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Long-term phosphorescence in cooled organic substances solid solutions – temporal dynamics and spectral memory effect

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Abstract: The paper presents the results of delayed phosphorescence study in organic substances solid solutions at cryogenic temperatures. This work continues the series of our works devoted to the study of the physical mechanism of excitation of long-term phosphorescence and the prospects for creating new active laser media based on an analogue of the Shpolsky matrix. The article also describes the observed effect of spectral memory in solid organic solutions upon excitation of long-term delayed phosphorescence by radiation from a mercury lamp.

Keywords: Long-term phosphorescence, organic compounds, cryogenic temperature, Shpolsky matrix, solid solutions, spectral memory effect

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1. INTRODUCTION

Complex organic compounds under normal conditions have luminescence spectra in the form of continuous wide bands. Because of this, it is difficult to extract information about the structure of molecules and their composition from such spectra. To solve this problem, E.V. Shpolsky and his collaborators [1-3] proposed in the middle of the last century to use the

effect discovered by them of the appearance of quasilinear electronic-vibrational spectra in complex organic compounds cooled to cryogenic temperatures. This effect allowed researchers to analyze spectra consisting of narrow spectral lines instead of broadband spectra. Subsequently, the development of research methods based on the Shpolsky effect led to the creation of optical selective laser spectroscopy of impurity molecules in solid solutions [4-6]. At present, optical spectroscopy of impurity molecules in solid solutions is widely used in solving problems in biophysics, quantum optics, physical chemistry, and technological applications.

In [7-8], the authors proposed the creation of active laser media based on analogues of the Shpolsky matrices. An experimental setup created for these purposes is described. This setup makes possible to study the phosphorescence of matrices cooled up to cryogenic temperatures. In the experiments described in [8-10], the “photon flame” effect previously discovered in [11] was additionally investigated. “Photon flame” is a long-term phosphorescence from 1 to 12 s when nanostructured matrices based on artificial opal SiO_2 are excited by a single-mode radiation of a giant ruby laser pulse.

The matrices were filled with various liquids based on organic substances (acetone, ethanol) and cooled up to liquid nitrogen temperature. Based on the results of processing the experimental data obtained in [8-9], it was concluded that ultralong-term phosphorescence (up to 60 s) in solid solutions of organic substances frozen to cryogenic temperatures can be initiated without the use of single-mode laser radiation and an opal matrix. It turned out that to excite ultra-high-power phosphorescence, it is sufficient to apply broadband radiation from a mercury lamp in the region of 240-310 nm as a pump.

In [10], studies of the temporal and spectral characteristics of ethanol $\text{C}_2\text{H}_5\text{OH}$, isopropyl $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$, and benzyl $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ alcohols cooled to cryogenic temperatures were continued when their phosphorescence spectra were excited for 10 s by ultraviolet radiation from a mercury lamp.

An analysis of the data obtained in [7-10] and literature [12-18] allows us to conclude that the phosphorescence spectra of various substances cooled to cryogenic temperatures can degrade over time, and the spectrum itself can “shift” depending on the phosphorescent molecule or atom matrix in which it is “placed”.

Several mechanisms are proposed to explain the microscopic effects of the radiation of an artificial opal arising in a crystal under the action of high-power pulsed laser radiation: the mechanism of four-photon parametric scattering and the mechanism of successive three-frequency wave interactions in periodically inhomogeneous media. In this case, the efficiency of stimulated emission in the blue-green region is provided by anomalies in the density of photon states near the edges of the Brillouin zone. The effect is observed only at low temperatures, since then the relaxation processes of photon decay with the transition of light energy into the thermal energy of the crystal lattice are suppressed [11].

We believe that the long afterglow in the blue-green region of ethyl alcohol or acetone samples frozen to cryogenic temperatures under the influence of pumping with ultraviolet radiation indicates the possibility of other, non-threshold mechanisms for the occurrence of this phenomenon, not related to photonic crystals and pulsed laser radiation.

It was also found in [8] that with increasing temperature, the afterglow effect decreases and in the region of 165 K the effect disappears. In this case, the main spectrum of long-term phosphorescence of the substances studied in

[8] is in the region of 400-555 nm. The relative intensity of the phosphorescence spectra of the studied samples differs markedly. For example, as was found in [9] from a comparison, the relative intensity under the same conditions of excitation of phosphorescence in Kalosha gasoline is about 3000 rel. units, for immersion oil – about 1800 rel. units, while ethanol has only 180 rel. units.

There is also a difference in the temporal dynamics of the phosphorescence spectra shapes of various substances. Over time, the phosphorescence spectra of ethanol and Kalosha gasoline decay proportionally over the entire range from 300 to 600 nm [9]. At the same time, the decay dynamics of the phosphorescence spectrum of immersion oil is different: the short-wavelength part (range 350-425 nm) of the phosphorescence spectrum decays faster than the long-wavelength part (range 475-525 nm), as a result of which the shape of the spectra recorded after 0.5 and 1.0 s is significantly differs from the spectra shape recorded after 2.0 and 5.5 s.

The effect of long-term phosphorescence is usually associated with a nonradiative transition in the triplet radiation scheme [10-17]. At the same time, the authors of the article consider other possible models for describing this phenomenon. For example, related to the mechanism of capture and long-term retention of electromagnetic radiation by the field of an atom or molecule within the framework of the extended space model [19-20].

In the presented work, new results of our experimental studies of the spectral characteristics of phosphorescence of organic substances cooled to the temperature of liquid nitrogen are presented. In particular, the observed effect of spectral memory in solid organic solutions upon excitation of long-term phosphorescence by radiation from a mercury lamp is described.

2. DESCRIPTION OF THE INSTALLATION AND MEASUREMENT TECHNIQUE

To study the spectral properties of organic substances cooled up to the temperature of liquid nitrogen, a laboratory setup was created, which is schematically shown in **Fig. 1**. A pulsed YAG:Nd³⁺ laser with a frequency doubler (radiation wavelength 1064, 532 nm, 15 mJ/pulse, 15 ns duration, repetition rate 50 Hz) or continuous radiation from a DRT-230 mercury lamp could be used as a pump source in the setup.

The pump radiation from a mercury lamp 1 passed through a replaceable light filter combined with a mechanical radiation interrupter 2. Next, the radiation was focused onto the surface of the test sample using a collimator 3, a rotary prism 4, and a focusing quartz lens 5 into liquid nitrogen, which was poured into a thermos cuvette open at the top. The time of irradiation of samples with pump radiation varied and ranged from several minutes to 5 s in different experimental series.

The phosphorescence of the samples was recorded by a digital spectrum analyzer 7

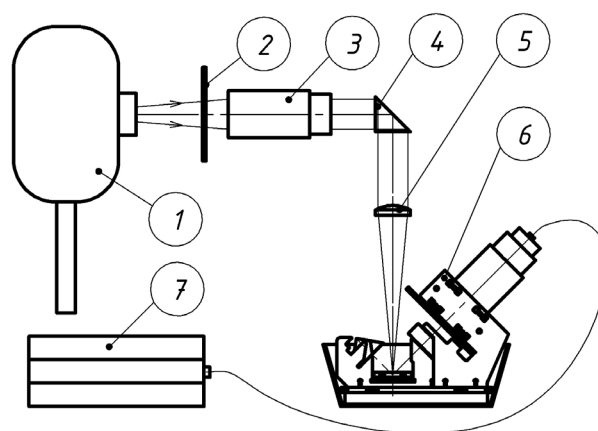


Fig. 1. Installation diagram. 1 – mercury lamp; 2 – replaceable light filter/mechanical radiation interrupter; 3 – collimator of a mercury lamp; 4 – rotary prism; 5 – focusing lens; 6 – sample exposure unit; 7 – spectrometer.

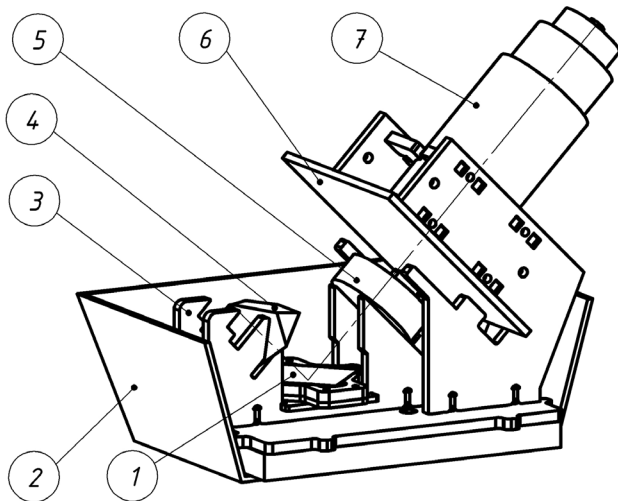


Fig. 2. Arrangement of the sample exposure unit. 1 – frozen sample; 2 – cell body for liquid nitrogen (section); 3 – constructive from PMMA (polymethyl methacrylate); 4 – replaceable rear mirror (trippelprism); 5 – replaceable front mirror; 6 – replaceable light filter; 7 – collimator of the light guide of the spectrometer.

connected to a computer or a digital camera after the pump radiation was blocked by a mechanical chopper.

Fig. 2 shows in more detail the arrangement of the unit for exposing samples, which is schematically shown. When designing the assembly for exposure, we took into account the features in measuring the optical characteristics of the Shpolsky matrices, which we obtained in the study of similar objects [7-8].

The design of the exposure unit made it possible to work with samples of organic substances partially immersed in liquid nitrogen without fogging the prism/mirrors 4, 5 and collimator 7. To measure the phosphorescence spectra, the cooled sample was illuminated by pump radiation for 30-60 s. After the end of irradiation, the light flux from the mercury lamp was mechanically blocked by an opaque metal shutter. Before measuring the experimental spectra, we recorded the control noise spectrum of the ruler, which was then subtracted from the working spectra. The exposure time of the noise and experimental

spectra in each experimental series was the same. To estimate the scatter in the intensity of the spectral data, series of 10-15 spectra of the same samples were recorded under the same conditions. The resolution of the Ocean Optics HR4000 spectrometer was about 0.75 nm/channel, the measurement range was 200-1100 nm.

Fig. 3 shows the spectrum of scattered radiation of a DRT-230 mercury lamp from liquid nitrogen in a steel cell, obtained on our experimental setup.

It should be noted that the radiation of a mercury lamp depends on the design and type of the lamp (DRT-230 is an arc mercury-helium high-pressure quartz lamp) and is variable in time as the mercury lamp heats up during operation [21,22]. Therefore, when using a mercury lamp as a fluorescence excitation source, in each series of experiments, before and at the end of the measurements, we controlled the initial radiation spectrum from the DRT-230. According to the manufacturer's passport data, the power consumption of the DRT-230 lamp is 230 W, the radiant flux in the range $\lambda = 240-320$ nm is 24.6 W, and the radiation power distribution in regions A, B, and C with respect to the entire radiation power: region A: 315-400 nm – 21%; region B: 280-315 nm – 25% and region C: 230-280 nm – 11%. As can be seen from Fig. 3, the strongest emission lines

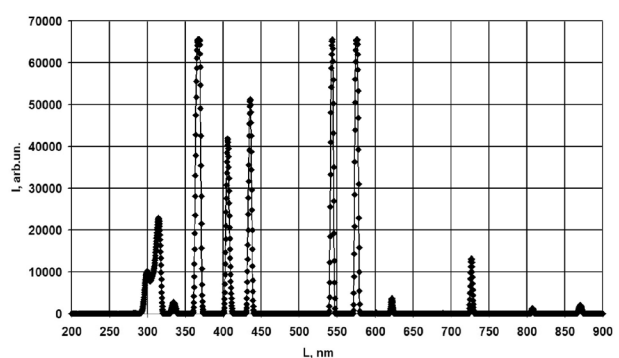


Fig. 3. Scattered radiation spectrum of a DRT-230 mercury lamp in liquid nitrogen in a steel cell.

of DRT-230 are located in the areas: 300-315; 336; 368; 406; 435; 544; 576; 622 and 727 nm.

When conducting research, we also took into account the results of studies of the spectral composition and temporal dynamics of radiation from various types of mercury lamps [21-22].

The measurement technique described above allowed us to control the spectral parameters of the exciting radiation and consistently obtain well-repeated results of spectral measurements from identical samples in different experimental series.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Below we present the results of further studies initiated in a series of works [7-10].

The magnitude of the excitation efficiency of long-term phosphorescence at cryogenic temperatures was studied in complex organic substances having a similar composition.

As samples for comparison, we examined Cosmofen PMMA Cosmo SL-650.110 diffuse adhesives; Cosmo SL-650.120 and Cosmo SL-660.210 (manufactured by Weiss Chemie). Cosmo SL-650.110 and Cosmo SL-650.120 are PMMA diffuse acrylic adhesives in solvent. The SL-650.110 specified by the manufacturer contains dichloromethane CH_2Cl_2 , acetone $\text{C}_3\text{H}_6\text{O}$ and butanone $\text{C}_4\text{H}_8\text{O}$, in contrast to the specified Cosmo SL-650.120. It was found that under the same excitation conditions, the relative intensity of the phosphorescence spectra of Cosmo SL-650.110 is approximately 70 times greater than that of Cosmo SL-650.120 **Fig. 4**.

In Fig. 4, the phosphorescence intensity of Cosmo SL-650.110 cooled to 77.4 K is displayed on a logarithmic scale and refers to the left scale, and the intensity of the phosphorescence spectrum of SL-650.120

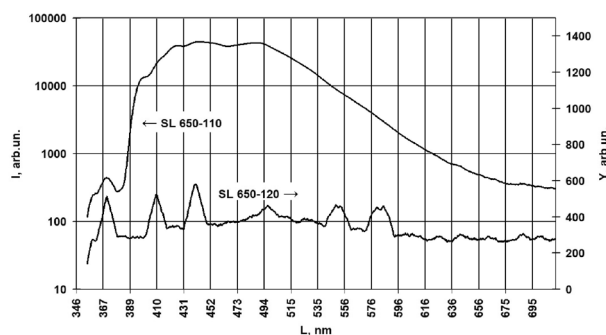


Fig. 4. Phosphorescence spectra of cooled to 77.4 K Cosmo SL-650.110 and Cosmo SL-650.120 exposure 200 ms, the spectra were recorded 400 ms after the excitation radiation from the DRT-230 mercury lamp was blocked.

cooled to 77.4 K refers to the linear scale located in Fig. 4 on the right.

Such a large difference in the intensity of the excited phosphorescent spectra can be attributed to the above three substances that are included in Cosmo SL-650.110 and are absent in Cosmo SL-650.120.

However, in our further experiments with Cosmo SL-650.120, which contains both acetone $\text{C}_3\text{H}_6\text{O}$ and butanone $\text{C}_4\text{H}_8\text{O}$, an extremely weak delayed phosphorescence was recorded. Therefore, we come to the conclusion that almost two orders of magnitude more efficient excitation of phosphorescence in the Cosmo SL-650.110 sample cooled to liquid nitrogen temperature compared to Cosmo SL-650.120 and in Cosmo SL-650.120 is associated only with the presence of dichloromethane CH_2Cl_2 in its composition.

It is necessary to note one more effect that we discovered in the study of the phosphorescence spectra of organic substances cooled to cryogenic temperatures. On the phosphorescence spectra of Cosmo SL-650.110 and Cosmo SL-650.120 Fig. 4, one can see broad lines that coincide with the arrangement of emission lines of a mercury lamp. From the comparison of Fig. 3 and

Fig. 4, it can be seen that the Cosmo SL-650.120 sample has broad lines in the 363-372 nm regions in the phosphorescence spectrum; 402-410; 431-448; 539-558 and 570-590 nm corresponding to the arrangement of emission lines of a mercury lamp. For the Cosmo SL-650.120 sample, the spectrum shown in Fig. 4 this effect is clearly visible in the region of 363-372 nm, relatively weakly in the regions of 402-410; 431-448 nm, and is not observed in the regions of 539-558 and 570-590 nm. This effect of the spectral memory of organic substances cooled to 77.4 K was recorded on the phosphorescence spectra recorded 400 ms after the complete overlap of radiation from the DRT-230 source, with an exposure time of 200 ms.

A similar result, in the time range from 0.2 to 8.0 s, was obtained by us in the study of phosphorescence of isopropanol C₃H₈O cooled to 77.4 K. On **Fig. 5** shows the temporal dynamics of the phosphorescence spectra of isopropanol. The total time of visually observed superlong phosphorescence

of isopropanol cooled to a temperature of 77.4 K was about 60 s.

As can be seen from the data shown in Fig. 5, the effect of spectral memory in solid organic solutions cooled to 77.4 K upon excitation of long-term phosphorescence by radiation from a mercury lamp is well observed in isopropanol in the range of time delays from 0.2 to 3.2 s.

In this case, as can be seen, the dynamics of the effect is different in different wavelength ranges. Comparison of the attenuation of broad lines of isopropanol phosphorescence in areas coinciding with the radiation of a mercury lamp in the ranges: 363-372; 402-410; 431-448; 539-558 and 570-590 nm shows that in the regions of 363-372 and 431-448 nm the effect of spectral memory is manifested in all seven spectra; in area 402-410; 539-558 and 570-590 nm the effect is reliably identified only in the first two spectra taken with a delay of 200 and 400 ms.

4. CONCLUSION

Many works have been devoted to the study of the spectral properties of organic and inorganic substances at cryogenic temperatures [23-30]. Literature analysis allows us to draw the following conclusions: the effect of long-term phosphorescence is usually associated with a nonradiative transition in the triplet radiation scheme. It was also found that the phosphorescence spectra of samples can degrade over time. The phosphorescence spectrum can also be shifted to the short-wavelength or long-wavelength region, depending on the matrix in which the phosphorescent molecule or atom is "placed".

Our results are in qualitative agreement with the above properties of cryogenic phosphorescence of organic compounds described in the authors' works [3-6;12-18]. Experimental results show the promise of

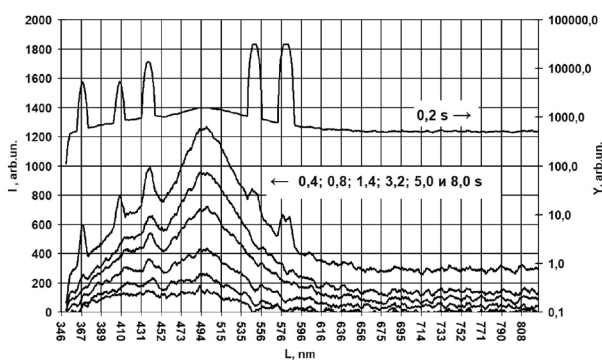


Fig. 5. Time dynamics of phosphorescence spectra of isopropanol cooled to 77.4 K. The exposure time of the spectra is 200 ms, the delay times of the recorded spectra are from 0.2 to 8.0 s. The spectrum taken with a delay of 0.2 s corresponds to the right logarithmic intensity scale, the remaining spectra with delays from 0.4 to 8.0 s corresponds to the left linear scale.

studying the possibility of creating cryogenic lasers based on organic compounds [7-8].

The observed effect of spectral memory in solid solutions of organic substances cooled to cryogenic temperatures upon excitation of phosphorescence by radiation from a mercury lamp deserves further detailed experimental study in the opinion of the authors.

The studies carried out indicate the possibility of the appearance in the sample of a potential well capable of capturing and retaining optical radiation for a long time in solid solutions of organic substances cooled up to a liquid nitrogen temperature of 77.4 K under the influence of the ultraviolet part of the radiation of a mercury lamp shorter than 300 nm.

To describe this phenomenon, we plan to study in subsequent works the possibility of using the mechanism of capture and long-term retention of electromagnetic radiation by the field of an atom or molecule as a model for describing this phenomenon within the framework of the extended space model [19-20].

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