Journal of the Mexican Chemical Society
ISSN: 1870-249X
editor.jmcs@gmail.com
Sociedad Química de México
México

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Journal of the Mexican Chemical Society, vol. 49, núm. 4, 2005, pp. 344-352
Sociedad Química de México
Distrito Federal, México

Article

J. Mex. Chem. Soc. **2005**, *49(4), 344-352*

ISSN 1870-249X

Ab Initio Study and Hydrogen Bonding Calculations of Nitrogen and Carbon Chemical Shifts in Serine-Water Complexes

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Recibido el 18 de junio del 2005; aceptado el 30 de noviembre del 2005

Abstract. The hydrogen bonding (HB) effects on the NMR shielding of selected atoms in a few Ser-nH_2O complexes have been investigated with quantum mechanical calculations of the ^{15}N and ^{13}C tensors. Interaction with water molecules causes important changes in geometry and electronic structure of serine. Chemical shift calculations, geometry optimization and energies have been performed with *ab initio* method at HF/6-31G* and HF/6-31G** levels with magnetic properties of the gauge-including atomic orbital method. There is evidence that intermolecular effects are important in determining the ^{15}N chemical shifts of free amino acid residue, to assign principal axes of the tensors, and some systematic trends appear from the analysis of the calculated values.
Formation of each interaction (in ten orientations) results in a change of the bridging hydrogen's chemical shifts of N…H bond that indicate the most stabilized compound. The $C^{\alpha}H$…O bond plays an important role in the interactions of amino acids residue upon the structure and function of a protein. This paper represents comparison between theoretical and experimental values of NMR resonances. Calculations at HF/6-31G** level produce results in better agreement with the experimental data.
Keywords: Isotropy and Anisotropy, chemical shift, *ab initio* serine, $C^{\alpha}H$…O, hydrogen bonding.

Resumen. Los efectos de protección que ejercen en RMN los puentes de de hidrógeno (PH) en ciertos átomos del complejo Ser-nH_2O fueron investigados mediante cálculos de mecánica cuántica y tensores de ^{15}N y ^{13}C. La interacción con moléculas de agua causa cambios importantes en la geometría y en la estructura electrónica de la serina.
Los cálculos de desplazamientos químicos, optimizaciones de la geometría y los cálculos de energía se llevaron a cabo mediante métodos *ab-initio* a niveles HF/6-31G* y HF/6-31G** con propiedades magnéticas incluyendo el método del orbital atómico. Hay evidencia de que los efectos intermoleculares son importantes en la determinación de los desplazamientos químicos de ^{15}N del residuo libre del aminoácido para la asignación de los ejes principales de los tensores, y se observaron algunas tendencias sistemáticas a partir del análisis de los valores calculados. La formación de cada interacción (en diez orientaciones) resulta en un cambio de los desplazamientos químicos de la unión N…H, lo que indica un compuesto mas estabilizado. La unión $C^{\alpha}H$…O desempeña un papel importante en la estructura y en la función de una proteína. Este artículo representa una comparación entre los valores teóricos y experimentales de RMN. Los cálculos al nivel HF/6-31G** produce resultados de mayor concordancia con los datos experimentales.
Palabras clave: Isotropía, anisotropía, desplazamiento químico, *ab-initio*, serina, puentes de hidrógeno

Introduction

The serine proteases are a common type of enzymes that cut certain peptide bonds in other proteins and in mammalian body, serine proteases perform many important functions, especially in digestion, blood clothing, putative neurotransmitters and the complement system because it is a constituent of brain proteins and nerve coverings and is also important in the formation of cell membranes [3].

Serine is first isolated in 1856 from sericin, a silk protein, and is a nonessential amino acid and can be synthesized in the body from glycine [1].

Serine plays an important role in intermediary metabolism of fat, tissue growth and the immune system as it assists in the production of immunoglobulins and antibodies in human pregnancy as a source of one carbon pool for nucleotide biosynthesis, as an endogenous ligand for the glycine, and as a contributor to cysteine biosynthesis [2].

Most of the current investigations in theoretical chemistry are based on the study of molecules immersed in a solvent phase.

As far as the amino acids are concerned, due to their chemical structure the majority of H-bond interactions between them and water are of the following types: C=O…H, N-H…O and N…H-O. In this work, we focus our attention on serine with water molecules.

The hydrogen bond is one of the least well understood compounds in the energy decomposition that is used to predict the folding of biological complexes such as proteins. Its importance stems from its directionality and modest bonding energies midway between strong covalent and weak Van der Waals bonds. For this reason, the hydrogen bond is characterized by a certain amount of charge transfer which could be determined in a compound.

Recent improvements in *ab initio* quantum chemical methodologies, when combined with similar improvements in computer hardware, have recently permitted the first successful predictions of the ^{15}N , ^{13}C and ^{19}F nuclear magnetic resonance spectra of proteins in solution, [4,5] and have led to methods for refining existing solution structures [6].

In the last few years, the ^{15}N isotope has become a prominent messenger protein. Successful interpretation of ^{15}N NMR

data requires an accurate knowledge of the chemical shifts anisotropy (CSA) and tensor for asymmetric (CSA_a) [7-10].

The calculation of nuclear magnetic resonance (NMR) parameters using semi-empirical and *ab initio* techniques has become a major and powerful tool in the investigation of how variations in the molecular structure occur. The ability to quickly evaluate and correlate the magnitude and orientation of the chemical shielding anisotropy (CSA) tensor with variations in bond length, bond angles, and local coordination and nearest neighbor interactions has seen a number of recent applications in the investigation of molecular structure [11-15].

The calculations also provide valuable information for exploring the experimental NMR chemical shifts with the molecular geometry and environment [16, 17].

NMR chemical shifts are quite sensitive to intermolecular interactions. Recent works indicate that the ^{15}N chemical shifts principal values. These results suggest that it may be possible to obtain explicit relationships between ^{15}N chemical shifts and hydrogen bonding and compounds [18].

Although conventional hydrogen bonds that involve electronegative atoms like oxygen and nitrogen have been thoroughly studied over the decades since their first introduction into the literature and are presently well understood [19-21], but the CH…O interaction is thought to be crucial in a large of molecular complexes and crystal structures [22-26].

This being the case, it would be surprising indeed if the CH…O bond were any less important in biological systems. In fact, after some early propels of CH…O contacts [27-29].

There is an increasing body of evidence that CH…O contacts occur with some regularity in protein as well. It was noted some time ago that the various amino acids contain these interactions [30-36].

By far the most prevalent CH group in proteins involves the C^{α} of each amino acid residue, so its possible involvement in H-bonds is of profound consequences. Even if individually weak, the sheer number of such $C^{\alpha}H$…O H-bonds could exert an enormous influence upon the structure and function of a protein [37, 38].

Computational and Theoretical Method

There is thus reason to be optimistic that in the future, when combined with experimental shielding tensor element measurements, may enable new general approaches to structure determination of proteins in solution.

This work describes the performance of quantum chemical and theoretical method in calculating the geometry coordination, energies, charges and chemical shift tensors of hydration of serine.

The ^{15}N and ^{13}C tensors and the energy minimized structures for both the serine and serine-nH_2O complexes (n=1, 2,… 10) were calculated using the parallel of the GAUSSIAN 98 software package on a computer.

The gauge-including atomic orbital (GIAO) method at the Hartree-Fock (HF) level of theory with 6-31G* and 6-31G** basis sets was employed.

This study involves calculations by keywords OPT and NMR, for optimization and chemical shift calculations, respectively.

The choice of this basis set is based on the consideration that in order to obtain reliable properties of hydrogen bonded complexes.

Typically it is only necessary to report the three principal compounds (or eignvalues) of the ^{15}N and ^{13}C CSA_a tensors (σ_{11}, σ_{22}, σ_{33}) when is discussing the magnitude of the shielding tensor.

The ^{15}N and ^{13}C CSA_a tensors can also be described by three additional parameters; The isotropic value, σ_{iso}, the anisotropy of the tensor, σ_{aniso}, nonsymmetric shielding tensor, $\Delta\sigma$,asymmetric of chemical shielding anisotropy, CSA_a, effective chemical shielding, σ_{eff} and chemical shift, δ.

In this paper these parameters have been calculated to suggest the solvation model of serine to estimate the most stabilized of serine-nH_2O complexes.

Results and Discussions

Our results point out the possibility that the charge transfer electronic states may play a significant role in the, up to now, quite mysterious process of methods. It would be quite interesting to carry out a detailed experimental exploration of these systems using various techniques.

a) Modeling of the hydration of serine:

In practice, if the system is described using quantum mechanics, the applicability of the model is restricted to a selected number of configurations of a solute surrounded by a few solvent molecules. Several studies necessary for a more complete understanding for hydrogen bonding in serine proteases are planned.

Firstly, we have tried with one water molecule in ten positions, the structure of all possible monohydrated complexes was fully optimized, and small difference of energy appears among these conformations. Then a second water molecule is added, and the hydrated complex having the lowest energy is found in the same way. Such a procedure is repeated 10 water molecules are arranged around the aminoacid (Figure 1).

Comparison of the geometry of isolated and hydrated serine (optimized bond lengths, bond angles and torsion angles) reveals that the interaction with water molecules noticeably influences the molecular structure of amino acid under consideration (Table 1).

Considering to this results shows that HF/6-31G**optimized geometry of serine is closer to experimental results [39] than HF/6-31G* optimized data.And complexes of serine-10H_2O is more stable than other complexes of these indicated this compound.

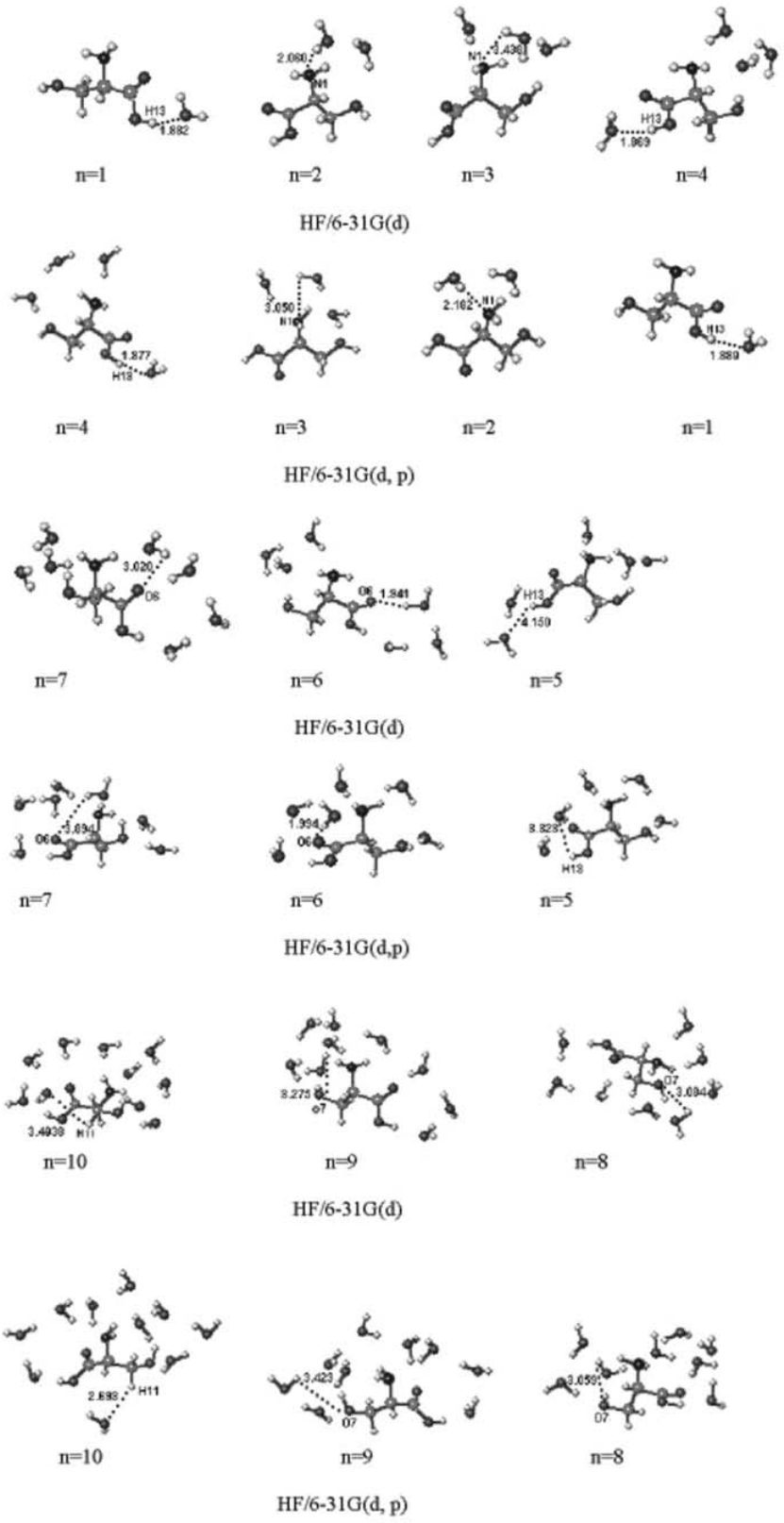

Fig. 1. Optimized structures of serine nH_2O (n = 1, 2, 10) with the HF/6-31G* and HF/6-31G** Level/bases set.

Table 1. The molecular geometries of serine in ten orientations with water molecules at Hartree Fock level of theory.

number of water	length bond(Å)	6-31G*	6-31G**	bond angle(D)	6-31G*	6-31G**	torsion angle(D)	6-31G*	6-31G**
n=1	r (O_1.....H_{13})	1.88269	1.88942	< ($O_1H_{13}O_5$)	158.404	**158.207**	<($O_1H_{13}O_5C_3$)	3.00546	2.72022
n=2	r (H_3.....N_1)	2.06055	2.18273	<($H_3N_1C_2$)	106.128	**97.908**	< ($H_3N_1C_2C_4$)	133.991	147.85
n=3	r (H_3.....N_1)	3.43810	3.05028	< ($H_3N_1C_2$)	22.2401	**114.866**	< ($H_3N_1C_2C_4$)	-133.902	110.862
n=4	r (O_1.....H_{13})	1.86949	1.87707	< ($O_1H_{13}O_5$)	159.110	**158.619**	< ($O_1H_{13}O_5C_3$)	1.65087	2.24362
n=5	r (O_1.....H_{13})	4.15093	3.32319	< ($O_1H_{13}O_5$)	146.601	**99.1396**	< ($O_1H_{13}O_5C_3$)	-90.3051	72.3252
n=6	r (H_3.....O_6)	1.94185	1.99438	< ($H_3O_6C_3$)	154.075	**20.2725**	< ($H_3O_6C_3C_2$)	-177.488	176.873
n=7	r (H_3.....O_6)	3.20990	3.89493	< ($H_3O_6C_3$)	113.344	**99.4293**	< ($H_3O_6C_3C_2$)	-64.0079	16.2121
n=8	r (H_2.....O_7)	3.08496	3.05970	< ($H_2O_7C_4$)	19.7628	**115.371**	< ($H_2O_7C_4C_2$)	-110.626	63.4316
n=9	r (H_3.....O_7)	3.27508	3.42329	< ($H_3O_7C_4$)	102.866	140.400	< ($H_3O_7C_4C_2$)	97.9674	105.706
n=10	r (O_1.....H_{11})	3.49383	2.69336	< ($O_1H_{11}C_4$)	91.2867	**133.042**	< ($O_1H_{11}C_4C_2$)	-110.096	18.8472

b) Stabilization energy in the various orientations:

Here, hydration of serine in water solvent causes that the stabilization energies to be more negative than non-hydrated this compound. Ab initio calculations on serine complexes have shown the lowest energy at HF/6-31G** level including water molecules making two simultaneous H-bonds either with the (H and O) atom pair.

The interaction energy of each of the serine complexes with water as the proton acceptor is reported as E in Table 2, under the convention that a negative energy corresponds to a favorable binding energy. This energy of this model with water was greater than single serine. One can assume therefore that binding energies for each of the amino acids in Table 2 would be more negative by a like amount when the residue is surrounded by peptide groups.

These observations are important since they suggest a route to structure determination, or at least refinement, an approach which should find particular utility in investigating the structures of peptides and proteins.

Table 2. Comparison between calculated binding energies of serine nH_2O complexes in two basis set of *ab initio* method in kcal mol^{-1}

number of		HF/6-31G*		HF/6-31G**	
Water		E	ΔE	E	ΔE
n=o		-248937.4641	0	-248953.3149	0
	I	-296640.1682	-47702.7041	-296664.0177	-47710.7028
	II	-296638.0623	-47700.5982	-296661.3827	-47708.0678
	III	-296640.0447	-47702.5806	-296663.9454	-47710.6305
	IV	-296644.9025	-47707.4384	-296668.7056	-47715.3907
	V	296645.2595	-47707.7954	-296669.0421	-47715.7272
	VI	-296640.9006	-47703.4365	-296664.7171	-47711.4022
	VII	-296638.0625	-47700.5984	-296661.9732	-47708.6583
	VIII	-296641.6224	-47704.1583	-296665.4881	-47712.1732
	XI	-296645.2595	-47707.8185	-296669.0421	-47715.7272
	X	296640.8971	-47703.4330	-296664.7171	-47711.4022
n=2		-344346.7976	-95409.3335	-344377.4959	-95424.1810
n=3		-392058.0743	-143120.6102	-392090.7285	-143137.4136
n=4		-439765.5655	-190828.1014	-439806.8567	-190853.5418
n=5		-487469.2116	-238531.7475	-487524.0328	-238570.7179
n=6		-535179.7125	-286242.2484	-535237.3892	-286284.0743
n=7		-582882.5316	-333945.0675	-582957.1605	-334003.8456
n=8		-630593.1603	-381655.6962	-630675.6698	-381722.3549
n=9		-678300.4842	-429363.0201	-678390.6718	-429437.3569
n=10		-725985.3147	-477047.8506	-726099.6411	-477146.3262

c) Effect of ^{15}N NMR on the formation of serine-nH_2O complexes:

NMR determination of N-H dipolar couplings in oriented samples with the separated local field approach also imply the essentially planar nature of the peptide bond. It therefore seems likely that the majority of peptide groups are planar, in actual protein [40].

During past few years, ^{15}N isotope has become prominent messenger of biopolymer dynamics in protein. For this amino acid, we found a good correlation between the experimentally observed ^{15}N and shift and those computed *ab initio*, which led us to develop methods for the refinement of serine in protein in solution [39].

We first consider the principal components of the ^{15}N shielding tensor for the serine and serine-nH_2O complexes (up to ten H_2O) to determine the effects of side chain substitution.

The water molecule has been taken as the oxygen proton acceptor in the hydrogen bonds discussed here. While HOH is in fact one of the acceptor molecules that one would expect to participate in such interactions, it also adequately mimics the hydroxyl group that occurs on such residues as serine.

The hydrogen bond length has a strong influence on the chemical shielding tensor of both imino proton and nitrogen, on their orientation. As the length of the hydrogen bond decreases, the least shielding component σ11, σ_{22}, σ_{33}, δ deflects from the N-H vector and the shielding tensor becomes increasingly asymmetric. Since the N-H is a substituent electronegative group, one might anticipate only a minor perturbation upon the chemical shift tensors in the complexes with water. This seemingly opposite behavior with increasing of water molecules in two basis sets of theoretical level (Table 3, 4).

d) The effect of $C^{\alpha}H\ldots O$ hydrogen bond in the protein folding:

Whereas the C^{α} of an amino acid is surrounded by NH_2 and COOH groups, it lies adjacent to full peptide groups within the context of a protein.

The $C^{\alpha}H\ldots O$ hydrogen bond are important determinants of stability, specificity and, depending on in membrane protein folding.

This works indicate the shielding of σ_{iso}, σ_{11}, σ_{22} and σ_{33} has permitted the successful prediction of coordination and structure of serine with use of C^{α} shielding tensor. Some confidence can, therefore, be placed in the quality of the calculations, since not only are the well-known isotropic chemical shift differences between 1 to 10 water molecules (Tables 5).

Figure 2 we show Ramachandran shielding surfaces for asymmetric of chemical shielding anisotropy, CSA_a for C^{α} of serine hydrated in two level (HF/6-31G* and HF/6-31G**) of *ab initio* calculations.

The results given in Table 5 and Figure 2 show that, with increasing of water molecules to stabilized molecule, the shift is increased, also has been seen in the axially asymmetric case, that $CSA_a = \Delta\sigma$.

More ever the basis set dependence, the influence of the relaxation of the geometry, therefore in most cases for these complexes in this paper, there is a uniform increase in shielding for each tensor element upon 6-31G** basis set.

The $C^{\alpha}H\ldots O$ could then be a more controllable and cooperative alternative than N-H…O bonds for exploiting the strength and directionality of hydrogen bonds in the hydrophobic environment and achieving,simultaneously,stability and specificity in transmembrane interactions.

As mentioned earlier, the structures of the various complexes have been optimized under the restriction of a linear $C^{\alpha}H\ldots O$ arrangement. As a result the optimized complex is not, strictly speaking, a true minimum on the entire potential energy surface. The large deshielding predicted for H is especially interesting since it has been implicated in a possible HB with the C=O group of serine. As expected, relaxation of this restriction permits the water molecule to swing around toward the COOH group, forming an H-bond between the carbonyl oxygen of the COOH and one of the water hydrogens, a bond that is stronger than the $C^{\alpha}H\ldots O$ interaction of interest. Since the $C^{\alpha}H$ group of each of amino acid residue in a protein is directly adjacent to a pair of electronegative groups (the N and C ends of two amide groups),it is logical to presume that its ability to form an H-bond is comparable in complexes of serine-n H_2O and we have indicated active site , Therefore $C^{\alpha}H\ldots O$ H-bond is important factor in the folding from one side and unfolding from active side of protein molecule(Figure 3).

Conclusion

The results presented in this paper show that:

1. The degree of agreement between correlated theoretical data and experimental methods mentioned will give us important insights into the nature of molecular interactions in the studied compounds and will provide us with an evaluation of the accuracy limits of these methods.
2. Creating and adapting tool for extracting information from the data bycomputercalculations has been always important task for producing labile character of the structure of hydration surrounding amino acid of serine.
3. Important probe of hydrogen bonding within protein, effect on proton chemical shifts and fractionation factors will be investigated. NMR chemical shifts (^{15}N and ^{13}C NMR Shielding Tensors) in hydrated serine has been performed by *ab initio* methods.
4. Optimization at the 6-31G** level yields molecular geometries in good agreement with experimental values for serine, and superior to those previously obtained theoretically. Complex of serine-10H_2O has been more stabilized than the other indicated compounds with this level of theory.
5. The existence of $C^{\alpha}H\ldots O$ hydrogen bonds between the water molecules and hydrophobic part of the amino acid has established. It seems that the $C^{\alpha}H\ldots O$ interaction appears to be a true H-bond that has significant role in folding of protein.

Table 3. ^{15}N pricipal values of the chemical shifts in hydrated serine with by HF/6-31G* method

			Shielding (ppm)					
			HF/6-31G*					
number of water			σ_{11}	σ_{22}	σ_{33}	σiso	σaniso	δ
n=0		N_1	253.6743	259.7206	255.6233	256.3394	37.1299	716.93185
n=1	I	N_1	186.0184	186.1557	266.3328	212.8357	107.7791	6.9569
		H	26.2118	32.2058	36.6325	31.6834	10.1821	11.80368
		H	28.219	31.8027	30.2099	30.0772	9.3717	452.3112
	II	H_3	38.6481	31.4995	26.3642	32.1706	11.7065	12.08108
		O	30.6701	4307885	-130.923	-18.8214	322.2546	0.6642
	III	H_4	31.2734	31.6408	36.5487	33.1543	14.2121	18.5347
		O	320.5857	324.434	284.0274	309.6824	33.5995	25.14206
	IV	H_{11}	32.3905	31.4725	24.4481	29.437	5.8616	12.80102
		O	325.4773	291.5984	290.0746	302.3835	38.0335	50.13248
	V	H_{12}	30.4788	31.0745	26.8159	29.4564	5.6905	23.31123
		O	310.8187	288.612	257.5587	285.6631	55.1167	21.32871
	VI	O_8	127.44	251.7521	181.9307	187.0409	167.5952	74.20298
		H	31.3173	25.0341	38.9264	31.7593	16.8094	7.86251
		H	39.7547	26.5513	31.8643	32.7234	16.9718	77.18077
	VII	H_{13}	36.8755	24.7313	23.2091	28.272	12.9226	12.16828
		O	292.6545	302.8488	274.3271	289.9434	27.8961	38.13344
	VIII	O_9	10.5679	-22.7842	-33.2881	-15.1681	542.3204	-0.6742
		H	39.9969	27.8312	26.2889	31.3723	19.4836	13.34305
		H	30.8739	39.1384	24.0218	31.3447	18.5369	9.56073
	IX	O_{10}	318.4822	348.9479	341.923	336.451	103.7971	121.97187
		H	28.0827	31.3666	33.4073	30.9522	19.8191	24.21461
		H	37.5847	29.0595	26.0804	30.9082	20.4655	13.80425
	X	H_{14}	47.9985	16.5618	18.513	27.6911	35.9472	7.03417
		O	327.6903	321.3658	301.6373	316.8978	21.8699	42.53177
n=2		N_1	143.9991	238.9196	250.7176	211.2121	108.7233	9.69279
n=3		N_1	221.3478	141.9555	246.8644	203.3892	108.9908	8.35656
n=4		N_1	267.7929	238.4789	260.4591	255.577	23.6829	103.6996
		O_{10}	337.4007	333.1921	349.3448	339.9792	33.8623	71.6017
n=5		N_1	268.3715	239.5889	259.1384	255.6996	24.0834	147.7144
		O_{10}	336.5795	331.8009	351.4163	339.9322	33.7174	58.2005
n=6		N_1	267.4132	237.1508	263.6631	256.0757	24.9641	66.5002
		O_{10}	342.6685	344.6405	352.4871	346.5987	35.835	116.7225
		O_9	-96.9357	33.0506	-215.9188	6.7321	525.2192	1.0604
n=7		N_1	428.3687	442.6103	427.0753	432.6848	23.4186	155.2685
		O_{10}	447.3363	530.0487	506.2675	494.5508	74.3376	83.4181
		O_9	440.7425	503.3905	397.4221	447.185	86.261	18.9726
n=8		N_1	269.3384	249.7545	241.6485	253.5804	37.7836	43.5046
		O_{10}	330.7265	378.6866	323.1445	344.1859	52.4194	33.7151
		O_9	-80.9778	53.652	80.2789	17.651	506.8979	-0.4363
		O_8	122.6155	218.8514	189.617	177.028	123.4824	27.1242
n=9		N_1	270.262	248.5581	240.5655	253.1285	37.817	41.2974
		O_{10}	325.9021	329.9044	213.9467	289.9177	71.4409	8.6323
		O_9	-75.4001	60.8983	91.0074	25.5019	496.078	-0.2214
		O_8	113.536	220.4737	203.8877	179.2992	122.3049	13.584
n=10		N_1	269.3026	259.0878	234.0759	254.1555	28.0908	26.3148
		O_{10}	331.9091	348.3967	365.9064	348.7374	69.0262	39.624
		O_9	-99.255	-159.3304	314.0594	18.4913	507.2701	-0.8748
		O_8	129.3333	129.2711	239.2611	165.9551	123.7535	3.5277
		H_{13}	39.2891	16.6404	13.1827	23.0374	25.2413	4.6381

Table 4. ^{15}N pricipal values of the chemical shifts in hydrated serine with by HF/6-31G** method

			Shielding (ppm)					
			HF/6 -31G**					
number of water			σ_{11}	σ_{22}	σ_{33}	σiso	σaniso	δ
n=0		N_1	258.4747	267.0775	258.4347	261.3289	34.4043	181.6068
n=1	I	N_1	204.1078	181.5718	271.3171	218.9989	105.3871	7.3718
		H	27.5711	29.0148	33.5905	30.0588	9.2253	16.0223
		H	29.189	29.5048	33.7294	30.8077	8.4184	20.0889
	II	H_3	38.521	30.6055	25.3104	31.479	12.4392	11.2062
		O	37.0967	39.8517	-141.0693	-21.3736	329.1668	0.6428
	III	H_4	30.4088	31.0862	35.9787	32.4912	15.1229	17.6329
		O	330.7324	330.728	293.9804	318.4803	30.159	26.9984
	IV	H_{11}	31.931	31.1385	23.8011	28.9569	6.3929	12.2327
		O	335.9749	300.7701	298.5742	311.773	40.0653	48.2426
	V	H_{12}	32.0589	25.388	31.1451	29.5307	6.1939	35.584
		O	321.4552	299.6348	265.5132	295.5344	56.8731	20.6884
	VI	O_8	126.8409	261.5211	190.6732	193.0117	168.8735	166.0731
		H	30.5566	23.8817	38.4831	30.9738	17.6965	7.2495
		H	39.3257	25.4468	31.0475	31.94	17.8647	72.5742
	VII	H_{13}	36.8089	23.7324	22.191	27.5774	13.9511	11.2396
		O	299.5878	313.0828	278.6869	297.1192	31.5581	33.2389
	VIII	O_9	15.9611	-9.1927	-55.0793	-16.1036	543.4092	0.1736
		H	39.477	26.912	25.262	30.5503	20.735	12.5539
		H	30.0247	38.785	22.7729	30.5275	19.8086	8.8734
	IX	O_{10}	326.6236	354.0795	348.221	342.9747	94.2007	129.7491
		H	27.0219	30.2156	33.0854	30.1076	21.0982	19.2214
		H	37.3844	27.753	25.0571	30.0648	21.7642	13.0074
	X	H_{14}	48.0236	15.0454	17.2335	26.7675	38.0406	6.6152
		O	338.3405	329.4603	312.2647	326.6885	19.7568	46.2985
n=2		N_1	175.2098	231.2987	247.7853	218.098	110.5696	13.6901
n=3		N_1	207.5271	178.4962	239.5407	208.5214	100.1774	12.4446
n=4		N_1	233.8947	247.9274	269.3099	250.3774	32.7627	25.4494
		O_{10}	328.3657	375.1997	329.0163	344.1939	85.1012	46.3555
n=5		N_1	262.2139	245.601	257.6576	255.1575	30.3885	203.1178
		O_{10}	314.0724	368.1856	347.6984	343.3188	90.5765	155.7809
n=6		N_1	243.2382	261.1946	257.6637	254.0322	32.785	138.9048
		O_{10}	362.7113	372.5611	312.8693	349.3806	103.3873	20.1382
		O_9	-69.101	296.9161	-254.6396	-8.9415	547.9134	0.9272
n=7		N_1	231.8715	272.3104	258.5	254.2273	32.4356	118.0007
		O_{10}	382.9371	363.2688	310.843	352.3496	90.5266	17.978
		O_9	-15.3302	42.012	53.7211	26.801	477.3335	0.9911
n=8		N_1	234.1439	273.4852	270.1046	259.2445	23.0452	46.7425
		O_{10}	331.5069	320.3209	245.7117	299.1798	74.4384	12.1909
		O_9	-40.1716	-134.5594	301.1537	42.1409	458.8627	-0.6746
		O_8	118.0917	187.4419	223.2772	176.2703	113.3164	6.4997
n=9		N_1	238.2246	268.9921	258.1479	255.1215	38.318	167.5973
		O_{10}	329.1215	289.0299	261.0661	293.0725	70.7452	19.3133
		O_9	-40.4923	-105.4859	256.8089	36.9436	472.9448	-0.6639
		O_8	121.6774	201.9194	205.7247	176.4405	117.8017	11.0502
n=10		N_1	231.9486	266.2162	268.8015	255.6554	42.867	37.8945
		O_{10}	338.8995	357.1206	350.2424	348.7541	38.7386	467.6611
		O_9	-60.4968	42.3263	126.9183	36.2493	473.1345	-0.2004
		O_8	151.4255	213.5376	170.6064	178.5231	116.096	46.1004
		H_{13}	39.7554	14.0932	10.7095	21.5194	27.8234	4.9814

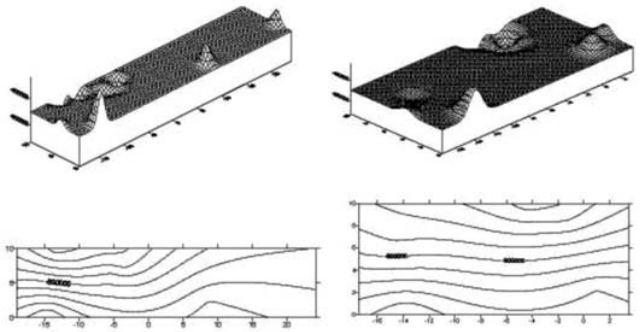

Fig. 2. Computed shielding tensor elementos for Ca in complexes of serine-nH_2O (n = 1,... 10) obtained by using a Hartree Fock method with 6-31G* and 6-31G** basis set respectively: (a, A') CSA.

Table 5. Summary of representative computed C^a shielding tensor elements for serine nH_2O complexes by HF/6-31G* and HF/6-31G** calculations

			HF/6-31G*								
number of water			s11	s22	s33	siso	saniso	d	?s	seff	CSAa
n=0		C2	156.9311	154.4894	141.9502	151.1236	20.4112	33.9482	-13.7600	13.92158	-13.7602
n=1	I	C2	118.3307	142.3975	136.0745	132.2676	60.0618	68.4883	5.7104	21.6105	5.7180
	II	C2	147.8866	158.8738	121.6353	142.7986	43.6602	14.4949	-31.7449	33.1403	-31.7540
	III	C2	162.1958	150.7911	138.8080	150.5983	22.3831	26.5461	-17.6854	20.2564	-17.6900
	IV	C2	162.0951	145.8679	141.7994	149.9208	22.7421	37.9199	-12.1821	18.5982	-12.1883
	V	C2	152.2066	153.8259	147.6862	151.2396	18.5976	861238	-5.3300	5.5114	-5.3300
	VI	C2	156.0470	155.2207	142.0268	151.0981	20.7081	34.3134	-13.6070	13.6258	-13.6070
	VII	C2	161.8889	150.4708	138.2100	150.1899	21.6286	26.0736	-17.9698	20.5108	-17.9745
	VIII	C2	155.5102	141.8870	155.4381	150.9451	21.2727	66.1912	6.7395	13.5873	6.7417
	IX	C2	161.2227	149.5443	141.4624	150.7432	21.3396	33.4849	-13.9211	17.2070	-13.9248
	X	C2	155.2968	155.6724	140.5865	150.5186	19.3963	31.3095	-14.8981	14.9016	-14.8981
n=2		C2	120.9477	146.9535	134.9518	134.2843	32.9366	401.3501	1.0012	22.4995	1.0027
n=3		C2	163.9415	102.4147	136.6162	134.3241	61.9586	116.2062	3.4381	53.3945	3.4675
n=4		C2	162.1261	149.1472	138.1685	149.8139	21.3622	26.7292	-17.4681	20.7719	-17.474
n=5		C2	161.9409	148.8148	138.3621	149.7059	21.5206	27.3943	-17.0157	20.4653	-17.0216
n=6		C2	162.8984	146.3688	139.9400	149.7424	23.6101	31.5522	-14.7036	20.5090	-14.7115
n=7		C2	344.5373	347.5276	348.7815	346.9488	15.7375	377.6204	2.74905	3.8078	2.47905
n=8		C2	162.0916	140.4713	147.9454	150.1695	24.5474	136.0383	-3.33605	19.0186	-3.3389
n=9		C2	160.6611	139.9508	148.7995	149.8038	24.5453	299.3248	-1.50645	17.9987	-1.50765
n=10		C2	165.1750	138.0970	147.3387	150.2036	27.1559	105.85779	-4.2973	37.6832	-4.3032

			HF/6-31G**								
number of water			s11	s22	s33	siso	saniso	d	?s	seff	CSAa
n=0		C2	157.3627	155.3354	141.8354	151.5111	21.481	32.3178	-14.5136	14.1945	-14.5137
n=1	I	C2	122.2075	141.6789	135.5261	133.1375	61.3892	110.4774	3.5829	17.2391	3.5860
	II	C2	147.7495	159.1047	122.4153	143.0898	44.1110	14.8421	-31.012	32.5336	-31.0212
	III	C2	162.9402	151.2716	138.7323	150.9814	23.4179	25.6518	-18.3736	20.9691	-18.3785
	IV	C2	162.9479	146.6008	141.5883	150.3790	23.7005	35.2132	-13.1860	19.3466	-13.1998
	V	C2	152.4775	154.9411	147.4992	151.6393	19.6487	74.2539	-6.2101	6.5663	-6.2101
	VI	C2	156.4781	156.0938	141.9432	151.5050	21.7579	32.6896	-14.3427	14.3466	-14.3427
	VII	C2	162.8143	150.8259	138.0797	150.5733	22.7093	25.1040	-18.7404	21.4241	-18.7458
	VIII	C2	155.9573	141.9291	156.2845	151.3903	22.4326	60.8651	-7.3413	14.1946	-7.3438
	IX	C2	162.0252	150.1896	141.2692	151.1613	22.3829	31.5620	-14.8382	18.0342	-14.8422
	X	C2	155.6747	156.5783	140.5133	150.9221	20.4344	29.9989	-15.6132	10.8132	-15.6132
n=2		C2	117.2555	141.0126	137.9765	132.0815	41.9036	43.81138	8.8424	22.3939	8.8538
n=3		C2	135.7501	102.0783	143.1026	126.9770	49.7557	14.7485	24.1884	37.8869	24.2509
n=4		C2	163.2849	155.7641	140.7162	153.2551	26.0503	25.4447	-18.8083	19.9166	-18.8103
n=5		C2	164.9982	151.5695	139.3194	151.9624	24.9020	25.0389	-18.9644	22.2462	-18.9711
n=6		C2	162.0410	146.1924	148.6893	152.3076	25.2923	85.1873	-5.4274	14.7594	-5.4299
n=7		C2	162.5162	145.4715	146.8590	151.6156	22.8342	64.7495	-7.1348	16.3960	-7.1387
n=8		C2	167.0905	140.5622	150.5321	152.7282	24.6028	140.0904	-3.2942	23.2091	-3.2984
n=9		C2	162.5798	141.5393	141.9578	148.6923	22.4991	45.1583	-10.1017	20.8344	-10.1105
n=10		C2	163.0150	143.3670	139.8300	148.7373	22.7180	34.3967	-13.3610	21.6344	-13.3713

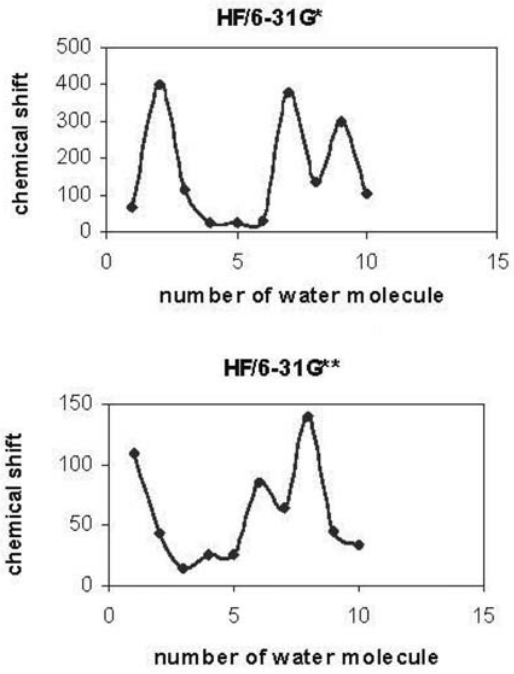

Fig. 3. Computed chemical shifts elements, □, for C□ in complexex of serine nH_2O (n = 1,... 10).

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