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Definitive confirmation for through-space bond dominance in the outermost π-orbitals of norbornadiene

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Abstract

High-resolution electron momentum spectroscopy (EMS) has been used to determine the character of the two outermost π-orbitals of norbornadiene. Definitive evidence, from comparisons of measured and calculated momentum distributions, for the dominance of the through-space interaction is presented. This through-space bond dominance is consistent with previous hypotheses based on molecular orbital considerations [Acc. Chem. Res. 4 (1971) 1; J. Am. Chem. Soc. 92 (1970) 706; J. Am. Chem. Soc. 112 (1990) 1710]. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

The electronic structure of norbornadiene (bicyclo[2.2.1]heptadiene) has been of considerable interest as it is the prototypical molecule for the study of through-space and through-bond interactions, concepts originally introduced by Hoffmann and colleagues [1,2,4] and incorporated into an SCF scheme by Heilbronner and Schmelzer [5]. The assignment of the first two ionic states, which arise from the ejection of an electron from the symmetric

(π_+) and antisymmetric (π_-) linear combination of the two ethylenic π bond orbitals: $\pi_\pm = \pi_a \pm \pi_b$, would give information on whether the through-space or through-bond interaction dominates. This follows as if the through-space interaction were to dominate, π_- would be expected [1–4] to be the highest occupied molecular orbital (HOMO), while if the through-bond interaction were to dominate, π_+ would be expected [1–4] to be the HOMO.

Electron momentum spectroscopy (EMS) measures momentum distributions for binding-energy selected electrons. The momentum distributions for transitions to different final states reflect the orbital symmetries [6] and permit allocation of each transition to a particular orbital manifold. This leads to

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clarification in orbital ordering, which thus makes EMS an ideal technique to definitively determine the dominant interaction in the outer most π orbitals for norbornadiene (NBD). Specifically, if the π_- antisymmetric orbital was the HOMO we would expect to observe an experimental momentum distribution (MD) for the HOMO that had small intensity at low momentum [6], whereas if the π_+ symmetric orbital was the HOMO the converse would be true, i.e. its experimental MD would have appreciable intensity at low momentum [6].

Previous photoelectron spectroscopy (PES) studies into the valence electronic structure of NBD include the He(I) measurement from Bischof et al. [7] and the He(II) measurement from Bieri et al. [8]. These results were interpreted by von Niessen and Diercksen [9], using an ab initio many-body Green's function method, to indicate that the HOMO is the $5b_2(\pi)$ orbital (which is essentially the π_- combination). Consequently, von Niessen and Diercksen [9] argued that it is the through-space interaction which dominates between the orbitals π_a and π_b in NBD. This result was consistent with the earlier conclusion of Heilbronner and Martin [10] although, as noted by both von Niessen and Diercksen [9] and Galasso [11], the ordering of the orbital energies is not uniformly reproduced by the calculations so that we believe its definitive confirmation remained open.

In light of this situation Takahashi et al. [12] undertook the pioneering, low-resolution, EMS study on NBD. This work was conducted at a total energy (E) of 1200 eV and an energy resolution (ΔE_{coin}) of 1.5 eV (FWHM). Unfortunately, the HOMO and next-highest-occupied-molecular orbital (NHOMO) in NBD are only separated by 0.85 eV, [7,8] so that they could not resolve them in their binding-energy spectra [12]. In addition, with this broad energy resolution, contributions from the next highest $2a_2$ orbital to the HOMO and NHOMO flux can also not be ruled out. To try and circumvent these difficulties Takahashi et al. [12] used a spectral deconvolution procedure, but the uniqueness of this procedure is debateable in this case as is reflected by the scatter in their data [12] for the HOMO and NHOMO momentum distributions. Thus while their [12] results were consistent with the conclusion of von Niessen and Diercksen [9], for the dominance of the through-space interaction, they are by no means definitive.

Consequently we have made new high-resolution EMS measurements ($\Delta E_{coin} \sim 0.55$ eV, FWHM) and performed plane wave impulse approximation (PWIA) and density functional theory (DFT) calculations, in an attempt to establish beyond doubt whether the through-space or through-bond interaction is dominant in NBD.

2. Experimental and computational details

A detailed description of the experimental apparatus [13] and multiparameter coincidence techniques [14] used in the present non-coplanar symmetric EMS study can be found elsewhere. Briefly, the incident electron energy (E_0) is 1500 eV plus the binding-energy of the struck electron. The binding-energy range of interest is stepped through sequentially at each of a chosen set of angles ϕ ($\phi = 0° - 27.5°$) using a binning mode [14], through the entire set of azimuthal angles ϕ. Scanning through a range of ϕ is equivalent to sampling different target electron momenta (p). Typical binding-energy (ϵ_f) spectra for the complete valence shell of NBD (C_7H_8) in the region 6–33 eV and at a total energy of 1500 eV are given in Fig. 1a ($\phi = 0°$) and b ($\phi = 10°$). Also shown in these spectra are enhancements for the regions of interest to this study. Fig. 1a and b clearly show that peaks 1 and 2 (HOMO and NHOMO, respectively) are resolvable from one another and that both these peaks are well separated from the $2a_2$ orbital [9] (peak 3).

The binding-energy spectra are analysed with a least-squares-fit deconvolution technique [15]. The results of the fit are indicated by the Gaussian curves in Fig. 1, the envelope of the fit being represented by the solid line. The peak positions of the respective Gaussians were set, where available, by the PES results [7,8], while their widths were set from a convolution of the instrumental energy resolution (ΔE_{coin}) and the natural line widths of the various transitions, the latter also estimated from the relevant PES spectrum [8]. This deconvolution analysis then allowed us to derive the required MDs for all [16] the respective valence orbitals of (C_7H_8), including the HOMO and NHOMO that are of specific importance to this paper. Note that while NBD has 18 valence electronic states, 28 Gaussians were actually
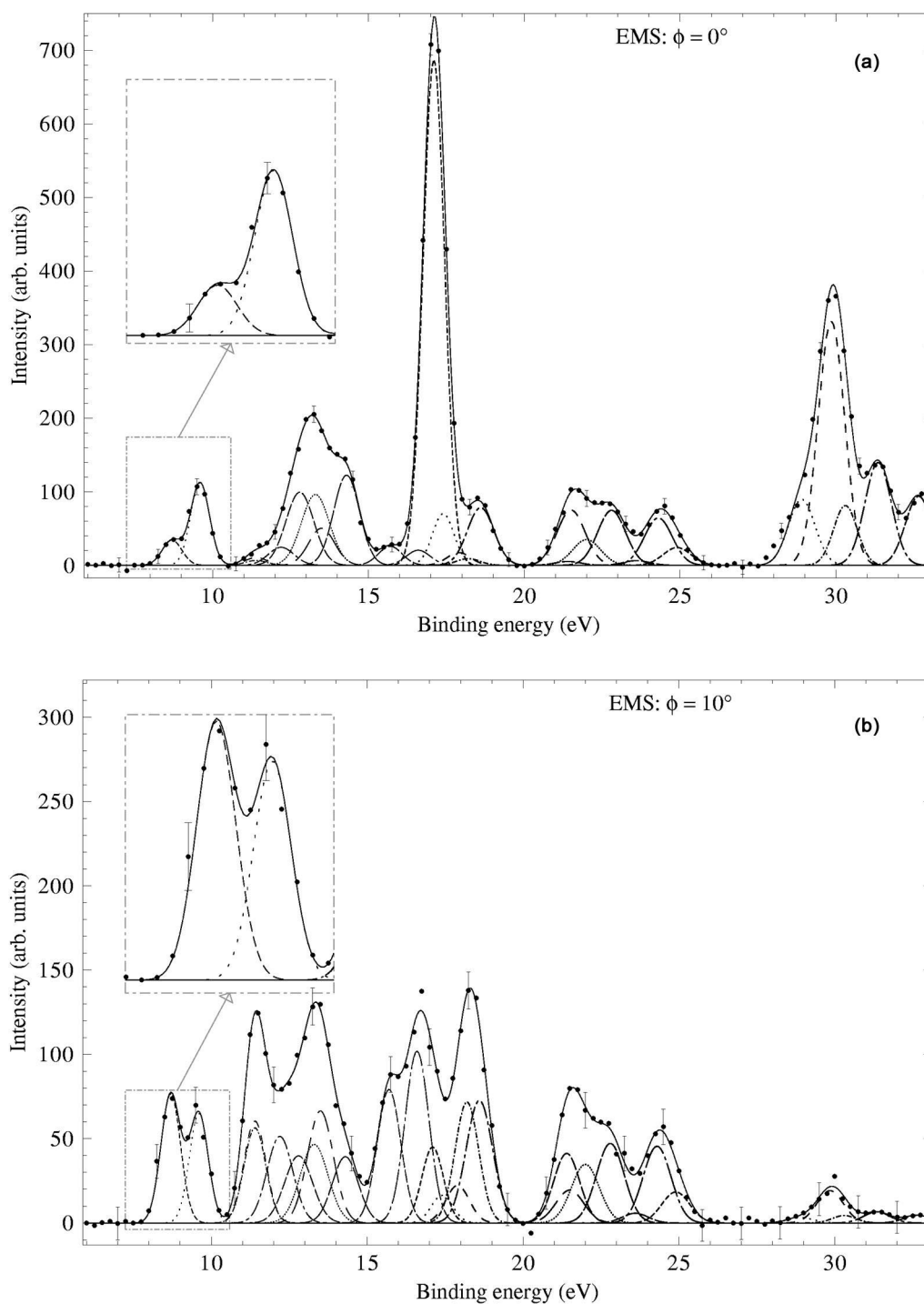
Fig. 1. Typical binding-energy spectra from our 1500 eV non-coplanar symmetric EMS investigation into norbornadiene. The curves show the fits to the spectra at (a) $\phi = 0°$ and (b) $\phi = 10°$ using the known energy resolution.

needed to fit the measured binding-energy spectra. The ten additional Gaussians reflect the effect of final-state correlations on the measured spectra [6], particularly in the inner valence region, as is well known from the results of many-body Green's function calculations [8].

The energy resolution, as noted above, of the present work is $\Delta E_{coin} \sim 0.55$ eV (FWHM). This was determined from measurements of the binding-energy spectrum of helium. The present angular resolution was typically 1.2° (FWHM), as determined from the electron optics and apertures and from a consideration of the argon 3p angular correlation. Commercially available NBD (Aldrich) was distilled under N_2 to ensure high purity. In addition it was degassed in situ by repeated freeze–pump–thaw cycles before being introduced into the interaction region via a leak valve and the EMS experiment performed. Note that there were no detectable impurities observed in any of our binding-energy spectra.

The PWIA is employed to analyse the measured MDs. Using the Born–Oppenheimer approximation for the target and ion wavefunctions, the EMS MD (σ), for randomly oriented molecules and unresolved rotational and vibrational states, is given by: [6,14]

$$\sigma = K \int d\Omega \, |\langle \, p \Psi_f^{N-1} | \Psi_i^N \rangle|^2 \qquad (1)$$

where K is a kinematical factor which is essentially constant in the present experimental set up, Ψ_f^{N-1} and Ψ_i^N are the electronic many-body wavefunctions for the final ion and target ground states, and p is the momentum of the stuck electron at the instant of ionisation. The $\int d\Omega$ denotes an integral over all angles due to averaging over all initial rotational states.

The momentum space target-ion overlap $\langle p\Psi_f^{N-1} | \Psi_i^N \rangle$ is usually evaluated in the weak-coupling approximation [14], so that it is replaced by the relevant orbital of, typically, the Hartree–Fock or Kohn–Sham [17] ground state Φ_0, multiplied by a spectroscopic amplitude. With these approximations, Eq. (1) reduces to:

$$\sigma = K S_j^{(f)} \int d\Omega |\phi_j(p)|^2 \qquad (2)$$

where $\phi_j(p)$ is the momentum space orbital. The spectroscopic factor $S_j^{(f)}$ may be considered as the probability of finding the one-hole configuration j in the many-body wavefunction of the ion. Note that to enable a valid comparison to be made between the theoretical and experimental MDs, the theory was folded with the experimental angular resolution using the planar grid method [14].

The comparisons of calculated MDs with experiment may be viewed as an exceptionally detailed test of the quality of the basis set [6]. In this investigation we have used three basis sets in the DFT computations. These basis sets are denoted by the acronyms: DZVP, DZVP2 and TZVP. The notations DZ and TZ denote basis sets of double- or triple-ζ quality. 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 reactive core orbitals. The inclusion of long-range polarisation functions is denoted by P. The DZVP, DZVP2 and TZVP basis sets are specially designed for DFT calculations [18,19] giving the respective contraction schemes of (621/41/1), (721/51/1) and (7111/411/1) for carbon and (41), (41/1) and (3111/1) for hydrogen. The auxillary basis set corresponding to the DZVP, DZVP2 and TZVP orbital basis sets is called A2 [20], in which the s-, p- and d-orbital exponents were determined separately from an optimisation that reproduces as accurately as possible the energy from an atomic DFT calculation. The contraction schemes of the A2 basis sets for H and C are (4/1) and (8/4/4), respectively.

The DFT calculations were performed using generalised gradient approximation (GGA) methods in the geometry optimisations. In general, our calculations of molecular geometries using the TZVP basis set are in very good agreement with other experimentally determined geometries [25,26]. This point is examined in detail elsewhere [16]. The GGA methods use gradient-corrected functionals based on the Becke–Perdew (BP) exchange-correlation (XC) functionals [21–23] and the Becke–Lee–Yang–Perdew [24] XC functionals in the calculations. All the calculations were performed on an SGI-2 work station and a CRAY J90se/82048 computer employing the computer distribution technique.

The MDs measured in the current EMS study are not absolute, although relative magnitudes for the different transitions are obtained [14]. In this work the experimental MDs are placed on an absolute

scale by summing the experimental flux for each measured ϕ (or p) for the first nine ($5b_2$, $7a_1$, $2a_2$, $4b_1$, $4b_2$, $6a_1$, $3b_1$, $5a_1$ and $3b_2$) outer valence orbitals, and then normalising this to the corresponding sum from the results of our PWIA DFT-BP/TZVP calculation.

3. Results and discussion

The momentum distributions for the first two peaks (HOMO and NHOMO) in our binding energy spectra (see Fig. 1a and b) are given, respectively, in Figs. 2 and 3. It is clear from Figs. 2 and 3 that these

MDs differ significantly from one another. Note that the present results for two independent runs (A and B) are plotted in these figures, and that in all cases for both orbitals they are consistent with each other. Also plotted in these figures are the corresponding (1200 eV total energy) momentum distributions from Takahashi et al. [12] and the MD results from our PWIA-DFT computations for the $5b_2$ and $7a_1$ orbitals. The $5b_2$ orbital PWIA MD results, with BP/DZVP, BP/DZVP2, BP/TZVP and BLYP/TZVP basis sets and XC functionals, reproduce very well the present experimental MD for the HOMO (see Fig. 2). This is a strong indication that the HOMO is the π_- antisymmetric orbital. Similarly, the $7a_1$
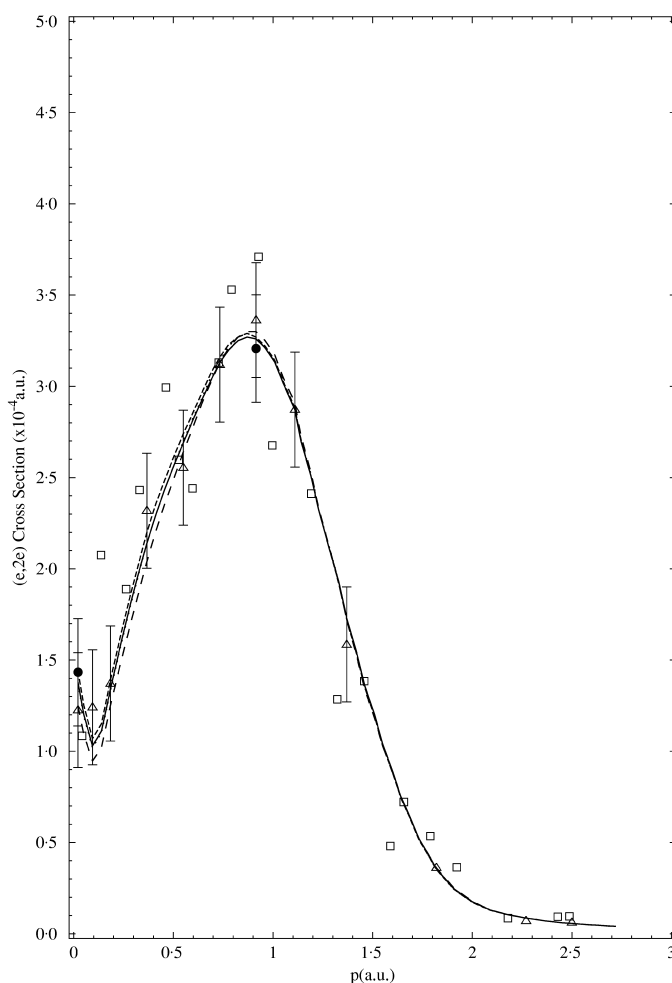

Fig. 2. The 1500 eV symmetric non-coplanar momentum distribution for the $5b_2$ HOMO of norbornadiene. The present data Run A (●) and Run B (△) and the earlier data of Takahashi et al. [12] (□) are compared against the results of our PWIA-DFT calculations: (- –) BLYP/TZVP, (—) BP/TZVP, (- - - - -) BP/DZVP2 and (· –) BP/DZVP. Acronyms are defined in the text.
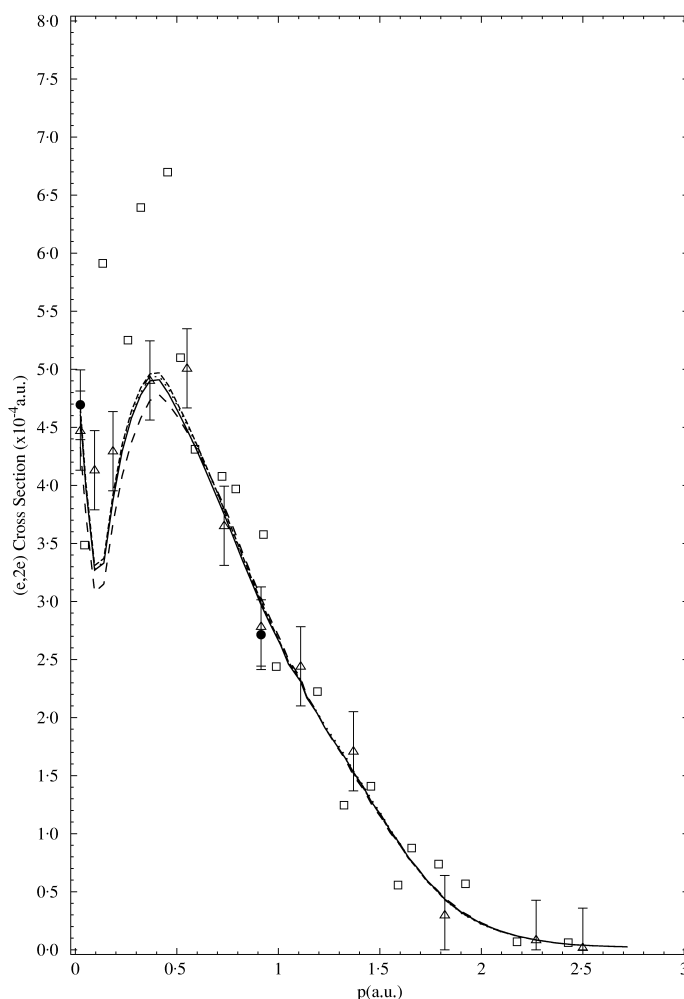
Fig. 3. The 1500 eV symmetric non-coplanar momentum distribution for the $7a_1$ NHOMO of norbornadiene. The legend is the same as that for Fig. 2.

orbital PWIA MD results, again with BP/DZVP, BP/DZVP2, BP/TZVP and BLYP/TZVP DFT basis sets and XC functionals, in this case reproduce very well the present experimental MD for the NHOMO (see Fig. 3). The only exception to this observation is that our $7a_1$ theory momentum distribution with BP/DZVP basis tends to somewhat underestimate the magnitude of the (e,2e) cross section for $p \lesssim 0.4$ a.u., thereby suggesting a limitation with the accuracy of BP/DZVP. Nonetheless, the generally good agreement between our experimental NHOMO MD and our theoretical $7a_1$ MDs is important evidence for the NHOMO being the π_+ symmetric orbital.

While the earlier MD data of Takahashi et al. [12] exhibit more scatter than the present, and have larger uncertainties (not plotted) than the current results, the trend is clear. Namely, for both the HOMO and NHOMO the momentum distribution results of Takahashi et al. [12] are in good qualitative accord with our corresponding measurements. Another interesting observation from the HOMO and NHOMO MDs is that for both these orbitals there is a local minimum in the PWIA-DFT results for $p \sim 0.1$ a.u. The present experimental data provides some support for the existence of these local minima, which may possibly arise due to electron correlation effects.

This behaviour was also observed in our recent EMS study on allene [27], and was considered at length in that paper. In essence Wang et al. [27] found that when electron correlation effects were 'turned off' in the calculations, the minima disappeared. Another possible rationale for the existence of these local minima does, however, exist. Brunger et al. [28] found that such behaviour was also observed when distortion effects became important in the scattering process. However in their case [28] they were considering core states, whereas here we are looking at the outer valence HOMO and NHOMO.

The most exciting result from Figs. 2 and 3 is, however, the following. It is clear from these figures that the (e, 2e) cross section for the HOMO is relatively small at $p = 0$ a.u. (see Fig. 2), while that of the NHOMO (see Fig. 3) has significant strength in the lower momentum region. Since only totally symmetric orbitals can have an appreciable (e, 2e) cross section [6] at $p = 0$ a.u., our result in Fig. 3 unequivocally demonstrates the NHOMO is the symmetric π_+ orbital. Consequently, consistent with the HOMO having a relatively small (e, 2e) cross section at $p = 0$ a.u., the HOMO must be the antisymmetric π_- orbital. Hence the present measurements definitively confirm the dominance of the through-space bond interaction between π_a and π_b in NBD.

Acknowledgements

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