Observation of Ultracold Ground-State Potassium Molecules

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Ultracold potassium molecules are produced in the $X\,^1\Sigma_g^+$ electronic ground state by photoassociation in a magneto-optical trap. They are detected sensitively and selectively by use of two-color resonant ionization, followed by time-of-flight mass spectroscopy. We observe deeply bound molecules with $\nu \cong 36$, at a temperature of about 300 μK. Presently about 1000 molecules/sec are produced, and much higher production rates should be attainable in the future. [S0031-9007(98)08237-4]

Although there has been a great deal of progress in the production of ultracold ($T < 1$ mK) atoms [1], similar efforts with molecules have only recently begun to bear fruit. There is significant motivation to extend many of the successful applications of ultracold atoms to molecules, e.g., precision spectroscopy, collisional interactions, and quantum collective effects. In addition, because they are composite particles, there are many new phenomena to be investigated with ultracold molecules including atom-molecule collisions, chemical reactions, and cluster formation. The spectral complexity of molecules, due to vibration and rotation, has been the main impediment to producing ultracold samples. Laser cooling of atoms relies on the existence of a "cycling" transition that allows multiple photon absorptions. Since this type of transition is generally not available in molecules, standard laser cooling is not applicable. Various proposals have been offered to overcome this difficulty, including cooling by a multiple-frequency laser [2], buffer gas cooling [3,4], and ultracold molecule production by photoassociation (PA) of ultracold atoms [5–7].

Only very recently have direct observations of ultracold molecules been reported. Fioretti *et al.* [8] have produced ultracold ($T \sim 300$ μK) cesium molecules in the metastable lowest triplet state by PA in a magneto-optical trap (MOT), then detected them with a one-color, two-photon ionization scheme. Subsequently, Takekoshi, Patterson, and Knize also observed ultracold Cs_2, probably also in the metastable lowest triplet state [9,10]. They have trapped a small number of these Cs_2 molecules in an optical trap formed with a CO_2 laser [9]. Finally, Weinstein *et al.* have cooled CaH molecules with ^{3}He buffer gas and confined up to 10^8 of them in a magnetic trap [11], although at a much hotter 400 mK.

Here, we report the production and detection of ultracold potassium molecules in deeply bound vibrational levels of the ground $X\,^1\Sigma_g^+$ state. The molecules are produced by the radiative decay of $A\,^1\Sigma_u^+$ state molecules, which are themselves produced by PA of ultracold potassium atoms in a vapor-cell MOT. Sensitive and selective detection is provided using two-color photoionization with nanosecond pulses. To the best of our knowledge,

this is the first direct observation of ultracold molecules in the electronic ground state. For many applications, the possibility of inelastic processes (e.g., vibrational quenching [12,13]) will require that the ultracold molecules be in their lowest possible internal state. Producing them in the lowest electronic state is an important step in this direction. Also, experiments involving interactions of deeply bound ultracold molecules (as opposed to barely bound, long-range molecules) will allow interesting comparisons with similar work at higher temperatures.

Our photoassociation scheme is nearly identical to the one used by Wang, Gould, and Stwalley [14,15] to study long-range states of K_2. We use a vapor cell "dark-spot" MOT that traps at least 10^7 atoms with $T \cong 300$ μK and a density of about 10^{11} cm^{-3}. A cw single-mode Ti:sapphire laser (Coherent 899-29) is used to photoassociate atoms to bound molecular levels near the K($4\,^2S_{1/2}$) + K($4\,^2P_{1/2}$) asymptote. Figure 1 shows the relevant molecular potential curves. In our earlier work [14], free-bound transitions to several states converging to this limit were observed by trap loss spectroscopy. Of these states, only the $A\,^1\Sigma_u^+$ state (0_u^+ at long range) decays directly to the ground $X\,^1\Sigma_g^+$ state at short range. Vibrational levels down to about 191 were observed and assigned, although the vibrational numbering is still uncertain by a small integer. These levels radiate primarily to the continuum of the ground state, but our calculations of the Franck-Condon factors indicate that a small fraction, about 0.15% for $\nu' = 191$, decays into bound levels of the X state. Much higher production efficiencies should be attainable using proposed multilaser arrangements [5–7]. However, we have opted with the simpler single-laser scheme for our initial experiments, because this configuration is readily calculable and more easily implemented in the laboratory.

Figure 2 shows our calculations of the Franck-Condon distribution from A, $\nu' = 191$, which is qualitatively similar to the distribution from any other high vibrational level of the A state. The potentials were taken from Refs. [16] and [17], and conjoined with the long-range potentials of Ref. [14]. The Franck-Condon distribution peaks for $\nu'' = 36$, slightly more than halfway up the
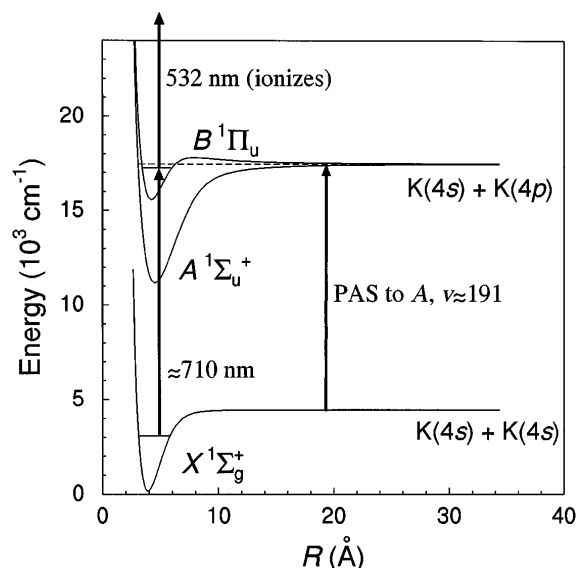
FIG. 1. Potential curves of the K_2 molecule, from Ref. [17]. Ultracold A state molecules are formed by PA of ^{39}K atoms in a MOT. Ultracold molecules in the $X\,^1\Sigma_g^+$ ground state are then formed by radiative decay (not shown), and detected by two-color resonant ionization via the B state.

potential well, where the inner turning points of the A state and the X state are almost vertically aligned. Three weaker maxima are predicted near $\nu'' = 46$, 55, and 67.

To detect these ground-state molecules we use near-resonant two-photon ionization, with one tunable pulsed laser and one fixed-frequency pulsed laser. Transitions from the X state to the $B\,^1\Pi_u$ state are driven by a pulsed dye laser tunable from 700–712 nm, with a bandwidth of about 0.3 cm^{-1} and a pulse duration of 7 nsec. The beam diameter is 2.5 mm and the energy is approximately 200 μJ, sufficient to saturate the signal even when the
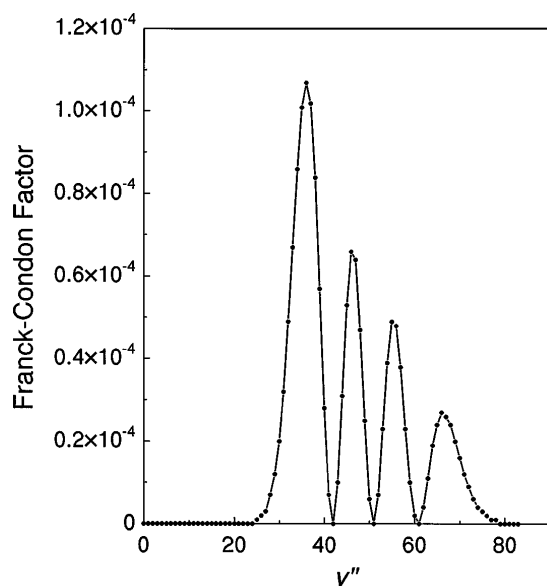

FIG. 2. Calculated Franck-Condon factors from A, $\nu' = 191$ to the ground X state.

laser is not tuned to an exact $B \leftarrow X$ resonance. The molecules are ionized from the B state by 532 nm light from a frequency-doubled neodymium-yttrium aluminum garnet (Nd:YAG) laser, with a pulse energy of 0.7 mJ and a beam diameter of 3 mm. At this irradiance, the 532 nm radiation saturates the ionization step for two-color detection, without producing detectable signals in the absence of the red $B \leftarrow X$ laser. The 532 nm wavelength is nearly ideal for this purpose, because at this wavelength the cross section for two-photon ionization of ground-state molecules is unusually low. This occurs because the photon energy lies well above all the bound states converging to the K(4S) + K(4P) asymptotes, but also well below the lowest ungerade states converging to the K(4S) + K(5S) and K(4S) + K(3D) asymptotes. The 532 nm laser is overlapped temporally and spatially with the red laser, and the merged lasers incorporate the entire MOT cloud, which has a diameter of about 1 mm.

The trapping beams are switched off with an acousto-optic modulator about 500 ns prior to the introduction of the pulsed detection beams. This is done to reduce the number of excited $4P$ atoms in the trap, since the $4P$-$8S$ atomic transition is nearly resonant with the frequency-doubled Nd:YAG laser. This precaution proved largely unnecessary, because the $8S$ atoms have a very low ionization probability at the irradiances used. The ions are detected by a channeltron (Galileo model 4869) with a bias voltage of 2000 V, sufficient to reliably detect single ions. Since the ion production rate is low, we use a gated photon counter (SRS model SR 400) to count the number of ions arriving at the detector during an appropriate time window. By varying the window timing we can observe well-separated atomic and molecular ion peaks, with flight times in the expected ratio of $1:\sqrt{2}$. Under optimal conditions the molecular and atomic ion signals are roughly equal in amplitude, demonstrating the effectiveness of the two-color detection scheme for discriminating against the atoms, which are more numerous than molecules by a factor of about 10^6. The atomic ions are produced predominantly by the 532 nm Nd:YAG laser, and their rate is roughly consistent with the measured ionization rates for ground-state potassium atoms [18].

Figure 3 shows a rotationally resolved spectrum of the A state observed by detecting K_2^+ ions while scanning the PA laser. As expected, the ion signal vanishes if either of the detection lasers is blocked, removing the $B \leftarrow X$ resonance, and also if the PA laser is detuned from resonance with the A state. We have observed transitions to several consecutive vibrational levels of the A state, with binding energies ranging from 11 to 14 cm^{-1} below the atomic $4S_{1/2} + 4P_{1/2}$ asymptote. Although this rotational spectrum has not been fully assigned, the strongest feature in each spectrum appears to be a blend of the $J' = 0$ and $J' = 1$ rotational levels.

Although the counting rate is low, at best about 50 counts/sec at a 10 Hz repetition rate, the low background rate, about 1 count/sec, allows very high
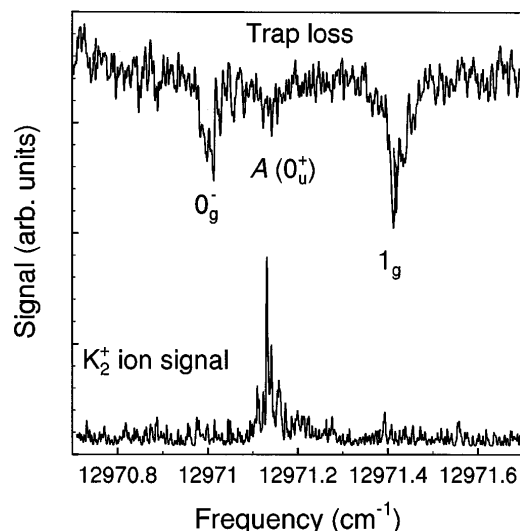
FIG. 3. K_2^+ signal showing resonances to the A state as the PA laser is scanned. The trap-loss spectrum [14] observed in an earlier measurement is also shown.

sensitivity. The signal and background counting rates are both strongly dependent on the potassium vapor pressure in the MOT chamber. The highest yields are obtained for potassium vapor pressures approximately 3 times higher than that which optimizes trap-loss measurements of photoassociation spectra. This difference is due to the fact that PA-induced trap loss must compete with background-atom collisional loss, while total molecule production rates, such as we measure here, do not.

We can estimate the molecule production rate by taking into account the ion detector efficiency of roughly 50% and the detection duty factor of 0.05–0.1 (the detection occurs at 10 Hz, but the molecules are formed continuously, and they leave the detection volume ballistically in 5–10 msec). The resulting rate of 1000–2000 molecules/sec is consistent with our estimated PA rate of 10^6 to 10^7 per sec and the Franck-Condon factors for $A \rightarrow X$ decay. Given the very low background level, this molecule production rate is already sufficient to permit further experiments. These deeply bound ultracold molecules offer a multitude of possibilities for high-resolution spectroscopy and collisional studies.

To confirm that our signals are produced by ground-state molecules, we have performed several additional checks as follows.

(1) When the PA laser is scanned, only transitions to the A state can be observed. This is in sharp contrast to trap-loss spectra, also shown in Fig. 3, where transitions to other states that do not decay to the ground state are much stronger than the A state transitions.

(2) When the PA laser is switched off with an acousto-optic modulator, the molecular signal decays slowly, with a time constant of about 5–10 msec. Figure 4 shows a typical decay curve, which is consistent with stable ul-

tracold molecules leaving the cylindrical detection region with velocities of about 30 cm/sec ($T \sim 300 \mu K$). It is not consistent either with the A state lifetime (roughly 20 nsec [19]) or with room-temperature thermal velocities. We can also measure the buildup time for the ultracold molecule signal, by switching on the PA laser at a variable time before the detection laser pulse. The buildup is very nearly a mirror image of the decay, with the same time constant within our considerable uncertainty ($\pm 50\%$).

(3) When the red detection laser is scanned, some spectral features are observed, and several transitions have been tentatively assigned to $B \leftarrow X$ transitions from $\nu'' = 35$ and 36 in the X state. There is a substantial wavelength-independent background from nonresonant detection of the ultracold molecules. We believe that this occurs because vibrational levels of the ground state with ν'' greater than about 43 can be ionized through the continua of the A or B states. We have been partially successful in efforts to quench this nonresonant ionization by introducing an additional cw laser (200 mW at 698 nm) to photodissociate high-ν'' molecules prior to the detection pulse. This laser can photodissociate X state vibrational levels bound by less than 1000 cm^{-1}. The added "photodissociation" laser decreases the overall signal count by a factor of 2–5, but improves the signal to background ratio by as much as a factor of 3 under optimal conditions. Figure 5 shows a scan of the red pulsed detection laser with the photodissociation laser present. The PA laser is fixed on a transition producing $A\ ^1\Sigma_u^+$ molecules, with $\nu' \cong 191$ and $J' = 1$. To avoid power broadening and excessive background levels, we obtain the spectrum using a reduced laser energy of only about 4 μJ. We observe that 20 μJ of red laser
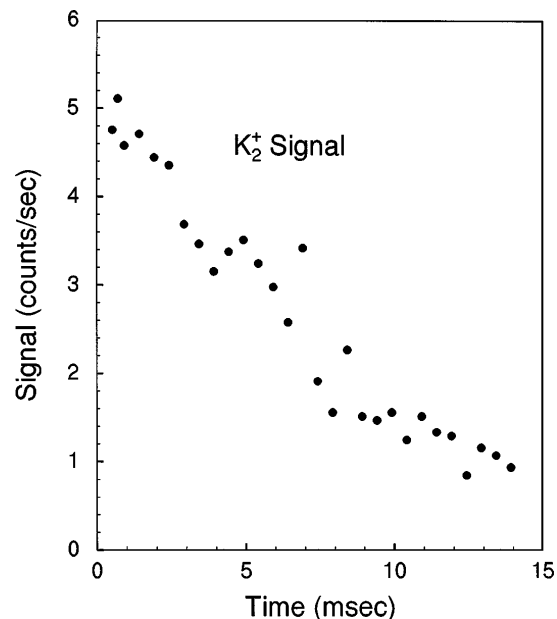

FIG. 4. Decay of the K_2^+ signal after the PA laser is switched off with an acousto-optic modulator.
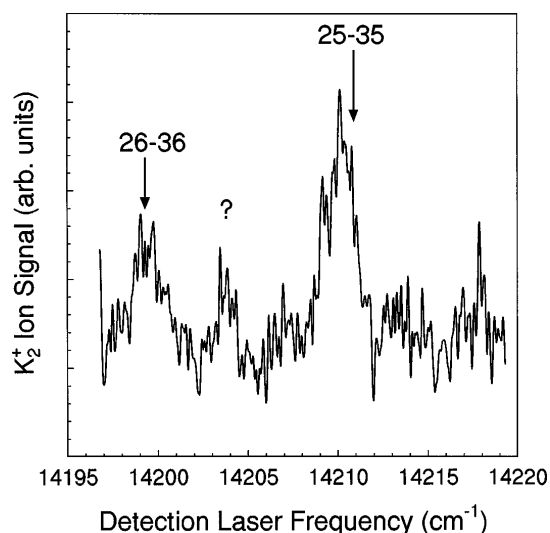
FIG. 5. Partially resolved $B \leftarrow X$ spectrum, observed by scanning the detection laser wavelength. Predicted $B(\nu', J' = 0) \leftarrow X(\nu'', J'' = 0)$ transitions are marked with arrows, based on high resolution spectra by Heinze *et al.* [21] and Amiot [22]. Unfortunately, vibrational band overlaps and laser scan nonlinearities of about 1 cm^{-1} prevent definitive assignments.

energy saturates the strongest transition, which probably belongs predominantly to the 25-35 band, but is also overlapped by predicted transitions from $\nu'' = 23$, 39, and 42.

A number of improvements on the present arrangement are underway or planned. The broadband detection laser will be replaced with a pulse-amplified cw laser, retaining time resolution while improving the bandwidth to about 50 MHz, easily sufficient to fully resolve $B \leftarrow X$ transitions. The MOT density will be transiently increased by ramping the magnetic trapping field about 10 msec prior to the detection laser pulse. We will also attempt two-laser transfer schemes, such as those proposed in Refs. [5–7].

It will, of course, be particularly significant to seek efficient methods for producing ultracold molecules in selected vibrational levels. The just-referenced two-laser schemes offer good prospects for efficient population of low-ν'' states, including $\nu'' = 0$. This will be highly desirable or even essential for future studies of ultracold molecule physics, such as quantum collisions, and the possible realization of a molecular Bose-Einstein condensate or a "molecule laser" [20]. Alternatively, it should also be possible to efficiently prepare X state molecules in very high vibrational levels. For example, in a variation of the present method, PA to A state levels with $\nu' = 162$ would be followed by radiative decay predominantly to the $\nu'' = 83$ level of the X state, with a Franck-Condon factor of 0.073.

In summary, we have observed ultracold molecules in the ground $X\,{}^1\Sigma_g^+$ electronic state, produced in a MOT of potassium atoms by photoassociation followed by radiative decay. The temperature is roughly 300 μK,

similar to that of the atoms. Partially resolved spectra of $B \leftarrow X$ transitions have been observed using a two-color resonant ionization scheme. These results point the way to future studies on the physics of ground-state molecules at ultracold temperatures.

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