Laser-assisted Electron Diffraction for Probing Femtosecond Nuclear Dynamics of Gas-phase Molecules

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Abstract: By detecting 1 keV electrons scattered by CCl_4 in a femtosecond laser field, we observed laser-assisted electron diffraction images with which we can probe ultrafast molecular dynamics with <10 fs and ~0.01 Å resolutions.
OCIS codes: (020.2649) Strong field laser physics; (020.4180) Multiphoton processes

1. Introduction

When an electron is scattered by an atom or a molecule in a laser field, the electron can change its kinetic energy by multiples of the photon energy ($\hbar\omega$). This scattering process is called laser-assisted electron scattering (LAES) or free-free transition of electrons. Recently we proposed an ultrafast electron diffraction method called laser-assisted electron diffraction (LAED) [1] as an application of the LAES process. Because the LAES process occurs only in the presence of the laser field, the temporal resolution of the LAED method can be as short as the laser pulse duration (< 10fs), which is more than two orders of magnitude higher than a few picoseconds achieved by the pulsed gas-phase electron diffraction method [2].

In the present study, we recorded LAED patterns of gas-phase CCl_4, i.e., electron diffraction patterns appearing through the interference among LAES electrons scattered by the respective atoms within a molecule at the energy shifts (ΔE) of $\pm\hbar\omega$. Through the comparison with the numerical simulations, we show that the LAED pattern carries the information of the geometrical structure of molecules during the ultrashort duration of the laser irradiation.

2. Experiment

In Fig.1, we show the schematic of our femtosecond-LAED apparatus. A linearly polarized output of a Ti:sapphire chirped pulse amplification laser system (λ = 800 nm, 5 kHz repetition rate, 0.6 mJ/pulse) was stretched to τ = 520 fs and focused into a vacuum chamber. The peak field intensity is estimated to be 6×10^{11} W/cm^2. A part of the laser pulse before a pulse compressor is split and converted to a UV pulse (λ = 266 nm, τ = 15 ps) by BBO crystals. The UV pulse is focused to a gold photocathode in an electron gun to generate an electron pulse. The electron pulse is accelerated to 1 keV and crosses both an effusive CCl_4 beam and the laser beam at right angles. The scattered electrons are introduced into a toroidal energy analyzer and are detected by a delay-line anode detector. The delay time (Δt) between the electron pulse and the laser pulse was varied by moving an optical delay stage for the UV pulse. The further details of the apparatus have been described elsewhere [3,4].

3. Results and Discussion

We show the kinetic energy spectrum of the scattered electrons at Δt = 0 as red circles in Fig. 2, which was obtained by integrating the scattered electron signals over the scattering angle θ ($2.5^\circ \le \theta \le 12.5^\circ$). The spectral intensities are normalized by the intensity of the peak at ΔE = 0. The increases in the signal intensities originating from the LAES processes are recognized at $\Delta E = \pm\hbar\omega$ (1.55 eV) and $\pm2\hbar\omega$ (3.10 eV). For comparison, in Fig. 2 as black squares, we show the kinetic energy spectrum recorded at Δt = +70 ps. In this spectrum, we cannot find any peaks originating

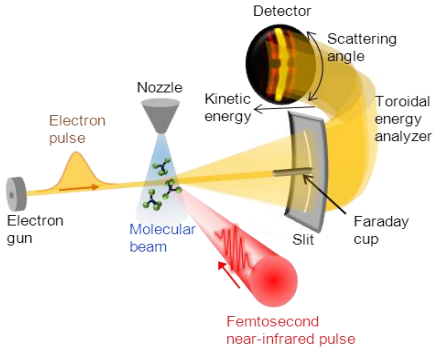

Fig.1. Schematics of experimental set-up.

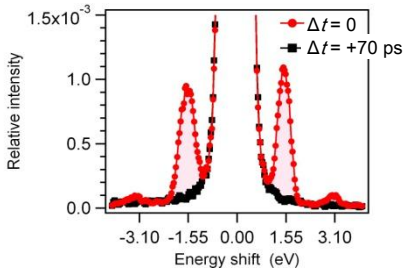

Fig.2. Kinetic energy spectra of scattered electrons by CCl_4 at Δt = 0 (red circles) and Δt = +70 ps (black squares).

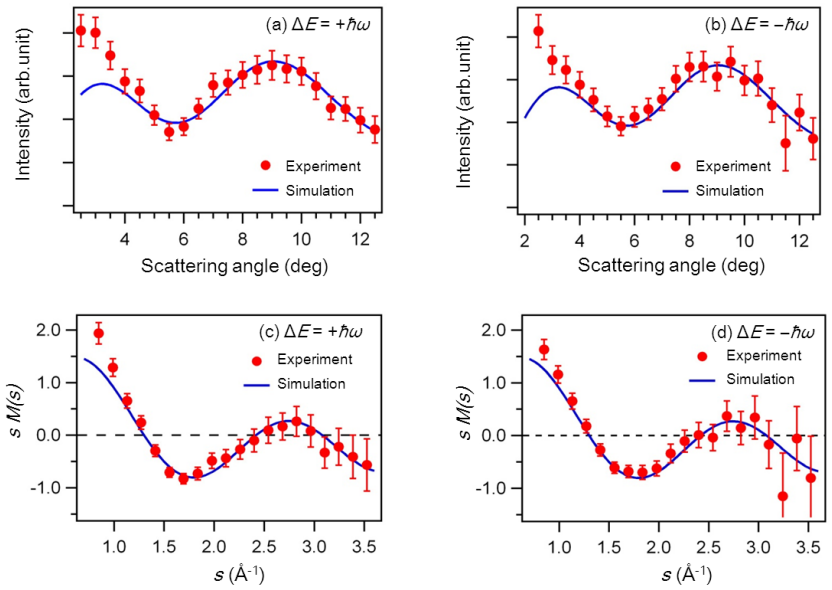

Fig. 3. Upper panels: laser-assisted electron diffraction pattern of CCl_4 at $\Delta E = +\hbar\omega$ (a) and at $\Delta E = -\hbar\omega$ (b). Lower panels: modified molecular scattering intensities calculated from the LAED patterns at $\Delta E = +\hbar\omega$ (c) and at $\Delta E = -\hbar\omega$ (d). Filled circles: experimental data. Solid curves: results of the simulation.

from the LAES processes, demonstrating that the LAES processes are induced only in the presence of laser fields.

The angular distributions of one-photon LAES signals ($\Delta E = \pm\hbar\omega$) are shown in Figs. 3 (a) and (b) as red circles. In both of the angular distributions, we observed clear interference structures with a minimum around 5.5º and a maximum around 9.0º. In order to confirm the origin of the interference patterns, we conducted a numerical simulation based on the Kroll-Watson approximation [5] and on the independent atomic model (IAM) [6] with corrections for the polarization effect induced by the incident electrons and the chemical bonding effect. We adopted the structural parameters of CCl_4 at room temperature [7] determined by the conventional gas-phase electron diffraction (GED). The details of the simulation are given in Ref. [4]. The simulated LAES angular distributions represented by solid blue curves in Figs. 3(a) and (b) are in good agreement with the experimental distributions. This agreement shows that the observed interference patterns are the electron diffraction patterns of CCl_4.

We calculated a modified molecular scattering intensity, $sM(s)$, which is commonly used for the determination of geometrical structures of molecules in the conventional GED [6]. In Figs. 3(c) and (d), we show $sM(s)$ calculated from the observed LAED patterns as red circles. For comparison, we show simulated $sM(s)$ based on IAM as blue curves. The agreement between the experimentally obtained $sM(s)$ and the simulated $sM(s)$ shows that the molecular structures at the moment of the laser irradiation can be determined from the analysis of LAED patterns with precision as high as 0.01 Å that can be achieved in the conventional GED.

4. Conclusion

We reported the observation of LAED patterns of CCl_4 at $\Delta E = \pm\hbar\omega$. The observed LAED patterns are reproduced by the numerical simulations in which the field-free geometrical structure of CCl_4 is adopted. The present study confirms that ultrafast nuclear dynamics can be probed in real time with high temporal (<10 fs) and spatial (~0.01 Å) resolutions if molecules are pumped by an ultrashort laser pulse and are probed by the LAED method.

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