

Excited electronic states and predissociation dynamics of Rb₂ 430 nm system

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In the Rb₂ 430 nm system, there are three bound states, 3 ¹Σ_u⁺, 3 ³Π_u, and 3 ¹Π_u in the Franck-Condon region from the X ¹Σ_g⁺ v = 0 level and several continuum states (2 ¹Π_u, 2 ³Π_u, 3 ³Σ_u⁺, and 1 ³Δ_u states) corresponding to the 4 ²D_{5/2,3/2} + 5 ²S_{1/2} limits can contribute to the predissociation dynamics.⁽¹⁾ Tsi-Zé and San-Tsiang observed band spectra near 430 nm and reported *T_e* and *ω_e* values of the 3 ¹Π_u state in 1937.⁽²⁾ Since their work, several studies on the predissociation of the 3 ¹Π_u state have been reported.⁽³⁻⁵⁾ The bound excited states overlapping the 3 ¹Π_u state, however, have not yet been identified and the combined interpretation of the previous works⁽³⁻⁵⁾ on the predissociation suggests that there is a subtler dynamics due to long-range potential interaction.

We have investigated the Rb₂ 430 nm system by resonance enhanced two-photon ionization (RE2PI) and photofragment yield (PFY) spectroscopy.⁽⁶⁾ Four electronically excited states have been assigned and their two-channel (*fast* and *slow*) predissociation has been observed.

We prepared Rb₂ by expanding Rb vapor with Ar gas (stagnation pressure, 760 Torr) through a modified fuel injection valve. The temperature of the nozzle was maintained at 330°C in this experiment. The nozzle diameter was 800 μm. The pulsed jet was collimated by a 1.2 mm diameter skimmer located 7 cm from the nozzle. Rb₂⁺ ions were regenerated by the absorption of two photons from a dye laser (Lambda Physik Scanmate 2E) pumped by the third harmonic of a Nd:YAG laser (Spectra Physics GCR-150). Photofragmented Rb atoms were ionized simultaneously with the excited Rb₂ by the dye laser. The ions were detected by a time-of-flight (TOF) mass spectrometer. Since Rb has two naturally occurring isotopes, Rb₂ has three different isotopomers (⁸⁵Rb₂, 52.1%; ⁸⁵Rb⁸⁷Rb, 40.2%; ⁸⁷Rb₂, 7.8%), which are well separated by our TOF mass spectrometer (m/Δm = 500). The linewidth of the dye laser is 0.12 cm⁻¹. The wavelength of the dye laser was calibrated by the Burleigh WA-4500 wavemeter and Ne optogalvanic spectrum

We have obtained mass-resolved RE2PI spectra of three isotopomers of Rb₂ (⁸⁵Rb₂, ⁸⁵Rb⁸⁷Rb, and ⁸⁷Rb₂) and ⁸⁵Rb PFY spectrum. From the vibrational progressions observed in our RE2PI spectrum, *T_e*, *ω_e*, and *ω_eX_e* have been determined and their electronic states have been identified. In our ⁸⁵Rb PFY spectrum, the sharp energy threshold of the *fast* predissociation channel is located between the isotopically shifted 3 ¹Π_u v = 14 levels of ⁸⁵Rb₂ and ⁸⁵Rb⁸⁷Rb. This indicates that the predissociating perturber corresponds to the 4 ²D_{5/2} + 5 ²S_{1/2} atomic fine-structure limit located between the 3 ¹Π_u v = 14 levels of ⁸⁵Rb₂ and ⁸⁵Rb⁸⁷Rb. Between the possible candidate continuum states, 1 ³Δ_u and 3 ³Σ_u⁺, corresponding to the 4 ²D_{5/2} + 5 ²S_{1/2} limit, we assign the 1 ³Δ_u state to the predissociating perturber from the calculations of the relative bound (3 ¹Π_u) continuum (1 ³Δ_u or 3 ³Σ_u⁺) predissociation rates. In the case of 3 ¹Π_u 1 ³Δ_u, the observed sharp threshold energy and the trend of PFY agree well

with the calculation. Also, the effect of long-range potential crossing among the continuum states corresponding to the different atomic fine-structure limits has been observed in our PFY spectrum. This suggests that the fast predissociation channel branches out into two finer product channels above the higher-lying $4\ ^2D_{3/2} + 5\ ^2S_{1/2}$ limit.

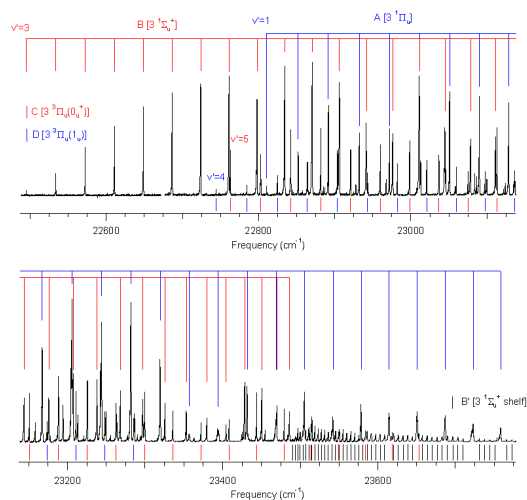


Figure 1. RE2PI spectrum of $^{85}\text{Rb}_2$.

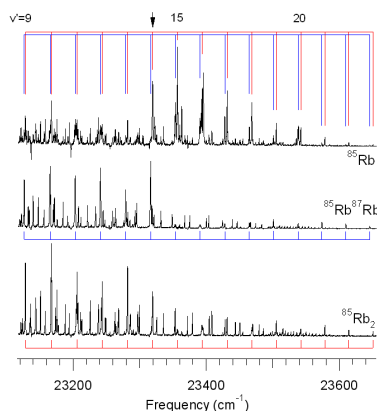


Figure 2. RE2PI spectra of $^{85}\text{Rb}_2$ and $^{85}\text{Rb}^{87}\text{Rb}$ and ^{85}Rb PFY spectrum.

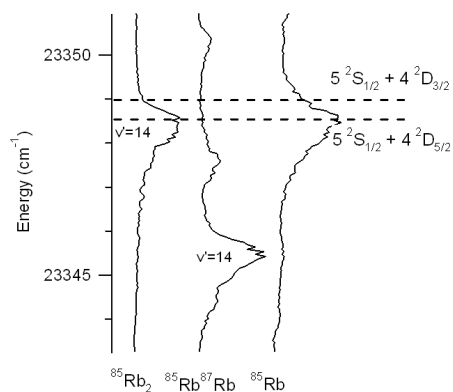


Figure 3. Expanded spectrum of Fig. 2 around the $5s + 4d$ atomic limit.

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