Heteronuclear Rydberg molecules

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We report the creation of heteronuclear ultralong-range Rydberg-molecule dimers by excitation of minority 88Sr atoms to 5snp3S1 Rydberg states (n = 31–39) in a dense background of 84Sr. We observe an isotope shift of the ν = 0 vibrational state over this range of n and compare our measurements with a theoretical prediction and a simple scaling argument. At low principal quantum number the isotope shift is sufficiently large to produce heteronuclear dimers with almost perfect fidelity. When the spectral selectivity is limited, we obtain a lower bound on the ratio of heteronuclear to homonuclear excitation probability of 30 to 1 by measuring the scaling of the molecular excitation rate with varying relative densities of 88Sr and 84Sr in the ultracold mixture.

Ultrasrange Rydberg molecules (RMs) are formed by the scattering between an excited Rydberg electron and at least one nearby neutral atom in a dense gas. Initially predicted theoretically [1], these molecules have been the subject of intense study following their initial observation in Rb [2] and subsequent observations in Cs [3] and Sr [4]. The internuclear potential inherits its shape from the Rydberg-electron probability distribution and supports bound states with bond lengths on the order of the radius of the Rydberg orbital Rν ∼ 2n2, ∼ 100 nm at n = 35. Recent studies have focused on the large permanent electric dipole moments of so-called trilobite and butterfly RMs [3, 5], ultracold chemistry and the stability of RMs in dense cold gases [6, 7], and on methods to use RMs to study low energy atom-ion scattering [8] and probe the pair-correlation function of quantum gases [9].

In this work we demonstrate photo-excitation of heteronuclear RM dimers using a mixture of 88Sr and 84Sr. We observe an isotope shift in the binding energy between the ground vibrational state of 84Sr + 84Sr, 88Sr + 84Sr and 88Sr + 88Sr RMs, and measure the scaling of molecule production with 88Sr and 84Sr density. Through the isotope shift, heteronuclear molecules provide a new probe of the underlying molecular potentials and the quantum statistics. Excitation of heteronuclear RM dimers from varied and well-controlled atomic constituents will enable the study of spatial correlations and collisional wavefunctions in atomic mixtures [9]. The combination of 88Sr and 84Sr is particularly interesting in this context because the system possesses an extremely large scattering length, a88−84 ~ 1800 a0, where a0 is the Bohr radius [10, 11].

The interaction of an excited Rydberg electron and a ground-state atom gives rise to a potential similar to that shown in Figure 1. The potential experienced by a ground-state atom, at distance R from the Rydberg atom nucleus, can be described in the Born-Oppenheimer approximation by a modified Fermi pseudopotential [12, 13],

\[ V(R) = \frac{2\pi\hbar^2 A_s(k)}{m_e} |\psi_{ns}(R)|^2 + \frac{6\pi\hbar^2 A_p^3}{m_e} |\nabla\psi_{ns}(R)|^2, \]

where \( \psi_{ns}(R) \) is the Rydberg electron wavefunction, \( m_e \) is the electron mass, and \( A_s(k) \) and \( A_p \) are s-wave and p-wave scattering lengths, respectively. For simplicity momentum \( k \) dependence of the scattering length is only included for the s-wave interaction. For strontium \( A_s(0) = -13.3 a_0 \) and \( A_p = 9.7 a_0 \) giving rise to an attractive potential. This attractive potential supports a manifold of vibrational states labeled by the quantum number \( \nu \) that appear as resonances red detuned from the atomic Rydberg state as shown in Figure 1. The binding energies of these molecular states scale as \( n^{-6} \). For each principal quantum number, the potential supports many bound states, but we focus on the highly localized \( \nu = 0 \) state for \( n = 31 − 39 \) here. The polarization potential between the background atom and ion core is negligible for these states.

In the present experiment we create \( \nu = 0 \) homonuclear RM dimers comprised of 88Sr + 88Sr and 84Sr + 84Sr, and heteronuclear dimers of 88Sr + 84Sr, where the star indicates the atom in the Rydberg state. Homonuclear dimers are excited from ultracold samples of either pure 88Sr or pure 84Sr. The chosen isotope is laser cooled in a broadband magneto-optical trap (MOT) operating on the 5s1 1S0 → 5s5p 3P1 cycling transition at 461 nm, from which a fraction of the atoms spontaneously decay into the metastable 5s5p 3P2 state and are magnetically trapped in the quadrupole field of the MOT [14]. The atoms are repumped to the ground state and further laser cooled using a narrow-band MOT operating on the 5s2 1S0 → 5s5p 3P1 intercombination line at 689 nm and are then loaded into an optical dipole trap (ODT) formed by two perpendicular light sheets at 1064 nm as described elsewhere [15]. We reduce the intensity of the ODT beams over an interval of 500 ms to allow for evaporative cooling after which 84Sr reaches a temperature of \( \sim 800 \) nK and a density of \( 9 \times 10^{13} \) cm\(^{-3} \). The weak interactions between 88Sr atoms (s-wave scattering length \( a = -2 a_0 \)) make evaporative cooling less efficient,
resulting in a final temperature of 1.1 μK and density of $6 \times 10^{12}$ cm$^{-3}$ for $^{88}$Sr at the same trap depth.

To create heteronuclear RMs we prepare an ultracold mixture of $^{88}$Sr and $^{84}$Sr. The two isotopes are sequentially laser cooled in the broadband MOT and loaded into the magnetic trap. From the magnetic trap the atoms are simultaneously repumped and cooled in a dual-isotope narrow-band MOT using laser light tuned to each isotope. The isotope shift of the $5s5p^1P_1$ intercombination line is sufficiently large that the $^{88}$Sr and $^{84}$Sr MOTs do not interfere with each other. From the narrow-line MOT, the mixture is loaded into the ODT and evaporatively cooled to the same trap depth as above. The sample temperature is set to $\sim 750$ nK, and the large interspecies scattering length and resulting high collision rate ensures that the mixture is in thermal equilibrium. We can selectively measure the number and temperature of each isotope using absorption imaging on the $5s5p^1P_1$ line and find that the temperatures of the two isotopes are equal to within 10% at the end of the evaporation. During the evaporation stage there is rapid atom loss due to the large three-body recombination rate associated with the strong interspecies interactions, which limits the maximum attainable density. We work with a relatively low peak density of $5 \times 10^{12}$ cm$^{-3}$, which yields samples with lifetimes on the order of a few hundred milliseconds. We can adjust the relative densities of the two isotopes by varying the load times of the broadband MOT. The ratio of $^{88}$Sr to $^{84}$Sr density is varied from 0.03 to 1 while maintaining approximately the same total number density and atom number $N \sim 3 \times 10^9$.

RMs are created in these ultracold samples using a two-photon excitation comprised of a fixed-wavelength 689 nm photon tuned near the $5s5p^1P_1$ level of the selected isotope and a 320 nm photon tuned to select the target Rydberg state. The target atom is excited to the $5sns^3S_1$ state with $n = 31 - 39$. For excitation of homonuclear $^{88}$Sr ($^{84}$Sr) molecules, we apply a 689 nm photon detuned 15 MHz (80 MHz) from the $5s5p^3P_1$ state. To excite heteronuclear molecules we selectively excite $^{88}$Sr to the $5sns^3S_1$ state in a background of $^{84}$Sr using the same laser detunings used to create homonuclear $^{88}$Sr molecules. The isotope shift of the $5sns^3S_1$ level between $^{88}$Sr and $^{84}$Sr is 445 MHz over the range of principal quantum numbers studied in this work and ensures complete isotope selectivity of the atom that is excited electronically. The detuning of the 689 nm photon from the $5s5p^3P_1$ level of $^{84}$Sr is sufficiently large that off-resonant scattering does not cause heating of the sample.

We generate spectra such as those shown in Figures 1 and 2 by scanning the energy of the 320 nm photon. We apply a 20 μs excitation pulse followed by an electric field ramp that ionizes any excited Rydberg atoms or molecules present in the sample. The liberated electrons are guided to a microchannel plate (MCP) detector where they are detected and counted. We repeat the excitation process 500 times per sample over 100 ms to build up statistics. The ODT beams are turned off during excitation to avoid AC stark shifts. To preclude the effects of Rydberg-Rydberg interactions we lower the power of the excitation lasers to ensure that fewer than one Rydberg state is created per excitation pulse on average.

The first evidence for production of heteronuclear Rydberg molecules is provided by the presence of an isotope shift in the binding energy of the $\nu = 0$ dimer state. In Figure 2 we show normalized excitation spectra for $\nu = 0$ RM dimers in three different samples: a pure $^{88}$Sr sample, excitation of a minority $^{88}$Sr in a majority $^{84}$Sr background, and a pure $^{84}$Sr sample for principal quantum numbers between $n = 31 - 39$. Spectra are plotted versus the detuning from the atomic Rydberg line of the electronically excited isotope, shifted by the detuning corresponding to the $\nu = 0$ line for $^{88}$Sr$^+ + ^{84}$Sr. Resonances for molecules with lighter reduced mass are shifted closer to the atomic line as is expected.

The isotope shift increases with decreasing principal quantum number with a scaling that can be understood with a simple model that is valid for the range of quantum numbers studied here. The molecular potential is approximated as harmonic around $R = R_c$ at which the RM potential has a minimum value $V(R_c) = -d$, i.e.,

$$V(R) \approx \frac{1}{2} \mu \omega^2 (R - R_c)^2 - d$$

(2)

with $\mu$ the reduced mass of the dimer pair. Because the $\nu = 0$ state is highly localized in the most outer well (see Fig. 1), the binding energy can be approximated by $E_{\nu=0} = -d - \hbar \omega/2$. Mass-dependent effects on the RM potential, such as variation of the reduced mass of the electron and background atom are negligible on the level of our measurement accuracy. Effects beyond the Born-Oppenheimer approximation, such as mass po-
The potential felt by the neutral atom follows the Rydberg line of the excited isotope, shifted by the detuning for the $88\text{Sr}^+ + 88\text{Sr}$ $\nu = 0$ dimer state, $\Delta_{\nu=0}^{(88)}$. Resonances for molecules with smaller reduced mass are shifted closer to the atomic line as expected. All spectra are taken in the same trap and with similar total densities (see text). For the heteronuclear spectra the ratio of the $88\text{Sr}$ and $84\text{Sr}$ densities is $\sim 0.1$.

The molecular energy levels can be obtained by numerical diagonalization of the Hamilton matrix formed using the molecular potential (Eq. 1). Due to the difference in reduced mass, the calculated energies are isotope dependent. The excitation spectra are weighted by the Franck-Condon factor and averaged over the thermal distribution of atoms, which shifts the peak of the excitation spectrum from the binding energy by $\sim 10$ kHz for the $\nu = 0$ vibrational state between $n = 30$ and 40. This shift is isotope independent. A small temperature difference between samples of different isotopes would change the apparent isotope shift, but this effect is estimated to be small ($\sim 1$ kHz). Moreover, the heteronuclear RM dimers are excited from a pair of distinguishable bosons and the RM dimers with rotational quantum number of $L = 1$ can be excited [18]. This can lead to an additional contribution to the isotope shift but it is small in the regime of current study (1-2 kHz). The measured and calculated isotope shifts are shown in Figure 3, the scalings agree reasonably with the expected $n^{-4}$. Relatively large deviations between the measurements and the calculations observed for the $88\text{Sr}^+ + 84\text{Sr}$ RM may be associated with the large scattering length $a_{84-88}$ affecting the Franck-Condon factor.

The presence of the isotope shift discussed above is conclusive evidence of the creation of heteronuclear RMs. For future applications one key quantity of interest is the fidelity with which heteronuclear RMs can be produced. It is clear from Figure 2 that for lower quantum numbers ($n \lesssim 35$) and with a sufficiently narrow excitation-laser linewidth, one can excite heteronuclear molecules with almost perfect fidelity by taking advantage of the spectroscopic resolution of the isotope shift. However, when the involved electronic state, the combination of constituent isotopes, or the excitation laser system does not permit the required spectral selectivity, another method of determining excitation fidelity is required.

As an example we consider the excitation of heteronuclear RMs at $n = 39$ where the isotope shift is 48 kHz, which is about half of the linewidth of the Rydberg excitation limited by the linewidth of the 320 nm laser system. If we assume that the distribution of atom positions is governed by Poissonian statistics and that the total number density, $n$, is much less than one per Rydberg-orbital volume, the RM excitation rate from the excitation of $88\text{Sr}$ in a $88\text{Sr}^+ + 84\text{Sr}$ mixture as a function of laser

\[
\Delta \omega / \omega = - \frac{1}{2} \frac{\Delta \mu}{\mu}.
\]
frequency $\nu$ is

$$R(\nu) = \int d^3r \kappa \left( n_{88}(r)^2 F(\nu - \nu_0^{(88-88)}) + \cdots \right)$$

where $n_x(r)$ is the number density distribution for each isotope, $F(\nu - \nu_0)$ is a lineshape function with unit integral centered at laser frequency $\nu_0$, and $\kappa$ is a rate constant that is a function of isotope-independent quantities such as electronic matrix elements, laser power, and other experimental parameters that are held fixed here. The Bose-enhancement of the homonuclear RM excitation rate [10] is about 10% for $n = 39$ at these temperatures and is neglected in our analysis.

Frequency integration over the line shape gives the integrated rate, $S$,

$$S = \int dv R(\nu) = \kappa (n_0^{2,88} + n_{0,88} n_{0,84}) V.$$  

(5)

For a harmonic trap the effective volume that arises from the integration of the spatial density distribution is

$$V = \left( \frac{\pi k_B T}{m \bar{\omega}^2} \right)^{3/2}$$

(6)

with geometric mean of the trap frequencies $\bar{\omega}$ and the spatial density distribution $n_x(r)$ is assumed to be a Gaussian with the peak density $n_{0,x}$ for each isotope. The effective volume is, in principle, isotope dependent, but when the effective volumes for each isotope are calculated we find that they are equal to within 10% over all of the densities considered and we assume these volumes as equal. We normalize the integrated rate $S$ by $n_{0,88} V$ to obtain a relation that is a function of the ratio of the two isotope densities.

$$\frac{S}{V n_{0,88}} = \kappa \left( 1 + \frac{n_{0,84}}{n_{0,88}} \right).$$

(7)

We obtain RM excitation spectra in $^{88}$Sr$^+ + ^{84}$Sr mixtures where we vary the ratio of $^{88}$Sr density to $^{84}$Sr density from 0.03 to 1 as discussed above. We scan the laser detuning over a range that includes both the $^{88}$Sr$^+ + ^{88}$Sr and $^{88}$Sr$^+ + ^{84}$Sr lines and integrate the spectrum. The integrated spectra are normalized according to Equation (7) and fitted with a single constant, $\kappa$. As shown in Figure 4, the measured data are well described by this scaling relation. For the lowest $^{88}$Sr fraction, we have a heteronuclear production fidelity of about 30 to 1. This fidelity is only a lower bound, however, as we have integrated over the entire spectrum and neglected any spectral selectivity. We can easily improve the heteronuclear excitation fidelity if spectral resolution is utilized, even for $n = 39$.

In summary, we have observed the excitation of heteronuclear and homonuclear production. When the isotope shift is large compared to the spectral linewidth, essentially pure samples of heteronuclear molecules can
be created. In the limit of unresolved lines, we have demonstrated homonuclear impurity below 1 part in 30. Heteronuclear RMs present many new opportunities for studying quantum systems such as probing interparticle and interspecies pair correlation functions in multicomponent many body systems [19, 20] using the methods of [9]. We can probe the scattering wavefunction of a strongly interacting mixture such as the \(^{88}\text{Sr} + ^{84}\text{Sr}\) combination used in this work. Such an \textit{in situ} measurement of the pair-correlation function in the presence of strong interactions can be related to the Tan contact [21, 22], and the temporal resolution available with RM excitation could provide a probe of the dynamics of the contact after an interaction quench. This new variety of RMs opens paths to explore the sensitivity of the isotope shift to the mass polarization energy for Rydberg trimers or larger molecules, and RMs involving high \(L\) Rydberg states. In lighter atomic species, e.g., Li, the isotope shift is expected to be much larger than observed in this work [8]. Heteronuclear RMs could also enable studies of new types of Rydberg impurities in quantum gases [23].

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