Mapping attosecond electron wavepacket motion in a molecule by using two-color laser pulses

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We measure high harmonic generation spectra of D_2, N_2, CO_2, N_2O and hydrocarbons by using simultaneously 800nm and 400 nm laser pulses generated with perpendicular polarization. The intensity of high harmonic spectra is modulated as we change the relative phase of the two pulses. The phase of intensity modulation depends on the symmetry of molecular orbitals from which high harmonics are emitted. We show that this allows us to identity any molecular orbital that can contribute high harmonic generation even randomly aligned molecule. Using this approach, we also show the observation of electron wavepacket motion occurring in a few-hundred attoseconds.

A high harmonic generation spectrum contains information on vibration, electronic structure, and its dynamics of molecules from which high harmonics are generated. Molecular orbital tomography approach allows us to measure the amplitude of an electron wavefunction [1]. However, the experimental example of this approach has been limited to the N_2 molecular orbital.

Recently, another route for orbital tomography was demonstrated by using orthogonally polarized, 800nm and 400 nm laser pulses [2]. We extend this approach to identify molecular orbital symmetry and observe the dynamical motion occurring within a few-hundred attosecond time-scale.

To identify molecular orbital symmetry, we use the following method. High harmonic emission is generally polarized. The polarization angle (ϕ_{HHG}) depends on both angle of electron re-collision (θ_c) and the symmetry of molecular orbital that contributes high harmonic generation. Therefore, by measuring the relationship between the two angles, we identify the molecular orbital symmetry. If molecular orbital changes in the spatial distribution of amplitude and phase until electron re-collision, then the ϕ_{HHG} also must be changed. From this, dynamical changes of molecular orbital can be measurable. For non-aligned molecules, harmonics are preferentially generated from that portion of the ensemble which dominates the ionization probability. It allows us to apply this method without aligning molecule.

We generate 400nm laser pulses from 35fs, 800nm laser pulses ($\sim1.5 \times 10^{14}$W/cm^2) by passing a BBO crystal. We measure high harmonic generation spectra as a function of the relative delay. Changing the delay between the two pulses changes the θ_c. We obtain the ϕ_{HHG} by comparing the relative intensity between two adjacent harmonic pairs (*i.e.*, 13th and 14th) as a function of harmonic number and the delay.

We observe that at the θ_c of ~0 degrees, the ϕ_{HHG} is ~0 for D_2 and N_2,while the ϕ_{HHG} is ~90 degrees for CO_2 and N_2. At the θ_c is ~45 degrees, the ϕ_{HHG} is ~45 degrees for D_2 and N_2, while the ϕ_{HHG} is ~0 degrees for CO_2 and N_2O. This observation is consistent with the calculated results when the high harmonics are generated from the σ_g state for D_2 and N_2, while the π_g (or quasi-π_g) state for CO_2 and N_2O. Since CO_2's (or N_2's) highest occupied molecular orbital (HOMO) has π_g (or σ_g) symmetry, the experiments suggest that HOMO is a dominant role for high harmonic generation process in the present laser intensity.

For the hydrocarbon, we observe the double peak structure of the ϕ_{HHG} as a function of the delay. Our analysis indicates that the molecular orbital symmetry changes as the harmonic number increases. The result cannot be accounted for two independent orbital contribution. Instead, the observation agrees with the result of calculation where the molecular orbital changes its spatial distribution in the range1.3 ~1.7fs after the tunnel ionization due to coherent superposition of two states.

References

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