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A UniChem and Electron Momentum Spectroscopy Investigation into the Valence Electronic Structure of trans 1,3 Butadiene

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The experimental (e,2e) coincidence spectroscopy, known as electron momentum spectroscopy (EMS), was applied to the trans 1,3 butadiene (C_4H_6) molecule with detailed binding energy spectra and orbital momentum distributions (MDs) being measured. A small selection of this data is presented. We also report on the utilisation of UniChem computational chemistry codes and the Flinders-developed AMOLD program, which together allow us to calculate theoretical MDs for each orbital, to help elucidate the valence electronic structure of butadiene. In this latter regard we, in addition, present results of our many-body Green's function calculation, to the ADC(3) level, for the binding energies and spectroscopic factors of the respective orbitals of C_4H_6 . A critical comparison between the experimental and theoretical MDs allows us to determine the optimum wavefunction from the basis sets we studied. The determination of this wavefunction then allows us to make further use of the UniChem package to derive butadiene's chemically interesting molecular properties. A summary of these results and comparison of them with the previous results of other workers is presented with the level of agreement typically being good.

1. Introduction

The unique ability of electron momentum spectroscopy (EMS) to measure the orbital momentum profile for binding-energy-selected electrons (McCarthy and Weigold 1991) has made it a powerful technique for evaluating the quality of theoretical wavefunctions in quantum chemistry (Bawagan *et al.* 1987). This property of EMS when combined with high-quality wavefunctions, as calculated using SCF or density functional theory (DFT) procedures in conjunction with sophisticated sets of basis states, allows you to *a priori* judge the validity of the physical representation provided by that wavefunction and hence, in turn, assess the pedigree of the molecular property information derived from the wavefunction. In this paper we report the results from just such a joint study into the complete valence electronic structure for the molecule trans 1,3 butadiene.

In the independent-particle approximation the ground state valence shell electronic configuration of butadiene (C_{2h} symmetry) may be given as $(3a_g)^2 (3b_u)^2 (4a_g)^2 (4b_u)^2 (5b_u)^2 (5a_g)^2 (6a_g)^2 (6b_u)^2 (7a_g)^2 (1a_u)^2 (1b_g)^2$ 1A_g with the two lowest lying virtual orbitals, $2a_u$ and $2b_g$, having π^* character (Jorgensen and Salem 1973). Previous studies into the valence electronic structure of butadiene have been restricted to photoelectron spectroscopy (PES) investigations (see Holland *et al.* 1996 and references therein).

Theoretical investigations into the electronic structure of butadiene have largely concentrated on calculating binding energies and spectroscopic strengths for the respective

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valence states. Greens' function method results due to Cederbaum *et al.* (1978) and Holland *et al.* (1996) are available in the literature, with the latter calculation being very similar to that which we later report. An *ab initio* configuration interaction (CI) level calculation has also recently been reported by Fronzoni *et al.* (1994). However it is clear that, until the present work, no calculations of theoretical MDs for the valence states of butadiene had been performed.

In section 2 we briefly discuss some of the experimental aspects of the EMS technique used in our work, while in section 3 details of our structure calculations are presented. An example of our results for the experimental and theoretical MDs is presented in section 4 with the molecular property information, as obtained from our "optimum" wavefunction, being given in section 5. Finally, in section 6, conclusions from the results of the present study are drawn.

2. Experimental Considerations

A detailed description of the experimental apparatus and multiparameter coincidence techniques used in the present EMS investigation of butadiene can be found elsewhere (McCarthy and Weigold 1991). Briefly, in the present work noncoplanar symmetric kinematics is employed with the two outgoing electrons having essentially equal energies (750eV) and making equal polar angles ($\theta = 45^\circ$) with respect to the incident electron beam. The incident electron energy E_0 is 1500eV plus the binding energy (ϵ_f) of the struck electron. The binding energy range of interest ($\epsilon_f = 4-40$ eV) is stepped through sequentially at each of a chosen set of angles ϕ ($\phi = 0-20^\circ$) using a binning mode (McCarthy and Weigold 1991) through the entire set of azimuthal angles ϕ . Scanning through a range of ϕ is equivalent to sampling different target electron momenta (p).

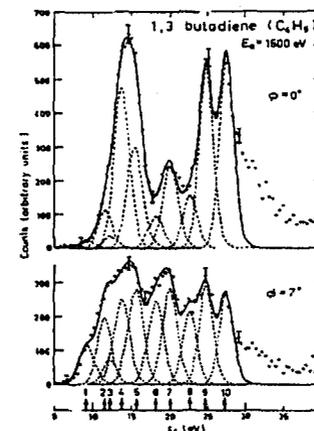


FIGURE 1. Typical binding energy spectra from our 1500eV noncoplanar symmetric EMS investigation into butadiene. The curves show the fits to spectra at $\phi = 0^\circ$ and $\phi = 7^\circ$ using the known energy resolution.

Typical binding energy spectra of C_4H_6 in the region 4-40eV and at a total energy of 1500eV are given in Fig.1. Note that the correspondence between the arrows, denoting the Gaussians used in the fit of these spectra, and the appropriate valence orbitals is detailed in Table 2. These spectra are analysed with a least squares fit deconvolution technique (Bevington and Robinson 1990) in the manner described fully by McCarthy and Weigold (1991). This analysis then allowed us to derive the required momentum distributions for the respective valence states of butadiene.

The energy resolution of the present work, as determined from measurements of the binding energy spectrum of beryllium, is 1.60eV (fwhm). However, due to the natural line widths of the various transitions, as estimated from the PES spectrum of Bieri and Asbrink (1980), the fitted resolutions of the spectral peaks in Fig. 1 for butadiene varied from 2.0 - 2.3eV (fwhm). The angular resolution was $\Delta\phi = 1.2^\circ$, $\Delta\theta = 0.6^\circ$, as determined from the electron optics and apertures and from a consideration of the argon 3p angular correlation. Butadiene of very high purity was introduced into the interaction region via a variable leak valve.

3. Reaction Mechanism and Structure Calculation Details

The plane-wave-impulse approximation (PWIA) is generally used to analyse the measured cross sections for high-momentum transfer ($e,2e$) collisions. In this approximation, and within the Born-Oppenheimer and target Hartree-Fock (THFA) or target Kohn-Sham (TKSA) (Duffy *et al.* 1994) approximations, the ($e,2e$) differential cross section, σ , for randomly orientated molecules is given by,

$$\sigma = K S_j^{(f)} \int d\Omega_p |\phi_j(p)|^2, \quad (3.1)$$

where K is a kinematical factor which is essentially constant in the present experimental arrangement, $\phi_j(p)$ is the momentum space wavefunction for the Hartree-Fock or Kohn-Sham orbital j from which the electron was removed. The spectroscopic factor, $S_j^{(f)}$, is the probability of finding the one-hole configuration j in the expansion of the final ion state f and satisfies the sum rule

$$\sum_j S_j^{(f)} = 1. \quad (3.2)$$

The present SCF wavefunction was computed from basis sets of Gaussian functions. It was constructed at the triple zeta plus polarisation level and employed (11s, 6p, 1d)/[5s, 3p, 1d] for each carbon atom and (5s, 1p)/[3s, 1p] for each hydrogen atom and came from the basis set of Dunning (1971). This SCF wavefunction was computed with the GAMESS program (Schmidt *et al.* 1984) which, in conjunction with the PWIA, allowed us to calculate the theoretical MDs for comparison with experiment. Note that the total SCF energy obtained for this wavefunction was -154.965485 au. Another SCF wavefunction due to Snyder and Basch (1972) was also employed in this study.

In the current theoretical studies we have, however, mainly made use of Density Functional Theory (DFT). Here, to compute the Kohn-Sham (KS) orbital ψ_i , we employed DGauss, a program developed for CRAY Research (Andzelm and Wimmer 1992), which is itself a part of UniChem, a suite of computational quantum chemistry programs. Using DGauss and UniChem we employed various basis sets to build a model butadiene molecule, then we minimised the energy. The molecular coordinates at the optimum geometry (minimum energy) and the Gaussian molecular orbital parameters (coeffi-

cients and exponents) were next treated as input to the Flinders-developed AMOLD program, which computes the momentum-space spherically-averaged molecular structure factor. This is the quantity that is in turn directly comparable to the scattering cross section as measured in the EMS experiment. These comparisons may be viewed as an exceptionally detailed test of the quality of the basis set.

In addition to the two SCF wavefunctions described earlier, we have also used the following seven basis sets in the DFT (DGauss) computations: DZ94, DZ94p, DZVP, DZVP2, TZ94, TZ94p, TZVP. In DGauss, atomic-centered Gaussian atomic orbitals are used to represent the molecular orbitals ϕ_i

$$\phi_i(r) = \sum_{\mu} C_{\mu i} \chi_{\mu}(r) \quad (3.3)$$

The atomic orbital χ_{μ} , centred on atom A , is expressed in terms of a linear combination of Gaussian basis functions and is called a contracted Gaussian:

$$\chi_{\mu}(r) = \sum_{j(l)} d_{j(l)} r^l \exp[-\zeta_j (r - r_A)^2] \quad (3.4)$$

where $l = 0, 1, 2$ labels the type of orbital with $s = 0$, $p = 1$ and $d = 2$; typically, $1 \leq j \leq 10$. In a minimal basis, the number of contracted functions is equal to the number of atomic orbitals occupied in the neutral atom. The double-zeta (DZ) basis, named after the ζ exponent, contains twice as many functions as the neutral atom. Similarly the triple-zeta (TZ) basis contains three times as many functions as the neutral atom. If functions with higher angular momentum than in the isolated atom are included in the set, they are called polarization functions (denoted by p or P). The atomic basis sets in DGauss are designed to provide a DZ or TZ basis for the important valence region, while using a single function to represent the less chemically reactive core orbitals. This is called a double-zeta-valence (DZV) or triple-zeta-valence (TZV) basis, as appropriate. The DGauss basis sets were developed specifically for DFT (Godbout *et al.* 1992).

Table 1 lists the basis sets available in DGauss for the hydrogen and carbon atoms. We used all of them in our studies of butadiene. The notation indicates the number of primitive Gaussians and the contraction scheme. For example, (621/41/1) means there are 3 contracted s -, 2 contracted p - and 1 contracted d -functions. The s -functions consist of 6, 2 and 1 primitive Gaussians while the p -functions consists of 4 and 1 primitive Gaussians.

TABLE 1. Local Spin-Density optimised basis sets used in the DGauss computations

	DZ94	DZ94p	DZVP	DZVP2	TZ94	TZ94p	TZVP
H	(41)	(41)	(41)	(41/1)	(311)	(311/1)	(3111/1)
C	(621/41)	(621/41/1)	(621/41/1)	(721/51/1)	(7111/411)	(7111/411/1)	(7111/411/1)

The present Green's function based calculations on butadiene were performed on the experimental structure (Landolt-Börnstein 1976) using the program system MOLCAS2 (Anderson *et al.* 1991). The basis set employed in this work derives from the atomic natural orbital (ANO) basis set of Widmark *et al.* (1990). For the C atoms it is (14s, 9p, 4d)/[5s, 3p, 1d] and for the H atoms it is (8s, 4p)/[3s, 1p]. The current third-order algebraic diagrammatic contraction (ADC(3)) results for the binding energies and spectroscopic factors are given in Table 2 below along with the corresponding PES results for the orbital energies (Bieri and Asbrink 1980) and the respective orbital binding energies

as calculated from the present SCF wavefunction. Also included in this table are the present EMS results for the binding energies and spectroscopic factors which are found to be in fair accord with those predicted by our ADC(3) - level calculation and with the similar calculation of Holland *et al.* (1996).

TABLE 2. Butadiene binding energies (eV) and spectroscopic factors (in parentheses). Only calculated pole strengths ≥ 0.02 are shown in the table.

Orbital	Gaussian Number	PES	SCF-present	EMS-present	ADC(3)-present
1b _g	1	9.20	8.81	9.20(0.65 ± 0.05) 13.70(0.35 ± 0.05)	8.93(0.87) 14.68(0.02)
1a _u	2	11.50	12.07	11.50(0.70 ± 0.05) 15.50(0.20 ± 0.05) 20.00(0.10 ± 0.05)	11.32(0.61) 13.98(0.28)
7a _g	3	12.20	13.43	12.20(0.87 ± 0.13)	12.25(0.89)
6b _u	4	13.40	14.95	13.70(~1)	13.48(0.86)
6a _g	4	13.90	15.11	13.70(~1)	13.87(0.88)
5a _g	5	15.50	17.51	15.50(~1)	15.39(0.78)
5b _u	5	15.50	17.55	15.50(~1)	19.09(0.05) 15.55(0.20) 15.88(0.61) 20.12(0.04)
4b _u	6	18.10	20.68	18.10(0.85 ± 0.06)	17.40(0.02) 17.92(0.06) 18.17(0.51) 18.91(0.16) 19.50(0.03) 20.12(0.04)
4a _g	7	20.00	22.39	20.00(~1)	18.75(0.04) 19.23(0.12) 19.35(0.11) 19.50(0.21) 20.09(0.06) 20.16(0.03) 20.57(0.14) 20.80(0.03)
3b _u	8	22.60	27.49	22.60(0.62 ± 0.05)	21.87(0.02) 21.98(0.08) 22.85(0.02) 22.93(0.04) 23.03(0.03) 23.17(0.09) 23.29(0.11) 23.41(0.17) 24.03(0.03) 25.73(0.02) 26.67(0.04) 26.69(0.04) 27.38(0.03)
3a _g	9,10	24.80	29.87	13.70(0.07 ± 0.04) 15.50(0.10 ± 0.04) 24.80(0.37 ± 0.04) 27.50(0.38 ± 0.04)	22.02(0.02) 24.50(0.09) 25.14(0.19) 25.31(0.07) 25.63(0.06) 25.85(0.02) 27.74(0.05) 28.15(0.03) 28.23(0.02)

4. Comparison between experimental and theoretical Momentum Distributions

Although the measured momentum distributions are not absolute, relative magnitudes for the different transitions are obtained (McCarthy and Weigold 1991). In the current EMS investigation of the valence states of C₄H₆ the experimental MDs are placed on an absolute scale by summing the experimental flux for each measured ϕ (or momenta, p) for the outervalence states, and then normalising this to the corresponding sum from the result or our PWIA-DFT TZ94p calculation.

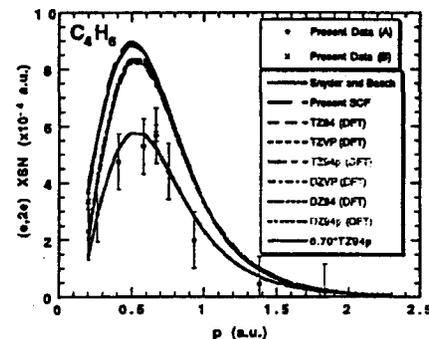


FIGURE 2. The 1500eV noncoplanar distribution for the 1a_u state of butadiene. The present data for runs A(•) and B(x) are compared against the results of our PWIA-SCF and PWIA-DFT calculations, with the respective results for the different basis states being as denoted on the figure.

In Figure 2 we compare our experimental MD for the 1a_u state of C₄H₆ with the results from our PWIA-SCF and PWIA-DFT calculations. It is clear that all the theoretical MDs overestimate the strength of this cross section. However, when our PWIA-DFT, with TZ94p basis, MD is scaled by a factor of 0.70 good agreement is now found between the experimental MD and this scaled theoretical MD. This value of 0.70 represents the experimental spectroscopic factor for the 1a_u state at $\epsilon_f = 11.50$ eV and, as can be seen from Table 2, it is in quite good agreement with the corresponding value from our ADC(3) calculation. This breakdown of the single-particle model of ionisation for an outervalence state in an unsaturated hydrocarbon has been previously considered elsewhere (Holland *et al.* 1996) and whilst it is not common it is not unreasonable (Cederbaum *et al.* 1978).

Space restrictions prevent us from considering our other experimental MDs. However we note that when they are compared against the results of our PWIA-SCF and PWIA-DFT calculations a clear picture emerges. That is, the representation provided by our PWIA-DFT result with TZ94p basis provides the best description of the respective experimental MDs. A full comparison between the present experimental and theoretical momentum distributions will be provided elsewhere (Brunger *et al.* 1997). At this time we simply note that on the basis of that comparison our "optimum" wavefunction for butadiene is provided by the TZ94p basis, which we now employ in determining some of the molecular properties of butadiene.

5. Molecular Properties

Experimental validation of density functional basis sets using EMS may provide a route to optimum basis sets for other molecular properties, such as molecular geometries, bond orders, charge distributions and orbital energies. Previous work (e.g. Traetteberg *et al.* 1994, Wiberg *et al.* 1990) has used *ab initio* molecular orbital approaches to determine structural and electronic properties of butadiene.

TABLE 3: Molecular properties of trans-1,3 butadiene.

Property	Exp. Value	MP2/6-31G*[∞]	MP2/6-31G*[♡]	HF/6-31G*[♡]	TZ94p Present
$r_{C=C}(\text{Å})$	1.341{†} 1.345(2){*} 1.349(1){‡}	1.344	1.343	1.323	1.341
$r_{C-C}(\text{Å})$	1.464{†} 1.465(3){*} 1.467(2){‡}	1.458	1.456	1.468	1.446
$r_{C-H}(\text{Å})$	1.090{†} 1.108(4){*} 1.108(1){‡}	-	1.086 av	1.076av	1.095av
$\angle CCC(^{\circ})$	123.3{†} 123.3(3){*} 124.4(1){‡}	123.7	123.7	124.1	123.9
E(Hartree)	-	-155.423	-155.442	-154.916	-155.448
Bond Order C-C					1.23 (Mayer) 1.27 (ED‡)
Bond Order C=C					1.64 (Mayer) 1.83 (ED‡)

[∞] Traetteberg *et al.* (1994); [♡] Wiberg *et al.* (1990); {†} Bock *et al.* (1989); {*} Landolt-Börnstein (1976); {‡} Kveseth *et al.* (1980); {‡} derived from electron densities at bond critical points.

The results of our DFT calculations using the TZ94p basis set were in good agreement with experimentally-determined molecular properties, and compared favourably with the results from other MO calculations (Traetteberg *et al.* 1994, Wiberg *et al.* 1990). These results are summarised in Table 3.

We also investigated the electron density in the carbon-carbon bonding regions of 1,3 butadiene. In this regard we carried out a study analogous to that of Wiberg *et al.* (1987 a,b) to estimate the electron density (ρ_b) at the bond critical point (Wiberg *et al.* 1987b). We obtained a value of $\rho_b = 0.311 \text{ a.u.}^{-3}$ for the C=C density and 0.258 a.u.^{-3} for the C-C density. We used Wiberg's empirical method to calculate bond orders (n) from the DFT electron densities at the bond critical points:

$$n = \exp\{7.004(\rho_b - 0.224)\} \quad (5.5)$$

This relationship yielded butadiene bond orders of 1.27 for the C-C bonds and 1.83 for the C=C bonds. We also calculated the bond order of the single and double bonds using Mayer population analysis. The C-C bond order of 1.23 and C=C bond order of 1.64 were in good agreement with our values derived from the bond critical point electron densities. Delocalisation was also apparent from the calculated Mayer bond orders and those derived from electron densities.

6. Conclusions

Using EMS techniques we have been able to *a priori* assess, for the large range of basis states we investigated, the quality of these basis states and therefore the validity of the physical representation provided by our respective butadiene wavefunctions. This procedure enabled us to select our optimum wavefunction for butadiene, in this case one calculated within a DFT framework at the triple zeta plus polarisation level, from which the subsequently determined molecular properties were found to be in good accord with the available experimental data and other calculations.

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