

Supplemental Materials: Sub-hertz optical transitions in excited Yb⁺

Magnetic dipole decays between J_1K -coupled states

The lifetimes of the J_1K -coupled states of interest are limited by magnetic dipole decays to other J_1K -coupled states. Thus, the magnetic dipole matrix elements between two unique J_1K -coupled states must be computed to estimate their lifetimes. In J_1K -coupling, the angular momenta are coupled in the following order:

$$\begin{aligned}\vec{L}_c + \vec{S}_c &= \vec{J}_c \\ \vec{J}_c + \vec{L}_o &= \vec{K} \\ \vec{K} + \vec{S}_o &= \vec{J}\end{aligned}$$

where the individual operators are in units of $\hbar$ and the subscripts c and o denote the core and outer electrons, respectively. The reduced matrix element of interest can then be found by applying the Wigner-Eckart theorem:

$$\langle \gamma', J', M'_J | T_q^{(1)}[\vec{\mu}] | \gamma, J, M_J \rangle = (-1)^{J'-M'_J} \begin{pmatrix} J' & 1 & J \\ -M'_J & q & M_J \end{pmatrix} \langle \gamma', J' || T^{(1)}[\vec{\mu}] || \gamma, J \rangle$$

where $\gamma \equiv \{L_c, S_c, J_c, L_o, K, S_o\}$. The magnetic dipole operator (in units of μ_B) is the sum of the magnetic dipoles of the core and outer electrons $\vec{\mu} \equiv \vec{\mu}_c + \vec{\mu}_o$, where each can be decomposed as $\vec{\mu}_i = -\vec{L}_i - g_s \vec{S}_i$. The reduced matrix element can then be rewritten as a sum of two terms:

$$\begin{aligned}\langle \gamma', J' || T^{(1)}[\vec{\mu}] || \gamma, J \rangle &= \langle \gamma', J' || T^{(1)}[\vec{\mu}_c - \vec{L}_o - g_s \vec{S}_o] || \gamma, J \rangle \\ &= \langle \gamma', J' || T^{(1)}[\vec{\mu}_c - \vec{L}_o] || \gamma, J \rangle - g_s \langle \gamma', J' || T^{(1)}[\vec{S}_o] || \gamma, J \rangle.\end{aligned}\quad (\text{S1})$$

The operators are grouped in this fashion because both $\vec{\mu}_c$ and $\vec{L}_o$ act on K . Because the two terms in S1 each act on one subspace of J , they can then be evaluated by multiple applications of the “spectator theorem” [1]. Starting with the second term in S1 (the simpler

of the two terms), we have

$$\langle L'_c, S'_c, J'_c, L'_o, K', S'_o, J' \| T^{(1)}[\vec{S}_o] \| L_c, S_c, J_c, L_o, K, S_o, J \rangle =$$

$$\delta_{K',K} (-1)^{K'+S_o+J'+1} \sqrt{(2J'+1)(2J+1)} \begin{Bmatrix} S'_o & J' & K' \\ J & S_o & 1 \end{Bmatrix} \delta_{S'_o, S_o} \sqrt{S_o(2S_o+1)(S_o+1)}.$$

For the first term in (S1), the same procedure yields

$$\langle L'_c, S'_c, J'_c, L'_o, K', S'_o, J' \| T^{(1)}[\vec{\mu}_c - \vec{L}_o] \| L_c, S_c, J_c, L_o, K, S_o, J \rangle =$$

$$\delta_{S'_o, S_o} (-1)^{K'+S'_o+J+1} \sqrt{(2J'+1)(2J+1)} \begin{Bmatrix} K' & J' & S'_o \\ J & K & 1 \end{Bmatrix}$$

$$\times \langle L'_c, S'_c, J'_c, L'_o, K' \| T^{(1)}[\vec{\mu}_c - \vec{L}_o] \| L_c, S_c, J_c, L_o, K \rangle.$$

With the matrix element on the right hand side reduced down to K , we once again decompose into two terms:

$$\langle L'_c, S'_c, J'_c, L'_o, K' \| T^{(1)}[\vec{\mu}_c - \vec{L}_o] \| L_c, S_c, J_c, L_o, K \rangle =$$

$$\langle L'_c, S'_c, J'_c, L'_o, K' \| T^{(1)}[\vec{\mu}_c] \| L_c, S_c, J_c, L_o, K \rangle - \langle L'_c, S'_c, J'_c, L'_o, K' \| T^{(1)}[\vec{L}_o] \| L_c, S_c, J_c, L_o, K \rangle.$$

Each term can be evaluated with more applications of the spectator theorem, starting with

$$\langle L'_c, S'_c, J'_c, L'_o, K' \| T^{(1)}[\vec{L}_o] \| L_c, S_c, J_c, L_o, K \rangle =$$

$$\delta_{J'_c, J_c} \delta_{L'_c, L_c} (-1)^{J'_c+L_o+K'+1} \sqrt{(2K'+1)(2K+1)L_o(2L_o+1)(L_o+1)} \begin{Bmatrix} L'_o & K' & J'_c \\ J_c & L_o & 1 \end{Bmatrix}$$

and on to

$$\langle L'_c, S'_c, J'_c, L'_o, K' \| T^{(1)}[\vec{\mu}_c] \| L_c, S_c, J_c, L_o, K \rangle =$$

$$\delta_{L'_o, L_o} (-1)^{J'_c+L'_o+K+1} \sqrt{(2K'+1)(2K+1)} \begin{Bmatrix} J'_c & K' & L'_o \\ K & J_c & 1 \end{Bmatrix} \langle L'_c, S'_c, J'_c \| T^{(1)}[\vec{\mu}_c] \| L_c, S_c, J_c \rangle.$$

For the matrix element on the right hand side, we decompose $\vec{\mu}_c = -\vec{L}_c - g_s \vec{S}_c$ to obtain

$$\langle L'_c, S'_c, J'_c \| T^{(1)}[\vec{\mu}_c] \| L_c, S_c, J_c \rangle$$

$$\begin{aligned}
&= -\delta_{S'_c, S_c} \delta_{L'_c, L_c} \sqrt{(2J'_c + 1)(2J_c + 1)} (-1)^{L_c + S_c + 1} \left[(-1)^{J_c} \begin{Bmatrix} L'_c & J'_c & S'_c \\ J_c & L_c & 1 \end{Bmatrix} \sqrt{L_c(2L_c + 1)(L_c + 1)} \right. \\
&\quad \left. + g_s (-1)^{J'_c} \begin{Bmatrix} S'_c & J'_c & L'_c \\ J_c & S_c & 1 \end{Bmatrix} \sqrt{S_c(2S_c + 1)(S_c + 1)} \right]. \tag{S2}
\end{aligned}$$

Estimation of $M1$ Lifetime

The $M1$ spontaneous emission rate between two $J_1 K$ -coupled states can be written as

$$A_{M1} = \frac{\omega^3}{3\pi\epsilon_0\hbar c^5} \mu_B^2 \frac{|\langle L'_c, S'_c, J'_c, K', S'_o, J' \| T^{(1)}[\vec{\mu}] \| L_c, S_c, J_c, K, S_o, J \rangle|^2}{2J' + 1} \tag{S3}$$

Usually, the next step is to simply calculate A_{M1} for all possible decay paths from the upper state and compute the lifetime as

$$\tau = \frac{1}{\sum_i A_i}$$

Lower Level (cm ⁻¹)	Term	%	M1-allowed Component
30224.33	³ [11/2] _{9/2}	96	³ [9/2] _{9/2} only
30224.33	³ [9/2] _{9/2}	2	Both
30562.79	³ [11/2] _{11/2}	92	³ [9/2] _{9/2} only
31979.90	³ [5/2] _{7/2}	69	³ [7/2] _{9/2} only
31979.90	³ [7/2] _{7/2}	28	Both

TABLE S1: Allowed $M1$ decay channels from the leading-order (71% ³[7/2]_{9/2}) and second-leading-order (23%³[9/2]_{9/2}) components of the 33052.29 cm⁻¹ level.

This approach is not used mainly because the J_1K -coupling scheme for these states is imperfect, which results in second-leading-order contributions. Table S1 provides an example of how the secondary-leading-order term of each of the J_1K -coupled states contributes the $M1$ -allowed decay pathways and therefore to the lifetime. To properly account for the contribution of each term for a given level, the relative phase between the terms must be considered. This phase can be roughly estimated based on the g -factors and state fractions provided by the NIST ASD. To do so, we start with the definition of the magnetic dipole moment operator (in units of μ_B):

$$\vec{\mu}_J = -g_J \vec{J} \quad (S4)$$

with $\vec{J} = \vec{K} + \vec{S}_o$. We define our state as a superposition of the first- and second-leading-order terms with an unknown relative phase

$$|\psi\rangle \equiv \alpha |\psi_\alpha\rangle + \beta |\psi_\beta\rangle \quad (S5)$$

where $|\alpha|^2$ and $|\beta|^2$ represent the state fraction first- and second-leading-order state fractions respectively, and the relative phase information is stored in $\beta = e^{i\phi}|\beta|$, leaving $\alpha \in \mathbb{R}$. Starting with the first-order Zeeman effect, the g -factor can then be written in terms of the matrix elements as

$$\begin{aligned} -g_J \langle \psi | \vec{J} \cdot \vec{B} | \psi \rangle &= \langle \psi | \vec{\mu}_J \cdot \vec{B} | \psi \rangle \\ g_J m_J B &= -B (|\alpha|^2 \mu_{\alpha\alpha} + |\beta|^2 \mu_{\beta\beta} + \alpha^* \beta \mu_{\alpha\beta} + \alpha \beta^* \mu_{\beta\alpha}) \\ g_J &= -\frac{1}{m_J} (|\alpha|^2 \mu_{\alpha\alpha} + |\beta|^2 \mu_{\beta\beta} + \alpha^* \beta \mu_{\alpha\beta} + \alpha \beta^* \mu_{\beta\alpha}) \end{aligned} \quad (S6)$$

where $\vec{B} = B\hat{z}$ and $\mu_{ij} \equiv \langle \psi_i | \mu_z | \psi_j \rangle$. Because the $q = 0$ component of $\boldsymbol{\mu}$ is being evaluated, $\mu_{\alpha\beta} = \mu_{\beta\alpha}$, and thus the relative phase can be written as:

$$\phi = \arccos \left(-\frac{g_J J + |\alpha|^2 \mu_{\alpha\alpha} + |\beta|^2 \mu_{\beta\beta}}{2|\alpha||\beta|\mu_{\alpha\beta}} \right) \quad (S7)$$

where the stretch state $m_J = J$ has been chosen for both $|\psi_\alpha\rangle$ and $|\psi_\beta\rangle$. In cases where the off-diagonal matrix element $\mu_{\alpha\beta}$ is nonzero, the relative phase can be calculated and thus A_{M1} should be computed by replacing each J_1K -coupled state with $|\psi\rangle = \alpha |\psi_\alpha\rangle + \beta |\psi_\beta\rangle$ in the matrix element of S3. In the cases where the off-diagonal matrix element $\mu_{\alpha\beta} = 0$, the relative phase cannot be computed using this method, so it is assumed that the contribution from each term is incoherent. In both cases, each decay rate A_{M1} must be properly weighted

by the state fraction of the upper and lower states when computing the $M1$ -only lifetime.

The results from this calculation method for the lowest-lying odd-parity states with $J \geq 9/2$ are shown in table S2. Higher-energy levels tend to have shorter $M1$ -only lifetimes due to the increase in the number of allowed $M1$ decay channels and the emitted photon's energy. The level at $38\,342.02\text{ cm}^{-1}$ is an outlier of this trend because both its leading order term and second-leading-order term ([2], not presented in the table) have spin singlets outside the core, thus reducing the available decay pathways. The second-leading-order term of the $34\,784.95\text{ cm}^{-1}$ level has a spin triplet outside the core, which explains why the leading-order spin singlet appears to follow the trend of decreasing lifetime.

Level	Leading Term	λ_F (nm)	M1-Lifetime (s)
46 169.78	$^3[7/2]_{9/2}^o$	404	1.1×10^{-3}
42 915.13	$^3[9/2]_{11/2}^o$	465	3.5×10^{-3}
40 917.91	$^3[9/2]_{9/2}^o$	512	0.011
38 342.02	$^1[9/2]_{9/2}^o$	590	22
35 831.68	$^3[9/2]_{11/2}^o$	693	0.51
35 019.13	$^3[9/2]_{9/2}^o$	735	0.24
34 784.95	$^1[11/2]_{11/2}^o$	748	0.41
33 052.29	$^3[7/2]_{9/2}^o$	860	9.9
30 562.79	$^3[11/2]_{11/2}^o$	1093	1.3×10^3
30 224.33	$^3[11/2]_{9/2}^o$	1135	—

TABLE S2: Estimated $M1$ -only lifetimes of potentially metastable odd-parity states from the $4f^{13}(^2F_{7/2}^o)5d6s$ electron configuration with $J \geq 9/2$. λ_F indicates the wavelength of the transition from $^2F_{7/2}^o$ to the corresponding level. Note that the $30\,224.33\text{ cm}^{-1}$ level does not have an obvious $M1$ -decay pathway.

Beyond the states shown in Table S2, there are a handful of other states with the same electron configuration but lower J that may be metastable owing to the need for a $\Delta l_i > 1$

change in the electron configuration to effect an $E1$ decay to the 2D_J states. Candidates in this regard include the $^3[5/2]_{5/2}^o$ state ($32\,371.10\text{ cm}^{-1}$, $\tau_{\text{calc}} = 36.8\text{ ms}$ [3]) and the $^3[5/2]_{7/2}^o$ state ($31\,979.90\text{ cm}^{-1}$, $\tau_{\text{calc}} = 19.7\text{ ms}$ [3], 13.1 ms [4]). The decays from these states to the 2D_J manifold do not appear in theoretical databases [3, 5], which establishes an upper bound of $\log gf = -4.0$ for the calculated oscillator strengths of these transitions. As a result, the lower bounds on the $E1$ -only lifetimes of the $^3[5/2]_{5/2}^o$ and $^3[5/2]_{7/2}^o$ states are $\geq 0.59\text{ ms}$ and $\geq 2.1\text{ ms}$ respectively.

The low-lying $^3[3/2]_{5/2}^o$ state is metastable with a lifetime recently measured by Ackerman *et al.* to be $\tau = 920(80)\text{ ms}$ [4]. The transition to this state from $^2F_{7/2}^o$ is in the infrared at $\lambda_F \approx 1.87\text{ }\mu\text{m}$, which may constrain the Lamb-Dicke factor achievable for applications requiring coupling to motion from $^2F_{7/2}^o$, but is unlikely to affect its usefulness for internal-state operations, precision spectroscopy, or transitions from lower levels. Odd-parity states with the electron configuration $4f^{13}(^2F_{7/2}^o)5d^2$ and $J \geq 9/2$ may also be metastable, though there is potential that a small amount of configuration interaction with $6s$ could quench these through $M1$ channels, as they lie $\approx 10\,000\text{ cm}^{-1}$ above many states with $4f^{13}(^2F_{7/2}^o)5d\,6s$ configurations.

Spin-motion coupling in the $^{171}\text{Yb}^+$ m -type qubit

In an omg -encoded architecture, there are three defined qubit subspaces: the g -type (ground state) qubit, the m -type (metastable state) qubit, and o -type (optical) qubit. Application of the omg scheme in $^{171}\text{Yb}^+$ and several gate operations are depicted in figure S1.

The $^2F_{7/2}$ state has access to many excited states via $E1$ and $E2$ transitions. The lowest lying even-parity (J_1, J_2) -coupled states are attractive candidates for $E1$ -mediated stimulated Raman transitions, as depicted in figure S2a. A less attractive feature of these states is their nanosecond lifetimes [6], due to a large number of strong spontaneous emission channels. Alternatively, the excited J_1K -coupled states could provide a more robust platform for performing spin-motion coupling via $E2$ mediated light shift gates, as depicted in figure S2b. These states primarily decay via $M1$ decay pathways, resulting in estimated lifetimes on the order of seconds. Therefore, the $^2F_{7/2}^o \leftrightarrow ^3[11/2]_{11/2}^o$ and $^2F_{7/2}^o \leftrightarrow ^3[11/2]_{9/2}^o$ transitions are attractive candidates for implementing qubit-motion coupling owing to the readily available

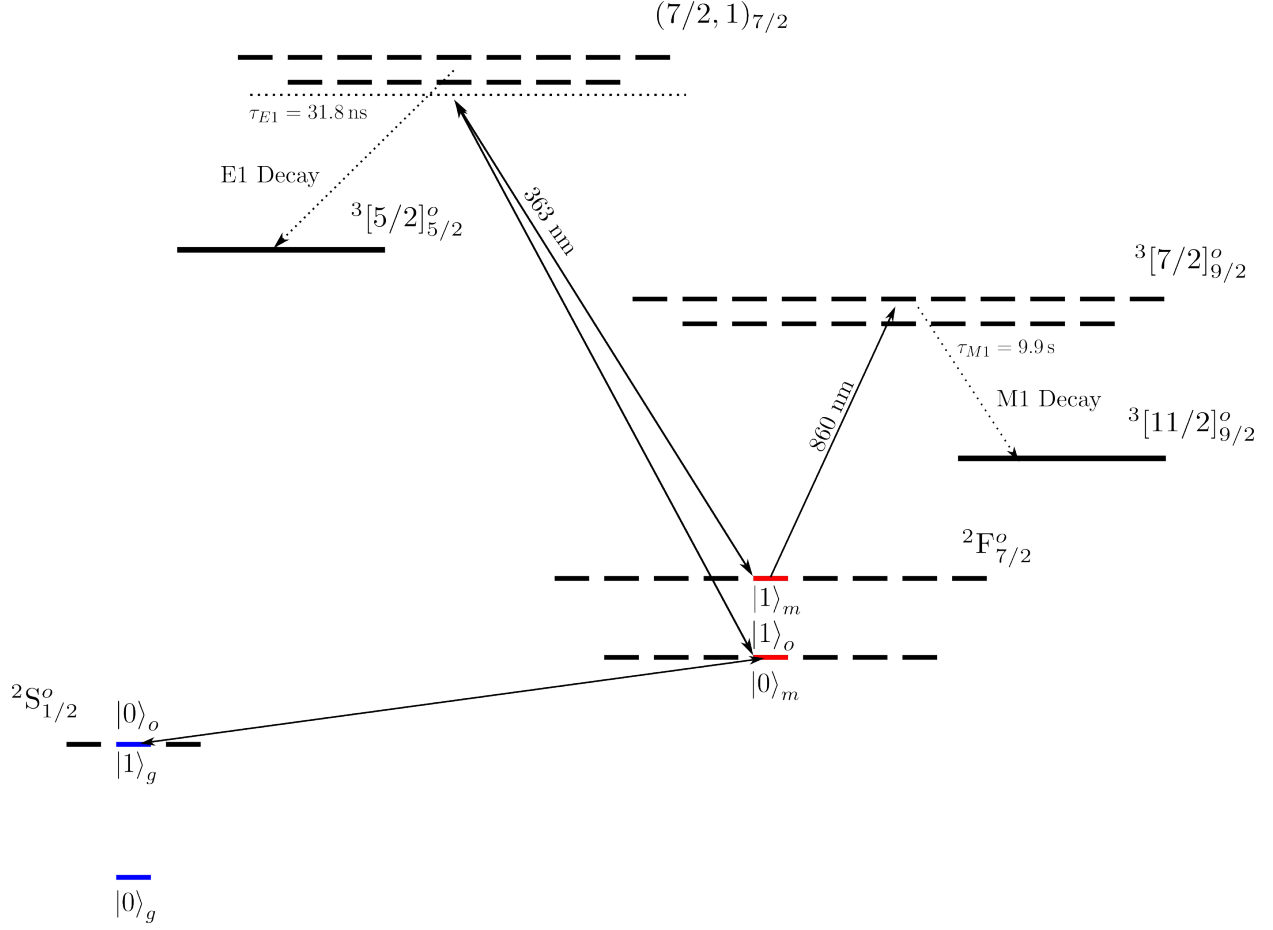


FIG. S1: Gate operations within the *omg* scheme on the metastable qubit in $^{171}\text{Yb}^+$. The ground and metastable qubit subspaces are represented via the blue and red hyperfine, magnetic-field insensitive levels respectively. The optical qubit is defined on the narrow $E3$ transition between hyperfine sublevels of the ground and metastable qubits. Only the highest branching ratio decay paths per excited state are shown.

laser sources and the extremely long $M1$ lifetimes of these two low-lying excited states.

Two-level system approximation of the rate model

The spontaneous emission rate A_{E2} and the matrix element of the $2F_{7/2}^o \leftrightarrow 3[7/2]_o^o$ transition were extracted by fitting the data from figure 6 to a two-level system rate model. The full three-level system, visualized in figure S3, includes the $M1$ decay path and follows the

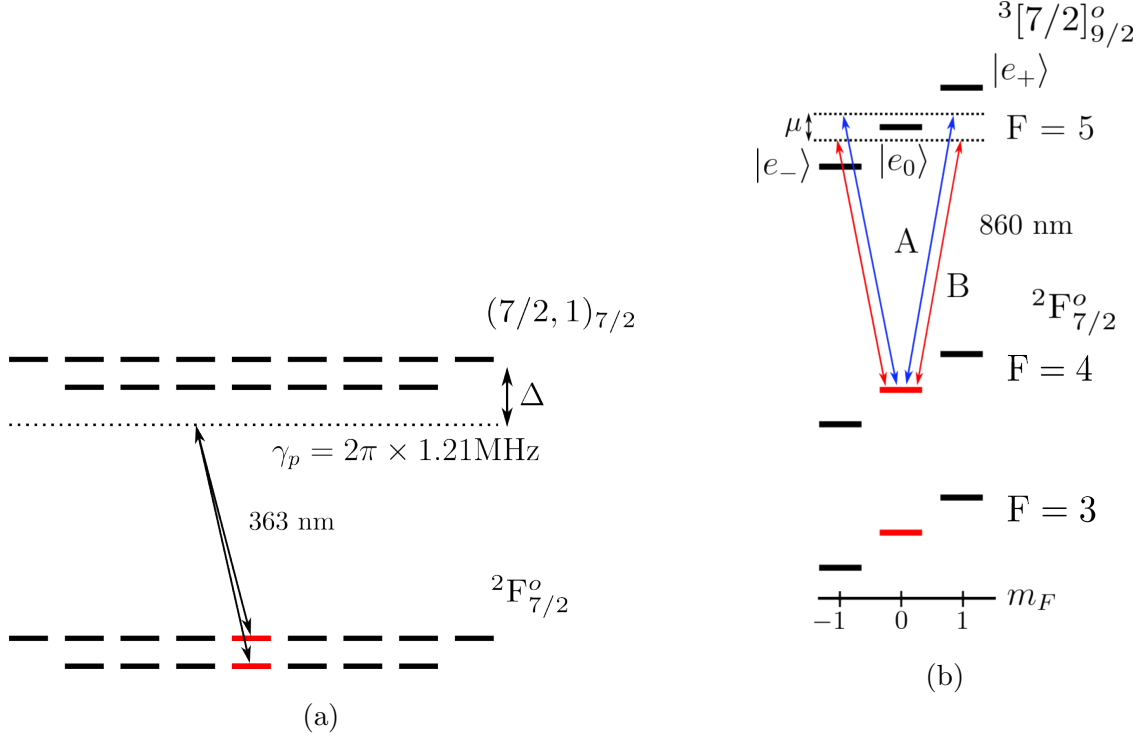


FIG. S2: **(a)** $E1$ -mediated stimulated Raman transition between the metastable qubit states via the excited state $(7/2, 1)_{7/2}$. The partial linewidth γ_p is given by Roman *et al.* [6]. **(b)** Light-shift (LS) gate on the metastable qubit. Two non-copropagating lasers are tuned to $\pm\mu/2$ from resonance between the one of the metastable qubit states and the $m_F = 0$ excited state $|e_0\rangle$. A full explanation of the light-shift gate is detailed by C.H. Baldwin *et al.* [7].

Einstein rate model below:

$$\begin{aligned}
 \dot{N}_g(t) &= A_{E2}N_e(t) + B\rho(\omega)(N_e(t) - fN_g(t)) \\
 \dot{N}_e(t) &= -\dot{N}_g(t) - \dot{N}_d(t) \\
 \dot{N}_d(t) &= N_eA_{M1}
 \end{aligned}
 \tag{S8}$$

However, because the stimulated emission rate $B\rho(\omega)$ is much higher than the estimated $M1$ spontaneous decay rate, we found that fitting the data to a two-level system rate model that omitted A_{M1} yielded similar results and was a justified approximation. A comparison between the models is shown in figure S4.

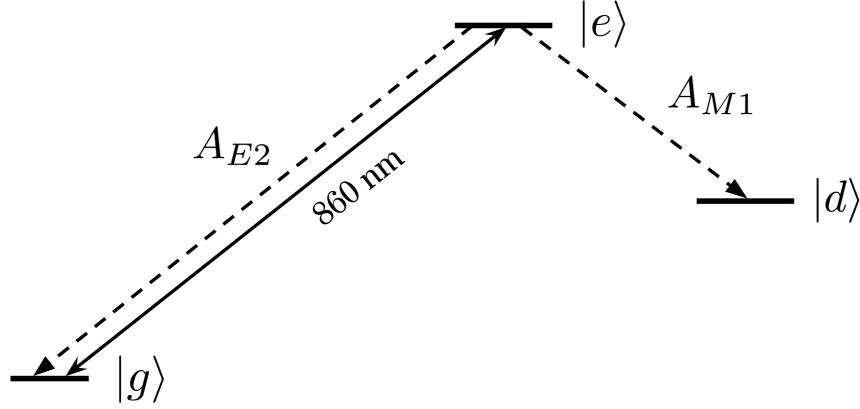


FIG. S3: Three level system in which only $|g\rangle \leftrightarrow |e\rangle$ transition is driven. The dark state $|d\rangle$ is a superposition of the $M1$ decay products from the excited state $^3[7/2]_{9/2}^o$, which is represented by $|e\rangle$. The “ground” state $|g\rangle$ in this model is the metastable state $^2F_{7/2}^o$. The corresponding rate model is displayed in equation S8.

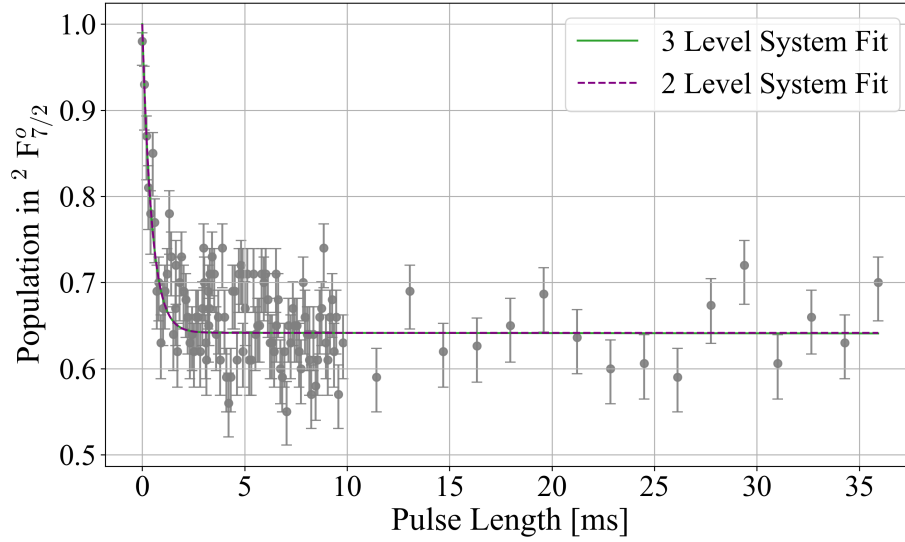


FIG. S4: Comparison between the three- and two-level system rate models.

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