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Effect of a dielectric spacer on electronic and electromagnetic interactions at play in molecular exciton decay at surfaces and in plasmonic gaps

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Abstract

The deposition of individual molecules, molecular networks, and molecular layers at surfaces is at the core of the surface reactivity, energy harvesting, molecular electronics, and (single) photon sources. Yet, strong adsorbate-substrate interaction on metallic surfaces quenches the excited molecular states and harms many practical applications. Here, we theoretically address the role of NaCl ionic crystal spacer layer in decoupling an adsorbate from the substrate, and therefore changing the interplay between the competing decay channels of an excited molecule driven by electronic and electromagnetic interactions. A quantitative assessment of the corresponding decay rates allows us to establish the minimum thickness of the spacer required for the observation of molecular luminescence from the junction of the scanning tunneling microscope. Our work provides a solid quantitative theoretical basis relevant for several fields of nanotechnology where engineering of ionic crystal spacers allows for adsorbate charge manipulation, reactivity, and photon emission in nanocavities.

Keywords

electroluminescence, plasmon, excited state, scanning tunneling microscope, nanoantenna, resonant electron transfer

Introduction

The evolution of electronically excited states of molecules adsorbed at metallic surfaces is often at the core of key physical and chemical processes in energy harvesting,¹⁻³ surface reactivity,⁴⁻⁶ and molecular (opto-) electronics.⁷⁻⁹ The interest to the excited state dynamics is further fueled by the current developments of techniques such as scanning tunneling microscopy (STM), capable to trigger and to monitor the surface reactions at the atomic scale,¹⁰⁻¹⁴ as well as to produce the photo- and electro-luminescence from adsorbed molecules

with possibility to engineer the nanosources of (single) photons.¹⁵⁻¹⁸ To understand the dynamics of molecular excited states in the proximity of a metallic surface, and to find ways to control their decay into different de-excitation channels is this of paramount importance in molecular nanotechnologies.

Atomic and molecular adsorbates on metal surfaces represent canonical examples of a discrete state-continuum interaction¹⁹ where the electronic orbitals localized at the adsorbate hybridise with the continuum of electronic states of the substrate. This leads to extremely short, at the femtosecond (fs) scale, lifetimes of the adsorbate-localised states.²⁰⁻²² The excited electron promptly escapes from the adsorbate into the unoccupied electronic states of the metal valence band via energy-conserving resonant electron transfer (RET).^{3,5,6,20,21,23,24} Similarly, the excited state can be quenched by RET from the occupied electronic states of the metal into the adsorbate.²⁵⁻²⁸

The short lifetime of an excited state localized on an adsorbed molecule represents a bottleneck for many processes requiring energy transfer from the electronic excitation to nuclear motion (surface reactivity), or to the electromagnetic field with photon or plasmon emission.^{6,29-32} This problem can be solved by locating organic overlayers, ionic crystal or oxide films, as well as 2D materials (hBN)^{32,33} as spacers between adsorbate and substrate in order to electronically decouple both, thus preventing the RET process. This approach is thoroughly used in studies of individual molecules by local probes, allowing e.g. to obtain atomically-resolved maps of electronic orbitals of neutral and charged species,³⁴⁻⁴³ and of the energy transfer from tunneling electrons to atomic motion.^{12-14,44,45} Blocking the RET renders an excited state lifetime long enough to probe redox reactions,⁴⁶ and to observe the light emission from excited molecules and associated vibrational signatures in the luminescence spectra.⁴⁷⁻⁵⁰ In this context, an extreme electromagnetic field localization by atomic scale protrusions at a STM tip is behind the spectacular advances in atomic-scale resolution of single-molecule luminescence in plasmonic STM junctions,^{14,28,49,51-55} and in atomic-scale control of electromagnetic interactions between individual molecules.⁵⁶⁻⁵⁸

Despite these spectacular advances, the broad empirical use, and the extensive experimental and theoretical studies of excited states localised on metal-organic interfaces,^{3,59–61} the quantitative characterization of the decoupling role of the spacer layer is still not achieved for individual molecular adsorbates. In this work we quantitatively address the effect of the ionic crystal (NaCl) spacer layer between an adsorbed molecule and a metal substrate on the interplay between the different decay channels of the molecular exciton. To this end we apply a quantum mechanical description of the RET between the excited molecular orbital and the substrate owing to the electronic coupling, and a classical description of the radiative and nonradiative decay of the molecular exciton due to electromagnetic interactions. The quantitative results and robust trends obtained in this work provide a theoretical basis for using spacer layers as a tool to engineer dynamics of excited states in molecular adsorbates as well as photon emission from individual molecules.

Excited state decay

Depending on the energies of the initial and final states of the reaction, and on the position of the Fermi level of the substrate, the RET between adsorbed molecules and metal substrates might involve various steps and intermediate states. This is particularly the case for the molecules located within the junction of a STM, where an applied bias can be used to control the electron transfer channels^{28,40} as we illustrated in the Supporting Information (SI). The purpose of the present work is to provide a robust and generalizable order-of-magnitude comparison between the efficiencies of the leading decay channels of the excited electronic states localized on adsorbed molecules. In particular, we focus our study on the RET as well as on the non-radiative and radiative deexcitation owing to the electromagnetic interactions discussed below, and on their evolution with the thickness of the ionic crystal layer introduced between the molecule and the substrate. To this end, we choose a representative system with an energy level alignment shown in Fig. 1a as considered in numerous experimental and

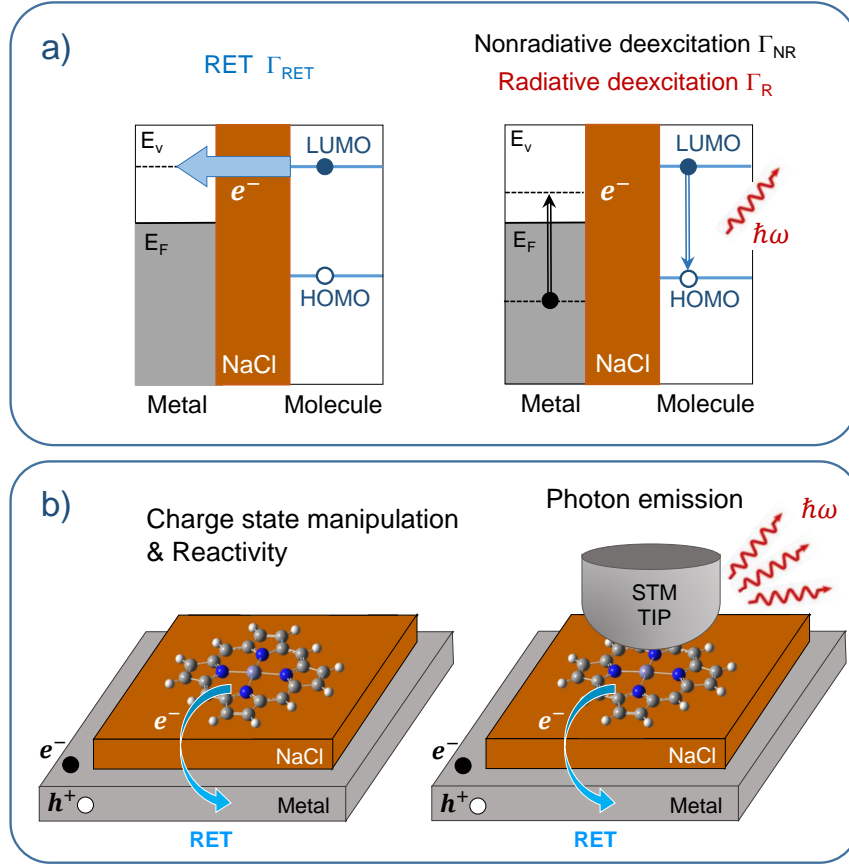


Figure 1: **a**: Energy diagram of the electronic states of an excited molecular adsorbate and of a metal substrate, and schematic representation of the processes leading to the excited state decay. E_v and E_F stands for the vacuum and Fermi energy levels, respectively. An excited electron occupies the π^* LUMO orbital of the molecule and corresponding hole is left in the HOMO orbital. **a, left**: The RET (rate Γ_{RET}). An excited electron tunnels through a NaCl spacer into the empty states of the metal valence band at energy resonance with LUMO and above E_F . **a, right**: The intra-molecular de-excitation given by the LUMO \rightarrow HOMO transition. The excess energy is transferred to an emitted photon (radiative transition, rate Γ_{R}) or to electronic excitations of the substrate, as exemplified with an electron-hole pair creation (nonradiative transition, rate Γ_{NR}). **b**: Adsorption systems and relevant processes. **b, left**: For the molecule (here Zn-porphyrin) deposited on the NaCl/Metal substrate the RET and the nonradiative de-excitation (schematized as electron-hole pair creation, e^- , h^+) are decisive for the charge-state manipulation and surface reactivity. The radiative de-excitation rate is small in this case. **b, right**: A plasmonic gap configuration of the STM junction greatly enhances the quantum efficiency for photon emission into the far field.

theoretical works.^{3,10,32,50,53,56,62–66}

The energy diagram shown in Fig. 1a corresponds to adsorbate/substrate configurations with energies $E_{\text{Mol}^+} - E_{\text{Mol}^0} > \Phi$, and $E_{\text{Mol}^+} - E_{\text{Mol}^*} < \Phi$, where Φ is the work function of the

metal, E_{Mol^0} (E_{Mol^*}) is the energy of the system where the ground state (excited) molecule is adsorbed at the surface, and E_{Mol^+} is the energy of the positive molecular ion adsorbed at the surface with an electron at the vacuum level. Within the one active electron approximation, the electronic structure of the molecular ion (excited molecule) is represented by the electron removal from the HOMO (HOMO \rightarrow LUMO transition). By using the total energies referred to E_{Mol^+} , one arrives to the sketch of the energy levels and processes relevant to the decay of electronically excited states localised on molecules adsorbed on metal surfaces as that shown in Fig. 1a.

The electronic coupling between molecular adsorbate and the substrate leads to the possibility of electron tunneling through the NaCl spacer. An electron initially located at the adsorbate-localised excited orbital escapes into the empty metal continuum states above the Fermi level.^{3,5,6,19,20} This RET process of *electron loss* by the adsorbate is characterized by a transfer rate Γ_{RET} and it leads to a change of the charge state of the adsorbate $M^q \rightarrow M^{q+1}$, where $q = 0, \pm 1, \dots$. Note also that in a situation where the total energy balance of the system sets the energy of molecular orbital involved in the RET below the Fermi level of the substrate, the RET process of *electron capture* from the substrate can be considered. Within the picture of the single active electron, if only the Fermi energy is changed for the same binding energy of the molecular orbital, the electron capture process will be characterized by the same discrete state/continuum couplings as the electron loss. Aside from the spin statistical factors,⁶⁷ the electron capture and loss rates will be the same so that our results and conclusions for the effect of the NaCl layer also apply to the quenching of the excited state via electron capture from the substrate illustrated in Supporting Information (SI).

Along with RET, the decay of the excited state can also involve the intra-molecular de-excitation via an *excited-state* \rightarrow *ground-state* transition with photon emission (radiative decay, rate Γ_{R}) or with non-radiative excitation transfer to the substrate also identified as ohmic losses (non-radiative de-excitation, rate Γ_{NR}).^{3,32,68-73} A quantum treatment incorporating the nonlocality of the metal response^{68,69,74-76} can be more adequate to describe these

processes when the molecule is adsorbed directly at the metal surface. However, the presence of the spacer layer between the emitter and metal surface reduces the effect of nonlocality and allows us to use classical local electrodynamics to properly estimate these two decay channels, as determined by the electromagnetic interactions between the adsorbate and the substrate.^{69,71,76}

We neglect here Penning-type deexcitation process^{27,77} involving an electron transfer between the substrate and adsorbate. Being two-electron in nature, it is essentially slower than the one-electron RET.

The interplay between the RET and the de-excitation determines the charge manipulation, the reactivity and the luminescence of individual molecules on metal substrates (see Fig. 1b). In the latter case, the use of a plasmonic gap configuration, as naturally formed in a STM junction, is of particular importance. The plasmonic gap shows an intense antenna effect which overrides the well known quenching of quantum emitters located at nanometric distances from the metal surface,^{71,72,78,79} and allows for the far field emission.⁸⁰ We emphasize that in the configuration of photoluminescence studies⁵⁴ adopted here, the unbiased STM tip is considered as a nanoantenna which only affects the electromagnetic interactions and rates. The opening/closing of the excited state decay channels owing to an applied bias is discussed in SI, but its effect on the RET is beyond the scope of the present work. Similarly, we assume a regime in which the RET between the tip and the molecule can be neglected.

Electronic coupling and RET

In the absence of a spacer, the RET typically proceeds at fs time-scales.^{21,22,81} It is orders of magnitude faster than the radiative and nonradiative intra-molecular de-excitation, and the luminescence is quenched even for the most optimal plasmonic gap configuration in a STM setup^{16,53} (see below). We thus first address the reduction of the RET by the ionic crystal

NaCl spacer layer, as this is a necessary condition for the other processes to be operative.

To reveal the robust underlying physics, independent of the specific adsorbate/substrate combination, we selected several representative systems. As adsorbates we consider the nitroethylene ($C_2H_3NO_2$) and Zn-porphyrin (ZnPP) molecules, and the metal substrate is represented by a Cu(100) surface as well as by a free-electron jellium metal surface. The $C_2H_3NO_2$ and ZnPP molecules (see Fig. 2), allow for sampling the adsorbates with different wave functions of the excited orbital while keeping its LUMO π^* character, typical of fluorophores in experimental studies of light emission. Along the same lines, the electronic structure of the Cu(100) surface is characterized by the projected band gap, typical of noble metals,^{20,82} while the jellium metal⁸³ is the simplest substrate with free-electron dispersion of the valence band states. Because of hybridization with the metal, the excited π^* orbital becomes quasistationary, i.e. its electronic population decays in time. It appears as resonance in the electronic density of states, with a resonance width given by the rate of the π^* population decay via irreversible RET into the continuum of empty electronic states of the substrate^{19,20} (see Fig. 1).

To trace the dynamics of the RET we apply a wave packet propagation approach (WPP).^{20,21} The method allows for a complete characterization of the molecule-localized π^* resonance, including its energy, wave function, and RET rate. In brief, one explicitly solves the time-dependent Schrödinger equation for the electron active in the transitions between the molecule and the substrate. The electron wave function is represented on a 3D spatial mesh and the effective one-electron potential of the system is obtained on the basis of the *ab initio* description of the adsorbed molecule and the model representation of the metal surface and of the NaCl layer. The details on the WPP can be found in Ref.²¹ and in SI.

The *ab initio* calculations of the excited states of the adsorbed molecule represent a real theoretical challenge.^{23,84,85} We then apply a strategy based on the similarity between the molecular anion neutralization and the decay of an excited molecule. Indeed, both processes involve the RET from the LUMO π^* orbital into the substrate. Thus, within the

one electron picture, both processes imply the same coupling matrix elements between the molecule-localized discrete state (π^*) and the continuum of the propagating electronic states of the metal substrate. Albeit these couplings must be taken at different energies. We then (i) calculate the π^* electron loss rate for the nitroethylene ($\text{C}_2\text{H}_3\text{NO}_2$) and Zn-porphyrin (ZnPP) molecular anions, and (ii) generalize the WPP results obtained for the molecular anions to the electron loss by the excited molecule. Obviously, the energy of the system where the molecular anion is located in front of the surface, E_{Mol^-} , has to be referred to the E_{Mol^0} configuration, which would define the energy position of the LUMO orbital in the schematics of Fig. 1. The HOMO orbital remains double occupied during the reaction.

The WPP results summarized in Fig. 2 reveal an extremely strong effect of the NaCl spacer layer on the RET. The bound state-continuum electronic coupling leads to the existence of two regions of space featuring distinctly different character of the electron density $n(\vec{r})$, associated with the decaying π^* resonance of the ZnPP molecule adsorbed on the NaCl/Cu(100) surface (Fig. 2a). The electron density around the adsorbed molecule lying nearly flat at the surface⁸⁷⁻⁹⁰ (see SI for calculations of the adsorption geometry) reflects the LUMO π^* orbital. The RET appears as an outgoing electron flux inside the Cu substrate, where the oscillating structure reflect the successive atomic planes of Cu(100). The energy E_{π^*} of the π^* resonance with respect to the Fermi level of the metal is 1.79 eV for 1ML NaCl, 1.93 eV for 2ML NaCl, and 2.11 eV for 3ML NaCl as obtained with WPP. Here, the energy change with increasing molecule-surface distance reflects the image potential interaction between the molecular anion and the metal surface. The π^* resonance is thus inside the projected band gap of Cu(100), located between 1.6 eV and 7.7 eV.⁸² In such a situation, the RET along the surface normal is not possible (white region in the metal below the molecule), and the electron escapes from the molecule at finite angle with respect to the z -axis.^{20,21,91} Note that the symmetry of the ZnPP molecule also imposes the nodal structure of the wave function along the $(x = 0, z)$ -axis. However, this symmetry effect is specific to ZnPP. This is while the effect of the projected band gap on the shape of the outgoing electron flux results

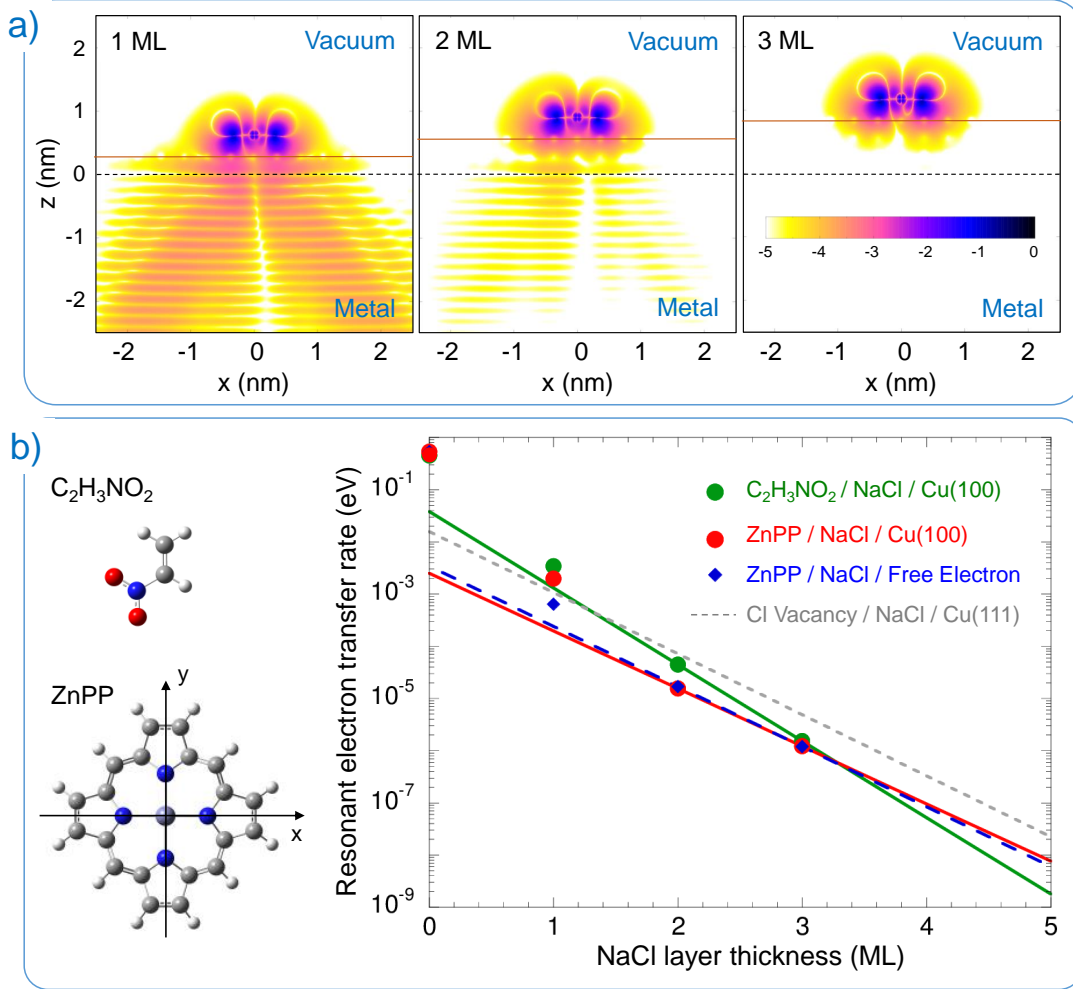


Figure 2: Analysis of the RET between the ZnPP molecule and Cu(100) surface coated with NaCl film. **a**: Logarithm of the electron density $\log_{10}[n(\vec{r})]$ of the wave function associated with the quasistationary π^* orbital. Results are shown in the (x, z) plane perpendicular to the surface plane. The horizontal brown line defines the topmost atomic layer of the NaCl crystal, and the dashed black line defines the position of the surface layer of Cu atoms set as the $(x, y, z = 0)$ -plane. The density maps are shown for the 1 ML, 2 ML, and 3 ML thickness of the NaCl film as indicated (1ML= 2.8\AA). The color code is explained in the insert. **b-left**: Sketch of the atomic structure of the $C_2H_3NO_2$ and ZnPP molecules. The atoms are represented as colored spheres: C (grey), O (red), N (blue), and H (white). **b-right**: Analysis of the dependence of the RET rate, Γ_{RET} , on the thickness of the NaCl spacer layer measured in monolayers, ML. Symbols: WPP results as explained in the insert. Lines of the corresponding color: extrapolation of the WPP data obtained by fitting the WPP results for the 2 ML and 3 ML films by $\Gamma_{RET} \propto e^{-\gamma N_{ML}}$ dependence. $\gamma = 3.38 \text{ ML}^{-1}$ (green), 2.5 ML^{-1} (red), and 2.67 ML^{-1} (blue). The dashed grey line shows the Γ_{RET} dependence on the NaCl coverage as deduced from the experimental STM data in Ref.⁸⁶ For further details see the text.

from the substrate electronic structure, and thus it is robust and adsorbate independent. This is further confirmed with the example of the $\text{C}_2\text{H}_3\text{NO}_2$ anion considered in SI (see Fig. 7 of SI).

When the thickness of the NaCl film increases, the weight of the continuum part of the wave function promptly decreases. For 3ML of NaCl, the outgoing electron flux inside the metal is not visible at the scale of the figure indicating that the RET rate, Γ_{RET} , is dramatically reduced by the tunneling barrier created by the ionic crystal spacer. The quantitative assessment of this effect is performed in Fig. 2b by plotting the dependence of the RET rate, Γ_{RET} , on the thickness of the NaCl spacer. Similar results are obtained for the molecule/substrate systems characterized by very different atomistic and electronic structure. Thus, for the molecules adsorbed on a metal surface, the fast RET with $\Gamma_{\text{RET}} \simeq 0.5$ eV corresponds to a very short lifetime of the electron population of the π^* orbital $\tau = 1/\Gamma_{\text{RET}} \simeq 1$ fs typical for such systems.^{21,22,81} According to our calculation, the monolayer (1ML) of NaCl introduced between the molecule and the metal reduces the Γ_{RET} by nearly two orders of magnitude. Considering that the band gap of NaCl (and thus its effect on RET) is fully developed for the film thickness ≥ 2 ML,⁹²⁻⁹⁴ we fit the WPP results for the 2ML and 3ML coverage with an exponential dependence $\Gamma_{\text{RET}} \propto e^{-\gamma N_{\text{ML}}}$. Here N_{ML} is the NaCl film thickness measured in number of monolayers. We then obtain quite similar γ within the range $\gamma \simeq 2.5 - 3.38$ ML⁻¹ (see Fig. 2b) for the different adsorbate/substrate combinations used in our study. Noteworthy, $\gamma = 2.7$ ML⁻¹, i.e. within the same range, has been reported in the STM study of the lifetimes of the Cl^- vacancy states in the external layer of much thicker NaCl films.^{86,95} Here, as a spacer we consider the defect free NaCl between the metal and the topmost NaCl layer with Cl^- vacancy defect.

This existence of a nearly universal $\Gamma_{\text{RET}}(N_{\text{ML}})$ dependence points out at a robust underlying physics: (i) the strong hybridization between the adsorbate-localized and substrate electronic states, and thus fast RET in the case of direct adsorption on the metal surface; and (ii) the dramatic reduction of the Γ_{RET} by an effective tunneling barrier introduced by

the NaCl film owing to the large band gap of the ionic crystal (9 eV).⁹⁶⁻⁹⁸ Here, because of the midgap alignment with the Fermi level of the metal,⁹⁹ and the 0.5 – 1 eV reduction of the work function by the ionic crystal film,^{87,100,101} the π^* resonance of the fluorophores is typically well below the onset on the NaCl conduction band^{53,66,87,89} (see Fig. 1). According to the semi-classical tunneling theory,^{102,103} the transmission of the tunneling barrier created by the NaCl spacer should be then similar for these adsorbates. It can be expressed as $e^{-\gamma N_{ML}}$, where $\mathcal{T} = e^{-\gamma}$ is the transmission factor of the tunneling barrier formed by 1ML of NaCl. For the vacuum barrier between the molecule and the substrate one would expect

$$\gamma_v = 2h_{NaCl}\sqrt{2(E_v - E_{\pi^*})/27.211}, \quad (1)$$

resulting in $\gamma_v = 3.63 \text{ ML}^{-1}$. In Eq. 1 the thickness of the NaCl layer is $h_{NaCl} = 5.3 a_0$ ^{86,104-106} (a_0 is the Bohr radius), and the energy of the vacuum level with respect to the Fermi level of the substrate $E_v = 3.6 \text{ eV}$ (here we took into account that the work function of Cu(100) $\Phi = 4.6 \text{ eV}$ ⁸² is reduced by 1 eV by NaCl film^{87,106}). The decoupling efficiency of the NaCl layer calculated in our work is given by $\gamma \simeq 2.5 - 3.38 \text{ ML}^{-1}$. It is thus very similar to that of the vacuum barrier.

Since the reduction of the RET rate is mainly a property of the NaCl spacer, our results can be generalized to many practical situations. In particular, when considering the RET between the molecular orbital and the substrate (both electron capture and electron loss processes, depending on the energy level alignment and the work function), the effect of the spacer layer on the RET rate can be estimated from $\gamma \simeq 0.8\gamma_v$. In Eq. 1 one then has to use $E_v - E_{\pi^*} \rightarrow \Delta E$, where ΔE is the binding energy of the molecular orbital involved in the charge transfer reaction. It is defined from the total energies of the initial and final states. Obviously, the higher is the binding energy of the molecular orbital, the stronger is the decoupling effect of the spacer layer.

Electromagnetic interactions

Classical calculations of the radiative and non-radiative de-excitation owing to electromagnetic interactions are performed with the COMSOL package.¹⁰⁷ As expected from the well-known effect of radiation quenching in the vicinity of metal,^{71,72,78,79} for a quantum emitter located above the NaCl/Ag metal surface, $\Gamma_{\text{NR}} \gg \Gamma_{\text{R}}$. This result holds within the entire NaCl coverage range studied here (from 0 to 10ML). Thus, while the NaCl spacer (see below for required width) electronically decouples an adsorbate from the substrate so that the RET is negligible, the molecular luminescence is strongly reduced by the ohmic losses into the metal. Nevertheless, increase of the quantum efficiency with the film thickness (see Fig 4) results in the possibility to observe molecular luminescence for the thick NaCl films.^{108,109}

This situation changes radically when a molecule is located in a plasmonic gap formed by an STM junction (see schematic in Fig. 1). The metallic tip-substrate system acts as a very efficient optical nanoantenna. It provides orders of magnitude enhancement of the decay rates, and most importantly, it leads to $\Gamma_{\text{R}} \gtrsim \Gamma_{\text{NR}}$ which favours light emission from the cavity.^{72,80,110}

We illustrate the effect of radiative decay enhancement by a plasmonic cavity in Fig 3, where we analyse the quantum efficiency, $QE = \Gamma_{\text{R}} / [\Gamma_{\text{R}} + \Gamma_{\text{NR}}]$, of light emission as function of the transition frequency of the point dipole and thickness of NaCl film. We recall that Γ_{R} is the rate of the radiative decay and Γ_{NR} is the rate of the non-radiative excitation transfer to the substrate. Thus QE takes into account only the electromagnetic interactions in the system. Below we will also use the quantum efficiency defined as $QE_{\text{RET}} = \Gamma_{\text{R}} / [\Gamma_{\text{R}} + \Gamma_{\text{NR}} + \Gamma_{\text{RET}}]$ which accounts for the RET as an additional decay channel of molecular exciton. Results shown in Fig 3 are obtained from classical electromagnetic calculations for the point dipole located in the middle of a 1 nm gap formed by an Ag tip and a NaCl spacer layer deposited on an Ag substrate. The thickness of the layer h is given by $h = 2.8\text{\AA} \cdot N_{\text{ML}}$ as deduced from experimental and theoretical data.^{86,104–106} In most of the luminescence experiments, the transition dipole of the adsorbed molecule is oriented parallel

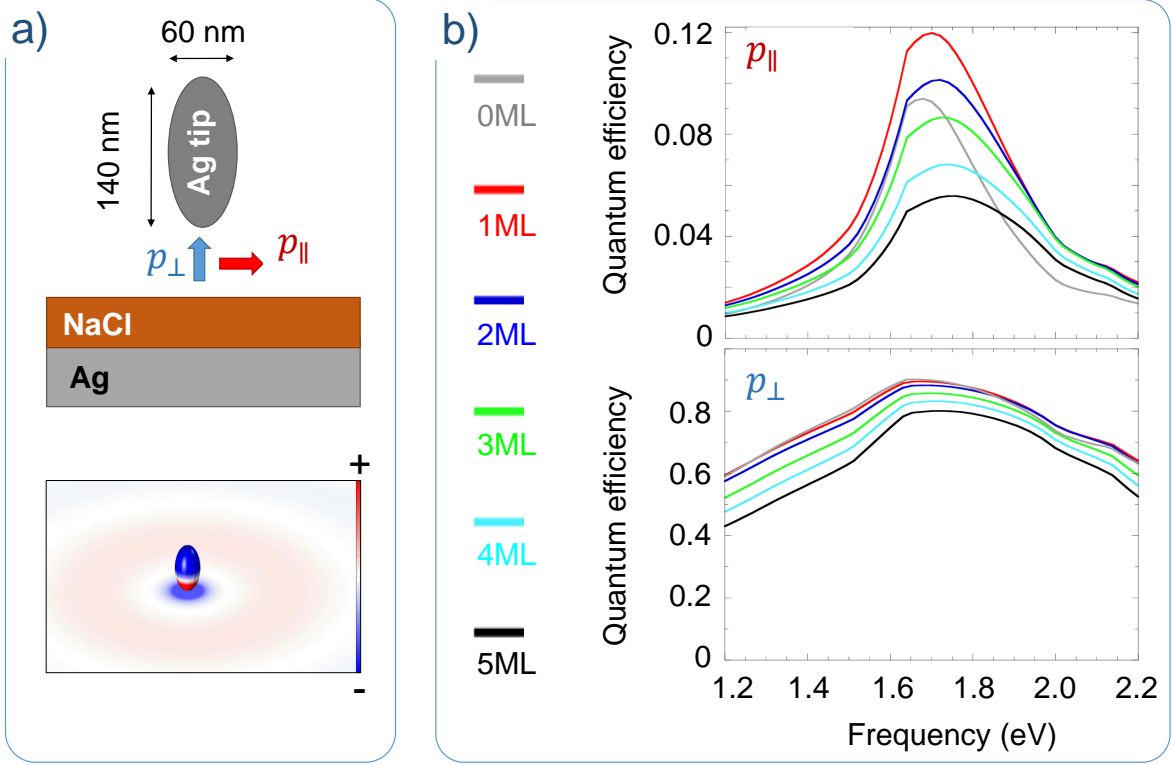


Figure 3: Classical electromagnetic results for a radiating point dipole located in a plasmonic gap between an Ag tip and a NaCl/Ag surface. **a**: Sketch of the system geometry and of the induced charge density (positive-red, negative-blue) associated with plasmon mode characterised by the dipolar excitation of the tip. The molecule in the STM junction is represented by a vertical (p_{\perp}) or horizontal (p_{\parallel}) point dipole. The STM tip is modelled as an Ag prolate spheroid of the dimensions set such that the dipolar plasmon resonance of the interacting tip-substrate system is at 1.8 eV. **b**: Quantum efficiency, QE, for light emission $QE = \Gamma_R / [\Gamma_R + \Gamma_{NR}]$ as a function of the transition frequency of the point dipole. Here Γ_R (Γ_{NR}) is the rate of radiative (non-radiative) de-excitation of the point dipole emitter owing to electromagnetic interactions. Results are shown for NaCl layers of various thickness and for p_{\parallel} and p_{\perp} orientations of the point dipole as indicated in the inserts.

to the surface, p_{\parallel} . In this situation, we consider the point dipole to be shifted by 1 nm from the tip axis.^{14,54,111} Such configuration enables the coupling between molecular exciton and the plasmon. Indeed, since the plasmonic local field is perpendicular to the surface at the symmetry axis of the system, placing the p_{\parallel} point dipole at this position would result in zero coupling with gap plasmon. For the sake of completeness we also show the results obtained for a Ag–Ag junction (no spacer) where the p_{\parallel} point dipole is located at 0.5 nm from the metal surface in the middle of the junction. As well we show the results obtained with a p_{\perp}

transition dipole oriented along the symmetry axis of the tip. In this latter case the molecular transition dipole strongly couples to the gap plasmon enhancing the nanoantenna effect of the STM tip.⁸⁰ The geometry of the Ag tip is such that the nanogap plasmon associated with the dipolar excitation of the tip is resonant with the molecular exciton at 1.8 eV (see Fig 3a). The choice of the system and of the resonant frequency is relevant to correctly quantify the emission in the actual experimental conditions.^{14,47,52,53,112} The situation where high-order plasmon modes are resonant with molecular exciton is considered in SI, leading to the similar qualitative results.

The calculated QE features a resonant enhancement as function of the emitter frequency. The maximum QE is reached at resonance with the gap plasmon (which is red-shifting when the gap narrows). Most importantly, for both orientations of the point dipole, the QE is nearly three orders of magnitude larger than in a situation without the tip. It reaches ~ 0.12 for p_{\parallel} , and ~ 0.9 for p_{\perp} dipole. Thus, the classical theory predicts that in a STM configuration molecular luminescence should be observed without NaCl spacer inline with earlier findings⁸⁰ and for any thickness of the spacer within the range considered here.

Interplay of decay channels

The classical prediction of light emission in a gap does not account for the decay of the molecular excited state population via RET. It needs to be completely revised for thin spacers in light of our results shown in Fig. 4. In this figure we analyse how the interplay between the different decay channels of molecular exciton in plasmonic STM gap changes with the thickness of the NaCl spacer. To compare the decay rates owing to electronic and electromagnetic interactions we focus on the Purcell factor and radiative rate enhancement calculated at the gap plasmon resonance frequency $\omega = 1.8$ eV using classical electrodynamics simulations. Resonant Γ_R and Γ_{NR} are then obtained considering the typical value of the transition dipole $\mu = 3.9$ a.u. (3.3×10^{-29} C m) characterising ZnPP, ZnPc, and H2Pc

molecular luminescence.^{56,113–115} For Γ_{RET} we relied on the robust character of the RET rates calculated for different molecule/surface combinations (see discussion of Fig. 2). For the discussion based on the order of magnitude comparison between different decay channels (see the vertical scale on Fig. 4) we then used the WPP results for the ZnPP/NaCl/Cu(100) case.

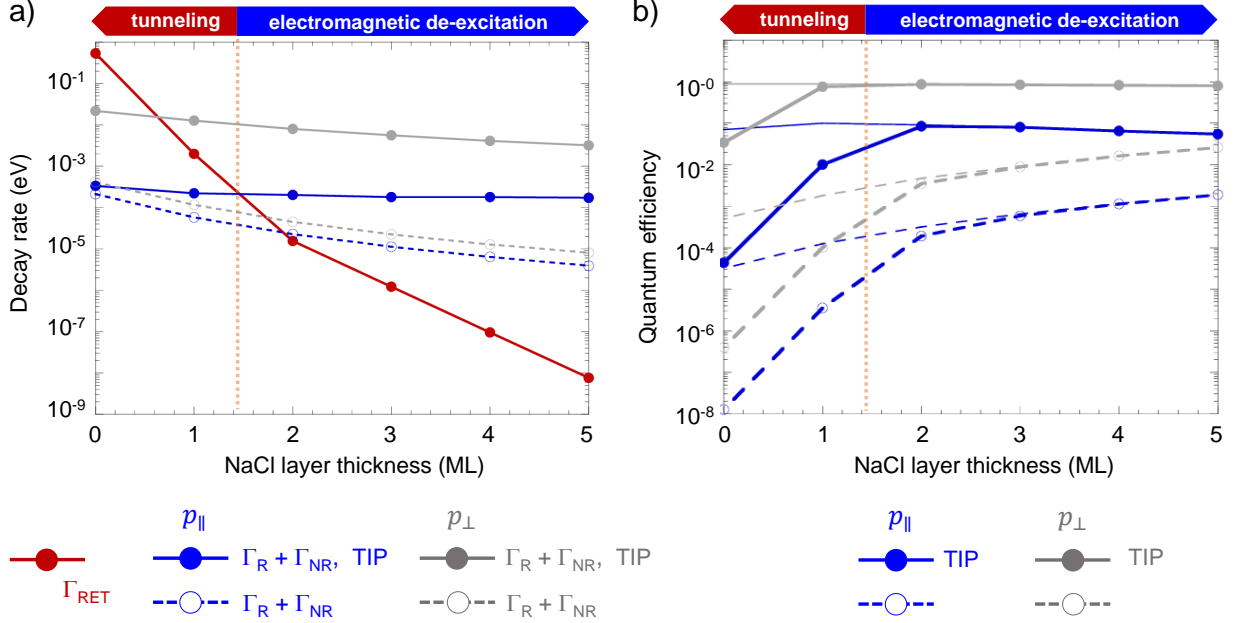


Figure 4: Analysis of the excited state decay for the ZnPP molecule separated from the metal surface by a NaCl spacer. Solid lines: plasmonic gap geometry of the STM junction. Dashed lines: flat NaCl/metal surface geometry (no tip). Results are shown at the transition frequency $\omega = 1.8$ eV resonant with gap plasmon as a function of the thickness of the NaCl layer measured in monolayers, ML. The ranges of NaCl coverage where the excited state decay is dominated by electronic (red, tunneling) or electromagnetic (blue, de-excitation) interactions are indicated on top of both panels. The vertical dashed line indicates the transition between these two regimes. **a, Decay rates:** Red line with dots: the rate of the RET from the molecule-localized excited orbital into the metal, Γ_{RET} . Blue (grey) lines: de-excitation rate given by the sum of radiative and non-radiative electromagnetic contributions, $\Gamma_{\text{R}} + \Gamma_{\text{NR}}$, for the p_{\perp} (p_{\parallel}) orientation of the point dipole. **b, Quantum efficiency:** Quantum efficiency of light emission calculated including the excited state decay via electron tunneling into the substrate, $QE_{\text{RET}} = \Gamma_{\text{R}} / [\Gamma_{\text{R}} + \Gamma_{\text{NR}} + \Gamma_{\text{RET}}]$ is shown with thick lines with symbols. Quantum efficiency calculated without account for the RET, $QE = \Gamma_{\text{R}} / [\Gamma_{\text{R}} + \Gamma_{\text{NR}}]$ is shown with thin lines. For further details see the legends.

The data presented in Fig. 4a reveals two characteristic ranges of thickness of the spacer layer according to the leading mechanism (electronic or electromagnetic) of the decay of the

excited state. For p_{\parallel} orientation of the transition dipole relevant to describe molecular luminescence in STM junction, the excited state decay is driven by the electron tunneling when the width of the NaCl spacer is below 2ML. A thicker NaCl spacer (2ML and above) electronically decouples the adsorbate from the substrate. In that situation, the electromagnetic interactions determine the excited state decay with energy transfer to photons (radiative channel), and to ohmic losses in metal (non-radiative channel). Interestingly, because of the essentially stronger coupling with the gap plasmon,⁸⁰ for p_{\perp} transition dipole the electromagnetic de-excitation dominated regime is reached already for 1ML of NaCl. Note that in the absence of the STM tip the de-excitation rates are reduced by several orders of magnitude. However, also in this situation, the exponential damping of the RET rate by the NaCl barrier results in the excited state decay to be dominated by the electromagnetic interactions (in this case the non radiative decay) for the width of the spacer of 3ML and above.

The quantum efficiency of light emission calculated at the gap plasmon frequency is shown Fig. 4b as a function of the NaCl film thickness measured in monolayers. At low NaCl coverage (below 2ML), the RET strongly harms the light emission as follows from the comparison between the data calculated with (QE_{RET} , thick lines with symbols), and without (QE , thin lines) inclusion of the electronic coupling. For thicker spacer, the RET becomes negligible and the far field radiation is determined by the Purcell factor and radiative decay rate^{73,116} resulting from the electromagnetic interactions in the system. Therefore, owing to the antenna effect of the STM junction, molecular luminescence in a STM setup can be observed for NaCl spacer of 2ML and thicker. Otherwise the excited state population is quenched by RET at the time scales too short as compared with the radiative decay. This result is in full agreement with experimental data,^{16,53} and it provides a consistent explanation of the empirical choice of the width of the ionic crystal spacer used throughout numerous experiments studying molecular luminescence at surfaces.

Summary and Conclusions

In summary, by using quantum mechanical calculations based on the WPP approach and classical electromagnetic theory, we have quantitatively addressed the competing pathways of decay of an excited molecule separated from the metallic substrate by a dielectric spacer. Namely, we considered an excited electron escape from the adsorbate into the substrate via resonant electron transfer resulting from the adsorbate–substrate electronic coupling, and the *excited-state* \rightarrow *ground-state* de-excitation resulting from the electromagnetic interactions. We considered flat surface and plasmonic STM junction geometry highly relevant for current developments in nanotechnology.

For the case of a NaCl spacer commonly used in local probe studies of surface reactivity and single molecule luminescence, we established the relationship between the width of the spacer and the dominant decay mechanism of a molecular exciton. Typically, for molecule deposited on a NaCl/metal surface the resonant electron transfer into the metal dominates the excited state decay below 2ML thickness of NaCl spacer. For the 3ML of NaCl and above, the decay of a molecular exciton is dominated by the electromagnetic interactions resulting in radiation quenching because of the ohmic losses in the metal. The antenna effect of the plasmonic gap configuration of the STM junction, allows for lifting the radiation quenching. As a result, starting from a 2ML NaCl coverage the molecular luminescence can be observed in the far field which explains a wealth of experimental data in tunneling configurations.

The results reported here are of general validity, and mainly depend on the electron transmission through the ionic crystal, as well as on the near-field enhancement and radiative decay enhancement in the plasmonic junction. Our study paves the way towards a quantitative description and engineering of the spacer layers for the adsorbate exciton and charge-state manipulation with implications in surface reactivity and in implementation of single-molecule spectroscopy and microscopy. Our findings are particularly interesting in the context of the quest for controllable exciton dynamics in nanojunctions.

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Supporting Information Available

The following files are available free of charge.

The Supporting Information providing the details on the theoretical approaches and extending results of the main text. It contains:

- The discussion on the resonant electron transfer processes relevant for the quenching (and formation) of excited molecule;
- The description of the wave packet propagation method;
- The description of the ab initio calculations of the adsorption geometry and molecular structure;
- The model of the NaCl ionic crystal used to capture the spacer effect on the resonant electron transfer between the adsorbed molecule and the substrate;
- The results of the classical electromagnetic calculations of the optical response of the STM tip antenna in front of the metal surface;

- The results of the classical electromagnetic calculations of the decay of the quantum emitter located in plasmonic gap formed by the STM tip and metal substrate.

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TOC Graphic

