Laser-Assisted Photoelectric Effect from Liquids

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The laser-assisted photoelectric effect from liquid surfaces is reported for the first time. Photoelectrons generated by 35.6 eV radiation from a liquid microjet of water under vacuum are dressed with a $\hbar\omega = 1.55$ eV laser field. The subsequent redistribution of the photoelectron energies consists in the appearance of sidebands shifted by energies equivalent to $\hbar\omega$, $2\hbar\omega$, and $3\hbar\omega$. The response has been modeled to the third order and combined with energy-resolved measurements. This result opens the possibility to investigate the dynamics at surfaces of liquid solutions and provide information about the electron emission process from a liquid.

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Photoelectron spectroscopy (PES) of liquids was first introduced by Siegbahn and co-workers in the early 1970s [1], but it is only recently that it really developed into a routine technique thanks to the works of Faubel, Winter, and their co-workers [2,3]. It was extended to the ultrafast time domain by Suzuki and co-workers [4], Neumark and co-workers [5], and Lübcke and co-workers [6,7] using ultraviolet (< 10 eV) pulses, while Abel, Faubel, and their co-workers [8,9] were the first to introduce the use of ultrashort extreme ultraviolet (EUV) probe pulses produced by high harmonic generation. In the latter experiments on liquid water, short IR pulses were used to vibrationally excite the liquid, and the authors studied the heating of water over tens of picoseconds while the resolution of the experiment was 0.5 ps. In the meantime, other groups have started to implement ultrafast optical pump and PES probe experiments using ultrashort EUV pulses [10–12] and working towards measuring attosecond dynamics [13]. These developments, coupled with strong field laser pulses used to pump the system under study, call for an understanding of the strong field physics occurring when the pump laser field temporally overlaps the probe EUV pulse.

In time-resolved PES, the probe field maps the electron distribution of the system under study onto a detector via photoemission. A pump pulse perturbs the system which can take the form or combination of a change in the ground state electron configuration [14,15], a change to the local potential of the environment (charging) [16], or a dressing of the emitted photoelectrons by the pump laser field [17]. When the source of photoelectrons has a duration (i.e., either the probe pulse temporal width or lifetime of the observed state) that is longer than the half-cycle duration of the dressing field and a monochromatic probe source is used, a phenomenon called the laser-assisted photoelectric effect (LAPE) can occur, which manifests itself as a redistribution of the emitted photoelectrons energies into sidebands of the unperturbed spectrum. This effect has previously been observed in the gas phase [18,19] and from solid surfaces [20,21]. Murnane and co-workers [22] used it to extract the lifetime of core-excited levels of an adsorbate by mapping the LAPE from the substrate Pt(111) with the Auger decay process from an absorbed Xe atom. Reported here for the first time is the observation of the LAPE from electrons emitted from a liquid-vacuum interface.

For a molecular system, the energy redistribution of emitted photoelectrons can be described as

$$S^{+} + e^{\dagger} \leftarrow \gamma + S + \hbar\omega, \tag{1}$$

where S is the neutral molecule, S^{+} is the molecular ion, γ is an EUV photon, $\hbar\omega$ is the dressing or pump laser field photon energy, and $e^{\dagger}$ is an electron with kinetic energy given by

$$e^{\dagger} = e_0 \pm j\hbar\omega, \tag{2}$$

where $j = 0, 1, 2, 3, \ldots$ and e_0 is an electron with kinetic energy given by the ionization process in the absence of the pump laser field. In the presence of a strong laser field, the photoemitted electron populates a Volkov state [23] in the continuum and is unaffected by the molecular potential. The interaction of this electron with the dressing field manifests itself as an exchange of photons as the electron changes levels in the continuum, producing sidebands in the collected photoelectron spectrum. The sidebands appear at both higher and lower electron kinetic energy owing to the absorption and emission of j dressing field photons, respectively. The amplitude of the sidebands α_j is given by [23]

$$\alpha_j = J_j^2(x), \tag{3}$$

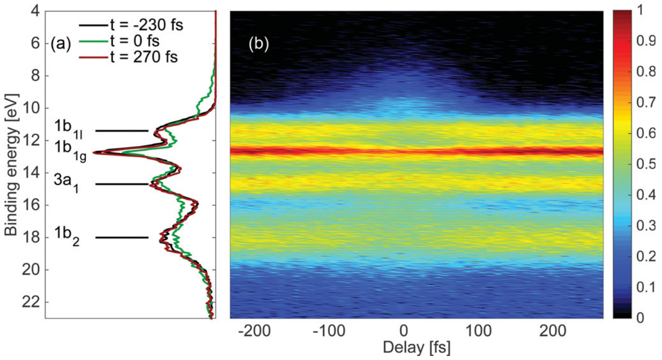

FIG. 1. (a) Photoelectron spectrum of water at $t = -230$ fs (black curve), $t = 0$ fs (green curve), and $t = 270$ fs (red curve). The first PE bands of water are shown with assigned molecular orbitals (subscript l refers to the liquid phase, subscript g to the gas phase, and no subscript to liquid and gas phase). (b) Evolution of the photoelectron spectrum as a function of the laser-pump or EUV probe time delay. The pump is at 1.55 eV with an intensity of 4×10^{11} W/cm^2.

where J_j is an ordinary Bessel function of the first kind whose order j is determined by the number of photons exchanged with the dressing field. The argument x is equal to

$$x = \sqrt{\frac{16\pi\kappa I E_{\mathrm{kin}}}{m_e \hbar\omega^4}}, \tag{4}$$

where κ is the fine structure constant, I is the dressing laser field intensity, and E_{kin} is the photoelectron kinetic energy [24]. Under the experimental conditions here, the amplitude α_j is proportional to the dressing field intensity, the photoelectron kinetic energy, and the dressing field wavelength to the fourth power.

The measurements reported here were performed with the Harmonium EUV light source of the Lausanne Centre for Ultrafast Science. A detailed description of the source and experimental setup is given in Ref. [10]. Briefly, a 35.6 eV (FWHM $\simeq$ 0.2 eV), 140 fs (FWHM) pulse was spatially and temporally overlapped with a 1.55 eV, 45 fs (FWHM) laser pulse delivering 4×10^{11} W/cm^2 on an 18 μm diameter liquid microjet positioned $\sim$300 μm in front of a time-of-flight electron spectrometer designed for liquids [25]. The temporal delay between the EUV and the 1.55 eV fields was scanned in steps of 10 fs from -230 to $+270$ fs (0 fs taken as the overlap of the pulse envelope maxima). A photoelectron spectrum was collected in 60 000 laser shots at each time delay.

Figure 1(b) shows the time-resolved PE measurement, i.e., the binding energy spectrum as a function of time. Photoelectron spectra at $t = -230$ fs (black curve), $t = 0$ fs (green curve), and $t = 270$ fs (red curve) are displayed in Fig. 1(a), showing the extent of the spectral intensity redistribution from $t = -230$ fs to $t = 0$ fs. Because of evaporation of water molecules, the photoelectron spectrum contains overlapping contributions from both liquid and gas phases, separated by $\sim$1.5 eV predominantly due to the Gibbs free energy of solvation [3]. The relative contributions of the liquid and gas phase for the spectra in Fig. 1 were 70% liquid and 30% gas. Immediately clear from Fig. 1(a) is the redistribution of the photoelectron spectral intensity in the vicinity of zero time delay between the 35.6 and 1.55 eV pulses. Most notable is the increase in intensity between 7 and 10 eV, and to a lesser extent between 15 and 17 eV and 20 and 23 eV, accompanied by a decrease in the intensity of all the water PE bands, i.e., between $\sim$10 and 20 eV. After the short-lived perturbation ($\sim$150 fs), the spectral intensity returns to the unperturbed distribution, as shown by the red curve at $t = 270$ fs.

Population of a short-lived excited state by the pump field is unlikely under these conditions: The excited state population would be small given the absorption cross section of liquid water at 800 nm (3×10^{-24} cm^2 [26] producing an $\sim 10^{-4}$ excited population) and would not account for the $\sim$20% intensity change of the $1b_1$ orbital [Fig. 1(a)].

The redistribution observed in Fig. 1 would be expected from the interaction of the dressing laser field with the photoemitted electron in a Volkov state of the continuum. In other words, what is observed at $t = 0$ fs is the partial redistribution of the spectral intensity of the unperturbed spectrum into sidebands. To confirm this interpretation, the redistribution was modeled with the following response function and was fitted by a genetic algorithm (GA) to the photoelectron spectrum at $t = 0$ fs:

$$\begin{aligned} N(E-E_0) = {} & \frac{1-2\alpha_1-2\alpha_2-2\alpha_3}{\sqrt{2\pi\sigma^2}} \exp[(E-E_0)^2/2\sigma^2] \\ & + \sum_{\pm}^{j=1,2,3} \left\{ \frac{\alpha_j}{\sqrt{2\pi\sigma^2}} \exp[(E-E_0 \pm j\hbar\omega)^2/2\sigma^2] \right\}, \end{aligned} \tag{5}$$

where $\hbar\omega$ is the dressing field photon energy, $\alpha_{1,2,3}$ are the amplitudes of the first-, second-, and third-order sidebands, $\sigma * 2.355$ is the FWHM bandwidth of the dressing field, and E_0 is the photoelectron energy in the absence of the LAPE. The fitting parameters of the GA were $\hbar\omega$, σ, and α_1. Using Eq. (3), the corresponding values of the second- and third-order Bessel functions were calculated from the value of α_1. The optimization was performed by minimizing the square of the residuals between a convolution of the function in Eq. (5) with the spectrum at $t = -230$ fs and the spectrum at $t = 0$ fs.

The space charge produced when the pump field has sufficient intensity to ionize the target has been observed to shift the collected photoelectron kinetic energy [11] and was accounted for with an additional space charge correction term in the GA.

The result of the optimization is shown in Fig. 2(a), where the convoluted signal follows the shift and magnitude of the

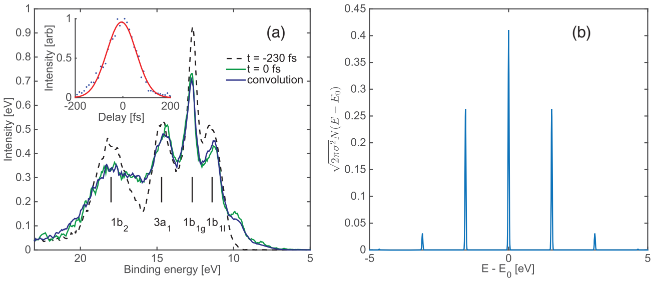

FIG. 2. (a) Black dashed curve: Photoelectron spectrum of liquid and gas phase water at $t = -230$ fs; green curve: photoelectron spectrum at $t = 0$ fs; blue curve: convolution of the black dashed curve and Eq. (5) including the space charge correction (0.09 eV). Water orbitals are labeled as in Fig. 1. Inset: Integrated photoelectron counts between 9.3 and 9.7 eV with a FWHM of 150 fs. (b) LAPE response function plotted with the fitted values of $\hbar\omega$, $\alpha_{1,2,3}$, and σ given by a genetic algorithm. See the text for details.

signal at $t = 0$ fs. The optimized values in Eq. (5) were $\hbar\omega = 1.55$ eV, $\sigma = 0.02$ eV, and the amplitude $\alpha_1 = 0.263$, giving $\alpha_{2,3}$ as 0.0301 and 0.0014, respectively. The space-charge-induced energy shift between the spectrum at $t = -230$ fs and $t = 0$ fs was 0.09 eV, and the fitted values of $\hbar\omega$ and σ are consistent with the central wavelength and bandwidth of the IR dressing field. The fitted LAPE response function for liquid and gas phase water is plotted in Fig. 2(b), showing the redistribution of detected photoelectrons from the unperturbed spectrum into three orders of symmetrical sidebands.

There is good agreement between the convoluted curve and the signal at $t = 0$ fs confirming the presence of the LAPE. The retrieved value of $\alpha_1 = 0.263$ is in remarkably good agreement with the value given by Eqs. (3) and (4) of 0.267 using the experimental parameters of dressing field intensity, $I = 4 \times 10^{11}$ W/cm^2 and the average photoelectron kinetic energy $E_{\text{kin}} = 20.4$ eV. This interpretation is further evidenced by the cross-correlation signal shown in the inset in Fig. 2(a) with a FWHM of 150 fs. For the dressing laser field intensities and photoelectron kinetic energies under these experimental conditions, the cross-correlation signal is linear with intensity [24]. As the LAPE occurs only in the presence of the two pulses, the FWHM of the measured cross-correlation signal should agree with the experimental parameters. Given a FWHM of 45 fs of the dressing laser field, the cross-correlation signal gives a FWHM of the EUV pulse of 143 fs, consistent with the monochromator temporal response [10].

Using a different approach, the liquid and gas phase sideband nature of the response was investigated by fitting Gaussian peaks to the spectrum at $t = 0$ fs. To reduce the permutations possible and to provide a conclusive fit, the spectral region investigated was limited to below 13 eV. This region contains the $1b_1$ gas and liquid orbitals (centred at 12.6 and 11.2 eV, respectively) with their associated sidebands resulting from the absorption of $j = 1$ and $j = 2$ dressing field photons as well as the first sideband from an emission ($j = -1$) of a photon associated with the $1b_1$ liquid orbital. Seven Gaussians were fitted, with a constraint that the width of sidebands from a given orbital were equal. The fitted Gaussians are shown in Fig. 3 (Gaussians for the $1b_1$ gas and liquid orbitals are omitted from the figure for clarity). The ratios of the first- and second-order sideband heights for the liquid and gas phase (0.12 and 0.13) match the ratio of $\alpha_1/\alpha_2 = 0.12$ found by the GA approach well.

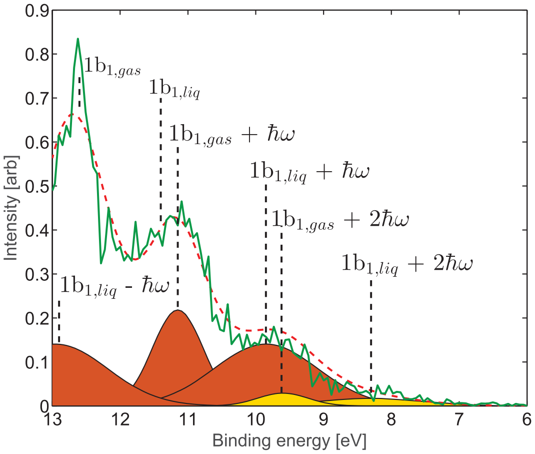

FIG. 3. Sidebands obtained from the Gaussian fit. The first-order sidebands are shown in orange and the second-order are shown in yellow. Red dashed curve: Sum of sidebands and the unperturbed water PE bands. Green curve: Photoelectron spectrum measured at zero time delay between the EUV and 1.55 eV pulses.

The close agreement between the two approaches (Gaussian fitting and convolution) is significant. While the convolution approach combines both the liquid and gas phase LAPE response, the use of Gaussians separates the two. The agreement between both methods and the ratio of the liquid and gas phase sidebands suggests that the LAPE response of the two phases is very similar. For the photon energies used here, the photoemission from the liquid with 35.6 eV is limited to, or very close to, the surface (~1 nm depth) due to a short inelastic mean free path of the photoelectron [27]. As such, photoelectrons from the liquid phase will be exposed to a very similar electric field strength from the dressing laser field as for the gas phase.

The observation of the LAPE from liquids reported here raises a certain number of issues. The dominance of the LAPE in perturbing the photoelectron signal around time zero when the sample is pumped with an ultrashort laser field offers an *in situ* laser or EUV cross-correlation. This will be particularly useful for photoinduced transitions occurring on a time scale longer than the cross-correlation. For experiments at a high time resolution, it could be used to study interfacial effects such as demonstrated for adsorbates on solids by Murnane and co-workers [22].

In this respect, simulations have shown that liquid surfaces of halide salt solutions have a higher concentration of halide; the heavier it is, the higher [28]. In a similar fashion to Ref. [22], this suggests the possibility to measure core-level relaxation dynamics occurring in solvated species near the interface.

In this study, momentum conservation during photon exchange has not been considered, and, as with surfaces, any change in the final electron energy would likely be small and below the energy resolution of the detection system [24]. However, the observation of the LAPE from liquid surfaces opens the possibility to investigate the phenomena with angular-resolved electron detection and could provide insights into the electron emission process from solutes and solvents. In a similar vein, the photoemitted electron in a liquid will undergo scattering events with other molecules where a photon exchange with the field will be possible. This may impart information in the observed sidebands about these scattering events, similar to the use of a recolliding electron as a probe of molecular potentials and ionization [29,30].

On the other hand, the intensity redistribution of the PE spectrum from the LAPE may mean the spectral features of the system under study may be blurred. Since α_j in Eq. (3) scales as λ^4, this implies that the pump laser wavelength has to be appropriately chosen. Luckily, in most photoinduced phenomena of solutes in solutions, shorter pump wavelengths are used. Finally understanding the effect allows the perturbation to be quantified and will permit the underlying electronic or vibrational perturbations evolving on a time scale similar to the pump and probe cross-correlation to be deconvoluted from the collected signal. As shown here, this can be done with high reliability when the experimental parameters of the dressing field are known.

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