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Electrochemical Shot Noise of a Redox Monolayer

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Redox monolayers are the base for a wide variety of devices including high-frequency molecular diodes or biomolecular sensors. We introduce a formalism to describe the electrochemical shot noise of such a monolayer, confirmed experimentally at room temperature in liquid. The proposed method, carried out at equilibrium, avoids parasitic capacitance, increases the sensitivity, and allows us to obtain quantitative information such as the electronic coupling (or standard electron transfer rates), its dispersion, and the number of molecules. Unlike in solid-state physics, the homogeneity in energy levels and transfer rates in the monolayer yields a Lorentzian spectrum. This first step for shot noise studies in molecular electrochemical systems opens perspectives for quantum transport studies in a liquid environment at room temperature as well as highly sensitive measurements for bioelectrochemical sensors.

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Self-assembled monolayers (SAMs) composed of nanometric-long redox molecules are building blocks for molecular electronics and electrochemistry. They can behave as molecular diodes operating at ultrahigh frequency (potentially as a rectenna in the visible spectrum) [1,2], with an on-off ratio breaking the Landauer limit [3,4], and show interesting features such as signatures of collective quantum interference effects at room temperature [5–7]. In addition, their operation in liquid offers a direct link between quantum transport and electrochemistry [8–10] that provides unique opportunities. For example, the nanoscale measurements of electrochemical signals remains extremely challenging while key to the development of nanobiosensors [11]. Several approaches have been explored to tackle the challenge, using redox cycling [12], high frequency measurements [13], and fluorescence [14]. The underlying challenges arise from the presence of parasitic capacitances and from the fact that under typical measurement conditions, the current scales with the sensor area, leading to difficulties in retrieving the signal with micro- and nanoscale electrodes. Simultaneously, these systems offer unique properties as quantum devices. Probably the most intriguing aspect for the solid-state physics community is the potential for millions of single-energy level quantum dots simultaneously operating at room temperature, with extremely small dispersion, tunable electronic coupling [15], and the Frank Condon effect [16].

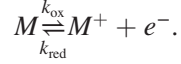
We propose here to exploit and formalize the shot noise induced by reversible single electron transfers of electroactive molecules attached to an electrode as a new, very sensitive electrochemical technique and as a way to characterize the homogeneity in the electronic properties of these assembled molecular quantum dots. Shot noise has been extensively studied in solid-state physics [17] and more recently in molecular electronics [18,19], but not in electrochemistry, except for the shot noise due to a variation of the number of molecules in a nanogap [20–23]. Such measurements are usually challenging because of the ubiquitous $1/f$ noise (e.g., in solid-state physics [24], quantum transport [25], molecular electronics [26], or in liquid [27]) which is typically circumvented by low-temperature measurements and by measurements at higher relative frequencies.

The $1/f$ noise here is not dominant thanks to the well-defined energy level and electron transfer rates of the redox molecules of the monolayer, allowing us to study its low-frequency shot noise arising from the sum of single-electron trapping and detrapping events to each molecule with a narrow distribution in time constants. A simple and straight-forward equation of the shot noise is proposed, giving direct access to the distribution of the charge transfer rates and the number of charge carriers. This approach provides clearly readable signals even when Faradaic currents become unmeasurable, avoids the parasitic capacitance issue, and allows for measurements without extra excitation other than the thermal noise.

Electroactive redox molecules can be seen as single-electron quantum dots with extremely small energy dispersion, even in liquid and at ambient temperature [5]. The equilibrium reaction of an ideally reversible redox

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couple M^+/M attached to a metallic electrode and held at a distance z from the electrode [insets Fig. 1(a)] can be written as



Using the Marcus-Hush formalism to describe the electron transfer rates gives [28]

$$k_{\text{ox,red}}^{MH} = \frac{\rho H^2}{\hbar} \sqrt{\frac{\pi}{k_B T \lambda}} \int_{-\infty}^{+\infty} \frac{1}{1 + e^{\frac{x}{k_B T}}} e^{-\frac{(x-\lambda \pm \eta)^2}{4\lambda k_B T}} dx \quad (1)$$

with k_{ox} the oxidation rate, k_{red} the reduction rate, ρ the density of state in the metallic electrode, H^2 the electronic coupling, \hbar the reduced Planck constant, λ the reorganization energy (the Frank Condon effect due to water molecules reorganizing after charging the redox molecule), T the temperature, k_B the Boltzmann constant, and $\eta = q(E - E^0)$ with E the potential at the electrode, E^0 the standard potential of the molecule, and q the elementary charge. Equation (1) is analogue to the Landauer formalism in solid-state physics [8]. The specificity of the redox molecules is their energy level broadening due to the large reorganization energy. Equation (1) can be simplified to

Eqs. (2) and (3) (Buttler-Volmer model) when $|\eta| \ll \lambda$ which is often the case. It will be used here initially for its simplicity.

$$k_{\text{ox}}^{\text{BV}} = k_0 e^{-\beta z} e^{\alpha \frac{\eta}{k_B T}}, \quad (2)$$

$$k_{\text{red}}^{\text{BV}} = k_0 e^{-\beta z} e^{-(1-\alpha) \frac{\eta}{k_B T}}, \quad (3)$$

with β the tunneling decay coefficient (1 \AA^{-1}), α the charge transfer coefficient, and k_0 the standard electron transfer rate at a distance $z = 0$ (in s^{-1}). The exponential decay part is formally contained in the electronic coupling term H^2 in Eq. (1) but is usually extracted for convenience to be included in the Butler-Volmer model [28].

Sampled current staircase voltammetry (SCV) is the electrochemical technique used to interrogate the surface-attached redox species [29], analogue to the charge pumping technique in semiconductors [30]. The electrode potential is raised in small steps of height E_{step} , and the current is recorded as a function of time, up to a time t_{step} , corresponding to the steps duration [Fig. 1(c)].

The current I , in the case of slow scan rate and long sampling time (i.e., $k_{\text{sum}} = k_{\text{ox}}^{\text{BV}} + k_{\text{red}}^{\text{BV}} \gg 1/t$), can be expressed as (details in SM)

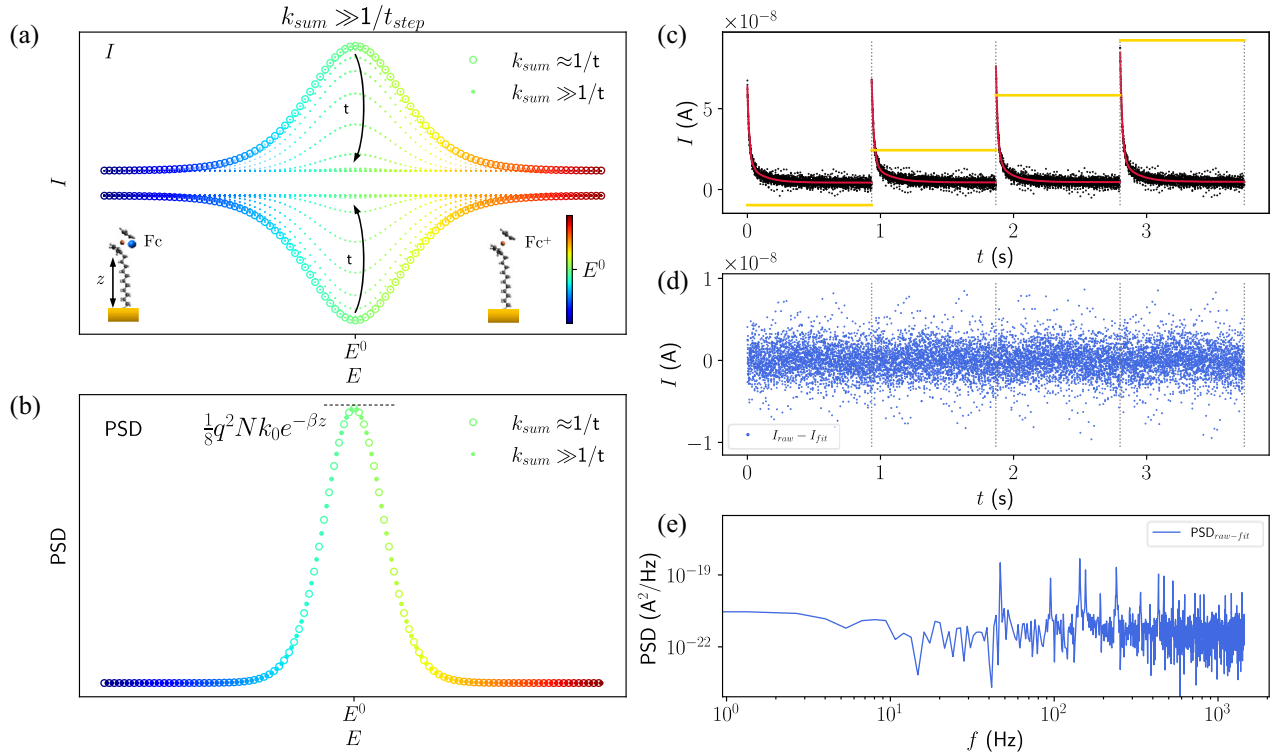


FIG. 1. Illustration of current and noise versus time and voltage, considering a slow scan rate compared to the electron transfer rates ($k_{\text{sum}} \gg 1/t_{\text{step}}$). (a) I vs E , with the evolution of I as the time after voltage step is increased. (b) Voltnoisograms (PSD vs E) taken at low frequency [Eq. (8)] corresponding to the same conditions as in (a). (c) Sampled staircase voltammetry example, with the raw current data (black dots), a double exponential decay fit of the current (red), and the voltage steps (yellow). In this example, each voltage step is of 2.25 mV, starting at 195 mV. (d) Raw currents subtracted with exponential fits (blue). (e) PSD spectrum of one current time trace in (d).

$$I = \frac{Nq\nu}{4k_B T} \frac{1}{\cosh^2\left(\frac{\eta}{2k_B T}\right)} \quad (4)$$

with N the total number of molecules and $\nu = E_{\text{step}}/t_{\text{step}}$ the voltage scan rate. Note that such current represents the transition of the charges at a certain scan rate, and not an equilibrium value of the current at a given potential. Figure 1(a) shows I versus applied voltage E at a given scan rate and at different times t after the voltage step, exhibiting a quick decrease of amplitude.

One way to consider the noise of the current versus time [Fig. 1(b)] is to look at its power spectrum density (PSD, noted S in equations). The PSD [Figs. 1(b) and 1(e)] can be seen as a description of how the variance of the measured signal is spread in the frequency domain. The system under study has two states related to the oxidized and reduced states of the molecules, here attached to a single electrode. Each molecule is expected to lead to the so-called random telegraph signal (RTS) which is a shot noise due to individual transfer of electrons in and out of the single-electron boxes. To avoid confusion, in such a single-electrode system, the shot noise is not expected to be compared to $2qI$ because at equilibrium, where both oxidation and reduction reactions compensate each other, $I = 0$ while $S > 0$ (discussion in SM) [31]. In general, the RTS is typically associated with $1/f$ noise due to the wide range of energy levels and electron transfer rates [32,33]. However, an ensemble of reversible redox couples, like those found in a redox SAM in liquid, can be thought of as an ensemble of quantum dots with very similar energy levels because the molecules that make up the SAM have strictly identical atomic structures and may differ only in their orientation relative to the surface [5]. Assuming first that all N molecules have identical energy levels E^0 and charge transfer rates k_{ox} and k_{red} for oxidation and reduction, respectively, the PSD can be expressed as [32]

$$S(f, \eta, N) = 4N\Delta I^2 \frac{k_{\text{ox}}k_{\text{red}}}{k_{\text{ox}} + k_{\text{red}}} \frac{1}{(k_{\text{ox}} + k_{\text{red}})^2 + (2\pi f)^2} \quad (5)$$

with f the frequency and ΔI the current corresponding to the oxidation (or reduction) of one molecule. If we consider ΔI as the transfer of one electron of charge q per the average time taken for transferring one electron (i.e., $\Delta I = \{q/[(1/k_{\text{ox}}) + (1/k_{\text{red}})]\}$), S can be rewritten as

$$S(f, \eta, N) = 4Nq^2 \frac{(k_{\text{ox}}k_{\text{red}})^3}{(k_{\text{ox}} + k_{\text{red}})^3} \frac{1}{(k_{\text{ox}} + k_{\text{red}})^2 + (2\pi f)^2} \quad (6)$$

which becomes at low frequency (assuming $\alpha = 0.5$)

$$\lim_{f \rightarrow 0} S(\eta, N) = 4Nq^2 \frac{(k_{\text{ox}}k_{\text{red}})^3}{(k_{\text{ox}} + k_{\text{red}})^5}, \quad (7)$$

$$= \frac{1}{8} Nq^2 \frac{k_0 e^{-\beta z}}{\cosh^5\left(\frac{\eta}{2k_B T}\right)}. \quad (8)$$

This equation expresses the dependence of the low frequency electrochemical shot noise of the redox SAM versus the electrode potential. The corresponding curve is plotted in Fig. 1(b). Similarly to current SCV signals, it presents a peak at E^0 , but narrower than that of the SCV peak, with a full width at half-maximum (FWHM)

$$E_{\text{FWHM}}^S = 4 \operatorname{acosh}(\sqrt[5]{2}) \frac{k_B T}{q} \approx 56 \text{ mV}. \quad (9)$$

Note that unlike the current, S does not depend on ν as the PSD is considered for a system at equilibrium. S is also independent of the potential scan direction. Interestingly, the limiting cases of $\eta \rightarrow 0$ and $f \rightarrow 0$ give access to the electron transfer rate k_0 and the total number of molecules N .

$$\lim_{\eta \rightarrow 0} S(f, N) = \frac{1}{2} Nq^2 k_0 e^{-\beta z} \frac{1}{4 + \left(\frac{2\pi f}{k_0 e^{-\beta z}}\right)^2} \quad (10)$$

with the corner frequency $f_c = (1/2\pi)k_0 e^{-\beta z}$:

$$\lim_{\eta \rightarrow 0, f \rightarrow 0} S(N) = \frac{1}{8} Nq^2 k_0 e^{-\beta z}. \quad (11)$$

The main result of the present work is Eq. (11), linking directly and simply k_0 and N to the noise measured at low frequency for $E = E^0$. Provided the corner frequency of the PSD f_c can be measured [Fig. S1(b)], the individual values of k_0 and N are obtained from Eq. (10) and Eq. (11). Alternatively, if N is known independently, k_0 can be straightforwardly derived from S at $E = E^0$ [Eq. (11)].

To demonstrate the validity of the previous analysis, an experiment is set using ferrocene undecanethiol $\text{Fc}(\text{CH}_2)_{11}\text{SH}$ self-assembled on a gold microelectrode. A two-electrode electrochemical cell setup is used in a Faraday cage, using a $[\text{NaClO}_4] = 0.5 \text{ M}$ aqueous electrolyte and a Ag/AgCl electrode (3 M NaCl) acting as both reference and counter electrode. Details about the sample preparation and the measurement setup can be found in the Supplemental Material ([34] Figs. S2 and S3). The system is interrogated using staircase voltammetry [Fig. S1(c)], which is equivalent to linear cyclic voltammetry (CV) at slow scan rates [43]. Our motivation is to offer a comparison of the well-known technique of cyclic voltammetry with the results obtained looking at the shot noise of the system.

The Fig. 2 shows an example of current CVs at different (low) scan rates ν . The signal is centered around a potential value of $E^0 = 0.35 \pm 0.02 \text{ V}$ vs Ag/AgCl , which corresponds to the expected standard potential for such surface-attached Fc molecules [44–46]. The density is estimated here at $4.2 \times 10^{-10} \text{ mol}/\text{cm}^2$, close to the values reported in the literature for packed SAMs ($4.4 \sim 4.9 \times 10^{-10} \text{ mol}/\text{cm}^2$) [1,47]. The peak currents of the CV exhibit the usual behavior

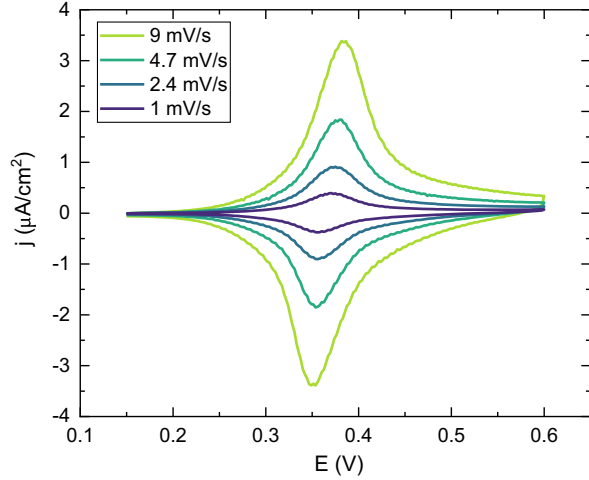


FIG. 2. Example of current CVs obtained at different ν (electrode area $\approx 45 \text{ mm}^2$, E vs Ag/AgCl (3 M NaCl), electrolyte: $[\text{NaClO}_4] = 0.5 \text{ M}$).

for a surface-confined reversible couple, with a linear dependency of the current versus ν (example data Fig. S11).

PSD signals were measured at several scan rates (see details in SM), their magnitude at 20 Hz versus E (called “voltnoisogram” for concision) shown in Fig. 3(a), (full set Fig. S12). Similar data without the Fc molecules can be found in Fig. S10. The PSD voltnoisograms behave as expected with a peak-shaped curve centered around $E^0 \approx 0.35 \text{ V}$, close to the standard potential of Fc. As predicted from Eq. (8), the peak value of the PSD voltnoisograms [Fig. 3(b)] remains quasiconstant for $\nu < 3 \text{ mV/s}$ (see details in SM Fig. 3).

Figure 4(a) shows a CV scan at $\nu = 0.014 \text{ mV/s}$ where no faradaic current signal can be identified. Figure 4(b) shows PSD values at $E < E^0$, $E \approx E^0$, and $E > E^0$ on the forward scan. Figure 4(c) shows the variation of PSD at 10 Hz as a function of the voltage, showing a clear peak. These results demonstrate the ability to detect an electrochemical reaction at an electrode through shot noise measurements, even when the average current signal from the CV does not show any reaction. The number of molecules $N = 7.5 \times 10^{10}$ is calculated from the CV data at higher scan rates (Fig. S11), and using this value and Eq. (11), the peak amplitude of PSD data shown in Fig. 3 yields $k_0 = 6.3 \times 10^7 \text{ s}^{-1}$ ($z = 1 \text{ nm}$), in good agreement with literature values for this molecule [15,20].

The FWHM of the PSD peaks on Fig. 4 is $\approx 90 \text{ mV}$, broader than the 56 mV predicted by Eq. (9). Taking $\eta = 0$ in the Eq. (1) gives an expression for k_0 , notably showing dependencies with H and λ [28]. Previous work [15] showed that variations of λ within physically reasonable limits do not significantly impact the electron transfer rates. However, the electronic coupling term H typically varies following lognormal distributions [5] and can impact significantly the resulting value of k_0 with

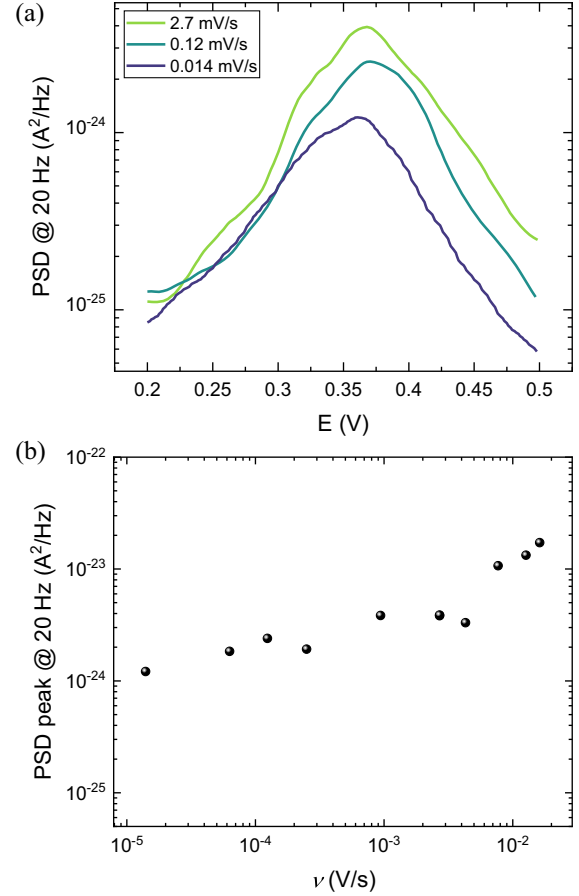


FIG. 3. (a) PSD of the current versus E obtained at different ν , at $f \approx 20 \text{ Hz}$. (b) PSD at $f \approx 20 \text{ Hz}$ and $E = 0.35 \text{ V}$ versus ν .

variations of just a few percent of its average value (see Figs. S13 and S14). If a lognormal distribution of the fluctuation of H (and thus, of k_0 as well) is assumed, a standard deviation of $\sigma \approx 4\%$, comparable to what was reported in Ref. [5] ($\approx 2\%$), can explain the broadening observed in PSD [Fig. 4(c), dashed line].

There is a significant difference between molecular monolayers in liquid and solid-state devices in terms of electrostatic forces. In the first case, the electrostatic interactions between neighboring molecules are greatly reduced thanks to the high permittivity of water. Previous research on Coulomb repulsion φ [Eq. (12)] within similar Fc SAMs showed negligible impact on current CV [5,48].

$$\varphi = q \frac{1 - \left[1 + \left(\frac{r_a}{d}\right)^2\right]^{-0.5}}{4\pi\epsilon_0\epsilon_r d} \quad (12)$$

with d the intermolecular distance, r_a the distance to counterions, ϵ_0 the permittivity of the vacuum, and $\epsilon_r = \epsilon_{\text{H}_2\text{O}}/\epsilon_{\text{SiO}_2}$ the permittivity of the medium under consideration. Taking the same formalism and distribution of d as in [5] for φ but changing $\epsilon_{\text{H}_2\text{O}} = 79$ to $\epsilon_{\text{SiO}_2} = 3.9$ results in

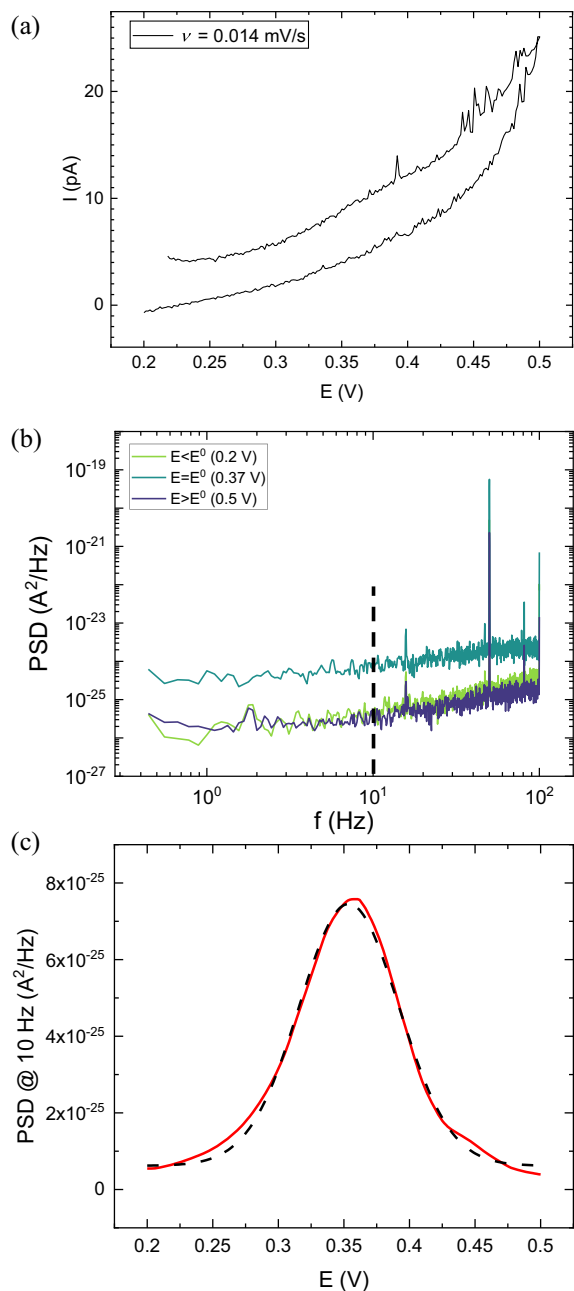


FIG. 4. (a) CV of a FcC_{11}SH SAM on gold. (b) PSD measured at 0.014 mV/s at $E < E^0$, $E \approx E^0$, and $E > E^0$. (c) PSD versus potential at 10 Hz . The dashed line is fitted using Eq. (7) considering a lognormal distribution of H with $\sigma = 3.97\%$ of the mean value of H .

variations of E_{FWHM}^S from 1% to 45%, respectively (see Figs. S15 and S16). As a result the screening of electrostatic interaction by water avoids a dispersion of the energy levels, such as the one observed in nanotransistors [33], and thus, avoids the domination of a $1/f$ noise resulting from the sum of multiple Lorentzian spectra with different amplitude and corner frequencies.

In conclusion, we demonstrated the measurement of the shot noise generated by an ensemble of surface-attached Fc

redox molecules, which can be seen as identical single-electron boxes, in liquid and in ambient conditions. A formalism is proposed to understand it and exhibit dependencies between such noise and electronic coupling. This constitutes a further step toward nanoelectrochemistry and single molecule measurements, which could be practically achieved using our technique combined with a transducer such as a nanotransistor and be extended to other systems such as quantum dot monolayer [49].

Our technique allows for the measurement of electron transfer rates at low frequencies without the need for highly time-resolved instrumentation. Although we compared our technique with traditional voltammetry techniques, exhibiting a clear signal in PSD when I tended to zero, the very concept of a “potential scan” is actually not required to perform noise measurements. As few as two points at potentials far from E^0 and one at E^0 can suffice to resolve the eventual background noise of the experiment and the noise due to the attached molecule, yielding k_0 and N provided the knowledge of β and z . Concurrently, since the measurements are carried out at equilibrium, capacitive contributions are altogether avoided, improving the signal and simplifying drastically the interpretation of the data. This opens perspectives in the field of biosensors [11], where the limit of detection of existing techniques could be further extended by shot noise analysis; and in high-frequency molecular diodes, where the electron transfer rate can be estimated through the low-frequency noise.

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- [1] J. Trasobares, D. Vuillaume, D. Théron, and N. Clément, *Nat. Commun.* **7**, 12850 (2016).
- [2] C. Reynaud, D. Duché, J.-J. Simon, E. Sanchez-Adaime, O. Margeat, J. Ackermann, V. Jangid, C. Lebouin, D. Brunel, F. Dumur, D. Gimes, G. Berginc, C. Nijhuis, and L. Escoubas, *Prog. Quantum Electron.* **72**, 100265 (2020).
- [3] N. Clement and A. Fujiwara, *Nat. Nanotechnol.* **12**, 725 (2017).
- [4] X. Chen, M. Roemer, L. Yuan, W. Du, D. Thompson, E. del Barco, and C. A. Nijhuis, *Nat. Nanotechnol.* **12**, 797 (2017).

- [5] J. Trasobares, J. Rech, T. Jonckheere, T. Martin, O. Aleveque, E. Levillain, V. Diez-Cabanes, Y. Olivier, J. Cornil, J.P. Nys, R. Sivakumarasamy, K. Smaali, P. Leclere, A. Fujiwara, D. Théron, D. Vuillaume, and N. Clément, *Nano Lett.* **17**, 3215 (2017).
- [6] Y. Li, D. Wang, W. Peng, L. Jiang, X. Yu, D. Thompson, and C. A. Nijhuis, *Nano Today* **44**, 101497 (2022).
- [7] P. Gehring, J. M. Thijssen, and H. S. J. van der Zant, *Nat. Rev. Phys.* **1**, 381 (2019).
- [8] K. H. Bevan, M. S. Hossain, A. Iqbal, and Z. Wang, *J. Phys. Chem. C* **120**, 179 (2016).
- [9] A. Nitzan and M. A. Ratner, *Science* **300**, 1384 (2003).
- [10] R. A. Marcus, *J. Chem. Phys.* **24**, 966 (1956).
- [11] S. Li, Y. Coffinier, C. Lagadec, F. Cleri, K. Nishiguchi, A. Fujiwara, T. Fujii, S.-H. Kim, and N. Clément, *Biosens. Bioelectron.* **216**, 114643 (2022).
- [12] F.-R. F. Fan, J. Kwak, and A. J. Bard, *J. Am. Chem. Soc.* **118**, 9669 (1996).
- [13] S. Grall, I. Alić, E. Pavoni, M. Awadein, T. Fujii, S. Müllegger, M. Farina, N. Clément, and G. Gramse, *Small* **17**, 2101253 (2021).
- [14] S. Huang, M. Romero-Ruiz, O. K. Castell, H. Bayley, and M. I. Wallace, *Nat. Nanotechnol.* **10**, 986 (2015).
- [15] C. E. D. Chidsey, *Science* **251**, 919 (1991).
- [16] C. Demaille, N. Clément, A. Chovin, S. H. Kim, and Z. Zheng, *Chem. Sci.* **14**, 3652 (2023).
- [17] Y. Blanter and M. Büttiker, *Phys. Rep.* **336**, 1 (2000).
- [18] D. Djukic and J. M. van Ruitenbeek, *Nano Lett.* **6**, 789 (2006).
- [19] O. S. Lumbroso, L. Simine, A. Nitzan, D. Segal, and O. Tal, *Nature (London)* **562**, 240 (2018).
- [20] M. A. G. Zevenbergen, B. L. Wolfrum, E. D. Goluch, P. S. Singh, and S. G. Lemay, *J. Am. Chem. Soc.* **131**, 11471 (2009).
- [21] K. Mathwig, D. Mampallil, S. Kang, and S. G. Lemay, *Phys. Rev. Lett.* **109**, 118302 (2012).
- [22] E. Kätelhön, K. J. Krause, P. S. Singh, S. G. Lemay, and B. Wolfrum, *J. Am. Chem. Soc.* **135**, 8874 (2013).
- [23] P. S. Singh and S. G. Lemay, *Anal. Chem.* **88**, 5017 (2016).
- [24] P. Karnatak, T. Paul, S. Islam, and A. Ghosh, *Adv. Phys.* **2**, 428 (2017).
- [25] E. Paladino, Y. M. Galperin, G. Falci, and B. L. Altshuler, *Rev. Mod. Phys.* **86**, 361 (2014).
- [26] N. Clément, S. Pleutin, O. Seitz, S. Lenfant, and D. Vuillaume, *Phys. Rev. B* **76**, 205407 (2007).
- [27] A. Fragasso, S. Schmid, and C. Dekker, *ACS Nano* **14**, 1338 (2020).
- [28] J. F. Smalley, S. W. Feldberg, C. E. D. Chidsey, M. R. Linford, M. D. Newton, and Y.-P. Liu, *J. Phys. Chem.* **99**, 13141 (1995).
- [29] H. A. Heering, M. S. Mondal, and F. A. Armstrong, *Anal. Chem.* **71**, 174 (1999).
- [30] A. Fujiwara, K. Nishiguchi, and Y. Ono, *Appl. Phys. Lett.* **92**, 042102 (2008).
- [31] R. Sarpeshkar, T. Delbruck, and C. Mead, *IEEE Circuits Dev. Mag.* **9**, 23 (1993).
- [32] S. Machlup, *J. Appl. Phys.* **25**, 341 (1954).
- [33] N. Clément, K. Nishiguchi, A. Fujiwara, and D. Vuillaume, *Nat. Commun.* **1**, 92 (2010).
- [34] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevLett.130.218001> for discussions on the nature of the noise, the derivation of the current, and the impact of the electron coupling, which includes the Refs. [35–42].
- [35] E. Laviron, *J. Electroanal. Chem. Interfacial Electrochem.* **101**, 19 (1979).
- [36] K.-C. Huang and R. J. White, *J. Am. Chem. Soc.* **135**, 12808 (2013).
- [37] S. Westerlund and L. Ekstam, *IEEE Trans. Dielectr. Electr. Insul.* **1**, 826 (1994).
- [38] C. Wen, S. Zeng, K. Arstila, T. Sajavaara, Y. Zhu, Z. Zhang, and S.-L. Zhang, *ACS Sens.* **2**, 300 (2017).
- [39] N. Clément, S. Pleutin, D. Guérin, and D. Vuillaume, *Phys. Rev. B* **82**, 035404 (2010).
- [40] K. Prabha and H. S. Jayanna, *Open J. Polym. Chem.* **05**, 47 (2015).
- [41] N. E. Israeloff, *Phys. Rev. B* **53**, R11913 (1996).
- [42] W. Schottky, *Ann. Phys. (Berlin)* **362**, 541 (1918).
- [43] J. H. Christie and P. J. Lingane, *J. Electroanal. Chem.* (1959) **10**, 176 (1965).
- [44] H. Tian, Y. Dai, H. Shao, and H.-Z. Yu, *J. Phys. Chem. C* **117**, 1006 (2013).
- [45] N. Nerngchamnong, D. Thompson, L. Cao, L. Yuan, L. Jiang, M. Roemer, and C. A. Nijhuis, *J. Phys. Chem. C* **119**, 21978 (2015).
- [46] N. K. Gupta, E. A. Wilkinson, S. K. Karuppanan, L. Bailey, A. Vilan, Z. Zhang, D.-C. Qi, A. Tadich, E. M. Tuite, A. R. Pike, J. H. R. Tucker, and C. A. Nijhuis, *J. Am. Chem. Soc.* **143**, 20309 (2021).
- [47] C. A. Nijhuis, W. F. Reus, and G. M. Whitesides, *J. Am. Chem. Soc.* **131**, 17814 (2009).
- [48] M. G. Reuter, M. C. Hersam, T. Seideman, and M. A. Ratner, *Nano Lett.* **12**, 2243 (2012).
- [49] J. M. Fruhman, H. P. Astier, B. Ehrler, M. L. Böhm, L. F. L. Eyre, P. R. Kidambi, U. Sassi, D. De Fazio, J. P. Griffiths, A. J. Robson, B. J. Robinson, S. Hofmann, A. C. Ferrari, and C. J. B. Ford, *Nat. Commun.* **12**, 4307 (2021).