

## Application of the reduced-potential curve method for the detection of errors or inaccuracies in the analysis of spectra and for the construction of internuclear potentials of diatomic molecules: Alkali diatomic molecules

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Errors in the Rydberg-Klein-Rees potentials for the ground and  $B$ -excited states of LiNa and LiK and in the ground-state potential of RbCs are detected using the reduced-potential curve (RPC) method and shown to be due to errors or inaccuracies in the analysis of the spectrum. Using the rules of the RPC scheme, estimates for the left limbs of the ground- and  $B$ -state potentials of LiNa and LiK are given which are quite accurate for the ground states. With the use of the RPC method, we also give estimates of the ground-state potentials of Rb<sub>2</sub> and RbCs up to the dissociation limit. The RPC method is further employed for a calculation of accurate internuclear potentials from inaccurate theoretical *ab initio* potential curves for a series of molecules. These procedures could be useful for a prediction of the spectrum. The examples should illustrate the predictive and constructive power of the RPC method.

### I. INTRODUCTION

The reduced-potential curve (RPC) method<sup>1</sup> serves for a systematic comparative study of internuclear potentials of diatomic molecules and has disclosed interesting regularities.<sup>1-3</sup> (The formulas of the reduced potential are briefly explained in the Appendix.) In particular, important results have been found for the very accurate Rydberg-Klein-Rees (RKR) potentials<sup>4</sup> of the ground states of a series of alkali diatomic molecules<sup>3</sup> obtained on the basis of modern laser spectroscopy. On the other hand, discrepancies have been found for the ground-state potentials<sup>5</sup> of LiK and LiRb which evidently are due to inaccuracies in the analysis of the spectrum.<sup>3</sup> In the present paper, we show that similar discrepancies exist also in the RKR ground-state potential of LiNa (from Ref. 6), in the ground-state RKR potential of RbCs (from Ref. 7), and in the  $B$  <sup>1</sup>Π excited-state potentials of LiNa and LiK (from Refs. 6 and 5, respectively).

Let us briefly describe the regularities observed in the RPC scheme. In contradistinction to the earlier hypothesis (cf. Ref. 1), the dependence of the RPC on  $Z_1$ ,  $Z_2$ , and  $n$  is rather complicated (monotonic dependence on  $Z_1$  and  $Z_2$  holds only as a rough rule for nonmetal molecules). The study of ground-state potentials of a large number of neutral molecules revealed regularities that we loosely called "a periodic system of diatomic molecules;"<sup>3</sup> they may be characterized as follows.

(1) By definition, the RPC's of different diatomics have a common minimum (1,0). (2) There are groups of chemically related molecules (e.g., alkali hydrides,<sup>2(a),2(b)</sup> nonmetal hydrides,<sup>2(c)</sup> hydrides of metals of the IIb group,<sup>2(d)</sup> and other metal hydrides,<sup>2(e)</sup> nonmetal homonuclear molecules of the fifth, sixth, and seventh column of the Periodic Table,<sup>2(f)</sup> mercury halides,<sup>2(g)</sup> etc.) in which the following rules hold. (a) The RPC's of different diatomics of the group do not intersect anywhere. (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). The noncrossing rule holds for all diatomics 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.<sup>3</sup> (4) The RPC's of the rare gases (ground states) coincide approximately and form the right-hand boundary of the admissible RPC region in the  $\rho$  versus  $(u+1)$  diagram (i.e., no ground-state RPC lies to the right of this curve). For nonmetal molecules, the left-hand boundary of this region is formed by the RPC of H<sub>2</sub>. (5) The differences in  $\rho$  between the RPC's are very small in the left limb, i.e., the "quasiparallel" RPC's of all diatomics lie close together in the left limb. Molecular ions form similar separate schemes.<sup>8</sup>

The situation is clearly much more complicated for excited states (where perturbations may also occur); nevertheless, similar regularities as described above are observed for excited states of the same type.<sup>8</sup> However, differences may exist, e.g., between homonuclear and heteronuclear alkali diatomic molecules and the RPC's of the excited states may, for some states, be quite distant from the RPC of the ground state. As a rule, the RPC of the first excited state almost coincides with the RPC of the ground state and the RPC's of the excited states frequently lie to the right of the RPC of the ground state in the  $\rho$  versus  $u+1$  diagram ("are more weakly bounded in the reduced sense,"<sup>1,8</sup> which, of course, does not hold, e.g., for excimers.<sup>8</sup>) There exist interesting anomalies (like, e.g., the  $A$  <sup>1</sup>Σ<sup>+</sup> state of LiH). At any rate, it seems that, in a normal case, the RPC's of the excited states do not intersect with the ground-state RPC's and do not cross in the potential well (unless there is a hump on the potential curve).

Inaccuracies or errors in the analysis of the spectrum or in the values of the molecular constants are indicated by salient deviations from the RPC scheme described above. So with the use of the RPC method, inaccuracies in the analysis of the spectrum could be detected<sup>1</sup> for the ground state of  $\text{Cl}_2$  and for the ground state of  $\text{Bi}_2$  [Refs. 9(a), 2(g), and 2(h), respectively]; in the same way, errors in extrapolations of the RKR curves could be shown.<sup>2(d), 2(e), 2(g), 9(b), 10</sup>

Alkali diatomic molecules ( $\text{Li}_2$ ,  $\text{Na}_2$ ,  $\text{K}_2$ ,  $\text{Rb}_2$ ,  $\text{Cs}_2$ , and  $\text{NaK}$ ) obey these rules quite accurately,<sup>3</sup> in particular the differences between the ground-state RPC's of the molecules of this group are very small in the left limb (discrepancies with respect to the ordering are of the order of  $10^{-4}$  Å). Thus the RPC method may be used for a quite accurate estimate of the left limb of the internuclear ground-state potential of a molecule of this group as explained in Sec. II. Of necessity, this paper contains numerous figures; the RPC method is essentially a graphical method and the proofs of our statements are contained in the figures.

## II. METHODS OF THE CALCULATION OF THE POTENTIAL

(i) Let the atomic numbers of the molecule in question be  $Z_1$  and  $Z_2$ . One takes two (neutral) alkali diatomic molecules such that  $Z_1^{(1)} \leq Z_1$ ,  $Z_2^{(1)} \leq Z_2$  and  $Z_1^{(2)} \geq Z_1$ ,  $Z_2^{(2)} \geq Z_2$ , respectively, and such that their RKR potentials and molecular constants  $r_e$ ,  $D_e$ , and  $k_e$  are known to sufficient accuracy. From the RPC's of these two molecules, left- and right-hand boundaries for the internuclear potential of the molecule in question are obtained by inverting the RPC formula with the use of the molecular constants  $r_e$ ,  $D_e$ , and  $k_e$  of this molecule. It is clear that this procedure is meaningful *only* if these molecular constants of the molecule in question are known to sufficient accuracy.

Since the differences between the RPC's of affiliated molecules are very small in the left limb, such boundaries already give a useful estimate for the left limb of the potential, if the potential is not known. On the other hand, if the low portion of the potential could be constructed by the RKR method, one may then extend this potential up to the dissociation limit in both limbs in estimating the extension of the reduced potential in the RPC scheme, using the ordering of the RPC's with respect to increasing atomic numbers as a guide (cf. Sec. V).

(ii) Another version of the application of the RPC method for the determination of the potential is the following:<sup>1,11</sup> *ab initio* internuclear potential is calculated using the configuration-interaction method based on self-consistent molecular orbitals [CI-MO(SCF)] method (or, possibly, another sufficiently reliable method) and the *theoretical* RPC is calculated with the use of the corresponding *theoretical* values of the molecular constants  $r_e$ ,  $D_e$ , and  $k_e$ . An estimate of the true potential is then obtained by inverting the RPC formulas with the use of the *experimentally* determined values of these molecular constants. As explained in Refs. 1 and 11, *slight* errors may occur if the uncertainties in the theoretical values of  $D_e$

and  $k_e$  are not eliminated; however, the method may be at any rate safely used unless very fine differences should be discussed. It appears that *even a not very accurate ab initio* potential approximately coincides in reduced form with the reduced RKR potential if  $D_e$  is approximated to more than about 80% of the experimental value.<sup>1,11</sup>

The RPC method is used in this paper for the detection of inaccuracies in the analysis of the spectra of the  $X$  and  $B^1\Pi$  states of the molecules  $\text{LiK}$  and  $\text{LiNa}$  and for rather accurate estimates of the left limb of the potentials. We also use the RPC method to demonstrate inaccuracies in the ground-state potential of  $\text{RbCs}$  by Kato and Kobayashi.<sup>7</sup> While writing this paper, we received a paper<sup>12</sup> containing a new RKR ground-state potential of  $\text{RbCs}$ , based on new measurements of the spectrum, which fully confirms our argument (cf. Sec. III). We use this opportunity to construct an extension of the ground-state potentials of  $\text{RbCs}$  (from Ref. 12) and also of  $\text{Rb}_2$  (from Ref. 13) up to the dissociation limit with the use of the RPC method (Sec. V).

## III. DETECTION OF ERRORS OR INACCURACIES IN THE ANALYSIS OF THE SPECTRA

### A. Ground states

#### 1. $\text{LiNa}$ and $\text{LiK}$

Figure 1 illustrates the discrepancies found for the ground-state RPC's of  $\text{LiNa}$  and  $\text{LiK}$ . The RPC's of  $\text{LiK}$  and  $\text{LiNa}$  were calculated from the RKR potentials of Refs. 5 and 6, respectively, which were both based on the spectrum of the  $B-X$  transition. The experimental values of the molecular constants are given in Table I. Whereas the RPC's of the other alkali diatomic molecules are "quasiparallel" and do not intersect anywhere (cf. also Ref. 3) the RPC of  $\text{LiK}$  intersects with the RPC of  $\text{Li}_2$  for relatively low value of  $u+1$  in the left limb and turns then wildly to the left, while the RPC of  $\text{LiNa}$  shows a salient deviation to the right.

In fact, according to the RPC rules (Sec. I), the RPC's of both  $\text{LiNa}$  and  $\text{LiK}$  should lie between the RPC's of

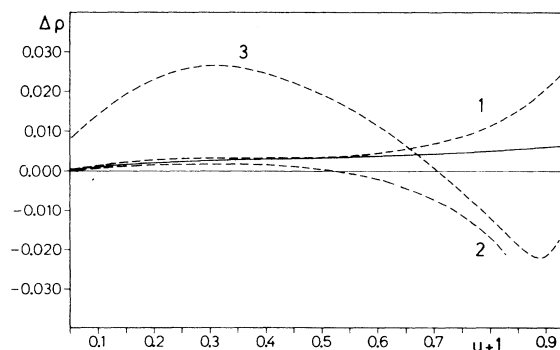


FIG. 1. Left limb. Differences in  $\rho$  from the ground-state RPC of  $\text{Li}_2$  (zero line). —, ground-state RPC of  $\text{Cs}_2$ ; - - -, incorrect ground-state RPC's of  $\text{LiNa}$ ,  $\text{LiK}$ , and  $\text{RbCs}$ . Curve 1,  $\text{LiNa}$  (Ref. 6); curve 2,  $\text{LiK}$  (Ref. 5); curve 3,  $\text{RbCs}$  (Ref. 7). All RPC's should lie between the RPC of  $\text{Li}_2$  and the RPC of  $\text{Cs}_2$ .

$\text{Li}_2$  and  $\text{NaK}$ , to be sure. The RKR potentials and the values of the molecular constants of  $\text{Li}_2$  and  $\text{NaK}$  are known to high accuracy. The deviations shown in Fig. 1 cannot be due to an error in the values of  $D_e(\text{LiNa})$  or  $D_e(\text{LiK})$ : errors in the molecular constants  $r_e$ ,  $k_e$ , and  $D_e$  only lead to a turning of the RPC around the minimum (plus a shift in the case of  $r_e$ ); they cannot cause its deformation with a change of the sign of the curvature.<sup>1</sup> Moreover, the RPC is rather insensitive to a small change in the  $D_e$  value in the left limb,<sup>14</sup> and the values of  $r_e$  and  $Y_{10}$  are still considered sufficiently accurate by the experimenters.<sup>15</sup> Thus the deviation must be due to inaccuracies in the spectral constants or errors in the analysis of the spectrum.

A possible explanation of such inaccuracies was attempted in Ref. 3 for  $\text{LiK}$ ; it seems, however, that in fact the reason could be the difficulties in the analysis of the spectrum of the  $B$ - $X$  transition.<sup>15</sup> Therefore, e.g., errors in assignment might have occurred in the middle part of the spectrum of the  $B$ - $X$  transition where the spectral data were not so complete.

The deviation of the RPC of  $\text{LiK}$  is seen also in the right limb (Fig. 2) where it crosses the RPC of  $\text{Na}_2$  thus violating rule 2(a) of the RPC scheme (cf. Sec. I). The RPC of  $\text{LiNa}$  also crosses the RPC of  $\text{Na}_2$  in the right limb. However, whereas the RPC of  $\text{LiK}$  behaves

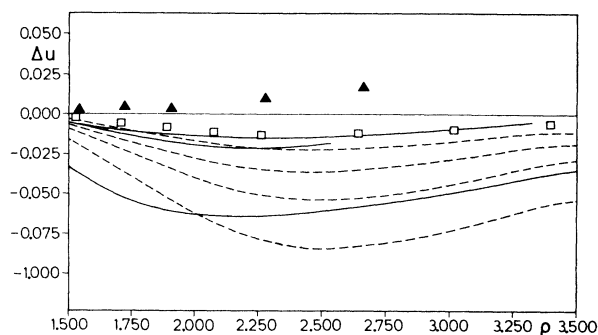


FIG. 2. Right limb. Differences in  $u$  from the ground state RPC of  $\text{Li}_2$  (zero line). — — —, correct ground state RPC's: from top to bottom they are  $\text{Na}_2$ ,  $\text{NaK}$ ,  $\text{K}_2$ , and  $\text{Cs}_2$ . — — —, incorrect ground-state RPC's of  $\text{LiNa}$ ,  $\text{LiK}$ , and  $\text{RbCs}$ : from top to bottom they are  $\text{LiNa}$  (Ref. 6),  $\text{LiK}$  (Ref. 5), and  $\text{RbCs}$  (Ref. 7). □, theoretical ground-state RPC of  $\text{LiNa}$  (Ref. 16); ▲, theoretical ground-state RPC of  $\text{LiNa}$  (Ref. 24).

correctly in the lowest portion of the potential, the RPC of  $\text{LiNa}$  crosses the RPC of  $\text{NaK}$  already for low vibrational levels (Fig. 3); for very low energies, it lies here to the right of the RPC's of  $\text{LiK}$  and  $\text{NaK}$ . Possibly also errors in the vibrational constants are involved. The deviations of the ground-state RPC's of  $\text{LiNa}$  and  $\text{LiK}$  are of

TABLE I. Values of molecular constants.

Molecule	State	$r_e$ (Å)	$Y_{10}$ ( $\text{cm}^{-1}$ )	$D_e$ ( $\text{cm}^{-1}$ )	$\rho_{ij}$ (Å)
$^7\text{Li}_2$	$X$	2.673 24 <sup>a</sup>	351.390 <sup>a</sup>	8516.78 <sup>a</sup>	1.172 85
$^7\text{LiNa}^b$	$X$	2.885 0 <sup>c</sup>	256.99 <sup>c</sup>	7067.81 <sup>c</sup>	1.454 98
$\text{Na}_2$	$X$	3.079 08 <sup>d</sup>	159.177 <sup>d</sup>	6022.6 <sup>d</sup>	1.691 47
$\text{LiK}^e$	$X$	3.316 87 <sup>f</sup>	211.910 <sup>f</sup>	6150 <sup>f</sup>	1.889 96
$\text{NaK}$	$X$	3.496 80 <sup>g</sup>	124.0124 <sup>g</sup>	5274.9 <sup>g</sup>	2.129 21
$\text{K}_2$	$X$	3.924 34 <sup>h</sup>	92.3985 <sup>h</sup>	4441.0 <sup>h</sup>	2.624 81
$\text{NaCs}$	$X$	3.850 00 <sup>i</sup>	98.8851 <sup>i</sup>	4950 <sup>i</sup>	2.564 50
$\text{Rb}_2$	$X$	4.209 90 <sup>j</sup>	57.7810 <sup>j</sup>	3950 <sup>k</sup>	3.045 29
$\text{RbCs}$	$X$	4.427 1 <sup>l</sup>	50.0116 <sup>l</sup>	3833.0 <sup>m</sup>	3.306 76
$\text{Cs}_2$	$X$	4.648 0 <sup>n</sup>	42.0203 <sup>n</sup>	3649.5 <sup>n</sup>	3.600 19
$^7\text{LiNa}^o$	$B$	3.119 0 <sup>p</sup>	209.63 <sup>p</sup>	1904.3 <sup>p</sup>	3.577 97
$^7\text{LiK}^o$	$B$	3.700 8 <sup>f</sup>	141.11 <sup>f</sup>	1800.0 <sup>f</sup>	3.471 42
$\text{NaK}$	$B$	4.015 6 <sup>q</sup>	71.4893 <sup>q</sup>	1325.2 <sup>q</sup>	3.761 89

<sup>a</sup> Reference 19(a).

<sup>b</sup> Small errors, in particular in  $D_e$ , are possible. In Ref. 16 the value  $D_e(\text{LiNa})=7093.0$  is recommended. For new values of  $Y_{10}$  and  $r_e$  [Ref. 19(e)] cf. Sec. IV.

<sup>c</sup> Reference 6.

<sup>d</sup> Reference 19(b).

<sup>e</sup> Small errors are possible, in particular in  $D_e$ .

<sup>f</sup> Reference 5.

<sup>g</sup> Reference 19(c).

<sup>h</sup> Reference 17(c).

<sup>i</sup> Reference 20.

<sup>j</sup> Reference 13.

<sup>k</sup> See Ref. 28. We regret the misprint in Table I of Ref. 3 where the value 3649.5 is erroneously given.

<sup>l</sup> Reference 12.

<sup>m</sup> Reference 7.

<sup>n</sup> Reference 19(d).

<sup>o</sup> Small errors are probable, in particular in  $D_e$ .

<sup>p</sup> Reference 6.

<sup>q</sup> Reference 21.

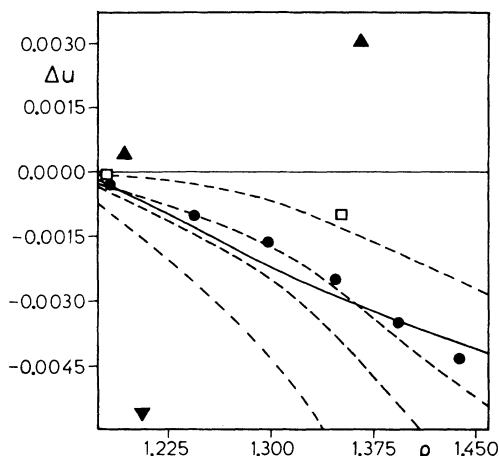


FIG. 3. Lowest part of the right limb. Differences in  $u$  from the ground-state RPC of  $\text{Li}_2$  (zero line). —, (incorrect) ground-state RPC of LiNa (Ref. 6). - - -, correct ground-state RPC's: from top to bottom they are  $\text{Na}_2$ , NaK,  $\text{K}_2$ , and  $\text{Cs}_2$ . ●, (incorrect) ground-state RPC of LiK. ▼, (incorrect) ground-state RPC of RbCs; □, theoretical ground-state RPC of LiNa (Ref. 16); ▲, theoretical ground-state RPC of LiNa (Ref. 24).

the same sign for a molecule in the left and right limb: the RPC of LiNa seems to be turned to the right, the RPC of LiK is turned to the left (similarly as was the RPC of LiRb in Ref. 3). The RPC diagnosis for the LiNa molecule is fully confirmed by the theoretical ground-state potential of LiNa recently obtained in a very accurate *ab initio* calculation<sup>16</sup> (Figs. 4 and 5). The theoretical ground state RPC of LiNa fulfils all the RPC rules perfectly.

## 2. RbCs

Let us now discuss the case of the RbCs molecule. According to the RPC rules (cf. Sec. I), the ground-state

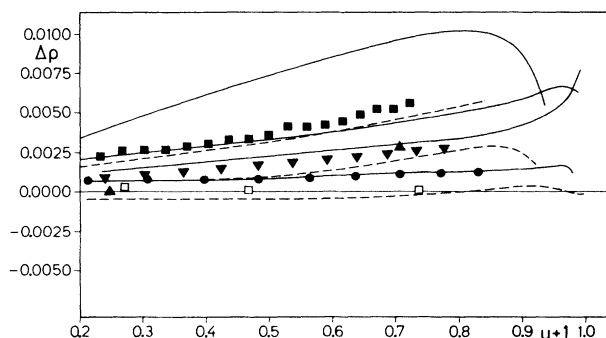


FIG. 4. Left limb. Differences in  $\rho$  of ground state RPC's from the ground-state RPC of  $\text{Li}_2$  (zero line). —, from top to bottom, NaCs,  $\text{Cs}_2$ , NaK, and  $\text{K}_2$  [Ref. 17(c)]. - - -, from top to bottom,  $\text{Rb}_2$ ,  $\text{K}_2$  [Ref. 17(b)], and  $\text{Na}_2$ . ■, RbCs; ▼, NaK (Ref. 18); ●,  $\text{K}_2$  [Ref. 17(a)]; □, LiNa (theoretical, Ref. 16); ▲, LiNa (theoretical, Ref. 24). The  $\rho$  scale is four times more sensitive than in Fig. 1.

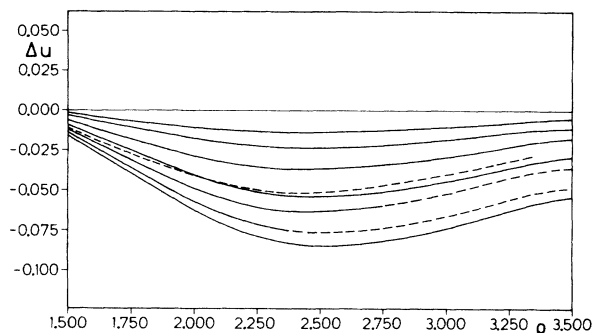


FIG. 5. Right limb. Differences in  $u$  of ground-state RPC's from the ground-state RPC of  $\text{Li}_2$  (zero line). —, from top to bottom, LiNa (theoretical, Ref. 16),  $\text{Na}_2$ , NaK,  $\text{K}_2$  [Ref. 17(c)],  $\text{Rb}_2$  (from RKR curve of Ref. 13), RbCs (from RKR curve of Ref. 12), and  $\text{Cs}_2$ . - - -, from top to bottom, NaCs (Ref. 20), extension of the RPC of  $\text{Rb}_2$  by the RPC method, and extension of the RPC of RbCs by the RPC method.

RPC of RbCs should, of course, lie between the RPC's of  $\text{Li}_2$  and  $\text{Cs}_2$ . Figure 1 shows that the potential of Ref. 7 is incorrect. The deviation of the RPC of RbCs is unusually large already for low vibrational levels. Figure 2 contains the right limbs of the RPC's corresponding to the incorrect RKR potentials of LiNa, LiK, and RbCs. Again, a very large deviation appears already in the low portion of the RPC of RbCs (from Ref. 7) which is deformed to the right in both limbs. On the other hand, the new RKR potential based on new data (from Ref. 12) satisfies all RPC rules in both limbs as may be clearly seen in Figs. 4 and 5 which contain the RPC's corresponding to the correct RKR [or inverted perturbation approach (IPA)] potentials. In the left limb the new potential<sup>12</sup> of RbCs almost coincides with the potentials of  $\text{Rb}_2$  and  $\text{Cs}_2$  in reduced form (possible discrepancies being of the order of  $10^{-4}$  Å) and it lies between the RPC's of  $\text{Rb}_2$  and  $\text{Cs}_2$  in the right limb. The errors in the spectroscopic constants, here disclosed by the RPC method, may be verified by comparing the corresponding tables in Refs. 7 and 12. Both RPC's of RbCs were calculated using the value  $D_e(\text{RbCs})=3833 \text{ cm}^{-1}$  recommended in Ref. 7, since no estimate of  $D_e$  was given in Ref. 12. As the analysis of the spectrum and the potential of Ref. 7 are not correct, the error limits  $\Delta D_e = \pm 5 \text{ cm}^{-1}$  given in Ref. 7 are not reliable. However, Fig. 6 shows that differences of  $+100 \text{ cm}^{-1}$  or  $-150 \text{ cm}^{-1}$  are already impossible, since then the RPC of RbCs would cross one of the neighboring RPC's, i.e., the RPC of  $\text{Rb}_2$  or  $\text{Cs}_2$ . (Unfortunately, the RPC scheme does not allow here any better estimate, since in Ref. 12 only the lower portion of the RbCs potential could be determined where the RPC is still not sufficiently sensitive to a change in  $D_e$ ). In fact, the value  $3833 \text{ cm}^{-1}$  leads to an acceptable shape of the RPC of RbCs in the RPC scheme (Fig. 5) so that the error in  $D_e$  probably is not too large.

Nevertheless, in view of the slight discrepancy in the ordering of the RPC's in the left limb (RbCs and  $\text{Cs}_2$ ), slight errors could exist also in the new RbCs potential of Ref. 12, in particular for  $u+1 > 0.5$ ). This slight

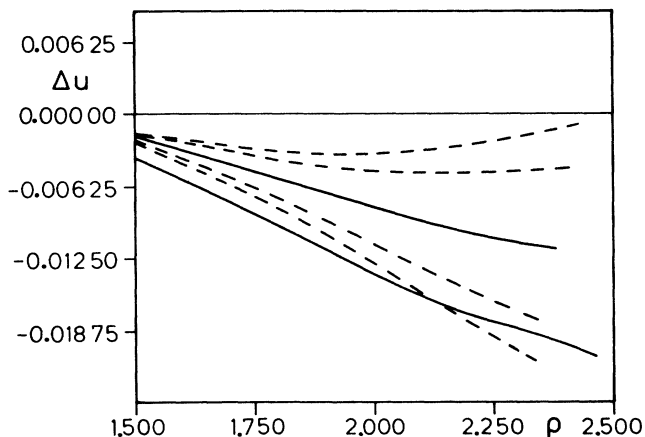


FIG. 6. Right limb. Differences in  $u$  of ground-state RPC's from the ground-state RPC of  $\text{Rb}_2$  (zero line). —, from top to bottom, RbCs for  $D_e = 3833 \text{ cm}^{-1}$  [recommended by experimenters (Ref. 7)] and  $\text{Cs}_2$ . - - -, from top to bottom, RbCs for  $D_e - 150 \text{ cm}^{-1}$ , RbCs for  $D_e - 100 \text{ cm}^{-1}$ ,  $D_e + 100 \text{ cm}^{-1}$ , and RbCs for  $D_e + 150 \text{ cm}^{-1}$ .

discrepancy cannot be due to an error in  $D_e$ : because of the insensitivity of the left limb to a change in the  $D_e$  value, only a too large change in  $D_e$  could produce this effect, and would then lead to a crossing of the RPC's in the right limb.

### 3. $\text{K}_2$

In Figs. 1–5, in addition to the RPC calculated from the RKR potential of Ref. 17(a) that was also employed in Ref. 3, we show also the new ground-state potential of  $\text{K}_2$  obtained by Doppler-free polarization spectroscopy up to very high vibrational levels and extended by the Le Roy-Bernstein method.<sup>17(c)</sup> It is a corrected and extended potential of Ref. 17(b). The potentials of Refs. 17(a) and 17(c) coincide quite accurately in the common range of  $\rho$  [there are small differences from the potential of Ref. 17(b)]. There is a slight discrepancy in the ordering of the RPC's of  $\text{K}_2$  and  $\text{NaK}$  in the left limb, which, however, is smaller than 0.001 in  $\rho$  (Fig. 4). In fact, this difference is reduced to the half if the ground-state potential of  $\text{NaK}$  of Refs. 15 and 18 is used, which shows that such seeming discrepancies easily arise through a slight inaccuracy in the experimental data and even lie at the limit of the accuracy of the RKR method. Indeed, slight inaccuracies seem to exist in the spectroscopic constants of  $\text{NaK}$  of Ref. 19(c) as disclosed by the curious bend of the highest portion of the left limb of the potential (Fig. 4). The ground-state RKR potential of  $\text{Li}_2$  and  $\text{Na}_2$  and the IPA potentials of  $\text{Rb}_2$  and  $\text{Cs}_2$  were taken from Refs. 19(a), 19(b), 13, and 19(d), respectively, and are considered as reliable and accurate.

### 4. $\text{NaCs}$

The new ground-state RKR potential of  $\text{K}_2$  [Ref. 17(c)], the new ground-state potential of  $\text{RbCs}$  (Ref. 12), and the accurate theoretical ground-state potential<sup>16</sup> of

$\text{LiNa}$  seem to confirm our hypothesis formulated in Ref. 3: we surmise that slight errors in the ground-state potential of  $\text{NaCs}$  (Ref. 20) exist. Figures 4 and 5 show that all RPC rules are practically satisfied by the molecules  $\text{Li}_2$ ,  $\text{Na}_2$ ,  $\text{K}_2$ ,  $\text{Rb}_2$ ,  $\text{Cs}_2$ ,  $\text{LiNa}$ ,  $\text{NaK}$ , and  $\text{RbCs}$ . Thus separate ordering of the homo- and heteronuclear molecules with respect to the increasing atomic numbers as two distinct series of molecules is improbable. Hence the RPC of  $\text{NaCs}$  should lie below the RPC of  $\text{RbCs}$  in Fig. 4. However, the RPC of  $\text{NaCs}$  is displaced strikingly to the left in the left limb (Fig. 4) which is then compensated by a curious bend to the right in the upper portion, which, in other cases, has been found to be due to inaccuracies in the spectroscopic constants.<sup>3</sup> In the right limb, the RPC of  $\text{NaCs}$  lies to the right of the RPC of  $\text{K}_2$  in the lower portion, then it crosses the two coinciding RPC's of  $\text{K}_2$  which were obtained by different authors from the spectra of different transitions [ $B-X$  in Ref. 17(a) and  $A-X$  in Ref. 17(c)]. The discrepancy in  $\rho$  is much larger in the right limb (Fig. 7) where it could be caused by an error in  $D_e$ . Although slight differences between homo- and heteronuclear molecules cannot be definitively excluded, the discrepancy in the left limb should be due to some errors.

### 5. Excited states

Figure 8 shows the deviations of the RPC's of the  $B^1\Pi$  state of  $\text{LiNa}$  and  $\text{LiK}$ . The RKR potentials were again taken from Refs. 6 and 5, respectively, and the RKR curve for the  $B$  state of  $\text{NaK}$  was taken from Ref. 21. The  $B^1\Pi$  RPC's of both molecules should lie between the RPC of the ground state of  $\text{Li}_2$  and the RPC of the  $B$  state of  $\text{NaK}$  in the left limb.<sup>8</sup> In contradistinction to Fig. 4, these two curves may evidently give only much less narrow boundaries for the  $B^1\Pi$  potential than the boundaries obtained for the ground-state RPC's of  $\text{LiNa}$  and  $\text{LiK}$  from the ground-state RPC's of  $\text{Li}_2$  and  $\text{NaK}$ . However, also the deviations (errors) of the RKR potentials are larger for the  $B^1\Pi$  states; therefore we show in Fig. 8 the RPC's directly, taking a sufficiently sensitive  $\rho$  scale. The RKR potentials of the  $X$  and  $B$  states of  $\text{LiK}$  and  $\text{LiNa}$  were obtained from the analysis of the spectrum of the  $B-X$  transition essentially by the same method.<sup>5,6</sup> The RPC analysis of the RKR potentials sug-

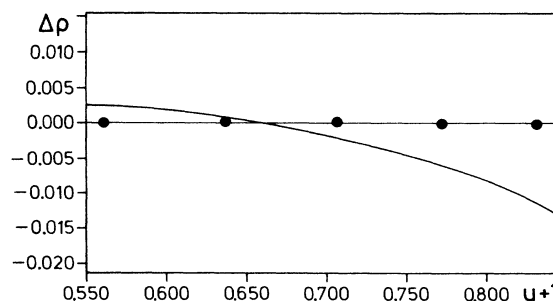


FIG. 7. Crossing of the ground-state RPC's of  $\text{K}_2$  and  $\text{NaCs}$  in the right limb. Differences in  $\rho$  from the ground-state RPC of  $\text{K}_2$  [Ref. 17(c), zero line]. —,  $\text{NaCs}$  (Ref. 20); ●,  $\text{K}_2$  [Ref. 17(a)]. [For  $D_e(\text{NaCs}) = 4950 \text{ cm}^{-1}$ .]

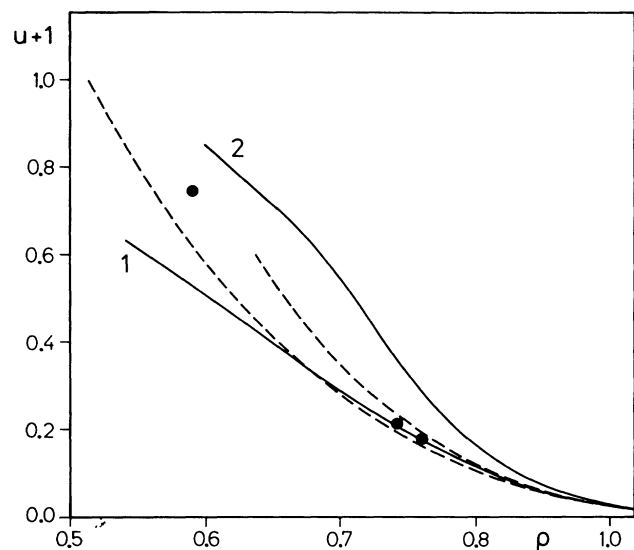


FIG. 8.  $B\ ^1\Pi$ -state RPC's (left limb). —: curve 1, LiK; curve 2, LiNa. - - -, from left to right, ground state RPC of  $\text{Li}_2$ ; RPC of the  $B\ ^1\Pi$  state of NaK. ●, theoretical RPC of the  $B\ ^1\Pi$  state of LiNa (Ref. 16).

gests that there should exist some systematical error in the analysis of the spectrum, since the deviations of both the ground-state and the  $B$ -state potentials are of the same type for each molecule (cf. also Figs. 9 and 11 and Figs. 10 and 12, respectively). The type of deviation for LiNa is opposite to that of LiK. The discrepancies in  $\rho$ , i.e., in  $r$ , seem to be larger in the right limb than in the left limb.

#### IV. ESTIMATION OF THE POTENTIALS

We recently received a paper on LiNa,<sup>19(e)</sup> containing results of an evaluation of the  $B$ - $X$  transition spectrum of LiNa using laser-induced fluorescence (Fourier transform) spectrometry. Unfortunately, only a low portion of the RKR potential of the ground state of LiNa could be determined (up to  $v=20$ ), however, this part of the potential is fully in accord with the RPC scheme, satisfying the RPC ordering rule (with respect to increasing atomic numbers). The corresponding RPC coincides to high accuracy with the theoretical RPC of Ref. 16 in both limbs, so that the anomalous crossing in Figs. 1–3 disappears. The values of  $\omega_e$  and  $r_e$  have changed by about 0.15% ( $Y_{10}=256.541\text{ cm}^{-1}$ ,  $r_e=2.889\text{ \AA}$ ) which caused a shift of the boundaries calculated in Tables II and III and of the potentials calculated with the use of the RPC method B (Tables XI and XII) by about  $0.0025\text{ \AA}$  in both limbs of the potential well (something more in the horizontal tail of the potential). The small changes in the potentials of Tables II, III, XI, and XII are not visible in the format of Figs. 9 and 10. Tables II, III, XI, and XII have been recalculated using these new constants. Commenting on Fig. 3 in Sec. III A, we suspected errors also in the vibrational constants; indeed, in addition to the small error in  $Y_{10}$ , there is an error of about 2% in  $Y_{20}$  and an error in

order of  $Y_{30}$ . Since the value of  $D_e(\text{LiNa}, X)=7068\text{ cm}^{-1}$ , recommended by the experimenters,<sup>6</sup> seems too small and the value  $7093\text{ cm}^{-1}$ , recommended by the theoreticians,<sup>16</sup> seems too large, we add Table XXIV, where an estimate of the potential of LiNa( $X$ ) is calculated using the value  $D_e=7080\text{ cm}^{-1}$ .

With respect to all the estimates of the potentials contained in the tables, we would like to emphasize that even very small differences in energy lead, of course, to large differences in the internuclear distance in the "horizontal" tail of the potential in the right limb. One should also note, that the noncrossing of the RPC's in Fig. 16 (cf. Sec. V) does not prove the correctness of the  $D_e$  values of LiNa,  $\text{Rb}_2$ , and  $\text{RbCs}$  (since they were used for the extension of the potentials), it only shows the compatibility of the extended potentials with the RPC scheme (and indicates that possible errors in the  $D_e$  values are not large). Let us now proceed to the discussion of the results obtained by the RPC methods A and B.

#### A. Method A

Figures 9–12 show the boundaries calculated by method A for the left limb of ground-state potentials of LiNa and LiK, and for the  $B$ -state potentials of these two molecules, respectively, compared with the corresponding RKR potentials; in the figures, the values of  $r_e$  and  $D_e$  of the respective state and molecule are taken as units for distance and energy, respectively. The deviations of

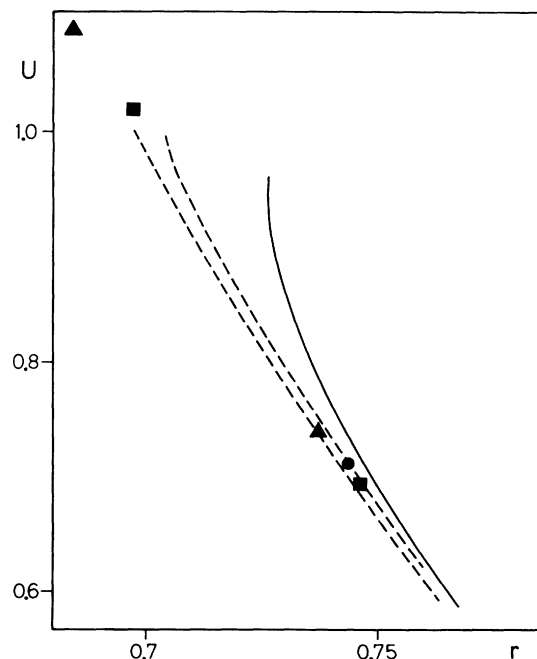


FIG. 9. Estimates of the ground-state potential of LiNa in the left limb. —, RKR potential (Ref. 6); - - -, left and right boundaries for the potential, calculated by RPC method A. Estimates of the potential calculated by RPC method B: ▲, from Ref. 16; ●, from Ref. 24; ■, calculation based on the theoretical potential of  $\text{Na}_2$  [Ref. 27(a)]. The experimental values of  $r_e$  and  $D_e$  are taken as units for internuclear distance and for energy, respectively.

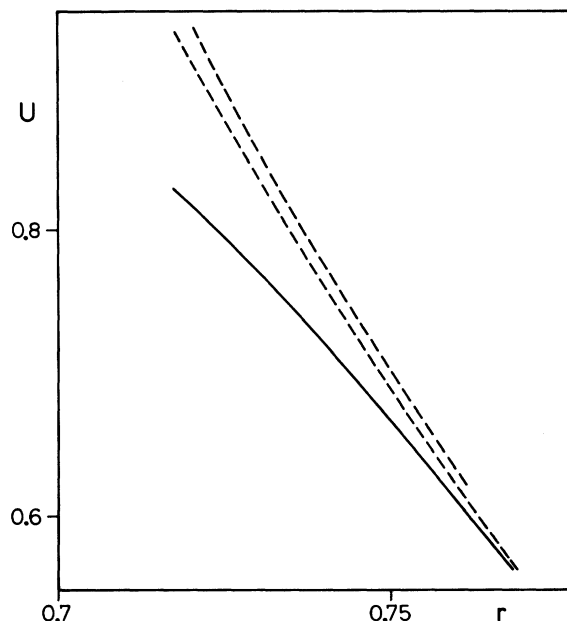


FIG. 10. Estimates of the ground-state potential of LiK in the left limb. —, RKR potential (Ref. 5); - - -, left and right boundaries for the potential, calculated by RPC method A. For comments cf. text to Fig. 9.

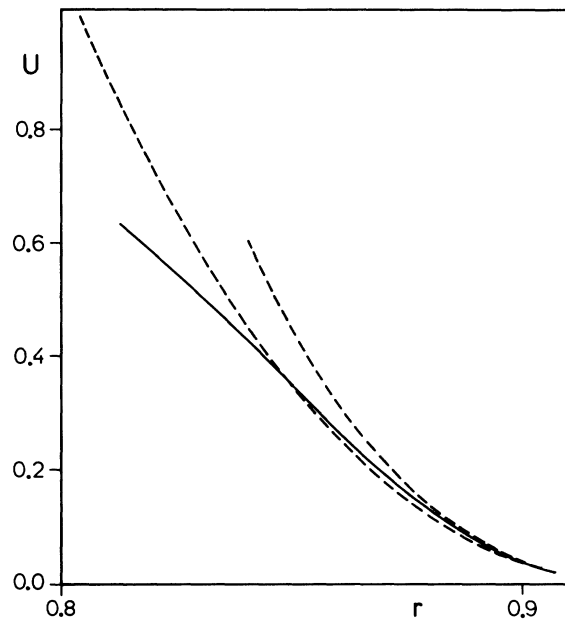


FIG. 12. Estimates of the  $B^1\Pi$ -state potential of LiK in the left limb. —, RKR potential (Ref. 5); - - -, left and right boundaries for the potential, calculated by RPC method A. For comments cf. text to Fig. 9.

the RKR potential from the "permitted" region are relatively large. This result shows again that—as in the case of  $\text{Cl}_2$  [Ref. 9(a)] and  $\text{Bi}_2$  [Ref. 2(h)]—even small inaccuracies in the analysis of the spectrum (spectral constants) may lead to relatively significant errors in the RKR potential. Fortunately, such errors can be detected with the

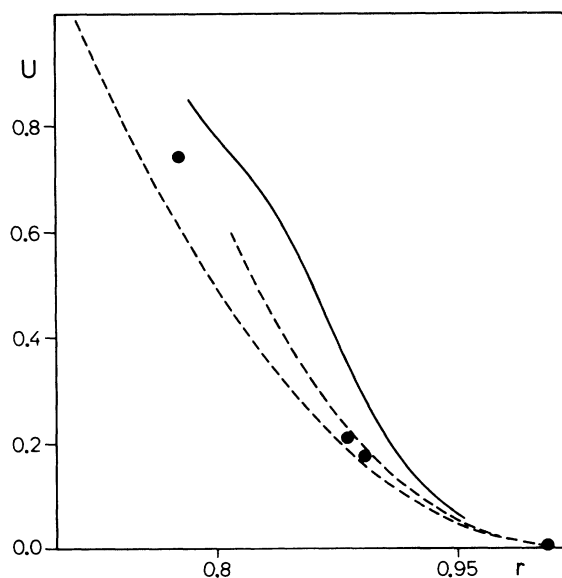


FIG. 11. Estimates of the  $B^1\Pi$ -state potential of LiNa in the left limb. —, RKR potential (Ref. 6); - - -, left and right boundaries for the potential, calculated by RPC method A; ●, estimate of the potential calculated by RPC method B (theoretical potential from Ref. 16). For comments cf. text to Fig. 9.

use of the RPC method.

The "boundary" potential curves of these figures are tabulated in Tables II–IX. The units for internuclear distance and energy are  $\text{Å}$  and  $\text{cm}^{-1}$ , respectively. A sufficient number of points and digits are given to permit an accurate interpolation for a comparison with newly calculated RKR potentials which, of course, will be determined for different values of the internuclear distance. To facilitate calculations, the points are currently numbered by the index  $i$ .

The *necessary condition for the validity* of these estimates is, of course, the assumption that possible errors in the molecular constants  $r_e$  and  $k_e$  are negligible and that the error in  $D_e$  is not substantial (for the ground state of LiNa, the new values<sup>19(e)</sup> of  $r_e$  and  $Y_{10}$  were used). For this reason, we did not discuss here the LiRb molecule, since the uncertainties in the  $D_e$  values are here too large<sup>5(b)</sup> and the deviations of the RPC's are also too large in the left limb.<sup>3</sup> So some inaccuracies in the values of  $r_e$  and  $\omega_e$  could here also exist, which would make our estimates rather dubious.

The boundaries for the  $B$ -state potentials are rather wide, since few RKR curves of heteronuclear alkali diatomic molecules are known and the ground-state RKR curve of  $\text{Li}_2$  had to be taken for the calculation of the left-hand boundary. If an accurate RKR curve for the  $B^1\Pi$  state of LiNa were known then, together with the RKR for the  $B^1\Pi$  state of NaK, it would, of course, yield essentially narrower boundaries for the  $B$ -state potential of LiK (cf. Fig. 11).

Estimation of the potential by the RPC method A is much more difficult in the right limb where the differences between the RPC's of various molecules

TABLE II. Left-hand boundary for the ground-state potential of LiNa in the left limb (calculated by RPC method A from the ground-state RPC of Li<sub>2</sub>).

<i>i</i>	<i>r</i> ( <i>i</i> ) (Å)	<i>U</i> ( <i>i</i> ) (cm <sup>-1</sup> )	<i>i</i>	<i>r</i> ( <i>i</i> ) (Å)	<i>U</i> ( <i>i</i> ) (cm <sup>-1</sup> )
1	2.014 926	7066.1479	21	2.128 071	4998.0156
2	2.015 201	7060.3926	22	2.140 130	4805.5259
3	2.015 826	7047.2822	23	2.152 936	4606.9331
4	2.016 941	7023.9800	24	2.166 459	4402.3979
5	2.018 632	6988.8335	25	2.180 807	4192.1108
6	2.020 934	6941.2773	26	2.196 063	3976.2561
7	2.023 865	6881.2964	27	2.212 251	3754.9700
8	2.027 183	6809.2666	28	2.229 438	3528.3789
9	2.031 367	6725.6494	29	2.247 770	3296.6226
10	2.036 208	6630.9971	30	2.267 380	3059.8169
11	2.041 642	6525.8467	31	2.288 433	2818.0667
12	2.047 662	6410.7168	32	2.311 136	2571.4656
13	2.054 312	6286.1509	33	2.335 753	2320.0989
14	2.061 354	6152.5171	34	2.362 633	2064.0425
15	2.069 188	6010.3711	35	2.392 250	1803.3647
16	2.077 528	5860.0518	36	2.425 276	1538.1265
17	2.086 435	5701.9399	37	2.462 711	1268.3822
18	2.095 992	5536.3848	38	2.506 167	994.1807
19	2.106 116	5363.7026	39	2.558 555	715.5662
20	2.116 688	5184.1475	40	2.626 267	432.5783

TABLE III. Right-hand boundary for the ground-state potential of LiNa in the left limb (calculated by RPC method A from the ground state RPC of NaK).

<i>i</i>	<i>r</i> ( <i>i</i> ) (Å)	<i>U</i> ( <i>i</i> ) (cm <sup>-1</sup> )	<i>i</i>	<i>r</i> ( <i>i</i> ) (Å)	<i>U</i> ( <i>i</i> ) (cm <sup>-1</sup> )
1	2.032 422	7016.1743	34	2.156 996	4629.3975
2	2.032 788	6997.1572	35	2.164 486	4513.1348
3	2.033 219	6974.3647	36	2.172 243	4394.9331
4	2.033 737	6947.7139	37	2.180 265	4274.8281
5	2.034 427	6917.1685	38	2.188 554	4152.8545
6	2.035 462	6882.7290	39	2.197 110	4029.0486
7	2.036 843	6844.4204	40	2.206 021	3903.4414
8	2.038 397	6802.2920	41	2.215 200	3776.0627
9	2.040 296	6756.4106	42	2.224 736	3646.9438
10	2.042 454	6706.8491	43	2.234 628	3516.1140
11	2.044 786	6653.6938	44	2.244 879	3383.5984
12	2.047 290	6597.0352	45	2.255 575	3249.4214
13	2.050 141	6536.9624	46	2.266 719	3113.6108
14	2.053 165	6473.5693	47	2.278 223	2976.1873
15	2.056 362	6406.9487	48	2.290 265	2837.1743
16	2.059 734	6337.1899	49	2.302 846	2696.5928
17	2.063 365	6264.3784	50	2.315 966	2554.4636
18	2.067 257	6188.6021	51	2.329 805	2410.8027
19	2.071 323	6109.9409	52	2.344 276	2265.6318
20	2.075 564	6028.4736	53	2.359 469	2118.9670
21	2.079 979	5944.2734	54	2.375 564	1970.8254
22	2.084 655	5857.4136	55	2.392 652	1821.2223
23	2.089 506	5767.9595	56	2.410 737	1670.1719
24	2.094 619	5675.9775	57	2.430 090	1517.6892
25	2.099 907	5581.5278	58	2.450 983	1363.7875
26	2.105 371	5484.6714	59	2.473 511	1208.4805
27	2.111 011	5385.4609	60	2.498 129	1051.7784
28	2.116 913	5283.9546	61	2.525 295	893.6936
29	2.123 079	5180.2012	62	2.555 921	734.2354
30	2.129 421	5074.2505	63	2.591 106	573.4146
31	2.135 939	4966.1504	64	2.633 050	411.2431
32	2.142 723	4880.0649	65	2.686 606	247.7291
33	2.149 770	4743.6812	66	2.768 550	82.8845



TABLE IV. Left-hand boundary for the ground-state potential of LiK in the left limb (calculated by RPC method A from the ground-state RPC of Li<sub>2</sub>).

<i>i</i>	<i>r</i> ( <i>i</i> ) (Å)	<i>U</i> ( <i>i</i> ) (cm <sup>-1</sup> )	<i>i</i>	<i>r</i> ( <i>i</i> ) (Å)	<i>U</i> ( <i>i</i> ) (cm <sup>-1</sup> )
1	2.359 488	6148.5537	22	2.499 026	4181.4907
2	2.359 795	6143.5459	23	2.513 251	4008.6873
3	2.360 494	6132.1377	24	2.528 265	3830.7122
4	2.361 740	6111.8618	25	2.544 183	3647.7327
5	2.363 630	6081.2788	26	2.561 095	3459.9084
6	2.366 203	6039.8984	27	2.579 029	3267.3579
7	2.369 478	5987.7065	28	2.598 053	3070.1917
8	2.373 185	5925.0303	29	2.618 330	2868.5305
9	2.377 858	5852.2715	30	2.640 000	2662.4761
10	2.383 265	5769.9106	31	2.663 242	2452.1189
11	2.389 332	5678.4146	32	2.688 279	2237.5408
12	2.396 052	5578.2354	33	2.715 398	2018.8160
13	2.403 473	5469.8457	34	2.744 974	1796.0106
14	2.411 329	5353.5649	35	2.777 520	1569.1838
15	2.420 064	5229.8779	36	2.813 757	1338.3888
16	2.429 361	5099.0786	37	2.854 766	1103.6729
17	2.439 286	4961.4985	38	2.902 282	865.0786
18	2.449 929	4817.4424	39	2.959 438	622.6443
19	2.461 200	4667.1846	40	3.033 112	376.4047
20	2.472 963	4510.9453	41	3.147 065	126.3913
21	2.485 623	4348.9844			

TABLE V. Right-hand boundary for the ground-state potential of LiK in the left limb (calculated by RPC method A from the ground-state RPC of NaK).

<i>i</i>	<i>r</i> ( <i>i</i> ) (Å)	<i>U</i> ( <i>i</i> ) (cm <sup>-1</sup> )	<i>i</i>	<i>r</i> ( <i>i</i> ) (Å)	<i>U</i> ( <i>i</i> ) (cm <sup>-1</sup> )
1	2.378 675	6118.4507	35	2.517 760	4028.2341
2	2.379 060	6105.0698	36	2.526 075	3927.0691
3	2.379 445	6088.5220	37	2.534 682	3824.2170
4	2.379 927	6068.6895	38	2.543 581	3719.7083
5	2.380 505	6045.4995	39	2.552 772	3613.5740
6	2.381 276	6018.9204	40	2.562 256	3505.8452
7	2.382 433	5988.9531	41	2.572 129	3396.5491
8	2.383 975	5955.6191	42	2.582 295	3285.7117
9	2.385 710	5918.9619	43	2.592 850	3173.3599
10	2.387 830	5879.0386	44	2.603 796	3059.5193
11	2.390 239	5835.9126	45	2.615 133	2944.2119
12	2.392 842	5789.6602	46	2.626 957	2827.4587
13	2.395 637	5740.3589	47	2.639 269	2709.2842
14	2.398 818	5688.0869	48	2.651 973	2589.7063
15	2.402 193	5632.9263	49	2.665 263	2468.7454
16	2.405 760	5574.9565	50	2.679 140	2346.4194
17	2.409 521	5514.2563	51	2.693 603	2222.7466
18	2.413 571	5450.9004	52	2.708 849	2097.7412
19	2.417 912	5384.9639	53	2.724 780	1971.4219
20	2.422 445	5316.5176	54	2.741 495	1843.8027
21	2.427 171	5245.6294	55	2.759 189	1714.8984
22	2.432 092	5172.3633	56	2.777 961	1584.7224
23	2.437 302	5096.7827	57	2.797 812	1453.2871
24	2.442 706	5018.9453	58	2.819 035	1320.6055
25	2.448 401	4938.9077	59	2.841 926	1186.6891
26	2.454 289	4856.7231	60	2.866 584	1051.5498
27	2.460 371	4772.4443	61	2.893 500	915.1968
28	2.466 647	4686.1172	62	2.923 167	777.6406
29	2.473 213	4597.7920	63	2.956 567	638.8892
30	2.480 071	4507.5117	64	2.994 884	498.9522
31	2.487 123	4415.3198	65	3.040 479	357.8400
32	2.494 369	4321.2573	66	3.098 572	215.5595
33	2.501 907	4246.3506	67	3.187 190	72.1213
34	2.509 736	4127.6777			

TABLE VI. Left-hand boundary for the  $B^1\Pi$ -state potential of LiNa in the left limb (calculated by RPC method A from the ground-state RPC of  $\text{Li}_2$ ).

$i$	$r(i)$ (Å)	$U(i)$ ( $\text{cm}^{-1}$ )	$i$	$r(i)$ (Å)	$U(i)$ ( $\text{cm}^{-1}$ )
1	2.469 923	1903.8522	22	2.575 547	1294.7664
2	2.470 160	1902.3015	23	2.586 091	1241.2590
3	2.470 699	1898.7692	24	2.597 174	1186.1505
4	2.471 659	1892.4908	25	2.608 875	1129.4922
5	2.473 116	1883.0211	26	2.621 251	1071.3339
6	2.475 098	1870.2079	27	2.634 311	1011.7122
7	2.477 618	1854.0471	28	2.648 097	950.6611
8	2.480 469	1834.6399	29	2.662 709	888.2183
9	2.484 059	1812.1107	30	2.678 236	824.4152
10	2.488 206	1786.6083	31	2.694 786	759.2797
11	2.492 853	1758.2772	32	2.712 496	692.8372
12	2.497 990	1727.2576	33	2.731 541	625.1108
13	2.503 653	1693.6954	34	2.752 149	556.1208
14	2.509 634	1657.6901	35	2.774 631	485.8857
15	2.516 271	1619.3912	36	2.799 426	414.4218
16	2.523 317	1578.8904	37	2.827 186	341.7438
17	2.530 818	1536.2897	38	2.858 958	267.8649
18	2.538 841	1491.6838	39	2.896 623	192.7970
19	2.547 311	1445.1576	40	2.944 294	116.5508
20	2.556 124	1396.7794	41	3.016 124	39.1361
21	2.565 576	1346.6295			

of the group are much larger. Uncertainty in the experimental value of  $D_e$  may pose further problems: for instance, in Ref. 5(a), the authors give error limits for  $D_e(\text{LiK}, X^1\Sigma^+)$  as  $\pm 125 \text{ cm}^{-1}$ . Error limits in  $D_e(\text{LiNa}, X^1\Sigma^+)$  of  $\pm 4 \text{ cm}^{-1}$  are given in Ref. 6; however, in view of evident inaccuracies in the analysis of the spectrum disclosed by the RPC method, a more significant error in the  $D_e$  value  $7068 \text{ cm}^{-1}$  of Ref. 6 must be taken into account; Schmidt-Mink *et al.*<sup>16</sup> suggested the value of  $7093 \text{ cm}^{-1}$  on the basis of a compar-

TABLE VII. Right-hand boundary for the  $B^1\Pi$ -state potential of LiNa in the left limb (calculated by RPC method A from the RPC of the  $B$  state of NaK).

$i$	$r(i)$ (Å)	$U(i)$ ( $\text{cm}^{-1}$ )
1	2.670 527	1140.2205
2	2.680 043	1082.3859
3	2.690 400	1021.8110
4	2.701 664	958.3967
5	2.713 974	892.0536
6	2.727 466	822.6829
7	2.742 346	750.1967
8	2.758 886	674.5191
9	2.773 147	595.5751
10	2.798 306	513.3060
11	2.822 551	427.6599
12	2.851 172	338.6039
13	2.886 266	246.1148
14	2.932 560	150.1914
15	3.006 074	50.8479

ison of their *ab initio*  $G(v)$  values with the  $G(v)$  values of Ref. 6, which means a difference of  $25 \text{ cm}^{-1}$ . Such differences in  $D_e$  are here relatively unimportant in the left limb where the RPC is rather insensitive to a change in  $D_e$ ;<sup>14</sup> for LiNa or LiK, a change of  $\pm 150 \text{ cm}^{-1}$  would produce a shift in  $\rho$  of the order of  $10^{-4} \text{ Å}$ , hence no visible change in Figs. 9 and 10 would result in this format. The RPC is, however, essentially more sensitive to a change in  $D_e$  in the right limb.<sup>14</sup> Since also the maximal differences between the RPC's of the various molecules are much larger here (of the order  $10^{-2}D_e$ , i.e., approximately  $50\text{--}70 \text{ cm}^{-1}$ ), one might in general obtain only rather crude estimates of the potential with the use of the RPC method A, which would, for instance, represent a multiple of the error which we assume here for the RKR ground-state potential of LiNa. Such an estimate could, of course, be still meaningful if the accuracy of the  $D_e$  value should be guaranteed or if the potential should be known only for a few vibrational levels.

However, let us emphasize that an accurate estimate of the left limb alone is also important for the determination of the whole potential if the vibrational constants may be considered as reliable: the errors in the rotational constants alone lead only to a shift of the RKR curve while the width of the potential well remains correct. Hence fixing the left limb, one obtains the correct potential by shifting the RKR potential in the due direction.<sup>4,22,23</sup>

On the other hand, if the accurate values of the molecular constants  $D_e$ ,  $r_e$ , and  $k_e$  are known, RPC method B may yield a quite accurate estimate of the potential if the *ab initio* calculation is correct. This point will be discussed in the next section.

TABLE VIII. Left-hand boundary for the  $B^1\Pi$ -state potential of LiK in the left limb (calculated by RPC method A from the ground-state RPC of  $\text{Li}_2$ ).

$i$	$r(i)$ (Å)	$U(i)$ ( $\text{cm}^{-1}$ )	$i$	$r(i)$ (Å)	$U(i)$ ( $\text{cm}^{-1}$ )
1	2.845 799	1799.5768	22	2.980 459	1223.8510
2	2.846 099	1798.1110	23	2.993 987	1173.2743
3	2.846 782	1794.7721	24	3.008 224	1121.1841
4	2.848 001	1788.8376	25	3.023 274	1067.6290
5	2.849 848	1779.8866	26	3.039 215	1012.6561
6	2.852 360	1767.7751	27	3.056 062	956.2999
7	2.855 558	1752.4995	28	3.073 870	898.5927
8	2.859 175	1734.1552	29	3.092 778	839.5699
9	2.863 732	1712.8600	30	3.112 906	779.2613
10	2.868 998	1688.7543	31	3.134 399	717.6933
11	2.874 901	1661.9750	32	3.157 445	654.8900
12	2.881 431	1632.6543	33	3.182 282	590.8730
13	2.888 633	1600.9304	34	3.209 222	525.6616
14	2.896 245	1566.8971	35	3.238 688	459.2733
15	2.904 696	1530.6959	36	3.271 279	391.7235
16	2.913 676	1492.4133	37	3.307 886	323.0262
17	2.923 244	1452.1459	38	3.349 938	253.1937
18	2.933 486	1409.9832	39	3.400 011	182.2374
19	2.944 308	1366.0051	40	3.463 736	110.1672
20	2.955 578	1320.2767	41	3.560 514	36.9926
21	2.967 679	1272.8735			

### B. Method B

The theoretical potentials for the ground state of LiNa are taken from Refs. 16 and 24, the theoretical potential for the  $B^1\Pi$  state of LiNa is taken from Ref. 16, since only a poor approximation was obtained in Ref. 24 for this state. (No point exists in this region in the calculation of Ref. 25 where also only the ground state was calculated with the use of the configuration-interaction (CI) method.) No theoretical calculations of the potentials of LiK are available (cf, e.g., Ref. 26, where—as in many similar papers—the tabulated potentials were not pub-

TABLE IX. Right-hand boundary for the  $B^1\Pi$  state potential of LiK in the left limb (calculated by RPC method A from the  $B$ -state RPC of NaK).

$i$	$r(i)$ (Å)	$U(i)$ ( $\text{cm}^{-1}$ )
1	3.102 908	1077.7698
2	3.115 251	1023.1028
3	3.128 699	965.8456
4	3.143 344	905.9045
5	3.159 371	843.1951
6	3.176 964	777.6240
7	3.196 398	709.1079
8	3.218 043	637.5751
9	3.236 740	562.9550
10	3.269 805	485.1918
11	3.301 764	404.2366
12	3.339 617	320.0583
13	3.386 218	232.6349
14	3.448 013	141.9653
15	3.546 916	48.0629

lished and could not be obtained on repeated request).

There are essential differences between the  $B^1\Pi$  states of homonuclear and heteronuclear alkali diatomic molecules<sup>8</sup> so that RKR potentials or theoretical potentials of the homonuclear molecules cannot be used for the estimation of the potentials of the heteronuclear molecules. (For instance, the  $B$ -state potential curves of homonuclear molecules have a hump due to avoided crossing; on the other hand, complicated perturbations exist in the heteronuclear case that are not encountered in the homonuclear case.<sup>15</sup>) The RPC's of the  $B^1\Pi$  states of homonuclear alkali diatomic molecules almost coincide and are very close to the corresponding ground state RPC's, whereas the  $B$ -state RPC's of heteronuclear molecules are strongly turned to the right.<sup>8</sup> Table X contains the corresponding theoretical values of the molecular constants, expressed as percentage of the experimental value. It is important to note<sup>1,11</sup> that even not very accurate *ab initio* calculations may be used in the RPC method.

The results of method B for the ground state of LiNa are shown in Fig. 9. Table XI contains the points of the ground-state potential of LiNa in the left limb, calculated by the RPC method B. Units for internuclear distance and energy are Å and  $\text{cm}^{-1}$ , respectively. We also show the points of the ground-state potential of LiNa calculated by inverting the theoretical ground state RPC of  $\text{Na}_2$ , based on the calculation of Ref. 27(a). All potentials behave correctly, i.e., they lie between the "boundary potential curves" obtained from the RPC's of  $\text{Li}_2$  and NaK (based on RKR potentials). The results presented in Figs. 11 and 12 for the  $B^1\Pi$  state of LiNa (and probably also of LiK) must indeed be taken with some reservation,

TABLE X. Theoretical values of the molecular constants expressed as a percentage of the experimental value.

Molecule	State	$r_e$ (Å)	$\omega_e$	$D_e$	Ref.
Li <sub>2</sub>	X	100.73	99.01	97.42	30(a)
Li <sub>2</sub>	X	100.01	99.90	99.41	30(b)
Na <sub>2</sub>	X	103.11	95.25	95.06	27(a)
Na <sub>2</sub>	X	100.27	99.88	98.73	27(b)
LiNa <sup>a</sup>	X	100.16	99.93	99.84	16
LiNa <sup>a</sup>	X	99.48	97.28	93.88	24
NaK	X	97.69	101.76	104.08	31
LiNa <sup>b</sup>	B	103.23	87.18	97.89	16

<sup>a</sup> A small error in the experimental value of  $D_e$  could exist; in Ref. 16, the value  $D_e(\text{LiNa})=7093.0 \text{ cm}^{-1}$  was suggested. The percentage for  $D_e$  would then be 99.48% in Ref. 16 and 93.55% in Ref. 24, respectively.

<sup>b</sup> Small errors in the experimental values of the molecular constants (in particular  $D_e$ ) could exist.

as crude estimates, since in this case, also an error in the value of  $\omega_e$  seems possible.

Full CI-MO(SCF) *ab initio* calculations certainly are more reliable and should be preferred. They seem to reflect the structure of the problem correctly,<sup>1,11</sup> and hence are suitable for the application of method B. One may hope that also effective core-potential methods may give good results if account is taken of electronic correlation and polarization in an adequate way; so the potential obtained by inverting the theoretical RPC based on the "model potential" calculation of Ref. 24 also gives a correct result in Fig. 9 (however, not in Fig. 3).

In Ref. 11, we have shown that the differences between the RKR potential and the theoretically calculated potential are very significantly diminished in the reduced form of the potentials; method B then leads to an essential improvement of the theoretical potential through the following steps: (1) theoretical potential and theoretical molecular constants, (2) reduced theoretical potential, (3) inversion of the reduced theoretical potential with the use of the experimental values of the molecular constants, (4) improved theoretical potential. The advantage is that, quite generally, method B may give accurate results also in the right limb if a sufficiently accurate *ab initio* method is used for the calculation of the theoretical potential and

if sufficiently accurate experimental values of the molecular constants  $r_e$ ,  $k_e$ , and also  $D_e$  are known. So this method may be used for an extension of the whole potential up to the dissociation limit if the RKR potential could be determined only for lower vibrational levels which, for heavier molecules, is often the case. Accurate values of  $r_e$  and  $\omega_e(Y_{10})$  are then often known and the value of  $k_e$  can be determined if the validity of the Dunham relation may be supposed [cf. Eq. (5) of the Appendix]. The value of  $D_e$  is often accurately determined from predissociation of some excited state [e.g., in Ref. 17(a)] or by other methods (e.g., for the HCl molecule, cf. Refs. 28 and 29).

The use of such improved potentials could be of practical importance if it is used for a numerical calculation of the energy levels and the spectrum (Numerov-Cooley method) in a region where the spectrum could not be measured which, in some cases, could be a hint for the experimentalist. The theoretical calculations for heavier molecules are in general not accurate enough to permit a meaningful approximation of the (unknown)  $\Delta G(v)$  and  $B(v)$  values. The RPC method is a new method of the calculation of the interatomic potential and it might be worthwhile to take it into consideration.

Figures 13 and 14 illustrate the use of this method on the examples of the ground states of the molecules Li<sub>2</sub>, Na<sub>2</sub>, and NaK, where the RKR curves and molecular constants are known to high accuracy.<sup>3</sup> The theoretical potentials were taken from Refs. 27, 30, and 31, respectively; the theoretical values of the molecular constants are given in Table X as percentage of the corresponding experimental values. The theoretical potentials calculated in Refs. 26 and 32 have not been published and could not be obtained on request. The potentials of Ref. 33 contain only one point of the left limb so that a reliable determination of the corresponding theoretical values of the molecular constants  $r_e$ ,  $k_e$ , and  $D_e$  is impossible. Figures 13 and 14 show the differences of the theoretical potential and of our potential, calculated with the use of RPC method B, from the RKR potential in the left and right limb, respectively. To save space, we bring the potentials of all three molecules in one figure, however, the scales in these figures have different meaning for different molecules: the experimental values of  $r_e$  and  $D_e$  of a mol-

TABLE XI. Estimated ground-state potential of LiNa (method B) for  $D_e(\text{LiNa})=7067.81 \text{ cm}^{-1}$  (recommended by the experimenters Ref. 6).

$i$	$r(i)$ (Å)	$U(i)$ (cm <sup>-1</sup> )	$i$	$r(i)$ (Å)	$U(i)$ (cm <sup>-1</sup> )
1	1.982 827	7718.4824	11	3.970 939	2964.8367
2	2.115 210	5210.9751	12	4.236 340	3847.6411
3	2.247 617	3301.8237	13	4.501 793	4613.9399
4	2.380 049	1911.4504	14	4.767 292	5242.6299
5	2.644 984	369.6207	15	5.298 396	6107.6284
6	2.884 566	0.1002	16	5.829 600	6577.6074
7	2.910 012	2.2989	17	6.360 864	6816.1143
8	3.175 128	353.1342	18	7.157 806	6969.3301
9	3.440 326	1098.5497	19	7.954 745	7024.7251
10	3.705 599	2017.6244	20	9.017 275	7050.8843

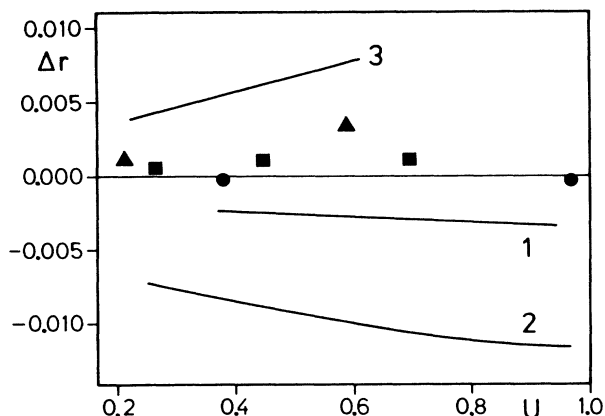


FIG. 13. Differences in  $r$  of the ground-state theoretical potential and our ground-state potential (method B) of  $\text{Li}_2$ ,  $\text{Na}_2$ , and  $\text{NaK}$  from the RKR potential of each molecule, respectively (left limb). The zero horizontal line represents for each molecule its RKR potential. For each molecule, its experimental values of  $r_e$  and  $D_e$  are taken as the units of internuclear distance and energy, respectively. All potential curves are shifted to the common minimum. —, theoretical potentials: curve 1,  $\text{Li}_2$  [Ref. 30(a)]; curve 2,  $\text{Na}_2$  [Ref. 27(a)]; curve 3,  $\text{NaK}$  (Ref. 31). Our potentials (method B): ●,  $\text{Li}_2$ ; ■,  $\text{Na}_2$ ; ▲,  $\text{NaK}$ . The theoretical potential of the small molecule  $\text{Li}_2$  of Ref. 30(b) coincides with our potential and with the RKR potential in the left limb in this format. The same holds for the theoretical  $\text{Na}_2$  potential of Ref. 27(b).

ecule are taken as units for the internuclear distance and the energy, respectively, for all potentials of this molecule. It is to be noted that the theoretical potential for the ground state of  $\text{NaK}$  was calculated only by an

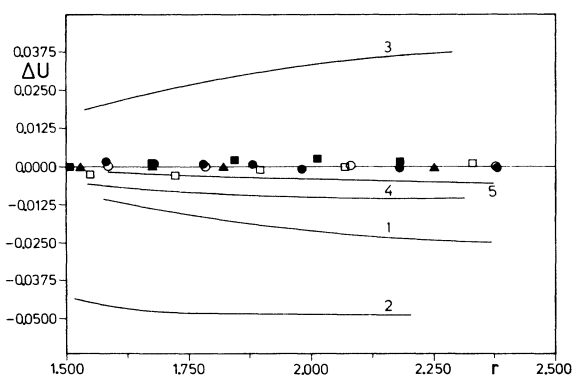


FIG. 14. Differences in energy  $U$  of the theoretical ground-state potential and our ground-state potential (method B) of  $\text{Li}_2$ ,  $\text{Na}_2$ , and  $\text{NaK}$  from the RKR potential of each molecule, respectively, in the right limb (for comments cf. text to Fig. 13). —, theoretical potentials: curve 1,  $\text{Li}_2$  [Ref. 30(a)]; curve 2,  $\text{Na}_2$  [Ref. 27(a)]; curve 3,  $\text{NaK}$  (Ref. 31); curve 4,  $\text{Na}_2$  [Ref. 27(b)]; curve 5,  $\text{Li}_2$  [Ref. 30(b)]. Our potentials: ●,  $\text{Li}_2$  [Ref. 30(a)]; ■,  $\text{Na}_2$  [Ref. 27(a)]; ▲,  $\text{NaK}$ ; ○,  $\text{Li}_2$  [Ref. 30(b)]; □,  $\text{Na}_2$  [Ref. 27(b)]. The references denote the theoretical potential used for our calculation.

effective core-potential method where the core-valence correlation effects were not treated in a sufficiently accurate way,<sup>31</sup> which may lead to the fact that the deviations in the left limb are slightly larger than for  $\text{Li}_2$  and  $\text{Na}_2$ . Note that the errors in  $k_e$  for  $\text{Na}_2$  or the error in  $r_e$  for  $\text{NaK}$  (Table X) would bring about a very large deviation of the RPC calculated from the RKR potential.<sup>11</sup> At any rate, the results prove without any doubt the efficiency of the RPC method B for a construction of accurate potentials from less-accurate theoretical potentials. The more accurate and more correctly structured the theoretical calculations are, the better the results of method B are. In the potential well, the RPC is not too sensitive to very small errors in the  $D_e$  value (of the order of 0.1%, say). It is, however, very sensitive in the tail of the right limb<sup>3</sup> so that method B should be used for the calculation of the (horizontal) tail of the potential only if both the experimental and theoretical value of  $D_e$  are accurately determined. It is clear that a primitive multiplication of the theoretical potential energy values by the factor  $D_e(\text{expt})/D_e(\text{theor})$  could not bring such an improvement of the theoretical potential and could even cause serious errors; at any rate it would be inefficient in the left limb.

The *ab initio* calculation on the  $\text{LiNa}$  molecule of Ref. 16 is a very accurate theoretical work; nevertheless, as illustrated in Figs. 13 and 14, we hope that the ground-state potential may be still slightly improved with the use of the RPC method B. The  $D_e$  value given by the experimenters<sup>6</sup> is  $7068 \text{ cm}^{-1}$ , the *ab initio* calculated value<sup>16</sup> is  $7057 \text{ cm}^{-1}$ , the value recommended in Ref. 16 is  $7093 \text{ cm}^{-1}$ . The difference of  $25 \text{ cm}^{-1}$  between the experimentally found and the recommended value already produces differences in the right limb of the potential calculated with the use of our RPC method B. Since the value  $7068 \text{ cm}^{-1}$  seems to represent the lower limit of  $D_e''(\text{LiNa})$ , we calculated the ground-state potential of  $\text{LiNa}$  by the RPC method B for both values,  $7068$  and  $7093 \text{ cm}^{-1}$ , in the right limb. These two curves tabulated in Tables XI and XII should give the (very narrow) boundaries of the right limb of the potential. The difference of  $25 \text{ cm}^{-1}$  in  $D_e$  (about 0.3%) is insignificant for Fig. 9 (left limb) in its format (cf. the introduction to this section).

As a last remark, we have to say that the application of method B is in reality difficult for the following reasons. Although some authors still keep to publishing also the tabulated theoretical (*ab initio*) potentials even for a series of excited states, many authors publish only figures and values of the molecular constants; the numerical data of the potential then are difficult to obtain, even from recent publications (e.g., Refs. 26 and 34). This seems a bit strange, since the potential determines the physics of the molecule and contains the key information; however, it then cannot be used for further calculations. In other papers, only few points of the potential are calculated either only in the neighborhood of the minimum or so dispersed that a reliable determination of the molecular constants is difficult. This certainly does not facilitate our work. We hope that this remark could explain the interest in the publication of the numerical values of the potentials and perhaps could help.

TABLE XII. Estimated ground-state potential of LiNa [method B for  $D_e(\text{LiNa})=7093.0 \text{ cm}^{-1}$  recommended in Ref. 16].

$i$	$r(i)$ (Å)	$U(i)$ ( $\text{cm}^{-1}$ )	$i$	$r(i)$ (Å)	$U(i)$ ( $\text{cm}^{-1}$ )
1	1.981 706	7745.9917	11	3.973 462	2975.4036
2	2.114 189	5229.5474	12	4.239 637	3861.3542
3	2.246 718	3313.5916	13	4.505 910	4630.3843
4	2.379 294	1918.2629	14	4.772 270	5261.3149
5	2.644 584	370.9380	15	5.305 192	6129.3965
6	2.884 558	0.1005	16	5.838 304	6601.0503
7	2.910 050	2.3071	17	6.371 527	6840.4072
8	3.175 683	354.3928	18	7.171 447	6994.1689
9	3.441 471	1102.4650	19	7.971 361	7049.7612
10	3.707 403	2024.8153	20	9.037 806	7076.0137

### V. EXTENSION OF THE INTERATOMIC POTENTIALS WITH THE USE OF THE RPC METHOD

The regular ordering of the ground-state RPC's of alkali diatomic molecules (Figs. 4 and 5) suggests the following practical application of the RPC scheme: if, for a molecule, the molecular constants  $r_e$ ,  $k_e$ , and  $D_e$  are known, but, however, the RKR potential could be constructed only in the lower portion of the potential well, then it might be extended as the most probable curve complying with the RPC scheme ("quasiparallelity" of the RPC's). This extension of the potential is a relatively easy task in the left limb, because of the very small differences of the RPC's in the left limb. However, in the right limb, maximal differences between the RPC's of various molecules are of the order  $10^{-2}$ .  $D_e$  (i.e., approximately of the order of  $50 \text{ cm}^{-1}$ ), so one could make relatively large errors in the estimate. Technically, the estimation is facilitated in using the generalized RPC formula of Jenč<sup>35</sup> which makes the RPC's almost coincide in the region relevant for the extension. The extension of the potential of the molecule in question is then obtained by inverting the RPC's of another alkali molecule whose potential is known up to the dissociation limit using the generalized RPC formula. The extension of the potential is supposed to be more accurate the closer the RPC's of the two molecules lie, i.e., the closer the atomic numbers of the two molecules. The maximum of the error appears in the region of the highest curvature of the potential in the right limb (about 85% of  $D_e$ ).

We have calculated such extensions for the ground-state potentials of  $\text{Rb}_2$  (from  $\text{K}_2$ ) and of  $\text{RbCs}$  (from  $\text{Cs}_2$ ) in the right limb. We believe that the maximal error in energy is essentially less than 0.1% of  $D_e$  (i.e., less than about  $4 \text{ cm}^{-1}$ ). The extensions were calculated by several different procedures; the maximal order of the differences was  $10^{-4}D_e$ . As a check, we calculated using this method an extension of the (known) potential of NaK from the potential of  $\text{Na}_2$  up from the same value of  $\rho$  as was necessary for  $\text{Rb}_2$  ( $\rho > 2.73$ ). The differences from the RKR potential [Ref. 19(c)] were found to be much less than 0.1% of  $D_e$  (cf. Fig. 15). Similarly, we calculated the ground-state potential of NaK from the

potential of  $\text{K}_2$  extending it up from the same value of  $\rho$  as was necessary for  $\text{RbCs}$  ( $\rho > 2.37$ ). The result is shown again in Fig. 15 and evidently is more than satisfactory.

The generalized RPC formulas and the extension method are still being studied and we hope to improve the method in the future which, however, appears to be a rather laborious task. At present we offer the best estimates available and we believe that our estimates are better than estimates obtained by any other existing method. As mentioned in Sec. I, various methods of extrapolation of the RKR potential have been shown to lead to relatively very large errors. Let us mention in passing that Morse-function-type approximation is very poor for alkali diatomic molecules.

It is clear that, making the extension of the potential, we take the ground-state potentials of  $\text{Rb}_2$  and  $\text{RbCs}$  for granted; *any error in these potentials naturally induces errors in our extension*. Such errors are, of course, more probable for the highest points of the potential where the extension starts. Therefore, speaking in terms of differences of the order of  $10^{-4}D_e$ , we prefer an extension curve which also approximates well the lower portion of

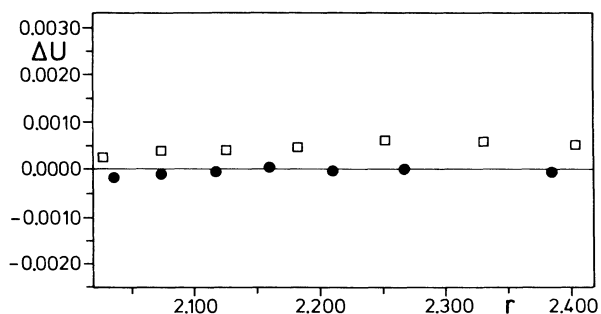


FIG. 15. Right limb of the potentials. Differences in energy from the RKR potential of NaK [Ref. 20(c)]. □, simulated extension of the NaK potential by the RPC method (using the generalized RPC formula and the RKR potential of  $\text{Na}_2$ ); ●, simulated extension of the NaK potential using the RKR potential of  $\text{K}_2$  [Ref. 17(c)]. The values of  $r_e(\text{NaK})$  and  $D_e(\text{NaK})$  were taken as units of internuclear distance and energy, respectively (extended from  $r = 1.6$ , and  $r = 1.35$ , respectively).

TABLE XIII. Extension of the left limb of the ground-state potential of Rb<sub>2</sub>.

<i>i</i>	<i>r</i> ( <i>i</i> ) (Å)	<i>U</i> ( <i>i</i> ) (cm <sup>-1</sup> )	<i>i</i>	<i>r</i> ( <i>i</i> ) (Å)	<i>U</i> ( <i>i</i> ) (cm <sup>-1</sup> )
6	3.131 202	3927.9194	17	3.152 020	3751.9385
7	3.131 525	3924.1538	18	3.155 107	3724.1772
8	3.132 335	3915.3835	19	3.158 461	3694.5720
9	3.133 716	3904.8643	20	3.161 908	3663.1594
10	3.135 383	3892.5117	21	3.165 641	3629.9768
11	3.137 253	3878.2637	22	3.169 622	3595.0627
12	3.139 289	3862.0806	23	3.173 872	3558.4568
13	3.141 500	3843.9426	24	3.178 389	3520.1982
14	3.143 867	3823.8469	25	3.183 175	3480.3259
15	3.146 410	3801.8005	26	3.188 228	3438.8767
16	3.149 127	3777.8223			

TABLE XIV. Extension of the left limb of the ground-state potential of RbCs.

<i>i</i>	<i>r</i> ( <i>i</i> ) (Å)	<i>U</i> ( <i>i</i> ) (cm <sup>-1</sup> )	<i>i</i>	<i>r</i> ( <i>i</i> ) (Å)	<i>U</i> ( <i>i</i> ) (cm <sup>-1</sup> )
6	3.311 487	3811.5735	22	3.351 363	3488.5762
7	3.311 821	3807.9194	23	3.355 773	3453.0544
8	3.312 662	3799.4089	24	3.360 461	3415.9292
9	3.314 096	3789.2012	25	3.365 427	3377.2378
10	3.315 827	3777.2144	26	3.370 670	3337.0164
11	3.317 768	3763.3884	27	3.376 182	3295.3025
12	3.319 880	3747.6846	28	3.381 953	3252.1306
13	3.322 175	3730.0840	29	3.387 974	3207.5347
14	3.324 633	3710.5837	30	3.394 214	3161.5483
15	3.327 271	3689.1902	31	3.400 696	3114.2043
16	3.330 092	3665.9221	32	3.407 398	3065.5344
17	3.333 095	3640.8052	33	3.414 340	3015.5686
18	3.336 299	3613.8662	34	3.421 532	2964.3369
19	3.339 780	3585.1379	35	3.428 974	2911.8679
20	3.343 357	3554.6555	36	3.436 695	2858.1902
21	3.347 231	3522.4561			

TABLE XV. Extension of the left limb of the ground-state potential of Rb<sub>2</sub> assuming coincidence of the RPC with the RPC of Cs<sub>2</sub>.

<i>i</i>	<i>r</i> ( <i>i</i> ) (Å)	<i>U</i> ( <i>i</i> ) (cm <sup>-1</sup> )	<i>i</i>	<i>r</i> ( <i>i</i> ) (Å)	<i>U</i> ( <i>i</i> ) (cm <sup>-1</sup> )
6	3.130 055	3927.9194	18	3.154 009	3724.1772
7	3.130 378	3924.1538	19	3.157 370	3694.5720
8	3.131 190	3915.3835	20	3.160 824	3663.1594
9	3.132 574	3904.8643	21	3.164 564	3629.9768
10	3.134 245	3892.5117	22	3.168 554	3595.0627
11	3.136 118	3878.2637	23	3.172 812	3558.4568
12	3.138 158	3862.0806	24	3.177 338	3520.1982
13	3.140 373	3843.9426	25	3.182 133	3480.3259
14	3.142 746	3823.8469	26	3.187 197	3438.8767
15	3.145 294	3801.8005	27	3.192 519	3395.8894
16	3.148 017	3777.8223	28	3.198 092	3351.3999
17	3.150 916	3751.9385			

TABLE XVI. Extension of the left limb of the ground-state potential of RbCs assuming coincidence of the RPC with the RPC of Cs<sub>2</sub>.

<i>i</i>	<i>r</i> ( <i>i</i> ) (Å)	<i>U</i> ( <i>i</i> ) (cm <sup>-1</sup> )	<i>i</i>	<i>r</i> ( <i>i</i> ) (Å)	<i>U</i> ( <i>i</i> ) (cm <sup>-1</sup> )
6	3.307 841	3811.5735	22	3.347 969	3488.5762
7	3.308 178	3807.9194	23	3.352 406	3453.0544
8	3.309 025	3799.4089	24	3.357 123	3415.9292
9	3.310 468	3789.2012	25	3.362 119	3377.2378
10	3.312 209	3777.2144	26	3.367 395	3337.0164
11	3.314 162	3763.3884	27	3.372 940	3295.3025
12	3.316 289	3747.6846	28	3.378 746	3252.1306
13	3.318 598	3730.0840	29	3.384 803	3207.5347
14	3.321 071	3710.5837	30	3.391 081	3161.5483
15	3.323 727	3689.1902	31	3.397 601	3114.2043
16	3.326 565	3665.9221	32	3.404 342	3065.5344
17	3.329 587	3640.8052	33	3.411 325	3015.5686
18	3.332 811	3613.8662	34	3.418 559	2964.3369
19	3.336 314	3585.1379	35	3.426 044	2911.8679
20	3.339 913	3554.6555	36	3.433 810	2858.1902
21	3.343 811	3522.4561			

the potential to an exact connection of the extension with the highest points of the potential. The extension of the left limb of the potentials of Rb<sub>2</sub> and RbCs was calculated from the potential of Cs<sub>2</sub> (Tables XIII and XIV). Nevertheless, if the *potential* of Cs<sub>2</sub> may be *taken for granted*, the RPC's of Rb<sub>2</sub> and RbCs should lie to the left of the RPC of Cs<sub>2</sub> in the left limb. Hence we also show extensions of the potentials of Rb<sub>2</sub> and RbCs obtained with the assumption that the RPC's of these molecules coincide with the RPC of Cs<sub>2</sub> in the left limb. The differences are, of course, *very small* (Tables XV and XVI).

If the RKR potentials and molecular constants of RbCs and Rb<sub>2</sub> are correct, the deviations of the extended potentials from the RKR potentials should be smaller than 0.001 Å in *r* in the left limb and smaller than 2–3 cm<sup>-1</sup> in energy in the right limb. Such differences often appear in a reevaluation of the RKR potentials on the basis of new data [cf., e.g., Refs. 17(b) and 17(c)]. If er-

rors in the value of *D<sub>e</sub>* exist, differences of the same order appear in the tail of the right limb, decreasing rapidly for smaller *r*. The extensions of the right limb of the potentials of Rb<sub>2</sub> and RbCs are shown in Tables XVII and XVIII and in Fig. 5. The difference curves for the ground state potentials for large *ρ* may be seen in Fig. 16; there are no crossings. The accuracy of our extrapolations may be verified when accurate analysis of the spectrum up to the dissociation limit is known and accurate RKR (IPA) potentials are constructed.

The practical use of such applications of the RPC method is clear: since these estimates are relatively accurate, any spectroscopist may calculate the *ΔG* and *B* values from the potential using the standard Numerov-Cooley method and thus estimate the system of still not measured spectral lines. (Such a calculation certainly is not the subject of this paper which should only illustrate the application of the RPC method for the construction

TABLE XVII. Extension of the right limb of the ground-state potential of Rb<sub>2</sub> for *D<sub>e</sub>*(Rb<sub>2</sub>)=3950.0 cm<sup>-1</sup> [recommended by experimenters (Ref. 28)].

<i>i</i>	<i>r</i> ( <i>i</i> ) (Å)	<i>U</i> ( <i>i</i> ) (cm <sup>-1</sup> )	<i>i</i>	<i>r</i> ( <i>i</i> ) (Å)	<i>U</i> ( <i>i</i> ) (cm <sup>-1</sup> )
1	6.816 580	3322.6250	14	7.910 170	3761.7910
2	6.879 807	3364.1440	15	8.034 538	3785.6067
3	6.945 337	3404.4766	16	8.169 404	3807.8257
4	7.013 388	3443.5977	17	8.316 712	3828.4109
5	7.084 206	3481.4797	18	8.478 995	3847.3213
6	7.158 071	3518.0955	19	8.659 631	3864.5161
7	7.235 304	3553.4150	20	8.863 268	3879.9531
8	7.316 270	3587.4104	21	9.285 243	3902.5776
9	7.401 394	3620.0510	22	10.283 672	3928.8511
10	7.491 169	3651.3040	23	11.226 095	3938.8772
11	7.586 176	3681.1396	24	12.218 856	3943.8274
12	7.687 100	3709.5215	25	13.157 643	3946.2515
13	7.794 765	3736.4175	26	14.098 558	3947.6245



TABLE XVIII. Extension of the right limb of the ground-state potential of RbCs for  $D_e(\text{RbCs})=3833.0 \text{ cm}^{-1}$  [recommended by experimenters (Ref. 7)].

$i$	$r(i) (\text{\AA})$	$U(i) (\text{cm}^{-1})$	$i$	$r(i) (\text{\AA})$	$U(i) (\text{cm}^{-1})$
1	6.671 159	2858.1902	19	8.192 904	3613.8662
2	6.730 468	2911.8679	20	8.331 289	3640.8052
3	6.791 433	2964.3369	21	8.481 295	3665.9221
4	6.854 211	3015.5686	22	8.644 854	3689.1902
5	6.918 939	3065.5344	23	8.824 364	3710.5837
6	6.985 814	3114.2043	24	9.022 816	3730.0840
7	7.055 040	3161.5483	25	9.243 964	3747.6846
8	7.126 825	3207.5347	26	9.492 549	3763.3884
9	7.201 443	3252.1306	27	9.774 611	3777.2144
10	7.279 179	3295.3025	28	10.097 975	3789.2012
11	7.360 354	3337.0164	29	10.473 213	3799.4089
12	7.445 333	3377.2378	30	10.914 417	3807.9194
13	7.534 558	3415.9292	31	11.164 721	3811.5735
14	7.628 509	3453.0544	32	12.017 165	3820.4387
15	7.727 765	3488.5762	33	13.491 453	3827.0347
16	7.832 992	3522.4561	34	13.983 056	3828.2527
17	7.944 949	3554.6555	35	14.376 379	3829.0090
18	8.064 555	3585.1379			

TABLE XIX. Extension of the right limb of the ground-state potential of  $\text{Rb}_2$  for  $D_e(\text{Rb}_2)=3939.0 \text{ cm}^{-1}$ .

$i$	$r(i) (\text{\AA})$	$U(i) (\text{cm}^{-1})$	$i$	$r(i) (\text{\AA})$	$U(i) (\text{cm}^{-1})$
1	6.803 123	3313.3723	14	7.885 483	3751.3152
2	6.865 785	3354.756	15	8.008 301	3775.0645
3	6.930 717	3394.9958	16	8.141 633	3797.2214
4	6.998 135	3434.0078	17	8.287 123	3817.7495
5	7.068 282	3471.7847	18	8.447 349	3836.6072
6	7.141 433	3508.2981	19	8.625 631	3853.7542
7	7.217 904	3543.5193	20	8.826 539	3869.1482
8	7.298 056	3577.4202	21	9.242 618	3891.7097
9	7.382 306	3609.9700	22	10.225 988	3917.9099
10	7.471 138	3641.1357	23	11.153 121	3927.9082
11	7.565 126	3670.8882	24	12.129 067	3932.8445
12	7.664 945	3699.1912	25	13.052 599	3935.2620
13	7.771 403	3726.0122	26	13.976 174	3936.6311

TABLE XX. Extension of the right limb of the ground-state potential of  $\text{Rb}_2$  for  $D_e(\text{Rb}_2)=3960.0 \text{ cm}^{-1}$ . The fitting procedure using the generalized RPC formula suggests that the correct value of  $D_e(\text{Rb}_2)$  is larger than  $3950 \text{ cm}^{-1}$ .

$i$	$r(i) (\text{\AA})$	$U(i) (\text{cm}^{-1})$	$i$	$r(i) (\text{\AA})$	$U(i) (\text{cm}^{-1})$
1	6.828 753	3331.0369	14	7.932 492	3771.3147
2	6.892 492	3372.6609	15	8.058 181	3795.1904
3	6.958 562	3413.0955	16	8.194 512	3817.4656
4	7.027 184	3452.3154	17	8.343 463	3838.1030
5	7.098 609	3490.2937	18	8.507 603	3857.0613
6	7.173 120	3527.0020	19	8.690 361	3874.2998
7	7.251 041	3562.4109	20	8.896 460	3889.7756
8	7.332 745	3596.4924	21	9.323 750	3912.4575
9	7.418 659	3629.2158	22	10.335 725	3938.7976
10	7.509 286	3660.5476	23	11.291 859	3948.8491
11	7.605 213	3690.4590	24	12.299 645	3953.8118
12	7.707 137	3718.9126	25	13.253 911	3956.2422
13	7.815 892	3745.8767	26	14.208 335	3957.6184

TABLE XXI. Extension of the right limb of the ground-state potential of RbCs for  $D_e(\text{RbCs})=3823.0 \text{ cm}^{-1}$ .

$i$	$r(i) (\text{Å})$	$U(i) (\text{cm}^{-1})$	$i$	$r(i) (\text{Å})$	$U(i) (\text{cm}^{-1})$
1	6.605 673	2796.0164	19	8.046 148	3575.7844
2	6.663 122	2850.7334	20	8.173 335	3604.4377
3	6.722 075	2904.2712	21	8.310 431	3631.3064
4	6.782 664	2956.6033	22	8.458 993	3656.3582
5	6.845 048	3007.7012	23	8.620 928	3679.5654
6	6.909 361	3057.5366	24	8.798 594	3700.9031
7	6.975 798	3106.0798	25	8.994 935	3720.3525
8	7.044 560	3153.3000	26	9.213 641	3737.9072
9	7.115 854	3199.1665	27	9.459 374	3753.5701
10	7.189 948	3243.6460	28	9.738 066	3767.3599
11	7.267 126	3286.7051	29	10.057 399	3779.3154
12	7.347 705	3328.3103	30	10.427 746	3789.4966
13	7.432 045	3368.4268	31	10.862 927	3797.9849
14	7.520 583	3407.0173	32	11.109 694	3801.6294
15	7.613 791	3444.0457	33	11.949 514	3810.4717
16	7.712 242	3479.4746	34	13.400 352	3817.0500
17	7.816 594	3513.2664	35	13.883 822	3818.2651
18	7.927 593	3545.3818	36	14.270 567	3819.0193

of interatomic potentials.) The values  $D_e(\text{Rb}_2)=3950 \text{ cm}^{-1}$  and  $D_e(\text{RbCs})=3833 \text{ cm}^{-1}$  are not guaranteed; hence we alternatively calculated boundary extensions of the potentials also for  $D_e(\text{Rb}_2)=3939 \text{ cm}^{-1}$  (the lower limit<sup>3</sup>) and  $3960 \text{ cm}^{-1}$ , and for  $D_e(\text{RbCs})=3823$  and  $3843 \text{ cm}^{-1}$ . The limits of  $D_e(\text{Rb}_2)$  have been discussed in Ref. 3; as has already been mentioned in Sec. III, large errors in  $D_e(\text{RbCs})$  also seem improbable, so the error limits  $\pm 10 \text{ cm}^{-1}$  seem sufficient (Tables XIX–XXIV). (This change of  $D_e$  is practically insignificant for the left limb.)

## VI. CONCLUSIONS

The results of the present paper lead to the following conclusions.

(1) Even small inaccuracies in the analysis of the spectrum (spectral constants) may lead to relatively significant errors in the RKR potential.

(2) The RPC method is sensitive enough to detect such inaccuracies in the analysis of the spectrum. Thus we have shown that the RKR potentials of the ground state

TABLE XXII. Extension of the right limb of the ground-state potential of RbCs for  $D_e(\text{RbCs})=3843.0 \text{ cm}^{-1}$ . The fitting procedure using the generalized RPC formula suggests that this value of  $D_e(\text{RbCs})$  is more probable than the lower values used in Tables XVIII and XXI.

$i$	$r(i) (\text{Å})$	$U(i) (\text{cm}^{-1})$	$i$	$r(i) (\text{Å})$	$U(i) (\text{cm}^{-1})$
1	6.563 414	2754.4797	19	7.959 752	3563.9294
2	6.620 086	2810.6436	20	8.080 235	3594.4912
3	6.678 163	2865.6470	21	8.209 550	3623.2944
4	6.737 772	2919.4648	22	8.349 000	3650.3037
5	6.799 052	2972.0706	23	8.500 212	3675.4863
6	6.862 161	3023.4358	24	8.665 119	3698.8149
7	6.927 239	3073.5322	25	8.846 161	3720.2642
8	6.994 482	3122.3291	26	9.046 364	3739.8154
9	7.064 098	3169.7964	27	9.269 535	3757.4622
10	7.136 296	3215.9028	28	9.520 484	3773.2068
11	7.211 352	3260.6152	29	9.805 337	3787.0688
12	7.289 554	3303.8997	30	10.132 038	3799.0869
13	7.371 228	3345.7224	31	10.511 323	3809.3213
14	7.456 743	3386.0488	32	10.957 508	3817.8540
15	7.546 542	3424.8411	33	11.210 736	3821.5176
16	7.641 113	3462.0632	34	12.073 612	3830.4060
17	7.741 040	3497.6775	35	13.567 261	3837.0190
18	7.846 998	3531.6460	36	14.065 573	3838.2402

TABLE XXIII. Comparison of the value of  $k_e$  [expressed as  $\omega_e$  according to Eq. (5)] obtained by our interpolation method (Ref. 11) (including  $r_e$ ) for the theoretical potential of the  $B$  state of LiNa of Ref. 16 and for a Morse potential with the same values of the molecular constants as calculated by the interpolation of the theoretical potential ( $\omega_e = 182.76 \text{ cm}^{-1}$ ).  $n$  is the degree of the interpolation polynomial. For a discussion cf. Ref. 16.

$n$	$\omega_e(\text{theor.})$	$\omega_e(\text{Morse})$
4	182.6480	180.5492
5	182.6481	183.0026
6	182.7176	182.7993
7	182.8412	182.7688
8	182.8694	182.7625
9	182.7463	182.7608
10	182.7800	182.7603
11	182.7464	182.7601
12	182.6827	182.7601
13	182.5997	182.7599

and the  $B^1\Pi$  state of LiNa and LiK (Refs. 6 and 5) and the ground-state potential of RbCs of Ref. 7 are incorrect and that this failure is due to errors or inaccuracies in the analysis of the spectrum.

(3) With the use of the RPC method A, one may eventually give rather accurate boundaries for the internuclear potential. This method is particularly suitable for the left limb of the potential where the RPC is relatively insensitive to a possible error (uncertainty) in the experimental value of  $D_e$  and the differences between the RPC's of affiliated molecules are very small.

(4) In the right limb, the application of method A will in general give only a less accurate estimate. Application of method B may here be more efficient if a sufficiently accurate theoretical potential has been calculated by means of a correct method<sup>11</sup> for sufficiently high energies and sufficiently many points in such a way that a correct and accurate determination of the corresponding theoretical values of the molecular constants  $r_e$ ,  $D_e$ , and  $k_e$  is possible (which also implies a suitable choice of the points of the calculated theoretical potential). In that case, this method may be used for an essential improvement of the theoretical potential and thus also for a more reliable guess of the spectrum. At present, this method is not realistic for too heavy molecules for which accurate

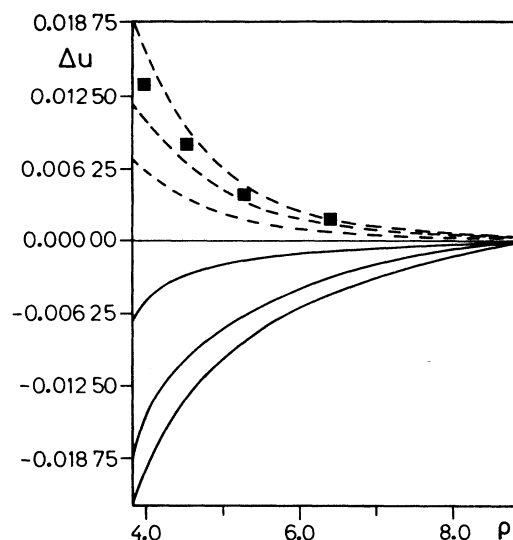


FIG. 16. Tails of the right limb of the ground-state RPC's. Differences in  $u$  of the ground-state RPC's from the ground-state RPC of  $K_2$  [Ref. 17(c), zero line]. —, from top to bottom, extended RPC of  $Rb_2$ ; extended RPC of  $RbCs$ ;  $Cs_2$ . - - -, from top to bottom,  $Li_2$ ,  $Na_2$ , and  $NaK$ . ■, theoretical ground-state RPC of LiNa (Ref. 16).

*ab initio* results are not available; any theoretical calculation also offers fewer points of the potential than the RKR method.

(5) Sufficiently accurate experimental values of the molecular constants  $r_e$  and  $k_e$  are needed for the application of the RPC method so that, in a current case, a sufficiently accurate analysis of the spectrum for a certain number of lower vibrational levels will be needed. The RPC method then makes an extension of the RKR potential for higher vibrational levels possible, in principle up to the dissociation limit, as has been illustrated by the examples of  $Rb_2$  and  $RbCs$ .

(6) Irregularities and anomalies may occur more frequently in the whole system of the excited states.<sup>8</sup> Therefore RPC method B should be considered as the more suitable method for the construction of the potentials of excited states if the reliability of the theoretical calculation may be supposed.<sup>8</sup> One should, of course, carefully check if the accuracy of the method is guaranteed also

TABLE XXIV. Estimated ground-state potential of LiNa (method B) for  $D_e(\text{LiNa}) = 7080 \text{ cm}^{-1}$ .

$i$	$r(i) (\text{\AA})$	$U(i) (\text{cm}^{-1})$	$i$	$r(i) (\text{\AA})$	$U(i) (\text{cm}^{-1})$
1	1.982 285	7731.7949	12	4.237 936	3854.2771
2	2.114 715	5219.9629	13	4.503 787	4621.8975
3	2.247 182	3307.5186	14	4.769 702	5251.6719
4	2.379 683	1914.7472	15	5.301 686	6118.1626
5	2.644 790	370.2582	16	5.833 815	6588.9521
6	2.884 562	0.1003	17	6.366 028	6827.8701
7	2.910 030	2.3029	18	7.164 413	6981.3501
8	3.175 397	353.7433	19	7.962 794	7036.8408
9	3.440 881	1100.4443	20	9.027 221	7063.0449
10	3.706 472	2021.1042	21	10.623 650	7074.7148
11	3.972 161	2969.9502	22	15.944 046	7079.7803

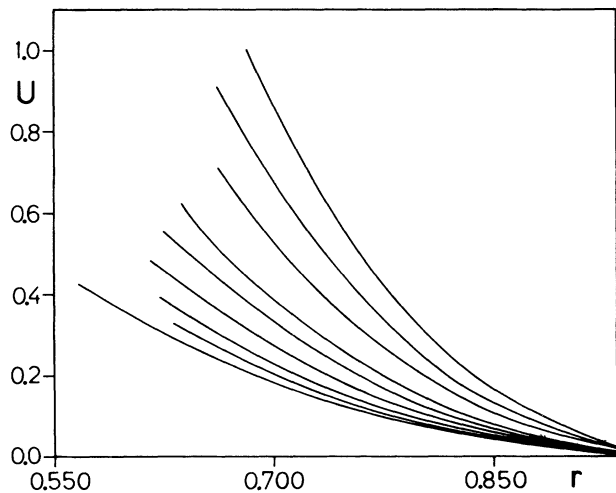


FIG. 17. Left limb. RKR (IPA) ground-state potentials. —, from top to bottom,  $\text{Li}_2$ ,  $\text{LiNa}$  (theoretical, Ref. 16),  $\text{Na}_2$ ,  $\text{NaK}$ ,  $\text{NaCs}$ ,  $\text{K}_2$ ,  $\text{Rb}_2$ ,  $\text{RbCs}$ ,  $\text{Cs}_2$ .  $r_e(\text{Li}_2)$  and  $D_e(\text{Li}_2)$  are used as units for distance and energy, respectively. All curves are shifted to a common minimum. The  $\rho$  scale is essentially more sensitive than in Fig. 18.

for higher excitation. For heavy molecules, full CI *ab initio* calculations are still rather expensive; on the other hand, the reliability of the effective core-potential method and similar procedures should still be checked. If the core-valence electron correlation is not adequately represented in the calculation, structural errors in the left limb may result, which are then also reflected in the RPC-method calculation. The *structural consistency* of the calculation (and not only the *values* of the molecular constants or the potential) is the proper criterion for the use of the RPC method.<sup>11</sup>

(7) Recently a comment on our paper on nonmetal hydrides<sup>2(c)</sup> was made as regards the usefulness of the RPC, which certainly gave us pause. Possibly others may question its worth. (We have encountered people who think that sooner or later the spectra and the potentials will be measured or calculated, and hence take the RPC method only for a useless method.) In the present modest contribution to a systematic study of diatomic molecules, we also tried to show explicitly the practical usefulness of the RPC method. We hope that at least some readers might be satisfied.

To develop a feeling for the merits of the RPC method, it is certainly worthwhile to have a look on Figs. 17 and 18 which show the (not-reduced) RKR potentials of the alkali diatomic molecules; the value of  $r_e$  and  $D_e$  of  $\text{Li}_2$  were taken as units for internuclear distance and for energy, respectively, and all curves were shifted to a common minimum. Though a certain (not quite the same) ordering of the potentials is already seen in these figures, we doubt that anybody could use these figures for an estimation of any quantity. Since there is a large difference in the atomic numbers of alkali diatomic molecules, the differences between the RPC's of different molecules of this group are relatively large in the right limb, i.e., much

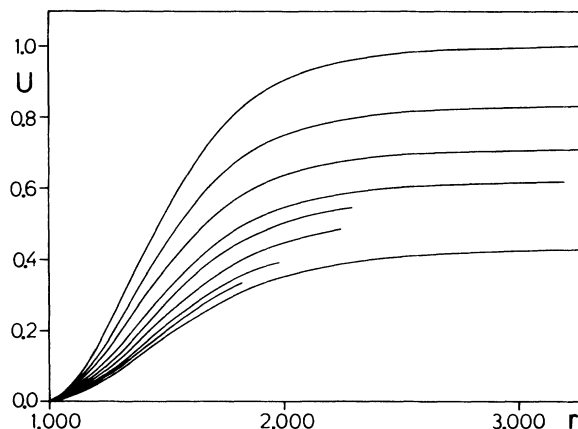


FIG. 18. Right limb. RKR (IPA) ground-state potentials. —, from top to bottom,  $\text{Li}_2$ ,  $\text{LiNa}$  (theoretical, Ref. 16),  $\text{Na}_2$ ,  $\text{NaK}$ ,  $\text{NaCs}$ ,  $\text{K}_2$ ,  $\text{Rb}_2$ ,  $\text{RbCs}$ ,  $\text{Cs}_2$ .  $r_e(\text{Li}_2)$  and  $D_e(\text{Li}_2)$  were taken as units for distance and energy, respectively. All curves are shifted to a common minimum.

larger than, e.g., for alkali hydrides<sup>2(a),2(b)</sup> or light non-metal hydrides.<sup>2(c)</sup> It is clear that if, e.g., for a light non-metal hydride, the accurate value of  $D_e''$  (and  $r_e''$  and  $k_e''$ ) should be known, a rather accurate estimation of its ground-state potential up to the dissociation limit could be given using the methods described in this paper.

Nevertheless, we would like to stress that we consider the practical applications described here rather as a by-product. We feel that the regularities (or laws) exhibited by the RPC scheme are most important and should merit further scientific research.

*Note added in proof.* Recent new information (C. Amiot, private communication) indicates that the correct value of  $D_e(\text{Rb}_2)$  should be about  $3980 \text{ cm}^{-1}$ . This change would produce a difference of about  $20 \text{ cm}^{-1}$  (+0.5%) in the extreme tail of the potential of Table XX, the difference diminishing rapidly with decreasing  $r$ ; the left limb (Table XIII) is not affected.

#### ACKNOWLEDGMENTS

Thanks are due to Professor Engelke for valuable discussions. We also thank Mrs. Schmidt-Mink, Miss Ross, and Dr. Heinze who kindly sent us the results from their Ph.D. theses on  $\text{Na}_2$ ,  $\text{NaK}$ , and  $\text{K}_2$ , respectively. We thank also Professor J. Vergès who kindly sent us a copy of Refs. 12 and 19(e) before publication.

#### APPENDIX

The reduced internuclear distance  $\rho$  and the reduced potential energy  $u$  are defined as follows:

$$u = U/D_e, \quad (1)$$

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

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

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

$r_e$  and  $D_e$  are the coordinates of the minimum of  $U(r)$ . For practical reasons,  $\rho$  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):

$$k_e = \mu \omega^2 = 4\pi^2 c^2 \mu \omega_e^2 \quad (5)$$

Here  $\mu$  is the reduced mass of the diatomic system,  $\omega$  is the harmonic vibration frequency determined from the spectrum,  $\omega_e$  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).  $\omega_e$  is in a very good approximation equal to the Dunham coefficient  $Y_{10}$  (e.g., for NaK  $^1\Sigma^+$ ,  $B_e^2/4\omega_e^2 = 1.47 \times 10^{-7}$ ).

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<sup>5</sup>(a) F. Engelke, H. Hage, and U. Sprick, *Chem. Phys.* **88**, 443 (1984); (b) H. Hage, Ph.D. thesis, University of Bielefeld, 1985.

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<sup>14</sup>The RPC is insensitive to a small change in the  $D_e$  value in the left limb (Ref. 1). It is much more sensitive to such a change in the right limb and extremely sensitive in the upper (quasihorizontal) portion of the right limb. This differentiated sensitivity of the RPC with respect to a change in the value of  $D_e$  is a very useful property: so while the insensitivity in the left limb makes accurate estimates of the left limb of the potential possible even if a small inaccuracy in  $D_e$  exists, its extreme sensitivity in the upper portion of the right limb may be used for an accurate estimation of the value of  $D_e$  [Refs. 2(a), 2(b), and 3].

<sup>15</sup>F. Engelke (private communication). New measurements on LiNa are in course and it will be interesting to compare the resulting RKR potentials with the results of the present paper. Experimenters believe that the values of  $r_e$  and  $\omega_e$  communicated for LiNa in Ref. 6 and for LiK in Ref. 5 remain valid; experimenters maintain that evaluation of the spectrum of the  $A-X$  transition of LiNa has essentially confirmed the  $k_e$  and  $r_e$  values for the ground state of LiNa.

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This value of  $k_e$  and Eq. (5) lead to the value  $182.76 \text{ cm}^{-1}$  whereas the value  $191.78 \text{ cm}^{-1}$  is given in Ref. 16. Our value of  $k_e$  seems correct which may be seen, e.g., on the values obtained by polynomial fitting by the procedure described in the Appendix of Ref. 11. [All eight calculations (Ref. 11) agree, for brevity we show only the results of one calculation and the corresponding Morse function check.] Table XXIII gives values of  $\omega_e$  [calculated from our  $k_e$  by means of Eq. (5)] in parallel for the theoretical potential of Ref. 16 and for a Morse potential which has the same values of the molecular constants as obtained through our interpolation of the theoretical potential. The Morse potential is interpolated for the same values of the internuclear distance as the theoretical potential; this calculation *only* serves as a check on the functioning of the method (Ref. 11).

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<sup>19</sup>(a) B. Barakat, R. Bacis, F. Carrot, S. Churassy, P. Crozet, F. Martin, and J. Vergès, *Chem. Phys.* **102**, 215 (1986); (b) K. Hussein, Ph.D. thesis, Université Claude Bernard, Lyon, France, 1985; (c) A. J. Ross, C. Effantin, J. d'Incan, and R. F. Barrow, *Mol. Phys.* **56**, 903 (1985); (d) W. Weickenmeier, U. Diemer, M. Wahl, M. Raab, and W. Demtröder, *J. Chem. Phys.* **82**, 5354 (1985); (e) C. F. Fellows, J. Vergès, and C. Amiot, *Mol. Phys.* **63**, 1115 (1988).

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- <sup>34</sup>M. Bettendorf and S. D. Peyerimhoff, *Chem. Phys.* **104**, 29 (1986) and references therein.
- <sup>35</sup>F. Jenč (unpublished). The generalized RPC formula is the subject of present research with the purpose of an improvement of the RPC method (not a simple thing at all), and will not be discussed in the present paper. The particular formulas employed here for the estimation of the potentials were used only as technical tools for the calculation and cannot replace the RPC formula of the Appendix.