Photoassociation Spectrum of Ultracold Rb Atoms

J. D. Miller, R. A. Cline, and D. J. Heinzen
Department of Physics, The University of Texas, Austin, Texas 78712
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We study the photoassociative collisional loss of laser-cooled Rb atoms from a far-off resonance optical dipole force atom trap. We obtain a well-resolved photoassociation spectrum from 50 cm^{-1} to 980 cm^{-1} below the first excited dissociation limit of the Rb_2 molecule. Two vibrational series associated with excited Rb_2 $^3\Sigma_g^+$ states are clearly visible. Oscillations in the associated Franck-Condon factors reflect the structure of the triplet ground state wave function. Our results clearly demonstrate the potential of photoassociation spectroscopy as a new probe of molecular structure.

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Recent and ongoing studies of ultracold ($T < 1$ mK) atomic collisions are revealing a rich variety of new phenomena [1–3]. Many new features arise because these collisions occur so slowly that the probability of stimulated and spontaneous radiative transitions during a collision can approach unity. Such optical transitions have been shown to play crucial roles in the dominant collisional loss processes in optical atom traps [1–4], and in the associative ionization of ultracold atoms [2,3]. Another dramatic possibility, first discussed by Thorsheim, Weiner, and Julienne (TWJ) [5], is that colliding, ultracold atoms could display a resolved photoassociation spectrum. As illustrated in Fig. 1, in this process a colliding pair of atoms initially has an energy $\sim k_B T$ relative to the dissociation limit of the ground state dimer. During the collision, these atoms can resonantly absorb a laser photon of frequency ω_L to produce a bound, excited molecule. As ω_L is tuned, resonant absorption peaks can occur when $\hbar\omega_L$ matches the energy difference between bound excited molecular states and the initially free state. A crucial point is that the energy spread of the initial collisional state is so small at low temperature (e.g., $k_B T/h = 21$ MHz at $T = 1$ mK) that the free-bound absorption lines can have a sharpness comparable to those normally associated with spectroscopy between bound states [5]. Furthermore, the photoassociation rate for ultracold collisions can be very large because of the large near-threshold free-bound Franck-Condon factors [5]. Cold atom photoassociation is of interest as a novel bond-formation mechanism and as a new spectroscopic method. Because the Franck-Condon factors are largest for transitions at long range, it is well suited to probing highly excited, long range molecular states which are difficult to reach with conventional bound-bound molecular spectroscopy. (Multiphoton techniques to do this have been developed in some cases [6].) Also, because the initial state is formed in a collision, both singlet and triplet states may be probed [5].

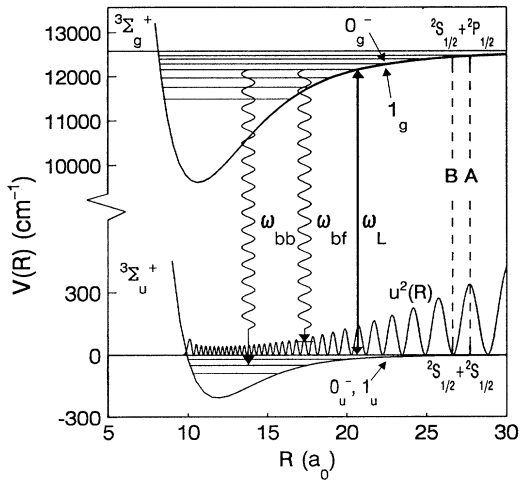

FIG. 1. Cold atom photoassociation in the lowest triplet states of Rb_2. Excitation of a colliding pair of Rb atoms by a photon of frequency ω_L forms an excited Rb_2 molecule, and is followed by spontaneous decay at frequency ω_{bb} or ω_{bf}. The excited $^3\Sigma_g^+$ state splits into 0_g^- and 1_g long-range states before converging to the first excited dissociation limit. The square of an approximate ground state radial wave function $u(R)$ of the initial collisional state is also shown.

In this paper, we present a photoassociation spectrum obtained in an experiment with Rb atoms confined in a far-off resonance optical dipole force atom trap [7,8]. We detect the free-bound absorption peaks by measuring the resulting loss of atoms from our trap rather than detecting the subsequent spontaneously emitted photons [5]. Our work differs substantially from previous cold atom collision experiments in that bound level structure plays a dominant role and that we probe a much larger region of tuning—up to 980 cm^{-1} below the first excited dissociation limit of Rb_2. For previous studies of trap loss collisions the laser detuning was much less than 1 cm^{-1}, and the collisional mechanisms could be understood without reference to bound molecular structure [1,4]. Evidence of resolved structure has been seen in recent Na "photoassociative ionization" experiments [2], and a resolved spectrum spanning a range up to 3 cm^{-1} from the excited Na_2 dissociation limit has recently been ob-

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tained [3]. Together with our work, these observations constitute the first well-resolved free-bound absorption spectra.

In our experiment, ^{85}Rb atoms are loaded into a far-off resonance optical dipole force trap (FORT) [7,8] from a vapor cell magneto-optical atom trap (MOT) [9], as described previously [8]. Briefly, the FORT consists of a single, linearly polarized, TEM_{00} mode Gaussian laser beam focused to a waist $w_0 = 10.2 \pm 1.2$ μm. Its power is between 1.3 and 1.6 W, its linewidth is 0.4 cm^{-1}, and its wavelength λ_L is varied between 798 and 860 nm, which is always to the red of the $5^2S_{1/2}$-$5^2P_{1/2}$ ($D1$) transition of Rb at 795 nm. To load the trap, we first turn on the MOT continuously for 25 ms. Then, we superimpose the FORT trapping beam onto the MOT for 25 ms, alternating at 200 kHz between the MOT and FORT trapping beams. We then turn the MOT off and the FORT fully on. Approximately 2700 atoms are loaded into the FORT, and from previous studies [8] we expect that their temperature is between 0.4 and 0.7 mK, and that their peak density n_0 at $\lambda_L = 822$ nm is between 3×10^{11} and 4×10^{12} cm^{-3}.

After each loading cycle we wait for an additional delay time of 100 ms. During this time, stimulated free-bound transitions are driven by the trapping laser at frequency $\omega_L = 2\pi c/\lambda_L$ (Fig. 1). In our experiment, any colliding pair which absorbs a photon will be lost from the experiment with a probability of order 1. A subsequent spontaneous decay by emission of a photon at frequency $\omega_{bf} < \omega_L$ will occur predominantly to free states of much higher kinetic energy than the initial state, which quickly escape from the trap (Fig. 1). Decay by emission of a photon of frequency $\omega_{bb} > \omega_L$ will produce a bound, ground state molecule which also results in the loss of trapped atoms. After the delay time, we probe the number of atoms remaining in the trap with laser-induced fluorescence. In order to produce a spectrum we repeat the measurement cycle at a succession of frequencies separated by about 0.18 cm^{-1}. We calibrate the laser frequency sweep to an accuracy of ± 0.1 cm^{-1} with an optogalvanic signal from a U hollow cathode discharge lamp, and interference fringes from two quartz etalons.

The results of the experiment are illustrated in Fig. 2. This spectrum was obtained with 27 500 loading, delay, and measurement cycles. The signal is proportional to the number of atoms remaining in the trap after the delay time, with increasing signal plotted downward from origin at the top of the graph. Remarkably, a spectrum consisting of more than 150 well-resolved lines is observed. The density of lines in the spectrum increases as the dissociation limit is approached, as expected from the increasing density of states for the roughly $1/R^3$ excited state potentials [10]. Also, the intensity of the lines increases as the dissociation limit is approached, which is expected because the free-bound Franck-Condon factors become larger and because the atomic density in our trap increases.

In order to understand the spectrum in more detail, we compared it to the vibrational energy eigenvalues of analytical model potentials. (Rotational structure may be ignored because only a few rotational states are excited in these low temperature collisions, with spacings that are less than the experimental resolution.) Little experimental information is available for the Rb_2 excited states, so we chose potentials which closely matched theoretical Rb_2 potentials [11,12]. There are six long-range attractive states which possess bound states in the energy range of interest and are optically coupled to the ground state [11]. The 0_g^-, 1_g, and 0_u^+ long range states which connect to the $5^2S_{1/2}+5^2P_{1/2}$ asymptote should dominate the spectrum because they are the longest range states throughout the energy range probed in the experiment, and therefore have the highest density of states and largest Franck-Condon factors. The 0_g^- and 1_g states connect at short range to the $^3\Sigma_g^+$ state (Fig. 1). The 0_u^+ state connects to the $^1\Sigma_u^+$ state and should contribute somewhat less strongly because the collisions create 3 times fewer singlet than triplet states. The remaining states connect to the $^1\Pi_g$ and $^3\Pi_u$ states at short range.

One striking feature of the spectrum is the two regular vibrational series labeled by the solid and dashed vertical lines in Fig. 2. These series correspond very closely to the calculated spectra for the 0_g^- and 1_g states shown in Fig. 1, with the level spacings agreeing to a few percent. Also, like the model spectra, the spacings of the two series are very close to each other, with the 0_g^- series having one more line than the 1_g series between 11 700 and 12 300 cm^{-1}. We therefore identify the series labeled by solid lines as belonging to $^3\Sigma_g^+(0_g^-,v) \leftrightarrow {}^3\Sigma_u^+(E=0)$ transitions, and the series labeled by dashed lines as belonging to $^3\Sigma_g^+(1_g,v) \leftrightarrow {}^3\Sigma_u^+(E=0)$ transitions, where $v \approx 70$ to 125 for the labeled peaks. $E=0$ corresponds to the ground state dissociation limit. These two series account for about 65% of the identifiable lines, and the remaining lines do not show additional vibrational series of the same completeness as the first two. In several parts of the spectrum three or four successive lines are observed with spacings that are consistent with our calculated 0_u^+ spectrum, but not enough of the series is visible to positively identify it. Also, there are more lines than can be accounted for by just the 0_u^+ state, so some of the additional lines must come from levels associated with the excited Π states.

A further very noticeable feature of the spectrum is the oscillation in the intensity of the lines, as illustrated by the inset curves of Fig. 2 for the 0_g^- and 1_g series. These oscillations are similar to those predicted by TWJ [5], and can be understood from a simple model in which the excited state wave function is assumed to be concentrated near its outer turning point. If this outer turning point lies above an antinode in the initial ground state wave function $u(R)$, the Franck-Condon factor will be large, as illustrated by the dashed line "A" in Fig. 1. At a slightly lower energy the outer turning point will lie above

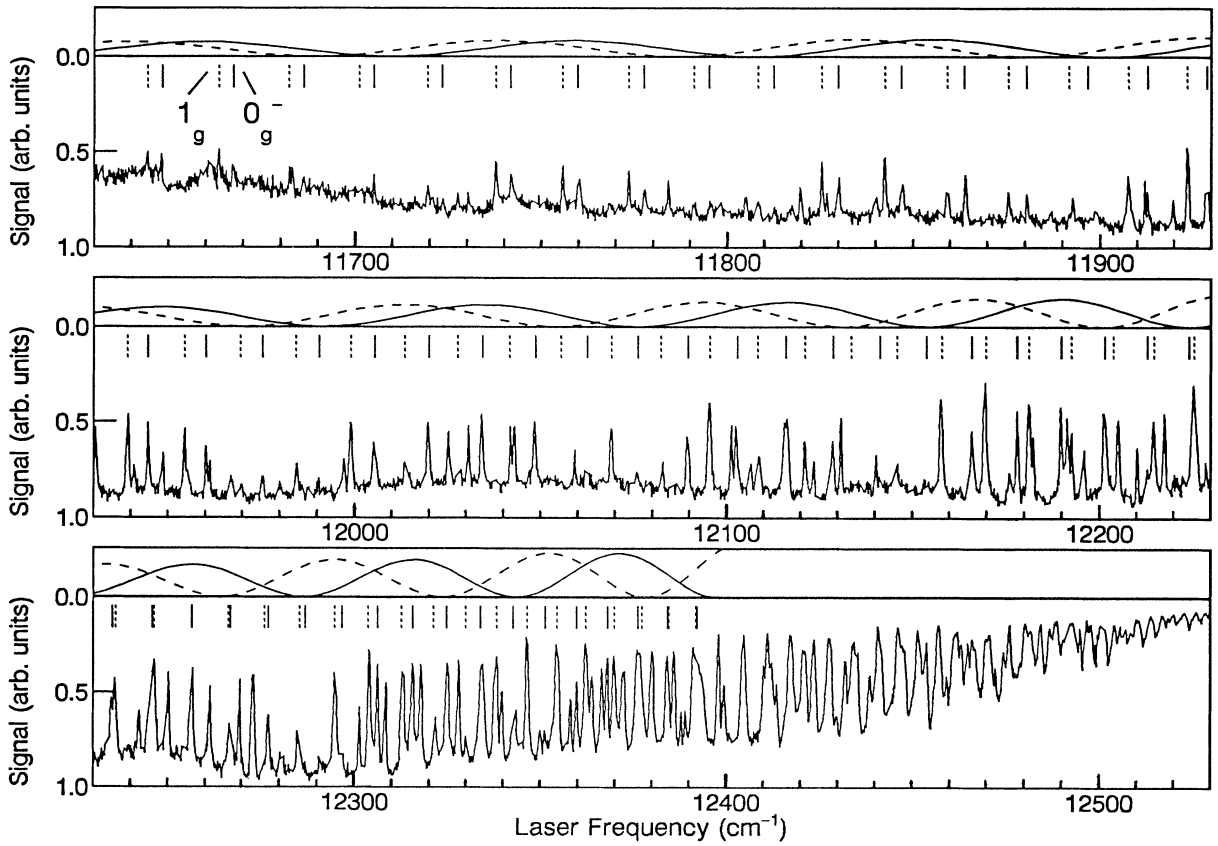

FIG. 2. Photoassociation spectrum of laser-cooled Rb atoms. The vertical axis corresponds to increased photoassociative loss of atoms from a far-off resonance optical dipole trap. The atomic $D1$ resonance occurs at 12578.9 cm^{-1}. Two vibrational series, indicated by the dashed and solid vertical lines, are clearly visible and are associated with the vibrational levels of the $^3\Sigma_g^+$ states illustrated in Fig. 1. The inset curves show the approximate variations in the Franck-Condon factors for these two series.

a node in $u(R)$ and the Franck-Condon factor will be small, as illustrated by the dashed line "B" of Fig. 1. In this way a further lowering of the energy will produce a series of maxima and minima. Our theoretical $u^2(R)$, when projected onto the outer turning points of our excited state potential curves, predicts Franck-Condon oscillations which are very similar to those shown in Fig. 2. An important point is that given the excited state potentials, these Franck-Condon oscillations provide information about the ground state potential [12].

In our experimental regime, photoassociation appears as a very efficient trap loss process. We measured trap decay curves on the photoassociation peaks and found that they have the nonexponential shape expected for trap loss collisions [1]. On the peak at 12170 cm^{-1}, the volume-averaged initial decay rate is $\langle \beta n \rangle = 18.2 \pm 0.4$ s^{-1}, which corresponds to a rate coefficient β between 1.4×10^{-11} and 1.7×10^{-10} cm^3/s. This is in rough agreement with the saturated rate constant for Na calculated by TWJ [5], when extrapolated to 0.5 mK. Even with our large laser bandwidth, our laser intensity should be near saturation. For our conditions, the spectrum becomes practically continuous and the trap loss rate becomes very large within 100 cm^{-1} of atomic resonance. These results explain our earlier observations of wavelength-dependent loss of atoms from the FORT [8]. The very large rate constant above 12500 cm^{-1} may be partly a result of attractive interactions between the atomic dipoles induced by the trapping laser.

We envision a variety of interesting extensions of this work. With further work it should be possible to more completely assign the spectrum. Experiments with spin-polarized atoms would yield only triplet states in a collision and give a simpler spectrum [12,13]. With a two-laser experiment, one laser could trap the atoms with negligible trap loss, and a second lower intensity, high-resolution laser could be scanned over the photoassociation spectrum. In this way a high-resolution spectrum extending to both the $^2S_{1/2}+{}^2P_{1/2}$ and $^2S_{1/2}+{}^2P_{3/2}$ dissociation limits could be obtained, possibly allowing an absolute assignment of the lines relative to the last bound state. Resolved rotational or hyperfine structure could

aid in the spectral assignment. Shape resonances arising from the ground state centrifugal barrier may be observable [5]. A rich variety of other novel features expected for these weakly bound, long-range molecules might be studied [14]. "Pure long range" molecular states which have both turning points at long range might be visible [15]. Free-bound-bound double optical resonance experiments to probe the molecular ground states would be of interest. Of the order of 10% of the excited molecules will decay to produce bound ground state molecules [5]. These product molecules might be detectable with ionization followed by mass-selective ion detection. An interesting point is that these molecules would be ultracold and may possibly be trapped in the FORT. These techniques should also be applicable to any diatomic species in which the two elements can be laser cooled and held in a dipole trap.

In summary, we have obtained a photoassociation spectrum of ultracold Rb atoms by measuring trap loss in a far-off resonance optical dipole trap. For our trapping conditions, photoassociation is the dominant trap loss mechanism for laser tunings within 100 cm^{-1} of atomic resonance. Two vibrational series associated with the first excited triplet states of the Rb dimer have been identified, and Franck-Condon oscillations which are reflective of the ground state structure of the initial state have been observed. Many further applications of this technique are apparent, and it appears that photoassociation spectroscopy could be a powerful new probe of molecular structure.

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