STUDY OF THE PHOTOPHYSICAL PROCESSES IN THE MOLECULE OF 3,4-BENZPYRENE IN CONNECTION WITH THE PROBLEM OF ITS DETECTION IN THE ENVIRONMENT

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The analysis of photophysical processes in the 3,4-benzpyrene molecule has been done. Different approaches to solution of the problem on detecting 3,4-benzpyrene are considered and a new one is being proposed.

INTRODUCTION

The 3,4-benzpyrene (benz-(a)-pyrene) belongs to the type of polycyclic aromatic compounds (PAC). It is a byproduct of the processes in the manufacture of asphalt concrete, in metallurgy, oil-processing, and oil-chemistry, and represents cancerigenic substance assigned to the first class of hazardous substances. The maximum permissible concentration of the 3,4-benzpyrene (BP) in the populated areas is extremely low: 10^{-15} g/cm^3, or $2.4 \cdot 10^6$ cm^{-3}, Ref. 1. It is known that at 0°C 100% of BP in air is in the aerosol phase, whereas at 19°C 1% BP is in the gas phase, and 99% in the aerosol one. Hence, the necessity arises of sampling sufficiently large volumes of air on suitable filters as well as of extracting precipitated substance by benzene or *n*-hexane, concentrating the obtained solution to use it in subseCuent analysis.

Standard analytical approaches[2] use two spectroscopic methods, namely the fluorescent and, more rarely, the absorption one. The problem of selectivity to BP arises when employing one or other of these methods, since, besides the BP, a great number of other organic compounds (like heterocyclic and oxygen-containing compounds, olefins, and paraffins) pass into the solution at extraction of samples from filters. So, the problem of chemical interference of compounds may arise in the analysis. In standard approaches the chromatographic separation of the extract is used to overcome these difficulties that make the process too complicated and laborious.

The aim of our research is to analyze the photophysical processes in the BP molecule, in order to be able to formulate approaches to its detection in air, enabling one to increase the analysis selectivity and to simplify it.

CALCULATED RESULTS OF AND THEIR DISCUSSION

The structure of the BP molecule and numbering of its atoms is presented on Fig. 1. It was the plane geometry that was calculated according to the

crystallographic data.[3] The electronic energy levels of the molecule have been calculated by the method of partial ignorance of the differential overlap (PIDO) of the levels and using the parametrization enabling one to correctly calculate the excited states of different nature and multiplicity in molecules of complex aromatic and heterocyclic compounds, Refs. 4–6. The rate constants of the radiative decay of excited states as well as internal and intercombination conversion in the system of singlet and triplet levels were calculated using approaches outlined in Refs. 5–7. All in all, 300 single excited configurations have been taken into account in calculations of the excited electronic states, with 9 occupied and 5 vacant molecular orbitals of π-type. The calculated results are given in Tables I–IV.
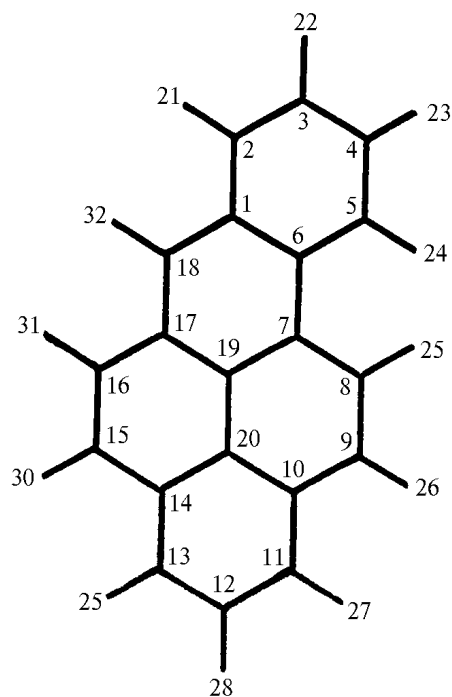

FIG. 1. Structure and numbering of the atoms of 3,4-benzpyrene molecule.

In Tables I and III the calculated $S_0 \rightarrow S_n$ and $S_0 \rightarrow T_n$ spectra are presented in a comparison with the experimental data. It follows from these results, that the first two electronic transitions are connected with π-electron excitation. According to the symmetry classification of the wave functions, Ref. 8, Ψ^- function corresponds to S_1 state whereas Ψ^+ to the S_2 state. Since the ground-state wave function is of the Ψ^- type, the $S_0 \rightarrow S_1$ transition is forbidden ($k_r = 3.6 \cdot 10^6$ s^{-1}), whereas $S_0 \rightarrow S_2$ transition is allowed ($k_r = 3.5 \cdot 10^8$ s^{-1}). These states strongly interact through the mechanism of internal conversion $k_{ic}(S_2 \rightarrow S_1) \approx 10^{13}$ s^{-1}. It is just because of this strong interaction (intensity borrowing) that the $S_0 \rightarrow S_1$ electronic transition becomes allowed and is experimentally observed in Ref. 9: $\varepsilon(S_0 \rightarrow S_1) = 6000$ l/(mole·cm), $\varepsilon(S_0 \rightarrow S_2) = 12000$ l/(mole·cm). The estimates of rate constants of internal conversion in systems of singlet and triplet electronic states are given in Tables II and IV. It is obvious from these results that internal conversion between the states of different molecular-orbital nature ($\pi\pi^* \Leftrightarrow \pi\sigma^*$) is a forbidden photoprocess. The rate constant value follows from the symmetry selection rule for the transitions between the states of one and the same molecular-orbital nature (transitions $\Psi^- \Leftrightarrow \Psi^-$ and $\Psi^+ \Leftrightarrow \Psi^+$ are forbidden).

TABLE I. *Calculated and experimental, Ref. 9, characteristics of the singlet electronic transitions in the 3,4-benzpyrene molecule: energy (nm, cm^{-1}) rate constant of radiative decay (s^{-1}), extinction coefficient (1/(mole·cm)).*

	$S_0 \rightarrow S_1$ $\pi\pi^*$	$S_0 \rightarrow S_2$ $\pi\pi^*$	$S_0 \rightarrow S_3$ $\pi\pi^*$	$S_0 \rightarrow S_4$ $\pi\pi^*$	$S_0 \rightarrow S_5$ $\pi\sigma^*$	$S_0 \rightarrow S_6$ $\pi\sigma^*$
#	396.8	391.0	315,8	296.8	296.6	286.6
	25202	25576	31665	33688	33721	34776
	$3.6 \cdot 10^6$	$3.5 \cdot 10^8$	$4.7 \cdot 10^6$	$2.9 \cdot 10^7$	$1.3 \cdot 10^4$	$2.9 \cdot 10^8$
##	402.0	388.0				
	24820	25745				
	$\varepsilon = 6000$	$\varepsilon = 12000$				

Calculation
Experiment

TABLE II. *Calculated rate constants of the internal conversion $S_i \rightarrow S_j$ in 3,4-benzpyrene molecule (s^{-1}).*

	$S_1(\pi\pi^*)$	$S_2(\pi\pi^*)$	$S_3(\pi\pi^*)$	$S_4(\pi\pi^*)$	$S_5(\pi\pi^*)$	$S_6(\pi\pi^*)$
S_0	$4.1 \cdot 10^4$	$2.0 \cdot 10^6$	$5.4 \cdot 10^4$	$1.6 \cdot 10^4$	$1.4 \cdot 10^{-7}$	$1.3 \cdot 10^4$
$S_1(\pi\pi^*)$		$9,6 \cdot 10^{12}$	$8.5 \cdot 10^9$	$1.2 \cdot 10^9$	$1.1 \cdot 10^0$	$4.2 \cdot 10^9$
$S_2(\pi\pi^*)$			$5.0 \cdot 10^{10}$	$5.5 \cdot 10^9$	$9.5 \cdot 10^0$	$3.1 \cdot 10^9$
$S_3(\pi\pi^*)$				$3.0 \cdot 10^{11}$	$2.5 \cdot 10^2$	$4.9 \cdot 10^{11}$
$S_4(\pi\pi^*)$					$1.1 \cdot 10^5$	$5.6 \cdot 10^{12}$
$S_5(\pi\pi^*)$						$9.6 \cdot 10^3$

The diagram of the energy levels and the main photophysical processes for low states of 3,4-benzpyrene molecule, modeled using results of Quantum-chemical

calculations, is presented in Fig. 2. It is seen from Fig. 2 and Table I that regions of maximum absorption correspond to molecule 3,4-benzpyrene excitation to S_2 ($\lambda = 391$ nm) and S_6 ($\lambda = 287.6$ nm) states. The internal conversion into S_1 ($k_{ic} \approx 10^{13}$ s^{-1}) state is the main channel of the S_2 state decay. Radiative decay and intercombination conversion of the T-state have significantly lower rate ($\approx 10^8$ s^{-1}). On excitation of the molecule to S_6 state with the energy of ≈ 34800 cm^{-1}, several photophysical processes are possible: radiative decay with the rate constant $k_r = 2.9 \cdot 10^8$ s^{-1}, internal conversion $k_{ic}(S_6 \rightarrow S_4) = 5.6 \cdot 10^{12}$ s^{-1}, and intercombination conversion into the close by energy triplet states, T_8 to T_{12}. The latter constant can be evaluated as a total $k_{icc}(S_6 \rightarrow T) = 5.6 \cdot 10^9$ s^{-1}. It is seen from the ratio among the rate constants of different photoprocesses that the internal conversion is again the main channel of the S_6 state decay. This process of the decay will be the main one for all excited singlet states, except for the S_1 state. As follows from calculations two competitive mechanisms are responsible for the S_1 state decay: the radiative decay with the rate constant $k_r = 3.6 \cdot 10^6$ s^{-1}, and the intercombination conversion into the triplet states $T_2 \rightarrow T_4$ $k_{icc}(S_1 \rightarrow T) = 5 \cdot 10^7$ s^{-1}. In this case the calculated Quantum yield of fluorescence is $\varphi = 0.07$. In the experiment the Quantum yield of the fluorescence may be several times as large because of the above mentioned vibronic interaction between the S_1 and S_2 states with the radiative transition $S_2 \rightarrow S_0$ being allowed.
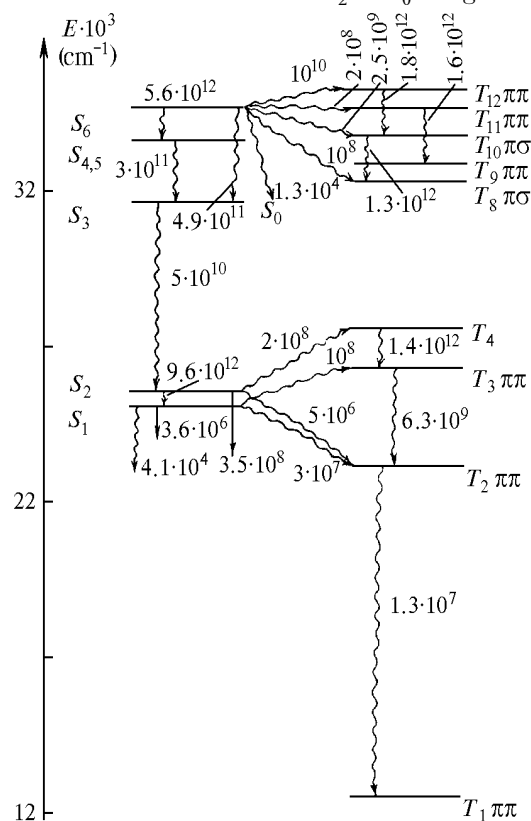

FIG. 2 *Scheme of the energy levels and the main photophysical processes for low electronic states of 3,4-benzpyrene molecule.*

TABLE III. Calculated and experimental energies (nm, cm⁻¹) of $S_0 \to T_n$ electronic transitions in 3,4-benzpyrene molecule.

	$S_0 \to T_1$ $\pi\pi^*$	$S_0 \to T_2$ $\pi\pi^*$	$S_0 \to T_3$ $\pi\pi^*$	$S_0 \to T_4$ $\pi\pi^*$	$S_0 \to T_5$ $\pi\sigma^*$	$S_0 \to T_6$ $\pi\pi^*$	$S_0 \to T_7$ $\pi\pi^*$	$S_0 \to T_8$ $\pi\sigma^*$	$S_0 \to T_9$ $\pi\pi^*$	$S_0 \to T_{10}$ $\pi\sigma^*$	$S_0 \to T_{11}$ $\pi\pi^*$	$S_0 \to T_{12}$ $\pi\sigma^*$	$S_0 \to T_{13}$ $\pi\sigma^*$	$S_0 \to T_{14}$ $\pi\pi^*$	$S_0 \to T_{15}$ $\pi\sigma^*$
Calculation	729.8	431.0	378.1	360.9	356.1	349.9	334.7	308.6	302.7	295.0	287.0	282.5	276.7	272.3	268.7
	12613	23203	26446	27709	28086	28577	29874	32405	330037	33902	34849	35402	36136	36720	37219
Experiment	14600	–	–	–	–	–	–	–	–	–	–	–	–	–	–

TABLE IV. Calculated rate constants of the internal conversion $T_i \to T_j$ in 3,4-benzpyrene molecule (s⁻¹).

	$T_2(\pi\pi^*)$	$T_3(\pi\pi^*)$	$T_4(\pi\pi^*)$	$T_5(\pi\sigma^*)$	$T_6(\pi\pi^*)$	$T_7(\pi\pi^*)$	$T_8(\pi\sigma^*)$	$T_9(\pi\pi^*)$	$T_{10}(\pi\sigma^*)$	$T_{11}(\pi\pi^*)$	$T_{12}(\pi\sigma^*)$	$T_{13}(\pi\sigma^*)$	$T_{14}(\pi\pi^*)$	$T_{15}(\pi\sigma^*)$
$T_1(\pi\pi^*)$	$1.3 \cdot 10^7$	$8.5 \cdot 10^6$	$1.8 \cdot 10^7$	$2.6 \cdot 10^{-5}$	$4.4 \cdot 10^7$	$5.7 \cdot 10^5$	$7.1 \cdot 10^{-6}$	$2.8 \cdot 10^5$	$2.2 \cdot 10^{-5}$	$3.5 \cdot 10^5$	$1.7 \cdot 10^{-5}$	$1.9 \cdot 10^{-5}$	$9.8 \cdot 10^5$	$3.0 \cdot 10^{-5}$
$T_2(\pi\pi^*)$		$6.3 \cdot 10^9$	$4.7 \cdot 10^{10}$	$8.4 \cdot 10^{-2}$	$9.5 \cdot 10^{10}$	$2.6 \cdot 10^8$	$3.6 \cdot 10^{-3}$	$1.3 \cdot 10^8$	$8.6 \cdot 10^{-3}$	$1.6 \cdot 10^8$	$5.4 \cdot 10^{-3}$	$3.0 \cdot 10^{-3}$	$2.1 \cdot 10^8$	$1.5 \cdot 10^{-2}$
$T_3(\pi\pi^*)$			$1.4 \cdot 10^{12}$	$5.7 \cdot 10^1$	$1.1 \cdot 10^{12}$	$8.4 \cdot 10^9$	$1.6 \cdot 10^{-1}$	$2.8 \cdot 10^8$	$2.2 \cdot 10^{-1}$	$1.1 \cdot 10^9$	$9.3 \cdot 10^{-2}$	$1.4 \cdot 10^{-1}$	$3.2 \cdot 10^9$	$6.7 \cdot 10^{-1}$
$T_4(\pi\pi^*)$				$4.0 \cdot 10^1$	$1.4 \cdot 10^{13}$	$2.6 \cdot 10^{11}$	$1.3 \cdot 10^{-1}$	$3.0 \cdot 10^{10}$	$4.0 \cdot 10^{-1}$	$1.3 \cdot 10^{10}$	$2.2 \cdot 10^{-1}$	$7.3 \cdot 10^{-2}$	$3.2 \cdot 10^9$	$8.8 \cdot 10^{-1}$
$T_5(\pi\sigma^*)$					$9.7 \cdot 10^1$	$5.5 \cdot 10^0$	$5.1 \cdot 10^{10}$	$2.4 \cdot 10^{-1}$	$1.5 \cdot 10^{10}$	$2.2 \cdot 10^{-1}$	$5.2 \cdot 10^9$	$4.6 \cdot 10^9$	$3.1 \cdot 10^{-1}$	$1.2 \cdot 10^9$
$T_6(\pi\pi^*)$						$5.6 \cdot 10^{12}$	$1.2 \cdot 10^0$	$2.2 \cdot 10^{11}$	$7.6 \cdot 10^{-1}$	$3.8 \cdot 10^{10}$	$5.6 \cdot 10^{-1}$	$5.6 \cdot 10^{-1}$	$4.6 \cdot 10^9$	$3.8 \cdot 10^0$
$T_7(\pi\pi^*)$							$9.2 \cdot 10^{-1}$	$5.6 \cdot 10^9$	$4.8 \cdot 10^{-1}$	$9.7 \cdot 10^9$	$2.1 \cdot 10^{-1}$	$2.7 \cdot 10^{-1}$	$9.9 \cdot 10^9$	$4.9 \cdot 10^{-1}$
$T_8(\pi\sigma^*)$								$3.5 \cdot 10^1$	$1.3 \cdot 10^{12}$	$2.2 \cdot 10^1$	$2.0 \cdot 10^{11}$	$9.2 \cdot 10^{10}$	$3.0 \cdot 10^0$	$2.9 \cdot 10^{10}$
$T_9(\pi\pi^*)$									$1.2 \cdot 10^2$	$7.6 \cdot 10^{11}$	$1.3 \cdot 10^1$	$6.1 \cdot 10^0$	$3.1 \cdot 10^{11}$	$1.7 \cdot 10^1$
$T_{10}(\pi\sigma^*)$										$4.0 \cdot 10^2$	$1.8 \cdot 10^{12}$	$4.9 \cdot 10^{11}$	$1.8 \cdot 10^1$	$5.6 \cdot 10^{10}$
$T_{11}(\pi\pi^*)$											$4.5 \cdot 10^2$	$1.8 \cdot 10^2$	$2.1 \cdot 10^{12}$	$3.2 \cdot 10^2$
$T_{12}(\pi\sigma^*)$												$2.9 \cdot 10^{12}$	$2.0 \cdot 10^2$	$3.7 \cdot 10^{11}$
$T_{13}(\pi\sigma^*)$													$1.3 \cdot 10^3$	$4.5 \cdot 10^{11}$
$T_{14}(\pi\pi^*)$														$1.1 \cdot 10^4$

Let us return to the S_6 state. The energy of this state roughly corresponds to the dissociation energy of the C–H bond in aromatic molecules (≈ 35000 cm^{-1} ≈ 4.4 eV), that is, the energy of the hydrogen atom separation in the ground state of the molecule. With the rate constant $k_{ic}(S_6 \to S_0) \approx 1.3 \cdot 10^4$ s^{-1}, the quantum yield of this process approximately equals to 10^{-9}.

Assuming that the break of the C–H bond is preceded by its weakening, an attempt has been done to find an excited electronic state in which essential weakening of the bond takes place. The bond strength was evaluated from the population (that is from electronic density value between A and B atoms[10]):

$$P_{AB} = 2 \sum_{i=1}^{\max} \sum_{\substack{\mu \in A \\ \nu \in B}} c_{i\mu}^A c_{i\nu}^B S_{\mu\nu} \,,$$

where $c_{i\mu}^A$, $c_{i\nu}^B$ are the coefficients of molecular orbital expansion over the atomic orbitals; $S_{\mu\nu}$ is the integral of the atomic orbitals overlap. Coefficients $c_{i\mu}^A$ and $c_{i\nu}^B$ correspond to non-orthogonal basis of the atomic orbitals (AO).

The search for the states with minimum P_{CH} value has been performed using special computer code to determine stability of the C–H bond. The results are given in Tables V and VI. The P_{CH} values in the ground state of the molecule are given in the second column of these tables, for a comparison. Data from Tables V and VI indicate that the C–H bond population variations are insignificant even in highly excited S_i and T_i states.

TABLE V. Minimum values of P_{CH} in singlet states.

Bond C–H	Number of the state P_{CH} value						
2–21	0	227	271	291	297	295	300	252
	0.887	0.719	0.721	0.729	0.732	0.734	0.739	0.740
3–22	0	300	298	295	291	271	282	145
	0.889	0.613	0.614	0.616	0.618	0.623	0.623	0.626
4–23	0	300	22	295	298	291	282	145
	0.890	0.607	0.624	0.627	0.631	0.635	0.642	0.651
5–24	0	290	232	289	138	15	164	292
	0.895	0.708	0.715	0.744	0.748	0.749	0.749	0.760
8–25	0	232	290	15	289	35	138	111
	0.892	0.652	0.656	0.685	0.689	0.708	0.709	0.719
9–26	0	232	290	239	289	250	15	241
	0.886	0.777	0.777	0.779	0.788	0.789	0.792	0.792
11–27	0	291	300	295	298	282	297	145
	0.887	0.696	0.709	0.715	0.717	0.723	0.723	0.724
12–28	0	295	300	298	291	282	22	145
	0.888	0.655	0.657	0.660	0.660	0.666	0.669	0.669
13–29	0	288	293	13	285	148	213	119
	0.887	0.717	0.743	0.749	0.754	0.771	0.776	0.779
15–30	0	288	293	13	285	148	213	208
	0.885	0.661	0.698	0.704	0.731	0.736	0.737	0.742
16–31	0	288	293	13	285	148	213	208
	0.885	0.693	0.701	0.708	0.729	0.740	0.748	0.749
18–32	0	10	239	273	290	61	232	235
	0.883	0.740	0.771	0.772	0.779	0.779	0.784	0.785

The above picture of photophysical processes well agrees with the peculiarities of experimentally measured absorption and fluorescence spectra of 3,4-benzpyrene molecule presented in Figs. 3 and 4, Ref. 9. The fluorescence peak at $\lambda = 402$ nm in Fig. 3 corresponds to the radiative transition $S_1 \to S_0$. Similar peak in the absorption spectrum (Fig. 4) corresponds to $S_0 \to S_1$ transition. The structure at $\lambda < 400$ nm represents the vibronic spectrum connected with $S_0 \to S_2$ transition. The maximum cross-section value in this region, at $\lambda < 388.6$nm, corresponds to pure electronic transition $0 \to 0$.

TABLE VI. Minimum values of P_{CH} in triplet states.

| Bond C–H	Number of the state P_{CH} value						
2–21	0	297	274	228	382	292	300	296
	0.887	0.730	0.734	0.736	0.736	0.736	0.736	0.739
3–22	0	274	296	300	298	292	103	284
	0.889	0.596	0.609	0.613	0.615	0.618	0.623	0.625
4–23	0	296	300	103	292	274	298	284
	0.890	0.607	0.609	0.610	0.630	0.632	0.636	0.643
5–24	0	290	234	155	289	97	95	36
	0.895	0.711	0.721	0.729	0.742	0.745	0.754	0.754
8–25	0	234	290	95	289	155	20	97
	0.892	0.663	0.666	0.685	0.686	0.693	0.703	0.704
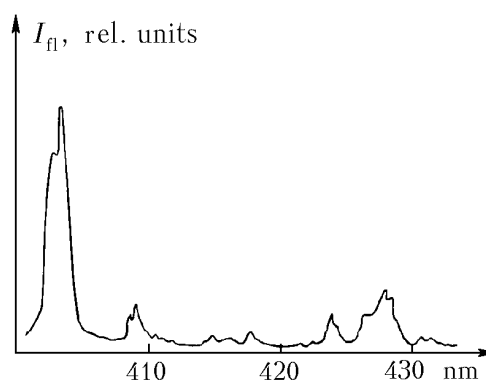
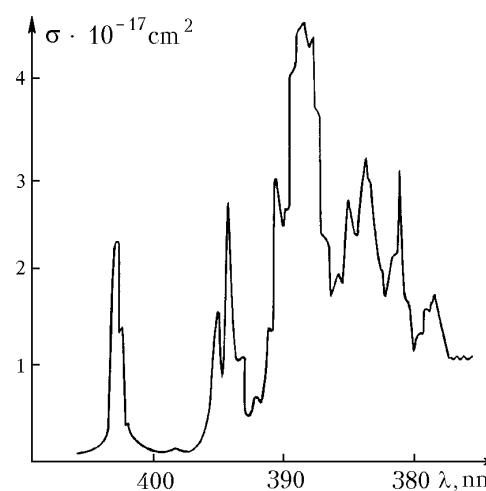*FIG. 3. Fluorescence spectrum of the 3,4-benzpyrene molecule in n-octane at 77 K, Ref. 9.*

FIG. 4. Absorption spectrum of the 3,4-benzpyrene molecule in n-octane at 77 K, Ref. 9.

It follows from Fig. 4 that $\lambda_0 < 388.6$ nm with $\sigma(\lambda_0) = 4.6 \cdot 10^{-17}$ cm^2, and $\lambda_1 = 400$ nm with $\sigma(\lambda_1) \approx 0$ are the optimal pair of wavelengths for the differential absorption (DA) method. Since at atmospheric temperatures the 3,4-benzpyrene is practically all in the aerosol phase, the attempt to measure its content directly by DA method is an illusive goal.

Pumping of 100 m^3 of air through the filter, yields about 10^{-7} g of 3,4-benzpyrene (at the level of maximum permissible concentration) collected on it. As a result of its subsequent extraction into a solvent and concentration of the solution to 1 cm^3-volume sample, the concentrations of $\approx 10^{-7}$ g/cm^3 or $N = 2.4 \cdot 10^{13}$ cm^{-3} may be obtained. For measurement path of 1 cm length at the above indicated wavelengths and cross-sections, $N_{\min} = 2.2 \cdot 10^{13}$ cm^{-3}, that means that the DA method is applicable in this case. However, the problem of influence of other impurities coming into the solution from the filter remains open.

It seems likely (the experimental check is necessary) that this problem can be solved by modification of standard approaches,[2] that use the influence of induced fluorescence. In these approaches a sample, after chromatic separation of fractions, is illuminated by the UV radiation. The fluorescence signal recorded at 402.4 nm wavelength, corresponding to pure electronic transition $S_1 \rightarrow S_0$, is then used for quantitatively estimating the 3,4-benzpyrene concentration.

In different approaches different wavelengths of exciting radiation are used: 254, 338, and 367.4 nm. Based on the above results regarding the mechanisms of the photophysical processes occurring in the molecule, one may state that wide spread of the wavelengths does not influence significantly the final result. In all cases the fluorescence occurs from the S_1 state, provided that the influence of hindering impurities is eliminated by pre-separation of the fractions. The view of the 3,4-benzpyrene absorption spectrum, presented in Fig. 4, and peculiarities of the photophysical processes considered make up the basis for modifying the standard techniques in the way we propose here. Excitation of the extract, which was not previously subjected to separation into fractions, should be alternately done at 338.6 and 400 nm wavelengths. The radiation at the first one efficiently excites the 3,4-benzpyrene fluorescence at 402.4 nm wavelength while the radiation at the second one practically does not produce any fluorescence. Taking into account that both these wavelengths are close one can assume that the excitation of the noise response from impurities at 402.4 nm wavelength occurs with the same efficiency and one may arrive at a conclusion that use of analytical signal $I_{BP}^{402.4} = I_{BP}^{402.4}(388.6 \text{ nm}) - I_{BP}^{402.4}(400 \text{ nm})$ in standard approaches (without chromatographic separation of fractions) can provide for the same precision of analysis while making it less laborious.

The most efficient, in our opinion, solution to the problem of 3,4-benzpyrene diagnostics, that excludes the necessity of using complicated physicochemical methods, characteristic of standard approaches, could be the use of mass-spectroscopy methods in combination with the selective laser photoionization of this molecule. Addressing to Fig. 2, let us note that after the S_2 state excitation, practically all molecules convert into the S_1 state due to nonradiative internal conversion mechanism. As mentioned above, only about 10% of molecules in this state decay through the radiative channel. The remaining 90% will convert into the triplet states due to the nonradiative mechanism of the intercombination conversion and will be accumulated in the T_1 state since the link of the latter with S_0 state is weak $k(T_1 \rightarrow S_0) < 1$ s^{-1}. The experimental value of the T_1 level position is 14670 cm^{-1}, whereas the lowest 3,4-benzpyrene ionization potential is of 57416 cm^{-1}, Ref. 12. Hence, the light quantum of the energy of 42546 cm^{-1} (5.3 eV, 235 nm) is needed to excite the molecule from T_1 state into an ionized state. Thus, using two-photon excitation ($\lambda_1 = 388$ nm, $\lambda_2 = 235$ nm) one can achieve the selective character of molecule ionization. The third degree of the selection is performed in time-of-light-travel type mass-spectrometer while recording current pulses corresponding to arrival, at the detector, of ions with mass number $M = 252$. The sensitivity of the method discussed is very high, according to modern estimations, it comprises of $5 \cdot 10^{-18}$ g, Ref. 13. The possibility of using supersonic gas jets in the ionization volume is the additional attractive feature of this method. In this case the deep freezing of the vibrational degrees of freedom takes place, comparable with that when using liquid helium in the Schpol'skii spectra analysis. As a result, the selectivity of analysis can be significantly increased in the process of laser-induced ionization, the latter may be being performed in this case due to the two-photon mechanism using only one laser and intermediate levels S_2 or S_6.

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