

MOLECULAR MECHANICS AND QUANTUM MECHANICS STUDY INTERACTION BETWEEN Zn (II) IONS AND CHITIN-CONTAINING SORBENTS

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Abstract

Chitin, chitosan and various derivative of chitin is effective sorbents of metal ions from water solutions. In our work was researched mechanism of sorption zinc ion on chitin-containing sorbents (ChCS) which were prepared from waste of biotechnological production of citric acid in Cherkassy region. We have performed analyses of IR spectra of different derivatives obtained in our laboratory. Quantum chemical calculations have been performed by the density functional theory (DFT) and by MNDO and PM3 semiempirical SCF methods. First we have optimized geometry of the chains containing up to 3-5 monomers with different sequence along the chain by molecular mechanics simulation. Shorter chains and their complexes with hydrate of Zn(II) ions have been studied by DFT and PM3 methods with calculations of the ultraviolet, NMR spectra, Hessian matrices, IR frequencies and IR intensity. From comparison with experimental data some conclusions about the chitin complexes chemical structures have been obtained.

Introduction

Chitosans is a family of linear heteropolysaccharides which include varying amounts of (1-4) linked 2-acetamido-2-deoxy-beta-D-glucopyranose (GlcNAc; A-unit) and 2-amino-2-deoxy-beta-D-glucopyranose (GlcN; D-unit) (Muzzarelli, 1977). Chemical structure of chitosans is characterized by the ratio between the two monomers, and their distributions in the chains. The chemical structure can be established by NMR and IR spectra, however the distribution of the GlcNAc and GlcN monomers is still discussed (Muzzarelli, 1977; Guibal, Milot, Eterradosi, Gauffier, & Domard, 1999; Muzzarelli, Tanfani, & Emmanuelli, 1984; Hirano, & Ohe, 1975).

The use of biopolymers to collect and remove metal ions from dilute solutions for the treatment of waste water is a popular subject of many researches (Guibal, Milot, Eterradosi, Gauffier, & Domard, 1999; Muzzarelli, Tanfani, & Emmanuelli, 1984). Chitin and chitosan are well-known biosorbents of metal ions (Muzzarelli, 1977). Sorption capability of native forms of these biopolymers have been extensively studied, but few data are available on the mechanisms and reactions between metal ions and the sorption sites (Guibal, Milot, Eterradosi, Gauffier, & Domard, 1999).

In the present work we have studied the mechanism of Zn(II) ion sorption by chitin-containing sorbents, which have been obtained from fungus mycelium of the *Aspergillus niger* – the waste of biotechnology production of citric acid at the Smela plant of the Cherkassy region.

Methods and materials

Fungus mycelium of the *Aspergillus niger* have been treated by 2% water solvent of NaOH at the heating up to 60°C, then by successive treatment by NaClO solvent (0.003 mole/liter) and by HCl

solvent (concentration 0.1 mole/liter). Every time the product has been washed by water. The obtained sorbent has been dried at 25-30°C. The yield is 43% in terms of the dry mycelium. Sorption of the hydrated Zn(II) ions from water solvents has been studied at the static condition of the experiment: to the water solvent of zinc sulfate ($V = 100$ ml) with the Zn(II) ion concentration of 0.000125 mole/l the sorbent (20 mg) has been added and the mixture has been stirred until full saturation of the sorbent. At the end the filtrate has been analyzed for the residual zinc ions. Concentration of the Zn(II) ions in solvent has been determined by atomic absorption spectrophotometer AA240FS Varian. High-dispersed powder of the sorbent deposited on the surface of the polished plane-parallel male die has been tablet at the pressure of 15 mPa. Infra-red (IR) spectra has been recorded with the IR spectrophotometer Specord IR-75. The models of chitin and chitosan polymers containing 2-5 monomer units has been optimized by molecular mechanics (MM+) method. Chelate complexes formed during sorption of the zinc ions by chitin have been simulated with the models where metal coordination has been arranged by the nitrogen and by the oxygen of the acetamido group as the most probable. Geometry optimization and IR spectrum of the chitin monomer and its complexes with $Zn(OH)_2 \cdot H_2O$ have been performed by the self-consistent field method in the PM3 (Stewart, 1990) and MNDO approximations (Dewar, & Thiel, 1977; Dewar, & Metz, 1986). Density functional theory (DFT) (Frisch, Trucks, Schlegel, Scuseria, Robb, et al. 1988) has also been applied for chitin monomer and its complex with Zn(II) ion with the 6-31G basis set (Hehre, Ditchfield, & Pople, 1972) and the B3LYP functional (Becke, 1993). After comparison of different methods the most results are presented in the framework of the MNDO approach.

Results and discussions

The optimized structures of N-acetylglucosamine (GlcNAc) and of its complexes with Zn(II) ion (GlcNAc+O-Zn and GlcNAc+N-Zn) are presented at Figures 1-3; some calculated parameters are given in Tables 1-2. Analysis of the optimized geometry by MNDO method of chitin monomer (GlcNAc) and its complex with Zn(II)-(OH)₂·H₂O species, where Zn ion is coordinated by oxygen atom of the carbonyl group (GlcNAc+O-Zn) indicates a small change in the glucopyranose ring, not only in the N-acetyl group. Similar results are obtained by DFT method; since vibrational calculations have not been done with DFT, we present here only the MNDO results.

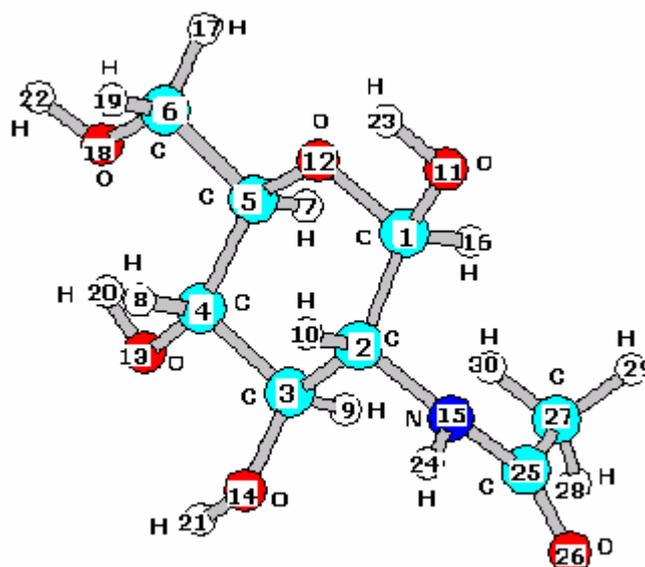


Figure 1 : The optimized structure of 2-acetamido-2-deoxy- β -D-glucopyranose (GlcNAc)

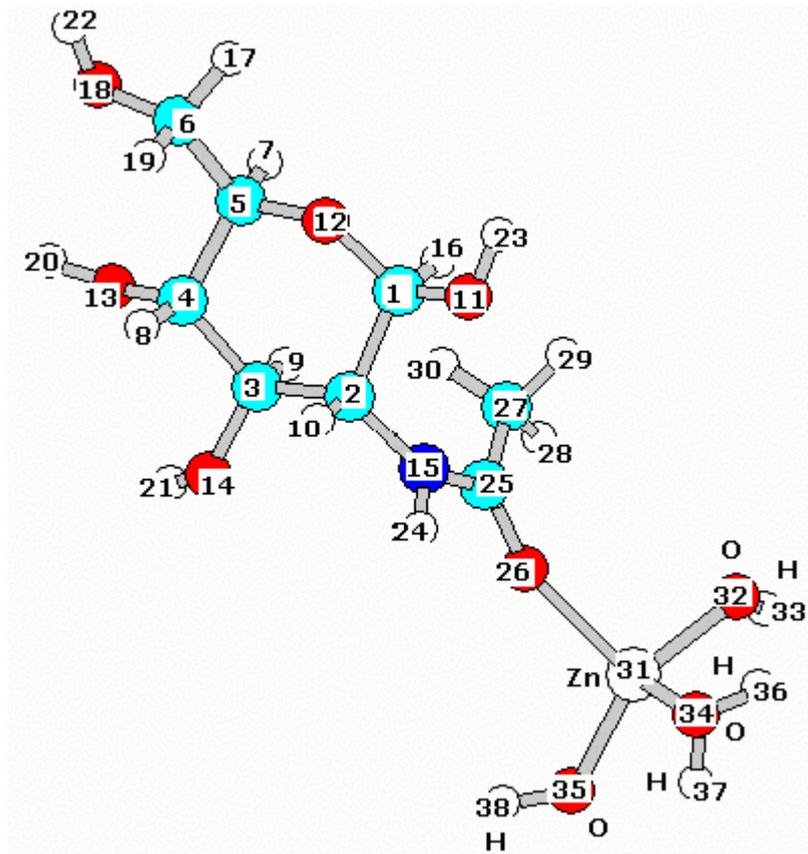


Figure 2 : The optimized structures of complexes 2-acetamido-2-deoxy- β -D-glucopyranose and Zn(II) ion (GlcNAc+O+Zn)

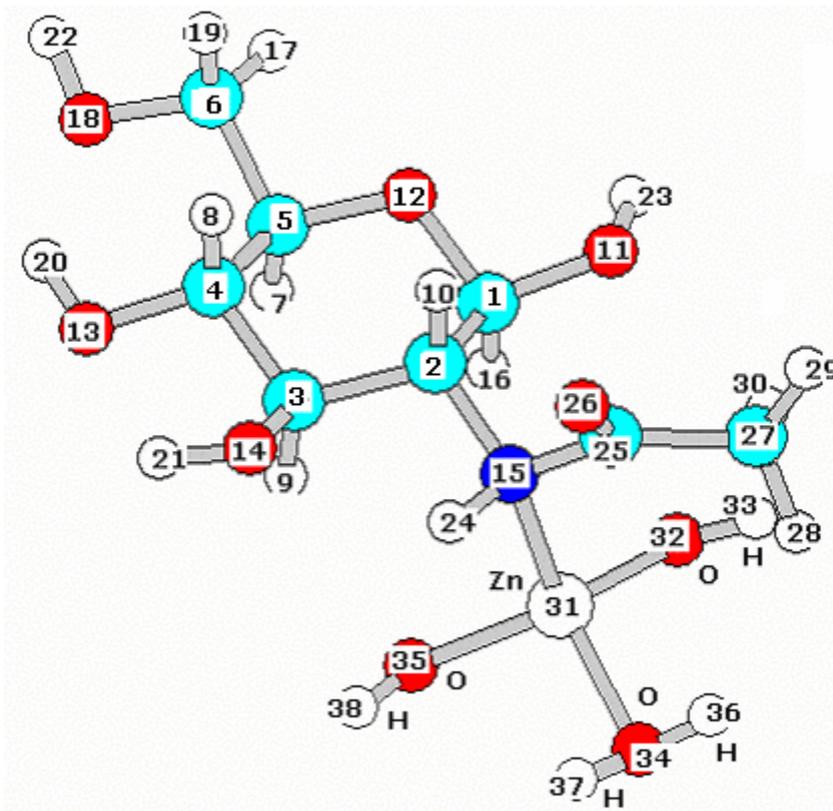


Figure 3 : The optimized structures of complexes 2-acetamido-2-deoxy- β -D-glucopyranose and Zn(II) ion (GlcNAc+N+Zn)

The C⁵-O¹² chemical bond in the ring is getting longer (by 0.001 Å, Table 1); similar response indicate the C⁵-C⁴ and C²-N¹⁵ chemical bonds. The C¹-O¹² and N¹⁵-C²⁵ (acetimido group) chemical bonds are strongly shorten (by 0.003 and 0.005 Å, respectively; Table 1). The carbonyl bond indicates elongation by 0.016 Å, Table 1. At the same time the calculated IR spectrum predicts an increase of vibrational frequency of the C=O group upon coordination with the Zn(II) ion in a good agreement with our measurements (Table 2, Fig.4.).

Table 1: Bond lengths (Å) of 2-acetamido-2-deoxy- β -D-glucopyranose and its complexes with Zn (II) ions

Bond	Method of calculation		
	MNDO		
	GlcNAc	GlcNAc+O+Zn	GlcNAc+N+Zn
O ¹² – C ⁵	1,405	1,406	1,425
C ⁵ – C ⁴	1,586	1,588	1,546
C ⁴ – C ³	1,591	1,592	1,536
C ³ – C ²	1,577	1,577	1,531
C ² – C ¹	1,586	1,585	1,538
C ¹ – O ¹²	1,414	1,411	1,419
C ⁵ – C ⁶	1,576	1,576	1,538
C ⁶ – H ¹⁷	1,123	1,228	1,091
C ⁶ – O ¹⁸	1,396	1,396	1,414
C ² – N ¹⁵	1,458	1,460	1,489
N ¹⁵ – H ²⁴	1,002	1,009	1,010
N ¹⁵ – C ²⁵	1,404	1,399	1,389
C ²⁵ – O ²⁶	1,230	1,246	1,229
C ²⁵ – C ²⁷	1,527	1,525	1,531

The high-frequency shift (about 30 cm⁻¹) is in contradiction with a simple theory of IR spectra; the longer (and weaker) bond with smaller force constant (k) has to provide the lower harmonic vibrational frequency (ν):

$$\nu = \frac{1}{2\pi} \frac{\sqrt{k}}{\sqrt{m}},$$

where m is a reduced mass. This puzzle can be explained by analysis of the calculated form of normal vibrations; this mode includes not only the characteristic vibration of the C=O group, but also intermolecular vibration of the whole C=O...Zn moiety. The complex formation influences carbonyl group in such a way that vibration of the C=O group modifies its nature and the vibrational frequency is not determined by the C=O force constant, but by the whole force field, created during reaction of the complex formation. Besides the frequency shift, a strong intensity increase is also predicted in qualitative agreement with observation. Other calculated and observed changes in IR absorption spectra also agree with the model of complex formation by C=O group.

Table 2: Calculated and experimental frequency (ν , cm^{-1}) of normal vibrations, calculated intensity (I, km/mole) of the IR spectrum of 2-acetamido-2-deoxy- β -D-glucopyranose and the complexe with Zn (II) ions

Type of vibration ^{**}	GlcNAc			GlcNAc+O+Zn		
	ν^* , cm^{-1} , calcul.	I, km/mole	$\nu_{\text{exper.}}$, cm^{-1}	ν^* , cm^{-1} , calcul.	I, km/mole	$\nu_{\text{exper.}}$, cm^{-1}
$\nu(\text{O}^{35}-\text{H}^{38})$				3817	2,46	3840
$\nu(\text{O}^{32}-\text{H}^{33})$				3805	3,76	
$\nu(\text{O}^{34}-\text{H}^{37})$; $\nu_{\text{as}}(\text{O}^{34}-\text{H}^{36})$				3736	14,6	3790
$\nu(\text{O}^{34}-\text{H}^{37})$; $\nu_{\text{s}}(\text{O}^{34}-\text{H}^{36})$				3701	30,8	
$\nu(\text{O}^{18}-\text{H}^{22})$	3477	7,9	3460	3467	16	3480
$\nu(\text{O}^{14}-\text{H}^{21})$	3466	10,1		3454	18,7	
$\nu(\text{O}^{11}-\text{H}^{23})$	3400	11,2	3415	3450		3410
$\nu(\text{O}^{13}-\text{H}^{20})$	3379	58,4		3448	0,28	
$\nu(\text{N}^{15}-\text{H}^{24})$	3326	6,3	3320	3342	38,5	3330
$\nu_{\text{as}}(\text{C}^{27}-\text{H}^{28})$	3049	3,7	3040	3105	1,4	3090
$\nu_{\text{as}}(\text{C}^1-\text{H}^{16})$	2755	0,4		2960	13,9	
$\nu(\text{C}^{25}-\text{O}^{26})$	1632	173	1630	1657	354	1660, 1605
$\delta(\text{N}^{15}-\text{H}^{24})$	1430	38	1450	1490	41,9	1480
$\delta_{\text{as}}(\text{C}^5-\text{O}^{12})$	1346	4,8	1350	1390	33	1375, 1345
$\delta(\text{C}^4-\text{O}^{18})$	1316	11,5	1310	1325	87	1310
$\delta_{\text{as,s}}(\text{C}^5-\text{O}^{12}-\text{C}^1)_{\text{as, sym}}$	1228- 992	25-2,8	1200- 950	1240- 987	21,3- 3,05	1205- 960
$\nu_{\text{s}}(\text{C}^{25}-\text{C}^{27})$; $\nu_{\text{s}}(\text{N}^{15}-\text{H}^{24})$	871	7,5	880	849	8,8	885
$\rho(\text{C}^2-\text{N}^{15}-\text{C}^{25})$	778	8,01	780	825	25,6	800
$\rho(\text{N}^{15}-\text{H}^{24})$	679	42,4	650	679	3,9	685
$\rho(\text{C}^5-\text{O}^{12})$; $\rho(\text{C}^1-\text{O}^{11})$	595	21,7	590	650	7,2	625, 605
$\rho(\text{O}^{13}-\text{H}^{20})$	507	34	500	530	19	505
$\rho(\text{Zn}^{31}-\text{O}^{32})$, $\rho(\text{Zn}^{31}-\text{O}^{35})$				480	24,7	485
$\rho(\text{O}^{34}-\text{H}^{36})$, $\rho(\text{O}^{34}-\text{H}^{37})$				345	100	
$\rho(\text{O}^{35}-\text{H}^{38})$, $\rho(\text{O}^{34}-\text{H}^{36})$				123	40,6	

*¹) – scaling factor in the range 0,85-0,89 are used for OH and CO vibrations.

**²) ν – stretching vibration; δ – internal deformation vibration (bending);

ρ – external deformation vibration.

Coordination by nitrogen atom provides no agreement with the observed changes in IR absorption; calculations predict completely different picture of complex formation by NH group in terms of IR frequency shifts, bond lengths and electron density redistribution. The heat of formation for the oxygen-coordinated complex is much lower in all methods studied. This is in agreement with the recent DFT calculations for the copper II ion sorption (Terreux, Domard, Viton, & Domard, 2005).

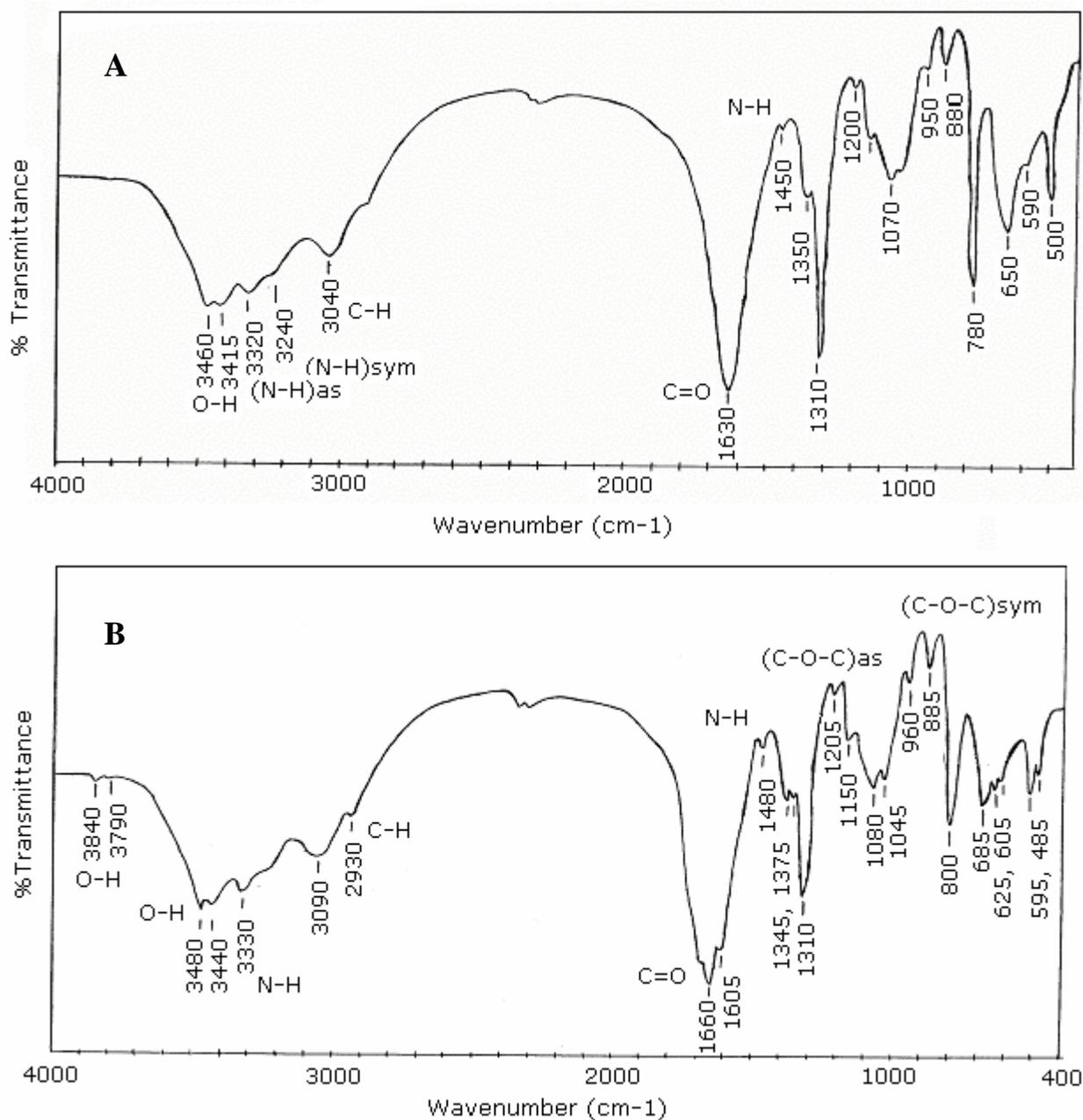


Figure 4 : FT-IR spectrum of citrin-containing sorbent (A) isolated from the mycelium *Aspergillus niger* (ChCS), citrin-containing sorbent after sorption Zn(II) ions (B).

The characterization of the chitin and chitosan structures by IR spectra has been studied in a number of works (Muzzarelli, 1977; Muzzarelli, Tanfani, & Emmanuelli, 1984; Guibal, Milot, Etteradossi, Gauffier, & Domard, 1999). Though the main absorption bands are now clearly identified, the assignments of several transitions are still a subject of controversy. The IR spectra can be influenced by the degree of deacetylation and by crystallinity (Guibal, Milot, Etteradossi, Gauffier, & Domard, 1999). The infrared absorption of chitosan corresponds to a convolution of IR bands specific to both carbohydrates and the signals due to amine and amide groups (Muzzarelli, 1977). It is well-known that within the range 2900-3500 cm^{-1} IR absorption bands can be identified as hydroxyl, N-H and C-H stretching, but these bands are not indicative for the identification of metal sorption mechanism (Guibal, Milot, Etteradossi, Gauffier, & Domard, 1999). From our calculations we have assigned very weak bands at 3840 and 3790 cm^{-1} to hydroxo groups, coordinated at the Zn(II) ion and to the asymmetric O-H stretching vibrations of water molecule. We have identified

the C-H stretching of the methyl group at 3040 cm^{-1} and its shift to 3090 cm^{-1} with intensity reduction upon metal sorption (Table 2). A small shift of the N-H band from 3320 to 3330 cm^{-1} is also well reproduced by our calculation (Table 2). We have found an interesting response of O-H vibrations to interaction with metal ion. The band 3460 cm^{-1} , responsible for the $\text{O}^{18}\text{-H}^{22}$ vibration of the CH_2OH group, is shifted and increased by complex formation.

Most IR studies on metal sorption usually concern the wave-number range $1660\text{-}400\text{ cm}^{-1}$ (Guibal, Milot, Eterradosi, Gauffier, & Domard, 1999). We have predicted a number of low-frequency bending vibrations for the Zn-coordinated O-H vibrations (345 and 123 cm^{-1}) with rather high IR intensity (Table 2) which are of intermolecular nature. The Zn-O vibration in the complex with chitin is calculated at 485 cm^{-1} and is seen in the IR spectrum. A number of shifted IR bands connected with C-O-C and other glucopyranose ring vibrations can be identified from our calculation and experimental IR measurements (Table 2, Fig. 4).

Calculations of the NMR spectra by DFT method (Frisch, Trucks, Schlegel, Scuseria, Robb, et al. 1988) indicate that the chemical shifts can be interpreted in terms of diamagnetic contributions which correlate with atomic charges. One can see from Table 3, which the positive charge at the C^{25} atom of the carbonyl group increases upon complexation through the oxygen atom O^{26} . Thus we predict the low-field shift of the C^{25} NMR signal.

Quantum chemical calculations of N-acetylglucosamine (GlcNAc) and of its complexes with Zn(II) ion (GlcNAc+O-Zn and GlcNAc+N-Zn) explain quite well the IR spectra of them species. Comparison of the optimized geometry of chitin monomer (GlcNAc) and its complex with Zn(II)-(OH)₂-H₂O species, where Zn ion is coordinated by oxygen atom of the carbonyl group indicates a small change in the glucopyranose ring, not only in the N-acetyl group. This complex is more stable than the other one with coordination at the nitrogen atom.

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References

- [1] Muzzarelli, R. A. A. (1977). Chitin. Oxford: Pergamon Press (pp. 22-138).
- [2] Guibal, E., Milot, C., Eterradosi, O., Gauffier, C., & Domard, A., International Journal of Biological Macromolecules, 24(1999) 49-59.
- [3] Muzzarelli, R. A. A., Tanfani, F., & Emmanuelli, M., Carbohydrate Polymers, 4(1984) 137-151.
- [4] Strand, S. P., Smidsrod, O., & Varum, K. M., Advances in Chitin Science, 6(2003) 27-34.
- [5] Hirano, S., & Ohe, Y., Carbohydrates Researches, 41(1975) 1-14.
- [6] Terreux, R., Domard, M., Viton, C., & Domard, A., Advances in Chitin Science, 8(2005), 390-398.
- [7] Stewart, J. J. P., Journal of Computer Aided Molecular Design, 4(1990) 1-22.
- [8] Frisch, M. J., Trucks, G. W. S., Schlegel, H. B., Scuseria, G. E., Robb, M.A., et al., Gaussian-98, Gaussian Inc., Pittsburg, PA. (1988).
- [9] Hehre, W. J., Ditchfield, R., & Pople, J. A., Journal of Chemical Physics, 56(1972) 2257-2261.
- [10] Dewar, M. J. S., & Thiel, W., Journal of the American Chemical Society, 99(1977) 4899-4998.
- [11] Dewar, M. J. S., & Metz, K. M. J., Organometalics, 5(1986) 1494-1496.
- [12] Becke, A.D., Journal of Chemical Physics, 98(1993) 5684-5690.