Interpretation of the Experimental Electron Momentum Spectra of $5e_{1/2}$ and $5e_{3/2}$ Orbitals of $CF_3I$ with Relativistic Calculations

# Interpretation of the Experimental Electron Momentum Spectra of $5e_{1/2}$ and $5e_{3/2}$ Orbitals of CF$_3$I with Relativistic Calculations *

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*With our newly developed method, we calculate the spin-orbit splitting states $5e_{1/2}$ and $5e_{3/2}$ of the CF$_3$I molecule incorporating the relativistic effects. Our theoretical results agree excellently with the recent experimental observations. The present study shows that relativistic effects can evidently change the electron momentum distributions of molecular orbitals when a medium Z element is included, such as iodine.*

Relativistic effects in high-$Z$ atoms and molecules including high-$Z$ elements have attracted wide interest recently[1−8] with the development of experimental techniques and theoretical methods, which can observe and interpret them. A well-known experimental technique that can observe relativistic effects in atoms or molecules is photoelectron spectroscopy. Spin-orbit coupling effects will split the energy level of the different electronic spin states. With the relativistic effects, an orbital with low-$l$ states ($s$ and $p$) usually shrinks and energetically becomes more stable, while the higher-$l$ states ($d$ and $f$) radially expand and energetically become less bound. Besides the energy splitting, the change of electron density distributions due to relativistic effects can also be measured using the electron momentum spectroscopic technique.

Electron momentum spectroscopy (EMS)[9−15] has shown to be a powerful technique to investigate the electronic structures and impact ionization dynamics. General techniques only measure the energy information, while EMS can obtain both the orbital binding spectra and the electron momentum profiles for each individual orbital. This advantage has made EMS a unique tool to investigate the relativistic effects. Cook et al.[3] conducted the first seminal work on the relativistic effects of Xe using the EMS method in 1984. Since then, several relativistic EMS works on heavy atoms have been reported,[4,5] but no work on molecular targets has been reported due to the difficulty of the relativistic theoretical calculations of electron momentum distributions. Recently, Li et al.[6] reported the EMS work of the CF$_3$I molecule. They partly took account of the relativistic effects in their calculations through the pseudopotential of iodine. The pseudopotential CRENBL they used did not include the spin-orbit coupling effect, so a relativistic method

including spin-orbit coupling is needed to fully explain the experimental results. In combination with the Amsterdam density functional (ADF)[16,17] program, our group developed a new program to generate the electron momentum distribution using scalar or two-component relativistic wavefunctions.[7] With this program, we have investigated relativistic effects in I$_2$ and Au$_2$,[7] UF$_6$,[8] and W(CO)$_6$ using the EMS method.

In the present work, we report the electron momentum distributions of $5e_{1/2}$ and $5e_{3/2}$ molecular orbitals of CF$_3$I. Our theoretical calculation agrees excellently with the recent experimental results of Li et al.[6]

Electron momentum spectroscopy is based on the kinematical complete $(e, 2e)$ collision single ionization process, where an incident electron "knocks out" an electron from the target and is scattered itself. The triple differential cross section $\sigma_{\mathrm{EMS}}$ for the $(e, 2e)$ process can be simplified using the target Kohn–Sham approximation (TKSA) of DFT, which is given by[18]

$$\sigma_{\mathrm{EMS}} \propto \int d\Omega \left| \psi_j^{\mathrm{KS}}(p) \right|^2, \tag{1}$$

where $\psi_j^{\mathrm{KS}}(p)$ is the momentum space Kohn–Sham orbital for the $j$th electron. The $\int d\Omega$ indicates the spherical average due to the randomly oriented gas phase target. According to Eq. (1), the EMS is able to image the electron density of individual orbitals selected according to their binding energies.

There are two steps in the calculation of the theoretical momentum profiles of $5e_{1/2}$ and $5e_{3/2}$ orbitals. The wavefunctions of spin-orbit states in position space are first calculated using the ADF 2008 program, and then the theoretical momentum profiles are calculated through Fourier transform and spherical integral on the wavefunctions in position space.

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The ADF program can perform relativistic and non-relativistic density functional theory (DFT) calculations for atoms and molecules. The relativistic calculations include scalar relativistic and spin-orbit relativistic methods. The latter is a kind of two-component relativistic method which can provide spin-orbit splitting components. In the present work, the spin-orbit relativistic method along with ZORA[19]/TZ2P basis sets and the standard hybrid B3LYP functional is used. The geometrical structure of $CF_3I$ is optimized at the ZORA/TZ2P level, and then is used in the spin-orbit relativistic calculations.
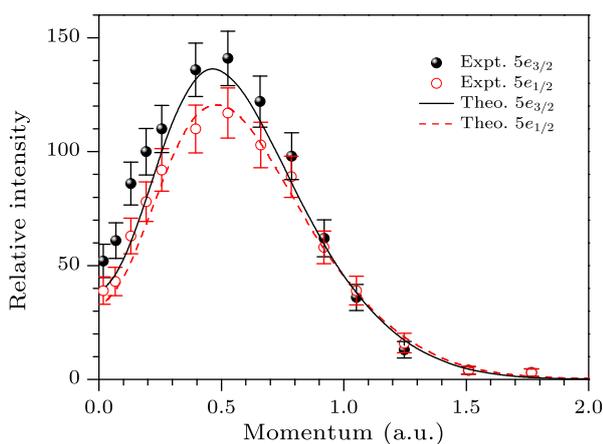


**Fig. 1.** The momentum distribution for the orbital $5e_{1/2}$ and $5e_{3/2}$. The experimental data are taken from Ref. [6].

Our newly developed ADFCOVT[7] and NEMS[20] program can extract wavefunction information of orbitals from the output file of ADF and calculate theoretical momentum profiles. The molecular orbital generated using the spin-orbit relativistic ADF calculation has the following form:

$$\Psi(r) = \Psi_\alpha(r) \cdot \alpha + \Psi_\beta(r) \cdot \beta, \qquad (2)$$

where $\alpha$ and $\beta$ are the spin variables and are orthogonal with each other. $\Psi_\alpha(r)$ and $\Psi_\beta(r)$ are the space wavefunction components for the spins $\alpha$ and $\beta$, respectively. The momentum distributions $|\Psi(p)|^2$ for the two-component molecular orbitals are given by

$$|\Psi(p)|^2 = |\Psi_\alpha(p)|^2 + |\Psi_\beta(p)|^2, \qquad (3)$$

where $|\Psi_\alpha(p)|^2$ and $|\Psi_\beta(p)|^2$ are the momentum distributions of the spin $\alpha$ and $\beta$ components.

The $CF_3I$ molecule has $C_{3v}$ point-group symmetry and its electronic configuration in the ground state can be written as

$$(\text{core})^{54} \underbrace{(1a_1)^2(1e)^4(2a_1)^2(3a_1)^2}_{\text{inner valence}}$$
$$\underbrace{(2e)^4(4a_1)^2(3e)^4(4e)^4(1a_2)^2(5a_1)^2(5e)^4}_{\text{outer valence}}.$$

The highest occupied orbital (HOMO) $5e$ is split into $5e_{1/2}$ and $5e_{3/2}$ states due to the spin-orbtial coupling.

The binding energies of $5e_{1/2}$ and $5e_{3/2}$ are shown in Table 1. The theoretical values are obtained by the present work, and the experimental ones are from high resolution PES.[21] It can be found that DFT theoretical energies all underestimate the respective experimental binding energies by $\sim 2.8$ eV. However, the calculated energy level interval between $5e_{1/2}$ and $5e_{3/2}$ agrees well with the experimental results.

The electron momentum profiles of spin-orbit components $5e_{1/2}$ and $5e_{3/2}$ are shown in Fig. 1. The experimental data are taken from the work of Li et al.,[6] and the curves are our theoretical results. Considering the resolution of the spectrometer, all the theoretical results have convolved the experimental momentum resolution. Since the experimental intensity is at a relative scale, all the theoretical results have been multiplied by the same factor for normalization. It can be found that our theoretical results provide an excellent agreement with the experimental data.

Table 1. The binding energies of $5e_{1/2}$ and $5e_{3/2}$ of $CF_3I$.

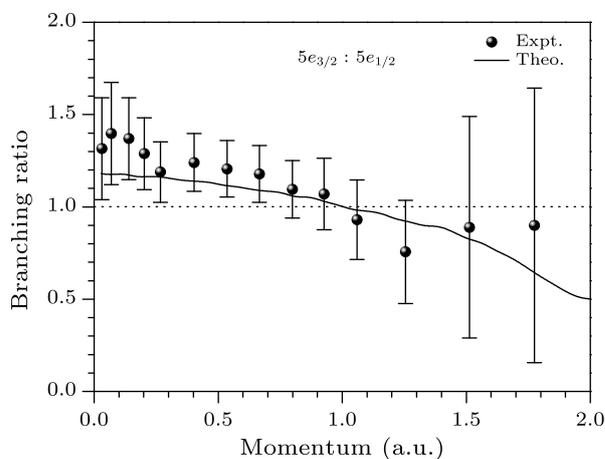| Orbital | Theoretical value (eV) | Experimental value (eV)[a] |
|---|---|---|
| $5e_{1/2}$ | 8.29 | 11.18 |
| $5e_{3/2}$ | 7.65 | 10.45 |
| Level interval | 0.64 | 0.73 |

[a] From Ref. [21].



**Fig. 2.** The branching ratio of $5e_{3/2}$ and $5e_{1/2}$ as a function of momentum for $CF_3I$. The experimental data are taken from Ref. [6].

To remove the uncertainty of normalization, the branching ratio of $5e_{3/2}$ and $5e_{1/2}$ as a function of the momentum is shown in Fig. 2. The differences between the momentum profiles of $5e_{3/2}$ and $5e_{1/2}$ can be clearly shown in Fig. 2. The experimental data are also from the recent work of Li et al.,[6] and the curves are our theoretical results obtained by the spin-orbit relativistic calculations. The non-relativistic method cannot calculate the spin-orbit splitting components, so the branching ratio is equal to the statistical weight of

the two spin-orbit splitting components, namely 1 : 1, shown as a dashed line. However, the branching ratio given by the experiment obviously deviates from the value of 1. The theoretical curve given by this work features the experimental data excellently, i.e., the intensity of $5e_{3/2}$ is greater than $5e_{1/2}$ in the momentum region $p < 1.0$ a.u. and smaller in the momentum region $p > 1.0$ a.u.

In summary, with our newly developed method, the theoretical electron momentum distributions for spin-orbit splitting states $5e_{1/2}$ and $5e_{3/2}$ of $CF_3I$ are calculated, and compared with the recent experimental measurement. The results indicate that the theoretical calculations agree with the experimental data very well, and the spin-orbit relativistic quantum chemical calculations can describe the relativistic effects on the electron momentum distributions of molecule orbitals.

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