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PAPER

Verification of the quantum nonequilibrium work relation in the presence of decoherence

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Abstract

Although nonequilibrium work and fluctuation relations have been studied in detail within classical statistical physics, extending these results to open quantum systems has proven to be conceptually difficult. For systems that undergo decoherence but not dissipation, we argue that it is natural to define quantum work exactly as for isolated quantum systems, using the two-point measurement protocol. Complementing previous theoretical analysis using quantum channels, we show that the nonequilibrium work relation remains valid in this situation, and we test this assertion experimentally using a system engineered from a trapped ion, adding external noise to produce the effects of decoherence. Our experimental results reveal the work relation's validity over a variety of driving speeds, decoherence rates, and effective temperatures and represent the first confirmation of the work relation for evolution described by a non-unitary master equation.

1. Introduction

Statements of the second law of thermodynamics are generally expressed as inequalities. For instance the work performed on a system during an isothermal process must not exceed the net change in its free energy: $W \geqslant \Delta F$. When statistical fluctuations are appropriately included these inequalities can be reformulated as equalities, such as the nonequilibrium work relation [1]

$$\langle \mathrm{e}^{-\beta W} \rangle = \mathrm{e}^{-\beta \Delta F}, \tag{1}$$

where β is an inverse temperature and angular brackets denote an average over repetitions of the process. For classical systems, this prediction and related *fluctuation theorems* have been extensively studied both theoretically [2] and experimentally [3–10], and have been applied to the numerical estimation of free energy differences [11, 12].

The last decade has seen growing interest in extending these results to quantum systems [13]. This pursuit is made challenging both by the fact that classical work is defined in terms of trajectories—a notion that is typically absent in the quantum setting—and by the lack of a quantum 'work operator' [14]. To avoid these difficulties, many studies have focused on closed quantum systems, which evolve unitarily. In the absence of a heat bath there is no heat transfer to or from the system and the first law of thermodynamics reads,

$$W = \Delta U \equiv E_f - E_i. \tag{2}$$

Here the classical work depends only on a system's initial and final configuration and can be determined from two measurements. This idea is easily lifted to the quantum regime through the two-point measurement (TPM)

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protocol [15–17], according to which the work performed during a single experimental run is the difference between energy values E_i and E_f resulting from initial and final projective measurements.

If a system is prepared in equilibrium at inverse temperature β with initial Hamiltonian $\hat{H}(0) = \sum \epsilon_n |n\rangle\langle n|$, then evolves unitarily as the Hamiltonian is varied from $\hat{H}(0)$ at $t = 0$ to $\hat{H}(\tau) = \sum \bar{\epsilon}_m |\bar{m}\rangle\langle \bar{m}|$ at $t = \tau$, the TPM work distribution is given by

$$p(W) = \sum_{nm} p_n \, p_{\bar{m}|n} \, \delta[W - (\bar{\epsilon}_m - \epsilon_n)]. \tag{3}$$

Here $p_n = Z_0^{-1} \mathrm{e}^{-\beta\epsilon_n}$ is the probability to obtain the value $E_i = \epsilon_n$ during the initial energy measurement, $p_{\bar{m}|n}$ is the conditional probability to obtain the final energy value $E_f = \bar{\epsilon}_m$, given the initial value ϵ_n, and Z_0 is the partition function for the initial equilibrium state. To date, both proposed [18–21] and implemented [22–25] experimental tests of the quantum work relation (1) have focused on evaluating equation (3) for a closed system.

Subtle conceptual issues arise if the system's initial state contains coherences in the energy basis, since such states are disturbed by the initial measurement [26, 27]. Even in this situation equation (1) remains valid under the TPM scheme, provided the diagonal elements of the initial density matrix are given by Boltzmann factors [28]. These issues will not affect our analysis, as we will always assume our system begins in equilibrium, and is thus described by a diagonal (in the energy basis) density matrix.

A number of authors have proposed definitions of work and derived fluctuation theorems for quantum systems in contact with general thermal environments [29–35]. Our more focused aim in this paper is to consider a quantum system in contact with a thermal environment that produces decoherence but no dissipation. From a theoretical viewpoint, we argue that the TPM protocol provides a natural definition of quantum work in this situation, and we give an elementary, physically motivated derivation of equation (1) that agrees with more general results obtained by previous authors [36–40]. We then describe an experimental implementation constructed from trapped ions that makes use of noise to achieve the effects of a bath which causes decoherence but no dissipation. From the data we verify the validity of the quantum work relation, providing the first experimental confirmation of equation (1) for a system undergoing decoherence.

2. Theoretical development

When a quantum system is coupled to a thermal environment, there arise two distinct departures from unitary dynamics: dissipation, that is the exchange of energy, and decoherence, the leakage of the system's quantum coherences into the environment [41]. *We will consider situations in which dissipation is negligible over experimentally relevant time scales, but decoherence is substantial.* Under such conditions the environment is a *decohering* (or *dephasing*) environment: it suppresses coherences but does not exchange energy.

Consider a system in contact with a decohering environment. At $t = 0$, following a projective energy measurement, the system begins in an energy eigenstate $|\epsilon_n\rangle$, then it evolves as its Hamiltonian is varied with time. At $t = \tau$ its energy is again measured, yielding $\bar{\epsilon}_m$. By assumption, no energy is exchanged with the environment, therefore we claim that it is natural to identify work to be the difference between the initial and final energies, $W = \bar{\epsilon}_m - \epsilon_n$, just as for a closed quantum system (see equation (2)). If we accept this as a plausible definition of work in the presence of a decohering environment, then does equation (1) remain valid in this situation? This question can be answered affirmatively within the general framework of quantum channels [37, 38, 40]. We now take a phenomenological approach to arrive at the same answer.

We begin by modeling the dynamics of the system. In the energy representation, a decohering environment does not affect the diagonal elements (populations) of the system's density matrix $\hat{\rho}(t)$, but may cause off-diagonal matrix elements (coherences) to decay. We capture these features with the equation

$$\frac{\mathrm{d}\hat{\rho}}{\mathrm{d}t} = -\frac{\mathrm{i}}{\hbar}[\hat{H}(t), \hat{\rho}] - \sum_{\mathrm{i}\neq j} \gamma_{ij} \rho_{ij} |i\rangle\langle j| \equiv \mathcal{L}\hat{\rho}, \tag{4}$$

which describes both unitary evolution under $\hat{H}(t)$ and the decohering effects of the environment. Here $\gamma_{ij} \geqslant 0$ are phenomenological decay rates for the coherences $\rho_{ij} \equiv \langle i|\hat{\rho}|j\rangle$, in the instantaneous eigenbasis of $\hat{H}(t)$.

Although we have motivated equation (4) heuristically, it can also be obtained from the perspective of quantum detailed balance master equations (QDBME) [42]. These equations are a special type of Lindblad master equation and are of physical relevance as they rigorously describe a quantum system coupled to an infinite, thermal quantum reservoir under appropriate assumptions of weak interaction and separation of time scales [43–45].

For an N-level quantum system with no degenerate energy gaps as shown in appendix A.1, the QDBME governing the evolution of the density operator can be written in the form

$$\frac{\mathrm{d}\hat{\rho}}{\mathrm{d}t} = -\frac{\mathrm{i}}{\hbar}[\hat{H},\,\hat{\rho}] + \sum_{ij} J_{ij}|i\rangle\langle i| + \sum_{i\neq j}\Gamma_{ij}|i\rangle\langle j|,$$
$$J_{ij} \equiv R_{ij}\rho_{jj} - R_{ji}\rho_{ii},$$
$$\Gamma_{ij} \equiv (R_{ii} + R_{jj} - \gamma_{ij})\rho_{ij} < 0,$$
$$\gamma_{ij} \equiv \sum_k d_k(O_{ki} - O_{kj})^2 \geqslant 0, \tag{5}$$

where the R_{ij}'s form a stochastic rate matrix [46] satisfying detailed balance, the O_{ij}'s form a real orthogonal matrix, and $d_k > 0$ for all k. The three terms on the right side of equation (5) respectively describe unitary evolution, dissipation, and decoherence. The dissipative term evolves the diagonal elements of $\hat{\rho}$ (populations) according to a classical Markov process described by the rate matrix R, whereas the decohering term causes the decay of off-diagonal elements (coherences). To model a decohering environment we set all $R_{ij} = 0$, thereby suppressing thermally induced transitions between energy eigenstates. This leads immediately to equation (4).

Earlier, we had motivated our definition of work in the presence of a decohering environment, $W = \bar{\epsilon}_m - \epsilon_n$, heuristically. With equation (4) this argument can be strengthened using a simple microscopic model, as we describe appendix A.2.

Note that evolution under equation (4) preserves the identity, $\mathcal{L}\hat{I} = 0$, hence this evolution is *unital*, and equation (1) follows as an immediate consequence of a general result derived by Rastegin [37]. To keep our presentation self-contained, we now derive equation (1) assuming only a linear master equation that preserves the identity.

Let $\Lambda_\tau : \hat{\rho}_0 \to \hat{\rho}_\tau$ denote the quantum evolution that maps an initial density matrix to a final density matrix, under the dynamics of equation (4). After initial equilibration, an energy measurement at time $t = 0$ yields an energy eigenvalue ϵ_n with probability $p_n = Z_0^{-1}\mathrm{e}^{-\beta\epsilon_n}$, and 'collapses' the system into a pure state $\hat{\rho}_0 = |n\rangle\langle n|$. This state then evolves under equation (4) to $\hat{\rho}_\tau = \Lambda_\tau(\hat{\rho}_0)$ and a final energy measurement at $t = \tau$ yields a value $\bar{\epsilon}_m$ with probability $p_{\bar{m}|n} = \langle\bar{m}|\hat{\rho}_\tau|\bar{m}\rangle$. Summing over all possible measurement outcomes, and using the linearity and identity preservation of Λ_τ, we have [37]

$$\begin{aligned}\langle\mathrm{e}^{-\beta W}\rangle &= \sum_{nm} p_n\, p_{\bar{m}|n}\, \mathrm{e}^{-\beta(\bar{\epsilon}_m - \epsilon_n)} \\ &= \sum_{nm} \frac{\mathrm{e}^{-\beta\epsilon_n}}{Z_0}\langle\bar{m}|\Lambda_\tau(|n\rangle\langle n|)|\bar{m}\rangle\,\mathrm{e}^{-\beta(\bar{\epsilon}_m - \epsilon_n)} \\ &= \frac{1}{Z_0}\sum_m \mathrm{e}^{-\beta\bar{\epsilon}_m}\langle\bar{m}|\Lambda_\tau(\hat{I})|\bar{m}\rangle = \frac{Z_\tau}{Z_0} = \mathrm{e}^{-\beta\Delta F}.\end{aligned}$$

3. Experimental verification

To test equation (1) experimentally, we employ a two state system engineered from a $^{171}\mathrm{Yb}^+$ ion's orbital degrees of freedom, using the energy levels $|F = 0,\ m_F = 0\rangle \equiv |\downarrow\rangle$ and $|F = 1,\ m_F = -1\rangle \equiv |\uparrow\rangle$ belonging to the ground-state manifold of $^2S_{1/2}$ [47]. By applying microwave pulses resonant to our states' energy difference $\omega_0 \equiv \omega_{\mathrm{HF}} - \omega_Z$, where $\omega_{\mathrm{HF}} = (2\pi)12.642\ 821$ GHz and $\omega_Z = (2\pi)13.586$ MHz, the system can be driven according to the Hamiltonian

$$\hat{H}(t) = \frac{\hbar\Omega(t)}{2}[\hat{\sigma}_x\cos\phi(t) + \hat{\sigma}_y\sin\phi(t)]. \tag{6}$$

Here $\hat{\sigma}_{x,y}$ are the standard Pauli matrices in the $\{|\uparrow\rangle,\ |\downarrow\rangle\}$ basis while Ω and ϕ are parameters controlled through the amplitude and phase of the microwave pulses. In our experiment, we use the driving protocols

$$\Omega(t) = \Omega_0\left(1 - \frac{t}{2\tau}\right);\ \ \phi(t) = \frac{\pi t}{2\tau}, \tag{7}$$

where τ is the duration of the process. Together equations (6) and (7) represent the Hamiltonian portion of our system's dynamics. The decohering term of equation (4) is realized by the addition of noise in the microwave pulse sequence. In our setup this adds a stochastic term $\Omega_0\xi(t)$ to the protocol $\Omega(t)$ where $\xi(t)$ is gaussian white noise characterized by zero mean $\langle\xi(t)\rangle = 0$ and variance $\langle\Delta\xi(t)\xi(t+\tau)\rangle = \alpha^2\delta(\tau)$. Averaging over all realizations of the noise $\xi(t)$ produces an equation of motion identical to equation (4) with $\gamma_{ij} = \gamma = \frac{1}{2}\alpha^2\Omega_0^2$ [48–51] (see also appendix A.3).

Given this setup, the procedure for measuring the work applied during a single experimental trial involves four steps: (i) thermal state preparation, (ii) initial energy measurement, (iii) application of the driving protocol, and (iv) final energy measurement, as shown in figure 1(a).

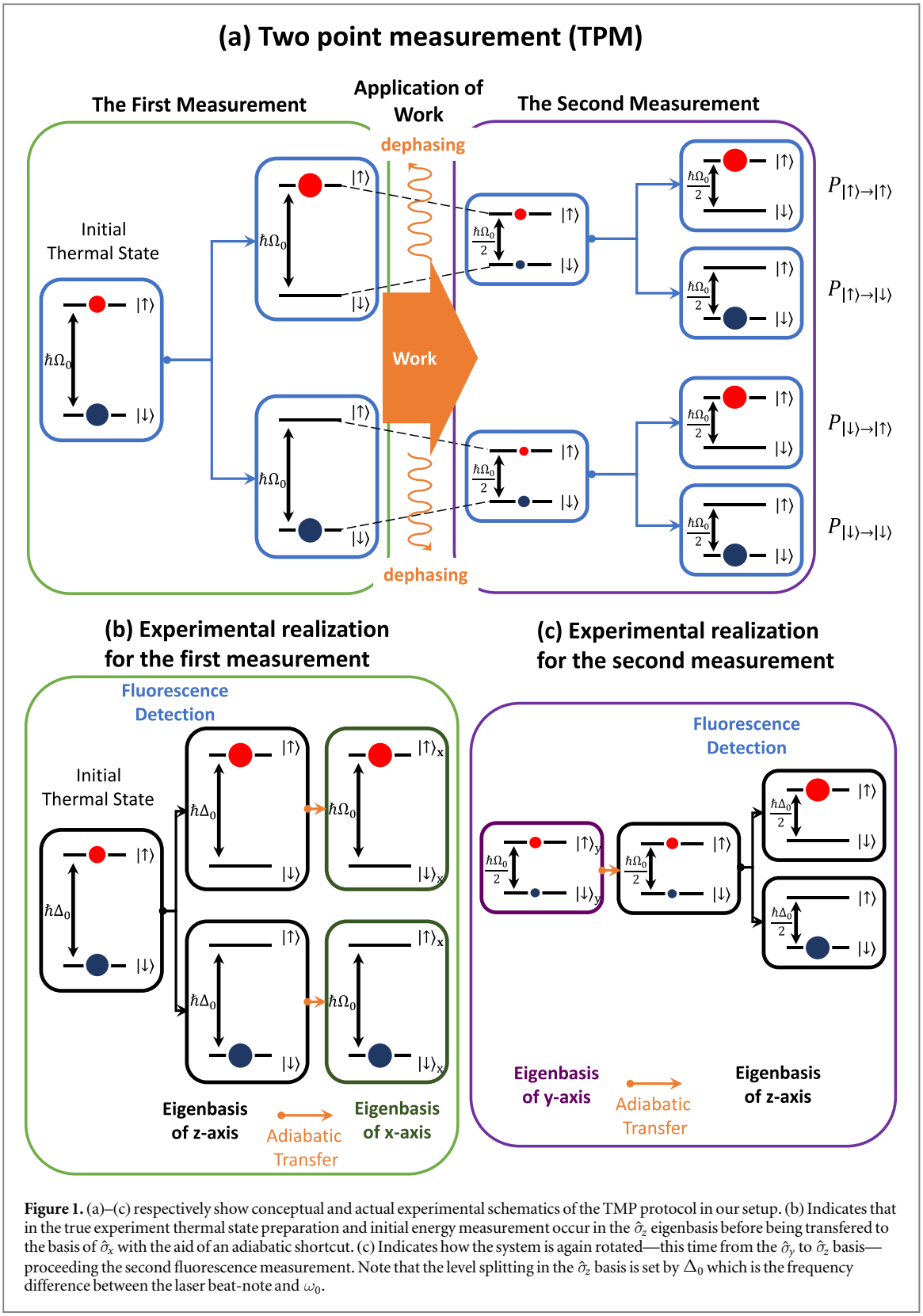


Figure 1. (a)–(c) respectively show conceptual and actual experimental schematics of the TMP protocol in our setup. (b) Indicates that in the true experiment thermal state preparation and initial energy measurement occur in the $\hat{\sigma}_z$ eigenbasis before being transfered to the basis of $\hat{\sigma}_x$ with the aid of an adiabatic shortcut. (c) Indicates how the system is again rotated—this time from the $\hat{\sigma}_y$ to $\hat{\sigma}_z$ basis—proceeding the second fluorescence measurement. Note that the level splitting in the $\hat{\sigma}_z$ basis is set by Δ_0 which is the frequency difference between the laser beat-note and ω_0.

Our Hamiltonian has the form $\hat{H}(t) = \mathbf{B}(t) \cdot \hat{\boldsymbol{\sigma}}$, where the field $\mathbf{B}(t)$ undergoes rotation by 90° in the *xy*-plane (see equation (6)). For technical reasons the initial thermalization and both measurements are performed in the $\hat{\sigma}_z$ basis. Therefore after the initial thermalization and measurement we rotate the system from the *z*-axis into the *xy*-plane, then we implement the driving as per equation (6), and finally we rotate the system back to the *z*-axis to perform the final measurement. These rotations do not affect the work distribution. The rotations are achieved with *adiabatic shortcuts* [52–54], which produce transformations equivalent to adiabatically switching

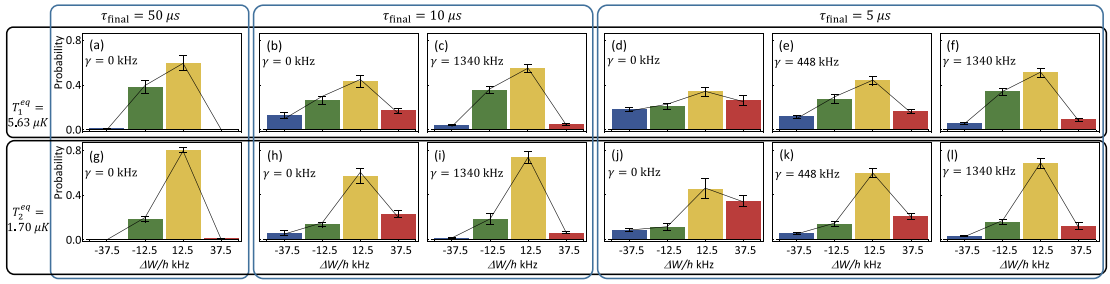


Figure 2. The work distributions (a)–(f) correspond to an initial temperature of $T_1 = 5.63\ \mu$K while (g)–(l) have $T_2 = 1.70\ \mu$K. The driving times $\tau = 50\ \mu$s, $\tau = 10\ \mu$s, and $\tau = 5\ \mu$s represent near adiabatic (a), (g), moderate (a), (c), (h), (i), and fast (d)–(f), (j), (k), (i) driving regimes. The dephasing rate γ took values of 0, 448, and 1340 kHz for the cases of no (a), (b) (d), (g), (h), (j), intermediate (e), (k), large (c), (f), (i), (l) dephasing respectively.

the system's Hamiltonian, but in a finite time (see appendix A.6). Figures 1(b) and (c) show detailed schematics of the measurement protocols, including these shortcuts.

(i) Thermal state preparation—We create the initial thermal state using the following procedure. First we prepare the pure state $|\psi\rangle = c_\uparrow|\uparrow\rangle + c_\downarrow|\downarrow\rangle$ using a standard optical pumping sequence followed by the application of resonant microwaves over a proper duration. After waiting more than 10 times the coherence time (see appendix A.4), the state becomes a mixed-state described by the density operator $\hat{\rho}_{\text{ini}} = |c_\uparrow|^2|\uparrow\rangle\langle\uparrow| + |c_\downarrow|^2|\downarrow\rangle\langle\downarrow|$, which is identical to thermal equilibrium state $\exp(-\hat{H}(0)/k_B T)$ with an effective temperature

$$T = \frac{\hbar\Omega_0}{k_B \ln(|c_\downarrow|^2/|c_\uparrow|^2)}. \tag{8}$$

For our experiment, $\Omega_0 = 2\pi \times 50$ kHz while $|c_\downarrow|^2$ took values of 0.605 ± 0.041 and 0.804 ± 0.034, corresponding to effective initial state temperatures of $T_1 = 5.63\ \mu$K and $T_2 = 1.70\ \mu$K, respectively.

(ii) Initial energy measurement—Following initial state preparation, the energy of the system is measured using a standard state-sensitive fluorescence detection sequence. In this procedure, fluorescence or the absence of fluorescence during the detection sequence indicate a measurement of the $|\uparrow\rangle$ or $|\downarrow\rangle$ state respectively. When the ground state $|\downarrow\rangle$ (dark state) is measured, we continue to the next step of the experiment. If the excited state $|\uparrow\rangle$ (bright state) is detected, we re-prepare the $|\uparrow\rangle$ state before continuing (see appendix A.5). As noted above, the actual measurements are performed with respect to the Hamiltonian $\hbar\Omega_0\hat{\sigma}_z/2$ which is then switched to $\hbar\Omega_0\hat{\sigma}_x/2$ using an adiabatic shortcut (see appendix A.6).

(iii) Application of driving with dephasing—At this point noisy microwave pulses are applied to the system resulting in evolution according to the Hamiltonian (6) with the protocols (7) and decoherence. For our trials, τ took values 50, 10, and 5 μs representing near adiabatic, intermediate, and fast driving speeds. The decoherence rate γ in equation (4) was set to 0, 448, or 1340 kHz which correspond to the cases of no, intermediate, or large dephasing strength respectively.

(iv) The final energy measurement—Prior to the final energy measurement, another adiabatic shortcut is used to switch the system's Hamiltonian—this time from $\hbar\Omega_0\hat{\sigma}_y/4$ to $\hbar\Omega_0\hat{\sigma}_z/4$. Following this transfer, the energy of the system is once again measured using a state-sensitive fluorescence detection sequence. By calculating the difference between the initial and final energy measurements, a work value for the experimental trial is obtained.

Figure 2 shows the work distributions resulting from experiments conducted with twelve different combinations of effective temperature T, driving time τ, and decoherence rate γ. From the data, it is clear that decoherence non-trivially affects the work distribution for a given process—for instance compare (d)–(f) in figure 2. A more careful inspection reveals that the qualitative behavior of the work distribution is governed by a competition between driving speed and decoherence. For near-adiabatic driving, the work distribution is peaked at values $W = \bar{\epsilon}_i - \epsilon_i$ corresponding to the measurement of two energies with the same quantum number. Increasing driving speed (decreasing τ) tends to induce transitions among energy states with different quantum numbers, thereby broadening the work distribution. This effect is exemplified in figure 2 by distributions (a), (b), and (d). In contrast, decoherence in the eigenbasis of $\hat{H}(t)$ suppresses these transitions bringing the work distribution closer to its adiabatic form. This can be seen by comparing the near adiabatic distribution (a) with the fast driving cases (d)–(f) which have varying degrees of decoherence. Interpreting this decoherence as environmental measurement of the system's energy, one can see that the system is forced to follow the adiabatic trajectory due to wave function collapse. When the collapse rate γ becomes large, the system becomes trapped in an eigenstate of the instantaneous Hamiltonian—a scenario analogous to the quantum Zeno effect.

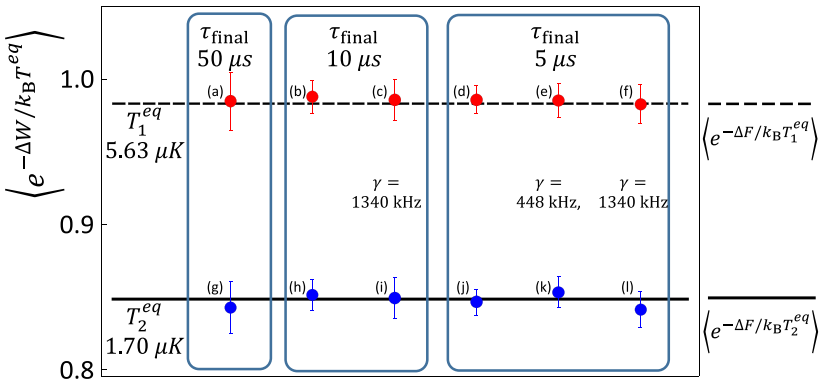


Figure 3. Comparison of the exponential average of work for distributions (a)–(l) in figure 2 to the exponential of the free energy difference calculated from the initial and final energy levels of $\hat{H}(t)$.

With these distributions, the work relation can be tested for each choice of the experimental parameters T, τ, and γ by direct comparison of the left- and right-hand sides of equation (1). Note that the quantity $\langle e^{-\beta W} \rangle$ is calculated using the work distribution while $e^{-\beta \Delta F}$ follows straightforwardly from knowledge of the energy levels of $\hat{H}(0)$ and $\hat{H}(\tau)$. The results of these calculations, shown in figure 3, agree to within the error of the experiment and hence validate the work relation.

4. Multiple interpretations

While our theoretical development focuses on environment-induced decoherence, the dephasing master equation (4) can be interpreted in various ways. For instance, (a) the same master equation describes—at the ensemble level—a system that evolves unitarily but is interrupted at random by projective measurements. More precisely if our experimenter makes measurements in the instantaneous eigenbasis of $\hat{H}(t)$ at times dictated by a Poisson process with rate γ, then the density operator resulting from averaging over all measurement realizations obeys equation (4), with $\gamma_{ij} = \gamma$. Yet another interpretation of the dephasing master equation arises when (b) one averages over noise that is introduced by adding an appropriately designed, randomly fluctuating term to the bare system Hamiltonian $\hat{H}(t)$ [48, 49]. The validity of equation (1) in case (a) has been noted explicitly by Campisi *et al* [55, 56], and in case (b) by Campisi, Pekola and Fazio [57]. More generally, both interpretations, (a) and (b), support a fluctuation theorem because the system evolves according to a unital channel during each realization, and the average of any number of unital maps is again unital, hence Rastegin's general analysis [37] applies.

Thus the non-unitary dephasing term appearing in equation (4) can arise either due to weak coupling to a bath, as described earlier, or due to externally imposed randomness, as described in the previous paragraph. In this paper we focus on the former interpretation because it most closely resembles the canonical setup for fluctuation theorems, namely a small system coupled to a bath in thermal equilibrium. As outlined in the experimental section of this manuscript, we simulate the effects of a decohering bath by the addition of noise to produce dephasing. Of course, our experiments can equally well serve as a direct verification of the above-mentioned prediction of [57].

5. Discussion and conclusions

Throughout this manuscript we have considered systems that experience only decoherence, but significant theoretical progress has been made in understanding quantum fluctuation theorems in situations where dissipation is also important. We outline some of these advances as they give context for our results and provide direction for future experimental work.

Perhaps the most conceptually appealing framework that addresses general thermal environments is based on considering the system and environment jointly as a closed composite system [33–35, 58]. Here the TPM scheme can be employed as the work is simply the change in energy of the joint system. (In the weak coupling limit, work can also be defined as $\Delta U - Q$ where the energy change ΔU and the heat Q are obtained by applying the TPM protocol separately to the system and environment.) Despite defining a work distribution that satisfies equation (1), this approach suffers from the need to measure bath degrees of freedom, which is difficult to realize in practice.

Other studies of the work relation overcome this issue by defining work at the system level without referencing an environment. In this vein there are several equivalent formalisms for treating QDBME [59–65] of which we focus on the quantum jump trajectory method [40, 61, 62, 66–69]. Originally developed in the field of quantum optics [70], this approach treats a system's density operator as an average over pure states evolving according to stochastic trajectories. The construction of these trajectories is called an *unraveling* and is generally not unique. When this unraveling is chosen properly, a consistent trajectory-based thermodynamics can be defined in a manner similar to classical stochastic thermodynamics, and the work relation remains valid [40, 61, 62, 66–69]. When applied to the decohering master equation (4), the quantum trajectory approach agrees with the theoretical development section of this paper.

Various approaches might be taken in future experimental tests of quantum fluctuation theorems. For instance, rather than producing decoherence through the addition of noise, the results of this manuscript could be complimented with an experiment using a true decohering bath engineered from an interaction commuting (at all times) with the bare Hamiltonians of the system and environment. For systems with dissipation, the quantum work relation could be tested for general thermal environments using the TPM protocol and a continuous environmental measurement technique [71–74] such as single photon detection in a cavity QED experiment. Alternatively using only the TPM protocol on a dissipative system, one could test the energy change fluctuation theorem which is a modified version of equation (1) devised by Pekola and co-workers [75]. For non-unital dynamics, Goold *et al* [76] have obtained fluctuationlike relations for *heat*, in the context of the quantum Landauer Principle. It remains an open, interesting question whether the quite general approach of [76] can be used to obtain an experimentally testable version of the nonequilibrium work relation (1) when both decoherence and dissipation are present. Alternative frameworks for defining heat and work present yet another direction for potential experimental tests of quantum fluctuation theorems. For example, in Elouard *et al* [77–79], energy changes are expressed in terms of three contributions—work, classical heat, and quantum heat. In the interpretation developed in [77], work is defined differently than in the present manuscript, and the energy changes measured in our experiment include contributions from quantum heat. Using a definition of work similar to that of [77], Deffner *et al* [80] have derived a modified version of equation (1) that accounts for the thermodynamic cost of projective measurements.

In summary, we have studied the quantum work relation for a system in contact with a decohering bath. We obtained equation (1) within a simple, phenomenological model that complements the more general approaches of unital quantum channels and quantum trajectories. Using a system constructed from trapped ions subjected to noisy dynamics, we conducted an experiment that demonstrated the work relation's validity for a dephasing process and represents the first test of equation (1) beyond the regime of closed quantum systems. These results demonstrate the applicability of fluctuation theorems to open quantum systems, at least for the special case of a decohering heat bath, and may spur additional tests of the work relation for systems with dissipation.

While this manuscript was under review, we learned that Naghiloo *et al* [24], also under review, describes experimental work verifying equation (1) for an open quantum system in which feedback control is used to compensate for the heat exchanged with the environment.

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Appendix

A.1. Detailed balance master equation

Consider a QDBME with a Hamiltonian $\hat{H} = \sum \epsilon_i |i\rangle \langle i|$ and an equilibrium state $\hat{\rho}^{\rm eq}$ satisfying the standard thermal relation

$$\hat{\rho}^{\mathrm{eq}} = \frac{\mathrm{e}^{-\beta\hat{H}}}{\mathrm{Tr}[\mathrm{e}^{-\beta\hat{H}}]}. \tag{9}$$

Additionally assume that the gaps $\epsilon_i - \epsilon_j$ in the spectrum of $\hat{H}$ are non-degenerate. Under these conditions, Alicki showed [42] that the master equation may be written in the form

$$\frac{\mathrm{d}\hat{\rho}}{\mathrm{d}t} = -\frac{\mathrm{i}}{\hbar}[\hat{H}, \hat{\rho}] + \sum_{\mathrm{i},j=1}^{N} D_{ij}\{[\hat{X}_{ij}, \hat{\rho}\hat{X}_{ij}^{\dagger}] + [\hat{X}_{ij}\hat{\rho}, \hat{X}_{ij}^{\dagger}]\}, \tag{10}$$

where N is the dimension of the system's Hilbert space and the real numbers D_{ij} and operators $\hat{X}_{ij}$ satisfy the conditions

$$D_{ij}\mathrm{e}^{-\beta\epsilon_j} = D_{ji}\mathrm{e}^{-\beta\epsilon_i}\,;\ D_{ij} \geqslant 0, \tag{11}$$

$$[\hat{H}, \hat{X}_{ij}] = (\epsilon_i - \epsilon_j)\hat{X}_{ij}, \tag{12}$$

$$\mathrm{Tr}[\hat{X}_{ij}^{\dagger}\hat{X}_{kl}] = \delta_{ik}\delta_{jl}, \tag{13}$$

$$\hat{X}_{ij} = \hat{X}_{ji}^{\dagger}. \tag{14}$$

In what follows, we will use the non-degenerate gaps of $\hat{H}$ along with conditions (11)–(14) to gain insight into the constants D_{ij} and operators $\hat{X}_{ij}$. This in turn will allow for equation (10) to be written in a form where the processes of relaxation and decoherence are manifest.

Constants D_{ij}—The constants D_{ij} can largely be interpreted within the framework of a classical continuous time Markov process [46]. Assuming discrete states indexed by i, such processes describe the evolution of a probability distribution p_i according to

$$\frac{\mathrm{d}p_i}{\mathrm{d}t} = \sum_j r_{ij}p_j, \tag{15}$$

where r_{ij} is a transition rate matrix with the properties

$$r_{ij}\begin{cases}\geqslant 0; & (i \neq j),\\ = -\sum_{k\neq i} r_{ki} & (i = j).\end{cases} \tag{16}$$

Furthermore the matrix r_{ij} is said to satisfy detailed balance with respect to an equilibrium probability distribution p_i^{eq} when

$$r_{ij}p_j^{\mathrm{eq}} - r_{ji}p_i^{\mathrm{eq}} = 0. \tag{17}$$

Given these definitions, one immediately recognizes from condition (11) that the off diagonal elements of D_{ij} coincide with the elements of a transition rate matrix satisfying the detailed balance condition (17) with $p_i^{\mathrm{eq}} \propto \exp(-\beta\epsilon_i)$. In what follows, we will find that the energy populations $\rho_{ii} = \langle i|\hat{\rho}|i\rangle$ relax thermally according to

$$\begin{aligned}\frac{\mathrm{d}\rho_{ii}}{\mathrm{d}t} &= \sum_{j\neq i}(2D_{ij})\rho_{jj} + \left(-2\sum_{j\neq i}D_{ji}\right)\rho_{ii}\\ &= \sum_{j\neq i} r_{ij}\rho_{jj} + r_{ii}\rho_{ii}.\end{aligned} \tag{18}$$

Hence for $i \neq j$ we will interpret D_{ij} as half the thermally induced transition rate from energy state j to state i. Note that r_{ii} is defined according to equation (16) and $D_{ii} \neq r_{ii}/2$. Condition (11) only constrains the constants D_{ii} to be positive. These numbers will later be interpreted in terms of decoherence rates. Anticipating these connections, the elements of D_{ij} will be redefined according to

$$D_{ij} = \begin{cases} r_{ij}/2 & (i \neq j),\\ d_i & (i = j).\end{cases} \tag{19}$$

Operators $\hat{X}_{ij}$—Before finding the explicit form of the operators $\hat{X}_{ij}$, it is instructive to recast conditions (12) and (13) in the language of linear algebra. Specifically note that condition (12) dictates that $\hat{X}_{ij}$ is an eigen-operator of the super-operator $[\hat{H}, \cdot]$ with eigenvalue $\epsilon_i - \epsilon_j$ while condition (13) asserts that the operators $\hat{X}_{ij}$ form an orthonormal set with respect to the matrix inner product $\langle\hat{A}, \hat{B}\rangle = \mathrm{Tr}[\hat{A}^{\dagger}\hat{B}]$.

First consider the operators $\hat{X}_{ij}$ for which $i \neq j$. In this case, each eigenvalue $\epsilon_i - \epsilon_j$ of equation (12) is non-degenerate (due to the gap structure of $\hat{H}$) and hence the corresponding eigen-operator $\hat{X}_{ij}$ is confined to a one-dimensional eigenspace. By inspection this eigenspace is determined to be $\{\alpha|i\rangle\langle j| : \alpha \in \mathbb{C}\}$. The normalization condition (13) further gives the constraint that $|\alpha|^2 = 1$. Without loss of generality, it is now possible to set

$$\hat{X}_{ij} = |i\rangle\langle j| \quad (i \neq j) \tag{20}$$

due to the fact that the master equation (10) is independent of the phase of α since $\hat{X}_{ij}$ and $\hat{X}_{ij}^{\dagger}$ appear in conjugate pairs.

For the case where $i = j$, the eigenvalue in equation (12) vanishes and corresponds to the N dimensional eigenspace $\{\sum_k O_{ik}|k\rangle\langle k| : O_{ik} \in \mathbb{C}\}$. Application of conditions (13) and (14) gives

$$O_{ik} \in \mathbb{R}\,;\ \sum_k O_{ik}O_{jk} = \delta_{ij} \tag{21}$$

which is exactly the condition that the matrix O_{ik} belong to the set of real orthogonal matrices $O(N)$. In conclusion

$$\hat{X}_{ii} = \sum_k O_{ik}|k\rangle\langle k|\,;\ O_{ik} \in O(N). \tag{22}$$

The form of the detailed balance master equation in the main body of this manuscript can now be deduced. Following substitution of equations (19), (20), and (22) into the master equation (10) and some manipulation, the result is given by

$$\begin{aligned}
\frac{\mathrm{d}\hat{\rho}}{\mathrm{d}t} &= -\frac{\mathrm{i}}{\hbar}[\hat{H},\,\hat{\rho}] + \sum_{ij} J_{ij}|i\rangle\langle i| + \sum_{i\neq j}\Gamma_{ij}|i\rangle\langle j|,\\
J_{ij} &\equiv r_{ij}\rho_{jj} - r_{ji}\rho_{ii},\\
\Gamma_{ij} &\equiv [(r_{ii} + r_{jj})/2 - \gamma_{ij}]\rho_{ij} \leqslant 0,\\
\gamma_{ij} &\equiv \sum_k d_k(O_{ki} - O_{kj})^2 \geqslant 0.
\end{aligned} \tag{23}$$

As stated earlier, the virtue of writing the master equation in the above form is that the processes of relaxation and decoherence are clearly displayed—they are the second and third terms on the right-hand side of equation (23) respectively. The relaxation is seen to shuffle the diagonal elements of the density operator according to a Markov process while the decoherence term causes exponential decay of off-diagonal elements.

A.2. The decohering master equation from a Hamiltonian model

In our main theoretical development, we argued that it is plausible no heating occurs during a decohering process and hence it is reasonable to determine work values using the TPM protocol. Here we strengthen this argument by presenting a specific microscopic model where our intuition can be verified according to the definitions of heat and work presented by Campisi *et al* [58].

Specifically, we consider a simple repeated interaction model where the bath is represented by a stream of identical auxiliary systems which we will refer to as *units*. Each unit begins in a thermal state $\hat{\omega}$ and interacts with the system of interest for a time δt. Over every interaction interval, the total Hamiltonian (system plus units) is fixed but the system's Hamiltonian and the interaction may change suddenly between intervals. We will denote the total Hamiltonian during the nth interval by

$$\hat{H}_n = \hat{H}_n^{(S)} \otimes \hat{I}^{(U)} + \hat{I}^{(S)} \otimes \hat{H}^{(U)} + \lambda\hat{V}_n, \tag{24}$$

where $\hat{H}_n^{(S)}$ is the system's Hamiltonian, $\hat{H}^{(U)}$ is the Hamiltonian of the non-interacting units which each have individual Hamiltonians $\hat{h}^{(U)}$, λ is the interaction strength, and $\hat{V}_n$ is an interaction that acts only on the system and nth unit. Furthermore to assure the process only produces dephasing in the system of interest, we assume that the interaction is of the form

$$\hat{V}_n = \hat{A}_n \otimes \hat{B}, \tag{25}$$

where $\hat{A}_n$ acts on the system and commutes with $\hat{H}_n^{(S)}$ while $\hat{B}$ acts on the nth unit and commutes with $\hat{h}^{(U)}$. In the following, we outline two important properties of this model: (1) the existence of a regime where the system's dynamics are described by a decohering master equation and (2) the absence of heat transfer between the system and units.

In order to show (1), we take

$$\hat{H}_n^{(S)} = \hat{H}^{(S)}(n\delta t), \tag{26}$$

$$\hat{A}_n = \hat{A}(n\delta t), \tag{27}$$

where $\hat{H}^{(S)}(t)$ and $\hat{A}(t)$ are operators that vary continuously with time and make the standard assumption [73] that $\mathrm{Tr}[\hat{\omega}\hat{B}] = 0$. Taking the limit $\delta t \to 0$ while simultaneously letting the interaction strength grow according to $\lambda = k\delta t^{-1/2}$ where k is a positive real constant, it can be shown [81] that

$$\frac{\mathrm{d}\rho^{(S)}}{\mathrm{d}t} = -\frac{\mathrm{i}}{\hbar}[\hat{H}^{(S)}(t),\ \rho^{(S)}] - C\left[\hat{A}(t)\rho^{(S)}\hat{A}(t) - \frac{1}{2}\{\hat{A}^2(t),\ \rho^{(S)}\}\right],$$
$$C = \frac{2k\mathrm{Tr}[\hat{B}^2\hat{\omega}]}{\hbar^2}. \tag{28}$$

Since $\hat{H}(t)$ and $\hat{A}(t)$ commute at all times, they share a common eigenbasis $\{|i(t)\rangle\}$. Rewriting the dissipator (second term on the rhs of equation (29)) in in this basis, the master equation becomes

$$\frac{\mathrm{d}\rho^{(S)}}{\mathrm{d}t} = -\frac{\mathrm{i}}{\hbar}[\hat{H}^{(S)}(t),\ \rho^{(S)}] - \sum_{i\neq j}\gamma_{ij}|i(t)\rangle\langle i(t)|\rho^{(S)}|j(t)\rangle\langle j(t)|,$$
$$\gamma_{ij} = \frac{\mathrm{Tr}[\hat{B}^2\hat{\omega}]}{\hbar^2}(a_i - a_j)^2, \tag{29}$$

where a_i are the eigenvalues of $\hat{A}$.

We now show property (2) holds according to the definitions of heat and work proposed in [58]. In this setup, work is determined (for initially thermal states) by applying the two point measurement protocol to the joint system and environment. Assuming that the system is decoupled from the units at the beginning and end of the process, the work performed during a single realization is given by $W = \epsilon_m^{(S)} + \epsilon_k^{(U)} - \epsilon_n^{(S)} - \epsilon_l^{(U)}$ where $\epsilon_m^{(S)} + \epsilon_k^{(U)}$ and $\epsilon_n^{(S)} + \epsilon_l^{(U)}$ respectively are the initial and final energy measurements. Since the total Hamiltonian of the system and units commutes with $\hat{H}^{(U)}$ at all times, it follows that $\epsilon_k^{(U)} = \epsilon_l^{(U)}$ which implies that the work is fully determined by local measurements on the system of interest as claimed in the main text of this manuscript.

A.3. Stochastic noise and decoherence rate

In our experiment, decoherence is induced by the introduction of noise. The system is driven by the total Hamiltonian

$$\hat{H}(t) = \frac{\hbar[\Omega(t) + \Omega_0\xi(t)]}{2}\hat{\sigma}_{\vec{n}}(t), \tag{30}$$

where $\hat{\sigma}_{\vec{n}}(t) = \hat{\sigma}_x\cos\phi(t) + \hat{\sigma}_y\sin\phi(t)$ and $\xi(t)$ is Gaussian white noise characterized by $\langle\xi(t)\rangle = 0$ and $\langle\xi(t)\xi(t+\tau)\rangle = \alpha^2\delta(\tau)$. $\hat{H}(t)$ can be decomposed into a control part $\hat{H}_c(t) = \hbar\Omega(t)\hat{\sigma}_{\vec{n}}(t)/2$ and stochastic part $\hat{H}_s(t) = \hbar\Omega_0\xi(t)\hat{\sigma}_{\vec{n}}(t)/2$.

Taking the ensemble average over all noise realizations, the evolution of the system is described by the Lindblad master equation[46, 48, 82]

$$\frac{\mathrm{d}\hat{\rho}}{\mathrm{d}t} = -\frac{\mathrm{i}}{\hbar}[\hat{H}_c(t),\ \hat{\rho}] - \gamma(\rho_{\downarrow\uparrow}|\downarrow\rangle\langle\uparrow| + \rho_{\uparrow\downarrow}|\uparrow\rangle\langle\downarrow|), \tag{31}$$

where $|\uparrow\rangle$, $|\downarrow\rangle$ are the instantaneous eigenvectors of $\hat{H}_c(t)$ and γ is the decoherence rate which satisfies

$$\gamma = \frac{(\alpha\Omega_0)^2}{2}. \tag{32}$$

In practice we applied discrete noise with a sampling rate of R_s instead of ideal continuous-Gaussian white noise. When $R_s^{-1}/2$ is much less than the duration of the operation, the digital noise can be approximated as Gaussian white noise, with auto-correlation function $\langle\xi(t)\xi(t+\tau)\rangle = \sigma^2R_s^{-1}\delta(\tau)$. Figure 4 gives an example of power spectral density of discrete Gaussian white noise, which has finite bandwidth. Hence equation (32) should be revised as

$$\gamma = \frac{(\sigma\Omega_0)^2}{2R_s}. \tag{33}$$

In our experiment, the systems decoheres for durations of 5, 10 and 50 μs and the noise sampling rate is set to 1 MHz. Hence the decoherence rate is given by $\gamma_{\mathrm{exp}} = (\sigma\Omega_0)^2/2$ MHz when Ω_0 is measured in MHz. And figure 5 clearly shows this linear relation between decoherence rate and effective auto-correlation amplitude of applied discrete Gaussian white noise.

A.4. Thermal state preparation

We use the magnetic field sensitive states $|^2S_{1/2},\ F = 1,\ m_F = -1\rangle \equiv |\uparrow\rangle$ and $|^2S_{1/2},\ F = 0,\ m_F = 0\rangle \equiv |\downarrow\rangle$ to create an effective two state system with a typical coherence time of 0.14 ms. After preparing a superposition state with the desired populations, we wait 1.5 ms for the system to decohere. We confirm that the state is effectively

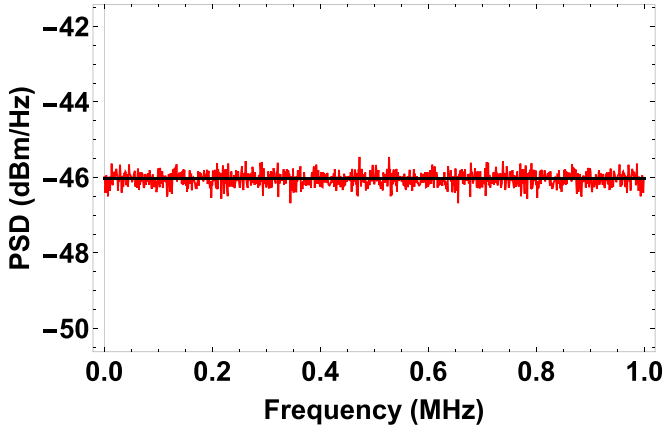


Figure 4. Power spectral density of discrete Gaussian white noise with standard deviation $\sigma = 5$ and sampling rate 1 MHz.

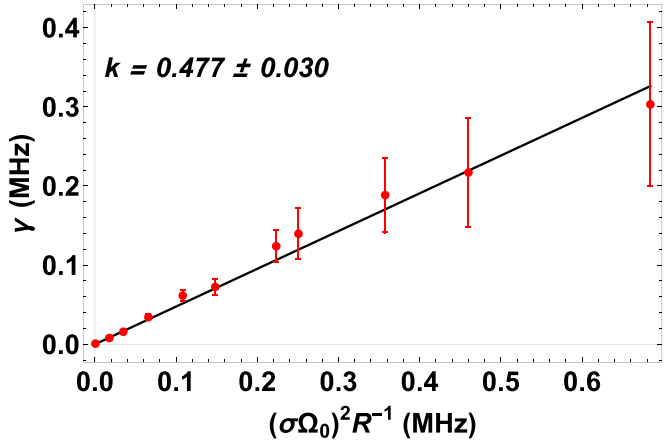


Figure 5. Experiment results of decoherence rate γ relation with $(\sigma\Omega_0)^2 R_s^{-1}$. Here sampling rate is set as 1 MHz.

thermal using state-tomography [47]. As shown in figure 6, the off-diagonal components of the density matrix are negligible for both effective temperatures used in our setup.

A.5. Energy measurements

The first and the second energy measurements are performed in the $\hat{\sigma}_z$ basis using standard fluorescence detection as shown in figure 7. Depending on whether the system is in the excited state $|\uparrow\rangle$ or ground state $|\downarrow\rangle$, fluorescence or no fluorescence respectively occurs during the detection sequence. When the ground state $|\downarrow\rangle$ (dark state) is measured, the system remains unchanged during the detection sequence and we simply continue to the next step of the experiment. If the excited state $|\uparrow\rangle$ (bright state) is detected, the system is left in a mixture of the three levels of $F = 1$ in ${}^2S_{1/2}$ manifold. Therefore, we re-prepare the $|\uparrow\rangle$ state using standard optical pumping and a π-pulse of microwaves before continuing the experiment. A fluorescence detection sequence is also used for the final measurement which constitutes the end of an experimental run.

A.6. Adiabatic rotation

For our setup, the initial and the final energy measurements are performed in the $\hat{\sigma}_z$ basis. Between the measurement sequences and the driving protocol, the state of the system must be transferred between the z-axis and x–y plane of the Bloch sphere. To accomplish this task, we use adiabatic shortcuts—a protocol that has the same effect as an adiabatic switching of the Hamiltonian but occurs in finite time [52–54]. Specifically we apply an additional counterdiabatic term to our Hamiltonian during the switching process to achieve the shortcut.

After thermal state preparation and the first energy measurement, our system collapses into the $|\uparrow\rangle$ or $|\downarrow\rangle$ state. In principle, we have to adiabatically rotate the $|\uparrow\rangle$ or $|\downarrow\rangle$ state to the corresponding state in the x-y plane of the Bloch sphere. In our experiment, the coherence time of a superposition of the $|\uparrow\rangle$ and $|\downarrow\rangle$ states is short and

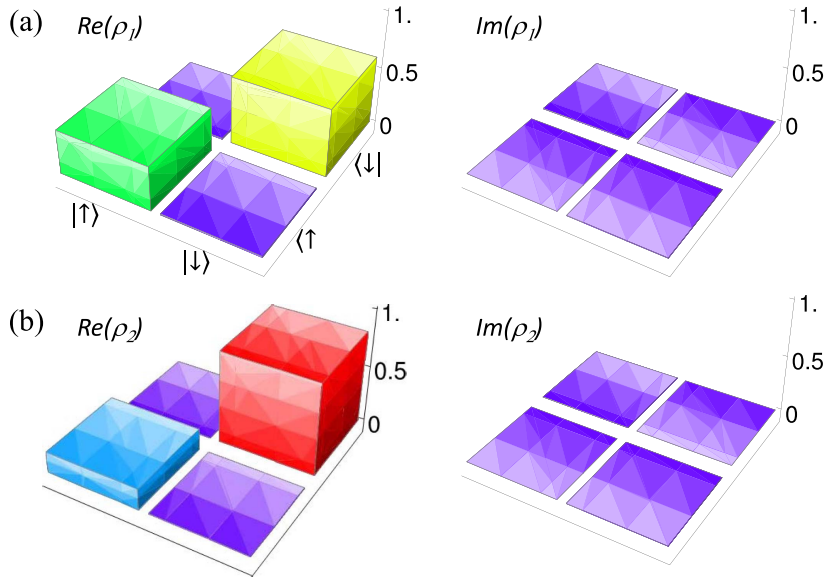


Figure 6. Density matrices after preparing effective thermal states, which are equivalent to (a) $T_1^{eq} = 5.63\ \mu$K and (b) $T_2^{eq} = 1.70\ \mu$K.

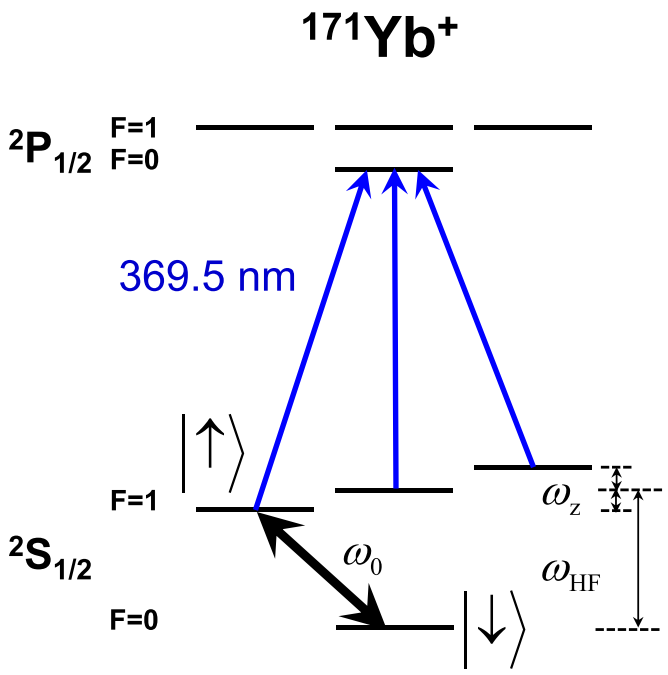


Figure 7. Energy levels of our $^{171}Yb^{+}$ ion system. The two level system used in our experiment is composed from the states $|\uparrow\rangle$ and $|\downarrow\rangle$. Transitions between these states are driven using resonant microwaves.

hence would introduce an error in the rotation if it were carried out in a truly adiabatic fashion. Therefore, we apply an adiabatic shortcut to reduce the time for the rotation. In this scheme, we change the Hamiltonian of the system according to

$$\hat{H}_1(t) = \frac{\Delta_0}{2}\hat{\sigma}_z \cos(\omega_1 t) + \frac{\Omega_0}{2}(\hat{\sigma}_x \sin(\omega_1 t) + \hat{\sigma}_y), \tag{34}$$

where $\omega_1 = \Omega_0 = \Delta_0 = (2\pi)50$ kHz and t varies from $t = 0$ to $t = \pi/2\omega_1 = 5\ \mu$s. The term proportional to $\hat{\sigma}_y$ is the counterdiabatic which suppresses the excitations. Note that true adiabatic rotation requires at least hundreds of μs, which is much longer than transfer time using the adiabatic shortcut.

After the driving sequence, we rotate the system's state back to the z-axis of the Bloch sphere using the Hamiltonian

$$\hat{H}_2(t) = \frac{\Omega_0}{4}(\hat{\sigma}_y \cos(\omega_2 t) + \hat{\sigma}_x) + \frac{\Delta_0}{4}\hat{\sigma}_z \sin(\omega_2 t), \tag{35}$$

where $\omega_2 = \Omega_0/2 = \Delta_0/2 = (2\pi)25$ kHz and t varies from $t = 0$ to $t = \pi/2\omega_2 = 10$ μs. This time the courterdiabatic term is proportional to $\hat{\sigma}_x$.

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