Low-frequency electron dynamics of organic charge-transfer salts studied by fluctuation spectroscopy

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Electronic fluctuations (noise) — often considered as an unwanted disturbance of the true measurement signal — reveal 'hidden' pieces of information, which are not present in the mean quantity, i.e. the resistance (or conductance) itself. The objective of this project is to utilize fluctuation spectroscopy as a new approach to investigate the low-frequency dynamics of interacting π-electrons in organic charge-transfer salts [1]. This method is non-invasive, since the dynamics can be studied without incepting additional electrons. Over the years, these molecular complexes have provided unprecedented model systems for exploring the physics of low-dimensional electron systems with both strong electron-electron and electron-phonon interactions. These combined effects give rise to the rich phenomenology of ground states encountered in these materials. Our aim is to extract information on the temperature, pressure, and electric- and magnetic-field dependence of the resistance (or conductance) noise power spectral density, which characterizes the dynamics of the charge fluctuations. The dynamical properties of electrons in turn play an important role in the vicinity of correlation-driven ordering phenomena and also when the carriers couple to different modes of structural (lattice) excitations.

[1] J. Müller, *ChemPhysChem* **2011**, 12, 1222 1245 (review article)

Charge carrier dynamics at the finite-temperature Mott critical endpoint

We investigate the dynamics of correlated charge carriers in the vicinity of the Mott metal-insulator transition in the quasi-two-dimensional organic charge-transfer salt κ-$(D_8\text{-ET})_2Cu[N(CN)_2]Br$, which is located near the second-order critical endpoint (p_0, T_0) of the first-order Mott transition. We observe fluctuations of general $1/f^{\alpha}$-type which quantitatively very well described by a phenomenological model based on the concept of non-exponential

kinetics. The main result is a correlation-induced enhancement of the fluctuations accompanied by a substantial shift of spectral weight to low frequencies in the vicinity of the Mott critical endpoint. This sudden slowing down of the electron dynamics, observed here in a pure Mott system, may be a universal feature of metal-insulator transitions. Our findings are compatible with an electronic phase separation in the critical region of the phase diagram and offer an explanation for the not yet understood absence of effective mass enhancement when crossing the Mott transition [2].

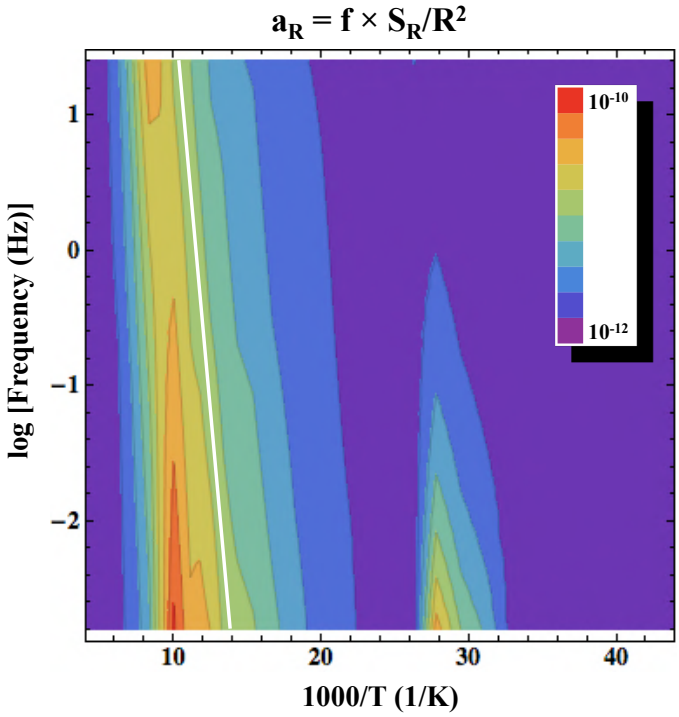

Figure 1: Contour diagram of the dimensionless relative noise level (color coded) as a function of temperature and frequency in an Arrhenius plot. The strong fluctuations at elevated temperatures $\sim 100\,\mathrm{K}$ occurring in the whole frequentcy range are due to structural, glass-like excitations of the donor ET molecules terminal ethylene groups. White line represents an activation energy of 260 meV. In addition, there is a drastic and abrupt increase of the fluctuations at $T_0 \sim 36\,\mathrm{K}$ occurring only at the lowest frequencies representing a sudden slowing down of the carrier dynamics die to the Mott critical endpoint.

Currently, we are investigating partially deuterated κ-[$(H_8$-ET$)_{0.2}(D_8$-ET$)_{0.8}]_2$Cu[N$(CN)_2$]Br, which can be tuned very close to and even through

the critical region in the generalized phase diagram. Our results confirm the measurements on the fully deuterated variant and indicate a near divergence of the low-frequency noise accompanied by the onset of a glassy carrier dynamics when approaching (p_0, T_0) [3].

[2] J. Brandenburg et al., *New. J. Phys.* **14**, 023033 (2012).

[3] B. Hartmann et al., in preparation.

Origin of the glass-like dynamics in molecular metals κ-(BEDT-TTF)$_2$X

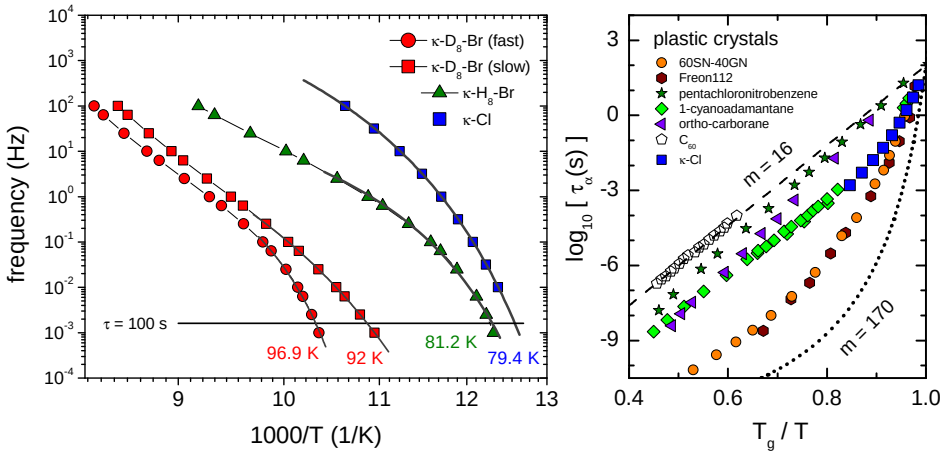

Figure 2: (a) Arrhenius plot of the distribution of the maxima of $S_R/R^2(T)$ at different frequencies (see Fig. 1) of selected systems of κ-(BEDT-TTF)$_2$X (see legend). The red lines are Vogel-Fulcher fits to the low-frequency data. Clearly visible is the strong deviation from thermally-activated behaviour. (b) The data for κ-(ET)$_2$Cu[N(CN)$_2$]Cl in comparison to other orientational glasses (taken from [5].

We have studied the low-frequency dynamics of the charge carriers in different organic charge-transfer salts κ-(BEDT-TTF)$_2$X with polymeric anions X by using resistance noise spectroscopy aiming to investigate the glass-like transition occurring at $T_g \sim 75-85\,\mathrm{K}$ for the different systems [4]. This glassy transition, which is of structural nature and believed to be caused by the rotational degrees of freedom of the BEDT-TTF molecules' terminal ethylene groups, is intimately related to a certain degree of intrinsic – and controllable – disorder in the lattice potential, and therefore of fundamental importance for the ground-state properties of the strongly-correlated electrons. Yet, mostly due to the non-applicability of dielectric spectroscopy in the relevant temperature range, the phenomenology of the glassy dynamics is only scarcely investigated and poorly understood. In our systematic studies of various different compounds we find that the resistance noise power spectral density exhibits a universal, pronounced Gaussian maximum at the glass transition, which is frequency dependent and accompanied by a strong shift of spectral weight from high to low frequencies upon cooling through T_g. The energy scale of the corresponding electronic fluctuations can be identified with the activation energy of the glass-like structural dynamics as determined from thermodynamic and NMR measurements. For the first time for this class of 'plastic crystals', we report a typical glassy property

of the relaxation time, namely a Vogel-Fulcher-Tamman law, and are able to determine the degree of fragility of the glassy system. Based on the comparison to other families of (BEDT-TTF)$_2$X salts and measurements of the linear coefficients of thermal expansion we argue that the collective dynamics of the BEDT-TTF molecules' orientational degrees of freedom and the polymeric anion chains are responsible for the occurrence of the glass transition.

[4] R. Rommel et al., in preparation.

[5] R. Brand et al., *J. Chem. Phys.* **116** 10386 (2002).

Nonlinear electronic transport in the anomalous metallic state of quasi-2D organic superconductors κ-(BEDT-TTF)$_2$X

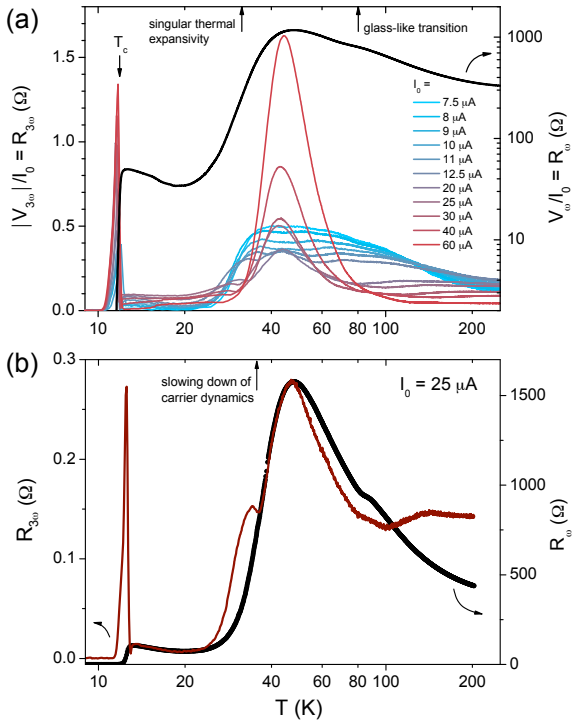

Figure 3: (a) Nonlinear and linear resistance of κ-D$_8$-Br, $R_{3\omega}(T)$ and $R_\omega(T)$, respectively, for various applied currents I_0 at a frequency of 17 Hz. Arrows indicate the glass-like transition due to $(CH_2)_2$-endgroup ordering and the singular thermal expansivity [7]. (b) Comparison of $R_{3\omega}$ and R_ω for $I_0 = 25\,\mu$A. Arrow indicates the sudden slowing down of the charge-carrier dynamics due to the vicinity of the Mott critical endpoint measured in the same sample [2].

We have performed measurements of the first- and third-harmonic voltage response in *ac* electronic transport measurements, representing the linear (ohmic) and nonlinear resistivity, respectively, of the quasi-two-dimensional (2D) organic superconductors κ-(BEDT-TTF)$_2$X. Nonlinear transport is a sensitive tool to probe the microgeometry of the electronic system in high-quality single crystals. For the title compounds, the normalconducting metallic state in the vicinity of the Mott metal-insulator transition and critical endpoint is known to be highly unusual. Our results reveal large current-induced intrinsic inhomogeneities, at high current densities most pronounced at the so-called T^* anomaly, which characterizes the anomalous metallic state. The observed nonlinearities in the interlayer transport do not depend on frequency and cannot be ascribed to a simple Joule heating mechanism in a resistor network. Furthermore, we find evidence supporting the notion of electronic phase separation induced by the Mott critical endpoint. The observed dependence of the generated third-harmonic voltage on the current density reveals a systematic behavior suggesting that current-induced electronic inhomogeneities are more pronounced for more strongly correlated systems.

[6] R. Rommel et al., *Phys. Status Solidi B* **250**, 568 (2013).

[7] L. Bartosch et al., *Phys. Rev. Lett.* **104**, 245701 (2010).