Interferometer-free Fourier-synthesized laser field generator estimated by molecular tunnelling ionization

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Abstract. Intense nanosecond four-colour Fourier-synthesized laser fields induce orientation-selective ionization based on directionally asymmetric molecular tunneling ionization. The interferometer-free laser field generator ensures high stability and high reproducibility. Phase-sensitive, orientation-selective molecular tunneling ionization provides a simple way to estimate the relative phase differences between the fundamental light and each harmonic by data-fitting analysis.

1. Introduction
Optical excitation using a two-color phase-controlled laser field consisting of the fundamental and its harmonic, has been theoretically explored by Brumer and Shapiro [1]. For weak laser fields \( I < 10^{12} \text{ W/cm}^2 \), a scheme involving quantum interference between two photo-transitions can be used to control the population of a targeted state by constructive or destructive interference [1]. In contrast, for intense laser fields \( I > 10^{12} \text{ W/cm}^2 \), a scheme involving phase-controlled electric fields that steer the motions of charges or dipoles has been studied. Typical examples of such schemes are found in tunneling ionization (TI) [2-4]. Phase-controlled two-color laser fields have been used to control such coherent electron motions in TI [5-16].

An extension of this methodology is the well-known synthesis by Fourier transformation theory of arbitrary light waveforms with a series consisting of a fundamental frequency of light and its harmonics. We have reported the use of Fourier-synthesized laser fields to achieve quantum control of molecular TI [17]. Directionally asymmetric molecular TI induced by intense \( I = 5 \times 10^{12} \text{ W/cm}^2 \) nanosecond Fourier-synthesized four-color laser fields consisting of fundamental, second-, third-, and fourth-harmonic light can make possible orientation-selective molecular TI (OSM-TI) and has been applied to the measurement of the three relative phase differences between the fundamental light and each of its harmonics [17]. In this study, we extend this technology to an interferometer-free Fourier-synthesized laser field generator. This methodology has enabled us to observe the phase-sensitive OSM-TI signals induced by Fourier-synthesized laser fields with high stability and reproducibility. This generator, however, does not separate each beam spatially; therefore, the three relative phase differences cannot be controlled and estimated independently. We have developed a procedure for analyzing the data that enables estimation of the three relative phase differences between the fundamental and each of its harmonics.

2. Experiment
The experimental setup consists of a pulsed Nd:YAG laser, an interferometer-free Fourier-synthesized laser field generator, and a time-of-flight mass spectrometer (TOF-MS) equipped with a supersonic...
molecular beam source. The Q-switched Nd:YAG laser (Spectra-Physics, LAB150) generated horizontally polarized laser pulses with a 10-ns duration and a bandwidth of 1.0 cm⁻¹ at a wavelength of 1064 nm and was operated at a repetition rate of 10 Hz without injection seeding. Fourier-synthesized laser fields consisting of a fundamental light and its harmonics—hereafter, ω, 2ω, 3ω, and 4ω (four-color) laser fields—were generated by an interferometer-free Fourier-synthesized laser field generator [Fig. 1]. All of the nonlinear optical crystals used in this study were β-barium borate, type I phase matching, with thicknesses of 10 mm for the 2ω pulses, 8 mm for the 3ω pulses, and 6 mm for the 4ω pulses. Then the vertical polarization component of ω + 2ω + 3ω + 4ω pulses was selectively transmitted by a polarizer (air-spaced Glan–Thompson prism). The electric field of the linearly polarized Fourier-synthesized laser field is given by

\[ E(t) = E_1 \cos(\omega t) + \sum_{n=2}^{4} E_n \cos(n\omega t + \phi_n), \]  

where \( E_i \) (i = 1, 2, 3, 4) is the amplitude of the electric field of each component and \( \phi_n \) (n = 2, 3, 4) is the relative phase difference between \( \omega \) and its harmonic field. The Fourier-synthesized laser fields were passed through a phase-shifting plate (synthesized quartz, thickness of 10 mm) that could be rotated around the incident angle of 45° to control the relative phase differences, \( \phi_n \). The value of \( \phi_n \) could be changed by the optical length, which was determined by the difference in the value of the refractive index due to dispersion. We note that because all the beams were transmitted through the phase-shifting plate, each \( \phi_n \) could not be controlled independently. A procedure was required to estimate each \( \phi_n \). The Fourier-synthesized \( \omega + 2\omega + 3\omega + 4\omega \) beams were directed toward the TOF-MS and were focused on the supersonic molecular beam by a concave mirror with a focal length of 120 mm. The total intensity \( I = I_1 + I_2 + I_3 + I_4 \) was \( 5 \times 10^{12} \) W/cm² at the focus, and the \( I_2/I_1, I_3/I_1, \) and \( I_4/I_1 \) ratios were about 0.56, 0.25, and 0.063, respectively, where \( I_1, I_2, I_3, \) and \( I_4 \) are the intensities of the \( \omega, 2\omega, 3\omega, \) and \( 4\omega \) pulses, respectively.

Figure 1. Schematics of the optics of a robust interferometer-free Fourier-synthesized laser field generator. The components are labeled as follows: HW, half-wave plate for the \( \omega \) laser beam; BBO(\( n \omega \)), nonlinear optical crystal for generation of the \( n \)th harmonic (\( n = 2, 3, 4 \)); DW, dual-wavelength wave plate (\( \lambda \) for the \( \omega \) laser beam and \( \lambda/2 \) for the \( 2\omega \) laser beam); P, polarizer; PS, phase-shifting plate; and M, mirror. The offset between the four beams is shown for clarity only, as the four beams overlapped completely in the experiment.

The principle of orientation-selective molecular tunneling ionization (OSM-TI) has been described previously [12,15]. Briefly, according to the most fundamental theory of molecular TI, the molecular Ammosov–Delone–Krainov model [18,19], photoelectrons are preferentially removed via tunneling from the large-amplitude lobe of the highest occupied molecular orbital in the opposite direction of the electric field vector. Because of the angular dependence of the TI rate between the electric field vector and the molecular axis, molecules oriented in a certain direction are selectively ionized in a randomly oriented gas-phase molecular ensemble. The amplitude of the electric field is larger in the positive direction than in the negative direction when \( (\phi_2, \phi_3, \phi_4) = (0, 0, 0) \) [17]. The directional asymmetry is reversed when \( (\phi_2, \phi_3, \phi_4) = (\pi, 0, \pi) \) (not shown). In the case of molecules with asymmetric structure, the TI rates of those with positive molecular orientations are expected to differ from those with
negative molecular orientations when TI occurs at the positive field maxima. As a result, the asymmetric waveform of the Fourier-synthesized laser field can selectively ionize molecules while discriminating the head-tail order of molecules with asymmetric structures, a distinction that cannot be achieved by single-frequency laser fields with symmetric waveforms [17]. The phase dependences of OSM-TI are applicable to the estimation of $\phi_n (n = 2, 3, 4)$ [17].

A TOF-MS equipped with a pulsed supersonic molecular beam source was used to detect the ionized molecules and their photo-fragments. TOF spectra were recorded with a digital oscilloscope. The polarization direction of the Fourier-synthesized laser fields was set to be vertical and parallel to the detection axis. We defined $\phi_n (n = 2, 3, 4) = 0$ as the indication that the electric field maxima were pointing toward the ion detector.

3. Results and Discussion

We selected carbonyl sulphide (OCS) as the focus of this study because we have already investigated its behavior by Fourier-synthesized laser fields generated by a multicolor Mach–Zehnder interferometer [17]. The OC$^+$ photo-fragments exhibited a pair of peaks in the TOF spectra. The first peak resulted from ions ejected directly toward the detector, and the second from ions that were first ejected in the backward direction before being accelerated toward the detector by the extraction field. The breaking of the forward-backward symmetry was clearly observed in the TOF spectra. The backward peak of the OC$^+$ ions predominated at $\theta = 45^\circ$. The forward-backward asymmetries of the S$^+$ photo-fragment ions were less pronounced when the OCS molecules were irradiated with Fourier-synthesized $\omega + 2\omega + 3\omega + 4\omega$ pulses because the photo-fragments induced by irradiation of only the $4\omega$ pulse, which is not phase-dependent with a symmetric signal shape, overlapped to cover up the forward-backward asymmetry.

![Figure 2. Yield asymmetries of OC$^+$ ions $A_{\text{yield}} = (I_F - I_B)/(I_F + I_B)$ as a function of angle incident to the phase-shifting plate $\theta$ for the $\omega + 2\omega + 3\omega + 4\omega$ field. The solid curve is the result of fitting analysis. The arrow shows the angle at forward asymmetry. $(\phi_{12}, \phi_{13}, \phi_{14}) = (-0.05\pi, -0.14\pi, 0.15\pi)$ at $\theta = 44.83^\circ$.

We define the forward-backward yield asymmetry of the photo-fragment ions by

$$A_{\text{yield}} = (I_F - I_B)/(I_F + I_B),$$

where $I_F$ ($I_B$) is the signal intensity of the forward (backward) photo-fragment emission. Figure 2 depicts $A_{\text{yield}}$ of the OC$^+$ photo-fragment as a function of the incident angle $\theta$ for the $\omega + 2\omega + 3\omega + 4\omega$ laser field. Clearly phase-dependent behaviors of $A_{\text{yield}}$ were observed for both OC$^+$ and S$^+$. The behavior of the $A_{\text{yield}}$ as a function of incident angle $\theta$ for the $\omega + 2\omega + 3\omega + 4\omega$ laser field was complicated because $A_{\text{yield}}$ was scanned through $\theta$ as a function of $\phi_{12}$, $\phi_{13}$, and $\phi_{14}$ for the $\omega + 2\omega + 3\omega + 4\omega$ laser field. The yield asymmetries of the OC$^+$ and S$^+$ ions were completely out of phase with each other (not shown). These results show that Fourier-synthesized $\omega + 2\omega + 3\omega + 4\omega$ pulses can distinguish the molecular orientation of the head-tail order [17]. Despite the fact that $A_{\text{yield}}$ behaved in a complicated way as a function of the incident angle $\theta$ for the $\omega + 2\omega + 3\omega + 4\omega$ laser field, we have found the phase-sensitive signals $A_{\text{yield}}$ induced by Fourier-synthesized laser fields to be highly stable and reproducible.
We now discuss the data-fitting procedure for estimating all of the $\phi_n$ values from the phase-dependent OSM-TI. To estimate all of the $\phi_n$ values, we tried to fit the phase-dependent signal $A_{\text{yield}}$ to a calculated curve considering the difference of the optical lengths of the fundamental and its harmonics induced by the phase-shifting plate [20]. The solid curve in figure 2 shows the results of the fit. We could reproduce the complicated phase-dependent behaviour of $A_{\text{yield}}$ with respect to the incident angle $\theta$ for many periods. Having obtained the fitted curve, we could extract all the $\phi_n$ values at any incident angle $\theta$. The characteristic set of relative phase differences $(\phi_2, \phi_3, \phi_4)$ was $(-0.05\pi, -0.14\pi, 0.15\pi)$ at $\theta = 44.83^\circ$ with an uncertainty of $\pm 0.05\pi$. This procedure enabled us to estimate all the $\phi_n$ values through phase-dependent OSM-TI in an intuitive manner by using the molecular orientation of the head-tail order [20].

4. Conclusions
We have demonstrated robust generation of Fourier-synthesized laser fields and their estimation using the phase-sensitive behavior of OSM-TI induced by nanosecond four-color Fourier-synthesized laser fields. The interferometer-free laser field generator that ensures high stability and high reproducibility is significant in light of the previously reported work [17] where we used a multicolor Mach–Zehnder interferometer that is vulnerable to a variety of fluctuations. We have developed a procedure for analyzing the data that enables estimation of the three relative phase differences between the fundamental and each of its harmonics.

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