# LCAO–MO–SCF calculation of the metal–oxygen bonding in the $M_2O_2$ series: M = Li, Na, and K[a)]

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The geometry and infrared active vibrational frequencies of $M_2O_2$ peroxides (M = Li, Na, and K) have been calculated by the SCF method. The pseudopotential method has also been applied to the case of sodium and potassium peroxides and results of both methods are compared. The nature of the metal–molecular oxygen binding and the ability of pseudopotential methods to represent such bonds are discussed.

## I. INTRODUCTION

Structural information and spectroscopic data on the metal alkali oxides $MO_2$ and $M_2O_2$ have been accumulated during the past ten years mainly from IR, Raman, and ESR[1-12] experiments using the matrix isolation technique. In most cases the trapped species are intermediates in collisional inelastic processes which occur when molecular oxygen is mixed with the alkali metal atoms in the gas phase. Similar species have been obtained by vaporizing solid alkali metal oxide samples.[13,14] Both procedures may lead to the formation of isomeric species, as exemplified by the case of the Li species which have been studied with both methods.[1,2,5,7,8,13-15] Vaporization of lithium monoxide LiO leads to the formation of $(LiO)_n$ polymers, while in the gas mixing methods the ionic compounds containing a nondissociated oxygen–oxygen bond $(Li_2O_2)$ are predominant. These two species $(LiO)_2$ and $(Li_2O_2)$ have the same $D_{2h}$ symmetry but certainly different geometrical parameters and force fields which give rise to two frequencies for the same vibrational mode.[2,13,14] Accurate vibrational data for $MO_2$ and $M_2O_2$ species are presently restricted to lithium compounds. For heavier elements such as Na,[3,11] K,[4,6] Rb,[4,9,12] and Cs[9,10,12] the data are scarce and still insufficient to provide reliable information on the structure of these complexes. However, it seems that the structure remains planar and rhombic throughout the series and that the frequencies of the active IR vibrational modes $S_{B_{2u}}$ and $S_{B_{3u}}$ decrease continuously from lighter to heavier metal elements. In contrast, the $\nu_{O-O}$ frequency (Raman active) has a nonmonotonic behavior which reflects the degree of ionicity of the oxygen–oxygen bond involved in the complex.[10] Some aspects of the problem have been discussed qualitatively by Spratley and Pimentel[16] in terms of molecular orbitals in reference to the case of H and F atoms bonded to molecular oxygen. More recently, a series

of *ab initio* calculations have been performed on some MO species: M = Li,[17,18] Na,[19,20] K and Rb,[20] and on $LiO_2$[18,21,22] and $Li_2O_2$.[18,23,24] SCF and CI studies have only been performed on the lighter $MO$[17,25] systems, while only semiempirical SCF studies have been performed in the other cases. The case of LiO, where SCF and CI calculations are available, shows that the SCF level can be considered as a reliable approximation in treating these ionic compounds. A description of their properties can also be obtained either by using models such as the electron gas model,[26] or by introducing model interaction potentials such as the Rittner potential[8] or the improved form of the Rittner potential.[27]

Precisely, one of the aims of this study is the understanding of the metal–molecular oxygen bond, a general problem of interest in various fields of chemistry and catalysis. In view of the satisfactory results previously obtained by SCF calculations, we have attempted to give, in this framework, an outline of some of the structural and vibrational properties of the molecular species $M_2O_2$ with M = Li, Na, and K. Our approach is limited to minimal sets of basis functions. However, the validity of our results is checked either by comparison with previous calculations (in the case of $Li_2O_2$), or by using at some stages of the calculation an extended basis set of functions including polarization functions. We report also some calculations performed with the pseudopotential method of Barthelat and Durand[28] which can be of interest for further calculations on species containing heavy alkali atoms. The latter are carried out with extended basis sets. In Sec. II a description of the methods and of the various types of calculations used is given. Some details on the force constants and vibrational calculations are explained in Sec. III and the results are discussed in Sec. IV.

## II. METHOD

### A. All electron calculations

*Ab initio* LCAO–MO–SCF calculations have been performed with the PSIBMOL[28,29] program, which has the extra option of carrying our pseudopotential SCF calculations. For some calculations, however, the Whitten[30] SCF program together with the AGLO[31] integral package
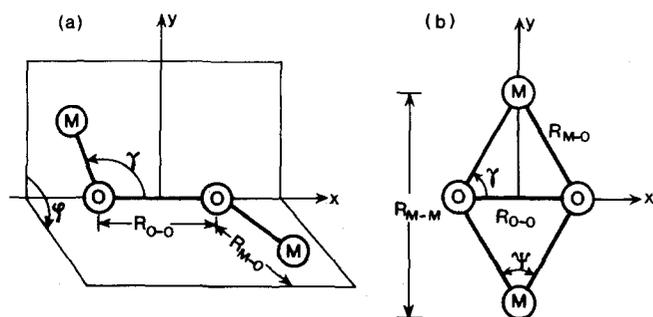
FIG. 1. Geometrical parameters characterizing (a) the $C_2$ conformation and (b) the $D_{2h}$ structure.

has been used. For the $Li_2O_2$ molecule we have used the oxygen $(7s, 3p)$ and lithium $(5s)$ primitive sets of Roos and Siegbahn[32] contracted into a single-zeta basis set. In the case of $Na_2O_2$ several basis sets have been used. The first calculations were performed in the single-zeta scheme using the $(7s, 3p)$ primitives contracted to $[5\,2/3]$ for oxygen. For sodium and potassium, the primitives used are $(10s, 4p)$ contracted to $[6\,2\,2/4]$ and $(12s, 6p)$ contracted to $[6\,2\,2\,2/4\,2]$, respectively. This set will be referenced later as set I.[32] The sodium case has also been studied with a double-zeta set consisting of the $O(7s, 3p)$ contracted to $[4\,1\,1\,1/2\,1]$ and $Na(11s, 4p)$[32] contracted to $[5\,2\,1\,1\,1\,1/3\,1]$, which will henceforth be referred to as set II. The extended basis set used in a double-zeta basis set consisting of $O(8s, 5p)$[33] contracted $[5\,1\,1\,1/4\,1]$ and $Na(12s, 6p)$[34] contracted to $[5\,3\,1\,1\,1\,1/4\,2]$ plus a $3p$ function on sodium. The latter was obtained by expanding a Slater $3p$ function with exponent $\zeta_{3p}$ $= 0.8357$[35] into three Gaussians, which in turn were contracted to one. This set is designated as III. Finally, a set IV was derived from set III by adding a $3d$ polarization function with exponent $1.33$ on the oxygen atoms[36].

The structures of the $M_2O_2$ complexes have been determined by varying the total energy with respect to the four geometrical parameters depicted on Fig. 1(a): $\phi$, the angle between the planes containing the OO and OM bonds: $\gamma$, the $\widehat{OOM}$ angle: $R_{O-O}$, the oxygen–oxygen distance; and $R_{M-O}$ (or $R_{M-M}$), the metal–oxygen distance. The geometrical deformations are performed by staring with the $C_2$ symmetry structure [Fig. 1(a)], which is progressively deformed towards the $D_{2h}$ conformation [Fig. 1(b)]. This latter structure may be characterized only by two parameters, namely, $R_{O-O}$ and $R_{M-M}$.

In the case of $Li_2O_2$ the calculations using set I lead to the $D_{2h}$ structure as being the most stable, in agreement with previous work.[24] No further refinements were attempted for this complex since the objective of this calculation was to confirm that the single-zeta basis set calculation is sufficiently accurate to give the correct symmetry of the most stable conformations in the $M_2O_2$ series.

More attention was paid to the $Na_2O_2$ intermediate case and several calculations were performed. First, exploratory calculations with set I were undertaken in order to distinguish between the two possible structures; again the $D_{2h}$ conformation was found to be the most stable. While using basis set II, the minimization procedure was refined by successive elongations of the $R_{O-O}$ and $R_{Na-Na}$ distances. Basis sets III and IV were used only to recalculate the ground state energy at the equilibrium position determined with basis set II in order to study the influence of polarization functions on the wave functions.

For the $K_2O_2$ complex, the calculations were performed only with basis set I and structural investigations were restricted to variations of the $R_{O-O}$ and $R_{K-K}$ parameters within an assumed planar rhombus geometry.

## B. Pseudopotential calculations

The treatment of alkali metals by pseudopotential methods is to some extent questionable since treating only the unique electron left out of the core may constitute a poor representation of the electronic distribution of the system. Therefore, a comparison with all electron methods may be of great interest, especially in view of the possibility of treating compounds containing heavy alkali elements. The pseudopotential method of Barthelat et al.[28] was used here for $Na_2O_2$ and $K_2O_2$. The same minimization method used for the all electron calculation was followed. Extended basis sets, $(4s, 4p)$ contracted to $[3\,1/3\,1]$ for O, $(4s, 3p)$ contracted to $[3\,1/2\,1]$ for Na, and $(4s, 1p)$ contracted $[3\,1/1]$ for K, have been used for these calculations. The $3p$ polarization function from basis set III was used for Na and the $p$ Gaussian with exponent $\zeta_{4p} = 0.039$ for K was obtained from a Slater $4p$ function with $\zeta = 0.85$.

The corresponding basis sets are given in Table I for oxygen and potassium; the optimized set for sodium has

TABLE I. Gaussian basis sets used in the pseudopotential calculations.

| Oxygen | | | | Potassium | | | |
|---|---|---|---|---|---|---|---|
| Orbital | Exp. | Coef. | Contraction | Orbital | Exp. | Coef. | Contraction |
| $2s$ | 121.549 | −0.007 267 | [3 1] | $4s$ | 0.650 501 | −0.013 301 | [3 1] |
|  | 15.550 6 | −0.047 267 |  |  | 0.223 283 | −0.216 178 |  |
|  | 0.895 851 | 0.541 678 |  |  | 0.038 307 | 0.690 038 |  |
|  | 0.284 882 | 0.525 713 |  |  | 0.016 469 | 0.439 469 |  |
| $2p$ | 15.876 2 | 0.045 789 | [3 1] | $4p$ | 0.039 | 1. | [1 1] |
|  | 3.690 41 | 0.236 858 |  |  |  |  |  |
|  | 1.018 69 | 0.505 227 |  |  |  |  |  |
|  | 0.271 689 | 0.452 936 |  |  |  |  |  |

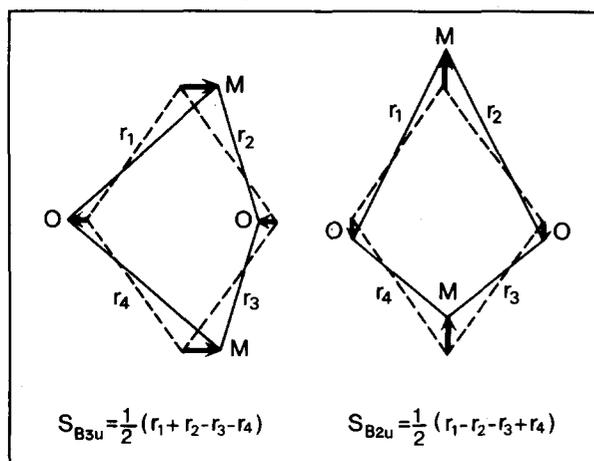$$S_{B3u} = \frac{1}{2}(r_1 + r_2 - r_3 - r_4) \qquad S_{B2u} = \frac{1}{2}(r_1 - r_2 - r_3 + r_4)$$

FIG. 2. The two IR-active normal modes studied in this work.

been reported previously.[37] Minimization of the conformational energy leads to the $D_{2h}$ structure for these two $M_2O_2$ complexes.

## III. FORCE CONSTANTS CALCULATIONS

The force constants were calculated as the second derivatives of a polynomial fitting the $E(X)$ curve, where $E$ is the total energy of the molecule and $X$ is a nuclear coordinate. Following Yates and Pitzer,[24] the energy was varied with respect to the symmetry coordinates in order to get rid of the interaction force constants. The vibrational analysis is based on the work of Berkowitz.[38] We have only calculated the frequencies of the two in-plane infrared active modes $B_{2u}$ and $B_{3u}$ without attempting to give any assignment to the low frequency out of plane mode $B_{1u}$. The choice of coordinates and the nature of the normal modes $B_{2u}$ and $B_{3u}$ are indicated in Fig. 2. The two vibrational frequencies are given in cm$^{-1}$ by

$$\nu_{Bnu} = (2\pi c)^{-1} (F_{Bnu} G_{Bnu})^{1/2} , \quad n = 2, 3 ,$$

where $c$ is the speed of light, the $F_{Bnu}$ are the symmetry

force constants, and the $G_{Bnu}$ are elements of the transformed kinetic energy matrix[39]

$$G_{Bnu} = (1/m_O + 1/m_M)[1 + (-)^n \cos\psi] ,$$

where $\psi$ is the $\widehat{OMO}$ angle [Fig. 1(b)] and $m_O$ and $m_M$ are, respectively, the oxygen and alkali metal atomic masses. Values of $S_{B_{2u}}$ and $S_{B_{3u}}$ are calculated by allowing those atomic displacements which leave the center of mass to be invariant during the deformation. The $S$ coordinates are varied by steps of 0.1 a.u. from 0 up to 0.5 to 1.0 a.u. and then the force constants are calculated by a natural spline interpolation.[40]

## IV. RESULTS AND DISCUSSION

Ground state electronic configurations, total energies, and charges on the oxygen atom at the equilibrium conformations are gathered in Table II for the all electron calculations as well as for the pseudopotential calculations. The corresponding geometrical parameters are given in Table III. The four $Na_2O_2$ calculations show that the total energy is particularly sensitive to the $3p$ polarization functions centered on the alkali metal atoms. This effect is mainly due to a small mixing of the $3p$ polarization orbitals into the $2b_{1g}$ molecular orbital of the total wave function. The $3d$ polarization functions on the oxygen atoms have negligible coefficients in the wave function. With basis set IV, a binding energy of 54.1 kcal/mol is found for sodium peroxide [$E(O) = -74.798834$ a.u., $E(Na) = -161.83605$ a.u.].

A comparison between the molecular orbital energy level diagrams obtained using basis set I for the three alkali oxides is depicted in Fig. 3. The cases of Li and Na are very similar, the binding being almost entirely represented by the mixing of the $ns$ ($n = 2, 3$) metal orbitals with the $\sigma_g$ $2p$ and $\pi_u$ $2p$ orbitals of molecular oxygen. The case of potassium is somehow different, since though the $4s$ energy level is still in the neighborhood of the $\pi_u$ $2p$ and $\sigma_g$ $2p$ levels of molecular oxygen, the $3p$ levels are now closer to the oxygen $\sigma_u$ $2s$. Consequently, there are two contributions to the binding represented by (i) the $4s$ metal orbital coupling with the

TABLE II. The $^1A_g$ states of the $M_2O_2$ molecules, total energy, and charge gain (fraction of electron) on the oxygen centers by Mulliken population analysis.

| Molecule | $^1A_g$ States | Basis set | Total energy (a.u.) | Charge on oxygen |
|---|---|---|---|---|
| Li₂O₂ | $(1a_g)^2 (1b_{3u})^2 (2a_g)^2 (1b_{2u})^2 (3a_g)^2 (2b_{3u})^2 (2b_{2u})^2$ $(1b_{1u})^2 (4a_g)^2 (1b_{1g})^2 (1b_{2g})^2$ | I | -164.05678 | -0.77 |
| Na₂O₂ | $(1b_{2u})^2 (1a_g)^2 (1b_{3u})^2 (2a_g)^2 (2b_{2u})^2 (3a_g)^2 (4a_g)^2$ | I | -472.36969 | -0.73 |
|  | $(1b_{1u})^2 (1b_{3g})^2 (2b_{3u})^2 (1b_{1g})^2 (3b_{2u})^2 (5a_g)^2 (3b_{3u})^2$ | II | -472.97712 | -0.84 |
|  | $(4b_{2u})^2 (2b_{1u})^2 (6a_g)^2 (2b_{1g})^2 (1b_{2g})^2$ | III | -473.34459 | -0.88 |
|  |  | IV | -473.35588 | -0.88 |
| K₂O₂ | $(1b_{2u})^2 (1a_g)^2 (1b_{3u})^2 (2a_g)^2 (2b_{2u})^2 (3a_g)^2 (1b_{1u})^2$ $(1b_{3g})^2 (1b_{1g})^2 (2b_{3u})^2 (3b_{2u})^2 (4a_g)^2 (5a_g)^2 (4b_{2u})^2$ $(6a_g)^2 (3b_{3u})^2 (2b_{1u})^2 (2b_{3g})^2 (2b_{1g})^2 (5b_{2u})^2 (7a_g)^2$ $(4b_{3u})^2 (3b_{1u})^2 (6b_{2u})^2 (8a_g)^2 (3b_{1g})^2 (1b_{2g})^2$ | I | -1345.00071 | -0.69 |
| Na₂O₂ | $(1a_g)^2 (1b_{3u})^2 (1b_{2u})^2 (1b_{1u})^2 (2a_g)^2 (1b_{1g})^2 (1b_{2g})^2$ | Pseudopotential |  | -0.78 |
| K₂O₂ |  |  |  | -0.84 |

TABLE III. Values of the geometrical parameters of the $D_{2h}$ equilibrium conformation. The notation (I) and (II) corresponds to calculations using sets I and II, respectively; (P) stands for pseudopotential calculations.

| | | $R_{O-O}$ (a.u.) | | $R_{M-M}$ (a.u.) | | OMO (deg) | |
|---|---|---|---|---|---|---|---|
| $Li_2O_2$ | Experiment[2] | 2.85[a] | | 5.11 | | 58.5[b] | |
| | | | | 5.47 | | 55.0[c] | |
| | Ref. 24 | 2.83 | | 5.91 | | 51.2 | |
| | This work | 2.9 | (I) | 5.84 | (I) | 52.8 | (I) |
| $Na_2O_2$ | Experiment[3] | 2.83[a] | | 5.8 | | 51.7[b] | |
| | | | | 6.5 | | 46.6[c] | |
| | This work | 2.93 | (I) | 7.0 | (I) | 45.4 | (I) |
| | | 3.05 | (II) | 7.1 | (II) | 46.5 | (II) |
| | | 3.00 | (P) | 7.4 | (P) | 44.1 | (P) |
| $K_2O_2$ | Experiment[4] | 2.83[a] | | | | | |
| | This work | 2.97 | (I) | 8.6 | (I) | 38.1 | (I) |
| | | 2.95 | (P) | 8.5 | (P) | 38.3 | (P) |

[a]X-ray diffraction measurements on crystalline $M_2O_2$ complexes.
[b]Values obtained using the assumption that the symmetry force constants are equal $(F_{B_{2u}} = F_{B_{3u}})$.
[c]Assumed values.

$\pi_u$ $2p$, $\pi_g$ $2p$, and $\sigma_g$ $2p$ of oxygen and (ii) the $3p$ metal orbital coupling with the oxygen $\sigma_u$ $2s$. This latter has been already pointed out by Lindsay et al.[41] in their study of the monoxides NaO, RbO, and CsO and referred to as an inner shell type bonding. The Mulliken population analysis shows only small changes of the molecular occupation numbers along the series of complexes, i.e., in the three cases the $\pi_g$ $2p$ molecular oxygen orbital is almost completely occupied. The picture emerging from this analysis indicates that the metal outer electrons are transferred towards the oxygen molecule. However, the transfer diminishes when going from Li to K, while the O–O bond character shifts from an $O_2^-$ type bonding to an $O_2^-$ type bonding. These results are also confirmed by the variation of the oxygen atomic charges given in Table II. This trend can also be correlated to changes in the polarizabilities within the series Li, Na, K (22, 21.5, and 38 Å³, respectively).[42] Finally, it seems that the binding has essentially an ionic character as has already been emphasized by other authors. It is noteworthy to remark that the structure described here is quite different from the one occurring in $H_2O_2$, where the H atoms form covalent bonds with the oxygen atoms and therefore cannot arrange themselves symmetrically on both sides of the $O_2$ molecule. The geometrical parameters deduced from the energy minimization are given in Table III and compared to the best results of Yates and Pitzer[24]
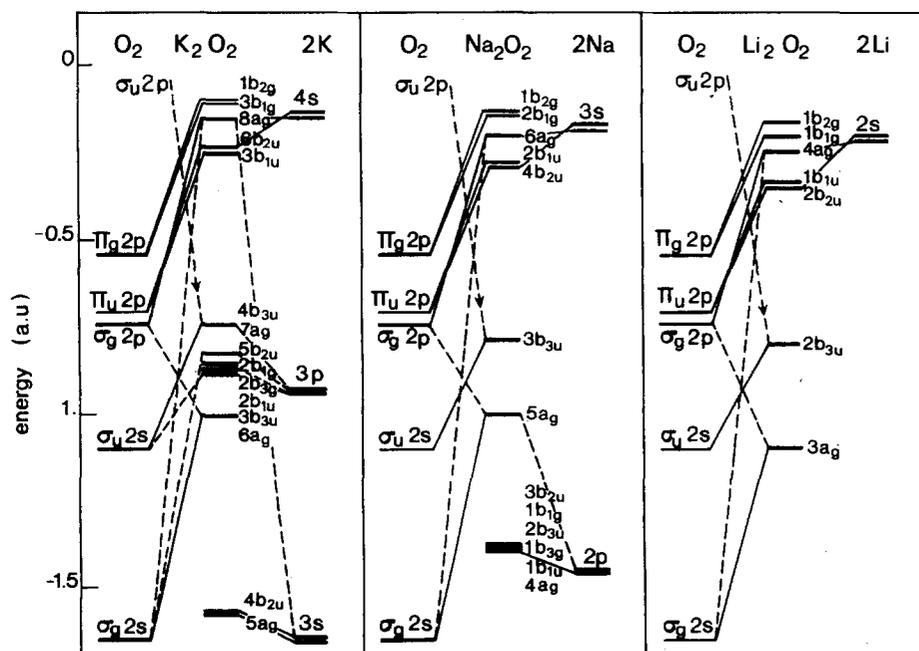


FIG. 3. Molecular orbital scheme of the three alkali peroxides. Full lines join the levels of the isolated components with the corresponding molecular levels. Dotted lines indicate contributions to the molecular states coming from the isolated components.

TABLE IV. Experimental and theoretical frequencies of the alkali peroxide IR-active normal modes $B_{2u}$ and $B_{3u}$. The notation (I) and (II) corresponds to calculations using sets I and II, respectively; (P) stands for pseudopotential.

| | | $B_{2u}$ | | $B_{3u}$ | |
|---|---|---|---|---|---|
| | | $F$ (mdyn/Å) | $\nu$ (cm$^{-1}$) | $F$ (mdyn/Å) | $\nu$ (cm$^{-1}$) |
| | Experiment[2] | 1.188[a] | | 1.188[a] | |
| | | | 796.0 | | 444.5 |
| $Li_2O_2$ | | 1.15[b] | | 1.333[b] | |
| | Ref. 24 | 1.38 | 883.4 | 1.52 | 445.6 |
| | This work | 1.29 | 852.2 | 1.84 | 505.2 |
| | Experiment[3] | 0.944[a] | | 0.944[a] | |
| $Na_2O_2$ | | 0.907[b] | 524.5 | 1.148[b] | 254.0 |
| | This work | 1.53 (I) | 684.0 | 1.61 (I) | 293.8 |
| | | 0.55 (P) | 412.4 | 0.92 (P) | 216.0 |
| | Experiment[4] | | 433.0 | | |
| $K_2O_2$ | This work | 0.85 (I) | 476.6 | 1.30 (I) | 203.5 |
| | | 0.42 (P) | 334.8 | 1.11 (P) | 189.0 |

[a]$\widehat{LiOLi} = 58.5°$, $\widehat{NaONa} = 51.7°$.   [b]$\widehat{LiOLi} = 55.0°$, $\widehat{NaONa} = 46.6°$.

for the case of $Li_2O_2$ and to the available experimental results.[2,3,4] The results are in satisfactory agreement, at least within the limit of experimental uncertainty. It is important to note that, to our knowledge, the conformational properties of the $M_2O_2$ complexes rest on a very limited amount of experimental data and are still uncertain. In fact, for the Li[2] and Na[3] peroxides the $\nu_{B_{2u}}$ and $\nu_{B_{3u}}$ vibrational frequencies are observed whereas for K and Rb only the $\nu_{B_{2u}}$ can be detected: the $\nu_{B_{3u}}$ being in the far IR, is still unmeasured. Only the $\nu_{O-O}$ frequency (Raman active) has been observed for the complete series.[8,9] In the peroxides of Li and Na, due to the large number of isotropic species measurements,[2,3] the $\widehat{OMO}$ angle can be deduced from the product rule. This is, nevertheless, an approximate value since no anharmonic corrections have been taken into account. A complete structural analysis needs the value of an extra parameter, the $R_{O-O}$ distance, which in lithium and sodium peroxides is taken from crystal data. Moreover, starting from a plausible $R_{O-M}$ bond distance, values of the bond angle in $Li_2O_2$ and $Na_2O_2$ have been assumed.[2,3] For potassium and rubidium the infrared and Raman data are still insufficient to give good structural information.

Once a plausible geometry is set up, a force field may be derived by adjustment of the observed frequencies. Two force fields have been derived for $Li_2O_2$,[2] one leading to $F_{B_{3u}} = F_{B_{2u}}$ and corresponding to the bond angle deduced form the product rule (58.5°), and the other one leading to $F_{B_{2u}} < F_{B_{3u}}$ and corresponding to an assumed bond angle (55°). Our calculated values (I) for $Li_2O_2$ agree well with the set of experimental data corresponding to $\widehat{OLiO} = 55°$ and are also close to the theoretical values of Yates and Pitzer.[24] Our set of force constants satisfy the condition $F_{B_{2u}} < F_{B_{3u}}$ but the calculated

frequencies are too high by about 20%, an effect partly due to the incorrect behavior of the Hartree-Fock approximation. These results are collected in Table IV. The same remarks are valid for sodium peroxide. The results for $K_2O_2$ rest at a predictable level. The pseudopotential calculations (P) lead to symmetry force constants which are systematically smaller than the ones deduced from the all electron calculations using basis set I and from experiment in the $Na_2O_2$ case. Though the order condition is obeyed, the difference $F_{B_{2u}} - F_{B_{3u}}$ $= f_{12} - f_{14}$ is in the Na and K cases larger for the pseudopotential than for the all electron calculation ($f_{12}$ and $f_{14}$ are the stretch-stretch interaction force constants in internal coordinates). This is in contradiction with the commonly adopted assumption[3,13] $f_{12} \cong f_{14}$. Apparently, the pseudopotential calculation overestimates one of the interaction force constants. This is not a general result but may be related to a deficient representation of the electronic distribution of the compound. Further studies using a modified pseudopotential for the alkali atom in which the outer $(n-1)p$ electrons are left as valence electrons may clarify this point.

## V. SUMMARY

A general outline of the structural properties of the $M_2O_2$ series has been given using SCF calculations with small basis sets. The bonds are essentially ionic in character and moreover, in agreement with previous results on MO compounds, our work also emphasizes the role of the $(n-1)p$ electronic shell in the binding of potassium with molecular oxygen. The pseudopotential method has been tentatively applied here and compared to the results derived from all electron methods. Its failure to reproduce the inner shell binding effect could be expected, but the geometrical parameters obtained

by both methods are close. From these preliminary results it may be stated that, for potassium and heavier alkali metals at least, the $(n-1)p$ shell should be left out of the electronic core. Work is presently in progress in that direction for the cases of $K_2O_2$ and $Rb_2O_2$.

## ACKNOWLEDGMENT

[1] L. Andrews, J. Am. Chem. Soc. 90, 7368 (1968).

[2] L. Andrews, J. Chem. Phys. 50, 4288 (1969).

[3] L. Andrews, J. Phys. Chem. 73, 3922 (1969).

[4] L. Andrews, J. Chem. Phys. 54, 4935 (1971).

[5] D. A. Hatzenbuhler and L. Andrews, J. Chem. Phys. 56, 3398 (1972).

[6] R. R. Snardzewski and L. Andrews, J. Chem. Phys. 57, 1327 (1972).

[7] H. Huber and G. A. Ozin, J. Mol. Spectrosc. 41, 595 (1972).

[8] L. Andrews and R. R. Smardzewski, J. Chem. Phys. 58, 2258 (1973).

[9] R. R. Smardzewski and L. Andrews, J. Phys. Chem. 77, 801 (1973).

[10] L. Andrews, J. T. Hwang, and C. Trindle, J. Phys. Chem. 77, 1065 (1973).

[11] F. J. Adrian, E. L. Cochran, and V. A. Bowers, J. Chem. Phys. 59, 56 (1973).

[12] D. M. Lindsay, D. F. Herschbach, and A. L. Kwiran, Chem. Phys. Lett. 25, 175 (1974).

[13] D. White, K. S. Seshadri, D. F. Dever, D. E. Mann, and M. J. Linevski, J. Chem. Phys. 39, 2463 (1963).

[14] K. S. Seshadri, D. White, and D. E. Mann, J. Chem. Phys. 45, 4697 (1966).

[15] C. H. Wu, H. Kudo, and H. R. Ihle, J. Chem. Phys. 70, 1815 (1979).

[16] R. D. Spratley and G. C. Pimentel, J. Am. Chem. Soc. 88, 2394 (1966).

[17] M. Yoshimine, J. Chem. Phys. 57, 1108 (1972).

[18] D. T. Grow and R. M. Pitzer, J. Chem. Phys. 67, 4019

[19] P. A. G. O'Hare and A. C. Wahl, J. Chem. Phys. 56, 4516 (1972).

[20] S. P. So and W. G. Richards, Chem. Phys. Lett. 32, 227 (1975).

[21] S. V. O'Neil, H. F. Schaefer III, and C. F. Bender, J. Chem. Phys. 59, 3608 (1973).

[22] F. P. Billingsley II and C. Trindle, J. Phys. Chem. 76, 2995 (1972).

[23] J. Peslak, Jr., J. Mol. Struct. 12, 235 (1972).

[24] J. H. Yates and R. M. Pitzer, J. Chem. Phys. 66, 3592 (1977).

[25] M. Yoshimine, A. D. McLean, and B. Liu, J. Chem. Phys. 58, 4412 (1973).

[26] M. J. Clugston and R. G. Gordon, J. Chem. Phys. 66, 244 (1977).

[27] M. H. Alexander, J. Chem. Phys. 69, 3502 (1978).

[28] C. Barthelat, Ph. Durand, and A. Serafini, Mol. Phys. 33, 159 (1977).

[29] E. Clementi and J. Mehl, IBM Res. J. p. 833 (1971).

[30] J. L. Whitten (private communication).

[31] H. LeRouzo and B. Silvi, Int. J. Quantum Chem. 13, 311 (1978).

[32] B. Roos and P. Siegbahn, Theor. Chim. Acta 17, 209 (1970).

[33] T. H. Dunning, Jr., J. Chem. Phys. 53, 2823 (1970).

[34] B. Roos, A. Veillard, and G. Vinot, Theor. Chim. Acta 20, 1 (1971).

[35] E. Clementi, "Tables of Atomic Functions," IBM J. Res. Dev. Suppl. 9, 2 (1965).

[36] T. H. Dunning, J. Chem. Phys. 55, 3958 (1971).

[37] J. Pineda, O. Novaro, J. P. Daudey, and E. Blaisten-Barojas, J. Chem. Phys. 71, 5124 (1979).

[38] J. Berkowitz, J. Chem. Phys. 29, 1386 (1958).

[39] E. B. Wilson, J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill, New York, 1955).

[40] T. N. E. Greville, *Mathematical Methods for Digital Computers*, edited by A. Ralston and H. S. Wilfred (Wiley, New York, 1967), Vol. 2, p. 156.

[41] D. M. Lindsay, D. R. Herschbach, and A. L. Kwiram, J. Chem. Phys. 60, 315 (1974).

[42] G. E. Chamberlain and J. C. Zorn, Phys. Rev. 129, 677 (1963).