

Two-Color Photoassociation Spectroscopy of Ground State Rb₂

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We determine the energies of twelve vibrational levels lying within 20 GHz of the lowest dissociation limit of ⁸⁵Rb₂ with two-color photoassociation spectroscopy of ultracold ⁸⁵Rb atoms. The levels lie in an energy range for which singlet and triplet states are mixed by the hyperfine interaction. We carry out a coupled channels bound state analysis of the level energies, and derive accurate values for ⁸⁵Rb₂ interaction parameters. The information obtained is sufficient to allow for quantitative calculations of arbitrary Rb ultracold collision properties. [S0031-9007(97)03822-2]

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An important reason for the interest in Bose-condensed, magnetically trapped alkali vapors [1–3] is that it is possible to understand many of their properties from first principles, starting with known atomic interactions. This close contact between theory and experiment requires accurate atomic interaction parameters such as elastic scattering lengths and inelastic collision cross sections. In principle these quantities can be computed from the atomic interaction potentials. Substantial progress has been made, for example, in the determination of Li [4–6], Na [7–9], and Rb [10–13] scattering lengths. Unfortunately, it has still not been possible to calculate many important collision properties because of uncertainties in the potential parameters.

In this Letter, we present new results that eliminate most of these uncertainties for Rb. We measure the energies of twelve of the highest bound vibrational levels of ground state ⁸⁵Rb₂ with two-color ultracold atom photoassociation spectroscopy. As illustrated in Fig. 1, ultracold ⁸⁵Rb atoms collide in the presence of two laser fields of frequency ν_1 and ν_2 . Resonances observed at specific values of the frequency difference $\nu_2 - \nu_1$ directly provide the level energies. We analyze the level energies with an inverse perturbation approach with coupled channels bound states, and obtain both singlet and triplet parameters. Two-color photoassociation spectroscopy has previously been used to obtain a single ground state level of Li₂ [5], and evidence for ground state levels of Na₂ [14]. Our work differs from this in that we obtain a much more complete spectrum, assignment, and analysis.

A unique aspect of our work is that we obtain a molecular spectrum for levels with binding energies comparable to the atomic hyperfine splitting. In this range singlet ($S = 0$) and triplet ($S = 1$) states are strongly mixed by the hyperfine interaction $V_{hf} = a(\mathbf{I}_1 \cdot \mathbf{S}_1 + \mathbf{I}_2 \cdot \mathbf{S}_2)$, so that molecular quantum numbers (S, I) are not good. Here $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$, $\mathbf{I} = \mathbf{I}_1 + \mathbf{I}_2$, and \mathbf{S}_i and \mathbf{I}_i are the electronic and nuclear spins of the two atoms ($i = 1, 2$), respectively. Atomic quantum numbers (f_1, f_2 , with $\mathbf{f}_i = \mathbf{S}_i + \mathbf{I}_i$) are not good either, since these states are mixed at short range by the exchange interaction. Only

the total spin quantum number F , with $\mathbf{F} = \mathbf{f}_1 + \mathbf{f}_2 = \mathbf{S} + \mathbf{I}$, is good at all internuclear distances. Adiabatic molecular potentials for ⁸⁵Rb₂ with the pure triplet ($F = 6$) potential subtracted off are shown in Fig. 2. The change between molecular and atomic (hyperfine) coupling occurs at about $24a_0$. Molecular vibrations on these potentials are not perfectly adiabatic, so that curves with the same F must be treated with a coupled channels approach.

The experiment is an extension of our previous one-color photoassociation experiments [10–12]. About 10^4 laser-cooled ⁸⁵Rb atoms, at a temperature of several hundred microKelvin and a density of about 10^{12} cm^{-3} , are spin-polarized in their $f = 3, m_f = 3$ state and held in a far-off resonance optical dipole force trap

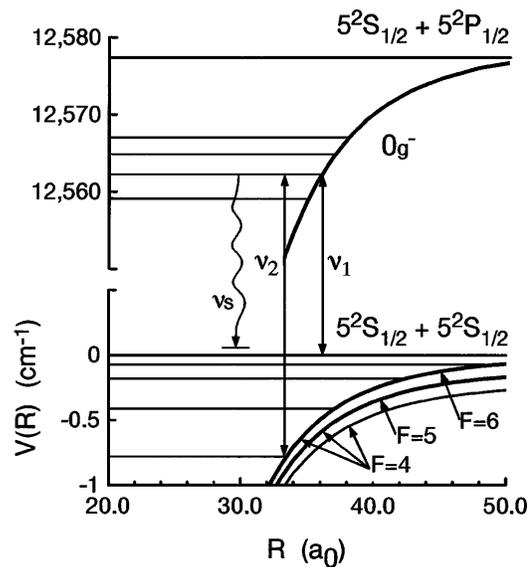


FIG. 1. Two-color photoassociation spectroscopy of ⁸⁵Rb₂. Colliding, trapped, ultracold ⁸⁵Rb atoms are irradiated by laser fields of frequency ν_1 and ν_2 . Spontaneous emission from the excited level at frequency ν_s leads to loss of the atoms from the trap. Optical double resonance (free-bound-bound) signals occur when the frequency difference $\nu_2 - \nu_1$ coincides with the binding energy of a ground state vibrational level.

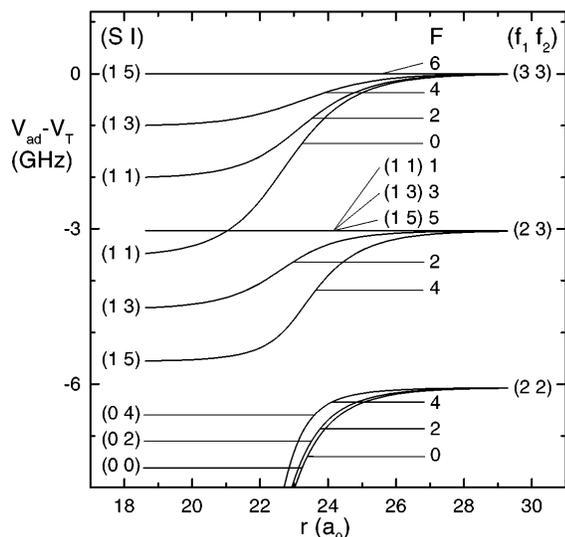


FIG. 2. Diagram showing the adiabatic molecular potentials for ground state $^{85}\text{Rb}_2$ with the pure triplet, $F = 6$ potential energy subtracted off. The potentials are labeled at short range by their molecular quantum numbers and at long range by their atomic quantum numbers.

(FORT) [15]. These atoms are irradiated for 200 ms with two laser fields of frequencies ν_1 and ν_2 , which have intensities of 1.6 kW/cm^2 , and $30\text{--}200 \text{ W/cm}^2$, respectively. These fields are alternated at 200 kHz with the FORT laser. The laser frequency ν_1 is fixed on a photoassociation resonance between the collision state and a $|0_g^-(\nu, J)\rangle$ excited state near the $5^2S_{1/2} + 5^2P_{1/2}$ dissociation limit, where ν is the vibrational quantum number and J the rotational quantum number. This induces substantial trap loss, since the excited states decay mostly to high kinetic energy atoms which escape from the trap. At the end of each 200 ms period, we measure the number of atoms remaining in the trap with laser-induced atomic fluorescence. We produce a two-color spectrum by stepping ν_2 through a succession of values.

A typical two-color photoassociation spectrum is shown in Fig. 3. We observe a decrease in the loss of atoms from the trap whenever ν_2 is tuned to a resonance between the intermediate level and a ground state level. This is due to power broadening of the excited state, which reduces the absorption rate of photons on the first step and therefore the trap loss. We took spectra with three different values of ν in the intermediate state, and with $J = 2$. The positions of the lines depended only on $\nu_2 - \nu_1$, and their widths varied from 0.060 to 0.30 GHz. We observed a total of twelve levels with the energies listed in Table I. In addition we supplemented the data with the energy of a g -wave shape resonance [12]. We estimated the errors from the differences between the positions of the same level in different spectra. We also took them to be at least $\pm 1/4$ of the linewidths, to allow for possible line shape effects [16], which we did not attempt to model. The highest level is bound by only 0.16 GHz. To our

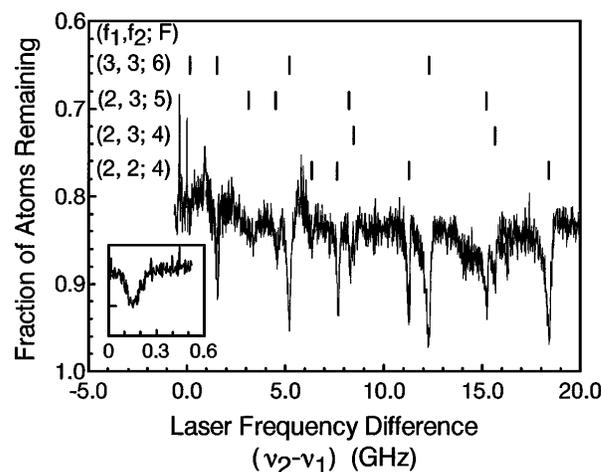


FIG. 3. Two-color photoassociation spectrum of $^{85}\text{Rb}_2$, with ν_1 tuned into resonance with a level at 12563.1 cm^{-1} . Double resonance signals are observable as a decrease in the trap loss. The positions and quantum numbers of the levels inferred from the analysis are also indicated. The inset at the lower left shows the highest level observed, with a binding energy of only 0.16 GHz.

knowledge, this is the most weakly bound level that has been spectroscopically observed in any molecule.

We assign the spectrum as follows. With a two-photon transition from the initial $M_F = 6$ state, only $F = 4, 5$, or 6 levels should appear in the spectrum. The $F = 6$ and $F = 5$ states are isolated, pure triplet channels, separated from each other by one unit of atomic hyperfine energy (3.036 GHz); see Fig. 2. Therefore, we may assign the vibrational progressions converging to the $(f_1, f_2) = (3, 3)$ and $(2, 3)$ limits to the $F = 6$ and $F = 5$ vibrational levels, respectively. The remaining levels must arise from

TABLE I. Experimental energy levels included in analysis and theoretical energy levels calculated with coupled-channel bound-states code, together with (f_1, f_2) progression and integer part of $\nu - \nu_D$. The $l = 4$ level included in the table is a shape resonance state observed in Ref. [12].

F	l	$E_{\text{exp}}(\text{GHz})$	$E_{\text{th}}(\text{GHz})$	$[\nu - \nu_D]$	(f_1, f_2)
6	4	$+0.015 \pm 0.002$	+0.013	-1	(3, 3)
6	2	-0.16 ± 0.03	-0.15	-1	(3, 3)
5	2		-3.18	-1	(2, 3)
4	2	-6.23 ± 0.06	-6.22	-1	(2, 2)
6	2	-1.52 ± 0.03	-1.50	-2	(3, 3)
5	2	-4.58 ± 0.06	-4.53	-2	(2, 3)
4	2	-7.61 ± 0.03	-7.57	-2	(2, 2)
6	2	-5.20 ± 0.03	-5.16	-3	(3, 3)
5	2		-8.20	-3	(2, 3)
4	2	-8.34 ± 0.06	-8.36	-3	(2, 3)
4	2	-11.27 ± 0.03	-11.24	-3	(2, 2)
6	2	-12.22 ± 0.06	-12.21	-4	(3, 3)
4	2		-12.51	-4	(3, 3)
5	2	-15.24 ± 0.06	-15.25	-4	(2, 3)
4	2	-15.67 ± 0.06	-15.68	-4	(2, 3)
4	2	-18.39 ± 0.06	-18.34	-4	(2, 2)

the three coupled, $F = 4$ potentials, and have mixed singlet and triplet character. As discussed previously [10], with the $0_g^- (\sim 5^2S_{1/2} + 5^2P_{1/2})$ intermediate state, we probe ground rotational states with $l = J = 2$.

To carry out an analysis of these spectra, we have developed an inverse perturbation approach for coupled bound states (coupled IPA). The usual (uncoupled) IPA [17] is a systematic approach to improve an approximate interaction potential $V^0(r)$ on the basis of a comparison of its bound-state energy eigenvalues E_n^0 with experimental values E_n . Changing the potential to $V^0(r) + \Delta V(r)$ changes the energies in first-order perturbation theory by

$$E_n - E_n^0 = \langle \phi_n^0 | \Delta V(r) | \phi_n^0 \rangle, \quad (1)$$

with known unperturbed eigenfunctions ϕ_n^0 . Writing the correction $\Delta V(r)$ as a linear combination of suitably chosen basis functions $f_i(r)$,

$$\Delta V(r) = \sum_i c_i f_i(r), \quad (2)$$

turns Eq. (1) into a set of linear equations which allows one to determine optimal expansion coefficients c_i .

Our method differs in two aspects from this approach. First, we incorporate coupled channels bound states, extending the expectation value (1) to a multichannel state. Second, we replace the atomic interaction inside $r = r_0$ with a boundary condition at r_0 on the phases ϕ_S and ϕ_T of the singlet and triplet radial wave functions [4]. We choose $r_0 = 20a_0$, small enough that singlet-triplet mixing inside r_0 is negligible, but large enough that the potentials outside r_0 have a simple description involving few parameters. In our version of IPA, we supplement the equation for the perturbation of the outer solution due to a change ΔV by an equation for the perturbation due to a change in ϕ_S and ϕ_T , making use of boundary perturbation theory [18]. An advantage of our method compared to the conventional IPA is that the set of parameters to be determined is more unique than in Eq. (2), where a subtle choice of basis functions is needed to avoid unrealistic adaptations of the potential. Our method also has the advantage that it treats singlet and triplet states simultaneously. A separate construction of singlet and triplet potentials from measured levels may lead to inconsistencies, as pointed out by Zhao *et al.* [19]. As in conventional IPA we apply our method in an iterative way. In each step we solve the equations for the first-order perturbations to find new parameter values. These then define the new unperturbed solution of Schrödinger's equation for the next step. The perturbation equations are also used to estimate error bars for the parameter values extracted from the coupled IPA analysis.

We write the long-range ($r > r_0$) interaction part of the two-atom Hamiltonian in the form

$$V = -C_6/r^6 - C_8/r^8 - C_{10}/r^{10} + V_{\text{exch}} + V_{\text{hf}}. \quad (3)$$

C_6 is taken to be 4550 ± 100 a.u. [12], the exchange part is from Smirnov and Chibisov [20], and C_8 and

C_{10} from Marinescu *et al.* [21]. We neglect the long range spin-dipolar interaction between the atoms, because its contribution to the level energies is small compared to the experimental accuracy. The inner part of the singlet potential has been determined by Amiot [22] by means of a conventional IPA. We adjust the zero of Amiot's energy scale to agree with a new, precise value of the Rb_2 dissociation energy $D_e = 3993.53 \pm 0.06 \text{ cm}^{-1}$ [23]. From this adjusted singlet potential, we calculate $\phi_S(E, l)$ for arbitrary energy E and relative orbital angular momentum l . We treat $\phi_S(0, 0)$ as a fit parameter in the analysis, and the calculated variation of $\phi_S(E, l)$ with E and l as boundary conditions for the $r > r_0$ IPA problem. For the triplet state no accurate potential is available, so we treat $\phi_T(0, 0)$ and its first derivatives with respect to E and $l(l+1)$ at $E = l = 0$ as variable parameters.

We begin by analyzing the pure triplet ($F = 5, 6$) states. The optimal phase parameters allow us to calculate the $^{85}\text{Rb} + ^{85}\text{Rb}$ triplet scattering length to be $a_T(^{85}\text{Rb}) = (-440 \pm 140)a_0$, consistent with the value $(-400 \pm 100)a_0$ from Ref. [12]. Uncertainties of 2% in C_6 and 4% in C_8 and C_{10} are accounted for in the final error limits. The corresponding nonintegral s -wave vibrational quantum number at dissociation $\nu_{DT}(\text{mod } 1)$ has the value 0.95 ± 0.01 , where the integer part of ν_{DT} is 37 ± 1 [12].

Next we analyze the complete set of levels. Varying $\phi_S(0, 0)$ alone, the six measured $F = 4$ levels fall in place within their experimental bounds. All of the theoretical $F \geq 4, l = 2$ eigenvalues in the last 20 GHz resulting from the combined optimization are presented in Table I. We obtain satisfactory agreement with the experimental levels. The triplet scattering length from the combined analysis is identical with the value given above. For the singlet scattering length, we find $+4500a_0 < a_S(^{85}\text{Rb}) < +\infty$ or $-\infty < a_S(^{85}\text{Rb}) < -1200a_0$. The corresponding ν_{DS} is 122.994 ± 0.012 , where in this case the integer part is quite certain. Our value shows a small discrepancy with the value $123.45(0.20)$ determined by Amiot [22].

A remarkable property of four of the observed $F = 4$ levels is their rather accurate triplet progression asymptotic to the $(f_1, f_2) = (2, 2)$ collision threshold. This results from an approximate equality between singlet and triplet phases for $^{85}\text{Rb}_2$ in the coupling region. Because of this, the highest parts of the uncoupled triplet and singlet bound state spectra approximately coincide, and the triplet and singlet interaction potentials are effectively interchangeable. The hyperfine mixing, which takes place almost exclusively at long range where the atoms are almost all of the time, then leads to a spin structure of the coupled states that is almost identical to that in the three asymptotic hyperfine channels. The calculation also shows similar $F = 4$ level progressions asymptotic to the $(f_1, f_2) = (2, 3)$ and $(3, 3)$ thresholds, and some of these levels are observed experimentally. In Table I we present for each predicted level the (f_1, f_2) combination

characterizing the progression it belongs to and its vibrational quantum number relative to ν_D . $F = 4$ levels above the $(f_1, f_2) = (2, 2)$ limit are not given since they are not bound. A very similar phase coincidence has been found to be responsible for the stability of a Bose-condensed mixture of two states of ^{87}Rb [24,25]. Considering the mass scaling of the wave function phases between ^{87}Rb and ^{85}Rb , it turns out that an approximate equality of ϕ_S and $\phi_T \pmod{\pi}$ in one isotope implies a similar equality in the other.

In combination with other recent results, our measurements have now determined Rb interaction parameters to sufficient accuracy to allow quantitative calculations of Rb cold collision cross sections to be carried out. Calculations based on these parameters [26] are in agreement with all known properties of cold Rb atom scattering [10–13,24,25]. The strong consistency among these measurements provides confirmation for their validity. In addition, it is now possible to precisely calculate other important cold collision properties such as the scattering lengths for arbitrary Rb sublevels, the location of magnetically tunable Feshbach resonances [26], inelastic collision rates, and the collisional frequency shift of a Rb atomic fountain clock [27]. We anticipate that future studies of ultracold Rb collisions will rest on a quantitative footing that is unusual in cold collision physics.

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- [1] M. H. Anderson, J. R. Ensher, M. R. Matthews, C. E. Wieman, and E. A. Cornell, *Science* **269**, 198 (1995).
- [2] K. B. Davis, M.-O. Mewes, M. R. Anderson, N. J. van Druten, D. S. Durfee, D. M. Kurn, and W. Ketterle, *Phys. Rev. Lett.* **75**, 3969 (1995).
- [3] C. C. Bradley, C. A. Sackett, and R. G. Hulet, *Phys. Rev. Lett.* **78**, 985 (1997).

- [4] A. J. Moerdijk, W. C. Stwalley, R. G. Hulet, and B. J. Verhaar, *Phys. Rev. Lett.* **72**, 40 (1994).
- [5] E. R. I. Abraham, W. I. McAlexander, C. A. Sackett, and R. G. Hulet, *Phys. Rev. Lett.* **74**, 1315 (1995).
- [6] E. R. I. Abraham *et al.*, *Phys. Rev. A* **53**, R3713 (1996).
- [7] A. J. Moerdijk and B. J. Verhaar, *Phys. Rev. Lett.* **73**, 518 (1994).
- [8] E. Tiesinga, C. J. Williams, P. S. Julienne, K. M. Jones, P. D. Lett, and W. D. Phillips, *J. Res. Natl. Inst. Stand. Technol.* **101**, 505 (1996).
- [9] K. B. Davis, M.-O. Mewes, M. A. Joffe, M. R. Andrews, and W. Ketterle, *Phys. Rev. Lett.* **74**, 5202 (1995).
- [10] J. R. Gardner, R. A. Cline, J. D. Miller, D. J. Heinzen, H. M. J. M. Boesten, and B. J. Verhaar, *Phys. Rev. Lett.* **74**, 3764 (1995).
- [11] H. M. J. M. Boesten, C. C. Tsai, J. R. Gardner, D. J. Heinzen, and B. J. Verhaar, *Phys. Rev. A* **55**, 636 (1997).
- [12] H. M. J. M. Boesten, C. C. Tsai, B. J. Verhaar, and D. J. Heinzen, *Phys. Rev. Lett.* **77**, 5194 (1996).
- [13] N. R. Newbury, C. J. Myatt, and C. E. Wieman, *Phys. Rev. A* **51**, R2680 (1995).
- [14] K. M. Jones, S. Maleki, L. P. Ratliff, and P. D. Lett, *J. Phys. B* **30**, 289 (1997).
- [15] J. D. Miller, R. A. Cline, and D. J. Heinzen, *Phys. Rev. A* **47**, R4567 (1993).
- [16] J. L. Bohn and P. S. Julienne, *Phys. Rev. A* **54**, R4637 (1996).
- [17] C. R. Vidal, *Comm. At. Mol. Phys.* **17**, 173 (1986).
- [18] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953).
- [19] G. Zhao *et al.*, *J. Chem. Phys.* **105**, 7976 (1996).
- [20] B. M. Smirnov and M. I. Chibisov, *JETP* **21**, 624 (1965).
- [21] M. Marinescu, H. R. Sadeghpour, and A. Dalgarno, *Phys. Rev. A* **49**, 982 (1994).
- [22] C. Amiot, *J. Chem. Phys.* **93**, 8591 (1990).
- [23] C. C. Tsai, J. D. Miller, R. A. Cline, and D. J. Heinzen (to be published).
- [24] C. J. Myatt, E. A. Burt, R. W. Ghrist, E. A. Cornell, and C. E. Wieman, *Phys. Rev. Lett.* **78**, 586 (1997).
- [25] S. J. J. M. F. Kokkelmans, H. M. J. M. Boesten, and B. J. Verhaar, *Phys. Rev. A* **55**, R1589 (1997); P. S. Julienne, F. H. Mies, E. Tiesinga, and C. J. Williams, *Phys. Rev. Lett.* **78**, 1880 (1997); J. P. Burke, Jr., J. L. Bohn, B. D. Esry, and C. H. Greene, *Phys. Rev. A* **55**, R2511 (1997).
- [26] J. M. Vogels, C. C. Tsai, R. S. Freeland, S. J. J. M. F. Kokkelmans, B. J. Verhaar, and D. J. Heinzen (to be published).
- [27] S. J. J. M. F. Kokkelmans, B. J. Verhaar, D. J. Heinzen, and K. Gibble (to be published).