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# Studies on the Failure of the First Born Approximation in Electron Diffraction

## VI. Ruthenium Tetraoxide

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Gaseous ruthenium tetraoxide has been studied by electron diffraction. Three sets of theoretical complex scattering amplitudes, $f(s) = |f(s)|\exp[i\eta(s)]$, have been considered. It was found experimentally that $(\eta_{Ru}-\eta_O) = \pi/2$ at $s = 20.2$ Å$^{-1}$ with an estimated standard deviation of 0.40 Å$^{-1}$. The corresponding theoretical $s$ values are: 21.5 Å$^{-1}$, 21.84 Å$^{-1}$, and 21.39 Å$^{-1}$.

No evidence is found for deviation from $T_d$ symmetry. The bond length is $1.705_8$ Å with an estimated standard deviation of 0.003 Å. The root-mean-square amplitude of vibration ($u$) for the Ru–O bonds is $0.036_5$ Å with a standard deviation of 0.0025 Å. This result is in good agreement with the value calculated from spectroscopic data.

Seven compounds ($UF_6$,[1] $OsO_4$,[2] $TeF_6$,[3] $MoF_6$,[4] $WF_6$,[4] $Mo(CO)_6$,[5] and $W(CO)_6$[5]) have already been studied in this series of investigations. The structural parameters (distances and $u$ values) and the $s$ values ($s_{\pi/2}$) corresponding to $(\eta_M-\eta_X) = \pi/2$ (M = metal, X = C, O, or F) have been determined for these compounds. This study was initiated mainly because we found $s_{\pi/2}$ for $\eta_{Os}-\eta_O$ (in $OsO_4$) to be greater than all the theoretical $s_{\pi/2}$ values. At least one of the theoretical $s_{\pi/2}$ values was greater than the experimental result in all the other compounds we have investigated.

The investigation of $RuO_4$ has been carried out in the same way as the previous investigations. The modified molecular intensity may be expressed by[6]

$$I(s) = \text{const} \sum_{i\neq j}\sum \alpha_{ij} g_{ij/kl}(s) \exp(-\tfrac{1}{2} u_{ij}^2 s^2) \frac{\sin[(r_{ij}-\varkappa_{ij}s^2)s]}{r_{ij}} \quad (1)$$

where

$$g_{ij/kl}(s) = \frac{|f_i||f_j|}{|f_k||f_l|} \cos(\eta_i-\eta_j) \quad (2)$$

The meaning of the symbols have been given previously.[1,2] As in the investigation of $OsO_4$ we used $|f_k| = |f_l| = |f_O|$. If $T_d$ symmetry is assumed and $\alpha_{ij} = 1$ and $\varkappa_{ij} = 0.0$, we may write:

$$I(s) = \text{const}(4\ g_{RuO/OO}(s)\ \exp(-\tfrac{1}{2}u_1^2\ s^2)\ \sin(r_1 s)/r_1 + 6\ \exp(-\tfrac{1}{2}u_2^2\ s^2)\ \sin(r_2 s)/r_2) \quad (3)$$

The changes in the notation should be self-explanatory.

Three sets of scattering amplitudes were considered in this investigation. Two of these sets have been applied before and were denoted by set II [7] and set III [8] (see Ref. 4). The last set, which will be denoted by set IV, has been obtained by the same computing program as set III. However, while a Thomas-Fermi-Dirac potential [9] was used for Ru in the calculation of set III, the Ru potential applied in set IV has been calculated by D. Lieberman *et al.*[10] using Dirac's relativistic equation in a self-consistent field calculation.[11] The exchange correction was as suggested by W. Kohn and L. J. Sham.[12] This correction is somewhat smaller than the one used in Ref. 11.

## EXPERIMENTAL

The sample of $RuO_4$ was synthetised from metallic Ru.[13] Diffraction photographs were taken with a nozzle temperature of about 15°C. Three sets of plates were used taken with, respectively, 48.10 cm, 19.39 cm, and 12.66 cm between nozzle and plate. The corresponding $s$ ranges are approximately 1.5—20.0 Å$^{-1}$, 7.0—44.0 Å$^{-1}$, and 15.0—60.0 Å$^{-1}$. The accelerating potential was $\approx$ 35 kV giving an electron wave length of 0.06473 Å. Four plates were selected out of the six plates in each set. The plates were photometered, and the intensity data were corrected in the usual way.[14]

## STRUCTURE ANALYSIS

Four observed intensity curves were obtained. Each of these were calculated using the data from one plate for each camera distance. Three of the intensity curves covered the $s$ range 1.50—58.25 Å$^{-1}$, while the last one covered 1.50—50.00 Å$^{-1}$, since the noise above $s = 50$ Å$^{-1}$ was higher in this case. Least-squares refinements of the molecular parameters were carried out with the scattering amplitudes denoted by set III. The theoretical intensity was calculated according to eqn. (3). Five parameters were refined independently, *i.e.* two distances, two $u$ values, and the scale factor. The estimates of the distances and $u$ values and their standard deviations obtained by the least-squares refinements are shown in Table 1 a, b, c, and d. The values in column e are the mean values and the standard deviations calculated from the results in the previous columns giving the results equal weights. The standard deviations for $r_1$ and $u_1$ are appreciably higher in column e than in the other columns. This is in agreement with the general experience, though the difference is somewhat greater than in most of the compounds studied previously. The standard deviation for $r_2$ in column e is slightly larger than the corresponding values in the other columns. It is seen that the $r_2$ distance given in column b is rather large, while the other three values are nearly equal.

*Table 1.* Results of least-squares calculations on four observed intensity curves (columns a—d), and mean values and standard deviations obtained from these results (e). (The standard deviations for the mean values in e are ½ times the values given in this column) The parameters ($r_g(1)$ and $u$) are in Å. The standard deviations are in $10^{-4}$ Å. The intensity data were in the $s$ ranges 1.50—58.25 Å$^{-1}$ (columns a, b, and c) or 1.50—50.00 Å$^{-1}$ (column d). The constants in the weight function were:[1] $s_1 = 5.0$ Å$^{-1}$, $s_2 = 30.0$ Å$^{-1}$, $W_1 = 0.10$, and $W_2 = 0.005$.

| | a | b | c | d | e |
|---|---|---|---|---|---|
| $r_1$ | $1.707_5$ (9) | $1.705_7$ (10) | $1.702_8$ (14) | $1.701_8$ (10) | $1.704_5$ (26) |
| $r_2$ | $2.785_6$ (48) | $2.799_2$ (49) | $2.787_2$ (53) | $2.787_1$ (55) | $2.789_3$ (63) |
| $u_1$ | $0.032_3$ (9) | $0.035_9$ (10) | $0.041_3$ (12) | $0.034_5$ (10) | $0.036_0$ (38) |
| $u_2$ | $0.064_2$ (41) | $0.065_2$ (41) | $0.067_4$ (44) | $0.072_6$ (46) | $0.067_4$ (37) |

*Table 2.* Least-squares results obtained from the three plate sets. The mean values and the standard deviations for the mean values have been calculated from four observations.

| | a | b | c |
|---|---|---|---|
| $s$ range (Å$^{-1}$) | 1.5—18.25 | 7.0—42.25 | 16.5—58.25 |
| $s_1$ (Å$^{-1}$) | 5.0 | 10.0 | 21.0 |
| $s_2$ (Å$^{-1}$) | 10.0 | 25.0 | 30.0 |
| $W_1$ | 0.05 | 0.05 | 0.05 |
| $W_2$ | 0.01 | 0.008 | 0.008 |
| $r_1$ (Å) | $1.704_8$ (30) | $1.706_3$ (18) | $1.704_0$ (15) |
| $r_2$ (Å) | $2.788_4$ (66) | $2.791_2$ (32) | $2.792_7$ (44) |
| $u_1$ (Å) | $0.054_4$ (70) | $0.033_6$ (22) | $0.035_5$ (18) |
| $u_2$ (Å) | $0.068_1$ (64) | $0.062_3$ (28) | $0.076_1$ (42) |

Table 2 gives the results obtained by least-squares refinements using the data from, respectively, the long (column a), the intermediate (column b), and the short (column c) camera distance. The mean values and the standard deviations for the mean values calculated from four observed results have been given. The agreement between the results from the different camera distances is in general satisfactory. $u_1$ is greater in column a than in the other columns, but this value is very sensitive to errors in the scattering amplitudes and to changes in the background. The difference between the values for $u_2$ in the columns b and c is rather large compared to the given standard deviations. However, it should be remembered that the standard deviations are based on only four observations.

The average of the four observed intensity curves was found and used in further calculations. The results in Table 3, column a, were obtained by using the intensity data in the $s$ range 1.50—50.25 Å$^{-1}$ and otherwise the same conditions as before.

*Table 3.* Various results (in Å) for the parameters in $RuO_4$. The distances obtained by least-squares refinements are given as $r_g(1)$. The standard deviations are in $10^{-4}$ Å.

| | a | b | c | d |
|---|---|---|---|---|
| $r_1$ | $1.704_6$ (7) | $1.704_1$ (7) | $1.704_5$ (6) | $1.706_9$ (15) |
| $r_2$ | $2.788_6$ (35) | $2.788_5$ (41) | $2.788_4$ (30) | $2.788_6$ (35) |
| $u_1$ | $0.035_7$ (7) | $0.036_5$ (6) | $0.037_1$ (6) | $0.035_7$ (7) |
| $u_2$ | $0.067_4$ (29) | $0.067_7$ (34) | $0.068_8$ (25) | $0.067_5$ (29) |

| | e | f | g | h |
|---|---|---|---|---|
| $r_1$ | $1.704_6$ (7) | $1.704_7$ (7) | $1.704_5$ | |
| $r_2$ | $2.788_6$ (35) | $2.788_3$ (28) | $2.787_9$ | |
| $u_1$ | $0.035_7$ (7) | $0.035_3$ (7) | | 0.0372 |
| $u_2$ | $0.066_7$ (37) | $0.065_1$ (30) | $0.065_8$ | 0.0750 |

[a] $\alpha = 1.0$ and $\varkappa = 0.0$ for both distances. The intensity data in the $s$ range 1.50–50.25 Å$^{-1}$ and the third set of scattering amplitudes were applied. The constants in the weight function were $s_1 = 5.0$ Å$^{-1}$, $s_2 = 30.0$ Å$^{-1}$, $W_1 = 0.100$, and $W_2 = 0.005$.

[b] All the observations were given the same weight. All other conditions as in a.

[c] The fourth set of scattering amplitudes was applied. All other conditions as in a.

[d] $\varkappa_1$ was refined. All other conditions as in a. Result: $\varkappa_1 = 2.0 \times 10^{-6}$ ($1.1 \times 10^{-6}$) Å$^3$.

[e] $\alpha_1$ was refined. All other conditions as in a. Result: $\alpha_1 = 1.018$ (0.055).

[f] The experimental $g$ function (*cf.* eqn. (4)) was applied and scaled by refining $\alpha_1$. The intensity data in the $s$ range 1.5–40.0 Å$^{-1}$ were applied. The weight function was as in a.

[h] Results obtained from RD curves.

[g] $u$ values obtained from spectroscopic data.[15]

The results in Table 3, column b, were obtained using a considerably different weight function. (All the observations were now given the same weight). The shift in the parameter $u_1$ is slightly larger than the corresponding standard deviation, while the shifts in the other parameters are smaller than the standard deviations.

The fourth set of scattering amplitudes was then applied in a least-squares calculation. The results are given in column c. (The weight function used to obtain the results in column a was applied in this refinement and in the refinements to be described below). The $u_1$ value given in column c is somewhat higher than the value given in column a. The shifts in the other parameters are quite small compared to the corresponding standard deviations. The standard deviations in column c are slightly smaller than those given in column a indicating that the agreement between experimental and theoretical intensities is improved when the fourth set of scattering amplitudes is applied. Further evidence for preferring the fourth set will be given in the next section.

Fig. 1 shows the average experimental intensity curve (A) and the theoretical curve (B) calculated according to eqn. (3) with the third set of scattering amplitudes and the parameters in Table 3, column a. Curve C shows the

difference between the curves A and B. The difference between the experimental curve (A) and the theoretical curve calculated with the fourth set of scattering amplitudes and the parameters given in Table 3, column c, is shown by curve D. The difference curve D is seen to be somewhat better than curve C in the $s$ region 10.0—30.0 Å$^{-1}$.

As in the previous investigations we have refined the asymmetry constant for the bond distance ($\varkappa_1$). (See Table 3, column d). The value obtained for $\varkappa_1$ is not unreasonable, but the standard deviation for this parameter is large.

The results in the following column (e) were obtained by refining $\alpha_1$ in addition to the distances and $u$ values. ($\varkappa_1 = 0.0$ was kept constant). If the present theory gives a sufficiently good approximation to the intensity, $\alpha$ should be unity. The result obtained is very close to the expected value.

We have also carried out least-squares calculations using the experimental $g$ function described in the next section. The function was scaled by refining $\alpha_1$. The intensity data in the $s$ range 1.5—40.0 Å$^{-1}$ were applied. The results are given in Table 3, column f. The parameters are close to the values given in column a.

The column g (Table 3) shows the results obtained from radial distribution (RD) curves. The RD functions shown in Fig. 2 have been calculated from the intensity curves in Fig. 1 using an artificial damping constant $k = 0.0009$ Å$^2$. An envelope has been subtracted from the experimental curve to compensate for the lack of data in the $s$ range 0.0—1.25 Å$^{-1}$. The theoretical curve was calculated using intensity data in the $s$ range 0.0—50.25 Å$^{-1}$. The value for

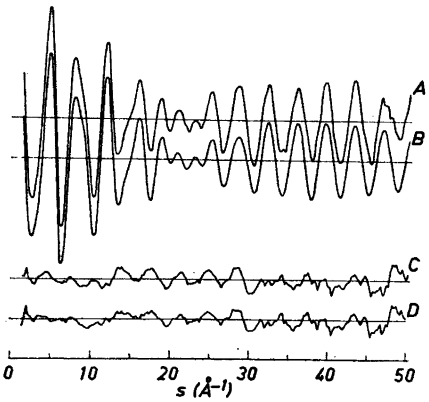


*Fig. 1.* Experimental (A) and theoretical (B) intensity functions. The theoretical curve was calculated according to eqn. (3) with the third set of scattering amplitudes and the parameters given in Table 3, column a. Curve C shows the difference between A and B, while D shows the difference between the experimental curve and the theoretical curve calculated with the fourth set of scattering amplitudes and the parameters in Table 3, column c.

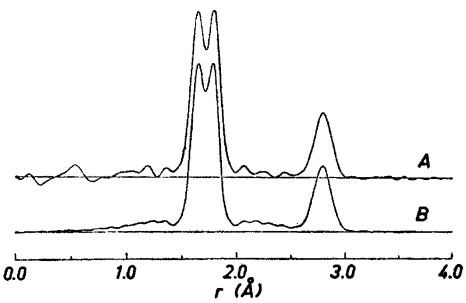


*Fig. 2.* Experimental (A) and theoretical (B) RD curves calculated with an artificial damping constant $k = 0.0009$ Å$^2$.

$r_1$ given in column g corresponds to the mean of the positions of the maxima of the double peak shown in Fig. 2 (curve A). The values given for $r_2$ and $u_2$ are the mean of the results obtained from the RD curves calculated with $k = 0.0009$ Å$^2$ (Fig. 2) and $k = 0.0020$ Å$^2$, $r_2$ corresponds to the maximum of the outer peak. The results in column g are seen to be in good agreement with the values obtained by least-squares refinements on the intensity curve.

The differences ($\Delta r$) between the positions of the maxima of the double peaks have been found from the experimental and the two theoretical RD curves calculated with $k = 0.0009$ Å$^2$. The results were:

| | $\Delta r$ (Å) |
|---|---|
| Experimental | $0.144_6$ |
| Theoretical (third set of scattering amplitudes) | $0.131_4$ |
| » (fourth » » » » ) | $0.139_2$ |

The theoretical values are both slightly smaller than the experimental result; the fourth set gives the best agreement.

Vibrational amplitudes have been calculated from spectroscopic data by Cyvin *et al.*[15] Their results are given in Table 3, column h. The $u$ values in column c (obtained by using the fourth set of scattering amplitudes) agree slightly better than the results in column a with the spectroscopic $u$ values.

From the values in Table 1, 2, and 3 we give as our final results:

$r_g$ (Ru—O): $1.705_8$ (0.0030) Å
$r_g$ (O···O): 2.790 (0.0050) »
$u$ (Ru—O): $0.036_5$ (0.0025) »
$u$ (O···O): 0.068 (0.0050) »

The standard deviations given in parentheses include an estimate of systematic errors. For a rigid molecule with $T_d$ symmetry one should have $r$(O ··O) = $1.633 \times r$(Ru—O) = 2.786 Å. The shrinkage effect in $RuO_4$ has been given by Cyvin *et al.*[15] as 0.002 Å. Thus we obtain $r_g$(O...O) = 2.784 Å from the bond length, which is slightly smaller than the result obtained by refining this parameter independently.

## SCATTERING AMPLITUDES

Experimental values for the function

$$g^{\text{exp}}_{\text{RuO/OO}}(s) = \frac{(|f_{\text{Ru}}|\ |f_{\text{O}}|)_{\text{exp}}}{(|f_{\text{O}}|^2)_{\text{theor}}} \cos\ (\eta_{\text{Ru}} - \eta_{\text{O}})_{\text{exp}} \qquad (4)$$

have been obtained as described previously.[3,4] Four experimental $g$ functions were obtained from the four observed intensity curves described in the previous section. The average calculated from these functions is shown in Fig. 3 (curve A). The two other curves show theoretical $g$ functions. The dotted curve (B) was obtained from the third set and the dashed curve (C) from the fourth set of scattering amplitudes. The scale of the experimental curve was found by refining $\alpha_1$ (*cf.* Table 3, column f). The experimental curve is very uncertain

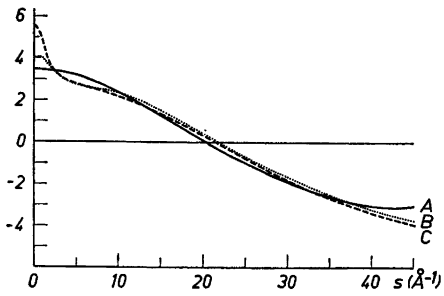


*Fig. 3.* Experimental (A) and theoretical (B, C) curves for $g_{RuO/OO}(s)$. Curve B (dotted) corresponds to the third and curve C (dashed) to the fourth set of scattering amplitudes.

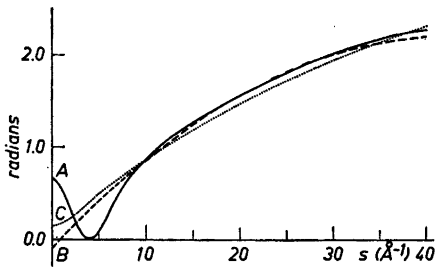


*Fig. 4.* Experimental (A, B) and theoretical (C) curves for $\Delta\eta_{RuO}(s)$. Curve A was found from the experimental $g$ function in Fig. 3, while B (dashed) was found by refining the constants in a polynomial of second degree (see text). Curve C (dotted) was calculated from the third set of scattering amplitudes.

for $s$ less than about 4 Å$^{-1}$ or greater than 40 Å$^{-1}$. The agreement between the theoretical curve C and curve A is somewhat better than between the curves B and A for intermediate $s$ values.

Values for $(\eta_{Ru}-\eta_O)$ were obtained as described previously [3,4] from the experimental $g$ function using theoretical values for the $|f|$ functions (third set). Fig. 4 shows $(\eta_{Ru}-\eta_O)$ obtained in this way (curve A). The region around the $s$ value corresponding to $(\eta_{Ru}-\eta_O) = \pi/2$ ($s_{\pi/2}$) is probably fairly accurate; the other parts of the curve are rather sensitive to changes in the scale factor used for the experimental $g$ function and to changes in the $|f|$ functions. The deep minimum near $s = 4$ Å$^{-1}$ may therefore not be real. Curve B (Fig. 4) was found by assuming $(\eta_{Ru}-\eta_O) = c_0 + c_1 s + c_2 s^2$. The constants $c_0$, $c_1$, and $c_2$ were refined by least-squares calculations using theoretical $|f|$ values (set III). The data in the $s$ range 5.5—40.0 Å$^{-1}$ were applied in the refinements.* The curves A and B are in good agreement in the $s$ range 10—30 Å$^{-1}$. Curve C is the theoretical $(\eta_{Ru}-\eta_O)$ function from the third set of scattering amplitudes.

The four experimental $g$ functions were zero (corresponding to $(\eta_{Ru}-\eta_O) = \pi/2$) at the $s$ values (Å$^{-1}$): 20.77, 19.35, 20.17, and 20.31. The mean value is 20.15 Å$^{-1}$, and the standard deviation for this mean value is 0.30 Å$^{-1}$. $s_{\pi/2}$ found from the polynomial described above is 20.22 Å$^{-1}$. The experimental and theoretical $s_{\pi/2}$ values are given below (in Å$^{-1}$):

| Experimental | Theoretical | | |
|---|---|---|---|
| | Set II | Set III | Set IV |
| 20.2 (0.40) | 21.5 | 21.84 | 21.39 |

* The parameters $\alpha_1$, $r_1$, $r_2$, $u_1$, $u_2$, and the scale factor were first refined using the theoretical $g$ function. These parameters were then kept constant, and $c_0$, $c_1$, and $c_2$ were refined.

The standard deviation given here is somewhat greater than the value obtained above to account for systematic errors. One would expect the fourth set of scattering amplitudes to be more accurate than the third set, since the only difference between these sets originates from the difference in the potentials applied for ruthenium (*cf.* p. 738). It is seen that the $s_{\pi/2}$ value from set IV agrees somewhat better than the value from set III with the experimental result. The $s_{\pi/2}$ value from set II is in rather good agreement with the experimental result in spite of the uncertainties in this set.[4]

The experimental $s_{\pi/2}$ value found in $RuO_4$ is thus smaller than the theoretical values as opposed to the result obtained for $s_{\pi/2}$ in $OsO_4$,[2] but in agreement with the results found for example in $MoF_6$[4] and $Mo(CO)_6$.[5] The results for $RuO_4$ will not be discussed more closely here, since a complete discussion of the results obtained for the eight compounds studied in this series of investigations will be given elsewhere.[6]

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