Precise study of asymptotic physics with subradiant ultracold molecules

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Weakly bound molecules have physical properties without atomic analogues, even as the bond length approaches dissociation. For instance, the internal symmetries of homonuclear diatomic molecules result in the formation of twobody superradiant and subradiant excited states. Whereas superradiance¹⁻³ has been demonstrated in a variety of systems, subradiance⁴⁻⁶ is more elusive owing to the inherently weak interaction with the environment. Here we characterize the properties of deeply subradiant molecular states with intrinsic quality factors exceeding 10¹³ via precise optical spectroscopy with the longest molecule-light coherent interaction times to date. We find that two competing effects limit the lifetimes of the subradiant molecules, with different asymptotic behaviours. The first is radiative decay via weak magnetic-dipole and electric-quadrupole interactions. We prove that its rate increases quadratically with the bond length, confirming quantum mechanical predictions. The second is non-radiative decay through weak gyroscopic predissociation, with a rate proportional to the vibrational mode spacing and sensitive to short-range physics. This work bridges the gap between atomic and molecular metrology based on lattice-clock techniques⁷, enhancing our understanding of long-range interatomic interactions.

Simple molecules provide a wealth of opportunities for precision measurements. Their richer internal structure compared to atoms enables experiments that push the boundaries in determinations of the electric-dipole moment of the electron⁸, the electron-to-proton mass ratio and its variations^{9,10}, and parity violation¹¹. Diatomic molecules are moving to the forefront of many-body science¹² and quantum chemistry¹³, providing glimpses into fundamental laws¹⁴. However, this attractive complexity of molecular structure has historically posed difficulties for manipulation and modelling¹⁵. This work removes many of these barriers by employing techniques of optical lattice atomic clocks^{16,17} to control the quantum states of weakly bound homonuclear diatomic strontium molecules, in particular by using state-insensitive optical lattices¹⁸ for molecular transitions with three types of optical transition moments. We observe strongly forbidden optical transitions in this asymptotic diatomic system, an ideal regime for studying the breakdown of the ubiquitous dipole approximation where the size of the quantum particle is a significant fraction of the resonant wavelength λ . We explain these observations with a state-of-the-art ab initio molecular model¹⁹ and asymptotic scaling laws. The results prove that the quantum mechanical effect of subradiance can be exploited for precision spectroscopy, and demonstrate the promise of combining precise state control, coherent manipulation and



Figure 1 | Optical transitions to superradiant and subradiant molecular states. a, Electric-dipole (E1), magnetic-dipole (M1) and electric-quadrupole (E2) transitions in homonuclear diatomic molecules, from the gerade ground state to ungerade or gerade excited states. **b**, Measurements and predictions of E1, M1 and E2 oscillator strengths in the weakly bound ⁸⁸Sr₂ molecule. All values are normalized to the oscillator strength of an E1 transition to a superradiant 1_u level. The error bars are standard errors of the mean of all *Q* determinations. For the M1 transition to v' = -2, the error bar was increased fourfold to reduce the difference between direct and Rabi-frequency measurements to two standard deviations.

accurate *ab initio* calculations with recently available ultracold molecular systems.

We create Sr_2 molecules by photoassociation²⁰ from an ultracold cloud of spinless strontium atoms, ⁸⁸Sr, in an optical lattice satisfying the Lamb–Dicke and resolved-sideband conditions²¹ (Methods). The weak optical coupling of the ground ¹S₀ state to the excited ³P₁ atomic state (22 µs lifetime²²) in Sr atoms enables spectroscopic resolution of molecular structure in the immediate proximity to

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Figure 2 | **Direct and spectroscopic measurements of subradiant state lifetimes.** For all states, J' = 1. **a**, Rabi oscillations between ground and excited gerade molecules that set the π -pulse lengths for lifetime measurements. a.u., arbitrary units. **b**, Excited-state population decay, fitted with an exponential curve. The cartoon illustrates the four-step measurement sequence used for all the gerade states but the least-bound one. **c**, The least-bound gerade state is strongly coupled to the atomic continuum owing to its large bond length $R \approx 130 a_0$. The optical transition to the ${}^{3}P_{1} + {}^{3}P_{1}$ continuum corresponds to the right-hand peak (or shelf¹³), and the ${}^{1}S_{0} + {}^{1}S_{0}$ continuum to the left-hand oppositely facing peak. **d**, Lifetime measurement of the least-bound state. The cartoon shows the simplified measurement sequence, using the right peak in **c**. The lower curve that was subtracted from the signal shows spontaneous fragmentation to the ${}^{1}S_{0} + {}^{1}S_{0}$ continuum during the wait time. **e**-**h**, Optical spectra of the four J' = 1 subradiant states, with their binding energies indicated in Table 1. Dashed red lines indicate lineshapes deduced from direct lifetime measurements as in **b**,**d**. Only the narrowest spectra are limited by technical broadening such as the laser linewidth.

the ${}^{1}S_{0} + {}^{3}P_{1}$ atomic threshold without losses from photon scattering. This 689 nm intercombination (spin-changing) transition is electric-dipole (E1) allowed, where the photon couples states with opposite parity. The magnetic-dipole (M1) and electric-quadrupole (E2) transitions are strictly forbidden. Owing to quantum mechanical symmetrization, these higher-order transitions become allowed in bound homonuclear dimers, as illustrated in Fig. 1a. In the molecular ground state with the asymptotic electronic wavefunction $|X^{1}\Sigma_{g}^{+}\rangle \approx |{}^{1}S_{0}\rangle|{}^{1}S_{0}\rangle$, only gerade (even) symmetry is possible, allowing optical E1 transitions only to ungerade (odd) excited molecular states. However, M1 and E2 transitions are possible from $X^{1}\Sigma_{g}^{+}$ to gerade molecular states such as those near the ${}^{1}S_{0} + {}^{3}P_{1}$ threshold, because these higher moments couple states of the same symmetry. Such transitions are very weak owing to their spin- and electric-dipole-forbidden nature. As a result, the gerade molecular states are subradiant, whereas the ungerade states are superradiant. That is, if the E1 atomic radiative decay rate of ${}^{3}P_{1}$ to ${}^{1}S_{0}$ is Γ , then the equivalent rates are approximately 2Γ and 0 for the superradiant

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Figure 3 | Natural linewidths of weakly bound subradiant and

superradiant molecular states. a, The dominant contribution to the natural lifetime of the long-range subradiant states is gyroscopic predissociation sensitive to short-range physics, as schematically shown here. ${\bf b},$ Four least-bound subradiant states of ⁸⁸Sr₂ with the lowest angular momentum J' = 1 are measured, covering the range of bond lengths $R \sim 40-130 a_0$. The threshold between superradiant and subradiant behaviour is marked, as well as measurements of two representative superradiant states. Calculations of subradiant widths include both radiative and non-radiative contributions. The former scale as $\propto R^2$ (the line is *ab initio* theory), and the latter as the vibrational energy spacing (the line is theory fit to the data with a single scaling parameter; ab initio theory points are also shown). The error bars correspond to standard errors of the fitted exponential decay rates (as in Fig. 2b,d) for subradiant states or the Lorentzian widths (as in Fig. 2e-h) for superradiant states. For v' = -4, the error bar is twice the standard error of the mean of the two measurement techniques to account for a larger statistical discrepancy.

and subradiant molecular states. Asymptotically, these states correspond to the superpositions $1/\sqrt{2}(|^{1}S_{0}\rangle|^{3}P_{1}\rangle - |^{3}P_{1}\rangle|^{1}S_{0}\rangle)$ and $1/\sqrt{2}(|^{1}S_{0}\rangle|^{3}P_{1}\rangle + |^{3}P_{1}\rangle|^{1}S_{0}\rangle)$ of atomic states, respectively. In this work, the subradiant states belong to the excited 1_g molecular potential (where '1' refers to the total electronic angular momentum projection onto the molecular axis and 'g' to the symmetry of the electronic wavefunction), and couple to the ground state only via the higher-order M1 and E2 transitions. We probe optical transition strengths to the subradiant molecular states to establish their asymptotic quadratic dependence on *R*, the classical expectation value of the bond length²³. This behaviour is in stark contrast to the

 Table 1 | Measured and calculated contributions to the subradiant state linewidths.

	<i>J'</i> = 1				J'=3			
v'	E _b	γ_{rad}	$\gamma_{\rm pre}$	γ_{exp}	Eb	γ_{rad}	$\gamma_{\rm pre}$	γ _{exp}
-1	19.0420(38)	5.7	19.7	28.5(2.0)	-			
-2	316	1.6	166	156.3(5.3)	193	1.7	819	<6E3
-3	1,669	0.8	555	525(30)	1,438	0.9	3,102	<13E3
_4	5,168	0.6	1,243	1,250(90)	4,826	0.6	7,033	<11E3

The binding energies E_b are in MHz and the widths are in Hz. The theoretical widths γ_{rad} and γ_{pre} are *ab initio*. The value and small uncertainty for the v' = -1, J' = 1 binding energy come from extrapolating a peak-to-shelf frequency difference¹³ to zero magnetic field and probe and lattice light powers. The binding energy uncertainties for the remaining levels are 1 MHz.

asymptotic E1 transition strengths of the superradiant states, which are constant with *R*.

We have precisely quantified the optical transition oscillator strengths from $X^{l}\Sigma_{p}^{+}$ to the subradiant states. The 1_{g} levels have vibrational quantum numbers v' between -1 and -4 (counting from the continuum) and total angular momenta J' = 1, 2. The oscillator strengths were measured via optical absorption spectra, with areas normalized by the probe light power P and pulse time τ . For each transition, the experimentally obtained quantity is $Q \equiv B_{12}/(c\pi^2 w_0^2) = A/(\tau P)$, where B_{12} is an Einstein *B* coefficient, w_0 is the waist of the probe beam and A is the Lorentzian area of the natural logarithm of the absorption spectrum (Supplementary Information). In Fig. 1b, the Q values for the M1 and E2 transitions $(\Delta J = 1 \text{ and } 2, \text{ respectively, all starting from a } J = 0 \text{ ground state})$ are normalized to the Q for an E1 transition near the same atomic threshold, giving ratios of absorption oscillator strengths. We find M1 and E2 Q values that are four to five orders of magnitude suppressed compared to E1, as expected from the $Q \sim \pi^2/4 (R/\lambda)^2$ ratio of the M1 and E1 transition moments²³. Alternatively, oscillator strengths are proportional to the ratios of the squares of the Rabi frequencies to P, which were measured for M1 in the time domain by observing coherent Rabi oscillations (Supplementary Information). The two methods yield similar results. We performed ab initio calculations of these doubly forbidden transition strengths. The results shown in Fig. 1b are in excellent agreement with measurements, confirming the asymptotic divergence of the M1 and E2 transition moments with *R*. In the absence of this linear growth, the oscillator strengths would be governed by the rovibrational wavefunction overlaps (Franck-Condon factors), resulting in ratios different from our observations by about an order of magnitude.

We have also measured the lifetimes of the subradiant states. The long molecule-light coherence times enable optical Rabi oscillations as shown in Fig. 2a, with the fringe decay times limited by the natural lifetimes of the 1_g states. The Rabi period was used to determine the length of a π -pulse needed to excite the ground-state molecules into subradiant states. After a variable wait time, the molecules were returned to the ground state and imaged via excitation to the ${}^{1}S_{0} + {}^{3}P_{1}$ continuum followed by spontaneous decay²⁰, as in the cartoon of Fig. 2b. A typical exponential lifetime curve is shown in Fig. 2b. Although this approach was used for lifetime measurements of the 1_g states with $\nu' = -2, -3, -4$, the leastbound level allowed a simplified method. The spectrum in Fig. 2c shows two bound-free optical transitions from v' = -1 to atomic continua. The process at the higher laser frequency corresponds to fragmentation via the doubly excited ${}^{3}P_{1} + {}^{3}P_{1}$ continuum and is harnessed for direct lifetime measurements, as depicted in Fig. 2d, where a plot of the recovered atom number versus wait time is shown with an exponential fit. Even without an imaging pulse, some of the weakly bound v' = -1 molecules decay to ground-state atoms, and we subtract this small contribution from the signal. All known

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Figure 4 | **Magnetic-field tuning of subradiant lifetimes.** The long-range subradiant states have linewidths that are highly tunable with small magnetic fields *B*. **a**, The four linewidths of the transitions to J' = 1 are shown versus *B* in the range of 0.2–11 G. The low-field values are distinct (as in Fig. 3b), whereas at fields exceeding ~ 3 G all widths increase quadratically with magnetic field at rates of $\sim 300-500$ Hz G⁻². The open points are from direct lifetime measurements, the filled points are spectroscopic linewidths, and the dotted lines are drawn to guide the eye and indicate zero-field widths. **b**-**e**, The broader widths of the J' = 2 partners decrease with applied field for v' = -2, -3. All error bars are standard errors of the fitted Lorentzian widths or exponential decay rates.

systematic effects were controlled (Methods). The lifetime results are presented in Table 1.

Because the molecules are trapped in the Doppler-free regime, their absorption linewidths can also yield lifetimes. Unlike the direct lifetime measurements in Fig. 2b,d, this technique is sensitive to inhomogeneous broadening from stray magnetic fields and the lattice. Therefore, we engineered state-insensitive optical lattices for molecular transitions to the deeply subradiant states. The polarization and wavelength were chosen to ensure light shifts $\leq 1 \text{ Hz mW}^{-1}$, leading to inhomogeneous broadening < 50 Hzfor 150 mW of lattice light power (Supplementary Information and Supplementary Fig. 1). We nulled the ambient magnetic field to $\leq 20 \text{ mG}$ by using the linear Zeeman effect in Sr₂, and applied a bias field of 0.43 G with angle control of $\lesssim 2^{\circ}$ to define the quantization axis. The four resulting spectra for transitions from $X^1\Sigma_g^+$ to $\nu'=-1,-2,-3,-4$ are shown in Fig. 2e-h, and are compared with lineshapes expected from direct lifetime measurements. For the narrowest lines, the spectroscopic method overestimates the widths, as a result of broadening caused by the intrinsic linewidth of the probe laser (<200 Hz), magnetic quenching (<90 Hz, discussed below) and the finite probe pulse (<50 Hz).

The radiative lifetimes of the 1_g states were calculated from the *ab initio* model by considering doubly forbidden M1 and E2 transitions to the ground state. The resulting contributions γ_{rad} to the linewidths are in the range $\sim 1-6$ Hz (Table 1). Any contributions from decay to other states below the ${}^{1}S_{0} + {}^{3}P_{1}$ asymptote, as well as from black-body radiation²⁴, are negligible. Unlike for atoms, the radiative lifetimes alone do not suffice to explain the observed linewidths.

Non-radiative decay is a dominant contributor to the subradiant lifetimes. As shown in Fig. 3a, the 1_g bound states can couple to the long-lived ${}^1S_0 + {}^3P_0$ continuum of the $0_g^$ state. The nature of this coupling is non-adiabatic Coriolis mixing^{13,19,25} leading to weak gyroscopic predissociation. An estimate of the predissociation rate follows from the Fermi golden rule, $2\pi \gamma_{\rm pre} \approx 2\pi /\hbar |\langle 1_g, \nu', J', m'| \hat{H}_R | 0_g^-, E, J', m' \rangle|^2$, where \hat{H}_R is the Coriolis interaction and $|0_g^-, E, J', m' \rangle$ are energy-normalized continuum scattering states with energy *E*. This coupling vanishes at long range owing to the different dissociation thresholds of the 1_g and $0_g^$ potentials, but not at short range (Supplementary Information). We calculated the predissociative linewidths from the *ab initio* model, which was slightly tuned by scaling the ${}^3\Pi_g$ potential by 1.2% to improve agreement with experiment. Moreover, we can obtain accurate predissociative linewidth ratios without precise knowledge of the short-range physics. The amplitude of a bound-state rovibrational wavefunction is $\psi_v(R) \propto (\partial E_v / \partial v)^{1/2}$, where $\partial E_v / \partial v$ is the known vibrational energy spacing²⁶ (Supplementary Information). Thus $\gamma_{pre} = p (\partial E_v / \partial v)_{E=E_v}$, where the parameter *p* can be related to the ${}^{1}S_0 + {}^{3}P_1$ inelastic collision cross-section^{25,27}. The γ_{pre} values were obtained both from *ab initio* theory and by fitting $p = 2.48 \times 10^{-7}$ to the measured 1_g level linewidths.

The results of the lifetime measurements and calculations are shown in Fig. 3b, where the natural widths are plotted versus *R*. Note that our $R/\lambda \lesssim 0.01$, which is less than 0.5% of the range formerly explored with trapped ions⁴. The four 1_g subradiant states are marked, as well as two typical nearby superradiant states (from the 0⁺_u and 1_u potentials). The predictions for both non-radiative and radiative contributions are also shown. The radiative contribution exhibits $\propto R^2$ asymptotic scaling. The non-radiative contribution shows a change from roughly $\propto R^{-4}$ to $\propto R^{-2.5}$ scaling, reflecting the shift of long-range interaction from a *C*₆ to a *C*₃ character that occurs near $R \sim 80 a_0$ for the 1_g potential of Sr₂ (ref. 22). This scaling can be understood from the LeRoy–Bernstein formula²⁸, relating the inverse density of states to the long-range *C_n/Rⁿ* behaviour as $\partial E_v/\partial v \propto E_v^{(n+2)/(2n)} \propto R^{-(n+2)/2}$.

Table 1 summarizes the measurements and *ab initio* calculations for the 1_g levels. Moreover, we found that the lifetimes of the subradiant states are tunable by orders of magnitude with modest magnetic fields up to ~10 G. Figure 4a shows the natural linewidths of the four 1_g states versus field strength. They broaden with a quadratic coefficient of ~300 Hz G⁻² (or ~500 Hz G⁻² for v' = -2). This broadening could be qualitatively explained via Zeeman mixing with nearby even-J' levels that seem to be short-lived owing to their more complex mixing dynamics, which is further substantiated by the narrowing trend of the J'=2 widths as shown in Fig. 4b–e.

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The Sr₂ state with the narrowest natural linewidth ($\nu' = -1$) has a measured lifetime longer than that of the atomic ${}^{3}P_{1}$ state by an unprecedented factor of nearly 300, opening the door to ultrahighresolution molecular metrology. Our precise determinations of the binding energies and Zeeman coefficients of molecular states in this deeply subradiant regime (Supplementary Information and Supplementary Table 1) should allow fine tuning of parameters in the *ab initio* molecular model to reach agreement with measurements at the experimental accuracy, which would be a major achievement of quantum chemistry. Furthermore, Fig. 2c hints at the intriguing possibility of using long-lived states for ultracold molecule photodissociation²⁹. The shown transition from the least-bound subradiant excited state to the ground-state continuum should have an ultimate width limited by the subradiant state lifetime, corresponding to excess fragment energies of only a nanokelvin.

Methods

⁸⁸Sr atoms were laser-cooled in a two-stage magneto-optical trap (MOT) and loaded into a one-dimensional optical lattice with a depth of $30\,\mu\mathrm{K}$ and a wavelength near 900 nm. The lattice was generated by a diode laser and semiconductor tapered amplifier, where a diffraction grating removed any amplified spontaneous-emission light. Atoms were photoassociated into 3 µK molecules with a density of $\leq 10^{12}$ cm⁻³, which were optically imaged by a photodissociation pulse with a high spectral resolution²⁰. The molecules can be selectively created in either of the two least-bound vibrational levels (v = -1 or -2) of the electronic ground state. They are distributed among two rotational levels with the total angular momentum J = 0 or 2, which are well resolved spectroscopically. These molecules near the ${}^{1}S_{0} + {}^{1}S_{0}$ ground-state atomic threshold are the starting point for probing electronically excited molecules near the ${}^{1}S_{0} + {}^{3}P_{1}$ asymptote. Narrow molecular transitions were induced with a laser that was phase-locked to the narrow-linewidth 689 nm cooling laser. The trapping magnetic coils were pulsed off during spectroscopy, and other sources of magnetic-field gradients and noise were eliminated. For lifetime measurements, the following parameters were systematically controlled: lattice light power, molecule density by adjusting the photoassociation light pulse detuning, magnetic field by adjusting the current in a set of Helmholtz coils, and probe light power (for spectroscopic linewidth measurements). No systematic shifts of the lifetime values were detected for the accessible densities and lattice intensities, which were each varied by roughly a factor of two. Magnetic fields quench the lifetimes as in Fig. 4, so the ambient fields were carefully nulled.

The *ab initio* potentials for the ${}^{3}\Pi_{g}$ (${}^{'}S+{}^{3}P$), ${}^{3}\Sigma_{g}^{+}$ (${}^{1}S+{}^{3}P$) and ${}^{1}\Pi_{g}$ (${}^{1}S+{}^{1}P$) electronic states (Supplementary Information and Supplementary Fig. 2) were calculated using linear response theory within the coupled-cluster singles and doubles framework. The ground-state $X^{1}\Sigma_{g}^{+}$ empirical potential was used³⁰. Excited-state potentials were fitted to analytical functions¹⁹. Spin–orbit couplings between the non-relativistic states were fixed at their asymptotic values related to the atomic fine structure. Rovibrational level calculations were set up in the Hund's case (a) framework by including the ${}^{3}\Pi_{g}$, ${}^{3}\Sigma_{g}^{+}$ and ${}^{1}\Pi_{g}$ electronic states for the 1_g symmetry, and ${}^{3}\Pi_{g}$ and ${}^{3}\Sigma_{g}^{+}$ states for the 0_g⁻ symmetry. Diagonalization of the multisurface Hamiltonian for a given *J'* was performed via the discrete variable representation method.

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Author contributions

B.H.M., M.M., G.Z.I. and T.Z. designed the experiments. B.H.M., M.M., G.Z.I., M.G.T. and T.Z. carried out the measurements and interpreted the data. B.H.M. and M.M. co-led the experimental efforts. W.S. and R.M. carried out the theoretical calculations and interpreted the data. All authors contributed to the manuscript.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to T.Z.

Competing financial interests

The authors declare no competing financial interests.