Spectroscopy of $^{39}$K$^{85}$Rb triplet excited states using ultracold a $3\Sigma^+$ state molecules formed by photoassociation

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Abstract. Convenient state-selective detection methods are proposed for exploring triplet Rydberg states from the metastable a $3\Sigma^+$ state of ultracold KRb molecules by resonance-enhanced two-photon ionization and time-of-flight (TOF) mass spectroscopy. This would allow the first accurate determination of the ionization potential. Particularly suitable resonant intermediate states include the $2\,3\Pi_\Omega$, $3\,3\Sigma^+$ and $4\,3\Sigma^+$ states, and we report spectroscopic studies of these states. For the $2\,3\Pi_\Omega$ state, the spin–orbit components ($\Omega = 0^+, 0^-, 1$ and 2) have been investigated and a shallow long-range state ($5(0^+)$) at $\sim$9.3 Å has been observed. We compare our observations of these three states with predictions based on ab initio potential energy curves. Such studies may also permit the direct observation of autoionizing resonances leading to efficient formation of low-lying rovibrational levels of the $2\Sigma^+$ ground state of KRb$, ideally in the $v^+ = 0$, $N^+ = 0$ level.

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1. Introduction

Ultracold plasma formation [1, 2] has opened new interesting features in high-resolution laser spectroscopy. A plasma with an initial ion translational temperature of \( \sim 200 \, \mu K \) can be formed by photoionizing laser-cooled atoms. To understand the reactive collision dynamics of cold molecular ions in the ground state \( (X^2\Sigma^+, \nu^+ = 0, N^+ = 0) \) with neutral atoms and molecules and their ions are needed. However, the uncertainty of the IP of the neutral KRb molecule is large \( (\sim 100 \, \text{cm}^{-1}) \). No experimental IP measurements have apparently been carried out.

Thus, we propose IP measurements for KRb by measuring a series of triplet Rydberg states with pump–probe techniques. This scheme was successfully exploited in Na\(_2\) [4, 5] by exciting singlet Rydberg \( np\sigma_u \) states with \( n \leq 119 \) from the ground singlet state. Multichannel quantum defect theory (MQDT) [6] was used to analyze the Rydberg states and a precise IP of the Na\(_2\) molecule was obtained [5]. The HD molecular IP [7] was also extrapolated from the Rydberg \( np \) (\( n = 40–80 \)) states using MQDT. Very recently, Liu et al [8] have improved the IP of H\(_2\) to \( \pm 0.00043 \, \text{cm}^{-1} \) by measuring 54p Rydberg states. A recent re-examination of the HD spectrum [9] extended all the way to \( n = 150 \), although there was no actual improvement in the accuracy of the IP. A similar approach can be applied to triplet Rydberg states of Rb\(_2\) formed from ultracold molecules [10], where the IP is also significantly uncertain \( (\sim 400 \, \text{cm}^{-1}) \) [3].

Ideally, the equilibrium distance of the intermediate state potential used for two-step excitation of KRb Rydberg states should be similar to that of the ground-state KRb\(^+\) ion, so there will be large Franck–Condon factors (FCFs) between the low-lying rovibrational levels of the intermediate state and the triplet Rydberg states converging to the \( \nu^+ = 0, N^+ = 0 \) level of the ion. We expect to observe one or two vibrational progressions to the Rydberg states when we use such an intermediate state for resonant ionization.

Spectroscopy of the triplet Rydberg states with low \( N \) rather than high \( N \) simplifies the assignments of the spectra. Also low-\( N \) Rydberg states are required to access the lowest rotational quantum number \( (N^+ = 0) \) of the KRb\(^+\) ion. In our ultracold experiments, low rotational levels in the intermediate state are easily produced since the molecules formed by photoassociation are exclusively in low rotational levels [11].

High-lying triplet Rydberg states of diatomic molecules have not been investigated extensively, although, for example, Lindsay et al [12] observed 35 different triplet Rydberg...
states of the H$_2$ molecule with $n = 10$–22. A study [13] of predissociation and autoionization from the metastable $^3\Pi_u^-$ state to nd Rydberg states ($n = 12$–20) in H$_2$ was also carried out.

Mixed singlet–triplet states have previously been used as intermediate states to study high-lying triplet states because the initial state is the ground singlet state in a molecular beam or heat pipe oven experiment. However, the powerful photoassociation experimental technique provides an alternative pathway for investigating high-lying triplet states because it can be used to produce pure triplet a $^3\Sigma^+$ state molecules as well as molecules in the singlet ground state. However, the intermediate triplet states and the a $^3\Sigma^+$ state should be well characterized. Ultracold KRb molecules have been formed in our laboratory by PA of ultracold $^{39}$K and $^{85}$Rb atoms, followed by spontaneous emission (SE). These molecules can be formed in high vibrational levels of the $X^1\Sigma^+$ ground state and the a $^3\Sigma^+$ lowest triplet state [14, 15]. The a $^3\Sigma^+$ state has also been observed using Fourier transform spectroscopy [16]. This work determined the absolute vibrational numbering in the a $^3\Sigma^+$ state by the isotope shift and generated high-quality potential curves for the $X^1\Sigma^+$ and a $^3\Sigma^+$ states. Zemke et al [17] have previously calculated the potential and vibrational energies for all $X^1\Sigma^+$ levels.

Based on the \textit{ab initio} potential energy curves of Rousseau et al [18], there are many possible intermediate states such as 1 $^3\Pi$, 2 $^3\Sigma^+$, 2 $^3\Pi$, 3 $^3\Sigma^+$, 4 $^3\Sigma^+$, 3 $^3\Pi$, 5 $^3\Sigma^+$, etc which could be used to generate high-lying triplet Rydberg states and the ground state ($v^+ = 0, N^+ = 0$) of KRb$^+$. High-lying vibrational levels of the 1 $^3\Pi$ and 2 $^3\Sigma^+$ states can be reached from high vibrational levels of the a $^3\Sigma^+$ state. However, in those two cases we need very long-wavelength lasers to reach low vibrational levels having good FCFs to the $v^+ = 0$ level of the molecular ion; moreover, the FCFs from the a $^3\Sigma^+$ state to the appropriate levels of the 1 $^3\Pi$ and 2 $^3\Sigma^+$ states are very small. In the energy region above about 16 600 cm$^{-1}$ (where the 3 $^3\Pi$, 5 $^3\Sigma^+$, etc states occur), there is a high density of spectral lines such that it is not easy to assign the spectra (see figure 2 of [15]). Thus there are three particularly promising intermediate states for pump–probe spectroscopy to the Rydberg triplet states and the molecular ion ground state: 2 $^3\Pi$, 3 $^3\Sigma^+$ and 4 $^3\Sigma^+$, shown in figure 1.

The 2 $^3\Pi$, 3 $^3\Sigma^+$ and 4 $^3\Sigma^+$ states have been investigated theoretically and experimentally. The 2 $^3\Pi$ state is known from the diffuse bands, was observed with absorption and laser-induced fluorescence methods [19]. Three satellite bands from the a $^3\Sigma^+$ state to this state were also measured by absorption [20]. Vibrationally resolved emission spectra from the 2 $^3\Pi$ state to the a $^3\Sigma^+$ state in KRb on helium nanodroplets [21] were also observed.

Lee et al [22] observed spin-forbidden transitions to the 3 $^3\Sigma^+$ state for vibrational quantum numbers between $v' = 1$ and 8 from the ground $X^1\Sigma^+$ state in a pulsed molecular beam and determined that the hyperfine splitting in the 3 $^3\Sigma^+$ state is mainly from the Fermi contact interaction. Spin-forbidden transitions between singlet and triplet states occur due to triplet–singlet mixing. Other examples of such forbidden transitions were recently analyzed [23, 24].

We have previously used resonance-enhanced two-photon ionization (RE2PI) through the 4 $^3\Sigma^+$ state to determine the a $^3\Sigma^+$ vibrational levels populated in our experiments and partially characterized the vibrational levels of the 4 $^3\Sigma^+$ state [14, 15]. More than ten vibrational progressions of the 4 $^3\Sigma^+$ state from the $v'' = 20$ and 21 levels of the a $^3\Sigma^+$ state (according to new vibrational assignments by Pashov et al [16]) were observed previously.

Here, we report the observation of vibrational levels between $v' = 4$ and 12 of the 3 $^3\Sigma^+$ state and between $v' = 0$ and 6 of the various 2 $^3\Pi$ states. Also, the spin–orbit interaction
Figure 1. Proposed scheme for observation of high-lying triplet states via intermediate states (2 $^3\Pi$, 3 $^3\Sigma^+$ and 4 $^3\Sigma^+$). KRb is formed in the metastable a $^3\Sigma^+$ state via PA followed by SE. The Rydberg states will be populated by two-photon (pump–probe) excitation. The intermediate state spectroscopy reported here is performed by vibrational-state-selective RE2PI.

and an intermediate long-range shallow well in the 2 $^3\Pi$ state have been investigated. Then we analyze promising ionization routes from the a $^3\Sigma^+$ state to triplet Rydberg states in low rotational levels through the intermediate 2 $^3\Pi$, 3 $^3\Sigma^+$ and 4 $^3\Sigma^+$ states. Such routes also represent promising approaches for reaching autoionizing levels that could produce exclusively the (v$^+$ = 0, N$^+$ = 0) level of the $X^2\Sigma^+$ ground state of KRb$^+$ under ultracold conditions.

2. Experiment

The experimental set-up is well described in a previous paper [25], and is summarized here briefly, with an emphasis on the scheme for exciting and observing the 3 $^3\Sigma^+$, 2 $^3\Pi$ and 4 $^3\Sigma^+$ states. $^{39}$K and $^{85}$Rb dark-spot magneto-optical traps (MOTs) with densities of 3 × 10$^{10}$ and 1 × 10 cm$^{-3}$ and temperatures of 300 and 100 $\mu$K, respectively, are generated and overlapped at the center of the chamber. For the Rb MOT, a depump beam is used to reduce the fraction of atoms in the bright state. The two MOTs are overlapped by optimally adjusting each MOT position. A CW PA laser is applied to generate excited molecular states near the K(4s) + Rb(5p$_{1/2}$) asymptote. The PA laser (Coherent 899–29) has a typical power of 1 W with a frequency jitter of $\sim$1 MHz. The alignment of the PA laser with the center of the MOT is confirmed by optimizing the destruction of the Rb MOT when the laser is tuned to the Rb atomic transition frequency near 12 579.00 cm$^{-1}$. To study excited triplet states, the 3(0$^-$) state is chosen for PA because this state decays exclusively to the triplet a $^3\Sigma^+$ state and has negligible hyperfine structure. Then a pulsed laser beam with 0.2 cm$^{-1}$ linewidth, $\sim$7 ns pulse width, 10 Hz repetition rate, and a few mJ pulse energy illuminates the overlapped MOTs to provide state-selective RE2PI detection. This laser (Continuum ND6000) is pumped by a frequency-doubled Nd:YAG laser.
DCM dye with a 600–680 nm tuning range is used for this experiment. The scanned spectra were calibrated using a wavemeter. The probe laser linewidth resolution is 0.2 cm\(^{-1}\), but the fitted uncertainty for the line positions is nearly 0.3 cm\(^{-1}\) due to laser scan nonlinearity in this frequency region.

The KRb\(^+\) ions produced by this laser are accelerated into a Channeltron ion detector. These molecular ions are separated from Rb\(^+\), Rb\(_2\)^+ and K\(^+\) ions by their time of flight to the detector and selected using a boxcar integrator. The resulting KRb\(^+\) ion signal is sent to a personal computer through an analog-to-digital converter. A typical production rate of \(\sim 4 \times 10^4\) molecules s\(^{-1}\), yielding 10–60 KRb\(^+\) ions per laser shot, is obtained for strong PA signals [26]. The background (off resonance) level of KRb\(^+\) ions is \(\sim 1.7\) ions laser pulse\(^{-1}\).

Figure 1 shows selected potential curves from [18] relevant to the experiment. The 3(0\(^-\)) molecular state with \(J' = 1\) is formed by PA from two colliding atoms. This state decays to high vibrational levels of the a \(\Sigma^+\) state with rotational levels [11] \(J'' = 0\) and 2, then the detection laser probes the intermediate triplet states by RE2PI.

The pulsed RE2PI scheme lacks rotational resolution. This can be obtained in the future using a novel ion depletion spectroscopy already demonstrated for other KRb states [11]. In the present experiments, we seek only to identify vibrational levels of the 2 \(\Pi\), 3 \(\Sigma^+\) and 4 \(\Sigma^+\) states useful for double resonance excitation of high Rydberg states. In the proposed IP experiments, CW lasers will be applied to excite high Rydberg states and ultimately to ionize the molecules from the intermediate state. For the molecular ion no measurements have been carried out, so we use theoretical values by Korek \textit{et al} [27] for the energetics of this state. The estimated error in the dissociation energy of KRb\(^+\) is estimated to be 2\%, based on the differences between the experimental and observed \(T_e\) values. An ionization limit for \(^{85}\)Rb of 33 690.7987 cm\(^{-1}\) was used [28]. The estimated IP for KRb is 32 162(100) cm\(^{-1}\) with respect to the potential minimum of the ground state of KRb, and 27 982(100) cm\(^{-1}\) with respect to the K(4s) + Rb(5s) limit [28]. Thus, the frequencies of the probe laser can be connected to the energies of the intermediate levels. For excitation through the 2 \(\Pi_2(v' = 0), 2 \Pi_1(v' = 0), 2 \Pi_0(v' = 0), 3 \Sigma^+(v' = 4)\) and 4 \(\Sigma^+(v' = 3)\) states, the required probe laser frequencies (which will be discussed in section 3) correspond to the readily available values of 14 739, 14 773, 14 810, 13 312 and 11 875 cm\(^{-1}\), respectively.

3. Results and discussion

3.1. The 3 \(\Sigma^+\) state

This state has a barrier at \(\sim 5\) Å and converges to the K(4p\(_{3/2}\)) + Rb(5s\(_{1/2}\)) asymptote. There are 14 quasibound vibrational levels predicted using the theoretical potential curve [18]. Most of the lowest vibrational levels (\(v' = 1–8\)) of this state have been observed by Lee \textit{et al} [22] in a molecular beam. Because we start in high \(v''\) levels of the a \(\Sigma^+\) state, it is most favorable to excite from the region of the inner turning point of the initial state to the region of the outer turning point of the 3 \(\Sigma^+\) state. This does not allow access to the lowest vibrational levels of the 3 \(\Sigma^+\) state due to the small FCFs.

Figure 2 shows spectra corresponding to vibrational levels \(v' = 4–12\) of the 3 \(\Sigma^+\) state observed in the K\(^+\) and KRb\(^+\) ionization signals. These two spectra are similar where they overlap except for a few strong atomic lines [29] marked in the figure. The K\(^+\) signal is presumably due to photofragmentation of KRb\(^+\), but this has not been investigated. For the
Figure 2. Observed $3^3\Sigma^+ \leftrightarrow a^3\Sigma^+$ spectra ($v' = 4–12$): the bottom trace is from the KRb$^+$ channel and the top trace is from the K$^+$ channel. Solid rectangles indicate observed vibrational levels. The # indicates the one-photon atomic transition $K(4p_{3/2}) \rightarrow K(4f)$, the asterisk indicates the two-photon transition $K(4s) \rightarrow K(5d)$, the open circle indicates the two-photon transition $K(4s) \rightarrow K(7s)$, and the closed circle indicates the two-photon transition from Rb$(5s) \rightarrow$ Rb$(7d)$. To better compare both channels (KRb$^+$ and K$^+$) the K$^+$ channel is offset vertically.

The two highest vibrational levels ($v' \leq 12$ and 13), we expect tunneling through the barrier and dissociation to the $K(4p_{3/2}) + Rb(5s_{1/2})$ asymptote will be more rapid than SE as discussed below. The absolute vibrational quantum numbering is based on the Lee et al data for $v' = 1–8$ [22]. For the overlapped vibrational quantum numbers, our results agree well with Lee et al [22] as shown in table 1. However, the difference between theoretical term values from [18] and both sets of experimental term values is approximately 30 cm$^{-1}$. On the other hand, the experimental vibrational spacings in the $3^3\Sigma^+$ state do agree well with those calculated for the theoretical potential [18], as shown in figure 3, showing that the shape of the potential is approximately correct.

The highest observed vibrational quantum number $v' = 12$ is predicted to be just one vibrational quantum number below the potential barrier. The predicted highest level ($v' = 13$) is not observed, presumably due to rapid tunneling through the barrier. Calculated tunneling lifetimes for the $3^3\Sigma^+$ levels based on the theoretical potential [18] are also given in table 1. The final $v' = 13$ level of the $3^3\Sigma^+$ state has a very large tunneling width (0.46 cm$^{-1}$) and short lifetime ($1.1 \times 10^{-11}$ s) and even the $v' = 12$ level we observe may decay primarily by tunneling rather than radiative emission.

In our spectra there is no resolved rotational-hyperfine structure; a narrowband laser could be used to observe this structure by depletion spectroscopy [11]. In [22], there is no hyperfine structure in the $X^1\Sigma^+$ ground state so that the observed hyperfine structure is only in the upper excited state. In our case, we would need to consider the hyperfine structure in the $a^3\Sigma^+$ state.
Table 1. Comparison between our observed term values $T_{v'}$ (cm$^{-1}$) and those of Lee et al [22] for the $3 \Sigma^+$ state. Tunneling lifetimes and term values calculated quantum mechanically from the potential of [18] are also shown.

| $v'$ | This work | [22] | [18] | Tunneling lifetimes (s) |
|------|-----------|------|------|------------------------|
| 0    | 14 443.2  | 14 507.7 | 2.7 $\times 10^{28}$ |
| 1    | 14 480.306 | 14 507.7 | 6.6 $\times 10^{23}$ |
| 2    | 14 544.135 | 14 572.1 | 4.7 $\times 10^{19}$ |
| 3    | 14 607.522 | 14 635.9 | 7.0 $\times 10^{15}$ |
| 4    | 14 670.2147 | 14 699.4 | 1.9 $\times 10^{12}$ |
| 5    | 14 732.7 | 14 762.2 | 8.7 $\times 10^{8}$ |
| 6    | 14 794.7 | 14 824.4 | 6.5 $\times 10^{5}$ |
| 7    | 14 856.016 | 14 886.0 | 7.5 $\times 10^{2}$ |
| 8    | 14 916.608 | 14 946.7 | 1.3 |
| 9    | 14 976.4 | 15 006.7 | 3.4 $\times 10^{-3}$ |
| 10   | 15 035.2 | 15 065.7 | 1.3 $\times 10^{-5}$ |
| 11   | 15 093.0 | 15 123.3 | 7.8 $\times 10^{-8}$ |
| 12   | 15 148.9 | 15 179.0 | 7.1 $\times 10^{-10}$ |
| 13   | 15 231.2 | 1.1 $\times 10^{-11}$ |

Figure 3. $\Delta G_{v'+1/2}$ comparison for the $3 \Sigma^+$ state between theory (○), experiment (+) from Lee et al [22] and our experiment (△). The experimental vibrational spacings agree well with those calculated from the theoretical potential of Rousseau et al [18]. Our highest observed vibrational quantum number is just one vibrational quantum number below the potential barrier.
Figure 4. Expanded spectra for a specific vibrational progression of the $3\,^3\Sigma^+ \leftarrow a\,^3\Sigma^+$ bands in the energy range between 14 915 and 14 955 cm$^{-1}$. Vertical dashed lines indicate the vibrational levels corresponding to the $a\,^3\Sigma^+$ potential of Pashov et al [16].

as well as in the $3\,^3\Sigma^+$ state. The hyperfine structure of the $a\,^3\Sigma^+$ state [16] is expected to result mainly from the magnetic dipole–dipole interaction between the nuclear spins and the unpaired electrons in $\sigma$ orbitals.

Figure 4 shows an expanded KRb$^+$ spectrum for a specific vibrational progression ($v' = 8$) between the $a\,^3\Sigma^+$ state and the $3\,^3\Sigma^+$ state in the energy range between 14 915 and 14 955 cm$^{-1}$. The vertical dashed lines represent observed positions of the $a\,^3\Sigma^+$ vibrational levels from Pashov et al [16]. Our observed $a\,^3\Sigma^+$ vibrational levels match well with those of [16]. The $v'' = 20$ and 21 levels have strong intensities while the levels below $v'' = 20$ are not observed.

FCFs for the $3\,^3\Sigma^+ \leftarrow a\,^3\Sigma^+$ transition (shown in figure 5) are calculated using the $a\,^3\Sigma^+$ state potential of Pashov et al [16] and the $3\,^3\Sigma^+$ state of Rousseau et al [18]. The calculated minimum of the FCFs between specific $v'$ levels of the $3\,^3\Sigma^+$ state and $v'' = 21$ of the $a\,^3\Sigma^+$ state is at $v'' = 10$ of the $3\,^3\Sigma^+$ state. The observed relative intensities from the KRb$^+$ spectrum in figure 2 are compared with these calculated FCFs in figure 5. The observed intensities agree well with calculated FCFs except for $v' = 11$. It is not easy to access lower levels ($v' = 0–3$) of the $3\,^3\Sigma^+$ state from $v'' = 21$ of the $a\,^3\Sigma^+$ state as already discussed.

Considering our measurements and FCF calculations between the $3\,^3\Sigma^+$ state and the ground state of KRb$^+$ (shown in figure 6), a plausible $3\,^3\Sigma^+$ vibrational level for access to $v'' = 0$ of the ground state of the ion is $v' = 4$. Thus, a promising route for observing high-lying triplet Rydberg states is a $3\,^3\Sigma^+ (v'' = 21) \rightarrow 3\,^3\Sigma^+ (v' = 4) \rightarrow$ Rydberg states. The probe laser frequency to access high-$n$ Rydberg states is 13 312(100) cm$^{-1}$ using our estimated IP. These states can be detected by pulsed field ionization or autoionization. For sufficiently high $v$, high Rydberg states can autoionize to the ground state ($v'' = 0, N^+ = 0$) of the KRb$^+$ ion.
Figure 5. Intensity comparison between theoretical FCFs and experimental relative intensities for the $3 \Sigma^+(v') \leftarrow a \Sigma^+(v''=21)$ transitions. The patterned and solid bars represent calculated FCFs and experimental relative intensities from the spectrum shown in figure 2, respectively.

Figure 6. Theoretical FCFs for formation of KRb$^+$ $X^2 \Sigma^+(v^+=0)$ by ionization of vibrational levels $v'$ of the $3 \Sigma^+$ state of KRb.

3.2. The $2 \Pi$ state

The $2 \Pi$ state has eight quasibound vibrational levels according to the eigenvalues calculated using the theoretical potential curve [18], which ignores spin–orbit splittings (see table 2). However, the tunneling lifetimes of the lower levels are extremely long ($8.6 \times 10^{29}$ s for $v'=0$), while the tunneling lifetime of the highest vibrational level is quite short ($4.4 \times 10^{-12}$ s for $v'=7$). Thus, the predissociation of only the highest two quasibound levels is predicted to be competitive with radiative decay.
are 33.6, 22.3 and 14 respectively. These relatively small differences for \( \omega_1 \Omega \) are due to the difference between theoretically obtained spin–orbit interaction parameters and those experimentally obtained ones, which will be discussed. However, we have not detected the

| \( \nu' \) | \( T_{\nu'} (\text{cm}^{-1}) \) | Tunneling lifetimes (s) |
|---|---|---|
| 0 | 13 230.9 | \( 8.5 \times 10^{-29} \) |
| 1 | 13 268.3 | \( 4.8 \times 10^{-29} \) |
| 2 | 13 303.9 | \( 8.0 \times 10^{-12} \) |
| 3 | 13 337.6 | \( 1.8 \times 10^{6} \) |
| 4 | 13 369.3 | \( 3.0 \times 10^{6} \) |
| 5 | 13 398.3 | \( 3.6 \times 10^{-5} \) |
| 6 | 13 423.9 | \( 3.0 \times 10^{-9} \) |
| 7 | 13 443.7 | \( 4.4 \times 10^{-12} \) |

Considering the spin–orbit interaction, one finds that this state has four different potentials with \( \Omega = \Lambda + \Sigma \), where \( \Sigma = 1, 0, -1 \) and \( \Lambda = 1 \). Note the \( \Omega = 0^+ \) and \( 0^- \) states are distinct but very nearly degenerate. The \( 2^3 \Pi_0^- \) state at long range (5(0+) in Hund’s case (c)) has a shallow outer well with four quasibound vibrational levels.

The uncertainties in the best KRb theoretical potential calculations [18] are usually less than 100 cm\(^{-1}\). Thus, we have examined the previous experimental absorption data [20] to determine where we expect to observe the rovibrational levels of the \( 2^3 \Pi_\Omega=0,1,2 \) states. Three distinct triplet satellite bands [20] assigned as \( 2^3 \Pi_\Omega \leftarrow 2^3 \Sigma^+ \) absorption were observed at 700 °C. This triplet structure clearly indicates the importance of spin–orbit coupling. Such satellite bands are due to the local extrema of the potential differences between the \( a^3 \Sigma^+ \) state and the \( 2^3 \Pi_\Omega=0,1,2 \) states. In [20], three distinct peaks were measured that match with the theoretical local extrema of the potential differences within 16 cm\(^{-1}\). We have also checked this by using the experimental potential of the \( a^3 \Sigma^+ \) state from [16] and the theoretical potentials of the \( 2^3 \Pi_\Omega \) states from [18]. From this, the local extrema of the potential differences at 6.2 Å correspond to 13 639.7, 13 682.0 and 13 720.7 cm\(^{-1}\) for the \( \Omega = 0^\pm \), 1 and 2 components, respectively. The measured satellite peaks for \( \Omega = 0^\pm \), 1 and 2 measured by Skenderovic \textit{et al} in [20] are 13 610.3, 13 659.3 and 13 697.3 cm\(^{-1}\), respectively. Thus, the differences between theory and experiment for \( \Omega = 0^\pm \), 1 and 2 are 29.4, 22.7 and 23.4 cm\(^{-1}\), respectively. We have used these potentials with the spin–orbit interaction included to refine our eigenvalue calculations for the various \( \Omega \) components of the \( 2^3 \Pi \) state, as given in table 3. The theoretical and experimental values of \( \Delta G_{\nu'+1/2} \) are in good agreement. The differences between experimental and theoretical \( T_{\nu'=0} \) values for the \( 2^3 \Pi_0^- \sim 5(0^+) \) state inner well, the \( 2^3 \Pi_1 \sim 6(1) \) state, and the \( 2^3 \Pi_2 \sim 2(2) \) state in table 3 are 33.6, 22.3 and 14.6 cm\(^{-1}\), respectively. These relatively small differences for \( \Omega = 1 \) and 2 compared with that for \( \Omega = 0 \) are due to the difference between theoretically obtained spin–orbit interaction parameters and experimentally obtained ones, which will be discussed.

For the \( \Omega = 0^- \) state, there is a long-range local minimum at 13 221.3 cm\(^{-1}\) near 9.4 Å. This is observed as a satellite band with a measured peak [20] at 13 236.1 cm\(^{-1}\). This minimum is due to the double-minimum nature of the potential of the \( 2^3 \Pi_\Omega=0^- \sim 5(0^+) \) state. Three levels in the outer well have been detected as discussed below. However, we have not detected the

**Table 2.** The predicted term values (with respect to the K(4s) + Rb(5s) asymptote) calculated from the potential of [18] for the \( 2^3 \Pi \) state (ignoring spin–orbit splittings). Tunneling lifetimes calculated from the potential of [18] are also shown.

| \( \nu' \) | \( T_{\nu'} (\text{cm}^{-1}) \) | Tunneling lifetimes (s) |
|---|---|---|
| 0 | 13 230.9 | \( 8.5 \times 10^{-29} \) |
| 1 | 13 268.3 | \( 4.8 \times 10^{-29} \) |
| 2 | 13 303.9 | \( 8.0 \times 10^{-12} \) |
| 3 | 13 337.6 | \( 1.8 \times 10^{6} \) |
| 4 | 13 369.3 | \( 3.0 \times 10^{6} \) |
| 5 | 13 398.3 | \( 3.6 \times 10^{-5} \) |
| 6 | 13 423.9 | \( 3.0 \times 10^{-9} \) |
| 7 | 13 443.7 | \( 4.4 \times 10^{-12} \) |
Table 3. Theoretically predicted term values (cm$^{-1}$) for the $2 \text{ } ^3 \Pi_0^e \sim 5(0^+)$: inner and outer well, $2 \text{ } ^3 \Pi_0^e \sim 4(0^-)$, $2 \text{ } ^3 \Pi_1 \sim 6(1)$ and $2 \text{ } ^3 \Pi_2 \sim 2(2)$ states of KRb, using the theoretical potential energy curves (including spin–orbit) of [18]. Also given are the predicted spacings $\Delta G_{v' + 1/2}$ (cm$^{-1}$) and the term values and spacings experimentally observed based on assignments shown in figure 8. The $2 \text{ } ^3 \Pi_0^e$ states are not resolved experimentally.

| $\nu'$ | Theoretically | Experimentally | $\Delta G_{v' + 1/2}$ |
|--------|---------------|----------------|----------------------|
|        | Theoretically | Experimentally |                      |
| $2 \text{ } ^3 \Pi_0^e \sim 5(0^+)$: inner well | | |
| 0      | 13 205.3/13 203.3 | 13 171.6 | 36.6/36.3 | 37.5 |
| 1      | 13 241.9/13 240.0 | 13 209.1 | 34.9/35.0 | 34.0 |
| 2      | 13 276.8/13 275.0 | 13 243.1 | 33.0/32.9 | 32.5 |
| 3      | 13 309.8/13 307.9 | 13 275.6 | 30.8/30.7 | 30.0 |
| 4      | 13 340.6/13 338.6 | 13 305.5 | 27.5/27.8 | (28.7) |
| 5      | 13 368.1/13 366.4 | (13 334.2)$^a$ | 23.8/23.6 | – |
| 6      | 13 391.9/13 390.0 | – | –/– | – |
| $2 \text{ } ^3 \Pi_0^e \sim 5(0^-)$: outer well | | |
| 0      | 13 187.2 | 13 149.3 | 13.4 | 14.0 |
| 1      | 13 200.6 | 13 163.3 | 11.8 | 11.7 |
| 2      | 13 212.4 | 13 175.0 | 10.0 | – |
| 3      | 13 222.4 | – | – | – |
| $2 \text{ } ^3 \Pi_1 \sim 6(1)$ | | |
| 0      | 13 231.5 | 13 209.1 | 37.4 | 37.2 |
| 1      | 13 268.9 | 13 246.3 | 35.6 | 34.8 |
| 2      | 13 304.5 | 13 281.1 | 33.8 | 33.0 |
| 3      | 13 338.3 | 13 314.1 | 31.6 | 31.6 |
| 4      | 13 369.9 | 13 345.7 | 29.1 | 28.4 |
| 5      | 13 399.0 | 13 374.1 | 25.6 | (24.8) |
| 6      | 13 424.6 | (13 399.0)$^b$ | 20.2 | – |
| 7      | 13 444.8 | – | – | – |
| $2 \text{ } ^3 \Pi_2 \sim 2(2)$ | | |
| 0      | 13 257.7 | 13 243.1 | 38.2 | 38.0 |
| 1      | 13 295.9 | 13 281.1 | 36.3 | 35.4 |
| 2      | 13 332.2 | 13 316.5 | 34.5 | (33.8) |
| 3      | 13 366.7 | (13 350.3)$^c$ | 32.5 | (31.7) |
| 4      | 13 399.2 | 13 382.0 | 30.0 | (29.4) |
| 5      | 13 429.2 | (13 411.5)$^c$ | 27.1 | (25.8) |
| 6      | 13 456.3 | 13 437.3 | 22.8 | – |
| 7      | 13 479.1 | – | – | – |

$a$ The line corresponding to $\nu' = 5$ (inner well) is weak and its position is less certain.

$b$ According to figure 9, $\nu' = 0 - 5$ are observed, while $\nu = 6$ is weak and its position is less certain.

$c$ According to figure 9, $\nu' = 3$ and 5 are weak and their positions are less certain.
\( \nu' = 3 \) level, which according to [20] rapidly predissociates. Possibly this state can be measured with rotational resolution in a future ion depletion PA experiment [11]. According to our FCF calculations, the largest FCF is between \( \nu' = 3 \) of this long-range outer well of the \( 2 \;^3\Pi_0^- \) state and \( \nu'' = 20 \) of the \( a \;^3\Sigma^+ \) state. Thus, the population of the \( \nu'' = 20 \) level of the \( a \;^3\Sigma^+ \) state could be detected by RE2PI via the \( \nu' = 3 \) outer well level. However, predissociation due to tunneling and potential curve crossings with other \( \Omega \) states, as shown in figure 7, may significantly broaden the RE2PI spectrum.

Guided by these estimates, we have observed the \( 2 \;^3\Pi_0^- \) state with vibrational resolution. Because the \( 2 \;^3\Pi_0^- \leftarrow a \;^3\Sigma^+ \) laser alone cannot two-photon ionize the molecule, a second photon from a delayed doubled Nd:YAG laser is used for ionization from the resonant intermediate state.

From scanned and calibrated spectra the signals were sorted out and the vibrational progressions for the \( a \;^3\Sigma^+ \) state were checked. One (weak) example of an \( a \;^3\Sigma^+ \) state progression is shown in figure 8. In this figure, the dotted vertical lines show the positions of the levels of the \( a \;^3\Sigma^+ \) state. The vibrational progressions of the \( 2 \;^3\Pi_0^- \) state were assigned as shown in figure 9, with assignments of the \( \nu' = 0-6 \) levels of the \( 2 \;^3\Pi_0^- \sim 5(0^+) \), \( 2 \;^3\Pi_0^- \sim 4(0^-) \), \( 2 \;^3\Pi_1 \sim 6(1) \) and \( 2 \;^3\Pi_2 \sim 2(2) \) states. Here, solid vertical lines are observed lines and dotted vertical lines are predicted lines from \( \nu'' = 20 \) for each vibrational quantum number \( \nu' \) of the \( 2 \;^3\Pi_0^- \) state. Some of the strong signals are from \( \nu'' = 21 \).
Table 4. Fitted $T_e$ and $\omega_e$ comparisons (in cm$^{-1}$). The origin of energy for these $T_e$ values is the $\text{K}(4s) + \text{Rb}(5s)$ limit.

| State | Reference | $5(0^+)/4(0^-)$ | 6(1) | 2(2) | Outer well: $5(0^+)$ |
|-------|-----------|------------------|------|------|----------------------|
| $T_e$ | This work | 13 152           | 13 191 | 13 224 | 13 143               |
|       | [18]      | 13 187/13 185   | 13 213 | 13 239 | 13 180               |
|       | [30]      | 13 014           | 13 043 | 13 065 |                       |
|       | [31]      | 12 447           | 12 510 | 12 555 |                       |
| $\omega_e$ | This work | 39.4             | 37.7  | 39.0  | 12.8                 |
|        | [18]      | 37.2/36.6        | 37.4  | 38.7  | 15.2                 |
|        | [30]      | 38/39            | 40     | 40     |                       |

Figure 8. The $a^3\Sigma^+ (v''')$ state progression for one of the weak signals ($v' = 4$) of the $2\,^3\Pi_2$ state.

The linewidths of the features in the spectrum often approach 1 cm$^{-1}$ due to power broadening and unresolved rotational and hyperfine structure. However, many of the intense features show a doublet structure with an approximate 4.23 cm$^{-1}$ spacing, the difference between the $v'' = 20$ and 21 levels of the $a^3\Sigma^+$ state [16]. Both of these levels are populated by the initial PA.

The observed term energies are fitted to obtain $T_e$ and $\omega_e$, as shown in table 4 for each $\Omega$ component. The fitted molecular constants match well with other results. The poorer match in $\Omega = 0$ may be due to the unresolved $\Omega = 0^\pm$ components and the broad linewidth. For example, the assigned $v' = 2$ level has a linewidth of 1.2 cm$^{-1}$.

Our assigned term values (table 4) are typically $\sim30$ cm$^{-1}$ below the theoretically predicted values for $\Omega = 0$, while the $\Delta G_{v'1/2}$ values are in good agreement. Other components ($\Omega = 1$ and 2) have somewhat smaller differences and again the $\Delta G_{v'1/2}$ values agree well. We checked the separations ($\Delta(E_{\Omega=2} - E_{\Omega=1})$ and $\Delta(E_{\Omega=1} - E_{\Omega=0})$) between $\Omega$ components for each...
Figure 9. Observed spectra in the predicted region of the $2^3\Pi_\Omega \leftarrow a^3\Sigma^+$ bands, with tentative assignments to the vibrational levels of the $2^3\Pi_\Omega$ component states. The strong lines at 13 155.3 and 13 495.1 cm$^{-1}$ are a two-photon transition Rb(5s) $\rightarrow$ Rb(7s) and a one-photon transition Rb(5p$_{3/2}$) $\rightarrow$ Rb(7s), respectively. $\bigcirc$, vibrational levels of the $\Omega = 0^\pm$ states starting from $v' = 0$; $\bigbox$, vibrational levels of the $\Omega = 1$ state starting from $v' = 0$; $\bigtriangleup$, vibrational levels of the $\Omega = 2$ state starting from $v' = 0$. The outer well region assignments are not shown here, but rather in figure 13.

vibrational quantum number. The separations $\Delta(E_{\Omega=1} - E_{\Omega=0})$ are nearly 3 cm$^{-1}$ larger than the separations $\Delta(E_{\Omega=2} - E_{\Omega=1})$. If there is spin–orbit mixing between electronic states, the splittings between the $\Omega$ components are unequal. In this energy region, there is the possibility of the $1^1\Pi$ state interacting with the $2^3\Pi_\Omega$ states.

The total energy separation between $T_{v' = 0}$ of the $2^3\Pi_2 \sim 2(2)$ state and $T_{v' = 0}$ of the $2^3\Pi_0 \sim 5(0^+)$ state (inner well) is 71.5 cm$^{-1}$, which is larger than the atomic K spin–orbit interaction separation of 57.7 cm$^{-1}$. The roughly linear increase of the spin–orbit interaction with vibrational quantum number is shown in figure 10. The total spin–orbit separation lies in between the spin–orbit separation of the potassium atom (57.7 cm$^{-1}$) and the rubidium atom (237.6 cm$^{-1}$). According to Park et al [30] the $2^3\Pi_\Omega$ state has a mixed configuration {0.13$s\sigma$(K), 0.87$p\tau$(K), 0.87$s\sigma$(Rb), 0.13$p\tau$(Rb)} near $R_e$, so that it has more K(4p) + Rb(5s) character than K(4s) + Rb(5p) character. Thus, the molecular spin–orbit separation should be larger than the spin–orbit separation of the potassium atom. This spin–orbit measurement...
Figure 10. Separations \(\Delta (E_{\Omega=2} - E_{\Omega=1})\) and \(\Delta (E_{\Omega=1} - E_{\Omega=0})\) between the \(\Omega\) components for each vibrational quantum number. The separation \(\Delta (E_{\Omega=2} - E_{\Omega=1})\) is smaller by nearly 3 cm\(^{-1}\) than the separation \(\Delta (E_{\Omega=1} - E_{\Omega=0})\).

provides information on the variation of the spin–orbit function for comparison with KRb \textit{ab initio} calculations. According to the calculation of Rousseau \textit{et al} \cite{18}, near the maximum of the potential barrier the spin–orbit separation between the 2 \(^3\Pi_2 \sim 5(0^+\rangle\) state and the 2 \(^3\Pi_2 \sim 2(2)\) state is larger than 87 cm\(^{-1}\), which also implies mixing of the K(4p) and Rb(5p) atomic configurations. Compared to the value of 71.5 cm\(^{-1}\) at \(R_e\), this suggests the barrier region has more K(4s) + Rb(5p) character and less K(4p) + Rb(5s) character. The \(v' = 7\) levels of the 2 \(^3\Pi_1 \sim 6(1)\) and 2 \(^3\Pi_2 \sim 2(2)\) states (as well as the \(v' = 6\) levels of the 2 \(^3\Pi_{0+} \sim 5(0^+)/(4(0^-)\) states) are not observed, presumably because of rapid tunneling predissociation.

It is worth noting that the experimental barrier maxima are also about 25 cm\(^{-1}\) below the calculated maxima. According to the \textit{ab initio} calculations the outer well near 9.3 Å has four quasi-bound levels. The lowest level of the inner well is above the \(v' = 1\) vibrational level of the outer well. The outer well vibrational energies and wavefunctions are shown in figure 11. This figure shows that inner well wavefunctions for each vibrational quantum number do not tunnel rapidly through the barrier between the inner well and the outer well except for the highest vibrational quantum number near the barrier maximum. The highest vibrational levels for the inner and the outer well can be rapidly predissociated by tunneling. We realized that the rather weak noisy signals in the marked region shown in figure 9 are also from a \(^3\Sigma^+\) state progressions, so this region was expanded and investigated in detail. The FCF calculation shows that there are plausibly strong FCFs between the \(^3\Sigma^+\) state and the \(5(0^\circ)\) outer well although there is a small transition probability between them near 9.3 Å according to \cite{18}. Without considering a transition dipole moment function, the calculated FCFs between the \(^3\Sigma^+\) state and the \(5(0^\circ)\) outer well state are shown in figure 12. For \(v' = 0\) (without any node) strong FCFs occur at \(v''_\alpha = 16\) and 17. For \(v' = 1\) or 2 the FCF distribution is broader. Also, the \(v' = 3\) level has rapid tunneling predissociation, so that it has not been observed even though it has strong FCFs compared with other lower \(v'\) levels. However, the observed strength of the outer well
Figure 11. The energy positions and the wavefunctions for the outer well of the $5(0^+)$ state. The $2\,3\Pi_0^- \sim 5(0^+)$ theoretical potential curve plus the vibrational wavefunctions for $v_{\text{in}}'=0$ and 6 and $v_{\text{out}}'=0$ and 3 are shown. Inner well wavefunctions for each vibrational quantum number do not interact with the outer well wavefunctions due to broad barrier width between inner well and outer well.

Figure 12. FCF distribution between the outer well $v'=0$ level of the $5(0^+)$ state and the $a\,3\Sigma^+$ state $v''$ level. FCFs between $v'' = 20$ and 21 and the outer well $v'=0$ are quite small.

transitions is much weaker than inner well transitions. This may be due to a smaller transition dipole moment in the region of the outer well. This is because the inner well of the $5(0^+)$ state has more triplet character than the outer well according to the transition dipole moment [20] between the $5(0^+)$ state and the lowest triplet state.
Figure 13. Outer well spectrum of the 5(0') state. The solid vertical lines indicate observed levels and dotted vertical lines are expected positions for the a 3Σ⁺ progression for each vibrational level of the 5(0') state. In this energy region, eight vibrational levels are expected: \( v' = 0, 1, 2 \) and 3 for the outer well of the 5(0') state and \( v' = 0 \) and 1 for the inner well of the 5(0') and the 4(0⁻) states. This results in a complicated spectrum.

According to FCF calculations between the a 3Σ⁺ state and the upper levels formed in PA, strong decays from the upper PA level to \( v''_a = 20 \) and 21 of the a 3Σ⁺ state are expected. Thus, the ionization of the \( v'' = 20 \) and 21 levels of the a 3Σ⁺ state may be expected to be strong through the intermediate 2 3Π states. However, the FCFs between the a 3Σ⁺ state and the 5(0⁻) state in the outer well are small so that stronger intensities for the \( v'' = 15, 16 \) and 17 levels are expected, as shown in figure 12. For \( v' = 1, 2 \) and 3, a broader FCF distribution is expected according to FCF calculations.

There are three vibrational levels for the outer well and four for the inner well (5(0⁺) and 4(0⁻)) with vibrational progressions of the a state in a range of \( \sim 80 \text{ cm}^{-1} \) in figure 13, so that complicated spectra can be expected. The matches between the observed and the theoretical \( \Delta G_{v'+1/2} \) values are good. This observed outer well, which can be used as a long-range intermediate state, reveals the weakly bound potential well centered at \( \sim 9.3 \text{ Å} \).

We also note that the 2 3Π states have a possible alternative application as the upper state in a Raman transfer scheme to produce ultracold molecules in low-\( v'' \) levels of the a 3Σ⁺ state. The FCFs for bound–bound emission from higher vibrational levels of the 2 3Π states to a 3Σ⁺ (\( v'' = 0 \)) are large (>1% for \( v' \geq 3 \), 35% for \( v' = 6 \) and 38% for \( v' = 7 \)). Thus, the expectation is that 2 3Π (\( v' = 6 \)) levels should allow preparation of ultracold KRb molecules in the a 3Σ⁺ (\( v'' = 0, J'' = 0 \)) state. Returning to two-step Rydberg excitation schemes, use of the 2 3Π \( v' = 0 \) levels will simplify the assignments of Rydberg levels because only one or two vibrational bands will be expected. The \( v' = 0 \) levels of the 2 3Π states can be reached from the \( v'' = 20 \) or 21 levels of the a 3Σ⁺ state because of the large FCFs. Also, the FCF between the \( v' = 0 \) levels of the 2 3Π states and the \( v'' = 0 \) vibrational level of the ion ground state is very large, 0.6. Thus, a promising route to triplet Rydberg states is a 3Σ⁺ (\( v'' = 20 \)) \( \rightarrow \) 2 3Π (\( v' = 0 \)) \( \rightarrow \) Rydberg state. For ionization through the \( v' = 0 \) levels of the 2 3Π states, probe laser frequencies of 14 739 (\( \Omega = 2 \)), 14 773 (\( \Omega = 1 \)), and 14 810 (\( \Omega = 0 \)) (±100 cm⁻¹) are needed, using our estimated IP.

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3.3. The $4^3 \Sigma^+$ state

The potential curve of this state has a broad minimum so that it is quite convenient for accessing the ground state of the ion. In previous experiments [14, 15], $v' = 0$–16 vibrational levels of the $4^3 \Sigma^+$ state were observed from the $v'' = 20$ and 21 levels of the $a^3 \Sigma^+$ state (see figure 2 of [15]). (Note, however, that the preliminary assignments of levels as given in [14, 15] were incorrect. It is now certain that these two levels are actually $v'' = 20$ and 21 [16].) The observed vibrational levels and spacings of the $4^3 \Sigma^+$ state agree well with those predicted based on the eigenvalue calculations using the theoretical $4^3 \Sigma^+$ potential of [18], as discussed in [15] (see figure 3 in [15] and the supplementary material for [15], which compares the theoretical and experimental term values).

Unfortunately in our experimental scans of this region, the ion signal is saturated so that it is difficult to compare the transition strengths with calculated $4^3 \Sigma^+ \leftarrow a^3 \Sigma^+$ FCFs. However, if we look at FCFs between the $v'$ levels of the $4^3 \Sigma^+$ state (of KRb) and the $v'' = 0$ level of the $X^2 \Sigma^+$ state of KRb$^+$ in figure 14, the $v' = 3$ level has the largest FCF. Thus, the optimal route for Rydberg excitations via the $4^3 \Sigma^+$ state appears to be a $3^3 \Sigma^+ (v'' = 20) \rightarrow 4^3 \Sigma^+ (v' = 3) \rightarrow$ Rydberg state. For ionization through the $v' = 3$ level of the $4^3 \Sigma^+$ state, probe laser frequencies above 11 875 (100) cm$^{-1}$ are needed, using our estimated IP.

4. Conclusions

We have observed the $3^3 \Sigma^+$ and the $2^3 \Pi_\Omega$ states of $^{39}$K$^{85}$Rb from ultracold a $^3 \Sigma^+$ state molecules in high $v''$ levels formed by photoassociation, complementing our earlier observations of the $4^3 \Sigma^+$ state [14]. The spin–orbit interaction and an intermediate long-range state with a shallow potential well for the $2^3 \Pi_\Omega$ state have been investigated.

State-selective detection methods for exploring triplet Rydberg states with low rotational quantum numbers from the metastable a $^3 \Sigma^+$ state of ultracold KRb molecules are proposed. There are three promising intermediate triplet states that will allow access, with high resolution,
**Table 5.** Promising intermediate levels for KRb$^+$ ($v^+, N^+ = 0$) formation from the a $^3\Sigma^+$ ($v'' = 20, J'' = 1$) state. Note that the energies listed are the rotationally unresolved vibrational levels, not the ($v', J' = 1$) levels. The origin of energy for these $T_v$ values is the K(4s) + Rb(5s) limit.

| Intermediate levels         | $T_v$ (cm$^{-1}$) |
|-----------------------------|------------------|
| $2\,^3\Pi_0$ ($v' = 20, J' = 1$): inner well | 13 171.6          |
| $2\,^3\Pi_0$ ($v' = 0, J' = 1$): outer well    | 13 149.3          |
| $2\,^3\Pi_1$ ($v' = 0, J' = 1$)                  | 13 209.1          |
| $2\,^3\Pi_2$ ($v' = 0, J' = 1$)                  | 13 243.1          |
| $3\,^3\Sigma^+$ ($v' = 4, J' = 0$)               | 14 670.2          |
| $4\,^3\Sigma^+$ ($v' = 3, J' = 0$)               | 16 031.6          |

to the high-lying triplet Rydberg states, enabling a precise determination of the IP of KRb. We also hope to observe autoionizing resonances leading to the formation of low-lying rovibrational levels (ideally $v^+ = 0, N^+ = 0$) of the ground $X^2\Sigma^+$ state of the ultracold KRb$^+$ ion. Promising routes for producing KRb$^+$ ($v^+ = 0, N^+ = 0$) from the ($v'' = 20, J'' = 1$) level of the a $^3\Sigma^+$ state are summarized in table 5. The low rotational levels ($J'$) and low vibrational levels ($v'$) of the $2\,^3\Pi_{1\Omega}, 3\,^3\Sigma^+$ and $4\,^3\Sigma^+$ intermediate states we observed should be optimal for observation of triplet Rydberg states converging to KRb$^+$ ($v^+ = 0$).

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