Optomechanical heat transfer between molecules in a nanoplasmonic cavity

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We explore whether localized surface plasmon polariton modes can transfer heat between molecules placed in the hot spot of a nanoplasmonic cavity through optomechanical interaction with the molecular vibrations. We demonstrate that external driving of the plasmon resonance indeed induces an effective molecule-molecule interaction corresponding to a new heat transfer mechanism, which can even be more effective in cooling the hotter molecule than its heating due to the vibrational pumping by the plasmon. This novel mechanism allows to actively control the rate of heat flow between molecules through the intensity and frequency of the driving laser.

I. INTRODUCTION

Achieving thermal control of molecular systems is a topic of current interest in various fields, such as quantum thermodynamics, quantum biology and quantum chemistry [1–8]. In order to achieve this, it is necessary to gain a fundamental understanding of the transfer of heat, and energy in general, between molecules. In addition to well-known mechanisms like advection, convection, conduction and radiation, which are responsible for the majority of heat transfer on macroscopic scales, additional mechanisms can play an important role in microscopic and/or quantum systems. Some examples of such mechanisms are seen in single-atom junctions [9], the driven non-equilibrium spin-boson model [10], or in spatially separated molecules entangled through strong coupling to cavity modes [11, 12]. In particular, optomechanical systems in which photonic modes are coupled to mechanical degrees of freedom, have been studied in detail in this context [13–15].

In this article, we demonstrate that localized surface plasmon polariton modes can transfer heat between molecules placed in the hot spot of a plasmonic cavity. This transfer is mediated through the molecular optomechanical interaction between electromagnetic modes and molecular vibrations, and is made possible by the fact that such systems can reach a high optomechanical coupling rate within the resolved-sideband limit [16–21]. While “traditional” optomechanics is concerned with the interaction of electromagnetic modes with macroscopic mechanical resonators (often the mirrors forming the cavity), with implementations in diverse setups such as optical Fabry-Perot cavities, optomechanical crystals, microwave LC-circuits or membrane-in-the-middle setups [22], it was recently shown that the interaction between vibrational modes of single molecules and plasmonic cavities can be understood within the same framework, as first applied in the context of Surface-Enhanced Raman Scattering (SERS) [16, 19]. The optomechanical interaction then occurs between two non-resonant (approximately) harmonic oscillators, a localized surface plasmon resonance (LSPR) functioning as the optical mode, and nuclear motion in the molecule functioning as the mechanical resonator, with vibrational displacement of the nuclei causing a dispersive shift of the LSPR frequency. While both quantum and classical molecular optomechanics (QMO and CMO, respectively) correctly describe elementary characteristics of Raman scattering, namely the dependence of Raman signal on the power and frequency of the incident laser, and on the temperature [20], QMO predicts several phenomena that are not seen within CMO, such as dynamical back-action amplification of the vibrational mode [19], and gives access to non-classical observables such as correlations of the emitted photons [18]. Furthermore, it allows to distinguish two adjacent molecules with similar chemical structure by the splitting of the transparency peak [23].

We here demonstrate heat transfer between the vibrational degrees of freedom of two molecules interacting with a single plasmonic cavity mode that is driven by an external laser, as sketched in Fig. 1. The paper is organized as follows: in section II, we introduce the QMO model for the system and describe our theoretical approach. In section III, we present our results for heat transfer between the molecules, both for the symmetric case of identical molecules (section IIIA), and the asymmetric case where...
the molecules and thus their vibrational modes are different (section III B). We conclude with a summary and discussion of the results in section IV. In the following, we use atomic units (\(\hbar = 1\)) unless otherwise stated.

II. THEORETICAL FRAMEWORK AND MODEL

The aim of our work is to investigate the heat transfer between the vibrational modes of two molecules placed in the hot spot of a LSPR mode that mediates the heat transfer, as shown in Fig. 1. The theoretical approach then follows from a straightforward extension of single-molecule descriptions [16, 20], sketched in the following. We assume that the plasmonic resonance is far-detuned from any transition within the molecule, and treat a single vibrational mode (approximated by a harmonic oscillator) in each molecule. The interaction between a molecular vibration and the quantized LSPR mode can then be described by the interaction Hamiltonian

\[
H_{\text{int}} = -\frac{1}{2} \hat{P}(t) \cdot \hat{E}(t),
\]

in which \(\hat{P}(t)\) and \(\hat{E}(t)\) are the molecular polarization and LSPR electric field operator, respectively. Under the assumption that the plasmonic resonance frequency is much larger than the molecular vibrational frequency, \(\omega_c \gg \omega_m\), this can be expressed through a “standard” optomechanical interaction [16, 20], given by

\[
H_{\text{int}} = -ga\hat{a}^\dagger \hat{a} (\hat{b} + \hat{b}^\dagger).
\]

Here, \(\hat{a}\) and \(\hat{b}\) are the annihilation operators for optical and vibrational modes, respectively, and \(g_0 = \frac{Q_0^R R_0 \omega_c}{\varepsilon_0 \varepsilon_0 V}\) is the optomechanical coupling constant. This coupling depends on both the properties of the nanocavity (permittivity of the surrounding medium \(\varepsilon_0\), effective mode volume \(V\) and central frequency \(\omega_c\)) and of the molecule (isotropic Raman tensor \(R_0\) and zero-point amplitude of the vibration \(Q_0^R\)). We now assume that we have two molecules, separated by a distance \(R\), as well as an external laser driving the LSPR mode. The full Hamiltonian in the rotating frame of the laser is then given by

\[
\hat{H} = \delta_0 \hat{a}^\dagger \hat{a} + \omega_1 \hat{b}^\dagger \hat{b}_1 + \omega_2 \hat{b}^\dagger_2 \hat{b}_2
- g_{01} \hat{a}^\dagger \hat{a} (\hat{b}^\dagger_1 + \hat{b}_1) - g_{02} \hat{a}^\dagger \hat{a} (\hat{b}^\dagger_2 + \hat{b}_2)
- \lambda (\hat{b}^\dagger_1 + \hat{b}_1) (\hat{b}^\dagger_2 + \hat{b}_2) + i\Omega (\hat{a}^\dagger - \hat{a}),
\]

where

\[
\lambda = \frac{\epsilon^2}{4\pi\varepsilon_0 R^3 \sqrt{m_1 m_2} \sqrt{\omega_1 \omega_2}}
\]

is the dipole-dipole coupling constant between the molecules, \(\delta_0 = \omega_c - \omega_1\) is plasmon-pump detuning and \(\Omega\) determines the laser pump intensity. Furthermore, we assume that the molecules are coupled to independent heat baths at temperatures \(T_1\) and \(T_2\), as sketched in Fig. 1(b). Plasmonic hotspots are typically very small (\(\ll 100\) nm), such that having different local temperatures for the molecules would require a very local source of heating. This could be achieved, e.g., with nanometric tips used as near-field thermal probes and for radiative heat transfer experiments [24–27], or through frequency-selective resonant laser heating of different bath molecules (e.g., by using DNA origami to precisely control molecular positions [28]). Alternatively, it would be possible to place the two molecules in different hot spots of the same LSPR mode, as, e.g., provided by triangular plasmonic nanoparticles [29].

In addition to the coherent dynamics described by Eq. (3), we include the coupling to external baths within a Lindblad master equation description [30, 31]:

\[
\frac{d\hat{\rho}}{dt} = \frac{1}{i} [\hat{H}, \hat{\rho}] + L_{\hat{a}} \hat{\rho} + L_{\hat{b}_1} \hat{\rho} + L_{\hat{b}_2} \hat{\rho},
\]

where

\[
L_{\hat{a}} \hat{\rho} = \frac{\gamma_1}{2} (\hat{n}_i + 1) D_{\hat{a}} \hat{\rho} + \frac{\gamma_1}{2} \hat{n}_i D_{\hat{a}}^\dagger \hat{\rho}
\]

\[
L_{\hat{b}_i} \hat{\rho} = \frac{\kappa}{2} D_{\hat{b}_i} \hat{\rho},
\]

where \(\kappa\) describes the decay of the plasmon, and \(\gamma_1, \gamma_2\) are the coupling rates of the first and second molecule to their respective thermal baths, while \(D_{\hat{C}} \hat{\rho}\) is a standard Lindblad superoperator,

\[
D_{\hat{C}} \hat{\rho} = 2\hat{C} \hat{\rho} \hat{C}^\dagger - \hat{C}^\dagger \hat{C} \hat{\rho} - \hat{\rho} \hat{C}^\dagger \hat{C}.
\]

The temperature of the two baths is encoded in the mean phonon occupation numbers \((\bar{n}_1, \bar{n}_2)\), given by [30, 31]

\[
\bar{n}_i = \frac{1}{\exp \left(\frac{\omega_i}{k_B T_i}\right) - 1},
\]

where \(k_B\) is the Boltzmann constant. If the molecule-molecule and molecule-plasmon interaction is negligible, each molecule will reach thermal equilibrium with its bath, with the populations of the vibrational levels decaying exponentially following a Boltzmann distribution. The average phonon number, i.e., the expectation value \(n_i = \langle \hat{b}^\dagger_i \hat{b}_i \rangle_{\text{ss}} = \text{Tr}(\hat{b}^\dagger_i \hat{b}_i \rho_{\text{ss}})\), where \(\rho_{\text{ss}}\) is the steady-state density matrix, then becomes equal to \(\bar{n}_i\).

The dipole-dipole and optomechanical interaction between molecules can modify the temperature, and more generally, the steady-state distributions. We then define an effective temperature based on the average phonon number, i.e.,

\[
T_i^\text{eff} = \frac{\omega_i}{k_B \log (1 + 1/n_i)}.
\]

In order for this effective temperature to correspond to a physical temperature, the population of the separate
levels should again follow a thermal distribution. We have checked for all the results presented below that this is indeed the case, i.e., that the steady-state distributions of the phonon populations are well-approximated by thermal Boltzmann distributions, and the effective temperatures obtained can thus indeed be interpreted as the steady-state physical temperatures of the respective vibrational modes.

Finally, we mention that all the numerical results shown here are obtained using the open-source QuTiP package [32, 33]. In the numerical calculations, we have used a cutoff of $N = 6$ for the maximum phonon and photon numbers. We have checked that this provides converged results for all the parameters considered below.

III. RESULTS

A. Identical molecules

We first show the direct heat transfer due to the dipole-dipole interaction $\lambda$ between the molecules when there is no interaction with the plasmon mode, shown in Fig. 2. Here and in the following, we choose phonon mode frequencies of $\omega_1 = \omega_2 = 50 \text{ meV}$, with the external baths at temperatures of $T_1 = 77 \text{ K}$ and $T_2 = 300 \text{ K}$, and molecule-bath coupling rates given by $\gamma_1 = \gamma_2 = 0.25 \text{ meV}$. Not surprisingly, as $\lambda$ is increased, the molecules can exchange energy more efficiently, causing heat to flow between them and their effective temperatures to approach each other. When $\lambda$ becomes comparable to $\gamma_1 = \gamma_2$, i.e., energy exchange between the molecules is comparably fast to the molecule-bath coupling, the steady-state temperatures of the two molecules become almost equal. We also note that due to the symmetry of the system in this case, the change in mean phonon numbers (not shown) induced by the coupling is symmetric, $\delta n_1 = -\delta n_2$, such that the total phonon number in both molecules is conserved as $\lambda$ is increased.

By comparison, in Fig. 3 we study the case where there is no direct dipole-dipole interaction, but the optomechanical coupling to the plasmon is nonzero, and the plasmon mode is driven by an external driving laser. We use a plasmonic resonance frequency of $\omega_1 = 1.36 \text{ eV}$ with linewidth $\kappa = 68 \text{ meV}$, corresponding to a quality factor of $Q = 20$. The optomechanical coupling rate is taken as $g_{01} = g_{02} = 10 \text{ meV}$, similar to values derived in the literature [16, 18, 20], and the laser-plasmon detuning is set to $\delta_0 = 150 \text{ meV}$. Due to the dispersive nature of the plasmon-phonon interaction Eq. (1), the plasmon mode does not have any influence on the phonon population when there is no driving, since in that case $\langle \hat{a}^\dagger \hat{a} \rangle = 0$. When the external laser drives the plasmon mode, the molecules can be driven out of equilibrium with their local heat baths. This leads to two possible effects on the molecular temperature: On the one hand, vibrational pumping of phonons through Stokes (anti-Stokes) transitions can heat (cool) the molecules [20]. This is a well-known single-molecule effect that also occurs when each molecule is alone in the cavity, as shown in dashed lines in Fig. 3. On the other hand, the effective molecule-molecule interaction mediated by the plasmon additionally enables heat transfer between the molecules, leading to deviations of the molecular temperatures compared to the single-molecule picture (solid lines in Fig. 3), even though there is no direct molecule-molecule interaction ($\lambda = 0$). As would be expected, the plasmon-mediated interaction again makes the molecular temperatures approach each other. Noticeably, this can even reverse the trend in the change of the temperature of the hotter molecule: Although it gets heated by the plasmon when it is in the cavity by itself, its temperature decreases in the presence of the colder molecule due to their effective coupling induced by the plasmon.
FIG. 4. Effective temperature of the molecules as a function of (a) the cavity damping rate $\kappa$ and (b) the molecular damping rate $\gamma = \gamma_1 = \gamma_2$. In both panels, all other parameters are kept constant at the values given in the main text.

This finding is consistent with analytical results for the heat transfer between coupled harmonic oscillators [34] obtained by adiabatic elimination of the photon mode in the linearized limit of optomechanics [22], i.e., when the cavity mode is coherently excited with a relatively large amplitude $\alpha = \langle \hat{a} \rangle$ and dropping the quadratic term is valid after the replacement $\hat{a} \rightarrow \alpha + \hat{a}$ (where $\alpha$ is a complex number). In this regime, it has been shown (for identical oscillators) that the common coupling to a photonic mode is equivalent to an effective coupling $\lambda$ between the oscillators (molecules in our case), as well as a coupling of both oscillators to a common heat bath [34]. The analytical results predicted by this approximation are shown in Fig. 3 as symbols.

We next study the influence of various parameters on the results obtained above. The effectiveness of the plasmon-mediated heat transport, as measured by the deviation of the full results from those with each molecule by itself in a cavity, is reduced when the cavity loss rate $\kappa$ increases (keeping all other parameters constant), as shown in Fig. 4(a). Similarly, increasing the molecule-bath coupling $\gamma_1 = \gamma_2$ leads to more efficient thermalization of each molecule with its individual bath, such that their temperatures approach those of their baths, as seen in Fig. 4(b). However, plasmon-mediated heat transfer still constitutes an important channel and leads to significant deviations between the individual-molecule results and the coupled system. We note that changing the optomechanical coupling rates $g_{01} = g_{02}$ (not shown) is equivalent to changing the external driving $\Omega$ (see Fig. 3), and leads to more efficient energy transfer (and also more efficient heating).

FIG. 5. Effective temperature of both molecules as a function of the frequency $\omega_2$ of the hotter molecule.

B. Non-symmetric system

In this section, we investigate the non-symmetric situation where two molecules with different vibrational mode frequencies are coupled to the same plasmonic resonance. For simplicity, we only change the mode frequency of molecule 2 and keep all other parameters (couplings and bandwidths) constant, and thus identical for both molecules. In Fig. 5, we show the temperature of both molecules when changing the frequency of the hotter molecule, with all other parameters as in Fig. 3 (in particular, $\omega_1 = 50$ meV). It can immediately be appreciated that plasmon-induced heat transfer between the molecules is only efficient when the two vibrational modes are close to resonance, with a central peak visible where the hotter (colder) molecule is cooled (heated) compared to the single-molecule case. We note that the width of these peaks is determined by the width of the vibrational modes $\gamma_1 = \gamma_2$. 
Interestingly, while the hotter molecule displays an almost Lorentzian-like lineshape, i.e., it is more efficiently cooled the closer the two molecules are to resonance, the colder molecule shows a Fano-like lineshape as a function of frequency difference, with the temperature actually decreasing below the single-molecule value at the same driving when the hotter molecule is at a slightly lower frequency than the colder one. This implies that there is a kind of destructive interference between the heating process induced by the coupling to the plasmonic resonance itself and the plasmon-mediated heat transfer to the hotter molecule.

More insight into the origin of this resonance condition is gained by studying the power spectral density of the molecular vibrations and the plasmon, respectively. The PSD, defined as

$$S_\epsilon(\omega) = \int_0^\infty e^{-i\omega t} \langle \hat{c}^\dagger(t)\hat{c}(0) \rangle_{\text{av}}dt,$$  \hspace{1cm} (10)

gives a measure of the oscillation spectrum of a mode as a function of frequency [30]. For the symmetric case of identical molecules, Fig. 6(a), the plasmonic resonance is modulated at the same frequency as the vibrational modes, leading to efficient effective coupling between the two modes. Interestingly, the effective coupling between the vibrational modes induced by the plasmonic mode becomes large enough for the parameters used here that normal mode splitting between the two vibrational modes occurs, and the PSD of the molecules shows a pronounced double-peak structure. In contrast, when the two molecular vibrations have different frequencies, as shown in Fig. 6(b) for $\omega_1 = 50$ meV, $\omega_2 = 45$ meV, they each induce a separate modulation onto the plasmonic mode, and each molecule only is influenced by the plasmonic mode modulation at its own frequency, such that no effective coupling between molecules takes place. In this figure, it can also be appreciated that the hot molecule induces much stronger fluctuations on the plasmonic mode than the cold one.

In order to understand the onset of normal mode splitting between the molecules, we plot the PSD of the two molecules for various values of the driving intensity $\Omega$ in Fig. 7. As can be seen, for weak driving, the two molecules only oscillate at their natural frequency. However, as $\Omega$ is increased above about 30 meV, the driving of the plasmonic mode induces a large enough effective coupling between the molecules to overcome losses and lead to normal mode splitting (or “strong coupling”) between the vibrational modes. Within the approximation of adiabatic elimination of the plasmon mode [34], this can be understood as being due to the effective molecule-molecule coupling $\lambda$. The results within this approximation are included in Fig. 7 as dashed black lines, which also demonstrates that the quality of this approximation actually decreases with increasing driving, and the observed splitting is larger than predicted.

IV. SUMMARY & DISCUSSION

To summarize, we have demonstrated that mutual coupling of two molecular vibrations to a localized surface plasmon resonance in the optomechanical regime can lead to efficient plasmon-mediated heat transfer between the molecules. Importantly, this plasmon-mediated channel is only active when the plasmonic mode is driven by an external laser field. This could enable active control of heat transfer between molecules through an external laser field. Additionally, in some parameter regimes, this optomechanically induced plasmon-mediated heat transfer is more efficient than bare plasmon-induced heating, such that the hotter molecule can effectively be cooled even though it is actively heated by a relatively intense laser pulse. This is reminiscent of radiative cooling under sunlight [35], with the additional twist that here it is the external laser field itself that induces the cooling by opening a new heat transport channel to a colder reservoir.
Furthermore, we have shown that in the case of non-identical molecules, heat transfer only efficiently takes place if the relevant vibrational modes are close to resonance with each other, due to the each one only interacting with modulations of its own frequency imprinted on the plasmon mode. Interestingly, inducing a slight detuning between the vibrational frequencies can lead to Fano-resonance like effects where the effective heat transfer of two in principle positive contributions leads to “destructive interference” and thus less heating of the colder molecule than by the laser-driven plasmon mode itself.

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