# Molecular Structure of Molybdenum Tetrafluoride Oxide Studied by Gas Electron Diffraction

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The molecular structure of molybdenum tetrafluoride oxide was determined to be square-pyramidal by a sector-microphotometer method of gas electron diffraction. The following molecular parameters were obtained by a least-squares method: $r_g$(Mo–F)=1.836±0.003 Å, $r_g$(Mo–O)=1.650±0.007 Å, and $r_g$(F···F(s))=2.522± 0.005 Å. The molecular structure is similar to those of $WCl_4O$ and $MoCl_4O$, but significantly different from those of $XeF_4O$ and $IF_5$. The molecular intensities calculated using the TFD or RHFS phase angle for molybdenum atom were in disagreement with the observed ones.

The molecular structures of $WCl_4O$,[1] $MoCl_4O$,[2] $XeF_4O$,[3,4] $IF_5$,[4,5] $BrF_5$,[4] and $ClF_5$[4] were reported to be square-pyramidal in gas phases, but the oxygen-metal-chlorine angles in $WCl_4O$ and $MoCl_4O$ differ significantly from the corresponding angles in the other compounds. Although the $MoF_4O$ molecule in the solid state is octahedral in consequence of bridging through fluorine atoms,[6] the molecule in the gas phase is monomeric with $C_{4v}$ symmetry as predicted from spectroscopic studies.[6–8] The present study was undertaken in order to determine the structure of gaseous $MoF_4O$ by means of gas electron diffraction. It is interesting to compare the molecular structure of $MoF_4O$ with those of $MoCl_4O$ and other square-pyramidal molecules. Seip and Seip noted from the electron diffraction analysis of $MoF_6$[9] that the observed cut-off point for Mo–F pair disagrees with the theoretical value. This problem was also checked in the present study.

## Experimental

The chlorine atoms in molybdenum tetrachloride oxide which was prepared by the method described before[10] were substituted with fluorine atoms by the reaction with anhydrous hydrogen fluoride.[11] The sample was purified by repeated sublimations *in vacuo*. It was vaporized at 70—80 °C, and electron-diffraction photographs were taken with an $r^3$-sector at the camera distance of 144 mm. The accelerating voltage was 40 kV, the exposure time 30 s, and the electron-beam current 0.8 μA. The pressure of the diffraction chamber was below $3\times10^{-5}$ Torr during a photographic exposure. The electron wavelength was calibrated by gold powder patterns. The lattice constant of gold was calibrated by means of X-ray diffraction, and checked by electron diffraction studies of thallium chloride[12] and carbon disulfide.[13] Photographs were recorded on Fuji process hard plates, and the photographic densities of four plates were measured with a digital microphotometer at intervals of 0.4 mm. The intensities of each plate were used independently for the structure analysis. The electron diffraction unit and digital microphotometer used in the present study were described elsewhere.[14]

## Analysis

Intensities were leveled by the theoretical background which was calculated by using the elastic scattering factors of Kimura *et al.*[15] and the inelastic scattering factors of Cromer and Mann.[16] The leveled intensities were obtained in a range $s$=5.3—32.0 Å$^{-1}$ at intervals $\Delta s=\pi/10$.

The radial distribution curve is shown in Fig. 1. The $N_{ij}$ functions which fit $\mu_{ij}$[1,17] in a whole range of scattering angle were as follows;

$$N_{Mo-F} = 1.097 + 0.104\exp(-0.0034\,s^2)$$
$$N_{Mo-O} = 1.118 + 0.153\exp(-0.0089\,s^2)$$
$$N_{F\cdots F} = 1.355 + 0.713\exp(-0.0057\,s^2)$$
$$N_{F\cdots O} = 1.380 + 0.814\exp(-0.0072\,s^2)$$

The radial distribution curve suggests that the molecular structure of $MoF_4O$ is square-pyramidal.

The index of resolution, $r$(Mo–F), $r$(Mo–O), $r$(F···F(s)), and five root-mean-square amplitudes $l$(Mo–F), $l$(Mo–O), $l$(F···F(s)), $l$(F···F(l)), and $l$(F···O) were determined by the least-squares calculations[2,18,19] with the assumption of $C_{4v}$ symmetry. Asymmetry parameters for bonded distances were estimated by a diatomic molecule approximation[20] to be $1.2\times10^{-6}$ and $0.6\times10^{-6}$ Å$^3$ for Mo–F and Mo–O, respectively. The parameter, $a$, in the Morse function was assumed to be 2.0 Å$^{-1}$. The asymmetry parameters for non-bonded distances were ignored.

At the first stage of analysis a large difference between the observed and theoretical molecular intensities was found in the range $s$=22—32 Å$^{-1}$, as shown in Fig. 2. The cut-off point for Mo–F pair is observed at $s$=23.2 ±0.6 Å$^{-1}$, but the theoretical value is $s$=27.0 Å$^{-1}$.

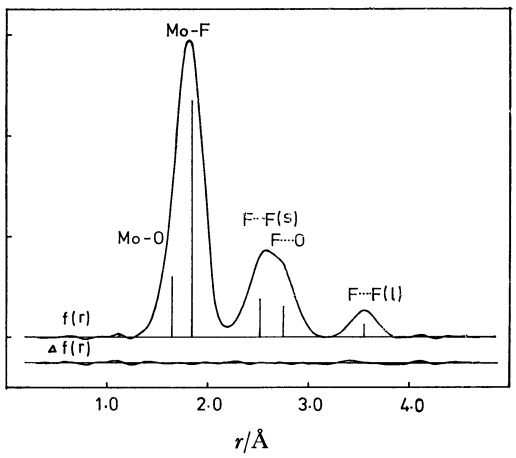


Fig. 1. Experimental radial distribution, $f(r)$, and the difference between the experimental and theoretical ones, $\Delta f(r)$. A damping function of $\exp(-0.0020\,s^2)$ was used.

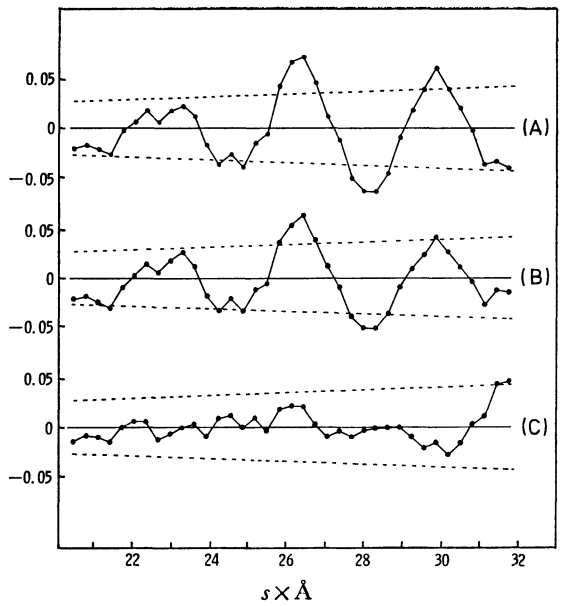


Fig. 2. The observed minus theoretical molecular intensities. The observed values were an average of intensities from four plates, and the theoretical ones in (A), (B), and (C) curves were calculated by using parameters of (A), (B), and (C) in Table 1, respectively. The broken curves show the limits of error in the $sM(s)$.

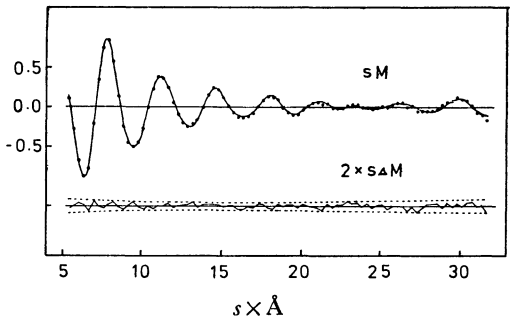


Fig. 3. Observed and theoretical molecular intensities. Typical observed values are shown in dots, and the best-fit theoretical ones are shown in the solid curve. The lower solid and broken curves represent the residuals and the limits of error, respectively, in the $sM(s)$.

The phase angles, $\eta$, obtained from the Thomas-Fermi-Dirac (TFD) and Hartree-Fock (HF) potentials[15] were used for molybdenum and fluorine atoms, respectively. The phase angle from the relativistic Hartree-Fock-Slater (RHFS) potential[21] was also used for molybdenum atom, and the theoretical cut-off point is $s=26.1$ Å$^{-1}$. The disagreement between the observed and theoretical molecular intensities may be due to the uncertainty in molybdenum phase angle, $\eta_{Mo}$, used in the anlysis. The theoretical cut-off point for Pd–F pair calculated using the TFD phase angle for palladium atom is $s=23.7$ Å$^{-1}$, in agreement with the observed value for the Mo–F pair. Since the absolute value of atomic scattering factor, $|f|$, for molybdenum atom had a negligible effect on molecular parameters, the analysis using $|f_{Mo}|$ and $\eta_{Pd}$ for molybdenum atom was carried out, and the calculated intensities gave the best fit to the observed ones. The results of least-squares analyses, where the TFD and RHFS phase angles of molybdenum and the TFD phase angle of palladium were used, are listed in Table 1.

Table 1. Results of least-squares analyses (in Å)

| | (A)[b] | (B)[b] | (C)[b] |
|---|---|---|---|
| $r_g$(Mo-F) | 1.838 (2) | 1.836 (1) | 1.836 (1) |
| $r_g$(Mo-O) | 1.654 (7) | 1.649 (6) | 1.650 (5) |
| $r_g$(F···F(s)) | 2.524 (4) | 2.519 (4) | 2.522 (3) |
| $l$(Mo-F) | 0.059 (3) | 0.057 (3) | 0.046 (3) |
| $l$(Mo-O) | 0.045(21) | 0.040(16) | 0.034(10) |
| $l$(F···F(s)) | 0.098 (8) | 0.100 (7) | 0.098 (5) |
| $l$(F···F(l)) | 0.084(14) | 0.086(12) | 0.084 (9) |
| $l$(F···O) | 0.101(10) | 0.104 (8) | 0.101 (7) |
| $R$[a] | 0.978(36) | 1.019(43) | 0.979(38) |

Estimated random errors ($2.5\sigma$) are shown in parentheses ($\times 10^3$). a) The index of resolution, $R$, is dimensionless. b) (A), (B), and (C) are the results of analyses using TFD $f_{Mo}$, RHFS $f_{Mo}$, and TFD $|f_{Mo}|$ and $\eta_{Pd}$, respectively, for molybdenum atom.

Table 2. Distances and mean amplitudes (in Å)

| | $r_g$ | $l$ |
|---|---|---|
| Mo-F | 1.836±0.003 | 0.046±0.013 |
| Mo-O | 1.650±0.007 | 0.034±0.015 |
| F···F(s) | 2.522±0.005 | 0.098±0.005 |
| F···F(l) | 3.563±0.008 | 0.084±0.009 |
| F···O | 2.752±0.009 | 0.101±0.008 |
| ∠OMoF | 103.8±0.6° | |
| ∠FMoF | 86.7±0.3° | |

The final results of the analysis are given in Table 2, where parameter values were obtained from the analysis using palladium phase angle for molybdenum atom. Random errors were given by 2.5 times the larger of $\sigma_1$ and $\sigma_2$.[19,22] The uncertainty in phase angle for molybdenum atom was taken into account as systematic errors in bond distances and amplitudes. The error in lattice constant of a reference material (0.06%) and the errors in measurements of diffraction patterns of the reference (0.09%) and of the camera distance (0.04%) were also taken into account as systematic errors in bond distances. The correlation matrix[23] is given in Table 3, and the best-fit theoretical intensity curve is shown in Fig. 3.[24] The least-squares calculations were carried out by use of a FACOM 230-60 computer at the Nagoya University Computing Center.

## Discussion

The phase angle for molybdenum was not sensitive to the distances of the atomic pairs relating to molybdenum, but was considerably sensitive to the amplitudes as shown in Table 1. The Mo–F and Mo–O amplitudes obtained using $\eta_{Pd}$ in place of $\eta_{Mo}$ were in fair agreement with 0.040 and 0.035 Å calculated from the Mo–F and Mo–O vibrational frequencies,[7,25] respectively. The analysis using $\eta_{Pd}$ gave the smallest

Table 3. Correlation matrix for molecular parameters of $MoF_4O$[a)]

| | $r$(Mo-F) | $r$(Mo-O) | $r$(F···F(s)) | $l$(Mo-F) | $l$(Mo-O) | $l$(F···F(s)) | $l$(F···F(1)) | $l$(F···O) | $R$ |
|---|---|---|---|---|---|---|---|---|---|
| $r$(Mo-F) | 1.0 | 0.13 | 0.38 | 0.05 | −0.26 | 0.04 | 0.02 | 0.08 | 0.13 |
| $r$(Mo-O) | | 1.0 | 0.54 | −0.11 | −0.07 | −0.21 | −0.07 | −0.12 | −0.50 |
| $r$(F···F(s)) | | | 1.0 | −0.16 | −0.16 | −0.05 | −0.06 | 0.03 | −0.36 |
| $l$(Mo-F) | | | | 1.0 | 0.34 | 0.24 | 0.09 | 0.19 | 0.65 |
| $l$(Mo-O) | | | | | 1.0 | 0.06 | 0.01 | 0.04 | 0.15 |
| $l$(F···F(s)) | | | | | | 1.0 | 0.06 | 0.62 | 0.39 |
| $l$(F···F(1)) | | | | | | | 1.0 | 0.04 | 0.15 |
| $l$(F···O) | | | | | | | | 1.0 | 0.30 |
| $R$ | | | | | | | | | 1.0 |

a) The elements are defined as $\rho_{ij}=B_{ij}^{-1}/(B_{ii}^{-1}\times B_{jj}^{-1})^{1/2}$.

standard deviations for parameters. The cut-off point for Mo–F pair, $s=23.2$ Å$^{-1}$, obtained at the accelerating voltage of 40 kV in the present study is estimated to be equivalent to about 22 Å$^{-1}$ at 35 kV by use of the formula.[26)] This value is in good agreement with 22.2±0.4 Å$^{-1}$ from the experiment of $MoF_6$ at 35 kV.[9)]

The molecular structure of $MoF_4O$ is square-pyramidal in the gas phase, but in the crystal state[6)] it is distorted by bridging of fluorine to another molecule and forms a nearly octahedral arrangement around a molybdenum atom. The Mo–F and Mo–O distances in the crystal, 1.81—1.84 and 1.62—1.65 Å, respectively, are in agreement with the corresponding distances in the gas phase. However, the average OMoF (terminal) angle in the crystal, 100.4°, is a little smaller than that in the gas phase because of an octahedral arrangement.

The gaseous $MoF_4O$ has the same structure as the gaseous $WCl_4O$[1)] or $MoCl_4O$,[2)] but it is apparently distinguished from those of $XeF_4O$[3,4)] and $IF_5$[4,5)] with respect to the XMY angle, where M is a central atom. The angles of the latter molecules are about 90° or less, and can be explained by considering the repulsions between bonding electron pairs and a nonbonding electron pair of central atoms.[27)]

There are only small differences between $MoF_4O$ and $MoCl_4O$ with respect to Mo–O distance and OMX angle. However, the Mo–F distance, 1.836±0.003 Å, is shorter than the Mo–Cl distance, 2.279±0.003 Å, by about 0.44 Å. The force constant for the Mo–O bond in $MoF_4O$ is estimated to be 8.6 mdyn/Å from the frequency of Mo–O stretching vibration in the gas phase[7)] and is nearly equal to that in $MoCl_4O$, 8.29 mdyn/Å.[2)] The distance and force constant for the Mo–O bond in gaseous $MoF_4O$ give a good fit to the correlation curve between them,[28)] and its bond order is estimated to be 3. The Mo–F distance in $MoF_4O$ is greater than that in $MoF_6$ (1.820±0.003 Å[9)]) by about 1%. The lengthening of the Mo–F distance may be interpreted as the effect of the Mo–O multiple bond.

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