

MODELING THE STRUCTURE AND VIBRATIONAL SPECTRA FOR OXOURANIUM DICHLORIDE MONOMER AND DIMER

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Structural models are designed and spectral characteristics are computed for the monomer and dimer of the oxouranium dichloride (UOCl₂) molecule based on ab initio calculations. The calculations were carried out in the LANL2DZ effective core potential approximation for the uranium atom and all-electron basis sets using DFT methods for oxygen and chlorine atoms (B3LYP/cc-pVDZ). A close-to-planar Y-shaped equilibrium configuration with C_s symmetry is obtained for the UOCl₂ monomer. The formation of the dimer is accompanied by both significant changes in the structure of the monomeric fragments and the actual loss of their identities. The obtained spectral characteristics are analyzed and compared with experimental data. The adequacy of the proposed models and qualitative agreement between calculation and experiment are demonstrated.

Keywords: *ab initio calculation, effective core potential, IR spectrum, oxouranium dichloride.*

Introduction. Oxouranium dichloride, UOCl₂, is one of the products from reaction of UO₂ with halogens. It is an intermediate link between uranyls and uranates. Its structure has not been determined although, like dioxouranium chloride UO₂Cl, it has practical significance. Therefore, it seemed interesting to use spectroscopic and quantum-chemical methods to establish its structural features and to find analytical vibrational frequencies in order to identify this compound.

Results and Discussion. Structural and spectral characteristics of UOCl₂ monomer and dimer were calculated using the applied quantum-chemical set GAMESS-US [1, 2]. Results were visualized using the program MacMolPlt [3]. The LANL2DZ effective core potential (ECP) approximation [4] that replaces the 78 inner electrons was used for the U atom. DZ-basis sets that were specially developed for this ECP were used for the remaining U electrons. The O and Cl atoms were described based on the standard all-electron basis set cc-pVDZ [5]. The ECP and corresponding basis sets were generated using the Extensible Computational Chemistry Environment Basis Set Database [6–8]. The hybrid exchange-correlated functional B3LYP was also used in all calculations [9–11]. Calculations of the structural and spectral characteristics of UO₂Cl monomer and dimer that were carried out previously [12] in an analogous approximation demonstrated that the employed model was effective.

The starting structure for finding the equilibrium configuration of UOCl₂ monomer was a non-planar pyramid with point symmetry C₁. Optimization of the geometry produced a nearly planar (deviation of the UO bond angle from the ClUCI plane 5°) Y-shaped equilibrium configuration with C_s symmetry (Fig. 1a). Calculation of the force-constant and vibrational-frequency matrices demonstrated that imaginary frequencies were absent and confirmed that such a configuration was stable.

Table 1 presents the calculated geometric parameters of UOCl₂ monomer. The UO (1.801 Å) and UCl (2.623 Å) bond lengths agree with those for dioxouranium chloride [12]. The UCl bond lengths from x-ray and neutron-scattering structure studies for various U compounds vary over a broad range of 2.414–2.514 Å for UCl₆ (depending on the position of the U atom in the crystal lattice) [13], 2.73–2.75 Å for UO₂Cl₂ [14], 2.82 Å for the ion UO₂Cl₄^{2–} [15], and 2.931–2.938 Å for UCl₃ [16]. Moreover, quantum-chemical calculations [17] that were carried out also using the ECP approximation gave UCl bond lengths of 2.42–2.51 Å for isolated UCl₆ depending on the em-

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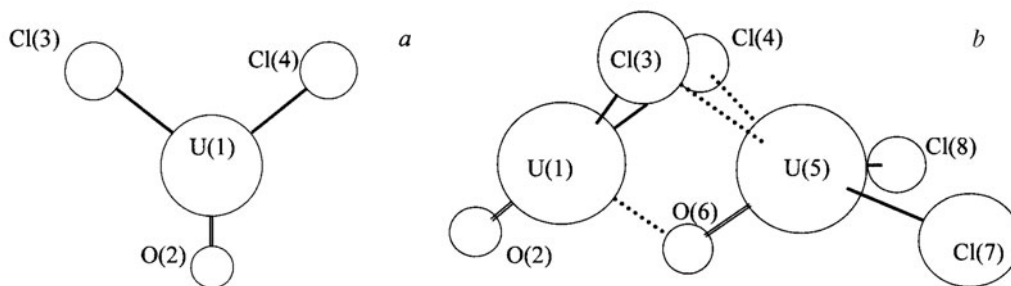


Fig. 1. Equilibrium structures of UOCl_2 monomer (a) and dimer (b).

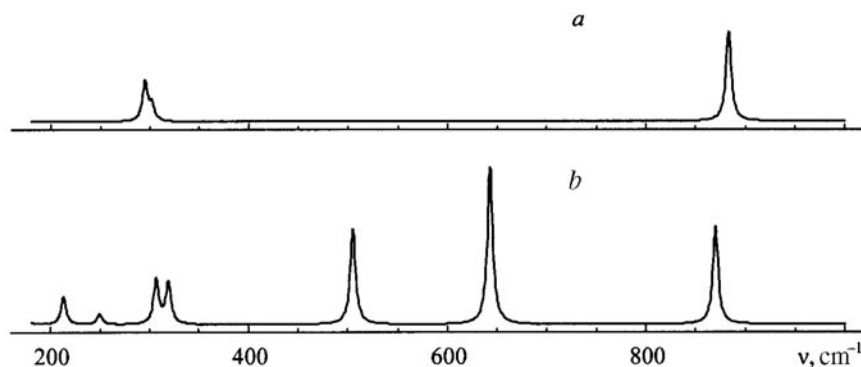


Fig. 2. Calculated IR spectra of UOCl_2 monomer (a) and dimer (b).

ployed exchange-correlated functional. Thus, it can be assumed that our calculation reproduced adequately the equilibrium structure of UOCl_2 monomer.

Figure 2a shows the calculated IR spectrum of UOCl_2 monomer. Table 2 gives the assignments of vibrational frequencies to particular types of vibrations and intensities of the corresponding bands. The strong band at 883 cm^{-1} corresponds to a UO stretching vibration and agrees with commonly accepted representations. Symmetric and antisymmetric UCl_2 stretching vibrations appear as a split band near $\approx 300\text{ cm}^{-1}$. Bending vibrations of UOCl_2 monomer appear in the region below 120 cm^{-1} . The calculations agree with experimental data for UO_2Cl_2 [18, 19].

The geometry of UOCl_2 dimer was optimized assuming that it had C_s symmetry. Figure 1b shows the structure of UOCl_2 dimer. Table 1 presents its geometric parameters. Each of the monomeric fragments retains local C_s symmetry in combining into the dimer.

By analogy with previous terminology [12], we call one of the monomeric fragments $\text{U(1)O(2)Cl(3)Cl(4)}$ constituting the dimer the "base"; the other $\text{U(5)O(6)Cl(7)Cl(8)}$, the "satellite." It is noteworthy that the separation of the dimer structural fragments is recognized to be somewhat arbitrary in nature in this instance, in contrast with the UO_2Cl dimer. This occurs because the monomeric fragments UOCl_2 undergo a significant loss of identity upon combining into the dimer, which is in essence a new structural unit because the intermolecular bond in UOCl_2 dimer is formed not only by a $\text{UO}\cdots\text{U}$ bridge but also by two $\text{U}\cdots\text{Cl}$ bonds. The multiplicities of the UCl bonds in the base fragment and the $\text{U}\cdots\text{Cl}$ intermolecular bonds have comparable values (0.54 and 0.44) whereas the multiplicity of the UCl bonds in the satellite is 1.07 and is practically the same as the corresponding values in the monomer (0.98). A similar redistribution of electron density occurs in the $\text{UO}\cdots\text{U}$ bridge. The multiplicity of the satellite UO bond is 1.29; of the $\text{U}\cdots\text{O}$ intermolecular bond, 0.73. The multiplicity of the UO bond of the base fragment retains the value characteristic of the monomer (2.26).

Table 1 and Fig. 1 indicate that the structural characteristics of the monomeric fragments constituting the dimer change significantly. First, these changes are reflected in the structure of the satellite fragment, the shape of

TABLE 1. Equilibrium Geometric Parameters* for UOCl_2 Monomer and Dimer

Parameter	Monomer	Dimer
U(1)O(2)	1.801	1.811
U(1)Cl(3)	2.623	2.835
U(1)Cl(4)	2.623	2.835
U(5)O(6)	–	2.040
U(5)Cl(7)	–	2.568
U(5)Cl(8)	–	2.568
U(1)...O(6)	–	2.200
U(5)...Cl(3)	–	2.922
U(5)...Cl(4)	–	2.922
$\angle \text{Cl}(3)\text{U}(1)\text{Cl}(4)$	102.02	75.62
$\angle \text{O}(2)\text{Cl}(3)\text{U}(1)\text{Cl}(4)$	4.89	5.03
$\angle \text{Cl}(7)\text{U}(5)\text{Cl}(8)$	–	117.08
$\angle \text{O}(6)\text{Cl}(7)\text{U}(5)\text{Cl}(8)$	–	46.41
$\angle \text{U}(1)\dots\text{O}(6)\text{U}(5)$	–	117.26
$\angle \text{O}(2)\text{U}(1)\dots\text{O}(6)$	–	107.81

* All bond lengths are given in Å; angles, in degrees.

TABLE 2. Calculated Frequencies (ν , cm^{-1}) and Intensities [I , $\text{D}^2/(\text{amu}\cdot\text{\AA}^2)$] in IR Spectra of UOCl_2 Monomer and Dimer

Vibration assignment	Monomer		Dimer	
	ν	I	ν	I
UO stretching of base fragment (monomer)	883.3	5.23	869.4	5.72
UO stretching of satellite	–	–	642.4	9.19
U...O stretching and U...OU bending	–	–	504.7	5.63
UCl_2 symmetric stretching of satellite	–	–	318.4	2.44
UCl_2 antisymmetric stretching of satellite	–	–	306.3	2.62
UCl_2 symmetric stretching of base fragment (monomer)	302.1	0.89	248.9	0.60
UCl_2 antisymmetric stretching of base fragment (monomer)	295.3	2.24	244.5	0.01
OU...OU out-of-plane	–	–	212.3	1.61
OUCl_2 out-of-plane of base fragment (monomer)	114.7	1.03	172.2	0.82
UO...O, U...OU, $\text{UCl}\dots\text{U}$ bendings	–	–	149.9	0.05
UO in-plane swinging of base fragment (monomer)	50.8	1.11	138.2	0.39
U...Cl symmetric stretchings	–	–	133.6	0.22
ClUCl symmetric bending of base fragment (monomer)	58.0	0.10	118.2	0.17
ClUCl antisymmetric bending of base fragment	–	–	109.8	0.07
ClUCl symmetric bending of satellite	–	–	85.2	0.05
ClUCl antisymmetric bending of satellite	–	–	61.3	0.05
OUCl_2 symmetric out-of-plane of satellite	–	–	58.9	0.19
OUCl_2 antisymmetric out-of-plane of satellite	–	–	38.3i	0.01

which is considerably different from planar. The bond lengths and angles of both monomeric fragments also undergo changes upon forming the dimer. The UO and UCl bonds of the base fragment are elongated. The ClUCl angle decreased noticeably. The UO bond of the satellite also lengthens whereas the UCl bond, conversely, is shorter. The ClUCl angle increases. The intermolecular U...Cl bond lengths (2.922 Å) approach the values for UCl of the base fragment (2.835 Å).

This analysis of the structure of the UOCl_2 dimer suggests that the structures of the base monomeric fragment and its satellite are different. This should be reflected in the vibrational spectrum of the dimer when compared with that of the monomer. Like for dimers of UO_2Cl [12], the presence in the UOCl_2 dimer of two nonequivalent monomeric fragments causes a doubling of its stretching frequencies. The formation of intermolecular bonds gives rise to new strong absorption bands (Table 2 and Fig. 2).

The formation of a U...O intermolecular bond and the redistribution of electron density from UO to U...O that is associated with it are accompanied by a weakening of the UO bond. This produces a significant long-wavelength shift of the UO frequency in the satellite fragment of the dimer (642 cm^{-1}) relative to its position in the spectrum of the monomer (883 cm^{-1}). The frequency of the free UO group of the base fragment is also shifted to long wavelength (869 cm^{-1}). The U...O stretching vibration (504 cm^{-1}) of the intermolecular bond is rather strong. The frequencies of UCl_2 stretching vibrations in the dimer show both insignificant short-wavelength shifts (16 and 11 cm^{-1}) due to contraction and strengthening of the satellite UCl bonds and more substantial long-wavelength shifts (53 and 51 cm^{-1}) due to lengthening of the UCl bonds of the base fragment. The spectral shifts are accompanied by a noticeable redistribution of band strengths.

Calculation of the dimer spectrum enabled assignment with certainty of the 565 , 523 , and 455 cm^{-1} bands in the experimental IR spectrum of UOCl_2 [20] to stretching and bending vibrations of U...OU intermolecular bridges; at 290 and 250 cm^{-1} , to stretching vibrations of bound and free UCl bonds in the polymeric structure.

Conclusion. Structural models of UOCl_2 monomer and dimer are constructed based on quantum-chemical calculations. It is shown that formation of the dimer is accompanied by substantial structural rearrangements of the monomeric fragments included in it. This is reflected in a significant complication of the vibrational spectrum. The calculated IR spectrum of the dimer agrees with experimental results and indicates that the proposed structural model is adequate.

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