Supplementary Materials for

Production of trilobite Rydberg molecule dimers with kilo-Debye permanent electric dipole moments

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Experiment

The Rydberg molecules were produced in a 1064 nm crossed far-off resonance trap (FORT) loaded from a Zeeman slower-loaded magneto-optical trap (MOT). The experimental setup has been described elsewhere [9,26].

The crossed FORT was created using a 50 W Yb fiber laser at 1064 nm. The laser was focused to a \( (1/e^2) \) spot size of \( 98 \pm 1.0 \mu m \). The beam was passed through the trapping region twice, with the second pass at a 22.5° angle to the first, resulting in an aspect ratio of approximately 2:1. The beams were not interferometrically stabilized, so a \( \lambda/2 \) waveplate was used to rotate the polarization of the second pass to prevent interference fringes. The trap depth was \( T \sim 5 \) mK. The trap frequencies were \( 2\pi \times 3.58 \) kHz on the short axis and \( 2\pi \times 1.0 \) kHz on the long axis. The crossed FORT was loaded to a peak density of \( 5 \times 10^{13} \) cm\(^{-3} \). The atoms inside the trap were optically pumped into the \( 6S_{1/2}(F = 3) \) hyperfine ground state to avoid collisional losses from the trap. The temperature of the atoms in the FORT was \( T = 40 \mu K \).

A two-photon process was used to photoassociate the molecular states in the dipole trap. The first step was generated by a near-infrared photon blue-detuned by 275 MHz from the \( 6S_{1/2}(F = 3) \rightarrow 6P_{3/2}(F' = 4) \) transition. The second step of the excitation was generated by a tunable dye laser at \( \sim 511 \) nm, near a transition to an \( nS_{1/2} \) Rydberg state. The detuning of the first step was chosen to place the frequencies of the hyperfine ghost peaks outside the
frequency range of interest; i.e. to the red of the atomic Rydberg line when scanning with the second step laser. This required a blue detuning on the first step to move the hyperfine ghosts outside that range.

The lasers were switched and frequency-shifted by acousto-optic modulators (AOMs) and coupled into optical fibers to transport the light to the experiment. The first step laser had a power of $\sim 5 \text{ mW}$ and was collimated to a spot size of $1 \text{ mm}$. The second step laser had a power of $70 \text{ mW}$ and was focused to a spot size of $44 \mu\text{m}$. The second step laser co-propagated with the second pass of the FORT beam. The angle between the first step and second step beams was $112.5^\circ$.

A train of 1000 laser pulses at $2 \text{ kHz}$ began $20 \text{ ms}$ after the end of the FORT loading period, lasting for $500 \text{ ms}$. The first step and second step lasers were pulsed simultaneously. Each laser pulse was $10 \mu\text{s}$ long. After a delay of $5 \mu\text{s}$ to allow the FORT beam to photoionize excited atoms, the ions were projected onto a microchannel plate (MCP) detector using an electric field pulse with a duration of $500 \text{ ns}$ and amplitude $F_p = 67 \text{ V cm}^{-1}$. The electric field plates were also used to generate background electric fields for the Stark shift measurements. After the pulse train was complete, the second-step laser frequency was incremented and the FORT was reloaded.

The spectra were produced by counting the pulses on the MCP at each frequency step, discriminating Cs$^+$ and Cs$_2^+$ ions based on the time of flight. No Cs$_2^+$ ion signal was detected in the experiment. The trilobite states appear as satellite peaks to the red of the atomic $nS$ Rydberg line in the Cs$^+$ signal. Ten scans were averaged for each spectrum. Spectra were taken from $\sim 1 \text{ GHz}$ red of the $nS_{1/2}$ line. The peak molecular signals were $\sim 4$–$5$ orders of magnitude weaker than the atomic $nS_{1/2}$ Rydberg signal. Two principal reasons for the small signal amplitude, as compared to Rb, are the smaller admixture of $S$-state character in the electronic wave functions, and the fact that the outer potential wells shown in Fig. 1B are
located at internuclear separations that are less than the average separation between the atoms in the gas.

The frequency of the first step laser was monitored using a saturated absorption setup. AOMs were used to shift the light in the saturated absorption setup so that it was resonant with the $6S_{1/2}(F = 3) \rightarrow 6P_{3/2}(F' = 4)$ transition. Additionally, an electromagnetically-induced transparency setup using a room-temperature Cs vapor cell was used to provide frequency markers for the spectra. The horizontal background electric field, $F_h$ was measured by recording a Stark spectrum of the Cs $126D$ Rydberg state with the applied (vertical) electric field, $F_a$, zeroed.

Lifetimes of the trilobite states were measured by varying the time between excitation and ionization. To prevent photoionization from contaminating the lifetime measurement by ionizing Rydberg atoms early, the FORT was switched off for 40 $\mu$s, starting 15 $\mu$s before the excitation laser pulses. The FORT was completely off when the laser excitation pulses occurred. The atoms were field ionized at $F_p = 356$ V cm$^{-1}$. Switching the FORT off increased losses from the trap due to thermal expansion of the atomic cloud during the off period. To mitigate this problem, the pulse train was reduced to 100 pulses in 50 ms. The experiment was performed by holding both steps of the two-photon transition in resonance with the trilobite state and counting ions during a 100,000 pulse period for each delay. The length of the excitation pulse for the lifetime experiment, 5 $\mu$s, caused an uncertainty of $\pm 2.5$ $\mu$s in each delay measurement. Tunneling of the system out of the potential wells studied in this paper is not relevant, as the tunneling times are far longer than any of the timescales present in the experiments.

**Theory**

Due to the large spatial extent of these molecules and the fairly short lifetimes, $\sim 10$ $\mu$s, the excited molecular states are localized angular wave packets, oriented relative to the external
electric field. The orientation is determined by the detuning of the excitation from the field free molecular energy. The spectra that result are the same as those obtained for molecules whose dipole moments are randomly oriented with respect to the electric field. There is a constant probability density of finding molecules oriented with a given projection of dipole moment along the electric field direction. As a result, the linear Stark shift manifests as a broad flat feature in the absorption spectrum that spans \( \Delta \omega = \pm dF \) where \( d \) is the molecular dipole moment and \( F = \sqrt{F_h^2 + F_a^2} \) is the total external field amplitude. Because the laser has a finite linewidth and the final electronic state is metastable, the spectral line has the shape of a step function of width \( 2dF \) convolved with a Lorentzian. This spectral lineshape was used to characterize the molecular Stark shifts.

The peak widths as a function of applied electric field are shown in Fig. 1C. The fitting function is,

\[
\frac{A}{2dF} \left[ \tan^{-1} \left( \frac{x - x_0 + dF}{\gamma/2} \right) - \tan^{-1} \left( \frac{x - x_0 - dF}{\gamma/2} \right) \right], \quad (S1)
\]

where the transition probability \( A \), the peak center \( x_0 \), and the spectral line broadening \( dF \) are fit parameters. The parameter \( x_0 \) is the field-free vibrational energy, \( \gamma \sim 3 \text{ MHz} \) is the width of the bare molecular transition, determined by the linewidth of the two-photon transition, and the transition probability \( A \) is proportional to the square of the s-wave electron probability amplitude matrix element between the initial and final molecular vibrational states. Thermal averaging over the initial states creates additional broadening on the order of 1 MHz; this additional broadening is incorporated into the width of the bare molecular transition, \( \gamma \). It is assumed that the initial state is a homogeneous distribution of Cs atoms. Taking into account the background field, the line broadening increases with electric field as \( d\sqrt{F_a^2 + F_h^2} \).

In atomic units the Fermi contact interaction is given by

\[
V_{\text{e-atom}}(\mathbf{r}, \mathbf{R}) = 2\pi A_4(k)\delta(\mathbf{r} - \mathbf{R}) + 6\pi A_6^3(k)\delta(\mathbf{r} - \mathbf{R}) \widehat{\nabla} \cdot \widehat{\nabla} \quad (S2)
\]
where $A_s(k)$ and $A_p(k)$ are the energy dependent $s$- and $p$-wave scattering lengths of the electron-perturber atom collision system, respectively, $r$ is the Rydberg electron position vector from the ionic core, and $R$ is the position vector of the neutral ground state perturbing atom to the Rydberg core. The electron momentum, $k$, is defined within the semi-classical approximation where $E_b = k^2/2 - 1/R$. In this expression, $E_b$ is the binding energy of the isolated Rydberg atom. Here, we used the triplet $s$- and $p$-wave scattering lengths found in [9,27,28]. Because the experiment is carried out in a FORT, rather than a magnetic trap, singlet Rydberg-ground state molecule states are present. However, the Cs singlet scattering lengths are small [21] and these states are not included in the calculations. To account for the spin-orbit splitting, the $p$-wave scattering volume is defined by

$$A_p^3 = \sum_{J=0}^{2} \left[ C_{L_1M_1,SM_S}^{JM_J} \right]^2 A_{p,J}^3,$$  

where $C_{L_1M_1,SM_S}^{JM_J}$ is a Clebsch-Gordan coefficient that couples the angular momentum of the Rydberg electron ($L_1, M_1$) to the total spin of the Rydberg electron-ground state atom system ($S, M_s$). We set the $^3P_1$ resonance position to 8 meV [28] and the spin-orbit splitting of the $^3P_0$ and $^3P_1$ resonances to the calculated values in [27]. For the electron to experience the $s$-wave contact interaction in Eq. S2, it must have a non-zero probability to be found along the internuclear axis of the ultralong-range Cs dimer. As a consequence, only states with total orbital angular momentum projection, $M_L = 0$, along this axis, contribute to the potentials.

In Rb Rydberg molecules (6), the resulting electronic states are dominated by the $nS$ Rydberg states and the $s$-wave electron-atom scattering. For Rb, the interaction potential mimics the Rydberg electron density function. In contrast, due to the accidental near-degeneracy present in Cs between the $nS$ and $(n - 4)l > 2$ Rydberg states, scattering of the Cs Rydberg electron between different Rydberg states must be considered. Recall that the ground state atom scattering center lies off-center from the Rydberg atom. This means that in an $s$-wave collision, the
electron can scatter from one angular momentum state into another. Such multiple scatterings result in highly-localized electronic wave functions, dominated by a nearly degenerate manifold of hydrogenic \((n-4)l > 2\) states.

In other previously studied Rydberg molecule systems [6,14], \(p\)-wave spin-orbit splittings were small, and could be treated as a single pole in the \(p\)-wave scattering length. Due to the large spin-orbit splitting in Cs, the \(p\)-wave scattering length in Eq. S3 leads to multiple sets of narrow avoided crossings. The Clebsch-Gordan coefficients in Eq. S3 create two different families of potentials, classified with \(|M_J| = 0\) and \(|M_J| = 1\). For the potential wells in which the states of interest reside, the \(M_J = 0\) and \(M_J = \pm 1\) projections are nearly degenerate, and not distinguishable in the experiment.

For the calculation of the BO potentials, the electronic wave function is dominated by the \((n-4)(l > 2)\) hydrogenic manifold and the \(ns\) state, however, a larger basis set is needed to achieve agreement with the experimental results. The convergence properties of the PECs with respect to basis set size is subtle for pathological potentials, such as the \(\delta\)-function interaction here. In this work, we used a basis set that includes all of the Rydberg orbits between the \((n \pm 1)S\) Rydberg states including the \((n-3)(l > 2)\) nearly degenerate manifold, just above the \((n + 1)S\) Rydberg threshold. Specifically we include the \(nS, (n \pm 1)S, nP, (n - 1)P, (n - 1)D,\) and \((n - 2)D\) states as well the \((n - 3)(l > 2), (n - 4)(l > 2),\) and \((n - 5)(l > 2)\) degenerate manifolds. As an example, for the \(n = 37\) state, this results in a basis set consisting of 97 Rydberg states. For the comparison between theory and experiment the zero-energy \(s\)-wave electron-perturber scattering length is adjusted to reproduce the lowest vibrational level belonging to the Cs(40S+6S) \(^3\Sigma^+\) molecular state. The basis set used here was selected to best reproduce the first vibration splitting in the Cs(40S+6S) \(^3\Sigma^+\) molecular state. In addition, a 25 MHz average AC Stark shift of the ground state due to the FORT laser was accounted for by shifting the experimental spectra. The FORT-induced AC Stark shift was measured by com-
paring the spectral position of each Rydberg state in the MOT, used to load the FORT, with the spectral position of the Rydberg state in the FORT. The ionization energy of the trilobite molecular states is nearly the same as for the nearby Rydberg states; the classical saddle point ionizing electric field for Cs(40S) is approximately 200 V/cm, several orders of magnitude larger than the applied electric fields. However, very large electric fields can significantly perturb the PECs [9].
References


20. See supplementary materials on Science Online.


