

Effect of an applied magnetic field on $^{84}\text{Sr } n^1D_2$ ultralong-range Rydberg dimers

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(Received 20 May 2026; accepted 22 July 2026; published 13 August 2026)

Photoassociation of $5snd\ ^1D_2 - 5s^2\ ^1S_0$ ultralong-range Rydberg dimers from an ultracold ^{84}Sr atomic gas in a magnetic field is studied. In the absence of magnetic fields, the electronic wave function is aligned along the rotating molecular axis through electron-atom scattering. With increasing magnetic field strength, the symmetry axis of the electron wave function becomes determined by the applied field. While the ground-state atom has no spin or net charge to interact directly with the magnetic field, the dimer wave function in the limit of strong magnetic field becomes aligned along the applied field. Photoassociation spectra show that with increasing field, an increasing number of rovibrational states are excited, indicating strong coupling between rotational states within the Rydberg dimer.

DOI: [10.1103/PhysRevA.114.022814](https://doi.org/10.1103/PhysRevA.114.022814)

I. INTRODUCTION

Ultralong-range Rydberg molecules (ULRRMs) comprise a Rydberg atom whose electron cloud contains one or more ground-state atoms weakly bound by scattering of the Rydberg electron from the ground-state atom, resulting in an unusually large chemical bond length that is comparable to the size of the Rydberg atom itself [1]. Many earlier studies of such novel species have been reported [2–6] and they have been used, for example, to probe electron-atom scattering and spatial correlations in quantum gases [7–10]. Whereas the majority of the earlier studies of dimer formation have been undertaken in zero or weak electric fields, relatively few studies of dimer formation in magnetic fields have been reported. However, as has been demonstrated using ^{87}Rb Rydberg states, an external magnetic field can dramatically influence dimer formation [11–13]. The presence of a magnetic field $\gtrsim 10$ G was found to induce alignment of s -state Rydberg molecules [13]. Studies with $^2D_{3/2}$ and $^2D_{5/2}$ Rydberg states demonstrated the effects of molecular alignment and anti-alignment with the external field on dimer formation [11]. This work showed that the dimer binding energies for low- m “axial” states were substantially larger than for high- m “toroidal” states.

In the present work, we use $^{84}\text{Sr } ^1D_2$ Rydberg states to examine further the effects of a magnetic field on dimer formation and the changes that occur as the magnetic field is increased from zero to the strong-field regime. Different from rubidium Rydberg dimers, bosonic ^{84}Sr has no hyperfine structure ($I = 0$) and, for singlet states, the total electron spin S is zero. The ground-state atom does not interact directly with magnetic fields, but only indirectly through the

interaction with the Rydberg electron. Figure 1 shows representative photoassociation spectra recorded when creating $5s50d\ ^1D_2 - 5s^2\ ^1S_0$ Rydberg dimers (and $5s50d\ ^1D_2$ Rydberg atoms) in a cold (1.1 μK) ^{84}Sr atomic gas in several different applied magnetic fields. As noted earlier [14], molecular states can be characterized by the total angular momentum K and its projection m . In the zero field, a series of sharp features is observed associated with the formation of dimers in different rotational and vibrational states with binding energies extending up to ~ 9 MHz [14]. The spectra are independent of laser polarizations, indicating the rotational symmetry of the molecular states. In a weak field (0.2 G), Zeeman splitting of the atomic line is evident, but the dimer lines remain essentially unchanged. At fields of 1.0 and 2.0 G, where the Zeeman splitting of the atomic line becomes sizable, significant changes and shifts in the dimer formation spectra become evident, although the shifts are not of the same magnitude as the atomic Zeeman shifts. In stronger fields, 6.0 G, where the Zeeman shifts are large, a well-resolved dimer series associated with each (Zeeman-shifted) atomic m level can be seen.

These observations raise a number of interesting questions. For example, why, in a weak field, do the dimer levels not show any significant Zeeman shifts, and why, at somewhat stronger fields, do they not shift in proportion to the atomic Zeeman shifts? In strong fields, the binding energies of the most prominent dimer features, relative to their associated Zeeman-shifted atomic state, become much smaller than in weak magnetic fields. To address these, and other, questions, we develop a theoretical model that includes both intramolecular angular momentum mixing and the presence of an external field. The mixing of the electronic orbital angular momentum and the rotational angular momentum plays a key role in understanding the energy shifts of molecular levels in a magnetic field. We probe the transition from the weak-field regime, where the interaction between m levels induced by the electron-atom scattering is larger than the Zeeman splitting, to the strong-field regime where interactions with the magnetic field become dominant. In the absence of a magnetic field, the

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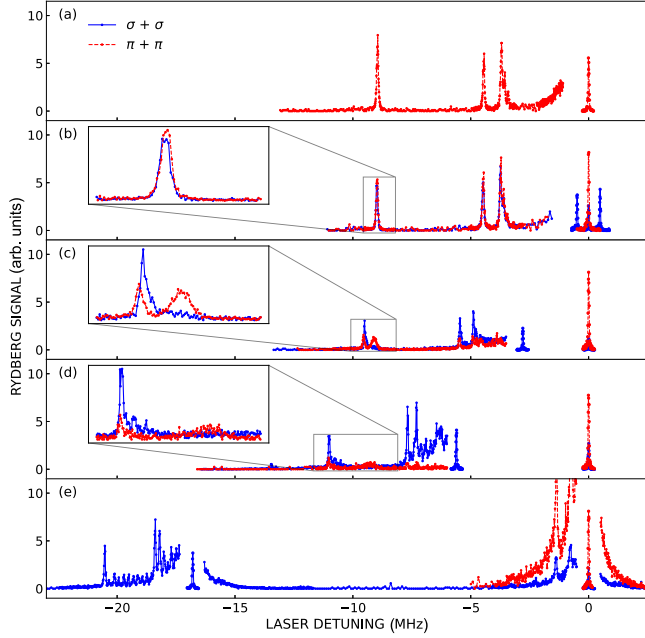


FIG. 1. Photoassociation spectra recorded when creating $5s50d\ ^1D_2$ dimers in the magnetic fields: (a) 0, (b) 0.2, (c) 1.0, (d) 2.0, and (e) 6.0 G. The laser polarizations ($\sigma + \sigma$, $\pi + \pi$) (see text) were selected to probe the population of $m = 0$ and ± 2 states in each molecular eigenstate. The atomic excitation lines are also included and form the sharp features present in each spectrum. The laser powers used to obtain the dimer spectra were ~ 400 times larger than those used to obtain the atomic spectra. The detunings are measured from the $m = 0$ atomic line and only those parts of the spectra seen at negative detunings are included.

molecular states are rotationally symmetric. The application of a magnetic field breaks this symmetry and, in the limit of strong fields, the molecular state becomes cylindrically symmetric around the magnetic field, forming axial and toroidal states aligned along and perpendicular, respectively, to the field axis.

The model predictions are in good agreement with the experimental measurements and account for many of the features seen in the data. They also provide insights into the transition from weak- to strong-field behavior. In Sec. II, we describe the experimental apparatus used for dimer photoassociation studies. Section III describes the theory, followed in Sec. IV by its application in the zero-field limit, Sec. V to the strong-field limit, and Sec. VI in intermediate fields.

Section VII provides detailed comparisons between model predictions and the experimental observations.

II. EXPERIMENTAL APPARATUS

A schematic of the present apparatus is shown in Fig. 2 and is described in detail elsewhere [8]. Briefly, ^{84}Sr atoms are cooled and loaded into a crossed optical dipole trap (ODT). Evaporative cooling is used to control the temperature of the atoms in the trap, which typically contains $\sim 10^6$ atoms with a peak density of $\sim 7 \times 10^{12} \text{ cm}^{-3}$. A series of six square coils arranged as the sides of a cube are positioned on the outside of the apparatus. These are used to null the Earth's magnetic field, but can also be used to generate a magnetic field of up to a maximum of $\sim 6\text{G}$ along the z axis, indicated in Fig. 2. The Rydberg atoms are created by two-photon excitation, $5s^2\ ^1S_0 \rightarrow 5s5p\ ^1P_1 \rightarrow 5snd\ ^1D_2$, using counterpropagating lasers operating at 461 and 413 nm, respectively. The 461 nm laser is blue detuned by 18 GHz to limit heating of the sample through scattering. The lasers are linearly polarized and their planes of polarization, defined relative to the magnetic field axis, can be controlled to permit selective excitation of $m = 0$ ($\pi + \pi$), ± 1 ($\sigma + \pi$), or 0 and ± 2 states ($\sigma + \sigma$). The high degree of linear polarization that is achieved is demonstrated by the fact that when scanning the atomic line in a magnetic field using, say, $\pi + \pi$ laser polarizations the number of $m = \pm 1$ states that are excited is less than 3% of the number of $m = 0$ states that are created. This observation also shows that any mixing of m levels by stray electric fields is negligible. The lasers are frequency stabilized using a high-finesse ultralow-expansion cavity. Rydberg atoms and molecules are detected using selective field ionization (SFI) in a field generated by applying potential differences to the electrodes shown in Fig. 2. The product electrons are directed to a microchannel plate for detection.

A cold ($T \sim 1.1\ \mu\text{K}$) atomic gas of ^{84}Sr is first prepared. Concurrent laser pulses of $20\ \mu\text{s}$ duration are then applied to create Rydberg atoms and molecules. The number of Rydberg atoms and molecules created per laser pulse is kept low, $\lesssim 1$, to avoid Rydberg-Rydberg interactions. Photoassociation spectra are built up through multiple cycles at each laser frequency. Typically ~ 100 such experimental cycles can be performed using a single cold-atom sample before significant heating of the sample occurs. At the end of each series of experimental cycles, the atom number and temperature are determined by releasing atoms from the trap and monitoring the expansion of the atomic cloud via absorption imaging on the $5s^2\ ^1S_0 \rightarrow 5s5p\ ^1P_1$ transition. A new cold-atom sample

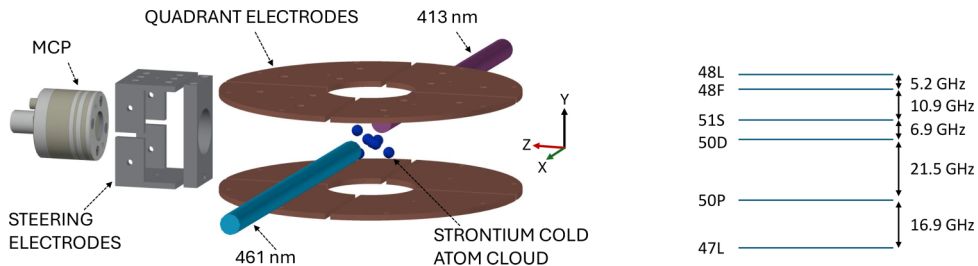


FIG. 2. Apparatus schematic and energy diagram around the $5s50d\ ^1D_2$ Rydberg state of strontium.

is then prepared and the process repeated for the next data point in the spectrum.

III. THEORY

The $5snd^1D_2$ Rydberg dimer is treated as a three-body system comprising the Rydberg electron, the Rydberg core ion, and the ground-state atom. In the presence of an external magnetic field, $\vec{B} = B\hat{z}$, the effective three-body system can be represented by the Hamiltonian

$$H \simeq \frac{p^2}{2\mu} + \frac{p^2}{2m_e} + V_c(r) + V(\vec{r} - \vec{R}) + \frac{e}{2m_e} \ell_z B, \quad (1)$$

where $\vec{r}$ and $\vec{R}$ are the positions of the electron and ground-state atom relative to the nucleus, $\mu = m_a/2$ the reduced mass of the dimer (m_a is the mass of an ^{84}Sr atom), m_e the electron mass, e the elementary charge, $\vec{p}$ the electron momentum, $\vec{P}$ the momentum of the ground-state atom, ℓ_z the projection of electronic orbital angular momentum onto the z axis, $V_c(r)$ the electron-Sr $^+$ ion core interaction, and $V(\vec{r} - \vec{R})$ the electron-ground-state atom interaction, which is approximated by

$$V(\vec{r} - \vec{R}) \simeq \frac{2\pi\hbar^2}{m_e} a_s(k) \delta(\vec{r} - \vec{R}) + \frac{6\pi\hbar^2}{m_e} a_p^3 \vec{\nabla} \delta(\vec{r} - \vec{R}) \vec{\nabla}. \quad (2)$$

The energy-dependent s -wave scattering length, $a_s(k) = -13.84a_0 + (\pi/3)\alpha k$ (a_0 : Bohr radius; α : ground-state atom polarizability), and the p -wave scattering length, $a_p = 9.7a_0$, are taken from earlier measurements in zero magnetic field [14]. For strontium, the low-energy p -wave shape resonance present in the alkalis is absent and D states are well isolated from adjacent ℓ states (Fig. 2) when compared to the typical molecular binding energies (~ 10 MHz at $n = 50$). Therefore, the molecular potential of a D state does not cross with those of other ℓ states. Assuming that the electronic wave function $\langle \vec{r} | n, \ell, m \rangle = \rho_{n,\ell}(r) Y_\ell^m(\hat{r})$ is unperturbed by the presence of the ground-state atom, we use an ansatz for the κ th molecular eigenstate,

$$\begin{aligned} & \langle \vec{r}, \vec{R} | nD; \kappa, M_K \rangle \\ &= \sum_{\nu, N} \sum_{m+M_N=M_K} \rho_{n,\ell=2}(r) \mathcal{R}_{\nu, N, m}^{(\kappa)}(R) Y_\ell^m(\hat{r}) Y_N^{M_N}(\hat{R}). \end{aligned} \quad (3)$$

N and M_N are the rotational angular momentum and its projection. Using this ansatz, the time-independent Schrödinger equation can be written as coupled partial differential equations for the radial wave functions $\mathcal{R}_{\nu, N, m}^{(\kappa)}(R)$, which are solved numerically to obtain the molecular eigenenergies and eigenwave functions (see details in [14]). [We choose to use unnormalized radial wave functions such that the population of the configuration (ν, N, M) in the molecular eigenstate κ is proportional to the square of the norm of $\mathcal{R}_{\nu, N, m}^{(\kappa)}(R)$.] M_K is a projection of the total angular momentum $\vec{K} = \vec{\ell} + \vec{N}$ onto the z axis. (The effects of electron spin are neglected for the present n^1D states.) In the presence of a magnetic field, M_K is a good quantum number, but not K .

The two-photon transition amplitude from the initial scattering state $|5s^2 \ ^1S_0; k, N', M'_N\rangle$ is given by

$$\begin{aligned} & F_{\kappa, M_K}(k, N', M'_N) \\ &= \langle nD; \kappa, M_K | d_2 d_1 | 5s^2 \ ^1S_0; k, N', M'_N \rangle \\ &= \sum_{\nu} D_{m=M_K-M'_N} \int dR R^2 j_{N'}(kR) \mathcal{R}_{\nu, N=N', m}^{(\kappa)}(R). \end{aligned} \quad (4)$$

Here the atomic wave function of the initial scattering state is represented as a spherical wave $j_{N'}(kR) Y_{N'}^{M'_N}(\hat{R})$. $j_{N'}(kR)$ is a spherical Bessel function for $N' > 0$, while for $N' = 0$, $j_0(kR) = \sin[k(R - A_s)]/(kR)$ including the scattering length ($A_s = 123a_0$) between ^{84}Sr atoms. $d_{1,2} = y$ or z specify the polarizations of the two excitation lasers (σ or π) and D_m is the electronic two-photon transition matrix element. This transition amplitude is similar to the Franck-Condon factor, but including the electronic dipole transition amplitudes to account for the angular momentum coupling. For a nonzero sample temperature T , the photoassociation spectrum as a function of laser frequency ω can be evaluated as

$$\begin{aligned} f(\omega) &= \left(\frac{\hbar^2}{2\pi\mu k_B T} \right)^{3/2} \int dk \sum_{N', M'_N} 4\pi k^2 e^{-\hbar^2 k^2 / (2\mu k_B T)} \\ &\times \sum_{\kappa, M_K} L_{\kappa, M_K}(k, \omega) |F_{\kappa, M_K}(k, N', M'_N)|^2, \end{aligned} \quad (5)$$

where $L_{\kappa, M_K}(k, \omega)$ is a Voigt profile centered at the molecular eigenenergy E_{κ, M_K} . The spatial distribution of the ground-state atom in the Rydberg dimer can be calculated by tracing over the electronic wave function,

$$\begin{aligned} \mathcal{Q}_{\kappa, M_K}(R, \theta_R) &= \int d^3r |\langle \vec{r}, \vec{R} | nD; \kappa, M_K \rangle|^2 \\ &= \sum_m \left| \sum_{\nu, N} \mathcal{R}_{\nu, N, m}^{(\kappa)}(R) Y_N^{M_N=M_K-m}(\hat{R}) \right|^2. \end{aligned} \quad (6)$$

The wave function is cylindrically symmetric around the magnetic field (i.e., z axis) and depends on $R = |\vec{R}|$ and the angle θ_R between $\vec{R}$ and the z axis.

For the current study, all numerical results are obtained using rotational states up to $N = 50$, including the contributions from both s - and p -wave scattering and also from both Σ and Π molecular states. The convergence of the photoassociation spectra was confirmed by comparison with simulations including states up to $N = 100$. In the next sections, we analyze two extreme limits (without magnetic field and with strong field). The full numerical calculations can be interpreted using an approximation containing only the dominant contributions from Σ states.

IV. ZERO MAGNETIC FIELD

In the absence of a magnetic field, the Rydberg molecule has rotational symmetry and the total angular momentum K is a good quantum number. Since the centrifugal energies and coupling to Π states are typically negligible, the molecular radial wave function can be approximately calculated using

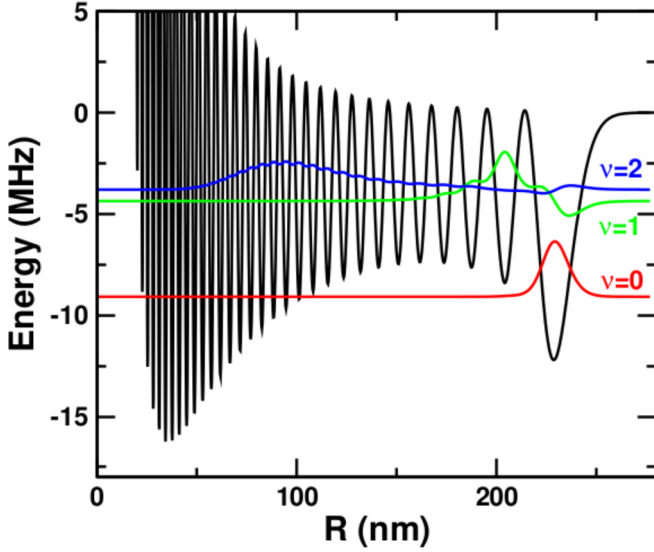


FIG. 3. Effective molecular potential [Eq. (7)] for the vibrational motion of a $50\ ^1D_2$ Rydberg dimer (black). Zero energy is set to that of a $50\ ^1D_2$ Rydberg atom (without the ground-state atom). Radial wavefunctions $R\chi_v(R)$ for $v = 0, 1, 2$ are also shown. Their base lines correspond to their binding energies.

the effective potential

$$V_M(R) \simeq \frac{\hbar^2(2\ell + 1)}{2m_e} a_s(k) |\rho_{n,\ell}(R)|^2 + \frac{3\hbar^2}{2m_e} (2\ell + 1) a_p^3 |\partial_R \rho_{n,\ell}(R)|^2 \quad (7)$$

(see Fig. 3) and is nearly independent of N and m . We denote the resulting N - and m -independent normalized radial wave function by $\chi_v^{(\kappa)}(R)$. Consequently, the molecular wave function can be approximated as [14]

$$\begin{aligned} \langle \vec{r}, \vec{R} | nD, v, K, M_K \rangle &\simeq \rho_{nd}(r) \chi_v^{(\kappa)}(R) \sum_{m,N} C_{m,N}(K) Y_\ell^m(\hat{r}) Y_N^{M_K-M_K-m}(\hat{R}) \\ &= (-1)^K \sqrt{\frac{2\ell + 1}{4\pi}} \rho_{nd}(r) \chi_v^{(\kappa)}(R) P_{\ell=2}(\hat{r} \cdot \hat{R}) Y_K^{M_K}(\hat{R}), \end{aligned} \quad (8)$$

where the coefficient

$$C_{m,N}(K) = (-1)^{\ell-N+M_K} \sqrt{(2N+1)(2K+1)} \times \begin{pmatrix} \ell & N & K \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell & N & K \\ m & M_K - m & -M_K \end{pmatrix} \quad (9)$$

is defined using the Wigner $3j$ symbols. A molecular state is a superposition of all m states ($-2 \leq m \leq 2$) and a few N levels ($|\ell - K| \leq N \leq \ell + K$). A selection rule defined from a Wigner $3j$ symbol indicates that $\ell + N + K$ has to be even. For an initial gas of bosons, only rotational states with even N' are present. Consequently, assuming a vertical transition $N = N'$, only molecular states with even K can be photoassociated for $\ell = 2$. For example, at the sample temperature of $1\ \mu\text{K}$ (i.e., the average relative momentum for a pair of atoms, $\hbar k \simeq 7 \times 10^{-4}$ a.u.), the initial gas is dominated by the partial waves satisfying $N' \lesssim \hbar k R$. In particular, around $R = 210\ \text{nm} \simeq 4000$ a.u., $N' = 0$ and $= 2$ rotational states are dominant

and molecular states with $K = 0, 2, 4$ are principally excited for $\ell = 2$.

The calculated photoassociation spectrum for $5s50d\ ^1D_2$ dimers at a sample temperature of $1.1\ \mu\text{K}$ in the absence of magnetic field is calculated using the three-body Hamiltonian introduced in Sec. III [Fig. 4(a)]. We interpret the results using the approximation described earlier [Eq. (8)]. For this temperature and dimers with $R_n \simeq 200\ \text{nm}$, the initial scattering states correlate primarily with $N = 0, 2$ rotational states. Indeed, the peak seen at $-9\ \text{MHz}$ corresponds to the production of dimers in the ground vibrational state ($v = 0$) with contributions from the $K = 0, 2, 4$ levels. Though the energy splittings between those K levels at $n = 50$ are too small ($\sim 30\ \text{kHz}$) to resolve, such line broadening has been observed at lower n [14]. The wave functions $R^2\varrho(R, \theta_R)$ [Eq. (6)] for $K = 0, 2, 4$ [Figs. 4(c)–4(e)] with $M_K = 0$ are localized in R around $R \simeq 230\ \text{nm}$ [or $\sim 1.8(n - \delta)^2 a_0$] and the excitations (nodal structures) are seen in angular coordinate θ_R . Indeed, the angular distribution is proportional to $|Y_K^{M_K}(\hat{R})|^2$ [Eq. (8)]. While the wave function with $M_K = 0$ is mostly aligned along the z axis, due to the M_K -level degeneracy, the wave functions with a superposition of M_K states can have any orientation. Only in the defined limit of low temperature, i.e., when the scattering states with $N' = M'_N = 0$ are dominant, can the laser polarization break the rotational symmetry and allow selective excitation of aligned molecular states (along z by $\pi + \pi$ and y by $\sigma + \sigma$). Whereas only a few K levels are visible in the calculated photoassociation spectrum, many more excited rovibrational states are found in the calculations [Fig. 4(b)]. As expected, as the expectation value $\langle N \rangle$ for each molecular state increases, its binding energy decreases. However, the standard deviation $\langle (\Delta N)^2 \rangle^{1/2}$ stays constant, limited by the condition $|K - 2| \leq N \leq K + 2$.

At the second peak around $\sim -4.3\ \text{MHz}$, the wave function of the molecular state [Fig. 4(f)] with the largest Franck-Condon factor within this peak possesses a radial distribution shifted towards smaller R ($\sim 200\ \text{nm}$), which points to the excitation of $v = 1$ states (see Fig. 3). The angular distribution with two nodes indicates the formation of the $K = 2$ state. Several vibrational states are densely distributed around $-3.6\ \text{MHz}$. That with the largest Franck-Condon factor ($v = 3$ and $K = 2$) is shown in Fig. 4(g).

V. STRONG-FIELD LIMIT

In the limit of strong magnetic field, Zeeman splittings become so large that the mixing of m levels induced by scattering from the ground-state atom becomes negligible [11], allowing the molecular eigenstates to be calculated by diagonalizing the Hamiltonian [Eq. (1)] for each m level separately. We note that the “strong”-field limit in this section means that the field is strong enough to uncouple m levels, but not so strong as to induce the coupling between ℓ levels or to introduce significant diamagnetic energies ($\sim 50\ \text{kHz}$ for $n = 50$ at $B \simeq 6\ \text{G}$). Figure 5 shows the calculated photoassociation spectra for the creation of $5s50d\ ^1D_2$ dimers with (a) $m = -2$ and (b) $m = -1$, in the limit of a strong magnetic field. When the dimer binding energies are referenced to the corresponding Zeeman-shifted [by $emB/(2m_e)$] atomic lines, their binding energies of $< 3\ \text{MHz}$ are seen to be significantly smaller than

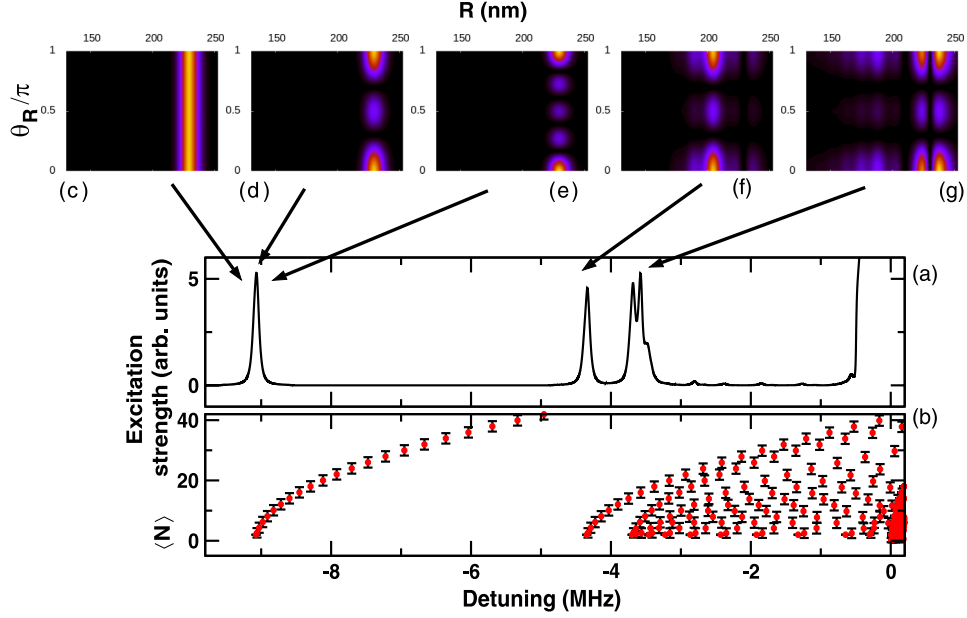


FIG. 4. (a) Calculated spectrum for the photoassociation of $5s50d\ ^1D_2$ Rydberg dimers in the absence of a magnetic field with a sample temperature $T = 1.1\ \mu\text{K}$. The detuning is referenced to the atomic Rydberg state. The contributions from M_K states in the range $[-6, 6]$ are summed. (b) Expectation value $\langle N \rangle$ (red dots) of the molecular $M_K = 0$ eigenstates. The error bars indicate the standard deviations. The molecular wave functions $R^2 Q(R, \theta_R)$ are shown for $\nu = 0$ with (c) $K = 0$, (d) $K = 2$, and (e) $K = 4$, and for (f) $\nu = 1$ and $K = 2$, and (g) $\nu = 3$ and $K = 2$.

those in the absence of a magnetic field, ~ 9 MHz (see Fig. 4). In the strong-field limit, an effective molecular potential can be evaluated for each m level separately and approximated by

$$\begin{aligned}
 U_M(\vec{R}) &\simeq \frac{e}{2m_e}mB + \left[\frac{2\pi\hbar^2}{m_e}a_s(k)|\rho_{n,\ell}(R)|^2 \right. \\
 &\quad \left. + \frac{6\pi\hbar^2}{m_e}a_p^3|\partial_R\rho_{n,\ell}(R)|^2 \right] |Y_\ell^m(\hat{R})|^2 \\
 &= \frac{e}{2m_e}mB + V_M(R) \frac{4\pi}{2\ell+1} |Y_\ell^m(\hat{R})|^2. \quad (10)
 \end{aligned}$$

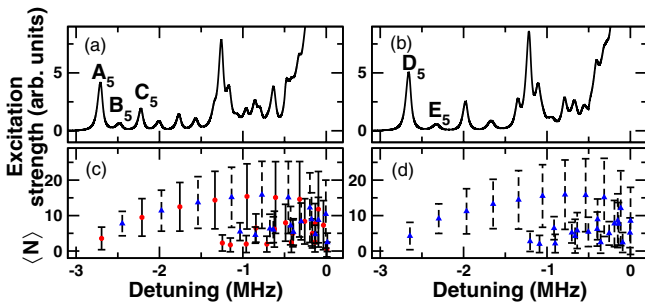


FIG. 5. Calculated photoassociation spectra for $5s50d\ ^1D_2$ Rydberg dimers for (a) $m = -2$ and (b) $m = -1$ in the limit of strong magnetic field. The sample temperature is set to $T = 1.1\ \mu\text{K}$. Contributions from M_K states in the range $[-6, 6]$ are summed. The laser polarizations are (a) $\sigma + \sigma$ and (b) $\sigma + \pi$. Detuning is defined with respect to the Zeeman-shifted atomic line. Expectation value $\langle N \rangle$ for (c) $m = -2$ and (d) $m = -1$. The red dots correspond to states with $M_K = -2$ and the blue triangles are states with $M_K = -1$. In (d), the states with $M_K = -2$ are not shown as they are nearly identical to those of $M_K = -1$. The error bars indicate the standard deviations.

The Zeeman shift, $emB/(2m_e)$, is constant within a single m manifold and the rest is separable into the radial part $V_M(R)$ (Fig. 3) obtained in the absence of a magnetic field [Eq. (7)] and the angular part $-|Y_\ell^m(\hat{R})|^2$. The latter is depicted in Fig. 6. We note that due to the negative scattering length $a_s(0)$, the angular potential is plotted with a minus sign. The depths of the angular potentials are $3/8 = 0.375$ for $|m| = 1, 2$ and the molecular binding energies [Figs. 5(a) and 5(b)] become smaller than those for $B = 0$ (Fig. 4).

The molecular wave functions (Fig. 7) are consistent with the angular part of molecular potentials (Fig. 6) and localized around $\theta_R = \pi/2$ for $m = -2$ (A_5, B_5, C_5), and $\pm\pi/4$ for $m = -1$ (D_5, E_5). The expectation value $\langle N \rangle$ increases as the binding energy decreases [Figs. 5(c) and 5(d)] until the next excited vibrational state around -1.5 MHz is found. In

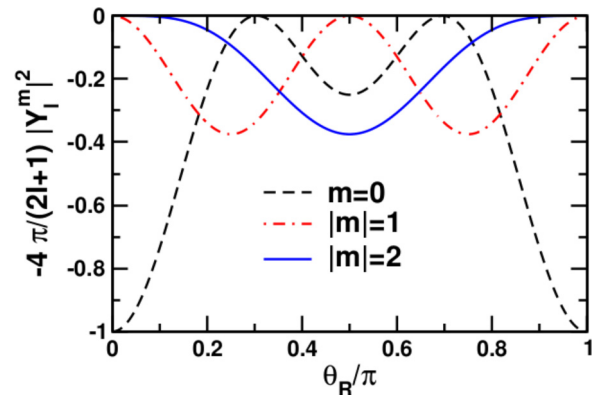


FIG. 6. Angular parts of the effective potential for (a) $|m| = 2$, (b) $|m| = 1$, and (c) $|m| = 0$.

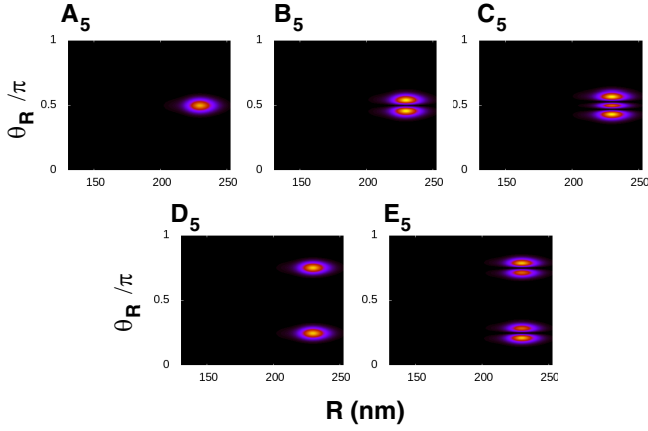


FIG. 7. Molecular wave functions $R^2 Q(R, \theta_R)$ corresponding to the peaks indicated as A_5 to E_5 in the photoassociation spectra in Fig. 5. A_5 and C_5 are for $m = -2$ and $M_K = -2$, B_5 is for $m = -2$ and $M_K = -1$. D_5 and E_5 are for $m = -1$ and $M_K = -1$.

contrast to the zero-field case (Fig. 4), the standard deviation also increases with $\langle N \rangle$, implying that highly excited rovibrational states contain a wide range of N states, including low- N states, which can be photoassociated in an ultracold gas. The wave functions (Fig. 7) show narrower distributions in θ_R than those for $B = 0$ (Fig. 4), confirming larger standard deviations $\langle (\Delta N)^2 \rangle^{1/2}$. The excitation strength of each molecular state is closely related to the symmetry of the angular wave function. The Franck-Condon factor is enhanced (suppressed) when the number of nodes within a single potential well in θ_R is even (as in A_5, C_5, D_5) (odd as in B_5 and E_5). Additional information on the symmetry of molecular wave functions can be extracted from the quantum number M_K , which could be controlled by

the laser polarizations in the limit of ultracold gas (i.e., $N' = M'_N = 0$). The angular wave function is even with respect to $\theta_R = \pi/2$ for even M_K and odd for odd M_K . For $m = -2$, the effective potential has a single well around $\theta_R = \pi/2$ and the symmetric wave functions with even M_K have sizable excitation strengths. On the other hand, for $m = -1$, i.e., in the double-well potential in θ_R (Fig. 6), M_K determines the gerade and ungerade symmetry between these two wells. In the current case, they are nearly degenerate and even and odd M_K states cannot be distinguished in the photoassociation spectra. We note that the above analysis shown for negative values of m is also applicable for positive m .

For $m = 0$, the angular potential (Fig. 6) shows multiple wells at $\theta_R = 0$ and $\pm\pi$ with different depths. Calculated photoassociation spectra [Fig. 8(a)] also show small peaks below -2 MHz [clearly seen in the logarithmic scale in Fig. 8(b)] corresponding to the deep wells at $\theta_R = 0, \pi$ and large sharp peaks above -2 MHz for the shallow well at $\theta_R = 0$. The molecular wave functions (Fig. 9) confirm the localization at $\theta_R = 0, \pi$ (axial states) for the small peaks (A_8, B_8, C_8) and $\theta_R = \pi/2$ (toroidal states) for the dominant peaks (D_8, E_8, F_8) [11]. As expected from Fig. 6, the binding energies for the axial states are comparable to those without magnetic fields (Fig. 4). Below -4 MHz, increasing $\langle N \rangle$ indicates the excitation of rovibrational states. Since the molecular states are subject to different boundary conditions at $\theta_R = 0, \pi$ (see Fig. 9), no degeneracy is seen between different M_K states. The first excited vibrational state is present around -4 MHz (with small $\langle N \rangle$), but the photoassociation strength is not significantly larger than is the case for $m = -1, -2$ (Fig. 5). This can be recognized in the photoassociation spectra as a change in the interval between peaks.

The binding energies for the toroidal states (> -4 MHz) are suppressed by a factor ~ 0.25 (Fig. 8) compared to those

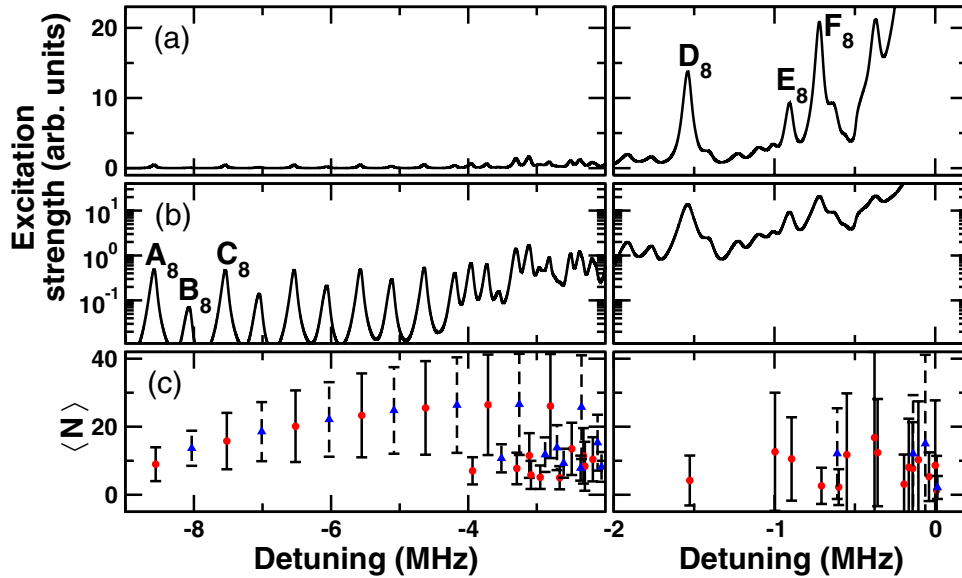


FIG. 8. (a) Calculated photoassociation spectrum of $5s50d$ $^1D_2$ Rydberg dimers with $m = 0$ in the strong-field limit. The sample temperature is set to $T = 1.1$ μ K. All contributions from M_K states in the range $[-6, 6]$ are summed. The laser polarization is $\pi + \pi$. Detuning is defined with respect to the Zeeman-shifted atomic line. (b) Same as (a), but on a logarithmic scale to visualize the small peaks. (c) Expectation value $\langle N \rangle$ for $M_K = 0$ (red dots) and $M_K = -1$ (blue triangles). Above -2 MHz, only states with significant Franck-Condon factors are shown. The error bars indicate the standard deviations.

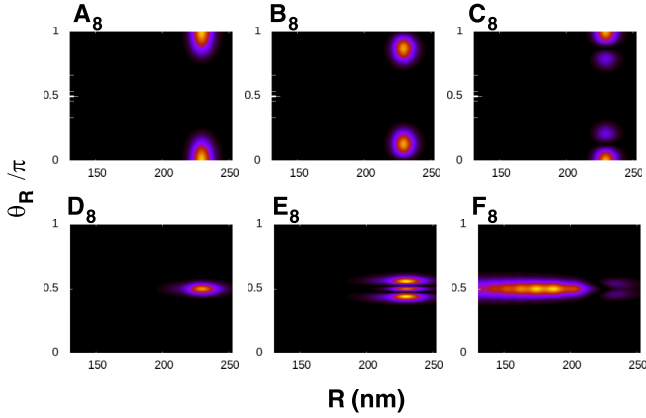


FIG. 9. Molecular wave functions $R^2 \rho(R, \theta_R)$ for $m = 0$ corresponding to the peaks indicated as A_8 to F_8 in the photoassociation spectra in Fig. 8. B_8 is for $M_K = -1$ and all others are for $M_K = 0$. To visualize the wave function near the boundary, in A_8 , B_8 , and C_8 , the θ_R axis is scaled by a power law $[\propto (\theta_R - 1/2)^5]$.

without magnetic fields (Fig. 4). The prominent peaks in the photoassociation spectrum correspond to the lowest-energy toroidal state (Fig. 9, D_8), the first excited rotational state (Fig. 9, E_8), and an excited vibrational state (Fig. 9, F_8). Due to the presence of excited background axial states, the detailed structure in the other molecular levels cannot be clearly resolved, as is the case for $m = -1, -2$. Due to the large standard deviations in N , the wave functions are well localized in θ_R for both axial and toroidal states. Consequently, the axial states have very small Franck-Condon factors when photoassociated from an isotropic distribution of atoms. The observation of such axial states, therefore, would require sizable laser powers [11].

VI. INTERMEDIATE-FIELD REGIME

When the Zeeman splitting is smaller or comparable to the interaction energy between the Rydberg electron and the ground-state atom, the couplings between m levels induced by the electron-atom scattering must be considered. The molecular energy levels in the intermediate-field regime calculated by diagonalizing the Hamiltonian [Eq. (1)] including the mixing of m levels are shown for $5s50d\ ^1D_2$ $M_K = 0$ dimers as a function of magnetic field applied along the z axis together with the Zeeman-shifted atomic levels (Fig. 10). Only those dimer states with $\langle R \rangle < 2.2(n - \delta)^2 a_0$ are considered as bound. For each bound state κ , the weight on each N state,

$$w_N^{(\kappa)} = \sum_m \int dR R^2 \left| \sum_v \mathcal{R}_{v,N,m}^{(\kappa)}(R) \right|^2, \quad (11)$$

is evaluated. States with the sum $\sum_{N=0,2} w_N^{(\kappa)}$ of $N = 0$ and $N = 2$ populations over 1% are plotted in red in Fig. 10 to highlight those states that can be accessed optically in a cold gas. At $B = 0$, only a few rotational states centered on the different vibrational states are optically accessible and can be populated. However, as illustrated by the black lines in Fig. 10, many additional molecular levels exist that are not optically accessible.

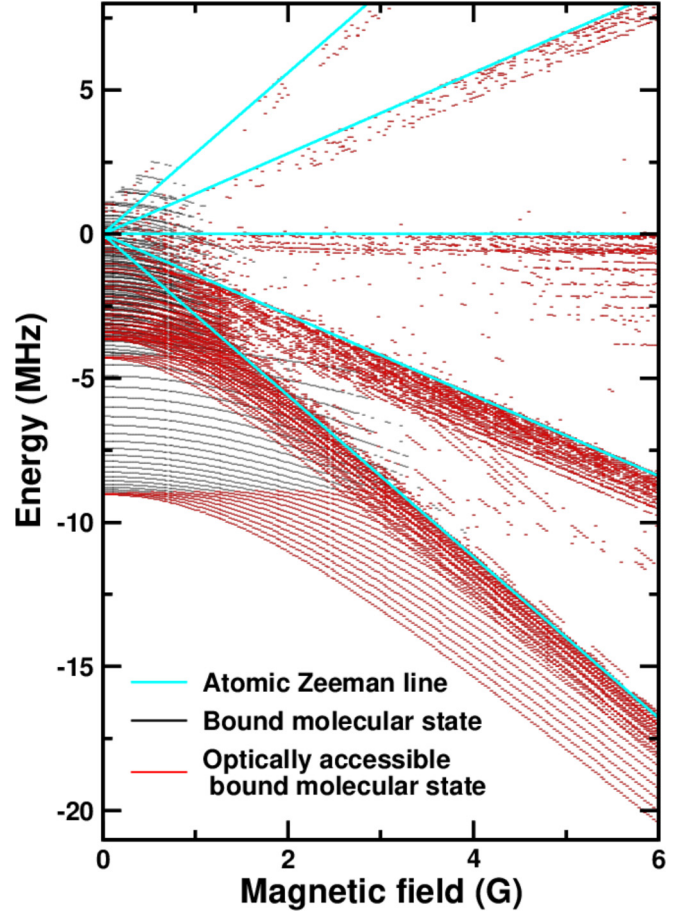


FIG. 10. Calculated bound molecular energy levels for $5s50d\ ^1D_2$ dimers ($M_K = 0$) as a function of magnetic field. The bound molecular states are defined by an average bond length satisfying $\langle R \rangle < 2.2(n - \delta)^2 a_0$. Those bound molecular states with $N = 0$ and 2 populations greater than 1% are highlighted in red (see text). The dissociation thresholds (i.e., atomic Zeeman lines) are also shown.

As B increases, the dimer levels begin to shift and split. Those with small level shifts, dE/dB , correspond to states with small expectation values of m , i.e., $\langle m \rangle \sim 0$, as $dE/dB = e\langle m \rangle / (2m_e)$. Many of these molecular states with energies between -4 and -9 MHz are not optically accessible from an ultracold gas in a weak magnetic field. However, with increasing magnetic field, the energies of some of these states shift below -9 MHz, whereupon they become optically accessible due to the coupling between rotational states, opening up the possibility of photoassociating weakly aligned molecules. Other states show larger B -field dependences, pointing to larger values of $\langle m \rangle$ and contributions from higher m states. Indeed, at the highest field in Fig. 10, the most strongly bound states have values of dE/dB characteristic of $m = -2$ states, i.e., of toroidal states. Also, at the higher fields, the dimer binding energies, relative to the corresponding Zeeman-shifted atomic level, become much reduced.

We note that the “bound” states associated with all but the $m = -2$ level lie above the dissociation threshold for one or more other m states. Therefore, they couple strongly with scattering states above the dissociation thresholds of other m states. These quasibound states are defined by the condition

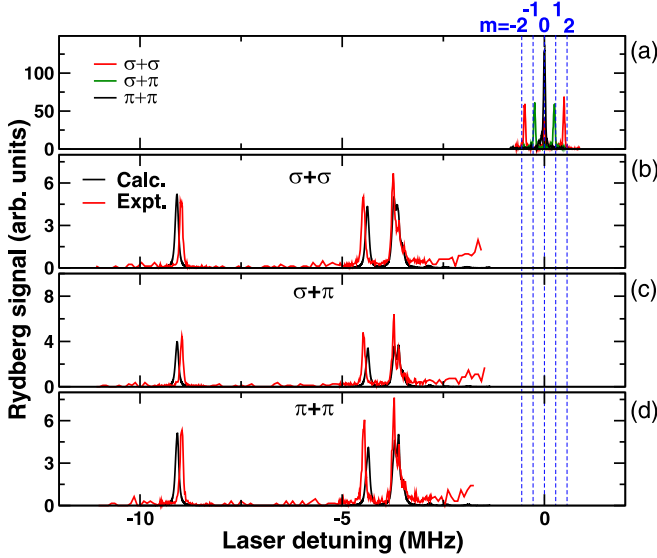


FIG. 11. (a) Rydberg excitation spectra recorded in a magnetic field $B = 0.2$ G using the combinations of laser polarizations indicated. (b)–(d), Comparison, on an expanded vertical scale, of the measured $5s50d\ ^1D_2$ dimer production rates with those predicted using the present model. The sample temperature is $1.1\ \mu\text{K}$ and the calculations include the sum of contributions for $-6 \leq M_K \leq 6$. The dashed blue lines indicate the positions of the Zeeman-shifted atomic lines.

$\langle R \rangle < 2.2(n - \delta)^2 a_0$, but are sensitive to the chosen threshold $\langle R \rangle$ value. The quasibound states displayed as nearly solid lines are close to true bound states and those as broken lines have expectation values $\langle R \rangle$ close to the threshold value, indicating strong coupling to scattering states.

VII. RESULTS AND DISCUSSION

Figures 11–13 show photoassociation spectra recorded in selected magnetic fields using different combinations of laser polarizations to selectively excite different m levels. (Note that because of small misalignments of the laser and magnetic fields, the spectra contain small contributions from the excitation of atomic m states other than those targeted. However, as noted previously, their excitation strengths are very small and therefore they and their associated dimers do not provide a significant contribution to the measured molecular photoassociation spectra.) Each spectrum is referenced to the $m = 0$ atomic line.

Figure 11 shows spectra recorded in a 0.2 G magnetic field. These match closely with those seen in zero magnetic field and contain three prominent narrow features associated with the creation of $v = 0, 1$, and 3 vibrational states having binding energies of $\sim 9, 4.3$, and 3.4 MHz (see Fig. 4). The model predictions agree well with the experimental measurements. The lack of any significant energy shifts is consistent with Fig. 10, confirming that in this regime, the dimer properties are governed simply by Rydberg electron scattering from the ground-state atom.

At $B = 1$ G (Fig. 12) and $B = 2$ G (Fig. 13), significant changes in the dimer spectra become apparent that depend markedly on the choice of laser polarizations and are again

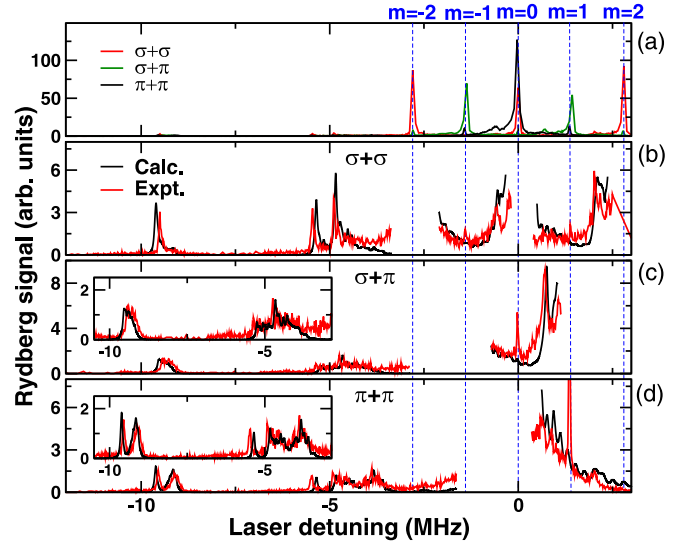


FIG. 12. (a) Rydberg excitation spectra recorded in a magnetic field $B = 1.0$ G in the vicinity of $n = 50$ using the combinations of laser polarizations indicated. (b)–(d) Comparison, on an expanded vertical scale, of the measured $5s50d\ ^1D_2$ dimer production rates with those predicted using the present model. All other conditions are as in Fig. 11.

well described by the model. For $\sigma + \pi$ polarization, pronounced broadening is seen, resulting from the creation of multiple rovibrational levels. For $\sigma + \sigma$ polarization, a significant change in binding energy is evident, from ~ 9 MHz at $B = 0$ to ~ 11 MHz at $B = 2$ G, as might be expected from its $m = -2$ character. For $\pi + \pi$ polarization, a peak at ~ -9 MHz is still present at both $B = 1$ and $B = 2$ G, consistent with the production of $\langle m \rangle \simeq 0$ states (Fig. 10),

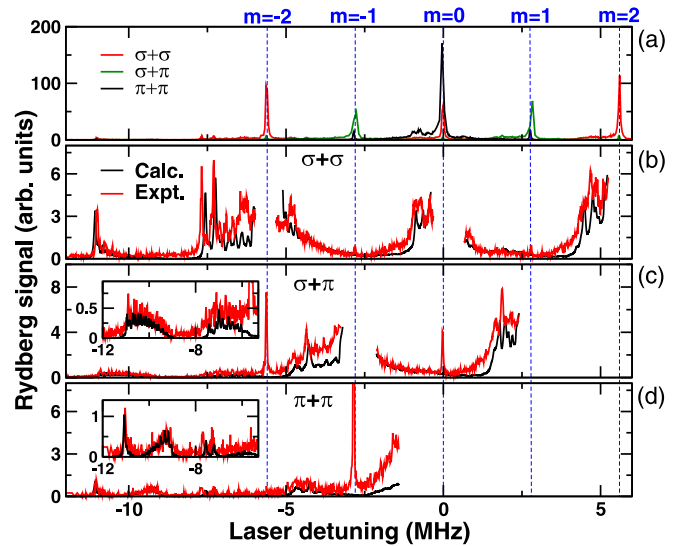


FIG. 13. (a) Rydberg excitation spectra recorded in a magnetic field $B = 2.0$ G in the vicinity of $n = 50$ using the combinations of laser polarizations indicated. (b)–(d) Comparison, on an expanded vertical scale, of the measured $5s50d\ ^1D_2$ dimer production rates with those predicted using the present model. All other conditions are as in Fig. 11.

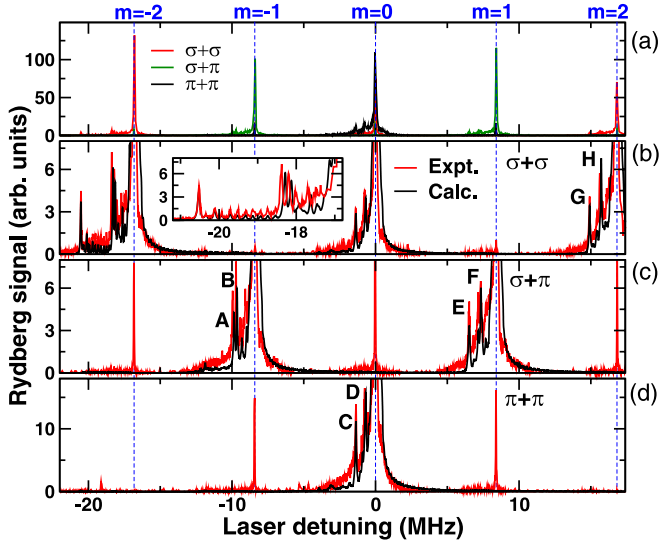


FIG. 14. (a) Comparison of the Rydberg excitation spectra recorded in a magnetic field $B = 6.0$ G in the vicinity of $n = 50$ using the combinations of laser polarizations indicated. (b)–(d) Comparison, on an expanded scale, of the measured $5s50d\ ^1D_2$ dimer production rates with those predicted using the present model. All other conditions are as in Fig. 11.

implying the presence of an aligned $M_K = 0$ molecular state. At $T = 1.1\ \mu\text{K}$ and $R_n \simeq 200$ nm, the initial gas of atoms has a non-negligible population of $K = 2$ states. The observed peak at -9 MHz may contain contributions from other M_K states, $|M_K| \leq 2$, that are not aligned to the magnetic field. However, at lower temperatures or for smaller n , the $M_K = 0$ states can become dominant and aligned molecules can be created. Moreover, the features corresponding to quasibound molecular states above the dissociation threshold for $m = -2$ states become sizable.

We note that the calculations are implemented in a finite-size box with $R \leq 500$ nm. Therefore, the states above dissociation thresholds are not accurately represented. This

leads to some discrepancies with the measured data, in particular the line width near the Zeeman-shifted atomic lines.

At $B = 6.0$ G (Fig. 14), the system approaches the strong-field limit (Sec. V). The spectra contain a series of isolated subspectra, each of which converges to a particular atomic m level. As predicted, the detailed structure of the individual contributions depends markedly on the value of m . Rydberg dimers observed below -16 MHz using $\sigma + \sigma$ laser polarization are dominated by the $m = -2$ state, which contributes more than 90% of the observed signal. The spectra contain multiple sharp peaks that correspond to vibrational excitations and small (quasiperiodic) peaks associated with rovibrational excitations [see the inset of Fig. 14(b)]. Quasibound molecular states belonging to other m states are embedded in the sea of highly excited (dissociated) dimer states of lower m (see Fig. 10). While coupling between m states induced by electron scattering is still sizable, for quasibound molecular states, the molecular wave functions [Eq. (6)] reveal that they are dominated by the nearby Zeeman-shifted m state. The distribution in angle θ_R (see Fig. 15) is well localized within the potential wells (see Fig. 6) associated with the corresponding value of m . For $m = 0$ (C,D), as expected in the strong-field limit (Sec. V), the localization around $\theta_R = \pi/2$ indicates the dominance of toroidal states, although a small admixture of axial states is also seen. Axial states with energies of -9 to -8 MHz (Fig. 8) are expected but are strongly perturbed by other m states as they overlay the $m = -1$ Zeeman line. Similar to toroidal states (Fig. 1), the angular distribution of axial states becomes narrower with increasing magnetic field. As the axial state aligns more sharply with the magnetic field, the corresponding Franck-Condon factor becomes smaller.

VIII. CONCLUSIONS

The present work shows that the presence of a magnetic field can have a dramatic effect on the structure of ^{84}Sr dimers. Although, in the absence of electronic and nuclear spins ($I = S = 0$), the ground-state atom barely interacts with magnetic

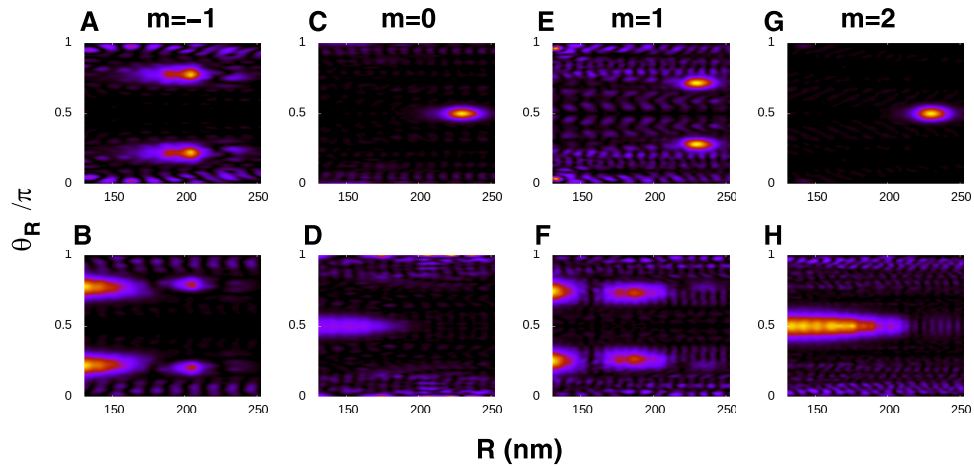


FIG. 15. Molecular wave functions $R^2 Q(R, \theta_R)$ corresponding to the peaks indicated as A to H in the photoassociation spectra in Fig. 14. A and B with $M_K = -1$, C and D with $M_K = 0$, E and F with $M_K = 1$, and G and H with $M_K = 2$.

fields, in the case of the dimer, indirect interactions through scattering of the Rydberg electron can affect the geometry of the molecular wave function. From an isotropic distribution of atoms, dimer states with toroidal wave functions perpendicular to the applied magnetic field have large photoassociation rates. Dimers aligned along the magnetic field (axial states) might also be photoassociated in a weak magnetic field in the limit of low temperature or in a strong field using high-power lasers. In future studies, it will be interesting to examine the production of $n^3D_{1,2,3}$ Rydberg dimers and the effects of nonzero total electron spin. Measurements of dimer binding energies in the presence of an electric field are also of interest, with emphasis on the creation of quasi-one-dimensional Stark

states for which the electron probability density is strongly localized on one side of the nucleus [15].

ACKNOWLEDGMENTS

Research was supported by the NSF under Grant No. PHY 2409598. The calculations were undertaken using the Austrian Scientific Computing infrastructure. The authors acknowledge TU Wien Bibliothek for financial support through its Open Access Funding Programme.

DATA AVAILABILITY

The data that support the findings of this article are openly available [16].

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