Quantum-Chemical Modelling of Clusters $NH_3 \cdot (H_2O)_N$, Forming in Processes of Gas and Oil - Refining Industry.

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Abstract

A number of significant structures of $NH_3 (H_2O)_n$ (n= 1- 6) clusters have been identified by the quantum chemical methods (RHF/3-21G, RHF/6-31G**, B3LYP/6-31G**, MP2/6-31G**). The cluster's geometry configurations and intermolecular energy have been calculated.

Key words:

Quantum-chemical calculations, ammonia, RHF/3-21G, RHF/6-31G**, B3LYP/6-31G**, MP2/6-31G**, cluster.

ملخص البحث :

تكمن أهمية البحث في معرفة ودراسة التركيب الجزيئي و نوع وطبيعة الارتباطات بين جزيئات المستحلبات المتكونة من عمليه تنقية الغازات المنبعثة من الصناعات النفطية وتخليصها من الغازات الحامضية (CO_2, H_2S) , بواسطة المحاليل المائية للأمونيا والأمينات العضوية والتي تستخدم على نطاق واسع في الصناعات النفطية ومعامل تكرير النفط, وذلك لأنها ستسمح لنا بتحديد خواص وسلوك التفاعلات الكيميائية التي ستحدث خلال عملية التنقية وإكمال هذه العملية بالشكل المطلوب.

حيث إن دراسة تركيب وخواص المذيبات الأيونية له مجال نظري وعملي واسع النطاق لأن تأثير المذيب سوف يغير من السلوك الكيميائي للمركب أو المعقد الناتج . وكذلك نتائج هذه الدراسة يمكن أن تكون مفيدة لفهم عملية :

The process of the partitioning of ammonia

في بحثنا هذا درسنا نظريا بواسطة طرق كيمياء الكم

(RHF/3-21G, RHF/6-31G**, B3LYP/6-31G**, MP2/6-31G**)

التركيب الجزيئي وخواص الارتباطات بين جزيئات المستحلبات المتكونة من عملية تنقية الغازات و المتمثلة $NH_3 (H_2O)_n$ (n= 1- 6) , من خلال مجموعة برامج (Hyperchem و Gamess) والتي تبين لنا الحد الأدنى من الطاقة الكامنة Potential energy لسطح المستحلبات المتكونة.

Introduction

The processes of gas purification of impurities aqueous solutions of ammonia and organic amines are widely used in gas and oil - refining industry [1]. The study of molecular structural association (clusters, molecular, complexes) in these solutions is important, because it allows identification of specific internal features of condensed matter and their influence on the course of the reaction in the implementation of the chemical - engineering processes [2].

The study of the structure and properties of solvated ionic species is an active field of theoretical and experimental research. Solvation effects alter the chemical behavior of compounds. Knowledge of the interactions controlling the arrangement and the number of the solvent molecules necessary to stabilize the ions is prerequisite to the understanding of the solvation process. When a molecule of a compound more basic than water is dissolved in aqueous solution, a water molecule donates one of its protons and ions are formed. Solutions

of ammonia in water have been used as a prototypical system for the study of this type of reactions. The formation of NH_4^+ and OH^- in solution has been established [5].

NH3 has recently attracted considerable interest for its possible role in atmospheric aerosol formation [6, 7]. The results of this study can be valuable to understand the process of the partitioning of ammonia between the droplets and the gas phase in the troposphere. The $NH_3(H_2O)_n$ complex has been experimentally studied by microwave and far-infrared spectroscopy[9, 10] and theoretically by the quantum chemical methods (RHF/3-21G, RHF/6-31G**, B3LYP/6-31G**, MP2/6-31G**)have shown the existence of a minimum energy structure in the

potential energy surface of the $NH_3(H_2O)_4$ cluster, which is the result of one proton transfer from a water molecule to the ammonia molecule [8, 9]. They also postulated that with less than four molecules of water the formation of the double ionic cluster is not possible [10, 14 , 15].

Experimental

We have carried out quantum-chemical calculations of molecular Complexes $NH_3 \cdot (H_2O)n$ (n = 1 - 6) (Software HyperChem and GAMESS [3, 4]), using methods RHF/3-21G, RHF/6-31G **, B3LYP/6-31G ** and MP2/6-31G ** and discrete model of solvent approximation of molecules. Equilibrium configuration of the molecular complexes (see table 1) is obtained through the full optimization of geometry.

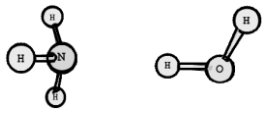
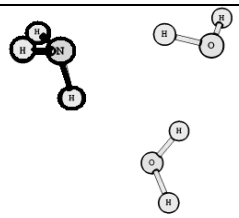
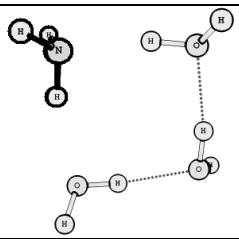
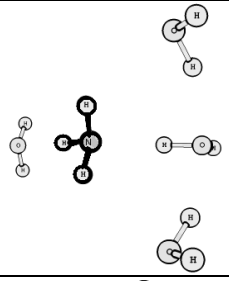
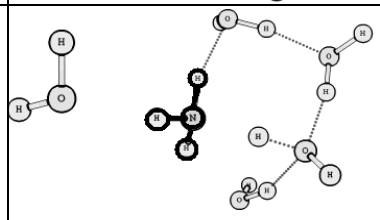
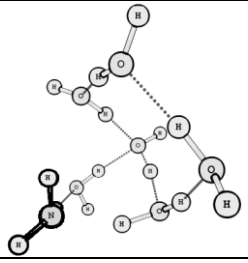
Results and Conclusions

The calculations show that all the methods (RHF/3-21G, RHF/6-31G **, B3LYP/6-31G ** and MP2/6-31G **) used to simulate the relative position of molecules in a cluster. In the H_2O molecule complexes (n = 1- 4) (see table 1) form a hydrate shell around the NH_3 molecule (see geometrical parameters a to e). The further addition of molecules in a cluster of H_2O leading to the displacement of molecules so that all molecules of H_2O, the combined network of hydrogen bonds are grouped together on one side of NH_3 (see table 1) to assess the value of the interaction energy between the cluster molecules, but excluding the energy of intermolecular interactions between the molecules of solvent H_2O $\Delta E_{\text{interaction}}$, we have a single account system, which consists H_2O molecules in the equilibrium configuration of the cluster.

The results calculation show that $\Delta E_{interaction}$ uniformly increases with the n =1 to 4 (Fig.1), (Fig.2) and (Fig.3). When n = 5, only for RHF/3-21G calculation showed growing $\Delta E_{interaction}$, all the other methods showed slightly change in value $\Delta E_{interaction}$. Further increase in the number of molecules of H_2O in the cluster leads to a reduction in the value of $\Delta E_{interaction}$. This is most likely linked to the-completion of filling the first ydrate shell of the molecule NH_3. Thus, to calculate the clusters formed in the process of gas purification of water solutions of NH_3 in the approximation molecule sufficiently take into account the 4 water molecules, the calculation of the equilibrium configurations to carry out the method RHF/3-21G, and the energy of intermolecular interaction specify complicating the base set and the method of calculation

.

Table 1- Equilibrium configuration and energy parameters of molecular complexes $NH_3 \cdot (H_2O)_n$

№	n	System Configuration $NH_3 \cdot (H_2O)_n$	E total , Kcal/mol.			
			RHF/ 3-21G	*RHF/ 6-31G(d,p)*	*B3LYP/ 6-31G(d,p)*	*MP2/ 6-31G(d,p)*
1	1		-82501,9* -47430,8**	-82975,2 -47705,45	-83453,0 -47954,0	-83217,6 -47828,6
2	2		-129953,9 -94871,5	-130690,4 -95416,3	-131422,1 -95915,1	-131059,8 -95663,8
3	3		-177407,4 -142316,9	-178406,5 -143129,4	-179391,4 -143878,8	-178902,19 -143501,2
4	4		-224836,7 -189738,4	-226110,7 -190830,6	-227344,5 -191826,8	-226730,6 -191324,8
5	5		-272290,7 -237181,6	-273830,6 -238550,1	-275319,2 -239799,4	-274578,3 -239170,9
6	6		-319759,2 -284671,8	-321553,2 -286277,9	-323293,1 -287781,5	-322429,3 -287030,2

* - Above the horizontal line shows the total value of energy for the complexes $NH_3 \cdot (H2O)_n$

** - Under the horizontal line shows the total value of energy for the complexes $(H_2O)_n$ in the geometry of the complexes of $NH_3 \cdot (H2O)_n$

Table 2 - The values of the total energy E_{total} of the isolated molecules NH3 and H_2O .

№	molecule	E_{total} , Kcal/mol.			
		RHF/3-21G	*RHF/6-31G***	*B3LYP/6-31G***	*MP2/6-31G***
1	**NH_3**	**-35060,3**	**-35263,2**	**-35490,6**	**-35381,0**
2	**H_2O**	**-47430,9**	**-47705,5**	**-47954,1**	**-47828,6**

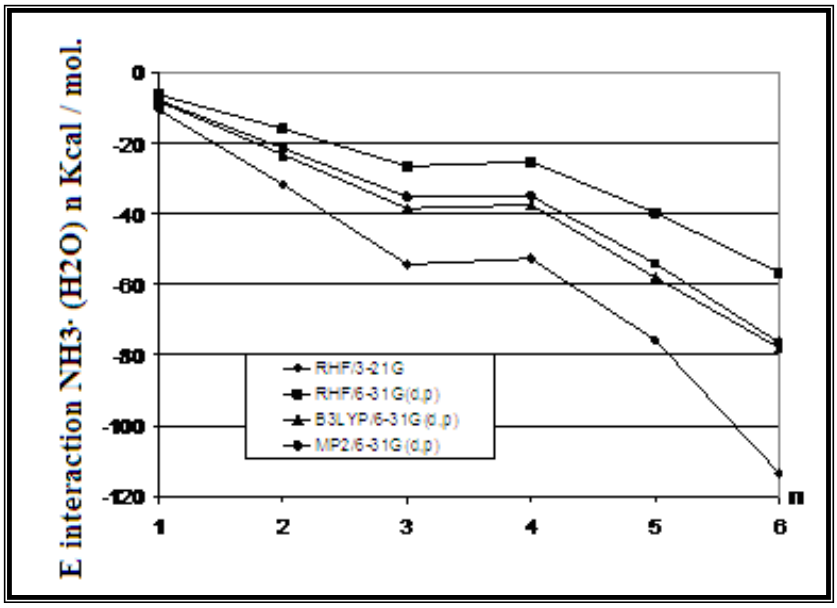


Fig. 1. Energy cooperation between all the molecules cluster

$E_{interaction}\ NH_3 \cdot (H_2O)_n = E_{total}\ NH_3 \cdot (H_2O)_n - (E_{total}\ NH_3 + n\ E_{total}\ H_2O)$

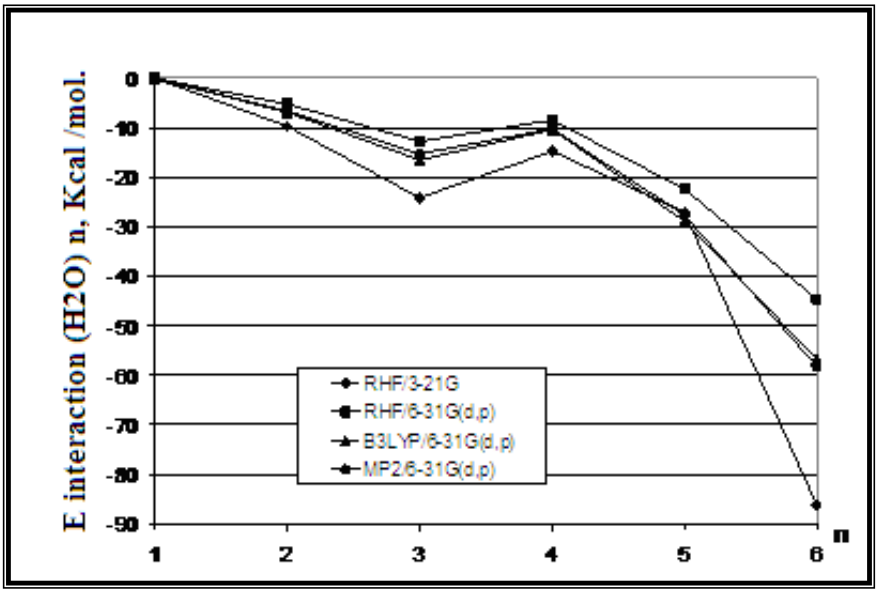


Fig. 2. The energy of interaction between the molecules of solvent in the equilibrium configuration of the cluster

$$E_{interaction}(H_2O)_n = E_{total}(H_2O)_n - n\,E_{total}\,H_2O$$

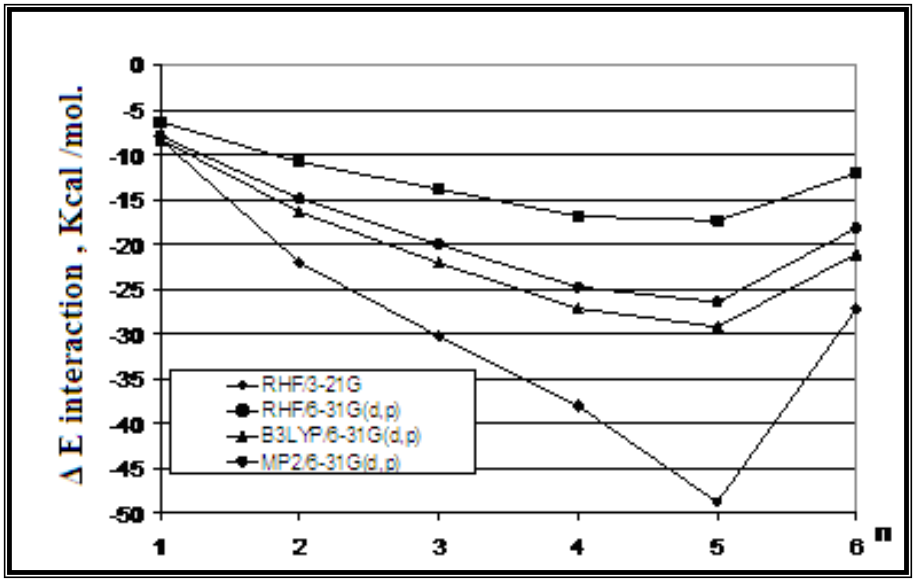


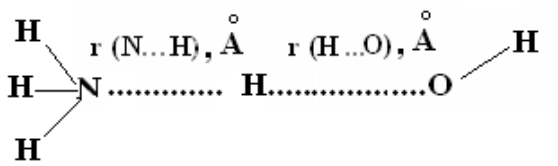
Fig. 3. Interaction energy of NH_3 molecules with solvent molecules in the cluster $\Delta E_{interaction} = E_{interaction}\,NH_3 \cdot (H_2O)_n - E_{interaction}(H2O)_n$

Increasing the number of molecules in the complexes of $NH_3 \cdot (H_2O)_n$ leads to a reduction in the inter atomic distance r (N ... H) , see (Fig.4) .

- (1.935 Aº to 1.417 Aº RHF/3-21G).
- (2.100 Aº to 1.818 Aº RHF/6-31G **) .
- (1.949 Aº to 1.555 AºB3LYP/6-31G **).
- (1.991 Aº to 1.661 AºMP2/6-31G **).

And the growth of the inter atomic distance r (O ... H), (see Fig.5 and geometrical parameters a to e).

- (0.979 Aº to 1.110 Aº RHF/3- 21G).
- (0.951 Aº to 0.972 Aº RHF/6-31G **).
- (1.980 Aº to 1.052 Aº B3LYP/6-31G **).
- (0.973 Aº to 1.027 Aº MP2/6-31G **).



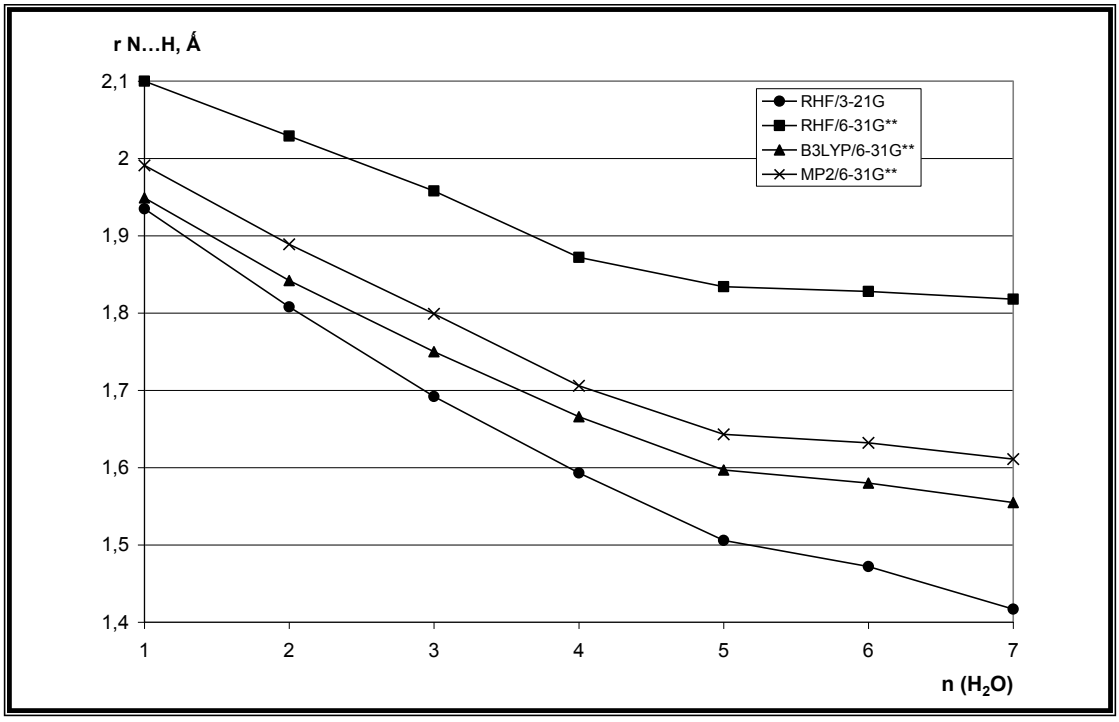


Fig. 4. Relationship inter atomic distance r (N ... N), Aº of the number of H_2O molecules in complexes $NH_3 \cdot (H_2O)_n$.

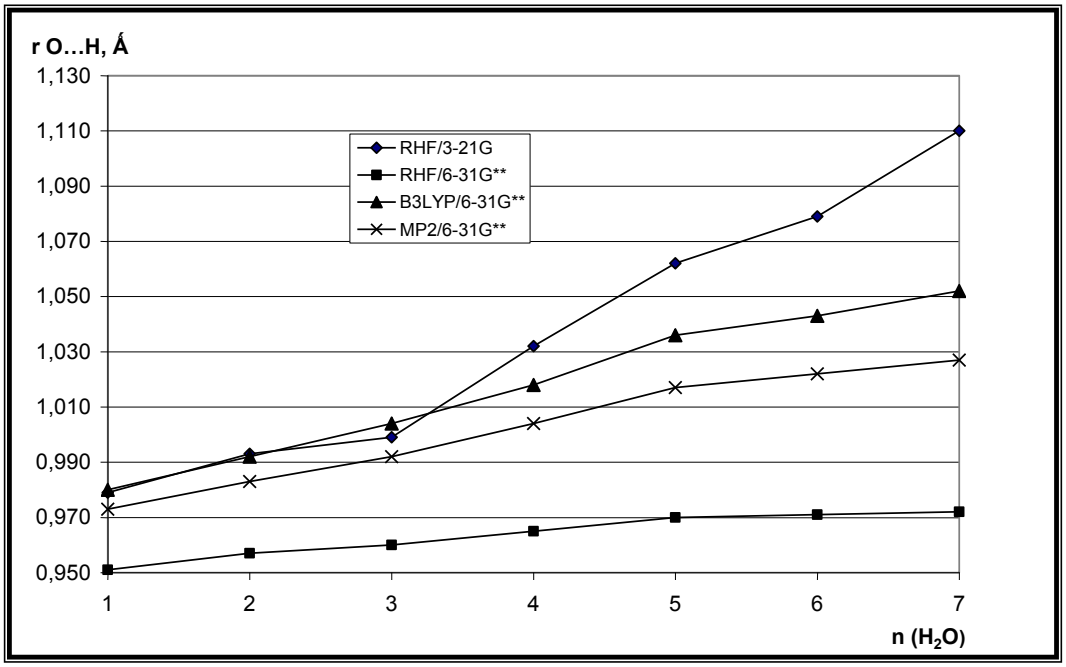
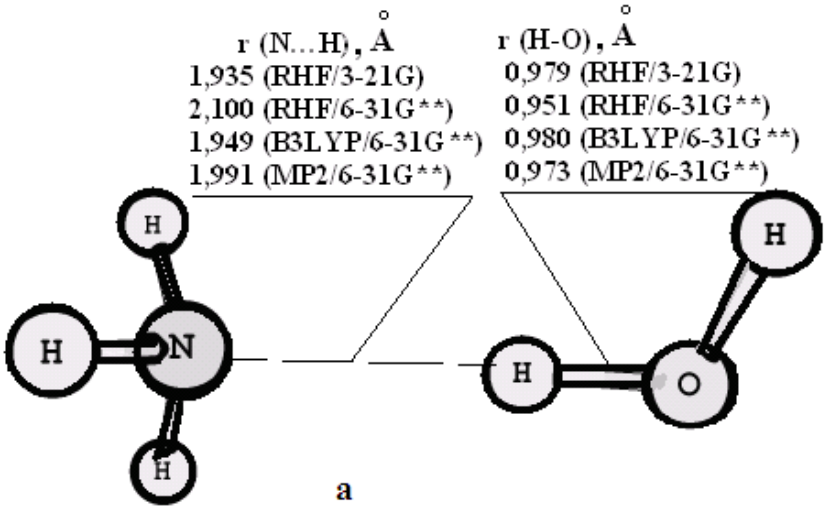
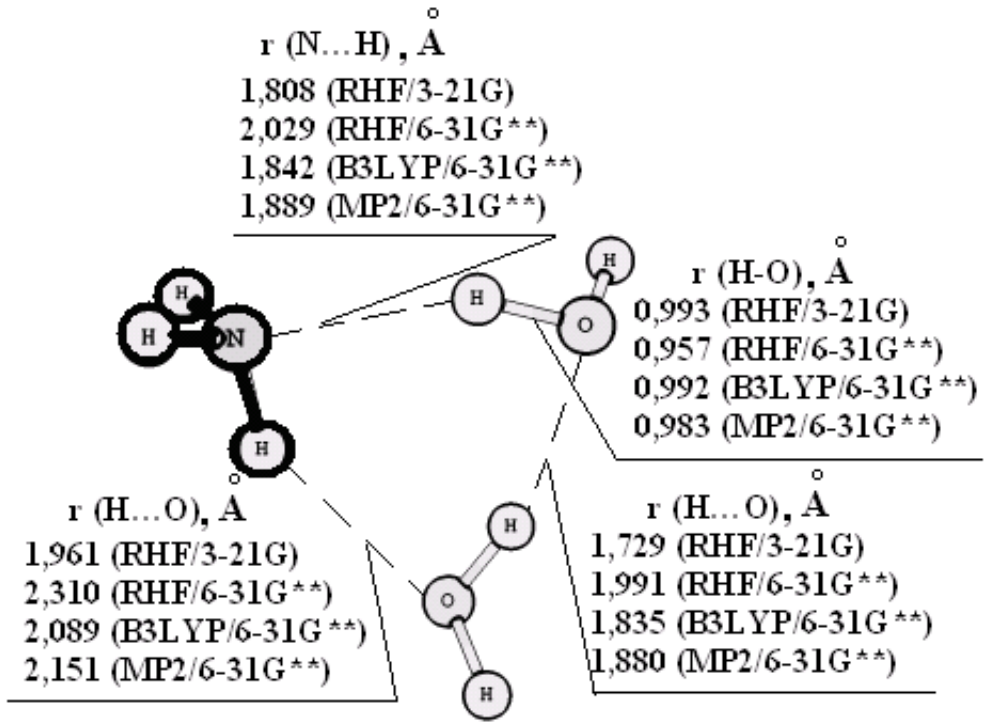
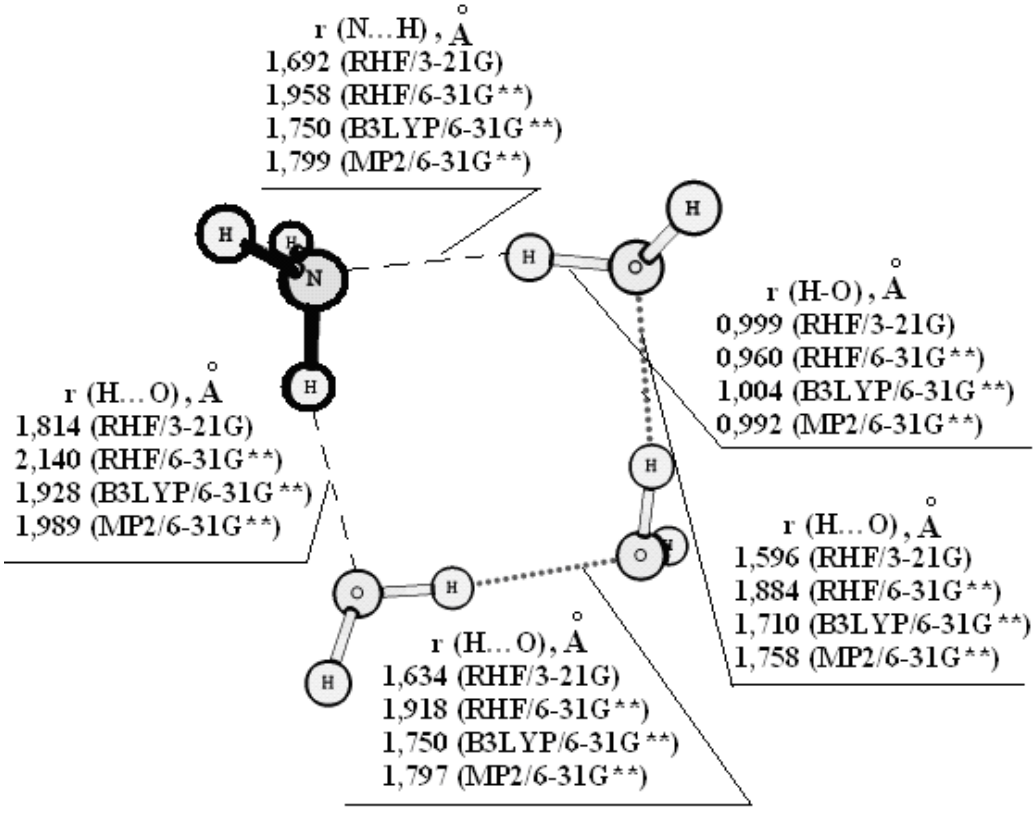


Fig. 5. Relationship inter atomic distance r (O ... H), Aº of the number of H_2O molecules in complexes $NH_3 \cdot (H_2O)_n$.

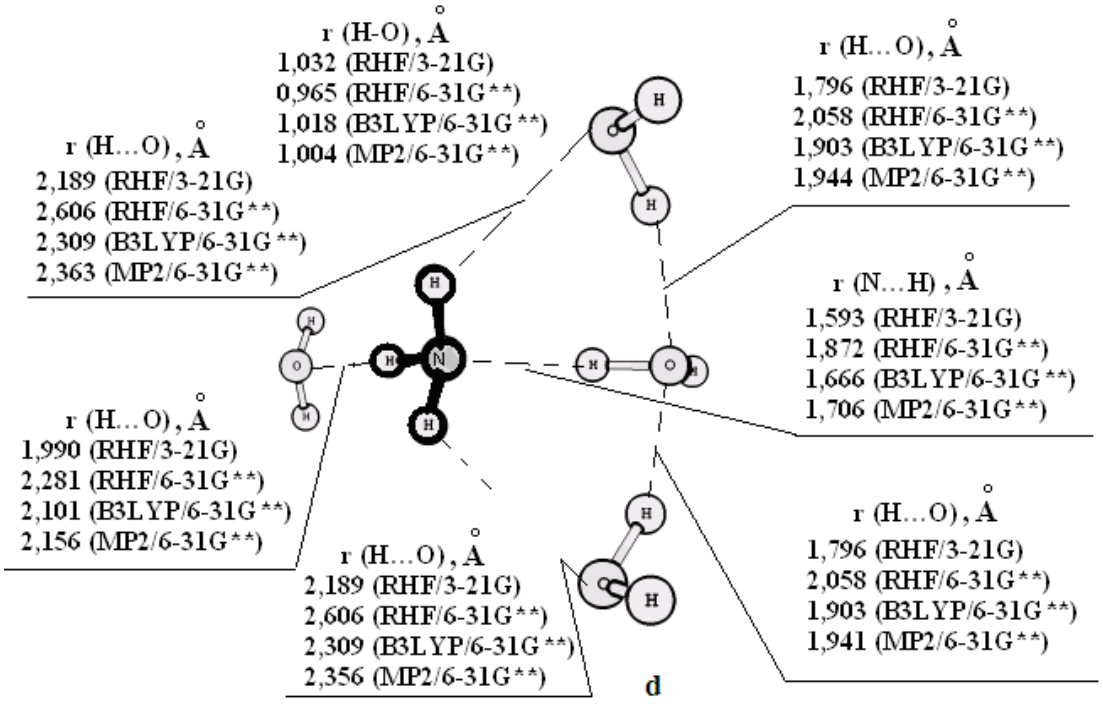


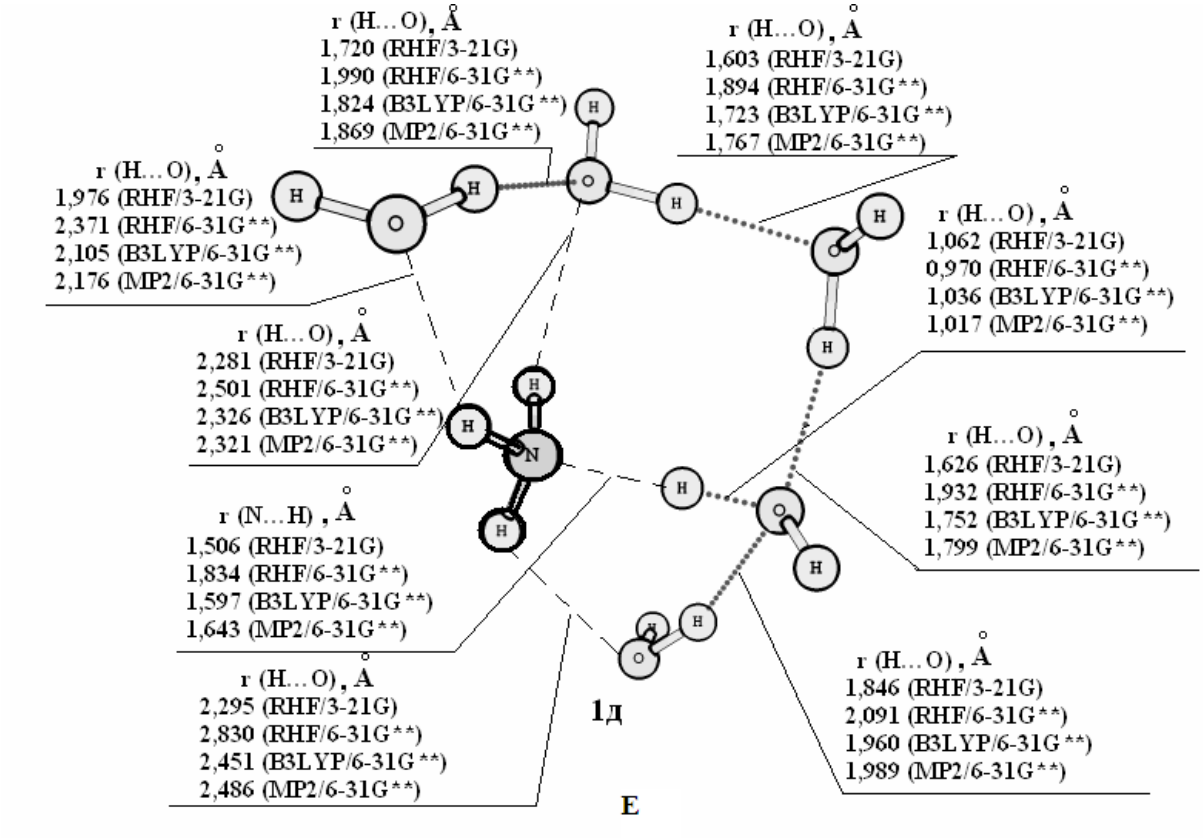

r (N…H), Å
1,808 (RHF/3-21G)
2,029 (RHF/6-31G**)
1,842 (B3LYP/6-31G**)
1,889 (MP2/6-31G**)
r (H-O), Å
0,993 (RHF/3-21G)
0,957 (RHF/6-31G**)
0,992 (B3LYP/6-31G**)
0,983 (MP2/6-31G**)
r (H…O), Å
1,961 (RHF/3-21G)
2,310 (RHF/6-31G**)
2,089 (B3LYP/6-31G**)
2,151 (MP2/6-31G**)
r (H…O), Å
1,729 (RHF/3-21G)
1,991 (RHF/6-31G**)
1,835 (B3LYP/6-31G**)
1,880 (MP2/6-31G**)

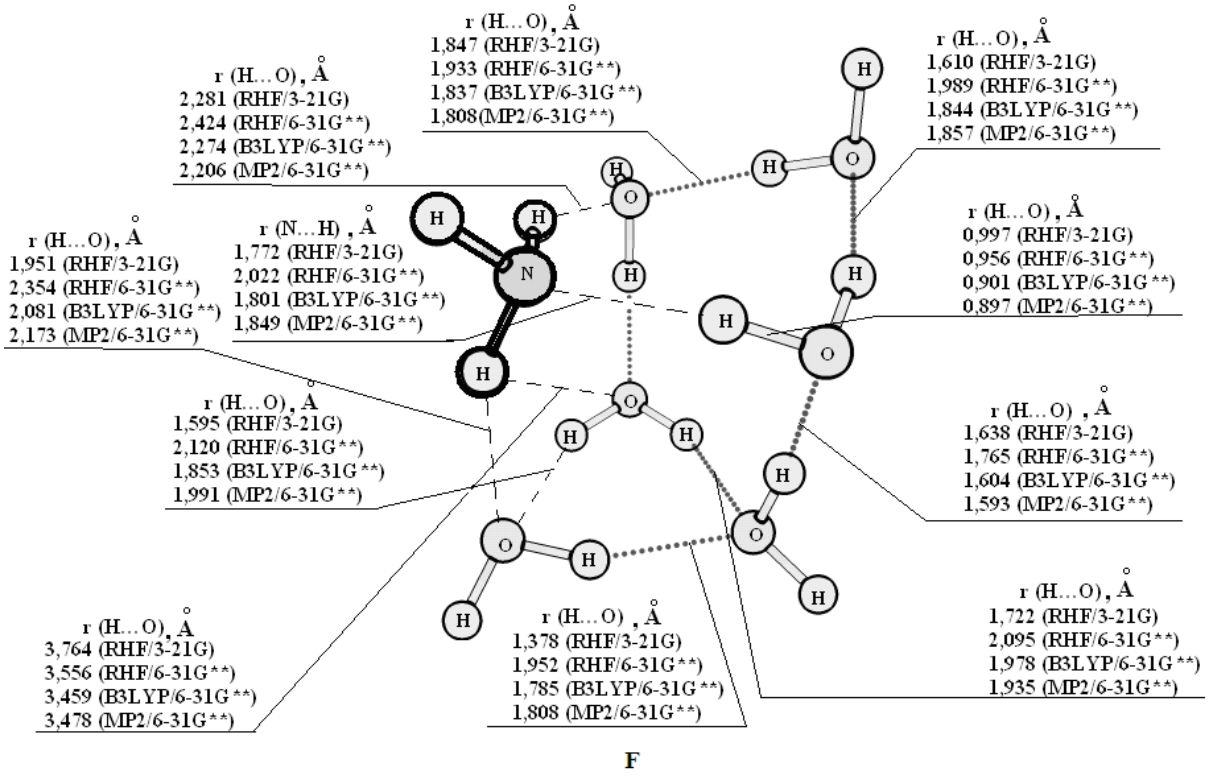
b


r (N…H), Å
1,692 (RHF/3-21G)
1,958 (RHF/6-31G**)
1,750 (B3LYP/6-31G**)
1,799 (MP2/6-31G**)
r (H-O), Å
0,999 (RHF/3-21G)
0,960 (RHF/6-31G**)
1,004 (B3LYP/6-31G**)
0,992 (MP2/6-31G**)
r (H…O), Å
1,814 (RHF/3-21G)
2,140 (RHF/6-31G**)
1,928 (B3LYP/6-31G**)
1,989 (MP2/6-31G**)
r (H…O), Å
1,596 (RHF/3-21G)
1,884 (RHF/6-31G**)
1,710 (B3LYP/6-31G**)
1,758 (MP2/6-31G**)
r (H…O), Å
1,634 (RHF/3-21G)
1,918 (RHF/6-31G**)
1,750 (B3LYP/6-31G**)
1,797 (MP2/6-31G**)

c


r (H-O), Å
1,032 (RHF/3-21G)
0,965 (RHF/6-31G**)
1,018 (B3LYP/6-31G**)
1,004 (MP2/6-31G**)
r (H...O), Å
1,796 (RHF/3-21G)
2,058 (RHF/6-31G**)
1,903 (B3LYP/6-31G**)
1,944 (MP2/6-31G**)
r (H...O), Å
2,189 (RHF/3-21G)
2,606 (RHF/6-31G**)
2,309 (B3LYP/6-31G**)
2,363 (MP2/6-31G**)
r (N...H), Å
1,593 (RHF/3-21G)
1,872 (RHF/6-31G**)
1,666 (B3LYP/6-31G**)
1,706 (MP2/6-31G**)
r (H...O), Å
1,990 (RHF/3-21G)
2,281 (RHF/6-31G**)
2,101 (B3LYP/6-31G**)
2,156 (MP2/6-31G**)
r (H...O), Å
1,796 (RHF/3-21G)
2,058 (RHF/6-31G**)
1,903 (B3LYP/6-31G**)
1,941 (MP2/6-31G**)
r (H...O), Å
2,189 (RHF/3-21G)
2,606 (RHF/6-31G**)
2,309 (B3LYP/6-31G**)
2,356 (MP2/6-31G**)
d





Geometrical parameters of complexes $NH_3 \cdot (H_2O)_n$, n = 1- 6

Thus, the dependence illustrate the trend of making the molecular complex $(H_3N \ldots H_2O).(H_2O)_{n-1}$ in the complex, intermediate between molecular and ionic $(H_4N^+ \ldots OH^-).(H_2O)_{n-1}$ with an increase in the number of molecules of H_2O.

Known [11, 12, 13] that in aqueous solution of ammonia ionization occurs with the formation of NH_4OH alkaline reaction medium (PH = 11.77) .

Thus, the results of calculation show that used to simulate the relative position of molecules in a cluster give the same. Quantum-chemical calculations of all methods confirm that the education of classical ion complex $(H_4N^+ \ldots OH^-) \cdot (H_2O)_{n-1}$ in aqueous solutions does not occur.

Figure captions

Fig. 1. Energy cooperation between all the molecules cluster $E_{\text{interaction}}\ NH_3 \cdot (H_2O)_n = E_{\text{total}}\ NH_3 \cdot (H_2O)_n - (E_{\text{total}}\ NH_3 + n\ E_{\text{total}}\ H_2O)$.

the cluster $\Delta E_{\text{interaction}} = E_{\text{interaction}}\ NH_3 \cdot (H_2O)_n - E_{\text{interaction}}\ (H_2O)_n$.

Fig. 2. The energy of interaction between the molecules of solvent in the equilibrium configuration of the cluster $E_{\text{interaction}}\ (H_2O)_n = E_{\text{total}}\ (H_2O)_n - n\ E_{\text{total}}\ H_2O$.

Fig. 3. Interaction energy of NH3 molecules with solvent molecules in.

Fig. 4. Relationship inter atomic distance r (N ... N), Aº of the number of H_2O molecules in complexes $NH_3 \cdot (H_2O)_n$.

Fig. 5. Relationship inter atomic distance r (O ... H), Aº of the number of H_2O molecules in complexes $NH_3 \cdot (H_2O)_n$.

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الاســـــم الثلاثي : نجلاء زكي رجب .

العنوان الوظيفي : كيمياوي أقدم .

المواليـــــــــد : 1978.

الشركـــــــــــة : شركة نفط الجنوب / قسم البحوث و السيطرة النوعية.

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