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Why Are $(MgO)_n$ Clusters and Crystalline MgO So Reactive?

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The electronic structures and chemical reactivities (toward H, Li, Li_2, and H_2) are examined for small $(MgO)_n$ clusters. It is postulated that decreases in the clusters' reactivity toward the above prototypical species as the cluster size (n) increases is related to the decrease in valence unsaturation that accompanies increases in n. Further, it is suggested that the known high reactivity of MgO powder and crystal is likely related to surface or defect sites that possess high levels of valence unsaturation.

Introduction

It is well-known in chemistry that pure and doped solid MgO are good catalysts of many chemical processes, while the valence isoelectronic LiF and NaCl crystals are not. Presumably, the catalytic action involves either or both of the constituent ionic centers coupling to the catalyzed species. Why does MgO work but LiF and NaCl do not?

If we view these crystals as formed from closed-shell ions (Mg^{2+} and O^{2-} for MgO and Li^+ and F^- for LiF), one would expect LiF and MgO to behave similarly because neither O^{2-} nor F^- would be able to form additional chemical bonds. Likewise, Mg^{+2} and Li^+ should not be highly active except toward species having lone-pair electrons. From these perspectives, the very different behavior in the chemical activity of MgO, LiF, and NaCl crystals is a puzzle.

It occurred to us, and we examine the possibility in this paper, that the more reactive nature of MgO may be related to the divalent nature of its constituents and the ability to form either Mg═O or Mg−O type bonding, the latter of which involves two centers ($Mg^\bullet$ and $O^\bullet$) with potential to covalently bond to catalyzed species. In an earlier series of articles,[1−6] it has been shown that diatomic MgO (and BeO) do not actually have M^{2+} and O^{2-} charges, but rather charges closer to M^+ and O^-. Analysis of the complete active space self-consistent field (CASSCF) and configuration interaction (CI) wave functions of BeO and MgO[1−3] has shown that their ground states are *not* well represented by the highly ionic configuration that describes Mg═O (or Mg^{2+} and O^{2-}). The proper wave functions have large contributions from electronic configurations which describe single bonded Mg−O with two unpaired electrons that are singlet coupled. As result, the oxygen does not have a full octet of valence electrons, is not fully closed-shell, and can form very stable bonds with other species by using its unpaired electron density. For example, we earlier have shown that the oxygen centers in BeO[5] and in MgO[6] may form additional very stable bonds with Be or Mg resulting BeOBe and MgOMg. The dissociation energy of the second Be−O and Mg−O bonds in the latter molecules are almost the same as the former.[5,6] Castleman and co-workers[7−11] experimentally observed an unusually high intensity mass spectral peak for Mg_2O^+ cations, in agreement with our theoretical prediction of the exceptional stability of neutral Mg_2O[6a] as well as the Mg_2O^+ cation.[6b] Moreover, Thompson and Andrews[12] observed BeOBe in solid argon as a result of the reaction of laser ablated Be atoms with O_2, and their computational results on a BeOBe molecule are similar to ours.

If the charge distribution in diatomic MgO is really closer to +1 and −1, it is interesting to inquire about what kind of charge distribution one can expect for various size $(MgO)_n$ clusters and for MgO crystal. Could it be that charges intermediate between +1 and −1 and +2 and −2 are responsible for the high catalytic activity of MgO crystal? In this work we address these questions on the basis of the results of our ab initio calculations on MgO, Mg_2O_2, and Mg_4O_4 (and LiF). We also examine the reactive encounters of these clusters with hydrogen and lithium atoms and molecules, which serve as prototypical monovalent reactant species of very different electron negativity.

The reactivity of MgO, Mg_2O_2, Mg_4O_4, and Mg_6O_6 clusters with H_2 as a model for adsorbtion of a hydrogen molecule onto a MgO (100) surface has been intensively studied previously.[13−16] It was found that hydrogen atoms favor coordination to oxygen atoms in Mg_4O_4.[13] When the number of atoms in the cluster $(MgO)_n$ increases, the enegy of "chemisorbtion" decreases.[16] Moreover, Li doping (substitution of Li for one Mg atom in the cluster) enhances the "catalitic" activity of MgO by creating O^- centers which strengthen the donor−acceptor interactions with H_2.[15,16] However, the reactivity of atomic hydrogen and lithium with these doped clusters have not yet been examined.

Computational Methods

The geometries of MgOH, HMgOH, LiFH, HLiFH, LiOMg, and LiOMgLi were optimized employing analytical gradients[17] with a polarized split-valence basis set (6-311++G**[18]) at the MP2(full) and QCISD levels. Analytical second derivatives were used at the MP2(full) level and 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[19] and by the (U)QCISD(T) method[20] using 6-311++G(2df,2pd) basis sets. The UHF wave functions for open-shell systems were projected to pure spectroscopic states (PUHF, PMP2, PMP3, and PMP4[21]).

The geometries of Mg_2O_2, Mg_2O_2H, and Mg_2O_2Li were optimized employing analytical gradients with a polarized split-valence basis set (6-311++G**) at the MP2(full) level. The MP2(full)/6-311++G** geometries were used to evaluate electron correlation in the MP4 and the (U)QCISD(T) method using 6-311++G(2df,2pd) basis sets.

Finally, the geometries of Mg_4O_4, Mg_4O_4H and Mg_4O_4Li were optimized employing analytical gradients with a polarized

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TABLE 1: Calculated Effective Atomic Charges in MgO, LiF, Na_2O, Mg_2O_2, and Mg_4O_4

method	E_{tot}, au	R_e, Å	μ, D	Q_O, Mulliken[a]	Q_O, dipole[b]	Q_O, CHelpG[c]	Q_O, MK[d]	Q_O, NBO[e]
MgO								
SCF/6−311+G*	−274.361 07	1.758	8.91	−0.661	−1.056	−1.058	−1.080	−1.410
MP2(full)/6-311+G*	−274.794 48	1.759	7.30	−0.559	−0.865	−0.871	−0.904	−1.402
CISD/6-311+G*	−274.609 87	1.787	7.02	−0.555	−0.817	−0.831	−0.858	−1.240
QCISD/6-311+G*	−274.643 56	1.810	6.08	−0.471	−0.700	−0.720	−0.755	−1.137
QCISD(T)/6-311+G(2df)	−274.700 56	1.778	8.91[f]	−0.641[f]	−0.751[f]	−0.768[f]	−0.800[f]	−1.208[f]
SCF/QZ2D2Dif	−274.381 75	1.724	9.12	−0.885	−1.101	−1.090	−1.116	−1.492
MP2(full)/QZ2D2Dif	−274.877 93	1.745	9.05	−0.877	−0.842	−0.841	−0.874	−1.404
QCISD/QZ2D2Dif	−274.700 60	1.774	8.93	−0.866	−0.756	−0.773	−0.801	−1.239
LiF								
SCF/6-311+G*	−106.975 11	1.576	6.65	−0.696	−0.879	−0.881	−0.879	−0.976
MP2(full)/6-311+G*	−107.205 15	1.595	6.53	−0.651	−0.853	−0.854	−0.851	−0.956
QCISD/6-311+G*	−107.203 64	1.595	6.74	−0.702	−0.854	−0.856	−0.853	−0.952
NaONa								
SCF/6-311+G*	−398.528 98	1.981	0	−1.481	−1.797	−1.759	−1.797	−1.955
MP2(full)/6-311+G*	−399.071 97	2.036	0	−1.476	−1.552	−1.492	−1.552	−1.850
QCISD/6-311+G*	−398.785 72	2.050	0	−1.475	−1.210	−1.172	−1.210	−1.529
Mg_2O_2 (D_{2h})								
SCF/6-311+G*	−548.990 15	1.857	0	−0.882	−1.503	−1.468	−1.503	−1.832
MP2(full)/6-311+G*	−549.778 93	1.910	0	−0.676	−1.325	−1.273	−1.325	−1.706
QCISD/6-311+G*[g]	−549.475 14	1.910[g]	0	−0.720	−1.340	−1.292	−1.340	−1.700
Mg_4O_4 (T_d)								
SCF/6-311+G*	−1 098.261 75	1.946	0	−0.849	−1.594	−1.552	−1.594	−1.846
MP2/6-311+G*[h]	−1 099.220 96	1.946[h]	0	−0.667	−1.510	−1.450	−1.510	−1.768

[a] Mulliken population analysis. [b] Dipole method that produces charges to fit the potential constrain to reproduce the dipole moment. [c] Fitting charges to the potential at points selected accorsding to the ChelpG scheme. [d] Fitting charges to the electrostatic potential at points selected according to the Merz−Singh−Kollman scheme. [e] Natural population analysis. [f] At QCISD/6-311+G(2df) level. [g] At MP2(full)/6-311+G* geometry. [h] At SCF/6-311+G* geometry.

split-valence basis set (6-311++G**[13]) at the MP2 level. All calculations were carried out with the Gaussian 94 program,[22] with valence, core, and core-valence electron correlation fully included at the MP2(full) level.

Quantum Chemical Charges in MgO, Mg_2O_2, and Mg_4O_4

A straightforward way to define atomic charges in MgO, $(MgO)_n$ clusters, and MgO crystal is to perform conventional quantum chemical calculations and to examine the various resonance structures in the resulting wave functions. However, because there is no quantum mechanical operator that rigorously defines atomic charges in molecules, there is a degree of arbitrariness in assigning electron densities to the atoms. Many different methods have been developed for the quantum chemical calculation of atomic charges. We explored five popular methods: Mulliken population analysis,[23] the Merz−Kollman method,[24,25] which produces partial charges fit to the electrostatic potential at points selected according to the Merz−Singh−Kollman scheme, the CHelpG method that produces charges fit to the electrostatic potential at points selected according to the CHelpG scheme,[26] the dipole method that produces charges to fit the potential constrained to reproduce the dipole moment[22] and the natural bond analysis[27] method of Weinhold. We believe it essential to examine various methods to make certain that any conclusions we draw do not depend on using any *particular* definition of atomic charges.

LiF, Na_2O, and MgO. Let us first consider the charges in diatomic MgO and compare them with charges in LiF and Na_2O which are expected to be close to +1 and −1 and +1, −2, +1, respectively. For MgO we used two conventional 6-311+G* and 6-311+G(2df) basis sets as well as the more extensive (12s6p/7s7p)Mg+ (11s7p/6s4p)O basis set developed by Ahlrichs at al.[28] augmented by 2d1f functions from the Gaussian-94 library and two sets of diffuse functions on every atom: $\alpha_{p8}(Mg) = 0.0179$, $\alpha_{p9}(Mg) = 0.00597$, $\alpha_{p5}(O) = 0.0494$, and $\alpha_{p6}(O) = 0.0165$ (QZ2D2Dif basis set). For the other molecules and clusters, only the 6-311+G* basis set was used because this basis was deemed to be reliable for MgO and remains computationally feasible for the larger systems we studied next. Four theoretical methods, SCF, MP2, CISD, and QCISD, have been used for MgO and (except CISD) for the other molecules.

Our results on MgO, LiF, and Na_2O are presented in Table 1 along with those for Mg_2O_2 and Mg_4O_4. As expected, the calculated effective atomic charges vary substantially from method to method and among basis sets. However, certain features clearly stand out independent of the method used to define the charges:

(1) As expected, the charge on F in LiF is very close to −1, ranging from ca. −0.7 in the Mulliken scheme to ca. −1.0 in the NBO scheme. Neither variation in basis set nor in ab initio method causes these charges to vary greatly. Even at the SCF level, the charges remain in these ranges.

(2) For Na_2O, the charge on O varies from ca. −1.2 to −2.0. As electron correlation is included (i.e., moving beyond the SCF treatment), the charges decrease somewhat in magnitude and then range from −1.2 to −1.5.

(3) For MgO, the O charges range from −0.5 to −1.4; for the best basis sets and highest levels of correlation, they do not exceed −1.2 in magnitude.

(4) The O in MgO is seen to have an atomic charge closer to that of F in LiF than to the O in Na_2O independent of the choice of basis set or method used to define atomic charges.

Mg_2O_2 and Mg_4O_4. We earlier proposed[6] that MgO might be viewed as a pseudobiradical because the pair of electrons involved in forming the second Mg−O bond is very weakly coupled (e.g., the singlet−triplet splitting between the two states of these weakly coupled electrons is only 0.326 eV[29]). Moreover, these electrons are localized mostly on opposite ends of the molecule. If this description of the bonding in MgO is correct, one might expect that MgO could form a cyclic Mg_2O_2 dimer in which the atomic charges would be close to +2 (Mg)

TABLE 2: Calculated Molecular Properties of HMgO, MgOH, and HMgOH

MgOH ($C_{\infty v}$, $^2\Sigma^+$)	HMgO ($C_{\infty v}$, $^2\Sigma^+$)	HMgOH (C_s, $^1A'$)	HMgOH ($C_{\infty v}$, $^1\Sigma^+$)
$1\sigma^2 2\sigma^2 1\pi^4 3\sigma^1$	$1\sigma^2 2\sigma^2 1\pi^4 3\sigma^1$	$1a'^2 2a'^2 3a'^2 1a''^2 4a'^2$	$1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2$
MP2(full)/6-311++G**	MP2(full)/6-311++G**		MP2(full)/6-311++G**
$R(Mg-O) = 1.805$ Å	$R(Mg-O) = 1.766$ Å		$R(Mg-O) = 1.796$ Å
$R(O-H) = 0.949$ Å	$R(H-Mg) = 2.727$ Å		$R(H-Mg) = 1.690$ Å
			$R(O-H) = 0.949$ Å
$E_{mp2(full)} = -275.477\,76$ au	$E_{mp2(full)} = -275.294\,98$ au		$E_{mp2(full)} = -276.079\,83$ au
$\langle S^2 \rangle = 0.751$	$\langle S^2 \rangle = 0.757$		$\nu_1(\sigma) = 4104$ cm^{-1}
$\nu_1(\sigma) = 4089$ cm^{-1}	$\nu_1(\sigma) = 985$ cm^{-1}		$\nu_2(\sigma) = 1691$ cm^{-1}
$\nu_2(\sigma) = 731$ cm^{-1}	$\nu_2(\sigma) = 240$ cm^{-1}		$\nu_3(\sigma) = 748$ cm^{-1}
$\nu_3(\pi) = 163$ cm^{-1}	$\nu_3(\pi) = 53$ cm^{-1}		$\nu_4(\pi) = 337$ cm^{-1}
			$\nu_5(\pi) = 147$ cm^{-1}
ZPE = 7.36 kcal/mol	ZPE = 1.90 kcal/mol		ZPE = 10.74 kcal/mol
$\Delta E_{mp2(full)} = 0.0$ kcal/mol	$\Delta E_{mp2(full)} = 114.7$ kcal/mol		
QCISD/6-311++G**	QCISD/6-311++G**	QCISD/6-311++G**	QCISD/6-311++G**
$R(Mg-O) = 1.801$ Å	$R(Mg-O) = 1.823$ Å	$R(Mg-O) = 1.793$ Å	$R(Mg-O) = 1.792$ Å
$R(O-H) = 0.948$ Å	$R(H-Mg) = 1.687$ Å	$R(H-Mg) = 1.695$ Å	$R(H-Mg) = 1.695$ Å
		$R(O-H) = 0.947$ Å	$R(O-H) = 0.947$ Å
		$\angle MgOH = 174.6°$	
		$\angle HMgO = 179.0°$	
$E_{qcisd} = -275.33418$ au	$E_{qcisd} = -275.22489$ au	$E_{qcisd} = -275.94357$ au	$E_{qcisd} = -275.94357$ au
$\langle S^2 \rangle = 0.751$	$\langle S^2 \rangle = 0.759$	$\nu_1(a') = 4120$ cm^{-1}	$\nu_1(\sigma) = 4122$ cm^{-1}
$\nu_1(\sigma) = 4100$ cm^{-1}	$\nu_1(\sigma) = 1672$ cm^{-1}	$\nu_2(a') = 1657$ cm^{-1}	$\nu_2(\sigma) = 1657$ cm^{-1}
$\nu_2(\sigma) = 736$ cm^{-1}	$\nu_2(\sigma) = 680$ cm^{-1}	$\nu_3(a') = 752$ cm^{-1}	$\nu_3(\sigma) = 753$ cm^{-1}
$\nu_3(\pi) = 104$ cm^{-1}	$\nu_3(\pi) = 304$ cm^{-1}	$\nu_4(a') = 322$ cm^{-1}	$\nu_4(\pi) = 321$ cm^{-1}
		$\nu_5(a') = 46$ cm^{-1}	$\nu_5(\pi) = 28i$ cm^{-1}
		$\nu_6(a'') = 322$ cm^{-1}	
ZPE = 7.21 kcal/mol	ZPE = 4.23 kcal/mol	ZPE = 10.32 kcal/mol	ZPE = 10.25 kcal/mol
$\Delta E_{qcisd} = 0.0$ kcal/mol	$\Delta E_{qcisd} = 68.6$ kcal/mol	$\Delta E_{qcisd} = 0.0$ kcal/mol	$\Delta E_{qcisd} = 0.000\,25$ kcal/mol
QCISD/6-311++G(2df,2pd)	QCISD/6-311++G(2df,2pd)	QCISD/6-311++G(2df,2pd)	
$E_{qcisd(t)} = -275.390\,93$	$E_{qcisd(t)} = -275.279\,76$	$E_{qcisd(t)} = -276.004\,66$	
$E_{qcisd} = -275.382\,03$	$E_{qcisd} = -275.273\,31$	$E_{qcisd} = -275.995\,99$	
$\Delta E_{qcisd(t)} = 0.0$ kcal/mol	$\Delta E_{qcisd(t)} = 69.8$ kcal/mol		

and −2 (O). We calculated the effective atomic charges in Mg_2O_2 using the same five methods detailed above for MgO and indeed found the charges in Mg_2O_2 to be ca. 0.5 unit larger than in MgO but only the NBO atomic charges are close to 2.

The data presented in Table 1 for Mg_2O_2 as well as that for Mg_4O_4 (T_d, $^1A_1$) clearly show the following:

(1) The O atoms in Mg_2O_2 are more negative (and thus the Mg atoms more positive) than in diatomic MgO, and are close to the O atom charges in Na_2O.

(2) The charges in Mg_4O_4 are not much different from those in Mg_2O_2.

(3) The inclusion of electron correlation tends to decrease the magnitude of the O atom charges in Mg_2O_2 and in Mg_4O_4 by ca. the same amount as in MgO and Na_2O.

The data overviewed above suggest that the partial atomic charges in $(MgO)_n$ differ significantly from ±2 and increase in magnitude as n increases. Although the findings discussed thus far may shed some light on what is different between MgO and LiF or NaCl, we do not feel that such equilibrium average charge densities provide a definitive resolution. For this reason, we decided to also examine differences in how Mg_nO_n and LiF behave when confronted with H_2, Li_2, H, or Li reactants. Our findings in this area are discussed in the following section.

Comparing Interactions of Mg_nO_n and LiF with H and Li Atoms and Diatomic Molecules

MgO + H or H_2. The results of our calculations for MgOH, HMgO, and HMgOH are presented in Table 2. While HMgO is a true minimum on the potential energy surface, this isomer is substantially higher in energy (by 69 kcal/mol at QCISD/6-311++G**) than the global minimum structure MgOH. This means that the hydrogen atom favors bonding to the oxygen end of MgO, which is by no means surprising. The dissociation energy D_e(MgOH into MgO + H) = 120 kcal/mol is more than twice that for the HMgO isomer D_e(HMgO into MgO + H) = 50 kcal/mol (all numbers at QCISD(T)/6-311++G(2df,2pd)).

At our highest theoretical level (QCISD/6-311++G**), R_e(Mg−O) = 1.801 Å in MgOH while R_e(Mg−O) = 1.823 Å in HMgO; both are very close to our computed bond length R_e(Mg−O) = 1.810 Å in diatomic MgO and somewhat longer than the experimental values 1.749 Å in MgO[30] and 1.76087 Å in MgOH.[31] The bond-length discrepancies are related to limitations in both basis sets and theoretical method. The use of larger basis sets somewhat improves the agreement with experiment: R(Mg−O) = 1.778 Å for MgO and R(Mg−O) = 1.781 Å for MgOH, both at QCISD/6-311++G(2df,2pd); however, we can not use such extended basis sets for the larger systems, so we restrict our analogies to data obtained with the more modest bases.

The dissociation energy of MgO (57 kcal/mol; this value and others are at the QCISD(T)/6-311++G(2df,2pd) level) is close to the dissociation energy of the Mg−O bond in MgOH (72 kcal/mol), but it is substantially lower than the dissociation energy of the Mg−O bond in HMgOH (112 kcal/mol). However, to correctly compare these energies, we need to take into account the so-called promotion energy (the excitation energy of the Mg atom from the ^1S to the ^3P state, which is 59.7 kcal/mol at QCISD(T)/6-311+G(2df)) that the Mg atom gains in both MgO → Mg + O and MgOH → Mg + OH, but does *not* gain in HMgOH → HMg + OH. Therefore, we need to compare the dissociation energy of HMgOH → HMg + OH (112 kcal/mol) with the dissociation energies of MgO → Mg (^3P) +O (117 kcal/mol) and MgOH → Mg (^3P) + OH (132 kcal/mol). The trend is clear; the strength of the "double" Mg═O bond in MgO is about the same as the single Mg−O bonds in both MgOH and HMgOH. Therefore we conclude that the "second" bond is very weak in MgO (i.e., 5−20 kcal/mol).

TABLE 3: Calculated Molecular Properties of LiMgO, MgOLi, and LiMgOLi

MgOLi ($C_{\infty v}$, $^2\Sigma^+$)	LiMgO ($C_{\infty v}$, $^2\Sigma^+$)	LiMgOLi ($Ck_{\infty v}$, $^1\Sigma^+$)
$1\sigma^2 2\sigma^2 1\pi^4 3\sigma^1$	$1\sigma^2 2\sigma^2 1\pi^4 3\sigma^1$	$1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2$
MP2(full)/6-311++G**	MP2(full)/6-311++G**	MP2(full)/6-311++G**
R(Mg−O) = 1.834 Å	R(Mg−O) = 1.856 Å	R(Mg−O) = 1.844 Å
R(O−Li) = 1.649 Å	R(Li−Mg) = 2.735 Å	R(Li−Mg) = 2.781 Å
		R(O−Li) = 1.644 Å
$E_{\text{mp2(full)}} = -282.384\,55$ au	$E_{\text{mp2(full)}} = -282.253\,43$ au	$E_{\text{mp2(full)}} = -289.873\,16$ au
$\langle S^2\rangle = 0.752$	$\langle S^2\rangle = 0.774$	$\nu_1(\sigma) = 961$ cm^{-1}
$\nu_1(\sigma) = 959$ cm^{-1}	$\nu_1(\sigma) = 643$ cm^{-1}	$\nu_2(\sigma) = 604$ cm^{-1}
$\nu_2(\sigma) = 601$ cm^{-1}	$\nu_2(\sigma) = 338$ cm^{-1}	$\nu_3(\sigma) = 319$ cm^{-1}
$\nu_3(\pi) = 92$ cm^{-1}	$\nu_3(\pi) = 105$ cm^{-1}	$\nu_4(\pi) = 125$ cm^{-1}
		$\nu_5(\pi) = 63$ cm^{-1}
ZPE = 2.49 kcal/mol	ZPE = 1.70 kcal/mol	ZPE = 3.23 kcal/mol
$\Delta E_{\text{mp2(full)}} = 0.0$ kcal/mol	$\Delta E_{\text{mp2(full)}} = 82.3$ kcal/mol	
QCISD/6-311++G**	QCISD/6-311++G**	QCISD/6-311+*G**
R(Mg−O) = 1.823 Å	R(Mg−O) = 1.841 Å	R(Mg−O) = 1.832 Å
R(O−Li) = 1.645 Å	R(Li−Mg) = 2.744 Å	R(Li−Mg) = 2.761 Å
		R(O−Li) = 1.641 Å
$E_{\text{qcisd}} = -282.221\,10$ au	$E_{\text{qcisd}} = -282.117\,53$ au	$\mathrm{E}_{\text{qcisd}} = -289.704\,53$ au
$\langle S^2\rangle = 0.752$	$\langle S^2\rangle = 0.774$	$\nu_1(\sigma) = 975$ cm^{-1}
$\nu_1(\sigma) = 971$ cm^{-1}	$\nu_1(\sigma) = 656$ cm^{-1}	$\nu_2(\sigma) = 616$ cm^{-1}
$\nu_2(\sigma) = 611$ cm^{-1}	$\nu_2(\sigma) = 326$ cm^{-1}	$\nu_3(\sigma) = 324$ cm^{-1}
$\nu_3(\pi) = 92$ cm^{-1}	$\nu_3(\pi) = 100$ cm^{-1}	$\nu_4(\pi) = 126$ cm^{-1}
		$\nu_5(\pi) = 64$ cm^{-1}
ZPE = 2.53 kcal/mol	ZPE = 1.70 kcal/mol	ZPE = 3.28 kcal/mol
$\Delta E_{\text{qcisd}} = 0.0$ kcal/mol	$\Delta E_{\text{qcisd}} = 65.0$ kcal/mol	
QCISD/6−311+G(2df)	QCISD/6−311+G(2df)	QCISD/6−311+G(2df)
$E_{\text{qcisd}(t)} = -282.280\,22$	$E_{\text{qcisd}(t)} = -282.169\,41$	$E_{\text{qcisd}(t)} = -289.765\,48$
$E_{\text{qcisd}} = -282.268\,45$	$E_{\text{qcisd}} = -282.161\,87$	$E_{\text{qcisd}} = -289.753\,10$
$\Delta E_{\text{qcisd}(t)} = 0.0$ kcal/mol	$\Delta E_{\text{qcisd}(t)} = 69.5$ kcal/mol	

The exothermicity or energy of “chemisorption” of H_2 on the MgO diatomic molecule with the formation of HMgOH is 82.7 kcal/mol. This is expected to exceed the chemisorption energy for H_2 molecules on other $(MgO)_n$ clusters and MgO crystal because, as was shown above, the magnesium and oxygen atoms have the lowest atomic charges in the diatomic molecule and therefore should have the highest reactivity. Anchel and Glendening[16] found in their ab initio calculations of the $H_2(MgO)_n$, $n = 1-4$ clusters that indeed the chemisorption energy of H_2 to $(MgO)_n$ is highest for $n = 1$. Their chemisorption energy of 88.5 kcal/mol is somewhat larger than ours because they used MP2 level theory and smaller basis sets than in this work.

If MgO has more of a single bond than a double bond, one can expect the energy of the reaction MgO + 2H → HMgOH to be nearly the sum of the energies of the reactions MgOH + H → HMgOH and HMgO + H → HMgOH. Indeed, the energy of the former reaction (191 kcal/mol) is close to the sum of energies (213 kcal/mol) of the last two reactions. According to these numbers, the effect due to partial binding of the second pair of electrons in MgO is ca. 22 kcal/mol which is similar to the 5−20 kcal/mol range noted earlier in this section.

In summary, the direct comparison of the bond length and bond energy of the “double” Mg═O or $Mg^{2+}O^{2-}$ bond in MgO with normal single Mg−O bonds demonstrates that MgO does not possess a conventional double bond and therefore can form strong bonds with hydrogen giving MgOH, HMgO, and HMgOH.

MgO + Li or Li_2. The results of our calculations for MgOLi, LiMgO, and LiMgOLi are presented in Table 3. LiOMg ($^2\Sigma^+$) was found to be the global minimum. The linear LiMgO ($^2\Sigma^+$) structure is a local minimum which is 70 kcal/mol (at QCISD(T)/6-311+G(2df)) less stable than LiOMg.

The LiOMg molecule is found to be very stable $D_e = 70$ kcal/mol for dissociation into LiO ($^2\Pi$) + Mg (^{1}S) and $D_e = 93$ kcal/mol for breaking into MgO ($^1\Sigma^+$) + Li (^{2}S) at QCISD(T)/6-311+G(2df). The latter dissociation energy is comparable to the dissociation energy $D_e = 80$ kcal/mol of LiO, and the dissociation energy into Mg + LiO is comparable to the dissociation energy $D_e = 57$ kcal/mol of MgO (both at QCISD(T)/6-311+G(2df)), again supporting the view that the oxygen atom in MgO has charge closer to −1 than to −2.

The energy of “chemisorption” of Li_2 on the MgO diatomic molecule to form LiMgOLi is 102 kcal/mol (QCISD(T)/6-311+G(2df)), which is higher than the corresponding energy $\Delta E = 82.7$ kcal/mol reported in the preceding section for H_2. This difference is due to the low dissociation energy of Li_2 (23.6 kcal/mol at QCISD(T)/6-311+G(2df)/24.6 kcal/mol experiment[30]) compared to H_2 (108.1 kcal/mol at QCISD(T)/6-311+G(2df)/109.5 kcal/mol experiment[30]). The dissociation energy $D_e = 99$ kcal/mol of LiOMgLi into LiMg ($^2\Sigma^+$) + LiO ($^2\Pi$) is somewhat lower than the dissociation energy $D_e = 112$ kcal/mol of HMgOH into HMg ($^2\Sigma^+$) + HO ($^2\Pi$) and both are somewhat lower than the dissociation energy $D_e = 117$ kcal/mol of MgO into Mg (^{3}P) + O (^{3}P).

From these data it is clear that the difference between the dissociation energy of MgO and LiOMgLi (or HMgOH) is too small to support the existence of a significant double bond in MgO. They are consistent with bonding in the range 5−20 kcal/mol.

LiF + H or H_2. Because LiF is valence isoelectronic to MgO, one might expect LiF to couple with hydrogen similar to MgO. We studied the full potential energy surface of LiFH and found two minima which are, in fact, only weak van der Waals complexes (see Table 4). The global minimum structure is the FH···Li (C_s, $^2A'$) structure with a strong F−H bond and a weak van der Waals bond between FH and Li. At our highest level of theory (QCISD(T)/6-311++ G(2df,2pd)) the binding energy of FH and Li is 5.8 kcal/mol.

The local minimum structure is FLi···H ($C_{\infty v}$, $^2\Sigma^+$) with a strong F−Li bond and weak van der Waals bond between FLi and H. This structure is 10.6 kcal/mol less stable than the global minimum.

From these data one can conclude that LiF can form only

TABLE 4: Calculated Molecular Properties of LiFH and LiFHH

HFLi (C_s, $^2A'$)	HLiF ($C_{\infty v}$, $^2\Sigma^+$)	LiFHH ($C_{\infty v}$, $^1\Sigma^+$)	LiHHF ($C_{\infty v}$, $^1\Sigma^+$)	HLiFH ($C_{\infty v}$, $^1\Sigma^+$)
$1a'^2 2a'^2 3a'^2 1a''^2 4a'^1$	$1\sigma^2 2\sigma^2 1\pi^4 3\sigma^1$	$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4$	$1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2$	$1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2$
MP2(full)/6-311++G**	MP2(full)/6-311++G**	MP2(full)/6-311++G**	MP2(full)/6-311++G**	MP2(full)/6-311++G**
R(Li−F) = 1.926 Å	R(Li−H) = 2.405 Å	R(Li−F) = 1.597 Å	R(Li−H) = 1.576 Å	R(Li−H) = 1.608 Å
R(F−H) = 0.928 Å	R(Li−F) = 1.596 Å	R(F−H) = 2.370 Å	R(H−H) = 1.394 Å	R(Li−F) = 1.909 Å
∠LiFH = 114.3°		R(H−H) = 0.743 Å	R(F−H) = 0.950	R(F−H) = 0.920
$E_{\text{mp2(full)}} = -107.75152$ au	$E_{\text{mp2(full)}} = -107.73856$ au	$E_{\text{mp2(full)}} = -108.40010$ au	$E_{\text{mp2(full)}} = -108.34128$ au	$E_{\text{mp2(full)}} = -108.33769$ au
$\langle S^2\rangle = 0.750$	$\langle S^2\rangle = 0.750$	$\nu_1(\sigma) = 4459$ cm^{-1}	$\nu_1(\sigma) = 3429$ cm^{-1}	$\nu_1(\sigma) = 4153$ cm^{-1}
$\nu_1(a') = 3957$ cm^{-1}	$\nu_1(\sigma) = 886$ cm^{-1}	$\nu_2(\sigma) = 881$ cm^{-1}	$\nu_2(\sigma) = 1635$ cm^{-1}	$\nu_2(\sigma) = 1397$ cm^{-1}
$\nu_2(a') = 378$ cm^{-1}	$\nu_2(\sigma) = 251$ cm^{-1}	$\nu_3(\sigma) = 188$ cm^{-1}	$\nu_3(\sigma) = 271$ cm^{-1}	$\nu_3(\sigma) = 344$ cm^{-1}
$\nu_3(a') = 339$ cm^{-1}	$\nu_3(\pi) = 60$ cm^{-1}	$\nu_4(\pi) = 440$ cm^{-1}	$\nu_4(\pi) = 791$ cm^{-1}	$\nu_4(\pi) = 152$ cm^{-1}
		$\nu_5(\pi) = 35$ cm^{-1}	$\nu_5(\pi) = 229i$ cm^{-1}	$\nu_5(\pi) = 200i$ cm^{-1}
ZPE = 6.68 kcal/mol	ZPE = 1.80 kcal/mol	ZPE = 9.26 kcal/mol	ZPE = 9.89 kcal/mol	ZPE = 8.86 kcal/mol
$\Delta E_{\text{mp2(full)}} = 0.0$ kcal/mol	$\Delta E_{\text{mp2(full)}} = 8.1$ kcal/mol	$\Delta E_{\text{mp2(full)}} = 0.0$ kcal/mol	$\Delta E_{\text{mp2(full)}} = 36.9$ kcal/mol	$\Delta E_{\text{mp2(full)}} = 39.2$ kcal/mol
QCISD/6-311++G**	QCISD/6-311++G**	QCISD/6-311++G**	QCISD/6-311++G**	QCISD/6-311++G**
R(Li−F) = 1.929 Å	R(Li−H) = 2.412 Å	R(Li−F) = 1.597 Å	R(Li−H) = 1.582 Å	R(Li−H) = 1.614 Å
R(F−H) = 0.927 Å	R(Li−F) = 1.596 Å	R(F−H) = 2.379 Å	R(H−H) = 1.440 Å	R(Li−F) = 1.915 Å
∠LiFH = 114.7°		R(H−H) = 0.747 Å	R(F−H) = 0.943 Å	R(F−H) = 0.918 Å
$E_{\text{qcisd}} = -107.72210$ au	$E_{\text{qcisd}} = -107.70448$ au	$E_{\text{qcisd}} = -108.37410$ au	$E_{\text{qcisd}} = -\ 108.31764$ au	$E_{\text{qcisd}} = -108.31534$ au
$\langle S^2\rangle = 0.750$	$\langle S^2\rangle = 0.750$	$\nu_1(\sigma) = 4363$ cm^{-1}	$\nu_1(\sigma) = 3568$ cm^{-1}	$\nu_1(\sigma) = 4177$ cm^{-1}
$\nu_1(a') = 3970$ cm^{-1}	$\nu_1(\sigma) = 887$ cm^{-1}	$\nu_2(\sigma) = 884$ cm^{-1}	$\nu_2(\sigma) = 1600$ cm^{-1}	$\nu_2(\sigma) = 1371$ cm^{-1}
$\nu_2(a') = 378$ cm^{-1}	$\nu_2(\sigma) = 244$ cm^{-1}	$\nu_3(\sigma) = 188$ cm^{-1}	$\nu_3(\sigma) = 258$ cm^{-1}	$\nu_3(\sigma) = 336$ cm^{-1}
$\nu_3(a') = 340$ cm^{-1}	$\nu_3(\pi) = 49$ cm^{-1}	$\nu_4(\pi) = 411$ cm^{-1}	$\nu_4(\pi) = 684$ cm^{-1}	$\nu_4(\pi) = 148$ cm^{-1}
		$\nu_5(\pi) = 29$ cm^{-1}	$\nu_5(\pi) = 304$i cm^{-1}	$\nu_5(\pi) = 227$i cm^{-1}
ZPE = 6.70 kcal/mol	ZPE = 1.76 kcal/mol	ZPE = 9.03 kcal/mol	ZPE = 9.71 kcal/mol	ZPE = 8.83 kcal/mol
$\Delta E_{\text{qcisd}} = 0.0$ kcal/mol	$\Delta E_{\text{qcisd}} = 11.1$ kcal/mol	$\Delta E_{\text{qcisd}} = 0.0$ kcal/mol	$\Delta E_{\text{qcisd}} = 35.4$ kcal/mol	$\Delta E_{\text{qcisd}} = 36.9$ kcal/mol
QCISD/6-311++G(2df2pd)	QCISD/6-311++G(2df2pd)	QCISD/6-311++G(2df2pd)	QCISD/6-311++G(2df2pd)	QCISD/6-311++G(2df2pd)
$E_{\text{qcisd}(t)} = -107.777\ 59$	$E_{\text{qcisd}(t)} = -107.760\ 54$	$E_{\text{qcisd}(t)} = -108.434\ 53$	$E_{\text{qcisd}(t)} = -108.378\ 96$	$E_{\text{qcisd}(t)} = -108.374\ 69$
$E_{\text{qcisd}} = -107.77095$	$E_{\text{qcisd}} = -107.75368$	$E_{\text{qcisd}} = -108.42757$	$E_{\text{qcisd}} = -108.37204$	$E_{\text{qcisd}} = -108.36848$
$\Delta E_{\text{qcisd}(t)} = 0.0$ kcal/mol	$\Delta E_{\text{qcisd}(t)} = 10.7$ kcal/mol	$\Delta E_{\text{qcisd}(t)} = 0.0$ kcal/mol	$\Delta E_{\text{qcisd}(t)} = 34.9$ kcal/mol	$\Delta E_{\text{qcisd}(t)} = 37.5$ kcal/mol

weak van der Waals complexes with H, which is consistent with our earlier observation that the charges are close to ±1 and that F^- has a full octet.

LiF also does not react chemically with H_2. The most stable structure of $LiFH_2$ stoichiometry (Table 4) is a van der Waals complex between H_2 and LiF. The global minimum structure has a linear H−H···F−Li ($C_{\infty v}$, $^1\Sigma^+$) structure (Table 4), which is bound only by 1.7 kcal/mol (QCISD(T)/6-311++G(2df,2pd)). Again, this is completely different from the reactivity of MgO and H_2.

Li_2F, Li_2Cl, Na_2F, Na_2Cl, Cs_2F, and Cs_2Cl have also been the subject of theoretical and experimental studies.[32−42] While MgO and BeO reacting with Li form a very strongly bound MgOLi and BeOLi, the valence isoelectronic alkali-metal halides (Hal) reacting with alkali atoms (Alk) form relatively weakly bound Alk_2Hal molecules ($D_e < 34$ kcal/mol[38]), where the atomic charge distributions are close to Alk_2^+ and Hal^-. In other words, the extra alkali atom does not form an additional bond with the halogen but rather reacts with the first alkali atom; hence, the electronic structures of these molecules are completely different from those of the isoelectronic MgOLi, BeOLi, etc.

From all of the above data it is clear that LiF is indeed a valence-saturated molecule whose ions have very stable full octet electronic structures, while MgO behaves more like a psudobiradical.

2MgO → Mg_2O_2. One might expect that dimerization of MgO would diminish the •Mg−O• character by tying up the reactive sites and increase atomic charges and might lead to an unusually large dimerization energy and to a larger singlet−triplet splitting in the dimer.

This is exactly what we find in our calculations. At our highest level of theory (QCISD(T)/6-311+G(2df)), the dimerization energy is found to be 125 kcal/mol, which is substantially higher than the dimerization energy 61.2 kcal/mol for the isoelectronic NaF.[43] If MgO involves appreciable •Mg−O• character as claimed earlier, the 125 kcal/mol released in the reaction 2MgO → Mg_2O_2 should be close to twice the dissociation energy of the Mg−O bond in Mg−O−Mg, which is 75 kcal/mol (QCISD(T)/6-311+G(2df)).

Another sign that electrons forming the weak second bond in MgO couple to form new bonds upon dimerization is provided by the large increase in singlet triplet splitting that accompanies dimerization. We performed calculations of several triplet states: $^3B_{1g}$ ($1a_g^2 1b_{2u}^2 2a_g^2 1b_{1u}^2 1b_{3u}^2\ 1b_{3g}^2 2b_{2u}^2 1b_{1g}^1 3a_g^1$), $^3B_{2u}$ ($1a_g^2 1b_{2u}^2 2a_g^2 1b_{1u}^2 1b_{3u}^2 1b_{3g}^2 2b_{2u}^1\ 1b_{1g}^2 3a_g^1$), $^3B_{3g}$, ($1a_g^2 1b_{2u}^2\ 2a_g^2 1b_{1u}^2 1b_{3u}^2 1b_{3g}^2 2b_{2u}^1 1b_{1g}^2 2b_{1u}^1$), and ^3A_u ($1a_g^2 1b_{2u}^2 2a_g^2 1b_{1u}^2 1b_{3u}^2\ 1b_{3g}^2 2b_{2u}^2 1b_{1g}^1 2b_{1u}^1$), and our data are summarized in Table 5. The $^3B_{2u}$ state is the lowest vertical excited state and has an excitation energy of 2.14 eV at QCISD(T)/6-311+G(2df) level. This energy gap is substantially higher than the singlet−triplet excitation in MgO, (0.24 eV).

On the basis of the large singlet−triplet splitting in Mg_2O_2 and the large dimerization energy for MgO, one might conclude that the dimer (and larger clusters) may consist of Mg^{2+} and O^{2-} ions even though MgO does not. However, the dimer is still quite far from the ionic limit as the charge densities shown in Table 1 indicate. Below we present our study of the reaction of Mg_2O_2 and Mg_4O_4 with hydrogen and lithium which clearly demonstrate the ability of the dimer to form strong bonds with hydrogen and lithium, thus showing that even in $(MgO)_2$ the Mg and O sites remain quite reactive.

$(MgO)_2$ + H. For Mg_2O_2H we assumed that the most stable structure has hydrogen attached to oxygen. We then studied three doublet $^2A_1$ ($1a_1^2 2a_1^2 3a_1^2 1b_2^2 1b_1^2 4a_1^2 2b_2^2 2b_1^2 5a_1^1$), $^2B_2$ ($1a_1^2 2a_1^2 3a_1^2 1b_2^2 1b_1^2 4a_1^2 2b_2^2 2b_1^2 3b_2^1$), and $^2B_1$ ($1a_1^2 2a_1^2 3a_1^2 1b_2^2 1b_1^2 4a_1^2 2b_2^2 2b_1^2 3b_1^1$) and three quartet $^4A_2$ ($1a_1^2 2a_1^2 3a_1^2 1b_2^2 1b_1^2 4a_1^2 2b_2^2\ 2b_1^1 5a_1^1 3b_2^1$), $^4B_2$ ($1a_1^2 2a_1^2 3a_1^2 1b_2^2 1b_1^2 4a_1^2 2b_2^2 2b_1^1 5a_1^1 1a_2^1$), and $^4A_1$ ($1a_1^2 2a_1^2 3a_1^2 1b_2^2 1b_1^2 4a_1^2 2b_2^1 2b_1^2 5a_1^1 3b_2^1$) states of Mg_2O_2H. Results for the two lowest doublet $^2B_2$ and $^2A_1$ and two lowest quartet $^4A_2$ and $^4A_1$ states are summarized in Table 6.

At our highest level of theory (QCISD(T)/6-311++G(2df,-

TABLE 5: Calculated Molecular Properties of the Singlet and Triplet States of Mg_2O

Mg_2O_2 (D_{2h}, ^1A_g)	Mg_2O_2 (D_{2h}, $^3B_{2u}$)	Mg_2O_2 (D_{2h}, $^3B_{3g)}$	Mg_2O_2 (D_{2h}, $^3B_{1g}$)	Mg_2O_2 (D_{2h}, ^3A_u)
$1a_g^2 1b_{2u}^2 2a_g^2 1b_{1u}^2 1b_{3u}^2$ $1b_{3g}^2 2b_{2u}^2 1b_{1g}^2 3a_g^0 3b_{1u}^0$	$1a_g^2 1b_{2u}^2 2a_g^2 1b_{1u}^2 1b_{3u}^2$ $1b_{3g}^2 2b_{2u}^1 1b_{1g}^2 3a_g^1$	$1a_g^2 1b_{2u}^2 2a_g^2 1b_{1u}^2 1b_{3u}^2$ $1b_{3g}^2 2b_{2u}^1 1b_{1g}^2 2b_{1u}^1$	$1a_g^2 1b_{2u}^2 2a_g^2 1b_{1u}^2 1b_{3u}^2$ $1b_{3g}^2 2b_{2u}^2 1b_{1g}^1 3a_g^1$	$1a_g^2 1b_{2u}^2 2a_g^2 1b_{1u}^2 1b_{3u}^2$ $1b_{3g}^2 2b_{2u}^2 1b_{1g}^1 2b_{1u}^1$
MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*
R(Mg−O) = 1.911 Å	R(Mg−O) = 1.904 Å	R(Mg−O) = 1.904 Å	R(Mg−O) = 1.911 Å	R(Mg−O) = 1.927 Å
R(Mg−Mg) = 2.455	R(Mg−Mg) = 2.903 Å	R(Mg−Mg) = 2.909 Å	R(Mg−Mg) = 2.720 Å	R(Mg−Mg) = 2.740 Å
R(O−O) = 2.930 Å	R(O−O) = 2.465 Å	R(O−O) = 2.455 Å	R(O−O) = 2.685 Å	R(O−O) = 2.709 Å
$E_{mp2(full)} = -549.77893$ au	$E_{mp2(full)} = -549.70720$ au	$E_{mp2(full)} = -549.67523$ au	$E_{mp2(full)} = -549.67445$ au	$E_{mp2(full)} = -549.64262$ au
	$\langle S^2 \rangle = 2.077$	$\langle S^2 \rangle = 2.107$	$\langle S^2 \rangle = 2.264$	$\langle S^2 \rangle = 2.299$
$\nu_1(a_g) = 631\ cm^{-1}$	$\nu_1(a_g) = 656\ cm^{-1}$	$\nu_1(a_g) = 652cm^{-1}$	$\nu_1(a_g) = 656\ cm^{-1}$	$\nu_1(a_g) = 626\ cm^{-1}$
$\nu_2(a_g) = 416\ cm^{-1}$	$\nu_2(a_g) = 340\ cm^{-1}$	$\nu_2(a_g) = 343\ cm^{-1}$	$\nu_2(a_g) = 367\ cm^{-1}$	$\nu_2(a_g) = 372\ cm^{-1}$
$\nu_3(b_{3g}) = 545\ cm^{-1}$	$\nu_3(b_{3g}) = 596\ cm^{-1}$	$\nu_3(b_{3g}) = 593\ cm^{-1}$	$\nu_3(b_{3g}) = 588\ cm^{-1}$	$\nu_3(b_{3g}) = 559\ cm^{-1}$
$\nu_4(b_{1u}) = 569\ cm^{-1}$	$\nu_4(b_{1u}) = 1934\ cm^{-1}$ [a]	$\nu_4(b_{1u}) = 892\ cm^{-1}$	$\nu_4(b_{1u}) = 1629\ cm^{-1,a}$	$\nu_4(b_{1u}) = 792\ cm^{-1}$
$\nu_5(b_{2u}) = 619\ cm^{-1}$	$\nu_5(b_{2u}) = 781\ cm^{-1}$	$\nu_5(b_{2u}) = 970\ cm^{-1}$	$\nu_5(b_{2u}) = 324i\ cm^{-1}$	$\nu_5(b_{2u}) = 878i\ cm^{-1}$
$\nu_6(b_{3u}) = 257\ cm^{-1}$	$\nu_6(b_{3u}) = 155\ cm^{-1}$	$\nu_6(b_{3u}) = 135\ cm^{-1}$	$\nu_6(b_{3u}) = 143\ cm^{-1}$	$\nu_6(b_{3u}) = 62\ cm^{-1}$
ZPE = 4.34 kcal/mol	ZPE = 6.38 kcal/mol	ZPE = 5.13 kcal/mol	ZPE = 4.84 kcal/mol	ZPE = 3.44 kcal/mol
$\Delta E_{mp2(full)} = 0.0$ eV	$\Delta E_{mp2(full)} = 1.95$ eV	$\Delta E_{mp2(full)} = 2.82$ eV	$\Delta E_{mp2(full)} = 2.84$ eV	$\Delta E_{mp2(full)} = 3.70$ eV
QCISD/6-311+G(2df)	QCISD/6-311+G(2df)			
$E_{qcisd(t)} = -549.600\ 55$	$E_{qcisd(t)} = -549.543\ 15$			
$E_{qcisd\ =} -549.575\ 43$	$E_{qcisd} = -549.518\ 18$			
$\Delta E_{qcisd(t)} = 0.0$ kcal/mol	$\Delta E_{qcisd(t)} = 1.56$ eV			

[a] This frequency could be affected by a symmetry-broken problem.

TABLE 6: Calculated Molecular Properties of Mg_2O_2H

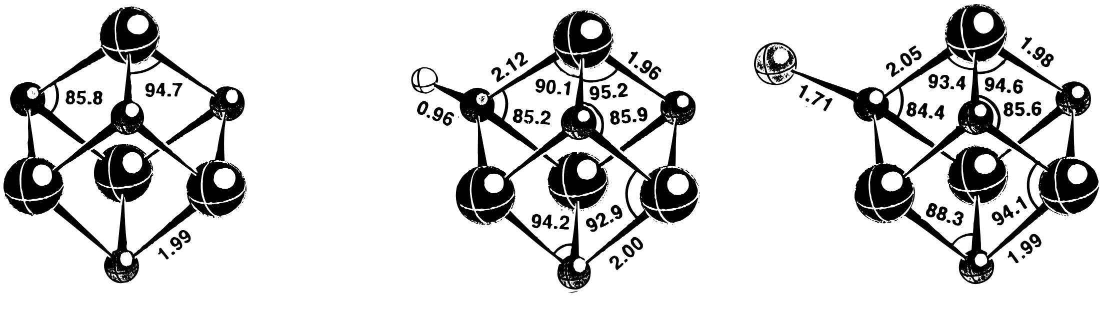
Mg_2O_2H (C_{2v}, $^2A_1$)	Mg_2O_2H (C_{2v}, $^2B_2$)	Mg_2O_2H (C_{2v}, $^4A_2$)	Mg_2O_2H (C_{2v}, $^4A_1$)
$1a_1^2 2a_1^2 3a_1^2 1b_2^2 1b_1^2 4a_1^2$ $2b_2^2 2b_1^2 5a_1^1$	$1a_1^2 2a_1^2 3a_1^2 1b_2^2 1b_1^2 2b_2^2 4a_1^2$ $2b_1^2 3b_2^1$	$1a_1^2 2a_1^2 3a_1^2 1b_2^2 1b_1^2 4a_1^2$ $2b_2^2 2b_1^1 5a_1^1 3b_2^1$	$1a_1^2 2a_1^2 3a_1^2 1b_2^2 1b_1^2 4a_1^2 2b_2^1$ $2b_1^2 5a_1^1 3b_2^1$
MP2(full)/6-311++G**	MP2(full)/6-311++G**	MP2(full)/6-311++G**	MP2(full)/6-311++G**
R(Mg−OH) = 1.976 Å	R(Mg−OH) = 2.005 Å	R(Mg−OH) = 1.990 Å	R(Mg−OH) = 1.965 Å
R(Mg−Mg) = 3.107 Å	R(Mg−Mg) = 2.710 Å	R(Mg−Mg) = 3.049 Å	R(Mg−Mg) = 2.961 Å
R(O−O) = 2.555 Å	R(O−O) = 2.795 Å	R(O−O) = 2.674 Å	R(O−O) = 2.805 Å
R(O−H) = 0.966 Å	R(O−H) = 0.956 Å	R(O−H) = 0.958	R(O−H) = 0.957
$E_{mp2(full)} = -550.356\ 75$	$E_{mp2(full)} = -550.376\ 38$ au	$E_{mp2(full)} = -550.343\ 72$ au	$E_{mp2(full)} = -550.313\ 07$ au
$\langle S^2 \rangle = 0.823$	$\langle S^2 \rangle = 0.755$	$\langle S^2 \rangle = 3.757$	$\langle S^2 \rangle = 3.756$
$\nu_1(a_1) = 3847\ cm^{-1}$	$\nu_1(a_1) = 3977\ cm^{-1}$	$\nu_1(a_1) = 3962\ cm^{-1}$	$\nu_1(a_1) = 3979\ cm^{-1}$
$\nu_2(a_1) = 563\ cm^{-1}$	$\nu_2(a_1) = 600\ cm^{-1}$	$\nu_2(a_1) = 509\ cm^{-1}$	$\nu_2(a_1) = 527\ cm^{-1}$
$\nu_3(a_1) = 499\ cm^{-1}$	$\nu_3(a_1) = 512\ cm^{-1}$	$\nu_3(a_1) = 441\ cm^{-1}$	$\nu_3(a_1) = 404\ cm^{-1}$
$\nu_4(a_1) = 359\ cm^{-1}$	$\nu_4(a_1) = 366\ cm^{-1}$	$\nu_4(a_1) = 304\ cm^{-1}$	$\nu_4(a_1) = 301\ cm^{-1}$
$\nu_5(b_1) = 278\ cm^{-1}$	$\nu_5(b_1) = 395\ cm^{-1}$	$\nu_5(b_1) = 444\ cm^{-1}$	$\nu_5(b_1) = 398\ cm^{-1}$
$\nu_6(b_1) = 54\ cm^{-1}$	$\nu_6(b_1) = 187\ cm^{-1}$	$\nu_6(b_1) = 69\ cm^{-1}$	$\nu_6(b_1) = 142\ cm^{-1}$
$\nu_7(b_2) = 772\ cm^{-1}$	$\nu_7(b_2) = 784\ cm^{-1}$	$\nu_7(b_2) = 735\ cm^{-1}$	$\nu_7(b_2) = 717\ cm^{-1}$
$\nu_8(b_2) = 622\ cm^{-1}$	$\nu_8(b_2) = 674\ cm^{-1}$	$\nu_8(b_2) = 495\ cm^{-1}$	$\nu_8(b_2) = 514\ cm^{-1}$
$\nu_9(b_2) = 432\ cm^{-1}$	$\nu_9(b_2) = 431\ cm^{-1}$	$\nu_9(b_2) = 411\ cm^{-1}$	$\nu_9(b_2) = 313\ cm^{-1}$
ZPE = 10.62 kcal/mol	ZPE = 11.33 kcal/mol	ZPE = 10.53 kcal/mol	ZPE = 10.43 kcal/mol
$\Delta E_{mp2(full)} = 0.0$ eV	$\Delta E_{mp2(full)} = -0.53$ eV	$\Delta E_{mp2(full)} = 0.36$ eV	$\Delta E_{mp2(full)} = 1.19$ eV
QCISD(T)/6-311++G(2df,2pd)	QCISD(T)/6-311++G(2df,2pd)	QCISD(T)/6-311++G(2df,2pd)	QCISD(T)/6-311++G(2df,2pd)
$E_{qcisd(t)} = -550.204\ 99$	$E_{qcisd(t)} = -550.204\ 23$	$E_{qcisd(t)} = -550.169\ 85$	$E_{qcisd(t)} = -550.140\ 37$
$E_{qcisd} = -550.173\ 74$	$E_{qcisd} = -550.180\ 84$	$E_{qcisd} = -550.153\ 98$	$E_{qcisd} = -550.124\ 30$
$\Delta E_{qcisd(t)} = 0.0$ eV	$\Delta E_{qcisd(t)} = 0.02$ eV	$\Delta E_{qcisd(t)} = 0.96$ eV	$\Delta E_{qcisd(t)} = 1.76$ eV

2pd)) the $^2A_1$ and $^2B_2$ states of Mg_2O_2H were found to have nearly the same energy, and both states are predicted to be true local minima in C_{2v} symmetry. In the $^2B_2$ state, the unpaired electron is located on the magnesium sites (50% at each Mg atom), while in the $^2A_1$ state, the unpaired electron is located 65% at the oxygen atom not bound to the hydrogen with the rest of the unpaired electron density located on the magnesium atoms.

The lowest $^4A_2$ quartet state is only 0.96 eV less stable than the $^2A_1$ and $^2B_2$ states. In this state, the unpaired electron density is located (1.1 e) at the oxygen atom not bound to the hydrogen and (0.94 e) at every magnesium atom. The doublet-quartet excitation energy in Mg_2O_2H is substantially less than the singlet−triplet excitation (1.56 eV) energy in the pure Mg_2O_2 dimer. We interpret this to mean that hydrogen atom "chemisorption" to an O site of Mg_2O_2 partially restores the radical-like activity of the species. The energy released in the reaction of a H atom with $(MgO)_2$ is 58 kcal/mol at the QCISD(T)/6-311++G(2df,2pd) level which is considerably less than that released when a H atom reacts with MgO (120 kcal/mol). The reactivity of the dimer is lower than that of the monomer, but the dimer remains a very reactive molecule, able to form a strong bond to H.

$(MgO)_2$ + Li. For Mg_2O_2Li we studied the analogous doublet and quartet states (see Table 7). The doublet $^2A_1$ state is a true minimum on the potential energy surface and is the lowest electronic state for this molecule. The $^2B_2$ lowest excited state is a local minimum too that is 0.96 eV (at QCISD(T)/6-311+G(2df)) less stable than the ground state, which is different from the Mg_2O_2H case where both $^2A_1$ and $^2B_2$ states were found to have essentially the same energy. However, the electronic structures of the $^2A_1$ states are different for Mg_2O_2H and Mg_2O_2Li. In the former molecule, the unpaired electron is located mostly at the oxygen atom not bound to the hydrogen, while in Mg_2O_2Li the unpaired electron is located on two magnesium atoms.

Coordination of a hydrogen or lithium atom to Mg_2O_2 creates unpaired electron density at the magnesium atoms in the lowest electronic states. The lowest $^4B_2$ quartet state of Mg_2O_2Li is a local minimum but is 1.75 eV (at QCISD(T)/6-311+G(2df))



Mg_4O_4 (T_d, $^1A_1$) Mg_4O_4H (C_{3v}, $^2A_1$) Mg_4O_4Li (C_{3v}, $^2A_1$)

Figure 1. Optimized geometries (at MP2/6-311+G*) of the Mg_4O_4 (T_d, $^1A_1$), Mg_4O_4H (C_{3v}, $^2A_1$), and Mg_4O_4Li (C_{3v}, $^2A_1$) clusters. Distances in angstroms and bond angles in degrees.

TABLE 7: Calculated Molecular Properties of Mg_2O_2Li

Mg_2O_2Li (C_{2v}, $^2A_1$)	Mg_2O_2Li (C_{2v}, $^2B_2$)	Mg_2O_2Li (C_{2v}, $^4B_2$)	Mg_2O_2Li (C_{2v}, $^4A_2$)
$1a_1^2 2a_1^2 3a_1^2 1b_2^2 1b_1^2 2b_2^2$ $4a_1^2 2b_1^2 5a_1^1$	$1a_1^2 2a_1^2 3a_1^2 1b_2^2 1b_1^2 4a_1^2$ $2b_2^2 2b_1^2 3b_2^1$	$1a_1^2 2a_1^2 3a_1^2 1b_2^2 1b_1^2 2b_2^2$ $2b_1^2 4a_1^1 5a_1^1 3b_2^1$	$1a_1^2 2a_1^2 3a_1^2 1b_2^2 1b_1^2 4a_1^2$ $2b_2^2 2b_1^1 5a_1^1 3b_2^1$
MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*
R(Mg−OLi) = 1.970 Å	R(Mg−OLi) = 1.978 Å	R(Mg−OLi) = 1.957 Å	R(Mg−OLi) = 1.946 Å
R(Mg−Mg) = 2.548 Å	R(Mg−Mg) = 2.591 Å	R(Mg−Mg) = 3.041 Å	R(Mg−Mg) = 2.891 Å
R(O−O) = 2.870 Å	R(O−O) = 2.890 Å	R(O−O) = 2.539 Å	R(O−O) = 2.803 Å
R(O−Li) = 1.688 Å	R(O−Li) = 1.681 Å	R(O−Li) = 1.687	R(O−Li) = 1.688
$E_{mp2(full)} = -557.325\ 47$ au	$E_{mp2(full)} = -557.288\ 15$	$E_{mp2(full)} = -557.258\ 30$ au	$E_{mp2(full)} = -557.259\ 78$ au
$\langle S^2 \rangle = 0.817$	$\langle S^2 \rangle = 0.755$	$\langle S^2 \rangle = 3.761$	$\langle S^2 \rangle = 3.758$
$\nu_1(a_1) = 1135$ cm^{-1}	$\nu_1(a_1) = 860$ cm^{-1}	$\nu_1(a_1) = 845$ cm^{-1}	$\nu_1(a_1) = 853$ cm^{-1}
$\nu_2(a_1) = 865$ cm^{-1}	$\nu_2(a_1) = 598$ cm^{-1}	$\nu_2(a_1) = 490$ cm^{-1}	$\nu_2(a_1) = 480$ cm^{-1}
$\nu_3(a_1) = 481$ cm^{-1}	$\nu_3(a_1) = 474$ cm^{-1}	$\nu_3(a_1) = 430$ cm^{-1}	$\nu_3(a_1) = 442$ cm^{-1}
$\nu_4(a_1) = 385$ cm^{-1}	$\nu_4(a_1) = 371$ cm^{-1}	$\nu_4(a_1) = 292$ cm^{-1}	$\nu_4(a_1) = 316$ cm^{-1}
$\nu_5(b_1) = 237$ cm^{-1}	$\nu_5(b_1) = 215$ cm^{-1}	$\nu_5(b_1) = 145$ cm^{-1}	$\nu_5(b_1) = 149$ cm^{-1}
$\nu_6(b_1) = 81$ cm^{-1}	$\nu_6(b_1) = 107$ cm^{-1}	$\nu_6(b_1) = 31$ cm^{-1}	$\nu_6(b_1) = 87$ cm^{-1}
$\nu_7(b_2) = 702$ cm^{-1}	$\nu_7(b_2) = 673$ cm^{-1}	$\nu_7(b_2) = 577$ cm^{-1}	$\nu_7(b_2) = 562$ cm^{-1}
$\nu_8(b_2) = 538$ cm^{-1}	$\nu_8(b_2) = 483$ cm^{-1}	$\nu_8(b_2) = 452$ cm^{-1}	$\nu_8(b_2) = 384$ cm^{-1}
$\nu_9(b_2) = 110$ cm^{-1}	$\nu_9(b_2) = 59$ cm^{-1}	$\nu_9(b_2) = 105$ cm^{-1}	$\nu_9(b_2) = 97$ cm^{-1}
ZPE = 6.48 kcal/mol	ZPE = 5.49 kcal/mol	ZPE = 4.81 kcal/mol	ZPE = 4.82 kcal/mol
$\Delta E_{mp2(full)} = 0.0$	$\Delta E_{mp2(full)} = 1.02$ eV	$\Delta E_{mp2(full)} = 1.83$ eV	$\Delta E_{mp2(full)} = 1.79$ eV
QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)
$E_{qcisd(t)} = -557.136\ 10$	$E_{qcisd(t)} = -557.100\ 70$	$E_{qcisd(t)} = -557.071\ 67$	$E_{qcisd(t)} = -557.070\ 93$
$E_{qcisd} = -557.109\ 51$	$E_{qcisd} = -557.074\ 94$	$E_{qcisd} = -557.052\ 74$	$E_{qcisd} = -557.052\ 71$
$\Delta E_{qcisd(t)} = 0.0$ eV	$\Delta E_{qcisd(t)} = 0.96$ eV	$\Delta E_{qcisd(t)} = 1.75$ eV	$\Delta E_{qcisd(t)} = 1.77$ eV

less stable than the $^2A_1$ ground state. The electron density distribution in this quartet state is very similar to that of Mg_2O_2H $^4A_2$. The unpaired electron density is located (1.0 e) at the oxygen atom not bound to the hydrogen and (1.0 e) at each magnesium atom.

The dissociation energy of Mg_2O_2Li ($^2A_1$) into Mg_2O_2 + Li was found to be 65 kcal/mol, which compares with 93 kcal/mol for the dissociation of MgOLi into MgO + Li (all at QCISD(T)/6-311+G(2df)).

While the dissociation energies of Mg_2O_2H into Mg_2O_2 + H and of Mg_2O_2Li into Mg_2O_2 + Li are lower than the corresponding dissociation energies of MgOH into MgO + H and MgOLi into MgO + Li, we conclude that the Mg_2O_2 dimer is still a very reactive species, a result of the remaining pseudobiradical character and atomic charges that differ from ±2.

$(MgO)_4$, + H or Li. For Mg_4O_4 we studied only one T_d ($^1A_1$) structure (see Figure 1). As we observed earlier, MgO dimerization diminishes the $^{\bullet}$Mg−O$^{\bullet}$ character, as a result of which, the charges in the dimer are closer to the +2 and −2 limit and consequently Mg_2O_2 is less reactive (to H_2 or H or Li) than MgO. As one can see in Table 1, the atomic charges do not change much when moving from the dimer to the tetramer, although they become somewhat closer to the ionic limit.

The exothermicity of the reaction $2Mg_2O_2 \rightarrow Mg_4O_4$ was found to be 159 kcal/mol (at MP2/6-311+G*) which is larger than that (120 kcal/mol at MP2/6-311+G*) of the $2MgO \rightarrow Mg_2O_2$ reaction. The energy gain per molecule (100 kcal/mol) upon formation of Mg_4O_4 from MgO is also higher than the energy of the formation Mg_2O_2 from MgO per molecule (60 kcal/mol).

Because we used H and Li atoms as probes for reactivity of MgO and Mg_2O_2, we performed similar calculations for Mg_4O_4H and Mg_4O_4Li but at a lower level of theory (MP2/6-311++G**) due to computational constraints.

For Mg_4O_4H, we studied only one C_{3v} ($^2A_1$) structure with the hydrogen coordinated to the oxygen (as shown in Figure 1). We believe this to be the most stable isomer based on our experience with the smaller clusters. Because of the relatively large size of this molecule, vibrational frequency calculations were not performed. The exothermicity of $Mg_4O_4 + H \rightarrow Mg_4O_4H$ was found to be 57 kcal/mol (at PMP2/6-311++G**) which compares to 61 kcal/mol (at MP2(full)/6-311++G**) for $Mg_2O_2 + H \rightarrow Mg_2O_2H$ and to 126 kcal/mol (at MP2(full)/6-311++G**) for $MgO + H \rightarrow MgOH$.

For Mg_4O_4Li we also studied only one C_{3v} ($^2A_1$) structure with lithium coordinated to oxygen (see Figure 1). Again because of the relatively large size of this molecule, frequency calculations were not performed. The exothermicity of this reaction was found to be 44 kcal/mol (at PMP2/6-311++G**) which compares to 64 kcal/mol (at MP2(full)/6-311++G**) for $Mg_2O_2 + Li \rightarrow Mg_2O_2Li$ and to 102 kcal/mol (at MP2(full)/6-311++G**) for $MgO + Li \rightarrow MgOLi$.

The exothermicities for the addition reactions of lithium and hydrogen atoms to $(MgO)_n$ clusters are seen to decrease with the size of the cluster. This is in agreement with the view that the extent of valence saturation moves closer to the ionic limit as the coordination number in the cluster grows. One can speculate that in the bulk MgO crystal, the oxygen sites are valence saturated and thus not as reactive as at less coordinated sites. Oxygen atoms on the surface are not valence saturated nor are atoms on steps, kinks, and other defect sites, so these sites are likely to be more reactive. This view is in agreement with the experimental fact that highly dispersed MgO is very reactive.[44]

Conclusion

On the basis of the electronic structure findings reported here, we speculate that the unusual catalytic action of MgO in the powder or crystal states relates to the partially saturated valence nature of the ions in these crystals. In NaF and other alkali halides, the ions have full octets of electrons and therefore are valence saturated; this, we claim, makes the alkali halides nonreactive. Although MgO and other alkaline-earth oxides may contain valence saturated ions in the bulk, the ions in small clusters, at defect sites in the crystal, and at various surface sites likely do not contain valence saturated ions. As a result, such sites may form additional bonds to chemisorbed species. Thus, we speculate that it is the dual character of the ions in MgO (e.g., being intermediate between O^{2-} and O^{-}) that makes these compounds catalytically active.

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References and Notes

(1) (a) Bauschlicher, C. W., Jr.; Yarkony, D. R. *J. Chem. Phys*. **1980**, *72*, 1138. (b) Bauschlicher, C. W., Jr.; Silver, D. M.; Yarkony, D. R. *J. Chem. Phys*. **1980**, *73*, 2867. (c) Bauschlicher, C. W., Jr.; Lengsfield, B. H., III; Silver, D. M.; Yarkony, D. R. *J. Chem. Phys*. **1981**, *74*, 2379. (d) Bauschlicher, C. W., Jr.; Lengsfield, B. H., III; Liu, B. *J. Chem. Phys*. **1982**, *77*, 4084.

(2) Liu, B.; Olson, R. E.; Saxon, R. P. *J. Chem. Phys*. **1981**, *74*, 4216.

(3) Langhoff, S. R.; Bauschlicher, C. W., Jr.; Partridge, H. *J. Chem. Phys*. **1986**, *84*, 4474.

(4) (a) Rice, S. F.; Martin, H.; Field, R. W. *J. Chem. Phys.* **1985**, *82*, 5023. (b) Baldwin, D. P.; Hill, E. J.; Field, R. W. *J. Am. Chem. Soc.* **1990,** *112*, 9156. (c) Harris, N. A.; Field, R. W. *J. Chem. Phys*. **1993**, *98*, 2642.

(5) Boldyrev, A. I.; Simons, J. *J. Phys. Chem*. **1995**, *99*, 15041.

(6) (a) Boldyrev, A. I.; Shamovsky, I. L.; Schleyer, P. V. R. *J. Am. Chem. Soc*. **1992**, *114*, 6469. (b) Boldyrev, A. I.; Simons, J.; Schleyer, P. v. R. *Chem. Phys. Lett*. **1995**, *233*, 266.

(7) Deng, H. T.; Okada, Y.; Foltin, M.; Castleman, A. W., Jr. *J. Phys. Chem.* **1994**, *98*, 9350.

(8) Ziemann, P. J.; Castleman, A. W., Jr. *J. Chem. Phys*. **1991**, *94*, 718.

(9) Ziemann, P. J.; Castleman, A. W., Jr. *Phys. Rev. B* **1991**, *44*, 6488.

(10) Ziemann, P. J.; Castleman, A. W., Jr. *Z. Phys. D* **1991**, *20*, 97.

(11) Ziemann, P. J.; Castleman, A. W., Jr. *Phys. Rev. B* **1992**, *46*, 482.

(12) Thompson, C. A.; Andrews, L. *J. Chem. Phys*. **1994**, *100*, 8689.

(13) Kobayashi, H; Yamaguchi, M.; Ito, T. *J. Phys. Chem*. **1990**, *94*, 7206.

(14) Sawabe, K.; Koga, N.; Morokuma, K.; Iwasawa, Y. *J. Chem. Phys*. **1992**, *97*, 6871.

(15) Anchell, J. L.; Morokuma, K.; Hess, A. C. *J. Chem. Phys.* **1993**, *99*, 6004.

(16) Anchell, J. L.; Glendening, E. D. *J. Phys. Chem*. **1994**, *98*, 11582.

(17) Schlegel, H. B. *J. Comput. Chem*. **1982**, *3*, 214.

(18) (a) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys*. **1980**, *72*, 650. (b) McLean, A. D.; Chandler, G. S. *J. Chem. Phys*. **1980**, *72*, 5639. (c) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem*. **1983**, *4*, 294. (d) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys*. **1984**, *80*, 3265.

(19) Krishnan, R.; Pople, J. A. *Int. J. Quantum Chem*. **1978**, *14*, 91.

(20) Pople, J. A.; Head-Gordon, M. Raghavachari, K. *J. Chem. Phys*. **1987**, *87*, 5968.

(21) Schlegel, H. B. *J. Chem. Phys*. **1984**, *84*, 4530.

(22) *GAUSSIAN 94*, Revision A.1; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chem, W.; Wong, M. W.; Anders, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P; Head-Gordon, M.; Gonzalez, C.; Pople J. A.; Gaussian Inc.: Pittsburgh, PA, 1995.

(23) Mulliken, R. S. *J. Chem. Phys*. **1955**, *23*, 1833.

(24) Besler, B. H.; Merz, K. M.; Kollman, P. A. *J. Comput. Chem*. **1990**, *11*, 431.

(25) Singh, U. C.; Kollman, P. A. *J. Comput. Chem*. **1984**, *5*, 129.

(26) Breneman, C. M.; Wiberg, K. B. *J. Comput. Chem*. **1990**, *11*, 361.

(27) Reed, A. E.; Curtiss, L. A.; Weinhold, F.*Chem. Rev*. **1988**, *88*, 899.

(28) Schafer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys*. **1992**, *97*, 2571.

(29) Ikeda, T.; Wong, N. B.; Harris, D. O.; Field, R. W. *J. Mol. Spectrosc*. **1977**, *68*, 452.

(30) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure. Constants of Diatomic Molecules*; van Nostrand Reinhold: New York, 1979.

(31) Bunker, P. R.; Kolbuszewski, M.; Jensen, P.; Brumm, M.; Anderson, M. A.; Barclay, W. L., Jr.; Ziurys, L. M.; Ni, Y.; Harris, D. O. *Chem. Phys. Lett.* **1995**, *239*, 217.

(32) Gutsev, G. L.; Boldyrev, A. I. *Chem. Phys. Lett*. **1982**, *92*, 262.

(33) Howard, W. F.; Andrews, L. *Inorg. Chem.* **1975**, *14*, 409.

(34) Peterson, K. I.; Dao, P. D.; Castleman, A. W., Jr. *J. Chem. Phys*. **1983**, *79*, 777.

(35) Sannigrahi, A. B.; Nandi, P. K.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1993**, *204*, 73.

(36) Cai, Z.-L.; Hirsch, G.; Buenker, R. J. *Chem. Phys. Lett.* **1995**, *246*, 529.

(37) Kappes, M.; Radi, P.; Schar, M.; Schumacher, E. *Chem. Phys. Lett.* **1985**, *113*, 243.

(38) Galli, G.; Andreoni, W.; Tosi, M. *Phys. Rev*. **1986**, *A34*, 3580.

(39) Thompson, J. W.; Child, M. S. *Chem. Phys. Lett*. **1989**, *157*, 343.

(40) Pollack, S.; Wang, C. R. C.; Kappes, M. M. *Chem. Phys. Lett*. **1990**, *175*, 209.

(41) Rehm, E.; Boldyrev, A. I.; Schleyer, P. v. R. Schleyer. *Inorg. Chem*. **1992**, *31*, 4834.

(42) Gutowski, M.; Simons, J. *J. Chem. Phys.* **1994**, *100*, 1308.

(43) Sidorov L. N.; Akishin, P. A.; Belousov, B. I.; Sholtz, V. B. *Russ. J. Phys. Chem.* **1964**, *38*, 146.

(44) Knozinger, E.; Jacob, K.-H.; Hofmann, P. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 1101.

JP953617P