Two-Electron Photon Emission from Metallic Quantum Wells

Gernar Hoffmann and Richard Berndt
Institut für Experimentelle und Angewandte Physik,
Christian-Albrechts-Universität zu Kiel, D-24098 Kiel, Germany

Peter Johansson
Department of Natural Sciences, University of Örebro, S–701 82 Örebro, Sweden

(Dated: March 22, 2022)

Unusual emission of visible light is observed in scanning tunneling microscopy of the quantum well system Na on Cu(111). Photons are emitted at energies exceeding the energy of the tunneling electrons. Model calculations of two-electron processes which lead to quantum well transitions reproduce the experimental fluorescence spectra, the quantum yield, and the power-law variation of the intensity with the excitation current.

PACS numbers: 73.20.At, 68.37.Ef, 73.20.Mf, 73.21.Fg

Tunneling electrons in a scanning tunneling microscope (STM) can excite vibrational or electronic modes of the sample by inelastic tunneling provided that their energy exceeds the excitation energy. These excitations have been detected either by their contribution to the tunneling current or by investigating light that is being emitted from the tunneling gap. Thus, inelastic tunneling spectroscopies have been performed. Usually, tunneling electrons can safely be assumed to be independent of each other in these spectroscopies. Even at a high tunneling current \( I = 100 \text{ nA} \) the average time between two consecutive tunneling events is \( \sim 1.6 \text{ ps} \). Assuming Poisson statistics, two electrons are rather unlikely to interact in the tunneling gap. As a consequence, inelastic processes which involve multiple electrons have only been observed in the particular case of STM-induced desorption of H from Si. The lifetime of the H-Si stretch mode which is involved in desorption is in the range of nanoseconds enabling an interaction with several consecutive electrons before deexcitation.

Here, we report on unusual emission of visible light from Na on Cu(111), a metallic system which exhibits well-studied quantum well states (QWS) near the Fermi energy \( E_F \). Surprisingly, fluorescence spectra reveal the emission of “forbidden” photons whose energy \( h \nu \) significantly exceeds the energy of a tunneling electron \( eU \), where \( U \) is the sample voltage. The intensity of the “forbidden” light increases approximately like \( I^{1.5} \) where \( I \) is the tunneling current, with the exponent decreasing to 1.2 at the highest currents used. Its quantum efficiency reaches values of up to \( \sim 10^{-7} \) photons per tunneling electron at large \( I \).

Electron lifetimes at the Na/Cu(111) surface being on a fs timescale we are lead to conclude that two-electron processes are involved which do not rely on a stepwise accumulation of energy in an excited mode. We propose a model where two electrons tunnel more or less simultaneously. Once they are in the vacuum-barrier region between tip and sample they may exchange energy through the Coulomb interaction which is relatively unscreened there. As a result of this Auger-like process, one of the electrons can emit a photon with \( h \nu > eU \). Despite the simplicity of the model, calculated fluorescence spectra and the current dependence of the quantum efficiencies are comparable to the experimental data.

Spectral structure extending beyond the condition \( h \nu < eU \) has been reported for photon emission from Au films investigated at ambient temperature. However, no explanation of this intriguing result is currently available. Uehara et al. reported on light emission at \( h \nu = 2eU \) from superconducting Nb tips and samples at \( T = 4.7 \text{ K} \) and explained this emission in terms of Cooper-pair tunneling. Photon emission at large \( h \nu \) has also been observed from metal point contacts which emit black-body radiation at elevated currents.

Our experiments were performed with a ultra-high vacuum (UHV) STM operated at a temperature \( T = 4.6 \text{ K} \). W tips were prepared by electrochemical etching and subsequent sputtering and annealing in UHV. The Cu(111) surface was cleaned by repeated cycles of Ar-ion bombardment and annealing. Na films were evaporated from outgassed SAES Getters sources onto the Cu crystal held at room temperature. Na coverages were calibrated using the binding energies of the lowest QWS. After preparation at room temperature the samples were transferred to the STM and cooled to \( T = 4.6 \text{ K} \). Photons in the energy range 1.1 eV < \( h \nu < 3.5 \text{ eV} \) were detected with a lens-system in UHV, coupling the light to a grating spectrometer and a liquid nitrogen cooled CCD camera. The spectra have been corrected for the wavelength dependency of the detection efficiency. For the voltages used here, up to currents of \( \sim 100 \text{ nA} \), surface modifications was rarely observed on flat surfaces. While surface modification becomes more probable at higher currents, during acquisition of the data sets shown here no such events occured as verified from STM images and simultaneous monitoring of the vertical tip position.

Figure 1 displays fluorescence spectra recorded at el-
Fluorescence spectra reveal a maximum which shifts with the tip Fermi level to the lower QWS and emit photons. The data of Fig. 1 appear to be consistent with this picture. Two spectral components are discernible, an emission at low photon energies below ~1.25 eV the correction is reliable only at higher photon energies. The insets show the uncorrected data as measured (in counts vs. wavelength in nm).

Two-electron processes provide a natural explanation of the unusual emission in Fig. 1. Since such processes imply a nonlinear variation of the intensity with the tunneling current \( I \) we recorded series of some 800 fluorescence spectra while varying \( I \) and evaluated the "forbidden" intensity. The double-logarithmic plot in Fig. 2 reveals that the intensity scales approximately like \( I^{1.5} \) confirming the above explanation. As a consequence, the "forbidden" emission is weak at low tunneling currents. That is why it has been overlooked previously. In addition to its variation with \( I \), the intensity of the quantum well emission from 0.6 ML Na also depends strongly on the voltage \( U \) for \( U < 2 \) V. Consequently, the quantum efficiency of the "forbidden" emission varies significantly depending on the specific \( I \) and \( U \) chosen. We estimate an efficiency on the order of \( 10^{-7} \) photons per tunneling electron at \( I = 100 \) nA and \( U = 1.8 \) V from 0.6 ML Na.

A possible explanation of the observed two-electron processes appears to be tunneling of an electron into a long-lived empty state of the Na/Cu(111) surface and subsequent further excitation of this electron via interaction with a second tunneling electron. We estimated the probability of such processes assuming a Poisson distribution of the intervals between tunneling events. To obtain the observed quantum efficiencies an excited electronic state with a lifetime \( \tau \approx 1 \) ps needs to be postulated. This value is much larger than typical electronic lifetimes at surfaces. Moreover, it is unclear why an electron should remain localized under the tip over this extended period of time. We therefore discard this type of mechanism.

We have instead considered two other two-electron mechanisms that we believe cause emission of photons with an energy exceeding \( eU \): (i) A coherent Auger-like process in which energy is transferred from one tunnel-
ing electron to another. (ii) Decay of the hot holes \( \Phi^e \) that are injected into the tip because most of the tunneling current passes through the lower QWS. The decaying holes create hot electrons in the tip which subsequently can tunnel into the upper QWS and thereby cause photon emission.

The Keldysh Green’s function (GF) formalism provides a suitable theoretical framework for calculating the intensity of the emitted light from a system out of equilibrium such as an STM under finite bias. The intensity can be written

\[
\frac{dP}{d\Omega(d\hbar\omega)} = \frac{\omega^2}{16\pi^2\epsilon_0^3\hbar} \int_V d^3r \int d^3r' \, i \Pi^<(\vec{r}, \vec{r}', \omega). \tag{1}
\]

The integrations run over a volume between the tip and sample where the electrons and photons interact efficiently. \( G \) is a factor describing the enhancement of the electromagnetic vacuum fluctuations in the tip-sample cavity, and \( \Pi^< \) is the Fourier transform of the current-current GF, \(-i(j(z, \vec{r}', 0)j(z, \vec{r}, t))\), which in the case of allowed light emission can be expressed in terms of a current matrix element between the initial and final electron states \( |k_1, k_2, q\rangle \). The detailed calculations of electron states and matrix elements employ a one-dimensional model for the system. The Cu potential is corrugated to yield a band gap of 5 eV at the Brillouin zone boundary, while the potential in the Na layer and the tip are assumed to be constant \( \epsilon \). A tilted square barrier, rounded and lowered by image-potential contributions, separates the electrodes. In addition, the potential in the Na layer is given an imaginary part \(-i\Gamma\), with \( \Gamma = 0.1 \) eV, to mimic the electron scattering processes that limit the lifetime of the quantum well states.

For forbidden light emission through an Auger-like process, the leading contribution to the integrals in Eq. \( \tag{1} \) can be written in terms of a sum of the squares of second-order matrix elements,

\[
\frac{dP}{d\Omega(d\hbar\omega)} = \frac{\omega^2}{16\pi^2\epsilon_0^3\hbar} \sum_{k_1, k_2, q} |M_{k_1, k_2, q}|^2 \\
\times \delta(E_{k_1} + E_{k_2} - E_{1, k_1, q} - E_{1, k_2, q} - \hbar\omega). \tag{2}
\]

\( M_{k_1, k_2, q} \) describes how two electrons in the tip labeled by the momenta \( k_1 \) and \( k_2 \) first interact through a screened Coulomb interaction, \( e^2e^{-\kappa|\vec{r}_1 - \vec{r}_2|}/(4\pi\epsilon_0|\vec{r}_1 - \vec{r}_2|) \) and exchange energy and momentum \( \hbar^2(k_1 + \vec{q})^2/(2m) \). One electron goes into the lower QWS (with in-plane momentum \( k_{1, q} + \vec{q} \)) and energy \( E_{1, k_1, q} = E_1 + \hbar^2(k_{1, q} + \vec{q})^2/(2m) \) and takes no further part in the process, while the other eventually emits a photon in a transition from an intermediate state into the lower QWS (with in-plane momentum \( k_{2, q} - \vec{q} \) and energy \( E_{1, k_2, q} \)). When the two electrons have opposite spin we can write

\[
M_{k_1, k_2, q} = -\frac{ie\hbar}{2m} \int_V d^3r \int_V d^3r_1 \int_V d^3r_2 \\
\times \left\{ \phi^e_{k_2, -q}(\vec{r}) \frac{\partial\phi^f_{k_2, q}}{\partial z}(\vec{r}_2) - \frac{\partial\phi^f_{k_2, -q}}{\partial z}(\vec{r}_2) \right\} \\
\times \phi^e_{k_1 + q}(\vec{r}_1) \frac{e^{2e^{-\kappa|\vec{r}_1 - \vec{r}_2|}}}{4\pi\epsilon_0|\vec{r}_1 - \vec{r}_2|} \psi_{k_2}(\vec{r}_2) \psi_{k_1}(\vec{r}_1), \tag{3}
\]

where \( \phi \) denotes the QWS wave function, while \( \psi \) stands for tip wave functions. The retarded electron Green’s function \( g^r \) describes the propagation of the electron in the intermediate state before photon emission. For energy and momentum conservatism to hold in the photon emission process the energy and in-plane momentum in the intermediate state must be \( E_{1, k_2, q} + \hbar\omega \) and \( k_{2, q} - \vec{q} \), respectively. The electron Green’s function has a resonance when its energy argument coincides with the energy of the upper QWS which explains why, as we will see, the forbidden light emission mainly produces photons with energy \( \hbar\omega = E_2 - E_1 \).

We have also calculated the light emission intensity as a result of hot-hole decay. To this end we studied a semiclassical model based on Ref. \( \tag{22} \) for hot-hole-electron cascade and diffusion (with an elastic mean free path of 2 nm) in the tip, and calculated the influx of secondary hot electrons onto the tip apex. This influx was then used as input in a calculation of the light emission intensity along the line of Ref. \( \tag{19} \).

![Figure 3: "Allowed" and "forbidden" light emission calculated for a model system with QWS at \( E_1 = 0.2 \) eV and \( E_2 = 2.5 \) eV. Results are shown for various currents indicated in the figure and a voltage \( U = 2 \) V. The thickness of the Na overlayer was set to 0.613 nm, corresponding to 2 monolayers.](image-url)

Figure 3 displays results from our model calculations obtained for \( U = 2 \) V and \( J = 10, 100, \) and 300 nA, respectively. The model potential leads to \( E_1 = 0.2 \) eV and \( E_2 = 2.5 \) eV at \( U = 2 \) V. Under these conditions, the upper quantum well state at \( E_2 \) is not accessible. Moreover, the energy \( eU \) of a single electron is not sufficient for exciting the corresponding quantum well transition. As a result, one-electron processes (solid lines in Fig. 3)
give rise to plasmon mediated emission by inelastic tunneling from the tip Fermi level only to the lower QWS. The emission occurs predominantly at $h\nu < eU - E_1$ as expected.

The emission calculated for the Auger-like and hot-hole processes, respectively, are indicated by dashed lines. We do find sizable emission, which is about one order of magnitude stronger for the Auger process than the hot-hole mechanism, peaked at $h\nu \sim 2.3$ eV (thus $h\nu > eU$) due to quantum well transitions. The electron that eventually causes the light emission gains enough energy (i.e. $\approx 0.5$ eV), either through Coulomb interactions with another electron while tunneling, or in the hot-hole-electron cascade in the tip, to be promoted to the upper quantum well resonance situated above the tip Fermi level in energy. We note that the particular electronic structure of Na on Cu(111) with states at well-defined energies is essential in achieving significant signal levels.

The calculations predict quantum yields of up to $10^{-7}$ photons per electron for the Auger-like mechanism at $I=100$ nA and $U=2.3$ V in reasonable agreement with the experimental value. Given the experimental uncertainty of absolute photon intensities, as well as the approximations involved in the calculations, a comparison of its variation with $I$ is more significant. The Auger-like process yields $I^{1.5}$ close to the experimental data. The hot-hole process gives a slightly larger exponent, 1.6. While both mechanisms must be considered as plausible explanations for the forbidden light emission the larger calculated intensities indicate that the Auger process is the dominating one.

In summary, we reported on unusual STM-induced photon emission from a metallic quantum well system at photon energies exceeding the limit $h\nu \leq eU$. Model calculations revealed that owing to the particular electronic structure of Na on Cu(111) two-electron processes can cause quantum well transitions and corresponding fluorescence. Similar effects may be observable in other quantum confined systems.

We acknowledge support by the European Commission (TMR EMIT), the Deutsche Forschungsgemeinschaft and the Swedish Research Council (VR).

[1] J.R. Hahn and W. Ho, Phys. Rev. Lett. 87, 196102 (2001) and references therein.
[2] J. K. Gimzewski, J. K. Sass, R. R. Schlittler, and J. Schott, Europhys. Lett. 8, 435 (1989).
[3] G. Hoffmann, J. Kliwer, and R. Berndt, Phys. Rev. Lett. 87, 176803 (2001) and references therein.
[4] E. T. Foley, A. F. Kam, J.W. Lyding, and Ph. Avouris, Phys. Rev. Lett. 80, 1336 (1998).
[5] S.-A. Lindgren and L. Walldén, Solid State Commun. 34, 671 (1980).
[6] S.-A. Lindgren and L. Walldén, Phys. Rev. Lett. 59, 3003 (1987).
[7] N. Fischer, S. Schuppler, R. Fischer, Th. Fauster, and W. Steimann, Phys. Rev. B 43, 14722 (1991).
[8] R. Dudde, L. S. O. Johansson, and B. Reihl, Phys. Rev. B 44, 1198 (1991).
[9] N. Fischer, S. Schuppler, Th. Fauster, and W. Steimann, Surf. Sci. 314, 89 (1994).
[10] A. Carlsson, B. Hellings, S.-A. Lindgren, and L. Walldén, Phys. Rev. B 56, 1593 (1997).
[11] J. M. Carlsson and B. Hellings, Phys. Rev. B 61, 13973 (2000).
[12] J. Kliwer and R. Berndt, Phys. Rev. B 65, 035412 (2001).
[13] R. Pechou, R. Coratger, F. Ajustron, and J. Beauvillain, Appl. Phys. Lett. 72, 671 (1998) and private communication.
[14] Y. Uehara, T. Fujita, M. Iwami, and S. Ushioda, Sol. State Commun. 116, 539 (2001).
[15] A. Downes, Ph. Dumas, and M.E. Welland, Appl. Phys. Lett. 81, 1252 (2002).
[16] J. Kliwer, Ph.D. thesis, RWTH Aachen, D-52056 Aachen, Germany, 2000.
[17] G. Hoffmann, J. Kröger, and R. Berndt, Rev. Sci. Instrum. 73, 305 (2002).
[18] The binding energies depend on the tunneling parameters $(I, U)$ since the electric field in the tunneling gap causes a Stark shift of the QWS. A change of the tunneling current by two orders of magnitude imposes a shift of $< 5$ meV for $E_1$ and $\sim$ 200 meV for $E_2$ at 0.6 ML. A detailed discussion and model calculation of these shifts will be presented elsewhere (G. Hoffman, R. Berndt, P. Johansson, in preparation).
[19] P. Johansson, G. Hoffmann, and R. Berndt, Phys. Rev. B 66, 245415 (2002).
[20] J. W. Gadzuk and E. W. Plummer, Phys. Rev. Lett. 26, 92 (1971).
[21] S.-A. Lindgren and L. Walldén, Phys. Rev. B 38, 3060 (1988).
[22] The phenomenological screening parameter $\kappa$ is introduced because Coulomb interactions in the vacuum region are screened by image charges induced in the nearby electrodes. We have used the constant value $\kappa = (1$ nm)$^{-1}$ consistent with typical experimental values for the tip-sample separation.
[23] R. H. Ritchie, J. Appl. Phys. 37, 2276 (1966).
[24] This value deviates from the intuitive expectation of an exponent 2 for two-electron processes. A more detailed analysis reveals that the exponent is affected by the effective thickness of the tunneling barrier that an electron has to overcome. This thickness decreases for increasing energy of the tunneling electrons. Consequently, a change of the tip-sample distance leading to a given increase of the total tunneling current is comprised of a weaker current increase of high energy electrons and a larger increase at low energies. As a result, the calculated exponent 1.5 for two-electron processes, i.e. electrons at high energies, is smaller than 2. (This last note was omitted from the published paper for lack of space.)