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The gas electron diffraction data recorded for UCl_4 cannot be ascribed to the chloride oxide $UOCl_4$

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A suggestion that gas electron diffraction data previously recorded for UCl_4 and found to be consistent with a tetrahedral molecular model are due to $UOCl_4$ is refuted.

Two years ago we published the results of a molecular structure determination of UCl_4 at 900 K by gas electron diffraction (GED).[1] The diffraction pattern was found to be in good agreement with a molecular model of tetrahedral symmetry and a U−Cl bond distance of $r_a = 250.3(3)$ pm.[1] Structure optimisation of a model of D_{2d} symmetry by density functional theory (DFT) calculations collapsed to tetrahedral symmetry and yielded a bond distance in good agreement with experiment. The gas-phase IR spectrum contained two bands which were assigned as the two IR-active bands expected for a tetrahedral AX_4 molecule. The entropy of gaseous UCl_4 calculated on the basis of T_d symmetry, the experimental bond distance and vibrational frequencies from the IR spectrum and the DFT force field was in excellent agreement with the experimental, Third Law, counterpart.[1] As in the case of a previous investigation of $PbCl_4$,[2] we found indications for the presence of Cl_2 in the molecular beam and when the mole fraction of Cl_2 was included in the least-squares calculations the *R* factor decreased from 6.7 to 5.2%.†

Our conclusions were, however, at variance with the results of two earlier GED investigations published by Ezhov *et al.*,[3] who had found that their GED data were incompatible with T_d symmetry, and in a recent Letter Ezhov[4] suggests that our gaseous sample consisted of uranium tetrachloride oxide, $UOCl_4$, rather than UCl_4 and Cl_2. Ezhov attempted to reproduce our experimental data by calculating the intensity curves for the mixture of tetrahedral UCl_4 and Cl_2 and adding 5% 'random noise' (though it is not specified how this noise is generated), found that the resulting intensity curve was consistent with $UOCl_4$ gas, and proceeded to estimate the molecular structure parameters of the latter.

Ezhov writes that 'it is well known that uranium halides UCl_n ($n < 6$) exposed to oxygen are easily oxidised to uranium oxohalides' and refers to the Russian edition of Katz and Seaborg's 'The Chemistry of the Actinide Elements' for support.[5] We have consulted an English language edition[6] and find reference to the reaction of solid UCl_4 with O_2 at 350 °C to yield solid UO_2Cl_2 and Cl_2, but cannot find that the formation $UOCl_4$ is mentioned. Early workers in the field speculated that $UOCl_4$ was formed as an intermediate, but the most recent publication on the kinetics of the reaction concludes that it occurs in one step.[7] According to an edition of Gmelins Handbook which covers the literature through 1977,[8] solid $UOCl_4$ has never been characterised and no reference is made to observation of the gaseous molecule. In this connection it may also be pertinent to record that solid UOF_4 decomposes in vacuum at temperatures above 100 °C to yield gaseous UF_6 and an unidentified uranium oxide.[9] A search of *Chemical Abstracts* from 1977 to the present yielded only one reference to $UOCl_4$, namely Ezhov's suggestion that it should have been produced inadvertently in our electron diffraction unit.

Our samples of UCl_4 were prepared as described elsewhere by careful dehydration of hydrated UO_2Cl_2 in a stream of gaseous hydrogen chloride and characterised by X-ray diffraction.[10] No indications for impurities were found. The samples were stored under argon and were at no time exposed to air or oxygen.

The gas-phase IR spectra of UCl_4 from 25 to 3400 cm^{-1} were recorded in silica or stainless-steel cells at temperatures ranging from 700 to 900 K. Only two bands, at 338 and 72 cm^{-1}, were observed.[1] These were assigned as the two IR-active bands expected for tetrahedral symmetry. (A third band at 618 cm^{-1} persisted on cooling to room temperature and was assigned to $SiCl_4$.) No bands indicating the presence of species with U=O double bonds were observed. (A very strong band at 892 cm^{-1} in the IR spectrum of solid UOF_4 has been assigned as a U=O stretching mode.[9,11])

The gas electron diffraction data were recorded with reservoir and nozzle temperatures of 900 ± 10 K with nozzle-to-plate distances of about 50 and 25 cm. The plates were photometers and processed by standard procedures. The total intensity curve derived from each plate was 'levelled' through division with the calculated atomic intensity and backgrounds drawn as least-squares-adjusted sixth-degree polynomials to the difference between the total experimental and calculated molecular intensity curves. The backgrounds thus obtained are shown in Fig. 1. Final intensity curves ranged from $s = 25.00$ to 120.00 nm^{-1} (50 cm) and from $s = 35.00$ to 260.00 nm^{-1} (25 cm). Final least-squares refinements of the U−Cl bond distance, the U−Cl and $Cl\cdots Cl$ vibrational amplitudes and the mole fraction of Cl_2 yielded an *R* factor of 4.9%.‡ Calculated and experimental radial distribution curves are compared in Fig. 2.

Are our data compatible with gaseous $UOCl_4$? Refining the scale factor for a model of $UOCl_4$ with the structure parameters estimated by Ezhov[4] we obtain an *R* factor of 36%. Calculated and experimental radial distribution curves are compared in Fig. 3. Note that the curve calculated for $UOCl_4$ contains a double peak representing the U=O double bond distance at about 180 pm which is absent in the experimental counterpart. We find the agreement unacceptable. Attempts to refine the structure parameters of $UOCl_4$ (two bond distances, one independent valence angle and five vibrational amplitudes) led

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† $R = [\Sigma w(I_{obs} - I_{calc})^2/\Sigma w I_{obs}{}^2]^{\frac{1}{2}} \times 100\%$.

‡ The data used in the last GED investigation by Ezhov *et al.*[3] extended from s = about 20 to about 130 nm^{-1} and refinement of the eight independent parameters characterising their C_{2v} model yielded an *R* factor of 10.8%. Subtraction of high-frequency noise from the experimental intensity curve reduced the *R* factor to 1.9%.

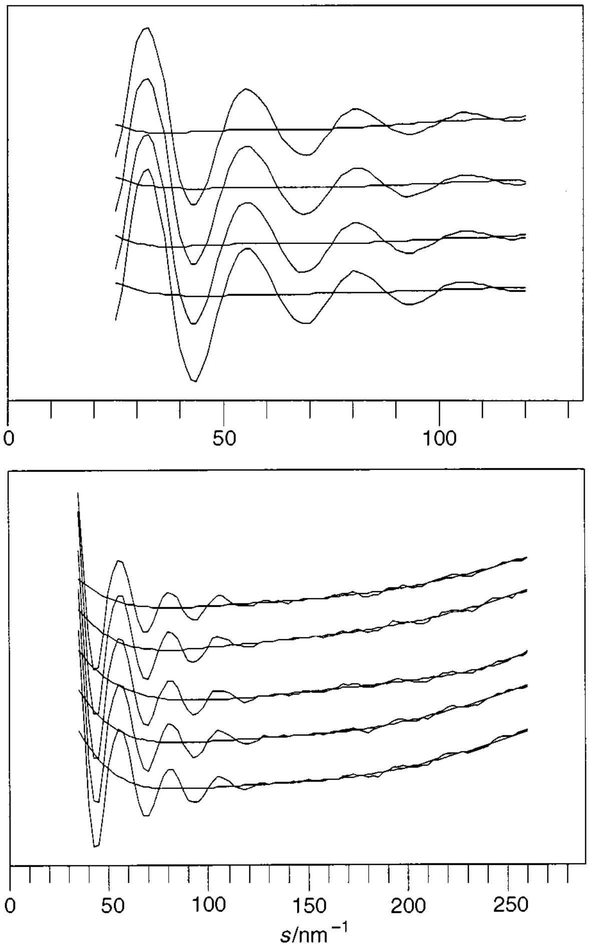

Fig. 1 Experimental gas electron diffraction intensities and backgrounds of UCl_4. Above, 50 cm plates; below, 25 cm plates

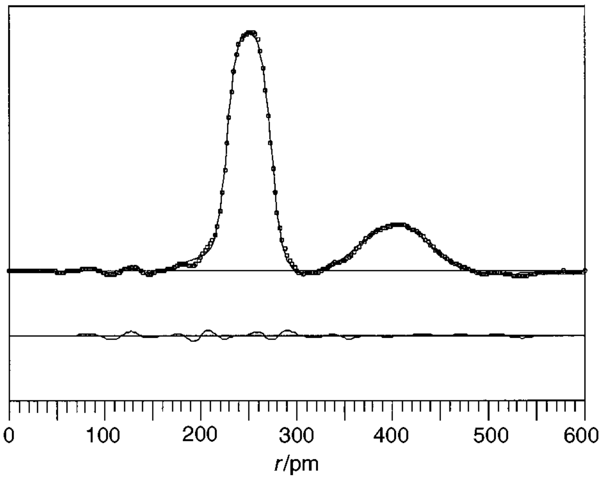

Fig. 2 Experimental (*) and calculated (—) radial distribution curves for the best model of UCl_4 of T_d symmetry. The difference curve is given below. Artificial damping constant $k = 25$ pm^2

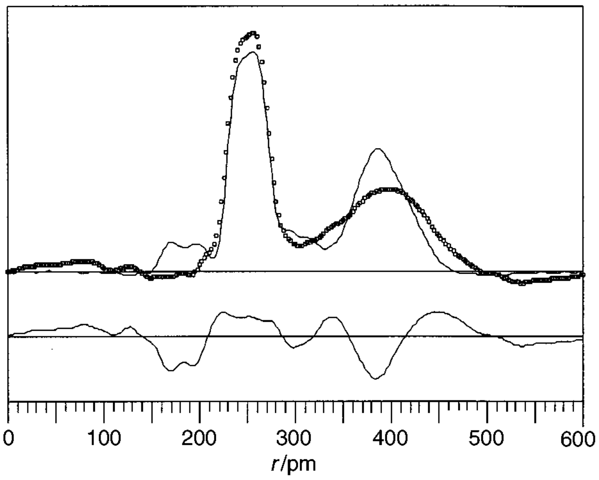

Fig. 3 Experimental radial distribution curve (*) calculated by Fourier inversion of the experimental molecular intensity curve of UCl_4 after addition of the molecular intensity curve calculated for $UOCl_4$ in the region below $s = 22.50$ nm^{-1}. Full line: calculated radial distribution curve for $UOCl_4$. The difference curve is given below. Artificial damping constant $k = 25$ pm^2

to divergence: depending on the starting parameters and the damping of the shifts, either the amplitude of the U=O bond distance or the amplitude of distance between Cl atoms at opposite corners of the square base (or both) went to infinity. We conclude that there are no such distances in the compound for which the data were recorded. Since it might be objected that backgrounds had been drawn to favour a tetrahedral model of UCl_4, they were redrawn to the difference between the total experimental intensities and molecular intensities calculated for $UOCl_4$ using the same degree of polynomials as before. The backgrounds obtained for the 25 cm plates were unaltered, while the new backgrounds for the 50 cm plates contained oscillations corresponding to an interatomic distance of about 150 pm. New least-squares refinements nevertheless yielded an R factor of 35%. We conclude that the observed intensity curves are incompatible with a gas consisting of $UOCl_4$.

In conclusion we point out that our work on UCl_4 prompted the reinvestigation of UF_4 which had also been believed to have C_{2v} symmetry. The U–F stretching frequency in the gas-phase IR spectrum was found at much lower wavenumber than previously supposed, and new structure refinements showed that the GED data were in good agreement with a tetrahedral model.[12]

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