Organic molecule fluorescence as an experimental test-bed for quantum jumps in thermodynamics

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We demonstrate with an experiment how molecules are a natural test-bed for probing fundamental quantum thermodynamics. Single-molecule spectroscopy has undergone transformative change in the past decade with the advent of techniques permitting individual molecules to be distinguished and probed. By considering the time-resolved emission spectrum of organic molecules as arising from quantum jumps between states, we demonstrate that the quantum Jarzynski equality is satisfied in this set-up. This relates the heat dissipated into the environment to the free energy difference between the initial and final state. We demonstrate also how utilizing the quantum Jarzynski equality allows for the detection of energy shifts within a molecule, beyond the relative shift.

Marrying the language of thermodynamics with quantum phenomena is giving rise to a quantum thermodynamics whose development defines a new frontier where the transfer of energy at the level of individual quantum objects can now be studied. The success of thermodynamics owes much to being open to experimental testing in a variety of systems [1]. These have included systems operating in the quantum regime and exhibiting features like quantum coherence, such as quantum dots [2]. Here we seek to demonstrate that the fluorescence of organic molecules forms a natural testbed for these theories. Our result provides an important proof of concept for the validity of quantum thermodynamics in this regime, and opens the door for more advanced tests of the theory.

Non-equilibrium thermodynamics is evolving rapidly, and a key result is the Jarzynski equality [1, 3, 4]. This concerns the probability distribution of work into a driven system in contact with a heat bath. It essentially equates the average of the exponential work with something which is constant regardless of the driving rate. That constant is the exponential of the equilibrium free energy, i.e. the free energy between a thermal state at the initial boundary conditions and at the final respectively. A key use of this equation is to determine the equilibrium free energy difference from non-equilibrium experiments [5, 6]. The equation also holds for quantum systems [8, 9]. One important area within this field, which has received a large amount of recent attention, is the development of experimental techniques and protocols which can test the theoretical predictions [10, 11].

Parallel developments in physical chemistry with the advent of single molecule spectroscopy [12] over the past decade have opened up unprecedented opportunities for the study of single quantum systems. Unlike studies in bulk where spectroscopic signatures are washed out by the averaging effect of ensembles, these novel techniques now allow individual molecules to be identified, tracked and probed. Thus it is becoming possible to study energy transfers at the level of single molecules, some of which offer ideal test-beds owing to their well-defined spectroscopic signatures and quantum state dynamics. Their properties are extremely reproducible, more so than rival quantum systems such as quantum dots and nanocrystals [12].

![Schematic of a two-level molecule driven by laser pulses generating single photons from decaying electronic states with our thermodynamical representation of the process below it.](image)

FIG. 1: Schematic of a two-level molecule driven by laser pulses generating single photons from decaying electronic states with our thermodynamical representation of the process below it.

In this work we connect these two approaches, namely quantum thermodynamics and molecular spectroscopy. We consider the spontaneous emission of photons from a single excited organic molecule as a thermodynamic process. We determine the probability distribution of work and heat in the experiment, see [1] and find that it satisfies the quantum Jarzynski equality. A key point is to

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treat the free space around the molecule as an extremely low excitation heat bath, and the fluorescent light as heat transferred into that environment. The laser applied initially corresponds to the driving force, as depicted in Fig. 1. In the theoretical analysis we use quantum jumps. The core concept in the quantum jump formalism is that the system always occupies a distinct state that undergoes a stochastic evolution which enables it to transition between different energy levels \( \text{[2, 13]} \) as illustrated in Figs. 2 and 3. Furthermore, we demonstrate how use of the quantum Jarzynski equality can be used to infer absolute energy-level shifts in molecules from the emitted photons, as opposed to just the relative shift. We thus establish that these organic molecules are a natural and powerful test-bed for non-equilibrium thermodynamics and suggest how they have use in the enhanced detection of force fields.

I. RESULTS

We examine the spectroscopic data from spontaneous emission of the organic molecule dibenzoterrylene (DBT) in an anthracene crystal. The molecular system is effectively described by two energy eigenstates that are delocalized across the DBT. The molecule is coupled to a low excitation heat bath, and the joint system number state basis evolves unitarily under the action of:

\[
U = \begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & \mu -\nu^* & 0 & 0 \\
0 & \nu & \mu^* & 0 \\
0 & 0 & 0 & 1 \\
\end{pmatrix},
\]

where \(|\mu|^2 + |\nu|^2 = 1\). This coupling can be viewed as a partial swap between qubit and environment, parametrized by \(\mu, \nu\). It has the effect of transferring \(\Delta E = E_2 - E_1\) (\(E_i\) is the energy of the \(i^{th}\) level) between the molecule and the environment, with a probability dependent on the coupling strength. Within this experiment all of the photons are emitted along the zero phonon line, and as such we do not observe the effects of transitions within the vibrational modes. If we perform periodic measurements on the output field we can perform a partial measurement on the state of the molecule, and measure the heat flux from the molecule to the environment. This produces trajectories of the joint system which are shown in Fig. 3. We convert the time resolved trace of the photon statistics into the heat distribution which we find to be consistent with:

\[
\begin{align*}
P(Q + \Delta E) &= \alpha + \beta |\mu|^{2n} \\
P(Q - \Delta E) &= \beta (1 - |\mu|^{2n}),
\end{align*}
\]

where \(\alpha, \beta\) are the initial occupation probabilities of each level. The heat distribution is plotted in Fig. 4 for two different laser intensities.

By examining the heat distribution given above we can directly evaluate the Jarzynski equality. In particular we find that the system satisfies \(\langle e^{-\beta (\Delta U - Q)} \rangle = 1\) for all time points during the period of spontaneous emission. This demonstrates that the decay of organic molecules from an excited to the ground state is a thermodynamic process, even when it is considered at the level of single photon emission events.

We can utilize the Jarzynski equality to detect shifts in the energy spectra of the molecule. If we consider taking the energy levels from:

\[
\begin{align*}
E_1 &\rightarrow E_1 + \delta \\
E_2 &\rightarrow E_2 + \delta + \epsilon,
\end{align*}
\]

FIG. 2: (a) Dibenzolettylene (DBT) and anthracene structures consist of corrugated planar assemblies of aromatic hydrocarbons. Two possible DBT insertion sites in the extended anthracene host crystal lattice act as defects giving rise to two distinct spectral lines at 785 nm and 795 nm. In this study we chose to probe the brighter blue-shifted site with a characteristic transition line at 785 nm. (b) The energy level structure of DBT reduces to two-level atom-like states typical of organic fluorescent dyes despite the relative complexity of the organic molecules. We pumped DBT above resonance at 4 K to generate excited states that decayed non-radiatively on pico-second timescales into the first excited state \(S_{1,0}\). Decay from \(S_{1,0}\) into the ground state \(S_{0,0}\) gave rise to a sharp lifetime limited line (30MHz), which, in a single molecule, gives rise to the emission of a single photon for each decay. The narrow width of the Zero Phonon Line (ZPL is lifetime-limited with a width of approx. 30MHz. (c) Waveform of the decay of excited electronic states in DBT at a temperature of 4K obtained by time-resolved fluorescence spectroscopy. The waveform represents a probability distribution of the arrival times of single photons from the decaying state rather than the shape of an optical signal. The time-resolved technique relies on time-correlated single photon counting of pulses obtained by exciting the sample with a 730 nm pulsed laser with a repetition rate of 80MHz. The probability of detecting more than one photon per excitation period is negligible. The excited state which gives to the ZPL emission line is found to have a characteristic lifetime of 5ns after fitting the exponential decay constant.
FIG. 3: A sample of the different trajectories the system can–
according to the model– take after interacting with the envi-
ronment several times, after having been initialized in a mixed
state. Each trajectory is formed by alternating a period of
evolution under the joint Hamiltonian and then performing
a projective measurement on the environment. As there is
only one photon during the protocol and the probability of
spontaneous excitation of the molecule is negligible, once the
photon has moved into the environment there are no further
branchings.

where $\delta$ is a common shift of the energies and $\epsilon$ is the
difference in shifts between energy levels 1 and 2. This
operation produces a change in the equilibrium free en-
ergy ($F = -k_B T \ln Z$) of the molecule:

$$\Delta F = k_B T \ln \left( \frac{Z_f}{Z_i} \right) = -\delta + k_B T \ln \left( \frac{1 + e^{-\beta \Delta E'}}{1 + e^{-\beta \Delta E}} \right).$$ (4)

Here we have defined $\Delta E = E_2 - E_1$ and $\Delta E' = \Delta E +
\epsilon$. By observing the fluorescence emitted by the excited
molecules we can determine the value of both of these
quantities. Combining this relation with the Jarzynski
equality for heat we can determine the value of $\delta$. This
would allow for probing the strengths of local field effects
with high sensitivity.

II. DISCUSSION

Recently there has been substantial interest in devel-
opling systems which can be used to test quantum ther-
modynamics, [10, 11]. Here we have demonstrated that
the photon emission from organic molecules satisfies one
of the fundamental relationships of the field. This is true
for the single photon emission from the molecules, at all
points during the relaxation time. We believe that this
provides an important platform for the study of quantum
thermodynamics in real systems. Organic spectroscopy
is a well developed and established field of physics, and
here we demonstrate that it possible to tap into these re-
sources to investigate fundamental questions in quantum
thermodynamics.

In the initial set up of this investigation we focused on
emissions along the zero phonon line. One major advan-
tage of investigating quantum thermodynamics by uti-
lizing fluorescence from organic molecules is that it is
experimentally straightforward to relax this assumption
and probe how the situation changes when we incorpo-
rate the phononic transitions. This would have the ef-
fect of creating an extra heat bath for energy transferred
into the molecule to dissipate into, and would also provide for a much larger number of potential trajectories to be taken. With single molecule spectroscopy it is possible to have sufficient resolution of the photons emitted to determine how much energy is being “lost” to the phonon modes. We would then be able to determine if the Jarzynski equality is still satisfied in this open system.

In this analysis of the molecule-heat bath system we have modelled it as initially being in a mixed state. We believe this initial condition to be reasonable as the lifetime of any entanglement between the molecule and environment is very short lived. If instead the molecule were to be left in a superposition of energy eigenstates (e.g. $|\psi\rangle = |g0\rangle + |e0\rangle$) after the work is done on it then in the current setup there is no difference in the measured heat statistics relative to the corresponding de-phased mixed state. The reason this occurs is due to the repeated suppression of the coherence in the heat bath via measurement in the photon number basis and discarding the measurement outcomes. However as the initial state before the spontaneous emission is very close to a pure product state between the molecule and the heat bath, and the Hamiltonian time evolution is unitary, the total state before measurements is approximately pure, and there will exist a basis in which measurements would not destroy coherence. As is well known, see e.g. [14], coherence implies extra extractable work so it would be valuable to identify how to implement this alternative basis measurement experimentally.

III. METHODS

Consider the two level molecule. We assume it is initially in a thermal state at the same temperature as the environment. In this set-up and for the modes of concern this means both the molecule and the environment are essentially in the ground state with a very small probability of a thermal excitation. The system is then pulsed by a laser which causes a swap in the occupation probabilities of the joint state. (The laser is non-resonant but there is then near-instantaneous vibrational de-excitation to the excited level of interest-see Fig. 2.) Now the joint system undergoes evolution under its own Hamiltonian which has the effect of inducing a partial swap, parametrized by $|\mu|^2$, see Eq. [1]. This unitary arises naturally from the Jaynes-Cummings Hamiltonian which describes the coupling between the environment and the molecule [15]. This corresponds to the emission of a photon to the environment as the molecule is de-excited.

Framing this in the language of quantum jumps, such that we can evaluate the Jarzynski equality à la [9], produces the trajectories in Table I. These trajectories are defined by considering an infinitesimal time step during which one of two events happens - either the system evolves under the joint Hamiltonian or we perform a projective measurement on the environment. The sequence of pure states produces a trajectory.

| Traj | W | Q | ΔU | Prob |
|------|---|---|----|-----|
| 1    | $|g\rangle \rightarrow |e\rangle \rightarrow |g\rangle$ | ΔE | −ΔE | 0 | $P(|g\rangle)P_{gg}$ |
| 2    | $|g\rangle \rightarrow |e\rangle \rightarrow |e\rangle$ | ΔE | 0 | ΔE | $P(|g\rangle)P_{ee}$ |
| 3    | $|e\rangle \rightarrow |g\rangle \rightarrow |e\rangle$ | −ΔE | 0 | −ΔE | $P(|e\rangle)P_{ge}$ |
| 4    | $|e\rangle \rightarrow |g\rangle \rightarrow |g\rangle$ | −ΔE | ΔE | 0 | $P(|e\rangle)P_{gg}$ |

TABLE I: Possible trajectories of the local state of the molecule.

In this framework we consider the system to always be occupying a definite state and determine what possible evolutions each state can take. Each of these evolutions constitutes a possible trajectory the system can undertake, which have associated values of internal energy change, work and heat.

Having identified what the possible trajectories are, we must now determine which correspond to the experimental data we obtain. As we are detecting photon emission from the molecules using an avalanche photodiode (APD), in principle we detect trajectories 1, 3 and 4. However due to the electronics of the APD there is a delay in time in receiving the signal from the photons [16]. Trajectories 3 and 4 occur on a very fast time scale due to the stimulating effect of the laser causing the transition and so are unobserved. As such, we only observe clicks in the detector due to traj. 1. The probabilities of the remaining trajectories turn out, as described below, to be determined uniquely by the initial state being assumed to be thermal together with demanding that the probabilities of all the trajectories sum to 1.

The time resolution is very high and the probability of receiving more than one photon in a given time-bin is negligible here, even taking into account the number of molecules scattered in the illuminated part of the crystal. Thus one click means one photon.

Having established the concurrence between clicks and photons, we now treat the environment as a low excitation heat bath. The emitted photons are then simply the heat flux into the bath, and by relating the cumulative probability of emission to the heat distribution, Eq. [2] we can determine the values of $\alpha, \beta$ and $|\mu|^2$, see Fig. 6. This information corresponds to trajectories 1 and 2, and by employing the fact that $P(Traj3) + P(Traj4) = P(|e\rangle)$ we can explicitly calculate the Jarzynski equality. This equality is plotted in Fig. 4.

Conclusion

We conclude that this fluorescence experiment amounts to a scenario where Jarzynski’s equality holds. As further evidence that this experimental set-up is promising for probing quantum thermodynamics we note/reiterate the following: (i) molecular spectroscopy is a powerful and well-established technique, (ii) the set-up maps naturally to the quantum jumps model for work
FIG. 5: The swapping parameter that controls the interaction with environment is plotted as a function of temperature and the time. It can be seen that the swapping parameter is very stable for the majority of time during the experiment, indicating that the model we employ to interpret the data is sound, see Eq. [1]. We utilize this in connecting the experimental data to the quantum jumps model that enables us to evaluate the Jarzynski equality.

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