CALCULATION OF VIBRATIONAL SPECTRA FOR DIOXOURANIUM MONOCHLORIDE MONOMER AND DIMERS

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Structural models were built and spectral characteristics were calculated based on ab initio calculations for the monomer and dimers of dioxouranium monochloride UO₂Cl. The calculations were carried out in the effective core potential LANL2DZ approximation for the uranium atom and all-electron basis sets using DFT methods for oxygen and chlorine atoms (B3LYP/cc-pVDZ). The monomer UO₂Cl was found to possess an equilibrium planar (close to T-shaped) configuration with C₂v symmetry. The obtained spectral characteristics were analyzed and compared with experimental data. The adequacy of the proposed models and the qualitative agreement between calculation and experiment were demonstrated.

Keywords: ab initio calculations, effective core potential, IR spectrum, dioxouranium monochloride.

Introduction. The actinide elements react with oxygen to form many stoichiometric and non-stoichiometric compounds. In this respect, the uranium–oxygen system is unparalleled in complexity. Uranium behaves as a multivalent element in compounds with oxygen and forms stoichiometric and non-stoichiometric phases, some of which are unstable at room temperature [1–3].

Despite the variety of uranium oxides, only three are commonly mentioned in the literature: UO₂, U₃O₈, and UO₃. These have high practical significance because they are the most important intermediates for producing uranium metal and its fluorides among such compounds as ammonium uranyl nitrate dihydrate, uranium peroxide, and ammonium uranyl tricarbonate. One of the most important applications of UO₂ is in fuel rods of many types of modern nuclear reactors. UO₂, being a ceramic fuel for nuclear reactors, is highly resistant to corrosion, radiation, and heat. This makes it possible to attain significantly higher temperatures in reactors than if metallic uranium were used [4, 5]. The principal method for synthesizing UO₂ is calcination of uranium salts with subsequent reduction [4]. The drawbacks of this method are the many steps and duration in addition to the use of high temperatures (up to 2000 K) and explosive oxygen. Another convenient method for synthesizing UO₂ is direct reduction of uranyl nitrate hexahydrate in a saturated alcohol solution in an autoclave at 473–453 K for 0.5–1.0 h. The proposed methods for synthesizing UO₂ could simplify the process and decrease significantly its temperature and time.

One of the reaction products of UO₂, for example, with halogens, is dioxouranium monochloride UO₂Cl, which has definite practical value [3, 4] and is a water-insoluble dark-brown compound. The DTA curve of UO₂Cl (Fig. 3, curve 1 in [6]) shows one endotherm at 665°C. The TG curve (curve 2 of the same reference) contains a mass loss of 11.5% in the temperature range 620–710°C. Analysis of the thermogram for Cl showed that the only endotherm corresponded to loss of one mole of Cl. The final decomposition product according to chemical and x-ray analyses was UO₂.

Therefore, it seemed interesting to determine the spectral and structural features of UO₂Cl in order to use them for analytical purposes. Keeping in mind the possibility of forming a polymeric system [6], we examine UO₂Cl monomer and dimers, the latter as a model of the simplest fragment of the polymeric structure.

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Results and Discussion. The structure of UO$_2$Cl monomer (Fig. 1a) was modeled based on results of numerous investigations of hexavalent uranium compounds [7, 8], for which the basic structural element is UO$_2^{2+}$ (so-called uranyl ion). Uranyl is a linear complex of high symmetry. This has been proven by direct methods (neutron diffraction) and by spectroscopy (the alternative forbidden rule is obeyed well). However, the UO$_2^{2+}$ group can also have non-linear geometry if the symmetry is lowered (for example, with a non-uniform equatorial ligand environment around UO$_2^{2+}$ or by establishing additional bonds through polymerization). As a result, all frequencies of this structural unit are activated in the vibrational spectra (IR absorption and Raman). Keeping in mind that the experimental spectrum of UO$_2$Cl exhibits two strong absorption bands [6] near 850 and 950 cm$^{-1}$ (characteristic of uranyl ion in complexes [7]), we hypothesized that UO$_2$Cl may contain a similar analog of this group. The fact that the aforementioned frequencies are active in the IR absorption spectrum (the alternative forbidden rule is violated) indicates that the UO$_2$ group in the monomer is bent; the fact that they are split into two components each, that these groups are nonequivalent in the actual structure or that their shoulders are significantly asymmetric because of the different environments of the axial oxygens in a field of rather low symmetry. Such an effect was also observed in uranyl compounds, especially when the equatorial environment of UO$_2^{2+}$ is unsaturated and additional bonds between the complexes are formed through the uranyl O atom [7]. This suggested that the simplest bound systems may exist as dimers.

The structures and spectral characteristics of UO$_2$Cl monomer and dimers were calculated using the applied quantum-chemical program GAMESS-US [9, 10]. Results were visualized using the program MacMolPlt [11]. Calculations were performed using DFT methods with pseudo-potentials or effective core potentials (ECP) [12]. A certain number of inner (core) electrons is replaced by the pseudo-potential. The LANL2DZ ECP, which replaces the 78 core electrons of the uranium atom, was used as the effective core potential [13]. DZ-basis sets that were specially developed for this ECP were used for the remaining electrons. The O and Cl atoms were described based on the standard fully electronic basis set cc-pVDZ [14]. Pseudo-potentials and the corresponding basis sets were generated using the Extensible Computational Chemistry Environment Basis Set Database [15–17]. The hybrid exchange-correlated functional B3LYP was used in all calculations [18, 19].

The geometry was optimized and the vibrational spectrum of the isolated uranyl ion UO$_2^{2+}$, for which a stable linear configuration was obtained, was calculated in a preliminary stage in order to estimate the accuracy of the aforementioned approximations for the examined species. The UO bond length was 1.709 Å. The frequency of the UO$_2$ anti-symmetric stretching vibration $v_3 = 1102$ cm$^{-1}$; fully symmetric $v_1 = 1006$ cm$^{-1}$; bending $v_2 = 259$ cm$^{-1}$. Experimental data on the structure and vibrational frequencies of free uranyl ion have not been published. The UO bond length for uranyl complexes lies in the range 1.60–1.95 Å, depending on the environment. Frequency $v_3 = 800$–1020 cm$^{-1}$; $v_1 = 780$–900 cm$^{-1}$; $v_2 = 190$–210 cm$^{-1}$ [7, 8, 20]. The ratio of $v_3$ and $v_1$ for a whole range of compounds.