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# The Peculiarities of the RNA Luminescence

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*The optical absorption, fluorescence and phosphorescence spectra of the RNA and ribonucleotides are investigated. Positions of the first excited singlet and triplet electronic energy levels of the RNA bases are evaluated. It is shown the energy structure of the RNA is determined mainly by the individual properties of the ribonucleotides π-electron systems. Comparing the phosphorescence spectra of the DNA, RNA and ribonucleotides two types of triplet excitations traps in the RNA are found: (1) adenosine groups and (2) the centers of unknown nature that manifest structureless long-wave phosphorescence and are not the same as for the DNA.*

**Keywords:** optical absorption; phosphorescence; ribonucleotides; RNA; triplet excitations

## 1. INTRODUCTION

The biologic macromolecules – nucleic acids (DNA and RNA) – are known π-electron-containing macromolecules that are natural functional systems and vitally important for any live creature. They are the main objects of the transfer, storage and realization of the genetic information, protein biosynthesis, etc. Therefore the investigation of photophysical processes in these biopolymers is in the great interest

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not only of photophysics but photobiology and applied medicine too. Our previous works [1,2] on the DNA, the separated deoxyribonucleotides and the synthetic polynucleotides and oligonucleotides with the predetermined energy structure showed that AT-sequences in the DNA are main traps of triplet excitations; the DNA phosphorescence is due to the complex formed by these AT-sequences. It is known the triplet excitations are initiated the photochemical reactions in organic macromolecules (for example, photodestruction). We believe the fact of triplet excitations localization on AT-sequences is connected with the existence of the DNA self-protection mechanism and the Nature have designed namely such mechanism in the DNA connected with the logic displacement of the excited electronic singlet and triplet energy levels of the nucleotides. In this connection the question arises: is the possibility for such self-protection mechanism to exist in the RNA macromolecule? Furthermore the nature of the luminescent centers of the RNA is not clear completely until now. This paper that presents the investigations results on the electronic excitations dynamics and the nature of the absorbing and emitting centers in the RNA gives some version of answer on the question asked above.



## 2. EXPERIMENTAL

The human neuroblastoma RNA, yeast RNA, colibacillus RNA and the model compounds – monophosphates of 5′-adenosine (rAMP), 5′-uridine (rUMP), 5′-guanosine (rGMP) and 5′-cytidine (rCMP) were obtained from the Institute of Molecular Biology and Genetics (IMBG) of the NAS of Ukraine. The brewery yeast RNA was obtained from Biologic Department of Kyiv Taras Shevchenko National University. The total chicken erythrocytes DNA was purchased from Sigma. The steady state fluorescence measurements were performed with Hitachi MPF-4 spectrofluorometer; absorption spectra were recorded on a Specord UV-VIS spectrophotometer. The phosphorescence spectra were obtained using laboratory-designed equipment. The spectral measurements were carried out at 4.2 K, 77 K and ambient temperatures. The irradiation of the investigated compound samples were performed using 1 kW Hg-lamp.

## 3. RESULTS AND DISCUSSION

### 3.1. The Singlet and Triplet Electronic Sites of the RNA

It is known [3] the electronic absorption spectrum of the DNA is close to the additive sum of the spectra of the corresponding nucleotides

that is confirmed by us in [1,2]; this is typical for nonconjugated $\pi$-electron-containing polymers. It is logically to suppose the same have to be with the RNA. Really, our experimental data confirm this (Fig. 1). Thus the nucleotides are practically independent absorbing centers in the RNA macromolecule and electronic processes in it start from initially excited the RNA bases. This gives the ground to consider the ribonucleotides (rAMP, rUMP, rGMP and rCMP) as the model compounds for the RNA elementary links (bases). We beleive the excited electronic levels of these compounds are the excited levels of the RNA macromolecule.

The absorption (at $T = 300\,K$), fluorescence (Fig. 2) and phosphorescence (Fig. 3) at $T = 4.2\,K$ and $77\,K$ spectra of the ribonucleotides (mentioned above) were investigated. These spectra are similar to some extent with the correspondent ribonucleotides spectra obtained in [4–6]. The absorption and fluorescence spectra obtained in our experiments (Fig. 2) give the positions of the first excited singlet energy level (Fig. 4) of the rAMP, rUMP, rGMP and rCMP (since the displacement of the first singlet excited level is obtained by intersection of the long-wave edge of absorption and the blue edge of fluorescence spectra curves normalized on the first absorption maxima). The spectral properties of the fifth ribonucleotide – monophosphates of 5′-inosine (rIMP)–that is found scarce in the cells of some bacteria also were investigated. But no total luminescence at $77\,K$ and no phosphorescence at $4{,}2\,K$ of this compound were observed. The reasons of these phenomena are under discussion now.

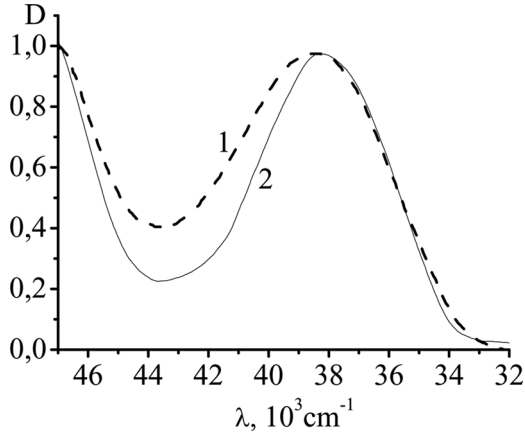


**FIGURE 1** The absorption spectra of the RNA (1) and additive sum of the spectra of ribonucleotides (2).

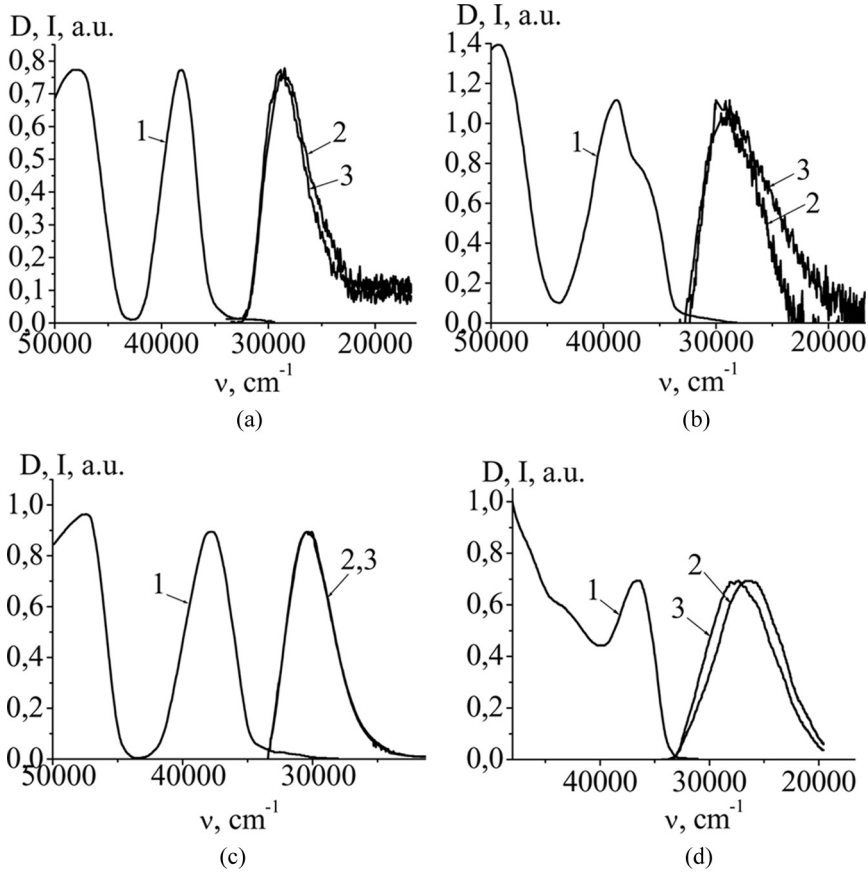


**FIGURE 2** The absorption spectra at 300 K (1) and fluorescence spectra at 77 K (2), at 4.2 K (3) (excitation 260 nm) of: rAMP (a), rGMP (b), rUMP (c), rCMP (d). Aqueous solutions, $C = 10^{-4}$ M.

The positions of the first excited triplet ($T_1$) electronic energy levels (Fig. 4) of the RNA bases were evaluated using blue edges of the phosphorescence spectra (Fig. 3) of the ribonucleotides (rAMP, rUMP, rGMP and rCMP).

## 3.2. The Nature of Singlet and Triplet Excitations Capture Centers in the RNA

The fluorescence (Fig. 5) and phosphorescence (Fig. 6) spectra at $T = 4.2$ K and 77 K of the RNA of the various origin were investigated.

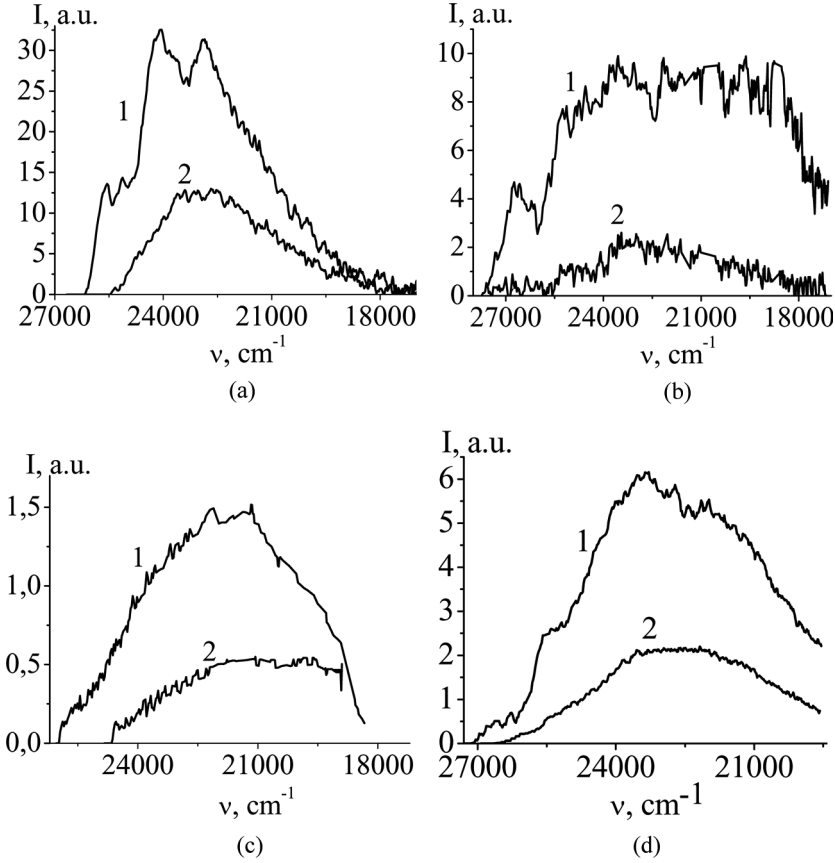


**FIGURE 3** The phosphorescence spectra at T = 4.2 K (1) and T = 77 K (2) of: rAMP (a), rGMP (b), rUMP (c), rCMP (d). Excitation 260 nm. Aqueous solutions, $C = 10^{-4}$ M.

At both temperatures the fluorescence of all investigated samples of the RNA with the wide structureless band with the maxima at 350–380 nm was observed. Furthermore this band is similar to the DNA fluorescence band that observes at 350 nm [1,2]. This is the reason to suggest the nature of singlet excitations localization centers is connected with cytidine and guanosine bases (or their complex) as it is shown for the DNA.

The comparison of the phosphorescence spectra of all investigated RNA and the ribonucleotides (rAMP, rGMP, rCMP, rUMP) shows that here are two type of triplet excitations traps: (1) adenosine

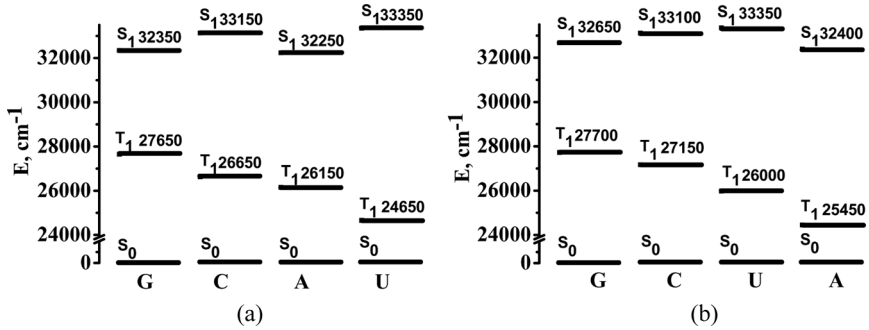


**FIGURE 4** The position of singlet and triplet energy levels of the RNA bases at T = 4.2 K (a) and T = 77 K (b).

groups and (2) the centers of unknown nature that manifested phosphorescence: structureless and shifted long-wave for the colibacillus RNA; shifted short-wave for the human neuroblastoma RNA; and practically without such bands for the yeast RNA (Fig. 6). One of versions of these bands nature is the contribution of residual impurity "small" molecules in the RNA luminescence. The results obtained on the RNA were compared with the results obtained on the DNA. The phosphorescence spectrum of all investigated RNA do not coincide with the DNA phosphorescence spectrum. Thus, since the

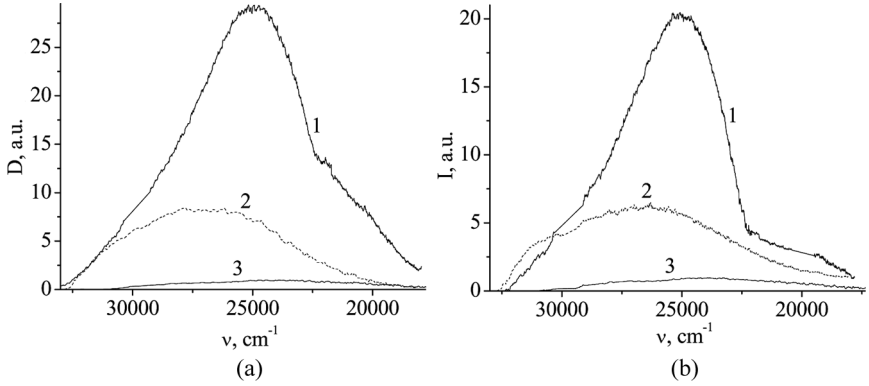


**FIGURE 5** The fluorescence spectra at T = 4.2 K (a) and T = 77 K (b) of: The human neuroblastoma RNA (1), yeast RNA (2) and colibacillus RNA (3). Excitation 260 nm. Aqueous solutions, $C = 10^{-4}$ M.

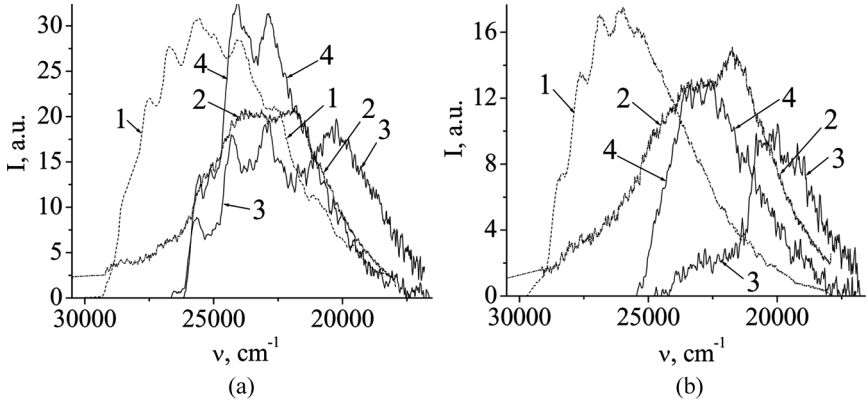


**FIGURE 6** The phosphorescence spectra at T = 4.2 K (a) and T = 77 K (b) of: The human neuroblastoma RNA (1), yeast RNA (2), colibacillus RNA (3), rAMP (4). Excitation 260 nm. Aqueous solutions, $C = 10^{-4}$ M.

photochemical properties of the majority of $\pi$-electron-containing compounds are determined mainly by the nature of triplet excitations localization centers, the different spectral properties and different photophysical and photochemical processes take place in the RNA and DNA macromolecules in spite of the similarity in the chemical structure. Furthermore the different origin of the RNA leads to the partly different photophysical and photochemical processes too.

## 4. CONCLUSIONS

1. While the displacement of the first excited electronic singlet and triplet levels of the RNA (as well as of the DNA) are determined by the properties of individual nucleotides, the fluorescence and phosphorescence of the RNA are due to electronic excitation energy migration to the correspondent intramolecular traps.
2. The comparative studies of the RNA and DNA show that traps for the singlet excitons in the RNA macromolecule could be guanine and cytidine bases or their complexes.
3. There are two types of triplet excitations traps in the RNA: (1) adenosine groups and (2) the centers of unknown nature that are not the same as for the DNA.

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