

The $2\Sigma^+$ states of HBeO, HMgO, and HCaO

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The $2\Sigma^+$ states of HBeO, HMgO, and HCaO have been studied at the CASSCF level with a basis set of at least triple-zeta plus double polarization quality. The correlation treatment includes the nine valence electrons and ten orbitals resulting in an active space denoted by (622). The optimized structures of HMO (M=Be, Mg, and Ca) are all linear and the energy of HMO lies around 250 kJ/mol (2.6 eV) above that of MOH. The M–O bond length in HMO is predicted to be longer than that in the corresponding MOH by amounts ranging from 0.01 Å to 0.05 Å. The M–O stretching frequencies are very similar for the two structures. The H–M bond lengths and stretching frequencies in HMO are very similar to the same properties in the corresponding diatomic molecule. Analysis of the electronic structures suggests that HBeO has two polarized covalent bonds formed from the *sp* hybrids of Be; HMgO has one covalent bond (between H and Mg) and one ionic bond and can be viewed as (HMg)⁺O[−], HCaO has two ionic bonds represented by H[−]Ca²⁺O[−]. © 1996 American Institute of Physics. [S0021-9606(96)02509-1]

I. INTRODUCTION

With the exception of BeOH, the alkaline–earth hydroxides are considered to be ionic compounds; the ionic character increases from BeOH to BaOH. Theoretical studies^{1,2} show that BeOH is bent while the other members of the series are linear. Experiments show that CaOH (Ref. 3) and SrOH (Ref. 4) are linear and that MgOH is quasilinear.⁵ The linearity suggests the dominance of ionic character, for otherwise the lone-pairs on oxygen would force the molecules to bend if the bonding were predominantly covalent. Bauschlicher and Partridge⁶ obtained favorable agreement with the experimental⁷ dissociation energies of CaOH and LiOH to ions by using the restricted-open-shell-Hartree–Fock (ROHF) method with a large basis set of at least triple-zeta plus double polarization quality and assuming that most of the correlation energy is embedded in the ions. In a subsequent paper Bauschlicher *et al.*² studied the structures and energetics of the ground states of the alkali and alkaline–earth monohydroxides at the singles plus doubles configuration interaction (CISD) level with the same basis set. In addition to predicting the metal–ligand equilibrium distance and the dissociation energy, the vibrational frequencies and bending potentials were also calculated and the bending potentials were used to discuss the relative proportions of ionic and covalent characters.

More recently the permanent dipole moments of the $X\ 2\Sigma^+$, $A\ 2\Pi^+$, and $B\ 2\Sigma^+$ states of CaOH were calculated at the computed equilibrium geometries with the coupled-pair functional (CPF) and modified CPF (MCPF) methods.⁸ The dipole moment of the ground state of CaOH was measured experimentally⁹ two years later. The geometries and bending potentials of BeOH and MgOH were also studied using fourth-order Møller–Plesset perturbation theory by Palke and Kirtman.¹ Ortiz studied the ground and excited states of CaL (L=CH₃, NH₂, OH, and F) by means of electron propagator calculations.¹⁰ Semiempirical models, based on the ionic character of the bonding between the metal (except Be)

and oxygen, were also proposed^{11–14} to calculate the binding energies, excitation energies, and dipole moments of these molecules. In the simple ionic model, the metal gives up one *s* electron to form the ligand OH[−] and the two parts are held together electrostatically. The low-lying electronic states are formed by promoting the unpaired electron from the *ns* orbital of the metal to the *np(n−1)d* and the $(n+1)s$ orbitals. The models were based on the classic electrostatic interaction plus the polarization of M⁺ and L[−]. Furthermore the excited states were treated in a fashion closely related to ligand field theory. The predictions compared well to experimental and *ab initio* data after the polarization effect on the heavy metals was included. With the development of laser spectroscopy, important physical quantities such as permanent electric dipole moments⁹ and the Renner–Teller and Fermi resonance parameters have been accurately measured^{15,16,17} in addition to geometries and frequencies.

In our recent CI studies of the energy hypersurface of CaOH, we have found a second minimum corresponding to HCaO.¹⁸ The new structure is linear with equilibrium H–Ca and Ca–O bond lengths and stretching frequencies of 2.021 Å, 1288 cm^{−1}, and 2.002 Å, 515 cm^{−1}, respectively, at the CISD level. The H–Ca bond is comparable with that of CaH (2.0025 Å and 1298 cm^{−1}, experimental values¹⁹) and the Ca–O bond is slightly weaker than that of CaOH (1.975 Å, 617 cm^{−1}, experimental values¹⁵). The finding of this new structure motivated us to explore the possibility of HBeO and HMgO and to try to understand the bonding of these new structures. Thus extensive *ab initio* CASSCF calculations for HMO (M=Be, Mg, and Ca) were carried out for the lowest $2\Sigma^+$ state, which is the ground state of MOH.

II. METHODS

In this study, the complete-active-space-self-consistent-field (CASSCF) method was chosen because the availability of CASSCF analytical gradients makes the full geometry optimization feasible. Moreover, a multiconfiguration approach

TABLE I. The bond lengths r_e (in Å), frequencies ω_e (in cm^{-1}), and dipole moments μ (in D) of HMO and MOH at the CASSCF and SCF (in parentheses) levels.

	H-M		M-O		O-H		Bending ω_e	μ
	r_e	ω_e	r_e	ω_e	r_e	ω_e		
HBeO	1.324(1.324)	2258(2261)	1.425(1.405)	1120(1163)			579(583)	0.637
HMgO	1.723(1.692)	1592(1751)	1.851(1.823)	652(663)			197(227)	2.318
HCaO	2.102(2.072)	1210(1314)	2.043(2.027)	543(564)			163(156)	0.107
BeOH (bent) ^a			1.415(1.391)	1257(1327)	0.955(0.934)	3975(4280)	422(409)	1.260
BeOH (linear)			1.390(1.372)	1311(1367)	0.949(0.929)	4056(4346)	109i(222i)	1.802
MgOH			1.802(1.774)	676(688)	0.951(0.931)	4012(4311)	516(601)	1.754
CaOH			2.027(2.004)	597(620)	0.956(0.934)	3925(4240)	407(418)	0.605

^aThe CASSCF bending angle is 139° , compared with 147° at the CISD level (Ref. 2).

is required for the study of the isomerization of HMO/MOH, one of the objectives of our research. The CASSCF method can potentially perform better than the single reference CISD method. For example, in their benchmark study of the radical OH, Bauschlicher and Langhoff²⁰ found that CASSCF gives spectroscopic constants such as the equilibrium bond length, frequency, dipole moment, and dissociation energy closer to the full-CI result than the single reference CISD method, when oxygen virtual p orbitals with π symmetry are included in the active space.

In this study, in addition to the bonding and antibonding σ orbitals, the occupied and virtual orbitals pertaining to the O $2s$ electrons were also included resulting in six a_1 orbitals in the CASSCF active space. In addition, the occupied and virtual p orbitals of oxygen—two b_1 orbitals and two b_2 orbitals—are also included in the active space. The final active space is composed of 9 electrons and ten orbitals and can be denoted as (622). Although including the $(n-1)$ shell of metal atoms might lead to better quantitative results, it would be prohibitively expensive. We also carried out CISD calculations with a single reference for comparison. The GAMESS program²¹ was used for all the calculations in this paper.

The extensive basis sets used are the same as those in the Bauschlicher *et al.*² study of MOH. The Be ($11s5p2d/6s3p2d$) contracted basis set was formed from the $11s$ primitive set of van Duijneveldt²² to which five sets of p functions²³ and two sets of d functions²⁴ were added. The Mg ($12s9p5d/6s5p4d$) contracted basis set was extracted from McLean and Chandler's²⁵ modification of the original Huzinaga ($12s9p$) basis set,²⁶ to which five sets of d functions² were added. The s and p functions of the Ca ($15s13p7d2f/9s9p6d2f$) basis set start from the $14s9p$ basis set of Wachters²⁷ with the addition of his two diffuse, $4p$ -like functions, as well as two additional p functions and a diffuse s function. The exponents and contraction coefficients for the d and f polarization functions are from the literature.² The O basis set uses the ($11s6p$) primitive set of van Duijneveldt²² contracted to $[6s3p]$. This is supplemented with a diffuse set of p functions optimized for the negative ion, three sets of d functions and one set of f functions, resulting in ($11s7p3d1f/6s4p3d1f$). The H basis set is the ($6s$) set of van Duijneveldt²² contracted to $[3s]$ to

which two diffuse s functions and four sets of p functions are added and the p functions are further contracted,² resulting in ($8s4p/5s3p$).

III. SPECTROSCOPIC PARAMETERS AND ENERGETICS

The CASSCF optimized spectroscopic parameters—bond lengths, stretching and bending harmonic frequencies and dipole moments—of HBeO, HMgO, and HCaO are listed in Table I. All of these molecules favor the linear structure. In contrast with the hydroxides in which the central oxygen atom has lone pairs, the linearity is expected even if the bonds are covalent. The CASSCF spectroscopic parameters of MOH are listed in Table I for comparison. It can be seen that the M–O bond length of HMO is slightly longer than that of MOH, by amounts ranging from 0.01 \AA for BeOH to 0.05 \AA for MgOH. The M–O bond stretching frequency of HMO does not differ much from that of MOH except for $M=\text{Be}$ where the former is more than 100 cm^{-1} lower than the latter. The implication of this observation will be discussed in the next section.

The SCF (ROHF) results are also listed in Table I (in parentheses) for comparison. From Bauschlicher *et al.*'s study² of MOH, the difference between the SCF and CISD optimized M–O bond lengths (at a fixed O–H bond length of 0.947 \AA) are 0.001 \AA for Be and Mg and 0.018 \AA for Ca. The M–O stretching frequency also differs by only 7 cm^{-1} at most. Considering the numbers were obtained with a parabolic fit, the differences are trivial. Our CASSCF M–O stretching frequencies for both MOH and HMO show the same trend as they are only slightly smaller than our SCF frequencies whereas the CASSCF stretching frequencies for the covalent O–H bonds differ significantly from the SCF results. The CASSCF M–O bond lengths are longer by $\sim 0.02\text{--}0.03 \text{ \AA}$. Compared with the experimental results for CaOH,¹⁷ the CASSCF M–O is 0.05 \AA too long and the CASSCF M–O frequency is 19 cm^{-1} too low, whereas the O–H bond length is in excellent agreement with experiment (0.956 vs 0.954 \AA). In fact, the SCF Ca–O bond length is closer to experiment than the CASSCF one. This is because the $(n-1)$ shell of the metal atoms is not included in our correlation calculations. A previous study of the alkaline–

earth monohalides²⁸ has shown that the pair–pair terms, the double excitations where one electron is excited from an M^+ orbital and the other from an L^- orbital, are increasingly important when M and L are getting close and tend to make the bond short. All the CASSCF bending frequencies are smaller than the SCF ones except for HCaO which is consistent with our previous CISD results¹⁸ where the CISD bending frequency is larger than the SCF one. Overall, SCF is a good zero-order approximation. The SCF method was also found to be effective for understanding the polarization of Ca^+ in CaOH.⁸

Since there is no experimental O–H stretching frequency for OH^- as a ligand, an estimate based on the experimental frequencies of OH and OH^- is usually made for the processing of experimental data. The experimental bond lengths and harmonic frequencies are available^{19,29,30} for these two molecules (0.970 Å and 3739 cm^{-1} for OH, 0.964 Å and 3738 cm^{-1} for OH^-) and agree remarkably well with the theoretical predictions.³¹ In their theoretical study of the alkaline hydroxides, Bauschlicher *et al.*² used 3700 cm^{-1} as the O–H stretching frequency in MOH and the O–H bond length was fixed at 0.947 Å. Although our CASSCF calculated values of the O–H bond length are in agreement with their representative CISD value of 0.95 ± 0.01 Å, our stretching frequency of 4000 cm^{-1} is much larger than that of OH and OH^- . In order to determine the accuracy of our O–H frequency, we also calculated the frequency of free OH^- with the (322) active space in the CASSCF calculation. The harmonic frequency (3728 cm^{-1}) and the bond length (0.969 Å) are in excellent agreement with experiment. The increase of the O–H frequency from a free anion to a ligand in MOH is probably due to the polarization effect of M^+ on OH^- . We believe that the previous estimates of the O–H stretching frequency are too small, although this error will probably not have much effect on calculations of other stretching frequencies.

By the means of the MCPF method Bauschlicher *et al.*⁸ predicted the permanent dipole moment of CaOH to be 0.980 D with an estimated uncertainty of 0.2 D, which is smaller than the experimental value of 1.465(61) D obtained from a supersonic molecular beam optical Stark effect study.⁹ Our CASSCF result of 0.605 D is smaller than the Bauschlicher *et al.* MCPF value but better than the CISD result⁸ of 0.449 D. Therefore the CASSCF dipole moments can only be used for qualitative comparison. The CASSCF dipole moment of MgOH (1.75 D) is larger than that of CaOH, and larger than a semiempirical prediction¹⁴ of 1.2 D. (The same study also predicted that CaOH and MgOH have the same dipole moment. It would be reasonable to expect MgOH to have a larger dipole moment because Mg^+ is smaller than Ca^+ and less polarizable. The dipole moments of HMO reach a maximum at $M=Mg$. This will be discussed in the next section.

Table II lists the energy difference ΔE between HMO and MOH at various levels of theory. It can be seen that all energy differences are around 0.1 hartree, or more than 240 kJ/mol after correction for the zero-point energy. This large energy difference may explain why no experimental observation of HMO has been reported. The situation is quite

TABLE II. The energy differences ΔE (in hartree) between HMO and MOH ($M=Be, Mg, \text{ and } Ca$) at various theoretical levels. The energy differences with zero-point energy correction (in kJ/mol) are given in parentheses.

	$\Delta E(\text{SCF})$	$\Delta E(\text{CASSCF})$	$\Delta E(\text{CISD})$
HBeOH/BeOH	0.086 85 (220)	0.107 89 (278)	0.100 80
HMgO/MgOH	0.103 36 (251)	0.099 98 (244)	0.117 75
HCaO/CaOH	0.094 89 (229)	0.113 33 (278)	0.102 54

different for the Group III (IUPAC XIII) elements. For the latter, HBO is more stable than BOH, whereas AlOH is more stable than HAIO.³²

IV. DISCUSSION

The focus of past theoretical studies of alkaline earth hydroxides has been on their similarity with the alkali hydroxides as both of them are ionic compounds. The possible existence of HMO makes it desirable to compare with group III elements, which have occupied p orbitals and can be trivalent when the s and p orbitals are hybridized, or monovalent when only a p orbital is used for bonding. For example, the Lewis structures of HBO and BOH can be easily drawn. In the recent *ab initio* studies^{32,33} of the isomerization of HBO/BOH and HAIO/AlOH, it has been noticed that monovalent species become more stable when moving down the group III elements. This has been attributed to the lower efficiency of sp hybridization due to the presence of both s and p core orbitals and used to explain why HBO is more stable than BOH whereas AlOH is more stable than HAIO.

Group II elements have empty valence p orbitals and therefore sp hybridization is even less efficient than for the group III elements. Any possible bivalency of these elements can only be understood with at least one ionic bond (except, perhaps, Be which does not have a core p shell) because the valence p orbital will be too diffuse to hybridize with the valence s orbital. Since the SCF wave function is a good zeroth-order approximation for describing HMO/MOH, a generalized bond order analysis based on it, as proposed by Mayer,³⁴ will be used to assist the analysis of the bonding. This bond-order analysis method can be used to indicate the degree of ionic character of a bond, e.g., the bond order for a complete ionic bond will be zero whereas the bond order for a nonpolarized covalent single bond will be 1. Since H is much lighter than all the other elements involved, the H– M and M –O stretching frequencies will be used for comparison of the bond strengths of these two bonds.

In order to understand the bonding of the HMO molecules, it is helpful to compare the H– M and M –O bonds in MH and MO in addition to those in MOH. Table III lists the CASSCF bond lengths and stretching frequencies and the SCF bond orders in the $^+\Sigma$ states of HMO, MOH, MH, MH^+ , MO, and MO^+ . The cations are included because of the possibility of ionic bonds.

TABLE III. The CASSCF bond lengths (in Å), frequencies (in cm^{-1}), and SCF bond orders of HMO, MOH, MH, MH^+ , MO, and MO^+ in their lowest Σ^+ states.

	H–M bond				M–O bond		
	r_e	ω_e	Bond order		r_e	ω_e	Bond order
HBeO	1.324	2258	0.94		1.425	1120	0.97
BeOH ^a					1.390	1311	1.26
BeH	1.358	2016	1.02	BeO	1.335	1534	2.13
BeH ⁺	1.344	2073	1.01	BeO ⁺	1.349	1434	1.43
HMgO	1.723	1592	0.91		1.851	652	0.13
MgOH					1.802	676	<0.05
MgH	1.788	1461	0.84	MgO	1.788	664	1.12
MgH ⁺	1.695	1644	0.86	MgO ⁺	1.734	699	0.29
HCaO	2.102	1210	0.50		2.043	543	0.48
CaOH					2.027	597	0.47
CaH	2.073	1531	0.61	CaO	1.852	732	1.48
CaH ⁺	1.963	1393	0.81	CaO ⁺	1.927	670	0.68

^aLinear structure.

A. HBeO

The relationship between Be and the rest of the group II elements is similar to that of B to the rest of the group III elements. Since there are no inner p orbitals, the empty p orbitals of Be are relatively compact and can be used for hybrid orbitals to form covalent bonds. For instance, both BeOH and BOH are bent whereas the hydroxides of the other elements in both groups are linear, the Be_4 cluster is strongly bonded due to the efficiency of sp hybridization, whereas Mg_4 and Ca_4 are only weakly bonded at the correlated level (CISD).²⁴

The calculations for the $2\Sigma^+$ state of HBeO show that Be forms two sp hybrid orbitals, one of which is used to form the covalent bond (doubly occupied molecular orbital) with H $1s$ and the other to form a covalent bond (singly occupied molecular orbital) with the empty O $2p_z$. The two doubly occupied π orbitals (O p_x and p_y) overlap with the empty Be p_x and p_y and form two weak π bonds to give a Be–O bond order of about 1 rather than the 0.5 expected from the Lewis structure. This bond order is also the same as the Be–O bond in BeOH, which also indicates that the Be–O bond in HBeO is covalent, similar to that in BeOH.

It is interesting to compare HBeO with BeH and BeO. In BeH, Be forms two sp hybrid orbitals, one of which forms a covalent bond with H. The other sp hybrid orbital is singly occupied, remains localized on Be and is slightly antibonding. When the unpaired electron is removed to form BeH^+ , the bonding is strengthened a little.

The bonding in BeO can be understood as a covalent bond between $\text{Be}^+(2s^1)$ and $\text{O}^-(p_x^2 p_y^2 p_z^1)$. The two doubly occupied π orbitals ($\text{O}^- p_x$ and p_y) overlap with the empty $\text{Be}^+ p_x$ and p_y to form two weak conjugate π bonds so that the overall bond order is 2. A similar conjugation effect also happens in HBO and makes the B–O bond length shorter than a normal B–O double bond.³² When one electron is removed from the σ bonding orbital, the bonding is weakened, as shown by the decrease of the frequency, the increase of the bond length and the decrease of the bond order by 0.5. Table I shows that the H–Be bond in HBeO is more similar

to that in BeH and BeH^+ than the Be–O bond is in HBeO to BeO and BeO^+ . The reason for this is that the sp hybrid orbitals used for bonding in HBeO are more diffuse than the Be $2s$ orbital used in BeO and BeO^+ for bonding and therefore the Be–O bond in HBeO is significantly weaker and longer. The Be–O bond order is smaller too as the longer bond length makes the conjugate π bonds weaker.

B. HMgO

In contrast to BeOH, MgOH has been recognized as being ionic due to its linear structure. The near-zero bond order of the Mg–O bond in MgOH is consistent with this argument. Similar to BeH and BeH^+ , the bonding of MgH and MgH^+ is still mainly covalent but more polarized, as indicated by a bond order somewhat smaller than 1.0. The bond length and frequency of H–Mg in HMgO lie between MgH and MgH^+ and closer to the latter. Similar to BeO, MgO can still be described as being covalently bonded between Mg^+ and O^- , but its bond order is smaller than that of BeO and close to that of a single bond (1.0) due to the lower efficiency of π conjugation because the Mg p orbitals are more diffuse. MgO^+ is more or less like Mg^{2+}O^- and ionic, as the small bond order and large SCF Mulliken charges of Mg(1.58) and O(–0.58) indicate, which also shows the tendency of Mg to form an ionic bond with oxygen. The Mg–O bond in HMgO has a very small bond order, suggesting that it is ionic, as in MgOH and MgO^+ , but only a little bit weaker. Therefore, the molecule looks like $(\text{HMg})^+\text{O}^-$. This viewpoint is also consistent with the large negative Mulliken charge on O(–0.75) compared to H(–0.33) and the much larger dipole moment of HMgO relative to HBeO.

C. HCaO

Since Ca is further down the Periodic Table, it has a lower ionization energy than Be and Mg, and therefore it has a greater tendency to form ionic bonds. The H–M bond in CaH and CaH^+ is much more ionic than its Mg counterparts, as indicated by the large Mulliken charges (–0.41 on H and

1.41 on Ca in CaH^+), as well as the smaller bond order. The H–Ca bond in HCaO is weaker than that of CaH and CaH^+ , and more ionic than the H–Mg bond in HMgO, as shown by the large magnitude of the Mulliken charge on H (–0.69). The similarity of the Ca–O frequency and bond order in HCaO and to those of CaOH suggests that the Ca–O bond in HCaO is ionic. All the bond orders involving Ca, however, are larger than those of Mg, contrary to what one would expect for a more ionic bond. But this is consistent with the argument of the polarization of Ca^+ in CaOH, which was used to explain why the dipole moment of CaOH is extraordinarily small.⁸ We think that part of the reason is the compactness of the inner unoccupied $3d$ orbitals of Ca, which can hybridize efficiently with Ca $4s$ orbitals. One indication of this is the high Mulliken population of the d orbitals (0.2). The properties of Ca are often closer to those of Be than to Mg. For example, MgOH has the lowest dissociation energy among alkaline earth monohydroxides² and the dissociation energy of MgH is smaller than that of BeH and CaH.¹⁹ Overall, we suggest that HCaO is ionic and resembles $\text{H}^-\text{Ca}^{2+}\text{O}^-$.

V. CONCLUSIONS

The alkaline–earth metal monohydroxides MOH have long been considered to be simple ionic compounds, similar to the alkali metal monohydroxides. Our CASSCF calculations show that they also have isomers with the formula HMO. The $2\Sigma^+$ states of HBeO, HMgO, and HCaO have been studied at the CASSCF level with basis sets of at least triple-zeta plus double polarization quality. The correlation includes all the valence electrons, resulting in an active space denoted by (622). The optimized structures are all linear. The M–O bond distance in HMO is slightly longer than that in MOH with similar stretching frequencies. The H–M bond length in HMO is comparable with that in MH with similar stretching frequencies.

The existence of HMO for alkaline earth metals makes it interesting to compare with group III elements for which both HMO and MOH structures exist. Group III elements have both covalent and ionic characters and the bonding of HMO can be easily understood as being covalent (sp hybrids) with increasing ionic character and instability as the atomic number increases. That is MOH becomes progressively more stable than HMO as the atomic number increases. Since group II elements have empty p orbitals, the sp hybrids will be less efficient and the bonding of HMO for group II elements will be expected to be more ionic. The ionic character increases with atomic number; HBeO has two polarized covalent bonds formed from the sp hybrids of Be; HMgO has one covalent bond (between H and Mg) and one ionic bond (between Mg and O) and can be viewed as $(\text{HMg})^+\text{O}^-$, HCaO has two ionic bonds represented by $\text{H}^-\text{Ca}^{2+}\text{O}^-$. This point of view is supported by comparison with the bonding in MOH, MH, MH^+ , MO, and MO^+ . The larger ionic character also helps to explain the similar relative stability of HMO and MOH in contrast to the group III case. The increasing ease of removing two valence electrons

of group II elements stabilizes the ionic bonds between M and H, O, compensating for the decreasing efficiency of sp hybridization.

The geometries and spectroscopic parameters of MOH for the alkaline–earth elements have also been calculated for the purpose of comparison. It is worthwhile to note that the OH^- stretching frequency in MOH is much larger than in free OH^- , in contrast to the assumption in previous publications.

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