

M. BAUER[✉]
M. WESSENDORF
D. HOFFMANN
C. WIEMANN
A. MÖNNICH
M. AESCHLIMANN

Time-resolved 2PPE: Probing adsorbate motion on femtosecond time-scales – what is the role of the laser bandwidth?

Department of Physics, TU Kaiserslautern, Erwin-Schrödingerstr. 46, 67663 Kaiserslautern, Germany

Received: 10 March 2004/Accepted: 22 October 2004

Published online: 23 February 2005 • © Springer-Verlag 2005

ABSTRACT Recently it has been shown that time-resolved two photon photoemission spectroscopy (TR 2PPE) is capable of probing the atomic motion of an adsorbate after excitation by a femtosecond laser-pulse. In this paper we address the question in how far the bandwidth of the used laser pulse is of importance with respect to the sensitivity of TR 2PPE to the actual nuclear dynamics. In particular, we find that the use of laser pulses of different spectral bandwidth may simplify the interpretation of the measured TR 2PPE autocorrelation traces and help to distinguish between purely electron related contributions and the nuclear dynamics. Our experimental results indicate that for pulses of small bandwidth only the lifetime of the electronic adsorbate excitation at the ground state equilibrium distance is probed. This information can be used as input for the interpretation of autocorrelation traces obtained with large bandwidth pulses, which in addition contain information about the nuclear dynamics of the adsorbate.

1 Introduction

The investigation of dynamical processes at surfaces on a femtosecond time-scale has attracted a lot of attention in recent years. In particular the decay dynamics of electron excitations at surfaces and the coupling of these excitations to translational and vibrational degrees of freedom of an adsorbate is a key point for the description of a variety of surface reactions and in particular of photon- and electron-stimulated reactions [1]. One of the most successful workhorses in this field is the technique of time-resolved two-photon photoemission spectroscopy (TR 2PPE). Over the last decade, the application of this technique to the investigation of the lifetime of bulk and surface located electronic excitations has contributed to the identification of ultrafast mechanisms responsible for the above mentioned surface processes in a crucial way [2]. With respect to the investigation of the lifetime of adsorbate excitations, the adsorption of alkali atoms on noble metals has been identified as an ideal and flexible model system [3–7]. Bauer and coworkers were the first who identified a long-lived excited state of a Cesium atom adsorbed on Cu(111) surface and reported a lifetime

of 12 fs [3]. Due to its energy and symmetry properties the authors assigned this excitation to the population of a $6s-6p_z$ hybrid state of the alkali [3, 8]. In further works it could be shown that this behavior is quite general for alkali adsorption on noble metal surfaces where the excited state is in resonance with a localized band-gap of the substrate at $k_{\parallel} = 0$ [9–11]. In a theoretical work Borisov and coworkers identified efficient blocking of resonant charge transfer as origin for the stabilization of the alkali excitation so that electron–electron scattering becomes a relevant decay mechanism [6, 7, 12]. This blocking is result of hybridization of the excited alkali state in combination with the presence of the substrate projected band gap. Recently, Petek and coworkers observed for the system Cs/Cu(111) that the measured TR 2PPE signal from an excited cesium state contains additionally information about the dynamics of the atomic motion of the cesium consequent to the electronic excitation of the adsorbate [5]. One of the important key points in Petek’s experiment in comparison to former studies [3, 9] was the use of extremely short laser-pulses (13 fs). This goes along with a spectral broadening of the laser light to values beyond 100 meV. In this way they were able to observe a systematic energy shift of the electronic excitation of the cesium atom as function of time. In addition they found significant distortions of the 2PPE autocorrelation (AC) traces measured at and close to the resonance energy of the Cs excitation [4]. Both signatures could be related to the motion of the cesium atom away from the surface after excitation. This interpretation was later supported by calculations by Borisov et al. [13], who could qualitatively reproduce the experimental results.

In this paper we address the question which of the two pulse parameters – pulse-length or bandwidth – are responsible for the observed distortions in the autocorrelation traces measured by Petek et al. In agreement with theoretical predictions [13] we find that the bandwidth is the important parameter and determines the sensitivity of the experiment to the atomic motion. Furthermore, we observe that for temporal delays < 30 fs the experimental result does not depend on pulse- and bandwidth of the used laser system. Under consideration of the dynamics of the nucleus motion after excitation we propose that within this time regime the experimental 2PPE autocorrelation probes the lifetime of the cesium excitation at the cesium-surface distance corresponding to the ground state equilibrium position.

✉ Fax: +49-631-205-3903, E-mail: mkbauer@physik.uni-kl.de

2 Experimental

The principle scheme of the monochromatic time-resolved 2PPE setup has been described in detail elsewhere [9]. In contrast to earlier investigations, we used three different femtosecond Ti:sapphire laser systems for the present studies delivering pulses at different pulse- and bandwidth, which in the following are labeled system A, B, and C. The relevant specifications of these systems are summarized in Table 1. Of particular importance for the discussion in Sect. 4 are the spectral and temporal characteristics of the second harmonic of the laser output obtained by frequency doubling in 0.2 mm thick nonlinear crystal (BBO), which is used to initiate the two photon photoemission process. The temporal widths of these pulses have been determined from 2PPE autocorrelation traces obtained by photoemission from the occupied Shockley-type ($n = 0$) surface state of a Cu(111) single crystal surface as proposed in [14]. For the 40 fs pulse (narrow-band TSUNAMI (A)) the pulse-bandwidth product indicates a transform limited laser-pulse, whereas for the other two systems (broad-band TSUNAMI (B) and FEMTOSOURCE (C)) complete compensation of temporal dispersion added to the pulse was not possible anymore. We account for this deviation from the transform-limited case to third and fourth order dispersion which becomes more critical in case of broadband laser-pulses. However, in comparison to the broadening of the experimental 2PPE autocorrelation trace induced by the lifetime of the adsorbate state probed in the present study, these small deviations from pulse optimum are negligible (see also Fig. 2).

The Cu(111)-sample was routinely cleaned by repeated argon ion sputtering and annealing (1000 V, 800 K). The sample state was checked by AES, LEED, and 2PPE spectroscopy. The cesium was deposited by resistive heated getter sources. The pressure during evaporation was maintained in the 10^{-10} mbar range. All experiments were performed at room temperature.

3 Experimental results

The relevant electronic structure of the Cs/Cu(111) system and the energy scheme of the 2PPE process involved in the present investigations are summarized in Fig. 1: Cu(111) has a gap of ~ 5 eV around the Fermi-Level in the projected

	Wavelength	Pulse-width	Band-width	Pulse-width	Band-width
		(laser)	(laser)	(SHG)	(SHG)
Laser A	780 nm	50 fs	20 nm	40 fs	6 nm
Laser B	790 nm	30 fs	40 nm	30 fs	9.5 nm
Laser C	795 nm	18 fs	50 nm	25 fs	12.5 nm

TABLE 1 Summary of specifications of the three Ti:sapphire laser systems used for the experiments. Of particular importance with respect to the discussion of the results are pulse- and bandwidth of the SHG-signal of the lasers

band structure at the Γ -point (L_2 - L_1 -gap). As a result of the termination of the crystal at the surface an occupied Shockley type surface state (labeled S) appears in this gap which represents a quasi-two-dimensional electron gas [15, 16]. The binding energy of the surface state at the Γ -point is 375 meV at room temperature [17]. The LUMO level of a single adsorbed cesium is located at about 3 eV with respect to E_F and is derived from the (occupied) 6s orbital of the free Cs-atom. The distortion of the atomic Cs potential by the surface induces mixing of the Cs 6s state with higher lying Cs orbitals (in particular the Cs $6p_z$ state) resulting in a polarization of the orbital wave-function into vacuum [6]. An additional, attractive contribution to the binding potential of the Cs-Cu(111) bond is induced by surrounding alkali atoms. This leads to a down-shift of the level energy when the alkali metal coverage is increased (see Fig. 1, right). This dependence can be used to tune the transition between surface state and Cs state in resonance to the photon energy of the used laser system ($h\nu \approx 3$ eV). Even though in the relevant energy range the experimental outcome is not affected by this tuning [4, 9], resonant enhancement allows reduction of background contributions to the autocorrelation (AC) traces arising from electron excitations in the bulk. All experiments presented in this work were performed at a coverages of about 0.04 ML [18].

Figure 2 shows time-resolved 2PPE results for the three different laser-systems obtained under similar conditions of the sample state for resonant excitation of the Cs-state (only positive temporal delays are displayed). For comparison also simulated 2PPE autocorrelation traces are shown (dashed line), calculated within the framework of the density-matrix formalism for a three level system corresponding to initial

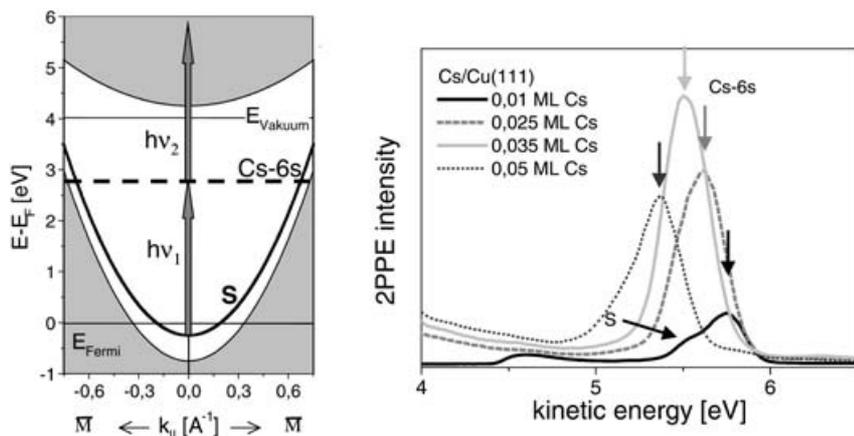


FIGURE 1 Left: projected band-structure of the system Cs/Cu(111), corresponding to the experimental conditions. Main features of the Cu(111) substrate are the L_2 - L_1 -gap crossing the Fermi edge and extending over an energy range of about 5 eV at the Γ -point and the Shockley type surface state S. The lowest unoccupied Cs state (Cs-6s) is located at an energy of about 3 eV in the zero-coverage limit and shifts down in energy with increasing coverage. The indicated energy of the Cs-resonance corresponds to the situation, where resonant excitation from the surface state S can be achieved within a 2PPE process using 400 nm laser-light; right: 2PPE spectra obtained for different Cs coverages; clearly visible is the resonance enhancement of the excitation at about 0.035 ML

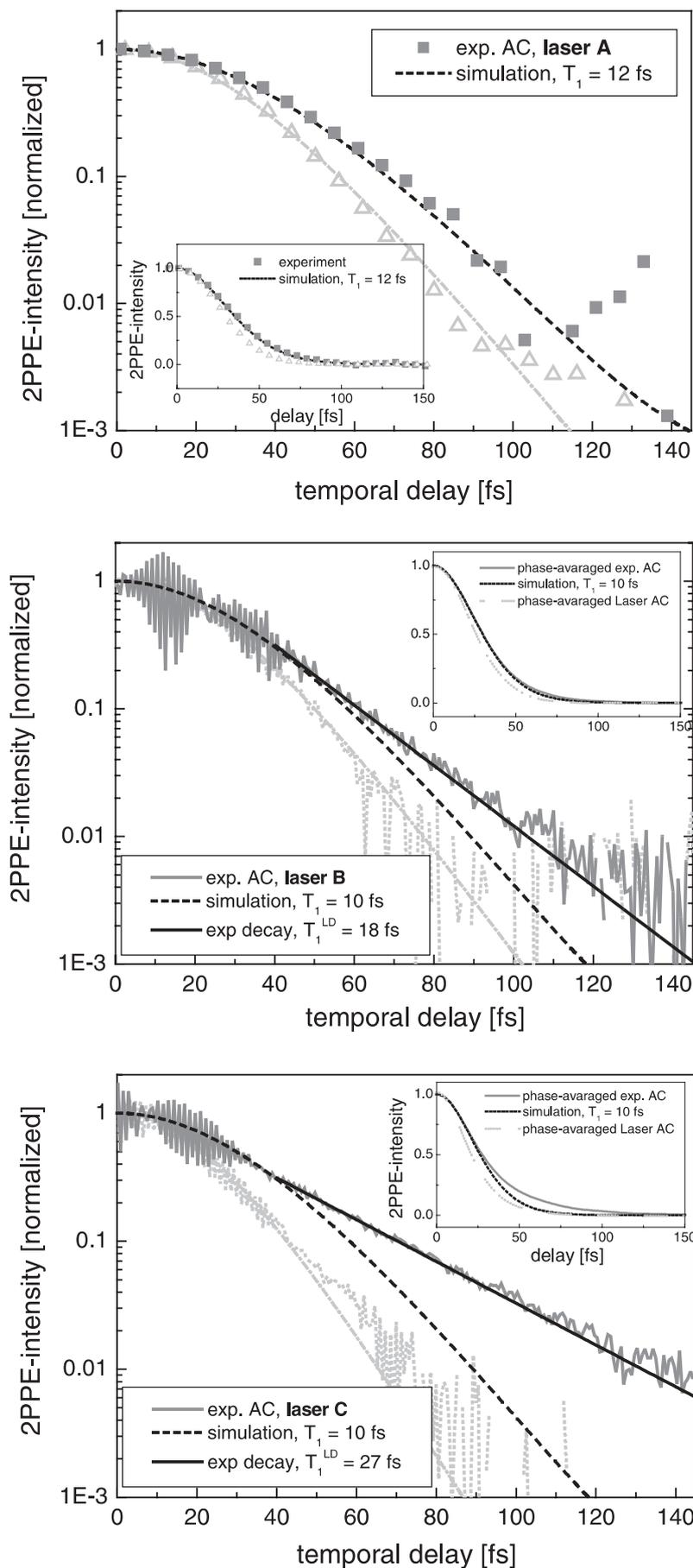


FIGURE 2 Experimental TR 2PPE autocorrelation traces obtained for the three different laser systems used in comparison to corresponding simulations. The experimental data were recorded at the intensity maximum of the 2PPE spectrum at a kinetic energy of about 5.5 eV (4 V bias applied to the sample, see Fig. 1; right). We find excellent agreement between experiment and simulation for all three data sets for temporal delays below 30 to 40 fs (see in particular linear scale representation of the *inset*). These results point to a lifetime T_1 of the Cs excitation in the range of 10 fs (laser B and C) to 12 fs (laser A) [20]. For large delays the shapes of the autocorrelation traces shows significant quantitative differences (see logarithmic scale). The AC corresponding to the long-pulse laser-system (system A) fits very well to the simulated traces even up to delays of more than 100 fs. For system B, however, we observe deviations from the calculated traces indicating lifetimes $T_1 > 10$ fs. This effect is even enhanced for measurements using laser system C. *Open triangles* (laser A) and *dotted lines* (laser B,C) to the measured autocorrelation trace of the respective SHG-pulse as determined from 2PPE of the ($n = 0$) surface state of the Cu(111) surface. *Dash-dotted lines* in bright gray represent the simulated laser AC used as input for our simulations of AC's within the density matrix formalism

state (surface state), intermediate state (Cs resonance) and final state (inverse LEED state) of the 2Photon absorption process [19]. Details such as the choice of the relevant parameters for a numerical simulation of the 2PPE excitation process of an alkali resonance are described in [9]. The calculated traces correspond to a lifetime T_1 of the Cs resonance of 10 fs (laser B and C) and 12 fs (laser A), the dephasing time T_2 between exciting laser pulse and excitation was set to its maximum possible value of $2T_1$ [20]. In all three cases the simulations resemble the experimental traces almost perfectly for small temporal delays ($\Delta t < 30$ fs) corresponding to short times after the population of the Cs resonance (see inset of Fig. 2). For larger delays, however, starting between 30 and 40 fs, quantitative differences of the experimental AC traces in comparison to theory are observed, best visible on a logarithmic scale. For excitation with 40 fs laser pulses (bandwidth 6 nm (FWHM), laser-system A), we find a perfect overlap over more than two orders of magnitude up to a temporal delay of 100 fs. The statistic scatter of the signal at higher delays prevents any further statements beyond this point. In contrast, experimental traces recorded using the 30 fs pulses (bandwidth 9.5 nm (FWHM), laser-system B) show significant deviations from the simulated traces at increased temporal delay to larger values. An exponential fit to the experimental data in this delay regime supports the significance of this deviations: the average decay of the experimental trace seems to be slowed down by a factor of about two from an initial value of $T_1 = 10$ fs to a value of 18 fs at large temporal delays (in the following labeled T_1^{LD}). This deviation is even more enhanced if we consider experiments performed with a 25 fs pulse (bandwidth 12 nm (FWHM), laser-system C). In this case the deviation from the calculated trace at delays > 40 fs is already clearly visible on a linear scale (see inset), the average lifetime is increased by almost a factor of three to a value of T_1^{LD} of 27 fs. Interestingly, this value is very close to a lifetime of the Cs-resonance of 23 fs reported in [4] for similar experimental conditions as for laser system C and obtained from an exponential fit to the large delay range.

Note that any other choice of T_1 does not improve the correspondence between experiment and simulation. This is evident for the longest pulses (laser A) where the overlap is almost perfect. In case of the shorter pulses, we will obtain a seemingly improved overlap of the traces at larger delays on the cost of agreement below 30 to 40 fs. However, in no case any part of the trace is reproduced as well as for $T_1 = 10$ fs and at small delays. Note also that variations in T_2 within the limits given by T_1 and the line-width of the Cs-resonance cannot account for the deviations observed for the short pulse experiments.

Also the differences in the temporal width of the laser pulses, respectively the temporal resolution that can be achieved with each of the laser systems, cannot account for the experimental deviations. Taking into account the differing laser parameters, we simulated autocorrelation traces for a decay-time of 27 fs corresponding to T_1^{LD} obtained with laser C for all three laser systems. We find that the slope of these simulated autocorrelation traces for delay times > 50 fs is independent of the used laser parameters.

In short, our experimental result can be summarized as follows: For temporal delays < 30 fs, the choice of parameters

of the exciting laser source does not affect the measurements and a consistent lifetime T_1 of the Cs resonance of 11 fs is found (laser A: $T_1 = 12$ fs, laser B and C: $T_1 = 10$ fs). On the other hand, for temporal delays beyond 40 fs the experimental results seem to be not consistent any more delivering a value of T_1^{LD} that critically depends on the specific laser parameters.

4 Discussion

For a qualitative explanation of the obtained differences, it is not sufficient just to consider the electronic degrees of freedom of the Cs-excitation. To actually obtain a consistent description of a time-resolved 2PPE experiment, the atomic motion of the adsorbate after excitation has also to be taken into account, as has been shown by Petek et al. [5], and Borisov et al. [13]. To elucidate the interaction of electronic excitation and atomic motion for the Cs–Cu(111) case a schematic potential energy diagram of the Cs ground and excited states adapted from reference [5] is shown in Fig. 3. The dynamical processes induced by the absorption of the laser pulse follow a Menzel–Gomer–Redhead (MGR) scenario for photo-desorption [21]. With respect to the nucleus motion the absorption process, i.e., the population of the Cs-6s resonance, can be considered as almost instantaneous. Consequently it induces a vertical lift up of the Cs-wavepacket from its ionic ground state into a neutralized excited state potential energy surface. Due to the consequent modifications in the charge distribution of the adsorbate the Cs–Cu(111) interaction in the (electronically) excited state is weakened, resulting in a shift of the potential energy minimum to larger Cs–Cu(111) separations. Attracted by this minimum, the Cs atom will start moving away from the Cu(111) giving rise to a transformation of electronic energy into translational energy. It is the feedback of this movement to the electronic degrees of freedom which can significantly affect the shape of experimental autocorrelation traces:

1. Along with the increase in alkali-surface distance the coupling between Cs excitation and surface electronic

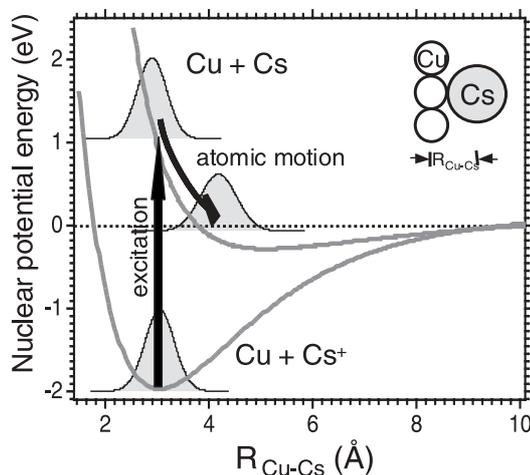


FIGURE 3 Schematic potential energy diagram for ground (ionic) and excited (neutral) state of the Cs atom. The shift in potential energy minimum in the excited state to larger Cs–Cu distances in comparison to the ground-state initiates the atomic motion after the electronic excitation

structure and, hence, the lifetime of the Cs resonance, is modified. This modification may follow the well known monotonic, exponential behavior as observed e.g., for the interaction of the ‘sensor atom’ at the top of a STM tip with a surface. In general, however, this dependence is not necessarily a monotonic function and can show a quite complicated structure as has been shown e.g., for resonant charge transfer processes for alkali–noble metal systems [6].

2. Additionally, a change in adsorbate substrate distance modifies the electronic structure, i.e., the degree of intra-atomic ($6s$ - $6p_z$) and inter-atomic ($6s$ -substrate) hybridization. In consequence the energy level of the excited state resonance shifts in energy. For the present case the Cs resonance shifts towards the Fermi-edge with increasing Cs–Cu(111) distance [6]. Experimental [5] and calculated [13] values of the induced level shifts as function of temporal delay between pump and probe are shown in Fig. 4a. In particular these modifications have been proposed to significantly modify measured 2PPE autocorrelation traces and have been suggested to be responsible for the distortions reported in [4].

Combination of both effects – time-dependent decay ‘constant’ $T_1(\Delta t)$ and energy level shift – under consideration of the respective bandwidth of the different laser sources can also account for the differences in our results as shown in Fig. 2.

Consider a detection scheme for TR-2PPE as used for the present investigations (see Fig. 5): To measure the resonance lifetime of the Cs-state, the used electron energy analyzer is set to a kinetic energy corresponding to the final state of the 2PPE process populated by resonant excitation from the intermediate Cs-state (see e.g. Fig. 1, right). However, as the energy of the Cs-level shifts as function of time (temporal delay between pump and probe laser pulse), it will at some point leave the detection window determined by a) the energy resolution of the analyzer and b) the bandwidth of the used laser system. Exactly this scenario has been quantified in [13] for model-like parameters and a laser-pulse characteristics corresponding to laser-system (C). As pointed out by the authors, it is the actual bandwidth of the laser that determines how long the Cs-resonance is probed, as long as all other experimental parameters (in particular detector resolution) are kept fixed. The use of different laser systems can, therefore, considerably modify the actual detection window and, hence,

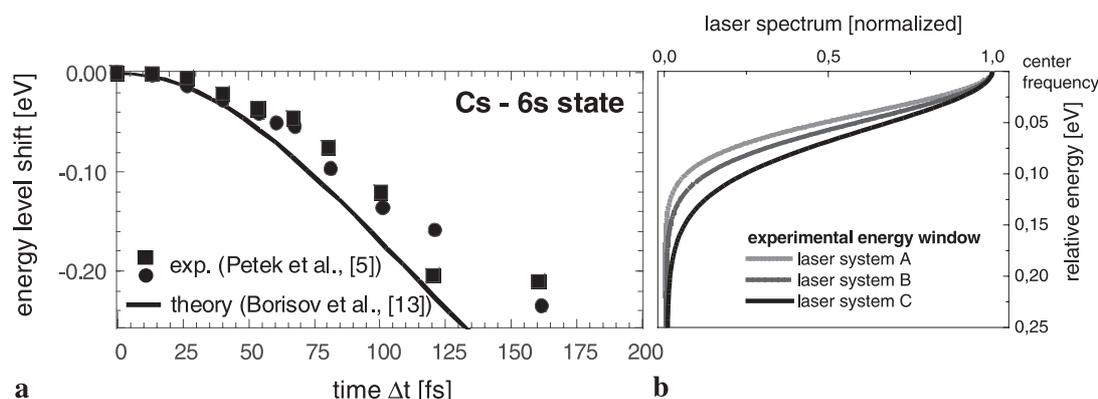


FIGURE 4 (a) Calculated (*full line*) and measured (*dots*) energy level shifts of the Cs-6s state as function of temporal delay induced by the motion of the Cs atom away from the surface. Experimental data have been published by Petek and coworkers [5], Borisov and coworkers have performed the corresponding calculations [13]. The parabolic dependence arises from the accelerated motion of the Cs-atom. To the right (b) the spectral distribution of the SHG signal obtained from laser system A, B, and C are displayed for comparison. The width of these distributions determine the energetic detection window of the experiment. It is obvious that the relation between energy level shift and laser band-width will affect the experimental autocorrelation trace. To account for the influence of the energy resolution of the used electron analyzer ($\Delta E = 80$ meV), the laser spectra have been convoluted with the analyzer resolution function

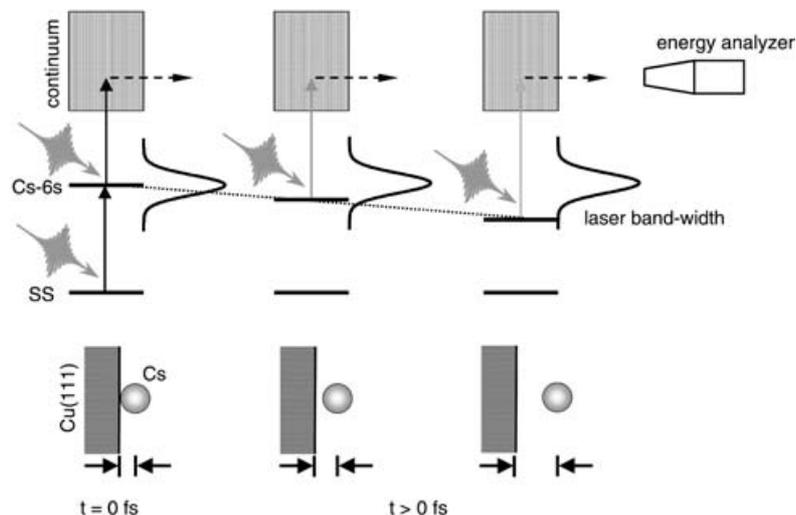


FIGURE 5 Detection scheme of a TR-2PPE experiment probing the resonant excitation of the Cs-6s level from the Cu(111) surface state. Due to the Cs motion, the 6s energy level shifts down in energy as function of time and will leave at some point the energetic detection window as e.g., determined by the bandwidth of the used laser

the time the Cs-state is actually probed. For the present situation level shift and bandwidth of laser systems A, B, and C are compared in Fig. 4. For the broad band laser (C) the Cs-resonance leaves the detection window at relatively large delays where the actual lifetime $T_1(\Delta t)$ may have increased significantly in comparison to the initial lifetime describing the static case. For laser-system (A) the maximum probed distance is much smaller, so that less deviations from the idealized static case are expected. The bandwidth of laser-system (B) corresponds to an intermediate situation in correspondence to our observations.

The effect of level shift as function of delay becomes also visible, if experimental AC traces at different electron kinetic energy are compared as the Cs 6s resonance is passed. Figure 6 shows three AC traces measured with laser system B at energies as indicated by the arrows in the inset. Two quite general features are observed and are represented by these AC's: (i) we typically measure the maximum temporal width of the AC at energies slightly below the intensity maximum of the 6s-resonance in the 2PPE spectrum (in Fig. 6 see AC at $E_{\text{kin}} \approx 5.7$ eV in comparison to AC at $E_{\text{kin}} \approx 5.8$ eV). (ii) AC's at the low energy side of the 6s resonances show a broadening at large temporal delays (in Fig. 6 see AC at $E_{\text{kin}} \approx 5.6$ eV) as result of the delay dependent energy shift of the resonance into the respective energy window of the detector. Such a broadening is not visible for AC's measured at the high energy side of the Cs resonance.

So far we were able to give a qualitative picture for the observed deviations in our measurements. In view of this explanation it may be rather surprising that we find an almost perfect agreement of the data for short delays ($T_1 = 11 \pm 1$ fs), right after population of the alkali excitation. To understand this agreement we have to consider the dynamics of the atomic

motion in more detail. In correspondence to [5] and [13] the cesium motion after excitation can be considered as follows:

The excitation of the Cs starts from the equilibrium position in the ground state (static case). Consequently, right after the optical excitation the Cs atom is initially at rest. The actual slope of the excited potential energy surface $\frac{dV}{dz}$ corresponds to an accelerating force acting on the Cs atom with the mass M . One thus gets a displacement of the adsorbate with respect to the surface, ΔZ , equal to:

$$\Delta Z = \frac{1}{2} \frac{dV}{dZ} \frac{t^2}{M} \quad (1)$$

For small displacements of the Cs atom, the assumption of a constant potential gradient is reasonable so that the relative change in adsorbate–surface distance as function of time increases quadratically with time t . Part of this dependence is indirectly reflected in the energy–time diagram in Fig. 4a, summarizing experimental and theoretical data from [5, 13]: the energy shift of the resonance shows a non-linear (parabolic) dependence as function of delay. It is in particular important to notice that due to the inertia of the relatively heavy Cs atom only a very small overall energy shift of the Cs-resonance < 20 meV can be observed for small temporal delays, i.e., $\Delta t < 30$ fs, corresponding to an effective displacement of the Cs-atom of < 0.05 Å, only [5]. Within this time interval the excited cesium atom is still very close to its ground state equilibrium position and may, therefore, be treated within a static model. Due to the accelerated motion of the cesium, the increase in adsorbate displacement ΔZ becomes more important for large time delays. In an equivalent manner changes in the adsorbate-substrate interaction and consequently changes in the lifetime of the excitation become relevant. For a correct description of the dynamics of the alkali excitation these changes have also to be taken into account. In this view we consider the value of T_1 of 10 to 12 fs consistently obtained from our fits to all three autocorrelation traces at small temporal delays $\Delta t < 30$ fs (Fig. 2) as the lifetime of the Cs-resonance corresponding to a static situation at/close to adsorption distance (under the assumption of $T_2 = 2T_1$).

In contrast, T_1^{LD} , the time constant obtained from the exponential fit to the slope of the autocorrelation trace at large delays is rather result of a lifetime averaging over the distance range between equilibrium position and the position, where the Cs resonance leaves the detection window and where we expect a significant change in the lifetime of the adsorbate excitation. This value is determined by the width of the detection window, i.e., by the bandwidth of the used laser-system and additionally by the change in lifetime of the Cs atom. It is obvious that this observation is of importance with respect to a comparison of experimental data achieved with different laser systems (e.g., data published in [4] in comparison to data published in [3]). Both studies reported on the surprisingly long lifetime of the Cs-resonance for adsorption on Cu(111). The reported lifetime values differ, however, by a factor of 4–5 (12 fs vs. 50 fs). Borisov and coworkers [13] proposed differences in the thermal population of the various vibrational levels in the Cs adsorption to be responsible for quantitative differences in the measured lifetimes. Where the experiments by Bauer et al. have been performed at room temperature experiments [3], experimental data by Ogawa et al. [4], were

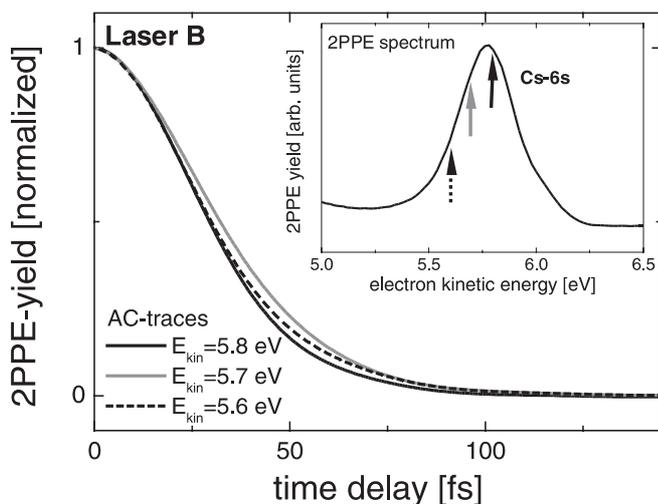


FIGURE 6 Experimental AC (phase-averaged) at different kinetic electron energies in the vicinity of the Cs-6s resonance as observed by 2PPE (see inset) measured with laser system B. We typically find that the maximum AC width is found at energies slightly lower than the intensity maximum in the 2PPE spectrum (here: 5.7 eV). For even smaller energies distortions of the AC are visible at large temporal delays mimicking an increased lifetime. We relate these distortions to the energy level shift of the Cs-resonance to lower energies as function of temporal delay into the respective energy detection window (see Fig. 4, left)

achieved at temperatures as low as 33 K. However, the obviously significant effect of the bandwidth of the different laser-systems used in both experiments (FWHM = 6 nm [3] and 13 nm [4, 22], respectively) haven't been considered, yet.

We would like to add that a quantitative analysis of the presented autocorrelation traces may even allow to trace back the dynamics of the atomic motion in detail. In the following we present a first, preliminary approach into this direction. The two effects responsible for the distortion of the autocorrelation trace are parameterized in terms of two corresponding delay dependent decay times T_1^{Cs} and T_1^{BW} . $T_1^{\text{Cs}}(\Delta t)$ accounts for the change in the coupling between adsorbate and surface with increasing alkali–Cu(111) separation and is a system intrinsic property not affected by the used laser system. $T_1^{\text{BW}}(\Delta t)$ quantifies the 'decay' out of the detection window as result of the level shift, and is, therefore, a function of the laser bandwidth. In correspondence with Matthiessen's rule, the measured total decay rate $1/T_1$ results from the sum of these two (independent) contributions:

$$\frac{1}{T_1} = \frac{1}{T_1^{\text{Cs}}(\Delta t)} + \frac{1}{T_1^{\text{BW}}(\Delta t)}. \quad (2)$$

Assumption of a linear dependence of T_1^{Cs} of adsorbate-substrate distance and consideration of (1) leads to the following expression:

$$T_1^{\text{Cs}}(\Delta t) = T_1^0 + a\Delta t^2. \quad (3)$$

T_1^0 corresponds to the lifetime at ground-state equilibrium distance, i.e., in the present case $T_1^0 = 11$ fs. The quadratic dependence of Δt arises from the accelerated motion of the alkali atom (see (1)). Any dependence of T_1^{BW} of Δt is neglected in first order. Of more importance is the relation of T_1^{BW} to the laser bandwidth. The $1/e$ intensity level of the spectral laser distribution in comparison to the energy level of the Cs-resonance gives a good estimate at which time Δt the alkali atom leaves the detection window (see Fig. 4). In this way T_1^{BW} is set constant and equals the value of Δt , where the Cs-state is in resonance with the $1/e$ intensity level of the detection window. From Fig. 4 we find a value of $T_1^{\text{BW}} = 65$ fs for laser system B. Under consideration of (2) and (3), we simulated autocorrelation traces for laser system B within a classical rate equation model (rapid dephasing, $T_2 \rightarrow 0$ fs) (Fig. 7). The dashed line corresponds to a static scenario (no Cs motion) at a constant lifetime of $T_1 = 11$ fs. The full line is the result for a quadratic dependence of T_1^{Cs} as defined by (3). The free parameter a was adjusted for best reproduction of the shape of the experimental AC (also shown in Fig. 7). An optimum value of $a = 1 \times 10^{-3} \text{ fs}^{-1}$ was found.

These simulations indicate that the use of a delay dependent lifetime T_1 accounting for modifications in the adsorbate–substrate coupling and consideration of the level shift of the Cs-resonance induced by the adsorbate motion is a reasonable Ansatz to simulate the experimental AC's as discussed in this paper. For a real quantification, however, the model has to be further refined. A consistent reproduction of the experimental AC-traces from laser B and C at the same time is not possible within this model, yet. However, we have to admit that the chosen ΔT_1^{Cs} dependence is somewhat

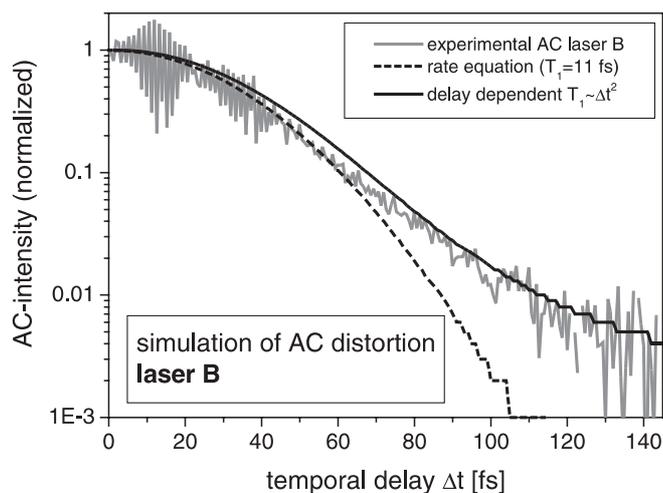


FIGURE 7 Simulated AC traces for laser system B for different T_1 -dependence of the temporal delay Δt (details see text). The step-like features are numerical artefacts

arbitrary and that a delay dependent T_1^{BW} may be more reasonable, too. In addition the thermal broadening of the alkali excitation due to low energy vibrational excitations of the Cs atom as observed in room temperature experiments should be considered, too [9, 13].

5 Summary

Depending on the bandwidth of the exciting laser-source we observe significant quantitative differences in TR 2PPE results for a long-lived excited Cs-resonance. Consistent results for different laser systems can only be obtained from a quantitative analysis of the autocorrelation traces at small temporal delay. For large delays the apparent lifetime differs by a factor of three within the set of laser parameters chosen in the present study. We show that an interpretation of the experimental data has to take into account the atomic motion of the Cs after photo-excitation and the energy level shift of the Cs resonance accompanied with this motion. With respect to the laser system the relevant parameter for the shape of the autocorrelation trace at long delays is the laser bandwidth. We propose that the lifetime extracted from an analysis of the short term contribution to the TR 2PPE signal corresponds to the actual excited state lifetime at adsorption distance, whereas the lifetime extracted from the TR 2PPE signal at delays > 40 fs probes i.e., the change of the lifetime as the Cs–Cu(111) distance increases. It describes the dynamical and, hence, the rather complex scenario of the Cs motion.

ACKNOWLEDGEMENTS Special thanks go to J.P. Gauyacq for critical comments on various aspects of this manuscript. This work was supported by the Deutsche Forschungsgemeinschaft through SPP 1093.

REFERENCES

- 1 See e.g. J.W. Gadzuk, L.J. Richter, S.A. Buntin, R.R. Cavanagh: Surf. Sci. **235**, 317 (1990); J.A. Misewich, T.F. Heinz, D.M. Newns: Phys. Rev. Lett. **68**, 3737 (1992); S.M. Harris, S. Holloway, G.R. Darling: J.Chem.Phys. **102**, 8235 (1995); J.W. Gadzuk: Surf. Sci. **342**, 345 (1995)
- 2 See e.g. R.W. Schoenlein, W.Z. Lin, J.G. Fujimoto, G.L. Eesley: Phys. Rev. Lett. **58**, 1680 (1987), U. Höfer, I.L. Shumay, C. Reuß,

- U. Thomann, W. Wallauer, T. Fauster: *Science* **277**, 1480 (1997); N.H. Ge, C.M. Wong, R.L. Lingle, J.D. McNeill, K.J. Gaffney, C.B. Harris: *Science* **279**, 202 (1998); L. Bartels, G. Meyer, K.-H. Rieder, D. Velic, E. Knoesel, A. Hotzel, M. Wolf, G. Ertl: *Phys. Rev. Lett.* **80**, 2004 (1998)
- 3 M. Bauer, S. Pawlik, M. Aeschlimann: *Phys. Rev. B* **55**, 10040 (1997)
- 4 S. Ogawa, H. Nagano, H. Petek: *Phys. Rev. Lett.* **82**, 1931 (1999)
- 5 H. Petek, M.J. Weida, H. Nagano, S. Ogawa: *Science* **288**, 1402 (2000)
- 6 A.G. Borisov, A.K. Kazansky, J.P. Gauyacq: *Surf. Sci.* **430**, 165 (1999)
- 7 A.G. Borisov, J.P. Gauyacq, A.K. Kazansky, E.V. Chulkov, V.M. Silkin, P.M. Echenique: *Phys. Rev. Lett.* **86**, 488 (2001)
- 8 M. Bauer, S. Pawlik, R. Burgermeister, M. Aeschlimann: *Surf. Sci.* **402–404**, 62 (1998)
- 9 M. Bauer, S. Pawlik, M. Aeschlimann: *Phys. Rev. B* **60**, 5016 (1999)
- 10 S. Ogawa, H. Nagano, H. Petek: *Appl. Phys. B* **68**, 611 (1999)
- 11 H. Petek, M.J. Weida, H. Nagano, S. Ogawa: *Surf. Sci.* **451**, 22 (2000)
- 12 A.G. Borisov, J.P. Gauyacq, E.V. Chulkov, V.M. Silkin, P.M. Echenique: *Phys. Rev. B* **65**, 235 434 (2002)
- 13 A.G. Borisov, A.K. Kazansky, J.P. Gauyacq: *Phys. Rev. B* **64**, 201 105(R) (2001)
- 14 T. Hertel, E. Knoesel, M. Wolf, G. Ertl: *Phys. Rev. Lett.* **76**, 535 (1996)
- 15 W. Shockley: *Phys. Rev.* **56**, 317 (1939)
- 16 P.O. Gartland, B.J. Slagsvold: *Phys. Rev. B* **12**, 4047 (1975)
- 17 R. Panagio, R. Matzdorf, G. Meister, A. Goldmann: *Surf. Sci.* **336**, 113 (1995)
- 18 1 ML corresponds to a closely packed alkali layer at the substrate
- 19 R. Loudon: *The Quantum Theory of Light* (Oxford University Press, Oxford 1973)
- 20 In [9] we reported a lifetime for the Cs-resonance of 15 ± 6 fs as average of two limiting cases for T_2 : the depopulation time T_1 and the line-width of the Cs-resonance as observed in the 2PPE spectrum. The best fit in this reference for the former case corresponding to the assumptions made in the present paper results in a lifetime T_1 of 12 fs
- 21 D. Menzel, R. Gomer: *J. Chem. Phys.* **41**, 3311 (1964)
- 22 This value is estimated from the intensity pulse width of 13 fs given in [4] assuming a transform limited, sech^2 temporal shaped pulse