Non-thermal energy fluctuations of a diamond spin qutrit with feedback-controlled dissipative dynamics

S. Hernández-Gómez,1,2,3 S. Gherardini,1,3,4 N. Staudenmaier,1,2,* F. Poggiali,1,2,† M. Campisi,5,2,6 A. Trombetta,4,7 F. S. Cataliotti,1,3, P. Cappellaro,6 and N. Fabbri1,3,‡

1 European Laboratory for Non-linear Spectroscopy (LENS), Università di Firenze, I-50019 Sesto Fiorentino, Italy
2 Dipartimento di Fisica e Astronomia, Università di Firenze, I-50019, Sesto Fiorentino, Italy
3 Istituto Nazionale di Ottica del Consiglio Nazionale delle Ricerche (CNR-INO), I-50019 Sesto Fiorentino, Italy
4 Scuola Internazionale Superiore di Studi Avanzati (SISSA), I-34136 Trieste, Italy
5 NEST, Istituto Nanoscienze-CNR and Scuola Normale Superiore, I-56127 Pisa, Italy
6 INFN - Sezione di Pisa, I-56127 Pisa, Italy
7 CNR-IOM DEMOCRITOS Simulation Center, I-34136 Trieste, Italy
8 Department of Nuclear Science and Engineering, Department of Physics, Massachusetts Institute of Technology, Cambridge, MA 02139

Engineered dynamical maps that combine not only coherent, but also unital and dissipative transformations of quantum states, have demonstrated a number of technological applications, and promise to be a beneficial tool also in quantum thermodynamic processes. Here, we exploit control of a spin qutrit to investigate energy exchange fluctuations of an open quantum system. The qutrit engineer dynamics can be understood as an autonomous feedback process, where random measurement events condition the subsequent dissipative evolution. To analyze this dynamical process, we introduce a generalization of the Sagawa-Ueda-Tasaki relation for dissipative dynamics and verify it experimentally. Not only we characterize the efficacy of the autonomous feedback protocol, but also find that the characteristic function of energy variations $G(\eta)$ becomes insensitive to the process details at a single specific value of its argument. This allows us to demonstrate that a fluctuation theorem of the Jarzynski type holds for this general dissipative feedback dynamics, while previous relations were limited to unital dynamics. Moreover, in addition to the feedback efficacy, we find a witness of unitality associated with the fixed point of the dynamics.

I. INTRODUCTION

The interaction of a quantum system with its environment has often a detrimental effect, inducing decoherence and information losses [1]. However, a proper control and design of the system-environment coupling via the combination of coherent and non-unitary operations is a fundamental resource for quantum information processing [2, 3], quantum simulation [4], quantum sensing [5–7], and quantum thermodynamics [8–10]. Dissipative operations—achieved e.g. by means of optical pumping, dark states, or through the quantum Zeno effect—can be used to produce quantum states of interest such as non-equilibrium steady states, strongly correlated states, or to prepare and stabilize robust phases and entanglement [11–15]. A relevant feature of dissipative dynamics is the appearance of stationary states, non necessarily in thermal equilibrium [16, 17], as a generalization of thermalization processes. Moreover, among non-unitary operations, measurement lies at the core of the relationship between thermodynamics and information. Quantum projective measurements contribute as a purely quantum component to heat exchange [18, 19], and enable feedback mechanisms acting on the system dynamics. Feedback mechanisms, where information is converted into usable energy [20, 21] by a so-called Maxwell’s demon [22–24], play a crucial role in the investigation of quantum information thermodynamics and may find applications in information-powered quantum refrigerator or heat engine [25, 26], quantum heat transport [27], quantum computation and error correction [28], and metrology [29].

Information and energy exchanges of an open quantum system with its environment inherently involve fluctuations. Quantum measurements, randomizing the system evolution, introduce quantum energy fluctuations, which impact the observable distribution obtained by averaging over many quantum trajectories [30, 31]. These fluctuations can drive the quantum system towards novel—often out-of-equilibrium—dynamical regimes that could not be otherwise achieved. Quantum fluctuation relations (QFR) [32, 33] provide a powerful framework to characterize such energy fluctuations in thermodynamic processes.

Experimental investigations of quantum fluctuation relations have been recently conducted on different platforms, including single trapped ions [34, 35], NMR systems [36, 37], atom chip [38], superconducting qubits [39], Nitrogen-Vacancy (NV) centers in diamond [40], and entangled photon pairs [41]. These studies cover closed system dynamics [34–36, 38, 39], and certain open dy-
FIG. 1. (a,b) Scheme of the spin system $S$ in the presence of a green laser. Upon interaction with a laser pulse, the spin is subject to a quantum measurement ($Q_m$) of $S_z$, and dissipation ($Q_D$) towards the $m_S=0$ spin projection. This irreversible dissipation is analogous to putting the system in contact with an out-of-equilibrium reservoir $R$. Since the interaction between the system and the reservoir is conditioned by the application of a quantum measurement, the dissipation acts as an intrinsic feedback mechanism. The unitary part of the dynamics is defined by the Hamiltonian $H$, with eigenstates $|E_i\rangle$, $i=1,2,3$.

(c) Protocol to measure energy conditional probabilities. The stochastic-dissipative map $M$ is a combination of a train of $N_L$ equidistant short laser pulses and a continuous driving under the Hamiltonian $H$ that can be either $H_{NV}$ or $H_{mw}$ (see text). The total time of the experiment $t_{\text{fin}}=N_L\tau$ is defined in terms of the number of laser pulses and the time $\tau$ between them. The laser pulse duration $t_L$ is negligible with respect to the continuous driving. The gates $G_i: |0\rangle \rightarrow |E_i\rangle$ and $G_j^{-1}: |E_j\rangle \rightarrow |0\rangle$ enable to prepare and readout the Hamiltonian eigenstates, respectively, by exploiting the optical properties of the NV center.

A unified framework to describe energy fluctuations in quantum systems under controllable feedback mechanisms, including non-unitary (even non-unital) operations, is still missing. Here, we explore this open issue both experimentally and theoretically. We realize an autonomous dissipative Maxwell demon with a spin qutrit formed by a Nitrogen-Vacancy (NV) center in diamond at room temperature, and we investigate its purely quantum (non-Gibbsian) energy fluctuations. The intrinsic feedback mechanism acting on a dissipative dynamics is achieved by performing random measurements followed by conditioned and tunable optical pumping. The resulting dynamics generates non-thermal steady states in the energy basis, independent of the initial state. We thus set up a formalism that includes both information and quantum energy fluctuations for dissipative Maxwell demons. In the case of conditioned unitary evolutions, the Sagawa-Ueda-Tasaki (SUT) relation establishes a fundamental connection between the thermodynamic properties of non-equilibrium quantum processes and information-theoretic quantities, evaluated by measuring and manipulating the system [22, 42–44]. Our work generalizes the SUT relation to conditioned dissipative dynamics, verifying it experimentally by measuring the energy change statistics of the spin qutrit. We also find, both theoretically and experimentally, that the characteristic function $G(\eta)$ of energy changes—where $\eta$ defines the energy scale—becomes insensitive to the process details and time independent, at a single specific value $\eta^*$ of its argument. Thus, an effective Jarzynski-like fluctuation theorem holds, despite lack of unitality of the qutrit evolution. Indeed, we find that the very quantity $\eta^*$—only dependent on the initial state and the final steady-state of the qutrit—provides information on the lack of unitality of the thermodynamic process, similarly to the efficacy of the feedback mechanism [27, 45, 46].

II. FEEDBACK-CONTROLLED DISSIPATIVE DYNAMICS

We now describe the intrinsic-feedback dissipative dynamics realized with a diamond spin qutrit, and we model it in terms of a Lindbladian master equation.

The negatively-charged NV center, a quantum defect comprising a substitutional nitrogen atom next to a va-
cancy in the diamond lattice, forms an electronic spin triplet \( S = 1 \) in its orbital ground state. The intrinsic electron spin-spin interaction separates in energy the state \(| m_S = 0 \rangle \) from the degenerate \(| m_S = \pm 1 \rangle \) (where \(| m_S \rangle \) are the eigenstates of the spin operator \( S_z \), along the NV symmetry axis \( z \)), while an applied magnetic field \( B \) aligned along \( z \) removes the degeneracy of the electronic spin states \(| \pm \rangle \), and leads to the formation of a three-level system. Each of the three states \(| m_S \rangle \) is further split into hyperfine sublevels due to coupling to the NV \( ^{14}\text{N} \) nuclear spin \( I = 1 \) \([47]\), however we restrict our analysis to the hyperfine subspace with nuclear spin projection \( m_I = +1 \), since the other states are depleted as a part of the initialization procedure and then are out of resonance in the following experiments, thus not contributing to the spin dynamics.

The spin qutrit is coherently driven by bichromatic on-resonant microwave radiation, with frequency components \( \omega_{\pm} \). The spin dynamics under the continuous double driving is described by the Hamiltonian \( H(t) = H_{\text{NV}} + \omega \cos(\omega t)|+1\rangle\langle 0| + \cos(\omega t)|-1\rangle\langle 0| + \text{h.c.} \), where \( \omega \) is the driving Rabi frequency. When \( \omega \) vanishes, this reduces to the intrinsic spin Hamiltonian

\[
H_{\text{nv}} = \Delta S_z^2 + \gamma_e B S_z, \tag{1}
\]

where \( \Delta \approx 2.87 \text{ GHz} \) is the zero-field-splitting, and \( \gamma_e \) is the NV gyromagnetic ratio. When the microwave driving is on, with \( \omega_{\pm} = \Delta \pm \gamma_e B \), in the rotating-wave approximation the spin Hamiltonian simplifies as follows:

\[
H_{\text{mw}} = \omega S_x. \tag{2}
\]

We performed different experiments while using each of the two Hamiltonians \([\text{Eq. (1) and (2)}]\) to determine the unitary part of dissipative maps, and the energy basis in which fluctuations are evaluated.

On top of the unitary evolution, the system is intermittently opened by means of its interaction with a train of short laser pulses, as illustrated in Fig. 1(a-b). Although laser pulses are equidistant, photon absorption events follow a binomial random distribution in time, due to the finite photon absorption probability \( (p_a < 1) \). While a long laser pulse would produce a complete optical pumping in the \(| 0 \rangle \) state \([48]\), the interaction with a short laser pulse—as used here—can be simply modeled as follows: If photons are not absorbed, the state of the system is unperturbed; if a photon is absorbed, the system is subjected to a projective measurement in the \( S_z \)-basis \([49]\) accompanied by optical pumping of the spin towards the state \(| m_S = 0 \rangle \). In other words, the optical pumping induces irreversible dissipation on the spin system. Thus, the interaction between the three-level system (3LS) and a short laser pulse can be described by a positive operator-measured value (POVM) followed by a dissipation operator conditioned on the POVM result.

The combined effect of unitary evolution, POVMs, and dissipation result in a quantum dissipative map \( \mathcal{M} \) that involves an intrinsic feedback mechanism. The feedback-controlled dissipative map \( \mathcal{M} \), applied to the spin qutrit, can be decomposed as a sequence of blocks, each representing the unitary evolution \( U = e^{-i\tau H} \) followed by the interaction of the system with a short laser pulse. In the superoperator formalism \([50]\), the unitary evolution of a given density matrix \( \rho \) is described as \( \text{col}[(U \rho U^\dagger)] = U \text{col}[\rho] \), where \( \text{col}[\rho] \) denotes the vectorization of \( \rho \), obtained by stacking the columns of \( \rho \) to form a ‘column’ vector, and \( U \equiv \exp(-i\tau (H \otimes \mathbb{1}_{3x3} - \mathbb{1}_{3x3} \otimes H')) \) with \( \otimes \) representing the Kronecker product. On the other hand, the interaction with a single short laser pulse of duration \( t_L \) transforms a density matrix \( \rho \) into \( \mathcal{A} \text{col}[\rho] \), where the Liouville superoperator \( \mathcal{A} \) is formally written as

\[
\mathcal{A} \equiv \sum_{j=1}^{4} \mathcal{D}_j m_j. \tag{3}
\]

In Eq. (S4), \( m_j \) is the \( j \)-th \((j = 1, \ldots, 4)\) measurement superoperator associated with the POVM (see Eqs. (A3) in Appendix A) and \( \mathcal{D}_j \) is the dissipation operator that depends on the result of the POVM:

\[
\mathcal{D}_j = \begin{cases} 
1_{9\times9}, & \text{if } j = 4 \\
\mathcal{L}, & \text{otherwise}
\end{cases} \tag{4}
\]

where the Lindbladian superoperator \( \mathcal{L} \) models the irreversible optical pumping. More details about this model are given in Appendix A.

Here, it is worth noting that the action of the dissipation operator is conditioned on the result of the previously-applied POVM. Thus, this mechanism effectively realizes an autonomous Maxwell demon, whose action is defined by the specific photodynamics of the NV center. Overall, the effect of the feedback-controlled dissipative map \( \mathcal{M} \), after \( N_l \) laser pulses, is thus modeled as \( \mathcal{M}[\rho] \to \mathcal{B}^{N_l}\text{col}[\rho] \), where \( \mathcal{B} \) is the superoperator that describes a single block of the dynamics

\[
\mathcal{B} \equiv \mathcal{A} U. \tag{5}
\]

The study of energy variation fluctuations induced by the map \( \mathcal{M} \) is the central issue of this article.

III. ENERGY FLUCTUATIONS MEASUREMENT

We characterize the quantum (non-thermal) energy fluctuations of the NV spin induced by the dissipative map \( \mathcal{M} \) in two independent experiments:

1. Coherent double driving and short laser pulses. The unitary part of the map \( \mathcal{M} \) is ruled by the Hamiltonian \( H_{\text{nv}} \) defined in Eq. (2), with eigenstates \(| E_1 \rangle = | -\omega \rangle \), \(| E_2 \rangle = | 0 \rangle \), and \(| E_3 \rangle = | +\omega \rangle \), where \(| \pm\omega \rangle \equiv \frac{1}{2} (| -1 \rangle \pm \sqrt{2} | 0 \rangle + | 1 \rangle) \), and \(| 0 \rangle \equiv \frac{1}{\sqrt{2}} (| -1 \rangle - | 1 \rangle) \).

2. Undriven spin, subject to short laser pulses. The spin Hamiltonian is \( H_{\text{NV}} \) with eigenstates \(| E_1 \rangle = | 0 \rangle \), \(| E_2 \rangle = | -1 \rangle \), and \(| E_3 \rangle = | +1 \rangle \).
The effect of the map $\mathcal{M}$ on the spin energy is characterized by measuring the energy jump probabilities, i.e., the conditional probabilities associated with the energy variation in a given time interval. The protocol used to measure conditional probabilities, as depicted in Fig. 1(c) consists in the following steps:

a) Initialize the system into one of the Hamiltonian eigenstates, say $|E_i\rangle$;

b) Evolve the system under the map $\mathcal{M}$ up to time $t_{\text{fin}}$;

c) Read out the probability of the spin to be in the Hamiltonian eigenstate $|E_j\rangle$ at final time $t_{\text{fin}}$;

d) Repeat the procedure for each initial and final Hamiltonian eigenstates.

A. Spin initialization and readout

The NV spin is initially prepared in the spin qutrit Hamiltonian eigenstate $|E_i\rangle$. The starting point of the initialization is a thermal spin mixture $\rho = \sum_{m_S,m_I} |m_S,m_I\rangle \langle m_S,m_I|$, within the $9 \times 9$ space described by the hyperfine manifold within orbital ground state. The quantum gate $G_0$ prepares the hyperfine state $|m_S,m_I\rangle = |0,1\rangle$ (see Fig. 1). First, a long laser pulse populates the hyperfine manifold $|0,m_I\rangle$ without initializing the nitrogen nuclear spin due to the relatively weak magnetic bias field ($B \approx 100$ MHz/$\gamma_c$). This is followed by electronic (hyperfine-selective) and nuclear spin operations that deplete the nuclear spin projections $m_I = \{0,-1\}$, as described in the Supplemental Material at [URL will be inserted by publisher]. Pure electron spin states in the energy basis ($|E_i\rangle$) are then prepared by applying opportune two-level-system quantum gates ($G_i$, in Fig. 1) realized by means of nuclear spin selective monochromatic microwave pulses resonant with the electronic transitions $|0\rangle \rightarrow |+1\rangle$ or $|0\rangle \rightarrow |-1\rangle$ as described in Appendix B.

After a spin evolution under the dissipative map $\mathcal{M}$, the state readout is performed by exploiting the difference in the NV center photoluminescence (PL) intensity, among states $|\pm 1\rangle$ and states $|\pm 0\rangle$, upon illumination with green laser light. To measure the probability of the spin to be measured in each of the three Hamiltonian eigenstates $|E_j\rangle$ at the end of the protocol, that eigenstate is projected into the $S_z$ eigenstate $|0\rangle$ (quantum gate $G_{-1}^z$ in Fig. 1), then the PL intensity is recorded. The description of the gates $G_i$ and $G_{-1}^z$ for each of the initial and final eigenstates can be found in Appendix B. Since the readout process is destructive, each experiment is composed by three different runs, where the probability of each of the three eigenstates is recorded. Due to limited diamond PL collection efficiency and to photon shot noise, each experiment is repeated $\sim 10^6$ times.

Notice that the duration of each realization of the experiment is much shorter than the nuclear spin lifetime so that the three-dimensional hyperfine spin subspace is well defined for the whole experiment duration.

B. Conditional probabilities

The conditional probabilities $P_{ji}$ associated with energy jumps from the initial ($|E_i\rangle$) to the final ($|E_j\rangle$) eigenstates are shown in Fig. 2, as a function of the number of laser pulses $N_L$ applied before performing the readout. The experimental data are shown together with the theoretical model of the dynamics, described in Sec. II. The experimental results show that the conditional probabilities $P_{ji}$ tend to a single constant value in the long-time regime (large $N_L$). In other words, the spin state asymptotically approaches a steady state in the energy basis (SSE) that does not depend on the initial state, thus confirming the dissipative nature of the map $\mathcal{M}$. In the case of $\mathcal{H} = \mathcal{H}_{\text{NV}}$ [Fig. 2(b)], the asymptotic state is $\rho_{\text{NV}}^\infty = \sum_{\ell=-1}^{+1} \rho_{\ell}^\infty |\ell\rangle \langle \ell|$, with populations, obtained from the experimental data, $p_{-1}^\infty = (-0.01 \pm 0.01)$, $p_0^\infty = (1.01 \pm 0.01)$, and $p_{+1}^\infty = (0.00 \pm 0.01)$. The protocol is equivalent to an initialization procedure into $\rho_{\text{NV}}^\infty = |0\rangle \langle 0|$. On the other hand, if $\mathcal{H} = \mathcal{H}_{\text{mw}}$ [Fig. 2(a)], the asymptotic state significantly differ from $|0\rangle = \frac{1}{\sqrt{2}} (|+\omega\rangle - |-\omega\rangle)$. Although the interaction with each laser pulse pushes the system towards $|0\rangle$, the unitary evolution modifies the density operator populations in the $S_z$ basis, thus changing the SSE at large times. In such case, the asymptotic state is $\rho_{\text{mw}}^\infty = \sum_{\ell=-\omega}^{+\omega} \rho_{\ell}^\infty |\ell\rangle \langle \ell|$, with populations, obtained from the experimental data, $p_{-\omega}^\infty = (0.41 \pm 0.01)$, $p_0^\infty = (0.20 \pm 0.02)$, and $p_{+\omega}^\infty = (0.40 \pm 0.01)$, as shown in Fig. 2(a).

C. Energy variation distribution

For an initial thermal state, measuring the conditional probabilities $P_{ji}$ gives access to the statistics of $\Delta E$

$$P_{\Delta E} \equiv \text{Prob}(\Delta E) = \sum_{i,j} \delta(\Delta E - \Delta E_{j,i}) P_{ji} P_i$$

where $\Delta E_{j,i} \equiv E_j - E_i$ and $P_i$ is the probability to obtain $E_i$ as a result of the energy measurement of an initial thermal state. In contrast with the usual two-point measurement (TPM) protocol [51], where $P_i$ is measured by performing an energy projective measurement on the initial state, we initialize the spin into each of the eigenstates of the Hamiltonian [Sec. III], and we obtain mixed (equilibrium) states as statistical mixture of the eigenstates with probabilities $P_i$ as weight factors. Our protocol gives equivalent results to a TPM protocol, owing to the large number of experimental realizations, [40, 52], while overcoming the difficulties to prepare an initial thermal state. Moreover, the protocol removes possible experimental errors inherent in the first energy measurement, and allows to use one single set of measurements to study different initial states.

Once provided the energy variation distribution $P_{\Delta E}$, the characteristic function $G(\eta) \equiv \langle e^{iu\Delta E} \rangle_{u,i=\eta}$ of $P_{\Delta E}$
FIG. 2. Probability $P_{ji}$ of measuring the state $|E_j\rangle$ after applying the map $M$ to the state $|E_i\rangle$ as a function of the number of laser pulses $N_L$, where $|E_i\rangle$ and $|E_j\rangle$ represent each of the eigenstates of the 3LS Hamiltonian (a) $H_{mw}$ and (b) $H_{NV}$. In both cases, the duration of the laser pulses is $t_L = 41$ ns, and the time between pulses is $\tau = 424$ ns. Each panel corresponds to a different initial eigenstate: (a) $\{|+\omega\rangle, |\emptyset\rangle, |-\omega\rangle\}$ and (b) $\{+1\rangle, |0\rangle, |-1\rangle\}$. The markers with errorbars represent the experimental data, and each solid line corresponds to the calculation performed with the theoretical model of the map $M$, as described in Sec. II. Experimental error bars are mainly due to photon shot noise.

can be experimentally computed as

$$G(\eta) = \sum_{i,j} e^{-\eta \Delta E_{ji}} P_{ji} P_i.$$

IV. DISSIPATIVE SAGAWA-UEDA-TASAKI RELATION

In our context, QFR [33] provide a powerful framework to characterize fluctuations of energy by inspecting its characteristic function. The quantum fluctuation relation for dynamics under measurements and feedback control, also known as the quantum Sagawa-Ueda-Tasaki (SUT) relation, was originally proposed for protocols where specific unitary operations are applied to the quantum system depending on the outcomes of a sequence of projective measurements [42, 43]. Here, we propose an extension of the quantum SUT relation to the case in which POVMs are performed instead of projective measurements, and the dynamics after the measurements are described by completely positive trace-preserving (CPTP) maps, conditioned on the result of the POVMs, instead of unitary operators.

The protocol is the following: An $n$-dimensional quantum system evolves under the Hamiltonian $H_0$; then, a POVM is performed on the system. The quantum measurement is defined by a set of positive semidefinite operators $\Pi_1, \ldots, \Pi_{n'}$ such that $\sum_{k=1}^{n'} \Pi_k = \mathbb{1}_{n \times n}$. According to a feedback mechanism, the measurement outcome $k$ determines the CPTP map $\Phi_k$ under which the system continues to evolve. Since $\Phi_k$ is a CPTP map, we can define the superoperator propagator $\Phi_k$ such that the evolution of a generic density matrix $\rho$ is described as $\text{col}[\Phi_k[\rho]] = \Phi_k \text{col}[\rho]$ [50]. Hence, the complete feedback map $M_\Phi$ transforms the density matrix $\rho$ into

$$\text{col}[M_\Phi[\rho]] = \sum_{k=1}^{n'} \text{col}[\Phi_k \Pi_k U_0 \text{col}[\rho]],$$

where $U_0 = \exp(-it(H_0 \otimes \mathbb{1}_{n \times n} - \mathbb{1}_{n \times n} \otimes H_0^*))$ is the superoperator that describes the unitary evolution before the POVM, and $\Pi_k \equiv \Pi_k \otimes \Pi_k$ represents the action of the measurement operators on the quantum system. As in the original SUT relation, a TPM measurement scheme is used to characterize the statistics of the energy variation, by initializing the quantum system in the thermal state $\rho_{th}$. As a result, the characteristic function of the energy variation is equal to a parameter $\gamma$ that represents the efficacy of the feedback mechanism:

$$G(\beta) = \gamma \equiv \sum_{k=1}^{n'} \text{Tr}_{n \times n} \left[ \Pi_k^\dagger \Phi_k \text{col}[\rho_{th}^\text{th}] \right],$$

where $\beta$ is the inverse temperature of the initial thermal state, $\rho_{th}^\text{th}$ is a thermal state at the final time of the TPM.
protocol, the symbol $\dagger$ denotes conjugate-transpose, and $\text{Tr}_{n \times n}[\text{col}[]] \equiv \text{Tr}[]$. The efficacy of a feedback mechanism defines the amount of energy that can be extracted from the system, depending on the value of $\gamma$ (see also Sec. VI). The mathematical proof of Eq. (9) can be found in Appendix C (see Corollary 1). The proof is based on the fact that the map $\mathcal{M}_k$ is itself a CPTP map, meaning that Eq. (9) is a particular case of the general quantum fluctuation relation for CPTP maps [43, 45, 53–56]. It is worth observing that Eq. (9) reduces to the original quantum SUT relation [42] in the specific case where the intermediate quantum measurements are projective and $\Phi_k$ are unitary evolution operators. Moreover, if $\Phi_k$ are unital CPTP maps, then $\Phi_k^\dagger$ is trace preserving [50], hence $\gamma = 1$ [53, 54] for any time-independent Hamiltonian. In contrast, for non-unital maps where microreversibility is not satisfied, the value of $\gamma$ can be different from 1 and, in general, involves non trace-preserving operators $\Phi_k^\dagger$.

Equations (8) and (9) refer to a feedback operation on the quantum system enabled by applying a single POVM measurement, and they can be simplified by defining $\mathcal{B}_\Phi \equiv \sum_{k=1}^N \Phi_k \Pi_k$ that leads to $\gamma = \text{Tr}_{n \times n}[\mathcal{B}_\Phi \text{col}[\rho^{\text{th}}]]$. Therefore, the protocol to the scenario where measurements and feedback are applied repeatedly is quite straightforward: After $N$ repetitions $\gamma = \text{Tr}_{n \times n}[(\mathcal{B}_\Phi^N) \text{col}[\rho^{\text{th}}]]$. Expressing $\gamma$ in this way significantly simplifies its computation, because it removes the requirement to calculate every possible quantum trajectory originated by the system dynamics; compare for example with Refs. [27, 42]. This advantage may be significant since the number of trajectories scales exponentially with the number of measurements. In addition, for any CPTP dissipative map, whereby the system asymptotically reaches the single SSE $\text{col}[\rho^\infty] \equiv \lim_{n \to \infty} \mathcal{B}_\Phi^N \text{col}[\rho]$, for a generic initial state $\rho$, we can write the asymptotic value of $\gamma$ as (see also Corollary 2 in Appendix C)

$$\gamma^\infty \equiv \lim_{t \to \infty} \gamma = n\langle \rho^\infty, \rho^{\text{th}} \rangle_{\text{hs}}$$

(10)

where $\langle \rho_1, \rho_2 \rangle_{\text{hs}} \equiv \text{Tr}[\rho_1 \rho_2]$ denotes the Hilbert-Schmidt inner product, and $n$ is the dimension of the quantum system. Remarkably, the quantity in Eq. (10) can be measured experimentally, even for non-unital maps.

Experimentally, we have studied the non-unital quantum dissipative map $\mathcal{M}$ affecting a three level spin system, as described in Sec. II. We have independently measured the characteristic function $\mathcal{G}(\beta)$ and the value of $\gamma^\infty$. The results are shown in Fig. 3(a-b). The agreement between $\mathcal{G}(\beta)$ and $\gamma^\infty$ represents the experimental verification of the generalized SUT fluctuation relation [Eq. (9)], in the SSE regime, for an open three-level system under quantum (non-thermalizing) dissipative dynamics conditioned by POVM quantum measurements. Let us observe that the theoretical model of the map $\mathcal{M}$ [Sec. II] allows us to calculate the efficacy $\gamma$ also in the transient regime, as

$$\gamma = \text{Tr}_{3 \times 3} \left[ (\mathcal{B}^\dagger)^N \text{col}[\rho^{\text{th}}] \right]$$

(11)

with $\mathcal{B}$ defined in Eq. (5). Here, it is worth noting that the ‘backwards’ superoperator $\mathcal{B}^\dagger$ is not trace preserving, a clear sign of the non-reversibility associated with the dissipative process [27]. In the transient regime, the values of $\gamma$ [Eq. (11)] were compared with the experimental values of the characteristic function $\mathcal{G}(\beta)$, as a function of the number of laser pulses. As shown in Fig. 3(a-b), there is an excellent agreement between the two quantities. This leads us to conclude that the dynamics of the system is very well described by an autonomous feedback mechanism.

In the specific case of $\mathcal{H} = \mathcal{H}_{\text{NV}}$, where the Hamiltonian commutes with the POVM operators and with the dissipative operator, we can derive an analytic expression for the efficacy $\gamma$ defined in Eq. (11) as

$$\gamma = \mu^{N_L} + 3(1 - \mu^{N_L}) e^{\beta F}$$

(12)

where $F \equiv -\beta^{-1} \ln Z$ is the initial free energy of the system, with $Z \equiv \sum_{k=1}^N e^{-\beta E_k}$, and $\mu \equiv 1 - p_d p_a \in [0, 1]$ defines the probability for the system to not be subjected to feedback. We also recall that $p_a$ denotes the laser pulse absorption probability, and $p_d \equiv (1 - e^{-t_L \Gamma})$ is the dissipation probability for the interaction with a single laser pulse (see appendix A). The mathematical proof of Eq. (12) is given in the Supplemental Material at [URL will be inserted by publisher]. As one would expect, $\gamma = 1$ if $p_a = 0$ (closed quantum system), or in case of pure projective measurements without dissipation $e^{-t_L \Gamma} = 1$ (no feedback). In addition, since $Z < 3$ for $\beta \neq 0$, Eq. (12) implies that $\gamma > 1$. Hence, if $\mathcal{H} = \mathcal{H}_{\text{NV}}$, energy extraction from the system is always possible for the open dynamical case with feedback. As final remark, notice that $\gamma$ in Eq. (12) is defined in terms of macroscopic quantities – it does not depend on the trajectories followed by the system. In the inset of Fig. 3(b), we show the behavior of the asymptotic value of $\gamma^\infty = 3 e^{\beta F}$ obtained from Eq. (12) in the SSE regime, as a function of the inverse initial temperature $\beta$. This result is in agreement with Eq. (10) for the asymptotic state $\rho^\infty_{\text{NV}} = |0\rangle \langle 0|$. 

V. FLUCTUATION RELATION FOR STATIONARY STEADY STATES

While classical fluctuation relations remarkably connect out-of-equilibrium quantities to equilibrium properties of the system [32], in QFR the characteristic function often depend on the details of the process [33]. In this section, we investigate the conditions under which the characteristic function of energy $\mathcal{G}(\eta)$ is constant, and thus independent of the system dynamics in the transient regime. Specifically, we aim at finding the values of an energy scale factor $\eta^*$ that allows the equality

$$\mathcal{G}(\eta^*) = 1$$

(13)
in the SSE regime, for a generic (out-of-equilibrium) quantum system under dissipation. Afterwards, we verify experimentally the validity of such relation.

As mentioned before, dissipative dynamics brings the system into a SSE, i.e., a state for which, on average, the open system does not exchange energy with the external environment, despite the active presence of interaction dynamics (indeed, the quantum system is not closed). Therefore, in the SSE regime, the mean energy value of the system is time independent. However, for values of \( \eta \) chosen without a specific criterion, \( \mathcal{G}(\eta) \) is not equal to one, and its value depends on the choice of the initial state of the system and on the parameters involved in its dynamical evolution. An example of this was shown in the previous section [Sec. IV] where \( \eta = \beta \) leads to the relation \( \langle \exp(-\beta \Delta E) \rangle = 3 \text{Tr}[\rho^\infty \rho^\text{th}] \) in the SSE regime. Instead, as proven in the Appendix D for a generic finite dimensional system, there exists a unique value of the scale energy factor \( \eta^* \) such that Eq. (13) is satisfied. This is a direct consequence of the presence of the dissipative channel. Moreover, dissipation brings the system into a SSE that is independent of the initial state, meaning that the energy variation probabilities can be factorized \( P_{j,i} = P_j P_i \). Thus, the value of \( \eta^* \) depends only on the initial and asymptotic states of the system. Only in the limit case where the asymptotic state is thermal with inverse temperature \( \beta_\infty \), the value of the energy scale factor is \( \eta^* = \Delta \beta \equiv \beta - \beta_\infty \) assuming that also the initial state is thermal with inverse temperature \( \beta \). In such case, equation (13) corresponds to the exchange fluctuation relation for a quantum system under thermalizing dynamics [57, 58], or under effective thermalizing dynamics [40].

After the last energy measurement, the quantum system reaches, on average, a non-Gibbsian mixed state. This means that the effects of the dissipative channel on the analyzed 3LS may not be modeled by the effective interaction of the system with a thermal reservoir. However, also in this case, the validity of Eq. (13) is expected to hold in the SSE regime. Once the asymptotic state
is known, the unique constant value of $\eta^*$ can be determined by numerically solving an algebraic equation. In this regard, refer to Supplemental Material at [URL will be inserted by publisher] for details on the algebraic method to obtain $\eta^*$. Remarkably, for an initial thermal state with inverse temperature $\beta$, equation (13) holds also for transient times, as it is shown experimentally in Fig. 3(c-d). Here, it is worth mentioning that, by expressing $\eta^*$ as a function of $\beta$, a non-linear relation is obtained [inset of Fig. 3 (c)]. This means that the quantity $\eta^* - \beta$ depends on both the initial and asymptotic states, and therefore cannot be associated, in general, with an inverse temperature.

VI. NON-UNITALITY OF A QUANTUM DISSIPATIVE MAP

As already known, the value of $G(\beta)$ can be used as a witness of non-unitality of open quantum maps [27, 45, 46]. Here, starting from the fluctuation relations studied in sections IV and V, we show that also $\gamma^\infty \neq 1$ or $\eta^* \neq \beta$ (when $\beta \neq 0$) are sufficient conditions for non-unitality. In addition, we connect these parameters to the possibility of extracting energy from the system mediated by the autonomous feedback mechanism.

For an $n$-dimensional quantum system under the generic dissipative map $\Phi_d$ with a unique fixed point $\rho^\infty$ that is asymptotically achieved for any initial state, we first demonstrate the following statements:

$$\Phi_d \text{ unital} \Leftrightarrow \rho^\infty = \frac{1}{n} \Rightarrow \gamma^\infty = 1 \Leftrightarrow \eta^* = \beta. \quad (14)$$

We prove the validity of each of the three statements separately, under the hypothesis that $\beta \neq 0$ [59]. The validity of the statement $\Leftrightarrow$ is based on the assumption that $\Phi_d$ is a dissipative map with a unique fixed point $\rho^\infty$, which is reached asymptotically and does not depend on the initial state. Hence, the definition of unitality, $\Phi_d \left[ \frac{1}{2} \right] = \frac{1}{2}$, can be satisfied only when $\rho^\infty = \frac{1}{n}$. Instead, the validity of the statement $\Rightarrow$ is ensured by the equality (10), while the statement $\Leftrightarrow$ is (3) the unique point of the equations, i.e., $\eta^* = \beta$. Accordingly, the map $\Phi_d$ is non-unitary if $\eta^* \neq \beta$ or $\gamma^\infty \neq 1$ are sufficient conditions for the non-unitarity of a dissipative map with unique fixed point.

Let us comment on the physical meaning of equation (14). It is important to stress that $\gamma^\infty = 1$ does not necessarily imply $\rho^\infty = \frac{1}{n}$. By writing the asymptotic state after the second energy measurement, $\rho^\infty$, according to its spectral decomposition, i.e., $\rho^\infty = \sum_{k=0}^{n-1} |E_k\rangle\langle E_k| \rho^\infty_k$, it can be easily shown that

$$\gamma^\infty = 1 \Leftrightarrow \sum_{k=1}^{n-1} (p_k - \frac{1}{n}) (e^{-\beta E_0} - e^{-\beta E_k}) = 0. \quad (15)$$

Clearly, the state $\rho^\infty = \frac{1}{n}$ is a solution of equation (15), but it is not the only one. An example of this is shown in Fig. 4, where $(\eta^* - \beta) \omega$ is plotted as a function of two populations of the asymptotic state for a 3LS with Hamiltonian $H = H_{\text{nw}}$ (as in our experiments). In such figure, the black solid line represents all the asymptotic states for which $\eta^* = \beta$, i.e., $\gamma^\infty = 1$ given the link among $\gamma^\infty$ and $\eta^*$ in Eq. (14). Such values of the asymptotic state do not allow to make statements about neither the non-unitality degree of the dissipative map nor the possibility to extract energy from the system. This can be done, instead, for the other configurations of $\rho^\infty$ (not lying on the black solid line), where the map is non-unitary and the autonomous Maxwell demon prevents or enables the possibility to extract energy from the system when $\eta^* < 0$, and is ceded to the system otherwise $(\eta^* > 0)$.

VII. CONCLUSIONS

In conclusion, we have used the electronic spin qutrit associated to an NV center in diamond at room temperature to realize an autonomous dissipative Maxwell de-
The conditioned dissipative spin qutrit dynamics consists in a non-unitary part originated by the interaction with a train of short laser pulses, which provide random measurements followed by conditioned dissipation, and in a unitary part set by a time-independent continuous driving Hamiltonian. Asymptotically, the spin qutrit approaches a non-Gibbsian steady state in the energy basis, independent of the initial state, and determined by the value of the commutator between the Hamiltonian and the spin operator $S_z$ (in which basis the dissipation operator is diagonal). Exploiting the POVM formalism to model the interaction of the NV spin qutrit with the short laser pulses, we have shown that the application of stochastically intermittent dissipative (Lindbladian) operators is effectively described by an intrinsic feedback process.

In this setting, measurement and feedback mechanisms actively condition the onset, over time, of dissipative dynamics with distinct features. This can be interpreted as the action of a quantum Maxwell demon that changes the open dynamics of the quantum system depending on which measurement operator occurs in a sequence of POVMs. The demon can be effectively considered as being autonomous, since the feedback mechanism is inherent in the photodynamics of the NV spin interacting with a properly-tuned train of laser pulses. As other Maxwell demons, the thermodynamics of an autonomous dissipative Maxwell demon is well-described by means of fluctuation relations; here, we show that the best description of a quantum dissipative demon is through an appropriate generalization of the Sagawa-Ueda-Tasaki formalism for feedback processes. Our study of the energy change statistics of the qutrit verifies for the first time, experimentally and theoretically, the Sagawa-Ueda-Tasaki relation in a scenario of conditioned dissipative dynamics. Moreover, as expected, we recover that the asymptotic value $\gamma^\infty$ provides information on non-unitality of the process also in our experimental case study.

In addition, we demonstrate that for the specific dynamics of our system, the characteristic function $G(\eta)$ of energy changes becomes independent of the process details, at a single specific value $\eta^*$ of its argument. This may suggest that the dissipative quantum map $\mathcal{M}$ stems from a Markovian process. We show that, for a quantum dynamics that leads to an asymptotic non-Gibbsian state, the energy scale factor $\eta^*$ cannot be interpreted as a (pseudo)temperature, but it depends only on the initial state and on the final steady-state. Notably, this demonstrates an effective fluctuation theorem of the Jarzynski type, which holds despite lack of unitality of the spin evolution. Moreover, we have shown that also the quantity $\eta^*$ is a witness of non-unitality for dissipative (and, more broadly, open) quantum maps with a unique fixed point.

Our results pave the way for the use of NV centers in diamond to further investigate open quantum system dynamics and thermodynamics. In particular, by applying cyclic interactions with the non-thermal reservoir, it has been conjectured the possibility to create a non-Gibbsian quantum heat engine [60], where quantum correlations affect the total amount of heat during the interaction processes. In addition, the proposed experimental protocol to measure energy variation statistics can be adjusted to one-time measurements schemes [61–63] or to quasi-probability measurements [64] with the aim to investigate the role of coherence in energy exchange mechanisms, with the final goal of understanding the effects of genuine quantum features in thermodynamic variables. Moreover, other forms of quantum fluctuation relations based on observables that do not commute with the system Hamiltonian may be measured to explore quantum synchronization [65], and the relation of the latter with quantum mutual information and with entanglement between the quantum system and its dissipative environment. Such kind of studies could also be exploited to realize multipartite entangled systems [66] formed by single NV electronic spins and nuclear spins inside the diamond. Indeed, the high degree of control and long coherence time for such complex spin systems would represent a very useful test-bed for the relation of quantum information and quantum thermodynamics at the nanoscale.

Appendix A: Short laser pulses interaction as POVM

The interaction between the NV center and a green laser pulse can be modeled by means of a master equation that involves orbital states not mentioned in the main text. The details about this interaction have been extensively studied, one can refer for example to Refs. [40, 49]. For the purposes of this work, i.e., to measure the statistics of energy variation in a quantum three level system, this interaction is modeled as a POVM followed by dissipation, as described below. In the following description, we ignore the coherent evolution of the system state because the Rabi periods associated with the unitary evolution of the system are much longer than the duration of a single short laser pulse.

The interaction of the 3LS with a short laser pulse is modeled as follows: If the laser pulse is not absorbed, the state of the system remains unchanged and there is no dissipation. If the laser pulse is absorbed, the system is subject to a quantum projective measurement in the $S_z$ basis, hence projecting its state into one of the spin states. Then, the system is subject to a dissipative operator, modeled by means of a Lindbladian master equation. We will use the formalism described in Ref. [50] for superoperators represented as $N^2 \times N^2$ matrices, where $N = 3$ is the dimension of the Hilbert space of the 3LS. According to this formalism, a given density matrix $\rho$ that interacts with a laser pulse of duration $t_L$ is trans-
formed into
\[ \text{col}[\rho(t_L)] = \mathcal{A} \text{col}[\rho] \] (A1)
where \( \text{col}[\rho] \) denotes the result of stacking the columns of \( \rho \) to form a ‘column’ vector, and the superoperator \( \mathcal{A} \) models the mean effect of a single short laser pulse. Taking into account all the possible outcomes of this interaction, \( \mathcal{A} \) is written as
\[ \mathcal{A} \equiv \sum_{j=1}^{4} \mathcal{D}_j m_j \] (A2)
where \( m_j \equiv m_j \otimes m_j \) is one of the measurement superoperator associated with the POVM \( \{m_1, m_2, m_3, m_4\} \) with
\begin{align*}
m_1 &\equiv \sqrt{p_d} | -1 \rangle \langle -1 | \quad \text{(A3a)} \\
m_2 &\equiv \sqrt{p_d} | 0 \rangle \langle 0 | \quad \text{(A3b)} \\
m_3 &\equiv \sqrt{p_d} | +1 \rangle \langle +1 | \quad \text{(A3c)} \\
m_4 &\equiv \sqrt{(1-p_d)} \mathbb{1}_{3 \times 3}, \quad \text{(A3d)}
\end{align*}
such that \( \sum_{j=1}^{4} m_j m_j^\dagger = \mathbb{1}_{3 \times 3} \), and \( \mathcal{D}_j \) represents the action of a superoperator conditioned to the result of the POVM:
\[ \mathcal{D}_j = \begin{cases} \mathbb{1}_{9 \times 9}, & \text{if } j = 4 \\ \mathcal{L}, & \text{otherwise} \end{cases} \] (A4)
with
\[ \mathcal{L} \equiv \exp \left( t_L \sum_{\ell=0}^{1} L_\ell^\dagger \otimes L_\ell - \frac{1}{2} \mathbb{1}_{3 \times 3} ^\dagger \otimes L_\ell L_\ell \right. \\
\left. - \frac{1}{2} (L_\ell L_\ell^\dagger)^\dagger \otimes \mathbb{1}_{3 \times 3} \right) \] (A5)
where \((\cdot)^\dagger\) denotes complex conjugate, \( \otimes \) denotes Kronecker product, and \( L_0, L_1 \) are the Lindbladian jump operators \( \{L_0, L_1\} = \{\sqrt{\Gamma} | 0 \rangle \langle +1 |, \sqrt{\Gamma} | 0 \rangle \langle -1 | \} \), describing the dissipation towards the state \( |0\rangle \). In Eq. (A2), the term for \( j = 4 \) corresponds to the case where the laser pulse is not absorbed, while the other three terms model the absorption of a single laser pulse. The Lindbladian dissipative super-operator \( \mathcal{L} \) is defined in terms of the product between the effective decay rate and the laser duration \( \Gamma t_L \), which dictates the strength of the dissipation that brings the system towards \( |0\rangle \); the dissipation probability is \( p_d \equiv (1 - e^{-\Gamma t_L}) \). The explicit expression of \( \mathcal{L} \) can be found in the Supplemental Material at [URL will be inserted by publisher]. Using short laser pulses with \( t_L = 41 \text{ ns} \), we experimentally characterized the strength of this decay rate resulting in a value such that \( \Gamma t_L \simeq 1/2 \). It is important to mention that, given the effective nature of this model, the value of \( \Gamma \) might vary for different NV centers and under different experimental conditions.

Notice that for a long laser pulse \( (t_L \Gamma \gg 1) \) any given state \( \rho \) is transformed into \( \mathcal{L} \text{col}[\rho] = \text{col}[|0\rangle \langle 0|] \), which is consistent with the usual protocol employed to optically initialize the electronic spin state.

Notice also that, in the hypothetical limit where \( p_d = 0 \), then no dissipation will occur \( (\mathcal{L} = \mathbb{1}_{9 \times 9}) \) and consequently \( \mathcal{D}_j = \mathbb{1}_{9 \times 9} \).

Appendix B: Hamiltonian eigenstate preparation and final readout gates

As shown in Fig. 1, the preparation of the Hamiltonian initial eigenstate requires the application of the quantum gate \( G^{(i)}_j: |0\rangle \rightarrow |E_j\rangle \), while the readout of the eigenstate \( |E_j\rangle \) requires a second quantum gate, i.e., \( G^{-1}_j: |E_j\rangle \rightarrow |0\rangle \). In this section we describe these gates for each of the possible states \( |E_i\rangle \) and \( |E_j\rangle \).

There are two possibilities for preparing the Hamiltonian eigenstates. One is with a double-driving microwave (MW) gate driving transitions between \( |0\rangle \) and \( |\pm 1\rangle \), and the other is with two MW pulses applied subsequently to transfer parts of the population from \( |0\rangle \) to \( | -1 \rangle \) and \( | +1 \rangle \) separately. In our experimental setup we have opted for the latter method due to easier handling of the MW operations. To induce the transition \( |0\rangle \rightarrow |0\rangle \equiv \frac{1}{\sqrt{2}} (| -1 \rangle - | +1 \rangle) \), the population in \( |0\rangle \) has to be transferred in equal parts to \( |\pm 1\rangle \) where both parts have an opposite phase. This is achieved by applying a \( \pi/2 \)-pulse that transfers half of the population to \( | -1 \rangle \), and subsequently applying a \( \pi \)-pulse to transfer the remaining population in \( |0\rangle \) to \( | +1 \rangle \). To obtain the correct phase between the \( |\pm 1\rangle \), it is required that the phase of both pulses is \( \pi/2 \) (or \(-\pi/2\)), as one can verify by calculation. Also the preparation of \( |\pm \omega\rangle \equiv \frac{1}{\sqrt{2}} (| -1 \rangle \pm \sqrt{2} |0\rangle \pm | +1 \rangle) \) works in a very similar way. A \( \pi/3 \)-pulse has to be applied to transfer one quarter of the population to \( | -1 \rangle \) and, then, an \( \arccos(1/3) \)-pulse transfers another one quarter of population from \( |0\rangle \) to \( | +1 \rangle \). Calculation shows that the phases of the MWs have to be \( \mp \pi/2 \) and \( \pm \pi/2 \), respectively for the first and second MW, if we aim to prepare \( |\pm \omega\rangle \).

The second quantum gate \( G^{(j)}_i^{-1} \equiv G^{(j)}_i \) applies the reversed process with respect to the preparation one. Thus \( G^{(j)}_2 \) is obtained by performing the operations of the state preparation in reversed order and assigning to the implemented MW pulses an opposite phase.

Appendix C: Derivation of the dissipative SUT relation

In this Appendix, we first demonstrate the validity of the general QFR, for an \( n \)-level quantum system under a completely-positive trace-preserving (CPTP) map \( \Phi \). We recall that the validity of the general QFR for CPTP map has been proved before \([45, 53, 54, 56] \). Then we demonstrate the validity of Eq. (9), as a corollary of the previous proof. Finally, we demonstrate the validity of
the dissipative SUT relation for a dissipative map with a unique fixed point.

Assuming a two-point-measurement scheme, the system energy is measured at the beginning of the protocol, then the system evolves under a CPTP map, and finally its energy is measured again. The Hamiltonian of the system can be decomposed in terms of the energy eigenstates that define the projectors $P_i \equiv |E_i\rangle\langle E_i|$. In agreement with the superoperator formalism [50] used in Appendix A, the state after an ideal energy measurement is given by $\text{col}[\rho_0,\rho_1]=\mathcal{P}_i \text{col}[\rho]$, where $\mathcal{P}_i \equiv P_i \otimes P_i$. Therefore, the joint probability to obtain $E_i$ in the first energy measurement, and $E_f$ in the final one, is written as

$$P_{f,i} = \text{Tr}_{n \times n} [\mathcal{P}_f \mathcal{J} \mathcal{P}_i \text{col}[\rho^{th}]] \quad (C1)$$

where $\rho^{th}$ is the initial thermal state, $\text{Tr}_{n \times n}[\cdot] \equiv \text{Tr}[\cdot]$, and $\mathcal{J}$ is the superoperator propagator associated with the CPTP map $\Phi$. The characteristic function $\mathcal{G}(\beta) \equiv \langle e^{-\beta \Delta E} \rangle$ of the energy variation distribution can be then written as

$$\mathcal{G}(\beta) = \sum_{i,j=1}^{n} P_{f,i} e^{-\beta(E_f-E_i)} \quad (C2)$$

By expressing the initial thermal state as $\rho^{th} \equiv \sum_{k=1}^{n} \mathcal{P}_k e^{-\beta E_k}/Z$ with $Z \equiv \sum_{k=1}^{n} e^{-\beta E_k}$, we obtain the following:

$$\mathcal{G}(\beta) = \sum_{f,i,k=1}^{n} P_{f,i} e^{-\beta(E_f-E_i)}$$
$$= \sum_{f,i,k=1}^{n} \text{Tr}_{n \times n} [\mathcal{P}_f \mathcal{J} \mathcal{P}_i \text{col}[\mathcal{P}_k]] e^{-\beta(E_f-E_i+E_k)}/Z$$
$$= \sum_{f,k=1}^{n} \text{Tr}_{n \times n} [\mathcal{P}_f \mathcal{J} \text{col}[\mathcal{P}_k]] e^{-\beta E_f}/Z \quad (C3)$$

where we have used the equality $\text{col}[\mathcal{P}_i \text{col}[\mathcal{P}_k]] = \text{col}[\mathcal{P}_i \mathcal{P}_k \mathcal{P}_i] = \text{col}[\mathcal{P}_k] \delta_{k,i}$, with $\delta_{k,i}$ the Kronecker delta. On the other hand, we know that $\text{Tr}_{n \times n}[\mathcal{P}_f \text{col}[\rho]] = (\text{col}[\mathcal{P}_f])^\dagger \text{col}[\rho]$, for any given density matrix $\rho$. Hence, from Eq. (C3) we get

$$\mathcal{G}(\beta) = \sum_{f,k=1}^{n} (\text{col}[\mathcal{P}_k])^\dagger \mathcal{J} \text{col}[\mathcal{P}_k] e^{-\beta E_f}/Z$$
$$= \sum_{f,k=1}^{n} (\mathcal{J} \text{col}[\mathcal{P}_k])^\dagger \mathcal{P}_f e^{-\beta E_f}/Z$$
$$= \sum_{f,k=1}^{n} (\text{col}[\mathcal{P}_k])^\dagger \mathcal{J}^\dagger \text{col}[\mathcal{P}_f] e^{-\beta E_f}/Z$$
$$= \sum_{k=1}^{n} \text{Tr}_{n \times n} [\mathcal{P}_k \mathcal{J}^\dagger \text{col}[\rho^{th}]] \quad (C4)$$
$$= \text{Tr}_{n \times n} [\mathcal{J}^\dagger \text{col}[\rho^{th}]] \quad (C5)$$

where $\rho^{th}$ denotes the thermal state at inverse temperature $\beta$ taking the system Hamiltonian at the time instant in which the second energy measurement of the TPM protocol is performed. Equation (C5) concludes the proof.

**Corollary 1:** Let us assume that the quantum system is under the feedback map $\mathcal{M}_\Phi$ described in Sec. IV. Given the fact that $\mathcal{M}_\Phi$ is formed by a combination of a POVM followed by CPTP maps, it is easy to prove that the map $\mathcal{M}_\Phi$ is itself a CPTP map, such that $\text{col}[\mathcal{M}_\Phi[\rho]] = \mathcal{J}_{\Phi} \text{col}[\rho]$, with $\mathcal{J}_{\Phi} \equiv \sum_{k=1}^{n'} \Phi_k \Pi_k U_0$. Therefore, using Eq. (C5) we obtain that $\mathcal{G}(\beta) = \gamma = \text{Tr}_{n \times n} [\sum_{k=1}^{n'} \Pi_k \Phi_k \text{col}[\rho^{th}]]$, hence proving the validity of Eq. (9).

**Corollary 2:** Assuming that the CPTP map is a dissipative map $\Phi_d$ with a unique fixed point $\rho^\infty$, then we can write $\lim_{t \to \infty} \mathcal{J} \text{col}[\rho_k] = \text{col}[\rho^\infty]$, for every value of $k \in \{1, \ldots, n\}$. Hence, from Eq. (C4) one gets $\gamma^\infty = \lim_{t \to \infty} \gamma = n \text{Tr}[\rho^\infty \rho^{th}]$.

Note that, in the particular case of the dissipative map $\mathcal{M}$ used in during our experiments, $\mathcal{J} = \mathcal{B}^{N_L}$, which describes the effect of the dissipative map after $N_L$ laser pulses.

**Appendix D:** Energy steady state regime enabling fluctuation relations

Now, we discuss the connection between the stationary state SSE of an arbitrary quantum system and the existence of a unique finite and time-independent value of $\eta^*$, obeying the fluctuation relation $\mathcal{G}(\eta^*) \equiv \langle \exp(-\eta^* \Delta E) \rangle = 1$ for any time instant $t$ of a quantum dissipative process. A sketch of the formal derivation of this result is presented below.

As a first step, we show that the equality $\mathcal{G}(\eta) = 1$ is fulfilled only for two values of $\eta$, namely $\eta = 0$ (trivial solution), and $\eta \neq 0$ with $\eta$ finite real number. This result stems directly from the convexity of the characteristic function $\mathcal{G}(\eta) = \sum_{i,j} \eta П_{j|i} П_i e^{-\eta \Delta E_{ij}} \eta$, with respect to the energy scale $\eta$ [67, 68], where $\Delta E_{ij} \equiv E_j - E_i$, $P_i$ denotes the probability of measuring $E_i$ at the beginning of the protocol, $P_{j|i}$ is the conditional probability of measuring $E_j$ at the end of the protocol, and the sum $\sum_{i,j}$ is performed over all the possible initial $i$ and final $j$ measured energies. It is worth noting that these probabilities define the probability distribution $P_{\Delta E}$ of Eq. (6) in the main text. Thus, being convex, $\mathcal{G}(\eta)$ is a twice differentiable real-valued function with positive concavity. Then, one needs to verify the validity of the following two conditions: (i) $\eta = 0$ is a zero of $g(\eta) \equiv \mathcal{G}(\eta) - 1 = 0$; (ii) the minimum value of $g(\eta)$ is equal or smaller than zero. Indeed, if both these conditions hold, then $g(\eta)$ has only another zero $\eta \neq 0$, since $G(\eta)$ and $q(\eta)$ are functions with positive concavity. Condition (i) is straightforwardly verified, as $\eta = 0$ is the trivial solution of the fluctuation relation $\mathcal{G}(\eta) = 1$. Instead, to verify the validity of condition (ii), one has to check if the derivative $\partial g(\eta)/\partial \eta$ evaluated in $\eta = 0$ is different from zero for
all system parameters, except for special cases. One has
\[ \frac{\partial g(\eta)}{\partial \eta} \bigg|_{\eta=0} = -\langle E_\infty \rangle + \langle E_{\text{in}} \rangle, \]  
\[ \text{(D1)} \]
which is zero if and only if \( \langle E_\infty \rangle = \langle E_{\text{in}} \rangle \), namely if the initial and final mean energy values are the same. This happens when the effects of the presence of the dissipative channel are negligible, e.g., when the steady state reached by the system is thermal with the same temperature than the initial thermal state, i.e., \( \beta_\infty = \beta \). This confirms that the minimum value of \( G(\eta) \) – convex function – is necessarily equal or smaller than 1 that implies the existence of a unique value of \( \eta \) different from zero, obeying the fluctuation relation \( G(\eta) = 1 \).

As a second step, let us demonstrate that, for any dissipative quantum dynamics, the steady state regime implies that the unique finite zero of \( G(\eta) \) only depends on the initial and the stationary states. In doing this, let us assume that the quantum system is at the steady state. In this regard, notice that the energy steady state is attained when the current state of the system, solution of the dynamical equation of motion, has constant energy and does not depend on the initial state. This condition can be translated in a property of \( \langle \exp(-\eta \Delta E) \rangle \). In the SSE regime, the conditional probabilities \( P_{ji} \) are invariant with respect to the initially measured energy value, with the result that
\[ P_{j|1} = P_{j|2} = \ldots = P_{j|n} \equiv \tilde{P}_j \]  
\[ \text{(D2)} \]
for any \( j \), with \( n \) denoting the dimension of the quantum system. By assuming the validity of Eq. (D2), \( \langle \exp(-\eta \Delta E) \rangle \) can be decomposed as
\[ \langle \exp(-\eta \Delta E) \rangle = \sum_i P_i e^{\eta E_i} \sum_j \tilde{P}_j e^{-\eta E_j} \]
\[ = \text{Tr} \left[ e^{\eta \mathcal{H}} \rho_0 \right] \text{Tr} \left[ e^{-\eta \mathcal{H}} \rho_\infty \right] \]  
\[ \text{(D3)} \]
that is still a convex function with respect to \( \eta \). Thus, there exists a unique value of \( \eta \) different from zero that verifies the equality \( \langle \exp(-\eta \Delta E) \rangle = 1 \). From the decomposition of Eq. (D3), one can state that \( \eta \) depends only on the set of probabilities \( \{P_i\} \) and \( \{\tilde{P}_j\} \), corresponding to the initial and the stationary states, and on the system energy values.

**Corollary:** If the dissipation is such that the asymptotic state is a completely mixed state, then \( \eta = \beta \) is the non-trivial solution of \( g(\eta) = 0 \). This can be easily proven by making the substitution \( \eta = \beta \) and \( \tilde{P}_j = 1/n \) in Eq. (D3).

As a final remark, note that if we would define \( g(\eta, a) = G(\eta) - a \), with \( a \) being a real and positive number not necessarily equal to 1, the value \( \eta = 0 \) is not longer solution of \( g(\eta, a) = 0 \). Therefore, if \( g(\eta, a) = 0 \) has only two solutions in \( \eta \), only \( a = 1 \) guarantees the existence of a unique non-trivial solution \( \eta \). Note also that \( a = 1 \) is

the appropriate physical choice for the exchange fluctuation relation in arbitrary quantum systems governed by a time-independent Hamiltonian, which do not entails any free-energy variation, irrespective of possible dissipative processes.
SUPPLEMENTAL MATERIAL

1. Nitrogen nuclear spin initialization

The electronic spin of the NV center is intrinsically coupled to the nuclear spin of the nitrogen atom. The NV center we work with is coupled to a $^{14}\text{N}$ atom with nuclear spin $I = 1$. For that reason each of the electronic spin levels is split into three hyperfine sub-levels for the nuclear spin projections $m_I = 0, \pm 1$. In order to obtain a genuine three-level system of the electronic spin, we polarize the nuclear spin in the $m_I = -1$ projection. This is done with a sequence of selective microwave and radio-frequency $\pi$-pulses, as illustrated schematically in Figure S1. We assume to have as initial state a completely mixed state involving the nine hyperfine sublevels, although this polarizing protocol is adequate for any initial state. The NV center electronic spin is initialized into the $m_S = 0$ state by means of a long laser pulse. The external magnetic field is far away from the excited-state level anti-crossing (ESLAC) [47, 69], hence the nuclear spin is unaffected by the interaction with laser pulses. From now on we adopt the notation $|m_S, m_I\rangle$ to describe a state of the joint system. In the first step, the population of $|0, 1\rangle$ is transferred to $|1, 1\rangle$ by a controlled-NOT operation on the electronic spin (selective MW $\pi$-pulse) and subsequently transferred to $|1, 0\rangle$ by a controlled-NOT operation on the nuclear spin (selective RF $\pi$-pulse). Then a long laser pulse pumps the population to $|0, 0\rangle$ while leaving unchanged the population that was already in the $m_S = 0$ level. Analogously, in a second step the resulting population in $|0, 0\rangle$ is transferred to $|0, -1\rangle$ passing through $|1, 0\rangle$ and $|1, -1\rangle$. Among the possibilities of initializing a different $m_I$ using different controlled-NOT operations, we have chosen the described one as it gave the best polarization result. We have measured an initialization fidelity of 79%, measured with a standard electron spin resonance (ESR) experiment, Figure S2.

As a part of the nuclear spin remains in the undesired $m_I = 0, +1$ a normalization of the measured fluorescence has to be done that is different from the standard references of $m_S = 0$ and $m_S = \pm 1$ where the nuclear spin is not relevant. For that reason spin-lock measurements after the initialization gates for the Hamiltonian eigenstates (see Appendix B of the main text) have been done. In this way the correct function of the initialization gates is proven and the fluorescence references for the correct normalization are obtained.

Note that in the presence of a relatively weak magnetic bias field ($B \approx 100\text{ MHz}/\gamma_e$), as used in our experiments, the nitrogen nuclear spin lifetime is expected to be of the order of milliseconds [70, 71], much longer than a single experimental realization ($\sim 10\text{ ms}$).

2. Lindbladian dissipation super-operator

As also described in the Appendix A of the main text, the interaction between the NV center and a green laser pulse can modeled as a POVM followed by a dissipation operator, and, overall, the dynamics of the open quantum system can be described by a master equation in Lindblad form. In this section, we will explicitly provide the expression of this Lindbladian dissipation operator.

For this purpose, from now on we will express operators in their matrix representation (with respect to the $S_z$-basis), such that

$$
|{-1}\rangle|{-1}\rangle = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad |0\rangle|0\rangle = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad |+1\rangle|+1\rangle = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}.
$$

(S1)

In addition, we will use indistinguishably the term matrix or operator, unless otherwise specified, and we will adopt the formalism described in Ref. [50] for superoperators represented by $N^2 \times N^2$ matrices, where $N = 3$ is the dimension of the quantum system’s Hilbert space.

In this formalism, the Lindbladian dissipation super-operator (defined in Appendix A) is written as

$$
\mathcal{L}^{(t_\Gamma)} = \begin{pmatrix}
\begin{array}{cccccccc}
e^{-t_\Gamma \Gamma} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \ne^{-t_\Gamma \Gamma/2} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \ne^{-t_\Gamma \Gamma} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & \ne^{-t_\Gamma \Gamma/2} & 0 & 0 & 0 & 0 \\
1 - \ne^{-t_\Gamma \Gamma} & 0 & 0 & 0 & \ne^{-t_\Gamma \Gamma/2} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \ne^{-t_\Gamma \Gamma} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & \ne^{-t_\Gamma \Gamma/2} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \ne^{-t_\Gamma \Gamma} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \ne^{-t_\Gamma \Gamma/2} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{array}
\end{pmatrix}
$$

(S2)
FIG. S1. Scheme for nuclear spin initialization of the $^{14}$N nucleus. (a) Initially the population is distributed among the $m_I = 0, \pm 1$. (b, c) With selective MW and RF pulses the population is first transferred from $m_I = +1$ to $m_I = 0$ and then to $m_I = -1$ to initialize/polarize the nuclear spin. The laser is used to pump population in $m_S = 1$ back to $m_S = 0$. (d) Pulse protocol for the initialization process.

FIG. S2. Nitrogen nuclear spin polarization. Results from an electron spin resonance (ESR) experiment performed immediately after the nuclear spin polarization protocol.

where $t_L$ denotes the laser duration, and $\Gamma$ is an effective decay rate. Using laser pulses with $t_L = 41$ ns, we characterized that the effective decay rate equals $\Gamma \sim 12.2$ MHz.

3. Analytic $\gamma$ in the case of $\mathcal{H} = \mathcal{H}_{NV}$

As explained in the main text, the effect of applying a single laser pulse can be described by the superoperator

$$\mathcal{A} = \sum_{j=1}^{4} \mathcal{D}_j m_j.$$  \hspace{1cm} (S3)

This superoperator can be computed explicitly from the definitions of $\mathcal{D}_j$ and $m_j$ [see also Appendix A in main text]. In this regard, by introducing the auxiliary matrices

$$A_1 \equiv \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}; \quad A_2 \equiv \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}; \quad A_3 \equiv I_{9 \times 9} - A_1,$$
it holds that
\[ \mathcal{A} = \mu A_1 + (1 - \mu) A_2 + A_3(1 - p_{\text{abs}}), \tag{S4} \]
where
\[ \mu = 1 - (1 - e^{-t L \Gamma}) p_{\text{abs}}. \tag{S5} \]

It is no surprising that, if \( p_{\text{abs}} = 0 \), then \( \mathcal{A}_{(p_{\text{abs}}=0)} = 1_{9 \times 9} \). On the other hand, if \( p_{\text{abs}} = 1 \), then the POVM is actually a quantum projective measurement in the \( S_z \)-basis. This is the reason why \( \mathcal{A}_{(p_{\text{abs}}=1)} = e^{-t L \Gamma} A_1 + (1 - e^{-t L \Gamma}) A_2 \) is practically equal to the Lindbladian dissipation super-operator \( \mathcal{L} \) [Eq. (S2)], but without the terms involving coherences that is a signature of have applied a quantum projective measurement. Moreover, another special case occurs when \( e^{-t L \Gamma} = 1 \), namely the case without dissipation, where Eq. (S4) can be rewritten as \( \mathcal{A} = A_1 p_{\text{abs}} + 1_{9 \times 9}(1 - p_{\text{abs}}) \) that identifies the mean effect of applying a quantum projective measurement of \( S_z \) with probability \( p_{\text{abs}} \).

On the other hand, by taking \( \mathcal{H} = \mathcal{H}_{\text{NV}} \), the unitary evolution of the system is described by the following superoperator:

\[ U(\tau) \equiv \exp(-i \tau (\mathcal{H} \otimes 1_{3 \times 3} - 1_{3 \times 3} \otimes \mathcal{H})) \]

\[ = \begin{pmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & e^+ & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & e^+ & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
\end{pmatrix}, \]

where \( e^\pm \equiv e^{-i \tau E^\pm} \). Therefore, \( B \equiv A U \) can be written as

\[ B = \mu A_1 + (1 - \mu) A_2 + U_1(\tau)(1 - p_{\text{abs}}) \tag{S6} \]

with \( U_1(\tau) \equiv U(\tau) - A_1 \). Writing \( B \) as in Eq. (S6) is very useful, because the following properties hold:

\[ A_i^2 = A_i \text{ for } i \in \{1, 2, 3\} \]
\[ A_1 A_3 = A_3 A_1 = A_2 A_3 = A_3 A_2 = 0_{9 \times 9} \]
\[ A_1 A_2 = A_2 A_1 = A_2 \]
\[ (U_1(\tau))^n = U_1(n\tau) \]
\[ A_i U_1(\tau) = U_1(\tau) A_i = 0_{9 \times 9} \text{ for } i \in \{1, 2\}, \]

thus implying that

\[ B^{NL} = \mu^{NL} A_1 + (1 - \mu^{NL}) A_2 + U_1(NL, \tau)(1 - p_{\text{abs}})^{NL} \tag{S7} \]

Moreover, being in the case of \( \mathcal{H} = \mathcal{H}_{\text{NV}} \), a thermal state \( \rho^\text{th} \) can be written according to the superoperators formalism [50] in the following way:

\[ \text{col}(\rho^\text{th}) = \frac{1}{\mathcal{Z}} \text{col} \left( \begin{bmatrix} e^{-\beta E_{+1}} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{-\beta E_{-1}} \end{bmatrix} \right) = \frac{1}{\mathcal{Z}} \begin{bmatrix} e^{-\beta E_{+1}} \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \end{bmatrix} \]
where $Z \equiv \sum_{k=-1}^{1} e^{-\beta E_k}$. Hence, as final calculation, by exploiting that $A_1^\dagger \text{col}(\rho^{\text{th}}) = (U_1(N_L)) \text{col}(\rho^{\text{th}}) = \text{col}(\rho^{\text{th}})$, and $A_2^\dagger \text{col}(\rho^{\text{th}}) = \text{col}(1_{3 \times 3})/Z$, the use of Eq. (S7) allows us to obtain an analytic expression for $\gamma$, namely

$$\gamma = \text{Tr}_{3 \times 3}[(B^\dagger N_L) \text{col}(\rho^{\text{th}})]$$

$$\gamma = \mu N_L + \frac{3}{Z} (1 - \mu N_L).$$

(S8)

Let us observe that, apart the special cases mentioned before,

$$\lim_{N_L \to \infty} \mu N_L = 0,$$

meaning that

$$\lim_{N_L \to \infty} \gamma = \frac{3}{Z}.$$

(S9)

4. An algebraic recipe to get $\eta^*$ with experimental data

Let us consider a 3LS initialized in the thermal state $\rho^{\text{th}} \equiv \exp(-\beta H)/Z_\beta$ with $Z_\beta \equiv \text{Tr}[\exp(-\beta H)]$. By diagonalizing the system Hamiltonian as $H = \sum_i E_i |E_i \rangle \langle E_i |$, the initial thermal initial state is equal to

$$\rho^{\text{th}} = \sum_i e^{-\beta E_i} |E_i \rangle \langle E_i | = \sum_i P_i |E_i \rangle \langle E_i |$$

where $P_i \equiv \exp(-\beta E_i)/Z_\beta$.

Then, let us introduce the mean value of the exponentiated energy variation $\Delta E$, i.e.,

$$\langle \exp(-\eta \Delta E) \rangle = \sum_{i,j} P_i P_j e^{-\eta (E_j - E_i)}$$

(S10)

which strictly depends on the energy scaling factor $\eta$. Note that the average $\langle \exp(-\eta \Delta E) \rangle$ is defined by the sets $\{P_i\}$ and $\{P_j|i\}$, corresponding respectively to the probabilities to measure the initial energies of the system and the conditional probabilities to get $E_j$ at the end of the procedure after having measured $E_i$.

In the SSE regime, as described in the main text, the conditional probabilities $P_j|i$ does not depend upon the initially measured energies $E_i$. This entails that

$$P_{j|1} = P_{j|2} = P_{j|3} \equiv \tilde{P}_j$$

(S11)

for any $j$ such that

$$\langle \exp(-\eta \Delta E) \rangle = \sum_{i,j} P_i \tilde{P}_j e^{-\eta (E_j - E_i)},$$

(S12)

whereby the quantum state $\rho_{\text{fin}}$ after the application of the 2nd energy projective measurement of the TPM measurement protocol is a mixed state, not necessarily thermal but completely described by the probabilities $\tilde{P}_j$, namely

$$\rho_{\text{fin}} = \sum_j \tilde{P}_j |E_j \rangle \langle E_j |.$$  

Now, to make our derivation compatible with the experimental setup and in particular with the case of $H = H_{\text{mw}}$, we assume that the energy values are symmetric around zero, and, for the sake of brevity, we call $E_1 = -\bar{E}$, $E_2 = 0$ and $E_3 = \bar{E}$, with $\bar{E}$ constant value (in the experiment $\bar{E} = \hbar \omega/2$). In this way, by means of the substitution

$$x \equiv e^{\eta \bar{E}} \iff \eta^* = \frac{1}{\bar{E}} \ln x,$$

(S13)

the equation

$$\sum_{i,j} P_i \tilde{P}_j e^{-\eta^* (E_j - E_i)} = 1$$

can be rewritten as the following polynomial equation:

\[ (x - 1) \left( P_1 \tilde{P}_3 x^3 + (P_1 \tilde{P}_2 + P_1 \tilde{P}_3 + P_2 \tilde{P}_3)x^2 - (P_2 \tilde{P}_1 + P_3 \tilde{P}_1 + P_3 \tilde{P}_2)x - P_3 \tilde{P}_1 \right) = 0 \]  

(S14)

Clearly, Eq. (S14) contains the trivial solution \( x = 1 \), i.e., \( \eta^* = 0 \), while solving the third-order algebraic equation

\[ P_1 \tilde{P}_3 x^3 + (P_1 \tilde{P}_2 + P_1 \tilde{P}_3 + P_2 \tilde{P}_3)x^2 - (P_2 \tilde{P}_1 + P_3 \tilde{P}_1 + P_3 \tilde{P}_2)x - P_3 \tilde{P}_1 = 0 \]  

(S15)

provides us the other value of \( \eta^* \neq 0 \) that obeys the fluctuation relation \( \mathcal{G}(\eta^*) = 1 \). In this regard, it is worth noting that, by applying the well-known Routh-Hurwitz criterion to the polynomial (S15), we can also prove that just only root of Eq. (S15) has positive real part. Indeed, according to the Routh-Hurwitz criterion, we recall that to each variation (permanence) of the sign of the coefficients of the first column of the Routh table corresponds to a root of the polynomial with a positive (negative) real part. In our case, there are always 2 sign-permanences and only 1 variation, for any possible value of the probabilities \( P_i \) and \( \tilde{P}_j \). Being \( \eta^* \propto \ln x \), only the unique solution \( x \neq 0 \) with positive real part is physical, thus providing us the (unique) non-trivial energy scaling factor \( \eta^* \) such that \( \mathcal{G}(\eta^*) = 1 \).

Non-equilibrium steady-state condition fulfilled by \( \eta^* \)

Here, let us provide some more insights on the interpretation of \( \eta^* \), and the condition that it has to fulfill by imposing the validity of the equality \( \mathcal{G}(\eta^*) = 1 \).

For this purpose, each probability \( \tilde{P}_j \) is decomposed in the product of two contributions: One is thermal and is associated to the inverse temperature \( \beta_{\text{fin}} \), while the other is a correction term that accounts for the (geometric) distance \( \lambda \) concerning \( \rho_{\text{fin}} \) from being thermal [72]. Specifically, given the set \( \{ E_j \} \) of the system energies after the application of the measurement protocol, \( \tilde{P}_j \) can be written as

\[
\tilde{P}_1 = \frac{e^{-\beta_{\text{fin}} E_1} e^{\lambda(E_2 - E_3)^2}}{Z_{\beta_{\text{fin}}}(\lambda)}; \quad \tilde{P}_2 = \frac{e^{-\beta_{\text{fin}} E_2} e^{\lambda(E_3 - E_1)^2}}{Z_{\beta_{\text{fin}}}(\lambda)}; \quad \tilde{P}_3 = \frac{e^{-\beta_{\text{fin}} E_3} e^{\lambda(E_1 - E_2)^2}}{Z_{\beta_{\text{fin}}}(\lambda)},
\]

(S16)

where

\[
Z_{\beta_{\text{fin}}}(\lambda) = \exp(-\beta_{\text{fin}} A + 2\lambda B), \quad \text{with} \ A = \sum_j E_j \text{ and } B = \sum_j E_j^2 - E_1 E_2 - E_2 E_3 - E_3 E_1,
\]

denotes the corresponding discrete partition function. It is worth noting that the probabilities \( \tilde{P}_1, \tilde{P}_2 \) and \( \tilde{P}_3 = 1 - \tilde{P}_1 - \tilde{P}_2 \) are written as a function of two free-parameters. Thus, known the energies \( E_j \) and experimentally obtained the values of the probabilities \( \tilde{P}_j \) with \( j = 1, 2, 3 \), \( \beta_{\text{fin}} \) and \( \lambda \) can be derived by means of standard non-linear regression techniques.

Now, let us consider that \( \mathcal{H} = \mathcal{H}_{\text{mw}} \), which is the more involved one among the cases we have analyzed so far. In accordance with the experimental setup, the energies can be assumed symmetric around zero, as even shown above. In this way, by substituting the relations of Eq. (S16) into Eq. (S12) and imposing \( \mathcal{G}(\eta^*) = 1 \), after simple calculations we can end up in the following equality that corresponds to a non-equilibrium steady-state condition for the analysed open 3LS:

\[
Z_\beta Z_{\beta_{\text{fin}}} + C(\lambda) \left( 3 - Z_{\beta + \beta_{\text{fin}}} \right) = C(\lambda) \left( Z_\beta + Z_{\beta_{\text{fin}}} - 2\eta^* \right) + C(\lambda)^2 Z_\beta - \eta^*.
\]

(S17)

where

\[
C(\lambda) = e^{\lambda \mathcal{E}^2}; \quad Z_{\beta + \eta^*} = \sum_{k=-1}^{1} e^{-k \mathcal{E}(\beta + \eta^*)}; \quad Z_{\beta_{\text{fin}} + \eta^*} = \sum_{k=-1}^{1} e^{-k \mathcal{E}(\beta_{\text{fin}} + \eta^*)};
\]

\[
Z_{\beta_{\text{fin}}} = \sum_{k=-1}^{1} e^{-k \mathcal{E}(\beta_{\text{fin}} - 2\eta^*)}; \quad Z_{\beta_{\text{fin}}} = \sum_{k=-1}^{1} e^{-k \mathcal{E}(\beta_{\text{fin}} - 2\eta^*)}.
\]

Let us observe that \( \eta^* = 0 \) is always solution of Eq. (S17) for any value of \( \lambda \), while for \( \lambda = 0 \) the non-trivial solution \( \eta^* \) of Eq. (S17) is \( \eta^* = \beta - \beta_{\text{fin}} \) in perfect agreement with the Jarzynski-Wójcik relation [57]. Instead, for a value of \( \lambda \neq 0 \), Eq. (S17) is numerically solved as a function of \( \eta \), whereby the non-trivial solution \( \eta^* \) is provided by the real and positive value of \( \eta \) obeying the energy exchange fluctuation relation \( \exp(-\eta^* \Delta \mathcal{E}) = 1 \).
M. Sbroscia, L. Buffoni, M. Paternostro, and F. Caruso, npj Quantum Information 6, 96 (2020).
[59] The case of $\beta = 0$ is not useful to evaluate the non-unitality of the map $\Phi_d$ by using fluctuation relations since $G(0) = 1$ by definition.