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Infrared Spectra of the Group 2 Metal Dihydroxide Molecules

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Group 2 metal atoms (Mg, Ca, Sr, and Ba) react on ultraviolet photoexcitation with O_2, H_2 mixtures in solid argon at 10 K to produce new absorptions in the O–H and O–M–O stretching regions. The effect of detailed isotopic substitution on these two absorptions identifies the $M(OH)_2$ molecules. The stepwise decrease in the O–H stretching modes in this chemical family demonstrates an increase in ionic character, which parallels the increase in base strength for the analogous solid compounds.

Group 2 metal dihydroxides are stable solids known to most chemists for their increasing strength as bases with the heavier metals.[1] However, the isolated $M(OH)_2$ molecules have received little experimental investigation. The strongest infrared absorption of $Ca(OH)_2$ was observed in the metal−oxide stretching region on photolysis of argon matrix samples containing Ca atoms and water.[2] The $Be(OH)_2$ species was produced in the reaction of laser-ablated Be atoms and water, and a C_2 structure with a linear OBeO linkage was computed for this molecule at the B3LYP level.[3] Further electronic structure calculations have been done for the $M(OH)_2$ molecules with the MP2 method (M = Be, Mg, Ca) and at the HF level (M = Ca, Sr, Ba).[4,5] The Be species retains C_2 symmetry, and the Mg and Ca dihydroxides favor linear structures, but the Sr and Ba dihydroxides give bent structures at the HF level of theory. Finally, the $M(OH)_2$ molecules have not been observed in the gas phase as even the MOH molecules require the $MO + H_2$ or $M + H_2O$ reaction for mass spectrometer measurement of dissociation energies.[6]

More extensive electronic structure calculations have been done on the group 2 MOH molecules.[7−10] Trends in the bending potentials from calculations and experimental observations for these linear molecules[11−15] suggested increased ionic character in this series, which also corresponds with a major increase in solubility of the solid $M(OH)_2$ compounds.[1]

Oxidative insertion reactions of Mg, Ca, Sr, and Ba atoms with water have been investigated in solid argon matrices.[2] On photoexcitation of the metal atom, the major product is the metal hydroxy hydride molecule, HMOH. With a second water molecule present in the matrix cage, the $Ca(OH)_2$ molecule is also formed.[2] However, water as a reagent in matrix-isolation investigations has some disadvantages: the O−H stretching region often masks important product absorptions, and contamination with water impurity in the system prevents pure isotopic substitution. We have discovered that reactions of metal atoms with mixtures of O_2 and H_2 provide some but not all of the same products as water without the above disadvantages. These reactions first form the OMO dioxide, which inserts into H_2 to produce the $M(OH)_2$ molecule.

Laser-ablated Mg, Ca, Sr, and Ba atom reactions with O_2 and H_2 in excess argon during condensation at 10 K were performed as described in detail previously.[16−19] The Nd:YAG laser fundamental (1064 nm, 10 Hz repetition rate with 10 ns pulse width, 5 mJ/pulse) was focused onto the rotating metal target. FTIR spectra were recorded at 0.5 cm^{-1} resolution on a Nicolet 750 with 0.1 cm^{-1} accuracy using a HgCdTe detector. Matrix samples were annealed at different temperatures and irradiated by a mercury arc lamp (Philips,

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Table 1. New Infrared Absorptions (cm^{-1}) Produced on Ultraviolet Irradiation of M/O_2/H_2 Samples in Excess Argon

M	$^{16}O_2 + H_2$	$^{16,18}O_2 + H_2$	$^{18}O_2 + H_2$	$^{16}O_2 + HD$	$^{18}O_2 + HD$	$^{16}O_2 + D_2$	$^{18}O_2 + D_2$
Mg	3829.8	3829.7, 3817.6	3817.7	3829.7, 2825.5		2825.5	2807.5
	867.2	867.2, 858.9, 850.0	850.0	861.6		854.8	837.8
Ca	3784.6	3784.3, 3772.3	3772.4	3784.4, 2791.8	3772.3, 2774.4	2792.0	2774.6
	592.4	592.4, 585.1, 575.3	575.3	593.6	578.6	594.8	581.0
Sr	3760.6	3760.8, 3749.2	3748.9	3760.2, 2773.8		2773.6	2756.6
	479.0	479.3, 459.9	460.3	480.2, 471.0		470.6	452.8
Ba	3724.2	3724, 3712	3712.6	3724.2, 2746.6		2746.6	
	422.8	422.8, 413	404 sh	417.4		414.4	

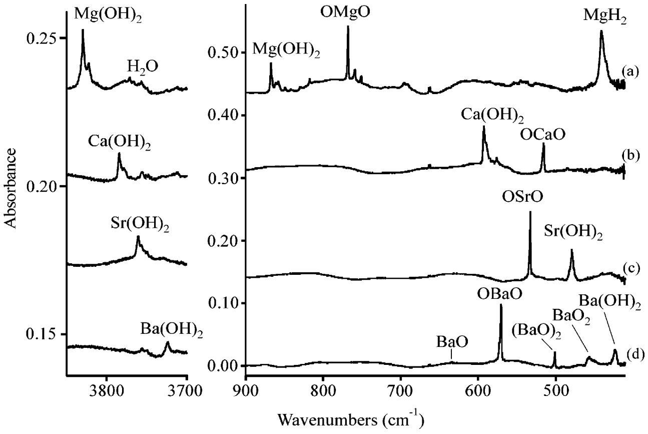

Figure 1. Infrared spectra in the 3850−3700 and 900−410 cm^{-1} regions for ultraviolet photochemical reactions of laser-ablated Mg, Ca, Sr, and Ba atoms with 0.4% O_2 and 6% H_2 in solid argon at 10 K: (a) Mg, (b) Ca, (c) Sr, and (d) Ba.

175 W, globe removed) using optical filters for 20 min periods. Complementary B3LYP calculations were performed using the Gaussian 98 program,[20] the 6-311++G(3df,3pd) basis for H, Mg, and Ca, and the SDD pseudopotential and basis for Sr and Ba.

Infrared spectra of the products of Mg, Ca, Sr, and Ba reactions with O_2 and H_2 in excess argon after ultraviolet mercury arc irradiation are illustrated in Figure 1. New associated absorptions observed in the O−H and M−O stretching regions, not found in previous investigations with each reagent separately,[16−19] are listed in Table 1. These bands exhibited $^{18}O_2$ and D_2 shifts, and diagostic information was obtained with the mixed isotopic $^{16}O_2$ + $^{16}O^{18}O$ +$^{18}O_2$ and HD reagents. The effect of isotopic substitution on the spectra is shown in Figure 2 for the Ca system. The triplet absorption with the scrambled isotopic oxygen sample shows that two equivalent O atoms are involved in this product molecule, just as is found for the bent OCaO calcium dioxide molecule.[17] The HD reagent gave almost the same bands in the O−H and O−D stretching region as H_2 and D_2 and one new band in the Ca−O stretching region. This shows that two O−H(O−D) groups are part of this molecule. Analogous spectra are observed for the other metals. In the Mg case, natural ^{25}Mg and ^{26}Mg splittings on the strong ^{24}Mg product band show that a single Mg atom is involved, like that observed for OMgO.[16] Thus, from isotopic substitution at all atomic positions, we have identified the $M(OH)_2$ molecules.

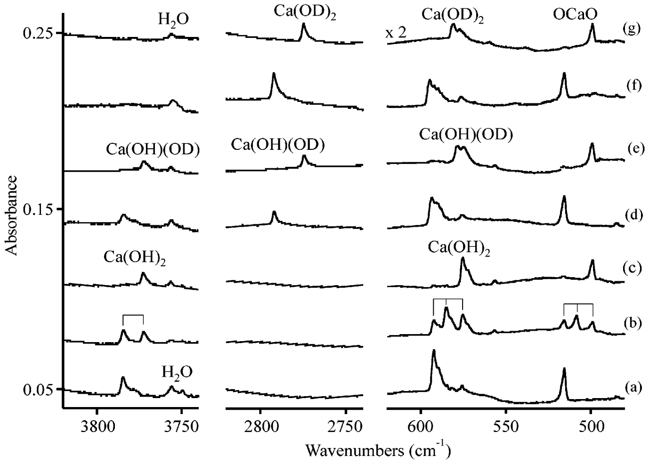

Figure 2. Infrared spectra in the 3820−3740, 2820−2740, and 620−480 cm^{-1} regions for ultraviolet photochemical reactions of laser-ablated Ca atoms with 0.4% O_2 and 6% H_2 in solid argon at 10 K: (a) $^{16}O_2 + H_2$, (b) $^{16,18}O_2 + H_2$, (c) $^{18}O_2 + H_2$, (d) $^{16}O_2$ + HD, (e) $^{18}O_2$ + HD, (f) $^{16}O_2 + D_2$, and (g) $^{18}O_2 + D_2$. Absorbance scale × 2 for the lowest region.

The 3829.4, 3784.6, 3760.6, and 3724.2 cm^{-1} bands are assigned to the antisymmetric O−H stretching mode in the $M(OH)_2$ molecules. The H/D isotopic frequency ratios (1.3555 ± 0.0001) and 16/18 isotopic frequency ratios (1.00317 ± 0.00005) attest to this assignment. The 867.2, 592.4, 479.0, and 422.8 cm^{-1} bands are due to antisymmetric O−M−O stretching modes, and their 16/18 ratios are near those found for the O−M−O dioxide molecules.[16,17]

The 3784.6 and 592.4 cm^{-1} absorptions we observe for $Ca(OH)_2$ in solid argon are very close to the 3778 and 610 cm^{-1} fundamentals for gaseous CaOH.[14] This indicates similar bonding in the group 2 mono- and dihydroxide molecules, and our calculations predict the same O−H bond length. We expect the O−H stretching modes for the gaseous $M(OH)_2$ molecules to be about 20 cm^{-1} higher than the argon matrix values.

The calculation of floppy molecules with flat bending potentials is a difficult theoretical problem,[5,7−10] but B3LYP computations provide useful information to help assign infrared spectra for the $M(OH)_2$ molecules. Calculation of $Mg(OH)_2$ gave a Mg−O−H angle of 155.6° and real

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Table 2. Frequencies, Bond Lengths, and Charges Calculated on the Metal Center for HOMOH Molecules Converged at the B3LYP Level

metal	M−O, O−H, Å	O−M−O, deg	*q* (M)	frequencies, cm^{-1} (infrared intensities, km/mol)[a]
Mg	1.772, 0.949	180	+1.05	4032(1), 4032(157), 906(198), 610(1), 162(1), 153(29), 153(50), 118(224), 21(219)
Ca	2.038, 0.954	170	+1.56	3960(2), 3960(82), 619(397), 525(1), 439(0), 438(1), 432(282), 432(268), 41(41)
Sr	2.186, 0.955	155	+1.58	3941(43), 3941(3), 491(3), 491(312), 433(0), 424(268), 423(257), 420(4), 29(32)
Ba	2.302, 0.956	127	+1.51	3918(29), 3918(9), 470(30), 441(307), 393(292), 388(0), 366(272), 329(30), 91(17)

[a] Symmetric or antisymmetric O−H, antisymmetric or symmetric O−M−O stretching, M−O−H and O−M−O bending modes, respectively.

frequencies. However, for the Ca, Sr, and Ba dihydroxide molecules, it was necessary to fix the M−O−H angle as linear, as found for the MOH molecules,[7−15] to obtain convergence with all real frequencies. Table 2 summarizes the most important results of our calculations. Notice that the O−H bond length increases, the O−H stretching frequency decreases, and the Mulliken charge on the metal center increases going down the family group. This points to an increase in ionic character that matches the base strength of the solid compounds.[1] However, cation−anion polarization and $p_\pi \rightarrow d_\pi$ interaction prevent these frequencies from reaching the ionic limit of gaseous OH^- (3556 cm^{-1}).[21] The calculations predict the strong O−H and O−M−O stretching modes (2−5% too high) and describe the observed patterns of isotopic substitution, which substantiates our assignments to the $M(OH)_2$ molecules.

This first combined experimental and theoretical investigation of two strong infrared absorptions for the alkaline earth metal dihydroxide molecules provides evidence that the HOMOH molecules bend more at the metal center with increasing mass, just as found in HF level calculations[5] and for the metal dihalides[22] and dihydrides,[18,19] which again underscores the importance of metal d orbital participation in the small metal valence populations and polarization of the subvalence shell.[23] Kaupp and Schleyer discuss how π-type bonding contributions keep the group 2 metal dihydroxides from bending as much as the difluorides.[23] We cannot rule out a linear structure for $Ca(OH)_2$, as computed earlier.[4,5] Finally, we observe a decrease in the O−H stretching frequency in the family series, which parallels an increase in ionic character for the molecules and base strength for the solid compounds.[1]

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