High-harmonic spectroscopy of low-energy electron-scattering dynamics in liquids

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ABSTRACT

High-harmonic spectroscopy is an all-optical nonlinear technique with inherent attosecond temporal resolution. It has been applied to a variety of systems in the gas phase and solid state. Here we extend its use to liquid samples. By studying high-harmonic generation over a broad range of wavelengths and intensities, we show that the cut-off energy is independent of the wavelength beyond a threshold intensity and that it is a characteristic property of the studied liquid. We explain these observations with a semi-classical model based on electron trajectories that are limited by the electron scattering. This is further confirmed by measurements performed with elliptically polarized light and with ab-initio time-dependent density functional theory calculations. Our results propose high-harmonic spectroscopy as an all-optical approach for determining the effective mean free paths of slow electrons in liquids. This regime is extremely difficult to access with other methodologies, but is critical for understanding radiation damage to living tissues. Our work also indicates the possibility of resolving subfemtosecond electron dynamics in liquids offering an all-optical approach to attosecond spectroscopy of chemical processes in their native liquid environment.

Keywords: high-harmonic generation; condensed-matter phase; liquids; ab initio simulation; time-dependent density functional theory

1. INTRODUCTION

The success of high-harmonic spectroscopy in unravelling attosecond electron dynamics in gases can be attributed to the robustness of the semi-classical three-step TSM, especially in predicting properties like the $(E\lambda)^2$ scaling of $E_c$ \cite{1}. The results of this approach are usually in good agreement with those of full ab-initio calculations, and can be used to extract dynamical information from high-harmonic spectroscopy. This has made temporal mapping of molecular orbitals and charge-migration dynamics \cite{2, 3} possible. In crystalline solids a linear $E\lambda$ scaling of $E_c$ was proposed based on a trajectory model in momentum space \cite{4}. Since the lack of single-particle approximation (like in gases) or long-range order (like in crystalline solids) make numerical simulations challenging for liquids, and experiments are scarce no such intuitive model exists thus far. Here, we show that the $E_c$ for liquid water and alcohols, measured over a broad spectrum of drivers, is wavelength independent and significantly lower than the TSM prediction.
2. METHODOLOGY AND RESULTS

The experimental set-up is shown in Fig. 1 a. It consists of a laser system delivering ~30–40 fs laser pulses with an adjustable central wavelength (800–1,800 nm) and a high-vacuum chamber containing the liquid flat-jet system and a flat-field imaging spectrometer. Unlike in gases and solids [3,4], the $E_c$ for liquid $H_2O$, $D_2O$ and alcohols is found to be independent of $\lambda$ and minimally dependent on the laser intensity and pulse duration, see Fig. 1 b. Using a combination of ab-initio simulations, based on real-time real-space time-dependent density functional theory, we explain these observations, see Fig. 1 c, and develop a scattering-limited trajectory model for HHG in liquids [5]. Our model successfully reproduces the wavelength independence of $E_c$ and identifies the effective mean-free path ($\lambda_{MFP}$) as the principal factor in defining $E_c$. We support this conclusion by showing that increasing $\lambda_{MFP}$ (by decreasing the liquid density), in both experiments and simulations, increases $E_c$ because longer trajectories with higher kinetic energies are able to recombine with the parent molecule.

We finally use our model to derive an analytical expression of the energy cutoff as a function of the mean-free path. A direct consequence of this relation is that it allows us to retrieve this quantity from the experimental spectra, provided that they were recorded under conditions where the wavelength-independence of the cut-off is observed, which is the case here. Electron MFPs play a very important role in describing electron-driven processes in the liquid phase, but they are notoriously difficult to measure and calculate, especially at low energies. The interest in developing new methods for accessing these quantities is, therefore, considerable and relevant for many physical and chemical processes. Here we do not attempt to determine the MFPs with high precision because this would require a more sophisticated scattering model, including a large number of different scattering channels (see ref. 43 and references therein). Instead, we aim at retrieving an effective MFP ($\lambda_{MFP}$), which is best thought of as accounting for all types of scattering processes. Since the elastic scattering cross sections are by far dominant at the very low kinetic energies (~10 eV) of interest here, we compare our results to the elastic MFPs in Fig. 2.
To summarize, we explored here the microscopic mechanisms responsible for liquid-phase HHG with a combination of experimental and theoretical methods. Our measurements of water and ethanol show that, contrary to crystals and gases, the cut-off energy in liquid-phase HHG is mostly independent of the laser wavelength. Microscopic quantum mechanical calculations based on both supercells and clusters agree with this result and show that it extends to other liquids and laser conditions. We showed that an extended semi-classical model that incorporates the effects of the ultrafast scattering of electrons off neighbouring molecules is capable of explaining the reduced HHG cut-off of liquids compared to the gas phase. The model reproduces well the wavelength-independence of the HHG cut-off and highlights the importance of the electron MFP in liquids, indicating that this quantity is imprinted onto the high-harmonic spectra and can be retrieved.

Our results provide the first intuitive picture of liquid-phase HHG and pave the way for attosecond spectroscopy of bio-chemical processes in their native liquid environment. We also expect that our results are highly relevant for HHG from amorphous solids. Our work may pave the way to a deeper understanding of the strong-field dynamics in disordered condensed phases and to resolving attosecond dynamics in liquids.

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