The Molecule of the Month --- October, 2004

n-Butane

Recognition of Chemical Bonding Mechanism of Normal Butane Conformers In Momentum Space

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Introduction

Butane (C_4H_{10}) is a colorless, flammable hydrocarbon that is present natural gas and can be obtained when petroleum is refined. Butane is a gaseous alkane. It is extremely stable, has no corrosive action to metal, slightly soluble in water and readily soluble in alcohol, ether and chloroform.

Butane is typically used in the manufacture in the following areas

- Aviation fuels and organic chemicals,
- As fuel for cigarette lighters and portable stoves,
- A raw material for synthetic rubber and high octane liquid fluids,
- Manufacture of ethylene and solvent, propellant in aerosols,
- A calibration gas for temperature and pressure gauges and as a heating fuel.
- Butane is also added to gasoline in order to increase its volatility (evaporation rate) in cold climates.
- Recent concerns about the destruction of the ozone layer by freon gases has led to an increase use of isobutene gas in refrigerating systems.

Butane exists as two isomers: **n-butane** is a fully hydrogenated linear chain of four carbon atoms: $CH_3CH_2CH_2CH_3$ and **i-butane**, or **isobutane**, has the formula $CH_3CH(CH_3)_2$, and the systematic name **2-methylpropane**. Butane is also a protoype in organic and structural chemistry for structural (constitutional) isomers and conformational (stereoisomers) isomers. Normal butane is known as n-butane and its chemical structure looks like

```
    H   H   H   H
    |   |   |   |
H - C - C - C - C - H
    |   |   |   |
    H   H   H   H
```

Conformational isomers have the same attachment of atoms but different spatial arrangements caused by rotation about single bonds [1]. Although conformers are usually difficult to isolate, in any group of conformers one form is likely to be more stable than any other, and therefore all molecules of that compound will spend most of their time in the most stable conformation. The process of conformational analysis allows one to predict relative stability of various conformations, and to gain insight into the behavior of that compound in a chemical reaction.

Of particular interest and importance are the normal butane conformers produced by rotation about the central carbon-carbon bond ($C_{(1)}$-$C_{(2)}$), as shown in Figure 1.

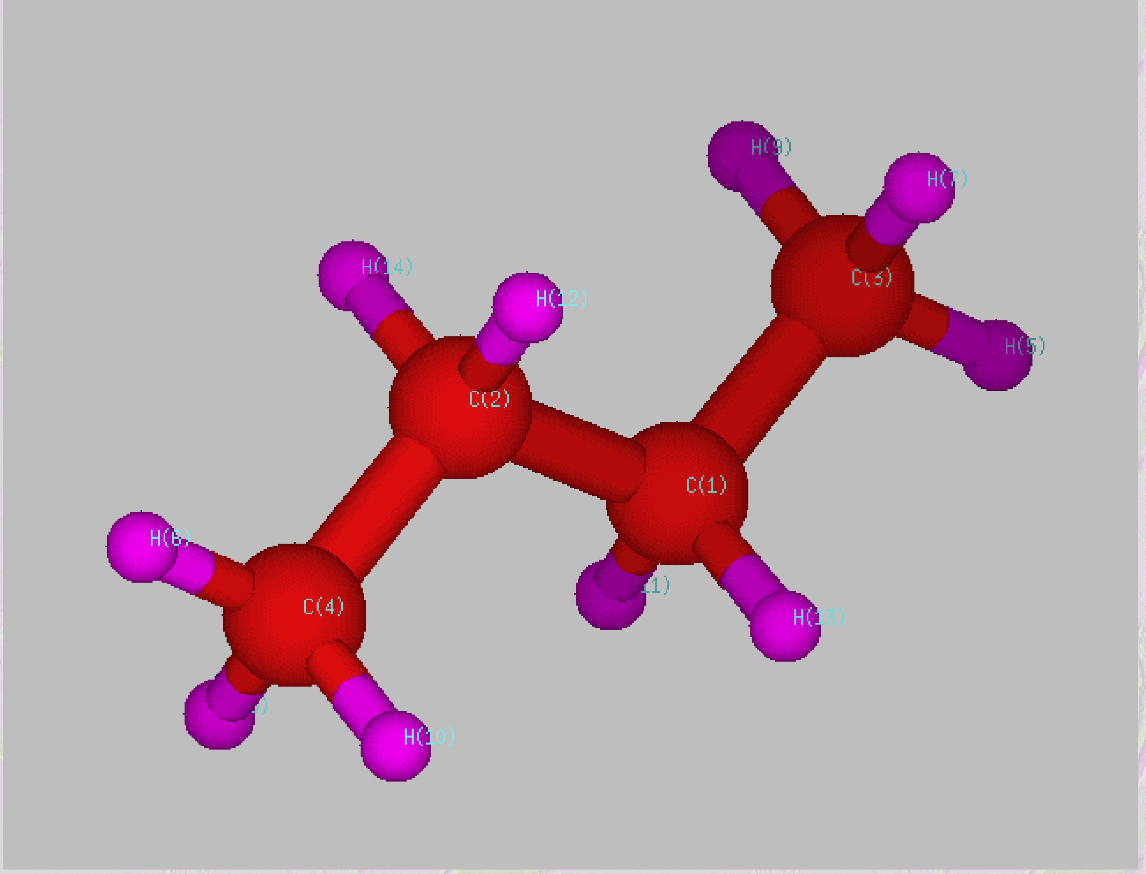

Fig. 1 Normal butane structure (A).

Conformers of n-Butane

Among these rotationally generated n-butane comformational isomers, we shall focus on two staggered conformers (**A & C**) and two eclipsed conformers (**B & D**), shown below in Figure 2 as the representable positions on the rotational potential energy curve [2].

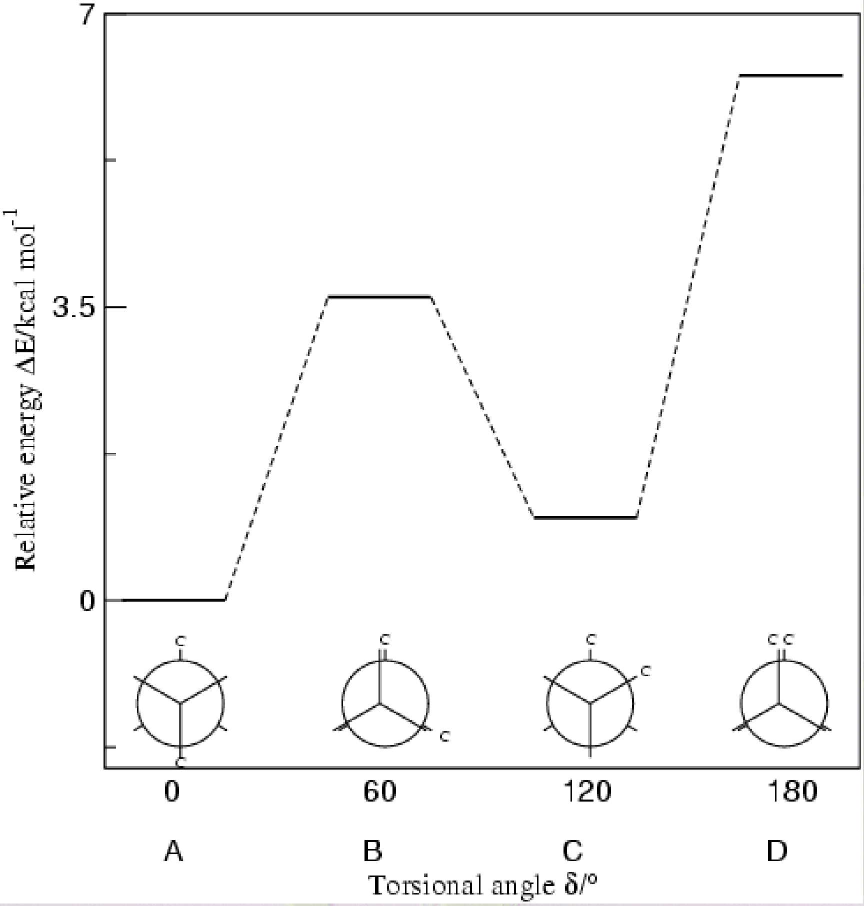

Fig. 2 Rotational energy curve of n-butane calculated by B3LYP/TZVP model.

The stereo-representation of the butane conformers presented in above potential energy curve is given below in Fig.3. The staggered conformers are more stable than the eclipsed conformers by 2.8 to 4.5 kcal/mol. Since the staggered conformers represent the chief components of a butane sample they have been given the identifying prefix designations **anti** for A and **gauche** for C [3].

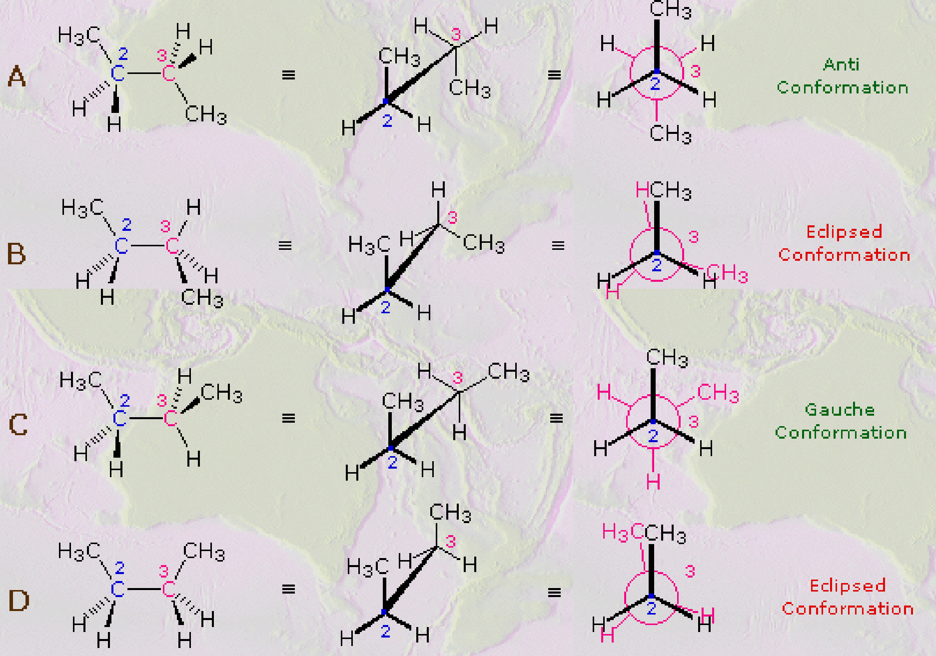

Figure 3 shows the normal butane conformers in several stereo-representations.

As these n-butane conformers exhibit very small energy differences in their structures, which results in demanding on the experiemental resolution to observe (when isolation is possible). Theoretical methods such as quantum mechanical means therefore, plays an important role in the study of conformers of organic and biological species. In the conventional coordinate space, however, the energy insensitive properties such as anisotropic (angular dependent) properties and chemical bonding mechanisms, are challenges to design new and sensitive experimental means for their observation.

Electron Momentum Spectroscopy and Dual Space Analysis

Electron momentum spectroscopy (EMS) in conjuction with momentum space quantum mechanics is able to reveal additional informaton to study orbitals and chemical bonding mechanisms of molecules [10-11]. Figure 4 demonstrates how EMS exepriment directly link to binding energy spectrum [12] and individual orbital momentum distributions (cross sections) [4, 13,14],. And how quantum mechanics closely works with EMS experiment in both prediction of the measurable properties and measurement of predictable properties of molecules and materials.

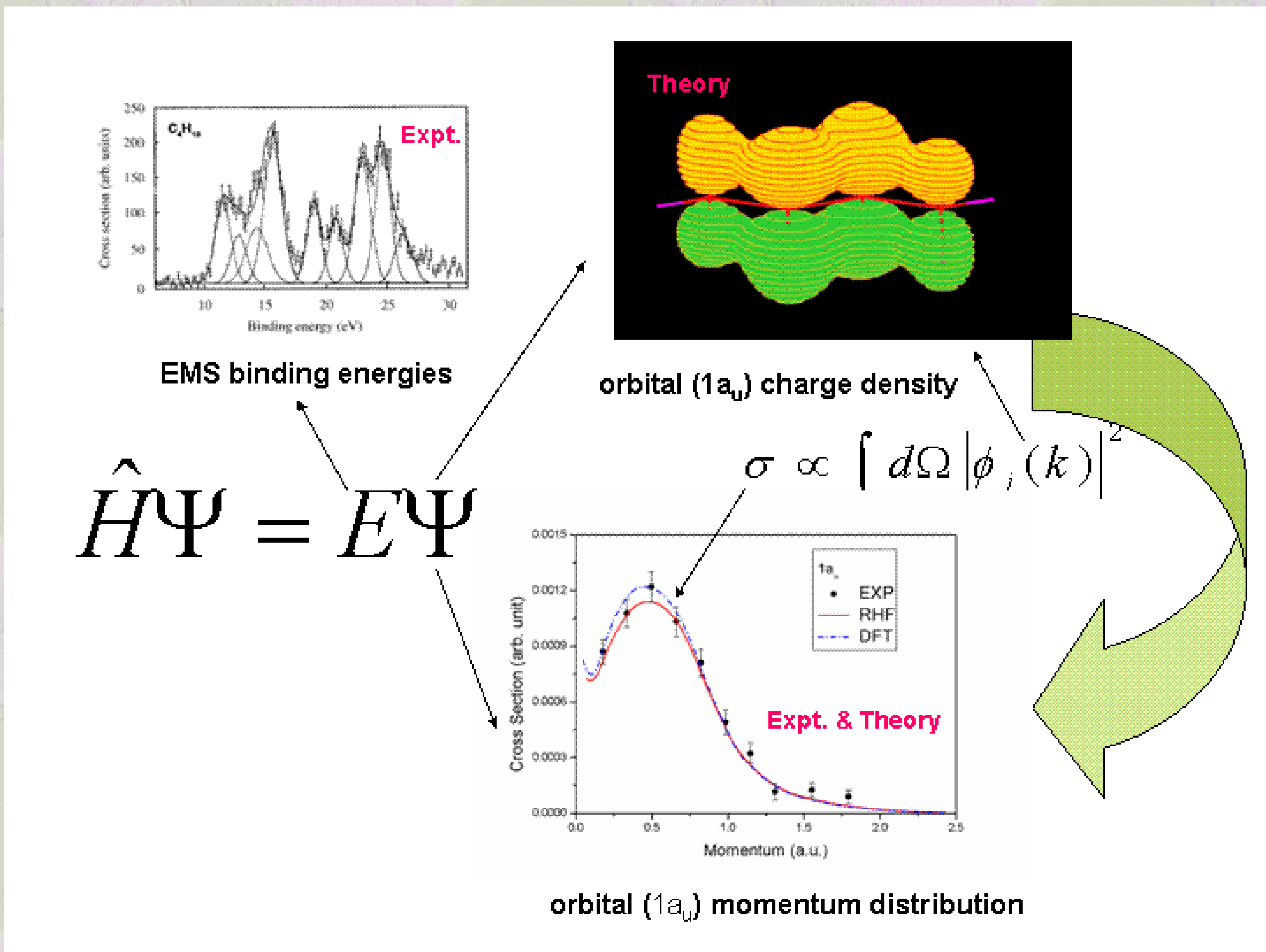

Fig.4 shows how quantum mechnics works with EMS experimental measurements on n-buatne orbital $1a_u$.

As can be seen from Figure 4 that quantum mechanical studies of molecules could reach better understanding if electronic information in both coordinate space and momentum space can be achieved. To this regards, dual space anaylsis (DSA) [4] was introduced to study bonding mechanism of molecules and to achieve a more comprehensive understanding of comformers [2,5-6] as well as tautomers [7] of species without signaficant energy difference. DSA could also help EMS experiment in distinguishing clustered orbitals in the outer valence shell due to exeprimental instrumental resolution of the technique. For example, the three outer most velance orbitals ($7a_g$, $2b_g$ and $6a_g$) of n-butane cannot be resolved due to the experimental instrumental resolution

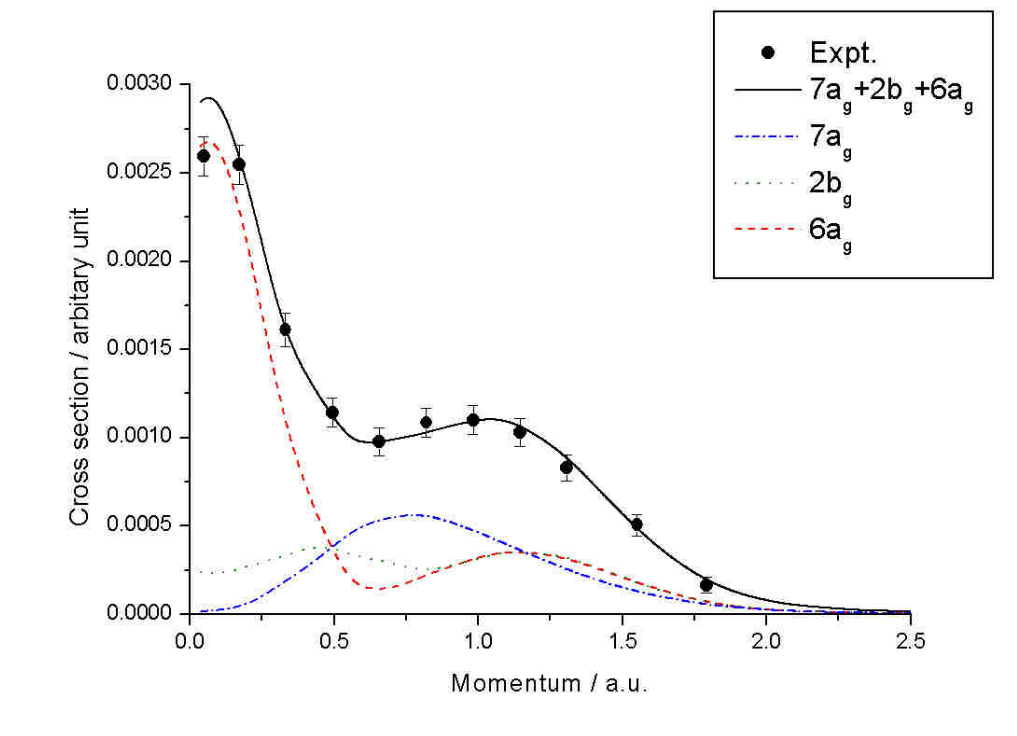

Fig. 5. The outer most cluster of orbitals of n-butane observed by EMS [11-12, 3] (dots) with theoretically synthesed orbital clusters and decomposed orbitals.

The highest occupied molecular orbitals (HOMO) of organic molecules are the target of studies of bonding mechanism and chemical reaction etc. in organic chemistry since they are very active in chemical processes. As a result, theoretical DSA method is used to decompose the cluster of orbitals observed by EMS [4]. The individual orbital momentum distributions (MDs) of this clustered orbitals of n-butane are shown in the same Figure with colored curves. It is seen that while exhibit the same point group symmetry, orbitals $6a_g$ and $7a_g$ have very different bonding characters: orbital $7a_g$ is strictly p-like but $6a_g$ is formed by a mixture of s- (smaller momentum region) and p-electrons (larger momentum region). To arrive a more familiar view of the orbitals, Figure 6 gives the charge density distributions of the orbitals in coordnate space calculated using the B3LYP/TZVP model [4].

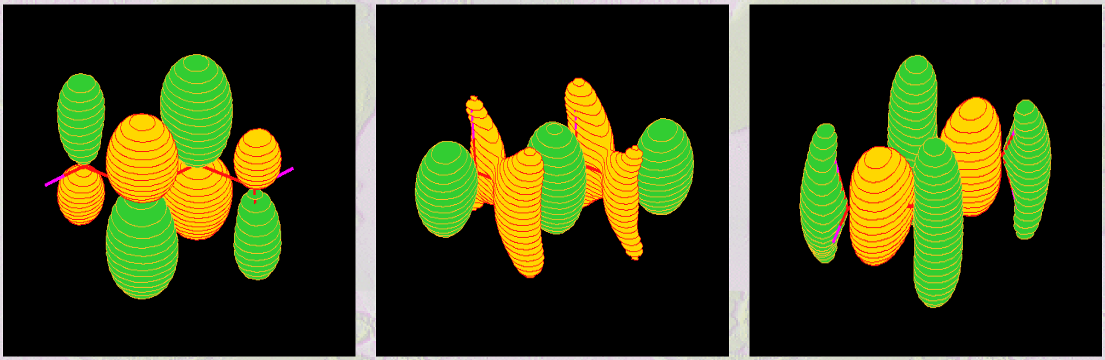

Fig.6 (a) $7a_g$ orbital. Fig.6 (b) $2b_g$ orbital. Fig.6 (c) $6a_g$ orbital.

Application to Structure and Bonding Mechanism Studies

Next question is how could DSA/EMS achieve an insight understanding of conformers of n-butane? Let's look at the four most significant rotational conformers of n-butane A (point group symmetry is C_{2h}, ground electronic state is ^1A_g), B(C_2, ^1A), C(C_2, ^1A) and D(C_{2v}, $^1A_1$). As can be seen from Fig.2, only A and C may be isolated as they represent the global minimum and local minimum positions on the n-butane rotational potential energy surface. For example, the outermost orbital, HOMO, of n-buatne will change when the molecule rotates around its $C_{(1)}$-$C_{(2)}$ bond (see Fig. 1). Fig.7 demonstrates such changes in both coordinate space and momentum space [8],

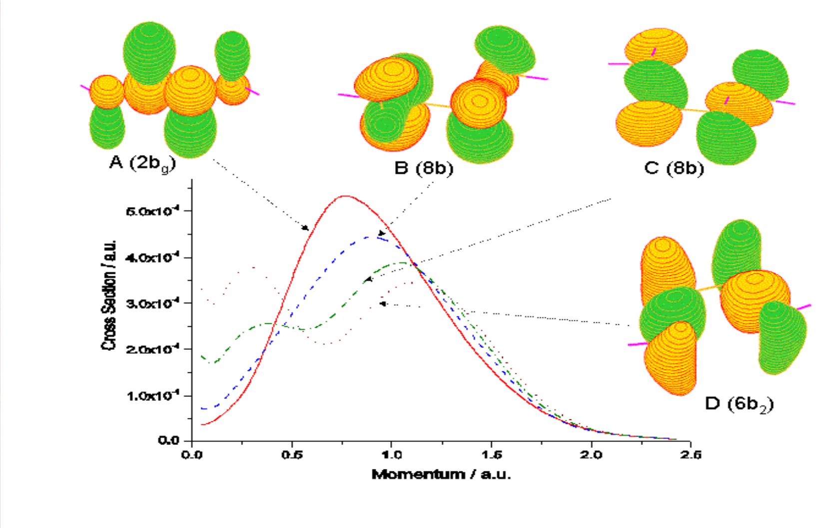

Fig.7 HOMOs of A-B-C-D n-butane in their ground electronic states.

Application to Core Orbitals of n-Butane Conformers

One of the most significant challenges in computational chemistry is to extend the prediction power into areas which experiment could not reach at the moment. To this regard, DSA has been extended into the core region to study core orbital behaviour of n-butane whent the central $C_{(1)}$-$C_{(2)}$ bond is rotating [9]. Because in coordinate space, the information is sensitive when energy is involved but insensitive when orbitals are in the equivalent positions in the space, whereas in momentum space, the information such as equivalent positions in space which cause energy degenerate states and "invisible" in coordinate space could be significant. For example, the four core orbitals of n-butane are two-fold degenerate calculated using RHF/TZVP as shown in Figure 8 [5],

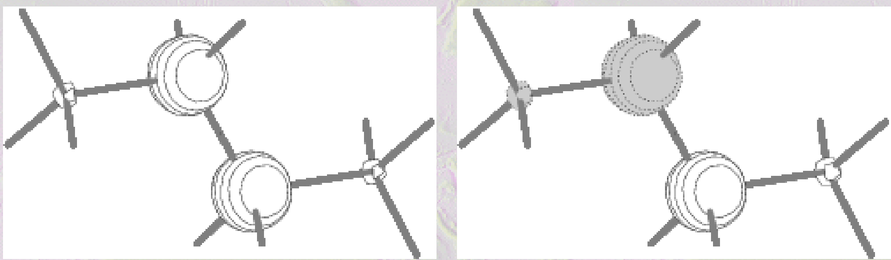

Fig.8(a) Two **inner** energy degenerate core orbitals of n-butane
($1a_g$ and $1b_u$ E=305.13 eV).

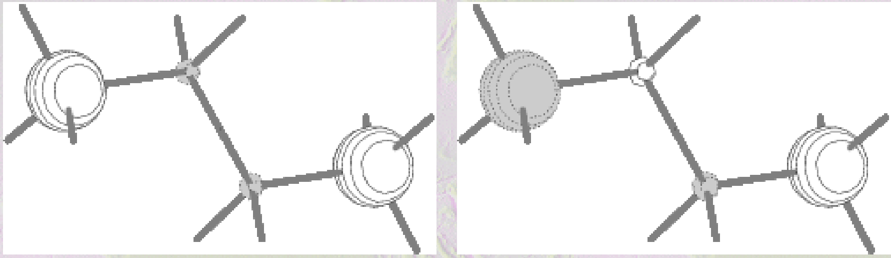

Fig.8(b) Two **outer** energy degenerate core orbitals of n-butane
($2a_g$ and $2b_u$ E=304.98 eV).

The orbital momentum distributions of the four core orbitals for the A, B, C and D conformers are shown in Fig.9 [5],

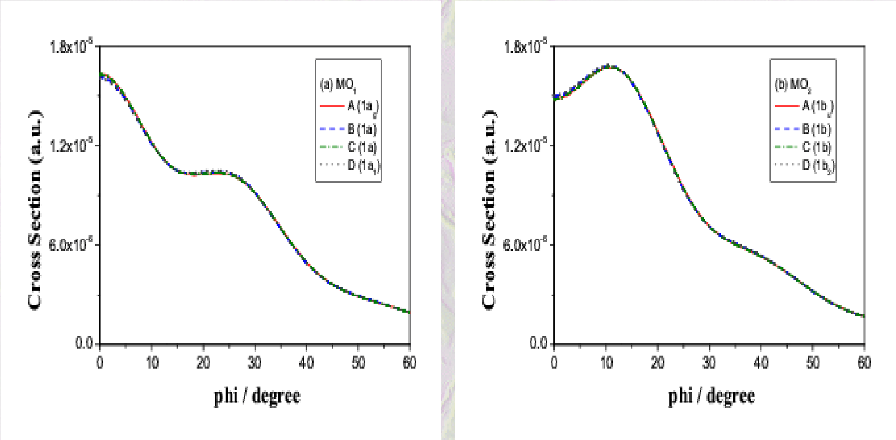

Fig.9(a) Two inner energy degenerate core orbitals of n-butane ($1a_g$ and $1b_u$) are also "degenerate" in momentum space.

The inner pair of core orbitals of the four butane conformers does not change while the molecules rotates around the central bond, $C_{(1)}$-$C_{(2)}$ in both coordinate space and momentum space, as the positions of $C_{(1)}$ and $C_{(2)}$ do not change at all. Only the torsional forces changes in the rotation. As indicated in Figure 9 (a). However, the $C_{(1)}$-$C_{(2)}$ bond rotation causes $C_{(3)}$ and $C_{(4)}$ atoms move to the equivalent positions in space, as a result, the energy of the orbital pair exhibits degeneracy but in momentum space, the orbital pair split so that the conformers can be identified even though the energies are the same. Figure 9 (b) demonstrate the splitting in momentum space.

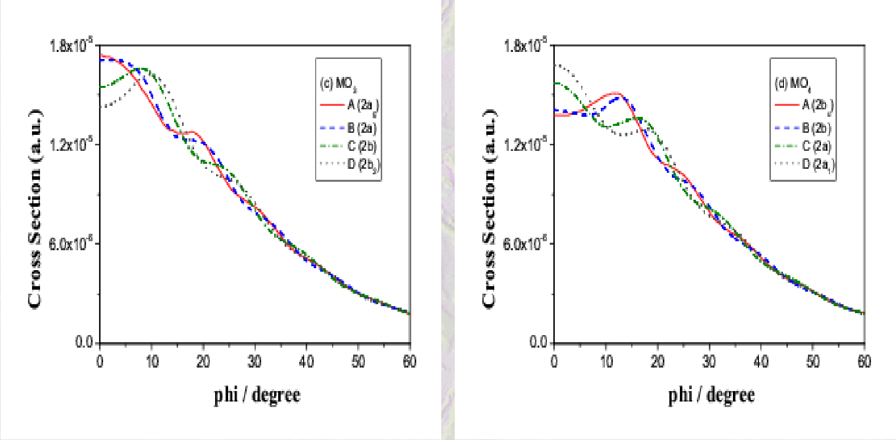

Fig.9(b) Two outer energy degenerate core orbitals of n-butane ($2a_g$ and $2b_u$) split in momentum space.

Conclusion

In conclusion, the combined dual space analysis (DSA) and electron momentum spectroscopy (EMS) could provide an additional dimension (momentum) of information to assist insight understanding of molecules such as butane, which has been extensively studied in coordinate space. The information in momentum space could provide novel information which has been largely "invisible" in the conventional coordinate space. As conformers and tautomers largely exist in biological molecules, DSA is expected to play important role of their structural information anaylsis.

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