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Prospects for narrow-line cooling of KRb molecules in the rovibrational ground state

J. Kobayashi,* K. Aikawa,† K. Oasa,‡ and S. Inouye
School of Engineering, University of Tokyo, Yayoi, Bunkyo-ku, Tokyo 113-8656, Japan
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We propose and experimentally investigate a scheme for narrow-line cooling of KRb molecules in the rovibrational ground state. We show that the spin-forbidden $X\,^1\Sigma^+ \rightarrow b\,^3\Pi_{0^+}$ transition of KRb is well suited for realizing narrow-line laser cooling of molecules because it has highly diagonal Franck-Condon factors and a narrow line width. To confirm the prediction, we performed optical and microwave spectroscopy of ultracold $^{41}K^{87}Rb$ molecules, and determined the line width [$2\pi\times$ 4.9(4) kHz] and Franck-Condon factors for the $X\,^1\Sigma^+(v''=0) \rightarrow b\,^3\Pi_{0^+}(v'=0)$ transition [0.9474(1)]. This result opens the door towards all-optical production of polar molecules at sub-microkelvin temperatures.

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Recently significant progress has been made in the field of cold molecules. Innovative ideas have been implemented one after another, making cold molecules an attractive new tool to test fundamental physics [1–3]. However, in spite of serious efforts by many groups, a quantum degenerate gas of polar molecules remains an elusive goal. The JILA group has obtained results closest to this goal by combining magneto-association with stimulated Raman adiabatic passage (STIRAP), and they attained a phase-space density on the order of 0.1 [4]. In that experiment, they were limited by the magneto-association efficiency, which was determined by the density overlap of the rubidium and potassium clouds [5].

Motivated by these results, we studied the possibility of laser cooling bi-alkali-metal molecules in the rovibrational ground state. Typically laser cooling of molecules is difficult because molecules have vibrational and rotational degrees of freedom. Recently, however, several groups succeeded in laser cooling molecules by selecting special types of molecules (such as SrF [6], YO [7], and CaF [8]) and constructing a quasicycling transition with minimal increase in laser complexity. The solution to the problem was to find an optical transition with highly diagonal Franck-Condon factors [9]. We have now observed such a transition in KRb: one of the most popular species in the field of cold molecules.

We claim that the intercombination transition $X\,^1\Sigma^+(v=0) \rightarrow b\,^3\Pi_{0^+}(v'=0)$ of KRb is well suited for realizing narrow-line cooling of the ground-state molecule because it has (i) near-unity spatial overlap between the ground and excited vibrational wave functions, (ii) a narrow line width, and (iii) negligible leakage to other (i.e., triplet) ground states.

To test our expectations, we experimentally investigated the rovibrational spectrum of ultracold $^{41}K^{87}Rb$ molecules using STIRAP and RF spectroscopy. From the experimental data, we determined the natural line width of $b\,^3\Pi_{0^+}(v'=0)$ to be $\Gamma = 2\pi \times 4.9(4)$ kHz while the Franck-Condon factor for the $X\,^1\Sigma^+(v''=0) \rightarrow b\,^3\Pi_{0^+}(v'=0)$ transition was established as 0.9474(1) [10]. Based on these values, we conclude that $^{41}K^{87}Rb$ is an ideal system for sub-microkelvin three-dimensional laser cooling of molecules. By combining this narrow-line cooling with photoassociation and STIRAP, cooling of polar molecules to the sub-microkelvin temperatures is possible by all-optical means [11].

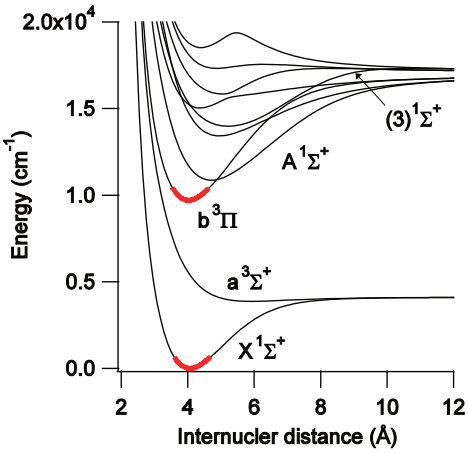

FIG. 1. (Color online) Potential energy curves for KRb [12]. The curves for $X\,^1\Sigma^+$ and $b\,^3\Pi$ states are quite similar (highlighted in red), suggesting highly diagonal Franck-Condon factors for transitions between these two states. The decay of the $v'=0$ level of the $b\,^3\Pi_{0^+}$ state into the $a\,^3\Sigma^+$ state is strongly suppressed because of the extremely small transition dipole moments [13].

Figure 1 shows the potential energy curve of KRb as a function of internuclear separation. The potential energy curves of $X\,^1\Sigma^+$ and $b\,^3\Pi$ look surprisingly similar, which suggests highly diagonal Franck-Condon factors for $X\,^1\Sigma^+ \rightarrow b\,^3\Pi_{0^+}$ transitions. Furthermore, radiative decay from $b\,^3\Pi_{0^+}(v'=0)$ into the dissociative continuum of the $a\,^3\Sigma^+$ triplet ground state is strongly suppressed because of the small electronic transition dipole moment (TDM) of the $a\,^3\Sigma^+$-$b\,^3\Pi_{0^+}$ transition at the bottom of the $b\,^3\Pi_{0^+}$ potential [$d = 0.006(4)\,ea_0$, where e is the electron charge and a_0 is the Bohr radius] [13,14]. The calculated decay rate of the $v'=0$ level of the $b\,^3\Pi_{0^+}$ to both the continuum and bound states of $a\,^3\Sigma^+$ is on the order of 1 Hz, which does not play a major roll unless narrow-line cooling is applied for more than 100 ms.

To test our prediction, we performed an experiment involving ultracold KRb molecules. Our experimental procedure for producing KRb molecules in the rovibrational ground state is described in detail in Ref. [11]. In brief, KRb molecules

*kobayashi@atomtrap.t.u-tokyo.ac.jp
†Present address: Universität Innsbruck, 6020 Innsbruck, Austria.
‡Present address: Toshiba Corporation, Tokyo 105-8001, Japan.

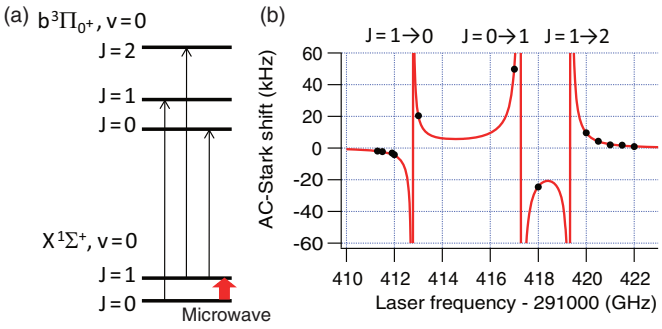

FIG. 2. (Color online) (a) Schematic of double-resonance spectroscopy for locating the $|X,0\rangle$-$|b,0\rangle$ transition. The ac Stark shift induced by a laser beam tuned close to the $|X,0\rangle$-$|b,0\rangle$ transition was detected by the microwave transition between the rotational levels in the $|X,0\rangle$ state. (b) The observed ac Stark shifts. The measured shifts exhibited a dispersive feature characteristic of ac Stark shifts. The solid curve is a fit to the data for extracting resonance frequencies.

in the $X\,^1\Sigma^+(v=91,J=0)$ state (or $|X,91,0\rangle$ state, for short) were made by photoassociation in a magneto-optical trap (MOT) of ^{87}Rb and ^{41}K atoms. Next, the molecules in the $|X,91,0\rangle$ state were transferred to the $|X,0,0\rangle$ state by STIRAP via the intermediate state $|(3)^1\Sigma^+,41,1\rangle$ by using two lasers of wavelength 875 and 641 nm. The use of 5 ns pulses from a tunable dye laser and a micro-channel plate provides for vibrationally selective detection by resonance-enhanced multiphoton ionization (REMPI).

Until now, the $X\,^1\Sigma^+(v''=0)\rightarrow b\,^3\Pi_{0^+}(v'=0)$ transition (or $|X,0\rangle$-$|b,0\rangle$ transition, for short) of KRb has not been observed. The transition wavelengths predicted by *ab initio* calculations range from 1026.4 to 1036.9 nm [12,15–17], which is nine orders of magnitude larger than the expected natural line width. To overcome this uncertainty, we looked for a dispersive signal rather than an absorptive signal because the signal falls off as $1/\Delta$ instead of $1/\Delta^2$ (where Δ is the detuning from resonance). We monitored the microwave transition frequency between rotational levels ($|X,0,0\rangle$ and $|X,0,1\rangle$), and looked for the ac Stark shift induced by near-resonant light, as described in Fig. 2(a). Employing this method resulted in the observance of three transitions $|X,0\rangle$-$|b,0\rangle$, $|X,0\rangle$-$|b,1\rangle$, and $|X,0\rangle$-$|b^3\Pi_1,0\rangle$ with clearly resolved rotational structures, as shown in Fig. 2(b). Their transition wavelengths without rotational energies were determined to be 1028.7397(7), 1020.9746(7), and 1022.6870(7) nm, respectively, where the accuracies were limited only by the accuracy of our wave meter.

We determined the natural line width and Doppler broadening of the $|X,0\rangle$-$|b,0\rangle$ transition by directly exciting molecules with a narrow-line width laser [18]. Figure 3(a) shows a schematic of the transitions examined by the experiment. Assuming almost diagonal Franck-Condon factors, prolonged excitation optically pumps molecules into different rotational states (in this case, mostly to $|X,0,2\rangle$). The number of molecules in the $|X,0,2\rangle$ state was detected by REMPI, which is sensitive to the rotational state [19]. First, we saturated the transition using a laser beam with an intensity three orders of magnitude greater than the saturation intensity. Here power broadening of the transition was larger than the hyperfine

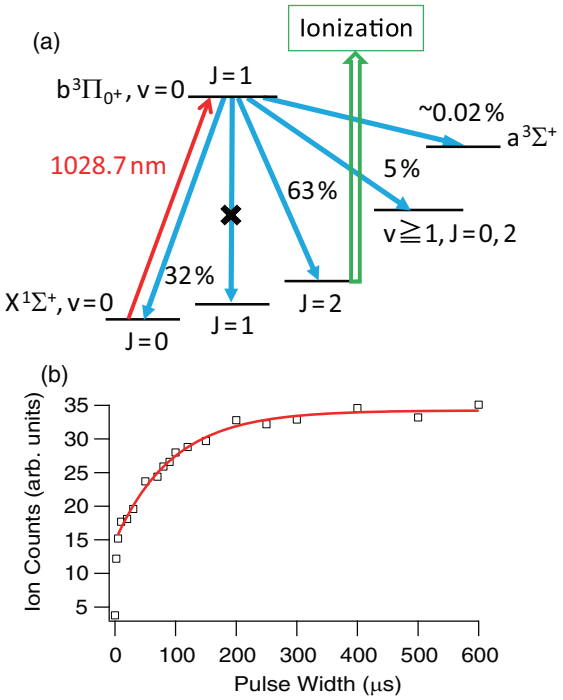

FIG. 3. (Color online) (a) Schematic of optical pumping spectroscopy of the $|b,0,1\rangle$ state (see text). The branching ratios for transitions from the $|b,0,1\rangle$ state were calculated using the Hönl-London and Franck-Condon factors. Most of the molecules in the $|X,0,0\rangle$ state were optically pumped into the $|X,0,2\rangle$ state by the 1028.7 nm laser, which was resonant with the transition between $|X,0,0\rangle$ and $|b,0,1\rangle$. Subsequently molecules in $|X,0,2\rangle$ were selectively detected by resonance-enhanced multiphoton ionization based on their rotational state [19]. (b) Measurement of the time constant of optical pumping in the saturated regime. Ion counts of the molecules in the $|X,0,2\rangle$ state were measured as a function of the pulse duration of the optical pumping laser. The measured time constant for optical pumping [95(7) μs] was converted into the lifetime of $|b,0,1\rangle$ [32.5(24) μs] using the branching ratios shown in panel (a).

splitting in the ground state, which is $\sim 2\pi\times 5$ kHz for $|X,0,0\rangle$ [20,21]. From the optical pumping time constant, determined as shown in Fig. 3(b) and the branching ratios shown in Fig. 3(a), we obtained the lifetime and natural line width of the $|b,0,1\rangle$ state, which was 32.5(24) μs and $2\pi\times$ 4.9(4) kHz, respectively. Second, we measured the molecule temperature by observing the optical pumping spectrum in the nonsaturating regime. The typical temperature and mean velocity were 130 μK and 130 mm/s, respectively. The observed velocity is about 43 times the recoil velocity of the $|X,0\rangle$-$|b,0\rangle$ transition.

Franck-Condon factors are sensitive to rotational constants because both are directly related to the equilibrium internuclear distance. To exploit this, we performed detailed analysis of $|b,0,0\rangle$, $|b,0,1\rangle$, $|b,1,0\rangle$, and $|b,1,1\rangle$ states by acquiring hyperfine-resolved optical pumping spectra, as shown in Fig. 4. We assigned the hyperfine structures based on the Hamiltonian discussed in Refs. [20,21], which describes the interactions between two atomic nuclear spins and the rotation of diatomic molecules [22]. The potential energy curve for a ground-state molecule was also refined using STIRAP spectra of the $|X,1,0\rangle$ and $|X,1,2\rangle$ states.

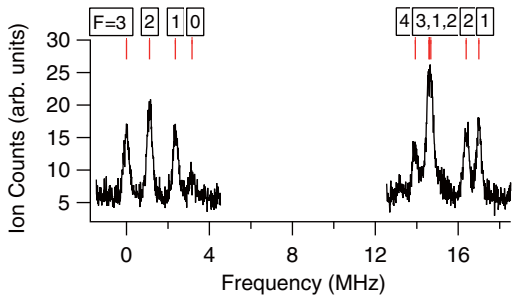

FIG. 4. (Color online) Spectrum of the $|b,0,1\rangle$ state obtained by optical pumping as described in Fig. 3(a). The horizontal axis shows the frequency of the optical pumping laser relative to the leftmost signal (which has been assigned a frequency of zero). The hyperfine structure of the $|b,0,1\rangle$ state was thereby observed.

From the spectra, we determined vibrational and rotational energies, which are listed in Table I. The X-state values agree well with the predictions of Ref. [23]. To calculate the Franck-Condon factors, we determined the potential energy curves of X and b states. We assumed that the potential energy curves in the low energy region of X and b states could be written as

$$V(r) = \sum_{n=2}^{n_{\max}} a_n (r - r_e)^n + V_0, \tag{1}$$

where r is the internuclear distance. r_e (the equilibrium distance), a_n, and V_0 are the fitting parameters. Setting $n_{\max} = 3$ and fitting these curves to the experimental data, we determined these parameters for X and b potentials, as listed in Table II [24]. Because the difference in equilibrium distance between X and b states (∼4.1 pm) is much smaller than the harmonic oscillator lengths for both potentials (∼80 pm), the Franck-Condon factors between these states are highly diagonal. Using the obtained potential energy curves, we determined the Franck-Condon factors of $|X,0\rangle$-$|b,0\rangle$, $|X,1\rangle$-$|b,0\rangle$, and $|X,v \geqslant 2\rangle$-$|b,0\rangle$ transitions to be 0.9474(1), 0.0500(1), and $2.60(1) \times 10^{-3}$, respectively, as illustrated in Fig. 5 [25].

The model dependence of the Franck-Condon factors is important because it could be a major source of systematic errors. In addition to the polynomial expansion shown in Eq. (1), we also tried other fitting functions like the expanded Morse oscillator function [26] and the function adopted by the Hannover group [27]. Surprisingly, the Franck-Condon factors obtained by all these methods were nearly identical to each other, well within the confines of statistical error. This fact indicates that the shape of the potential around the equilibrium point is not sensitive to the details of the model. We also replaced the potential energy curve for the X state with that described in Ref. [23] and calculated the Franck-Condon factors, but the difference was again smaller than the statistical error.

We now discuss using the $X\,^1\Sigma^+ \rightarrow b\,^3\Pi_{0^+}$ transition for realizing narrow-line cooling of KRb molecules. The proposed scheme is as follows. Ground-state KRb molecules at a few hundred microkelvin are prepared by photoassociation in a dual-species MOT followed by STIRAP. The cooling beam is red-detuned from the $|X,0,1\rangle$-$|b,0,0\rangle$ transition, whereas the repumping beam is resonant with the $|X,1,1\rangle$-$|b,0,0\rangle$ transition. Both beams irradiate molecules from all six directions. Because the cooling beam is red detuned, molecules should predominantly scatter photons from the counterpropagating beam; therefore their velocities are reduced. The actual spectra of the cooling and repumping beams must be optimized both for accessing all the hyperfine states and for increasing the ranges of the capture velocity.

Several necessary conditions must be satisfied for cooling the molecules. First, the cooling transition should be highly closed. From the experimentally obtained Franck-Condon factors, KRb molecules can scatter $\sim 1/2.60(1) \times 10^{-3} \sim 400$ photons before being pumped into other vibrational levels. This number is sufficiently large for capturing molecules in this setup because the mean velocity of the initial cloud was ∼43 times the recoil velocity.

TABLE I. Experimentally obtained rotational and vibrational energies for molecular potentials of $X\,^1\Sigma^+$ and $b\,^3\Pi_{0^+}$. The energy difference between $v = 0(J = 0)$ and $v = 1(J = 0)$ states is given by $E(v = 1) - E(v = 0)$. The accuracy was limited by the accuracy of our wavemeter (∼ 100 MHz). B is the rotational constant. The accuracy of the rotational transition frequencies is higher since the measurement was done using narrow line-width lasers and a stable optical cavity (see Ref. [18] for details). The value with the highest accuracy (B for $|X,0\rangle$) was obtained by directly driving the microwave transition.

	$X\,^1\Sigma^+$	$b\,^3\Pi_{0^+}$
$E(v = 1) - E(v = 0)$ (cm^{-1})	73.845(3)	73.936(3)
$B(v = 0)$ (MHz)	1095.3772(1)	1118.37(1)
$B(v = 1)$ (MHz)	1091.93(1)	1116.26(1)

TABLE II. Obtained parameters for molecular potentials of $X\,^1\Sigma^+$ and $b\,^3\Pi_{0^+}$ states. Similarity between the two potentials can be seen by the values obtained for a_2,a_3, and r_e (see text). Only statistical errors are shown. For estimates on systematic errors, see text.

	$X\,^1\Sigma^+$	$b\,^3\Pi_{0^+}$
a_2 (cm^{-1} Å^{-2})	2286.3(2)	2279.2(2)
a_3 (cm^{-1} Å^{-3})	−1133.5(8)	−906.5(1.5)
r_e (Å)	4.067792(5)	4.02698(2)
V_0 (cm^{-1})	0	9720.531(3)

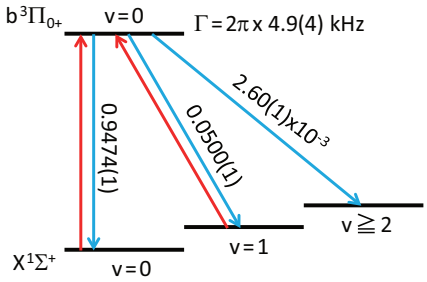

FIG. 5. (Color online) Franck-Condon factors and natural line width for $X\,^1\Sigma^+$-$b\,^3\Pi_{0^+}$ transitions. A cooling laser red-detuned from the $|X,0,1\rangle$-$|b,0,0\rangle$ transition and repumping laser resonant with the $|X,1,1\rangle$-$|b,0,0\rangle$ transition can form a highly closed cooling transition.

Second, the dark Zeeman substates, which are inevitably formed in this ($J'' = 1 \rightarrow J' = 0$) type of rotationally closed transition, should be eliminated. As described in Ref. [28], these dark states can be mixed with bright states by applying a proper magnetic field such that the Larmor precession frequency in the ground state nearly equals the natural line width of the cooling transition. For the ^{41}K^{87}Rb molecule, this condition can be fulfilled by a magnetic field of about 4 G, which is easily applied in the experiment.

Finally, the cooling transition should be sufficiently strong. The natural line width obtained for the $X\,^1\Sigma^+ \rightarrow b\,^3\Pi_{0^+}$ transition is $2\pi \times 4.9(4)$ kHz; therefore, the thermal expansion of the molecular cloud during laser cooling ($\sim$6 ms [29]) is estimated to be only $\sim$1 mm. Thus, we can apply narrow-line cooling to molecules in free space, since we can complete the cooling process before the molecules diffuse away from the trap center. In addition, the maximum acceleration for this transition, which is ~ 22 m/s^2 ($=\hbar k\Gamma/4m$, where m is the mass of the molecule), is more than twice the acceleration due to gravity.

From the above considerations, we conclude that three-dimensional laser cooling can be achieved by this system [30]. Because the natural line width of the cooling transition is comparable to its recoil frequency ($2\pi \times 1.5$ kHz), laser cooling to the recoil temperature (140 nK) can be realized, as has been successfully performed with strontium atoms [31].

In summary, we investigated the optical transitions between the low-lying vibrational states of the $X\,^1\Sigma^+$ and $b\,^3\Pi_{0^+}$ states for KRb molecule and determined its natural line width and Franck-Condon factors. These results suggest a novel all-optical scheme for producing sub-microkelvin molecules, where molecules formed by photoassociation (and STIRAP) are cooled to the photon recoil temperature by three-dimensional laser cooling using $|X,0,1\rangle$-$|b,0,0\rangle$ and $|X,1,1\rangle$-$|b,0,0\rangle$ transitions. Because alkali-metal dimers have similar properties, this scheme is applicable to other homo- and heteronuclear alkali-metal-dimers, in addition to other isotopic KRb molecules. Because this scheme allows sub-microkelvin molecules to be rapidly produced, it could prove a powerful method for molecular precision spectroscopies. Furthermore, optically trapping molecules cooled by this scheme can be a novel strategy for realizing a quantum degenerate molecular gas.

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[29] The time it takes for capturing molecules traveling with 43 times the recoil velocity can be estimated as $t_{\text{capture}} \sim \frac{1}{2\pi \times 5\text{kHz}} \times 4 \times 43 \sim 6\,\text{ms}$.

[30] Although Doppler cooling is our prime interest, three-dimensional MOT is also a possible extension [7]. Repumping lasers, which are resonant to the $|X,v \geqslant 2,1\rangle - |b,0,0\rangle$ transitions, should make the trapping time of molecular MOT longer.

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