Supplemental material

I.   ION MOTION AMPLIFICATION

In an 1D harmonic oscillator with normal frequency ω_0, the position and velocity of a single ion at time t are

$$x(t) = x_0 \cos \omega_0 t, \tag{S1}$$

$$v(t) = x_0 \omega_0 \sin \omega_0 t, \tag{S2}$$

where x_0 is the motion amplitude.

A light field with k-vector $\vec{k}_L$ couples to the ion motion through photon scatterings. We define $\vec{k}_L \cdot \hat{x} < 0$, and the light force on the ion at time t is

$$F(t) = F(\omega) = s(\omega)\hbar c \vec{k}_L \cdot \hat{x}, \tag{S3}$$

where $s(\omega)$ is the scattering rate at Doppler shifted light frequency $\omega = \omega(v(t)) = ck_L\sqrt{(c+v(t))/(c-v(t))} \approx \omega_L(1 + v(t)/c)$, where $\omega_L = ck_L$ is the light frequency in the lab frame.

From the work-energy theorem, the energy gained by the ion after a cycle of motion is

$$\Delta E = \int_{x_0}^{-x_0} F'(x)\mathrm{d}x + \int_{-x_0}^{x_0} F''(x)\mathrm{d}x, \tag{S4}$$

where $F'(x)$ is the light force as a function of ion position in the first half of the cycle $(0 < t < \frac{\pi}{\omega_0})$, and $F''(x)$ is the light force in the second half of the cycle $(\frac{\pi}{\omega_0} < t < \frac{2\pi}{\omega_0})$. By changing the integration variable in Eq. S4 from x to t,

$$\Delta E = \int_0^{\frac{\pi}{\omega_0}} F(\omega)v(t)\mathrm{d}t + \int_{\frac{\pi}{\omega_0}}^{\frac{2\pi}{\omega_0}} F(\omega)v(t)\mathrm{d}t. \tag{S5}$$

From Eq. S2,

$$v(t) = -v(\frac{2\pi}{\omega_0} - t). \tag{S6}$$

With this, Eq. S5 becomes,

$$\begin{aligned}
\Delta E &= \int_0^{\frac{\pi}{\omega_0}} F(\omega(v(t)))v(t)\mathrm{d}t + \int_{\frac{\pi}{\omega_0}}^{\frac{2\pi}{\omega_0}} F(\omega(-v(\frac{2\pi}{\omega_0} - t)))(-v(\frac{2\pi}{\omega_0} - t))\mathrm{d}t \\
&= \int_0^{\frac{\pi}{\omega_0}} F(\omega(v(t)))v(t)\mathrm{d}t + \int_{\frac{2\pi}{\omega_0}}^{\frac{\pi}{\omega_0}} F(\omega(-v(\frac{2\pi}{\omega_0} - t)))v(\frac{2\pi}{\omega_0} - t)\mathrm{d}t.
\end{aligned} \tag{S7}$$

We define $t' = \frac{2\pi}{\omega_0} - t$, and

$$\Delta E = \int_0^{\frac{\pi}{\omega_0}} F(\omega(v(t)))v(t)\mathrm{d}t - \int_0^{\frac{\pi}{\omega_0}} F(\omega(-v(t')))v(t')\mathrm{d}t'$$
$$= \int_0^{\frac{\pi}{\omega_0}} [F(\omega(v(t))) - F(\omega(-v(t)))]v(t)\mathrm{d}t. \tag{S8}$$

From Eq. S3,

$$\Delta E = \hbar c \vec{k}_L \cdot \hat{x} \int_0^{\frac{\pi}{\omega_0}} [s(\omega(v)) - s(\omega(-v))]v(t)\mathrm{d}t. \tag{S9}$$

If $\Delta E > 0$, the ion's motion will be amplified after a cycle. If $\Delta E < 0$, the motional amplitude decreases after a cycle until reaching the Doppler cooling limit [1]. From Eq. S9, the difference between scattering rates $s(\omega(v))$ and $s(\omega(-v))$ for $0 < t \leq \frac{\pi}{\omega_0}$ determines the sign of ΔE.

Note that for small oscillation amplitude x_0 so that the scattering rate $s(\omega)$ is linear with ω,

$$\Delta E \propto \lim_{v \to 0}[s(\omega(v)) - s(\omega(-v))] \propto -\left.\frac{\mathrm{d}s}{\mathrm{d}v}\right|_0 \propto -\left.\frac{\mathrm{d}s}{\mathrm{d}\omega}\right|_{\omega_L}, \tag{S10}$$

which gives the well-known result that the ion is cooled (heated) when the sign of the spectrum slope is positive (negative).

For spectra with multiple peaks, as in Fig. 2 in the main text, the ion is locally heated as the sign of the spectrum slope at $\omega = \omega_L$ is positive, but is globally cooled due to the contribution of light that is Doppler shifted when the ion motion is large that $\omega - \omega_L$ is no longer small compared to sizes of the CPT features. Therefore, the ion's motion is amplified up to a stable orbit due to an equilibrium between "local heating" and "global cooling" effects.
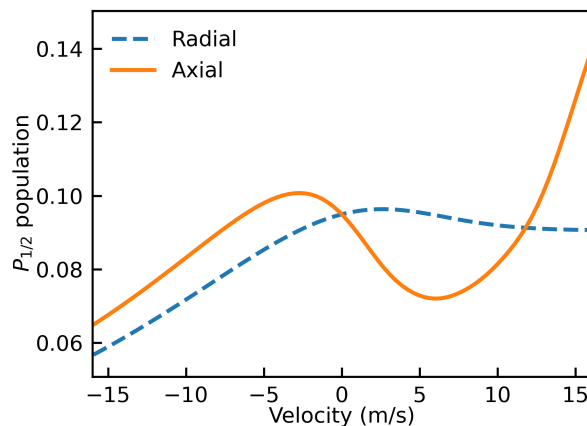

FIG. S1. $P_{1/2}$ state population vs. radial and axial ion velocities. From the ion velocity we can calculate the Doppler shifted 468 nm and 1079 nm light frequencies, and the $P_{1/2}$ state population can be calculated from the light frequencies. The positive axes are defined so $\vec{k}_{468} \cdot \hat{x} < 0$.

We further analyze the ion's motion in the trap radial and axial directions given the experimental setup in Fig. 1 described in the main text. The 468 nm and 1079 nm k-vectors are perpendicular to each other, leading to anisotropy

in axial and radial motion if we consider Doppler shifts to both the 468 nm and 1079 nm light: When the ion moves radially, the 468 and 1079 nm Doppler shifts have the same sign, and when the ion moves axially, the Doppler shifts have the opposite signs. We calculate the $P_{1/2}$ state population separately for ion velocities in the radial and axial directions, see Fig. S1, using the fitted parameters in Fig. 2 of the main text. According to Eq. S10, the ion is cooled if the slope of the scattering rate, which is proportional to the $P_{1/2}$ state population, at $v = 0$ is positive (radial directions), and the ion is heated if the slope of the scattering rate at $v = 0$ is negative (axial direction). Therefore, the ion motion is selectively amplified in the axial direction.

We note that if multiple modes can be excited, mode competition will lead to stable amplification of only one mode [2], and the amplified coherent motion of the dominant mode can be used in OMS to measure ion masses.

II.   SECULAR FREQUENCIES OF A LINEAR ION CRYSTAL

Formulas for the axial center-of-mass (COM) mode of a linear ion crystal with 1 to 3 ions are summarized.

We define the axial Mathieu parameter [3]

$$a_z = \frac{8Q\kappa U_0}{m z_0{}^2 \Omega_{\rm rf}{}^2},\tag{S11}$$

where Q is the ion's charge, m is the ion mass, κ is a dimensionless factor related to shielding of the axial electric field by the radial electrodes, U_0 is the dc voltage on the two endcap electrodes, and z_0 is the distance from the endcap electrode to the trap center.

For a single ion, the axial secular frequency in the approximation of $a_z \ll 1$ is [3]

$$\omega_{z,1} = \frac{\Omega_{\rm rf}}{2}\sqrt{a_z}.\tag{S12}$$

For a linear 2-ion crystal with ion masses M and m, the axial COM mode frequency is [4]

$$\omega_{z,2} = \omega_{z,1}\sqrt{1 + \frac{1}{\mu} - \sqrt{1 + \frac{1}{\mu^2} - \frac{1}{\mu}}},\tag{S13}$$

where μ is the mass ratio M/m.

For a linear 3-ion crystal with two ions of mass m on each end, and an ion of mass M at the center, the axial COM mode frequency is [5]

$$\omega_{z,3} = \omega_{z,1}\sqrt{\frac{13}{10} + \frac{1}{10\mu}(21 - \sqrt{441 - 34\mu + 169\mu^2})}.\tag{S14}$$

III.   OMS SYSTEMATICS

A.   Mass calibration

We calculate the molecular ion masses using an OMS calibration measurement directly before introducing reactants, and the systematic shift is the difference between the ion mass using the most recent calibration data and that using

the initial calibration shown in Fig. 3 in the main text. We do not report an uncertainty for this systematic as all calibrations have the same statistical uncertainty.

B. Trap potential drift

The secular frequency may drift in the time between mass calibration and molecular mass spectrometry (typically < 1 hour), due to for example material deposited on the trap electrodes during ion loading. We measure the axial secular frequency of a single Ra^+ as a function of time using the OMS for a period of ~ 5 hours to measure the drift of the trapping potential, and the results are shown in Fig. S2. During the measurement, the maximum fractional frequency drift during an 1 hour period is 6×10^{-5}, which we use for the systematic error due to trap potential drift. The corresponding mass uncertainties are calculated.
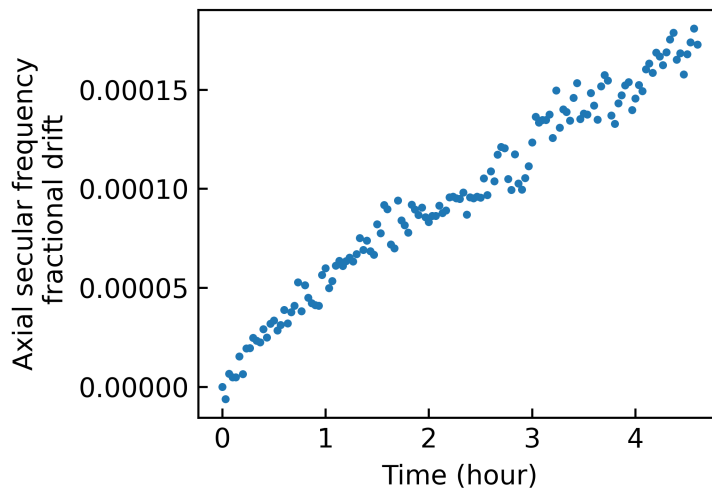

FIG. S2. Fractional drift in the axial secular frequency of a single Ra^+.

C. Secular motion amplitude shift

The axial COM secular frequency is amplitude-dependent due to trap anharmonicity [6]. We measure the axial COM mode secular frequency for a 3 Ra^+ crystal as a function of the oscillation amplitude [See Fig. S3]. With a motional amplitude of $22(3)\,\mu m$ that is used in the measurement, the maximum fractional secular frequency shift due to oscillation amplitude uncertainty is 5×10^{-5}, which translates to mass uncertainties that are less than 0.1 dalton.

The systematic shifts and uncertainties of measured masses are summarized in Table S1, along with the statistical results. The total systematic shift is a linear sum of the individual shifts, and the total uncertainty is a quadrature sum of the individual uncertainties.
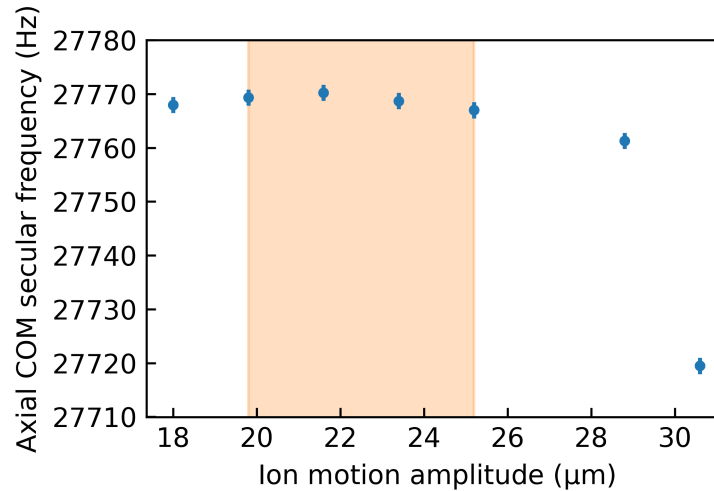
FIG. S3. Secular frequency vs. ion secular motion amplitude for 3 Ra^+. The orange shaded region indicates secular motion amplitudes used for OMS measurements.

	$RaOH^+$	$RaOD^+$	$RaOCH_3^+$	$RaOCD_3^+$
Calibration shift	0.01	0.21	0.34	0.22
Trap potential drift	0.00(9)	0.00(9)	0.00(9)	0.00(9)
Motion amplitude shift	0.00(7)	0.00(7)	0.00(8)	0.00(8)
Total systematic	0.01(11)	0.21(11)	0.34(11)	0.22(11)

TABLE S1. Systematic shifts and uncertainties of the measured molecular ion masses in daltons.

[1] P. D. Lett, W. D. Phillips, S. L. Rolston, C. E. Tanner, R. N. Watts, and C. I. Westbrook, Optical molasses, J. Opt. Soc. Am. B **6**, 2084 (1989).

[2] U. Kemiktarak, M. Durand, M. Metcalfe, and J. Lawall, Mode competition and anomalous cooling in a multimode phonon laser, Phys. Rev. Lett. **113**, 030802 (2014).

[3] D. J. Berkeland, J. D. Miller, J. C. Bergquist, W. M. Itano, and D. J. Wineland, Minimization of ion micromotion in a paul trap, J. Appl. Phys. **83**, 5025 (1998).

[4] G. Morigi and H. Walther, Two-species coulomb chains for quantum information, The European Physical Journal D - Atomic, Molecular, Optical and Plasma Physics **13**, 261 (2001).

[5] D. Kielpinski, B. E. King, C. J. Myatt, C. A. Sackett, Q. A. Turchette, W. M. Itano, C. Monroe, D. J. Wineland, and W. H. Zurek, Sympathetic cooling of trapped ions for quantum logic, Phys. Rev. A **61**, 032310 (2000).

[6] N. Akerman, S. Kotler, Y. Glickman, Y. Dallal, A. Keselman, and R. Ozeri, Single-ion nonlinear mechanical oscillator, Phys. Rev. A **82**, 061402 (2010).