High harmonic generation from multiple molecular orbitals of \( \text{N}_2 \)

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Abstract. We observe the contribution of the HOMO and HOMO-1 orbitals in high harmonics from \( \text{N}_2 \) and discuss the harmonic modulation in the rotational revivals.

Introduction

High harmonic generation (HHG) proceeds in three steps: (1) A part of the electron wave function tunnels out of the valence orbital; (2) The liberated electron wave packet accelerates in the laser field; (3) The electron wave packet coherently recombines with the initially ionized orbital [1]. For molecules, the highest occupied molecular orbital (HOMO) is generally thought to be responsible for ionization and recombination. The spectrum has been transformed to produce an image of the HOMO’s \( \sigma_g \) electronic structure [2]. We have obtained new experimental evidence that other orbitals apart from the HOMO, namely the HOMO-1 with its \( \pi_u \) symmetry, contribute to HHG. We reproduce the experimental features with semi-classical simulations of the recombination process on the HOMO and HOMO-1. This opens the route to imaging coherent superpositions of electronic orbitals.

Experimental Methods

An ultrashort laser pulse from a Ti:Sapphire amplifier interacts with the anisotropic polarizability of \( \text{N}_2 \) molecules in a supersonic jet and creates a rotational wave packet that results in molecular alignment at wavepacket revivals [3]. We concentrate on the half rotational revival in Fig. 1. At 4.1 ps after the alignment pulse, the molecular ensemble is aligned along the pulse polarization with a prolate distribution, followed by an oblate distribution at 4.3 ps. A second laser pulse with a variable intensity from \( 1.6 \) to \( 2.3 \times 10^{14} \) \( \text{W/cm}^2 \) generates high harmonics in the aligned molecules. Since the signal we attribute to the HOMO-1 is most pronounced under 90 degrees relative polarization of alignment and generation pulse, we concentrate on this configuration. The HHG beam passes through a thin Al filter and aperture which reject the fundamental as well as harmonics from long electron trajectories. The remaining harmonics are dispersed by a flat-field grating and detected by a MCP-phosphor screen unit. The HHG signal as a function of delay between alignment and harmonic generating pulse is given in Fig. 1 for a selection of harmonics from 15 to 39.

Results and Discussion

Figure 1 b) shows the harmonic signal for perpendicular polarizations of alignment and high harmonic generating laser pulses for a harmonic generation intensity of \( 2.3 \times 10^{14} \) \( \text{W/cm}^2 \). As seen in the inset Fig. 1a), the molecular axes are preferentially
perpendicular with respect to the harmonic generating polarization at 4.1 ps and a decrease of the signal at harmonic 15 is observed compared to the unaligned case prior to 3.6 ps. At 4.3 ps the molecular axes are partially parallel to the harmonic generating polarization and an increase of the harmonic radiation compared to the unaligned case is observed on harmonic 15. However, as the harmonic number increases above number 25, a peak grows out of the minimum at 4.1 ps. At the 39th harmonic the peak is most pronounced and the temporal modulation compared to harmonic 15 is inverted. For lower intensities of 1.9 and $1.6 \times 10^{14}$ W/cm$^2$ (c and d), the single peak at 4.1 ps is visible, however at lower harmonics. The peak at 4.1 ps is always most pronounced in the cutoff region.

![Graph](image.png)

**Fig. 1.** a) At 4.1 ps a prolate distribution of molecular axes is created standing orthogonal to the generation polarization, whereas at 4.3 ps an oblate ensemble is generated, which has axes partwise parallel to the generation polarization. The alignment polarization is perpendicular to the generation polarization. b)-d) For harmonic 15, a modulation by a minimum at 4.1 ps followed by a maximum at 4.3 ps is visible. At higher harmonics, the signal modulation is reversed. We attribute the peak visible at 4.1 ps for the higher harmonics to ionization and recombination to the HOMO-1.

We interpret the data in terms of tunnel ionization and recombination for the molecular orbitals in Fig. 2 a) and b). For tunnel ionization the magnitude of the molecular wave function far away from the nuclei and in direction of the generation polarization is important. Thus, the $\sigma_g$ HOMO orbital ionizes more easily if the generation polarization is parallel to the internuclear axis as compared to the perpendicular case. Also the recombination dipole is larger if the molecular axis is aligned with the generation polarization, since the recombination dipole has a larger amplitude in the long direction of the orbital. For the HOMO, ionization and recombination maximize the signal for molecules standing parallel to the HHG polarization and minimize the signal in the perpendicular configuration explaining the observed experimental trend in harmonics 15-25 in Fig. 1 b)-d).

The peak growing out of the minimum at harmonic 25-39 can be explained by reversed conditions for effective and ineffective HHG. The HOMO-1 fulfills exactly