Distinguishing thermal from non-thermal ("hot") carriers in illuminated molecular junctions

Yonatan Dubi¹, Ieng Wai Un², Yonatan Sivan²

¹. Department of Chemistry, Ben-Gurion University; 2. School of Electrical and Computer Engineering, Ben-Gurion University

sivanyon@bgu.ac.il

Abstract: We develop the theory necessary to explain the experimental measurement of the non-thermal electron distribution in a plasmonic molecular junction in [2]. This reveals that the original interpretation of the measurements was inaccurate. © 2023 The Author(s)

When a plasmonic nanostructure is continuously illuminated, the system unavoidably heats up, and non-thermal (so-called “hot”) carriers are being generated [1]. The separation between these different carriers is very challenging, because the number of the high excess-energy non-thermal electrons is many orders of magnitude smaller compared to the number of thermal (i.e., low excess energy) carriers. In an attempt to circumvent this problem, Reddy co-authors [2] measured the I-V curves through a molecular junction (MJ) under illumination and in the dark, and assessed the effect of illumination on the electronic distribution in an illuminated Au electrode. Here [3], we interpret the results of [2] by combining the standard Landauer theory of transport through MJJs with the analytic form for the electron non-equilibrium distribution of an illuminated metal [1]. This shows that the main results in [2] have a satisfactory explanation as mere heating of the bottom electrode, whereas additional measurements of a different molecule (discussed in the SI of [2]) provides (probably for the first time) a direct observation of non-thermal electrons, but not in the way interpreted in the original manuscript. This finding confirms the original theoretical prediction [1] in a reasonable quantitative manner, and thus confirms the claims on the extremely small role played by non-thermal electron in general [1], and specifically in plasmon-assisted photocatalysis experiments [4].

References
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Fig. 1 (Left) Schematic depiction of the experimental setup, comprising an Au slab with surface plasmons excited at the nanofabricated gratings, and a molecular junction formed between the slab and an STM tip. (Right) A fits to experimental data of [2] for a 6 nm thick slab, assuming that the tip is not heated but the slab right under it is. Black squares are the experimental data, and red circles are the fits.