INTRODUCTION

To form an idea about the mechanism of molecule photoisomerization, a certain type of interactions between various molecule isomeric states is considered [1]. In this work, the results of mathematical modeling of photoisomerization are given taking into account interaction between various isomeric states of a molecule which appears when these states experience collective decay with energy transfer into a common reservoir formed by phonons of molecule vibrational degrees of freedom in an excited electronic state. Such interactions were not considered earlier. Modeling was performed for photoisomerization accompanied by changes in the stable proton position on an intramolecular H-bond (proton phototransfer).

Much attention has been given to the special features of photoisomerization accompanied by proton phototransfer (see [2] and the references therein). In recent years, the photoisomerization of H-bonded molecules the secondary radiation spectra of which contain two fluorescence bands spaced far apart (“two-band” fluorescence) has been the focus of special interest. Such molecules are treated as fluorescent probes for promising sensors of various medium properties [3, 4].

The origin of two-band fluorescence is related to the possibility of the emission of a secondary radiation photon at two transitions between molecule states with different energies in both the ground and first excited electronic states. In H-bonded molecules, these can be the following transitions:

1. The transition from the ground electronic state $N$ of a molecule in the “normal” (enol) form into an excited electronic state $N^*$ of the molecules in the same form,
2. The transition from state $N^*$ into state $T^*$ of a molecule in the “tautomeric” (keto) excited electronic state form,
3. The transition from state $T^*$ to state $T$ of the tautomeric form in the ground electronic state.

For instance, the band at about 406 nm in the secondary radiation spectrum of 3-hydroxyflavone (3-HF) is assigned to the $N^* \rightarrow N$ transition and called a “normal” fluorescence band, and the band at about 535 nm is assigned to the $T^* \rightarrow T$ transition and called a “tautomeric” fluorescence band (see review [5]).

A change in the state of a molecule involved in the $N^* \rightarrow T^*$ radiationless transition is accompanied by H-bond proton transfer from the oxygen atom of the hydroxyl group to the oxygen atom of the keto group, as for instance in the 3-HF molecule, or to the nitrogen atom, as in 2-(2-hydroxyphenyl)benzotriazole and other molecules (see [6]). This proton phototransfer is called ESIPT (Excited State Intramolecular Proton Transfer) [7]. For definiteness, H-bond proton shifts between oxygen atoms (as in 3-HF) will be considered.

In forming ideas about the mechanism of proton phototransfer and the origin of two-band fluorescence, potentials determining H-bond proton posi-
tions in the ground and excited electronic states and interactions between various isomeric states of a molecule are considered first of all.

It is usually assumed that potentials have the form of two asymmetric wells separated by a barrier. The well corresponding to the $T^*$ state is deeper than the well corresponding to the $N^*$ state, and the well corresponding to the $N$ state is deeper than the well corresponding to the $T$ state. The relative positions of the minima of these wells are determined by differences of the frequencies of the highest-intensity bands in fluorescence spectra. This is usually $6000–10000 \text{ cm}^{-1}$.

Different authors select different potential parameters. For instance, several authors starting with [8] explained the origin of two-band fluorescence of 3-HF based on the assumption of asymmetric two-well potentials with an insignificant (see Fig. 1 in [9]) barrier height, however, sufficient for proton tunneling in the excited electronic state of the molecule. According to other authors (e.g., see [10]), the barrier in the excited electronic state of 3-HF is low to the extent that the depth of the proton potential well is insufficient for the existence of a stationary proton vibrational state in this well, and proton shifts in the $N^* \rightarrow T^*$ transition are explained by irreversible vibrational relaxation processes.

A more detailed idea of the mechanism of proton phototransfer is formed with augmenting the selection of the potentials determining H–bond proton position and the type of interactions of various molecule isomeric states by an analysis of the ratios between the constants characterizing the rates of radiation and radiationless decays of molecule states mentioned above. These constants are estimated from the homogeneous width of fluorescence bands and the so-called time of the appearance (rise time) of tautomeric fluorescence ($\tau_R$), that is, the interval between the time of the maximum irradiation pulse intensity at the place where the molecule occurs initially in state $N$ and the time of the maximum intensity $I_T(t)$ of the tautomeric fluorescence pulse. For the conclusions concerning the mechanism of proton phototransfer and the origin of two-band fluorescence drawn on the basis of these experimental data, e.g., see [5, 7, 10–12].

To form a comprehensive idea of the process of molecule photoisomerization, knowledge of the corresponding intramolecular dynamics is necessary. For this purpose, we must analyze the results of mathematical modeling of changes in molecule state populations. We can restrict ourselves to the use of the simplest molecule models, which, however, take into account its fundamental properties, to fairly completely describe the mechanism of the process under consideration.

Intramolecular dynamics was modeled in [13] using a five-level molecular model. A possible photo-