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# The long-range potential of the $K_2 X^1\Sigma_g^+$ ground electronic state up to 15 Å

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Titanium sapphire laser induced fluorescence spectra of the  $A^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$  electronic system have been recorded at high resolution by Fourier transform spectroscopy. Ground state vibrational levels are observed up to  $v=81$  corresponding to an internuclear distance of 15.4 Å and to 99.96% of the potential well depth. A long range study of the potential energy curves (RKR and IPA) allowed the determination of the coefficients of the dispersion energy (multipolar expansion representation) and of the exchange energy (exponential representation). The dissociation energy is found to be  $4450.75 \pm 0.15 \text{ cm}^{-1}$ . © 1995 American Institute of Physics.

## I. INTRODUCTION

Advances in laser cooling and trapping technology have lead to new interest in the knowledge of the long-range forces between atoms in diatomic molecules. In fact, confinement of alkali-metal atoms at sub-Kelvin temperatures depends strongly on the asymptotic long-range properties.<sup>1-3</sup>

Up to now, experimental determination of this long-range part of the potential in the alkali dimers has been reported mainly for the molecules  $\text{Li}_2$  (Refs. 4 and 5) and  $\text{Na}_2$ .<sup>6,7</sup>

In a recent paper<sup>8</sup> we studied the  $K_2$  ground electronic state potential energy curve up to  $v=73$  and we determined the dissociation energy value as  $4451 \text{ cm}^{-1}$  with a rather large uncertainty of  $\pm 1.5 \text{ cm}^{-1}$ . In fact, the last observed vibrational level, with  $v=73$ , is located at about  $46 \text{ cm}^{-1}$  below the dissociation limit energy, well inside the “LeRoy radius” (noted  $R_L$ ), equal to 10.8 Å, where exchange energy is expected to be negligible.<sup>9</sup>

Subsequently, Zemke, Tsai, and Stwalley<sup>10</sup> determined an improved value for the dissociation energy as  $D_e = 4449.1 \pm 1 \text{ cm}^{-1}$ , by considering both  $X^1\Sigma_g^+$  experimental data from Ref. 1, the  $a^3\Sigma_u^+$  data from Li *et al.*,<sup>11</sup> and the dispersion and exchange contributions to the energy as reported by Marinescu *et al.*<sup>12</sup> The highest considered internuclear distance in Ref. 10 was equal to 9.335 Å in the ground state and to 10.515 Å in the  $a^3\Sigma_u^+$  state, both distances being smaller than  $R_L$ . Although the two previously reported values for  $D_e$  are consistent within their stated uncertainties, it appeared that an experimental observation of vibrational levels corresponding to internuclear distances longer than  $R_L$  would be more satisfactory.

The first part of the paper deals with the experimental procedure used to obtain the spectroscopic data. In Sec. III, we present the method employed for the data reduction and for the determination of the potential energy curves. The long-range analysis is presented in Sec. IV. The dissociation energy value, the dispersion coefficients, and the exchange energy determined in the present work are compared to previously reported evaluations and are discussed in Sec. V.

Finally, conclusions are presented in Sec. VI.

## II. EXPERIMENT

The experimental arrangement has been described previously.<sup>13</sup> About 1 g of potassium metal was loaded into a stainless steel heat pipe oven. Argon gas at 10 mbar pressure was used as a buffer gas. The potassium vapor pressure was about 0.6 mm Hg at the operating temperature of 600 K. The vapor contains 0.5%  $K_2$  molecules.<sup>14</sup>

The molecules are excited by the radiations emitted by a titanium:sapphire laser (Coherent Radiation model 899-21) between 731 nm and 755 nm. This laser, delivering 2.3 W of power, operates in monomode and frequency stabilized conditions during the recording time of FTS spectra, typically 3 h. The fluorescence light emitted in the opposite direction of the laser beam is collected through a pierced mirror and is sent towards a Fourier spectrometer. The spectral resolution of this apparatus,  $0.01 \text{ cm}^{-1}$ , is lower than the spectral lines Doppler width in the studied spectral range which extends between 9 500 and 12 500  $\text{cm}^{-1}$ . Relative wave numbers accuracy is better than  $10^{-3} \text{ cm}^{-1}$ .

A typical example of a spectrum involving the highest observed vibrational level of the ground electronic state is shown in Fig. 1. After excitation with the 737.71 nm laser radiation, a fluorescence series of doublets ( $J'=18$ ) has been observed up to  $v''=81$ . The  $P$  line of the last observed doublet has a poor signal to noise ratio and was considered only after that a preliminary calculation, involving only the  $R$  line, has reasonably predicted its spectral position.

## III. DATA REDUCTION. POTENTIAL ENERGY CURVE

Fifty new fluorescence series were added to our previously reported data set.<sup>8</sup> The data field ( $J', v''$ ) involving the vibrational levels with a vibrational quantum number greater than 73, i.e., from  $v''=74$  to  $v''=81$ , is represented in Fig. 2. It is worth noting that the LeRoy radius corresponds to an effective vibrational level  $v$  of about 76.5 and that only one series is observed up to  $v=81$ .

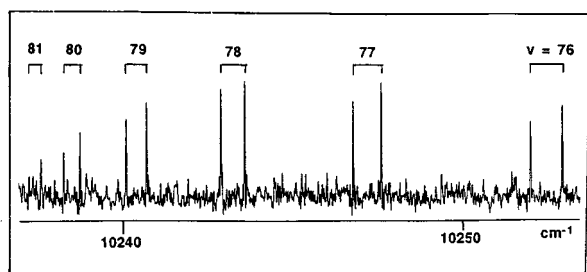


FIG. 1. Fluorescence spectrum induced by the 737.71 nm radiation of a Ti:Sa laser in the  $10\,240\text{ cm}^{-1}$  spectral region. The upper  $A \ ^1\Sigma_u^+$  level has  $J' = 18$ . The  $v$  values in the ground state are noted from  $v = 76$  to  $v = 81$ .

In all 4076 spectral lines quantum numbers were assigned. Their wave numbers were reduced to usual “Dunham-type”  $Y_{ij}$  parameters with a standard deviation between observed and calculated quantities equal to  $2.6 \times 10^{-3} \text{ cm}^{-1}$ . The effective  $Y_{ij}$  parameters are listed in Table I with their respective standard deviations. Only significative parameters improving the quality of the fit are included and some sets  $i, j$  of powers has been excluded. The molecular constants for the newly observed levels are gathered in Table II. They comprise the vibrational  $G(v) + Y_{00}$  values and the rotational  $B, D, H$ , and  $L$  parameters. These constants are deduced from the Dunham power series rather than from fitting the individual levels.

An associated Rydberg–Klein–Rees (RKR) potential energy curve, for  $v$  all the way to a value of  $v = 81$ , was determined using the spectroscopic constants  $Y_{i0}$  and  $Y_{i1}$  of Table I. The RKR1 Computer Code of LeRoy was used for this purpose.<sup>15</sup> This program allows, for the higher vibrational levels to correct for possible slight irregular behavior of the inner potential wall (here after  $v = 75$ ). The slope of

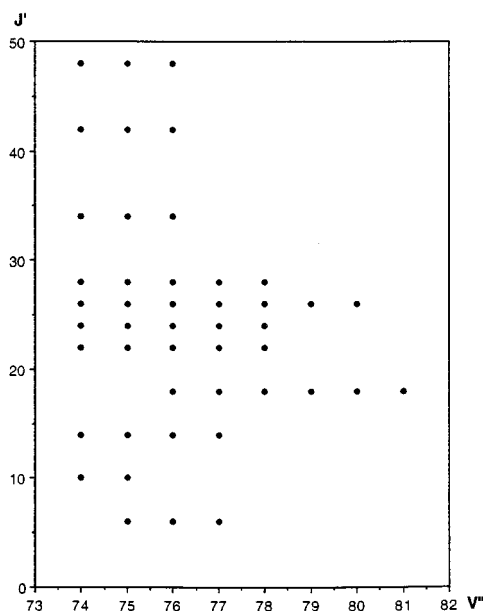


FIG. 2. Data field ( $J', v''$ ) of the observed levels of the  $X \ ^1\Sigma_g^+$  ground state (with  $v''$  larger than 73).

TABLE I. “Dunham-type” coefficients  $Y_{ij}$  of the development  $G(v) = \sum Y_{ij}(v + 1/2)^i [J(J+1)]^j$ , the notation s.d. indicates one standard deviation and % is the percent ratio between s.d. and  $Y_{ij}$ .

$i$	$j$	$Y_{ij}$	s.d.	%
1	0	0.923 976 600 4D+02	0.47D-03	0.001
2	0	-0.324 847 838 1D+00	0.12D-03	0.038
3	0	-0.780 811 444 9D-03	0.14D-04	1.844
4	0	0.932 739 387 2D-05	0.81D-06	8.730
5	0	-0.561 520 887 0D-06	0.19D-07	3.375
9	0	0.216 446 729 6D-11	0.49D-13	2.263
10	0	-0.180 054 189 6D-12	0.37D-14	2.060
11	0	0.690 435 353 4D-14	0.13D-15	1.891
12	0	-0.154 351 001 2D-15	0.27D-17	1.748
13	0	0.213 963 015 2D-17	0.35D-19	1.623
14	0	-0.182 069 398 8D-19	0.28D-21	1.514
15	0	0.874 491 819 4D-22	0.12D-23	1.417
16	0	-0.181 957 495 0D-24	0.24D-26	1.331
0	1	0.561 862 184 5D-01	0.84D-06	0.001
1	1	-0.212 408 654 3D-03	0.89D-07	0.042
2	1	-0.958 898 570 8D-06	0.17D-07	1.747
3	1	-0.441 319 311 6D-07	0.14D-08	3.127
4	1	0.978 264 534 6D-09	0.50D-10	5.161
5	1	-0.174 374 285 1D-10	0.70D-12	4.006
10	1	0.133 072 401 7D-18	0.50D-20	3.782
11	1	-0.603 729 520 9D-20	0.21D-21	3.552
12	1	0.109 475 970 5D-21	0.37D-23	3.354
13	1	-0.929 710 849 9D-24	0.29D-25	3.165
14	1	0.309 211 906 4D-26	0.92D-28	2.976
0	2	-0.827 263 937 1D-07	0.68D-10	0.082
1	2	-0.608 757 022 7D-09	0.39D-11	0.639
2	2	-0.188 425 534 2D-10	0.67D-12	3.530
3	2	0.118 557 391 7D-11	0.57D-13	4.766
4	2	-0.462 313 523 9D-13	0.20D-14	4.235
5	2	0.516 955 628 7D-15	0.24D-16	4.651
10	2	-0.556 976 633 2D-24	0.22D-25	3.919
12	2	0.242 844 470 8D-27	0.87D-29	3.578
13	2	-0.218 233 613 3D-29	0.70D-31	3.225
0	3	0.933 240 506 0D-13	0.15D-14	1.585
3	3	-0.720 592 372 4D-17	0.27D-18	3.774
5	3	0.124 135 681 5D-19	0.41D-21	3.303
6	3	-0.232 486 874 5D-21	0.66D-23	2.835
12	3	0.312 043 412 2D-32	0.15D-33	4.802
13	3	-0.497 432 358 9D-34	0.20D-35	4.084
1	4	-0.726 924 572 6D-20	0.16D-20	22.693
2	4	0.179 227 618 5D-20	0.14D-21	8.027
4	4	-0.293 889 444 6D-23	0.69D-25	2.343

this part of the curve is kept to be correct by fitting the energy values of this inner part of the RKR curve to the formula

$$V(R) = A + B e^{-CR}. \quad (1)$$

TABLE II. Molecular constants (in  $\text{cm}^{-1}$ ) for the observed vibrational levels from  $v = 74$  to  $v = 81$ .

$v$	$G(v)$	$B \times 10^3$	$D \times 10^7$	$H \times 10^{11}$	$L \times 10^{16}$
74	4415.380	16.056 98	5.675	-3.126	-0.81
75	4424.194	14.630 39	6.334	-3.740	-0.86
76	4431.433	13.180 84	7.122	-4.472	-0.91
77	4437.220	11.721 69	8.066	-5.342	-0.96
78	4441.705	10.271 36	9.201	-6.374	-1.01
79	4445.054	8.854 74	10.564	-7.597	-1.07
80	4447.436	7.504 83	12.202	-9.042	-1.13
81	4449.004	6.264 77	14.171	-10.748	-1.18

TABLE III. The RKR potential energy curve  $V(R)$  based on the coefficients of Table I. The quantity  $V(R)$  is equal to  $G(v) + Y_{00}$ , where  $Y_{00} = -0.022 \text{ cm}^{-1}$ .  $R$  in Å is the outer turning point. The internuclear distances relative to the vibrational levels are also indicated.

$v$	$R(\text{Å})$	$V(R) \text{ cm}^{-1} \text{ }^a$
77	11.070 71	4437.198
	11.226 26	4438.435
	11.390 73	4439.593
	11.564 12	4440.675
78	11.747 17	4441.683
	11.940 71	4442.620
	12.145 69	4443.489
	12.363 17	4444.292
79	12.594 42	4445.032
	12.840 93	4445.712
	13.104 50	4446.334
	13.387 38	4446.900
80	13.692 39	4447.414
	14.023 25	4447.878
	14.384 94	4448.292
	14.784 46	4448.660
81	15.231 96	4448.982

<sup>a</sup>Inner wall  $V(R)$  after  $v=75$  (in  $\text{cm}^{-1}$ ):  $V(R) = 500.6612 + 0.106\,791 \times 10^8 \exp(-2.753\,948\,9 \times R)$ .

The behavior of the  $C$  values, as a function of  $R$ , allows to determine whether there exists some energy above which the directly calculated inner potential wall can no longer be trusted. If so, for a certain  $v$  value, the program is rerun with the inner wall calculated with Eq. (1) and the outer turning point is then obtained by adding the  $R2(v) - R1(v)$  quantity to the inner turning point.

The basic data kept for the derivation of the long range parameters involve  $R$  values greater than 11 Å, i.e., well beyond the  $R_L$  limit. They are summarized in Table III with the corresponding energy values  $G(v) + Y_{00}$ . They correspond to vibrational levels from  $v=77$  to  $v=81$ . Also reported are artificial quarters of  $v$  values ranging from  $v=77.25$  to  $80.75$ . These values are interpolated ones and are equivalent to “tensioned cubic spline of RKR points” used to define quasicontinuous potential curves.<sup>10</sup>

An IPA potential curve was also derived following the methods outlined by Vidal *et al.*<sup>16</sup> The differences in energy with the RKR curve being lower than  $0.02 \text{ cm}^{-1}$  we shall consider below only the RKR curve.

#### IV. LONG-RANGE ANALYSIS: DISSOCIATION ENERGY

Several approaches can be used to perform the long-range analysis and to derive the dissociation energy value.

##### A. From the RKR potential energy curve

The ground electronic state of  $K_2$  dissociates into two ground state  $4s^2S$  atoms. At large internuclear distances, the potential energy can be written as a sum of the dissociation energy  $D_e$  and of a quantity  $\Delta V_X$ ,

$$V_X(R) = D_e(X^1\Sigma_g^+) + \Delta V_X(R). \quad (2)$$

When the atomic overlap is small, i.e., at long range, the deviation  $\Delta V_X(R)$  from the dissociation energy can be de-

TABLE IV. The long-range parameters deduced from a fit of the data of Table III (from  $v=77$  to  $v=80$ ) to the expression  $\sum C_n R^{-n} + A \exp^{-aR}$ .<sup>a</sup>

$D_e$	4450.711(5)
$C_6$	17.434 77 (6 050) $\times 10^6$
$C_8$	6.955 97 (6 530) $\times 10^8$
$C_{10}$	1.837 66 (1 930) $\times 10^{10}$
$A$	4.864 98 (20 500) $\times 10^6$
$a$	1.501 152 (5 920)

<sup>a</sup> $D_e$  and  $A$  are expressed in  $\text{cm}^{-1}$ ,  $a$  in  $(\text{Å})^{-1}$ , and  $C_n$  is in  $\text{Å}^n \text{ cm}^{-1}$ .

composed into the sum of a dispersion contribution (or Coulombic)  $\Delta V_c$  and of an exchange contribution  $\Delta V_e$ ,

$$\Delta V_X(R) = \Delta V_c(R) + \Delta V_e(R); \quad (3)$$

$\Delta V_x$ ,  $\Delta V_c$ , and  $\Delta V_e$  being negative quantities.

The second-order Coulombic component or dispersion energy, at large  $R$  values, can be calculated from separated atomic properties and is usually represented as a multipolar expansion in powers of  $R^{-1}$ ,

$$\Delta V_c(R) = -C^6 R^{-6} - C^8 R^{-8} - C^{10} R^{-10} \dots \quad (4)$$

Each term in this series correspond to a particular multipole moment of the charge-charge interaction; dipole-dipole  $C_6$ , dipole-quadrupole  $C_8$ , and dipole-octupole and quadrupole-quadrupole  $C_{10}$ .<sup>17-20</sup>

The exchange energy  $\Delta V_e$  is well represented by the approximate formula, suitable at large internuclear distance

$$\Delta V_e(R) = -A e^{-aR}. \quad (5)$$

The  $V(R)$  [or  $G(v) + Y_{00}$ ] values of the RKR outer turning points, reported in Table III, have then been fitted to the following expression:

$$V(R) = D_e - C^6 R^{-6} - C^8 R^{-8} - C^{10} R^{-10} - A e^{-aR}. \quad (6)$$

As starting parameters we chose the  $C_n$  constants calculated by Marinescu *et al.*<sup>12</sup> and for the exchange energy the values determined by Zemke *et al.*<sup>10</sup> To derive the parameters  $A$  and  $a$  of Eq. (5) these authors fitted the difference of the calculated potentials for the  $X$  and  $a$  state, as derived by Magnier.<sup>21,22</sup>

In a first fit, if we constrain the  $D_e$  and  $C_n$  values to the one used in Ref. 10, the experimental energies cannot be reproduced; the rms of the deviations between observed and calculated wave numbers being larger than  $1 \text{ cm}^{-1}$ . If only the coefficient  $D_e$  is left free to vary, with the coefficients  $C_n$ ,  $A$ , and  $a$  fixed, it is found  $D_e = 4450.70(11) \text{ cm}^{-1}$ . As the number of experimental points to be employed to determine the coefficients of Eq. (6) is limited to five, multiple and successive fits were performed. The coefficients  $D_e$ ,  $C_6$ ,  $C_8$ ,  $C_{10}$  were first constrained;  $D_e$  to the preceeding value and the  $C_i$  to the calculated values.<sup>12</sup> The derived  $A$  and  $a$  parameters were then constrained in a second fit where  $D_e$ ,  $C_6$ , and  $C_8$  were left free. After four cycles convergence is achieved and the constants reported in Table IV are obtained. They allow one to reproduce the observed wave numbers to about  $10^{-3} \text{ cm}^{-1}$ . In Table V are also given, for each  $R$  value, the contributions  $-\Delta V_c(R)$  and  $-\Delta V_e(R)$  and the derived  $D_e$  values obtained by summing  $V(R)$  to  $-\Delta V_c(R)$

TABLE V. Coulombic energies  $-\Delta V_c$ , exchange energies  $-\Delta V_e$  and their sum  $V(R) - \Delta V_c - \Delta V_e$  as a function of the internuclear distance  $R$ . The quantities  $-\Delta V_c$  and  $-\Delta V_e$  are obtained from the parameters of Table IV.<sup>a</sup>

$R$	$G(v) + Y_{00} = V(R)$	$-\Delta V_c$	$-\Delta V_e$	$V(R) - \Delta V_c - \Delta V_e$
11.070 71	4437.1978	13.218	0.295	4450.7104
11.226 26	4438.4349	12.045	0.233	4450.7133
11.390 73	4439.5930	10.936	0.182	4450.7115
11.564 12	4440.6748	9.895	0.141	4450.7103
11.747 17	4441.6829	8.920	0.107	4450.7098
11.940 71	4442.6199	8.010	0.080	4450.7097
12.145 69	4443.4886	7.163	0.059	4450.7103
12.363 17	4444.2916	6.377	0.042	4450.7111
12.594 42	4445.0317	5.651	0.030	4450.7121
12.840 93	4445.7115	4.981	0.021	4450.7129
13.104 50	4446.3336	4.366	0.014	4450.7130
13.387 38	4446.9004	3.802	0.009	4450.7117
13.692 39	4447.4144	3.288	0.006	4450.7082
14.023 25	4447.8777	2.820	0.004	4450.7014
14.384 94	4448.2924	2.396	0.002	4450.6900
14.784 46	4448.6600	2.011	0.001	4450.6722
15.231 96	4448.9822	1.663	0.0005	4450.6461

<sup>a</sup> $R$  is in Å and other quantities in  $\text{cm}^{-1}$ .

and to  $-\Delta V_e(R)$ . A representation of  $-\Delta V_c(R)$  is plotted in Fig. 3 both using the  $C_n$  parameters derived in the present paper and those calculated by Marinescu *et al.*<sup>12</sup> The exchange energy, in a logarithmic scale, is depicted in Fig. 4. The figure shows clearly the validity of the exponential representation for  $\Delta V_e$ . Also, in the studied spectral range of internuclear distance, the exchange contribution is much lower than the dispersion one since  $\Delta V_e \leq (2/100) \Delta V_c$ .

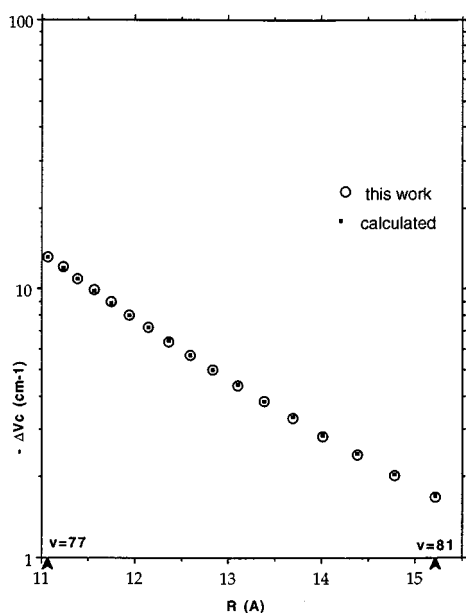


FIG. 3. Plot, on a logarithmic scale, of the dispersion energy  $-\Delta V_c$  (in  $\text{cm}^{-1}$ ) as a function of  $R$ . The calculated values are derived from the calculated parameters quoted in Ref. 12.

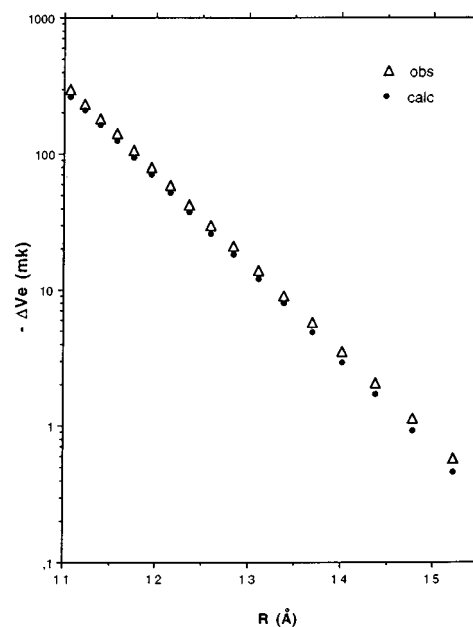


FIG. 4. Plot, on a logarithmic scale, of the exchange energy  $-\Delta V_e$  in mk ( $10^{-3} \text{ cm}^{-1}$ ) as a function of the internuclear distance  $R$ . The calculated values are derived from the calculated parameters quoted in Ref. 12.

## B. From the near-dissociation expansion (NDE) theory of LeRoy (Ref. 23)

For most bound electronic states of diatomic molecules the very long-range potential asymptotically takes on the simple inverse-power form if the exchange energy is neglected,

$$V(R) = D_e - C_n R^{-n}. \quad (7)$$

Here only one term is retained in the expansion development (5). LeRoy has shown that the limiting near-dissociation behavior of the vibrational level energies is given by

$$G(v) = D - X_0(n)(v_D - v)^{2n/n-2}. \quad (8)$$

In this expression  $v_D$  is an effective noninteger vibrational index at dissociation,  $n$  is equal to 6 in the case of the  $4s\ ^2S + 4s\ ^2S\ K_2$  ground state, and  $X_0(n)$  is a numerical factor depending on  $n$  and on physical constants like the reduced mass and  $C_n$ . Near-dissociation expansions (NDE) in fact incorporate the correct limiting behavior into empirical expansions taking account of all the set of observed energy levels. As an example, an “outer” 3/5 expansion is represented by the following Padé approximants:

$$G(v) = D - X_0(6)(v_D - v)^3 L/M, \quad (9)$$

with

$$L = 1 + p_1 z^2 + p_2 z^3 + p_3 z^4,$$

and

$$M = 1 + q_1 z^2 + q_2 z^3 + q_3 z^4 + q_4 z^5 + q_5 z^6,$$

where

$$z = v_D - v.$$

TABLE VI. Coefficients  $p_i$  and  $q_i$  (in  $\text{cm}^{-1}$ ) of the “Padé” development of the  $G(v) + Y_{00}$  values (from  $v=0$  to  $v=80$ ) obtained applying the NDE method.<sup>a</sup>

$p_1$	$0.542\,459\,273\,62 \times 10^{-2}$
$p_2$	$0.411\,090\,175\,37 \times 10^{-3}$
$p_3$	$-0.553\,619\,319\,92 \times 10^{-6}$
$q_1$	$0.482\,811\,513\,29 \times 10^{-2}$
$q_2$	$0.189\,025\,751\,08 \times 10^{-3}$
$q_3$	$0.845\,102\,694\,43 \times 10^{-5}$
$q_4$	$0.680\,301\,101\,14 \times 10^{-7}$
$q_5$	$-0.206\,250\,998\,02 \times 10^{-9}$

<sup>a</sup> $v_D = 85.284$ ;  $X_0 = 0.2209 \text{ cm}^{-1}$ , and  $D_e + Y_{00} = 4450.792 (10) \text{ cm}^{-1}$ .

The 81 experimental energies, all weighted equally from  $v=0$  to  $v=81$ , were fitted with  $X_0(6) = 0.2209 \times 10^{-1} \text{ cm}^{-1}$  (taking  $C_6$  from Table IV). The rms of the deviations between observed and calculated wave numbers was  $1.7 \times 10^{-3} \text{ cm}^{-1}$ . The Padé coefficients  $p_i$  and  $q_i$  are summarized in Table VI. From this particular fit it was found that  $v_D = 85.284(10)$  and  $D_e = 4450.792(14) \text{ cm}^{-1}$ .

As noticed by LeRoy<sup>23</sup> the method “replaces blind extrapolations by an interpolation between experimental data for levels lying far from dissociation, and the exactly-known functional behavior for that property at the limit.”

Fits to different NDE functions (varying the number of Padé coefficients) yield slightly different estimates for the parameters  $D$  and  $v_D$ . The values of all the resulting parameters has then been averaged using a particular weighting. The recommended values are then  $D_e = 4450.78(8) \text{ cm}^{-1}$  and  $v_D = 85.27(6)$ .

The value of the predissociation energy compares favorably to the direct determination quoted in Table IV and to the above given value.

### C. From $dG(v)/dv$ as a function of $G(v)$ or $v$

Bernstein<sup>24</sup> demonstrated that if the long-range potential can be approximated by a dominant effective term like in Eq. (7), the following relation holds:

$$dG(v)/dv = (K_n/\mu^{0.5} C_n^{0.5}) [D_e - G(v)]^{(n+2)/2n}.$$

In the case of  $K_2$  the expression becomes

$$G(v) = D_e - 0.020\,037 C_6^{0.25} [dG(v)/dv]^{1.5}.$$

The quantity  $[dG(v)/dv]^{1.5}$  vs  $G(v)$  is represented in Fig. 5. The curve is linear and a fit gave a dissociation energy  $D_e$  of  $4450.8 \text{ cm}^{-1}$ . From the slope of the plot,  $C_6$  was calculated to be  $14.9 \times 10^6 \text{ cm}^{-1} \text{ Å}^6$ .

LeRoy also showed that an integral form of the previous expression becomes, in the case of  $K_2$ ,

$$v = v_D - 0.060\,113 C_6^{0.25} [dG(v)/dv]^{0.5}.$$

Thus  $[dG(v)/dv]^{0.5}$  is a linear function of  $v$ , and as shown in Fig. 6, the linearity appears to extend over a large number of vibrational levels. From the slope and intercept of the least-squares linear fit to the represented points, we found that  $C_6 = 18.07 \times 10^6 \text{ cm}^{-1} \text{ Å}^6$  and  $v_D = 85.25$ . It is worth

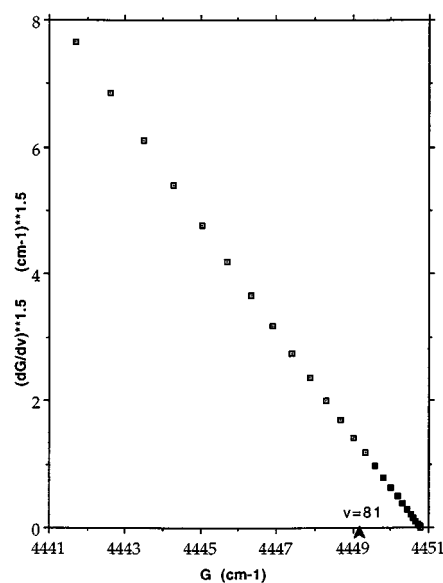


FIG. 5. Plot of  $[dG(v)/dv]^{1.5}$  as a function of  $G(v)$ . After  $v=81$  (black squares), the data are extrapolated using a NDE-based RKR potential (Table VI).

to note that all the previously reported determinations are consistent. Our recommended value is the one derived from the NDE method i.e.,

$$D_e = 4450.78 \pm 0.15 \text{ cm}^{-1}.$$

The associated accuracy takes account of the dispersion of the different determinations.

To summarize the results, a representation of the potential at very large internuclear distances, as obtained by the NDE extrapolation method, is shown in Fig. 7. Also the

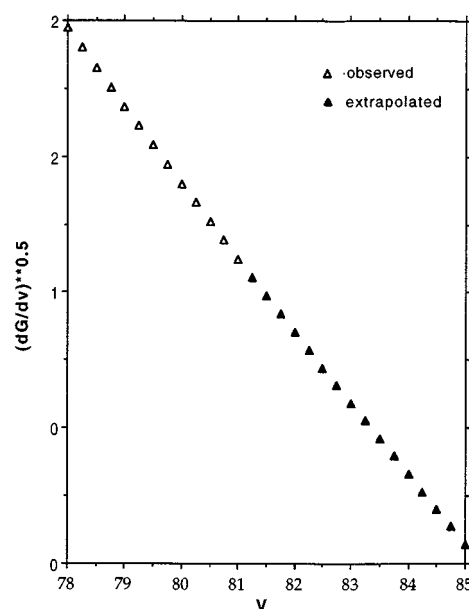


FIG. 6. Plot of  $[dG(v)/dv]^{0.5}$  as a function of  $v$ . Extrapolated values after  $v=81$  (black triangles) are obtained from a RKR potential constructed with the NDE parameters of Table VI.

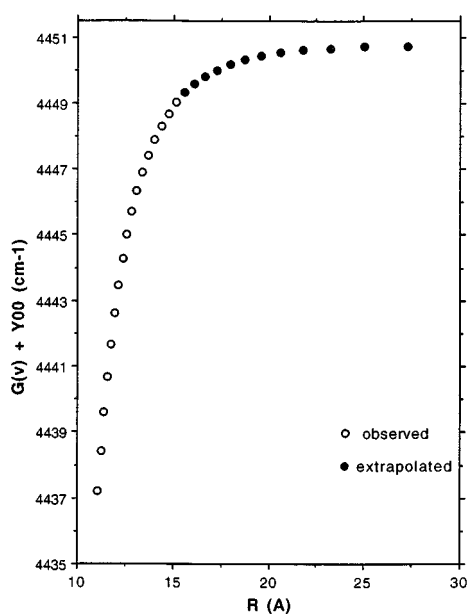


FIG. 7. Outer part of the RKR potential curve as a function of the internuclear distance  $R$ . Extrapolation up to 30 Å is obtained with a NDE-based RKR potential.

graph of Fig. 8 represents the variation of the last quantum numbers  $v$  as a function of the internuclear distance  $R$ .

## V. DISCUSSION

### A. Comparison of the $C_n$ parameters

Many theoretical studies have been reported using a variety of methods for the evaluation of the multipole polarizabilities of the alkali-metal atoms.<sup>25,32</sup> A comparison of the previously reported  $C_n$  parameters is presented in Table VII. The agreement is generally good with all the determinations,

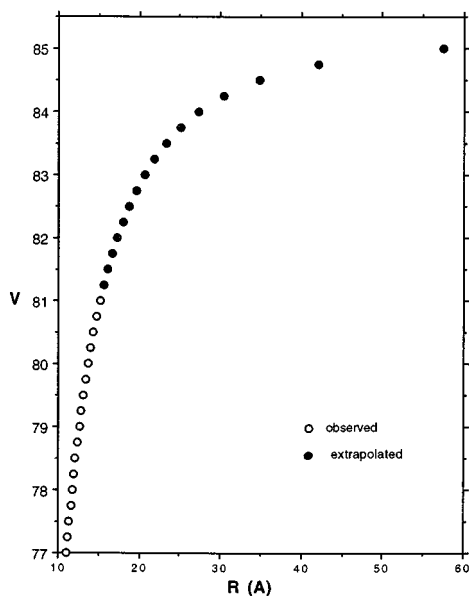


FIG. 8. Representation of the vibrational number  $v$  as a function of  $R$ . Extrapolation up to 60 Å is obtained through a RKR-NDE curve.

TABLE VII. Comparison of the  $C_n$  coefficients (in  $\text{cm}^{-1}$ ).  $C_n$  values should be multiplied by  $10^n$ . Conversions to atomic units can be obtained with  $a_0 = 0.529\,177\,25\text{ Å}$  and  $1\text{ hartree} = 219\,474.631\,418\text{ cm}^{-1}$ .

Reference	$C_6$	$C_8$	$C_{10}$
25	18.4100		
18 and 26	19.7595		
	17.7353		
27	18.7474	6.0190	2.0748
28	19.0125	5.1742	1.7089
29	17.2245		
30	18.2173		
31	22.7523	5.2552	1.5377
32	17.5281	5.4131	2.0525
12	18.3763	5.5278	1.9833
10	18.3763	5.5278	1.9833
	(7711)	(2160)	(758)
This work	17.4348	6.956	1.8377
	(605)	(65)	(193)

especially with the values of Spelsberg *et al.*<sup>32</sup> It is often assumed<sup>5</sup> that the coefficient  $C_{10}$  is nearly equal to  $1.3\,C_8^2/C_6$ . From the values reported in Table IV the ratio is 0.662. Our derived  $C_8$  coefficient seems too high.

### B. Comparison of the exchange energies

Differences between the two potential energy curves for the  $X \ ^1\Sigma_g^+$  and  $a \ ^3\Sigma_u^+$  electronic states have been calculated using predictive asymptotic surface integral methods by Aubert-Frécon.<sup>33</sup> A comparison of the  $\Delta V_e$  values is presented in Fig. 9. The agreement is quite satisfactory since the differences decrease from  $0.2\text{ cm}^{-1}$  to less than  $0.001\text{ cm}^{-1}$  when the distance  $R$  varies from  $10\text{ Å}$  to  $15\text{ Å}$ . It is worth to note that our determination is based on a study of the internuclear distance ranging from  $11\text{ Å}$  to  $15\text{ Å}$ . Near smaller  $R$

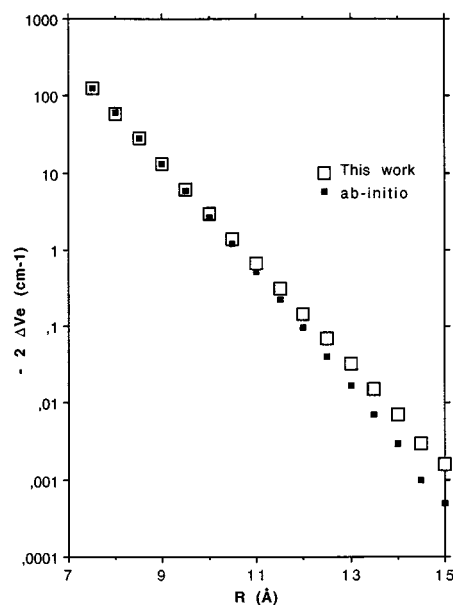


FIG. 9. Plot of the differences of the  $-2\Delta V_e$  quantities (in  $10^{-3}\text{ cm}^{-1}$ ) obtained from this work (using the data between  $11\text{ Å}$  and  $15\text{ Å}$ ) and from the *ab initio* results of Ref. 33.

values the predicted asymptotic results remain consistent with our derivations down to 7.5 Å where the differences is only 0.8 cm<sup>-1</sup>.

### C. Comparison of $D_e$ determinations

In a recent paper, Zemke *et al.*<sup>10</sup> found a smaller value for  $D_e$ , i.e., 4449.1±1 cm<sup>-1</sup>. The authors perform a mean between the  $D_e$  determinations obtained for the  $X\ ^1\Sigma_g^+$  and a  $^3\Sigma_u^+$  electronic states. For the  $X$  state, using our previously derived parameters,<sup>8</sup> a total energy of 4449.1±1.8 cm<sup>-1</sup> is found at  $R=9.33$  Å, in agreement with the calculations reported in the present work. The low evaluation of  $D_e$  seems due to the potential of the  $a$  state. In the “experimental” work of Li *et al.*,<sup>11</sup> an accuracy of ±2 cm<sup>-1</sup> was given for  $D_e$  ( $a\ ^3\Sigma^+$ ). Later on Zemke *et al.*<sup>10</sup> correct their RKR curve using theoretical calculations reported by Magnier.<sup>21,22</sup> They shifted the uppermost  $v=14-17$  turning points to slightly smaller internuclear distances. This treatment is perhaps responsible for the lowering of the  $D_e$  values obtained using the triplet potential curve. In any way, the very good agreement of the “experimental” and theoretical exchange energies shows that at 15 Å such a low total energy cannot be obtained.

### VI. CONCLUSIONS

Following our results, the LeRoy criterion at or outside the “LeRoy radius” (10.8 Å) is confirmed for the interaction of two ground state potassium atoms. The long-range forms of the dispersion energy  $\Delta V_c = -\Sigma C_n R^{-n}$  and of the exchange energy  $\Delta V_e = -Ae^{-aR}$  are in good agreement with the most recent calculations.<sup>12,33</sup> The potential energy curves determined in the present work range from high on the inner wall above the dissociation energy to very large internuclear distances. However, new experiments are still necessary to improve the accuracy of the energies for  $R$  larger than 15 Å. Use of photoassociation spectroscopy would be a nice tool for such experiments.

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