Ultrafast Nonradiative Decay Rates on Metallic Surfaces by Comparing Surface-Enhanced Raman and Fluorescence Signals of Single Molecules

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By the simultaneous observation of surface-enhanced Raman scattering and surface-enhanced fluorescence signals from a single molecule, we can measure and quantify the modification of the total decay rate of emitters in very close proximity to metals, even down to adsorbed molecules. This modified decay rate is shown to be largely dominated by its nonradiative component, which would be extremely difficult to estimate with conventional approaches. The method provides an indirect measurement of ultrafast (~25 fs) mechanisms, which would be impossible to gain with time-resolved spectroscopy of a single molecule.

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The interest in the optical properties of molecules close to metal surfaces has recently soared, driven by the many potential applications of surface-enhanced Raman spectroscopy (SERS) [1,2] and surface-enhanced fluorescence (SEF) [1]. The basic theory of surface-enhanced spectroscopies was extensively developed in the 1970s–1980s [3–6], but it is only recently that experimental advances have allowed the confirmation of various aspects [7–12] and foresee more elaborate applications. SEF is the modification (quenching or enhancement) of the fluorescence intensities and lifetimes for molecules adsorbed on (or close to, by a few nm) a metal surface. This arises from the strong electromagnetic (EM) response of metallic objects, particularly when localized surface plasmon resonances (LSPRs) are excited [3–6,13]; these resonances are also the origin of the large enhancements observed in SERS, allowing the detection of single molecules under appropriate conditions [14–17]. Although the underlying SERS and SEF EM enhancements are related, they are rarely studied together [4,18,19]. SEF studies are mostly carried out for molecules that are *not* directly adsorbed on the metal surface (typically a few nm away). This dramatically improves the SEF intensity, which then overwhelms any residual SERS signal. Contrariwise, SERS is usually studied for molecules directly on the surface, for which it was until recently believed that fluorescence is entirely quenched. This assumption has however been recently revisited [1,10,12,20], and it was shown that fluorescence, although partially quenched, should still be observable (albeit spectrally modified) under typical SERS conditions, which could be the origin of the much-debated SERS continuum [1,10].

In this Letter, we propose a method that uses such joint SERS/SEF spectra to extract the total (i.e., radiative + nonradiative) decay rate enhancement factor, and therefore to quantify indirectly the decay rate. This is demonstrated experimentally under single-molecule SERS/SEF conditions, and allows us to infer the ultrafast (subpicosecond) decay rate that is expected from molecules directly adsorbed on metallic surfaces [4], without resorting to time-resolved measurements [21] (which would be impossible here in single-molecule conditions). It is shown that this total decay rate is entirely dominated by the nonradiative decay into dissipative modes of the metal substrate, in agreement with EM predictions.

The classical EM model of SERS and SEF is well understood and has been numerously discussed in the literature [1,10,12,18–20,22,23]. We sketch here briefly the points relevant to this study to define the notation (after Refs. [1,10]). We ignore any tensorial effects for simplicity, since they are secondary and can be included later if necessary [1,11]. For clarity, we write explicitly the dependencies with the excitation (λ_L) and emission (λ_S) wavelengths (fluorescence or Raman). First, the local field intensity for a molecule in the vicinity of a metallic surface is modified by an enhancement factor $M_{\mathrm{Loc}}(\lambda_L)$, which can be calculated using standard EM theory. This factor will typically amplify the absorption cross section of a fluorophore. Second, considering now a dipolar emitter at the same position, its radiated power in a given direction (toward the detector) is also modified by a factor $M^d_{\mathrm{Rad}}(\lambda_S)$. For a fluorophore in its excited state, this factor characterizes the modification of its differential radiative decay rate [1]. Finally, the total (radiative + nonradiative) EM decay rate is modified by a factor $M_{\mathrm{Tot}}(\lambda_S)$ with respect to its normal radiative decay rate. If the spectral profile modification of the fluorescence is taken into account [10], then this factor should be replaced by an effective EF $\bar{M}_{\mathrm{Tot}}$, which does not depend on λ_S. Note that any intrinsic nonradiative decay is assumed to be unmodified by the metal.

The enhancement factors for SERS and SEF can then be deduced from these three aforementioned EFs. The fluorescence EF is [1,10,22,23]:

$$M_{\mathrm{SEF}}(\lambda_L, \lambda_S) = \frac{M_{\mathrm{Loc}}(\lambda_L) M^d_{\mathrm{Rad}}(\lambda_S)}{Q^0 \bar{M}_{\mathrm{Tot}}}, \qquad (1)$$

where Q^0 denotes the (nonmodified) quantum yield of the fluorophore. Quenching or enhancement of the fluorescence can therefore be observed depending on the situation and on the competition between radiative and nonradiative decays. In the case of scattering, i.e., SERS, there is no competition between radiative and nonradiative channels. Both M_{Loc} and M^d_{Rad} contribute multiplicatively to the SERS EF resulting in [1,10,24]:

$$M_{\mathrm{SERS}}(\lambda_L, \lambda_S) = M_{\mathrm{Loc}}(\lambda_L) M^d_{\mathrm{Rad}}(\lambda_S). \qquad (2)$$

It is important to reemphasize that these EFs relate the modified properties, differential radiative fluorescence or Raman cross section with respect to those of the bare molecule (i.e., in the absence of the metal). Many aspects of this model have been verified experimentally [7,10,12,20,21,23], but the total decay rates have remained out of reach. Theory predicts that total decay rate enhancements may be as large as $\bar{M}_{\mathrm{Tot}} = 10^5$–$10^6$ for molecules located at ~1 nm or less from the surface. This implies decay rates well into the sub-ps regime, making a direct measurement (time-resolved) very challenging. Here, we propose to extract this from the ratio R_{EF} of the SERS and fluorescence EFs which—according to the previous expressions—simplifies to

$$R_{\mathrm{EF}}(\lambda_L, \lambda_S) = \frac{M_{\mathrm{SERS}}(\lambda_L, \lambda_S)}{M_{\mathrm{SEF}}(\lambda_L, \lambda_S)} = Q^0 \bar{M}_{\mathrm{Tot}}. \qquad (3)$$

Note that this ratio is not the ratio R_{Metal} of SERS and SEF intensities, but a ratio of enhancement factors. The ratio R_{Bare} of Raman to fluorescence intensity of the bare molecule must therefore also be measured, from which $R_{\mathrm{EF}} = R_{\mathrm{Metal}}/R_{\mathrm{Bare}}$ can be deduced. These steps are illustrated in Fig. 1. One of the advantages of this approach is that it is *self-normalizing*. Since $M_{\mathrm{Loc}}(\lambda_L)$ and $M^d_{\mathrm{Rad}}(\lambda_S)$ cancel out in the ratio, R_{EF} is independent of the LSPR position, of the magnitude of the local field enhancements, and of the actual SERS EF. It is also insensitive to any photobleaching effect, a common problem in SERS/SEF [25,26]. Finally, it is independent of the Raman (SERS) peak used for the calculation (i.e., of λ_S), as confirmed experimentally in Ref. [12]. It is hence possible to check for the self-consistency of the method and improve its accuracy by calculating R_{EF} for several SERS peaks.

We shall demonstrate a particular implementation of this method. The SERS substrate consists of Lee-Meisel Ag colloids [27], partially aggregated with KCl (10 mM final concentration) as reported elsewhere [16,17]. Such a substrate allows the study of relatively large numbers of single-molecule SERS events produced by Brownian motion of aggregates in solution. SERS/SEF spectra were obtained at 633 nm excitation (4.1 mW to 36 μW) with a ×100 immersion objective and 0.1 s integration time. In practice, a number of additional constraints have to be considered. (i) First, we need to measure the bare Raman and fluorescence of the molecule. This is (paradoxically) more challenging than SERS/SEF in many cases, for fluorescence typically overwhelms the spectrum making it impossible to extract any resonance Raman cross section. This may be circumvented using a more sophisticated approach [28,29], but we choose here a specific fluorophore, Crystal Violet (CV), for which this problem is absent because of its particularly poor fluorescence quantum yield. Its quantum yield in water at 633 nm excitation (which is also required) was determined from the relative fluorescence and absorption cross sections of a 10 μM solution. We obtained $Q^0 = 5.2 \times 10^{-5}$, in agreement with reported values [30]. (ii) Second, because $\bar{M}_{\mathrm{Tot}}$ may vary with the molecule position (in particular its distance

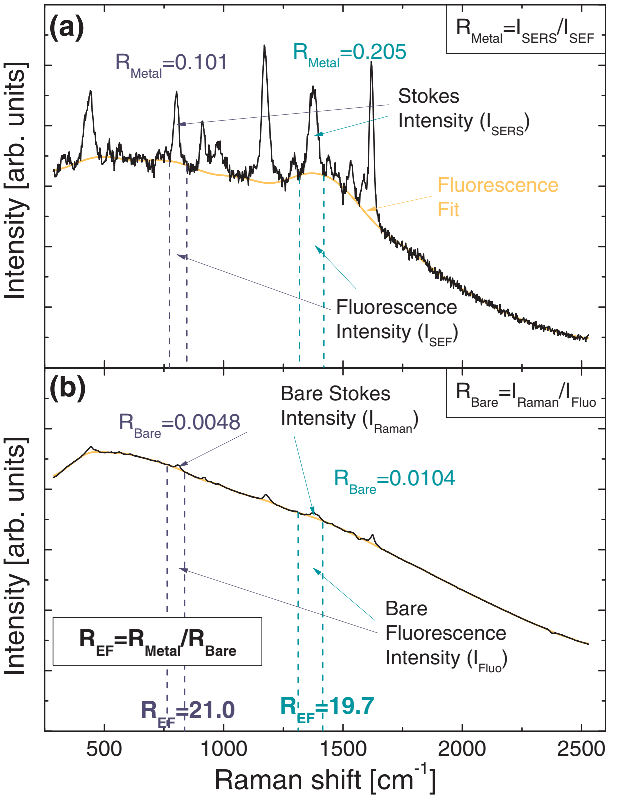

FIG. 1 (color online). Raman and fluorescence spectra after extrinsic background subtraction: (a) modified, and (b) unmodified by the metallic nanoparticles. The Raman to fluorescence ratio is calculated in each case (R_{Metal} and R_{Bare}) by measuring the intensity of the Raman peak (I_{SERS} and I_{Raman}) and the fluorescence intensity over a fixed Raman-shift window fixed beneath it (I_{SEF} and I_{Fluo}). Note that the actual values of R_{Metal} and R_{Bare} depend on various parameters, but their ratio has a precise physical meaning: the quotient of the Raman to fluorescence ratios under surface-enhanced and unmodified conditions gives $R_{\mathrm{EF}} = R_{\mathrm{Metal}}/R_{\mathrm{Bare}}$, and this is equivalent to taking the ratio of the SERS to SEF enhancement factors. As predicted, the same R_{EF} is obtained for both peaks measured from the same single-molecule event.

from the surface), Eq. (3) is only valid in *single-molecule conditions*. The concentration of CV was here adjusted to 1 nM, for which we checked beforehand (using the bi-analyte SERS method [16]) that the majority of signals were indeed single-molecule (SM) events. (iii) Third, special attention is needed for the extraction of the SEF intensities for the spectra. Unlike SERS peaks, which are easily measured above the background, the SEF spectrum is broad and may be mixed with extrinsic backgrounds not related to adsorbed molecules (i.e., signals from water itself and/or fluorescence from nonadsorbed molecules). In order to address this issue, the SERS solution was centrifuged at 14 500 rpm for 10 min and the residual signal from the supernatant measured under the same conditions. The resulting background was then subtracted off from all SERS/SEF spectra to reveal the true SEF background. (iv) Finally, for the technique to work, one must be able to measure the ratio of SERS to SEF intensities with adequate accuracy in single-molecule conditions. This restricts the fluorophores that may be used. The problem is here the opposite of that in (i) for the bare molecule: the SEF signal may be quenched too much, to a point where its intensity may become unmeasurable. For fluorophores directly adsorbed on the metal and resonantly excited (like CV here at 633 nm), the strong quenching is compensated by the large intrinsic absorption cross section, resulting in comparable SERS and SEF. This is explicitly shown in Fig. 1, where the details of the extraction of $\bar{M}_{\text{Tot}}$ for a single representative SERS/SEF spectrum are summarized. The ratio of Raman to fluorescence intensities is measured in both SERS/SEF and bare conditions for several peaks. The quotient R_{EF} of these ratios can be extracted, and the value of $\bar{M}_{\text{Tot}}$ is deduced from the knowledge of Q^0.

Figure 1 demonstrates the principles of our approach. However, in order to draw further conclusions, it is desirable to obtain data from a much larger set of single-molecule events. This can be done easily in colloidal solutions, whereby Brownian motion provides a natural mechanism for sampling clusters. Hence, we measured 3000 spectra as a function of time for three incident laser powers, and analyzed those where a measurable signal was obtained (only a small fraction of them because of the low concentration necessary to ensure single-molecule detection). For each event, $\bar{M}_{\text{Tot}}$ was extracted from the measurement of R_{EF} at five of the most prominent Raman peaks of CV. In all cases, the value of $\bar{M}_{\text{Tot}}$ extracted for a given SM event from the 5 Raman peaks were similar and the average over these 5 values, $\bar{M}_{\text{Tot}}^{\text{Ave}}$, therefore provides a more reliable estimate of $\bar{M}_{\text{Tot}}$ for that event. To quantify this further, it is instructive to consider the average over all events $\langle \bar{M}_{\text{Tot}} \rangle$ for each Raman peak along with $\langle \bar{M}_{\text{Tot}}^{\text{Ave}} \rangle$. As shown in Table I, there are minor systematic differences between the 5 cases. These can be attributed partly to experimental uncertainties in R_{Bare} for the bare molecule. They may also be the result of real physical mechanisms, for example, minor changes in the electronic structure or Raman polarizability of CV adsorbed on the metal, or surface selection rules [1,31,32], which may mildly affect the relative SERS intensities of different modes. But overall, these small fluctuations are within the expected experimental accuracy. For a given SM event, $\bar{M}_{\text{Tot}}$ for each of the 5 Raman peaks typically fluctuates by no more than $\sim \pm 20\%$ of their average. $\bar{M}_{\text{Tot}}^{\text{Ave}}$ therefore represents a reliable measure of $\bar{M}_{\text{Tot}}$ for any individual SM events.

TABLE I. Average $\bar{M}_{\text{Tot}}$ (over all SM events) obtained from analysis of 5 Raman peaks at different incident powers. $\langle \bar{M}_{\text{Tot}}^{\text{Ave}} \rangle$ is the average of these 5 values.

	$\langle \bar{M}_{\text{Tot}} \rangle$ $(\times 10^5)$					
	Raman shift [cm^{-1}]					
Power	441	804	1176	1386	1622	$\langle \bar{M}_{\text{Tot}}^{\text{Ave}} \rangle$ $(\times 10^5)$
4.1 mW	4.96	4.36	3.80	4.06	3.91	4.21
430 μW	5.22	4.78	3.84	4.23	4.08	4.43
36 μW	5.66	4.75	3.79	3.85	3.74	4.36

We focus now on the actual value of $\bar{M}_{\text{Tot}}^{\text{Ave}}$ and how it varies from event to event. There are, as in most SM-SERS experiments, large fluctuations in SERS/SEF intensities from event to event. This can be quantified by determining the SERS enhancement factor M_{SERS} for each event (following the method of Ref. [17]). Figure 2 illustrates how the measured $\bar{M}_{\text{Tot}}^{\text{Ave}}$ for each SM event varies with the event intensity, as quantified by $(M_{\text{SERS}})^{1/2}$. First, it is clear from Table I and Fig. 2 that $\bar{M}_{\text{Tot}}$ is not affected by the incident laser power. This is one of the attractive features of this

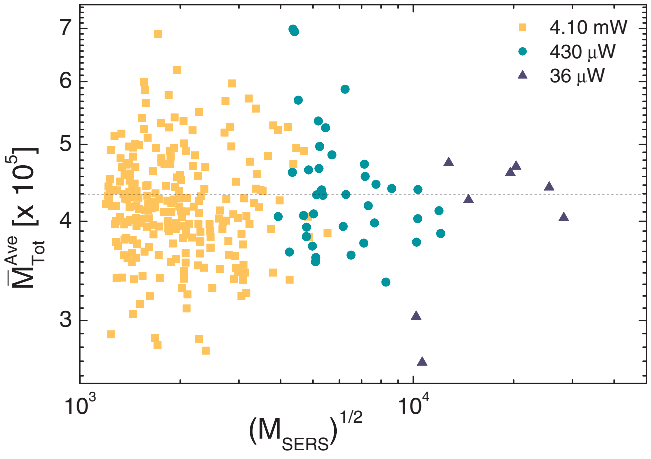

FIG. 2 (color online). Variations of $\bar{M}_{\text{Tot}}^{\text{Ave}}$ (from event to event), plotted against the square root of the SERS enhancement factor, $(M_{\text{SERS}})^{1/2}$ (calculated from the Stokes intensities) at three incident powers. For each SM event, $\bar{M}_{\text{Tot}}^{\text{Ave}}$ is the average over the 5 values obtained from analysis of 5 different Raman peaks. It is clearly unaffected by incident power, and remains independent of the event intensity, quantified here by $(M_{\text{SERS}})^{1/2}$. The dashed line marks the average (over events): $\langle \bar{M}_{\text{Tot}}^{\text{Ave}} \rangle = 4.3 \times 10^5$.

approach: it is insensitive to photobleaching, even if it is clearly affecting here the SERS and SEF intensities at the largest power, as evidenced in Fig. 2: the maximum measured SERS EF are clearly lower at the largest power. This is the result of fast photobleaching of fluorophores (faster than the integration time), as discussed extensively in Ref. [26]. Under the present conditions, photobleaching effects only become negligible for the lowest power of 36 μW [26]. Second, despite the spread in M_{SERS} over more than 2 orders of magnitude, the data in Fig. 2 show that $\bar{M}_{\mathrm{Tot}}$ remains approximately constant, independent of the actual SERS EF. In fact, within the $|E|^4$-approximation [1,24], we may assume that $M_{\mathrm{Loc}} \approx M^d_{\mathrm{Rad}}$, which means that $(M_{\mathrm{SERS}})^{1/2}$ is an order-of-magnitude estimate of M^d_{Rad}. It is clear in Fig. 2 that $\bar{M}_{\mathrm{Tot}}$ is always much larger than M^d_{Rad}. However, $\bar{M}_{\mathrm{Tot}}$ should correspond to the sum of a radiative contribution of the order of M^d_{Rad} and a nonradiative one M_{NR}. Hence, our results indicate that $\bar{M}_{\mathrm{Tot}}$ is entirely dominated by nonradiative effects, which enables us to derive an estimated average value of $M_{\mathrm{NR}} \approx 4.3 \times 10^5$ (and in the range 3–7 $\times 10^5$ for individual events).

Such a conclusion is in agreement with standard EM theory, which predicts that M_{NR} increases dramatically, as the distance d between the molecule and the surface decreases, and should therefore dominate any radiative enhancement at small distances, in particular, for adsorbed molecules. More precisely, the nonradiative EM decay rate EF can be approximately described at short distances by a simple image dipole model [23], which (ignoring nonlocal effects) gives [1,23]:

$$M_{\mathrm{NR}} \approx \frac{3}{16(k_M d)^3} \frac{2|\mathbf{p}_\perp|^2 + |\mathbf{p}_\parallel|^2}{|\mathbf{p}_\perp|^2 + |\mathbf{p}_\parallel|^2} \mathrm{Im}\left(\frac{\epsilon - \epsilon_M}{\epsilon + \epsilon_M}\right), \qquad (4)$$

where k_M is the wave vector, ϵ and ϵ_M are the dielectric constants of the metal (silver) and the embedding medium (water) at an average emission wavelength (we use 660 nm here), and $\mathbf{p}_{\parallel,\perp}$ the $\parallel$, $\perp$ are the components of the dipole with respect to the surface. Such a model would imply a separation between CV and the metal surface of the order of 1.9 Å (depending on orientation). At such low separations, more sophisticated models including nonlocal effects [6,19,33] are necessary and would result in a larger value for d. For example, the nonlocal correction predicted by the model of Ref. [33] results in $d \approx$ 6–7 Å, in agreement with what is typically expected for an adsorbed molecule of the size of CV. Independent of the actual value of d, the fact that M_{NR} is fairly constant from event to event must be a consequence of d being approximately constant, something expected for molecules directly adsorbed on the surface. The small fluctuations of M_{NR} (by a factor ~2–3) may then be interpreted as small fluctuations in d or in orientation for different molecules.

In closing, we proposed and demonstrated a method to estimate the large total decay rate enhancements for emitters on metallic surfaces, without relying on time-resolved measurements. In the case of CV on Ag particles, it was shown that the nonradiative decay entirely dominates and is linked to the close distance of CV to the metal surface. The power of this method is perhaps more spectacularly highlighted when the actual measured lifetime is considered: the (nonmodified) radiative lifetime of CV in water is of the order of ~10 ns. Hence, a value of $\bar{M}_{\mathrm{Tot}} \approx 4.3 \times 10^5$ implies a modified lifetime of the order of ~25 fs. This method therefore provides a unique insight into ultrafast processes of single molecules on metal surfaces (which would otherwise be inaccessible with conventional approaches) and bestows a unified picture of SERS and SEF highlighting their common microscopic origin and their physical consistency.

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[1] E. C. Le Ru and P. G. Etchegoin, *Principles of Surface-Enhanced Raman Spectroscopy and Related Plasmonic Effects* (Elsevier, Amsterdam, 2009).
[2] R. Aroca, *Surface-Enhanced Vibrational Spectroscopy* (John Wiley & Sons, Chichester, 2006).
[3] R. R. Chance *et al.*, Adv. Chem. Phys. **37**, 1 (1978).
[4] J. Gersten and A. Nitzan, J. Chem. Phys. **75**, 1139 (1981).
[5] H. Metiu, Prog. Surf. Sci. **17**, 153 (1984).
[6] G. W. Ford and W. H. Weber, Phys. Rep. **113**, 195 (1984).
[7] E. Dulkeith *et al.*, Phys. Rev. Lett. **89**, 203002 (2002).
[8] S. Kühn *et al.*, Phys. Rev. Lett. **97**, 017402 (2006).
[9] P. Anger *et al.*, Phys. Rev. Lett. **96**, 113002 (2006).
[10] E. C. Le Ru *et al.*, J. Phys. Chem. C **111**, 16 076 (2007).
[11] E. C. Le Ru *et al.*, J. Phys. Chem. C **112**, 8117 (2008).
[12] K. Yoshida *et al.*, Phys. Rev. B **79**, 085419 (2009).
[13] L. Novotny and B. Hecht, *Principles of Nano-Optics* (Cambridge University Press, Cambridge, England, 2006).
[14] S. Nie and S. R. Emory, Science **275**, 1102 (1997).
[15] K. Kneipp *et al.*, Phys. Rev. Lett. **78**, 1667 (1997).
[16] E. C. Le Ru *et al.*, J. Phys. Chem. B **110**, 1944 (2006).
[17] E. C. Le Ru *et al.*, J. Phys. Chem. C **111**, 13 794 (2007).
[18] H. Xu *et al.*, Phys. Rev. Lett. **93**, 243002 (2004).
[19] P. Johansson *et al.*, Phys. Rev. B **72**, 035427 (2005).
[20] M. Ringler *et al.*, Phys. Rev. Lett. **100**, 203002 (2008).
[21] A. Leitner *et al.*, Appl. Phys. B **36**, 105 (1985).
[22] R. Carminati *et al.*, Opt. Commun. **261**, 368 (2006).
[23] P. Bharadwaj and L. Novotny, Opt. Express **15**, 14 266 (2007).
[24] E. C. Le Ru and P. G. Etchegoin, Chem. Phys. Lett. **423**, 63 (2006).
[25] E. J. Bjerneld *et al.*, J. Phys. Chem. A **108**, 4187 (2004).
[26] P. G. Etchegoin *et al.*, Anal. Chem. **81**, 682 (2009).
[27] P. C. Lee and D. Meisel, J. Phys. Chem. **86**, 3391 (1982).
[28] S. Shim *et al.*, Chem. Phys. Chem. **9**, 697 (2008).
[29] P. Matousek *et al.*, J. Raman Spectrosc. **33**, 238 (2002).
[30] M. S. Baptista and G. L. Indig, J. Phys. Chem. B **102**, 4678 (1998).
[31] M. Moskovits, J. Chem. Phys. **77**, 4408 (1982).
[32] E. C. Le Ru *et al.*, J. Raman Spectrosc. **39**, 1127 (2008).
[33] I. A. Larkin *et al.*, Phys. Rev. B **69**, 121403 (2004).