SPECIAL PROPERTIES OF THE FLUORESCENCE OF VAPORS OF ANTHRACENE DERIVATIVES

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Abstract

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SPECIAL PROPERTIES OF THE FLUORESCENCE OF VAPORS OF ANTHRACENE DERIVATIVES

Usually the quantum yield γ and the lifetime τ of fluorescence of dilute vapors, when the frequency of the exciting radiation ν_v and the temperature T are increased, remain constant or decrease (1,2). In work (3) it was found that the quantum yield of vapors of 9,10-dimethylanthracene upon excitation by radiation with $\lambda_\mathrm{v} = 313$ mμ is higher than upon excitation by radiation with $\lambda_\mathrm{v} = 365$ mμ. Subsequently V. P. Klochkov and A. M. Makushenko (4,5) observed an increase in the quantum yield with increasing ν_v for vapors of 9-methylanthracene, and an increase in the quantum yield of vapors of these two anthracene derivatives with increasing temperature.

The quantum yield of vapor fluorescence is related to the average probabilities of radiative $A(E^*)$ and nonradiative $d(E^*)$ transitions by the relation (2)

$$\gamma = A(E^*)/[A(E^*) + d(E^*)]. \qquad (1)$$

The decrease in the quantum yield with increasing store of vibrational energy E^* of the excited molecules is explained by an increase in the probability of nonradiative transitions $d(E^*)$. The probability of emission $A(E^*)$ is then assumed to be constant. The authors of works (4,5) suggested that the increase in the quantum yield of the compounds studied with increasing store of vibrational energy of the excited molecules is connected with an increase in the probability of radiative transitions $A(E^*)$.

To explain the special properties of the fluorescence of vapors of the abovementioned anthracene derivatives, in the present work a parallel study was carried out of the quantum yield and the fluorescence lifetime of vapors of 9,10-dimethylanthracene over a wide range of temperatures and wavelengths of the exciting radiation.

Figure 1 shows the dependence of the quantum yield (1) and lifetime (2) of fluorescence of vapors of 9,10-dimethylanthracene on the frequency of the exciting radiation. The values of γ and τ for $\lambda_\mathrm{v} = 365$ mμ are taken as unity. The

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

fluorescence spectra (3) for $\lambda_\text{v} = 365$ mμ and absorption (4) are also given there. Table 1 gives the absolute values of γ and τ for $T = 423°$ K.

Table 1

λ_v, mμ	380	365	334	320	313	254	248
γ	–	0.11	0.16	–	–	0.06	0.06
$\tau \cdot 10^9$, sec	2.8	3.0	3.8	4.1	4.1	–	–

The wavelengths $\lambda_\text{v} = 380$; 365; 334; 313 mμ belong to the first, and $\lambda_\text{v} = 254$; 248 mμ to the second electronic absorption band. Yield measurements were carried out by the method described in (^{6}); the fluorescence lifetime was measured on a phase fluorometer*. The vapor pressure upon excitation of fluorescence in the first absorption band was $5 \cdot 10^{-2}$ mm Hg, and in the second $5 \cdot 10^{-3}$ mm (^{7}).

From Fig. 1 it is seen that with increasing ν_v not only γ, but also τ, increases. The quantum yield increases somewhat faster than the fluorescence lifetime. Upon excitation of fluorescence in the second absorption band the quantum yield decreases markedly (see Table 1).

* We express our gratitude to M. Ya. Kostko for assistance in the measurements of τ.

The dependence of the quantum yield* and the fluorescence lifetime of 9,10-dimethylanthracene vapors on temperature is illustrated in Fig. 2. Attention is drawn to the fact that, upon excitation of fluorescence in the first absorption band ($\lambda_\text{v} = 365$; 334 mμ), γ increases with increasing temperature, whereas upon excitation in the second band ($\lambda_\text{v} = 254$; 248 mμ) the usual temperature quenching is observed. The change with temperature of the fluorescence lifetime for $\lambda_\text{v} = 365$; 334 mμ qualitatively

Fig. 1. Dependence of the quantum yield (1) and fluorescence lifetime (2) of 9,10-dimethylanthracene vapors on the frequency of the exciting radiation ν_v. 3 —fluorescence spectrum, 4—absorption spectrum.

Fig. 2. Dependence of the quantum yield (solid lines, 1, 2, 4, 5) and fluorescence lifetime of vapors (dashed lines, 1′, 2′, 3′) of 9,10-dimethylanthracene on

temperature T. $1, 1'$—$\lambda_{\text{v}} = 365$ mμ; $2, 2'$—$\lambda_{\text{v}} = 334$ mμ; $3'$—$\lambda_{\text{v}} = 313$ mμ; 4—$\lambda_{\text{v}} = 254$ mμ; 5—$\lambda_{\text{v}} = 248$ mμ.

repeats the change in the quantum yield, although τ increases somewhat more slowly with increasing T. The fluorescence lifetime upon excitation of the vapors by radiation with $\lambda_{\text{v}} = 313$ mμ does not depend on T. Therefore one should expect that γ for $\lambda_{\text{v}} = 313$ mμ will also be practically independent of temperature. Thus

* The relative changes of the quantum yield with ν_{v} and T agree with those obtained in works ([3–5]). The absolute values of γ differ considerably.

Thus, on going from long-wavelength excitation to short-wavelength excitation, the temperature increase of the quantum yield gradually slows down and, upon excitation of fluorescence in the second absorption band, turns into temperature quenching.

As already noted, the authors of works ([4], [5]) explained the increase of γ with increasing vibrational energy reserve by an increase in the probability of radiative transitions $A(E^*)$. In doing so they proceeded from the observed increase, with increasing temperature, of the oscillator strength (the Kravets integral). According to our measurements, the oscillator strength of the vapor of 9,10-dimethylanthracene is practically independent of temperature. The probabilities $A(E^*)$ calculated from these data are: $5.9 \cdot 10^7$ s^{-1} for $T = 423°$ K, $6.0 \cdot 10^7$ s^{-1} for 523 and 583° K. The ratio γ/τ increases only slightly with increasing ν_{v} and T. From this, however, it does not follow that $A(E^*)$ depends on the vibrational energy reserve of the excited molecules, since for dilute vapors this ratio is not strictly equal to the probability $A(E^*)$ ([2], [8], [9]).

Using the values found for the probability $A(E^*)$, one can calculate, by formula (1), the probabilities of nonradiative transitions $d(E^*)$. They prove to be an order of magnitude larger than $A(E^*)$ and decrease with increasing vibrational energy reserve of the excited molecules of 9,10-dimethylanthracene. The decrease in $d(E^*)$ is also indicated by the fact that, with increasing ν_{v} and T, the lifetime of the excited state increases.

Within one class of compounds, three possible cases are encountered for the dependence of $d(E^*)$ on the vibrational energy reserve. Thus, the quantum yield and the lifetime of the excited state of anthracene vapor do not depend on ν_{v} and T ([2], [3], [10], [11]), and consequently it may be considered that $d(E^*)$ does not depend on the vibrational energy reserve. For 9-diacetylaminoanthracene ([3]-[5]), the case usual for vapors is observed—an increase in $d(E^*)$ with increasing ν_{v} and T. A decrease in the probability $d(E^*)$ with increasing vibrational energy reserve is discussed in the present work.

Recently it has been considered that nonradiative deactivation of electronic energy proceeds mainly through triplet states ([12]). In works ([13], [14]) it was suggested that, in anthracene derivatives, depending on the character and position of the substituents, the arrangement of the triplet levels changes, and apparently the different character of the dependence of the probability of nonradiative transitions on the vibrational energy reserve of the excited molecules is connected with this.

The different course of the temperature dependence of the quantum yield of 9,10-dimethylanthracene vapor upon excitation of fluorescence in the first and second electronic absorption bands should be associated with the existence of nonradiative deactivation of the second excited state, in which the fluorescent state does not participate ([2], [15]).

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