

Coherence and Decoherence of a Localized Excitation on a Surface Adatom *

GAO Shi-Wu(高世武)¹, H. Petek², J. Aizpurua¹, P. Apell¹¹Department of Applied Physics, Chalmers and Göteborg University, SE-412 96 Göteborg, Sweden²Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh, PA 15260, USA

(Received and accepted 13 May 2002 by WANG Ding-Sheng)

A theory of coherent excitation of a localized state on an adatom by two-photon photoemission spectroscopy (TR-2PPE) is presented within a microscopic model and the time-dependent formalism. Coherent oscillation and incoherent population decay of the excitation are obtained, and are shown to attain well-defined lifetime constants only in the long-delay limit. In addition, we have found a competing excitation channel via electron transfer. The theory is applied to Cs/Cu (111), which reproduces a few qualitative features observed in recent experiments. The effect of atomic motion on the 2PPE spectra, which manifests dominantly as a redshift in the spectrum, has been analysed.

PACS: 78.47.+p, 78.20.Bh, 68.43.Tj

Ultrafast laser spectroscopy has become a powerful tool to probe and control the short-time dynamics of atoms and molecules in gas phase and condensed matter environments.^[1] Recent experiments using interferometric two pulse correlation (I2PC) scans have made it possible to generate, resolve and control various coherent phenomena, including the exciton dynamics in quantum wells,^[2] rovibrational motion in molecules,^[3] electronic relaxation in He clusters,^[4] attosecond pulse generation,^[5] plasma dephasing in nanoclusters,^[6] and hole dynamics in metals.^[7] In the probe of nuclear motion in the condensed phase, coherent excitation has recently been generated in the surface bands and adsorbate states. Such local excitations couple strongly to nuclear degrees of freedom, leading to vibrational excitations and even desorptive motion.^[8] By following the two-photon photoemission (2PPE) spectra as a function of time delay, the femtosecond atomic motion has been mapped out in the time domain.

The interpretation and understanding of 2PPE spectra and I2PC scans has so far been based on simulations with a three-level model and the optical Bloch equation (OBE),^[9] with fitting parameters chosen to mimic the relaxation processes within the system. This approach, which treats coherence explicitly, is inadequate for describing the coupled electron–nuclear system in a complex environment, where multiple channels of excitation and dissipation may coexist and compete on the same timescale. More elaborate models^[10,20] have recently been developed to describe in greater detail the electronic and/or nuclear dynamics. These works have not yet, however, considered quantum coherence, which is central in the I2PC-type experiments.

In this Letter, we present a theory of 2PPE spectra from a moving atom at the surface, a simple localized excitation in a condensed environment, based on an extended Anderson–Newns model and the time-dependent formalism. In particular, we treat coherence and electron–nuclear dynamics on an equal foot-

ing. The atom and the surface were represented by a resonance state embedded in the substrate continuum. The two pulses and the atomic motion are treated explicitly as the time-dependent or position-dependent coupling. The main results from our formulation include the following. (1) The dynamics of both the phase coherence and the incoherent population decay are obtained. In the long time limit, both components decay exponentially with well-defined time constants, fulfilling the identity $T_2 = 2T_1$, which is expected in the absence of pure dephasing. However, such a simple relationship does not exist in the intermediate to short time regime. (2) The effect of atomic motion on the spectra has been analysed in terms of the time-dependent and position-dependent quantities. Our model establishes the dynamical relationship between the position-dependent coupling and the time-resolved spectrum. (3) We found that there is a new competing excitation channel via electron transfer, which was not considered in the earlier OBE model^[9] or more sophisticated modelling,^[10] but comes straightforwardly from our formulation. We point out that this channel may contribute significantly to the 2PPE spectra in certain systems. When applied to the model system, Cs/Cu(111), our theory reproduces all basic features of the dynamical spectra observed experimentally.

The laser–electron–atom system is described by an extended Anderson–Newns-type model Hamiltonian as follows

$$H = H_e + V_{em}, \quad (1)$$

$$H_e = \epsilon_a(t)c_a^\dagger c_a + \sum_k \epsilon_k c_k^\dagger c_k + \sum_p \epsilon_p c_p^\dagger c_p + \sum_k [v_k(t)c_a^\dagger c_k + \text{H.c.}], \quad (2)$$

$$V_{em} = \sum_k [A_k(t)c_a^\dagger c_k + \text{H.c.}] + \sum_p [B_p(t)c_a^\dagger c_p + \text{H.c.}], \quad (3)$$

where Eq. (2) is the Anderson–Newns model^[12] for a local resonance state, state a , in a continuum band, $\{k\}$, of the surface. The coupling term $v_k(t)$ and

* Supported by the Swedish Natural Science Research Council (NFR).

the resonance state energy $\epsilon_a(t)$ depend on the atom-surface distance $z(t)$, which is time-dependent as the atom moves. The final states of the photo-emitted electrons are represented by a continuum band ($\{p\}$) in the vacuum. The laser-surface coupling is modelled by the absorption and emission matrix elements, $A_l(t)$ and $B_p(t)$, as shown in Eq. (3). The latter can be factorized into the dipole transition matrix and laser profile function, i.e. $A_l(t) = \langle l|z|a\rangle E_A(t)e^{-i\omega_A t}$ and $B_p(t) = \langle p|z|a\rangle E_B(t)e^{-i\omega_B t}$, where $E_A(t)$ and $E_B(t)$ are the envelope functions of the pump and probe pulses, respectively. An experiment with I2PC scans can be treated as a special case of this coupling, where $\omega_A = \omega_B = \omega$ and the envelope functions are identical

$$E(t, \delta) = \frac{1}{\sqrt{2\pi\tau^2}} (e^{-t^2/2\tau^2} + e^{-(t-\delta)^2/2\tau^2} e^{i\omega\delta}) \quad (4)$$

Here τ is the width of the pulse, and δ is the delay between the two pulses.

The model Hamiltonian of Eq. (2), without laser coupling, has been widely used to treat a number of static and dynamical problems,^[13,14] including dynamical charge transfer^[15,16] and resonance tunnelling through a double barrier and an atom.^[17] With the laser coupling terms, it can also be solved with the time-dependent formalism, if the fields are not extremely strong. While the detailed solution will be given elsewhere, we sketch here the major steps and results briefly. Firstly, the spectral function $I(\epsilon_p, \delta) = \langle c_p^\dagger c_p(t \rightarrow \infty) \rangle$ of the emitted electrons with final-state energy ϵ_p can be generally expressed as a convolution of the dipole transitions and a correlation functions of the atomic state

$$I(\epsilon_p, \delta) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} B_p^*(t') B_p(t'') \langle c_a^\dagger(t') c_a(t'') \rangle \cdot \exp[-i\epsilon_p(t' - t'')] dt' dt'' \quad (5)$$

This result indicates that the correlation function $\langle c_a^\dagger(t') c_a(t'') \rangle$ of the excited atomic state contains all the dynamics beyond the last probe transitions. The whole problem reduces to deriving this correlation function of the atomic state, in the dynamical system.

The time evolution of the atomic state was obtained by solving the coupled Heisenberg equations for the field operators. In the weak coupling limit, $c_a(t)$ can be derived as

$$c_a(t) = -i \sum_l c_l \int_{t_0}^t G_a(t, t') A_l(t') e^{-i\epsilon_l(t'-t_0)} dt' - i \sum_k c_k \int_{t_0}^t G_a(t, t') v_k^*(t') e^{-i\epsilon_k(t'-t_0)} dt' \quad (6)$$

Here the first term describes the pump excitation from initial state $|l\rangle$ at the surface by the laser pulses, while the second term describes the electron-transfer excitation caused by tunnelling. The latter channel, which has not been considered in earlier modelling, comes straightforwardly from our model. We later discuss the possible roles of this term, and the conditions that

this term may contribute to 2PPE. The electron propagator G_a is defined by

$$G_a(t, t') = \exp\left(-\int_{t'}^t [i\epsilon_a(t'') + \gamma_a(t'')] dt''\right). \quad (7)$$

The resonance energy and the imaginary term depend generally on the atom-surface distance, and are functions of time if the atom moves. With the classical trajectory approximation, we have $\epsilon_a(t) = \epsilon_a[z(t)]$ and $\gamma_a(t) = \pi \sum_k v_k(z(t))^2 \delta(\epsilon - \epsilon_k)$. By this expression, we neglect the laser-induced energy shift of the atomic level, which should be small if the applied fields are not extremely strong.

One key quantity characterizing the atomic dynamics is the time-dependent population of the resonance state. It is in our model given by

$$n_a(t) = \sum_l A_l^2 \left| \int_{-\infty}^t dt' G_a(t, t') E_A(t', \delta) e^{-i(\omega+\epsilon_l)t'} \right|^2 + \sum_k f(\epsilon_k) \left| \int_{-\infty}^t dt' G_a(t, t') v_k(t') e^{-i(\omega+\epsilon_k)t'} \right|^2 \quad (8)$$

If the atomic resonance is far above the Fermi level (for example, in the Cs/Cu(111) case at low Cs coverage, it is 3 eV above the Fermi level), the contribution from the second term of Eq. (8) should be small. In this case, the direct two-photon excitation dominates. The spectral function corresponding to the direct channel is given by

$$I(\epsilon_p, \delta) = \sum_l A_l^2 B_p^2 \left| \int_{-\infty}^{\infty} dt' E_B(t', \delta) e^{-i(\omega-\epsilon_p)t'} \cdot \int_{-\infty}^{t'} dt'' G_a(t', t'') E_A(t'', \delta) e^{-i(\omega+\epsilon_l)t''} \right|^2 \quad (9)$$

This expression can be easily interpreted as follows. One electron is first pumped into the resonance state $|a\rangle$ at time t'' . The electron then propagates on the atom from t'' to a later time t' . It is then emitted by the probe pulse at t' . Equations (8) and (9) are the main formal results of our theory. The solution of Eq. (9) is in general complicated, as it involves evaluation of the many transition matrices and double time integrations.

To achieve qualitative physical insight into the spectral data and the dynamics of the excited electrons, we consider first a special case of 2PPE where the atom does not move. We have then $\epsilon_a(t) = \epsilon_0$, $\gamma_a(t) = \gamma$ and $G_a(t, t') = e^{-(i\epsilon_a + \gamma_a)(t-t')}$. Assuming a Gaussian laser pulse specified above, one arrives at the following analytical expression for the 2PPE spectra

$$I_{2PPE}(\epsilon_p) = I_0 e^{-2\gamma\delta} e^{-(\epsilon_p - \omega_B - \epsilon_a)^2 \tau^2}, \quad (10)$$

where $I_0 = 2\pi\tau^2 \Gamma_A B_p^2 e^{\gamma^2 \tau^2}$, with $\Gamma_A(\epsilon) = \pi \sum_l A_l^2 \delta(\epsilon - \epsilon_l)$, which measures the cross section for pump excitation. Equation (10) is simply a Gaussian spectrum

located at one photon energy above the resonance state. It should be noted that the linewidth of the spectrum is determined by the duration of the laser pulse τ^{-1} , rather than the lifetime of the resonance state, as in conventional photoemission spectroscopy. The 2PPE intensity decays exponentially as a function of delay, which suggests that the lifetime of the excited state can be obtained by scanning intensity versus delay in a real-time pump–probe measurement. In comparison with experiments, Gaussian spectra have been observed in almost all systems, and the real-time measurement has been used to extract the lifetime in both bulk excitations, surface states and adsorbate states.

For I2PC scans, the analytical expression for non-moving atoms can be derived only in the long delay limit, i.e. $\delta \gg \tau$. In this limit, the profile function can be approximated by delta functions, $E_A = E_B = \delta(t) + \exp(i\omega\delta)\delta(t - \delta)$. Equation (9) then leads to

$$I_{I2PC} = \sum_l \frac{1}{8} f_l A_l^2 B_p^2 \{1 + 2e^{-2\gamma\delta} + 2e^{-\gamma\delta} \cdot [\cos(\epsilon_p - \epsilon_a) + \cos(\epsilon_a - \epsilon_l)] + \cos(\epsilon_p - \epsilon_l)\}. \quad (11)$$

The summation is dominated by the initial states whose energy is in resonance with the photons, i.e. $\epsilon_a - \epsilon_l \simeq \omega$. It is also obvious that the photo-emitted electrons are dominated by the states with energy near resonance with the photons, $\epsilon_p - \epsilon_a \simeq \omega$. Neglecting the energy dependence of the transition matrix, the I2PC signal for near-resonant excitations then has the following simple form

$$I_{I2PC} = I_{2p} [a_0 + a_1 \cos(\omega\delta) + a_2 \cos(2\omega\delta)], \quad (12)$$

where $a_0 = (1 + 2e^{-2\gamma\delta})$, $a_1 = 4e^{-\gamma\delta}$, $a_2 = 1$, and $I_{2p} = \sum_l f_l A_l^2 B_p^2 / 8$. The I2PC scans contain therefore a population decay term (the first term) and two oscillation terms with frequency ω and 2ω . The latter corresponds to the coherent oscillation driven by the pump and probe pulses, and the weak interference between the initial and final states, respectively. The exponents in a_0 and a_1 attain the physical meaning as the lifetime for the excited state $T_1 = (2\gamma)^{-1}$, and the decoherence time $T_2 = \gamma^{-1}$. This justifies the relation, $T_2 = 2T_1$, as usually expected by the OBE approach. Such an assignment of time constants does not exist in the short delay limit, when the dynamics of the coherent excitations are entangled with those of the laser pulses.

Figure 1 shows the numerical simulation of a typical I2PC. Parameters have been chosen to mimic the Cs/Cu(111) system, where experimental data are available. Specifically, we used $\epsilon_a = 3.0$ eV and $\omega = 3.08$ eV. The laser pulses have a Gaussian envelope with $\tau = 13$ fs. The lifetime of the 6s resonance state was chosen to be 50 fs. To simulate a continuous band, some 80 initial states were chosen at around the resonance energy. The final state was set to be 6.0 eV above the Fermi level, which is nearly resonant with

the photon energy. The simulated I2PC spectra indicate that the I2PC intensity decays exponentially as a function of delay. The I2PC signal shows coherent oscillations at short delays, which die off gradually at large delays. The dashed line shows the phase averaged envelope of the I2PC. The inset shows the power spectrum of the I2PC obtained by Fourier analysis. It exhibits two peaks with frequencies at around ω and 2ω , which are oscillations of the coherent polarization, as expected from Eq. (12). Compared to experiment, similar coherent oscillations have been observed on several systems in the I2PC experiment. In particular, very similar features were observed on both Cs/Cu(111) and Cs/Ag(111), and Rb/Cu(111).^[18,19]

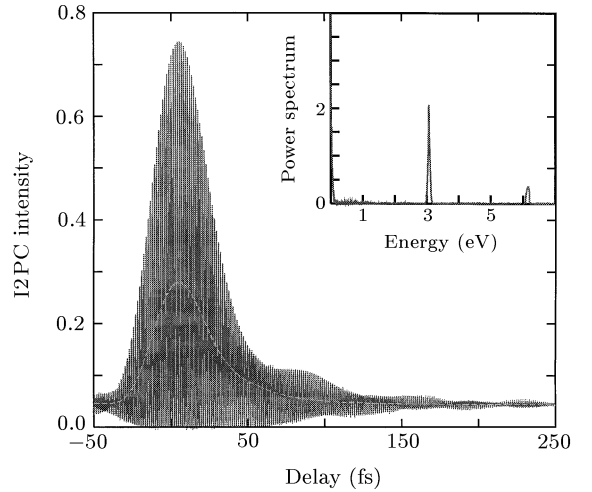


Fig. 1. Intensity of the I2PC scan for Cs/Cu(111). The two pulses are defined by a field, $E(t, \delta) = e^{i\omega t} [e^{-t^2/2\tau^2} + e^{i\omega\delta(t-\delta)^2/2\tau^2}]$, with $\omega = 3.08$ eV and $\tau = 13$ fs. The inset shows the power spectrum of the I2PC.

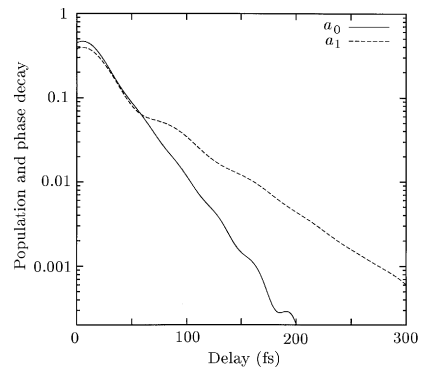


Fig. 2. Envelope function of the population decay, a_0 , and the coherent oscillations at frequency ω , a_1 , extracted from the I2PC spectrum shown in Fig. 1.

By fitting the I2PC spectra with the three components shown in the power spectrum, we obtain the envelope function of the coherent oscillations, which are shown in Fig. 2. It is seen that the ω component, the a_1 term, decays much slower than the population decay, the a_0 term. By fitting the coherent oscillations at long delays, we can deduce a decoherence time, $T_2 = 96$ fs, which is approximately twice that of the

lifetime of the excited state, 50 fs, for the Cs/Cu(111) system.

Now we turn to study the effect of atomic motion on the 2PPE/I2PC spectra, as observed in recent experiments.^[8,18,19] To consider the atomic motion, one needs to treat the following processes: (i) the events of electronic transition to the excited state; (ii) the nuclear motion on the excited state; and (iii) the quenching of the excited state and the dissipative dynamics when back on the ground-state potential. While detailed treatments of these processes are subjects of their own, we adopt a simple trajectory approach for atomic dynamics to understand the qualitative features of atomic motion in the 2PPE/I2PC spectra. Thus, we have treated the electronic excitation–de-excitation cycle using a simple Monte Carlo approach. To accelerate simulations, we only simulate those inelastic events involving electron–atom energy transfer.

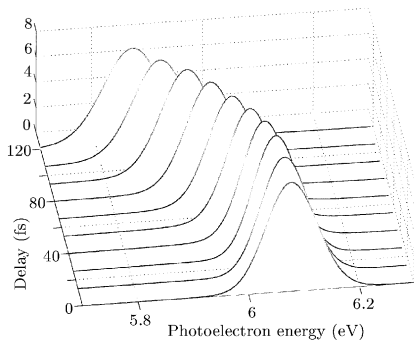


Fig. 3. Two-photon photoemission spectra versus delay when the Cs atom moves on the excited state, which is simply described by an excitation force $F = 0.018$ eV/a.u. A number, 1000, of trajectories of excitation–de-excitation were simulated.

Figure 3 shows the 2PPE spectra as a function of delay. We have simulated 1000 events of transitions. Each of these was excited at around $t = 0$, where the pump pulse was applied, and their motion on the excited state was simulated by a driving force $F = 0.018$ eV/a.u., estimated from the Cs/Cu(111) excited state. The lifetime of the excited state was simulated stochastically with a mean lifetime of 50 fs for the Cs atom. It is obvious that the spectra shift to a lower energy as the delay increases, due to the desorptive motion of the Cs atom. We assumed an exponential dependence of the energy as a function of atom–surface distance, $\epsilon_a(z(t)) = \epsilon_a e^{-\alpha z(t)}$, with $\alpha = 0.44$ a.u.⁻¹. The motion on the excited state was determined by classical molecular dynamics. In Fig. 4, we have plotted the energy shift as a function of delay obtained from our simulation. The dashed line represents the experimental data. Good agreement is found at short delay. Earlier studies with a different approach also obtained a similar behaviour.^[20] At longer delays, the model gives larger values due to the fact that we have assumed a simple constant force at all distances, where in reality the force should die off at large distances.

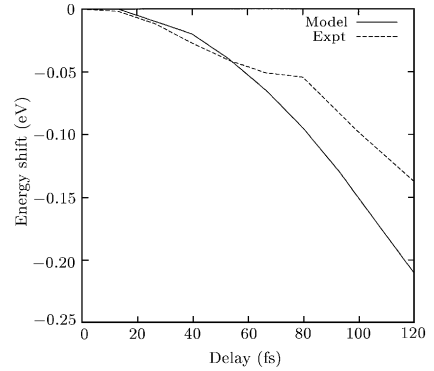


Fig. 4. Peak energy shift as a function of delay. The solid line is from the model simulation in Fig. 3, while the dashed line is the experimental data.

Finally, we like to point out the possible role of the indirect excitation channel via electron transfer. For those states far above the Fermi level, 3 eV for Cs/Cu(111), the probability of electron transfer is small due to off-resonance. The contribution of the second channel is probably negligible. However, for systems whose excitations are closer to the Fermi level, atomic motion may further lower the atomic state. Electron tunnelling may lead to auto-neutralization and excitation, and thus contribute to 2PPE/I2PC. It will be interesting in the future to investigate the effect of this channel both experimentally and theoretically.

S. Gao acknowledges partial support from the Materials Consortium–ATOMICS, funded by the Swedish Foundation for Strategic Research (SSF). H. Petek acknowledges funding from the NSF under Grant No DMR-0116034.

References

- [1] Petek H and Ogawa S 1997 *Prog. Surf. Sci.* **56** 239
- [2] Heberle A P *et al.* 1995 *Phys. Rev. Lett.* **75** 2598
- [3] Blanchet V *et al.* 1997 *Phys. Rev. Lett.* **78** 2716
- [4] Stienkemeier F *et al.* 1999 *Phys. Rev. Lett.* **83** 2320
- [5] Papadogiannis N A *et al.* 1999 *Phys. Rev. Lett.* **83** 4289
- [6] Lamprecht B *et al.* 1999 *Phys. Rev. Lett.* **83** 4421
- [7] Ogawa S *et al.* 1997 *Phys. Rev. Lett.* **78** 1339;
Ogawa S *et al.* 1999 *Phys. Rev. Lett.* **83** 832
- [8] Petek H *et al.* 2000 *Science* **288** 1402
- [9] Weida M J *et al.* 2000 *J. Opt. Soc. Am. B* **17** 1443
- [10] Sakaue M, Kasai M and Okiji A 2001 *Surf. Sci.* **482** 1169
Sakaue M, Kasai M and Okiji A 2001 *Surf. Sci.* **493** 292.
- [11] Borisov A G *et al.* 2001 *Phys. Rev. Lett.* **64** 221105
- [12] Anderson P W 1961 *Phys. Rev.* **124** 41
Newns D M 1969 *Phys. Rev.* **178** 1123
- [13] Blandin A *et al.* 1976 *J. Physique* **37** 369
- [14] Brako R and Newns D M 1978 *Surf. Sci.* **108** 253
- [15] Langreth D C and Nordlander P 1991 *Phys. Rev. Lett.* **43** 2541
- [16] Shao H *et al.* 1996 *Phys. Rev. Lett.* **76** 102
- [17] Gao S *et al.* 1997 *Phys. Rev. B* **55** 4825
- [18] Petek H *et al.* 2001 *J. Phys. Chem. B* **105** 6767
- [19] Petek H and Ogawa S 2002 *Ann. Rev. Phys. Chem.* **53** 507
- [20] Borisov A G *et al.* 2001 *Phys. Rev. B* **64** 221105