Precise Determination of ^{6}Li Cold Collision Parameters by Radio-Frequency Spectroscopy on Weakly Bound Molecules

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We employ radio-frequency spectroscopy on weakly bound ^{6}Li$_2$ molecules to precisely determine the molecular binding energies and the energy splittings between molecular states for different magnetic fields. These measurements allow us to extract the interaction parameters of ultracold ^{6}Li atoms based on a multichannel quantum scattering model. We determine the singlet and triplet scattering lengths to be $a_s = 45.167(8)a_0$ and $a_t = -2140(18)a_0$ ($1a_0 = 0.0529177$ nm), and the positions of the broad Feshbach resonances in the energetically lowest three s-wave scattering channels to be 83.41(15), 69.04(5), and 81.12(10) mT.

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Molecular level structure near a collision threshold uniquely determines the scattering properties of ultracold atoms. When a molecular state is tuned near the scattering threshold, the atomic scattering amplitude can be resonantly altered. Magnetically tuned Feshbach resonances [1] in ultracold fermionic gases have recently led to ground-breaking observations, including the condensation of molecules [2–6] and the studies of the crossover physics from a molecular Bose-Einstein condensate (BEC) to atomic Cooper pairs in the Bardeen-Cooper-Schrieffer state (BEC-BCS crossover) [5,7,8]. These studies are of general importance in physics as the ultracold Fermi gas provides a unique model system for other strongly interacting fermionic systems [9].

In spin mixtures of ^{6}Li atoms, a broad Feshbach resonance in the energetically lowest s-wave channel [10] allows for precise interaction tuning. This, together with the extraordinary stability of the system against inelastic decay [2,11], makes ^{6}Li the prime candidate for BEC-BCS crossover studies. A precise knowledge of the magnetic-field dependent scattering properties is crucial for a quantitative comparison of the experimental results with crossover theories. Of particular importance is the precise value of the magnetic field where the s-wave scattering diverges. At this unique point, the strongly interacting fermionic quantum gas is expected to exhibit universal properties [12]. Previous experiments explored the ^{6}Li resonance by measuring inelastic decay [13], elastic collisions [14,15], and the interaction energy [16], but could locate the exact resonance point only to within a range between 80 and 85 mT.

An ultracold gas of weakly bound molecules is an excellent starting point to explore the molecular energy structure near threshold [17]. An improved knowledge on the exact ^{6}Li resonance position was recently obtained in an experiment that observed the controlled dissociation of weakly bound ^{6}Li$_2$ molecules induced by magnetic-field ramps [18]. These measurements provided a lower bound of 82.2 mT for the resonance position. Studies of systematic effects suggested an upper bound of 83.4 mT. Within this uncertainty range, however, we observe the physical behavior of the ultracold gas to exhibit a substantial dependence on the magnetic field [8]. In this Letter, we apply radio-frequency (rf) spectroscopy [17,19] on weakly bound molecules to precisely determine the interaction parameters of cold ^{6}Li atoms. Together with a multichannel quantum scattering model, we obtain a full characterization of the two-body scattering properties, essential for BEC-BCS crossover physics.

The relevant atomic states are the lowest three sublevels in the ^{6}Li ground state manifold, denoted by $|1\rangle$, $|2\rangle$, and $|3\rangle$. Within the magnetic-field range investigated in this experiment, these levels form a triplet of states, essentially differing by the orientation of the nuclear spin ($m_I = 1, 0, -1$). Figure 1 shows the energy level structure of the two scattering channels $|1\rangle + |2\rangle$ and $|1\rangle + |3\rangle$, denoted by $(1, 2)$ and $(1, 3)$, respectively. The broad Feshbach resonance occurs in the $(1, 2)$ channel near 83 mT. When the magnetic field is tuned below the resonance, atoms in the $(1, 2)$ channel can form weakly bound molecules [20]. For the $(1, 3)$ channel, a similar Feshbach resonance [19] occurs near 69 mT.

Starting with molecules formed in the $(1, 2)$ channel, we drive the rf transition to the $(1, 3)$ channel at various magnetic-field values B. The rf excitation can dissociate a molecule into two free atoms (bound-free transition; see Fig. 1) [17] or, for $B < 69$ mT, it can also drive the transition between the molecular states in the $(1, 2)$ and $(1, 3)$ channels (bound-bound transition). In both processes, the rf excitation results in loss of molecules in the

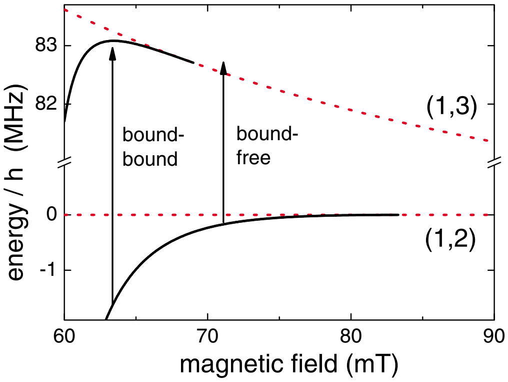

FIG. 1 (color online). Energy level structure near the Li_2 dissociation threshold as a function of magnetic field B. The threshold energy of the (1, 3) scattering channel (upper dotted line) is plotted relative to the (1, 2) threshold (lower dotted line). In the (1, 2) channel, a molecular state (lower solid line) exists below the Feshbach resonance at ~83 mT. In the (1, 3) channel, another molecular state (upper solid line) exists below the resonance at ~69 mT. The bound-free and bound-bound transitions of molecules in the (1, 2) channel are illustrated by the arrows.

(1, 2) channel. This loss constitutes our experimental signal. We perform measurements at different magnetic fields for both the bound-free and the bound-bound transitions.

Our experimental procedure is similar to Ref. [8]. The optically trapped sample is cooled by forced evaporation at a magnetic field of 76.4 mT. With deep cooling we routinely produce a BEC of 2×10^5 molecules [2], which at the lowest trap laser power of 3.8 mW has a peak density of 4×10^{12} cm^{-3}. After evaporation we linearly ramp the field to a specific value between 66 and 72 mT in typically 200 ms. We then apply a single rf pulse for 200 ms with its frequency tuned close to the atomic transition $|2\rangle$ to $|3\rangle$. Following the rf pulse, we apply state-selective absorption imaging, which is sensitive to free atoms in state $|2\rangle$ and molecules in the (1, 2) channel.

To precisely determine the magnetic field, we employ rf spectroscopy on a "hot" thermal sample of 2×10^6 atoms at a temperature $T \approx 90$ μK (about 6 times the Fermi temperature T_F) with the highest trap laser power of 10.5 W. Under these conditions we do not observe any density-dependent frequency shifts, in agreement with [19]. The rf transition energy then corresponds to the internal energy difference hf_0 between the states $|2\rangle$ and $|3\rangle$, where h is Planck's constant. This energy is magnetic-field dependent and the transition frequency is about 83 MHz in the magnetic-field range we study. The measured transition has a narrow linewidth of less than 1 kHz, and the center position can be determined to within a few hundred Hz. This high resolution allows us to calibrate our magnetic field to an accuracy of a few μT based on the Breit-Rabi formula and the ^{6}Li parameters given in [21].

For bound-free transitions, the molecules in the (1, 2) channel make a transition to the (1, 3) scattering continuum. The excitation rate from a stationary molecule to an atomic scattering state with kinetic energy $2E_k$ is determined by the Franck-Condon factor between the bound and free wave functions [22]. From energy conservation, $2E_k$ is related to the rf transition energy hf by $hf = hf_0 + E_b + 2E_k$, where E_b is the binding energy of the molecules in the (1, 2) channel. The variation of the Franck-Condon factor with atomic kinetic energy leads to a broad and asymmetric dissociation line shape [22].

Rf dissociation spectra taken at 72.0 and 69.5 mT for a molecular BEC in a weak optical trap are shown in Fig. 2. An important feature of the spectra is the sharp rising edge on the low frequency side. This threshold corresponds to the dissociation of a molecule into two atoms with zero relative momentum. Therefore, the position of the edge relative to the atomic transition directly indicates the molecular binding energy.

We determine the dissociation threshold and thus the molecular binding energy by fitting the full line shape. The line shape function [22] depends on both the (1, 2) molecular binding energy E_b and the scattering length a_{13} in the (1, 3) channel. In the range of magnetic fields we investigate, a_{13} is much larger than the interaction range of the van der Waals potential of $\sim 30a_0$. The line shape function $P(E)$ is then well approximated by [22]

$$P(E) \propto E^{-2}(E - E_b)^{1/2}(E - E_b + E')^{-1}, \qquad (1)$$

where $E = hf - hf_0$ and $E' = \hbar^2/ma_{13}^2$. From the fits to the experimental data [23], we determine the threshold positions, given in Table I. Together with the atomic transition frequencies, we conclude that the molecular binding energies are $E_b = h \times 134(2)$ kHz at 72.013(4) mT and $E_b = h \times 277(2)$ kHz at 69.483(4) mT.

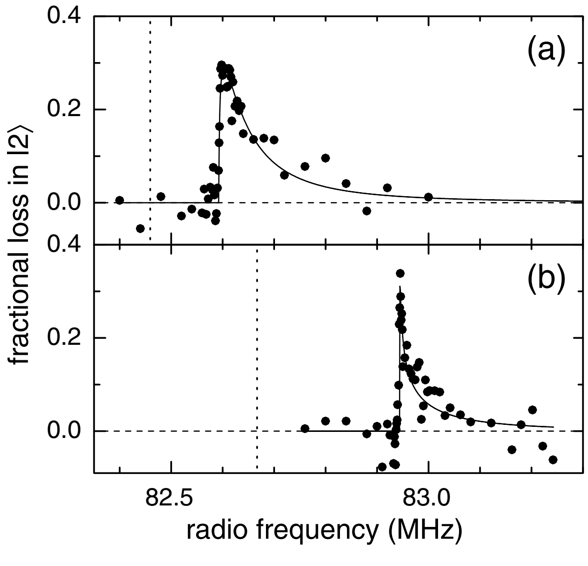

FIG. 2. Bound-free rf spectra at 72.013(4) mT (a) and 69.483(4) mT (b). Fractional loss in state $|2\rangle$ is measured as a function of the radio frequency. The solid lines represent a fit based on Eq. (1). The atomic transition frequencies, which are measured independently, are indicated by the vertical dashed lines.

TABLE I. Comparison between our experimental and theoretical results. The magnetic field B is determined from the measured atomic transition frequency f_0. The molecular transition frequency f_{mol} refers to the resonance peak for bound-bound transitions (upper two rows) or the dissociation threshold (lower two rows). The values in parentheses indicate 1σ uncertainties.

		f_{mol} (MHz)	
B (mT)	f_0 (MHz)	Experimental	Theory
66.1436(20)	82.968 08(20)	83.6645(3)	83.6640(10)
67.6090(30)	82.831 84(30)	83.2966(5)	83.2973(10)
69.4826(40)	82.666 86(30)	82.9438(20)	82.9419(13)
72.0131(40)	82.459 06(30)	82.5928(20)	82.5910(13)

For magnetic field $B < 69$ mT, we can drive the rf transition between the $(1, 2)$ and $(1, 3)$ molecular states. Here, the resonance frequency is given by the energy difference of the two molecular states. To avoid possible systematic mean-field shifts at these lower magnetic fields [19], we prepare a thermal mixture of atoms and molecules with temperature $T \approx T_{\mathrm{F}}$ by a controlled heating method [8]. Rf spectroscopy is performed at 67.6 and 66.1 mT. The bound-bound transition signal at 66.1 mT is shown in Fig. 3. By fitting the narrow transition line with a Lorentzian profile, we determine the resonance frequency; see Table I. Notably, below the resonance in the $(1, 3)$ channel at ~69 mT, the bound-free transition is much weaker due to a Fano-type interference effect [22].

Because of the high precision of the measured transition frequencies, a careful analysis of systematic effects is necessary. Possible systematic shifts include differential light shifts of the two molecular states and density-dependent many-body shifts. In order to characterize these possible systematic errors, we experimentally investigate these shifts by varying the trap depth of the optical potential. In a deeper trap, both the differential light shifts and mean-field shifts are expected to increase. We repeat the bound-free and bound-bound rf spectroscopy for different trap laser powers in a range between 3.8 and 310 mW. At a typical magnetic field of $B = 69$ mT the peak number density of a molecular BEC is thereby varied between 8×10^{12} cm^{-3} and 5×10^{13} cm^{-3}. Within our statistical uncertainties we do not see any systematic density-dependent shifts.

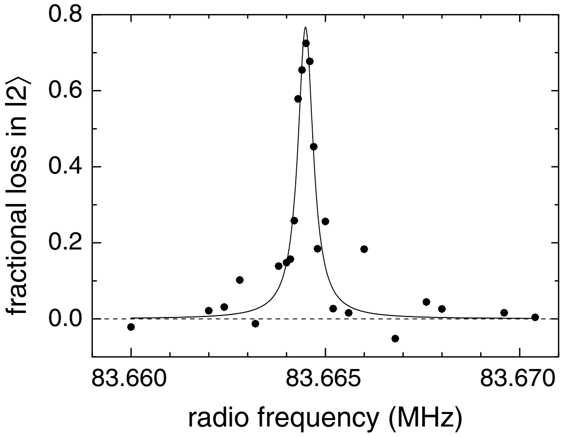

FIG. 3. Bound-bound rf spectrum at 66.144(2) mT. The fractional population loss in state $|2\rangle$ shows a narrow resonance. We determine the center position to be 83.6645(3) MHz from a Lorentzian fit (solid line).

Given the measured data summarized in Table I, it is possible to predict the location of the scattering resonances in the $(1, 2)$, $(1, 3)$, and $(2, 3)$ channels if we have an accurate theoretical model of the collision. We use a standard multichannel model for the interaction of two ^{2}S atoms with nuclear spin [24] to calculate the scattering lengths and bound state energies for these channels. It is necessary to include s waves only in the basis set, since we find that there is a negligible change within the experimental uncertainties if we also include higher partial waves in the basis set. The interaction potential model is the same as described in Ref. [14]. It uses a combination of Rydberg-Klein-Rees and *ab initio* potentials for the singlet ($^1\Sigma_g^+$) and triplet ($^3\Sigma_u^+$) states at short range and joins them smoothly onto long range potentials based on the exchange [25] and van der Waals dispersion energy [26], the lead term of which is $C_6 = 1393.39(16)$ au (1 au $= 9.573\,44 \times 10^{-26}$ J nm^6). As in Ref. [14], the singlet $^1\Sigma_g^+$ and triplet $^3\Sigma_u^+$ scattering lengths, a_s and a_t, respectively, are varied by making small variations to the inner wall of the potential. Once a_s and a_t are specified, all other scattering and bound state properties for all channels of two ^{6}Li atoms are uniquely determined, including the positions of the resonances. Consequently, varying a_s and a_t to fit the binding energies and energy differences from rf spectroscopy determines the values of these two free parameters.

Fitting the data of the present experiment determines $a_s = 45.167(8)a_0$ and $a_t = -2140(18)a_0$. The uncertainty includes both the uncertainty in the measured value of the magnetic field and the uncertainty in the rf measurements. Our scattering lengths agree within the uncertainties with previous determinations: $a_s = 45.1591(16)a_0$ [18] and $a_t = -2160(250)a_0$ [27]. Table I shows a comparison of the measured and best fit calculated energies. The calculated positions of the broad s-wave resonances for the $(1, 2)$, $(1, 3)$, and $(2, 3)$ channels are 83.41(15), 69.04(5), and 81.12(10) mT, respectively.

Figure 4 shows the scattering lengths calculated for several different channels in the magnetic-field range of interest to BEC-BCS crossover experiments. We find that the formula $a = a_b[1 + \Delta(B - B_0)^{-1}][1 + \alpha(B - B_0)]$ fits the calculated scattering lengths to better than 99% over the range of 60 to 120 mT. This expression includes the standard Feshbach resonance term [28] with the background scattering length a_b, resonance position B_0, and resonance width Δ, and a leading-order correction parametrized by α. The respective values for a_b, B_0, Δ, and α are $-1405a_0$, 83.4149 mT, 30.0 mT, and 0.0040 mT^{-1} for channel $(1, 2)$, $-1727a_0$, 69.043 mT, 12.23 mT, and

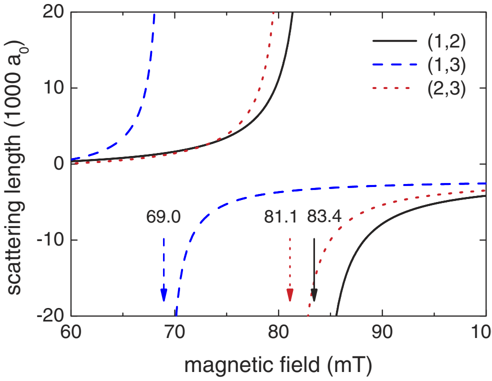

FIG. 4 (color online). Scattering lengths versus magnetic field from multichannel quantum scattering calculations for the (1, 2), (1, 3), and (2, 3) scattering channels. The arrows indicate the resonance positions.

0.0020 mT^{-1} for channel (1, 3), and $-1490a_0$, 81.122 mT, 22.23 mT, and 0.003 95 mT^{-1} for channel (2, 3).

The (1, 3) channel molecular bound state can decay to the (1, 2) channel by a very weak spin-dipolar coupling. We have used the methods of Ref. [29] to calculate the two-body lifetime of the (1, 3) bound state due to predissociation to the (1, 2) channel and find that it is very long, greater than 10 s at 60.0 mT, increasing to 1000 s at 68.5 mT very close to resonance. However, (1, 3) molecules might be quenched by collisions with $|2\rangle$ atoms or (1, 2) channel molecules, since with three different spin states involved in the collision, there would be no fermionic suppression of collision rates according to the mechanism of Ref. [11].

In conclusion, radio-frequency spectroscopy on ultracold, weakly bound molecules allowed us to precisely determine the molecular binding energies and the energy splittings between two molecular states for different magnetic fields. Based on the measured data and a multichannel quantum scattering model, we determine the scattering lengths as a function of magnetic field and the Feshbach resonance positions in the lowest three channels with unprecedented precision. With these data, we can fully characterize the interaction strength between particles in the BEC-BCS crossover regime for future experiments based on ^{6}Li atoms.

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