

Experimental Characterization of Singlet Scattering Channels in Long-Range Rydberg Molecules

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We observe the formation of long-range Cs₂ Rydberg molecules consisting of a Rydberg and a ground-state atom by photoassociation spectroscopy in an ultracold Cs gas near $6s_{1/2}(F=3,4) \rightarrow np_{3/2}$ resonances ($n=26-34$). The spectra reveal two types of molecular states recently predicted by D. A. Anderson, S. A. Miller, and G. Raithel [Phys. Rev. A 90, 062518 (2014)]: states bound purely by triplet s -wave scattering with binding energies ranging from 400 MHz at $n=26$ to 80 MHz at $n=34$, and states bound by mixed singlet-triplet s -wave scattering with smaller and F -dependent binding energies. The experimental observations are accounted for by an effective Hamiltonian including s -wave scattering pseudopotentials, the hyperfine interaction of the ground-state atom, and the spin-orbit interaction of the Rydberg atom. The analysis enables the characterization of the role of singlet scattering in the formation of long-range Rydberg molecules and the determination of an effective singlet s -wave scattering length for low-energy-electron-Cs collisions.

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Atoms in Rydberg states of high principal quantum number n are weakly bound systems and are extremely sensitive to their environment. In 1934, Amaldi and Segrè [1] observed the pressure-dependent shift and broadening of the Rydberg series of alkali atoms in a gas cell, an effect that was explained by Fermi [2] as originating from the elastic scattering between slow Rydberg electrons and ground-state atoms within the Rydberg orbit. He modeled the pressure shift using a pseudopotential

$$V(R) = 2\pi a |\Psi(\mathbf{R})|^2, \quad (1)$$

where a is the scattering length and $|\Psi(\mathbf{R})|^2$ is the probability density of the Rydberg electron at the position \mathbf{R} of the neutral perturber. Measurements of pressure shifts in Rydberg states thus provide information on the cross sections of elastic collisions between slow electrons and atoms and molecules [2,3]. Equation (1) implies the existence of oscillating interaction potentials between Rydberg and ground-state atoms [4,5]. Manifestations of such potentials are long-range diatomic molecules in which a ground-state atom having a negative s -wave scattering length is attached to a Rydberg atom at a distance corresponding to an antinode of $\Psi(\mathbf{R})$, as was first pointed out by Greene *et al.* [6]. Such molecules were first observed experimentally by Bendkowsky *et al.* [7] following excitation of Rb atoms close to $ns_{1/2}$ Rydberg states with $n=35-37$. Later investigations led to the detection of long-range Rb₂ molecules correlated to $np_{1/2,3/2}$ ($n=7-12$) [8], $nd_{3/2,5/2}$ ($n=34-40$) [9], and $nd_{3/2,5/2}$ ($n=40-49$) [10] dissociation asymptotes and long-range Cs₂ molecules correlated to $ns_{1/2}$ ($n=31-34$) [11] and $ns_{1/2}$ ($n=37, 39, 40$) [12] asymptotes. The analysis of the experimental

data confirmed the overall validity of Eq. (1), revealed contributions from triplet p -wave scattering channels, and enabled the determination of triplet s - and p -wave scattering lengths that confirmed theoretical predictions [13].

Singlet s -wave scattering lengths are expected to be either positive or much smaller than triplet scattering lengths [14,15] and thus scattering in singlet channels has not been included in the analysis of the experimental data. Anderson *et al.* [16] have recently predicted that the hyperfine coupling in the ground-state atom should effectively mix triplet and singlet scattering channels and lead to shallow bound states in addition to the more strongly bound states resulting from pure triplet scattering.

Here, we report on the observation of these shallow bound states correlated to $np_{3/2}$ Rydberg states in the range $n=26-34$ in an ultracold Cs gas. We show that the well depths of these shallow states depend on the hyperfine component ($F=3$ or $F=4$) in which the ground-state atoms are prepared, model the experimental observations theoretically, and extract an effective singlet s -wave scattering length for low-energy e^- -Cs collisions from the experimental data.

Following Ref. [16], we model the interaction between the Rydberg and the ground-state atom using

$$\hat{H} = \hat{H}_0 + \hat{H}_{\text{SO}} + \hat{H}_{\text{HF}} + \hat{P}_S \cdot \hat{V}_S + \hat{P}_T \cdot \hat{V}_T, \quad (2)$$

where \hat{H}_0 is the Hamiltonian of the Rydberg atom without spin-orbit interaction, $\hat{H}_{\text{SO}} = A_{\text{SO}} \mathcal{L}_r \otimes s_r$ is the spin-orbit interaction of the Rydberg electron with angular momentum \mathcal{L}_r and electron spin s_r , and $\hat{H}_{\text{HF}} = A_{\text{HF}} \mathbf{i}_g \otimes s_g$ is the hyperfine interaction of the ground-state atom with nuclear

spin i_g and electron spin s_g . Separate terms for singlet (S) and triplet (T) scattering are obtained by using the projection operators $\hat{P}_S = -s_r \otimes s_g + \frac{1}{4} \cdot \hat{1}$ and $\hat{P}_T = s_r \otimes s_g + \frac{3}{4} \cdot \hat{1}$ and representing the corresponding Fermi-contact-interaction operators by $\hat{V}_i = 2\pi a_i \delta^3(\mathbf{r} - R\hat{z})$, with $i = S, T$, for s -wave scattering between the Rydberg electron at position \mathbf{r} and the ground-state atom located at distance R along the molecular z axis [17]. We neglect the rotational motion of the molecule, because the spacings between the accessible rotational levels are less than their natural linewidths. The hyperfine structure of the Rydberg atom is also neglected, because the corresponding interaction is much weaker than all other relevant interactions [18]. To reproduce experimental binding energies, we adjust the zero-energy limit of the energy-dependent scattering lengths [Ref. [14], Eqs. (1, 4–6)]. The spin-orbit coupling constants A_{SO} are extracted from experimental fine-structure splittings [19] and we use the hyperfine coupling constant A_{HFS} from Ref. [20].

The Hamiltonian matrix corresponding to Eq. (2) is set up in the uncoupled basis $|\ell_r, \lambda_r\rangle |s_r, \sigma_r\rangle |s_g, \sigma_g\rangle |i_g, \omega_{i,g}\rangle$ ($i_g = 7/2$ for ^{133}Cs) for a single np Rydberg state and the energetically closest Rydberg state $(n-1)d$. The quantum number $\Omega_{\text{tot}} \equiv \lambda_r + \sigma_r + \sigma_g + \omega_{i,g}$ of the projection of the total angular momentum on the internuclear axis is a good quantum number. The ground-state atom can be in either of the two $F = 3, 4$ ($F \equiv i_g + s_g$) hyperfine levels, and the np Rydberg atom can be in either the $np_{3/2}$ ($\omega_r \equiv \lambda_r + \sigma_r = -3/2, -1/2, 1/2, 3/2$) or the $np_{1/2}$ ($\omega_r = -1/2, 1/2$) spin-orbit levels. The spin-orbit interaction of the Rydberg electron completely mixes the $\lambda_r = 0$ and $|\lambda_r| = 1$ components of the $|\omega_r| = 1/2$ levels, whereas the $|\omega_r| = 3/2$ levels have pure Π character. Because we restrict the e^- -Cs interaction to s -wave scattering, only the $\lambda_r = 0$ (Σ^+) components of the Rydberg wave function contribute to the binding [17]. The $|\omega_r| = 3/2$ levels are thus non-bonding and the strength of the bond of the $|\omega_r| = 1/2$ levels is proportional to their $\lambda_r = 0$ (Σ^+) character. The selection of the $\lambda_r = 0$ component in the interaction terms \hat{V}_S and \hat{V}_T implies that ω_r equals σ_r in all components of the wave functions contributing to binding and that s -wave singlet and triplet channels of the e^- -Cs scattering interaction are not mixed by \hat{H}_{SO} . These channels can, however, be mixed by \hat{H}_{HF} . Remarkably, the eigenstates of Eq. (2) form two distinct subgroups, one containing states that do not possess any $^1\Sigma^+$ character (but $^3\Sigma^+$, $^1\Pi$, and $^3\Pi$) and for which the binding is entirely dictated by the triplet s -wave interaction, and one containing states which possess both $^3\Sigma^+$ and $^1\Sigma^+$ (as well as $^1\Pi$ and $^3\Pi$) character and for which the binding results from both singlet and triplet s -wave scattering interactions. Table I gives an overview of the character and degeneracy factors of the resulting bound states. For simplicity we refer to the states bound via the $^3\Sigma^+$ component as $^3\Sigma$ states and to those for which the

TABLE I. Asymptotes and binding mechanism. First column: fine-structure asymptote of the Rydberg atom. Second column: symmetries contributing to the molecular state. Third and fourth column: degeneracies g_3 and g_4 of the molecular states associated with Cs, np_j , $6s_{1/2}$ ($F = 3, 4$) asymptotes. Last column: s -wave scattering lengths contributing to the binding.

Rydberg asymptote	Contributions	g_3	g_4	Binding via	
$np_{1/2}$	$ \omega_r = 1/2$	$^1\Sigma^+, ^3\Sigma^+, ^1\Pi, ^3\Pi$	8	8	a_S, a_T
		$^3\Sigma^+, ^1\Pi, ^3\Pi$	6	10	a_T
$np_{3/2}$	$ \omega_r = 1/2$	$^1\Sigma^+, ^3\Sigma^+, ^1\Pi, ^3\Pi$	8	8	a_S, a_T
		$^3\Sigma^+, ^1\Pi, ^3\Pi$	6	10	a_T
	$ \omega_r = 3/2$	$^1\Pi, ^3\Pi$	14	18	...

binding results from both $^3\Sigma^+$ and $^1\Sigma^+$ components as $^{1,3}\Sigma$ states. The $^3\Sigma$ states are those that have been observed in previous experiments [7–9].

A Cooper minimum in the $6s_{1/2} \rightarrow np_{1/2}$ photoexcitation cross section of Cs [21] prevents the observation of states correlated to $np_{1/2}$ asymptotes and we thus focus on the states correlated to $np_{3/2}$ asymptotes. Potential-energy curves (PECs) for the long-range molecules are obtained by determining the eigenvalues of Eq. (2) as a function of the separation R between the atoms. We use the mapped Fourier-grid method [22] to obtain the vibronic eigenstates of these PECs. The PECs and vibrational wave functions of the $26p_{3/2}, ^3\Sigma$ and $26p_{3/2}, ^{1,3}\Sigma$ states, calculated for parameters derived from the analysis of our spectroscopic data, are depicted in Fig. 1. The $^3\Sigma$ PECs do not depend on the hyperfine state of the ground-state atom, while the $^{1,3}\Sigma$ state correlated to the $F = 3$ asymptote is more strongly bound than the $^{1,3}\Sigma$ state correlated to the $F = 4$ asymptote.

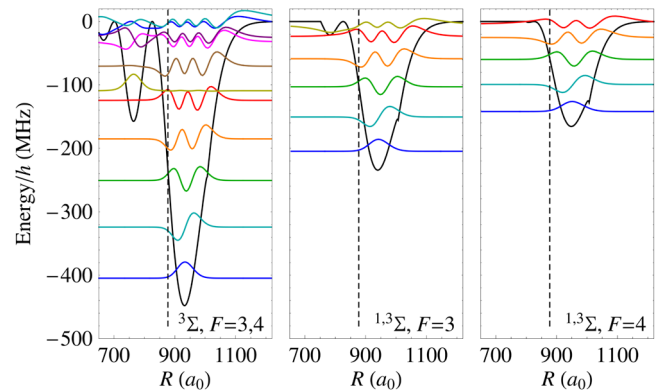


FIG. 1 (color online). Potential-energy curves (black lines) and vibrational wave functions (colored lines) for $^3\Sigma$ states dissociating to the $26p_{3/2}, 6s_{1/2}$ ($F = 3, 4$) asymptotes (left panel), and the $^{1,3}\Sigma$ states dissociating to the $26p_{3/2}, 6s_{1/2}$ ($F = 3$) asymptote (middle panel) and $26p_{3/2}, 6s_{1/2}$ ($F = 4$) asymptote (right panel). Vertical dashed lines mark the positions where the semiclassical Rydberg-electron energy equals the energy of the 3P_0 Cs- e^- scattering resonance (see text).

The long-range Cs_2 molecules are photoassociated from samples of ultracold Cs atoms (3×10^8 atoms at a density of $2 \times 10^{11} \text{ cm}^{-3}$ and a temperature of $40 \mu\text{K}$), released from a vapor-loaded compressed magneto-optical trap [23]. Stray magnetic and electric fields are compensated to below 2 mG and 20 mV/cm, respectively [18,24]. The atoms are optically pumped into one of the two hyperfine states ($F = 3, 4$) of the $6s_{1/2}$ ground state and excited with a single-mode cw UV laser (100 mW power, 5 MHz linewidth, $40 \mu\text{s}$ excitation pulse length) using intensities around 100 W/cm^2 . The frequency relative to the $np_{3/2}$ atomic resonance is calibrated at an accuracy of 5 MHz using a scanning Fabry-Perot cavity and a frequency-stabilized HeNe laser. After excitation, spontaneously formed ions [25] are detected with a microchannel-plate detector. On molecular resonances, we observe both atomic Cs^+ (attributed to Penning ionization) and molecular Cs_2^+ ions (attributed to associative ionization), the relative strength of the former increasing with the density of excited molecules.

Figure 2 presents photoassociation spectra of Cs atoms prepared in the $F = 3$ and $F = 4$ hyperfine levels to long-range Cs_2 molecules correlated to $np_{3/2}$ Rydberg states ($n = 26, 28, 32$, and 33). Several photoassociation resonances are observed on the low-frequency side of the strongly saturated atomic $6s_{1/2}(F = 3, 4) \rightarrow np_{3/2}$

resonances. The two most intense photoassociation resonances are assigned to the vibronic ground state of the $^3\Sigma$ and $^{1,3}\Sigma$ states. We determine the binding energies of the $^3\Sigma(v = 0)$ and $^{1,3}\Sigma(v = 0)$ levels for all n values between 26 and 34. In Fig. 3 these energies are compared to binding energies calculated with the model outlined above after adjustment of the zero-energy s -wave singlet ($a_{S,0}$) and triplet ($a_{T,0}$) scattering lengths, to $a_{T,0} = (-21.8 \pm 0.2)a_0$ and $a_{S,0} = (-3.5 \pm 0.4)a_0$, in a least-squares fit [26]. The fact that the adjustment of only two parameters permits the reproduction of 36 resonances within their experimental uncertainty of 5 MHz leaves no doubt concerning the validity of the assignments. As predicted by the model calculations (see also Fig. 1), the positions of the $^3\Sigma(v = 0)$ levels are identical for $F = 3$ and $F = 4$ within the experimental uncertainty whereas the $(F = 4), ^{1,3}\Sigma(v = 0)$ levels are less strongly bound than the $(F = 3), ^{1,3}\Sigma(v = 0)$ levels. An exception is found at $n = 32$, where the $^{1,3}\Sigma(v = 0)$ levels correlated to $32p_{3/2}, 6s_{1/2}(F = 3)$ and $32p_{3/2}, 6s_{1/2}(F = 4)$ have almost identical binding energies. This irregularity is well described by our model, which indicates that it originates from an accidental perturbation of the $32p_{3/2}, 6s_{1/2}(F = 3)$ state by the almost degenerate $32p_{1/2}, 6s_{1/2}(F = 4)$ state. Indeed, at $n = 32$, the $np_{1/2}-np_{3/2}$ fine-structure splitting, which scales as n^{*-3} , almost exactly matches the ground-state

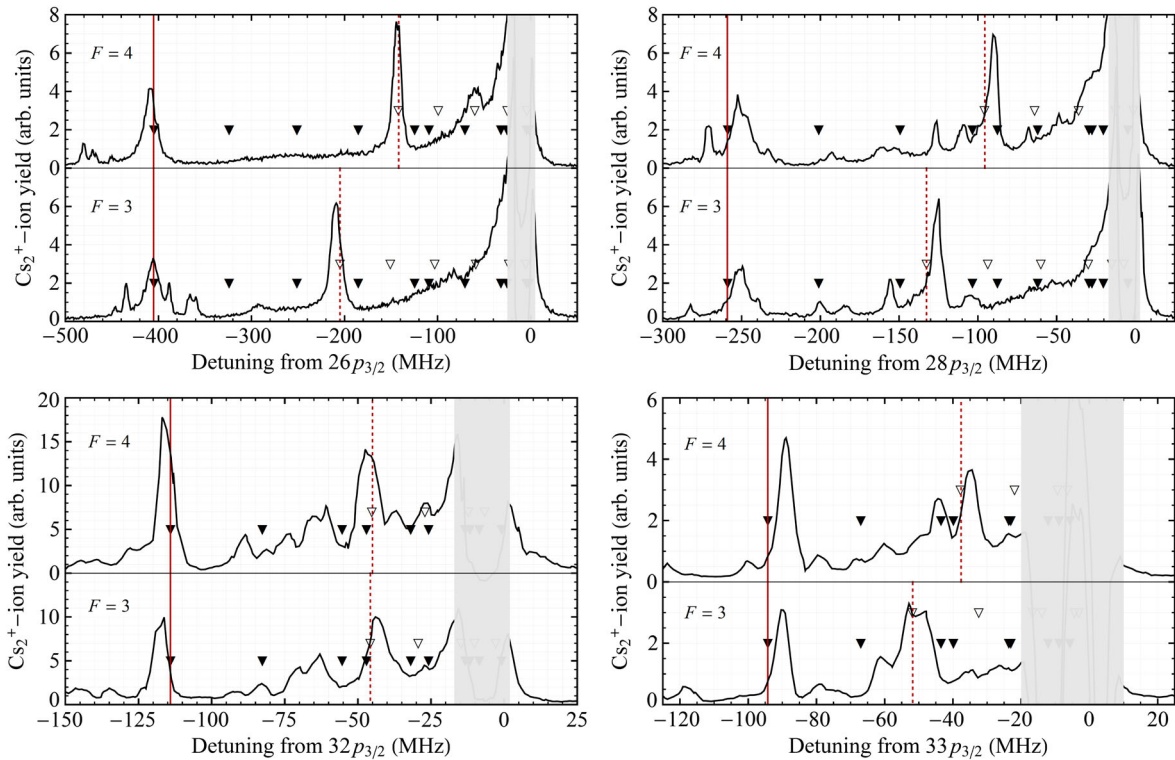


FIG. 2 (color online). Detected Cs_2^+ ions as a function of laser frequency relative to the $np_{3/2}, 6s_{1/2}(F = 3, 4)$ asymptotes. Solid (dashed) red lines mark the calculated positions of the $v = 0$ levels of $^3\Sigma$ ($^{1,3}\Sigma$) states. Calculated positions of higher vibrational levels are also shown (full and open triangles, respectively). The strongly saturated atomic transitions correspond to the gray areas.

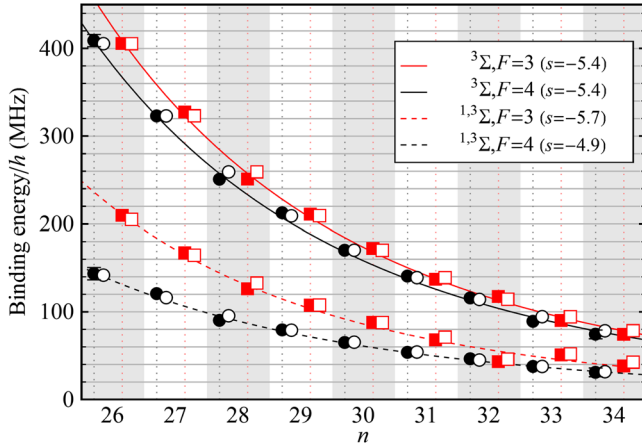


FIG. 3 (color online). Comparison of experimental (full symbols) and calculated (open symbols) binding energies of the ${}^3\Sigma(v=0)$ and ${}^{1,3}\Sigma(v=0)$ levels. The solid and dashed lines are fits of a $(n^*)^s$ scaling law to the experimental binding energies to guide the eye. Black and red symbols designate states with the ground-state atoms prepared in the $F=4$ and $F=3$ hyperfine level, respectively.

hyperfine splitting. The dependence of the ${}^3\Sigma(v=0)$ binding energies on the effective quantum number n^* deviates from the previously encountered n^{*-6} scaling [7] (see Fig. 3). Our calculation shows that this deviation is caused by the increasing contribution of higher-order, energy-dependent terms of the scattering length at lower n values.

Our values of the triplet and singlet s -wave scattering lengths are effective, model-based values obtained assuming that p -wave scattering is negligible. This assumption is fulfilled for low electron energies and in the absence of scattering resonances. The lowest p -wave scattering resonance (the 3P_0 shape resonance in Cs^- [27]) is located at an electron kinetic energy $p_c^2/(2m_e)$ of 4 meV [11], which is (in a semiclassical description) reached by the Rydberg electron at the critical radius r_c corresponding to $p_c^2 = [-(1/n^{*2}) + (2/r_c)]$, and marked in Fig. 1 by vertical dashed lines. Although the minima of the outermost potential wells are located beyond r_c and the $v=0$ levels should not be strongly affected by p -wave scattering for $n \geq 26$, Fig. 1 indicates that PECs for lower n values and excited vibrational levels of the outermost well could be significantly impacted by p -wave scattering channels. We believe this to be the reason for the inability of our effective s -wave scattering model to reliably predict the positions of excited vibrational levels, which are marked by triangles in Fig. 2, and of further resonances observed in our experiments for $n = 19$ –25.

Fabrikant [14] and, more recently, Bahrim *et al.* [15] calculated the e^- -Cs s -wave scattering lengths to be $a_{T,0} = -22.7a_0$ and $a_{S,0} = -2.4a_0$, and $a_{T,0} = -21.7a_0$ and $a_{S,0} = -1.33a_0$, respectively, from an effective-range-theory analysis of higher-energy scattering data. As a

measure of the deviation between experiment and theory, we consider the absolute error in the zero-energy scattering phase shift $\delta_0 = \arctan(a_i/R_{\text{pol}}) + \pi/4$ [28], where $R_{\text{pol}} = \sqrt{\alpha} = 20.05a_0$ is the typical range of the e^- -Cs interaction and α is the polarizability of the Cs ground-state atom. The deviation between experiment and theory is at most 0.1 rad and the agreement can thus be regarded as good. Our fitted model-based values may include effects of higher partial waves in the e^- -Cs scattering and interactions with Rydberg states other than the neighboring $(n-1)d_{3/2,5/2}$ states in an effective manner. The fact that our model reproduces the experimental observations well over a broad range of n from 26 to 34 suggests that these effects are not dominant.

The interaction operators \hat{V}_i in Eq. (2) mix the neighboring np and $(n-1)d$ Rydberg states and induce an electric dipole moment in the molecular frame [9,11,29]. For the $32p_{3/2}, 6s_{1/2}(F=4), {}^3\Sigma(v=0)$ states, our model predicts dipole moments between 21.0 and 25.8 D (mean value 24.4 D) for $|\Omega_{\text{tot}}|$ between 1/2 and 9/2. The dipole moments of the $32p_{3/2}, 6s_{1/2}(F=4), {}^{1,3}\Sigma(v=0)$ states are smaller and range from -0.5 to 12.0 D (mean value 5.6 D) for $|\Omega_{\text{tot}}|$ between 1/2 and 7/2. In an electric field we observe broadenings for these states that are in qualitative agreement with the expected Stark shifts; however, the spectra also reveal the strong perturbations due to field-induced state mixing [30] as observed in long-range Rb_2 dimers [29].

The prominent contributions of the long-range molecules in ${}^{1,3}\Sigma$ states to the photoassociation spectrum of Cs near the $np_{3/2}, 6s_{1/2}$ asymptotes implies that these states should also be observable in other systems. In Refs. [7,13], long-range Rb_2 molecules were studied by photoassociation of Rb atoms prepared in the $5s_{1/2}(F=2, m_F=2)$ level in a magnetic trap. Thus, only the shallow ${}^{1,3}\Sigma$ states correlating to the $ns_{1/2}, 5s_{1/2}(F=2)$ asymptotes could have been observed. Using a triplet s -wave scattering length of $a_{T,0} = -18.5a_0$ [7] and the literature value for $a_{S,0} = +0.627a_0$ [15] we predict the positions of the $v=0$ levels of the $n = 35$ –37 ${}^{1,3}\Sigma$ shallow potential wells listed in the column $E_{2,1,3\Sigma}^{\text{theor}}$ of Table II. Near these positions, all spectra

TABLE II. Experimental positions E_2^{expt} (MHz) of the ${}^3\Sigma(v=0)$ resonances correlated to ${}^{87}\text{Rb}, ns_{1/2}, 5s_{1/2}(F=2)$ asymptotes from Ref. [13], and calculated positions E^{theor} of $v=0$ levels in ${}^3\Sigma$ and ${}^{1,3}\Sigma$ states. Also given are $v=0$ binding energies $E_{F,1,3\Sigma}^*$ for $F=1, 2$ based on optimized values $a_{T,0} = -18.7a_0$ and $a_{S,0} = +1.0a_0$.

n	$E_{2,3\Sigma}^{\text{expt}}$	$E_{2,\uparrow}^{\text{expt}}$	$E_{2,3\Sigma}^{\text{theor}}$	$E_{2,1,3\Sigma}^{\text{theor}}$	$E_{2,1,3\Sigma}^*$	$E_{1,1,3\Sigma}^*$
35	-23.0	-3.8	-23.1	-3.9	-3.6	-11.0
36	-19.0	-2.9	-19.2	-3.2	-2.9	-9.1
37	-16.2	-2.3	-16.0	-2.6	-2.4	-7.5

presented in Fig. 2 of Ref. [13] show features marked by dashed lines at positions given in the column $E_{2,\dagger}^{\text{expt}}$ of Table II. After a small adjustment of $a_{S,0}$ to $1.0a_0$, our calculations of the positions of the $^{1,3}\Sigma(v=0)$ levels for $F=2$ match all experimental peak positions within 0.2 MHz (see column $E_{2,1,3\Sigma}^*$ in Table II). In Ref. [13], these resonances were, however, attributed to a purely atomic transition, the shift being the electron-spin Zeeman shift of the $ns_{1/2}$ Rydberg level. Our calculations for the $^{1,3}\Sigma(v=0)$ levels associated with the $F=1$ component of the ground-state level predict larger binding energies (see column $E_{1,1,3\Sigma}^*$ in Table II) and we hope that our predictions will be confirmed by future experiments with ultracold Rb samples prepared in the $F=1$ hyperfine component.

In previous studies of $^3\Sigma$ long-range Rb molecules correlated to $ns_{1/2}$ Rydberg states, not only dimers, but also trimers and even larger Rb_m molecules have been observed [31], the binding energies being proportional to the number $(m-1)$ of ground-state atoms. We have not observed any long-range molecules consisting of more than two atoms. We attribute this nonobservation to a reduction of the excitation probability of $m=3$ long-range Rydberg molecules by a factor of $(4\pi)^{-1}$ resulting from the change from spherical to linear geometry (imposed by the anisotropy of the p orbitals) when going from ns to np Rydberg levels.

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