Pump-Probe Noise Spectroscopy of Molecular Junctions

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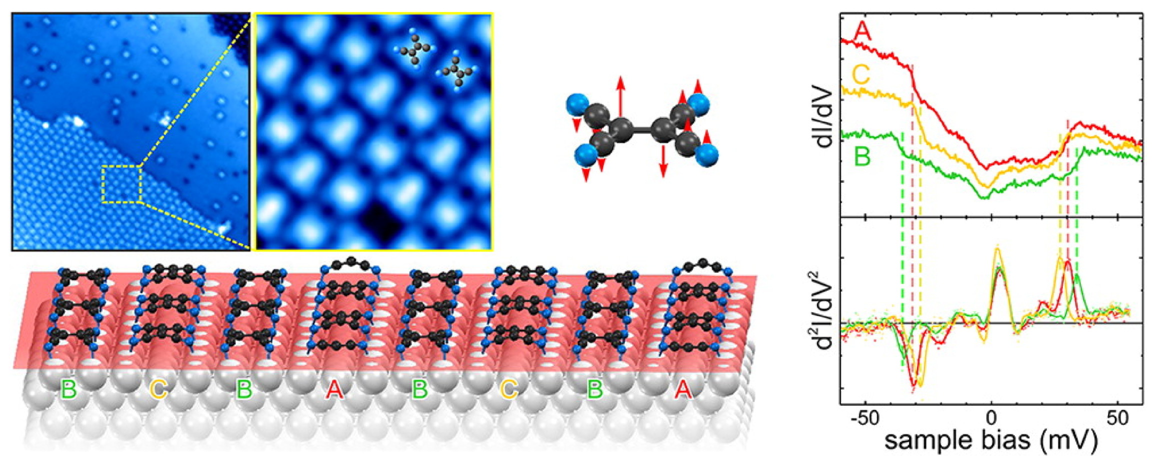
Summary

A pump-probe *dc* shot noise spectroscopy for molecular junctions is proposed as a suitable technique to identify intramolecular dynamics on the sub-picosecond time scale. We show that intramolecular dynamical processes not directly related to charge transfer in the current direction are captured by noise and missed by current measurements.

Molecular Spectroscopies

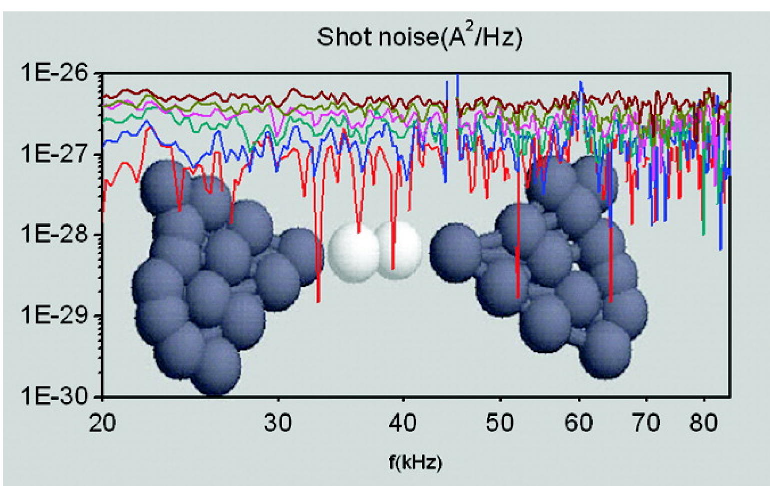
Several spectroscopic techniques have been succesfully adpated to the study and characterization of molecular junctions such as Inelastic Tunneling Spectroscopy, Noise Spectroscopy and Surface Enhanced Raman Spectroscopy.

IETS ✓



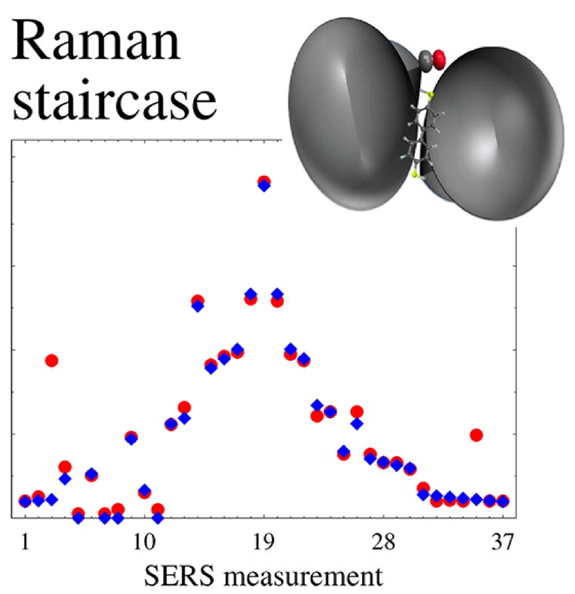
Wegner, D. et. al *Nano Lett.* **2013**, 13, 2346-2350

Shot Noise ✓

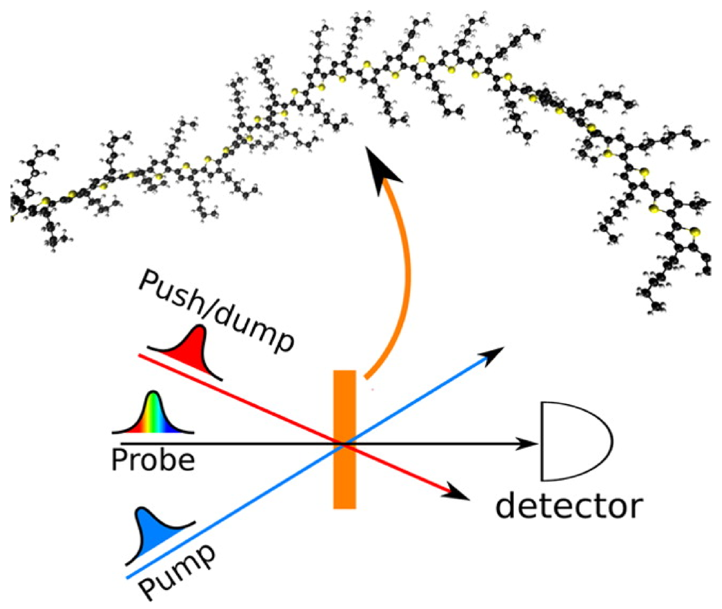


Djukic, D.; van Ruitenbeek, J. M.
Nano Lett. **2006**, 6, 789-793

SERS ✓



Banik, M. et. al.
J. Phys. Chem. Lett. **2013**, 4, 88-92

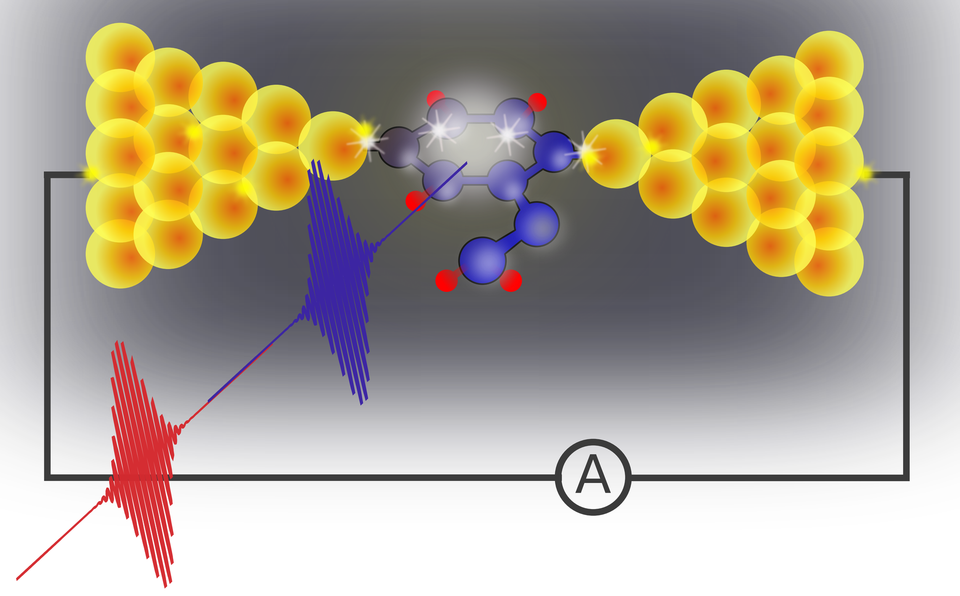


Pump-probe Spectroscopy (?)
However, pump-probe-type spectroscopy has not been realized in junctions!

Kee, T. W.
J. Phys. Chem. Lett. **2014**, 5, 3231-3240

Setting for a Pump-Probe Noise Spectroscopy

A pump-probe spectroscopy for molecular junctions, utilizing laser pulse pair sequences (LPPS) is presented. The setting consists of a junction that is externally perturbated by an LPPS, with a repetition period t_{fi}. The pulses are identical in amplitude, frequency and pulse width, and they are also characterized by a delay time t_d. Optical excitation results in current through the junction.



Intramolecular dynamics: Rabi oscillations

The *dc* noise measurement provides information about intramolecular dynamics. Note that the sub-picosecond time scale (the time scale of the intramolecular processes)is not accessible from direct measurements. We find that transient dynamics which is not directly related to charge transfer in the current direction of the junction is missed by the *dc* current but recovered with a noise measurement.

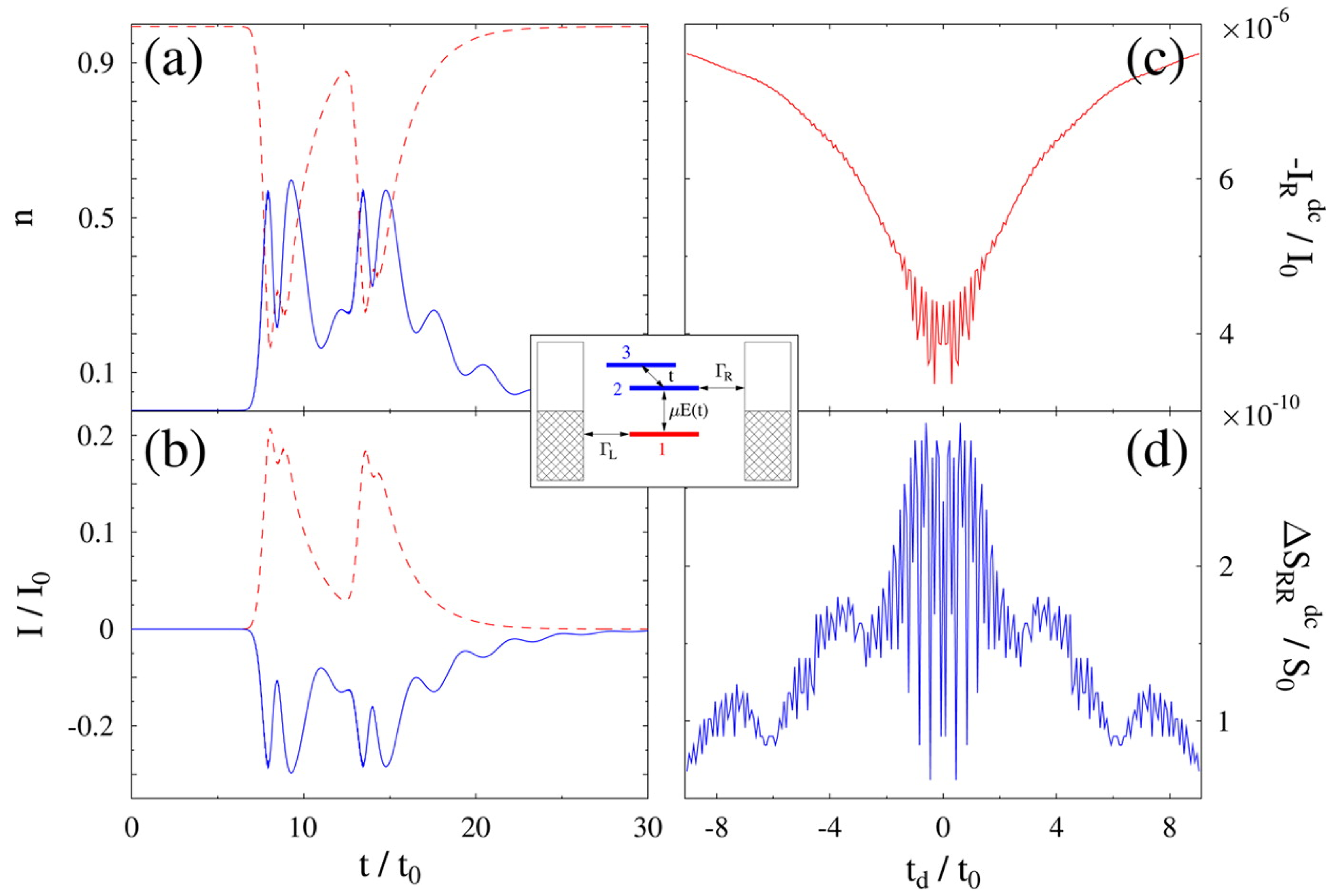


Figure : 1 (a) transient populations of the HOMO (dashed line, red) and LUMO level 2 (solid line, blue) and (b) transient currents at the left (dashed line, red) and right (solid line, blue) molecule-contacts interfaces. Average transport characteristics of the junction are (c) *dc* current and (d) shot *dc* noise $\Delta S^{dc}_{RR}(t_d)$ at the right molecule-contact interface as functions of the pair pulse delay time, t_d . Parameters are $k_B T = 0.045$, $\varepsilon_1 = -25$, $\varepsilon_2 = \varepsilon_3 = 25$, $t = 1$, pulse amplitude $A = 5$, pulse frequency $\Omega = \varepsilon_2 - \varepsilon_1$, $t_i = 9.1$, $\tau = 0.75$, $t_d = 6$, and $t_{fi} = 3 \times 10^5$.

Theory

If $\hat{I}_K$ represents the current operator at the molecule-contact interface K, the time-dependent expectation is given by $I_K(t) = \langle \hat{I}_K(t) \rangle$ and that for noise is $S_{K,K}(t_1,t_2) = \frac{1}{2}\langle\{\hat{I}_K(t_1), \hat{I}_K(t_2)\}\rangle$. We calculate the corresponding, experimentally accesible, average *dc* counterparts.

dc Current $$I^{dc}_K(t_d) = \frac{1}{t_{fi}}\int_0^{t_{fi}} I_K(t)dt$$

dc Noise $$S^{dc}_{K,K'}(t_d) = \frac{1}{t_{fi}}\int_0^{t_{fi}} dt_1 \int_0^{t_{fi}} dt_2 S_{K,K'}(t_1,t_2)$$

Intramolecular dynamics: circular currents

In the presence of a magnetic field, a circular current may be induced in the junction. Here we notice again that the average current will miss the corresponding dynamics. On the contrary, the *dc* noise measurements do allow us to reveal the dynamics.

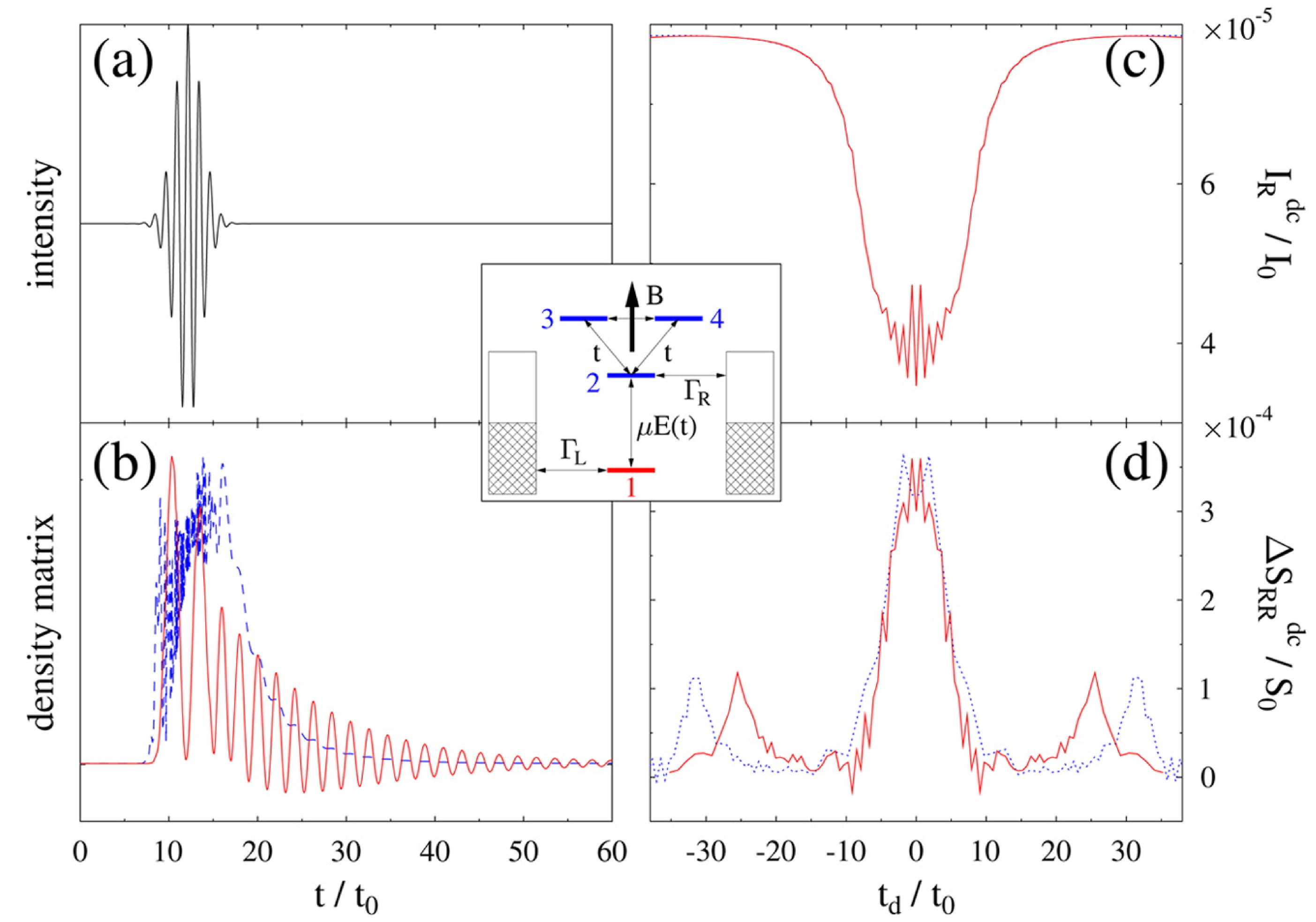


Figure : 2 Response of a junction with a ring structure in the presence of magnetic field B. Shown are (a) single pulse and (b) transient response of the system - population of the LUMO level 2 (dashed line, blue) and coherence between levels 3 and 4 (solid line, red). In this case $B = 5T$. (c) *dc* current and (d) *dc* shot noise $\Delta S^{dc}_{RR}(t_d)$ at the right molecule-contact interface as functions of the pair pulse delay time,t_d . Here, $B = 5T$ (dotted line, blue) and $B = 10T$ (solid line, red). Parameters are $k_B T = 0.45$, $\varepsilon_1 = -2.5$, $\varepsilon_2 = \varepsilon_3 = \varepsilon_4 = 2.5$, $t = 1$,

In this case the peaks corresponding to the intramolecular process are satellites of the central peak. Shift in the peak positions account for change of the Larmor frequency for different magnetic field strengths.

Conclusions

- The *dc* response to LPPS yields information on the dynamics at sub-picosecond time scale.
- The *dc* noise measurements contain richer information than the corresponding current data.
- Pump-probe noise spectroscopy is potentially a new powerful tool to characterize time-dependent and transient dynamics in junctions.

Acknowledgements

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