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A single hydrogen molecule as an intensity chopper in an electrically-driven plasmonic nanocavity

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Abstract

Photon statistics is a powerful tool for characterizing the emission dynamics of nanoscopic systems and their photophysics. Recent advances that combine correlation spectroscopy with scanning tunneling microscopy-induced luminescence (STML) have allowed measuring the emission dynamics from individual molecules and defects demonstrating their nature as single photon emitters. The application of correlation spectroscopy to the analysis of the dynamics of a well-characterized adsorbate system in ultrahigh vacuum remained to be shown. Here we combine single photon time correlations with STML to measure the dynamics of individual H₂ molecules between a gold tip and a Au(111) surface. An adsorbed H₂ molecule performs recurrent excursions below the tip apex. We use the fact that the presence of the H₂ molecule in the junction modifies plasmon emission to study the adsorbate dynamics. Using the H₂ molecule as a chopper for STM-induced optical emission intensity we demonstrate bunching in the plasmonic photon train in a single measurement over six orders of magnitude in the time domain (from μs to s) that takes only a few seconds. Our findings illustrate the power of using photon statistics to measure the diffusion dynamics of adsorbates with STML.

Keywords

STML; Physisorbed hydrogen; Plasmonic antenna; Molecular dynamics; Correlation spectroscopy; Photon bunching

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Author contribution.

P.M., K. Ku, and K.Ke conceived of the experiments. P.M., A.R., C.C.L, C.Gr and A.G. carried out the measurements. C.Go performed the DFT calculations. P.M. analyzed the data and wrote the manuscript. P.M., K.Ku., and K.Ke supervised the project. All authors discussed the results and contributed to the manuscript.

Notes.

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Light permits dynamical studies of nanoscopic systems and has been employed to complement the nanoscale analytical power of scanning probe microscopy.¹ In contrast to electric currents, light can be easily detected at the single quantum limit i.e. at the single photon level.² This property permits one to characterize processes in regimes (e.g. low currents) that are not readily accessible by electronic means.³ Such conditions are often needed in the study of weakly bound atomic-scale systems, like individual molecules, in order to preserve their structural integrity and intrinsic properties during measurements. When a small molecule is adsorbed on a surface, it can exchange energy and momentum with the local environment, making the adsorbate prone to diffusion.⁴ For individual molecules confined on surfaces at cryogenic temperatures, the diffusion dynamics typically occur on the nanometer length scale and on a time scale in the microsecond to second range.⁵ Dynamical processes can be routinely accessed on the nanoscale with scanning tunneling microscopy (STM) but achieving high temporal resolution below the millisecond range of individual adsorbates has remained a challenge because of the limited bandwidth of the necessary current preamplifier.^{6,7} Photon correlations, by contrast, allow emission properties to be probed on the picosecond scale.⁸ Efforts to combine the temporal resolution of correlation spectroscopy with the spatial resolution of STM have been made earlier and while great advances have been obtained in the study of single photon emitters,^{9,10} investigating the diffusion dynamics of well-characterized adsorbate systems with photon correlations has not seen much progress recently.^{11–13}

Here we report on the dynamics of an individual hydrogen molecule (H_2) adsorbed on a crystalline Au(111) surface. Profiting from the tip-induced plasmonic electroluminescence and combining time-resolved photon detection with STML,⁹ we can monitor the motion of H_2 with a time resolution down to a microsecond. Importantly, our experiments require only a few seconds of integration and can be easily extended to other molecular systems on surfaces. The technique is based on the observed change of plasmon emission intensity when a molecule is present in the STM tunnel junction. Inelastic electron tunneling processes excite plasmon nanocavity modes which can be detected as photons in the far field.¹⁴ When H_2 moves into the junction, we observe a jump to higher conductance and a reduction of emission efficiency due to the fact that electrons preferably tunnel through the first empty molecular orbital,^{15,16} which reduces the branching ratio between inelastic and elastic tunneling and results in plasmonic emission being suppressed. Since the increase of conductance is, however, much larger than the reduction of emission efficiency, we observe a significant increase in the total plasmon emission intensity. By calculating the second order correlation function of the photon intensity train, $g^{(2)}(\tau)$, we are able to assess the dynamics of the molecule in the junction. Because the diffusion of adsorbates is a common process in STM studies and many adsorbates modify plasmonic emission intensity, the measurement of plasmon modulation statistics in molecular tunnel junctions can be widely extended to measure the dynamics of adsorbates on metal surfaces. Compared to the well-established method of evaluating telegraphic noise in the tunnel current,^{7,17,18} our technique allows for an efficient analysis of the system time constants over many orders of magnitude using an optoelectronic approach.

In Fig. 1 we present constant current STM images of a Au(111) surface covered with H_2 measured at 4K. Fig. 1a shows a high resolution large scale image of three H_2 /Au(111)

terraces separated by monatomic steps obtained at a bias voltage of +3.23 V applied to the sample. H₂ molecules exhibit a long-range ordered hexagonal superstructure with an average periodicity of ≈ 2 nm, templated by the herringbone reconstruction of Au(111). This intermolecular distance is approximately half the surface state Fermi wavelength ($\lambda_F/2 = 1.9$ nm)¹⁹ suggestive of a surface-state-mediated electronic intermolecular interaction.^{20–22} In Fermi superlattices the adsorbates scatter substrate electrons which generate electronic density oscillations. Charge fluctuations induce an oscillatory potential between adsorbates, with a characteristic periodicity proportional to the electron wave vector at the Fermi energy.²⁰ Such long-range ordered superstructures mediated by surface electrons are known to be low-temperature metastable configurations for a number of small physisorbed adsorbates and have been observed on densely-packed noble metal interfaces bearing surface states.^{20,23} Hydrogen is known to form coverage-dependent superlattices on semiconductors and metal surfaces^{24–29} and condensed hydrogen structures have been reported on Au(111) around surface defects such as single molecules³⁰ or metal clusters.³¹ Here we report the observation of a two-dimensional surface-state-mediated H₂ superlattice on Au(111) for the first time.

Hydrogen adsorbates have earlier been studied by means of scanning tunneling spectroscopy (STS) and inelastic electron tunneling spectroscopy (IETS) and are known to exhibit a characteristic vibrational structure that permits their identification.^{24,25,27,29,30,32,33} The inset in Fig. 2a shows a STS curve obtained on top of a molecular adsorbate with the characteristic double peak around the Fermi level originating from the $\nu = 0 \rightarrow 1$ vibrational mode of H₂ adsorbates while they are trapped between tip and substrate.^{32,33} In our experiments, we rationalize the formation of the surface-state mediated H₂ superlattice by the condensation of a coverage-dependent network of H₂ appearing in the presence of residual hydrogen in the cryogenic vacuum of our low temperature STM. Assuming that each protrusion corresponds to a single molecule, the molecular coverage is 2% with respect to the reconstructed Au(111) surface atom density.³⁴ However, the value may vary since H₂/Au(111) is an extremely bias-dependent system and scanning at the required higher voltages can stimulate partial H₂ desorption.

To gain further insights into the nanocavity geometry and electronic structure we have performed DFT simulations of the complete STM tip - H₂ - Au(111) system with tip-surface distances of 5 Å and 7 Å (see S.I. for further details).³⁵ Such separations are characteristic for the tunnel regime in STM. We find that in the relaxed structure of the system a H₂ molecule is vertically aligned between tip and sample. The molecule is tensile-stretched which produces a weakened H-H bond. The H atom closest to the tip has a tendency to be below the apex due to the higher reactivity of the last protruding Au atom of the tip. The H atom closest to the sample is located in an atop position of the Au surface. To theoretically explore the dynamical processes, we have performed *ab initio* molecular dynamics (AIMD) calculations and simulated the energy input from tunneling electrons. After an energy of ~ 3 eV is equally distributed between the atoms of the relaxed unit cell, the system is allowed to evolve following the quantum mechanically induced force fields and resulting motions. Under these conditions we find that the H₂ molecule oscillates between two configurations, one where the H₂ is vertically aligned and the other where the molecule is submitted to a high degree of strain. During its vibrations, the molecule performs excursions outside and

inside the tunnel junction, (see S.I) which is made apparent by the bistable emission condition observed in the experiments, as we will discuss in more detail below.

Next we address the spatially-resolved STM-induced luminescence (STML). A lens collects the light from the tunnel junction and guides it to a single photon avalanche photodiode (SPAD) which enables measuring the STML intensity while raster scanning the tip over the surface. Fig. 1c and 1d show luminescence maps measured simultaneously with the constant current topographies presented in Fig. 1a and 1b, respectively. The color scales represent the spectrally integrated photon intensity. Comparing topographic STM images with photon maps leads us to the observation that light efficiency decreases at the positions where H₂ molecules are present. Height maxima coincide with minima in the photon maps (Fig. 1e). Moreover, clean Au(111) regions correlate with higher photon efficiencies; at the bottom left of Fig. 1b one molecule is missing in the topographic map which results in the extraordinarily high experimental quantum efficiency (detected photons per tunneling electron) on that region in Fig. 1d.

To understand the origin of the quantum efficiency decrease on top of the molecule we study the electronic structure and the charge transport mechanisms of the H₂/Au(111) system with experiments and *ab-initio* calculations. Let us first consider a metallic tunnel junction formed between a metal tip and a Au(111) surface without H₂ adsorbates. The schematic energy diagram of such a “clean” tunnel junction is presented in Fig. 2b. When a positive bias is applied to the sample, it results in the tunneling of electrons from the tip to the sample. At a bias of +3 V, inelastic electron processes excite tip-sample nanocavity plasmon modes with a quantum efficiency up to 1.5×10^{-4} photons/electron^{1,14} (Fig. 1 c,d). Due to the large number of initial and final states available for inelastic tunneling (marked with red arrows in Fig 2b) a broad emission spectrum of around 100 nm width is typically observed (see S.I.). Broadband plasmonic spectra are characteristic of the electroluminescence of coinage-metal tunnel junctions, even in the presence of molecular adsorbates.^{1,36}

When H₂ is present in the junction, its molecular orbitals modify the tunneling matrix elements of charge carriers and reduce the probability for the inelastic tunneling events that are responsible for plasmon emission. In Fig. 2a we present the dI/dU spectrum measured on a H₂ adsorbate on Au(111) with a clean metallic tip. Since dI/dU is proportional to the local density of states (LDOS), Fig. 2a reflects the electronic structure of the H₂/Au(111) system. The strong feature at +3.3V corresponds to the lowest unoccupied molecular orbital (LUMO) of the adsorbed species and may be related to the antibonding $1\sigma^*$ state of H₂. We calculated the LDOS of a H₂ molecule adsorbed on a Au(111) surface within the density functional theory (DFT) framework and found the presence of an antibonding molecular state at an energy of +2.58 V, in reasonable agreement with the experimental observation (see S.I). The molecular orbital-derived state at +3.3V is associated with two important facts: the observation of H₂ in the tunnel junction and the simultaneous reduction of STML quantum efficiency. The lack of molecular states at negative voltages hinders tunneling to the molecule in this voltage range, which explains the apparent absence of H₂ under these tunneling conditions (see S.I.). Once the tunnel voltage reaches the molecular state at +3.3V, the probability for elastic tunneling processes is increased at the expense of the inelastic processes involving plasmon generation.¹⁵ Hence, the resonant tunneling of electrons from

the tip to the +3.3 eV state of the molecule results in a decrease of the rate of inelastic tunneling events and in an effective reduction of plasmon emission efficiency as is observed in the constant current photon maps.

Concurrent with modification of plasmonic emission in the nanocavity, the H₂ molecule gets transiently charged and its molecular vibrational and translational modes become excited.^{32,33,37} The negative differential resistance feature observed around 3.5 eV is a clear indication that energy dissipation channels are opened when tunneling into the antibonding 1σ* state. Energy loss by excitation of translational modes of H₂ can lead to molecular diffusion across the Au(111) surface.³⁸ As a consequence of a migration process the tip-sample junction may become emptied of H₂. However, the surface-state mediated potential between adsorbates will drive the molecule back below the tip to its minimum energy position within the Fermi lattice. The schematic in Fig. 3 shows a cartoon of the dynamical processes occurring in the tip - H₂ - Au(111) junction during the single photon time correlation experiments. The presence of the molecule modifies the elastic and inelastic branching ratios and results in a lower plasmon efficiency. However, the increase in tunnel current at open feedback (i.e. constant height) conditions overcompensates this reduction and results in a net increase of the observed plasmonic intensity (see S.I.). The molecule in the junction will eventually get charged and performs a migration process leaving the tunnel junction. When the tunnel junction is clean of H₂ adsorbates it will produce low plasmon emission intensity at a fixed tip – Au(111) distance. When the molecule returns to its position below the tip apex the junction becomes bright again. The two alternating states result in periods of low and high photon count rates. Therefore, the resulting light intensity trace will exhibit photon bunches interrupted by time intervals that correspond to the time when the H₂ molecule is out of the tip-sample junction.

A means for analyzing the relative time delay between photons in a stream is the normalized second order correlation function of the light intensity $I(t)$:

$$g^{(2)}(\tau) = \frac{\langle I(t)I(t+\tau) \rangle}{\langle I(t) \rangle \langle I(t+\tau) \rangle} \quad [1]$$

$g^{(2)}(\tau)$ expresses the probability that two photons are detected with a time difference τ and is proportional to the number of all photon pairs observed with time τ between them. We use $g^{(2)}(\tau)$ to analyze the STM-induced luminescence of the H₂/Au(111) system and assess the dynamics of the excursions of the H₂ molecule in the junction. For this aim we connect one SPAD to a time-correlated single photon counting (TCSPC) module and record the arrival time of every detected photon.³⁹ We calculate $g^{(2)}(\tau)$ and access time constants down to the low microsecond range. The timescale of our set-up is limited of the electronic detector afterpulsing which generates artifacts at times $< 1 \mu\text{s}$.³⁹

In Fig. 4c we present the $g^{(2)}(\tau)$ function obtained on a Au(111) region without H₂. $g^{(2)}(\tau)$ is exactly unity over more than five orders of magnitude in the time domain. This is an important reference measurement since mechanical noise in the experimental set-up or tip instabilities, even when small, will become obvious in spurious photon bunching features.

Moreover, all $g^{(2)}(\tau)$ measurements were performed in constant height mode, to avoid the possible damping artifacts which can be introduced by the feedback loop. In comparison, the $g^{(2)}(\tau)$ function measured over a H_2 molecule at the same tunneling conditions (Fig. 4d) demonstrates notable bunching reflected by a $g^{(2)}(0) = 1.4$. The bunching can also be qualitatively visualized in the intensity traces. In Fig. 4a and 4b we present the first 25 ms of the intensity traces evaluated in Fig. 4c and 4d, respectively. In the traces, each detected photon is represented by a vertical line at its arrival time. When a H_2 molecule moves in and out of the junction it strongly modulates the light emission (see for example a blank space around $\tau = 10$ ms in Fig. 4b). In contrast, the photon stream emitted from the empty Au(111) junction is more regular and shows a Poissonian photon distribution (Fig. 4a). By fitting $g^{(2)}(\tau)$ in Fig. 4d (see blue dashed line) with one exponential function we can determine the characteristic time constant related to the dynamics of the molecule. Deviations from unity, indicate that photons within the stream are not emitted independently of each other but are related by some photophysical mechanism. Note that the time axis in Fig. 4d is logarithmic and an exponential function thus appears as a smooth step between two values with the step extending over two orders of magnitude on the time scale. We find the dominating transition with a time constant T_1 in the millisecond range with a value of 2.37 ms.

To quantify the dynamics in more detail we use a time-dependent model permitting us to estimate the periods when the molecule stays below the tip with enhanced emission and the excursion periods with low photon intensity. We employ a two level rate model where the system is always in one of the two states, either in the bright state (molecule inside the junction) or in the dark state (molecule outside the junction). For simplicity we further assume that light emission in the latter state is negligible. We define the rate constants k_{OUT} and k_{IN} , accounting for the molecule to change from the bright to the dark state and from the dark to the bright state, respectively. The rates are the inverses of the average residence times of the molecule outside (T_{DARK}) and inside (T_{BRIGHT}) the junction. The analytical solution yields:

$$g^{(2)}(\tau) = 1 + \frac{k_{OUT}}{k_{IN}} e^{-(k_{IN} + k_{OUT})\tau} \quad [2]$$

where:

$$k_{OUT} = \frac{1}{T_{BRIGHT}} \quad ; \quad k_{IN} = \frac{1}{T_{DARK}} \quad [3]$$

Therefore:

$$g^{(2)}(0) = 1 + \frac{k_{OUT}}{k_{IN}} \quad [4]$$

$$T_1 = \frac{1}{k_{IN} + k_{OUT}} = \frac{T_{DARK} T_{BRIGHT}}{T_{DARK} + T_{BRIGHT}} \quad [5]$$

Fitting the experimental $g^{(2)}(\tau)$ in Fig. 4d to the single exponential from equation [2] we obtain the values $k_{OUT} = 99 \pm 7 \text{ s}^{-1}$ and $k_{IN} = 318 \pm 25 \text{ s}^{-1}$, which correspond to an average residence time for the molecule inside and outside the junction of $T_{BRIGHT} = 10.1 \text{ ms}$ and $T_{DARK} = 3.1 \text{ ms}$, respectively.

Minor deviations from this model are accounted for by extending the fitting function to a total of three exponentials. We then find two more time constants, T_2 and T_3 , which are in the microsecond ($31 \text{ }\mu\text{s}$) and millisecond range (87 ms), accounting for 11% and 9% of the bunching, respectively (see S.I). The physical origin of T_2 and T_3 is not clear at the present stage. These time constants may pertain to alternative processes which modify the light emission to a minor degree, e.g. molecular vibration, rotation or dissociation [33,37,40] and may be the subject of future investigations.

In summary, we combine STM and single photon time correlation spectroscopy for studying the dynamics of H_2 molecules on a gold surface using plasmon intensity modulations by individual adsorbate molecules. Measuring the arrival time of photons in light emission streams permits obtaining the characteristic time constants of adsorbates on noble metals in relatively short measurements. Theoretical calculations confirm that H_2 molecules have a strong tendency to stay below the tip apex and perform short excursions upon energy dissipation thus corroborating the experimental observation. Since most organic molecules adsorbed on coinage metal surfaces modify the emission from nanocavity plasmon modes we expect a wide range of dynamical systems to be good candidates for characterization via photon correlations. Dependence of the dynamics on stimuli such as current, electric field or external light sources will open new research directions in molecular nanophotonics. The present study explores the dynamics down to the microsecond scale; the use of two detector Hanbury-Brown Twiss interferometry will permit accessing dynamic time constants down to the low ps range and, in combination with standard electronic telegraphic noise measurements, may open new insights into quantum plasmonics.⁸

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

a. Constant current topography STM image of H₂ on Au(111). Every white protrusion can be ascribed to a single H₂ molecule. The H₂ molecules are weakly physisorbed and form a surface-state mediated superlattice. $50 \times 31 \text{ nm}^2$, $U = +3.23 \text{ V}$, $I = 120 \text{ pA}$. **b.** STM high resolution image of the H₂/Au(111) surface. $15 \times 15 \text{ nm}^2$, $U = +2.76 \text{ V}$, $I = 40 \text{ pA}$. **c. d.** Luminescence efficiency maps recorded simultaneously with the constant current topography images in panels a and b, respectively. The color scale bar in the insets represent the spectrally integrated experimental quantum efficiency (in detected photons per tunneling

electron). e. Topography and photon intensity profiles obtained along the dashed lines in images b and d. The weakest light intensity is detected at the position where the H₂ molecules are located with the highest probability.

Figure 2.

a. Scanning tunneling spectroscopy of a H_2 molecule on Au(111). The state located at +3.3V corresponds to the LUMO of the H_2 molecules. The inset shows the characteristic double-lobed zero-bias spectrum of H_2 around the Fermi level. **b.** Energy diagram representing a "clean" tunnel junction without adsorbate. The electron paths are represented by red arrows, while the plasmonic emission is symbolized by a multicolor wave. **c.** Energy diagram with a H_2 molecule in the tunnel junction between tip and sample. The molecular electronic state enhances resonant tunneling of electrons from the tip to the molecule. The molecule remains

transiently charged before the electron finally tunnels to the substrate. This resonant tunnel process suppresses the plasmonic emission efficiency shown in b.

Figure 3.

Schematics of the experiment; the H_2 performs excursions in the tip-sample nanocavity. The sequence shows a tunnel junction with a H_2 adsorbate (marked Molecule IN) that emits photons with high intensity. The H_2 molecule performs an excursion below the tip (marked Molecule OUT). During the time that the H_2 molecule resides below the tip apex the inelastic channel responsible for plasmon excitation is less efficient and resonant tunneling to the LUMO of the molecules is enhanced. However due to the strong increase in the number of tunneling electrons, the total plasmon intensity increases. During the course of transient charging and discharging of the molecule, vibrational and translational modes of the adsorbate get excited permitting the molecule to perform excursions, which again modifies the plasmon intensity.

Figure 4.

a. 25 ms sample of a photon train measured on a clean Au(111) region with no H₂ adsorbates present. The arrival time of each photon is marked by a vertical line. Panel **c** below shows the evaluation of the full train. **b.** 25 ms section of a photon train recorded on H₂/Au(111). Panel **d** below shows the evaluation of the full train. **c.** Second order autocorrelation function, $g^{(2)}(\tau)$, calculated from a photon train on a clean Au(111) surface recorded at $U_{\text{bias}} = +3$ V, current set point $I = 250$ pA. During data acquisition the constant-current feedback was disabled. Within the measuring time of 8.1 s a total of 392367 photons were detected in the train. The line indicates the value 1 which is expected for emission following Poissonian statistics. **d.** Second order autocorrelation function, $g^{(2)}(\tau)$, calculated from a photon train on H₂/Au(111), recorded with the same STM settings as the data in **c**. Within the measuring time of 35.7 s a total of 338875 photons were detected in the train. The dashed curve is a best fit using eq. [2] describing the pronounced bunching of the light emission.