

# Spectroscopic investigation of the double-minimum $2^1\Sigma_u^+$ state of the potassium dimer

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The double-minimum  $2^1\Sigma_u^+$  state was investigated in  $^{39}\text{K}_2$  and  $^{39}\text{K}^{41}\text{K}$  molecules by analyzing spectra of the  $2^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$  band system, simplified by polarization labeling. A wide range of rovibrational levels  $21 \leq v \leq 97$ ,  $18 \leq J \leq 159$  was observed. By using the inverted perturbation approach to construct the exotic potential-energy curve, an accurate, isotopically consistent description of the  $2^1\Sigma_u^+$  state has been obtained.

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## I. INTRODUCTION

Excited electronic states of diatomic alkali-metal molecules often display exotic potential curves which result from avoided crossings between diabatic Rydberg and covalent potentials at short internuclear distances and also ion pair potentials at large distances. Such states are subjects of much interest and curiosity since experimental observation of them can provide sensitive tests of methods and models used in theoretical calculations. Well known examples are the double-minimum (DM)  $2^1\Sigma_u^+$  states of homonuclear  $\text{Li}_2$ ,  $\text{Na}_2$ , and  $\text{K}_2$  dimers, first predicted theoretically nearly two decades ago [1,2]. For lithium and sodium dimers, the predictions have been largely confirmed in subsequent experiments [3–8]. The experimental information about the  $2^1\Sigma_u^+$  state in  $\text{K}_2$  is rather scarce. In the sole spectroscopic investigation [9], only 21 (of more than 150 expected) vibrational levels were studied at rotational resolution, all of them situated above the internal potential barrier. With the best theoretical calculations available at that time being only of qualitative accuracy [10] and giving no definite hint about the lowest energy levels missing in observation, this did not suffice to assign absolute vibrational numbering to the  $2^1\Sigma_u^+$  state and thus the constructed potential-energy curve was only of tentative character.

In this paper, we discuss our recent experiment in which the  $2^1\Sigma_u^+$  state of potassium dimer has been reinvestigated by means of polarization labeling spectroscopy on the  $2^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$  band system. 763 rovibrational levels in the DM state of  $^{39}\text{K}_2$  spanning  $v' = 21-97$  were measured with resolution better than  $0.1 \text{ cm}^{-1}$ . Due to unfavorable Franck-Condon factors, we did not directly observe transitions terminating on the lowest vibrational levels, belonging to the separate inner and outer potential wells. However, using the inverted perturbation approach (IPA) to our experimental data and aided by the high-quality calculations of Magnier [11,12], we have successfully obtained a rotationless potential curve of the  $2^1\Sigma_u^+$  state which reproduces the observed energy levels with a standard deviation of  $0.07 \text{ cm}^{-1}$ . The absolute vibrational numbering of the levels has been established by observation of spectrum of the  $^{39}\text{K}^{41}\text{K}$  isotopomer.

## II. EXPERIMENT

The experimental method and setup have been described previously [13] and only the essential features will be sum-

marized here. Potassium dimers (natural isotopic composition) were formed in a heatpipe oven at 590 K with a background pressure of 4 Torr helium. The pump and probe laser beams were copropagated through the center of the oven. As the probe laser, we employed one of the fixed frequency lasers (He-Ne,  $\lambda = 632.8 \text{ nm}$  and  $\text{Kr}^+$ ,  $\lambda = 647.1 \text{ nm}$ , 30–50 mW power) which excite a few molecular transitions in the  $B^1\Pi_u \leftarrow X^1\Sigma_g^+$  system of potassium dimers, thus labeling the involved rovibrational levels in the ground electronic state (see Table I). The probe beam had to pass two crossed polarizers placed in front of and behind the oven, to be, in principle, totally extinguished. The pump laser (pulsed dye laser and XeCl excimer laser system, 2 mJ pulse energy,  $0.1 \text{ cm}^{-1}$  spectral width) was tuned across the investigated band system, in the spectral range  $21\,000-23\,200 \text{ cm}^{-1}$ . The laser wavelength was calibrated against both the optogalvanic spectrum of argon and the transmission fringes of a Fabry-Pérot interferometer 0.5 cm long, to absolute accuracy better than  $0.1 \text{ cm}^{-1}$ . At resonance with any molecular transition, the strong polarized pump beam produced optical anisotropy in the lower and upper molecular levels involved. Whenever lower levels for both the pump and probe transitions coincided, the probe light changed its original polarization and passed partially through the second polarizer. Therefore, the information about the excitation spectrum of the molecules was contained in the transmitted intensity of the probe light.

## III. RESULTS AND ANALYSIS

Throughout the observed spectrum, several vibronic  $v'$  progressions belonging to the  $2^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$  system were observed. Small vibrational spacing in the upper state made the initial assignment of lines rather confusing (see Fig. 1). However, making use of the preliminary molecular constants of the  $2^1\Sigma_u^+$  state [9], we were able to identify progressions involving the lowest rotational levels observed. Then, gradually proceeding towards higher  $J'$  levels, we assigned a total of 763 transitions in the main isotopic form  $^{39}\text{K}_2$  spanning 73 vibrational levels of the DM state with  $J'$  ranging between 18 and 159. Moreover, 491 lines from the heads of 18 bands, studied at  $0.04 \text{ cm}^{-1}$  resolution in the previous molecular-beam experiment [9], were added to the analysis. Figure 2 shows the data field ( $v', J'$ ) taken into account [14].

The wave numbers of the identified lines were described by the relation

TABLE I. Observed transitions in the  $B^1\Pi_u \leftarrow X^1\Sigma_g^+$  band system of  $K_2$  excited by the He-Ne and Kr<sup>+</sup> lasers used as probe lasers. The asterisks indicate excitation of both  $^{39}K_2$  and  $^{39}K^{41}K$ ; otherwise only  $^{39}K_2$  was excited.

Laser line	Excited transition ( $v', J'$ ) $\leftarrow$ ( $v'', J''$ )
He-Ne, 632.8 nm (15 798.0 cm <sup>-1</sup> )	(6,18) $\leftarrow$ (0,19)
	(7,82) $\leftarrow$ (0,83)
	(8,73) $\leftarrow$ (1,73)
	(9,55) $\leftarrow$ (2,55)
	(12,70) $\leftarrow$ (4,70)
	(13,46) $\leftarrow$ (5,47)
	(16,137) $\leftarrow$ (5,137)
Kr <sup>+</sup> , 647.1 nm (15 449.6 cm <sup>-1</sup> )	(16,112) $\leftarrow$ (6,111)
	(2,82) $\leftarrow$ (0,83)*
	(2,95) $\leftarrow$ (0,94)*
	(4,159) $\leftarrow$ (0,158)
	(9,103) $\leftarrow$ (5,104)
	(10,92) $\leftarrow$ (6,93)
	(11,91) $\leftarrow$ (7,90)

$$\tilde{\nu} = T'(v', J') - T''(v'', J''), \quad (1)$$

where  $T'(v', J')$  and  $T''(v'', J'')$  are the term values of the excited and of the lower states, respectively. Since the term values of the ground  $X^1\Sigma_g^+$  state have been accurately measured by Ross *et al.* [15] covering all the levels labeled in our experiment, we added the known values  $T''(v'', J'')$  to our measured line positions  $\tilde{\nu}$  and obtained the term values  $T'(v', J')$  of the  $2^1\Sigma_u^+$  state according to Eq. (1) [14]. The experimental errors of Ross *et al.* are about an order of magnitude smaller than those of our measurements, hence no additional errors are introduced into the analysis of the  $2^1\Sigma_u^+$  state.

In the case of electronic states with double-minimum potentials, the traditional methods of description clearly fail, since energies of rovibrational levels cannot be represented

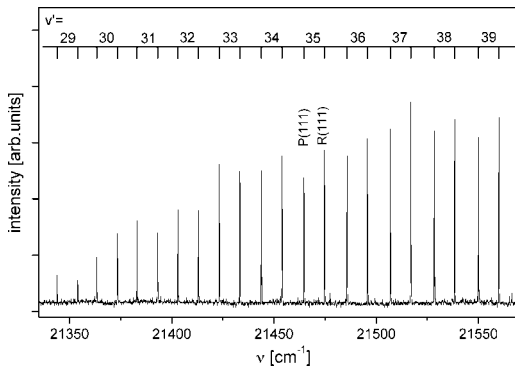


FIG. 1. A portion of the polarization spectrum of  $K_2$  obtained with a He-Ne laser as the probe laser and a circularly polarized pump beam. The assigned vibrational progression corresponds to the transition  $2^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$  from the  $v''=6, J''=111$  level labeled in the ground state. Two rotational  $P$  and  $R$  lines are marked for easier reading of the spectrum.

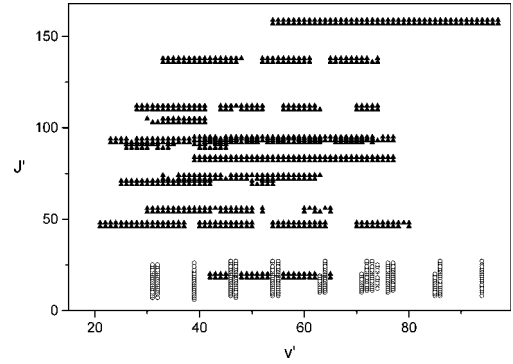


FIG. 2. Distribution of the data used in the present analysis of the  $2^1\Sigma_u^+$  state in  $K_2$ . Full triangles, present measurements; open circles, data from Ref. [9].

by a Dunham expansion and the semiclassical Rydberg-Klein-Rees technique is no longer applicable for construction of the potential. The alternative way is to represent the investigated state exclusively by its potential curve built by a fully quantum-mechanical variational procedure, known as the inverted perturbation approach (IPA; for a review, see [16]). In this method, one starts with some estimated approximate potential curve and iteratively seeks corrections to it until the quantum-mechanical eigenenergies calculated from the improved curve agree with the spectroscopic term values within the experimental uncertainty. The method is not subject to limitations imposed by semiclassical techniques and, in principle, can provide a potential of any desired shape.

In our realization of the IPA algorithm [17], we used a cubic spline function for construction of the molecular potential. This function is flexible enough to handle potentials with multiple minima. A serious problem was to generate a reasonable initial potential-energy curve of the DM  $2^1\Sigma_u^+$  state. Fortunately, reliable *ab initio* calculations by Magnier [11,12] have been available. We tried to adopt the theoretical potential by shifting it slightly in energy (by  $\pm 200$  cm<sup>-1</sup>) to match approximately the positions of the observed vibrational levels. However, as  $\Delta G_v$  values for various pairs of levels in the  $2^1\Sigma_u^+$  state are rather similar and not very characteristic, no optimum match could have been found this way. Therefore, several initial potentials have been assumed, each of them imposing a different vibrational numbering on the observed levels. Starting from them as first approximations, several potential curves have been generated by the IPA method, every curve reproducing well the experimental term values. But only one of these curves allowed us to predict correctly positions of more than 50 spectral lines in two  $v'$  progressions, recorded in the experiment and attributed to the  $^{39}K^{41}K$  isotopomer. This unique potential of the DM  $2^1\Sigma_u^+$  state in  $K_2$  is given in Table II in a grid of 60 equidistant points. To interpolate it to any point between 2.38 and 15 Å, the natural cubic spline [18] should be used. The quantum-mechanical energy eigenvalues of the generated potential reproduce all measured term values for  $v' = 21-97, J' = 6-159$  within a standard error of 0.07 cm<sup>-1</sup>. The potential may be somewhat rough around its minima due to the lack of observed levels in the inner and outer wells.

TABLE II. The rotationless IPA potential-energy curve of the  $2^1\Sigma_u^+$  state in  $K_2$ . The positions of the inner and outer minima and of the top of the potential barrier are  $R_{\min}^{\text{in}}=4.91 \text{ \AA}$ ,  $E_{\min}^{\text{in}}=22\,019.9 \text{ cm}^{-1}$ ;  $R_{\min}^{\text{out}}=7.43 \text{ \AA}$ ,  $E_{\min}^{\text{out}}=21\,726.5 \text{ cm}^{-1}$ ;  $R_{\max}=5.56 \text{ \AA}$ ,  $E_{\max}=22\,081.8 \text{ cm}^{-1}$ .

$R \text{ (\AA)}$	$U \text{ (cm}^{-1}\text{)}$	$R \text{ (\AA)}$	$U \text{ (cm}^{-1}\text{)}$	$R \text{ (\AA)}$	$U \text{ (cm}^{-1}\text{)}$
2.3800	55 360.7376	6.6580	21 852.6084	10.9359	23 889.6964
2.5939	42 292.8277	6.8719	21 796.6172	11.1498	24 061.6938
2.8078	33 417.5725	7.0858	21 754.5625	11.3637	24 230.8223
3.0217	29 496.5500	7.2997	21 730.6959	11.5776	24 391.4830
3.2356	26 878.4292	7.5136	21 727.8818	11.7915	24 537.2973
3.4495	25 167.8862	7.7275	21 746.2570	12.0054	24 671.8676
3.6634	23 991.2843	7.9414	21 789.0650	12.2193	24 800.0581
3.8773	23 174.9265	8.1553	21 861.6102	12.4332	24 916.7209
4.0912	22 632.2352	8.3692	21 957.6424	12.6471	25 016.4026
4.3051	22 298.5116	8.5831	22 066.1754	12.8610	25 099.3574
4.5190	22 117.2686	8.7969	22 187.5409	13.0749	25 167.6804
4.7329	22 037.5519	9.0108	22 326.2755	13.2888	25 222.7191
4.9468	22 020.5780	9.2247	22 480.0663	13.5027	25 266.1653
5.1607	22 043.8114	9.4386	22 644.2574	13.7166	25 300.2390
5.3746	22 072.8560	9.6525	22 815.8869	13.9305	25 326.9405
5.5885	22 081.4900	9.8664	22 992.6135	14.1444	25 347.5678
5.8024	22 065.9834	10.0803	23 172.3010	14.3583	25 363.2021
6.0163	22 028.8626	10.2942	23 353.6057	14.5722	25 374.9504
6.2302	21 976.8811	10.5081	23 535.2215	14.7861	25 383.9119
6.4441	21 916.1578	10.7220	23 714.5125	15.0000	25 391.0914

Therefore, there is considerable interest in trying to locate experimentally the lowest vibrational levels of the  $2^1\Sigma_u^+$  state in order to improve the knowledge of the bottom of this state.

In the case of double-minimum states which originate from an avoided curve crossing of two diabatic potential-energy curves, it is always advisable to check whether the investigated state can indeed be described within the adiabatic approximation implicitly assumed in the IPA method. A general criterion is provided by the adiabaticity parameter  $\gamma$  introduced by Dressler [19],  $\gamma=H_{\text{el}}/h\nu$ , where the elec-

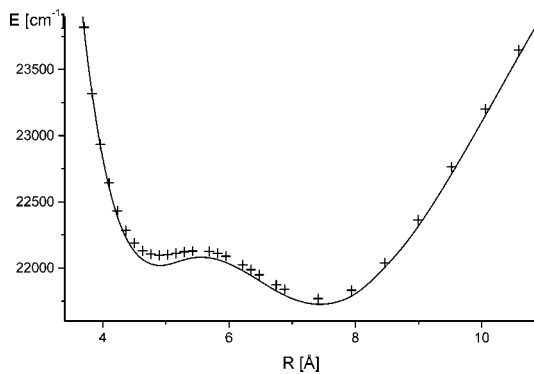


FIG. 3. The generated potential curve of the double-minimum  $2^1\Sigma_u^+$  state (solid line) compared with Magnier's calculation [12] (pluses).

TABLE III. Dunham-type coefficients representing term values for the  $2^1\Sigma_u^+$  state in  $^{39}\text{K}_2$  with the rms deviation  $0.09 \text{ cm}^{-1}$ . All values are given in  $\text{cm}^{-1}$ . The coefficients are meaningful only for  $v'=29-91$ ,  $J'=6-159$ .

Constant	Value	Constant	Value
$Y_{00}$	21 965.31	$Y_{01}$	0.025 296 7
$Y_{10}$	-0.884 74	$10^{+4} Y_{11}$	-0.751 9
$Y_{20}$	0.648 934	$10^{+6} Y_{21}$	0.538 95
$10^{+2} Y_{30}$	-0.952 101 8	$10^{+8} Y_{31}$	-0.319 36
$10^{+4} Y_{40}$	0.867 425 2	$10^{+7} Y_{02}$	-0.305 0
$10^{+6} Y_{50}$	-0.445 162	$10^{+10} Y_{12}$	0.630 7
$10^{+9} Y_{60}$	0.960 26	$10^{+12} Y_{03}$	-0.126 3

tronic matrix element  $H_{\text{el}}$  between the diabatic states giving rise to a double-minimum state is compared with the vibrational frequency  $\nu$  in the upper one of the resulting two adiabatic states. The parameter distinguishes between the diabatic ( $\gamma \ll 1$ ) and adiabatic ( $\gamma \gg 1$ ) limits. With  $\gamma \approx 12.1$  for the pair of  $2^1\Sigma_u^+$  and  $3^1\Sigma_u^+$  states in  $\text{K}_2$  the latter case is evidently approached, thus validating the use of the IPA method. The bottom of the  $3^1\Sigma_u^+$  state potential is placed about  $23\,673 \text{ cm}^{-1}$  [13], close to the upper boundary of the energy region sampled in the present experiment. No traces of the  $2^1\Sigma_u^+ \sim 3^1\Sigma_u^+$  perturbation have been detected in the observed spectra, probably due to negligible overlap of vibrational wave functions belonging to both states. For the same reason also the  $C^1\Pi_u$  state with  $T_e \approx 22\,968 \text{ cm}^{-1}$  [20] apparently does not perturb the double-minimum state to a measurable extent. As a result, all of the observed spectral lines in the  $2^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$  system were used in our analysis of the  $2^1\Sigma_u^+$  state.

In Fig. 3, the constructed double-minimum potential is compared in the range  $3.7-10.6 \text{ \AA}$  with the theoretical curve furnished by Magnier [12] (points outside this range are listed in Table II only in order to ensure proper boundary conditions for solving the Schrödinger equation). The discrepancy between the experimental and theoretical potentials never exceeds  $75 \text{ cm}^{-1}$ , thus proving the high quality of Magnier's calculation. It must be noted that the experimental term values of the  $2^1\Sigma_u^+$  state can be reproduced with a reasonable accuracy by a set of Dunham-like coefficients, which are listed in Table III. We have to stress that they have no direct physical meaning and the applicability of them is strictly limited to the range of  $v'$  and  $J'$  quantum numbers used for their definition. However, we find them more handy for predicting rovibrational energies than by numerically solving the Schrödinger equation with the potential of Table II.

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- [1] A. Valance and Q. Nguyen Tuan, *Phys. Lett.* **82A**, 116 (1981).
- [2] D. D. Konowalow and J. L. Fish, *Chem. Phys.* **84**, 463 (1984).
- [3] C. Linton, F. Martin, R. Bacis, and J. Vergès, *J. Mol. Spectrosc.* **137**, 235 (1989).
- [4] A. J. Ross, P. Crozet, C. Linton, F. Martin, I. Russier, and A. Yiannopoulou, *J. Mol. Spectrosc.* **191**, 28 (1998).
- [5] S. Kasahara, P. Kowalczyk, Md. H. Kabir, M. Baba, and H. Katô, *J. Chem. Phys.* (to be published).
- [6] J. Vergès, C. Effantin, J. d'Incan, D. L. Cooper, and R. F. Barrow, *Phys. Rev. Lett.* **53**, 46 (1984).
- [7] D. L. Cooper, R. F. Barrow, J. Vergès, C. Effantin, and J. d'Incan, *Can. J. Phys.* **62**, 1543 (1984).
- [8] A. Pashov, W. Jastrzebski, W. Jaśniecki, V. Bednarska, and P. Kowalczyk, *J. Mol. Spectrosc.* (to be published).
- [9] P. Kowalczyk, A. Katern, and F. Engelke, *Z. Phys. D: At., Mol. Clusters* **17**, 47 (1990).
- [10] G. Jeung and A. Ross, *J. Phys. B* **21**, 1473 (1988).
- [11] S. Magnier and Ph. Millié, *Phys. Rev. A* **54**, 204 (1996).
- [12] S. Magnier (private communication).
- [13] W. Jastrzebski and P. Kowalczyk, *Phys. Rev. A* **51**, 1046 (1995).
- [14] See EPAPS Document No. E-PLRAAN-62-064010 for a list of the measured transitions with the assignments and term values used in the IPA procedure. This document may be retrieved via the EPAPS homepage (<http://www.aip.org/pubservs/epaps.html>) or from <ftp.aip.org> in the directory/epaps/. See the EPAPS homepage for more information.
- [15] A. J. Ross, P. Crozet, J. d'Incan, and C. Effantin, *J. Phys. B* **19**, L145 (1986).
- [16] C. R. Vidal, *Comments At. Mol. Phys.* **17**, 173 (1986).
- [17] A. Pashov, W. Jastrzebski, and P. Kowalczyk, *Comput. Phys. Commun.* **128**, 622 (2000).
- [18] C. De Boor, *A Practical Guide to Splines* (Springer, New York 1978).
- [19] K. Dressler, in *Photophysics and Photochemistry Above 6 eV*, edited by F. Lahmani (Elsevier, Amsterdam, 1985), p. 327.
- [20] I. Jackowska, W. Jastrzebski, and P. Kowalczyk, *J. Phys. B* **29**, L561 (1996).