500 nm System of RbCs: Assignments and Intensity Anomalies

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We have investigated the RbCs 500 nm system by mass-resolved resonance enhanced two-photon ionization in a cold molecular beam. The $4^3\Pi_0 \rightarrow 10-39$, $4^3\Pi_1 \rightarrow 14-28$, and $6^1\Sigma^+ \rightarrow 12-28 \sim X^1\Sigma^+ \rightarrow 0$ transitions have been observed and assigned for the first time. The $4^3\Pi_0 \rightarrow X^1\Sigma^+ \rightarrow 0$ transitions abnormally show double maxima of the vibronic-band intensity distribution around $\nu = 22$ and 38. The intensities of the transitions to the lower vibrational levels ($4^3\Pi_0 \rightarrow 10-32$) are explained well by the direct transitions from the $X^1\Sigma^+ \rightarrow 0$ level following the Franck-Condon principle. The transitions to the higher vibrational levels ($4^3\Pi_0 \rightarrow \nu \geq 33$) borrow intensities through the interaction with nearby $6^1\Sigma^+$ perturber levels.

1. Introduction

The ultracold molecules that have extremely low internal energies can be ideal samples for fundamental physics and chemistry.1-7 Cold polar molecules attract particular interest because of their long-range anisotropic interactions8 and prospect for a novel physical realization of a quantum computer.8 DeMille proposed ultracold RbCs, produced by photoassociation of laser-cooled Rb and Cs atoms and the subsequent population transfer,9 as one of the promising candidates for the quantum qubit generator.9 As indicated by Ni et al., a suitable level in the excited electronic states should be employed for the stimulated Raman passage (STIRAP) to the ground $X^1\Sigma^+$ level following the Franck-Condon principle. The electronic term values and equilibrium internuclear distances ($Y.L.$); bongsoo@kaist.ac.kr (B.K.). Fax: +82-62-970-3359 (Y.L.); +82-42-350-2810 (B.K.).

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In this work, we have investigated the complicated vibronic structures of RbCs near 500 nm by mass-resolved RE2PI spectroscopy in a cold molecular beam. The $4^3\Pi_0 \rightarrow 10-39$, $4^3\Pi_1 \rightarrow 14-28$, and $6^1\Sigma^+ \rightarrow 12-28 \sim X^1\Sigma^+ \rightarrow 0$ transitions are newly identified. While the intensity distributions of the $4^3\Pi_0 \rightarrow \nu \leq 32 \sim X^1\Sigma^+ \rightarrow 0$ transitions are explained well by the Franck-Condon (FC) principle, the transitions to the higher levels ($4^3\Pi_0 \rightarrow \nu \geq 33$) show abnormally strong intensities. This is found to originate from the perturbation with the nearby bright $6^1\Sigma^+$ levels.

2. Experiment

Details of our experimental apparatus and techniques have been discussed previously.22 Briefly, RbCs was produced by expanding Rb and Cs vapor with Kr or Ar gas through a high-temperature pulsed nozzle with a 800 μm diameter orifice. The alkali metal sample was heated to 350 °C. The pulsed jet was collimated by a 1.2 mm diameter skimmer. Two photons from a Nd:YAG pumped dye laser excited and ionized RbCs. The resulting ions of two isotopomers (68Rb13Cs and 83Rb13Cs) were separately and simultaneously detected by a linear time-of-flight (TOF) mass spectrometer (m/Δm ≈ 500). Vibronic and rotational structures were revealed by 0.12 and 0.02 cm−1 laser resolutions (Δνlaser, respectively). Wavelength calibration of the dye laser was conducted using a wavemeter, Ne optogalvanic spectra, and I2 LIF spectra23 obtained simultaneously.

3. Results and Discussion

3.1. Assignments. Figure 1 shows the nonrelativistic ab initio potential energy curves (PECs) of the $5^1\Sigma^+$, $6^1\Sigma^+$, $4^1\Pi$, $5^1\Sigma^+$, and $4^1\Pi$ states.18 The vertical dotted line represents the FC region excited from the $X^1\Sigma^+ \rightarrow 0$ level. Between 20000 and 21000 cm−1, the inner walls of the $6^1\Sigma^+$ and $4^1\Pi$ PECs are located in the FC region. According to the selection rule of electric dipole transitions in Hund’s case (c) ($\Delta\Omega = 0, \pm 1$), two parallel ($\Delta\Omega = 0, 6^1\Sigma^+$) and $4^1\Pi \rightarrow X^1\Sigma^+$ transitions and one perpendicular ($\Delta\Omega = \pm 1, 4^1\Pi \rightarrow X^1\Sigma^+$) transition are predicted to be observed in this energy region.24

Figure 2 shows the low-resolution RE2PI spectra of $85\text{RbCs}$ and $87\text{RbCs}$ isotopomers around 20000 cm−1 obtained by
coexpanding Kr carrier gas at 760 Torr. In the energy region below 20410 cm⁻¹ (region I), four vibrational progressions, denoted as α, β, γ, and δ in Figure 2, are identified. Above 20410 cm⁻¹ (region II), the spectra show very complex and rich vibronic structures. Here, we focus on the vibronic structures and intensity distributions in region I. The vibronic-band intensity distribution of the β progression shows double maxima around 19950 and 20375 cm⁻¹. This is very abnormal because the Franck–Condon distribution of vibronic-band intensities from the X 1Σ⁺ state ν′ = 0 level can never have more than one maximum aside from very unusual R-dependence of the transition moment function or strong perturbation effects. Despite the intensity anomalies and significant red shifts of the vibronic bands, the vibrational spacing of the β progression shows a smooth connection at around 20225 cm⁻¹. The plot of the vibrational spacing of the β progression can be found in the Supporting Information. The vibronic-band intensity anomalies in the β progression will be discussed in section 3.2.

The upper electronic states of α, β, γ, and δ progressions are assigned as follows. The α progression is easily assigned to the 5 1Σ⁺ ν′ = 29–35 → X 1Σ⁺ ν′′ = 0 transitions by comparing the observed vibronic-band positions with those reported by Yoon et al.11 Candidates for the upper electronic states of the β, γ, and δ progressions are the 6 1Σ⁺, 4 3Π₁, and 4 3Π₁ states, as predicted by theoretical calculations.18–20 The β and γ bands progress parallel to each other with an almost constant spacing between the nearby bands. This indicates that their upper electronic states are the Ω = 0 (A = 1, Σ = −1) and 1 (A = 1, Σ = 0) substates of the 4 3Π₁ state. In this case, the shapes of both PECs in Hund’s case (c) would be very similar and split by the magnitude of the 4 3Π₁ diagonal spin–orbit (SO) interaction constant.21 The upper-state Ω (Ω′) values of the β and γ bands are assigned below by their rotational structures. Then, the upper electronic state of the δ progression is assigned logically to the 6 1Σ⁺ state.

Absolute vibrational-quantum numbers can be determined from the isotope shifts, ΔTᵣ = Tᵣ(⁸⁷RbCs) − Tᵣ(⁸⁵RbCs).12,25 The vibrational term values, Tᵣ, of isotopomers were fitted simultaneously by the following mass-reduced relation:

\[ Tᵣ = Tₑ + ωₑρ(ν′ + 1/2) - ωₓχₓ[ρ(ν′ + 1/2)]^2 \]  (1)

The term values Tₑ, ωₑ, and ωₓχₓ are the electronic term value, harmonic vibrational frequency, and anharmonic vibrational constant, respectively. The constant ρ (1 for ⁸⁷RbCs and 0.992963624 for ⁸⁵RbCs)26 is (μ/μiso)½, where μ and μiso are the reduced masses of ⁸⁷RbCs and ⁸⁵RbCs, respectively. The vibronic bands in the ranges of ν′ = 10–32, 14–28, and 12–23 were fitted for β, γ, and δ progressions, respectively. The fitted ΔTᵣ values were calculated from the fitted parameters using the following equation:

\[ ΔTᵣ = ωₑ(ν′ + 1/2) - ωₓχₓ[ν′ + 1/2] - [ωₑρ(ν′ + 1/2) - ωₓχₓρ²(ν′ + 1/2)] \]  (2)

Figure 3 compares the observed isotope shifts of the β, γ, and δ bands and the calculated values. For the calculations, ν′s of the lowest-lying β, γ, and δ bands were assumed to be 9, 10, and 11 (for β), 13, 14, and 15 (for γ), and 11, 12, and 13 (for δ). The assigned ν′s of the lowest-lying β, γ, and δ bands are designated for each progression in Figure 2. On this basis, we assign minimum ν′ = 10, 14, and 12 to the β, γ, and δ bands, respectively.

The Ω′ values of β and γ bands are revealed by their rotational structures. Parallel and perpendicular electric dipole transitions can be distinguished by rotational branches of an observed vibronic band.24 Parallel bands (ΔΛ = 0 in Hund’s case (a) or ΔΩ = 0 in Hund’s case (c)) consist of P (ΔJ = −1) and R (ΔJ = +1) branches of similar intensity. Perpendicular bands (ΔΛ = ±1 in Hund’s case (a) or ΔΩ = ±1 in Hund’s case (c)) have a strong Q (ΔJ = 0) branch of approximately twice the intensity of the P and R branches. Figure 4 compares the rotationally resolved spectra of the β (ν′ = 17 → ν′′ = 0), γ (ν′ = 21 → ν′′ = 0), and δ (ν′ = 23 → ν′′ = 0) bands with the simulations assuming Ω′ = 0 and 1. The experimental spectra were analyzed by line position fits using the following equation:

\[ ν = ν₀ + Bᵥ(J′ + 1) - Dᵥ[J′(J′ + 1)]² - \{BᵥJ''(J'' + 1) - Dᵥ[J''(J'' + 1)]²\} \]  (3)

ν, ν₀, Bᵥ, Dᵥ, J', J'' and J'' are the observed rotational line position, band origin, upper- and lower-state rotational constants, upper- and lower-state centrifugal distortion constants, and upper- and lower-state rotational quantum numbers, respectively. Bᵥ (=0.016592237 cm⁻¹) and Dᵥ (=7.3075 × 10⁻⁵ cm⁻¹) were fixed at the values reported by Fellows et al.27 In our experiment, the rovibronic transitions are limited to low J' levels less than 26. Thus, the Dᵥ values could not be determined accurately and were not included in the final fit. The observed rotational line positions, their assignments of J' and J'' numbers, and the fitted band origins and Bᵥ values can be found in the Supporting Information. As shown in Figure 4, the β (ν′ = 17 → ν′′ = 0) bands show both P and R branches (Ω′ = 0) and the γ (ν′ = 21 → ν′′ = 0) band is closer to the simulation with Ω′ = 1 than that with Ω′ = 0. Consequently, the upper electronic states of β and γ progressions are assigned to the 4 3Π₁ and 4 3Π₁ states, respectively. For the δ (ν′ = 23 → ν′′ = 0) band, the simulation indicates that the Ω′ value is 0, confirming the assignment of the upper electronic state to the 6 1Σ⁺ state.

In Table 1, the experimentally determined and theoretically predicted molecular constants18,20 are listed. Comparing the experimental and theoretical Tₑ and ωₑ values, the upper
Figure 2. Low-resolution RE2PI spectra of (top) $^8$RbCs and (bottom) $^6$RbCs between 19525 and 20550 cm$^{-1}$ obtained by expanding Kr carrier gas at 760 Torr. $\alpha$, $\beta$, $\gamma$, and $\delta$ progressions and their vibrational quantum numbers are indicated.

electronic states of the $\beta$, $\gamma$, and $\delta$ bands are assigned to $4\,^3\Pi_0$, $4\,^1\Pi_1$, and $6\,^1\Sigma^+$, respectively. This is consistent with the assignment from the rotational structures. The lists of $T_V$ values of the $\beta$, $\gamma$, and $\delta$ bands are given in the Supporting Information.

The diagonal matrix element of the SO coupling operator observed as the splitting of fine-structure levels is expressed as $\langle \Lambda, \Sigma, \Omega, v|H_{SO}|\Lambda', \Sigma', v \rangle = A_{\Lambda,\Sigma} \Lambda \Sigma$. For the $^3\Pi$ state, this indicates that the vibrational levels of the different $\Omega (=0, 1, \text{and } 2)$ substates are equally separated by the SO coupling constant, $A_{\Sigma}$. From this analysis, the $4\,^3\Pi$ state is found to be split by 70 cm$^{-1}$ ($T_x = 19262$ cm$^{-1}$ for $4\,^3\Pi_0$ and $T_x = 19332$ cm$^{-1}$ for $4\,^3\Pi_1$). This becomes an estimation of the SO coupling constant of the $4\,^3\Pi$ state.

3.2. Intensity Anomalies. Figure 5 shows (a) the observed vibronic-band intensity distributions of the $\beta$ and $\delta$ progressions and (b) the FC factors of the $4\,^3\Pi_0$ $v_{\Pi} \leftarrow X\,^3\Sigma^+ \nu_X = 0$ ($|v_{\Pi}|v_{\Sigma}^0)$ and $6\,^1\Sigma^+ \nu_{\Sigma} \leftarrow X\,^1\Sigma^+ \nu_X = 0$ ($|v_{\Sigma}|v_{\Sigma}^0)$ transitions. The FC factors were calculated by the LEVEL 7.7 program$^{28}$ using the empirical PEC of the $4\,^3\Pi_0$ state and the modified PEC of the $6\,^1\Sigma^+$ state from the ab initio PEC.$^{18}$

The empirical PEC of the $4\,^3\Pi_0$ state was constructed by the Rydberg–Klein–Rees (RKR) method$^{29}$ using the experimentally determined vibrational and rotational constants. The rotational constants were determined by analyses of rotationally resolved spectra of the $\beta$ ($v' = 16-25 \leftarrow v'' = 0$) bands. See the Supporting Information for the plot of the determined $B_V$ values of the $\beta$ bands as a function of $v'$. For the $6\,^1\Sigma^+$ state, the energy of the $ab\,\text{initio}$ PEC was scaled by a factor of 0.9365 with respect to $T_x$ and then $T_x$ was set to the experimental value. As mentioned above, the observed vibronic-band intensity distribution of the $\beta$ progression shows double maxima around $v' = 22$ and 38. The intensity distribution of the lower-lying $\beta$ bands ($v' \leq 32$) is explained well by the FC principle (compare the observed and calculated values in Figures 5a and 6b, respectively). However, the dramatic increase in the intensities of the higher-lying $\beta$ bands ($v' \geq 33$) cannot be rationalized by the direct vertical transitions from the $X\,^1\Sigma^+ \nu_X = 0$ level. In this energy region, we can define the $6\,^1\Sigma^+$ state as the “bright” state and the $4\,^3\Pi_0$ state as the “dark” state. The former can be directly excited from the $X\,^1\Sigma^+ \nu_X = 0$ level. On the other hand, direct transitions to the vibrational levels of the latter from the $X\,^1\Sigma^+ \nu_X = 0$ level are almost impossible due to very small FC factors. No bright states other than the $6\,^1\Sigma^+$ state are predicted by $ab\,\text{initio}$ calculations in the FC region around 20400 cm$^{-1}$. When a dark state interacts with a bright state, the borrowed transition moment can be estimated as follows:$^{24}$

$$
\langle \text{Dark}, v_{\text{Dark}}|\mu|X\,^1\Sigma^+, \nu_X = 0 \rangle = \sum_{v_{\text{Bright}}} \langle \text{Bright}|\mu|X\,^1\Sigma^+, \nu_X = v_{\text{Bright}} \rangle \langle v_{\text{Bright}}|v_X = 0 \rangle \langle v_{\text{Bright}}|a_{SO}|\text{Bright} \rangle \frac{\langle v_{\text{Dark}}|v_{\text{Bright}} \rangle}{E(v_{\text{Dark}}) - E(v_{\text{Bright}})}
$$

The first two terms in the above equation are the electric dipole transition moment and the FC factor between bright and ground states. The third term is the interaction matrix element between dark and bright states. In this case, we assume that the interaction is SO coupling, $H_{SO}$, between the $4\,^3\Pi_0$ and $6\,^1\Sigma^+$ states. The
last term is the vibrational overlap between dark and bright states divided by their energy level difference. The intensity borrowing mechanism of the dark state is, thus, described by the last two terms.

The $^4\Sigma^+$ vibrational overlap, $\langle v_\parallel | v_\parallel \rangle$, values were calculated by the LEVEL 7.7 program$^{28}$ using the same PECs employed for the calculation of FC factors shown in Figure 5b. From this calculation, we can gain an insight into the intensity borrowing mechanisms of the dark $^4\Pi_0$ levels. Figure 6 shows the maps of (a) $\langle v_\parallel | v_\parallel \rangle$ and (b) $| v_\parallel | v_\parallel \rangle/\Delta E\ell$ and the bar graphs of (c) $\langle v_\parallel | v_\parallel \rangle = 37|v_\parallel \rangle$ and (d) $| v_\parallel | v_\parallel \rangle/\Delta E\ell$. $\Delta E$ is the energy difference between the $v_\parallel$ and $v_\perp$ levels, $E(v_\parallel) - E(v_\perp)$. The two-dimensional maps of $\langle v_\perp | v_\perp \rangle$ and $| v_\perp | v_\perp \rangle/\Delta E\ell$ are plotted for the $v_\perp$ levels between 20000 and 20700 cm$^{-1}$ and the $v_\parallel$ levels between 20200 and 21000 cm$^{-1}$. In Figure 6a and b, white and red dotted lines indicate the regions of $\Delta E \approx 200$ and 0 cm$^{-1}$, respectively. The energy at the top of the barrier between the inner and outer wells of the $^6\Sigma^+$ double-minimum PEC is also indicated by the arrows in Figure 6a and b. The map shown in Figure 6a indicates that the remote $v_\perp$ levels ($\Delta E \approx 200$ cm$^{-1}$) provide the dark $v_\perp$ levels with particularly large $\langle v_\parallel | v_\parallel \rangle$ values. However, when $\Delta E$ is taken into account, the nearby $v_\perp$ levels ($\Delta E \approx 0$ cm$^{-1}$) are found to be more important to the intensity borrowing of the dark $v_\parallel$ levels. This energy-level proximity effect on the intensity borrowing of the $^4\Pi_0$ dark levels is shown for the $v_\parallel = 37$ level in Figure 6c and d. The horizontal dotted lines in Figure 6c and d indicate the energy of the $v_\perp = 37$ level at 20385 cm$^{-1}$. Due to the energy-level proximity effect, the contribution of the nearby $v_\perp$ perturbers to the borrowed transition moment of the $v_\parallel = 37$ level becomes $\sim 20$ times.

**Figure 3.** Observed isotope shifts of (a) $\beta$, (b) $\gamma$, and (c) $\delta$ progressions between $^{85}\text{RbCs}$ and $^{87}\text{RbCs}$ and the expected values assuming $\nu'$ of the lowest-lying $\beta$, $\gamma$, and $\delta$ bands to be 9, 10, and 11 (for $\beta$), 13, 14, and 15 (for $\gamma$), and 11, 12, and 13 (for $\delta$).

**Figure 4.** High-resolution RE2PI spectra of the (a) $\beta (\nu' = 17 \rightarrow \nu'' = 0)$, (b) $\gamma (\nu' = 21 \rightarrow \nu'' = 0)$, and (c) $\delta (\nu' = 23 \rightarrow \nu'' = 0)$ bands, and their simulations as parallel ($\Omega' = 0 \rightarrow \Omega'' = 0$) and perpendicular ($\Omega' = 1 \rightarrow \Omega'' = 0$) bands. For the simulations, rotational temperatures were set to 2.3, 2.4, and 2.6 K for the $\beta$, $\gamma$, and $\delta$ bands, respectively, and the stick spectra were convoluted by a Voigt profile ($\Delta v_{\text{Gauss}} = 0.02$ cm$^{-1}$ and $\Delta v_{\text{Lorentz}} = 0.01$ cm$^{-1}$). Between the simulations assuming $\Omega'' = 0$ and 1, the better fit is shown in red.

**TABLE 1: Experimental and Theoretical Molecular Constants**

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<th>$T_e$ (cm$^{-1}$)</th>
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<td>$\gamma$ [4 $^4\Pi_1$]</td>
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<td>29.497(37)</td>
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<tr>
<td>$\delta$ [6 $^6\Sigma^+$]</td>
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<td>37.92(11)</td>
<td>0.1971(31)</td>
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<td>6 $^6\Sigma^+$</td>
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$^a$ Reference 18. $^b$ Reference 20.
larger than that of the remote v_2 perturbers. Figure 7 shows the vibrational wave functions of the v_1 = 37 level at 20385 cm⁻¹ and the two v_2 levels at 20381 (nearby) and 20589 (remote) cm⁻¹. Between the v_1 and nearby v_2 levels, the ⟨v_1|v_2⟩ value (0.042) is mostly contributed by the 4 1Π_0–6 1Σ⁺ PEC crossing region. At the stationary phase point, the momenta are matched and the overlap integral accumulates. In other regions, ⟨v_1|v_2⟩ is canceled out by the out-of-phase oscillations of the wave functions. Between the v_1 and remote v_2 level, the ⟨v_1|v_2⟩ value (0.088) is larger than that between the nearby v_1 and v_2 levels. As shown in Figure 6a (see the region indicated by the white dotted line), the v_1 levels have the largest ⟨v_1|v_2⟩ with the remote v_2 levels. This is due to the in-phase oscillations of both vibrational wave functions. However, this large ⟨v_1|v_2⟩ is not effective because of large energy differences.

Consequently, we have found that the abnormally strong intensities of the β (ν'' = 33–39 ← ν' = 0) bands observed in the RE2PI spectra (see Figure 2) originate from the perturbations between the 4 1Π_0 and 6 1Σ⁺ states, and the nearby 6 1Σ⁺ perturber levels dominantly contribute to the intensity borrowing through the energy-level proximity effect. Figure 8 shows the differences between the fitted and observed T_v values for the β progression, T_v^fit − T_v^obs. The 4 1Π_0 ν'' = 33–39 levels are significantly red-shifted. This also indicates the existence of the nearby blue-side perturbers. Therefore, the whole vibronic-band intensity distribution of the 4 1Π_0 ν'' = 10–39 ← X 1Σ⁺ ν'' = 0 transitions comes from two different intensity borrowing mechanisms: (i) from the 6 1Σ⁺ remote perturber (ΔE ~ 200 cm⁻¹) to the lower-lying 4 1Π_0 ν'' levels and (ii) from the 6 1Σ⁺ nearby perturber (ΔE ~ 0 cm⁻¹) to the higher-lying ones. When multiple perturbers make comparable contributions to intensity borrowing of a dark state, the interference effects on the borrowed transition moments should be considered. Rotas et al. reported the representative example of the multiple-perturber contributions on the nominally spin-forbidden transitions. Here, it is worth considering whether the two different intensity
borrowing mechanisms of the $4 \Pi_0 \nu' \leftarrow X \Sigma^+ \nu'' = 0$ transitions can interfere or not. As shown in Figure 2, the two vibronic-band intensity distributions of $4 \Pi_0 \nu' \leftarrow X \Sigma^+ \nu'' = 0$ around $\nu' = 22$ and 38 are almost completely separated. This indicates the two different mechanisms dominate the $4 \Pi_0 \nu' \leftarrow X \Sigma^+ \nu'' = 0$ transitions in the different energy regions (divided at 20225 cm$^{-1}$). Under these circumstances, they can hardly interfere with each other.

The $4 \Pi_0$ dark levels above the barrier energy of the $6 \Sigma^+$ PEC can borrow the transition moments from the nearby $6 \Sigma^+$ levels (see Figure 6b). As shown in Figure 2, the vibronic structures in region II become very dense and complicated. The dense vibronic structure is probably due to abrupt expansion of the $6 \Sigma^+$ potential well above the barrier energy. The transitions to the higher $4 \Pi_0$ dark levels, however, may also contribute to the complicated vibronic spectra above 20410 cm$^{-1}$.

4. Conclusion

We have assigned the $4 \Pi_0 \nu' = 10 - 39$, $4 \Pi_0 \nu' = 14 - 28$, and $6 \Sigma^+ \nu' = 12 - 28 \leftarrow X \Sigma^+ \nu'' = 0$ transitions of RbCs near 500 nm for the first time. For the $4 \Pi_0 \nu' = 10 - 39 \leftarrow X \Sigma^+ \nu'' = 0$ transitions, abnormal double maxima of the vibronic-band intensity distribution were observed. The FC principle explains the intensity distribution of the $4 \Pi_0 \nu' = 10 - 32 \leftarrow X \Sigma^+ \nu'' = 0$ transitions well. However, the vibrational levels around the higher-lying maximum ($4 \Pi_0 \nu' = 33 - 39$) cannot be directly excited from the $X \Sigma^+ \nu'' = 0$ level because of negligible FC factors. We suggest the intensity borrowing mechanism of the transitions to the dark $4 \Pi_0$ levels. The nearby bright $6 \Sigma^+$ levels have been found to shed light on the $4 \Pi_0$ levels.

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Supporting Information Available: Data of the RbCs 500 nm system by RE2PI spectroscopy: (i) a plot of the vibrational spacing, $\Delta G_\nu$, of $\beta$ bands as a function of $\nu'$; (ii) observed rotational line positions, their assignments of $J'$ and $J''$ numbers, and the fitted band origins and $B_\nu$ values of the $\beta$ ($\nu' = 17 \leftarrow \nu'' = 0$), $\gamma$ ($\nu' = 21 \leftarrow \nu'' = 0$), and $\delta$ ($\nu' = 23 \leftarrow \nu'' = 0$) bands; (iii) lists of $T_\nu$ values of $\beta$, $\gamma$, and $\delta$ progressions; and (iv) a plot of $B_\nu$ values of $\beta$ bands as a function of $\nu'$. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes