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快报

CF₂BrCl 分子近域轨道的电子动量谱学研究*

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Electron Momentum Spectroscopy of the Frontier Molecular Orbitals of CF₂BrCl*

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Abstract The frontier molecular orbitals (HOMO and NHOMO) of CF₂BrCl molecule have been firstly investigated by (e,2e) electron momentum spectroscopy. The experimental momentum profiles are compared with the theoretical profiles employing Hartree-Fock and density functional theory with 6-31G and 6-311 + G(d) basis sets. Both HF and DFT calculations using 6-311 + G(d) basis set can well describe the experiment, whereas those calculated using 6-31G basis set largely underestimate the experiment at the low momentum region. Furthermore, orbital electron density images show that HOMO and NHOMO have a mixed character of the bromine and chlorine lone pairs.

Key words Electron momentum spectroscopy, Hartree-Fock, Density functional theory

Bromochlorodifluoromethane (CF₂BrCl), also known as Halon 1211 in industry, is a main agent widely used for fire suppression applications and has received considerable attention because of its potential for stratospheric ozone depletion^[1,2]. The detailed information on properties of CF₂BrCl molecule such as ionization potential, chemical bonding character and electron density distribution of molecular orbitals, especially of the frontier molecular orbitals, is believed to be important for chemical reaction and possible molecular recognition according to the frontier orbital

theory of Fukui^[3]. Electron momentum spectroscopy (EMS) is particularly sensitive to the chemically important low momentum (outer spatial) electron density of valence orbitals, and has become one of premier tools in the study of electronic structures of atoms and molecules due to its unique ability to directly obtain spherically averaged electron momentum distribution for individual orbital^[4-6].

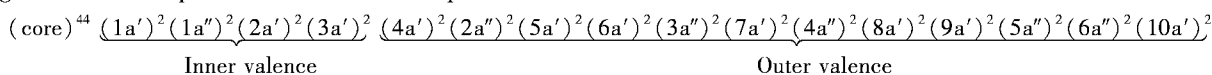
The electronic structure of CF₂BrCl molecule has been studied by the photoelectron spectra (PES)^[7,8]. To our best knowledge, no EMS measurement on

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CF₂BrCl has been reported so far. In this letter, we report the first investigation on the frontier molecular orbitals (HOMO and NHOMO) of CF₂BrCl by EMS, and present the experimental and theoretical momentum profiles (XMPs and TMPs). A detailed description of the experimental apparatus has been given elsewhere^[9,10]. The coincident energy resolution of the present spectrometer was measured to be 1.2 eV (FWHM) using Ar 3p ionization. The momentum resolution was estimated to be 0.15 a. u. by comparing the XMPs and TMPs of Ar 3p orbital.

EMS is based on the kinematically complete (e, 2e) collision experiment which is an electron impact single ionization process. Within the plane wave



The assignment of the order of these valence orbitals is based on the PES^[8] and our present molecular orbital calculation using B3LYP method with 6-311 + G(d) basis set. Due to the low symmetry, the bromine lone pair in CF₂BrCl splits two non-degenerate HOMO 10a' and NHOMO 6a'' orbitals with the ionization energy of 11.51 and 11.81 eV, respectively^[8].

Sixteen binding energy spectra (BES) of CF₂BrCl molecule over the energy range 5 ~ 30 eV have been measured at sixteen different azimuthal angles, which cover all twelve outer valence orbitals. Fig. 1 shows the BES measured at azimuthal angles $\phi = 2^\circ$. Gaussian peaks fitted to the individual transitions are shown by dotted curves while their sum is by a solid curve. The positions of individual Gaussian peaks are estimated by

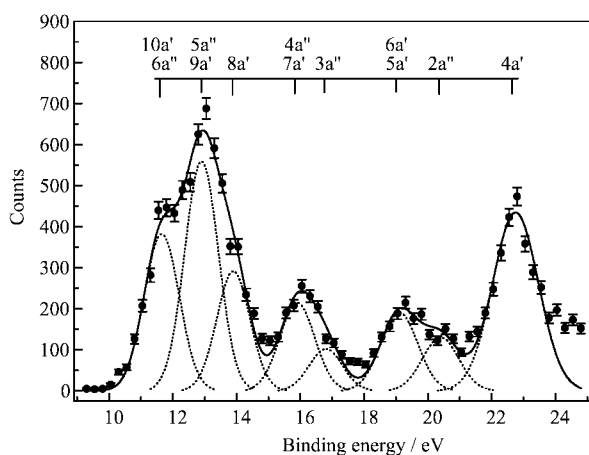


Fig. 1 Binding energy spectrum of CF₂BrCl at $\phi = 2^\circ$

impulse approximation, as well as the target Hartree-Fock approximation or target Kohn-Sham approximation, the triple differential cross section of the (e, 2e) reaction can be written as^[4,11]

$$\sigma_{\text{EMS}} \propto \int d\Omega_p |\varphi_q(p)|^2 \quad (1)$$

where φ_q is the one-electron momentum space canonical Hartree-Fock or Kohn-Sham wavefunction for the q th orbital from which the electron is knocked out. The integral in the expression (1) is the spherically averaged electron momentum distribution.

The CF₂BrCl molecule contains 76 electrons and has C_s point group symmetry. Its ground electronic configuration can be written as

the ionization potentials determined by PES^[7,8]. The widths of the Gaussian peaks are the combinations of EMS instrumental energy resolution and Frank-Condon width of the corresponding bands determined by PES^[7,8]. The first Gaussian peak at about 11.65 eV corresponds to the ionization from the HOMO 10a' and NHOMO 6a'' orbitals, and it is partly resolved in the BES.

The XMPs can be obtained by plotting the area of the corresponding Gaussian peak in BES versus the orbital electron momentum converted by the azimuthal angles. The TMPs according to the expression (1) were calculated using Hartree-Fock (HF) and B3LYP methods with 6-31G and 6-311 + G(d) basis sets in the GUASSIAN 98W program^[12]. In order to compare with the XMPs, the TMPs were convoluted with the instrumental angular resolution utilizing the Gaussian-weighted planar grid method^[13] and normalized to the common intensity scale by the comparison of the XMPs and TMPs calculated using B3LYP/6-311 + G(d). Fig. 2 shows the summed XMPs and TMPs for the HOMO 10a' and NHOMO 6a'' orbitals of CF₂BrCl, together with the TMPs of bromine atom 4p orbital. It can be seen that the momentum profile of HOMO and NHOMO orbitals exhibits a p-type character. Both HF and DFT calculations using 6-311 + G(d) basis set well describe the experiment whereas those calculated

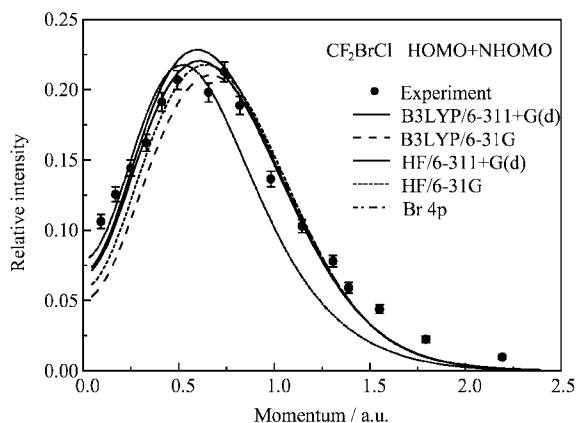


Fig. 2 The XMPs and TMPs for HOMO and NHOMO orbitals of CF₂BrCl

using 6-31G basis set largely underestimate the experiment at the low momentum region. In addition, the XMPs and TMPs of HOMO and NHOMO are obviously more diffuse than the TMPs of bromine atom 4p lone-pair orbital, indicating that the bromine lone pair in CF₂BrCl possibly suffers a strong interaction. As shown in Fig. 3, HOMO and NHOMO orbital electron density

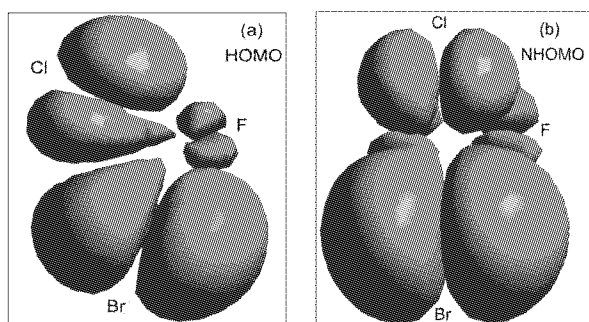


Fig. 3 Orbital electron density images in position space for HOMO and NHOMO of CF₂BrCl calculated using B3LYP method with 6-311 + G(d) basis set

images in position space show that these two outermost orbitals have a mixed character of the bromine and chlorine lone pairs, and the HOMO orbital displays an obvious intramolecular repulsion interaction between the bromine and chlorine lone pairs in CF₂BrCl, which does not agree with the slight interaction predicted by Doucet *et al.* [7].

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