Polarisation Labelling Spectroscopy of Highly Excited (Rydberg) $^1\Pi_\mathrm{u}$ States in Potassium Dimer

W. Jastrzebski*

Institute of Physics, Polish Academy of Sciences
al. Lotników 32/46, 02-668 Warsaw, Poland

AND P. Kowalczyk

Institute of Experimental Physics, Warsaw University
Hoża 69, 00-681 Warsaw, Poland

Two previously unknown electronic states of K_2, both of $^1\Pi_\mathrm{u}$ symmetry, have been observed by polarisation labelling spectroscopy technique in the energy region of 31500–33100 cm^{-1} above the bottom of the molecular ground state potential well. Major molecular constants have been determined for these states and the potential curves have been constructed using the Rydberg–Klein–Rees method. The correlation of the observed states with atomic limits is discussed.

PACS numbers: 31.50.Df, 33.20.Lg, 33.20.Vq

1. Introduction

Excited electronic states of potassium dimer have been a subject of intensive laser spectroscopic studies for many years. Most experiments concentrated on states of singlet gerade symmetry, readily accessible via two-step transitions through the well-known intermediate $A\,^1\Sigma_\mathrm{u}^+$ and $B\,^1\Pi_\mathrm{u}$ states. As a result several Rydberg $^1\Lambda_\mathrm{g}$ series of K_2 have been studied thoroughly: $^1\Delta_\mathrm{g}(4s + nd)$ up to

*corresponding author; e-mail: jastr@ifpan.edu.pl

$n = 43$, $^1\Sigma_g^+(4s + ns)$ to $n = 20$, $^1\Sigma_g^+(4s + nd)$ to $n = 14$, $^1\Pi_g(4s + nd)$ to $n = 6$ [1–9] and extrapolation of the longest $^1\Delta_g$ series to $n \to \infty$ provided a reliable value of the molecular ionisation potential [1].

Definitely less is known about the excited singlet ungerade states of K_2. Although they can be reached by one-photon transitions from the molecular ground state, $X^1\Sigma_g^+$, but even for medium excited states wavelengths of the necessary photons fall into a rather inconvenient ultraviolet spectral range. In the experiments reported in the laser age the $7\,^1\Pi_u(4s + 6p)$ state, located approximately 29000 cm^{-1} above the bottom of the ground state potential, is to the best of our knowledge the highest one studied experimentally [10]. This state has been observed by us in the last of a series of investigations on potassium dimer, employing the polarisation labelling spectroscopy technique [11–16]. Recently we were able to extend the range of excitation energies in K_2 up to 33100 cm^{-1}. This paper deals with two previously unobserved $^1\Pi_u$ states placed in the newly opened range.

2. Apparatus

The experimental arrangement and the employed V-type optical–optical double resonance polarisation spectroscopy scheme were similar to that described in our previous papers [10, 17]. Figure 1 presents a schematic diagram of the apparatus used in the present work. In brief, the K_2 molecules were produced in a stainless steel heat pipe oven by heating potassium metal (of natural isotopic composition) to 600 K with helium at a pressure of 4 Torr as a buffer gas. The pump and probe laser beams were copropagated through the centre of the oven. As sources of the probe light we used the fixed wavelength lasers: He–Ne (Carl Zeiss HNA 188-1, $\lambda = 632.8$ nm, 30 mW) or Kr$^+$ (Carl Zeiss ILM 120, $\lambda = 647.1$ nm, 40 mW). Both of them excite well-known transitions in the $B\,^1\Pi_u \leftarrow X^1\Sigma_g^+$ band system of K_2 [13], thus labelling the involved rovibrational levels in the ground electronic state. A parametric oscillator/amplifier system (OPO/OPA, Sunlite Ex, Continuum) provided with a frequency doubler (FX-1) and pumped with the third harmonic of an injection seeded Nd:YAG laser (Powerlite 8000) generated the pump light. The system produced pulsed UV radiation with a typical energy of 3 mJ, 10 ns duration and a spectral width below 0.16 cm, tuneable for purposes of the present experiment in the range of 300–330 nm. The laser frequency was calibrated with argon atomic lines [18] obtained by the optogalvanic effect in a hollow cathode discharge. For additional control of the linearity of the laser scan a fraction of the pump beam was additionally sampled with a Fabry–Pérot interferometer 0.5 cm long. The estimated accuracy of the measured laser wave numbers was 0.1 cm^{-1}. Crossed polarisers were placed at both sides of the heat pipe oven in the path of the probe beam. At the frequencies, at which transitions induced by the pump beam shared the same lower level with any of the probe transitions, the probe light passed through the analyser. It was subsequently detected by a photomultiplier placed behind a 0.3 m monochromator centred at the
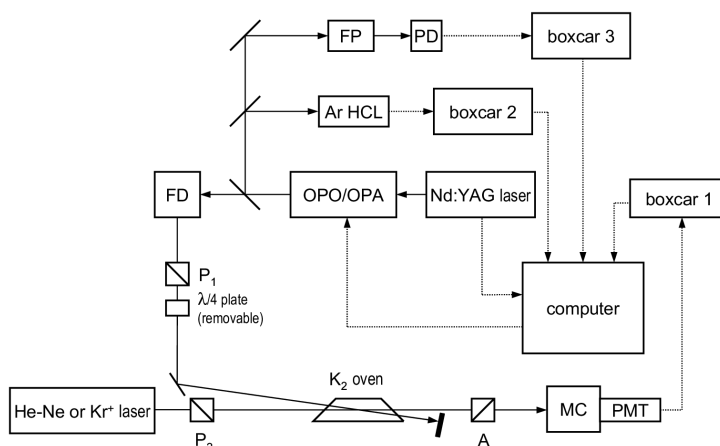
Fig. 1.   Block diagram of the experimental set-up: A — analyser, FD — frequency dou-bler, FP — Fabry–Pérot interferometer, HC — hollow cathode lamp, MC — monochro-mator, OPO/OPA — optical parametric oscillator and amplifier, P_1, P_2 — polarisers, PD — photodiode, and PMT — photomultiplier tube.

probe laser wavelength. The photoelectric current representing the polarisation spectrum of K_2, as well as calibration signals, were averaged with three boxcar integrators (Stanford Research Systems SR250), recorded in a digital form with a personal computer and stored for further analysis. Apart from data acquisition, the computer was used to control tuning of the OPO/OPA system.

3. Results and analysis

We have scanned the energy region of 30500–33100 cm^{-1} above the mini-mum of the ground state potential well. Despite the expected simplification of the spectra due to the used polarisation labelling method, they remained highly con-gested and intricate. According to the selection rules $\Delta\Lambda = 0, \pm1$, $\Delta S = 0$, g $\leftrightarrow$ u and $\Sigma^+ \leftrightarrow \Sigma^+$, from the ground $X^1\Sigma_g^+$ state only $^1\Sigma_u^+$ and $^1\Pi_u$ states are accessible by single photon excitation. However, since in the inves-tigated energy range molecular states of such symmetries can be formed from $4s + ns$ $(n \geq 7)$, $4s + np$ $(n \geq 7)$, $4s + nd$ $(n \geq 6)$, $4s + nf$ $(n \geq 5), \ldots$ atoms, and the density of these atomic asymptotes increases as n^3, a multitude of states could have been potentially observed in our experiment. In addition, earlier obser-vations of highly excited molecular states in alkali dimers [10, 15, 19] have shown that perturbations between them become increasingly frequent and cause both shifts in line positions and changes in intensities, adding to the complexity of the spectra. As a result in the recorded mass of spectral lines we were not able to iden-tify unambiguously transitions to any molecular state below the excitation energy of 31500 cm^{-1}. At still higher excitation energies the spectra grew simpler again.

A few vibrational progressions became recognisable and we succeeded in assigning them to two partially overlapping band systems having the ground $X^1\Sigma_g^+$ state of K_2 as the lower state. The symmetry of the upper states in both transitions is clearly $^1\Pi_u$ as indicated by the presence of strong Q lines in the spectra; for the sake of clarity in further text we designate the observed states as the $\alpha\,^1\Pi_u$ and $\beta\,^1\Pi_u$, respectively. It could be easily noticed that both band systems are strongly perturbed. Even perfunctory inspection of the spectra reveals highly irregular patterns of P, Q, and R lines in the observed progressions; in many cases only Q lines can be assigned without doubt. Since in a given $^1\Pi_u$ state the e parity levels are expected to be more prone to perturbations (mainly by the neighbouring $^1\Sigma_u^+$ states, containing only levels of e parity) than the f parity levels, we confined our analysis to the latter ones, observed via Q lines in the spectra. This problem had been encountered in our previous studies of the $5\,^1\Pi_u$ and $7\,^1\Pi_u$ states in K_2 [10, 15] and solved in a similar way. Initially we were able to assign $55Q$ lines to the lower $^1\Pi_u$ state and $54Q$ lines to the upper one, all of them corresponding to the most abundant $^{39}K_2$ isotopomer. It must be remembered, however, that perturbations by other nearby states, $^3\Sigma_u^+$, $^{1,3}\Pi_u$, and $^{1,3}\Delta_u$, involve both e and f parity levels of a $^1\Pi_u$ state and the observed Q lines could also be perturbed. Indeed, even the identified progressions were far from regular, and occasionally perturbations manifested themselves clearly by doubling of rotational lines. In such instances we applied a model of perturbation of two levels, in which the ratio of intensities of the main (perturbed) and the extra line equals to the inverse ratio of their spectral shifts [20], $I_1 : I_2 = \Delta_2 : \Delta_1$. Assuming that the extra lines appear only when the mutually perturbed levels become degenerate, we were able then to infer the unperturbed positions of lines from the experimental ratio of intensities ($I_1 : I_2$) and the distance between the main and the extra ones ($\Delta_1 + \Delta_2$). Even if this method of deperturbation may be oversimplified, we believe that it has yielded improved positions of some lines.

The wave numbers of spectral lines corresponding to both band systems were converted to energies of levels in the upper states referred to the bottom of the $X^1\Sigma_g^+$ state potential using the ground state constants of Amiot et al. [21]. The energies of levels for each electronic state were fitted with the conventional Dunham expansion

$$T(v, J) = T_e + \sum_{m,n} Y_{mn}(v + 1/2)^m [J(J+1) - 1]^n, \tag{1}$$

where the symbols T_e, Y_{mn}, v, and J have their usual meanings. The rotational numbering could be obtained unambiguously because the J quantum numbers of the labelled ground state levels were exactly known. On the other hand, to assign vibrational quantum numbers to all levels in a given state, identification of the $v = 0$ level in this state was necessary. Unfortunately, the unfavourable Frank–Condon factors made observation of the lowest vibrational levels in the α and β states questionable. Therefore, during the progress of our analysis many determi-

nations of the Dunham coefficients were made for various vibrational numberings of the observed levels. Basing on a given set of coefficients we constructed then a potential energy curve with the Rydberg–Klein–Rees (RKR) method and calculated the Franck–Condon factors for transitions from the molecular ground state. The Franck–Condon factors obtained with the correct assignment of the vibrational numbering should give the most satisfactory agreement with the experimental intensities of spectral lines. In general, the agreement was rather qualitative than quantitative, and we had to rely mainly on comparison of zeros in theoretical and experimental intensity distributions. Having established the most plausible vibrational assignment we tried to confirm it by employing the isotope effect, i.e. by searching for lines corresponding to the $^{39}K^{41}K$ isotopomer. Eventually, we were able to include into the fits 8 such lines for the $\alpha\,^1\Pi_u \leftarrow X^1\Sigma_g^+$ transition and 4 lines for the $\beta\,^1\Pi_u \leftarrow X^1\Sigma_g^+$ transition. But also this argument is not conclusive because of rather large deviations between line positions measured and calculated for both states and consequently the vibrational numberings proposed by us should be treated with caution.

The obtained Dunham coefficients are listed in Table I. For each state we used the smallest number of coefficients that reproduce the measured line positions. After removing a few deviant points, still present in the data, we find that the root mean square error of the fit is 0.17 cm^{-1} for the $\alpha\,^1\Pi_u$ state and 0.28 cm^{-1} for the $\beta\,^1\Pi_u$ state. Both values exceed the estimated uncertainty in making a single measurement, 0.1 cm^{-1}, which again exemplifies perturbations of both states.

TABLE I

The experimentally determined Dunham coefficients for the $\alpha\,^1\Pi_u$ and $\beta\,^1\Pi_u$ states of $^{39}K_2$ (the coefficients and rms errors all in units of cm^{-1}).

	$\alpha\,^1\Pi_u$ state	$\beta\,^1\Pi_u$ state
T_e	31389.15(36)[a]	31929.81(19)
Y_{10}	64.241(56)	66.289(44)
Y_{20}	−0.0157(24)	0.0401(24)
Y_{01}	0.039100(49)	0.039829(22)
Y_{11}	0.130(41)×10^{-4}	—
rms error of the fit	0.17	0.28
No. of levels in the fit	51	55
range of v	4–17	0–15
range of J	55–94	55–94
atomic asymptote[b]	$4s + 9p$	$4s + 10p$

[a]the numbers in parentheses are 1σ uncertainties,

[b]see the text for discussion.

It must be also noted that all the available data correspond to relatively high rotational quantum numbers $J \geq 55$. The RKR potential energy curves calculated using the determined Dunham coefficients are given in Tables II and III.

TABLE II

Rotationless potential energy curve for the $\alpha\,^1\Pi_{\mathrm{u}}$ state of K_2.

v	V [cm^{-1}]	$R_{\min}$ [Å]	$R_{\max}$ [Å]
	0.0	4.704[a]	
0	32.121	4.543	4.871
1	96.331	4.428	4.996
2	160.509	4.350	5.084
3	224.656	4.288	5.157
4	288.772	4.235	5.221
5	352.856	4.188	5.278
6	416.910	4.146	5.331
7	480.932	4.107	5.380
8	544.922	4.071	5.426
9	608.882	4.039	5.471
10	672.810	4.005	5.513
11	736.706	3.975	5.553
12	800.572	3.947	5.592
13	864.406	3.919	5.630
14	928.208	3.893	5.666
15	991.980	3.868	5.702
16	1055.720	3.844	5.736
17	1119.429	3.821	5.770

[a]The first line refers to the bottom of the potential curve: R is the equilibrium distance.

In the absence of theoretical calculations concerning Rydberg states of K_2 (see [22] for the most extensive results) and of direct experimental observations, we can try to assign atomic asymptotes to the observed states only tentatively and by indirect arguments. First, we resort to a general rule that in case of transitions to highly excited molecular states the strongest ones are expected to be those corresponding to the allowed transitions between the asymptotic atomic limits of the molecular states [2, 23, 24]. Since the observed transitions originate from the ground $X\,^1\Sigma_{\mathrm{g}}^{+}$ state, which dissociates to $4s + 4s$ potassium atoms, it is concluded that the two investigated $^1\Pi_{\mathrm{u}}$ states correspond to $4s + np$ and $4s + (n+1)p$ asymptotes. The principal quantum number n can be assigned by

TABLE III

Rotationless potential energy curve for
the $\beta\,^1\Pi_{\mathrm{u}}$ state of K_2.

v	V [cm^{-1}]	$R_{\min}$ [Å]	$R_{\max}$ [Å]
	0.0	4.661^a	
0	33.175	4.502	4.825
1	99.544	4.390	4.949
2	165.994	4.314	5.036
3	232.523	4.254	5.107
4	299.133	4.202	5.170
5	365.823	4.157	5.226
6	432.593	4.116	5.278
7	499.444	4.079	5.326
8	566.374	4.045	5.371
9	633.385	4.013	5.414
10	700.475	3.982	5.455
11	767.646	3.954	5.495
12	834.897	3.927	5.533
13	902.228	3.901	5.569
14	969.640	3.877	5.604
15	1037.131	3.853	5.638

^{a}The first line refers to the bottom of
the potential curve: R is the equilib-
rium distance.

comparing separation of the potential wells of the $\alpha\,^1\Pi_{\mathrm{u}}$ and $\beta\,^1\Pi_{\mathrm{u}}$ states with
energy differences between successive np atomic levels of potassium [25], the com-
parison based on an assumption that the molecular dissociation energies of the
highly excited (Rydberg) states are not significantly influenced by a distant Ryd-
berg electron. The separation $T_e(\beta\,^1\Pi_{\mathrm{u}}) - T_e(\alpha\,^1\Pi_{\mathrm{u}}) \approx 541$ cm^{-1} is relatively close
to $\Delta_{10p-9p} = 469$ cm^{-1} and $\Delta_{9p-8p} = 713$ cm^{-1}. Thus we conclude that $n = 9$ or,
less likely, $n = 8$. The first assignment would lead to dissociation energies of the α
and β states 6004 and 5932 cm^{-1}, respectively, the second to 5291 and 5463 cm^{-1}
(we make use of the experimental dissociation energy of the $X\,^1\Sigma_{\mathrm{g}}^+$ state [21] for
this calculation). These values can be compared to the known dissociation energy
of the ground $X\,^2\Sigma_{\mathrm{g}}^+$ state of the K_2^+ ion, $D_e = 6669$ cm^{-1} [4], being the limit
of the $^1\Pi_{\mathrm{u}}(4s + np)$ Rydberg series. Both sets of dissociation energies seem to
be in contradiction with a simple model of the $^1\Pi_{\mathrm{u}}$ Rydberg states of K_2. In
all these states one valence electron is in a strongly bonding $4s\sigma_{\mathrm{g}}$ orbital. The
orbital for the second valence electron is $np\pi_{\mathrm{u}}$, also bonding and with the bond
strength decreasing with increasing n [26]. Therefore the dissociation energy of

the $^1\Pi_u$ states may be expected to decrease when n rises, approaching $D_e(K_2^+)$ at $n \to \infty$. However, this model, based on a single configuration approximation for electron wave functions, is certainly oversimplified (in particular it suggests incorrectly that the molecular ion K_2^+ should be weaker bound than the ground state K_2) and cannot be used to choose between the two possible assignments. Therefore we accept both correlations with atomic asymptotes discussed above as plausible, with a preference for $n = 9$ value.

4. Conclusion

In the range of 31500–33100 cm^{-1} above the bottom of the ground state of K_2 we observed two highly excited states of $^1\Pi_u$ symmetry, which we identified as members of the $4s + np$ Rydberg series. The Dunham coefficients and potential energy curves for both states were determined. Our experiment shows that further simplification of the experimental excitation spectra of K_2 is required, in particular to study the energy range between 30000 and 31500 cm^{-1}, not analysable at present. Identification of all lower $^1\Pi_u$ states would provide a direct answer concerning asymptotic correlation of the α and β states. For this purpose a polarisation spectroscopy experiment with a single mode, tuneable probe laser used for labelling of chosen, single rovibrational levels in the ground state is planned. On the other hand, theoretical calculations of potential curves for Rydberg states in K_2 are highly desirable as they also could greatly help in interpretation of experimental results.

Acknowledgments

References

[1] M. Broyer, J. Chevaleyre, G. Delacretaz, S. Martin, L. Wöste, *Chem. Phys. Lett.* **99**, 206 (1983).

[2] P. Kowalczyk, U. Schühle, F. Engelke, *Z. Phys. D* **13**, 231 (1989).

[3] H. Wang, Li Li, A.M. Lyyra, W.C. Stwalley, *J. Mol. Spectrosc.* **137**, 304 (1989).

[4] H. Wang, W.C. Stwalley, A.M. Lyyra, *J. Chem. Phys.* **96**, 7965 (1992).

[5] G. Jong, H. Wang, C.C. Tsai, W.C. Stwalley, *J. Mol. Spectrosc.* **154**, 324 (1992).

[6] J.T. Kim, C.C. Tsai, W.C. Stwalley, *J. Mol. Spectrosc.* **171**, 200 (1995).

[7] J.T. Kim, C.C. Tsai, H. Wang, J.T. Bahns, W.C. Stwalley, *J. Mol. Spectrosc.* **172**, 183 (1995).

[8] J.T. Kim, H. Wang, J.T. Bahns, W.C. Stwalley, *J. Chem. Phys.* **102**, 6966 (1995).

[9] J.T. Kim, C.C. Tsai, W.C. Stwalley, *J. Mol. Spectrosc.* **177**, 194 (1996).

[10] A. Grochola, W. Jastrzebski, P. Kowalczyk, S. Magnier, M. Aubert-Frécon, *J. Mol. Spectrosc.* **224**, 151 (2004).

[11] W. Jastrzębski, P. Kowalczyk, *Chem. Phys. Lett.* **206**, 69 (1993).

[12] W. Jastrzębski, P. Kowalczyk, *Chem. Phys. Lett.* **227**, 283 (1994).

[13] W. Jastrzębski, P. Kowalczyk, *Phys. Rev. A* **51**, 1046 (1995).

[14] I. Jackowska, W. Jastrzębski, P. Kowalczyk, *J. Phys. B* **29**, L561 (1996).

[15] I. Jackowska, W. Jastrzębski, P. Kowalczyk, *J. Mol. Spectrosc.* **185**, 173 (1997).

[16] W. Jastrzebski, W. Jaśniecki, P. Kowalczyk, R. Nadyak, A. Pashov, *Phys. Rev. A* **62**, 042509 (2000).

[17] R. Ferber, W. Jastrzębski, P. Kowalczyk, *J. Quant. Spectrosc. Radiat. Transfer* **58**, 53 (1997).

[18] A.R. Striganov, G.A. Odincova, *Tablicy Spektralnych Linii Atomov i Ionov*, Energoizdat, Moscow 1982 (in Russian).

[19] C.C. Tsai, J.T. Bahns, W.C. Stwalley, *Chem. Phys. Lett.* **236**, 553 (1995).

[20] I. Kovacs, *Rotational Structure in the Spectra of Diatomic Molecules*, Amer. Elsevier, New York 1969, p. 209.

[21] C. Amiot, J. Vergès, C.E. Fellows, *J. Chem. Phys.* **103**, 3350 (1995).

[22] S. Magnier, M. Aubert-Frécon, A.R. Allouche, *J. Chem. Phys.* **121**, 1771 (2004).

[23] N.W. Carlson, A.J. Taylor, K.M. Jones, A.L. Schawlow, *Phys. Rev. A* **24**, 822 (1981).

[24] B. Hemmerling, R. Bombach, W. Demtröder, N. Spies, *Z. Phys. D* **5**, 165 (1987).

[25] W.L. Wiese, M.W. Smith, B.M. Miles, *Atomic Transition Probabilities*, NSRDS-NBS 22, US Govt. Printing Office, Washington 1969.

[26] R. McWeeny, *Coulson's VALENCE*, Oxford University Press, Oxford 1979.