Intramolecular diffraction in (e, 2e) reactions of CX_4 (X=F, Cl, Br)

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Synopsis The remarkable discrepancies between the experimental momentum distributions and the calculated distributions within the plane wave impulse approximation (PWIA) were observed in (e, 2e) reaction of CF_4, CCl_4, and CBr_4. The discrepancies evidently depend on the impact energy of electrons. One possible explanation is the intramolecular diffraction.

If the wavelength of an electron is comparable with the atomic distances in a molecule, we expect to see diffraction in the scattering. Recently, the diffraction effect in the x-ray photoelectron spectroscopy has been reported [1,2]. In the electron momentum spectroscopy (EMS), the typical electron energies are several hundreds eV. The wavelength of scattered electrons with a kinetic energy of 300 eV is 0.71Å, 0.50 Å for 600 eV, which are comparable with bond lengths of molecules. For example, the CF bond length d_{CF} of CF_4 is 1.315 Å, and $d_{CCl}(CCl_4)$=1.767 Å, $d_{CBr}(CBr_4)$=1.942 Å. Since the (e,2e) accompanying diffractions is a higher order effect as compared with the direct (e,2e) binary collision, it may be overwhelmed by the direct (e,2e) intensity. However, the direct (e, 2e) intensity may become very small at the low momentum region for some anti-symmetric molecular orbitals. Therefore, the diffraction effect can become observable.

Figure 1 plots the highest occupied molecular orbitals (HOMOs) of CF_4, CCl_4, and CBr_4, which have four anti-symmetrical lobe-like pairs. As shown in Figure 2, the calculated (e, 2e) intensity at low momentum region under PWIA is approximately zero. For example, the calculated intensity is very low as the momentum less than 0.5 a.u. for HOMO of CF_4. The four symmetrically located F, Cl, Br atoms can enhance the diffraction due to the interference. Indeed, there are remarkable discrepancies between the experimental momentum distributions and the calculation without considering diffractions. The experimental intensity at low momentum region is remarkably higher than the PWIA calculation, and the discrepancy decreases as the impact energy increases from 600 eV to 1200 eV. This agrees with the diffraction explanation since the wavelength become further shorter than atomic distances as the energy of electrons increases. The further calculations including diffraction effects are needed for explaining the details.

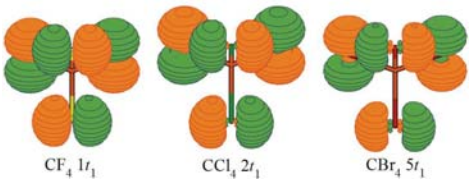

Figure 1. Plots of HOMOs of CF_4, CCl_4, and CBr_4 with the contour value 0.05.

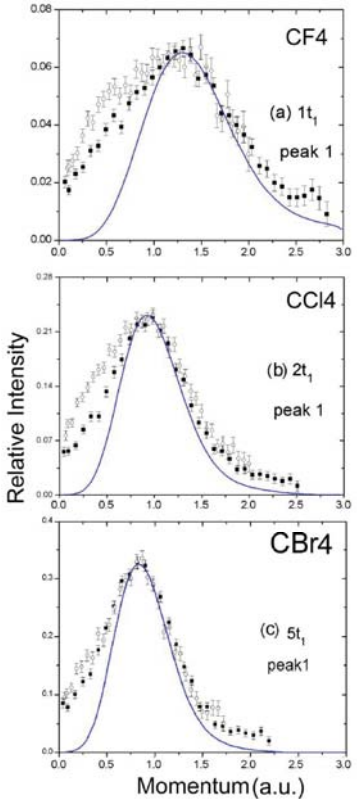

Figure 2. Experimental momentum distributions of HOMOs of CF_4, CCl_4, and CBr_4 (open circles at 600 eV, and solid at 1200eV) compared with calculations using B3LYP/Aug-cc-pVTZ under PWIA (solid lines). The experimental resolution has been convoluted in the calculations.

References

[1] F Krasniqi *et al* 2011 *Phys. Rev. A* **81** 033411
[2] A Landers *et al* 2001 *Phys. Rev. Lett.* **87** 013002

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