

# Nature of the Autodetaching Sub $2P_{1/2}$ Threshold States of the Alkali Anions

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## Introduction

Patterson et al. [1] observed window-type resonances in the photodetachment of  $Rb^-$  and  $Cs^-$  lying slightly below ( $\sim 0.5$ – $3.0$  meV) the threshold for the  $2P_{1/2}$  channel openings. Evidence for the existence of a similar resonance was also obtained for  $K^-$ . Moores and Norcross [2, 3] performed photodetachment calculations on  $K^-$  and  $Cs^-$  and on  $Li^-$ ,  $Na^-$ , and  $K^-$  using configuration interaction (CI) wave functions for the ground-state anions and close-coupling wave functions for the continuum states. The results of these calculations were used to explain the experimentally observed window resonances as being due to the existence of metastable anion states, which lie slightly below the  $2P_{1/2}$  atomic states and which couple with the  $2S_{1/2}$   $kp$  continua of the ground-state atoms (via the  $r_{ij}^{-1}$  electronic interaction) to autodetach. Moores and Norcross indicate [2, 3] that the electronic configurations of the metastable states seem to be dominated by the  $np(n+1)s^1P$  and  $nnpnd^1P$  structures (e.g.,  $2p3s$ ,  $2p3d$  for  $Li^-$ ,  $4p5s$ ,  $4p3d$  for  $K^-$ , and  $6p7s$ ,  $6p5d$  for  $Cs^-$ ). This description is consistent with a wave function whose localized component consists of a valence  $p$ -electron coupled to another electron that exists in an "sd hybrid" orbital. The physical significance of such an "sd hybrid" is easily understood in terms of the motion of a loosely bound electron in the field of an atom having a single valence electron in a  $p$  orbital. The atomic valence electron can be viewed as occupying a  $p_{\pm 1}$  orbital which, to minimize Coulombic repulsion, is oriented at  $90^\circ$  relative to the axis of the  $sd$  hybrid. The  $s$  and  $d$  orbitals hybridize in order to localize the outer electron's charge density in a region of space that is away from the atomic  $p_{\pm 1}$  electron. Of course, the continuum part of this anion wave function is the  $2S_{1/2}$   $kp$  state of the alkali atom and free electron. The lifetimes of the resonance states are determined by densities of final states and by the magnitudes of the configuration coupling matrix elements  $\langle np(1)sd(2)|r_{12}^{-1}|kp(1)ns(2) \rangle$  (and their exchange integrals). Here,  $sd$  represents the  $sd$  hybrid orbital involved in the localized component of the resonance state. Certainly the calculations of Moores and Norcross seem to provide a reasonably accurate quantitative description of the sub  $2P_{1/2}$  threshold resonance states. However, it is natural to wonder whether the existence of these states should be considered as surprising. In other words, is there anything special about the fact that these states exist in anions, or do they also exist in the respective isoelectronic neutrals and positively charged ions? The answer to this question is not at all obvious because of the qualitatively different potentials (charge-induced dipole versus Coulomb) experienced by the outer electron in the anions and neutrals or cations. The primary purpose of this paper is to attempt to shed further light on the physical nature of these resonance excited states of the alkali anions and to indicate that these states do indeed exist in the respective isoelectronic species. Arguments are developed in support of the assignments originally made by Patterson et al. [1] and Moores and Norcross [2, 3] by employing currently available experimental data and performing extrapolations within isoelectronic series.

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## Symmetry Considerations

Because the ground electronic states of the alkali anions have  $1S$  symmetry, the electric-dipole accessible excited states must have  $1P_1$  symmetry and must be odd under inversion ( $1P_1^o$ ). For the heavier alkali's, where spin-orbit coupling is important, the  $3P_1$  states, which are odd under inversion ( $3P_1^o$ ), must also be considered. The  $np^2(3P_1)$  anion states, which Norcross [4] found, in a completely separate piece of work, to be bound relative to the alkali  $2P_{1/2}$  states (see Table I), are clearly not playing a role in these window resonances. Both spin and parity considerations allow one to exclude these  $np^2$  states. By no means are we implying that Norcross attempted to connect the  $P^2 3P_1$  anion states with the autodetaching resonances. We only mention these states in order to make it clear that they must be viewed as being distinct from and unrelated to the window resonances, which are the primary topic of discussion here.

*ns np Configurations*

The possibility that the  $nsnp\ v^1P_1$  or  $3P_1$  anion states contribute to the resonances can be ruled out on two grounds. First, the  $ns^2 \rightarrow nsnp$  excitation energies would be expected (because of the large  $ns^2$  Coulomb repulsion) to be smaller than the neutrals' corresponding  $ns \rightarrow np$  energy differences, which are [5] 14,900, 17,000, 13,000, 12,600, and 11,200  $\text{cm}^{-1}$  for the alkali atoms Li–Cs. The window resonances occur slightly below the  $ns^2 \rightarrow np\ ks$  channel openings, which have excitation energies of 19,900, 21,350, 17,040, 16,520, and 15,010  $\text{cm}^{-1}$  for Li–Cs (see Table I). Secondly, extrapolation of isoelectronic [6]  $ns^2 \rightarrow nsnp$  excitation energies (e.g.,  $N^{+3}$ ,  $C^{+2}$ ,  $B^{+1}$ , Be to predict  $Li^-$ ;  $P^{+3}$ ,  $Si^{+2}$ ,  $Al^{+1}$ , Mg to predict  $Na^-$ ), yield  $1P_1$  excitation energies of 13,500 and 11,000  $\text{cm}^{-1}$  for  $Li^-$  and  $Na^-$ , and  $3P_1$  excitation energies that are even smaller. Clearly, neither the  $1P_1$  nor the  $3P_1\ nsnp$  states lie close to the  $np\ ks$  channel openings; instead, they are buried in the  $1P_1$  (or  $3P_1$ )  $ns\ kp$  continua to which they are strongly coupled.

*np n's and np n''d Configurations*

Because the states contributing to the window resonances were found to lie very near the  $np\ ks$  channel opening, it is natural to consider the family of anion states that could be formed by adding an electron to an excited ( $2P_{1/2}$ ) alkali atom. To produce a state which has  $1P_1^o$  or  $3P_1^o$  symmetry, this  $2P_{1/2}$  alkali atom

TABLE I. Alkali anion state energies ( $\text{cm}^{-1}$ ).

Ion	$2P_{1/2}$ threshold <sup>a</sup>	$p^2(3P)^b$	$np(n+1)s\ (1P)^c$	$npn'd(1P)^c$
$Li^-$	19,900	- (20,700) <sup>c</sup>	22,000	>19,200
$Na^-$	21,350	20,850 (22,000) <sup>c</sup>	15,000	>22,900
$K^-$	17,040	16,081	<16,000 <sup>d</sup>	
$Rb^-$	16,520	15,358	<15,000 <sup>d</sup>	
$Cs^-$	15,010	13,701	<13,500 <sup>d</sup>	

<sup>a</sup> Obtained as the sum of the alkali electron affinity (Ref. 1) and the alkali  $2S \rightarrow 2P_{1/2}$  excitation energy (Ref. 5).

<sup>b</sup> From Norcross [4]. All energies are relative to the  $s^2(1S)$  anion ground state. Norcross did not observe a bound  $p^2(3P)$  state for  $Li^-$ .

<sup>c</sup> Obtained from isoelectronic extrapolation as discussed in the text.

<sup>d</sup> See the text for explanation.

state may be coupled with  $^2S_{1/2}$ ,  $^2D_{3/2}$ , or  $^2D_{1/2}$  states of the "extra" electron. (The  $^3P_1$   $np^2$  metastable states investigated by Norcross [4] are obtained by coupling the  $^2P_{1/2}$  alkali atom with  $^2P_{3/2,1/2}$  "extra" electron functions.) To form the lowest energy  $^1P_1^0$  (or  $^3P_1^0$ ) anion state, it is natural to employ the lowest lying "empty"  $s$  and  $d$  orbitals of the alkali anion (e.g.,  $3s$ ,  $3d$  for  $\text{Li}^-$ ;  $4s$ ,  $3d$  for  $\text{Na}^-$ ;  $5s$ ,  $3d$  for  $\text{K}^-$ ) in describing the  $^2S_{1/2}$  and  $^2D_{3/2,1/2}$  functions for the "extra" electron. In this way, one can form  $np\ n's$  and  $np\ n'd$  configurations of the alkali anions, which are likely to contribute strongly to the anion states which lie below the  $np$  alkali levels and which autodetach *via* coupling with the  $ns\ kp$  continua.

### Results for $\text{Li}^-$ and $\text{Na}^-$

To investigate the possibility that the  $np\ n's$  and  $np\ n'd$  configurations play dominant roles in the window resonance states, as Patterson et al. [1] and Moores and Norcross [2, 3] indicated, it is useful to employ experimental data on isoelectronic species. By simply extrapolating the  $2s^2 \rightarrow 2p3s$  ( $^3P$ ) excitation energies of Be,  $\text{B}^+$ ,  $\text{C}^{2+}$ ,  $\text{N}^{3+}$ , and  $\text{O}^{4+}$ , one predicts that the  $2p3s$  ( $^3P$ ) state of  $\text{Li}^-$  should lie  $20,600\text{ cm}^{-1}$  above the  $^1S$  ground state. (As a concrete example of the kind of extrapolation procedure employed, consider the  $2p3s$  ( $^3P$ ) excitation energies of Be,  $\text{B}^+$ ,  $\text{C}^{2+}$ ,  $\text{N}^{3+}$ , and  $\text{O}^{4+}$ . They are [5] 85,557, 181,655, 308,196; 465,300; and  $653,262\text{ cm}^{-1}$ , respectively. The differences between successive numbers are (approximately) 96,000; 127,000; 157,000; and  $188,000\text{ cm}^{-1}$ . The differences between successive members of this sequence are nearly the same, i.e.,  $31,000\text{ cm}^{-1}$ . Hence we predict the  $2p3s$  ( $^3P$ ) state of  $\text{Li}^-$  to lie at  $85,557 - (96,000 - 31,000) \approx 20,600\text{ cm}^{-1}$ .) A similar extrapolation (for Mg,  $\text{Al}^+$ ,  $\text{Si}^{2+}$ ,  $\text{P}^{3+}$ , and  $\text{S}^{4+}$ ) leads to a  $3s^2 \rightarrow 3p4s$  ( $^3P$ ) excitation energy of  $13,800\text{ cm}^{-1}$  for  $\text{Na}^-$ . Unfortunately, the  $^1P$  excitation energies are, to the best of our knowledge, not available for the above isoelectronic series. By considering the singlet-triplet splittings [5] in the  $2s\ 3s$  and  $2s\ 3p$  states of Be,  $\text{B}^+$ , etc., and the  $3s\ 4s$  and  $3s\ 4p$  states of Mg,  $\text{Al}^+$ ,  $\text{Si}^{2+}$ , etc., and assuming that the splittings in the  $2p\ 3p$  states of  $\text{Li}^-$  and the  $3p\ 4s$  states of  $\text{Na}^-$  will be of similar magnitude, one estimates the  $^1P$  states of  $\text{Li}^-$  and  $\text{Na}^-$  to lie  $22,000\text{ cm}^{-1}$  and  $15,000\text{ cm}^{-1}$  above their respective ground states. Recall that the  $^2P_{1/2}$  channel openings occur at  $19,900$  and  $21,350\text{ cm}^{-1}$  for  $\text{Li}^-$  and  $\text{Na}^-$ , respectively.

The  $2p\ 3d$  ( $^3P$ ) state of  $\text{Li}^-$  and the  $3p\ 3d$  ( $^3P$ ) state of  $\text{Na}^-$  are estimated, after performing similar extrapolations of these particular state energies for the above two isoelectronic series, to lie  $19,200$  and  $22,900\text{ cm}^{-1}$  above their respective ground states. On the basis of arguments similar to those put forth in the preceding paragraph, the  $pd$  ( $^1P$ ) states of  $\text{Li}^-$  and  $\text{Na}^-$  would be expected to lie slightly ( $200$ – $1500\text{ cm}^{-1}$ ) above these triplet states. The results of both sets of extrapolations are summarized in Table I.

To gain some feeling for the precision that is to be expected from the kind of isoelectronic extrapolation technique employed here, one can compute the  $ns^2 \rightarrow np^2$  ( $^3P$ ) excitation energies to be compared with those of Norcross [4]. By using data [5] on the isoelectronic series already discussed, one obtains extrapolated  $p^2$  ( $^3P$ ) state energies of  $20,700$  and  $22,000\text{ cm}^{-1}$  for  $\text{Li}^-$  and  $\text{Na}^-$ , respectively, the latter of which compares reasonably well with the results of Norcross ( $20,850\text{ cm}^{-1}$ ).

### Estimates for the Heavier Alkalies

The use of isoelectronic extrapolations to predict the relative stabilities of the  $ps$ ,  $pd$ , and  $p^2$  states of the heavier alkali anions is hampered by a lack of data for many of the elements involved. However, it is possible to make a few observations that may provide hints about the stabilities of these anion states. It is well known that the  $ns^2 \rightarrow ns(n+1)p$  and  $ns^2 \rightarrow (n+1)s\ np$  excitation energies are usually quite similar in magnitude. Because all of the alkaline earth atoms (Be–Ba) are found [5] to possess  $p^2$  ( $^3P$ ) and  $ns(n+1)p$  ( $^3P$ ) states that are quite close to one another in energy, one is led to believe that these atoms also have  $np(n+1)s$  ( $^3P$ ) states in this same energy range. Secondly, Ca, Sr, and Ba are known to have  $np(n-1)d$  ( $^3P$ ) states that lie slightly above their respective  $np^2$  ( $^3P$ ) states. The  $3p\ 3d$  ( $^3P$ ) state of Mg and the  $2p\ 3d$  ( $^3P$ ) state of Be do not lie near the respective  $p^2$  ( $^3P$ ) states probably because of the higher  $d$ -orbital quantum number involved in these cases.

Certainly these observations about the existence of  $np(n+1)s$  and  $np\ n'd$  states of the alkaline earth elements do not apply directly to the alkali anions. One must be able to predict what is likely to happen to the relative energies of these states as the nuclear charge is decreased by one unit (i.e., in going from the alkaline earths to the alkali anions). From elementary considerations of screening, one would expect



the  $np(n+1)s$  ( $^3P$ ) states to become stabilized relative to the  $np^2$  ( $^3P$ ) states as the nuclear charge is decreased by one, although both states would be destabilized in an absolute sense. Hence the  $np(n+1)s$  ( $^3P$ ) states of the alkali anions should lie further below the respective  $np^2$  ( $^3P$ ) states than was the case for the alkaline earths. Moreover, as the nuclear charge is decreased in going from the alkaline earths to the alkali anions, one expects the  $2p\ 3d$  and  $3p\ 3d$  states to become stabilized relative to the  $2p^2$  and  $3p^2$  states, thus bringing the  $pd$  ( $^3P$ ) states of  $\text{Li}^-$  and  $\text{Na}^-$  closer to their respective  $p^2$  ( $^3P$ ) states than was the case for  $\text{Be}$  and  $\text{Mg}$ . The relative energetics of the  $4p\ 3d$ ,  $5p\ 4d$ , and  $6p\ 5d$  states versus the  $4p^2$ ,  $5p^2$ , and  $6p^2$  states does not seem to be as sensitive to the change in nuclear charge. Hence it is likely that these states of the alkali anions are energetically similar, relative to their  $p^2$  ( $^3P$ ) states, to those of the alkaline earths, which were discussed above.

### Summary

Although the arguments presented above do tend to support the existence of both  $np(n+1)s$  ( $^3P$ ) (and hence  $^1P$ ) and  $npn'd$  ( $^3P$ ) (and hence  $^1P$ ) states of the heavier alkali anions, they do not comprise as convincing a case as our extrapolations gave for  $\text{Li}^-$  and  $\text{Na}^-$ . Thus we are not in a very good position to predict that  $\text{K}^-$ ,  $\text{Rb}^-$ , and  $\text{Cs}^-$  possess  $np(n+1)s$  ( $^1P$ ) and  $np(n-1)d$  ( $^1P$ ) states whose energies are close to the  $np^2$  ( $^3P$ ) states and, thus, close to the  $2P_{1/2}$  channel openings. All we can say at this stage is that the data of Moores and Norcross [2, 3] combined with our isoelectronic extrapolation strongly suggest that such states do exist in the near-threshold energy range for  $\text{Li}^-$  and  $\text{Na}^-$ . The lack of experimental data does not permit us to be as confident in the cases of the heavier alkali anions, although the conclusions of Moores and Norcross [2, 3] and of Patterson et al. [1] are (weakly) supported by our qualitative arguments, which attempt to link the alkaline earth atoms to the alkali anions as the nuclear charge is decreased by one unit. Clearly, no new experimental or theoretical data have been introduced in putting forth these arguments. Our intent was to employ available experimental information, simple isoelectronic extrapolations, and the known nuclear charge dependence of atomic orbital energies to examine the relative energetics of the  $np^2$  ( $^3P$ ),  $np(n+1)s$  ( $^1P$ ), and  $npn'd$  ( $^1P$ ) states of the alkali anions and to demonstrate that the states giving rise to the window resonances are not unique to the alkali anions. The same metastable states occur in the alkaline earth atoms and in isoelectronic cations. It is our hope that this exposition has shed some light on the physics involved in the binding of an "extra" electron to the  $np(2P_{1/2})$  excited states of neutral alkali atoms.

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