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LUMINESCENCE PROPERTIES AND VIBRATIONAL STRUCTURE OF PHOSPHORESCENCE SPECTRA OF QUINAZOLINE IN SHPOLSKII-TYPE HYDROCARBON MATRICES*,**

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The quasilinear phosphorescence spectra of quinazoline in n-pentane and isooctane were obtained at 77 K. The vibrational analysis of the spectra was carried out, and 11 fundamental vibrations belonging to a' modes and 5 belonging to a'' modes were identified. Weak activity of out-of-plane modes in the quinazoline phosphorescence spectrum, compared with their activity in the quinoxaline phosphorescence spectrum, points to some lesser significance of second-order vibronic spin-orbit couplings in the mechanism of quinazoline phosphorescence. The lifetime of quinazoline phosphorescence in frozen n-pentane is 0.52 s, and in frozen ethanol 0.68 s. No fluorescence of quinazoline was detected.

1. *Introduction*

Not many papers concerning the phosphorescence of quinazoline (1,3-diazanaphthalene) have been published so far. Dörr et al. [1, 2] described the phosphorescence band spectrum of quinazoline in frozen ethanol and proved the emission to originate from $T_1(\pi, \pi^*)$ state. In Jordan and Ross' [3] paper, dealing with the analysis of highly resolved quinazoline absorption spectra $S_1(n, \pi^*) \leftarrow S_0$, there is a brief notice concerning the structure of quinazoline phosphorescence spectrum in a durene crystal at 4 K.

In this paper we present the results of our research in the highly resolved quinazoline phosphorescence spectra in the Shpolskii-type hydrocarbon matrices at 77 K, as well as the results of measurements of the phosphorescence lifetimes. We also tried to obtain quasilinear quinazoline absorption spectra in the Shpolskii matrices. Recently, similar trials yielded a positive result in case of another diazanaphthalene, i. e. quinoxaline [4].

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2. *Experimental*

Quinazoline (purum, Fluka A. G.) was prepurified by vacuum sublimation, and then purified chromatographically. The purity of the product obtained was checked with the gas-liquid chromatography method.

The origin as well as the methods of purification and drying of hydrocarbon solvents (n-pentane, n-hexane, methylcyclohexane, isooctane) have been given in [4] and [5]. There were also used n-heptane "per spettrofotometria UV", C. Erba, Milano, cyclohexane "für UV Spektroskopie", Fluka, A. G., and specially purified ethanol, POCh, Gliwice. The purified solvents showed no own luminescence after freezing.

Low-temperature (LT) and high-temperature (HT) modifications of isooctane matrix were obtained, respectively, by quick and slow freezing, like in [4].

The phosphorescence of the solutions ($c = 10^{-3}$–10^{-5} M) solidified at 77 K was excited by means of a mercury arc lamp HBO 500 through a filter transmitting the radiation of Hg lines group of about 313 nm. The spectra were recorded photographically with the use of a Zeiss triprismatic spectrograph provided with $F = 270$ mm and $F = 700$ mm cameras.

The source of continuous radiation for absorption measurements was an XBO-1001 high-pressure xenon lamp. The absorption spectra were recorded with an ISP-22 spectrograph and the phosphorescence decay curves, as described in [5].

3. *Results and discussion*

The best resolved quasilinear structure of phosphorescence spectra is shown by quinazoline in n-pentane and HT-modification isooctane matrices. In frozen hexane, cyclohexane, crystalline methylcyclohexane and LT-modification of frozen isooctane, the lines are rather broadened, particularly in the long-wave part of the spectrum. In frozen n-heptane the spectrum is composed of narrow bands.

The quasilinear quinazoline phosphorescence spectra have a multiplet structure in the Shpolskii meaning [6]. In the quinazoline phosphorescence spectrum in n-pentane matrix the quartet of lines 21925, 21894, 21767 and 21711 cm^{-1} corresponds to 0–0 transition. However, nearly all the lines of vibronic transitions observed in this spectrum originate from the first, most intensive component of the 0–0 quartet. In HT-isooctane matrix the 0–0 multiplet consists of five lines and in n-hexane matrix of three lines. The difference between wave numbers of extreme components of the 0–0 multiplet is 214 cm^{-1} for quinazoline in n-pentane matrix, nearly the same (211 cm^{-1}) in HT-isooctane matrix, 188 cm^{-1} in n-hexane matrix and similarly in other matrices. Such considerable splittings of 0–0 multiplet are rather rarely observed in Shpolskii matrices, though the splitting of 0–0 doublet of the quinazoline phosphorescence spectrum in durene is also high, reaching up to 205 cm^{-1} [3].

In the phosphorescence spectrum of quinazoline in frozen n-pentane (Fig. 1(a) and (b)) 68 quasilines were observed in the range 22000–16000 cm^{-1}. Vibrational analysis allowed for identification of 16 fundamental vibration frequencies of quinazoline molecule, appearing in this spectrum (Table, column 1).

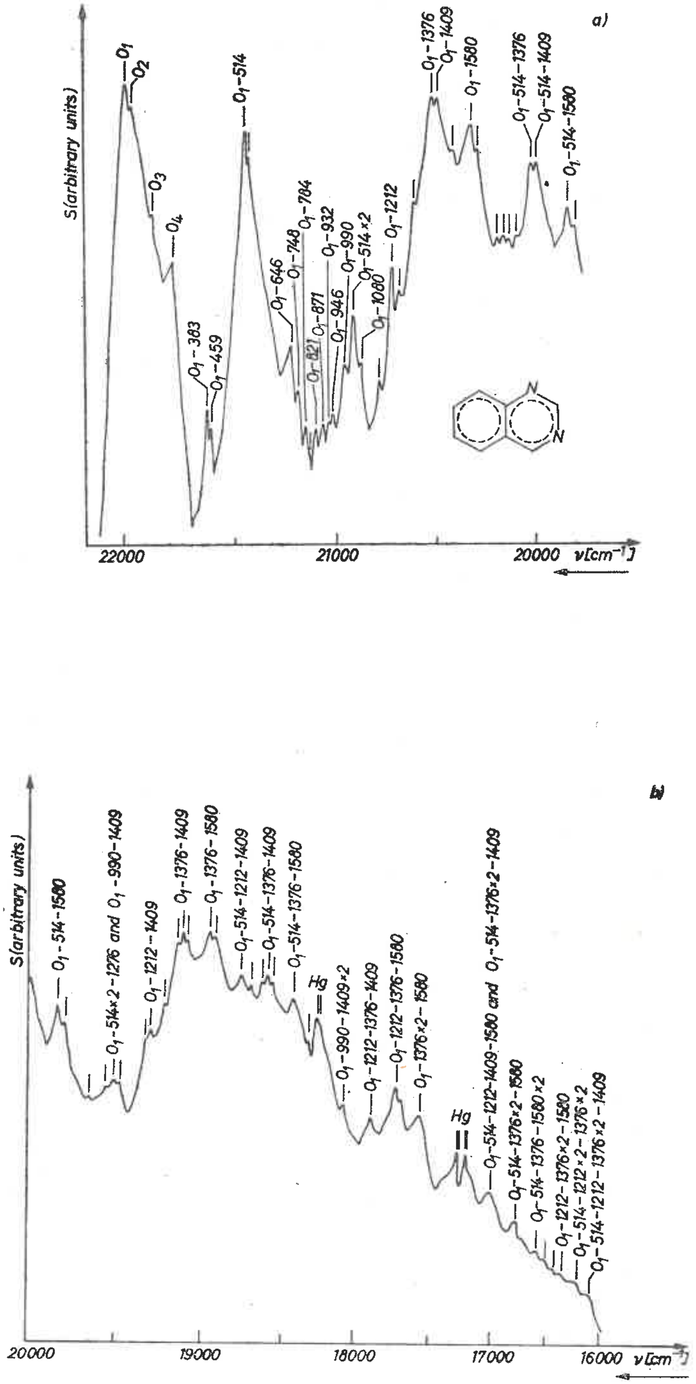

Fig. 1. Microphotometer curve (redrawn) of the phosphorescence spectrum of quinazoline in n-pentane matrix, at 77K; a) — region of fundamental frequencies, b) — region of combinations

The same — within the measurement accuracy — fundamental vibration frequencies were found in the phosphorescence spectrum of quinazoline in isooctane HT-matrix (Table, column 2). The only difference is the vibration of 374 cm^{-1}, to which in this spectrum, a distinct line corresponds, imperceptible in the spectrum shown in Fig. 1(a).

TABLE

Fundamental vibration frequencies of quinazoline molecule active in the $T_1 \rightarrow S_0$ transition

Phosphorescence		Corresponding vibrations in IR and Raman Spectra (from [7, 8])		
n-pentane matrix $\tilde{\nu}$ (cm^{-1})	isooctane matrix $\tilde{\nu}$ (cm^{-1})	$\tilde{\nu}$ (cm^{-1})	Symmetry	Approximate description
not observed	374	374	a'	skeletal distortion
383	387	385	a''	skeletal distortion
459	452	451	a''	skeletal distortion
514	514	517	a'	skeletal distortion
646	641	640	a' or a''	skeletal distortion
748	750	752	a''	skeletal distortion
784	783	779	a'	skeletal distortion
821	825	822	a'	skeletal breathing
871	868	870	a''	CH bending
932	925	926	a''	?
946	944	943	a' or a''	CH bending
990	985	985	a''	CH bending
1080	1071	1071	a'	skeletal breathing
1212	1207	1208	a'	CH bending
1376	1377	1375, 1382	a'	ring stretching
1409	1411	1406	a'	CH bending
1580	1578	1583	a'	ring stretching

All the fundamental vibrations identified in quinazoline phosphorescence spectra are known from the examinations of IR and Raman spectra of this compound. Respective frequencies taken from [7] and assignments of these vibrations from papers [7] and [8] are given in columns 3–5 of the Table. The compatibility of numerical values in column 3 with those in columns 1 and 2 is very good in all cases.

The vibrations most active in the phosphorescence spectra, i. e. those giving the most intensive lines and appearing in the greatest number of combinations, are in-plane skeletal vibrations (a') 514, 1376 and 1580 cm^{-1} and in-plane CH bending ones 1212 and 1409 cm^{-1} (cf. Table and Fig. 1, (a) and (b)).

From among 13 possible out-of-plane (a'') modes of quinazoline molecule, in the $T_1 \rightarrow S_0$ spectrum there appear at least 6. Here belong the skeletal vibrations 383, 459 and 748 cm^{-1} as well as CH bending ones 871 and 990 cm^{-1}; the latter also occur in several combinations with the most active a' modes. The frequency 871 cm^{-1} could correspond to out-of-plane vibration of the hydrogen atoms of CH groups in the heteroaromatic ring of quinazoline (cf. e. g. [9]).

The frequency 932 cm^{-1} (926 cm^{-1} in IR spectrum) corresponds — according to Chappell and Ross [8] — to out-of-plane vibration. However, those authors' discussion does not univocally answer the question whether the fundamentals 646 (641) cm^{-1} and 946 (944) cm^{-1} appearing in the quinazoline phosphorescence spectra (see Table, columns 1 and 2), belong to a' or a'' modes.

The presence of out-of-plane vibrational modes in quinazoline phosphorescence spectrum proves that beside the direct spin-orbit coupling of $T_1(\pi, \pi^*)$ state with $^1(n, \pi^*)$ state (states) there occurs — like in the quinoxaline molecule [4, 10] — a second-order vibronic spin-orbit coupling with participation of $^1(n, \pi^*)$ and/or $^3(n, \pi^*)$ states. Lim and Yu [10] found the signs of such coupling in the polarization spectra of quinazoline phosphorescence, but they considered it to be of much less importance in the phosphorescence mechanism of this compound than in the phosphorescence of quinoxaline. This conclusion seems to be confirmed by relatively weak activity of rather numerous out-of-plane modes in the phosphorescence spectrum of quinazoline as compared with activity of similar modes in the phosphorescence spectrum of quinoxaline in the Shpolskii matrices [4].

The mean lifetime of quinazoline phosphorescence in n-pentane matrix is 0.52 ± 0.04 s, in isooctane matrix 0.56 ± 0.04 s, while in deaerated frozen ethanol it increases up to 0.68 ± 0.02 s. This increase can be caused by a shift of n, π^* states in hydroxylic medium towards higher energies, resulting in weakening of their couplings with $T_1(\pi, \pi^*)$ state.

Quinazoline shows a measurable fluorescence neither in Shpolskii matrices, nor in hydroxylic glass; it was not detected either while examining quinazoline in aromatic matrices [3]. This fact can be explained, as in the case of quinoxaline, by rapid intersystem crossing $S_1(n, \pi^*) \rightsquigarrow T_1(\pi, \pi^*)$ (comp. [4] and literature cited there).

We have not succeeded in obtaining highly resolved $S_1(n, \pi^*) \leftarrow S_0$ absorption spectra of quinazoline molecules isolated in the Shpolskii matrices. The spectrum obtained was composed of few narrow bands ($\tilde{\nu}_{0-0} = 27220$ cm^{-1} in isooctane matrix). Now, in the $S_2(\pi, \pi^*) \leftarrow S_0$ spectrum there appeared broad bands only, which had been also observed in [3]; to the maximum of the first band in isooctane matrix corresponded $\tilde{\nu} = 32160$ cm^{-1}.

The $S_1(n, \pi^*) \leftarrow S_0$ spectrum of quinazoline molecules isolated in the Shpolskii matrices is shifted towards red in relation to the spectrum of this transition in pure quinazoline crystal [3]. Such a spectral shift could be explained, as in the case of 9, 10-diazaphenanthrene [11], by a decrease in the dipole moment of excited molecules in the $S_1(n, \pi^*)$ state.

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