Electron Diffraction Investigation of Gaseous Mercury(II) Chloride

Kuniaki Kashiwabara*, Shigehiro Konaka, and Masao Kimura**
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo

(Received July 26, 1972)

The molecular structure of mercury(II) chloride has been determined by the sector-microphotometer method of gas-phase electron diffraction at accelerating voltages of 29 and 42 kV. The parameter values obtained are: r_g(Hg–Cl), 2.252±0.005 Å; l(Hg–Cl), 0.052±0.005 Å; r_g(Cl–Cl), 4.48±0.04 Å; and l(Cl–Cl), 0.09±0.04 Å. A linear structure has been confirmed within an error of 16°. The experimental mean amplitudes are consistent with the estimated values based on the spectroscopic data. No appreciable differences in the structure parameters have been found between the results of analysis carried out on the basis of the Thomas-Fermi-Dirac and the relativistic Hartree-Fock-Slater scattering factors.

Mercuric chloride has $D_{\infty h}$ symmetry in the normal state. The electronic[1] and vibrational spectra[2–4] measured in the gas phase and the result of mass-spectrometric observation[5] are all consistent with this symmetry. In earlier electron diffraction studies by means of the visual method,[6–8] the bond angle was not observed because of the relatively weak scattering power of the Cl–Cl atom pair. Later, Akishin *et al.* confirmed the linear structure within an error of 40°.[9] The bond lengths reported previously are 2.28,[6] 2.34±0.01,[7] 2.27±0.03,[8] and 2.29±0.02 Å,[9] all involving large uncertainties.

It has been known that the scattering theory based on the first Born approximation is insufficient for the interpretation of the diffraction patterns of about 40 keV electrons by molecules containing both heavy and light atoms. An improvement of the scattering theory has been made by replacing the Born-approximation atomic scattering factors by the complex scattering factors calculated by the partial-waves method.[10] The use of such complex scattering factors is essential for a precise structure analysis of such a molecule as $HgCl_2$, because phase factors have a large effect on the molecular scattering intensity. The complex scattering factors for heavy atoms have been calculated from the Thomas-Fermi-Dirac (TFD) potential[11] and also recently, from the relativistic Hartree-Fock-Slater (RHFS)[12] and the SCF Hartree-Fock (SCF HF)[13] wavefunctions. In a recent work on $Pb(CH_3)_4$, an appreciable discrepancy has been found between the theoretical and observed scattering intensities;[14] in connection with this, further investigations have been desired into the scattering factors for heavy atoms. An improvement of the scattering theory has also been made by adding intramolecular multiple scattering to the simple kinematical framework of the theory.[15] For linear molecules, however, the multiple scattering does not give interference terms dependent on the internuclear distances, at least, not in the first order approximation.[15]

The purposes of the present study are to determine the structure more accurately by the sector-microphotometer method of electron diffraction, to examine the adequacy of the reported scattering factors for mercury, and at the same time, to see whether or not the use of two sets of available scattering factors for mercury produces any difference in the results of analyses. Since the scattering factors are dependent on the accelerating voltage, diffraction photographs were taken at two different voltages, 29 and 42 kV.

Experimental

Research-grade mercuric chloride (about 99.5% pure) obtained from Wako Pure Chemical Industries, Inc., was used as the sample. A high-temperature nozzle[16] made of stainless steel was used to obtain a sufficient vapor pressure. Diffraction patterns were taken on Fuji process hard plates by using an r^3-sector with a diffraction unit which has been described elsewhere.[17] Three sets of experimental data were taken under the conditions shown in Table 1. The accelerating voltages were stabilized within 0.01%. Carbon disulfide was used as the reference material for the determination of the scale factors except for a set of plates taken at 29 kV and at a camera length of 25.89 cm. This set of data was scaled so that the molecular scattering intensities became

---

* Present address: Chisso Polypropylene Fiber Industries, Ltd., Moriyama, Shiga.

** To whom correspondence should be addressed.

1) a) M. Wherli, *Helv. Phys. Acta*, **11**, 339 (1938); **13**, 153 (1940); b) H. Sponer and E. Teller, *Rev. Mod. Phys.*, **13**, 75 (1941).

2) H. Braune and G. Engelbrecht, *Z. Phys. Chem.*, **B19**, 303 (1932).

3) W. Klemperer and L. Lindeman, *J. Chem. Phys.*, **25**, 397 (1956).

4) W. Klemperer, *J. Electrochem. Soc.*, **110**, 1023 (1963).

5) A. Büchler, J. L. Stauffer, and W. Klemperer, *J. Chem. Phys.*, **40**, 3471 (1964).

6) H. Braune and S. Knoke, *Z. Phys. Chem.*, **B23**, 163 (1932).

7) A. H. Gregg, G. C. Hampson, G. I. Jenkins, P. L. F. Jones, and L. E. Sutton, *Trans. Faraday Soc.*, **33**, 852 (1937).

8) L. R. Maxwell and V. M. Moseley, *Phys. Rev.*, **57**, 21 (1940).

9) P. A. Akishin, V. P. Spiridinov, and A. N. Khodchenkov, *Zhur. Fiz. Khim.*, **33**, 20 (1959).

10) a) J. A. Hoerni and J. A. Ibers, *Phys. Rev.*, **91**, 1182 (1952). b) J. A. Ibers and J. A. Hoerni, *Acta Crystallogr.*, **7**, 405 (1954).

11) a) M. Kimura, S. Konaka, and M. Ogasawara, *J. Chem. Phys.*, **46**, 2599 (1967); b) M. Ogasawara, S. Konaka, and M. Kimura, *ibid.*, **50**, 1488 (1969).

12) L. Schäfer, A. C. Yates, and R. A. Bonham, *ibid.*, **55**, 3055 (1971).

13) D. T. Cromer, *ibid.*, **50**, 4857 (1969).

14) T. Oyamada, T. Iijima, and M. Kimura, This Bulletin, **44**, 2638 (1971).

15) a) P. J. Bunyan, *Proc. Phys. Soc. London*, **82**, 1051 (1963); b) J. Gjønnes, *Acta Crystallogr.*, **17**, 1075 (1964); c) J. W. Liu and R. A. Bonham, *J. Mol. Structure*, **11**, 297 (1972). d) L. S. Bartell and T. C. Wong, *J. Chem. Phys.*, **56**, 2364 (1972).

16) M. Ogasawara and M. Kimura, Symposium on Molecular Structure, Chemical Society of Japan, October, 1967.

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

Table 1. Experimental conditions

Accelerating voltage (kV)	Camera length (cm)	Temperature (°C)	Beam current (μA)	Exposure time (min)	Observed range (q)	Number of plates
42	12.39	160—170	0.27	3—6	17—104	3
29	12.39	160—170	0.29	2—5	12—91	2
29	25.89	160—170	0.19	2—4	6—45	3

consistent with the interatomic distances determined by the other sets of data; it was used only for the examination of background intensities at small angles. The optical densities of the diffraction patterns, D, were measured with a digital microphotometer and were converted to the intensities, E, by assuming the relation, $E=D(1+0.03D)$, and the intensities were corrected for the imperfection of the sector shape.[18]

Analysis of Data

The elastic scattering factors for Hg and Cl used for the data analysis described in this section were those calculated by the partial-waves method based on the Thomas-Fermi-Dirac and the Hartree-Fock (HF) potentials respectively.[11] As for the inelastic scattering factors, the values based on the SCF HF wavefunction[13] and the HF potential[19] were used for Hg and Cl respectively. The 42 kV data were also analyzed using the RHFS elastic scattering factors for Hg, but no significant change was found in the result of analysis. This will be discussed in a later section.

The experimental scattered intensities were leveled by the theoretical background, to which the contribution from the elastic scattering factors for Hg is dominant. The experimental molecular intensities, $qM(q)$, were calculated as $q(I_T-I_B)/I_B$, where I_B is a smooth background drawn through the total intensity curve, I_T. The theoretical expression of $qM(q)$ is given by;

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

with the usual notations.[20]

The background curves were revised by the use of the non-negativity criterion for radial distribution curves. For this purpose, the following g_{ij} functions were chosen so as to fit theoretical $\mu_{ij}\cos(\Delta\eta_{ij})$.[18] For 42 kV:

$$g_{Hg-Cl} = 1.45\cos(0.0283q)$$

$$g_{Cl-Cl} = 2.2$$

and for 29 kV:

$$g_{Hg-Cl} = 1.45\cos(0.0326q)$$

$$g_{Cl-Cl} = 1.64\exp(-3.1\times10^{-4}q^2).$$

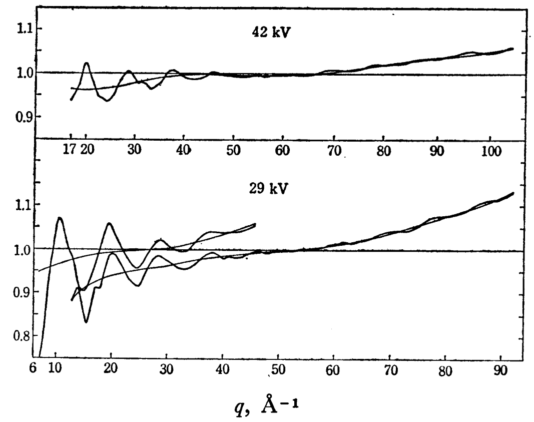

Fig. 1. Leveled total intensities and backgrounds.

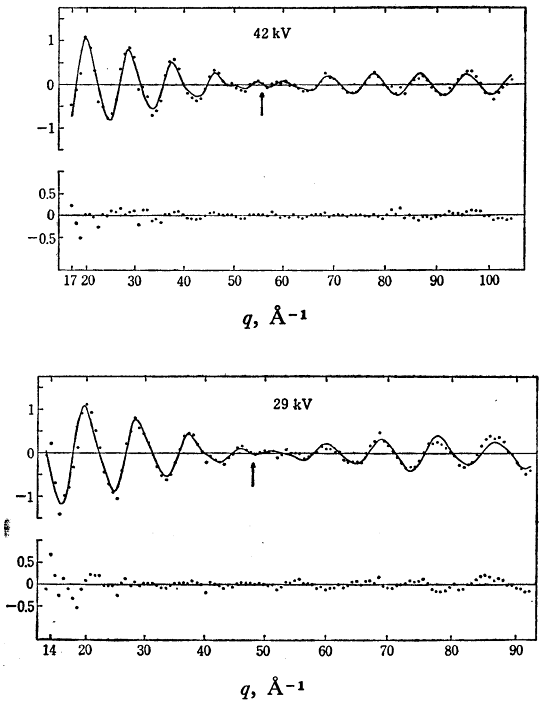

Fig. 2. Molecular intensities and the residuals.
Dots and solid curves show the observed values and the best-fit theoretical curves respectively. The arrows indicate the theoretical cut-off points based on the TFD scattering factors.

One of the leveled total intensities and its background thus obtained[21] are shown in Fig. 1 for each of the three combinations of accelerating voltage and camera length listed in Table 1.

The interatomic distances, r_a(Hg–Cl) and r_a(Cl–Cl), the mean amplitudes, l(Hg–Cl) and l(Cl–Cl), and the index of resolution, k, were determined by least-squares fittings of the experimental molecular intensities to

---

[18] S. Konaka and M. Kimura, This Bulletin, **43**, 1693 (1970).

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

[20] S. Konaka, Y. Murata, K. Kuchitsu, and Y. Morino, This Bulletin, **39**, 1134 (1966).

[21] Numerical experimental data of the leveled total intensity have been deposited with the Chemical Society of Japan. (Document No. 7305).

TABLE 2. RESULTS OF THE LEAST-SQUARES ANALYSIS[a)] (r_a AND l in Å UNITS)

		average	σ_1	σ_2
42 kV	k	0.852	0.023	0.028
	r_a(Hg-Cl)	2.2528	0.0018	0.0022
	r_a(Cl-Cl)	4.4720	0.0157	0.0192
	l(Hg-Cl)	0.0508	0.0019	0.0023
	l(Cl-Cl)	0.0777	0.0132	0.0162
29 kV	k	0.903	0.013	0.018
	r_a(Hg-Cl)	2.2501	0.0018	0.0026
	r_a(Cl-Cl)	4.4835	0.0200	0.0283
	l(Hg-Cl)	0.0540	0.0020	0.0024
	l(Cl-Cl)	0.0992	0.0166	0.0235

a) The weighted average of results from three plates for 42 kV and those from two plates for 29 kV are listed.

TABLE 3. Error matrix[a)]

	r_a(Hg-Cl)	l(Cl-Cl)	r_a(Cl-Cl)	l(Cl-Cl)	k
r_a(Hg-Cl)	24	3	−3	−1	16
l(Hg-Cl)		26	10	18	69
r_a(Cl-Cl)			182	−17	37
l(Cl-Cl)				156	80
k					312

a) Elements of the matrix are given by $\sigma_{ij}=\mathrm{sgn}(B^{-1})_{ij}\{|(B^{-1})_{ij}|V'PV/(N-m)\}^{1/2}$, where the notations follow Ref. 23. Units ($\times 10^{-4}$) for r_a and l are Å and the index of resolution, k, is dimensionless.

the theoretical expression with our conventional weighting scheme.18) The asymmetry parameter, $\kappa_{\mathrm{Hg-Cl}}$, was fixed at an estimated value of 5.3×10^{-6} Å^3 in a diatomic approximation,22) and the $\kappa_{\mathrm{Cl-Cl}}$ was assumed to be zero. The data analysis was made by using the computer program used for AsF_3.18) The experimental molecular intensities, the theoretical curve calculated from the best-fit parameters, and the difference curves are shown in Fig. 2.

The results of the analyses are given in Table 2. An error matrix for a plate taken at 42 kV is given in Table 3. As may be seen in Table 2, the data at different accelerating voltages led to results consistent with each other. For the determination of the molecular parameters, the two results were averaged with weights inversely proportional to the squares of the limits of error, which were estimated from both random and systematic errors as follows. Since the standard deviations, σ_2, estimated from the fluctuations in the results are slightly larger than the standard errors, σ_1, as estimated by the least-squares treatment, $2.6\sigma_2$ was chosen as the random error corresponding to the 99% confidence interval.18) The systematic error estimated for the interatomic distance includes the uncertainty in the scale factor and the errors associated with ambiguities in the κ values. For the means amplitudes, an error due to the uncertainty in the nozzle temperature was taken into account.

TABLE 4. DISTANCES, MEAN AMPLITUDES AND SHRINKAGE (IN Å UNITS)

	r_g	l	δ_g
Hg-Cl	2.252±0.005	0.052±0.005	0.024±0.045
Cl-Cl	4.480±0.044	0.09±0.04	

Other systematic errors were ignored since they were estimated to be much smaller than the random error. The final results thus determined are listed in Table 4. The shrinkage, δ_g, given in this table was calculated as $2r_g$(Hg–Cl)$-r_g$(Cl–Cl).24)

Discussion of the results

The mean amplitudes and shrinkage can be calculated from the vibrational frequencies according to an ordinary harmonic approximation.24) The fundamental frequencies of $HgCl_2$ observed in the gas phase have been summarized by Klemperer *et al.* as follows4,5): ν_1, 360 cm^{-1} (the average of the frequencies from the Raman2) and electronic spectra1)); ν_2, 70 cm^{-1} (a value from the electronic spectra1) which is close to the value of 71 cm^{-1} deduced by statistical thermodynamics6)); and ν_3, 413 cm^{-1} (a value from the infrared spectra3)). The values calculated from these frequencies at 165°C are as follows: l(Hg–Cl), 0.0506 Å; l(Cl–Cl), 0.0706 Å; and δ_g, 0.036 Å. They are consistent with the present experimental values. Since the bending frequency is very low, the above calculation might be insufficient for the l(Cl–Cl).25) However, no further treatment was made because of the large experimental uncertainties in the mean amplitude and vibrational frequencies.

If we assume the shrinkage in this molecule to be 0.036 Å, then the bond angle in the r_α-structure26) is found to equal 180°, within an uncertainty of 16°. The bond lengths obtained by the previous studies were too long, by from 0.02 to 0.09 Å.6–9)

Figure 1 shows that the theoretical backgrounds based on the TFD scattering factor are in agreement with the experimental values within their uncertainties. Although the experimental backgrounds deviate by 10% or less from unity, the possibility of this amount of deviation being caused by extraneous scattering cannot ruled out judging from the shape of the leveled intensity and the observed indices of resolution. The agreement of the observed mean amplitude, l(Hg–Cl), with the theoretical one is another support for the adequacy of the scattering factors used. No significant deviations are seen between the observed and calculated molecular intensities as shown by the difference curves in Fig. 2; the agreement near the cut-off points, 55.8 Å^{-1} for 42 kV and 48.1 Å^{-1} for

---

22) K. Kuchitsu, This Bulletin, **40**, 505 (1967).

23) K. Hedberg and M. Iwasaki, *Acta Crystallogr.*, **17**, 529 (1964).

24) S. J. Cyvin, "Molecular Vibrations and Mean Square Amplitudes," Universitetsforlaget, Oslo, and Elsevier Publishing Co., Amsterdam, 1968.

25) M. Tanimoto, K. Kuchitsu, and Y. Morino, This Bulletin, **43**, 2776 (1970).

26) Y. Morino, K. Kuchitsu, and T. Oka, *J. Chem. Phys.*, **36**, 1108 (1962).

29 kV in the q scale, is satisfactory for both accelerating voltages.

The data at 42 kV were also analyzed using the RHFS elastic scattering factor for Hg.[12)] Since the calculated values are available only at 10, 40, 70 and 100 kV, the values for 42 kV were estimated by referring to the TFD values calculated at 40 and 42 kV. The theoretical cut-off point derived from the RHFS scattering factor is about 3 Å^{-1} larger than that obtained from the TFD scattering factor.

The use of the RHFS scattering factor made the background curves in Fig. 1 closer to unity, and caused the index of resolution and mean amplitude, l(Hg–Cl), to decrease by 0.05 and 0.002 Å respectively. However, the magnitudes of the variations are within the experimental uncertainties or the limits of error. The other parameter values and their standard deviations were practically unchanged. In conclusion, both the TFD and the RHFS scattering factors are consistent with the results of the present experiment; they caused no significant difference in the results of the structure determination.

The authors wish to thank Professor Takao Iijima for his helpful discussions. The numerial computations were carried out on a FACOM 230—60 of the Hokkaido University Computing Center.