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Molecular Structure and Phase-shift of Tetramethyllead as Studied by Gas Electron Diffraction

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The molecular structure of tetramethyllead has been determined by the sector-microphotometer method of gas-phase electron diffraction. The structure parameters determined by a least-squares analysis on molecular intensities are, with estimated limits of error, as follows; r_g(Pb–C)=2.238±0.009 Å, r_g(Pb···H)=2.72±0.06 Å, r_g(C···C)=3.66±0.07 Å, and r_g(C–H)=1.08±0.02 Å. The experimental cut-off point was nearly 37 in q value for the 42.0 keV electrons; this was not in sufficient agreement with the theoretical value as calculated from the Thomas-Fermi-Dirac potential for Pb and from the Hartree-Fock potential for C. Moreover, the experimental background showed a significant deviation from its theoretical counterpart in the region of small q values. This discrepancy has not been accounted for even by the use of scattering factors based on a relativistic SCF calculation, or by the correction for the polarization effect available at present.

The electron diffraction study of tetramethyllead (abbreviated to TML) was previously carried out by Wong and Schomaker[1] by use of the visual technique. They pointed out that the use of the complex atomic scattering factors of Ibers and Hoerni,[2] instead of the first Born scattering factors, was essential to the interpretation of the electron-diffraction pattern of TML, which contains both heavy (Pb) and light (C, H) atoms. The effect of the phase-angle difference of the atomic scattering factors, occasionally called the phase-shift, had already been elucidated by Schomaker and Glauber.[3] Wong and Schomaker attempted the first experimental test of the then newly-calculated table of Ibers and Hoerni. They determined the molecular structure of TML to be r(Pb–C)=2.20_3±0.01_0 Å and r(Pb–H)=2.79±0.01 Å. The first cut-off point was determined as q^c_{Pb-C}=38.5±1.5 for the 39.7 keV electrons; they remarked that this was slightly larger than the theoretical value 35.8 obtained from the table of Ibers and Hoerni, which was based on the Thomas-Fermi potential. When the present study was initiated, it was anticipated that the use of the phase angles calculated by the Thomas-Fermi-Dirac (TFD) potential instead of by the Thomas-Fermi potential would improve the consistency between the experimental and theoretical cut-off points. Thus, the present investigation has the purpose of performing a more quantitative examination of the phase-effect as well as making a more precise determination of the structure parameters, which became possible by the use of a modern diffraction unit and by means of the microphotometric processing of the photographic plates.

Experimental

The sample of TML was kindly supplied by Mr. Y. Fujiwara of the Central Technical Research Laboratory, Nippon Oil Co., Ltd., in the form of toluene blend. (Blending with toluene is necessary in order to stabilize the TML. The rate of the blending of TML and toluene was about 2 to 3). The separation of toluene (mp −95°C) from TML was achieved by utilizing the higher melting point of TML (mp −30°C) as follows. In order to protect TML from oxidation by air, the blend was placed in a flask purged with a flow of dry nitrogen gas. It was then slowly cooled in a dry ice-acetone bath under gentle stirring in order to avoid rapid crystallization. This cooling process was continued for about three hours until nearly two-thirds of the total content had solidified. Then the liquid part (toluene) was removed by decantation. This process of separation was repeated three times. The sample thus obtained was then assumed to have sufficient purity, since it has been reported that a series of several freezings and decantations raises the purity of TML to above 99%.[4]

The separated TML was transferred into a glass sample holder in a dry box filled with nitrogen gas. The whole

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1) C. Wong and V. Schomaker, *J. Chem. Phys.*, **28**, 1007 (1958).
2) J. A. Ibers and J. A. Hoerni, *Acta Crystallogr.*, **7**, 405 (1954).
3) V. Schomaker and R. Glauber, *Nature* **170**, 290 (1952).
4) The separation and purification were carried out by referring to a technical report privately communicated by Mr. Fujiwara of Nippon Oil Co., Ltd.

procedure of separation and purification was carried out just before taking photographs. Since TML is a strong toxicant, full caution was used during the experimental procedures by following the advice in the Manual prepared by Ethyl Corporation.

Diffraction patterns were taken by means of a unit reported elsewhere,[5] with an r^3-sector at the camera length of 24.43 cm. The experimental conditions were as follows; accelerating voltage, ~42.0 kV; sample pressure, ~17.5 Torr; exposure time, 40~50 sec; electron-beam current, ~0.2 μA; and room temperature, 18°C. In order to make the calibration of the accelerating voltage, the diffraction patterns of carbon disulfide were taken just before taking those of the sample in the same sequence of exposures.

The optical densities of the diffraction photagraphs were measured by means of a double-beam microphotometer connected to an integral digital voltmeter. The data covered the range of $q=12$—62.

Analysis

The optical densities (0.25—0.50) were converted to the total intensities by assuming the proportionality between density and electron intensity. After the correction for the imperfection of the sector shape had been applied, the total intensities were interpolated at integral q values by Lagrange's method of three-point interpolation and were leveled by the theoretical background function. The experimental backgrounds and molecular intensities were determined by the calculation of the radial distribution curve and its inverse Fourier trans formation in the range of $r \leqq 0.8$ Å. In the calculation of the radial distribution curves, Bartell's correction for non-nuclear scattering[6] was modified in order to avoid difficulty arising from the large phase-angle difference. The method follows that of our previous paper.[7] The factors $\chi_{ij}=\mu_{ij}\cos\Delta\eta_{ij}$ were replaced by the following approximate functions:

$$\chi_{Pb,C} = 1.527 \cos\left\{0.1251\left(\frac{\pi}{10}q\right)\right\}$$

$$\chi_{Pb,H} = 1.933 \cos\left\{0.1488\left(\frac{\pi}{10}q\right)\right\}$$

$$\chi_{C,C} = 4.247 \exp\left\{-0.0143\left(\frac{\pi}{10}q\right)^2\right\}$$

$$\chi_{C,H} = 6.302 \exp\left\{-0.0135\left(\frac{\pi}{10}q\right)^2\right\}$$

$$\chi_{H,H} = 8.569 \exp\left\{-0.0133\left(\frac{\pi}{10}q\right)^2\right\}$$

The b value in the damping factor $\exp(-bq^2)$ was taken to be 0.00065.

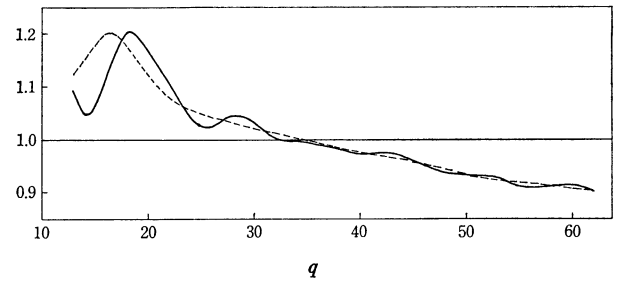

Fig. 1. Total intensity and experimental background of TML leveled by the theoretical background based on the TFD potential for Pb.

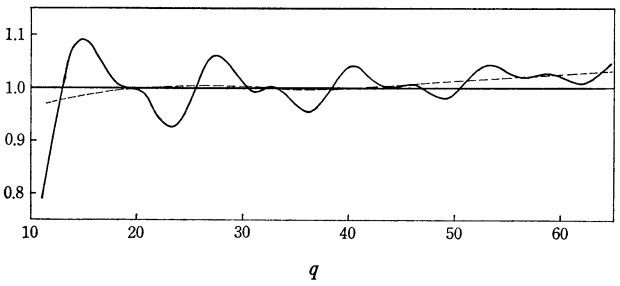

Fig. 2. Total intensity and experimental background of carbon disulfide leveled by the theoretical background.

One of the leveled total intensities and its background thus obtained are shown in Fig. 1 for TML[8] and in Fig. 2 for carbon disulfide, the reference molecule. The theoretical backgrounds were calculated by the use of elastic and inelastic scattering factors taken from the literature.[9-11] As is shown in Fig. 1, the background of TML rises sharply in the region of q values less than 19; this tendency is different from that of the theoretical value, which is a straight horizontal line at 1.00. On the other hand, the background of carbon disulfide, shown in Fig. 2, is not so different from its theoretical counterpart, except for the tailing up at large q values. This discrepancy in the background will be discussed in the next section.

The experimental molecular intensities obtained from the three best plates were analysed by the standard least-squares method.[12] The theoretical molecular intensity was calculated by the following equation, in which the notations have the usual significance:

$$qM(q) = k\sum_{ij}{}' A_{ij}\mu_{ij}\cos\Delta\eta_{ij}\exp\left\{-\frac{1}{2}\left(\frac{\pi}{10}q\right)^2 l_{ij}^2\right\} \times \sin\left[\frac{\pi}{10}q\left\{r_{aij}-\left(\frac{\pi}{10}q\right)^2\kappa_{ij}\right\}\right]$$

The index of resolution k, the distance r_a and the mean amplitude l were determined by the least-squares fitting of the theoretical expression to the experimental intensities. The nine parameters, the index of resolu-

5) Y. Murata, K. Kuchitsu, and M. Kimura, *Japan J. Appl. Phys.*, **9**, 591 (1970).

6) L. S. Bartell, L. O. Brockway, and R. H. Schwendeman, *J. Chem. Phys.*, **23**, 1854 (1955).

7) H. Fujii and M. Kimura, This Bulletin, **43**, 1933 (1970).

8) Numerical experimental data of the leveled total intensity have been deposited with the Chemical Society of Japan. (Document No. 7113). A copy may be secured by citing the document number and by remitting, in advance, ¥ 100 for photoprint. Pay by check or money order payable to: Chemical Society of Japan.

9) a) M. Kimura, S. Konaka, and M. Ogasawara, *J. Chem. Phys.*, **46**, 2559 (1967); b) M. Ogasawara, S. Konaka, and M. Kimura, *ibid.*, **50**, 1488 (1969).

10) C. Tavard, D. Nicolas, and M. Rouault, *J. Chim. Phys.*, **64**, 540 (1967).

11) L. Bewilogua, *Physik. Z.*, **32**, 740 (1931).

12) a) K. Hedberg and M. Iwasaki, *Acta Crystallogr.*, **17**, 529 (1964); b) Y. Morino, K. Kuchitsu, and Y. Murata, *ibid.*, **18**, 549 (1965).

tion, the distances and the mean amplitudes of Pb–C, Pb···H, C···C, and C–H atom pairs were adjusted without any constraint among them. All the non-bonded C···H and H···H pairs were ignored because of the negligibly small contribution of these terms. The asymmetry parameters κ for bonded pairs were fixed at the values estimated by the diatomic approximation:[13]

$$\kappa = \frac{1}{6}al^4\left\{1+\frac{8\varepsilon}{(1+\varepsilon)^2}\right\}, \quad \varepsilon = \exp\left(-\frac{h\nu}{kT}\right).$$

The Morse anharmonicity parameters, a, were assumed to be 1.7 Å^{-1} for the Pb–C atom pair and 2.0 Å^{-1} for the C–H atom pair.[14] The characteristic frequencies ν were taken to be 475 and 2998 cm^{-1} for Pb–C and C–H, respectively.[15] The estimated values were 49×10^{-7} Å^3 for κ_{Pb-C} and 123×10^{-7} Å^3 for κ_{C-H}. The parameters κ for the non-bonded pairs were assumed to be zero.

The results of the least-squares adjustment for the three plates were in excellent consistency with one another, as is shown in Table 1. The error matrix is shown in Table 2. The final values of the interatomic distances r_g and mean amplitudes are given in Table 3. The total limits of error were estimated by following the procedure described in previous papers.[7,16] The experimental molecular intensity and the theoretical one calculated by the best-fit parameters are shown in Figs. 3 and 4.

Table 1. Results of the least-squares analysis[a]
(r_a and l in Å units)

		σ_1[b]	σ_2[b]
k	0.947	0.035	0.026
r_a(Pb-C)	2.2364	0.0034	0.0017
l(Pb-C)	0.0550	0.0049	0.0023
r_a(Pb···H)	2.7102	0.0232	0.0065
l(Pb···H)	0.1739	0.0181	0.0081
r_a(C···C)	3.6455	0.0264	0.0117
l(C···C)	0.1726	0.0218	0.0040
r_a(C-H)	1.0791	0.0073	0.0062
l(C-H)	0.0868	0.0099	0.0094

a) The averages of the results of three plates are listed.
b) The definitions of σ_1 and σ_2 are given in Ref. 12(b).

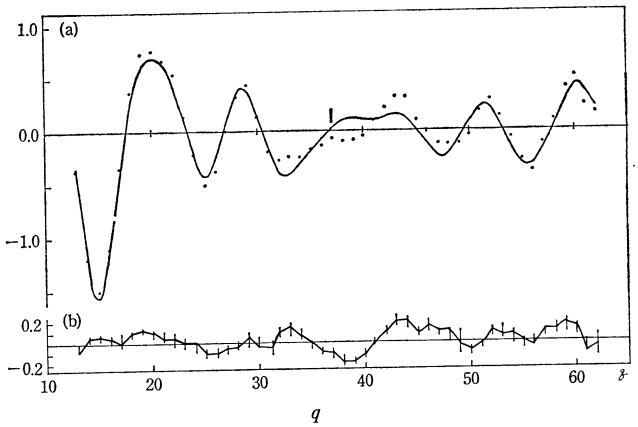

Fig. 3. (a) Molecular intensity of TML. Dots for experimental values and solid curve for the best-fit theoretical intensity. The heavy vertical bar at $q=37$ shows the experimental cut-off point for the Pb-C term. (b) The residuals. Vertical bars indicate the random scattering of residuals among six observed molecular intensities.

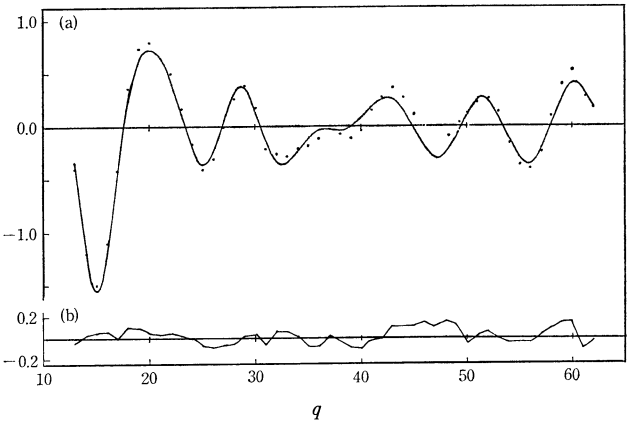

Fig. 4. (a) Molecular intensity of TML. Theoretical curve calculated by use of modified phase-angles for Pb (solid curve) and experimental values (dots). (b) The residuals.

Table 2. Error matrix[a]

	r_a(Pb-C)	l(Pb-C)	r_a(Pb···H)	l(Pb···H)	r_a(C···C)	l(C···C)	r_a(C-H)	l(C-H)	k
r_a(Pb-C)	62	22	130	7	−74	15	16	34	100
l(Pb-C)		87	120	−64	−73	72	16	59	184
r_a(Pb···H)			414	253	−289	152	54	152	469
l(Pb···H)				335	226	−201	15	−116	−341
r_a(C···C)					400	−151	−42	−93	−299
l(C···C)						338	11	95	276
r_a(C-H)							128	−41	65
l(C-H)								171	227
k									657

a) Elements of the matrix are given by $\sigma_{ij}=\mathrm{sgn}(\boldsymbol{B}^{-1})_{ij}\{|(\boldsymbol{B}^{-1})_{ij}|\boldsymbol{V}'\boldsymbol{P}\boldsymbol{V}/(N-m)\}^{1/2}$, where the notations follow Ref. 12(a). Units ($\times10^{-4}$) for r_a and l are Å and for the index of resolution k dimensionless.

13) K. Kuchitsu, This Bulletin, **40**, 505 (1967).
14) E. R. Lippincott and R. Schroeder, *J. Chem. Phys.*, **23**, 1131 (1955).
15) J. A. Jackson and J. R. Nielsen, *J. Mol. Spectrosc.*, **14**, 320 (1964).
16) S. Konaka and M. Kimura, This Bulletin, **43**, 1693 (1970).

Table 3. Distances and mean amplitudes of TML with estimated limits of error (in Å)

	r_g	l
Pb-C	2.238±0.009	0.055±0.012
Pb···H	2.721±0.058	0.174±0.045
C···C	3.656±0.066	0.173±0.055
C—H	1.083±0.020	0.087±0.025

A remarkable result seen in Fig. 3 is that the general features of the experimental molecular intensity are rather different from those of the theoretical curve in the region of $q=35-44$. This was systematically reproduced in each of the molecular intensities from the three plates. The reproducibility is demonstrated by the vertical bars in Fig. 3(b). Thus, the deviation has been considered to be significant, although its amount at each observed point is roughly twice the random scattering of data observed in current studies of other molecules using the same apparatus and analytical procedure. The cut-off points for the Pb–C and Pb···H bond pairs lie in this region. However, the contributions of the Pb···H and other terms to the molecular intensity are smaller in this region than that of the Pb–C term. The theoretical value for the first cut-off point, q^c_{Pb-C}, defined by $\Delta\eta_{Pb-C}=\pi/2$ at q^c_{Pb-C}, is 39.8 for the 42.0 keV electrons, according to the calculation based on the TFD potential for Pb and the Hartree-Fock potential for C.

Discussion

Structure. The bond angles, θ(CPbC) and θ(PbCH), calculated by use of the final values of the r_g distances are 109.5°±3.6° and 104.6°±5.4° respectively. Although the θ angle does not necessarily correspond to the geometrical conformation,[17] no further refinement was attempted on account of the large uncertainties of the non-bonded distances. The obtained θ(CPbC) value merely indicates the overall consistency of the present results with the symmetry of the molecule.

Mean Amplitudes. The vibrational mean amplitudes of TML were calculated by the following two simplified models: (a) A five-atom molecule with *Td* symmetry, where the methyl group was replaced by a point of mass; (b) A five-atom molecule, $PbCH_3$, with C_{3v} symmetry. In each of these models, a simple Urey-Bradley force field was determined from the normal frequencies observed by Jackson and Nielsen.[15] For the *Td*-model, the skeletal normal modes were selected from the observed frequencies. For the C_{3v}-model, the observed frequencies were assessed by considering the correlation between *Td* and C_{3v}. If nearly equivalent frequencies were found in the A_1 and F_2 species in the original assignment by Jackson and Nielsen, an average of them was taken; it was assumed to be an A_1 mode in the local C_{3v} molecule. Similarly, those found in both E and F_2 were assessed to be E-mode frequencies in the C_{3v}-model.

The values of these *observed* frequencies and those calculated by the use of the determined force constants are listed in Table 4. The calculated values of the mean amplitudes are shown in Table 5. In spite of the above simplification, the calculated values have sufficient accuracy because of the heavy central atom in TML. By comparing Tables 5 and 3, it may be seen that the observed mean amplitudes are in fair agreement with the calculated values.

Table 4. Vibrational frequencies of TML (in cm^{-1})

Td-model	obsd.[a]	calcd.	C_{3v}-model	obsd.[a]	cald.
A_1	462	462	A_1	2918	2931
				1153	1167
E	145	145		462	459
F_2	475	477	E	2998	2985
	130	131		1430	1431
				785	777

a) Values selected from the observed frequencies by Jackson and Nielsen.[15] (see Text)

Table 5. Calculated mean amplitudes of TML at 288°K (in Å)

	l(Pb-C)	l(C···C)	l(C-H)	l(Pb···H)
Td-model	0.0594	0.154	—	—
C_{3v}-model	0.0570	—	0.0782	0.138

Scattering Factors and Phase-angles. It has been found that the discrepancy in the molecular intensity shown in Fig. 3 can be alleviated if the cut-off point of the Pb–C term is moved to $q=37$, which is indicated by a heavy bar in Fig. 3. The phase-angle η of the Pb atom was modified in such a way as to make $\Delta\eta_{Pb-C}=\pi/2$ at $q=37$ by simply shifting the whole η *vs.* q curve slightly upwards. As is shown in Fig. 4, the general features of the theoretical intensity as calculated from the modified phase-angles are in better agreement with those of the experimental intensity in the region of $q=35$—44. This suggests that the phase-angles of Pb as calculated from the TFD potential are slightly smaller than the exact values.

In Table 6 are listed the structure parameters obtained by a least-squares fitting of the theoretical expression by the use of the modified phase-angles. The r_a distances are in agreement with the previous values given in Column II within their standard deviations.

Table 6. Results of the least-squares analysis of plate 3 (r_a and l in Å)

	I[a]	II[b]
k	0.992	0.961
r_a(Pb-C)	2.2368	2.2372
r_a(Pb···H)	2.735	2.720
r_a(C···C)	3.637	3.625
r_a(C-H)	1.077	1.081
l(Pb-C)	0.068	0.055
l(Pb···H)	0.182	0.158
l(C···C)	0.171	0.180
l(C-H)	0.091	0.089

a) By use of modified phase angles (see Text).
b) Previous results by use of unmodified phase angles.

17) K. Kuchitsu, *ibid.*, **44**, 96 (1971).

The mean amplitudes are slightly larger, but they are consistent within the total limits of error.

In the hope of accounting for the discrepancy in the background and the cut-off point, the scattering factors based on the relativistic SCF calculation and the correction for the polarization effect were employed. The background of TML was calculated by the use of the relativistic scattering factor for Pb, which was computed by Schäffer, Yates, and Bonham[18] from Liberman's Dirac-Slater atomic potentials. The phase-angles η taken from their table are graphically shown in Fig. 5. The background is shown in Fig. 6. The original values for the 40 keV electrons were converted to those for 42 keV by assuming that the $|f|$ and η curves, regarded as functions of the scattering angle, show no significant difference between 40 and 42 keV. Therefore, only the scaling of abscissa was corrected for the voltage difference in getting the $|f|$ and η *vs.* q curves for 42 keV. The validity of this assumption was confirmed by comparing the TFD scattering factors for 40 and 42 keV.

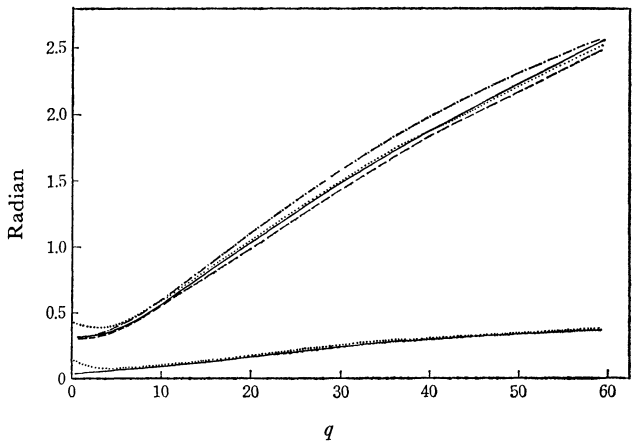

Fig. 5. Comparison of phase-angles; —— TFD for Pb and Hartree-Fock for C, ····· TFD corrected for the polarization effect for Pb and Hartree-Fock corrected for the polarization effect for C, ---- Dirac-Slater for Pb, —·—· modified phase-angle for Pb.

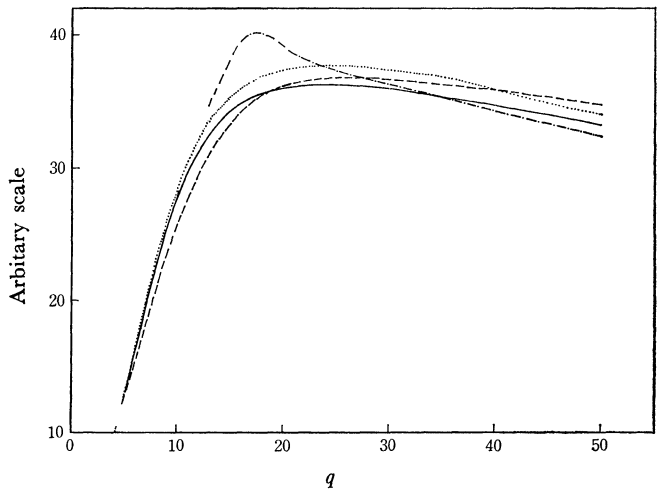

Fig. 6. Comparison of the background functions of TML. The elastic scattering factor of Pb is based on the atomic potential of TFD (——), TFD corrected for the polarization (·····), and Dirac-Slater (----). The observed background normalized to TFD at $q=35$ is shown by (—·—·).

18) L. Schäffer, A. C. Yates, and R. A. Bonham, *J. Chem. Phys.* to be published.

The correction for the polarization effect was computed by a program kindly offered by Professor Bonham.[19] As the numerical parameters for the computation, the following values of the total inelastic scattering cross sections σ_{inel} were employed, namely, $\sigma_{inel}(\mathrm{Pb})=0.2684$ Å^2 and $\sigma_{inel}(\mathrm{C})=0.0531$ Å^2. By this program, the corrections for the real part ΔR^{pol} and the imaginary part ΔIm^{pol} due to the polarization effect were computed. For the Pb atom, these values were added to the real part R^{TFD} and the imaginary part Im^{TFD} of the TFD scattering factors, and the magnitude $|f|$ and the phase angle η of the corrected scattering factors were obtained by:

$$|f| = \{(R^{\mathrm{TFD}}+\Delta R^{\mathrm{pol}})^2 + (Im^{\mathrm{TFD}}+\Delta Im^{\mathrm{pol}})^2\}^{1/2}$$

$$\eta = \tan^{-1}\{Im^{\mathrm{TFD}}+\Delta Im^{\mathrm{pol}})/(R^{\mathrm{TFD}}+\Delta R^{\mathrm{pol}})\}.$$

For the C atom, the same procedure was applied to the Hartree-Fock scattering factors.

The phase-angles and the backgrounds are compared in Figs. 5 and 6. It can be seen from these figures that the theoretical improvement by the use of relativistic scattering factors and the polarization correction is too small to account for the experimental results. The deviation in the background is too large in amount and opposite in direction to be interpreted in terms of the effect of chemical-bond formation.[20] In the diffraction studies of $HgCl_2$[21] and $BiCl_3$[22], however, the experimental results showed no discrepancy from the TFD-based theoretical values in either the cut-off points or the backgrounds. Thus, the possibility that this discrepancy is common in heavy atoms seems to have been excluded. Should the discrepancy observed in the present study be in fact real, then it must presumably be due to something specific to the lead atom. A future investigation of this matter in both experimental and theoretical aspects is to be hoped for.

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19) R. A. Bonham, *Phys. Revs. A*, **3**, 298 (1971).

20) a) T. Iijima, This Bulletin, **39**, 843 (1966); b) D. A. Kohl and R. A. Bonham, *J. Chem. Phys.*, **47**, 1634 (1967).

21) K. Kashiwabara and M. Kimura, The 24th Annual Meeting of the Chemical Society of Japan, (April, 1971) Osaka.

22) S. Konaka and M. Kimura, *ibid.*