

Studies on the Failure of the First Born Approximation In Electron Diffraction

II. Osmium Tetraoxide

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Gaseous osmium tetraoxide has been studied by electron diffraction. Two sets of complex scattering amplitudes have been used, and the agreement between observed and theoretical intensities is shown to be rather good in both cases. There is no evidence for deviation from T_d symmetry. The bond length is 1.711₆ Å with an estimated standard deviation of 0.003 Å. The root-mean-square amplitude of vibration for the Os—O bond is 0.036 ± 0.002 Å.

Osmium tetraoxide has been studied in the same way as uranium hexafluoride.¹ Some preliminary results have already been mentioned in a recent review article.²

The modified molecular intensity may usually be expressed as ¹

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

where

$$g_{ij/kl}(s) = \frac{(Z_i - F_i)(Z_j - F_j)}{(Z_k - F_k)(Z_l - F_l)} \quad (2)$$

in the classical (kinematic) theory, and

$$g_{ij/kl}(s) = \frac{|f_i| \cdot |f_j|}{|f_k| \cdot |f_l|} \cos(\Delta\eta_{ij}) \quad (3)$$

in the quantum mechanical (quasi-kinematic) theory.*

A radial distribution (RD) curve is defined by

$$\sigma(r)/r = \int I(s) \exp(-ks^2) \sin(rs) ds \quad (4)$$

* To clarify the notation we use four indices on g while only two indices (ij) were used in Ref. 1.

where k is an artificial damping constant. It is well known that the classical theory is satisfactory for molecules containing light atoms only. In these cases the radial distribution curve will consist of nearly Gaussian peaks where each peak represents an interatomic distance.

For osmium tetroxide it is necessary to use g from eqn. (3) because of the large difference in atomic numbers. ($Z_{\text{Os}} - Z_{\text{O}} = 68$). This study is included in a series of investigations of molecules with both heavy and light atoms. We want to investigate if reasonable agreement between theoretical and experimental intensity curves and radial distribution curves can be obtained by using eqn. (3) and the complex scattering amplitudes now available. As mentioned, results for UF_6 have already been published and investigations of MoF_6 , TeF_6 , WF_6 , RuO_4 , $\text{W}(\text{CO})_6$, and $\text{Mo}(\text{CO})_6$ are almost finished.

As in the study of UF_6 two sets of complex scattering amplitudes have been used. Set I was calculated at Indiana University Research Computing Center using the method described by Karle and Bonham.³ The calculation was carried out using the Hartree-Fock potential for oxygen and the Thomas-Fermi-Dirac potential for osmium at an accelerating potential of 35 kV. Set II was calculated by Ibers and Hoerni⁴ using Thomas-Fermi potentials and an accelerating potential of 40 kV. The corrections suggested in Ref. 4 were applied to make the values applicable to the potential used in this experiment. However, in this case we did not use the values given by Ibers and Hoerni for $|f_{\text{O}}|$, since the use of Thomas-Fermi potentials makes these values very uncertain for small s values.

Osmium tetroxide has been studied by electron diffraction quite a long time ago.⁵ Since the classical theory was used (*cf.* eqn. (2)) the results may be rather inaccurate. The bond distance was found to be 1.66 Å with an estimated error limit of ± 0.05 Å. A recent X-ray investigation⁶ gave 1.76 Å and 1.71 Å for the crystallographic independent Os—O bonds. Since the standard deviations are 0.03 Å the difference is probably not real. The infrared and Raman spectra of osmium tetroxide strongly indicate a tetrahedral structure.^{7,8}

EXPERIMENTAL

The sample of osmium tetroxide was obtained from L. Light & Company, England. Diffraction photographs were taken at a nozzle temperature of about 25°C and an accelerating potential of 35 kV. Three sets of plates were used, taken with the camera distances 48.13 cm, 19.43 cm, and 12.67 cm. Four plates were used for the intermediate distance while five plates were selected for the other distances. The plates were photometered and corrected in the usual way.⁹ An experimental background was subtracted from the mean intensity curve obtained from each set of plates. The resulting molecular intensity curves covered the ranges 1.50–20 Å⁻¹, 5–40 Å⁻¹, and 15–60 Å⁻¹. These curves were scaled, and the mean values were taken in the overlap regions.

STRUCTURE ANALYSIS

The experimental molecular intensity function was multiplied by $s/|f_{\text{O}}|^2$. The theoretical expression for the modified molecular intensity is then in the quasi-kinematic theory

$$I(s) = \text{const} \left[4 g_{\text{OsO/OO}}(s) \exp(-\frac{1}{2}u_1^2 s^2) \sin(r_1 s)/r_1 + 6 \exp(-\frac{1}{2}u_2^2 s^2) \sin(r_2 s)/r_2 \right] \quad (5)$$

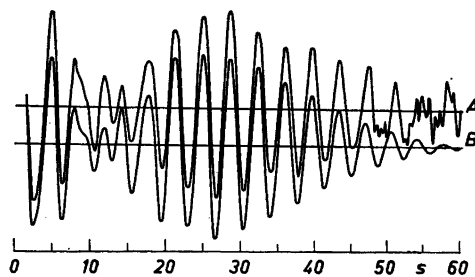


Fig. 1. Experimental (A) and theoretical (B) intensity curves. The theoretical curve was calculated according to eqn. (5) with the r and u values given in Table 1a, and scattering amplitudes from Karle and Bonham.

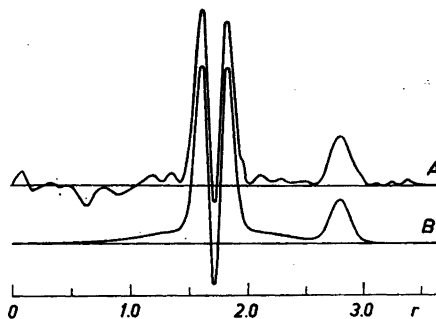


Fig. 2. Experimental (A) and theoretical (B) RD curves. ($k = 0.0009 \text{ \AA}^2$) These curves were obtained by a Fourier transformation of the curves shown in Fig. 1.

assuming harmonic vibrations* and a regular tetrahedral molecule (*cf.* eqn. (1)). Fig. 1 shows the experimental and theoretical intensity curves. The theoretical curve was obtained by using eqn. (5) with the distance- and u values given in Table 1a and scattering amplitudes according to Karle and Bonham. Fig. 2 shows the corresponding experimental and theoretical radial distribution curves calculated by a Fourier transformation of the intensity curves shown in Fig. 1. An artificial damping constant $k = 0.0009 \text{ \AA}^2$ was used. The bond distance corresponds to the minimum of the double peak or to the mean value of the positions of the two maxima. Comparison of Δr (the distance between the two maxima in the double peak) measured on theoretical and experimental RD curves, may indicate if the applied scattering amplitudes are reasonably correct. Various Δr values for OsO_4 are given below. Some values for UF_6 have been included for comparison.

	OsO_4	$k = 0.00 \text{ \AA}^2$	$k = 0.0009 \text{ \AA}^2$
Experimental		0.181 \AA	0.211 \AA
Theoretical (with first set of f values)		0.191 \AA	0.221 \AA
Theoretical (» second » » f »)		0.182 \AA	0.214 \AA
	UF_6		
Experimental		0.233 \AA	
Theoretical (f values according to Karle and Bonham)		0.224 \AA	

The theoretical curves have been calculated according to eqn. (5).

The agreement is somewhat better when the second set of f values are used for OsO_4 . Δr is smaller for OsO_4 than for UF_6 corresponding to the smaller difference in atomic numbers.

The distances and u values were refined by fitting the theoretical intensity curve to the experimental one by the least-squares method. The program permits a calculation of the theoretical intensity according to ¹

$$I(s) = \text{const} \sum_{i \neq j} \sum_l \alpha_{ij} g_{ij|kl}(s) \exp(-\frac{1}{2} u_{ij}^2 s^2) \frac{\sin[(r_{ij} - \kappa_{ij} s^2) s]}{r_{ij}} \quad (6)$$

* or rather Gaussian distance distributions.

The parameter κ_{ij} depends on the anharmonicity, and may often be kept equal to zero. The parameter α_{ij} was kept equal to 1 in most of the refinements performed. The weight function is

$$\begin{aligned} W &= \exp [-W_1(s-s_1)^2] && \text{for } s < s_1 \\ W &= 1.00 && \text{for } s_1 < s < s_2 \\ W &= \exp [-W_2(s_2-s)^2] && \text{for } s > s_2 \end{aligned}$$

where s_1 , s_2 , W_1 and W_2 are adjustable constants.

Table 1 (columns a-g) gives the results from various least-squares refine-

Table 1. Various results for the parameters in OsO_4 . Standard deviations are given in parenthesis. All values in Å.

	a	b	c	d	e
r_1	1.711 ₀ (0.0006)	1.710 ₆ (0.0006)	1.710 ₉ (0.0005)	1.713 ₃ (0.0013)	1.710 ₉ (0.0005)
r_2	2.791 (0.0079)	2.791 (0.0096)	2.791 (0.0071)	2.791 (0.0071)	2.794 (0.0069)
u_1	0.037 ₅ (0.0008)	0.036 ₅ (0.0009)	0.035 ₄ (0.0007)	0.035 ₃ (0.0008)	0.035 ₄ (0.0008)
u_2	0.069 (0.0066)	0.068 (0.0080)	0.067 (0.0059)	0.067 (0.0059)	0.083 (0.0072)

	f	g	h	i
r_1	1.711 ₄ (0.0006)	1.711 ₄ (0.0005)	1.710 ₈	
r_2	2.791 (0.0073)	2.791 (0.0069)	2.791	
u_1	0.035 ₅ (0.0008)	0.035 ₈ (0.0008)		0.0348
u_2	0.067 (0.0061)	0.074 (0.0072)	0.077	0.0700

The results in the columns a-g were obtained by least-squares refinements. The scattering amplitudes used are either

- (I) all values according to Karle and Bonham
 (II) $|f_{\text{O}}|$ according to Karle and Bonham, and η_{O} , f_{Os} according to Ibers and Hoerni.
 If nothing else is stated the following conditions were applied:

- Intensity data in the s range 1.5–60.0 Å⁻¹ were used.
- The scattering amplitudes denoted by II were used.
- The theoretical intensity was calculated according to eqn. (5), *i.e.* in the harmonic approximation.
- The constants in the weighting scheme were $s_1 = 4.00$ Å⁻¹, $s_2 = 25.00$ Å⁻¹, $W_1 = 0.1$, $W_2 = 0.002$.

Special conditions and results are given below.

- The scattering amplitudes denoted by I were used.
- The scattering amplitudes denoted by I and $s_2 = 40.00$ Å⁻¹ were used.
- No special conditions.
- The theoretical intensity was calculated including anharmonicity for the bond distance (*cf.* eqn. (6)). The refined value is $\kappa_{\text{Os-O}} = 2.3 \times 10^{-6}$ Å³ with a standard deviation of 1.1×10^{-6} Å³.
- $\alpha_{\text{Os-O}}$ was refined as an additional parameter (*cf.* eqn. (6)). ($\kappa_{\text{Os-O}}$ was kept equal to zero.) The refined value is $\alpha_{\text{Os-O}} = 0.713$ with a standard deviation of 0.059.
- Intensity data in the s range 1.5–45.0 Å⁻¹ were used.
- Intensity data in the s range 1.5–45.0 Å⁻¹ were used. The experimental g function (Fig. 3b) was applied and scaled by refining $\alpha_{\text{Os-O}}$. The refined value is $\alpha_{\text{Os-O}} = 0.857$.

- h. Results obtained from RD curves. r_1 was determined from the curve in Fig. 2. ($k = 0.0009 \text{ \AA}^2$). The mean of the positions of the maxima was used rather than the position of the minimum, since the latter value seems to vary more with the value of k . The values given for r_2 and u_2 are the mean of the results obtained from the RD curves calculated with $k = 0.0009 \text{ \AA}^2$ and $k = 0.002 \text{ \AA}^2$.
- i. Spectroscopic u values from Cyvin *et al.*

ments. Both the distances were treated as independent parameters in all cases. The experimental data range from $s = 1.5 \text{ \AA}^{-1}$ to $s = 60.0 \text{ \AA}^{-1}$ as mentioned. Two different weight functions were tried with scattering amplitudes according to Karle and Bonham (set I). The results are shown in Table 1a,b. The results are very similar even though the change in the weight on the outer data is considerable. The shift in r_1 and u_1 are of the same order of magnitude as the standard deviations while the other shifts are much smaller than the corresponding standard deviations.

The results in the next column (c) were obtained by using the second set of scattering amplitudes (see p. 386). These results should be compared to the values in column (a) which were obtained with the same weighting of the data. We notice that the shift in the u value for the bond distance is larger than the standard deviation. The changes in the other parameters are small compared to the corresponding standard deviations. A similar result was obtained for UF_6 .¹ The u values may be compared to the values obtained by Cyvin *et al.*¹⁰ from spectroscopic data (Table 1i). The electron diffraction value for u_1 in column c (obtained by using f values from Ibers and Hoerni) is in best agreement with the spectroscopic value.

The constant $\kappa_{\text{Os-O}}$ in eqn. (6) should be very small in this case because of the small u value for the Os—O bond. However, a refinement based on the anharmonic intensity expression was carried out. The results are given in Table 1d. The κ value obtained is reasonable, but the standard deviation is of course very large. A κ value different from zero corresponds to an unsymmetric double peak in the RD curve, *i.e.* for $\kappa > 0$ the inner peak is higher than the outer one.¹ Fig. 2 shows that this is the case for the Os—O double peak.

A theoretical RD curve was calculated by a Fourier transformation of the theoretical intensity obtained from eqn. (6) and the parameters given in Table 1d. The difference in the peak heights was found to be somewhat smaller on the theoretical curve than on the experimental one. This is probably due to noise in the outer part of the intensity curve (Fig. 1).

Refinements were performed introducing $\alpha_{\text{Os-O}}$ as an additional parameter. Table 1e shows the results when the second set of scattering amplitudes was applied. The α value obtained is rather low ($\alpha_{\text{Os-O}} \approx 0.71$) and the shift in $u_{\text{O-O}}$ is great because of the correlation between these parameters. A somewhat higher α value was obtained with the first set of f values ($\alpha_{\text{Os-O}} \approx 0.81$, $u_{\text{O-O}} = 0.079 \text{ \AA}$).

It is seen from Fig. 1 that the experimental intensity data are very inaccurate for $s > 45 \text{ \AA}^{-1}$ because of noise. A refinement was therefore performed discarding the data above $s = 45 \text{ \AA}^{-1}$. The results (Table 1f) are very similar to those previously obtained (column c).

The experimental g function shown in Fig. 3b (*cf.* the next section) was used in a refinement on the intensity data in the s range 1.5–45.0 \AA^{-1} . The scale of this function was introduced as an additional parameter by refining $\alpha_{\text{Os-O}}$. The results (Table 1g) are very similar to those obtained by using the second set of theoretical scattering amplitudes.

Table 1h shows the parameters obtained from RD curves. The results are of course similar to those obtained by the least-squares refinements. The parameter u_2 is found to be between the values obtained by least-squares refinement keeping $\alpha_{\text{Os-O}}$ fixed (column c) and refining $\alpha_{\text{Os-O}}$ (column e).

If the distances given in Table 1c are corrected according to

$$r_g = r_g(1) + u^2/r$$

we get

$$r_g(\text{Os-O}) = 1.711_6 \text{ \AA}$$

$$r_g(\text{O-O}) = 2.793 \text{ \AA}$$

For a rigid molecule we calculate from the bond length $r_g(\text{O-O}) = 2.795 \text{ \AA}$. However, before a comparison is made to the observed value we must correct for the shrinkage effect. The shrinkage has been calculated by Cyvin *et al.*¹⁰ and is found to be 0.002 \AA . Thus $r_g(\text{O-O}) = 2.793 \text{ \AA}$ calculated from the bond distance which is exactly the same as found by refining this parameter independently.

We conclude that a very good agreement between theory and experiment is obtained by assuming T_d symmetry provided that complex scattering amplitudes are used. T_d symmetry was also found by spectroscopic investigations^{7,8} as already mentioned. There are some small differences in the experimental and theoretical intensity curves (Fig. 1). Complete agreement is not to be expected for large s values because of noise in the experimental data. The agreement is not quite satisfactory near $s = 13 \text{ \AA}^{-1}$. This is probably due to inaccurate theoretical scattering amplitudes (see next section). However, we are also investigating if inclusion of multiple scattering¹¹ may improve the agreement.

The bond length (r_g) is $1.711_6 \text{ \AA} \pm 0.003 \text{ \AA}$ where the standard deviation includes an estimate of the systematic errors.² This result is seen to be between the values found by the two earlier investigations (see p. 386) and, because of the great uncertainty in the previous determinations, within the error limits of both. The standard deviation for the u value of the bond length must certainly be greater than given in Table 1. This is partly due to uncertainties in the theoretical scattering amplitudes. The u values are, however, also sensitive to errors in the applied blackness correction. To estimate this error a blackness correction, known to be much too low, was applied. The change in u_1 was nearly 0.003 \AA , while the shifts in the other parameters were much less than the corresponding standard deviations. A reasonable estimate for u_1 seems to be 0.036 \AA with a standard deviation of 0.002 \AA .

Table 2. Results of least-squares refinements of parts of the intensity data.

	a	b	c	d	e	f
r_1	1.711 ₄ (0.0019)	1.711 ₃ (0.0006)	1.711 ₀ (0.0005)	1.711 ₀ (0.0017)	1.711 ₂ (0.0006)	1.711 ₀ (0.0005)
r_2	2.791 (0.0091)	2.787 (0.0106)	2.752 (0.0154)	2.793 (0.0089)	2.785 (0.0102)	2.752 (0.0154)
u_1	0.049 ₁ (0.0027)	0.034 ₁ (0.0021)	0.033 ₁ (0.0015)	0.036 ₀ (0.0032)	0.036 ₁ (0.0020)	0.034 ₀ (0.0014)
u_2	0.071 (0.0089)	0.066 (0.0075)	0.062 (0.0082)	0.062 (0.0088)	0.069 (0.0070)	0.064 (0.0081)

The results in a, b and c were obtained by using scattering amplitudes from Karle and Bonham.
 The results in d, e and f were obtained by using scattering amplitudes from Ibers and Hoerni.

The range of data and the constants in the weighting scheme were

	δ_{\min}	δ_{\max}	δ_1	δ_2	W_1	W_2
a,d	1.50	23.00	4.50	23.00	0.1	0.0
b,e	15.50	35.00	15.50	25.00	0.0	0.004
c,f	25.50	60.00	25.50	30.00	0.0	0.004

SCATTERING AMPLITUDES

We have analysed the intensity data more closely by using least-squares refinements on three ranges of the intensity curve (*i.e.* 1.5–23.0 Å⁻¹, 15.5–35.0 Å⁻¹, and 25.5–60.0 Å⁻¹). The results are given in Table 2 for both sets of scattering amplitudes. The values in a, b, and c were obtained by using set I, the values in d, e, and f by set II, (*cf.* p. 386). We observe that the inner part of the intensity curve gives a very high estimate for u_1 when the first set of scattering amplitudes is used (column a), while column (d) shows a value in excellent agreement with the values given in Table 1 found by using all the experimental data. The result obtained for u_1 will clearly be very sensitive to errors in $g_{\text{OsO/OO}}(s)$ near the first zero point (the beat-out) because of the rapid change of $g(s)$ with s in this region. The results in Table 2 may thus indicate a small error in the position of the beat-out calculated with scattering amplitudes from Karle and Bonham.

Experimental values for the $g_{\text{OsO/OO}}(s)$ function* were now obtained in essentially the same way as described for UF₆.¹ The contribution from the Os—O bonds to the experimental intensity is obtained by a Fourier transformation of the double peak in the RD curve. In this case the double peak in Fig. 2 was used, giving an artificially damped intensity curve. The absolute value of the damped Os—O intensity was plotted for s values to the left of the beat out. To the right all values were made negative and then plotted (see Fig. 4). The envelope of this curve is — when multiplied by $\exp[(\frac{1}{2}u_1^2 + k)s^2]$ — proportional to the experimental function. Fig. 3a shows the resulting experimental g function when u_1 from Table 1a is used. The theoretical g function according to Karle and Bonham is shown for comparison. Similarly Fig. 3b shows the second theoretical function compared to the experimental curve obtained by using u_1 from Table 1c. The experimental curves are scaled to give the same minimum value as the theoretical curves. The experimental curves are very uncertain above $s = 45$ Å⁻¹ because of noise in the experimental data (*cf.* Fig. 1). In this region the curves are also very sensitive to changes in the values used for u_1 .

However, the region near the beat-out should be rather well determined. It is seen that the agreement is better in Fig. 3b than in Fig. 3a indicating that the scattering amplitudes from Ibers and Hoerni are somewhat better than those calculated by Karle and Bonham in this case. The beat-out is at $s = 12.9$ Å⁻¹ on the experimental curve compared to $s = 11.8$ Å⁻¹ (Fig. 3a) and $s = 12.4$ Å⁻¹ (Fig. 3b) on the theoretical ones. However, for UF₆ the values from Karle and Bonham proved to be the best ones.¹

* In a more precise notation we could write

$$g_{\text{OsO/OO}}^{\text{exp}}(s) = \frac{(|f_{\text{Os}}| |f_{\text{O}}|)_{\text{exp}}}{(|f_{\text{O}}|^2)_{\text{theor}}} \cos(\Delta\eta_{\text{OsO}})_{\text{exp}} \quad (7)$$

$|f_{\text{O}}|_{\text{exp}}$ is probably very nearly equal to $|f_{\text{O}}|_{\text{theor}}$.

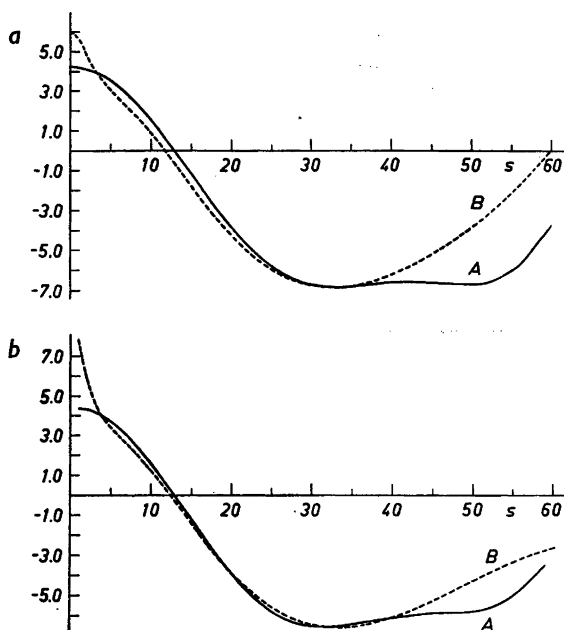


Fig. 3a, b. Comparison of experimental (A) and theoretical (B) curves for the g function. The first set of scattering amplitudes (Karle and Bonham) was used in a; the second set (Ibers and Hoerni) used in b.

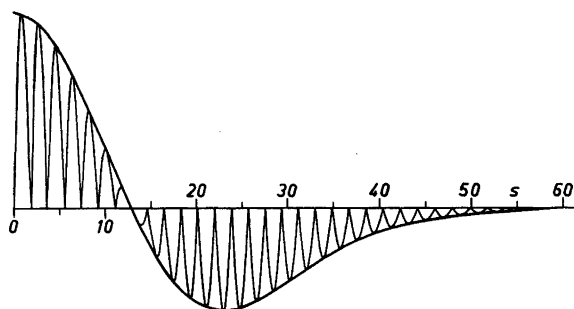


Fig. 4. The Os—O contribution to the experimental intensity (artificially damped) was found by a Fourier transformation of the double peak in Fig. 2. This function was plotted after making all values positive to the left, and all values negative to the right of the beat-out.

The experimental g function was divided by the theoretical function $|f_{Os}| / |f_O|$. The function $\Delta\eta_{OsO}$ could then be calculated.¹ The curves obtained are compared to theoretical $\Delta\eta(s)$ functions in Figs. 5a and 5b.

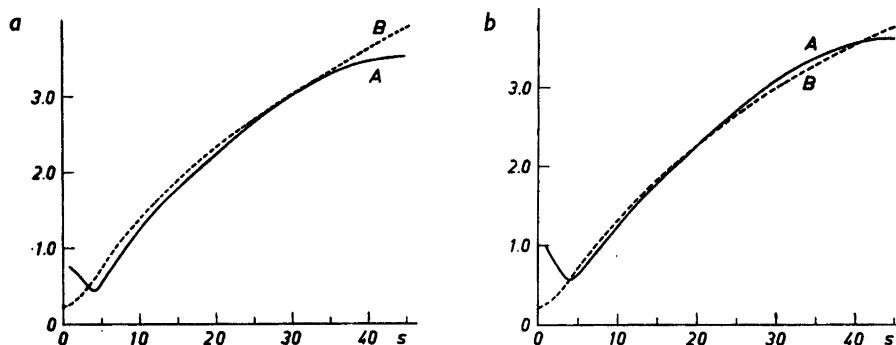


Fig. 5a, b. $\Delta\eta_{\text{Os-O}}(s)$ obtained from the experimental g functions shown in Fig. 3 and theoretical $|f|$ values (A) compared to theoretical $\Delta\eta_{\text{Os-O}}(s)$ functions (B).
 a) The experimental g function in Fig. 3a and theoretical values from set I were used.
 b) The experimental g function in Fig. 3b and theoretical values from set II were used.

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