Efficient Production of Ground-State Potassium Molecules at Sub-mK Temperatures by Two-Step Photoassociation

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We have developed a two-step "R-transfer" method that efficiently produces translationally ultracold potassium molecules in the $X\,^1\Sigma_g^+$ electronic ground state. Laser-cooled atoms are initially photoassociated at large internuclear separation R to form molecules in high vibrational levels of the $1\,^1\Pi_g$ state, which are in turn excited by an additional laser to shorter-range Rydberg states such as $5\,^1\Pi_u$ and $6\,^1\Pi_u$. Subsequent radiative decay produces ground-state molecules at rates up to 10^5 molecules/second per vibrational level.

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In the past two years, it has become possible for the first time to produce and detect stable diatomic molecules with sub-mK translational temperatures [1–6]. With improved methods for producing and trapping these molecules, it should soon be possible to study ultracold molecular collisions, reactions, and quantum collective effects. Ultracold molecules are also expected to find use in precision spectroscopy and tests of fundamental symmetries. Many of these experiments will require ultracold ground-state molecules in low vibrational levels, to avoid vibrational quenching by atom-molecule or molecule-molecule collisions [7]. Most of the experimental work until now has relied on single-photon photoassociation of ultracold alkali atoms in a magneto-optical trap (MOT). Photoassociation produces excited-state molecules which, depending on their symmetry, can radiatively decay to the ground $X\,^1\Sigma_g^+$ state or the $a\,^3\Sigma_u^+$ triplet metastable state. However, this approach cannot efficiently produce molecules in low vibrational levels of the ground X state, with $R \approx 7.4a_0$ for K_2, because photoassociation is efficient only at large internuclear separations, typically $R \approx 50a_0$. Excited-state molecules are produced only in long-range states, which radiate predominantly either back to the vibrational continuum or to bound states with high vibrational quantum numbers.

Recent experimental results have reflected this restriction. Triplet Cs_2 molecules have been produced by Fioretti *et al.*, at rates up to 10^6/second [1], and they also reported significant production rates for very high vibrational levels of the singlet ground state [8]. By contrast, in our own previous work [2] on deeply bound levels of the singlet ground state of K_2, we produced only about 10^3 molecules/second in vibrational levels near $v = 35$. The lowest vibrational levels were not populated at all. Until now, the only method that has successfully circumvented this problem is the alternative approach of buffer-gas cooling [9]. Doyle and co-workers have cooled laser-ablated molecules by collisions with cold ^{3}He [10], and recently they were able to load up to 10^8 ground-state CaH molecules into a magnetic trap [11]. Compared with photoassociation, buffer-gas cooling produces much hotter molecules, with typical temperatures of 400 mK as opposed to 200–600 μK. In the future it may be possible to evaporatively cool trapped molecules produced by buffer-gas cooling. However, this requires a deep magnetic trap formed by a superconducting magnet, and is feasible only for paramagnetic species. Thus photoassociative production of cold molecules is clearly preferable for nonparamagnetic species such as singlet-state alkali dimers, and for experiments that cannot tolerate large magnetic fields.

In this Letter, we report results from a two-step photoassociation scheme that produces ultracold ground-state molecules with greatly improved efficiency, and with a vibrational distribution that includes some of the lowest vibrational levels. Our scheme, depicted in Fig. 1, is conceptually similar to one proposed several years ago by Band and Julienne [12]. In the first step, ground-state atoms are photoassociated to form long-range molecules in a selected high vibrational level of the $1\,^1\Pi_g$ state, with an outer turning point of about $45a_0$. In the second step, the molecules are further excited to a selected rovibrational level of a Rydberg state, in this case the $5\,^1\Pi_u$ or the $6\,^1\Pi_u$ state. This provides an opportunity for "R transfer" to internuclear separations more typical of ground-state molecules. Because the second step is a bound-bound transition, efficient excitation is possible with moderate laser powers ($\approx$100 mW) even if the Franck-Condon factors are small. Ideally, this upper state should be free from predissociation and should radiate principally to the ground X state. Radiative decay will then produce X state molecules with a vibrational distribution that can be manipulated by selecting the vibrational level of the upper state.

The $5\,^1\Pi_u$ and $6\,^1\Pi_u$ states were selected as candidates for the upper state because the required laser wavelengths near 850 nm are convenient, and because the higher rotational levels of these states have been previously observed in high-resolution laser spectra [13]. This simplifies the search for the low rotational levels and makes it possible to estimate Franck-Condon factors to the X state.

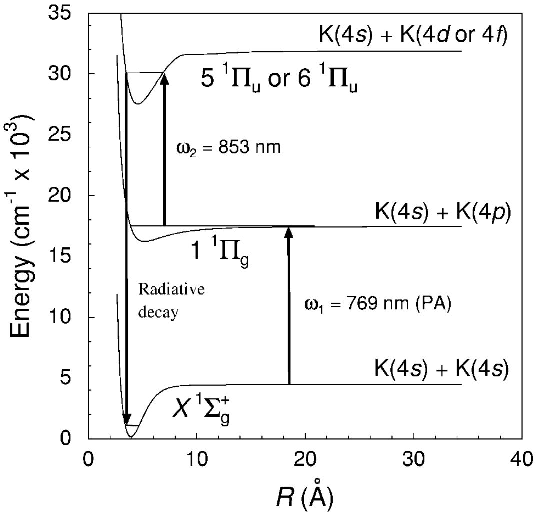

FIG. 1. Formation of ground-state potassium molecules by two-step photoassociation. Potential curves are from Ref. [14]. The second excitation step accomplishes an "R transfer" to short internuclear distances. The ground state can be populated both by direct radiative decay and cascades through intermediate singlet states.

For example, using the Rydberg-Klein-Rees potential of Ref. [13], we calculate a Franck-Condon factor of 0.1 from the $v = 13$ level of the $6\,^1\Pi_u$ state to the $v = 0$ level of the ground state. There is a price to pay for this, because the Franck-Condon factor for excitation from the $1\,^1\Pi_g$ intermediate state with $v = 89$ is only about 1×10^{-3}, but the laser power requirements are moderated by the narrow bandwidth of this bound-bound transition. After starting our experiments, we learned that the dipole transition moment from the $6\,^1\Pi_u$ state to the ground state is small and strongly R dependent [14], so the X state vibrational distribution is modified by non-Franck-Condon behavior and possibly by indirect population via radiative cascades from the $6\,^1\Pi_u$ state through lower excited singlet states. Nevertheless, the $6\,^1\Pi_u$ state turns out to be a suitable upper state for the "R-transfer" scheme.

In our experiments, we use a "dark-spot" vapor cell MOT to trap about 10^7 atoms of ^{39}K. The trap was previously described [15,16], and is modified only by increasing the power of the trapping laser by about 50%, and by approximately doubling the repump laser power. The MOT produces an atomic density of $>10^{11}$ cm^{-3} with a loading time of 400–600 ms. At least 75% of the atoms are in the $F = 1$ hyperfine "dark" state.

We photoassociate pairs of atoms to the intermediate $1\,^1\Pi_g$ state using a single-mode ring dye laser (Coherent 899-29) at 769 nm, producing $\simeq$200 mW focused to a $1/e^2$ radius of about $\omega_0 \simeq 450$ μm. At large internuclear separations, the $1\,^1\Pi_g$ state correlates to a potential curve of 1_g symmetry in Hund's coupling case (c), converging to the $4S + 4P_{3/2}$ dissociation limit. We chose to photoassociate to the $v = 89$ level, bound by 32.18 cm^{-1}, as an acceptable compromise between three conflicting criteria: (i) Cross sections for photoassociation increase with vibration, because the outer turning point moves to larger R. (ii) The Franck-Condon factors for $6\,^1\Pi_u \leftarrow 1\,^1\Pi_g$ excitation decrease with vibration, making saturation impossible above about $v = 95$ of the $1\,^1\Pi_g$ state. (iii) Vibrational levels with $90 < v < 106$ are observed to predissociate weakly [17], although the predissociation rates are believed to be slower than the radiative decay rates. We found it necessary to directly detect the photoassociated $1\,^1\Pi_g$ molecules in order to facilitate tuning the laser to exact resonance, and to permit optimization of the MOT parameters for maximum photoassociation rates. To do this, we introduce an auxiliary laser, a single-mode cw ring dye laser (Coherent 699-29) tuned to resonance from the $1\,^1\Pi_g$ state to unassigned bound levels observed just below the $4S + 5D$ dissociation limit. Excitation of these levels produces a cw ion signal, probably via autoionization [16,18]. With about 400 mW of detection laser power, the $1\,^1\Pi_g$ spectrum can be observed with a signal-to-noise ratio greater than 100:1. The rotational structure of the $1\,^1\Pi_g$ state is almost fully resolved, allowing us to selectively produce the $J = 1$, $J = 2$, or $J = 3$ rotational levels.

After the photoassociation step is optimized, the second step is excited by introducing light from a single-mode cw Ti:sapphire laser. It operates at 830–855 nm, producing 400 mW, and is focused to a radius of $\omega_0 \simeq 670$ μm. To monitor transitions to the $5\,^1\Pi_u$ and $6\,^1\Pi_u$ states, we again make use of a cw ionization signal, produced predominantly by the absorption of one additional photon from the photoassociation laser. Figure 2 shows a scan of this second-step laser. As a starting point in locating these transitions, transition frequencies to the $5\,^1\Pi_u$ and $6\,^1\Pi_u$ states were calculated using the molecular constants of Ref. [13]. However, these constants were derived from spectra of high rotational levels, and the extrapolation to low J introduces considerable uncertainties. Still, we were easily able to locate transitions to four vibrational

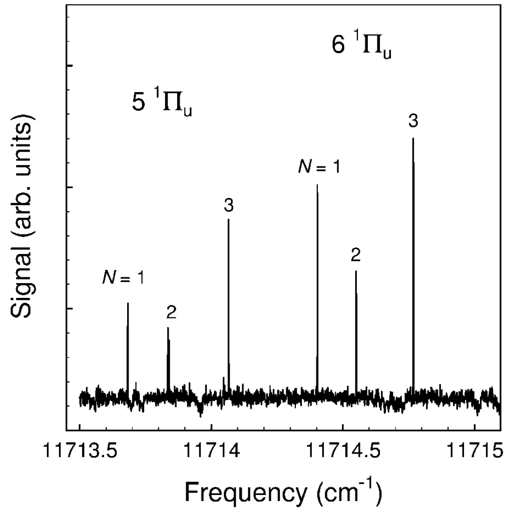

FIG. 2. Scan of the second-step excitation laser at 853 nm, showing transitions from the $1\,^1\Pi_g$, $v = 89$, $J = 2$ level to rotational levels of $5\,^1\Pi_u$, $v = 28$ and $6\,^1\Pi_u$, $v = 13$.

levels of the $6\,^1\Pi_u$ state, shifted by 2.8 ± 0.1 cm^{-1} above the predicted positions. Transitions to the $5\,^1\Pi_u$ state were also observed, as well as transitions to at least one other electronic state that has yet to be positively identified. The linewidths of all of these transitions are very narrow, comparable to the $1\,^1\Pi_g$ state hyperfine structure of about 20 MHz. This sets a lower limit of 8 ns for the excited-state lifetimes, indicating that they are sufficiently stable against predissociation to allow efficient radiative decay. The well-resolved rotational branches allow us to select a well-defined rotational level, and thereby manipulate the distribution of ground-state rotational levels populated by radiative decay.

We monitor the radiative formation of ultracold molecules in the ground X state using a pulsed ionization scheme nearly identical to the one used in our previous work [2]. It employs two-color resonant ionization through the $B\,^1\Pi_u$ state by use of nanosecond laser pulses, a detection scheme that is selective, sensitive, and highly efficient. $B \leftarrow X$ transitions are excited with a red tunable pulsed laser at 630–640 nm, with energies of 1–10 μJ in a 6 ns pulse with a beam radius of $\omega_0 \simeq 3$ mm. The B state molecules are then ionized by a pulsed Nd:YAG laser, using 30–140 μJ in a beam radius of $\omega_0 \simeq 2.2$ mm. Atomic and molecular ions are easily distinguished by their time of flight using a gated integrator. During the detection process, the trapping laser is switched off for 500 ns. We have observed ground-state molecules produced from both the $5\,^1\Pi_u$ and $6\,^1\Pi_u$ upper states, but the majority of our work was done using the $6\,^1\Pi_u$ state.

By scanning the detection laser, the $B \leftarrow X$ vibrational bands can be partially resolved, though the pulsed laser resolution of about 0.5 cm^{-1} causes considerable overlap. Figure 3 shows one such spectrum. A few vibrational bands, such as (42–25), can be uniquely identified, while most other spectral features have two or more possible assignments. To simplify the spectrum and further confirm that we are observing ground-state molecules, we introduced an additional cw photodissociation laser that can dissociate ground-state vibrational levels having $v > 17$ over the barrier of the B state potential curve. The results, shown in the light trace on Fig. 3, confirm that transitions from higher X state vibrational levels are depleted preferentially. The survival of a feature near 15 589 cm^{-1} strongly suggests that $v = 0$ molecules are present. Analysis of these and other spectra indicates that the ground-state vibrational distribution includes roughly ten levels with large populations. Unfortunately, an accurate quantitative determination of the vibrational distribution is not possible, because the detection efficiency can vary considerably from one vibrational level to another. However, the distribution definitely includes low vibrational levels with $v < 10$, including $v = 0$. In a forthcoming publication, we will provide a much more complete description of the $B \leftarrow X$ spectra obtained for various choices of the upper level in the $5\,^1\Pi_u$ or the $6\,^1\Pi_u$ state [19].

The production rate for ground-state molecules can be estimated from the size of the ion signals. For the $v = 25$ level of the X state, which gives one of the stronger spectral features that can be uniquely identified, we estimate that we are producing at least 9×10^4 molecules/second. This number is based on knowledge of the detection laser energies and saturation intensities, detection duty cycle, and channeltron quantum efficiency [20]. In addition, we observe maximum production rates well in excess of 10^5 molecules/second for unresolved vibrational levels. These production rates contrast sharply with our previous single-photon production scheme, which yielded total rates of $1\text{–}2 \times 10^3$ molecules/second.

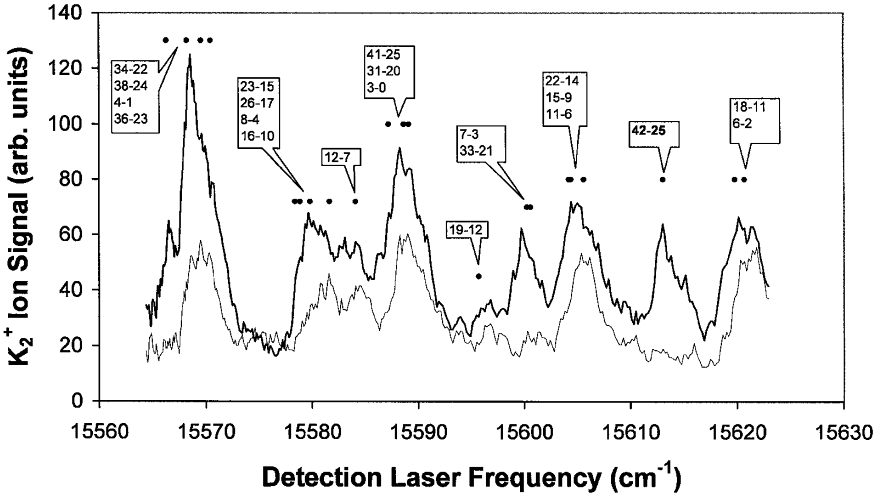

FIG. 3. Low resolution spectrum of a $B \leftarrow X$ transition, showing all possibilities for vibrational assignments ($v' - v''$) of the most prominent features. The photoassociation laser is set to the $1\,^1\Pi_g$, $v = 89$, $J = 2$ level and the second-step laser is set to the $6\,^1\Pi_u$, $v = 15$, $N = 1$ level. The transition frequencies are uncertain by 1 cm^{-1}. The lower trace is taken in the presence of an additional "photodissociation" laser at 16 304.3 cm^{-1}, which can dissociate high-v levels. Predicted line positions are based on results from high resolution spectra obtained by Heinze *et al.* [21] and Amiot [22].

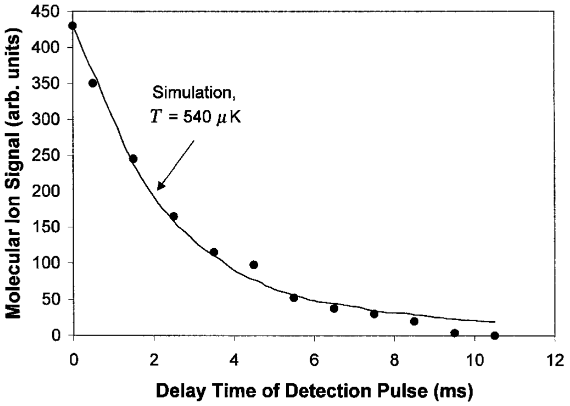

FIG. 4. Decay of the K_2^+ signal after the 853 nm laser is switched off with an acousto-optic modulator. Simulation results depend slightly on the length of the detection region, here taken to be 5 mm, somewhat shorter than estimated by other methods.

The temperature of the ground-state molecules can be estimated by measuring the decay of the molecular ion signal after gating off the second step laser with an acousto-optic modulator. Figure 4 shows a typical decay curve. We have simulated this decay with a Monte-Carlo calculation, assuming that the molecules leave with ballistic trajectories. A Maxwell-Boltzmann distribution is assumed, though the actual velocity distribution may be somewhat different because of the velocity dependence of the photoassociation cross section. Reasonable fits can be obtained for temperatures in the range 450–650 μK, near the upper end of the range of atomic temperatures normally encountered in our potassium MOT.

In summary, we have demonstrated a novel production scheme for ultracold K_2 molecules in the ground $X\,^1\Sigma_g^+$ state. The method utilizes two-step photoassociation, followed by radiative decay, to form tightly bound dimers starting from free ultracold atoms at long range. The present results are a dramatic improvement over our previous work [2] in two regards. First, the production rate has been increased by a factor of ~ 100, yielding $\sim 10^5$ molecules per second in certain vibrational levels. Second, we are able to populate low vibrational states, likely including $v = 0$. Both factors will be important to future applications of ultracold molecules. Most applications will require large molecular samples, and the lowest rovibrational level of the ground state is the only state that is stable against quenching collisions with atoms or molecules. The prospects for optically trapping large numbers of ultracold molecules appear promising, opening the door for collisional studies, precision spectroscopy, and possibly quantum collective effects.

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[20] We calibrate our counting rates by integrating the molecular ion signal detected during a 6 nsec time window and dividing by the single ion response of the channeltron detector, taken to be 20%. We then account for the detection duty cycle: as a result of our finite detection volume and the small molecular velocities, each detection pulse counts molecules that are produced during the 3 msec prior to the pulse. The pulse repetition rate for detection is 10 Hz. Finally, we scale the detected molecule rate to reflect the efficiency of pulsed laser ionization, in this case about 10%, making a conservative estimate because the ionization efficiency was not accurately determined.

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