Spectroscopic investigation of the $A$ and $3 1 \Sigma^+$ states of $^{39}$K$^{85}$Rb

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By using a combination of molecular beam (MB) excitation spectra and two distinct ultracold molecule excitation spectra (UM+ and UM−), we have assigned high vibrational levels of the $A$ and $3 1 \Sigma^+$ states from absorption spectra of the mutually strongly perturbed $A 1 \Sigma^+ - 3 1 \Sigma^+$ and $1 1 \Pi - 2 3 \Sigma^+ - b 3 \Pi$ states of ultracold $^{39}$K$^{85}$Rb molecules in the energy region between 15 116 and 16 225 cm$^{-1}$ above the minimum of the ground $X 1 \Sigma^+$ state. The ultracold molecules (UM+ and UM−) are formed by radiative decay following photoassociation (PA) to a specific level of the $3(0^+)$ state (UM+) or to a specific level of the $3(0^-)$ state (UM−). We observe that the $A$ and $3 1 \Sigma^+$ states are observable in the UM+ spectra, but absent from the UM− spectra. This is explained by considering Hund’s case (c) selection rules and transition dipole moments between the upper excited $A 1 \Sigma^+$ ($2(0^+)$) state and the three $\Omega$ components ($0^+, 0^–, 1^+$) at the ground-state dissociation limit. We propose further investigations of the extended potential wells of the $A$ and $3 1 \Sigma^+$ states by combining short-range MB excitation spectra in a narrow Franck-Condon (FC) window near $R_e$ of the $X 1 \Sigma^+$ state, and long-range UM (and PA) excitation spectra, which have much larger FC windows. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4771661]

I. INTRODUCTION

In recent decades, spectroscopic investigations of heteronuclear alkali diatomic molecules such as LiCs, NaCs, KRb, KCs, and RbCs1–7 have been carried out to support the production and study of these species at ultracold temperatures. These dipolar molecules have important applications such as quantum degenerate gases, quantum computation, novel quantum phases, and chemical reaction control at the quantum-state level. Much progress has been made towards the production of dense samples of cold and ultracold heteronuclear molecules in their absolute ground state.5 One crucial requirement for these techniques is to identify the most suitable optical transitions for preparation of the lowest vibrational level of the ground state. This requires a precise knowledge of the molecular spectra, which are congested by the many excited electronic states involved and the couplings among them, as well as by hyperfine structure.

Since Ross et al.8 first reported high-resolution spectroscopic information on the ground state of KRb, its visible and near infrared spectrum3,8–23 has become the best understood of the heteronuclear alkali dimers, partially because highly accurate ab initio calculations24,25 of the electronic states are also available.

The KRb heteronuclear diatomic molecule has large spin-orbit interactions at the first four excited $K(4s) + Rb(5p_{1/2, 3/2})$ and $K(4p_{1/2, 3/2}) + Rb(5s)$ asymptotic limits. These limits correlate to eight electronic states in Hund’s case (a), or sixteen in case (c): $[A 1 \Sigma^+ (2(0^+)), 3 1 \Sigma^+ (4(0^+)), 1 1 \Pi (4(1)), 2 1 \Pi (5(1)), 2 3 \Sigma^+ (2(0^-) and 2(1)), b 3 \Pi (3(0^+), 3(0^-), 3(1), and 1(2)), 3 3 \Sigma^+ (5(0^-) and 7(1)), 2 1 \Pi (5(0^-), 4(0^-), 6(1), and 2(2))]$. These states lead to complicated spectra, particularly given the global perturbations among them due to the large spin-orbit interactions, especially for the Rb atom. Assigning the observed molecular transitions in these congested spectra poses considerable challenges.

These states have potential well depths between 400 and 7000 cm$^{-1}$, and some of them have not been systematically studied. Also, for the states with a deep potential well, it is not always possible to investigate the entire potential because of the limited range of the Franck-Condon (FC) windows for excitation. Thus, it is worthwhile to combine several experimental methods to more completely study the full range of the potentials.3,26

High-resolution spectroscopic information on the ground and excited electronic states of KRb has been accumulated using KRb molecules formed in a heat-pipe oven,9,10,12,13,15,16,27,28 in a supersonic molecular beam (MB),3,18–22 in photoassociation (PA) of ultracold atoms,11 and in the spectra of ultracold molecules (UMs)3,9,17,23 formed from the radiative decay of levels formed by PA. While the first two approaches provide information primarily at short range near the equilibrium distance of the ground state, the latter two provide information primarily at long range, but with some overlap at intermediate range.

We have published detailed reviews of the previously observed electronic states of KRb ($A 1 \Sigma^+, 3 1 \Sigma^+, 1 1 \Pi, 2 1 \Pi,$ etc.)
2 $^3\Sigma^+$, and $b$ $^3\Pi$) in earlier articles.\textsuperscript{3,29} Only a few of the low vibrational levels of these have been reported with the exceptions of heat-pipe oven studies of the $1^1\Pi$ and $2^1\Pi$ states\textsuperscript{15} and our UM experiments.\textsuperscript{3,9,17,23} Thus, information on the low-lying electronic states of the KRb molecule is still incomplete. Among these eight Hund’s case (a) electronic states, the $A$ and $3^1\Sigma^+$ states, which have ion-pair character at intermediate internuclear distance, are not yet well known. The $3^1\Sigma^+$ state, with its ion-pair character arising from K$^-$ and Rb$^+$, as predicted by Mulliken,\textsuperscript{30} has an unusual distribution of vibrational level spacings at short range.

Recently, we have extensively studied the spectra of $^{39\text{K}}\text{Rb}$ ultracold molecules formed by PA to a level of the $3(0^-)$ state.\textsuperscript{3,29} The spectra of molecules in the high-lying $v_a = 21$ level of the $a$ $^3\Sigma^+$ state (formed by spontaneous emission (SE) from a specifically excited rovibrational PA level of the $3(0^-)$ state) are designated here as UM$-$ spectra. The decay of the $3(0^-)$ state is consistent with the dipole transition selection rules in Hund’s case (c), where an $\Omega = 0^-$ state can emit only to $\Omega = 0^-$ and 1 states. These UM$-$ spectra have been combined with MB spectra to assign and analyze the complex perturbations among the $1^1\Pi - 2^3\Sigma^+ - b$ $^3\Pi$ states.\textsuperscript{3} These UM$-$ spectra have also been used to determine optimal paths for stimulated Raman adiabatic passage to populate the lowest rovibrational level in the X state from a specific rovibrational level in the $a$ state.\textsuperscript{29}

Here we combine these prior results, which we label MB and UM$-$ with a new UM experiment, labeled UM$+$. In the UM$+$ experiment, PA is used to form a specific rovibrational level of the $3(0^+)$ state instead of the $3(0^-)$ state. It is the combination of these three experiments, which we will examine in this manuscript. Note that both here and in our prior work, we assume the absence of collisions which might interconvert the three $\Omega$ components at the ground-state dissociation limit, in accordance with our experimental conditions. We have explored the UM$+$, UM$-$, and MB excitation spectra in the energy region between 14 890 cm$^{-1}$ and 16 300 cm$^{-1}$ above the minimum of the ground $X$ $^1\Sigma^+$ state. We have newly assigned many high vibrational levels of the $A$ $^1\Sigma^+$ and $3^1\Sigma^+$ states using these three spectra.

The $A$ $^1\Sigma^+$ and $3^1\Sigma^+$ states are absent in the UM$-$ spectra, and we explain this in Sec. III C by considering Hund’s case (c) selection rules and transition dipole moment (TDM) calculations of Kotochigova et al.\textsuperscript{31} between the upper excited $A$ $^1\Sigma^+$ ($2(0^+)$) state and the three $\Omega$ components at the ground-state dissociation limit.

As shown in Fig. 1, the FC windows in the MB and UM experiments are quite different. In the MB experiments, the window is narrowly localized near the equilibrium internuclear distance of the ground-state potential. However, in the UM experiments, the windows are broad, especially for levels near the dissociation limit. To investigate the entire potential up to the dissociation limit, combined spectroscopic investigations using multiple methods are required. This has been accomplished for the $K_2$ molecule, where short-range laser-induced fluorescence spectra and long-range PA spectra in the $1^2\Pi_g$ state were combined.\textsuperscript{26} Here we propose similar investigations of the extended potential well of the $A$ $^1\Sigma^+$ and $3^1\Sigma^+$ states by combining short-range spectra from MB experiments and long-range spectra from UM experiments.

![FIG. 1. Ab initio potential energy curves of the $A$ $^1\Sigma^+$, $1^1\Pi$, 2 $^3\Sigma^+$, and 3 $^1\Pi$ states dissociating to the K(4$s$) + Rb(5$p$) asymptotic limit and the $3^1\Sigma^+$, $2^1\Pi$, 2 $^3\Pi$, and 3 $^1\Sigma^+$ states dissociating to the K(4$p$) + Rb(5$s$) asymptotic limit. An energy scale referred to the minimum of the ground X state is used (i.e., theoretical energies are shifted up by 4217.822 cm$^{-1}$) where 4217.822 cm$^{-1}$ is the value of the ground-state dissociation limit from Ref. 9. The MB experiment has a narrow FC window near 4.1 Å and the UM$-$ experiment has a FC window extending a long distance outside 5.6 Å. Thus, the UM$-$ experiment accesses a wide range of high vibrational levels of the electronic states. The newly reported UM$+$ experiment has broad FC windows, one for the X state and one for the $a$ state. The X state UM$+$ window extends across both the MB and UM$-$ windows shown as well as the gap between them. The $a$ state UM$+$ window is similar to the UM$-$ window as shown.](http://jcp.aip.org/about/rights_and_permissions)
levels as zero in defining the ground-state dissociation limit. In $^{39}\text{K}^{85}\text{Rb}$, the lowest hyperfine asymptote is 0.069 cm$^{-1}$ below the center of gravity. The $X^1\Sigma^+$ zero point level hyperfine splittings are too small to resolve in our experiments. It might also be noted that the UM$^+$ and UM$^-$ spectra both originate from $\Omega = 0$ states that have very small hyperfine splittings. The observed widths in both the UM$^+$ and UM$^-$ spectra are dominated by the rotational splitting between the $J'' = 0$ and 2 rotational levels, both of which are populated. Hence, we will not consider hyperfine structure here.

A. UM excitation spectrum

As described previously, dark-SPOT magneto-optical traps (MOTs) of $^{39}\text{K}$ and $^{85}\text{Rb}$ are generated and overlapped at the center of a vacuum chamber pumped by an ion pump. Densities of $3 \times 10^{10}$ cm$^{-3}$ and $1 \times 10^{11}$ cm$^{-3}$ and temperatures of 300 $\mu$K and 100 $\mu$K are obtained for the $^{39}\text{K}$ and $^{85}\text{Rb}$ MOTs, respectively. A continuous-wave Ti:sapphire laser ($\sim 1$ W power and $\sim 1$ MHz frequency jitter) is used to photoassociate atoms into molecular states below the K (4s) $+ \text{Rb}(5p_{1/2})$ asymptote. One specific vibrational level from each of the $3(0^-$) and $3(0^+)$ states, with $J' = 1$, is chosen for formation by PA. These levels decay radiatively to the $a$ and 2 levels of highly excited vibrational levels of the $X^1\Sigma^+$ and $a^1\Sigma^+$ states. The energies of the $3(0^-)$ and $3(0^+)$ levels are at 12 520.36 (16 738.18) cm$^{-1}$ and 12 569.94 (16 877.76) cm$^{-1}$ with respect to the ground-state dissociation limit (with respect to the minimum of the ground-state potential).

A pulsed dye laser with 0.2 cm$^{-1}$ linewidth, 5 ns pulse width, 10 Hz repetition rate, and a few mJ pulse energy is used to excite UM spectra from the high-$\nu''$ levels of the $X$ and $a$ states. The spectra are observed using two-color resonance-enhanced two-photon ionization (RE2PI) by introducing an additional pulsed laser, a frequency-doubled Nd:YAG laser at 532 nm. The resulting $^{39}\text{K}^{85}\text{Rb}^+$ ions are accelerated into a Channeltron ion detector in a time-of-flight (TOF) mass spectrometer and KRb$^+$ TOF signals are collected by a box car integrator.

B. MB excitation spectrum

A supersonic MB of KRb molecules is produced by expanding $^{39}\text{K}$ ($^{41}\text{K}$ and $^{85}\text{Rb}$) and $^{85}\text{Rb}$ ($^{85}\text{Rb}$ and $^{87}\text{Rb}$) vapor with Kr gas through a 300 $^\circ$C pulsed nozzle, with a backing pressure of 530–550 Torr, into a vacuum chamber. Four different isotopologues ($^{39}\text{K}^{85}\text{Rb}$, 67.3%; $^{39}\text{K}^{87}\text{Rb}$, 26.0%; $^{41}\text{K}^{85}\text{Rb}$, 4.9%; $^{41}\text{K}^{87}\text{Rb}$, 1.9%) are produced in the molecular beam. The pulsed jet is collimated by a 1.2 mm diameter skimmer. A Nd:YAG pumped dye laser with 0.12 cm$^{-1}$ linewidth, 5 ns pulse width, 5 Hz repetition rate, and less than 1 mJ pulse energy excites and ionizes KRb by one-color REMPI through intermediate states such as $3\Sigma^+$, $1\Pi$, $2\Sigma^+$, and $b\Sigma^+$. The ion signal at the mass-to-charge ratio of $m/Z = 124$ ($^{39}\text{K}^{85}\text{Rb}^+$) is well separated from the ion signals of the minor isotopologues ($^{39}\text{K}^{87}\text{Rb}^+$, $^{41}\text{K}^{85}\text{Rb}^+$, and $^{41}\text{K}^{87}\text{Rb}^+$) by a TOF mass spectrometer with a dual microchannel plate detector ($m/\Delta m \approx 500$).

III. RESULTS AND DISCUSSION

There are four excited asymptotic limits of interest: $K(4s) + \text{Rb}(5p_{1/2})$ at 16 796.78 cm$^{-1}$, $K(4s) + \text{Rb}(5p_{3/2})$ at 17 034.38 cm$^{-1}$, $K(4p_{1/2}) + \text{Rb}(5s)$ at 17 202.99 cm$^{-1}$, and $K(4p_{3/2}) + \text{Rb}(5s)$ at 17 260.71 cm$^{-1}$ above the minimum of the ground-state potential. These correlate to eight Hund’s case (a) states (four singlets and four triplets: $A^1\Sigma^+$, $3^1\Sigma^+$, $1^1\Pi$, $2^1\Pi$, $2^3\Sigma^+$, $b^3\Pi$, $3^3\Sigma^+$, and $2^3\Pi$) as shown in Fig. 1 where zero energy is referred to the minimum of the ground X state. If the spin-orbit interaction is considered, the component states at long range split into sublevels with various $\Omega$ values which correlate to the four excited asymptotic limits. However, if spin-orbit interaction is neglected, there are only two asymptotic limits. Thus, in theoretical calculations that neglect the spin-orbit interaction, the asymptotic limit of the $A^1\Sigma^+$, $1^1\Pi$, $2^3\Sigma^+$, and $b^3\Pi$ states is taken to be 16 955.18 cm$^{-1}$ (the weighted mean of 16 796.78 and 17 034.38 cm$^{-1}$) and that of the $3^1\Sigma^+$, $2^1\Pi$, $3^3\Sigma^+$, and $2^3\Pi$ states is taken to be 17 241.47 cm$^{-1}$ (the weighted mean of 17 202.99 and 17 260.71 cm$^{-1}$ above the minimum of the ground-state potential.

Our experiments span the energy region between 14 890 cm$^{-1}$ and 16 300 cm$^{-1}$ above the minimum of the ground $X^1\Sigma^+$ state, marked with horizontal dotted lines in Fig. 1. As previously mentioned, the spectra are complicated due to the many perturbations among the states, especially near their crossings, due primarily to spin-orbit interactions. In this energy region, we observe the $A^1\Sigma^+$, $3^1\Sigma^+$, $1^1\Pi$, $2^3\Sigma^+$, and $b^3\Pi$ states.

A. The MB spectra

Our MB experiment employs a very sensitive detection method with which we can observe quite weak molecular signals. Simulation of the rotational contours obtained in the MB experiment shows that only low $J''$ components (typically $J''_{\text{max}} = 5$) are involved. The electronic TDM of the $3^1\Sigma^+$ $\leftarrow X^1\Sigma^+$ transition and the Franck-Condon factors (FCFs) between the $3^1\Sigma^+$ and $X^1\Sigma^+$ states are predicted to be very small. Nevertheless, we observe a regular and very weak vibrational progression assignable to the $3^1\Sigma^+$ ($\nu'$) $\leftarrow X^1\Sigma^+$ ($\nu''$) transition in the MB excitation spectrum as shown in Fig. 2, where the intensity scale has been expanded. The strongest signals, assigned to vibrational levels of the $1^1\Pi$ state in our previous paper, are about 100 times stronger in signal intensity than the peaks assigned here to vibrational levels of the $3^1\Sigma^+$ state.

After eliminating bands of the $1^1\Pi$, $b\Sigma^+$, and $2\Sigma^+$ states assigned previously (including the weak $\nu'' = 1$ “hot bands” marked by the symbol (*) in Fig. 2), only one regular vibrational progression with very weak signal intensities in the MB experiment remains unassigned. The vibrational spacing of this progression ($\sim 39$ cm$^{-1}$) is close to that calculated for the $3^1\Sigma^+$ state. Thus, we assign this progression to the $3^1\Sigma^+$ state ($\nu'' = 24–43$) as shown in Fig. 2. Experimental $T_{\nu''}$ values of the $A$ and $3^1\Sigma^+$ states are obtained from the MB and UM$^+$ spectra. We compare these experimental $T_{\nu''}$ values of the $A$ and $3^1\Sigma^+$ states with theoretical $T_{\nu''}$ values, where eigenvalues of the $A$ and $3^1\Sigma^+$ states are obtained from the MB and UM$^+$ spectra.
Ref. 24 have been shifted up by the experimental ground-state dissociation energy 4217.822 cm\(^{-1}\), those observed in the UM experimental assignments have been made by comparing theoretical limits of the theoretical potentials into coincidence with per state eigenvalues, since it brings the ground-state dissociation to the 3\(^1\Sigma^+\) state. Hot bands from the \(\nu' = 1\) level of the X\(^1\Sigma^+\) state and unassigned vibrational levels are marked by the symbols (*) and (+), respectively. The energy is given with respect to the minimum of the ground \(X\) state potential well (i.e., the spectrum is shifted up by \(E(X, \nu' = 0, J' = 0) = 37.864\) cm\(^{-1}\) to the excitation laser frequency in cm\(^{-1}\)).

\((\nu', J' = 0)\) states from the theoretical potential curves of Ref. 24 have been shifted up by the experimental ground-state dissociation energy 4217.822 cm\(^{-1}\), since the theoretical curves use the ground-state dissociation limit as their energy zero while we use the minimum of the experimental ground-state potential as our energy zero. We note that the theoretical calculations from Ref. 24 underestimate the ground-state potential well depth by 107.822 cm\(^{-1}\), and this shift of 4217.822 cm\(^{-1}\) effectively removes this ground-state error from the upper state eigenvalues, since it brings the ground-state dissociation limit of the theoretical potentials into coincidence with the experimental ground-state dissociation limit. The vibrational assignments have been made by comparing theoretical \(T_v\) with experimental \(T_v\) as shown in the supplementary material, and the numbering may be uncertain by one or possibly two. The observed energies of the \(\nu' = 35–43\) levels of the 3\(^1\Sigma^+\) state in the MB experiment overlap well with those observed in the UM experiment (\(\nu' = 35–51\)) as discussed below. Most lines have been assigned in the strongly perturbed region above 15 140 cm\(^{-1}\) as shown in Fig. 2(b). We could not assign some of the observed weak lines marked by a symbol (+) for energies below 15 140 cm\(^{-1}\). This region includes the avoided crossings of the \(\Omega = 0^-\) and 1 potential curves of the \(b\,^3\Pi\) and \(2\,^3\Sigma^+\) electronic states at \(\sim 6.4\) Å visible in Fig. 1. Further investigation will be needed to understand these unassigned perturbed spectra.

**B. The UM spectra**

We used two different PA levels (one \(3(0^+)\) and one \(3(0^-)\)) to obtain UM spectra (UM+ and UM−, respectively).

Both of the UM spectra have only vibrational resolution, but only low \(J\) components are involved because only the \(J = 1\) levels of the \(3(0^+)\) and \(3(0^-)\) states are initially excited by PA. These two levels have different symmetries, so their selection rules are different. Radiative decay from the 3\((0^-)\) level can occur only to the \(a\) state because of the symmetry selection rules. However, the 3\((0^+)\) level decays to both the \(X\) and \(a\) states. More specifically, in the UM+ spectra, \(X(\nu'' = 87–90)\) and \(a(\nu_a = 19–23)\) are populated from the decay of the 3\((0^+)\) PA level, while in the UM− spectra, only \(a(\nu_a = 20 \text{ and } 21)\) are populated. Also the \(A\) and \(3\,^1\Sigma^+\) states are observed differently: they are absent in the UM− spectra, but present in the UM+ spectra, as we discuss in Sec. III C. For all of these reasons, the UM+ spectra from high-lying vibrational levels of the \(X\) and \(a\) states are more complicated than the UM− spectra. Thus, initially it was not easy to assign them.

However, by a stepwise process we have been able to assign all possible levels of the \(A\,^1\Sigma^+, 3\,^1\Sigma^+, 1\,^1\Pi, 2\,^3\Sigma^+, \) and \(b\,^3\Pi\) states in the energy region below the first excited dissociation asymptote. First we assigned the \(1\,^1\Pi, 2\,^3\Sigma^+, \) and \(b\,^3\Pi\) states by combining the strong transitions in the MB and UM− spectra from high-lying vibrational levels of the \(a\,^3\Sigma^+\) state. In the MB experiment, as explained in Sec. III A, we first assign weak transitions to lower vibrational levels of the 3\(^1\Sigma^+\) state. We then extend the vibrational assignments of that state to higher vibrational levels by using the UM+ spectra, which include excitation from the higher vibrational levels of the \(X\) and \(a\) states. Finally, we assign the \(A\,^1\Sigma^+\) state to the transitions which still remain unassigned, confirming the identifications by comparing the spectra from the \(X\,^1\Sigma^+\) and \(a\,^3\Sigma^+\) vibrational levels. The energies of the assigned \(A\,^1\Sigma^+\) levels are close to theoretical predictions in the supplementary material. We successfully sort out the \(A\,^1\Sigma^+\) and \(3\,^1\Sigma^+\) states among the many observed spectroscopic lines to the \(A\,^1\Sigma^+, 3\,^1\Sigma^+, 1\,^1\Pi, 2\,^3\Sigma^+, \) and \(b\,^3\Pi\) states by using UM+ and MB experiments in the strongly perturbed energy region between 14 890 cm\(^{-1}\) and 16 300 cm\(^{-1}\) above the minimum of the ground \(X\) state.

Previously assigned UM− spectra, of the 1\(^1\Pi, 2\,^3\Sigma^+, \) and \(b\,^3\Pi\) states from high vibrational levels of the \(a\) state, formed by decay from a specific PA level of the 3\((0^-)\) state, are shown in Fig. 3(a). The assigned vibrational levels of the electronic states are from \(\nu_a = 21\) (and 20) of the \(a\) state.

Newly assigned UM+ spectra of the \(A\,^1\Sigma^+, 3\,^1\Sigma^+, 1\,^1\Pi, 2\,^3\Sigma^+, \) and \(b\,^3\Pi\) states, starting in high vibrational levels of the \(a\) and \(X\) states, are shown in Fig. 3(b). All assigned electronic states which match well with assigned vibrational levels in Figs. 3(a) and 3(c) are marked by the symbol (o) in Fig. 3(b). The assigned vibrational levels of the initial electronic states include the \(\nu'' = 89\) level of the \(X\) state and \(\nu_a = 21\) level of the \(a\) state. Other (usually weaker) lines are from \(\nu_a = 19, 20, 22, \) and 23 of the \(a\) state and from \(\nu'' = 87, 88, \) and 90 of the \(X\) state. We note that the energy splitting (3.61 cm\(^{-1}\)) between \(\nu_a = 21\) and \(\nu_a = 22\) of the \(a\) state is only slightly larger than that between \(\nu'' = 89\) and \(\nu'' = 90\) of the \(X\) state. Transitions from the \(a\) state to the excited upper states are weaker than those from the \(X\) state to the excited upper states. Two unassigned transitions marked by the symbol (?) still remain in this energy region. Vibrational levels...
and MB spectra shown in Fig. 3 are shifted up by the energies $\epsilon_l$ so that the excited from high vibrational levels of the states, populated by decay from a specific level of the $3(0^+)$ state (formed by PA), (b) Newly assigned UM+ spectra of the $A^1\Sigma^+$, $3\Sigma^+$, $1\Pi$, $2\Sigma^+$, and $b^3\Pi$ levels excited from high vibrational levels of the $X$ and $a$ states formed by decay from a specific level of the $3(0^+)$ state (formed by PA). (c) Assigned MB spectra of the $3\Sigma^+$, $1\Pi$, $b^3\Pi$, and $2\Sigma^+$ states excited from low vibrational levels of the $X$ state. Hot bands from the $v'' = 1$ level of the $X^1\Sigma^+$ state vibrational levels are marked by the symbol ($\star$). All of the assigned electronic levels in panel (b) that match well with assigned vibrational levels in Figs. 3(a) and 3(c) are marked by the symbol (o). It should be noted that the energy scales in the MB, UM+, and UM$-$ spectra are all the same and are relative to the minimum of the ground $X$ state potential. Thus, each spectrum is shifted up by the energy of the lower level of the excitation (relative to the bottom of the ground-state potential well): the frequency axes of the UM$-$, UM+, and MB spectra shown in Fig. 3 are shifted up by the energies $E(0, v_n = 21, l_s = 0)$ [4202.976 cm$^{-1}$], $E(X, v'' = 89, j'' = 0)$ [4204.762 cm$^{-1}$], and $E(X, v'' = 0, j'' = 0)$ [37.864 cm$^{-1}$] relative to the excitation laser frequency in cm$^{-1}$, respectively.

$v'' = 35 - 51$ of the $3\Sigma^+$ state and $v'' = 93 - 122$ of the $A^1\Sigma^+$ state have been observed in the UM+ experiment.

In Fig. 3(c), the assigned vibrational levels of the $3\Sigma^+$, $1\Pi$, $2\Sigma^+$, and $b^3\Pi$ states from the MB experiment are shown. The energy positions of the assigned vibrational levels of the $3\Sigma^+$ state in the MB spectra match well with the assigned levels of that state in the UM+ spectra. The supplementary material shows tables of vibrational number assignments and term energies for the $A$ and $3\Sigma^+$ states, made by comparing the energies from theoretical calculations with the assigned MB, UM+, and UM$-$ experimental energies.

The $\Delta G_{v+1/2}$ values of the $A$ and $3\Sigma^+$ states are shown in Fig. 4 as a function of energy, where zero energy is referred to the minimum of the ground-state potential. The $\Delta G_{v+1/2}$ values of the $A^1\Sigma^+$ state are intermittently observed due to the distribution of FCFs. They are more irregular than those of the $3\Sigma^+$ state due to the perturbations, and also smaller in the energy region above 15 618 cm$^{-1}$.

It is characteristic of ion-pair states such as $3\Sigma^+$ for the intervals $\Delta G_{v+1/2}$ to initially increase with energy, then pass through a maximum before decreasing as for a covalent potential. The $3\Sigma^+$ state dissociates adiabatically to the $A^1\Pi + \text{Rb}(5s)$ limit. The $2\Pi$, $2\Pi$, and $3\Sigma^+$ states, which lie far above the $3\Sigma^+$ state in our experimental energy region, also dissociate to the excited $K$ dissociation limits as shown in Fig. 1. However, the $A$ state dissociates to the $K(4s) + \text{Rb}(5p_{1/2})$ limit and is perturbed strongly by nearby electronic states such as $1\Pi$, $2\Sigma^+$, and $b^3\Pi$ due to the spin-orbit interaction. Thus, we expect the $3\Sigma^+$ state to be perturbed less strongly by these states, accounting for its more regular vibrational progression compared to the $A^1\Sigma^+$ state.

C. Selection rules and TDMs

As already mentioned, the previously reported UM$-$ spectra did not show transitions to the $A^1\Sigma^+$ or $3\Sigma^+$ states. However, the UM+ spectra include several transitions to vibrational levels of the $A^1\Sigma^+$ state with term energies between 15 116 and 16 225 cm$^{-1}$ above the minimum of the ground $X^1\Sigma^+$ state.

If a $3(0^+)$ level is formed by PA, it can decay only to the $\Omega = 1$ component of the $4\Sigma^+$ state or to the $X^1\Sigma^+$ state ($\Omega = 0^+$), because transitions between the $1(0^+)$ and $3(0^+)$ states are forbidden. The dominant transition from our specific level of the $3(0^+)$ state to the $X^1\Sigma^+$ state is to $v'' = 89$, and the dominant transition to the $a^3\Sigma^+$ state is to $v_a = 21$.

According to Kotochigova’s TDM calculations [Figs. 6 and 7 of Ref. 31, showing the TDM between the $1(0^+)$ and $2(0^+)$ states, and between the $1(0^+)$ and $2(0^+)$ states, respectively], the TDM is large between the $X$ and $A$ state in the region of FC overlap between $v'' = 89$ and the $A$ state vibrational levels in the energy region between 15 116 and

FIG. 4. Vibrational spacings $\Delta G_{v+1/2}$ of the $A^1\Sigma^+$ and $3\Sigma^+$ states with an energy scale referred to the minimum of the ground-state potential. Theoretical energies are shifted up by 4217.822 cm$^{-1}$, where 4217.822 cm$^{-1}$ is the value of the ground-state dissociation energy from Ref. 9. Our experimental observations of the $A^1\Sigma^+$ and $3\Sigma^+$ states are marked by symbols ($\bigcirc$) and (o), respectively. Theoretical $\Delta G_{v+1/2}$ values of the $A^1\Sigma^+$ and $3\Sigma^+$ states based on the potential curves of Rousseau et al. are marked by symbols ($\bigstar$) and ($\Diamond$), respectively. Theoretical $\Delta G_{v+1/2}$ values of the $2(0^+)$ and $4(0^+)$ states based on the potential curves of Rousseau et al. are marked by solid lines. Prior experimental values for the $3\Sigma^+$ state by Amiot et al. are marked by the symbol ($\bigtriangleup$). The $\Delta G_{v+1/2}$ plot for the $3\Sigma^+$ state has a maximum in the lower energy region reflecting the ion-pair character of the potential. Note that the $3\Sigma^+$ state is less perturbed than the $A^1\Sigma^+$ state, as indicated by its more regular $\Delta G_{v+1/2}$ spacings. At the high-$v''$ limit, $3\Sigma^+$ and $4(0^+)$ states have 9 and 6 quasibound levels, respectively. The last levels of the $3\Sigma^+$ and $4(0^+)$ states are the only ones which predominantly predissociate by tunneling rather than radiate, with very short estimated theoretical lifetimes of $1.0 \times 10^{-10}$ s and $3.9 \times 10^{-12}$ s, respectively.
16 225 cm$^{-1}$ above the minimum of the ground $X\, ^1\Sigma^+$ state. However, the TDM between $v_a = 21$ of $a\, ^3\Sigma^+$ ($\Omega = 1$) state and these vibrational levels of the $A\, ^1\Sigma^+$ state is quite small.

If instead a $3(0^+)$ level is formed by PA, it can only decay to the $a\, ^3\Sigma^+$ state ($\Omega = 1$ and 0$^-$ components) because transitions between the $3(0^-)$ and $1(0^+)$ states are forbidden. As mentioned previously, most of the a state population is in the level $v_a = 21$. Electric dipole transitions are not allowed between the $\Omega = 0^-$ component of the $a\, ^3\Sigma^+$ state and the $A\, ^1\Sigma^+$ ($\Omega = 0^+$) state. Also, the TDM for the $\Omega = 1$ component is quite small in the region of FC overlap between $v_a = 21$ and the energetically accessible levels of the A state.

We may apply the same argument used for the A state to explain the absence of the $3\, ^1\Sigma^+$ state in the UM$^-$ spectra. However, Kotochigova et al. did not calculate the TDM between the $4(0^+)$ and $1(1)$ states, or between the $4(0^-)$ and $1(0^+)$ states. If those calculations were available, it would help us to clarify the reason why the $3\, ^1\Sigma^+$ state is missing in the UM$^-$ spectra, but present in the UM$^+$ spectra. Note that there are also TDM calculations for the $A\, ^1\Sigma^+ - X\, ^1\Sigma^+$ and $3\, ^1\Sigma^+ - X\, ^1\Sigma^+$ transitions from Beuc et al., but they do not incorporate the spin-orbit coupling.

**D. Proposal for future investigation of long-range structure and dynamics**

Sixteen Hund’s case (c) states correlate to the four lowest excited K and Rb atomic asymptotes at large internuclear distance. Figure 5 shows the Hund’s case (c) potentials of the $2(0^+)$, $3(0^+)$, and $4(0^+)$ states and the Hund’s case (a) potentials of the $A$ and $3\, ^1\Sigma^+$ states. The $2(0^+)$ state has an avoided crossing near 5.2 Å with the $3(0^+)$ state. The $A\, ^1\Sigma^+$ state crosses the $b\, ^3\Pi$ state diabatically near 5.2 Å. The $3(0^+)$ state has an avoided crossing with the $4(0^+)$ curve at 7.1 Å.

![FIG. 5. Theoretical potential curves of the 2(0+), 3(0+), and 4(0+) states of Hund’s case (c) and the A 1Σ+ and 3 1Σ+ states of Hund’s case (a). Theoretical energies are shifted up by 4217.822 cm$^{-1}$, where 4217.822 cm$^{-1}$ is the value of the ground-state dissociation energy from Ref. 9. The 2(0+) state has an avoided crossing near 5.2 Å with the 3(0+) state. The A 1Σ+ state crosses diabatically the Ω = 0− component of the b 3Π state near 5.2 Å. The 0− component of the b 3Π state correlates to the 3(0+) state at long range which dissociates to the K(4s) + Rb(5p) asymptote. The 3 1Σ+ state at 7.1 Å, then correlates to the 4(0+) state at long range. The 4(0+) state avoids the 3(0+) state (a component of the 2 3Π state) at ~10 Å and dissociates to the K(4p) + Rb(5s) asymptote. Note that the 2(0+) and A 1Σ+ potentials are nearly identical between 5.2 Å and 10 Å, and the 4(0+) and 3 1Σ+ potentials are nearly identical inside ~9.5 Å.](Image)

As shown in Fig. 5, the asymptotic limit of the $3\, ^1\Sigma^+$ state (K(4p) + Rb(5s)) is above the dissociation limits K(4s) + Rb(5p) and K(4s) + Rb(5p). Other asymptotes for other states are described in another paper.

Possible full characterization of the potential curves, predissociation, and the dissociation limits with UM$^+$, UM$^-$, and MB spectra up to the dissociation limit would extend our knowledge of this molecule. There are several reasons to carry out these long-range investigations. First, predissociation due to the potential crossings near the dissociation limit may show interesting behavior. The vibrational levels of the $3\, ^1\Sigma^+$ state above the K(4s) + Rb(5p) limit may be predissociated. Second, it is interesting to explore the boundary between the Hund’s case (a) and Hund’s case (c) behavior of various levels. According to Kotochigova et al., abrupt boundaries between Hund’s case (a) and Hund’s case (c) are evident in the TDMs with respect to internuclear distance.

Conventional methods such as heat-pipe ovens and supersonic molecular beams prepare populations near the equilibrium point of the potential wells so that it is not easy to access the long-range levels, although there are several exceptions if one has access to very sensitive observation methods.

The UM and PA methods give us wide access to the excited states in the long-range region, so that the combination of the two methods can provide the full potential of a state. UM spectroscopy can also be connected to the levels observed by PA very near the dissociation limit. The two datasets differ in FCFs between the initial and final states and in the different symmetries of the initial states. Combining rovibrational levels in the long-range region previously observed in PA spectra with those observed in these UM$^+$ spectra can be readily carried out.

Figure 6(a) shows that there are broad FCF distributions up to vibrational levels of the $A$ state near the dissociation limit, for transitions starting from the $v'' = 90$ level of the $X\, ^1\Sigma^+$ state. For $v'' = 92$ in Fig. 6(b), the strongest FCFs between the $X$ and $A$ states are above the K(4s) + Rb(5p) asymptote, so that vibrational levels above this limit may be predissociated and have wider linewidths compared to those below this limit. Because the $3(0^+)$ level used in our present UM$^+$ experiment mainly decays to $v'' = 89$ and 90, other higher-energy PA levels of the $3(0^+)$ state should be used to preferentially populate to $v'' = 92$. For MB spectra, the FCF distribution between the $X\, ^1\Sigma^+$ ($v'' = 0$) level and the vibrational levels of the $A\, ^1\Sigma^+$ state is localized in low $v'$ vibrational levels so that high vibrational levels of the $A\, ^1\Sigma^+$ state cannot be observed. FCFs between the $X\, ^1\Sigma^+$ ($v'' = 90$) level and the vibrational levels of the $3\, ^1\Sigma^+$ state are even smaller than those between the $X\, ^1\Sigma^+$ ($v'' = 0$) level and the vibrational levels of the $3\, ^1\Sigma^+$ state as shown in Fig. 6(c), but these vibrational levels have already been observed up to $v'' = 51$ in the UM$^+$ experiment. The highest rovibrational levels of the $A\, ^1\Sigma^+$ states near the dissociation limit should be observable.

At long range, the $2(0^+)$, $2(0^-)$, $2(1)$, $3(0^+)$, $3(0^-)$, $3(1)$, $4(1)$, $5(1)$, and $1(2)$ Hund’s case (c) states have been studied by PA below the K(4s) + Rb(5p) asymptotic limit. However, the PA levels near the dissociation limit are congested and perturbed so that only preliminary assignments have been made and some high-lying levels have been left...
FIG. 6. (a) FCFs between the $X^1\Sigma^+$ ($v' = 0$ and 90) levels and vibrational levels $v''$ of the $A^1\Sigma^+$ state. (b) FCFs between the $X^1\Sigma^+$ ($v' = 0$ and 92) levels and vibrational levels $v''$ of the $A^1\Sigma^+$ state. (c) FCFs between the $X^1\Sigma^+$ ($v' = 0$ and 90) levels and the vibrational levels $v''$ of the 3 $1^3\Sigma^+$ state. Higher vibrational levels of the ground state for UM experiments have a wider FCF distribution and larger FCFs for transitions up to levels near the dissociation limit compared to the $v'' = 0$ vibrational level of the ground state for MB spectra. FCFs with very small magnitudes are shown with numbers.

unassigned. Moreover, exploring the energy region blue-detuned above the K(4$s$) + Rb($5p_{1/2}$) asymptote should also be quite interesting, with many additional perturbations and predissociations.35

IV. CONCLUSIONS

We have observed the $A$ and $3 \ 1^1\Sigma^+$ states of ultracold $^{85}$Rb molecules in the energy region between 15 116 and 16 225 cm$^{-1}$ above the minimum of the ground $X^1\Sigma^+$ state by using a combination of MB, UM$-$, and UM$+$ excitation spectra. Unexpectedly, many high vibrational levels ($v' = 24–51$) of the $3^1\Sigma^+$ state, with a small TDM from the $X$ state,32 have been observed. The observed energies of the $v' = 35 – 43$ levels obtained from UM$+$ experiment match well with those observed from molecular beam experiments. This state, which dissociates adiabatically to the K(4$p_{1/2}$) + Rb($5s$) asymptotic limit and is well below the observed energy region for other electronic states with the same dissociation limit or the next higher K(4$p_{3/2}$) + Rb($5s$) limit, is weakly perturbed. In contrast, the $A^1\Sigma^+$ state is strongly perturbed by the $1^1\Sigma^-$–$2^3\Sigma^+$–$b^1\Pi$ states. Many high vibrational levels ($v' = 93–122$) of the $A^1\Sigma^+$ state with ion-pair character have also been observed.

Recently we have reported that molecules formed by using the 3(0$^-$) PA level (i.e., the UM$-$ spectra) are not excited to the $A$ and $3^1\Sigma^+$ states in the same energy region.3,29 The contrast between UM$-$ and UM$+$ spectra of the $A$ and $3^1\Sigma^+$ states has been explained by considering Hund’s case (c) selection rules in conjunction with TDM calculations of Kotochigova et al.31 between the upper excited $A^1\Sigma^+$ (2(0$^+$)) state and the three $\Omega$ components at the ground-state dissociation limit.

We also propose future investigations of the entire potential wells of these states, including the long-range region, by combining short-range MB spectra with intermediate and long-range UM spectra and PA spectra. This investigation of high vibrational levels near the dissociation limit may also reveal interesting predissociations of the vibrational levels. Exploring the boundary between the Hund’s case (a) and case (c) behavior of various levels should provide further understanding of Hund’s case changes.

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37See supplementary material at http://dx.doi.org/10.1063/1.4771661 for $T_v$ values of the $A$ and $3 \Sigma^+$ states obtained from the MB and UM+ spectra and from the experimental dissociation energy and theoretical potentials.