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Dielectric Constant Measurement on Organic Crystalline Powder

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The microwave cavity perturbation method was applied for the measurement of the dielectric constants for polycrystalline samples of ten aromatic compounds (naphthalene, anthracene, phenanthrene, pyrene, chrysene, perylene, durene, acenaphthene, biphenyl, and *p*-terphenyl.) The method is shown to give a reasonable result, if the effect of the second order perturbation term is properly included and if Böttcher's equation is carefully applied in transforming an apparent dielectric constant obtained on a powder sample into the mean dielectric constant of a crystal. The nature of the ordinarily used cavity perturbation equation and of Böttcher's transformation equation is discussed in this respect. The obtained mean dielectric constants are; naphthalene 2.87, anthracene 3.12, phenanthrene 2.96, pyrene 3.14, chrysene 3.09, perylene 3.34, durene 2.55, acenaphthene 2.94, biphenyl 2.88, and *p*-terphenyl 2.98. The molecular polarization calculated from these values agreed quite well with the values estimated from the bond polarization given by Le Fèvre *et al.*

Only few measurements have been reported on the dielectric constants of aromatic molecular crystals, although the dielectric properties are of essential significance in understanding their electric behaviors. The reason for this may be attributable to the difficulties most frequently found in the shape and the amount of a sample when the usual method of dielectric constant measurement is applied. In the usual method, we must fill up the whole space between the electrodes with a fairly good amount of sample.[2] However, it is difficult to obtain a single crystal of sufficient size and shape in the case of molecular crystal of interest. When a compressed powder specimen is used, there are a problem in fitting itself to electrode surfaces and other apprehensions[3] that the crystallites may be oriented in some direction on compression.

It is, therefore, desirable to establish a simple method to measure the dielectric constant on a small amount of crystalline material. For this purpose, we adopted the cavity perturbation method in the X-band microwave region. This method is found to be useful for polycrystalline samples if applied with proper care. In this paper we will describe the experimental procedures, and the dielectric constants of ten polycrystalline aromatic compounds determined with this method. We will discuss also some fundamental problems related to the cavity perturbation method.

Method of Measurement

Cavity Perturbation Method. In the cavity perturbation method, the change in the resonant frequency of the microwave cavity is related to the dielectric constant of the sample inserted into the cavity.

If a small sample, of which the dielectric constant and the magnetic permeability are given respectively

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2) See, for example, C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill, New York, (1955), Chapter VI.

3) C. C. Meredith and G. F. Wright, *Can. J. Chem.*, **38**, 1177, (1960).

by ε_1 and μ_1, is inserted into a resonant cavity, the change in the resonant frequency, f_1-f_0, is given[4] by,

$$-\frac{f_1-f_0}{f_1}=\frac{\int_{V_1}(\varepsilon_1-\varepsilon_0)\boldsymbol{E}_1\cdot\boldsymbol{E}_0^*\mathrm{d}v+\int_{V_1}(\mu_1-\mu_0)\boldsymbol{H}_1\cdot\boldsymbol{H}_0^*\mathrm{d}v}{\varepsilon_0\int_V\boldsymbol{E}_0\cdot\boldsymbol{E}_0^*\mathrm{d}v+\mu_0\int_V\boldsymbol{H}_0\cdot\boldsymbol{H}_0^*\mathrm{d}v} \tag{1}$$

where f_0 and f_1 are the resonant frequencies of the cavity, in the absence and presence of the sample, respectively, ε_0 and μ_0 denote the dielectric constant and magnetic permeability of vacuum, $\boldsymbol{E}_0$ and $\boldsymbol{H}_0$ the undisturbed electric and magnetic field vectors and $\boldsymbol{E}_1$ and $\boldsymbol{H}_1$ the resulting field vectors when the sample is loaded. V_1 and V indicate that the integration should be carried out within the volume of the sample and whole volume of the cavity, respectively.

The frequency, the dielectric constant and the magnetic permeability should, in general, be considered as complex quantities. However, in the case of low-dielectric-loss and diamagnetic material, we assume that all the quantities are real, and also that μ_1 is equal to μ_0. Then using the relation,

$$\varepsilon_0\int_V\boldsymbol{E}_0\cdot\boldsymbol{E}_0^*\mathrm{d}v=\mu_0\int_V\boldsymbol{H}_0\cdot\boldsymbol{H}_0^*\mathrm{d}v, \tag{2}$$

one gets Eq. (3) which concerns only the electrical field and the dielectric constant.

$$-(f_1-f_0)/f_1=(\varepsilon_s-1)\left(\int_{V_1}\boldsymbol{E}_1\cdot\boldsymbol{E}_0^*\mathrm{d}v\right)\Big/2\left(\int_V\boldsymbol{E}_0\cdot\boldsymbol{E}_0^*\mathrm{d}v\right), \tag{3}$$

where $\varepsilon_s=\varepsilon_1/\varepsilon_0$.

In the usual measurement of the dielectric constant, the equation in the first order approximation has been used[5,6] by assuming that the dielectric constant of a sample is small, and/or that its volume is also small compared with that of the cavity. In this case, putting $\boldsymbol{E}_1$ equal to $\boldsymbol{E}_0$, the dielectric constant of the sample is calculated by an equation which includes only the known electric field $\boldsymbol{E}_0$. For a rectangular cavity of the reasonance mode of TE_{k0m}, assuming that $\boldsymbol{E}_0$ is constant in the sample, this equation is written as[5]

$$-(f_1-f_0)/f_1=2(\varepsilon_s-1)\cdot V_1/V. \tag{4}$$

For a sample of relatively large volume and large dielectric constant, on the other hand, the first order equation is not promised to hold. Kaminow and Harding[7] and Hatta[8] gave equations of higher approximation which contain the quadratic term of ε_s. However, since the physical meanings of these equations are not given plainly, and since these equations lead to quite different results,[9] we tried to use another equation which was derived according to the general perturbation theory.[10]

Considering a wave equation in a cavity, and regarding the sample inserted into the cavity as a perturbation, one may derive an equation in which the square of the resulting resonant frequency is given by an expansion in ε_s-1. If one takes the first three terms of Eq. (I, 3) in Appendix I, he obtains a quadratic equation of ε_s (see Appendix I),

$$\frac{f_1^2-f_0^2}{f_1^2}=-(\varepsilon_s-1)\frac{\int_{V_1}\boldsymbol{E}_0\cdot\boldsymbol{E}_0^*\mathrm{d}v}{\int_V\boldsymbol{E}_0\cdot\boldsymbol{E}_0^*\mathrm{d}v}+(\varepsilon_s-1)^2\cdot\mathrm{A}, \tag{5}$$

where A is the factor which represents the second order perturbation effects.

Calculation of the factor A (see Appendix II) indicated that the second order term is not negligible under the experimental condition in this work. This term has a large value when ε_s is large and sometimes well exceeds five percent of the first order term in spite of our intention to get ε_s-1 with an accuracy within several percent. Therefore we explicitly took account of this term and calculated ε_s by solving the quadratic equation.

Calculation of Mean Dielectric Constant of Crystal. Many formulae have been proposed for the calculation of the dielectric constant of a crystal (which we denote by ε) from the apparent dielectric constant measured on a powder sample. We employed Böttcher's equation for the calculation of the dielectric constant of a molecular crystal, since it gives a relatively good result[11] among those equations.

Assuming that the environment of a spherical powder particle is continuous dielectric, Böttcher derived the following equation;[12]

$$\varepsilon=\frac{3\delta\varepsilon_a+2\varepsilon_a(\varepsilon_a-1)}{3\delta\varepsilon_a-(\varepsilon_a-1)}, \tag{6}$$

where ε_a is the apparent dielectric constant of the sample and δ is the ratio of the volume actually occupied by the microcrystals to the apparent volume of the powder filled in the sample cell. Polder and van Santen[13] showed that this equation also hold for non-spherical particles when the dielectric constant of the crystal is not large. Therefore we adopted it for our powder samples without correction.

We should note that ε is the mean dielectric constant of a crystal when it has anisotropic dielectric constant.

Experimental

Apparatus. The block diagram of the apparatus is shown in Fig. 1. The microwave generated by the klystron was introduced into the test cavity, of which the resonance mode is TE_{105}. The klystron was frequency-swept at a 50 Hz rate around the resonant frequency of the cavity, and the resonance was detected with a crystal detector and displayed on an oscilloscope. The output of the klystron was partly introduced into a cavity wavemeter, Hitachi M240B, through a directional coupler. Representing the resonance of it

4) F. E. Borgnis and C. H. Papas, "Encyclopedia of Physics," Vol. 16, ed. by S. Flügge, Springer, Berlin, (1958), p. 285.
5) G. Birnbaum and J. Franeau, *J. Appl. Phys.*, **20**, 817 (1949).
6) E. Nakamura and J. Furuichi, *J. Phys. Soc. Japan*, **15**, 2101 (1960).
7) I. P. Kaminow and G. O. Harding. *Phys. Rev.*, **129**, 1562 (1963).
8) I. Hatta, *J. Phys. Soc. Japan*, **24**, 1043 (1968).
9) M. Hosoya and E. Nakamura, *Japanese J. Appl. Phys.*, **9**, 552 (1970).
10) This treatment was originally proposed by Hosoya and Nakamura (Ref. 9). The authors wish to thank Dr. Hosoya for his kindness to draw our attention to their paper.
11) J. C. van Vessem and J. M. Bijvoet, *Rec. Trav. Chim.*, **67**, 191 (1948).
12) C. J. F. Böttcher, "Theory of Electric Polarization," Elsevier, Amsterdam, (1952).
13) D. Polder and J. H. van Santen, *Physica*, **12**, 257 (1946).

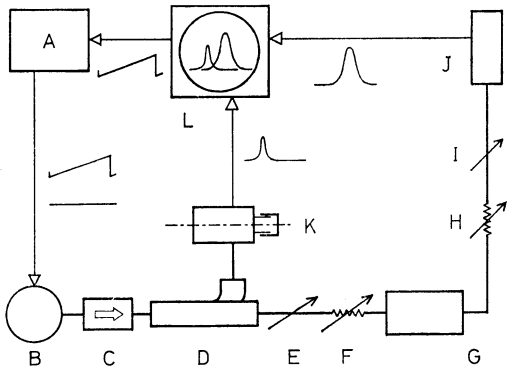

Fig. 1. Schematic diagram of the apparatus.
A: Powder supply for the klystron, B: Klystron, 2K25, C: Isolator, D: Directional coupler, E and I: Phase shifters, F and H: Attenuaters, G: Test cavity, J: Crystal detector, K: Cavity wavemeter, L: Oscilloscope. The klystron is frequency-swept by the saw-tooth wave oscillator included in the oscilloscope through the power supply. The components, from B to K, compose the wave guide circuit.

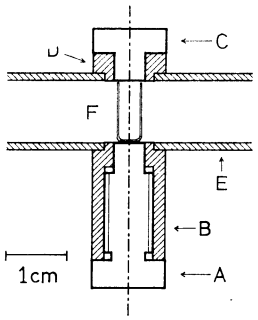

Fig. 2. The sample holder and the cell.
A and C; Brass sample holder and cap. B and D: Brass guides for the holder and the cap, bound to the copper cavity, E, with solder. F: Fused quartz sample cell.

simultaneously on the oscilloscope, the resonant frequency of the test cavity was measured.

The test cavity was made with copper waveguide and copper plates. Its volume is 25.7 cm^3. The resonant frequency and the Q-factor are about 9.36 GHz and 4500, respectively, when it contains the empty sample cell.

The sample holder and the cell are shown in Fig. 2. The sample cell made with fused quartz was bound on the brass holder with a small amount of binding agent of cyanoacrylate, and was inserted into the cavity at the point of the maximum electric field. The outer diameter of the cell is 4.0 mm, and the volume is measured to be 89.9 mm^3 by weighing cyclohexane, *n*-heptane and benzene filled in the cell.

All the measurements were carried out in atmosphere and at room temperature.

Samples. Organic liquids were used after distillation over calcium chloride. In the case of *p*-xylene, in addition to this procedure, fractional crystallization was repeated for several times. The solid samples were used after purification by sublimation *in vacuo* or recrystallization followed by drying under a reduced pressure.

The powder sample was prepared by grinding crystals in an agate mortar just before the measurement, and stuffed into the cell without pressure. The volume fraction δ was determined using the total volume of the microcrystals which was calculated from the weight and the crystal density. By changing the amount of powder and stuffing procedure, we were able to vary δ in the range around 0.4—0.5.

Table 1. Dielectric constants of organic liquids[a)]

Substance	1st Order	Corrected 1ts Order	2nd Order	Literature[b)]
n-Heptane	1.94	1.97	1.94	1.924
Cyclohexane	2.04	2.07	2.03	2.023
p-Xylene	2.30	2.34	2.28	2.270
Benzene	2.31	2.35	2.29	2.284

a) The measurement was carried out at room temperature around 20 °C.
b) A. A. Maryott and E. R. Smith, Nat. Bur. Standards Circ. 514, August 10, 1951. (At 20 °C)

Results

Dielectric Constants of Organic Liquids. For the first we measured the dielectric constants of organic liquids to ascertain the adequacy of the cavity perturbation method. In Table 1 the results for four organic liquids calculated by three different methods are shown. The results in the second column (1st Order) are obtained using Eq. (4). The results shown in the next column (Corrected 1st Order) are obtained by introducing a factor of 0.971 in the right-hand side of Eq. (4) as a correction for the ununiform electric field in the specimen. The fourth column (2nd Order) shows the results obtained by solving Eq. (5). The numeric factor, A, in the second order term was calculated for the test cavity and the sample cell used, using the computer, HITAC 5020E, of the Computer Center of the Tokyo University, and found to be $0.035 \times 4V_s/V_c$ (see Appendix II). In the last column, the dielectric constants reported for these liquids are given for comparison. One can see that the second order perturbation method gives better results.

Dielectric Constants of Aromatic Molecular Crystals. Since, as stated before, crystalline powder was used as the sample in this work, we calculated first the apparent dielectric constant of the specimen (including the empty space between the microcrystals) by the method of the second order perturbation, and then the mean dielectric constant of the crystal was calculated by Böttcher's equation.

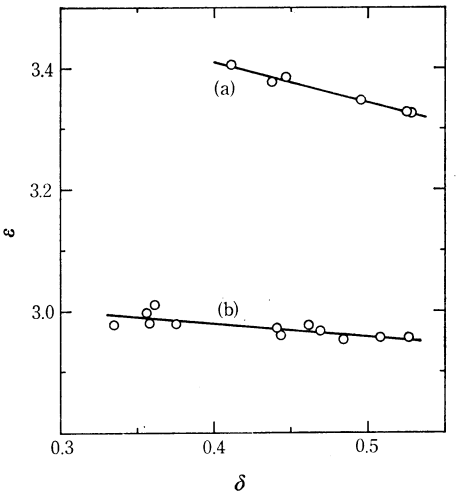

Fig. 3. The variations of ε with δ for (a) perylene and (b) phenanthrene.

In Fig. 3, the results for perylene and phenanthrene are shown as the examples. If Böttcher's equation was quite adequate to this calculation, ε should be independent of δ. However, as shown in this figure, ε calculated by the equation varies with δ. Similar variation was seen for all the substances studied.

After examining the experimental results, the following properties of the calculated ε and its relation to δ became clear;

(1) The δ-dependence of ε can be approximated by a linear line when δ is in the region from 0.4 to 0.55.

(2) When the mean dielectric constant of the crystal is considered to be small (about three or smaller), in most of the cases, the line shows small negative slope. For the substances of which the dielectric constant are reported, ε's calculated by this method almosts agree with those values.

(3) When the dielectric constant is large, the inclination of the line has a large negative value, and ε is small compared with the reported value. In Fig. 4, the results for NaCl is shown as an example of this case.[14]

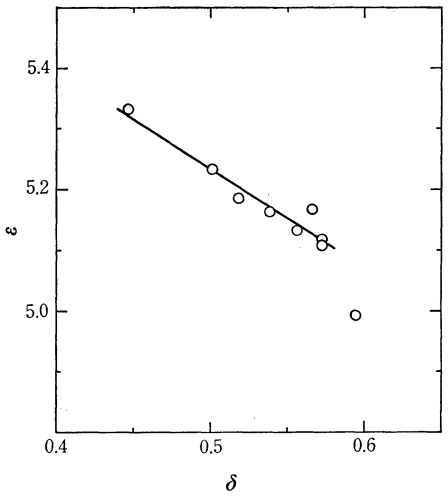

Fig. 4. The variation of ε with δ for NaCl, for which the dielectric constant is reported to be 5.90 (Ref. 15).

For the substances of which ε does not exceed four, we tentatively adopt the value of ε, as the mean dielectric constant of the crystal, which is obtained by interpolating or extrapolating the linear line to the point of δ equal to 0.5. The reason for this estimation will be discussed later. The results obtained for ten aromatic molecular crystals are shown in Table 2. In this table, are also given the value of the crystal density, which was used to calculate δ, and the inclination of the δ-dependence of ε. In addition, the reported dielectric constants are given for some substances.

When the dielectric constant of a crystal is larger than four, it seems a little difficult to get a reliable value of the mean dielectric constant by this simple method.

14) Almost the same results were obtained by N. L. Conger and and S. E. Tung, *Rev. Sci. Instr.*, **38**, 384 (1967). For NaCl, they obtained 5.28 as ε for $\delta=0.54$ by the usual first order method. The results for KCl given in Table 2 in their paper are not consistent together. The value, 4.76 in the sixth column is considered to be incorrect.

Table 2. Mean dielectric constants of aromatic molecular crystals

Substance	Mean dielectric constant	Density	Inclination[a]	Literature[b]
Naphthalene	2.87	1.169	0.02	2.85[c] 2.8[d]
Anthracene	3.12	1.250	−0.21	
Phenanthrene	2.96	1.209	−0.21	
Pyrene	3.14	1.271	−0.55	
Chrysene	3.09	1.274	−0.28	
Perylene	3.34	1.35	−0.66	
Durene	2.55	1.03	−0.20	
Acenaphthene	2.94	1.217	−0.35	
Biphenyl	2.88	1.18	0.16	
p-Terphenyl	2.98	1.230	0.11	2.95— 3.20[c] 2.95[d]

a) $d\varepsilon/d\delta$.
b) Ref. 16.
c) Frequency; $\leq 10^7$ Hz.
d) Frequency; 3×10^9 Hz.

Discussion

Contribution of Second Order Term in Cavity Perturbation Method. Although the cavity perturbation method has been applied to the dielectric and/or magnetic measurement by several investigators, very few attempts have been made to experimentally examine whether this method gives a proper value of dielectric constant or magnetic permeability. In most of the studies using this method, the absolute value of dielectric constant obtained was discussed only qualitatively.

In this work, we attempted to settle the procedure for obtaining a reliable value of dielectric constant on solid materials, especially organic molecular crystals.

The treatment using the second order perturbation theory reduced the ambiguity inherent to the ordinary first-order perturbation method.

The results for the organic liquids given in Table 1 show the characteristics of the three different calculation methods. In the cases shown there, we can compare the dielectric constant at microwave frequency with the values reported for the lower frequency, because all these liquids are non-polar. In this work, the ordinary first order method gives a good result when the dielectric constant of the sample is around two. However, for the sample of which the dielectric constant is larger, it has a tendency to give a little larger value than the reported value. Furthermore, if we consider a correction for the smallness of the electric field at the off-center part in the specimen, the values become still larger as they are shown in the third column in Table 1.

By starting from the general perturbation theory, the higher order perturbation terms are introduced without any special consideration. The second order term has a value of 0.035 (ε_s-1) time of the absolute value of the field-uncoreected first order term for the sample cell used here, and contributes to ε_s as a deducting term. One can now understand the reason why the ordinary first order equation gives a reasonable

result in this work when ε_s is around two. In that case, the field correction and the higher order terms are cancelling each other.

The results obtained by including the second order term are shown in the fourth column of the table. These values are quite reasonable, although they are also larger than the reported values by about 0.01. We consider that this small deviation comes from the error in the estimated volumes of the cavity and the sample cell. It is also possible that the differences are due to small amounts of water and/or organic impurity in the sample.

Böttcher's Equation. As already described Böttcher's equation does not give constant results when δ is changed. It ought to be ascertained, therfore, whether the δ-dependence of ε is the intrinsic character of this equation or this dependence appears only when this equation is applied to the result of the cavity perturbation method.

van Vessem and Bijvoet[11] extensively studied on the correction equations for dielectric constants measured on powder sample. They measured dielectric constants on powder samples of some ionic crystals, and concluded that Böttcher's equation gives a relatively good result when the grain-size is sufficiently small compared to the dimension of the electrodes. Their conclusion is based on the fact that the apparent dielectric constant of the powder sample calculated from the known dielectric constant of the crystal agreed well with the observed apparent dielectric constant for a wide range of δ. However, inversely calculating ε from their experimental values of the apparent dielectric constant, we found that their results did not give constant ε either. Two examples are shown in Fig. 5. The inclination has obviously a large negative value for the sample of which the dielectric constant of the crystal is very large compared with that of the surrounding medium. Seemingly, the δ-dependence is the intrinsic nature of this equation although it is small when the dielectric constant of the crystal is not very large compared with that of the surroundnig medium. By examing their data, we found that Böttcher's equation gives reasonable value of ε when δ is around 0.5, and that it gives improperly small ε for very large δ (say, larger than 0.6).

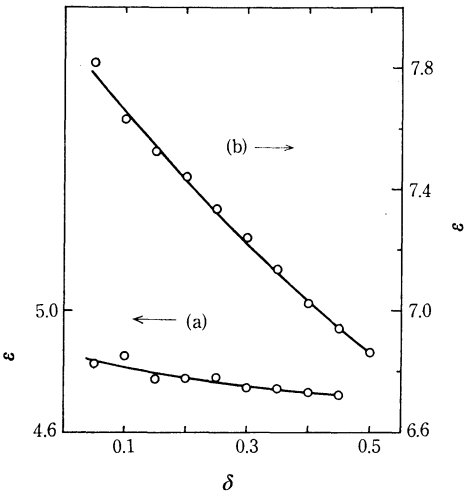

Fig. 5. The variations of ε with δ for (a) KCl and (b) NH_4Cl, where the values of ε are calculated from the apparent dielectric constants measured in the suspenders, CCl_4–CBr_4 and CCl_4–C_6H_6 mixtures, by van Vessem and Bijvoet (Ref. 11). The dielectric constants they used in their calculation are 4.70 for KCl, 2.372 for CCl_4–CBr_4 mixture, 6.85 for NH_4Cl and 2.234 for CCl_4–C_6H_6 mixture.

Although the cause of this δ-dependence of ε is not clear yet, we consider that it results from the basic assumption made by Böttcher. He assumed that the environment of a spherical particle in the powder sample can be considered as a continuous dielectric with the dielectric constant equal to the apparent dielectric constant of the sample. Starting from it and homogeneously distributing the polarization in the particles into the whole space in the specimen, he obtained the field which is identical with the field where a single spherical particle is placed. However, the actual "local" external field, in which a powder particle is placed, is the superposition of the external field and the field which results from the polarization of the surrounding particles. The latter field is a superposition of the fields which are the functions of the distances between the particle considered and the charges and/or the dipoles on other particles. Therefore, when δ is small, the particle is more polarized than expected by Böttcher's equation. Consequently, this equation gives large ε for small δ. The deviation may be pronounced in the case of a material of large dielectric constant.

As to the effect of the size of the particle, it was found[11] that the apparent dielectric constant appears smaller for the larger grain-size powder when δ's are equal. Therefore, although Böttcher's equation is derived without imposing any assumption on the size of the particle, it may be inadequate to apply this equation for the sample of large grain-size.

The shape of the powder particle seems to affect the δ-dependence of ε. The positive inclinations given in Table 2 for some substances are considered to manifest the effect of it. However, since the inclinations are not large, we need not make much of this effect in this work.

The experimental error in our result of ε is large when δ is small, because the errors accompanied in the measured weight and the frequency change become serious in this case. On the other hand, the result for very large δ (say, larger than 0.55) is not reliable. It may be due to the inhomogeneous stacking of the sample in the cell.

Taking account of our experimental results and above considerations, we arrived at the following conclusions.

(1) Böttcher's equation gives reasonable results for a material of small dielectric constant when δ is in the region around 0.5 and the grain-size of the powder is sufficiently small.

(2) When the difference between the dielectric constant of a crystal and that of the surrounding medium is large, the δ-dependence of ε is serious and it is rather difficult to estimate the proper value of the dielectric constant of the crystal. In this case, the effects of the shape and the size of the particle may be also important.

Mean Dielectric Constants and Molecular Polarizations of Aromatic Molecular Crystals. The mean dielectric constants were estimated for the aromatic molecular crystals given in Table 2. Unfortunately, so far as we know, very few reliable data have been reported for the dielectric constants of organic molecular crystals. The data given in the table are the ones quoted from the book edited by von Hippel.[15] The mean dielectric constants estimated from our simple measurement agree well with these data. For anthracene, anisotropic dielectric constants of a single crystal at low frequency were recently reported.[16] The mean dielectric constant estimated in the present work qualitatively agrees with these single crystal data.

Using the mean dielectric constant obtained, we calculated molecular polarization, P, defined by,

$$P = M(\varepsilon-1)/d(\varepsilon+2),$$

where M is the molecular weight and d is the crystal density, and ε is the isotropic dielectric constant of the crystal, for which we used the mean dielectric constant. The molecular polarization is estimated in good approximation as the sum of the values characteristic to atoms or bonds.[17]

Table 3. Molecular polarization[a]

Substance	Experiment	Calculated[b]	Difference
Naphthalene	42.1	41.2	0.9
Anthracene	59.0	57.2	1.8
Phenanthrene	58.3	57.2	1.1
Pyrene	66.3	64.8	1.5
Chrysene	73.6	73.2	0.4
Perylene	81.9	80.8	1.1
Durene	44.4	43.3	1.1
Acenaphthene	49.8	48.2	1.6
Biphenyl	50.3	49.5	0.8
p-Terphenyl	74.4	73.9	0.5

a) Unit; cm^3/mol.
b) See text.

In Table 3, the molecular polarization calculated from the mean dielectric constants are given in the second column. The values given in the third column are calculated using the "electronic" bond polarizations estimated by Lè Fevre and Steel.[17,18] They estimated those quantities by assuming a dispersion equation and extrapolating the bond refractions to the limit of the infinite wavelength. Therefore the polarization calculated using their values is considered to give the "electronic" molecular polarization at the infinite wavelength. As shown in the last column, the difference between the experimental value and the estimated one is, in general, small positive value. Although these small differences cannot be discussed quantitatively, it is not impossible to attribute the differences to the contribution from the "atomic" polarization.[19] The good agreement for many substances seems to imply that the additivity of the bond polarization is valid in these aromatic molecules.

The authors wish to thank Professor Hideo Akamatu for his kind encouragement throughout this work. They are also indebted to Dr. Toshiaki Ohta for making the computer program for the calculation of the second order perturbation term.

Appendix I

The electric field, $\boldsymbol{E}$, in a resonant cavity containing a low-loss dielectric specimen satisfies the wave equation,

$$\nabla^2\boldsymbol{E} + \omega^2\varepsilon_r\varepsilon_0\mu_0\boldsymbol{E} = 0, \qquad \text{(I, 1)}$$

where ε_r is equal to ε_s, the dielectric constant of the specimen relative to the vacuum, inside the specimen and unity outside of it. Substituting $\omega^2\varepsilon_0\mu_0$ by $-\chi$ and adding the factor $\chi\boldsymbol{E}$ to the both sides of this equation, one gets

$$\{\nabla^2-(\varepsilon_r-1)\chi\}\boldsymbol{E} = \chi\boldsymbol{E}. \qquad \text{(I, 2)}$$

If one regards the second term in the left-hand-side of this equation as a perturbation, according to the usual treatment of the perturbation theory, one gets the n-th eigen-value of $\boldsymbol{E}$, χ_n, as

$$\chi_n = \chi_{n,0} + \langle\boldsymbol{E}_{n,0}|-(\varepsilon_r-1)\chi_n|\boldsymbol{E}_{n,0}\rangle + \sum_{k\neq n}\frac{1}{\chi_{n,0}-\chi_{k,0}}|\langle\boldsymbol{E}_{n,0}|-(\varepsilon_r-1)\chi_n|\boldsymbol{E}_{k,0}\rangle|^2 + \cdots, \qquad \text{(I, 3)}$$

where $\boldsymbol{E}_{n,0}$ and $\boldsymbol{E}_{k,0}$ are the n-th and k-th eigen-states of the electric field in the non-perturbed cavity, and $\chi_{n,0}$ and $\chi_{k,0}$ are the corresponding eigen-values of them. This equation is considered to give a more general expression to the relation between the dielectric constant of a specimen and the change of the resonant frequency, since it was obtained without imposing any restriction on the dielectric constant and the volume of the specimen.

If one takes account of the first three terms in the right-hand-side of Eq. (I, 3), rearranging χ_n and $\chi_{n,0}'$ one gets

$$\frac{\chi_n-\chi_{n,0}}{\chi_n} = \langle\boldsymbol{E}_{n,0}|-(\varepsilon_r-1)|\boldsymbol{E}_{n,0}\rangle + \sum_{k\neq n}\frac{\chi_n}{\chi_{n,0}-\chi_{k,0}}|\langle\boldsymbol{E}_{n,0}|-(\varepsilon_r-1)|\boldsymbol{E}_{k,0}\rangle|^2. \qquad \text{(I, 4)}$$

Since ε_r-1 has the finite value only in the volume of the specimen, rewriting χ in the form of frequency, $f=\omega/2\pi$, one gets the same equation as Eq. (5), in which $f_{n,0}$, f_n, $\boldsymbol{E}_{n,0}$ and ε_r in the specimen are written as f_0, f_1, $\boldsymbol{E}_0$ and ε_s, respectively. The factor A is

$$\sum_k{}'\frac{f_1^2}{f_0^2-f_{k.0}^2}\left(\int_{V_1}\boldsymbol{E}_0\cdot\boldsymbol{E}_{k.0}^*\mathrm{d}v\right)^2, \qquad \text{(I, 5)}$$

where the summation should be carried out for all the normal modes of the unperturbed cavity except the n-th mode.

When the perturbation is considered to be very small, and if one takes the first two terms in the right-hand-side of Eq. (I, 3) one gets the same result as Eq. (3) by rewriting the equation as before and assuming $f_1+f_0=2f_1$.

15) A. R. von Hippel, ed., "Dielectric Materials and Applications," The Technology Press of M. I. T. and John Wiley & Sons, Inc., New York (1954).
16) N. Karl, H. Rohrbacher and D. Siebert, *Phys. Stat. Sol.*, (a) **4**, 105 (1971).
17) R. J. W. Le Fèvre, "Advances in Physical Organic Chemistry," Vol. 3, ed. by V. Gold, Academic Press, London (1965), p. 1.
18) R. J. W. Le Fèvre and K. D. Steel, *Chem. & Ind.*, London, 670 (1961).
19) Since most of the molecules dealt with in this work are non-polar, the molecular polarization can be explained with the electronic and atomic polarizations. The latter may be in a magnitude of only several percent of the former for these substances (see, for instance, Chapter XIV of Ref. 1).

Appendix II

For a rectangular cavity of the resonance mode $TE_{k,0,m}$, the electric field is given by,

$$E_y = B \sin \frac{k\pi x}{a} \sin \frac{m\pi z}{c}, \qquad \text{(II, 1)}$$

where a and c are the width and the length of the cavity, and B is a function of time which gives the amplitude of the standing wave. The electric fields of other directions, E_x and E_z, do not exist for this resonance mode.

If a cylindrical specimen, of which the height is identical with that of the cavity, b, is placed at the point of the maximum electric field of TE_{105} mode, it is easily shown that the normal modes, which have finite values of overlap integrals with the TE_{105} mode in the volume of the specimen, are only $TE_{k',0,m'}$ modes with odd k' and $(k', 0, m') \neq (1, 0, 5)$.

Substituting the electrical fields of these normal modes into Eq. (I, 5), one obtains

$$\frac{16}{(abc)^2} \sum_{k',m'} \frac{f_1^2}{f_0^2 - f_{k'0.m'.0}^2} \times \left(\int_{V_1} \sin \frac{\pi x}{a} \sin \frac{5\pi z}{c} \sin \frac{k'\pi x}{a} \sin \frac{m'\pi z}{c} dv \right)^2 \qquad \text{(II, 2)}$$

as the factor A, where $16/(abc)^2$ is the normalization constant.

The sum was calculated by the numerical integration and found to converge sufficiently when we took account of the modes of the resonant frequency up to about 200 GHz. Since the resulting frequency f_1 is not varied so much with the specimens, we can assume the formula (II, 2) as a constant. It was found to be $0.035 \times 4\ V_s/V_c$ for the geometry of the cavity and the sample cell used.