# *Studies on Molecular Structure by the Measurement of the Dielectric Constants of Gases and Vapors. I. Construction of an Apparatus and the Dipole Moment and the Molecular Structure of 1, 1-Dichloroacetone*

By Takehiko CHIBA

(Received June 5, 1954)

The measurement of dipole moment is one of the most powerful tools for the study of molecular structure. However by the dilute solution method usually employed it is difficult to obtain the true dipole moment of free molecules. The determination of atomic polarization and the measurement of the moment for the substances which are insoluble in nonpolar solvents as well as those which have a moment of small magnitude can only be made by a gas method. In spite of its importance, gas measurements reported so far are very scarce, because a very high precision is required in this method compared with the solution method. The purpose of this research is to study many interesting problems on molecular structure by precise determination of the dielectric constants in the gaseous state.

The present paper deals with the details of the construction of the apparatus and the result of the measurement of the dipole moment of 1,1-dichloroacetone.

## I. Apparatus

The measuring apparatus is shown in Fig. 1,

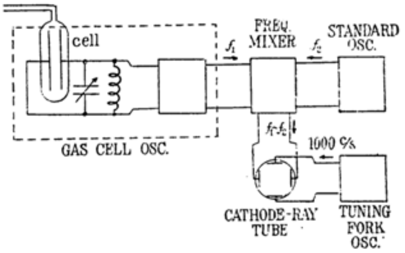


Fig. 1. Block-diagram of the measuring system.

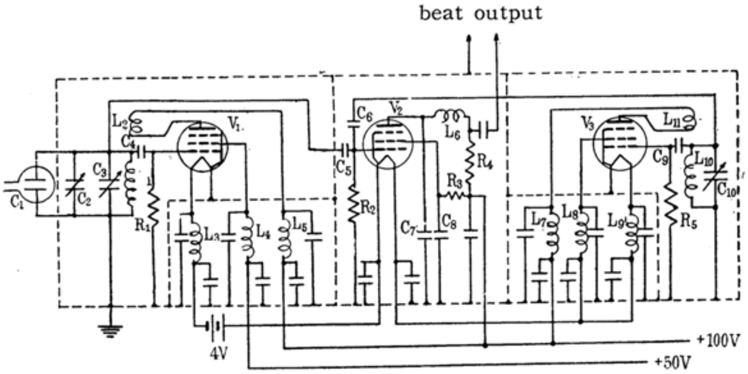


Fig. 2. Oscillators and mixer circuit.

$C_1$ Gas cell
$C_2$ Precision condenser
$C_3$ Variable air condenser
(max. capacity, ca. 90$\mu\mu$F)
$C_4$, $C_9$ 100$\mu\mu$F
$C_5$, $C_6$ $\sim$1$\mu\mu$F
$C_7$ 250$\mu\mu$F
$C_8$ 0.01$\mu$F
$C_{10}$ Variable air condenser
(max. capacity, ca. 860$\mu\mu$F)
All the other capacitors have values of 0.1$\mu$F.

$R_1$, $R_5$ 200k$\Omega$
$R_2$ 1M$\Omega$
$R_3$ 100k$\Omega$
$R_4$ 50k$\Omega$

$L_1$ 41 turns of 0.4mm diameter enamel wire space-wound on 60 mm. diameter "steatite" bobbin.
$L_2$ 10 turns of 0.32 mm. diameter silk-covered wire close-wound on the same bobbin as $L_1$, with $L_2$ spaced 7 mm. from $L_1$.
$L_{10}$ and $L_{11}$ same as $L_1$ and $L_2$
$L_3$, $L_9$ 200$\mu$H
$L_4$, $L_5$, $L_6$, $L_7$, $L_8$ 4mH
$V_1$, $V_2$, $V_3$ 1N5-GT

which is similar to that employed by Groves[1]. A beat output from two oscillators, one of which is a standard oscillator and the other one which has a gas cell and a precision condenser in its tank circuit, is fed to one deflection plate of a cathode-ray tube, and 1000-cycle output from a tuning fork oscillator to the other plate to form a Lissajous figure on the screen. The change in the cell capacity by the introduction into the cell of a vapor of a sample is measured by the decrease of the capacity of the precision condenser until the figure takes the original form.

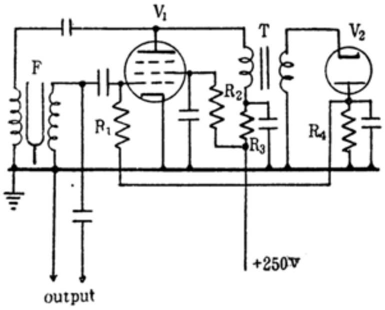
**1. Oscillators and Mixer.**—The circuit connexion of the oscillators and the mixer is shown in Fig. 2. The gas cell oscillator and the standard one are constructed as similarly as possible, their operating frequency being about one megacycle. The outputs of the two oscillators are fed to the mixer, where a beat frequency is formed.

In the course of the construction of the oscillators, several points are found to be important for maintaining the oscillation frequency in extremely high stability which is necessary for the measurement of a dielectric constant in the gaseous state.

These are as follows: Air condensers exclusively are used for the tank circuit capacity because a mica or titanate condenser gives time drift to the frequency. The tank circuit is designed so as to give the least loss, and, accordingly, both the grid leak and the plate resistance of the vacuum tube circuit are made high (electron coupling circuit is used). The fluctuation of the plate resistance is minimized by not inserting a carbon resistor in the screen grid circuit for potential drop. In order to avoid heat emission from the tube a dry cell tube 1N5-GT is empolyed. The oscillators and the mixer are all battery-operated. They are placed in a wooden box lined with brass plates. The high frequency filters of both high tension and filament supplies for the oscillators are placed in a shielded chassis to avoid inter-oscillator coupling. The earth line is made of a stout brass pipe well soldered to water piping.

The circuit thus constructed proved to be very stable: the drift of the beat frequency was found to be less than one cycle per hour, which corresponds to $2\times10^{-4}$ per cent per hour in the cell capacity change.

The circuit of the tuning fork oscillator is shown in Fig. 3. A slight change in the frequency is noticed by an occasional change in the amplitude of oscillation, a diode amplitude limiter being attached to it.



| | | | |
|---|---|---|---|
| $R_1$ | 1MΩ | T | A.F. transformer |
| $R_2$ | 150kΩ | F | Tuning fork |
| $R_3$ | 30kΩ | $V_1$ | 6SK7 |
| $R_4$ | 500kΩ | $V_2$ | 6H6 |

Capacitors are all 0.01μF.

Fig. 3. Tuning fork oscillator circuit.

**2. Precision Condenser.**—The precision condenser is a micrometer variable condenser[2] shown in Fig. 4. The capacity change produced by 1-mm. step of the micrometer condenser is about 0.06μμF, so that a change of capacity can be read to the order of $6\times10^{-4}$μμF.

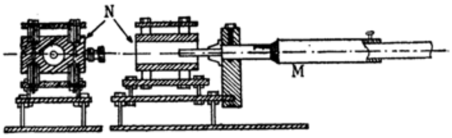


Fig. 4. Precision micrometer condenser.

**3. Gas Cell.**—The gas cell is the most important part of the apparatus since the plate surface inevitably comes into contact with various kinds of vapors at high temperatures, and a change in its state affects sensitively the observed value. The cell must be fixed rigidly in order to keep the capacity constant over a long period of time and over a wide range of temperatures. Thus, four kinds of cells shown in Table I are tested. Cell A is that used by Watanabe[3]: the small distance between the plates seems to make serious the capacity instability which occurs in the case of adsorption or condensation of a sample onto the plates. Cell B is constructed with wide gaps but it has mica spacers which were proved to be the cause of an abnormally large increase in the capacity recorded even with far less filling of a sample vapor below its saturation pressure. Cells C and D are constructed so as to eliminate these shortcomings. The

---

[1] L. G. Groves, *J. Chem. Soc.*, **1939**, 1144.

[2] H. E. Watson et al., *Proc. Roy. Soc.*, **143**, 558 (1934).

[3] I. Watanabe, *Bull. Inst. Phys. Chem. Research (Tokyo)*, **20**, 681 (1941).

TABLE I

DATA OF THE GAS CELLS USED

| | Plate material | Diam. (mm.) | Length (mm.) | No. of plates | Gaps (mm.) | Spacing insulator | Capacity (μμf) |
|---|---|---|---|---|---|---|---|
| A | Nickel | 45 | 130 | 4 | approx. 1 | Mica | approx. 540 |
| B | Brass (gold plated) | 46 | 130 | 5 | „ 1.5 | Mica | „ 450 |
| C | Nickel | 35 | 120 | 3 | „ 1.3 | Glass | „ 160 |
| D | Nickel (gold Plated) | 46 | 137 | 3 | „ 1.3 | Glass | „ 200 |

spacing of these cells is as follows. Short nickel wires are silver-soldered at three points, each 120° apart at both ends of each cylinder plate, these three plates are placed in a coaxial position, and glass beads are melted on three nickel wires at each corner (Fig. 5b). The cell is designed to have a capacity of 150 to 200μμF, since, on account of the high stability of the oscillation, it is unnecessary to use a cell of so large a capacity as was previously thought requisite. The middle plate of Cell D is made 2 mm. shorter than the two other plates and the nickel wires are shielded by small guard pieces to reduce stray capacity. Cell D was found to be the most satisfactory.

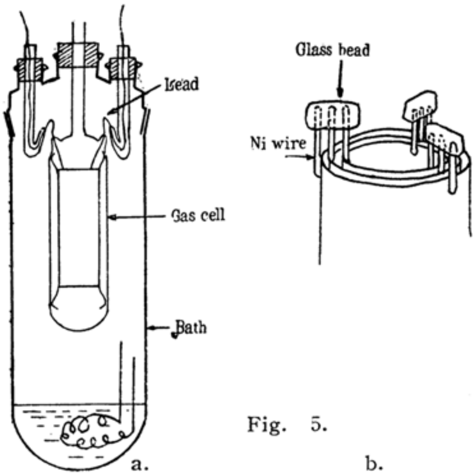


Fig. 5.

a. Gas cell in the vapor bath

b. Spacing of the plates

**4. Gas Filling Apparatus and Manometer.**—The equipment of gas filling as shown in Fig. 6 is constructed as a modification of Groves' method[1]. A sample in gaseous state is introduced from the cock $C_2$, while that in a liquid state is first poured into S, cooled from outside, and the whole system is evacuated. Then the cock $C_4$ is closed and $C_5$ opened to admit air through the cock $C_6$ so that the liquid goes up slowly to the capillary U-tube. The path from the cell to the point P is heated with a nichrome wire to nearly the same temperature as that of the cell. The liquid evaporates at the point P, where a small piece of gold is placed to prevent bumping. Air is admitted from the flow controllable leak-cock $C_6$ and $C_7$ so as to keep the liquid in contact with the gold piece, whereby the velocity of the air flow is so adjusted that the liquid meniscus in the manometer side of the U-tube remains at about the middle. Fine pneumatic control is facilitated by connecting cocks, $C_6$ and $C_7$, to an air reservoir, V, the pressure in which is kept at about 15 to 30 cmHg. When a desired amount of the vapor is introduced, the two cocks are closed after bringing the liquid menisci of both arms to an equal level; the pressure of the vapor is then directly read by the manometer. The measurement is repeated by evacuating the whole system, condensing the vapor at S, and then carrying out the same operation as stated above. For a sample having a rather high vapor pressure at room temperature, the measurement becomes difficult since it readily condenses on the manometer wall.

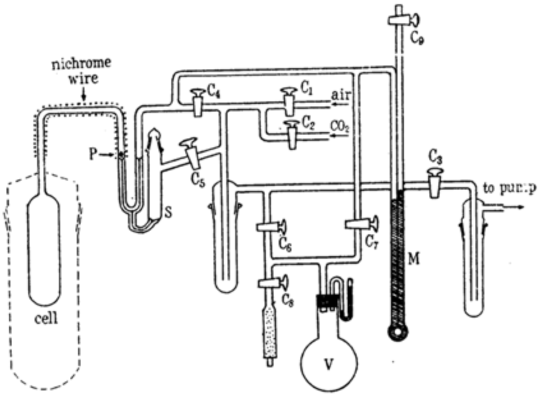


Fig. 6. Apparatus for gas filling and manometer.

**5. Vapor Bath.**—The cell is maintained at a constant temperature by the use of a vapor bath thermostat (Fig. 5a). Since the lead-wires to the cell are stretched in the vapor of the bath, dew-drops condense on them, followed by a rapid change in stray capacity disturbing a stationary Lissajous figure at a balancing point. This difficulty is eliminated by covering the lead with glass tubes so that dew does not touch the leads directly (Fig. 5a).

Methanol, benzene, heptane, toluene, xylene, bromobenzene, and decaline are employed for the bath at 65°, 80°, 98°, 111°, 140°, 156° and 192°, respectively.

## II. Calibration and Measuring Procedures

**1. Calibration of the Micrometer condenser.**—It is not necessary to know the absolute capacity of the micrometer condenser accurately, but its linearity must be checked. This is done by observing at each point of the micrometer the difference of the two micrometer readings which occur when the oscillation frequency shifts from a constant frequency to one higher by a given frequency (for instance, 100 cycles). The actual procedure is conveniently carried out by employing two tuning fork oscillators of 1000 and 700 cycles, respectively, and adjusting the beat frequency first to the first overtone of 1000 cycles and then to the second one of 700 cycles. By this procedure it is found that the deviation of capacity from linearity is less than 0.2 percent in the region of 8 to 23 mm. of its readings.

**2. Measuring Procedure.**—A sample is first introduced to a few mmHg, $p_1$, by the method described above, and the micrometer reading of the condenser is taken, $l_1$. The vapor is again filled to the pressure $p_2$, and the micrometer reading $l_2$ is taken. The polarization, $P$, is then given by

$$P=\frac{1}{3}\times\frac{\Delta l}{l_0}\times\frac{RT}{\Delta p}=20790\times\frac{\Delta l}{\Delta p}\times\frac{T}{l_0},$$

where $\Delta l=l_2-l_1$, $\Delta p=p_2-p_1$, $T$ is the absolute temperature of the vapor, and $l_0$ is the cell constant in the unit of capacity of 1 mm. of the micrometer condenser. $l_0$ is determined by known substances. Air and carbon dioxide are convenient for this purpose, but these substances have such small polarizations that measurements at several hundred mm. filling have to be carried out. Usually, however, gradual capacity change is observed in such cases, resulting in large fluctuation of $l_0$ values observed. Therefore mesitylene, on account of its moderate vapor pressure, is used for this purpose and $l_0$ is measured at three temperatures, 111°, 141°, and 192°. The measured values are constant within experimental errors, $l_0$ is taken to be their mean value, i. e. 3545 mm. in Cell D.[4] The additional check of the cell constant is made at room temperature using carbon dioxide with a large number of observations of different $\Delta p$'s. The resultant $l_0$ is in good accord with the value mentioned above.

The same frequency is used in every measurement, since otherwise a change of the cell constant cannot be avoided if there exists non-negligible inductance between the cell and the other part of the tank circuit.

Samples are filled to about 5 to 15 cmHg. The pressure should not exceed about two-thirds of its saturation pressure, because otherwise abnormally large values are often observed.

In all measurements gas is assumed to be ideal, for the correction of gas imperfection is 0.3 per cent at most and is usually far less than experimental errors. A mean value of $\Delta l/\Delta p$ is used instead of the value extrapolated to zero pressure, since, though it is more rigorous to use the latter, the observed value is always proved to be approximately the same within experimental errors throughout all the values of $\Delta p$. In most cases, the error in the observed polarization is 1 to 2 percent in each observation, and the error originates from the pressure readings as well as from the capacity measurement. By several runs of observation, however, it is easy to reduce the error to less than 0.5 per cent.

## III. The Dipole Moment and the Molecular Structure of 1.1-Dichloroacetone

**1. Experimental and the Result of the Measurement.**—1.1-Dichloroacetone was prepared by passing chlorine gas into a mixture of acetone, granulated marble, and water. One volume of the raw product was washed with ten volumes of water to separate monochloroacetone, dried over calcium chloride, and fractionally distilled; b.p. 118–120°C. The main contamination in this product is monochloroacetone, whose absence was confirmed by the observation of the infrared spectrum.

The results of the measurement are given in Table II. The plot of the molecular polarisation, $P$, against $1/T$ is found to be almost a straight line. If the dipole moment is assumed to be independent of temperature, the inclination of this straight line gives the moment of 1.52 D, and the intercept of this line with the axis of $P$ affords the atomic polarization $P_A$ of 29 cc. It is impossible, however, to allow such a large value to the atomic polarization, since it is well known that in most cases the atomic polarization dose not exceed 10 percent of the electronic polarization, and $MR_D$ of this compound is

---

[4] The polarization of mesitylene is taken to be 41.5 cc.

only 25.8 cc. Thus, by the usual assumption that $P_E+P_A=1.05MR_D=27.1$ cc., it must be concluded that the moment of this molecule increases with the temperature as listed in Table II.

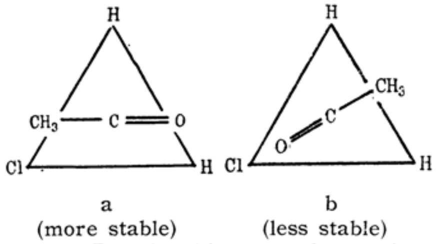
TABLE II
THE OBSERVED POLARIZATION AND DIPOLE MOMENT OF 1, 1-DICHLOROACETONE

$MR_D=25.8$ cc. $P_E+P_A=1.05MR_D$ (assumed) $=27.1$ cc.

| $T°$ | $p$ | $n$ | $P$ | $\Delta P$ | $\mu$ |
|---|---|---|---|---|---|
| K | mmHg | | cc. | cc. | D |
| 338.3 | 65–90 | 7 | 92.6 | 0.5 | 1.91 |
| 371.1 | 66–117 | 7 | 89.0 | 0.2 | 1.94 |
| 413.3 | 72–120 | 7 | 85.2 | 0.3 | 1.99 |
| 467.5 | 85–113 | 9 | 81.5 | 0.4 | 2.05 |

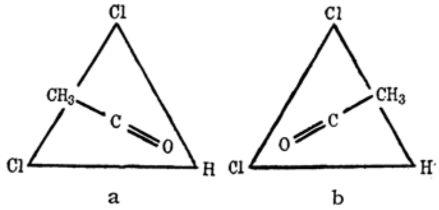
$p$: pressure range of the observations.
$n$: number of the observations.
$\Delta P$: mean deviation of $P$.

**2. Discussion.**—It is found that the dipole moment increases with the temperature, which shows clearly that the molecules are distributed over a range of positions with small moment to that with larger moment, and that the former position is more stable than the latter. In the case of monochloroacetone, a small dependence of its moment on temperature was observed by Zahn.[5] The molecular structure of the compounds with a carbonyl group at one end of the axis of internal rotation has been studied extensively through molecular spectra[6] and electron diffraction.[7] According to a spectroscopic study[8] of monochloroacetone, it was concluded, taking Zahn's data into account, that there are two forms of rotational isomers corresponding to the internal rotational angle of 150° and 0°, respectively, taking the *trans*-posistion of the chlorine atom with respect to the methyl group as 0° (Fig. 7a, 7b). It was further concluded that in the gaseous state the former is more stable than the latter, the energy difference being estimated as 1 to 2 kcal./mole.[9] The recent molecular spectroscopic study of dichloroacetone[10] revealed that there exist also two rotational isomers in this case. In analogy to the case of monochloroacetone, it may safely be assumed that these isomers take the forms shown in Fig. 2a (the angle $\theta$ is taken as 0° at this position) and b ($\theta=120°$). These two forms are considered as well-defined isomers, since they may be separated by a potential barrier of a considerable height due to the steric repulsion between the chlorine atoms and the methyl group.



a (more stable) b (less stable)

Fig. 7. Rotational isomers of monochloro acetone.



a (more stable) b (less stable)

Fig. 8. Rotational isomers of 1.1-dichloroacetone.

The dipole moment of this molecule is estimated as follows. The bond moments and the bond angles are taken to be $\mu_{C-Cl}=1.86$ D, $\mu_{C=O}=2.50$ D, $\angle CCCl=\angle ClCCl=$ tetrahedral, and $\angle CCO=123°$. For the correction of the induction effect, the rule suggested by Miyagawa and Morino[11] is used, whereby the amount of induction moment by C=O dipole is taken as being equal to the amount of induction by C-Cl bond dipole multiplied by a factor $\mu_{C=O}/\mu_{C-Cl}=2.50/1.86$. The moments calculated are shown in Table III. As described above, the more stable form is the one with the smallest moment. Therefore, it should be form (a), corresponding to $\theta=0°$. By assuming the moment of this form to be 1.30 D it is found from the observed temperature dependence of the moment that the difference in energy between the two isomers, $\Delta E$, is about 800 cal./mole., together with the moment of the less stable form of 2.7 D, a value close to the calculated moment for the 120°−form. It should be pointed out that this value of $\Delta E$ is smaller than that of mo-

TABLE III
THE CALCULATED MOMENT OF 1, 1-DICHLOROACETONE AT VARIOUS POSITIONS OF INTERNAL ROTATION

| $\theta$ | 0° | 30° | 60° | 90° | 120° | 150° | 180° |
|---|---|---|---|---|---|---|---|
| $\mu$ | 1.30 | 1.53 | 2.01 | 2.54 | 2.96 | 3.24 | 3.34 |

---

[5] C. T. Zahn, *Phys. Rev.*, **33**, 686 (1932).
[6] (a) S. Mizushima, et. al., *J. Chem. Phys.*, **20**, 1720 (1952); (b) S. Mizushima, et al., *J. Chem. Phys.*, **21**, 815 (1953).
[7] Y. Morino, et al., *J. Chem. Soc. Japan (Pure Chem. Sect.)*, **75**, 647, 721 (1954).
[8] Ref. 6(b).
[9] T. Miyazawa, private communication.
[10] T. Miyazawa, private communication.
[11] Y. Morino, I. Miyagawa, and T. Oiwa, *Bochu-Kagaku*, **15**, 181 (1950).

nochloroacetone (1–2 kcal./mole). It may easily be understood from the comparison of Figs. 1 and 2 that the difference in the steric energy between the two forms of dichloroacetone is not so far from that between the corresponding two forms of monochloroacetone. The difference in the dipole interaction energy would also be nearly the same in both cases, if the moment of C-Cl and C=O bonds in the former is equal to those in the latter. Actually, however, the two chlorine atoms in dichloroacetone are attached to the same carbon atom so that the C-Cl bond moments must be reduced considerably by the mutual induction, and consequently the energy difference between the two isomers would also be diminished.

Now the dipole interaction energy in these molecules will be computed in the following way by simple assumptions. The bond dipoles are assumed to converge to dipoles at the contact points of the atomic radii in each bond, their magnitudes being taken to be equal to the corrected bond moments. The assumed dimensions of the molecules are such that $R_{cc}=1.54$ Å, the radius of $-C=0.77$ Å, and of $=C=0.67$ Å, and the bond angles are the same as described above. The calculation shows that the energy difernce of the two isomers is 1.3 kcal./mole in dichloroacetone and 2.2 kcal./mole in monochloroacetone. Because of the approximation of the assumptions used here, it might be too much to expect a quantitative agreement between the calculated and the observed values of $\Delta E$, but it is very interesting to note that the calculated values are parallel to the observed $\Delta E$'s. It may, therefore, be concluded from this that the greater part of the energy difference in these molecules is due to the electrostatic energy of dipole interaction, and the lowering of $\Delta E$ in dichloroacetone is the result of the reduced moment of the C-Cl bonds by mutual induction. This result is in accord with the conclusion obtained by Mizushima, Morino, and Shimanouchi[13] and that by Miyagawa[14] in the case of haloethanes.

The author expresses his sincere thanks to Professor Y. Morino for his kind guidance in this study and to Dr. I. Miyagawa for his valuable advice.

## Summary

An apparatus for the measurement of dielectric constant in the gaseous state is constructed. The electrical circuit is a heterodyne double-beat type, the oscillators with a remarkably high frequency stability are constrcuted. By testing several types of gas cell, it was found that one of them (cell D) can be used satisfactorily for the present purpose. For the gas filling system, a modification of Groves' method is employed. Using this apparatus dielectric constant measurement with an error of less than 0.5 per cent can be obtained.

The dipole moment of 1,1-dichloroacetone was measured in this apparatus. The moment was found to increase with temperature. This increase is attributed to the increase of the more polar isomer (b), which coexists with the form (a). The energy difference of the two isomers was found to be about 800 cal./mole. This value is smaller than that of monochloroacetone, and the lowering of $\Delta E$ was considered to be due mainly to the reduced moment of the C-Cl bonds by mutual induction. It was thereby concluded that the energy difference in these molecules is electrostatic in nature rather than steric.

*Department of Chemistry, Faculty of Science, Tokyo University, Tokyo*

---

[12] As for the method of determining $\Delta E$ from the temperature dependence of the moment, see I. Miyagawa, *J. Chem. Soc. Japan* (*Pure Chem. Sect.*), 75, 970 (1954).

[13] S. Mizushima, Y. Morino and T. Shimanouchi, *J. Phys. Chem.*, 56, 324 (1952).

[14] I. Miyagawa, *J. Chem. Soc. Japan* (*Pure Chem. Sect.*), 75, 1169, 1173, 1177 (1954).