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Citation: *The Journal of Chemical Physics* **5**, 1 (1937); doi: 10.1063/1.1749922

View online: <http://dx.doi.org/10.1063/1.1749922>

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THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 5

JANUARY, 1937

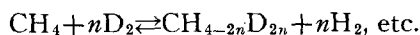
NUMBER 1

The Analysis of Isotopic Mixtures of Deuteromethanes and Ethanes by Infrared Absorption Spectra

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(Received October 16, 1936)

The infrared absorption spectra of a large number of deuterium-containing methane samples, and a few of ethane, have been studied with a rocksalt spectrometer. All the observable fundamental frequencies of each individual methane isotope have been identified, and from the relative intensity of absorption at various characteristic wave-lengths the composition of any mixture of these isotopes may be determined. The infrared spectra of deuterioethanes including C_2D_6 have been observed.

THE exchange reactions between deuterium and various hydrogen-containing compounds have yielded much information of chemical interest concerning the stability of these compounds. In several preliminary notes¹ we have given the chief results of such studies on the simplest hydrocarbons, methane and ethane. In the present paper, one of a series of more detailed communications, the others of which are appearing in the *Journal of the American Chemical Society*, we will describe the general method of analysis of our samples, involving the infrared spectra of these compounds, some of which have not been previously reported. A subsequent paper will deal with the theoretical and experimental determination of the equilibrium of the reactions



The use of infrared spectroscopy for the analysis of isotope exchanges appears to be new. The advantage of absorption spectroscopy in analyzing isotopic mixtures is that the presence

of each individual isotopic molecule is made known by its characteristic absorption bands. Infrared absorption is made necessary in the case of saturated hydrocarbons by the absence of any banded absorption in the visible or ultraviolet regions, which made the semiquantitative analysis of exchange in ammonia² and benzene³ so convenient. The comparative tedium of the infrared technique is more than compensated, however, by the quantitative accuracy obtainable; and after experience and a number of calibrating analyses throughout the entire infrared spectrum have disclosed the few wave-lengths at which the absorption is most significant, a complete analysis giving the composition of a mixture of deuteromethanes to within 1 or 2 percent for each isotopic constituent is a matter of a very few hours.

PREPARATION OF SAMPLES

In addition to determining the infrared absorption of a large number of "unknown"

¹ Taylor, Morikawa and Benedict, *J. Am. Chem. Soc.* **57**, 383 (1935); *ibid.* **57**, 592 (1935); *ibid.* **57**, 2735 (1935).

² Taylor and Jungers, *J. Chem. Phys.* **2**, 373 (1934).
³ Bowman, Benedict and Taylor, *J. Am. Chem. Soc.* **57**, 960 (1935).

samples of methane of varying D content the preparation of which forms the subject of other papers, "standard" samples were prepared as follows.

CH_4 and CD_4 were prepared by reduction of CO with H_2 or D_2 on a nickel catalyst. The preparation of the catalyst and the purification of the gases are described in detail elsewhere.⁴ The resulting CD_4 contained small amounts of CD_3H , which could be estimated from the spectra. The samples used varied from 93 to 98.4 percent C—D content. Samples containing $33\frac{1}{3}$ percent, 50 percent and $66\frac{2}{3}$ percent C—D were also prepared by reduction of CO with the appropriate $\text{H}_2 : \text{D}_2$ mixtures. The composition of the resulting gases is subject to a slight uncertainty, due to the possibilities of dilution with H or D excess present on the catalyst, and differential isotope exchange in the reaction. Equilibrium mixtures of methanes not subject to these uncertainties were prepared by bringing a mixture of CH_4 and CD_4 in the desired proportions to equilibrium on a nickel catalyst at 302° . The catalyst had been previously washed with a $\text{H}_2 : \text{D}_2$ mixture of the same proportions. Two samples of each mixture were prepared and gave concordant results. In this way equilibrium mixtures of 9.5, 18.1, 79.8 and 88.6 percent C—D content were secured. Correction was made for the H content of the CD_4 samples used.

CH_3D was prepared by the Grignard reaction, using CH_3I and D_2O . It was subjected several times to fractional extraction at liquid-air temperatures. The product was spectroscopically free from CH_2D_2 , but contained a small amount of CH_4 .

To prepare CH_2D_2 , CH_2I_2 was added drop by drop to $\text{C}_2\text{H}_5\text{OD} + \text{D}_2\text{O} + \text{Zn dust}$.⁵ The reaction being highly exothermic, it was necessary to cool the mixture at first, later raising the temperature. The gas was collected in a liquid-air trap and subjected to repeated fractionation. The $\text{C}_2\text{H}_5\text{OD}$ was prepared from $(\text{C}_2\text{H}_5\text{O})_3\text{Al}$ and D_2O , according to directions suggested by Dr. John Turkevich. The resulting gas was far from pure CH_2D_2 containing considerable CH_3D , as well as smaller amounts of CHD_3 and CH_4 .

A similar method was attempted in the preparation of CHD_3 , using a mixture of CHI_3 and CHCl_3 in place of CH_2I_2 . Again the resulting gas contained considerable amounts of CH_2D_2 , CH_3D and CD_4 , though preponderantly CHD_3 .

To prepare C_2H_6 , tank ethylene was fractionated, the middle fraction hydrogenated on nickel catalyst at room temperature, and excess hydrogen removed by $\text{Cu} - \text{CuO}$ at 302° as water.

To prepare C_2D_6 , purified tank ethylene was hydrogenated with D_2 and then subjected to the exchange reaction with twice the quantity of D_2 seven times on nickel catalyst. Details are described in another paper.^{4b} The resulting C_2D_6 showed only very weak absorption due to $\text{C}_2\text{D}_5\text{H}$ and may be estimated as containing 95–98 percent C—D bonds.

INFRARED SPECTRA

Technique

For infrared analysis, the gaseous samples were transferred at known pressures into cylindrical Pyrex absorption cells, with rocksalt windows. Two such cells were used in the present work, 20.6 and 24.4 cm in optical length, respectively. The spectrometer was a rocksalt prism instrument of the Wadsworth type, described by Barnes.⁶ The high magnification of the photorelay made possible the use of comparatively narrow slits and high accuracy of absorption measurements even to long wave-lengths. At 10μ the galvanometer deflections due to the energy spectrum reached 500 mm reproducible to 2 mm, and the working limit of the spectrum was 16μ . The absorption cell was raised and lowered in and out of the light beam, alternate readings in, out, out and in being taken at each wave-length. At some times the galvanometer zero showed a steady drift; hence the average of the deflections obtained on raising and lowering the shutter was taken. The deflections obtained were to a slight extent a function of the position of the galvanometer zero, due to nonlinearity of the amplification; hence the zero was brought back to approximately the same position for each reading; and to ensure further the accuracy of the ratio of the absorbed to the unabsorbed deflections, the latter was raised by a factor of two at

⁴ Morikawa, Benedict and Taylor, J. Am. Chem. Soc. (a) 58, 1445 (1936); (b) 58, 1795 (1936).

⁵ Sabanejew, Ber. 9 (1870).

⁶ Barnes, Brattain and Seitz, Phys. Rev. 48, 582 (1935).

any given important wave-length. Using all these precautions for quantitative accuracy, the percentage absorption of a given sample, or of similar samples at different times, was reproducible to 1 percent. For absorption under average conditions, the accuracy is 2-3 percent. In the earliest experiments the accuracy is considerably less, as at that time there was no device for raising and lowering the absorption cell. The energy spectrum was first mapped with the cell in; then with it out; and smoothed curves for each were plotted, and then the ratio was taken.

Correction for the effect of rocksalt window

The observed transmission ratio of energy: cell-in/energy: cell-out must be corrected for the absorptions and reflections of the rocksalt windows. This depends on wave-length and the position of the cell in its carrier. The following procedure was adopted: Wave-lengths were found at which there was zero absorption, as proven both by experiment at high gas pressures, and backed by theory. The transmission was always observed at these wave-lengths; the transmission of the cell at intermediate wave-lengths, where there was gas absorption, was determined from these by plotting a smooth curve, in accordance with measurements made on an evacuated cell. For the methane experiments, the reference wave-lengths were 25.05 scale divisions = 3400 cm^{-1} ; 24.45 = 2520 cm^{-1} ; 23.60 = 1900 cm^{-1} ; and 17.00 = 850 cm^{-1} . From evacuated-cell measurements, $\text{trans } 3000 \text{ cm}^{-1} = (\text{trans}_{3400} + \text{trans}_{2520})/2$, and $\text{trans } 2250 \text{ cm}^{-1} = (2 \cdot \text{trans}_{2520} + \text{trans}_{1700})/3$. Similar standard procedure prevailed for other wave-lengths.

Absorption coefficient and pressure

The percent absorption, $1 - (I/I_0)$, then was given by $1 - (\text{observed transmission}/\text{calc. cell transmission})$. To correct for the effect of gas density and cell length, these are converted into extinction coefficients, $K = (-\log_{10} I/I_0/pl)$, where p is the gas pressure in mm Hg, corrected to 25°C; and l is the cell length in cm. That K is rarely a true constant, but varies with pressure, i.e., that Beer's law does not hold, is a familiar phenomenon in infrared work.⁷ This is particu-

larly true when using a rocksalt spectrometer and spectra consisting of unresolved single lines. Here the slit width is much greater than the true line width, and the observed transmission is the average of narrow peaks of true absorption and wide valleys of transmission. When the absorption of the peaks is already high, increasing the pressures does not increase the over-all absorption linearly. Moreover, the effects of pressure broadening on line shapes are often appreciable. However, for low absorptions and for moderate absorptions in bands where the lines are numerous and closely spaced (i.e., the unsymmetrical methanes), Beer's law should be expected to hold. This is indeed the case, experimentally. The K 's determined from $I/I_0 > 70$ percent, or those for the unsymmetrical methanes (except the 1300 cm^{-1} band of CH_3D) up to $I/I_0 > 50$ percent are nicely constant; for higher gas pressures K falls with pressures to perhaps 70 percent of its true value. In practice, therefore, the pressure was chosen to bring as many points as possible between the limits of absorption too low to be accurately measured $I/I_0 > 95$ percent and too high to obey Beer's law. Since this could not be attained for all wave-lengths, the pressure of a series of corresponding samples was kept constant, so that even though the K 's might fall below their true values, they would be directly comparable one with another.

Effect of H_2 or D_2 pressure

Many of the unknown samples contained H_2 or D_2 in addition to methanes. The effect of such nonabsorbing foreign gas on the absorption coefficients was therefore tested on the 18.1 percent D sample. Addition of 190 mm D_2 to the 190 mm sample had no effect greater than 10 percent on K for any wave-lengths although such an increase was observed in some bands. Hence deviations from Beer's law due to pressure broadening by H_2 are of no great consequence.

Absorption coefficients and mole fraction

The K 's observed were computed on the bases of the total pressure of methane of whatever isotopic nature in the cell. If several methanes are present, $K_{\text{obs}} = \sum K_i x_i$, where K_i is K for any pure constituent and x_i its mole fraction. The accuracy of this expression is testified to by the

⁷ von Bahr, Ann. d. Physik **29**, 780 (1909); Bartholome, Zeits. f. physik. Chemie **23**, 131 (1933).

coherence of all the observed data. The K for any given sample is quite accurately decomposable for all wave-lengths into the sum of the K 's for the pure components, and their mole fractions, due allowance being made for Beer's law deviations.

The wave-length calibration curve of the instrument was obtained from the known absorption bands of various substances. One calibration point, the energy minimum due to atmospheric CO_2 absorption at 2353 cm^{-1} , was rechecked for every run.

Observed spectra

The observed absorption spectra of the methanes may for convenience be divided into two regions, those of the "valence" vibrations, $2000\text{--}3200\text{ cm}^{-1}$, and of the "deformation" vibrations, $1500\text{--}900\text{ cm}^{-1}$.

(1) *Region $2000\text{--}3200\text{ cm}^{-1}$.*—In the first region, the fundamental frequencies correspond closely to two values, one characteristic of the C—H band, 3000 cm^{-1} , and one to the C—D band, 2250 cm^{-1} . In all the methanes, the bands of strongest absorptive power lie within 50 cm^{-1} of these values, so that, under the low resolving power of a rocksalt spectrometer in this region, the absorption of samples of widely different C—D content show only these two bands roughly similar in position and structure, but differing in intensity. Because of the similarity and the low resolution, no curves of the absorption in this region will be presented. The values of the extinction coefficient at the two maxima of absorption, designated by K_H and K_D , respectively, are given with the plots of absorption in the second region. The position of the K_H maximum was constant, within the accuracy at this region

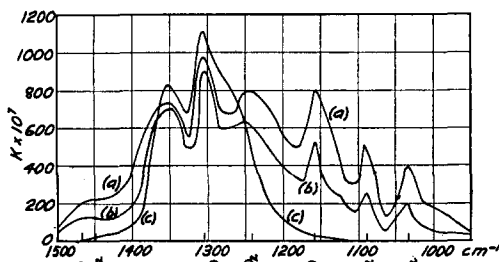


FIG. 1. Absorption spectra of equilibrium methanes of low C—D content. $P = \sim 180\text{ mm}$. (a) 18.1 percent; (b) 9.5 percent; (c) 0 percent.

of $\pm 40\text{ cm}^{-1}$, at 3020 cm^{-1} , with the exception of the very weak band observed in the CD_4 of highest purity. Here, of course, there should be no absorption corresponding to a C—H fundamental. Actually there is a weak, broad band, with a badly defined maximum at about 3200 cm^{-1} , as well as some absorption at 3000 cm^{-1} due to the small percentage of CD_3H remaining in the sample. The 3200 cm^{-1} absorption is undoubtedly due to the CD_4 molecule, and corresponds to the CH_4 absorption at 4300 cm^{-1} , due to "combination" bands of valence and deformation frequencies. In the 2250 cm^{-1} region, the accuracy of wave-length determination is somewhat improved, so that the maximum of samples of lowest D content is found at 2210 cm^{-1} , the position of the single CH_3D , C—D fundamental. CH_2D_2 and CHD_3 each have two fundamentals in this region, but those at 2255 and 2270 cm^{-1} , respectively, appear by far the stronger, as the maximum occurs there, with only a slight asymmetry of the band, lower frequencies indicating the presence of the other fundamentals, known from Raman measurements⁸ to occur at 2139 and 2141 cm^{-1} . Similarly, the weaker C—H frequencies, CH_3D , 2922 cm^{-1} and CH_2D_2 , 2974 cm^{-1} do not appear strong enough to shift the maximum observably.

(2) *Region $1500\text{--}900\text{ cm}^{-1}$.*—Representative curves of absorption in the second region are presented in Figs. 1–3. Frequencies in cm^{-1} are plotted

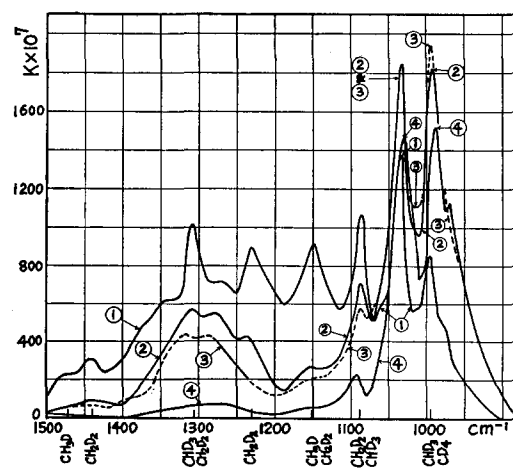


FIG. 2. Absorption spectra of equilibrium methanes of high C—D content. (1) 46 percent; (2) 79.8 percent; (3) 88.6 percent; (4) 98.2 percent.

⁸ MacWood and Urey, *J. Chem. Phys.* 4, 402 (1936).

TABLE I. K of individual isotopes.

MOLECULE ν $\text{CM}^{-1} \rightarrow$	3020	2250	1460	1305	1180-1160	1090	1035
CH_4	380	—	—	1110	80-0	—	—
CH_3D	1200	300	350	800	1100-1900	550	—
CH_2D_2	1200	1500	500	500	700-700	2400	2400
CHD_3	733	2200	—	1400	300-300	400	2500
CD_4	70	450	—	—	—	250	1400

against $K \times 10^7$. The gradual appearance and disappearance of bands C—D, as the percent expressed in the form $(\text{C—D}/\text{C—H} + \text{C—D}) \times 100$, increases, in Figs. 1 and 2, is the justification for their assignment to individual molecules, at the foot of the figures. These assignments are corroborated by the curves of Fig. 3, which represent the absorption of the samples prepared to give the pure individual isotopes. As can easily be seen, the desired goal was not achieved. The CH_3D is quite free from other isotopes, but the “ CH_2D_2 ” and “ CHD_3 ” curves show bands due to both molecules, as well as CH_3D .

In order further to demonstrate how the observed absorption may be represented as the sum of the contributions of each individual isotopic molecule, we may plot, for any desired wave-length, K against the percent C—D. The mol fractions of each molecular species may be calculated, given the equilibrium constants of the equations $\text{CH}_4 + \text{CH}_2\text{D}_2 \rightleftharpoons 2\text{CH}_3\text{D}$, $\text{CH}_3\text{D} + \text{CHD}_3 \rightleftharpoons 2\text{CH}_2\text{D}_2$, and $\text{CH}_2\text{D}_2 + \text{CD}_4 \rightleftharpoons 2\text{CHD}_3$ and the total percent C—D. The equilibrium constants are obtained, and the mol fractions calculated therefrom, in a later paper. The result is given in Fig. 10, where the heavy lines represent the resulting mole fractions. These are seen to deviate but slightly from the classical result, if all the equilibrium constants equal 1, given by the

broken lines. Given the mole fractions, K_i 's may now be found so that $K_{\text{obs}} = \sum X_i K_i$. This has been done, and the results plotted, for significant wave-lengths of maximum absorption, K_{H} and K_{D} are given in Fig. 4, and K_{1460} , K_{1305} , $K_{1180-1160}$, K_{1090} and K_{1035} in Figs. 5-9. The light lines in Fig. 4 are $X_i K_i$ computed from the X_i 's of Fig. 10 and the K_i 's of Table I, the heavy lines are the resultant K 's. The observed points, as shown in Figs. 4-9, are marked by circles.

Analysis of mixtures

Figs. 4-9 thus gives a series of calibration curves, obtained both experimentally and theoretically from which it is possible to determine the percent C—D of any unknown sample, assuming equilibrium distribution among the methanes. This has been done many times (see the other papers^{1, 4}) always with gratifying concordance among the results obtained from various wave-lengths. It must be admitted that the observed K 's for all the wave-lengths given do not fall on the curves, if the pressure of the sample differs too much from the $p \cong 170$ mm obtaining in the standard samples, due to the deviations from Beer's law mentioned above. In such cases, however, it has been feasible to apply concordant corrections, such that the values then fall on the curves. For example, for samples in the neighborhood of 50 percent C—D, the observed results for K_{H} and K_{D} fall uniformly below the values plotted in Fig. 4. The ratio $K_{\text{H}}/K_{\text{D}}$ is then a good measure of the percent C—D in the sample. Similarly, if it be attempted to estimate the composition of the samples whose curves are plotted in Fig. 3 (taken at higher pressures), the result will not add up to 100 percent. It is believed, however, that the ratios of one isotopic molecule to the other obtained from the K 's of Table I are substantially correct.

Also, the calibration curve for 1305 cm^{-1} could not be relied upon in the range 0-60 percent C—D,

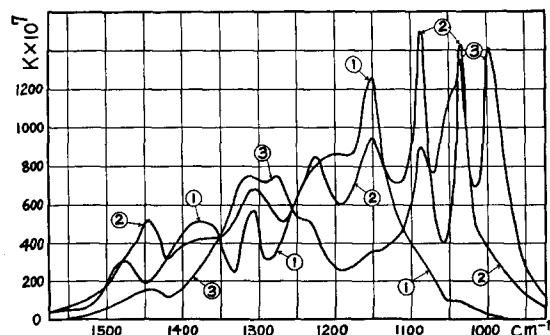


FIG. 3. Absorption spectra of methanes prepared by reduction of halides. (1) CH_3D ; (2) CH_2D_2 ; (3) CHD_3 .

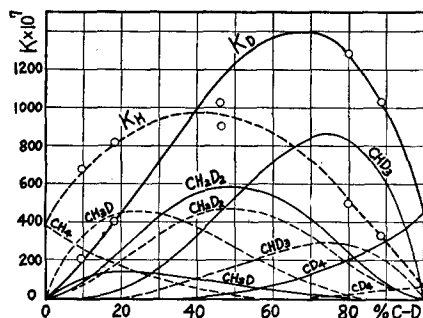


FIG. 4. Contribution of individual isotopes to K_H (3020 cm^{-1}) and K_D (2250 cm^{-1}).

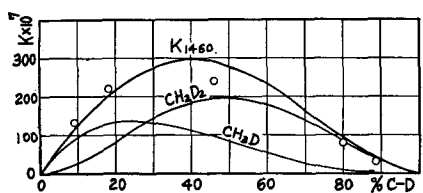


FIG. 5. Contributions of individual isotopes to $K_{1460} \text{ cm}^{-1}$.

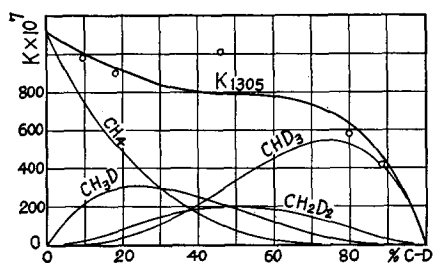


FIG. 6. Contribution of individual isotopes to $K_{1305} \text{ cm}^{-1}$.

as seen from the bad agreement of observed and computed points. This is believed due to the abnormally large Beer's law variations for the 1305 cm^{-1} band of CH_4 . In the range 60–100 percent C–D, where CD_3H is the principal absorber, the calibration curve may be relied upon, as results obtained were consistent with those from other wave-lengths.

In practice, it sufficed to measure K_H and K_D with the utmost accuracy, and to dispense with further measurements, unless it was believed that nonequilibrium conditions prevailed. This was done in most of the early work on the attainment of equilibrium on catalytic surfaces. Nonequilibrium samples were found under several conditions, however. For example, CH_4 and CD_4 were mixed on catalytic surfaces for times less than that corresponding to equilibrium. If percent conversion, X , is understood to be the fractional

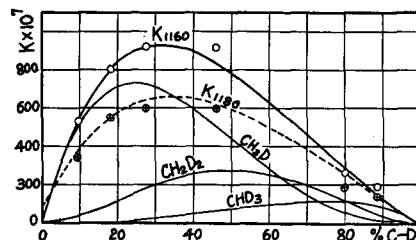


FIG. 7. Contributions of individual isotopes to $K_{1160} \text{ cm}^{-1}$.

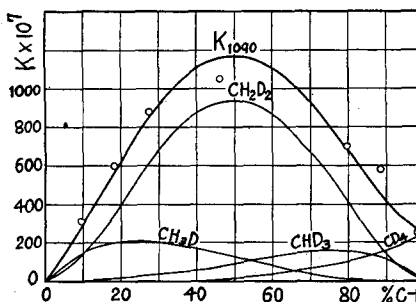


FIG. 8. Contribution of individual isotopes to $K_{1090} \text{ cm}^{-1}$.

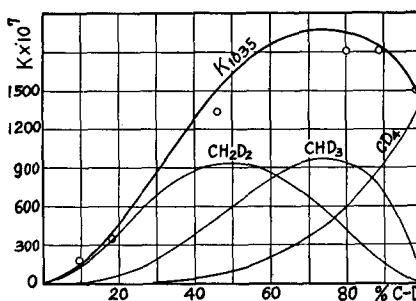


FIG. 9. Contribution of individual isotopes to $K_{1036} \text{ cm}^{-1}$.

amount by which both CH_4 and CD_4 have approached the equilibrium state, this may easily be found by drawing new plots similar to Figs. 4–9 in which the abscissa, X , runs from 0–100 percent and the ordinates are the average of the K 's corresponding to percent C–D = $X/2$ and percent C–D = percent C–D in $\text{CD}_4 - X/2$. Again the results from varying wave-lengths were concordant. In other cases, mentioned in the catalytic papers,⁴ the reaction $\text{CH}_4 + \text{D}_2$ sometimes progressed with the heavier isotopes, CH_2D_2 and CHD_3 appearing in quantities beyond the equilibrium amounts. Recourse to the curves will always make possible estimates of the composition of any mixture, however, once the necessity for taking absorption readings at a number of wave-lengths is established.

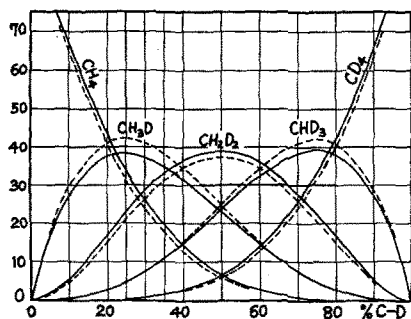


FIG. 10. Mole percentages of individual isotopic molecules: — Equilibrium at 302°. --- Ideal equilibrium (infinitely high temp.).

Effects of ethanes on absorption coefficients of methanes

Another series of discrepancies between the percent C-D estimated from K_H and K_D and from the other K 's appeared in certain photochemical experiments (the results of which will appear later in this Journal) in which K_H and K_D were higher than expected from the percent C-D estimated from K_{1160} , for example. Since the C_2H_6 molecule has a K_H much higher than CH_4 it was thought that there might be traces of $C_2H_xD_{6-x}$ present; the abnormally high values of K_{1460} in these samples corroborated this view, as C_2H_6 also has a strong band at 1460 cm^{-1} . Subsequent chemical analysis of similarly prepared

samples proved the presence of the ethanes, etc. It was hardly possible to estimate the ethane quantitatively from the absorption coefficients, however, as the small amounts of ethane involved contributed markedly only to K_H and K_D , and there was no guarantee that the percent C-D was the same in the methane and the ethane. Accordingly, the percent C-D of the methane was determined from the curves of Fig. 6-9, and the differences between the observed and calculated values of K_H and K_D serve as a semi-quantitative indication of the amount of ethane. In some of the early experiments only K_H and K_D were measured; for these runs the percent C-D in the methane can be roughly found by assuming ethane absorption equal to that determined for analogous samples by the more exact later measurements.

Ethane spectra

Although no attempt was made to prepare and analyze the entire range of deuterioethane samples as we have done for deuteromethane, absorption curves were run for several catalytically prepared deuterioethane samples, including one of nearly pure C_2D_6 . These are presented in Fig. 11. The exact percentage C-D in samples 2, 3 and 4 was not measured, but may be estimated from the spectra. In C_2H_6 there are three main regions of

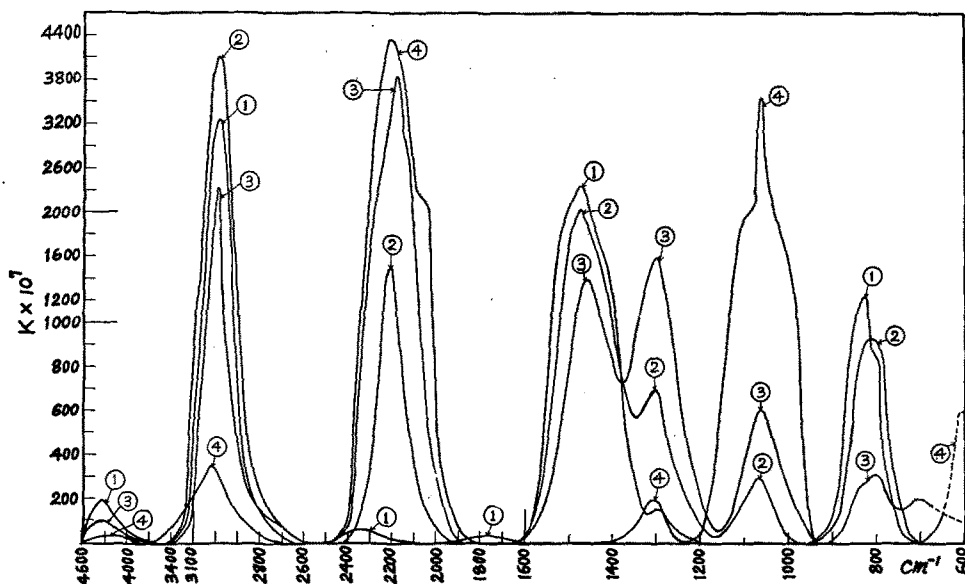


FIG. 11. Absorption spectra of ethanes of varying C-D contents. (1) 0 percent (C_2H_6); (2) ~15 percent; (3) ~45 percent; (4) ~95 percent.

absorption, 2980 cm^{-1} , 1470 cm^{-1} and 827 cm^{-1} , corresponding, respectively, to C—H valence, C—H deformation, and C—C deformation vibrations, to adopt Mecke's⁹ terminology. The first two regions have been shown, under high resolution¹⁰ to be composite, each corresponding to several infrared active modes of vibration. In addition to these strong bands we observe, with gas pressures of one atmosphere, weak bands at 4280 , 2350 , 1770 and 1305 cm^{-1} . The first is $\nu_{\text{H}} + \delta_{\text{H}}$; the second and third do not appear to have been previously reported, but may readily be ascribed to combination bands $\nu_{\text{C-C}} + \delta_{\text{H}}$ and $\nu_{\text{C-C}} + \delta_{\text{C}}$. ($\nu_{\text{C-C}}$ is well known from Raman spectra and equals 990 cm^{-1} .) The 1305 cm^{-1} absorption is probably due to a trace of CH_4 as impurity.

Deuteroethanes spectra

Now in spectrum No. 2 these same bands are present, not noticeably shifted in position but in addition new bands have appeared at 2210 cm^{-1} (ν_{D}) 1300 cm^{-1} ($\delta_{\text{H-D}}$), and 1070 cm^{-1} (δ_{D}). The K_{H} has increased slightly, and $K_{\text{D}} = 0.4 K_{\text{H}}$. In spectrum No. 3, the new bands have increased appreciably in intensity, ν_{D} shifting to 2180 cm^{-1} , with $K_{\text{D}} = 1.5 K_{\text{H}}$, $K_{1300} > K_{1480}$, and with much weaker and very irregular absorption in the region $< 900\text{ cm}^{-1}$. Obviously here the characteristic bands of C_2H_6 have almost completely disappeared, the observed absorption being a composite of bands of the many possible deuteroethanes of intermediate composition. The simplicity of absorption in the regions of shorter wave-length is another instance of the paradoxical fact that the more complicated the molecule the simpler the vibrational spectrum, in that the vibrations within radicals preserve closely their characteristic values, interrational forces being small. Thus 1470 cm^{-1} is a characteristic frequency of CH_3 or CH_2 radicals, whether in CH_3X , CH_3D , CH_3-CH_3 , CH_2D_2 , or $\text{CH}_2\text{D}-\text{CH}_2\text{D}$; 1305 cm^{-1} is characteristic of CHD ; and 1070 cm^{-1} of CD_3 or CD_2 . The ν_{H} and ν_{D} absorptions show the same characteristic as in CH_4 , namely, that the wave-length shifts but slightly with changing percent D; but that the K increases as asymmetry increases. As $K_{\text{D}} > K_{\text{H}}$ in No. 3, we may conclude that the percent C—D

corresponds to equilibrium, as this sample was prepared from $1\text{ C}_2\text{H}_6 : 2\text{ D}_2$, or equilibrium of ~ 45 percent C—D. From relative intensities No. 2 is then between 10 and 20 percent C—D.

In spectrum 4, the purest C_2D_6 , the simplicity of the C_2H_6 spectrum is almost but not quite reattained. ν_{D} is now at 2210 cm^{-1} and the greater resolution obtainable here gives unmistakable evidence that a second fundamental lies at about 2080 cm^{-1} . δ_{D} is a sharp band at 1067 cm^{-1} , and $\delta_{\text{C-C}}$ has shifted to wave-lengths just beyond the reach of the instrument, absorption being manifest at $\sim 600\text{ cm}^{-1}$, but the energy being insufficient to establish the position of the maximum with any accuracy. Other weak bands appear at 1305 cm^{-1} ($\delta_{\text{H-D}}$); 3020 cm^{-1} , a combination of $\nu_{\text{D}} + \delta_{\text{D}}$ and ν_{H} ; and 4300 cm^{-1} ($2\nu_{\text{D}}$). From the weakness of the first two ($K\delta_{\text{D}} : K\delta_{\text{H}} = 16 : 1$ and $K_{\text{D}} : K_{\text{H}} \cong 25 : 1$) we may estimate that the sample contains 95–98 percent C—D.

Discussion of methane spectra

The results reported in this paper make nearly complete the tabulation of all the fundamental frequencies of all the methane isotopes. Those of CH_4 have been long known; those of CH_3D and some of CH_2D_2 are known from the accurate infrared work of Ginsburg and Barker,¹¹ while MacWood and Urey⁸ have recently reported on the Raman spectra of all the methanes. In one or two cases these last results disagree with the infrared measurements. The observed values for the frequencies are tabulated in Table II, where the nomenclature follows that of previous authors. The calculated values are taken from a forthcoming paper by one of us, and include corrections for the harmonic terms in the energy, taken so as to give exact agreement with the CH_4 and CD_4 frequencies; hence the somewhat better agreement than with previous calculated values.¹²

The agreement of the Raman and infrared measurements is good, with one or two exceptions. The line found by MacWood and Urey in CH_3D at 1330 cm^{-1} is hard to explain, as the origin of ν_{4ab} is unquestionably the strong zero branch found by Ginsburg and Barker at 1307 cm^{-1} and confirmed in this work. Similarly, the line found by them in CH_2D_2 at 1333 cm^{-1} is out

⁹ Mecke, Zeits. f. physik. Chemie **B16**, 409 (1932).

¹⁰ Leven and Meyer, J. Am. Chem. Soc. **16**, 137 (1928).

¹¹ Ginsburg and Barker, J. Chem. Phys. **3**, 668 (1935).

¹² Dennison and Johnson, Phys. Rev. **47**, 93 (1935).

TABLE II. *Frequencies of the deuteromethanes.*

FREQUENCY	ν_1	$\nu_2(2)$	$\nu_3(3)$	$\nu_4(3)$
CH ₄ , OBS. AND CALC.	2915 (RAM.)	1519	3020 (RAM. I-R)	1306 (I-R)
CH ₃ D { OBS. I-R (G-B)	2950 (?)	1474	3031 2205	1156 1307
{ OBS. RAM.		$2\nu_2 = 2921.7$	2199.5	$2\nu_{4c} = 2314.8$ 1330(?)
{ CALC.	2961	1458	3032 2193	1147 1311
CH ₂ D ₂ { OBS. I-R (G-B)		1450	$\leftarrow 3020 \ 2255 \rightarrow$	1035 1091 1235
{ OBS. RAM.	2139.0	$2\nu_2 = 2916$ 1285.6	2974.2	1033.1 $2\nu_{4c} = 2179.6$ 1333(?)
{ CALC.	2144	1450 1290	3027 2980 2265	1038 1085 1227
CHD ₃ { OBS. I-R (THIS PAPER)		$\left(\begin{matrix} 1290 \\ 1299.2 \\ 1293 \end{matrix} \right) \rightarrow$	3000 2260	988 988(?)
{ OBS. RAM.	2141		2268.6	$2\nu_{4ab} = 1963.4$ $2\nu_{4c} = 2092.8$
{ CALC.	2127		3015 2263	995 997
CD ₄ , OBS. AND CALC.	2085 (RAM.)	1052	2258 (RAM. AND THIS PAPER)	988 (THIS PAPER)

of place in our scheme, as we confirm the occurrence of ν_{4a} at 1235 cm^{-1} , thus making the Raman line at 1285.6 be ν_{2a} , in agreement with calculation. Reference to Ginsburg and Barker's curves will show the complete agreement with ours of all maxima attributed to CH₃D and CH₂D₂. The relative intensity of our bands also agrees with their curves; and, as far as it is possible to calculate extinction coefficients from their data, rough agreement is also obtained. The grating intensities are somewhat higher, as should be expected from the narrower slits used. For CHD₃, we prefer to interpret the two strong absorption peaks at 988 and $1035\text{--}1040 \text{ cm}^{-1}$ as being the *Q* and *R* branches of both ν_{4cb} and ν_{4c} , the origin of both bands being at 988 cm^{-1} , although perhaps the *Q* branch of ν_{4c} is at 1035 , as suggested by the Raman assignments. A justification of our assignment, based on the expected envelopes of the bands, will be given in the forthcoming paper. That the *Q* branch of CD₄ is located at 988 cm^{-1} cannot be questioned, as the similarity in envelope with ν_4 of CH₄ is apparent. The weak absorption appearing at 1095 cm^{-1} in CD₄ must be attributed to a difference band, $\nu_1 - \nu_4 = 2085 - 988 = 1097 \text{ cm}^{-1}$.

The relative intensities of the methane bands is a matter of some interest. As we have emphasized, not too much importance can be attached to absolute intensities, because of the low resolving power of the apparatus; thus the apparent greater intensity of ν_D over ν_H in CH₂D₂, or in

CD₄ over CH₄, may not be real, as the band width is much greater compared with the slit width at 2250 cm^{-1} than at 3000 cm^{-1} . There can be no question, however, that K_H and K_D are much greater for the unsymmetrical methanes than for CH₄ and CD₄, as Fig. 4 clearly and startlingly indicates. This result is all the more surprising, as in CH₂D₂ the weight of the active upper state is only two (and practically only one, as we have seen that the bands at 3020 and 2255 contribute most to the absorption), compared with three for the tetrahedrally symmetric molecules. Moreover, a simple calculation of the expected intensities, assuming a dipole in each C-H or C-D band, $\mu = \mu_0 + \mu_1 \partial dr$, indicates that the intensities should be roughly equal for each active fundamental, and be less for a ν_D than a ν_H , because of the smaller amplitudes involved. The peculiar relations observed can only be explained by assuming a complicated behavior of the dipole moment as a function of the C-H distance, and probably interaction terms between the separate C-H bands play a role also. No satisfactory quantitative explanation has been obtained. It is of interest to note that the few samples of heavy ethanes observed showed a similar though somewhat smaller increase of K_H for the intermediate molecules, pointing to a definite property of the C-H dipole in all hydrocarbons. Accurate absolute intensity measurements and further calculations on this point would be of interest.