



Electronic transitions of Rb_2 above $25\,000\text{ cm}^{-1}$

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ABSTRACT

Rubidium dimers were formed by thermal vaporization of the metal followed by continuous co-expansion with argon through a small pinhole into a vacuum chamber. The dimers were detected by laser-induced fluorescence. Vibrationally resolved excitation spectra were recorded for two new band systems in the wavelength regions around 394 nm and 353 nm. The well known $D-X$ system near 430 nm was also observed. All three band systems exhibited long vibrational progressions, indicative of substantial changes in the equilibrium bond lengths on electronic excitation. Isotope splittings between the bands of $^{85}\text{Rb}_2$ and $^{85}\text{Rb}^{87}\text{Rb}$ were resolved for the band system centered at 353 nm. Vibrational analyses were carried out, and the upper state vibrational constants are reported. Possible assignments of the electronic configurations for the newly observed states are considered.

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1. Introduction

Spectroscopic and dynamic studies of the rubidium dimer (Rb_2) have been pursued for several decades [1–15]. In recent years, rubidium has been used in laser cooling and trapping experiments, where cold rubidium molecules have been formed from ultra-cold atoms using Feshbach resonances [16–18], or by photoassociation [19–22]. In addition to being molecules of fundamental interest, Rb_2 and the other alkali metal dimers may also be used as the active species in optically pumped laser systems [23,24].

The potential energy curve and molecular constants for the ground state Rb_2 ($X^1\Sigma_g^+$) have been obtained very precisely with a dissociation $D_e = 3993.5082\text{ cm}^{-1}$ [3,25]. Several electronic band systems of Rb_2 have been analyzed, resulting in detailed characterizations of at least 13 low-lying electronically excited states [1–15]. The highest energy states were found in a complex series of bands that are centered near 430 nm. This system, originally discovered by Tsi-Zé and San-Tsiang [15], was assigned to the $(2)^1\Pi_u-X^1\Sigma_g^+$ and $(3)^1\Pi_u-X^1\Sigma_g^+$ transitions (labeled $D-X$ in earlier literature). The 420–445 nm spectral range was revisited by Lee et al. [2] who used laser excitation and jet cooling techniques to obtain more highly resolved spectra. Bands of the $(3)^1\Sigma_u^+-X^1\Sigma_g^+$ and $(3)^3\Pi_u-X^1\Sigma_g^+$ transitions were observed for the first time.

As the alkali atoms have just a single valence electron, the alkali dimers are useful benchmarks for testing the quality of electronic structure calculations for excited states. Several computational studies of Rb_2 have been reported [26–28]. In the context of the present work, the extensive calculations reported by Spiegelmann et al. [26] and Park et al. [27] are of particular relevance.

Spiegelmann et al. [26] predicted potential energy curves for the 56 lowest states of Rb_2 up to the $\text{Rb}(5s) + \text{Rb}(7s)$ dissociation asymptote. Their calculations used a relativistic core pseudopotential (36 electrons), configuration interaction and a perturbative treatment of the core–valence interactions. The calculated transition energies were mostly within $\sim 400\text{ cm}^{-1}$ of the measured values. Subsequently, Park et al. [27] calculated potentials for 58 states from the same set of configurations. They used a large scale configuration interaction method in combination with a small core relativistic pseudopotential (28 electrons). This approach reduced the discrepancies between the measured and calculated transition energies to $\sim 100\text{ cm}^{-1}$.

The energy ranges explored in the previous experimental studies accessed states that could be associated with $\text{Rb}(5s) + \text{Rb}(6p)$ as the highest energy dissociation asymptote. In the present work we have recorded spectra for Rb_2 that reveal higher energy band systems, centered near 394 and 353 nm. Vibronic analyses of these bands have been carried out, and spectroscopic constants for the excited states are presented. Tentative assignments for the excited states are proposed based on comparisons with theoretical predictions and consideration of the possible asymptotic dissociation limits.

2. Experimental

The Rb_2 dimer was generated in a free jet expansion and characterized by means of laser induced fluorescence (LIF) spectroscopy. The main vacuum chamber consisted of a 6-way stainless steel cross, evacuated by a Roots blower (nominal pumping speed 50 cfm). The chamber pressure was monitored by a capacitance manometer (Baratron MKS, 0–10 Torr range). Rb atoms were generated by thermal vaporization of the metal in a small heated

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sample chamber. The metal vapor was entrained in a continuous Ar (or Ar/He mixture) carrier flow and expanded through a pinhole into the main chamber. The sample chamber was constructed from a commercial stainless steel in-line filter (Swagelok) which had $\frac{1}{4}$ " Swagelok type of connectors on both ends and a center diameter of about 0.7". One end of the chamber was sealed with a $\frac{1}{4}$ " stainless cap. A hole of about 0.2 mm diameter was made in the center of the cap by laser ablation using a focused Nd:YAG laser. The cap and stainless steel chamber body were encapsulated in two copper heating blocks that had outer diameters of 1" to make the heating more efficient and uniform. The cap and chamber were heated by two separate nozzle heaters (mineral insulated, 1"-ID and 1"-width, 150 W). Power for the heaters was provided by two variable autotransformers. The temperatures of the two heaters were monitored using K-type thermocouples. The heater temperatures were kept around 600 K, with the nozzle held 30–50 K higher to reduce the occurrence of pinhole clogging. The input end of the sample chamber was connected to the gas supply by $\frac{1}{4}$ " stainless tubing. The mount for the heated nozzle assembly permitted two-dimensional adjustment (distance and height relative to the center of the main chamber) while the system was under vacuum.

A dye laser (Lambda Physik, FL 3002) pumped by an XeCl excimer laser (Coherent COMPexPro 201) was used for the laser excitation of Rb₂. The laser dyes used to cover the spectral range of interest were DMQ, BiBuQ, PBBO, and Stilbene3. The linewidth of the laser was approximately 0.4 cm⁻¹. The laser beam was propagated along an axis that was perpendicular to the direction of the gas flow from the nozzle. Typically a distance of 5–10 mm between the nozzle orifice and the axis of the laser beam yielded good laser induced fluorescence signals from Rb₂.

Laser induced fluorescence from Rb₂ was collected along an axis that was perpendicular to both the expansion and the laser beam. An imaging lens was used to focus the fluorescence through the entrance slit of a 0.25 m monochromator. A long-pass optical filter (50% transmission point at 400 nm), placed before the monochromator, was used to reduce the interference from scattered laser light. A photomultiplier tube (PMT, EMI 9558 QB) was used for the LIF detection. The PMT output signal was preamplified (SRS model 240A) and recorded by a digital oscilloscope (Lecroy Wavesurfer 24Xs). The signal was averaged by the oscilloscope, and the entire system was controlled by a lab computer.

Since rubidium reacts violently with moisture, the sample required careful handling. The metal was supplied in sealed glass ampoules (Sigma Aldrich Corp, 99.6% purity). Transfer of the metal to the sample chamber was carried out in a glove box in an atmosphere of dry nitrogen. The carrier gases were ultra-high purity grade, and nozzle source pressures in the range of 1–4 atmospheres were found to be optimal.

3. Results

Figs. 1 and 2 show the LIF spectra of the new band systems of Rb₂. In the following we refer to these transitions as systems I and II. These traces were recorded using Ar as the carrier gas, with a source pressure of 3–4 atm. The two strong lines on the low energy side of Fig. 2 are the Rb 7p ²P_{1/2}–5s and 7p ²P_{3/2}–5s transitions, which provide useful calibration markers.

The intensities of the new band systems were markedly dependent on the concentration of the Rb vapor in the heated source chamber. This provided one indication that the bands were associated with Rb₂. Further support for this assignment was provided by the observation of the Rb₂ (3)¹Π_u – X¹Σ_g⁺ system under the same experimental conditions that optimized the intensities of the new bands.

The vapor pressure of Rb is strongly dependent on temperature, and the production of Rb₂ increased dramatically as the tempera-

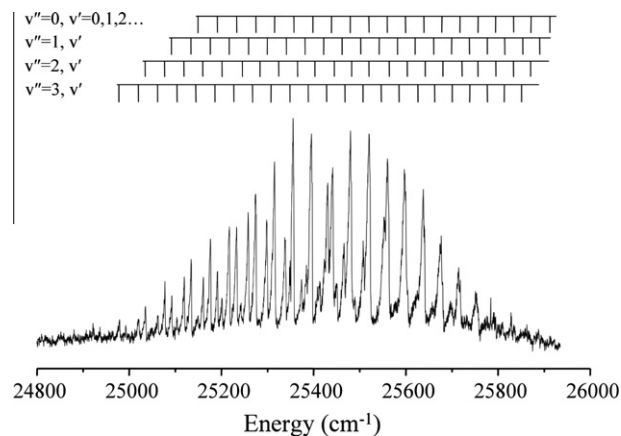


Fig. 1. Laser induced fluorescence spectrum of Rb₂, band system I.

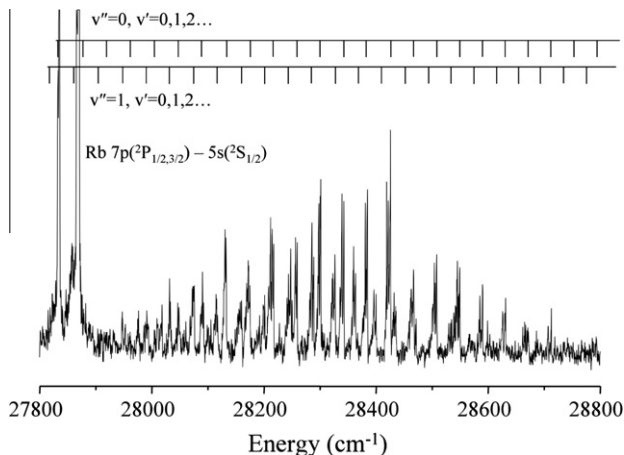


Fig. 2. Laser induced fluorescence spectrum of Rb₂, band system II.

ture of the source chamber was increased. However, the rate of sample consumption imposed a practical upper bound on the temperature that could be used. The data reported here were recorded with a source temperature near 600 K, which corresponds to a Rb vapor pressure of approximately 5 Torr.

For LIF detection the monochromator slits were set to a width of 2 mm, corresponding to a band-pass filter with a width of 10 nm. Excitation spectra for the new band systems were recorded with the monochromator diffraction grating set to the zeroth order position. In this configuration the monochromator acted as a spatial filter. Long-pass filters (LP 400 and LP 630) were then used to block scattered laser light. The (3)¹Π_u – X¹Σ_g⁺ bands of Rb₂ were recorded using a LP 445 filter.

The dye laser power was monitored for correction of the spectral intensities. For the (3)¹Π_u – X¹Σ_g⁺ bands and band system II, Rb atomic lines were observed in the same spectral range, and these were used to establish the wavelength calibration. For band system I the nearest atomic lines (6p–5s, 23715.19 and 23792.69 cm⁻¹) were not quite as close to the new spectral features, but the calibration required only a short extrapolation.

A dispersed fluorescence spectrum was recorded over the range 400–850 nm using excitation of the system II band at 28467.1 cm⁻¹. This trace exhibited the Rb 6p → 5s and 5p → 5s atomic lines, but did not show features that could be assigned to emission from Rb₂.

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