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

V. Molybdenum- and Tungsten Hexacarbonyl

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Molybdenum- and tungsten hexacarbonyl have been studied by electron diffraction. Three sets of scattering amplitudes [$f(s) = |f(s)| \cdot \exp(i\eta(s))$] have been considered. The experimental and theoretical s values corresponding to $\eta_M - \eta_X = \pi/2$ (M = W or Mo, X = C or O) are given below. The theoretical values are in parentheses. WC: 12.3 (11.79, 11.8, 12.38) Å^{-1}, WO: 12.4 (12.03, 12.6, 12.91) Å^{-1}, MoC: 18.4 (20.43, 20.4, 21.16) Å^{-1}, and MoO: 20.8 (21.98, 22.9, 23.21) Å^{-1}. Thus, while the agreement is satisfactory for $\eta_W - \eta_C$ and $\eta_W - \eta_O$, there seems to be a significant difference between experimental and theoretical values at least for $\eta_{Mo} - \eta_C$. The bond lengths (with estimated standard deviations) are: r(C–O) = 1.148_0 (0.0025) Å, r(W–C) = 2.058_6 (0.0030) Å in $W(CO)_6$, and r(C-O) = 1.145_0 (0.0020) Å, r(Mo–C) = 2.063_2 (0.0030) Å in $Mo(CO_6)$. There is no evidence for deviation from O_h symmetry. The results obtained for the root-mean-square amplitudes of vibration for $Mo(CO)_6$ show satisfactory agreement with the values obtained from spectroscopic data for most of the distances.

Five compounds (UF_6,[1] OsO_4,[2] TeF_6,[3] MoF_6,[4] and WF_6[4]) have already been studied in this series of investigations. It is convenient to modify the molecular intensity by multiplication by a function, which in this case is chosen to be $s/|f_O|^2$ (*cf.* Ref. 1). The general expression for the modified molecular intensity is given by eqn. (1) in the preceding paper.[4] For $Mo(CO)_6$ and $W(CO)_6$ we have the following g functions (eqn. (2), Ref. (4)):

$$g_{MC/OO}(s) = \frac{|f_M| \cdot f_C|}{|f_O|^2} \cos(\eta_M - \eta_C)$$

$$g_{MO/OO}(s) = \frac{|f_M|}{|f_O|} \cos(\eta_M - \eta_O)$$

$$g_{CO/OO}(s) = \frac{|f_C|}{|f_O|} \cos(\eta_C - \eta_O)$$

$$g_{CC/OO}(s) = \frac{|f_C|^2}{|f_O|^2}$$

$$g_{OO/OO}(s) = 1$$

where M is Mo or W.

Two sets of scattering amplitudes were used in the investigations of UF_6, OsO_4, and TeF_6. One additional set was included in the studies of MoF_6 and WF_6. All the three sets described in Ref. 4 were considered in this case. Since the values given for $|f_O|$ by Ibers and Hoerni [5] (set II) are very uncertain (because of the use of a TF potential), we have not carried out least-squares refinements using this set. However, we have compared the s values giving $\eta_M - \eta_C = \pi/2$ and $\eta_M - \eta_O = \pi/2$ (*i.e.* $g_{MC/OO} = 0$ and $g_{MO/OO} = 0$) for these scattering amplitudes with the corresponding values obtained experimentally.

Electron diffraction studies of $Mo(CO)_6$ and $W(CO)_6$ were carried out by Brockway *et al.* in 1938.[6] O_h symmetry was found for both compounds in spite of the use of the first Born approximation. The reported bond distances (with estimated error limits) are:

	$Mo(CO)_6$	$W(CO)_6$
C—O	1.15 ± 0.05 Å	1.13 ± 0.05 Å
M—C	2.08 ± 0.04 »	2.06 ± 0.04 »

The vibrational spectrum of $Mo(CO)_6$ was studied by Hawkins *et al.*[7] and by Kawai and Murata.[8] More recently the Raman- and infrared spectra of $Mo(CO)_6$ and $W(CO)_6$ have been discussed by Jones [9] and Amster *et al.*[10] Brunvoll [11] has calculated the root-mean-square amplitudes of vibration and shrinkage effects for $Mo(CO)_6$.

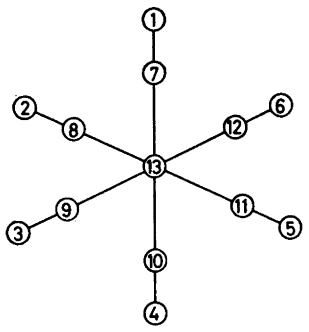

Fig. 1. The numbering of the atoms in $M(CO)_6$.

EXPERIMENTAL

The samples of $Mo(CO)_6$ and $W(CO)_6$ were obtained from L. Light & Co. Ltd. and used without further purification. Diffraction photographs were recorded in the usual way [12] applying an accelerating potential of approximately 35 kV. The nozzle temperature was approximately 75°C for $Mo(CO)_6$ and 90°C for $W(CO)_6$. Four sets of plates were used for each compound. The nozzle to plate distances and the corresponding s ranges were:

	Nozzle to plate distance (cm)	Approximate s range ($Å^{-1}$)
$Mo(CO)_6$:	130.06	0.5 — 7.75
	48.00	1.5 —19.75
	19.35	7.0 —45.0
	14.56	12.0 —55.0
$W(CO)_6$:	130.13	0.5 — 7.75
	48.08	1.5 —20.00
	22.37	5.5 —41.00
	14.66	10.25—56.00

Sixteen plates (four for each nozzle to plate distance) were used for each compound. The plates were photometered, and the intensity values were read off at intervals Δs = 0.25 $Å^{-1}$ and corrected in the usual way.[12]

STRUCTURE ANALYSIS

These investigations have been carried out mainly in the same way as the previous investigations.[4] We have applied least-squares refinements on the intensity data, but also calculated experimental and theoretical radial distribution (RD) curves. The least-squares refinement program is the same as used previously [1] and permits a calculation of the theoretical intensity according to eqn. (1) of Ref. 4. The numbering of the atoms is shown in Fig. 1. Assuming octahedral symmetry there are 9 different distances in these molecules, but if shrinkage effects are neglected (or known), only two of these distances are independent.

a. $Mo(CO)_6$. The investigation was initiated without the plates taken with the longest camera distance. Four observed intensity curves were obtained, all ranging from s = 1.50 $Å^{-1}$ to 55.0 $Å^{-1}$. The first set of scattering amplitudes (Ref. 4, p. 2699) was used and least-squares calculations carried out on these four curves separately. We soon realized that the experimental data were rather inaccurate for s less than 3.5 $Å^{-1}$. These data were then discarded. An attempt to refine 9 independent distances, the corresponding vibrational amplitudes, and of course the scale factor, did not work out very well. Two distances ($C_7 \cdots C_8$ and $O_1 \cdots O_2$) were therefore kept constant in the refinements. The results of these calculations are shown in Table 1a, b, c, and d.

If these results are given equal weights, the mean values and standard deviations in column e are found. The agreement between the results is seen to be satisfactory compared to the corresponding standard deviations, perhaps with r_1 as an exception. However, it is a very general experience that the

Table 1. $Mo(CO)_6$. Least-squares results (in Å) for $r_g(1)$ and u obtained from four observed intensity curves covering the s range 3.50 — 55.0 $Å^{-1}$. The standard deviations given in parentheses are in 10^{-4} Å. The two distances $r(C_7 \cdots C_8)$ = 2.91 Å and $r(O_1 \cdots O_2)$ = 4.51 Å were not refined.

	a		b	
	r	u	r	u
C_7-O_1	1.145_7 (12)	0.035_0 (15)	1.142_1 (13)	0.037_0 (16)
$Mo_{13}-C_7$	2.061_4 (27)	0.065_3 (29)	2.061_7 (31)	0.068_5 (35)
$Mo_{13} \cdots O_1$	3.193_5 (29)	0.056_0 (29)	3.194_1 (32)	0.056_6 (33)
$C_{10} \cdots O_1$	5.253 (143)	0.078 (116)	5.250 (145)	0.075 (118)
$O_1 \cdots O_4$	6.389 (203)	0.065 (173)	6.382 (231)	0.067 (195)
$C_7 \cdots C_{10}$	4.133 (250)	0.068 (205)	4.095 (357)	0.081 (280)
$C_7 \cdots C_8$	—	0.138 (102)	—	0.130 (102)
$C_8 \cdots O_1$	3.800 (163)	0.232 (114)	3.791 (183)	0.235 (134)
$O_1 \cdots O_2$	—	0.279 (330)	—	0.280 (362)

c		d		e	
r	u	r	u	r	u
1.143_6 (13)	0.035_2 (16)	1.145_4 (11)	0.035_2 (13)	1.144_2 (17)	0.035_6 (9)
2.061_4 (29)	0.062_9 (30)	2.063_1 (25)	0.066_7 (28)	2.061_9 (8)	0.065_9 (24)
3.192_1 (33)	0.056_2 (33)	3.192_9 (28)	0.058_2 (29)	3.193_5 (9)	0.056_8 (10)
5.264 (144)	0.073 (118)	5.250 (126)	0.076 (103)	5.255 (64)	0.075 (22)
6.377 (270)	0.072 (224)	6.368 (279)	0.086 (228)	6.379 (89)	0.073 (92)
4.104 (299)	0.072 (240)	4.114 (315)	0.083 (249)	4.112 (163)	0.076 (71)
—	0.134 (109)	—	0.127 (83)	—	0.132 (45)
3.784 (205)	0.247 (147)	3.798 (150)	0.232 (107)	3.793 (70)	0.236 (72)
—	0.302 (442)	—	0.252 (245)	—	0.278 (203)

a—d: Results obtained from the individual intensity curves using the first set of scattering amplitudes. The constants in the weight function[1] were s_1 = 5.0 $Å^{-1}$, s_2 = 20.0 $Å^{-1}$, W_1 = 0.2, W_2 = 0.003.

e: Mean values and standard deviations calculated from the results in the columns a—d.

standard deviations obtained for the most accurately determined parameters tend to be rather small.[1,4]

The average intensity curve was then calculated from the four observed intensity curves. In order to obtain independent estimates of all the r and u parameters it was decided to include the intensities from plates taken with approximately 130 cm between nozzle and plate. The complete intensity curve obtained covered now the s range 0.5—55.0 $Å^{-1}$. Various least-squares refinements were carried out using the total intensity curve, and it proved possible to refine all r and u values independently. In most of the calculations performed we thus had 19 parameters. The results in Table 2a were obtained using the first set of scattering amplitudes.[4] The theoretical intensity curve corresponding to these parameters is shown in Fig. 2 (curve B). Curve A (Fig. 2) shows the averaged observed intensity, and curve C gives the differences

Table 2. Various results (in Å) for the parameters ($r_g(1)$ and u) in $Mo(CO)_6$. The standard deviations given in parentheses are in 10^{-4} Å. Intensity data in the s range 0.5 — 55.0 Å were used in all these calculations.

	a		b		c	
	r	u	r	u	r	u
C_7-O_1	1.144_2 (8)	0.034_2 (10)	1.144_2 (9)	0.032_5 (11)	1.144_5 (8)	0.035_6 (12)
$Mo_{13}-C_7$	2.061_7 (19)	0.062_6 (18)	2.061_2 (23)	0.062_3 (22)	2.061_0 (17)	0.067_1 (22)
$Mo_{13}\cdots O_1$	3.199_3 (23)	0.055_4 (19)	3.198_3 (28)	0.057_1 (26)	3.198_7 (22)	0.059_5 (27)
$C_{10}\cdots O_1$	5.260_7 (95)	0.073_3 (78)	5.261_3 (112)	0.072_1 (91)	5.259_7 (79)	0.073_7 (66)
$O_1\cdots O_4$	6.379_5 (175)	0.073_2 (144)	6.379_6 (206)	0.073_1 (170)	6.379_4 (138)	0.071_4 (119)
$C_7\cdots C_{10}$	4.116_0 (203)	0.072_2 (159)	4.115_1 (239)	0.070_9 (186)	4.118_8 (163)	0.071_2 (133)
$C_7\cdots C_8$	2.949_0 (96)	0.131_3 (73)	2.948_1 (114)	0.123_3 (83)	2.945_3 (85)	0.135_7 (68)
$C_8\cdots O_1$	3.799_8 (122)	0.217_7 (83)	3.799_3 (151)	0.216_5 (101)	3.800_3 (99)	0.217_9 (68)
$O_1\cdots O_2$	4.507_1 (441)	0.294_3 (265)	4.496_9 (549)	0.302_5 (329)	4.510_9 (349)	0.291_8 (211)

d		e	
r	u	r	u
1.144_3 (8)	0.035_9 (10)	1.143_6 (8)	0.035_1 (9)
2.062_1 (18)	0.062_0 (18)	2.061_1 (15)	0.063_9 (19)
3.200_1 (23)	0.053_8 (21)	(3.200_7)	0.056_3 (20)
5.260_5 (94)	0.075_2 (77)	(5.246_9)	0.076_1 (84)
6.380_3 (172)	0.074_9 (142)	(6.380_2)	0.074_0 (150)
4.117_1 (202)	0.074_8 (160)	(4.111_4)	0.073_2 (166)
2.959_3 (121)	0.137_8 (80)	(2.909_1)	0.137_9 (75)
3.801_2 (106)	0.224_4 (82)	(3.793_2)	0.221_6 (79)
4.524_5 (351)	0.291_5 (223)	(4.503_1)	0.290_8 (242)

: The constants in the weight function[1] were $s_1 = 5.0$ Å^{-1}, $s_2 = 20.0$ Å^{-1}, $W_1 = 0.150$, $W_2 = 0.002$. For all the distances $\alpha = 1.0$ and $\varkappa = 0.0$ were kept constant. Altogether 19 parameters (9 distances, 9 u values, and the scale factor) were refined. The first set of scattering amplitudes was applied.
: The third set of scattering amplitudes was applied. All other conditions as in a.
: The weight function was changed by using $W_2 = 0.008$. All other conditions as in a.
: α_2 and α_3 were refined in addition to the previous parameters. (Results: $\alpha_2 = 0.950$ (0.020), $\alpha_3 = 0.913$(0.036)). All other conditions as in a.
: All the non-bonded distances were considered as dependent parameters (*i.e.* only 12 parameters were refined). The values obtained for the dependent distances are given in parentheses. All other conditions as in a.

between the experimental and theoretical intensities. The agreement seems satisfactory, though some small deviations occur. The intensity curves from the individual plates indicate that the differences in the s ranges (Å^{-1}): 15.5 — 17.5, 27.0 — 28.5, and (with some uncertainty) 20.0 — 22.5, are not due to noise. These deviations may originate from errors in the applied scattering amplitudes, since the theoretical intensity is very sensitive to such errors near the s values where $g_{MoC/OO}$ and $g_{MoO/OO}$ are zero. (see Fig. 7). The other deviations between the intensity curves in Fig. 2 are probably due to noise or to an incorrect drawing of the experimental background.

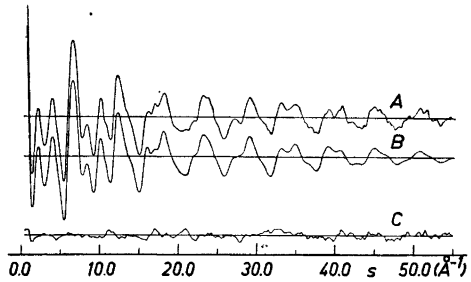

Fig. 2. $Mo(CO)_6$. Experimental (A) and theoretical (B) intensity curves. The theoretical curve was obtained by using the results in Table 2a and the first set of scattering amplitudes. Curve C shows the difference between the curves A and B.

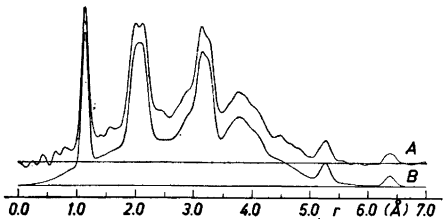

Fig. 3. $Mo(CO)_6$. Experimental (A) and theoretical (B) RD curves calculated from the intensity curves shown in Fig. 2 with an artificial damping constant $k = 0.0009$ Å^2.

The RD curves in Fig. 3 were obtained by Fourier transformations of the intensity curves in Fig. 2. Theoretical intensity values were used for $s < 0.5$ Å^{-1}, and the integrations performed in the s range 0 — 55 Å^{-1}. A small artificial damping constant ($k = 0.0009$ Å^2) was applied. The sharp inner peak corresponds to the C—O bond distance. Then the experimental curve shows a double peak with a small minimum corresponding to the Mo—C distance, while the theoretical curve shows a flat maximum. This fact seems to indicate errors in the theoretical function $g_{MoC/OO}(s)$, though the minimum on the experimental curve could perhaps be due to noise. The small shoulder on the next peak gives the $C_7 \cdots C_8$ contribution, while the peak itself corresponds to the Mo···O distance. The complex around 4 Å contains the $C_8 \cdots O_1$ and $C_7 \cdots C_{10}$ contributions, while the $O_1 \cdots O_2$ contribution corresponds to a very broad peak near 4.5 Å. The two outer peaks give the $C_{10} \cdots O_1$ and $O_1 \cdots O_4$ distances.

The results in Table 2 will be discussed closely later (*cf.* point c, p. 2719).

b. $W(CO)_6$. The structure analysis of $W(CO)_6$ was carried out in the same way as described for $Mo(CO)_6$. However, in this case the plates taken with the longest camera distance ($\approx$ 130 cm) were included from the beginning. Four observed intensity curves were obtained ranging from $s = 0.75$ Å^{-1} to 50.0 Å^{-1}. The data for $s > 50$ Å^{-1} had to be discarded because of noise. It is more difficult to obtain reliable data for high s values in this case than for $Mo(CO)_6$ for two reasons: 1) The atomic scattering (the background) is greater compared to the molecular scattering. 2) The functions $g_{MC/OO}(s)$ and $g_{MO/OO}(s)$ have their second zero point near $s = 60$ Å^{-1} and $s = 65$ Å^{-1} for M = W, while these points are at much higher s values for M = Mo (*cf.* Figs. 7 and 8).

Since these intensity curves started at a lower s value than the corresponding curves for $Mo(CO)_6$, it proved possible to refine all r and u parameters and the scale factor. The results are given in Table 3a, b, c, and d. The mean and standard deviations calculated from these values are shown in column e. The agreement between the different determinations is not as good as for $Mo(CO)_6$ (Table 1). Some of the values, especially in column c, deviate appreciably

Table 3. $W(CO)_6$. Least-squares results (in Å) for $r_g(1)$ and u obtained from four observed intensity curves covering the s range 0.75—50.0 $Å^{-1}$. The standard deviations given in parentheses are in 10^{-4} Å.

	a		b	
	r	u	r	u
$C_7—O_1$	1.146_1 (14)	0.037_3 (19)	1.148_5 (17)	0.038_2 (22)
$W_{13}—C_7$	2.055_5 (11)	0.061_6 (9)	2.059_4 (12)	0.059_1 (10)
$W_{13}\cdots O_1$	3.191_4 (14)	0.061_7 (10)	3.196_5 (15)	0.058_9 (12)
$C_{10}\cdots O_1$	5.241 (120)	0.067 (102)	5.228 (175)	0.077 (145)
$O_1\cdots O_4$	6.349 (397)	0.100 (321)	6.346 (374)	0.085 (306)
$C_7\cdots C_{10}$	4.088 (236)	0.062 (197)	4.127 (227)	0.053 (205)
$C_7\cdots C_8$	2.928 (168)	0.168 (140)	2.934 (178)	0.153 (149)
$C_8\cdots O_1$	3.818 (133)	0.204 (102)	3.806 (144)	0.193 (106)
$O_1\cdots O_2$	4.505 (533)	0.300 (348)	4.455 (463)	0.256 (313)

c		d		e	
r	u	r	u	r	u
1.146_7 (21)	0.026_9 (37)	1.150_6 (20)	0.041_6 (25)	1.148_0 (20)	0.036_0 (63)
2.056_9 (14)	0.0524 (14)	2.057_0 (13)	0.059_8 (12)	2.057_2 (16)	0.058_2 (40)
3.194_4 (18)	0.0520 (16)	3.194_6 (19)	0.062_4 (14)	3.194_2 (21)	0.058_8 (47)
5.246 (211)	0.066 (180)	5.250 (207)	0.080 (170)	5.241 (98)	0.072 (71)
6.375 (750)	0.102 (607)	6.372 (320)	0.072 (270)	6.361 (150)	0.090 (142)
4.122 (500)	0.069 (402)	4.130 (758)	0.118 (618)	4.117 (196)	0.075 (290)
2.972 (307)	0.169 (258)	2.929 (246)	0.178 (200)	2.941 (211)	0.167 (100)
3.811 (214)	0.189 (165)	3.818 (175)	0.200 (140)	3.813 (58)	0.196 (68)
4.435 (971)	0.305 (677)	4.538 (680)	0.292 (460)	4.483 (467)	0.288 (220)

a—d: Results obtained from the individual intensity curves using the first set of scattering amplitudes. The constants in the weight function were $s_1 = 5.0$ $Å^{-1}$, $s_2 = 25.0$ $Å^{-1}$, $W_1 = 0.15$, $W_2 = 0.015$.

e: Mean values and standard deviations calculated from the results in the columns a—d.

from the mean values. Obviously these four intensity curves were not of the same quality. This is also reflected in the standard deviations given in the first four columns of Table 3. The standard deviations in column c are larger than the corresponding values in the other columns for most of the parameters.

Weighted mean values and the corresponding standard deviations were therefore calculated and are shown in Table 4f. The weights were inversely proportional to the square of the standard deviations given in Table 3. The standard deviations in Table 4f may be compared to 1/2 times the corresponding values in Table 3e, since the former values give the standard deviation for the mean of four observations.

A weighted average of the four observed intensity curves was then found and used in more least-squares calculations. The results in Table 4a were

Table 4. Various results (in Å) for the parameters ($r_g(1)$ and u) in $W(CO)_6$. The standard deviations given in parentheses are in 10^{-4} Å. Intensity data in the s range 0.75 — 50.0 $Å^{-1}$ were used in all cases.

	a		b		c	
	r	u	r	u	r	u
C_7-O_1	1.147_7 (13)	0.037_1 (18)	1.147_5 (11)	0.036_6 (15)	1.147_2 (15)	0.038_9 (25)
$W_{13}-C_7$	2.057_2 (9)	0.059_0 (8)	2.057_1 (8)	0.056_0 (7)	2.058_1 (12)	0.062_3 (12)
$W_{13}\cdots O_1$	3.194_0 (12)	0.059_5 (9)	3.194_2 (10)	0.056_1 (8)	3.193_7 (18)	0.064_0 (14)
$C_{10}\cdots O_1$	5.239_2 (128)	0.072_7 (106)	5.240_1 (111)	0.072_4 (92)	5.239_5 (119)	0.078_6 (109)
$O_1\cdots O_4$	6.354_8 (336)	0.092_2 (273)	6.353_9 (299)	0.095_0 (243)	6.351_7 (270)	0.092_8 (234)
$C_7\cdots C_{10}$	4.115_2 (279)	0.072_9 (226)	4.113_6 (254)	0.074_4 (201)	4.117_4 (227)	0.069_2 (217)
$C_7\cdots C_8$	2.936_3 (156)	0.166_6 (130)	2.903_4 (116)	0.139_4 (91)	2.932_0 (125)	0.168_9 (107)
$C_8\cdots O_1$	3.812_6 (120)	0.197_4 (90)	3.806_1 (112)	0.202_1 (83)	3.813_2 (94)	0.197_6 (71)
$O_1\cdots O_2$	4.484_2 (461)	0.286_4 (308)	4.488_2 (423)	0.297_5 (280)	4.488_4 (352)	0.283_3 (235)

d		e		f	
r	u	r	u	r	u
1.147_7 (13)	0.040_5 (19)	1.144_7 (10)	0.038_2 (18)	1.147_7 (10)	0.037_5 (23)
2.057_2 (9)	0.058_5 (9)	2.056_0 (9)	0.059_5 (8)	2.057_1 (9)	0.059_1 (17)
3.194_0 (12)	0.057_2 (15)	(3.196_6)	0.059_8 (10)	3.194_0 (12)	0.059_6 (20)
5.239_7 (125)	0.076_1 (103)	(5.237_5)	0.073_4 (110)	5.240_3 (43)	0.071_1 (33)
6.354_2 (328)	0.096_3 (266)	(6.371_6)	0.093_4 (286)	6.359_0 (72)	0.085_2 (69)
4.121_6 (297)	0.079_9 (236)	(4.100_8)	0.072_7 (228)	4.110_1 (110)	0.061_5 (77)
2.965_0 (195)	0.168_0 (127)	(2.898_0)	0.163_5 (125)	2.935_1 (78)	0.164_8 (51)
3.817_2 (123)	0.209_7 (101)	(3.789_0)	0.202_4 (90)	3.813_4 (31)	0.197_6 (33)
4.522_8 (423)	0.279_7 (271)	(4.498_4)	0.296_2 (316)	4.484_0 (204)	0.281_4 (121)

a: The constants in the weight function were $s_1 = 5.0$ $Å^{-1}$, $s_2 = 25.0$ $Å^{-1}$, $W_1 = 0.15$, $W_2 = 0.015$. For all the distances $\alpha = 1.0$ and $\varkappa = 0.0$ were kept constant. Altogether 19 parameters (9 distances, 9 u values, and the scale factor) were refined. The first set of scattering amplitudes was applied.

b: The third set of scattering amplitudes was applied. All other conditions as in a.

c: The weight function was changed by using $s_2 = 15.0$ $Å^{-1}$. All other conditions as in a.

d: α_2 and α_3 were refined in addition to the previous parameters. (Results: $\alpha_2 = 0.919$ (0.025), $\alpha_3 = 0.860$ (0.046)). All other conditions as in a.

e: All the non-bonded distances were treated as dependent parameters (*i. e.* only 12 parameters were refined). All other conditions as in a.

f: Weighted mean values and standard deviations obtained from the results in Table 3 a, b, c, and d.

obtained applying the first set of scattering amplitudes. The corresponding experimental (A) and theoretical (B) intensity curves are shown in Fig. 4. Curve C gives the difference between the curves A and B. We notice that the agreement for s larger than say 35 $Å^{-1}$ was somewhat better for $Mo(CO)_6$ (Fig. 2). In this case we have $\eta_W - \eta_C = \pi/2$ and $\eta_W - \eta_O = \pi/2$ at $s \approx 12$ $Å^{-1}$. The agreement is rather good in the region around this s value indicating that there are no great errors in the applied functions $g_{WC/OO}$ and $g_{WO/OO}$.

Fig. 5 shows the RD curves corresponding to the intensity curves in Fig. 4 ($k = 0.002$ $Å^2$). The main differences between the RD curves for $Mo(CO)_6$

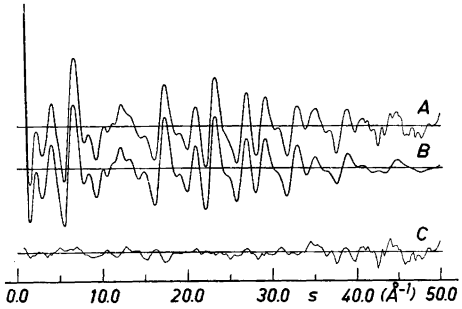

Fig. 4. $W(CO)_6$. Experimental (A) and theoretical (B) intensity curves. The theoretical curve was obtained by using the results in Table 4a and the first set of scattering amplitudes. Curve C shows the difference between the curves A and B.

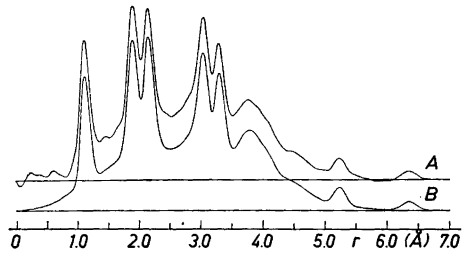

Fig. 5. $W(CO)_6$. Experimental (A) and theoretical (B) RD curves calculated from the intensity curves shown in Fig. 4 with an artificial damping constant $k = 0.0020$ Å^2.

and $W(CO)_6$ are found in the M—C and M···O contributions since W is much heavier than Mo. In Fig. 3 a small minimum is observed corresponding to the Mo—C distance, while Fig. 5 shows deep minima corresponding to the W—C and W···O distances in spite of the larger damping constant applied in this case. Some values for the difference between the positions of the maxima of the double peaks (Δr) are given below. These results were obtained from RD curves calculated with $k = 0.0009$ Å^2.

	Δr (Å) W—C	W···O
Experimental (mean of four determinations):	0.237	0.232
Theoretical (first set of scattering ampl.):	0.243	0.241
» (third » » » :	0.235	0.229

The results in Table 4 are discussed further below.

c. *Discussion of the results obtained for $Mo(CO)_6$ and $W(CO)_6$.* Some results of least-squares calculations are shown in Table 2 ($Mo(CO)_6$) and Table 4 ($W(CO)_6$). The columns a and b in these tables show the results obtained using the first and the third set of scattering amplitudes,[4] respectively. The differences between the parameter values in Table 2a and b and between the values in Table 4a and b, are in general small compared to the corresponding standard deviations. $u(C_7—O_1)$ and to a smaller degree $u(Mo_{13}\cdots O_1)$ and $u(C_7\cdots C_8)$ are exceptions for $Mo(CO)_6$. For $W(CO)_6$ the shifts are rather great for $u(W_{13}—C_7)$, u $(W_{13}\cdots O_1)$, $r(C_7\cdots C_8)$, and $u(C_7\cdots C_8)$. Since $g_{MC/OO}$ and $g_{MO/OO}$ are somewhat different in the two sets, changes in the u values for the M—C and M···O distances were to be expected. The changes in the parameters for the $C_7\cdots C_8$ distances are not very surprising. In the RD curves (Figs. 3

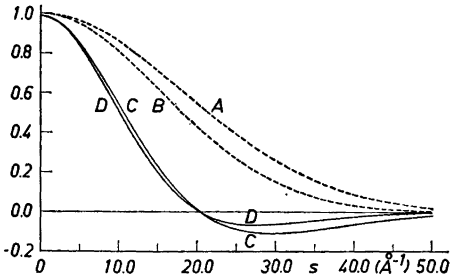

Fig. 6. The curves A and B show exp $(-\frac{1}{2}u^2s^2)$ with $u = 0.055$ Å and $u = 0.065$ Å, respectively. The lower curves (C and D) show $\cos(\eta_{Mo} - \eta_C) \cdot \exp(-\frac{1}{2}u^2s^2)$ for the same u values.

and 5) the small shoulder on the M···O peak was identified as the $C_7 \cdots C_8$ contribution. It is thus a large correlation between the Mo···O and the $C_7 \cdots C_8$ parameters, and it is difficult to obtain reliable estimates for the latter, since the contribution from the $C_7 \cdots C_8$ distances is relatively small.

Refinements were then carried out applying weight functions considerably different from those used in the other calculations. The data at high s values were now given weights that seemed unrealistically small. The results obtained are given in Table 2c and Table 4c. The u values for the M—C and M···O distances increased as a result of these changes in the weights.

These shifts in the u values may seem rather large. Fig. 6 illustrates why it is more difficult to obtain a reliable estimate of the u value for a distance between a heavy and a light atom, than of a similar u value for a distance between two equal atoms. The dashed curves show $\exp(-\frac{1}{2}u^2s^2)$ with $u = 0.055$ Å and $u = 0.065$ Å, respectively. The two other curves (C and D) show $\cos(\eta_{Mo} - \eta_C) \cdot \exp(-\frac{1}{2}u^2s^2)$ for the same u values. Thus, the cosine factor has a small value in the region where the difference between the exponential curves is large. The standard deviation for the u value for a distance between a heavy and a light atom should of course reflect this fact. However, the errors in the intensity curve are not completely random. More or less systematic errors (for example in blackness correction, background, scattering amplitudes, or in transferring the photometer trace to paper) reduce the reliability of the standard deviations as discussed by Almenningen *et al.*[13] It is also obvious that rather small changes in the applied η functions may cause considerable shifts in the u value.

The parameters α_{MC} and α_{MO} were then refined in addition to the parameters used previously. The results for the α values were somewhat less than unity in all cases (Table 2d and Table 4d), but the changes in the distances and u values are rather small for most of the parameters.

The results in Tables 2e and 4e were obtained by considering the nonbonded distances as dependent parameters. These distances were calculated from the bond lengths and corrected for shrinkage effects. Brunvoll[11] has given the shrinkage effects corresponding to r_g distances in $Mo(CO)_6$ (see Table 5d). The least-squares program calculates distance parameters which may be denoted by $r_g(1)$ where

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

Table 5. Parameters (r_g and u) in $Mo(CO)_6$ and $W(CO)_6$. Comparison of the u values and shrinkage effects found by electron diffraction and from spectroscopic data.

	$Mo(CO)_6$						$W(CO)_6$			
	a		b	c	d	e	f		g	h
C_7-O_1	1.145_2	0.034_2	—	—	—	0.0350	1.148_8	0.037_5	—	—
$M_{13}-C_7$	2.063_4	0.063_0	—	—	—	0.0664	2.058_9	0.058_0	—	—
$M_{13}\cdots O_1$	3.200_0	0.056_0	3.208_6	0.008_6	0.0059	0.0675	3.195_1	0.058_5	3.207_7	0.012_6
$C_{10}\cdots O_1$	5.262	0.073	5.272	0.010	0.0227	0.0751	5.241	0.073	5.267	0.026
$O_1\cdots O_4$	6.381	0.073	6.417	0.036	0.0342	0.0760	6.357	0.092	6.415	0.058
$C_7\cdots C_{10}$	4.117	0.072	4.127	0.010	0.0133	0.0740	4.116	0.071	4.118	0.002
$C_7\cdots C_8$	2.955	0.131	2.918	−0.037	0.0025	0.1840	2.939	0.160	2.912	−0.027
$C_8\cdots O_1$	3.813	0.218	3.815	0.002	0.0082	0.2157	3.821	0.198	3.812	−0.009
$O_1\cdots O_2$	4.526	0.294	4.538	0.012	0.0140	0.2764	4.503	0.286	4.536	0.033

a,f: Final distances (r_g) and u values in $Mo(CO)_6$ and $W(CO)_6$ obtained by least-squares refinements with no dependent parameters.
b,g: The non-bonded distances in $Mo(CO)_6$ and $W(CO)_6$ calculated from the bond distances assuming rigid molecules with O_h symmetry.
c,h: Observed shrinkage effects in $Mo(CO)_6$ and $W(CO)_6$
d: Shrinkage values calculated by Brunvoll.[11]
e: u values calculated by Brunvoll.[11]

Shrinkage corresponding to $r_g(1)$ distances was therefore calculated from the values given by Brunvoll, and the u values given in Table 2a. Since the shrinkage for $W(CO)_6$ is unknown, we assumed that the values for $Mo(CO)_6$ (Table 5d) could be applied.* This assumption seems rather reasonable when the similarity of the fundamental frequencies,[8-10] force constants, and the structure parameters in Tables 2 and 4 are considered. The least-squares calculations were performed using the first set of scattering amplitudes for both compounds. The results in the columns e should therefore be compared to the results in the columns a in the Tables 2 and 4. The shifts in the bond distances were negative (−0.0006 Å and −0.0006 Å in $Mo(CO)_6$, and −0.0030 Å and −0.0012 Å in $W(CO)_6$). The shifts in the u values are all rather small. It is interesting to compare the values obtained for

$$\sum \text{Weight} \cdot (I_{obs} - S \cdot I_{calc})^2$$

in the calculations with 19 (column a) and only 12 (column e) independent parameters. (The sum is over all observations, and S is the scale factor). The increase in this sum by reducing the number of distance parameters was 13 % in both cases.

Table 5 (a and f) gives our results for the distances (r_g) (with the 9 distances determined independently) and u values in $Mo(CO)_6$ and $W(CO)_6$. These estimates are based mainly on the results in Tables 2a and 4a, but a slight adjustment has been made in some cases according to the results in the other

* The shrinkage corresponding to $r_g(1)$ distances was calculated using the u parameters in Table 4a.

least-squares calculations with no dependent parameters. The non-bonded distances were then calculated from the bond lengths (columns b and g), and the differences between the latter values and the distances in the columns a and f were found (columns c and h). The agreement between our values and the shrinkage calculated for $Mo(CO)_6$ by Brunvoll [11] (column d) seems satisfactory except for $C_7 \cdots C_8$ where we obtain a rather large negative value. Our value for Mo···O is slightly large. The results for $W(CO)_6$ (column h) show an unlikely great value for W···O and a negative value for $C_7 \cdots C_8$.

Table 5e gives the u values calculated for $Mo(CO)_6$ by Brunvoll.[11] The agreement with our results is seen to be satisfactory except for the Mo···O and $C_7 \cdots C_8$ distances, *i.e.* the distances that showed deviations in the shrinkage values as discussed above. Our result for u(Mo···O) seems too low compared to the result for u(Mo—C). This may be due to errors in the applied g functions. The large correlation between the M···O and $C_7 \cdots C_8$ parameters described previously may also cause the discrepancies discussed above. The disagreements are in any case too small to be regarded as evidence for deviation from O_h symmetry.

Our final values for the lengths (r_g) and vibrational amplitudes of the bonds in $Mo(CO)_6$ and $W(CO)_6$ are given below. The standard deviations given (in Å) include an estimate of the systematic errors.

	$Mo(CO)_6$		$W(CO)_6$	
	r_g	u	r_g	u
C—O	1.145_0(0.0020)	0.034_2(0.0020)	1.148_0(0.0025)	0.037_1(0.0030)
M—C	2.063_2(0.0030)	0.063_0(0.0040)	2.058_6(0.0030)	0.059_0(0.0030)

All the distances are slightly smaller than the corresponding values in Table 5, to take into account the results obtained using dependent distance parameters. We have two reasons for not using the bond distances in Tables 2e and 4e as our final results: 1) There is some uncertainty in the values used for the shrinkage effects, especially for $W(CO)_6$. 2) The bond-lengths are well separated from the other distances, while some of the non-bonded distances overlap rather strongly. The results obtained for the bond lengths are in such cases more sensitive to systematic errors (for example in the scattering amplitudes and blackness correction) if the non-bonded distances are treated as dependent parameters.

The bond lengths given above are the same as obtained by Brockway *et al.* (p. 2712) within the experimental error limits. The corresponding distances and u values obtained for $Mo(CO)_6$ and $W(CO)_6$ are very similar. None of the parameters for the bonds are significantly different in the two compounds according to the standard deviations given above. Even though it is likely that possible systematic errors are in the same direction in both compounds, our results give only an indication of possible differences. Jones [9]

has found a small difference in the CO stretching force constants in $Mo(CO)_6$ (18.122 mdyn/Å) and in $W(CO)_6$ (17.695 mdyn/Å). The bond length and the force constant in the CO molecule are 1.128 Å (r_e) and 19.02 mdyn/Å. The C—O bond lengths are thus in the order to be expected from the force constants. By applying Badger's rule [14] ($1/k^{1/3} = a_{ij}(r_e - b_{ij})$) the force constants suggest a 0.0037 Å longer CO bond in $W(CO)_6$ than in $Mo(CO)_6$. The difference between the CO bond lengths in $W(CO)_6$ and the CO molecule is estimated to 0.011 Å from the force constants. The observed difference is somewhat greater ($\approx$ 0.015 Å). (We have assumed $r_g - r_e = 3/2\ au^2$ for the CO bond in $W(CO)_6$ with $a = 2.48$ Å^{-1} as in the CO molecule).

Jones gives a slightly smaller value for k(Mo—C) than for k(W—C). In agreement with his results we obtain a slightly greater value for u(Mo—C) than for u(W—C).

SCATTERING AMPLITUDES

A method to obtain experimental g functions,

$$g^{\text{exp}}_{\text{MX/OO}}(s) = \frac{(|f_M| \cdot |f_X|)_{\text{exp}}}{(|f_O|^2)_{\text{theor}}} \cos(\eta_M - \eta_X)_{\text{exp}}$$

(M = Mo or W, X = C or O)
has been described previously.[2,3] The contribution from, *e.g.*, the W—C distances in $W(CO)_6$ is a much smaller fraction of the total molecular intensity than the W—F contribution in WF_6. The u values for the distances in question are furthermore much larger in the $M(CO)_6$ molecules than in the MF_6 molecules. It is therefore more difficult to obtain reliable experimental g functions for these molecules than for those studied previously. However, it seems that the s values corresponding to $\eta_M - \eta_X = \pi/2$ (*i.e.* zero points in the g functions) are fairly well determined especially for the M—C distances. The RD curves in Figs. 3 and 5 show that the contributions from the $C_7 \cdots C_8$ distances must be subtracted before the M···O contributions are Fourier transformed, which of course introduces an additional uncertainty.

The RD curves (Figs. 3 and 5) show further that the MX peaks have non-negligible contributions for rather large values of $|r_{MX} - r|$. The contribution far from the mean r value is difficult to obtain from the experimental curves because of the overlap with other contributions. An envelope was therefore subtracted before the peaks were Fourier transformed. This will affect the inner part of the experimental g functions. However, the determination of the zero points is still reliable. This was checked by drawing a similar envelope in the theoretical RD curves, and Fourier transform the MX peaks. The theoretical zero points were reproduced to within 0.1 Å^{-1} in all cases.

Four independent determinations of the g functions were made for both compounds. The four experimental intensity curves described previously for $W(CO)_6$, could be used directly. A damping constant $k = 0.001$ Å^2 was used in the Fourier transformations of these intensity curves. The individual curves for $Mo(CO)_6$ did not include the data from the plates taken with the longest camera distance. Since the intensity curves from these plates had been averaged before the background was subtracted, we decided to connect this aver-

Table 6. s values (Å^{-1}) corresponding to $\eta_M - \eta_C = \pi/2$ and $\eta_M - \eta_O = \pi/2$ determined from 4 experimental intensity curves for each compound.

M	X				
Mo	C	18.97	18.32	18.32	17.95
Mo	O	19.78	20.00	21.52	21.85
W	C	12.30	12.50	12.20	12.35
W	O	12.35	12.46	12.44	12.39

aged curve to the four individual curves already obtained. The intensity values for $s > 5$ Å^{-1} were not changed, and the determinations of the zero points (near $s = 20$ Å^{-1}) are therefore practically independent. The experimental intensity curves were Fourier transformed without any artificial damping.

The experimental s values corresponding to $\eta_M - \eta_X = \pi/2$ found from the individual intensity curves, are given in Table 6. In Table 7 we have compared the mean values obtained from the results in Table 6 to the corresponding

Table 7. Experimental and theoretical s values (Å^{-1}) corresponding to $\eta_M - \eta_C = \pi/2$ and $\eta_M - \eta_O = \pi/2$. The values in parentheses are estimated standard deviations.

M	X	a	b	c	d
Mo	C	18.3_9 (0.40)	20.43	20.4	21.16
Mo	O	20.7_9 (0.80)	21.98	22.9	23.21
W	C	12.3_4 (0.30)	11.79	11.8	12.38
W	O	12.4_1 (0.40)	12.03	12.6	12.91

a. Experimental values.
b—d. Theoretical values from b) the first set, c) the second set, and d) the third set of scattering amplitudes.

theoretical values found from the three sets of scattering amplitudes.[4] The standard deviations given for the mean experimental values are considerably larger than the values in Table 6 indicate: We have changed the applied damping constants and the envelopes, and we have smoothed out the peaks in somewhat different ways, to obtain a more realistic estimate of the errors.

Table 7 shows that the experimental results are lower than all the theoretical values for $Mo(CO)_6$. The agreement is better for set I than for set III, but at least the difference found for Mo—C seems significant also in the former case. The experimental values for $W(CO)_6$ do not in any case differ from the theoretical values by more than twice the standard deviations. The theoretical value from set III is very close to the experimental result in the case of W—C, while the values from set I and set III are almost equally

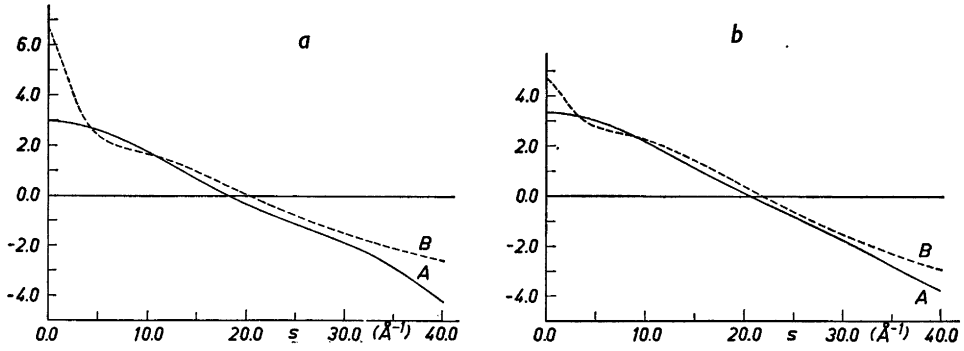

Fig. 7. $Mo(CO)_6$. Comparison of experimental (A) and theoretical (B) g functions.
a. $g_{MoC/OO}(s)$. b. $g_{MoO/OO}(s)$.

close to the experimental result for W···O. As mentioned on p. 2719 the experimental split of both the W—C and W—O peaks was found to be between the corresponding theoretical values. When $\Delta\eta$ is calculated from set II the points do not fall exactly on a smooth curve. These values have also been corrected for the difference in the accelerating potential used in this experiment and the value assumed in the calculations. In spite of these uncertainties the agreement with the experimental values is quite good, for Mo—C and W···O even better than for the other sets.

The results in Table 7 agree very well with the results obtained previously for WF_6 and MoF_6.[4] The experimental s value corresponding to $\Delta\eta_{MoF} = \pi/2$ was found to be lower than the theoretical values and in best agreement with set I. The experimental result for WF_6 was between the theoretical values from set I and set III.

Figs. 7a and b show the averaged functions $g^{exp}_{MoC/OO}(s)$ and $g^{exp}_{MoO/OO}(s)$ compared to the theoretical g functions calculated from set I. Figs. 8a and

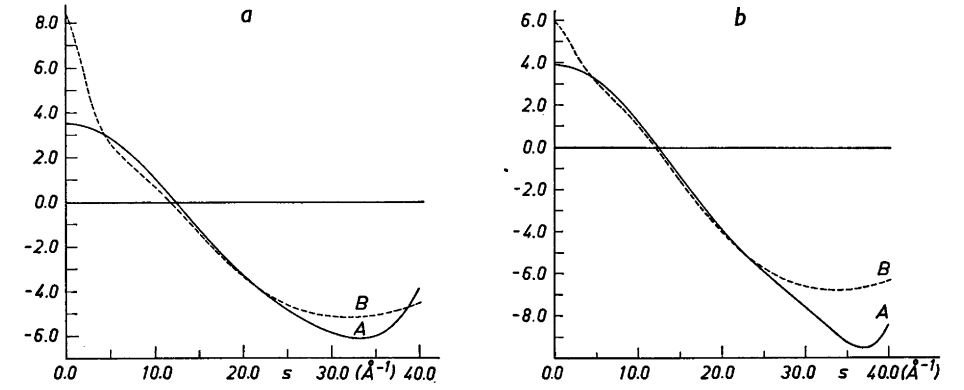

Fig. 8. $W(CO)_6$. Comparison of experimental (A) and theoretical (B) g functions.
a. $g_{WC/OO}(s)$. b. $g_{WO/OO}(s)$.

b show the corresponding curves for $W(CO)_6$. To determine the scale of the experimental functions least-squares calculations were carried out using the experimental g functions and refining α_{MC} and α_{MO} in addition to all the r and u values. The intensity data in the s range 0.5 — 36.0 Å^{-1} were applied for $Mo(CO)_6$, while the range 0.75 — 40.0 Å^{-1} was used for $W(CO)_6$. The shifts in all the r and u values were rather small. The ratios $\alpha_{MoC}/\alpha_{MoO} = 1.05$ and $\alpha_{WC}/\alpha_{WO} = 1.07$ do not deviate more from unity than is to be expected.* The scales were now found by dividing the α values obtained above by the corresponding α values in the Tables 2d and 4d obtained using the theoretical g functions (*cf.* p. 2708 of Ref. 4). It was mentioned in the beginning of this section that the experimental g functions are less reliable than the corresponding functions for the hexafluorides.[4] The inner parts of the curves (say s less than 3 Å^{-1}) depend heavily on the envelope as already mentioned, and the deviations from the theoretical values in this region cannot be considered significant. The outer parts of the experimental curves (but of course not the zero points) are very sensitive to changes in the applied u values. Nevertheless, there is a great resemblance between the curves in Figs. 7 and 8 and the corresponding curves in Ref. 4 (Figs. 6 and 8).

Note added in proof. J. Brunvoll (private communication) has recently applied the fundamental frequencies given by L. H. Jones [9] and by R. L. Amster *et al.*[10] to calculate u values and shrinkage effects in $Mo(CO)_6$ and $W(CO)_6$ at 25°C. The results in the columns a below were obtained using the frequencies in Ref. 9. The results in the columns b were obtained with CO stretching frequencies as given by L. H. Jones [9] (these frequencies have been corrected for anharmonicity), and the rest of the frequencies according to Ref. 10.

	$Mo(CO)_6$				$W(CO)_6$			
	a		b		a		b	
	u	Shrinkage	u	Shrinkage	u	Shrinkage	u	Shrinkage
C_7-O_1	0.0342		0.0342		0.0344		0.0344	
$M_{13}-C_7$	0.0574		0.0557		0.0534		0.0517	
$M_{13}\cdots O_1$	0.0571	0.0060	0.0556	0.0062	0.0532	0.0060	0.0516	0.0062
$C_{10}\cdots O_1$	0.0734	0.0272	0.0686	0.0274	0.0704	0.0244	0.0656	0.0246
$O_1\cdots O_4$	0.0737	0.0397	0.0691	0.0402	0.0707	0.0360	0.0662	0.0365
$C_7\cdots C_{10}$	0.0729	0.0170	0.0680	0.0169	0.0700	0.0146	0.0649	0.0146
$C_7\cdots C_8$	0.1747	0.0042	0.1624	0.0035	0.1653	0.0038	0.1509	0.0031
$O_8\cdots O_1$	0.2086	0.0099	0.1945	0.0094	0.1976	0.0094	0.1812	0.0089
$O_1\cdots O_2$	0.2737	0.0159	0.2581	0.0153	0.2591	0.0151	0.2407	0.0145

The u values given above for the Mo—C and Mo···O distances differ considerably from those in Table 5 column e. By comparing our results (Table 5, columns a and f) to the spectroscopic values given above, we find a very good agreement for u(Mo···O), while our values for u(Mo—C), u(W—C), and u(W···O) are somewhat higher than the spectroscopic results.

* The functions $g^{exp}_{MO/OO}(s)$ have been multiplied by (r_{MO}/r_{MC}) before the least-squares refinements since the contribution from a distance to the RD curve is inversely proportional to r.

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