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An electron momentum spectroscopy study of the highest occupied molecular orbital of difluoromethane

G.L. Su, C.G. Ning, S.F. Zhang, X.G. Ren, H. Zhou, B. Li, F. Huang,
G.Q. Li, J.K. Deng *, Y. Wang

Department of Physics, Tsinghua University, Beijing 100084, PR China
Key Laboratory for Quantum Information and Measurements, MOE, PR China

Abstract

The highest occupied molecular orbital (HOMO) of difluoromethane (CH_2F_2) has been firstly studied by binary (e, 2e) electron momentum spectroscopy (EMS), at the impact energy of 1200 eV plus binding energy, and using symmetric non-coplanar kinematics. The experimental momentum profile of the HOMO is compared with Hartree–Fock (HF) and density functional theory (DFT) methods with various basis sets. The experimental measurement is well described by the HF and DFT calculations except for the low-momentum region.
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1. Introduction

Difluoromethane, also known as HFC32 (CH_2F_2), is an important refrigerating medium and fire extinguishing agent. Recently, it is called a green refrigerating medium because it does not damage the ozone layer and has the potential contribution to global warming [1]. Furthermore, it has become a chlorofluorocarbon replacement of hydrofluorocarbon (HFC) in industrial applications [2]. Otherwise, the detailed molecular mechanism of the action of difluoromethane remains unknown in all cases. Requirements for such understanding include a detailed knowledge of the chemically important part of the molecular electron density, particularly the part of the wave function corresponding to the highest occupied molecular orbital (HOMO) as well as the lowest unoccupied molecular orbital (LUMO), since factors such as orbital electron density distributions are believed to be important for reaction chemistry [3,4] and molecular similarity and recognition [5]. Thus far electron momentum spectroscopy (EMS) is the only experimental technique able to

effectively image individual valence orbital electron density distributions. The EMS experiments which have been developed extensively for investigating the electronic structures of atoms, molecules and condensed matter [6–10], carried out in momentum space, together with appropriate Hartree–Fock (HF) or density functional theory (DFT) quantum mechanical calculations have been able to provide detailed quantitative information on the reactive parts of molecular electron densities. It should also be noted that EMS is particularly sensitive to the low momentum part of the frontier orbital densities that may be important in molecular recognition and the initial processes involved in the early stages of a chemical reaction. Cooper et al. [11] have shown that the assessment of electron density topographies is much more effectively carried out in momentum space than in the more commonly used position space.

Difluoromethane has been widely studied not only by HeI and HeII photoelectron spectroscopy (PES) [12,13] and X-ray photoelectron spectroscopy (XPS) [14], but also by the theoretical works [15]. To our best knowledge, no EMS study of difluoromethane has been reported so far. In this Letter, we report the binding energy spectra of difluoromethane and electron mo-

mentum profile of its HOMO using (e, 2e) electron momentum spectrometer at an impact energy of 1200 eV plus binding energy with the symmetric non-coplanar geometry. The measured momentum profile is compared with the HF and DFT calculations using different basis sets.

2. Theoretical and experimental background

Electron momentum spectroscopy is based on a so-called binary (e, 2e) experiment, which is an electron impact ionization process. Within several approximations [6], of which the most important are the plane wave impulse approximation (PWIA), and the binary encounter approximation as well as the target HF approximation (THFA), the triple differential EMS cross-section for randomly oriented molecules is then given [6] by

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

where $\psi_j(\boldsymbol{p})$ is the one-electron momentum space canonical Hartree–Fock orbital wavefunction for the jth electron, corresponding to the orbital from which the electron was ionized. The $\int d\Omega$ represents the spherical average due to the randomly oriented target. The integral in Eq. (1) is known as the spherically averaged one-electron momentum distribution. To this extent EMS has the ability to image the electron density in individual 'orbitals' selected according to their binding energies.

The triple differential EMS cross-section has recently been re-interpreted [16] in the context of Kohn–Sham DFT and the target Kohn–Sham approximation (TKSA) gives a result similar to Eq. (1) but with the canonical Hartree–Fock orbital replaced by a momentum space Kohn–Sham orbital $\psi_j^{KS}(\boldsymbol{p})$

$$\sigma_{EMS} \propto \int d\Omega |\psi_j^{KS}(\boldsymbol{p})|^2. \tag{2}$$

It should be noted that accounting of electron correlation effects in the target ground state is included in the TKSA via the exchange correlation potential. A more detailed description of the TKSA-DFT method may be found elsewhere [16].

Theoretical calculations of the momentum profiles were carried out using the GAUSSIAN98 program. The optimized geometry of difluoromethane has been used for all the calculations.

A detailed description of the present constructed electron momentum spectrometer has been reported elsewhere [17]. Therefore, it is described briefly here. It consists of an electron gun, a reaction chamber, and two hemispherical electron energy analyzers each having a five-element cylindrical retarding lens and a one-dimension position sensitive detector. In the present work,

the polar angles of both analyzers are kept fixed at 45°. One analyzer turntable is kept in a fixed position while the other one is rotated over a range of ±30°. The incident electron energy was 1200 eV plus binding energy and the two outgoing electrons have essentially equal energies (600 eV). The coincidence energy resolution of the spectrometer was measured to be 1.15 eV FWHM using argon 3p ionization. The experimental momentum resolution is estimated to be ∼0.1 a.u. from a consideration of the argon 3p angular correlation. The sample of difluoromethane (99.0% purity) was used without further purification. No impurities were evident in the binding energy spectra.

3. Results and discussion

Difluoromethane (CH_2F_2) contains 26 electrons and has C_{2V} symmetry point group. The ground state electronic configuration can be written as

$$(core)^6 \underbrace{(3a_1)^2(2b_2)^2(4a_1)^2}_{\text{inner valence}} \underbrace{(5a_1)^2(3b_2)^2(1b_1)^2(1a_2)^2(6a_1)^2(4b_2)^2(2b_1)^2}_{\text{Outer valence}}.$$

The valence-shell contains 10 molecular orbitals and can be divided into two sets of three inner valence and seven outer valence orbitals. The order of these valence orbitals has been established both by PES and molecular calculations [13].

In order to obtain the experimental momentum profiles, twelve binding energy spectra over the energy range of 7–32 eV which cover seven outer valence orbitals and one inner valence orbital were collected at the out-of-plane azimuth angles $\varphi = 0°, 1°, 2°, 3°, 4°, 6°, 8°, 10°, 12°, 14°, 16°$ and $21°$ in a series of sequential repetitive scans. The binding energy spectra of difluoromethane in the range 7–32 eV for measurements at $\varphi = 1°$ and $\varphi = 10°$ are shown in Fig. 1 at the incident energy of 1200eV plus the binding energy. The spectra in Fig. 1 are fitted with a set of individual Gaussian peaks. The fitted Gaussians for individual peaks are indicated by dashed lines while their sum, i.e. the overall fitted spectra, are represented by the solid lines. The widths of the peaks are combinations of the EMS instrumental energy resolution and the corresponding Franck–Condon widths derived from high resolution PES data [13].

The PES spectrum of the seven outer valence and one inner valence region has been reported by Bieri et al. [13]. In this work, the vertical ionization potentials of the $2b_1, 4b_2, 6a_1, 1a_2, 1b_1, 3b_2, 5a_1$ and $4a_1$ orbitals were determined to be 13.3, 15.4, 15.4, 15.8, 19.1, 19.1, 19.1 and 24.0 eV, respectively.

In the EMS binding energy spectra of Fig. 1, however, only four structures could be clearly identified. The ionization peak for the HOMO, $2b_1$, at 13.3 eV is well resolved. The next three outer valences orbitals with the 15.4 eV average vertical ionization potential, $4b_2, 6a_1$
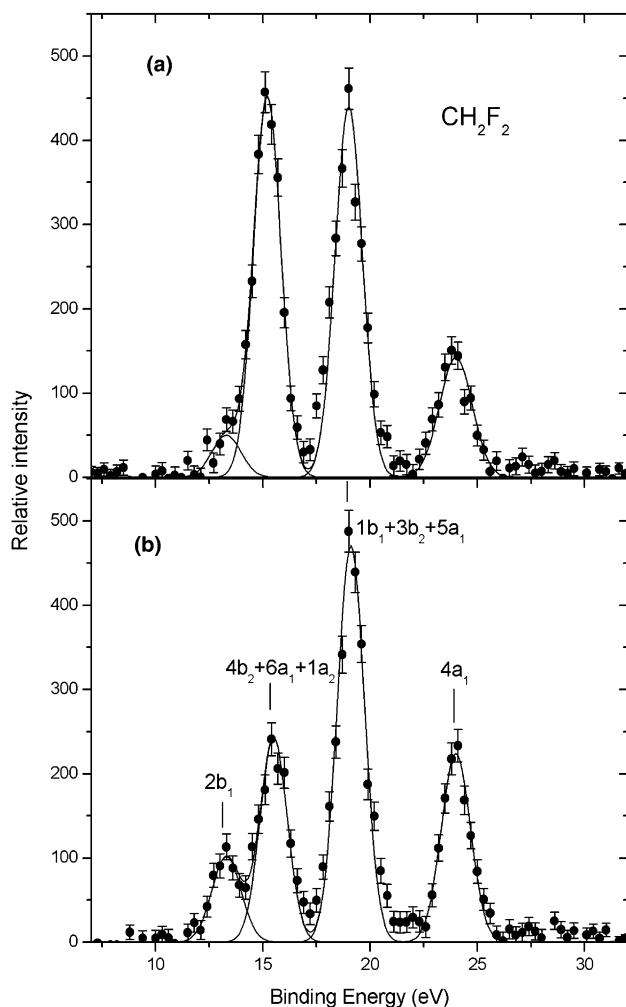
Fig. 1. Valence shell binding energy spectra for difluoromethane at (a) $\phi = 1°$ and (b) $\phi = 10°$. The dashed and solid lines represent individual and summed Gaussian fits, respectively.

cross-sections with the experimental electron momentum profile, the effects of the finite spectrometer acceptance angles in both θ and ϕ ($\Delta\theta = 0.6°$ and $\Delta\phi = \pm 1.2°$) were incorporated in the calculations using the UBC RESFOLD program based on the Gaussian-weighted planar grid method [18]. The experimental momentum distribution is compared, in Fig. 2, with four theoretical momentum profiles calculated using Hartree–Fock method (curves 3 and 4) and DFT-B3LYP method (curves 1 and 2) with the 6-311++G** and 6-31G basis sets. In the momentum range above 0.25 a.u., it can be seen that the experimental result is well described by the HF and DFT calculations. Whereas, the small residual experimental intensity is in excess of all the calculations for the HOMO of difluoromethane in the low momentum region below 0.25 a.u. The discrepancy between experiment and theory in the low momentum region is probably due to inaccuracies in the Gaussian fitting procedures since the nearby two ionization peaks, i.e., the first peak and the second peak in the binding energy spectra in Fig. 1 are close and the second peak, i.e., the $4b_2 + 6a_1 + 1a_2$ peak is large and could leak into the first peak i.e., the HOMO peak in the low momentum range. An other possible source for the discrepancy in the low momentum range could be because of the distorted wave effects in the following discussion. The momentum and position space density contour maps calculated by DFT-B3LYP/6-311++G** for the difluoromethane $2b_1$ orbital are shown in Figs. 3 and 4, respectively. The contour maps are slices of the orbital electron density in the position and momentum space. In the momentum density map of Fig. 3, it obviously shows that the momentum profile of the orbital is p-type which is the case as shown in our experiment. As shown in the case of the position density map of Fig. 4, the general shape of the orbital is similar to that
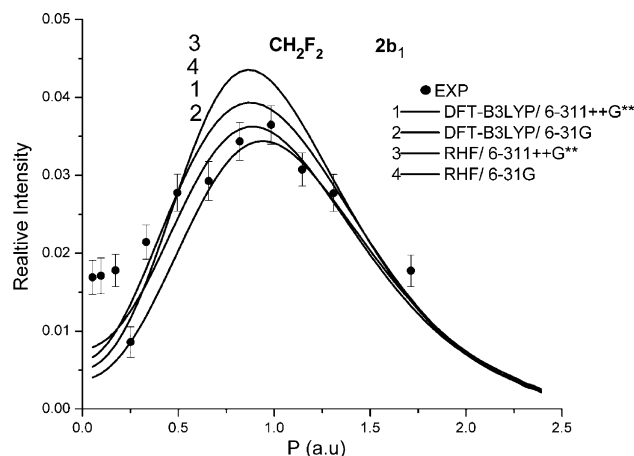
and $1a_2$, are not well separated experimentally due to their small energy separations [13]. The same is true of the next three outer valence orbitals with the 19.1 eV average vertical ionization potential, $1b_1$, $3b_2$ and $5a_1$, which even the high resolution PES could not resolve [13]. The band located at 24.0 eV corresponds to the ionization of the $4a_1$ orbital. Thus the EMS experimental binding energy spectra are consistent of the PES values [13]. Some weak structures above 26 eV are observed which may due to correlation effects in the target or in the final state of residual ion.

The experimental momentum profile (XMP) has been extracted by deconvolution of the sequentially obtained angular-correlated binding energy spectra, and therefore the relative normalization for the different transitions is maintained. For the HOMO, the various theoretical momentum profiles (TMPs) are obtained with the methods described above. The experimental result is normalized to the DFT-B3LYP/6-311++G** calculation for the HOMO. In order to compare the calculated

Fig. 2. The experimental and calculated momentum distributions for the HOMO of difluoromethane. The TMPs are calculated by using Hartree–Fock (curves 3 and 4) and DFT-B3LYP (curves 1 and 2) methods with the 6-311++G** and 6-31G basis sets.
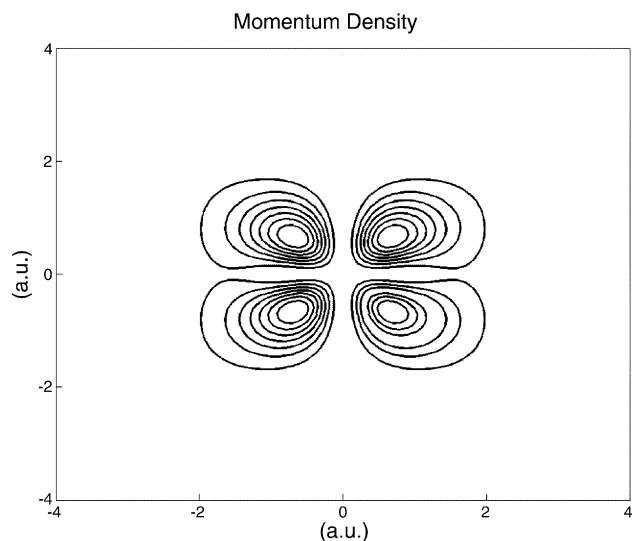
Momentum Density

Fig. 3. Momentum density contour map for the HOMO of difluoromethane calculated by DFT-B3LYP/6-311++G**.
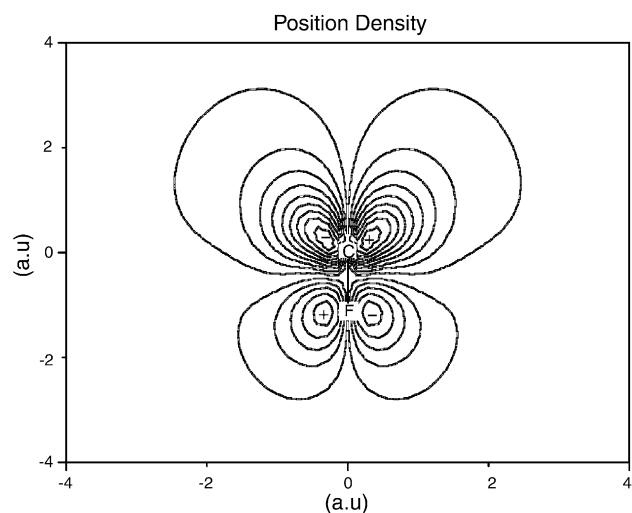
Position Density

Fig. 4. Position density contour map for the HOMO of difluoromethane calculated by DFT-B3LYP/6-311++G**. Relative signs of the wavefunctions are indicated by plus (+) and minus (−).

of a π^* orbital, which is in agreement with Brundle et al.'s conclusion that the orbital contains a large fraction C–F π antibonding character [19]. This 'π^* effect' is likely due to the d-like nature of π^* orbitals and could be attributed to distorted wave effects which increase the calculated cross-sections in the low momentum range to match the experimental measurements. Similar effects have been seen in atomic d-orbital XMPs [20] and some molecular XMPs [21,22].

4. Summary

In summary, we report the first measurements of the valence shell binding spectra and the HOMO momentum profile of difluoromethane. The experimental momentum profile is also compared with the theoretical momentum distributions calculated using Hartree–Fock (HF) and density functional theory (DFT) methods with various basis sets. In general, the experimental measurement is well described by the HF and DFT calculations except for the low-momentum range. The full details of the experimental results and the associated theoretical analysis for difluoromethane will be reported later.

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