# A study on the effect of medium acidity and basicity on the stability of tryptophan photoionization products

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## INTRODUCTION

Biosafety and environmental friendliness of metal nanoparticles are of great interest due to their promising use in biomedical applications. In this context, mono- and bimetallic silver and gold nanoparticles obtained in colloids in the presence of amino acid tryptophan (Trp) have a great potential for the cancer treatment without the need of their further functionalization. At the same time, the mechanism of metal reduction and particle stabilization in metal/Trp systems should be revealed, and the quantum-chemical calculations can help to elucidate it, starting from individual molecules.

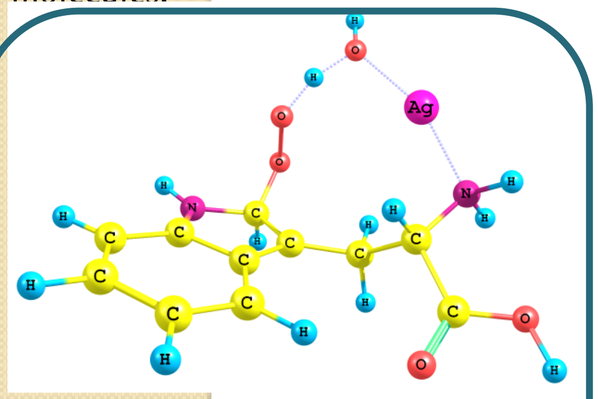

**Fig.2.** The intermediate complex model of tryptophan oxidation processes to NFK by silver ions in the presence of water and oxygen molecules

## MODELS AND METHODS

In this work, we performed quantum-chemical calculations of the energy characteristics of structural changes in the silver complex with Trp metabolite – N'-formylkynurenine (NFK) under the influence of acidity of the medium: neutral, acidic and alkaline media were analyzed. The optimal structures of single molecules of NFK and its complexes with hydrated $Ag^+$ ions and proton were studied by density functional theory (B3LYP/3-21G*) method.

The electronic absorption spectra of studied structures were calculated by the TDDFT method. On going from a neutral to an acidic medium, the NFK complex with silver decomposes with the formation of hydrated silver ions and the protonated form of NFK. In an alkaline environment the free form of NFK and the solid phase of silver hydroxide are formed.

## RESULTS

Based on the foregoing, coordination compounds based on silver and tryptophan can become a basis for drugs with a wide spectrum of action (Fig.1). For their purposeful development, it is necessary to first study the process of complexation of silver and tryptophan.

Coordination compounds of silver and tryptophan are usually obtained through the formation of an intermediate silver hydroxide (Fig.2). The formation of protonated coordination compounds occurs at pH 7-9; an increase in pH value due to hydroxide ions added to the system leads to their deprotonization [1]..

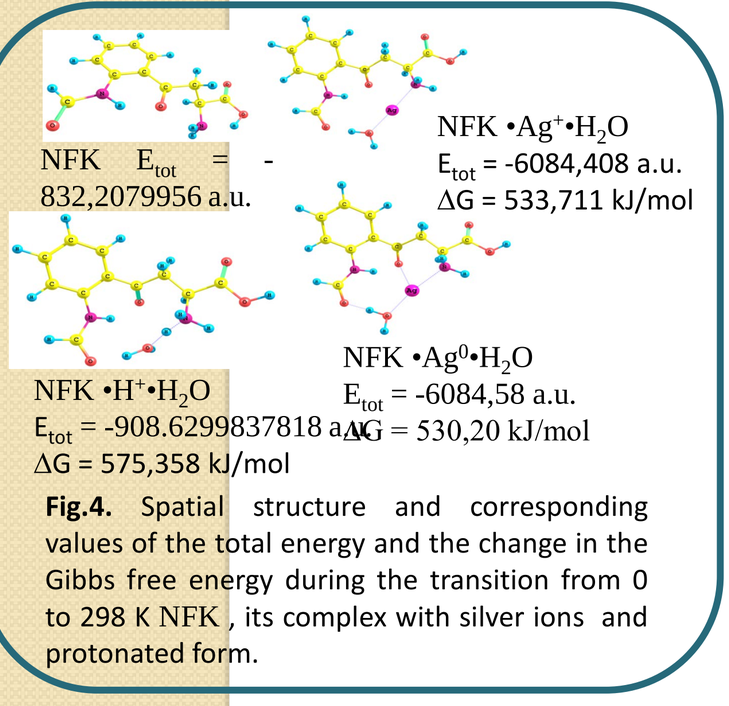


**Fig.4.** Spatial structure and corresponding values of the total energy and the change in the Gibbs free energy during the transition from 0 to 298 K NFK , its complex with silver ions and protonated form.

From the optical spectra of a stable colloid of silver nanoparticles obtained in the presence of tryptophan, it follows that with increasing ultraviolet irradiation, the intensity of the absorption band (about 270-290 nm) corresponding to tryptophan decreases whereas and the intensity of the absorption band (400-450 nm) corresponding to silver nanoparticles increases. This conclusion is supported by the results of quantum chemical calculations of the absorption spectra of the $Ag_{14}$ cluster (absorption maximum at 456 nm Fig. 3) and tryptophan molecules in a complex with 4 water molecules (absorption maximum at 265 nm).

The corresponding UV spectra of the reaction products (NFK) and its complex with silver ions and the protonated form) are shown in Fig. 4-5.

## CONCLUSION

When passing from a neutral to an acidic medium, the absorption bands of NFK shift hypsochromically from 367 to 340 nm, caused by the protonation of amino group. In an alkaline medium there is a bathochromic shift of absorption bands from 367 to 395 nm, that corresponds to the elimination of the neutral form NFK.

From the results of quantum chemical calculations, it follows that Based on the results of quantum chemical calculations, it can be assumed that the process proceeds more efficiently in an alkaline medium, since it is thermodynamically more advantageous than in an acidic medium.


**Fig.1.** UV spectra of tryptophan:changes of experimental absorption spectra of tryptophan/silver system in time

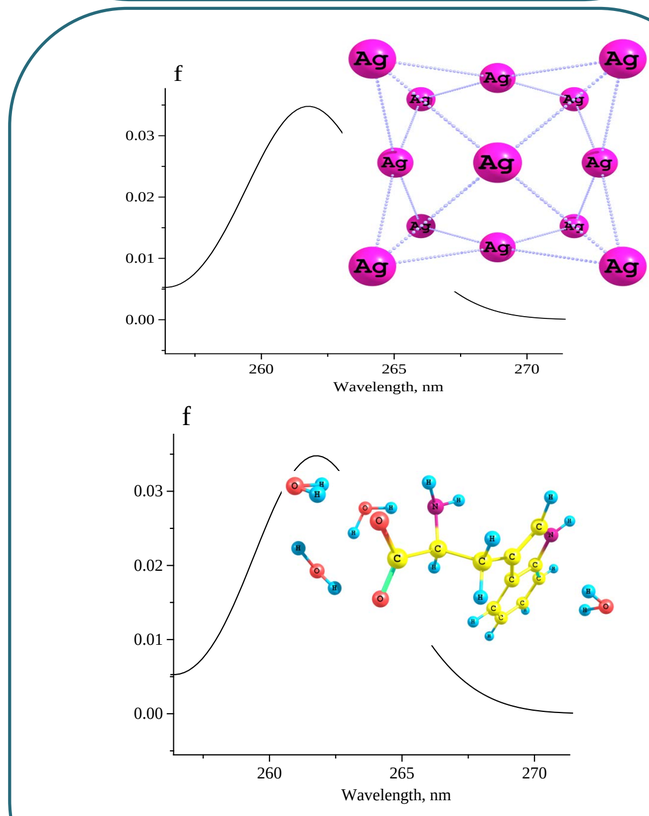


**Fig. 3.** Cluster and related UV spectrum $Ag_{14}$.(a) and Cluster Tr+2$H_2O$+OH) and related UV spectrum (*b*)

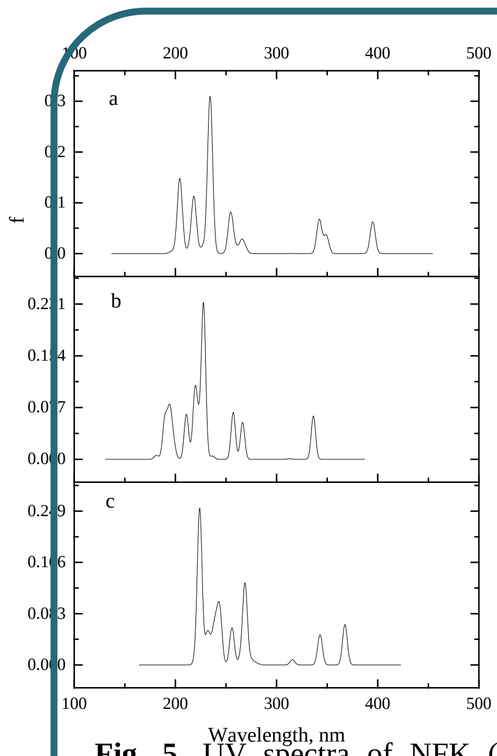


**Fig. 5.** UV spectra of NFK (*a*), its protonated form(*b*) and its complex with silver ions (*c*)

## REFERENCES

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