Formation of Ultracold Polar Molecules in the Rovibrational Ground State

J. Deiglmayr, A. Grochola,* M. Repp, K. Mörtlbauer, C. Glück, J. Lange, O. Dulieu,+ R. Wester, and M. Weidemüller‡
Albert-Ludwigs-Universität Freiburg, Physikalisches Institut, Hermann-Herder-Str. 3, 79104 Freiburg, Germany
(Received 20 July 2008; published 25 September 2008)

Ultracold LiCs molecules in the absolute ground state $X^1\Sigma^+$, $v''=0$, $J''=0$ are formed via a single photoassociation step starting from laser-cooled atoms. The selective production of $v''=0$, $J''=2$ molecules with a 50-fold higher rate is also demonstrated. The rotational and vibrational state of the ground state molecules is determined in a setup combining depletion spectroscopy with resonant-enhanced multiphoton ionization time-of-flight spectroscopy. Using the determined production rate of up to 5×10^3 molecules/s, we describe a simple scheme which can provide large samples of externally and internally cold dipolar molecules.

DOI: 10.1103/PhysRevLett.101.133004 PACS numbers: 37.10.Mn, 33.20.−t, 33.80.Rv

A gaseous cloud of translationally ultracold molecules, i.e., well below a temperature of 1 mK, in their rovibrational ground state is the starting point for many intriguing scientific applications, such as the exploration of quantum phases in dipolar gases [1,2], the development of quantum computation techniques [3], precision measurements of fundamental constants [4], and the investigation and control of ultracold chemical reactions [5]. A number of experimental approaches are currently being studied to prepare and manipulate ultracold molecules [6,7]. Up to now, the formation of ultracold molecules in the lowest vibrational level of the electronic ground state has been demonstrated for ultracold KRb [8], RbCs [9], and Cs_2 [10], in all cases using complex photoassociation schemes in an ultracold gas of atoms involving both continuous and pulsed laser fields. In an alternative approach, ultracold gaseous samples of magneto-associated, weakly bound molecules, so-called Feshbach molecules, have recently been transferred into deeply bound vibrational states, yet not the lowest state, by coherent adiabatic passage [11–13].

In this Letter, we demonstrate the production of ultracold LiCs molecules in the absolute vibrational *and* rotational ground state $X^1\Sigma^+$, $v''=0$, $J''=0$, by scattering the light of a single narrow-band photoassociation (PA) laser off pairs of magneto optically trapped lithium and cesium atoms. We unambiguously assign the produced quantum state using high resolution, rotationally selective depletion spectroscopy combined with resonance enhanced multiphoton ionization time-of-flight (REMPI-TOF) mass spectrometry. The sequence of the formation and detection steps is schematically shown in Fig. 1.

^{133}Cs and ^{7}Li atoms out of a double species oven are slowed in a Zeeman slower and trapped in an overlapped magneto-optical trap (MOT) for lithium and a forced dark-spot MOT (SPOT) [14] for cesium. We trap 4×10^7 cesium atoms and 10^8 lithium atoms at densities of 3×10^9 and 10^{10} cm^{-3}, respectively. Time-of-flight expansion was used to measure a cesium temperature of 250(50) μK. Because of the large photon recoil and unresolved hyperfine structure of the excited state, the lithium atoms have a temperature of hundreds of μK. In the cesium SPOT, 97% of the atoms are in the lower hyperfine ground state $F=3$, while in the lithium MOT, 80% of the atoms are in the upper hyperfine state $F=2$. Therefore, the atoms collide mainly on the $\text{Li}(2^2S_{1/2}, F=2)+\text{Cs}(6^2S_{1/2}, F=3)$ asymptote. For PA, 500 mW of light from a Ti:Sa laser is collimated to a waist of 1.0 mm and passed through the center of the trap region, left on continuously during all measurements. For the detection of formed molecules, first all cesium atoms in the trap are quenched to the ground state by blocking the cesium repumper, because two-photon ionization of excited cesium atoms would form a strong background signal for the detection of LiCs$^+$ ions. After 0.6 ms, a pulsed dye laser (pulse energy 4 mJ, pulse length 7 ns, bandwidth 2 GHz) ionizes ground state molecules. The laser beam is collimated to a waist of ~5 mm and is aligned to pass roughly one beam diameter below the trapped atoms in order to prevent excessive ionization of

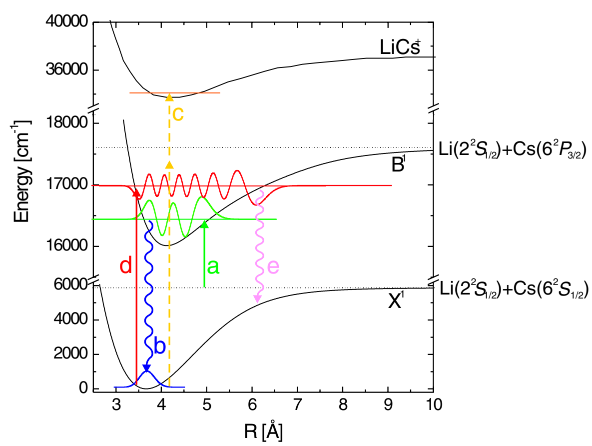

FIG. 1 (color online). Sketch of the excitation and detection scheme. (a) photoassociation by Ti:Sa laser at 946 nm, (b) spontaneous decay into deeply bound ground state molecules, (c) two-photon ionization with resonant intermediate state. For depletion spectroscopy: (d) excitation of ground state molecules, (e) redistribution of ground state population; potentials curves from Ref. [19,20,32].

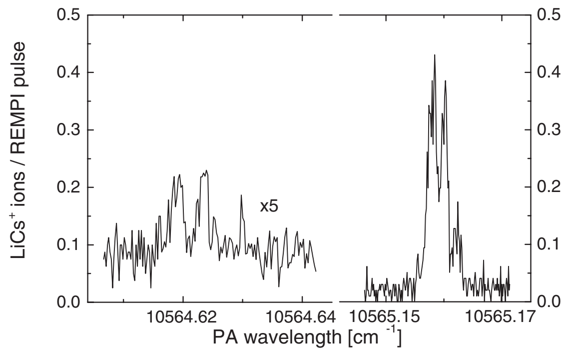

FIG. 2. The $v' = 4$, $J' = 1$ (left trace) and $J' = 2$ (right trace) PA resonances in the $B^1\Pi$ state. The $J' = 1$ trace has been enlarged by a factor of 5 for better visibility.

atoms. The ions are then detected in a high resolution time-of-flight mass spectrometer and are counted in a single-ion counting setup (for details, see Ref. [15,16]). The extraction fields of 47 V/cm are switched on only 0.5 ms before the ionization pulse for 1 ms, so that the PA is performed mainly under field-free conditions. This experimental cycle is repeated at 20 Hz.

We determine the relative collision energy of lithium and cesium atoms by fitting the shape of a narrow, temperature-broadened PA resonance with the model of Ref. [17]. Assuming a natural linewidth of $\gamma = 7$ MHz, we deduce a relative collision temperature of 530(80) μK, dominated by the temperature of the lithium atoms. This is well below the LiCs p-wave centrifugal barrier of 1.6 mK derived from the C_6 dispersion coefficient of Ref. [18]. Assuming a Boltzmann distribution of collision energies, we expect a p-wave contribution on the order of 5% and no contributions from higher partial waves.

For the production of ground state molecules, photoassociation is performed via the $B^1\Pi$ state correlated to the $\mathrm{Li}(2^2S_{1/2}) + \mathrm{Cs}(6^2P_{3/2})$ asymptote. We identify vibrational levels from $v' = 35$ just below the asymptote down to $v' = 4$ and find excellent agreement with the energies calculated from an experimental potential energy curve for this state [19].

For the experiments presented in this Letter, we focus on the $v' = 4$, $J' = 1$, and $J' = 2$ levels of the $B^1\Pi$ state which are addressed with PA light of 946.56 nm. Typical PA scans of the corresponding resonances are shown in Fig. 2. Both resonances show substructure which reflects the molecular hyperfine interactions. For PA, we always choose the strongest component. It is noteworthy to mention the strongly increased PA rate for the $J' = 2$ over the $J' = 1$ resonance by roughly a factor of 20. This is in contrast to ratios $\sim$1 observed in our experiment for higher vibrational levels $v' > 20$. A full analysis of the observed PA line shapes will be the subject of further studies.

The excited $B^1\Pi$, $v' = 4$ molecules decay spontaneously only into the $X^1\Sigma^+$ state [19]. Using the experimental potential curves from Ref. [19,20] and an *ab initio* R-dependent dipole moment function [21], Einstein A coefficients for the spontaneous decay from $B^1\Pi$, $v' = 4$ into $X^1\Sigma^+$ levels are calculated. Table I shows the deduced relative population of the $X^1\Sigma^+$ levels. From these calculations, 23% of all excited state molecules are expected to decay into the $X^1\Sigma^+$, $v'' = 0$ level. We note that nearly all excited $v' = 4$ molecules are expected to decay into bound molecules, since the sum over all Franck-Condon (FC) factors for decay into the $X^1\Sigma^+$ state is close to unity [23].

The formation of $X^1\Sigma^+$ molecules is detected by two-photon ionization with typical wavelengths in the range of 575 to 600 nm. At these energies, vibrational levels $v'' =$ 0–4 of the $X^1\Sigma^+$ state can be ionized via the well-known intermediate $B^1\Pi$ state. Figure 3 shows a REMPI scan together with expected positions for transitions from the $X^1\Sigma^+$, $v'' =$ 0–3 levels to intermediate levels in the $B^1\Pi$ state. Resonances are clearly visible at the expected positions for transitions from $X^1\Sigma^+$, $v'' = 0$ to intermediate levels $B^1\Pi$, $v' =$ 13–17. However, some of these resonances could also include contributions from higher vibrational states. The intensities required for the ionization of ground state molecules strongly saturate the first resonant bound-bound transitions; therefore, the rotational structures of the ground state levels is not resolved.

In order to further identify the internal quantum states of the ultracold ground state molecules, we perform depletion spectroscopy of the formed ground state molecules [24]. An additional narrow-band laser optically pumps population out of rovibrational levels of the $X^1\Sigma^+$ ground state (Fig. 1). Those levels are coupled to specific rovibrational levels in the $B^1\Pi$ potential from which spontaneous decay leads to higher-lying vibrational levels. The full scheme for the depletion spectroscopy is as follows: with the PA laser locked at a chosen resonance, the REMPI laser is set to selectively ionize one vibrational ground state and a cw dye laser (bandwidth $\sim$5 MHz, typically 40 mW, $\omega_0 =$ 0.7 mm), aligned collinear with the PA light, is scanned. Rotational components of the chosen vibrational level are detected as a reduction of the ion count rate when the narrow cw dye laser is resonant with transitions to excited state levels. The expected positions of the depletion resonances are given by $\hbar\omega_0 + B'J'(J'+1) - B''J''(J''+1)$ where $\hbar\omega_0$, the term energy difference between excited and ground state vibrational level, and B' (B''), the excited state (ground state) rotational constant, are calculated from experimental potential energy curves [19,20].

TABLE I. Calculated relative population of vibrational states in the $X^1\Sigma^+$ state after photoassociation via $B^1\Pi$, $v' = 4$.

$X^1\Sigma^+$, $v'' =$	**0**	1	2	3	4	5	6	7	8	9	10	Σ(11–20)	Σ(>20)
Rel. pop. [%]	**23**	1	12	2	3	8	2	1	5	6	2	35	0

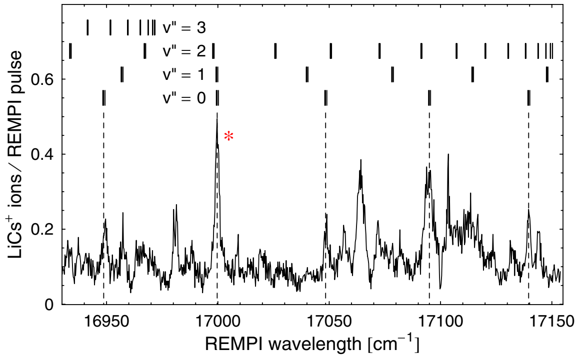

FIG. 3 (color online). Resonant-enhanced multiphoton ionization of ground state molecules produced by photoassociation via $B^1\Pi$, $v' = 4$, $J' = 2$. In the upper part, calculated line positions between all vibrational levels in the $X^1\Sigma^+$ and in the $B^1\Pi$ state are marked. The star (*) marks the resonance used in the depletion spectroscopy. At the moment, we do not have a full assignment of all observed resonances.

Depletion scans were performed for $X^1\Sigma^+$, $v'' = 0$ molecules, ionized via the intermediate $B^1\Pi$, $v' = 14$ level at an ionization wavelength of 16999.4 cm^{-1} (marked with a star in Fig. 3). In the scan of Fig. 4(a), the molecules are produced by PA via $B^1\Pi$, $v' = 4$, $J' = 2$ (Fig. 2, right trace). We observe that excitation on the transitions from $X^1\Sigma^+$, $v'' = 0$, $J'' = 2$ to $B^1\Pi$, $v' = 12$, $J' = 1$–3 reduces the ion count rate down to the background level. Therefore, the ions at this REMPI resonance originate predominantly in the $X^1\Sigma^+$, $v'' = 0$ level. The spontaneous decay of the $B^1\Pi$, $v' = 4$, $J' = 2$ level occurs only via the Q branch ($\Delta J = 0$) leading to the population of only $J'' = 2$ rotational levels, as shown by the rotational assignment in Fig. 4(a) [25]. From the measured spectrum, we derive the excited state rotational constant $B'' = 3.10(5)$ GHz in excellent agreement with the calculated value of 3.096 GHz. In combination with the calculated ground state rotational constant B'', one gets $\hbar\omega_0 = 16895.75(2)$ cm^{-1} which is also in very good agreement with the expected value of 16895.77 cm^{-1}. The depletion resonances show a width of about 2 GHz, which can be attributed to hyperfine broadening of the excited states (typically 500 MHz) and strong saturation of the transition. Hyperfine structure of deeply bound ground state levels is expected to be below 1 MHz and is therefore not resolved in the current experiment.

Figure 4(b) shows a depletion scan for $v'' = 0$ molecules produced via the PA resonance $B^1\Pi$, $v' = 4$, $J' = 1$ (Fig. 2, left trace). With $\hbar\omega_0$ and B' from the depletion spectrum of Fig. 4(a) and the calculated value for B'', the exact positions of the depletion resonances are known. Using the widths found for the $J' = 2$ depletion resonances and relative population strengths from Hönl-London-Factors, we fit spectra for different excited state parities to the data in Fig. 4(b). The only free fit parameters are the level of the undepleted ion signal and the depletion depth.

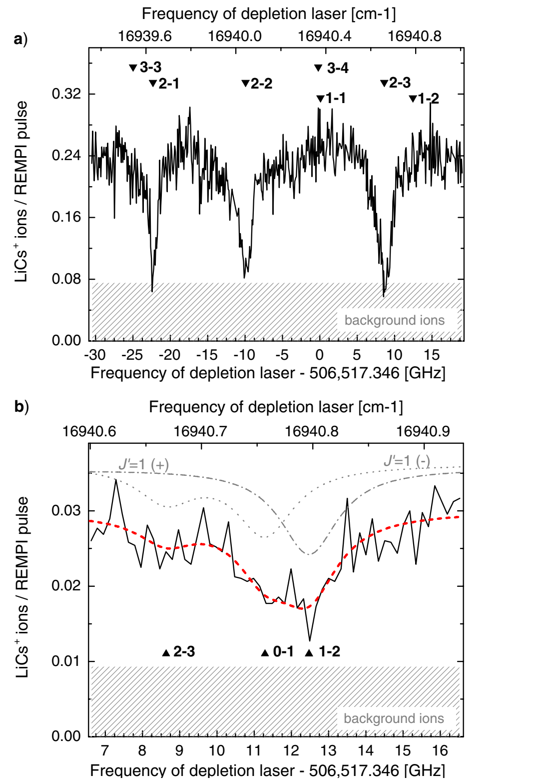

FIG. 4 (color online). Depletion laser scan with the PA laser resonant to the $B^1\Pi$, $v' = 4$, $J' = 2$ level (a) and to the $v' = 4$, $J' = 1$ level (b). In the upper part of the graphs, calculated wavelengths for transitions from $X^1\Sigma^+$, $v'' = 0$, J'' to $B^1\Pi$, $v' = 12$, J' (labeled J''-J') are marked. The dotted and dash-dotted gray lines in (b) are fitted spectra (see text for details) assuming PA via the (−) and (+) parity component of $J' = 1$, respectively, offset for visibility. The dashed (red) line is a fit combining both parities. The background at large formation rates as in (a) is dominated by $LiCs^+$ ions from off-resonant excitation of other vibrational ground state levels. For small formation rates as in (b), spurious detection of fast Cs^+ ions constitutes the main background [16].

The precisely known positions of the depletion resonances make a single excited state parity unlikely and we attribute the observed spectrum to PA via both parity components with equal strength leading to population of $X^1\Sigma^+$, $v'' = 0$, $J'' = 0$, 1, and 2 states [26].

For molecules in the absolute ground state $X^1\Sigma^+$, $v'' = 0$, $J'' = 0$, produced by PA via $B^1\Pi$, $v' = 4$, $J' = 1$, on average 5×10^{-3} $LiCs^+$ ions are detected per ionization pulse. Since the experiment is running at 20 Hz, this yields a detection rate of 0.1 ions/s. Taking into account a geometric overlap factor of 40%, a typical on-resonance ionization probability of 1%, and a detector efficiency of 20% [27], this results in a production rate of about 1×10^2 molecules/s in the $v'' = 0$, $J'' = 0$ absolute ground state. For molecules in the $X^1\Sigma^+$, $v'' = 0$, $J'' = 2$ state, produced by PA via $B^1\Pi$, $v' = 4$, $J' = 2$, on average 0.2 $LiCs^+$ ions per ionization pulse are detected. Following the same argument as above, this results in a production rate of about 5×10^3 molecules/s in the ground state level $v'' = 0$, comparable to the rate given in Ref. [9] for RbCs and roughly a factor 20 smaller than the rate given in Ref. [10] for the homonuclear Cs_2. However, we want to point out that we determine rates for the population of a single vibrational and rotational state, while in the cited references, the produced molecules are distributed over a range of rotational states. The translational temperature of the molecules is estimated based on the atomic values and a simple kinematic model to be about 260 μK, dominated by the temperature of the heavier cesium; contributions from photon recoil during the single absorption and emission cycle are not significant.

As the presented scheme for the formation of molecules relies on spontaneous decay, it allows the continuous accumulation of molecules in the absolute ground state. Because of the large vibrational level spacing in LiCs accidental reexcitation of formed molecules by the narrow-band PA laser is very unlikely. This accumulative approach is in contrast to schemes involving adiabatic transfer. The molecules produced in the presented setup could be trapped in an electrostatic trap [28]. Alternatively, one could start from a mixture of lithium and cesium atoms in an optical dipole trap [29], where typically tenfold increased densities could lead to a production rate on the order of 5×10^5 molecules/s for ground state molecules in $v'' = 0$, $J'' = 2$. On a time scale of seconds, a large part of the trapped atom pairs may therefore be transformed into molecules. In a final step of adiabatic transfer using microwaves at 22.5 and 11.2 GHz, the $J'' = 2$ molecules could be transferred to $J'' = 0$. Excited vibrational states would be constantly removed by inelastic collisions with ultracold atoms, as shown for $Cs_2 + Cs$ [30,31]. Sympathetic cooling in the dipole trap [29] may yield molecular samples with temperatures down to the nanokelvin regime. This may open up an efficient route to form stable quantum gases of molecules in their absolute internal ground state.

We thank S. D. Kraft and P. Staanum for contributions at the early stage of the experiment. We thank E. Tiemann and A. Pashov for providing experimental LiCs potentials before publication and, together with J. Hutson, for fruitful discussions. This work is supported by the DFG under WE2661/6-1 in the framework of the Collaborative Research Project QuDipMol within the ESF EUROCORES EuroQUAM program. J. D. acknowledges partial support of the French-German University. A. G. received support from the Alexander von Humboldt-Foundation.

Note added in proof.—After submission of this Letter, two other groups also reported the formation of ultracold molecules in the rovibrational ground state [33,34].

*Also at the Institute of Experimental Physics, Warsaw University, Poland
†Permanent address: Laboratoire Aimé Cotton, CNRS, Université Paris Sud XI, Orsay, France
‡weidemueller@physik.uni-freiburg.de

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