Ultrafast photoelectron spectroscopy of solutions: space-charge effect

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Abstract

The method of time-resolved XUV photoelectron spectroscopy is applied in a pump–probe experiment on a liquid micro-jet. We investigate how the XUV energy spectra of photoelectrons are influenced by the space charge created due to ionization of the liquid medium by the pump laser pulse. XUV light from high-order harmonic generation is used to probe the electron population of the valence shell of iron hexacyanide in water. By exposing the sample to a short UV pump pulse of 266 nm wavelength and ~55 fs duration, we observe an energy shift of the spectral component associated with XUV ionization from the Fe 3d(t2g) orbital as well as a shift of the water spectrum. Depending on the sequence of the pump and probe pulses, the arising energy shift of photoelectrons acquires a positive or negative value. It exhibits a sharp positive peak at small time delays, which facilitates to determine the temporal overlap between pump and probe pulses. The negative spectral shift is due to positive charge accumulated in the liquid medium during ionization. Its dissipation is found to occur on a (sub)nanosecond time scale and has a biexponential character. A simple mean-field model is provided to interpret the observations. A comparison between the intensity dependencies of the spectral shift and the UV ionization yield shows that the space-charge effect can be significantly reduced when the pump intensity is attenuated below the saturation level of water ionization. For the given experimental conditions, the saturation intensity lies at 6 × 10¹⁰ W cm⁻².

Introduction

The study of electronic and structural dynamics in solutions and at interfaces received much attention during the past years [1–9]. The interest and the importance of these studies arise from the fact that solutions represent a natural environment for most biochemical complexes [10–13]. Various non-radiative electronic transitions can be initiated by light in biochemical complexes. Charge transfer [14], electron solvation [1, 15], spin crossover [16, 17], and photooxidation [18] represent some of them. Depending on the transition character, the time scale of the complex dynamics can lie in the femtosecond range, requiring application of ultrafast spectroscopies to study photoreactions in detail. Different time-resolved spectroscopic methods are developed to follow the dynamics of a biochemical system under photoexcitation. Among these are transient absorption and fluorescence spectroscopies [18, 19] and transient electron photoemission spectroscopy (PES) [20–25]. In the present work we consider the latter approach. It is advantageous in the unambiguous determination of the electron population distribution among different states via mapping the electron density into the continuum and recording the arising kinetic energy spectrum. While the electron dynamics can be initiated by photons in the UV/visible wavelength range, application of XUV light from high-order harmonic generation (HHG) represents a suitable tool for monitoring the electron population at a given time delay after the excitation [5, 24–26]. The XUV photon energy is sufficient for probing the entire electronic structure of the valence shell in a one-
photon transition to the continuum. In the present work we employ a HHG setup which we recently developed for time-resolved spectroscopic studies on solutions [27].

Photoexcitation of the solute with the use of a short laser pulse imposes some specific conditions on the pump laser intensity. The reason is that the photoelectron spectrum, generated by the XUV probe pulse, is dominated by the ionization yield of the solvent due to its much higher number density. In order to distinguish changes in the kinetic energy spectra associated with the electron population dynamics of the solute, a substantial amount of the solute molecules should be initially excited by the pump pulse. For one-photon excitation, the transition probability can be estimated as

\[ W = \sigma \frac{I}{\hbar \omega} \tau, \]  

where \( \sigma \) is the photoabsorption cross section, \( I \) is the laser intensity, \( \hbar \omega \) is the photon energy, and \( \tau \) is the laser pulse duration. Equation (1) immediately implies that application of a shorter pulse requires a higher laser intensity in order to achieve the same yield of a given photoreaction process. The saturation condition, \( W \approx 1 \), represents the ideal case where all solute molecules in the interaction region are excited. In order to provide an estimate for the intensity value needed to achieve saturation, we consider for a moment photoexcitation by a laser pulse of 30 fs duration and 2 eV photon energy, and assume that the cross section \( \sigma \) is in the order of 1 Mb. With these parameters, we obtain that an intensity of \( 10^{13} \) W cm\(^{-2}\) is needed to saturate the process. The intensity requirement becomes weaker if the photoreaction cross section is resonantly enhanced due to population of an excited state. However, the laser field may still be strong enough to ionize the solvent medium efficiently. This leads to the formation of the space charge. Its effect on the XUV photoemission spectra of aqueous solutions represents the subject of our work.

The space–charge effect, induced in the process of electron emission, is of fundamental importance in PES studies. It causes spectral shifts and broadenings and often represents a limiting factor in experiment. Treatment of this effect is, therefore, a crucial issue. The charge effect was in the focus of many previous studies on ionization of gaseous media and from solid state surfaces with the use of a single laser pulse [28–31]. Recently, this effect was also reported in a few pump–probe PES experiments, where XUV light [32, 33] or soft x-ray [34] and hard x-ray [35] radiation was used to probe a solid-state sample irradiated by a laser pulse. It was found that the charge, generated due to electron emission in the field of the pump laser pulse, causes a shift of the core-level photoemission spectra to higher kinetic energies, and this shift is dependent on the time delay between pump and probe pulses. A systematic investigation of the charge dynamics due to the interaction between pump and probe photoelectron clouds emerging from a solid state surface is presented in [35]. In contrast to the reported studies, in the present experiment on aqueous solution we observe both positive and negative spectral energy shifts. Similar results were obtained for solutions with the use of other solvents, such as ethanol and DMSO. The difference in the manifestation of the space–charge effect in solids and liquids will be addressed below. We would like to stress that the present study focuses on the space–charge effect initiated via electron emission from the sample. Charge separation can also be induced by light at the (solid) medium surface without electron emission, resulting in a surface photovoltage (SPV). For n-type Si, it was shown that the SPV can cause a negative energy shift in the core-level photoemission spectra (see, e.g., [36, 37]). While such a spectral shift resembles the observation of our study, the charge dynamics in the SPV experiments is rather different since it does not involve the interaction between pump and probe electron clouds. In order to quantify the spectral shift and to follow its dependency on the time delay between the pump and probe pulses, it is practical to observe a well-distinguished energy peak in the XUV spectra and measure its energy position. For this purpose we apply a 500 mM aqueous solution of potassium ferrocyanide ([Fe(CN)₆]³⁻). Ionization from the Fe 3d(t₂₃) orbital of this complex gives rise to an energy peak which is well separated from the XUV water spectrum [38]. We record the position of this peak as a function of time delay and pump intensity to reveal the space–charge effect induced by a short UV laser pulse. The application of XUV light as a probe beam is an essential issue in this study, since its much higher photon energy allows to distinguish electrons generated by the probe beam.

**Experimental procedure**

A Ti:sapphire laser system producing 2.5 ml, 800 nm pulses at a repetition rate of 5 kHz and with a duration of 25 fs was used to generate the UV pump and XUV probe beams. Approximately 60% of the laser output was used for the frequency up–conversion via the HHG process in an argon–filled cell to generate XUV pulses. A detailed description of the HHG setup can be found in [27]. The 21st harmonic of the fundamental frequency, with a photon energy of 32.55 eV, was spectrally selected with the use of a reflection off-center zone plate and this XUV beam was refocused by a toroidal mirror into the experimental chamber. A focus spot size of approximately 60 μm was measured by scanning a razor blade across the beam while monitoring the current of a photodiode.
positioned behind the interaction region. An XUV pulse duration of 50 fs was inferred from a cross-correlation measurement in Ar with the use of the 800 nm beam [27]. The calibration curve of the photodiode was used to derive the XUV photon flux. This flux was attenuated to $10^6$ photons per pulse by decreasing the pump pulse energy of the HHG process to 1 mJ. At higher XUV intensities, ionization of the medium by the probe beam alone resulted in additional charging effect that distorted the photoelectron spectra. The rest of the laser output was used to generate the third harmonic with a photon energy of 4.65 eV, which was applied as the pump beam. This UV beam was focused with a lens outside the experimental vacuum chamber, and redirected toward the interaction region with a mirror positioned close to the XUV beam path in vacuum (see figure 1 for illustration).

With such a geometry, we could achieve a small angle of $\sim 1^\circ$ between the propagation directions of the pump and probe beams. The UV beam was loosely focused into a spot size of 100 $\mu$m. An optical delay stage was used in the pump beam path to vary the time delay between the pump and the probe pulses. The time delay was controlled with a precision of 1 fs.

In order to maintain high-vacuum conditions required for electron detection, the highly volatile aqueous solution was introduced into the interaction region as a liquid micro-jet [39, 40]. A quartz nozzle of 24 $\mu$m diameter forms a fast (approximately 40 m s\(^{-1}\)) jet with an initial laminar flow of a few millimeters length. A salt of NaCl with a concentration of 50 mM was added to the [Fe(CN)]\(^{4-}\) aqueous solution to prevent streaming potential caused by friction of the liquid flow in the nozzle capillary [41]. A few centimeters downstream the flow, the sample was collected by a nitrogen-cooled liquid trap, allowing for residual gas pressure below $10^{-4}$ mbar in the interaction chamber during the experiment. The pump and the probe beams were focused onto the same spot within the laminar region of the liquid jet. The region of the beam overlap was centered in front of the detector. Hence, slow electrons produced by XUV ionization of lower-lying bands of the water valence shell were not recorded. In the wide-angle collection mode, a predefined non-uniform electrostatic field is imposed to the drift region of the spectrometer, allowing to increase the acceptance angle to $\pm 15^\circ$. The kinetic energy scale, however, is limited to a certain range around a chosen pass energy. This mode was used for acquisition of spectra with a high signal-to-noise ratio in an energy range sufficient to reveal XUV ionization from the Fe 3d\((t_{2g})\) orbital of [Fe(CN)]\(^{4-}\).

As a part of the experiment, a cross correlation measurement was carried out to define the time resolution in the present setup. This was performed by overlapping the pump and the probe beams on a copper wire of 100 $\mu$m diameter, which was positioned in front of the skimmer of the TOF spectrometer instead of the micro-jet. The possibility of cross correlation measurements on a solid surface via the laser-assisted photoelectric effect with the use of XUV light was demonstrated in [43]. By recording the photoelectron yield in the range of higher kinetic energies as a function of the time delay between the pump and the probe pulses, we obtained a cross correlation trace with a width of $\sim 75$ fs (FWHM). This value represents a convolution of the UV pump and XUV probe pulse durations. Accordingly, the pump pulse duration is broadened to approximately 55 fs by dispersion as it propagates through beam optics. The cross correlation measurement also allowed to define the delay stage position at which the pump and probe pulses overlapped in time in the interaction region.

**Figure 1.** Schematic illustration of the interaction region of the UV pump and the XUV probe beams with the liquid micro-jet.
Experimental results

Figure 2 shows three representative kinetic energy spectra obtained for time delays of −12, 0, and 50 ps between the pump and the probe pulses. An XUV spectrum measured without applying the pump beam is also presented for comparison. All spectra were recorded with equal acquisition time and were not normalized to each other. A negative-time delay means that the probe pulse arrives first to the interaction region. The spectra were recorded with the pump pulse energy of 1 μJ, corresponding to a peak intensity of ~1.8 × 10^{11} W cm^{-2} in the laser focus. At such intensity, ionization of the sample by the UV pump pulse generates rather slow electrons. This was verified by applying a low voltage of a few volts to the low-energy filter in the spectrometer, which decreased the count rate of electrons produced by the third harmonic beam to zero. Thus, the presented in figure 2 spectra reveal only the XUV ionization signal. In the shown kinetic energy range ionization contributions of both [Fe(CN)₆]^{4−} and water are present, though ionization yield of water dominates the spectra by orders of magnitude (note the logarithmic scale of electron yield in figure 2). The 1b₁ and 3a₁ orbitals of water are identified according to results of previous studies [25, 44]. The signal of iron hexacyanide exhibits two spectral components. In the spectrum recorded without applying the pump beam (dotted line), they appear as a shoulder on the higher-energy side of the 1b₁ water band and a prominent peak at 26.4 eV kinetic energy. These components originate from ionization of the σ (ε₂) + π (mainly CN-donor contribution) and the Fe 3d(t₂₃) orbitals, respectively. This assignment is consistent with the results of previous studies of the [Fe(CN)₆]^{4−} valence-shell structure in aqueous solution [38, 45].

A remarkable feature apparent in figure 2 is the delay-dependent modification of the spectra which is well pronounced in the range of higher kinetic energies above 21 eV. In particular, the photoelectrons acquire a negative energy shift if the pump pulse arrives first to the interaction region (green curve), and the energy shift becomes positive if the pulse sequence is reversed (blue curve). It affects the ionization contributions of both the 1b₁ liquid-phase water band and the valence shell of [Fe(CN)₆]^{4−}. When the pump and probe pulses overlap in time, a nonlinear response of the liquid medium to the superposition of two electromagnetic fields leads to an additional distortion of the XUV spectrum (see red curve in figure 2). This nonlinear response consists in simultaneous absorption of one XUV photon and one (or several) laser photons, giving rise to a photoelectron signal which is analogous to the cross correlation signal recorded with the use of the copper wire in the pulse-diagnostic routine. The study of laser-assisted XUV ionization of liquids, however, lies beyond the scope of the present work and we do not consider below short time delays within ±100 fs where this effect is significant.

The spectral modifications shown in figure 2 are less pronounced at lower kinetic energies. One should note that the simultaneous detection of photoelectrons from gas-phase water surrounding the jet is unavoidable since the spot size of the XUV focus is much larger than the jet diameter. As demonstrated in a previous PES experiment with a water micro-jet, ionization of water vapor results in a substantial contribution to photoelectron spectra [44]. Indeed, the ionization yield from the 1b₁ orbital of gas-phase water is the largest in the spectra shown in figure 2. For the XUV photon energy of 32.55 eV used in the present study, the gas-phase water spectrum lies in a range of kinetic energies below 21 eV. Apparently, the space-charge effect induced by the pump beam is different in the gas phase compared to the liquid phase. We will address this issue below.
For a quantitative characterization of the observed effect, we consider the Fe 3d($t_{2g}$) ionization peak and follow its energy position as a function of time delay between the pump and probe pulses. Figure 3 displays a sequence of spectra obtained for a number of chosen time delays. A fit to a Gaussian profile was used to determine the central energy and the width of the Fe 3d($t_{2g}$) peak for each measurement. The fit results showed that the height and the area of the peak remain nearly constant over the delay scan. This implies that photooxidation of ferrocyanide, which represents the dominant photoreaction channel of $[\text{Fe(CN)}_6]^{4-}$ at the wavelength of 266 nm [18], is negligible at the applied peak intensity and pulse duration of the pump beam. One can see from figure 3 that the spectral shift of the Fe 3d($t_{2g}$) ionization peak is the dominant effect observed in the present experiment. The width of the Fe 3d($t_{2g}$) ionization peak, inferred from the Gaussian fit, is found to be nearly independent of the time delay and is the same as the unperturbed width, indicating that the spectral broadening due to the space-charge effect is small. Similar results were obtained for different peak intensities of the pump beam in the range up to $2.5 \times 10^{11}$ W cm$^{-2}$. Figure 4 shows the dependency of the central energy of the Fe 3d($t_{2g}$) ionization peak as a function of time delay, recorded at the highest peak intensity of $2.5 \times 10^{11}$ W cm$^{-2}$. In the figure, the dashed horizontal line indicates the unperturbed peak position obtained without applying the pump beam. One can see that the spectral shift exhibits a strong variation, as well as a change of sign, at short time delays. The observed variation amplitude reaches a value of $\sim 1.5$ eV. Such a spectral change is dramatic for spectroscopic measurements.

Intensity studies
In order to investigate the proportionality between the spectral shift and the charge of electrons created by the pump beam, we measured the dependencies of both the energy shift and the UV ionization yield on the peak intensity $I$ of the pump beam. The low-energy filter of the spectrometer was disabled in the measurements of the UV ionization yield. The functional dependency of the energy shift on the laser intensity was verified to be independent of the time delay. To gain higher signal-to-noise ratio, the energy shift was averaged over the range of positive time delays between 3 ps and 1 ns, where it has larger values of negative sign. The absolute values of the averaged shift are considered below. Both intensity dependencies are presented in figure 5 on a double logarithmic scale.
Let us consider first the yield curve. It reveals that ionization of water is saturated at laser intensities above \(6 \times 10^{10} \text{ W cm}^{-2}\). In the limit of low intensities, the non-saturated yield is proportional to \(I^{2.04 \pm 0.04}\), implying that ionization is rather a two-photon process. This was inferred from a fit of experimental data assuming that the fit function has different polynomial dependencies on \(I\) below and above the saturation intensity, respectively. The fit results are shown by the black solid line in figure 5. One should note that the photoemission threshold of liquid water lies at \(10.06 \text{ eV}\) above the ground state \([46]\), requiring absorption of three photons of the pump beam for an electron to be vertically excited from the valence band to the continuum. However, due to the possibility of solvent reorientation the gap between the valence and the conduction bands has a lower value of \(6.9 \text{ eV}\) \([47]\). It means that the excitation energy of \(9.3 \text{ eV}\) of two UV photons is sufficient to eject an electron into the conduction band via adiabatic transition. Relevant experiments on two-photon excitation of water, leading to electron solvation, were carried out in \([48]\). The conduction band of liquid water represents an intermediate state in the three-photon ionization process. Since this state is resonantly populated in a two-photon transition, the intensity dependency of the non-saturated ionization yield acquires a polynomial coefficient close to 2.

Considering water in the gas phase, the electronic structure of isolated molecules does not possess a conduction band lying below the photoemission threshold. Ionization of gas, thus, occurs via non-resonant three-photon absorption and requires a higher intensity to reach saturation. Therefore, the ionization degree of gas-water surrounding the jet is lower. This is confirmed by the fact that a very slight misalignment in the spatial overlap between the pump beam and the jet resulted in disappearance of the ionization signal. Consequently, the space-charge effect on the gas-phase contribution to the XUV spectra is less pronounced, which is consistent with our observations presented in figure 2.
In the saturation regime, the ionization yield is found to be proportional to $I^{0.87 \pm 0.02}$ (see figure 5). This dependency is defined by the geometry of the interaction volume where the ionization process is saturated. In the case of unconfined medium interacting with a focused Gaussian beam, the saturation regime is described by the $3/2$ power law [49]. In the present experiment, the interaction region is confined to the jet size and, therefore, the polynomial exponent is smaller than $3/2$ due to the partial elimination of interaction volume effects [50]. One should note that the saturation intensity is defined by the laser pulse duration and the ionization rate, which is dependent on the order of nonlinearity of the ionization process. Application of a laser pulse of longer wavelength would lead to a higher value of saturation intensity due to the increase of the nonlinearity exponent.

One can see from figure 5 that most of the measurements of the energy shift of XUV spectra were performed under the saturation regime of water ionization. At intensities below $2.5 \times 10^{10} \text{ W cm}^{-2}$ the shift was too small and could not be distinguished because of the limited energy resolution. By performing a similar fit (see red solid line in figure 5) as used in the analysis of the yield curve, we find that at higher intensities the spectral shift is proportional to $I^{1.0 \pm 0.3}$. Within the error bar of the exponential coefficient, this dependency is the same as for the ionization yield and we conclude that the spectral shift is directly proportional to the amount of electrons ionized by the pump beam.

**Modeling of space-charge effect**

As shown in [35], a simple mean-field model can accurately predict the spectral shift of core-level photoemission caused by the space-charge effect. In the cited work, it was sufficient to consider only the interaction between pump and probe electron clouds, ionized from a solid-state surface, and disregard the possible interaction of electrons with the positive charge created in the solid-state as a result of photoemission. This approximation is valid due to the high carrier mobility in solid state that leads to ultrafast dissipation of the induced positive charge. In the present case, however, the interaction medium is not a conductor and the positive space-charge effect needs to be taken into account as well. Below we present a mean-field model where this effect is included.

Let us consider that XUV photons ionize electrons from the sample with an initial kinetic energy $E_0$. As mentioned above, the intensity of the XUV beam was attenuated so that charging of the medium due to this beam can be neglected. Our goal is to determine the kinetic energy $E_f$ of the XUV-generated electrons in the far field (at the detector) when a strong laser pulse is applied at a negative or positive time delay $t_d$. The laser field ionizes the sample and, thus, a cloud of electrons with a total negative charge $-Q$ is created. We assume that the cloud formation by the pump pulse is instantaneous and the laser-generated electrons move toward the detector with a mean kinetic energy $E_f$ which is smaller than $E_0$, $E_f \ll E_0$. Accordingly, the liquid sample acquires a positive charge $+Q$ localized within the interaction region with the laser beam. We do not specify the size of the interaction region but denote the electric potential of positive charges at the sample surface by $U_r$. Since the positively charged particles are inertial, we do not consider their motion. However, a slow dissipation of the positive charge near the surface is possible due to the presence of carriers, e.g., anions in the solution or electrons generated in the bulk by the pump pulse. Their diffusion into the charged region of the medium leads to regeneration of charge neutrality. Therefore, we consider that the positive potential $U_r(t)$ is time-dependent and the characteristic time of this dependency, which we address below, is much larger than the time of the electron cloud dynamics. The potential $U_r(t)$ can be considered as being analogous to the above discussed SPV potential in $n$-type Si, where photoexcitation initiates electron motion from the surface into the bulk and, thus, the surface acquires a positive charge. In the present case, instead, we consider that the photoexcited electrons move into the outer space from the surface and leave the sample. The XUV-generated electrons experience the interaction with both the negative and the positive charges created by the laser pulse. Using the field superposition principle, we first consider these interactions separately and, then, add them together.

**Positive charge effect.** If the pump laser pulse interacts with the sample first, the XUV-electrons are emerging from the sample in the presence of the potential $U_r(t_d)$ (see figure 6(a) for illustration). This results in a decrease of their kinetic energy in the far field by $eU_r(t_d)$, where $-e$ is the electron charge. If the probe pulse arrives first (see figure 6(b)), the XUV-electrons have moved to the distance $z_0 = (2E_0/m_e)^{1/2}t_d$ from the interaction region by the instant when the pump pulse creates the positive charge. Here $m_e$ is the electron mass. In the latter case the positive charge effect results in a decrease of $E_f$ by $eQ/(4\pi\varepsilon_0\ell_0)$, where $\varepsilon_0$ is the electric constant.

**Negative charge effect.** For both pulse sequences, the negative charge effect leads to acceleration of the XUV-electrons. If these electrons are produced after the interaction of the pump laser pulse with the sample (see figure 6(a)), their kinetic energy is sufficiently high to reach the cloud of the laser-generated slow electrons and penetrate through it. Then, the acceleration mechanism can be described in the same manner as in the case illustrated in figure 6(b). The difference lies solely in the initial potential energy of the Coulomb interaction between the XUV electron and the cloud of the laser-generated electrons, which is equal to $eQ/(4\pi\varepsilon_0\ell_0)$ and $eQ/(4\pi\varepsilon_0\ell_L)$ for the
cases (a) and (b), respectively, depicted in figure 6. Here $\ell = (2E_f/m_e)^{1/2}|t_d|$ and $\ell_0$ is introduced above. To determine the energy gain due to acceleration, we solve the system of two equations representing the energy and the momentum conservation rules:

$$\frac{Q}{e} E_L + E_0 + \frac{eQ}{4\pi \varepsilon_0 \ell_0 L} = \frac{Q}{e} E_{L_f} + E_{f}',$$

$$\frac{Q}{e} E_{L_f}^{1/2} + E_0^{1/2} = \frac{Q}{e} E_{L_f}^{1/2} + E_{f}'^{1/2},$$

where the electron cloud is considered as a single object of mass $m_e Q/e$, and $E_{L_f}$ and $E_{f}'$ are the kinetic energies of the XUV- and the laser-generated electrons, respectively, in the far field.

The analytical solution of equations (2) and (3) is straightforward. Below we consider the limits of short ($|t_d| \to 0$) and long ($|t_d| \to \infty$) time delays, where the solution acquires a simple form. Adding the negative and positive charge effects together, the results for the energy change $E_f - E_0$ of XUV-generated electrons are presented in table 1. One should note that for both pulse sequences the predicted energy change as a function of $t_d$ has a singularity at $|t_d| \to 0$. This singularity is a consequence of the one-dimensional character of our model, where the Coulomb interaction of point charges is used to describe the interaction between the pump and probe electron clouds, and the interaction between the probe electron cloud and the laser-generated positive ions at $t_d < 0$. At short time delays, the initial distance between the point charges is small, giving rise to a high potential energy of their interaction which is transformed to the electron kinetic energy in the far field. This description corresponds well to the observed sharp increase in the energy shift at short time delays (see figure 4). The latter provides us with a method to achieve the temporal overlap of XUV and laser pulses with a sub-picosecond precision via optimizing the positive spectral energy shift.

The results of the model were fitted to the experimental data shown in figure 4. The positive charge dissipation was considered to have an exponential character. We found, however, that a single exponential decay is not sufficient to reproduce the experimental data in the full range of positive time delays. Therefore, the time dependency of $U_r (t_d)$ was considered to have two exponential decay constants, which were used as fit parameters. The red solid curve in figure 4 shows the fit results and demonstrates that the model describes well the measured time dependency of the spectral shift. The decay constants of $136 \pm 15$ ps and $1.5 \pm 0.3$ ns of the positive charge dissipation were obtained from the fit (see dotted–dashed line in figure 4 for the individual

**Figure 6.** Illustration of the charge dynamics in the vicinity of the interaction region for different sequences of the pump and the probe pulses: (a) ‘pump → probe’ sequence, (b) ‘probe → pump’ sequence.

**Table 1.** The time-delay dependency of the energy change $E_f - E_0$ of XUV electrons in the far field due to the charge dynamics initiated by the laser pulse. The results are given for different sequences of the pump and the probe pulses in the limit of short and long time delays. The coefficients are $a = eQ(m_e/2E_f)^{1/2}/(4\pi \varepsilon_0 L)$, $b = (eQ_2/8\pi \varepsilon_0 (m_e/2E_0)^{1/4})$, and $c = eQ(m_e E_f/2)^{1/2}/(4\pi \varepsilon_0 E_0)$.

| Pulse sequence | $|t_d| \to 0$ | $|t_d| \to \infty$ |
|----------------|--------------|-------------------|
| Pump → probe   | $-eU_r (t_d) + a | t_d |^{-1}$ | $-eU_r (t_d) + a | t_d |^{-1}$ |
| Probe → pump   | $b | t_d |^{-1/2}$ | $c | t_d |^{-1}$ |
The space–charge effect can be significantly reduced by decreasing the laser intensity below the ionization saturation level. At the laser wavelength and pulse duration applied in the present work, we have found that ionization of water is saturated at intensities above $6 \times 10^{10}$ W cm$^{-2}$. Alternatively, one needs to develop algorithms of data analysis taking the spectral shift due to the space-charge effect into account.

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