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The importance of valence *p* functions in the bonding of Na_2, K_2, and Cu_2 and their positive and negative ions*

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Summary. The relative importance of the valence *p* functions for describing the bonding in the valence isoelectronic Na_2, K_2, and Cu_2 molecules and their positive and negative ions is investigated. In absolute magnitude the contribution of the *p* functions to the dissociation energy follows the trend $Cu > Na > K$ while by percentage of the dissociation energy the importance of the *p* functions follows the polarizabilities, i.e. $K > Na > Cu$. The bonding in K_2, K_2^+, and K_2^- is analyzed to explain the observed trends.

Key words: Valence *p* functions – Na_2 – K_2 – Cu_2 – Bonding

1. Introduction

Cu_2, Na_2, and K_2 each have a single *s–s* bond, and thus a bond order of one, making them valence isoelectronic with H_2. However, the bonding in Cu_2, Na_2, and K_2 as well as their positive and negative ions is very different from that in H_2. For example, H_2^+ has a dissociation energy (D_e) that is only 60% of the D_e of H_2 [1]. In contrast, Na_2^+ and K_2^+ have larger D_e values than the neutral diatomics [1] and Cu_2^+ has a D_e that is 92% that of Cu_2 [2]. The negative ions also exhibit trends which are dissimilar to H_2^-: Na_2, K_2, and Cu_2 all have sizable electron affinities [3, 4], whereas H_2^- is unstable with respect to H_2 plus an electron.

The difference in the bonding arises because Na, K, and Cu are much more polarizable than H [5]. Removing an electron from H_2 to form H_2^+ reduces the bond order from one to one half. Hence if there were no relaxation of the orbitals a D_e of about one half that of the neutral would be expected. In reality, however, the pairing energy required to form the neutral bond, as well as relaxation of the bonding orbital in the ion, leads to a D_e for the ion that is somewhat more than half that of the neutral diatomic molecule. For Na, K, and Cu the atomic polarizabilities are much larger than for H leading to D_e values

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for the positive ions which are comparable to, or even larger than those of the neutral compounds. A similar effect occurs for the negative ion, where the "extra" electron is nominally in an antibonding combination of the valence *s* orbitals. As for the positive ion, the bond order is reduced from one to one half, and a significantly smaller D_e for the anion than the neutral molecule would be expected. However, the antibonding orbital is strongly polarized out of the bonding region becoming essentially nonbonding in character – see Fig. 1. The difference in the experimental D_e values for the neutral molecules and their ions indicates a large stabilization associated with this polarization. In this work we report *ab initio* calculations to quantify this effect for Na_2, K_2, and Cu_2 and their negative and positive ions.

2. Method of calculation

The Na primitive basis set is derived from the ($12s9p$) set of McLean and Chandler [6], while the K primitive set is derived from the ($14s9p$) set of Wachters [7]. Two diffuse *s* functions are added to these primitive sets to describe the negative ion. The exponents of the added functions are factors of 2.5 and 6.25 smaller than the most diffuse function in the original basis sets. In addition, three *p* functions (0.1236, 0.06261 and 0.02281) are added to K to describe the $4p$ orbital. Five even-tempered $3d$ polarization functions of the form $2.5^n \times \alpha_0$ are added to K, where $\alpha_0 = 0.0182$. Four even-tempered *d* functions of the same form are added to Na, but with $\alpha_0 = 0.0455$; a fifth more compact $3d$ function ($\alpha = 4.033668$) is also added to Na. The Cu basis set is that used in our previous study [8] of Cu_2^- and Cu_3^-; it is derived from the ($14s9p5d$) set of Wachters [7], supplemented with two *s* functions, three *p* functions, and two *d* functions. These primitive sets are contracted using the atomic natural orbital (ANO) procedure [9] based on the anions. For Na^- and K^- only the two valence *s* electrons are correlated, while for Cu^- the $3d$ and $4s$ electrons are correlated. The final basis sets are of the form: Na ($14s9p5d$)/[$5s3p2d$], K ($16s12p5d$)/[$6s4p2d$], and Cu ($16s12p7d$)/[$6s5p3d$]. Only the pure spherical harmonic components of the basis functions are employed in the calculations.

We use the self-consistent-field/modified coupled-pair functional (SCF/MCPF) approach [10]. For K_2 and Na_2 and their ions only the valence *s* electrons are correlated. The positive ion has only one valence electron and is treated using an SCF approach. Core-valence (CV) correlation substantially reduces the radial extent of the valence orbital and therefore its inclusion is required to compute accurate bond lengths for the alkali dimers [11–13]. For a given bond length, however, CV correlation not only reduces the repulsion, but also reduces the polarizability of the atoms. Thus the inclusion of CV correlation has only a small effect on the computed D_e and electron affinity (EA). While the effect of CV correlation on the atomic ionization potentials (IP) is somewhat larger (0.2 eV for Na and 0.3 eV for K), the effect on the D_e of Na_2^+ and K_2^+ is small [13] (0.02 eV). Thus CV correlation is not expected to significantly affect the discussion of the valence *p* functions and we neglect it in this work. For Cu_2^+, Cu_2, and Cu_2^- it is necessary to include both $3d$ and $4s$ correlation to obtain reasonable estimates of the D_e; a two-electron treatment of Cu_2 gives a D_e value that is only 85% of a treatment including $3d$ correlation, for example.

3. Results and discussion

The calculated bond lengths, dissociation energies, and electron affinities of the neutral molecules and negative ions are summarized in Table 1, along with the available experimental data. For Na_2 and K_2, the D_e values are in reasonably good agreement with experiment, but the r_e values are longer due to the neglect of core-valence correlation. The neglect of CV correlation also gives atomic polarizabilities that are much larger than experiment. However, like the D_e of the dimer, the atomic EA is quite accurate despite the neglect of CV correlation. These results are consistent with more accurate studies of the alkali dimers [11, 13].

The Cu 4*s* electron is bound more tightly than the valence electrons of Na or K. The larger EA and smaller polarizability of Cu compared to Na and K are indications of this (Table 1). The need to correlate more electrons (the 3*d* and the 4*s*) increases the computational requirements for a quantitative description and therefore it is not surprising that the errors in D_e and EA for Cu_2 and Cu_2^- are larger than for the alkali diatomics (Table 1). However, there is still qualitative agreement with experiment – the computed ratio of the binding energies, Cu_2^-/Cu_2, agrees well with experiment, indicating we are obtaining an equivalent treatment of both systems.

To investigate the importance of the valence polarization (largely the importance of the p functions), we delete all basis functions which correspond to p or

Table 1. Spectroscopic constants for the neutral molecules and negative ions[a]

	K			Na			Cu		
Diatomic molecules	r_e	D_e	EA	r_e	D_e	EA	r_e	D_e	EA
Experiment									
X_2	7.380^{b}	0.520^{b}		5.818^{b}	0.730^{b}		4.194^{c}	2.078^{d}	
X_2^-		0.509^{e}	0.493^{e}		0.608^{e}	0.430^{e}	4.431^{f}	1.57^{f}	0.842^{f}
Δ		−0.011			−0.122		0.237	−0.508	
ratio (X_2^-/X_2)		0.979			0.833			0.756	
Full basis set									
X_2	7.861	0.496		6.025	0.690		4.340	1.742	
X_2^-	8.862	0.486	0.475	6.886	0.589	0.430	4.592	1.376	0.618
Δ	1.001	−0.010		0.861	−0.101		0.252	−0.366	
ratio (X_2^-/X_2)		0.980			0.849			0.790	
Reduced basis set									
X_2	8.548	0.149		6.471	0.275		4.674	0.808	
X_2^-	9.369	0.174	0.056	7.268	0.214	0.001	5.148	0.570	−0.002
Δ	0.821	0.025		0.797	−0.061		0.474	−0.238	
Atom									
		α	EA		α	EA		α	EA
Experiment		293^{g}	0.501^{h}		159^{g}	0.546^{h}		53^{g}	1.235^{h}
Full basis set		399.2	0.485		187.5	0.531		66	0.984
Reduced basis set			0.031			0.060			0.236
Effect of extra orbitals			0.454			0.471			0.748

[a] r_e in a_0; D_e and EA in eV. [b] Ref. [1] [c] Ref. [14] [d] Ref. [15] [e] Ref. [3] [f] Ref. [4] [g] Ref. [5] [h] Ref. [16]

d virtual orbitals for the atoms; these orbitals are easily identified as we are using ANO basis sets. These results are also summarized in Table 1 and are labeled "reduced basis set"; in the text we refer to this as deleting the polarization functions to indicate that we are deleting the functions required to describe valence polarization. Deleting these functions has a dramatic effect on the dimer properties; the r_e values increase while the D_e and EA values decrease. The large reduction in the molecular EA parallels the reduction in the atomic EA. To illustrate the effect of the polarization, we also report the difference between the full and reduced basis set results in Table 2. The D_e of the neutral molecule is reduced more than that of the ion for each molecule. For K_2 and Na_2, the expansion of the bond length is larger for the neutral molecule than for the ion, whereas for Cu_2 the ion is affected by more than the neutral.

In Table 3 we compare the results for the positive ions with those of the neutral molecules. The computed ratios of D_e values are in good agreement with

Table 2. Effect of the polarization (*p* and *d*) functions on the calculated spectroscopic constants[a]

Diatomic molecule	r_e			D_e			EA/IP		
	K	Na	Cu	K	Na	Cu	K	Na	Cu
X_2	0.687	0.446	0.334	−0.347	−0.415	−0.934			
X_2^-	0.507	0.384	0.556	−0.312	−0.375	−0.806	−0.419	−0.429	−0.620
X_2^+	0.108	0.149	0.160	−0.421	−0.463	−0.856	+0.082	+0.052	−0.430

[a] r_e in a_0; D_e, EA and IP in eV

Table 3. Spectroscopic constants for the neutal molecules and positive ions[a]

	K		Na		Cu	
	r_e	D_e	r_e	D_e	r_e	D_e
Experiment						
X_2		0.520		0.730		2.078
X_2^+		0.8_5[b]		0.97[b]		1.908[c]
Δ		0.33		0.24		−0.170
ratio (X_2^+/X_2)		1.635		1.329		0.918
Full basis set						
X_2	7.861	0.496	6.025	0.690	4.340	1.742
X_2^+	9.076	0.777	7.032	0.942	4.725	1.666
Δ	1.215	0.281	1.007	0.252	0.385	−0.076
ratio (X_2^+/X_2)		1.567		1.365		0.956
Reduced basis set						
X_2	8.548	0.149	6.471	0.275	4.674	0.808
X_2^+	9.184	0.356	7.181	0.479	4.885	0.810
Δ	0.636	0.207	0.710	0.204	0.211	0.002

[a] r_e in a_0; D_e in eV. The calcualted atomic IP values (eV) are 4.949 (4.953), 4.004 (3.931), and 7.067 (6.637) for Na, K and Cu, respectively; where the reduced basis set results are in parentheses

[b] Ref. [1]

[c] Ref. [2]

experiment. The positive ion bond lengths are longer than those of the neutral molecules as a result of the reduction in the bond order. The positive ion bond lengths are noticeably longer than those of the negative ions even though each has a bond order of one half. This is due to increased repulsion of the two nuclei with only one bonding electron for shielding. The effect of polarization on the D_e is very large for the positive ions, leading to K_2^+ and Na_2^+ binding energies that are even larger than those for the neutral molecules.

Comparison of the ion and the neutral molecule results shows some interesting trends. With the full basis set, the bond lengths are in the order $X_2 < X_2^- < X_2^+$ while they are $X_2 < X_2^+ < X_2^-$ when the polarization functions are deleted. The polarization functions affect the bond length in the order $X_2 > X_2^- > X_2^+$ for K and Na, but for Cu the order is $X_2^- > X_2 > X_2^+$. The effect of the polarization functions on the dissociation energies show a different trend; $X_2^+ > X_2 > X_2^-$ for K and Na, but $X_2 > X_2^+ > X_2^-$ for Cu. That is, the negative ion where there is a dramatic polarization of the open-shell orbital, shows the smallest effect of the polarization functions. For K and Na, the positive ion with one valence electron has the largest effect.

Plots of the K valence orbital densities are given in Fig. 1. The $6\sigma_g$ bonding orbital in K_2 and K_2^- are clearly similar, but the $6\sigma_g$ orbital in K_2^+ is very different. For K_2 and K_2^- the $6\sigma_g$ orbital is essentially formed by the bonding combination of two s orbitals, while for K_2^+ the $6\sigma_g$ orbital shows a large contribution from the p orbitals. Hence, the importance of the p functions for K_2^+ is very reasonable – by mixing in p-orbital character the shielding of the positive charge is improved. For K_2^- the $6\sigma_u$ orbital also exhibits strong p character; in fact, the p-function contribution appears to be even larger than that found for K_2^+. Therefore the small energetic effect of the p-character for K_2^- appears contradictory.

One dramatic difference between Cu and the alkali diatomics is the effect of the polarization (p and d) functions on the IP – see Table 2. For Na_2 and K_2 the IP is larger in the reduced basis set since the polarization functions are more important for the positive ion. For Cu_2 the polarization functions are 0.08 eV more important for the D_e of the neutral than they are for the positive ion, therefore the IP is smaller in the reduced basis set. Comparison of the Cu_2 and Cu_2^+ SCF orbitals in Fig. 2 with the K_2 and K_2^+ orbitals in Fig. 1 shows that the smaller α of Cu leads to considerably less polarization in the positive ion. However, at the SCF level and for treatments that only correlate the $4s$ electrons, the IP is increased if the polarization functions are deleted; that is, the results are similar to those for Na_2 and K_2. Deleting the polarization functions virtually eliminates the d–d and d–s correlation contributions. This is supported by the 0.430 eV change in the IP of Cu atom when the polarization functions are deleted. Since the d correlation contributions are more important for Cu_2 than for Cu_2^+, the IP decreases when the polarization functions are deleted in a treatment that includes $3d$ and $4s$ valence electrons.

While the orbital plots give some insight into the trends, we decomposed the energetic contributions for K_2 to quantify the effects; the results are summarized in Table 4. The top part of the table lists the calculations performed, while the bottom part is a breakdown of the bonding based on these calculations. Note that, in the calculation of the dissociation energies, the fully relaxed orbitals are used for the fragment atoms and ions. The full basis set D_e for K_2 is the same as that reported in Tables 1 and 3, but the reduced basis set result is 0.019 eV smaller because the bond length is that of the full basis set.

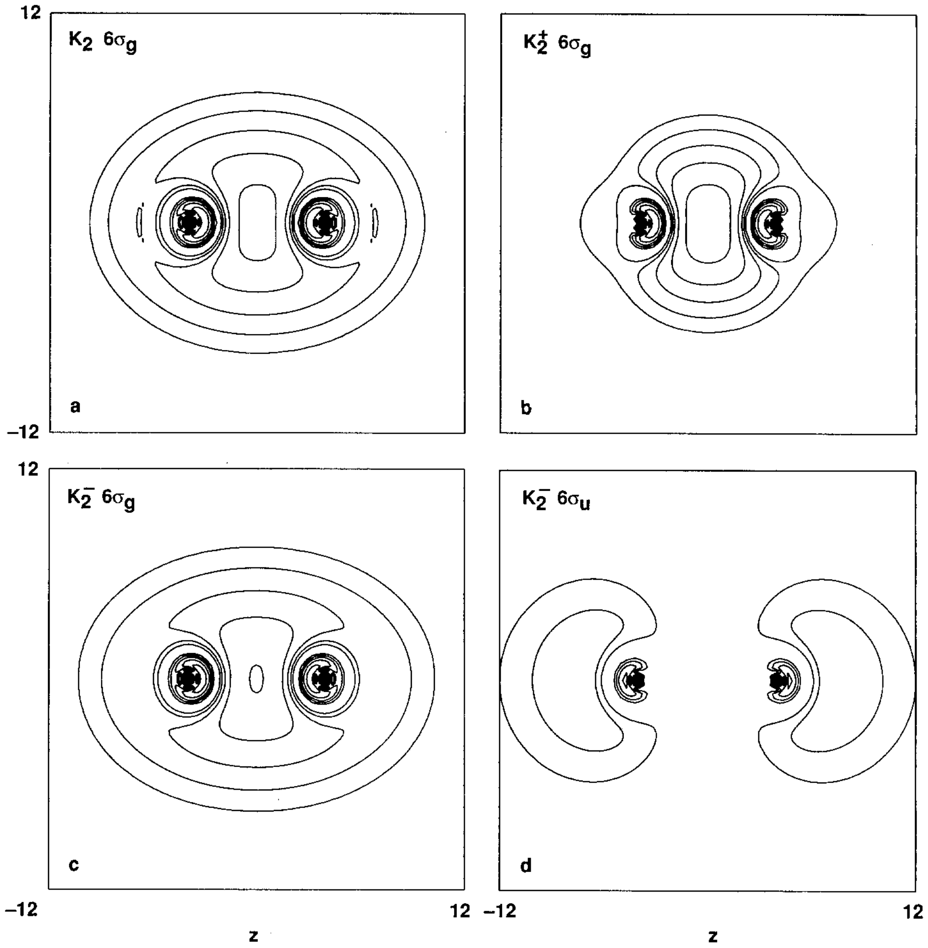

Fig. 1. A log plot of the SCF orbital density for K_2, K_2^+, and K_2^-

Deleting the polarization functions reduces the neutral D_e by 0.366 eV, which is 74% of the binding energy (line M). Evaluating the binding energy of K_2^+ using the K_2 orbitals and equilibrium geometry results in a value that is smaller than for K_2 (line K). Also, the effect of deleting the polarization functions is only 0.162 eV for the positive ion – a 46% reduction in D_e. Using this K_2^+ calculation we compute the pairing energy in the full basis to be 0.20 eV (line N). Allowing the K_2^+ orbitals to relax (line L) increases the bonding by 0.338 eV in the full basis but by only 0.103 eV in the reduced basis set. The energy lowering by optimizing the geometry in the reduced basis set is only about a quarter of the electronic relaxation. We find that the electronic relaxation energy makes the largest contribution to the increase of the binding energy of the positive ion relative to the neutral molecule, but the loss of binding in the neutral due to the pairing energy is 60% of the electronic relaxation in the ion. The energetic effect of the geometric relaxation is quite small in spite of the very large geometry

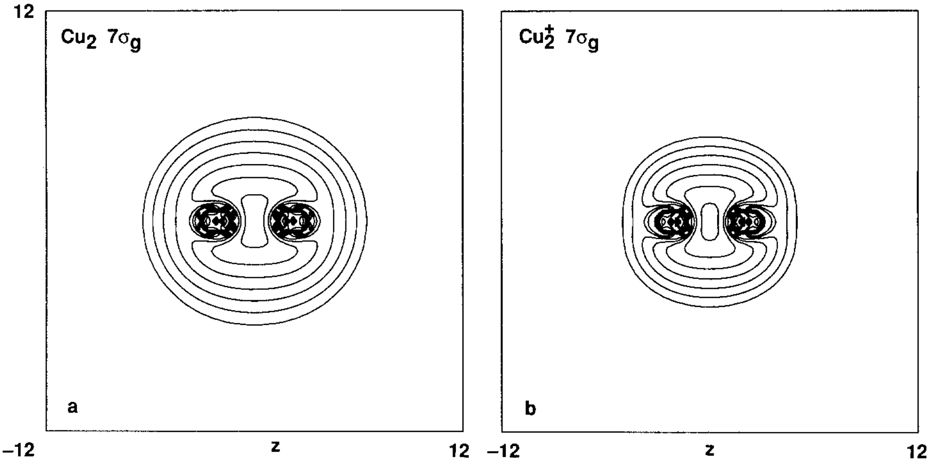

Fig. 2. A log plot of the SCF orbital density for Cu_2 and Cu_2^+

Table 4. Decomposition of the binding energy in K_2

Calculations (at K_2 for full basis r_e unless otherwise noted)
A. K_2 fully optimized SCF with CI.
B. K_2^+ with K_2 orbitals from A.
C. K_2^+ fully optimized SCF.
D. K_2^- with K_2 orbitals from A.
E. K_2^- with 4*s*-like orbitals optimized others from A.
F. K_2^- fully optimized SCF plus MCPF
G. K_2^+ fully optimized at full basis set K_2^+ r_e
H. K_2^- fully optimized at full basis set K_2^- r_e

	Basis set used		
	Full	Reduced	Δ
K_2^+			
I. C−B is electronic relaxation effect for K_2^+	0.338	0.103	0.235
J. G−C is geometric relaxation for K_2^+	0.090	0.065 (0.066)[a]	0.025
K. K_2^+ D_e from B	0.349	0.187	0.162
L. K_2^+ D_e from C	0.687	0.290	0.397
M. K_2 D_e from A (CI level)	0.496	0.130	0.366
N. Pairing energy 2*K−M	0.202	0.243	−0.041
K_2^-			
O. E−D is σ bond relaxation	0.082	0.076	0.006
P. F−E is core relaxation	0.006	0.005	0.001
Q. K_2^- D^e from F (MCPF level)	0.437	0.113	0.324
R. H−F is geometric relaxation	0.041	0.056 (0.061)[a]	−0.015

[a] The value in parentheses is computed using the optimal geometry from the reduced basis set

change. The total contribution of the polarization functions to the positive ion D_e $(0.162 + 0.235 = 0.397)$ is slightly larger than the 0.366 eV found for the neutral molecule.

If the doubly occupied orbitals are frozen and taken fom K_2, there is no relaxation of the open-shell orbital in the SCF calculation of K_2^-. The virtual orbital is the solution for adding an "extra" electron, and is therefore already polarized. If we construct a σ_u orbital as the antisymmetric combination of the *s* orbitals from K^- (which is Schmidt orthogonalized to the K_2 orbitals) we find a small relaxation of the open-shell orbital, 0.078 and 0.025 eV for the full and reduced basis sets, respectively. Allowing the $4s$–$4s$ bonding and open-shell orbitals to relax results in only a small increase in the energy, and the energetics are essentially unaffected by reducing the basis set. The core relaxation energy is very small, as is the geometrical relaxation. That is, in spite of the large distortion of the σ_u valence orbital there is less energy associated with polarization than for the positive ion and the neutral molecule.

4. Conclusions

We have investigated the effect of the *p* and *d* polarization functions on the bonding of Na_2, K_2, and Cu_2, and their positive and negative ions. As expected, functions required to describe the valence polarization are found to be very important in describing all of these systems; their removal dramatically increases the bond lengths and reduces the dissociation energy. However, the polarization functions contribute more (energetically) to the neutral and positive ion than the negative ion, in spite of the very large polarization of the σ_u orbital in the negative ion.

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