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Electron Diffraction Study of Dimethylmercury

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Electron scattering by dimethylmercury has been studied for 42 keV electrons. The theoretical scattering factors currently used have shown satisfactory conformity to the observed scattering intensity, with the following distance parameters: r_g(Hg–C)=2.083±0.005 Å, r_g(Hg···H)=2.71±0.02 Å, and r_g(C–H)=1.106 Å (assumed). A comparison of the background functions has revealed that the scattering factors based on the relativistic Hartree-Fock-Slater potential are better than those based on the Thomas-Fermi-Dirac and Thomas-Fermi potentials. The zero-point average distance determined from the spectroscopic data has shown significant inconsistency with the diffraction result. The diffraction value is shorter than the spectroscopic one by 0.015 Å.

The phase-shift of complex atomic scattering factors in gas-phase electron diffraction has been a long-lasting topic in both theoretical and experimental studies.[1] For almost all the molecules investigated so far, theoretical predictions of the cut-off points have been in reasonable agreement with the experimental results, although the conclusions have sometimes been obscured by large experimental errors. However, a recent study of tetramethyllead has claimed that there was considerable inconsistency between the experimental results and the theory,[2] not only in the cut-off point but also in the background intensity. To prove or disprove the possibility that the inconsistency is inherent in the heaviest members of the atoms, dimethylmercury was chosen for the present study as a practically usable compound which showed closest kinship to tetramethyllead. The present study has disproved the possibility mentioned above, in accordance with the results of a similar study of mercuric chloride.[3]

The vibrational[4] and rotational spectra[5] indicate that the present molecule has a linear structure. As for the Hg–C bond length, Rao *et al.* have derived an r_0 value of 2.094±0.005 Å from the rotational constants,[5] whereas an earlier electron-diffraction study by Gregg *et al.* gave a value of 2.23±0.04 Å.[6] The present paper will, then, present a more accurate Hg–C distance determined by means of the current electron-diffraction technique.

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The rotational constants obtained by Raman spectroscopy[5] were corrected for the vibrational effect, and the zero-point structure was compared with the diffraction results. There was a disparity in the Hg–C distances, which, unfortunately, was left unsettled.

Diffraction Experiment and Analysis

The sample of dimethylmercury was purchased from the K&K Co., Inc., U. S. A., and was used without further purification. The diffraction experiment and the data analysis were carried out by our routine procedure of the sector-microphotometer method.[7] The experimental conditions were as follows: accelerating voltage,~42 kV; camera length, 244.3 mm; electron beam current, ~0.07 μA; sample pressure, 40 Torr, and exposure times, 20—30 sec. The photographs were taken at room temperature. Carbon disulfide was used as the reference substance to calibrate the scale factor. The data covered the range of q= 8—63.

Background Intensities. Two sets of scattering factors for mercury were used in the analysis:

a) The Thomas-Fermi-Dirac(TFD)-based elastic scattering factors[8] and the Thomas-Fermi(TF)-based inelastic scattering factors.[9]

b) The relativistic Hartree-Fock-Slater(RHFS)-based elastic and Hartree-Fock(HF)-based inelastic scattering factors.[10]

For carbon and hydrogen atoms, the HF-based elastic[8] and inelastic scattering factors[11] were used.

The total intensities leveled by the theoretical background function are shown in Fig. 1.[12] The overall consistency between the theoretical and observed background intensities may be regarded as satisfactory, irrespective of the scattering factors employed. However, a close examination in the smaller q region reveals that the discrepancy between the theoretical and observed intensities is much less for the set b than for the set a. This improvement due to the use of the set b was more markedly observed in the region of still smaller q, $q \leqq 8$, by means of a counting method. The small angle scattering by dimethylmercury and other molecules containing heavy atoms will be reported in a forthcoming paper.[13]

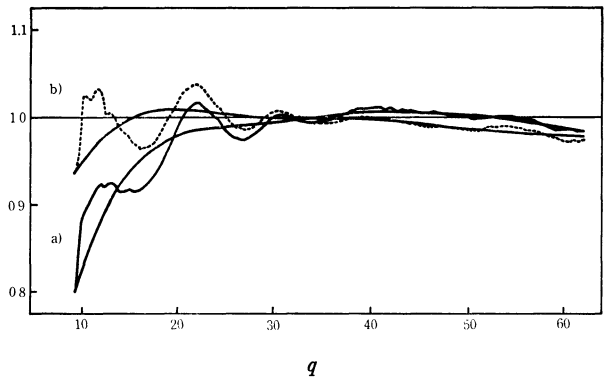

Fig. 1. The leveled total intensity. a): The set a of scattering factors was used, b): The set b was used. (see Text)

Molecular Structure. The bond distances were determined by a least-squares adjustment for the molecular intensity. Since the scattering power of the mercury atom is predominant, it is impracticable to determine the bond distances between light atoms. Thus, only the Hg–C and Hg···H distances were adjusted. The C–H distances were assumed to be 1.100 Å in r_a, and the other non-bonded distances, C···C, intramethyl H···H, and C···H, were constrained in r_α-parameters by assuming a linear structure. The intermethyl H···H distances were ignored, as the large mean amplitude caused by the nearly free rotation of the methyl tops[14] in addition to the small scattering power of hydrogen, makes the contribution from these terms less significant.

All the mean amplitudes were fixed at the values shown in Table 1, which were calculated by the use of the force constants determined by Miles *et al.*[15] The perpendicular amplitudes and the shrinkage corrections were also calculated as listed in Table 1. The calculated values of the parallel mean amplitudes are consistent with those given by Bribes and Gaufrès.[16] The torsional motion was neglected in these calculations. The r_α-values should, therefore, be interpreted as representing the average configuration where the torsional motion is frozen. The asymmetry parameters, κ, was estimated in the same way as in the previous paper.[2]

The results of the least-squares adjustment for the four best plates are summarized in Table 2. The indices of resolution were in the range of 0.86—1.05.

TABLE 1. MEAN AMPLITUDES AND SHRINKAGE CORRECTIONS OF DIMETHYLMERCURY AT 293 K (IN 10^{-4} Å UNITS)

	l_a	$r_a - r_\alpha$
Hg-C	551	34
Hg···H	1205	38
C···C	772	−13
C-H	785	102
C···H	1475	−27
H···H	1278	72

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Table 2. Bond distances of dimethylmercury (in Å units)

	r_g	σ_1	σ_2	Limit of error
Hg-C	2.083	0.004	0.002	0.005
Hg···H	2.712	0.014	0.003	0.018
C-H	1.106	(assumed)		

The results shown in Table 2 were obtained by the use of the RHFS and HF scattering factors (set b), since they were considered to be better expressions of the true scattering factors, because of the better agreement of the experimental background with the theoretical one as well as the theoretical sophistication of the atomic potential itself. The best-fit theoretical molecular intensity is shown in Fig. 2, along with the observed values and the residuals. The agreement is satisfactory.

The use of the set a instead of the set b produced longer Hg–C and Hg···H distances by 0.005 Å and 0.009 Å respectively, with standard deviations similar to those for the set b. The indices of resolution were 0.94—1.13.

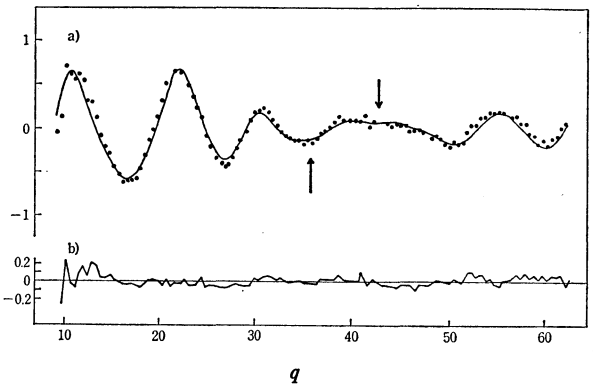

Fig. 2. a) The molecular intensity calculated by the best-fit model (solid curve). Dots are the observed values. The arrows indicate the theoretical cut-off points, $q^c_{Hg\cdots H}=35.8$ and $q^c_{Hg-C}=42.8$.

Zero-point Average Structure

The rotational constants of the normal and fully-deuterated species were observed by Rao *et al.*[5] The moments of inertia were corrected for the vibrational effect by the one-top formalism, which was reported elsewhere.[17] The effective and zero-point moments of inertia are listed in Table 3. The vibrational correction is relatively small for the *b*-constant of this molecule.

The zero-point average distance, r_z(Hg–C), was determined from the zero-point moments of inertia to be 2.095±0.006 Å. A relation between r_z(C–H) and ϕ_z(HCH) was also obtained, although neither of them can be determined separately. If, for instance, r_z(C–H) is assumed to be 1.096 Å, ϕ_z-(HCH) can then be evaluated as 109°20′. The r_z-(Hg–C) is insensitive to the possible isotope effect in the structure parameters of the methyl top as long as the effect is confined within reasonable limit.

Table 3. Moments of inertia of dimethylmercury (in amu Å² units)

	I_b^{eff} a)	ΔI_b b)	$I_b^{(z)}$ c)
Normal	145.06±0.13	0.17	145.23
d_6-species	184.83±0.20	0.21	185.04

a) Observed by Rao *et al.* Ref. 5. b) Vibrational corrections. c) Zero-point moments of inertia.

The r_g distance obtained by the diffraction experiment was converted to the r_α^0 distance which can be compared with the r_z value.[18] The value of r_α^0 thus obtained was 2.080±0.005 Å, which shows a significant difference from the spectroscopic r_z value. This is equivalent to the fact that the B_0(ED) is larger than B_0(Raman) by about 1%. A similar amount of disparity in B_0 was observed by Tanimoto *et al.*[19] in the case of diacetylene and was elucidated by taking the bending-stretching interaction into account. Dimethylmercury also has a low-lying bending mode (~160 cm^{-1}). However, the same treatment applied to the present molecule would require a negative interaction constant, in contradiction to the cases of diacetylene and several linear molecules.[19]

It may be worth considering that the Raman B_0 value might be obscured by overlapping hot bands, as was pointed out by Maki in the case of cyanogen.[20] The effect of the overlapping of bending hot bands is, however, in the direction of increasing the disparity in the present results. Besides the effects of hot bands due to vibrationally-excited states, the effect of the rotation-torsion-vibration coupling seems to be important. At least, with regard to the infrared rotation-vibration bands, it was suggested by Kirtman that such a treatment would be promising in order to study some anomalous features of the spectra.[21]

Judging from the recorded readings of monitoring accelerating voltages there was no indication that the scale factor of the present experiment contained an exceptionally large error.

Numerical computations were carried out on a FACOM 230—60 of the Hokkaido University Computing Center and also on a FACOM 270—20 of the laboratory of Professor Kimio Ohno, whom the authors wish to thank for allowing them to use the facilities.

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