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Theoretical investigation on the crossing states $^1\Sigma_g^+(^2P-{}^2P)$ and $X^2\Sigma_g^+$ of the dimers Li_2, Na_2, K_2 and their positive ions Li_2^+, Na_2^+ and K_2^+

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Calculation has been made of the potential energy curves of the crossing states $Me_2\,^1\Sigma_g^+(^2P-{}^2P)$ and $Me_2^+\,X^2\Sigma_g^+$, where Me = Li, Na, K. These crossings are the basis of the photodissociation occurring in alkali vapour lasers. The calculations are completely *ab initio*, following a group functions procedure.

Key words: Alkali vapour lasers—Alkali dimers—Potential energy curves.

1. Introduction

In the past few years much experimental work has been devoted to the photodissociation occurring in vapours of alkali metals by CW or pulsed light lasers [1–5]. A mechanism which has been proposed involves the following step

$$Me\,^2P + Me\,^2P \rightarrow Me_2^+\,^2\Sigma_g^+ + e^-$$

where Me = Li, Na or K. The process would imply i) an excitation of metal vapour atoms $ns \rightarrow np$ and a consequent large growth of the population of the excited state, ii) the formation of the ionic dimer ($X\,^2\Sigma_g^+$ state) and finally iii) its excitation to $A\,^2\Sigma_u^+$ state which dissociates as $Me\,^2S + Me^+\,^1S$. Although many calculations have recently been reported on ground and some excited states of Me_2 and Me_2^+ [6–17], no calculation is available for the excited states $^1\Sigma_g^+(^2P-{}^2P)$ of Me_2 which actually is the most interesting and the crucial point of the above-mentioned mechanism. It is to be pointed out that in the experimental conditions (very low vapour density) the probability of multiple atomic collisions is very low, so the dimer potential energy curves give a good representation of the actual physical situation. Therefore, we have considered the calculation of the potential energy curves of some electronic states of this group of molecules and ions useful. We have limited our calculations to the ground states $X^1\Sigma_g^+(\mathrm{Me}_2)$ and $X^2\Sigma_g^+(\mathrm{Me}_2^+)$ and to the excited states ${}^1\Sigma_g^+({}^2P-{}^2P)(\mathrm{Me}_2)$ and $A^2\Sigma_u^+(\mathrm{Me}_2^+)$. The ground states of Me_2 have been calculated only for a comparison with previous calculations.

2. Calculation scheme

The calculations of the present work are completely *ab initio*, while most previous calculations adopted a pseudopotential approach. We have employed the following scheme:

a) The wavefunction has been written as an antisymmetrized product of group functions. The strong orthogonality condition has been applied.

b) The electrons have been partitioned in three groups: two groups for the inner shells of the atoms, one for the valence electrons.

c) A single antisymmetrized product has been employed for every inner shell, without any variation with the internuclear distance. It has been verified that freezing the inner shells functions at the separated atoms value does not cause any appreciable worsening of the results. This fact can suggest that the polarization factors which have been introduced in some pseudopotential schemes are to be justified by the missing exchange integrals and not by a substantial variation of the core functions.

d) The valence electrons have been described by group functions which are able to give the right dissociation limit and to properly evaluate the correlation energy. Since the multiconfigurational scheme can give very slow and difficult convergence, we have employed wavefunctions with minimum number of determinants. The correlation energy has been evaluated afterwards by integrating a density matrix functional, following the method outlined in [18]. This calculation has been limited to the valence electrons. We think that this method produces reliable

Atom	Type	α
Li	*s*	0.008
Li	*p*	8.0
Li	*p*	3.0
Li	*p*	1.0
Li	*p*	0.3
Li	*p*	0.1
Li	*p*	0.03
Li	*p*	0.01
Na	*p*	0.1
Na	*p*	0.02
Na	*p*	0.004
Na	*p*	0.001
K	*s*	0.004
K	*p*	0.032
K	*p*	0.01
K	*p*	0.032

Table 1. Basis functions added to the literature basis sets

results also for the dependence of the correlation energy on the internuclear distance. The strong orthogonality between valence and core wavefunctions has been obtained by expanding the valence orbitals in a subspace which is rigorously orthogonal to the core orbitals subspace. Since the valence electrons are only two, this fact does not introduce any serious difficulty. In our calculations we employ the Modified Gaussians functions [19]. The orbital exponents are those given by Huzinaga (Li, Na) [20] and Wachters (K) [21], with the addition of some very expanded functions, as reported in Table 1.

3. Results and conclusions

For all the molecules examined we find a crossing of the ${}^1\Sigma_g^+({}^2P-{}^2P)$ state with the $X^2\Sigma_g^+$ state of the relevant ion. We have considered interesting an evaluation of the quantum number of the vibrational level closest to the crossing point. This

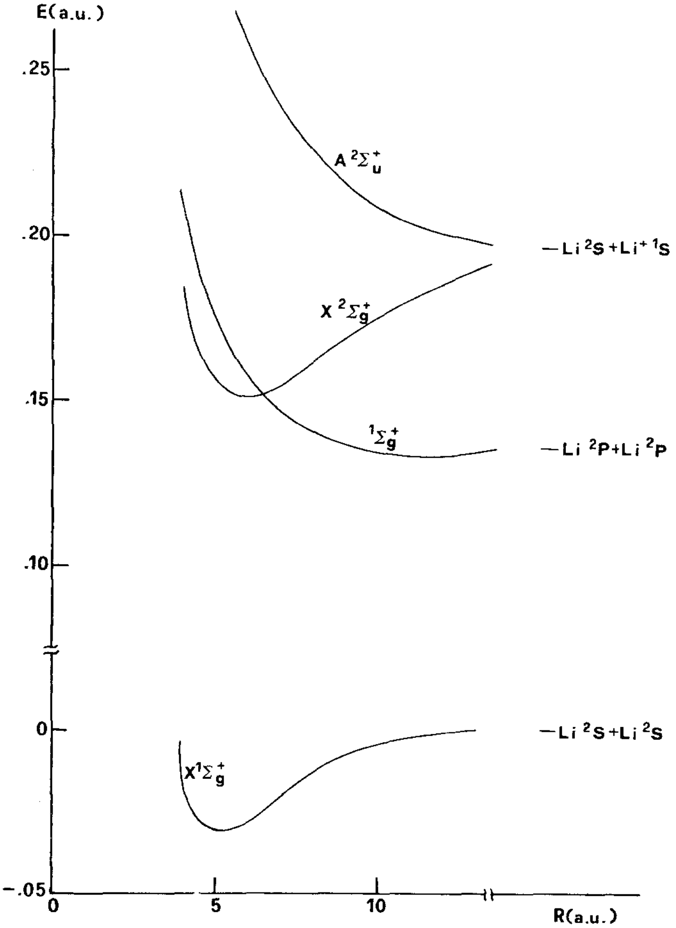

Fig. 1. Potential energy curves for the systems Li_2 and Li_2^+, including the correlation energy

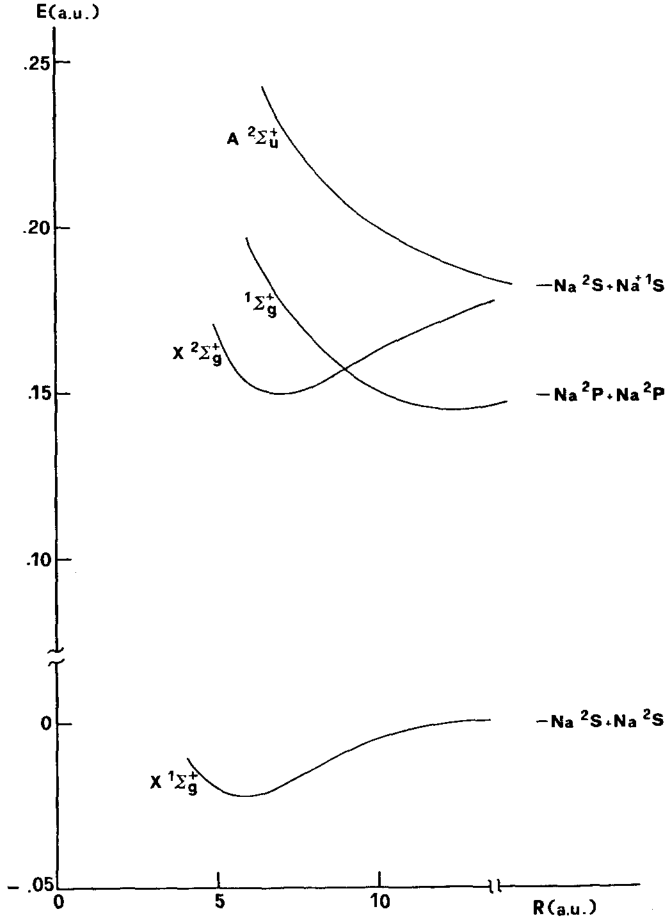

Fig. 2. As in Fig. 1, Na_2 and Na_2^+

Table 2. Li_2 and Li_2^+ potential energy curves. All energies (a.u.) are referred to Li dissociation limit

	Li_2		Li_2^+	
R	$X^1\Sigma_g^+$	$^1\Sigma_g^+(^2P-^2P)$	$X^2\Sigma_g^+$	$A^2\Sigma_u^+$
∞	0	0.1356	0.1963	0.1963
12	−0.0009	0.1334	0.1852	0.2005
10	−0.0045	0.1344	0.1755	0.2081
8	−0.0131	0.1407	0.1618	0.2250
7	−0.0205	0.1469	0.1549	—
6	−0.0284	0.1562	0.1509	0.2577
5	−0.0318	0.1728	0.1558	—
4	−0.0165	0.2077	0.1836	—

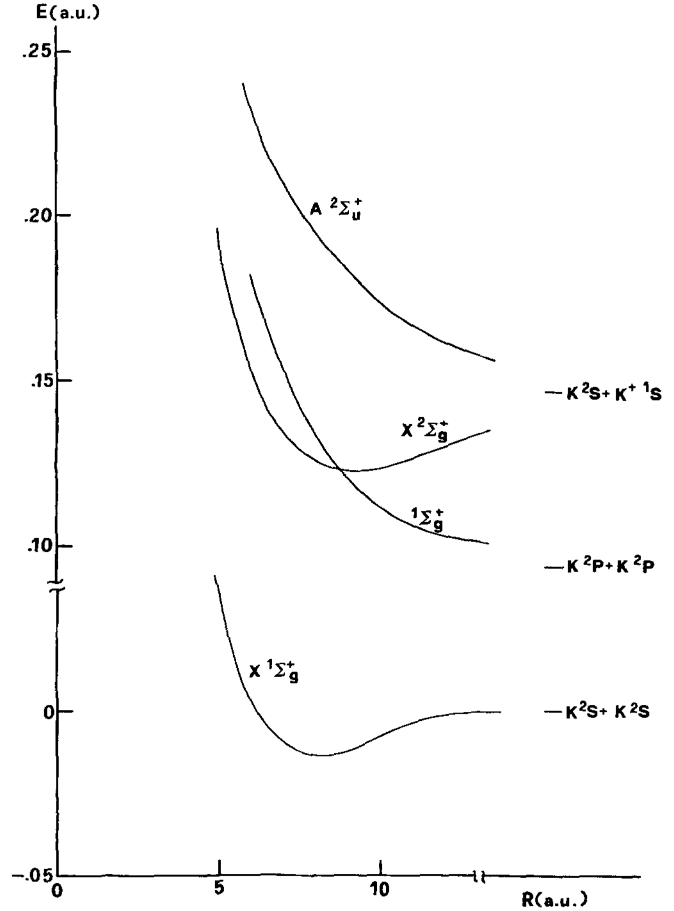

Fig. 3. As in Fig. 1, K_2 and K_2^+

Table 3. Na_2 and Na_2^+ potential energy curves. All energies (a.u.) are referred to Na dissociation limit

	Na_2		Na_2^+	
R	$X^1\Sigma_g^+$	$^1\Sigma_g^+(^2P-^2P)$	$X^2\Sigma_g^+$	$A^2\Sigma_u^+$
∞	0	0.1490	0.1821	0.1821
12	−0.0005	0.1445	0.1712	0.1890
10	−0.0050	0.1504	0.1629	—
9	−0.0089	0.1568	0.1577	—
8	−0.0138	0.1659	0.1525	0.2161
7	−0.0197	0.1771	0.1493	—
6	−0.0228	0.1958	0.1526	0.2510
5	−0.0198	—	0.1695	—

Table 4. K_2 and K_2^+ potential energy curves. All energies (a.u.) are referred to K dissociation limit

	K_2		K_2^+	
R	$X^1\Sigma_g^+$	$^1\Sigma_g^+(^2P-^2P)$	$X^2\Sigma_g^+$	$A^2\Sigma_u^+$
∞	0	0.0937	0.1464	0.1464
12	−0.0014	0.1025	0.1295	0.1616
11	−0.0044	0.1057	0.1262	0.1668
10	−0.0073	0.1102	0.1236	0.1736
9	−0.0110	0.1198	0.1227	0.1823
8	−0.0125	0.1328	0.1250	0.1929
7	−0.0091	0.1515	0.1335	0.2084
6	0.0034	0.1800	0.1528	0.2294
5	0.0356	—	0.1920	0.2682

quantum number has been evaluated in a very simple way, by the formula of the energetic levels of the Morse oscillator [22]. The calculated levels are $n=0$ (Li_2^+), $n=14$ (Na_2^+) and $n=0$ (K_2^+). The calculated quantum number for Na_2^+ is in good agreement with that given in Ref. [2].

In Figs. 1–3, as well as in Tables 2–4 we report the potential energy curves of Li_2 and Li_2^+, Na_2 and Na_2^+, K_2 and K_2^+, respectively. The effect of the correlation energy, for both ground and excited states, is very noticeable. In particular, the weak bond of $^1\Sigma_g^+(^2P-^2P)$ states is completely due to a correlative effect.

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