

Supplemental Materials

SCATTERING MODELS

Two scattering models considered in this paper (which we denote the “CDA” and “ ω^3 -theory” models) are explicitly given below. To establish a common set of notation that can be used for ions with similar atomic structure, we adopt the notation given in Fig. S1 and Table S.I. The Einstein A coefficients, electron angular momentum quantum numbers, and frequencies will be denoted with subscripts accordingly (*e.g.* $A_{e',g''}$, J_g , $\omega_{e,g'}$, *etc.*).

CDA theory model

First, the constant density of states approximation (CDA) theory model, which we base on the previous theory [1], is most valid when the laser detuning from an intermediate state is small compared to the laser’s frequency. The total spontaneous scattering rate (during a g -type, zero-field hyperfine clock-state qubit gate) is given by

$$\Gamma_{\text{total,CDA}} \equiv (A_{e,g} + A_{e,g'}) \times \frac{g^2}{3} \frac{1}{\Delta^2} + (A_{e',g} + A_{e',g'} + A_{e',g''}) \times \frac{g^2}{3} \frac{2}{(\Delta - \omega_{\text{FS}})^2} \quad (\text{S.1})$$

where $\Delta = \omega_\ell - E_{\text{P}_{1/2}}/\hbar$ is the detuning of the laser from the $^2\text{P}_{1/2}^o \leftrightarrow ^2\text{S}_{1/2}$ resonance. The spontaneous Rayleigh scattering rate is

$$\Gamma_{\text{Rayleigh,CDA}} \equiv A_{e',g} \frac{g^2}{3} \left(\frac{3\Delta^2 - 2\Delta\omega_{\text{FS}} + \omega_{\text{FS}}^2/3}{\Delta^2(\Delta - \omega_{\text{FS}})^2} \right), \quad (\text{S.2})$$

and the spontaneous Raman scattering rate is difference between these two, $\Gamma_{\text{Raman,CDA}} = \Gamma_{\text{total,CDA}} - \Gamma_{\text{Rayleigh,CDA}}$. The branching fraction of the spontaneous Raman scattering rate into $^2\text{D}_{5/2}$ is

$$\eta_{\text{D}_{5/2},\text{CDA}} \equiv \frac{\Gamma_{\text{D}_{5/2},\text{CDA}}}{\Gamma_{\text{Raman,CDA}}} = A_{e',g''} \times \frac{g^2}{3} \left(\frac{2}{(\Delta - \omega_{\text{FS}})^2} \right) / \Gamma_{\text{Raman,CDA}}. \quad (\text{S.3})$$

ω^3 -theory model

The ω^3 -theory model closely resembles the CDA theory model near resonance, but differs significantly far from resonance. The difference between the two is simply the addition of the dependence of the spontaneous scattering rate on the frequency of the spontaneously scattered photon. This necessarily includes a step function to ensure that spontaneous scattering events to excited final states turn off when the laser photons don’t have enough energy to populate those states (see Fig. 1b). The total spontaneous scattering rate in this model is given by

$$\begin{aligned} \Gamma_{\text{total},\omega^3} = & \left(\frac{\omega_\ell}{\omega_{e,g}} \right)^3 A_{e,g} \times \frac{g^2}{3} \left(\frac{1}{\Delta^2} \right) \\ & + \Theta(\omega_\ell - \omega_{g,g'}) \left(\frac{\omega_\ell - \omega_{g,g'}}{\omega_{e,g'}} \right)^3 A_{e,g'} \times \frac{g^2}{3} \left(\frac{1}{\Delta^2} \right) \\ & + \left(\frac{\omega_\ell}{\omega_{e',g}} \right)^3 A_{e',g} \times \frac{g^2}{3} \left(\frac{2}{(\Delta - \omega_{\text{FS}})^2} \right) \\ & + \Theta(\omega_\ell - \omega_{g,g'}) \left(\frac{\omega_\ell - \omega_{g,g'}}{\omega_{e',g'}} \right)^3 A_{e',g'} \times \frac{g^2}{3} \left(\frac{2}{(\Delta - \omega_{\text{FS}})^2} \right) \\ & + \Theta(\omega_\ell - \omega_{g,g''}) \left(\frac{\omega_\ell - \omega_{g,g''}}{\omega_{e',g''}} \right)^3 A_{e',g''} \times \frac{g^2}{3} \left(\frac{2}{(\Delta - \omega_{\text{FS}})^2} \right). \end{aligned} \quad (\text{S.4})$$

State	Shorthand	J	Energy ($/\hbar$)
$^2S_{1/2}$	g	$J_g = \frac{1}{2}$	$\equiv 0$
$^2P_{1/2}^o$	e	$J_e = \frac{1}{2}$	$\omega_{e,g}$
$^2P_{3/2}^o$	e'	$J_{e'} = \frac{3}{2}$	$\omega_{e',g}$
$^2D_{3/2}$	g'	$J_{g'} = \frac{3}{2}$	$\omega_{g',g}$
$^2D_{5/2}$	g''	$J_{g''} = \frac{5}{2}$	$\omega_{g'',g}$

TABLE S.I. Shorthand notation for the five manifolds under consideration.

The spontaneous Rayleigh scattering rate is similar to the CDA theory,

$$\Gamma_{\text{Rayleigh}, \omega^3} = \left(\frac{\omega_\ell}{\omega_{e',g}} \right)^3 A_{e',g} \frac{g^2}{3} \left(\frac{3\Delta^2 - 2\Delta\omega_{\text{FS}} + \omega_{\text{FS}}^2/3}{\Delta^2(\Delta - \omega_{\text{FS}})^2} \right) \quad (\text{S.5})$$

and the spontaneous Raman scattering rate is again given by the difference between the total and Rayleigh rates,

$$\begin{aligned} \Gamma_{\text{Raman}, \omega^3} &= \Gamma_{\text{total}, \omega^3} - \Gamma_{\text{Rayleigh}, \omega^3} \\ &= \left(\frac{\omega_\ell}{\omega_{e',g}} \right)^3 A_{e',g} \frac{2g^2}{9} \left(\frac{\omega_{\text{FS}}}{\Delta(\Delta - \omega_{\text{FS}})} \right)^2 \\ &\quad + \Theta(\omega_\ell - \omega_{g,g'}) \left(\frac{\omega_\ell - \omega_{g,g'}}{\omega_{e,g'}} \right)^3 A_{e,g'} \times \frac{g^2}{3} \left(\frac{1}{\Delta^2} \right) \\ &\quad + \Theta(\omega_\ell - \omega_{g,g'}) \left(\frac{\omega_\ell - \omega_{g,g'}}{\omega_{e',g'}} \right)^3 A_{e',g'} \times \frac{g^2}{3} \left(\frac{2}{(\Delta - \omega_{\text{FS}})^2} \right) \\ &\quad + \Theta(\omega_\ell - \omega_{g,g''}) \left(\frac{\omega_\ell - \omega_{g,g''}}{\omega_{e',g''}} \right)^3 A_{e',g''} \times \frac{g^2}{3} \left(\frac{2}{(\Delta - \omega_{\text{FS}})^2} \right) \end{aligned} \quad (\text{S.6})$$

where we have used $A_{e,g}/\omega_{e,g}^3 = A_{e,g'}/\omega_{e,g'}^3$. The branching fraction of the spontaneous Raman scattering to the $^2D_{5/2}$ manifold is

$$\eta_{D_{5/2}, \omega^3} = \Theta(\omega_\ell - \omega_{g,g''}) \left(\frac{\omega_\ell - \omega_{g,g''}}{\omega_{e',g''}} \right)^3 A_{e',g''} \times \frac{g^2}{3} \left(\frac{2}{(\Delta - \omega_{\text{FS}})^2} \right) / \Gamma_{\text{Raman}, \omega^3}. \quad (\text{S.7})$$

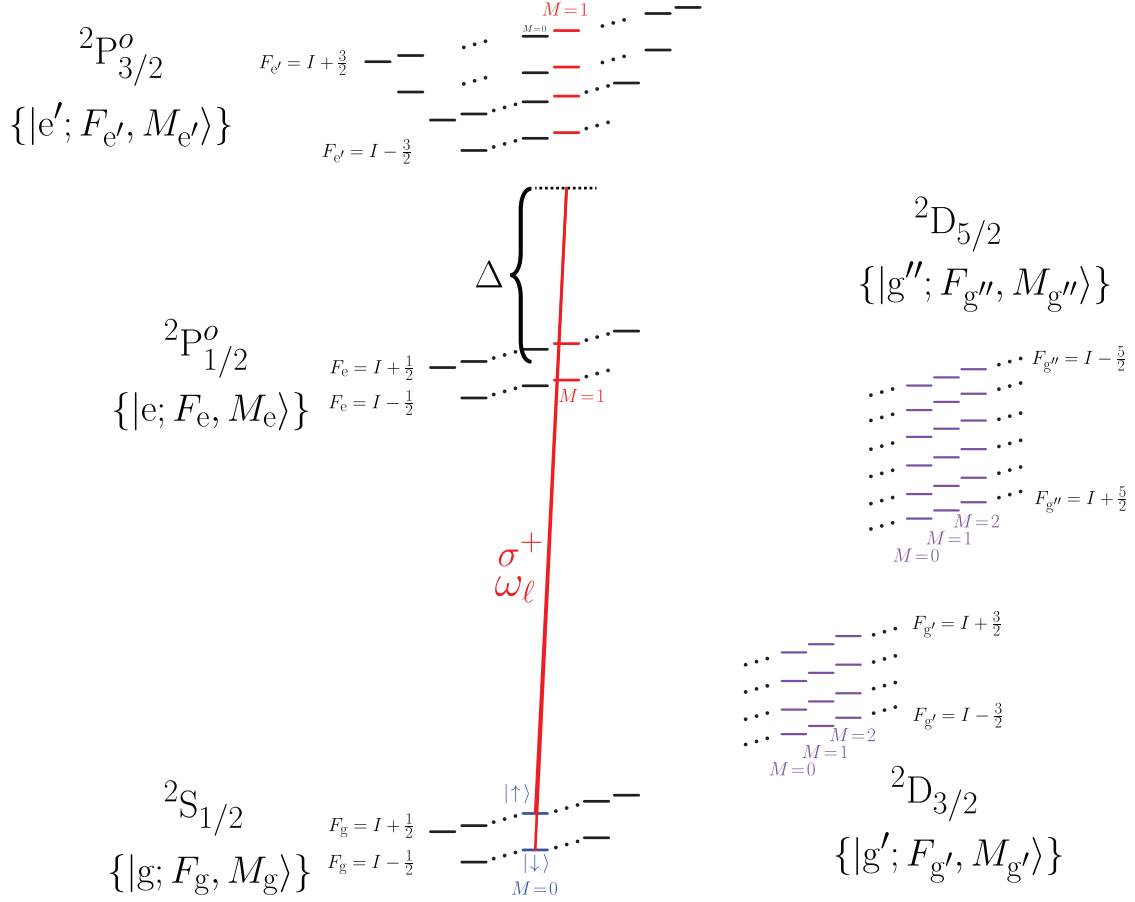


FIG. S1. Level diagram relevant for driving a stimulated Raman transition between zero-field g -type clock states in a half-integer-spin isotope of an alkaline earth ion with pure σ^+ light. For isotopes with $I < \frac{5}{2}$, the allowed values of F are constrained to $F \geq 0$.

The ω^3 -theory model, while being a fairly clear improvement over the CDA model in the regime explored experimentally in this paper, neglects a number of effects that should be considered before applying this analysis to other regimes. As discussed in Ref. [2], there are terms arising from emission-first processes that can play a role, as well as coupling to more excited states than just the five manifolds considered here (Fig. S1).

Experimental Sequence and Error Budget

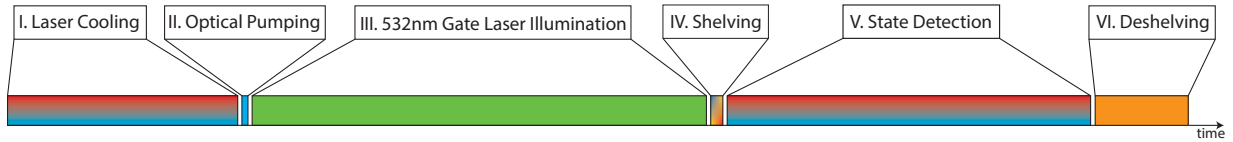


FIG. S2. Pulse Sequence Diagram outlining the 6 steps to each experimental cycle. I: First, the atom is laser cooled for 5ms. II: Next, using an EOM to phase modulate the 493 light, the ion is optically pumped to the $|S_{1/2}, F = 0 >$ state for $150 \mu s$. III: The atom is then illuminated by the high power 532nm laser when SRS can occur. IV: Then, for $300 \mu s$, the SRS error states of the atom are electron shelved to the $D_{5/2}$ metastable manifold. V: The cooling lasers are turned back on for 8ms and photon counts are collected to determine whether or not SRS has occurred. VI: Finally, a 614nm laser is used at the end to deshelve population back to the cooling manifold to repeat the experiment.

For this experiment, State Preparation and Measurement (SPAM) fidelity must be maximized due to the infrequent nature of Raman scattering. SPAM utilizes Electron shelving which uses electronic dipole transitions to quickly move population out of the $|S_{1/2}, F=1\rangle$ state to the $^2D_{5/2}$ manifold. Population in $|S_{1/2}, F=1\rangle$ is resonantly pumped to the $|P_{3/2}, F=2\rangle$ state with a tuned 455nm laser. This state will spontaneously decay to $^2S_{1/2}$, $^2D_{5/2}$, $^2D_{3/2}$ states. To rescue population from these states a 650nm and 585 nm laser, resonant with the $|P_{3/2}, F=2\rangle$ state, are applied along with the 455nm laser. Due to dipole selection rules, population in $|P_{3/2}, F=2\rangle$ cannot decay to the $|S_{1/2}, F=0\rangle$ state. The limiting factor in this shelving scheme is off resonant scatter from $|S_{1/2}, F=1\rangle \leftrightarrow |P_{3/2}, F=1\rangle$, where almost half of the spontaneous decays from this state to the $^2S_{1/2}$ are to $|S_{1/2}, F=0\rangle$. However, if the 455nm light is π -polarized, dipole selection rules forbid $\Delta F=0$, limiting this off resonant transition. The theoretical expected fidelity of this shelving scheme is $F_{SPAM} = 0.9998$. Experimentally, the SPAM fidelity was recorded to be $F_{SPAM} = .99971(3)$ [3]. This would give an infidelity of roughly $\epsilon_{SPAM} \approx 3 \cdot 10^{-4}$ during this Raman scattering experiment.

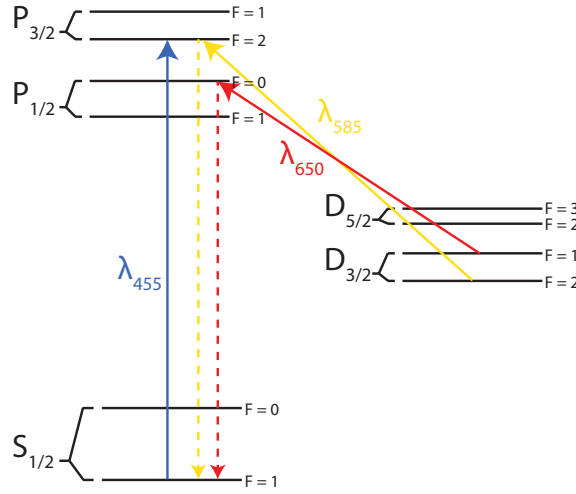


FIG. S3. Energy level diagram with applied shelving lasers.

Before and during each scattering rate data collection run, the 532nm laser was turned off and the experiment was run to determine the rate of erroneous background scattering events due to SPAM. These background events are due to off resonant shelving of the $|S_{1/2}, F=0\rangle$. These events look identical experimentally to SRS events and their rate must be well understood. This probability was measured to be $6(2) \cdot 10^{-4}$ and was subtracted from the measured scattering probability with the 532nm laser on. This probability is of the order of ϵ_{SPAM} with small differences in the quality of shelving parameters being the main factor in small error differences between these two studies.

Converting Stark Shift to Optical Intensity

The formula used for conversion from optical intensity to stark shift is [4],

$$\delta E_{nFMF}^{(2)} = \frac{1}{4\hbar^2} \sum_i \frac{|\langle m_s | \mathbf{d} \cdot \mathcal{E} \hat{\epsilon} | i \rangle|^2}{\Delta_i} \quad (\text{S.8})$$

Note $\mathcal{E}$ is the electric field amplitude. As stated in the letter, the laser illumination power ranged from .3-1.4 W. Using our measured beam waist of 40μ we can calculate an electric field amplitude and plug it into equation (S.8).

This electric field amplitude range corresponds to optical stark shifts of .32-1.5 Mhz. This range of stark shift values directly agree with the measured stark shift data points in the horizontal axis of Figure 2.



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