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[Index of Refraction of Methane in the Infra-Red and the Dipole Moment of the CH Bond

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The index of refraction of methane has been measured for 49 different wave-lengths in the infra-red between 1 and 15μ. These data have been interpreted in terms of the active infra-red frequencies of methane, and yield what may be considered estimates of the dipole moment of the CH bond and the rate of change of this moment with CH distance. The measurements show that the infra-red bands are only about one-sixth as strong as would be necessary to remove the discrepancy between $n_\infty - 1$ as obtained from indices of refraction measured at optical wave-lengths and extrapolated to infinite wave-length, and $\epsilon - 1$ as determined from dielectric constant measurements.

THE need for quantitative information on the intensities of infra-red bands of molecular gases has frequently been pointed out. Van Vleck[1] has called attention to the fact that such data would permit quantitative calculation of the contribution of "atomic polarization" to the dielectric constant, thus furnishing a check on dielectric constant measurements and increasing the accuracy of measurements of dipole moments. Dennison[2] and Mulliken[3] have used intensity measurements to calculate "effective charges" of the vibratng molecules (or the rate of change of the dipole moment with internuclear distance) and have pointed out the need for more quantitative data. This paper contains essentially the same information as would be obtained from accurate measurements of the intensities of the infra-red bands of methane. Since the reasons for measuring the refractive index instead of the intensity of absorption have already been pointed out by Van Vleck,[1] and have been fully explained in a previous communication,[4] they will not be repeated here.

The method consists in measuring the change in deviation produced by a change in pressure in a hollow prism containing the gas being studied. The apparatus used was essentially similar to that used for the measurements on HCl,[4] except for the thermopile. The thermopile, mounted on a comparator carriage, is used to locate the image. A new design of thermopile increased the speed of taking observations by a factor of about ten and decreased the uncertainty of measurements by a factor of six.

The new thermopile has two receivers, each 10 mm by 1 mm, mounted side by side, with the edges slightly overlapping but not in contact. Each receiver is mounted on a two-junction pile and the two piles are connected in opposition. Fig. 1 shows a typical curve of galvanometer deflection against position as this thermopile is moved across a slit image. In practice it was necessary to take only four or five points along the straight center portions of the curve, and the two zeros, in order to determine the image position. In the high energy regions of the spectrum, successive determinations of the image position would check to within 0.3 micron. For all the wave-lengths less than 11μ, variations of more than 2 microns were rare. The thermopile case was so constructed that thermal drift was eliminated, and since the thermopile was of the compensated type and the two compensating piles were almost identical, deflections due to electrical surges induced in the galvanometer-thermopile circuit by sparks in neighboring rooms were reduced to a minimum. A Kipp and Zonen type Z C galvanometer was used for all the measurements. When necessary, the deflections were magnified by a thermal relay. With this arrangement, when working at night, it was possible to reach the limit set by Brownian motion of the primary galvanometer.

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[1] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford, 1932), Chapter 3.

[2] D. M. Dennison, Phil. Mag. **1**, 216 (1926); Astrophys. J. **62**, 84 (1925).

[3] R. S. Mulliken, J. Chem. Phys. **2**, 400; **2**, 712 (1934).

[4] R. Rollefson and A. H. Rollefson, Phys. Rev. **48**, 779 (1935).

The methane for most of the measurements was obtained by heating sodium acetate and soda lime. The gas thus obtained was purified by repeated distillations in an all-glass system. The gas was generated several times and the agreement of the refraction measurements on the different samples indicated that the gas was sufficiently pure. However, since the absolute values of the indices of refraction which were obtained did not agree with the value obtained by extrapolating data available for wave-lengths in the visible region of the spectrum, several additional checks were made. Since the same apparatus had been used for measurements on HCl and CO, gases which are easily obtained in high purity and which had given results in close agreement (better than $\frac{1}{4}$ percent) with those obtained by extrapolating the data of Cuthbertson and Cuthbertson, it was decided that the most likely source of error in the measurements on methane was impurity of the gas. The vapor pressure of the methane was then measured at the boiling point of oxygen. The value obtained fitted on the vapor pressure curve as well as those tabulated in the *International Critical Tables*. This indicated that no volatile impurities, such as hydrogen, carbon monoxide, or air, could be present in sufficient quantity to cause a noticeable change of index of refraction. Then varying fractions of the methane condensed in the liquid-air trap were distilled into the hollow prism and the index of refraction measured for each fraction. No change in the index reduced to standard conditions was noted. This indicated that if any impurity were present it must have a vapor pressure curve almost identical with that of methane, or an index of refraction nearly equal to that of methane. An additional check on the less volatile impurities was furnished by the infra-red absorption spectrum of the gas used. Absorption measurements were customarily made throughout the spectrum in order to determine for which wave-lengths there was appreciable absorption, and therefore where measurements of the index of refraction could not be made by the prism method. No bands other than those belonging to methane were observed. It must be pointed out, however, that this constitutes merely corroborative evidence and not conclusive proof of purity, since the resolving power which was used was not high and some of the organic impurities which may have been present have their strongest bands in the same regions as those of methane.

When preliminary efforts at interpretation indicated that the data were not consistent with measurements in the visible, new runs were made for which the methane was generated by a slightly modified Grignard process. Both this process and the chemicals used in it were entirely different from the sodium acetate-soda lime process. The results of the new runs agreed with the old to within 0.5×10^{-6} for the absolute value of n, and so far as shape was concerned the new curves were indistinguishable from the old. Shortly thereafter new measurements[5] on the index of refraction of methane in the visible and ultraviolet appeared. These new values for n gave a dispersion curve which when extrapolated into the infra-red gave values much closer to those we obtained, although the disagreement was still 4×10^{-6}, or about 1 percent in the absolute value of $n-1$. The slope of the new extrapolated curve allowed a much more satisfactory

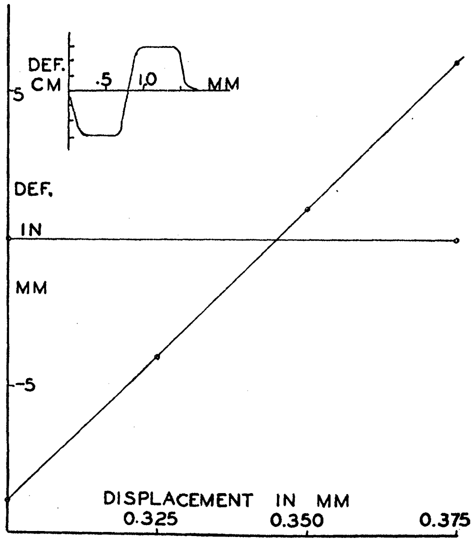

FIG. 1. Galvanometer deflection as a function of thermopile position. The upper diagram is an approximate curve for a large total displacement, while the lower curve is one actually obtained in the measurements on methane. With points as good as these, the position for zero deflection can be determined to 1μ or better if the comparator screw is reliable.

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[5] S. Friberg, Diss. Lund. (1933) quoted by T. Larsen, Zeits. f. Physik **105**, 166 (1937).

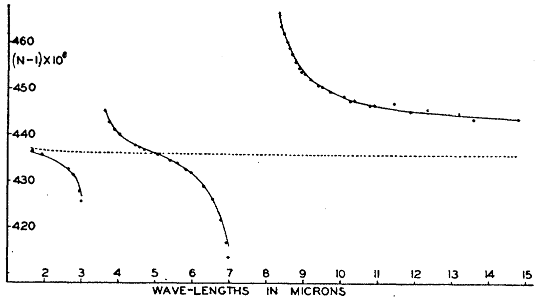

FIG. 2. Dispersion of methane. The solid curve is that given by theory; the points are averaged experimental results; the dotted curve is $(n-1)$ extrapolated.

interpretation of our results than the old. Even if the 1 percent difference which remains were due entirely to systematic error in the present experiments or impurity of the gas used, it would be of little importance in the interpretation of the results, since the changes of index which are important probably cannot be measured to within one percent. Any impurity which had active frequencies in the infra-red would of course cause trouble but would probably have been detected by its absorption.

The effect of purity of spectrum was tested by trying several different slit widths in the monochromator and gas spectrometer. The trials showed that changing slit widths over the range actually used had no effect. The values of the index of refraction which were obtained were reduced to standard conditions (0°, 760 mm) by means of coefficient of expansion and pv data given in the *International Critical Tables.* ($\alpha = 0.003683$; the pv correction was at most about $\frac{1}{4}$ percent.)

RESULTS

The index of refraction of methane was measured at 49 different wave-lengths between 1.6 and 14.8μ. The values of the index for the various wave-lengths are given in Table I and plotted in Fig. 2. The values given are averages for several runs. In taking these averages, runs which did not cover the whole range of wave-lengths used were adjusted to agree in absolute value with the average of the runs which included all wave-lengths; that is, the whole curve was shifted up or down a definite amount. This was obviously necessary in order to avoid spurious kinks in the dispersion curve which would be due only to the fact that certain regions of the spectrum were more thoroughly investigated than others. The largest shift was 1.1×10^{-6} in n, and most of the curves were not shifted at all.

The contribution of the overtone bands in the neighborhood of 2.3μ is small but easily noticeable. The measurements in this region cannot, however, yield quantitative values of the intensities of the overtones. Two bands overlap in this region, and in order to get estimates of their separate contributions to the index of refraction, measurements would have to be taken in regions very near the band center where there is appreciable absorption. Such measurements would not be reliable if obtained by the prism method, since unsymmetrical absorption of the slit image causes an apparent shift of the image. Since measurements in this wave-length region are not quantitative, they are not included in Table I or Fig. 2.

The only other measurements on the dispersion of methane in the infra-red which have come to the writers' attention are those of Koch[6] who used an interferometer and residual rays of wave-lengths 6.557μ and 8.678μ; that is, wave-lengths on each side of the 7.7μ band. His values for $(n-1) \times 10^6$ were 419.20 and 450.06, respectively, for the above two wave-lengths, while those obtained in the present work were 426.35 and 458.10. The quantity which is of most importance for the interpretation of the results is the difference between the values obtained for the two wave-lengths. For this difference Koch obtains 30.86 while we obtain 31.75. This must be considered satisfactory agreement, since we differ by 1.7 percent in the same direction on the absolute values.

INTERPRETATION OF RESULTS

The contribution of an infra-red band to the square of the index of refraction is given by $\Delta_i(n^2-1) = K_i/(\nu_i^2 - \nu^2)$ where ν_i is the resonance frequency, ν the frequency of the light used, and the K_i are constants. $\Delta(n-1)$ due to the infra-red bands was obtained by subtracting the experimental values of n from the values obtained by extrapolating into the infra-red the measure-

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[6] J. Koch, Nova Acta Soc. Upsala, 2, No. 5 (1909).

ments made by Friberg[5] in the visible and ultraviolet. The values of the K_i for the two active bands were adjusted by successive approximations until each K_i remained constant throughout the spectrum. In this adjustment the extrapolated curve was adjusted vertically to give the same value of K on both sides of a band, the assumption being that the visible and ultraviolet data gave the slope of the curve more accurately than the absolute value.

The final results are given in Table I. The average value of K_3 for the band for which $\nu_3=3019.6$ cm was 16.50. The average value of K_4 for the band $\nu_4=1304$ cm was 7.50. For the computation of these averages the various values are weighted according to the magnitude of $\Delta(n-1)$, and values beyond 11μ are not used since the energy available in this region is very small and the points consequently scatter rather badly compared with other regions of the spectrum. The values for some wave-lengths very near the absorption bands (those in parenthesis)

TABLE I. *Index of refraction of methane. Here* $(n-1)_{exp}$ *is the average experimental value of* $n-1$ *where* n *is the index of refraction;* $(n-1)_{ext}$ *is the value obtained by extrapolation of the data of Friberg;* Δ_3 *and* Δ_4 *are the contributions of* ν_3 *and* ν_4 *to the index of refraction, as determined experimentally.*

WAVE-LENGTHS IN MICRONS	$(n-1)_{\text{EXP}}\times10^6$	$(n-1)_{\text{EXT}}\times10^6$	$\Delta(n-1)\times10^6$	$\Delta_3\cdot(\nu_3^2-\nu^2)$	$\Delta_4\cdot(\nu_4^2-\nu^2)$	$(n-1)_{\text{CALC}}\times10^6$
1.680	436.50	437.07	0.57	9.21		436.22
1.940	435.70	436.74	1.04	12.91		435.49
2.670	432.70	436.40	3.70	15.16		432.43
2.790	431.50	436.35	4.85	15.58		431.25
2.960	427.80	436.30	8.50	17.72		428.34
3.000	425.85	436.30	10.45	(19.22)		427.22
3.640	445.25	436.17	9.08	16.29	8.24	445.38
3.750	442.80	436.15	6.65	16.11	8.54	442.99
3.900	441.10	436.12	4.98	16.59	7.36	441.07
4.040	440.10	436.11	3.99	17.03	6.72	439.92
4.450	437.80	436.08	1.72	16.10	7.84	437.90
4.570	437.30	436.07	1.23	15.85	7.96	437.45
4.700	436.80	436.06	0.74	15.55	8.09	437.01
5.060	435.80	436.04	0.24	16.46	7.52	435.81
5.400	434.55	436.02	1.47	16.32	7.56	434.58
5.600	434.00	436.02	2.02	17.90	7.15	433.76
5.840	432.60	436.01	3.41	16.57	7.48	432.59
5.980	432.05	436.00	3.95	18.27	7.19	431.77
6.330	429.05	435.99	6.94	16.43	7.51	429.06
6.560	426.30	435.98	9.68	16.00	7.54	426.38
6.790	421.8	435.98	14.18		(7.78)	422.40
6.940	416.8	435.97	19.17		(8.00)	418.21
7.000	413.6	435.97	22.37		(8.45)	416.39
8.36	466.5	435.9	30.6		7.67	465.9
8.42	463.6	435.9	27.7		7.40	464.0
8.48	462.0	435.9	26.1		7.44	462.2
8.57	460.3	435.9	24.4		7.54	460.2
8.63	459.0	435.9	23.1		7.50	459.0
8.70	457.7	435.9	21.8		7.48	457.7
8.80	456.0	435.9	20.1		7.36	456.3
8.89	454.7	435.9	18.8		7.25	455.3
8.95	453.8	435.9	17.9		7.14	454.6
9.05	453.4	435.9	17.5		7.38	453.7
9.20	452.2	435.9	16.3		7.36	452.5
9.41	450.9	435.9	15.0		7.35	451.2
9.52	450.6	435.9	14.7		7.52	450.6
9.73	449.6	435.9	13.7		7.52	449.6
10.11	448.6	435.9	12.7		7.72	448.3
10.28	447.6	435.9	11.7		7.30	447.9
10.38	447.7	435.9	11.8		7.56	447.6
10.80	446.5	435.9	10.6		7.24	446.8
10.94	446.7	435.9	10.8		7.60	446.6
11.46	447.1	435.9	11.2		(8.61)	445.9
11.89	445.3	435.9	9.4		(7.33)	445.5
12.36	445.8	435.9	9.9		(8.35)	445.0
13.20	445.0	435.9	9.1		(8.10)	444.5
13.60	443.7	435.9	7.8		(6.84)	444.3
14.00	448.4	435.9	12.5		(12.61)	444.1
14.8	443.8	435.9	7.9		(7.46)	443.8

are also left out in computing the weighted average, since in these regions the spread of the band due to rotation begins to have an appreciable effect. It may be noticed in Fig. 2 that near the bands the theoretical curve lies nearer to the extrapolated curve than the experimental points. Inclusion of all the points would change the averages by only about 1 percent. The agreement on the high frequency side of ν_3 is not very good, but it must be remembered that in this region the dispersion of the monochromator is at a minimum and that there are difficulties due to two overtone bands of methane and the absorption bands due to CO_2 and H_2O in the atmosphere.

In order to get a picture of what might be occurring in the methane molecule during vibration, a calculation was made to see how much charge would have to be placed on each of the hydrogen atoms (with, of course, four times as much on the carbon) in order to produce the observed effect on the index of refraction. The coordinates chosen for the calculation (shown in Fig. 3) were those given by Dennison and Johnston[7] except that the x, y, and z were reversed in direction. The expressions for the kinetic and potential energies were taken from Dennison and Johnston's paper and are

$$T=\tfrac{1}{2}\{\mu(\dot{x}^2+\dot{y}^2+\dot{z}^2)+(5m/8)(\dot{q}_1^2+\dot{q}_2^2+\dot{q}_3^2+\dot{q}_4^2+\dot{q}_5^2+\dot{q}_6^2)-2(m/8)(\dot{q}_1\dot{q}_3+\dot{q}_1\dot{q}_4+\dot{q}_1\dot{q}_5+\dot{q}_1\dot{q}_6+\dot{q}_2\dot{q}_3$$
$$+\dot{q}_2\dot{q}_4+\dot{q}_2\dot{q}_5+\dot{q}_2\dot{q}_6+\dot{q}_3\dot{q}_5+\dot{q}_3\dot{q}_6+\dot{q}_4\dot{q}_5+\dot{q}_4\dot{q}_6)+2(m/8)(\dot{q}_1\dot{q}_2+\dot{q}_3\dot{q}_4+\dot{q}_5\dot{q}_6)\},$$

where $\mu=4mM/(4m+M)$ and m and M are the masses of the hydrogen and carbon particles, respectively;

$$V=\tfrac{1}{2}\{a(x^2+y^2+z^2)+b(q_1^2+q_2^2+q_3^2+q_4^2+q_5^2+q_6^2)+2c(q_1q_3+q_1q_4+q_1q_5+q_1q_6+q_2q_3+q_2q_4+q_2q_5$$
$$+q_2q_6+q_3q_5+q_3q_6+q_4q_5+q_4q_6)+2d(q_1q_2+q_3q_4+q_5q_6)+2e[x(q_1-q_2)+y(q_3-q_4)+z(q_5-q_6)]\}.$$

If we let ε be the charge on each hydrogen atom, the potential energy due to an electric field $\mathcal{E}$ parallel to the x axis is $4\varepsilon\mathcal{E}x$. The Lagrange equations which involve x are then

$$\mu\ddot{x}+ax+e(q_1-q_2)=4\varepsilon\mathcal{E}, \tag{1}$$

$$(5m/8)\ddot{q}_1-(m/8)(\ddot{q}_3+\ddot{q}_4+\ddot{q}_5+\ddot{q}_6)+(m/8)\ddot{q}_2+bq_1+c(q_3+q_4+q_5+q_6)+dq_2+ex=0, \tag{2}$$

$$(5m/8)\ddot{q}_2-(m/8)(\ddot{q}_3+\ddot{q}_4+\ddot{q}_5+\ddot{q}_6)+(m/8)\ddot{q}_1+bq_2+c(q_3+q_4+q_5+q_6)+dq_1-ex=0. \tag{3}$$

The remaining equations, those involving y and z, will be of the same form as (1), (2), and (3), except that $\mathcal{E}_y=\mathcal{E}_z=0$, and will clearly be satisfied by $q_3=q_4=q_5=q_6=y=z=0$, $q_1+q_2=0$. Subtracting (3) from (2) we obtain

$$(5m/8)(\ddot{q}_1-\ddot{q}_2)-(m/8)(\ddot{q}_1-\ddot{q}_2)+b(q_1-q_2)-d(q_1-q_2)+2ex=0. \tag{4}$$

If the q_i are of the form $A\cos\omega t$, $\ddot{q}=-\omega^2 q$. If the applied field is given by $\mathcal{E}=\mathcal{E}_0\cos\omega t$ the polarization per molecule due to the forced vibrations may then be obtained by solving

$$\begin{aligned}(-\mu\omega^2+a)x-e(q_1-q_2)&=4\varepsilon\mathcal{E},\\ 2ex+[(-m/2)\omega^2+b-d](q_1-q_2)&=0.\end{aligned} \tag{5}$$

This gives for the polarization per molecule p

$$p=4\varepsilon x=\frac{(4\varepsilon)^2\mathcal{E}(-m/2)\omega^2+b-d}{(-\mu\omega^2+a)[(-m/2)\omega^2+b-d]-2e^2}. \tag{6}$$

Since it is more convenient to have the polarization expressed in terms of the resonance frequencies, Eq. (6) can be transformed as follows:

Let λ_3, λ_4 be the two values of ω^2 corresponding to the natural periods of (5). One has then

$$(m\mu/2)(\omega^2-\lambda_3)(\omega^2-\lambda_4)$$
$$=(-\mu\omega^2+a)[(-m/2)\omega^2+b-d]-2e^2,$$

so that

$$\lambda_3+\lambda_4=(2/m\mu)[\mu(b-d)+(m/2)a]$$
$$=2(b-d)/m+a/\mu,$$
$$\lambda_3\lambda_4=(2/m\mu)[a(b-d)-2e^2].$$

From the first of these:

$$2(b-d)/m=\lambda_3+\lambda_4-a/\mu. \tag{7}$$

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[7] M. Johnston and D. M. Dennison, Phys. Rev. **48**, 879 (1935).

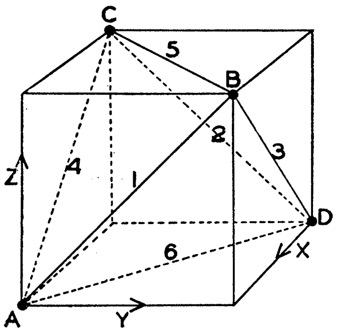

FIG. 3. Equilibrium coordinates for methane. The hydrogens are on corners a, b, c, d. The carbon is at the center of the cube and x, y, and z give the displacements of the carbon with respect to the center of gravity of the hydrogens. The $q_1 \cdots q_6$ give the increases in length of edges $1 \cdots 6$.

According to (6):

$$4\varepsilon x = \frac{16\varepsilon^2\mathcal{E}}{\mu}\,\frac{-\omega^2+(2/m)(b-d)}{(\omega^2-\lambda_3)(\omega^2-\lambda_4)}.$$

Substituting from (7) one obtains

$$4\varepsilon x = \frac{16\varepsilon^2\mathcal{E}}{\mu}\,\frac{\omega^2+\lambda_3+\lambda_4-a/\mu}{(\omega^2-\lambda_3)(\omega^2-\lambda_4)}$$

$$= \frac{16\varepsilon^2\mathcal{E}}{\mu}\left[\frac{(\lambda_4-a/\mu)/(\lambda_3-\lambda_4)}{\omega^2-\lambda_3} + \frac{(\lambda_3-a/\mu)/(\lambda_4-\lambda_3)}{\omega^2-\lambda_4}\right]. \quad (8)$$

Then if N is the number of molecules per cc

$$\Delta(n^2-1) = \frac{4\pi Np}{\mathcal{E}} = 4\pi N\frac{16\varepsilon^2}{\mu}\left[\frac{(\lambda_4-a/\mu)/(\lambda_3-\lambda_4)}{\omega^2-\lambda_3} + \frac{(\lambda_3-a/\mu)/(\lambda_4-\lambda_3)}{\omega^2-\lambda_4}\right]. \quad (9)$$

where the first term gives the contribution of ν_3, the resonance frequency corresponding to λ_3, and the second term gives the contribution of ν_4. Since the oscillator is isotropic the result is unchanged when averaged over all directions of polarization of the incident light and all orientations of the molecule. The above calculation has been made according to classical theory on the assumption that the carbon and the hydrogens carry fixed "effective charges." Comparison with experiment indicates that this hypothesis is too simple, and that the two active normal modes of vibration must have different ε's. Eq. (9) may then be rewritten

$$\Delta_3(n^2-1) = \frac{(16N\varepsilon_3^2/\pi\mu)(\lambda_4-a/\mu)/(\lambda_3-\lambda_4)}{\nu^2-\nu_3^2} = \frac{-K_3}{\nu^2-\nu_3^2}$$

and

$$\Delta_4(n^2-1) = \frac{(16N\varepsilon_4^2/\pi\mu)(\lambda_3-a/\mu)/(\lambda_3-\lambda_4)}{\nu^2-\nu_4^2} = \frac{-K_4}{\nu^2-\nu_4^2}.$$

where $(2\pi\nu)^2$ has been substituted for ω^2, $(2\pi\nu_3)^2$ for λ_3, $(2\pi\nu_4)^2$ for λ_4, and K_3, K_4, $\Delta_3(n^2-1)$ and $\Delta_4(n^2-1)$ have the same significance as when previously introduced in the interpretation of the data. It will be noted that a is the only potential constant which appears in the above expressions. This is reasonable since it is the constant connected with the displacement of the carbon away from the center of gravity of the hydrogens, which displacement can be expected to produce electrical dissymmetry in the molecule. It will be noticed that if e, the constant giving the coupling between x and q_1 and q_2, is set equal to zero, Δ_3 will reduce to the result for a simple oscillator of mass μ and charge 4ε and force constant a, while Δ_4 will be zero.

The above expressions were used to calculate the values of ε for the two active modes of vibration. In this calculation the following numerical constants were used: $\mu = 5.03\times10^{-24}$ gram; $a = 7.670\times10^5$ dynes/cm (Dennison and Johnston); $m = 1.67\times10^{-24}$ gram; $\lambda_3 = 32.4\times10^{28}$; $\lambda_4 = 6.04\times10^{28}$; $\nu_3 = 9.05\times10^{13}$ vib./sec.; $\nu_4 = 3.915\times10^{13}$ vib./sec.; c = velocity of light $= 3\times10^{10}$ cm/sec.; $N = 2.69\times10^{19}$ molecules/cc under standard conditions; and $e = 4.80\times10^{-10}$ e.s.u. = electronic charge. From this calculation we obtained for ε_3, the charge required on each H atom for the vibration ν_3, 0.562×10^{-10} e.s.u. or 0.117 e where e is the electronic charge. For ε_4 we obtain 0.277×10^{-10} e.s.u. or 0.0578 e. These results should not, of course, be interpreted as meaning that the H atoms in methane actually carry a charge of 0.562×10^{-10} e.s.u. for one mode

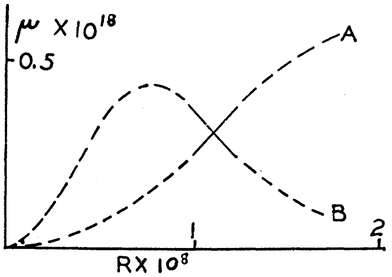

FIG. 4. Change of the dipole moment of the CH group as a function of CH distance. Curves *a* and *b* give two possibilities; the experiments yield only the value of μ and its derivative at the equilibrium position.

of vibration and 0.277×10^{-10} for the other. They merely mean that if that were the case the observed values of the index of refraction would be obtained. It is highly probable that the charge on the H atoms is not constant during a vibration. The refraction measurements which we have made cannot distinguish between the various ways in which the dipole moment of the molecule can vary during a vibration.

In order to gain further insight into what may actually be happening in the methane molecule, it is interesting to examine in closer detail the actual motions of the nuclei for each of the two active frequencies ν_3 and ν_4. For this calculation it is desirable to know the coefficients involved in the transformation to normal coordinates, and these are given in the appendix. A semi-classical calculation, which involves setting the potential energy at maximum displacement equal to $h\nu$ gives the following results: For ν_3, if only the one of the 3 equal frequency modes which involves displacement of the C in the X direction is excited, the carbon moves 0.0402×10^{-8} cm in the X direction with respect to the center of gravity of the hydrogens, q_1 decreases by 0.0906×10^{-8} cm, and q_2 increases by 0.0906A. Expressed in another way, the CH distance varies between the limits 1.045A and 1.17A while the angle between the CH bonds changes only from 109°0′ to 110°4′ or each CH bond vibrates only about $\frac{1}{2}$° on each side of its equilibrium position. For ν_4 the C moves 0.751A in the $+X$ direction while q_1 increases by 0.962A and q_2 decreases by 0.962A. In more pictorial language, the CH bond vibrates between 100°14′ and 118°42′ or 9° on each side of its equilibrium position, while the CH distance changes from 1.107A to 1.118A or only about 0.005A on each side of equilibrium.

One interesting possible interpretation then presents itself. In the vibration corresponding to ν_4 the charges on the hydrogens may remain nearly constant since the CH distance remains so nearly constant and the hydrogens are so far apart. (This, of course, neglects any directional effect of the carbon on the distribution of charge.) The ε_4 above then may be interpreted as actually the charge on the hydrogen and the electric moment of the CH bond may be computed. Since the equilibrium distance between the C and the H is 1.11A, the moment of the bond is $1.11\times10^{-8}\times0.277\times10^{-10}$ or 0.307×10^{-18}. This will of course be equal to the dipole moment of the CH_3 group in methane. For ν_3, since the angles remain so nearly constant, ε_3 may be interpreted as the rate of change of the dipole moment of the CH bond with respect to the CH distance. If this interpretation is correct, the dipole moment of the CH bond may vary with CH distance somewhat as shown in Fig. 4. In this connection it is interesting to note that from measurements of the intensity of absorption in overtone bands of several halogen derivatives of hydrocarbons, Timm and Mecke[8] estimate the moment of the CH bond to be between 0.3×10^{-18} and 0.4×10^{-18} e.s.u.

One further point which must be mentioned is the extrapolation to infinite wave-length, where n_∞^2-1 should be equal to $\epsilon-1$. If we take 435.9×10^{-6} as $n_\infty-1$ from measurements in the visible and ultraviolet regions of the spectrum and add 1.81×10^{-6} and 4.41×10^{-6} as the contributions of ν_3 and ν_4, we obtain $n_\infty-1=442.1\times10^{-6}$ and $n_\infty^2-1=884.4\times10^{-6}$. Sanger ob-

TABLE A. *Coefficients for transformation to normal coordinates for methane.*

	ξ_1	ξ_2	ξ_3	ξ_4
q_1	$(2/3m)^{\frac{1}{2}}$	a	D_1	E_1
q_2	$(2/3m)^{\frac{1}{2}}$	a	$-D_1$	$-E_1$
q_3	$(2/3m)^{\frac{1}{2}}$	$b-a$	D_2	E_2
q_4	$(2/3m)^{\frac{1}{2}}$	$b-a$	$-D_2$	$-E_2$
q_5	$(2/3m)^{\frac{1}{2}}$	$-b$	D_3	E_3
q_6	$(2/3m)^{\frac{1}{2}}$	$-b$	$-D_3$	$-E_3$
x	0	0	$2D_1e/(\mu\lambda_3-a)$	$2E_1e/(\mu\lambda_4-a)$
y	0	0	$2D_2e/(\mu\lambda_3-a)$	$2E_2e/(\mu\lambda_4-a)$
z	0	0	$2D_3e/(\mu\lambda_3-a)$	$2E_3e/(\mu\lambda_4-a)$

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[8] B. Timm and R. Mecke, Zeits. f. Physik **98**, 363 (1936).

tained 960×10^{-6} for $\epsilon-1$. The contribution of the infra-red bands thus reduces the discrpeancy between n_∞^2-1 optical and $\epsilon-1$ by only about 12.4×10^{-6} or 16 percent of the difference. The agreement between various determinations of $n_\infty-1$ makes it extremely improbable that changes in its value can reduce the discrepancy by more than 10 percent. The remainder must then be due to error in measurements of ϵ.

It is a pleasure to acknowledge the help received from Professor G. Breit in the interpretation of the results, and to thank the Wisconsin Alumni Research Foundation for a grant in aid.

APPENDIX

Table A gives the coefficients for the transformation to normal coordinates for methane. The $D_{1,2,3}$, $E_{1,2,3}$, a and b are constants which enter because of the degeneracy of the corresponding modes of vibration.

If T is to have the form

$$T=\tfrac{1}{2}(\dot{\xi}_1^2+\dot{\xi}_2^2+\dot{\xi}_3^2+\dot{\xi}_4^2)$$

there are the following restrictions on the constants:

$$a^2+b^2-ab=\tfrac{1}{4}m,$$

$$D_1^2+D_2^2+D_3^2=\left[\left(\frac{2e}{\mu\lambda_3-a}\right)^2\mu+m\right]^{-1},$$

$$E_1^2+E_2^2+E_3^2=\left[\left(\frac{2e}{\mu\lambda_4-a}\right)^2\mu+m\right]^{-1}.$$

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The Diffraction of Radio Ranges by Hills

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The scattering of electromagnetic waves by hemispherical obstacles on a conducting plane has been investigated. The results have been applied to the problem of the splitting of radio range beacons when the range passes over hilly country. The calculations refer particularly to long wavelengths (about 1000 meters) such as used in the Oakland range. It is found that even hills of moderate size can cause wide spatial fluctuations in the received signal strength. The results of numerical calculation for one simple model of the terrain are reported. The beam is found to split into several parallel courses, giving a pattern of the same type as is observed in the field. It is concluded that this phenomenon is a typical diffraction effect.

IN the standard system of radio ranges for the guidance of aircraft the radiating antenna array sends out two separate signals on the same frequency. One signal, modulated with the code letter *N* (—·) is strong in two opposite quadrants; the other, modulated with *A* (·—) is strong in the remaining quadrants. Along four lines passing through the station, the *A* and *N* signals are of equal intensity, and blend into a continuous sound. These lines form the courses or "beams" defined by the system. The radiation fields are vertically polarized to eliminate some of the troubles that occurred when earlier types of antenna systems were used.

In level country these range courses are reasonably well behaved, but over mountainous or even moderately hilly terrain curious effects often arise. In particular, instead of a single course of equal signal strength, there may appear a complicated pattern of several parallel courses spread over an angular distance of up to twenty degrees. This effect is very troublesome and dangerous to air traffic.

Early in 1939, field investigations of these phenomena were carried out on the range at Oakland, California, by Captain E. C. Dyer, U.S.M.C., and Lieutenant D. E. Wait, U.S.N. It was found that the seaward course was badly split and that this seemed to be related to the hills of the San Francisco peninsula and especially Mt. Tamalpais in Marin County north of the Gate. They requested the author to make