SPECTROSCOPY OF ATOMS
AND MOLECULES

Electron Impact Excitation of Gas-Phase Thymine Molecules

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Abstract—The electron impact excitation of gas-phase thymine molecules is studied optically in crossed electron and molecular beams. The emission spectrum of molecular bands is obtained and the bands are identified. The excitation functions of the most strong bands are measured.

INTRODUCTION

The investigation of the excitation of organic molecules (including thymine) in the condensed phase by UV and VUV radiation has been already reported earlier [1–3]. In these studies, a variety of phenomena occurring under the action of short-wavelength radiation passing through condensed media was pointed out. Among these phenomena, the most noteworthy is the generation of free (secondary) electrons, which is of general nature and arises when high-energy radiation of any kind passes through a substance. Note that the secondary electrons are mostly low-energy electrons [4]. Hence, it becomes important to elucidate the role of the secondary electrons in the excitation of organic molecules, primarily, those of biological origin. It is conceived that an adequate modeling of the excitation processes in a physical experiment is possible under the conditions of a very small effect of the environment. One can successfully cope with this problem provided that the objects in question are studied in the gas phase. Our first considerations on this matter were presented as early as in 1987 [5].

In this paper, we report the results of our study of the specific features of the excitation of gas-phase thymine molecules by slow electrons. Thymine, along with cytosine, adenine, uracil, and guanine, is a nucleotide base, being an important constituent of genetic DNA and RNA macromolecules.

EXPERIMENTAL

We carried out the experiments by the optical method, which had been used in our earlier works [6, 7]. The thymine molecules were transported as a molecular beam to the region of their interaction with an electron beam. The technique of crossed electron and heterocyclic biomolecular beams used in this study has been described in our previous papers [8, 9]. The molecular beam is formed by an effusion thermal source of a multichannel type and a system of collimating slits. This part of the technique was described in more detail in [9]. We used a thymine preparation of 99% purity acquired from Sigma Aldrich company.

A pentode gun with a tungsten cathode was used as an electron source. A low negative potential was applied to the first electrode of the gun [10], which hindered the low-energy portion of the cathode stream. The electron gun was placed in a longitudinal magnetic field with the induction $B = 1.2 \times 10^{-2}$ T. The zero point of the electron energy scale was determined from the position of the resonance peak of negative molecular ions SF_6 formed by the electron capture.

The radiation emitted from the crossing region of the molecular and electron beams was detected by a spectrophotometer consisting of an MDR-23 monochromator, PMT photon detector FEU-106, and 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 [7].

The experimental setup provided detection of the produced positive and negative ions using a measuring technique that was described in [9].

The experiments were performed under the following conditions: the electron beam current was within $(3–4) \times 10^{-5}$ A, the electron energy nonuniformity at the half-width of the energy distribution being $\Delta E_{1/2} \sim$ 0.5 eV; the concentration of the thymine molecules in the region of their interaction with the electron beam was $\sim 2 \times 10^{10}$ cm^3, and the vacuum was maintained at $\sim 10^{-5}$ Pa.

RESULTS AND DISCUSSION

In our experiments, we studied the electron impact excitation of the gas-phase thymine molecules. The emission (luminescence) spectra of thymine were
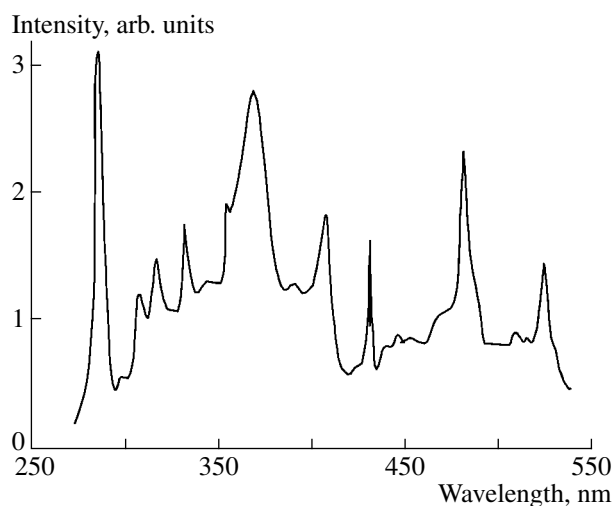
Fig. 1. Emission spectrum of thymine for an electron energy of 100 eV.

Fig. 2. Energy dependences of the excitation cross sections of the thymine spectral bands at $\lambda_p = (1)$ 482.2 and (2) 369.6 nm.

obtained in the wavelength range 200–600 nm, as well as the electron energy dependences of the effective excitation cross sections (excitation functions) of the molecular bands at their peaks. The electron beam energy was scanned within 0–200 eV.

Figure 1 depicts the emission spectrum of thymine for an excitation electron energy of 100 eV. Nine molecular bands whose peaks are located at 286.5, 307.5, 317.2, 333.2, 369.6, 408.1, 432.0, 482.2, and 525.0 nm are clearly exhibited in the spectrum. The band intensities are ascertained to be dependent on the electron energy. It can be assumed that the nature of the band origin is associated with the excitation of the electronic states of both the whole molecule and its fragments (dissociative excitation). Note that the spectrum depicted in Fig. 1 substantially differs from the luminescence spectra of the thymine molecules in solutions and polycrystalline films [1, 2].

It is very difficult to identify the spectral bands because of the extremely scarce data available in the literature. In this respect, a primary identification of the obtained spectra is possible basing on measuring the band excitation energy thresholds and analysis of the form of the relevant optical excitation functions. The wavelengths corresponding to the band peaks and band excitation energy thresholds are listed in the table, and the excitation functions for the strongest bands are shown in Figs. 2 and 3. We measured the ionization energy equal to 9.4 eV, which fairly agrees with the data of papers [11, 12]. The error in measurements of the excitation thresholds and ionization energy amounts to
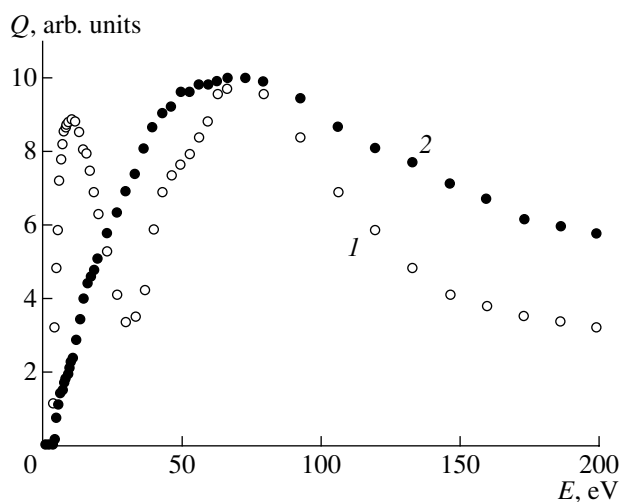
±0.2 eV. The excitation thresholds for the bands at $\lambda_p =$ 408.1 and 432.0 nm were not determined because of their low intensity in the near-threshold energy region.

The spectral bands presented in the table can be subdivided according to the excitation threshold into two groups, that are, those with the excitation energy lower and higher than the ionization energy (9.4 eV). The band excitation functions of the former group are of different shapes (see Fig. 2). For example, the excitation function for the band at $\lambda_p = 369.6$ nm is mildly sloping with the maximum at an energy of 80 eV, which is characteristic of the excitation of the singlet states. The excitation function for the band at $\lambda_p = 482.2$ nm has a maximum located near the threshold, which is characteristic of the excitation of the triplet states. It follows from the aforesaid that the upper electronic states of the bands at $\lambda_p = 369.6$ and 482.2 nm are the singlet and triplet states with excitation energies of 3.5 ± 0.2 and 3.0 ± 0.2 eV, respectively. It was assumed in [13] that the energy of the first singlet state of a thymine molecule equals ~3.9 eV; however, a possible error was not specified.

The molecular band at $\lambda_p = 286.5$ nm is the strongest one of the second group. The sum of the energy of this spectral transition (4.32 eV) and the ionization energy amounts to 13.7 eV, which coincides with the excitation energy of this band within the measurement error. In addition, as can be seen in Fig. 3, there is a slight kink in the energy dependence of the total ionization cross section (ionization function) at an energy of ≈14 eV. Therefore, the upper state of this band can be treated as

Wavelengths λ_p corresponding to the peaks of the thymine emission bands and the energy thresholds of their excitation E_{exc}

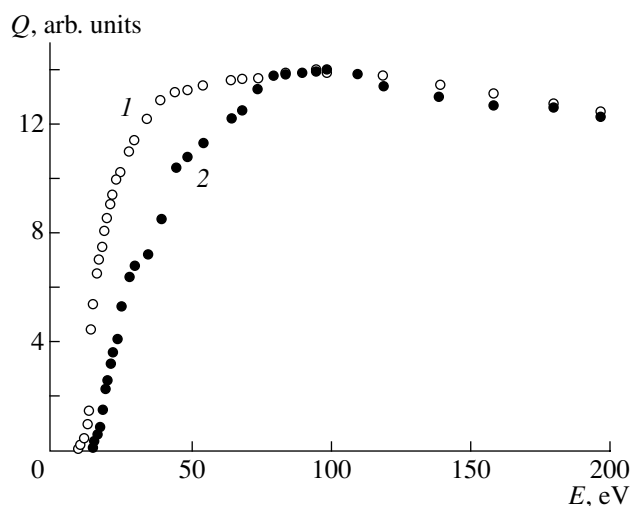| λ_p, nm	286.5	307.5	317.2	333.2	369.6	482.2	525.0
E_{exc}, eV	13.8	13.0	11.0	10.5	3.5	3.0	27.5

Fig. 3. Energy dependences of (*1*) the total ionization cross section of thymine and (*2*) the excitation cross section of the spectral band at $\lambda_p = 286.5$ nm.

the ionic state of a thymine molecule. Note that the maximum of the excitation function of the 286.5-nm band is located at the same energy as that of the ionization function.

Identification of the rest of the bands is difficult; however, based on the aforesaid and the data on the molecular electronic spectra and binding energies [14–16], it can be assumed that the bands at $\lambda_p = 307.5$, 317.2, and 333.2 nm are related to the dissociative excitation processes. In particular, the band at $\lambda_p = 317.2$ nm is associated with a pyrimidine ring ($\tilde{A} - \tilde{X}$ transition), and the band at $\lambda_p = 333.2$ nm is emitted from an NCN group ($^3\Pi_u$–$^3\Sigma_g$ transition). The molecular band at $\lambda_p = 525.0$ nm with the excitation energy of 27.5 eV is related to one of the dissociative ionization fragments.

CONCLUSIONS

It can be stated that the experimental approach used in this study made it possible to obtain new data on the electron impact excitation of thymine molecules. We intend to extend this study to molecules of other bases of the nucleic acids.

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