

## SPECTROSCOPY OF ATOMS AND MOLECULES

# Electron Impact Excitation of Luminescence of Uracil

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**Abstract**—We have measured the luminescence spectra of isolated uracil molecules in the wavelength range of 200–500 nm that were excited by slow electrons. Each spectrum contains more than 20 spectral bands and lines. We show that the luminescence spectrum of uracil is formed by processes of dissociative excitation of molecules, dissociative excitation with ionization, and excitation of electronic states of the initial molecule and molecular ion.

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## INTRODUCTION

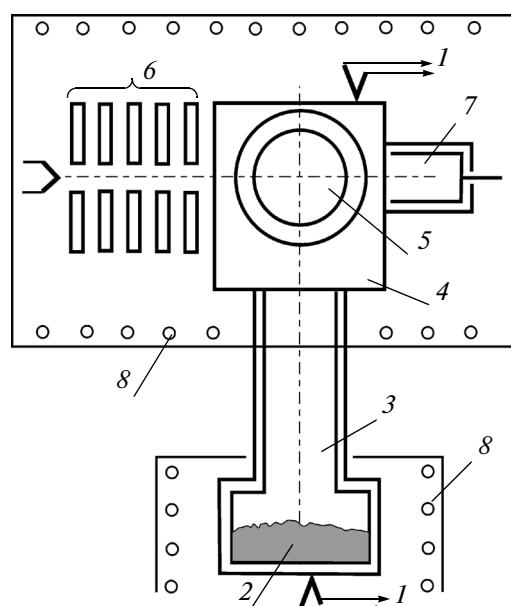
Information on the physical structure of molecules is necessary for understanding the role played by primary physical processes in ensuring the functioning of biosystems and the effect that various environmental factors have on these processes. Among these factors, special attention is paid to natural and artificial radioactivity. For the most part, the interaction of high-energy radiation with living cells does not lead to immediate degradation of biopolymer molecules, in particular, to breaking of covalent bonds in the primary structure of nucleic acids. This function is implemented by secondary electrons, which are formed in large numbers ( $4 \times 10^4$  electrons per 1 MeV of high-energy projectile particle) in a biocompound [1]. The majority of secondary electrons are low-energy (slow) particles, the energy of which varies from fractions of an electronvolt to tens of electronvolts [1]. At present, destructive changes that occur in biostructures on the molecular level are mainly associated precisely with slow electrons. In this case, DNA and RNA genetic macromolecules become the main target.

In previous works [2, 3], we investigated processes of excitation by slow electrons of molecules of nucleic acid bases such as cytosine and thymine in the gas phase. The present work is devoted to uracil.

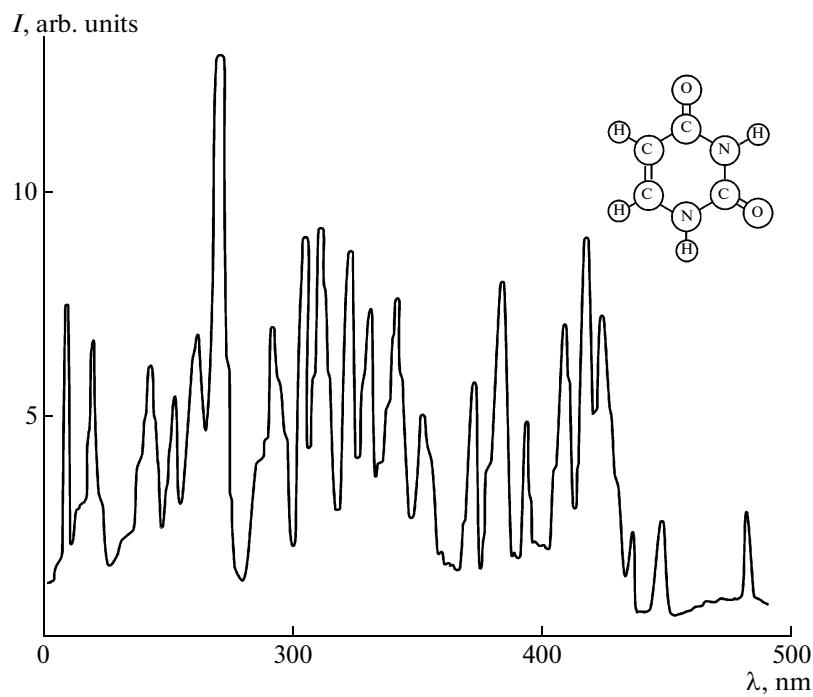
## EXPERIMENT

The gas phase of uracil was formed by heating of the compound under study in a separate metallic container (Fig. 1). The formed gas phase was fed to a cubic cell with a volume of  $\sim 2 \text{ cm}^3$  via a vapor line. The temperature of the container with uracil powder did not exceed 350 K. On one of the facets of the cell, a diaphragm (with a hole diameter of 1.5 mm) was mounted for introducing an electron beam. An elec-

tron beam source was arranged on this facet, while a detector of beam electrons (Faraday cup) was placed on the opposite facet. An electron beam was formed by a pentode gun with a tungsten cathode. The cell was placed in a magnetic field such that its lines of force were parallel to the electron beam. The energy scale of electrons was calibrated in terms of the energy excitation threshold of the band of molecular nitrogen with  $\lambda = 315.9 \text{ nm}$  (the electronic transition  $X^1\Sigma_g^+ - C^3\Pi_u$ ; the second positive system) with an error of  $\pm 0.25 \text{ eV}$ . The magnetic field induction was  $\sim 1.2 \times 10^{-2} \text{ T}$ . To couple radiation out of the cell, quartz windows were



**Fig. 1.** Scheme of formation of the gas phase of uracil: (1) thermocouple, (2) compound under study, (3) vapor line, (4) cell, (5) quartz window, (6) electron gun, (7) electron detector, and (8) heater.



**Fig. 2.** Luminescence spectrum of uracil molecules at an energy of exciting electrons of 100 eV.

mounted on its two facets such that the optical axes of the windows were perpendicular to the electron beam. The radiation was detected by a spectrophotometer consisting of a diffraction monochromator (MDR-23) with a reciprocal linear dispersion of 1 nm/mm, a photomultiplier (FEU-106), and a photosignal detection system. To enhance the signal-to-noise ratio, the system operated in the photoelectron pulse counting mode combined with the electron beam modulation [4].

The experiments were performed under the following conditions: the electron beam current was within  $(3\text{--}4) \times 10^{-5}$  A, the electron energy nonuniformity at the half-height of the energy distribution was  $\Delta E_{1/2} \sim 0.5$  eV, and the vacuum in the chamber with the cell was maintained at  $\sim 10^{-5}$  Pa. To avoid condensation of the uracil vapor on the windows and electrodes of the electron gun, the cell heated to a temperature of 370 K. The chemical purity of the sample was 99.9%.

## EXPERIMENTAL RESULTS AND DISCUSSION

The emission (luminescence) spectra of uracil were excited by electron impact and measured in the wavelength range of 200–500 nm for different energies of bombarding electrons. Figure 2 shows a photoemission spectrum of uracil at an electron energy of 100 eV. In the spectrum, molecular bands are clearly seen, with their maxima  $\lambda_m$  being at the following wavelengths:  $\lambda_m = 205.5, 218.5, 241.9, 254.0, 265.3, 277.4,$

297.2, 310.0, 317.1, 328.4, 333.5, 344.5, 35.3, 377.1, 387.9, 398.0, 412.3, 421.0, 427.3, 451.1, and 486.1 nm. As can be seen from Fig. 2, almost all bands are of a complex character, which points to their superposition nature. For comparison, we note that, upon photoexcitation of polycrystalline films and solutions of uracil, its luminescence spectrum is a continuous broad band in the wavelength range from  $\sim 300$  to  $\sim 550$  nm [5, 6].

Based on the data available from the literature, it is rather difficult to totally and correctly identify the observed spectral bands. However, we succeeded in performing the following analysis of the nature of bands in the obtained spectrum. For this purpose, we used the results of mass-spectrometric investigations of uracil, data on the integral ionization cross section and on the dissociative ionization cross section of uracil by electron impact [7–9], and analyzed the photoemission spectra of corresponding chemical compounds [10–13]. We also calculated electronic excitation levels of the uracil molecule.

In [7, 8], the absolute values of the total and partial formation cross sections of positive uracil ions were determined (table). These data indicate that the probability of fragmentation of the uracil molecule under electron impact is very high. Clearly, some of the charged fragments will be in excited states. In this case, the main attention should be paid to the fragments the partial cross sections of which are the largest. These are the molecular ion  $C_4H_4N_2O_2^+$  and fragments  $CO^+$ ,  $CNO$ ,  $C_3H_3NO^+$ ,  $C_3H_2NO^+$ , and

$\text{C}_4\text{H}_4\text{O}^+$ . In addition, the scheme of fragmentation of uracil also provides for the formation of neutral fragments, which also can be in excited states (dissociative excitation). First of all, these are fragments CO (upon decomposition of the ion  $\text{C}_3\text{H}_3\text{NO}^+$ ), HNCO,  $\text{C}_3\text{H}_3\text{NO}$  (upon decomposition of the molecular ion  $\text{C}_4\text{H}_4\text{N}_2\text{O}_2^+$ ), and H (upon decomposition of the ion  $\text{CHNO}^+$ ).

The radiative decay of excited states of charged and neutral fragments will manifest itself in the emission spectrum of uracil in the form of spectral bands and lines. Thus, it is clear that the band with a maximum at the wavelength  $\lambda = 205.5$  nm is a superposition of several emission bands that belong to the ion  $\text{CO}^+$  (the first negative system; the electronic transition  $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ ;  $\lambda_m = 206.8$ , 206.1, and 204.2 nm). The band with a maximum at the wavelength  $\lambda = 218.5$  nm is a superposition of emissions by the CO molecule (the fourth positive system; the transition  $A^1\Pi \rightarrow X^1\Sigma^+$ ;  $\lambda = 217$  nm) and by the  $\text{CO}^+$  ion (the first negative system; the electronic transition  $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ ;  $\lambda = 241.9$  nm) [14]. The bands with maxima at the wavelengths  $\lambda = 256.4$  and 297.2 nm contain bands of a neutral fragment CO (the third positive system; the transition  $A^1\Pi \rightarrow X^1\Sigma^+$ ;  $\lambda = 256.2$ , 297.3 nm). The band with a maximum at the wavelength  $\lambda = 265.3$  nm is evidently a superposition of two emission lines of the  $\text{CO}^+$  ion (the first negative system; the electronic transition  $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ ;  $\lambda_m = 267.2$ , 263.9 nm).

The most intense spectral band with a maximum at the wavelength  $\lambda = 275$  nm deserves special consideration. We believe that its occurrence is caused by the radiative decay of the first excited electronic-vibrational state of the molecular ion of uracil to its ground state. This can be confirmed by the following factors. First, the table shows that the formation cross sections of molecular ions are the highest. It is logically to assume that formation cross sections of molecular ions in excited states, first of all those that are the lowest-lying, will be greater than the formation cross sections of other charged fragments in excited states. This factor explains the highest intensity of the spectral band with a maximum at the wavelength  $\lambda = 275$  nm. Second, in the photoelectron spectrum of uracil that was reported [15], an intense peak at an energy of  $\sim 14$  eV was revealed. If we combine the energy of the spectral transition (at  $\lambda = 275$  nm) with the ionization energy of uracil, which, according to [8], is  $9.4 \pm 0.2$  eV, we obtain a value  $\sim 13.9$  eV, which almost coincides with the energy position of the peak in the photoelectron spectrum. Therefore, we can assume that the molecular ion of uracil has an excited electronic-vibrational state with the energy  $\sim 13.9$  eV, from which the radiative transition to the ground state of the ion can occur.

The band  $\lambda = 317.1$  nm can be emitted by the pyrimidine ring (transitions  $A-X$ ). To the formation of the

Absolute values of formation cross sections (in units of  $10^{-16} \text{ cm}^2$ ) of positive ions of the uracil molecule at an energy of electrons of 95 eV

$m/z$	Ion	Ref. [8]	Ref. [7]
112	$\text{C}_4\text{H}_4\text{N}_2\text{O}_2$	2.7	4.5
96	$\text{C}_4\text{H}_4\text{N}_2\text{O}$	0.1	
83	$\text{C}_3\text{H}_3\text{N}_2\text{O}$	0.3	
70	$\text{C}_3\text{H}_4\text{NO}$	0.3	
69	$\text{C}_3\text{H}_3\text{NO}$	1.1	2.3
68	$\text{C}_3\text{H}_2\text{NO}$ , $\text{C}_4\text{H}_4\text{O}$	0.6	
56	$\text{C}_2\text{H}_2\text{NO}$ , $\text{C}_3\text{H}_4\text{O}$	0.2	
42	$\text{CNO}$ , $\text{C}_2\text{H}_2\text{O}$ , $\text{CH}_2\text{N}_2$	1.0	2.0
41	$\text{CHN}_2$ , $\text{C}_2\text{H}_3\text{N}$	0.3	
40	$\text{C}_2\text{H}_2\text{N}$ , $\text{CN}_2$	0.3	
28	CO	0.5	

band at  $\lambda = 328.4$  nm, the emissions of the fragments  $\text{CN}^+$  (transitions  $c^1\Sigma - a^1\Sigma$ ) and NCN (transitions  $^3\Pi_u - ^3\Sigma_g$ ) contribute. The band with a maximum at  $\lambda = 333.5$  nm is emitted by the group NCN (the transition  $^3\Pi_u - ^3\Sigma_g$ ), and the bands with maxima at  $\lambda = 344.5$  and 357.3 nm belong to the group HNCN (transitions  $A-X$ ). In the bands with maxima at  $\lambda = 377.1$  and 388.3 nm, the emission of the neutral fragment CO of the comet system (379.6 nm) and the Herzberg system (389.3 nm) is manifested. In the formation of the band  $\lambda = 411.5$  nm, CO fragments (transitions in the Herzberg system; 412.5 nm) and hydrogen ( $\text{H}_\delta$ ; 410.1 nm) participate. An intense line at  $\lambda = 421.0$  nm belongs to the fragment  $\text{CH}^+$  (the transition  $A - X$ ;  $\lambda = 421.0$  nm). The emission of the neutral fragment CO is manifested in the band with a wavelength of 427.3 nm (the comet system;  $\lambda = 427.3$  nm) and in the band with a wavelength of 451.1 nm (the  $\lambda$  system;  $\lambda = 451.0$  nm). The excitation of the above-indicated bands of CO and  $\text{CO}^+$  by the electron impact was studied in detail in [14]. The results of these investigations we considered as especially important in identification of the uracil spectrum.

For some bands of the spectrum, it is likely that lines of the Balmer series of the hydrogen atom can contribute. In particular, these are bands with maxima at  $\lambda = 398.4$  nm ( $\text{H}_\epsilon = 397.07$  nm),  $\lambda = 412.3$  nm ( $\text{H}_\delta = 410.1$  nm),  $\lambda = 427.3$  nm ( $\text{H}_\gamma = 434.05$  nm). The  $\text{H}_\beta$  emission line of the hydrogen atom at  $\lambda = 486.1$  nm is especially clearly pronounced.

As can be seen from Fig. 2, in the wavelength range of 300–440 nm, two broad molecular bands are observed, which are partially overlapped and form a base (background) for narrow bands. We attribute the first of these bands to the emission of the singlet state of the uracil molecule, while the second band is asso-

ciated with the emission of the triplet state of this molecule. This interpretation does not contradict our calculations, which were performed by the AM1 semiempirical method using the HyperChem 8.0 software package. Thus, the energy of one of the vibrational levels of the first singlet state  $S_1$  of the uracil molecule was calculated to be 4.1 eV and the wavelength of the spectral transition from this state to the ground state is 301.5 nm. For the triplet state, our calculations yield the energy 2.8 eV, which corresponds to the transition at the wavelength  $\lambda = 442.2$  nm. It should be noted that, upon photoexcitation of polycrystalline uracil films, two maxima at  $\sim 350$  and  $\sim 420$  nm appear on the broad luminescence band of this compound [5, 6].

To more exactly and interpret the obtained data, it is necessary to experimentally study the excitation functions of corresponding spectral bands and their energy thresholds. We plan to perform such investigations in the future.

Therefore, summarizing the above analysis of the nature and reasons for the occurrence of a complicated photoemission spectrum of uracil molecules excited by low-energy electrons, we can state the following. The emission spectrum of uracil initiated by the electron impact in this energy range arises as a result of different processes. First, these are spectral transitions between electronic–vibrational–rotational states of the initial uracil molecule and its molecular ion. In this case, we call attention to the fact that, for this polyatomic molecule, the most probable transitions are only those that occur from the lowest singlet and triplet states to the ground state. The same is true for the molecular ion. Second, these are spectral transitions between electronic–vibrational–rotational states of fragments of the molecule that are formed under the electron impact (processes of dissociative excitation and dissociative ionization with excitation).

It should be emphasized that we obtained these results for a molecular object that is exceptionally biologically important. Uracil, along with other nitrogen bases (thymine, adenine, cytosine, and guanine), is an important constituent of genetic nucleic acid macromolecules. Ionization and fragmentation of molecules of nucleotide bases will lead to chemical changes in the structure of RNA and DNA. Due to this, even at insignificant energies of electrons in living cells, irreversible degradation and mutagenic processes will be initiated.

## CONCLUSIONS

The interaction of slow electrons with uracil molecules in the gas state is accompanied by the occurrence of a complicated emission spectrum in the range of 200–490 nm, which is indicative of an intense fragmentation of molecules. The emission spectrum of

uracil is formed by processes of dissociative excitation of molecules, dissociative excitation with ionization, and excitation of electronic levels of the initial molecule and molecular ion. The obtained data can be used to estimate radiation changes in DNA and RNA molecules upon internal  $\beta$  irradiation of bioobjects.

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