Ab Initio Study of the Strong Binding of BeO to Li, Be, and B Atoms in the Hyperstoichiometric LiOBe, BeOBe, and BeOB Molecules[†]

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The equilibrium geometries and fundamental vibrational frequencies of LiOBe, BeOBe, and BeOB have been calculated using MP2(full)/6-311+G* and QCISD/6-311+G* levels of theory. The linear LiOBe ($^2\Sigma^+$), BeOBe ($^1\Sigma g^+$), and BeOB ($^2\Sigma^+$) structures were found to be the most stable, with representative dissociation energies of LiOBe, 114 kcal/mol (into LiO + Be) and 116 kcal/mol (into BeO + Li); BeOBe, 100 kcal/mol (into BeO + Be); and BeOB, 59 kcal/mol (into BO + Be) and 168 kcal/mol (into BeO + B). The strong binding of BeO to Li, Be, and B is related to the nature of the bonding in BeO, in which the charge on O is significantly below −2. The bonding in BeO was further examined by comparing to the single Be−O bonds in BeOH and HBeOH. The bond in BeO was found to be only 0.06 Å shorter than the Be−O single bonds in HBeOH and BeOH and to have about the same dissociation energy as these single bonds, in agreement with our statement that BeO does not possess a conventional double bond.

I. Introduction

The formal −2 charge of the group VI atoms in AB diatomic molecules (AB, A = Be−Ba, B = O−Po) might lead one to conclude that these species should not be able to bond through the O to another atom because they have a full octet of valence electrons. However, Boldyrev, Shamovsky, and Schleyer have shown,[1] for example, that MgO is able to form a very stable linear Mg−O−Mg molecule, where the dissociation energy of the first Mg−O bond is comparable with the dissociation energy of the second. Castleman and co-workers[2−6] experimentally observed an unusually high intensity mass spectral peak for the Mg_2O^+ cation, in agreement with the theoretical prediction of exceptional stability of neutral Mg_2O^1 as well as Mg_2O^+ cation.[7]

The reason for the strong binding of MgO to the second Mg atom lies in the charge on the oxygen atom. It has been known for some time[8−10] that the oxygen charge in both the triplet and singlet states of MgO is close to −1 instead of −2. Hence, representations such as Mg=O are inappropriate. The singlet−triplet state splitting (0.326 eV in MgO[11]) is small because the covalent coupling of the second pair of "bonding" electrons is very weak. As a result, oxygen is able to form a second strong Mg−O bond in Mg−O−Mg.[1] We expect that all AB diatomics will be able to form an extra strong bond through the group VI atom to another electropositive atom X. In this article, we present our computational results which support such a bonding picture for BeO attached to Li, Be, and B atoms in LiOBe, BeOBe, and BeOB.

II. Computational Methods

The geometries of LiOBe, BeOBe, BeOB, LiO, BeO, and BO were optimized employing analytical gradients[12] with a polarized split-valence basis set (6-311+G*[13]) at the MP(full) and QCISD levels. Analytical second derivatives were used at the MP2(full) level; numerical second derivatives, at the QCISD level. The fundamental vibrational frequencies, normal coordinates, and zero-point energies (ZPE) were calculated by standard FG matrix methods. The QCISD/6-311+G* geometries were used to evaluate electron correlation in the frozen-

core approximation both by Møller−Plesset perturbation theory to full fourth order[14] and by the (U)QCISD(T) method[15] using 6-311+G(2df) basis sets. The UHF wave functions for open-shell systems were projected to pure spectroscopic states (PUHF, PMP2, PMP3, and PMP4[16]). All calculations were carried out with the Gaussian 92/DFT program.[17]

III. Results

LiOBe. We first studied two linear structures: LiOBe ($^2\Sigma^+$) and LiBeO ($^2\Sigma^+$) whose optimal geometries, vibrational frequencies, and relative energies are summarized in Table 1.

TABLE 1: Calculated Molecular Properties of the LiOBe Molecule

LiOBe ($C_{\infty v}$, $^2\Sigma^+$) $1\sigma^2 2\sigma^2 1\pi^4 3\sigma^1$	LiBeO ($C_{\infty v}$, $^2\Sigma^+$) $1\sigma^2 2\sigma^2 1\pi^4 3\sigma^1$
MP2(full)/6-311+G*	
$R(\text{Li}-\text{O}) = 1.664$ Å	$R(\text{Li}-\text{Be}) = 2.577$ Å
$R(\text{Be}-\text{O}) = 1.397$ Å	$R(\text{Be}-\text{O}) = 1.343$ Å
$E_{\text{mp2(full)}} = -97.321\ 74$ au	$E_{\text{mp2(full)}} = -97.225\ 79$ au
$\langle S^2 \rangle = 0.775^a$	$\langle S^2 \rangle = 0.825^a$
$\nu_1(\sigma) = 1333$ cm^{-1}	$\nu_1(\sigma) = 1697$ cm^{-1}
$\nu_2(\sigma) = 788$ cm^{-1}	$\nu_2(\sigma) = 312$ cm^{-1}
$\nu_3(\pi) = 69$ cm^{-1}	$\nu_3(\pi) = 80i$ cm^{-1}
ZPE = 3.22 kcal/mol	ZPE = 2.87 kcal/mol
$\Delta E_{\text{mp2(full)}} = 0.0$ kcal/mol	$\Delta E_{\text{mp2(full)}} = 60.2$ kcal/mol
QCISD/6-311+G*	
$R(\text{Li}-\text{O}) = 1.662$ Å	
$R(\text{Be}-\text{O}) = 1.392$ Å	
$E_{\text{qcisd}} = -97.273\ 39$ au	
$\langle S^2 \rangle = 0.775^a$	
$\nu_1(\sigma) = 1350$ cm^{-1}	
$\nu_2(\sigma) = 795$ cm^{-1}	
$\nu_3(\pi) = 76$ cm^{-1}	
ZPE = 3.28 kcal/mol	
QCISD(T)/6-311+G(2df)	
$E_{\text{qcisd(t)}} = -97.331\ 72$	
$E_{\text{qcisd}} = -97.320\ 60$	
$E_{\text{pmp4}} = -97.335\ 14$	
$E_{\text{pmp3}}\ -97.314\ 12$	
$E_{\text{pmp2}} = -97.322\ 30$	
$\langle S^2 \rangle = 0.755^a$	

a In all cases reported in these tables deviation from the anticipated $S(S + 1) = 0.75$ reflects the spin contamination presented in the UHF reference wave functions and is not a physical spin−orbit coupling effect.

TABLE 2: Calculated Molecular Properties of the BeOBe Molecule

BeOBe ($D_{\infty h}$, $^1\Sigma_g^+$) $1\sigma_g^2 1\sigma_u^2 1\pi_u^4 2\sigma_g^2$	BeOBe ($D_{\infty h}$, $^3\Sigma_u^+$) $1\sigma_g^2 1\sigma_u^2 1\pi_u^4 2\sigma_g^1 2\sigma_u^1$	Be$_2$O (C_{2v}, $^1A_1$) $1a_1^2 1b_2^2 2a_1^2 1b_1^2 3a_1^2$
	MP2(full)/6-311+G*	
R(Be$-$O) = 1.428 Å $E_{mp2(full)}$ = 104.475 81 au	R(Be$-$O) = 1.420 Å $E_{mp2(full)}$ = $-$104.503 46 au $\langle S^2 \rangle$ = 2.004	R(Be$-$Be) = 2.026 Å R(Be$-$O) = 1.439 Å $E_{mp2(full)}$ = $-$104.479 68
$\nu_1(\sigma_g)$ = 974 cm^{-1} $\nu_2(\sigma_u)$ = 1452 cm^{-1} $\nu_3(\pi_u)$ = 112 cm^{-1} ZPE = 3.79 kcal/mol $\Delta E_{mp2(full)}$ = 17.3 kcal/mol	$\nu_1(\sigma_g)$ = 1007 cm^{-1} $\nu_2(\sigma_u)$ = 1393 cm^{-1} $\nu_3(\pi_u)$ = 91 cm^{-1} ZPE = 3.69 kcal/mol $\Delta E_{mp2(full)}$ = 0.0 kcal/mol	$\nu_1(a_1)$ = 1170 cm^{-1} $\nu_2(a_1)$ = 375 cm^{-1} $\nu_3(b_2)$ = 1087 cm^{-1} ZPE = 3.76 kcal/mol $\Delta E_{mp2(full)}$ = 14.9 kcal/mol
	QCISD/6-311+G*	
R(Be$-$O) = 1.417 Å E_{qcisd} = 104.450 12 au	R(Be$-$O) = 1.417 Å E_{qcisd} = $-$104.456 42 au $\langle S^2 \rangle$ = 2.004	
$\nu_1(\sigma_g)$ = 1018 cm^{-1} $\nu_2(\sigma_u)$ = 1436 cm^{-1} $\nu_3(\pi_u)$ = 43 cm^{-1} ZPE = 3.63 kcal/mol ΔE_{qcisd} = 4.0 kcal/mol	$\nu_1(\sigma_g)$ = 1017 cm^{-1} $\nu_2(\sigma_u)$ = 1404 cm^{-1} $\nu_3(\pi_u)$ = 84 cm^{-1} ZPE = 3.70 kcal/mol ΔE_{qcisd} = 0.0 kcal/mol	geometry optimization started from MP2(full)/ 6-311+G* geometry leads to the BeOBe ($D_{\infty h}$, $^1\Sigma_g^+$) structure
	QCISD(T)/6-311+G(2df)	
$E_{qcisd(t)}$ = $-$104.524 94 E_{qcisd} = $-$104.501 16 E_{pmp4} = $-$104.528 10 E_{pmp3} = $-$104.489 19 E_{pmp2} = $-$114.479 63	$E_{qcisd(t)}$ = $-$104.518 91 E_{qcisd} = $-$104.508 21 E_{pmp4} = $-$104.520 53 E_{pmp3} = $-$104.503 41 E_{pmp2} = $-$104.506 30	
ΔE_{pmp4} = 0.0 kcal/mol $\Delta E_{qcisd(t)}$ = 0.0 kcal/mol	ΔE_{pmp4} = 4.7 kcal/mol $\Delta E_{qcisd(t)}$ = 3.8 kcal/mol	

BeBeO ($C_{\infty v}$, $^1\Sigma^+$) $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4$	BeBeO ($C_{\infty v}$, $^3\Sigma^+$) $1\sigma^2 2\sigma^2 3\sigma^1 1\pi^4 4\sigma^1$	BeBeO ($C_{\infty v}$, $^3\Sigma^-$) $1\sigma^2 2\sigma^2 1\pi^4 2\pi^2$
	MP2(full)/6-311+G*	
R(Be$-$O) = 1.359 Å R(Be$-$Be) = 2.098 Å $E_{mp2(full)}$ = $-$104.384 03 au	R(Be$-$O) = 1.329 Å R(Be$-$Be) = 2.423 $E_{mp2(full)}$ = $-$104.312 33 au $\langle S^2 \rangle$ = 2.092	R(Be$-$Be) = 1.903 Å R(Be$-$O) = 1.438 Å $E_{mp2(full)}$ = $-$104.146 43 $\langle S^2 \rangle$ = 3.003
$\nu_1(\sigma)$ = 1430 cm^{-1} $\nu_2(\sigma)$ = 416 cm^{-1} $\nu_3(\pi)$ = 84 cm^{-1} ZPE = 2.88 kcal/mol $\Delta E_{mp2(full)}$ = 74.9 kcal/mol	$\Delta E_{mp2(full)}$ = 119.9 kcal/mol	$\Delta E_{mp2(full)}$ = 224.0 kcal/mol

LiOBe ($^2\Sigma^+$) was found to be the global minimum. The linear LiBeO ($^2\Sigma^+$) structure has two imaginary frequencies (of π symmetry) and is a saddle point for rotation of Li around BeO, about 60 kcal/mol (at MP2(full)/6-311+G*) less stable than the LiOBe structure; hence such internal rotation is not accessible at moderate temperatures.

The LiOBe molecule is found to be very stable wtih respect to dissociation: D_0 = 114 (118) kcal/mol for dissociation of LiOBe into LiO + Be and D_0 = 95 (90) kcal/mol for breaking into BeO + Li at QCISD(T)/6-311+G(2df) (data in parentheses are given for the PMP4/6-311+G(2df) level). The second dissociation energy could be questionable, because it is known that the $^1\Sigma^+$ state of BeO is not well represented by a single reference configuration.[18] To test this, we calculated this D_0 employing the procedure of Langhoff et al.[10] The triplet $^3\Pi_i$ BeO state is reasonably well represented by a single configuration, and therefore we calculated D_0 for LiOBe breaking into BeO ($^3\Pi_i$) + Li and then reduced the energy by the experimental $^3\Pi_i \leftarrow X^1\Sigma^+$ BeO energy separation (24.5 kcal/mol[19]). The resulting dissociation energy is 92 kcal/mol at the QCISD(T)/ 6-311+G(2df) level, which is very close to the directly calculated dissociation energy D_0 = 95 kcal/mol reported above. The dissociation energy of LiOBe into BeO + Li is comparable to the dissociation energy D_0 = 80.5 kcal/mol[20] of LiO, again supporting the assumption that the oxygen atom in BeO has a charge closer to -1 than to -2.

BeOBe. We considered six structures of Be$_2$O at the MP2-(full)/6-311+G* level: BeOBe ($D_{\infty h}$, $^1\Sigma g^+$), BeOBe ($D_{\infty h}$, $^3\Sigma_u^+$), Be$_2$O (C_{2v}, $^1A_1$), BeBeO ($C_{\infty v}$, $^1\Sigma^+$), BeBeO ($C_{\infty v}$, $^3\Sigma^+$), and BeBeO ($C_{\infty v}$, $^3\Sigma^-$). Their optimal geometries, vibrational frequencies, and relative energies are presented in Table 2. The first three structures were found to be substantially more stable than the others and were selected for further examination at the QCISD/6-311+G* level. While BeOBe ($D_{\infty h}$, $^1\Sigma g^+$), BeOBe ($D_{\infty h}$, $^3\Sigma_u^+$), and Be$_2$O (C_{2v}, $^1A_1$) were found to be stable minima at the MP2(full)/6-311+G* level, Be$_2$O (C_{2v}, $^1A_1$) was found to be unstable and to collapse to BeOBe ($D_{\infty h}$, $^1\Sigma g^+$) upon optimization at the QCISD/6-311+G* level (see Table 2).

At our highest level of theory, the linear singlet BeOBe structure is more stable (by 4 kcal/mol, Table 2) than the triplet and is similar to the structure found for the MgOMg molecule.[1] Since the singlet state of BeOBe requires a multiconfiguration representation, we cannot predict with certainty which of the two spin states is the more stable. We calculated the dissociation energy D_0 for the triplet state of BeOBe ($D_{\infty h}$, $^3\Sigma_u^+$) into BeO ($^3\Pi_i$) + Be (^1S) to be 117 kcal/mol at the QCISD(T)/6-311+G-(2df)+ZPE level. While the singlet state of BeOBe requires multiconfigurational descriptions, only small singlet$-$triplet splitting is expected in this molecule. Hence, the dissociation energy of the triplet state should be a reasonable estimate for the dissociation energy of Be$_2$O ($D_{\infty h}$, $^1\Sigma g^+$) as well. The D_0 of Be$_2$O ($D_{\infty h}$, $^1\Sigma g^+$) was also estimated using the total energies

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TABLE 3: Calculated Molecular Properties of the BeOB Molecule

BeOB ($C_{\infty v}$, $^2\Sigma^+$) $1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2 4\sigma^1$	BeOB TS (C_s, 2A′) $1a''^2 2a'^2 3a'^2 1a''^2 4a'^2 5a'^1$	BeBO ($C_{\infty v}$, $^2\Sigma^+$) $1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2 4\sigma^1$
	MP2(full)/6-311+G*	
R(Be−O) = 1.452 Å	R(Be−O) = 2.054 Å	R(Be−B) = 1.866 Å
R(B−O) = 1.293 Å	R(B−O) = 1.234 Å	R(B−O) = 1.217 Å
$E_{\text{mp2(full)}}$ = −114.548 50 au	R(Be−B) = 1.815 Å	$E_{\text{mp2(full)}}$ = −114.553 62 au
$\langle S^2 \rangle$ = 0.751	$E_{\text{mp2(full)}}$ = −114.518 02 au	$\langle S^2 \rangle$ = 0.752
$\nu_1(\sigma)$ = 1522 cm^{-1}	$\langle S^2 \rangle$ = 0.781	$\nu_1(\sigma)$ = 1913 cm^{-1}
$\nu_2(\sigma)$ = 991 cm^{-1}	$\nu_1(a')$ = 1823 cm^{-1}	$\nu_2(\sigma)$ = 670 cm^{-1}
$\nu_3(\pi)$ = 60 cm^{-1}	$\nu_2(a')$ = 814 cm^{-1}	$\nu_3(\pi)$ = 287 cm^{-1}
ZPE = 3.76 kcal/mol	$\nu_3(a')$ = 282i cm^{-1}	ZPE = 4.51 kcal/mol
$\Delta E_{\text{mp2(full)}}$ = 3.2 kcal/mol	ZPE = 3.77 kcal/mol	$\Delta E_{\text{mp2(full)}}$ = 0.0 kcal/mol
	$\Delta E_{\text{mp2(full)}}$ = 22.3 kcal/mol	
	QCISD/6-311+G*	
R(Be−O) = 1.446 Å		R(Be−B) = 1.872 Å
R(B−O) = 1.297 Å		R(B−O) = 1.213 Å
E_{qcisd} = −114.512 28 au		E_{qcisd} = −114.511 17 au
$\langle S^2 \rangle$ = 0.751		$\langle S^2 \rangle$ = 0.752
$\nu_1(\sigma)$ = 1512 cm^{-1}		$\nu_1(\sigma)$ = 1937 cm^{-1}
$\nu_2(\sigma)$ = 1005 cm^{-1}		$\nu_2(\sigma)$ = 663 cm^{-1}
$\nu_3(\pi)$ = 51 cm^{-1}		$\nu_3(\pi)$ 288 cm^{-1}
ZPE = 3.74 kcal/mol		ZPE = 4.54 kcal/mol
ΔE_{qcisd} = 0.0 kcal/mol		ΔE_{qcisd} = 0.7 kcal/mol
	QCISD(T)/6-311+G(2df)	
$E_{\text{qcisd(t)}}$ = 114.580 15		$E_{\text{qcisd(t)}}$ = −114.574 31
E_{qcisd} = −114.566 93		E_{qcisd} = −114.559 19
E_{pmp4} = −114.579 80		E_{pmp4} = −114.578 31
E_{pmp3} = −114.559 61		E_{pmp3} = −114.549 07
E_{pmp2} = −114.553 66		E_{pmp2} = −114.552 43
$\langle S^2 \rangle$ = 0.751		$\langle S^2 \rangle$ = 0.752
ΔE_{pmp4} = 0.0 kcal/mol		ΔE_{pmp4} = 0.9 kcal/mol
$\Delta E_{\text{qcisd(t)}}$ = 0.0 kcal/mol		$\Delta E_{\text{qcisd(t)}}$ = 3.7 kcal/mol

of BeO ($^1\Sigma^+$), obtained as a sum of total energy of BeO ($^3\Pi_i$) and the experimental energy separation $^3\Pi_i \leftarrow {}^1\Sigma^+$ (24.5 kcal/mol[19]), and the calculated total energies of BeOBe ($D_{\infty h}$, $^1\Sigma_g^+$) and of BeO ($^1\Sigma^+$) + Be (^{1}S). The D_0 of Be$_2$O ($^1\Sigma_g^+$), 97 and 100 kcal/mol, respectively, obtained in these ways are very close, so we suggest that D_0(BeO−Be) for BeO ($^1\Sigma^+$) + Be is 100 ± 10 kcal/mol. This value is very close to the experimental dissociation energy D_0 = 106 kcal/mol[20] of BeO ($^1\Sigma^+$), again consistent with the expectation based on the assumption of the oxygen atomic charge being about −1 in BeO.

BeOB. Two linear BeOB ($^2\Sigma^+$) and BeBO ($^2\Sigma^+$) structures were found to be minima (see Table 3). The relative energies of these two structures are very sensitive to the basis sets and theoretical methods used. However, at our highest theoretical level (QCISD(T)/6-311+G(2df)), the BeOB ($^2\Sigma^+$) structure is the global minimum and the BeBO ($^2\Sigma^+$) structure is a local minimum. The energy difference between these two structures is about 4 kcal/mol (Table 3). The saddle point structure (C_s, 2A′) on the intramolecular rearrangement of BeOB into BeBO is 23 kcal/mol (at MP2(full)/6-311+G* level) above the former, which makes this rearrangement difficult at moderate temperature.

Both isomers are very stable toward dissociation. The two lowest dissociation pathways for BeOB ($^2\Sigma^+$) into BeO ($^1\Sigma^+$) + B (^{2}P) and into BO ($^2\Sigma^+$) + Be (^{1}S) have been examined. The dissociation energy for the first channel was computed employing the procedure of Langhoff et al.[10] as well as by direct calculation of the reactants and products. In the former approach, the total energy of BeO ($^1\Sigma^+$) was calculated as described above for the dissociation energy of LiBeO and BeOBe. The resulting D_0 is 144 kcal/mol at the QCISD(T)/6-311+G(2df)+ZPE level. In comparison, the difference between the total energies of BeOB ($^2\Sigma^+$) and the sum of BeO ($^1\Sigma^+$) and B (^{2}P) energies gives 147 kcal/mol at the same level. Again

agreement between these two methods is excellent. The energy for the BO ($^2\Sigma^+$) + Be (^{1}S) pathway, 59 kcal/mol (at the QCISD(T)/6-311+G(2df)+ZPE level), is substantially less than that for the B (^{2}P) + BeO ($^1\Sigma^+$) channel. Again the calculated dissociation energy of BeOB into BeO + B (D_0 = 147 kcal/mol) may be compared with the dissociation energy of the BO molecule, D_0 = 191 kcal/mol.[20]

IV. Comparing the BeO "Double" Bond with BeO Single Bonds

It is known that a double bond is usually shorter that the corresponding single bond by ca. 0.2 Å (R(C=C) = 1.337 Å in C$_2$H$_4$ vs R(C−C) = 1.536 Å in C$_2$H$_6$)[21] and is considerably stronger (D(C=C) = 167.4 kcal/mol in C$_2$H$_4$ vs D(C−C) = 83.9 kcal/mol in C$_2$H$_6$).[21] Let us compare the energy and the bond length of the "double" Be=O bond in BeO with the single Be−O bonds in BeOH and HBeOH. Results of our calculations for BeOH, HBeO, and HBeOH are presented in Tables 4 and 5. While HBeO is a true minimum on the potential energy surface, this isomer is substantially higher in energy (by 63.6 kcal/mol at QCISD(T)/6-311++G(2df,2pd)) than the global minimum structure BeOH.

At our highest theoretical level (QCISD(T)/6-311++G**), the bond length in BeO (1.36 Å (experimental value is 1.3309 Å)[20] is only 0.06 Å shorter than the Be−O bonds in BeOH and the HBeOH. The dissociation energy of BeO (100 kcal/mol; this value and others are at the QCISD(T)/6-311++G-(2df,2pd) level) is very close to the dissociation energy of the Be−O bond in BeOH (104 kcal/mol), but it is substantially lower than the dissociation energy of the Be−O bond in HBeOH (149 kcal/mol, see Table 5). However, to correctly compare these energies, we need to take into account the so-called promotion energy (the excitation energy of the Be atom from the ^{1}S to the ^{3}P state, which is 62.8 kcal/mol at QCISD(T)/6-

TABLE 4: Calculated Molecular Properties of HBeO, BeOH, and HBeOH

BeOH (C_s, $^2A'$) $1a''^2 2a'^2 3a'^2 1a''^2 4a'^1$	HBeO ($C_{\infty v}$, $^2\Sigma^+$) $1\sigma^2 2\sigma^2 1\pi^4 3\sigma^1$	HBeOH (C_s, $^1A'$) $1a''^2 2a'^2 3a'^2 1a''^2 4a'^2$
	MP2(full)/6-311++G**	
$R(\text{Be–O}) = 1.416$ Å	$R(\text{Be–O}) = 1.421$ Å	$R(\text{Be–O}) = 1.419$ Å
$R(\text{O–H}) = 0.953$ Å	$R(\text{H–Be}) = 1.320$ Å	$R(\text{H–Be}) = 1.326$ Å
$\angle$BeOH $= 135.1°$	$\angle$HBeO $= 180.0°$	$R(\text{O–H}) = 0.953$ Å
		$\angle$BeOH $= 133.9°$
		$\angle$HBeO $= 176.6°$
$E_{\text{mp2(full)}} = -90.391\ 76$ au	$E_{\text{mp2(full)}} = -90.279\ 69$ au	$E_{\text{mp2(full)}} = -91.032\ 20$ au
$\langle S^2 \rangle = 0.752$	$\langle S^2 \rangle = 0.759$	$\nu_1(a') = 4046$ cm^{-1}
$\nu_1(a') = 4037$ cm^{-1}	$\nu_1(\sigma) = 2232$ cm^{-1}	$\nu_2(a') = 2205$ cm^{-1}
$\nu_2(a') = 1230$ cm^{-1}	$\nu_2(\sigma) = 1108$ cm^{-1}	$\nu_3(a') = 1183$ cm^{-1}
$\nu_3(a') = 348$ cm^{-1}	$\nu_3(\pi) = 559$ cm^{-1}	$\nu_4(a') = 587$ cm^{-1}
		$\nu_5(a') = 388$ cm^{-1}
		$\nu_6(a'') = 583$ cm^{-1}
ZPE = 8.03 kcal/mol	ZPE = 6.37 kcal/mol	ZPE = 12.86 kcal/mol
$\Delta E_{\text{mp2(full)}} = 0.0$ kcal/mol	$\Delta E_{\text{mp2(full)}} = 70.3$ kcal/mol	
	QCISD/6-311++G**	
$R(\text{Be–O}) = 1.416$ Å	$R(\text{Be–O}) = 1.423$ Å	$R(\text{Be–O}) = 1.418$ Å
$R(\text{O–H}) = 0.952$ Å	$R(\text{H–Be}) = 1.324$ Å	$R(\text{H–Be}) = 1.329$ Å
$\angle$BeOH $= 133.5°$	$\angle$HBeO $= 180.0°$	$R(\text{O–H}) = 0.951$ Å
		$\angle$BeOH $= 133.1°$
		$\angle$HBeO $= 176.6°$
$E_{\text{qcisd}} = -90.362\ 26$ au	$E_{\text{qcisd}} = -90.265\ 32$ au	$E_{\text{qcisd}} = -91.009\ 20$ au
$\langle S^2 \rangle = 0.751$	$\langle S^2 \rangle = 0.759$	$\nu_1(a') = 4058$ cm^{-1}
$\nu_1(a') = 4043$ cm^{-1}	$\nu_1(\sigma) = 2197$ cm^{-1}	$\nu_2(a') = 2186$ cm^{-1}
$\nu_2(a') = 1232$ cm^{-1}	$\nu_2(\sigma) = 1108$ cm^{-1}	$\nu_3(a') = 1186$ cm^{-1}
$\nu_3(a') = 389$ cm^{-1}	$\nu_3(\pi) = 537$ cm^{-1}	$\nu_4(a') = 585$ cm^{-1}
		$\nu_5(a') = 413$ cm^{-1}
		$\nu_6(a'') = 570$ cm^{-1}
ZPE = 8.10 kcal/mol	ZPE = 6.26 kcal/mol	ZPE = 12.87 kcal/mol
$\Delta E_{\text{qcisd}} = 0.0$ kcal/mol	$\Delta E_{\text{qcisd}} = 60.8$ kcal/mol	

TABLE 5: Calculated Dissociation Energies of BeOH, HBeO, and HBeOH

reaction	ΔE (kcal/mol)^a
BeO ($^1\Sigma^+$) $\rightarrow$ Be (^{1}S) + O (^{3}P)^b	99.9
BeOH (^{2}A′) $\rightarrow$ Be (^{1}S) + OH ($^2\Pi$)^b	103.9
HBeOH (^{1}A′) $\rightarrow$ HBe ($^2\Sigma^+$) + OH ($^2\Pi$)	148.7
BeO ($^1\Sigma^+$) $\rightarrow$ Be (^{3}P) + O (^{3}P)	162.7
BeOH (^{2}A′) $\rightarrow$ Be (^{3}P) + OH ($^2\Pi$)	166.7
HBeOH (^{1}A′) $\rightarrow$ HBe ($^2\Sigma^+$) + OH ($^2\Pi$)	148.7
BeOH (^{2}A′) $\rightarrow$ BeO (Σ^+) + H (^{2}S)	108.6
HBeO ($^2\Sigma^+$) $\rightarrow$ BeO ($^1\Sigma^+$) + H (^{2}S)	45.0
HBeOH (^{1}A′) $\rightarrow$ HBeO ($^2\Sigma^+$) + H (^{2}S)	157.4
HBeOH (^{1}A′) $\rightarrow$ BeOH (^{2}A′) + H (^{2}S)	93.8
HBeOH (^{1}A′) $\rightarrow$ BeO ($^1\Sigma^+$) + H$_2$ ($^1\Sigma^+$)	94.0
HBeOH (^{1}A′) $\rightarrow$ Be (^{1}S) + H$_2$O (^{1}A$_1$)^b	73.8

^{a} At the QCISD(T)/6-311++G(2df,2pd) level using QCISD/6-311++G** optimal geometries. ^{b} Thermochemically the most favorable channel for the dissociation of the molecule.

311++G(2df)), that the Be atom gains in both BeO $\rightarrow$ Be + O and BeOH $\rightarrow$ Be + OH, but does not gain in HBeOH $\rightarrow$ HBe + OH. Therefore, we need to compare the dissociation energies of BeO $\rightarrow$ Be (^{3}P) + O (163 kcal/mol) and BeOH $\rightarrow$ Be (^{3}P) + OH (167 kcal/mol). The trend is clear now; the strength of the "double" Be=O bond in BeO is about the same as the single Be–O bonds in both BeOH and HBeOH, and therefore the "second" bond is very weak.

The direct comparison of the bond length and bond energy of the "double" Be=O bond in BeO with normal single Be–O bonds thus demonstrates that BeO does not possess a conventional double bond, which is the reason that both the oxygen and beryllium (and other alkaline earth metals) atoms in BeO (and in MO, where M is an alkaline earth atom) can form strong bonds with other atoms. Table 5 demonstrates that BeO can form strong bonds with hydrogen, giving BeOH, HBeO, and HBeOH.

V. Conclusions

We found that the BeO molecule reacting with Li, Be, or B atoms can form very stable molecules LiOBe, BeOBe, and BeOB. The dissociation energies of LiOBe into BeO + Li, BeOBe into BeO + Be, and BeOB into BeO + B are comparable with the dissociation energies of LiO, BeO, and BO, respectively. That means that the oxidation number of the oxygen atom in ground-state BeO is not −2 but rather closer to −1 and that the oxygen in BeO is able to form a second very strong ionic bond with other electropositive atoms. Taking into account similar results for MgO,[1-7] we predict that all AB (A = Be–Ba, B = O–Po) molecules are able to form strongly bound ABX species with electropositive X atoms. Field et al.[22] have examined electronic states of CaO and CaX (X = halide) and have also emphasized the role played by configurations with Ca$^+$O$^-$ (or Ca$^+$X$^-$) character.

Linear LiOBe ($^2\Sigma^+$), BeOBe ($^1\Sigma$g$^+$), and BeOB ($^2\Sigma^+$) structures were found to the global minima. Only the BeBO ($^2\Sigma^+$) isomer was found to be close in energy to the global minimum BeOB ($^2\Sigma^+$). LiOBe and BeOB do not have low-lying LiBeO and BeBeO isomers. However, the BeOBe triplet state ($^2\Sigma$u$^+$) is only about 4 kcal/mol less stable than the most stable singlet state.

The calculated geometric parameters and vibrational frequencies of LiOBe, BeOBe, and BeOB may help experimental identification of these species in the gas phase or in matrix isolation.

The direct comparison of the bond length and bond energy of the "double" Be=O bond in BeO with normal single Be–O bonds in BeOH and HBeOH further demonstrates that BeO does not possess a conventional double bond, which is the reason that both the oxygen and beryllium (and other alkaline earth metals) atoms in BeO (and in MO, where M is an alkaline earth atom) form strong bonds with other atoms including atoms such as hydrogen, giving BeOH, HBeO, and HBeOH.

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