Molecular Structure of Monomeric Uranium Tetrachloride determined by Gas Electron Diffraction at 900 K, Gas-phase Infrared Spectroscopy and Quantum-chemical Density-functional Calculations

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The gas electron diffraction pattern of monomeric UCl_4 has been recorded with a nozzle temperature of 900 K. The data are in good agreement with a model of T_d symmetry and a U–Cl bond distance of r_a = 250.3(3) pm. The root-mean-square vibrational amplitudes are l(U–Cl) = 8.9(3) pm and l(Cl $\cdots$ Cl) = 34.3(10) pm. The gas-phase infrared absorption spectra have been recorded from 25 to 3400 cm^{-1} at temperatures ranging from 700 to 900 K, and the t_2 stretching and deformation modes have been assigned at ν_3 337.4 and ν_4 71.7 cm^{-1} respectively. The molecular structure of UCl_4 has been optimised by density-functional calculations under D_{2d} symmetry. It is tetrahedral with bond distance r_e = 251 pm. The calculations yield values for the IR-active modes which are in good agreement with the experimental counterparts. The 'best values' for the two IR-inactive frequencies were obtained by refining a diagonal symmetry force field to the four calculated (density functional) frequencies, the two observed frequencies and the vibrational amplitudes obtained by gas electron diffraction. The entropies of gaseous UCl_4 calculated from these normal modes and a symmetry number of 12 corresponding to T_d symmetry are in good agreement with the experimental counterparts.

Uranium tetrachloride was first prepared by Peligot (from uranium oxide, chlorine gas and charcoal) in 1842.[1] At room temperature it forms crystals containing molecular UCl_4 species of D_{2d} symmetry which have the shape of elongated tetrahedra with Cl–U–Cl 66.4° (twice).[2] The U–Cl bond distance is 264 pm, about 14 pm longer than in the gase phase. In addition each U atom interacts with four more Cl atoms at a distance of 287 pm; the four Cl atoms at 264 pm and the other four at 287 pm form a dodecahedron.[2]

The vapour density of UCl_4 indicates that the gas is monomeric.[3] Investigation of the mass spectrum of the gas at 747 K demonstrated the presence of only very small amounts (less than 0.1 ppt) of the dimer.[4] The first investigation by gas electron diffraction (GED) was published in 1969 by a group working at the Institute of High Temperatures (IHT) in Moscow.[5] They found the molecular symmetry to be lower than tetrahedral, probably C_{2v}. The mean U–Cl bond distance was found to be 253 pm. In a reinvestigation published in 1988, the IHT group concluded that the molecular symmetry was indeed C_{2v},[6] see Fig. 1. One of the Cl–U–Cl angles bisected by the symmetry axis (α) was found to be 90 ± 10° and the four angles which are equal by symmetry (β) were 100 ± 10°. The mean U–Cl bond distance was 251.6(3) pm.

A metal tetrachloride of T_d symmetry would have only four vibrational modes, a totally symmetric a_1 stretching mode ν_1, an asymmetric stretching mode of t_2 symmetry ν_3, and deformation modes ν_2 and ν_4 of e and t_2 symmetries respectively. Only the two t_2 modes would be IR active. The infrared absorption spectrum of gaseous UCl_4 at 1120 K has been recorded by Gruber and Hecht.[7] Only two absorption bands, at 330 and 110 cm^{-1}, were detected in the expected frequency range and were assigned as ν_3 and ν_4 respectively.

The IR spectra of thorium and uranium tetrachlorides in argon and krypton matrices have been investigated by Arthers and Beattie.[8] It was concluded that the isotope pattern of the ν_3 band of $ThCl_4$ was incompatible with tetrahedral symmetry, but could be fitted by a species of C_{2v} symmetry. Similar results, though less detailed, were found for UCl_4. Later the same group recorded the IR spectra of the two tetrachlorides in neon matrices and found them to be consistent with tetrahedral symmetry.[9] The lowering of the symmetry observed in argon and krypton matrices was ascribed to matrix effects. The tetrahedral symmetry of $ThCl_4$ has been confirmed by a later gas electron diffraction study by Bazhanov *et al.*[10]

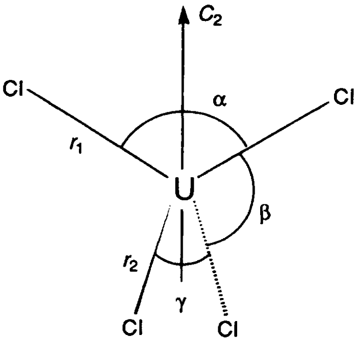

Fig. 1 A C_{2v} model of UCl_4 described by two independent bond distances, r_1 and r_2, and two independent valence angles, *e.g.* α and β

Boerrigter *et al.*[11] have optimized the structures of $ThCl_4$ and UCl_4 using relativistic Hartree–Fock–Slater (Xα) calculations. Models with D_{2d}, C_{2v} or C_{3v} symmetry all collapsed to T_d. Uranium tetrachloride is, however, an f^2 complex and might exhibit Jahn–Teller distortion.[11] Such a distortion would not be reproduced by the calculations which were carried out with equal, fractional occupation of all f orbitals.

Finally, Hildenbrand *et al.*[12] have compared experimental entropies of uranium and thorium tetrahalides with entropies calculated from spectroscopic data under the assumption of tetrahedral symmetry. The calculations on UCl_4 were based on the vibrational modes of $PbCl_4$,[13] *i.e.* ν_1 328, ν_2 93, ν_3 349 and ν_4 110 cm^{-1}. While the calculated entropy of $ThCl_4$ was in excellent agreement with the experimental counterpart, that of UCl_4 was found to be incompatible with the experimental value. Agreement could, however, be obtained by reducing the symmetry number from twelve to two, *i.e.* by assuming the symmetry of the UCl_4 molecule to be C_{2v} rather than T_d.[12]

Density-functional Calculations

These calculations were carried out with the program system ADF developed by Baerends and co-workers.[14]

The core orbitals of all atoms, *i.e.* up to and including the 2p orbitals on Cl, and up to and including the 5d orbital on U, were frozen in their atomic shape. The valence shell of the Cl atoms was described by two s-, two p- and one d-type Slater exponent, while that of U was described by three s-, three p-, three d- and three f-type Slater exponents.[15] The Vosko–Wilk–Nusair parametrisation[16] with the gradient corrections of Becke[17] for exchange and of Perdew[18] for correlation was used for the exchange-correlation energies. The corrections were added self-consistently. Relativistic effects were taken into account by using relativistic frozen cores and a perturbational treatment of the valence region.[19] Spin–orbit effects were not accounted for. The accuracy of the numerical integration was set to 10^{-8} for each integral, see te Velde and Baerends[20] for details. We believe this gives a numerical noise level of less than 0.1 kJ mol^{-1} for the final energies.

Uranium tetrachloride is an f^2 compound. Since spin–orbit effects have been neglected and because we have used spin-polarised calculations, the exact ground state could not be identified. All calculations were carried out with the two unpaired electrons distributed between the three f orbitals which were the most stable for the T_d equilibrium geometry.

The use of spin-polarised functions also introduced problems for the calculation of a consistent set of energies for structures of tetrahedral and lower symmetries (D_{2d} or C_{2v}): in order to obtain a consistent set of energies it was necessary to recompute the energy of the T_d conformation with the same symmetry restrictions as for the deformed models.

The calculations were run on IBM RS/6000 workstations.

Experimental

Samples of UCl_4 were prepared and characterised as previously described.[21]

Infrared Spectroscopy. — Infrared absorption spectra of the gas from 25 to 3400 cm^{-1} were recorded with a BOMEN DA3.02 Fourier-transform spectrometer equipped with a high-temperature gas cell (HTOC2). Details about the equipment have been published elsewhere.[22] The cell was assembled and loaded in an argon-filled glove-box in order to avoid contact with atmospheric gases; 10 mbar (10^3 Pa) argon buffer gas at room temperature was added. For the experiments approximately 3 g of the sample were heated in a silver vessel at the centre of the cell. Silica as well as steel cells were used. The silica cell contained a silver protection tube to prevent chemical reactions in the hot zone.

The following experimental arrangements were used: for the range 350–3400 cm^{-1} a globar light source, KRS-5 windows and a silicon–boron detector; for 25–375 cm^{-1} a mercury light source, silicon windows and a germanium bolometer operating at 4.2 or 1.6 K; 256 scans were co-added.

Gas Electron Diffraction.—The gas electron diffraction data of UCl_4 were recorded on a Baltzers Eldigraph KDG-2[23] with a new single-chamber radiation heater of stainless steel.[24] The nozzle temperature was 900 ± 10 K, the reservoir temperature some 50 K lower. Exposures were made with nozzle-to-photographic plate distances of about 50 and 25 cm. The plates were photometered on the Snoopy densitometer[25] and processed by a program written by Strand.[26] Complex atomic scattering factors, $|f'(s)|\exp[i\eta(s)]$ [$s = (4\pi/\lambda)\sin(\theta/2)$, where λ is the electron wavelength and θ the scattering angle], were taken from ref. 27. Backgrounds were drawn as least-squares-adjusted sixth-degree polynomials to the difference between total experimental intensities and calculated molecular intensities. The final modified molecular intensity curves extended from $s = 25.00$ to 120.00 nm^{-1} with increment 1.25 nm^{-1} (four 50 cm plates) and from $s = 35.00$ to 260.00 nm^{-1} with increment 2.50 nm^{-1} (five 25 cm plates), see Fig. 2.

The r_a bond distance of the Cl_2 impurity at the temperature of our experiment was calculated from the values of r_e, ω_e and $\omega_e x_e$ listed in ref. 28.[29] The root-mean-square (r.m.s.) vibrational amplitude was calculated as described by Cyvin.[30]

Structure refinements were carried out by least-squares calculations on the intensity curves using the program KCED25.[31] The molecular force field was refined on the basis of vibrational frequencies and r.m.s. vibrational amplitudes obtained by gas electron diffraction with the program ASYM20.[32] The same program was used to calculate the correction terms $D = r_\alpha - r_a$.

Results and Discussion

Gas-phase Infrared Spectra.—The four normal modes expected for UCl_4 of tetrahedral symmetry have been described in the Introduction. In the present study the spectrum of gaseous UCl_4 from 25 to 3400 cm^{-1} was measured in silica and stainless-steel cells at temperatures ranging from 700 to 900 K, see Fig. 3. Three distinct absorption maxima were observed at about 618, 338 and 72 cm^{-1}. The intensities of the last two bands were strongly temperature dependent, which suggests that they are due to gaseous UCl_4 species. The band at 618 cm^{-1} persisted on cooling to room temperature and was assigned to an $SiCl_4$ impurity which presumably had been formed by reaction of UCl_4 with an SiO_2 impurity in the sample.

Gaseous Fe_2Cl_6 has strong IR absorption bands at 268, 397, 468 and 504 cm^{-1},[33] gaseous $FeCl_2$ a strong band at 492 cm^{-1}.[34] The absence of bands in these regions, even when the spectra were recorded with the stainless-steel cell, shows that gaseous iron chlorides are not formed at the temperature of our experiments. This is particularly important, since the inlet system used for the recording of the GED data (below) was made from stainless steel.

The band at 337.4 cm^{-1} was assigned to the t_2 stretching mode ν_3. This value is in agreement with previous gas-phase studies, 330[7] and 345 cm^{-1}.[35] The band at 71.7 cm^{-1} was assigned to the t_2 deformation mode ν_4. This mode has previously been assigned at 110[8] and 85 cm^{-1}.[36]

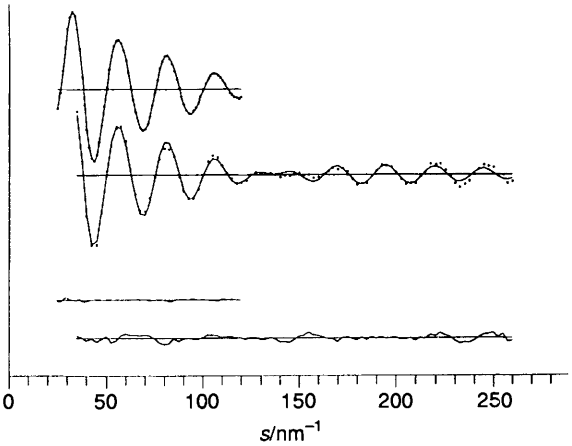

Fig. 2 Experimental modified molecular intensity curve (·) for UCl_4 at 900 K obtained with nozzle-to-plate distances of 50 and 25 cm and modified molecular intensity curves (—) calculated for the best model of T_d symmetry (refinement 2). The difference curves are shown below

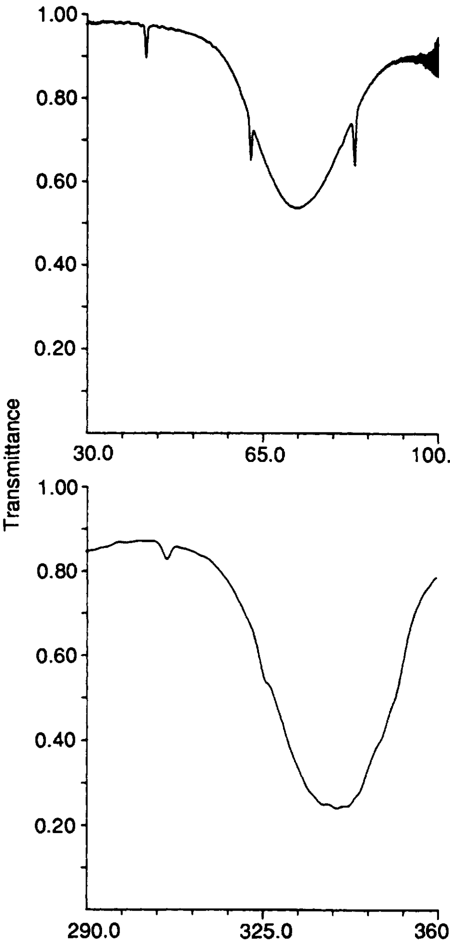

Fig. 3 The IR absorption spectrum of gaseous UCl_4. The band at 71.7 cm^{-1} is assigned to ν_4 (resolution 0.5 cm^{-1}) and that at 337.4 cm^{-1} to ν_3 (resolution 1.0 cm^{-1})

Distortion from T_d to C_{2v} symmetry would remove all degeneracies, giving a total of nine normal modes, eight of which would be IR active. The simplicity of the observed gas-phase spectrum is consistent with a tetrahedral UCl_4 molecule. If the symmetry is lower than T_d the distortion must be too small to yield detectable splitting of the t_2 modes or intensity of the e modes.

Density-functional Calculations.—The molecular structure of UCl_4 was first optimised under D_{2d} symmetry. The optimum structure was found to be tetrahedral with bond distance U–Cl 251 pm, in good agreement with the experimental value. This is in agreement with the results of Boerrigter *et al.*[11] who found models of D_{2d} or C_{2v} symmetry to optimise to tetrahedral symmetry. Since our calculations, like those of Boerrigter *et al.*, would be unable to reproduce a Jahn–Teller distortion due to the two unpaired f electrons, we did not attempt to optimise a C_{2v} structure.

In order to obtain a molecular force field we carried out calculations with the following geometries: (*a*) $\Delta r(\alpha) = \Delta r(\gamma) = 0$, $\Delta\alpha = \Delta\gamma = 20°$; (*b*) $\Delta r(\alpha) = \Delta r(\gamma) = 0$, $\Delta\alpha = \Delta\gamma = -20°$; (*c*) $\Delta r(\alpha) = 12.5$ pm, $\Delta r(\gamma) = -12.5$ pm, $\Delta\alpha = \Delta\gamma = 0°$; (*d*) $\Delta r(\alpha) = \Delta r(\gamma) = 0$, $\Delta\alpha = 20°$, $\Delta\gamma = -20°$. Here (*a*) and (*b*) represent models of D_{2d} symmetry, *i.e.* a flattened and an elongated tetrahedron respectively; (*c*) and (*d*) represent models of C_{2v} symmetry. All these geometries yielded higher energies than that of the tetrahedral model. The calculated energies for (*a*) and (*b*) were used to estimate the symmetry force constant F_{22}, and those of (*c*) and (*d*) to estimate the symmetry force constants F_{33} and F_{44} respectively. The force constant F_{11} was estimated by carrying out calculations on a tetrahedral molecule in which all U–Cl bond distances had been increased by 5.0 pm.

Table 1 Normal vibrational modes of UCl_4, wavenumbers (ν) and diagonal force constants (F_{ii}). IR = Gas-phase IR absorption spectroscopy; DF = density-functional calculations; FF = force-field refinement based on IR and DF wavenumbers and r.m.s. vibrational amplitudes (*l*) from gas electron diffraction

Mode no.	IR	DF calculations		FF refinement	
i	ν_i^a	F_{ii}	ν_i^a	F_{ii}	ν_i^a
1	—	2.24^b	328	2.23^b	326.6
2	—	1.93^c	67	1.64^c	61.5
3	337.4	2.01^b	341	1.98^b	337.4
4	71.7	2.28^c	68	2.52^c	71.7

^{a} In cm^{-1}. ^{b} In 10^{-8} J m^{-1}. ^{c} In 10^{-19} J rad^{-1}.

The resulting force constants and the normal modes calculated from them under the assumption that $F_{34} = 0$ are listed under the heading DF calculations in Table 1. The values thus obtained for ν_3 and ν_4 are seen to be in good agreement with the experimental counterparts.

Gas Electron Diffraction.—If the molecular symmetry of UCl_4 is T_d the structure is described by just one independent parameter, *i.e.* the U–Cl bond distance. This parameter was refined by least-squares calculations on the intensity data along with the root-mean-square vibrational amplitudes (*l*) of both the bond distance and the non-bonded Cl···Cl distance. The refinements converged to yield $R = [\Sigma w(I_{\text{exptl}} - I_{\text{calc}})^2/\Sigma wI_{\text{exptl}}^2]^{\frac{1}{2}} = 0.079$.

Comparison of calculated and experimental intensities made it clear that the complex atomic scattering factors did not reproduce the experimental 'beat-out', *i.e.* the *s* value at which the factor $\cos[\eta_U(s) - \eta_{Cl}(s)]$ is equal to zero. This is a situation which we have often encountered in gas electron diffraction studies of compounds containing heavy elements, for instance in our recent studies of $PbCl_4$ and WCl_6.[29,37] The discrepancy was, at least partly, removed by multiplying the phase angle $\eta_U(s)$ by 1.046. New refinements reduced the *R* factor to 0.067.*

A small shoulder to the low-*r* side of the bond-distance peak in the experimental radial distribution curve suggested the presence of an impurity with a bond distance of about 200 pm. In our study of $PbCl_4$ we found the gas to contain a mole fraction *x* of 0.19(3) gaseous Cl_2.[29] The refinement of UCl_4 was therefore repeated with the mole fraction of Cl_2 (with known bond distance and vibrational amplitude) as an additional adjustable parameter: the mole fraction was found to be $x(Cl_2) = 0.21(4)$ and the *R* factor decreased to 0.0517.

We note that the presence of Cl_2 in the cell would not be detected by IR absorption spectroscopy. As already described, the spectra did, however, indicate the presence of a $SiCl_4$ impurity. When the mole fraction of such an impurity was refined along with the Cl_2 content, the resulting value was $x(SiCl_4) = 0.000(6)$; we conclude that our molecular beam is uncontaminated by silicon tetrachloride, perhaps because of the flow-through nature of the GED experiment.

The parameter values obtained by refinement of the U–Cl bond distance, two vibrational amplitudes and $x(Cl_2)$ are

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* Dr. T. G. Strand of this laboratory is writing a program for least-squares refinements which will make it possible to include three-atom scattering in the expression for the calculated molecular intensity.[26] Preliminary calculations on UCl_4 with this program indicate that inclusion of three-atom scattering neither improves the fit between experimental and calculated intensities, nor leads to perceptible changes in the refined parameters. This is in agreement with Strand's results for $PbCl_4$.[26]

Table 2 Structure parameters of UCl_4, molecular symmetry T_d. Distances (r_a), r.m.s. vibrational amplitudes (l), vibrational correction terms (D) in pm and angles (°); e.s.d.s in parentheses in units of the last digit. Refinement 1 was carried out with vibrational correction terms set to zero. Vibrational correction terms and vibrational amplitudes calculated from the best molecular force field, see Table 1. These vibrational correction terms were then used in refinement 2 (our best model)

	GED Refinement 1		FF Refinement		GED Refinement 2	
	r_a	l	l	D	r_a	l
U–Cl	250.1(3)	8.7(3)	7.9	−3.81	250.3(3)	8.9(3)
Cl···Cl	408.3(5)	34.1(10)	33.5	−0.09	402.6(5)	34.3(10)
$x(Cl_2)$	0.24(5)				0.23(4)	
R	0.0517				0.0487	

listed in Table 2 under the heading refinement 1. Since the refinements were carried out with a diagonal weight matrix, the estimated standard deviations (e.s.d.s) computed by the program have been multiplied by a factor of 2 to include the added uncertainty due to data correlation[38] and further expanded to include an estimated scale uncertainty of 0.1%.

The observed values for the normal modes ν_3 and ν_4 were assigned an accuracy of 1 cm^{-1}, the calculated values for ν_1 and ν_2 were assigned an accuracy of 10 cm^{-1}, and the two r.m.s. vibrational amplitude accuracies corresponding to three e.s.d.s, and a diagonal symmetry force field refined with the use of the program ASYM20.[32]

The resulting correction terms for thermal vibrations $D = r_\alpha - r_a$, were used to carry out refinement of a geometrically consistent r_α structure which converged to yield slightly different values for the two amplitudes. Refinement of the force field and of the structure were alternated to self-consistency to yield the force constants, normal frequencies, vibrational amplitudes and D values listed under FF refinement in Table 1 and the structure parameters and overall R factor listed under refinement 2 in Table 2. Experimental and calculated intensities and radial distribution curves are compared in Figs. 2 and 4 respectively. We find the agreement satisfactory.

We have also carried out least-squares refinements on models of symmetry lower than T_d. Thus refinement of a D_{2d} model characterised by six adjustable parameters (*versus* four for the T_d model) reduced the R factor to 0.0473. The best model thus obtained was a flattened tetrahedron with Cl–U–Cl 120(4)° (twice). The standard deviation might be taken to indicate that the improvement of the model hovers at the edge of statistical significance. We do not draw this conclusion, but instead note that the improvement of the R factor (0.0014) is less than half of that associated with the introduction of corrections for thermal motions (0.0030).

The low values obtained for the deformation frequencies ν_2 and ν_4 and the large r.m.s. vibrational amplitude of the Cl···Cl distance shows that the molecule undergoes large-amplitude deformation motion at the temperature of our experiment. The algorithms used for calculation of the molecular intensity and for computation of the vibrational correction terms are both based on a molecular model where the atoms undergo small-amplitude, harmonic vibrations. Such a model is hardly valid in the present case. We believe, therefore, that the D_{2d} model leads to an improvement of the fit simply because it introduces two more adjustable parameters which improves the fit to the slightly non-gaussian shape of the Cl···Cl distance peak in the radial distribution curve. Refinement of a C_{2v} model characterised by six adjustable parameters did not improve the fit relative to the D_{2d} model.

Thus, while the IHT group found their gas electron diffraction data to be incompatible with tetrahedral symmetry,[6] we obtain good agreement for such a model. In Fig. 5 we compare a radial distribution curve calculated from our experimental intensities with a theoretical curve calculated from the best C_{2v} model of the IHT group. Their model is obviously incompatible with our data.

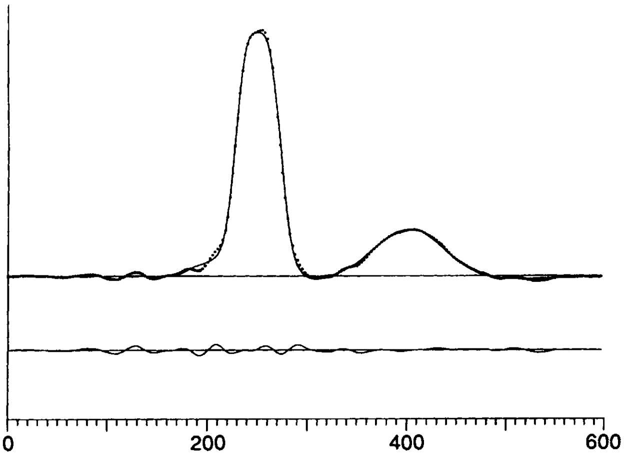

Fig. 4 Experimental radial distribution curve (·) of UCl_4 at 900 K and radial distribution curve (—) calculated for the best model of T_d symmetry (refinement 2). The difference curve is given below. Artificial damping constant, $k = 25$ pm^2

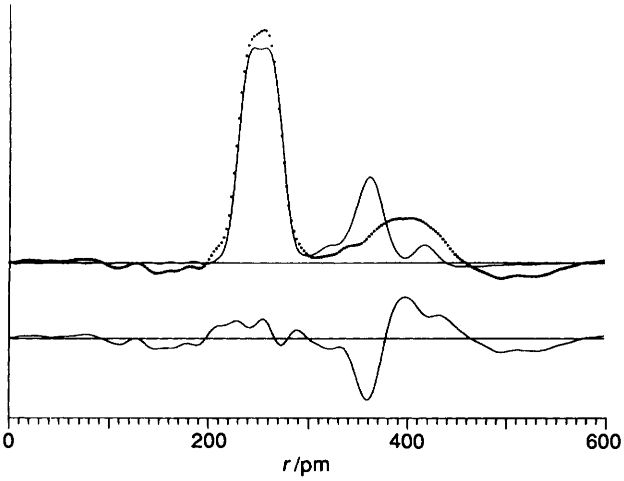

Fig. 5 Experimental radial distribution curve (·) of UCl_4 at 900 K and radial distribution curve (—) calculated for the best (C_{2v}) model of ref. 6. The difference curve is given below. Artificial damping constant, $k = 25$ pm^2

We should like to point out that while the IHT data extend only from about $s = 20$ to about 130 nm^{-1}, ours extend from $s = 22.50$ to 260.00 nm^{-1}, *i.e.* over twice the range. Secondly, while refinement of a C_{2v} model characterised by eight independent parameters to the IHT data yielded an R factor of 0.108, refinement of a T_d model characterised by three independent parameters plus the mole fraction of Cl_2 to our

Table 3 Calculation of standard entropies of $UCl_4(g)$

Molecular parameters used	
Symmetry group	T_d
Symmetry number	12
Molar mass/kg	0.379 839 7
Product of moments of inertia, $I_AI_BI_C$/kg^3 m^6	9.514×10^{-133}
Vibrational wavenumbers (cm^{-1}) with degeneracies in parentheses[a]	337.4 (3), 326.6 (1), 71.7 (3), 61.5 (2)
Electronic states (cm^{-1}) with degeneracies in parentheses[b]	0 (3), 710 (2), 1700 (3), 2500 (1), 4200 (5), 6200 (8), 7300 (3), 9100 (14)

	S°/J K^{-1} mol^{-1}	
T/K	Calc.	Exptl.[c]
298.15	409.4 ± 3.0	—
611	486.6 ± 3.0	485.0 ± 2.2
650	493.6 ± 3.0	492.5 ± 2.1
711	512.5 ± 3.0	509.5 ± 4.3

[a] From Table 1. [b] From ref. 7. [c] See text.

data yields an R factor of 0.024 for the 50 cm data which cover the same range as that of the IHT data, 0.139 for the 25 cm data which cover the wider-angle range, and 0.0487 overall.* We believe, therefore, that our results invalidate those of the previous gas electron diffraction studies.

Except for a slightly larger bond distance, the structure parameters of UCl_4 obtained in this study are in fact very similar to the corresponding parameters obtained by Bazhanov *et al.*[10] in their GED study of $ThCl_4$ at 850 K: T_d symmetry, r_a(Th–Cl) = 256.5(5), l(Th–Cl) = 7.3(6), l(Cl $\cdots$ Cl) = 31(5) pm.

Entropy Calculations.—The standard entropies of gaseous UCl_4 at 298.15, 611, 650 and 711 K were calculated from the observed bond distance, the normal modes obtained from the refined force field (Table 1) and energies and degeneracies of the electronic states listed in ref. 7, see Table 3. We believe these entropies to be accurate to within ± 3 kJ K^{-1} mol^{-1}.

Standard sublimation entropies, ΔS°, of UCl_4 at 611 and 650 K may be obtained from the Knudsen effusion measurements of Hildenbrand *et al.*,[12] the sublimation entropy at 771 K from the transpiration measurements of Cordfunke and Konings.[39] The standard entropy of solid UCl_4 at any temperature may be calculated from data given in ref. 40. Combination of solid-state and sublimation entropies yields the total experimental entropies of gaseous UCl_4 listed in Table 3. The experimental and calculated entropies are seen to be equal to well within the combined uncertainties.

The calculations reported by Hildenbrand *et al.*[12] indicated that it was necessary to assume that the symmetry number of gaseous UCl_4 was lower than 12 to obtain agreement between calculated and experimental entropies. Those calculations were, however, based on values for the doubly and triply degenerate deformation modes which were significantly higher than indicated by the IR absorption spectrum reported in this study, the r.m.s. vibrational amplitudes obtained by gas electron diffraction or the force field obtained by density-functional calculations.

Conclusion

Molecular symmetry, such as tetrahedral symmetry for the UCl_4 molecule, cannot be proven, deviations from symmetry can. At the outset of the present investigations there were two sets of observations which appeared to indicate that the symmetry must be lower than tetrahedral: gas electron diffraction data had been found to be incompatible with a tetrahedral model, and the entropy of gaseous UCl_4 calculated on the basis of a tetrahedral model and the normal frequencies observed for $PbCl_4$ was incompatible with the experimental value.

We have shown that the IR-active deformation mode of UCl_4 is found at much lower frequency than that of $PbCl_4$. We have also recorded a set of gas electron diffraction data which cover twice the range of the earlier studies, and which give twice as good a fit for a tetrahedral model as did the earlier study for a non-tetrahedral model with twice the number of adjustable parameters.

Using the two experimental frequencies of the two IR-active normal modes, estimates for the IR-inactive modes obtained from density-functional calculations, and the r.m.s. vibrational amplitudes obtained from GED, we obtain a molecular force field and frequencies for the IR-inactive modes which in turn give a calculated entropy for a T_d model which is in good agreement with the experimental counterpart.

The results obtained by density-functional calculations, gas-phase IR absorption spectroscopy, gas electron diffraction and entropy calculations are thus in good agreement with a tetrahedral model for UCl_4. The tetrahedral structure has not been proven, but earlier observations favouring models of lower symmetry have been invalidated.

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* The IHT group subtracted a high-frequency noise from their experimental molecular intensities and thus reduced the R factor in their final refinements to 0.02. Another aspect of the IHT study which tends to weaken their conclusions is that the least-squares refinements were not carried out on geometrically consistent models. Instead, the Cl $\cdots$ Cl distances spanning the α, β and γ angles were refined as three independent parameters. Using their best values for these distances spanning α and β, we calculate by geometry a value for the distance spanning γ which is 150 pm larger than the 'best value' listed in the IHT study.

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