AN INVESTIGATION OF THE ELECTRIC MOMENTS OF VARIOUS ORGANIC AND INORGANIC COMPOUNDS OF FLUORINE

Thesis for the Degree of M. S.

MICHIGAN STATE UNIVERSITY

Bruce L. Kennedy

1961

ABSTRACT

THE ELECTRIC DIPOLE MOMENTS OF SUBSTANCES IN THE VAPOR PHASE

by Bruce L. Kennedy

The electric dipole moments of various organic and inorganic compounds have been measured in the gas phase. The compounds are : pentafluoropropionitrile 1.33D, pentafluoropropionyl chloride .99D, trifluoromethyl propene 2.33D, vinyl methyl ether 1.05D, ethyl acetylene .76D, methallene .44D, perfluoropropylene 1.1D, and sulfur tetrafluoride .88D.

The method employed in this investigation was the heterodyne-beat method. This method takes advantage of the dependence of frequency in an oscillating circuit on the capacitance of the circuit. Therefore if a dielectric cell is included in this oscillating circuit, the capacitance will change in relation to the substance in the dielectric cell, thereby giving different frequencies for different substances in the cell. If one employs the method with the cell evacuated and then again with a substance in the cell, the frequency difference or capacitance change can be determined, and hence the dielectric constant of the substance can be calculated. The dielectric constant can then be related to the molar polarization by the Clausius-Mosotti equation. Then by determining the distortion polarization from refractive index data, the dipole moment of the substance can be determined.

The results of this investigation seem to indicate that ethylenic compounds with a substituted CF_3 group exhibit very large dipole moments. This is attributed to hyperconjugation of the CF_3 group. Compounds with a CF_3CF_2 group also exhibit very strong electron withdrawing properties as is indicated by considering the various effects which are occurring in the

molecules, $CF_3CF_2\overset{O}{\overset{\|}{C}}Cl$ and CF_3CF_2CN.

The dipole moments of methallene and ethyl acetylene also indicate that hyperconjugation is occurring in these molecules although not to the extent that it is occurring in the CF_3 and CF_3CF_2 groups.

The dipole moment of vinyl methyl ether is consistent with those of other ethers, but is slightly less, presumably because of resonance of the type,

$$CH_3-\overset{+}{O}=CH-\bar{C}H_2$$

The moment of sulfur tetrafluoride indicates that the sp^3d hybridization with an unshared pair occuping a hybrid orbital is very probable.

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A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemistry

1961

ACKNOWLEDGMENT

The writer wishes to express his appreciation to Professor M.T.Rogers for his assistance throughout the course of this work.

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I. Theoretical Background

When a dielectric material is subjected to an electric field, the molecules in the dielectric are said to be polarized by the field. Polarization occurs by distortion and by orientation. Distortion polarization is due to the fact that positive and negative charge centers in the molecules are made to separate, and hence a dipole is induced so as to line up with the field. Orientation polarization occurs when the molecule has a permanent dipole. When acted upon by the field, the permanent dipole tends to line up in the direction of the field. The first effect is independent of temperature since a dipole disturbed by thermal collisions from its equilibrium position is at once induced again by the field. The orientation polarization is dependent on temperature, decreasing with an increase in temperature. This is due to an increase in the number of thermal collisions at higher temperatures, and hence the force of alignment imposed by the field is being overcome.

The objective of this section is to derive a relationship from which the total polarization can be obtained (1), and then to show the relationship between polarization and the dipole moment.

Consider a polar dielectric material under the influence of an electric field. Let the small vibrations of the charges about their equilibrium configurations be specified by a set of normal coordinates $\xi_1, \xi_2, \ldots$ equal in number to the number of degrees of freedom of the elastic vibrations. One assumes the electrical moments $p_{x'}$, $p_{y'}$, and $p_{z'}$ along the principal axes of inertia x', y' and z' to be linear functions of the normal coordinates; therefore,

$$p_{x'} = u_{x'} + \sum_{i=1}^{s} c_{x'i}\xi_i \qquad (1)$$

where $u_{x'}$ is the component of the permanent moment along the principal axis of inertia, x', and the terms inside the summation are those representing polarizations acquired by virtue of the elastic vibrations.

Let θ, ϕ and ψ be the angles specifying the position of the principal axes of inertia x', y' and z' which are fixed in the molecule relative to another set of axes x, y, and z which are fixed in space. θ is the angle between z and z', and ϕ and ψ are the angles between the intersection of the xy and x'y' planes and the x and x' axes respectively. The kinetic energy of rotation of the molecule regarded as a rigid body is then

$$T = \frac{1}{2}\left(A_{x'}\Omega_{x'}^2,\ A_{y'}\Omega_{y'}^2,\ A_{z'}\Omega_{z'}^2, \right) \qquad (2)$$

$$\Omega_{x'} = \dot{\theta}\cos\psi + \dot{\phi}\sin\theta\sin\psi$$

$$\Omega_{y'} = \dot{\phi}\cos\psi\sin\theta - \dot{\theta}\sin\psi$$

$$\Omega_{z'} = \dot{\psi} + \dot{\phi}\cos\theta$$

where the A's are the principal moments of inertia and the Ω's are the components of angular velocity. Then the Hamiltonion function is given by

(3)

$$H = \left(\frac{1}{2A_{x'}}P^2 + \frac{1}{2A_{y'}}Q^2 + \frac{1}{2A_{z'}}R^2\right) + \frac{1}{2}\sum b_i p_{\xi_i}^2 + \frac{1}{2}\sum a_i \xi_i^2$$

$$-E\Big[(u_{x'} + \sum c_{x',i}\xi_i)\sin\theta\sin\psi + (u_{y'} + \sum c_{y',i}\xi_i)\sin\theta\cos\psi$$

$$+ (u_{z'} + \sum c_{z',i}\xi_i)\cos\theta\Big]$$

where

$$P = \cos\psi\, p_\theta + \sin\psi\,\mathrm{cosec}\,\theta\,(p_\phi - \cos\theta\, p_\psi)$$

$$Q = -\sin\psi\, p_\theta + \cos\psi\,\mathrm{cosec}\,\theta\,(p_\phi - \cos\theta\, p_\psi)$$

$$R = p_\psi$$

The first term is the kinetic energy of the molecule regarded as a rigid body, and the second and third terms are

the kinetic and potential energy respectively of the small vibrations. The fourth term is the potential energy due to the applied electric field.

The expression for the polarization involves the average moment of a large number of molecules. Such an average can be calculated if the probability that a molecule have any configuration is known. This probability is given by the Boltzmann distribution function. Then, by integrating over all possible configurations, the partition function for the system is,

$$Z = \iint \cdots \int e^{-H/kT} \; dp_{\xi_1} dp_{\xi_2} \cdots dp_\psi dp_\theta dp_\phi d\xi_1 d\xi_2 \cdots d\theta d\phi d\psi \quad (4)$$

In order to perform the integration it is convenient to change three of the variables p_θ, p_ϕ, p_ψ to P, Q and R. This transformation can be represented by

$$dp_\theta \, dp_\phi \, dp_\psi = \sin\theta \; dP \; dQ \; dR \quad (5)$$

Then the Hamiltonion takes the form,

$$H = f(PQR \; p_{\xi_1} \ldots\ldots) + g(\theta\phi\psi_{\xi_1} \ldots E) \quad (6)$$

and the partition function can be factored into,

$$Z = Z_1 Z_2 \quad (7)$$

where

$$Z_1 = \iint \cdots \int e^{-f/kT} \; dPdQdR \; dp_{\xi_1} dp_{\xi_2} \ldots\ldots \quad (8)$$
$$Z_2 = \iint \cdots \int e^{-g/kT} \; \sin\Theta \, d\theta d\phi d\psi d\xi_1 d\xi_2 \ldots\ldots$$

The electric susceptibility can then be obtained from,

$$\chi = \frac{NkT}{E} \frac{\partial}{\partial E} \ln Z = \frac{NkT}{E} \frac{\partial}{\partial E} (\ln Z_1 + \ln Z_2) \quad (9)$$

but since $Z_1 \neq Z_1(E)$, the Z_1 makes no contribution to the susceptibility and hence,

$$\mathcal{P} = \frac{NkT}{E}\frac{\partial}{\partial E}\ln Z_2 \qquad (10)$$

This means that the polarization is the same as though the kinetic energy were omitted entirely from the Hamiltonion function, provided the weight function $\sin\theta$ is retained. Hence, for Z_2

$$Z_2 = \int\cdots\int e^{-\frac{1}{2kT}\Sigma a_i\xi_i^2}\, e^{-\frac{E}{kT}(p_x,\sin\theta\sin\psi - p_y,\sin\theta\cos\psi - p_z,\cos\theta)} \sin\theta d\theta d\phi d\psi d\xi_1 \ldots (11)$$

In order to evaluate Z_2, Z_2 must be expanded in terms of E. Hence,

$$Z_2 = \int\cdots\int e^{-\frac{1}{2kT}\Sigma a_i\xi_i^2}\left[1 - \frac{E}{kT}(p_x,\sin\theta\sin\psi + p_y,\sin\theta\cos\psi + p_z,\cos\theta) + \frac{E^2}{2k^2T^2}(p_x,\sin\theta\sin\psi + p_y,\sin\theta\cos\psi + p_z,\cos\theta)^2 + \ldots\ldots\right]\sin\theta d\theta d\phi d\psi d\xi_1 \ldots\ldots \qquad (12)$$

In order to integrate, observe that the coefficients of E and E^2 are direction cosines. Therefore, since the mean square of any direction cosine is 1/3 and the mean of the first power of a direction cosine is zero, equation (12) becomes,

$$Z_2 = \int\cdots\int e^{-\frac{1}{2kT}\Sigma a_i\xi_i^2}\left[1 - \frac{E^2}{6k^2T^2}(u_x' + u_y' + u_z' + \Sigma c_{x'i}\xi_i + c_{y'i}\xi_i + c_{z'i}\xi_i)^2\right]\sin\theta d\theta d\phi d\psi d\xi_1 \ldots\ldots \qquad (13)$$

By multiplying out equation(13) and using the relationships

$$\mathcal{Y} = \frac{NkT}{E}\frac{\partial}{\partial E}\ln Z_2 \qquad (10)$$

This means that the polarization is the same as though the kinetic energy were omitted entirely from the Hamiltonion function, provided the weight function $\sin\theta$ is retained. Hence, for Z_2

$$Z_2 = \int\cdots\int e^{-\frac{1}{2kT}\sum a_i \xi_i^2}\; e^{-\frac{E}{kT}(p_x,\sin\theta\sin\psi - p_y,\sin\theta\cos\psi - p_z,\cos\theta)} \sin\theta d\theta d\phi d\psi d\xi_1 \ldots (11)$$

In order to evaluate Z_2, Z_2 must be expanded in terms of E. Hence,

$$Z_2 = \int\cdots\int e^{-\frac{1}{2kT}\sum a_i \xi_i^2}\left[1 - \frac{E}{kT}(p_x,\sin\theta\sin\psi + p_y,\sin\theta\cos\psi + p_z,\cos\theta) + \frac{E^2}{2k^2T^2}(p_x,\sin\theta\sin\psi + p_y,\sin\theta\cos\psi + p_z,\cos\theta)^2 + \ldots\ldots\right]\sin\theta d\theta d\phi d\psi d\xi_1 \ldots\ldots \qquad (12)$$

In order to integrate, observe that the coefficients of E and E^2 are direction cosines. Therefore, since the mean square of any direction cosine is 1/3 and the mean of the first power of a direction cosine is zero, equation (12) becomes,

$$Z_2 = \int\cdots\int e^{-\frac{1}{2kT}\sum a_i \xi_i^2}\left[1 - \frac{E^2}{6k^2T^2}(u_x' + u_y' + u_z' + \sum c_{x'i}\xi_i + c_{y'i}\xi_i + c_{z'i}\xi_i)^2\right]\sin\theta d\theta d\phi d\psi d\xi_1 \ldots\ldots \qquad (13)$$

By multiplying out equation(13) and using the relationships

$$\int_{-\infty}^{+\infty} \xi_i e^{-\beta \xi_i^2} d\xi_i = 0 \qquad 2\beta_i \int_{-\infty}^{\infty} \xi_i^2 e^{-\beta \xi_i^2} d\xi_i = \int_{-\infty}^{\infty} e^{-\beta \xi_i^2} d\xi_i$$

Z_2 can be expressed as,

$$Z_2 = \left[1 + \frac{E^2}{6k^2T^2} \left(u_{x'}^2 + u_{y'}^2 + u_{z'}^2 + kT \sum \frac{c_{x'i}^2 + c_{y'i}^2 + c_{z'i}^2}{a_i} \right) \int \cdots \int e^{-a_i \xi_i^2 / 2kT} \sin\theta \, d\theta \, d\phi \, d\psi \, d\xi_1 \cdots \right] \tag{14}$$

By substituting equation (14) into equation (10),

$$\chi = \frac{2\gamma NkT}{1 + E^2} \tag{15}$$

where γ is the coefficient of E^2 in equation (14). E^2 can be neglected in comparison to 1 in the denominator since the range of applicability of equation (15) is in the region of low fields. That is, the susceptibility is independent of field strength for low fields. Therefore,

$$\chi = 2\gamma NkT \tag{16}$$

or

$$\chi = N \sum_{i=1}^{S} \frac{c_{x'i}^2 + c_{y'i}^2 + c_{z'i}^2}{3a_i} + N \left(\frac{u_{x'}^2 + u_{y'}^2 + u_{z'}^2}{3kT} \right)$$

If the oscillations are due to isotropically bound charges,

$$c_{x'i}^2 = c_{y'i}^2 = c_{z'i}^2 = e_i^2 \tag{17}$$

Therefore,

$$\chi = N \sum_{i=0}^{S} \frac{e_i^2}{a_i} + \frac{Nu^2}{3kT} \tag{18}$$

where the first term is the molecular polarizability, α_o. Hence the polarization in a field of unit field strength is given by

$$P = \frac{4\pi N}{3}\left(\alpha_o + u^2/3kT\right) \qquad (19)$$

where the first term is the distortion polarization and the second term is the orientation polarization.

It is desirable to know the effective average field or the force to which a molecule is subjected when a field is applied (2). This force may be resolved into three parts:

$$\vec{F}_{local} = \vec{F}_1 + \vec{F}_2 + \vec{F}_3 \qquad (20)$$

$\vec{F}_1$ is the force due to the applied electric field and is given by

$$\vec{F}_1 = 4\pi\vec{\sigma} \qquad (21)$$

where $\vec{\sigma}$ is the surface charge density on the conducting plates between which a dielectric material has been placed. $\vec{F}_2$ takes into account the attractions and repulsions by other molecules polarized under the influence of the external field. $\vec{F}_2$ is given by,

$$\vec{F}_2 = -4\pi\vec{P} + \frac{4\pi\vec{P}}{3} \qquad (22)$$

where $\vec{P}$ is the polarization vector. $\vec{F}_3$ takes into consideration the internal field exerted by other charges within the same molecule. In general, $\vec{F}_3$ is very small and is taken as zero. However, it is a very complicated function and is temperature dependent. Neglecting $\vec{F}_3$, the local field is,

$$\vec{F}_{local} = 4\pi\vec{\sigma} - 4\pi\vec{P} + \frac{4\pi\vec{P}}{3} \qquad (23)$$

Using the relationships,

$$\vec{D} = 4\pi\vec{\sigma} \qquad (24)$$

and

$$\vec{E} = \vec{D} - 4\pi\vec{P} \qquad (25)$$

where $\vec{E}$ is the electric intensity vector and $\vec{D}$ is the electric

displacement vector, equation(23) becomes,

$$\vec{F}_{local} = \vec{E} + \frac{4\pi\vec{P}}{3} \qquad (26)$$

where the first term represents the average field throughout the dielectric, and the second term represents a correction for the fact that the other molecules of the dielectric exert an average force on the given molecule when the dielectric is subject to $\vec{E}$.

The average moment of one molecule is

$$\vec{m} = \alpha \vec{F}_{local} \qquad (27)$$

where α is the sum of the induced and permanent polarizability. The molar polarization is given by,

$$\vec{P} = n\vec{m} \qquad (28)$$

where n is the number of molecules/cm^3. By substituting equations 25 and 26 into 27,

$$\vec{P} = n\vec{m} = n\alpha\vec{F}_{local} = n\alpha\left(\vec{E} + \frac{4\pi\vec{P}}{3}\right) \qquad (29)$$

Using the relation, $\vec{D} = \epsilon E$, and equation 25, equation 29 becomes,

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi n}{3}\alpha \qquad (30)$$

where ϵ is the dielectric constant of the substance. Multiplying equation (30) through by the ratio of the molecular weight of the dielectric to its density gives,

$$\frac{M}{d}\left(\frac{\epsilon - 1}{\epsilon + 2}\right) = \frac{4\pi N \alpha}{3} \qquad (31)$$

where N is Avogadro's number. Since α was the sum of the induced and permanent polarizabilities, equation (31) is identical with equation (19). Hence,

$$P = \frac{(\epsilon - 1)}{(\epsilon + 2)}\frac{M}{d} \qquad (32)$$

Hence, the molar polarization can be obtained experimentally by measurements of dielectric constants and can then be related to the distortion and orientation polarization. However, in order to calculate dipole moments, the distortion polarization must be obtained. This is done by taking into consideration the fact that the dielectric constant is equal to the square of the refractive index at infinite wavelength. That is.

$$\epsilon = n^2 \qquad (34)$$

and therefore,

$$P_d = \frac{n^2 - 1}{n^2 + 2} \frac{M}{d} \qquad (35)$$

where P_d is the distortion polarization. It is significant to elaborate on this point. In order to measure the refractive index, visible light is used. The electromagnetic forces associated with visible light oscillate very rapidly in sign and hence don't act in any one direction long enough to orient molecules in any one direction. Hence the refractive index measured with visible light is due entirely to distortion polarization. Therefore, extrapolation of such data to infinite wave-length will yield only the part of the dielectric constant exclusive of orientation. Furthermore, the distortion polarization is the sum of two terms: atomic and electronic. The atomic polarization is due to vibrations of nuclei, but since nuclei generally have vibrational frequencies in the infra-red, the atomic polarization contributes very little to the distortion polarization when measured with visible light. Therefore, the distortion polarization is due almost entirely to electronic polarization when refractive indices are measured in this manner.

Hence the dipole moment can be readily calculated in terms of,

$$P = P_d + P_o = P_d + \frac{4\pi N}{3}\frac{u^2}{3kT} = \frac{\epsilon - 1}{\epsilon + 2}\frac{M}{d} \qquad (36)$$

or, by solving for u ,

$$u = \sqrt{\frac{9kT}{4\pi N}\left[\frac{(\epsilon - 1)\,M}{(\epsilon + 2)\,d} - P_d\right]} \qquad (37)$$

Experimental

The method employed was the heterodyne-beat method, and all samples were measured in the gaseous phase. This method takes advantage of the dependence of the frequency of an (3) electron tube oscillator upon resistance, inductance and capacitance in its tank circuit. A circuit with C, L and R will be set into oscillation if the capacitor is suddenly given a charge and then left to discharge. From this oscillating circuit, electromagnetic radiation is generated. If two such oscillators are loosely coupled, one a fixed oscillator generating a radiofrequency f_0 , and the other a variable oscillator generating a radiofrequency f , and if these signals are fed into a mixer tube whose function it is to produce in its output voltage a component of frequency $f - f_0$, this difference frequency or beat frequency will be in the audio range when f and f_0 are nearly equal. This can be detected by earphones or other suitable means. The frequency of the variable oscillator will be given very nearly by,

$$f = \frac{1}{2\pi\sqrt{LC}} \qquad (38)$$

where L and C are the inductance and capacity of the oscillating tuning circuit.

If for some capacitance setting, f is greater than f_0, the beat frequency will be outside the audible range. An increase in C (L is fixed) will lower the beat frequency which will pass through the audible range and will reach zero when $f = f_0$. A further increase in C will again produce a beat note which will now increase with C until it passes beyond audibility . The region of inaudibility is so narrow as to correspond to a point on a precision measuring condenser in the variable oscillator. This corresponds to

location of the beat frequency to within one cps, and hence the accuracy of this method is determined by the accuracy of setting and calibrating the standard condenser and by the stability of the variable and fixed oscillators.

Hence, by connecting a dielectric cell in parallel to the variable oscillator circuit, a change in capacitance can be effected by altering the medium witnin the cell. Then, a measurement of the beat frequency for inaudibility before and after introduction of a substance into the dielectric cell will give the capacitance of the substance.

In general, it is much harder to measure dielectric constants of gases since their dielectric constants are so close to unity, thereby causing capacitance changes to be very small. Hence, a third source of oscillations is employed. This source also has a fixed frequency. The beat frequency for inaudibility is then adjusted so that it is equal to this third source rather than to zero frequency. This eliminates the so-called locking-in effect of the fixed and variable oscillators initially described. That is, when f is brought close to f_o, low frequency beats cannot be distinguished because the more stable of the two oscillators exerts a synchronizing action on the less stable and over a considerable range the two oscillators are locked in step with one another and a sharp zero beat cannot be obtained. The third source of oscillations in this investigation generated a frequency of 400 cps. Then, when the beat frequency was 400 cps, one observed a one-to-one Lissajous figure on an oscilliscope.

Variable Oscillator

The variable frequency oscillator made use of a 6A8-type pentagrid converter tube (4) which exhibits a negative trans-

conductance between the signal grid and the anode grid. Under these conditions, the screen current remained fairly constant for wide variations in signal-grid voltage, and the frequency at which the tube oscillated was relatively independent of stray signal feedback through the plate. This design resulted in an oscillator of high frequency stability, and one which should not be affected by the frequency of the fixed oscillator.

Fixed Oscillator

A crystal replaced the tuning circuit found in most oscillators (4) , and hence the oscillator required no tuning adjustment and would work without change of components over a wide range of crystal frequencies. A 6SJ7 pentode tube was used as a triode oscillator, with the cathode and suppressor grid grounded. This provided screening against capacitance coupling of the oscillator to later stages, so that the frequency of oscillation was less affected by feedback through the plate.

Each oscillator was shielded by enclosure in a separate metal box, and the signal output of each was fed to the mixer tube through coaxial leads. The entire apparatus was enclosed in a thermally insulated aluminum box.

Precision Condenser

A General Radio Type 722-N precision condenser with a range of 1100 scale divisions was used to measure capacitance. Since this instrument was in scale divisions, it had to be calibrated in terms of capacitance. This was accomplished by determining the change in capacitance on the precision condenser relative to a primary standard capacitor. The primary standard capacitor (5) was designed so that the capacitance change per inch of travel on it was equal to 1.4800 uuf or .0001057 uuf per scale division. The error in determining capacitance by this method was about 1%, but since all measurements of capacitance involved capacitance increments, the error was minimized. Table I gives the data for the calibration.

Temperature Measurement

The temperature inside the dielectric cell was determined with a copper-constantan (60% Cu-40% Ni) thermocouple. The cold junction consisted of a crushed ice-distilled water mixture. All switches and connections were made of copper so that the only junctions of different metals were those of the thermocouples. The resulting electromotive force was measured with a K-2 type potentiometer (Leeds and Northrup). A plot of emf vs. temperature was made for the copper- constantan thermocouple, the data being taken from the National Bureau of Standards (6). Hence the temperature for any emf could be determined. The sensitivity was such that a change in temperature of 0.1 degree could easily be detected. Table II gives emf vs. temperature data.

Table I

Calibration of Precision Condenser

Scale Divisions (precision condenser)	Scale Divisions (standard condenser)
	100
0.0	125
43.5	150
87.2	175
131.4	200
173.2	225
217.6	250
262.8	275
307.0	300
354.1	325
396.1	350
429.2	375
481.8	400
524.0	425
565.3	450
604.9	475
643.7	500
683.4	525
722.1	550
760.0	575
797.6	600
834.7	625
872.3	650
909.1	675
944.8	700
981.8	725
1016.7	750
1051.8	775
1086.3	800
1121.8	825
1155.6	850
1188.9	875
1221.6	900
1255.3	925
1288.1	950
1321.7	975
1354.5	1000
1385.4	

*data are for position 1 on precision condenser

Table II

Temperature Measurement - Copper-Constantan Thermocouple

Temperature °C	EMF (millivolts)
0.0	0.0
10.0	0.39
20.0	0.79
30.0	1.19
40.0	1.61
50.0	2.03
60.0	2.47
70.0	2.91
80.0	3.36
90.0	3.81
100.0	4.28

Temperature Control

The dielectric cell was immersed in an asbestos bath. The temperature within the cell was controlled by a thermistor in a Wheatstone bridge circuit. The thermistor was of the glass-coated rod type with Pt-Ni alloy leads.* Its resistance varies from 145000 ohms at 0°C to 305 ohms at 200°C. The other resistors in the bridge set-up were a 4-decade resistance box with a range of 1 to 10,000 ohms and a ten-turn helical potentiometer. The heater current was controlled by a saturable reactor in series with a heater. The circuit was supposed to control the temperature within ±.05 degrees. However, temperature variations of as much as a degree were observed. A change in temperature of a degree during a measurement did not effect the value of the dipole moment to any appreciable extent provided no marked change in the replaceable capacitance of the cell accompanied this change. When the replaceable capacitance did change appreciably, the data obtained were no longer consistent, and hence one could tell if temperature changes were effecting the measurements. Inconsistent data due to temperature changes were discarded. For a more extensive description of the temperature control apparatus, see reference (7).

Gas Handling System

Before any gas was let into the system, the system was thoroughly evacuated with a Duo Seal Vacuum Pump**. Then, since the cell had to be calibrated before each use, the

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* Western Electric Company, Type 14-B

** W. M. Welsh Manufacturing Company

calibrating gas, ammonia, was let into the system at B and solidified in tube C with liquid air (see diagram, page 18). The ammonia was then condensed and re-solidified into tube D. The system was again evacuated so as to remove any traces of air that may have been present in the system or in the ammonia. This process was continued until any air present had been removed. Then the ammonia was vaporized the vapors flowing into the dielectric cell. The pressure of the gas within the system could then be determined by the mercury manometer.

After having calibrated the cell, the ammonia was pumped out, the vapor being solidified in a removable liquid air trap, E. After pumping on the system for a short period of time , the gas whose dielectric constant was to be measured was allowed to enter at A. The same process of condensation and solidification was again carried out until all traces of air had been removed. The gas was then allowed to enter the dielectric cell so as to make a measurement.

The entire gas handling system was constructed with high vacuum glass stopcocks. The stopcock grease used was Dow Corning high vacuum grease.

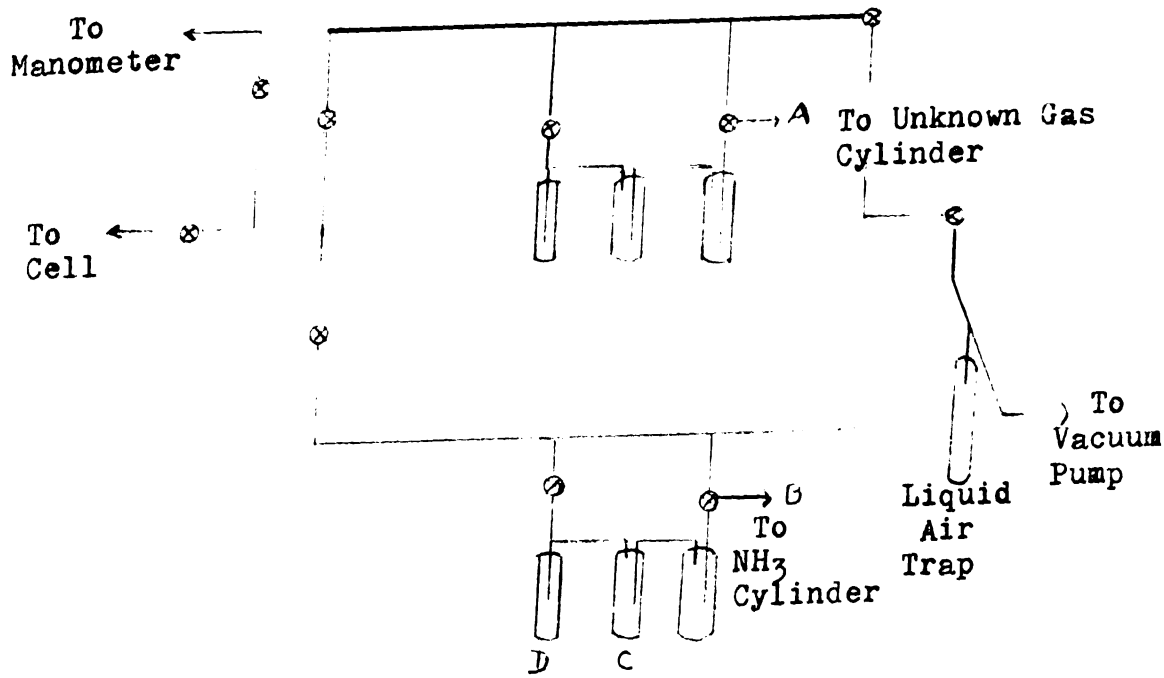
Dielectric Cell

The dielectric cell consisted of a series of nickel-plated copper cylinders insulated from each other by small Teflon spacers. The plates were sealed in glass so as not to allow any air to enter the cell. Platinum leads connected the cylinders to tungsten wires which were sealed through the glass casing. The tungsten wires were connected to the heterodyne-beat apparatus by a coaxial lead.

Since the capacitance is directly proportional to the area of the plates and inversely proportional to the distance

Figure I

Gas Handling System



⊗ Glass vacuum stopcocks

between them, the largest ratio of A/d would give the largest value for C_o, the replaceable capacitance . A large C_o is a necessity when working with gases since the capacitance increments are so small. However, the larger the ratio of A/d the greater the absorption error. Therefore, the cell described above (4) was constructed with these two factors in mind. As a result, the replaceable capacitance , which is a function of temperature, pressure, and humidity changed periodically, and since it was large relative to capacitance changes, a change in C_o had a marked effect on the measured quantities. Therefore, C_o had to be determined each time a series of measurements was to be made. The method of cell calibration will be described more fully in a following section. See page 20 for a diagram of the dielectric cell.

Experimental Method

Since the replaceable capacitance, C_o, changed periodically, the cell had to be calibrated each time a determination was to be made. This was done in the following manner:

The total capacitance of the evacuated cell is given by

$$C_v = C_o + C_f \qquad (39)$$

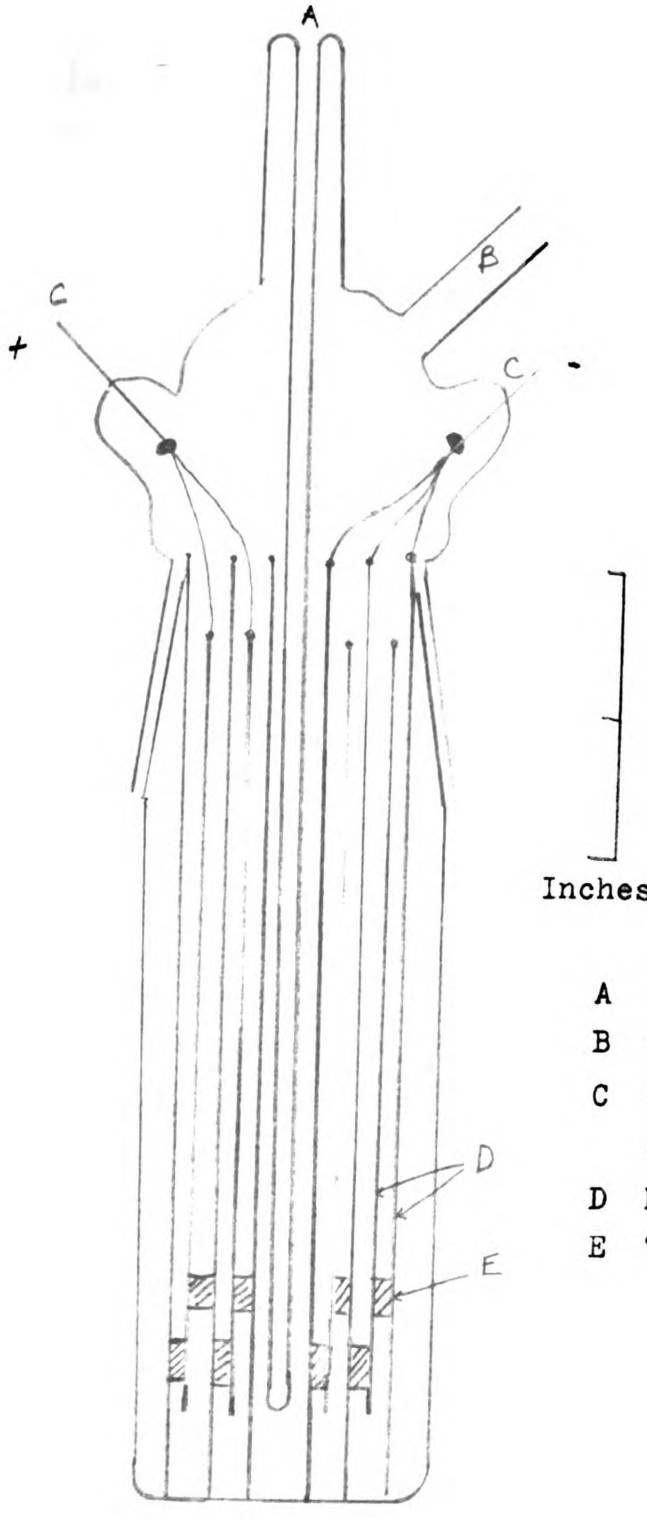
where C_f is the capacitance associated with leads and parts of the cell which can not be filled with gas. The total capacitance with a dielectric material in the cell is given by

$$C_g = \epsilon C_o + C_f \qquad (40)$$

where ϵ is the dielectric constant of the material in the cell. By solving these two equations simultaneously, C_f can be eliminated and the result is

$$C_o = \frac{C_g - C_v}{\epsilon - 1} = \frac{\Delta C}{\epsilon - 1} \qquad (41)$$

Figure II
Dielectric Cell



Inches

A Thermocouple Well
B Connection to vacuum line
C Leads to heterodyne-beat apparatus
D Nickel-plated copper cylinders
E Teflon insulators

where ΔC represents the difference in capacitance between the empty cell and the cell filled with a dielectric material. ΔC is given by $(dC/dP)760$; it is the capacitance change at a pressure of one atmosphere. Hence by knowing the variation of dielectric constant with temperature for some gas at a given pressure, ammonia in this investigation, the replaceable capacitance can be determined. Then the dielectric constant of a gas under investigation is given by,

$$\epsilon = \frac{\Delta C}{C_o} + 1 = \frac{(dC/dP)\ 760}{C_o} + 1 \qquad (42)$$

The method used to determine the slope, dC/dP, was as follows: The capacitance at a low pressure, about 200mm, and the capacitance at a higher pressure, about 300mm., was determined. This process was repeated as many times as was necessary to get good reproducibility in the quantity dC/dP.

Then, having determined the dielectric constant, it was related to the molar polarization by

$$P_m = \frac{\epsilon - 1}{\epsilon + 2}\left(\frac{M}{d}\right) \qquad (43)$$

where M/d was the molar volume of the gas. By assuming that the gases were ideal, $V_m = RT/1$. Then by using refractive index data to determine the distortion polarization, P_d, the dipole moment was determined from,

$$P_m = P_d + P_o \qquad (44)$$

and

$$u = \sqrt{\frac{9kT}{4\pi N}\left(P_m - P_d\right)} \qquad (45)$$

Table III

Dielectric Constants of Ammonia Vapor at Several Temperatures

Temperature (°C)	$(\epsilon - 1)\times 10^6$
29.95	5826
38.72	5522
47.59	5240
58.36	4916
71.44	4581
80.33	4369
92.21	4062
116.12	3498

* Data from Van Itterbeck and de Clippeleir, Physica, 14, 349 (1948).

DATA AND RESULTS

Materials

1. Sulfur Tetrafluoride - purity 90-94% - impurities, SOF_2 5-9%, Cl_2 .3% , - E. I. Du Pont de Nemours and Co., Inc., Wilmington, Delaware.
2. Perfluoropropylene - literature B.P. -33°C, observed B.P. -30°C - Peninsular ChemResearch, Inc., Gainesville, Florida.
3. Pentafluoropropionyl Chloride - literature B.P. 9.5°C, observed B.P. 7-9°C - Peninsular ChemResearch, Inc., Gainesville, Florida.
4. Pentafluoropropionitrile - literature B.P. ? , observed B.P. -30°C - Peninsular ChemResearch, Inc.,Gainesville, Florida.
5. Trifluoromethylpropene - literature B.P. 6.4°C, observed B.P. 6-7°C - Peninsular ChemResearch, Inc., Gainesville Florida.
6. Ammonia,anhydrous - purity 99.99% min. - Matheson Co., Inc., Joliet, Illinois.
7. Ethyl Acetylene - purity 95.0% min. - Matheson CO., Inc., Joliet, Illinois.
8. Vinyl methyl ether - purity 95.0% min. - Matheson CO., Inc., Joliet, Illinois.
9. Methallene - purity 98.0% min. - Columbia Organic Chemical Co.

Table IV

Calibration with Ammonia for Ethyl Acetylene (1st determination)

Pressure cm. of Hg	ΔP cm. of Hg	Precision Condenser	Standard Condenser	ΔC μμf	ΔC/ΔP μμf/cm
30.53	17.55	299.2	352.0	0.2495	0.01422
12.98		438.6	588.0		
30.96	17.45	287.7	332.0	.2421	.01388
13.51		422.2	561.0		
30.96	18.23	280.1	319.0	.2505	.01374
12.73		419.3	556.0		
30.86	17.84	265.0	291.0	.2537	.01422
13.02		404.0	531.0		

ΔC/ΔP average	$(\epsilon - 1)\times 10^6$ at 48.3°C	C_o
0.01402	5218	204.2

Table V

Ethyl Acetylene (1st determination)

Pressure cm. of Hg	ΔP cm. of Hg	Precision Condenser	Standard Condenser	ΔC µµf	$\Delta C/\Delta P$ µµf/cm
32.52	19.32	305.2	363.0	0.1723	0.008918
13.20		400.4	526.0		
32.01	18.92	247.1	258.0	.1723	.009106
13.09		339.1	421.0		
32.64	19.89	225.9	220.0	.1807	.009080
12.75		320.6	391.0		

$\Delta C/\Delta P$ average	ϵ at 48°C	P_d cm3	P_m cm3	P_∞ cm3	u Debye
0.009035	1.003363	18.88	29.57	10.69	0.75

Table VI

Calibration with Ammonia for Ethyl Acetylene
(2nd determination)

Pressure cm. of Hg	ΔP cm. of Hg	Precision Condenser	Standard Condenser	ΔC μμf	ΔC/ΔP μμf/cm
29.38	19.32	260.7	284.0	0.2716	0.01405
10.06		410.3	541.0		
30.45	16.75	246.6	257.0	.2357	.01408
13.70		373.7	480.0		
34.32	22.20	219.7	209.0	.3150	.01419
12.12		389.4	507.0		
30.86	16.96	249.4	262.0	.2368	.01396
13.90		377.4	486.0		

ΔC/ΔP average	$(\epsilon - 1)\times 10^6$ at 49.8 °C	C_o μμf
0.01407	5175	206.63

Table VII

Ethyl Acetylene (2nd determination)

Pressure cm. of Hg	ΔP cm. of Hg	Precision Condenser	Standard Condenser	ΔC uuf	ΔC/ΔP uuf/cm.
31.86	18.30	320.7	390.0	0.1723	0.009415
13.56		417.2	553.0		
32.81	18.94	320.3	388.0	.1744	.009208
13.87		416.8	553.0		
31.90	18.41	323.1	393.0	.1712	.009291
13.49		418.5	555.0		
32.29	18.38	305.4	363.0	.1712	.009315
13.91		400.4	525.0		

ΔC/ΔP average	ϵ at 49.6 °C	P_m cm3	Pd cm3	P_o cm3	u Debye
0.009307	1.003423	30.23	18.88	11.34	0.77

Table VIII

Calibration with Ammonia for Vinyl Methyl Ether

(1st determination)

Pressure cm. of Hg	ΔP cm. of Hg	Precision Condenser	Standard Condenser	ΔC μμf	ΔC/ΔP μμf/cm.
27.39	13.33	336.4	415.0	0.1924	0.01444
14.06		444.9	597.0		
30.77	17.33	313.2	376.0	.2516	.01452
13.44		455.8	614.0		
25.41	12.11	300.2	357.0	.1744	.01440
13.30		398.2	522.0		

ΔC/ΔP average	$(\epsilon - 1)\times10^6$ at 46.5 °C	C_o μμf
0.01445	5275	208.23

Table IX

Vinyl Methyl Ether (1st determination)

Pressure cm. of Hg	ΔP cm.of Hg	Precision Condenser	Standard Condenser	ΔC μμf	ΔC/ΔP μμf/cm.
32.14	19.40	312.6	478.0	0.2389	0.01231
12.74		514.3	704.0		
32.56	19.00	372.3	477.0	.2357	.01239
13.56		511.0	700.0		
32.62	19.31	377.0	486.0	.2273	.01177
13.31		512.0	701.0		
32.87	18.92	369.8	474.0	.2251	.01190
13.95		502.9	687.0		
32.85	19.43	373.0	479.0	.2484	.01278
13.42		519.9	714.0		

ΔC/ΔP average	ϵ at 46.0 °C	P_m cm3	P_d cm3	P_o cm3	u Debye
0.01223	1.004464	38.97	17.28	21.69	1.06

Table X

Calibration with Ammonia for Vinyl Methyl Ether

(2nd determination)

Pressure cm. of Hg	ΔP cm.of Hg	Precision Condenser	Standard Condenser	ΔC μμf	ΔC/ΔP μμf/cm.
31.42	17.11	334.4	412.0	0.2473	0.01445
14.31		476.4	646.0		
32.14	17.51	330.8	407.0	.2473	.01412
14.63		472.7	641.0		
32.21	18.58	309.6	370.0	.2695	.01450
13.63		462.6	625.0		

ΔC/ΔP average	$(\epsilon - 1)\times 10^6$ at 45.9°C	C_o μμf
0.01436	5292	206.23

Table XI

Vinyl Methyl Ether (2nd determination)

Pressure cm. of Hg	ΔP cm. of Hg	Precision Condenser	Standard Condenser	ΔC μμf	ΔC/ΔP μμf/cm.
32.42	19.79	374.2	480.0	0.2294	0.01159
12.63		508.7	697.0		
32.14	18.75	383.8	498.0	.2199	.01172
13.39		515.0	706.0		
32.46	18.63	377.8	487.0	.2347	.01251
13.83		517.4	709.0		
32.66	20.11	384.6	499.0	.2452	.01219
12.55		530.6	731.0		
33.15	19.40	386.4	502.0	.2368	.01221
13.75		528.4	726.0		

ΔC/ΔP average	ϵ at 45.7°C	P_{m_3} cm3	P_d cm3	P_o cm3	u Deybe
0.01204	1.004389	38.32	17.28	21.04	1.05

Table XII

Calibration with Ammonia for Pentafluoropropionitrile

(1st determination)

Pressure cm. of Hg	ΔP cm. of Hg	Precision Condenser	Standard Condenser	ΔC μμf	ΔC/ΔP μμf/cm.
34.30	22.13	496.9	678.0	0.3382	0.01528
12.17		711.2	998.0		
38.31	25.29	450.5	613.0	.3808	.01506
13.02		694.2	973.0		
38.17	25.69	464.5	628.0	.3932	.01531
12.48		713.0	1000.0		
39.81	26.37	450.3	605.0	.4069	.01543
13.44		706.1	990.0		

ΔC/ΔP average	$(\epsilon - 1)\times 10^6$ at 44.6°C	C_o μμf
0.01527	5335	217.5

Table XIII

Pentafluoropropionitrile (1st determination)

Pressure cm. of Hg	ΔP cm. of Hg	Precision Condenser	Standard Condenser	ΔC μμf	ΔC/ΔP μμf/cm.
39.94	29.42	487.6	664.0	0.4704	0.01598
10.52		790.6	1109.0		
37.53	26.46	504.1	689.0	.4186	.01582
11.07		773.4	1085.0		
38.18	26.85	497.6	680.0	.4228	.01575
11.33		769.8	1080.0		

ΔC/ΔP average	ϵ at 45.0 °C	P_m cm^3	P_d cm^3	P_o cm^3	u Debye
0.01585	1.005539	48.19	14.69	33.50	1.32

Table XIV

Calibration with Ammonia for Pentafluoropropionitrile

(2nd determination)

Pressure cm. of Hg	ΔP cm. of Hg.	Precision Condenser	Standard Condenser	ΔC μμf	ΔC/ΔP μμf/cm.
33.93	21.38	437.6	586.0	0.3160	0.01478
11.55		634.3	885.0		
36.86	23.92	405.7	534.0	.3425	.01432
12.94		616.2	858.0		
35.02	22.45	432.7	578.0	.3277	.01460
12.57		635.5	888.0		
34.91	21.94	440.9	592.0	.3224	.01470
12.97		641.7	897.0		
35.31	22.44	446.9	600.0	.3224	.01437
12.87		647.3	905.0		

ΔC/ΔP average	$(\epsilon - 1)\times 10^6$ at 48.2°C	C_o μμf
0.01455	5220	211.8

Table XV

Pentafluoropropionitrile (2nd determination)

Pressure cm. of Hg	ΔP cm.of Hg	Precision Condenser	Standard Condenser	ΔC μμf	ΔC/ΔP μμf/cm.
36.41	24.68	426.2	568.0	0.3953	0.01601
11.73		672.0	942.0		
37.23	25.42	434.6	581.0	.4006	.01576
11.81		683.9	960.0		
37.88	27.42	442.4	593.0	.4387	.01599
10.46		717.8	1008.0		

ΔC/ΔP average	∈ at 48.2 °C	P_m cm^3	P_d cm^3	P_o cm^3	u Debye
0.01592	1.005712	50.21	14.69	35.52	1.37

Table XVI

Calibration with Ammonia for Pentafluoropropionitrile

(3rd determination)

Pressure cm. in Hg	ΔP cm. in Hg	Precision Condenser	Standard Condenser	ΔC uuf	ΔC/ΔP μμf/cm.
29.86	16.73	495.4	675.0	0.2505	0.01497
13.13		651.4	912.0		
30.41	18.18	491.2	669.0	.2653	.01459
12.23		657.6	920.0		
32.41	19.64	487.3	663.0	.2949	.01502
12.77		672.5	942.0		

ΔC/ΔP average	$(\epsilon - 1)\times10^6$ at 47.2 °C	C_o *uuf*
0.01486	5250	213.2

Table XVII

Pentafluoropropionitrile (3rd determination)

Pressure cm. of Hg	ΔP cm. of Hg	Precision Condenser	Standard Condenser	ΔC μμf	ΔC/ΔP μμf/cm.
29.90	19.17	545.3	752.0	0.2917	0.01522
10.73		733.2	1028.0		
30.04	17.40	526.7	724.0	.2653	.01525
12.64		695.4	975.0		
29.74	17.95	530.0	729.0	.2748	.01531
11.79		705.0	989.0		

ΔC/ΔP average	ϵ at 47.2 °C	P_m cm^3	P_d cm^3	P_o cm^3	u Debye
0.01526	1.005439	47.66	14.69	32.97	1.32

Table XVIII

Calibration with Ammonia for 2-Trifluoromethylpropene

(1st determination)

Pressure cm. of Hg	ΔP cm. of Hg	Precision Condenser	Standard Condenser	ΔC μμf	ΔC/ΔP μμf/cm.
36.53	26.35	228.3	224.0	0.4059	0.01540
10.18		451.9	608.0		
39.27	29.96	207.4	186.5	.4603	.01537
9.31		460.8	622.0		
37.91	29.04	220.9	211.0	.4408	.01518
8.87		464.6	628.0		
38.08	28.77	215.2	200.0	.4344	.01509
9.31		454.0	611.0		
37.94	29.32	206.3	184.0	.4429	.01511
8.62		449.0	603.0		

ΔC/ΔP average	$(\epsilon - 1)\times 10^6$ at 31.4 °C	C_o μμf
0.01523	5778	200.32

Table XIX

2-Trifluoromethylpropene (1st determination)

Pressure cm. of Hg	ΔP cm. of Hg	Precision Condenser	Standard Condenser	ΔC μμf	ΔC/ΔP μμf/cm.
36.47	27.46	205.4	183.0	1.0063	0.03665
9.01		810.4	1135.0		
38.53	30.23	144.7	79.0	1.1172	.03696
8.33		810.9	1136.0		
39.16	29.53	109.5	16.0	1.0898	.03683
9.36		746.7	1047.0		

ΔC/ΔP average	ε at 31.4 °C	P_m cm^3	P_d cm^3	P_o cm^3	u Debye
0.03681	1.01397	115.4	14.33	101.1	2.26

Table XX

Calibration with Ammonia for 2-Trifluoromethylpropene

(2nd determination)

Pressure cm. of Hg	ΔP cm. of Hg	Precision Condenser	Standard Condenser	ΔC μμf	ΔC/ΔP μμf/cm.
35.64	25.39	194.0	164.0	0.3911	0.01540
10.25		406.3	534.0		
37.68	28.79	189.4	154.0	.4630	.01608
8.89		441.7	592.0		
38.45	27.41	204.3	181.0	.4291	.01565
11.04		438.0	587.0		
35.03	24.16	239.3	243.0	.3816	.01580
10.87		449.5	604.0		
35.19	25.81	246.5	257.0	.4091	.01585
9.38		475.0	644.0		
33.76	24.17	268.4	297.0	.3847	.01591
9.59		480.6	661.0		

ΔC/ΔP average	$(\epsilon - 1)\times 10^6$ at 30.0°C	C_o μμf
0.01583	5823	206.6

Table XXI

2-Trifluoromethylpropene (2nd determination)

Pressure cm. of Hg.	ΔP cm. of Hg	Precision Condenser	Standard Condenser	ΔC μμf	ΔC/ΔP μμf/cm.
36.05	26.05	148.0	84.0	1.031	0.03958
10.00		755.5	1059.0		
36.06	27.87	154.2	95.0	1.112	.03989
8.19		819.6	1147.0		
40.10	31.04	153.4	94.0	1.226	.03950
9.06		898.8	1254.0		
37.50	26.86	213.4	197.0	1.071	.03987
10.64		866.1	1210.0		
37.22	27.48	216.8	203.0	1.100	.04000
9.74		891.4	1244.0		

ΔC/ΔP average	∈ at 30.7 °C	P_m cm^3	P_d cm^3	P_o cm^3	u Debye
0.03978	1.01464	121.53	14.33	107.20	2.31

Table XXII

Calibration with Ammonia for 2-Trifluoromethylpropene

(3rd determination)

Pressure cm. of Hg	ΔP cm. of Hg	Precision Condenser	Standard Condenser	ΔC μμf	ΔC/ΔP μμf/cm.
33.92	24.33	146.1	81.0	0.3615	0.01486
9.59		340.6	423.0		
38.62	28.95	114.2	23.0	.4323	.01493
9.67		345.8	432.0		
36.55	26.70	134.2	60.0	.3974	.01488
9.85		347.7	436.0		
33.07	23.46	165.5	116.0	.3509	.01496
9.61		355.4	448.0		
35.12	26.05	153.8	95.0	.3911	.01501
9.07		364.6	465.0		

ΔC/ΔP average	$(\epsilon - 1)\times 10^6$ at 32.1 °C	C_o μμf
0.01493	5753	197.36

Table XXIII

2-Trifluoromethylpropene (3rd determination)

Pressure cm. of Hg	ΔP cm. of Hg	Precision Condenser	Standard Condenser	ΔC μμf	ΔC/ΔP μμf/cm.
34.89	24.12	216.1	202.0	1.003	0.04158
10.77		822.8	1151.0		
37.06	26.80	170.8	125.0	1.117	.04168
10.26		845.1	1182.0		
34.33	23.79	247.2	267.0	.9894	.04159
10.54		860.8	1203.0		

ΔC/ΔP average	ϵ at 32.9 °C	P_m cm^3	P_d cm^3	P_o cm^3	u Debye
0.04162	1.01603	134.20	14.33	119.9	2.45

Table XXIV

Calibration with Ammonia for Pentafluoropropionyl Chloride
(1st determination)

Pressure cm. of Hg	ΔP cm. of Hg	Precision Condenser	Standard Condenser	ΔC μμf	ΔC/ΔP μμf/cm.
33.72	21.41	488.4	665.0	0.3065	0.01432
12.31		680.6	955.0		
36.28	23.37	466.8	632.0	.3277	.01402
12.91		672.2	942.0		
37.06	25.48	453.4	610.0	.3530	.01382
11.58		673.4	944.0		
35.77	24.92	454.7	613.0	.3562	.01429
10.85		677.0	950.0		
34.29	22.47	477.7	648.0	.3277	.01458
11.82		683.4	958.0		
30.82	18.98	520.6	715.0	.2833	.01492
11.84		700.6	983.0		
33.58	21.00	500.1	683.0	.3171	.01510
12.58		701.0	983.0		
33.98	22.99	504.5	690.0	.3213	.01398
10.99		709.0	994.0		

ΔC/ΔP average	$(\epsilon - 1)\times 10^6$ at 47.5°C	C_o μμf
0.01438	4950	220.78

Table XXV

Pentafluoropropionyl Chloride (1st determination)

Pressure cm. of Hg	ΔP cm. of Hg	Precision Condenser	Standard Condenser	ΔC μμf	ΔC/ΔP μμf/cm.
35.59	24.31	513.6	704.0	0.3108	0.01279
11.28		711.2	998.0		
34.93	24.05	560.6	776.0	.3023	.01257
10.88		756.9	1062.0		
37.92	25.51	536.1	738.0	.3256	.01276
12.41		745.6	1046.0		
35.57	23.64	557.2	770.0	.3002	.01269
11.93		751.2	1054.0		

ΔC/ΔP average	ϵ at 48.0 °C	P_m cm^3	P_d cm^3	P_o cm^3	u Debye
0.01270	1.004371	38.38	19.68	18.70	0.991

Table XXVI

Calibration with Ammonia for Pentafluoropropionyl Chloride
(2nd determination)

Pressure cm. of Hg	ΔP cm. of Hg	Precision Condenser	Standard Condenser	ΔC μμf	ΔC/ΔP μμf/cm.
32.68	20.00	355.6	448.0	0.2928	0.01464
12.68		527.0	725.0		
35.59	23.47	313.6	377.0	.3583	.01527
12.12		521.1	716.0		
34.86	22.12	331.0	407.0	.3308	.01496
12.74		524.5	720.0		

ΔC/ΔP average	$(\epsilon - 1)\times 10^6$ at 45.6 °C	C_o μμf
0.01495	5303	214.2

Table XXVII

Pentafluoropropionyl Chloride (2nd determination)

Pressure cm. of Hg	ΔP cm. of Hg	Precision Condenser	Standard Condenser	ΔC μμf	ΔC/ΔP μμf/cm.
34.33	22.09	387.0	503.0	0.2822	0.01273
12.24		557.0	770.0		
33.49	21.98	422.0	562.0	.2780	.01265
11.51		593.8	825.0		
35.18	24.56	420.2	558.0	.3034	.01235
10.62		607.6	845.0		
33.71	22.31	441.0	591.0	.2769	.01241
11.40		612.8	853.0		
34.24	23.87	449.4	604.0	.2991	.01253
10.37		635.0	887.0		

ΔC/ΔP average	ϵ at 46.3 °C	P_m cm^3	P_d cm^3	P_o cm^3	u Debye
0.01253	1.004446	38.81	19.68	19.13	1.000

Table XXVIII

Calibration with Ammonia for Methallene (1st determination)

Pressure cm. of Hg	ΔP cm. of Hg	Precision Condenser	Standard Condenser	ΔC μμf	ΔC/ΔP μμf/cm.
34.73	24.27	208.6	189.0	0.3816	0.01572
10.46		415.4	550.0		
35.89	25.43	212.1	194.0	.4017	.01579
10.46		430.1	574.0		
38.09	26.84	212.7	196.0	.4091	.01524
11.25		436.0	583.0		
37.12	26.90	223.2	214.0	.4122	.01532
10.22		449.2	604.0		
35.98	24.83	234.1	234.0	.3795	.01528
11.15		441.8	593.0		
36.06	23.95	233.2	233.0	.3626	.01556
12.11		431.4	576.0		

ΔC/ΔP average	$(\epsilon - 1)x10^{6}$ at 31.8 °C	C_o μμf
0.01549	5760	204.4

Table XXIX

Methallene (1st determination)

Pressure cm. of Hg	ΔP cm. of Hg	Precision Condenser	Standard Condenser	ΔC μμf	ΔC/ΔP μμf/cm.
36.56	22.67	187.4	152.0	0.1659	0.007318
13.89		275.3	309.0		
37.91	25.02	183.0	146.0	.1881	.007518
12.89		283.2	324.0		
37.17	23.68	189.2	156.0	.1786	.007542
13.49		284.2	325.0		
34.11	21.11	202.8	180.0	.1649	.007812
13.00		289.2	336.0		

ΔC/ΔP average	∈ at 33.0 °C	P_m cm^3	P_d cm^3	P_o cm^3	u Debye
0.007548	1.002807	23.49	19.68	3.81	0.43

Table XXX

Calibration with Ammonia for Methallene (2nd determination)

Pressure cm. of Hg	ΔP cm. of Hg	Precision Condenser	Standard Condenser	ΔC μμf	ΔC/ΔP μμf/cm.
33.07	19.59	225.0	218.0	0.2938	0.01499
13.48		384.9	496.0		
35.16	23.04	194.8	166.0	.3467	.01504
12.12		381.8	494.0		
35.60	22.64	200.0	174.0	.3530	.01559
12.96		389.8	508.0		
36.50	23.84	204.3	182.0	.3721	.01561
12.66		405.9	534.0		
35.55	21.18	210.5	192.0	.3266	.01542
14.37		386.4	501.0		

ΔC/ΔP average	$(\epsilon - 1)\times 10^6$ at 33.6 °C	C_o μμf
0.01533	5700	204.4

Table XXXI

Methallene (2nd determination)

Pressure cm. of Hg	ΔP cm. of Hg	Precision Condenser	Standard Condenser	ΔC μμf	ΔC/ΔP μμf/cm.
36.95	23.55	159.1	104.0	0.1807	0.00767
13.40		256.2	275.0		
39.60	25.77	156.0	99.0	.1903	.00735
13.83		258.4	279.0		
35.68	23.40	134.0	59.0	.1755	.00750
12.28		229.1	225.0		

ΔC/ΔP average	ϵ at 33.7 °C	P_m cm^3	P_d cm^3	P_o cm^3	u Debye
0.00751	1.002792	23.44	19.68	3.76	0.435

Table XXXII

Calibration with Ammonia for Perfluoropropylene

Pressure cm. of Hg	Δ P cm. of Hg	Precision Condenser	Standard Condenser	∠C μμf	∠C/∠P μμf/cm.
27.72	13.52	186.6	152.0	0.20294	0.01501
14.20		290.4	344.0		
43.17	25.39	182.1	144.0	.4038	.01590
17.78		400.6	526.0		
46.77	27.98	433.9	580.0	.3953	.01413
18.79		680.1	954.0		
44.59	28.50	440.0	590.0	.4249	.01491
16.09		707.2	992.0		
44.29	28.41	439.5	590.0	.4376	.01540
15.88		715.9	1004.0		

ΔC/ΔP average	$(\epsilon - 1)\times 10^6$ at 77.6°C	C_o μμf
0.01509	4460	257.1

Table XXXIII

Perfluoropropylene

Pressure cm. of Hg	ΔP cm. of Hg	Precision Condenser	Standard Condenser	ΔC $\mu\mu$f	$\Delta C/\Delta P$ $\mu\mu f$/cm.
51.44	40.86	583.8	810.0	0.4006	0.00980
10.58		850.3	1189.0		
51.44	41.96	555.8	769.0	.4302	.01025
9.48		840.8	1176.0		
50.57	41.34	426.6	569.0	.4143	.01002
9.23		685.6	961.0		

$\Delta C/\Delta P$ average	ϵ at 77.5°C	P_m cm^3	P_d cm^3	P_o cm^3	u Debye
0.01002	1.002962	28.41	7.026	20.82	1.11

Table XXXIV

Calibration with Ammonia for Sulfur Tetrafluoride

(1st determination)

Pressure cm. of Hg	ΔP cm. of Hg	Precision Condenser	Standard Condenser	ΔC μμf	$\Delta C/\Delta P$ μμf/cm.
29.95	16.60	512.6	702.0	0.2600	0.01565
13.35		676.2	948.0		
28.20	14.37	524.4	748.0	.2114	.01471
13.83		676.3	948.0		
28.12	15.54	536.8	740.0	.2410	.01551
12.58		689.8	968.0		
30.60	19.05	521.6	716.0	.2843	.01493
11.55		702.0	985.0		
29.13	16.22	539.8	745.0	.2463	.01519
12.91		696.9	978.0		

$\Delta C/\Delta P$ average	$(\epsilon - 1)x10^6$ at 47.0°C	C_0 μμf
0.01520	5260	219.6

Table XXXV

Sulfur Tetrafluoride (1st determination)

Pressure cm. of Hg	ΔP cm. of Hg	Precision Condenser	Standard Condenser	ΔC μμf	ΔC/ΔP μμf/cm.
37.34	25.74	632.3	882.0	0.2389	0.009289
11.60		789.6	1108.0		
37.42	26.10	539.8	745.0	.2357	.009031
11.32		689.9	968.0		
37.65	26.12	537.4	740.0	.2304	.008821
11.53		683.2	958.0		
37.11	25.61	537.4	740.0	.2325	.009078
11.50		683.8	960.0		

ΔC/ΔP average	ϵ at 47.0°C	P_m cm^3	P_d cm^3	P_o cm^3	u Debye
0.009055	1.003134	27.45	11.7	15.75	0.91

Table XXXVI

Calibration with Ammonia for Sulfur Tetrafluoride

(2nd determination)

Pressure cm. of Hg.	ΔP cm. of Hg	Precision Condenser	Standard Condenser	ΔC μμf	ΔC/ΔP μμf/cm.
23.22	11.31	458.5	618.0	0.1702	0.01505
11.91		562.9	779.0		
25.38	14.83	458.3	617.0	.2251	.01517
10.55		597.2	830.0		
26.22	13.60	466.3	630.0	.2029	.01492
12.62		592.4	822.0		

ΔC/ΔP average	$(\epsilon - 1)\times10^6$ at 46.9°C	C_o μμf
0.01505	5263	217.3

Table XXXVII

Sulfur Tetrafluoride (2nd determination)

Pressure cm. of Hg	ΔP cm. of Hg	Precision Condenser	Standard Condenser	ΔC μμf	ΔC/ΔP μμf/cm.
32.39	21.28	508.2	695.0	0.1966	0.009239
11.11		630.6	881.0		
33.28	22.59	504.3	689.0	.2093	.009265
10.69		635.0	887.0		
33.65	21.23	513.8	704.0	.1945	.009162
12.42		636.0	888.0		

ΔC/ΔP average	ϵ at 47.2°C	P_m cm^3	P_d cm^3	P_o cm^3	u Debye
0.009222	1.003229	28.29	11.7	16.59	0.93

* The SF_4 contained about 5% impurity of SOF_2 which has a dipole[4] moment of 1.62D. After applying this correction to the average value of SF_4, the dipole moment of SF_4 was .88D. See page 24.

Table XXXVIII

Moments

COMPOUND	Dipole moment, D	Error, D
Ethyl Acetylene	0.76	±0.1
Vinyl Methyl Ether	1.06	.1
Pentafluoropropionitrile	1.33	.1
2-Trifluoromethylpropene	2.34	.1
Pentafluoropropionyl Chloride	0.99	.1
Methallene	0.44	.1
Perfluoropropylene	1.11	.2
Sulfur Tetrafluoride	0.88	.2

Discussion of Error

The most probable error in the replaceable capacitance can be obtained by differentiating equation (41) thereby obtaining,

$$\frac{dC_o}{C_o} = \frac{d\Delta C}{\Delta C} + \frac{d\epsilon_{NH_3}}{\epsilon_{NH_3} - 1}$$

Since the beat frequency could be determined within about 1 cps, the value of $d\Delta C$ was about 0.001 uuf. $\epsilon - 1$ for ammonia was about 5000×10^{-6} and $d\epsilon$ for ammonia was about 10^{-6}. Then by using the value of ΔC for ammonia, the quantity dC_o was obtained from the above equation. Since the replaceable capacitance was about 210 uuf, the error in determining it was about 7%.

To determine the maximum error in the dielectric constant of the material under investigation, differentiate equation (42); thus,

$$d\epsilon = \frac{d(\Delta C/\Delta P\ 76)}{C_o} + \frac{76\ \Delta C/\Delta P\ dC_o}{C_o^2}$$

Again, using the value of 0.001 for the error in the slope and the error in the replaceable capacitance as obtained above, the error in the measurement of the dielectric constant can be determined.

By differentiating equation(43), the error in the molar polarization is obtained from,

$$\frac{dP_m}{P_m} = \frac{d\epsilon}{\epsilon - 1} + \frac{dV_m}{V_m}$$

Since it was assumed that the gases investigated were behaving ideally, and since this is not really accurate, an error of about 0.1 in V_m was assumed.

Since this method of investigation does not take into account atomic polarization, the error in P_d was assumed to be about 10%. Then, by differentiating equation (44), the error in the orientation polarization was determined by,

$$dP_o = dP_m + dP_d$$

Finally, the error in the dipole moment was determined by differentiating equation (45) to give,

$$\frac{du}{u} = \frac{dP_o}{2P_o} + \frac{dT}{2T}$$

The second term in this equation however was negligible in comparison to the first since the temperature variation amounted to only about 0.1 of a degree.

When this method was applied to the compounds measured in this investigation, the maximum probable error was as follows:

Compound	u	Δu
CF_3CF_2CN	1.33D	± .1D
$CF_3CF{=}CF_2$	1.1D	± .2D
$CF_3-\underset{\underset{CH_3}{|}}{C}{=}CH_2$	2.34D	± .2D
CF_3CF_2CCl	0.99D	± .1D
$CH_3CH_2C{\equiv}CH$	0.76D	± .2D
$CH_3OCH{=}CH_2$	1.06D	± .2D
$CH_3CH{=}C{=}CH_2$	0.44 D	± .4D
SF_4	0.88 D	± .2D

The error involved seems to be quite large; however, the fact that the replaceable capitance was determined in the same manner as was the dielectric constant of the compound under investigation causes the error to be minimized. On this

basis, reporting the error as .1D for all of the compounds except $CF_3CF{=}CF_2$ and SF_4 is reasonable. Due to the fact that SF_4 has such a large atomic polarization, the error involved is about .2D. The perfluoropropylene must also be reported as about .2D since its dipole moment was determined only once.

IV. DISCUSSION

A dipole moment can yield valuable qualitative information about the structure of a molecule. Of special importance are the magnitude and direction of the moment since with this information one can compare a measured moment with the moments of similar compounds and thereby interpret changes in terms of differences in electronic environments. The interpretation can be based on resonance theory or on the classical theory of induced dipoles.

In terms of resonance, each structure can be thought of as contributing to the state of the molecule. Furthermore, structures with formal charges on them may be expected to contribute heavily toward the net moment of the molecule even though these structures may make only a small contribution to the state of the molecule. The particular type of resonance referred to in this investigation is hyperconjugation. This can be described by structures such as,

$$CH_3CH{=}CH_2 \longleftrightarrow \overset{H^+}{CH_2{=}CH{-}\bar{C}H_2}$$

Resonance energies due to hyperconjugation are usually of the order of 3 or 4 kcal/mole as measured from heats of hydrogenation. Hence, the hyperconjugated structure probably makes only a small contribution to the state of the molecule. However, as stated above, this small contribution may give rise to a large dipole moment. This seems to be especially true of molecules containing the CF_3 group. Further evidence of hyperconjugation has to do with the shortening and lengthening of bonds. For example, if propylene can be represented by hyperconjugated structures, one would expect a shortening of the $C(sp^3)$-$C(sp^2)$ bond and a lengthening of the carbon-carbon double bond. Microwave and electron diffraction measurements on bond distances seem to indicate that this is what occurs.

Classically, one might be able to account for variations in dipole moments by inductive effects. This effect may tend to increase or decrease the net dipole moment depending on the type of molecule. For example, consider the molecule CH_3Cl; the chlorine is more electronegative than the carbon atom , and hence the bonding electrons in the C-Cl bond are shifted toward the chlorine atom. This leaves the carbon atom positive relative to the chlorine atom. Hence the carbon atom tends to attract electrons from the hydrogen atoms, and thus a dipole is induced in the direction $\overline{H\text{-}C}$. In a molecule such as CF_3Cl, the fluorines are more electronegative than either the carbon or chlorine atoms. Therefore the bonding electrons in the C-F bond are shifted toward the fluorine atoms thereby leaving carbon positive relative to fluorine. Hence the carbon atom pulls electrons in the C-Cl bond toward itself, thereby inducing a moment in the C-Cl bond, so as to oppose the principal moment in the C-Cl bond. It is rather difficult to calculate an induced moment since the exact location of the electrons in the bond is unknown. However, the magnitudes are usually about 0.1 to 0.2D. From a standpoint of interpretation, the direction of the induced dipole is the important thing.

Nuclei, as well as electrons, can be displaced from their equilibrium positions so as to create an atomic dipole. This is especially true of molecules containing atoms with unshared electron pairs. When an unshared pair occupies an s or p, or any orbital in which the associated center of negative charge is coincident with the positively charged nucleus, an atomic dipole will not occur. Hence, an atomic dipole can exist only if the atomic orbital is a hybrid. The magnitude of such moments could be very large depending on the distance of the unshared pair from the nucleus.

Moments may also arise due to the differences in the electronegativity of carbon atoms in different states of

hybridization. Hence the moments of the $C(sp^3)$-$C(sp^2)$ bond, the $C(sp^3)$-C(sp) bond, and the $C(sp^2)$-C(sp) bonds are not zero. The actual value of these moments are difficult to determine, but the direction would be toward the more electronegative or more unsaturated carbon, (8).

In order to calculate approximate values for the dipole moment so as to make comparison with experimental quantities, one usually assumes that the molecule can be represented by a vector model, the resultant vector being the vector sum of the individual bond vectors or bond moments. The bond moments used to calculate the dipole moments of molecules in this investigation are:

C=O in $Cl_2C=O$	2.7 D
CF in CF_3H	1.2D
CCl in CH_3Cl	1.5D
CN	between 2 and 2.5 D
C-O in $(CH_3)O$	1.5D
C-H	0.4D

The direction of the C-H bond moment was according to (9),

$\overset{+}{C}(sp^3)\text{-}\overset{-}{H}$

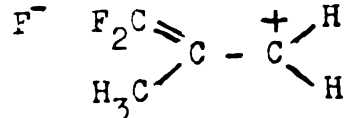
$\overset{-}{C}(sp^2)\text{-}\overset{+}{H}$

$\overset{-}{C}(sp)\text{-}\overset{+}{H}$

2-Trifluoromethylpropene

The dipole moment was measured as 2.33D. The value calculated from bond moments is much less than this figure, about 1.5D. However, a comparison of this compound with other compounds containing the trifluoromethyl group is in good agreement. It is to be noted that compounds with the CF_3 group exhibit very large dipole moments. This is attributed to the extremely high electron withdrawing power of the group. For example, $CF_3CCl{=}CCl_2$ has a dipole moment of 1.28D and $CF_3CF{=}CF_2$ has a dipole moment of 1.1D. Both of these compounds would be expected to have very small dipole moments. The large moments seem to imply that some sort of hyperconjugation of the CF_3 group is occurring.

Since the CF_3 group is extremely electron withdrawing, it would be expected that the sp^2 carbon would be polarized so as to induce a moment in the direction of the trifluoromethyl group. Such an effect could probably be represented by structures such as.

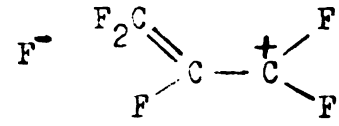


The effect of the methyl group, which might also undergo hyperconjugation, should be to decrease the moment. A comparison with $CF_3CH{=}CH_2$, 2.45D, shows that this is exactly what happens.

Perfluoropropylene

The dipole moment was found to be 1.1D. One would expect a very small moment for this compound by comparison with $CH_3CH{=}CH_2$, 0.35D, and $CCl_3CCl{=}CCl_2$, 0.4D. Evidently, the

type of hyperconjugation previously described for 2-trifluoromethylpropene is also significant in this compound. Hence, structures such as the following may account for the large large moment observed:



Pentafluoropropionitrile

The dipole moment was found to be 1.33D. It is difficult to calculate the dipole moment of this compound since no suitable bond moment for the C≡N bond is availible. That is, the value varies with the environment of the cyanide group. For example, in HCN the bond moment would be about 2.5D; in CH_3CN the value would be about 3.5D. This is due to the fact that the overall moment of these compounds is due to resonance structures of the type,

$$HCN \leftrightarrow H\text{-}\overset{+}{C}\text{=}\overset{-}{N} \leftrightarrow H^{+}\,CN^{-} \qquad H^{+}$$

$$CH_3CN \leftrightarrow CH_3\overset{+}{C}\text{=}N^{-} \leftrightarrow CH_3^{+}\,CN^{-} \leftrightarrow CH_2\text{=}\,C\text{=}N^{-}$$

Clearly, the hyperconjugated structure in CH_3CN would have no analog in CF_3CF_2CN due to the large electronegativity of F, and therefore there would be no justification for using the value 3.5D for the bond moment of CN. Similarly, the ionic structure in HCN has no analog in CF_3CF_2CN. On this basis, it is not expected that the CN bond moment will make such a large contribution to the moment of CF_3CF_2CN. The CN moment will then be due to a resonance structure such as,

$$CF_3CF_2\overset{+}{C} = N^{-}$$

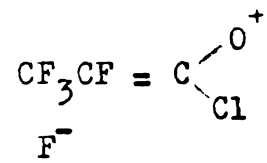
However, due to the large electron withdrawing power of the CF_3CF_2 group, structures such as,

$$CF_3CF = C = \overset{+}{N}$$
$$F^{-}$$

will also contribute heavily toward the overall moment. The direction of the resultant moment would probably still be toward the cyanide group.

Pentafluoropropionyl Chloride

The dipole moment was measured as 0.99D. The calculated value, based on the bond moment of C = O in phosgene and the bond moment of C-Cl in CH_3Cl, was about 1.35D. The lowering is accounted for by the large electron withdrawing power of the CF_3CF_2 group. The sp^2 carbon will be polarized by the CF_3CF_2 group so as to induce a moment in the direction of this group. In terms of hyperconjugation, this effect can be represented by structures such as,

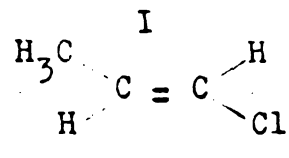


Methallene

The observed moment for methallene in this investigation was 0.44D. This value agrees extremely well with the value 0.401D determined by microwave spectroscopy (10). The value calculated on the basis of bond moments is about 0.8D with the resultant vector toward the methyl group. However, this value does not take into consideration a dipole contribution from hyperconjugation.

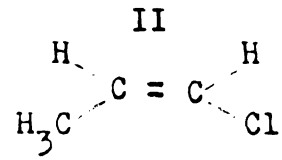
By examining the direction of the moment in the following two compounds, it can be shown that the direction of the

moment in methallene is toward the sp^2 carbon rather than toward the methyl group;



I

$u_{exp.} = 1.97D$



II

$u_{exp.} = 1.71D$

If the direction of the CH_3-C moment was toward the sp^3 carbon, compound II would be expected to have the larger dipole moment; experimentally, compound I has the larger moment. This indicates that the CH_3-C moment is in the direction of the sp^2 carbon. This also implies that hyperconjugation of the type,

$$CH_2 = CH - \bar{C} = CH_2$$
$$H^+$$

is occurring.

Evidence for hyperconjugation in methallene is supported to some extent by the shortening of the $C(sp^3)$-$C(sp^2)$ bond length by about .06A (10). Furthermore, compounds of this type exhibit resonance energies of several kilocalories per mole as obtained from heats of hydrogenation data.

Ethyl Acetylene

The dipole moment of ethyl acetylene was determined as 0.76D. This agrees well with the value previously determined, 0.80D (11) by a heterodyne-beat method. The value calculated on the basis of bond moments is about .8D in the direction of the ethyl group. Not included in the calculation is a polar contribution due to hyperconjugation. Such a contribution can be represented by structures such as,

$$CH_3CH = C = \bar{C}H$$
$$H^+$$

The hyperconjugation would be of sufficient magnitude to give a resultant moment in the direction of the acetylenic carbon.

Vinyl Methyl Ether

The dipole moment of vinyl methyl ether was determined to be 1.06D. The value calculated on the basis of bond moments is about 1.8D. A comparison of methyl ether, 1.29D, and vinyl ether, 1.06D suggests that the moment of vinyl ether is lowered relative to methyl ether by structures such as (12),

$$CH_2= CH-\overset{+}{O}=CH-\bar{C}H_2$$

Similarly, one would expect the moment of vinyl methyl ether to be decreased by structures such as,

$$CH_3-\overset{+}{O}=CH-\bar{C}H_2$$

Hence, a consideration of resonance would tend to lower the calculated value to some extent therby making the experimental value of 1.06 quite reasonable.

The resonance effect can be supported to some extent by heats of hydrogenation data (13) of similar compounds. The resonance energies obtained by this method for vinyl ether and ethyl vinyl ether are 3.4 and 3.6 kcal/mole respectively.

Sulfur Tetrafluoride

The dipole moment obtained in this investigation was 0.88D. This compares fairly well with the value of 1D obtained by another heterodyne-beat method (14). However, the value has been determined quite accurately by a microwave technique as 0.64D (15). The rather large difference between 0.85D and 0.64D is indicative of a large atomic polarization which was not taken into account in the present work.

The fact that SF_4 has a dipole moment immediately rules out structures utilizing hybrid orbitals which give planar and tetrahedral arrangements since they would have dipole moments of zero. The NMR spectrum of SF_4 shows two peaks with a chemical shift of 1920 cps, each peak being split into a triplet of equal intensity (16). Hence, two pairs of chemically different fluorines are indicated. This would be consistent with a trigonal bipyramid with the unshared pair in an equatorial position. The fact that the molecule has a dipole moment supports this structure.

The hybridization would probably be sp^3d with the unshared pair occupying a hybrid orbital. Hence the unshared pair would give rise to an atomic dipole which would contribute to the net moment of the molecule. This, too, is to be expected since the net moment is comparatively small, and since the large electronegativity difference of S-F, 1.5, indicates a rather large moment for the S-F bond.

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