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Experimental Momentum-Space Chemistry of Isobutene: Isomeric Effects on Orbital-Specific Electron Momentum Distributions in Isobutene and Its *cis* and *trans* Isomers

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Abstract: The valence-shell electronic structure of isobutene has been investigated by performing molecular (e, 2e) reactions in the symmetric noncoplanar geometry. Experimental momentum distributions (MDs) of selected ionic states have been determined and compared with *ab initio* calculations using self-consistent-field wave functions of 4-31G, 6-31G, and 6-31++G** basis sets. These MD measurements can be used to provide detailed information not only for the evaluation of the quality of *ab initio* wave functions but also for the assignments of two of the more prominent ionic states in the inner-valence region. Furthermore, together with our recent (e, 2e) work, the electronic structure and chemical bonding morphology of the isomeric series iso-, *cis*- and *trans*-butene can be investigated from the unique momentum-space perspective. In particular, although the calculated orbital energies for the corresponding orbitals appear to be similar among the butene isomers, the measured and calculated MDs are found to be qualitatively different, particularly for valence-shell orbitals involving in-plane bonding overlaps in these isomers. The sensitivity of MDs to the different isomeric arrangements of the methyl groups in butene will be discussed in terms of momentum-space chemical concepts.

1. Introduction

The studies of the electronic structure of ethylene and related derivatives continue to attract much recent attentions in quantum chemistry. Ethylene ($H_2C{=}CH_2$) and substituted ethylenes represent the simplest prototypical unsaturated organic molecules with a single C=C bond. A recent (e, 2e) study by Gorunganthu *et al.* discussed the trend in the electron momentum distributions of the highest occupied molecular orbitals (HOMOs) in ethylene and vinyl halides and the plausible relations between the momentum distributions of these frontier orbitals and the reactivities of these molecules.[1] The isoelectronic series of butene ($H_3CHC{=}CHCH_3$) in the iso, *cis*, and *trans* isomeric forms represents an unique homologous group of dimethyl-substituted ethylenes for the study of isomeric effects on the valence-shell electronic structure. This series is valence-isoelectronic to the isomeric series of dichloroethylenes reported earlier[2] and offers an opportunity for comparative study of ligand substitution effects (i.e., the methyl group in butenes vs the chlorine atom in dichloroethylenes). In addition to the numerous He–I photoelectron (PE) spectroscopic studies for all three butene isomers,[3] He II PE spectra were reported for iso- and *cis*-butene by Wiberg *et al.*[4] and for *cis*- and *trans*-butene by Bieri *et al.*[5] Furthermore, theoretical interpretations of the valence-shell photoelectron spectra using *ab initio* multireference configuration-interaction (CI) calculations have been provided by Palmer and co-workers.[6,7]

Recently, we reported the ionization energy (IE) spectra of the valence shells of iso-, *cis*-, and *trans*-butene using symmetric noncoplanar (e, 2e) spectroscopy and photoelectron spectroscopy with monochromatic synchrotron radiation at 100-eV photon energy.[8] A significant number of new many-body features in the inner-valence regions have been observed for the first time in these isomers. Although the PE spectra of all three isomers measured at 100-eV photon energy (corresponding to an effective electron momentum of ~2.5 au for the bound electron before photoejection) were found to be similar to one another, the corresponding (e, 2e) IE spectra measured at electron momenta of ~0 and ~0.7 au showed marked differences among the three butene isomers.[8] The observed differences in the electron-momentum-resolved (e, 2e) IE spectra are indicative of the underlying bonding and electronic structural differences in these isomers. In particular, the majority of the ionic states below ~20 eV are generally found to have p-like angular dependences, which are different for the three isomers. The spectral features above 20 eV are dominated by s-like contributions, and only minor differences in the momentum dependences of these states are observed between isobutene and the other two isomers in this region. The measured (e, 2e) spectra, unlike the PE spectra, are evidently more sensitive to the details of the electronic wave function, particularly in the low-momentum (<2 au) or spatially diffuse region of the molecule.

Spherically averaged electron momentum densities of selected ionic states in the valence region of *cis*- and *trans*-butene have also been determined recently.[9] These so-called momentum distributions (MDs) were compared with theoretical momentum densities of the appropriate orbitals calculated using *ab initio*

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self-consistent-field (SCF) wave functions. Although the MDs of the frontier orbitals (HOMOs) in these butene isomers were found to be very similar to one another, the MDs involving the in-plane σ-bonded orbitals (including, e.g., the next HOMOs or NHOMOs and the first and second inner-valence orbitals) showed prominent differences that are consistent with isomeric changes. In the present work, we present (e, 2e) MD measurements of the remaining isomer, isobutene. Like its *cis* and *trans* isomers, the large number of close-lying ionic states in isobutene precludes individual MD measurements of all the ionic states. However, direct MD measurements of the first two ionic states in the outer and inner valence regions of isobutene are possible. Plausible connection of the observed trends with other isomeric series and/or related C=C containing molecules will also be discussed.

2. Theoretical Background and Experimental Details

Symmetric noncoplanar (e, 2e) spectroscopy or electron momentum spectroscopy has become a powerful technique for probing valence-shell electronic structure and chemical bonding phenomena of atoms and molecules and condensed matter.[10] Details of the (e, 2e) technique for electronic structural investigation[10,11] and its importance to the development of modern quantum chemistry in the momentum-space perspective[12] have been discussed elsewhere. In a typical (e, 2e) reaction, a (gaseous) target is impact-ionized by a high-energy incident electron [with momentum p_0 and energy E_0 (1200 eV plus the ionization energy of interest)], and the resulting scattered and ejected electrons (with momenta p_1 and p_2 and energies E_1 and E_2) are detected in coincidence under appropriate kinematic conditions.[11] If the scattering takes place in a close, binary encounter condition, the momentum of the bound electron, p, is equal in magnitude but opposite in sign to the recoil momentum of the ion and is given by the conservation of momentum. In the symmetric noncoplanar geometry, the magnitude of the momentum p [$= \{[2p_1 \cos \theta_1]^2 + [2p_1 \sin \theta_1 \sin(\phi/2)]^2\}^{1/2}$] can be varied by changing the relative azimuthal angle ϕ [$= \pi - (\phi_1 + \phi_2)$] while keeping p_1 ($= p_2 = 1/2|p_0 - p|$) and θ_1 ($= \theta_2 = 45°$) fixed. Using the plane wave impulse approximation (PWIA) and the target Hartree–Fock approximation, the triple differential cross section can be shown to be proportional to the MD of a characteristic orbital preselected by the sampling IE.[11]

$$\frac{d^3\sigma_f}{d\Omega_1\, d\Omega_2\, dE_1} \propto \int d\Omega\, |\Psi_c(p)|^2 \qquad (1)$$

The MDs can therefore be used to provide insight into the electronic wave function and molecular bonding structure of the initial electronic state on an orbital-by-orbital basis, particularly in the low-momentum or spatially diffuse region.[10]

The symmetric noncoplanar (e, 2e) spectrometer used in the present work has been described previously.[13] Our spectrometer was capable of an energy resolution of 1.7 eV full-width-at-half-maximum (fwhm) and a momentum resolution of 0.12 au fwhm. All other operating conditions of the spectrometer remained effectively constant during the entire experiment and were similar to those in our previous work.[13,14] The sample of isobutene (CP grade, with a minimum purity of 99.0%) was purchased from Alphagaz and used without further purification.

3. Results and Discussion

By following our previous work on *cis-* and *trans*-butene,[9] the experimental MDs of isobutene are compared with spherically averaged momentum densities of the respective orbitals calculated with *ab initio* SCF wave functions using a custom-developed program described previously.[13] The restricted Hartree–Fock (RHF) calculations were performed using a commercial SCF code GAUSSIAN-90[15] with internally optimized geometries and three standard basis sets of different quality (4-31G, 6-31G, and 6-31G++G**). The parameters obtained from geometry optimization (for each of the three bases) were found to be similar to the experimental values reported in an earlier microwave study,[16] with the largest difference being less than 8%. The total energies and other wave function properties obtained for the internally optimized and experimental geometries were also found to be very similar to each other. In addition, the wave functions obtained from the three bases were of similar quality (i.e., near double-ζ quality) and all gave similar values for the total energy and orbital energies of individual orbitals, as well as the same ground-state electronic configuration with an identical orbital ordering. Detailed comparison of wave function properties among the basis sets for the three isomers have been given elsewhere.[8] Although the SCF calculations give orbital energies that are consistently larger than the corresponding experimental vertical ionization potentials (IPs) by ~0.5–2 eV in the outer-valence region, there appears to be remarkably good agreement for the outermost states: $(2b_1)^{-1}$ in isobutene and *cis*-butene and $(2a_u)^{-1}$ in *trans*-butene.[8] Moreover, the experimental IPs of the frontier-orbital states (and the orbital energies of the HOMOs) are found to be effectively identical for all three isomers. This observation is consistent with the presence of a common C=C π bond in these isomers. Furthermore, the IEs of the other outer-valence states for isobutene are found to be generally similar to those of the corresponding states for the *cis* and *trans* isomers. In the inner-valence region, the RHF calculations fail to predict the breakdown of Koopmans' ionization picture.[8] The empirically determined bands represent groups of excited ionic states including those predicted by the multireference CI calculations of Palmer and co-workers.[6,7]

The experimental MDs were obtained sequentially in repetitive sweeps and are therefore relatively normalized with respect to one another. As we are more interested in the trend analysis of individual orbitals in the isomeric series rather than detailed wave function evaluation, only shape comparison will be made in the present work. A p-like MD is single-point-normalized at the maximum to the calculated MD of the 6-31G wave function, and an s-like MD is area-normalized from 0 to 1.5 au to the corresponding 6-31G MD. It should be noted that area normalization is limited only to a momentum value of 1.5 au due to the possible breakdown of the PWIA at higher momentum. Calculated MDs generated from the 4-31G and 6-31++G** bases are then put on a common intensity scale as the corresponding 6-31G MD. In addition, the calculated MDs have been convoluted with an effective instrumental momentum resolution (0.12 au fwhm) before comparing with the experimental data.[13]

Theoretical momentum-space and position-space density contour maps in the appropriate cross sectional planes of the molecule are generated using the 4-31G basis set and are used to illustrate the bonding morphology of individual orbitals. The contour values correspond to 0.1, 0.3, 0.5, 0.7 (dashed lines), 1, 3, 5, 7 (dotted lines), 10, 30, 50, 70, and 90% (solid lines) of the maximum density. The center of the position density map is chosen to be at the C(2) position for isobutene and at the center of the C=C bond in the case of *cis-* or *trans*-butene. The α plane corresponds to the molecular plane that contains all four C atoms (i.e., a σ_v symmetry plane in iso-, *cis-*, and *trans*-butene). The orthogonal plane parallel to and containing the C=C bond is referred to as the β plane (which corresponds to a second σ_v symmetry plane in isobutene). The (remaining) orthogonal plane perpendicular to the C=C bond is denoted as the γ plane. The density maps are useful for qualitative interpretation of the observed features

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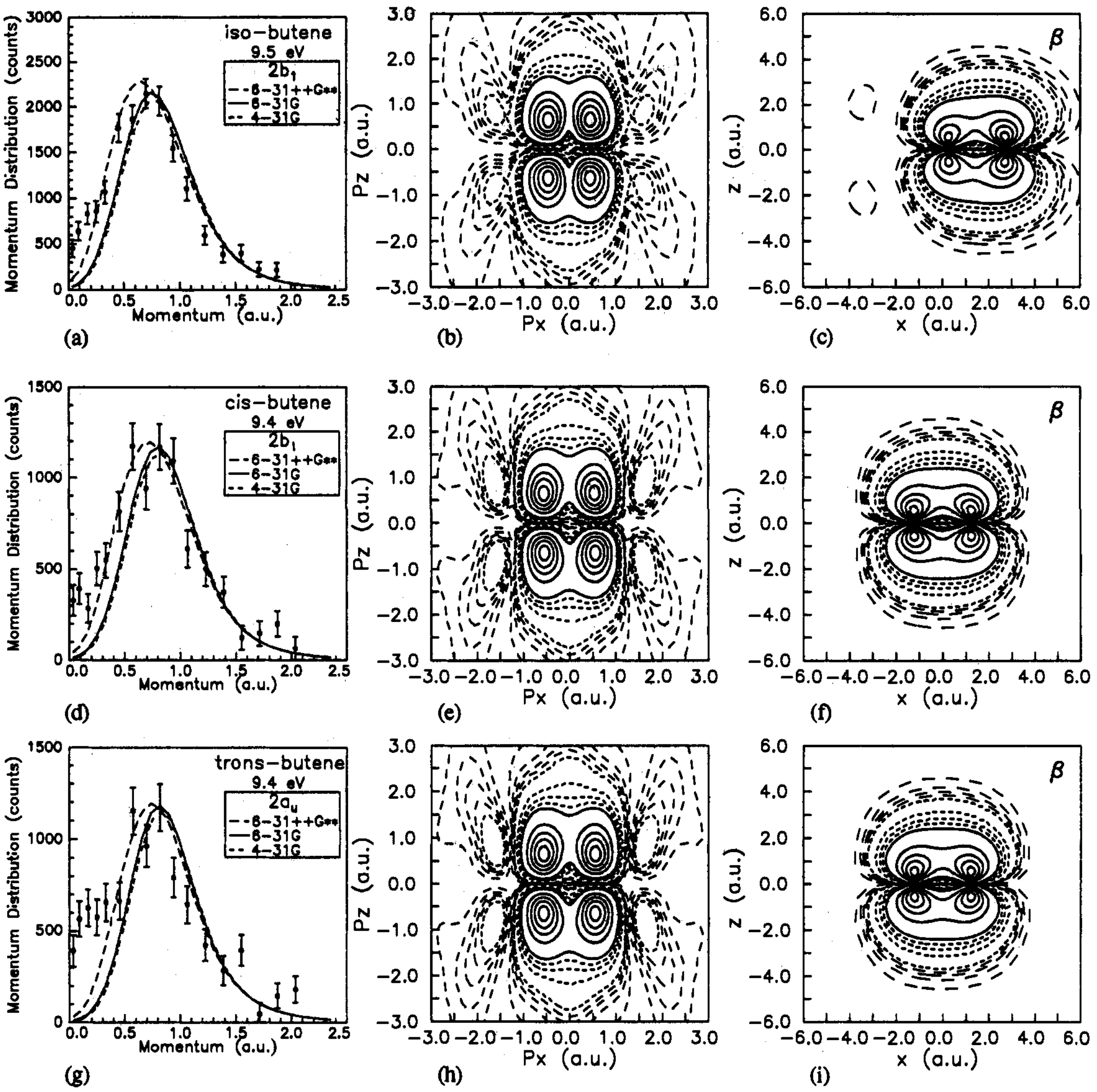

Figure 1. Experimental and calculated momentum distributions (left column) and calculated two-dimensional contour maps of orbital density in momentum space (center column) and position space (right column) for $2b_1$ of isobutene (top row), $2b_1$ of *cis*-butene (center row), and $2a_u$ of *trans*-butene (bottom row). The ionization energies used for the momentum distribution measurements are indicated in a, d, and g. The contour maps (of the predominant orbitals) were generated using the 4-31G basis set. The β contour plane contains the C=C bond and is orthogonal to the molecular plane (α) that contains all four carbon atoms. The contour values are 0.1, 0.3, 0.5, 0.7 (dashed lines), 1, 3, 5, 7 (dotted lines), 10, 30, 50, 70, and 90% (solid lines) of the maximum density.

in the corresponding MDs. In the present case, we may consider a butene molecule as consisting of a C=C backbone with hydrogen atoms and methyl groups attached. Two general types of bonding may be qualitatively classified: in-plane σ and π bonding in the molecular plane (α) and out-of-plane π bonding. In particular, we may identify several possible "elemental" bonding and antibonding components involving $\sigma(C_{2p,2s}-C_{2p,2s})$ and in-plane and out-of-plane $\pi(C_{2p}-C_{2p})$ overlaps between the two ethylenic carbons, $\sigma(C_{2p,2s}-C_{2p,2s})$ overlaps between an ethylenic carbon and its methyl carbon neighbor, $\sigma(C_{2p,2s}-H_{1s})$ overlaps between an ethylenic carbon and its hydrogen neighbor, and $\sigma(C_{2p,2s}-H_{1s})$ and out-of-plane π $(C_{2p,2s}-H_{1s})$ overlaps between a methyl carbon and its hydrogen neighbors (within a methyl group). The bonding features in the position density maps are related to those in the corresponding momentum density maps by the Fourier transform properties.[17,18] Even though a density feature in momentum space in general contains contributions from the entire position space, qualitative correlations between different regions of the molecular density in position space and those in momentum space can be made under appropriate conditions and/or in simple cases (such as diatomic and linear molecules).[10,17,18] For example, the conservation of symmetry properties, the presence of inversion symmetry in momentum space, and the inverse spatial reversal relation between momentum space and position space are evident.[10] Relations concerning different molecular density groups, such as bond directional reversal and bond oscillation effects, can be observed in the case of molecules. These and other aspects of momentum-space chemistry have been discussed in details elsewhere.[10,17,18]

Figures 1 and 2 compare, respectively, the experimental MDs of the HOMOs (X states) and NHOMOs (A states) of all three isomers. The calculated position density maps (obtained using the 4-31G basis set) shown in Figure 1 clearly indicate that the $2b_1$ orbital of isobutene and the HOMOs of the *cis* and *trans* isomers correspond essentially to the out-of-plane (β plane) π $(C_{2p}-C_{2p})$ overlap of the C=C structure and that the methyl groups are not involved. The position densities of the HOMOs of all three isomers are found to be remarkably similar to one another. In particular, the position density map of $2b_1$ in *cis*-butene (Figure 1f) is almost identical to that of $2a_u$ in *trans*-

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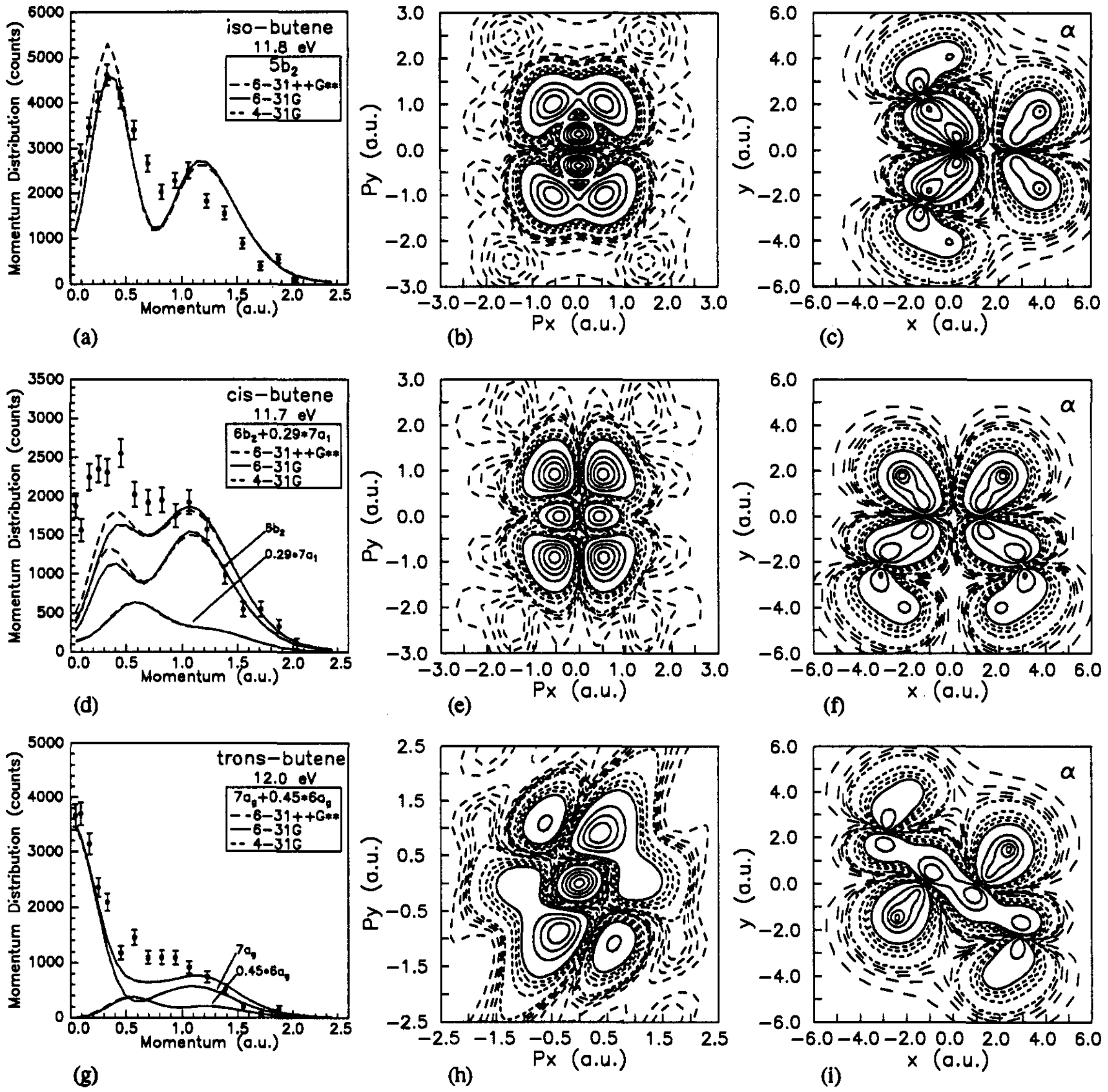

Figure 2. Experimental and calculated momentum distributions (left column) and calculated two-dimensional contour maps of orbital electron density in momentum space (center column) and position space (right column) for $5b_2$ of isobutene (top row), predominantly $6b_2$ of *cis*-butene (center row), and predominantly $7a_g$ of *trans*-butene (bottom row). See Figure 1.

butene (Figure 1i), while that of $2b_1$ in isobutene (Figure 1c) is only slightly distorted at the C(2) position on the side of the methyl groups, in comparison with those of the HOMOs of the other isomers. The corresponding momentum density maps and calculated MDs (of the 4-31G and 6-31G bases) reflect the similarity of the bonding morphology in these orbitals (Figure 1). The $2b_1$ MD of isobutene calculated using the 6-31++G** basis set (i.e., with more diffuse functions) is in good accord with the experimental MD measured at 9.5 eV, with a small discrepancy found below 0.2 au (Figure 1a). In contrast, a significant amount of discrepancy below 0.6 au is observed between the measured MD and the calculated MDs generated using the smaller 4-31G and 6-31G bases, which are similar to each other. The half-widths of the 4-31G and 6-31G MDs are also found to be generally smaller than that of the 6-31++G** MD. The similarity between the 4-31G and 6-31G MDs is to be expected because the addition of more basis functions to better describe the core orbitals (as in 6-31G) should have little effect on the wave functions of the valence orbitals. It is also of interest to note that the orbital energy derived using the 6-31G++G** basis set appears to give a slightly better agreement with the experimental IPs than those obtained with the smaller bases.[8] In the case of the MDs of the HOMOs of *cis*- and *trans*-butene, similar observations can be made. The 6-31++G** MDs again give better agreement with the experiment for these isomers.[9] Except for the location of the maximum at a lower momentum (~0.7 au instead of 0.8 au) and a slightly broader half-width, the 6-31++G** calculated MD of the $2b_1$ orbital of isobutene also closely resembles the corresponding MDs of the HOMOs in *cis*- and *trans*-butene, which are essentially identical to each other. The close resemblance among the measured MDs of the HOMOs of all three butene isomers also provides more direct independent evidence for a common C=C π bonding structure in these orbitals, as was previously suggested on the basis of the observation of essentially identical IEs of the X states found for these isomers.[8]

The position density maps in the α plane for the NHOMOs of isobutene and its *cis* and *trans* isomers (Figure 2) show that the NHOMOs are composed essentially of $\sigma(C_{2p}-C_{2p})$ bonding overlaps between the ethylenic and methyl carbons and $\sigma(C_{2p}-H_{1s})$ bonding overlaps between the ethylenic carbons and their nearest hydrogen atoms. An in-plane $\pi^*(C_{2p}-C_{2p})$ overlap between the ethylenic carbons in the C=C structure is also evident. The overall arrangement of the constituent density groups in the $5b_2$ orbital of isobutene (Figure 2c) is generally similar to that of $6b_2$ in *cis*-butene (Figure 2f), except for the more abrupt change in the σ $(C_{2p}-C_{2p})$ bonding overlaps between the ethylenic and methyl carbons in isobutene. Both density maps reflect the C_{2v} symmetry of the molecules, each with a C_{2v} nodal plane that is orthogonal to the molecular plane (α). The corresponding nodal planes (β plane for isobutene and γ plane for *cis*-butene) are preserved in the corresponding momentum density maps (Figure 2, parts b and e, respectively). In *trans*-butene, no nodal plane in the $7a_g$ orbital is observed in position or momentum space, even though nodal surfaces are evident. Figure 2 also compares the MDs of the A ionic states of the butene isomers. Due to the proximity of the nearby ionic states, the measured MD of the *cis* or *trans* isomer may contain, in addition to the dominant contribution from the NHOMO, a small contribution from a nearby orbital with the appropriate mixing ratio obtained from consideration of the IE spectra.[9] Although the contributions from the nearby states help to reduce the observed discrepancies, some notable differences between experiment and calculations remain and can be attributed to deficiencies in the SCF wave functions of the NHOMOs of these isomers.[9] Except for the 6-31++G** basis set which gives a stronger low-momentum component corresponding to the diffuse basis functions, all three basis functions give rather similar calculated MDs for the NHOMO of a given butene isomer. The measured MDs are, however, in generally poor agreement with the calculated MDs of the three different bases. In particular, the secondary maximum of the measured $5b_2$ MD in isobutene (Figure 2a) is found to be located at 1.1 au, about 0.2 au lower than the calculated MDs. The lower-momentum peak of the measured MD of this orbital with maximum at ~0.3 au is also found to be broader than the calculated ones. Moreover, discrepancies are found at ~0.7 au (i.e., in between the two peaks) and near the momentum origin. The observed $5b_2$ MD therefore indicates that there are more diffuse features (low-momentum components) not accounted for by the SCF wave functions, despite the inclusion of diffuse functions in the 6-31++G** basis. In the case of *cis*-butene, there is considerably more intensity below 0.7 au, relative to the peak at ~1.1 au, in the measured MD of the $6b_2$ orbital (Figure 2d) in contrast to the calculated MDs which contain a stronger higher-momentum peak. Furthermore, like the $5b_2$ MD of isobutene, the measured MD of the $7a_g$ orbital of *trans*-butene (Figure 2g) appears to be more intense in the 0.5–0.9-au region than the calculated MDs.

Unlike the HOMOs, the MDs of the NHOMOs show dramatic differences among the three isomers reflecting the differences in bonding morphology among the three isomers. In particular, the (calculated) MDs of the NHOMOs of both iso- and *cis*-butene contain a double-peak structure. The relative intensity and the location of the maximum for the higher-momentum peak in the *cis* MD (Figure 2d) are both found to be larger than those of the isobutene MD (Figure 2a). In marked contrast to the MDs of its isomers, the MD of the $7a_g$ orbital in *trans*-butene (Figure 2g) has a sp-like structure. Two regions of interest in the MDs can be empirically separated at ~0.7 au. We may qualitatively correlate the densities in these two momentum regions (i.e., $p < 0.7$ au and $p > 0.7$ au) to specific parts of the position-space orbital wave functions for the different spatial isomeric conformations (i.e., iso, *cis*, or *trans* arrangement of the methyl groups). For instance, the higher-momentum (>0.7 au) parts of the $5b_2$ MD of isobutene (Figure 2a) and of the $6b_2$ MD of *cis*-butene (Figure 2d) may be related to the more abrupt $\sigma\,(C_{2p}–C_{2p})$ overlaps between the ethylenic and methyl carbons, while the lower-momentum (<0.7 au) parts may be correlated with the more monotonous $\sigma(C_{2p}–H_{1s})$ overlaps between the ethylenic carbons and their nearest hydrogen atoms. The discrepancy observed in the momentum region between 0.5 and 0.9 au of the $5b_2$ MD of isobutene therefore suggests that the $5b_2$ orbital should be somewhat more localized in the appropriate spatial regions where there are intermediate wave functions gradients.[19] The discrepancy in the lower-momentum region of the $6b_2$ MD of *cis*-butene, on the other hand, suggests that the $6b_2$ orbital wave function should be more delocalized than predicted by the present *ab initio* calculations. Furthermore, the sp-like calculated MDs of the $7a_g$ orbital in *trans*-butene (Figure 2g) may also be empirically divided into two parts: a stronger lower-momentum (<0.7 au) s-like structure corresponding to single-center H 1s densities and a small bonding overlap in the C═C structure, and a relatively weaker higher-momentum (>0.7 au) p-like structure corresponding to single-center C 2p densities and double-center σ molecular overlap terms.[19] The discrepancy in a momentum range similar to that of the isobutene may again be attributed to deficiencies in the SCF wave functions as discussed above.

Figure 3a compares the experimental MD measured at 17.6 eV with calculated MDs of the $6a_1$ orbital of isobutene generated by three different basis sets. The corresponding position density map obtained with the 4-31G basis set shows that the $6a_1$ orbital consists of $\sigma\,[C(2)_{2s}–C(1)_{2p,2s}]$ bonding overlaps between the center ethylenic carbon [C(2)] and the CH_2 group in the C═C structure and of $\sigma(C_{2s}–C_{2p})$ bonding overlaps between the ethylenic carbon and the methyl groups (Figure 3c). The strong C 2s component of the center ethylenic carbon gives rise to a predominant s-like MD, with a secondary maximum (p-like) at ~0.8 au which corresponds to the σ overlaps (Figure 3a). Despite the apparently similar "elemental" bonding groups involved in the molecular orbitals, the $6a_1$ MD of isobutene is found to be quite different from the $4b_2$ MD of *cis*-butene (Figure 3d) and the $4b_u$ MD of *trans*-butene (Figure 3g); the latter MDs are both p-like. The latter two orbitals involve $\sigma^*(C_{2s,2p}–C_{2s,2p})$ overlaps between the ethylenic carbons, which are σ-bonded to the methyl groups.[9] Evidently, the different isomeric arrangements of individual elemental bonding groups give rise to very different MDs for this isomeric series of orbitals. Like the calculated MDs of the corresponding orbitals in the *cis* and *trans* isomers, there is little discernible difference among the calculated MDs of the $6a_1$ orbital generated using the three basis sets (Figure 3a), with the 6-31++G** basis again giving rise to a more intense low-momentum (s-like) component. For the $6a_1$ orbital, generally good accord between the measured and calculated MDs is observed except between 0.4 and 0.9 au, where the experimental MD is found to be larger.

The MD measured at 21.7 eV is compared with calculated MDs of different quality bases for the $5a_1$ orbital of isobutene in Figure 4a. Contributions from the $2b_2$ orbital at the sampling IE have also been included, with the appropriate mixing ratio determined from the IE spectra.[8] The $5a_1$ orbital may be considered as antibonding overlaps between the $\sigma[C(2)_{2p}–C(1)_{2s}]$ bond in the C═C structure and the C 2s orbitals of the methyl groups. Like the first inner-valence orbitals of the butene series, the second inner-valence orbitals again demonstrate the dramatic effect of isomeric arrangement on the molecular orbital densities. In particular, the position density maps show that both the $4a_1$ orbital of *cis*-butene (Figure 4f) and the $4a_g$ orbital of *trans*-butene (Figure 4i) may be regarded as consisting of $\sigma^*(C_{2s}–C_{2s})$ antibonding overlaps between the methyl groups and the C═C bond. The corresponding momentum densities (in the α plane) consist of a finite zero-momentum component due to a single-center contribution of C 2s orbitals and a p-like component corresponding to a two-center contribution arising from the spatial distributions of the C 2s groups.[19] Furthermore, different relative proportions of s-like and p-like components are evident in the MDs of the corresponding orbitals of the *cis* and *trans* isomers. In particular, the s-like component is found to be weaker, equally intense, and stronger than the p-like component in the MDs of the isobutene $5a_1$, *cis*-butene $4a_1$ and *trans*-butene $4a_g$ orbitals, respectively. In the case of the $5a_1$ MD of isobutene, there is essentially no difference among the calculated MDs generated by the three different basis sets (Figure 4a). For the corresponding orbitals in the *cis* and *trans* isomers, the calculated MDs of the 6-31++G** basis set are found to have a stronger low-momentum component in comparison with the MDs generated by the smaller

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(19) Leung, K. T.; Brion, C. E. *Chem. Phys.* **1983**, *82*, 113.

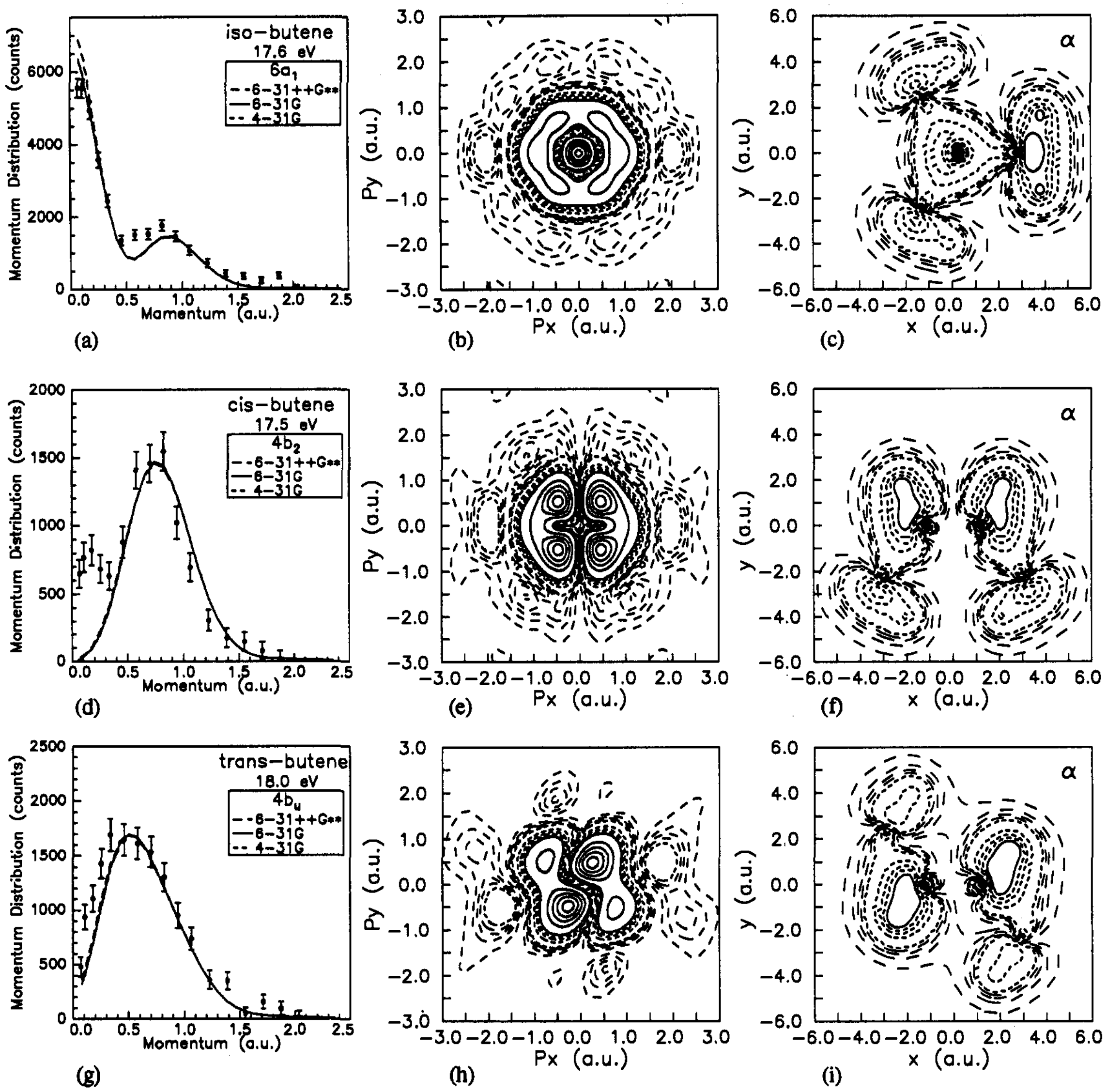

Figure 3. Experimental and calculated momentum distributions (left column) and calculated two-dimensional contour maps of orbital electron density in momentum space (center column) and position space (right column) for $6a_1$ of isobutene (top row), $4b_2$ of *cis*-butene (center row), and $4b_u$ of *trans*-butene (bottom row). See Figure 1.

bases (Figure 4d,g).[9] The experimental MDs of the second inner-valence orbitals are found to have the same general shapes as the corresponding calculated MDs. The MD measured at 21.7 eV (Figure 4a), however, appears to lie closer to the momentum origin than the calculated MDs of the $5a_1$ orbital of isobutene, with noticeable discrepancy below 0.5 au. The discrepancy in the low-momentum region suggests a more delocalized orbital wave function.

4. Summary

The present work compares the MDs of the first two outer-valence (frontier) orbitals and the first two inner-valence orbitals of isobutene with those of the corresponding orbitals of its *cis* and *trans* isomers. Except for the MDs of the HOMOs, the MDs of the other three orbitals are found to be quite different among the butene isomers. The similarities of the (observed and calculated) MDs of the HOMOs in the three isomers (Figure 1) are indicative of a similar underlying bonding structure in the $C{=}C$ π bond, as reflected also by the corresponding position and momentum density maps. In our recent work,[9] we compared the MDs of these π orbitals in *cis* and *trans* butene with those of the $C{=}C$ π orbitals of ethylene and vinyl halides reported by Gorunganthu *et al.*[1] Similar observations can be made in the case of isobutene. In particular, the momentum value corresponding to the maximum of the p-like MD, $p_{\max}$, for the HOMO of iso-, *cis*-, or *trans*-butene is found to be ~0.7 au, which appears to be closer to that of vinyl fluoride (0.64 au), chloride (0.72 au), or bromide (0.73 au) than to that of vinyl iodide (0.57 au) or ethylene (~0.5 au). The similarity in $p_{\max}$ further suggests the general transferability of the π bond density among the butene isomers and the lighter members of the vinyl halide series, although the electronegativity of the ligand(s) may affect the degree of delocalization in this bond.[20] There are also notable similarities between the MDs of the HOMOs of ethylene and vinyl halides and those of the butene isomers, particularly in the half-widths of the MDs (0.7–0.8 au) and the presence of small but finite intensity at zero momentum. The presence of finite intensity in the low-momentum region may indicate delocalization of the π bond as induced by the nearby ligand (halogen vs methyl group). In the calculated MDs of the HOMOs of the butene isomers, the 6-31++G** basis set gives a broader MD which is in better agreement with the experiment than the MDs generated by the smaller 4-31G and 6-31G bases (which are found to be similar to each other).

The measured MDs for the other three orbitals considered in the present work show rather dramatic differences as a result of

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(20) Coplan, M. A.; Moore, J. H.; Tossell, J. A.; Gupta, A. *J. Chem. Phys.* **1979**, *71*, 4005.

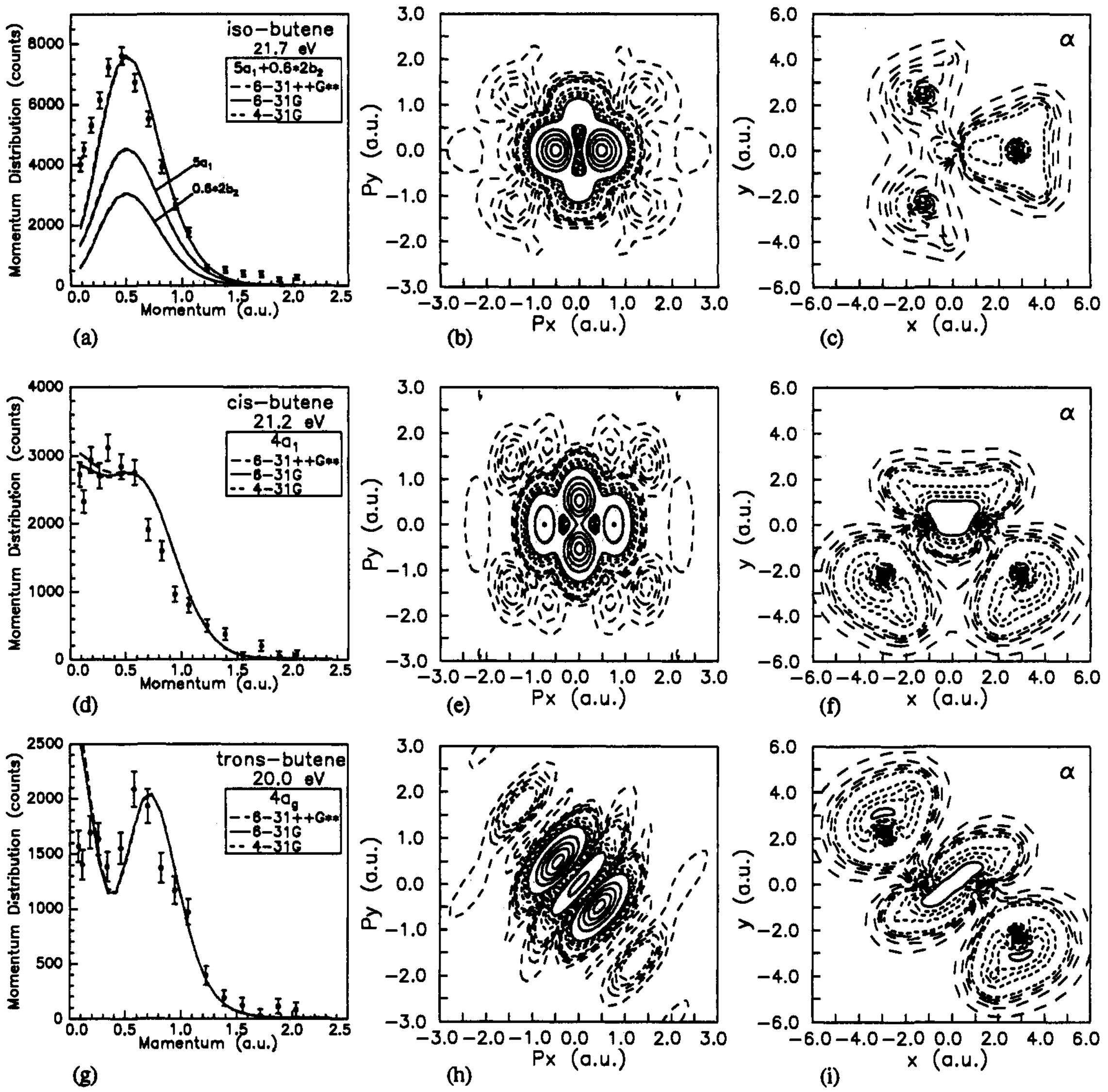

Figure 4. Experimental and calculated momentum distributions (left column) and calculated two-dimensional contour maps of orbital electron density in momentum space (center column) and position space (right column) for predominantly $5a_1$ of isobutene (top row), $4a_1$ of *cis*-butene (center row), and $4a_g$ of *trans*-butene (bottom row). See Figure 1.

the different isomeric arrangements of the constituent in-plane bonding groups. For instance, the NHOMO may be regarded as consisting of "elemental" $\sigma(C_{2p}–C_{2p})$ bonding overlaps between the ethylenic and methyl carbons and is therefore sensitive to the geometry of the isomer (Figure 2). The MDs of these orbitals in isobutene and its C_{2v} isomer (*cis*-butene) are both found to have a double-peak (or pp-like) structure, in marked contrast to the sp-like MD of the *trans* isomer with C_{2h} symmetry. Like the MDs of the HOMOs in these isomers, the 6-31++G** basis set again gives a more intense, broader peak in the low-momentum region of the calculated MD (relative to the MDs generated from the smaller bases) for the $5b_2$ orbital of isobutene (Figure 2a) and the $6b_2$ orbital of *cis*-butene (Figure 2d). The more intense low-momentum features found in the first two frontier orbitals are likely related to the more diffuse basis representation of the C 2p orbital in the 6-31++G** basis set. For the first two inner-valence orbitals, however, the isomers with the same point group symmetry (iso- and *cis*-butene) do not necessarily contain features in the corresponding MDs that resemble each other. In particular, the general features in the MDs of these orbitals for isobutene are distinctly different from those of the corresponding MDs for its *cis* and *trans* isomers (Figures 3 and 4). From the calculated position density maps of these inner-valence orbitals, it is evident that the "constituent" bonding groups are more alike between *cis*- and *trans*-butene. Indeed, the corresponding orbitals of isobutene are generally quite different; the dominant presence and essential absence of the C 2s density at the C(2) position appear to play an important role in the MDs of the $6a_1$ (sp-like) and $5a_1$ orbitals (p-like), respectively. The calculated MDs obtained from the three basis sets are found to be essentially identical, with the possible exception of the $6a_1$ orbital of isobutene (Figure 3a), the $4a_1$ orbital of *cis*-butene (Figure 4d), and the $4a_g$ orbital of *trans*-butene (Figure 4g), where the 6-31++G** basis gives a more intense low-momentum component in the respective MDs. Although the observed difference is consistent with the presence of more diffuse basis functions in the 6-31++G** representation of the C 2s and C 2p orbitals, the more intense low-momentum features are likely due to increased interactions in the "diffuse" two-center terms. It is of interest to note that despite some small discrepancies, there is good general agreement (in the shape) between experiment and calculations in the MDs of the $6a_1$ and $5a_1$ orbitals of isobutene. The observed agreement therefore provides an independent confirmation of the earlier photoelectron assignments of these inner-valence ionic states made by Wiberg *et al.*[4]

Finally, the present work demonstrates that the MD measurements provided by the (e, 2e) technique can offer useful bonding information that is sensitive to the isomeric changes in the butene series. Despite some notable discrepancies for some orbitals, the measured MDs investigated in the present work are in generally good agreement with the calculated MDs generated with the near-double-ζ quality wave functions. The (e, 2e) data therefore have enormous analytical value for elucidating the orbital parentage of individual ionic states in the valence shells of these isomers. Combined with *ab initio* calculations, the MD data are unique in providing new insight into ionic-state-specific bonding morphology associated with these isomeric effects (and the associated stereochemistry), particularly in molecules for which photoelectron data including β parameter measurements are not particularly sensitive.[21] The present work also demonstrates that a significant loss of information occurs due to spherical averaging. The continual development of new techniques to allow true three-dimensional mapping of electron momentum densities of individual ionic states will therefore be of great interest.

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(21) Mintz, D. M.; Kuppermann, A. *J. Chem. Phys.* **1979**, *71*, 3499.