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The Vibrational Frequencies of Ethylene*

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The infra-red spectrum of a mixture of deuterated ethylenes has been obtained, and the non-planar fundamentals analyzed. The assignment establishes the twisting frequency as 1027 cm^{-1} (C_2H_4). This result leads to a new and more satisfactory assignment of the fundamental vibrational frequencies of ethylene.

INTRODUCTION

THROUGH an attempt to prepare *cis*-dideutero-ethylene for another purpose, we obtained a mixture of all seven deuterio-isotopic ethylenes. To our pleased surprise, the infra-red absorption spectrum of this mixture proved to be analyzable with regard to the non-planar vibrations. The most significant result of our analysis is the location of the twisting frequency of ethylene (C_2H_4) at 1027 cm^{-1} . With this information and the remeasurement of the low frequency band in C_2H_4 , we found it possible to make a most satisfactory assignment of all fundamentals and all observed frequencies for C_2H_4 and C_2D_4 .

EXPERIMENTAL

The deuterated ethylenes were prepared by passing heavy water (D_2O) vapor over calcium carbide and

subjecting the resulting dideutero-acetylene to catalytic hydrogenation (H_2 on Pd) to convert it to the olefin. The heavy water used contained 99.9 percent D_2O and the usual precautions were taken to remove H_2O from the apparatus and from the carbide.

The gas resulting from the hydrogenation reaction contained both ethane and unchanged acetylene as impurities. The latter component was effectively removed by bubbling the gas through a solution of alkaline mercuric cyanide. Chemical analysis of the final product revealed the composition: acetylene two percent, ethylene 85 percent, and ethane 13 percent.

After the spectrum of this sample was obtained, the gas was completely hydrogenated (H_2 on Pt) to ethane. This product was 98 ± 2 percent pure. The spectrum of this ethane was used to locate the ethane bands which were expected in the ethylene spectra. The records made at several pressures revealed that only one region

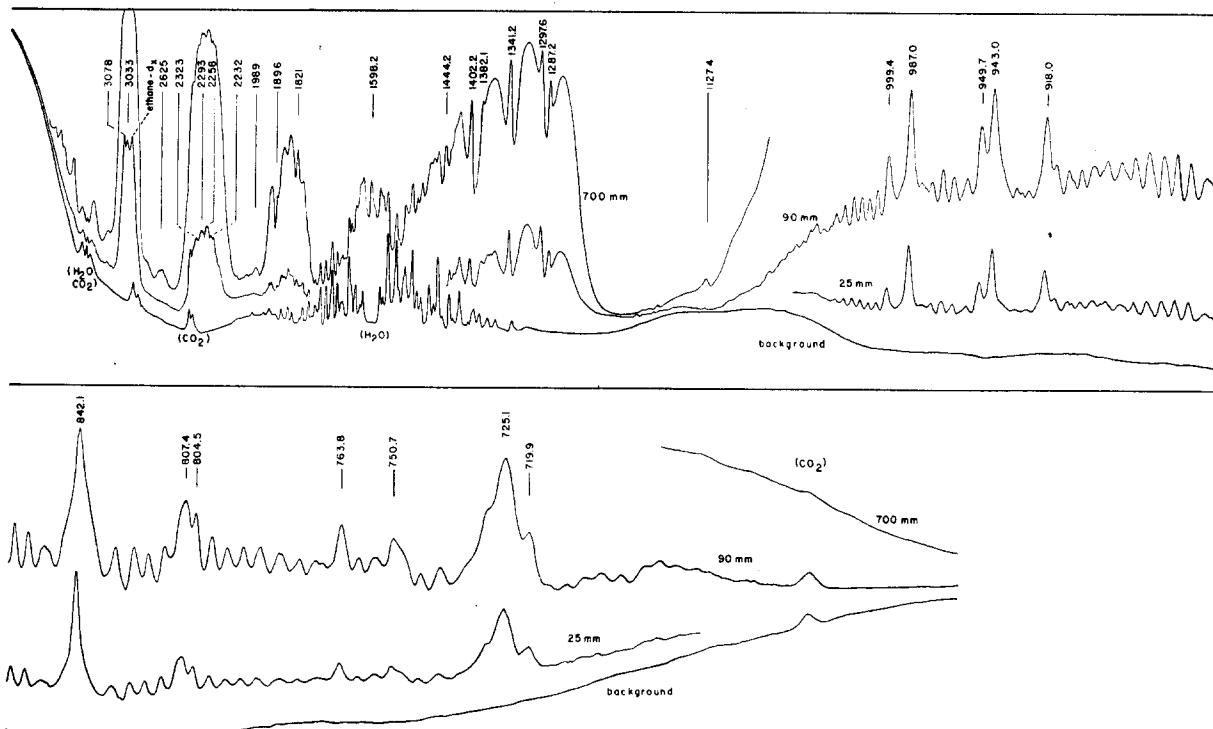


FIG. 1. Spectrum of deuterated ethylene mixture (NaCl). Cell length 10 cm.

* From a dissertation submitted by Raymond L. Arnett to the Graduate Faculty of the University of Minnesota in partial fulfillment of the requirement for the degree of Doctor of Philosophy.

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of absorption of the paraffin was sufficiently intense to be observed in the olefin spectrum.

The qualitative composition of the ethylene as to the isotopic molecules present was deduced from the mass spectrum of the ethane. The appearance of mass number 34 ($C_2H_2D_4$) makes it almost certain (in view of the method of preparation) that all the isotopic ethylenes were present in the olefin sample. This received confirmation through the analysis of the non-planar vibrational frequencies.

The infra-red absorption spectra were obtained from Model 12-C (for the rocksalt region) and Model 12-B (for the potassium-bromide region) Perkin-Elmer recording spectrometers. The 12-C instrument was fitted with a continuous slit drive adjusted to give approximately constant incident energy as the spectrum was traversed. The degree to which this is achieved can be seen from the lowest curves (marked "background") in Figs. 1 and 3. The 12-B spectrometer was not so equipped and its background changes rapidly with wave-length (Fig. 2).

For the deuterated ethylene, records in the rocksalt region were obtained at 25, 90, 135, and 700 mm Hg pressure. Traces obtained at each of these pressures (save 135 mm) are reproduced in Fig. 1; the 135-mm record is omitted for the sake of clarity. As many of the weak bands are seen only at the highest pressure, records at 700 mm were obtained in triplicate. All observations appearing in Tables I and II are thus the means of at least three measurements. Frequencies are corrected to vacuum conditions.

TABLE I. Ethylene- d_x absorption maxima below 1100 cm^{-1} (Figs. 1 and 2).

| Line | Assignment | Line | Assignment | Line | Assignment |
|--------------------|-------------------------|--------------------|-------------------------------|--------------------|-------------------------|
| 637 | | 802.3 | | 899.0 ⁺ | |
| 644 | | 804.5 ^Q | $2\omega_7-\omega_7\ C_2H_3D$ | 902.8 | |
| 694.6 | | 807.4 ^Q | $\omega_7\ C_2H_3D$ | 905.9 ⁺ | |
| 697.5 | | 809.5 ⁺ | | 908.3 | |
| 702.0 | | 812.0 ⁺ | | 913.0 | |
| 705.9 | | 814.1 | | 918.0 ^Q | $\omega_8\ C_2HD_3$ |
| 709.6 | | 817.2 ⁺ | | 921.9 ⁺ | |
| 712.5 | | 819.3 | | 926.6 | |
| 719.9 ^Q | $\omega_7\ C_2D_4$ | 823.8 | | 929.9 | |
| 725.1 ^Q | $\omega_7\ t-C_2H_2D_2$ | 829.8 | | 932.5 | |
| 729.0 | | 838.2 ⁺ | | 943.0 ^Q | $\omega_8\ a-C_2H_2D_2$ |
| 739.1 | | 842.1 ^Q | $\omega_7\ c-C_2H_2D_2$ | 949.7 ^Q | $\omega_7\ C_2H_4$ |
| 744.1 | | 845.3 ⁺ | | 957.0 | |
| 750.7 ^Q | $\omega_7\ a-C_2H_2D_2$ | 853.0 ⁺ | | 964.3 | |
| 753.9 | | 855.1 | | 969.7 | |
| 755.9 ⁺ | | 860.2 | | 975.4 | |
| 759.4 | | 865.3 | | 980.7 | |
| 761.9 ⁺ | | 870.3 | | 987.0 ^Q | $\omega_4\ t-C_2H_2D_2$ |
| 763.8 ^Q | $\omega_4\ C_2HD_3$ | 875.5 | | 999.4 ^Q | $\omega_4\ C_2H_3D$ |
| 785.7 | | 880.7 | | 1005.9 | |
| 788.0 ⁺ | | 884.8 ⁺ | | 1011.1 | |
| 790.8 | | 886.8 | | 1015.9 | |
| 793.0 ⁺ | | 892.1 | | 1020.8 | |
| 794.7 | | 894.1 ⁺ | | 1026.0 | |
| 799.6 | | 897.1 | | 1031.2 | |

Note.—Frequencies marked with Q are the labeled Type C bands in Fig. 1; those marked (*) do not appear in Fig. 1 as they are so weak or so close to a neighbor that the compression of the scale does not permit their showing.

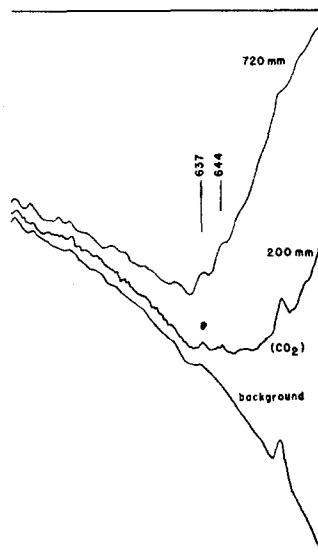


FIG. 2. Spectrum of deuterated ethylene mixture (KBr). Cell length 10 cm.

The material is transparent in the KBr region except for a very feeble absorption near 640 cm^{-1} . Two weak maxima appear here at 637 and 644 cm^{-1} (Fig. 2).

Since the ethylene sample contained an appreciable amount of ethane, the spectrum of the latter was obtained to identify the ethane bands which might appear in the ethylene spectrum. The deuterated ethane spectrum was obtained at three pressures, 16, 104, and 480 mm. Only the highest pressure is recorded here (Fig. 3), for the records at the lower pressures were blank except for a strong absorption at 3.4μ and a feeble one at 5.0μ . Duplicate runs were made at the highest pressure; the observed frequencies are listed in Table III.

The ethane proved to be completely transparent in the KBr region event at the highest pressure (480 mm). Only one ethane band, then, appears in the ethylene spectrum. This band is marked in Fig. 1.

Ohio Chemical Company ethylene (99.5–99.7 per cent) was used to obtain the record of the 810.3-cm^{-1} band shown in Fig. 4; the line positions are listed in

TABLE II. Ethylene- d_x absorption bands above 1100 cm^{-1} (Fig. 1).

| ω | Maxima | ω | Maxima |
|----------|--------|----------|------------------|
| 1127.4 | | 1802 | $P(?)$ |
| 1269 | P | 1821 | Q |
| 1287.2 | Q | 1847 | R |
| 1297.6 | Q | 1868 | P |
| 1314 | R, P | 1896 | Q |
| 1341.2 | Q | 1920 | R |
| 1362 | R, P | 1989 | |
| 1382.1 | Q | 2232 | |
| 1402.2 | Q | 2258 | |
| 1419 | R, P | 2293 | |
| 1444.2 | Q | 2323 | |
| 1464 | P | 2625 | |
| 1515(?) | | 2972 | (ethane- d_x) |
| 1577 | P | 3033 | |
| 1598.2 | Q | 3078 | |
| 1618 | R | | |

Note.—Frequencies marked with Q and those unmarked as to branch are labeled in Fig. 1. Region from 1400 to 1800 cm^{-1} uncertain due to H_2O absorption.

Table IV. Records were obtained at six pressures from 12 to 700 mm. Evidence of the band is faintly observable at 50 but not at 12 mm.

MATHEMATICAL MACHINERY

Normal Coordinates

For our analysis we shall need the mathematical relations among the frequencies. The method employed in obtaining these is that of Wilson.¹ As valence-force coordinates, R , we select the five interatomic distances

| U | r_{12} | r_{13} | r_{15} | r_{24} | r_{26} | $r_0\alpha_1$ | $r_0\alpha_2$ | $r_0\beta_1$ | $r_0\beta_2$ | $\Gamma r_0\eta_1$ | $\Gamma r_0\eta_2$ | $\Sigma r_0\delta$ |
|------------------|----------|---------------|----------------|----------------|----------------|---------------|---------------|--------------|---------------|--------------------|--------------------|--------------------|
| $A_{1g}: S_1$ | 0 | $\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| S_2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| S_3 | 0 | 0 | 0 | 0 | 0 | $1/\sqrt{2}$ | $1/\sqrt{2}$ | 0 | 0 | 0 | 0 | 0 |
| $A_{1u}: S_4$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |
| $B_{1g}: S_5$ | 0 | $\frac{1}{2}$ | $-\frac{1}{2}$ | $-\frac{1}{2}$ | $\frac{1}{2}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| S_6 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | $1/\sqrt{2}$ | $-1/\sqrt{2}$ | 0 | 0 | 0 |
| $B_{1u}: S_7$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | $1/\sqrt{2}$ | $1/\sqrt{2}$ | 0 |
| $B_{2g}: S_8$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | $1/\sqrt{2}$ | $-1/\sqrt{2}$ | 0 |
| $B_{2u}: S_9$ | 0 | $\frac{1}{2}$ | $-\frac{1}{2}$ | $\frac{1}{2}$ | $-\frac{1}{2}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| S_{10} | 0 | 0 | 0 | 0 | 0 | 0 | 0 | $1/\sqrt{2}$ | $1/\sqrt{2}$ | 0 | 0 | 0 |
| $B_{3u}: S_{11}$ | 0 | $\frac{1}{2}$ | $\frac{1}{2}$ | $-\frac{1}{2}$ | $-\frac{1}{2}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| S_{12} | 0 | 0 | 0 | 0 | 0 | $1/\sqrt{2}$ | $-1/\sqrt{2}$ | 0 | 0 | 0 | 0 | 0 |

Following Wilson's procedure, we obtain the following factored F and G matrices (\bar{F} , \bar{G}) arranged for study of the hydrogen-deuterium isotopic molecules. The original F matrix included all interaction terms; the zeros in \bar{F} are required by symmetry if our valence-force coordinates are used in defining the potential.

In addition to the elements in the \bar{G} matrix in Table V, there are certain off-diagonal "perturbation" terms. All of these elements vanish for V_h symmetry (C_2H_4 , C_2D_4) but some will not for the ethylenes having less symmetry. Whenever such an element does not vanish, the two (or more) so "linked" species of V_h combine to form one species of the new point group (C_{2v} , C_{2h} , or C_s). These off-diagonal sub-matrices are given in Table VI.

between bonded atoms plus the following seven angles: $\alpha_i = HC_iH$ angle; $\beta_i =$ angle between C—C bond and bisector of the C_iH_2 angle; $\eta_i =$ angle between C—C bond and C_iH_2 plane; $\delta =$ angle between the two CH_2 planes caused by rotation about a common axis which includes the C atoms. The numbering of the atoms is shown in Fig. 5.

Symmetry coordinates, S , obtained from these valence-force coordinates by the matrix transformation, $S = UR$, are identified by use of the orthogonal U matrix shown.

In our calculations, we took $\alpha = 119^\circ 55'$, $r_{12}^0 = 1.353A$, $r_{13}^0 = 1.071A$; we used atomic weights on the chemical scale, and the Birge 1941 values of the physical constants.²

Anharmonic Correction

Because of the lack of agreement of the isotopic relations for species B_{3u} where the frequencies of both C_2H_4 and C_2D_4 are precisely known, and the good agreement in species B_{1u} (also B_{2g}) where frequencies are also precisely known, we felt that an anharmonic correction was necessary but that it should be applied only to the C—H (C—D) bond-stretching vibrations. We used the following arbitrary procedure: (i) Assume all the anharmonicity arises from bond-stretching vibrations

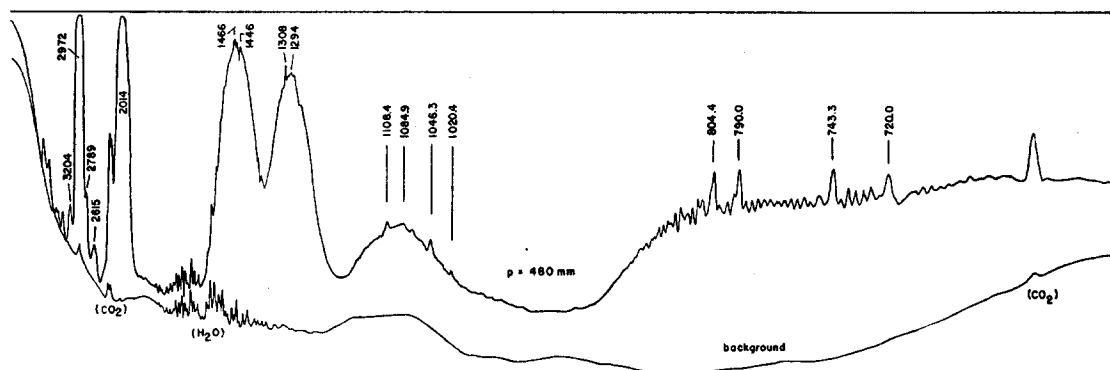


FIG. 3. Spectrum of deuterated ethane mixture (NaCl). Cell length 10 cm.

¹ E. B. Wilson, Jr., J. Chem. Phys. 7, 1047 (1939); 9, 76 (1941).

² R. T. Birge, Rev. Mod. Phys. 13, 233 (1941).

TABLE III. Ethane- d_x absorption maxima (Fig. 3).

| | | | |
|--------|--------|---------|---------|
| 720.0Q | 766.3 | 804.4Q | 1046.3Q |
| 726.9 | 769.8 | 810.9 | 1084.9Q |
| 730.1 | 773.5 | 813.6 | 1108.4Q |
| 733.7 | 776.9 | 816.4 | 1294Q |
| 736.6 | 779.8 | 819.5 | 1308Q |
| 739.8 | 783.0 | 823.7 | 1446Q |
| 743.3Q | 786.6 | 826.9 | 1466Q |
| 749.9 | 790.0Q | 831.7 | 2014Q |
| 754.2 | 792.8 | 834.7 | 2615Q |
| 756.9 | 796.1 | 837.7 | 2789Q |
| 759.8 | 801.1 | 1020.4Q | 2972Q |
| 763.1 | | | 3204Q |

Note.—Frequencies marked with Q are positions of maxima labeled in Fig. 3.

involving H or D atoms. (ii) For the anharmonic vibrations so defined, we use the relation between observed, ω_0 , and harmonic, ω_e , frequencies found to hold for diatomic molecules; i.e. (for fundamentals), $\omega_0 = \omega_e - 2x_e\omega_e$. (iii) Assume the anharmonic correction, x_e , is constant for all defined anharmonic vibrations.

The constant, x_e , may be found with the aid of isotopic molecules. If we let primes refer to the heavier molecule and let ρ be the mass function relating ω_e and ω_e' ($\omega_e' = \rho\omega_e$), we have for the two isotopic molecules³

$$\omega_0' = \rho\omega_e(1 - 2\rho x_e); \quad \omega_0 = \omega_e(1 - 2x_e)$$

and from the ratio ω_0'/ω_0 ,

$$x_e = (\rho - r)/2(\rho^2 - r),$$

where $r = \omega_0'/\omega_0$. On applying this to species B_{3u} of C_2H_4 and C_2D_4 , we find $x_e = 0.0445$.

INTERPRETATION OF OUR DATA

Previous work on C_2H_4 and C_2D_4 ⁴ has established eight of the twelve fundamentals beyond question (see Table IX). The values of the twisting frequency $\omega_4(A_{1u})$, the planar rocking frequencies $\omega_{10}(B_{2u})$ and $\omega_6(B_{1g})$, and the CH stretching frequency $\omega_5(B_{1g})$ were still far from certain.

Deuterated Ethylenes

In the sample prepared here, all seven isotopic ethylenes are present: C_2H_4 , C_2H_3D , *cis*-, *trans*-, and

TABLE IV. Line positions in the 810.3-cm⁻¹ C_2H_4 band (Fig. 4).

| K | $\nu_Q(K)$ | K | $\nu_Q(K)$ |
|---|------------|----|------------|
| 1 | 805.7 | | 744.9 |
| 2 | 796.2 | 8 | 738.6 |
| 3 | 786.8 | 9 | 728.7 |
| 4 | 777.7 | 10 | 718.4 |
| 5 | 767.9 | 11 | 708.2 |
| 6 | 758.4 | | 696.6 |
| 7 | 748.7 | | |

³ G. Herzberg, *Diatomic Molecules* (Prentice-Hall, Inc., New York, 1939), pp. 152.

⁴ Thoroughly discussed and summarized by G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., New York, 1945), p. 325.

asymmetric- $C_2H_2D_2$, C_2HD_3 , and C_2D_4 . A convincing detailed interpretation of the spectrum obtained is possible only for those bands lying in the range 700 cm⁻¹ to 1000 cm⁻¹. There are twelve bands observed in this region, all with prominent Q branches. Also, the rotational spacings are such as to enable the positive identification of each as a Type C band. (Since the moments of inertia of the less symmetric isotopic ethylenes are intermediate between those of C_2H_4 and C_2D_4 , their absorption bands may be expected to be similar to those known for C_2H_4 and C_2D_4 .) No other Type C bands were observed in the range investigated, 420 cm⁻¹ to 3300 cm⁻¹. Our analysis is therefore limited to the Type C bands.

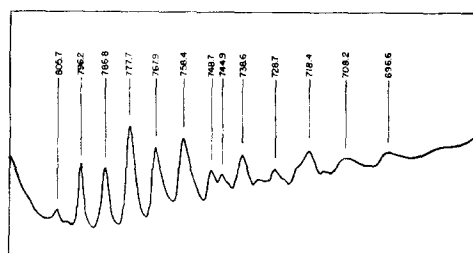


FIG. 4. The 810.3-cm⁻¹ band in C_2H_4 . Cell length 10 cm ($p = 700$ mm Hg.).

The use of measured rotational spacings to identify the molecular species causing an observed band is impractical for the spectra presented here. Firstly, the bands are so close together that identification of the subbands is impossible; secondly, the expected differences among the spacings are so small as to be almost within the precision of the measurements. We turn then to the secular equations for aid in the interpretation.

Type C bands correspond, for all the isotopic molecules, to the non-planar vibrations, ω_4 , ω_7 , ω_8 . Not all are allowed in every case, of course, but it appears reasonable that our twelve observed bands are due to these vibrations. Consequently, they should be related through the mass factors and three potential constants, one of which is already known accurately from the known value of ω_7 in C_2H_4 and C_2D_4 . Another is known approximately from the Raman observation of ω_8 , but liquid frequencies may be shifted somewhat. We should therefore be able to account for these 12 observed bands in terms of (say) one-and-a-half adjustable parameters, the force constants. We proceed along this line.⁵

The equations which relate the frequencies of the several isotopic molecules to the appropriate masses and force constants are obtained from the \tilde{F} and \tilde{G} matrices. On substituting numerical values in the \tilde{G} matrix, these equations for the non-planar frequen-

⁵ We may note that, since we use the most general potential function, there is no question here of "estimated" or "transferred" force constants. The only neglect here is of anharmonic corrections.

cies are:

| C_2H_4 | C_2D_4 |
|--|--|
| $A_{1u}: (\omega_4)^2 = 16.844148\Delta$ | $A_{1u}': (\omega_4)^2 = 8.428463\Delta$ |
| $B_{1u}: (\omega_7)^2 = 9.835438H_1$ | $B_{1u}': (\omega_7)^2 = 5.627595H_1$ |
| $B_{2g}: (\omega_8)^2 = 12.963655H_2$ | $B_{2g}': (\omega_8)^2 = 8.755812H_2$ |

In these equations as in all the subsequent numerical work, the square of the frequency is in units of 10^5 cm^{-2} and the force constants are in units of 10^5 dynes/cm .

From the accurate values of ω_7 for C_2H_4 and C_2D_4 (949.85 and 720.30 cm^{-1} , respectively) we find $H_1 = 0.918996$ as the arithmetic mean of (B_{1u}) and (B_{1u}') .

This value of H_1 is put into the equations of the other molecules so that only the constants Δ and H_2 appear as undetermined. These remaining equations follow with the selection rules indicated:

$$\text{trans-}C_2H_2D_2(A_u IR; B_g R)$$

$$\begin{aligned} A_u: (\omega_4)^2 + (\omega_7)^2 &= 12.636305\Delta + 7.105232 \\ (\omega_4)^2(\omega_7)^2 &= 81.648039\Delta \\ B_g: (\omega_8)^2 &= 10.859731H_2 \end{aligned}$$

$$\text{cis-}C_2H_2D_2(B_2 IR; A_2 R)$$

$$\begin{aligned} A_2: (\omega_4)^2 + (\omega_8)^2 &= 12.636305\Delta + 10.859731H_2 \\ (\omega_4)^2(\omega_8)^2 &= 128.373904\Delta H_2 \\ B_2: (\omega_7)^2 &= 7.731516H_1 = 7.105232 \end{aligned}$$

$$\text{asym-}C_2H_2D_2(B_2 IR; A_2 R)$$

$$\begin{aligned} A_2: (\omega_4)^2 &= 12.636305\Delta \\ B_2: (\omega_7)^2 + (\omega_8)^2 &= 7.105232 + 10.859731H_2 \\ (\omega_7)^2(\omega_8)^2 &= 73.092987H_2 \end{aligned}$$

$$C_2H_3D(A'' IR, R)$$

$$\begin{aligned} A'': (\omega_4)^2 + (\omega_7)^2 + (\omega_8)^2 &= 14.740227\Delta + 11.911689H_2 \\ &+ 8.071980 \\ (\omega_4)^2[(\omega_7)^2 + (\omega_8)^2] + (\omega_7)^2(\omega_8)^2 &= 116.948856\Delta \\ &+ 95.133934H_2 + 173.367757\Delta H_2 \\ (\omega_4)^2(\omega_7)^2(\omega_8)^2 &= 1355.923353\Delta H_2 \end{aligned}$$

$$C_2HD_3(A'' IR, R)$$

$$\begin{aligned} A'': (\omega_4)^2 + (\omega_7)^2 + (\omega_8)^2 &= 10.532384\Delta + 9.807768H_2 \\ &+ 6.138485 \\ (\omega_4)^2[(\omega_7)^2 + (\omega_8)^2] + (\omega_7)^2(\omega_8)^2 &= 62.618920\Delta \\ &+ 59.187856H_2 + 101.085936\Delta H_2 \\ (\omega_4)^2(\omega_7)^2(\omega_8)^2 &= 594.133947\Delta H_2. \end{aligned}$$

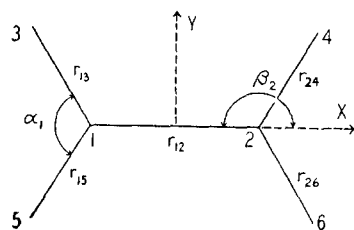


FIG. 5. Coordinates for ethylene.

Now ω_7 of *cis*- $C_2H_2D_2$ is immediately given; we find $\omega_7 = 842.93 \text{ cm}^{-1}$. A strong band is observed at 842.1 cm^{-1} and we unhesitatingly assign it to ω_7 (*cis*- $C_2H_2D_2$).

To make any further assignments it is necessary to know the constants Δ and H_2 . Let us examine the equations for species A_u of *trans*- $C_2H_2D_2$, where only Δ enters. There are here two independent relations in the three unknown quantities ω_4 , ω_7 , and Δ . By eliminating Δ we obtain one relation containing the symmetric pair ω_4 and ω_7 ,

$$(\omega')^2 = 6.461385(\omega^2 - 7.105232)/(\omega^2 - 6.461385)$$

where one member of the pair is designated by ω' and the other by ω . We may now take an observed frequency as one member of the pair and calculate its companion. If we do this for all observed frequencies (Table I) of the appropriate magnitude, then only the ones whose calculated companions fall reasonably near an observed band are eligible for assignment to the A_u species of *trans*- $C_2H_2D_2$.

In like manner the constant, H_2 may be eliminated from the equations for species B_2 of *asym*- $C_2H_2D_2$ to obtain an equation relating ω_7 and ω_8 for that molecule. The equation so obtained is used to assign the two frequencies for this species.

Having now tentative assignments for A_u (*trans*- $C_2H_2D_2$) and B_2 (*asym*- $C_2H_2D_2$), the force constants Δ and H_2 are calculated and used in turn in the equation for species A'' of C_2HD_3 and C_2H_3D as a check on the previous work and to complete the assignment. The resulting assignment of all the observed Type C bands is shown in Table I, while the calculated frequencies for the non-planar vibrations of all the ethylenes are compared with observed values, where this is possible, in Table VII.

It is apparent from the calculated values that the frequencies ω_8 of C_2H_3D and *asym*- $C_2H_2D_2$ are very close together, perhaps within a few tenths of a wave number. The same can be said for ω_7 of C_2HD_3 and *trans*- $C_2H_2D_2$. Thus with the resolution obtained in these measurements, the 943.0 band may represent both C_2H_3D and *asym*- $C_2H_2D_2$, while the broad (as it appears on our records) 725.1 band may also break into two Q branches under better resolution. We feel that the intensity of bands from the di-deuterium molecules will be greater than those from the mono- and tri-deuterium compounds,⁶ therefore the 725.1 cm^{-1} band is assigned to ω_7 .

⁶ According to an intensity sum rule derived by B. L. Crawford, Jr. (in press) for isotopic molecules, the sum of the integrated intensities of all ethylene bands in a given symmetry species is equal to the same quantity for an isotopic molecule of the same total symmetry; the integrated intensities being weighted by the inverse squares of the frequencies of the bands involved. In C_2H_4 and C_2D_4 (point group V_h) this intensity is concentrated in one band (ω_7); in *trans*- $C_2H_2D_2$ and in *asym*- $C_2H_2D_2$, this intensity is distributed among two bands (ω_4 , ω_7 for the former and ω_7 , ω_8 for the latter), while the mono- and tri-deuterated compounds have three active bands to absorb the intensity. Although overlapping of the observed bands and lack of knowledge as to the composition of the gas mixture prevent a quantitative application of the intensity rule, one may base qualitative arguments on it leading to the conclusion stated in the text.

TABLE V.*

| Species | Coordinate | \bar{F} | \bar{G} |
|----------|------------|--|--|
| A_{1g} | S^1 | $\begin{bmatrix} K_1 & 2k_2^1 & \sqrt{2}k_1 \\ K_0 & & \sqrt{2}k_6^1 \\ & & A_1 \end{bmatrix}$ | $\begin{bmatrix} (\mu_1' + \mu_2')/4 + c/M & -2\Gamma/M & -\sqrt{2}s/M \\ & 2/M & 2\sqrt{2}\Sigma/M \\ & & (\mu_1' + \mu_2')/2 - 2c/M \end{bmatrix}$ |
| | S^2 | | |
| | S^3 | | |
| A_{1u} | S^4 | $[\Delta]$ | $[(m_1' + m_2')/4]$ |
| B_{1g} | S^5 | $\begin{bmatrix} K_2 & 0 \\ & B_1 \end{bmatrix}$ | $\begin{bmatrix} (\mu_1' + \mu_2')/4 - c/M & -\sqrt{2}(2\rho + \Gamma)\Sigma/M \\ & (m_1' + m_2')/8 + (2\rho + \Gamma)^2/M \end{bmatrix}$ |
| | S^6 | | |
| B_{1u} | S^7 | $[H_1]$ | $[(m_1' + m_2')/8 + 1/M]$ |
| B_{2g} | S^8 | $[H_2]$ | $[(m_1' + m_2')/8 + (1 + 2\rho\Gamma)^2/M]$ |
| B_{2u} | S^9 | $\begin{bmatrix} K_3 & 0 \\ & B_2 \end{bmatrix}$ | $\begin{bmatrix} (\mu_1' + \mu_2')/4 - c/M & -\sqrt{2}s/2M \\ & (\mu_1' + \mu_2')/8 + c/2M \end{bmatrix}$ |
| | S^{10} | | |
| B_{3u} | S^{11} | $\begin{bmatrix} K_4 & \sqrt{2}k_2 \\ & A_2 \end{bmatrix}$ | $\begin{bmatrix} (\mu_1' + \mu_2')/4 + c/M & -\sqrt{2}s/M \\ & (\mu_1' + \mu_2')/2 - 2c/M \end{bmatrix}$ |
| | S^{12} | | |

* Symbols are defined under Table VI.

of *trans*-C₂H₂D₂ (rather than C₂HD₃) and 943.0 cm⁻¹ to ω_8 of *asym*.-C₂H₂D₂ (rather than C₂H₃D).

The sample of C₂D₄ used by Gallaway and Barker⁷ contained some C₂HD₃. The Type C band measured by them to be 919.0 cm⁻¹ and assigned to C₂HD₃ is unquestionably the same band we observed at 918.0 cm⁻¹. The band they observed at 723.38 cm⁻¹ was assigned by them to $2\omega_7 - \omega_7$ of C₂D₄, but in the light of the additional data of this research we assign it to ω_7 of C₂HD₃ and so enter it in Table VII. Indeed, the presence of the two bands (723.38 and 763.8 cm⁻¹) of

C₂HD₃ within the structure of the 720.30 band of C₂D₄ would adequately account for the complex structure of the latter observed by Gallaway and Barker.

One other observed frequency listed in Table VII needs comment here, namely, ω_8 of *trans*-C₂H₂D₂. The value given here is that of a Raman shift reported by deHemptinne, Jungers, and Delfosse⁸ in a mixture of partially deuterated ethylenes.

The force constants used in this frequency computation are given in Table VIII together with the coordinates appropriate to these numerical values.

TABLE VI. Perturbation sub-matrices of the \bar{G} matrix.

| | | | |
|----------|--|--|---|
| A_{1g} | B_{1g} | B_{2u} | B_{3u} |
| | $\begin{bmatrix} (m_1'' - m_2'')/4 & 0 \\ 0 & 0 \\ 0 & -(m_1'' - m_2'')/4 \end{bmatrix}$ | $\begin{bmatrix} (m_1'' + m_2'')/4 & 0 \\ 0 & 0 \\ 0 & -(m_1'' + m_2'')/4 \end{bmatrix}$ | $\begin{bmatrix} (m_1' - m_2')/4 & 0 \\ 0 & 0 \\ 0 & (m_1' - m_2')/2 \end{bmatrix}$ |
| A_{1u} | B_{1u} | B_{2g} | |
| | $[\sqrt{2}s(m_1'' - m_2'')/8]$ | $[\sqrt{2}(m_1'' + m_2'')/8]$ | |
| B_{1g} | B_{2u} | B_{3u} | |
| | $\begin{bmatrix} (m_1' - m_2')/4 & 0 \\ 0 & (m_1' - m_2')/8 \end{bmatrix}$ | $\begin{bmatrix} (m_1'' + m_2'')/4 & 0 \\ 0 & -(m_1'' + m_2'')/4 \end{bmatrix}$ | |
| B_{1u} | B_{2g} | B_{3u} | |
| | $[(m_1' - m_2')/8]$ | | |
| B_{2u} | | B_{3u} | |
| | | $\begin{bmatrix} (m_1'' - m_2'')/4 & 0 \\ 0 & -(m_1'' - m_2'')/4 \end{bmatrix}$ | |

Note.—

α = equilibrium value of H-C-H angle.
 $\Gamma = \cos \alpha/2$, $c = \cos \alpha$.
 $\Sigma = \sin \alpha/2$, $s = \sin \alpha$.
 ρ = ratio of equilibrium C-H to C-C distance.
 m_i = mass of i 'th hydrogen atom.
 M = mass of carbon atom.
 $1/\mu_i = 1/m_i + 1/M$.

$m_1' = 1/m_3 + 1/m_5$.
 $m_1'' = 1/m_3 - 1/m_5$.
 $m_2' = 1/m_4 + 1/m_6$.
 $m_2'' = 1/m_4 - 1/m_6$.
 $\mu_1' = 1/\mu_3 + 1/\mu_5$.
 $\mu_1'' = 1/\mu_3 - 1/\mu_5$.
 $\mu_2' = 1/\mu_4 + 1/\mu_6$.
 $\mu_2'' = 1/\mu_4 - 1/\mu_6$.

⁷ W. S. Gallaway and E. F. Barker, J. Chem. Phys. 10, 88 (1942).⁸ deHemptinne, Jungers, and Delfosse, J. Chem. Phys. 6, 319 (1938).

The 810.3-cm⁻¹ C₂H₄ Band

We have reexamined the low frequency C₂H₄ band reported by Rasmussen and Brattain⁹ and by Thompson and Harris.¹⁰ In general contour, this band (Fig. 4) has the appearance of one branch (the *P*) of a Type *B* band; particularly when compared with the resolved curve of this species (ω_9 at 3105.5 cm⁻¹) obtained by Gallaway and Barker. Through this comparison we make the assignment of the observed lines given in Table IV. The distinct alternating intensity of the sub-bands leaves no choice as to which lines have an even value of *K* so that a comparison of the contour of this band with that of its species companion makes the assignment given almost unavoidable.

The position of the band center, ω_0 , is found from the equation

$${}^PQ(K) = \omega_0 + (A' - \bar{B}') - 2(A' - \bar{B}')K + [(A' - \bar{B}') - (A'' - \bar{B}'')]K^2 \quad (1)$$

given by Herzberg¹¹ for asymmetric tops. Here *A*, *B*, and *C* are ($h/8\pi^2c$) times the reciprocals of the principal moments of inertia *I_a*, *I_b*, and *I_c*, respectively; primes refer to the upper and double primes to the lower vibrational states and \bar{B} is the arithmetic mean of *B* and *C*. By taking the difference ${}^PQ(K) - {}^PQ(K+1)$ the rotational spacing is given as a linear function of *K*. The data in Table IV were fitted to this function by the method of least squares yielding $A' - \bar{B}' = 4.555$ and $A'' - \bar{B}'' = 4.609$. On substituting these values in (1), the band center is determined from each line. The arithmetic mean of these is 810.3 cm⁻¹.

TABLE VII. Non-planar vibrational frequencies of all the ethylenes.

| | C ₂ H ₄ | C ₂ H ₂ D ₂ | C ₂ H ₂ D ₂ | C ₂ H ₂ D ₂ | C ₂ H ₂ D ₂ | C ₂ H ₂ D ₂ | C ₂ D ₄ |
|-------------------|-------------------------------|--|--|--|--|--|-------------------------------|
| ω_4 (obs.) | — | 999.4 | 987.0 | (—) | (—) | 763.8 | — |
| (calc.) | 1026.9 | 1001.8 | 990.0 | 981.6 | 889.4 | 759.8 | 726.4 |
| ω_7 (obs.) | 949.85 | 807.4 | 725.1 | 842.1 | 750.7 | 723.38 | 720.30 |
| (calc.) | 950.7 | 804.5 | 722.2 | 842.9 | 747.9 | 722.1 | 719.2 |
| ω_8 (obs.) | (943) | — | (863.4) | (—) | 943.0 | 918.0 | (780.0) |
| (calc.) | 942.0 | 945.8 | 862.2 | 755.7 | 945.9 | 919.7 | 774.2 |

Note.—Values in parenthesis are liquid-phase Raman observations. The root-mean-square deviation is 2.7 cm⁻¹ for the 15 instances where comparison is possible.

TABLE VIII. Force constants involved in the non-planar vibrations ($\Delta = 0.6260$; $H_1 = 0.9190$; $H_2 = 0.6846$).

| Coordinate | $\Sigma r_0 \delta$ | $\Gamma r_0 \eta_1$ | $\Gamma r_0 \eta_2$ |
|---------------------|---------------------|---------------------|---------------------|
| $\Sigma r_0 \delta$ | 0.6260 | 0 | 0 |
| $\Gamma r_0 \eta_1$ | 0 | 0.8018 | 0.1172 |
| $\Gamma r_0 \eta_2$ | 0 | 0.1172 | 0.8018 |

Note.—Values in units of 10⁶ dynes/cm.

⁹ R. W. Rasmussen and R. Robert Brattain, J. Chem. Phys. **15**, 120 (1947).

¹⁰ H. W. Thompson and G. P. Harris, Trans. Faraday Soc. **40**, 295 (1944).

¹¹ G. Herzberg, reference 4, p. 424.

FINAL ASSIGNMENTS FOR C₂H₄ AND C₂D₄

As pointed out earlier, the assignments of eight C₂H₄ fundamentals have been unquestionably correct and need no further comment here. Of the four uncertain frequencies, one, Raman active ω_5 , is not settled by this research. The other three are ω_4 (twisting, inactive), ω_6 (Raman-active but unobserved), and ω_{10} (infra-red-active). The twisting frequency has now been established by our work at 1027 cm⁻¹ and is most probably correct to within three wave numbers.

There have been two observed bands vying for ω_{10} . Gallaway and Barker⁷ assigned 995 cm⁻¹ as the frequency of this vibration while Rasmussen and Brattain⁹ would have it at 800 cm⁻¹ (our work fixes the band center at 810.3 cm⁻¹). Both these bands are perpendicular and both must be fundamentals. Specifically, one must be ω_{10} and the other ω_4 made weakly active by Coriolis interaction¹² with ω_{10} and ω_{12} . Having the frequency of ω_4 (=1027 cm⁻¹), it is possible to choose Gallaway and Barker's 995 band¹³ as resulting from Coriolis perturbation and the 810.3-cm⁻¹ band as ω_{10} . Knowing ω_{10} , the frequency of ω_6 is fixed from the certain combination band, $\omega_6 + \omega_{10}$ at 2046.5 cm⁻¹; we find $\omega_6 = 1236$ cm⁻¹.¹⁴

All the C₂D₄ fundamentals (save ω_6 , ω_{10}) are satisfactorily assigned for reasons entirely analogous to the C₂H₄ molecule. The frequency of the heavier isotopic molecule corresponding to 810.3 cm⁻¹ in C₂H₄ has not been observed; from the product rule we predict that it will be detected in the KBr region centering near 586 cm⁻¹. As a matter of fact, Conn and Sutherland's¹⁵ sylvine-prism curves covering this region do show faint

TABLE IX. New fundamental frequency assignment for C₂H₄ and C₂D₄.

| Species | Activity* | Number | C ₂ H ₄ | C ₂ D ₄ |
|------------------------|----------------------|---------------|-------------------------------|-------------------------------|
| <i>A</i> _{1g} | <i>R</i> , <i>p</i> | ω_1 | 3019.3 | 2251 |
| | | ω_2 | 1623.3 | 1515 |
| | | ω_3 | 1342.4 | 981 |
| <i>A</i> _{1u} | <i>I</i> <i>n</i> | ω_4 | 1027 | 726 |
| | | ω_5 | 3272.3 | 2304 |
| <i>B</i> _{1g} | <i>R</i> , <i>d</i> | ω_6 | 1236 ^a | 1009 ^b |
| | | ω_7 | 949.2 | 720.0 |
| <i>B</i> _{2g} | <i>IR</i> , <i>C</i> | ω_8 | 943 | 780 |
| <i>B</i> _{2u} | <i>R</i> , <i>d</i> | ω_9 | 3105.5 | 2345 |
| | | ω_{10} | 810.3 | 586 ^c |
| <i>B</i> _{3u} | <i>IR</i> , <i>A</i> | ω_{11} | 2989.5 | 2200.2 |
| | | ω_{12} | 1443.5 | 1077.9 |

* *R* = Raman, *IR* = infra-red, *I**n* = inactive; *p*, *d* = polarized, depolarized; *A*, *B*, *C* refer to band type.

^a Calculated from $\omega_6 + \omega_{10} = 2046.5$ for C₂H₄.

^b Calculated from $\omega_6 + \omega_{10} = 1595.1$ for C₂D₄.

^c Calculated from product rule.

¹² See G. Herzberg, reference 4, p. 467.

¹³ The most prominent maximum in this band occurs at 1028 cm⁻¹ (private communication from Professor Barker).

¹⁴ This assignment was transmitted to Professor D. H. Rank who was making polarization measurements on the Raman shifts of C₂H₄. He found a hitherto unreported line at 1236 ± 3 cm⁻¹ (see preceding paper, Rank, Shull, and Axford, J. Chem. Phys. **18**, 116 (1950)).

¹⁵ G. K. T. Conn and G. B. B. M. Sutherland, Proc. Roy. Soc. **A172**, 172 (1939).

TABLE X. Isotopic check on the assignment.

| Species | Observed | Theoretical | % difference |
|-----------------------------|----------|-------------|--------------|
| A_{1g} | 0.4952 | 0.5004 | 1.03 |
| A_{1u} | 0.7069 | 0.7074 | — |
| B_{1g} | 0.5606 | 0.6046 | 7.28 |
| B_{1g} (ω_6 only) | 0.8163 | 0.8107 | 0.69 |
| B_{1u} | 0.7585 | 0.7564 | 0.28 |
| B_{2g} | 0.8271 | 0.8218 | 0.64 |
| B_{2u} | 0.5351 | 0.5351 | — |
| B_{3u} | 0.5351 | 0.5351 | — |

indications of the existence of a band here. In the KBr records of the spectrum of our isotopic mixture, we found indications of this ω_{10} in two faint maxima near 637 cm^{-1} . The spacing is about that expected for a di-deuteroethylene.

With ω_{10} set at 586 cm^{-1} , we may use the combination band $\omega_6 + \omega_{10}$ ($=1595.1\text{ cm}^{-1}$) to establish ω_6 at 1009 cm^{-1} .

This leaves only ω_5 unaccounted for. The Raman line given by C_2D_4 at 2304 cm^{-1} is the only one available for this assignment, but there are two, 3075 and 3272.3 cm^{-1} , possibilities for C_2H_4 . Originally we favored 3075 as the fundamental, assigning the higher frequency to a resonance form of species A_{1g} . Rank,¹⁶ however, has

recently shown that both the 3075 and 3272.3 lines are depolarized. Since there is no binary combination which would give a depolarized Raman line of this frequency and a ternary (or higher) combination showing in the Raman effect is not likely, we must accept the 3272.3 line as the fundamental, ω_6 , even though the product rule is not well satisfied. The 3075 line could then be ω_9 appearing in the Raman effect due to a phase-change breakdown of the selection rules as suggested by Glockler and Renfrew.¹⁷

The complete assignments are shown in Table IX and the isotopic check in Table X. In making the computations for Table X, the anharmonic correction was applied. The frequencies ω_6 , in B_{1g} , were not obtained using the isotopic relation for this species so that the product rule serves as an independent check. The difference between theory and observation is not readily accounted for. It might appear that the ω_6 assignment is bad. In order to check this, we factored off the high frequency and so obtained a "reduced" product rule¹ for B_{1g} involving ω_6 only; this is also listed in Table X and it is seen that the agreement is good.

We have yet to discover what disposition is to be made of the remaining observed infra-red and Raman

TABLE XI. Assignment of infra-red absorption bands of C_2H_4 and C_2D_4 .

| Type | Intensity | Coblentz* (1905) | C_2H_4 L. + M.* (1928) | G. + B.* (1942) | Calc. | Assignment | C_2D_4 C. + S.* (1939) | G. + B.* (1942) | Calc. |
|------|-----------|---------------------|--------------------------------|---------------------|--------|---|--------------------------------|---------------------|-------|
| ? | w. | 847 | | | | $\omega_{10}B_{2u}$ | | | |
| C | v.s. | 952 | 949.5 | 949.20 ⁺ | | ω_7B_{1u} | 721.4 | 720.00 ⁺ | |
| C | s. | | | | | $t-C_2H_5D_2$ | 726.7 | | |
| B, C | v.w. | | | 995 | | ω_4A_{1u} | | | |
| C | | | | | | C_2HD_3 | | 919.0 ⁺ | |
| A | s. | | 1443.5 | | | $\omega_{12}B_{3u}$ | 1080.3 | 1077.9 | |
| A | | | | | | C_2HD_3 | 1291.5 | 1289.1 | |
| B | | 1724 | | 1766 | | impurity | | | |
| A | m. | 1887 | 1889.2 | 1889.6 ⁺ | 1892 | $\omega_7 + \omega_8B_{3u}$ | 1496.9 | 1495.7 ⁺ | 1500 |
| A | w. | | 2046.5 | | a | $\omega_6 + \omega_{10}B_{3u}$ | | 1595.1 ⁺ | a |
| ? | w. | 2315 | | | | impurity | | | |
| | | | | | 2263 | $\omega_4 + \omega_6B_{1u}$ | | | |
| A | s. | 3049 | 2987.4 | 2989.5 ⁺ | | $\omega_{11}B_{3u}$ | 2198 | 2200.2 ⁺ | |
| B | s. | | 3106.6 | 3105.5 ⁺ | | ω_8B_{2u} | 2353 | 2345 | |
| C | s. | | | | | $\omega_1 + \omega_7B_{1u}$ | 2969 | | 2971 |
| | | | | | | C_2HD_3 | | 3049.0 | |
| A | w. | | | | | $2\omega_8 + \omega_{12}B_{3u}$ | | | 3096 |
| | | | | | | $\omega_2 + \omega_7 + \omega_8$ | | | 3015 |
| B | w. | | 4206.7 | | 4226 | $\omega_6 + \omega_{11}B_{2u}$ | | 3204.3 | 3209 |
| A | m. | 4329 | 4323.1 | | 4303 | $\omega_2 + \omega_8 + \omega_{12}B_{2u}$ | | | |
| A | m. | | | | | $\omega_8 + \omega_9B_{3u}$ | | 3345.3 | 3354 |
| | | | | | | $\omega_1 + \omega_{12}B_{3u}$ | | | 3329 |
| B | m. | | 4514.3 | | 4510.3 | $\omega_2 + 2\omega_{12}B_{2u}$ | | | |
| B | v.w. | | 4727.7 | | 4715.8 | $\omega_5 + \omega_{12}B_{2u}$ | | 3387.8 | 3382 |
| | | | | | 4729 | $\omega_2 + \omega_9B_{2u}$ | | 3862.8 | 3860 |
| A | w. | | | | | $\omega_1 + \omega_{11}B_{3u}$ | | 4429.5 | 4451 |
| B | w. | | | | | $\omega_5 + \omega_{11}B_{2u}$ | | 4478.6 | 4504 |
| A | w. | | | | | $\omega_6 + \omega_9B_{3u}$ | | 4628.0 | 4649 |

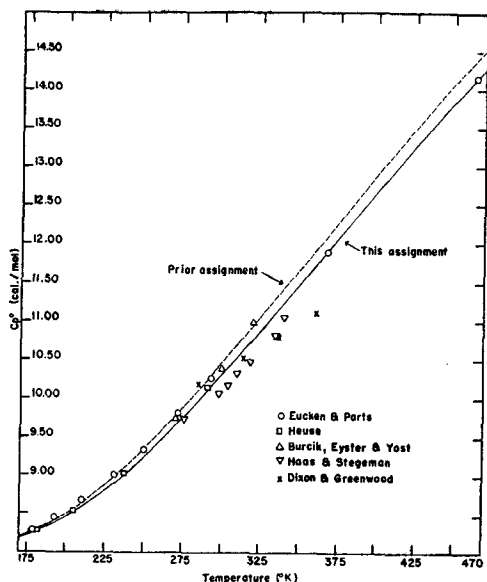
Note.—Values marked (+) indicate positions of band centers calculated from rotational structure rather than positions of minima or Q branch maxima.
* G. + B., Gallaway and Barker, reference 7; W. Coblentz, "Investigations of Infrared Spectra," Carn. Inst. Wash. Pub. No. 35, p. 45 (1905); L. + M., A. Levin and C. F. Meyer, J. Opt. Soc. Am. 16, 137 (1928); C. + S., G. K. T. Conn and G. B. B. M. Sutherland, Proc. Roy. Soc. A172, 172 (1939).

* Used to calculate ω_6 .

^b Although most workers ascribe this band of Coblentz to an impurity, it is more than likely that it is the absorption band whose center was fixed at 810.3 cm^{-1} by this work. As stated in the text, the band center has also been set at 770 cm^{-1} and at 800 cm^{-1} by Thompson and Harris and by Rasmussen and Brattain, respectively.

¹⁶ See Rank, Shull, and Axford, reference 14.

¹⁷ George Glockler and M. M. Renfrew, J. Chem. Phys. 6, 170, 409 (1938).

FIG. 6. Heat capacity of C_2H_4 .

frequencies in the light of the new assignment of fundamentals. The only Raman line whose assignment needs changing from that given by Herzberg¹⁸ is the 1656 line. Obviously it can no longer be $2\omega_4$; however it can be $2\omega_{10}$ if we allow a small positive anharmonicity so that $2\omega_{10}$ is not $1620.6 (=2 \times 810.3)$, but some value greater than 1623.3 cm^{-1} . With this, the Fermi resonance between the strong 1623.3 level and $2\omega_{10}$ may be expected to cause the latter to appear at the still higher frequency, 1656 cm^{-1} .

There are several changes necessary in the infra-red-active combination bands, most of these resulting in a reduction from quaternary to binary tones. Table XI gives the complete assignment of observed infra-red bands.

¹⁸ G. Herzberg, reference 4, p. 326.

It is interesting to make a comparison of the torsional frequencies in ethylene (1027 cm^{-1}) and allene (820 cm^{-1}). It seems reasonable to us that the greater separation (with one more intervening atom) and perpendicular configuration of the CH_2 groups in allene should result in a lower vibrational frequency than that for ethylene. The old assignment for C_2H_4 had them at the same level and made a perplexing problem for interpretation; the assignment given in Table IX removes the difficulty.

We turn now to heat-capacity data as extra-spectroscopic evidence in support of our assignment. In Fig. 6, the dotted line is the result of calculations to the harmonic-oscillator approximation using the old assignment as given by Herzberg,⁴ while the full curve results from similarly calculated values using our assignment (Table IX). The points represent the existing thermal measurements.¹⁹ The better fit over the whole temperature range is at once apparent.

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We are indebted also to Professor A. O. C. Nier for obtaining and interpreting the mass spectra for us. Without this information, the method of attack on the infra-red spectrum would not have been so immediately clear.

¹⁹ Wilhelm Heuse, *Ann. d. Physik* **59**, 86 (1919); A. Eucken and A. Parts, *Zeits. f. physik. Chemie* **B20**, 184 (1933); Burcik, Eyster, and Yost, *J. Chem. Phys.* **9**, 118 (1941); Harold B. Dixon and Gilbert Greenwood, *Proc. Roy. Soc. A* **105**, 199 (1924); Matthias E. Haas and Gebhard Stegeman, *J. Phys. Chem.* **36**, 2127 (1932).