

## Spectroscopic Determination of the $s$ -Wave Scattering Length of Lithium

E. R. I. Abraham, W. I. McAlexander, C. A. Sackett, and Randall G. Hulet

*Physics Department and Rice Quantum Institute, Rice University, Houston, Texas 77251-1892*

(Received 2 September 1994)

Two-photon photoassociation of colliding ultracold  ${}^7\text{Li}$  atoms is used to probe the  ${}^3\Sigma_u^+(a)$  ground state of  ${}^7\text{Li}_2$ . The binding energy of the least-bound state of this triplet potential,  $\nu = 10$ , is found to be  $12.47 \pm 0.04$  GHz. This spectroscopic information establishes that the  $s$ -wave scattering length for  ${}^7\text{Li}$  atoms in the  $F = 2$ ,  $m_F = 2$  state is  $(-27.3 \pm 0.8)a_0$ . The negative sign of the scattering length has important implications as to whether atoms at this doubly spin-polarized state can undergo a Bose-Einstein condensation.

PACS numbers: 33.20.Fb, 32.80.Pj, 34.20.Cf, 34.40.+n

Recent advances in the field of trapping and cooling spin-polarized atoms may lead to the observation of Bose-Einstein condensation (BEC) in a weakly interacting system [1,2]. This would enable, for the first time, investigations of quantum statistical effects in a regime where interactions may be treated perturbatively [3]. However, the formation of the condensate depends on the nature of the interaction between trapped atoms. It is well known that, at low temperatures, the effect of the interaction potential in a two-body collision can be described by a single parameter, the  $s$ -wave scattering length  $a$  [4]. For atoms colliding with relative momentum  $\hbar k$ , the scattering length is related to the phase shift  $\delta_0$  by  $a = -\lim_{k \rightarrow 0} \tan \delta_0 / k$ , and, for identical bosons, to the elastic scattering cross section  $\sigma$  by  $\sigma = 8\pi a^2$ . If  $a > 0$ , the potential is effectively repulsive, and the gas will be mechanically stable at low temperatures [4]. However, if  $a < 0$ , a spatially homogeneous gas is unstable and Bose-Einstein condensation is predicted not to occur [5]. It is less straightforward to determine whether a Bose-Einstein condensate can be metastable for  $a < 0$  in the homogeneous environment of an atom trap [6], but a recent theoretical investigation has shown that such a system will always undergo a gas-liquid or a gas-solid phase transition before it reaches the BEC phase transition point [7]. Consequently, it is crucial to determine the sign of  $a$  for the atomic systems proposed for attaining BEC. The magnitude of  $a$  is also important, since the elastic scattering cross section is desired to be large in order to facilitate schemes for evaporative cooling of trapped atoms [8–11].

The scattering length is determined entirely by the interaction potential, which in the case of spin-polarized hydrogen or alkali-metal atoms, is the  ${}^3\Sigma_u^+(a)$  potential. For H, this potential is not deep enough to support bound states, and is known theoretically well enough to determine with certainty that  $a > 0$  [12]. However, the situation is much more complex for the alkali-metal atom species. For these atoms, the triplet potential is deep enough to support many bound states. The  ${}^7\text{Li}_2$  triplet potential is predicted to support 11 bound states [13,14],

while heavier species, such as Cs, will have hundreds. The existence of bound states leads to the possibility of a zero-energy scattering resonance caused by a state very near the dissociation limit. A potential giving a state which is only weakly bound leads to a large positive value for  $a$ . However, if the potential is made slightly shallower so that this state is no longer bound,  $a$  changes discontinuously to a large and negative value [15].

The experimental and theoretical knowledge of the  $\text{Li}_2$  triplet potential is sufficient that reasonable predictions may be made as to the value of  $a$  for this case. Recent theoretical calculations for atoms in the  $F = 2$ ,  $m_F = 2$  doubly spin-polarized ground state give a value for  $a$  in the range  $-7a_0$  to  $-27a_0$ , where  $a_0$  is the Bohr radius [6,14]. However, if the actual binding energy of the least-bound state is found to be as little as  $0.1 \text{ cm}^{-1}$  different than the calculated value, the conclusion as to the sign of  $a$  could be reversed.

Recently, photoassociative spectroscopy of ultracold trapped atoms has proven to be a powerful spectroscopic tool for probing weakly bound, long-range excited molecular states [16,17]. We have extended this technique to probe ground-state molecular levels via a two-photon Raman process. We report the measurement of the binding energy of the least-bound vibrational state of the  ${}^7\text{Li}_2$   ${}^3\Sigma_u^+(a)$  potential and extract a value for the triplet  $s$ -wave scattering length. Vibrational levels  $\nu = 0-7$  have been observed previously for the  ${}^3\Sigma_u^+(a)$  state of  ${}^7\text{Li}_2$ , using single-photon Fourier transform spectroscopy [18]. Multiphoton techniques have also been developed to access high-lying vibrational levels of ground and excited states [19], and used to observe the  $\nu = 0-9$  triplet ground states of  ${}^7\text{Li}_2$  [20]. Since, for photoassociative spectroscopy, the highest vibrational levels are the most easily accessed and energies are measured relative to the dissociation energy, it is a complementary spectroscopic technique.

The experiment uses atoms confined to a magneto-optical trap (MOT) that are loaded from a laser-slowed lithium beam [2]. The six trap laser beams are derived from a stabilized ring dye laser offset locked to an

atomic lithium resonance line using saturated absorption in a lithium vapor cell. The trap laser beams are frequency modulated using a LiTaO<sub>3</sub> electro-optic modulator driven at 406.4 MHz to produce sideband frequencies resonant with transitions from both ground-state hyperfine levels of the <sup>7</sup>Li atom. The lower sideband drives the  $2S_{1/2}, F = 2 \leftrightarrow 2P_{3/2}, F = 3$  transition, and the upper sideband drives the  $2S_{1/2}, F = 1 \leftrightarrow 2P_{3/2}, F = 2$  transition, and both are detuned 17 MHz to the red of resonance. The combined power in the six beams in each of the first-order sideband components is 12.4 mW. The Gaussian waist ( $e^{-2}$  intensity radius) of each beam is 3.1 mm. The density of trapped <sup>7</sup>Li is approximately  $3 \times 10^{10} \text{ cm}^{-3}$ , and the Gaussian waist of the trapped atom cloud is approximately 300  $\mu\text{m}$ . The temperature of the trapped atoms is estimated to be several mK.

A second, independently tunable laser beam with frequency  $\omega_{\text{PA}}$  is directed through the trapped atom cloud to photoassociate colliding atoms into specific electronically excited molecular vibrational levels (Fig. 1). These newly formed diatomic molecules can decay into bound ground states of the molecule, or into a dissociative continuum of two ground-state atoms which may possess enough kinetic energy to escape the trap. These processes result in a reduction in the number of trapped atoms, which can be detected by monitoring

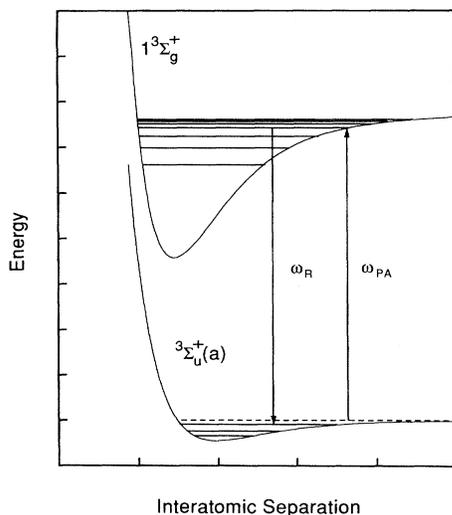


FIG. 1. Photoassociative spectroscopy of the ground-state triplet potential of <sup>7</sup>Li<sub>2</sub>. Two colliding ultracold atoms absorb a resonant photon of frequency  $\omega_{\text{PA}}$  and are excited to a high-lying vibrational level of the  $1^3\Sigma_g^+$  potential, which correlates asymptotically to  $2S_{1/2} + 2P_{1/2}$  atoms. These atoms may be lost from the trap through decay channels and will lead to a decrease in trap-laser-induced fluorescence. A laser of frequency  $\omega_R$  is tuned to resonance between a ground-state vibrational level and the excited-state vibrational level. This Raman laser reduces the excitation into the excited state, which decreases photoassociation and leads to an increase in the trap-laser-induced fluorescence.

the trap-laser-induced atomic fluorescence. Vibrational levels of the  $1^3\Sigma_g^+$  and  $1^1\Sigma_u^+$  molecular potentials, which correlate asymptotically to  $2S_{1/2} + 2P_{1/2}$  atoms, have been observed for both <sup>7</sup>Li<sub>2</sub> and <sup>6</sup>Li<sub>2</sub> [17]. The most deeply bound level observed for the  $1^3\Sigma_g^+$  potential of <sup>7</sup>Li<sub>2</sub> has a vibrational quantum number  $\nu = 62$ , a binding energy of 75  $\text{cm}^{-1}$ , and an outer classical turning point of  $32a_0$ . Because the overlap between free states and deeply bound states is small, this observation required a relatively high laser intensity of 100  $\text{W}/\text{cm}^2$ . Figure 2(a) shows a high-resolution photoassociation spectrum of the  $\nu = 64$  level. The observed structure is due to the hyperfine interaction. The spectrum is predominantly  $s$  wave, corresponding to the rotational quantum number  $N = 1$  [21]. Other rotational lines can be observed only at the highest laser intensities.

Two-photon stimulated Raman transitions may be used to probe bound states of the ground-state molecular potentials, as shown in Fig. 1. In this scheme, the frequency of the photoassociation laser is fixed on a resonance between the asymptotic energy of two ground-state atoms and an

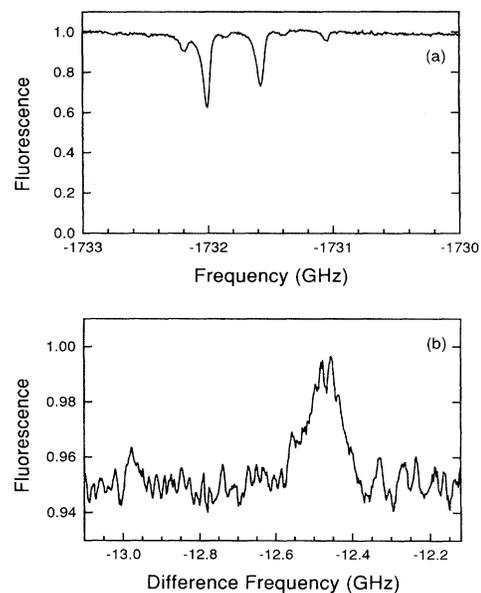


FIG. 2. (a) One-photon photoassociation of the  $\nu = 64$  vibrational level of the  $1^3\Sigma_g^+$  state of <sup>7</sup>Li<sub>2</sub>, using a laser beam with a power of 100 mW and a beam waist of 250  $\mu\text{m}$ . The frequency is measured relative to the  $2S_{1/2} \leftrightarrow 2P_{1/2}$  atomic transition frequency. The structure is due to the hyperfine interaction. (b) Two-photon photoassociation of the  $\nu = 10$  vibrational level of the  $3^3\Sigma_u^+(a)$  state. The baseline corresponds to the reduction of the fluorescence level due to the photoassociation laser beam. As  $\omega_R$  is tuned over the bound-bound transition frequency, the rate of photoassociative loss is reduced, thereby increasing the trap-laser-induced fluorescence. When  $\omega_R$  is tuned to resonance, nearly all of the fluorescence signal lost induced by the photoassociation laser is reclaimed. No additional features are observed above the noise.

excited vibrational level, while the frequency of the Raman laser,  $\omega_R$ , is tuned over the bound-bound transition frequency. Since the photoassociation laser is tuned to resonance, it causes a reduction in the number of trapped atoms, as in the one-photon case. As the Raman laser is tuned into resonance, it reduces the rate of loss of trapped atoms, producing an *increase* in the trap-laser-induced fluorescence. There are several possible mechanisms that give a reduction in the loss of trapped atoms. First, the Raman beam reduces the population in the excited molecular state, thereby reducing the rate of the spontaneous emission events which give rise to loss. Second, atoms which have decayed to the bound ground state being probed can be returned to the trap via a two-photon stimulated Raman transition; these atoms would otherwise be lost. Finally, if the Raman beam is sufficiently intense, it can split the excited molecular state into an Autler-Townes doublet [22], thereby shifting the photoassociation resonance away from  $\omega_{PA}$ . Modeling suggests that the first mechanism dominates at lower Raman beam intensities, while the third dominates at higher intensities. The Autler-Townes doublet has been observed by scanning  $\omega_{PA}$  while using an intense, fixed frequency Raman beam.

Figure 2(b) shows the Raman spectrum of the least-bound state of the  ${}^3\Sigma_u^+(a)$  potential, using the  $\nu = 64$  state of the  $1^3\Sigma_g^+$  as an intermediate resonance. In this spectrum, the Raman beam, which was derived from a dye laser, had a power of 35 mW and a beam waist of 250  $\mu\text{m}$ , while the photoassociation beam had a power of 7 mW and a beam waist of 200  $\mu\text{m}$ . The beams were directed through the trapped atom cloud and retroreflected. The photoassociation beam was produced by a nominally 20 mW diode laser [23], which was frequency narrowed using an external grating cavity. Acoustic vibrations produce frequency jitter in the output of this device of approximately 20 MHz. Although vibrational levels of the excited  $1^3\Sigma_g^+$  potential deeper than  $\nu = 64$  have greater overlap with the levels of the ground  ${}^3\Sigma_u^+(a)$  potential, we were constrained by the available photoassociation laser power.

The frequency scale of Fig. 2(b) is obtained by measuring  $\omega_{PA} - \omega_R$  with an optical spectrum analyzer. In order to check the consistency of the binding energy measured in this way, spectra were obtained using either  $\nu = 64$  or 65 of the  $1^3\Sigma_g^+$  potential as the intermediate state. As expected, the result is independent of the intermediate vibrational quantum number, eliminating the possibility that the two-photon resonance is to a doubly excited molecular state. Similarly, spectra were obtained using either of the two dominant hyperfine levels of the upper state, evident in Fig. 2(a). To the level of our precision, the binding energy of the ground state is independent of which of the two hyperfine levels is chosen as the intermediate state. Hyperfine structure would be of the order of the atomic ground-state hyperfine splitting

of 800 MHz, but none is discernable in the ground-state spectrum. We conclude that the total angular momentum  $F$  is at least partially conserved in the Raman transition. Significant power broadening caused by the Raman laser is observed at the highest intensities. For the spectrum shown in Fig. 2(b), the Raman laser was attenuated as much as possible to reduce the linewidth, while still maintaining adequate signal to noise.

The  ${}^3\Sigma_u^+(a)$  potential is well known since vibrational levels  $\nu = 0-7$  have been observed previously [18]. An accurate dense Rydberg-Klein-Rees (RKR) potential has been extracted from these data [13], and improved upon by means of an inverse perturbation analysis [6]. Furthermore, the ground-state long-range coefficients  $C_6, C_8$ , and  $C_{10}$  of the interaction potential have been calculated to high precision for  $\text{Li}_2$  [24]. Using this information, we can unambiguously assign the observed level to  $\nu = 10$ . Moerdijk *et al.* [6] and Côté *et al.* [14] have used this knowledge of the potential to predict the binding energy of the  $\nu = 10$  level and to derive a value for the  $s$ -wave scattering length. Both groups predict the binding energy to be 11.4 GHz [14,25], while our result is  $12.47 \pm 0.04$  GHz. The uncertainty in the measurement is due to the spectral width of the ground-state feature, the resolution of the spectrum analyzer, and the uncertainty in the zero of kinetic energy in the excited-state photoassociation line shape. Although it is remarkable that the error in the theoretically predicted binding energy is only  $10^{-4}$  of the depth of the potential well, the scattering length is extremely sensitive to this binding energy.

In order to estimate the scattering length implied by the experimental results, the model potential of Côté *et al.*, using the dense RKR data from Zemke and Stwalley [13], was modified to give a  $\nu = 10$  eigenvalue in agreement with the measured value. The energy of the  $\nu = 10$  level is sensitive to the value of the dissociation energy  $D_e$  used in the RKR potential, as well as the long-range coefficients, and is relatively insensitive to the other components of the potential. Côté *et al.* used the long-range coefficients recently published by Marinescu *et al.* [24]. Using these values, we find that  $D_e = 333.73 \pm 0.02$   $\text{cm}^{-1}$  yields the correct binding energy to within our experimental uncertainty. This is in reasonable agreement with Zemke and Stwalley who obtain  $D_e = 333.4 \pm 0.3$   $\text{cm}^{-1}$  [13]. Other published sets of long-range coefficients, referenced in [24] and [13], yield  $D_e$  in the range 333.67 to 334.12  $\text{cm}^{-1}$ .

The modified potential was then used to calculate  $a$ , by solving Schrödinger's equation for energies greater than zero. The resulting radial wave function was compared to a free-particle wave function in the asymptotic region to determine the phase shift. The scattering length was determined using the limiting value of the phase shift as the energy approached zero. Using the Marinescu *et al.* long-range coefficients, the scattering length was found to be between  $-26.8a_0$  and  $-27.7a_0$ . Including the

other sets of long-range coefficients broadens this range somewhat, so we find that the triplet  $s$ -wave scattering length for  ${}^7\text{Li}$  is  $(-27.3 \pm 0.8)a_0$ .

We conclude that BEC cannot be stable for atoms of  ${}^7\text{Li}$  in the  $F = 2$ ,  $m_F = 2$  doubly polarized state, because the sign of the  $s$ -wave scattering length is negative. This has important implications for an experimental effort to observe BEC of  ${}^7\text{Li}$  in a permanent magnetic trap [26]. Recent theoretical work, however, finds that the scattering length for  ${}^7\text{Li}$  in the  $F = 1$ ,  $m_F = -1$  state, which can also be confined by a magnetic field minimum, is positive [27]. An experiment similar to the present one to measure the binding energy of the least-bound singlet state would increase the accuracy of such calculations for any of the ground-state hyperfine levels. Extending this spectroscopic technique to the  $\nu = 9$  vibrational level of the  ${}^3\Sigma_u^+(a)$  state would establish a connection between levels measured from the dissociation limit to those measured relative to the bottom of the potential well [20].

We are grateful to K. Kobayashi of the NEC Corp. for providing diode lasers used for this experiment and to A. Dalgarno for providing the results of a calculation of the bound-bound matrix elements. This work is supported by the National Science Foundation, the Texas Advanced Technology Fellow Program, and the Welch Foundation. W.I.M. is a Fannie and John Hertz Foundation Fellow.

- [1] For reviews of BEC, see T.J. Greytak and D. Kleppner, in *New Trends in Atomic Physics*, edited by G. Grynberg and R. Stora (North-Holland, Amsterdam, 1984), Vol. 2, p. 1125; I.F. Silvera and J.T.N. Walraven, in *Progress in Low Temperature Physics*, edited by D.F. Brewer (North-Holland, Amsterdam, 1986), Vol. 10, p. 139.
- [2] See the special issues on laser cooling and atom trapping: *J. Opt. Soc. Am. B* **6**, 2020 (1989); *Laser Phys.* **4**, 829 (1994).
- [3] There have been observations of quantum statistical effects in *nondegenerate* gases, including the observation of spin waves in a dilute gas of spin-polarized H by N.P. Bigelow, J.H. Freed, and D.M. Lee [*Phys. Rev. Lett.* **63**, 1609 (1989)].
- [4] Cf. K. Huang, *Statistical Mechanics* (John Wiley & Sons, New York, 1987); A.L. Fetter and J.D. Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, New York, 1971).
- [5] H. T. C. Stoof, *Phys. Rev. A* **49**, 3824 (1994).
- [6] A. J. Moerdijk, W. C. Stwalley, R. G. Hulet, and B. J. Verhaar, *Phys. Rev. Lett.* **72**, 40 (1994).
- [7] H. T. C. Stoof (private communication).
- [8] H. F. Hess, G. P. Kochanski, J. M. Doyle, N. Masuhara, D. Kleppner, and T. J. Greytak, *Phys. Rev. Lett.* **59**, 672 (1987).
- [9] J. M. Doyle, J. C. Sandberg, I. A. Yu, C. L. Cesar, D. Kleppner, and T. J. Greytak, *Phys. Rev. Lett.* **67**, 603 (1991).
- [10] K. B. Davis, M.-O. Mewes, M. A. Joffe, and W. Ketterle in *Proceedings of the Fourteenth International Conference on Atomic Physics*, University of Colorado, Boulder, 1994 (unpublished).
- [11] W. Petrich, M. H. Anderson, J. R. Ensher, and E. A. Cornell (Ref. [10]).
- [12] D. G. Friend and R. D. Eppers, *J. Low Temp. Phys.* **39**, 409 (1980).
- [13] W. T. Zemke and W. C. Stwalley, *J. Phys. Chem.* **97**, 2053 (1993).
- [14] R. Côté, A. Dalgarno, and M. J. Jamieson, *Phys. Rev. A* **50**, 399 (1994).
- [15] Cf. C. J. Joachain, *Quantum Collision Theory* (Elsevier Science Publishers B. V., Amsterdam, 1975).
- [16] H. R. Thorsheim, J. Weiner, and P. S. Julienne, *Phys. Rev. Lett.* **58**, 2420 (1987); V. Bagnato, L. Marcassa, C. Tsao, Y. Wang, and J. Weiner, *Phys. Rev. Lett.* **70**, 3225 (1993); P. D. Lett, K. Helmerson, W. D. Phillips, L. P. Ratliff, S. L. Rolston, and M. E. Wagshul, *Phys. Rev. Lett.* **71**, 2200 (1993); L. P. Ratliff, M. E. Wagshul, P. D. Lett, S. L. Rolston, and W. D. Phillips, *J. Chem. Phys.* **101**, 2638 (1994); J. D. Miller, P. A. Cline, and D. J. Heinzen, *Phys. Rev. Lett.* **71**, 2204 (1993); R. A. Cline, J. D. Miller, and D. J. Heinzen, *Phys. Rev. Lett.* **73**, 632 (1994).
- [17] W. I. McAlexander, E. R. I. Abraham, N. W. M. Ritchie, C. J. Williams, H. T. C. Stoof, and R. G. Hulet, *Phys. Rev. A* **51**, 871 (1995).
- [18] C. Linton, T. L. Murphy, F. Martin, R. Bacis, and J. Verges, *J. Chem. Phys.* **91**, 6036 (1989).
- [19] A. M. Lyyra, H. Wang, T.-J. Whang, W. C. Stwalley, and L. Li, *Phys. Rev. Lett.* **66**, 2724 (1991).
- [20] A. M. Lyyra, L. Li, C. Linton, P. Crozet, A. J. Ross, and I. Russier (private communication).
- [21] Cf. M. Mizushima, *The Theory of Rotating Diatomic Molecules* (John Wiley & Sons, New York, 1975).
- [22] Cf. C. Cohen-Tannoudji, J. Dupont-Roc, and G. Grynberg, *Atom-Photon Interactions* (John Wiley & Sons, New York, 1992).
- [23] The diode laser is a noncommercial device provided by the NEC Corp.
- [24] M. Marinescu, H. R. Sadeghpour, and A. Dalgarno, *Phys. Rev. A* **49**, 982 (1994).
- [25] A. J. Moerdijk and B. J. Verhaar (private communication).
- [26] J. J. Tollett, C. C. Bradley, C. A. Sackett, and R. G. Hulet, *Phys. Rev. A* **51**, 22 (1995).
- [27] A. J. Moerdijk and B. J. Verhaar, *Phys. Rev. Lett.* **73**, 518 (1994).