STABILIZING SMALL PARTICLES OF LITHIUM HYDROXIDE WITH ADSORBED WATER MOLECULES: A QUANTUM CHEMICAL STUDY

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Abstract

Quantum chemical calculations have been carried out of the energetic and geometric characteristics of the lithium hydroxide molecular models within the frameworks of both semiempirical (the MNDO method) and *ab initio* (the STO-3G and 6-31G basises being used) approaches. The adsorption of water molecules has been shown to result in stabilizing small particles of the compound. The vibrational spectra of the LiOH microcrystallites have been also examined.

Introduction

Molecular models of solids are widely used now as effective tools for the study of their bulk and surface physicochemical properties [1]. The simulation of the compounds having structures with the great atomic coordination numbers is of particular interest because the taking frontier conditions into account in such cases meets definite difficulties and is a non-trivial problem [2].

The aim of this work is the construction and quantum chemical analysis of the molecular models of lithium hydroxide, the selection of them as objects for investigation being conditioned by its relatively simple structure and practicality [3]. This compound has a layered tetragonal system lattice with a "wafer" structure [4]. The coordination environment of any lithium atom is a distorted tetrahedron and any hydroxyl group has four lithium atoms as the nearest neighbours, all OH groups being stationed in the layers alternatively on either side of the plane of lithium atoms. Hydrogen bonds are absent between the layers.

The geometrical structure as well as the force field and vibrational spectra of the $Li_2(OH)_2$ molecule were examined theoretically in [5]. The detailed studies of the lithium hydroxide tetramers [6] and hexamers [7] lead the authors to the conclusion that small clusters of this compound must have equilibrium structures significantly distinct from that of the crystal. In this connection a question arises what factors cause stabilizing small lithium hydroxide clusters – precursors of the crystal.

There is a natural assumption that water molecules connected in definite way with the surface of lithium hydroxide microcrystallites can be ones of such factors. Their presence may be conditioned, firstly, by hygroscopic moisture, secondly, by the formation of condensation water, due to the equilibrium

$$2\ LiOH_{solid} \leftrightarrow Li_2O_{solid} + H_2O_{gas},$$
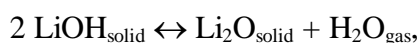
thirdly, due to the presence of the admixture of the crystal hydrate $LiOH \cdot H_2O$.

It is obvious that the firmer is the connection between water molecules and microcrystallite surface, the greater is their stabilizing effect. On evidence derived from [8, 9],

water molecules are the most tied ones on the oxide system surface when adsorbed on the "pared" Lewis surface sites formed at the expense of an elimination of the OH group that is the same for two metal atoms.

Models and Methods

The lithium hydroxide molecular models examined were built with consideration for the suggestions described above (see Fig.). Their structure and properties were studied by the SCF MO LCAO quantum chemical method within the frameworks of semiempirical MNDO approximation [10] by means of the program [11], and also in an *ab initio* way with use of the STO-3G and 6-31G basises, operating under the program [12].
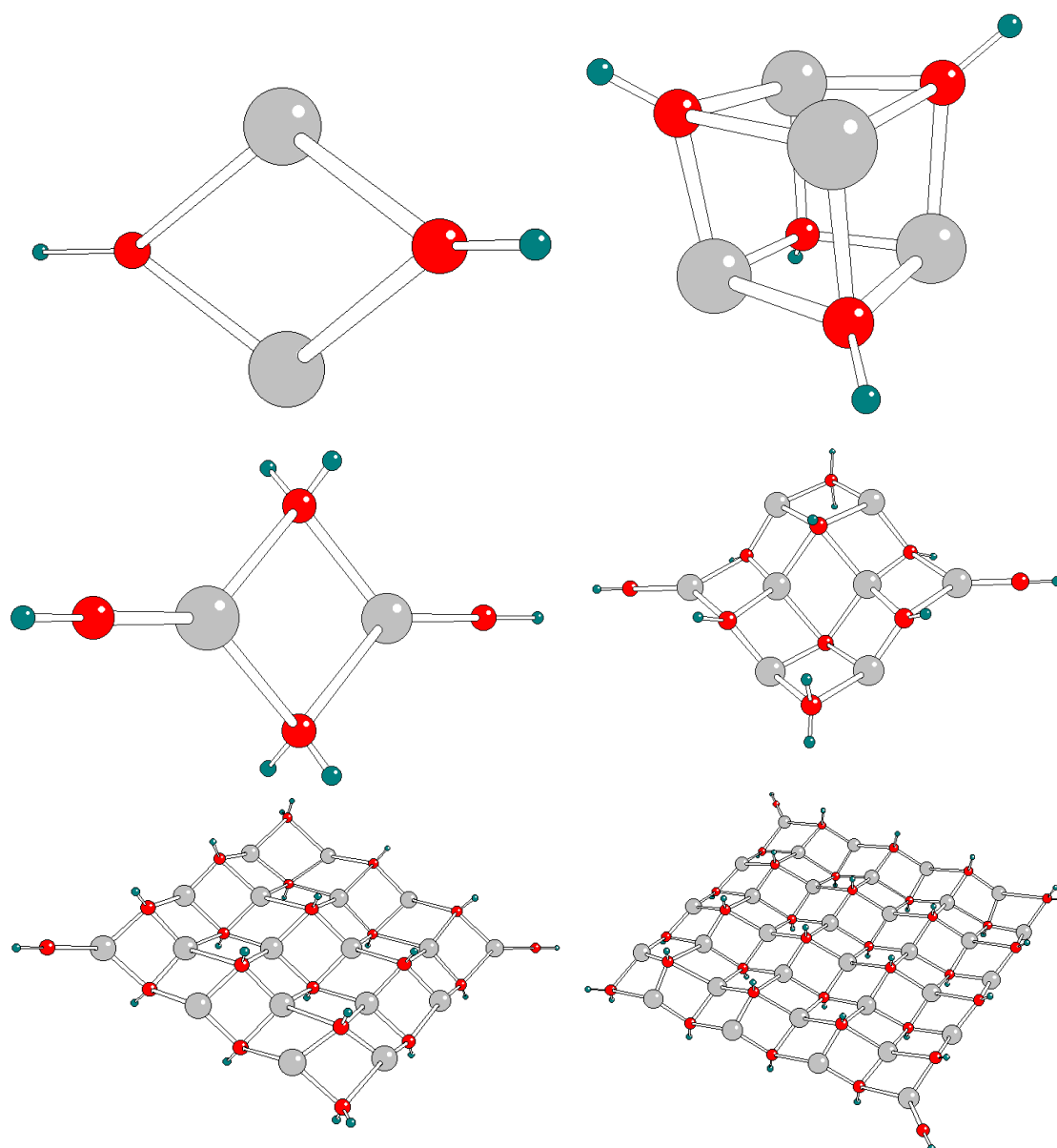

Fig. Molecular models for LiOH (big balls depict lithium atoms).

Results and Discussion

Let us consider at first the results obtained within frameworks of the MNDO method. A comparison of the experimental [4] parameters of the lithium hydroxide crystalline lattice with theoretical ones (see Table 1) shows that as a whole a semiquantitive agreement is observed between them that is only slightly affected by the model dimensions. Enlarged values of Li-O and Li-H distances as compared with the experimental ones engage our attention whereas the calculated values for the Li-Li separations fall far short of those in the crystal. As a consequence, the values of the Li-O-H angles are overestimated considerably. It seems likely that these deviations can be explained by shortcomings of the MNDO method parameterization what results in an overestimation of the values of coordination bond lengths.

Table 1. The averaged values of the equilibrium interatomic distances (pm) and valence angles (degrees) in the molecular models and in the crystal of lithium hydroxide (on evidence derived from the MNDO method).

Models	Interatomic distances				Valence angles		
	Li-Li	Li-O	Li-H	O-H	Li-O-Li	O-Li-O	Li-O-H
$(LiOH)_2$	237	193	272	92	76	104	142
$(LiOH)_4$	261	211	282	93	79	100	133
$(LiOH)_2 \cdot 2H_2O$	315	228	282	95	88	92	115
$(LiOH)_8 \cdot 2H_2O$	301	212	288	93	90	90	138
$(LiOH)_{18} \cdot 2H_2O$	305	216	281	94	90	90	125
$(LiOH)_{32} \cdot 2H_2O$	309	222	276	94	88	88	116
Exp. [4]	355	196	250	92	129	129	115

The values of the formation enthalpies of the lithium hydroxide molecular models calculated by the MNDO method (see Table 2) can be used for the evaluation of the corresponding theoretical value for the crystal of this compound provided the coordination compositions of these models are taken into consideration. Really, symbolizing a contribution into the models of the molecules with four-coordinated atoms (what answers the crystal) by the letter x, that of the molecules with three-coordinated atoms being symbolized by the letter y and the contribution of the $Li_2(OH)_2 \cdot 2H_2O$ fragment - by the letter a, we will obtain a system of equations:

$$18x + 12y + a = -13194 \qquad (1)$$
$$8x + 8y + a = -7454 \qquad (2)$$
$$2x + 4y + a = -3409 \qquad (3).$$

Subtracting both of the parts of the second equation from those of the first one and those of the third equation from the second one, another system is arrived at:

$$10x + 4y = -5740 \qquad (4)$$
$$6x + 4y = -4045 \qquad (5),$$

whence it follows that the required x value is of -424 kJ/mol what is fitted well with the experimental value that is equal to 440 kJ/mol [3]. The value y (-376 kJ/mol) coincides practically with the specific (attributed to the single molecule) formation enthalpy calculated for the globular model of $Li_4(OH)_4$ (-379 kJ/mol), and the value a (-1058 kJ/ mol) is somewhat lesser than the corresponding one for the model of $Li_2(OH)_2 \cdot 2H_2O$ (-1124 kJ/mol).

Table 2. The coordination composition and the values of the formation enthalpies calculated by the MNDO method (ΔH_f, kJ/mol) of the lithium hydroxide molecular models (upper indices indicate the atomic coordination numbers)

Models	ΔH_f
$Li^2_2(OH)^2_2$	-688
$Li^3_4(OH)^3_4$	-1516
$Li^3_2(OH)^1_2(OH_2)^2_2 \equiv Li_2(OH)_2 \cdot 2H_2O$	-1124
$Li^4_2(OH)^4_2 \cdot Li^3_4(OH)^3_4 \cdot Li_2(OH)_2 \cdot 2H_2O$	-3409
$Li^4_8(OH)^4_8 \cdot Li^3_8(OH)^3_8 \cdot Li_2(OH)_2 \cdot 2H_2O$	-7454
$Li^4_{18}(OH)^4_{18} \cdot Li^3_{12}(OH)^3_{12} \cdot Li_2(OH)_2 \cdot 2H_2O$	-13194

A comparison of the calculated vibrational spectra of the lithium hydroxide crystal [13] (see Table 3) shows the values of vibrational frequencies to be overestimated systematically. When dimensions of the models increase, the number of absorption bands grows, nevertheless for the most part they have very small intensivities (because of this, the values of frequencies are shown in the Table 3 for the most intensive bands), with the regions of vibrational frequencies of the two-coordinated Li-OH and OH_2 fragments differing from those of the vibrations of the fragments with three- and four-coordinated atoms.

In order to improve the results obtained by the MNDO method, *ab initio* calculations were carried out of the models including no more than eight lithium atoms, a minimal basis (STO-3G) and expanded one (6-31G) being used. The results of calculations are shown in the Table 4. A comparison of the data listed in the Table 1 and Table 4 testify the geometric parameters of the crystal to be reproduced, as a whole, better in the *ab initio* calculations rather in the semiempirical ones; in this case the change from the STO-3G basis to the 6-31G one, as a rule, improves considerably the accordance with the experiment.

The values of total energies of the models can be used for an estimation of the lithium hydroxide cohesion energy that is the difference between the compound formation enthalpy in the gaseous state and that in solid one (on evidence derived from [14], it is of 238 kJ/mol). Using the coordination formulae of the models with the compositions of $Li_2(OH)_2 \cdot 2H_2O$, $(LiOH)_4$, and $Li_8(OH)_8 \cdot 2H_2O$, it is an ease matter to find that the value

$$E = E[(LiOH)_8 \cdot 2H_2O] - E [(LiOH)_4] - E[Li_2(OH)_2 \cdot 2H_2O]$$

corresponds to the energy of two formula units of lithium hydroxide with four-coordinated atoms, i.e. to that of the crystalline state.

Table 3. The experimental (crystal [13]) and theoretically calculated values of the vibrational frequencies of the lithium hydroxide molecular models (ν, cm^{-1})

Vibrations	Exp.	$(LiOH)_2 \cdot 2H_2O$	$(LiOH)_8 \cdot 2H_2O$	$(LiOH)_{18} \cdot 2H_2O$	$(LiOH)_{32} \cdot 2H_2O$
A_{2u} (OH)	3677	3898	3980	3965	3960
A_{1g} (OH)	3664	3897	3949	3940	3938
E_g (T')	620	860	827	818	802
	519	593	717	697	666
A_{2u}(T')	495	518	586	527	508
E_u(T')	440	461	503	451	485
E_u (R)	419	395	423	420	444
A_{1g} (T')	329	362	366	327	369
B_{1g} (T')	299	286	331	306	338
E_g (R)	287	270	289	293	299

Table 4. The results of *ab inito* calculations on interatomic distances (pm) and valence angles (degrees) in the molecular models of lithium hydroxide

Models	Basis	Interatomic distances				Valence angles		
		Li-Li	Li-O	Li-H	O-H	Li-O-Li	O-Li-O	Li-O-H
$(LiOH)_2$	STO-3G	217	166	248	97	82	98	139
	6-31G	222	177	257	94	78	102	141
$(LiOH)_4$	STO-3G	230	177	252	98	81	98	131
	6-31G	242	189	262	95	80	99	132
$(LiOH)_2 \cdot 2H_2O$	STO-3G	267	186	242	97	91	89	116
	6-31G	278	202	257	95	87	93	114
$(LiOH)_8 \cdot 2H_2O$	STO-3G	325	187	243	97	121	121	114
	6-31G	346	204	249	94	116	116	108

Thus, we have for the STO-3G basis

$$2\,E(\text{STO-3G}) = -805.189967 - (-327.623029) - (-313.693358) = -163.873590 \text{ a.u.},$$

cohesion energy

$$E_{cohes} (STO\text{-}3G) = E(STO\text{-}3G) - E_{STO\text{-}3G}(LiOH) =$$
$$= \frac{1}{2} (-163.873590) - (-81.768565) = -0.16823 \text{ a.u. } (-442 \text{ kJ/mol}).$$

For the 6-31G basis

$$2 \, E(6\text{-}31G) = -815.776997 - (-331.914765) - (-317.868806) = -165.99043 \text{ a.u.,}$$

and cohesion energy

$$E_{cohes} (6\text{-}31G) = E(6\text{-}31G) - E_{6\text{-}31G}(LiOH) =$$
$$= \frac{1}{2} (-165.99043) - (-82.894883) = -0.10033 \text{ a.e. } (-263 \text{ kJ/mol}).$$

So, unlike those of the STO-3G basis, the calculations using the 6-31G basis let it possible to reproduce both geometrical and energetic characteristics of the lithium hydroxide crystal with small error. It should be noticed that the cohesion energy calculated by the MNDO method (E_{cohes} (MNDO) = -424 – (-230) = -194 kJ/mol) is slightly lesser than the experimental one (as an absolute quantity) whereas non-empirical calculations overestimates it.

Conclusions

An analysis of the calculated parameters of spatial structure, energetic and spectral characteristics of the models examined indicates their stability (what is secured by the adsorption of as few as two water molecules) and agreement with the experimental data. With the availability of sufficiently large amount of molecules in such associates, they can be considered as crystallites of the solid.

Acknowledgement

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