Direct Photoassociative Formation of Ultracold KRb Molecules in the Lowest Vibrational Levels of the Ground State

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We report continuous direct photoassociative formation of ultracold KRb molecules in the lowest vibrational levels ($v'' = 0 - 10$) of the electronic ground state ($X^1\Sigma^+$), starting from $^{39}$K and $^{85}$Rb atoms in a magneto-optical trap. The process exploits a newfound resonant coupling between the $2(1)$, $v' = 165$ and $4(1)$, $v' = 61$ levels, which exhibit an almost equal admixture of the uncoupled eigenstates. The production rate of the $X^1\Sigma^+ (v''=0)$ level is estimated to be $5 \times 10^3$ molecules/sec.

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I. INTRODUCTION

Ultracold heteronuclear alkali dimers have enjoyed extensive attention from researchers in fields ranging from atomic, molecular and optical (AMO) physics to physical chemistry and chemical physics for over a decade now [1, 2]. The presence of a large molecule-fixed electric dipole moment in the absolute rovibrational ground state ($v'' = 0$, $J'' = 0$) makes external control over the motion and internal quantum state very convenient, opening up the fields of ultracold chemical reactions and collisions [3], many body physics [4] and quantum computation [5].

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II. EXPERIMENT

A detailed description of the experimental apparatus is available in [16]. Briefly, it consists of overlapped dual species MOTs of $^{39}$K and $^{85}$Rb, operating in a “dark-SPOT” configuration [17], with atomic densities of $\sim 3 \times 10^{10}$ cm$^{-3}$ and $\sim 1 \times 10^{11}$ cm$^{-3}$ respectively.

The temperatures of the K and Rb MOTs are on the order of $300 \mu$K and $100 \mu$K respectively. A cw Titanium:sapphire ring laser focused at the MOT with power of about 1 W acts as the PA laser. The molecules thus formed by PA then radiatively decay to the $X$ and $a$ states correlating with two ground-state atoms and are detected via REMPI. The REMPI laser is a Continuum model ND6000 pulsed dye laser and produces 10 ns pulses.
of \(\sim 1\) mJ energy that are focused to a diameter (FWHM) of \(\sim 0.76\) mm at the MOT. The ions are then detected by a channeltron and the KRb\(^+\) ion signal is distinguished from K\(^+\), Rb\(^+\), K\(_2^+\) and Rb\(_2^+\) ions by time-of-flight mass spectroscopy. PA spectra are obtained by scanning the cw laser while keeping the pulsed REMPI laser fixed on a particular resonance. Similarly REMPI spectra are obtained by scanning the pulsed laser while fixing the PA laser on a known resonance. Figure 1 shows a schematic representation of our present work. The excited state potentials are \textit{ab initio} potentials obtained from \cite{18} and the X and a state potentials correlating with two ground-state atoms are obtained from the experimental work reported in \cite{19}.

![Figure 1](image1.png)

**FIG. 1.** (Color online) Schematic for formation and detection of ground-state KRb. The PA laser is detuned below the K(4s) + Rb(5p\(_{1/2}\)) asymptote. The intermediate states used for detection of the lowest vibrational levels of the ground-state KRb molecules are 2\(^3\Sigma^+\), 3\(^3\Sigma^+\) and 1\(^1\Pi\). At long-range, the 1\(^1\Pi\) state correlates to the 4(1) state and dissociates to the K(4s) + Rb(5p\(_{3/2}\)) asymptote while the 2\(^3\Sigma^+\) state diabatically correlates to the 2(1) and 2(0\(^-\)) states and dissociates to the K(4s) + Rb(5p\(_{1/2}\)) asymptote.

III. RESONANT COUPLING OF THE 2(1) AND 4(1) STATES

The coupled states used can be observed by scanning the PA laser in the vicinity of 12547.9 \(\text{cm}^{-1}\), red-detuned from the K(4s) + Rb(5p\(_{1/2}\)) asymptote by 31 \(\text{cm}^{-1}\). In the PA spectra of Figure 2, the two excited states are observed about \(\sim 0.3\) \(\text{cm}^{-1}\) apart. These are identified as \(v' = 165\) of 2(1) and \(v' = 61\) of 4(1), using Hund’s cases c) notation. In earlier work \cite{20}, these two states were observed using a pulsed REMPI laser with significantly broader linewidth and considerable amplified spontaneous emission, thus degrading the state selectivity but with the advantage of locating all PA resonances with some efficiency. In the present work PA spectra are obtained via REMPI using a narrow bandwidth (0.5 \(\text{cm}^{-1}\)) laser with a well-defined frequency.

Theoretical calculations predict that the long-range 2(1), \(v' = 165\) level should radiatively decay predominantly to high-\(v''\) levels of the X state. Similarly the intermediate-range 4(1), \(v' = 61\) level should emit predominantly to low-\(v''\) levels of the X state. However, the PA spectra in Figure 2 reveal a different picture. Although Figure 2a corresponds to detection of high-\(v''\) levels and Figure 2b to low-\(v''\) levels of the ground-state, both have the same ratios of 2(1) and 4(1) signals for all the \(J\) values. This suggests that the pair of excited states is strongly mixed by perturbative coupling.

Figure 3 depicts the behavior of the rotational constants for these two levels. The topmost 4(1), \(v' = 61\) and bottom-most 2(1), \(v' = 165\) lines depict theoretical prediction of \(B_e\) based on single channel calculations. The experimental results depicted by the middle two lines deviate significantly towards one another, as expected in case of resonant coupling. The values of \(B_e\) for 4(1), \(v' = 61\) and 2(1), \(v' = 165\) are quite similar and each deviates significantly from the single channel calculations or from simple linear interpolation between neighboring vibrational levels. This observation again suggests that these two excited states are strongly mixed. We also note
FIG. 3. (Color online) Plot of $E_J$ vs $J(J+1)$, where $J$ is the rotational quantum number and $E_J = J(J+1)B_v$. $B_v$ is the rotational constant. The theoretical values of $B_v$ are calculated using LEVEL. The single-channel potentials calculated by Rousseau et al. [13].

FIG. 4. (Color online) Comparison of hyperfine structure of the $2(1)$, $v' = 165$ (black, thicker width) and $4(1)$, $v' = 61$ (red, narrower width) states for $J' = 1, 2$ and 3. The detection laser frequency for all the PA scans is $16635.8 \text{ cm}^{-1}$. Also, as the scan speeds and laser powers were not closely matched, we do not consider the differences in the linewidths to be significant.

that if they are strongly mixed, their hyperfine structure (hfs) should be quite similar. This is indeed observed, as can be seen in Figure 4 for superposed plots of the hfs for $J' = 1, 2$ and 3.

The vibrational numbering of the $4(1)$ electronic state is absolute. This state was previously observed by Kasahara et al. [22] in an optical-optical double resonance experiment for higher values of $J$ and was later observed by our group [16] for lower values of $J$. However, the vibrational numbering of the long-range state of $2(1)$ is slightly uncertain. In previous work by our group [16], we observed many vibrational levels of $2(1)$ state, but not all. Based on a long-range extrapolation to the dissociation limit [16], we can definitively state that the $2(1)$ vibrational level in the present experiment is the 22nd level below the dissociation limit. Calculating the vibrational levels of $2(1)$ state using the LEVEL program [21] and the single-channel potential [18], we find that the energy of the $v' = 165$ calculated level corresponds closely to our experimental vibrational level. Hence, for ease of discussion we will denote this vibrational level of the $2(1)$ state to be $v' = 165$.

This mixing between $2(1)$ and $4(1)$ is even more apparent in the REMPI spectra of the $X$ and $a$ state molecules formed by radiative decay of the coupled PA states. These spectra are obtained by scanning the ionization laser with the PA laser fixed at $12547.6 \text{ cm}^{-1}$ ($2(1), v' = 165, J' = 1$) and then at $12547.92 \text{ cm}^{-1}$ ($4(1), v' = 61, J' = 1$), shown in Figure 5. These spectra are extremely congested and hence quite challenging to assign. Nevertheless comparing the two spectra reveals that they share the same spectral lines for the entire $400 \text{ cm}^{-1}$ scan except for six random peaks (out of ~110 reproducible peaks). For many years, in our group, we have studied REMPI spectra, which are usually very different for different electronic states. We have never observed two REMPI spectra arising from two different electronic states with such striking similarity. This implies a strong coupling between the participating electronic excited states and suggests that these coupled states are nearly an equal admixture of the $2(1)$ and $4(1)$ electronic states at least in the range of internuclear sep-

FIG. 5. (Color online) Near-identical REMPI spectra of KRb with the PA laser at A) $12547.6 \text{ cm}^{-1}$ and B) $12547.9 \text{ cm}^{-1}$. The line marked by an asterisk represents the detection frequency of $16635.8 \text{ cm}^{-1}$ used for the PA scans in Figure 2a and 4. Note that the intensity scales in A and B are the same.
FIG. 6. (Color online) REMPI detection spectra of KRb molecules, at lower laser frequencies. The vertical lines indicate assignments from $X^1\Sigma^+$, $v'' = 0$ to several levels of the intermediate states $1^1\Pi$, $2^3\Sigma^+$ and $3^1\Sigma^+$. The black circles (•) indicate $^{85}$Rb two photon transitions that leak into the molecular channel. The PA laser was set to the $4(1)$, $v' = 61$, $J' = 1$ level for this scan.

In an attempt to better understand the vibrational distribution of ground state molecules formed via these coupled excited states, we performed REMPI scans from $\sim$15000-15300 cm$^{-1}$, which is significantly below the scan range shown in Figure 5, since in that region the number of intermediate state resonances is fewer and hence the spectra are expected to be less complex.

The spectrum thus obtained, as shown in Figure 6, is still rather congested but nearly all of the lines have been successfully assigned. The assignments include numerous transitions from the lowest lying vibrational levels $v'' = 0 - 10$ of the $X^1\Sigma^+$ state, as well as from the levels $a^3\Sigma^+, v'' = 19 - 27$. In Figure 6, we have shown only the transitions from $X^1\Sigma^+, v'' = 0$ to the intermediate levels with the intention to avoid excessive congestion of assignments. The low-$v$ ground-state molecules, as observed by REMPI through the $1^1\Pi$, $2^3\Sigma^+$ and $3^1\Sigma^+$ excited electronic states, have been studied extensively in very recent molecular beam experiments [23-25]. Thus the vibrational energies of the ground state and intermediate states used to assign the REMPI spectra are all well known from experiments and hence there is very little uncertainty in the assignments of our spectra. Also, we have only assigned the lines in the REMPI spectrum which can be detected via the vibrational levels of the intermediate states already observed in [23-25]. As a result, there are a few lines that are still unassigned.

In order to provide a cleaner view of the dense spectrum, we show in Figure 7 an expanded view of the spectrum in Figure 6 focusing on the region $\sim$15105-15137 cm$^{-1}$. In this region, lines can be assigned to transitions from $X^1\Sigma^+, v'' = 0 - 3$ levels to various vibrational levels of the $2^3\Sigma^+$ and $3^1\Sigma^+$ states. Transitions corresponding to the lowest triplet state are also shown. However, in this region, no distinct lines can be assigned to the $1^1\Pi$ state. As is evident from the figure, there are still some unassigned lines in this region. These are likely to be transitions to vibrational levels of the same intermediate states beyond the range reported in [23-25].

Further evidence that KRb molecules are formed in the lowest lying vibrational levels of the ground state...
comes from our observation of very large KRb+ signals ionized using only a 532 nm pulsed laser. For molecules in high vibrational levels of the ground state, single-color ionization at 532 nm was previously observed to be quite inefficient. For $X^1\Sigma^+$, $v'' = 0$, the situation is much different because of a near resonance with the $3^3\Sigma^+$, $v' = 3$ level, which enhances two-photon ionization. Because the vibrational spacings are very similar in the $X$ and the $3^3\Sigma^+$ states, other $X$, low $v''$ levels are also enhanced.

The relative intensities of the REMPI intermediate states are also of interest. The spin selection rule $\Delta S = 0$ forbids transitions between singlet and triplet electronic states, so the $2^3\Sigma^+ \leftarrow X^1\Sigma^+$ transitions might be expected to be very weak. However, as is evident in Figure 6, the $2^3\Sigma^+ \leftarrow X^1\Sigma^+$ transitions are actually nearly as strong as the singlet-singlet REMPI transitions. Similarly efficient transitions between these two states are also reported in Ref. [23]. This occurs because there are five excited electronic states in this energy region, $2^1\Sigma^+, 1^1\Pi, 2^3\Sigma^+, 1^3\Pi$ and $3^3\Sigma^+$, which undergo mutual perturbations at various internuclear distances. This gives rise to very complicated coupling and hence the participating states are often not of pure singlet or triplet character. This is probably facilitating not only the detection of the lowest vibrational levels of $X^1\Sigma^+$ via the $2^3\Sigma^+$ state in KRb with very good efficiency [23, 24], but also the formation of these low-lying vibrational states by resonant coupling. At small internuclear distances the 2(1) state correlates to the 2$^3\Sigma^+$ state and the 4(1) state correlates to $1^3\Pi$. Hence the long range states 2(1)$\sim$4(1) used for PA are themselves participants in this five-state perturbation complex, so that further study may reveal the influence of other nearby states on this strongly coupled pair.

To estimate the formation rate of $X^1\Sigma^+$, $v'' = 0$ level via photoassociation, we calibrated the ion signal to determine the number of KRb+ ions/pulse. Taking the velocity of the KRb molecules as $\sim 0.3$ m/sec based on the MOT temperature of $\sim 300 \mu$K and estimating a detection volume of 0.45 mm$^3$ determined by the pulsed laser diameter of 0.76 mm and the nominal MOT thickness of 0.1 mm, the production rate of molecules in $v'' = 0$ state is approximately $5 \times 10^3$ molecules/second. Comparing with other recent results using single-step PA alone, this production rate is of the same order as the results [3] for LiCs and about a factor of ten smaller than for NaCs [10].

The main caveat in using a single-step photoassociation process rather than a method of coherent transfer is the unwanted population of various higher vibrational levels due to spontaneous radiative decay. However a pure sample of rovibrational ground state molecules is still achievable after the PA process by several possible methods. As discussed in Ref. [20], vibrational cooling of the sample is one option. For KRb molecules, the $2^1\Sigma^+ \sim 1^3\Pi$ complex can provide intermediate states for optical pumping of molecules in higher vibrational levels down to $v'' = 0$. Another option for obtaining a pure sample of absolute ground state molecules is to photodissociate the vibrationally excited molecules, so that the residue is a pure sample of $v'' = 0$. This process has been previously carried out successfully for K$_2$ [27]. Either method can be efficient, so the choice between them depends to some extent on the availability of suitable lasers.

V. SUMMARY

In summary, we have presented a simple, single-step path for the efficient formation of KRb molecules in the $v'' = 0$ level of the $X^1\Sigma^+$ state via photoassociation through a pair of strongly resonantly coupled levels of the 2(1)$\sim$4(1) excited electronic states. The process forms $\sim 5 \times 10^3$ KRb molecules/second in the $v'' = 0$ level of the ground state. It achieves this with just a single laser and works well at typical uncompressed MOT densities, with atomic temperatures of a few hundred $\mu$K. Further gains might be achieved by purifying the vibrational distribution into the $v'' = 0$ level and optically trapping them to allow studies of collisions and interactions. This process provides continuous production and accumulation of the absolute ground state molecules without complicated transfer techniques. Finally the observation of suitable...
pairs of resonantly coupled states for KRb, together with related observations in LiCs, NaCs and RbCs, inspires confidence that similar pathways can be found for other heteronuclear molecules as predicted in [15]. We gratefully acknowledge support from the National Science Foundation and the Air Force Office of Scientific Research (MURI).

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