental MDs was very good. This fulfills criterion (i) of Section 3. Hence criteria (i) – (iii) have all been fulfilled and thus, in some sense, this EMS study of Ar reports a definitive experiment for electron momentum spectroscopy.

5. CUBANE

Cubane is an unusual polycyclic molecule with carbon skeletal carbon bond angles near 90°, rather than the 109.5° typical of acyclic systems. The molecule has unusual chemical properties such as a very high strain energy, carbon acidity and kinetic stability. In addition cubane has potential for combinatorial chemistry, and as an energetic material precursor.
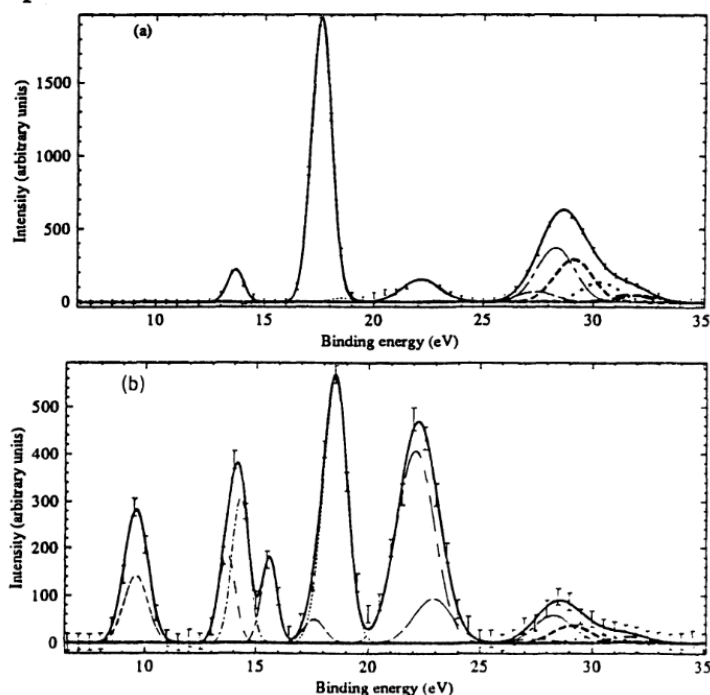

Figure 2: Typical binding–energy spectra from our 1000 eV noncoplanar symmetric EMS study of C_8H_8. The curves show the fit to the (a) ϕ = 0° and (b) ϕ = 10° spectra using the known resolution function.

Binding–energy spectra from our 1000 eV noncoplanar symmetric investigation into cubane at $\phi = 0°$ and $\phi = 10°$ are given above in Figure 2. We again highlight that our improved energy resolution has enabled us to measure "cleaner" spectra. Also note the present study is the first EMS investigation on this unique molecule.

From spectra such as Figure 2 we have derived MDs for all nine valence orbitals ($2t_{2g}$, $1t_{2u}$, $1e_g$, $2t_{1u}$, $1a_{2u}$, $2a_{1g}$, $1t_{2g}$, $1t_{1u}$ and $1a_{1g}$) of cubane. Figure 3, a representative example of this work, shows our theoretical PWIA-DFT MDs for the two outermost valence (degenerate) orbitals of cubane ($2t_{2g}$, $1t_{2u}$) and our corresponding experimental MD. Clearly the TZ94P basis functions are totally inadequate representations of the $2t_{2g}$ + $1t_{2u}$ orbitals, particularly for momenta $\phi < 12°$. Comparison of our experimental and theoretical MDs for each of the valence orbitals enabled us to select an 'optimum' DFT wavefunction for cubane. Here it was with the TZVP basis functions. This wavefunction was then used in conjunction with the UNICHEM package[3,4] to extract the chemically interesting molecular property information. In general, the molecular property data derived using the TZVP basis set was in very good agreement with those determined experimentally by other groups. A full discussion of this can be found elsewhere[7]. However, we note that the present results add to existing evidence[3,4] that *a priori* experimental validation of DFT basis sets using EMS provides a route to determine the most accurate molecular property information for a target of interest.
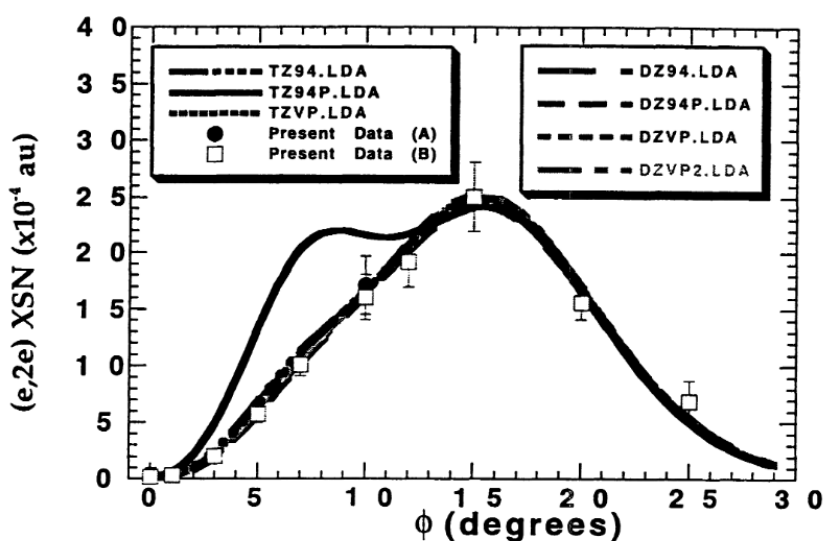

Figure 3: The 1000 eV noncoplanar symmetric MD for the $2t_{2g}$ + $1t_{2u}$ outermost valence states of cubane. The present data for runs A(•) and B(□) are compared against the results of our PWIA-DFT (LDA) calculations: (— -) DZ94, (- - -) DZ94P, (-----) DZVP, (— - -) DZVP2, (— - - - -) TZ94, (—) TZ94P and (- - - - - - - -) TZVP.

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