Luminescence spectra of uranyl ions adsorbed on disperse SiO_2 surfaces

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In this paper, the luminescene spectra of UO_2^{2+} molecular ions adsorbed on disperse SiO_2 surfaces were investigated under photoexcitation. It has been established that luminescence properties of this system are determined by the type and structure of the adsorption complexes (AC's) formed. Various AC's cause many elementary luminescence spectra (about 20) that were detected by means of selective laser excitation. It has been shown that uranyl ions are linked with the surface by water molecules. H_2O molecules coordinate uranium in water-uranyl complexes and take part in the formation of adsorption bonds. One can observe the so-called nonuniform broadening of the emisson spectra, which is due to variations of the degree of water-uranyl-complex perturbaton under AC formation. It is shown that there is a correlation between the emission maxima shift and perturbation degree of uranyl ions for each AC. We observe the phenomenon of resonant energy transfer among various AC's in their excited states. The resonant energy transfer is a result of the coincidence of the perturbation energy value and the energy of symmetrical and deformation vibrations in excited states. The rate of nonradiative energy relaxation among these AC's is consistent with the rate of vibrational relaxation in each concrete AC. The effect of heat pretreatment (320–1300 K) on the luminescence properties was also investigated. The water-uranyl-complex bond energies were obtained. We demonstrate the use of uranyl ions for the investigation of adsorption properties of the disperse SiO_2 surface.

INTRODUCTION

SiO_2 surfaces have attracted increasing interest due to their properties for numerous important applications in chemical, petrochemical, biochemical, and environmental industries, such as the electrochemical photolysis of water,[1] as a support material for catalysts,[2] and as a separation and purification of fluid mixtures by selective adsorption.[3,4] Disperse silicon dioxide is a complex heterogeneous system with a high specific surface (50–400 m^2/g). It is a set of small particles with sizes 10–100 nm and amorphous by volume. Its adsorption efficiency is caused by active surface centers, such as surface atoms, impurities, and self-defects.[5,6] In this work we use uranyl ions for adsorption efficiency determination. The emission properties of uranyl ions have been greatly studied.[7,8] It has long been known that UO_2^{2+} ions are characterized by the high sensitivity of their emission properties to weak perturbations which arise under interaction with their surroundings.[8]

In the present paper we will consider the luminescence properties of the adsorption system SiO_2-UO_2^{2+} under integral and selective laser excitations. The major line of this research was the employment of inorganic molecular ions for the study of the disperse SiO_2 surface adsorption activity. The basic idea of these investigations is the following. Molecular ions experience weak perturbation under interaction with the SiO_2 surface. The degree of the molecule-surface interaction and perturbation of molecular ions, respectively, is caused by the value of the bond energy in this adsorption system. These weak perturbations of molecular ions lead to the perturbation of their electronic structure and to changes of spectroscopic characteristics. The formation of adsorption complexes (AC's) initiates a shift of the 0-0-electronic transition and emission bands of molecular ions, resulting in broad and continuous adsorption and emission spectra. The investigation of these shifts offers a possibility to study the SiO_2 surface adsorption activity, bond energy for each concrete AC, as well as the nature of active centers on the SiO_2 surface.[9] The nonuniform broadening of the emission spectra is caused by the shifts of elementary luminescence spectra that were detected by means of selective laser excitation.[10]

In this connection, a selection of a type of molecular ions is of great importance. It is required of molecular ions that their properties must satisfy the following requirements.

(1) They must be effective luminophors.
(2) They must be characterized by narrow emission bands with well-detected position of maxima.
(3) The time constant of luminescence decay in the lowermost excited state must be equal for various AC's.
(4) They must be characterized by a fast time of nonradiative relaxation among the AC's in their lowermost and higher excited states by comparison with the time constant of luminescence decay.

We will show below that molecular ions UO_2^{2+} satisfy these requirements.

In this paper, the nature of the nonuniform broadening of the luminescence spectra and the contribution of elementary luminescence spectra into total intensity under integral excitation will also be discussed. The experimental spectra have been theoretically described and computer-calculated intensity distribution functions have been obtained. The model of adsorption complexes for

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the uranyl ions will be discussed. Finally, in the last section, the adsorption bond energies have been assessed using an electrostatic consideration and resonant energy-transfer conception.

EXPERIMENT

All samples for investigations were prepared by the following technique. Disperse silicon dioxide with the specific surface of 220 m^2/g (aerosil) was dehydrated at 700 K, during 2 h in air. The adsorption of UO_2^{2+} ions on the surface was carried out from an aqueous solution of $UO_2SO_4 \times 3H_2O$ salt. Then the modified sorbent was dehydrated in air (heat treatment under $T_{h.t.} = 320-1300$ K) and compacted. The compressed samples were obtained in a mold under pressure of 4.0×10^6 N/m^2. The content of adsorbed water and surface hydroxyls was inspected over infrared (IR) absorption spectra. A computer-controlled laser spectrometer was used for the measurements of luminescence spectra under selective laser excitation. The luminescence spectra were excited by an Ar^+ laser or tunable dye laser with N_2 laser pumping. All measurements were performed at liquid-helium temperature. All luminescence spectra have been corrected.

RESULTS

The adsorption system SiO_2-UO_2^{2+} is characterized by intensive luminescence at liquid-helium temperature.[9,11] The emission spectra of these samples were investigated for three temperature regions of sample heat pretreatment $T_{h.t.} = 320$ (I); 900 (II), and 1200 K (III). It has been shown previously[12] that the first region ($T_{h.t.} = 320-500$ K) corresponds to the hydrated and hydroxylated surface. The second region ($T_{h.t.} = 900-1000$ K) may correspond to the dehydrated surface rather than the dehydroxylated one. The third region ($T_{h.t.} = 1200-1300$ K) corresponds to the dehydrated and dehydroxylated surface. Thus, there are three temperature intervals that correspond to three dissimilar conditions of the silicon dioxide surface in reference to the water molecules and hydroxyl groups. These conclusions are confirmed by our IR-spectroscopy measurements in the stretching vibration region of the H_2O molecules and OH groups.

A. Spectra analysis

The luminescence spectra of the initial aqueous solution and SiO_2-UO_2^{2+} samples for the indicated temperature intervals under ultraviolet excitation are represented in Fig. 1 [spectra (b),(d),(f),(h)]. One can observe the vibrational structure in the luminescence spectra, which is caused by the interaction between 0-0-electronic transition and symmetrical vibrations of the UO_2^{2+} ion (ν_1) in its ground state.[8] It should be noted that the position of emission bands is shifted towards the long-wavelength side with increasing pretreatment temperature. The half width of the luminescence maxima for the SiO_2-UO_2^{2+} samples is greater than the respective maxima for the aqueous solution of $UO_2SO_4 \times 3H_2O$ salt. An additional structure of the luminescence spectra under visible laser

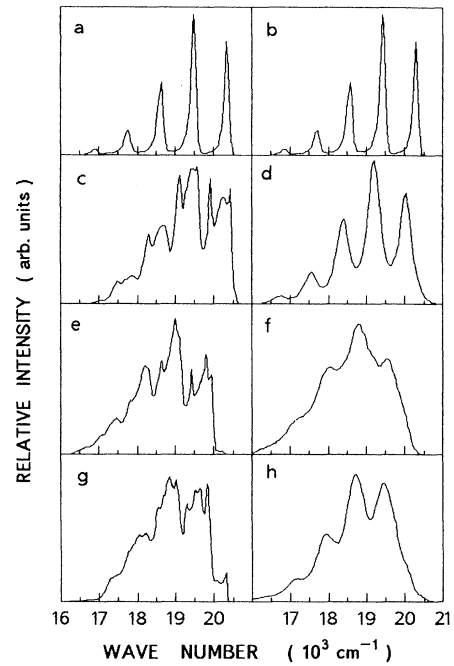

FIG. 1. The luminescence spectra of the aqueous solution of uranyl salt (a),(b) and the SiO_2-UO_2^{2+} samples (c)–(h) prepared at $T_{h.t.} = 320$ (c),(d); 900 (e),(f), and 1200 K (g),(h); $\lambda_{exc.} = 465.8$ (a); 472.7 (c); 488.0 (e); 476.1 (g); 337.1 nm (b),(d),(f),(h); $T_{reg.} = 4.2$ K.

excitation [Fig. 1, spectra (a),(c),(e),(g)] can be observed. The excitation wavelength changes in the interval ~480–515 nm, which allows one to obtain the many luminescence spectra that were detected under excitation in the 0-0-transition region and that we will be calling "elementary" (Figs. 2 and 3).

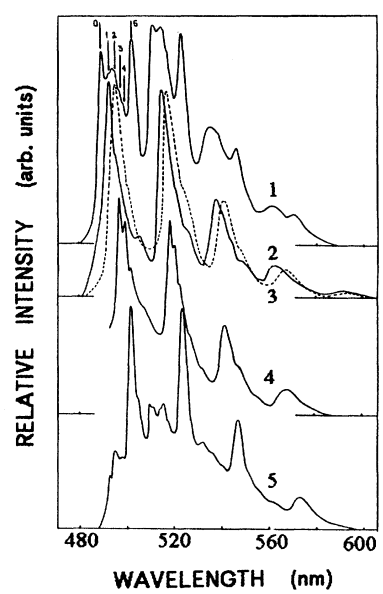

FIG. 2. The luminescence spectra ($T_{reg.} = 4.2$ K) of the SiO_2-UO_2^{2+} sample ($T_{h.t.} = 320$ K) under integral ($\lambda_{exc.} = 472.7$ nm) (1) and selective excitation [$\lambda_{exc.} - 476.5$ (2), 465.7 (3), 482.5 (4), and 488.0 nm (5)].

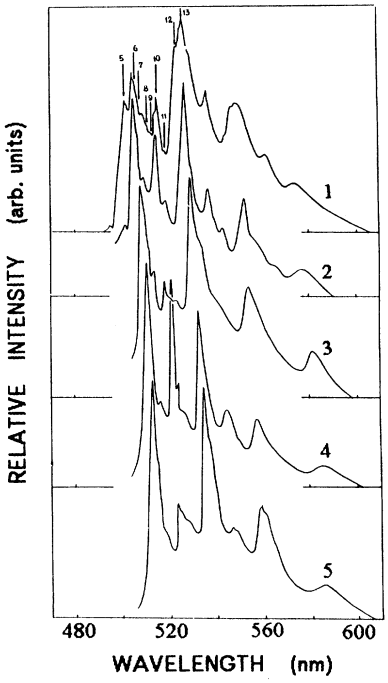

FIG. 3. The luminescence spectra ($T_{reg.}=4.2$ K) of the SiO_2-UO_2^{2+} sample ($T_{h.t.}=900$ K) under integral ($\lambda_{exc.}=488.0$ nm) (2) and selective excitation [$\lambda_{exc.}=493.0$ (2), 496.5 (3), 500.0 (4), and 501.7 nm (5)].

The half width of the luminescence maxima for the elementary luminescence spectra corresponds to the aqueous solution of $UO_2SO_4\times 3H_2O$ salt in the $T_{h.t.}=320-900$ K temperature region. However, from the annealing temperature $T_{h.t.}=1000$ K the half width of the luminescence maxima decreases. Figures 2 and 3 represent, for example, only some elementary luminescence spectra. The total number of the elementary spectra is 13 for samples prepared in the $T_{h.t.}=320-900$ K temperature region and 11 for samples prepared in the $T_{h.t.}=1000-1200$ K region. The position of the 0-0-transition and emission bands, respectively, for various elementary luminescence spectra is shifted towards the long-wavelength side corresponding to the position of the 0-0-transition for the aqueous solution of uranyl salt. One can observe a vibrational structure in each elementary luminescence spectrum, which is caused by the interaction between the respective 0-0-transition and the symmetrical vibration of UO_2^{2+} ions (ν_1), as well as by the deformation vibration of UO_2^{2+} ions (ν_2) in their ground state[8] and the libration vibration of water molecules ($\nu_{lib.}$), too.[13] All experimental parameters of these spectra are represented in the Table I.

Thus, there are three excitation wavelength regions characterized by three different types of luminescence spectra. The broadened luminescence spectrum with one vibrational series is observed under excitation in the ultraviolet region (first region). As a limiting value of excitation wavelength in the visible region is approached, we can detect the additional structure of emission spectra (second region) following the elementary luminescence spectra (third region) which can only be observed.

TABLE I. The experimental parameters of elementary luminescence spectra.

N (i)	$\nu_{00}^{(i)}$ (cm^{-1})	$\nu_1^{(i)}$ (cm^{-1})	$\nu_2^{(i)}$ (cm^{-1})	$\nu_{lib.}^{(i)}$ (cm^{-1})	$\nu_2^{(i)}+\nu_{lib.}^{(i)}$ (cm^{-1})
		SiO_2-UO_2^{2+} ($T_{h.t.}=320$ and 900 K)			
0	20 430	836			
1	20 293	831			
2	20 255	830			
3	20 100	817			
4	20 024	804			
5	19 924	814		303	536
6	19 759	800	203	346	518
7	19 672	790	218	368	553
8	19 587	795	229	397	580
9	19 489	802	207	401	581
10	19 425	800	216	406	618
11	19 316	790	247	420	
12	19 150	780		420	
13	19 019	764	212	425	
		SiO_2-UO_2^{2+} ($T_{h.t.}=1200$ K)			
0	20 328	860			
1	19 778	810	209	349	584
2	19 712	805	219	370	592
3	19 634	791	217	355	
4	19 569	800	223	368	
5	19 497	796	225	379	
6	19 448	788	217	393	
7	19 365	788		379	
8	19 303	785		407	
9	19 216	756		383	
10	19 048	763		405	
11	18 945	760		450	

To account for such facts as these, the excitation luminescence spectra for the lowermost excited state region were investigated, too (Fig. 4). According to Ref. 8, the 0-0-transitions for several excited electronic states

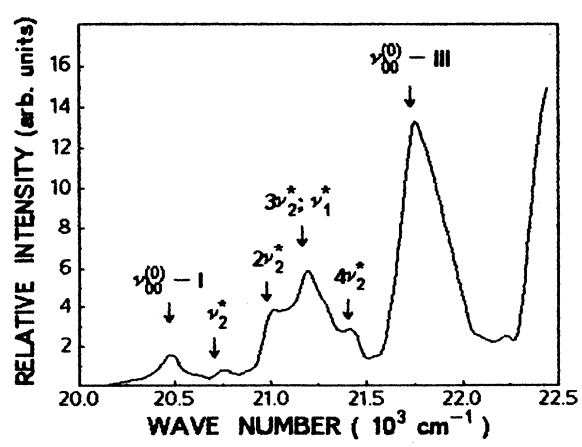

FIG. 4. The luminescence excitation spectra of the aqueous solution of uranyl salt. The arrows indicate the positions of 0-0-electronic transitions ($\nu_{00}^{(0)}$) and local vibrations (ν_L^*).

and respective vibrational series of ν_1 and ν_2 vibrations are observed in the excitation spectra. Maximum positions and their interpretation are shown in Fig. 4.

We have also investigated luminescence kinetic characteristics of the adsorption system SiO_2-UO_2^{2+}. It should be noted that the time constant of luminescence decay accounts for $\sim 10^{-4}$ s and does not vary in magnitude for different elementary luminescence spectra.

Thus, the adsorption system SiO_2-UO_2^{2+} shows intensive luminescence, which is characterized by narrow emission bands at liquid-helium temperature and the invariant value of the time constant of luminescence decay. Hence, these molecular ions satisfy the first three requirements as discussed in the Introduction. The fourth requirement will be considered below.

B. The model of adsorption complexes

The comparable analysis of the emission spectra by ultraviolet and visible laser excitations allows one to affirm that various AC's cause many elementary luminescence spectra that are detected by means of selective laser excitation. Evidently, variation of the concentration of various AC's causes a change of contributions of concrete AC to the total intensity of luminescence spectra and the shift of emission spectra under excitation in regions I and II towards the long-wavelength side.

The analysis of the spectral characteristics under selective laser excitation (region III) is sufficient to allow a conclusion that there is a correlation between the emission maxima shift and perturbation degree of uranyl ions in each concrete AC. It has been well known that H_2O molecules coordinate uranium in the water-uranyl complex in an aqueous solution of uranyl salts. The uranyl ion is surrounded by six water molecules, which are arranged at the equatorial plane.[8] Therefore, from our point of view, the perturbation of uranyl ions in the prepared at $T_{\text{h.t.}}=320-900$ K samples is the result of interaction between water molecules surrounding UO_2^{2+} ion and active centers of silicon dioxide surface. For samples prepared at $T_{\text{h.t.}}=1000-1200$ K, we shall consider the interaction of free uranyl ions with SiO_2 surface. These conclusions are confirmed by IR-spectroscopy measurements, too. Hence, the luminescence spectra of AC's vary from complex to complex both in wavelengths and in intensities. Since the total intensity of the luminescence spectra is due to the contribution of many elementary luminescence spectra corresponding to various AC's and, at the same time, the concentration of various active centers depends on the surface dehydration and dehydroxylation degree, there is a dependence of luminescence properties under ultraviolet excitation on pretreatment temperature. The position of the 0-0-transition for various AC's is marked in Figs. 2 and 3.

There are two AC types that correspond, in our opinion, to physical ($T_{\text{h.t.}}=320-900$ K) and chemical ($T_{\text{h.t.}}=700-1200$ K) adsorption states, because as the temperature increases prior to $T_{\text{h.t.}}=900$ K, the contribution of weakly perturbed AC's (with minimum shifts of 0-0 transition corresponding to the position of 0-0-transition for aqueous solution of uranyl salt) to the total intensity of the luminescence spectra is diminished (Fig. 1). It is safe to assume that the first type of complexes are fixed on surface hydroxyls and adsorbed water molecules by hydrogen bonds. The chemisorbed complexes are formed under interaction of water molecules creating water-uranyl complexes with surface silicon, bridging oxygen atoms, and surface structural defects. In the following, we will discuss the types of AC, the energy of the adsorption bonds of water-uranyl complexes with the silicon dioxide surface and mechanisms of energy transfer.

As stated above, extreme broadening of the luminescence spectra by adsorption of the uranyl salt aqueous solution on the silicon dioxide surface can be observed. It is the co-called nonuniform broadening of the emission spectra that is due to the change of the water-uranyl complexes perturbation degree by AC formation at $T_{\text{h.t.}}=320-900$ K. It is necessary to stress that the comparable analysis of the emission spectra by ultraviolet and visible laser excitations (regions I and II) allows one to affirm that there is a resonant energy transfer among AC's in their excited states (Fig. 1).

C. Spectra fittings

The total integral intensity of emission spectra under ultraviolet and visible excitations may be represented by

$$S=\sum_i \int_\nu I_i(\nu)d\nu \ , \tag{1}$$

where $I_i(\nu)$ is the intensity of the ith elementary luminescence spectrum corresponding to the aqueous solution. In the fittings below, we will assume that the electronic transition interacts with one (ν_1) or two (ν_1 and $\nu_{\text{lib.}}$) vibrations only. The intensity of electron-vibrational luminescence spectrum may be written as[14]

$$I_i(\nu)=C_i \sum_{n=0}^{4} \exp\left[-\left[\frac{\nu-(\nu_{00}^{(i)}-n\nu_1^{(i)})}{\gamma^{(i)}}\right]^2\right] \times \exp(-P_\lambda^{(i)})\frac{(P_\lambda^{(i)})^n}{n!} \ , \tag{2}$$

where each vibrational maximum of the ith luminescence spectrum is described by a Gaussian function and where n, $\nu_{00}^{(i)}$, $\nu_1^{(i)}$, $\gamma^{(i)}$, and $P_\lambda^{(i)}$ are the vibrational quantum number, electronic transition frequency, vibrational frequency in ground state, half width of the vibrational maxima, and electron-vibrational interaction parameter, respectively. In the case where two vibrations are used, we obtain analogously

$$I_i(\nu)=C_i \sum_{n=0}^{4} \sum_{k=0}^{1} \exp\left[-\left[\frac{\nu-(\nu_{00}^{(i)}-n\nu_1^{(i)}-k\nu_{\text{lib.}}^{(i)})}{\gamma^{(i)}}\right]^2\right] \times \exp(-P_\lambda^{(i)}-P_{\lambda(\text{lib.})}^{(i)})\frac{(P_\lambda^{(i)})^n(P_{\lambda(\text{lib.})}^{(i)})^k}{(n!k!)} . \tag{3}$$

In these fittings the following functions for minimization have been used:

$$\psi=\int_\nu I_{\text{exp.}}(\nu)d\nu-S \ , \tag{4}$$

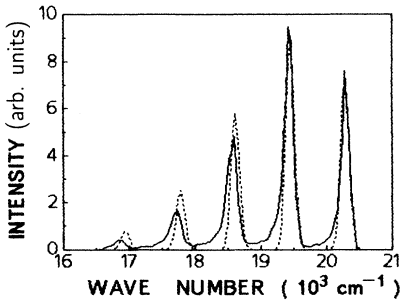

FIG. 5. The experimental (——) and calculated (— — —) spectra of the aqueous solution of uranyl salt $\lambda_{exc.}=337.1$ nm; $T_{reg.}=4.2$ K.

where $I_{exp.}(\nu)$ is the intensity of the experimental nonuniform broadened spectrum. The result of the approximate fittings for the spectra of the aqueous solution and samples prepared at $T_{h.t.}=320$ and 900 K are shown in Figs. 5–7. Calculated parameters of luminescence bands are given in Table II. One can easily see that there is a very good approach. Thus, the half width of the luminescence maxima can be explained by a nonuniform broadening of emission spectra. As this takes place, the relative error for these fittings is no greater than 1%.

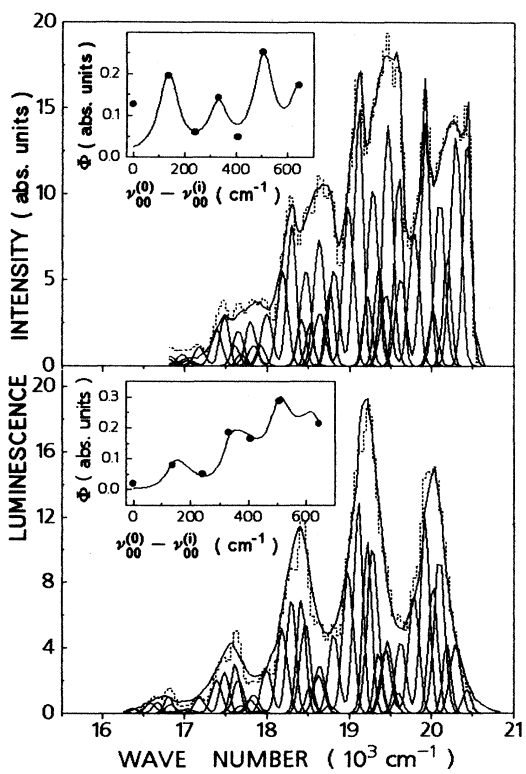

FIG. 6. The experimental (——) and calculated (— — —) spectra of the SiO_2-UO_2^{2+} samples prepared at $T_{h.t.}=320$ K; $\lambda_{exc.}=472.7$ nm (the upper part); $\lambda_{exc.}=337.1$ nm (the lower part). The elementary luminescence spectra are shown. The intensity distribution functions of contributions for elementary spectra (Φ) versus the 0-0-electronic transition shift are shown in insets.

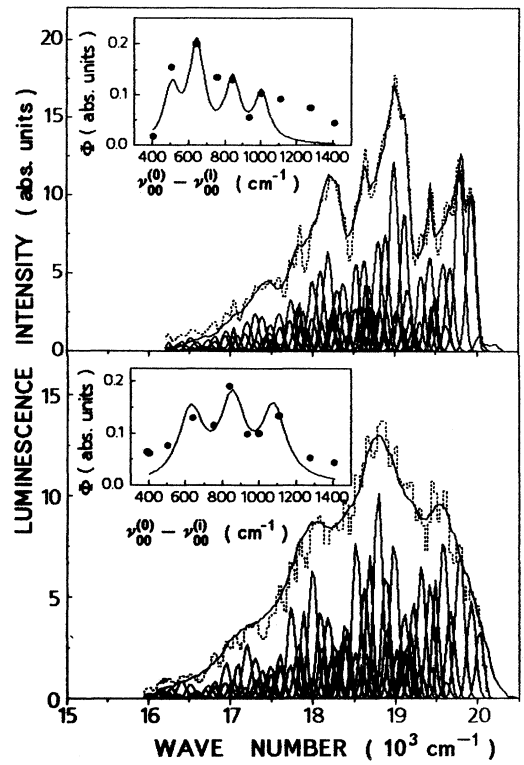

FIG. 7. The experimental (——) and calculated (— — —) spectra of the SiO_2-UO_2^{2+} sample prepared at $T_{h.t.}=900$ K; $\lambda_{exc.}=488.0$ nm (the upper part); $\lambda_{exc.}=337.1$ nm (the lower part). The intensity distribution functions of contributions for elementary spectra (Φ) versus the 0-0-electronic transition shift are shown in the insets.

D. Intensity distribution functions calculation

The calculations of distribution functions of contributions for elementary spectra Φ (insets in Figs. 6 and 7) follows the fastest gradient method, using function (4). The distribution function Φ may be represented as

$$\Phi=(\phi_1 \cdots \phi_m)\ , \quad \phi_i=\frac{\int_\nu I_i(\nu)d\nu}{S}\ , \tag{5}$$

where ϕ_i defines the contribution of the ith luminescence spectrum to the total integral intensity of the nonuniform broadened emission spectra. As this takes place, intensity distribution functions for luminescence spectra, which were excited in an ultraviolet region (first excitation region), were calculated by fixed parameters taken from the calculation of spectra excited in the visible region (second excitation region).

It should be noted that the distribution function is not simple. There are several resonance points for dependence of elementary spectra contributions to the total luminescence spectrum. From our point of view, these resonances are the result of the resonant energy transfer among AC's in their excited states. The mechanism of this process will be discussed below.

TABLE II. The typical calculated parameters of elementary luminescence spectra for samples prepared at $T_{h.t.}=320$ and 900 K.

N (i)	$\nu_{00}^{(i)}$ (cm^{-1})	$\nu_1^{(i)}$ (cm^{-1})	$\nu_{lib.}^{(i)}$ (cm^{-1})	$\gamma_1^{(i)}$ (cm^{-1})	$\gamma_{lib.}^{(i)}$ (cm^{-1})	$P_\lambda^{(i)}$	$P_{\lambda(lib.)}^{(i)}$
			SiO_2-UO_2^{2+} ($T_{h.t.}=320$ K)				
0	20 430	835		72.6		0.81	
1	20 293	831		90.0		1.04	
2	20 189	836		68.0		0.86	
3	20 100	817		90.0		1.08	
4	20 024	804		76.1		1.31	
5	19 924	814	301	77.2	90.0	1.07	1.02
6	19 786	800	346	90.0	90.0	1.18	0.63
			SiO_2-UO_2^{2+} ($T_{h.t.}=900$ K)				
4	20 024	804		64.0		1.40	
5	19 924	814	301	71.6	66.3	0.88	1.8
6	19 786	800	346	75.0	36.5	1.04	1.41
7	19 672	790	368	71.7	58.4	1.39	1.03
8	19 587	795	397	75.0	58.9	1.26	0.92
9	19 489	802	387	54.1	47.7	1.21	0.82
10	19 425	800	406	73.6	60.4	0.96	0.85
11	19 316	790	423	69.7	54.7	1.16	0.62
12	19 150	780	420	75.0	49.3	1.10	0.37
13	19 019	764	425	70.5	45.8	1.20	0.26

E. Resonant energy transfer for AC systems

An adiabatic potential for ground and excited states of uranyl ions will be considered for convenience as potential curves for two-atomic molecules. The water-uranyl complex-surface interaction leads to the attenuation of the bond between the uranyl ion and water molecules. This conclusion, according to Ref. 8, demonstrates a decrease of a frequency of the symmetrical vibrations of UO_2^{2+} ions (ν_1) with an increase of the perturbation degree (Table I). In turn, this causes the strengthening of the uranium-oxygen bonds. Hence, the bond becomes stronger and the system energy is reduced (Fig. 8). On the other hand, the reduction of the uranyl ion potential energy may be considered as a result of the interaction between the induced dipole of the UO_2^{2+} ion and the electric field of the water molecule induced dipole. In this case, the SiO_2 surface can be considered as, varying with position of atoms, the surface electrostatic field of the amorphous SiO_2. These dipole moments are equal in magnitude, but opposite in sign. Therefore, the interaction rate between the uranyl ion and water molecule decreases with increasing interaction of water molecules with the SiO_2 surface. The induced dipole moment of the UO_2^{2+} ion is determined by its value of the perturbation energy. Evidently the perturbation energy in excited states of uranyl ions will be larger than in the ground state:

$$\mu_1^* \mathcal{E} < \mu_2^* \mathcal{E} , \tag{6}$$

where μ_1^* and μ_2^* are the induced dipole moment of the UO_2^{2+} ion in the ground and excited states, respectively, and $\mathcal{E}$ is the electric-field strength of the water molecule induced dipole. Condition (6) explains the shift of elementary luminescence spectra towards the long-wavelength side with an increase in adsorption efficiency of the disperse SiO_2 surface. Thus, it is reasonably safe to suggest that the resonant energy transfer is a result of the coincidence of the perturbation energy value and symmetrical and deformation vibration energy in excited states.

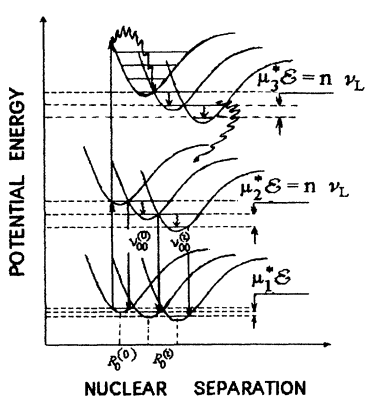

FIG. 8. A schematic energy-level diagram illustrating resonant energy transfer.

As indicated earlier, there are three excitation wavelength regions. The third excitation region, that the elementary luminescence spectra were excited, corresponds to the lowermost excited state and respective series of ν_1 and ν_2 vibrations (Fig. 4). Hence, the resonant energy transfer is observed when the perturbation energy and these lowermost excited states coincide. In a similar manner, the resonance energy transfers in higher states are realized.

These effects cause a manifestation of the additional structure of emission spectra (second excitation region). In such a case, it would be a good idea to take a second

look at the resonance characteristics. In the beginning, we consider the dependence between the elementary spectra shifts and respective perturbation energies. The Hamiltonian operator of the system may be written

$$\hat{H}=\hat{H}^0-\mu^*\mathcal{E} , \tag{7}$$

where μ^* is the induced dipole moment of the UO_2^{2+} ion. In the case $\mathcal{E}=0$ (nondisturbed system), we have the following simple solution for the energy of the electronic transition,

$$\nu_{00}^{(0)}=E_{20}^{(0)}-E_{10}^{(0)} , \tag{8}$$

where $\nu_{00}^{(0)}$ is the wave number of the 0-0-electronic transition (in cm^{-1}).

The first-order perturbation energy is the mean value of the perturbation operator in the ground and excited states, i.e.,

$$E_{10}=E_{10}^{(0)}-\mu_1^*\mathcal{E} , \quad E_{20}-E_{20}^{(0)}-\mu_2^*\mathcal{E} . \tag{9}$$

Hence, we can write

$$\nu_{00}^{(i)}=\nu_{00}^{(0)}-\Delta\mu^*\mathcal{E} , \quad \Delta\mu^*=\mu_2^*-\mu_1^* . \tag{10}$$

Thus, the value of the elementary luminescence spectrum shift is determined by the difference of the perturbation energy in the excited ($\mu_2^*\mathcal{E}$) and ground ($\mu_1^*\mathcal{E}$) states. Hence, the shifts of $\Delta\mu^*\mathcal{E}$ will be manifested in the luminescence response, whereas resonant energy transfer in the lowermost excited state is carried out by $\mu_2^*\mathcal{E}$ (Fig. 8). In this case, the resonance condition may be written as

$$\mu_2^*\mathcal{E}=\mu_1^*\mathcal{E}+\Delta\mu^*\mathcal{E}=n\nu_L^* , \tag{11}$$

where ν_L^* is the wave number of different local vibrations in the lowermost excited state. Therefore, in the luminescence spectra (second excitation region), the resonant energy transfer for AC's, characterized by the magnitude of shift equal to $n\nu_L^*-\mu_1^*\mathcal{E}$ will be manifested. For higher excited states (first excitation region), the resonance condition may be written in the following manner:

$$\mu_3^*\mathcal{E}=n\nu_L^* , \tag{12}$$

where now ν_L^* are different local vibrations in respective excited states. One can observe the resonance energy transfer up to 5 and 2 vibrational quantum for ν_1 and ν_2, respectively:

$$\mu_2^*\mathcal{E}=n_1\nu_1^* \ (n_1=1,2) , \quad \mu_2^*\mathcal{E}=n_2\nu_2^* \ (n_2=1,\ldots,5) , \tag{13}$$

where values of ν_1^* and ν_2^* are taken from excitation spectra. The resonant energy transfer parameters are given in Table III.

It has been well known that any resonance can be described by means of three parameters: a position, half width, and intensity. Therefore, we can use the following resonance functions by analogy with resonance functions for a mechanical vibration:

$$\Phi^{(1)}{}_{\text{non-rad.}}=A_n\left[\sum_{n=1}^{2}\frac{\left[\frac{\Gamma}{2}\right]^2}{(n\nu_1^*-\mu_3^*\mathcal{E})^2+\left[\frac{\Gamma}{2}\right]^2}+\sum_{n=1}^{5}\frac{\left[\frac{\Gamma}{2}\right]^2}{(n\nu_2^*-\mu_3^*\mathcal{E})^2+\left[\frac{\Gamma}{2}\right]^2}\right] , \tag{14}$$

$$\Phi^{(2)}_{\text{non-rad.}}=A_n\left[\sum_{n=1}^{2}\frac{\left[\frac{\Gamma}{2}\right]^2}{(n\nu_1^*-\Delta\mu^*\mathcal{E}-\mu_1^*\mathcal{E})^2+\left[\frac{\Gamma}{2}\right]^2}+\sum_{n=1}^{5}\frac{\left[\frac{\Gamma}{2}\right]^2}{(n\nu_2^*-\Delta\mu^*\mathcal{E}-\mu_1^*\mathcal{E})^2+\left[\frac{\Gamma}{2}\right]^2}\right] , \tag{15}$$

where $\Phi^{(1)}_{\text{non-rad.}}$ and $\Phi^{(2)}_{\text{non-rad.}}$ are functions that describe the nonradiative energy transfer resonance in the higher and lowermost excited states, respectively; A_n and $\Gamma/2$ are the resonance intensity and half width. Hence, the function $\Phi^{(2)}_{\text{non-rad.}}$ may be used for calculations of luminescence spectra excited in the visible region (second excitation region). For spectra excited in the ultraviolet region (first excitation region) the distribution function may be represented by using resonance function multiplication:

$$\Phi=N_i\times\Phi^{(1)}_{\text{non-rad.}}\times\Phi^{(2)}_{\text{non-rad.}} , \tag{16}$$

where N_i is the distribution of concentrations of various AC's, which is invariant for samples prepared at each concrete temperature. The parameter Γ in these resonance functions is the total width of resonance maximum. According to the indeterminacy relationship between energy and time, one can define the time of nonradiative energy relaxation among various complex excited states:

$$\tau=\frac{h}{\Gamma} . \tag{17}$$

The results of the calculations are given in the insets of Figs. 6 and 7 and in Table III.

We can conclude that the time of nonradiative energy relaxation in adsorption complex systems is consistent with the time of vibrational relaxation in each concrete adsorption complex and is much less that the luminescence decay time constant. Thus, emission efficiency in such adsorption systems is caused by the time constant of luminescence decay in the lowermost excited state and is independent of peculiarities of energy relaxation processes from higher excited states. Hence, molecular ions

TABLE III. Resonant energy-transfer parameters, their interpretation, and the time of nonradiative energy relaxation in the adsorption complexes system (τ).

$N(i)$		0	1	3	5	6	8	10
$\nu_{00}^{(i)}$ (cm^{-1})		20 430	20 293	20 100	19 924	19 786	19 587	19 425
$\Delta\mu\mathscr{E}$ (cm^{-1})		0	137	330	506	644	843	1005
ν_L^* (cm^{-1})	Lower-		230	460	710	920	1150	1420
Γ (cm^{-1})	most		92	92	95	95	100	100
τ (10^{-13} s)	excited state		3.63	3.63	3.52	3.52	3.34	3.34
ν_L^* (cm^{-1})	Higher		196	392	617	842	1067	1292
Γ (cm^{-1})	excited		128	128	140	150	160	160
τ (10^{-13} s)	state		2.61	2.61	2.39	2.22	2.08	2.08
Interpretation			ν_2^*	$2\nu_2^*$ or	ν_1^* or $3\nu_2^*$	$4\nu_2^*$	$5\nu_2^*$	$2\nu_1^*$

UO_2^{2+} satisfy the fourth requirement as discussed in the Introduction.

F. Bond energies assessment

The position of the uranyl ion 0-0-electronic transition for various AC's, which are indicated in Figs. 2 and 3, allows one to assess also the magnitude of the water-uranyl-complex adsorption bond energies. The potential between an atom and a solid can be written as[15–18]

$$V(r)=V_A(r)+V_R(r) , \tag{18}$$

where $V_R(r)$ is the repulsive part and $V_A(r)$ is the attractive one. The repulsive part takes account of a Lennard-Jones potential,[19]

$$\Phi^{LJ}(r)=\varepsilon\left[\left[\frac{r_0}{r}\right]^{12}-2\left[\frac{r_0}{r}\right]^{6}\right] , \tag{19}$$

where ε is the well depth with adsorption distance r_0. The term proportional to r^{-6} correctly describes the van der Waals interaction between H_2O molecules and surface active centers.

The attraction between the surface active center and water-uranyl complex may be represented by the sum of the Coulombic electrostatic interaction between a surface active center and the water molecule dipole moment and induction interaction between a surface center and the induced dipole moment of the water molecule. The induction interaction arises from the interaction between the induced dipole, due to polarization of the water molecule and the electrostatic field of the SiO_2 surface. The induction interaction caused by the polarization of surface centers in the field of water-uranyl complexes is negligibly small and is not considered. Thus, one may write the attractive part of $V(r)$ as

$$V_A(r)=V_C(r)+V_I(r) . \tag{20}$$

Subscripts C and I stand for Coulombic and induction interactions, respectively. This model has been successful in predicting the adsorption potential for the M-H_2O complexes (where M is either a cation or an anion).[20–23] In these papers, it has been shown that the M-H_2O complex has the same number of electron pairs as the dissociation products M and H_2O and the amount of charge transfer between the M and H_2O is quite small. Therefore, one can say with reasonable confidence that the basis for the water molecule-surface ion bond is the Coulombic electrostatic and induction interactions. Generally, using atom-atom potentials, the adsorption potential may be written in the following form:

$$V_{ijk}=\Phi_{ijk}^{LJ}-\left[\frac{q_{ij}^{\pm}q_k^{\pm}}{r_{ijk}}+\frac{\alpha_{ij}(q_k^{\pm})^2}{2r_{ijk}^4}\right] . \tag{21}$$

The first term is the Lennard-Jones potential for interactions of atom j of the ith water molecule with atom k in the adsorbent, the second term accounts for Coulombic interactions between the jth atom of the ith water molecule and a surface atom k, and the last term is for the energy of the induction interaction. In that event $q_{ij}^{\pm}$, α_{ij} are the charge and polarizability of atom j of the ith water molecule, $q_k^{\pm}$ the charge of the surface kth ion, r_{ijk} the distance between atom j of the ith water molecule and the kth ion.

On the other hand, the potential energy, due to a permanent dipole moment of the water molecule (μ) in the electric field of the surface ion (E), is simply

$$V_C=-\mu E . \tag{22}$$

The induction interaction may be represented as

$$V_I=-\tfrac{1}{2}\alpha E^2 , \tag{23}$$

where E is the magnitude of the electric field at the point moving from the surface atom on a distance, which is equal to the adsorption bond distance (r_0); α is the polarizability of water molecules. In this case, the Lennard-Jones potential is equal to ε and the adsorption potential value (V) is consistent with the adsorption bond energy (D). Then the adsorption bond energy may be represented in the following form:

$$D=-\sum_i(\varepsilon_i+\mu E_i+\tfrac{1}{2}\alpha E_i^2) , \tag{24}$$

where the summation is over all the water molecules of

the water-uranyl complex.

According to Ref. 8, one can consider the interaction between uranyl ions and ligands (water molecules) as dipole-dipole interaction. Hence, the position of adiabatic potentials of the uranyl ion ground and excited states may be changed by varying the water molecule dipole moment only [the last term in formula (21)]. Moreover, the work done at the water molecule polarization in the electric field of the surface charge is equal to the work done on the uranyl ion in the electric field of the induced dipole. Hence, we can write

$$(\boldsymbol{\mu}_1^* \times \mathcal{E}) = \sum_i \tfrac{1}{2}\alpha \mathbf{E}_i^2 \ . \tag{25}$$

Then Eq. (24) may be rewritten as

$$D = -\mu \left[\frac{2\mu_1^* \left| \sum_i \mathcal{E}_i \right|}{\alpha} \right]^{1/2} - \mu_1^* \left| \sum_i \mathcal{E}_i \right| \ . \tag{26}$$

where the contribution of the ε into adsorption bond energy is much less by comparison with Coulombic electrostatic and induction interactions and can be neglected. $\mathcal{E} = \sum_i \mathcal{E}_i$ is the vector sum of the electric-field strengths of the water molecule induced dipoles.

It can easily be shown that the adsorption bond energies in the calculation on one water molecule are as follows:

$$D_1 = -\mu \left[\frac{2\mu_1^* \mathcal{E}}{\alpha} \right]^{1/2} - \mu_1^* \mathcal{E} \ ,$$

$$D_2 = -\mu \left[\frac{2}{\sqrt{3}} \frac{\mu_1^* \mathcal{E}}{\alpha} \right]^{1/2} - \frac{1}{\sqrt{3}} \mu_1^* \mathcal{E} \ , \tag{27}$$

$$D_3 = -\mu \left[\frac{\mu_1^* \mathcal{E}}{\alpha} \right]^{1/2} - \tfrac{1}{2} \mu_1^* \mathcal{E} \ ,$$

for one and the two or three nearest water molecules of a water-uranyl complex, respectively. In these formulas, we assume that the uranyl ion arranged in a symmetric environment of the water molecules with the angles between nearest molecules are equal to $\pi/3$ and the adsorption bond energies for different H_2O molecules are equal in magnitude.

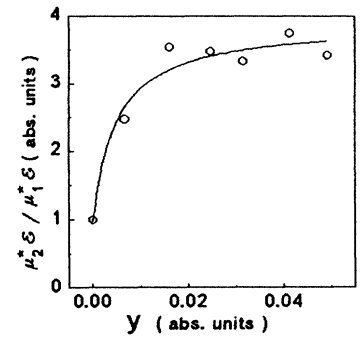

FIG. 9. The correlation $\mu_2^* \mathcal{E} / \mu_1^* \mathcal{E}$ versus relative shift of luminescence spectra (y).

Thus, the problem reduces to obtaining the correlation between perturbation energies in excited and ground states. Then from Eqs. (9) and (27) may be obtained the water-uranyl bond energy expressed in terms of spectral parameters.

On the other hand, resonant energy transfer, as stated above, is the result of the coincidence between the perturbation energy value and vibrational energy of UO_2^{2+}, ν_1, and ν_2 modes in the lowermost excited state. At the resonance position, the perturbation energy $\mu_2^* \mathcal{E}$ is equal to the vibrational energy. Therefore, one can obtain the correlation between perturbation energies in the ground and lowermost excited states. For convenience, one can study the correlation $\mu_2^* \mathcal{E} / \mu_1^* \mathcal{E}$ depending on the relative shift of the luminescence spectra,

$$y = \frac{\nu_{00}^{(0)} - \nu_{00}^{(i)}}{\nu_{00}^{(0)}} \ . \tag{28}$$

This dependence may be described by the following hy-

TABLE IV. The position of 0-0-electronic transitions of the elementary luminescence spectra ($\nu_{00}^{(i)}$), the difference of perturbation energies ($\Delta\mu^* \mathcal{E}$), the water-uranyl-complex adsorption bond energy ($-D_1$, $-D_2$, $-D_3$), and the electric-field strength of surface active centers (E).

N (i)	$\nu_{00}^{(i)}$ (cm^{-1})	$\Delta\mu^* \mathcal{E}$ (meV)	$-D_1$ (meV)	$-D_2$ (meV)	$-D_3$ (meV)	E (10^{10} V/m)
1	20 293	16.98	590.2	446.3	414.9	1.5
2	20 255	21.69	647.9	490.1	455.7	1.63
3	20 100	40.91	828.1	626.2	582.2	2.07
4	20 024	50.33	902.9	681.9	633.8	2.26
5	19 924	62.73	993.4	750.2	697.2	2.48
6	19 759	83.19	1125.8	849.2	788.9	2.8
7	19 672	93.98	1191.6	898.6	834.9	2.96
8	19 587	104.52	1251.5	943.9	877.1	3.1
9	19 489	116.67	1321.0	995.5	924.7	3.27
10	19 425	124.6	1362.0	1025.5	952.4	3.37
11	19 316	138.12	1431.1	1077.8	1001.0	3.54
12	19 150	158.7	1532.1	1153.2	1070.9	3.78
13	19 019	174.94	1604.0	1206.8	1120.7	3.95

perbolic expression (Fig. 9):

$$\frac{\mu_2^* \mathcal{E}}{\mu_1^* \mathcal{E}} \approx 3.9 - \frac{1.4\times 10^{-2}}{4.9\times 10^{-3}+y} , \tag{29}$$

where the point $y=0$ corresponds to the condition $\mu_1^* \mathcal{E} = \mu_2^* \mathcal{E}$ for a nonperturbed system. Thus, the correlation $\mu_2^* \mathcal{E}/\mu_1^* \mathcal{E}$ is characterized a saturation and approaches asymptotically the value ~ 3.9 with the increase of the uranyl ions perturbation degree. Finally, we can write

$$\mu_1^* \mathcal{E} \approx \frac{y \nu_{00}^{(0)}}{2.9 - \dfrac{1.4\times 10^{-2}}{(4.9\times 10^{-3}+y)}} . \tag{30}$$

Now the perturbation energy in the ground state is expressed in terms of spectral parameters and from Eq. (27) we can find the bond energy for each AC.

The results of assessments are given in Table IV, where we use the position of the 0-0-transition for a nonperturbed system, which corresponds to the aqueous solution ($\nu_{00}^{(0)} = 20\,430\ \mathrm{cm}^{-1}$).

DISCUSSION

The analysis of assessments allows one to affirm that the complexes with numbers 1–4 for samples prepared at 320 and 900 K may be fitted into physical adsorption states. These AC's are fixed on surface hydroxyls by hydrogen bonds. According to quantum-chemical calculations carried out earlier,[24,25] we can make a conclusion that the UO_2^{2+} ions are fixed on the surface by means of two or three water molecules forming water-uranyl complexes. Really, the value of the H bonds for one water molecule adsorbed on sylanol group (Si(OH)) is ~ 270 meV, but for two and three water molecules the values are ~ 640 and ~ 980 meV, respectively. These facts by comparison with our assessments (Table IV) and heat pretreatment behavior of the luminescence spectra allow one to satisfy the above-mentioned conclusion. The complexes with numbers 5–13 for samples prepared at 900 K and all complexes for samples prepared at 1200 K should be fitted into chemical adsorption states. Moreover, the chemisorbed complexes for samples prepared at $T_{\mathrm{h.t.}} = 320-900$ K are formed under the interaction of water molecules with surface silicon (sylanol group) and bridging oxygen atoms. According to Ref. 24, the value of the adsorption bond energy for one, two, and three water molecules located in the *cis* position with respect to surface silicon are ~ 400, ~ 700, and ~ 1050 meV, respectively. If it is remembered that these molecules form single hydrogen bonds, then we obtain for one and the two or three nearest water molecules of water-uranyl complex ~ 670, ~ 1340, and ~ 2030 meV. In our case (see, for example, spectrum number 5 in Table IV), we obtained ~ 990, ~ 1500, and ~ 2090 meV. The closest approach is for two and three water molecules. Hence, we can make a conclusion that in this case also the adsorption by means of two and three H_2O molecules predominantly must be considered. It should be noted also that an electric-field strength of the surface active centers (Table IV) corresponds to the quantum-chemical calculations, too. For example, according to Ref. 25, a charge on the surface silicon atom is $\sim 2.39\times 10^{-19}$ C and an equilibrium distance for adsorption of one water molecule in the *cis* position is 0.20 nm. Then, in the point charge approximation, we obtain the following value of the electric-field strength: $E \cong 5.37\times 10^{10}$ V/m. From our assessments (spectrum number 5 in Table IV) have been obtained the following values $\sim 2.48\times 10^{10}$, $\sim 4.29\times 10^{10}$, and $\sim 4.96\times 10^{10}$ V/m for one, two, and three H_2O molecules, respectively. Thus, we obtained again the result indicative of predominated adsorption of water-uranyl complexes by means of two and three water molecules.

On the other hand, the chemisorbed complexes for samples prepared at $T_{\mathrm{h.t.}} = 1000-1200$ K, from our point of view, are formed under interaction of free uranyl ions with surface silicon and bridging oxygen atoms and surface structural defects. Note, that in the case of free uranyl ions another model must be used for assessment of the AC bond energies. This is a particular problem and in this paper is not considered. We should finally mention that the total number of various AC's is determined by various peculiarities of their formation on the silicon dioxide surface.

CONCLUSIONS

This paper combines various spectroscopic techniques, such as luminescent spectroscopy under integral and selective laser excitation and IR vibration analysis, to provide experimental data on the adsorption efficiency of the disperse SiO_2 surface. It has been shown that uranyl ions are very convenient luminescent probes for investigations of adsorption properties different disperse oxygen materials. Our assessments of the water-uranyl adsorption bond energies show that the UO_2^{2+} ions are fixed on the surface by means of two or three water molecules forming water-uranyl complexes. The phenomenon of resonant energy transfer among various AC's in their excited states has been found experimentally. It has also been shown that the time of nonradiative energy relaxation among these AC's is consistent with the time of vibrational relaxation in each concrete AC. Values of the bond energies lend support to the validity of the water-uranyl model of AC and the electrostatic consideration used.

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