

EVIDENCE FOR QUANTIZATION FROM THE ELECTRIC  
POLARIZATION OF ACETIC ACID VAPOR

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## ABSTRACT

The dielectric constant of acetic acid vapor was measured at various pressures and temperatures. The results indicate a departure from Debye's theory which suggests an internal transition, with respect to temperature variation, from one type of single molecule to another. Near saturation there was detected a small amount of association of a kind increasing the molecular polarization. The anomaly is discussed from the point of view of the new quantum mechanics and it is suggested as an explanation that the effect is due to a transition from one state to a higher state of vibration associated with the OH group. The data are interpreted in terms of the proposed extension of Van Vleck's theory given in the following note. The Raman frequencies given by Dadiou and Kohlrausch indicate that the fundamental vibration frequency due to the OH group is of such a value as to produce transitions of quantum state in precisely the observed region of temperature. This is in agreement with the proposed theory, particularly since molecular polarization measurements in general indicate that the OH group always has associated with it a large electric moment.

The electric moment of the acetic acid molecule cannot be calculated accurately but the data indicate roughly a transition from  $1.4 \times 10^{-18}$  in the ground state to an average value greater than  $1.7 \times 10^{-18}$  c.g.s. e.s.u. in the upper states.

A discussion is given of the anomalous behavior of other physical properties of the vapor, regarding it as a statistical distribution of molecules, surrounded by different force fields associated with the change in electric moment. The possibility of attributing previously observed discrepancies between refractivities and the optical parts of the dielectric polarization to the above mentioned type of quantization is suggested.

**I**N THE measurement of the dielectric constant of vapors there have occurred occasional apparent deviations<sup>1</sup> from Debye's theory. These deviations are detected by a departure from linearity of the curve obtained by plotting the product of the molecular polarization and the absolute temperature against the absolute temperature itself. They occur always near the saturation point of the vapor, i.e., at low temperatures or high pressures. For this reason they have been attributed to association or adsorption on the condenser material. An associated molecule would give an increased contribution to the "optical" term of Debye's equation and a change in the "orientational" term corresponding to either an increased or a decreased electric moment.<sup>2</sup> The existence of association is to be detected by studying

<sup>1</sup> M. Jona, *Phys. Zeits.* **20**, 14 (1919); C. T. Zahn, *Phys. Rev.* **27**, 329 (1926); K. Wolf, *Phys. Zeits.* **27**, 588 (1926); K. Wolf, *Ann. d. Physik.* **83**, 884 (1927); F. Maske, *Phys. Zeits.* **28**, 533 (1927); J. B. Miles, Jr. *Phys. Rev.* **34**, 964 (1929).

<sup>2</sup> L. Ebert, *Zeits. f. Physik. Chem.* **113**, 1 (1924).

the variation of the polarization with pressure. Adsorption could be detected in the same manner, but there is sometimes introduced a complication due to accompanying conductivity between the condenser plates. An anomaly of the latter type was observed by the author<sup>3</sup> in the case of water vapor at room temperature. The effect seemed to set in sharply at about one-third the saturation pressure. This adsorption was explained qualitatively by the attraction of the dipole molecule for its image in the adsorbing surface. As the molecule approaches the surface its potential energy is lowered until it touches the surface. The ratio of the pressure at the surface to that far from the surface is obtained by the Boltzmann distribution law. When the pressure in the body of the vapor reaches a certain value, that on the surface reaches saturation and adsorption follows. Originally it was thought that the observed effect was due to the direct dielectric effect of the layer of water on the condenser plates. This required about 200 layers of water. Later experiments were made by K. Wolf on this effect, and it was shown that there is considerable conductivity between the plates of the condenser. The author has also made measurements of this conductivity which show that the observed apparent increase in dielectric polarization may be largely due to the indirect effect of conductivity across the thin layer of water adsorbed on the quartz insulators used. It is impossible to say how much of the effect is due to each of the three causes, association, adsorption layer on the plates, and conductivity across the insulators. Fraser<sup>4</sup> has shown by measurements of the polarization of light reflected from the adsorbing surface of glass that about 5 layers of water are present at saturation. Therefore in the case of water vapor the effect must be almost entirely due to conductivity and possibly association. Only in case there is no observable conductivity can one be sure that a variation in molecular polarization with pressure is due to association (or chemical reaction).

All the above effects can usually be eliminated by working at pressures considerably below saturation, when one is interested in the polarization of single molecules.<sup>5</sup> In cases where there is no appreciable leakage in the condenser the anomalies can be used to obtain information concerning the forces causing association.<sup>6</sup> On account of the general anomalous behavior of the physical properties of acetic acid vapor it was thought that measurements of its dielectric constant might prove of interest, particularly since it is known definitely to associate in the gaseous state. By making pressure runs at each temperature and using only the linear, or low pressure parts, the polarization corresponding to the single molecules can be obtained. The Debye line obtained from these data should enable one to calculate the electric moment of the molecule and thus to obtain an idea of the magnitude of the moment characteristic of the carboxyl group. The upper or high pressure parts of the curves should give an idea of the nature of the association.

<sup>3</sup> C. T. Zahn, *Phys. Rev.* **27**, 329 (1926).

<sup>4</sup> J. H. Fraser, *Phys. Rev.* **33**, 97 (1929).

<sup>5</sup> c.f. C.T. Zahn, *Phys. Rev.* **35**, 848 (1930)

<sup>6</sup> P. Debye, "Polar Molecules," p. 41.

## EXPERIMENTAL RESULTS

The experiments here described were made by the same method used by the author in a series of previous investigations.<sup>7</sup> Pressure curves were obtained at eleven different temperatures in the range 20–220° C. In Fig. 1 are shown two typical pressure curves, one for a high temperature, and the other for a low temperature where the gas was nearer saturation. The high temperature curve shows no departure from linearity and therefore no as-

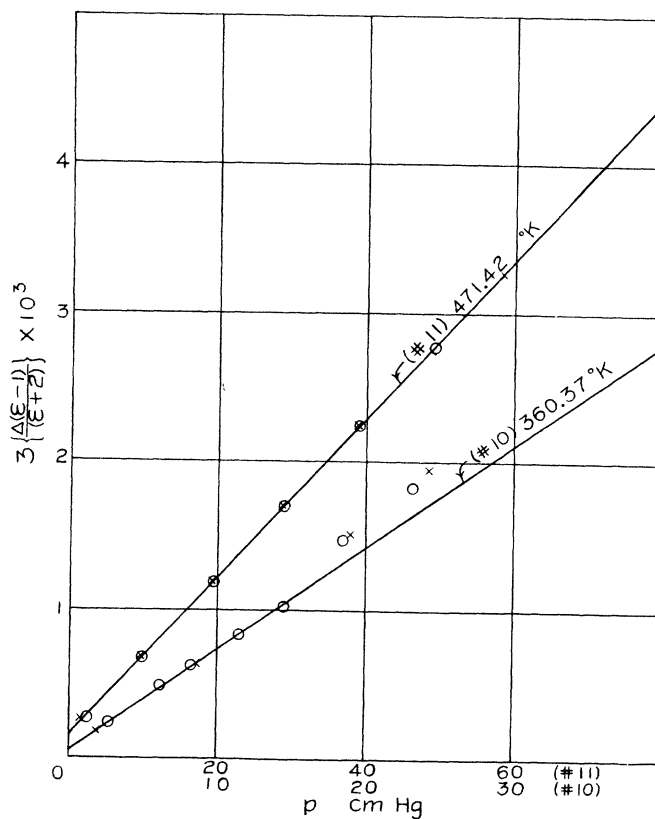


Fig. 1.

sociation. The low temperature curve has a linear portion at the lower pressures and an anomalous increase of the polarization for the higher pressure near saturation. Leakage tests showed no appreciable conductivity. Therefore there is association of such a nature that the electric moment is increased.

A more interesting feature of the results is seen when an attempt is made to plot a Debye line. In Table I are given the data taken from the lower portions of the pressure curves where the effect of association is negligible. For economy in space the individual pressure data are not included. In

<sup>7</sup> C. T. Zahn, Phys. Rev. **24**, 400 (1924), C. T. Zahn, Phys. Rev. **35**, 848 (1930).

column III is given the limiting slope of the pressure curve in the lower part for pressures expressed in atmospheres. This gives the value of  $(\epsilon-1) 10^6$  corresponding to an atmosphere of single molecules. Column IV gives values of  $3(\epsilon-1/\epsilon+2) (1/p_{at})$ ; and column V, values of  $3(\epsilon-1/\epsilon+2) v \cdot 10^6$  where

TABLE I.

No.	T°K	$\frac{\epsilon-1}{p_{at}} \cdot 10^6$	$3\left(\frac{\epsilon-1}{\epsilon+2}\right) \frac{10^6}{p_{at}}$	$3\left(\frac{\epsilon-1}{\epsilon+2}\right) v \cdot 10^6$	$3\left(\frac{\epsilon-1}{\epsilon+2}\right) vT$	P
1	410.84	4767	4760	7165	2.94 <sub>0</sub>	53.5
2	491.44	3742	3737	6724	3.30 <sub>4</sub>	50.2
3	357.78	5246	5235	6860	2.45 <sub>0</sub>	51.2
4	341.13	5461	5452	6809	2.32 <sub>3</sub>	50.8
5	389.64	5044	5036	7184	2.79 <sub>9</sub>	53.7
6	320.85	5791	5782	6792	2.17 <sub>9</sub>	50.7
7	450.09	4340	4334	7142	3.21 <sub>4</sub>	53.3
8	297.51	6764	6756	7359	2.18 <sub>9</sub>	55.0
9	493.86	3728	3724	6733	3.32 <sub>5</sub>	50.3
10	360.37	5246	5235	6907	2.48 <sub>9</sub>	51.6
11	471.42	4068	4063	7013	3.30 <sub>6</sub>	52.3

$v$  is calculated from the ideal gas law  $v = T/273.13p_{at}$ . The van der Waal correction would probably amount to about one percent. This correction was not made because of the lack of data. Column VI gives the ordinates for the Debye line:

$$3\left(\frac{\epsilon-1}{\epsilon+2}\right)vT = AT + B.$$

Column VII gives values of the molecular polarization  $P$ , i.e., the value of  $(\epsilon-1/\epsilon+2)$  corresponding to a gram molecule of single acetic acid molecules.

In Fig. 2 are plotted the values of columns VI and VII of the table. According to Debye's theory the upper curve should be a straight line of slope  $A$  and intercept  $B$ . The lower curve should be of the form:

$$P :: A + (B/T).$$

It is obvious that this is far from the case and that there is here represented a departure from Debye's theory which is due neither to association nor to conducting layers. Apart from the linearity of the pressure curves in their lower parts, if there were association, it would be practically absent at the higher temperatures and the upper portion of the curve of Fig. 2 would approach the supposed true Debye line. Then the anomalous *decrease* of  $3(\epsilon-1/\epsilon+2)vT$  for the lower temperatures would have to be attributed to association corresponding to *reduced* electric moment. On the other hand the pressure curves near saturation indicate that association occurs in such a way as to *increase* the electric moment of the molecule. Therefore an explanation of the departure from the Debye line based on the assumption of association leads to a contradiction.

The values for the lowest temperature, given in the table and shown in Fig. 2, were obtained under very difficult experimental conditions because of

the low vapor pressure, and are therefore subject to a much greater probable error. Association may not be completely eliminated. The slight rise in the upper curve is probably not correct, but the rise in the lower curve is probably only a little too great but definitely existing.

During the investigation it was thought that the observed anomalies could be due to an indirect effect of a small amount of water in the acid specimen. In order to test this supposition an especially pure specimen, of

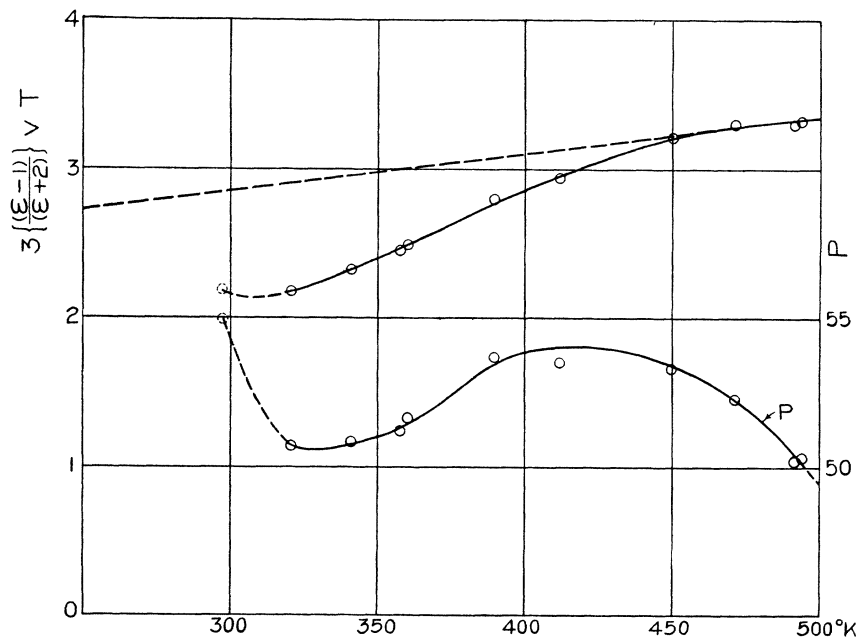


Fig. 2.

fusion point  $16.6^{\circ}$  C, was prepared and measurements were repeated at extreme temperatures. No appreciable difference was observed between the two specimens. In any case if the effect of water vapor is only its direct effect it would require a considerable amount to produce an appreciable change in the dielectric constant, since the two substances have nearly the same dielectric constant.

#### EVIDENCE FOR QUANTIZATION

The curves in Fig. 2 indicate roughly a transition from one value of  $A$  and  $B$  in the Debye equation to another. Since the pressure curves are linear this must correspond to an internal change in the molecule. On the quantum theory such a change would be a change from one stationary state to another, or to a redistribution among several states, according to the Boltzmann theorem. Van Vleck<sup>8</sup> has given a general derivation of the Debye formula in the new quantum mechanics. The Debye formula is found

<sup>8</sup> J. H. Van Vleck, *Phys. Rev.* **29**, 729 (1927); *Phys. Rev.* **30**, 31 (1927).

to hold for temperatures such that  $h\nu \ll kT$  where  $h\nu$  is the energy spacing of the rotational levels or other low energy levels. This means that deviations due to rotational quantization are small when  $T$  is such that the above inequality holds. To a second approximation the effect of rotational quantization gives the formula:

$$3 \left( \frac{\epsilon - 1}{\epsilon + 2} \right) = A + \frac{B}{T} - \frac{C}{T^2}$$

Van Vleck has calculated the constant  $C$  in terms of the moments of inertia of the molecules and the components of the electric moment along the principal axes of inertia. When  $T = h\nu/k$  the deviations are considerable and the above second approximation is not sufficient, of course. Debye<sup>9</sup> calls this latter temperature the "characteristic" temperature and finds that for HCl it is 14.7°K. At 0°C the correction due to rotational quantization is only about 2 percent, and it would be difficult to detect departures from the Debye formula unless measurements could be made near the characteristic temperature.

One can let each energy transition  $h\nu$  define a temperature such that  $h\nu = kT$ . In this sense a transition in the region of  $T = 400^\circ\text{K}$  could certainly not be attributed to rotational quantization since it would require a moment of inertia many times smaller than that of HCl. Van Vleck in his derivation of the Debye equation assumes that the electric moment of the molecule is invariant with respect to all quantum numbers producing low or medium frequency transitions. There are many substances which have vibrational energies in the region of measurable temperatures. If one admits the possibility of different "fixed" electric moment in different vibrational states the general behaviour of the curves in Fig. 2 can be explained as due to the statistical distribution in these states. In a note to follow Van Vleck's theory has been generalized to include such an assumption and Debye's formula is replaced by:

$$3 \left( \frac{\epsilon - 1}{\epsilon + 2} \right) = A + \frac{[\sum_v B_v e^{-h\nu_v/kT}]/[\sum_v e^{-h\nu_v/kT}]}{T}.$$

This does not include the small correction due to rotational quantization. The  $B$  of Debye's equation is replaced by a statistically averaged  $B$  over all vibrational states. The same is true of the square of the electric moment since it is proportional to  $B$ .

In case the changes in the electric moment  $\mu$  are due to a single type of vibration the various overtones  $\nu_v$  will be spaced relatively far apart on the temperature scale, and in the region of temperature around a particular value of  $\nu$  the transition will be roughly as from one value of  $\nu$  to one other value. The higher energy states will exist in only small amounts. The general shape of the distribution curve in the two states according to the Boltzmann theorem is like the upper curve of Fig. 2. If the overtones be taken into

<sup>9</sup> P. Debye, "Polar Molecules," p. 150.

account the shape of the curve is only slightly changed in this region. Judging from such a distribution curve one would expect the transition frequency  $h\nu$  to correspond to a temperature in the region from 420–450°K.

#### RELATION TO RAMAN SPECTRUM

Dadiou and Kohlrausch<sup>10</sup> have investigated the Raman spectrum of acetic acid in the liquid state and give lines of the following wave-numbers: 440 (0); 618 (1); 890 (4); 1430 ( $\frac{1}{2}$ ); 1656 (1); and 2935 (4). Salant and Sandow<sup>11</sup> have shown that for HCl there is a small shift of the infra-red lines on passing from the liquid to the vapor states on account of the Lorentz force in the liquid. The frequency in the gaseous state was found to be of the order of 4 percent higher. This would not alter the following qualitative discussion. In the sense defined by  $h\nu = kT$  these lines lie at temperatures: 307; 432; 622; 998; 1157; and 2050°K. Of these lines the only one definitely in the region of observed temperatures is the second at 432°K. This is a moderately strong line and is attributed by the above mentioned authors to the OH group of the molecule. This is in excellent agreement with what would be expected from the existing data on electric moments.<sup>12</sup> The OH group is known to have associated with it a large electric moment and therefore the Raman line associated with this group would be the most likely to produce changes in electric moment. The other lines in the Raman spectrum excepting the overtones of the OH line which are not sufficiently strong to appear, would probably cause only very small changes in electric moment. There may be also a small effect on the electric moment due to vibrations associated with the CO group, if the corresponding value of  $h\nu$  is near the observed temperature region.

If the potential energy function associated with the vibration is unsymmetrical about the minimum point, the average nuclear separations may be quite different for the different quantum states. Accompanying this the electric moment might have quite different values, particularly in cases of weak bonds such as exist in large organic molecules. On the other hand it is just here that one would expect interaction between rotation and vibration or centrifugal expansion; and that the sum rules, discussed by Van Vleck in connection with the high frequency or optical part of the susceptibility, might be invalidated. It does not seem impossible that such disturbing effects might be small even if the electric moment is altered by the vibration. As another possibility, in a complicated organic molecule there might be more than one minimum value of the potential energy of vibration with fairly strong binding forces around each one of them. For example, in the case of the ammonia molecule, the potential energy of the nitrogen nucleus along the axis of the molecule is probably symmetrical, or nearly symmetrical, with respect to the plane of the hydrogen triangle and there exist two minima

<sup>10</sup> A. Dadiou and K. W. F. Kohlrausch, *Monatsch. f. Chem.* **52**, 220 (1929).

<sup>11</sup> E. O. Salant and A. Sandow, *Phys. Rev.* **35**, 214 (1930).

<sup>12</sup> H. A. Stuart, *Phys. Zeits.* **31**, 80 (1930).

on opposite sides of the triangle. In an organic molecule such a bond might be unsymmetrical and hence give rise to two distinct energy levels.

In connection with the above mentioned high frequency part of the dielectric susceptibility there are in progress in this laboratory observations of the refractivity of acetic acid vapor under the same conditions of pressure and temperature as the present observations. These observations may indicate whether any of the temperature variation is due to the failure of the sum rules which are called upon to prove the invariance of the high frequency term with temperature. They should also be of interest in connection with the association of the vapor near saturation. An observed variation with temperature could also be due to a variation in refractivity from one vibration state to another.

#### ELECTRIC MOMENT

On account of the inability to resolve completely the effects of the different states and of the lack of accurate knowledge of the Raman frequency for the vapor, it is impossible to obtain from the present observations an *accurate* knowledge of the electric moment in either state. Using a value of the refractivity obtained from the liquid one can calculate roughly the effective electric moment at the various temperatures. This is, of course, the root mean square electric moment. The calculation indicates that the average moment varies from 1.4 to  $1.7 \times 10^{-18}$  c.g.s. e.s.u. The lower value is probably not far from the value corresponding to the ground state. At the highest temperature there are still present a considerable number of the molecules in the ground state, which would necessitate a moment still greater than  $1.7 \times 10^{-18}$  for the upper state.

C. P. Smyth has recently made measurements<sup>13</sup> of the molecular polarization of acetic acid solutions in benzene and in ether from 0 to 30°C. The values for the solution in benzene are in general abnormal. A calculation using the refractivity of acetic acid as above indicates an average moment of  $0.7 \times 10^{-18}$ . This may be due to a special type of association in the liquid state. For the solution in ether the behavior is normal and there is probably very little association as indicated by partition coefficient measurements. The value of the moment calculated by Smyth for this solution is  $1.40 \times 10^{-18}$ . At temperatures from 0 to 30°C all the molecules are probably in the ground state of vibration, judging from the curve of Fig. 2. The lower limit previously calculated from this curve, 1.4, is in good agreement with Smyth's value.

#### PHYSICAL PROPERTIES

In addition to the anomalous behavior here described acetic acid has long been known to behave anomalously with respect to van der Waal's equation. The value of  $(RT_k d_k)/(Mp_k)$ , which for most vapors is around 3.88, is abnormally high for acetic acid vapor, 4.99. Also Nasini<sup>14</sup> has recently measured

<sup>13</sup> To be published in the Jour. Amer. Chem. Soc.

<sup>14</sup> A. G. Nasini, Phil. Mag. **52**, 596 (1929).



the viscosity of acetic acid vapor at pressures of the order of 5 mm Hg and at temperatures from 90 to 250°C. At such low pressures there is no appreciable association, yet the temperature-viscosity curve shows at lower temperatures an opposite shape to those of other non-associated compounds.

If the interpretation of the behavior of acetic acid here suggested is correct it seems that the above mentioned deviations could be explained by the fact that such a vapor must be considered as a mixture of molecules surrounded by different force fields and distributed statistically. Any physical property depending on these force fields, such as van der Waal forces, mean free path, mobility, viscosity, etc., would be expected to behave abnormally with respect to temperature variation.

This effect of the variation of electric moment with vibrational state may be of some small importance even in molecules such as HCl where Debye's theory is apparently obeyed. If the vibration frequencies are not near the observed temperature region and if the moment is slightly different for different quanta of vibration, there may still be a first order linear correction to be applied. This would not alter the linearity of the Debye line but would give a slightly erroneous electric moment, and an erroneous value of the "optical" part,  $A$ , of the susceptibility. In a number of cases<sup>15</sup> where the electric moment is large there have been discrepancies between the value of  $A$  and the refractivity.  $A$  is usually higher than the refractivity. In the case of the halogen hydrides the discrepancy is larger the larger the electric moment. These discrepancies have been discussed by various authors, notably Van Vleck,<sup>16</sup> without obtaining a satisfactory explanation. For the case of HCl Van Vleck has made calculations to show that the effect of the vibrational spectrum on the dielectric constant is negligibly small. It should be noted in this connection that he has assumed an electric moment fixed with respect to the vibrational quantum number. In the case of CO<sub>2</sub> Fuchs<sup>17</sup> has shown that the atomic vibration frequencies are necessary for the extrapolation of the refractivity to infinite wave-length, and that the value so extrapolated agrees well with the polarization obtained from electrical measurements. The discrepancies then may be due either to an error in the refractivity by the failure to include the atomic vibration frequencies when they are important, or to an erroneous value of  $A$  caused by vibrational quantization, when there is a variable electric moment, and possibly to a much smaller extent by the rotational quantization. There may also be a temperature effect on the high frequency part  $A$  caused by the failure of the sum rules for molecules with loose bonds; and the value of  $A$  obtained from dielectric constant data on the assumption that it is constant would be in error.

<sup>15</sup> C. T. Zahn, Phys. Rev. **24**, 400 (1924).

<sup>16</sup> J. H. Van Vleck, Phys. Rev. **30**, 44-46 (1927).

<sup>17</sup> O. Fuchs, Zeits. f. Physik **46**, 519 (1928).