

Fluorescence as a Probe of Energy Dependence of Electron–Molecule Interaction

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The fluorescence intensity dependences on electron kinetic energy, or fluorescence excitation functions, for some aromatic (perylene and *p*-terphenyl) and heterocyclic (biphenylfuran, oxazoles, and oxadiazoles) compounds are studied. It is found that the addition of phenyl rings to the above molecules result in a moderate decrease in excitation function. On the other hand, introducing heteroatoms such as oxygen or nitrogen leads to a substantial decrease in excitation function.

KEY WORDS: Organic compound; electron; excitation function.

INTRODUCTION

Physics of interaction of complex organic molecules with electrons have been investigated very little. Growing interest in this problem is connected with the application of electric excitation in organic electroluminescent micro-electronic devices, because it was found that the main mechanism of organic excited-state formation is excitation of a molecule by direct electron impact [1]. Such data will be also useful in radiation chemistry, biology, and medicine.

A considerable contribution to understanding these questions can be made by luminescence investigations. One of the main problems is the study of the energy dependence of molecule excitation cross sections. But direct measurements of these data are practically impossible. As opposed to photonic excitation, electrons, upon passing through the matter, can initialize practically all the molecular electronic transitions. But the emitting state in almost all cases is a lower excited singlet state. Thus,

fluorescence measurements provide the possibility of determining the fluorescence intensity dependence on electron kinetic energy, which is an integral characteristic. Such a dependence is often called the fluorescence excitation function. This function is an analogue of the excitation spectrum in optical spectroscopy. The study of optical excitation functions of fluorescence is of great importance in determining the efficiency and the ways of transformation of energy received by polyatomic organic molecules into light radiation and the absolute cross section of molecular excitation by electron impact.

It is known that excitation functions of atoms are associated with the number of peaks that arise with the cascade transitions from higher-lying levels as well as the resonance effects of interaction between atoms and electrons [2]. Fluorescence excitation functions of complex organic molecules behave differently. It was shown in our previous works [1,3] that the fluorescence excitation function has a special behavior for some organic compounds in the vapor phase. Fluorescence appears at a threshold energy approximately equal to the $S_0-S_1^*$ transition energy. The maximum value of this function is reached in the region of $\sim 3 E_{th}$ or $\sim 4 E_{th}$, where E_{th} is the threshold energy of fluorescence excitation. A slow fall in excitation function values can be seen in a wide energy region. The shape of the excitation function

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reflects the intramolecular energetic of the complex molecule. Radiating properties of organic molecules excited by electron impact are defined by both electron–molecule interaction and internal molecular features. The purpose of this article is to study the role of molecular structure in the formation of excitation functions and the mechanism of its formation by using fluorescence measurements. We studied some aromatic (perylene and *p*-terphenyl) and heterocyclic (biphenylfuran, oxazoles, and oxadiazoles) compounds, which are known as good scintillators and laser media. They can also be used as model compounds for other systems and as active materials of electroluminescent devices.

EXPERIMENTAL

Fluorescence excitation functions are measured on an experimental setup [4], where a monokinetic electron beam enters the collision chamber with organic vapor at a pressure of about 10^{-3} Torr, to exclude reabsorption and secondary electron collisions. The required vapor pressure was reached by heating the chamber and reservoir with an organic substance. The current value at electron energy $E = 20$ eV was about 10^{-5} A, and kinetic

energy dispersion was less than 0.3 eV. The electron energy could be changed from 5 to 200 eV. The registered radiation passed through the windows in a chamber and vacuum setup. Fluorescence radiation was registered by a photomultiplier with photon counting using a grating monochromator.

The chemical structures of compounds under study are shown in Fig. 1. All the substances are radiation-stable. They have a high fluorescence quantum yield in solutions and in the vapor phase. In all experimental conditions in this work in the spectral range from 200 to 400 nm, there was no radiation of molecule fragments. The recorded fluorescence came from nondestructed molecules.

RESULTS AND DISCUSSION

The measurements of excitation functions of compounds under study are presented in Figs. 2 and 4. First, it is necessary to note that fluorescence excitation functions have several common regularities as reported earlier [1, 3]. But the increase and fall velocity were found to be different for all studied molecules. Their maxima are not coincided. In conclusion, the behavior of excitation

paraTerphenyl (PT)		2,5-Biphenylfuran (PPF)	
2,5-Biphenyloxazol (PPO)		2,5-Biphenyloxadiazol (PPD)	
2-(4-Biphenyl)-5- phenyloxazol (BPO)		2-Phenyl-5-(4- biphenyl)oxadiazol (PBD)	
2-(1-Naphtyl)-5- phenyloxazol (α- NPO)		1,4-Bi[2-(5- phenyloxazol)]benzene (POPOP)	
Perylene			

Fig. 1. Chemical structures of the compounds studied.

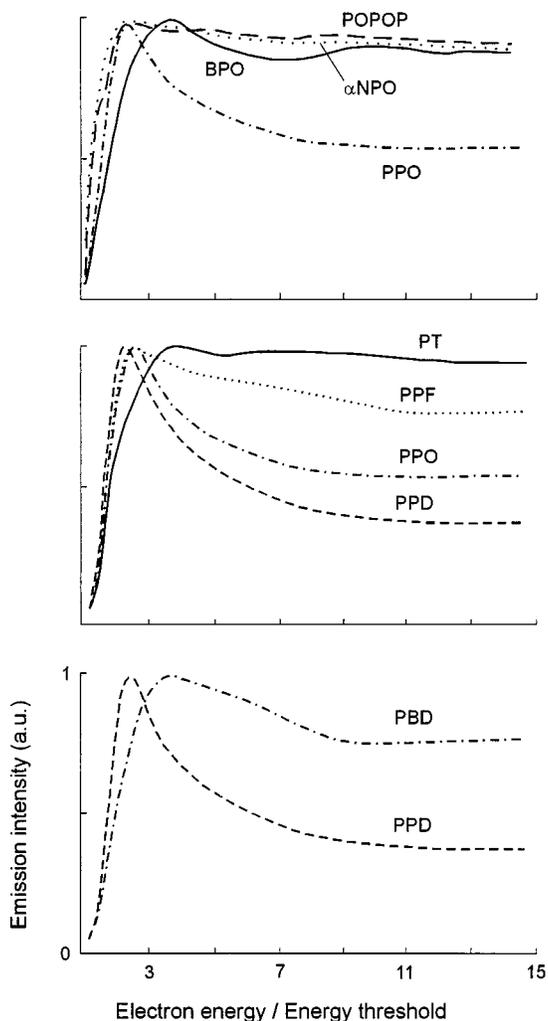


Fig. 2. Fluorescence excitation functions of *p*-terphenyl, 2,5-biphenylfuran, oxazoles, and oxadiazoles.

functions is not universal. Principally, there are two types of deactivation of higher excited singlet states S_n , which affect the behavior of excitation functions. (1) Fluorescence follows after the excitation to S_n singlet states. (2) The quantum yield of fluorescence at excitation to S_n ($n > 1$) equals zero, and these states will be deactivated by intercombination or internal conversion to the lowest singlet state. Unfortunately, fluorescence quantum yields are not measured in a wide spectral region. According to known data on quantum yields [5–7], perylene can be assigned to the first case, and the rest of the compounds to the second. Comparing the chemical structures of compounds under study with their fluorescence excitation functions in Figs. 2 and 4, two conclusions can be drawn. If we add phenyl rings to the molecule, resulting in extension of the π -electron system, a weaker excitation func-

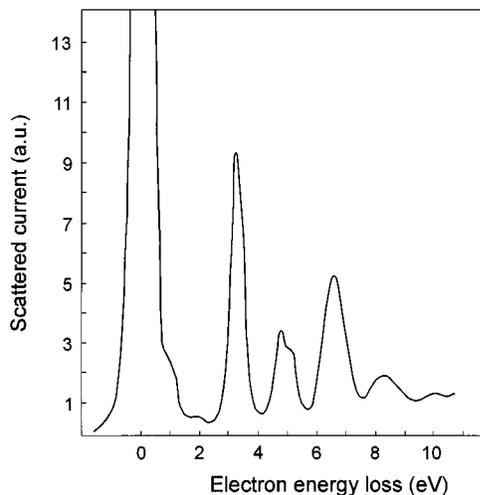


Fig. 3. Electron energy loss spectrum of perylene (scattered angle, 90° ; incident electron energy, 15 eV).

tion decrease can be noted (compare corresponding data for POPOP, α -NPO, BPO, and PBD with others). But introducing heteroatoms such as oxygen or nitrogen leads to a substantial decrease in excitation function. Figure 2 shows the behavior of excitation function on the consecutive addition of heteroatoms (compare the data for *p*-terphenyl, PPF, PPO, and PPD). An especially strong

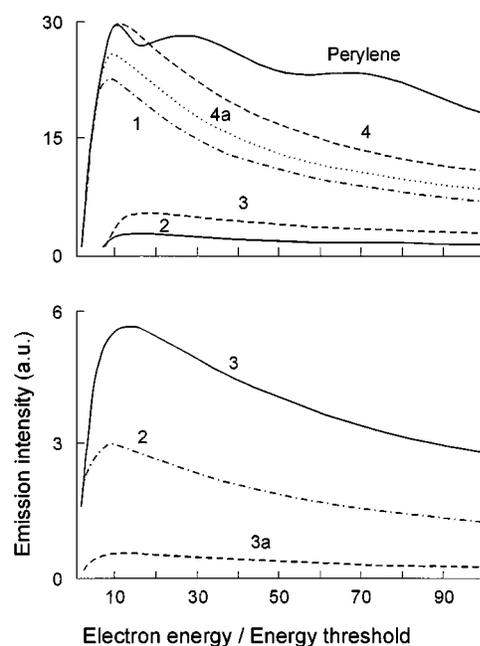


Fig. 4. Calculated fluorescence excitation functions of perylene. (1) Excitation of S_1^* ; (2) excitation of S_2^* ; (3) excitation of S_3^* ; (4) sum of 1–3; (3a, 4a) quantum yield under excitation into the S_3^* state divided by 10; upper curves, experiment.

effect of the fluorescence excitation function is caused by nitrogen heteroatoms. It is known that the nature of energy levels and photonics on optical excitation in *p*-terphenyl, PPF, and oxazoles are similar [8]; the observed difference therefore can be attributed to the peculiarities of electron–molecule interaction.

To explain the behavior of excitation function, the simple theoretical calculations of deposition of various processes are used. In a molecular ensemble, excitation of different levels n takes place, whose cross sections $\sigma_n(E)$ are determined by electron energy loss spectra. The probability of emission (which occurs from the lowest excited singlet state) is characterized by the corresponding value of the quantum yield γ_n . Then the fluorescence excitation function $W_n(E)$ can be defined as

$$W_n(E) = (j/e)n_0hv \sum_n \gamma_n \sigma_n(E) \quad (1)$$

where j is the current density, e is the electron charge, n_0 is the concentration of molecules, and hv is the fluorescence energy quantum, i.e., the fluorescence excitation function is proportional to the sum of the excitation cross sections over all the singlet states at different electron energies, which account for the fluorescence quantum yield.

Excitation cross sections of atoms and simple molecules have long been the subject of investigation. Despite certain differences, there are common regularities in the dependence of the cross sections on electron energy. For allowed transitions, the effective excitation cross section in the Bethe–Born approximation is given by the formula [9]

$$\sigma_n(E) = \sigma_n^{\max} \varphi(E/E_n) q \quad (2)$$

where $\sigma_n^{\max} = 1.48\pi a_0^2 (E_H/E_n)^2 f$, $\varphi(E/E_n) = 2.7(E_n/E) \ln(E/E_n)$, a_0 is the Bohr radius, E_H is the hydrogen atom ionization energy, E_n is the threshold excitation energy of the corresponding level, f is the strength of the transition oscillator, and q is the Frank–Condon factor. Values of fluorescence cross sections σ^{\max} were measured to be in the framework $0.47 \dots 5.6 \cdot 10^{-16} \text{ cm}^2$ for a number of well-luminescing organic molecules [10]. They are closely allied with corresponding data on optical excitation. The function $\varphi(E/E_n)$ is universal within the framework of errors. The cross section increases from the threshold to a maximum value at $E/E_n \approx 4$, then a slow decrease is observed, i.e., its behavior is similar to that of the excitation function measured. To analyze the formation of excitation functions, the cross sections of excitation processes are calculated in the Bethe–Born approximation [Eq. (2)].

We use perylene molecules, because its excitation function has distinct essential maxima, and it can fluo-

resce at excitation in different singlet states [5]. There are three intensive bands of singlet transition in perylene (see the electron energy loss spectrum in Fig. 3). Band intensities were taken from Fig. 3, and the quantum yield was supposed to be constant and equal to 0.3 [5]. The results of calculations of energy dependence cross sections and excitation function are presented in Fig. 4. It can be seen that, even for perylene, the main deposition to fluorescence intensity is connected with the excitation of the lowest excited singlet state (curve 4). The excitation of other singlet levels results in a shift of the maximum of the excitation function to the maximum of the experimental curve. But the fall of the theoretical function is faster than in the experimental curve, and no other maxima are observed. The velocity of the function decrease can apparently be explained by not only deposition to fluorescence intensity of higher excited singlet states, but also losses of electron energy on excitation of triplet states and ionization. In this case the cross sections of these processes have to decrease in accordance with Eq. (1). It is known that cross sections of triplet-level excitation have near-resonance behavior. As a result, the excitation function will become structural. Unfortunately, a convenient approximation for the triplet cross section is absent, and it is impossible to make these calculations. This value can be found precisely by solving the Boltzman equation.

CONCLUSION

The addition of phenyl rings to a molecule results in a weaker decrease in the fluorescence intensity dependence on electron kinetic energy. But introducing heteroatoms such as oxygen or nitrogen leads to a substantial decrease in excitation function.

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