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Alkali Oxides. Analysis of Bonding and Explanation of the Reversal in Ordering of the $^2\Pi$ and $^2\Sigma^+$ States

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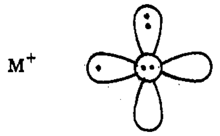
We analyze the bonding in alkali oxides, MO, for M = Li, Na, K, Rb, and Cs. Using ab initio correlated wave functions we find that the ground state is $^2\Pi$ for M = Li, Na, and K and that the ground state is $^2\Sigma^+$ for M = Rb and Cs. The origin of this effect is explained.

I. Introduction

Generally there is a close correspondence in the ground states of molecules in which atoms are replaced by other atoms of the same column from the periodic table. An exception to this occurs with the alkali oxides where LiO has a $^2\Pi$ ground state (as does HO), whereas CsO has a $^2\Sigma^+$ ground state.[1,2,20] In this paper we have carried out a series of ab initio calculations, Hartree–Fock (HF), generalized valence bond (GVB), and configuration interaction (CI), in order to elucidate the bonding in these systems and to explain this reversal. A synopsis of this work has appeared previously.[1]

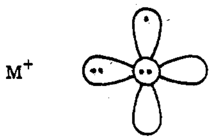
We find that the wave functions can be accurately characterized in terms of an ionic description, M^+O^-. There are two ways of orienting the O^-, leading to the $^2\Pi$ and $^2\Sigma^+$ states

$^2\Sigma^+$:



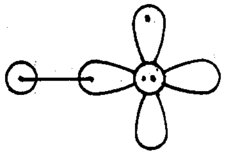
(1)

$^2\Pi$:



(2)

that are within 0.3 eV of each other for all alkali metals, M. In contrast, for a covalent bond as in HO or MeO



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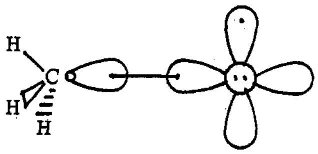
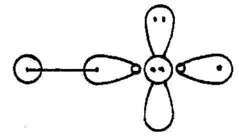


(4)

the ground state would clearly be $^2\Pi$ (or ^2E) with the $^2\Sigma^+$ (or $^2A_1$) state very high

$^2\Sigma^+$



(5)

Thus, for OH (2) $^2\Sigma^+$ is 4.05 eV above $^2\Pi$.

In section III we analyze the MO system and compare various spectroscopic properties with experiment. We find (section III.F) that an analysis of the ionic bonding in MO leads to an understanding of why the $^2\Pi$ and $^2\Sigma^+$ levels invert upon proceeding from M = Li to M = Cs. In section II we consider a similar analysis for a simpler system, NaCl, where available experimental data allow an assessment of accuracy for the theoretical results. Details of the calculations are included in the Appendix.

II. NaCl

For NaCl we considered four types of wave functions ($\mathcal{A}$ is the antisymmetrizer or determinant operator): (i) the simple valence bond (VB) wave function

$$\Psi_{VB} = \mathcal{A}[(\mathrm{Na^+\ core})(\mathrm{Cl^+\ core})(\phi_{3s}\phi_{3p_z} + \phi_{3p_z}\phi_{3s})(\alpha\beta - \beta\alpha)] \tag{6}$$

involving a bond between an Na 3s atomic orbital and a Cl $3p_z$ atomic orbital, (ii) the ionic wave function

$$\Psi_{\mathrm{ionic}} = \mathcal{A}[(\mathrm{Na^+\ core})(\mathrm{Cl^+\ core})(\phi_{3p_z}\phi_{3p_z})(\alpha\beta - \beta\alpha)] \tag{7}$$

involving Na^+ and Cl^- atomic wave functions, (iii) the GVB wave function

$$\Psi_{GVB} = \mathcal{A}[(\mathrm{Na^+\ core})(\mathrm{Cl^+\ core})(\phi_a\phi_b + \phi_b\phi_a)(\alpha\beta - \beta\alpha)] \tag{8}$$

where orbitals ϕ_a and ϕ_b are optimized self-consistently, and (iv) the singles and doubles CI wave function (CI-SD)

$$\Psi_{HF} = \mathcal{A}[(\mathrm{Na^+\ core})(\mathrm{Cl^{7+}\ core})\phi_{3s}\phi_{3s}\phi_{3p_x}\phi_{3p_x}\phi_{3p_y}\phi_{3p_y}\phi_a\phi_a(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)] \tag{9}$$

involving all single and double excitations from the HF wave function where ϕ_a is optimized self-consistently. For wave functions i–iii, we considered the frozen-core (FC) case where the Na^+ and Cl^+ cores are obtained from the ground state of Na and Cl atoms. For wave function ii we also considered the conventional ionic wave function using the self-consistent wave functions from infinite separation for Na^+ and Cl^-. For wavefunctions iii and iv we considered the self-consistent case (SCC), where the core orbitals are solved for self-consistently with the valence electrons.

In Figure 1 we compare the potential curves for the VB, ionic, HF, GVB, and CI wave functions. The VB description is poor, D_e = 0.014 eV, and R_e = 3.929 Å, whereas experimental values are D_e = 4.23 eV and R_e = 2.361 Å.[2] However, the ionic (FC)

[†] Fannie and John Hertz Foundation Fellow, 1979 to the present.

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[§] Contribution No. 6781.

(1) Janet N. Allison and William A. Goddard III, *J. Chem. Phys.*, **77**, 4259 (1982).

(2) K. P. Huber and G. Herzberg, "Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules", Van Nostrand, New York, 1979.

(3) The value of D_e quoted is for an all singles and doubles CI from the valence space using a double-ζ basis for Na and a DZ + d + negative ion functions on Cl. This CI is consistent with the Na^+ + Cl^- limit at infinity. This D_e was then corrected to a D_e appropriate to dissociation to neutral species using the experimental IP of Na and EA of Cl. This yields a D_e of 3.970 eV. A similar calculation was done without negative ion functions on Cl, yielding a D_e = 4.662 eV and R_e = 2.380 Å.

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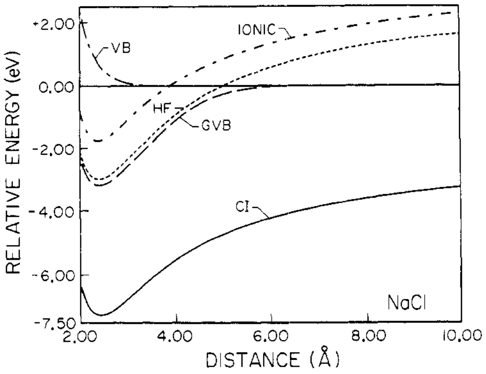

Figure 1. Energy of NaCl as a function of distance of various wave functions. The energy is referenced to HF Na and Cl atoms at infinity. The VB and ionic wave functions used a frozen core. The points at which energies were calculated are as follows (in angstroms): GVB, 2.0, 2.2, 2.4, 2.5, 3.0, 3.5, 4.7626, 6.0, 8.0, 10.0; HF, 2.0, 2.1, 2.2, 2.4, 2.5, 3.0, 3.5, 4.0, 4.7, 5.0, 6.0, 8.0, 10.0; VB, 2.0, 2.1, 2.2, 2.4, 2.5, 3.0, 3.4, 4.0, 4.5, 6.0, 8.0, 10.0; ionic, 2.0, 2.1, 2.2, 2.4, 2.5, 3.0, 3.3, 3.5, 4.7626, 6.0, 8.0, 10.0; CI, 2.0, 2.2, 2.3, 2.4, 2.5, 3.0, 3.3, 3.5, 4.7626, 6.0, 8.0, 10.0.

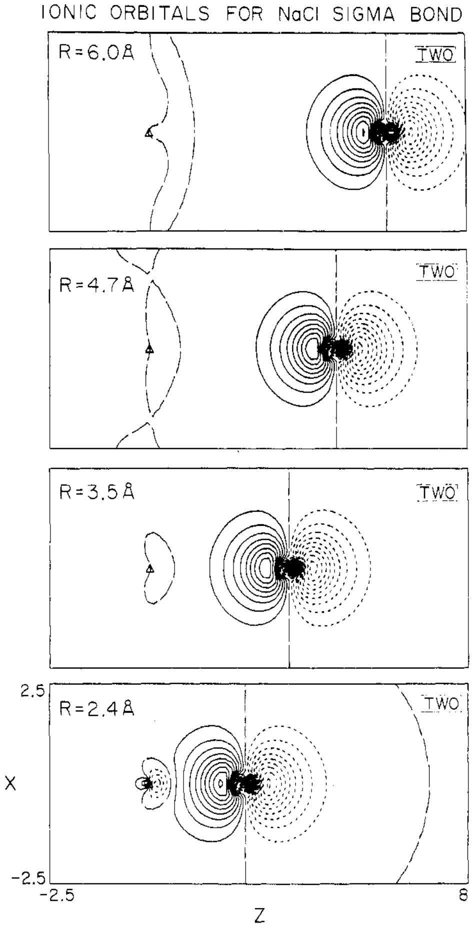

Figure 2. Doubly occupied Cl 3p$_z$ orbital as a function of internuclear distance from the ionic wave function. This illustrates the effect on the 3p$_z$ orbital of orthogonalization to the Na$^+$ core. The nodal surface is indicated by long dashes. Contour separation is 0.03 for all figures.

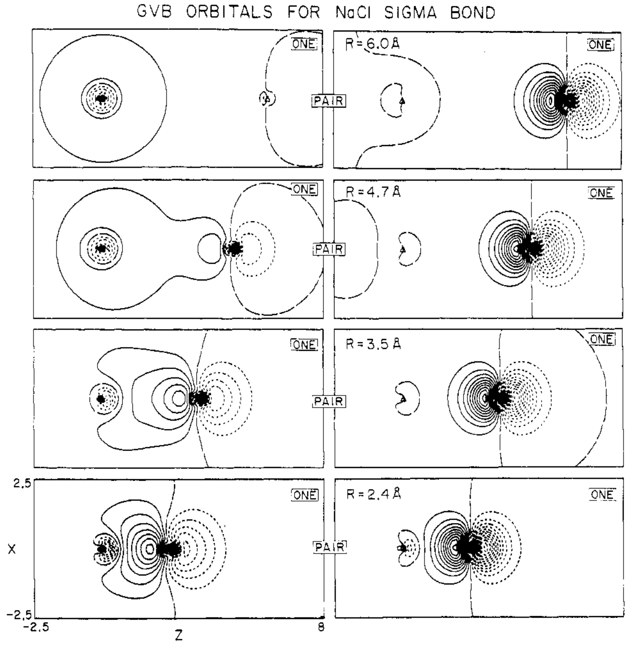

Figure 3. GVB orbitals for the σ bond of NaCl as a function of internuclear distance. Note the conversion from covalent to ionic behavior between 4.7 and 3.5 Å.

and GVB (FC) wave functions lead to R_e = 2.376 and 2.466 Å, respectively, and to bond energies of 1.739 and 2.451 eV, respectively. The conventional ionic wave function leads to R_e = 2.389 Å and D_e = 2.272 eV. Allowing self-consistent cores, the GVB and CI wave functions lead to D_e = 3.170 eV and R_e = 2.389 Å, and D_e = 3.970 eV^2 and R_e = 2.424 Å, respectively.

The bonding orbitals for the ionic and GVB(FC) wave functions of NaCl are shown in Figures 2 and 3, respectively. At 2.4 Å, the ionic and GVB orbitals are very similar, showing that the GVB wave function is largely ionic in character. In Figure 3 we see the conversion from covalent to ionic character between 4.7 and 3.5 Å.

If one defines the energy of M$^+$ + X$^-$ at infinity as E_0, the energy of the ionic wave functions at large distances (R) can be represented by eq 10,

$$E(R) = E_0 - 1/R + Q/R^3 \tag{10}$$

where $-1/R$ is the Coulombic potential for two point charges of opposite sign, and Q represents the quadrupole interactions (zero if the two charge distributions are spherically symmetric).[4] For smaller distances, E_0 is not a constant because of penetration of the charge distributions. The major term here arises from orthogonality of the orbitals of M$^+$ and X$^-$ due to the Pauli principle, and we will refer to

$$E_{\mathrm{PR}}(R) = E_0(R) - E_0(\infty) \tag{11}$$

as the Pauli repulsion term. This quantity is plotted in Figure 4a for the ionic wave function, and we see from Figure 4b that $E_{\mathrm{PR}}(R)$ has an exponential form for $R \leqslant 3.0$ Å.

The VB wave function for NaCl may be written as in (2), leading to an energy of the form

$$E_{\mathrm{VB}} = E_{\mathrm{core}} + E_{\mathrm{Cl}} + \tau/(1 + S^2) \tag{12}$$

where

$$E_{\mathrm{Cl}} = h_{3\mathrm{s},3\mathrm{s}} + h_{3\mathrm{p},3\mathrm{p}} + J_{3\mathrm{s},3\mathrm{p}} \tag{13}$$

$$\tau = E_{\mathrm{ex}} - S^2 E_{\mathrm{Cl}} \tag{14}$$

$$E_{\mathrm{ex}} = 2S h_{3\mathrm{s},3\mathrm{p}} + K_{3\mathrm{s},3\mathrm{p}} \tag{15}$$

and where E_{core} is the energy of FC Na$^+$ and Cl$^+$ wave functions at the given R, S is the overlap of the Na 3s and Cl 3p$_z$ orbitals

$$h_{\mathrm{ij}} = \langle \phi_{\mathrm{i}} | -\tfrac{1}{2}\nabla^2 + V_{\mathrm{core}} | \phi_{\mathrm{j}} \rangle$$

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(4) The quadrupole contribution to the electrostatic potential of the Cl used in the ionic (FC) wave function may be written as

$$-\tfrac{1}{3}(2\Theta_{zz}/R^3 - \Theta_{xx}/R^3 - \Theta_{yy}/R^3)$$

However, by symmetry, $\Theta_{xx} = \Theta_{yy}$, and, since the trace of the quadrupole moment tensor is zero, $\Theta_{xx} = -\Theta_{zz}/2$. Therefore, the total quadrupolar contribution to the electrostatic potential is $-\Theta_{zz}/R^3$. At long R we assume the Pauli repulsion is zero and estimate Θ_{zz} to be 6.16×10^{-28} esu·cm^2.

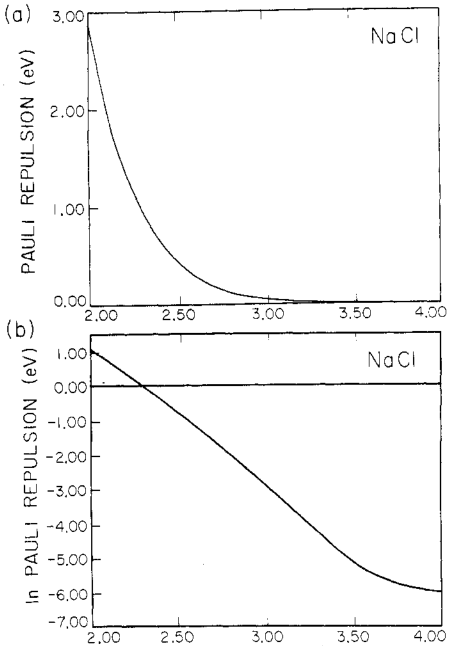

Figure 4. (a) Pauli repulsion for NaCl ionic wave function as a function of internuclear distance using eq 10 and 11. (b) Natural logarithm of the Pauli repulsion for the NaCl ionic wave function as a function of internuclear distance. In the region r = 2.0–2.5 Å, $E_{PR} = Ae^{-br}$, with A = 5920 eV and b = 3.82 Å^{-1}.

is the one-electron matrix element of the valence electron with all core electrons and with the nuclear charges, $J_{3s,3p}$ and $K_{3s,3p}$ are the usual Coulomb and exchange energies, and 3p is understood to refer to the 3p$_z$ orbital.

In this form there are two parts to the energy: (i) $E_{core} + E_{CI}$ provides a nonbonding repulsive contribution that includes the Pauli repulsion effects due to orthogonalization of overlapping doubly occupied orbitals; (ii) $\bar{\tau}/(1 + S^2)$ is the bonding portion of the wave function and may be considered as arising from interference effects of singly occupied orbitals. In this framework it is obvious why the covalent bonding is so weak in NaCl. Writing $\bar{\tau}$ as

$$\bar{\tau} = 2Sh_{3s,3p_z} + K_{3s,3p_z} - S^2(h_{3s,3s} + h_{3p,3p} + J_{3s,3p}) \quad (16)$$

and noting that

$$h_{3s,3p} \approx \tfrac{1}{2}S[h_{3s,3s} + h_{3p,3p}] \quad (17)$$

$$K_{3s,3p} \approx \tfrac{1}{4}S[J_{3s,3s} + J_{3p,3p} + 2J_{3s,3p}] \quad (18)$$

(from use of the Mulliken approximation), we see that all terms in $\bar{\tau}$ depend either explicitly or implicitly on S^2. A plot of S vs. distance for these two orbitals is shown in Figure 5. For VB, S never goes above 0.17 and therefore $\bar{\tau}$ is kept small. It is therefore the small overlap of the Na 3s and Cl 3p$_z$ that limits appreciable covalent bonding. Next we will use a similar analysis to examine the GVB-FC wave function to understand why its bonding is better than the ionic.

The GVB frozen-core wave function preserves the same orbitals (except for orthogonalization) as in the separated atom limit for all orbitals *except* for the Na 3s and Cl 3p$_z$. These orbitals are allowed to take any shape they want. Since it has already been illustrated that at R_e these orbitals have essentially the shape of the Cl$^-$ 3p$_z$ orbital, we might approximate them by a wave function that is mostly Na$^+$Cl$^-$ with a small amount of covalent character mixed in. This amounts to doing a two-orbital CI, the two states being the ionic and covalent wave functions

$$\Psi_{GVB} = C_I\Psi_I + C_C\Psi_C \quad (19)$$

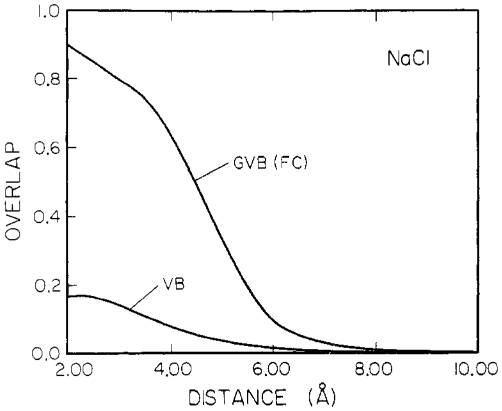

Figure 5. Overlap of bond orbitals for NaCl as a function of internuclear distance for VB and GVB(FC) wave functions.

For the ionic wave function we use the ionic (FC) wave function 7 since it has the same core orbitals as the GVB(FC) and VB wave functions. This should parallel the GVB(FC) case since any mixing will occur due to differences only in the bonding orbitals. In matrix form, we solve

$$\begin{pmatrix} H_{II} & H_{IC} \\ H_{CI} & H_{CC} \end{pmatrix}\begin{pmatrix} C_I \\ C_C \end{pmatrix} = E_{GVB}\begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix}\begin{pmatrix} C_I \\ C_C \end{pmatrix} \quad (20)$$

H_{II} and H_{CC} are exact. H_{IC} is obtained by using the Mulliken approximation.

At 10 Å, E_{GVB} is essentially the energy of the VB wave function. However, at 2.4 Å (near the minimum for experimental and GVB curves), the energy lowering due to mixing is substantial, with the wave function being predominantly ionic but containing some mixing of covalent. Thus, at 2.4 Å, the wave function is 78% ionic, with an energy lowering relative to the ionic (FC) wave function of 0.61 eV.

One might wonder why the energy lowering in going from ionic to GVB is so large, since the covalent wave function is repulsive at this distance. Analysis of the energy in eq 20 shows that H_{IC} (responsible for coupling ionic and covalent terms) has the form

$$H_{IC} \simeq \tau - \tfrac{1}{2}S\bar{\tau}/(1 + S^2)$$

where $\tau = h_{3s,3p} - \frac{1}{2}S(h_{3s,3s} + h_{3p,3p})$ is the quantity that dominates one-electron bonds, such as in H$_2^+$. The energy for such one-electron systems may be written as

$$E_{tot} = E_{CI} + \tau/(1 + S)$$

where E_{CI} is a repulsive term and τ is negative. Thus, large negative τ yields large bonding. We find that τ is also the major term responsible for coupling between the ionic and covalent wave functions. The form of τ suggests that it is approximately equal to $(\bar{\tau})^{1/2}$. However, since τ only goes as S rather than S^2, it is a good deal larger than $\bar{\tau}$ and is able to contribute substantial coupling between the two wave functions at this distance.

Therefore, although the valence bond wave function is not a good description of the overall bonding in NaCl, it does contribute significantly to the bonding because the coupling term between the ionic and covalent wave functions goes as S and not S^2.

In the following section we will use the above ideas to examine the trend in alkali oxide (M$^+$O$^-$) energies.

III. Alkali Oxides

A. Calculational Details. The basis sets were of valence double-ζ type on atoms but with polarization (d) functions and diffuse p functions on the oxygen. Three types of calculations were carried out: ionic, HF, and CI.

(*a*) *Ionic.* For the ionic wave function we calculated the wave function for M$^+$ and O$^-$ at $R = \infty$ and kept the shapes of the orbitals fixed as the atoms were brought together (and the wave functions properly antisymmetrized). For O$^-$ the singly occupied p orbital was allowed to have a shape different from the doubly occupied orbitals [see (1) and (2)].

(*b*) *HF.* Fully self-consistent HF calculations were carried out for both $^2\Sigma^+$ and $^2\Pi$ as a function of internuclear distance (R).

TABLE I: LiO, NaO, KO, RbO, and CsO Ionic, HF, and CI Wave Functions

M^+O^-	state		E (hartree), T (cm^{-1})[a]	ω_e,[b] cm^{-1}	D_e,[c] eV	R_e,[d] Å
LiO	$^2\Pi$	ionic	−82.268 077	792	2.93	1.79
		HF	−82.291 43	869	3.57	1.73
		CI	−82.449 16	772	3.45	1.76
	$^2\Sigma^+$	ionic	3 519	762	2.49	1.72
		HF	2 894	850	3.21	1.64
		CI	2 634	824	3.13	1.65
NaO	$^2\Pi$	ionic	−236.666 20	506	2.35	2.08
		HF	−236.673 17	507	2.66	2.06
		CI	−236.832 24	464	2.58	2.09
	$^2\Sigma^+$	ionic	2 220	487	2.08	2.01
		HF	2 088	514	2.40	1.97
		CI	2 177	493	2.31	2.00
KO	$^2\Pi$	ionic	−673.286 79	280	2.19	2.50
		HF	−673.294 26	401	2.39	2.45
		CI	−673.443 80	363	2.05	2.52
	$^2\Sigma^+$	ionic	352	351	2.14	2.38
		HF	233	389	2.36	2.32
		CI	831	403	1.95	2.37
RbO	$^2\Pi$	ionic	−3 010.197 30	324	2.06	2.66
		HF	−3 010.207 57	339	2.34	2.58
		CI	−3 010.363 58	399	2.18	2.67
	$^2\Sigma^+$	ionic	−71	300	2.07	2.53
		HF	−138	387	2.36	2.45
		CI	−114	452	2.19	2.52
CsO	$^2\Pi$	ionic	−7 622.202 57	264	2.00	2.87
		HF	−7 622.211 21	272	2.23	2.74
		CI	−7 622.367 21	236	2.07	2.84
	$^2\Sigma^+$	ionic	−587	301	2.07	2.71
		HF	−735	321	2.33	2.59
		CI	−846	286	2.18	2.67

[a] $^2\Pi$ total energy in hartrees E; $^2\Sigma^+$ excitation energy from $^2\Pi$ state, T_e (cm^{-1}). [b] Vibrational frequency. [c] Bond dissociation energy. [d] Optimized internuclear distance.

(*c*) *CI*. Starting with the HF wave functions, CI calculations allowing all single and double excitations from the occupied valence orbitals into all virtual orbitals were carried out as a function of R. For the $^2\Sigma^+$ state of CsO, this leads to 910 spatial configurations (2561 spin eigenfunctions or 4476 determinants).

The results of all calculations are presented in Table I. For all five molecules, all three types of calculations lead to the same order of states and the same trends in various properties. For the rest of this paper we will discuss only the results for the CI calculations as summarized in Table II.

B. Ground-State Symmetries. As discussed above, alkali oxides have two low-lying states, $^2\Pi$ and $^2\Sigma^+$, just as expected, for M^+O^-. It has been reported[5-7] that a change in ground state from $^2\Pi$ for LiO to $^2\Sigma^+$ for CsO occurs as one proceeds down the M^+O^- series LiO, NaO, KO, RbO, and CsO. The evidence is indeed strong that CsO has a $^2\Sigma^+$ ground state and that LiO and NaO have $^2\Pi$ ground states. For KO, evidence has been presented separately for both a $^2\Sigma^+$ ground state and a $^2\Pi$ ground state.[5,8] RbO has not been well characterized, although the ESR is consistent with a $^2\Sigma^+$ ground state. Generally, data on these systems are sparse and consequently we have carried out a series of moderately extensive calculations.

The calculated results for the $^2\Pi$ and $^2\Sigma^+$ states of all five molecules are given in Table I and summarized in Table II. The CI results are the most accurate and should be compared with experiment. We find that the $^2\Sigma^+$–$^2\Pi$ separation decreases monotonically from +0.327 eV for LiO, to +0.270 eV for NaO, to +0.103 eV for KO, to −0.014 eV for RbO, and to −0.105 eV for CsO. Thus, we find that $^2\Pi$ is the ground state for LiO, NaO, and KO, but that $^2\Sigma^+$ is the ground state for RbO and CsO. These results are consistent with the ESR studies that detect signals only for RbO and CsO ($^2\Pi$ would not lead to observable ESR).

A $^2\Pi$ ground state for LiO and NaO is consistent with previously reported spectroscopic and ESR results.[5-7] However, there has been disagreement regarding the ground state of KO. Lindsay, Herschbach, and Kwiram[8] find no observable ESR spectrum for K + N_2O under conditions that gave KO infrared absorption, which is consistent with a $^2\Pi$ ground state. However, So and Richards,[5] in HF calculations, report a ground state of KO to be $^2\Sigma^+$ with an excitation to the $^2\Pi$ KO of 0.04 eV. We find, in agreement with ESR, that $^2\Sigma^+$ KO lies above $^2\Pi$ by 0.10 eV.

C. Bond Energies. The CI calculations near equilibrium lead to a wave function of the form M^+O^-, and it is expected that the correlation errors in this wave function would be approximately independent of distance as long as the wave function has the character M^+O^-. Thus, the bond energy calculated with respect to the ionic limit

$$-D_e^{\text{ionic}} = E^{\text{CI}}(R_e) - E^{\text{CI}}(M^+) - E^{\text{CI}}(O^-) \qquad (21)$$

where the same CI is used for R_e and for $R = \infty$, is expected to be fairly accurate. The proper definition of the bond energy is, of course

$$-D_e^{\text{cov}} = E^{\text{CI}}(R_e) - E^{\text{CI}}(M) - E^{\text{CI}}(O) \qquad (22)$$

however, the level of correlation error in a covalent wave function for separated M and O will not be the same as for an ionic wave function (M^+O^-). Consequently, we have calculated bond energies (D_e^{cov}) as follows:[9-11]

$$\begin{aligned} -D_e^{\text{cov}} &= [E^{\text{CI}}(R_e) - E^{\text{CI}}(M^+) - E^{\text{CI}}(O^-)] + \\ &\qquad [E^{\text{exptl}}(O^-) - E^{\text{exptl}}(O)] + [E^{\text{exptl}}(M^+) - E^{\text{exptl}}(M)] \\ &= -D_e^{\text{ionic,CI}} - \text{EA}(O)^{\text{exptl}} - \text{IP}(M)^{\text{exptl}} \qquad (23) \end{aligned}$$

That this is a reliable way to obtain accurate bond energies from calculations is indicated by the close correspondence between the values of D_e^{cov} obtained by using eq 23 with HF or CI wave functions (0.1-eV error), despite the fact that the CI wave function has a total energy 4.3 eV lower than HF. Analogous calculations on NaCl lead to a calculated bond energy that is 0.28 eV smaller than the experimental value.

In order to compare with D_0 values from experiment, we have corrected our calculated D_e by including the calculated zero-point energies (see Table II).

Of the alkali oxides, reliable experimental bond energies are known only for LiO and NaO. For LiO($^2\Pi$) we calculate a bond energy of 3.40 eV, in good agreement with the thermochemical value of 3.49 ± 0.06 eV.[12] For NaO($^2\Pi$) we calculate a bond dissociation energy of 2.55 eV, also in good agreement with the experimental value of 2.61 ± 0.2 eV.[13]

There is no known reliable experimental bond energy for KO. Gusarov et al.[14] estimate the dimerization energy of KO to be ~3.52 eV by comparison with experimental data for LiO, Li_2O_2, and the alkali fluorides. From this they deduce $D_0(\text{KO}) \simeq 2.61 \pm 0.26$ eV. This value has been lowered by 0.17 eV to 2.43 ± 0.35 eV to be consistent with the chosen dissociation energy of LiO.[9] Our calculations for KO($^2\Pi$) lead to $D_e = 2.03$ eV. No experimental information is available for RbO and CsO bond energies. Our calculations for RbO($^2\Sigma^+$) lead to a $D_0 = 2.16$ eV and for CsO($^2\Sigma^+$) lead to a $D_0 = 2.14$ eV. The above results are

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TABLE II: Comparison of Experiment and Theory (CI-SD)

	$^2\Pi-^2\Sigma^+$ exctn energy,[h] cm^{-1}		ground state					
			bond energy, eV		vibr freq, cm^{-1}		bond distance, Å	
	theory[a]	expt	theory[a]	expt	theory	expt[b]	theory	expt
NaCl			3.949	4.23[c]	342	366[c]	2.424	2.361[c]
LiO	2634	>0	3.40	3.49 ± 0.06[d]	772	(752)[e]	1.76	
NaO	2177	>0	2.55	2.61 ± 0.20[f]	464		2.09	
KO	831		2.03		363	(384)[g]	2.52	
RbO	−114		2.16		452		2.52	
CsO	−846	<0	2.14		286	(314)[g] (322)[e]	2.67	

[a] Corrected for zero-point energy to obtain D_0. [b] All experimental values are in matrices and in all cases there is some uncertainty in the identity of the species as MO. [c] Reference 2. [d] Reference 12. [e] Reference 17. [f] Reference 13. [g] Reference 16. [h] Use $^2\Pi$ as reference.

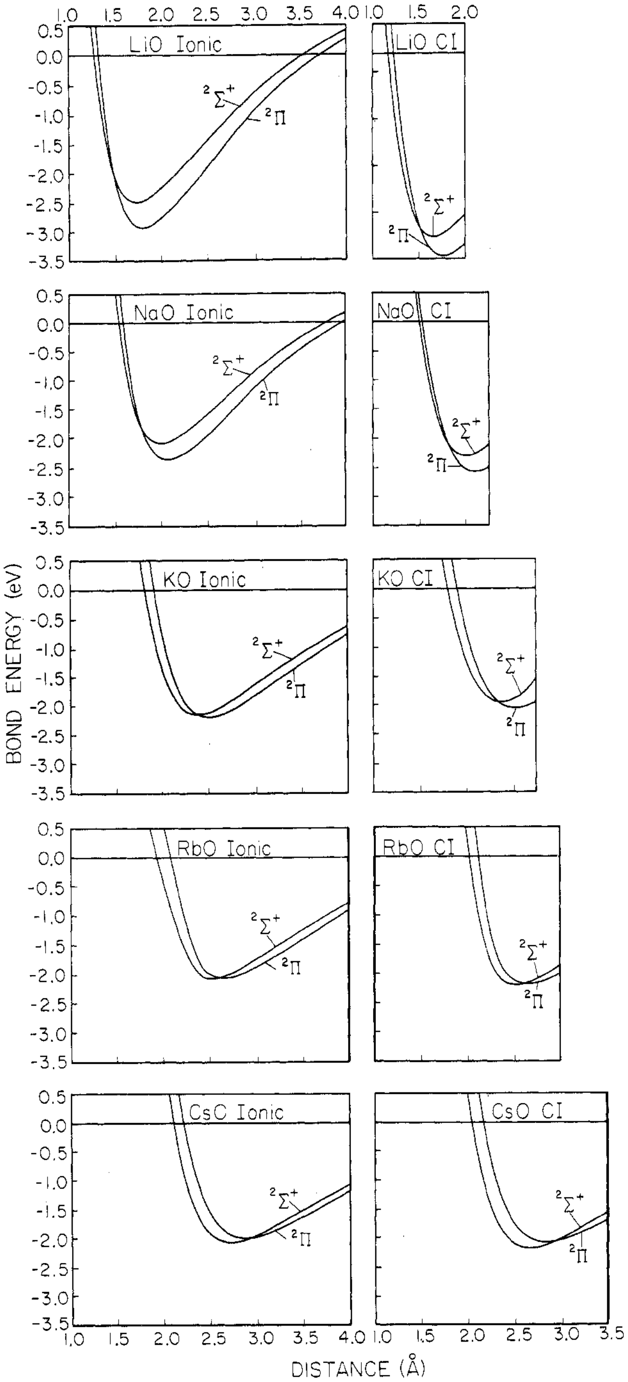

Figure 6. Potential curves for the $^2\Sigma$ and $^2\Pi$ states of the alkali oxides using ionic and CI wave functions.

shown in Table I, where it can be seen that bonds tend to be weaker as the size of M^+ is increased.

TABLE III: K[5s,4p] Contracted Basis[a]

s basis		p basis	
α_s	c_s	α_p	c_p
4604	1.97116167D-02	183.0	3.08410585D-02
691.4	1.37234789D-01	42.10	1.91276749D-01
155.4	4.74535636D-01	12.48	5.14236821D-01
42.09	4.90585110D-01	3.981	4.36694325D-01
155.4	−3.13185885D-02	12.48	−1.77900407D-02
42.09	−1.35692015D-01	3.981	2.42372456D-02
9.759	4.59054357D-01	1.088	5.39594678D-01
3.422	6.84412236D-01	0.3291	5.80210340D-01
3.422	−1.92816873D-01	0.05936	1.00000000D+00
0.8701	6.19277995D-01	0.01896	1.00000000D+00
0.3197	6.25422957D-01		
0.3197	−1.56768784D-01		
0.03276	7.59368522D-01		
0.01733	1.00000000D+00		

[a] $E = -598.46757$ hartrees, $\epsilon_{4s} = -0.147311$ hartree, $\epsilon_{4p} = -0.09504$ hartree.

D. Geometries. There are no experimentally known bond distances for the alkali oxides. In all cases we find that $^2\Pi$ states have equilibrium internuclear distances longer than the $^2\Sigma^+$ state by ~0.1 Å. The CI values calculated for LiO($^2\Pi$) and LiO($^2\Sigma^+$) are 1.76 and 1.65 Å and increase to 2.84 and 2.67 Å for CsO($^2\Pi$) and CsO($^2\Sigma^+$), respectively. The changes in bond length in going from LiO to CsO (a total of 1.08 Å for $^2\Pi$ and 1.02 Å for $^2\Sigma^+$) parallel the changes in ionic radii of the alkali metals as one proceeds down the periodic column (Li^+, 0.68 Å; Na^+, 0.95 Å; K^+, 1.33 Å; Rb^+, 1.48 Å; and Cs^+, 1.69 Å).[15]

E. Vibrational Frequencies. Infrared studies[16] of matrix reactions of Na, K, Rb, and Cs with N_2O yield KO and CsO absorptions at 384 and 314 cm^{-1}, respectively (our calculated values are 363 and 286 cm^{-1}, respectively). Absorptions due to RbO were too weak to be observed and no NaO was produced.[16] In the reaction of Na with O_2 in an argon matrix, NaO_2 and NaO_2Na were identified; however, no NaO was found.[17] The identification of the Na species is complicated by the fact that Na has only one stable isotope ($^{23}_{11}Na$ = 100%) so isotopic labeling studies must be ruled out for the alkali atom. Argon matrix infrared spectroscopy for Cs with O_3 produced assignments of CsO at 322 cm^{-1} (calculated value 286 cm^{-1}) and simultaneous mercury arc photolysis was required to assign the LiO absorption at 752 cm^{-1} (calculated value 772 cm^{-1}) from the Li/O_3/Ar matrix reaction.[18]

Comparing these experimental results with our calculated values (Table II) leads to discrepancies of less than 10%. The comparison is complicated because of uncertainty in the assignment of the observed species as MO and because of the presence of matrix effects in the experiments. Thus, for both KO and RbO it would even be possible that the matrix could shift the ordering of $^2\Sigma^+$

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(17) L. Andrews, *J. Phys. Chem.*, **73**, 3922 (1969).

(18) R. C. Spiker, Jr., and L. Andrews, *J. Chem. Phys.*, **59**, 1851 (1973).

TABLE IV: Rb[6s,5p,1d] Contracted Basis[a]

s basis		p basis		d basis	
α_s	c_s	α_p	c_p	α_d	c_d
17530	2.00793424D-02	828.2	2.91737936D-02	79.17	5.04823768D-02
2644	1.36687381D-01	194.3	1.89114031D-01	22.29	2.56450065D-01
597.4	4.83498105D-01	60.28	5.21392739D-01	7.426	5.15328715D-01
163.0	4.97110569D-01	20.81	4.29339554D-01	2.460	4.28291504D-01
229.1	−1.16149506D-01	14.81	5.87734209D-02		
41.34	4.24626708D-01	7.265	5.15026535D-01		
16.24	6.63064243D-01	2.603	5.15750600D-01		
21.48	−2.48078576D-01	6.286	−4.33381510D-02		
5.516	5.08310302D-01	0.6123	6.72247462D-01		
2.239	6.57264399D-01	0.1845	4.29976351D-01		
2.993	−2.98135436D-01	0.1845	−5.72514746D-02		
0.5029	8.06312511D-01	0.03882	1.02740267D+00		
0.1887	3.57686621D-01	0.01094	1.00000000D+00		
0.2131	−7.85297180D-01				
0.03544	1.23009464D+00				
0.01565	1.00000000D+00				

[a] $E = -2935.37820$ hartrees, $\epsilon_{5s} = -0.13653$ hartree, $\epsilon_{5p} = -0.08941$ hartree.

TABLE V: Cs[7s,6p,3d] Contracted Basis[a]

s basis		p basis		d basis	
α_s	c_s	α_p	c_p	α_d	c_d
38990	1.99721959D-02	1956	2.81362862D-02	254.6	3.95252870D-02
5879	1.38839643D-01	460.7	1.86251459D-01	74.25	2.26282568D-01
1329	4.83975871D-01	144.5	5.23106652D-01	26.38	5.24358534D-01
363.2	4.94928675D-01	50.75	4.26646071D-01	9.858	4.16269774D-01
519.0	−1.35465076D-01	30.87	6.54334473D-02	9.115	2.37506883D-01
99.95	4.04982358D-01	20.90	4.76009931D-01	3.769	8.15622204D-01
39.41	6.90811513D-01	8.502	5.25302242D-01	1.391	1.00000000D+00
56.10	−3.40125333D-01	17.26	−2.08933499D-02		
18.53	3.27712450D-01	3.692	5.47252619D-01		
7.597	8.77329020D-01	1.490	5.21178176D-01		
9.759	−4.82878105D-01	5.302	−3.88578526D-03		
3.753	4.48092239D-01	0.4849	5.53881730D-01		
1.475	8.57694277D-01	0.1729	5.22806920D-01		
1.738	−3.80047701D-01	0.2661	−1.07647483D-01		
0.3820	7.58660512D-01	0.02620	1.02110142D+00		
0.1567	4.57786203D-01	0.01140	1.00000000D+00		
0.2494	−5.78383788D-01				
0.02688	1.12132195D+00				
0.01313	1.00000000D+00				

[a] $E = -7547.38242$ hartrees, $\epsilon_{6s} = -0.12309$ hartree, $\epsilon_{6p} = -0.08388$ hartree.

and $^2\Pi$, changing the symmetry of the ground state.

We should point out here that the calculated ω_e is the curvature at the bottom of the potential surface (using a cubic spline fit), whereas the experimental values are ω_0, the separation of the $v = 0$ and $v = 1$ vibrational levels.

F. Explanation of the Reversal in $^2\Pi$–$^2\Sigma^+$ Ordering. The essence of our explanation of the shift in ground-state symmetry can be grasped by considering the energy curves for purely ionic wave functions corresponding to the $^2\Sigma^+$ and $^2\Pi$ states 1 and 2. These ionic curves are shown in Figure 6 for LiO through CsO. In all cases $^2\Pi$ is favored at longer distances, while $^2\Sigma^+$ is favored at shorter distances, leading always to a crossing of the $^2\Sigma^+$ and $^2\Pi$ states. The reason that $^2\Pi$ is lower at larger R is the greater electrostatic attraction caused by the orientation of the oxygen ion [see (1) and (2)]. In the $^2\Sigma^+$ state, the orientation of the oxygen ion is such that the quadrupole terms are repulsive (the hole is in the p_σ orbital). However, in the $^2\Pi$ state, the quadrupole terms are attractive (the hole is in the p_π orbital), thus lowering this state relative to the $^2\Sigma^+$ state.[19]

The reason that $^2\Sigma^+$ is lower than $^2\Pi$ at shorter R is due to Pauli repulsion effects arising from orthogonalizing the O p_σ orbital to the M^+ core. This term becomes important for small R and is roughly twice as large for $^2\Pi$ as than for $^2\Sigma^+$ due to the presence of two electrons in the p_σ orbital for $^2\Pi$ and only one for $^2\Sigma^+$. A plot of Pauli repulsion vs. distance for $^2\Pi$ and $^2\Sigma^+$ states of NaO is shown in Figure 7, a and b.

The equilibrium bond distance is determined by a balance of the attractive $1/R$ electrostatic term and the repulsive Pauli orthogonality term. As we move down the periodic table, the M core becomes larger, leading to a larger bond distance and hence a smaller bond energy. Indeed, the total bond energy scales roughly as $1/R_e$, so that the effective Pauli repulsion term (at R_e) scales as $1/R_e$. However, the $^2\Sigma^+$–$^2\Pi$ splitting involves a balance between Pauli repulsion (scaling as $1/R_e$) and a quadrupole term that scales as $(1/R_e)^3$. Thus, at R_e the $^2\Sigma^+$ states should be stabilized with respect to $^2\Pi$ as we move down the column.

Summarizing, the change in stability of $^2\Sigma^+$ with respect to $^2\Pi$ occurs because the balance between Pauli repulsion (favoring $^2\Sigma^+$)

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(19) The quadrupole terms in the electrostatic potentials for the ionic NaO wave functions are $-\Theta/R^3$ for $^2\Pi$ and $+2\Theta/R^3$ for $^2\Sigma^+$. At long R we assume the Pauli repulsion is zero for both states; therefore, the state separation is merely $3\Theta/R^3$. From this we estimate Θ to be 0.796 in atomic units. An explicit calculation of the O^- quadrupole moment yields 0.795. This is equal to 1.07×10^{-27} esu·cm^2.

(20) R. R. Herm and D. R. Herschbach, *J. Chem. Phys.*, **52**, 5783 (1970).

(21) T. H. Dunning, Jr., and P. J. Hay in "Methods of Electronic Structure Theory", H. F. Schaefer III, Ed., Plenum Press, New York, 1977, Chapter 1.

(22) A. K. Rappé and W. A. Goddard III, *J. Phys. Chem.*, to be submitted for publication.

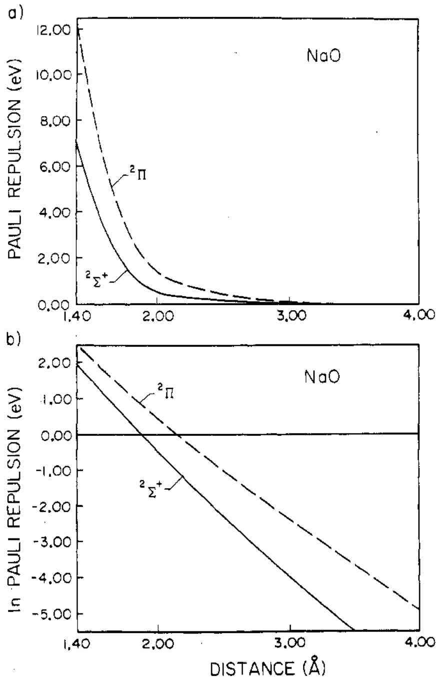

Figure 7. (a) Pauli repulsion for the NaO $^2\Sigma^+$ and $^2\Pi$ ionic wave functions as a function of internuclear distance. (b) Natural logarithm of the NaO Pauli repulsion as a function of distance for the $^2\Sigma^+$ and $^2\Pi$ states. Using the form $E_{PR} = Ae^{-br}$ and the calculated points at $R = 1.4$ and $R = 2.2$ leads to $A(^2\Pi) = 1270$ eV, $A(^2\Sigma^+) = 1780$ eV, $b(^2\Pi) = 3.3$ Å^{-1}, and $b(^2\Sigma^+) = 3.9$ Å^{-1}.

TABLE VI: Na[12s,8p] Contracted Basis[a]

s basis		p basis	
α_s	c_s	α_p	c_p
36 631.1	3.8000D-04	148.928	5.1300D-03
5 385.07	3.0500D-03	34.5149	3.7910D-02
1 216.20	1.5990D-02	10.6045	1.53410D-01
339.529	6.4270D-02	3.67106	3.53130D-01
109.563	1.94810D-01	1.28490	4.5550D-01
38.7834	4.0099D-01	0.430941	2.4372D-01
14.5790	3.9267D-01	0.067600	1.0000D+00
5.27901	8.2820D-02	0.020800	1.0000D+00
1.82902	1.0000D+00		
0.620535	1.0000D+00		
0.058065	1.0000D+00		
0.024617	1.0000D+00		

[a] $E = -161.84197$ hartrees, $\epsilon_{3s} = -0.18188$ hartree, $\epsilon_{3p} = -0.10931$ hartree.

and quadrupole interactions (favoring $^2\Pi$) is shifted toward the Pauli repulsion terms (and hence $^2\Sigma^+$) as we go to metal ions with larger cores.

Clugston and Gordon[23] have reported electron-gas-model calculations where in all cases a $^2\Pi$ ground state was found. (For RbO they find that $^2\Pi$ is stabilized by 2195 cm^{-1} and conclude that the electron-gas model is able to describe the $^2\Pi$ state but not the $^2\Sigma^+$ state.) They have suggested that the Π states are stable at larger R due to differential shielding effects and that the Σ states are stable at shorter R due to non-Coulombic terms (kinetic, exchange, and correlation).

Previously it has been suggested that the reversal of $^2\Pi$–$^2\Sigma^+$ ordering from LiO to CsO might be the result[8] of mixed covalency interactions of the alkali inner-shell electrons with the O$^-$, or that it might be due[20] to the more polarizable nature of the core electrons of Cs and Rb. The fact that we obtain the same ordering of states for ionic wave functions obtained from *atomic* M$^+$ combined with *atomic* O$^-$ shows that such mixed covalency effects cannot be responsible for the reversal in states. Our calculations do indicate that for the SCF wave functions of the $^2\Sigma^+$ state there is a small amount of radical character on the metal. For example, in CsO($^2\Sigma^+$) the p_σ singly occupied orbital of oxygen has the form $\phi_{O2p_z} + 0.096\phi_{Cs5s} + 0.167\phi_{Cs5p_z}$, leading to 1% Cs 5s character and 3% Cs 5p character in the radical orbital. These results are consistent with those found by Lindsay, Herschbach, and Kwiram.[8,24]

Acknowledgment. This work was supported in part by grants (DMR-79-19689 and DMR-82-15650) from the National Science Foundation.

Appendix

Basis Sets. The basis sets were as follows. For Li and O we used the Dunning [3s,2p] contraction of the [9s,5p] basis of Huzinaga.[21] For oxygen this was supplemented by diffuse p functions ($\alpha_p = 0.059$) and by polarization functions ($\alpha_d = 0.85$). For Cl we used the Dunning [6s,4p] contraction of the Huzinaga (11s,7p) basis.[20] We supplemented the Cl basis in all cases with polarization functions ($\alpha_d = 0.600$), and for the CI wave function the basis was also supplemented with diffuse p functions ($\alpha_p = 0.049$). For Na we used the [6s,4p] contraction of the (12s,8p) basis obtained by R. Bair (unpublished results) using functions from the Na(12s,6p) basis of Veillard.[25] For K, Rb, and Cs we used valence double-ζ contractions of basis sets recently obtained by Rappé and Goddard.[22]

Details of these basis sets for Na, K, Rb, and Cs are included in Tables III–VI.

Registry No. LiO, 12142-77-7; NaO, 12401-86-4; KO, 12401-70-6; RbO, 12509-27-2; CsO, 24774-39-8.

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(23) M. J. Clugston and R. G. Gordon, *J. Chem. Phys.*, **66**, 244 (1977).

(24) Neglecting overlap terms, Lindsay and Herschbach[8] estimate 2% Cs 5s and 6% Cs 5p. Including overlap terms should yield a decreased amplitude on the Cs. On the other hand, we have not included core polarization effects and hence obtain parameters that are too low.

(25) A. Veillard, *Theor. Chim. Acta*, **12**, 405 (1968).