Creation of vibrationally-excited ultralong-range Rydberg molecules in polarized and unpolarized cold gases of $^{87}\text{Sr}$

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Abstract

Photoexcitation rates for creation of ultralong-range Rydberg molecules with $31 \lesssim n \lesssim 41$ in both ground and excited vibrational levels in cold ($T \sim 900$ nK) gases of polarized and unpolarized $^{87}\text{Sr}$ are presented. The measured production rates of the $\nu = 0$, 1 and 2 vibrational levels reveal rather different $n$ dependences which are analyzed by evaluating the Franck–Condon factors associated with excitation of the different vibrational levels and molecular rotational states. In particular, for gases of spin-polarized fermions, only Rydberg dimers with odd rotational quantum numbers are excited due to the requirement that their wave functions be anti-symmetric with respect to exchange. The data also demonstrate that measurements of the formation of vibrationally-excited $\nu = 1$ molecules can furnish a probe of pair correlations over intermediate length scales.

Keywords: Rydberg molecules, ultracold atoms, spectroscopy

(Some figures may appear in colour only in the online journal)

1. Introduction

Ultralong-range Rydberg molecules (ULRM) have been the subject of much recent interest because of their novel physical and chemical properties [1]. In the present work we focus on Rydberg dimer molecules which comprise a Rydberg atom in whose electron cloud are embedded one, or more, weakly bound ground-state atoms. While the existence of such molecules was first predicted theoretically [2], they have now been observed using a variety of different atomic Rydberg states and a number of atomic species including rubidium, cesium, and strontium [1, 3–10]. Binding results from the scattering of the excited Rydberg electron from the ground state atom(s) and can be approximated using a Fermi pseudopotential [11]. The resulting molecular potential $V(R)$ can support a number of vibrational levels. For principal quantum numbers $n \sim 30$, such levels have binding energies of the order of 10 megahertz, necessitating their study in cold molecular gases, $T \lesssim 1$ mK. The binding energies decrease rapidly with increasing $n$ and scale as $\sim 1/n^5$.

An example of a molecular potential is depicted in figure 1 together with the radial component of the vibrational wave functions for the $\nu = 0$–4 vibrational levels. The structure present in the potential mirrors the modulations in the radial Rydberg electron probability density distribution. The wave function for the ground $\nu = 0$ vibrational state is strongly localized in the outermost well of the molecular potential located near the classical outer turning point of the electron. The probability of photoexciting a $\nu = 0$ dimer molecule is therefore governed by the likelihood of there being two ground-state atoms with the required internuclear separation, $R$. Thus, by varying $n$ and, hence, the location of the potential minimum, measurements of dimer formation can be used to probe the spatial dependence of the pair correlation function, $g^{(2)}(R)$, in a cold gas [12]. This has been exploited in earlier work to probe non-local pair correlations in cold gases of (bosonic) $^{86}\text{Sr}$ and (fermionic) $^{87}\text{Sr}$ over length scales of $\sim 50$–150 nm using Rydberg molecules with...
Figure 1. Calculated molecular potential for a 5s3p4s ¹Σg−1S0−5s2 ¹Σ0 strontium atom pair (see equation (1)) together with the calculated vibrational wave functions multiplied by the radial coordinate R for the \( \nu = 0 \) to \( \nu = 4 \) vibrational states. The horizontal axis for each wave function denotes its binding energy. The inset shows the pair correlation functions, \( g^\nu(R) \), for cold thermal gases of non-interacting identical bosons, fermions, and classical, i.e. distinguishable, particles [12]. The particle separations are expressed in units of the thermal de Broglie wavelength \( \lambda_{\text{th}} = h/\sqrt{2\pi m k_B T} \) where \( m \) is the atomic mass, \( k_B \) the Boltzmann constant, and \( T \) the temperature.

31 ≤ \( n \) ≤ 45 [13, 14]. These studies clearly demonstrated the effects of quantum statistics, i.e. of bunching in a thermal gas of \(^{84}\text{Sr}\) and antibunching due to Pauli exclusion in a spin-polarized gas of \(^{87}\text{Sr}\).

As seen in figure 1, the wave functions for higher excited vibrational states \( \nu = 1, 2, \cdots \) extend to smaller internuclear separations than for the \( \nu = 0 \) states, which suggests that measurements of the formation rates for the different vibrationally-excited dimer levels might be used to probe spatial correlations over a broader range of \( R \). We examine this in the present work by comparing results for the formation of the different molecular vibrational states in a cold (\( T \approx 900 \) nK) gas of spin-polarized \(^{87}\text{Sr}\) with results for an unpolarized \(^{87}\text{Sr}\) sample. \(^{87}\text{Sr}\) atoms have a sizable nuclear spin, \( I = 9/2 \), resulting in a total angular momentum \( F = 9/2 \) for the 5s2 ¹Σ0 ground state and a large number of magnetic sublevels, \( m_F = -9/2, -7/2, \ldots 7/2, 9/2 \). Because of this ten-fold degeneracy, a statistical population of ground-state \(^{87}\text{Sr}\) atoms provides a good approximation to a gas of uncorrelated, i.e. classical, particles. (The bosonic isotopes of strontium have \( I = 0 \) and thus no degeneracy in the ground state. Here, when we refer in general to bosonic isotopes, we assume they are spin polarized.)

The experimental results are interpreted through comparison to calculated rates for molecule formation that incorporate an effective Franck–Condon factor and account for pair correlations and for the thermal distribution of atoms in the gas. The theoretical work provides a rigorous derivation of molecular formation rates including the effects of quantum statistics and highlights the important role played by rotational angular momentum. This study also illuminates how different rotational levels contribute to total molecular production and how these contributions vary with temperature. In addition, the work provides a valuable test of the present theoretical understanding of the molecular potentials and wave functions involved and demonstrates that studies of vibrationally-excited states can be used to examine spatial correlations on intermediate length scales.

2. Experimental approach

As is apparent from the inset in figure 1, for cold gases of non-interacting identical bosons or fermions, quantum statistics have a significant effect on \( g^\nu(R) \) at small interparticle spacings \( R \lesssim 0.8 \lambda_{\text{th}} \), where \( \lambda_{\text{th}} \) is the thermal de Broglie wavelength. For a gas of \(^{87}\text{Sr}\) atoms at 900 nK, the de Broglie wavelength is \( \lambda_{\text{th}} \approx 200 \) nm, enabling study of the effects of quantum statistics at interparticle spacings \( \lesssim 160 \) nm. An interparticle spacing of 160 nm corresponds to the radius \( \sim 2(n - \delta)^2 a_0 \) of 5nm ¹Σ1 Rydberg atoms for \( n \approx 40 \), where \( \delta \approx 3.37 \) is the quantum defect and \( a_0 \) the Bohr radius. Smaller interparticle separations can be investigated through formation of molecules with smaller values of \( n \). However, it is difficult to extend measurements to values of \( n \lesssim 30 \) because production of a Rydberg molecule requires that the ground-state atom density, \( \rho \), in the trap is sufficient to provide a significant likelihood of finding ground-state atom pairs at the appropriate spacing. For \( n \approx 30 \), this necessitates densities \( \rho \gtrsim 3 \times 10^{13} \) cm\(^{-3}\). Conversely, measurements for \( n \gtrsim 45 \) are challenging as the spacings between neighboring vibrational levels, which decrease rapidly as \( n \) increases, become very small making them difficult to resolve with our existing laser linewidth of \( \sim 300 \) kHz.

To better compare molecule formation in polarized and unpolarized gases it is advantageous to use samples with similar temperatures and density distributions. To achieve sub-mK temperatures in \(^{87}\text{Sr}\) gases requires evaporative cooling. An unpolarized sample efficiently thermalizes through s-wave collisions as the trap depth is lowered, leading to efficient evaporation. In contrast, for a spin-polarized sample s-wave collisions are not allowed, and at these low temperatures collisions in higher partial waves are suppressed, frustrating the evaporation process. This problem can be overcome by using a mixture of \(^{84}\text{Sr}\) and \(^{87}\text{Sr}\) and employing sympathetic cooling to obtain the desired temperature.

The cooling protocol [15, 16] can be discussed with reference to the term diagram for strontium (figure 2). Strontium atoms are cooled to temperatures of a few millikelvin in a magnoeto-optical trap (MOT) utilizing the 461 nm 5s2 ¹Σ0−5s5p ¹P1 transition. Atoms in the 5s5p ¹P1 state have a small branching ratio for decay via the 5s4d ¹D2 state into the 5s5p ¹P2 metastable state. ¹P2 atoms created in weak-field-seeking states become trapped in the MOT magnetic field [17], allowing for accumulation of large numbers of atoms. \(^{87}\text{Sr}\) and \(^{84}\text{Sr}\) atoms are loaded sequentially into the magnetic trap to allow the 461 nm laser to be separately tuned for each isotope. (The relative populations of each isotope are varied by controlling the loading times.) After the magnetic trap is loaded, a repump laser operating on the 5s5p ¹P2−5p2 ¹P2 transition
transition at 481 nm returns atoms to the $\Sigma_0^+$ ground state via the $5s5p \ ^3P_1$ state.

As illustrated in figure 3, which shows the number of atoms returned to the ground state for different repump-laser detunings, the presence of hyperfine structure in $^{87}$Sr results in multiple spectral features, which complicates the repump process. (The observed splittings indicate that the structure is associated primarily with the hyperfine splitting of the lower $5s5p \ ^3P_1$ state.) Efficient and simultaneous repumping of all the $^{87}$Sr hyperfine states, as well as admixed $^{84}$Sr atoms, therefore requires the presence of multiple laser frequencies, which are generated by broadening the laser spectrum by modulating its drive current and superposing sidebands using an EOM.

Following repumping, both isotopes are simultaneously cooled to $\sim 2 \mu$K using a MOT operating on the 689 nm $5s^2 \ ^1S_0 \rightarrow 5s5p \ ^3P_1$ intercombination line. Three separate laser frequencies are applied to drive the $\Sigma_0^+ \rightarrow \Pi_1$ transition in $^{84}$Sr, and the $\Sigma_0^+ F = 9/2 \rightarrow \Pi_1 F = 11/2$ and $\Sigma_0^+ F = 9/2 \rightarrow \Pi_1 F = 9/2$ transitions in $^{87}$Sr [16]. The atoms are then loaded into an optical dipole trap (ODT) formed using a 1.06 $\mu$m laser beam that is formed into a sheet (width $\sim 260 \mu$m and thickness $\sim 26 \mu$m) in the center of which is a ‘dimple’ created using a second laser beam ($\sim 60 \mu$m diameter) incident near normal to the plane of the sheet and roughly parallel to gravity.

To obtain spin-polarized samples, $^{87}$Sr atoms are then optically pumped in the presence of a magnetic bias field of 7.6 G. Once optical pumping is complete the magnetic field is reduced to 1 G to preserve a quantization axis. Detailed spectroscopic measurements [13, 14] showed that optical pumping transfers $\sim 90\%$ of the ground-state atoms to the $m_f = +9/2$ magnetic sublevel. Experiments with unpolarized samples are undertaken in zero magnetic field.

Atoms held in the ODT are cooled to $\sim 900$ nK through evaporative cooling. Optical pumping causes heating of the $^{87}$Sr atoms due to photon scattering, and a higher temperature before evaporation. To obtain polarized and unpolarized samples with similar final densities and temperatures the ratio of $^{84}$Sr and $^{87}$Sr atoms loaded into the ODT is adjusted—the greater the fraction of $^{84}$Sr the colder the final sample. Once evaporation is complete, the $^{84}$Sr atoms are ejected from the trap through light scattering using a light pulse resonant with the $5s^2 \ ^1S_0 \rightarrow 5s5p \ ^3P_1$ transition in $^{84}$Sr. (Because of the $^{84}$Sr-$^{87}$Sr isotope shift, the laser pulse does not lead to any detectable heating of the $^{87}$Sr atoms.) The final atom number and temperature are determined with absorption imaging on the $5s^2 \ ^1S_0 \rightarrow 5s5p \ ^3P_1$ transition.

Following preparation of an $^{87}$Sr sample, Rydberg excitation spectra are obtained using pulsed two-photon excitation. The first (689 nm) photon is $\sigma^+$ polarized and blue detuned $\sim 14.8$ MHz from the transition to the $5s5p \ ^3P_1 F = 11/2$ level. The second (319 nm) photon has $\pi$ polarization and is tuned to excite final $5sns \ ^3S_{1/2} F = 11/2$ Rydberg states. To eliminate AC Stark shifts, the ODT is turned off during the excitation pulses. Voltage pulses are applied to electrodes surrounding the trap in order to detect Rydberg atoms/molecules through field ionization. Resulting electrons are directed to a microchannel plate detector whose output is recorded with a multichannel scalar. During each excitation pulse, the number of Rydberg atoms/molecules created is kept small to avoid blockade effects and detector saturation. To improve statistics, many laser pulses and ionization sequences are applied to a sample of trapped atoms.

3. Theoretical method

The interaction between the quasi-free Rydberg electron and the neutral ground state atom is very weak and dominated by the short-range Fermi pseudopotential [11]. The effective potential of an ULRM is therefore approximately given by

$$V(\vec{R}) = 2\pi \hbar^2 a_s |\psi(\vec{R})|^2 + 6\pi \hbar^2 a_p |\psi(\vec{R})|^2,$$

where $\psi(\vec{R})$ is the electronic wave function, $m_e$ the electron mass, $e$ the electronic charge, and $a_s$ and $a_p$ are the $s$- and $p$-wave scattering lengths. In the following we consider Rydberg
dimers formed by $5sns$ $S_1$ Rydberg states. For such a spherically symmetric charge cloud the molecular potential is isotropic and depends only on the internuclear distance $R$ between the Rydberg core and the ground state atom. Therefore, the eigenstates of Rydberg dimers can be written as \[ \Psi_{\nu, \Lambda, M}(R, \theta, \phi) = \mathcal{R}_{\nu, \Lambda}(R) Y^M_{\Lambda}(\theta, \phi), \] (2)

where $\mathcal{R}_{\nu, \Lambda}(R)$ is the radial wave function, $\nu$ is the vibrational quantum number, $\Lambda$ is the rotational quantum number, and $M$ is the projection of $\Lambda$ onto the magnetic field axis. (For Rydberg $S$-states the third Euler angle becomes cyclic and the Wigner rotation matrix reduces to a spherical harmonic $Y^M_{\Lambda}$.)

The rate of excitation of a Rydberg molecule is governed by experimental factors such as laser intensity and sample density as well as by the atomic dipole transition strength and a Franck–Condon-type factor for characterizing the overlap between the initial unbound ground-state atom-pair wave function and the ULRM wave function. Since the interaction between the Rydberg electron and the ground state atom is typically very weak, the molecular potential (equation (1)) is evaluated in first-order perturbation theory, i.e. the unperturbed electronic wave function of the Rydberg atom is used in equation (1). Moreover, the electronic transition strength depends only on the atomic Rydberg wave function, in particular on the principal quantum number $n$ and quantum defect $\delta$ of the Rydberg atom, $(\delta)^2 \approx (n - \delta)^2 \delta_0$, but is independent of the molecular level to be formed. The Franck–Condon factor governing the production rate from a particular initial two-body scattering state $\chi^\pm_k(R)$ is given by

\[ \mathcal{F}^\pm_{\nu, \Lambda, M}(\vec{k}) = \int d^3R \mathcal{R}_{\nu, \Lambda}(R) Y^M_{\Lambda}(\theta, \phi) \chi^\pm_k(\vec{R}), \] (3)

where $\vec{R}$ is the relative coordinate, $\pm$ is the parity, and $\vec{k}$ is the relative momentum of the two neighboring ground state atoms that eventually form the Rydberg dimer through photoexcitation of one of the atoms to a Rydberg state. Assuming that the interaction between the two ground-state atoms is negligibly small and that the potential of the ODT is constant over the length scale of the Rydberg atom, the properly symmeterized initial two-body scattering states are given by

\[ \chi^\pm_k(\vec{R}) = \frac{1}{\sqrt{2}} (e^{i\vec{k} \cdot \vec{R}} \pm e^{-i\vec{k} \cdot \vec{R}}). \] (4)

For ground-state $^{87}$Sr atoms, if the gas is spin polarized, the scattering state must have odd parity. Otherwise, the system can be described by an ensemble of scattering states with both parities.

By assuming a Lorentzian profile, we approximate the spectral excitation density for a given molecular state $(\nu, \Lambda, M_0)$, fixed relative wave vector $\vec{k}$, and parity $\pm$ as

\[ f^\pm_{\nu, \Lambda, M_0}(\vec{k}, \omega) = \frac{1}{2} \mathcal{F}^\pm_{\nu, \Lambda, M_0}(\vec{k})^2 \times \left( \frac{\Gamma}{\omega + \hbar^2 k^2/4\mu - E_{\nu, \Lambda}} / \Gamma/2 \right)^{1/2}, \] (5)

where $E_{\nu, \Lambda}$ is the binding energy of the Rydberg molecule, $\omega$ is the laser detuning from the resonant excitation of $5sns$ $S_1$ Rydberg atoms, and $\mu$ is the reduced mass which is half the $^{87}$Sr mass. In the current setting, the experimental resolution determines the effective width $\Gamma$ ($\sim 300$ kHz) which is much larger than the lifetime broadening of the Rydberg molecule. The total spectral excitation density from all states of parity $\pm$ follows then from equation (5) as the sum over all molecular states $(\nu, \Lambda, M_0)$ and the average over the thermal distribution at given temperature $T$ over the relative momenta of the atom pairs. Assuming the system is far from quantum degeneracy, this yields

\[ f^\pm(\omega) = \sum_{\nu, \Lambda, M_0} \left( \frac{\hbar^2}{2\pi\mu k_B T} \right)^{3/2} \times \int d^3k e^{-\hbar^2 k^2/(2\mu k_B T)} f^\pm_{\nu, \Lambda, M_0}(\vec{k}, \omega). \] (6)

Typically, the energy shifts associated with rotational excitation are small (for $n = 30$ and $\nu = 0$ the rotational constant is $\sim 20$ kHz) and individual rotational levels cannot be resolved. However, the vibrational levels $(\nu = 0, 1, 2)$ have significantly larger energy spacing ($\sim 30$ MHz at $n = 30$ and $\sim 4$ MHz at $n = 40$) and can be resolved. In such cases, an excitation strength for each vibrational level can be separately determined by summing over the thermally-averaged Franck–Condon factors $\langle \mathcal{F}^\pm_{\nu, \Lambda, M_0}(\vec{k}) \rangle$ from all rotational levels or approximated by integrating $f^\pm(\omega)$ over a frequency window centered at a given vibrational level

\[ P^\nu_{\Lambda} \approx \sum_{\Lambda, M_0} \langle \mathcal{F}^\pm_{\nu, \Lambda, M_0}(\vec{k}) \rangle \sim \int_{E_{\nu, \Lambda} - \Delta}^{E_{\nu, \Lambda} + \Delta} f^\pm(\omega) d\omega, \] (7)

where $\Delta$ is much larger than $\Gamma$ but is small compared to the vibrational level spacing, i.e. of the order of 1 MHz. When the radial wave function of a vibrational state is well localized at $R = R_0$, the excitation strength for states of $\pm$ parity can be approximated as

\[ P^\nu_{\Lambda} \approx 4\pi \mathcal{g}^{(2)}_{\nu, \Lambda}(R_0) \int dR R^2 \mathcal{R}_{\nu, \Lambda}(R)^2. \] (8)

The radius at which $\mathcal{R}_{\nu, \Lambda}(R)$ is localized follows the Coulomb scaling $R_0 \approx c s_{\nu, \Lambda}(n - \delta)^2$ of the Rydberg electronic wave function, while the exact position (encoded in $c_{\nu, \Lambda}$) depends on the vibrational state of the ULRM because of differences in the radial vibrational wave function. Appropriate expressions for $R_0$ corresponding to different states will be given throughout the paper.

For $30 \lesssim n \lesssim 41$, the centrifugal potential only adds a nearly constant energy shift to the molecular potential and the resulting molecular wave functions $\mathcal{R}_{\nu, \Lambda}(R)$ can be approximated as independent of $\Lambda$. In equation (8), we have introduced

\[ \mathcal{g}^{(2)}_{\nu, \Lambda}(R) = \frac{1}{4\pi} \sum_{\Lambda, M_0} \left( \frac{\hbar^2}{2\pi\mu k_B T} \right)^{3/2} \int d^3k e^{-\hbar^2 k^2/(2\mu k_B T)} \times \int d\cos \theta d\phi \chi^M_{\nu, \Lambda}(\theta, \phi) \chi^\pm_k(\vec{R})^2. \] (9)
Using the identity $\sum_{M_{\Lambda}} Y_{\Lambda}^{M_{F}}(\theta, \phi) Y_{\Lambda}^{-M_{F}}(\theta', \phi') = \delta(\cos \theta - \cos \theta') \delta(\phi - \phi')$ one obtains
\[ g_{+}^{(2)}(R) = \frac{1}{4\pi} \int d\cos \theta d\phi \left( \frac{-\hbar^{2}}{2\pi \mu_{B}T} \right)^{1/2} \times \int d^{3}k e^{-\hbar^{2}k^{2}/(2\mu_{B}T)} \left| \chi_{\Lambda}^{+}(\vec{R}) \right|^{2} = 1 + e^{-2\pi R^{2}/\lambda_{B}^{2}}. \] (10)

For a spin-polarized gas of $^{87}$Sr atoms, the excitation strength for a transition to a single localized vibrational state $\nu$ is $P_{\nu}^{\text{pol}} = Q_{\text{pol}}^{\nu} P_{\nu} + Q_{\text{pol}}^{-\nu} P_{\nu}$ with $Q_{\text{pol}}^{\nu} = 0$ and $Q_{\text{pol}}^{-\nu} = 1$ where $Q_{\text{pol}}^{-\nu}$ denotes the occupation probability of even/odd parity states. For unpolarized fermions in which all the $M_{F}$ levels are populated with equal probability the probability for two atoms to have the same value of $M_{F}$ is $1/(2F + 1)$ and the corresponding scattering states are anti-symmetric. For the other pairs that have different values of $M_{F}$ the scattering states can be symmetric or anti-symmetric with equal probability. Therefore the excitation strength becomes a statistical sum $P_{\nu}^{\text{pol/unpol}} = Q_{\text{pol}}^{\nu} P_{\nu} + Q_{\text{unpol}}^{\nu} P_{\nu}$ where
\[ Q_{\text{pol}}^{\nu} = \frac{1}{2F + 1} \left\{ \begin{array}{ll} F & \text{for } + \\ F + 1 & \text{for } - \end{array} \right. . \] (11)

We can thus express the excitation strength for both polarized and unpolarized gases for excitation to a vibrational state well localized at $R = R_{0}$ as
\[ P_{\nu}^{\text{pol/unpol}} \approx 4\pi g^{(2)}(R_{0}) \int dR R^{2}P_{\nu,\Lambda}(R) \frac{\hat{\chi}_{\nu}(\vec{R})}{\lambda_{B}}, \] (12)
where
\[ g^{(2)}(R) = Q- g^{(2)}(R) + Q+ g^{(2)}(R) = 1 - e^{-2\pi R^{2}/\lambda_{B}^{2}} \] (13)
is the appropriate pair correlation function for the sample, assuming weak interactions and thermal equilibrium far from quantum degeneracy. Here $\epsilon = Q- - Q+$. $g^{(2)}(R)$ takes the following forms: for spin polarized fermions
\[ g^{(2)}(R) = g_{\text{pol}}^{(2)}(R) = 1 - e^{-2\pi R^{2}/\lambda_{B}^{2}}, \] (14)
for an unpolarized ensemble with $F = 9/2$
\[ g^{(2)}(R) = g_{\text{unpol}}^{(2)}(R) = 1 - 0.1e^{-2\pi R^{2}/\lambda_{B}^{2}} \] (15)
and for a gas of spin polarized bosons
\[ g^{(2)}(R) = g_{\text{pol}}^{(2)}(R) = 1 + e^{-2\pi R^{2}/\lambda_{B}^{2}}. \] (16)

Equation (12) is accurate for transitions to the molecular ground state ($\nu = 0$) because this state is typically localized in the outer well of the potential at $R = R_{0}$ (figure 1) [14]. Thus, measurements of $P_{\nu = 0}$ can be used to extract information on the correlation function. Since the radial integrals in equation (12) are common for spin-polarized and unpolarized gases, the ratio $\xi_{\nu = 0} = P_{\nu = 0}^{\text{pol}} / P_{\nu = 0}^{\text{unpol}}$ can be directly related to the pair correlation function for spin-polarized gases [14]. Using equation (15) for the unpolarized gas, then $g^{(2)}(R)$ for the polarized gas is given by
\[ g^{(2)}(R) = \xi_{\nu = 0}(1 - 0.1e^{-2\pi R^{2}/\lambda_{B}^{2}}) \] (17)
and $\xi_{\nu = 0}$ can be found from the ratio of the experimental signal rates for transitions in polarized and unpolarized gases after taking into account different Clebsch–Gordan coefficients and any variations in experimental parameters such as laser intensities and sample densities and temperature [14].

Equation (9) can be decomposed into contributions to the pair correlation function from different rotational levels $\Lambda$. The plane waves (equation (4)) appearing in equation (9), can be expanded in partial waves with well-defined exchange symmetry (or parity),
\[ \chi_{\Lambda}^{\pm}(\vec{k}) = 4\sqrt{\pi} \sum_{\Lambda M_{\Lambda}} \sum_{\Lambda M_{\Lambda}} i^{\Lambda} \mathcal{P}_{\Lambda}^{\pm} Y_{\Lambda M_{\Lambda}}(\theta_{k}, \phi_{k}) Y_{\Lambda M_{\Lambda}}(\vec{R}) \] (18)
with $\theta_{k}, \phi_{k}$ the polar angles of $\vec{k}$,
\[ \chi_{\Lambda,\Lambda M_{\Lambda}}(\vec{R}) = j_{\Lambda}(kR) Y_{\Lambda M_{\Lambda}}(\theta, \phi) \] (19)
($j_{\Lambda}(kR)$: spherical Bessel function).
\[ \mathcal{P}_{\Lambda}^{\pm} = \frac{1}{2} (1 \pm (-1)^{\Lambda}) \] (20)
restricts the wave function to even angular momenta $\Lambda$ for symmetric (+) and odd $\Lambda$ for anti-symmetric (−) two-body scattering states. This yields
\[ g_{\pm}(R) = 8\pi \sum_{\Lambda} (2\Lambda + 1) \mathcal{P}_{\Lambda}^{\pm} \left( \frac{-\hbar^{2}}{2\pi \mu_{B}T} \right)^{1/2} \times \int dk k^{2}e^{-\hbar^{2}k^{2}/(2\mu_{B}T)} |j_{\Lambda}(kR)|^{2}. \] (21)
Figure 5. Excitation spectra (equation (6)) for ULRMs (black solid lines) associated with the $5\times30^5\text{Sr}$ dimer calculated for a spin-polarized $^{87}\text{Sr}$ gas at the various temperatures indicated. The contributions from each rotational level are also displayed (red dashed line: $\Lambda = 1$, green dotted–dashed line: $\Lambda = 3$, and blue dotted line: $\Lambda = 5$). At 1 $\mu$K the contributions from the $\Lambda = 3, 5$ rotational states are essentially zero.

Figure 4 shows the relative contributions to $g^{(2)}(R)$ associated with states with different values of $\Lambda$ as a function of $R/\lambda_{IB}$, for identical bosons and fermions. As expected, the maximum in $g^{(2)}(R)$ at small values of $R/\lambda_{IB}$ is associated primarily with $\Lambda = 0$ states, i.e. s-waves. As $R/\lambda_{IB}$ increases, due, for example, to an increase in sample temperature, higher-$\Lambda$ states become accessible and become increasingly important while the $\Lambda = 0$ contribution is reduced. Indeed, for $R/\lambda_{IB} \sim 1$, $\Lambda = 2$ states, i.e. the d-wave, becomes the dominant contribution to $g^{(2)}(R)$ which has then become close to its limiting value $g^{(2)}(R) = 1$. Further increase in $R/\lambda_{IB}$ results in little change of $g^{(2)}(R)$, although the relative contributions from higher-$\Lambda$ states steadily grow. For spin-polarized fermions, the s-wave contribution is excluded because of anti-symmetry and $g^{(2)}(R)$ vanishes for $R/\lambda_{IB} \rightarrow 0$. As $R/\lambda_{IB}$ increases, p-wave and successively higher odd-order partial waves become accessible and $g^{(2)}(R)$ approaches its limiting value of one.

The contributions from various $\Lambda$ levels to the calculated excitation spectra (equation (5)) are shown in figure 5. For spin-polarized fermions the excitation spectrum is dominated by the $\Lambda = 1$ rotational state at low temperature (1 $\mu$K). As temperature increases, the contributions from higher excited rotational levels become non-negligible. The peak positions of $f^−(\omega)$ for different $\Lambda$ nearly coincide since the spacing between different rotational levels are smaller than the thermal line broadening. Furthermore, since $\Lambda$ is preserved during the Franck–Condon transition, the contribution to rotational energy splitting from the centrifugal potential present in both the initial and final states largely cancels out. The contributions of different rotational channels to the Rydberg molecule excitation spectrum were recently discussed in [19].

Unlike the case for ground-state molecules, the molecular wave functions for excited Rydberg dimers span multiple wells (see figures 1, 6). We therefore explore the degree of localization of each ULRM molecular wave function in a specific well and how this affects the ability to use excitation spectra for excited dimers to extract information on $g^{(2)}(R)$. To this end we construct a set of pseudostates $|w^{(\eta)}\rangle$ ($\epsilon = 0, 1, \cdots$) that are eigenstates of each isolated potential well $\eta$ ($\eta = 1, 2, 3, \cdots$ with $\eta = 1$ the outermost well) thereby removing the influence of the adjacent potential wells. In analogy to tight-binding approximations, the molecular wave function can then be viewed as a coherent superposition of eigenstates $|w^{(\eta)}\rangle$ associated with each isolated well. For example, the lowest energy level $|w^{(0)}\rangle$ of the outermost well
\begin{align}
\langle |F_{\nu, \Lambda}|^2 \rangle & \propto \int dk \frac{k^2 e^{-\frac{\beta k^2}{2}}} {\langle \gamma(kR_{\nu, \eta=1}) \rangle} \int dR R^2 w_{\nu, 1}^{\eta=1}(R) \\
& \quad + c_{\eta=2} \int dR R^2 w_{\nu, 2}^{\eta=2}(R) \\
& = \text{(22)}
\end{align}

assuming that (for small $T$) the spherical Bessel functions for the $k$-values that contribute to the transitions are nearly constant within a single well centered at $R = R_{\nu, \eta}$. Because of the node in the wave function $w_{\nu, 1}^{\eta=1}(R)$ located in the $\eta = 1$ well, the overlap integral $\int dR R^2 w_{\nu, 1}^{\eta=1}(R)$ is typically small, and thus the Franck–Condon factor can be simplified to

\begin{align}
\langle |F_{\nu, \Lambda}|^2 \rangle & \propto \int dk \frac{k^2 e^{-\frac{\beta k^2}{2}}} {\langle \gamma(kR_{\nu, \eta=2}) \rangle} \int dR R^2 w_{\nu, 2}^{\eta=2}(R) \\
& = \text{(23)}
\end{align}

with $R_{\nu, \eta=2} = 1.6(n - \delta)^2 a_0$. Summing over contributions from all $\Lambda$ levels with appropriate weighting for the polarization state of the gas, the excitation strength becomes approximately

\begin{align}
P_{\nu=1} & \simeq 4\pi g^{2\nu}(R_{\nu, \eta=2}) \int dR R^2 w_{\nu, 2}^{\eta=2}(R) \\
& = \text{(24)}
\end{align}

With increasing $n$, the energy of $\left| w_{\nu, 2}^{\eta=2} \right|^2$ becomes smaller than $\left| w_{\nu, 1}^{\eta=1} \right|^2$ (see figure 6) and, correspondingly, the $\nu = 1$ molecular state becomes increasingly dominated by the $\left| w_{\nu, 2}^{\eta=2} \right|^2$ state. For Franck–Condon factors with well-localized transition points (equation 23) the ratio $\zeta_{\nu=1} = \rho_{\nu=1} / \rho_{\nu=1}$ can be used to probe the correlation function but over a range of $R$ different from that for the $\nu = 0$ states. However, as contributions from other wells ($\eta > 2$) become increasingly important (for example, for higher $n$) the ratio $\zeta_{\nu=1}$ no longer probes the pair correlation locally but provides an average of $g^{2\nu}(R)$ over a range of $R$ weighted by $|c_{\nu}|^2$. For even higher vibrational states (for example, $\nu = 2$), the contributions from inner wells ($\eta > 2$) can no longer be neglected. As the molecular wave function becomes increasingly delocalized reliable extraction of the pair correlation function becomes difficult.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7.png}
\caption{Experimental Rydberg excitation spectra recorded using (a), (c) polarized and (b), (d) unpolarized $^{87}$Sr cold gases with $T \sim 900 \text{nK}$. (a), (b) are the spectra for $5s4d^2 \Sigma^+_g - 5s^2 \Sigma^+_g$ molecules and (c), (d) are for $5s4d^2 \Sigma^+_g - 5s^2 \Sigma^+_g$ molecules. The spectra are normalized such that the peaks of the $\nu = 0$ features are of equal height. The solid lines show the predicted excitation spectra (see text). The calculated spectra have been convolved with a Lorentzian of 300 kHz width. Subtle differences between spectra for polarized and unpolarized gases are discussed in figure 8 and the text.}
\end{figure}

4. Results and discussion

Experimental Rydberg excitation spectra recorded at $n = 34$ and 40 using both polarized and unpolarized cold, $T \sim 900 \text{nK}$, $^{87}$Sr gases are shown in figure 7. The spectra are normalized such that the peaks associated with the formation of $\nu = 0$ ground-state Rydberg dimers are of equal height. The actual sizes of the excitation features seen in different experimental runs depend on many factors including the intensities of the excitation lasers, the trapped atom density, the laser detuning, the dipole matrix elements, the Clebsch–Gordan coefficients, and the excitation strengths $P_{\nu}$ (equations 7 and 12). Within a single panel in figure 7 all factors other than $P_{\nu}$ are the same, and the relative heights are proportional to $P_{\nu}$, thereby providing a more direct test of the calculated effective Franck–Condon factors and their underlying dependence on the pair correlation function. Multiple features are present in each spectrum that result from creation of different dimer vibrational states. Figure 7 also includes the predictions of calculations (equation 6) using the Fermi pseudopotential (equation 1). The scattering lengths, $a_s$ and $a_p$, were used as fitting parameters to obtain the best overall agreement with the experimental data for $31 \lesssim n \lesssim 41$, yielding the optimized values $a_s(k = 0) = -13.3a_0$ and $a_p = 9.7a_0$. The small differences in peak positions might result because other contributions to the molecular potential such as interactions...
between the Rydberg core ion and the ground-state atom, and higher partial waves for electron-atom scattering are not included. Nonetheless, the positions and relative sizes of the observed features are in good general agreement with the theoretical predictions. However, as seen in figure 7 the relative sizes of the $\nu = 1$ and $\nu = 2$ features are strongly $n$-dependent. For $n = 34$ the relative sizes of the $\nu = 1$ and $\nu = 2$ features are comparable, whereas for $n = 40$ the $\nu = 1$ feature is dominant.

Figure 8 shows the integrated experimental signals for transitions to the $\nu = 1$ (top) and $\nu = 2$ states (bottom), normalized by the integrated signals for the $**nu** = 0$ states, for various $n$. These ratios should equal the theoretically-calculated ratios of excitation strengths $P_{\nu=1}/P_{\nu=0}$. The integrated experimental signals were obtained by fitting the different features with a pseudo-Voigt profile and determining the area under the resulting curve. Interestingly, the relative excitation strengths of the $\nu = 1$ and $\nu = 2$ features display very different $n$-dependencies. The relative strength of the $\nu = 1$ feature decreases markedly with decreasing $n$, whereas that of the $\nu = 2$ feature increases substantially, behavior that is well reproduced by theory.

For $\nu = 1$ states, the calculated ratio of the excitation strengths for $\nu = 1$ and $\nu = 0$ states can be written by using equations (12) and (24) as

$$
\frac{P_{\nu=1}}{P_{\nu=0}} = \frac{[c_{\nu=2}]^2}{[c_{\nu=0}]^2} \frac{\int dR R^2 W_{\nu=2}^{0,2}(R) \xi_{\nu=2}}{\int dR R^2 W_{\nu=0}^{0,0}(R) \xi_{\nu=0}}.
$$

The $W_{\nu=1,2}^{0,2}$ states represent the ground states of nearly isolated harmonic potential wells pointing to similar $n$-dependencies of the integrals for both $\eta = 1$ and 2. Therefore, since $R_{\nu=0,1}$ and $R_{\nu=0,2}$ are similar, this results in a ratio of the $g^{(2)}(R)$ that remains close to unity for the present range of $n$. The strong $n$-dependence seen in the $\nu = 1$ to $\nu = 0$ production ratios must thus be associated primarily with the weights $|c_{\nu=2}|^2$. Furthermore, the calculated ratios $R_{\nu=1}/R_{\nu=0}$ for polarized samples are, on average, somewhat smaller than those for unpolarized samples. This is due to the fact that $R_{\nu=2}$ is slightly less than $R_{\nu=1}$ and thus the ratio $g^{(2)}(R_{\nu=2})/g^{(2)}(R_{\nu=1})$ for a polarized sample is slightly less than one (see the inset in figure 1) leading to the small decrease in $P_{\nu=1}/P_{\nu=0}$.

As discussed in the previous section (see figure 6), as $n$ increases the molecular state becomes increasingly dominated by the $|w_{\nu=0}^{10}|^2$ contribution and $|c_{\nu=2}|^2$ increases. Therefore, the observed $n$-dependence mirrors the dominance of the $|w_{\nu=0}^{10}|^2$ contribution to the $\nu = 1$ vibrational state. For $\nu = 2$, however, the contributions from other wells ($\eta > 2$) become more significant and the peaks in the molecular wave functions shift towards smaller values of $R$, relative to the size of the atom, with increasing $n$. This is reflected in the observed $n$-dependence of the $\nu = 2$ features.

As demonstrated in earlier work that focused on the $\nu = 0$ state [14], pair correlation functions can be obtained from measurements of the ratio, $\xi_{\nu=0} = \xi_{\nu=0,\text{pol}}/\xi_{\nu=0,\text{unpol}}$, which can be determined from the relative molecular production rates in polarized and unpolarized samples. Ideally such measurements should be undertaken using identical samples with the exception that one is polarized, the other unpolarized. While for the measurements reported here we attempt to match the sample conditions as closely as possible, differences remain. The ratio of the measured production rates must be corrected for small differences in the intensities of the photoexcitation lasers, in laser detunings, in the sample temperatures and densities and density distributions, as well as for the differences in the two-photon electronic transition matrix elements, i.e. Clebsch–Gordan coefficients, when creating Rydberg molecules in polarized and unpolarized gases.

Figure 9 shows the experimentally determined ratios of excitation strengths, $\xi_{\nu=1} = P_{\nu=1}^{\text{pol}}/P_{\nu=1}^{\text{unpol}}$, for the $\nu = 1$ level in polarized and unpolarized samples. Also included in figure 9 are the theoretically-predicted ratios of the excitation strengths, $\xi_{\nu=0}^{\text{theory}} = P_{\nu=0}^{\text{pol,theory}}/P_{\nu=0}^{\text{unpol,theory}}$ and $\xi_{\nu=1}^{\text{theory}} = P_{\nu=1}^{\text{pol,theory}}/P_{\nu=1}^{\text{unpol,theory}}$, for the $\nu = 0$ and $\nu = 1$ states, respectively. For reference, figure 9 also shows the ratio to be expected under the simple zeroth-order ‘ideal’ assumption that $\xi^{\text{ideal}} = g_{-1}^{(2)}(R)/g_{0}^{(2)}(R)$. As noted in earlier work [14], $\xi^{\text{theory}}$ closely matches $\xi^{\text{ideal}}$. The predicted values of $\xi^{\text{theory}}$ are somewhat smaller than $g_{\nu}^{(2)}$, which results because, while the contributions from potential wells other than $\eta = 2$ are small, they are significant. Nonetheless, the predicted values are in reasonable agreement with experiment, although the discrepancy seen at the largest values of $R_{\nu=0}$, i.e. the largest values of $n$, remains to be explained. However, the pronounced decrease in $g_{\nu}^{(2)}$ at the smaller values of $R$ provides clear evidence of the effects of antibunching, and the data demonstrate that (for $31 \leq n \leq 41$) measurements of the $\nu = 1$ vibrational state can provide a probe of pair correlation functions at values of $R$ that are somewhat smaller than can be realized using $\nu = 0$ states and where the effects of quantum statistics become increasingly important.
5. Conclusions

The present work demonstrates the important role that rotational angular momentum plays in molecular formation and how the contributions from different rotational states are influenced by quantum statistics and sample temperature. In addition, the measurements show that photoexcitation of vibrationally-excited ultralong-range Rydberg dimer molecules can provide an in situ probe of pair correlations in an ultracold gas that, with an appropriate choice of $n$, allows length scales of $\sim 20$ to $250$ nm to be explored, although the utility is more limited compared to ground-state molecules [14] because of delocalization of the wave function. Quantum gas microscopes can resolve correlations on length scales on the order of half the wavelength of light [20, 21] whereas inelastic loss from spin flips and three-body recombination probe two- and three-body spatial correlations at shorter length scales [22]. The use of ULRMs to probe correlations provides a valuable new window into intermediate-range phenomena such as the formation of Halo states [23, 24] and Efimov trimers [25], and allows study of correlation functions for scattering states involving atom pairs with large s-wave scattering lengths. Furthermore, since the time scale for molecule formation is short, $\sim 1\mu s$, the present approach is suitable for in situ probing of non-equilibrium dynamics in quantum gases.

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Figure 9. Ratios, $\xi_n$, of the ULRM excitation strengths in polarized and unpolarized samples of $^{87}$Sr as a function of $R/\lambda_{dB}$, with $R = 1.87(n-\delta)^2\lambda_0$ for $n=0$ states and $R = 1.6(n-\delta)^2\lambda_0$ for $n=1$ states. The figure includes the results of measurements, $\xi^\text{meas}$, for the $n=1$ state together with theoretical predictions for the $n=0$ and 1 states, $\xi^\text{theory}$, and the ‘ideal’ ratio $\xi^\text{ideal} = g^{(2)}(R)/g^{(2)}(R)$ (see text).