The Experimental Determination of the Intensities of InfraRed Absorption Bands. III. Carbon Dioxide, Methane, and Ethane

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The Experimental Determination of the Intensities of Infra-Red Absorption Bands. III. Carbon Dioxide, Methane, and Ethane*

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The absolute intensities of the chief infra-red absorption bands of carbon dioxide, methane, and ethane have been determined experimentally to be (in cycles per centimeter at N.T.P.):

Carbon dioxide	Methane	Ethane
670 cm⁻¹ band: 560×10^{10}	1306 cm⁻¹ band: 450×10^{10}	820 cm⁻¹ band: 73×10^{10}
2350 cm⁻¹ band: 8600×10^{10}	3020 cm⁻¹ band: 900×10^{10}	1450 cm⁻¹ bands: 230×10^{10}
		2950 cm⁻¹ bands: 2200×10^{10}

These results are in satisfactory agreement with available data on infra-red dispersion and atomic polarization. They may be interpreted in terms of dipole moments, μ', of bonds between vibrating atoms, and their rates of change with internuclear distance, $\partial \mu'/\partial r$. When this is done for the CH bond, however, unexpected variations in these quantities are found for the different vibrations and molecules studied. The average values are about $\mu' = 0.4 \times 10^{-18}$, $\partial \mu'/\partial r = \pm 0.6 \times 10^{-10}$. For the CO bond the values are considerably larger.

INTRODUCTION

THE light transmitted a distance, L, through a gas at pressure, p, is given by Eq. (1). Here $I_0(\nu)$ is the incident intensity,

$$I(\nu) = I_0(\nu) \exp[-\alpha(\nu)pL], \qquad (1)$$

and $\alpha(\nu)$ is the absorption coefficient. The intensity of absorption is defined by Eq. (2). Here

$$A_i \equiv \int_{i\text{th band}} \alpha(\nu)d\nu, \qquad (2)$$

A_i is the absolute intensity of the ith vibrational absorption band, the integral being taken over the band in question.

Direct measurement of the intensity is difficult because $\alpha(\nu)$ and $I(\nu)$ may fluctuate considerably even over the small frequency range transmitted by an infra-red spectrograph at any setting. A spectrograph with a finite effective slit width averages $I(\nu)$ over that frequency range, and it is not possible to obtain $\alpha(\nu)$ directly from such a measurement. In previous papers an extrapolation procedure has been described for deter-

mining A_i from absorption measurements made with a spectrograph of low resolving power,[1] and the application of this method to ethylene and nitrous oxide has been discussed.[2] The results of further measurements using this method will be reported in the following sections. The experimental procedure involves measuring the apparent value of the intensity—called the "integrated apparent absorption coefficient"—as a function of the partial pressure of the absorbing gas, with an inert (non-absorbing) gas added to a constant total pressure. The limit of this "integrated apparent absorption coefficient" as the absorbing gas pressure approaches zero is the true intensity.[1] The inert gas present serves to broaden the individual lines making up the absorption band and reduce the fluctuations in $\alpha(\nu)$ which cause the "integrated apparent absorption coefficient" to deviate from the true intensity.

The absorption of light by these infra-red bands is due to changes in the dipole moment of the vibrating molecule when the atoms are displaced from their equilibrium positions. The intensities are proportional to $|\partial \mathbf{\mu}/\partial Q|^2$, where $\mathbf{\mu}$ is the dipole moment of the molecule, and Q the normal coordinate for the vibrational mode in question.[2] The complete relationship is given in Eq. (3).

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[1] E. Bright Wilson, Jr. and A. J. Wells, J. Chem. Phys. 14, 578 (1946).

[2] A. M. Thorndike, A. J. Wells, and E. Bright Wilson, Jr., J. Chem. Phys. 15, 157 (1947).

$$A_i = (N\pi/3c)\{\,|\partial\mu_x/\partial Q_i|^2$$
$$+\,|\partial\mu_y/\partial Q_i|^2 + |\partial\mu_z/\partial Q_i|^2\}. \quad (3)$$

The intensities may be interpreted in terms of the structure of the molecule by assuming that the dipole moment, **μ**, of the molecule can be regarded as the sum of dipole moments, **μ**$_i'$, of the bonds forming the molecule. With such a picture the intensities of bending modes determine μ', stretching modes $\partial\mu'/\partial r$.[2] These quantities might reasonably be expected to be characteristic properties of any particular bond, constant for different vibrations and different molecules, but the results show that this is true only as a very rough approximation.

In the following sections values are given for the intensities of the fundamental bands of CO_2, CH_4, and C_2H_6. These are interpreted in terms of the properties of CO and CH bonds.

CARBON DIOXIDE

The intensities of the carbon dioxide bands are of special interest because: (a) measurements of infra-red dispersion are available[3] which may be compared with our values for the intensities, and (b) absorption of heat by CO_2 in the atmosphere is important in meteorology. Unfortunately our measurements on CO_2 are less reliable than those on other gases because of the difficulties involved in removing atmospheric CO_2 from the optical path of our spectrograph.

The CO_2 samples were admitted directly to the absorption cell from a Matheson lecture bottle.
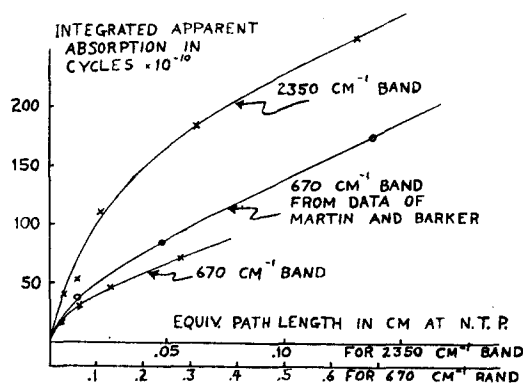

FIG. 1. Experimental data on absorption by carbon dioxide bands at a total pressure of one atmosphere.

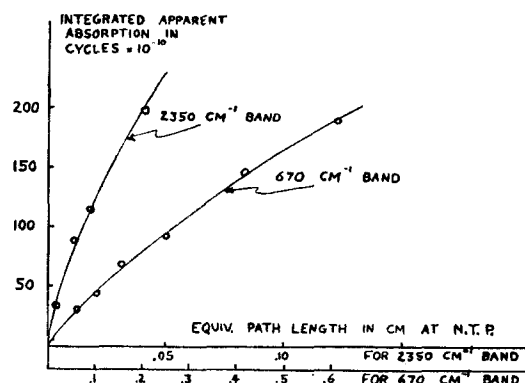[3] These are summarized by O. Fuchs, Zeits. f. Physik 46, 519 (1927).

FIG. 2. Experimental data on absorption by carbon dioxide bands at a total pressure of four atmospheres.

The broadening gas was nitrogen obtained from an Air Reduction Company high pressure cylinder. One set of measurements was made at a total pressure of one atmosphere; a second set at about four atmospheres total pressure using a pressure cell. One atmosphere was not enough to give complete pressure broadening, but was probably sufficient to give a fairly close approach to the limiting absorption curve which would have been obtained with complete broadening.

It is obviously necessary to eliminate the absorption by atmospheric CO_2 in the optical path of the spectrograph in order to measure the absorption of the CO_2 sample in the absorption cell even when a blank comparison cell is used. The presence of atmospheric CO_2 introduces an inadmissable frequency dependence of the incident intensity.[1] The atmospheric CO_2 would, in fact, absorb quite completely all frequencies corresponding to the lines in the CO_2 bands, so that addition of CO_2 in the absorption cell would have very little effect upon the transmitted light. The presence of atmospheric CO_2 would, therefore, make the absorption by the CO_2 in the sample cell much smaller than it should be.

In order to remove the CO_2 from the optical path, the spectrograph[2] was enclosed in a housing built of Masonite and plywood.*** The air inside was circulated through Drierite and Caroxite by means of a small blower. At the same time nitrogen was admitted to the housing at a rate of about 10 cubic feet per hour so as to maintain an outward flow through the many small leaks.

*** Dr. Oliver A. Schaeffer assisted in the setting up of this air-conditioning system.

TABLE I. Intensities of carbon dioxide bands
(units are cycles per cm at N.T.P.).

	670 cm^{-1}	2350 cm^{-1}
From data of Martin and Barker[a]	660×10^{10}	—
From our data with total pressure:		
1 atmosphere	560×10^{10}	7200×10^{10}
4 atmospheres	470×10^{10}	9600×10^{10}
4 atmospheres	—	8900×10^{10}[b]
Average	560×10^{10}	8600×10^{10}
From dispersion data of Fuchs[c]	538×10^{10}	7680×10^{10}

[a] See reference 4.
[b] A second set of data on the 2350 cm^{-1} band was taken giving this result.
[c] See reference 3.

This procedure, while inconvenient, reduced the CO_2 concentration so that no absorption by atmospheric CO_2 could be observed. In the first set of measurements, however, it was not possible to eliminate the atmospheric absorption completely, and it was necessary to introduce a correction for what remained.

The experimental data are given in Fig. 1 and Fig. 2. In Fig. 1 we also show a curve based on data published by Martin and Barker[4] for the 670 cm^{-1} band. Their resolving power was substantially greater than ours. Since the band at 670 cm^{-1} has a strong Q-branch, "envelope effect" is to be expected,[1] and it is likely that the difference between the two curves is due to the difference in resolving power.

The data given in Fig. 1 and Fig. 2 are values of the "integrated apparent absorption" defined by Eq. (4), where $\mathfrak{B}$ = "integrated apparent absorption,"

$$\mathfrak{B} = \int_{band} \ln(T_0/T) d\nu, \qquad (4)$$

T_0 = light transmitted by blank comparison cell, T = light transmitted by sample cell. The "integrated apparent absorption coefficient," B, defined by Eq. (5)

$$B = \mathfrak{B}/pL \qquad (5)$$

was calculated, as before,[2] from points on the smooth curves.

The resulting intensities are given in Table I. The different values are not in particularly good agreement. The experimental errors may, however, be somewhat larger for CO_2 than the 10 percent previously estimated,[2] so that the dis-

crepancies are no larger than should be expected on the basis of experimental errors.

In the case of the 670 cm^{-1} band, difference bands are listed as occurring at 618, 647, 668, 720, and 740 cm^{-1}.[5] We have not, however, tried to correct the observed intensity for contributions from these weak overlapping bands.

The comparison between our values of the intensity and those calculated from Fuchs' expression for the index of refraction is made in Table I. The agreement is satisfactory, considering the larger experimental errors for this substance.

If our intensities are used to calculate the atomic polarization, we obtain 0.68 cc. The value given by Watson and Ramaswamy[6] is 0.81 cc. Again the agreement is about as good as we expect.

The properties of the CO bond moment may readily be calculated from the observed intensities. Since the bending and stretching vibrations have different symmetry, it is only necessary to calculate the effective masses for the two modes. The final values obtained for the bond dipole moment are: $\mu' = \pm 1.17 \times 10^{-18}$, $\partial\mu'/\partial r = \pm 6.0 \times 10^{-10}$. These are similar to the results obtained for N_2O.[2]

This result for μ' may be compared with the conventional values of 2.3×10^{-18} assigned to C=O, and 0.7×10^{-18} assigned to C—O.[7] According to Pauling,[8] resonance in CO_2 involves three structures in about equal proportions:

$$
\begin{array}{ccc}
A & B & C \\
O=C=O & \overset{+}{O}\equiv C-\overset{-}{O} & \overset{-}{O}-C\equiv\overset{+}{O}
\end{array}
$$
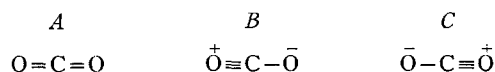
Since the formal charges cancel out, the observed value of μ' would be the average of that for single, double, and triple bonds. Our low value for μ' implies a small dipole moment of the triple bond. It is evident from the three resonant structures for CO_2 that stretching a CO bond will tend to make it a single bond (which has the greatest length), negative at the oxygen end, so

[4] P. E. Martin and E. F. Barker, Phys. Rev. 41, 291 (1932).

[5] See, for example, G. Herzberg, Infrared and Raman Spectra of Polyatomic Molecules (D. Van Nostrand Company, Inc., New York, 1945), p. 274.
[6] H. E. Watson and K. L. Ramaswamy, Proc. Roy. Soc. (London) A156, 144 (1936).
[7] S. Glasstone, Textbook of Physical Chemistry (D. Van Nostrand Company, Inc., New York, 1940), p. 542.
[8] L. Pauling, The Nature of the Chemical Bond (Cornell University Press, Ithaca, 1945), second edition, p. 196.

that $\partial\mu'/\partial r$ should be large, as it is, and negative. Since oxygen in more electronegative than carbon, we should select negative signs for both μ' and $\partial\mu'/\partial r$.

METHANE

In any study of the properties of hydrocarbons methane is a logical starting place. The intensities of the methane bands were not, however, the first to be measured, since it was anticipated that it would be very difficult to secure adequate pressure broadening for methane. The individual rotational lines would be widely spaced because of the molecule's small moment of inertia, and a pressure of one atmosphere would not be expected to provide sufficient pressure broadening. With the pressure cell, however, we were able to employ pressures up to five atmospheres. By using ammonia as a broadening gas considerably more effective pressure broadening was achieved than in the case of non-polar gases. In this way it was possible to make satisfactory measurements of intensities with methane.

The methane was used directly from a Matheson lecture bottle (C.P. grade), without further purification. Ammonia used for pressure broadening was obtained from the Ohio Chemical and Mfg. Company. The experimental data are plotted in Fig. 3. Values of the "integrated apparent absorption coefficient" calculated from these curves lead to the intensities given in Table II.

In Table II a comparison is again made with data based upon measurements of infra-red dispersion. The intensities obtained by the two methods are in good agreement, the differences being well within our experimental error.

As a final check upon these intensities for methane, we may calculate the atomic polarization from them. The result is 0.091 cc, whereas Watson and Ramaswamy[6] obtained 0.08 cc. The agreement is good.

A normal coordinate treatment of methane was made by Rollefson and Havens[9] to determine values of μ' and $\partial\mu'/\partial r$ for the CH bond. Our values are only slightly different, and were obtained by adjusting the values of Rollefson and Havens in proportion to the square root of the

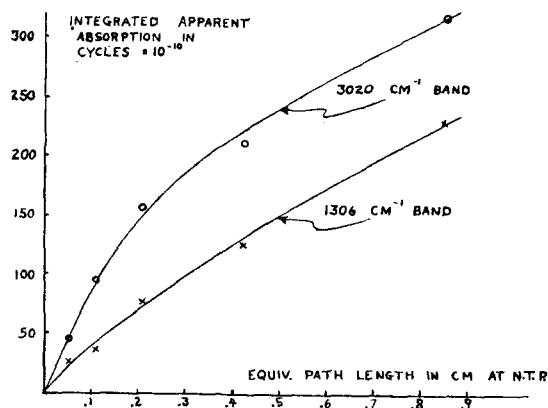[9] R. Rollefson and R. Havens, Phys. Rev. 57, 710 (1940).

FIG. 3. Experimental data on absorption by methane bands.

intensity. The results are $\mu' = 0.31 \times 10^{-18}$, $\partial\mu'/\partial r = \pm 0.55 \times 10^{-10}$.

These results are in fair agreement with the two values previously reported for the CH bond in ethylene, namely, 0.37×10^{-18} and 0.52×10^{-18} for μ', about $\pm 0.6 \times 10^{-10}$ for $\partial\mu'/\partial r$.[2] As before, the sign of $\partial\mu'/\partial r$ is undetermined. We have followed the usual convention in assuming the bond moment, μ', to be positive at the hydrogen end. Theoretical calculations by Coulson[10] led, however, to a negative value for μ'. Our results do not give any information concerning the sign of μ'.

ETHANE

Measurements were made on ethane following those on methane, since it was desired to compare the behavior of the CH bond in the two related molecules. Ethane was used from a Matheson lecture bottle without subsequent purification. One atmosphere of air was adequate as broadening gas. No attempt was made to reduce atmospheric absorption, which was appreciable only for the bands near 1400 cm^{-1}.

In these experiments it was not possible to

TABLE II. Intensities of methane bands (units are cycles per cm at N.T.P.).

Band	Intensity from these measurements	Intensity from dispersion measurements[a]
1306 cm^{-1}	450×10^{10}	444×10^{10}
3020 cm^{-1}	900×10^{10}	970×10^{10}

[a] See reference 9.

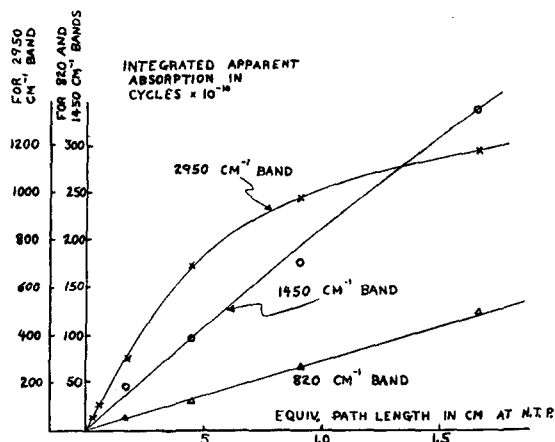[10] C. A. Coulson, Trans. Faraday Soc. 38, 433 (1937).

FIG. 4. Experimental data on absorption by ethane bands.

resolve the band at 2954 cm^{-1} from that at 2994 cm^{-1}, nor the band at 1379 cm^{-1} from that at 1486 cm^{-1}. Each of these overlapping pairs of bands is, therefore, considered as a single band in tabulations of experimental data. The frequencies are listed as 2950 cm^{-1} and 1450 cm^{-1}, respectively. The data are presented graphically in Fig. 4. Values of the "integrated apparent absorption coefficient" calculated from these curves lead to the intensities given in Table III.

Unfortunately there are no other data on ethane intensities available which could be used to confirm or deny these results. A very rough check is possible in terms of atomic polarization. Our intensities lead to a calculated atomic polarization of 0.14 cc, whereas the value given by Watson and Ramaswamy[6] is 0.09 cc. This is fairly good agreement, since small atomic polarizations could not be measured very accurately by Watson and Ramaswamy's method.

Values of the intensities of ethylene are also given in Table III. The most striking difference is in the low frequency bending mode which is

TABLE III. Intensities of ethane bands (units in cycles per cm at N.T.P.).

Band	Intensity
Ethane:	
820 cm^{-1}	73×10^{10}
1450 cm^{-1}	230×10^{10}
2950 cm^{-1}	2200×10^{10}
Ethylene:[a]	
950 cm^{-1}	1540×10^{10}
1444 cm^{-1}	210×10^{10}
3050 cm^{-1}	840×10^{10}

[a] From reference 2.

intense in ethylene but rather weak in ethane. Thus the abnormally great intensity of the out-of-plane bending mode of ethylene[11] has disappeared in ethane. The stretching modes, however, appear to be somewhat more intense for ethane than ethylene.

A more detailed interpretation of ethane intensities in terms of properties of the CH bond can be made if the intensities of the 1450 cm^{-1} and 2950 cm^{-1} "bands" are broken down into their individual components. Unfortunately, no good basis for estimating the intensities of the individual overlapping bands is available. The best published data appear to be those of Levin and Meyer[12] who, however, failed to resolve either pair completely. Qualitative estimates of the intensities are given by Herzberg.[13]

In the case of the 1379 cm^{-1} and 1486 cm^{-1} bands his estimates are "weak" and "strong," respectively. Levin and Meyer's data indicate fairly clearly that the 1379 cm^{-1} band is a good deal the weaker, and our absorption curves show a weak maximum at about 1375 cm^{-1}. As a rough estimate, therefore, we have assigned 30×10^{10} to the 1379 cm^{-1} band and 200×10^{10} to the 1486 cm^{-1} band.

In the case of the 2954 cm^{-1} and 2994 cm^{-1} bands Herzberg's designations are "strong" and "medium" respectively. The experimental data of Levin and Meyer are consistent with this estimate, but could apparently equally well arise from a weak band at 2954 and a strong one at 2994. In our data the two are completely unresolved. Qualitative consideration of the geometry of the molecule suggests, however, that the band at 2994 cm^{-1} is the stronger, since it is a perpendicular band.[14] On the basis of the

[11] Data on ethylene are discussed in detail in reference 2.
[12] A. Levin and C. F. Meyer, J. Opt. Soc. Am. 16, 137 (1928). Measurements at higher resolution have been reported (L. G. Smith and W. M. Woodward, Phys. Rev. 61, 386 (1942)) but no experimental curves given.
[13] See reference 5, p. 344.
[14] The reasoning is as follows: In the ethane molecule the CH bonds are almost perpendicular to the CC bond (the C−C−H angle being about 109°). Therefore a CH bond stretch will give rise to a contribution to μ whose component parallel to the CC bond is small and perpendicular to it is large. In a parallel type band the perpendicular components cancel out, while the parallel components add up to a small net dipole moment. In a perpendicular-type band the parallel components cancel out, while the perpendicular components add up to a large net dipole moment. Therefore the perpendicular type band should be the stronger one.

TABLE IV. Apportionment of ethane intensities.

Band	Frequency in cm^{-1}	Intensity in cycles per cm at N.T.P.	$\partial\mu/\partial Q$
ν_5	2954	200×10^{10}	$\pm\ 45.9$
ν_6	1379	30×10^{10}	$\pm\ 17.8$
ν_7	2994	$\left\{2000\times10^{10}\right.$	±103
ν_8	1486	$\tfrac{1}{2}\times\left\{200\times10^{10}\right.$	$\pm\ 32.5$
ν_9	820	$\left.7.3\times10^{10}\right.$	$\pm\ 19.7$

TABLE V. Characteristics of CH bond moment in ethane (c.g.s. units).

Type of vibration	μ'	μ'/s	$\partial\mu'/\partial r$
ν_6-bending	0.104×10^{-18} or 0.094×10^{-18}	0.096×10^{-10} or 0.086×10^{-10}	—
ν_8-bending	$0.35\ \times10^{-18}$ or $0.33\ \times10^{-18}$	$0.32\ \times10^{-10}$ or $0.30\ \times10^{-10}$	—
ν_9-bending	$0.30\ \times10^{-18}$ or $0.26\ \times10^{-18}$	$0.28\ \times10^{-10}$ or $0.24\ \times10^{-10}$	—
ν_5-stretching	—	—	$+0.69\times10^{-10}$ or -0.74×10^{-10}
ν_7-stretching	—	—	$+0.81\times10^{-10}$ or -0.74×10^{-10}

normal coordinate treatment, which will now be discussed, it was determined that the most consistent results were obtained by assigning an intensity of about 200×10^{10} to the 2954 cm^{-1} band and 2000×10^{10} to the 2994 cm^{-1} band. It should be emphasized, however, that these intensities are tentative estimates; only their sum has been accessible to direct measurement.

A simple normal coordinate treatment was carried out for ethane in order to determine the properties of the CH bond moment. It was assumed, following Howard,[15] that the potential function involves only two force constants and may be written as in Eq. (6).

$$2V=K_1\sum_i r_i^2+r_0^2K_2\left[\sum_i \beta_i^2+\sum_{jk}\alpha_{kj}^2\right]. \quad (6)$$

Here r_i=change in CH$_i$ bond distance, β_i =change in C—C—H$_i$ angle, and α_{jk}=change in H$_j$—C—H$_k$ angle. In the latter case the two hydrogens must obviously be attached to the same carbon. $K_1=4.79\times10^5$ dyne/cm, $K_2=0.46\times10^5$ dyne/cm. The method and terminology used follow that of Wilson.[16]

The configuration of the ethane molecule is uncertain to the extent that it may be either "staggered" or "eclipsed." Both lead, however, to the same relations between the observed intensities and properties of bond moments.[17] Our cal-

culations were made on the basis of the eclipsed configuration, but the final results are equally valid for the staggered case.

The symmetry coordinates for the infra-red active vibrations were taken to be:

Parallel-type modes

$$\mathfrak{R}_5=(6^{-\frac{1}{2}})(r_1+r_2+r_3-r_4-r_5-r_6),$$
$$\mathfrak{R}_6=(12^{-\frac{1}{2}})[\beta_1+\beta_2+\beta_3-\beta_4-\beta_5-\beta_6$$
$$-(\alpha_{23}+\alpha_{13}+\alpha_{12}-\alpha_{56}-\alpha_{46}-\alpha_{45})].$$

Perpendicular-type modes

$$\mathfrak{R}_{7a}=(3^{-\frac{1}{2}})[r_1+r_4-\tfrac{1}{2}(r_2+r_3+r_5+r_6)],$$
$$\mathfrak{R}_{7b}=\tfrac{1}{2}(r_2-r_3+r_5-r_6),$$
$$\mathfrak{R}_{8a}=(3^{-\frac{1}{2}})[\beta_1+\beta_4-\tfrac{1}{2}(\beta_2+\beta_3+\beta_5+\beta_6)],$$
$$\mathfrak{R}_{8b}=\tfrac{1}{2}[\beta_2-\beta_3+\beta_5-\beta_6],$$
$$\mathfrak{R}_{9a}=(3^{-\frac{1}{2}})[\alpha_{23}+\alpha_{56}-\tfrac{1}{2}(\alpha_{13}+\alpha_{12}+\alpha_{46}+\alpha_{45})],$$
$$\mathfrak{R}_{9b}=\tfrac{1}{2}(\alpha_{13}-\alpha_{12}+\alpha_{46}-\alpha_{45}).$$

In terms of these symmetry coordinates the normal coordinates are given by the transformation L^{-1} whose elements are tabulated below:

$$(L^{-1})_{55}=-1.276\times10^{-12},\quad (L^{-1})_{56}=-0.0177\times10^{-20},$$
$$(L^{-1})_{65}=+0.116\times10^{-12},\quad (L^{-1})_{66}=-0.903\times10^{-20},$$
$$(L^{-1})_{77}=1.225\times10^{-12},\quad (L^{-1})_{78}=-0.0040\times10^{-20},$$
$$(L^{-1})_{79}=0.0237\times10^{-20},$$
$$(L^{-1})_{87}=-0.0355\times10^{-12},\quad (L^{-1})_{88}=0.198\times10^{-20},$$
$$(L^{-1})_{89}=0.808\times10^{-20},$$
$$(L^{-1})_{97}=0.0914\times10^{-12},\quad (L^{-1})_{98}=-1.313\times10^{-20},$$
$$(L^{-1})_{99}=0.322\times10^{-20}.$$

[15] J. B. Howard, J. Chem. Phys. 5, 442 (1937).
[16] E. Bright Wilson, Jr., J. Chem. Phys. 9, 76 (1941).
[17] This may be shown in the following way: We can change from staggered to eclipsed forms by rotating one CH$_3$ group by 180° about the CC axis. The symmetry coordinates for vibrations parallel to this axis are unchanged, those for vibrations perpendicular to the axis must have coefficients of the internal coordinates belonging to the rotated CH$_3$ group changed in sign. For example, the symmetry coordinate $\mathfrak{R}_{7a}$ is given by $1/\sqrt{3}[r_1-r_4-\tfrac{1}{2}(r_2+r_3-r_6)]$ for the staggered case as contrasted with $1/\sqrt{3}[r_1+r_4-\tfrac{1}{2}(r_2+r_3+r_5+r_6)]$ for the eclipsed case. In order to set up the secular equation, following the method of reference 16, we calculate the vectors, S defined by Eq. (11) of reference 16 as $S_i^{(t)}=\sum_k U_{ik}s_{kt}$. In the case of $\mathfrak{R}_{7a}$ the s vectors are unit vectors along the CH bonds. The U_{ik} are coefficients which give $\mathfrak{R}_{7a}$ in terms of the r's. When one changes from eclipsed to staggered

configuration some of the s vectors change direction, but the corresponding U_{ik} coefficients change sign so that there is no net change in the S vectors or in the secular equation calculated from them. Either form for the molecule will then lead to the same set of L^{-1} coefficients (in terms of symmetry coordinates), and the same values of the $(\partial\mu/\partial\mathfrak{R}_k)$'s determined from the observed intensities. The interpretation of the $(\partial\mu/\partial\mathfrak{R}_k)$'s in terms of the $(\partial\mu/\partial R)$'s, which are properties of individual bonds, again involves the geometry of the molecule and the U_{ik} coefficients, but again in such a way that the changes in these two factors compensate in going from eclipsed to staggered form. Therefore the same results will be obtained for properties of bond moments whichever form of molecule is assumed.

The procedure for calculating the properties of bond dipole moments is the same as that previously described.[2] The perpendicular modes, ν_7, ν_8, and ν_9 are each twofold degenerate, so that only half the observed intensity should be ascribed to each member of these degenerate pairs. The resulting values of intensities and of $(\partial\mu/\partial Q)$'s are given in Table IV, $(\partial\mu/\partial Q)$'s being calculated by Eq. (3).

The values of the $(\partial\mu/\partial Q)$'s and (L^{-1})'s are substituted in Eq. (7) in order to obtain values of the $(\partial\mu/\partial\Re)$'s. From these

$$\partial\mathbf{u}/\partial\Re_k = \sum_i (\partial\mathbf{u}/\partial Q_i)(L^{-1})_{ik} \qquad (7)$$

latter and the geometry of the molecule the dipole moment, μ', and its rate of change with internuclear distance, $\partial\mu'/\partial r$, may be calculated. If we exclude negative values for the bond dipole moment as unreasonable, the final values are those given in Table V. (Here s is the equilibrium CH distance.) If $\partial\mu'/\partial r$ is positive, the choice of signs for the $(\partial\mu/\partial Q)$'s must be that leading to the top member of each pair of values in Table V. If negative, the bottom member is to be taken.

These results may be compared with those obtained for methane. The outstanding difference between the two molecules is the very low value of μ' obtained for the parallel-type band ν_6 of ethane. The intensity of this band is only about $\frac{1}{10}$ what would be required to give the expected value of μ'. The reason for this is not known and merits further investigation.[18] The values of μ' obtained from ν_8 and ν_9 agree well with that from methane, however, all being close to 0.3×10^{-18}. In the case of $\partial\mu'/\partial r$ the agreement is less satisfactory; values from ethane are about $\pm0.75\times10^{-10}$, whereas $\pm0.55\times10^{-10}$ had been obtained for methane.

These results cast some doubt upon the whole concept of additivity of bond dipole moments.

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[18] Such a large discrepancy as this could not be accounted for as an error in dividing the intensity of the "1450 cm^{-1} band" between ν_6 and ν_8. To give ν_6 ten times as much intensity we would have to assign to it all the intensity of the "1450 cm^{-1} band" and more, leaving nothing at all for ν_8.

It would seem that the apparent values of μ' and $\partial\mu'/\partial r$ change so much from one molecule to another and one type of vibration to another that strong interactions with neighboring bonds must frequently occur. One might think, however, that our normal coordinate treatment of ethane has been too simple. The potential function with only two force constants does not give very good solutions for the secular equation, and may introduce very considerable approximations in the normal coordinates. Nevertheless the fact remains that the stretching modes are, relatively, too intense in ethane, and the bending modes too weak. The conclusions concerning μ' and $\partial\mu'/\partial r$ are actually not at all sensitive to changes in the normal coordinate treatment.

CONCLUSIONS

Two fairly definite conclusions may be drawn from the results summarized in this and the preceding paper:

(1) Our intensities, obtained by direct measurement of absorption employing an extrapolation to zero absorption, are in satisfactory agreement with results obtained from measurement of infra-red dispersion in all cases where a comparison is possible. Our method may, therefore, be considered reliable and applied with confidence to other molecules.

(2) It is not yet possible to predict intensities of vibrational bands on the basis of empirically-assigned dipole moments for the chemical bonds making up a molecule. If this could be done, it would greatly extend the usefulness of infra-red spectroscopy in the analysis of molecular structure, since the infra-red intensities could be used to determine the numbers of various types of structure present. Further investigations are necessary to measure and explain the behavior of a variety of bond dipole moments under a variety of conditions.