ELECTRONIC STRUCTURE AND VIBRATIONAL ANALYSIS OF THE ALKALI PEROXIDES K_2O_2 AND Rb_2O_2

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The aim of this work is to emphasize the role of the outermost p shell of the alkali atoms in the binding of the heavy peroxides K_2O_2 and Rb_2O_2. It is shown that although the symmetry of the ground state is not changed as one increases the mass of the alkali atom, the molecular orbital energies are sufficiently changed as to point to K_2O_2 as being the least stable in the series M_2O_2 (M = Li, Na, K, Rb). Frequencies of the IR active modes are calculated as well.

Recently we studied the structural and vibrational properties of Li_2O_2, Na_2O_2 and K_2O_2 based on a LCAO MO SCF calculation [1]. Now we add results for the potassium and rubidium peroxides using extended basis sets and accurate pseudopotentials derived from the non-empirical method of Barthelat and Durand [2]. Our aim is to gain a better understanding of the bonding of molecular oxygen to metals in these molecules, and to determine the extent of the mixing between the O_2 valence orbitals and the $(n-1)$p shell of the alkali metals. We construct a pseudopotential for the metal atoms in such a way as to have a core that contains all occupied orbitals except the $(n-1)$p and ns functions ($n = 4$ for K, 5 for Rb). Table 1 shows the parameters for this pseudopotential; the oxygen pseudopotential is already given in the literature [3]. Our calculations ‡ were carried out using optimized GTOs contracted to (3,1) for the s and p symmetries with exponents and coefficients shown in table 2, one p-polarization function on the metal with exponent $\zeta = 0.0345$ for potassium, $\zeta = 0.0304$ for rubidium and one d-polarization function on each oxygen with $\zeta = 1.33$. In the K_2O_2 molecule, the polarization exponents were the same as those used in our previous all-electron calculation [1].

Table 3 and fig. 1 summarize the results. Table 3 gives the distances R_{O-O} (oxygen–oxygen along the x axis) and R_{M-M} (metal–metal along the y axis) of the rhomboidal conformation [1], the binding energy $E_B = E_{total} - 2(E_{oxygen} + E_{metal})$, the net atomic charges on the oxygen centers, the force constants and frequencies of the infrared active modes B_{2u} and B_{3u}, as well as the best results from ref. [1] and ref. [5] for LiO_2O_2 and Na_2O_2. Fig. 1 shows the energy level diagram of the ^1A_g states for K_2O_2 and Rb_2O_2. Full lines indicate strong contributions of the isolated components to the molecular levels while dots show less important contributions.

Two important facts are to be pointed out with respect to the molecular orbital scheme shown in fig.

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‡ PSHONDO, written by J.P. Daudey, includes the pseudopotentials [2] to HONDO [4].

Table 1
Pseudo-potential parameters in the expression [2] $W = z/r + \Sigma_l P_l \exp(-\alpha_l r^2)\Sigma_i c_i r^{n_i}$ where P_l is the projector on the lth space of the spherical harmonics, and $z = 7$ is the effective nuclear charge of the metals

Atom	Valence configuration	l	α_l	c_i	n_i
K	$3p^64s^1$	0	0.17653	7.01653	−1
				−1.86188	0
	$3p^64p^1$	1	2.07523	−1.26767	−2
				23.14104	−1
				−27.16609	0
Rb	$4p^65s^1$	0	0.17241	8.03584	−1
				−1.82971	0
	$4p^65p^1$	1	0.99971	17.03923	−1
				−15.23546	0
	$4p^64d^1$	2	0.26970	−3.11004	−1

Table 2
Gaussian basis sets used in the pseudopotential calculations. In all cases these were contracted into [3,1]

K			Rb			O		
orbital	exp.	coef.	orbital	exp.	coef.	orbital	exp.	coef.
3p	4.235258	−0.102160	4p	3.476912	−0.034924	2s	5.799125	−0.137734
	1.363821	0.364612		2.712410	0.149765		1.298338	0.292953
	0.547407	0.547638		0.606982	−0.665210		0.547297	0.531222
	0.199920	1.000000		0.207841	1.000000		0.226132	1.000000
4s	0.304753	0.149987	5s	0.292035	0.050359	2p	12.655163	0.068201
	0.220535	−0.411502		0.179776	−0.315967		2.953694	0.274403
	0.042922	0.579550		0.031979	0.801389		0.886188	0.482324
	0.018395	1.000000		0.013018	1.000000		0.259961	1.000000

1. First, an inversion between the molecular orbital energies b_{2u} and b_{1u} is present for K_2O_2 when compared with the spectra of the lighter peroxides. This inversion of levels was found in our previous SCF calculation [1] and it is due the covalent mixing of the oxygen $2p\pi_u$ with the alkali p orbitals. The D_{2h} symmetry allows the in-plane oxygen $2p\pi_u$ to take part in the mixing. Its antibonding combination with the alkali valence p_x functions produces the b_{2u} orbital which rises in energy above the out-of-plane b_{1u} orbital. As the energy of the alkali valence p orbitals approaches that of the molecular oxygen $2p\pi_u$ from below (when going from Na up to Rb), mixing is expected to increase in this direction. In the rubidium peroxide, the destabilization of the $2b_{2u}$ level is so strong as to produce an inversion with respect to the $3a_g$ level. The energy difference between these two orbitals, $\epsilon_{b2u} - \epsilon_{b1u}$ changes sign at potassium peroxide as one proceeds from Li to Rb: −0.022, −0.017, 0.008, 0.053 au, respectively. Secondly, the two outermost occupied levels b_{2g} and b_{1g} are almost pure $2p\pi_g$ from molecular oxygen, although a mixing arises in b_{1g} with the alkali metal p and s valence orbitals. The contribution starts to show up for the potassium peroxide and results in a repulsion between the two levels: the energy difference $\epsilon_{b2g} - \epsilon_{b1g}$ being 0.034, 0.010, 0.016, 0.040 au for Li, Na, K and Rb peroxides.

In summary, the molecular oxygen character of the highest occupied orbital is not lost along the series, although the binding of these molecules as they grow heavier is helped by the metal $(n-1)$p or-

Table 3
Geometry of the minimal energy conformation, binding energies, charge on the oxygens from a Mulliken population analysis, force constants and frequencies of the IR-active modes B_{2u} and B_{3u}

		R_{O-O} (au)	R_{M-M} (au)	E_B (kcal/mol)	Charge on oxygen	B_{2u}		B_{3u}	
						F (mdyn/A)	ν (cm^{-1})	F (mdyn/A)	ν (cm^{-1})
Li_2O_2	ref. [5]	3.0	6.24	177	−0.77	1.38	883.4	1.52	445.6
Na_2O_2	ref. [1]	3.0	7.0	54.1	−0.88	1.53	684.0	1.61	293.8
K_2O_2	this work	2.85	8.68	23.9	−0.85	0.87	483.8	1.23	189.3
	ref. [6]	2.83					389.0		
Rb_2O_2	this work	2.82	7.9	62.8	−0.91	1.08	491.4	1.72	221.6

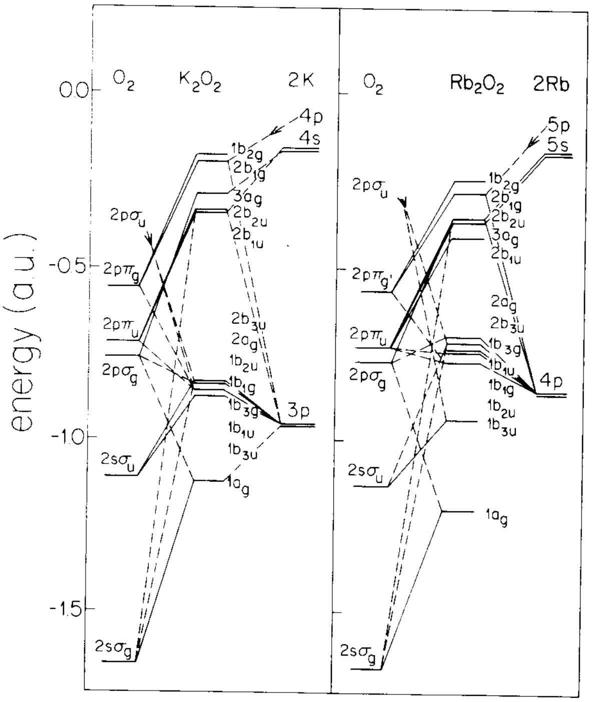

Fig. 1. Energy level diagram for K_2O_2 and Rb_2O_2 (^1A_g state). On the left of each diagram we draw the O_2 energy levels and on the right the alkali metal energy levels.

bitals. The overall effect of this valence p-shell contribution is not strong enough to result in changes of symmetry of the ^1A_g states as the mass of alkali atoms increases. The usual way to construct the Barthelat and Durand [2] pseudopotential for atoms such as the alkali metals is to include the $(n-1)$p shell in the core. The field that such a core produces for the free *n*s electron is not capable of simulating the effects that we have described above [7]. Let us emphasize that in this work, we omitted the $(n-1)$p functions from the core, thereby considering these functions as part of the valence orbitals.

The frequencies of the IR active modes, as well as the R_{M-M} distances as functions of the metal mass show an inflection point for the potassium peroxide (table 3). It would be interesting to have experimental data available for Rb_2O_2. Finally, the binding energy values E_B give trends making it possible to state that K_2O_2 is the least stable molecule of the series M_2O_2. From the above discussion, the potassium peroxide can be regarded as a transition case. Similar facts are also noticed for the alkali monoxides and superoxide series [8–11]. These peroxides, Li_2O_2 up to Rb_2O_2, are highly ionic species and might be good candidates for molecular oxygen storage.

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