The Experimental Determination of the Intensities of InfraRed Absorption Bands II. Measurements on Ethylene and Nitrous Oxide

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The Experimental Determination of the Intensities of Infra-Red Absorption Bands

II. Measurements on Ethylene and Nitrous Oxide

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The absolute intensities of the chief infra-red absorption bands of ethylene and nitrous oxide have been determined experimentally to be (in cycles per centimeter at N.T.P.):

Ethylene	Nitrous oxide
950 cm^{-1} band: 1540×10^{10}	590 cm^{-1} band: 120×10^{10}
1444 cm^{-1} band: 210×10^{10}	1285 cm^{-1} band: 1150×10^{10}
3050 cm^{-1} band: 840×10^{10}	2224 cm^{-1} band: 5600×10^{10}

From these intensities it is possible to calculate the dipole moments, μ, of bonds between vibrating atoms and also the rates of change of dipole moment with inter-nuclear distances, $\partial\mu/\partial r$. The values of μ obtained are all of the order of magnitude of 0.5×10^{-18} c.g.s. unit, while values of $\partial\mu/\partial r$ are of the order of 1×10^{-10} c.g.s. unit. The results are in agreement with available data on infra-red dispersion and on atomic polarization within the limits of experimental error, which are estimated to be approximately ±10 percent.

IN a recent paper[1] a method has been described for measuring the intensities of infra-red vibrational absorption bands. The integrated apparent absorption coefficient per molecule is measured at several partial pressures of absorbing gas and extrapolated to zero partial pressure. This limit can normally be expected to equal the true integrated absorption coefficient. The use of a non-absorbing gas to broaden the individual lines composing the band assures that the limit will be approached closely for measurable values of the absorption. This pressure broadening need not be so great as to merge completely the rotational lines, but must reduce the variations of $\alpha(\nu)$ across the spectrometer slit until the observed absorption by a given amount of gas is not appreciably increased by a further increase of non-absorbing foreign gas pressure. It has long been known that the addition of a non-absorbing gas causes, in some cases, an increase in the measured absorption. The increase caused by the first increment of foreign gas is considerable, but further additions produce smaller and smaller effects.[2] The pressure required in practice varies from zero to about 50 atmos., depending primarily upon the spacing between the rotational lines of the absorbing gas.

The experimental procedure is simplest for molecules whose lines are adequately broadened by one atmosphere total pressure. N$_2$O and

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

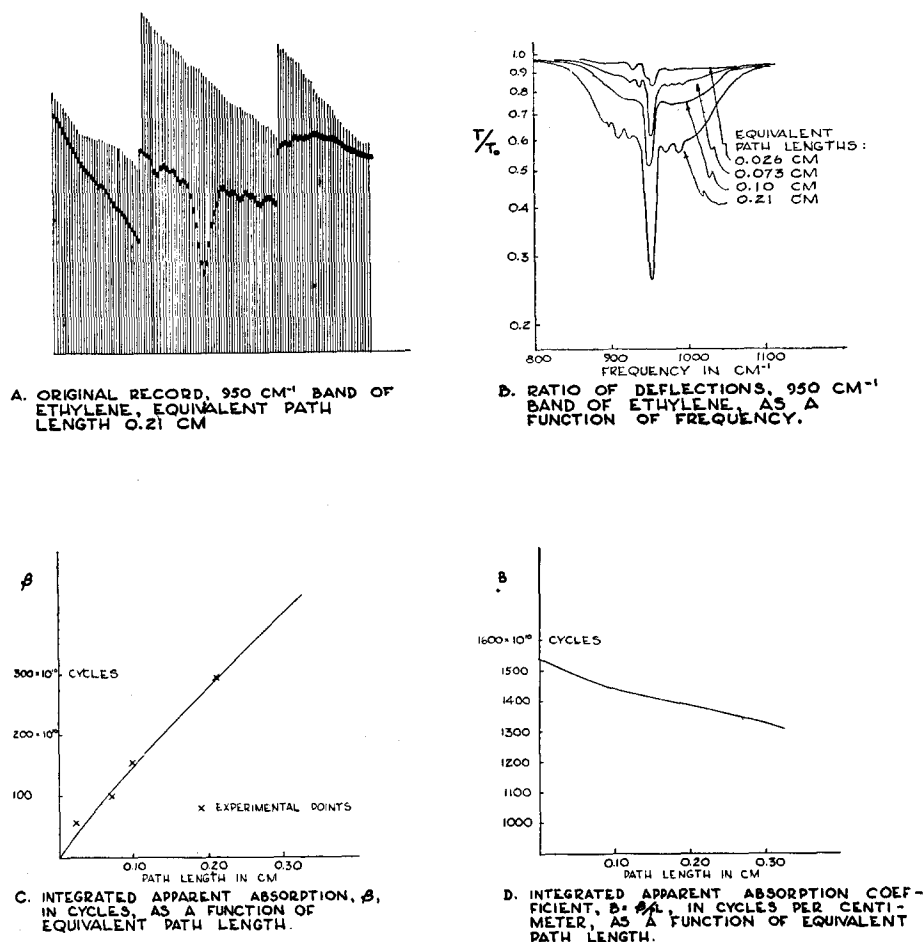[2] See, for example, E. von Bahr, Ann. d. Physik **29**, 780 (1909); **33**, 585 (1910).

A. ORIGINAL RECORD, 950 CM⁻¹ BAND OF ETHYLENE., EQUIVALENT PATH LENGTH 0.21 CM

B. RATIO OF DEFLECTIONS, 950 CM⁻¹ BAND OF ETHYLENE, AS A FUNCTION OF FREQUENCY.

C. INTEGRATED APPARENT ABSORPTION, β, IN CYCLES, AS A FUNCTION OF EQUIVALENT PATH LENGTH.

D. INTEGRATED APPARENT ABSORPTION COEFFICIENT, B+β/L, IN CYCLES PER CENTIMETER, AS A FUNCTION OF EQUIVALENT PATH LENGTH.

FIG. 1. Steps in calculating the intensity from experimental data (950 cm⁻¹ band of ethylene).

C_2H_4 were chosen as fulfilling this requirement[2] without having unduly complicated spectra. This paper describes measurements of the intensities of their fundamental bands.

EXPERIMENTAL PROCEDURE

The absorption of the gas under study is measured as a function of frequency for various partial pressures of absorbing gas, at a fixed total pressure, and the intensity is obtained from the extrapolation previously described.[1] An automatic recording prism spectrograph was employed[3] whose effective slit width varied from about 5 cm⁻¹ to 25 cm⁻¹ depending upon fre-

quency. The sample was enclosed in a cell 30 cm long, with NaCl or KBr windows. Air was added as a broadening gas to a total pressure of about one atmosphere. The partial pressure of the sample was varied from nearly an atmosphere down to about 0.1 mm Hg for an intense band. The data for low pressures (that is, those which lead to a maximum observed absorption not greater than about 30 percent) are most important in determining the intensity. The lower limit to the partial pressures employed was set by the fact that absorptions of less than about 10 percent were too small to be determined precisely from the record obtained.

The first measurements, made in 1940–41, have been repeated in 1946 with special emphasis on the low partial pressures.

The basic data were obtained as a record on

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[3] The instrument is that described by Gershinowitz and Wilson, J. Chem. Phys. 6, 197 (1938). Improved slits and a more sensitive thermocouple were used, and an off-axis parabolic mirror has replaced the original spherical one for the more recent of the measurements here discussed.

photographic paper of galvanometer deflections for sample (T) and blank cells (T_0) at frequency intervals averaging about 5 cm^{-1}. The ratio of these deflections was then plotted as a function of frequency on semi-logarithmic graph paper, and the area between the curve for zero pressure of absorbing gas and that for pressure p was measured to give the integrated apparent absorption, defined by (1), below:

$$\mathfrak{B} = pLB = \int \ln(T_0/T)d\nu \qquad (1)$$

where L is the cell length and ν the frequency. The integration is over the band.

While it is the integrated apparent absorption *coefficient*, B, that is extrapolated[1] to obtain the true intensity, A, this quantity is liable to fluctuate considerably if calculated directly from experimental data. It was most convenient to plot the integrated apparent absorption, $\mathfrak{B}$, draw a smooth curve through the experimental points and select smoothed values of $\mathfrak{B}$ from which to calculate B for extrapolation. These steps are

illustrated by data for the 950 cm^{-1} band of C_2H_4 in Fig. 1.

EXPERIMENTAL DATA

The integrated apparent absorption, $\mathfrak{B}$, is obtained from the basic data by unambiguous arithmetical reduction, whereas quantities obtained through smoothing and extrapolation involve individual judgment. The plotted values of $\mathfrak{B}$ in Figs. 2 and 3 are, therefore, a summary of the basic data, but the values of the intensities given in Table I involve judgment as well.

Data for N_2O are presented in Fig. 2, and those for C_2H_4 in Fig. 3. The case of N_2O is clear-cut, but that of C_2H_4 has some unsatisfactory aspects. In the first place, 1941 and 1946 data are not in agreement for the 950 cm^{-1} band, and the discrepancy is more than the expected limits of experimental error (see discussion below). In addition, both 3050 cm^{-1} and 950 cm^{-1} "bands" actually involve absorption by two vibrational modes which are not resolved. The separate contributions can only be estimated in these cases.
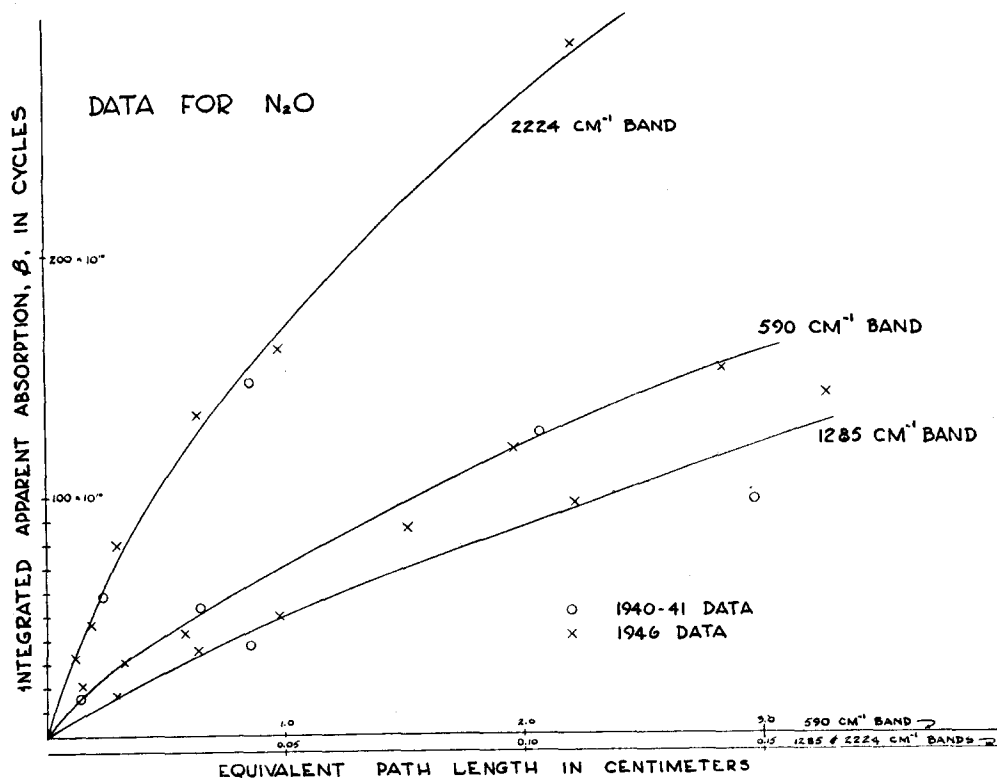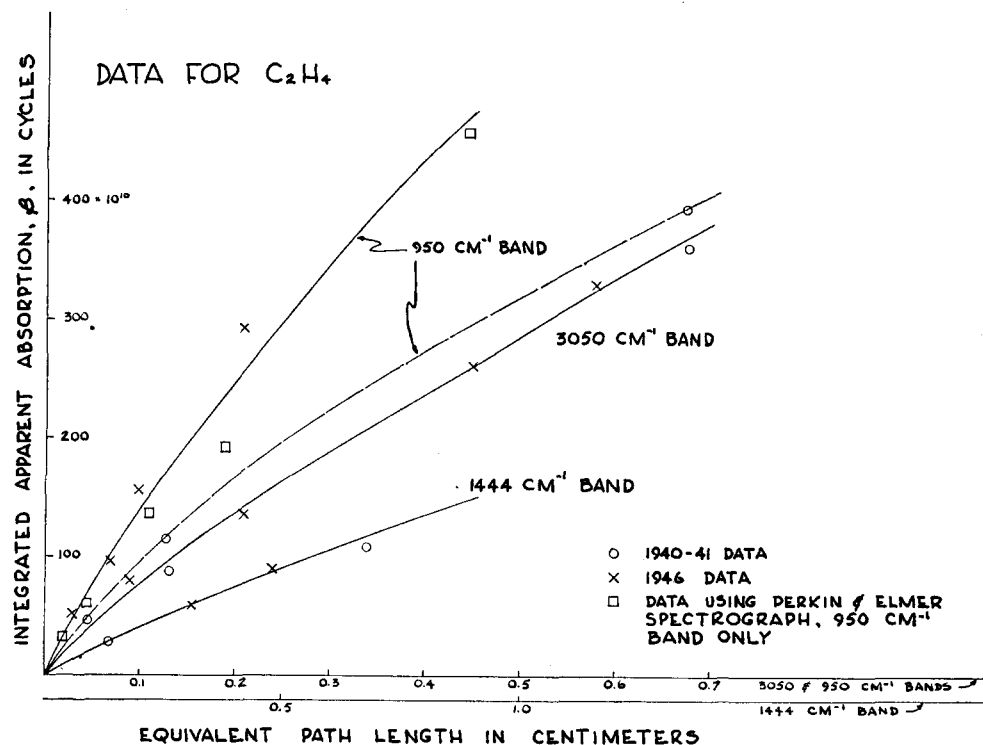

FIG. 2. Experimental results for N_2O.

FIG. 3. Experimental results for C_2H_4.

ACCURACY OF RESULTS AND LIMITATIONS OF METHOD

The most serious general limitation of the method is the critical importance of the low pressure measurements where a small absolute error results in a large percentage error. Inaccuracies in measuring records, and in determining the ratio of sample to blank deflections in the absence of absorbing gas, may be responsible for errors of 5–10 percent. By taking a very large number of measurements the error in the smoothed curve could be made less than this, but it is believed that the intensities given in Table I may be in error by about 10 percent.

A number of other sources of error may be minimized by proper procedure. Stray light must be corrected for, and this correction becomes a serious potential source of error if the contribution of stray light to the deflections is 20 percent or more. In the above data only the N_2O 590 cm^{-1} band was low enough in frequency to have appreciable stray (about 40 percent). Rapid fluctuations in the intensity of the incident beam, due to absorption by atmospheric CO_2 and H_2O,

are a potential source of error,[1] even if accurate ratios of transmission through the filled and blank cells are obtained. During the 1946 measurements an attempt to eliminate this absorption was made in the case of the 1444 cm^{-1} band of C_2H_4, the only one of the bands studied which lies in a region of strong atmospheric absorption. While the H_2O absorption was by no means eliminated, it was much reduced. Data on this band show good agreement between 1941 and 1946 data, suggesting that the errors due to atmospheric absorption are not serious in this case.[4]

A final source of error which is difficult to eliminate is that of "envelope effect" in the Q-branches of perpendicular bands, since these branches may be intense and narrower than the slit width of low resolving power spectrographs. To give the Q-branch a half-width of 10 cm^{-1} by pressure broadening (assuming it to be effectively a single line) would require about 100 atmos-

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[4] One would expect atmospheric absorption to have no effect if randomly distributed in frequency, but to have a serious effect if the lines are spaced regularly in relation to those of the absorbing gas.

pheres broadening gas pressure. To eliminate the envelope effect by extrapolation to zero equivalent path length may require measurements at impracticably low absorptions. This type of difficulty may well account for the difference between 1941 and 1946 data on the 950 cm^{-1} band of C_2H_4, since this band is the only one of those measured which has prominent multiple Q-branches (spaced about 10 cm^{-1} apart), and the resolution of the spectrograph was considerably better in 1946 than in 1941.

In order to ascertain whether the resolution of the spectrograph in 1946 (about 10 cm^{-1} effective slit width in this region) was adequate, a series of measurements was made on an instrument of considerably higher resolving power (a Perkin and Elmer spectrograph at Brown University).[5] While the fine structure was very much more pronounced on these records, the values of integrated apparent absorption were in good agreement with our 1946 data, and the extrapolated intensities very nearly the same. We may conclude that errors due to envelope effect are not serious in this case.

On the basis of these estimates of errors, it is considered that the results above may be in error by about 10 percent, but that certainly in no case should errors exceed 25 percent. In order to achieve this accuracy, considerable care must be employed in measuring the records and a sufficient number of pressures must be used.

The preliminary results,[6] published in 1941, were satisfactory for N_2O but were based on too few points to give good agreement with our final results on ethylene, even when adjusted to N.T.P.

INTERPRETATION OF RESULTS

The integrated intensity A_i is related to the matrix elements of the electric moment by

$$A_i \equiv \int_i \alpha(\nu)d\nu = (8\pi^3 N\nu_i/3hc)$$
$$\times \{ |\mu_{ix}^{1,0}|^2 + |\mu_{iy}^{1,0}|^2 + |\mu_{iz}^{1,0}|^2 \}, \quad (2)$$

in which the integration covers the ith band, of

frequency ν_i. $\alpha(\nu)$ is the true absorption coefficient, N is the number of molecules per cc, h is Planck's constant, and c the velocity of light. $\mu_{ix}^{1,0}$ etc., are the matrix elements of the components of the electric moment for a transition between the ground state and first-excited state of the ith normal mode.[7] This quantity may be calculated on the basis of various simple models.

If, for example, we assume the wave equation to have been separated in normal coordinates, Q_i, we can, to a first approximation, express the (vector) dipole moment, $\mathbf{\mu}$, as a linear function of the Q_i:

$$\mathbf{\mu} - \mathbf{\mu}_0 = \sum_i (\partial\mathbf{\mu}/\partial Q_i)Q_i, \quad (3)$$

whence

$$\mathbf{\mu}_i^{1,0} = (\partial\mathbf{\mu}/\partial Q_i)Q_i^{1,0}. \quad (4)$$

$Q_i^{1,0}$ is the matrix element of Q_i for the 0–1 transition in question; $\mathbf{\mu}_0$ is the constant part of the dipole moment. Each normal coordinate may be treated as a harmonic oscillator coordinate for which

$$Q_i^{1,0} = (h/8\pi^2\nu_i)^{\frac{1}{2}}. \quad (5)$$

Substituting (4) and (5) in (2) yields a simple relation between the observed intensity and the coefficient in Eq. (3):

$$A_i = (N\pi/3c)\{ |\partial\mu_x/\partial Q_i|^2$$
$$+ |\partial\mu_y/\partial Q_i|^2 + |\partial\mu_z/\partial Q_i|^2 \}. \quad (6)$$

In order to explain the observed values of the A_i with a smaller number of constants we might

TABLE I. Intensities obtained by extrapolation.

Substance	Band	Intensity (cycles per centimeter at N.T.P.)
N_2O	590 cm^{-1}	120×10^{10}
N_2O	1285 cm^{-1}	1150×10^{10}
N_2O	2224 cm^{-1}	5600×10^{10}
C_2H_4	950 cm^{-1}	1540×10^{10}a, b
C_2H_4	1444 cm^{-1}	210×10^{10}
C_2H_4	1890 cm^{-1} (combination)	67×10^{10}
C_2H_4	3050 cm^{-1}	840×10^{10}c

a The intensity of 1540×10^{10} for the 950 cm^{-1} "band" is based on 1946 data only. On account of better resolving power it is considered to be more accurate than that obtained in 1940–41.
b This includes a contribution from the weak 995 cm^{-1} band. From the observed asymmetry of this pair of overlapping bands we estimate that the total intensity should be apportioned as follows: 950 cm^{-1}: 1390 $\times10^{10}$ cycles; 995 cm^{-1}: 150×10^{10} cycles.
c There are two overlapping bands here, at 2990 and 3105 cm^{-1}. Using the relative intensities observed by Levin and Meyer, J. Opt. Soc. Am. 16, 137 (1928), we tentatively divide this observed intensity as follows. 2990 cm^{-1}: 270×10^{10} cycles; 3105 cm^{-1}: 570×10^{10} cycles.

[5] We are indebted to Professor Paul C. Cross, Professor Donald H. Hornig, and Mr. Earl Wilson of Brown University for their cooperation with these measurements.
[6] A. J. Wells and E. B. Wilson, Jr., J. Chem. Phys. 9, 659 (1941).

[7] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, New York, 1945), p. 261.

TABLE II. Normal coordinates for ethylene.

Mode	Symmetry	Frequency*	Normal coordinate
ν_{11}	B_{3u}	2989.5	$Q_{11} = 12.6 \times 10^{-13} S_4 - 1.95 \times 10^{-6} S_5$
ν_{12}	B_{3u}	1443.5	$Q_{12} = -1.12 \times 10^{-13} S_4 + 90.8 \times 10^{-6} S_5$
ν_9	B_{2u}	3105.5	$Q_9 = -12.2 \times 10^{-13} S_6 + 0.72 \times 10^{-6} S_7$
ν_{10}	B_{2u}	995	$Q_{10} = +0.91 \times 10^{-13} S_6 + 93.1 \times 10^{-6} S_7$
ν_7	B_{1u}	949.2	$Q_7 = 126 \times 10^{-6} S_{11}$

* See reference 7.

TABLE III. Experimentally determined characteristics of bond moments of C_2H_4 (c.g.s. units).

Bond	Bands involved	μ	μ/s	$\partial\mu/\partial r$
CH	ν_{11} out-of-plane bending	0.77×10^{-18}	0.72×10^{-10}	—
CH	ν_7 in-plane bending	0.52×10^{-18}	0.48×10^{-10}	—
CH	ν_5 in-plane bending	0.37×10^{-18}	0.33×10^{-10}	—
CH	ν_4 stretching	—	—	$+0.70 \times 10^{-10}$ or -0.60×10^{-10}
CH	ν_6 stretching	—	—	$+0.57 \times 10^{-10}$ or -0.53×10^{-10}

endeavor to reproduce the intensities by assigning fixed "effective charges" to each type of atom, and taking the form of the normal modes into account. Such a simplification would be too drastic, however, since the intensities calculated in this manner do not agree well with those observed. It is more satisfactory to assume, as has been done, for example, by Rollefson and Havens,[8] and Wolkenstein,[9] that the electric moments of the bonds are additive. Then the intensities of the stretching vibrations depend on $d\mathbf{\mu}/dr$, and those of the bending vibrations depend on $\mathbf{\mu}$, r being the bond length.

This relation can be written explicitly since the normal coordinates, Q_i, are linearly related to the internal coordinates, R_k (e.g., changes in inter-atomic distances, etc.), by the transformation

$$R_k = \sum_i L_{ki} Q_i, \quad Q_i = \sum_k (L^{-1})_{ik} R_k. \quad (7)$$

But the dipole moment of the molecule is related to the coordinates, Q_i, by the $\partial\mathbf{\mu}/\partial Q_i$ as in (3). From (3) and (7) we obtain

$$\mathbf{\mu} - \mathbf{\mu}_0 = \sum_i (\partial\mathbf{\mu}/\partial Q_i) Q_i$$
$$= \sum_{ik} (\partial\mathbf{\mu}/\partial Q_i)(L^{-1})_{ik} R_k$$
$$= \sum_k (\partial\mathbf{\mu}/\partial R_k) R_k,$$
$$\partial\mathbf{\mu}/\partial R_k = \sum_i (\partial\mathbf{\mu}/\partial Q_i)(L^{-1})_{ik}. \quad (8)$$

Since the transformation L^{-1} is easy to normalize,[10] this is a convenient method of determining the behavior of bond dipole moments with respect to stretching, bending, or other internal coordinates from the observed absorption intensities.[11]

This procedure involves one serious difficulty, however, arising from the fact that it is the squares of $\partial\mu_x/\partial Q_i$, $\partial\mu_y/\partial Q_i$, and $\partial\mu_z/\partial Q_i$ that enter into (6). The signs of these coefficients are, therefore, undetermined, and can be either positive or negative. When they are substituted in Eq. (8) a large number of combinations of signs are possible, each leading to a different value of $\partial\mathbf{\mu}/\partial R_k$. Other arguments must be introduced in order to eliminate as many of them as possible.

Following this procedure bond moments and their rates of change were calculated from the intensities given in Table I. In order to obtain the $(L^{-1})_{ik}$ coefficients normal coordinate treatments of N_2O and C_2H_4 were carried out using the methods previously described.[10]

Ethylene

In the case of C_2H_4 the normal coordinates were calculated from the observed frequencies on the assumption that the dependence of the potential energy upon the infra-red active symmetry coordinates can be expressed without interaction terms as

$$V = \tfrac{1}{2}\{f_{44} S_4^2 + f_{55} S_5^2 + f_{66} S_6^2 + f_{77} S_7^2 + f_{11\,11} S_{11}^2\},$$

TABLE IV. Normal coordinates for N_2O.

f_{12}	$f_1{}^a$	$f_2{}^a$	$(L^{-1})_{11}$	$(L^{-1})_{12}$	$(L^{-1})_{21}$	$(L^{-1})_{22}$
in units of 10^5			in units of 10^{-12}			
0.50	15.47	14.05	−2.30	+1.65	+3.24	+3.78
1.36	17.91	11.36	−2.72	+1.13	+2.89	+3.95
2.72	20.32	10.29	−3.03	+0.613	+2.48	+4.07
5.00	22.94	9.884	−3.42	−0.017	+2.05	+4.22
10.00	26.51	11.38	−3.85	−1.14	+1.05	+4.01

a There are, of course, two algebraic solutions for f_1 and f_2 with each value of f_{12} assumed, of which only one is tabulated. The other leads, in each case, to a solution with f_1 smaller than f_2, and was discarded since the $2\frac{1}{2}$-fold NN bond must surely be stiffer than the $1\frac{1}{2}$-fold NO bond.

[8] R. Rollefson and R. Havens, Phys. Rev. 57, 710 (1940).
[9] M. W. Wolkenstein, J. Phys. USSR, 5, 185 (1941).
[10] E. Bright Wilson, Jr., J. Chem. Phys. 9, 76 (1941).
[11] For symmetrical molecules it may be convenient to introduce internal symmetry coordinates, $\mathfrak{R}$, as an inter-

mediate step, determining first the $\partial\mathbf{\mu}/\partial\mathfrak{R}$ as in (8) and then the $\partial\mathbf{\mu}/\partial R_k$.

TABLE V. Characteristics of bond moments of N_2O (c.g.s. units).

f_{12}	$(\partial\mu/\partial r)_{NN}$	$(\partial\mu/\partial r)_{NO}$	μ_{NN}	μ_{NO}	μ_{NN}/s	μ_{NO}/s
1.0	-2.9×10^{-10}	-7.5×10^{-10}				
2.0	-4.1×10^{-10}	-6.6×10^{-10}				
3.0	-5.0×10^{-10}	-5.9×10^{-10}	-0.50×10^{-18}	-0.67×10^{-18}	-0.45×10^{-10}	-0.56×10^{-10}
5.0	-6.2×10^{-10}	-4.6×10^{-10}				
7.0	-7.1×10^{-10}	-3.4×10^{-10}				
10.0	-8.2×10^{-10}	-1.6×10^{-10}				

where

$$S_4=\tfrac{1}{2}\{r_1+r_2-r_3-r_4\},$$
$$S_5=\tfrac{1}{2}rR\{\gamma_1+\gamma_2-\gamma_3-\gamma_4\},$$

Along C−C axis

$$S_6=\tfrac{1}{2}\{r_1-r_2+r_3-r_4\},$$
$$S_7=\tfrac{1}{2}rR\{\gamma_1-\gamma_2+\gamma_3-\gamma_4\},$$

Perpendicular to C−C axis

$$S_{11}=[(-rR\cos\gamma)/\sqrt{2}]\{\delta_a+\delta_b\}.$$

The internal coordinates r_i and γ_i are changes in CH bond lengths and C−C−H bond angles, respectively, and δ_a and δ_b are out-of-plane bending angles of the H−C−H planes with respect to the C−C bond.

The force constants were determined to be

$$f_{44}=5.07\times10^5 \text{ dynes/cm},$$

$$f_{55}=6.33\times10^{20} \text{ dynes/cm}^3/\text{radian}^2,$$

$$f_{66}=5.08\times10^5 \text{ dynes/cm},$$

$$f_{77}=3.07\times10^{20} \text{ dynes/cm}^3/\text{radian}^2,$$

$$f_{11\ 11}=5.11\times10^{20} \text{ dynes/cm}^3/\text{radian}^2.$$

The corresponding normal coordinates are given in Table II.

The results for C_2H_4 are presented in Table III. Values are given for μ, $\partial\mu/\partial r$, and μ/s, where s is the equilibrium inter-atomic distance. (It is assumed throughout that the dipole moments are directed along the bond in question.) μ/s and $\partial\mu/\partial r$ have the dimensions of charge, and may be compared with the charge of -4.8×10^{-10} for an electron.

In Table III considerations of the electro-negativities of the atoms have been employed to determine the signs when possible. Since hydrogen is less electronegative than carbon, negative values for the CH bond moment would be unreasonable, and this restriction allows us to select the proper sign for three of the five $\partial\mu/\partial Q$'s for C_2H_4. The remaining two must have

opposite signs, leaving two possibilities which lead to the two values of $\partial\mu/\partial r$ for ν_{11} and ν_9. If the $\partial\mu/\partial Q$'s had the same signs, these two CH-stretching vibrations would involve values for $\partial\mu/\partial r$ of opposite sign, which seems quite impossible.

Nitrous Oxide

The case of N_2O is made more complicated by the existence of resonance between the two structures

(a) $\overset{-}{N}=\overset{+}{N}=O$, (b) $N\equiv\overset{+}{N}-\overset{-}{O}$.
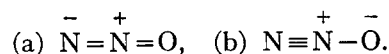
The potential energy must be expressed as

$$V=\tfrac{1}{2}\{f_1r_1^2+2f_{12}r_1r_2+f_2r_2^2+f_3\gamma^2\},$$

where $r_1=$ NN stretch, $r_2=$ NO stretch, and $\gamma=$ NNO bending. The interaction coefficient cannot be evaluated from the two observed frequencies, but is probably large (and positive) since a stretch of the NO bond will favor structure (b) which has the greater NO distance and thereby stiffen the NN bond considerably.

It was, therefore, necessary to calculate normal coordinates as a function of the variable f_{12}. The results of these calculations are summarized in Table IV, the indices being selected so that:

$$\nu_1=2224 \text{ cm}^{-1}, \quad Q_1=(L^{-1})_{11}r_1+(L^{-1})_{12}r_2.$$
$$\nu_2=1285 \text{ cm}^{-1}, \quad Q_2=(L^{-1})_{21}r_1+(L^{-1})_{22}r_2.$$

For the normal coordinates corresponding to each possible choice of f_{12} there are four possible combinations of signs for the $\partial\mu/\partial Q$'s that must be considered. The values are:

$$\partial\mu/\partial Q_1=\pm244, \quad \partial\mu/\partial Q_2=\pm111.$$

The choice is restricted, however, by the fact that stretching the NO bond will favor structure (b) above, and, therefore, give the molecule a dipole moment directed to the left, whereas
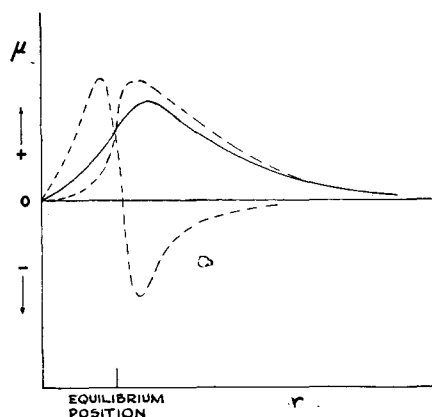
Fig. 4. Hypothetical curves for dipole moment, μ, as a function of internuclear distance, r.

stretching the NN bond will favor structure (a) and give a dipole moment directed to the right. Substitution of the above values for $\partial\mu/\partial Q_1$ and $\partial\mu/\partial Q_2$ with those from Table IV in Eq. (8) shows that this restriction is satisfied only if $\partial\mu/\partial Q_1$ and $\partial\mu/\partial Q_2$ are both positive. Possible values of $\partial\mu/\partial r_1$ (NN bond), and $\partial\mu/\partial r_2$ (NO bond), are given in Table V as a function of f_{12}. A positive contribution to the dipole moment on the part of the NN bond is defined as one which is directed from the central nitrogen to the end nitrogen. Similarly a positive contribution by the NO bond will be directed from nitrogen to oxygen.

Table V also includes values for the dipole moments themselves, determined from the intensity of the bending mode. These signs are also uniquely determined. Since oxygen is more electronegative than nitrogen, the moment of the NO bond must be negative. It will be assumed that the molecular dipole moment is directed toward the nitrogen end and that it has the value[12] 0.17×10^{-18}. These two conditions and the observed intensity determine the NO and NN bond moments using the hypothesis of additivity, though it should be remembered that in a resonant molecule any separation into individual bonds is somewhat artificial.

Behavior of Bond Dipole Moments

As might be expected, values of μ/s and $d\mu/dr$ vary from about 0.1 to 2.0 times the charge

of an electron. The slope, $d\mu/dr$ is in most cases greater than μ/s, but the values for CH are consistent with a simple curve such as that shown solid in Fig. 4. The values for NN and perhaps NO seem to require a steeper form like one or the other of the dotted curves. The value of μ for CH obtained from the 950 cm^{-1} band is almost twice that obtained from the 1444 cm^{-1} or 995 cm^{-1} bands. Apparently the electric moment behaves differently for this out-of-plane bending than for the in-plane modes because of some interaction with neighboring atoms.

COMPARISON WITH OTHER DATA

There are very few other measurements of infra-red intensities, and they are not directly comparable with those reported here. Bourgin[13] obtained 0.86×10^{-10} for $d\mu/dr$ in HCl, and Matheson[14] obtained 3.92×10^{-10} for CO. Foley[15] has given the "dipole moment" of the bending mode of HCN as 0.147×10^{-18}, from which we calculate the CH bond moment as 0.57×10^{-18}, $\mu/s=0.54\times10^{-10}$. This is intermediate between our values for in-plane and out-of-plane modes in C_2H_4.

The conventional value for the CH bond moment obtained from molecular moments[16] on
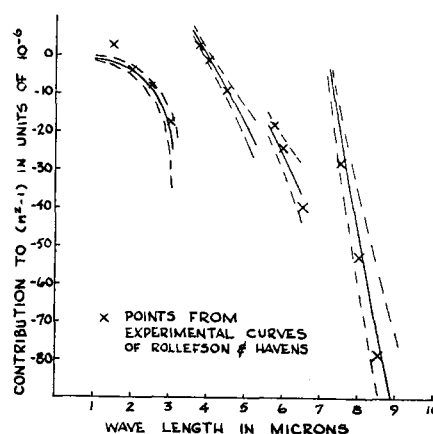

Fig. 5. Dispersion curve for ethylene calculated from intensity data and compared with experimental points from Rollefson and Havens. Dotted curves show limits of 20 percent error.

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[12] J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Clarendon Press, Oxford, 1932), Chap. III.

[13] D. G. Bourgin, Phys. Rev. **29**, 794 (1927); **32**, 237 (1928).
[14] L. A. Matheson, Phys. Rev. **40**, 813 (1932).
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the basis of additivity is 0.4×10^{-10}, agreeing well with our in-plane moment.

Measurements of infra-red dispersion also lead to values for bond dipole moments. In the case of methane Rollefson and Havens[8] concluded that $\mu = 0.307 \times 10^{-18}$, and $\partial\mu/\partial r = \pm 0.562 \times 10^{-10}$, in fair agreement with our in-plane moment and our values for $\partial\mu/\partial r$. Rollefson and Havens have also very kindly furnished us with some unpublished data on the index of refraction of ethylene, and we find that our values for the intensities reproduce their observed dispersion curve quite closely if the combination band at 1890 cm^{-1} is taken into account, as shown in Fig. 5. The agreement is well within an assumed maximum experimental error of 20 percent shown by the dotted curves except at the highest fre-

TABLE VI. Atomic polarizations.

Substance	Calculated from intensity data	From visible index and dielectric constant[a]
C_2H_4	0.40 cc	0.39 cc
N_2O	0.55 cc	0.41 cc (0.46[b])

[a] H. E. Watson and K. L. Ramaswamy, Proc. Roy. Soc. London, A156, 144 (1936).
[b] E. Czerlinsky, Zeits. f. Physik 88, 515 (1934).

quencies where contributions from electronic transitions should be taken into account.

A final comparison can be made with the atomic polarization obtained from measurements of dielectric constant. Table VI shows the contribution of infra-red vibration bands to the molar polarization as calculated from our intensities and from the difference of extrapolated visible indices of refraction and measured dielectric constants.[12] Again the agreement is good.