ELECTRON DIFFRACTION BY URANIUM TETRACHLORIDE

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UDC 539.193+541.63+539.27

Vapor electron diffraction has been applied to the molecular structure of uranium tetrachloride. The molecule is a distorted tetrahedron (symmetry group C_{2v}) having internuclear distances r_g in Å r(UCl$_1$) = 2.475(15), r(UCl$_2$) = 2.558(18), r(Cl$_1$-Cl$_2$) = 3.612(6), r(CL$_1$Cl$_1$') = 3.212(12), r(Cl$_2$Cl$_2$') = 4.178(12). The Cl$_i$ and Cl$_i$' lie in the same plane. The vibrational frequencies have been calculated.

We have measured [1] the mean r(UCl) = 2.53(1) Å internuclear distance for the UCl_4 molecule, where the ℓ(UCl) and k(UCl) were used to conclude that the geometrical configuration does not have T_d symmetry but most likely C_{2v}. Complete structural information had not then been obtained and is still lacking. Advances in high-temperature vapor electron diffraction have led us to make a fresh study on this tetrachloride, particularly since structural information on uranium tetrahalides is significant.

We used UCl_4 made by halogenating uranium oxalate with CCl_4 at about 500°C. The specimen was further purified by vapor recrystallization. The compound is hygroscopic, so the tubes were loaded in a drybox, and the specimen was not in contact with dry air for more than 1-1.5 min. The vapor composition under working conditions was monitored from patterns recorded with the ELPRIM apparatus at about 580 and 680 K. The substance evaporated from a platinum tube. The patterns did not alter as the temperature was raised or during the recording. Our r(UCl) and ℓ(UCl) agree with the previous ones [1], so there are no appreciable amounts of other molecular forms in the vapor, which agrees completely with the data [2] on the vapor above UCl_4(s) at 600-700 K.

We processed five patterns from three series recorded under the following conditions (we give the detailed data for one of them): T_{exp} = 578(5) K, U ≈ 50 keV (λ = 0.05355(1) Å), I_b = 5 μA, P = $(4.5 \pm 1.0)\cdot 10^{-2}$ Pa, L_p (plate-nozzle distance) = 421.9(1) mm, E = 50 sec, k = L_p/L_h = 1.0001(2).

The experimental molecular-component function was derived for 2.0-19.0 $Å^{-1}$; the error of measurement was comparable with the function itself for s > 15.0 $Å^{-1}$, so that range was neglected in refining the structure parameters by least squares. Figure 1 shows $sM(s)_{exp}$ in the comparison region. The theoretical analog for $sM(s)_{exp}$ in the least-squares analysis is

$$sM(s)_{\text{th}} = h\sum_m n_m g_m(s)\exp\times\left(-l_m^2 s^2/2\right)\sin s\left[r_m - k_m s^2\right]. \qquad (1)$$

The functions $g_m(s)$ in (1) were calculated with $|f(s)|$ and $\eta(s)$ for Cl from the [3] tables, while for U they were derived by extrapolation with respect to Z for the moduli and phases from the same tables. The $sM(s)_{exp}$ were derived by drawing the background line graphically in $I_\ell(s)_{exp}$ and from the automatic background obtained by the method of [5]. The least-squares analysis was performed for $sM(s)_{exp}$ by the usual method and for $M(s)_{exp}$ by the [4] one. In all cases, we obtained values for the parameters in agreement within 2σ (least squares), which indicates that the structural information is reliable.

The initial values in the LS analysis were taken as ones corresponding to various geometrical configurations for UCl_4 (tetrahedron, trigonal bipyramid, or distorted tetrahedron with various α and γ) but having r(UCl) = 2.53 Å. In all cases (apart from the tetrahedron) we obtained parameters corresponding to a distorted tetrahedron, whose model is shown in Fig. 1.

High Temperatures Institute, Academy of Sciences of the USSR. Translated from Zhurnal Strukturnoi Khimii, Vol. 29, No. 5, pp. 42-45, September-October, 1988. Original article submitted January 15, 1987.

0022-4766/88/2905-0692 $12.50

TABLE 1. LS Results for $sM(s)_{exp}$ for Uranium Tetrachloride (T_{exp} = 578 ± 5 K)

Model	1	2	3	4	5
Analysis conditions	$r_1=r_2$ Δ_1	$r_1=r_2$ Δ_2	T_d	$r_1\neq r_2$	$r_1\neq r_2$ $k_1=k_2=k$
r_1(UCl), Å	2,516(6)	2,516(3)	2,496(8)	2,473(6)	2,456(2)
r_2(UCl), Å	2,516(6)	2,516(3)	2,496(8)	2,556(8)	2,580(2)
r_3(ClCl), Å	3,210(16)	3,213(4)	—	3,210(4)	3,213(5)
r_4(ClCl), Å	3,605(11)	3,606(3)	3,54(1)	3,607(2)	3,606(3)
r_5(ClCl), Å	4,173(23)	4,173(5)	—	4,175(4)	4,173(5)
l_1(UCl), Å	0,094(6)	0,090(2)	0,091(8)	0,063 *	0,063 *
l_2(UCl), Å	0,094(6)	0,090(2)	0,091(8)	0,063 *	0,063 *
l_3(ClCl), Å	0,073(19)	0,094(5)	—	0,108(5)	0,096(4)
l_4(ClCl), Å	0,168(10)	0,172(3)	0,30(2)	0,173(2)	0,172(2)
l_5(ClCl), Å	0,094(25)	0,089(5)	—	0,085(5)	0,089(5)
10^4k_1(UCl), Å^3	3,6(6)	3,6(6)	0 *	1,6(4)	3,65 *
10^4k_2(UCl), Å^3	3,6(6)	3,6(6)	0 *	4,7(4)	3,65 *
h	1,69(4)	1,623(8)	1,65(3)	1,58(1)	1,619(8)
R_f, %	10,83	2,41	4,65	1,94	2,05

* Value fixed during the LS analysis.

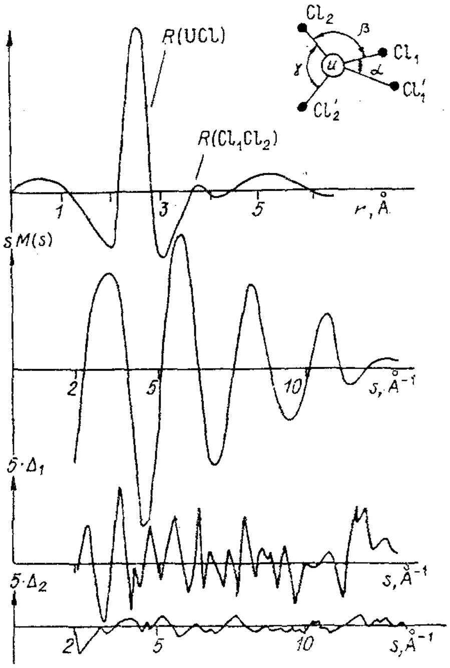

Fig. 1. Experimental $f(r/s_{min}, s_{max})$, $sM(s)$ and difference functions $\Delta sM(s)$ for the uranium tetrachloride molecule.

Table 1 (model 3) gives the parameters corresponding to T_d equilibrium symmetry for the UCl_4. It is clear firstly that R_f here is increased appreciably, and secondly, the $r(YY)/r(XY) = 1.42 \pm 0.01$ is much less than that expected for a tetrahedron (1.633), while thirdly, ℓ(UCl) and ℓ(ClCl) do not agree with the frequencies ν_{str} = 320-350 cm^{-1} and $\nu_{def} \approx$ 110 cm^{-1} [6-8]. Then the suggested T_d symmetry for UCl_4 is to be taken as not fitting the data.

The $sM(s)_{exp}$ LS analysis gave the model 1 parameters in Table 1. It was found that $\Delta sM(s) = sM(s)_{exp} - sM(s)_{th}$ hardly varied for the different forms and models, i.e., $sM(s)_{exp}$ has an additive component (Fig. 1 shows $\Delta_1 sM(s)$ corresponding to model 1). We derived that component from several $\Delta sM(s)$ corresponding to the different configurations and made the corresponding corrections to $sM(s)_{exp}$, which did not alter the parameters (see model 2) but reduced R_f and σ (LS). The difference function $\Delta_2 sM(s)$ corresponds to model 2,

TABLE 2. Molecular Constants for Uranium Tetrachloride

Parameter	Value	Parameter	Value
$r_e(UCl_1)$, Å	2,47(2)	$\nu_4(A_1)$, см^{-1}	85(10)
$r_e(UCl_2)$, Å	2,57(2)	$\nu_5(B_1)$, см^{-1}	335(10)
$\alpha_e(Cl_1UCl_1)$, °	95(5)	$\nu_6(B_1)$, см^{-1}	118(10)
$\beta_e(Cl_1UCl_2)$, °	100(5)	$\nu_7(B_2)$, см^{-1}	330(10)
$\nu_1(A_1)$, см^{-1}	350(10)	$\nu_8(B_2)$, см^{-1}	123(10)
$\nu_2(A_1)$, см^{-1}	325(10)	$\nu_9(A_2)$, см^{-1}	115(10)
$\nu_3(A_1)$, см^{-1}	123(10)		

which is also shown in Fig. 1. We suggest that this component is due to inexact $|f(s)|$ and $\eta(s)$ for U. Also, the background line for $I_\ell = I_{tot}/I_{bg}$ due to these functions may result in a systematic shift in $r_m(Cl_2Cl_2)$, which is responsible for the discrepancy in the r_m within a single model.

The $\ell(UCl)$ found in the LS analysis for model 2 ($r_1 = r_2$) agrees with the analogous quantity found in [1] but is appreciably larger than the $\ell(UCl)_{th} = 0.063$ Å calculated from the stretching frequencies, which may be due to $r_1(UCl_1)$ and $r_2(UCl_2)$ not being equivalent, which is confirmed by the differing values for the corresponding force constants ($f_r = 2.11$ mdyn·Å^{-1} and $f_d = 2.00$ mdyn·Å^{-1}). The possible difference between the $r_1(UCl_1)$ and $r_2(UCl_2)$ was estimated by LS with fixed $\ell(UCl) = \ell(UCl)_{th}$. To check for effects from correlation between $r(UCl)$, $\ell(UCl)$ and $k(UCl)$ (correlation coefficients about 0.9 in modulus), the minimization was also performed with fixed $k(UCl)$ (see models 4 and 5 in Table 1). The data show that $\Delta r(UCl) = 0.10 \pm 0.02$ Å with the mean $\bar{r}(UCl) = 1/2(r_1 + r_2) = 2.516 \pm 0.003$ Å.

The $r_g(M\Gamma)$ differ only slightly from $r_e(M\Gamma)$, where Γ is the halogen, whereas α_g is usually less than α_e and may differ greatly from it. The spectrum of UCl_4 in the stretching-frequency range has been recorded [6] in Ar and Kr matrices, where frequencies were recorded relating to UCl_4 molecules differing in isotope composition, so we processed that spectrum on the basis of our data, which showed that it can be described quantitatively (isotope shifts and intensity ratios) with the following values for the bond angles: $\alpha_e = 90 \pm 10°$ and $\beta_e = 100 \pm 10°$, which agree well with our α_g and β_g but are evidently more reliable.

The UCl_4 molecule has C_{2v} symmetry (Fig. 1) with α and $\beta \approx 100°$. The [6-8] spectral data enable one to select all the frequencies readily apart from $\nu_9(A_2)$. These may be processed along with the reliably determined $\ell(Cl_1Cl_2) = 0.176(6)$ Å to derive $\nu_9(A_2) = 115 \pm 10$ cm^{-1}, so we recommend the Table 2 molecular-constant set, which is required to calculate vapor-state thermodynamic functions for uranium tetrachloride.

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