

Photoassociation of $^{84}\text{Sr } n^1D_2$ ultralong-range Rydberg dimers

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Measurements of the production of $5snd\ ^1D_2\text{--}5s^2\ ^1S_0$ ultralong-range Rydberg dimers through photoassociation in an ultracold ^{84}Sr atomic gas are reported. The molecular potential associated with the Rydberg D state is anisotropic and the molecular states are characterized by the vibrational quantum number ν and the total angular momentum $\vec{K} = \vec{L} + \vec{N}$, where $\vec{L}$ and $\vec{N}$ are the electronic orbital angular momentum and rotational angular momentum, respectively. The measured molecular binding energies agree reasonably well with theoretical predictions. Additionally, the electron-atom scattering leads to broader line shapes in the photoassociation spectrum than might be expected simply from the angular momentum of the initial colliding cold-atom pairs.

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I. INTRODUCTION

Since their existence was first predicted theoretically in [1], much interest has focused on the production and properties of ultralong-range Rydberg molecules (ULRMs) which comprise a Rydberg atom in whose electron cloud are embedded one or more ground-state atoms weakly bound by their scattering of the Rydberg electron [2–8]. Such molecules represent a new type of molecular bond with bond lengths comparable to the size of the Rydberg atom, which increases rapidly with principal quantum number n scaling as n^2 . They have been exploited, for example, to study electron-atom scattering in an energy regime difficult to access using alternate techniques [3,9] and have provided a valuable probe of nonlocal spatial correlations in a quantum gas [10,11] as well as many-body effects such as the creation of Rydberg polarons [12,13].

Many early experiments utilized alkali-metal nS Rydberg atoms and demonstrated the production of not only dimer molecules, but also trimers, tetramers, etc., in both their ground and vibrationally excited states [12,14]. Several classes of ULRMs were identified associated with low- L states, with a quasidegenerate mix of high- L states (trilobite states), and with the p -wave shape resonance present in low-energy electron-alkali-metal scattering (butterfly states) [2,8]. Measurements were also extended to alkali-metal nP and nD states [15–18] whose anisotropies allowed, for example, the study of the effects of alignment and antialignment on ULRM formation when created in a magnetic field.

Ultralong-range Rydberg molecule studies have been extended to the alkaline-earth-metal elements, in particular strontium nS Rydberg molecules [10,11,19]. The

alkaline-earth-metal elements offer a number of advantages when comparing experiment to theory. The bosonic isotopes ^{84}Sr , ^{86}Sr , and ^{88}Sr have no hyperfine structure or low-energy p -wave shape resonance, which, in comparison to studies of rotational excitation in the alkali-metal atoms [20], significantly simplifies calculations and permits more straightforward comparisons to theory. Ultralong-range Rydberg molecules are typically analyzed using a Born-Oppenheimer (BO) molecular potential in which electron-ground-state-atom scattering is represented using a Fermi pseudopotential. Recently, the theoretical approach has been extended beyond the BO approximation to account for the excitation of vibrational motion through diabatic transitions caused by collisions between the Rydberg electron and the ground-state atom [21].

Here we extend high-resolution strontium photoassociation spectroscopy to $^{84}\text{Sr } n^1D_2$ dimers. Unlike n^1S_0 dimers, the molecular potential is anisotropic and the resulting molecular state is represented as a superposition of rotational levels [17,20]. Consequently, as illustrated in Fig. 1, the energy splittings of rovibrational levels are larger for n^1D_2 dimers than for n^1S_0 dimers. To analyze the rovibrational structure, we perform *ab initio* calculations that include effects beyond the BO approximation. We analyze the diabatic transitions between rotational levels induced by the anisotropic molecular potential. The resulting mixed molecular states are characterized by the total angular momentum $\vec{K} = \vec{L} + \vec{N}$, where $\vec{L}$ and $\vec{N}$ are the electronic orbital angular momentum and the molecular rotational angular momentum, respectively. The angular momentum coupling yields nondegenerate K levels that are each a superposition of several N levels. The energy splittings between K levels result in broadening of the photoassociation spectra larger than might be expected simply on the basis of the initial angular momentum of the colliding cold-atom pair. This is illustrated in Fig. 1, which shows calculations of the contributions from the different K levels to the n^1D_2 photoassociation spectra. On the other hand, the electron-atom scattering for n^1S_0 dimers does not yield an admixture of N levels due to vanishing L (i.e., $K = N$).

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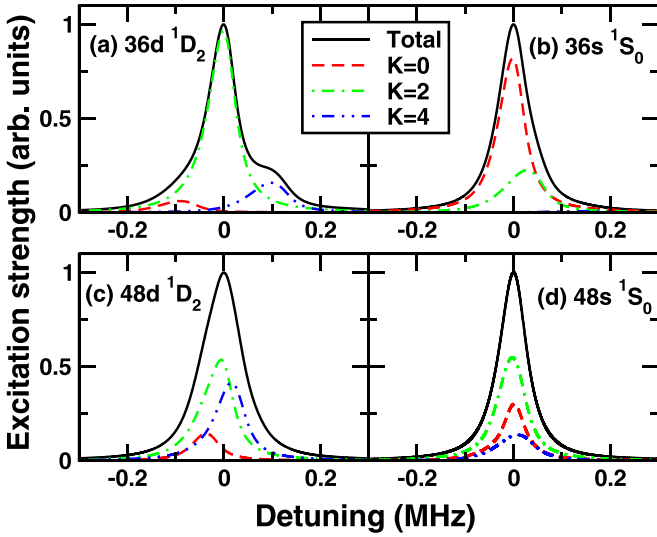


FIG. 1. Black solid lines show the calculated photoassociation spectra for (a) $5s36d\ ^1D_2$, (b) $5s36s\ ^1S_0$, (c) $5s48d\ ^1D_2$, and (d) $5s48s\ ^1S_0$ Rydberg dimers of ^{84}Sr . The temperature of the initial ultracold gas is set to $T = 1.1\ \mu\text{K}$ and the spectra are convolved with the measured instrumental linewidth. The contributions from individual K levels are also shown: $K = 0$ (red dashed line), $K = 2$ (green dash-dotted line), and $K = 4$ (blue dash-double-dotted line). In each case zero detuning is taken to be the peak in the photoassociation spectrum.

II. EXPERIMENTAL METHOD

The present apparatus is shown in Fig. 2 and has been described in detail elsewhere. Briefly, ^{84}Sr atoms are cooled and loaded into an optical dipole trap [10,11]. Evaporative cooling is used to control their temperature. The atom temperature and density are determined by releasing the atom cloud from the trap and monitoring its expansion through optical absorption. The Rydberg atoms are created in near-zero electric and magnetic fields by two-photon excitation $5s^2\ ^1S_0 \rightarrow 5s5p\ ^1P_1 \rightarrow 5snd\ ^1D_2$ using radiation provided by two lasers, both linearly polarized along the same axis, operating at 461 and 413 nm, respectively. The laser frequencies are stabilized using a high- Q ultralow-expansion cavity and their powers are monitored. Rydberg atoms or molecules are detected by selective field ionization (SFI) in an electric field produced by application of potential differences between the electrodes shown in Fig. 2. The product electrons are directed to a microchannel plate

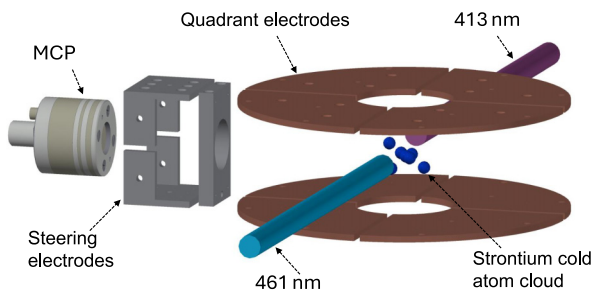


FIG. 2. Schematic diagram of the apparatus.

for detection. The signals are normalized to take into account variations in laser intensity and trap density.

A cold sample ($T \sim 1.1\ \mu\text{K}$, peak density approximately equal to $7 \times 10^{12}\ \text{cm}^{-3}$) is first prepared. In each experimental cycle concurrent 20- μs -duration laser pulses are used to create the Rydberg atoms or molecules, following which their number is determined by SFI. The number of Rydberg atoms or molecules created in a single pulse is kept low, less than approximately 1, to prevent Rydberg-Rydberg interactions, and photoassociation spectra are built up through multiple experimental cycles at each laser frequency. Up to approximately 100 experimental cycles can be conducted with a single cold-atom sample before any significant heating of the sample by the 461-nm laser (which was blue detuned by 18 GHz from the $^1S_0\text{-}^1P_1$ transition) can occur.

III. THEORETICAL MODEL

We model the Rydberg dimer as a three-body system consisting of a Rydberg electron, an ion core, and a ground-state atom. In the limit of heavy atomic mass, the Hamiltonian can be approximated as

$$H_M \simeq \frac{P^2}{2\mu} + \frac{p^2}{2m_e} + V_c(r) + V(\vec{r} - \vec{R}), \quad (1)$$

where $\mu = m/2$ is the reduced mass (m is the mass of a ^{84}Sr atom), m_e the electron mass, V_c the electron- Sr^+ ion core interaction, and $V(\vec{r} - \vec{R})$ the electron-ground-state-atom interaction approximated by the Fermi pseudopotential

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

Here $\vec{r}$ and $\vec{p}$ are the electron position and momentum with respect to the ion core, respectively, and $\vec{R}$ and $\vec{P}$ are those of the ground-state atom. Note that for the analysis of singlet $5snd$ states (i.e., $S = 0$) the electron spin is neglected in the following discussion. Additionally, the ion-atom interaction is also neglected. All other angular momenta are defined with the rotation center at the ion core. The molecular eigenstates are evaluated by numerically diagonalizing the two-body Hamiltonian. Due to the weak interaction between the ground-state atom and the Rydberg electron, the system can be confined within a subspace of Hilbert space in which the Rydberg electron is confined in a D state including all m levels. Due to this reduction of Hilbert space, the numerical diagonalization of the total Hamiltonian becomes feasible within an accessible computing time. Using this limited basis, we analyze the diabatic transitions between the molecular potentials associated with different values of m . We note that a_s and a_p in Eq. (2) are treated as effective scattering lengths and fitted to reproduce the measured molecular binding energies. This approach compensates for any weak couplings to neighboring L levels [22].

The electronic wave function $\langle \vec{r} | n, \ell, m \rangle = \rho_{n,\ell}(r) Y_\ell^m(\hat{r})$ of the Rydberg atom is assumed to be unperturbed by the presence of the ground-state atom. The quantum numbers n and ℓ are preserved. Interactions between the electron and

the ground-state atom mix different m levels and states of different rotational angular momentum $\tilde{N}$. The total angular momentum $\tilde{K} = \tilde{N} + \tilde{L}$ is a good quantum number due to the rotational symmetry of the Hamiltonian [Eq. (1)]. (We note that for singly excited Rydberg states the total electron angular momentum $\tilde{L}$ is the same as the angular momentum $\tilde{\ell}$ of the Rydberg electron.) For a rovibrational state with a given K and M_K , we assume an ansatz for

$$|nD, \nu, K, M_K\rangle = \sum_{\nu_N, N} C_{\nu_N, N} |n, \nu_N, (L=2, N)K, M_K\rangle. \quad (3)$$

The basis state $|n, \nu_N, (L=2, N)K, M_K\rangle$ is the eigenstate of the Hamiltonian within a subspace of a fixed value of N , i.e., without rotational-state couplings. The vibrational wave functions $\langle R | \nu_N, N \rangle = \mathcal{R}_{\nu_N, N}(R)$ with unperturbed eigenenergies $\tilde{E}_{\nu_N, N}$ can be numerically evaluated by solving the radial Schrödinger equation with the effective potential

$$V_M(R) = -\frac{\text{Ry}}{(n-\delta)^2} + \frac{\hbar^2 N(N+1)}{2\mu R^2} + U_S(N, N) |\rho_{n, \ell}(R)|^2 + U_P^{(1)}(N, N) |\partial_R \rho_{n, \ell}(R)|^2 + U_P^{(2)}(N, N) \frac{1}{R^2} |\rho_{n, \ell}(R)|^2, \quad (4)$$

where Ry is the Rydberg constant, $n - \delta$ is the effective quantum number of the Rydberg electron, and δ is the quantum defect. The matrix elements are defined by

$$U_S(N, N') = \frac{\hbar^2(2L+1)}{2m_e} a_s(k) \xi_N(K) \xi_{N'}(K), \quad (5)$$

$$U_P^{(1)}(N, N') = \frac{3\hbar^2}{2m_e} (2L+1) a_p(k)^3 \xi_N(K) \xi_{N'}(K), \quad (6)$$

and

$$U_P^{(2)}(N, N') = \frac{1 + (-1)^{N+N'}}{2} \frac{3\hbar^2}{2m_e} L(L+1)(2L+1) \times a_p(k)^3 \eta_N(K) \eta_{N'}(K), \quad (7)$$

with

$$\xi_N(K) = \sqrt{2N+1} \begin{pmatrix} L & N & K \\ 0 & 0 & 0 \end{pmatrix}, \quad \eta_N(K) = \sqrt{2N+1} \begin{pmatrix} L & N & K \\ 1 & 0 & -1 \end{pmatrix}. \quad (8)$$

Using this basis, the total Hamiltonian including the rotational-state coupling is expressed as

$$\begin{aligned} \langle n, \nu'_N, (L, N')K, M_K | H_M | n, \nu_N, (L, N)K, M_K \rangle \\ = \tilde{E}_{\nu_N, N} \delta_{\nu_N, \nu'_N} \delta_{N, N'} + (1 - \delta_{N, N'}) \\ \times \langle n, \nu'_N, (L, N')K, M_K | V | n, \nu_N, (L, N)K, M_K \rangle. \end{aligned} \quad (9)$$

By separating the short-range potential as $V = V_S + V_P$, the corresponding matrix elements can be written as

$$\begin{aligned} \langle n, \nu'_N, (L, N')K, M_K | V_S | n, \nu_N, (L, N)K, M_K \rangle \\ = U_S(N, N') \int dR R^2 |\rho_{n, \ell}(R)|^2 \mathcal{R}_{\nu'_N, N'}(R) \mathcal{R}_{\nu_N, N}(R) \end{aligned} \quad (10)$$

and

$$\begin{aligned} \langle n, \nu'_N, (L, N')K, M_K | V_P | n, \nu_N, (L, N)K, M_K \rangle \\ = U_P^{(1)}(N, N') \int dR R^2 |\partial_R \rho_{n, \ell}(R)|^2 \mathcal{R}_{\nu'_N, N'}(R) \mathcal{R}_{\nu_N, N}(R) \\ + U_P^{(2)}(N, N') \int dR |\rho_{n, \ell}(R)|^2 \mathcal{R}_{\nu'_N, N'}(R) \mathcal{R}_{\nu_N, N}(R). \end{aligned} \quad (11)$$

The Hamiltonian can be diagonalized numerically to obtain the binding energies $E_{\nu, K}$ of the rovibrational states. The interaction terms [Eqs. (10) and (11)] mix nondegenerate N states into a given K state.

The Franck-Condon factor is evaluated as the overlap between an initial scattering state and a Rydberg molecular state. We approximate the initial scattering states by spherical waves including the scattering phase shift for an s wave ($N' = 0$) while both valence electrons are in the ground state, i.e.,

$$\begin{aligned} \langle \vec{r}, \vec{R} | 5s^2; k, N'; K', M'_K \rangle \\ = \sqrt{\frac{2}{\pi}} j_{N'}(kR) \langle \vec{r} | 5s^2 \rangle \langle \hat{R} | N' = K', M'_N = M'_K \rangle, \end{aligned} \quad (12)$$

where $j_{N'}(kR)$ are the spherical Bessel functions when $N' \neq 0$ and for $N' = 0$, $j_0(kR) = \sin[k(R - a_s)]/kR$ including the scattering length ($a_s = 123a_0$). Neglecting photon momentum recoil, the transition amplitude for two-photon excitation to a molecular state [Eq. (3)] using lasers which are both linearly polarized along the z axis is

$$\begin{aligned} \langle nD, \nu, K, M_K | z^2 | 5s^2; k, N' = K'; K', M'_K \rangle \\ = \delta_{K', N'} \langle 5snd^1D_2 | z^2 | 5s^2 \rangle F_{\nu, K, M_K}(k, K', M'_K) \end{aligned} \quad (13)$$

and can be factorized to the electronic transition amplitude and the Franck-Condon overlap defined as

$$\begin{aligned} F_{\nu, K, M_K}(k, K', M'_K) = \delta_{M_K, M'_K} \sum_{\nu_N} C_{\nu_N, N=K'} \\ \times \left(\int dR R^2 \sqrt{\frac{2}{\pi}} j_{K'}(kR) \mathcal{R}_{\nu_N, N=K'}(R) \right) \\ \times \langle K, M_K | L=2, M=0; N=K', M'_K \rangle. \end{aligned} \quad (14)$$

The target molecular state is characterized by the total angular momentum K with a superposition of several N levels due to the electron-atom scattering. Assuming a vertical transition, only the $N = K'$ level contributes to photoassociation and therefore the Franck-Condon factor [Eq. (14)] is weighted by the factor $C_{\nu_N, N=K'}$ and the Clebsch-Gordan coefficient $\langle K, M_K | L=2, M=0; N=K', M'_K \rangle$. Finally, for a nonzero sample temperature T , the photoassociation spectrum can be evaluated as

$$\begin{aligned} f(\omega) = \left(\frac{\hbar^2}{2\pi \mu k_B T} \right)^{3/2} \int dk \sum_{K', M'_K} 4\pi k^2 e^{-\hbar^2 k^2 / 2\mu k_B T} \\ \times \sum_{\nu, K} L_{\nu, K, M_K=M'_K}(k, \omega) |F_{\nu, K, M_K=M'_K}(k, K', M'_K)|^2, \end{aligned} \quad (15)$$

where $L_{v,K,M_K}(k, \omega)$ is a Voigt profile centered at the molecular energy $E_{v,K}$. The integrated excitation strength of the ground vibrational level $v = 0$, summed over nearby K levels, is given by

$$\begin{aligned} Q_n &= \sum_K \langle |F_{v=0,K,M_K=M'_K}(k, K', M'_K)|^2 \rangle \\ &= \sum_K \sum_{K', M'_K} \left(\frac{\hbar^2}{2\pi\mu k_B T} \right)^{3/2} \int dk 4\pi k^2 e^{-\hbar^2 k^2 / 2\mu k_B T} \\ &\quad \times |F_{v=0,K,M_K=M'_K}(k, K', M'_K)|^2. \end{aligned} \quad (16)$$

In the photoassociation spectrum [Eq. (15)] the signal strength for each K level is determined by the angular momentum coupling through the weighted Franck-Condon factor [Eq. (14)]. However, once summed over K , the effects of angular momentum coupling will drop out in the integrated strength [Eq. (16)].

IV. DEEPLY BOUND ROVIBRATIONAL LEVELS

The *ab initio* calculations account for angular momentum couplings between $\vec{L}$ and $\vec{N}$. However, it is also instructive to compare these with results obtained using the BO approximation, in which the atomic and electronic motions are treated separately. Within the BO approximation, i.e., assuming fixed positions (in both the radial and angular coordinates) of the ground-state atom, the effective molecular potential for Σ states (i.e., $\Lambda = 0$ with the projection Λ of $\vec{L}$ along the molecular axis) is given by

$$\begin{aligned} V_M^{\text{BO}}(R) &= -\frac{\text{Ry}}{(n-\delta)^2} + \frac{\hbar^2(2\ell+1)}{2m_e} a_s(k) |\rho_{n,\ell}(R)|^2 \\ &\quad + \frac{3\hbar^2}{2m_e} (2\ell+1) a_p(k)^3 |\rho'_{n,\ell}(R)|^2. \end{aligned} \quad (17)$$

We denote the resulting vibrational wave functions by $\chi_v(R)$ with binding energies $\mathcal{E}_v^{\text{BO}}$. Since the adiabatic molecular potential $V_M^{\text{BO}}(R)$ (i.e., the eigenenergy of the electronic Hamiltonian) within the BO approximation is isotropic, the rotational quantum number is also conserved. Since the ground rovibrational state is well localized around $R = R_n \simeq 1.8(n-\delta)^2 a_0$ (see Fig. 3), the molecular energy including rotational excitation can be approximated as

$$E_{v,N}^{\text{BO}} \simeq \mathcal{E}_v^{\text{BO}} + \frac{\hbar^2 N(N+1)}{2\mu R_n^2}. \quad (18)$$

On the other hand, the molecular states obtained from the *ab initio* calculations can be approximated, in the limit of weak centrifugal energies and couplings to Π states, as

$$\begin{aligned} \langle \vec{r}, \vec{R} | nD, v, K, M_K \rangle \\ \simeq \langle r, R | nD; v \rangle \sum_N \xi_N(K) \langle \hat{r}, \hat{R} | (L=2, N) K, M_K \rangle \\ = (-1)^K \sqrt{\frac{2L+1}{4\pi}} \rho_{nd}(r) \chi_v(R) P_{\ell=2}(\hat{r} \cdot \hat{R}) Y_K^{M_K}(\hat{R}). \end{aligned} \quad (19)$$

The vibrational wave function, even when the rotational-state couplings are included, is well approximated by $\chi_v(R)$ from

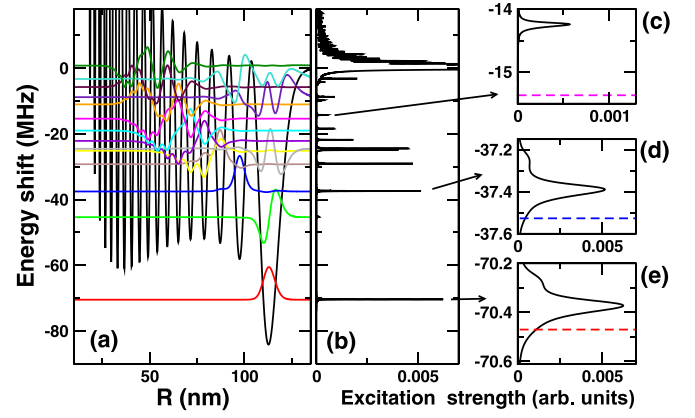


FIG. 3. (a) Calculated molecular potential for a $5s36d^1 D_2-5s^2 1S_0$ ^{84}Sr atom pair using the BO approximation. The calculated vibrational wave functions for the bound vibrational states are also shown. (b) Photoassociation spectrum evaluated using *ab initio* calculations of the molecular states (beyond the BO approximation). Spectra for (c) $v = 8$, (d) $v = 2$, and (e) $v = 0$ are shown on an expanded scale. The dashed lines indicate values $E_{v,N=0}^{\text{BO}}$ obtained for Σ states using the BO approximation.

the BO approximation. The Legendre polynomial $P_\ell(\hat{r} \cdot \hat{R})$ indicates the formation of a Σ state along the molecular axis. This angular part of the electronic state can be rewritten as

$$\sqrt{\frac{2\ell+1}{4\pi}} P_{\ell=2}(\hat{r} \cdot \hat{R}) = \sum_{m=-\ell}^{\ell} Y_\ell^m(\hat{r}) D_{m,0}^\ell(\phi_R, \theta_R, 0). \quad (20)$$

Here the Wigner D matrix $D_{m,0}^\ell(\phi_R, \theta_R, 0) = \sqrt{4\pi/(2\ell+1)} Y_\ell^m(\hat{R})^*$ rotates the molecular axis towards the z axis. This $\hat{R}$ -dependent part of the electronic wave function leads to diabatic transitions along the angular coordinates. These effects beyond the BO approximation are caused by scattering of the ground-state atom by the Rydberg electron. For the ground vibrational state localized around $R \simeq R_n$, the dominant part of binding energy is given by the BO approximation, i.e., $\mathcal{E}_v^{\text{BO}}$. The centrifugal energy beyond the BO approximation can be estimated as the first-order perturbative correction

$$\left\langle \frac{\hbar^2 N(N+1)}{2\mu R^2} \right\rangle_K \simeq \frac{\hbar^2 \langle N(N+1) \rangle_K}{2\mu R_n^2}, \quad (21)$$

with

$$\langle N(N+1) \rangle_K = \sum_N \xi_N(K)^2 N(N+1). \quad (22)$$

The *ab initio* calculation of molecular energy levels also confirms that the vibrational wave function is well localized, i.e., $\langle R^{-2} \rangle_K \simeq R_n^{-2}$ (Fig. 4). For an ultracold gas, the initial scattering state $|5s^2, K' = N' = 0, M'_K = 0\rangle$ is expected to be excited to a molecular state $E_{v,N=0}^{\text{BO}} = \mathcal{E}_v^{\text{BO}}$ with $N = N' = 0$ through a vertical transition within the BO approximation. The *ab initio* calculation indicates that molecular states with $K = 2$ are preferentially excited. The centrifugal energy for $n = 36$ and $K = 2$ is estimated as $\hbar^2 \langle N(N+1) \rangle_K / 2\mu R^2 \simeq 120$ kHz, which agrees well with the energy

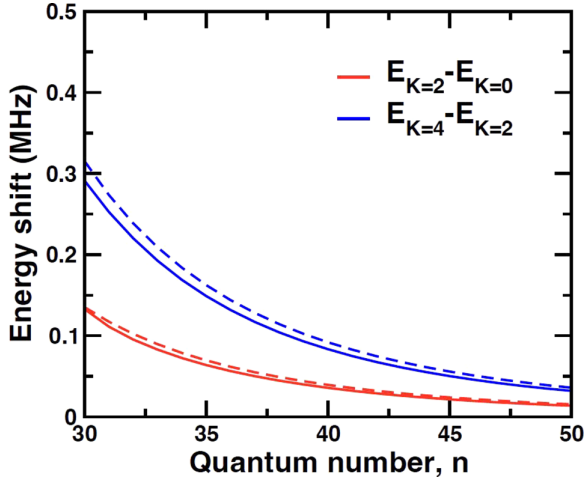


FIG. 4. Plot of the n dependence of the $\nu = 0$ K -level energy spacings calculated by the *ab initio* method (solid lines) together with those obtained using the first-order perturbation $\hbar^2 \langle N(N+1) \rangle_K / 2\mu R_n^2$ beyond the BO approximation (dashed lines).

difference $E_{\nu=0, K=2} - E_{\nu=0, N=0}^{\text{BO}}$ between the *ab initio* calculation (Sec. III) and the BO approximation using Eq. (17) [Fig. 3(e)]. The difference from the BO approximation increases with increasing ν and is on the order of megahertz for weakly bound molecular states with $E_{\nu, K} > -20$ MHz at $n = 36$ [see Fig. 3(c)]. The vibrational wave function extends towards small R as ν increases and the approximation [Eq. (21)] breaks down as $\langle R^{-2} \rangle_K > R_n^{-2}$ enhancing the centrifugal energy.

The density distribution of the ground-state atom with respect to the ion core can be obtained by tracing the squared wave function over the electronic coordinates

$$\begin{aligned} \varrho_{\nu, K, M_K}(\vec{R}) &= \int d^3r |\langle \vec{r}, \vec{R} | nD, \nu, K, M_K \rangle|^2 \\ &\simeq |\chi_\nu(R) Y_K^{M_K}(\hat{R})|^2. \end{aligned} \quad (23)$$

The angular distribution becomes approximately proportional to $|Y_K^{M_K}(\hat{R})|^2$ and is characterized by the quantum numbers K and M_K of the total angular momentum. For an initial scattering state $|5s^2; K' = N' = 0, M'_K = 0\rangle$, photoassociation by two lasers, each linearly polarized along the z axis, yields molecular states with $K = 2$ and $M_K = 0$. The calculated angular distributions $\Theta_K(\theta_R) = \int dR d\phi_R R^2 \varrho_{\nu=0, K, M_K=0}(\vec{R})$ of the ground vibrational state point to the alignment of the molecule along the laser polarization axis following the spherical harmonic $|Y_{K=2}^{M_K=0}(\hat{R})|^2$. However, at higher temperatures with the increasing population of initial scattering states with $N' = 2$ or larger, the quantum number M_K of the product molecular state becomes distributed over the range $[-2N' - 1, 2N' + 1]$ and the molecules are no longer aligned.

The Franck-Condon overlap [Eq. (14)] can be simplified as

$$\begin{aligned} F_{\nu, K, M_K}(k, K' = N', M'_K) \\ \simeq (-1)^{K+M_K} \left(\int dR R^2 \chi_\nu(R) \sqrt{\frac{2}{\pi}} j_{K'}(kR) \right) \\ \times \sqrt{(2K+1)(2K'+1)} \end{aligned}$$

$$\times \begin{pmatrix} K' & L & K \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} K' & L & K \\ M'_K & 0 & -M_K \end{pmatrix}. \quad (24)$$

The selection rule associated with the Wigner $3j$ symbol indicates that photoassociation from an initial ultracold gas of bosons (i.e., even N') yields molecular states with even K ($|K' - 2| \leq K \leq K' + 2$). For the ground vibrational state $\nu = 0$, the vibrational wave function is well localized around $R = R_n$ in a region much smaller than the wavelength $\lambda = 2\pi/k$ of the initial scattering states. In this limit, the Franck-Condon factor can be further approximated by

$$\begin{aligned} F_{\nu, K, M_K}(k, K', M'_K) \\ \simeq (-1)^{K+M_K} \sqrt{\frac{2}{\pi}} j_{K'}(kR_n) \left(\int dR R^2 \chi_\nu(R) \right) \\ \times \sqrt{(2K+1)(2K'+1)} \\ \times \begin{pmatrix} K' & L & K \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} K' & L & K \\ M'_K & 0 & -M_K \end{pmatrix} \end{aligned} \quad (25)$$

and the integrated excitation strength of the ground vibrational state [Eq. (16)] becomes

$$\begin{aligned} Q_n &\simeq \sum_{K'} \left\langle \frac{2}{\pi} j_{K'}^2(kR_n) \right\rangle \sum_{K, M_K, M'_K} |F_{\nu=0, K, M_K}(k, K', M'_K)|^2 \\ &= \left(\sum_{K'} 2(2K'+1) \langle j_{K'}^2(kR_n) \rangle \right) \\ &\times \frac{1}{\pi(2L+1)} \left(\int dR R^2 \chi_{\nu=0}(R) \right)^2. \end{aligned} \quad (26)$$

The first factor is the pair correlation in the initial ultracold gas, i.e.,

$$g^{(2)}(R_n) = \sum_{K'} 2(2K'+1) \langle j_{K'}^2(kR_n) \rangle. \quad (27)$$

For bosons (fermions), the summation is taken over even (odd) values of the rotational quantum number $K' = N'$.

V. RESULTS AND DISCUSSION

Photoassociation spectra recorded for several values of n are presented in Fig. 5. Each spectrum contains a number of rovibrational features and the binding energies of the more prominent of these, indicated by the squares in Fig. 5, are shown in Fig. 6(a) and decrease rapidly with increasing n . Their n -dependent scaling can be inferred from Fig. 6(b), which shows the measured (and calculated) binding energies multiplied by $(n - \delta)^6$ as a function of n . This clearly demonstrates that the binding energy of the ground vibrational state scales as approximately $1/(n - \delta)^6$. This behavior is similar to that seen in earlier studies [23] of dimer formation and reflects the scaling of the depth of the molecular potential, which is proportional to the electron probability density $|\psi_{n\ell}(\vec{R})|^2$.

Assuming that the vibrational wave function of the most deeply bound state is localized within the outermost well of the molecular potential and that the well is nearly harmonic, the molecular binding energy is given by $E \simeq V_0 + \hbar\omega(\nu + 1/2)$. The depth V_0 of the well scales as $(n - \delta)^{-6}$ while the trap frequency scales as $\omega \sim (n - \delta)^{-4}$ [24]. Therefore, the

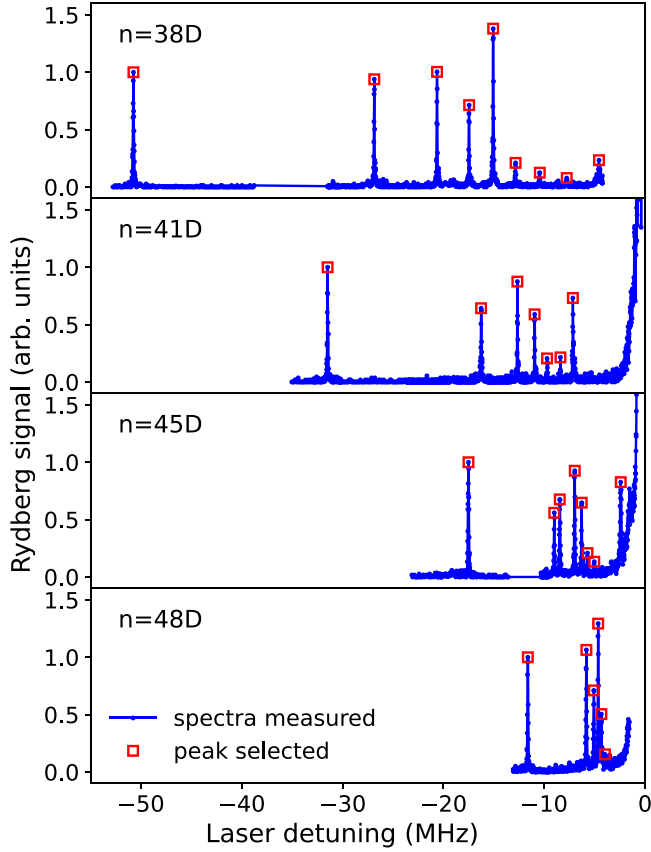


FIG. 5. Photoassociation spectra recorded for the values of n indicated. The major features used to generate the molecular binding energies shown in Fig. 6 are indicated by the squares. The detunings are referenced to the atomic line.

power-law scaling changes from $(n - \delta)^{-6}$ for deeply bound states ($V_0 \gg \hbar\omega\nu$) towards a smaller exponent at large ν . Further deviations can be induced by tunneling into adjacent wells in the molecular potential. Indeed, the first excited vibrational state $\nu = 1$ is invisible at low n in the measured data due to its antisymmetric wave function which is also localized in the outermost well [see Fig. 3(a)]. At higher n it becomes visible through the coupling with the lowest vibrational state of the neighboring well. Figure 6 shows the resulting avoided crossing of the $\nu = 1$ and $\nu = 2$ states near $n = 45$.

Figure 6 also includes representative $\nu = 0$ binding energies measured in earlier studies of n^3S_1 dimers [23]. The two data sets display qualitatively similar approximately $(n - \delta)^{-6}$ scaling, but the binding energies for the n^1D_2 dimers are larger by approximately a factor of $2L + 1$, which can be attributed to the higher local electron probability densities found in the anisotropic D -state wave functions.

We note that the calculated results in Fig. 6 use an s -wave scattering length tuned to optimize the fits to the data, $a_s = -13.84a_0$, which is very similar to the value $a_s = -13.3a_0$ derived from earlier studies using $^3S_1$ dimers. At $n = 36$, a variation in s -wave scattering length of $0.01a_0$ corresponds to a change of binding energy of about 10 kHz for the ground vibrational state. The p -wave scattering length $a_p = 9.7a_0$ obtained in the earlier $^3S_1$ dimer studies [25] provides the optimal fit in the present study.

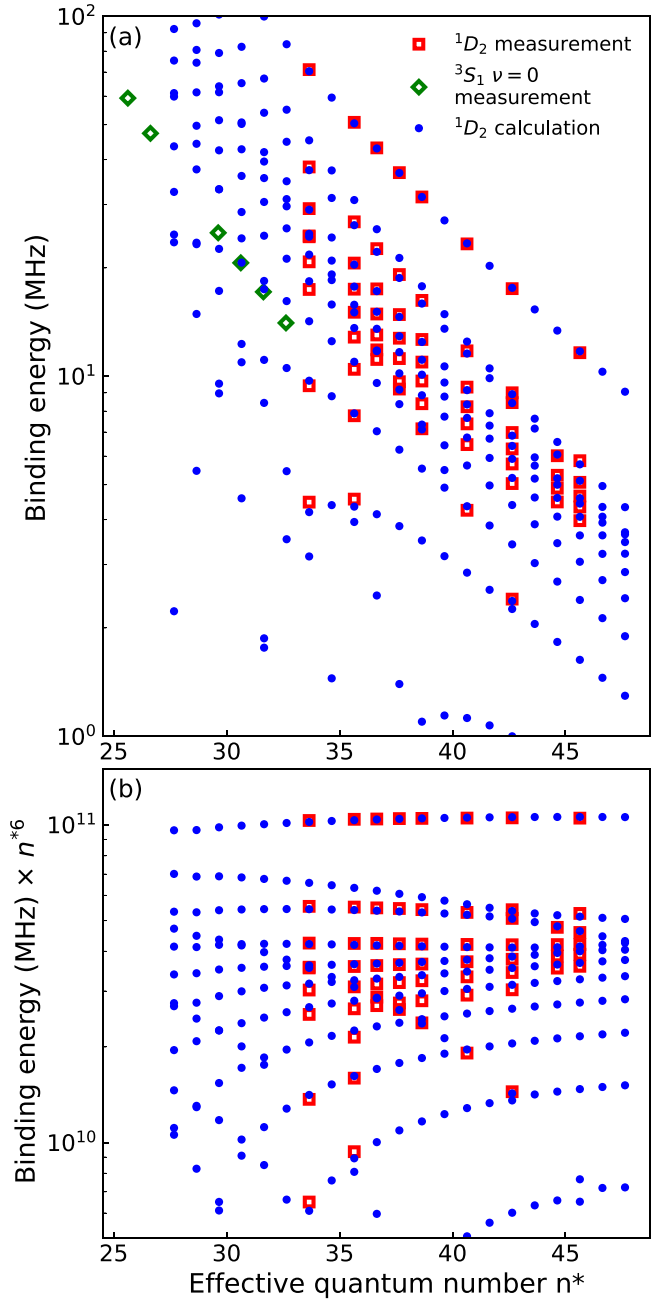


FIG. 6. (a) Measured binding energies of the most prominent vibrational states seen in the photoassociation spectra (open squares) and the calculated eigenenergies $E_{v,K}$ with $K = 2$ (circles) plotted as a function of $n^* = n - \delta$. For comparison, the binding energies of the ground vibrational state for $5sns\ ^3S_1$ – $5s^2\ ^1S_0$ dimers are also included (diamonds). The experimental uncertainties are less than the size of the data points. (b) Measured (open squares) and calculated (circles) vibrational energy levels scaled by $(n - \delta)^6$.

To examine the effects of coupling between angular momenta L and N , we examined the line profiles of the photoassociation spectra for dimer $\nu = 0$ vibrational states (Fig. 7). As noted earlier, the initial scattering states with the $N' = 0$ partial wave will be excited to molecular states with $K = 2$. At a temperature $T = 1.1\ \mu\text{K}$ another partial wave $N' = 2$ is also present with a small but non-negligible probability and can be excited to molecular states with $K = 0, 2, 4$.

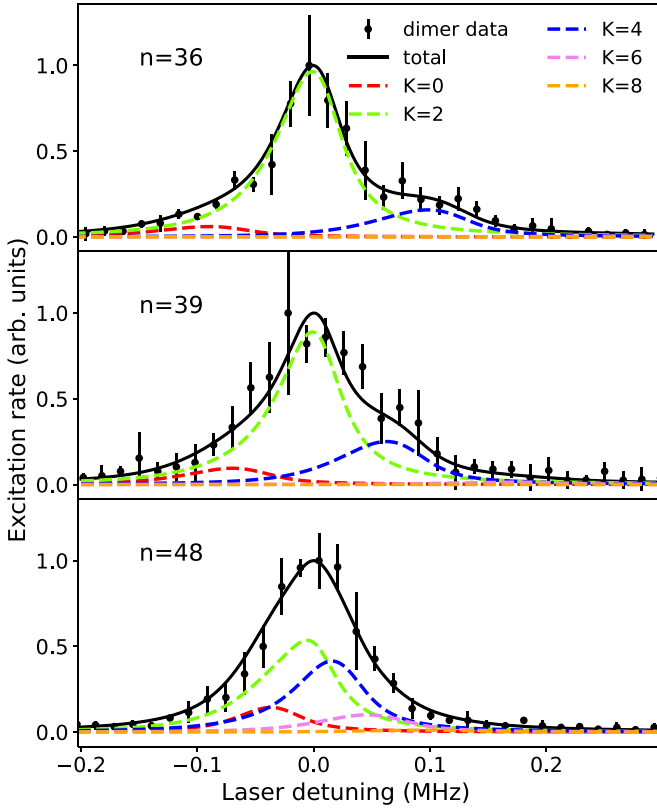


FIG. 7. Measured photoexcitation spectra for creation of $\nu = 0$ $^1D_2$ dimers with the values of n indicated, together with those predicted by the *ab initio* calculations. Model predictions of the separate contributions from each individual K state are also included. The calculated profiles are convolved with a 50-kHz FWHM Gaussian to account for the measured experimental linewidth. In each panel the peaks of the measured and predicted spectra are normalized to one and used to define zero detuning.

This is illustrated in Fig. 7, which shows the calculated line profiles for several $\nu = 0$ dimer vibrational state together with the relative contributions associated with the creation of the different K states. (The calculations are convolved with a Gaussian of 50 kHz FWHM to account for the experimental linewidth obtained from measurements of the photoexcitation of the parent Rydberg states.) Whereas $K = 2$ states are the major contributors to dimer production, the contributions from $K = 0$ and $K = 4$ states are significant. The measured molecular line profiles are also included in Fig. 7. As can be seen, the measured spectra are in good agreement with the model predictions. In particular, the data point to the creation of significant numbers of dimers in the $K = 4$ state.

As a further test of the present model, the n dependence of the integrated $\nu = 0$ dimer signals was measured. This signal can be written as

$$S_n \propto \alpha \frac{I_1 I_2}{\Delta^2} N_A \rho_0 \beta_n Q_n, \quad (28)$$

where α is the electron detection efficiency, I_1 and I_2 are the laser intensities, Δ is the intermediate state detuning, N_A is the atom number, ρ_0 is the peak density in the trap, β_n is the two-photon electronic transition matrix element, and Q_n is the integrated transition strength from Eq. (26). The signal

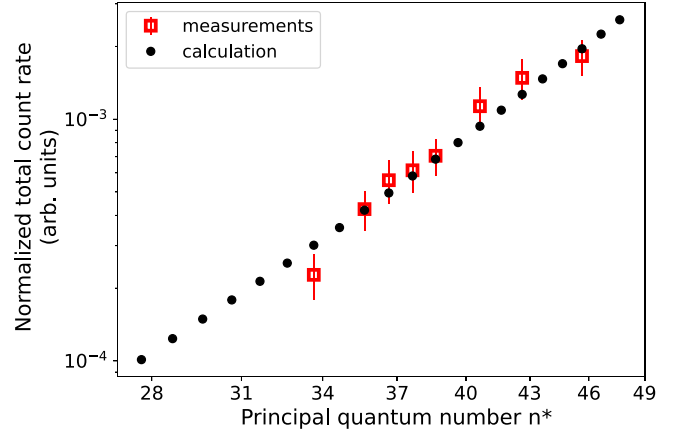


FIG. 8. Plot of the n dependence of the integrated dimer signal (see the text for details). For comparison, the calculated n dependence of this signal [Eq. (26)] is also included. The two data sets are normalized to each other at $n^* \sim 40$.

associated with the creation of the parent Rydberg atoms, S_{nd} , can be expressed as

$$S_{nd} \propto \alpha \frac{I'_1 I'_2}{\Delta^2} \beta_n N_A \quad (29)$$

when

$$\frac{S_n}{S_{nd}} \propto \frac{I_1 I_2}{I'_1 I'_2} \rho_0 Q_n, \quad (30)$$

whereupon Q_n can be written as

$$Q_n \propto \frac{S_n}{S_{nd}} \frac{I'_1 I'_2}{I_1 I_2} \frac{1}{\rho_0}. \quad (31)$$

The measured n dependence of Q_n obtained in this manner is presented in Fig. 8 together with that predicted by the model [Eq. (26)]. Both theory and experiment demonstrate very similar n dependences and show that Q_n scales approximately as the size of the Rydberg atom.

Note that for the present sample temperature the de Broglie wavelength λ_{dB} is approximately $3200a_0$ whereas, for the present range of n , R_n spans the range from approximately $2000a_0$ to approximately $3700a_0$. The corresponding values of R_n/λ_{dB} thus range from approximately 0.63 to 1.16, over which range the value of $g^{(2)}(R)$ remains essentially constant [$g^{(2)}(R) \sim 1$]. If $g^{(2)}(R_n)$ is assumed to be constant, Q_n may then be written as

$$Q_n \simeq \frac{1}{\pi(2L+1)} \left(\int dR R^2 \chi_{\nu=0}(R) \right)^2, \quad (32)$$

i.e., as proportional to the squared integral of the vibrational wave function.

VI. CONCLUSION

We have shown that the measured molecular binding energies of $^{84}\text{Sr } n^1D_2$ ULRMs agree well with theoretical calculations. Broadening of rotational spectra was observed consistent with electron-atom scattering which leads to population of a broader range of rotational states than expected simply from the angular momentum of the initial colliding cold-atom pair. Considering the earlier studies of alkali-metal nD states in a magnetic field [17,26], it will be interesting

to explore the evolution of the strontium n^1D_2 photoassociation spectra during the transition from the present case ($B = 0$) where electron–ground-state-atom interactions provide the dominant energy scale to that where magnetic interactions dominate.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [27].

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Correction: A typographical error in Eq. (4) has been fixed.