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Thermoelectricity in single-molecule devices

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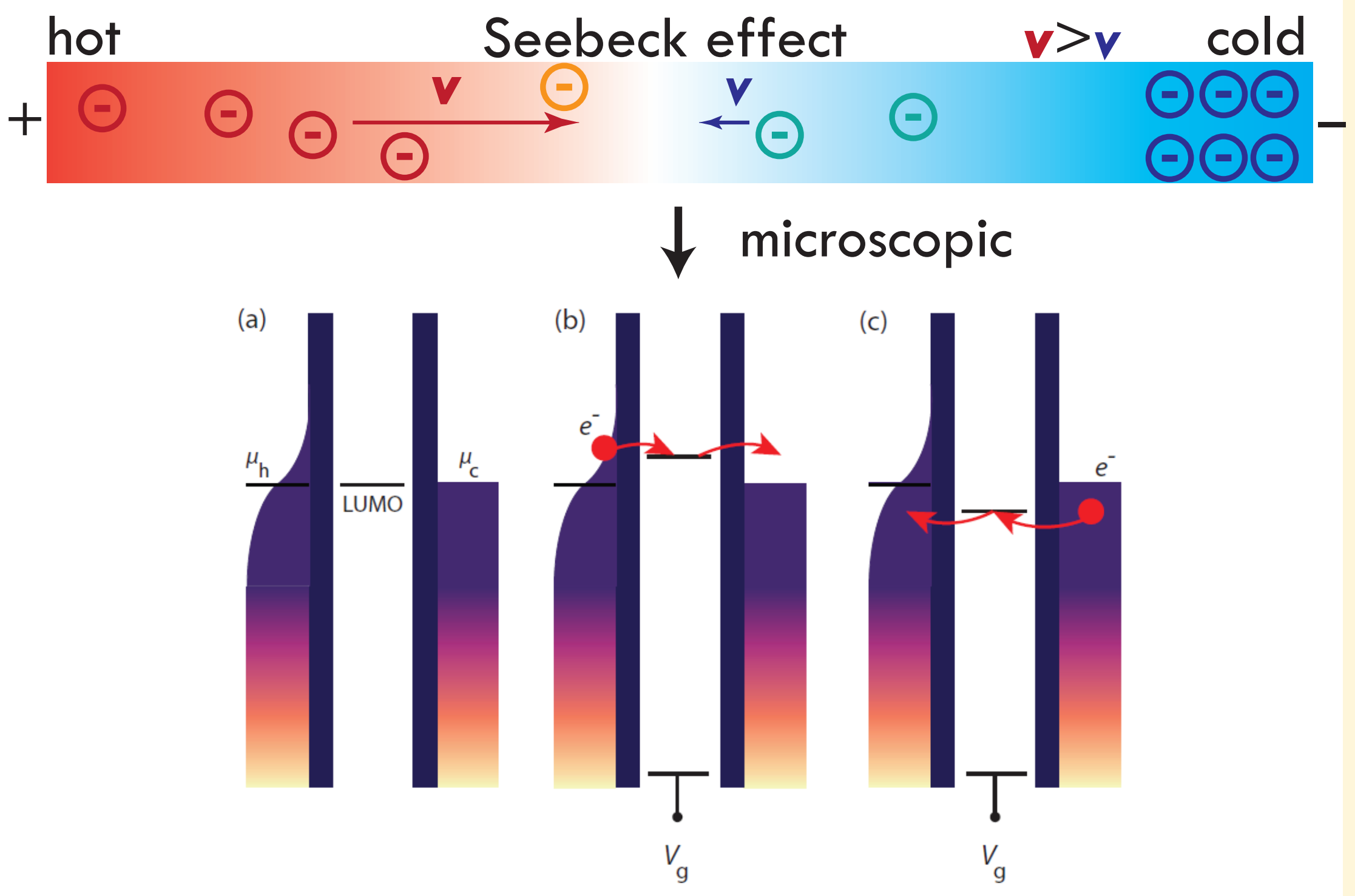
Thermoelectricity at the nanoscale

- Thermoelectricity is the conversion between temperature gradient and electric potential difference. The effect concerning the voltage created by a temperature gradient is called - the Seebeck effect: $V = -S\Delta T$, S is the Seebeck coefficient[1].
- In a simple classical open circuit, it can be seen as the charge accumulation in the cold arm. This is due to the higher momenta of the charges in the hot arm, resulting in more charges going from the hot to the cold side.
- At the nanoscale, the elastic phase-coherent microscopic picture can be captured in the Landauer formuism[2]:

$$I = \frac{2e}{h}\int_0^{\infty} \mathcal{T}(E)[f_L(E) - f_R(E)]\mathrm{d}E$$

As it can be seen from the drawing, a thermally broadened Fermi-Dirac Distribution can induce a current flow with its direction based on the carrier type (level alignment).



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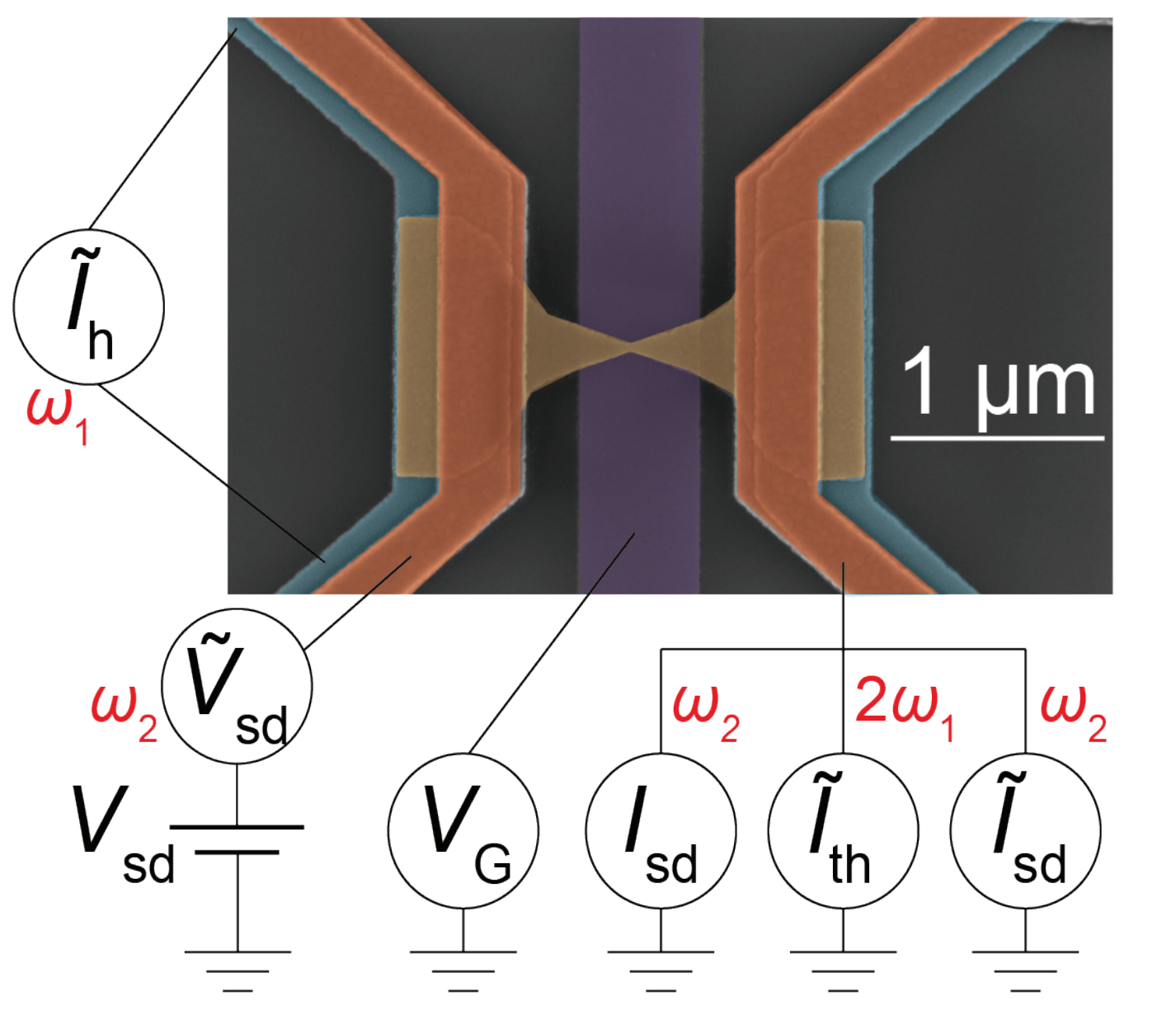
[1] ΔT is the temperature difference.
[2] I is the current, e is the electron charge, h is the Plank constant, $T(E)$ is the energy dependent transmission, $f(E)$ is the Fermi-Dirac distribution of the left or right lead.
Bottom drawing: van der Star, M. "Developing a single-molecule transistor for thermoelectric measurements" TU Delft MasterThesis 2019

Single-molecule thermoelectric device



- Nanoscale systems can form so-called "Quantum Dot" (QD) where electrons strongly interact with each other due to the small sizes.
- Single molecules are particularly interesting QD systems because they can be functionalized to host exotic states, such as a high-spin ground state. To contact a single molecule, electromigrated break junction (EMBJ) is used, where the molecule is drop-cast onto the electromigrated gold nanogap[3] (yellow constriction). Immediately after the junction formation, the system is cooled down to T = 2 K for stability and sharp Fermi-Dirac distributions for the thermoelectric study.
- By using the lock-in technique at 2 different frequencies, ω_1 = 3 Hz and ω_2 = 13 Hz, we can simultaneously detect the electrical and thermoelectric signals. The detected electrical current $\tilde{I}_{sd}$ is driven at ω_2 by a voltage source $\tilde{V}_{sd}$. The thermocurrent $\tilde{I}_{th}$ is detected at $2\omega_1$ driven by the temperature gradient generated by $\tilde{I}_h$ at ω_1 on the left. We note that the factor of 2 in the detection signal of $\tilde{I}_{th}$ is due to the Joule heating of the left lead, which takes the form: $P = I^2R \propto \sin^2\omega_1 \propto 1\text{-}\cos 2\omega_1$, which $\propto \Delta T$.

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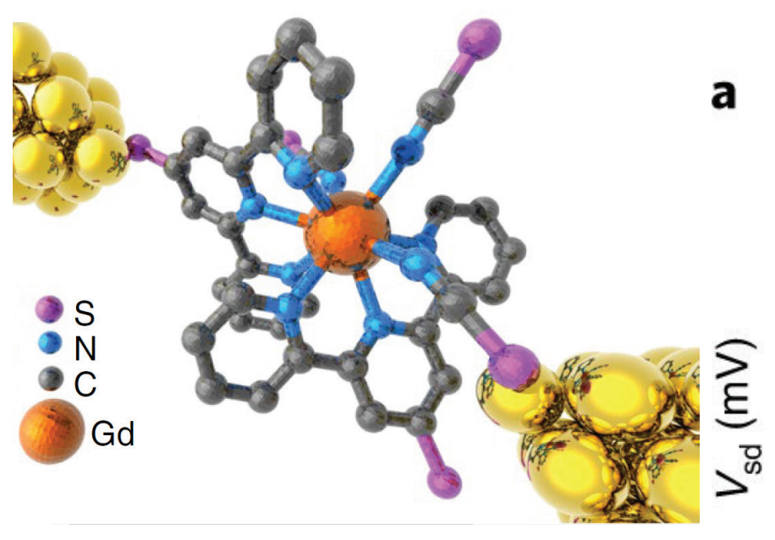
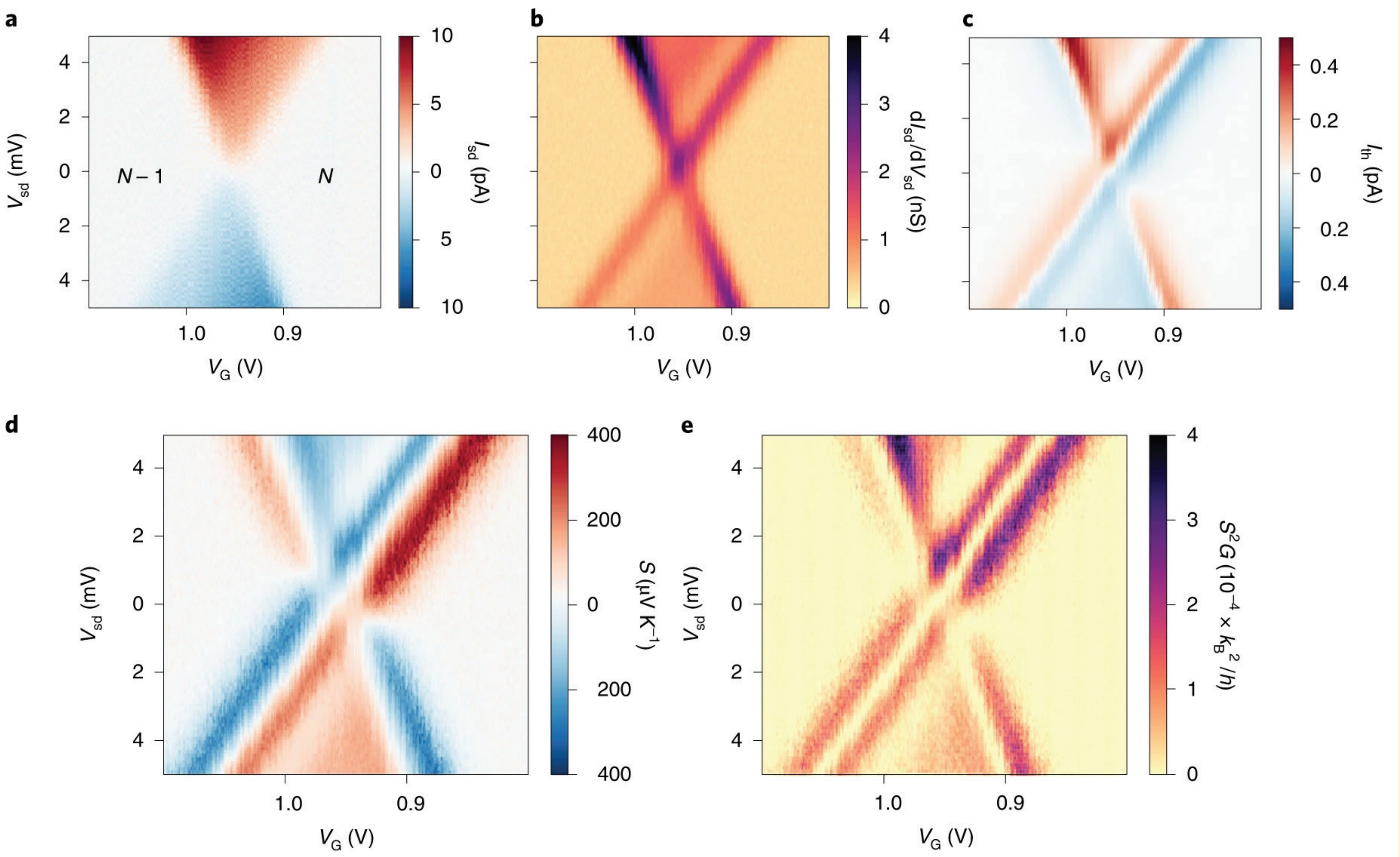
[3] The nanogap is opened at the yellow constriction in the center by the high current density during the electromigration process.
[4] The purple strip in the back is the gate, the blue feature indicates the heaters, the gold bridge is the EMBJ, the orange pattern is the contact/thermometer.

Complete mapping of the thermoelectric properties of a single molecule



- The above-described device can be used to map not only the electrical transport of the single-molecule QD but also the thermoelectric properties such as the Seebeck coefficient or the power factor.
- An example of the complete mapping of a single molecule is the Gadolinium (Gd) complex[5]. In this case the Coulomb stability diagram across N-1 to N -electron state is simultaneously mapped for: a. DC current, b. differential conductance, c. thermocurrent, d. Seebeck coefficient, and e. power factor.
- It is worth noting that the Seebeck coefficient is as high as S > 400 µV/K, which is comparable to the commonly used semiconductor, silicon. Another measure for the performance of a thermoelectric material is the figure of merit ZT, which takes the form $ZT = S^2GT/(K_{ph}+K_e)$[6]. Typically, a high performance device can reach $ZT \approx 2$ [7], yet decreases drastically (ZT<<1) when it goes to low temperature. The Gd complex device has a $ZT \approx 0.7$ at T = 2 K outperforming most of the semiconductor devices.
- Another important finding in this experiment is the asymmetry in the thermoccurent $-I_{th,min}/I_{th,max}$ =1.4 at zero-bias voltage. This suggests the different degeneracies, i.e. entropy, in the N-1 and N state. We estimate it from the conductance signal, which corresponds to a singlet-to-doublet transition.



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[5] Gehring, P.; Sowa, J. K.; Hsu, C.; de Bruijckere, J.; van der Star, M.; Le Roy, J. J.; Bogani, L.; Gauger, E. M.; van der Zant, H. S. J. Complete Mapping of the Thermoelectric Properties of a Single Molecule. Nat. Nanotechnol. 2021, 16 (4), 426–430.
[6] Here, G is the electrical conductance, T is the temperature, K_{ph} is the phononic thermal conductivity, and K_e is the electronic thermal conductivity.
[7] Zabek, D.; Morini, F. Solid State Generators and Energy Harvesters for Waste Heat Recovery and Thermal Energy Harvesting. Therm. Sci. Eng. Prog. 2019, 9 (November 2018), 235–247.

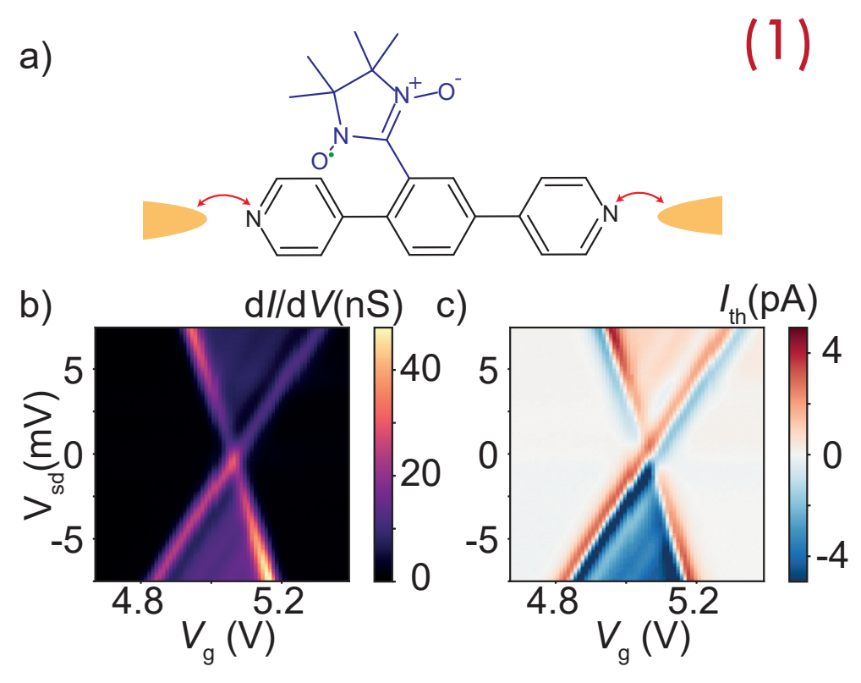
Entropy measurement

- While a conductance measurement can provide an estimate of the entropy change in a system, thermocurrent provides a more direct measure of the entropy change, since it is robust against parasitic conduction and background charge in the systems.
- We look into a different molecule with a nitronyl nitroxide side group by the same experimental technique[8] (1). In addition to the Coulomb stability, we also find the asymmetric I_{th} as a function of magnetic field (2).
- From a thermodynamic relation and rate equations, we find a relation between the thermoconductance, taking the form[9]:

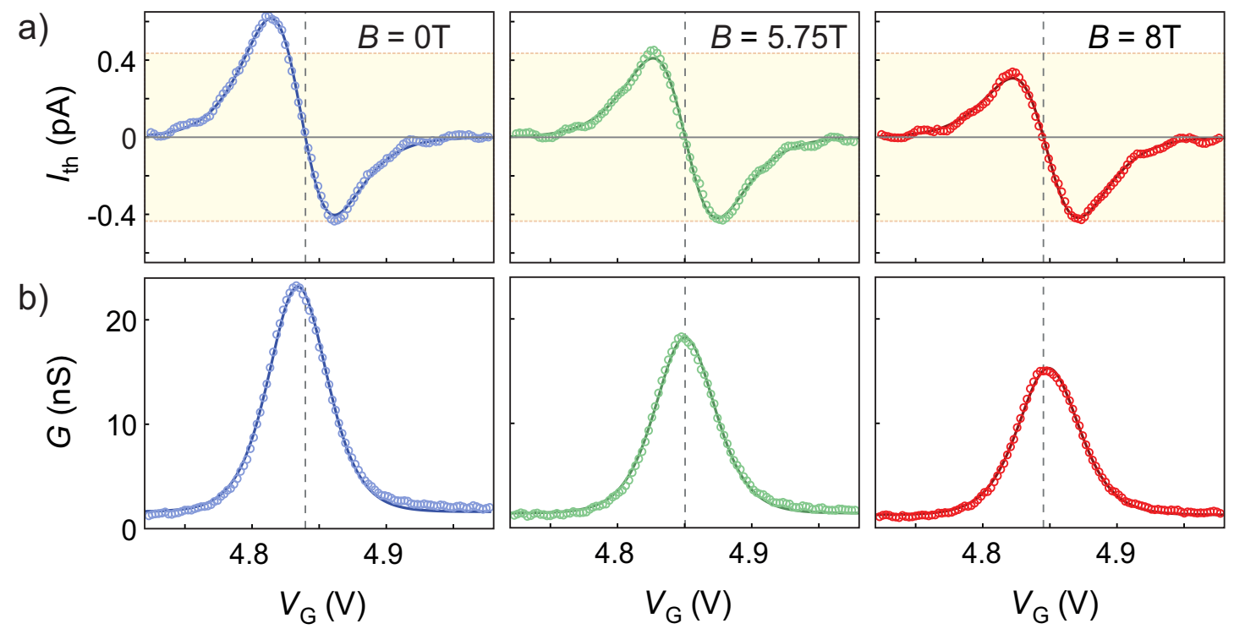
$$L \propto \frac{\varepsilon}{T^2}[1 - f(\varepsilon)]f(\varepsilon - T\Delta S)$$

- This clearly shows that N+1 ground state changes from singlet to ↓↓-triplet at higher magnetic field (3).

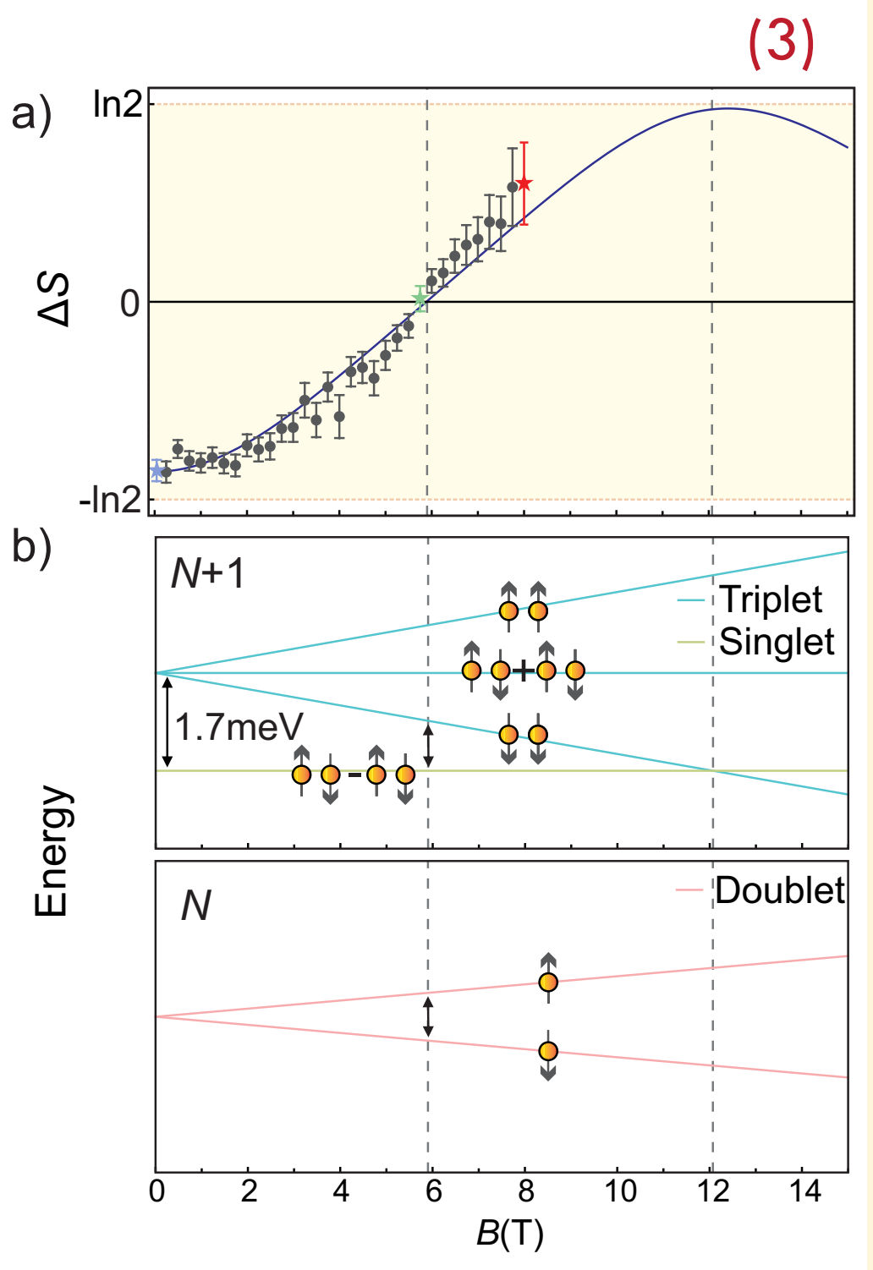
(1)



(2)



(3)



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[8] Pyurbeeva, E.; Hsu, C.; Vogel, D.; Wegeberg, C.; Mayor, M.; van der Zant, H.; Mol, J. A.; Gehring, P. Controlling the Entropy of a Single-Molecule Junction. Nano Lett. 2021, 21 (22), 9715–9719.
[9] Here, ε is the energy, T is the temperature, f is the Fermi-Dirac distribution, ΔS is the entropy change.

Summary & Conclusion

- Thermoelectricity at nanoscale is a crucial technological concept in modern electronics. Due to the high density and small size of electronic components, it is profitable to harvest energy from the waste heat. Equally important, the thermoelectric properties are key for the fundamental understanding of charge transport in nanoscale systems.
- We create single-molecule QD devices by nanofabrication, enabling the possibility to simultaneously characterize the full electrical and thermoelectric properties of such a system for the first time.
- From the estimated Seebeck coefficient and the figure of merit ZT, it is shown that single-molecule QD devices are a promising platform for exploring optimal thermoelectric device designs.
- It is shown that thermocurrent can also be used to study fundamental physical quantities such as the entropy change in a charge transition under different magnetic fields.
- For the future, it is appealing to study thermoelectricity with exotic physical phenomena, such as the strongly-correlated Kondo effect or high-spin ground states.

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