The healing mechanism for excited molecules near metallic surfaces

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Abstract. Radiation damage prevents the ability to obtain images from individual molecules. We suggest that this problem can be avoided for organic molecules by placing them in close proximity with a metallic surface. The molecules will then quickly dissipate any electronic excitation via their coupling to the metal surface. They may therefore be observed for a number of elastic scattering events that is sufficient to determine their structure.

Examining individual molecules at the atomic length scale is one of the most challenging modern problems of science. An analysis of elastic and inelastic cross-sections provides a basis for understanding why molecules can become fragmented beyond recognition long before the time necessary to accumulate sufficient counts for image reconstruction. In the case of organic molecules, most structural knowledge has been gained using crystalline samples, where damaging exposure is distributed over many identical molecules, and the image is almost the same as that of an undamaged molecule. For molecules which cannot be crystallized, there is an urgent need for methods that can give information on their structures.

In single-molecule diffraction techniques proposed using either femtosecond x-ray pulses [1] or high-energy electron beams [2], short wavelengths are used to image the atomic structure of individual molecules, but the radiation doses destroy the molecule after providing a diffraction pattern. Imaging with coherent electrons from low energy electron point sources (LEEPS) is a less-destructive method to characterize single molecules [3]. A holographic interference pattern can be generated by LEEPS from which one can reconstruct the object’s structure. For example, one can reconstruct the structure of single polymer strands like DNA [4]. Recently, another method using interference patterns with standing x-ray waves has been used to map the perylene-tetracarboxylic-dianhydride (PTCDA) molecule on a silver surface [5].
The use of positrons for microscopy is not as well known, but it has tremendous potential. Positrons, owing to their positive charge, have negative work functions in several materials, and they can be re-emitted spontaneously. This feature allows the control of slow positron beams having energies in the epithermal region. A positron microscope for imaging single molecules has been recently proposed by Mills and Platzman [6]. In order to get proper structural information with sufficient resolution, Mills and Platzman have estimated that each atom in a molecule of 200 atoms should suffer about 50 annihilations in the course of the positron diffraction. After the annihilation, the molecule is in an ionic excited state, and under normal circumstances, such a large number of ionizations would destroy or desorb the molecule.

Clearly, while exploring the opportunities of imaging single molecules with either x-rays, electrons or positrons, it is vital to reduce radiation damage at the level of individual molecules. In this paper, we analyse the neutralization process that occurs when a molecule is placed near a metallic surface—here called the healing mechanism—and propose that it may be applied to heal the radiation damage. The main idea is to fill the vacant molecular orbital by an electron from the metal in a time short compared to some characteristic vibration time of the molecule. Therefore, charge neutrality is restored before the onset of the vibrational modes which would lead to the destruction of the molecule. This healing mechanism can be decomposed in two main steps. In the first step, when the positive ion is sufficiently close to the surface, one conduction electron of the metal will tunnel under the influence of the strong electric field produced by the ion. In the second step, the tunnelling electron will fill the hole via an Auger process involving an electron–hole pair of the metal. The physics of the healing mechanism is closely related to various neutralization processes [7]–[14] and to the intermolecular Coulombic decay [15]. Most of this paper describes collisions of slow ions with solids. Our study involves the neutralization of physisorbed molecules on metallic surfaces. Given the wide range of estimates of the neutralization time in previous work [8], we must perform a conservative estimate to demonstrate the feasibility of the healing mechanism in our case.

A schematic of the healing mechanism setup is shown in figure 1. The molecule, in this example PTCDA, is on a metallic substrate, which should be chemically inert to preserve the integrity of the molecule. Gold, silver or other noble metals are possible substrates. In reality, the PTCDA geometry might slightly bend near the metallic substrate because of the readiness of some PTCDA atoms to form weak bonds with the surface [5].

When a positive charge is suddenly created on the molecule, the resulting electric field attracts the electrons of the metal. The probability $T$ that one electron escapes from the metal depends on the work function $\Phi$ and on the distance $d$ of the positive charge from the surface. An accurate determination of the tunnelling probability $T$ would require solving the Schrödinger equation, for example using the matching wavefunction method [16]. However, the result is mostly dominated by an exponential factor given by the WBK approximation [17]

$$T = \exp \left( -2 \int_0^s dz \sqrt{2m(V(z) - E_F)}/\hbar \right),$$

(1)

where $s$ is the width of the potential barrier and $E_F$ is the Fermi energy of the metal. The actual shape of the potential barrier $V(z)$ is complicated, but a linear approximation of the electrostatic potential at the metal–molecule interface yields a simple triangular barrier, and the penetration
Figure 1. Schematic of a typical healing mechanism setup: an ionized molecule is placed above a metallic substrate and the positive charge is at a distance \(d\) from the substrate. In this example, atoms of a PTCDA fragment are shown. The small grey spheres denote H, the large green spheres denote O and the large blue spheres denote C.

probability \(T\) becomes

\[
T(d) = \exp(-\sqrt{\frac{2}{3}} \Phi^{3/2} d^2),
\]

where atomic units have been used. Figure 2 shows that \(T\) under a barrier characterized by a work function \(\Phi = 5\) eV is still about 0.01 for a distance \(d = 4\) Å. Actually, our major assumption—the triangular barrier—underestimates \(T(d)\) since the electric field gets stronger as an electron approaches the molecule. Moreover, equation (2) gives a smaller penetration probability than self-consistent density functional calculations for metallic surfaces [19], since in our approximation we neglect the reduction of the potential barrier due to the field produced by the escaping electron. Both effects combined lead to a sizable underestimate of \(T(d)\).

An electron of the metal is expected to fall into the vacant orbital of the molecule. Indeed, a photoemission study [20] of the PTCDA organic molecule on a metal surface reveals the energy-level alignment shown in the schematic diagram of figure 3, where the highest occupied molecular orbital (HOMO) level is about 2 eV below \(E_F\). A similar diagram of energy levels has been obtained via first-principles calculations [21].

The energy separation \(\omega\) (see figure 3) between the state \(\psi_t\) of the electron spilling out from the metal\(^4\) and the molecular orbital of the hole \(\psi_n\) must be dissipated during the recombination. An Auger process involving an electron-hole excitation in the metal can mediate the capture of the electron in the state \(\psi_t\) into the vacant molecular state \(\psi_n\). There are several possible electron

\(^3\) We have assumed that the charge distribution on the molecule is spherical and we have used the method of images to determine the electric field. Near the metal–vacuum interface, along the direction from the metal surface to the positive charge, the electric field intensity is \(F = 2e^2/d^2\); see e.g. [18].

\(^4\) We have assumed that \(\psi_t\) is at the Fermi level \(E_F\).
transfer processes between molecules and surfaces [22]. For chemisorbed systems, a hole lifetime is much shorter than a typical vibration time [23], so that normally the hole would be filled before the molecule can fly apart. For N₂ molecules physisorbed on graphite, experiments suggest that the neutralization occurs with a characteristic time $\tau \approx 10^{-14}$ s [24]. In general, for a molecule far from the surface, the corresponding hole may not be filled for a while. In this case, the relevant process is the Auger neutralization as described by Propst [17]. The actual calculation of the Auger neutralization rate $1/\tau(d, \omega)$ is a difficult problem including subtle screening effects at
the metal–vacuum interface [8]. Nevertheless, it has been suggested by numerical calculations that, as a good approximation, the dependence on the distance \( d \) and the energy \( \omega \) factorize [9] as

\[
\frac{1}{\tau(d, \omega)} = f(d) \frac{1}{\tau_B(\omega)},
\]

(3)

where \( 1/\tau_B(\omega) \) is obtained using the formula for the molecule immersed in the bulk and \( f(d) \) is an unknown function, usually approximated by an exponential [9], which decays away from the metal surface. Propst [17], however, has shown that the distance of the molecule from the surface comes into play mostly through the WKB transmission probability. Therefore, we can assume \( f(d) \approx T(d) \).

The matrix element \( M_{\alpha}(q) \) of the Auger process in the bulk involves the ground-state \( u_0 \) of the metal, the excited state \( u_{\alpha} \) of the metal and the density operator \( \rho_q^* \) for excitations with momentum transfer \( q \). The actual form of \( M_{\alpha}(q) \) reads\(^5\)

\[
M_{\alpha}(q) = F(q) V_C(q) \langle u_{\alpha} | \rho_q^* | u_0 \rangle,
\]

(4)

where \( F(q) \) is a form factor given by

\[
F(q) = \int \mathrm{d}r \psi_n(r) \psi_t(r) \exp(iqr),
\]

(5)

\( V_C(q) \) is the Coulomb interaction Fourier transform

\[
V_C(q) = \frac{4\pi e^2}{q^2 L^3}
\]

(6)

and \( L^3 \) is the volume of the metallic sample. The rate of the Auger recombination can be calculated by using Fermi’s golden rule

\[
\frac{1}{\tau_B} = \sum_q \sum_\alpha |M_{\alpha}(q)|^2 \delta(\omega - \omega_{\alpha 0}),
\]

(7)

where \( \omega_{\alpha 0} \) is the energy difference between the metal ground-state \( u_0 \) and the excited state \( u_{\alpha} \). Equation (7) can be rewritten in the form

\[
\frac{1}{\tau_B} = \sum_q S(q, \omega) V_C(q)^2 F(q)^2,
\]

(8)

where \( S(q, \omega) \) is the dynamical structure factor [26] defined by

\[
S(q, \omega) = \sum_\alpha |\langle u_{\alpha} | \rho_q^* | u_0 \rangle|^2 \delta(\omega - \omega_{\alpha 0}).
\]

(9)

\(^5\) Related lifetimes have been used in the context of electron relaxation in quantum dots, see e.g. [25].
The fluctuation–dissipation theorem relates the dynamical structure factor $S(q, \omega)$ to the dielectric function $\epsilon(q, \omega)$ by the formula

$$S(q, \omega) = -\frac{1}{V_C(q)} \text{Im} \left[ \frac{1}{\epsilon(q, \omega)} \right].$$

(10)

Substituting equation (10) in equation (8), we obtain

$$\frac{1}{\tau_B} = -\int L^3 d^3q \frac{8}{8\pi^3} \text{Im} \left[ \frac{F(q)^2 V_C(q)}{\epsilon(q, \omega)} \right].$$

(11)

To extract an Auger rate estimate, one can use the Lindhard RPA formula [26] for the dielectric function $\epsilon(q, \omega)$. Density inhomogeneity effects, due to the lattice and the surface, and correlation corrections beyond the RPA are not considered in this study. For $\psi_n(r)$, one can use a Slater type of orbital (STO) [27] given by

$$\psi_n(r) = \sqrt{\frac{\xi^3}{\pi}} \exp(-\xi r).$$

(12)

where $1/\xi$ provides the size of the molecular orbital. Therefore, assuming that $\psi_t(r)$ is slowly varying, the main form factor contribution to the integral in equation (11) is given by

$$F(q) = \sqrt{\frac{8\xi^3}{\pi^2}} \frac{\xi^{5/2}}{(\xi^2 + q^2)^2}.$$

(13)

Figure 4 shows typical $1/\tau$ values in the energy range 2–10 eV for a gold surface (corresponding to an electron density parameter $r_s = 3.1$). Since this rate is proportional to the penetration probability $T$, we show $T^{-1}/\tau$ in the ordinate axis of the plot in figure 4. The grey region in figure 4 corresponds to an STO exponent $\xi$ ranging from 1 to $\infty$. For a distance of $\sim 4\text{Å}$, since $T$ is about 0.01 the Auger rate becomes of the order of $10^{13} \text{s}^{-1}$ in the lower part of the grey region in figure 4. This value is comparable to the highest vibration modes in molecules. All this implies that, within distances of less than 4 Å, the time to fill the hole is estimated to be fast enough to keep the molecule from being damaged by molecular vibrations. As mentioned previously, the value of the penetration probability $T$ given by equation (2) is a lower bound. This fact adds to the robustness of the present model. Nevertheless, our calculation is not meant to provide an accurate value of the healing time but instead to demonstrate the feasibility of the healing mechanism.

In conclusion, the effects of radiation damage on molecules are of concern, because they can be a major obstacle to the emergence of microscopy as a tool to determine the structure of
Figure 4. Auger rates in the energy range 2–10 eV for a metal with density parameter $r_s = 3.1$, as in gold. The grey region corresponds to $\zeta$ ranging from 1 to $\infty$. Note that the grey region extends beyond the frame of the picture.

delicate biological molecules. This is true whether x-rays, electrons or positrons are used as the illumination. We have shown that in favourable conditions, ionized molecules on a metal surface can quickly dissipate any electronic excitation via their coupling to the metal. The relaxation is achieved via an electron tunnelling from the metal to the molecule and falling into the vacant orbital. The falling electron gives up its energy to an excitation of the metal produced by an Auger process. If the molecule is within distances of about 4 Å from the metal surface, short lifetimes of the hole on the molecule (of the order of 10–100 fs) prevent the destruction or desorption of the molecule. Our model may in fact overestimate the healing time. This healing mechanism is particularly suitable for the positron microscope newly proposed by Mills and Platzman [6], but it can be applied also to other microscopes imaging single molecules. In all these cases, the molecule on the metallic surface may be observed without being damaged for a number of scattering events sufficient to determine its structure by speckle diffraction. These measurements would be ideal for studying delicate biological molecules which cannot be crystallized.

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