Saturation in heteronuclear photoassociation of $^{6}\text{Li}^{7}\text{Li}$

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We report heteronuclear photoassociation spectroscopy in a mixture of magneto-optically trapped $^{6}\text{Li}$ and $^{7}\text{Li}$. The laser-induced decrease in the $^{7}\text{Li}$ steady-state particle number, only appearing in the presence of $^{6}\text{Li}$, gives clear evidence of photoassociation to form $^{6}\text{Li}^{7}\text{Li}$. Hyperfine resolved spectra of the vibrational level $v=83$ of the singlet state $^1\Sigma_u^+$ have been taken up to intensities of 1000 W/cm$^2$. The absolute resonance frequencies and the rotational constant have been measured. Saturation of the photoassociation rate has been observed for two hyperfine transitions, which can be shown to be due to saturation of the rate coefficient near the unitarity limit. Saturation intensities on the order of 40 W/cm$^2$ can be determined.

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Photoassociation of cold atoms has been established as a versatile tool for the formation of cold molecules. Starting with atoms either from a magneto-optical trap or a Bose-Einstein condensate this technique has been shown to allow for efficient production of various cold alkali dimers \cite{1,2,3,4}. In single-photon photoassociation a pair of free atoms is optically excited into a rovibrational level of the electronically excited molecule. By spontaneous decay, either a pair of free atoms is formed, or, with small fractional probability, a translationally cold ground state molecule. In extension to this intrinsically incoherent process, also coherent processes, such as two-photon Raman-type transitions \cite{5,6,7,8}, have been investigated. In the degenerate regime, such methods should allow for coherent coupling between free atom-pair states and specific molecular ground states, similar to the recently observed atom-molecule coupling due to a Feshbach resonance \cite{9}. It is expected that quantum statistics will affect the initial atomic states as well as the molecular product, leading to what may be phrased as ‘superchemistry’ \cite{10}. In this context, mixtures between bosonic and fermionic gases are particularly interesting, as they offer not only the possibility of molecular Bose gases, but also of molecular Fermi gases.

A promising candidate for such experiments is lithium. It provides a stable fermionic and bosonic isotope, it can be routinely cooled to quantum degeneracy, and mixtures between Bose- and Fermi-gases have already been observed and studied \cite{11,12}. There is also extensive experience with photoassociation of homonuclear lithium dimers in the nondegenerate and in the degenerate regime \cite{13,14}. However, the formation of fermionic molecules requires two atomic species with different quantum statistics. In general, such heteronuclear photoassociation bears intrinsic difficulties \cite{15} and, although being very desirable as a universal tool \cite{16}, it has not yet been implemented successfully in binary mixtures. For studying heteronuclear photoassociation, lithium is again exceptionally suitable. The isotopic shift of only 10 GHz allows for resonant dipole-dipole interaction in the excited molecular state already at large internuclear separations, which is a crucial prerequisite for efficient photoassociation \cite{17}.

Even though the theory of photoassociation at high laser intensities is not yet fully understood \cite{18,19}, it is clear that for coherent coupling, optical excitation rates are required that are fast as compared to the other relevant time scales of the system (i.e. collision time and decoherence time due to spontaneous decay of the involved excited states). One indication for entering the regime of sufficiently strong excitation rates is the occurrence of saturation in the single-photon photoassociation signal. Saturation studies have been reported for several one-species experiments \cite{20,21}. However, a clear saturation of the photoassociation rate has not been observed yet.

In this paper we report on heteronuclear photoassociation in a mixture of magneto-optically trapped $^{6}\text{Li}$ and $^{7}\text{Li}$. We investigate photoassociation of $^{6}\text{Li}^{7}\text{Li}$ by monitoring the $^{6}\text{Li}$-induced decrease in the $^{7}\text{Li}$ steady-state particle number as a function of the photoassociation laser frequency and intensity. The number of $^{6}\text{Li}$ atoms exceeds that of $^{7}\text{Li}$ by a factor of 10 such that the photoassociation losses are significant only for $^{7}\text{Li}$ while the number of $^{6}\text{Li}$ atoms remains almost unaffected. This setup is possible only for heteronuclear photoassociation and substantially facilitates the quantitative analysis. Strong saturation of the photoassociation rate is observed for two of four studied hyperfine lines of the chosen singlet transition $v=83$. We derive values for the saturation intensities on the order of 40 W/cm$^2$ which are sufficiently low to encourage future experiments aiming at coherent control in the degenerate regime.

Our experimental setup has been described in detail in \cite{22}. The combined magneto-optical trap (MOT) is operated with two independent diode-laser systems and
loaded from a single Zeeman-slowed atomic beam. The particle numbers are monitored by two absorption lasers, tuned into resonance of the respective cooling transition, by means of a lock-in technique. The photoassociation light is provided by a tunable dye laser, which is focused to a 1/e^2 diameter of 300 µm, resulting in peak intensities up to 1000 W/cm^2. Its frequency is measured with a combination of a commercial wavemeter, a Fabry-Perot etalon and a doppler-free iodine fluorescence spectroscopy [21]. If the laser light is resonant with a molecular transition, losses in the two-species MOT are induced due to spontaneous decay of the excited molecule into a pair of free atoms or a ground state molecule. To simplify the quantitative analysis, we operate the MOTs such that the particle number of the ^6Li MOT is large compared to that of the ^7Li MOT. Therefore, losses in the ^6Li particle number due to heteronuclear photoassociation are small and the ^6Li MOT acts as a temporally constant background gas for the ^7Li MOT. Moreover, quadratic losses in the ^7Li particle number are negligible. In that special case the complicated solution of the coupled rate equations for a two-species system is reduced to the following simple form for the ^7Li steady-state particle number N_7:

\[ N_7 = \frac{L_7}{\alpha_7 + \beta_{PA}}. \]  

Here, L_7 is the ^7Li MOT loading rate, and \( \alpha_7 \) is the loss rate mainly due to collisions with hot atoms from the beam source. The photoassociation rate \( \beta_{PA} = K n_0 w r \), with the photoassociation rate coefficient K, the ^6Li peak density \( n_0 \), the factor w considering the relative atomic hyperfine ground-state populations, and the factor r accounting for the spatial overlap between the atomic clouds and the laser beam. Spectra are taken by monitoring the ^7Li steady-state atom number as a function of the photoassociation laser frequency. With 1.25 MHz/s, the scan rate was chosen slow as compared to the loading time of the MOTs. The positions of the heteronuclear resonances can be predicted theoretically within 1 GHz, by applying the method of mass-reduced quantum numbers [22] to the well-known data for homonuclear lithium [12]. To identify heteronuclear resonances we have recorded the ^7Li particle number with and without the other isotope present. The additional resonances give clear evidence of ^6Li^7Li photoassociation.

We have concentrated on the transition into the vibrational level \( v = 83 \) of the singlet series \( A_1 \Sigma^+_v \) near a detuning of 177 GHz to the red of the D1 line of ^6Li. Its outer turning point is placed at an internuclear separation of about 74 a_0. At this detuning, the singlet series of ^6Li^7Li is sufficiently separated from the heteronuclear triplet resonances as well as from the homonuclear ^9Li^6Li and ^7Li^6Li transitions, while at the same time the photoassociation rates are still large. A high-resolution photoassociation spectrum for an intensity of 420 W/cm^2 is shown in Fig. 1. The four strongest lines ((a)-(d)) can be assigned to transitions from the quartet of hyperfine entrance channels into the rotational level \( N = 1 \) of the excited state. This hyperfine structure reflects the different combinations of atomic hyperfine ground states (hyperfine splitting: 228 MHz for ^6Li and 804 MHz for ^7Li) and is a further clear indication of the heteronuclear structure of the molecule. The absolute transition frequency, adjusted to the hyperfine center of gravity, amounts to 14897.4015(7) cm^{-1}. Several lines to the excited-state levels \( N = 0 \) (resonances (a’)-(d’)) and \( N = 2 \) (resonance (a’’)) are also visible. From more sensitive spectra taken with a less focused laser beam (1.0 mm diameter), the rotational constant \( B/h \) can be determined as 301(2) MHz. The transitions into the \( N = 1 \) level can be assigned to s-wave collisions and the transitions into the levels \( N = 0, 2 \) to p-wave collisions. The contributing partial waves are determined in their parity by the selection rule on the change of angular momentum and in their number by the corresponding centrifugal barriers. For d-wave collisions the barrier amounts to 38 mK at an internuclear separation of 54 a_0, which strongly suppresses contributions from d-waves and above, even as shape resonances.

In the following we discuss the intensity dependence of the photoassociation rate. We took several series of spectra up to intensities of 1000 W/cm^2 and find, that the signal saturates. For all hyperfine transitions, we observe a remaining fraction of ^7Li atoms, that cannot be depleted, even in the limit of high laser intensities. Thus, particle losses due to photoassociation must be limited at high intensities. This limitation is to be explained by the intensity dependence of the photoassociation rate. Internal MOT processes, such as optical pumping, thermalization or diffusion, can be excluded as the origin of the

![Heteronuclear photoassociation spectrum of the singlet v = 83 level of ^6Li^7Li](image)
observed behaviour by a simple time scale argument. In order to lead to a limited depletion, the losses due to photoassociation must occur on the same time scale as the loading time of the MOT, which is about 10 s. Internal MOT processes happen on a much faster time scale and therefore cannot limit the losses.

For a quantitative analysis, one has to take into account that the experimentally observed steady-state particle number $N_T$ depends on the photoassociation rate in a nonlinear way (see Eq. 1). We assume a Lorentzian frequency dependence of the photoassociation rate $\beta_{PA} = a/((f - f_{res})^2 + \gamma^2/4)$, with the central frequency $f_{res}$, the linewidth $\gamma$ and a proportionality factor $a$. Inserting this expression in equation 1 yields:

$$N_T = \frac{N_{T,0}(1-cf)}{1 + a/\alpha(f - f_{res})^2 + \gamma^2/4}. \quad (2)$$

We account for slow drifts in the loading rate during the frequency scan and for partial overlap of the different lines by assuming a linear frequency dependence $\propto (1-cf)$ of the steady-state particle number without photoassociation laser present $N_{T,0}$. For the atomic-beam limited loss rate $\alpha_T$ we use the measured value of 0.11 s$^{-1}$. Up to intensities of 450 W/cm$^2$ for transitions (a) and (b) and of 600 W/cm$^2$ for transitions (c) and (d) the different hyperfine lines do not show any significant asymmetries and partial overlap of the different lines remains small, so that the resulting quasi-Lorentzian function represents the data sufficiently well. This is exemplarily shown in Fig. 2 for transition (a) at two intensities. Obviously, asymmetries due to thermal averaging over the different collision energies are negligible, since the natural linewidth of the excited level (12 MHz, 24, 25) plus the unresolved hyperfine-structure of the excited state is larger than the thermal broadening of about 10 MHz for the MOT temperature of 0.5 mK.

![FIG. 2: Spectra for the $f_{i}=3/2 + f_{j}=2$ transition (resonance (a)) at two different intensities. The solid line (lower panel) is a fit according to Eq. 2, the corresponding residuals are plotted in the upper panel. The frequency scale is relative to the central frequency.](image)

For the determination of the photoassociation rate one has to realize that the shape of the resonances can be influenced by various systematic effects. Due to the focusing of the photoassociation laser and due to inhomogeneities in the beam profile, the light shift varies spatially, which leads to inhomogeneous broadening. The different light shifts for the different hyperfine levels of the excited state contribute similarly. These broadening mechanisms lead to asymmetries at very high intensities and flatten the approximately Lorentzian lines at moderate laser intensities. However, the area of the frequency-integrated photoassociation rate is preserved, which has been checked numerically. Therefore, we correct the maximum photoassociation rate $4a/\gamma^2$, which we get from the fit, by multiplying with the ratio of the broadened linewidth $\gamma$ and the linewidth in the limit for zero intensity, $\gamma_{I=0}$, which gives $\beta_{PA,0} = 4a/\gamma_{I=0}\gamma_{I=0}$.

This corrected photoassociation rate $\beta_{PA,0}$ is proportional to the area of the rate and corresponds to the maximum rate in absence of any broadening mechanisms, both broadening due to systematic effects and power broadening due to saturation. Extrapolation of the broadened linewidths towards zero intensity leads to values for $\gamma_{I=0}$ of 51, 45, 33, 40 MHz for resonances (a)-(d) respectively. They include the natural linewidth, the unresolved structure of the different involved excited hyperfine states and thermal broadening. In Fig. 3 the photoassociation rate for the four different hyperfine transitions is presented as a function of the laser intensity. The data points are mean...
values of up to 4 spectra. The error bars indicate the statistical error. While the rates for the transitions (c) and (d) do not saturate in the given intensity range (the uncorrected rates \(4a/\gamma^2\), which seem to saturate are also indicated), strong saturation is observed for the transitions (a) and (b). As the \(^6\)Li density is nearly unaffected by the photoassociation, this saturation must be due to saturation of the rate coefficient \(K\).

For the interpretation we use a simplified model according to the close-coupled theory of Bohn and Julienne \([15]\). It yields an analytic expression for the rate coefficient for a two-level system and a specific scattering energy. To compare with the experimental corrected photoassociation rate, we have to adapt the theoretical expression by multiplying with the ratio of the power-broadened linewidth and the natural linewidth. For s-wave collisions this leads to the following intensity dependence for the corrected photoassociation rate coefficient:

\[
K_0 = \frac{\pi v}{k^2} \frac{4}{1 + I_{sat}/I}
\]

where \(v\) is the velocity and \(k\) is the wave number of the relative motion. \(I_{sat}\) is the energy-dependent saturation intensity, for which the natural linewidth equals the induced linewidth. This intensity dependence also applies for the thermally-averaged corrected rate coefficient with approximately the same saturation intensity, as checked by simulations. A full theoretical analysis would include a population-weighted summation over the different transitions from the magnetic ground-state sublevels to the various excited hyperfine states and has not been carried out yet. We thus assume the validity of the expression (Eq. 3) also for the full problem, and use it for a fit to the data of the saturating transitions. For the saturation intensities we obtain values of 28 W/cm\(^2\) for transition (a) and of 54 W/cm\(^2\) for transition (b). This is about \(10^4\) times the atomic saturation intensity and in good agreement with an estimation for a two-level system, which gives 33 W/cm\(^2\) for an energy of \(E/k_B = 0.5\) mK \([20]\).

For the corrected photoassociation rates, we receive maximum values of 0.06 s\(^{-1}\) for resonance (a) and 0.14 s\(^{-1}\) for resonance (b). Taking into account an estimated \(^6\)Li peak intensity of \(10^{10}\) cm\(^{-3}\), the overlap factor \(r = 0.22\), the population factor \(w\) (0.42 and 0.21 for the transitions (a) and (b) respectively, statistical distribution assumed), and the correction factor of 4 (see Eq. 3), the saturated photoassociation rate coefficient \(K\) can be estimated to be \((2 \cdot 10^{-11} - 8 \cdot 10^{-11})\) cm\(^3\)s\(^{-1}\). This value is close to the unitarity limit, where the scattering probability \(|S|^2 \rightarrow 1\). In this limit the rate coefficient is simply given by the product of the scattering cross-section \(\pi/k^2\) and the velocity \(v\), resulting in \(5 \cdot 10^{-10}\) cm\(^3\)s\(^{-1}\) for the temperature considered. For a more sophisticated analysis, knowledge of the different ground-state sublevel populations, of the various Clebsch-Gordan coefficients and of laser-polarization effects would be required.

In summary, we have observed heteronuclear photoassociation in \(^6\)Li\(^7\)Li. Studying the intensity dependence of the hyperfine resolved singlet spectrum, we have observed saturation of the rate coefficients for two of the four hyperfine lines and determined the corresponding saturation intensities. The observation of the unitarity limit has been possible, as it is orders of magnitude lower at MOT temperatures than at temperatures in the degenerate regime \([21]\). Reaching the unitarity limit is another proof that already at MOT temperatures quantum mechanical properties become apparent.

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