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Femtosecond time-resolved photoemission of electron dynamics in surface Rydberg states

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Femtosecond time-resolved photoelectron spectroscopy provides a unique tool to study the dynamics of optically excited electrons at surfaces directly in the time domain. We present a new model for two-photon photoelectron spectroscopy from surface and image potential (or Rydberg) states which is based on density matrix theory. The formalism accounts for the influence of both energy and phase relaxation on experimental spectra and thus permits the study of the nature of inelastic and elastic scattering processes at surfaces in more detail. The analysis of experimental data employing the proposed model reveals a new mechanism for optical excitation of electrons to normally unoccupied states at surfaces which is feasible due to the influence of electronic dephasing. We discuss the nature of different relaxation channels with respect to our studies of image state dynamics on the bare and Xe or Kr covered Cu(111) surfaces. © 1997 American Vacuum Society. [S0734-2101(97)57103-X]

I. INTRODUCTION

Investigations on the dynamics of charge transfer processes at surfaces can reveal insights into the interaction of electronic states localized at surfaces with the underlying substrates. Such localized states may either be surface states, which are supported by the projected bulk band structure, or they may be associated with the electronic states of adsorbates. Two-photon photoelectron spectroscopy (2PPE) provides high sensitivity and good energy resolution and may be used as a versatile tool for the investigation of normally unoccupied states that are energetically located between the vacuum and the Fermi level.^{1,2} One particular advantage of this method is its potential for time resolved pump-probe experiments which allow to study the lifetimes of electrons in normally unoccupied states directly in the time domain. In this article we describe a comprehensive model that can be used to investigate time resolved two-photon photoelectron spectra.

The majority of investigations employing 2PPE have focused on the properties of so-called image potential states on bare and adsorbate covered surfaces.^{1,2} This particular class of surface states is due to the Coulombic tail of the image potential in front of a surface which can give rise to a Rydberg-like series of normally unoccupied states. The binding energies of these states converge towards the vacuum level approximately with $0.85/n^2$ eV where n is the quantum number.³ In many aspects the spectroscopy of image potential states may serve as a model system for the investigation of electronically excited states at surfaces. On the one hand they have a relatively simple and well characterized electronic structure and on the other hand they are not very strongly coupled to the bulk which makes their lifetimes ac-

cessible with the capabilities of current time resolved pump-probe techniques. Thus, time resolved studies of electron dynamics in image states can be used to learn about fundamental properties of inelastic and elastic interactions of electronically excited surface states with the bulk. This may also improve our understanding of processes which lead to rapid deexcitation during photochemical surface reactions and thereby have a critical influence on photoreaction cross sections, for example.

Combined with ultrafast laser techniques, time resolved photoemission has been used as a powerful tool in a pump-probe scheme to investigate surface state lifetimes.⁴⁻¹⁰ In principle, time resolved 2PPE should also permit us to study lifetimes of temporary formed negative ions at surfaces directly in the time domain, and first steps towards this goal have been reported lately.¹¹ A simple theory for continuous wave two-photon photoelectron spectroscopy that could successfully describe many aspects of 2PPE has previously been presented by Ueba.¹² However, here we develop a comprehensive theoretical model for *time resolved* two-photon photoelectron spectroscopy which will allow to investigate the interaction of image potential states with the substrate in more detail. We will show in particular that electronic dephasing can play an important role in the 2PPE process.

The model is used to analyze time resolved 2PPE spectra from image potential states at the bare and rare gas (Kr, Xe) covered Cu(111) surface. The results indicate that the intensity of the image potential state and its linewidth is strongly influenced by so-called pure electronic dephasing. This is likely to be a consequence of elastic electron or phonon scattering events at the surface. Rare gas adsorbates are found to decouple the image potential states from the substrate and thereby reduce both elastic and inelastic interactions with the bulk. The temperature dependence of the 2PPE spectra also indicates the importance of image potential state interaction with phonons.

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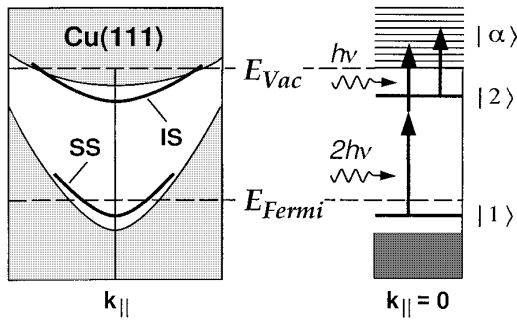


FIG. 1. Left side: projected band structure of the bare Cu(111) surface. Photoelectron spectra from this surface exhibit two sharp features due to nonresonant two-photon photoemission from the occupied surface state (SS) and due to photoemission from the transiently populated image state (IS). Right side: photoemission from the gamma point of the surface Brillouin zone can be modeled by the optical coupling of the image and surface state to the ionization continuum.

II. RESULTS

The experiments were performed with a 200 kHz Ti:sapphire seeded regenerative amplifier (Coherent, RegA 9000) which pumps an optical parametric amplifier (OPA, Coherent). The visible output of the OPA is compressed by a pair of prisms and we used a 0.2 mm thin beta barium borate crystal to generate the second harmonic ultraviolet (UV) pulses. Another prism sequence is used in the optical path of the UV beam before the p -polarized pump and probe beams were overlapped nearly collinearly (skew $< 0.5^\circ$) on the sample at 45° incidence angle. Two-photon photoelectron spectra were recorded for emission along the surface normal. The angular resolution of the analyzer is estimated to be better than 2° . The energy resolution in these experiments could be enhanced significantly to about 5 meV with respect to previous experiments due to improved time resolution of the counting electronics. More details about sample preparation and setup of the ultrahigh vacuum (UHV) chamber can be found in Refs. 11, 13, and 14.

We can model two-photon photoemission from the $\bar{\Gamma}$ point of the Cu(111) surface Brillouin zone and that of similar surfaces by the optical coupling of two discrete states to an ionization continuum. This can be understood if we take a brief look at the projected band structure of the bare Cu(111) surface in Fig. 1 which is typical for (111) surfaces of the late noble metals. The surface state band (SS) has its minimum at 0.42 eV below the Fermi level at $k_{||} = 0$ and the $n=1$ image potential state band (IS) stretches to 0.82 eV below the vacuum level. When investigated with two-photon photoelectron spectroscopy, two sharp features can be observed in the spectra, one resulting from nonresonant photoemission from the occupied surface state and one due to photoemission from the temporarily occupied intermediate image potential state.¹ A puzzling observation in the resulting 2PPE spectra is, however, that the image potential state is present even at photon energies where no direct optical transitions to the $n=1$ state at $k_{||} = 0$ are accessible, i.e., well below or above a photon energy of 4.45 eV at the bare Cu(111) surface, for example. It has therefore been specu-

lated that excitation of electrons to the image state at $k_{||} \neq 0$ followed by fast intraband relaxation of these electrons may lead to the observed population at $k_{||} = 0$. In contrast to this we will show that the experimental data can be accounted for by a new excitation mechanism which involves rapid electronic dephasing and does not require interband relaxation.

The electronic states that were included in the simulations are the initially occupied surface state (SS), the normally unoccupied image state (IS) and the continuum of final states as seen in the right panel of Fig. 1. To calculate the optical perturbation of this system we have used a density matrix formalism which accounts for energy and phase relaxation on a phenomenological basis. Energy relaxation here refers to the depopulation of the intermediate image state due to the coupling to a continuum of substrate excitations. After optical excitation the state of the system is given by a coherent superposition of the eigenfunctions $|1\rangle$, $|2\rangle$ and $|\alpha\rangle$ (see Fig. 1). Subsequent relaxation processes will not only lead to a decay of the excited state population but also to a loss of the phase relation between the coherently excited states. The interaction of the system with a bath also leads to the decay of coherence between the individual states, the so-called “pure” phase relaxation. Here this dephasing may be caused by elastic collisions of image state electrons with phonons, defects, or bulk electrons, for example. The optical coupling of final states $|\alpha\rangle$ could be neglected in the simulations and we, therefore, obtained spectra by investigating a variety of three level systems where only the final state energy—representative for different kinetic energies of the photoemitted electrons—was varied. The 2PPE spectra were then obtained by calculating the population which was transferred by the optical perturbation from the ground to the final state at various energies above the ionization threshold. For the propagation of the density matrix we used the Liouville–von Neumann equation

$$\frac{d}{dt} \rho = -\frac{i}{\hbar} [H, \rho] + \frac{d}{dt} \rho_{\text{diss}} \quad (1)$$

It describes the evolution of the system under the influence of a Hamiltonian H and a dissipative term $d/dt \rho_{\text{diss}}$. The time dependent Hamiltonian is determined by the frequency of the two laser pulses, their duration, and the optical transition matrix elements. The dissipative part, which describes the interaction with a bath, determines in detail how energy and coherence decay in the diagonal and off diagonal elements of the density matrix. This can be characterized by four rate constants which are determined by fitting calculated spectra to the experimental time resolved 2PPE spectra. The quality of the calculated spectra is very good (see below). An investigation of the wavelength dependence of calculated and experimental spectra for the same set of parameters in the calculation yields similar agreement for all photon energies. At the resonance energy, for example, the two peaks merge and we observe an increase of experimental and theoretical intensities of approximately two orders of magnitude.

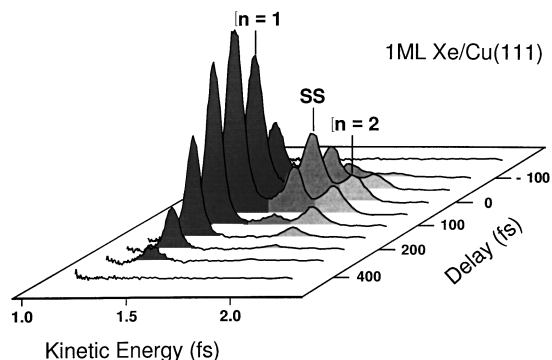


Fig. 2. Time resolved two-photon photoelectron spectra for the Xe covered Cu(111) surface (1 ML) as a function of the time delay between the pump ($2h\nu=4.32$ eV) and probe ($h\nu=2.16$ eV) pulses. The label SS refers to the surface state and $n=1$ as well as $n=2$ to the first and second image potential states, respectively.

A line shape analysis using voigt profiles reveals that the image potential state can be well described by a nearly Lorentzian line shape while the surface state can be approximated much better with a nearly Gaussian line shape. The lifetime of image state electrons, however, cannot be determined unambiguously from the homogeneous image state linewidth without knowledge of the contribution of pure dephasing. This is analogous to the optical excitation in a two level system as described by the optical Bloch equations where the excited state lifetime is given by the longitudinal relaxation time T_1 whereas the linewidth Γ is also influenced

by the so-called transverse or pure dephasing time T_2^* , i.e., $\Gamma = \hbar(1/T_1 + 2/T_2^*)$.¹⁵ Thus information on both energy and phase relaxation can only be determined by a combination of energy and time resolved measurements, for example, as shown in Fig. 2 for the xenon covered Cu(111) surface. Here we show two-photon photoelectron spectra as a function of the pump ($2h\nu$) and probe ($h\nu$) delay. Obviously the signal from the $n=1$ image state persists for a much longer time than the surface state signal (SS) which is given by the convolution of pump and probe pulses. The exact lifetime of the image state at the bare and rare gas covered Cu(111) surfaces can then be determined by fitting theoretical to experimental cross correlation traces as depicted in Fig. 3. From this we find that the adsorption of one monolayer of Kr leads to a dramatic increase of the $n=1$ image state lifetime from 18 fs to 60 fs, i.e., by a factor of 3.3, whereas the adsorption of a monolayer of Xe increases the $n=1$ image state lifetime even more to 70 fs, i.e., by a factor of 3.8. Adsorption of a second monolayer of Xe then leads to an additional increase of the lifetime to 135 fs by another factor of 2 (see Table I). This lengthening of the image state lifetime can be attributed to a decrease of the overlap of the image state wave function with the bulk metal as discussed below (see also Wolf *et al.*¹⁶). The lifetime of the $n=2$ image state behaves differently due to the degeneracy with bulk bands and has been discussed elsewhere.¹⁶ Recently Harris *et al.* have performed careful experiments with adsorbed xenon layers on Ag(111) and they also observe a strong increase in the $n=1$ image

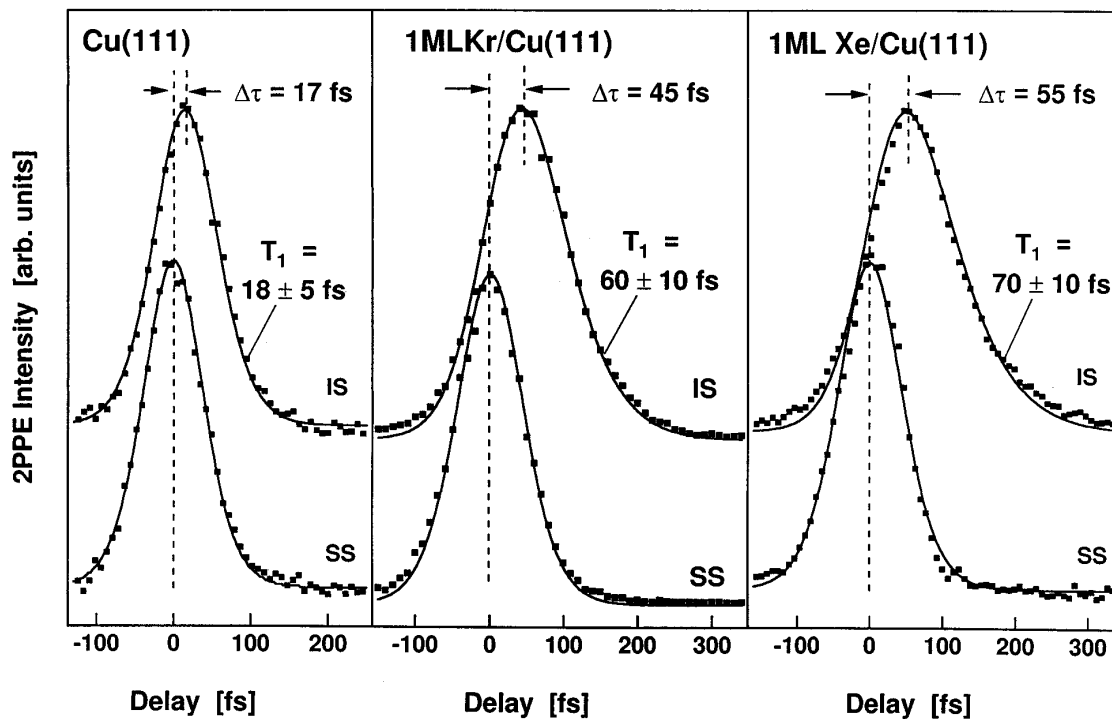


Fig. 3. Experimental and calculated cross correlation traces for the $n=1$ image potential state (IS) from the bare, Kr and Xe covered Cu(111) surfaces. The cross correlation of the surface state (SS) is used for determination of the precise time delay between pump and probe pulses. The shift of the cross correlation maximum $\Delta\tau$ can be used as a sensitive measure for the excited state lifetime in particular when the lifetime is comparable to the laser pulse duration.

TABLE I. Binding energies and lifetimes of the first and second image potential state on the bare and rare gas (Xe, Kr) covered Cu(111) surface. The dephasing time in the second column refers to the decay of coherence between the initial and intermediate state.

	Image state lifetime (fs)	Dephasing time (fs)	Binding energy (eV)	
Bare Cu(111)	($n=1$)	18 ± 5	19	0.83 ± 0.05
	($n=2$)	17 ± 5	...	0.25 ± 0.07
1 ML Kr/Cu(111)	($n=1$)	60 ± 10	...	0.57 ± 0.05
	($n=1$)	70 ± 10	37	0.66 ± 0.05
1 ML Xe/Cu(111)	($n=1$)	40 ± 10	...	0.18 ± 0.05
	($n=1$)	135 ± 20	...	0.56 ± 0.05

state lifetime with layer thickness.⁸ However, upon adsorption of a monolayer of xenon these authors report an even more pronounced increase of the $n=1$ lifetime from 32 fs on the bare surface by a factor of 6.5. It should be noted that these authors have also used a different approach for data analysis based on simple rate equations.

A careful investigation of experimental cross correlation traces furthermore reveals that the particular shape of the traces in Fig. 3 depends critically on the kinetic energy of the photoelectrons. This can be visualized if we plot the shift $\Delta\tau$ of the cross correlation maximum with respect to the time zero versus the kinetic energy of the photoemitted electrons (see Fig. 4). This shift, which is particularly sensitive to the excited state lifetime when the pulse duration is comparable to the lifetime itself, can be measured with high precision and may, therefore, be used for determination of ultrashort excited state lifetimes.⁷ The calculated shift $\Delta\tau$ of the cross correlation maximum is plotted along with the experimental values for the xenon covered surface (1 ML) and reproduces the experimental data very well. The largest shift of 55 fs is found exactly at the maximum of the image state peak and continuously decreases towards zero at the maximum of the surface state feature. This is consistent with the nonresonant nature of the 2PPE process from the surface state. The discrepancy between experimental and theoretical data at higher energies ($E_{\text{kin}} > 1.8$ eV) is due to the proximity of the $n=2$ image state which has not been included in the simulation. We note in passing that the cross correlation trace averaged over the entire image state feature is nearly identical to the cross correlation trace obtained from an evaluation with classical rate equations. Thus in this case the lifetime of the image state can be determined using Fermi's golden rule for the excitation process even though the promotion of the electron to the image state is not directly related to the coupling of a discrete level to a continuum.

A striking observation which is closely related to the energy dependence of the cross correlation shift $\Delta\tau$ is that the linewidth of the image state feature varies strongly with the delay between pump and probe pulses as seen from Fig. 5. Obviously the $n=1$ linewidth decreases from 83 meV at negative time delay (-50 fs) down to 51 meV for large positive time delay (250 fs). This can already be anticipated from the data in Fig. 4 where we find that the final state

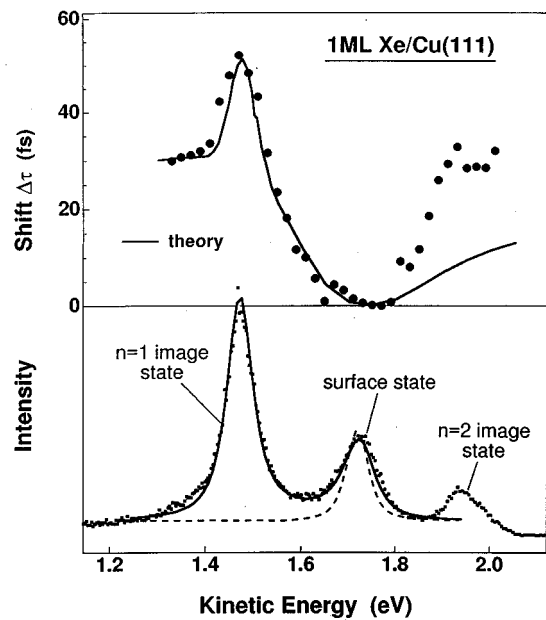


FIG. 4. The shift $\Delta\tau$ of the cross correlation maximum vs final state energy, i.e., vs the kinetic energy of photoemitted electrons. Calculated spectra for the xenon-covered Cu(111) surface (solid line) are in very good agreement with experimental data. The intensity of the image state feature in calculated spectra approaches zero when electronic dephasing between the ground and the intermediate states is not accounted for (dashed line).

response shows the slowest decay at the center of the image state peak and is significantly faster at all other energies. This implies that the photoelectron intensity in the wings of the image state will decay faster which thus leads to the observed narrowing of the image state linewidth. As seen

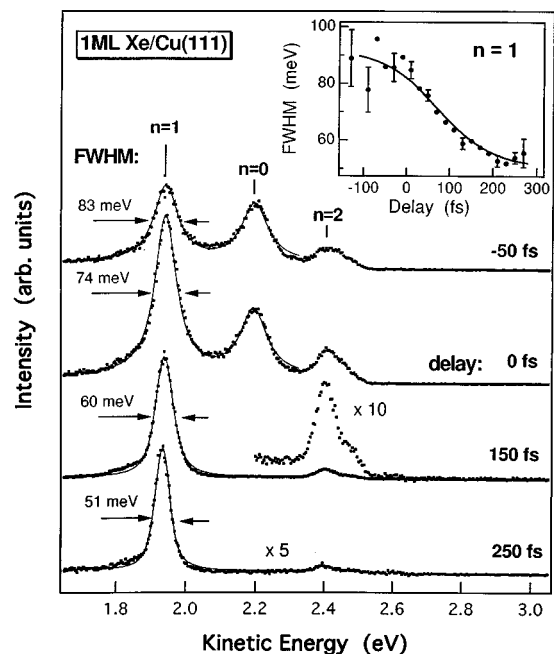


FIG. 5. Dependence of the image state linewidth on the pump-probe delay for the xenon covered surface. The inset shows the results of our calculations in comparison with the experimentally derived linewidths.

from the inset in Fig. 5, our model calculations nicely reproduce this trend. A similar observation of linewidth narrowing has also been reported by Zinth *et al.* in solutions using a transient Raman technique.¹⁷

Another key result of our simulations is that the image state feature can be reproduced by the calculations *only* if pure dephasing contributes to the decay of coherence between the ground and the intermediate state (see results for no dephasing between states $|1\rangle$ and $|2\rangle$, dashed line in Fig. 4). Again, in analogy to the optical Bloch equations, the effective decay of coherence is determined in part by the lifetime of the excited state T_1 and in addition to that by pure dephasing T_2^* . In particular, we find that the ratio of image to surface state intensities is approximately proportional to the rate of pure dephasing which contributes to the loss of coherence between the states $|1\rangle$ and $|2\rangle$. Thus we can determine the rate of pure dephasing between these two states by simply adjusting the calculated intensity ratio to the one found in experimental data. So far our investigation of time resolved spectra has revealed that the time constant for pure dephasing between the states $|1\rangle$ and $|2\rangle$ increases by about a factor of 2 from 19 fs on the bare Cu(111) surface to 37 fs on the surface covered with 1 ML of xenon (see Table I). Thus both energy and phase relaxation between image and surface state proceed significantly slower on the rare gas covered Cu(111) surface.

III. DISCUSSION

In the previous section we presented a comprehensive model which can be used to simulate time resolved two-photon photoelectron spectra and thereby allows a detailed study of the interaction of electronically excited states at a surface with the underlying substrate. One of the key results of our simulations was the apparent influence of electronic dephasing on experimental spectra. In particular we found that the homogeneous linewidth of the image state can only partially be attributed to lifetime broadening and that nearly 50% of the image state linewidth must be accounted for by the effect of pure electronic dephasing. Later on we will discuss possible microscopic mechanisms responsible for this phenomenon. For the moment we will just remind ourselves that pure electronic dephasing is related to the coupling of the surface states to the continuum of bulk excitations, irrespective of the nature of this process. Significant pure electronic dephasing between the surface and image potential states was also required to reproduce the image state feature observed in the 2PPE spectra at photon energies where no direct optical transitions to the image state are accessible, i.e., below or above 4.45 eV for the bare Cu(111) surface, for example. These observations show that pure electronic dephasing plays an important role in two-photon photoemission from image states and it reveals a new mechanism for the optical excitation of electrons to normally unoccupied states.

Typical decay channels which determine photoemission linewidths for valence hole or electron excitations at zero temperature are Auger-type electron hole pair generation,

phonon and impurity scattering.^{18–20} In general it is assumed that these processes are inelastic, i.e., that they are associated with an energy loss for the primary electron or hole. They should, therefore, be related to the corresponding lifetimes for energy relaxation as obtained from the time resolved data (see Table I). Energy and momentum conservation for the Cu(111) surface then require that image state electrons at $k_{\parallel}=0$ can only decay via electron hole pair generation into states with $k_{\parallel}\neq 0$, if we neglect impurity scattering for the moment. Tunneling into the bulk conduction band is obviously prohibited due to the Cu(111) projected band gap (see Fig. 1). Relatively good estimates of image state lifetimes due to Auger-type scattering events have been calculated by Echenique *et al.* and deAndres *et al.*,^{18,19} whereas the calculations by Gao and Lundqvist deviate severely from experimental image state lifetimes.²¹ Echenique *et al.* and deAndres *et al.* find an approximately linear dependence of the image state linewidth (at zero temperature) on the penetration of the image state wave function into the bulk. Using the phase analysis model by Smith,^{22,2} we have calculated the overlap of the $n=1$ image state wave function with the bulk from known band structure parameters.¹⁶ From this we can estimate that about 35% of the image state wave function should be inside the metal on the bare Cu(111) surface which would lead to a lifetime of 10 fs according to deAndres *et al.*¹⁹ This is in reasonable agreement with the measured image state lifetime and shows that the decay of image state electrons seems to be governed by their overlap with the bulk. An alternative approach to the determination of image state lifetimes was given by Cole and is based on the notion of an attempt frequency for states which are resonant with the bulk conduction band.^{23,24} For the Cu(111) and Ag(111) surfaces, however, this approach seems not to be appropriate due to the projected band gap where no bulk states are available at the energy of the image potential state (near $k_{\parallel}=0$).

The effect of adsorbed rare gases on the image state dynamics seems to be that they strongly decouple the image state wave functions from the substrate as seen from the dramatic increase of the image state lifetime in Table I. This should be caused by a reduction of the wave function overlap with the bulk which can be related to a combination of different effects. On the one hand the adsorption of 1 ML of xenon or krypton decreases the work function by 0.52 and 0.39 eV, respectively. This shifts the image state towards the center of the projected band gap and thus causes a stronger attenuation of the image state wave function in the bulk. Calculations which only account for the change in the work function and neglect screening effects or a change of the image plane upon rare gas adsorption would yield a reduction of the image state overlap with the bulk by a factor of approximately 3.¹⁶ Thus this effect could almost account for the observed increase of the image state lifetime by a factor of 3.3 for Kr and a factor of 3.8 for Xe upon adsorption of the rare gas monolayer. However, the adsorption of a second xenon layer, for example, leads to a further increase of the lifetime by another factor of 2 to 135 fs even though the energetic position of the image state with respect to the bulk

band structure hardly changes. This indicates that other effects like dielectric screening and shift of the image potential plane may also lead to a reduction of the wave function overlap with the bulk and hence to a decoupling from bulk states. This has been discussed in some detail by Harris and co-workers^{25–28,8} based on the aforementioned work by Cole.^{23,24}

So far we have focused our discussion on inelastic processes leading to a decay of the intermediate image state population. But the phenomenological rate constants appearing in the density matrix formalism [see Eq. (1)] not only determine the decay of energy (i.e., population) but also the loss of coherence (phase relation) due to interaction with the unobserved bath. We have seen from our calculations that pure dephasing between the ground and the intermediate state indeed is required to account for the existence of the image state feature in 2PPE spectra and that pure dephasing also does contribute significantly to the image state linewidth. For finite sample temperatures we suggest that a possible origin of pure dephasing may be due to elastic scattering with bulk phonons or electrons at the surface. The scattering of phonons at the surface, for example, may lead to a transient shift in the image potential and surface state energies. Using conventional photoelectron spectroscopy Paniago *et al.* have recently shown that the energetic position of surface states indeed depends on the substrate temperature.²⁹ Since the phase factor of excited and ground state wave functions is determined by the corresponding eigenenergies, this transient energy shift may cause a decay of coherence, in analogy to collisional line broadening in the gas phase, for example. It has also been shown that the surface state linewidth on Cu(111) critically depends on the substrate temperature indicative for the interaction of surface states with phonons.²⁰ The effective dephasing rates of $1/30 \text{ fs}^{-1}$ – $1/20 \text{ fs}^{-1}$ for the bare Cu(111) surface at room temperature, for example, also agree well with electron phonon scattering times known from the bulk metal.³⁰

Thus we hoped that the analysis of 2PPE spectra recorded at different sample temperatures might cast more light onto the role of phonons on pure dephasing in two-photon photoemission. The results of these investigations indeed indicate that pure dephasing rates tend to become faster with increasing temperature (see Fig. 6). Here the increase of the image state linewidth is most apparent and is reflected by the growth of the effective dephasing rate between intermediate and final states (solid squares) as obtained from our fit (solid lines). It should be noted, however, that the linewidth of the surface state was somewhat too large in these experiments, indicative for a higher defect density at the surface. This may mask some of the expected increase in effective dephasing rates between the other states. In analogy to the temperature dependence of the surface state,²⁹ the observed lowering of the image state energy may be attributed to the temperature dependence of the projected bulk band gap.

However, we still need to understand how electronic dephasing may lead to the appearance of the image state peak in calculated and experimental spectra for photon ener-

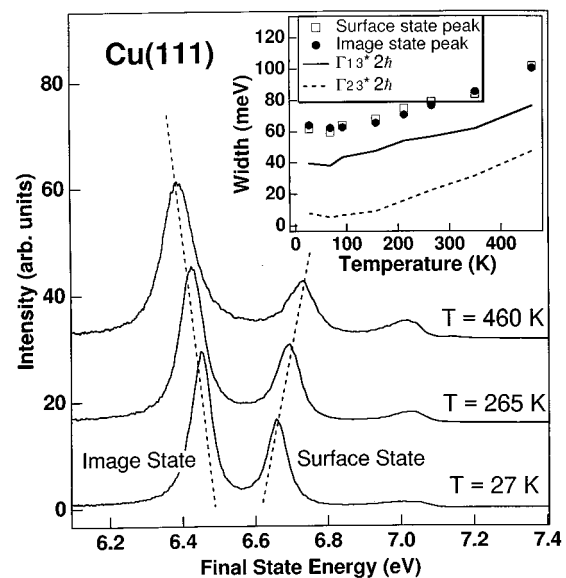


FIG. 6. Influence of substrate temperature on two-photon photoelectron spectra for the bare Cu(111) surface. Apart from the temperature induced shift of the line positions we also observe a pronounced increase of the image state linewidth. This can be attributed to the influence of elastic collisions with phonons on electronic dephasing. The dephasing rates Γ_{12} and Γ_{23} refer to the rates at which coherence decays between the corresponding levels; they were obtained from a fit of the model to experimental data.

gies far away from the resonance. On the one hand, if some type of rapid phasebreaking scattering events which occur during the excitation lead to the decay of coherence this will broaden the spectral excitation density and thereby create a small transient population in the image state even at photon energies far off resonance. A somewhat similar phenomenon has been observed in band-to-acceptor luminescence spectra from photoexcited carriers in GaAs where the spectral width of luminescence peaks also depends on the rate of electronic dephasing during the excitation process.^{31,32} Alternatively, a microscopic theory of dephasing by Gorini and Kossakowski suggests that a time dependent stochastic perturbation of the systems' eigenfunctions will also lead to pure dephasing.³³ According to this, we may argue that the effect of pure dephasing is to temporarily change the image and surface state resonance frequency such that the laser field may promote electrons to the excited state with small but finite probability.

The influence of an adsorbed rare gas on the dephasing dynamics is again similar to its influence on energy relaxation. So far we have analyzed the change of pure dephasing for adsorption of a Xe monolayer and find a pronounced increase of the dephasing rate between the initial and intermediate image state from $1/(19 \text{ fs})$ for the bare to $1/(37 \text{ fs})$ for the xenon covered surface, for example. This can also be attributed to a decoupling of the image state wave function from bulk excitations due to the reduced overlap with bulk states on the rare gas covered surface.

In conclusion, we have presented a time dependent approach to two-photon photoelectron spectroscopy which can

account for nearly all experimental observations and, thereby, allows to obtain reliable excited state lifetimes. In particular, we have used a formalism which allows to account for the role of coherence on the optical excitation process. This reveals that both the image state linewidth and its intensity is significantly influenced by pure electronic dephasing. This may cast some light onto the role of *elastic* (phase breaking) scattering processes with phonons or electrons at finite temperatures which apparently also allows to excite electrons with small but finite probability to normally unoccupied states using photon energies far away from the resonance frequency. Adsorbed rare gases were found to decouple the image states significantly from the continuum of bulk states as seen from the increase in image state lifetime and slower pure dephasing on the rare gas covered surface.

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