BERYLLIUM AND MAGNESIUM HYDROXIDES AND FLUORIDES

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A theoretical study of the reactivity of BeF_2, $Be(OH)_2$, BeF(OH), MgF_2, $Mg(OH)_2$ and MgF(OH) was carried out at the MPn ($n = 2, 3, 4$)/6-31G**//SCF/6-31G** and CCD/6-31G**//SCF/6-31G** levels. Geometries and harmonic frequencies of the normal vibrational modes of the studied molecules are tabulated. Reaction energies and heats of reaction of $MF_2 + OH^- \rightleftarrows MF(OH) + F^-$ and $MF(OH) + OH^- \rightleftarrows MF(OH)_2 + F^-$ (M = Be, Mg) have been calculated and estimates for analogous processes involving calcium have been provided.

This work is related to our long standing interest in the role of fluoridation in dental hydroxyapatite which is of great importance in preventive dentistry. On the basis of a cluster model for the solid phase, the interaction between hydroxyapatite and the fluoride anion was studied in our laboratory by means of extended Hückel theory[1]. The influence of temperature and hydration were approximately taken into consideration. It was concluded that fluoridation of hydroxyapatite is not thermodynamically favored and partial permanent substitution of OH^- in hydroxyapatite by F^- requires a permanent supply of fluoride ions. It seems this is a plausible conclusion in spite of the serious simplifications made and the extremely simple MO method used.

This paper concerns the first step in the theoretical reexamination of the process with a significantly better model at a much higher quantum chemical level. Even the following process is not easy to study at a reliable level with correlated wave functions quantum chemically:

$$3\,Ca_3(PO_4)_2.Ca(OH)_2 + 2\,F^- \rightleftarrows 3\,Ca_3(PO_4)_2.CaF_2 + 2\,OH^- . \qquad (1)$$

Therefore, we decided to begin with nonempirical computations of the fluorides and hydroxides of beryllium and magnesium for which reliable, sufficiently good basis sets are available within standard *ab initio* computer programs. In the future we shall search for somewhat simpler but well balanced basis sets for atoms ranging from H to Ca which will successfully reproduce the main results of the present study. We believe that such basis sets will also offer reliable results for calcium containing system.

There has been increasing interest recently in nonempirical studies of simple systems containing beryllium and magnesium. SCF and perturbation calculations of the bending potential[2] of BeOH and MgOH were reported; good agreement with experiment was found for MgOH. Nonempirical calculations were performed[3] for several Be and Mg containing molecules including MgF(OH) (linear structure found) and $Mg(OH)_2$. The structure and vibrational frequencies of BeH(OH) and MgH(OH) were investigated[4]. SCF-MO dissociation energies of fluorides of the first and second row elements are available[5]. In a sophisticated *ab initio* study[6] of the alkali-earth monohydroxides the following dissociation energies of BeOH, MgOH and CaOH were recommended: 4·70, 3·31, 4·15 eV. It was stated that these theoretical dissociation energies were strongly correlated with those of the corresponding fluorides and oxides. Further works dealt with the *ab initio* investigation of a set of Be containing molecules (including BeH(OH) and BeF_2) (ref.[7]), with BeF_2 (ref.[8]), and with laser spectroscopy of MgOH and MgOD (ref.[9]). The linear structure of Be and Mg hydroxide hydrides has been established quantum chemically in connection with theoretical studies of the interactions of metal atoms with water[10].

MODEL SYSTEMS AND COMPUTATIONS

The model molecular and ionic species of interest are summarized below. We are interested in molecular geometry and harmonic frequencies of normal vibrational modes, and, moreover, in reaction energies of the gas phase processes

BeF_2	$Be(OH)_2$	BeF(OH)	Be^{2+}	MgF_2	$Mg(OH)_2$
I	*II*	*III*	*IV*	*V*	*VI*

MgF(OH)	Mg^{2+}	F^-	OH^-
VII	*VIII*	*IX*	*X*

$$MF_2 + OH^- \rightleftarrows MF(OH) + F^- \tag{2}$$

$$MF(OH) + OH^- \rightleftarrows M(OH)_2 + F^- , \tag{3}$$

where M is either Be or Mg.

Nonempirical calculations were performed with the Gaussian 86 program at the MP2,3,4 and CCD//SCF/6-31G** levels; vibrational analyses were done at the SCF/6-31G**//SCF/6-31G** level.

DISCUSSION

Energy characteristics including zero-point energies (ZPE) are presented in Table I. Table II comprises geometrical and vibrational data. Energy characteristics of the processes (*2*) and (*3*) are summarized in Table III.

Both difluorides were found to be linear. The structures of the remaining molecules differ between those containing Be and Mg; the minima of the Mg containing species belong to higher point symmetry groups (C_{2h}, $C_{\infty h}$) than do the Be derivatives (C_2, C_1). While both hydroxides of Mg and Be have a linear arrangement of the central three atoms (O—M—O), all atoms of $Mg(OH)_2$ lie in a plane (C_{2h}), while all atoms in $Be(OH)_2$ do not (C_2). MgFOH was found to be linear ($C_{\infty v}$) while BeFOH is not only bent, but also is not planar (C_1). The reason for these differences is not obvious to us.

The calculated BeF bond length* in BeF_2 (1·37 Å) agrees well with the observed value[11] (1·36 Å); the agreement for MgF_2 is also satisfactory (1·73 vs 1·75 Å) (ref.[11]).

TABLE I

MPn and CCD/6-31G**//SCF/6-31G** total energies (with opposite sign) and zero-point energies (ZPE) of stationary points of molecules and ions *I*—*X* (a.u., 1 a.u. = 2 625·5 kJ/mol). Unless stated otherwise the points represent relative or absolute minima on the respective potential energy surface

Species	Symmetry	H.F.	MP2	MP3	MP4	CCD	ZPE
I	$D_{\infty h}$	213·67777	214·06249	214·05614	214·07468	214·07468	0·00710
IIa[a]	$D_{\infty h}$	165·64583	—	—	—	—	—
IIb[b]	C_{2v}	165·65048	—	—	—	—	—
IIc[c]	C_{2h}	165·65066	—	—	—	—	—
IId	C_2	165·05954	166·05954	166·06353	166·07941	166·06740	0·02950
III	C_1	189·66560	190·06196	190·06082	190·07798	190·06507	0·01800
IV		13·60980	13·60980	13·60980	13·60980	13·60980	—
V	$D_{\infty h}$	398·60243	398·98582	398·97712	398·99654	398·98236	0·00428
VIa[d]	$D_{\infty h}$	350·56230	350·96710	350·96861	350·98451	350·97348	—
VIb	C_{2h}	350·56229	350·96718	350·96865	350·98459	350·97354	0·02515
VII	$C_{\infty v}$	374·58313	374·97723	374·97362	374·99127	374·97869	0·01496
VIII	—	198·81211	198·81211	198·81211	198·81211	198·81211	—
IX	—	99·35048	99·52661	99·52751	99·53075	99·52916	—
X	—	75·33266	75·52584	75·52996	75·53442	75·53198	0·00770

[a] Four imaginary frequencies. [b] One imaginary frequency, 207 i cm^{-1}. [c] One imaginary frequency, 191 i cm^{-1}. [d] Two small imaginary frequencies, 16 i cm^{-1}.

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* 1 Å = 0·1 nm

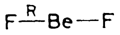
The calculated BeO and MgO bond lengths in *IId*, *III*, *VIb* and *VII* lie between those observed[11] for molecular beryllium and magnesium oxides and ionic lattices containing BeO bonds (in ZnO-type ionic lattices) and MgO bonds (in NaCl-type

TABLE II

6-31G** optimized geometry (Å, degrees) and harmonic frequencies of vibrational modes (cm^{-1}) for the studied species

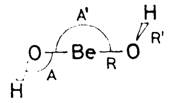
Species[a]	Symmetry	Geometry	Frequency
I	$D_{\infty h}$	$R = 1{\cdot}371$	337 (2×), 766, 1 675
IId[b]	C_2	$R = 1{\cdot}419$, $R' = 0{\cdot}937$, $A = 129{\cdot}1$, $A' = 180{\cdot}0$	206, 303, 323, 571, 772, 1 601, 4 299, 4 302
III[c]	C_1	$R = 1{\cdot}376$, $R' = 1{\cdot}410$, $R'' = 0{\cdot}936$, $A = 178{\cdot}6$, $A' = 132{\cdot}9$	305, 351, 515, 772, 1 643, 4 317
V	$D_{\infty h}$	$R = 1{\cdot}723$	150 (2×), 614, 962
VIb	C_{2h}	$R = 1{\cdot}728$, $R' = 1{\cdot}747$, $R'' = 0{\cdot}932$	88, 109, 116, 167, 168, 665, 967, 4 378, 4 379
VII	$C_{\infty v}$	$R = 1{\cdot}728$, $R' = 1{\cdot}717$, $R'' = 0{\cdot}932$	136 (2×), 158 (2×), 629, 967, 4 380

[a] For easier orientation, structural formulas are depicted below. [b] The dihedral angle H—O—O—H is 94·9°. [c] The dihedral angle F—Be—O—H is 170·8°.

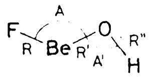


$\mathrm{F\overset{R}{-}Be-F}$

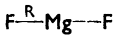
I



IId

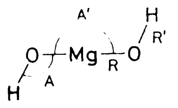


III

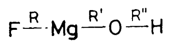


$\mathrm{F\overset{R}{-}Mg-F}$

V



VIb



$\mathrm{F\overset{R}{-}Mg\overset{R'}{-}O\overset{R''}{-}H}$

VII

ionic lattices). There is a great deal of similarity between the structural and geometrical features of FMgOH ($C_{\infty v}$, *VII*) and characteristics reported in ref.[10] for HMgOH ($C_{\infty v}$). In contrast to this FBeOH is bent (C_1) and HBeOH linear.

A number of saddle points were also located. The saddle point *VIa* represents an Eyring activated complex even though it possesses two degenerate imaginary frequencies; they are a consequence of the linearity of this system. The energy of the linear transition structure *VIa* is very similar to the degenerate minima (*VIb*) which it links. This is indicative of a very flat potential surface in this region. The motion connecting the C_2 form of the $Be(OH)_2$ minimum with an equivalent C_2 structure either via a C_{2v}(*IIb*) or C_{2h}(*IIc*) activated complex is more involved than in the case of $Mg(OH)_2$; it includes a bending motion and rotation.

The number of soft or relatively soft vibrational modes is very high in all the systems under study. This can be ascribed to some similarity of these systems to intermolecular complexes (van der Waals systems). In such a non-linear intermolecular complex consisting of two subunits having m and n atoms ($m > 2$, $n > 2$) there are six intermolecular (mostly soft) vibrational degrees of freedom[12]. From this point of view, the systems under study represent three interacting atoms (e.g., BeF_2), two atoms and a diatomic (e.g., BeF(OH)) and two diatomics and an atom (e.g., $Be(OH)_2$). It can be easily shown that a supersystem consisting of three subsystems (having m, n and o atoms, where $m, n, o > 2$) possesses 12 intermolecular vibrations. The above mentioned three specific cases in this study are non-linear (linear) supersystems with 3(4), 6(7) and 7(8) intermolecular vibrational modes. Frequencies of the perturbed OH^- groups lie in the region above 4 000 cm^{-1}. In case of the Mg containing species all the remaining frequencies are below 1 000 cm^{-1}; with Be containing molecules there is always one frequency in the region of 1 600 cm^{-1}.

By inspection of Table III it is obvious that (with respect to a very small entropy effect for reactions of type (*2*) and (*3*)) the studied equilibria are shifted to the left-

TABLE III

Energy characteristics of processes (*2*) and (*3*) (kcal/mol)

Process	M	ΔE					ΔH_0	
		H.F.[a]	MP2	MP3	MP4	CCD	MP4	CCD
(*2*)	Be	−3·545	−0·151	−1·399	0·232	−0·935	2·240	1·073
(*2*)	Mg	0·929	4·907	3·734	5·610	4·073	7·480	5·943
(*3*)	Be	−2·134	1·035	−0·163	1·406	0·307	3·790	2·692
(*3*)	Mg	1·889	5·823	4·656	6·495	5·001	1·663	0·169

[a] 6-31G**.

-hand side, i.e. to the side of the bonded fluoride anion and free hydroxide ion. In this connection the following consideration is topical. The published[13] heats of formation permit one to easily obtain the following heats of dissociation*:

$$BeF_2 \rightarrow BeF^{\bullet} + F^{\bullet} \quad \Delta H_{298} = 167\ \text{kcal/mol} \tag{4}$$

$$MgF_2 \rightarrow MgF^{\bullet} + F^{\bullet} \quad \Delta H_{298} = 139\ \text{kcal/mol} \tag{5}$$

$$CaF_2 \rightarrow CaF^{\bullet} + F^{\bullet} \quad \Delta H_{298} = 143\ \text{kcal/mol}\,. \tag{6}$$

In the cited paper[6] the following *ab initio* dissociation energies for BeOH, MgOH and CaOH were found: 108·4, 78·1 and 95·7 kcal/mol. There is, indeed, a close correlation with reaction heats of processes (*4*)–(*6*) as proposed in work[6]. This suggests that the still missing ΔH_0 value for reactions (*7*) and (*8*) will lie between the values given in Table III

$$CaF_2 + OH^- \rightarrow CaF(OH) + F^- \tag{7}$$

$$CaF(OH) + OH^- \rightarrow Ca(OH)_2 + F^- \tag{8}$$

for the Be and Mg derivatives.

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* 1 kcal/mol = 4·184 kJ/mol