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## Resonance Excitation of Photoluminescence in Crystalline Uranyl Acetate Dihydrate

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**Abstract**—A method for rapid identification of uranyl compounds based on resonance fiber-optic photoluminescence (PL) excitation by ultraviolet-laser or LED radiation is proposed. This method was used to measure the PL spectra of an extremely small volume ( $10^{-9}$  cm<sup>3</sup>) of crystalline uranyl acetate dehydrate  $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  with an exposure of  $10^{-3}$  s. Semiconductor LEDs with wavelengths of 369, 385, 410, and 466 nm and a repetitively pulsed nitrogen laser with a lasing wavelength of 337 nm served as sources of excitation radiation. The operating range of a small-sized minispectrometer used in these experiments was 200–1000 nm.

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### INTRODUCTION

The application of uranium compounds in nuclear-power engineering and the related issues of recycling and waste treatment are currently driving interest in these compounds [1]. Their spectra are being studied extensively [2, 3], with applied research in this field having commenced in the late 20th century [4]. Uranium compounds also have unique crystallochemical and physicochemical properties [5, 6]. One of these properties is intense luminescence [7] in the visible range, which is attributable to the electronic structure of the uranyl ion ( $\text{UO}_2$ )<sup>+</sup> [8].

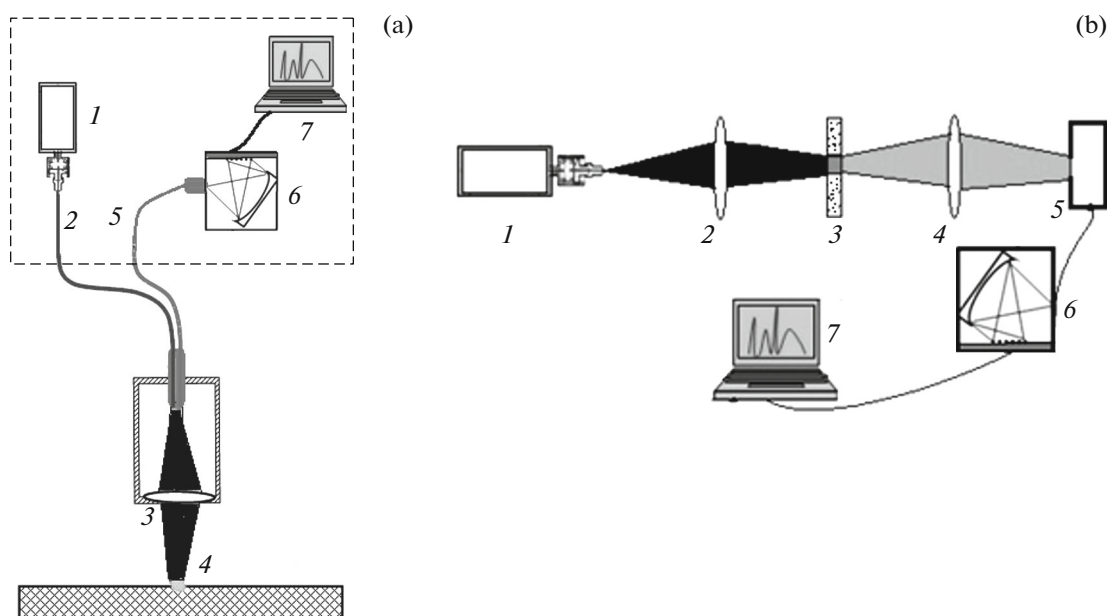
A great number of ultraviolet, infrared, and visible transitions are present in the spectrum of electronic states of this ion. General information regarding uranyl compounds and a discussion of their properties are found in [9]. The photoluminescence (PL) and absorption spectra of organic and inorganic uranyl-based complexes (uranyl silicate, uranyl perchlorate, uranyl nitrate, uranyl sulfate, uranyl fluoride, and uranyl oxalate) measured at different temperatures have been studied in [10–17]. It was found that the typical room-temperature PL spectra of uranyl compounds contain a system of equidistant diffuse bands located in the region of 450 nm. Depending on the measurement conditions, a total of four to eight PL bands with a frequency distance of approximately 860 cm<sup>-1</sup> between their maxima were detected. The spectral positions of these maxima depend on the chemical composition of the compound under study. The cooling of crystalline samples to the boiling point of liquid

oxygen or nitrogen is accompanied by splitting of the PL spectra of most uranyl compounds in the PL band with a FWHM of 20–40 cm<sup>-1</sup>. This splitting shapes the PL spectra structure under excitation by visible and ultraviolet radiation of different wavelengths [10, 18]. The formed structure is specific to each compound and is very sensitive to the presence of impurities.

The electronic configurations of several uranyl compounds have been examined thoroughly in [19–23]. The mechanisms of energy distribution between characteristic oscillations of crystals have also been characterized in detail. Experimental results agreed well with the results of group-theoretical analysis. Uranyl complexes were cooled to fairly low temperatures in the PL studies in [19–23].

It was found in experiments with uranyl chloride in [24] that excitation radiation with frequencies of 20 400 (490), 21 000 (476), 21 500 (465), 22 500 (445), 23 000 (434), 23 900 (418), 24 400 (410), 26 000 (384), and more than 27 000 cm<sup>-1</sup> (<370 nm) corresponds to the regions of strong absorption of the uranyl ion.

Uranyl acetate and uranyl nitrate rank are some of the uranium-containing compounds most commonly encountered in nature [25]. The optical properties related to their PL and absorption spectra have been studied in [26]. Reliable PL spectra were measured in these experiments only at low temperatures (4–78 K). A mercury lamp emitting at 365 nm was used to excite photoluminescence. The PL spectra of the studied samples had four bands with intensity maxima at 489,



**Fig. 1.** Experimental setup for PL excitation in crystalline uranyl acetate dehydrate. (a) “Reflection” geometry; optical excitation source 1, quartz waveguides 2 and 5, converging lens 3, sample cell 4, spectrometer 6, and computer 7 are indicated. (b) “Transmission” geometry; laser 1, converging lenses 2 and 4, sample 3, locking device 5, spectrometer 6, and computer 7 are indicated.

507, 534, and 559 nm. These wavelengths correspond to transitions from the first excited electronic state to vibrational sublevels of the uranyl group of the ground electronic state [27].

The room-temperature PL spectrum of crystals of sodium uranyl acetate  $\text{NaUO}_2(\text{CH}_3\text{COO})_3$  was obtained in [28]. Semiconductor LEDs and a laser with an operating wavelength of 266 nm served as the sources of excitation radiation. PL emission at 479, 498, 521, and 546 nm was detected. The redistribution of intensity in the PL spectrum in the band corresponding to 498 nm ( $21000 \text{ cm}^{-1}$ ) under repetitively pulsed excitation by a solid-state laser emitting at 266 nm was also observed. The authors of this work have hypothesized that uranyl ions may be capable of lasing (in a way similar in nature to dye lasing [29]).

The aim of the present study was to develop a method for rapid detection of uranyl components at room temperature. The proposed method was used to measure the PL spectra of uranyl acetate dehydrate  $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  polycrystals. The obtained spectra were compared to the available PL spectra of sodium uranyl acetate and several other compounds.

## EXPERIMENTAL

Uranyl acetate exists in the form of crystalline  $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  [30]. This polycrystal belongs to the orthorhombic system and is characterized by space group  $Pnam(D_{2h}^{16})$  with lattice parameters  $Z = 4$ ,  $a = 9.622$ ,  $b = 14.833$ , and  $c = 6.808 \text{ \AA}$ . Linear

$\text{UO}_2$  groups are positioned along the axis of point group  $D_{2h}$  of the crystal. The studied sample was yellow powder in a quartz cell. Microparticles of uranyl acetate polycrystals were  $\sim 100 \mu\text{m}$  in size. The PL spectra were measured at room temperature.

Two experimental setups were used (see Fig. 1). In the “reflection” setup (Fig. 1a), radiation was transferred via a quartz waveguide with a diameter of  $100 \mu\text{m}$  to the crystal surface so as to achieve almost normal incidence. The excited PL emission entered another waveguide [31].

The PL spectra of crystalline uranyl acetate dehydrate were measured under excitation by quasi-monochromatic semiconductor LEDs with wavelengths of 369 (3.36), 385 (3.24), 410 (3.02), and 466 nm (2.64 eV). The spectrum of optical excitation sources fell within the bands of strong absorption of the uranyl ion [24, 32]:  $27000 (370)$ ,  $26000 (384)$ ,  $24400 (410)$ , and  $21500 \text{ cm}^{-1} (465 \text{ nm})$ . Owing to this strong absorption, excitation radiation penetrated through only a thin layer of the sample (on the order of a single wavelength, i.e.,  $\sim 10^{-5} \text{ cm}$ ). Since the illuminated surface area was just  $\sim 10^{-4} \text{ cm}^2$ , the volume of luminescent material was  $\sim 10^{-9} \text{ cm}^3$ .

In the “transmission” setup (Fig. 1b), a repetitively pulsed nitrogen laser with an operating wavelength of 337 nm was used as the optical excitation source. The spectrum of this source also fell within the region of strong absorption of uranyl ( $>27000 \text{ cm}^{-1}$ ).

The obtained PL spectra were recorded by an FSD-8 digital spectrometer connected to a computer.

**Table 1.** Spectral positions of the PL intensity maxima of crystalline uranyl acetate dehydrate  $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  and  $\text{NaUO}_2(\text{CH}_3\text{COO})_3$ 

Wavelength, nm	Spectral positions of the intensity maxima of PL bands for $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ , $\text{cm}^{-1}$					Spectral positions of the intensity maxima of PL bands for $\text{NaUO}_2(\text{CH}_3\text{COO})_3$ , $\text{cm}^{-1}$				
337	17070	17914	18758	19653	20430	—	—	—	—	—
369	—	17850	18761	19646	20491	17490	18301	19192	20099	20875
385	—	17853	18759	19629	20491	17394	18315	19192	20035	20898
410	—	17851	18759	19629	20490	—	18281	19192	20099	20875
466	—	—	18755	19630	21052	—	18301	19192	20099	20875

The operating spectral range of this spectrometer is 200–1000 nm at a resolution of  $\sim 1$  nm. The exposure times were varied within the interval 0.1–128 ms.

## RESULTS

The PL spectra of uranyl acetate dehydrate polycrystals obtained under excitation by various sources are shown in Fig. 2. Photoluminescence was excited either by semiconductor LEDs with wavelengths of 369 (Fig. 2a), 385 (Fig. 2b), 410 (Fig. 2c), and 466 nm (Fig. 2d) or by the nitrogen laser at 337 nm (Fig. 2e). It can be seen that the PL spectra contain four (LED excitation; Figs. 2a–2c) or five (laser excitation; Fig. 2e) well-resolved bands. The PL spectrum shape varied with the excitation-radiation frequency.

The positions of the intensity maxima (in  $\text{cm}^{-1}$ ) of PL bands of uranyl acetate dehydrate determined in the present study are listed in Table 1. The data for sodium uranyl acetate obtained in similar measurements in [28] are given in Table 1 for comparison.

## DISCUSSION

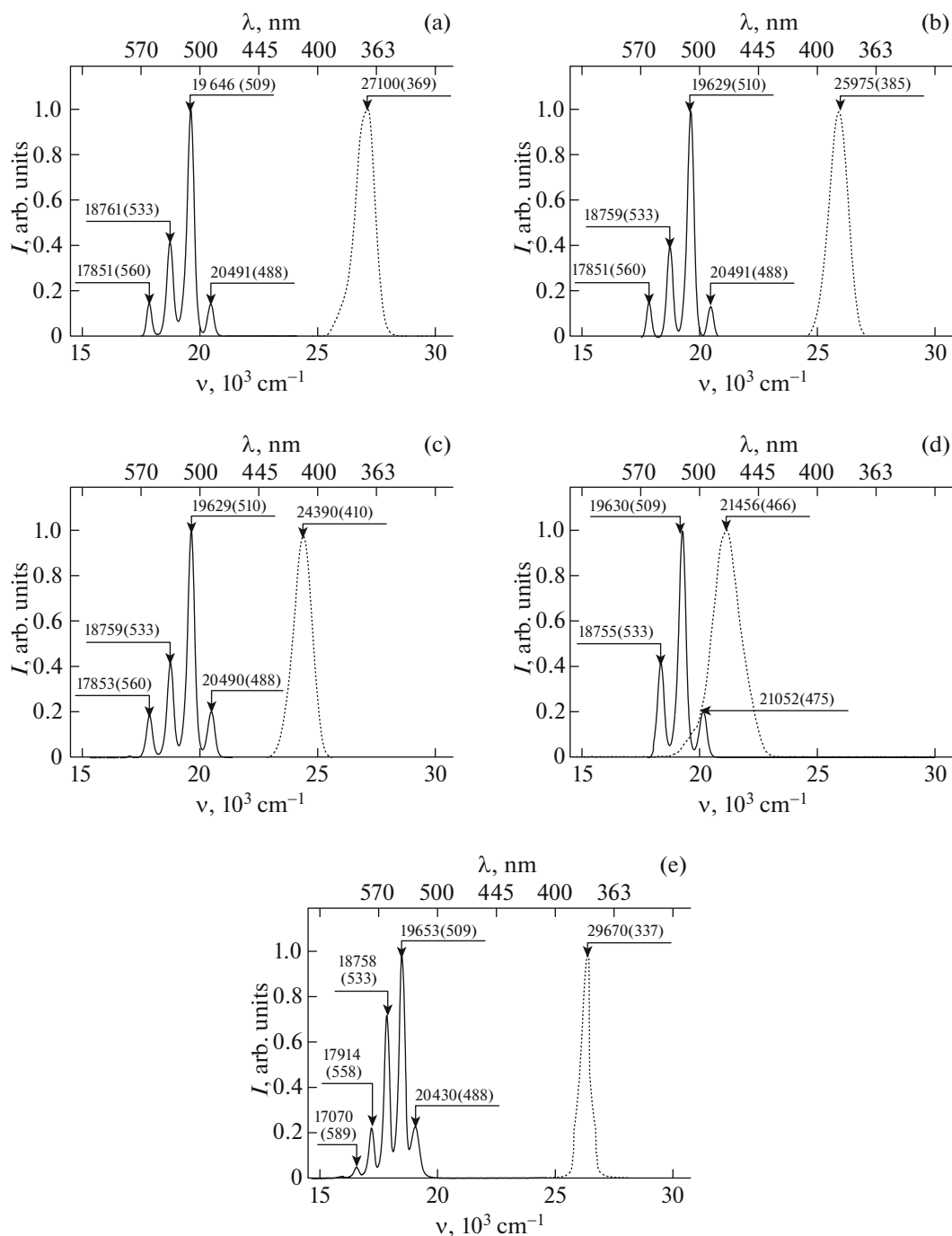
Thus, a method for rapid detection of uranyl complexes was proposed. This method is based on the effect of resonance excitation of uranyl ions observed when the excitation radiation frequency falls within the region of strong absorption of the studied sample. Ultraviolet LEDs emitting in a narrow spectral range may be used as excitation sources in such experiments. The PL spectra were recorded using fiber waveguides and an FSD-8 minispectrometer with short exposures ( $\sim 10^{-3}$  s) and extremely small irradiated volumes ( $10^{-9}$   $\text{cm}^3$ ).

The obtained PL spectra of crystalline uranyl acetate dehydrate contain four well-resolved bands with their intensity maxima at 17852, 18762, 19630, and 20490  $\text{cm}^{-1}$ . This agrees with the results presented in [26], where a large setup and a mercury lamp (excitation source) were used. The absorption and emission of light by uranyl ions is illustrated by the energy-level diagram [33] of crystalline uranyl acetate dehydrate shown in Fig. 3. The ground and excited electronic

states are denoted in this diagram as  $S_0$  and  $S_1$ . Each of these levels is composed of several vibrational–rotational sublevels (0, 1, 2, etc.). The absorption of uranyl ions ( $\text{UO}_2$ )<sup>+</sup> corresponds to transitions from the lowest ground electronic state  $S_0$  to excited state  $S_1$  and its sublevels.

The observed PL spectra represent [27] radiative transitions from energy level  $S_1$  of the uranyl ion to ground state  $S_0$  or to its vibrational sublevels of the ground state. Thus, the highest radiative transition frequency  $\nu_1 = 20490$   $\text{cm}^{-1}$  corresponds to the resonance frequency of the electronic transition to the lowest energy level. Frequencies  $\nu_2 = 19630$ ,  $\nu_3 = 18762$ , and  $\nu_4 = 17852$   $\text{cm}^{-1}$  correspond to transitions from the excited electronic state to the ground one (the first, the second, and the third vibrational sublevels, respectively). The frequencies of the PL intensity maxima for crystalline uranyl acetate dehydrate and sodium uranyl acetate are listed in Table 2. It follows that the observed PL bands are equidistant (within the measurement error): the frequency distance between the mentioned maxima (and, consequently, vibrational energy levels) is  $870 \pm 50$   $\text{cm}^{-1}$ . This frequency corresponds to symmetric stretch vibrations of the uranyl ion [27]. The PL intensity maxima for  $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  are shifted by 400  $\text{cm}^{-1}$  relative to the maxima for  $\text{NaUO}_2(\text{CH}_3\text{COO})_3$ . This is attributed to the difference in positions of the first excited electronic level. The resonance transition frequency for crystalline uranyl acetate dehydrate (20491  $\text{cm}^{-1}$ ) is 384  $\text{cm}^{-1}$  lower than that for sodium uranyl acetate (20875  $\text{cm}^{-1}$ ). Therefore, the first excited electronic level in sodium uranyl acetate is located 384  $\text{cm}^{-1}$  higher than the same level in crystalline uranyl acetate dehydrate. These levels correspond to the uranyl ion excitation in condensed media and depend on ligands.

The frequencies (in  $\text{cm}^{-1}$ ) of the PL maxima for several uranyl-based complexes mentioned in the Introduction are listed in Table 3. It can be seen that the PL properties of crystalline uranyl acetate dehydrate allow one to identify it unambiguously at room temperature. The small size of the used experimental

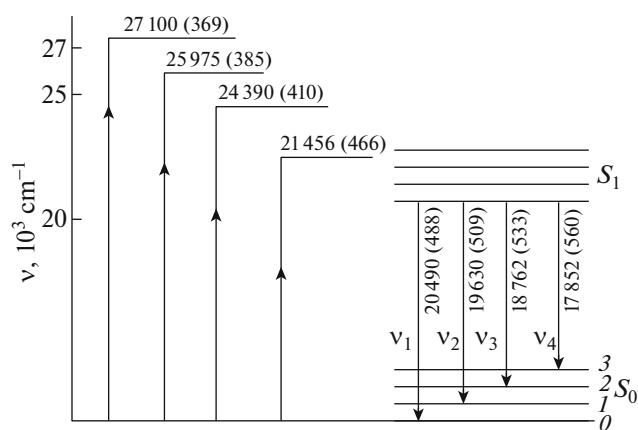


**Fig. 2.** PL spectra measured under excitation by diodes with wavelengths of (a) 369, (b) 385, (c) 410, and (d) 466 nm and (e) by the laser with  $\lambda = 337$  nm.

setup suggests that production of portable rapid-response analyzers designed to scan the environment for uranyl components is possible. Resonance excitation of  $(\text{UO}_2)^+$  and the excitation of the spectral region corresponding to strong electronic absorption of the uranyl ion provide efficient luminescence of the crystal. The PL band with its maximum at  $19630\text{ cm}^{-1}$ ,

which is shaped like a peak no more than 20 nm wide, is the most intense. The emergence of a narrow intense peak suggests that the emission of a photon with a frequency of  $19630\text{ cm}^{-1}$  in the process of photoluminescence is highly probable.

It should be noted that the effect of superluminescence has been observed in [28] when sodium uranyl



**Fig. 3.** Energy-level diagram of crystalline  $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ .

acetate was excited by a repetitively pulsed solid-state laser with a lasing wavelength of 266 nm and a four-level pumping scheme. Superluminescence mani-

fested itself in the intensification of PL in the band corresponding to 498 nm ( $20100 \text{ cm}^{-1}$ ).

The observation of superluminescence in sodium uranyl acetate crystals attests to the possibility of lasing in crystalline uranyl acetate dehydrate  $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ . In contrast to known dye lasers [34], sources utilizing the effect of superluminescence in uranyl compounds are characterized by high gain factors. The enhancement of intensity in crystalline uranyl acetate dehydrate should manifest itself at the frequency of  $19630 \text{ cm}^{-1}$  (due to the  $385 \text{ cm}^{-1}$  difference in positions of the first excited levels). It is proposed to use a solid-state laser with an operating wavelength of 266 nm as a pump source.

## CONCLUSIONS

The obtained results attest to the possibility of rapid identification of small amounts of crystalline uranyl acetate dehydrate in ambient environment by fiber-optic excitation of PL spectra with ultraviolet and blue semiconductor LEDs. It was found that four

**Table 2.** Numbers and differences between the frequencies of PL intensity maxima of  $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  and  $\text{NaUO}_2(\text{CH}_3\text{COO})_3$  crystals

Crystalline uranyl acetate dehydrate $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$		Sodium uranyl acetate $\text{NaUO}_2(\text{CH}_3\text{COO})_3$	
$\nu \pm 50, \text{ cm}^{-1}$ (position of the PL intensity maxima)	$\Delta\nu \pm 50, \text{ cm}^{-1}$	$\nu \pm 50, \text{ cm}^{-1}$ (position of the PL intensity maxima)	$\Delta\nu \pm 50, \text{ cm}^{-1}$
17851	906	18300	892
18757	873	19192	907
19630	861	20099	776
20491		20875	

**Table 3.** Comparison of the frequencies (in  $\text{cm}^{-1}$ ) of PL intensity maxima of uranyl-based complexes

Compound	$\nu_1, \text{ cm}^{-1}$ (peak 1)	$\nu_2, \text{ cm}^{-1}$ (peak 2)	$\nu_3, \text{ cm}^{-1}$ (peak 3)	$\nu_4, \text{ cm}^{-1}$ (peak 4)	$\nu_5, \text{ cm}^{-1}$ (peak 5)	$\nu_6, \text{ cm}^{-1}$ (peak 6)	$\nu_7, \text{ cm}^{-1}$ (peak 7)
Uranyl silicate $\text{K}(\text{UO}_2) \cdot (\text{SiO}_3\text{OH}) \cdot 15(\text{H}_2\text{O})$ [17]	19787	18685	17921	17259	—	—	—
Fluoride $\text{UO}_2\text{F}_2$ [11]	20234	19366	18500	17490	16640	—	—
Pure uranyl $\text{UO}_2$ [13]	20338	19459	18574	17746	16895	—	—
Perchlorate $\text{UO}_2(\text{ClO}_4) \cdot 6\text{H}_2\text{O}$ [15]	20408	19342	18691	—	—	—	—
Crystalline uranyl acetate dehydrate $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ [present study]	20491	19630	18757	17851	—	—	—
Nitrate $\text{UO}_2(\text{NO}_3)_2$ [12]	20703	19801	19011	18083	17152	—	—
Sodium uranyl acetate $\text{NaUO}_2(\text{CH}_3\text{COO})_3$ [28]	20875	20099	19192	18300	—	—	—
Sulfate $\text{K}_2(\text{UO}_2) \cdot (\text{SO}_4)_2$ [10]	20986	20325	19493	18657	17838	17004	16155

bands with their intensity maxima located at 17851, 18757, 19630, and 20491  $\text{cm}^{-1}$  are present in the PL spectrum. The PL spectra measured in the “reflection” geometry correspond to radiative transitions from excited electronic-energy levels of the uranyl ion to the ground state and to equidistant ( $860 \text{ cm}^{-1}$ ) vibrational sublevels. A similar spectral pattern was observed in the “transmission” geometry under repetitively pulsed laser excitation. The PL spectra of crystalline uranyl acetate dehydrate and sodium uranyl acetate were found to be similar. The vibronic structure in these spectra is governed by symmetric vibrations of the uranyl ion (type  $A_1$ ). The observed differences are attributed to the fact that the first excited electronic level in sodium uranyl acetate is located  $385 \text{ cm}^{-1}$  higher than the same level in crystalline uranyl acetate dehydrate. The possibility of lasing in  $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  crystals (similar to dye lasing with four-level pumping) was established.

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