Relationship between interference pattern and molecular orbital shape: a binary (e, 2e) study on SF_6

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Synopsis We report a binary (e, 2e) study on interference effects in the electron momentum density distributions of the molecular orbitals of SF_6. The (e, 2e) experiment on SF_6 has been performed in the symmetric noncoplanar geometry and interference patterns for each molecular orbital have then been obtained. It has been shown that the interference patterns provide information about not only the molecular geometry but also the spatial orientation of the constituent atomic orbitals even for this relatively complicated molecule.

Electron momentum spectroscopy (EMS), also known as binary (e, 2e) spectroscopy, is a powerful means for investigating the electronic structures of atoms and molecules. Within the plane wave impulse approximation (PWIA), the EMS cross section is directly related to the electron momentum density distribution of the ionized orbital. EMS thus enables one to look at individual electron orbitals in momentum-space (p-space).

A notable feature of p-space wave functions is that for molecules, the information about the nuclear positions appears only in phase factors introduced by the Dirac-Fourier transform. Hence, the electron momentum density distribution of a molecular orbital (MO) possesses cosinusoidal modulations, for instance, that with periodicity of $2\pi/R_{jk}$ along the direction of the line connecting atoms j and k, separated by the distance, R_{jk}. Furthermore, the interference pattern may provide a wealth of information on the spatial distribution and symmetry of the MO [1]. In this contribution, we report our recent EMS study on the interference effects for the five outermost molecular orbitals of SF_6, which are each constructed from the F 2p atomic orbitals (AOs) [2]. The principal aim of the present work is to elucidate the relationship between interference pattern and molecular orbital shape for SF_6.

An EMS experiment was carried out for the molecule at impact energy of 1.2 keV. In the experiment, two fast outgoing electrons having equal energies and making equal polar angles of 45° with respect to the incident electron beam axis were detected in coincidence. In this way, (e, 2e) data were obtained as a function of binding energy and the ion recoil momentum. Interference patterns for each MO were then obtained by dividing the experimental data by distorted-wave-Born-approximation cross section for an isolated F 2p AO.

Fig. 1 shows the experimental interference factors thus obtained for the $3e_g$ and $1t_{2g}$ orbitals as well as the associated PWIA calculation. A glance at the figure shows that the experimental results clearly exhibit oscillations, as expected, and that the interference patterns are largely dependent upon the MO shape. Further analysis has shown that they allow one to experimentally clarify the symmetries of the nonbonding MOs and also that they provide information about the degree of orientation of the 2p AOs and about the tilt angles of the AOs with respect to the internuclear directions.

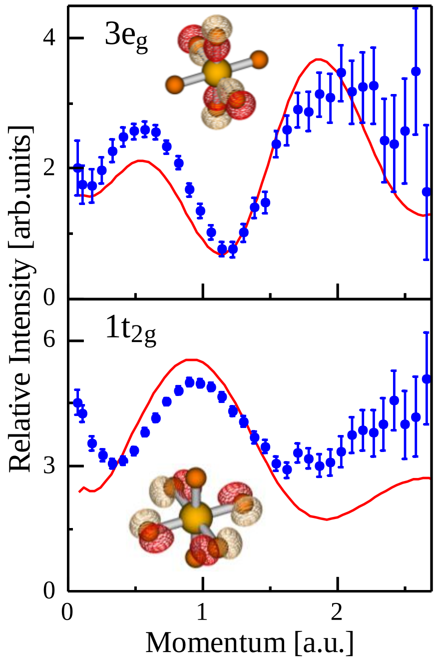

Figure 1. Interference patterns for the $3e_g$ and $1t_{2g}$ orbitals of SF_6.

References

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