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Singlet and triplet Σ^+ excited states of NaH and KH: undulating potential energy curves

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Abstract

The $^1\Sigma^+$ and $^3\Sigma^+$ states of NaH dissociating into the 3s–5s states of Na and the $^1\Sigma^+$ and $^3\Sigma^+$ states of KH dissociating into the 4s–6p states of K are calculated using the effective core potential with the core polarization potential and the configuration interactions. Apart from ionic-neutral avoided crossings in cascade for the singlet states and neutral-neutral avoided crossings in both singlet and triplet states, all these states also show the undulating potential curves discovered recently: Phys. Rev. A 59 (1999) 1178–1186. The apparently complex potential curves are analyzed in this work. © 2000 Published by Elsevier Science B.V.

1. Introduction

The alkali hydride diatomic molecules have been intensively studied in the past by experimentalists and theoreticians (for review see Refs. [1,2]). The best known states are the ground (X, 1 $^1\Sigma^+$) and the A (2 $^1\Sigma^+$) and B (1 $^1\Pi$) excited states. The A and X states are produced by avoided crossings between the neutral A(ns)H and the ionic A^+H^- configurations. A recent work on the C (3 $^1\Sigma^+$) state of LiH [3] has reported an avoided crossing between the valence Li(2p)H and Rydberg Li(3s)H configurations at short distances and another avoided crossing between the neutral valence A(2p)H and ionic configuration at longer distances, resulting in a double potential well separated by a low barrier. To analyze such a complicated state, accurate quantum chemical calculations were invaluable.

As higher and higher states are studied, further complexity can be added. Our recent work has revealed undulating potential curves having double or triple potential wells and having as many potential barriers [4]. These undulations have no relationship with any avoided crossing but are directly connected with the undulating atomic orbital structure. In fact, the existence of undulating potential curves (or surfaces) is believed to be general in the highly excited electronic states. A simple rule concerning the num-

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ber of potential barrier in diatomic molecules consisting of one alkali-metal atom (with the *m*s ground state) and a compact atom (like hydrogen atom or rare-gas atoms) or a compact molecule (like hydrogen molecule) has been proposed in [4]. The Σ molecular state made from the *n*s or *n*p alkali-metal atomic state has $n-m$ number of potential barrier and the Σ molecular state made from the *n*d alkali-metal state has $n-m-1$ number of potential barrier, and the Σ molecular state made from the *n*f alkali-metal atomic state has $n-m-2$ number of potential barrier.

The single potential barriers not originating from any avoided crossing has been known for the metal/rare-gas diatomics (see for example Ref. [5]). The Helium dimer has been reported to have strange potential barriers (or 'humps') which have been interpreted to originate from the Pauli-principle-induced Rydberg-core repulsion combined with an attractive core-core interaction [6,7]. These can be neatly explained in terms of the nodal structure of the Rydberg atomic orbital as has been given in our previous paper [4].

In this work, we have calculated the excited states of NaH and KH to investigate the existence of potential curve undulations. Our result shows complex potential curves, in particular for the singlet states. We analyze and explain these complexities according to the simple rule mentioned in above determining the number of the potential barrier and potential well.

2. Method of computation

The effective core potentials and the core polarization potentials are used to simulate the core electrons of the alkali atoms. We employed the effective core potential from the Stuttgart group [8,9]. The core polarization potential was initially proposed by Müller and Meyer [10]. The parameters for these effective potentials are available in a web site [11]. The large-core effective potentials were used in this work as the finite volume of the core electrons does not affect the molecular energy in the alkali hydrides except for very short distances. We have prepared basis sets to optimally represent the 3s, 3p, 4s, 3d, 4p and 5s states of Na and the 4s, 4p, 5s, 3d, 5p, 4d, 6s, 4f and 6p states of K (according to the order of increasing energy). For the potassium atom, the original parameters of the core polarization potential did not give satisfactory atomic energy differences. The cutoff radius was adjusted in such a way that the relative atomic energies for the above-mentioned states are optimally reproduced. The dipole polarizabilities and the cutoff radii for Na^+ and K^+ used in this work are listed in Table 1 together with the final basis sets. In the potassium case, the adjustment of the cutoff radius improved the excitation energies for the neutral states but the ionization potential became worse than before the adjustment.

The relative atomic energies calculated with our basis sets and the polarizabilities of the atomic core are reported in Table 2. We can see there an excel-

Table 1
Basis sets and the effective potential parameters for Na and K used in this work

Atom	l	Exponent								
Na [a]	s	2.352500	0.538490	0.059999	0.023897	0.014500	0.005530	0.002950		
	p	0.481406	0.087451	0.034403	0.024000	0.014523	0.005127			
	d	0.091093	0.039435	0.018060						
	f	0.101000								
K [b]	s	7.885550	3.956920	0.720896	0.326640	0.172479	0.027348	0.013012	0.004400	0.002200
	p	21.54020	1.103270	0.473652	0.224785	0.101648	0.045680	0.008400	0.00500	0.00200
	d	5.036370	1.256220	0.332781	0.079668	0.030362	0.009043	0.004000	0.001900	
	f	0.016500	0.006900	0.002800						

[a] $\alpha_d(Na^+) = 0.9947$; $R_c = 0.62$.
[b] $\alpha_d(K^+) = 5.354$; $R_c = 0.5731$.

Table 2
Calculated atomic energies of sodium and potassium (in cm^{-1})

Atom	State	Experimental	Calculation	Error
Na	IP	41438	41450	−12
	5s	33201	33193	−8
	4p	30271	30263	−8
	3d	29713	29709	−4
	4s	25740	25731	−9
	3p	16968	16957	−11
	3s	0	0	0
K	IP	35010	34829	−181
	6p	29005	29004	−1
	4f	28128	28120	−8
	6s	27451	27451	0
	4d	27397	27395	−2
	5p	24714	24712	−2
	3d	21535	21530	−5
	5s	21027	21027	0
	4p	13024	13017	−7
	4s	0	0	0

lent agreement between our calculated energies and the experimental data. For the hydrogen atom, the same basis set as has been used in Ref. [4] was used. This basis set yielded the electron affinity of 0.736 eV which is quite close to the experimental value, 0.756 eV [12]. However, the remaining error, 160 cm^{-1}, can still affect the quality of the potential curve as has been shown before [4] and as can be seen below. In this work, the spin–orbit coupling has not been taken into account.

For the molecular calculation, a large active space including at least all molecular orbitals made from the atomic orbitals for the above-mentioned atomic states and the 1s atomic orbital of hydrogen was used to correlate the two valence electrons of NaH and KH in all possible way within this active space. The state-averaged molecular orbitals (for 7 lowest $^1\Sigma^+$ states or 6 lowest $^3\Sigma^+$ states for the NaH, and 10 $^1\Sigma^+$ states or 9 lowest $^3\Sigma^+$ states for the KH) were generated from the multi-configuration self consistent field calculation. Then, all active and virtual orbitals were included in the multi-reference single and double configuration interactions. The MOLPRO [13] has been used in this work.

3. Result and discussion

The potential energy curves of NaH for five $^1\Sigma^+$ states dissociating adiabatically into the 4s, 3d, 4p, 5s and 4d states and four $^3\Sigma^+$ states dissociating into from 4s to 5s states are drawn in Fig. 1. The lowest two $^1\Sigma^+$ states and two $^3\Sigma^+$ states dissociating into 3s and 3p are omitted in this figure for the sake of clarity. The singlet states in Fig. 1(a) shows the ionic-neutral avoided crossings in cascade. The 3 $^1\Sigma^+$ state adibatically dissociating into 4s shows a coupling at short distances between the 3p and 4s configurations, resulting in an avoided crossing at short distances. According to the simple rule explained in Ref. [4], the neutral 3p state (both singlet and triplet) is entirely repulsive while the 4s state has a small potential well at short internuclear distances. This inner potential well has about the same characteristics as that of the ground state well of the cation, NaH^+, because the Rydberg electron is loosely bound to the cation and it does not contribute much to the bond energy at short distances. The potential barrier for the 4 $^1\Sigma^+$ state originates from a repulsive interaction between the maximum electron density part of the Na(4s) and the electron residing around the proton. The $^1\Sigma^+$ state made from the Na(3d) asymptote is repulsive with a potential well at short distances which is due to the low electron density region located between the core electron distribution and the 3d electron distribution. As the $^1\Sigma^+$ state made from the Na(4p) is only slightly repulsive with a small potential well at short distances, an avoided crossing between the 3d and 4p states takes place. Thus the 5 $^1\Sigma^+$ state has a 4p character at short distances. This state has a potential barrier originating from the repulsive interaction between the outer density maximum of the Na(4p) atomic orbital and the electron residing around the proton as in the Na(4s) case. The $^1\Sigma^+$ state made from the Na(5s) would have two potential barriers with the small inner potential well and a shallow outer potential well according to the rule of Ref. [4]. While there is a barrier at a long distance in the 7 $^1\Sigma^+$, the inner one is overridden by a mixing with the 3d state as the 3d state is repulsive. The 7 $^1\Sigma^+$ state appears to have another avoided crossing with higher state at short distances.

The potential curves for the $^3\Sigma^+$ states are simpler than the $^1\Sigma^+$ states because of no low-energy ionic state. The rule of Ref. [4] applies here without any complication except the coupling between the attractive 4p state and the repulsive 3d state. The 3

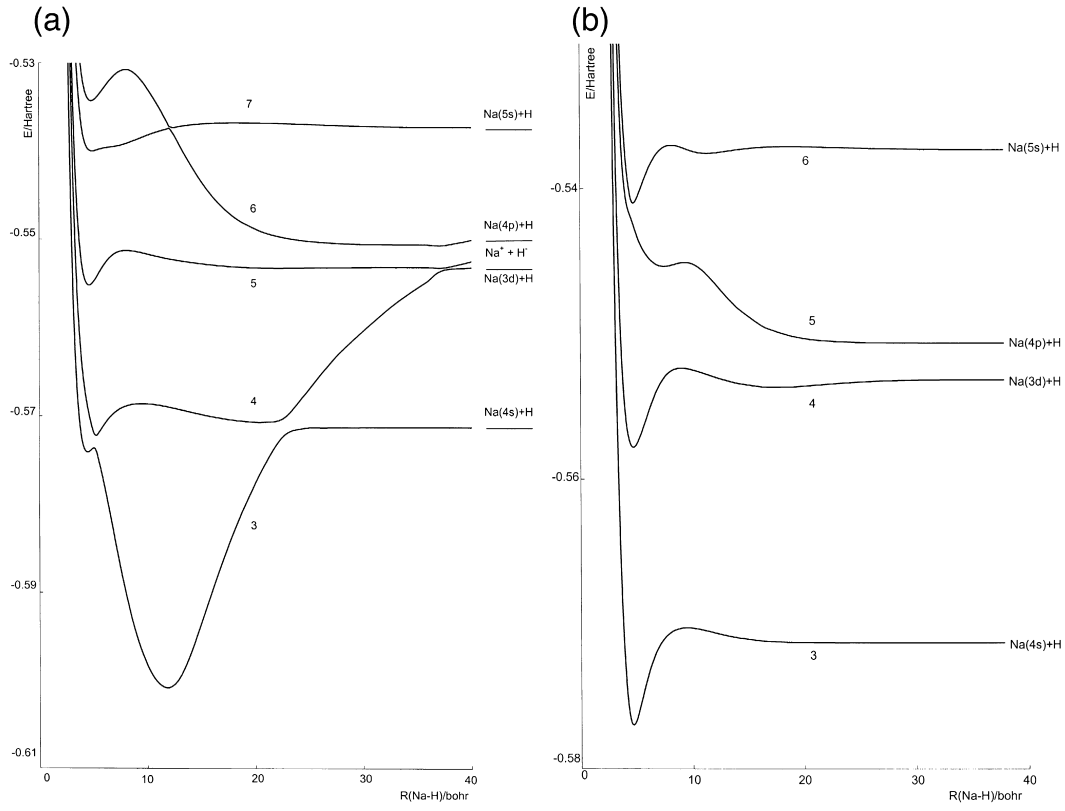

Fig. 1. Potential energy curves for the $^1\Sigma^+$ states (a) and the $^3\Sigma^+$ states (b) of NaH (E in hartree and R in bohr). The state numbering is in the order of increasing energy.

and 4 $^1\Sigma^+$ states coming from the 4s and 4p atomic configurations, respectively, have a single potential barrier. The 6 $^1\Sigma^+$ state coming from the 5s state has two potential barriers and two potential wells. The outer barrier is made from the interaction between the outer electron density maximum region of Na(5s) atomic orbital and the electron residing around the proton. The outer well is due to the interaction between the outer nodal area of Na(5s) atomic orbital and the H electron.

The potential energy curves of KH for eight $^1\Sigma^+$ states adiabatically dissociating into the 5s, 3d, 5p, 4d, 6s, 4f, 6p and 5d states and seven $^3\Sigma^+$ states dissociating into from 5s to 6p states are drawn in Fig. 2. The lowest two $^1\Sigma^+$ states and two $^3\Sigma^+$ states dissociating into 4s and 4p are not reported in this figure for the sake of clarity. The singlet states in Fig. 2(a) show the ionic-neutral avoided crossings in cascade as in the NaH case. The neutral part of these states exhibit differences between the singlet and the triplet states as in the NaH case. The Pauli exclusion principle does not allow a close contact between the two valence electrons in the triplet state while it is allowed for the singlet states. However, the singlet-triplet difference in KH is somewhat less marked than in NaH. This may be due to more diffuse electron distribution of the former in comparison with the latter. The 4 $^1\Sigma^+$ state diabatically dissociating into 5s is perturbed so strongly by mixing with the 3d configuration at short distances and with the ionic configuration at long distances that the expected single potential barrier is erased out. In contrast, the (5s) 3 $^3\Sigma^+$ state shows an intact barrier at 13.4 bohr. The mixing between the 3d and 5p configurations appears differently for the singlet state and the triplet state, too. A closely avoided crossing, meaning a small diabatic coupling, takes place in the 4 and 5 $^3\Sigma^+$ states, while the 5 and 6 $^1\Sigma^+$ states

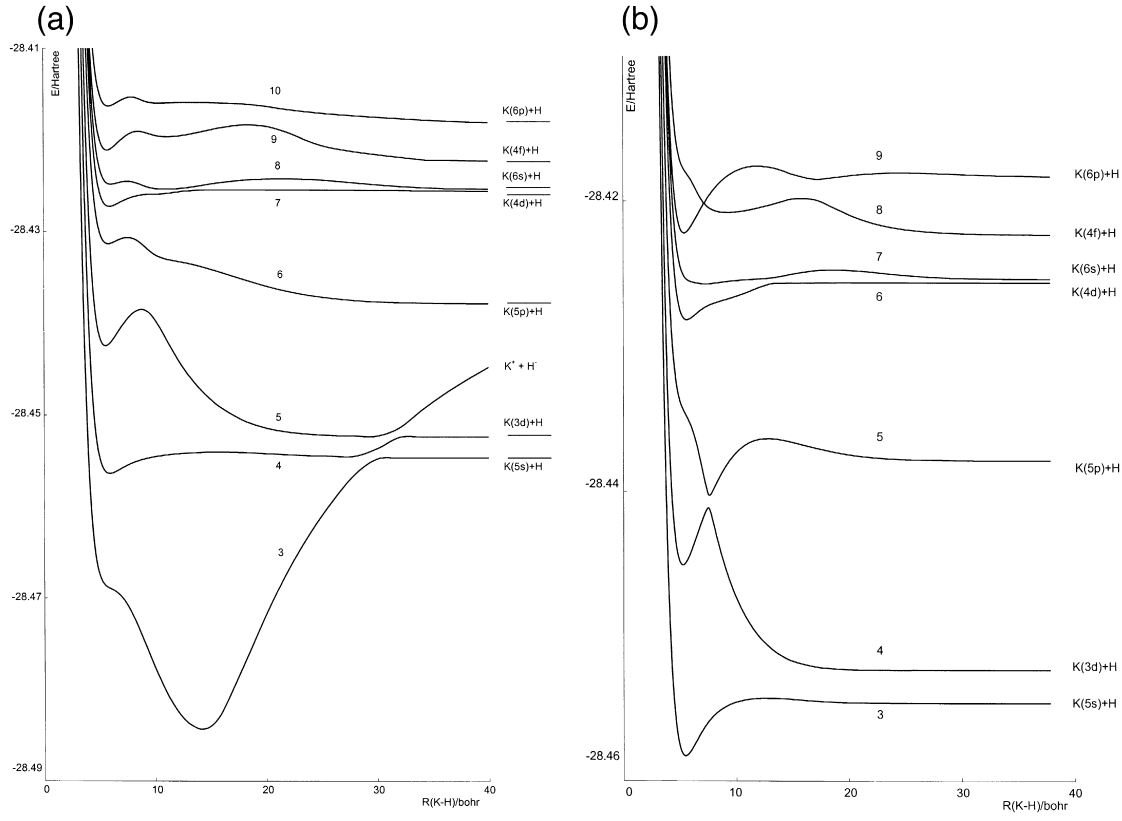

Fig. 2. Potential energy curves for the $^1\Sigma^+$ states (a) and the $^3\Sigma^+$ states (b) of KH (E in hartree and R in bohr). The state numbering is in the order of increasing energy.

make a larger avoided crossing, meaning a large diabatic coupling. (When comparing the singlet state to the corresponding triplet state, one should consider the intrusion of ionic part. As a consequence, their state numberings differ by one for the internuclear distances shorter than the ionic-neutral crossing distance but they are identical for longer distances.)

The K(4d) and K(6s) asymptotes are so close that a mixing between these two configurations could be unavoidable at short distances. Were these asymptotes well separated, the rule of Ref. [4] predicts a single barrier with the inner well for the 4d state and two barriers and two wells for the 6s state. Although the potential curves for these two states appear to be significantly perturbed both in the singlet (7 and 8 $^1\Sigma^+$) and triplet (6 and 7 $^3\Sigma^+$) states, the undulating characters do remain. The potential curve for the 4f state as it appears in the 9 $^1\Sigma^+$ state is typical as has been shown in the LiHe, LiNe and LiH cases [4]. In contrast, the 8 and 9 $^3\Sigma^+$ states are results of a closely avoided crossing between the 4f and 6p configurations.

The potential minima and maxima in the electronic states of NaH and KH are summarized in Table 3. The potential well of the X, A and C states and the outer well of the D state (4 $^1\Sigma^+$) are made from the ionic configurations, and the ionic part of the potential curve is usually difficult to calculate accurately. The experimental spectroscopic data for the ground state of NaH are: $R_e = 3.57$ bohr and $D_e = 15900$ cm^{-1}, while our calculation yielded 3.55 bohr and 15685 cm^{-1}, respectively. For the A state of NaH, the experimental data are 6.03 bohr and 10143 cm^{-1} against our values, 6.01 bohr and 9997 cm^{-1}. For the ground state of KH, the experimental data are 4.23 bohr and 14773 cm^{-1} against our

Table 3
Potential energy minima and maxima of the $^1\Sigma^+$ and $^3\Sigma^+$ states with respect to the corresponding adiabatic asymptotes in NaH and KH (R in bohr and E in cm^{-1})

Molecule	Electronic state	E_{min} (cm^{-1})	R_{min} (bohr)	E_{max} (cm^{-1})	R_{max} (bohr)
NaH	$7\,^1\Sigma^+$	−4149	4.84	−3372	8.06
		−4820	12.31	−4694	18.71
	$6\,^1\Sigma^+$	−4178	4.92	−3618	12.06
	$5\,^1\Sigma^+$	−3927	4.63	−3072	8.08
		−3508	22.46		
	$4\,^1\Sigma^+$	−4738	5.24	−3947	9.51
	$3\,^1\Sigma^+$	−612	4.48		
		−6490	11.83	−510	5.05
	$2\,^1\Sigma^+$	−9997	6.01		
	$1\,^1\Sigma^+$	−15683	3.55		
	$6\,^3\Sigma^+$	−812	4.75	62	8.18
‘		−60	11.32	43	18.79
	$5\,^3\Sigma^+$	1158	7.70	1218	9.37
	$4\,^3\Sigma^+$	−1020	4.71	173	9.02
		−114	17.55		
	$3\,^3\Sigma^+$	−1249	4.66	226	9.48
KH	$10\,^1\Sigma^+$	437	5.53	653	7.49
		510	9.77	528	12.58
	$9\,^1\Sigma^+$	−233	5.41	212	8.06
		86	10.52	370	17.49
	$8\,^1\Sigma^+$	−546	5.73	−476	7.13
		−660	10.30	−415	20.23
	$7\,^1\Sigma^+$	−416	5.60	−11	15.91
	$6\,^1\Sigma^+$	−1253	5.49	−1107	7.15
	$5\,^1\Sigma^+$	−1012	5.24	−142	8.31
	$4\,^1\Sigma^+$	−881	5.59	−365	14.97
	$3\,^1\Sigma^+$	−6516	13.40		
	$2\,^1\Sigma^+$	−8811	7.01		
	$1\,^1\Sigma^+$	−15066	4.22		
	$9\,^3\Sigma^+$	−390	7.17	176	11.95
		−20	17.15	76	24.67
	$8\,^3\Sigma^+$	24	5.40	476	7.19
		338	9.22	558	15.94
	$7\,^3\Sigma^+$	−77	7.30	136	18.70
	$6\,^3\Sigma^+$	−563	5.63		
	$5\,^3\Sigma^+$	−533	7.63	328	12.82
	$4\,^3\Sigma^+$	1596	5.27	2460	7.52
	$3\,^3\Sigma^+$	−799	5.48	75	12.81

values of 4.23 bohr and 15066 cm^{-1}. The experimental value for the A state of KH are 7.11 bohr and 8698 cm^{-1} against our values of 7.01 bohr and 8811 cm^{-1}. (All experimental data are taken from [1]). Curiously, our calculations underestimate the bond energy for the NaH while that of the KH is overestimated in comparison with the experimental data. This could be partially explained by the fact that the (ionization potential of the alkali atom) − (electron affinity of H) with Na is overestimated by 150 cm^{-1} while this quantity for K is underestimated by 20 cm^{-1} in our calculation in comparison with the experimental data. The other inner potential wells made from the neutral configurations are believed to be more accurate, although there are presently no experimental data to confirm this yet.

The double-well character of the D ($4\,^1\Sigma^+$)state of LiH has been recently found by Luh et al. [14] by

the optical-optical double resonance technique using the A and B states as the intermediate states. A close comparison between the observed data and the ab initio calculation [4] has proved the accuracy of the theoretical prediction. (In this case, the ab initio calculated $T(\nu', \nu'')$ transition energies, which is around 48000 cm^{-1}, differ from the observed spectra by from -10 to 71 cm^{-1}.) The extension of such experimental work may allow observation of the highly excited states predicted in this work.

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