PHYSICAL REVIEW A VOLUME 35, NUMBER 9 MAY 1, 1987

Ground-state reduced-potential curves and estimation of the dissociation energy of alkali-metal diatomic molecules

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(Received 22 November 1985; revised manuscript received 1 May 1986)

The Rydberg-Klein-Rees potentials for the ground states of alkali-metal diatomic molecules, recently obtained on the basis of new measurements employing modern techniques, have been analyzed with the use of the reduced-potential curve (RPC) method. It is shown that the behavior of this group of chemically related molecules is fully in accord with the overall regularities observed for many other groups of diatomic molecules. The RPC scheme seems to lead to a picture that might be loosely called "a periodic system of diatomic molecules." The method also permits a rather accurate estimation of dissociation energies and detection of errors in the analysis of the spectra or in the calculation of the potentials in general, which is applied to a critical evaluation of some papers on alkali-metal diatomic molecules.

I. INTRODUCTION

The interesting results obtained in a comparative study of the ground-state internuclear potentials of alkali-metal hydrides with the use of the reduced-potential curve (RPC) method[1] suggested that a similar analysis of the ground-state potentials of alkali-metal diatomic molecules should be worthwhile. The diatomic alkali-metal molecules are now of special interest, in particular in laser spectroscopy (alkali-metal dimer optically pumped lasers).

All fundamental spectroscopic concepts are defined in the framework of the adiabatic approximation[2] in which the internuclear potential of a diatomic system determines all interesting information on the system. Therefore, the knowledge and a systematic study of internuclear potentials of diatomic molecules are of fundamental interest. The RKR (Rydberg-Klein-Rees) method[3] of calculating the internuclear potentials of diatomic molecules from the measured spectral lines has now become a standard procedure where the adiabatic approximation may be considered as sufficiently accurate. Deperturbed, corrected RKR potentials are calculated if non-negligible perturbations are present.[4] The reliability of the RKR method is supported by many results (cf. Refs. 1 and 5). Modern experimental techniques (in particular, laser spectroscopic methods) have now made the determination of the potential well almost up to the dissociation limit possible. The accuracy of the rotational analysis of the spectrum, to which the RKR method is very sensitive, has also been improved. New spectroscopic results obtained with the use of such modern techniques also enabled the construction of the ground-state RKR potentials of diatomic alkali-metal molecules up to high vibrational levels, which certainly makes an RPC analysis of these potentials interesting. In the following section, we shall briefly sketch the essence and the results of the RPC method.

II. THE RPC (REDUCED-POTENTIAL CURVE) METHOD

The RPC method was developed to permit a visualization of the relations and differences between the internuclear potentials of various molecules and states in a unified geometrical picture. The values of the spectroscopic constants of various diatomic molecules, the shape of the potential curves, and their location in the r-U diagram (r is the internuclear distance, U is the energy) are so diversified that, without such a scheme, a systematic comparative study of the potentials of diatomic molecules is absolutely impossible. All internuclear potentials are here represented in terms of dimensionless "reduced" quantities ρ (the reduced internuclear distance) and u (the reduced-potential energy). The graph of the function $u(\rho)$ is the RPC. The reduced quantities are defined as follows:

$$u=U/D_e\ , \tag{1}$$

$$\rho=\frac{r-[1-\exp(-r/\rho_{ij})]\rho_{ij}}{r_e-[1-\exp(-r/\rho_{ij}]\rho_{ij}}\ , \tag{2}$$

$$\rho_{ij}=\frac{r_e-(\kappa D_e/k_e)^{1/2}}{1-\exp(-r_e/\rho_{ij})},\quad \kappa=3.96 \tag{3}$$

$$k_e=(d^2U/dr^2)_{r=r_e}\ . \tag{4}$$

r_e and $-D_e$ are the coordinates of the minimum of $U(r)$. For practical reasons ρ versus $u+1$ is always plotted in the figures (which makes both quantities positive).

In spectroscopy, one currently uses the following approximation for k_e, which appears to be very accurate in most cases (perhaps not all):

$$k_e=\mu\omega^2=4\pi^2c^2\mu\omega_e^2\ . \tag{5}$$

Here μ is the reduced mass of the diatomic system, ω is the harmonic vibration frequency determined from the spectrum, ω_e is the "harmonic" spectroscopic vibrational constant, and c is the velocity of light. For most ground states, the approximation of Eq. (5) is indeed acceptable and is used in the RPC method (and checked by interpolation). The RPC for an electronic state of a diatomic molecule may be calculated from the RKR potential, inserting the values of internuclear distance r and potential energy U in Eqs. (1)—(3). The shape of the RPC is very sensitive to a change in the value of r_e, rather sensitive to a change in the value of k_e, and rather insensitive to a change in the value of D_e (for the specific change of the geometry of RPC due to a change in the value of one of these constants cf. Ref. 5). Only the tail of the right limb is very sensitive to a small change of D_e, which may be used for checking the value of D_e.

Since there are only about 10^2 atoms, however, and about 10^4 diatomic molecules and (singly ionized) molecular ions, the RPC scheme should presumably be very complicated and will certainly contain many exceptions and anomalies. (By way of example let us mention the Be_2 molecule.[6]) Nevertheless, the importance of a unifying systematic scheme for diatomic molecules is clear and stimulates our interest in the RPC method. We consider worthwhile any pioneer (however difficult) attempt in this direction. Unfortunately, available spectroscopic data permits the construction of the RKR potentials only for a number of about 100 diatomic molecules and radicals; for many molecules, the potential still cannot be constructed for sufficiently high values of $u+1$ and in many cases it cannot be considered to be sufficiently reliable. Moreover, for many molecules the dissociation energy is not known or is only roughly estimated. Notwithstanding, the results obtained as yet for the ground states lead to interesting regularities.

The determination of the RKR potentials of heavy diatomic molecules up to large values of $u+1$, i.e., in the higher part of the potential well, has been made possible only recently with the use of modern laser techniques. The evaluation of the new data[1,6–10] required a reformulation of the RPC scheme. Whereas the results obtained previously suggested a monotonic dependence of the shape of the ground-state RPC on the atomic numbers of the molecules,[5] a comparative study of the ground-state RPC's, including also RPC's of heavier (in particular, metallic) molecules for sufficiently high values of $u+1$, has shown that the dependence on the atomic numbers is in fact more complicated. The RPC scheme seems to lead to a picture that might loosely be called "a periodic system of diatomic molecules."[6]

This scheme may be described as follows.

(i) By definition, the RPC's of different diatomics have a common minimum (1,0).

(ii) There are groups of chemically related molecules (e.g., nonmetallic hydrides; alkali-metal hydrides; hydrides of the II*a* and II*b* group; nonmetallic homonuclear molecules of the fifth, sixth, and seventh column of the Periodic Table; mercury halides; etc.) in which the following rules hold: (a) The RPC's of different diatomic molecules of the group do not intersect anywhere; and (b) the shape of the RPC within the group changes with increasing atomic numbers as follows. The RPC turns to the right around the common minimum while becoming broader ("the reduced attractive force decreases").

(iii) The noncrossing rule holds for all diatomic molecules in the left limb and it also approximately holds for many molecules in the right limb. Nevertheless, slight crossings of the RPC's of different groups may appear in particular in the highest parts of the right limb.

(iv) The RPC's of the rare gases (ground states!) coincide approximately and form the right-hand boundary of the admissible RPC region in the ρ versus $u+1$ diagram (i.e., no ground-state RPC lies to the right of this curve). For nonmetallic molecules, the left-hand boundary of this region[11] is formed by the RPC of H_2.

(v) The differences in ρ between the RPC's are very small in the left limb, i.e., the "quasiparallel" RPC's of all diatomic molecules lie close together in the left limb.[12]

In Ref. 1 (Figs. 1, 2, and 8) we already emphasized the interesting fact that even RPC's of many diatomic molecules with radically different values of molecular constants and different shape of the RKR potential curve may almost coincide in the reduced form and no significant crossing occurs anywhere.

Such results clearly show the existence of certain interesting laws expressed by the formula of the reduced potential. Crude deviations from the RPC scheme outlined above (in particular salient crossings) could as yet always be shown to be due to an error in the analysis of the spectrum, e.g., for Cl_2 (Refs. 10 and 13) and Bi_2 (Refs. 9 and 10), or to an error in the calculation of the RKR potential (in particular extrapolations), e.g., for mercury halides,[9] halogen hydrides,[14] and some metal hydrides,[15] or to incorrect values of the dissociation energy.[1,7] Thus the noncrossing rule may be used for quite accurate estimation of dissociation energy comparing the RPC's of diatomic molecules belonging to the same group (the tail of the RPC being very sensitive to a change in D_e) and for rough estimation comparing the RPC's of diatomic molecules belonging to different groups, if the RKR curves can be calculated for sufficiently high values of $u+1$. It may further be used for detection of errors in the analysis of the spectrum (errors in the constants) or errors in the calculation of the potential, as has been mentioned above. We shall employ this method also in the present paper to diatomic alkali molecules in Sec. III.

The RPC is admittedly an empirical method; however, no better method for a direct comparison of the potentials is known. A rigorous proof of the RPC formula is impossible.[5] So the method must be judged with respect to its practical results—as any other method. The results at least seem to be interesting. The RPC formulas are perhaps not ideal and could be improved.[5,6] Nevertheless, the regularities revealed by using these formulas, and the significance of a practical application of the method, are too salient to be overlooked.

III. THE DISSOCIATION ENERGIES AND THE GROUND-STATE RPC'S OF DIATOMIC ALKALI-METAL MOLECULES

The ground-state RKR potential curves and the corresponding molecular constants of nine diatomic alkali-metal molecules recently calculated on the basis of new spectroscopic data are analyzed here, i.e., the five alkali-metal dimers and four heteronuclear combinations: Li_2 (Ref. 16), Na_2 (Refs. 17 and 18), K_2 (Ref. 19), Rb_2 (Ref. 20), Cs_2 (Ref. 21), LiK (Ref. 22), LiRb [Ref. 22(b)], NaK [Ref. 23(a)], NaCs (Ref. 24).

The RKR curves could be constructed almost up to the dissociation limit for Li_2, Na_2, NaK, and Cs_2 and the dissociation energies of these molecules could be determined to high accuracy.[16,17,21,23] Also the dissociation energy of K_2 seems now to be fixed to high accuracy on the basis of the analysis of the $C\,^1\Pi_u$ state.[25] [A somewhat smaller value (4192 cm^{-1}) was previously accepted.[26]]

The limits of error for D_e(NaCs) proposed in Ref. 24 are ± 100 cm^{-1}. On the other hand, the values of the dissociation energies proposed by the experimenters for Rb_2 (Refs. 26–28), LiK (Ref. 22), and LiRb [Ref. 22(b)] must be considered as rather rough estimates.

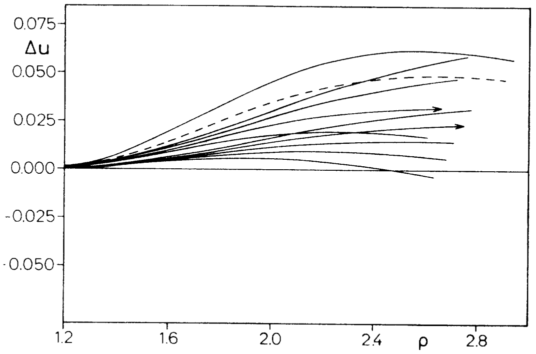

FIG. 1. Comparison of the ground-state RPC's (right limbs) of K_2 and Rb_2 for various values of D_e(cm^{-1}). Differences in u from the RPC of Cs_2 (zero straight line). Solid lines from top to bottom: Na_2; K_2 (4192); K_2 (4300); K_2 (4440); K_2 (4600); Rb_2 (3870); Rb_2 (3950); Rb_2 (4020); Rb_2 (4100); Rb_2 (4200). Dashed line: NaK. [Using the old value (Ref. 26) of $D_e(K_2)=4192$ cm^{-1} one obtains a salient crossing of the RPC's of K_2 and Na_2.] The arrows indicate the RPC's of K_2 and Rb_2 for values of D_e finally adopted.

Therefore, we first try to check the D_e values proposed by the experimentalists for Rb_2 with the use of the RPC method and shall test also different values of $D_e(K_2)$. (Such a test is meaningless for LiK and LiRb for reasons explained below.) Figure 1 shows the differences in u between the ground-state RPC's of the alkali-metal dimers in the right limb, the RPC of Cs_2 being chosen for comparison. The value 3939 cm^{-1} has been proposed by Breford and Engelke[27] as the lower limit for $D_e(Rb_2)$; no value was indicated in Ref. 20. Figure 1 shows that, indeed, the value 3950 cm^{-1}, proposed in Ref. 28 as the most probable value, seems reasonable, since it makes the RPC of Rb_2 "quasiparallel" to the accurate RPC of Na_2; the value 3870 cm^{-1} evidently seems too small and the values 4200 and even 4020 are too large, since they imply a crossing of the RPC of Cs_2. For K_2, the old value of $D_e(K_2)=4192$ cm^{-1} evidently is too small, since it leads to a crossing with the RPC of Na_2, and so is also the value 4300 (they would also lead to a crossing of the RPC of NaK). The value 4600 cm^{-1} is already too large, since it leads to a crossing with the RPC of Rb_2. The value $D_e(K_2)=4440$ recently proposed[25] seems, indeed, to be the most probable value. The values of the molecular constants finally adopted (together with the corresponding references) are given in Table I. Table II summarizes the

TABLE I. (a) Values of molecular constants. (The values are quoted as given in the reference; all the digits are, of course, not relevant for the graphical comparison.) (b) References for the molecular constants.

(a)

Molecule	Z_1	Z_2	r_e (Å)	ω_e (cm^{-1})	D_e (cm^{-1})	ρ_{ij} (Å)
$^7Li_2$	3	3	2.673 24	351.390	8516.78	1.172 85
Na_2	11	11	3.079 08	159.177	6022.6	1.691 47
K_2	19	19	3.924 43	92.3994	4440	2.625 49
Rb_2	37	37	4.209 90	57.7810	3649.5	3.045 29
Cs_2	55	55	4.648 00	42.0203	3650	3.600 19
LiK	3	19	3.316 87	211.910	6150	1.889 96
LiRb	3	37	3.456 59	195.230	6000	2.021 23
NaK	11	19	3.496 80	124.0124	5274.9	2.129 21
NaCs	11	55	3.850 00	98.8851	4950	2.564 50
H_2	1	1	0.741 44	4403.210	38 297	0.018 00
HF	1	9	0.916 81	4138.320	49 383	0.295 92

(b)

	Ref.	Ref.	Ref.
Li_2	16	16	16
Na_2	17,18	17,18	17,18
K_2	19	19	25
Rb_2	20	20	28
Cs_2	21	21	21
LiK	22	22	22
LiRb	22(b)	22(b)	22(b)
NaK	23(a)	23(a)	23(a)
NaCs	24	24	24
H_2	26	26	26
HF	26	26	26

TABLE II. References for the RKR curves of the diatomic alkali-metal molecules.

Molecule	RKR curves for the RPC's	Potential curves used for comparison
Li_2	16	31
Na_2	17,18	32
K_2	19	27
Rb_2	20	22(b)
Cs_2	21	
LiK	22	
LiRb	22(b)	
NaK	23(a)	23(b),23(c)
NaCs	24	

references for the RKR curves.

Figures 2—5 show the RPC's of the diatomic alkali-metal molecules studied in the global RPC scheme. The RPC's of H_2 and of the rare gases and the RPC of O_2 are shown for comparison[6] to convey a feeling for the significance of the differences. One may clearly see that the RPC's of the alkali-metal dimers lie close together and seem to obey rules ii(a) and ii(b) (Sec. II). They lie slightly more to the left-hand side of the RPC of H_2 than the RPC's of the (practically coinciding) RPC's of alkali-metal hydrides[1] in the left limb, as the comparison with the RPC of LiH shows (Fig. 2). In the right limb, the RPC's are not so closely coinciding as the RPC's of the alkali-metal hydrides, since there exist too large differences in the two atomic numbers: the RPC of the very heavy molecule Cs_2 ($Z=55$) already lies under the RPC of H_2 (Fig. 3); however, it lies very far to the left of the RPC of I_2 ($Z=53$). The (almost coinciding) RPC's of the alkali-metal hydrides would approximately lie between the RPC of Li_2 and the RPC of H_2.[1]

The potentials for LiK and LiRb have been calculated in Ref. 22(a) and in the Ph.D. thesis of Hage[22(b)] using the RKR method. However, the Dunham coefficients were not determined from a complete fit of the spectral data [Refs. 22(a) and 22(b)]; the two lowest vibrational constants and the rotational analysis relied essentially on the very accurate selectively detected laser induced fluorescence (SDLIF) data for $v''=0,1,2,3$. Though these constants appeared to be in a very good agreement with the data for the higher vibrational levels obtained from LIF (laser induced fluorescence),[22] the following important question arises: Are the molecular constants obtained by this procedure accurate enough for the calculation of a reliable RKR potential? One may assume that such a procedure might not be accurate enough and could in fact be considered as a sort of extrapolation; however, extrapolation procedures have been shown[5,7,9,14,15] to lead to significant errors in the RKR potential. Since the detection of errors in the RKR curves is a declared aim of the RPC method, an application of the RPC analysis for a critical

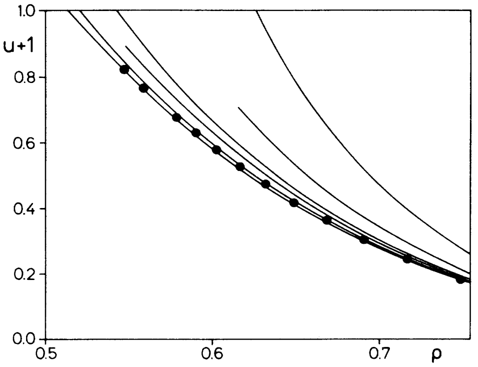

FIG. 2. Ground-state RPC's of alkali-metal dimers (left limbs). Solid lines from left to right: (practically) coinciding RPC's of Li_2 and Na_2; (practically) coinciding RPC's of Rb_2 and Cs_2; LiH; H_2; O_2; rare gases. ●: K_2. The ρ scale is about 14 times more sensitive than in Fig. 3 (right limbs). (RKR curves for H_2, O_2, and rare gases from Ref. 6.)

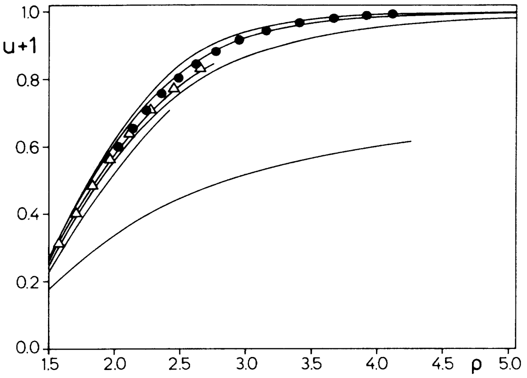

FIG. 3. Ground-state RPC's of alkali-metal dimers (right limbs). Solid lines from left to right: Li_2; Na_2; Rb_2; Cs_2; O_2; rare gases. ●, H_2; △, K_2.

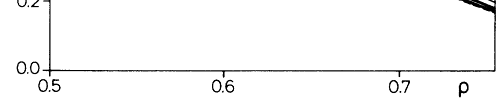

FIG. 4. Ground-state RPC's of heteronuclear diatomic alkali-metal molecules (left limbs). Solid lines from left to right: LiK; NaK; NaCs; H_2; LiRb; O_2; rare gases. Dashed line: Na_2. The ρ scale is about 14 times more sensitive than in Fig. 5 (right limbs). (RKR curves for H_2, O_2, and rare gases from Ref. 6.)

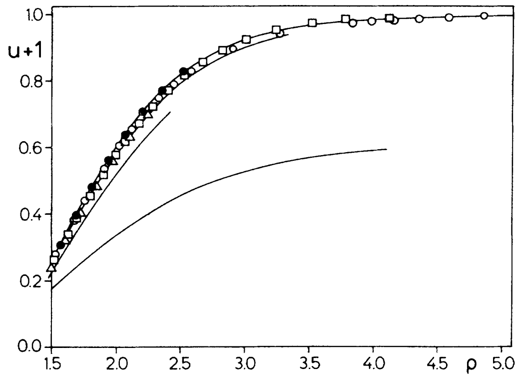

FIG. 5. Ground-state RPC's of heteronuclear diatomic alkali-metal molecules (right limb). Solid lines from left to right: Na_2; NaCs; O_2; rare gases; ●, LiK; ○, NaK; △, LiRb; □, H_2.

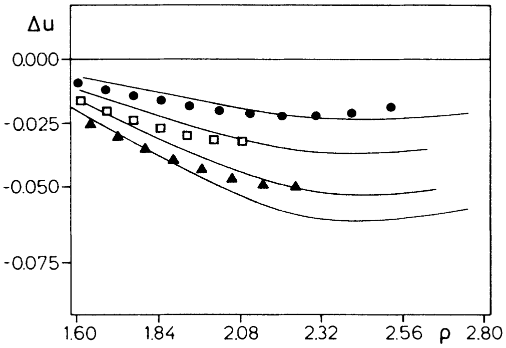

FIG. 7. Demonstration of errors. Differences in u from the RPC of Li_2 (zero straight line) in the right limb. Solid lines from top to bottom: Na_2, NaK, K_2, Rb_2. ●, LiK; ▲, LiRb; □, K_2 (RKR from Ref. 27). Cf. Ref. 22(b).

evaluation of these two RKR curves certainly seemed interesting.

The RPC analysis shows that both curves are not quite correct. In Fig. 6, the RPC of LiK shows a salient deviation in the left limb brutally crossing the RPC of Li_2 [violation of the fundamental rule ii(a)]. Deviations of this type, which were caused by errors in the analysis of the spectrum (constants) or by incorrect extrapolation, have been observed previously in many cases.[9,10,14,15] The crossing occurs already for $u+1=0.5$ and the deviation starts at $u+1=0.4$. As compared with the (reliable) RKR curve of NaK, the RKR curve of LiK seems to contain small errors already in its lowest portion. On the other hand, the RPC of LiRb is shifted too far to the right (Figs. 4 and 6) in the left limb even for low $u+1$.

In the right limb (Fig. 7), the RPC of LiK and LiRb cross the RPC's of Na_2 and Rb_2, respectively, thus again violating the fundamental noncrossing rule ii(a). A quite comparable deviation is observed in Fig. 7 for the RPC of K_2 based on a (certainly incorrect) RKR curve calculated with the use of previous less complete data[27] (in Ref. 27 a fit only for $v''=0,1,2$ was made so that, strictly speaking, the potential that was calculated up to $v''=35$, should again be considered as an extrapolation). Since the RPC's of LiK and LiRb probably are not correct, an estimation of D_e is meaningless; the value proposed by the experimenters for LiK seems, however, approximately acceptable. It appears that the discrepancy in the RPC of LiRb could not be removed only by a change in the value of D_e, so also here some other errors should be involved. That such larger errors may occur is illustrated on the example of the RPC of Rb_2 taken from Ref. 22(b); it is shown in Fig. 6 for $D_e(Rb_2)=3950$ cm^{-1} and also for the much higher value 4602 cm^{-1} proposed in Ref. 29 (Fig. 23). This old potential of Rb_2 evidently was quite erroneous (the analysis of the spectrum is very difficult because of the laborious separation of the isotopic spectra[30]).

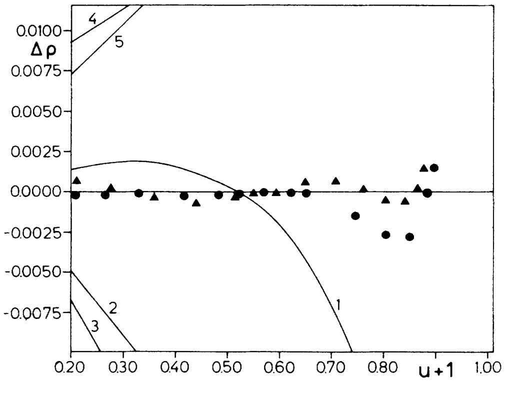

FIG. 6. Demonstration of errors. Differences in ρ from the RPC of Li_2 (zero straight line) in the left limb. Solid lines: 1, LiK; 2, Rb_2 (Ref. 27, $D_e=3950$ cm^{-1}); 3, Rb_2 (Ref. 27, $D_e=4602$ cm^{-1}); 4, LiRb; 5, H_2. ▲, Li_2 (Ref. 31); ●, Na_2 (Ref. 32). Cf. Ref. 22(b).

These deviations should be compared with the regular behavior of the RPC's of the other diatomic alkali-metal molecules. Figure 8 shows the differences in ρ of the

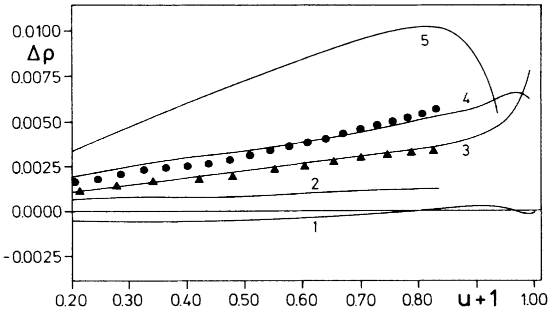

FIG. 8. Differences in ρ from the RPC of Li_2 (zero straight line) in the left limb. Solid lines: 1, Na_2; 2, K_2; 3, NaK [Ref. 23(a)]; 4, Cs_2; 5, NaCs; ●, Rb_2; ▲, NaK [Ref. 23(b)]. (Here 1×10^{-4} in ρ corresponds approximately to 2×10^{-4} Å in r.)

RPC's of the diatomic alkali-metal molecules from the RPC of Li_2 in the left limb. The "quasiparallel nature" of the RPC's is remarkable. The RPC's lie very close together and rules ii(a) and ii(b) of the RPC scheme (cf. Sec. II) are essentially fulfilled.

The discrepancies in the RPC's of Na_2 (or Li_2) and Rb_2 (or Cs_2) are of the order 10^{-4} Å and hence are absolutely insignificant with regard to the limited accuracy of the RKR method. Slight errors in the (probably rotational) spectroscopic constants seem to lead to the anomalous form of the highest portion of the RPC of NaK.

There also seem to exist small errors in the spectral analysis (constants) of NaCs which lead to the strange curvature in the highest portion. Similar deviations have been observed before in cases where such errors were present (cf. also the RPC of CsH in Ref. 1). This is illustrated by Fig. 6 where the RPC's of Li_2 and Na_2 from older calculations are shown (Refs. 31 and 32, respectively; for a discussion cf. also Ref. 33). Small errors in the shape of the whole curve may result in some cases. It is probable that such errors have also led to the global anomaly of the RPC of NaCs in the left limb. A check on the eigenvalues (which has not been made) or corrections with the use of the IPA method[34] might be interesting. (Only the potential curve of Rb_2 was calculated[20] with the use of the IPA method. Slight differences between the groups of homonuclear and heteronuclear molecules might exist.)

It should be emphasized in this context that no such "wiggles" appeared in the RKR curves of Li_2 of Ref. 16 and Na_2 of Refs. 17 and 18, where no corrections (extrapolations or rectifications) were made (confirmed by the authors[30]). Neither did such irregularities appear in the RKR curves of H_2 and HF shown in Ref. 1, for instance. Small errors of this type may be, however, quite significant in the framework of the RPC scheme as the example of CsH has shown.[1,39]

Finally, Fig. 9 shows the differences in u from the RPC of Li_2 of the RPC's of alkali-metal dimers and NaK and NaCs in the right limb. The *very nice* quasiparallel nature of the curves and the accurate fulfillment of rules ii(a) and ii(b) seem, indeed, interesting and yield an excellent demonstration of the laws of the RPC scheme. (Such nice results for difference curves can, of course, be obtained only using very accurate analysis of the spectrum and very accurate potentials.) Only the RKR curves of Li_2, Na_2, NaK, and Cs_2 have been calculated up to the dissociation limit and join asymptotically without crossing. Also the other RPC's in Fig. 9 seem to have the correct trend.

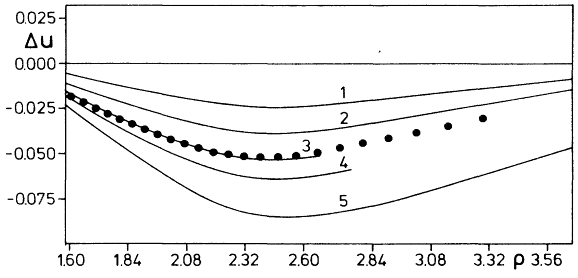

FIG. 9. Differences in u from the RPC of Li_2 (zero straight line) in the right limb. Solid lines: 1, Na_2; 2, NaK (practical coincidence of both 23a and 23b in the range of 23b); 3, K_2; 4, Rb_2; 5, Cs_2. ●, NaCs. (Here $\Delta u = 0.01$ means approximately 1% of D_e.)

The use of the noncrossing rule within the group would lead to very accurate estimates of D_e, the tail of the curve being very sensitive to a change in D_e. Figure 10 shows the accurate confluence for large ρ of the RPC's of Li_2 and Na_2, and also NaK and Cs_2. For instance, a change of about $1.10^{-3}D_e$ would produce a visible crossing of the RPC's of Li_2 and Na_2.[35-38] (A similarly excellent confluence was obtained, e.g., for H_2 and HF,[1] and LiH and KH.[39])

As has already been explained in Sec. II, slight crossings of RPC's of molecules belonging to *different* groups may occur in the right limb. For instance, before ultimate confluence, the RPC of Li_2 slightly crosses the (almost coinciding) RPC's of the alkali-metal hydrides in the region of the maximal bend, differently located for the group of alkali-metal hydrides and for the group of diatomic alkali-metal molecules (which seems to be due to avoided crossing in alkali-metal hydrides, cf. Ref. 1 for a discussion). This crossing corresponds to maximal difference in $u+1$ of only about 0.01.

The RPC of Na_2 slightly crosses the RPC of H_2 (and HF) before ultimate confluence; this crossing is avoided by using a value of $D_e(Na_2)$ which is about 30 cm^{-1} smaller than the now-accepted accurate value[17] 6022 cm^{-1}. So we would make here an error of only 30 cm^{-1} (about $0.005D_e$) in applying the noncrossing rule to molecules from *different* groups. A slight crossing in the lower portion of the right limb also seems to exist between the RPC of HF and the RPC's of NaCs, K_2, and Rb_2, maximal difference in $u+1$ being about 0.01. This is due to a slight difference in the shape of the close-lying RPC's of nonmetallic hydrides and diatomic alkali-metal molecules. It is not clear if this phenomenon could be excluded by an improvement of the definition of the RPC (Ref. 5) (not quite an easy task) or is inherent in the nature of the

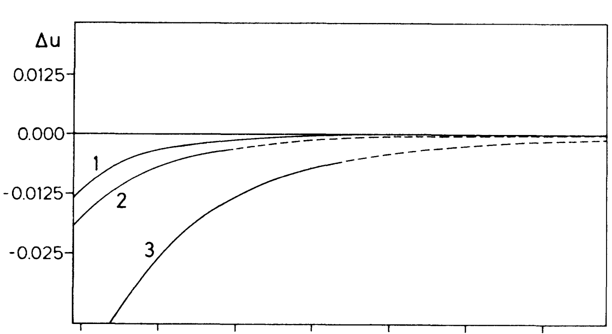

FIG. 10. Asymptotic confluence of the RPC's. Differences in u from the RPC of Li_2 (zero straight line). Solid lines: 1, Na_2; 2, NaK (Ref. 23a); 3, Cs_2. (Here the Δu scale is twice more sensitive than in Fig. 9. $\Delta u = 0.01$ means approximately 1% of D_e.) The dashed parts correspond to a Le Roy-Bernstein type extrapolation.

matter. However, as has been shown before,[1,7] the RPC method may be safely used to exclude gross errors in D_e, even comparing the RPC's of different groups.

Possibilities for perfecting the RPC formula are presently being studied; however, a serious attempt could be meaningful only when reliable RKR potentials up to dissociation limit are known for a sufficiently large series of molecules from different groups, including heavy molecules; such data is still not available.

IV. CONCLUSIONS

A comparative study of the ground-state RKR potentials of the diatomic alkali-metal molecules with the use of the RPC method confirms the global RPC scheme formulated in Sec. II and loosely called "a periodic system of diatomic molecules." The RPC's of diatomic alkali-metal molecules studied lie close together (especially in the left limb) and lie to the left of the RPC of H_2 (with the exception of the heaviest molecules in the right limb).

The RPC analysis shows again that the RPC method may be successfully employed for estimation of dissociation energy and for detection of errors in the molecular constants, in the analysis of the spectrum, or in the construction of the RKR potentials (e.g., extrapolations). Thus previous RKR curves of Rb_2 and K_2 and the RPC of LiK and LiRb are shown to be incorrect. According to the RPC analysis, there do not exist large errors in the D_e values proposed by the experimenters for the other diatomic alkali-metal molecules studied, i.e., the corresponding RPC's are essentially in accord with the RPC scheme.

The following remark seems in order: In some cases (e.g., for the previous RKR curve[27] of K_2), the spectral data may *a priori* seem insufficient to guarantee a quite accurate RKR curve. However, the demonstration of the deviations of the corresponding RPC's in Figs. 6 and 7 certainly is important for the following reasons.

(i) It shows that the RPC method is sensitive enough to disclose even very small errors or inaccuracies.

(ii) It clearly shows the order of magnitude of errors in the RKR curve due to the (unkown) inaccuracy of the analysis of the spectrum; it is hard to obtain such a good estimate by any other method. E.g., even very accurate *ab initio* calculations contain much larger errors in the potential and in the molecular constants.

(iii) Thus it makes clear that even very small inaccuracies in the analysis of the spectrum lead to relatively significant errors in the RKR curve.

(iv) It proves that the RPC method may yield good estimates of the correct RKR curve if one relies on the quasiparallel nature of the RPC's in a group of molecules if, at least for some molecules of the group, the RKR curves could be determined with sufficient accuracy (since larger discrepancies appear only for higher vibrational levels if the errors are not too large). Thus in Fig. 7, the correct RPC of K_2 is obtained in a very good approximation by prolonging the lowest portion of the incorrect RPC (RKR from Ref. 27) quasiparallel to the other RPC's of the diatomic alkali-metal group.

(v) It leads to the following admonition. It is *extremely* important to specify *exactly* the data field (and accuracy) for which the molecular constants have been determined (e.g., to calculate an RKR potential) and not to expect to be able to extrapolate [the computed line frequencies, the higher molecular constants, and the RKR potential (!!)] *significantly* beyond the range of the data field.

(vi) As explained in Ref. 5, p. 294, one might, of course, use rules (2) and (5), and the approximate coincidence of the RPC's of some diatomic alkali-metal molecules for a rather accurate estimate of the true potential. The "empirical" character of the RPC method should not be a point of criticism, since, in fact, the majority of computational methods in molecular physics are used in an empirical way.[40]

There will always be readers who will consider the regularities described here as not surprising and not interesting (though they have been so far unknown); on the contrary, to others they will still seem not exact enough, hence unconvincing. This modest attempt of an RPC guide through the jungle of diatomic molecules is devoted to readers who may find it useful or at least amusing.

Note added in proof. A remark on the sensitivity and the limits of the application of the RPC method. For Li_2, Na_2, NaK, and Cs_2, the RKR potentials were extrapolated using a Le Roy-Bernstein-type method, which makes a comparison of the RPC's for very large internuclear distances possible. Figure 11 shows that for $\rho > 8.0$, the final confluence of the RPC's of Li_2, Na_2, and NaK is perfect down to $\Delta u = 10^{-4}$. The confluence with the RPC of the heavy molecule Cs_2 is achieved for still larger values of ρ. (The RKR curve of Li_2 is extrapolated for $\rho > 7.7$.) In the context of Fig. 11, the following example may illustrate the limits of the application of the RPC method which is based on *reduced* quantities. Whereas in Ref. 23(a) the value of D_e'' (NaK) was determined from a Le Roy-Bernstein extrapolation of the ground-state potential, it was determined in Ref. 23(b) from the extrapolation of the excited $a\Sigma^+$-state potential, assuming the coincidence of both potential curves for very large r. The values obtained for the ground state and the a state, respectively,

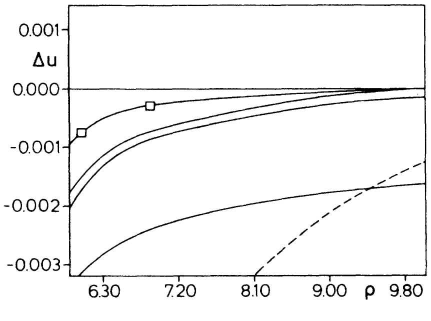

FIG. 11. Differences in u from the extrapolated RPC of Li_2 (zero straight line). The RPC's were calculated using Le Roy-Bernstein-type extrapolations of the RKR potentials [Refs. 16, 18, 23(a), 23(b), and 21]. Solid lines from top to bottom: Na_2; NaK [Ref. 23(b), from extrapolations of the $a\,^1\Sigma^+$ potential with $D_e''=5268.1$ cm^{-1}]; NaK [Ref. 23(a)]; NaK [Ref. 23(b), from extrapolation of the $a\,^1\Sigma^+$ potential with $D_e''=5274.9$ cm^{-1}]. Dashed line: Cs_2. □: last RKR points of Na_2. Δu scale is 12.5 times more sensitive than in Fig. 10.

were the following: D_e'' (NaK)$=5274.9$ cm^{-1}, D_e' (NaK)$=209.1$ cm^{-1} in Ref. 23(a); and D_e'' (NaK)$=5268.1$ cm^{-1}, D_e' (NaK)$=203.1$ cm^{-1} in Ref. 23(b). Hence a difference of about 6 cm^{-1} results (and a difference of 0.8 cm^{-1} in T_e). The value of D_e' (NaK)$=203.1$ cm^{-1} is, of course, used in the extrapolation for the a state in Ref. 23(b) which may serve for the determination of the tail of the ground-state potential, assuming coincidence of the ground- and excited-state potentials in this region. In Fig. 11, we show the tail of the RPC for the ground-state potential of Ref. 23(b) calculated in this way from the $a\,{}^3\Sigma^+$ potential (with $T_e=5065.00$ cm^{-1}) for the corresponding value $D_e''=5268.1$ and also for the value 5274.9.

Although the RPC method evidently is sensitive enough to exhibit the deviation caused by a difference of 6 cm^{-1} (about 0.1% of D_e'') for a definite potential, it cannot decide in this case which of both D_e'' values is correct, since here two *different* potentials and the corresponding D_e'' values are compared, i.e., *both* the potential and the D_e'' value are shifted by 6 cm^{-1}. Since the RPC method employs the reduced, i.e., relative energy $u+1=(U+D_e)\,|\,D_e$, the slight difference in $U+D_e$ and D_e compensates for large values in the tail of the potential in such a way that only a very slight difference between the two reduced curves remains (ρ also depends on D_e). In contradistinction to the potential well, the tail of the RPC is insensitive to the difference[23] in r_e. It seems impossible to make any judgment on the basis of such small differences. Anyway, the sensitivity of the RPC method—at least for this group of molecules where very accurate data was available—is surprising enough.

ACKNOWLEDGMENTS

The authors thank Professor W. Demtröder and Professor F. Engelke for kindly communicating unpublished results and valuable comments. We are especially obliged to Professor Engelke for his generous permission to use his unpublished calculation of the RKR curve for K_2 that was based on still insufficient spectral data and serves for the demonstration of the sensitivity of the RPC method in the detection of small errors or inaccuracies (Figs. 6 and 7), for sending us the Ph.D. thesis of Dr. Hage, and for valuable discussions. We thank Dr. Hage who kindly communicated to us the numerical results of his RKR calculations. Warm thanks are due to Professor J. Vergès who kindly sent us the Ph.D. thesis of K. Hussein, and the copies of Refs. 16 and 20. The RPC's were calculated using the REDPOT program of D. Merdes.

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p. 170]. For LiK, the RKR potential was further extended up to $v''=30$ $(u+1\approx 0.8)$ using the Hulburt-Hirschfelder formula. The potentials were then used for the calculation of Frank-Condon factors and for a confirmation of the vibrational assignment. A quite analogous procedure was employed for Rb_2, where, however, only data for $v''=0-2$ and $v'=4-11$ for $v''=0$, $v'=6-8$ for $v''=1$, and $v'=9$ for $v''=2$ $(J=0-50)$ were evaluated. Only small v values entered also into the analysis of the two-photon ionization spectra of K_2 in Ref. 27 ($v''=0,1,2$; $v'=0-12$; $J=0-100$). However, whereas, in Ref. 27, the errors in the potential of K_2 calculated by the RKR method are very small, the errors in Ref. 22(b) are rather large for Rb_2. [One should compare the Dunham coefficients in Refs. 19 and 27 for K_2 and in Refs. 20 and 22(b) for Rb_2, respectively.]

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