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The $(3)^1\Pi-(3)^1\Sigma^+$ system of KRb

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Abstract

Infrared fluorescence of the KRb molecule in the spectral range 6500–8000 cm^{-1} , arising when the levels of the $(3)^1\Pi$ state are excited by the 457.9, 465.8, 472.7, and 476.5 nm lines of an argon-ion laser, has been recorded by Fourier transform spectrometry. A part of the fluorescence is assigned to the system $(3)^1\Pi \rightarrow (3)^1\Sigma^+$. The $(3)^1\Sigma^+$ state energy levels up to $v = 15$ have been determined. The main spectroscopic constants for this state are $T_e = 13995.465(10) \text{ cm}^{-1}$, $\omega_e = 40.76310(40) \text{ cm}^{-1}$, $\omega_e x_e = -0.26988(71) \times 10^{-1} \text{ cm}^{-1}$, $B_e = 22.8215(28) \times 10^{-3} \text{ cm}^{-1}$, $R_e = 4.17125 \text{ Å}$. The unusual spacing of the vibrational levels reflects the ionic character of the state. Preliminary values for the strongly perturbed $(3)^1\Pi$ state are $T_e = 21762.0$, $\omega_e = 41.36$, $\omega_e x_e = 0.184$, $B_e = 28.82 \times 10^{-3} \text{ cm}^{-1}$. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The KRb molecule spectroscopy is of particular interest for two main reasons:

1. The dissociation channels $\text{K}(4s) + \text{Rb}(5s)$ and $\text{K}(4p) + \text{Rb}(5p)$ of the first excited atomic states are in close proximity since the energies of the four asymptotes are, in increasing order of magnitude: 12578.96 cm^{-1} ($\text{Rb } 5p^2P_{1/2}$), 12816.56 cm^{-1} ($\text{Rb } 5p^2P_{3/2}$), 12985.17 cm^{-1} ($\text{K } 4p^2P_{1/2}$) and 13042.89 cm^{-1} ($\text{K } 4p^2P_{3/2}$). Hence, the coupling between the electronic states calculated with these limits is expected to be large. This fact was confirmed by calculations of Bussery and Aubert-Frécon [1], of Patil and Tang [2] and, quite recently by Marinescu and Sadeghpour [3]. These calculations give dispersion force coefficients much larger for KRb than for any of the nine other heteronuclear alkali diatomic molecules;
2. By examining the excited long-range Hund’s case (*c*) molecular states of the 10 such molecules which support bound states and can be probed by ultracold photoassociative spectroscopy, Wang and Stwalley [4] found that the KRb system has very favourable Franck–Condon factors for the photoassociation process. Also, the collisions of unlike alkali-metal atoms can be driven by much shorter-range Van der Waals forces.

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Only a few spectroscopic studies on the electronic states of KRb have been so far reported. Long ago Walter and Baratt [5] observed a molecular band at 495.9 nm while diffuse bands at 597, 586.7 and 569 nm were reported by Beuc et al. [6]. The first high-resolution study of the ground state was reported by Ross et al. [7]. In this study, the $A^1\Sigma^+ \rightarrow X^1\Sigma^+$ system was excited using a Ti:Sapphire laser. Subsequent fluorescence spectra were recorded with a Bomem Fourier transform spectrometer using a resolution of 0.045 cm^{-1} . Rotational and vibrational constants were reported, covering the ranges $v = 0\text{--}44$ and $J = 28\text{--}141$.

Doppler-free optical-optical double-resonance polarization spectroscopy of the $B^1\Pi$ state was performed at high resolution by Okada et al. [8]. Accurate molecular constants were derived for this B state, up to $v = 12$, and the RKR potential energy curve was calculated. Numerous local perturbations were discovered in these spectra and the perturbing electronic states were characterized. Radiative lifetimes and collisional cross-section of the fluorescence quenching were also determined in this work.

From a theoretical point of view, the KRb molecule was studied through four methods:

1. the generalized reduced potential curve (GRPC) method was set up by Jenc and Brandt [9,10] and by Bludsky et al. [11] who derived provisional ground-state potential curves for several guesses of the dissociation energy value;
2. approximate ground-state spectroscopic constants for heteronuclear alkali dimers were obtained by Cavalière et al. [12] using interpolation methods;
3. ab initio calculations of the electronic states correlated with the first four excited separate atomic limits were reported by Leininger and Jeung [13], focusing on the weakly coupled $(1)^1\Pi$ and $(2)^1\Pi$ 'twin states'. Improvements of these results were later published by Leininger et al. [14] and by Yiannopoulou et al. [15]. Quite recently new ab initio determinations have been reported by Rousseau [16]; and
4. long-range studies and calculation of dispersion coefficients have been reported, as mentioned above, by Bussery and Aubert-Frécon [1], Patil and Tang [2] and Marinescu and Sadeghpour [3].

In this Letter, we report on the laser-induced fluorescence (LIF) of the transition $(3)^1\Pi \rightarrow (3)^1\Sigma^+$ recorded at high-resolution Fourier transform spectroscopy. The experimental apparatus and procedures are first described. The spectroscopic analysis and the results are then presented.

2. Experimental

The KRb molecules were produced in a stainless steel heat-pipe oven by heating a 1:4 mixture of potassium and rubidium metals (99.95% K and 99.7% Rb from Aldrich Chemical) with 11 Torr of argon as a buffer gas. The temperature was kept at 570 K where the vapor pressures of Rb, Rb_2 , K and K_2 are, respectively, 0.59, 0.003, 0.13, and 0.0004 Torr [17]. Isolated $X^1\Sigma^+ \rightarrow (3)^1\Pi$ rovibrational transitions were excited by an argon-ion laser (Spectra Physics 2080-155).

The experimental arrangement was similar to the one described in a previous work [18]: backward fluorescence from the heat pipe oven was collected and focused on the entrance iris of the Fourier spectrometer. Spectra were recorded between 6000 and 8500 cm^{-1} with a resolution of 0.010 cm^{-1} corresponding to the Doppler width at 8000 cm^{-1} . From the spectra 358 lines were assigned; other lines corresponding possibly to other electronic transitions. The relative spectral positions of the lines were measured with a typical accuracy of 0.0015 cm^{-1} . These transitions frequencies were arranged into 35 series spanning the vibrational range for the lower state $v'' = 0\text{--}15$. An example of a short portion of the spectrum, obtained after excitation with the 472.7 nm Ar^+ laser radiation, is depicted in Fig. 1. Both Q -type and P , R doublets of lines are observed.

3. Analysis and results

A preliminary analysis has shown that the energy levels of the $(3)^1\Pi$ state are perturbed while those of the lower $(3)^1\Sigma^+$ state are regular. The wavenumbers of the $(3)^1\Pi \rightarrow (3)^1\Sigma^+$ system were reduced by represent-

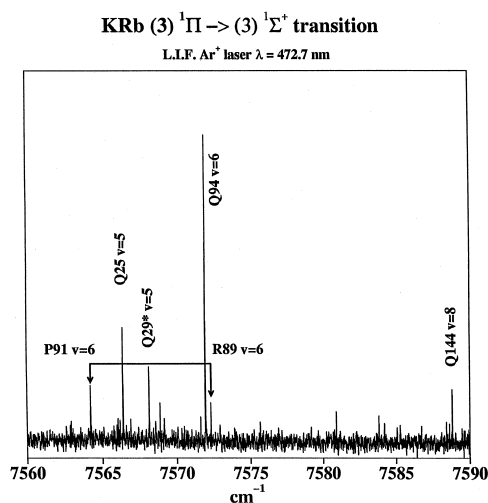


Fig. 1. The IR system (3)¹Π → (3)¹Σ⁺ of KRb excited by the 472.7 nm Ar⁺ laser line from 7560 to 7590 cm⁻¹. The line assignments J' , v'' are noted vertically for Q lines ($\Delta J = 0$) and horizontally for R -, P -type ones ($\Delta J = \pm 1$). The transition marked by an asterisk is due to the ³⁹K⁸⁷Rb isotopic species ($Q\ 29^*\ v=5$ means, for example, ³⁹K⁸⁷Rb Q -type transition with $J' = J''$ and $v'' = 5$).

ing the (3)¹Σ⁺ state term energy values by a polynomial development while those of the upper state are considered individually by their value T'_{vJ} .

The term energy values $E(v, J)$ for the (3)¹Σ state are then written as:

$$E(v, J) = \sum Y_{l,m} [\rho(v + 1/2)]^l \times [\rho^2(J(J + 1))]^m$$

where $Y_{l,m}$ are the usual Dunham coefficients, and ρ is the mass parameter. In the present work, the following atomic masses ³⁹K: 38.9637069, ⁸⁵Rb: 84.9117924; ⁸⁷Rb: 86.9091858 leads to the $\rho = 0.99637903$ referred to the principal isotopic species ³⁹K⁸⁵Rb.

Table 1

Dunham coefficients $Y_{l,m}$ for the (3)¹Σ⁺ state of ³⁹K⁸⁵Rb. The energy difference between X¹Σ⁺ ($v = -1/2$, $J = 0$) and (3)¹Σ⁺ ($v = -1/2$, $J = 0$) is equal to 13995.465(10) cm⁻¹

l m	$Y_{l,m}$	Std	%
1 0	0.40763096d+2	0.4d-3	0.0
2 0	0.2698869d-1	0.7d-4	0.3
3 0	-0.1098735d-2	0.5d-5	0.5
4 0	0.35287d-5	0.1d-6	4.6
0 1	0.228215068d-1	0.3d-5	0.0
1 1	-0.223124d-5	0.6d-7	2.6
2 1	-0.112758d-5	0.4d-8	0.4
3 1	0.124404d-7	0.1d-9	1.0
0 2	-0.2831284d-7	0.2d-9	0.7
1 2	0.154285d-9	0.4d-11	2.5
2 2	-0.43712d-11	0.2d-12	5.7
0 3	0.58387d-13	0.4d-14	6.6
1 3	-0.22692d-14	0.7d-16	3.2
2 3	0.62821d-16	0.5d-17	7.5

358 wavenumbers; rms = 0.0013 cm⁻¹; v lower than 16 and J lower than 196; std is the standard deviation associated with each parameter and % is the percentage ratio between std and $Y_{l,m}$.

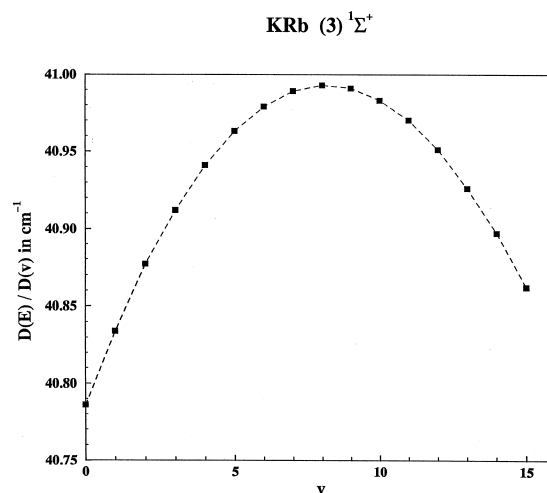


Fig. 2. The vibrational energy derivative $d(E)/d(v)$ as a function of the vibrational quantum number v .

The spectroscopic data for the two observed isotopic species were simultaneously reduced and the molecular constants $Y_{l,m}$ were obtained through a least-squares fit of these data. The standard deviation for the reduction of the 358 observations was 0.0013 cm^{-1} . The quality of this fit, including data for two isotopic species, unambiguously insures the vibrational numbering in the $(3)^1\Sigma^+$ state. The Dunham coefficients are listed in Table 1. The sign of some coefficients is unusual and this is reflected in the slope $d(E)/d(v)$ depicted in Fig. 2: the quantity first increases to a maximum at about $v = 8-9$ before decreasing with increasing v in the usual way. It is worth noticing that their anomalous shapes were previously observed in the other alkali molecules Li_2 , Na_2 , K_2 , Rb_2 and Cs_2 [19–23]. The maximum occurs at identical v values for the heavier molecules. This ion-pair interaction has long been predicted by Mulliken [24].

Table 2
The $(3)^1\Sigma^+$ state RKR potential energy curve

v	E_v (cm^{-1})	$[d(E)/d(v) - 40] \times 10^3$	R_{\min} (\AA)	R_{\max} (\AA)
–0.5	0	763	4.1713	4.1713
0	20.399	786	4.0341	4.3132
1	61.210	834	3.9369	4.4201
2	102.066	877	3.8717	4.4952
3	142.961	912	3.8198	4.5573
4	183.887	941	3.7757	4.6116
5	224.840	963	3.7370	4.6609
6	265.812	979	3.7022	4.7063
7	306.796	989	3.6705	4.7489
8	347.788	993	3.6412	4.7892
9	388.780	991	3.6140	4.8276
10	429.767	983	3.5886	4.8644
11	470.744	970	3.5646	4.8999
12	511.705	951	3.5419	4.9342
13	552.643	926	3.5203	4.9675
14	593.555	897	3.4998	4.9999
15	634.435	862	3.4803	5.0316

An RKR potential energy curve was calculated using the $Y_{l,0}$ and $Y_{l,1}$ parameters of Table 1. Table 2 lists, for each vibrational level from $v = 0$ to the last observed one $v = 15$, the term energy values (referred to the minimum of the potential curve), and the derivatives $d(E)/d(v)$, the turning points and the rotational constants.

The $(3)^1\Pi$ upper state study was performed using the previously determined 35 T'_{vJ} values. These data, represented with a polynomial development as usual, led to a fit of moderate accuracy ($\text{rms} = 0.34 \text{ cm}^{-1}$) due to the perturbations affecting the state; the six more strongly perturbed levels were discarded from the fit.

The absolute vibrational numbering in the state was obtained by comparing the intensities of the analysed fluorescence series to those derived from the corresponding calculated Franck–Condon factors. In Table 3 are gathered the spectroscopic data for the $(3)^1\Pi$ state: energy values are referred to the bottom of the $X^1\Sigma^+$ state potential curve ($v = -1/2, J = 0$).

Table 3

Term energy values (in cm^{-1}) for the $(3)^1\Pi$ state: (a) $^{39}\text{K}^{85}\text{Rb}$; (b) $^{39}\text{K}^{87}\text{Rb}$. Discarded term values in the fit are marked with a star

T'_{vJ} (cm^{-1})	v'	J'	Obs.–calc. (cm^{-1})
(a)			
21801.501	0	25	0.195
21807.661	0	29	0.055
22014.198	0	90	0.022
22034.356	0	94	−0.374
22102.369*	1	99	1.728
22140.524	1	106	0.439
22169.694	1	111	−0.055
22395.164	1	144	−0.056
22833.564	1	195	0.166
22008.437	2	71	0.778
22395.102	3	134	−0.332
22496.128	4	143	−0.226
22082.800*	5	60	−1.959
22035.847	6	21	−0.007
22396.185*	6	118	−2.861
22116.465	8	24	−0.144
22122.200	8	28	−0.149
22734.166*	9	152	−1.363
22373.725	10	86	0.505
22836.580	10	161	−0.034
22907.745	11	166	0.209
22440.258	12	85	0.096
22911.645	14	154	−0.225
(b)			
21807.280	0	29	−0.072
21914.446	0	68	−0.723
21833.212*	1	19	−0.981
21908.712*	1	54	1.647
22121.197	1	103	0.644
22228.997	2	115	−0.448
22208.735	3	105	0.546
22521.095	4	147	−0.468
22099.963	5	65	−0.385
22521.000	7	132	0.103
22115.150	8	24	−0.168
22631.467	8	143	0.102

Proposed preliminary molecular constants for the $(3)^1\Pi$ state are the following:

$$\begin{array}{lll} T_e = 21762.0(2) \text{ cm}^{-1}, & \omega_e = 41.36(6) \text{ cm}^{-1}, & \omega_e x_e = 0.184(5) \text{ cm}^{-1}, \\ B_e = 28.82(3) 10^{-3} \text{ cm}^{-1}, & \alpha_e = 1.96(2) 10^{-4} \text{ cm}^{-1}, & D_e = 5.50(7) 10^{-8} \text{ cm}^{-1}. \end{array}$$

A comparison with the results of Rousseau [16] is presented below, the first line referring to Ref. [16] and the second line to the present work (all values in cm^{-1}):

	T_e	ω_e	B_e
$(3)^1\Sigma^+$	13985.4	39.91	0.02318
	13995.46	40.763	0.022822
$(3)^1\Pi$	21903.0	38.44	0.02788
	21762.0	41.36	0.02882

Good agreement is observed, particularly for the non-perturbed $(3)^1\Sigma^+$ state.

4. Conclusion

High-resolution Fourier spectroscopy has provided the first experimental observation and accurate rotational analysis of the K₂Rb $(3)^1\Sigma^+$ state. Similarly to the other alkali dimer molecules a strong ionic character has been found for this state. However, only a moderate portion of the potential curve has been explored and it remains, in further work, to extend the observations towards the predicted potential curve hump.

The upper $(3)^1\Pi$ state was also observed for the first time. But from the present work on this strongly perturbed state only preliminary molecular constants can be derived.

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