

Experimental Verification of Minima in Excited Long-Range Rydberg States of Rb_2

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Recent theoretical studies with alkali atoms A^* excited to high Rydberg states predicted the existence of ultra-long-range molecular bound states. Such excited dimers have large electric dipole moments which, in combination with their long radiative lifetimes, make them excellent candidates for manipulation in applications. This Letter reports on experimental investigations of the self-broadening of Rb principal series lines, which revealed multiple satellites in the line wings. The positions of the satellites agree quantitatively with theoretically predicted minima in the excited long-range Rydberg states of Rb_2 .

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Two different types of bound Rydberg molecules have been proposed in recent years as intriguing candidates for possible study. In the first case [1–5], a bound state is created by the interaction between an excited atom (A^*) and a ground state atom (A). The properties of low-energy scattering of the quasifree electron of the Rydberg atom A^* on the perturber A create the attraction needed for dimer formation. These Rydberg molecules are comparable to the size of the excited atoms, and the corresponding electronic wave functions are characterized by specific spatial forms, two of which are the “trilobite” and “butterfly” states. These molecules are also predicted to be polar diatomic molecules possessing dipole moments (even the homonuclear species) that are huge compared to typical polar diatomic molecules. A growing body of theoretical evidence strongly suggests the existence of these unusual molecular states, whose Born-Oppenheimer potential curves oscillate like a wave function (see, e.g., Refs. [6–10]) But until now, their existence has not been confirmed experimentally. The second type of bound molecular Rydberg state is predicted to be created by the interaction of two Rydberg atoms $A^* + A^*$ at very large distances R [11]. Here, the potential energy curve can be exclusively described by the long-range electrostatic interaction.

Laser spectroscopic experiments performed in ultracold gases ([12–14] and references therein) have provided evidence for the existence of bound molecular Rydberg states of the $A^* + A^*$ type [12,14]. Our Letter is focused on the experimental verification of the oscillatory bound state potentials in the $\text{Rb}^* + \text{Rb}$ system associated with electron-atom scattering resonances. We apply the well-established method for spectral line wing absorption measurement under thermal conditions [15] that reveal satellites in the wings of collisionally broadened lines. The positions, shapes, and intensities of satellites depend on the difference potentials as functions of the interatomic separation R . We were encouraged to make such measure-

ments since peculiar satellite structures have been observed in the line wings of collisionally broadened principal series lines of Cs, dating back to more than 30 years ago [16,17]. The absolute satellite strengths in terms of reduced absorption coefficients were published later for the $6S - nP$ ($n = 8-13$) lines [18]. Similar satellite features have also been observed in Rb spectra (see remark in [18]), but never published, owing primarily to our poor understanding of the physical origin of these regular satellite features. The long history of investigations of far-wing alkali line broadening resulted, for the first resonance line of each species, in complete agreement between theory and experiment (see, e.g., [19]). Regarding the theory, there is a smooth transition between *ab initio* calculations and the perturbation approach using the long-range multipole interactions. Recent *ab initio* calculations also yielded a satisfactory explanation of the measured structure of the second principal series line of Rb, the $5S - 6P$ transition [20]. However, for the transitions to the third and higher resonance states neither *ab initio* nor the usual perturbation calculations can explain the pronounced satellite structures in the quasistatic region of the line wings.

The experiments were performed with a Rb vapor-filled heat pipe, using the classical white light absorption method with a tungsten-halogen lamp and a 0.75 m Czerny-Turner type monochromator supplied with a EMI 9789QA photomultiplier. Although the experimental arrangement is in principle very simple, the realization of the experiment required solving some technical problems connected with the production of a stable rubidium vapor at pressures of about 100 mbar (number density $N_{\text{Rb}} \geq 10^{18} \text{ cm}^{-3}$). This was necessary to get stable and measurable absorption in the line wings. The specific details of our experimental arrangement are given in [21] and will be repeated here only briefly. The rubidium vapor column was generated in the middle part of a stainless-steel heat pipe by the use of

an outer electric heater. Argon was used as a buffer gas to protect the quartz windows at the cold ends of the heat pipe oven from the corrosive influence of the hot rubidium vapor. The heat pipe was running in the heat pipe mode, i.e., the rubidium pressure was equal to the buffer gas pressure. It was possible to achieve a rubidium vapor pressure of about 200 mbar. However, it is well known that strong turbulent "fogs" (particle clouds) appear in the transition regions between the hot vapor and the cold buffer gas at vapor pressures larger than about 30 mbar. As shown in [21], this effect can be efficiently removed with a help of an additional rod heater built in along the heat pipe axis which accomplished stable rubidium vapor conditions by overheating the vapor. For example, for the maximum temperature of ~ 1100 K near to the central heater, the metal bath temperature at the heat pipe wall was ~ 800 K.

The absolute reduced absorption coefficients $k_R = k/N^2$ of the measured lines were obtained using the narrow triplet molecular band at 605 nm as a reference for N determination. The absorption of this molecular band was calibrated using the far-wing absorption of the first resonance lines [22], in the same way as for the corresponding potassium triplet band [18]. To avoid spectral interference of the line wings with the strongly temperature-dependent Rb dimer spectrum, we made spatially resolved absorption measurements in the overheated vapor. The spatially resolved absorption spectra were related to measurements in thin absorption columns at various distances from the heat pipe axis, i.e., in different temperature zones. By this the dissociation of the ground state dimers could be varied and dimer interferences with the atomic line shapes could be excluded. The reduced absorption coefficients of the principal series lines given below were found to be constant in the applied temperature range.

The measured reduced absorption coefficients $k_R = k/N^2$ of some principal series line are shown in Fig. 1. The satellite sequences in these spectra are similar to those found in the case of the Cs principal series lines [18]. As seen from Fig. 1, the shapes of higher $5S - nP$ lines become simpler. They are characterized by single sharp blue satellites and weak red shoulders. Because of their concise line shapes they seem to be appropriate candidates for the comparison of experiment and theory. Thus, our former calculations were extended from the high Rb Rydberg states around $n \sim 30$ [1,2,4] to the regime of lower-lying levels, from $9P$ to $12P$.

Previous studies of ultra-long-range Rb dimers have suggested that such extrema arise from two sources. First, the potential of the perturber interacting with any Rydberg state, even hydrogenic, gives rise to oscillatory features that reflect the underlying nodal structure of the Rydberg electron wavefunction. Second, for a nonhydrogenic molecule, the breaking of the degeneracy of a single n manifold due to the large quantum defects of the lower- l states places their energies at points intermediate to the

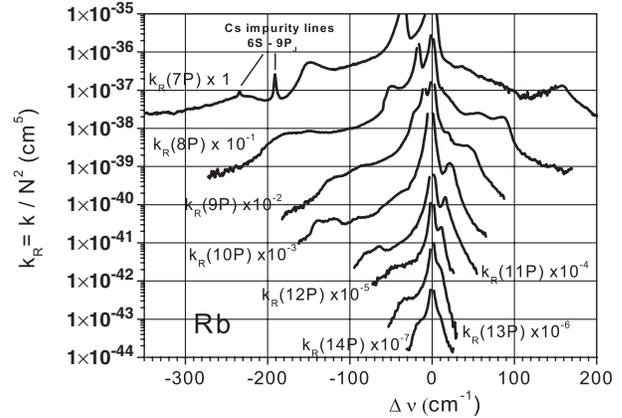


FIG. 1. The reduced absorption coefficients $k_R(nP) = k(nP)/N_{\text{Rb}}^2$ of the quasistatic wings of some Rb $5S - nP$ lines are plotted versus the wave number difference from the respective line centers. For better representation, the individual spectra have been multiplied by different factors of 10 as indicated.

energies of the high- l degenerate manifolds. Since the molecular Rydberg state includes some components of these states, the adiabatic potential can undergo avoided crossings with each of the unperturbed atomic potentials.

The short-ranged interaction of the Rydberg electron with the ground state perturber atom approaches a polarization potential far from the atom, and its center lies far from the ionic core where the Coulomb potential varies slowly with the radial electron-ion coordinate r . This allows the electron-perturber interaction to be approximated as the scattering of a quasifree electron of fixed local momentum from an atom. Far from the ion, a Rydberg electron has little kinetic energy. Importantly, the low-energy scattering of a p -wave electron from a neutral Rb atom displays a sharp triplet shape resonance [3,4]. It is this resonance that spawns avoided crossings and other extrema near the atomic nP absorption lines, and whose electronic structure resembles a butterfly when plotted as in Fig. 3 of [4]. Note that the previously predicted [1,2] trilobite states apparently have too little atomic P character to be visible in line-broadening experiments that excite directly out of the alkali atom ground states.

To perform a full *ab initio* calculation on the Rydberg electron states of such a molecule would be exceedingly difficult using existing quantum chemistry programs, due to the large number of coupled Rydberg states that contribute to the perturbed wave function and the large electron distances that are relevant. Through most of its range, however, the Rydberg electron is subject only to the Coulomb potential of the ionic core, modified by l -dependent quantum defects that cause the electron de Broglie waves to be phase shifted [23]. Only in the region of the perturber does the potential become more complicated. This has given reasonably accurate results using a zero-range approximation to the potential, as was generalized to higher- l scattering from the Fermi pseudo-

potential by Omont [24]. This method, however, suffers from instabilities related to divergent behavior close to a resonance energy, and thus becomes inaccurate in the regions of the potential giving rise to avoided crossings.

An alternative method that takes similar advantage of the simplicity of the potential away from the perturber utilizes the Coulomb Green's function, which gives an analytical solution to the wave function via the Kirchhoff integral method or similar techniques [4,5]. First the formal solution is written in terms of the Coulomb Green's function $G_c^{\text{mod}}(\vec{r}, \vec{r}')$, with appropriate modifying terms added to correct for the atomic Rydberg state quantum defects [5]. Application of Green's theorem converts the resulting expression into a surface integral over a sphere enclosing the perturber, which implies that we can interpret the ground state perturber as simply modifying the boundary conditions of the solution (for details see Eq. 14 of [3], or [25]). The matching surface must be sufficiently large that the scattering from the perturber can be described at that radius entirely in terms of the asymptotic phase shifts. Next the solution is expanded in partial waves at the boundary of the surface of integration using the spherical Bessel functions, $\Psi(\vec{r}) = \sum_{lm} A_{lm} [j_l(kx) \cos \delta_l - n_l(kx) \times \sin \delta_l] Y_{lm}(\theta_x, \phi_x)$. The effect of the perturber interaction is all contained in the phase shifts $\delta_l(\epsilon)$. Projecting Ψ onto the spherical harmonics gives a linear system of equations for the unknown coefficients A_{lm} . The bound state energies are associated with zeroes of a determinantal equation.

A detailed view of one absorption line is presented in Fig. 2, where the calculated difference potential curves around the Rb 11P level are compared with the measured shape of the 5S – 11P line. In the case of a single potential curve $V(R)$ the quasistatic formula for the reduced absorption coefficient is $k_R = \frac{4\pi^2 e^2 h}{mc} f(R) R^2 / |dV(R)/dR|$. At internuclear distances of interest the ground state potential is predominantly given by the van der Waals interaction [20]. According to data taken from [26], the corresponding C_6 coefficient is 4660 a.u., which, e.g., yields an interaction energy $\Delta E_0 \approx -0.065 \text{ cm}^{-1}$ at $R = 50$ a.u.. Therefore, the difference potential corresponds in practice to the excited state potential alone here. To calculate the theoretical line shape of k_R , the R -dependent oscillator strengths $f(R)$ are needed, but they have not yet been calculated in this study. Nevertheless, the correspondence between the extrema of the calculated potential curves and the satellite positions suggest that theory and experiment generally agree. This agreement for a range of n values seems unlikely to be fortuitous. Hence we regard this as a confirmation of the existence of oscillatory long-range potential curves in these Rydberg ground state molecule systems.

The general agreement between calculated potential curves and measured absorption profiles is illustrated in (Fig. 3.) Here the energy scale is converted to an effective quantum number scale using $E_n + \Delta E - E_0 = E_i -$

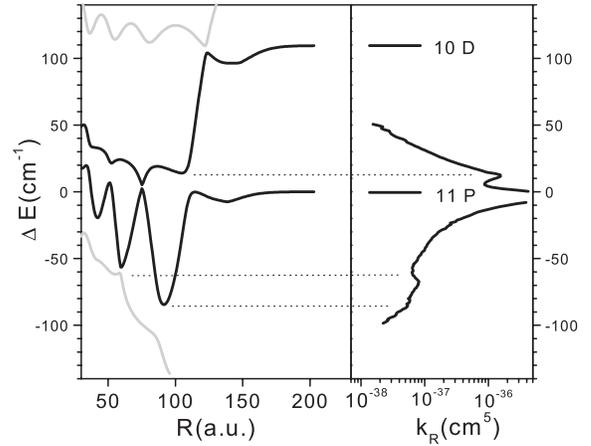


FIG. 2. $^3\Sigma$ Born-Oppenheimer difference potential curves in the vicinity of the Rb 11P level (left) compared with the measured reduced absorption coefficient of the Rb 5S – 11P line (right). The upper and lower gray potential curves are connected with the 12S and with the hydrogenic n, l states having $l \geq 3$, respectively. The strong blue satellite corresponds to the minimum of the potential curve that correlates adiabatically with the 10D level, the minimum originating from an avoided crossing between the steeply rising butterfly potential curve [4] and the 11P curve. The weak red-shifted shoulders correspond to minima in the potential curve that dissociates adiabatically to the 11P asymptote, but whose electronic character near the minima is also predominantly “butterflylike”.

$R_{\text{Rb}}/n_{\text{eff}}^2$, where E_i and R_{Rb} are the ionization limit and the Rydberg constant for Rb. On this scale, atomic and molecular levels with successive principal quantum numbers n are approximately equidistant, which provides insight into the theoretical and experimental regularities. The

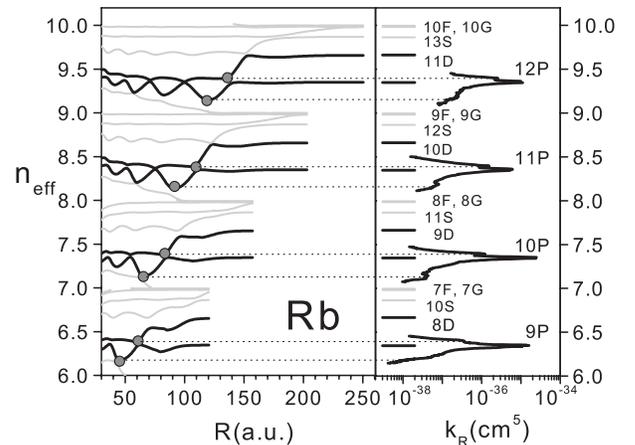


FIG. 3. Calculated $^3\Sigma$ Rb* – Rb Born-Oppenheimer excited state potential curves (left) and the relevant experimental line shapes (right) of the Rb 5S – nP ($n = 9, 10, 11, 12$) transitions. In contrast to Fig. 2, the energies are represented in terms of the effective principal quantum numbers n_{eff} . The positions of the potential curves minima which produce the line satellites are labeled by gray circles.

R values of the deepest potential minima expressed in Bohr radii scale roughly with $1.5n_{\text{eff}}^2$, as is expected for Rydberg state length scales. The positions of the line shoulders on the red line wings and the corresponding potential minima for the sequence are nearly constant ($\Delta n_{\text{eff}} = 0.25$). This means that an extrapolation of the experimental red satellites to the $5S - 30P$ line would reveal a potential depth of the $\text{Rb}^*(32P) - \text{Rb}(5S)$ molecular state comparable to what was predicted (≈ 30 GHz) in [4].

Preliminary absorption measurements of the self-broadening of the K principal series lines revealed very similar satellite structures as were found in Rb, although the strengths of the features were somewhat weaker. Thus the $\text{Cs}^* - \text{Cs}$ case, which displays the richest structure of multiple experimental satellites [18], appears to be the best example to study in order to refine the theory. However, it is necessary to include the spin-orbit coupling, much stronger than in Rb, because it has a nontrivial effect on the fine-structure intensity ratios, especially in the higher principal series lines (see, e.g., [27]).

In summary, we have presented experimental evidence for the phenomenon of oscillatory long-range potential curves, having the qualitative behavior that was predicted in Refs. [1,4,5]. Moreover, these unusual long-range Rydberg molecules provide an explanation for the origin of certain features that have been observed in line-broadening experiments for decades, but not successfully interpreted until now. To make the correspondence between theory and experiment clearer, it will be desirable to improve the Fermi-style zero-range description of the electron-perturber interaction potential. Because lower principal quantum numbers n are considered in the present experiment and theoretical analysis, higher electron-perturber collision energies occur than were important for the $n \sim 30$ states studied in Ref. [1]. This increased collision energy makes the zero-range theory less applicable for high precision quantitative purposes, but it nevertheless seems sufficient for the key points of the present interpretation. In the future it will be desirable to calculate the dipole matrix elements and to thereby hopefully achieve an understanding of the experimental spectra, at an improved level. Also interesting are $\text{K}^* - \text{K}$, which looks quite similar to $\text{Rb}^* - \text{Rb}$, and $\text{Cs}^* - \text{Cs}$, which shows many more oscillations and will stringently test theory because spin-orbit interactions are crucial. Experimentally, it is desirable to study higher principal quantum numbers, preferably in a multistep excitation that might permit the trilobite states to become observable.

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