中国科学技术大学

Valence electronic structure of isopropyl iodide investigated by electron momentum spectroscopy

--- Influence of intramolecular interactions

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Outline

1. Introduction

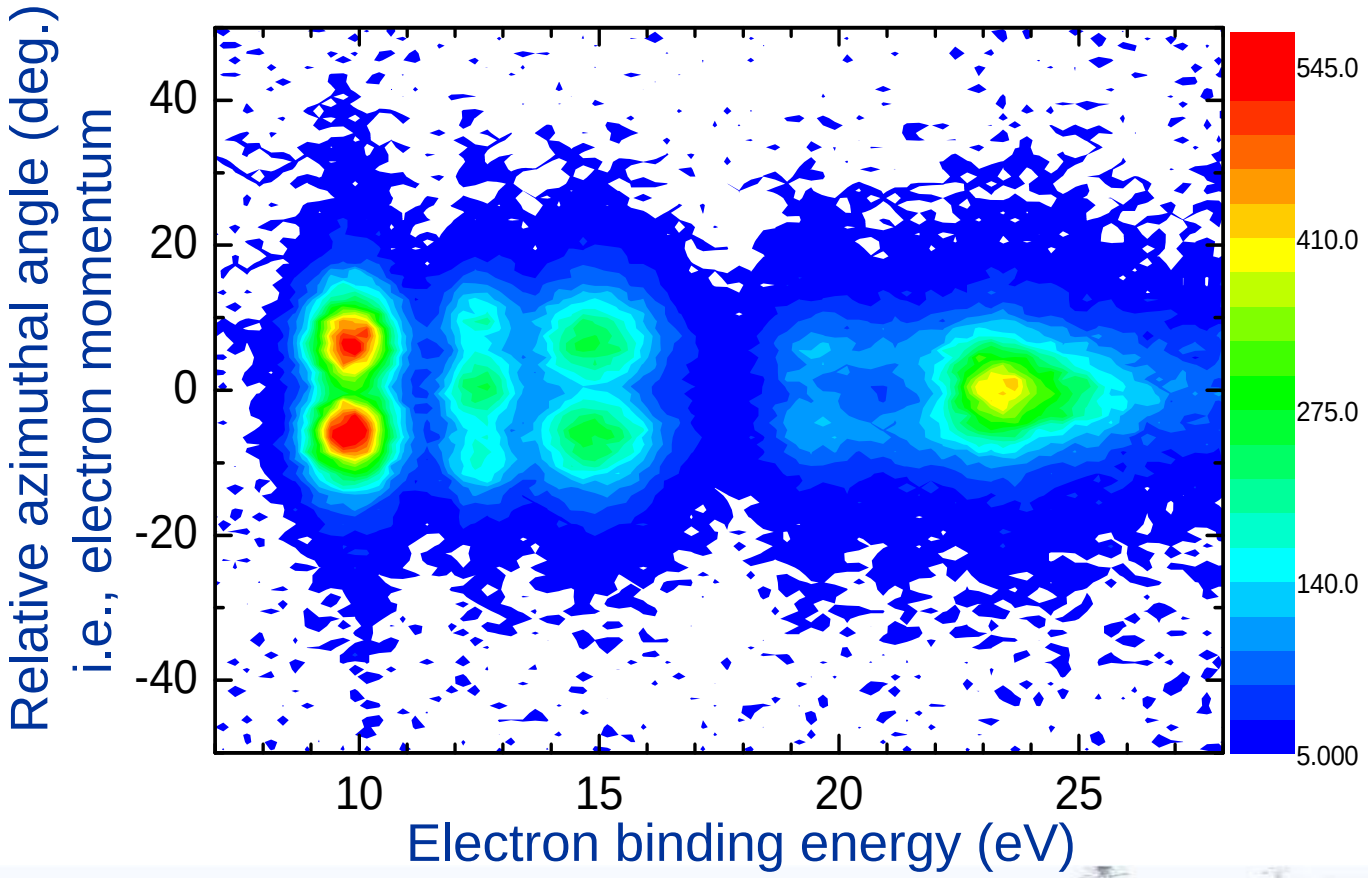
2. Experimental setup

3. Preliminary results of isopropyl iodide
   ---Electron binding energies
   ---Electron density distributions

4. Summary

Intramolecular interactions play an important role in electronic structures of molecules.

Molecular orbital imaging

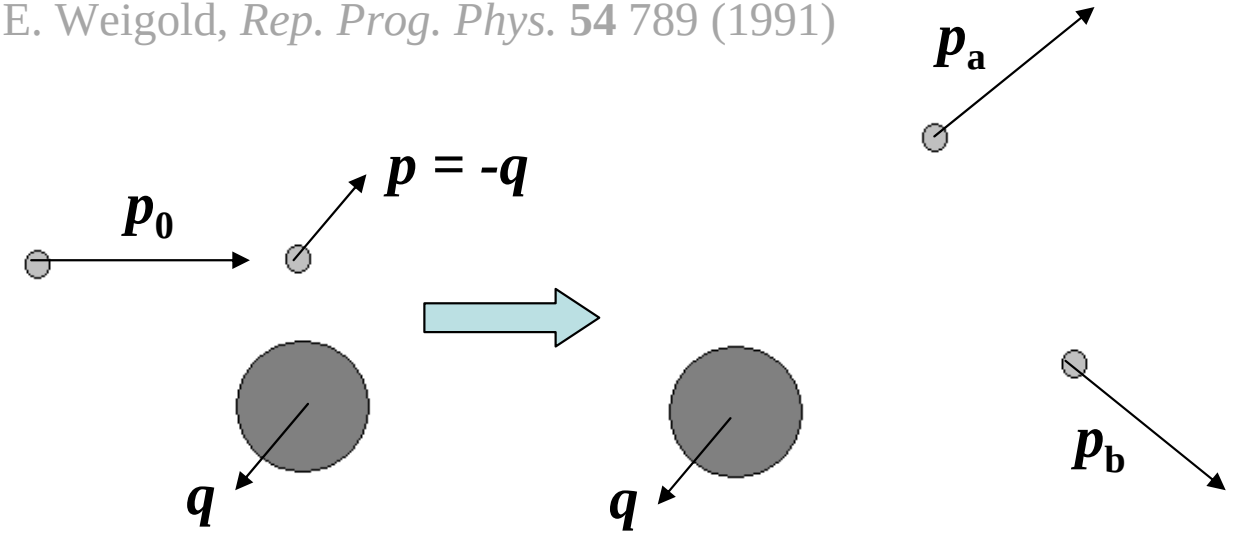


1. Introduction

Electron momentum spectroscopy (EMS) is an unique technique for imaging atomic or molecular orbitals in momentum space.

Binary (e,2e) process, in which the residual ion acts as a spectator.

I. E. McCarthy and E. Weigold, *Rep. Prog. Phys.* **54** 789 (1991)



By detecting two outgoing electrons in coincidence, we can obtain

$$\varepsilon_f = E_0 - \left(E_a + E_b\right) \qquad \boldsymbol{p} = -\boldsymbol{q} = \boldsymbol{p}_a + \boldsymbol{p}_b - \boldsymbol{p}_0$$

$$\frac{d^3\sigma}{dE_a d\Omega_a d\Omega_b} \propto \int d\Omega_p \left|\psi_j(p)\right|^2$$

i.e., Orbital imaging

1. Introduction

$$\frac{d^3\sigma}{dE_a d\Omega_a d\Omega_b} \propto \frac{1}{4\pi}\int d\Omega_p \left|\psi_j(p)\right|^2$$

⇩ measurement ⇩ calculation

Theoretical methods generally used in EMS:

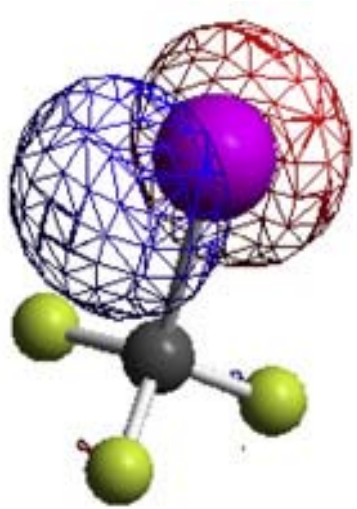
- Non-relativistic Hartree-Fock (HF), density functional theory (DFT-B3LYP), Configuration interaction (CI) approach, ect.
  Rep. Prog. Phys. **54** 789 (1991)

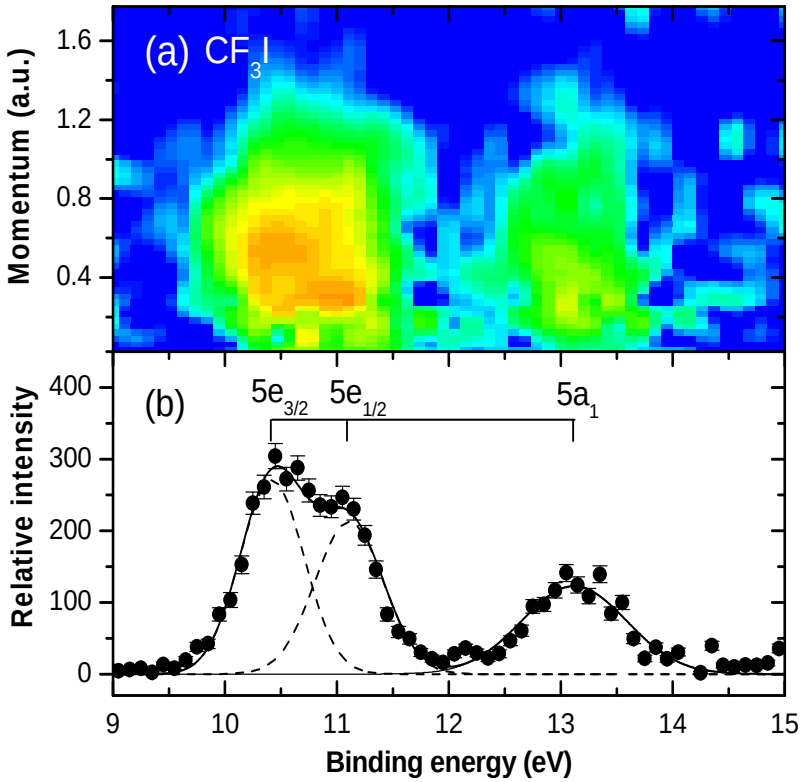
- Dirac-Fock and Relativistic density functional theory (ADF)
  Rep. Prog. Phys. **54** 789 (1991); J. Comput. Chem. **22** 931(2001)
- Natural bond orbitals (NBO) analysis;
  (donor-acceptor interaction) Chem. Rev. **88** 899 (1988)
- Harmonic analytical quantum mechanical approach;
  (vibrational effect) J. Chem. Phys. **68** 2053 (2012)
- …

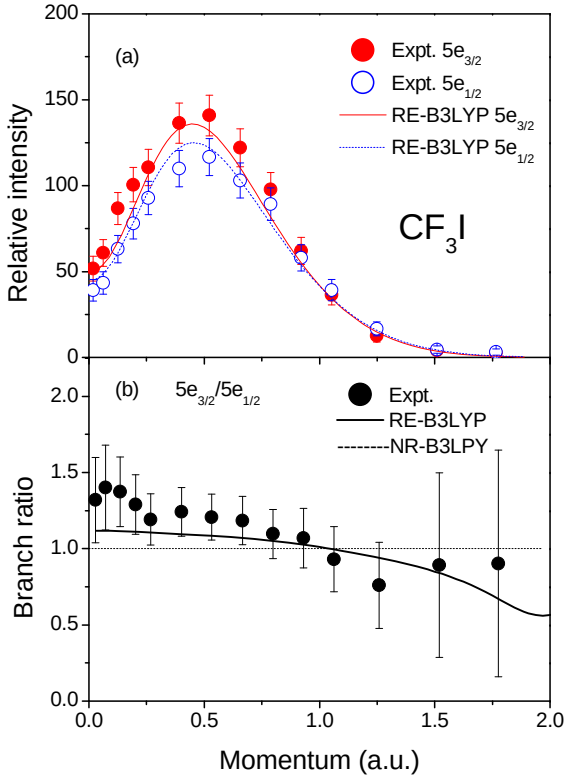
1. Introduction

Relativistic effects for valence electrons of molecules containing high-Z atoms may also be substantial.

e.g., CF_3I







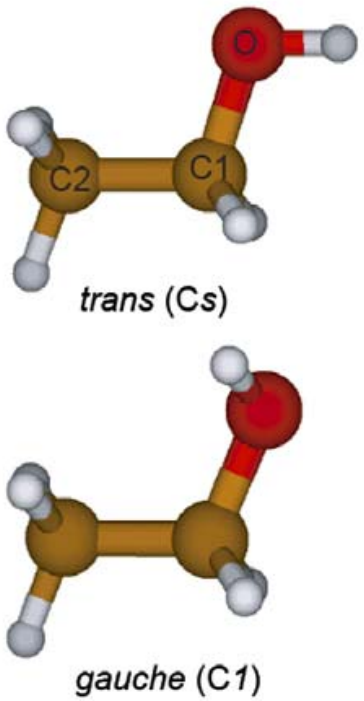
Spin-orbit coupling effect on electronic wavefunctions was observed clearly.

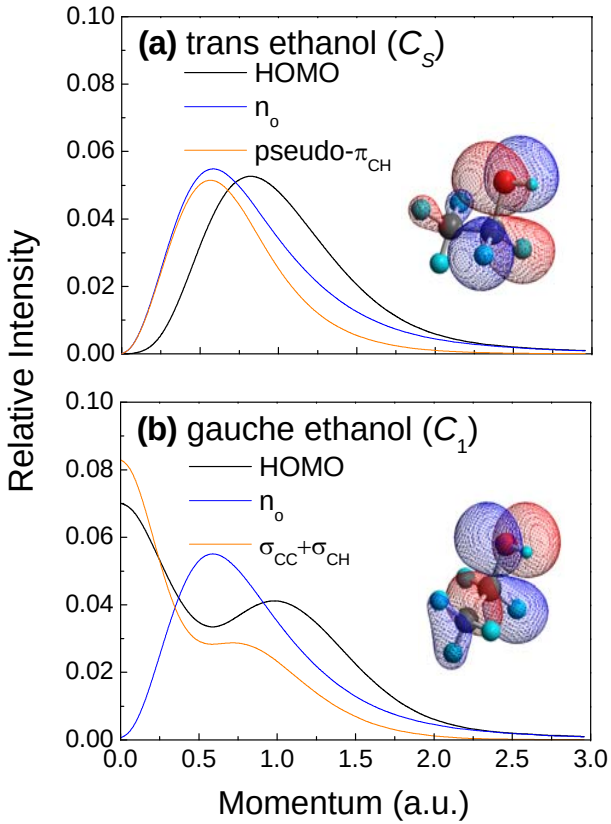
Z. J. Li, *et al.* Chem. Phys. Lett. **457** 45 (2008)

1. Introduction

Hyperconjugation: donor–acceptor interactions often occur in alkyl and other saturated substituents.

e.g., ethanol





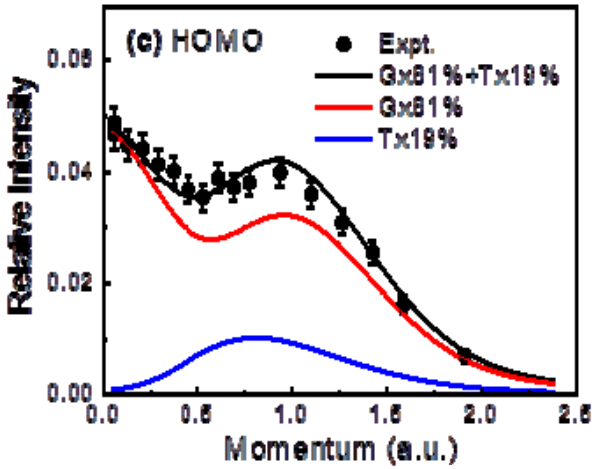
NBO analysis indicates

Trans: two equivalent $n_O \rightarrow \sigma_{CH}^*$ interactions (E(2) = 6.57 kcal/mol);

Gauche: two different interactions

$n_O \rightarrow \sigma_{CC}^*$ (E(2) = 4.93 kcal/mol)

$n_O \rightarrow \sigma_{CH}^*$ (E(2) = 7.03 kcal/mol)

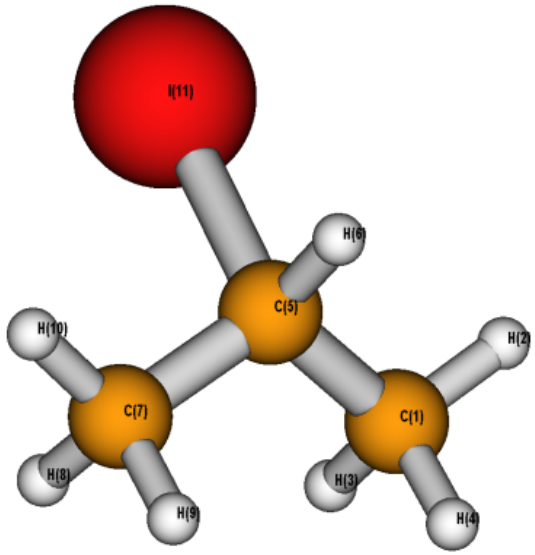


Hyperconjugative effect on electronic wavefunctions was clearly revealed.

X. J. Chen, *et al.* Chem. Phys. Lett. 472 (2009) 19

1. Introduction

Isopropyl iodide
(CH_3CHICH_3)



Kinds of intramolecular interactions coexist in one molecule:

- **relativistic effect,**
- **hyperconjugative effect,**
- **electron correlation effect,**

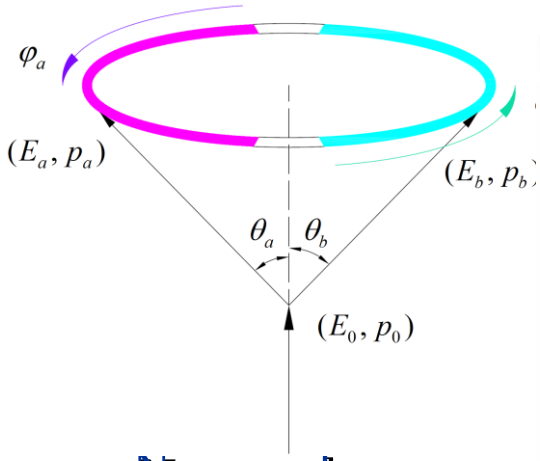
…

Motivation of the present work:

To study influences or competition of spin-orbit coupling and hyperconjugative effects

2. Experimental setup

high-sensitivity EMS spectrometer

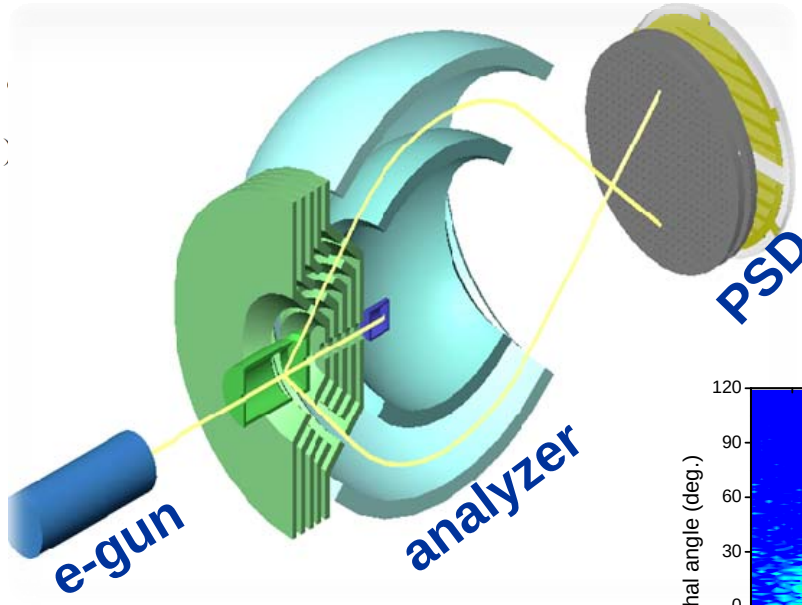


Non-coplanar
symmetric geometry

$E_0 = 1.2$ keV

$E_a \equiv E_b$

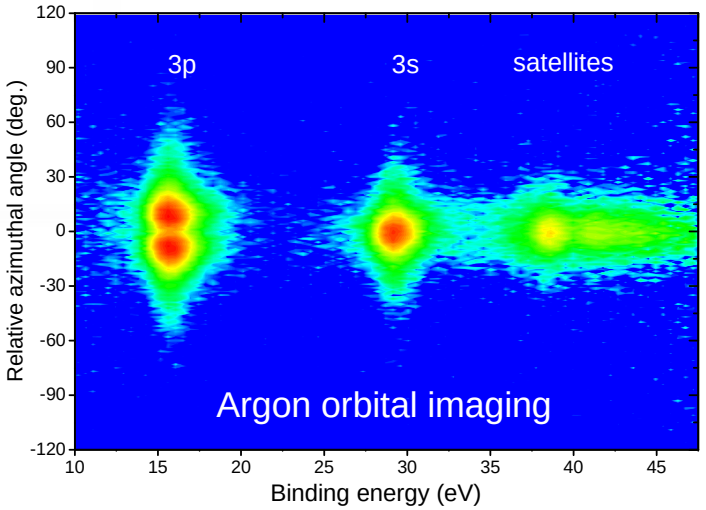
$\theta_a \equiv \theta_b \equiv \theta \equiv 45^\circ$



$$\varepsilon = E_0 - E_a - E_b$$

$$\boldsymbol{p} = \boldsymbol{p}_a + \boldsymbol{p}_b - \boldsymbol{p}_0$$

$$\sigma \propto \int d\Omega |\psi(p)|^2$$



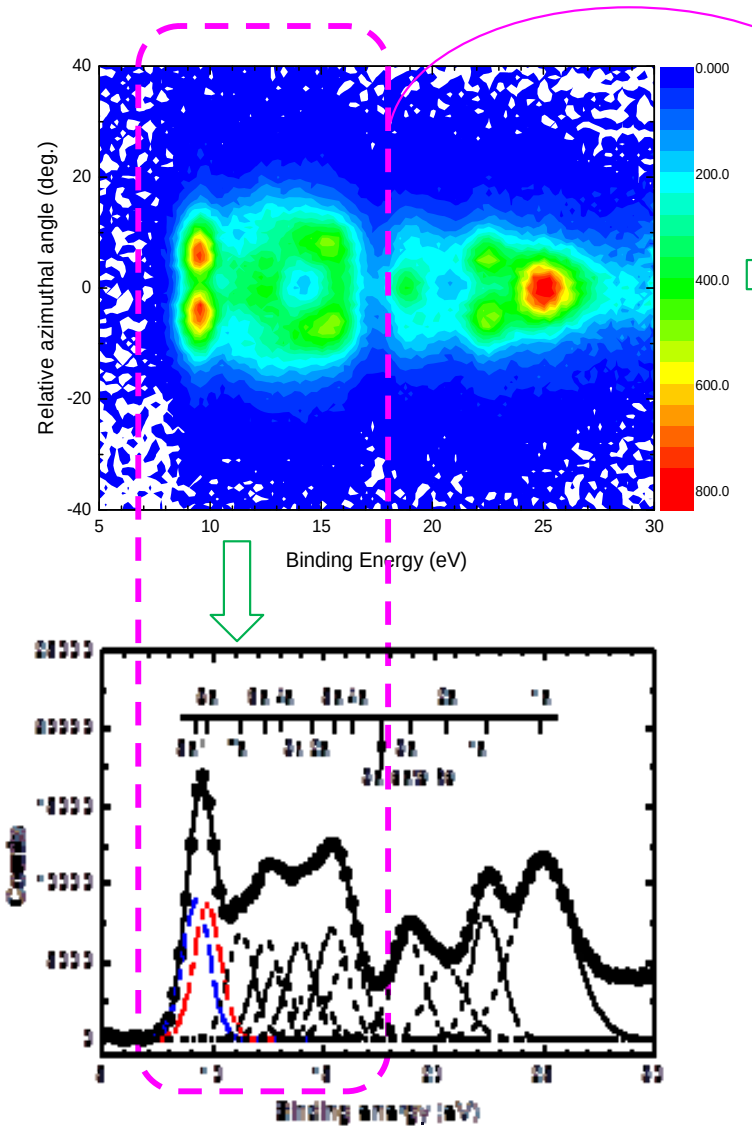
$$p = \left\{ \left(2p_a \cos\theta - p_0\right)^2 + \left[2p_a \sin\theta \sin\left(\frac{\varphi}{2}\right) \right]^2 \right\}^{1/2}$$

Almost 2 π angle simultaneous detection makes the sensitivity of spectrometer improved greatly.

Tian *et al* Rev. Sci. Instrum. **82** 033110 (2011)

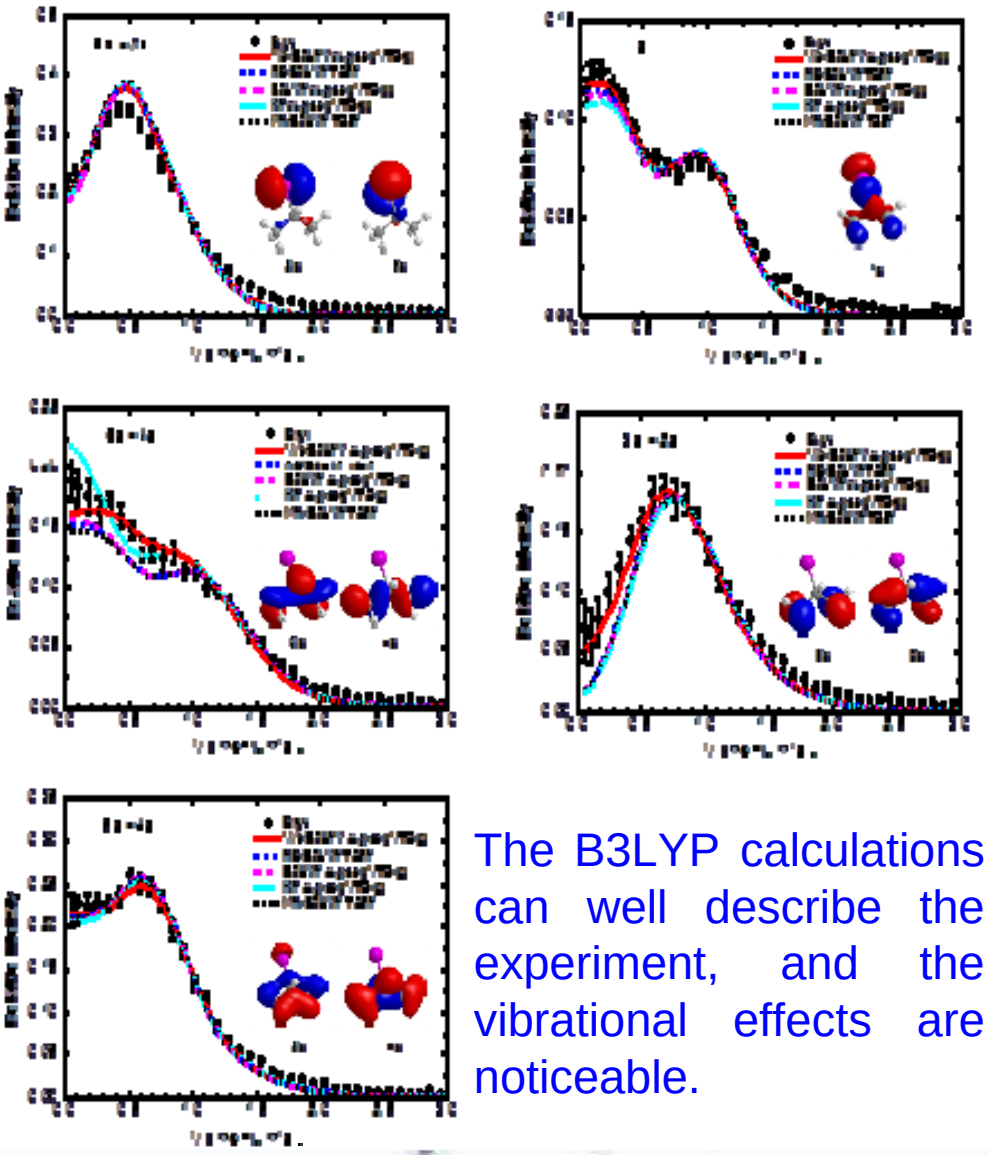
3. Results of isopropyl iodide

- **2D electron density map, i.e., molecular orbital images**



- **Binding energy spectrum**

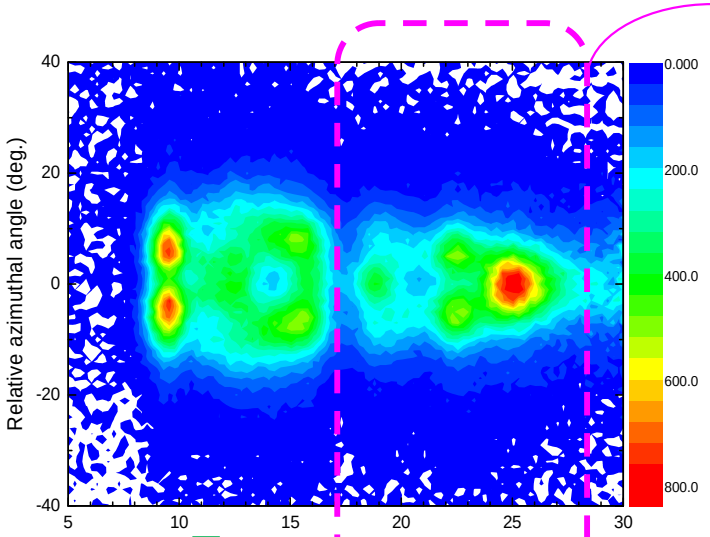
- **Outer-valence molecular orbital electron momentum distributions**

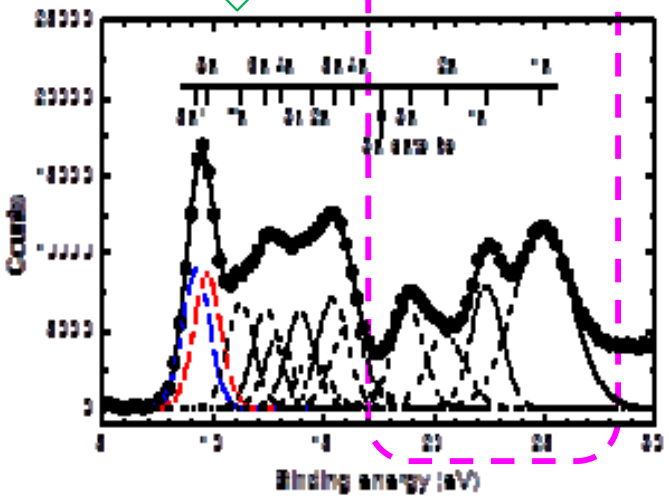


The B3LYP calculations can well describe the experiment, and the vibrational effects are noticeable.

3. Results of isopropyl iodide

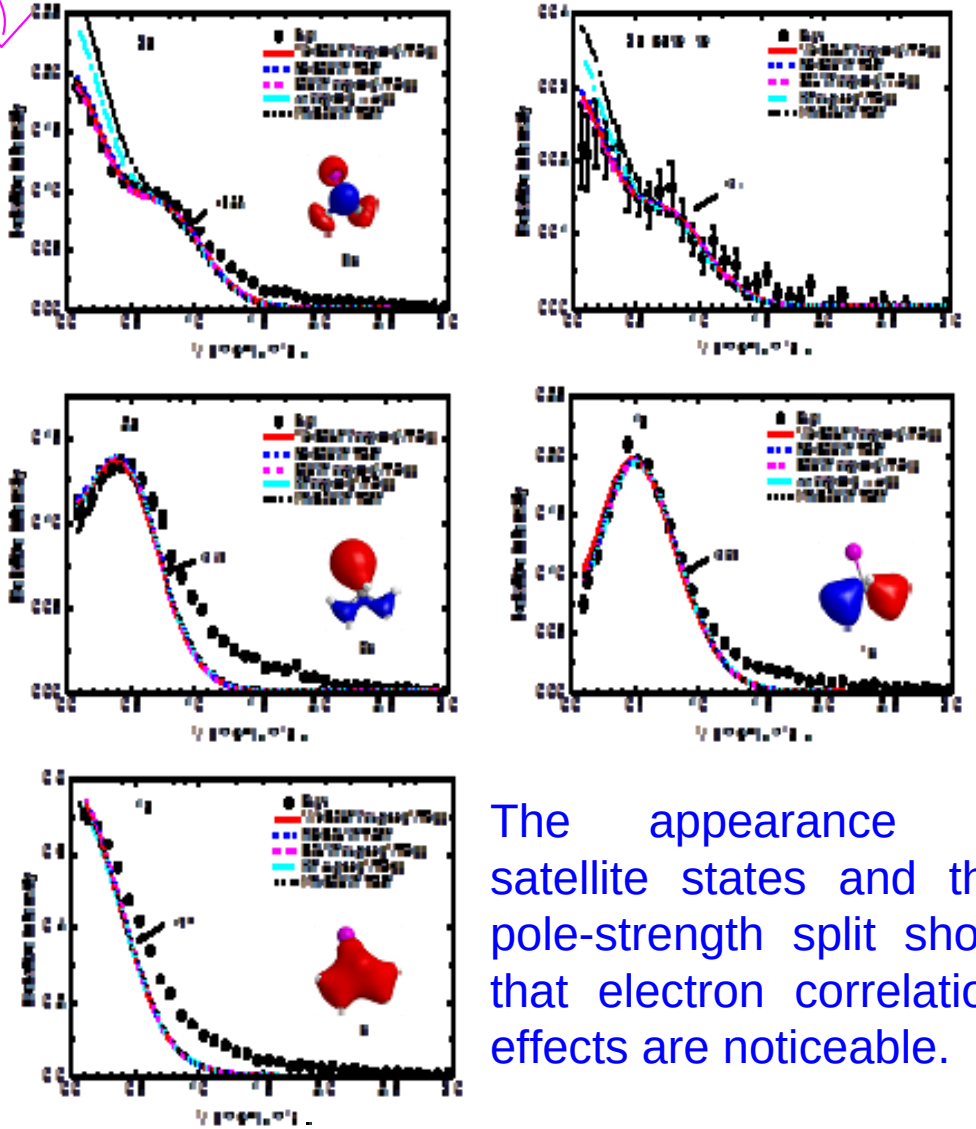
- **2D electron density map, i.e., molecular orbital images**





- **Binding energy spectrum**

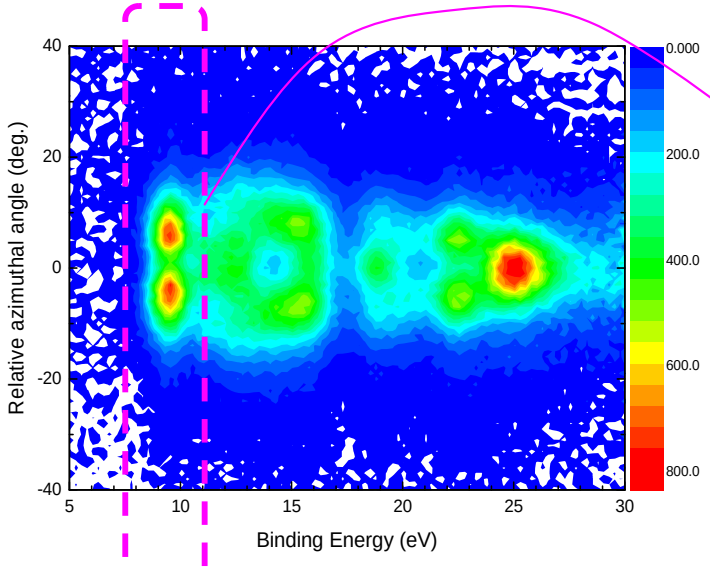
- **inner-valence molecular orbital electron momentum distributions**

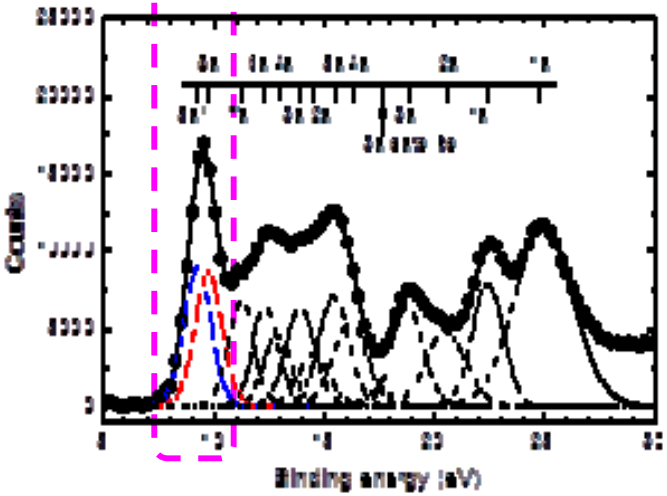


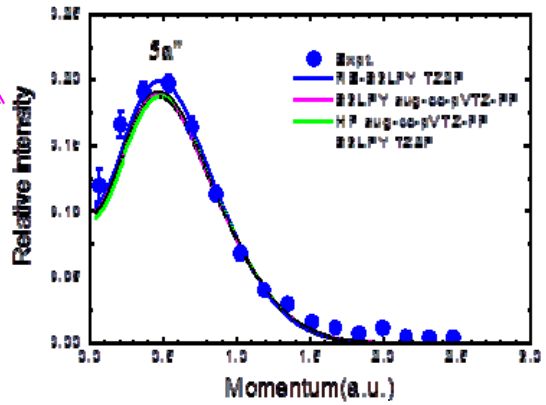
The appearance of satellite states and the pole-strength split show that electron correlation effects are noticeable.

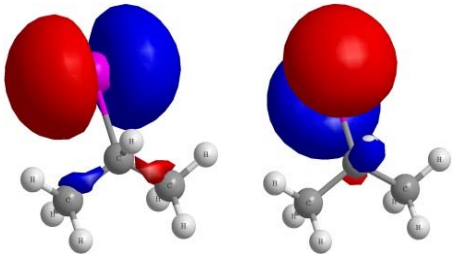
3. Results of isopropyl iodide

To reveal the relativistic effect on the HOMO orbital

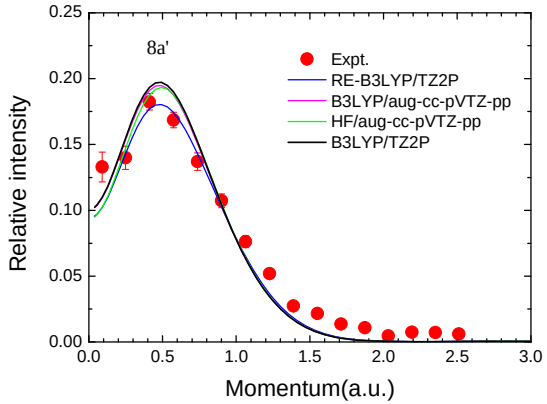


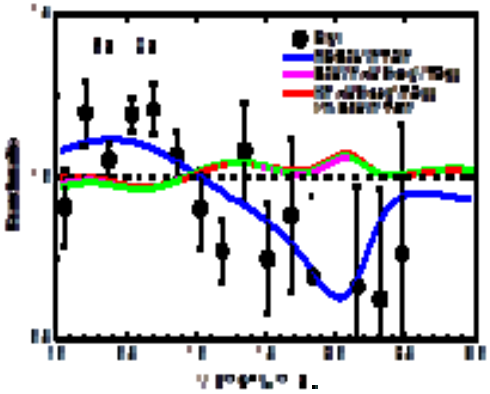






5a" 8a'

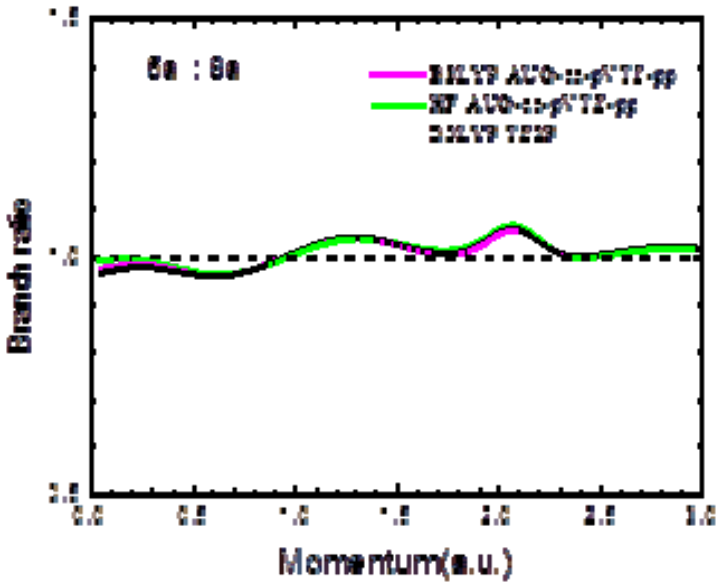


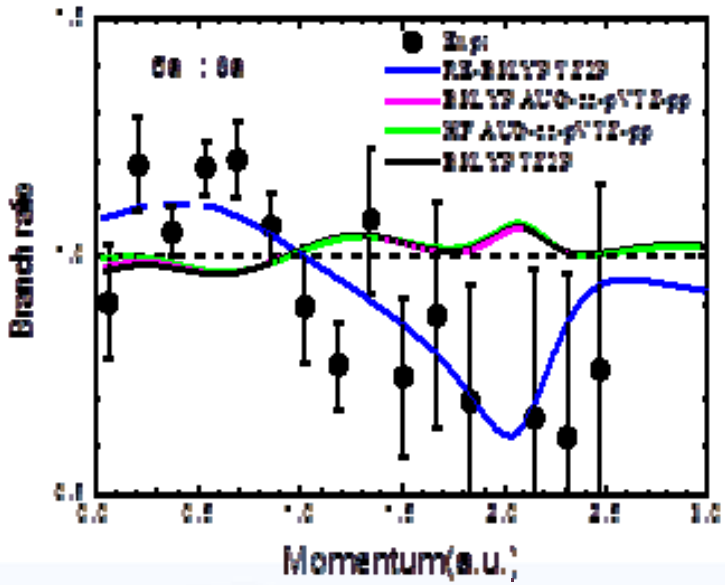


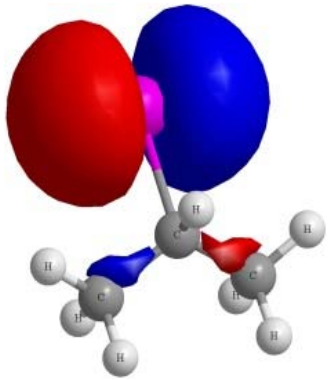
Spin-orbit coupling effect on electronic wavefunctions of HOMO was observed.

3. Results of isopropyl iodide

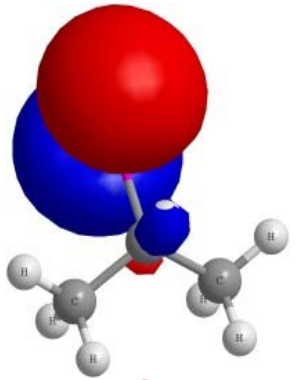
To reveal the hyperconjugative effect on the HOMO orbital







$5a''$



$8a'$

NBO analysis indicates hyperconjugative interaction and charge transfer occurred, but very small.

$$5a'' : n_I \rightarrow \sigma^*_{C\text{-}C} \qquad 8a' : n_I \rightarrow \sigma^*_{C\text{-}H}$$

$$\Delta E(2) : 2.58\,kcal/mol\,(5a''), 1.62\,kcal/mol\,(8a')$$

Such an effect can not be revealed by present experiment.

Summary

- Valence orbital electron momentum distributions of isopropyl iodide have been measured for the first time. The DFT calculations can describe the experiment well.

- Spin-orbit coupling effects on HOMO wavefunctions are observed clearly, as well as electron correlation or vibrational effects on some other orbitals.

- Hyperconjugative effects on HOMO wavefunctions are small, not be revealed by present experiment.

In the future, improve the energy resolution and sensitivity of EMS apparatus, to further study such intramolecular interactions.

Thank you for your attention!

NBO analysis transforms the canonical delocalized molecular orbitals into localized orbitals, and the hyperconjugative interaction can be treated by the second order perturbation energy,

$$E(2) = nF_{ij}^2/\Delta\varepsilon$$

where F_{ij} is the Fock matrix between the unperturbed occupied lone pair (donor, n_I) and unoccupied antibonding C—H or C—C natural orbitals (acceptor, σ *), n is the lone pair orbital population, and $\Delta\ \varepsilon$ is the energy difference between the unperturbed n_I and σ * orbitals.

Molecular orbital: $\psi = \sum c_i \phi_{donor} + \sum c_j \phi_{acceptor}$