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Molecular Structure of Gaseous $(TaF_5)_3$ by Electron Diffraction

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Gaseous tantalum pentafluoride is found to be mostly trimeric at the applied nozzle temperature of about 45 °C. Satisfactory agreement with the data is obtained for a D_{3h} symmetric molecule. Each of the three tantalum atoms is surrounded by six fluorine atoms in a distorted octahedral arrangement with structure parameters and standard deviations given by: Ta–F_a (axial) = 1.846(5), Ta–F_t (terminal) = 1.823(5), Ta–F_b (bridged) = 2.062(2) Å, ∠(F_a–Ta–F_a) = 173.1(2.1), ∠(F_t–Ta–F_t) = 96.4(1.5) and ∠(F_b–Ta–F_b) = 83.5(0.6)°.

Solid NbF_5 and TaF_5 are known to consist of tetrameric molecules,[1] and also the gaseous molecules are associated at lower temperatures according to earlier electron diffraction investigations.[2] The experimental molecular weight of gaseous NbF_5 results in an average degree of polymerization varying from 1.15 at 405 °C to 2.6 at 246 °C[3] indicating that a trimeric species may be present in the gas at lower temperatures. Recent mass-spectrometric investigations of gaseous TaF_5 indicate that trimeric molecules dominate at lower temperatures.[4]

In the present paper the results of a reinvestigation of gaseous TaF_5 by electron diffraction at a lower nozzle temperature are reported.

ESTIMATES AND CORRECTION TERMS

Initial results of the electron diffraction investigation favoured a trimeric molecule of D_{3h} symmetry. This model has 24 different distances, and therefore 24 root mean-square amplitudes of vibration, u, must be known or determined from the electron diffraction data. In addition, it is desirable to know the correction terms between the electron diffraction distances and the distances between the thermal average atomic positions, the D-values.[5]

The u- and D-values were estimated from a simple valence force field of the molecule. The force field of Tab. 1 gave a symmetry force field.[6] From this force field the transformation between symmetry coordinates and normal coordinates, the L matrix, was obtained. The computed frequencies were then replaced by experimental values[3] wherever possible, and vibrational amplitudes and D-values given in Tab. 2 were computed by means of this set of frequencies and the L matrix of the approximate force field.

ELECTRON DIFFRACTION INVESTIGATION

Tantalum pentafluoride was synthesized[8] and purified by vacuum distillation. Diffraction patterns

Table 1. Valence force constants (mdyn/Å) for D_{3h}-symmetric $(TaF_5)_3$.

Bond stretching		Angular bend		Torsion
Ta–F_a (axial)	5.0	F–Ta–F	0.1	0.03[a]
Ta–F_t (terminal)	5.5	Ta–F_b–Ta	0.01	
Ta–F_b (bridged)	2.0			

[a] Force constant for ring torsion, Ta–F_b–Ta–F_b.

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Table 2. Root-mean-square amplitudes of vibration, u (Å) and correction terms to the distances, D (Å), for $(TaF_5)_3$.

Distance[a]	D[b]	u[b]	u[c]	Group[d]
Tal–F4	−0.0162	0.0384	0.0394(15)	1
Tal–F2	−0.0181	0.0375	0.0385(15)	1
Tal–F6	−0.0040	0.0537	0.0547(15)	1
Tal···Ta7	0.0005	0.0712	0.0888(15)	2
F2···F3	−0.0192	0.1292	0.1264(35)	3
Tal···F9	0.0002	0.1590	0.1873(208)	4
Tal···F8	−0.0037	0.0917	0.1422(113)	5

[a] For numbering of the atoms see Fig. 2. [b] Computed from the force field of Table 1 modified by experimental frequencies for 20 °C. [c] Experimental values and standard deviations for refinement A of Table 4. [d] The u-values were refined in 5 groups, see text.

Table 3. Experimental conditions for the electron diffraction diagrams of TaF_5 at about 56 keV.

Camera distance (mm)	512.762	262.579
Wavelength (Å)[a]	0.05078(4)	0.05078(4)
Beam current (μA)	0.8	0.8
Nozzle temperature (°C)	45(2)	45(5)
Exposure time (s)	12–14	28–30
Blackness interval	0.15–0.35	0.15–0.35
Applied s-range (Å^{-1})[b]	3.0–18.0	7.0–31.0
Applied number of plates	6	6

[a] Determined from zinc oxide diffraction patterns. [b] Intervals of $s = 0.25$ Å^{-1} were applied.

were obtained using the improved apparatus[9] of the Moscow State University. The experimental conditions are summarized in Tab. 3.

The data were treated in the usual way[10] and $sM(s)$ molecular intensities were applied. The scattering factor of fluorine was computed[11] from an analytical representation of the potential[12] while the scattering factor of tantalum was obtained by interpolation of numerical tables.[13]

Initial least-squares refinements agreed with a trimeric molecule of D_{3h} symmetry. u- and D-values were computed for this model as explained in the previous section. The independent geometrical parameters applied are given in Tab. 4 and the geometry of the model was satisfied by correcting the electron diffraction distances by the computed D-values.

Table 4. Results of final least-squares refinements for TaF_5.

Parameter[a]	A[b]	B[b]
R(Tal–F4)	1.846(5)	1.849(6)
R(Tal–F2)	1.823(5)	1.813(6)
R(Tal–F6)	2.062(2)	2.076(3)
∠(F4–Tal–F5)	173.1(2.1)	173.0(2.9)
∠(F2–Tal–F3)	96.4(1.5)	94.7(2.2)
∠(F18–Tal–F6)	83.5(0.6)	87.0(0.7)
K_1	0.788(8)	0.774(11)
K_2	0.772(15)	0.748(18)
R_f	7.43	9.82

[a] Independent parameters (except R_f) for least-squares refinements applying a nondiagonal weighting matrix (Ref. 15) and keeping the intensities from each of the two camera distances separated. K_1 and K_2 are the scale factors for the data of the long and short camera distances, respectively. R_f is a weighted agreement factor in percent according to eqn. 16 of Ref. 15. Structure parameters for thermal average atomic positions are given. [b] The two refinements are identical except that contribution from triatomic scattering was added to the theoretical intensities in A.

The root mean-square amplitudes of the 24 different distances were assigned to one of five different groups. All the u-values belonging to one group were regarded as one independent parameter thereby getting the same shifts and standard deviations in the least-squares refinements. The refinements were started from the computed u-values. The different groups are indicated in Tab. 2. Group 1 included the u-values of the three bonded Ta–F distances and the Ta···Ta u-value was an independent parameter as the only member of group 2. Group 3 included the u-values of seven distances less than 3.9 Å, group 4 seven u-values of distances between 3.9 and 5.1 Å, and group 5 those of the six longest distances of the model. The u-values obtained in this way for refinement A of Tab. 4 are included in Tab. 2.

The two least-squares refinements, the results of which are given in Tab. 4, are identical except that the theoretical intensities of A also included contributions from intramolecular triatomic scattering computed by modifying eqn. 23 of Ref. 14 by $s/I_T^B(s)$, where $I_T^B(s)$ is the theoretical background, and applying values for the thermal damping functions estimated from the computed u-values. Only contributions from triangles deviating at least 10° from linearity and containing at least one Ta atom

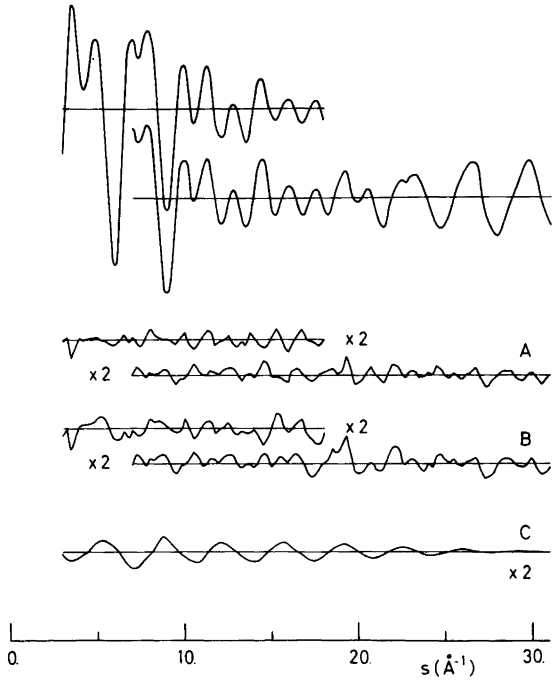

Fig. 1. $sM(s)$ average experimental intensities of $(TaF_5)_3$. The curves A and B give the differences between the experimental intensities and the intensities computed from the parameters of Table 4, A and B, respectively. Curve C illustrates the computed contribution from triatomic scattering.

were included. In this way contributions from 104 different triangles were calculated, representing 1782 of the possible 4896 terms of the triple sum over all different atoms of the molecule.

The molecular intensities are illustrated in Fig. 1 and Fig. 2 gives the radial distribution function of $(TaF_5)_3$. Correlation coefficients for the final refinement are given in Tab. 5.

DISCUSSION

Referring to the experimental radial distribution function of Fig. 2, the information about the degree of association of gaseous TaF_5 is found mostly in the shape of the peak due to the nonbonded Ta···Ta distance(s) and in the area of this peak relative to the areas of the peaks of the bonded Ta–F distances. The ratios of the numbers of bonded Ta–F to nonbonded Ta···Ta distances are for the dimeric, trimeric and tetrameric species 12/1, 18/3 and 24/6, and an incorrect degree of association should show up as discrepancies in the areas of these peaks. In addition a tetrameric species should have two types of nonbonded Ta···Ta distances. The agreement for the trimeric model of D_{3h} symmetry is satisfactory and very much of other species cannot be present. A refinement on a mixture of the tri- and tetrameric species converged to 99(2) % of the trimeric form.

The conclusion is that gaseous TaF_5 at the applied nozzle temperature mostly consists of trimeric molecules. The best estimate of the structure parameters for a model of D_{3h} symmetry is given in Tab. 4, A. The axial Ta–F distances are longer than the terminal ones by 0.023(11) Å and the axial atoms are distorted toward the threefold axis as shown in Fig. 2.

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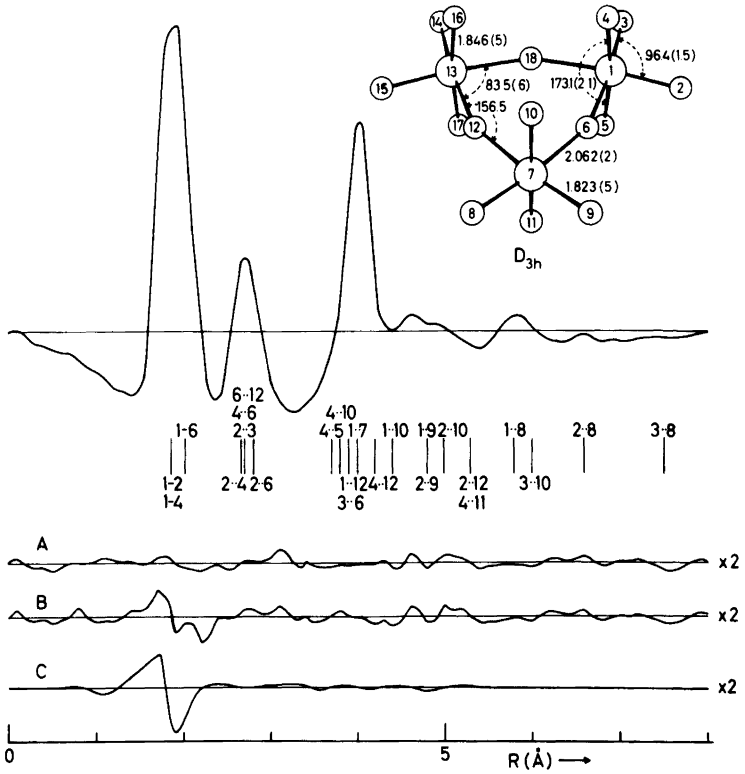

Fig. 2. Experimental radial distribution function of $(TaF_5)_3$ for a damping function of $\exp(-0.003\ s^2)$. Computed intensities were added inside $s = 3$ Å^{-1}. The curves A and B give the differences between the experimental radial distribution function and the functions computed for the parameters of Table 4, A and B, respectively. Curve C gives the Fourier transform of the intensities due to triatomic scattering for the same damping function, as applied in computing the radial distribution function.

Table 5. Correlation coefficients with absolute value greater than 0.5 for the parameters of least-squares refinement A of Table 4.

	R(Tal–F4)	R(Tal–F2)	R(Tal–F6)	∠(F4–Tal–F5)
R(Tal–F2)	−0.952			
∠(F2–Tal–F3)				0.736
∠(F18–Tal–F6)			0.943	
$u(1)^a$	−0.680	0.643		
$u(4)^a$				0.588

[a] Group Nos. 1 and 4 of u-values, see Table 2 and text.

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