Structure and charge transfer dynamics of uranyl ions in boron oxide and borosilicate glasses

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Laser spectroscopic experiments, molecular dynamics simulation, and charge transfer-lattice interaction modeling have been conducted for studing the electronic and structural properties of uranyl ion UO_2^{2+} in boron oxide and borosilicate glasses. The charge transfer electronic and vibrational energy levels for uranyl ions in the glass matrices were obtained from laser excitation and fluorescence spectra of UO_2^{2+}. A model structure for uranyl ions in the glass matrices was established using the method of molecular dynamics (MD) simulation in comparison with the results of extended X-ray absorption fine structure (EXAFS) for U^{6+} ions in the glasses we studied. The formation and stabilization of uranyl clusters in glass matrices are interpreted by charge transfer-lattice interactions on the basis of self-consistent charge transfer accompanied by lattice distortion. The latter is in the framework of the simultaneous action of pseudo-Jahn-Teller and pseudo-Jahn-Teller analog effects on charge transfers between oxyged–uranium ions.

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From uranium to americium, the lighter elements in the actinide series often bind with two oxygen anions to form actinyl ions. The uranyl ion, UO_2^{2+}, is extraordinarily stable in solutions as well as in crystals and glasses. Under blue or shorter wavelength light illumination, it emits visible fluorescence in the region of 500 to 700 nm. The fluorescence and spectral properties of uranyl in canary glass have been studied since the 19th century. After extensive and systematic investigation of actinyl properties that began in the middle of the last century, many current studies of the spectroscopic properties of actinyl species seek primarily to interpret their electronic structure and bonding, and eventually to provide fundamental understanding of the chemical and mechanical properties of nuclear waste-related phases.

After Jørgensen's initial work in 1957 [1] and subsequent studies by others [2–4], it is now well-understood that optical absorption and emission in the uranyl ion are due to oxygen-to-uranium charge transfer excitations. Significant contribution to the uranium-related impurity center studies was made by Feofilov and co-authors [5,6]. The optical transitions are due to electronic excitation primarily from the $2p$ state of the ligands to the $5f$ state of the uranium ion. The intense vibronic features and absence of zero-phonon lines in the optical transitions indicate that the charge transfer transition is strongly coupled to lattice vibrational modes. Therefore, the uranyl optical transitions indirectly probe the properties of local structure. Depending on the host materials, the lowest excited charge transfer state of UO_2^{2+} is on the order from 19 000 to 21 000 cm^{-1}, and the vibrational energy of the O–U–O symmetric stretch mode is typically 750 to 900 cm^{-1} for its ground state and much lower in its excited states. The lowering of vibrational energy in the excited uranyl states suggests strong structure distortion induced by charge transfer-lattice interaction [7,8]. Strong charge trasfer-lattice interaction also results in large different equilibrium positions of the uranyl potential that prevent observation of zero-phonon transitions and change the lifetime of the uranyl fluorescence.

It is also well known that vibronic states originating from the charge transfer-lattice interaction are quite localized. As a result, the absorption and emission spectra of the UO_2^{2+} ion in single crystals such as $Cs_2UO_4Cl_4$ indeed exhibit extremely sharp lines [9]. At low temperature, optical lines are as narrow as $\sim 1\,\mathrm{cm}^{-1}$, so that energy levels of various vibrational modes and even the isotopic shift resulting from substitution of oxygen-18 for exygen-16 is clearly observable [10]. However, due to structural disorder in amorphous environments, inhomogeneous line broadening is often significant and obscures the spectral structure of vibronic transitions. The inhomogeneous line broadening, which often can be partially eliminated using selective laser excitation [11], provides „fingerprint“ information about the uranyl local structure. Namely, one expects to observe sharp lines in the absorption and emission spectra of uranyl ions in crystalline phases [9], where the charge transfer transitions can be so broad that the characteristic vibronic features become obscured for uranyl ions in amorphous phases. It has been realized that lanthanide and actinide ions in oxide glasses, such as borosilicate glass, have an ordered local structure [11,12]. This means that an f-element ion has a definite coordination number and bond distance with its first shell ligands, although there is no long-range order in the glass matrix.

Although the electronic properties of uranyl itself and its bonding in crystalline phases were extensively studied [4], there is still lack of knowledge about its bonding property in glasses. In the present paper, we report the results of experimental investigation and theoretical modeling of uranyl coordination in boron oxide and borosilicate glasses. It is shown that the uranyl ions have a well-defined local structure that includes four additional oxygen ions in its equatorial plane to form a UO_6 tetrahedral cluster in the glass matrix. A model structure of uranyl in boron oxide and borosilicate glasses is established using a molecular dynamics (MD) simulation method. The symmetry and stability of the uranyl cluster are interpreted based on the microscopic mechanisms of charge transfer-lattice interaction.

1. Experimental results and discussion

Samples of boron oxide (B_2O_3) and borosilicate (12% B_2O_3, 63% SiO_2, 20% Na_2O, 5% Al_2O_3, by weight) glass containing 0.1 and 1% (weight) uranium were prepared for this work. After the host glasses were made, a nitric acid solution of natural isotopic abundance uranium as uranyl was added to the ground glass, and the mixture was melted in a furnace by heating up to 1000°C for the boron oxide glass and 1600°C for the borosilicate glass before quenching to room temperature. Laser excitation and fluorescence spectra and fluorescence decay were recorded for the samples with 0.1 and 1% (by weight) uranium at room temperature and liquid helium temperature.

As shown in Fig. 1 for 0.1% UO_2 in the boron oxide glass, the fluorescence spectrum consists of 5 sharp bands from 20 278 to 16 722 cm^{-1} that are due to vibronic transitions from the excited state to the ground state of uranyl charge transfer configuration. Fig. 1 also includes a section of the excitation spectrum that shows the lowest two groups of excited states, one centered at 21 030 cm^{-1}, and another at 21 570 cm^{-1}. No zero-phonon line was observed in the fluorescence spectrum. The spectrum is remarkably sharp and little inhomogeneous line broadening due to structure disorder was observed. No significant differences were registered between the spectra of the 0.1 and 1% uranyl samples. Uranyl ions in samples of different concentration have the same line width and positions. The results shown in Fig. 1 suggest that UO_2^{2+} in the B_2O_3 glass matrix has a well-defined local environment. This means that the uranyl ions have the same coordination number and local crystalline lattice, and disorder in the first shell of ligands is insignificant.

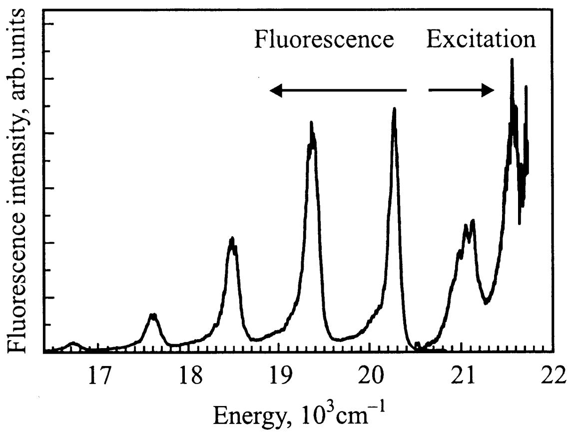

Figure 1. Ambient temperature excitation and fluorescence spectra of uranyl in B_2O_3 glass that contained 0.1% uranium.

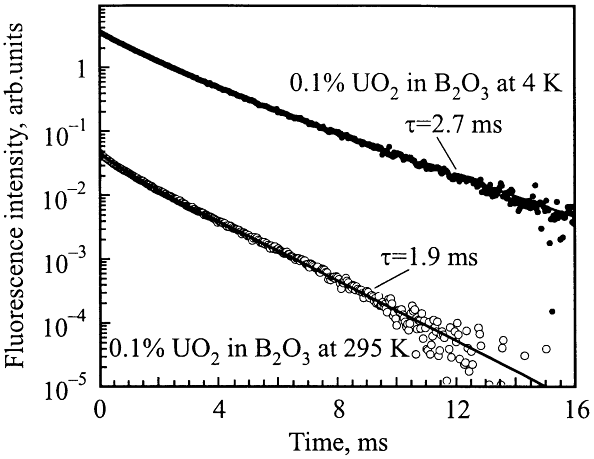

Figure 2. Fluorescence decay of uranyl in boron oxide glass.

The lifetime of the uranyl ion in the lowest excited state is longer than 1 ms, which is extremely long in comparison with the μs scale of fluorescence decay dynamics for many other uranyl compounds. As shown in Fig. 2, the fluorescence decay curves of uranyl in the B_2O_3 glass are nonexponential immediately following the laser pulse due to the energy transfer and approaches to a single exponential decay time of 2.7 ms at 4 K and 1.9 ms at room temperature. The single exponential decay suggests that most uranyl ions have similar local environments in the sample we studied. The uranyl fluorescence decay in the boron oxide glass decay curves is insensitive to temperature from ambient temperature to 4 K. The initial decay rate at room temperature is slightly larger than that at low temperatures. Without considering this faster decay at short times, the decay curves are not sensitive either to temperature or uranium concentration. This result indicates that the two most common relaxation mechanisms, namely, phonon relaxation and energy transfer between uranyle ions are not strong in the samples we studied. Without much contribution from these two relaxation mechanisms, the ms-scale lifetime of uranyl in the lowest excited state confirms that the charge transfer state is metastable, and the recombination process with electronic relaxation to the ground states is extremely slow. This will be discussed later with regard to the mechanisms of charge transfer-lattice interaction.

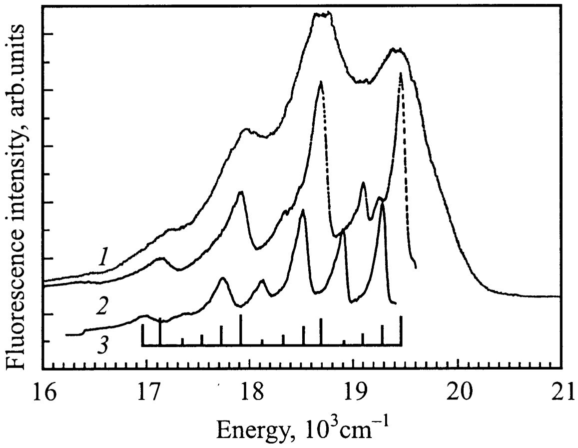

Figure 3. Fluorescence spectra of uranyl in borosilicate glass that contained 0.1% uranium with laser excitation at 28 169 (*1*), 19 806 (*2*), and 19 550 cm^{-1} (*3*). All spectra were recorded at 4 K.

As expected for uranyl ions in the borosilicate glass, the lines of the fluorescence spectrum are much broader than those in the boron oxide glass. Fig. 3 (curve *1*) shows the fluorescence spectrum recorded at 4 K and wiht laser excitation at 28 170 cm^{-1}. It is apparent that uranyl ions have a common local structure, in which they have different electronic energy levels and vibronic energies than in the B_2O_3 glass. It is also clearly shown in Fig. 3 (curves *2* and *3*) that selective excitation at lower laser energies resulted in fluorescence line narrowing and distinguished four different types of uranyl species that evidently are due to UO_2 at different local environments. These site-resolved spectra are shifted from each other by approximately 200 cm^{-1} and have similar vibronic peaks that the separated by 750 to 760 cm^{-1}. In comparison with the broad spectrum obtained with 28 170 cm^{-1} excitation, the strongest set of peaks in Fig. 3 (curve *2*) is attributed to uranyl ions surrounded by SiO_2, the major constituent of the glass compositions. And the other three groups of lines in weaker intensity likely arise from uranyl ions that are coordinated with the other three constituents of the glass, namely Na_2O, Ba_2O_3, and Al_2O_3. One also anticipates that in borosilicate glass a uranyl ion may be coordinated with more than one type of these four metal oxides, more possibly, the presence of a different type of metal oxides near the uranyl cluster that is coordinated with one type of the metal oxides in its first shell. The mixture of the surrounding metal oxides is expected to shift the uranyl electronic energy levels. In the spectra obtained from our sample, only four sets of spectra can be identified, although emission line shifting was observed when the laser excitation energy was varied. We believe that the line shifting, indicative of inhomogeneous line broadening, is largely due to the mixtures of different metal oxides in the surrounding environment of uranyl ions.

It should be pointed out that in contrast to our selective laser excitation spectra revealed four types of different uranyl sites plus significant inhomogeneous line broadening on each set of the site-resolved spectra, the EXAFS data [13,14] suggest only one type of uranyl cluster exist in the same borosilicate glass. It is presumably because that EXAFS is not capable of resulting in site selective spectrum and also has sensitivity much less than that of the laser-induced fluorescence detectrion, so that minor sits was not resolved in the EXAFS spectrum. Given that the three sets of laser-detect uranyl sits indeed have much weaker intensity in comparison with the major site shown in Fig. 3 (curves *1* and *2*), these results can be interpreted consistently with the assumption that in the borosilicate glass most of the uranyl ions coordinate with four SiO_2 tetrahedra in their equatorial plane. This means that a uranyl ion tends to bond with SiO_2 and excludes other metal oxides in formation of a uranyl tetrahedral cluster. This hypothesis was verified in MD simulation.

2. Molecular dynamics simulation

It is generally believed that there is no long-range order in glasses even though short range structural order is common. This usually means that the structure order is limited to a metal ion and its nearest neighbor ligands. In B_2O_3 glass, for example, the BO_3^{3-} cluster in a form of a plane triangle is the basic unit of the disordered glass matrix. The present results show that for uranium in the glasses that we studeied not only is the linear structure of uranyl ion well defined and stable, but also structure ordering extends to the next nearest neighbors to from a larger crystalline cluster. At present, EXAFS and laser spectroscopic experiments provide the best experimental techniques for resolving in detail the structure of the uranyl clusters diluted in glasses. The structure and vibrational spectrum of uranyl in vitreous glass have been studied using a MD simulation method [15–17].

Our MD calculations utilize the Born–Mayer–Huggins and Coulomb pair potentials and the Stillinger–Weber three-body potential [18]. We simulated two systems, one is UO_2–B_2O_3, and another UO_2–(70% mol)SiO_2(30% mol)B_2O_3. The first system contained 2 124 atoms including four U^{6+} ions, and the second contained 3 000 atoms including nine U^{6+} ions. As a procedure of the MD simulation, the assignment of effective charge is -2 for each of the axial oxygen in the uranyl ions and -1.5 for other four oxygen ions that located as the nearest ligands of the uranium. The same structure configuration was always obtained in our MD simulations regardless of initial conditions as long as the simulated system undergoes a virtual quenching from the initial temperature at 6000 to 1000°C, then from 1000°C to room temperature in 10^5 time steps (0.5 fs/step). Partial random distribution functions (RDFs) of ion pair distances were calculated from the MD model systems

Pair distances between U and it ligands in various uranyl phases (pm)

Ion pair	$UO_2B_2O_3$ MD/EXAFS [14]	$UO_2SiO_2^*$ MD/EXAFS [14]	$UO_2(NO_3)(H_2O)_2$ [20]	$UO_2(SO_4)(H_2O)_2$ [20]
U–O_{ax}	176/180	182/182	174	180
U–O_{eq}	248/249	222/223	249	264
U–B (Si, N, S)	340/335	367/	304	308

* Borosilicate glass studied in this work.

for structure indentification and comparison with EXAFS experiments [13,14].

From the simulated glass systems, we can visualize the exact atomic structure in which a uranyl is centered. Fig. 4 shows the cluster structure of uranyl in B_2O_3 glass matrix. In addition to the six oxygen ions that are directly coordinated with the core uranium ion, we see four boron ions in connection with additional oxygen ions in the form of four BO_3 triangles. The BO_3 triangle units that are bonded with the uranyl are slightly bent and twisted, which is understood because these BO_3 groups are connected with other such groups that are randomly oriented in the glass matrix. The B–O bond length of the four BO_3 groups in the uranyl cluster varies from 0.132 to 0.153 nm in comparison with 0.136–0.138 nm for the intrinsic B–O bond. It is always the case that the two axial oxygen ions are not actively bonded with any boron (or Si) ions in the glass matrix. In agreement with this observation, calculations of molecular bonding using quantum theory also suggest that no stable bonding can be established on the top of an actinyl ion along its axis [19]. The reality of the model structure is based, of course, on the agreement between the EXAFS data and the calculated RDF for the uranium ion and its ligands, and the agreement between the simulated glass matrices and that previously extablished by Raman and neutron scattering techniques. The calculated ion pair distances are listed in the Table in comparison with those obtained from EXAFS [14] and *ab initio* calculations [20]. It is also supported by comparison between the vibrational energies measured in the laser spectra and those calculated for the simulated system of uranyl in B_2O_3 glass [21].

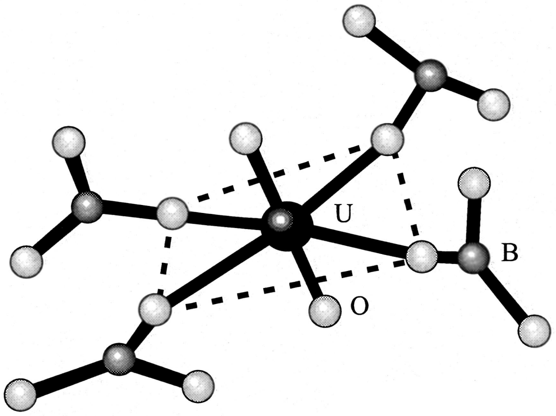

Figure 4. Model structure of uranyl cluster in B_2O_3 glass established using a molecular dynamics simulation.

3. The mechanism of charge transfer-lattice interaction

While our MD simulations provide a model structure for uranyl clusters in boron oxide and borosilicate glasses that is in excellent agreement with the experimental observation, one of the main purposes of the present work is to construct a theoretical model of charge transfer-lattice interaction that helps to explain the formation of uranyl clusters in glass environments. The basic consideration is to take into account an ionic-covalent bonding between the six oxygen ions as well as between uranium and uxyden ions both with charge transfer-lattice interaction in the UO_6 cluster (see Fig. 5).

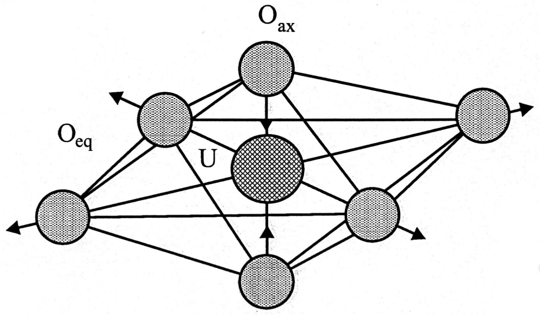

Figure 5. Charge transfer channels and vibronic distortion of in UO_6 cluster that contains uranyl. The lines indicate charge transfer channels and the arrows indicate distortion modes.

The mechanism of charge transfer-lattice interaction can be realized based on the following phenomena that are simultaneously active.

The first phenomenon is a self-consistent charge transfer-lattice distortion. There are three actual channels of the charge transfer in the UO_6 cluster, namely oxygen $2p$–oxygen $2p$ charge transfer (q_1) between the six active oxygen ions, oxygen $2p, 2s$–uranium $6p$ (q_2), and oxygen $2p$–uranium $5f$ (q_3) charge transfers. Such charge transfers are self-consistent with the local lattice displacements. The latter is due to the vibronic-type charge transfer-lattice interaction proposed recently in the framework of consideration of the problem of charge transfer vibronic excitons (CTVE) [7,8]. The CTVE is the electronic polaron–hole polaron correlated pair with strong vibronic interaction of polaronic origin [7]. Namely, the small pllaron nature of the electronic and hole states of CTVE is responsible for the high strength of the vibronic interaction in the case of the uranyl cluster.

The important peculiarity of CTVE in the uranyl system is the charge transfer between the same type of active ions. This is mainly due to the possible strong equilibrium charge transfer between different oxygen ions within the degenerated states, which significantly reduces the quadratic increasing of cluster energy with charge transfer and hence, produces rather soft conditions for the CTVE formation even in the ground charge transfer state.

The oxygen $2p(2s)$–uranium $6p$ charge transfer should also be considered. It induces additional strengthening of CTVE effect in the cluster under discussion. The pseudo-Jahn-Teller type mechanism of such charge transfer presumably exists in the present case. The equilibrium charge transfer in the oxygen–uranium channel becomes important when taking into account of the simultaneous action of the charge transfer analog of the pseudo-Jahn-Teller effect (PJTE) and PJTE on the active tetragonal distortion of the cluster. Both types of PJTE are realized in the framework of oxygen $2p, 2s$–uranium $6p$ states mixing. Moreover, this type of charge transfer is responsible for the effective indirect and two step mechanism of the oxygen $2p$–oxygen $2p$ charge transfer resulting from the oxygen $2p$–uranium $6p$–oxygen $2p$ charge transfer via the intermediate uranium $6p$ state.

Last but not least, the classical [1–4] oxygen $2p$–uranium $5f$ charge transfer also phays an important role in the uranyl formation. Here, the PJTE mechanism of charge transfer also has actual contribution. Again the equilibrium charge transfer becomes significant when taking into account the simultaneous action of charge transfer analog of PJTE width oxygen $2p$–uranium $5f$ states mixing as well as PJTE on structure-distortion with the same active electronic states.

The strong local displacements of oxygen ions that were detected in the experiments on the uranyl cluster need very definite conditions for charge transfer-lattice interaction even in the frame of the CTVE-model. This situation takes place within the second phenomenon mentioned above. Namely, there is an increase in the ionicity of the two active oxygen ions of UO_2^{2+} due to charge transfer under consideration (tending to O^{2-} final states where the ionic radius is decreased). Correspondingly, a decrease of the Born–Mayer repulsion radius with an increasing ionicity will lead to significant softening of the quasi-local vibration for these two oxygen ions. The latter induces local configurational instability (LCI) caused by charge transfer-lattice interaction under discussion. Such LCI is accompanied by strong equilibrium tetragonal lattice distortion for the UO_6 cluster in the glass matrix (with displacements of two axial oxygen ions towards to each others). Therefore, the microscopic nature of the above mentioned charge transfer-lattice interaction (direct influence of charge transfer on the local vibrational dynamics of active ions) explains the uncommonly strong increase in vibronic interaction with charge transfer. It is important to underline that this CTVE-effect is mainly formed by the competition between cluster energy increasing due to oxygen–oxygen charge transfer and cluster energy decreasing due to lattice distortion as a result of LCI.

The uranyl ground state structure can be treated as an oxygen-related CTVE-pair trapped by the central U^{6+} ion. The tetragonal structure of such CTVE-pair leads to cluster energy minimum due to Coulomb repulsion between two electronic polarons (two oxygen ions with increased negative charges and corresponding high ionicity). Another origin of the geometry with tetragonal symmetry for the UO_6 cluster connects with specific hybridization of the states in the framework of PJTE. The role of the central U^{6+} ion is essential in the construction of the uranyl structure. Because of significant U–O state overlapping, the indirect mechanism of O(1)–O(2) effective charge transfer between two different oxygen ions via successive O(1)–U and U–O(2) channels of state mixing becomes important. The latter strongly decreases the electronic part of cluster energy, which is characterized by enhancement in charge transfer. As a result, the energy of the localized CTVE-pair of O–O type goes down due to softening of the corresponding CTVE-pair trapping by the U^{6+} ion.

It should be stressed that there is another important source of the U^{6+} ion influence on the uranyl structure and properties. This is the PJTE due to the mixing of the $6p-5f$ uranium ion states unduced by linear vibronic interaction with active tetragonal distortion of the cluster coordinate. This PJTE-mechanism of the $6p-5f$ states mixing accompanied by an equilibrium distortion can explain the linear geometry of the uranyl structure. It should be also pointed out that the importance of the $6p-5f$ hybridization for the stability of a linear geometry was discussed for the uranyl ion in the review article [4]. We have proposed here the microscopic mechanism of such a phenomenon.

The CTVE-effect under discussion can be described in the framework of a semiphenomenological approach. The latter is based on the cluster potential expansion into the powers of active variables. It corresponds to the strong PJTE case, and to the two successive adiabatic approximations within the hierarchy of the characteristic rates of active subsystems. Namely, the latter hierarchy is realized within the interacted „very fast“ subsystem of electronic degrees of freedom of ionic states, „intermediately fast“ subsystem of charge transfer degrees of freedom, and „slow“ subsystem of quasi-local vibrations of the ionic cluster under consideration. A solution for the problem can be found from analysis of successive potential energy minimization in accord with the subsystem hierarchy mentioned above. „Intermediate“ adiabatic potential of a UO_6 cluster embedded in the matrix of B_2O_3 (or SiO_2) contains the leading charge transfer-lattice interaction, and depends on three types of charge transfer variables $\{q_1, q_2, q_3\}$ as well as the „slow" vibration variable x. We obtain the adiabatic potential for the „slow" subsystem after minimization of the „intermediate" potential on the $\{q_1, q_2, q_3\}$ variables. Its expansion on the powers of x-displacements can be presented in the usual form but with strongly renormalized coefficients by charge transfer

$$U = D(x)^2 + \beta(x)^4 + \gamma(x)^6 + \dots . \qquad (1)$$

Here two different types of the solutions are realized. Namely, in the case of $D < 0$, $\beta > 0$ (LCI of the second order) we have to deal with equilibrium cluster distortion accompanied by correspondent equilibrium charge transfer both induced by leading vibration instability. This is the case of CTVE trapped to the ground state. In contrast to this case, in the situation of $D > 0$, but with $\beta < 0$, $\gamma > 0$, pure CTVE-type solution is realized (with equilibrium charge transfer in the corresponding anharmonic excited state of the system). Both solutions are possible depending on the parameter values. But the first case is adequate to the real situation for uranyl ion. Strong vibronic charge transfer-lattice interaction is responsible here for strong enough equilibrium charge transfer and cluster distortion within the LCI phenomenon.

The model proposed in the present work is in agreement with EXAFS and MD simulation, and can explain the stability of the uranyl cluster on the basis of uncommonly high CTVE-pair lattice distortion. In addition, the long lifetime of the uranyl fluorescence also finds the explanation due to vibronic reduction that appears in the framework of recombination process with electronic transition between states with strongly different equilibrium positions of cluster ions. The latter results from strong lattice distortion in the framework of CTVE-effect.

Thus, we have investigated experimentally and theoretically the formation of a locally ordered structure of uranyl ions in B_2O_3 glass and borosilicate glass. Our experimental results show a ordered local structure in which a UO_2^{2+} ion is coordinated with its surrounding ligands consisting of four BO_3 triangles in the case of boron oxide glass and SiO_4 tetrahedra in the borosilicate glass. Our MD simulations reproduced the EXAFS results and demonstrated that a U^{6+} ion in vitreous B_2O_3 and SiO_2 matrices has strong capacity to form a crystalline-like, ordered UO_6 cluster, which consists of a linear uranyl ion with additional four oxygen ions in its equatorial phane in a tetragonal symmetry. This crystalline-like cluster is very stable in the glass matrix although the U–O distances vary (depending on the O–B (or O–Si) bonding strength). It is also observed that in the borosilicate glass uranyl primarily coordinates with four metal oxide ligand units of the same type, mainly four SiO_4 tetrahedra. The model of charge transfer-lattice interaction explains the stability of the uranyl cluster of the basis of uncommonly high CTVE-pair lattice distortion. In the framework of this theoretical model, charge transfer channels in the uranyl ion (UO_2) and a larger cluster (UO_6) are considered important in formation of a crystalline-like cluster. The predicted structural and electronic properties for the uranyl cluster are in agreement with the spectroscopic experiments and MD simulation. In addition, the long lifetime of the uranyl fluorescence is also explained based on the vibronic reduction of the recombination process in the electronic transitions between states with strongly defferent equilibrium positions of cluster ions.

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