Determining Conformational Preference for Molecules by Electron Momentum Spectroscopy

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Abstract. Many molecules can rotate internally around one or more bonds so that during 360° rotation, they will change between unstable and relative stable conformers. The internal rotation of molecules can lead to much different electron density distributions for certain molecular orbitals (MOs). By comparing the measured electron momentum profiles with the calculated ones, the relative stability of different conformers of 1-butene has been determined, demonstrating that the electron momentum spectroscopy (EMS) is a feasible experimental method to study the conformational preference of molecules.

1. Introduction
Conformational phenomena exist in numerous molecules from simple inorganic compounds to large biomolecules [1-2]. The relative stabilities of conformers (i.e. conformational preference) attract great interest both of theoretical and experimental studies due to the importance in stereochemistry [3-4]. The enthalpy differences of conformers in gas, liquid, or solid phases as well as the relative abundances at various temperatures have been investigated extensively by means of NMR, Raman, infrared, microwave spectroscopy, and various theoretical calculations. Most of these experimental and theoretical studies focused on the determination of the relative stability between conformers in the energetic domain. The conformational effects can also be reflected by the variance of molecular electronic structures. The internal rotation of molecules can lead to much different electron density distributions for certain molecular orbitals. Electron momentum spectroscopy (EMS) is an experimental technique which can effectively image the electron density distributions in momentum space for individual atomic and molecular orbitals [5]. By comparing the measured electron momentum profiles with the calculated ones for the conformers, it is possible to determine the Boltzmann-weighted abundances and thus to predict the relative stability for different conformers involved in the experiment. The conformational effect is taken into account for the first time in the EMS study of electron densities of valence orbital of glycine by Brion and co-workers [6]. More recently, the importance of this effect in explaining the electron momentum profiles of molecules with conformers was further confirmed by the EMS studies of n-butane by Deleuze et al. [7] and Wang et al. [8]. Our recent EMS studies of series molecules have shown that EMS can be a feasible experimental method to study the conformational preference of molecules. In this talk, the results of 1-butene are presented as an example.

The molecule 1-butene, one of the simplest alkene, exists as an equilibrium mixture of high- and low-energy conformers at room temperature. The previous theoretical investigation on the energy barriers of the torsional potential energy surface predicts four low-lying conformers for 1-butene: skew, syn, anti, and gauche. Only the skew and syn conformers have been confirmed by the experiments [9]. However, up to now, the precise equilibrium between these two conformers of 1-butene has not been determined. The skew-syn enthalpy differences in gas, liquid, or solid phases have been investigated extensively by means of NMR, Raman, far-infrared, mid-infrared, microwave spectra, and various theoretical calculations (e.g. CBS-Q, G2) [9-14]. In general, two
contradictory conclusions of the skew-syn conformational stabilities have been derived by the microwave spectroscopy [12] and the calculation studies [9] on one side, and the Raman [11], infrared [10, 14] and NMR [13] spectroscopy on the other side, respectively. In these experiments, the enthalpy is regarded as the key to determine the relative conformational stabilities. The microwave spectroscopy study indicates that the skew conformer is a little more energetically favorable and has a small enthalpy difference 0.15±0.15 kcal/mol with respect to the syn conformer [12]. The Raman [11], NMR [13] and IR [10, 14] studies indicate that the enthalpy of the syn conformer is lower by 0.220 kcal/mol (Raman), 0.10 ± 0.05 kcal/mol (NMR) in the liquid phase and by 0.209± 0.017 kcal/mol (IR) in gas phase than the skew conformer. The CBS-Q and G2 theoretical calculations predicted that the skew conformer is preferred by the enthalpy difference 0.37 kcal/mol and 0.30 kcal/mol with respect to the syn conformer in the gas phase [9]. In this work, the relative stability of the two conformers of 1-butene has been determined by comparing the measured electron momentum profiles with the calculated ones.

2. Experimental and theoretical background

The details of the present EMS spectrometer have been given elsewhere [15]. Briefly, the gas phase target molecules are ionized by the impact with a high-energy incident electron beam (1200 eV + binding energy). The outgoing scattered and ejected electrons which have equal scattering polar angles ($\theta_1 = \theta_2 = 45^\circ$) and energies ($E_1 = E_2$) are received by two hemispherical electron energy analyzers with a five-element electron optical lens system. The relative azimuthal angle $\phi$ between the two outgoing electrons is variable over wide range ($0^\circ \sim \pm 30^\circ$) by rotating one analyzer around the incident electron beam and keeping another one fixed. According to the energy and momentum conservation, the binding energy and momentum the target electron can be obtained by measuring the energies and momenta of the incident ($E_0, p_0$) and two outgoing electrons ($E_1, p_1$ and $E_2, p_2$). At non-coplanar symmetric geometry ($p_1 = p_2$), the magnitude of momentum of the target electron is given by

$$p = \left\{ \left( 2p_1 \cos \theta - p_0 \right)^2 + \left[ 2p_1 \sin \theta \sin (\phi/2) \right]^2 \right\}^{1/2}$$

where $p_0, p_1$ are the magnitudes of momenta of incoming and outgoing electrons, $\theta$ and $\phi$ are the polar angle and relative azimuthal angle, respectively. The energy and momentum resolution of the present EMS spectrometer is determined to be ~1.1 eV [full width at half maximum (FWHM)] and 0.15 a.u., respectively, by measuring Ar $3p$ ionization.

In such experimental condition, the plane wave impulse approximation (PWIA) provides a good description for electron-impact single ionization process. Within the target Hartree-Fock approximation (THFA) or Kohn-Sham approximation (TKSA), the triple differential cross-section (TDCS) $\sigma_{EMS}$ for randomly oriented gas phase molecules can be described as [5,16]

$$\sigma_{EMS} \propto \int d\Omega_p \left| \varphi_q(p) \right|^2$$

where $\varphi_q(p)$ is the momentum space one-electron canonical HF or the KS wavefunction for the $q$th MO from which the electron ejected. The integral in Equation (2) is known as the spherically averaged electron momentum distribution, or electron momentum profile.

Density functional theory (DFT) calculation using B3LYP hybrid functional with the 6-311++G** basis set was employed to optimize the molecular geometries of the skew, syn, conformers of 1-butene. The optimized geometrical parameters are in good agreement with the microwave experimental values [12]. The theoretical momentum profiles (TMPs) for the valence orbitals of the skew and syn conformers were calculated using Equation (2) with the Kohn-Sham orbitals obtained by B3LYP/6-311++G**. All the present calculations were carried out using GAUSSIAN 03 program [17].
3. Results and Discussions

3.1. Binding energy spectra

The skew and syn conformers of 1-butene are $C_1$ and $C_s$ symmetries, respectively. Their corresponding ground state electronic configurations are

\[
\text{(core)}^8 (1a)^2(2a)^2(3a)^2(4a)^2(5a)^2(6a)^2(7a)^2(8a)^2(9a)^2(10a)^2(11a)^2(12a)^2 \quad \text{(skew conformer)}
\]

\[
\text{inner–valence} \quad \text{outer–valence}
\]

and

\[
\text{(core)}^8 (1a)^2(2a)^2(3a)^2(4a)^2(5a)^2(1a)^2(6a)^2(7a)^2(2a)^2(8a)^2(9a)^2(3a)^2 \quad \text{(syn conformer)}.
\]

\[
\text{inner–valence} \quad \text{outer–valence}
\]

The 32-electron molecule of 1-butene has 12 individual valence orbitals. The binding energy spectra (BES) in the range of 6-27 eV have been measured at 16 different relative azimuthal angles ($\phi$). The ones at the $\phi = 1^\circ$ and $9^\circ$ are displayed in figure 1. Due to the low energy resolution of the present EMS experiments, only nine Gaussian peaks (p1-p9 in figure 1) are fitted to the BES in which 12 valence MOs are included. The widths for the Gaussian peaks are determined by the EMS instrumental energy resolution (1.1eV in the present work) convoluting the Frank-Condon widths of the corresponding bands observed in the HeI UPS [18].

![Figure 1.](image_url)
(for p1 to p6) and those observed in SRPES [19] (for p7 to p9). The positions of each Gaussian peaks are determined by the ionization potentials reported by high-resolution PES experiment [18, 19]. Small adjustments have been applied to compensate the asymmetries of the shape of the Frank-Condon profiles. The nine fitted peaks are indicated by dashed lines while the overall fitted spectra are represented by the solid lines.

As shown in figure 1, the first peak (p1) at 10.0 eV is well resolved and corresponds to the ionization from the high occupied molecular orbitals (HOMO) of 1-butene, i.e., 12a orbital for the skew and 3a″ orbital for the syn conformers. The next four peaks (p2 –p5) located at 12.0 eV, 13.4 eV, 14.8 eV and 15.9 eV represent ionizations from the MOs of 11a′+10a/9a″′+8a′ (p2), 9a+8a/2a″′+7a′′ (p3), 7a/6a′ (p4) and 6a+5a/1a″′+5a′ (p5). The last four peaks (p6 –p9) located at 18.3 eV, 20.5 eV, 22.7 eV and 24.4 eV correspond to ionizations from the four innermost valence orbitals, i.e., 4a/4a′ (p6), 3a/3a′′ (p7), 2a/2a′ (p8) and 1a/1a′′ (p9).

3.2. Conformational Preference Determined by Electron Momentum Profiles

The experimental momentum profiles (XMPs) are extracted by deconvoluting the respective peaks from the sequentially obtained binding energy spectra at 16 different azimuthal angles φ and plotting area under the corresponding fitted peaks as a function of momentum p. To compare the TMPs with the XMPs, a momentum resolution of δp = 0.15 a.u. of the spectrometer was folded into the TMPs. The experimental and theoretical results are placed on a common intensity scale by normalizing the TMP for HOMO (12a/3a″′) to XMP.

![Figure 2.](image)

**Figure 2.** (a) The summed experimental and theoretical momentum profiles of 1-butene for ionization bands at peak4 and 5 of BES. (b)-(d) Theoretical momentum profiles and density surface plots (B3LYP/6-311++G**) for individual orbitals of the two conformers of 1-butene.

The summed XMP for peaks 4 and 5 located at 14.8 eV and 15.9 eV, which can not be well resolved by the present energy resolution, are shown as solid circles in figure 2a. Since 1-butene
coexists in two conformers, peak 4 and 5 actually contains ionizations from six orbitals, 7a (skew), 6a’ (syn) in peak 4 and 6a, 5a (skew), 1a”, 5a’ (syn) in peak 5. The TMPs for individual orbitals are shown in figure 2b-2d respectively. The corresponding orbital density surface plots in position space for the two conformers are also displayed on the right hand side of each figure. The discrepancies between the individual TMPs of the two conformers are obvious, especially in the low momentum region. As can be seen in figure 2b, the TMP for 7a orbital of the skew conformer displays a ‘sp-type’ character with a secondary maximum at $p \sim 1.0$ a.u. and the orbital plot exhibits that the electron density mainly distributes on the C=C double bond and the ethyl group. On the other hand, the momentum profile of 6a’ orbital of the syn conformer presents mainly a ‘p-type’ character with a maximum at $p \sim 0.4$ a.u.. The orbital plot shows that the electron density also distributes mainly on the C=C double bond and the ethyl group. The different symmetry of momentum profiles for these two orbitals can clearly be attributed to the orientation of methyl group leading to the two conformers of 1-butene. The orbital plots in figure 2c show that both 6a orbital of skew conformer and 1a” of syn conformer have electron densities predominantly distributed on the ethyl group and exhibit pseudo $\pi$ character. In this way, the TMPs for these two orbitals are both ‘p-type’ in nature with maximum at $p \sim 0.5$ a.u.(syn) and 0.6 a.u.(skew) respectively. The TMPs for 5a’ orbital of the syn conformer and 5a orbital of the skew conformer display more complicated shapes as shown in figure 2d. But the discrepancy at low momentum region is discernable. Both of these two orbitals are mainly C=C $\pi$ orbitals with obvious electron density distributions on ethyl group as depicted by orbital plots. Significant differences in electron momentum profiles between the skew and syn conformers for individual orbitals can be observed in summed TMPs for two conformers (dotted line for skew and dashed line for syn) as shown in figure 2a. In order to best fit the summed XMP, relative conformational abundances of 65% for skew conformer and 35% for syn conformer should be taken into account in summing the conformational TMPs. The result is shown as solid line in figure 2a. In this way, the Boltzmann-weighted abundances for different conformers of 1-butene at room temperature (298K) are then determined, indicating that the skew conformer is the preferential one.

Table 1. Skew-Syn Relative Energies for 1-Butene at Room Temperature (298K).

|                | Theoretical[9] | Experimental |
|----------------|----------------|--------------|
|                | CBS-Q          | G2           | MW[12] | Raman[11] | NMR[13] | IR[10] | EMSa |
| $\Delta G$ (kcal/mol) | 0.47           | 0.40         | 0.37   |           |         |        |      |
| $\Delta H$ (kcal/mol) | 0.37           | 0.30         | 0.15±0.15 | -0.220 | -0.10±0.05 | -0.209±0.017 |

* This work

As mentioned in the introduction, the relative stability of the conformers of 1-butene is still a controversial issue. In general, all the previous experiments predicated that the syn conformer is more stable than skew except the MW work [10-14], while various levels of theoretical calculations predict an inverse order [9]. The skew-syn relative enthalpies $\Delta H$ obtained by the previous experiments are listed in Table 1, together with the theoretically calculated skew-syn relative Gibbs free energies $\Delta G$ and enthalpies $\Delta H$ by CBS-Q and G2 methods. The exact equilibrium conformational abundances depend on the Gibbs free energy difference $\Delta G$ of the two conformers. The conformation equilibrium constant ($K_T$) can be simply estimated by the following equation:

$$\ln K_T = -\frac{\Delta G}{RT}$$

(3)

where $RT = 0.592$ kcal/mol at room temperature and the Gibbs free energy has a relationship with enthalpy and entropy as $\Delta G=\Delta H-T\Delta S$. By substituting the above-gained relative conformational abundances in Equation (3), a relative Gibbs energy of 0.37 kcal/mol can be obtained, which is in a good agreement with the previous results of G2 calculations [9].
4. Conclusions

In summary, the investigation of the conformational preference for 1-butene by comparing the XMP with the conformation-weighted TMPs has been reported. Relative conformational abundances of 65% for skew conformer and 35% for syn conformer were obtained and skew-syn relative Gibbs energy of 0.37 kcal/mol was deduced, indicating that the skew conformer is the preferential one for the molecule of 1-butene.

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References

[1] Tarnovsky A N, Sundstrom V, Akesson E and Pascher T 2005 J. Phys. Chem. A. 109 954
[2] Ha T K, Wakahara T, Nagase S and Kobayashi K 1993 J. Am. Chem. Soc. 115 11939
[3] Saha S, Feng W, Falzon C T and Brunger M J 2005 J. Chem. Phys. 123 124315
[4] Galasso V 1995 J. Chem. Phys. 102 7158
[5] McCarthy I E and Weigold E 1991 Rep. Prog. Phys. 54, 789
[6] Neville J J, Zheng Y and Brion C E 1996 J. Am. Chem. Soc. 118 10533
[7] Deleuze M S, Pang W N, Salam A and Shang R C 2001 J. Am. Chem. Soc. 123 4049
[8] Wang F and Downton M 2004 J. Phys. B: At. Mol. Opt. Phys. 37 557
[9] Murcko M A, Castejon H and Wiberg K B J. Phys. Chem.100 16162
[10] Bell S, Drew B R, Guirgis G A and Durig I R 2000 J. Mol. Struct. 553 199
[11] Durig J R and Compton D A C 1980 J. Phys. Chem. 84 773
[12] Kondo S, Hirota E and Morino Y 1968 J. Mol. Spectrosc. 28 471
[13] Bothner-By A A and Naar-Colin C 1961 J. Am. Chem. Soc. 83 231
[14] Gallinella E and Cadioli B 1997 Vibr. Spectrosc. 13 163
[15] Yang B, Chen X J, Pang W N and Chen M H 1997 Acta. Phys. Sin. 5 862
[16] Duffy P, Chong D P, Casida M E, Salahub D R 1994 Phys. Rev. A50, 4707
[17] Firsch M J, Trucks G M and Schlegel H B 2003 GAUSSIAN 03 Revision B 04 Gaussian Inc. Pittsburgh PA
[18] White R M, Carlson T A and Spears D P 1974 J. Electron. Spectrosc. 3 59
[19] Bawagan A D O, Desjardins S J, Dailey R and Davidson E R 1997 J. Chem. Phys. 107 4295