J. Braz. Chem. Soc., Vol. 17, No. 4, 741-745, 2006.
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0103 - 5053 $6.00+0.00

Article

Computational Study of the Solid-State Vibrations and Force Field of Magnesium and Calcium Hydroxides

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As vibrações no estado sólido dos hidróxidos de magnésio e cálcio foram estudadas através da análise de coordenadas normais. Usando um campo de força simples, de curto alcance, foram obtidas boas concordâncias entre as freqüências calculadas das vibrações normais e as fundamentais experimentalmente observadas. Algumas bandas fundamentais foram estimadas por meio de cálculos. Os cálculos de freqüência para os três modelos de cluster, através do método Hartree-Fock, indicam que o desdobramento dos estiramentos do grupo hidroxila pelo campo de correlação é principalmente originado em interações entre camadas.

The solid-state vibrations of magnesium and calcium hydroxides have been studied by normal coordinate analysis. Using a simple short-range force field, the calculated frequencies of normal vibrations are in good agreement with the experimentally observed fundamentals. Some fundamental bands have been estimated by calculations. Hartree-Fock frequency calculations on three model clusters suggest that the correlation field splitting of the hydroxyl group stretching vibrations mainly originates in the interlayer interactions.

Keywords: magnesium hydroxide, calcium hydroxide, normal coordinate analysis, solid-state vibrations

Introduction

After a long controversy about interpretation of low-frequency infrared bands, a new assignment has been proposed for the brucite-type metal hydroxides.[1-3] According to the empirical linear relationship of the infrared OH stretching frequencies against physical-chemical data that characterizes the solid-state metal hydroxides, magnesium and calcium hydroxides belong to the same group of hydroxides.[4-7] This new proposal in assignment of magnesium hydroxide seems to be consistent with the assignment of the calcium analogue by Lutz *et al.*[8] With respect to the Raman spectra, the Raman active fundamentals are well established for both the hydroxides by aid of a single crystal Raman polarization measurement.[9-11] Hence, the fundamental frequencies of the solid-state vibrations of the magnesium and calcium hydroxides are almost completely known from experiment for the normal compounds and their deuterated analogues. Although Oehler and Günthard[12] reported the frequency calculations of the solid-state calcium hydroxide, band assignment of the observed spectral data based on the dispersion surface calculations is not in agreement with the later vibrational analysis.[8-11]

In this article, normal coordinate analysis for single crystals was carried out on the magnesium and calcium hydroxides, using a simple short-range force field. The eight force constants were refined to fit the calculated normal frequencies to the fundamental frequencies observed in the infrared and Raman spectra. The interactions between the polarized OH groups, which are responsible to correlate field band splitting on the OH stretching vibrations (νOH), are discussed in terms of the force constants and also based on the quantum chemical calculations performed on three types of clusters.

Crystal structure and selection rule

Crystal structure of the hydroxide of interest ($P\overline{3}\,ml \equiv D_{3d}^{3}$) is illustrated in Figure 1. The layer structure consists of trigonal sheets of metal ions attached by hydroxide groups on both sides of the sheets. The nearest neighbor layers interact on each other by interlayer force, which mainly arises from electrostatic interactions of the

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closed and oppositely directed hydroxide groups. According to neutron diffraction structural analysis, the lattice constants are a = 3.148 Å, c = 4.779 Å, z_O = 0.2187 and z_H = 0.4169 for $Mg(OH)_2$ and a = 3.589 Å, c = 4.911 Å, z_O = 0.2337 and z_H = 0.4256 for $Ca(OH)_2$.[13,14] Since the unit cell of brucite-type crystals contains one formula unit of $M(OH)_2$, factor group analysis at the Brillouin zone center (**k**=0) yields the structure of the reduced representation: $\Gamma = 2A_{1g} + 2E_g + 2A_{2u} + 2E_u$. The vibrations of A_{1g} and E_g species are Raman active, while the vibrations of A_{2u} and E_u species are active in infrared spectra.

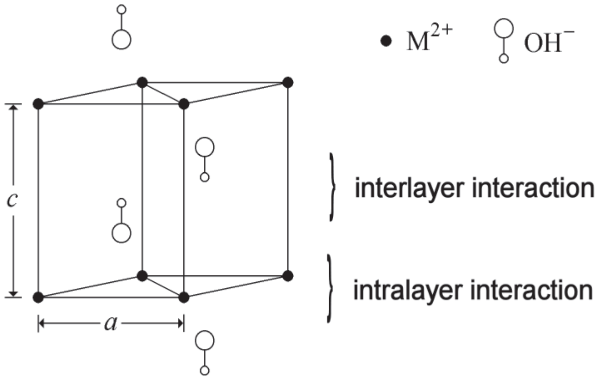

Figure 1. Unit-cell structure of brucite-like $M(OH)_2$, showing lattice constants a and c.

Results and Discussion

Single crystal normal coordinate analysis, based on Cartesian symmetry coordinates, was carried out in accordance to the Wilson's GF matrix method, using the NCT program package.[15] The short-range force field is expressed by two bond stretch force constants, f(OH) and f(MO), and three non-bonded neighbor interactions f(H...H), f(O...H) and f(O...O). Three additional cross-terms, f(OH/OH), f(MO/OM) and f(MO/OM)', are also necessary for good reproduction of the experimental fundamentals. Table 1 summarizes the final values of the force constants refined against the experimental frequencies. The observed and calculated frequencies are given in Table 2 (magnesium hydroxide) and Table 3 (calcium hydroxide).

Table 1. Force constants (mdyn Å^{-1})

Force Constant	$Mg(OH)_2$ and $Mg(OD)_2$ Set 1	Set 2	$Ca(OH)_2$ and $Ca(OD)_2$ Set 1	Set 2
f(OH)	7.397	7.324 (H) 7.534 (D)	7.315	7.254 (H) 7.429 (D)
f(OH/OH)	-0.092	-0.092	-0.066	-0.066
f(MO)	0.955	0.954	0.780	0.779
f(MO/OM)	0.367	0.367	0.274	0.273
f(MO/OM)'	-0.041	-0.041	-0.008	-0.009
f(H...H)	0.077	0.077	0.071	0.071
f(O...H)	0.143	0.143	0.087	0.087
f(O...O)	-0.028	-0.028	-0.027	-0.027

Set 1 force constants were refined with the observed frequencies of both of the normal hydroxide and its deuterium analogue. The values of f(OH) for the Mg compound (7.397 mdyn Å^{-1}) and the Ca compound (7.315 mdyn Å^{-1}) are almost the same. Agreement between the calculated and observed frequencies is very good for such a simple potential function and discrepancies are found only in the hydroxyl group stretching bands. Set 2 force constants were determined similarly, but based on a consideration that the value of f(OH) can be different between the OH and OD compounds, possibly to compensate the effect of an anharmonicity under harmonic approximations. The hydroxyl group stretching frequencies become very close to the experimental fundamentals. It is worth noting that the differentiated f(OH) force constants do not affect the optimized values of the remaining force constants, consequently the frequencies of the external vibrations. The ratios of f(OH) between isotopic hydroxides (7.534/7.324 = 1.029 for Mg and 7.429/7.254 = 1.024 for Ca) are comparable to the mean value (1.026) computed for diverse molecular systems.[16]

Table 2. Observed and calculated frequencies (cm^{-1}) of magnesium hydroxide

	$Mg(OH)_2$				$Mg(OD)_2$			
	Obs.		Calc.		Obs.		Calc.	
	Raman[a]	Infrared[b]	Set 1	Set 2	Raman[a]	Infrared[b]	Set 1	Set 2
A_{1g}	3652		3673	3655	2696		2668	2692
	443		445	444	434		433	433
E_g	725		720	720	506		513	513
	280		279	279	277		278	278
A_{2u}		3698 s	3713	3695		2725 s	2705	2729
		562 w	562	562		(549)[c]	555	555
E_u		462 s	461	462		410 s	406	406
		368 s	373	373		305 s	305	305

[a]Reference 9; [b]reference 2; [c]shoulder band (not used for refinement).

Table 3. Observed and calculated frequencies (cm^{-1}) of calcium hydroxide

	$Ca(OH)_2$				$Ca(OD)_2$			
	Obs.		Calc.		Obs.		Calc.	
	Raman[a]	Infrared[b]	Set 1	Set 2	Raman[a]	Infrared[b]	Set 1	Set 2
A_{1g}	3620		3634	3619	2661		2643	2663
	357		359	358	350		349	349
E_g	680		676	676	475		480	480
	254		254	254	252		252	252
A_{2u}		3645	3661	3646		2689	2667	2686
		(415)[c]	418	418		411	411	411
E_u		392	391	392		(303)[d]	347	347
		312	312	312		(275)[d]	253	253

[a]Reference 9; [b]reference 8; [c]shoulder band (not used for refinement); [d]see text (not used for refinement).

To describe the weak interaction functions between hydroxyl group sheets, two types of forces might be considered; non-bonded forces acting between two near neighbor atoms and the dipole-dipole interaction force. Inclusion of three atom-atom neighbor interaction force constants f(H...H), f(O...H) and f(O...O) is necessary to reproduce some external vibration frequencies. However, these terms alone are insufficient to express an effective correlation field band splitting observed for the OH stretching vibrations. On the other hand, the dipole-dipole interaction force constant f(OH/OH) does not contribute in any way to the lattice modes of vibration, but the small values, -0.092 mdyn Å^{-1} (Mg) and -0.066 mdyn Å^{-1} (Ca), are needed and cause correlation field separation of the OH stretching bands.

In normal coordinate analysis in the form applied in the present study, however, the OH/OH interaction term is interpretable as a case of close-neighbor interlayer interactions, as an intra-layer interaction of two opposite side hydroxyl anions on same metal ion plane or as the global sum of two types of interactions. Then, to understand better the correlation field splitting, *ab-initio* calculations were performed at the Hartree-Fock (HF) level for the three cluster models illustrated in Figure 2, $[M_8(OH)_2]^{14+}$, $[M_{10}(OH)_2]^{18+}$ and $[M_{16}(OH)_6]^{26+}$, by the GAMESS program,[17] using the valence only basis sets with core effective potentials CEP-31G for Mg and Ca, while the 6-31G standard Pople valence split basis sets were used for O and H. Additional polarization and diffuse functions were also considered in these calculations. During geometry optimization, all metal-oxygen distances were kept unchanged to the values given by neutron diffraction studies,[13,14] whereas moving hydrogen atoms along the c-axis was allowed to optimize the OH bond distances. Analytical frequency calculations were performed for the respective optimized cluster structures. Although, the OH stretching frequencies might be useful to interpret the effect of the correlation field on the νOH bands, the external normal vibrations computed for such model calculations are, of course, meaningless and not analyzed.

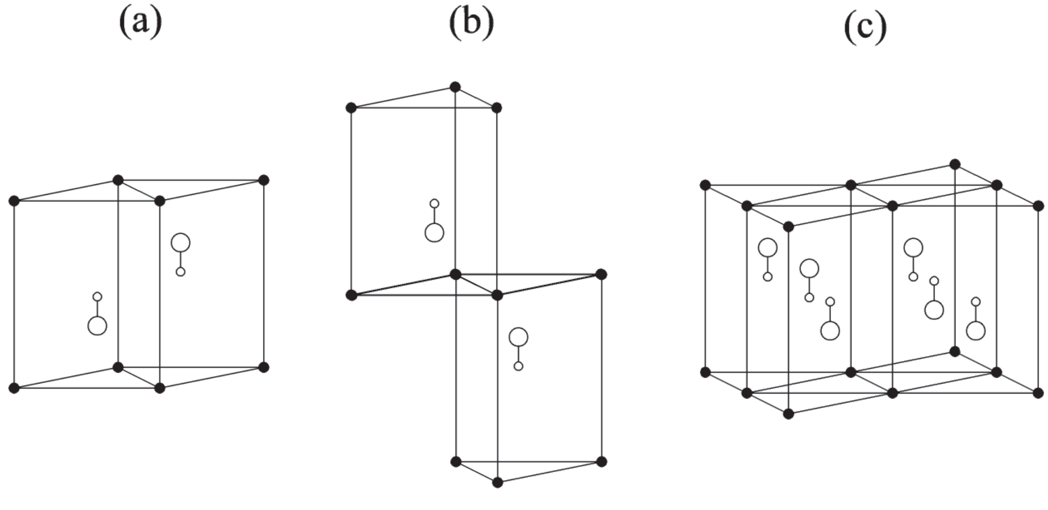

Figure 2. Model clusters: (a) $[M_8(OH)_2]^{14+}$, (b) $[M_{10}(OH)_2]^{18+}$ and (c) $[M_{16}(OH)_6]^{26+}$.

Table 4. Basis set, ab-initio OH stretching wavenumbers (in cm^{-1}; $\tilde{\nu}_u$, out of phase; $\tilde{\nu}_g$, in phase) and correlation field splitting ($\Delta\tilde{\nu} = \tilde{\nu}_u - \tilde{\nu}_g$) of $[M_8(OH)_2]^{14+}$, $[M_{10}(OH)_2]^{18+}$ and $[M_{16}(OH)_6]^{26+}$ clusters

Bases set		$[Mg_8(OH)_2]^{14+}$			$[Mg_{10}(OH)_2]^{18+}$			$[Mg_{16}(OH)_6]^{26+}$		
Mg	O,H	$\tilde{\nu}_u$	$\tilde{\nu}_g$	$\Delta\tilde{\nu}$	$\tilde{\nu}_u$	$\tilde{\nu}_g$	$\Delta\tilde{\nu}$	$\tilde{\nu}_u$	$\tilde{\nu}_g$	$\Delta\tilde{\nu}$
CEP-31G	6-31G	4244	4231	13	4279	4277	2	4027	4008	19
CEP-31G*	6-31+G*	4271	4259	12	4309	4307	2	4057	4043	14
CEP-31G*	6-31++G**	4332	4317	15	4376	4375	1	4109	4092	17
Bases set		$[Ca_8(OH)_2]^{14+}$			$[Ca_{10}(OH)_2]^{18+}$			$[Ca_{16}(OH)_6]^{26+}$		
Ca	O,H	$\tilde{\nu}_u$	$\tilde{\nu}_g$	$\Delta\tilde{\nu}$	$\tilde{\nu}_u$	$\tilde{\nu}_g$	$\Delta\tilde{\nu}$	$\tilde{\nu}_u$	$\tilde{\nu}_g$	$\Delta\tilde{\nu}$
CEP-31G	6-31G	4169	4165	4	4182	4178	4	4044	4033	11
CEP-31G*	6-31+G*	4240	4235	5	4250	4246	4	4095	4084	11
CEP-31G*	6-31++G**	4311	4304	7	4326	4322	4	4155	4143	12

Figure 2(a) is a cluster $[M_8(OH)_2]^{14+}$ to estimate close interlayer interaction of one hydroxyl group pair surrounded by metal ions, while the intra-layer pair interaction is modeled as a cluster $[M_{10}(OH)_2]^{18+}$ in Figure 2(b). Table 4 summarizes the calculated νOH frequencies and the splitting ($\Delta\tilde{\nu} = \tilde{\nu}_u - \tilde{\nu}_g$) between the asymmetric ($\tilde{\nu}_u$) and symmetric ($\tilde{\nu}_g$) modes for the basis sets employed in this study. The experimental correlation field separations, between the infrared and Raman active O-H stretching bands, are 46 cm^{-1} for $Mg(OH)_2$ and 29 cm^{-1} for $Mg(OD)_2$ (Table 2).[2,9] The theoretically simulated separations of ~10 cm^{-1} are counted to $[Mg_8(OH)_2]^{14+}$ and few wavenumbers are to $[Mg_{10}(OH)_2]^{18+}$. So that, it is found that the intra-layer interaction force is too small to explain the correlation field. The aspect is different for calcium hydroxide, only some wavenumbers of separation are computed for both clusters, $[Ca_8(OH)_2]^{14+}$ and $[Ca_{10}(OH)_2]^{18+}$, nevertheless the experimental $\Delta\tilde{\nu}$ is measured as 25 cm^{-1} for $Ca(OH)_2$ and 27 cm^{-1} for $Ca(OD)_2$ (Table 3).[8,9] Hence, further calculations were performed on the interlayer system using an extended $[M_{16}(OH)_6]^{26+}$ cluster in which each central hydroxyl group is surrounded by three groups of neighbor layers, just as seen in crystals. The band separation between two central hydroxyl vibrations is about 15 cm^{-1} for this $[Mg_{16}(OH)_6]^{26+}$ cluster, larger than the value for $[Mg_8(OH)_2]^{14+}$, and is approximately half of the experimental band splitting. For the $[Ca_{16}(OH)_6]^{26+}$ cluster, a band separation of about 10 cm^{-1} is calculated, also approximately half of the experimental value. Then, it is concluded that the crystal correlation effect on the nOH fundamentals is principally due to interlayer forces between the piled hydroxyl groups. The larger band splitting in magnesium hydroxide compared with the splitting in calcium hydroxide obtained from the calculation is consistent with the experimental observation.

With respect to the cation-anion interactions, the metal-oxygen bond force constants, f(MO), are 0.955 mdyn Å^{-1} (Mg) and 0.780 mdyn Å^{-1} (Ca). The difference of about 20% indicates that the MO stretching band frequencies are not simply explained by the metal atomic masses, but also essentially due to the MO bonding character. Two metal-oxygen bond-bond interaction force constants, f(MO/OM) and f(MO/OM)', describe *cis*-interaction between two M-O bonds connected to a common metal atom in an MO_6 octahedral coordination structural unit. The first, f(MO/OM), relates to the same side hydroxyl groups attached about the metal ion sheet, the second, f(MO/OM)', is between two opposite side hydroxyl groups. The former interaction force, 0.367 mdyn Å^{-1} (Mg) and 0.274 mdyn Å^{-1} (Ca), has an important contribution to express the potential function of the brucite-type hydroxides, while the opposite side interaction force, -0.041 mdyn Å^{-1} (Mg) and -0.008 mdyn Å^{-1} (Ca), carries a complementary role.

The normal coordinate analysis predicted values of the experimentally uncertain fundamental frequencies are included in Tables 2 and 3. In the case of magnesium hydroxide, only one infrared active A_{2u} frequency of $Mg(OD)_2$ is missing. The computed frequency of 555 cm^{-1} is close to the estimated one at 549 cm^{-1}, which was derived from the corresponding $Mg(OH)_2$ weak band at 562 cm^{-1} by application of the isotope product rule and located on high wavenumber side shoulder of the asymmetrically broad band at 410 cm^{-1}.[2,3] In $Ca(OH)_2$, the calculated low-frequency A_{2u} mode of 418 cm^{-1} is in agreement with the assignment of ~415 cm^{-1} on shoulder of the strong and broad band at 392 cm^{-1} and shifts to 411 cm^{-1} on deuteration.[8] Lutz *et al.* assigned two infrared bands of $Ca(OH)_2$ at 392 and 312 cm^{-1} as the E_u fundamentals. On the other hand, the infrared spectra of $Ca(OD)_2$ give only one band (303 cm^{-1}) at room temperature, while two peaks (310 and 265 cm^{-1}) are found at 95 K. So that, the E_u bands of

$Ca(OD)_2$ were not used to refine the force constants. The calculated E_u frequencies for the optimized force constants are 347 and 253 cm^{-1}; those are not in good agreement with the experimental fundamental frequencies.

Conclusions

The results of normal coordinate analysis supported the band assignments of the solid-state vibrations of magnesium and calcium hydroxides proposed in literature.[2,8,9] The calculated frequencies are in good agreement with the fundamentals observed in both internal and external vibrations and well-reproduced isotopic shifts of the infrared and Raman bands. Some experimentally uncertain fundamental band positions were also predicted by normal coordinate calculations.

The refined force field parameters showed that the dipole-dipole interaction force constant f(OH/OH) was necessary to express the correlation field band splitting of the OH stretching vibrations. Moreover, the Hartree-Fock cluster model calculations revealed that the interlayer interactions of the hydroxyl groups are responsible to this correlation effect. On the other hand, the neighbor atom-atom interaction force constants f(H…H), f(O…H) and f(O…O) were needed to estimate the low-frequency lattice vibrations.

Acknowledgments

This work was financially supported in part by FAEP/UNICAMP. Professor C. H. Collins' assistance in revising this manuscript is gratefully acknowledged.

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Received: July 20, 2005
Published on the web: May 26, 2006

FAPESP helped in meeting the publication costs of this article.