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TITLE THE POTENTIAL CONSTANTS OF THE ETHANE MOLECULE

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THE POTENTIAL CONSTANTS OF THE ETHANE MOLECULE

by

Gordon E. Hansen

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of the requirements for the degree of
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CHAPTER I

INTRODUCTION

Because of its relative simplicity, the ethane molecule, C_2H_6, was an early target for research into the structure of polyatomic molecules. The accumulation of basic spectroscopic data began about twenty years ago with the investigations of the infra-red absorption by Levin and Meyer[1] and the Raman effect by Daure[2]. This early data revealed over one-half of the twelve fundamental vibrational frequencies, and, through the fine structure of the bands, gave direct proof that ethane is a symmetric top molecule. Analysis of these observed frequencies led to the construction of simplified potential functions[3,4] which gave information about the restoring forces and also greatly aided the later assignment of the other fundamental frequencies. In 1937, Howard[5] proved that the observed fine structure of the perpendicular bands was incompatible with the existence of free axial rotation of the two methyl groups with respect to one another and concluded that there must exist a potential barrier, hindering torsional motion, with a height of at least 700 cm^{-1}. Shortly thereafter, specific heat measurements led to a value of 965 cm^{-1} for this barrier height[6,7]. By 1938, Crawford, Avery, and Linnett were able to give a complete summary of the fundamental frequencies which found general acceptance[8]. The next year, Stitt observed the infra-red and Raman spectra of the isotopic molecule, C_2D_6, and determined its fundamental frequencies[9]. This work nearly doubled the amount of data capable of giving information about the potential

function of ethane. In order to predict this new data quantitatively, it was found necessary to add several new interaction terms to the previously constructed potential functions. Thus Stitt determined nine characteristic force constants which indicated the magnitudes of the mutual interactions between remote parts of the molecule as well as the forces directly giving the bond bendings and bond stretchings.

Throughout this period, the equilibrium configuration of ethane remained uncertain. The rotational fine structure showed ethane to be a symmetric top and the distribution of the activity of the fundamental vibrations in the infra-red absorption and Raman spectra disclosed that it possesses dihedral symmetry, in other words, that the two methyl groups are of the same size and shape. However, the spectroscopic evidence was insufficient to decide between the "staggered" model, D_{3d}, (center of symmetry) and the "eclipsed" model, D_{3h} (reflection plane perpendicular to the symmetry axis)[8,9].

The classification of the normal vibrations of ethane is well known and will be described in detail later. The notation employed by Herzberg[I] ("Infra-red and Raman Spectra") will be used and is the following: ν_1, ν_2, and ν_3 denote the symmetrical parallel frequencies (carbon atoms move along the symmetry axis) which are Raman active but infra-red inactive. ν_4 is the torsional vibration which is inactive in both the Raman and infra-red spectra. ν_5 and ν_6 are the unsymmetrical parallel vibrations which are infra-red active but Raman inactive. ν_7, ν_8, and ν_9 are the perpendicular vibrations (carbon atoms move perpendicular to the symmetry axis) which are active in the infra-red but absent

from the Raman spectra, while ν_{10}, ν_{11}, and ν_{12} are the perpendicular vibrations which are Raman active but infra-red inactive. The last named six vibrations are each doubly degenerate and hence may exhibit the phenomena of internal angular momentum.

In 1942, Smith[10] completed high resolution observations on ethane over a large range of the infra-red region, determining with high precision the centers and rotational spacings of many fundamental and combination bands. The rotational spacings yielded an accurate determination of the principal moments of inertia and these, together with the less accurate value of the carbon-carbon distance obtained by electron diffraction, permitted the calculation of the dimensions of ethane. The observed combination bands gave direct evidence for the D_{3d} or "staggered" equilibrium configuration. Also, from the rotational spacings associated with the degenerate vibrational bands, Smith determined a set of ζ values. These zeta values give a measure of the internal or vibrational angular momentum along the symmetry axis. The notation is due to Teller who introduced the concept in his explanation of the anomalous rotational spacings found in all symmetric top molecules.[11] As was first shown by Johnston and Dennison[12] the zeta values serve as powerful aids in the determination of potential constants.

Of the possible potential constants permitted by the symmetry of ethane, nine of the more important ones have already been determined. Strictly speaking, these latter con-

stants are "effective" force constants[13] since their numerical values not only depend on the adopted form of the simplified potential function but also include anharmonic contributions. After Smith's work, it appeared that the total information either available or at least readily obtainable would be sufficient to make a more complete determination of these force constants.

We may formulate the present problem as that of a precise determination of the potential constants of ethane.

The justifications for this precision determination are manifold. For example, all further calculations on ethane or any of its isotopes require a knowledge of these constants. One may cite two instances where such calculations have been made and applied to the ammonia molecule: (1) the observed convergence in the pure rotation spectrum of ammonia[14] has been quantitatively explained by the effect of centrifugal stretching on the moments of inertia[15], and (2) the anomalous values of certain of the microwave lines of NH_3 have been successfully computed on the basis of a K-type doubling induced by the combined effect of the Coriolis and harmonic restoring forces[16]. The potential constants are well known only for a very few polyatomic molecules, namely water vapor, carbon dioxide, ammonia, acetylene, and methane. An extension of this list is desirable for comparisons between typical polyatomic molecules.

There are a number of difficulties associated with the determination of the so-called potential constants of a

molecule. These constants are defined as the coefficients of the quadratic terms in the representation of the potential energy as a power series in the relative nuclear displacements. Since these relative nuclear displacements are quite small for a vibrating molecule, the quadratic terms essentially control the motion and the higher order or anharmonic terms may be treated as small perturbations. (The nuclear displacements are measured from equilibrium positions and hence there are no linear terms.) The number, N, of these potential constants is dependent upon the number of distinct fundamental vibrations and its decomposition in terms of the symmetry classes associated with the geometrical configuration of the molecule. The explicit expression is $N = \text{Sum } n_i\ (n_i + 1)/2$ where n_i is the number of distinct fundamental vibrations belonging to the i^{th} symmetry class. Thus ethane has 22 potential constants as compared with 12 distinct fundamental vibrations. Neglecting for the moment any effects due to anharmonicity, it might seem that a measurement of the 24 fundamental frequencies of ethane and heavy ethane would constitute a basis for the determination of these 22 constants, but actually there are five relationships among these 24 frequencies as embodied in the Teller product rule. If one designates the i^{th} fundamental frequencies of two isotopic molecules by ν_i and ν_i^*, then this rule states that for each symmetry class the product ratio $\pi\ \nu_i/\nu_i^*$ depends only on the masses and dimensions and not on the force constants. It is only with the addition of the zeta values that the number of independent measurements equals, and in fact

exceeds, the number of potential constants. One could determine then, using the theory of vibrations of infinitesimal amplitude, the potential constants as functions of the fundamental frequencies and zeta values. This determination would only be approximate since the vibrations do take place with appreciable amplitude and the anharmonic potential terms produce a shift in the vibrational frequencies. One may thus consider the fundamental frequencies as composed of two parts, the one part, termed the normal frequency, being produced by the quadratic terms of the potential energy, and the second part, termed the anharmonicity shift or correction, being produced by the higher order or anharmonic potential terms. In order to determine the potential constants, one requires a complete knowledge of the normal frequencies. In principle, these normal frequencies may be determined from the observed fundamental frequencies together with the frequencies of all simple combination bands. For ethane, this procedure is impractical as there is a total of over 150 simple combination bands most of which have not been observed. This is a real difficulty but the saving feature is the relative smallness of the difference between the fundamental and normal frequencies. It has been shown[13] that the relations among the normal frequencies given by the product rule can often serve to estimate this difference. This method of estimation is not rigorous but its use is necessitated by a lack of information which has not been and probably cannot be obtained experimentally. Another difficulty arises in connection with the accuracy to which the fundamental

frequencies of ethane and heavy ethane have been determined. This accuracy is limited by the resolution of the spectrometers employed, by distortions in the fine structure which confuse the positions of the band centers, by Fermi resonances which cause anomalous shifts of the vibrational frequencies, and finally through the estimation from combination bands of the several fundamental frequencies which have not been observed directly.

In ethane as well as other symmetric top molecules, there are slight deviations between the observed and predicted zeta values for various combination bands. There are numerous perturbations not considered in these predictions which may contribute to these observed deviations. However it does not appear possible at present to introduce systematic corrections, and the measured zeta values are interpreted on the basis that these perturbations are absent or at least negligible.

Summary of Results

The values obtained for the general valence force constants are listed below. The symbolism is defined on pages 103-108. The indexing code is r ≅ C-H stretching, R ≅ C-C stretching, ψ ≅ H-C-C angle bending, θ ≅ H-C-H angle bending, and the use of primes indicates that the interaction is between the two methyl groups.

Simple valence force constants. (in units of 10^5 dynes/cm.)

(1) $k_r = 5.35$

(2) $k_\theta = .51$

(3) $k_\psi = .63$

(4) $k_R = 4.57$

Valence force constants involving interactions between adjacent bonds.

(5) $k_{r\psi_\beta} = -1.89 \pm .20$

(6) $k_{R\psi} = 0.60 \pm .04$

(7) $k_{r\theta} = -0.20 \pm .02$

(8) $k_{\theta\psi} = -0.07 \pm .02$

(9) $k_{r\psi} = -0.07 \pm .15$

(10) $k_{rr} = -0.04 \pm .04$

(11) $k_{\psi\psi} = 0.03 \pm .04$

(12) $k_{Rr} = 0.00 \pm .20$

Valence force constants involving remote coupling.

(13) $k_{\psi\psi'} = 0.11 \pm .02$

(14) $k_{\theta\psi'} = 0.07 \pm .03$

(15) $k_{r\theta'} = -0.03 \pm .02$

(16) $k_{\theta\theta'} = -0.02 \pm .02$

(17) $k_{rr'_\beta} = -0.08 \pm .04$

(18) $k_{rr'} = 0.08 \pm .04$

(19) $k_{r\psi'_\beta} = 0.35 \pm .20$

(20) $k_{r\psi'} = -0.13 \pm .15$

(21) $k_{\psi\psi'_\beta} = 0.00 \pm .05$

The Torsion constant.

(22) $a = 0.055$

The spectrum of heavy ethane, C_2D_6, was examined experimentally to obtain data necessary for the evaluation of the potential constants. The results of these observations are listed in the following table:

Assignment	Frequency $cm.^{-1}$	Rotational Spacing $cm.^{-1}$	ζ Value
ν_5^*	1077	---	---
ν_6^*	2087.3 2139.7	0.922_0 ---	---
ν_7^*	2236°	---	---
ν_8^*	1082	2.76	-0.423
ν_9^*	593.7	1.197	0.182

The rotational spacing of the low frequency component of ν_6^* establishes the large moment of inertia as $60.7_1 \times 10^{-40}$ $gm.cm^2$ (for the vibrational ground state) and combined with Smith's results gives the following dimensions for ethane.

C-H distance = 1.102 Angstroms

C-C distance = 1.544 Angstroms

H-C-C angle = 109° 37'

H-C-H angle = 109° 19'

° The value 2236 $cm.^{-1}$ was also obtained by Stitt. The present work served only to verify this result.

CHAPTER II

INFRA-RED ABSORPTION BY C_2D_6

The purpose of reinvestigating the infra-red spectrum of heavy ethane, first measured by Stitt using a prism spectrometer, was to obtain (1) more accurate positions of the fundamental frequencies, (2) the zeta values associated with the degenerate vibrations, and (3) the large moment of inertia.

The absorption measurements were made by means of a high resolution grating spectrometer and automatic recording system such as described by W. E. Anderson[18]. The C_2D_6 was prepared by the deuteration of heavy acetylene in the presence of a platinum black catalyst[9]. The deuterium and heavy acetylene, in turn, were produced by the reaction of heavy water° with calcium metal and calcium carbide. The complete preparation is schematically diagrammed in Figure 1.

Before giving the experimental results, it seems well to give a few definitions and qualitative features concerning the vibrational infra-red spectra of symmetric top molecules.

Those vibrations of a symmetric top molecule for which the electric moments are parallel to the symmetry axis are called "parallel vibrations" while if the alternating moments are perpendicular to the symmetry axis, the vibrations are called "perpendicular vibrations". The rotational fine structures of parallel and perpendicular vibrational bands are quite different and qualitatively this is easily understood.

° The heavy water was obtained through the permission of the Atomic Energy Commission.

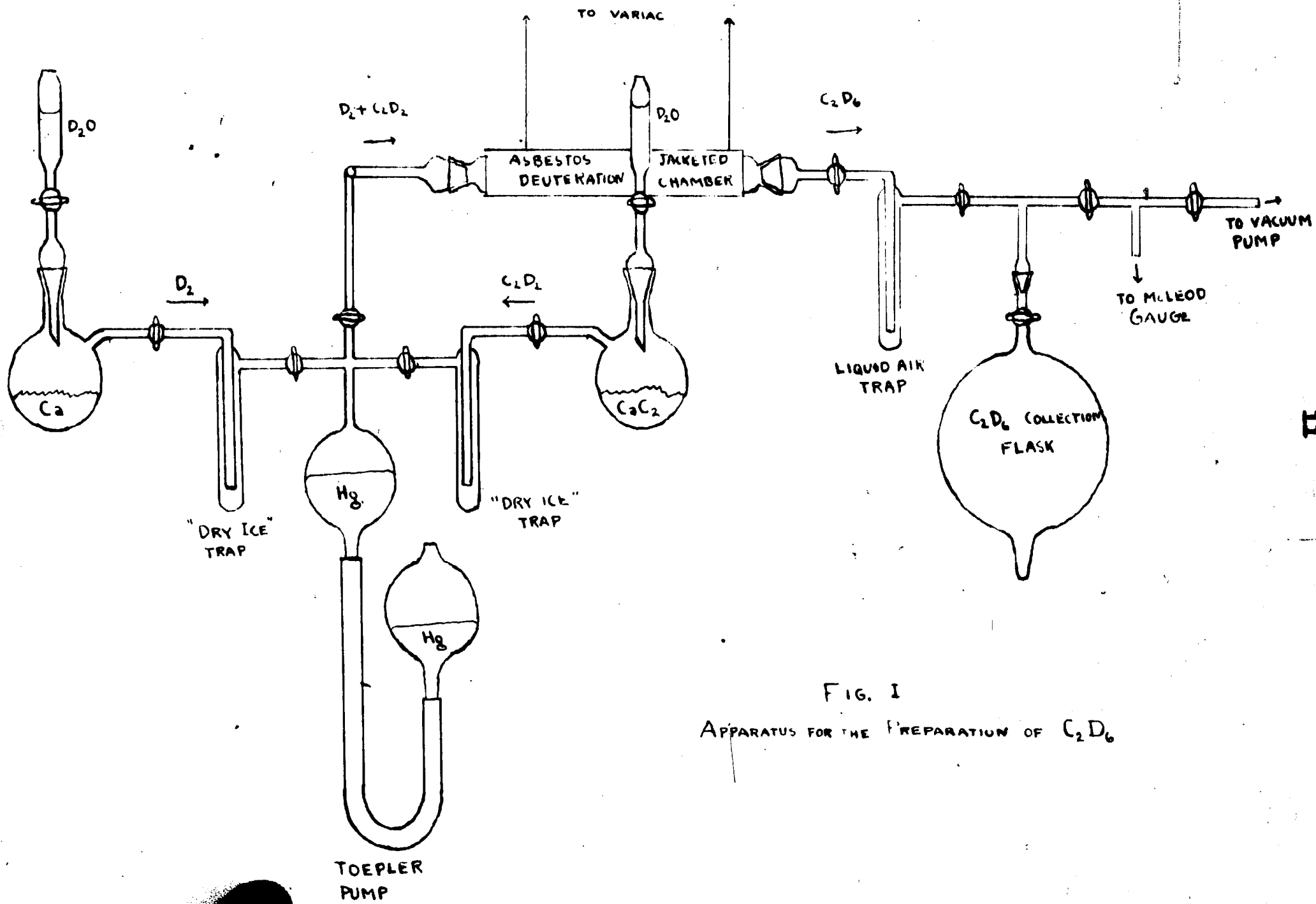


FIG. I

APPARATUS FOR THE PREPARATION OF C_2D_6

In the case of parallel vibrations, rotation of the molecule about its symmetry axis does not affect the vibrational electric moment, and the spectrum of frequencies associated with such a vibration consists of a strong central line, called the "Q line", whose frequency is that of the vibration, and two "wings" produced by the modulation of the vibrational electric moment by rotations of the molecule perpendicular to the symmetry axis. In the case of perpendicular vibrations, rotations about as well as perpendicular to the symmetry axis modulate the vibrational electric moment and the associated spectrum of frequencies is considerably more complicated. This spectrum may be considered as composed of a series of incomplete parallel bands uniformly displaced with respect to each other. The set of equally spaced Q lines of these parallel bands is the characteristic feature of a perpendicular band. The line positions are given by the well known equations (see Herzberg).

Parallel band:
$$\begin{cases} \Delta K=0,\ \Delta J=0 \rightarrow \nu=\nu_0 \equiv \text{vibrational frequency} \\ \Delta K=0,\ \Delta J=1 \rightarrow \nu=\nu_0+2B(J+1) \equiv \text{"R" branch} \\ \Delta K=0,\ \Delta J=-1 \rightarrow \nu=\nu_0-2BJ \equiv \text{"P" branch} \end{cases}$$

Q lines of a Perpendicular band: $\Delta v=1, \Delta J=0 \rightarrow \nu=\nu_0+[A(1-\zeta)-B]+2[A(1-\zeta)-B]K$

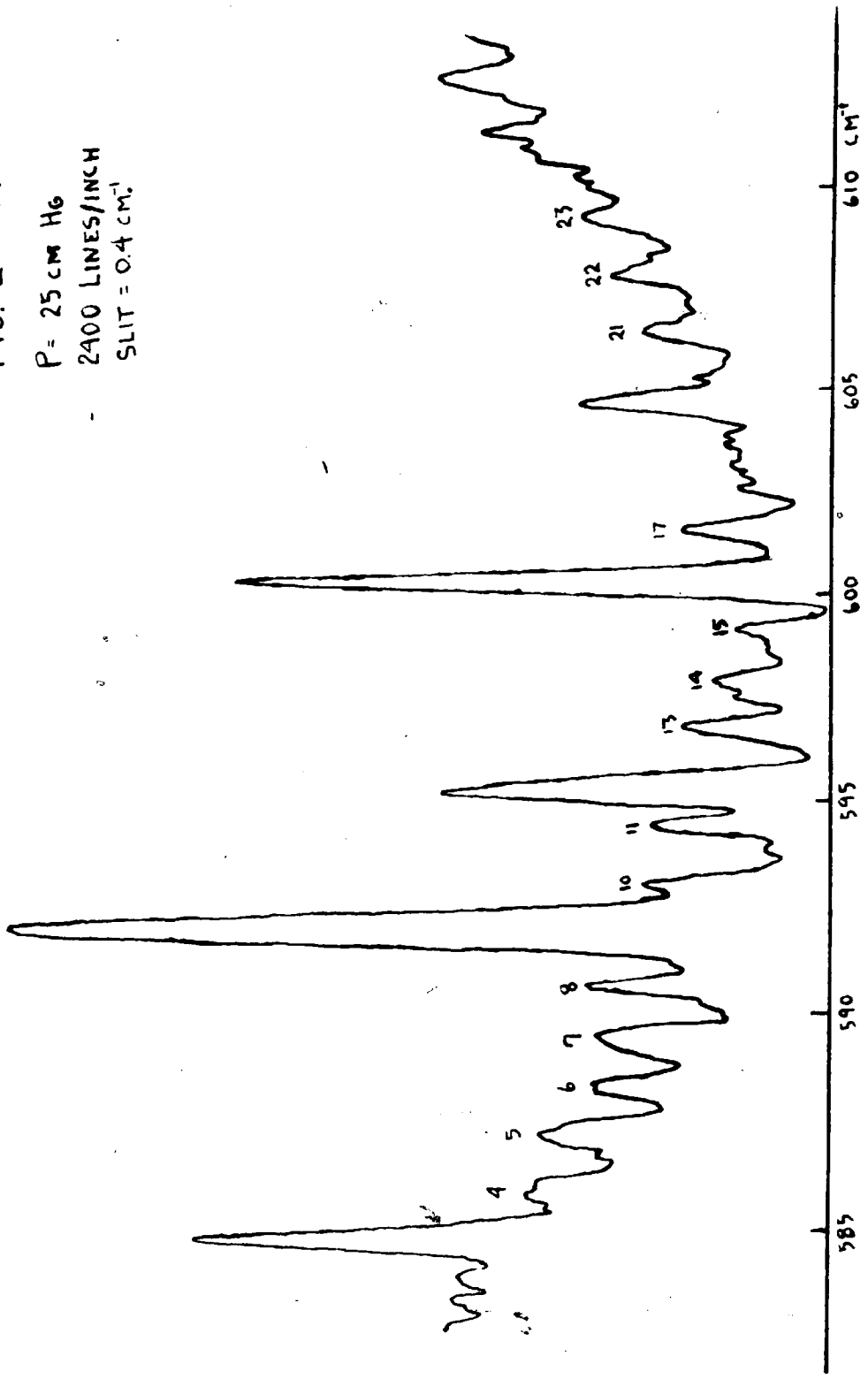
where A and B are called the rotational constants and depend on the principal moments of inertia.

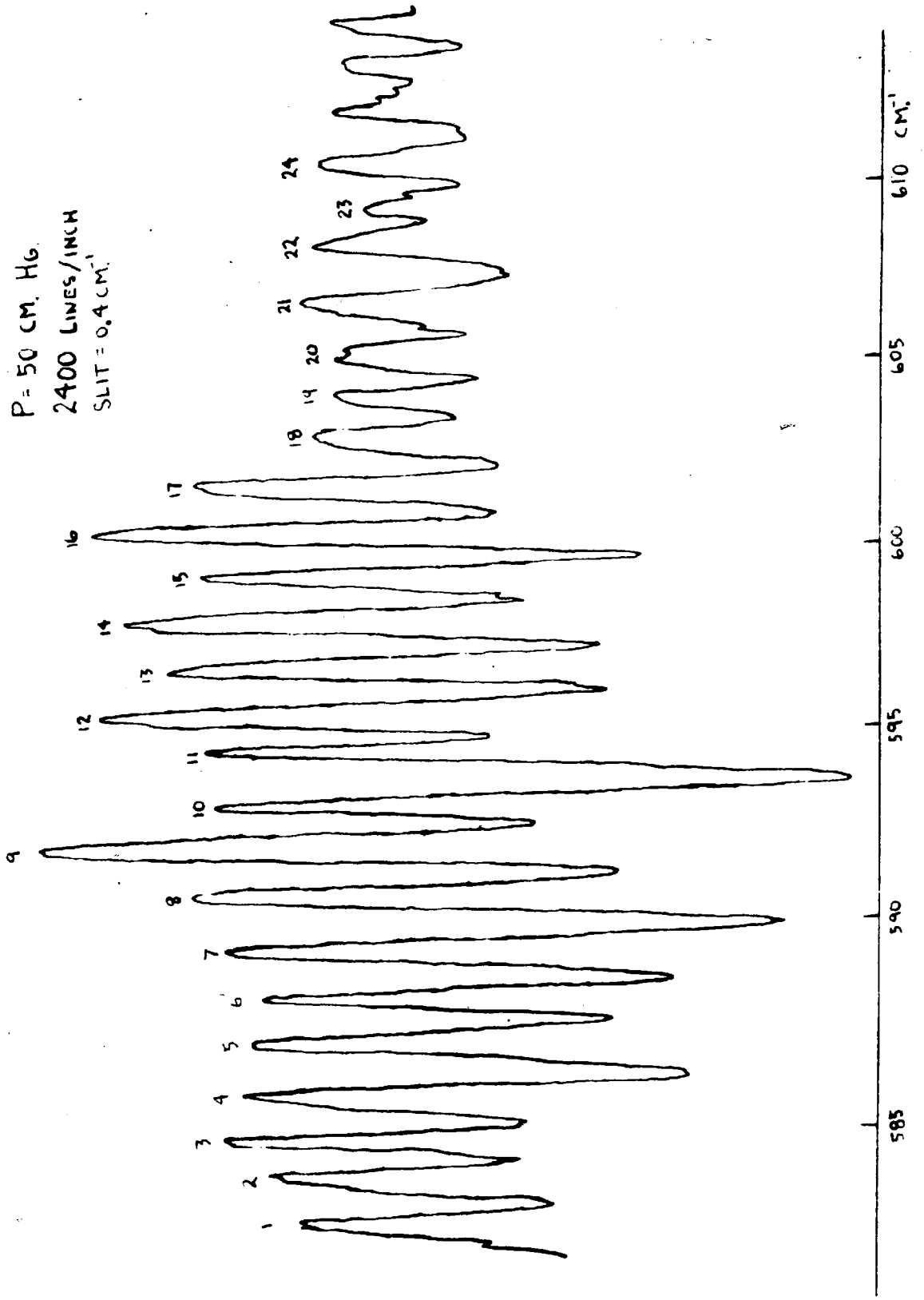
A. Absorption at 17 microns.

The absorption by C_2D_6 in this region results from the perpendicular vibration ν_9^*. Two spectrograms of this region are given in Figures 2 and 3. The first spectrogram (Figure 2)

FIG. 2 ABSORPTION BY ν_4^*

P = 25 cm Hg
2400 LINES/INCH
SLIT = 0.4 cm^{-1}




FIG. 3. ABSORPTION BY ν_4^*
P = 50 CM. Hg
2400 LINES/INCH
SLIT = 0.4 CM.$^{-1}$
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
585
590
595
600
605
610 CM.$^{-1}$

was obtained using an absorption cell 2 cm. in length and filled to a gas pressure of 25 cm. Hg. and served to determine the background absorption due to the presence of atmospheric water vapor. The second spectrogram (Figure 3) was obtained using a 10 cm. absorption cell filled to 50 cm. of pressure, and in this case the effect of the water vapor was fairly well masked through the strong absorption by C_2D_6. The presence of a small amount of heavy acetylene as an impurity in the heavy ethane prevented the safe extension of the measurements below 580 cm^{-1}. (C_2D_2 has an absorption band at 540 cm^{-1}.)

The criteria used for the determination of the band center and the quantum number assignments of the rotational lines were the customary ones that the band center lies between the two strongest Q lines and in the vicinity of minimum absorption by the unresolved sub-structure. In table I is presented the measured positions of the Q lines together with the rotational quantum numbers K and K' of the initial and final states. After the moments of inertia were established, the band center was computed to lie at

$$\nu_9^* = 593.7 \text{ cm}^{-1}.$$

and the rotational spacing of 1.197 $cm.^{-1}$ gives a computed value $\zeta_9^* = .192$.

B. Absorption at 9.2 microns.

Two vibrational bands contribute to the absorption in this region - the parallel band ν_6^*, and the perpendicular band ν_8^*. The upper of the two spectrograms shown in Figure 4 was obtained using a 10 cm. cell and a pressure of 50 cm. while

Table I

Wave numbers of the lines shown in Figure 3.

Line No.	K	K'	cm^{-1}
1	10	9	582.3
2	9	8	583.6
3	8	7	584.7
4	7	6	585.9
5	6	5	587.1
6	5	4	588.1
7	4	3	589.3
8	3	2	590.6
9	2	1	591.8
10	1	0	593.0
11	0	1	594.3
12	1	2	595.3
13	2	3	596.5
14	3	4	597.7
15	4	5	598.9
16	5	6	600.2
17	6	7	601.3
18	7	8	602.5
19	8	9	603.8
20	9	10	605.1
21	10	11	606.4
22	11	12	607.8
23	12	13	609.1
24	13	14	610.4

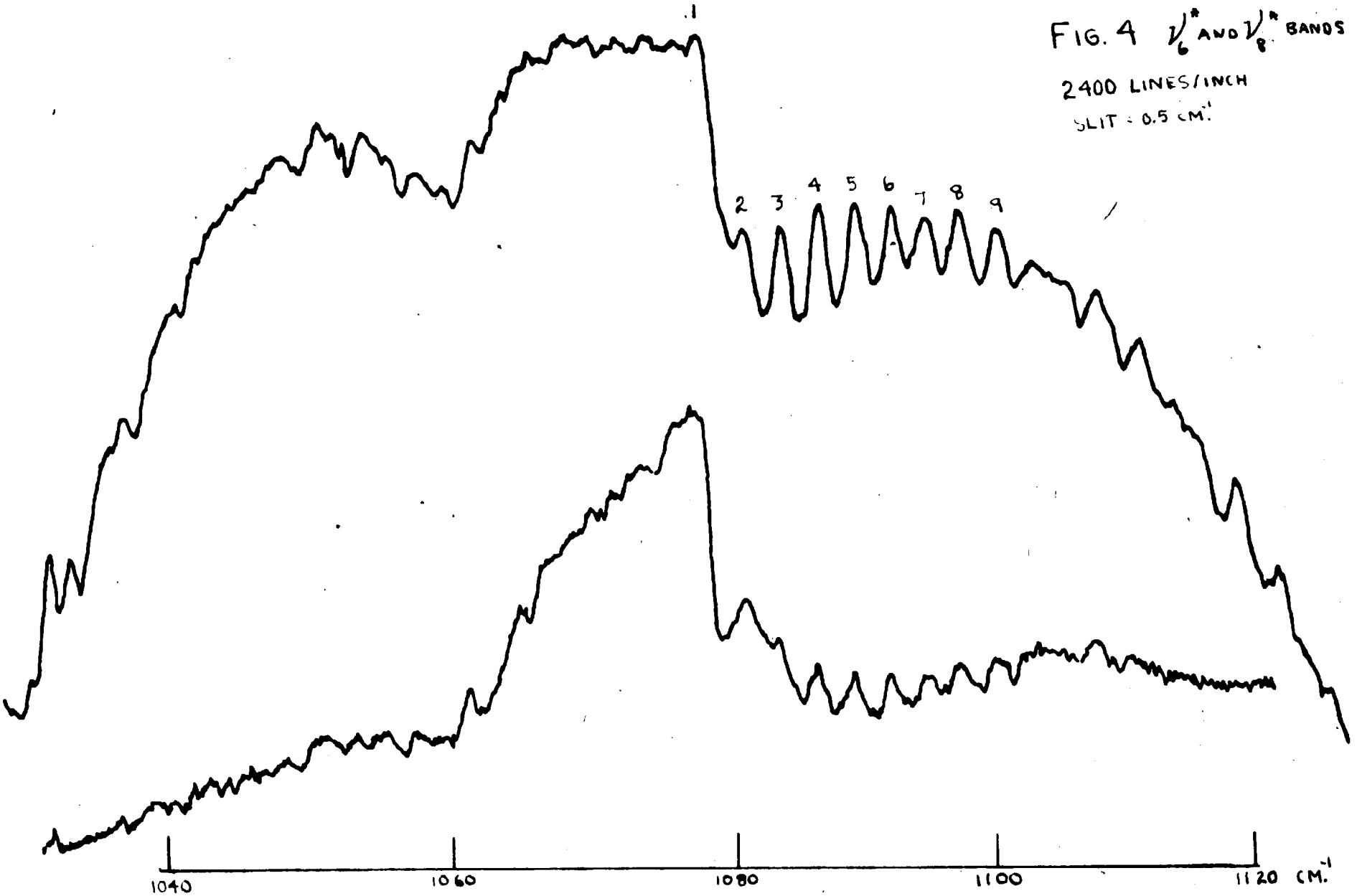


FIG. 4 ν_6^* AND ν_8^* BANDS

2400 LINES/INCH

SLIT = 0.5 CM.-1

the lower one was obtained using a 2 cm. cell and a pressure of 25 cm. Hg. Eight of the Q lines of the perpendicular band are clearly visible above 1080 cm^{-1}, but their normal intensities are obscured by the presence of the parallel band. The broad absorption peak just under 1080 cm^{-1} is interpreted as the strongly broadened Q "line" of this parallel band and with this interpretation, the vibrational frequency of ν_6^* is established at

$$\nu_6^* = 1077 \text{ cm}^{-1}.$$

The band center of the perpendicular vibrational band is estimated to lie between the lines 2 and 3 and the vibrational frequency and assignments of the Q lines are established on this basis. The measured positions of the absorption lines and their rotational quantum number assignments are given in table II. The vibrational frequency and rotational spacing of ν_8^* are computed to be

$$\nu_8^* = 1082 \text{ cm}^{-1}$$
$$\Delta\nu_8^* = 2.76 \text{ cm}^{-1}.$$

C. Absorption at 5.2 microns.

The lower of the two spectrograms shown in Figure 5 gives the background absorption by water vapor while the upper one establishes the frequency of the parallel combination band $\nu_{3+6}^* = 1902.5 \text{ cm}^{-1}$.

D. Absorption between 4.2 and 5 microns.

The general character of the absorption in this region is

Table II

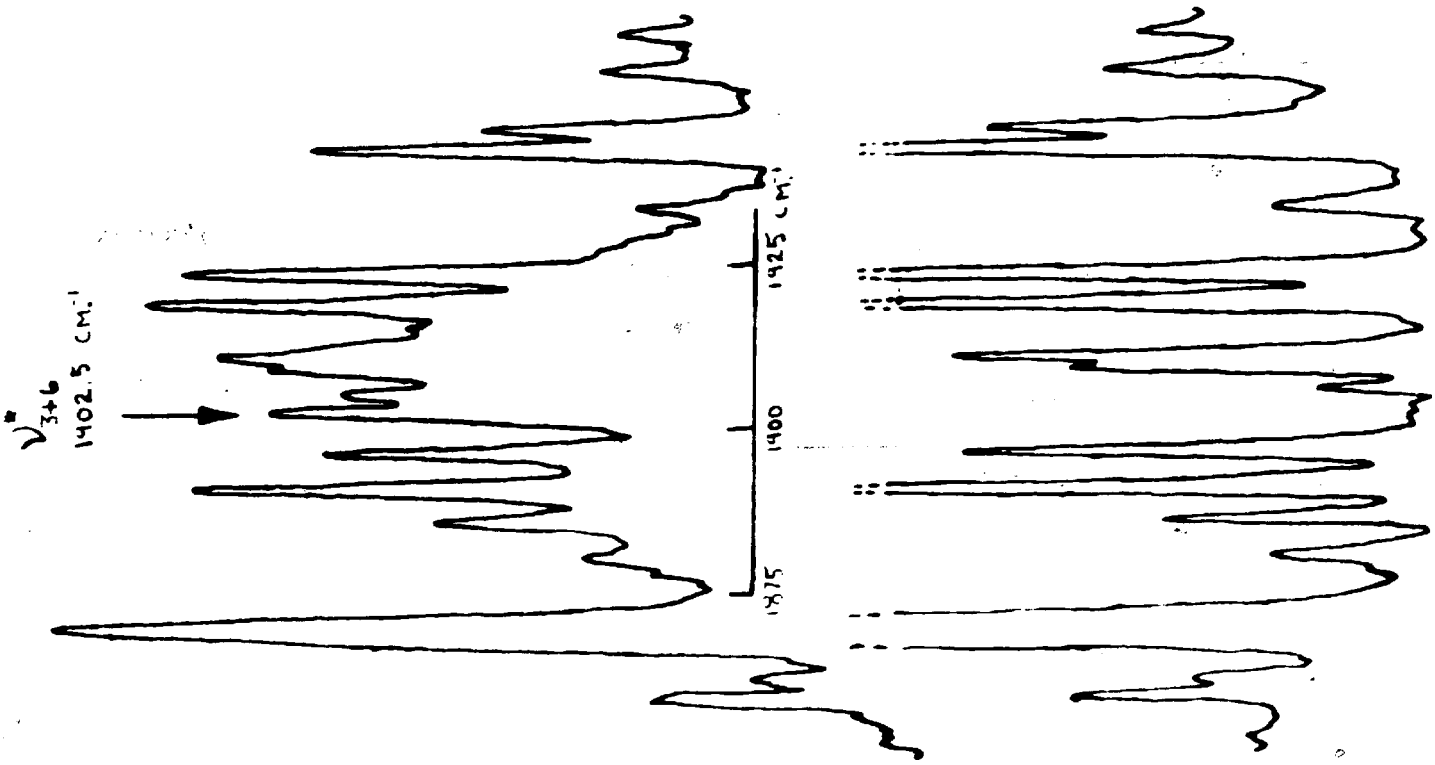
Wave numbers of the lines shown in Figure 4.

Line no.	J	J'	cm^{-1}
1	0	0	1077.1
	K	K'	
2	1	0	1080.4
3	0	1	1083.2
4	1	2	1086.2
5	2	3	1089.0
6	3	4	1091.6
7	4	5	1094.2
8	5	6	1096.9
9	6	7	1099.7

FIG. 5

3600 LINES/INCH

SLIT ~1.5 CM.$^{-1}$



shown by the spectrograms in Figure 6. (The lower spectrogram gives the background absorption.) The strong parallel band at 2087.3 cm^{-1} and the weaker parallel band at 2139.7 cm^{-1} are the result of the parallel vibrations ν_5^* and ν_{8+11}^* between which there is presumed to exist a weak resonance interaction. The broad absorption band centered at 2236 $cm.^{-1}$ is caused by the perpendicular vibration ν_7^*. This recording was obtained using a 10 cm. cell and a gas pressure of approximately 10 cm. Hg.

The parallel band at 2087.3 $cm.^{-1}$ was chosen for the determination of the large moment of inertia. Since the resolution of the spectrometer was only slightly better than the spacing of the rotational lines, this band was scanned several times using 3600, 4800, and 7200 lines/inch gratings. A typical spectrogram is given in Figure 7, and the measured positions and assignments of the rotational lines are given in Table III. The rotational constant $B_o = h/8\pi^2 cI_x$ for the ground vibrational state was determined using the "method of combination differences" given by Herzberg. Specifically, designating the difference ν (J') (R branch) - ν (J') (P branch) by X(J'), the theoretical relationship is

$$X(J') = 4B(J' + 1/2)$$

and the least squares solution for B_o is

$$4B_o = \text{Sum } (J' + 1/2)X(J')/\text{Sum } (J' + 1/2)^2$$

The B_o values obtained from four separate sets of measure-

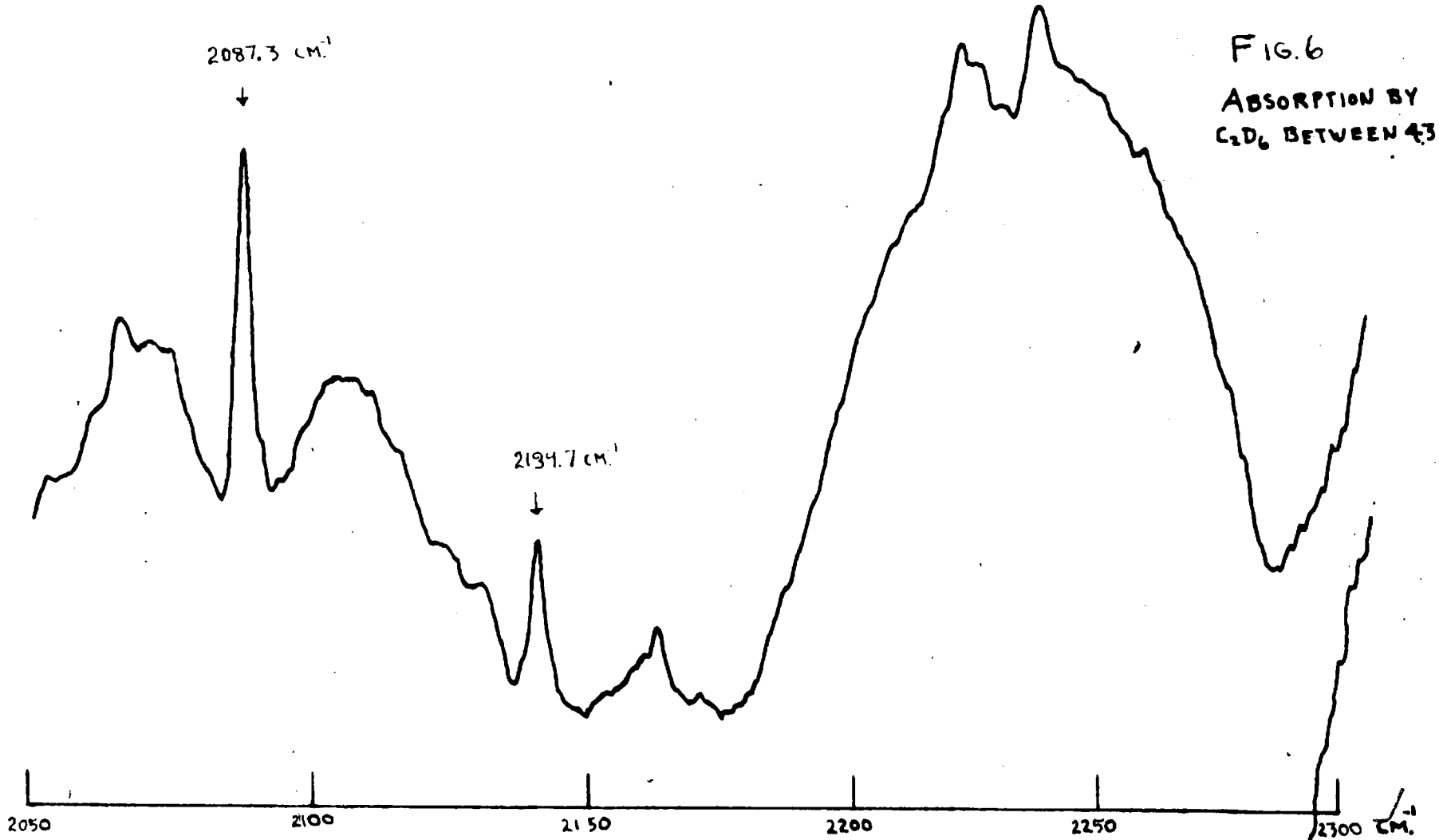


FIG. 6

ABSORPTION BY C_2D_6 BETWEEN 4.3 AND 5 μ.

FIG. 7 ABSORPTION BY ν_5^*

P = 25 CM. Hg

4800 LINES/INCH

SLIT = 0.4 CM.$^{-1}$

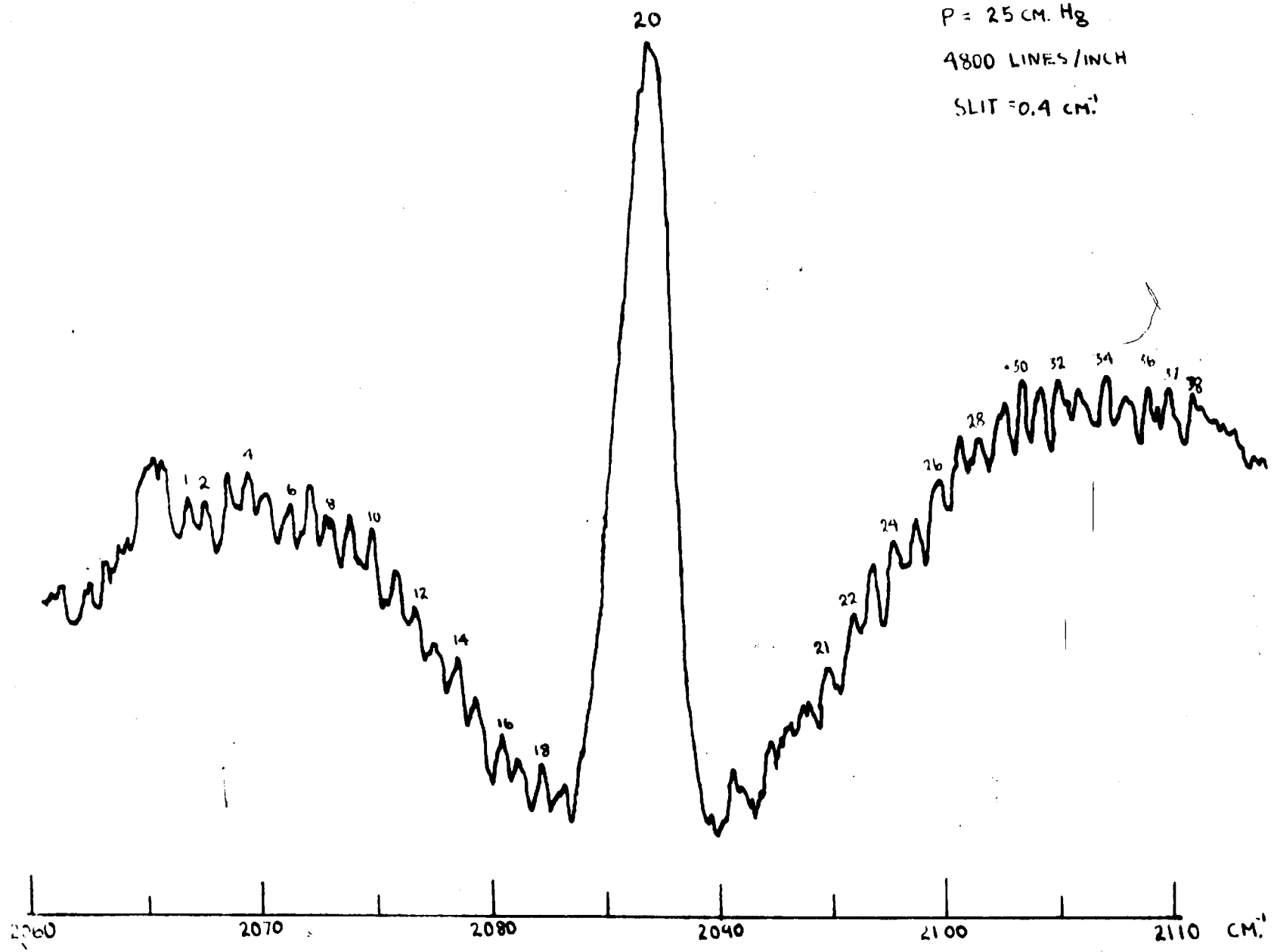


Table III

Wave numbers of the lines shown in Figure 7.

Line no.	J	J'	cm^{-1}
1	23	22	2066.38
2	22	21	2067.52
3	21	20	2068.51
4	20	19	2069.40
5	19	18	2070.05
6	18	17	2071.15
7	17	16	2072.03
8	16	15	2072.83
9	15	14	2073.67
10	14	13	2074.65
11	13	12	2075.66
12	12	11	2076.48
13	11	10	2077.34
14	10	9	2078.28
15	9	8	2079.08
16	8	7	2080.21
17	7	6	2080.88
18	6	5	2082.10
19	5	4	2082.93
20	0	0	2087.3
21	7	8	2094.59
22	8	9	2095.73
23	9	10	2096.62
24	10	11	2097.51

Table III (cont.)

Line no.	J	J'	cm^{-1}
25	11	12	2098.53
26	12	13	2099.58
27	13	14	2100.58
28	14	15	2101.47
29	15	16	2102.51
30	16	17	2103.40
31	17	18	2104.20
32	18	19	2105.04
33	19	20	2105.97
34	20	21	2107.20
35	21	22	2108.07
36	22	23	2109.02
37	23	24	2109.70
38	24	25	2111.07

ments are:

(1) $B_o = 0.460 \pm .001$ cm.$^{-1}$ (from values given in Table III)

(2) $B_o = 0.461 \pm .001$ " (3600 lines/inch grating; 1st order)

(3) $B_o = 0.461 \pm .001$ (4800 lines/inch grating)

(4) $B_o = 0.462 \pm .001$ (7200 lines/inch grating)

Adopted value: $B_o = 0.461_0$ cm.$^{-1}$

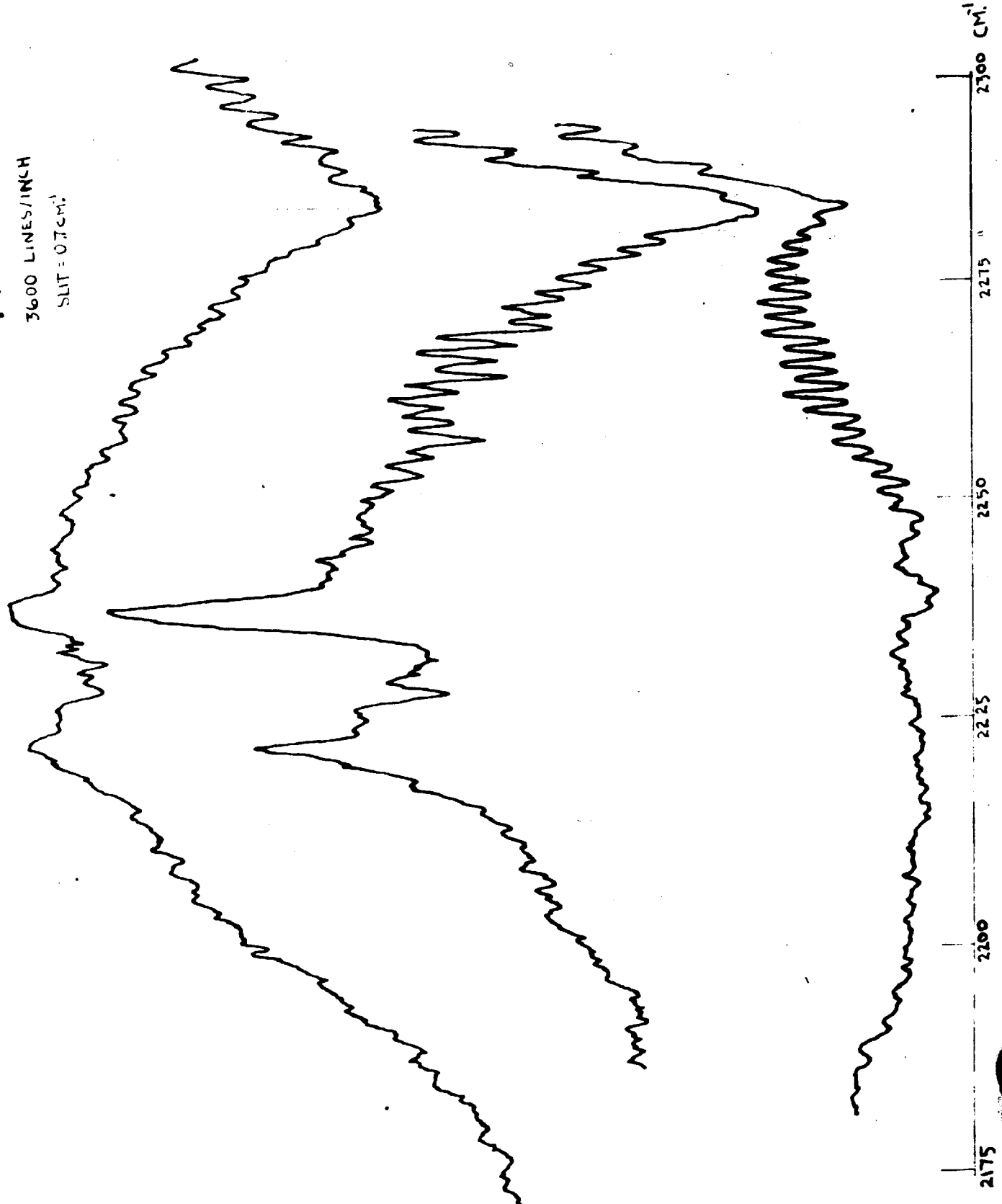
This value for the rotational constant, B, leads to the value $I_x = 60.7_1 \times 10^{-40}$ gm. cm.^{2}.

Attempts to resolve the rotational fine structure of the broad absorption band at 2236 cm.$^{-1}$ were unsuccessful. However, certain characteristic features are evident from the spectrograms given in Figure 8. (The lowest tracing gives the background atmospheric absorption.) Thus, the absorption by C_2D_6 is apparently due to more than just the perpendicular vibration ν_7^*. The combination band ν_{2+6}^* lies in this region ($\nu_2^* + \nu_6^* = 1158 + 1077 = 2235$ cm.$^{-1}$) and could well contribute to the absorption pattern either through it normal infra-red activity (the equivalent band in ethane is moderately intense) or by Coriolis interaction with ν_7^*, or by a combination of both. The existence of such a Coriolis interaction between the parallel band ν_{2+6}^* and the perpendicular band ν_7^* is suggested by the presence of the two prominent absorption peaks at about 2222 and 2238 cm^{-1}. Qualitatively, such an interaction would be dependent upon the quantity $(J^2 - K^2)$ and would be most pronounced when the interacting rotational levels ($\Delta K = \pm 1$, $\Delta J = 0$) were of equal energy. The effect on the spectrum would be a broadening of the Q line of the parallel band ν_{2+6}^*

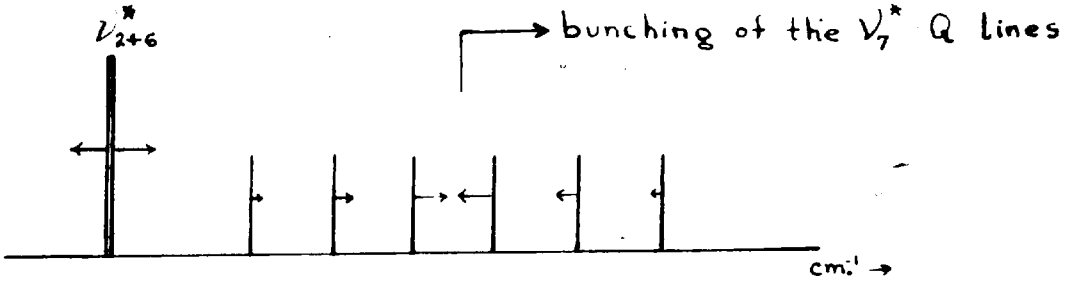
FIG. 8 ABSORPTION BY ν_7^*

3600 LINES/INCH

SLIT = 0.7 CM.$^{-1}$



and a broadening of the Q lines of the perpendicular band ν_7^* in such a way that there would be an apparent bunching of these lines at the resonance position. This may be illustrated by the following type diagram where the normal Q line positions are given together with arrows which give the direction of broadening.



The preceeding diagram could have been drawn equally well with ν_{2+6}^* on the high frequency side of the bunched Q lines. The exact interpretation is obscure and it is felt that the present observations of this band are not such as to warrant a change in the value $\nu_7^* = 2236$ cm^{-1} reported earlier by Stitt.

The program set forth at the beginning of this section has been successfully accomplished except for the determination of the normal rotational spacing of the perpendicular band ν_7^*. The measurement of this spacing would have been most welcome since it, together with the spacings of ν_5^*, ν_8^*, and ν_9^*, would have permitted the direct spectroscopic determination of the small moment of inertia of C_2D_6. Since the small moments for C_2D_6 and C_2H_6 stand in the ratio of the known masses of the deuteron and the proton, this would have given a direct

check on the validity of the perturbation scheme through which the value of the small moment of C_2H_6 was determined (see Chapter V). However, such a determination of the rotational spacing of ν_7^* would also require the use of a perturbation scheme, probably with ν_{2+6}^* but possibly also with ν_{2+8}^* ($\nu_2^* + \nu_8^* = 1158 + 1082 = 2240$ cm.$^{-1}$). The broadened Q line of the parallel band $\nu_6^* = 1077$ cm^{-1} is also presumably due to Coriolis interaction with the perpendicular band ν_8^* and the observed spacing of the Q lines may differ slightly from the normal or unperturbed spacing.

CHAPTER III

THE GENERAL PROCEDURE

The great number of variables associated with a polyatomic molecule makes it necessary to utilize any properties which enable one to investigate the molecule in a stepwise fashion. One of these properties is the approximate separability of electronic, vibrational, rotational, and nuclear spin motions. Up to the present time, most of the investigations of polyatomic molecules have been concerned with the vibrational and rotational motions associated with the electronic ground states of these molecules. The methods of observation have generally been such that the hyperfine structure produced by the nuclear spin motions is not resolved and the existence of the spin variables is made known only through their effect on the statistical weights of the rotational states. (Microwave techniques represent an exception.) Another property of a molecule, which enables one to subdivide and classify these motions further, is its symmetry. It is the theory of groups and group representations that formalizes the methods for this additional simplification.

It can readily be shown that the normal coordinates (those coordinates along whose axes the motions of the normal vibrations can take place) are the bases for irreducible representations of the point group which characterizes the symmetry of the equilibrium configuration of the molecule. The activity in infra-red absorption and Raman effect of any vibration depends on its symmetry type, that is, on the irreducible re-

presentation which it generates, and it is by the use of these predicted activities or selection rules that one determines from the spectroscopic data the equilibrium configuration of a molecule.

The collection of normal coordinates having the same symmetry type generate a characteristic subspace of the configuration space of internal coordinates. If the vibrations are non degenerate, then any (non-singular) linear transformation of these normal coordinates will generate a new set of coordinates which again will have this same symmetry type. If the vibrations are doubly degenerate, any linear transformation of the associated pairs of normal coordinates will generate a new set of associated pairs of coordinates with the same symmetry type. Similarly for higher orders of degeneracy. When expressed in terms of symmetry coordinates, both the kinetic energy and the quadratic terms of the potential energy appear in a considerably simplified form in which there are no cross products involving symmetry coordinates belonging to different symmetry types. The Hamiltonian for the harmonic vibrations thus appears separated into a sum of Hamiltonians, one for the vibrations of each symmetry class (type). The use of symmetry coordinates, then, permits one to investigate the vibrations of a single symmetry class without considerations of the remaining vibrations. This is the separation given by the symmetry conditions. Any further separation requires detailed knowledge of the forces.

Under the operations of the point group (i.e. 3-fold

rotations about a symmetry axis, reflections, etc.), each of these characteristic sub spaces is mapped onto itself. Moreover, if the vibrations are non degenerate, each symmetry coordinate will either remain unchanged or change sign only. If the vibrations are doubly degenerate, the two dimensional space of each associated pair of symmetry coordinates is mapped onto itself while the individual components of each associated pair undergo a linear transformation characteristic of the particular point group operation. The transformation properties (with respect to the point group operations) of the symmetry coordinates for a given symmetry class are identical and in general these properties are sufficiently well expressed by the set of traces or characters of the transformation matrices.

The character table for the irreducible representations of the point group D_{3d}, presumably the point group to which ethane belongs, is given in Table IV (character tables for this and various other point groups are given by Herzberg).

For ethane, there are two classes of fundamental vibrations in which the carbon nuclei move along the symmetry axis, and two classes in which these nuclei move perpendicular to this axis. It is convenient to generalize the earlier definition of parallel and perpendicular vibrations, letting parallel and perpendicular refer to the motion, relative to the symmetry axis, of the carbon nuclei rather than the electric moment. In this manner A_{2u} and A_{1g} are called respectively "parallel active" and "parallel inactive" vibra-

tions, while E_u and E_g vibrations are called respectively "perpendicular active" and "perpendicular inactive" vibrations. The "active" or "inactive" refers to the presence or absence of an electric moment and thus indicates whether or not these vibrations will emit and absorb infra-red radiation. A list of the symmetry types of the normal vibrations of ethane and their spectral activity is given in Table V and the normal vibrations themselves are schematically pictured in Figure 9.

The outline of the general procedure for determining the potential constants of ethane may be expressed as follows:

I Collection of the data associated with a given symmetry class of vibrations.

(a) Fundamental frequencies.

(b) ζ values.

II Definition of the force constants and the determination of the equations which relate these force constants to this data.

(a) Relations between the force constants and the normal frequencies.

(b) Relations between the normal frequencies and the fundamental frequencies.

(c) Relations between the ζ values and the force constants.

III Solution of these equations for the force constants.

It is the present purpose to give a brief description of the general relations between the force constants, the fundamental frequencies, and the zeta values.

Table IV

Character table of D_{3d}.

	I	$2S_6$	$2C_3$	i	$3C_2$	$3\sigma_d$
A_{1g} :	1	1	1	1	1	1
A_{1u} :	1	-1	1	-1	1	-1
A_{2g} :	1	1	1	1	-1	-1
A_{2u} :	1	-1	1	-1	-1	1
E_g :	2	-1	-1	2	0	0
E_u :	2	1	-1	-2	0	0

The operations of the point group have the following definitions:

I = the identity operation.

S_6 = rotation by $2\pi/6$ about the symmetry axis (z-axis) followed by the reflection through the xy plane.

$C_3 = S_6^2$ = rotation by $2\pi/3$ about the symmetry axis.

i = inversion.

C_2 = rotation by π about one of the three 2-fold axes perpendicular to the z-axis.

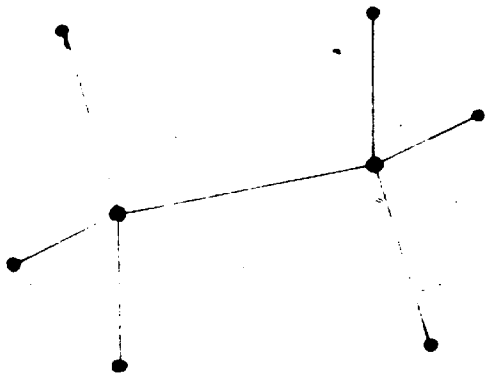
σ_d = reflection through one of the three planes of symmetry.

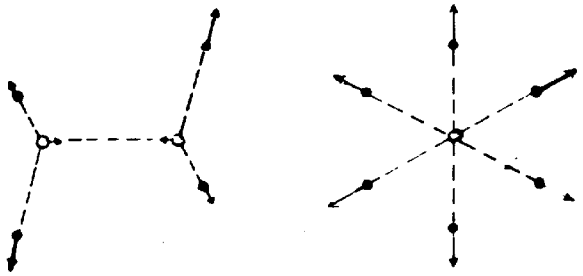
Table V

Symmetry types of the normal vibrations of ethane.

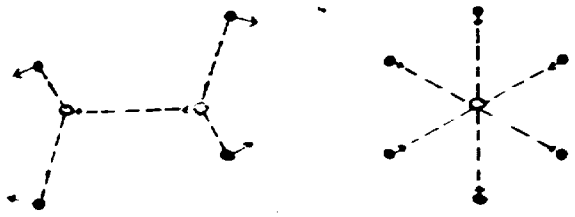
Classification	Vibration	Activity
A_{1g} : Parallel inactive vibrations	ν_1, ν_2, ν_3	Raman, polarized
A_{1u} : Torsional vibration	ν_4	inactive
A_{2u} : Parallel active vibrations	ν_5, ν_6	Infra-red, parallel
E_u : Perpendicular active vibrations	ν_7, ν_8, ν_9	Infra-red, perpendicular
E_g : Perpendicular inactive vibrations	ν_{10}, ν_{11}, ν_{12}	Raman, depolarized

NORMAL VIBRATIONS OF ETHANE FIG. 9

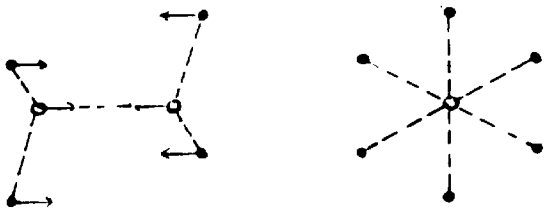




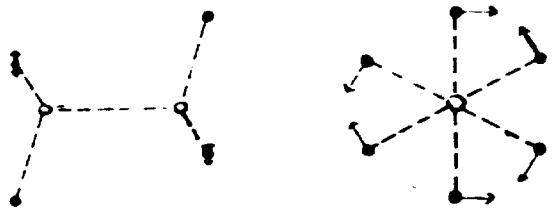
ν_1



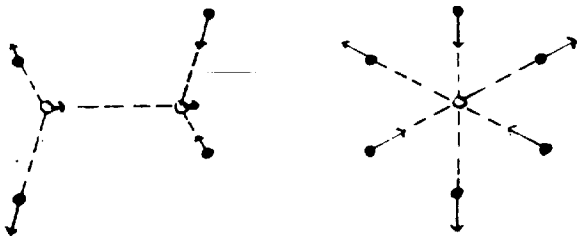
ν_2



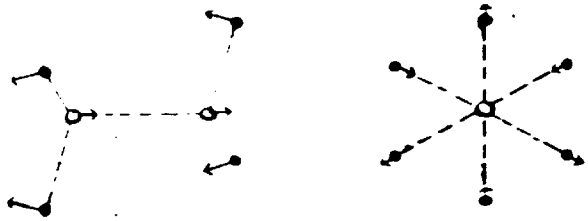
ν_3



ν_4

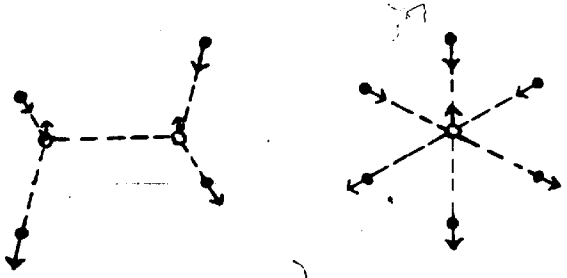


ν_5

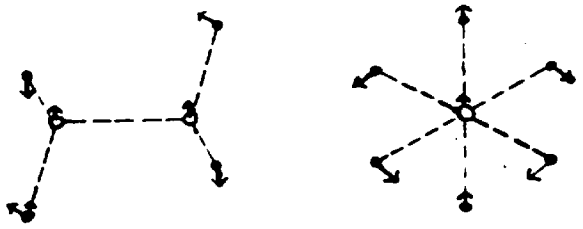


ν_6

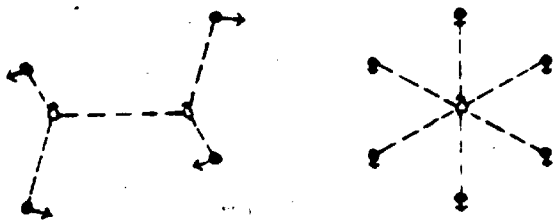
FIG. 9 (CONCL.)



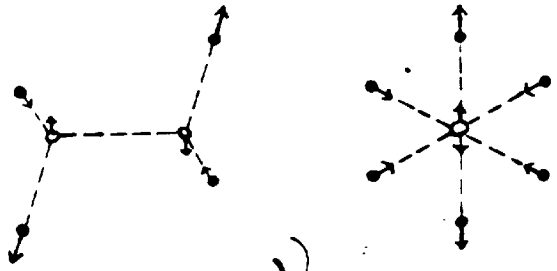
ν_7



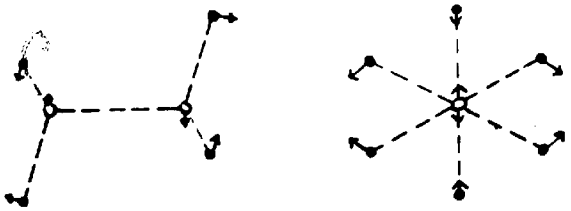
ν_8



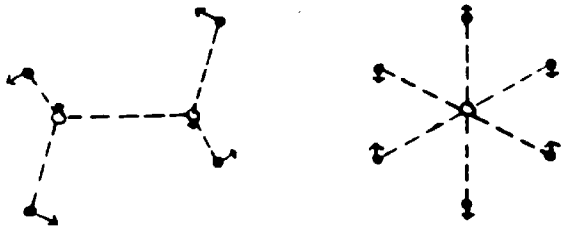
ν_9



ν_{10}



ν_{11}



ν_{12}

The vibrational energy associated with a given symmetry class of normal vibrations may be expressed as:

$$T + V = \tfrac{1}{2} \sum \mu_{ij} \dot{\xi}_i \dot{\xi}_j + \tfrac{1}{2} \sum a_{ij} \xi_i \xi_j \quad \text{for } C_2H_6$$

$$T^* + V^* = \tfrac{1}{2} \sum \mu^*_{ij} \dot{\xi}_i \dot{\xi}_j + \tfrac{1}{2} \sum a_{ij} \xi_i \xi_j \quad \text{for } C_2D_6$$

where ξ_i and $\dot{\xi}_i$ are the i^{th} symmetry coordinate and its time derivative, the μ_{ij} and μ^*_{ij} are known functions of the masses and dimensions of C_2H_6 and C_2D_6, and the a_{ij} define the potential constants to be determined. (In order that the potential energies of C_2H_6 and C_2D_6 shall have the same explicit form, it is necessary that the symmetry coordinates ξ_i represent definite geometrical distortions of the configuration of the molecule. The coordinates must also (1) give displacements from equilibrium, and (2) conserve linear and angular momenta.)

The relations between the potential constants and the normal frequencies ω_α for C_2H_6 and ω^*_α for C_2D_6 are given by the roots of the secular determinants

$$\left| \mu_{ij}\omega_\alpha^2 - a_{ij} \right| = 0 = \left| \mu^*_{ij}\omega^{*2}_\alpha - a_{ij} \right|$$

It is the relations between the normal frequencies and the fundamental frequencies which present certain difficulties. As was mentioned in the Introduction, one is unable to give rigorous relations, but, with the aid of the Teller product rule, can make plausible estimates. This procedure, due to Dennison[13], involves a generalization of the known relations between the fundamental and normal frequencies of isotopic diatomic molecules. Thus, for a diatomic molecule, the normal vibrations and fundamental vibrations are governed by the respective energy expressions

I Normal Vibration: $T + V = \frac{1}{2}\mu\dot{\xi}^2 + \frac{1}{2}k\xi^2 \rightarrow \omega = \sqrt{k/\mu}$

II Fundamental Vibration: $T + V = \frac{1}{2}\mu\dot{\xi}^2 + \frac{1}{2}k\xi^2 + \frac{1}{6}k_2\xi^3 + \frac{1}{24}k_3\xi^4 + \ldots$

For the second equation, by neglecting terms in ξ^5 and higher, and treating the cubic and quartic terms by perturbation theory, one predicts the fundamental frequency

$$\nu = \omega(1 - \alpha\omega) \tag{1}$$

where α is a function of the coefficients k, k_2 and k_3 and not of the reduced mass μ. Hence for the isotopic diatomic molecule, one obtains

$$\nu^* = \omega^*(1 - \alpha\omega^*) \tag{2}$$

Finally, the product rule gives a third equation

$$\omega/\omega^* = \sqrt{\mu^*/\mu} \tag{3}$$

From these equations one may determine the normal frequencies ω and ω^* in terms of the observed fundamental frequencies ν and ν^* and the known reduced masses μ and μ^*. The quantity $\alpha\omega$ is called the anharmonicity factor and will be designated as x. The content of the first two equations is incorporated in the single equation

$$X^* = \frac{\omega^*}{\omega} X$$

The similarities between the vibrations of two isotopic polyatomic molecules (belonging to the same point group) leads to the very plausible "first" assumption that, if x_i is the anharmonicity factor associated with the fundamental vibration ν_i, then the anharmonicity factor x_i^* for the similar vibration of the isotopic molecule will be given approximately by the equation

$$X_i^* = \frac{\nu_i^*}{\nu_i} X_i$$

In order to establish the normal frequencies from the fundamental frequencies, it is necessary to know each one of the x_i and x_i^* values. The use of the above set of relations reduces this problem to the determination of the x_i alone. The product rule gives only one relation among these anharmonicity factors, namely

$$\sqrt{\frac{|\mu_{ii}|}{|\mu_{ii}^*|}} = \prod_i \frac{\omega_i}{\omega_i^*} = \prod_i \frac{\nu_i(1-x_i^*)}{\nu_i^*(1-x_i)} = \prod_i \frac{\nu_i/\nu_i^* - x_i}{1-x_i},$$

Of course, if there is only one vibration associated with the particular symmetry class, this condition is sufficient,

but such a case is exactly equivalent to the case of diatomic molecules. Thus, in general, further conditions are required to specify the x_i values.

For the few polyatomic molecules where the values are known, these anharmonicity factors are generally positive and of the order of magnitude of two to five percent. If, for a given class of vibrations, one defines the average anharmonicity factor, $\bar{x}$, by the equation

$$\sqrt{\frac{|\mu_{ii}|}{|\mu_{ii}^*|}} = \prod_i \left(\frac{\nu_i/\nu_i^* - \bar{x}}{1 - \bar{x}} \right)$$

then the best apriori estimate of the value of x_i is obtained by setting $x_i = \bar{x}$. However, many of the vibrations of ethane are similar to those of methane for which the anharmonicity factors are known[13], and this information permits closer estimation of the x_i values for ethane. Thus, the C-H stretching and H-C-H bending frequencies of ethane agree within a few percent of the corresponding frequencies in methane. One might expect the agreement between the associated anharmonicity factors to be intermediate between this few percent and the agreement between the bond energies. The procedure adopted is to choose the x_i values for ethane to agree as closely as possible with the corresponding values for methane and still be consistent with the requirements of the product rules. This partly constrained choice constitutes the "second" and last assumption required to determine the normal frequencies. It is unfortunate that the differences between the fundamental

and normal frequencies cannot be rigorously determined, but the estimations as obtained by means of the above assumptions should be considerably better than ignoring these differences altogether.

We may summarize the method by which the fundamental frequencies are utilized in the determination of the potential constants:

I The fundamental frequencies ν_i serve to determine a set of normal frequencies ω_i through the defining equations

$$\nu_i = \omega_i(1 - x_i)$$
$$\nu_i^* = \omega_i^*(1 - x_i^*)$$

and the two empirical relations

(1) $$x_i^* = \nu_i^*/\nu_i \, x_i$$

(2) $$x_i(C_2H_6) \cong x_i'(CH_4)$$ subject to the condition $$\sqrt{\frac{|\mu_{ij}|}{|\mu_{ij}^*|}} = \prod_i \left(\frac{\nu_i/\nu_i^* - x_i}{1 - x_i}\right)$$

II The normal frequencies determine relations among the potential constants through the roots of the secular determinants

$$\left| \mu_{ij}\omega_\alpha^2 - a_{ij} \right| = 0 = \left| \mu_{ij}^*\omega_\alpha^{*2} - a_{ij} \right|$$

For the parallel active and parallel inactive vibrations, there are no additional data beyond the fundamental frequencies. For the parallel active vibrations, the fundamental frequencies are sufficient to determine the associated set of potential constants but in the case of the parallel inactive vibrations, the data must be supplemented by one additional condition.

For the perpendicular active and perpendicular inactive

vibrations, the additional data, required for the determination of the associated potential constants, are supplied by the ζ values. It is the purpose now to give the relations between the force constants and these zeta values.

The Hamiltonian generally used for the rotational energy of a symmetric top molecule may be expressed as[17]

$$H = \frac{(P_x - p_x)^2 + (P_y - p_y)^2}{2I_x} + \frac{(P_z - p_z)^2}{2I_z}$$

where P_x, P_y, P_z, and p_x, p_y, p_z are the components of the total and vibrational (or internal) angular momentum and I_x and I_z are the principal moments of inertia.

To the first order of approximation, the energy spectrum is given by[12]

$$E = \frac{\hbar^2 J(J+1)}{2I_x} + \frac{\hbar^2}{2}\left(\frac{1}{I_z} - \frac{1}{I_x}\right)K^2 - \frac{\hbar^2 \zeta}{I_z} K$$

where $\hbar\zeta$ is the expectation value of p_z and the rotational quantum number, K, is considered positive or negative depending on whether the rotational and vibrational phases advance in the same or in opposite senses. (The fundamental perpendicular bands are generated by transitions $K \rightarrow K + 1$; ground vibrational state $\rightarrow$ 1st excited vibrational state.)

For a given symmetry class of degenerate vibrations, the z-component of the internal angular momentum has the form

$$p_z = \sum \zeta_{ij}(\xi_i^\circ p_{\eta_j^\circ} - \eta_j^\circ p_{\xi_i^\circ}) \quad ; \quad \zeta_{ij} = \zeta_{ji}$$

where $\xi_i^\circ, \eta_i^\circ$ are the pair of normal coordinates associated with the i^{th} normal vibration.and $P_{\xi_i}^\circ, P_{\eta_i}^\circ$, are their conjugate momenta. If the i^{th} normal vibration is singly excited, the expectation value of p_z is

$$P_z = \pm \hbar \zeta_{ii} \equiv \pm \hbar \zeta_i$$

The value of ζ_i, determined from the rotational spacing of the i^{th} fundamental vibrational band, is related to the potential constants through their dependence on the transformation matrix between the normal coordinates and the symmetry coordinates. Thus, one can construct p_z as a function of the symmetry coordinates, their conjugate momenta, and a known set of constant coefficients, and then by re-expression in terms of the normal coordinates, solve for the ζ_{ij} in terms of the known set of coefficients and the components of the transformation matrix.

For both the perpendicular active and perpendicular inactive classes of ethane, we have chosen symmetry coordinates such that the kinetic energy expression contains no cross product terms and each of the square terms have the same coefficient. By normalizing the symmetry coordinates so that this constant coefficient is unity, then the transformation matrix between these normalized symmetry coordinates and the normal coordinates is a unitary matrix. In terms of these normalized coordinates,

$$P_z = \sum Z_{ij}(\xi_i P_{\eta_j} - \eta_j P_{\xi_i}) \quad ; \quad Z_{ij} = Z_{ji}$$

The unitary transformation matrix $S_{i\alpha}$, defined by the equations $\xi_i = \sum S_{i\alpha} \xi^0_\alpha$, is determined from the equations (since $\mu_{ij} = \delta_{ij}$)

$$\sum_j \left(\omega_\alpha^2 \delta_{ij} - a_{ij} \right) S_{j\alpha} = 0 \qquad (1)$$

Since $S_{i\alpha}$ is unitary, $p_{\xi_i} = \sum S_{i\alpha} p_{\xi^0_\alpha}$, and one obtains the following equations for the ζ_α.

$$\zeta_\alpha = \sum_{i,j} Z_{ij} S_{i\alpha} S_{j\alpha} \qquad (2)$$

Equations (1) and (2) give the desired relations between the observed zeta values and the potential constants. This, then, concludes the general procedure for determining the potential constants of ethane.

The above relations between the measured zeta values and the potential constants are "first order" equations. These equations neglect the effect upon internal angular momentum of the anharmonicity of the vibrations as well as the terms involving the ζ_{ij}. Although usually these effects are small, it is occasionally necessary to make allowance for their presence as will be done in the cases of ν_8 and ν_{10}. Certain of the qualitative features of these higher order contributions to the zeta values will be presented in the next chapter.

CHAPTER IV

HIGHER ORDER CONTRIBUTIONS TO THE ZETA VALUES

The first order expression for the rotational energy of a symmetric top molecule was given on page 45 and is of the form

$$E = \alpha J(J+1) + \beta K^2 + \gamma K \quad \text{where} \quad \gamma = -\frac{\hbar^2 \zeta}{I_z}$$

When the energy is calculated to second order, the above expression is modified in two ways; (1) small terms proportional to quartic powers of J and K occur, and (2) the coefficients α, β, and γ now contain small terms proportional to the vibrational quantum numbers. These new values for the coefficients will be designated α', β', and γ'. By the higher order contributions to the zeta values is meant those contributions to the energy which are linear in the quantum number K and cause the inequality $\gamma \neq \gamma'$. (In the special case of resonance, the energy is not expressable as a power series in the rotational quantum numbers and the meaning of γ' is ambiguous.) The present purpose is to determine those contributions to γ' which arise from the interaction terms

$$T' = -\frac{(P_x p_x + P_y p_y)}{I_x} - \frac{P_z \sum_{\alpha,\beta} \zeta_{\alpha\beta}(\xi_\alpha p_\beta - \eta_\alpha p_\xi)}{I_z}$$

The operator T' has no diagonal matrix elements in the representation based on the first order wave functions, and the energy contributions are proportional to $P_x^2 \sim P_y^2 \sim J^2 - K^2$ and $P_z^2 \sim K^2$. Thus the contributions of T' alone do not affect the zeta values. However, due to the first order vibration-

rotation interaction energy, the term

$$-\frac{P_z \sum_{i \neq j} \zeta_{ij} (\xi_i P_{\eta_j} - \eta_i P_{\xi_i})}{I_z}$$

has matrix connections in common with the relatively large anharmonic terms and "interference" occurs which produces an energy correction linear in K. The physical picture of how the zeta values are changed by this interaction is rather simple. In the actual symmetric top molecule undergoing degenerate vibrations, an individual nucleus moves in a small elliptic orbit inclined at some angle, θ_i, to the symmetry axis. The resultant internal angular momentum, due to the sum of these nuclear contributions, lies along the symmetry axis and has the value $h\zeta$, where ζ is a weighted average of the $\cos \theta_i$. If the restoring forces are harmonic, then as the vibrations become more energetic and the elliptic orbits become larger, the tilt or pitch angles, θ_i, do not change. However, in the presence of anharmonic forces, the angles θ_i, in general will depend on the size of the orbits. The first order ζ values are based on infintesimal amplitudes of vibration and hence on limiting values of the θ_i as the elliptic orbits are shrunk to zero. By determining the "interference" between anharmonicity and vibration rotation interaction, one is thus determining the modification in the pitch angles which occurs due to the finite size of the actual nuclear orbits.

For the actual calculation of this "interference" contribution to the energy, it is convenient to use the polar

normal coordinates ρ_i, φ_i rather than the cartesian normal coordinates ξ_i°, η_i°. In terms of these polar coordinates

$$\text{I} \quad -P_z \sum_{i,j} \zeta_{ij}(\xi_i^\circ P_{\eta_j}^\circ - \eta_j^\circ P_{\xi_i}^\circ) = -\frac{\hbar^2 K}{2I_z} \sum \zeta_{ij} e^{i(\varphi_i-\varphi_j)} \left\{ \rho_j\left(\frac{\partial}{\partial\rho_i} + \frac{1}{i\rho_i}\frac{\partial}{\partial\varphi_i}\right) - \rho_i\left(\frac{\partial}{\partial\rho_j} - \frac{1}{i\rho_j}\frac{\partial}{\partial\varphi_j}\right)\right\}$$

If n_i, l_i represent the vibrational quantum numbers of the i^{th} two dimensional oscillator, then the matrix connections for the above (i,j) terms are of the form

$$\begin{matrix} n_i, n_j, n_k \longleftrightarrow n_i \pm 1, n_j \pm 1, n_k \\ l_i, l_j, l_k \longleftrightarrow l_i \pm 1, l_j \pm 1, l_k \end{matrix} \quad \text{where } k \neq i,j$$

The lowest order anharmonic terms having these same connections are quartic terms of the form

$$\text{II} \qquad V' = \sum_{i<j} \left\{ \alpha_{ij} \rho_i^3 \rho_j + \alpha_{ji} \rho_j^3 \rho_i \right\} \left\{ e^{i(\varphi_i-\varphi_j)} + e^{-i(\varphi_i-\varphi_j)} \right\}$$

The interference energy contribution to the vibrational state, (n,l) is

$$\Delta E_{(n,l)} = \sum_{(n',l')} \frac{2\,|T'|^{(n',l')}_{(n,l)}\,|V'|^{(n,l)}_{(n',l')}}{E^\circ_{(n,l)} - E^\circ_{(n',l')}}$$

The evaluation of this sum requires the matrix elements of the following operators

(a) $\rho e^{\pm i\varphi}$

(b) $\rho^3 e^{\pm i\varphi}$

(c) $e^{\mp i\varphi}\left\{\frac{\partial}{\partial\rho} \pm \frac{1}{i\rho}\frac{\partial}{\partial\varphi}\right\}$

The wave functions for the two dimensional harmonic oscillator are[19]

$$\Psi_{n,l} = \left(\tfrac{n+l}{2}!\right)^{1/2}\left(\tfrac{n-l}{2}!\right)(-1)^{\frac{n-l}{2}} e^{-\frac{\rho_o^2}{2}} \rho_o^l e^{\pm il\varphi} \left[L^l_{\frac{n+l}{2}} \equiv \sum \frac{(-1)^\beta \rho_o^{2\beta}}{(l+\beta)!\,\beta!\,(\frac{n-l}{2}-\beta)!} \right]$$

where ρ_0 is related to the normal coordinate, ρ , and the vibrational angular velocity, ω, by the equation

$$\rho = \sqrt{\frac{\hbar}{\omega}}\,\rho_0$$

From the above expression for $\psi_{n,l}$, one may obtain the following recursion formulae which give directly the required matrix elements.

(a) $$\rho_0 e^{\pm i\varphi}\psi_{n,l} = \left(\frac{n\pm l}{2}+1\right)^{1/2}\psi_{n+1,l\pm1} + \left(\frac{n\mp l}{2}\right)^{1/2}\psi_{n-1,l\pm1}$$

(b) $$\rho_0^3 e^{\pm i\varphi}\psi_{n,l} = \left(\frac{n\pm l}{2}+1\right)^{1/2}\left(\frac{n\pm l}{2}+2\right)^{1/2}\left(\frac{n\mp l}{2}+1\right)^{1/2}\psi_{n+3,l\pm1}$$
$$+ \frac{3n+4\mp l}{2}\left(\frac{n\pm l}{2}+1\right)^{1/2}\psi_{n+1,l\pm1} + \frac{3n+2\pm l}{2}\left(\frac{n\mp l}{2}\right)^{1/2}\psi_{n-1,l\pm1}$$
$$+ \left(\frac{n\mp l}{2}\right)^{1/2}\left(\frac{n\mp l}{2}-1\right)^{1/2}\left(\frac{n\pm l}{2}\right)^{1/2}\psi_{n-3,l\pm1}$$

(c) $$e^{\mp i\varphi}\left(\frac{\partial}{\partial\rho_0} \pm \frac{1}{i\rho_0}\frac{\partial}{\partial\varphi}\right)\psi_{n,l} = -\left(\frac{n\mp l}{2}+1\right)^{1/2}\psi_{n+1,l\mp1} + \left(\frac{n\pm l}{2}\right)^{1/2}\psi_{n-1,l\mp1}$$

For the general vibrational state (n,1), the energy contribution given by equation III' may then be computed as

IV $$\Delta E_{(n,l)} = \sum_{i\neq j}\frac{4\hbar}{I_z}K\zeta_{ij}\,\frac{(\omega_i\omega_j)^{1/2}(2l_j-l_i)(n_i+1)\left[\alpha_{ij}\left(\frac{\hbar}{\omega_i}\right)^{3/2}\left(\frac{\hbar}{\omega_j}\right)^{1/2}\right]}{\omega_i^2-\omega_j^2}$$

Letting

$$\frac{4\zeta_{ij}(\omega_i\omega_j)^{1/2}\left[\alpha_{ij}\left(\frac{\hbar}{\omega_i}\right)^{3/2}\left(\frac{\hbar}{\omega_j}\right)^{1/2}\right]}{\hbar(\omega_i^2-\omega_j^2)} \equiv \beta_{ij}$$

then the contribution to the zeta value is

V $$\Delta\zeta_{(n,l)} \equiv -\frac{I_z}{\hbar^2 K}\Delta E_{(n,l)} = \sum_{i\neq j}\beta_{ij}(l_i-2l_j)(n_i+1)$$

The coefficients of the quartic potential terms are not known for ethane and hence one cannot make a direct numerical calculation of $\Delta\zeta$. However, an estimate can be made of this correction. Thus, barring near resonances, β_{ij} is of the order of the ratio of the energy contributions of the quartic potential terms to the quadratic potential terms. For CO_2, some of the quartic terms have been determined[13] and the corresponding ratio is about 1%. The magnitude of $\Delta\zeta$ for low quantum number vibrational states is then about

$$\Delta\zeta \simeq .01$$

Although relatively small, this correction is a factor ten larger than the uncertainty of high resolution measurements. Specializing equation V to the cases of fundamental and simple combination vibrations one obtains

Case 1. Fundamental vibrations: $n_i = \ell_i = 1$; $n_j = \ell_j = 0$.

$$\Delta\zeta_i = \sum_j 2(\beta_{ij} - \beta_{jj})$$

If one designates the measured zeta value by Z and the theoretical first order zeta value by ζ , then

$$(1) \qquad Z_i \equiv \zeta_i + \Delta\zeta_i = \zeta_i + \sum_j 2(\beta_{ij} - \beta_{jj})$$

From the form of $\Delta\zeta_i$, it immediately follows that

$$\sum_i Z_i = \sum_i \zeta_i$$

and hence the Teller Zeta Sum rule should hold for the Z_i as well as for the ζ_i .

Case 2. (A) First harmonic vibrations: $n_i = \ell_i = 2$; $n_j = \ell_j = 0$.

$$\Delta\zeta_{i,i} = \sum_j 6\beta_{ij} - 4\beta_{jj} = 2\Delta\zeta_i + \sum_j 2\beta_{ij}$$

and since $Z_{i+i} = 2\zeta_i + \Delta\zeta_{i+i}$

one obtains

$$(2) \qquad Z_{i+i} = 2Z_i + \sum_j 2\beta_{ij}$$

Case 2. (B) Simple combination bands: $n_i = l_i = 1$; $n_k = l_k = 1$; $n_j = l_j = 0$.

$$\Delta\zeta_{i+k} = \sum_j 2(\beta_{ij} - \beta_{ji}) + \sum_j 2(\beta_{kj} - \beta_{jk}) - 2(\beta_{ik} + \beta_{ki})$$

$$= \Delta\zeta_i + \Delta\zeta_k - 2(\beta_{ik} + \beta_{ki})$$

$$Z_{i+k} = \zeta_i + \zeta_k + \Delta\zeta_{i+k}$$

$$(3) \qquad Z_{i+k} = Z_i + Z_k - 2(\beta_{ik} + \beta_{ki})$$

The question arises whether one may determine the $\Delta\zeta_i$ from measurements of the rotational spacings of the fundamental and simple combination vibrational bands and thus be able to "measure" the theoretical first order ζ_i values without knowing the coefficients of the quartic potential terms, (assuming of course that the $\Delta\zeta_i$ values are the result of the above interference mechanism.) If there are N fundamental vibrations belonging to the same degenerate symmetry class, then in principle one can measure N rotational spacings of the fundamentals and $N(N+1)/2$ rotational spacings of the harmonic and simple combination bands. In order that these measurements suffice to determine the N first order ζ_i values and the $N(N-1)$ unknown β_{ij}, the number N must satisfy the condition

$$N + N(N+1)/2 \geq N + N(N-1) \quad \text{or} \quad N \leq 3$$

For ammonia, there are two degenerate vibrations and hence the rotational spacings could serve not only to determine the ζ_i and β_{ij} values but also to check the predicted behavior of the Z_i values. With ethane N = 3 for both the perpendicular active and the perpendicular inactive vibrations and a complete set of combination band spacings would be required for determining the higher order corrections to the zeta values. Unfortunately, when there is a large number of fundamental and simple combination bands, there are invariably cases of near resonance. In such cases, the rotational spacings of the interacting vibrational bands tend to become equal, and the corrections to the first order zeta values are not of the same form as given by equation V. The effects of resonance on the zeta values of ν_8 and ν_{10} of ethane will be considered individually as the occasions arise.

CHAPTER V

THE " ν_8 PROBLEM"

The fine structure of the ν_8 vibrational band as measured by Smith (Figure 10) has a ragged appearance suggesting the presence of resonance interaction with another vibrational band. The determination of the fundamental frequency and the unperturbed rotational spacing requires the detailed interpretation of this fine structure.

The problem consists of two parts. First, the assignment of a quantum number K to each Q line, and second, the determination of the unperturbed rotational spacing and perturbation parameters which quantitatively predict the observed positions of the Q lines.

As guides to the assignment of quantum numbers, one utilizes the analyticity of the unknown function $\nu(K)$ in order to obtain relative assignments as well as any recognizable characteristics of the spectrum which can lead to the absolute assignment of the lines. Fortunately, the fine structure of ν_8 becomes regular at the high frequency side of the band indicating that the influence of the local perturbing forces vanishes in this direction. By coincidence, the spacings associated with the $\Delta J = \pm 1$ transitions are almost exactly 1/4 of the Q line spacings and the usually broad background associated with these transitions becomes bunched into clearly resolved "lines". Using the Q line spacing at the high frequency side of the band in order to determine a rough value for the small moment of inertia, one may calculate

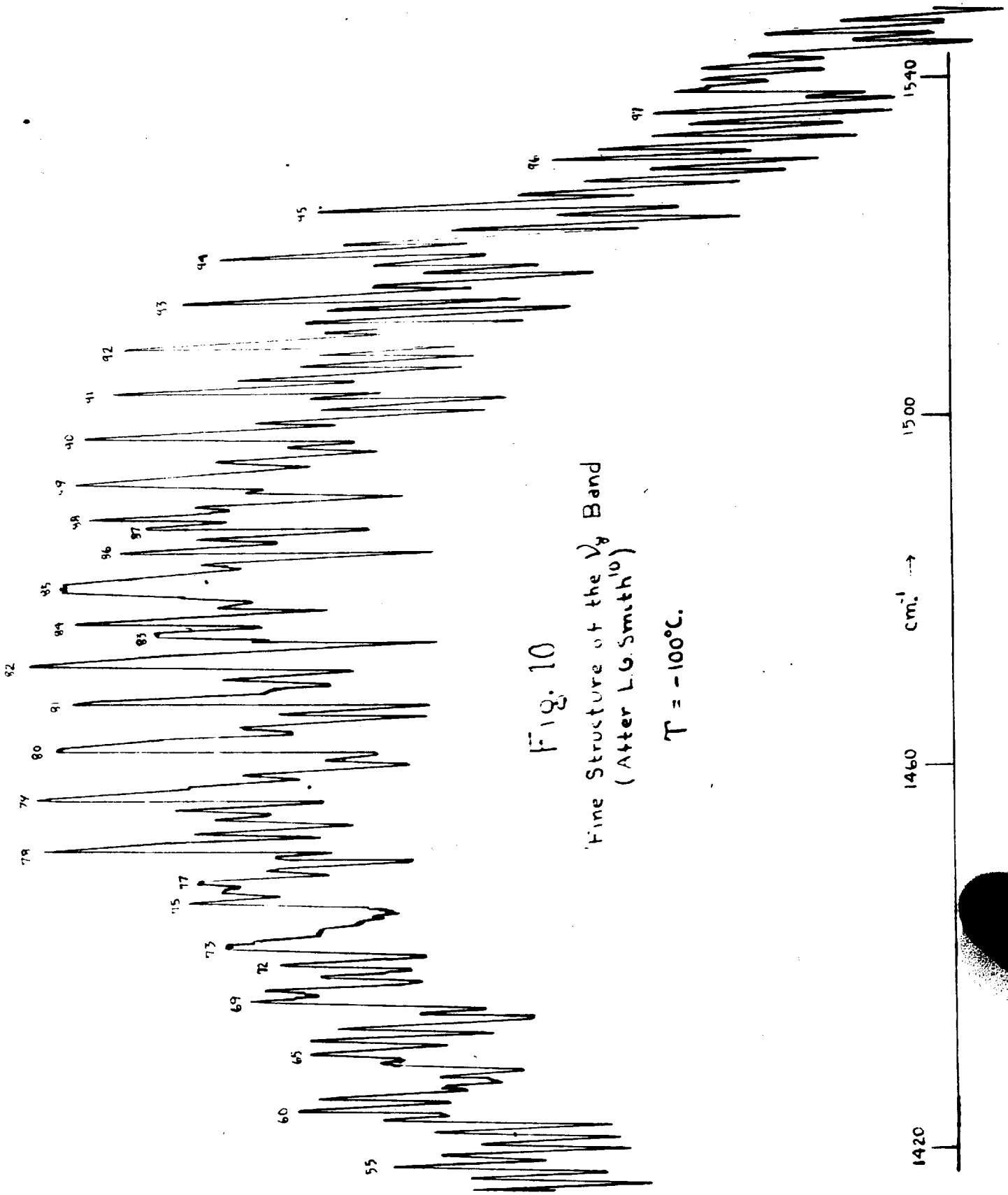


Fig. 10

Fine Structure of the ν_4 Band
(After L.G. Smith[10])

a theoretical intensity distribution for the equivalent unperturbed band. This predicted intensity distribution is pictured in Figure 11 and includes the statistical effect of nuclear spin which enhances by a factor 6/5[20] the intensity of those Q lines identified with K (ground state) equal to a multiple of three. A comparison of the observed and predicted fadings of the Q lines into the substructure gives an identification of these lines with their proper quantum numbers.

From his examination of the ν_8 band, Smith concluded that two distinct regions of perturbation were present and suggested that these perturbations were the result of Fermi and Coriolis interactions with the combination band ν_{4+12} which presumably lies in this region. The general nature of resonance curves, $\nu(K)$, is well known, and forewarned that two such curves may be present in the ν_8 band, one can proceed with the stepwise assignment of the Q lines starting from the high frequency side. The results of this procedure do indeed give two resonance like curves for the function $\nu_8(K)$. However, all of the observed Q lines are not accounted for by this procedure and these "extra" Q lines do not fall on the resonance curves. Yet, as will be shown, the existence and position of these "extra" lines are actually a consequence of the interaction scheme suggested by Smith. If this interaction scheme is correct, two interesting conclusions immediately follow. First, this scheme is permitted only if the equilibrium configuration of ethane is the staggered form D_{3d}

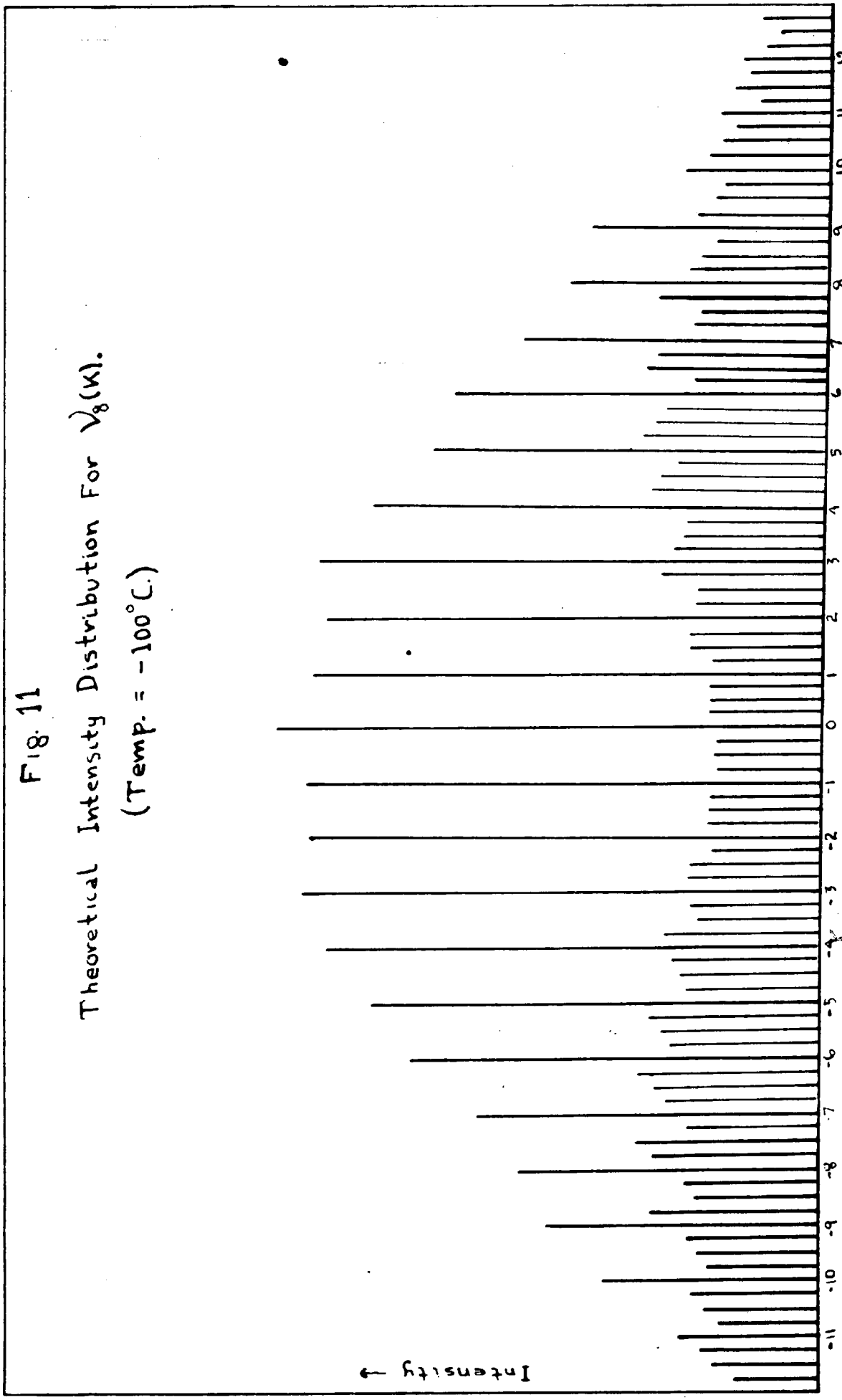


Fig. 11

Theoretical Intensity Distribution For $\nu_8(K)$.

(Temp. = -100°C.)

and hence the presence of these perturbations gives an alternate proof of this equilibrium configuration. Second, since the torsion frequency, ν_4 is known, the value for the frequency ν_{12}, often called the "uncertain frequency" of ethane, can be estimated from the calculated position of the combination band ν_{4+12}.

If the line assignments, given in Table VI, are correct, then without any perturbation calculations, the unperturbed rotational spacing can be determined. These assignments moreover, indicate that the resonances occur near the middle of the band, and hence the line positions at the high and low frequency limits are approaching asymptotically the hypothetical positions of the resonance-free band. From the measurement of these two asymptotes (one at each limit of the band), one can determine the normal band center, and the spacing and convergence of the resonance-free Q lines associated with ν_8. This procedure gives

$$\nu_8 = 1472.2 \text{ cm.}^{-1}$$

$$\Delta\nu_8 = 5.563 \text{ cm.}^{-1} \text{ at the band center}$$

For the quantitative determination of the structure of ν_8, one has three essential perturbation parameters, (1) the vibrational frequency of ν_{4+12}, (2) the strength of the Coriolis coupling term, and (3) the strength of the Fermi coupling term. These parameters enter in the following way.

(a) The lowest order anharmonic term which can couple the vibrational states ν_8 and ν_{4+12} is

Table VI

Line Assignments for the $_8$ band.

Line no.°	K	K'	line position° cm.$^{-1}$	observed° $_8(K) - _8(K)$ cm.$^{-1}$	predicted $_8(K) - _8(K)$ cm.$^{-1}$
55	10	9	1418.71	-.39	-.41
60	9	8	1424.56	-.33	-.43
65	8	7	1430.34	-.31	-.46
69	7	6	1435.65	-.74	-.49
72	6	5	1439.63	-2.47	-2.04
73	6	5	1441.36	-.74	-.26
75	5	4	1446.38	-1.41	-1.19
77	5	4	1448.52	.73	.36
78	4	3	1452.41	-1.04	-1.07
79	3	2	1457.91	-1.18	-1.05
80	2	1	1463.48	-1.21	-1.45
81	1	0	1468.45	-1.84	-1.90
82	0	1	1472.95	-2.90	-2.74
83	0	1	1475.87	.02	.17
84	1	2	1477.78	-3.91	-3.95
85	1	2	1481.49	.14	.97
	2	3		-5.41	-5.93
86	1	2	1485.64	4.25	4.34
87	2	3	1488.28	1.38	1.66
88	2	3	1489.29	2.39	3.21
89	3	4	1493.68	1.29	1.62
90	4	5	1498.90	1.05	1.38

° From the data of L. G. Smith

Table VI (Concl.)

Line no.	K	K'	line position $cm.^{-1}$	observed $s(K) - s(K)\ cm.^{-1}$	predicted $s(K) - s(K)\ cm.^{-1}$
91	5	6	1504.13	.84	1.09
92	6	7	1509.47	.77	.90
93	7	8	1514.65	.56	.78
94	8	9	1519.85	.40	.67
95	9	10	1525.14	.35	.59
96	10	11	1530.51	.41	.53
97	11	12	1535.80	.41	.48

$$b\,\xi_4\rho_8\rho_{12}\left(\frac{e^{i[\varphi_8-\varphi_{12}]}-e^{-i[\varphi_8-\varphi_{12}]}}{2i}\right)$$

where b is an unknown coefficient and ξ_4 is the torsional normal coordinate, etc. As this is a purely vibrational coupling, the matrix connections of this term obey the selection rules $\Delta J = \Delta K = 0$. Designating the two components of the vibrational state ν_8 by ν_8^+ and ν_8^-, then the matrix connections between ν_8 and ν_{4+12} are of the form

$$\left|b\,\xi_4\rho_8\rho_{12}\left(\frac{e^{i[\varphi_8-\varphi_{12}]}-e^{-i[\varphi_8-\varphi_{12}]}}{2i}\right)\right| \equiv \Delta \quad \text{for } \nu_8^+ \rightarrow \nu_{4+12}^+$$

$$= \Delta^* = -\Delta \quad \text{for } \nu_8^- \rightarrow \nu_{4+12}^-$$

$$= 0 \quad \text{for } \nu_8^+ \leftrightarrow \nu_{4+12}^- \text{ or } \nu_8^- \leftrightarrow \nu_{4+12}^+$$

The pure imaginary number Δ is taken as the Fermi coupling parameter.

(b) The general Coriolis interaction terms are

(1) $(P_x p_x + P_y p_y)/I_x$

(2) $P_z p_z / I_z$

These two terms would in general give two perturbation parameters. However, the selection rules for the second term are the same as for the Fermi interaction and although its interaction strength is dependent upon the quantum number K, its presence would be somewhat masked by the Fermi interaction.

Thus the combined actions of the Fermi coupling term and this Coriolis coupling term can be characterized fairly well by the single parameter Δ . The selection rules for the matrix connections of the term $(P_x p_x + P_y p_y)/I_x$ are

$$\begin{aligned} \nu_8^+(K) &\longleftrightarrow \nu_{4+12}^-(K+1) \\ \nu_8^-(K+1) &\longleftrightarrow \nu_{4+12}^+(K) \end{aligned} \qquad ; \quad \Delta J = 0$$

The form of the matrix elements for these connections is

$$d\sqrt{(J-K)(J+K+1)} \qquad ; \quad d^* = -d$$

In the harmonic oscillator approximation of the vibrations, there is no coupling between ν_8 and ν_{4+12}, and the non-vanishing of the coupling coefficient d depends on the anharmonic potential energy terms. Although the interaction strength depends on the quantum numbers J and K, we shall use a value obtained by averaging over the J values. Since near the band center, $\bar{J} >> K$, this average value is essentially $\bar{J}\, d \equiv f$, a pure imaginary number independent of K. This procedure focuses attention on the centers of the Q lines and the number f is the strength parameter for the Coriolis interaction.

The energy contributions due to the Fermi and Coriolis interactions are determined as the eigenvalues of the 4 x 4 matrices

$$\begin{vmatrix} E_8^+(K) & \Delta & 0 & f \\ \Delta^* & E_{4+12}^+(K) & f^* & 0 \\ 0 & f & E_8^-(K+1) & \Delta^* \\ f^* & 0 & \Delta & E_{4+12}^-(K+1) \end{vmatrix}$$

where $E_8^+(K)$ is the energy of the K^{th} rotational level of the state ν_8^+ in the absence of the perturbing terms Δ and f. Thus,

$$E_8^+(K) = E_8(0) + \frac{\hbar^2}{2}\left(\frac{1}{I_z} - \frac{1}{I_x}\right)K^2 - \frac{\hbar^2}{I_z}\zeta_8 K$$

$$E_{4+12}^+(K) = E_{4+12}(0) + \frac{\hbar^2}{2}\left(\frac{1}{I_z} - \frac{1}{I_x}\right)K^2 - \frac{\hbar^2}{I_z}\zeta_{12} K$$

$$E_8^-(K+1) = E_8(0) + \frac{\hbar^2}{2}\left(\frac{1}{I_z} - \frac{1}{I_x}\right)(K+1)^2 + \frac{\hbar^2}{I_z}\zeta_8(K+1)$$

$$E_{4+12}^-(K+1) = E_{4+12}(0) + \frac{\hbar^2}{2}\left(\frac{1}{I_z} - \frac{1}{I_x}\right)(K+1)^2 + \frac{\hbar^2}{I_z}\zeta_{12}(K+1)$$

(c) The third and last perturbation parameter gives the position of the vibrational frequency of ν_{4+12} relative to ν_8 and is defined as

$$a \equiv E_{4+12}(0) - E_8(0)$$

Starting with Smith's initial values for the moments of inertia and zeta values[21]

$$\hbar/4\pi c I_z = 2.524 \text{ cm.}^{-1} \qquad \zeta_8 = -.238$$
$$\hbar/4\pi c I_x = 0.663 \text{ cm.}^{-1} \qquad \zeta_{12} = .380$$

one obtains fairly good agreement between the observed and predicted fine structure of ν_8 with the choice (in wave-number units)

$$a = 7.0 \text{ cm}^{-1}$$
$$ff^* = 1 \text{ cm}^{-2}$$
$$\Delta\Delta^* = 16 \text{ cm}^{-2}$$

Letting $\nu_8^\circ(K)$ represent the positions which the Q lines would have in the absence of the resonance interactions, the difference

functions

$$\nu_3(K)\ \{\text{observed}\} - \nu_8^{\circ}(K)$$

and $$\nu_3(K)\ \{\text{predicted}\} - \nu_8^{\circ}(K)$$

are given in Figure 12.

As an example of the calculations, consider the interacting quadruplet of states

$$\nu_8^{+}(K = 3)$$
$$\nu_{4+12}^{+}(3)$$
$$\nu_8^{-}(4)$$
$$\nu_{4+12}^{-}(4)$$

Relative to the energy of $\nu_8^{+}(3)$, the unperturbed energies are

$$\nu_8^{+}(3) = 0 \text{ cm.}^{-1}$$
$$\nu_{4+12}^{+}(3) = -3.12 \text{ cm.}^{-1}$$
$$\nu_8^{-}(4) = 2.35 \text{ cm.}^{-1}$$
$$\nu_{4+12}^{-}(4) = 23.34 \text{ cm.}^{-1}$$

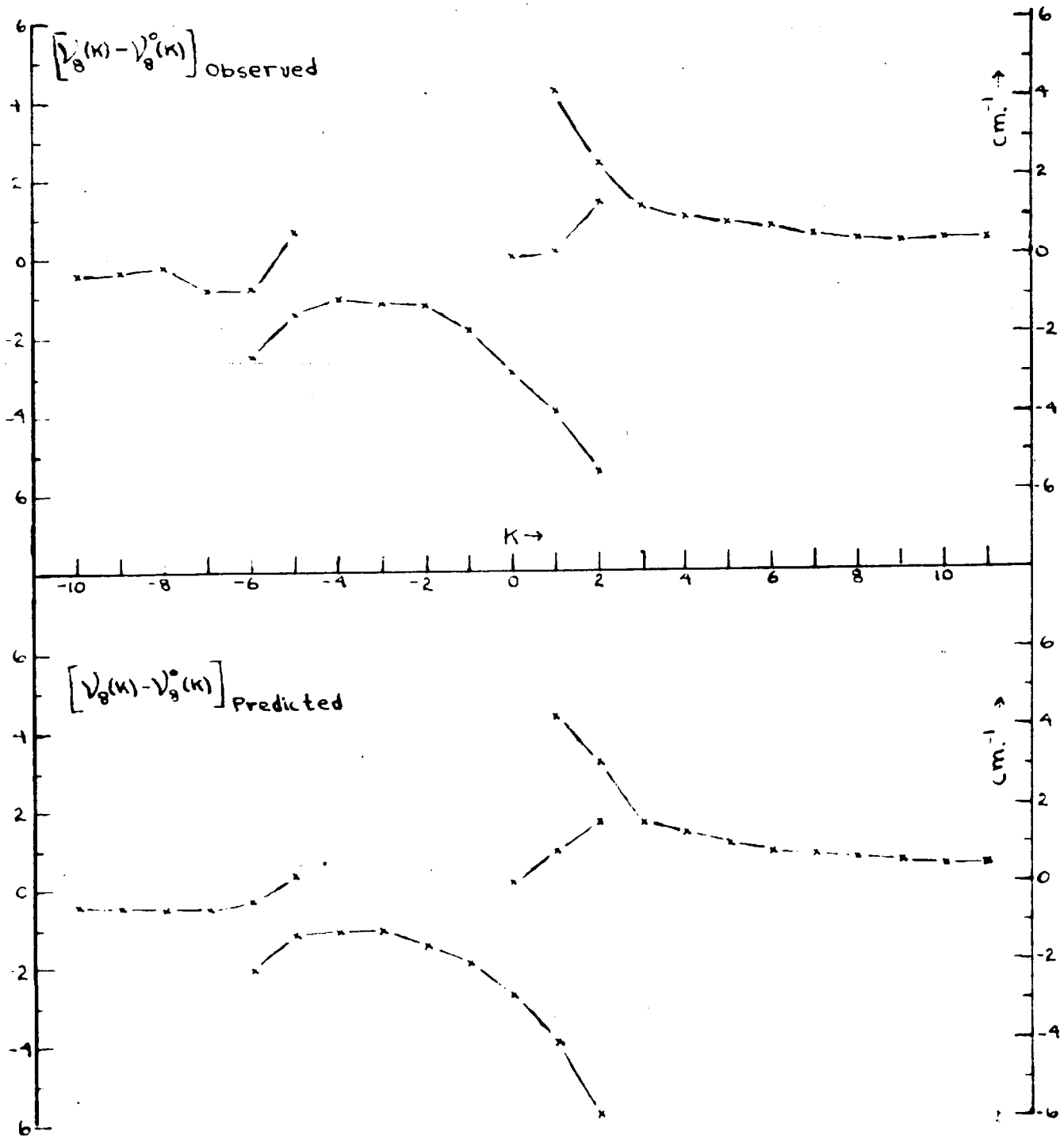
The eigenvalues of the corresponding 4 x 4 matrix and the compositions of the perturbed states are

State	Energy	$\%\nu_8^{+}(3)$	$\%\nu_{4+12}^{+}(3)$	$\%\nu_8^{-}(4)$	$\%\nu_{4+12}^{-}(4)$
I.	3.21 cm.$^{-1}$	43.0	25.4	31.0	0.6
II.	-5.93 cm.$^{-1}$	31.0	68.1	0.8	0.0
III.	1.66 cm.$^{-1}$	25.8	6.6	64.6	2.9
IV.	24.13 cm.$^{-1}$	0.0	0.0	3.5	96.5

Since the selection rules for transitions to the vibrational ground state $\nu_o(K)$ are

Fig 12.

Predicted versus Observed Line Positions of the ν_8 Band



$$\nu_8^+(K) \rightarrow \nu_0(K-1)$$
$$\nu_8^-(K) \rightarrow \nu_0(K+1)$$

one can conclude, for example, that the perturbed level labelled I above can make transi tions to

either $\nu_0(2)$ 43% relative intensity

or $\nu_0(5)$ 30% relative intensity

The absorption line $\nu_0(2) \longrightarrow I$ will lie 3.21 $cm.^{-1}$ above the normal position of the unperturbed Q line $\nu_0(2) \longrightarrow \nu_8^+(3)$. The absorption line $\nu_0(5) \rightarrow I$ will lie 3.21 - 2.85 = 0.36 $cm.^{-1}$ above the normal position of the unperturbed Q line $\nu_0(5) \longrightarrow \nu_8^+(4)$. It is these shifts which constitute the difference functions plotted in Figure 12.

The agreement between the predicted and observed line positions of the ν_8 band might be improved somewhat by a more careful determination of the perturbation parameters. However, the values chosen are such as to show the essential correctness of the perturbation scheme. The result of the Fermi and Coriolis coupling is not equivalent to the simple superposition of these two interactions. The "extra" Q lines are one of the characteristic features of the spectrum and these may be thought of as arising from a self resonance between the rotational levels of ν_8 caused by the combined action of the Fermi and Coriolis interactions. (Two different rotational levels of ν_8 are coupled to one another via a third level of ν_{4+12}.)

CHAPTER VI

SOLUTION OF THE GENERAL POTENTIAL CONSTANTS

The definition and solution of the general potential constants is presented for each symmetry class in the following order:

A. E_u: The perpendicular active vibrations

B. E_g: The perpendicular inactive vibrations

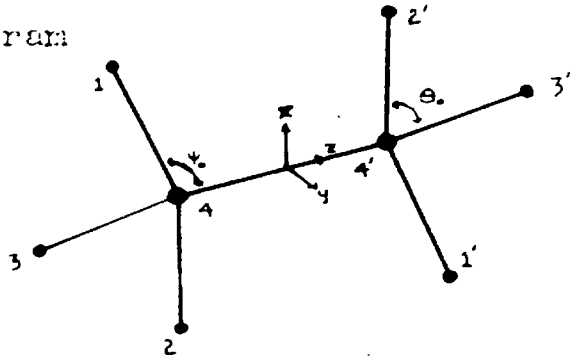
C. A_{2u}: The parallel active vibrations

D. A_{1g}: The parallel inactive vibrations

E. A_{1u}: The torsional vibration

For each class, the procedure is (1) to define the symmetry coordinates and to establish the required relations between the potential constants and the normal frequencies (and zeta values), (2) to present the spectroscopic data and estimate the normal frequencies, and (3) to give the calculated values for the potential constants and the predicted values for the normal frequencies (and zeta values).

In the subsequent pages, the nuclei are indexed according to the diagram

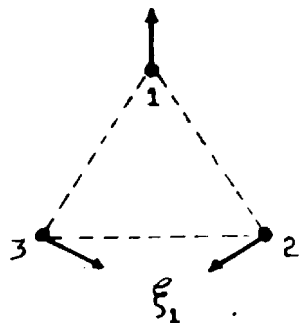


and m, m^*, and L denote the masses of the H, D, and C atoms.

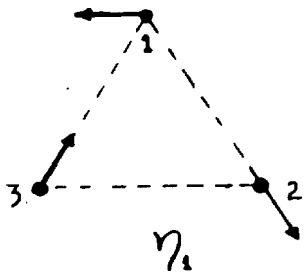
A. The perpendicular active vibrations.

The three pairs of symmetry coordinates were chosen as follows:

(1) The distortion of the "hydrogen triangle".



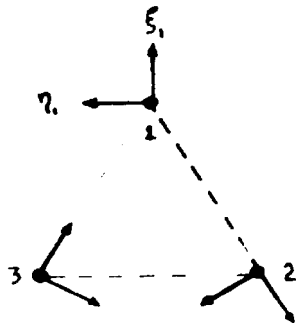
ξ_1



η_1

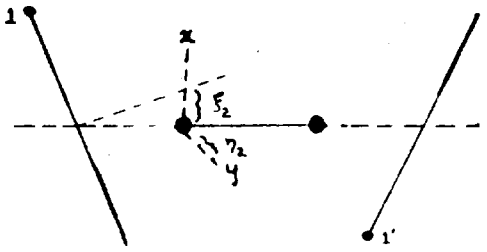
The displacements of the nuclei of the opposing or "primed" hydrogen triangle are specified by the symmetry conditions $x_{1'} = x_1$; $y_{1'} = y_1$ and hence need not be schematically indicated. By convention, the equal magnitude vector displacements shown above correspond to positive values of ξ_1, and η_1. For normalization purposes, the units of ξ_1 and η_1 are chosen so that the magnitude of any hydrogen displacement is given by $\sqrt{(\xi_1^2+\eta_1^2)/6}$.

We shall adopt the more brief presentation



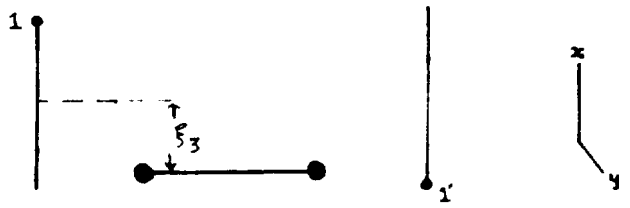
scale factor: $6^{-1/2} = .4082_5$

(2) Rocking of the hydrogen triangles:



scale factor: $(3\tan^2\psi_0)^{-1/2} = .2058_3$

(3) Translation of the hydrogen triangles:



scale factor: $\sqrt{\frac{3m+M}{6M}} = .4571_6$

For η_3 positive, the hydrogens move out on the y axis.

It will be noted that these coordinates uniquely specify the configuration of the molecule whatever the ratio of carbon and hydrogen masses may be. They are thus geometric coordinates in the sense used by Johnston and Dennison[12].

In terms of these coordinates, the expressions for the kinetic energies are

$$2T = m\left\{(\dot{\xi}_1^2+\dot{\eta}_1^2)+(\dot{\xi}_2^2+\dot{\eta}_2^2)+(\dot{\xi}_3^2+\dot{\eta}_3^2)\right\} \qquad \text{for } C_2H_6$$

$$2T^* = m^*\left\{(\dot{\xi}_1^2+\dot{\eta}_1^2)+(\dot{\xi}_2^2+\dot{\eta}_2^2)+\frac{(\dot{\xi}_3^2+\dot{\eta}_3^2)}{\sigma}\right\} \qquad \text{for } C_2D_6$$

where $\sigma = \frac{3m^*+M}{3m+M} = 1.2010$

The most general form of the quadratic potential energy function is

$$2V = 2V^* = a_{11}(\xi_1^2+\eta_1^2) + a_{22}(\xi_2^2+\eta_2^2) + a_{33}(\xi_3^2+\eta_3^2)$$
$$+ 2a_{12}(\xi_1\xi_2+\eta_1\eta_2) + 2a_{13}(\xi_1\xi_3+\eta_1\eta_3) + 2a_{23}(\xi_2\xi_3+\eta_2\eta_3)$$

The component of vibrational angular momentum along the symmetry axis is

$$p_z = -(\xi_1 p_{\eta_1} - \eta_1 p_{\xi_1}) + (\xi_3 p_{\eta_3} - \eta_3 p_{\xi_3})$$

Hence, $Z_{11} = -1$; $Z_{33} = 1$ and all other $Z_{ii} = 0$

The zeta sum rule is thus

$$\sum \zeta_i = 0$$

The required relations among the potential constants are given by the roots of the two secular determinants

$$\begin{vmatrix} m\omega^2 - a_{11} & -a_{12} & -a_{13} \\ -a_{12} & m\omega^2 - a_{22} & -a_{23} \\ -a_{13} & -a_{23} & m\omega^2 - a_{33} \end{vmatrix} = 0 = \begin{vmatrix} m^*\omega^{*2} - a_{11} & -a_{12} & -a_{13} \\ -a_{12} & m^*\omega^{*2} - a_{22} & -a_{23} \\ -a_{13} & -a_{23} & \frac{m^*}{\sigma}\omega^{*2} - a_{33} \end{vmatrix}$$

(the product rule is thus: $\frac{\omega_7\omega_8\omega_9}{\omega_7^*\omega_8^*\omega_9^*} = \sqrt{\frac{m^{*3}}{\sigma m^3}} = 2.5781$)

and the zeta transformation equations.

$$\zeta_{ij} = -S_{i1}S_{j1} + S_{i3}S_{j3}$$
$$\zeta_{ij}^* = -S_{i1}^*S_{j1}^* + S_{i3}^*S_{j3}^*$$

Where the S_i and S_i^* are the unitary transformation matrices defined in Ch. III.

The spectroscopic data available for the perpendicular active vibrations is quite complete and unambiguous (the exceptions have already been discussed in Chapters III and V). A listing of the observed fundamental frequencies and zeta values is given in Table VII.

For the estimation of the normal frequencies we have used the following set of anharmonicity factors:

$x_7 = .0440$

$x_8 = .0350$

$x_9 = .0004$

The values of x_7 and x_8 were chosen, in accordance with the principles outlined in Chapter III, to agree roughly with the anharmonicity factors .046 and .039 of the corresponding normal frequencies of Methane. The value of x_8 was slightly lowered to .0350 so that the Teller product would have a positive value for x_9.

The potential constants were determined using least squares and a weighting scheme based on the estimate that a normal frequency is equivalent to an error in a zeta value. A listing of the calculated potential constants is given in Table VIII together with the corresponding matrices. Table IX gives a listing of the experimental values of the normal frequencies

Table VII

Spectroscopic Data for the perpendicular active vibrations

Vibration	Fundamental Frequency cm^{-1}	zeta value	Reference
ν_7	2095.5	.095	(10)
ν_8	1472.2	-.331	(10)
ν_9	881.52	.336	(10)
ν_7^*	2330	---	(9)
ν_8^*	1082	-.423	Ch.II
ν_9^*	593.7	.132	Ch.II

Table VIII

Potential constants for the perpendicular active vibrations:

(in units of 10^5 dynes/cm.)

a_{11} = 2.3823 $\quad$ a_{12} = 1.1819

a_{22} = 1.4346 $\quad$ a_{13} = 1.7900

a_{33} = 2.2328 $\quad$ a_{23} = 1.6934

Calculated components of the zeta matrices:

$\zeta_{7,7}$ = .398 $\quad$ $\zeta_{7,8} = \zeta_{8,7}$ = .851

$\zeta_{8,8}$ = -.334 $\quad$ $\zeta_{8,9} = \zeta_{9,8}$ = .315

$\zeta_{9,9}$ = .338 $\quad$ $\zeta_{7,9} = \zeta_{9,7}$ = .296

$\zeta^*_{7,7}$ = .313 $\quad$ $\zeta^*_{7,8} = \zeta^*_{8,7}$ = .845

$\zeta^*_{8,8}$ = -.403 $\quad$ $\zeta^*_{8,9} = \zeta^*_{9,8}$ = .295

$\zeta^*_{9,9}$ = .199 $\quad$ $\zeta^*_{7,9} = \zeta^*_{9,7}$ = .279

Calculated components of the unitary transformation matrices:

S_{71} = .001 $\quad$ S_{72} = .422 $\quad$ S_{73} = .678

S_{81} = -.717 $\quad$ S_{82} = .383 $\quad$ S_{83} = .548

S_{91} = .313 $\quad$ S_{92} = -.871 $\quad$ S_{93} = .489

$$\begin{pmatrix} \xi_7 \\ \xi_8 \\ \xi_9 \end{pmatrix} = S \begin{pmatrix} \xi_1 \\ \xi_2 \\ \xi_3 \end{pmatrix}$$

S^*_{71} = .550 $\quad$ S^*_{72} = .404 $\quad$ S^*_{73} = .725

S^*_{81} = -.123 $\quad$ S^*_{82} = .193 $\quad$ S^*_{83} = .529

S^*_{91} = .074 $\quad$ S^*_{92} = -.894 $\quad$ S^*_{93} = .442

$$\begin{pmatrix} \xi^*_7 \\ \xi^*_8 \\ \xi^*_9 \end{pmatrix} = S^* \begin{pmatrix} \xi_1 \\ \xi_2 \\ \xi_3/\sqrt{\sigma} \end{pmatrix}$$

Table IX

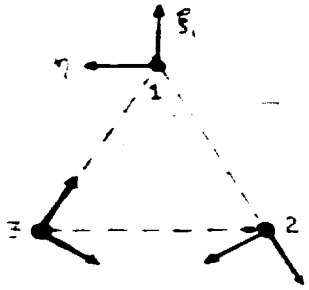
Predicted versus "observed" normal frequencies and zeta values for the perpendicular active vibrations.

Vibration	Normal frequencies ($cm.^{-1}$) Predicted	Observed	Zeta values Predicted	Observed
ω_7	3136.9	3139.9	.098	.095
ω_8	1526.9	1525.6	-.334	-.331
ω_9	825.1	821.8	.236	.236
ω^*_7	2321.3	2315.5	.213	--
ω^*_8	1109.3	1110.5	-.403	-.423
ω^*_9	595.2	593.9	.190	.182

B. The perpendicular inactive vibrations.

The three pairs of symmetry coordinates were chosen as follows:

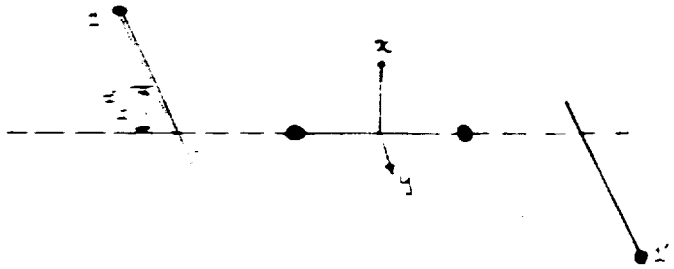
(1) The distortion of the hydrogen triangle.



Scale factor: $6^{-1/2} = .4082_5$

The nuclei of the opposing or primed hydrogen triangle undergo displacements governed by the condition $x_{i'} = -x_i$; $y_{i'} = -y_i$.

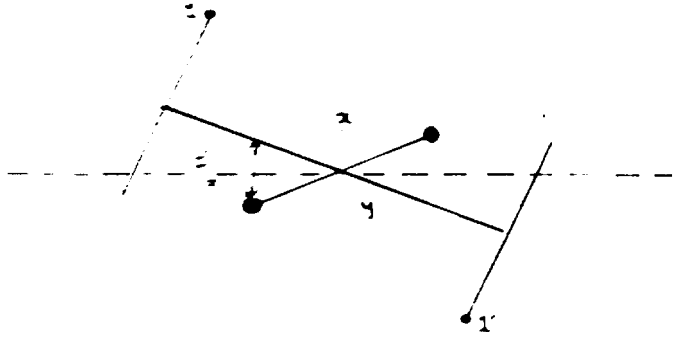
(2) Shearing of the hydrogen triangles (also could be called the lateral distortion of the hydrogen cylinder).



Scale factor: $\sqrt{I_z/12\,I_c} = .2207_2$

where I_c is the moment of inertia of the hydrogen cylinder about an axis perpendicular to the symmetry axis. For positive values of γ_2, the center of the hydrogen triangle (1,2,3) is displaced out along the positive y- direction (by an amount $.2270_2 \gamma_2$ cm.)

(3) Rocking of the hydrogen cylinder.



Scale factor: $\sqrt{\frac{m I_x}{2 I_c M}} = .3096_5$

The displacement of the hydrogen triangle (1,2,3) is in the positive y direction for positive values of η_3.

In terms of these coordinates, the expression for the kinetic energies are

$$2T = m\left\{\left(\dot{\xi}_1^2+\dot{\eta}_1^2\right)+\left(\dot{\xi}_2^2+\dot{\eta}_2^2\right)+\left(\dot{\xi}_3^2+\dot{\eta}_3^2\right)\right\}$$

$$2T^* = m^*\left\{\left(\dot{\xi}_1^2+\dot{\eta}_1^2\right)+\left(\dot{\xi}_2^2+\dot{\eta}_2^2\right)+\left(\frac{\dot{\xi}_3^2+\dot{\eta}_3^2}{\sigma}\right)\right\}$$

where $\sigma = I_x^* / I_x = 1.4372_6$

The most general form for the potential energies is

$$2V = 2V^* = a_{11}\left(\xi_1^2+\eta_1^2\right)+a_{22}\left(\xi_2^2+\eta_2^2\right)+a_{33}\left(\xi_3^2+\eta_3^2\right)$$
$$+2a_{12}\left(\xi_1\xi_2+\eta_1\eta_2\right)+2a_{13}\left(\xi_1\xi_3+\eta_1\eta_3\right)+2a_{23}\left(\xi_2\xi_3+\eta_2\eta_3\right)$$

The component of the vibrational angular momentum along the symmetry axis is

$$P_z = -\left(\xi_1 P_{\eta_1}-\eta_1 P_{\xi_1}\right)+\frac{I_z}{2I_c}\left(\xi_2 P_{\eta_2}-\eta_2 P_{\xi_2}\right)+\left(1-\frac{I_z}{2I_c}+\frac{I_z}{2I_x}\right)\left(\xi_3 P_{\eta_3}-\eta_3 P_{\xi_3}\right)$$
$$+\left\{\frac{I_z}{2I_c}\left(1-\frac{I_z}{2I_c}\right)\left(\frac{I_x-I_c}{I_x}\right)\right\}^{1/2}\left\{\left(\xi_2 P_{\eta_3}-\eta_3 P_{\xi_2}\right)+\left(\xi_3 P_{\eta_2}-\eta_2 P_{\xi_3}\right)\right\}$$

for C_2H_6:

With the normalized coordinates $\xi_1^* = \xi_1$; $\xi_2^* = \xi_2$; $\xi_3^* = \xi_3/\sqrt{\sigma}$, the expression for the vibrational angular momentum of C_2H_6 is the same as above but with all quantities starred.

In these coordinates, the components of the zeta matrices are thus

$Z_{11} = -1$ $\qquad Z_{23} = Z_{32} = \left\{ \frac{I_z}{2I_c}\left(1 - \frac{I_z}{2I_c}\right)\left(\frac{I_x - I_c}{I_x}\right)\right\}^{1/2} = .3410$

$Z_{22} = I_z/2I_c = .2923$ $\qquad Z_{13} = Z_{31} = 0$

$Z_{33} = \left(1 - \frac{I_z}{2I_c} + \frac{I_z}{2I_x}\right) = .8357$ $\qquad Z_{12} = Z_{21} = 0$

$Z_{11}^* = -1$ $\qquad Z_{23}^* = Z_{32}^* = .2844$

$Z_{22}^* = .2923$ $\qquad Z_{13}^* = Z_{31}^* = 0$

$Z_{33}^* = .8857$ $\qquad Z_{12}^* = Z_{21}^* = 0$

The zeta sum rules are $\sum \zeta_i = I_z/2I_x = .128$; $\sum \zeta_i^* = .178$

The fundamental frequencies and zeta values for the perpendicular inactive vibrations are listed in Table X. Unlike the case of the perpendicular active vibrations, some of these adopted values require additional explanations. The values in questior are (1) the fundamental frequency and zeta value for ν_{12}, and (2) the fundamental frequency and zeta value for ν_{10}.

The frequency, ν_{12}, has been termed the "uncertain frequency" of ethane since it has consistently avoided direct detection by Raman effect. The localization of the region in which this frequency must lie has been established by a series of indirect methods, and Herzberg reports an average value of 1155 $cm.^{-1}$. However, Smith's recent data suffices for a more accurate determination. The value $\nu_{4+12} = 1480$ $cm.^{-1}$ obtained from the analysis of the ν_8 band together with the value

Table X

Fundamental Frequencies and zeta values for the perpendicular inactive vibrations.

Vibration	Fundamental frequency $cm.^{-1}$	zeta value	reference
ν_{10}	2955	---	(p. [illegible])
ν_{11}	1460	-.354	(8,10)
ν_{12}	1190	.490	(p. [illegible])
ν^*_{10}	2225	---	(9)
ν^*_{11}	1055	---	(9)
ν^*_{12}	970	---	(9)

$\nu_4 = 290$ cm.$^{-1}$ [10], gives the adopted value $\nu_{12} = 1190$ cm.$^{-1}$ As further support for this value, there are the highly plausible assignments

$\nu_{12+9} = 2081.6$ cm.$^{-1} \rightarrow \nu'_{12} \sim \nu_{12+9} - \nu_9 = 1200.1$ cm.$^{-1}$
$\nu_{12+8} \cong 2383$ cm.$^{-1} \rightarrow \nu_{12} \sim \nu_{12+8} - \nu_8 \cong 1181$ cm.$^{-1}$
$\nu_{12+7} = 4178.9$ cm.$^{-1} \rightarrow \nu_{12} \sim \nu_{12+7} - \nu_7 = 1183$ cm.$^{-1}$

The zeta values for ν_{12} may be determined from the rotational spacings of the bands ν_{12+9} and ν_{12+7}. (The rotational structure of ν'_{12+8} is complicated presumably by a Fermi and Coriolis interaction with $\nu_{12+12+4}$ and possibly also by the overlapping of ν_{10-4}.)

$\Delta\nu_{12+9} = 7.60$ cm.$^{-1}$ ° ; $-\zeta_{12+9} = .725 \xrightarrow{\circ\circ} \zeta_{12} = .489$
$\Delta\nu'_{12+7} = 6.89$ cm.$^{-1}$; $-\zeta_{12+7} = .587 \longrightarrow \zeta_{12} = .492$

Adopted Value: $\zeta_{12} = .490$

The information concerning ν_{10} is abundant yet at first sight rather paradoxical. It is expected apriori that the frequency ν_{10} will be approximately equal to that of the analogous perpendicular active vibration ν_7, namely 2995 cm.$^{-1}$ The observed Raman displacements in this region are given below

° Smith reported these spacings as 7.64 and 7.02 cm.$^{-1}$ respectively, but reexamination of his data seems to indicate the above listed values to be preferable.

°°The dipole coupling between a combination level and the vibrational ground state is such that if $l_1, l_2 \ldots$ represent the azimuthal quantum numbers, the apparent ζ value for the combination band is $\zeta_{\Sigma l_i} = +(\Sigma l_i \zeta_i)$ or $-(\Sigma l_i \zeta_i)$ as $|\Sigma l_i| = 3n+1$ or $3n-1$.[12]

Lewis and Houston Ethane gas[22]	Glockler and Renfrew Ethand liquid[23]
2899.2 $cm.^{-1}$ (strong)	2844 $cm.^{-1}$ (strong)
2939.5 $cm.^{-1}$ (weak)	2922 $cm.^{-1}$ (diffuse)
2955.1 $cm.^{-1}$ (strong)	2941 $cm.^{-1}$ (strong)
2969.5 $cm.^{-1}$	2963 $cm.^{-1}$ (diffuse)
2979.0 $cm.^{-1}$	
2989.5 $cm.^{-1}$ (Stokes lines)	
2999.4 $cm.^{-1}$	
3008.3 $cm.^{-1}$	

The strong lines are polarized and have been assigned as parallel inactive (symmetric) vibrations[8]. Glockler and Renfrew considered the diffuse pair of lines at 2922 and 2963 $cm.^{-1}$ as a resonance doublet involving ν_{10}, and, in their 1938 summary, Crawford, Avery, and Linnett adopted the value $\nu_{10} = 2963$ $cm.^{-1}$ Lewis and Houston attempted to correlate the Stokes lines with the strong line at 2955.1 $cm.^{-1}$, but pointed out that the initial spacing was inconsistent with theory.

If the vibration ν_{10} is in resonance with some combination band as suggested by Glockler and Renfrew, then the fundamental frequency of ν_{10} should lie somewhere between the limits of the resonant doublet. That such a resonance exists is clearly shown by Smith's data on rotational spacings. We hence postulate an interaction between ν_{10} and the harmonic vibration ν_{8+8} and will show that this interaction is consistent with the observations.

First it is necessary to develop a simple formula involving the behavior of zeta values for resonant vibrations. Designating the higher and lower of the two unperturbed

energy levels by $E_H(K)$ and $E_L(K)$ and the higher and lower energies of the resonant doublet by $E_{H^*}(K)$ and $E_{L^*}(K)$, then perturbation theory gives the relations

$$2E_{H^*}(K) = E_L + E_H + \left\{ (E_H - E_L)^2 + 4\triangle^2 \right\}^{1/2}$$

$$2E_{L^*}(K) = E_L + E_H - \left\{ (E_H - E_L)^2 + 4\triangle^2 \right\}^{1/2}$$

where $\triangle$ is the interaction constant. The high frequency component of the resonant doublet involves the energy levels $E_{H^*}(K)$ and its rotational spacing is characterized by a ζ_{H^*} defined by the relation

$$E_{H^*}(K) = \frac{\hbar}{2}\left(\frac{1}{I_z} - \frac{1}{I_x}\right)K^2 - \frac{\hbar}{I_z}\zeta_{H^*}K$$

Expressing ζ_{H^*} and ζ_{L^*} in terms of ζ_H and ζ_L,

$$\zeta_{H^*} = (\zeta_H + \zeta_L)/2 - \frac{(\zeta_H - \zeta_L)}{2}\left\{ \begin{matrix} E_H & E_L \\ F_{H^*} & F_{L^*} \end{matrix} \right\}$$

$$\zeta_{L^*} = (\zeta_H + \zeta_L)/2 - \frac{(\zeta_H - \zeta_L)}{2}\left\{ \begin{matrix} E_H & E_L \\ F_{H^*} & E_{L^*} \end{matrix} \right\}$$

The qualitative features desired from these relations are:

(1) At complete resonance, $E_H = E_L$, the ζ_* values for the resonant doublet are the same and equal to the average of the ζ values for the unperturbed bands.

(2) At incomplete resonance, ζ_{H^*} has a value between ζ_H and $(\zeta_H + \zeta_L)/2$.

(3) If the fine structure of only one component of the doublet is observed, it can be recognized as the high or low energy component depending on whether the ζ_* values increase or decrease in going towards the lower frequency limit of the band.

Utilizing the zeta sum rule and the already assigned values for ζ_{11} and ζ_{12}, one obtains the calculated value, $\zeta_{10} = -.008$ for the unperturbed vibration. Similarly the zeta value for the unperturbed harmonic vibration ν_{8+8} is $\zeta_{8+8} = -2\zeta_8 = .662$. One concludes then, that any interaction between ν_{10} and ν_{8+8} will result in a perturbed ζ_{10^*} value lying between the limits $-.008$ and $-.327 = (.662 - .008)/2$.

A list of band centers and zeta values obtained by Smith and presumably involving ν_{10^*} are

ν_{4+10^*}	$= 3258$ cm.$^{-1}$	$\rightarrow$	ν_{10^*}	$\cong 2968$ cm.$^{-1}$
ζ_{4+10^*}	$= .164$		ζ_{10^*}	$\cong .164$
ν_{6+10^*}	$= 4334$ cm.$^{-1}$	$\rightarrow$	ν_{10^*}	$\cong 2955$ cm.$^{-1}$
ζ_{6+10^*}	$= .147$		ζ_{10^*}	$\cong .147$
ν_{8+10^*}	$= 4416$ cm.$^{-1}$	$\rightarrow$	ν_{10^*}	$\cong 2944$ cm.$^{-1}$
ζ_{8+10^*}	$= -.039$		ζ_{10^*}	$\cong .370$
ν_{7+10^*}	$= 5950$ cm.$^{-1}$	$\rightarrow$	ν_{10^*}	$\cong 2955$ cm.$^{-1}$
ζ_{7+10^*}	$= -.228$		ζ_{10^*}	$= .135$

The vibrations listed above as ν_{10^*} may be considered as composed of X% ν_{10} and (100-X)% ν_{8+8} where X is defined by the equation

$$\zeta_{10^*} = \frac{X}{100}\zeta_{10} + \frac{(100-X)}{100}\zeta_{8+8}$$

Thus the vibration ν_{8+10^*} is composed of 44% ν_{8+10} and 56% $\nu_{8+(8+8)}$ and hence should preferably be labelled

$\nu_{8+(8+8)^*}$. The variation of the ζ_{10^*} values between the different combination bands is just what one should expect since the general effect of anharmonicity is to cause the energy spacings between the various combinations levels $\nu_{i+10} - \nu_{i+(8+8)}$ to shift and hence vary the resonant coupling.

Of course these percentage values only have significance at the band centers where the above zeta values were measured. Only in the 325[ ] $cm.^{-1}$ band was the fine structure sufficiently clear to give an accurate determination of the convergence. In this case, the spacing of the Q lines decreases, and hence the ζ_* values increase, in going towards the low frequency limit of the band. From the qualitative results listed previously, one concludes that the band at 3258 $cm.^{-1}$ is the high frequency component of a weakly resolved doublet and hence that the frequency of the unperturbed vibration ν_{4+10} is less than 3258 $cm.^{-1}$ and $\nu_{10} < \sim 2963$ $cm.^{-1}$. As a lower limit, one has $\nu_{10} \geq \nu_{8+8} \sim 2\nu_8 = 2x1472 = 2944$ $cm.^{-1}$. The mean of these two limits gives the adopted value $\nu_{10} = 2955$ $cm.^{-1}$. This value is the best estimate from the infra-red data.

Returning to the Raman data of Lewis and Houston, it will be observed that the Stokes lines fit into a series of which the 2939.5 $cm.^{-1}$ line is a member. This series, having a rotational spacing of 10.0 $cm.^{-1}$ is missing two lines, one at 2949.5 and the other at 2959.5 $cm.^{-1}$. Assuming that the former of these is obscured by the strong 2955 $cm.^{-1}$ line, then the Stokes lines may be interpreted as $^{S}Q_K$ lines and the 2939.5 $cm.^{-1}$ line as the first $^{O}Q_K$ line associated with the vibration $\nu_{(8+8)^*}$. (These are Q lines of a perpendicular band which originate from the

transitions $\Delta K = \pm 2$, $\Delta J = 0$). The theoretical line positions are given by the formula (Herzberg pg. 443)

$$\nu(K) = \nu_0 + [4A(1+\zeta) - 4B] \pm 4[A(1+\zeta/2) - B]K$$

From the observed positions and spacings of the Stokes lines plus the line at 2939.5 cm.$^{-1}$ one obtains

$$\nu_0 = \nu'_{(8+8)^*} = 2947.2 \text{ cm.}^{-1}$$
$$\zeta = \zeta_{(8+8)^*} = .444 \quad \rightarrow \quad \nu_{(8+8)^*} \equiv 67\% \nu_{8+8} ; 53 \nu_{10}$$

Thus with this interpretation of the Stokes lines, the Raman data also indicates the presence of a resonance interaction between ν_{10} and ν_{8+8}, and gives a lower limit for ν_{10} of 2947.2 cm.$^{-1}$ in good agreement with the infra-red data.

The value $\zeta_{10} = -.008$ has been omitted from Table X since it is not directly observed but calculated from the zeta sum rule.

It is necessary to mention an alternate interpretation of the rotational spacings considered above. The simplest combination bands involving the perpendicular inactive vibrations are

$$\nu_{4+10} = 3257.8 \text{ cm.}^{-1} ; \quad \zeta_{4+10} = .164 \rightarrow \zeta_{10} = .164$$
$$\nu_{4+11} = 1747.1 \text{ cm.}^{-1} ; \quad \zeta_{4+11} = -.354 \rightarrow \zeta_{11} = -.354$$

One may consider the band ν_{4+10} free from resonance interactions and hence that the zeta value of ν_{10} is actually $\zeta_{10} = .164$. Using the zeta sum rule, one may then calculate $\zeta_{12} = .312$. The following difficulties arise:

(1) The anomalously large convergence of the 3257.8 cm.$^{-1}$

band and the anomalous variations of the ζ_{10} values in the different combinations bands remain unexplained.

(2) The spacing of the Stokes lines is unexplained.

(3) The very large spacings of the combination bands ν_{9+12} and ν_{7+12} are unexplained. (These spacings are inconsistent with the value $\zeta_{12} = .312$. This inconsistency cannot be removed by reassignment or by postulating some resonance interaction with neighboring bands since there are no neighboring bands with the requisite zeta values more negative than the respectively observed values -.725 and -.537).

To summarize, it is felt that the adopted interpretation of the rotational spacings ($\zeta_{10} = -.008$; $\zeta_{11} = -.354$; $\zeta_{12} = .490$) permits a simple explanation of the available data whereas the alternate interpretation does not.

The normal frequencies for the perpendicular inactive vibrations were estimated from the following set of anharmonicity factors.

$$x_{10} = .0694$$
$$x_{11} = .0590$$
$$x_{12} = .0450$$

These values are the consequences of the listed fundamental frequencies, the product rule and the two assumptions

(1) the ratio, x_{11}/x_{10} is equal to the ratio of the anharmonicity factors for the analogous triply degenerate vibrations of methane; .039/.046 = .85.

(2) $x_{12} = .045$.

The second assumption is based on the following sequence of C-C-H bending vibrations°

	Acetylene	Ethylene	Ethane
Vibration:	$\nu_4(\pi_g)$	$\nu_8(B_{2g})$	$\nu_{12}(E_g)$
Frequency:	611.8 $cm.^{-1}$	943 $cm.^{-1}$	1190 $cm.^{-1}$
Anharmonicity:	.032	.036	(.045)

As allowance for the uncertainties in the ζ_{10} and ζ_{12} values, the potential constants for the perpendicular inactive vibrations were determined so as to give (1) exact agreement between the predicted and "observed" normal frequencies, (2) exact agreement between the predicted and observed ζ_{11} value, and (3) the closest agreement between the predicted and observed ζ_{12} value consistent with the first two conditions. The values for these potential constants are listed in Table XI together with the calculated values for the components of the zeta and transformation matrices. Table XII gives the predicted and "observed" normal frequencies and zeta values for the perpendicular inactive vibrations. The agreement between the predicted and observed values of ζ_{12} is not very good. However, this should not be taken as evidence that the resonance scheme

° The data requisite for the construction of this table has been taken directly from Herzberg except for the π_g bending frequency of C_2D_2. This frequency is listed by Herzberg as 505 $cm.^{-1}$, a value obtained as the difference of ν_{5+4} = 1044 $cm.^{-1}$ and ν_5 = 539 $cm.^{-1}$. We have used the value 513 $cm.^{-1}$ obtained as the difference of ν_3 = 2440 $cm.^{-1}$ (determined as a C_2D_2 impurity band in the present measurements of C_2D_6) and ν_{3-4} = 1927 $cm.^{-1}$ [24].

for ν_{10} is incorrect. The "observed" ζ_{12} value was determined from the rotational specings of combination bands and in such bands the deviations from first order theoretical predictions are considerably greater than for fundamental bands.

Table XI

Potential constants for the perpendicular inactive vibrations.

(in units of 10^5 dynes/cm.)

$a_{11} = 3.2438$	$a_{12} = 1.7778$
$a_{22} = 3.1594$	$a_{13} = 1.4010$
$a_{33} = 1.9345$	$a_{23} = 1.4563$

Components of the zeta matrices.

$\zeta_{10,10} = .069$	$\zeta_{10,11} = .750$
$\zeta_{11,11} = -.354$	$\zeta_{10,12} = -.544$
$\zeta_{12,12} = .413$	$\zeta_{11,12} = -.012$

$\zeta^*_{10,10} = .190$	$\zeta^*_{10,11} = .804$
$\zeta^*_{11,11} = -.395$	$\zeta^*_{10,12} = -.446$
$\zeta^*_{12,12} = .383$	$\zeta^*_{11,12} = -.027$

Components of the unitary transformation matrices.

$S_{10,1} = .636$	$S_{10,2} = .630$	$S_{10,3} = .446$
$S_{11,1} = -.734$	$S_{11,2} = .672$	$S_{11,3} = .097$
$S_{12,1} = .239$	$S_{12,2} = .389$	$S_{12,3} = -.890$

$$\begin{pmatrix} \xi_{10} \\ \xi_{11} \\ \xi_{12} \end{pmatrix} = S \begin{pmatrix} \xi_1 \\ \xi_2 \\ \xi_3 \end{pmatrix}$$

$S^*_{10,1} = .596$	$S^*_{10,2} = .593$	$S^*_{10,3} = .542$
$S^*_{11,1} = -.743$	$S^*_{11,2} = .573$	$S^*_{11,3} = .223$
$S^*_{12,1} = .178$	$S^*_{12,2} = .560$	$S^*_{12,3} = -.809$

$$\begin{pmatrix} \xi^*_{10} \\ \xi^*_{11} \\ \xi^*_{12} \end{pmatrix} = S^* \begin{pmatrix} \xi_1 \\ \xi_2 \\ \xi_3/\sqrt{\sigma} \end{pmatrix}$$

Table XII

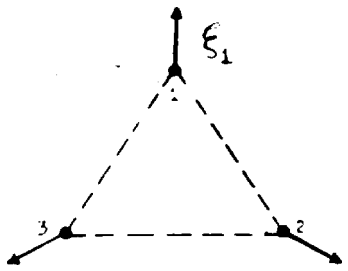
Predicted versus "observed" normal frequencies and zeta values for the perpendicular inactive vibrations.

Vibration	Normal frequencies ($cm.^{-1}$) Predicted	Observed	Zeta values Predicted	Observed
ν_{10}	3175.6	3175.1	.069	(-.008)
ν_{11}	1551.6	1551.6	-.354	-.354
ν_{12}	1246.0	1246.0	.413	.490
ν_{10}^{*}	2347.8	2347.8	.190	--
ν_{11}^{*}	1102.0	1102.0	-.395	--
ν_{12}^{*}	1006.9	1006.9	.383	--

C. The parallel active vibrations.

The two symmetry coordinates were chosen as follows:

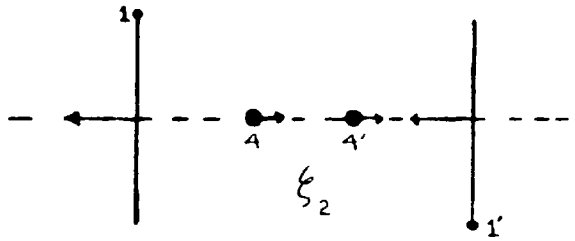
(1) Stretching of the hydrogen triangle.



scale factor:
$6^{-1/2} = .4082_5$

The displacements of the hydrogen nuclei of the opposing or primed triangle are governed by the conditions $x_{1'} = x_1$; $y_{1'} = y_1$.

(2) Axial translation of the hydrogen cylinder.



scale factor:
$\left(\frac{3m + M}{6M}\right)^{1/2} = .4571_6$
$\xi_2 = .4571_6(z_4 - z_1)$

The kinetic energy for this class of motions is

$$2T = m(\dot{\xi}_1^2 + \dot{\xi}_2^2)$$
$$2T^* = m^*(\dot{\xi}_1^2 + \dot{\xi}_2^2/\sigma)$$

where $= \frac{3m^* + M}{3m + M} = 1.2009_4$

The most general expression for the potential energy is

$$2V - 2V^* = a_{11}\xi_1^2 + a_{22}\xi_2^2 + 2a_{12}\xi_1\xi_2$$

The fundamental frequencies of the parallel active vibrations are listed in Table XIII. The vibrations ν_5 and ν_5^* are in resonance presumably with the parallel active components of the combination vibrations ν_{8+11} and ν_{8+11}^*. The adopted values lie between the limits of the observed doublets

$$\nu_5 \; ; \; \nu_{8+11} \rightarrow \begin{cases} 2895.6 \text{ cm.}^{-1} \\ 2954.0 \text{ cm.}^{-1} \end{cases} \quad \text{(Reference 10)}$$

$$\nu_5^* \; ; \; \nu_{8+11}^* \rightarrow \begin{cases} 2087.3 \text{ cm.}^{-1} \\ 2139.7 \text{ cm.}^{-1} \end{cases} \quad \text{(Chapter II)}$$

In each case, the low frequency component is more intense. With the customary assumption that the intensities of fundamental bands are greater than those of combination bands, one can conclude that the fundamental frequencies of ν_5 and ν_5^* lie between the lower limits and arithmetical means of the doublets.

$$2895.6 < \nu_5 < 2924.8$$
$$2087.3 < \nu_5^* < 2113.5$$

Pressing the argument still further, the nearly equal intensities of the ethane doublet suggests that ν_5 is closer to the mean doublet frequency than to the lower limit, while the quite different intensities of the heavy ethane doublet suggests that ν_5^* is closer to the low frequency limit than to the mean doublet frequency. In view of these intensity considerations, we have used the 2:1 weighted averages--

$$\nu_5 = (2895.6 + 2 \times 2924.8)/3 \cong 2915 \text{ cm.}^{-1}$$
$$\nu_5^* = (2 \times 2087.3 + 2113.4)/3 \cong 2095 \text{ cm.}^{-1}$$

Table XIII

Fundamental frequencies, normal frequencies, and the potential constants of the parallel active vibrations.

Vibration	Fundamental frequency ($cm.^{-1}$)	Reference	Normal frequency ($cm.^{-1}$)
ν_5	2915	(pgs.90,92)	3061.0
ν_6	1379.2	(10)	1437.5
ν_5'	2095	(pgs.90,92)	2169.4
ν_6'	1077	Ch.II	1112.2

Potential constants (in units of 10^5 dynes/cm.)

$a_{11} = 5.4342$

$a_{22} = 1.3051$

$a_{33} = 0.5775$

These values of ν_5 and ν_5^* have been estimated using only the positions and intensities of the doublets. One may check these values by another method. Since the action of resonance displaces the upper and lower components symmetrically from a mean position, the frequency ν_5 may be determined from the frequencies ν_{8+11} and the doublet components (ν_H and ν_L) by the equation

$$\nu_5 + \nu_{8+11} = \nu_H + \nu_L$$

Approximating the frequency of ν_{8+11} as the sum $\nu_8 + \nu_{11}$, one obtains the values $\nu_5 \simeq 2917$ cm.$^{-1}$ and $\nu_5^* \simeq 2090$ cm.$^{-1}$ in good agreement with the values obtained above.

The normal frequencies were estimated from the following set of anharmonicity factors.

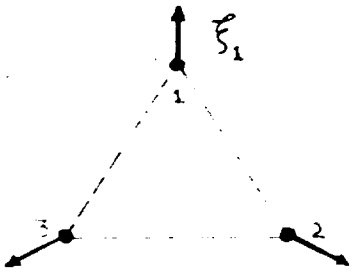
$$x_5 = .0477$$
$$x_6 = .0405$$

These values are consequences of the product rule and the assumption that the ratio x_5/x_6 is the same as the ratio of the anharmonicity factors for the triply degenerate vibrations of methane, namely 0.85. The three independent normal frequencies just suffice to determine the three potential constants. The predicted and "observed" normal frequencies are the same and these together with the calculated potential constants are listed in Table XIII.

D. The parallel inactive vibrations.

The symmetry coordinates were chosen as follows:

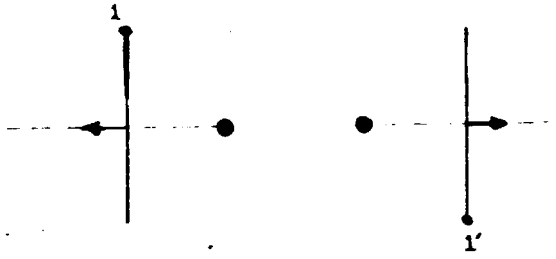
(1) Stretching of the hydrogen triangle



Scale factor:
$6^{-1/2} = .4082_5$

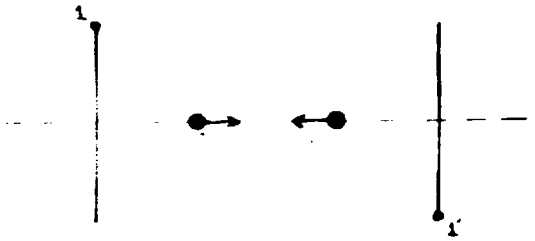
The displacements of the hydrogen nuclei in the opposing triangle are governed by the conditions $x_{1'} = x_1$; $y_{1'} = y_1$.

(2) Stretching of the hydrogen cylinder.



Scale factor:
$6^{-1/2} = .4082_5$

(3) Carbon-Carbon Stretching.



Scale factor:
$(m/2M)^{1/2} = .2049_1$

The expression for the kinetic energies are

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

$$2T^* = m^*(\dot{\xi}_1^2 + \dot{\xi}_2^2 + \dot{\xi}_3^2/\gamma)$$

where $\gamma = m^*/m = 1.9985$

The general form for the potential energies is

$$2V = 2V^* = a_{11}\xi_1^2 + a_{22}\xi_2^2 + a_{33}\xi_3^2 + 2a_{12}\xi_1\xi_2 + 2a_{13}\xi_1\xi_3 + 2a_{23}\xi_2\xi_3$$

The fundamental frequencies for the parallel inactive vibrations are listed in Table XIV. The values adopted for ν_1 and ν_1^* as well as ν_2 require some explanations.

The high frequency vibrations ν_1 and ν_1^* are in resonance presumably with the symmetric components of the harmonic vibrations of either ν_8 or ν_{11}. The observed doublets are tabulated below:

C_2H_6		C_2D_6	
gas[22]	liquid[23]	gas	liquid[9]
2909.2 $cm.^{-1}$	2844 $cm.^{-1}$	(2093 $cm.^{-1}$)	2083 $cm.^{-1}$
2955.1 $cm.^{-1}$	2941 $cm.^{-1}$	(2157 $cm.^{-1}$)	2147 $cm.^{-1}$

(The "gas" values for C_2D_6 have been estimated on the basis that in going from gas to liquid, the percentage frequency shift for C_2D_6 should be the same as the corresponding shift for C_2H_6. This type of frequency shift has an empirical basis in the work of West and Edwards[25]. According to these authors, Kirkwood has shown that a percentage frequency shift is also a theoretical consequence of a molecule interacting with a dielectric medium.) The intensities of the doublet components are very nearly equal for both C_2H_6 and C_2D_6 and this fact suggests that in each case the resonance is nearly complete and that the fundamental frequencies ν_1 and ν_1^* should lie near the mean values of the resonant doublets. The magnitudes of the doublet separations, however, indicate that the resonance should not be complete for

Table XIV

Fundamental frequencies, normal frequencies, and potential constants of the parallel inactive vibrations.

Vibration	Fundamental frequency ($cm.^{-1}$)	Reference	Normal frequency ($cm.^{-1}$)
l_1	2915	(pgs. 94-98)	3042.8
l_2	1400	(pgs. 94-98)	1449.3
l_3	993	(8)	1015.8
l'_1	2100	(9)	2165.5
l'_2	1158	(9)	1191.5
l'_3	852	(9)	868.8

Adopted values for the potential constants (in units of 10^5 dynes/cm.)

$a_{11} = 5.3295$ $\quad a_{12} = 0.7047$

$a_{22} = 1.2380$ $\quad a_{13} = 0.4311$

$a_{33} = 0.7886$ $\quad a_{23} = 0.3510$

C_2D_6. For if ν_1^* is in complete resonance, then on the basis that ν_1 and ν_1^* are similar vibrations, perturbation theory gives the following inequality relation between the doublet separations $\Delta\nu^* = 64$ cm.$^{-1}$ of C_2D_6 and $\Delta\nu$ of C_2H_6

$$\Delta\nu^* \leq \left[\nu_1^*/\nu_1\right]^{3/2} \Delta\nu = 35 \text{ cm.}^{-1}$$

The difference between the observed $\Delta\nu^*$ and the upper limit given by the inequality relation represents an argument that the vibration ν_1^* is only slightly perturbed. Stitt[9] has used the value $\nu_1^* = 2100$ cm.$^{-1}$ and this is the value given in Table XIII. The adopted value $\nu_1 = 2915$ cm.$^{-1}$ is based on the value of ν_5 and the similarity between the resonant doublets of the parallel active and the parallel inactive vibrations. (A rather unsatisfactory check on this value for ν_1 is given by the fact that certain of the potential constants become imaginary if the frequency ν_1 is chosen near the upper limit of the resonant doublet.)

The frequency of the vibration ν_2 is not observed directly. Crawford[8] has used the value $\nu_2 = 1375$ cm.$^{-1}$ based on the combination band $\nu_{2+6} = 2753$ cm.$^{-1}$ and as a consequence has assigned the Raman lines at 2744 and 2778 cm.$^{-1}$ to ν_{2+2} and ν_{6+6} respectively. The addition to the above data of the infrared band at 221[9] cm.$^{-1}$ observed by Smith favors a higher value for ν_2. From the fact that the zeta value for this band is 0.22, it must almost certainly be interpreted as ν_{2+9}. Also on the basis that the frequencies of combination bands are generally less than the sum of the component frequencies, it is preferable to reverse the above Raman assignments for ν_{2+2} and ν_{6+6}.

The following data are available for the determination of ν_2.

$$\nu_2^* = 1158 \text{ cm.}^{-1}$$ [9]

$\nu_6 = 1379.2$ cm.$^{-1}$ [10]
$\nu_9 = 821.5$ cm.$^{-1}$ [10]
$\nu_{2+9} = 2218$ cm.$^{-1}$ [10]
$\nu_{2+6} = 2753.3$ cm.$^{-1}$ [8]
$\nu_{6+6} = 2744$ cm.$^{-1}$ [8]
$\nu_{2+2} = 2778$ cm.$^{-1}$

$$\nu_{2+2}^* = 2300 \text{ cm.}^{-1}$$ [9]

The simple differences give

$$\nu_2 \sim \nu_{2+6} - \nu_6 = 1374 \text{ cm.}^{-1}$$
$$\nu_2 \sim \nu_{2+9} - \nu_6 = 1396 \text{ cm.}^{-1}$$
$$\nu_2 \sim 1/2\,\nu_{2+2} = 1389 \text{ cm.}^{-1}$$

These values for ν_2 will tend to be low due to anharmonicity. The following estimates of ν_2 should be preferable in that they roughly take into account the presence of this anharmonicity.

(1) Using the approximate isotope relations

$$\nu_{2+2} = 2\,\nu_2(1-X)$$
$$\nu_{2+2}^* = 2\,\nu_2^*\left(1-\frac{\nu_2^*}{\nu_2}X\right)$$

one obtains the value $\nu_2 = 1401$ cm.$^{-1}$

(2) Using the same anharmonicity factor for analogous vibrations

$$\nu_2/\nu_{2+2} = \nu_6/\nu_{6+6}$$

one obtains the value $\nu_2 = 1396$ cm.$^{-1}$

We have adopted the average value $\nu_2 = 1400$ cm.$^{-1}$.

The normal frequencies were estimated from the following set of anharmonicity factors:

$$x_1 = .042$$
$$x_2 = .034$$
$$x_3 = .0225$$

The values of the anharmonicity factors for the triply degenerate vibrations of methane were employed for the estimation of x_1 and x_2 and the value x_3 then determined by means of the product rule. (The physical condition that the potential constants be real imposes the two mathematical conditions $x_1 < .062$ and $\frac{x_2 + x_3}{2} > .010$.)

The five independent normal frequencies are not sufficient to determine the six potential constants of the parallel inactive vibrations. In order to establish a set of values for these potential constants, we are forced to make one assumption regarding the specific valence force coupling constants. It is probable that the coupling constant k_{Rr} which couples the carbon-carbon and carbon-hydrogen stretchings is small and may be chosen to be zero. The five relations among the potential constants given by the normal frequencies permits the expression of these constants in terms of k_{Rr}. As an indication of how

the calculated potential constants depend on the value of this one parameter, Table XV gives three sets of potential constants in the vicinity of the point where the value of k_{Rr} vanishes. Table XV also includes the variations of the calculated C-C stretching constant, k_R, and the coupling constant $k_{R\psi}$ which couples the C-C stretching and H-C-C angle bending. The normal frequencies and the adopted set of potential constants for the parallel inactive vibrations are listed in Table XIV.

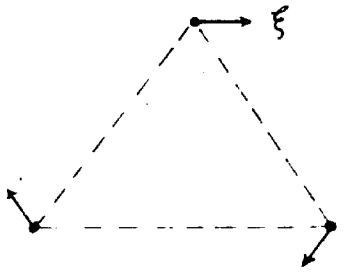
Table XV

Parametric tabulation of possible potential constants for the parallel inactive vibrations (in units of 10^5 dynes/cm.).

$a_{11} = 5.2412$	$a_{12} = 0.9220$	$k_R = 4.570$
$a_{22} = 1.3262$	$a_{13} = 0.4125$	$k_{R\psi} = 0.552$
$a_{33} = 0.7886$	$a_{23} = 0.3538$	$k_{Rr} = 0.303$
$a_{11} = 5.3295$	$a_{12} = 0.7047$	$k_R = 4.574$
$a_{22} = 1.2380$	$a_{13} = 0.4311$	$k_{R\psi} = 0.597$
$a_{33} = 0.7886$	$a_{23} = 0.3310$	$k_{Rr} = 0.049$
$a_{11} = 5.4179$	$a_{12} = 0.3568$	$k_R = 4.662$
$a_{22} = 1.1497$	$a_{13} = 0.4570$	$k_{R\psi} = 0.717$
$a_{33} = 0.7886$	$a_{23} = 0.2940$	$k_{Rr} = -0.332$

E. The torsional vibration.

The coordinate specifying the torsonal motion is chosen as follows:



Scale factor:
$6^{-1/2} = .4082_5$

The expressions for the kinetic and potential energies are:

$$T = 1/2\, m \dot{\xi}^2$$
$$T^* = 1/2\, m^* \dot{\xi}^2$$
$$V = V^* = 1/2\, a \xi^2$$

and the secular equations become:

$$m\omega^2 - a = 0$$
$$m^*\omega^{*2} - a = 0$$

From specific heat measurements, Kistiakowsky, Lacher, and Stitt[7] have obtained the values:

$$\nu_4 = 275 \text{ cm.}^{-1} \; ; \; \nu_4^* = 200 \text{ cm.}^{-1}$$

The ratio ν_4/ν_4^* and the product rule give an anharmonicity factor $x_4 = .0933$ and this leads to the results:

$$\omega_4 = 303.3 \text{ cm.}^{-1}$$
$$\omega_4^* = 214.6 \text{ cm.}^{-1}$$
$$a = 0.0546 \times 10^5 \text{ dynes/cm.}$$

The torsional vibration is both Raman and infra-red inactive and the spectroscopic determination of its fundamental

frequency can be obtained only from combination bands. For C_2H_6, Smith has determined the average value $\nu_4 = 290$ cm.$^{-1}$ from the two bands ν_{4+11} and ν_{4+10} while for C_2D_6, Stitt's observation $\nu^*_{4+10} = 2415$ cm.$^{-1}$ gives $\nu_4 = 190$ cm.$^{-1}$. For these two values, the ratio $\nu_4/\nu_4^* = 1.526$ differs so markedly from the product rule ratio $\sqrt{m'/m} = 1.414$ as to indicate a real inconsistency. Although in general, spectroscopic methods are the more accurate, in this case the specific heat measurements give the more concordant results.

To summarize, in this chapter we have evaluated the general potential constants of ethane corresponding to a symmetry coordinate expression of the potential energy function. This symmetry coordinate formulation has a minimum of complexity and also possesses the advantage that uncertainties in the data associated with one symmetry class are not propagated to the calculated potential constants of any other symmetry class. For the determination of those potential constants associated with the parallel inactive vibrations, it was necessary to supplement the data with an assumption concerning the nature of the coupling between the different parts of the molecule. Although the data does not establish each of the listed potential constants with the same precision, each value is given to four figures beyond the decimal point. This insures best agreement between predicted and observed frequencies and zeta values and gives the best basis for further calculations on ethane or any of its isotopes. The discussion of uncertainties in calculated values will be reserved for the valence force

constants where an improperly claimed accuracy could be misleading in the correlations between ethane and other molecules.

CHAPTER VII

THE VALENCE FORCE CONSTANTS

With the general set of potential constants determined in the last chapter, it is now possible to calculate the restoring forces associated with arbitrary small distortions of ethane such as the stretching of one of the C-H bonds or the bending of one of the H-C-H bond angles. The force constants for such specific distortions are required for comparisons with other molecules which possess similar elements.

When, for example, one of these bonds is stretched, the other bonds will deform in such a way as to minimize the potential energy. These distortions are characterized by the "coupling force constants" which indicate the strength of the coupling forces between the various parts of the molecule. It is well known that the vibrational spectra of many molecules may be explained quite accurately using simplified expressions for the potential functions in which most of the possible coupling terms are absent. One thus expects, apriori, that many of the coupling terms for ethane will be very small, especially those terms which represent coupling between remote parts of the molecule. In fact, one may consider it a requisite property of the general set of potential constants to yield values in accordance with these expectations.

These bond stretching, bond angle bending, and coupling force constants are the potential constants associated with a "valence coordinate" expression of the potential energy

function. They may be determined, then, in terms of our general set of potential constants and the transformation matrix between the valence coordinates and the symmetry coordinates. The symmetry coordinate for the torsional vibration is also a valence coordinate, and the dependence of the potential energy on this coordinate will be unchanged by the above transformation. The single valence force constant associated with the torsional motion has thus already been evaluated and we may focus our attention on the remaining undetermined constants.

For the determination of these valence force constants, the following procedure is used.

I. The general form of the potential energy is expressed in terms of the valence coordinates and the unknown valence force constants.

II. The valence coordinates are determined as functions of the symmetry coordinates and these functions substituted into the energy expression. The resulting constant coefficients are equated to the known potential constants and the values of the valence force constants determined.

The 19 bond distances and bond angles of ethane give rise to 19 valence coordinates having the definitions:

(1) R = the C-C' distance minus the equilibrium C-C' distance (R_o).

(2-7) r_i = the C-H_i distance minus the equilibrium C-H_i distance (r_o).

(8-13) ψ_i = the H_i-C-C' angle minus the equilibrium H_i-C-C' angle (ψ_o).

(14-19) θ_i = the H_{i+1}-C-H_{i-1} angle minus the equilibrium H_{i+1}-C-H_{i-1} angle (θ_o).

These coordinates are not all independent but satisfy the two conditions:

(a) $(\theta_1 + \theta_2 + \theta_3)\sin\theta_0 = (\psi_1 + \psi_2 + \psi_3)(3\sin\psi_0\cos\psi_0)$

(b) $(\theta_{1'} + \theta_{2'} + \theta_{3'})\sin\theta_0 = (\psi_{1'} + \psi_{2'} + \psi_{3'})(3\sin\psi_0\cos\psi_0)$

These two equations are equivalent to the conditions that there be (1) no net rotation about the symmetry axis, and (2) no rotation of one methyl group relative to the other. Thus, the 12 valence coordinates possess the 12 degree of freedom required to express the vibrations of ethane (exclusive of torsion).

Excluding torsion, the 21 valence force constants permitted by the symmetry of ethane may be divided into three categories.

(A) Stretching and bending force constants (4 independent constants).

(B) Force constants coupling adjacent parts of the molecule (8 independent constants).

(C) Force constants coupling remote parts of the molecule (9 independent constants).

The redundancy of the coordinate system permits a certain lattitude in the expression of the potential energy. 21 independent force constants may be defined as follows:

(A) Stretching and bending force constants.

Nature of the constant	Symbol	Contribution to the Potential Energy
(1) C-H_1 stretching	k_r	$\frac{1}{2}k_r(r_1^2 + r_2^2 + r_3^2 + r_{1'}^2 + r_{2'}^2 + r_{3'}^2)$
(2) H-C-C bending	k_ψ	$\frac{1}{2}k_\psi r_0^2(\psi_1^2 + \psi_2^2 + \psi_3^2 + \psi_{1'}^2 + \psi_{2'}^2 + \psi_{3'}^2)$

(3) H-C-H bending k_θ $\quad \tfrac{1}{2} k_\theta r_0^2 (\theta_1^2 + \theta_2^2 + \theta_3^2 + \theta_{1'}^2 + \theta_{2'}^2 + \theta_{3'}^2)$

(4) C-C stretching k_R $\quad \tfrac{1}{2} k_R R^2$

(B) Force constants coupling adjacent parts of the molecule.

(5) $\left\{\begin{matrix}\text{C-H stretching} \\ \text{C-H stretching}\end{matrix}\right.$ $\quad \tfrac{1}{2} k_{rr} (r_1 r_2 + r_2 r_3 + r_3 r_1 + r_{1'} r_{2'} + r_{2'} r_{3'} + r_{3'} r_{1'})$

(6) $\left\{\begin{matrix}\text{H-C-C bending} \\ \text{H-C-C bending}\end{matrix}\right.$ $\quad \tfrac{1}{2} k_{\psi\psi} r_0^2 (\psi_1 \psi_2 + \psi_2 \psi_3 + \psi_3 \psi_1 + \psi_{1'} \psi_{2'} + \psi_{2'} \psi_{3'} + \psi_{3'} \psi_{1'})$

(7) $\left\{\begin{matrix}\text{H}_i\text{-C-C bending} \\ \text{H}_{i+1}\text{-C-H}_{i-1}\text{ bending}\end{matrix}\right.$ $\quad \tfrac{1}{2} k_{\theta\psi} r_0^2 (\theta_1 \psi_{1'} + \theta_2 \psi_{2'} + \theta_3 \psi_{3'} + \theta_{1'} \psi_1 + \theta_{2'} \psi_2 + \theta_{3'} \psi_3)$

(8) $\left\{\begin{matrix}\text{H}_i\text{-C stretching} \\ \text{H}_{i+1}\text{-C-C bending}\end{matrix}\right.$ $\quad \tfrac{1}{4} k_{r\psi_3} r_0 \left\{\begin{matrix} r_1(\psi_2+\psi_3) + r_2(\psi_3+\psi_1) + r_3(\psi_1+\psi_2) + \\ r_{1'}(\psi_{2'}+\psi_{3'}) + r_{2'}(\psi_{3'}+\psi_{1'}) + r_{3'}(\psi_{1'}+\psi_{2'}) \end{matrix}\right\}$

(9) $\left\{\begin{matrix}\text{H}_i\text{-C stretching} \\ \text{H}_{i+1}\text{-C-H}_{i-1}\text{ bending}\end{matrix}\right.$ $\quad \tfrac{1}{2} k_{r\theta} r_0 (r_1 \theta_1 + r_2 \theta_2 + r_3 \theta_3 + r_{1'} \theta_{1'} + r_{2'} \theta_{2'} + r_{3'} \theta_{3'})$

(10) $\left\{\begin{matrix}\text{H}_i\text{-C stretching} \\ \text{H}_i\text{-C-C bending}\end{matrix}\right.$ $\quad \tfrac{1}{2} k_{r\psi} r_0 (r_1 \psi_{1'} + r_2 \psi_{2'} + r_3 \psi_{3'} + r_{1'} \psi_1 + r_{2'} \psi_2 + r_{3'} \psi_3)$

(11) $\left\{\begin{matrix}\text{H-C stretching} \\ \text{C-C stretching}\end{matrix}\right.$ $\quad \tfrac{1}{2} k_{Rr} R (r_1 + r_2 + r_3 + r_{1'} + r_{2'} + r_{3'})$

(12) $\left\{\begin{matrix}\text{C-C stretching} \\ \text{H-C-C bending}\end{matrix}\right.$ $\quad \tfrac{1}{2} k_{R\psi} r_0 R (\psi_1 + \psi_2 + \psi_3 + \psi_{1'} + \psi_{2'} + \psi_{3'})$

(C) Force constants coupling remote parts of the molecule.

Nature of the constant	Contribution to the potential energy
(13) $\left\{\begin{matrix}\text{H}_i\text{-C stretching} \\ \text{H}_{i'}\text{-C stretching}\end{matrix}\right.$	$k_{rr'} (r_1 r_{1'} + r_2 r_{2'} + r_3 r_{3'})$
(14) $\left\{\begin{matrix}\text{H}_i\text{-C stretching} \\ \text{H}_{(i+1)'}\text{-C stretching}\end{matrix}\right.$	$\tfrac{1}{2} k_{rr'_3} (r_1 r_{2'} + r_2 r_{3'} + r_3 r_{1'} + r_{1'} r_{3'} + r_{2'} r_{1'} + r_{3'} r_{2'})$
(15) $\left\{\begin{matrix}\text{H}_i\text{-C stretching} \\ \text{C-C'-H}_{(i+1)'}\text{ bending}\end{matrix}\right.$	$\tfrac{1}{4} k_{r\psi_3} r_0 \left\{\begin{matrix} r_1(\psi_{2'}+\psi_{3'}) + r_2(\psi_{3'}+\psi_{1'}) + r_3(\psi_{1'}+\psi_{2'}) \\ + r_{1'}(\psi_2+\psi_3) + r_{2'}(\psi_1+\psi_3) + r_{3'}(\psi_1+\psi_2) \end{matrix}\right\}$
(16) $\left\{\begin{matrix}\text{H}_i\text{-C stretching} \\ \text{C-C'-H}_{(i')}\text{ bending}\end{matrix}\right.$	$\tfrac{1}{2} k_{r\psi'} r_0 (r_1 \psi_{1'} + r_2 \psi_{2'} + r_3 \psi_{3'} + r_{1'} \psi_1 + r_{2'} \psi_2 + r_{3'} \psi_3)$

Nature of the constant	Contribution to the potential energy
(17) $\begin{cases} H_i\text{-C stretching} \\ H_{(i+1)'}\text{-C-}H_{(i-1)'} \text{ bending} \end{cases}$	$\frac{1}{2} k_{r\theta} r_0 (r_1\theta_{1'} + r_2\theta_{2'} + r_3\theta_{3'} + r_{1'}\theta_1 + r_{2'}\theta_2 + r_{3'}\theta_3)$
(18) $\begin{cases} H_i\text{-C-C' bending} \\ C\text{-C'-}H_{i'} \text{ bending} \end{cases}$	$k_{\psi\psi'} r_0^2 (\psi_1\psi_{1'} + \psi_2\psi_{2'} + \psi_3\psi_{3'})$
(19) $\begin{cases} H_i\text{-C-C' bending} \\ C\text{-C'-}H_{(i+1)'} \text{ bending} \end{cases}$	$\frac{1}{2} k_{\psi\psi'_3} r_0^2 (\psi_1\psi_{2'} + \psi_1\psi_{3'} + \psi_2\psi_{1'} + \psi_2\psi_{3'} + \psi_3\psi_{1'} + \psi_3\psi_{2'})$
(20) $\begin{cases} H_{i+1}\text{-C-}H_{i-1} \text{ bending} \\ H_{(i+1)'}\text{-C-}H_{(i-1)'} \text{ bending} \end{cases}$	$k_{\theta\theta'} r_0^2 (\theta_1\theta_{1'} + \theta_2\theta_{2'} + \theta_3\theta_{3'})$
(21) $\begin{cases} H_{i+1}\text{-C-}H_{i-1} \text{ bending} \\ C\text{-C'-}H_{i'} \text{ bending} \end{cases}$	$k_{\theta\psi'} r_0^2 (\theta_1\psi_{1'} + \theta_2\psi_{2'} + \theta_3\psi_{3'})$

One may think of other coupling constants such as

$$\begin{cases} \text{C-C stretching to} \\ H_{i+1}\text{-C-}H_{i-1} \text{ bending coupling} \end{cases} \longrightarrow \frac{1}{2} k_{R\theta} r_0 R (\theta_1 + \theta_2 + \theta_3 + \theta_{1'} + \theta_{2'} + \theta_{3'})$$

However, the quadratic form $k_{R\theta} r_0 R (\theta_1 + \theta_2 + \theta_3 + \theta_{1'} + \theta_{2'} + \theta_{3'})$ is proportional to $k_{R\psi} r_0 R (\psi_1 + \psi_2 + \psi_3 + \psi_{1'} + \psi_{2'} + \psi_{3'})$. This indicates that, due to the redundancy of the valence coordinate system, one can characterize the same distortion by either of two coupling constants. Thus, in this case, when the carbon-carbon bond is stretched, the methyl groups will tend to open or close somewhat like umbrellas depending on the sign of the interactions between these distortions. This opening or closing of the methyl groups can be expressed either as

$$(\theta_1 + \theta_2 + \theta_3 + \theta_{1'} + \theta_{2'} + \theta_{3'}) \longrightarrow \text{coupling constant } k_{R\theta}$$

or

$$(\psi_1 + \psi_2 + \psi_3 + \psi_{1'} + \psi_{2'} + \psi_{3'}) \longrightarrow \text{coupling constant } k_{R\psi}$$

We have arbitrarily chosen the second of these equivalent expressions. It suffices to say that since the 21 listed quadratic forms in the valence coordinates are independent and satisfy the symmetry requirements, their 21 coefficients represent a complete set of force constants.

The 21 potential terms listed above constitute the quadratic terms in a power series expansion of the potential energy function. The sum of these quadratic terms represents the total potential energy for infinitesimal distortions of the molecule. By the transformation from valence coordinates to symmetry coordinates, one means the linear transformation which relates infinitesimal values of the valence coordinates to the infinitesimal values of the symmetry coordinates In this sense, the valence coordinates are linear functions of the symmetry coordinates. The linear functions of the symmetry coordinates of each symmetry class are given separately in the order (A) A_{1g}, (B) A_{2u}, (C) E_u, (D) E_g.

A. Dependence of the valence coordinates on the A_{1g} (parallel inactive) symmetry coordinates (ξ_1 , ξ_2 , ξ_3).

$$r_1 = r_2 = r_3 = r_{1'} = r_{2'} = r_{3'} = \frac{\sin\psi_0}{\sqrt{6}}\xi_1 - \frac{\cos\psi_0}{\sqrt{6}}\xi_2 - \sqrt{\frac{m}{2M}}\cos\psi_0\,\xi_3$$

$$r_0(\psi_1 = \psi_2 = \psi_3 = \psi_{1'} = \psi_{2'} = \psi_{3'}) = \frac{\cos\psi_0}{\sqrt{6}}\xi_1 + \frac{\sin\psi_0}{\sqrt{6}}\xi_2 + \sqrt{\frac{m}{2M}}\sin\psi_0\,\xi_3$$

$$r_0(\theta_1 = \theta_2 = \theta_3 = \theta_{1'} = \theta_{2'} = \theta_{3'}) = \frac{3\sin\psi_0\cos^2\psi_0}{\sqrt{6}\sin\theta_0}\xi_1 + \frac{3\sin^2\psi_0\cos\psi_0}{\sqrt{6}\sin\theta_0}\xi_2$$

$$+ 3\sqrt{\frac{m}{2M}}\,\frac{\sin^2\psi_0\cos\psi_0}{\sin\theta_0}\,\xi_3$$

$$R = -2\sqrt{\frac{m}{2M}}\,\xi_3$$

Substituting these expressions for the valence coordinates in the potential energy function (consisting of the 21 terms listed on pages 106-108), one obtains the following six equations among the force constants.

$$a_{11} = .8872K_1 + .1128K_2 - .3163K_3$$

$$a_{22} = .1128K_1 + .8872K_2 + .3163K_3$$

$$a_{12} = .3163K_1 - .3163K_2 + .3872K_3$$

$$a_{33} = .0284K_1 + .2235K_2 + .0797K_3 + .1380k_R - .1692k_{Rr} - .4746k_{R\psi}$$

$$a_{13} = .1588K_1 - .1588K_2 + .1944K_3 - .4728k_{Rr} + .1685k_{R\psi}$$

$$a_{23} = .0566K_1 + .4453K_2 + .1588K_3 - .1685k_{Rr} - .4728k_{R\psi}$$

where $K_1 = k_r + k_{rr} + k_{rr'} + k_{rr'_\beta}$

$$K_2 = k_\psi + k_{\psi\psi} + k_{\psi\psi'} + k_{\psi\psi'_\beta} + (3 \sin\psi_o \cos\psi_o / \sin\theta_o)^2 (k_\theta + k_{\theta\theta'}) + (3 \sin\psi_o \cos\psi_o / \sin\theta_o)(k_{\theta\psi} + k_{\theta\psi'})$$

$$K_3 = k_{r\psi} + k_{r\psi_\beta} + k_{r\psi'} + k_{r\psi'_\beta} + (3 \sin\psi_o \cos\psi_o / \sin\theta_o)(k_{r\theta} + k_{r\theta'})$$

and the a_{ij} are the general potential constants for the parallel inactive vibrations.

B. Dependence of the valence coordinates on the A_{2u} (parallel active) symmetry coordinates (ξ_1, ξ_2).

$$r_1 = r_2 = r_3 = -r_{1'} = -r_{2'} = -r_{3'} = \frac{\sin\psi_o}{\sqrt{6}}\xi_1 - \cos\psi_o\sqrt{\frac{3m+M}{6M}}\xi_2$$

$$r_o(\psi_1 = \psi_2 = \psi_3 = -\psi_{1'} = -\psi_{2'} = -\psi_{3'}) = \frac{\cos\psi_o}{\sqrt{6}}\xi_1 + \sin\psi_o\sqrt{\frac{3m+M}{6M}}\xi_2$$

$$r_o(\theta_1 = \theta_2 = \theta_3 = -\theta_{1'} = -\theta_{2'} = -\theta_{3'}) = \frac{3\sin\psi_o\cos^2\psi_o}{\sqrt{6}\sin\theta_o}\xi_1$$

$$+ \frac{3\sin^2\psi_o\cos\psi_o}{\sin\theta_o}\sqrt{\frac{3m+M}{6M}}\xi_2$$

$$R = 0$$

Substituting these expressions for the valence coordinates in the potential energy function, one obtains the following three equations among the force constants.

$$a_{11} = .8872L_1 + .1128L_2 - .3163L_3$$

$$a_{22} = .1412L_1 + 1.1107L_2 + .3960L_3$$

$$a_{12} = .3539L_1 - .3539L_2 + .4332L_3$$

where

$$L_1 = k_r + k_{rr} - k_{rr'} - k_{rr'_\beta}$$

$$L_2 = k_\psi + k_{\psi\psi} - k_{\psi\psi'} - k_{\psi\psi'_\beta} + (3 \sin\psi_o \cos\psi_o / \sin\theta_o)^2 (k_\theta - k_{\theta\theta'}) + (3 \sin\psi_o \cos\psi_o / \sin\theta_o)(k_{\theta\psi} - k_{\theta\psi'})$$

$$L_3 = k_{r\psi} + k_{r\psi_\beta} - k_{r\psi'} - k_{r\psi'_\beta} + (3 \sin\psi_o \cos\psi_o / \sin\theta_o)(k_{r\theta} - k_{r\theta'})$$

and the a_{ij} are the general potential constants for the parallel active vibrations.

c. Dependence of the valence coordinates on the E_u (perpendicular active) symmetry coordinates ($\xi_1, \eta_1, \xi_2, \eta_2, \xi_3, \eta_3$).

$$r_1 = -r_{1'} = \frac{\sin\psi_o}{\sqrt{6}}\xi_1 - \frac{\cos\psi_o}{\sqrt{3}}\xi_2 + \sqrt{\frac{3m+M}{6M}}\sin\psi_o\,\xi_3$$

$$r_o(\psi_1 = -\psi_{1'}) = \frac{\cos\psi_o}{\sqrt{6}}\xi_1 + \frac{\sin\psi_o}{\sqrt{3}}\xi_2 + \sqrt{\frac{3m+M}{6M}}\cos\psi_o\,\xi_3$$

$$r_o(\theta_1 = -\theta_{1'}) = -\tfrac{3}{2}\frac{\sin\psi_o(1+\cos^2\psi_o)}{\sqrt{6}\sin\theta_o}\xi_1 - \tfrac{3}{2}\frac{\sin^2\psi_o\cos\psi_o}{\sqrt{3}\sin\theta_o}\xi_2 + \tfrac{3}{2}\frac{\sin^3\psi_o}{\sin\theta_o}\sqrt{\frac{3m+M}{6M}}\,\xi_3$$

$$R = 0$$

$r_2 = -r_{2'}$ is obtained from r_1 by substituting $(-\tfrac{1}{2}\xi_i + \sqrt{3}/2\,\eta_i)$ for ξ_i. Similarly for $r_o(\psi_2 = -\psi_{2'})$ and $r_o(\theta_2 = -\theta_{2'})$.

$r_3 = -r_{3'}$ is obtained from r_1 by substituting $(-\tfrac{1}{2}\xi_i - \sqrt{3}/2\,\eta_i)$ for ξ_i. Similarly for $r_o(\psi_3 = -\psi_{3'})$ and $r_o(\theta_3 = -\theta_{3'})$.

Substituting these expressions for the valence coordinates in the potential energy function, one obtains the following six equations among the force constants.

$$a_{11} = .4436M_1 + .0564M_2 - .1582M_3 + 1.3879M_4 - .7847M_5 + .2798M_6$$
$$a_{22} = .1128M_1 + .3872M_2 + .3163M_3 + .2243M_4 + .1590M_5 + .4461M_6$$
$$a_{33} = .5554M_1 + .0706M_2 - .1980M_3 + 1.1046M_4 + .7833M_5 - .2792M_6$$
$$a_{12} = .2257M_1 - .2237M_2 + .2738M_3 - .5579M_4 - .0401M_5 - .6110M_6$$
$$a_{13} = .4963M_1 + .0631M_2 - .1770M_3 - 1.2382M_4 - .0890M_5 + .0317M_6$$
$$a_{23} = .2503M_1 - .2503M_2 + .3063M_3 + .4977M_4 + .3529M_5 + .4321M_6$$

where

$$M_1 = k_r - 1/2k_{rr} - k_{rr'} + 1/2k_{rr'_\beta}$$
$$M_2 = k_\psi - 1/2k_{\psi\psi} - k_{\psi\psi'} + 1/2k_{\psi\psi'_\beta}$$
$$M_3 = k_{r\psi} - 1/2k_{r\psi_\beta} - k_{r\psi'} + 1/2k_{r\psi'_\beta}$$
$$M_4 = k_\theta - k_{\theta\theta'}$$
$$M_5 = k_{r\theta} - k_{r\theta'}$$
$$M_6 = k_{e\psi} - k_{\theta\psi'}$$

and the a_{ij} are the general potential constants for the perpendicular active vibrations.

D. Dependence of the valence coordinates on the E_g (perpendicular inactive) symmetry coordinates ($\xi_1, \eta_1, \xi_2, \eta_2, \xi_3, \eta_3$).

$$r_1 = r_{1'} = \frac{\sin\psi_o}{\sqrt{6}}\xi_1 + \sqrt{\frac{I_z}{12I_c}}\left\{\sin\psi_o - \cos\psi_o\left(\frac{R_o}{r_o} - 2\cos\psi_o\right)\right\}\xi_2 + \sqrt{\frac{mI_z}{2MI_c}}\sin\psi_o\,\xi_3$$

$$r_o(\psi_1 = \psi_{1'}) = \frac{\cos\psi_o}{\sqrt{6}}\xi_1 + \sqrt{\frac{I_z}{12I_c}}\left(\frac{R_o}{r_o} - \cos\psi_o\right)\xi_2 + \sqrt{\frac{mI_z}{2MI_c}}\left(\cos\psi_o - 2\frac{R_o}{R_o}\right)\xi_3$$

$$r_o(\theta_1 = \theta_{1'}) = -3/2\,\frac{\sin^3\psi_o(1+\cos^2\psi_o)}{\sqrt{6}\,\sin\theta_o}\xi_1 + \frac{3/2\sin\psi_o}{\sin\theta_o}\sqrt{\frac{I_z}{12I_c}}\left\{1+\cos^2\psi_o - \frac{R_o}{r_o}\cos\psi_o\right\}\xi_2$$

$$+ 3/2\,\frac{\sin^3\psi_o}{\sin\theta_o}\sqrt{\frac{mI_z}{2MI_c}}\,\xi_3$$

$$R = 0$$

$r_2 = r_{2'}$ is obtained from r_1 by substituting $(-1/2\,\xi_1 + \sqrt{3}/2\,\eta_1)$ for ξ_1. Similarly for $r_o(\psi_2 = \psi_{2'})$ and $r_o(\theta_2 = \theta_{2'})$.
$r_3 = r_{3'}$ is obtained from r_1 by substituting $(-1/2\,\xi_1 - \sqrt{3}/2\,\eta_1)$ for ξ_1. Similarly for $r_o(\psi_3 = \psi_{3'})$ and $r_o(\theta_3 = \theta_{3'})$.
Substituting these expressions for the valence coordinates in the potential energy function, one obtains the following six equations among the force constants.

$$a_{11} = .4436N_1 + .0564N_2 - .1582N_3 + 1.3879N_4 - .7847N_5 + .2798N_6$$

$$a_{22} = .4130N_1 + .4409N_2 + .4267N_3 + .8213N_4 + .3264N_5 + .6018N_6$$

$$a_{33} = .2552N_1 + .8944N_2 - .4778N_3 + .5077N_4 + .3600N_5 - .6738N_6$$

$$a_{12} = .4280N_1 - .1577N_2 + .1448N_3 - 1.0677N_4 + .0897N_5 - .4987N_6$$

$$a_{13} = .3565N_1 + .2246N_2 - .3749N_3 - .3394N_4 - .0603N_5 + .4725N_6$$

$$a_{23} = .3247N_1 - .6280N_2 - .1562N_3 + .6457N_4 + .4720N_5 - .1920N_6$$

where

$$N_1 = k_r - 1/2k_{rr} + k_{rr'} - 1/2k_{rr'_\beta}$$

$$N_2 = k_\psi - 1/2k_{\psi\psi} + k_{\psi\psi'} - 1/2k_{\psi\psi'_\beta}$$

$$N_3 = k_{r\psi} - 1/2k_{r\psi_\beta} + k_{r\psi'} - 1/2k_{r\psi'_\beta}$$

$$N_4 = k_\theta + k_{\theta\theta'}$$

$$N_5 = k_{r\theta} + k_{r\theta'}$$

$$N_6 = k_{\theta\psi} + k_{\theta\psi'}$$

and the a_{ij} are the general potential constants for the perpendicular inactive vibrations.

The valence force constants may now be expressed in terms of the "secondary" force constants K_1, L_1, M_1, and N_1 defined in the previous pages.

$$k_r = (K_1 + L_1 + 2M_1 + 2N_1)/6$$
$$k_{rr'} = (K_1 + L_1 - M_1 - N_1)/3$$
$$k_{rr'} = (K_1 - L_1 - M_1 + 2N_1)/6$$
$$k_{rr'\beta} = (K_1 - L_1 + M_1 - N_1)/3$$
$$k_\theta = (K_4 + N_4)/2$$
$$k_{\theta\theta'} = (-K_4 + N_4)/2$$
$$k_{r\theta} = (K_5 + N_5)/2$$
$$k_{r\theta'} = (-K_5 + N_5)/2$$
$$k_{\theta\psi} = (K_6 + N_6)/2$$
$$k_{\theta\psi'} = (-K_6 + N_6)/2$$
$$k_\psi = (K_2 + L_2 + 2M_2 + 2N_2 - 1.0112N_4 - 1.0112M_4 + 1.0056N_6 + 1.0056M_6)/6$$
$$k_{\psi\psi} = (K_2 + L_2 - M_2 - N_2 - 1.0112N_4 - 1.0112M_4 + 1.0056N_6 + 1.0056M_6)/3$$
$$k_{\psi\psi'} = (K_2 - L_2 - M_2 + 2N_2 - 1.0112N_4 + 1.0112M_4 + 1.0056N_6 - 1.0056M_6)/6$$
$$k_{\psi\psi'\beta} = (K_2 - L_2 + M_2 - N_2 - 1.0112N_4 + 1.0112M_4 + 1.0056N_6 - 1.0056M_6)/3$$
$$k_{r\psi} = (K_3 + L_3 + M_3 + 2N_3 + 1.0056N_5 + 1.0056M_5)/6$$
$$k_{r\psi\beta} = (K_3 + L_3 - M_3 - N_3 + 1.0056N_5 + 1.0056M_5)/3$$
$$k_{r\psi'} = (K_3 - L_3 - M_3 + 2N_3 + 1.0056N_5 - 1.0056M_5)/6$$
$$k_{r\psi'\beta} = (K_3 - L_3 + M_3 - N_3 + 1.0056N_5 - 1.0056M_5)/3$$
$$k_R = k_R$$
$$k_{Rr} = k_{Rr}$$
$$k_{R\psi} = k_{R\psi}$$

The numerical values for these force constants are listed in Table XVI. The "uncertainty" values for these force constants,

Table XVI

The valence force constants of ethane.

(all constants are expressed in units of 10^5 dynes/cm.)

Stretching and bending force constants

(1) $k_r = 5.35 \pm .03$

(2) $k_\theta = 0.51 \pm .02$

(3) $k_\psi = 0.63 \pm .02$

(4) $k_R = 4.57 \pm .03$

Coupling constants for adjacent components

(5) $k_{r\psi_\beta} = -1.89 \pm .20$

(6) $k_{R\psi} = 0.60 \pm .04$

(7) $k_{r\theta} = -0.20 \pm .02$

(8) $k_{\theta\psi} = -0.07 \pm .02$

(9) $k_{r\psi} = -0.07 \pm .15$

(10) $k_{rr} = -0.04 \pm .04$

(11) $k_{\psi\psi} = 0.03 \pm .04$

(12) $k_{Rr} = 0.00 \pm .20$

Coupling constants for remote components

(13) $k_{\psi\psi'} = 0.11 \pm .02$

(14) $k_{\theta\psi'} = 0.07 \pm .03$

(15) $k_{r\theta'} = -0.03 \pm .02$

(16) $k_{\theta\theta'} = -0.02 \pm .02$

(17) $k_{rr'_\beta} = -0.08 \pm .04$

(18) $k_{rr'} = 0.08 \pm .04$

(19) $k_{r\psi'_\beta} = 0.35 \pm .20$

(20) $k_{r\psi'} = -0.13 \pm .15$

(21) $k_{\psi\psi'_\beta} = 0.00 \pm .05$

which are also listed in this Table, have been defined by the following recipe (there does not exist a statistical basis for the calculation of probable errors). Letting β_i represent the deviation of the value of the i^{th} datum from the adopted value, then we have chosen limiting values of the β_i for several of the least well established datum and in each case determined the associated set of valence force constants. Letting Δk_{ji} represent the change in the j^{th} force constant when β_i changes from zero to $\beta_i(\text{max.})$, then the "uncertainty" in the value of the j^{th} force constant, Δk_j, has been defined by the equation

$$\Delta k_j = \left\{ \sum_i (\Delta k_{ji})^2 \right\}^{1/2}$$

The chosen β_i and their assigned limiting values are as follows:

(1) The limiting range of the parallel inactive potential constants which satisfy the five normal frequency equations and the inequality condition

$$|k_{Rr}| \leq 0.2 \times 10^5 \text{ dynes/cm.}$$

is associated with the symbolic uncertainty parameter β_1. This uncertainty is concerned with the supplementary assumption that $k_{Rr} = 0$. (The assumed limit values of $\pm 0.2 \times 10^5$ dynes/cm. are large compared to any of the C-H to C-H stretching coupling constant values.)

(2) Due to its determination from the positions of a resonant doublet, the fundamental frequency ν_1 was assigned

the limiting values 2915 ± 15 $cm.^{-1}$. In order to obtain normal frequencies which satisfy the Teller product rule, it was necessary also to change the anharmonicity factors. Thus the upper limit of the uncertainty parameter β_2 was chosen to correspond to the values

$$\nu_1 = 2930 \text{ cm.}^{-1}$$

$$x_1 = x_2 = x_3 = 0.0267$$

(The above choice of equal anharmonicity factor was adopted since the more customary ratios with $x_1 > x_2 > x_3$ lead to non-real values for the potential constants.)

(3) The third parameter, β_3, was chosen to represent a 10 $cm.^{-1}$ change in the fundamental frequency $\nu_5 = 2915$ $cm.^{-1}$, which like ν_1, was determined from the limits of a resonant doublet.

(4) For the perpendicular active vibrations, the six fundamental frequencies and four independent zeta values should be expected to yield reliable values for the six associated potential constants. However, in the least squares method used for the solution of these potential constants, it is found that there is a path along which the sum of the squared deviations remains very close to its minimum value. In one direction along this path, the agreement between the predicted and "observed" normal frequencies becomes better while the agreement between the predicted and observed zeta values becomes worse. (In the opposite direction along this

path, the reverse is true.) As the upper limit of the fourth parameter, β_4, we have chosen that "distance" along the path which results in a doubling of the sum of the squared deviations of the zeta values. The values for the k_{j4} were doubled as partial compensation for a similar condition existing in the case of the perpendicular inactive vibrations.

This recipe for estimating the uncertainties in the calculated values of the valence force constants is admittedly very crude. It does give information, however, on the sensitivity of the calculated values with respect to the values of the initial data.

As was expected, many of the coupling constants listed in Table XVI are small, and, within the estimated limits of precision, may be assumed as zero. This result, then, tends to confirm the interpretations of the spectroscopic data of ethane and heavy ethane.

CHAPTER VIII

CORRELATION OF THE FORCE CONSTANTS OF ETHANE AND METHANE

The potential function of methane has been determined by Denison[13] and is characterized by a set of five potential constants. In terms of valence coordinates, these constants may be given as follows:

Nature of constant	Symbol and value (in units of 10^5 dynes/cm.)	Contribution to the energy
(1) C-H stretching	$K_r = 5.394$	$\frac{1}{2}(r_1^2 + r_2^2 + r_3^2 + r_4^2)$
(2) H-C-H bending	$K_\psi = 0.420$	$\frac{1}{2} K_\psi r_0^2 (\psi_{12}^2 + \psi_{13}^2 + \psi_{14}^2 + \psi_{23}^2 + \psi_{24}^2 + \psi_{34}^2)$
(3) $C\text{-}H_i$ to $C\text{-}H_j$ coupling	$K_{rr} = 0.037$	$\frac{1}{2} K_{rr} (r_1 r_2 + r_1 r_3 + r_1 r_4 + r_2 r_3 + r_2 r_4 + r_3 r_4)$
(4) $C\text{-}H_i$ to $H_j\text{-}C\text{-}H_k$ coupling	$K_4 = -0.276$	$\frac{1}{2} K_4 r_0 \{ r_1(\psi_{23}+\psi_{24}+\psi_{34}) + r_2(\psi_{34}+\psi_{14}+\psi_{13}) + r_3(\psi_{12}+\psi_{14}+\psi_{24}) + r_4(\psi_{12}+\psi_{13}+\psi_{23}) \}$
(5) $H_i\text{-}C\text{-}H_j$ to $H_k\text{-}C\text{-}H_l$ coupling	$K_5 = -0.075$	$\frac{1}{2} K_5 r_0^2 (\psi_{12}\psi_{34} + \psi_{13}\psi_{24} + \psi_{14}\psi_{23})$

As in the case of ethane, these valence coordinates for methane comprise a redundant set having the one relation $\psi_{12} + \psi_{13} + \psi_{14} + \psi_{23} + \psi_{24} + \psi_{34} = 0$. Again this redundancy permits one to express the potential energy in numerous equivalent ways, and the values of the coupling constants such as K_4 depend on the specific expression. In order to establish the correlation between these force constants of methane and the force constants of ethane, we rephrase the above expression of the potential function of methane in the asymetrical notation (which emphasizes the hydrogen nucleus indexed 4)

CHAPTER VIII

CORRELATION OF THE FORCE CONSTANTS OF ETHANE AND METHANE

The potential function of methane has been determined by Dennison[13] and is characterized by a set of five potential constants. In terms of valence coordinates, these constants may be given as follows:

Nature of constant	Symbol and value (in units of 10^5 dynes/cm.)	Contribution to the energy
(1) C-H stretching	$K_r = 5.394$	$\frac{1}{2}(r_1^2 + r_2^2 + r_3^2 + r_4^2)$
(2) H-C-H bending	$K_\psi = 0.420$	$\frac{1}{2} K_\psi r_0^2 (\psi_{12}^2 + \psi_{13}^2 + \psi_{14}^2 + \psi_{23}^2 + \psi_{24}^2 + \psi_{34}^2)$
(3) $C\text{-}H_i$ to $C\text{-}H_j$ coupling	$K_{rr} = 0.037$	$\frac{1}{2} K_{rr} (r_1 r_2 + r_1 r_3 + r_1 r_4 + r_2 r_3 + r_2 r_4 + r_3 r_4)$
(4) $C\text{-}H_i$ to $H_j\text{-}C\text{-}H_k$ coupling	$K_4 = -0.276$	$\frac{1}{2} K_4 r_0 \{ r_1(\psi_{23}+\psi_{24}+\psi_{34}) + r_2(\psi_{34}+\psi_{14}+\psi_{13}) + r_3(\psi_{12}+\psi_{14}+\psi_{24}) + r_4(\psi_{12}+\psi_{13}+\psi_{23}) \}$
(5) $H_i\text{-}C\text{-}H_j$ to $H_k\text{-}C\text{-}H_l$ coupling	$K_5 = -0.075$	$\frac{1}{2} K_5 r_0^2 (\psi\psi_{34} + \psi_{13}\psi_{24} + \psi_{14}\psi_{23})$

As in the case of ethane, these valence coordinates for methane comprise a redundant set having the one relation $\psi_{12} + \psi_{13} + \psi_{14} + \psi_{23} + \psi_{24} + \psi_{34} = 0$. Again this redundancy permits one to express the potential energy in numerous equivalent ways, and the values of the coupling constants such as K_4 depend on the specific expression. In order to establish the correlation between these force constants of methane and the force constants of ethane, we rephrase the above expression of the potential function of methane in the asymetrical notation (which emphasizes the hydrogen nucleus indexed 4)

$$\psi_{12} = \theta_3 \qquad \psi_{14} = \psi_1$$
$$\psi_{13} = \theta_2 \qquad \psi_{24} = \psi_2 \qquad r_4 = R$$
$$\psi_{23} = \theta_1 \qquad \psi_{34} = \psi_3$$

By direct substitution, one obtains

$$2V = k_r(r_1^2+r_2^2+r_3^2) + k_\psi r_o^2(\psi_1^2+\psi_2^2+\psi_3^2) + k_\psi r_o^2(\theta_1^2+\theta_2^2+\theta_3^2)$$
$$+ k_r R^2 + k_{rr}(r_1r_2+r_1r_3+r_2r_3) + k_{rr}R(r_1+r_2+r_3)$$
$$+ k_4 r_o(r_1\theta_1+r_2\theta_2+r_3\theta_3) + k_4 r_o(r_1[\psi_2+\psi_3]+r_2[\psi_1+\psi_3]+r_3[\psi_1+\psi_2])$$
$$+ k_5 r_o^2(\theta_1\psi_1+\theta_2\psi_2+\theta_3\psi_3) + k_4 r_o R(\theta_1+\theta_2+\theta_3)$$

This expression is not analogous to the expression chosen for ethane due to the presence of the last term $k_4 r_o R(\theta_1+\theta_2+\theta_3)$. The analogy can be restored, however, by replacing $k_4 r_o R \cdot (\theta_1+\theta_2+\theta_3)$ by the equivalent term $-k_4 r_o R(\psi_1+\psi_2+\psi_3)$. As a further illustration, if we had chosen to represent the C-H to H-C-H coupling by the suitable term

$$-k_4 r_o[r_1(\psi_{12}+\psi_{13}+\psi_{14})+r_2(\psi_{12}+\psi_{23}+\psi_{24})+r_3(\psi_{13}+\psi_{23}+\psi_{34})]$$

then there would have appeared, in the asymetrical expression of the potential function, the two terms

$$-k_4 r_o[r_1(\theta_2+\theta_3)+r_2(\theta_1+\theta_3)+r_3(\theta_1+\theta_2)] - k_4 r_o[r_1\psi_1+r_2\psi_2+r_3\psi_3]$$

Although the latter term appears in the expression for ethane (coupling constant $k_{r\psi}$), the former term does not and hence must be reexpressed using the relations $\theta_2+\theta_3 = -\theta_1-\psi_1-\psi_2-\psi_3$, etc. This rephrasing, of course, always leads to the same result. It should be noticed, that as a consequence of expressing

the r-θ coupling in methane as $k_4 r_0 (r_1\theta_1 + r_2\theta_2 + r_3\theta_3)$, the potential energy function does not include a term of the form $k^*_{r\psi} r_0 (r_1\psi_1 + r_2\psi_2 + r_3\psi_3)$. One may attribute this fact to the equivalent nature of the angles θ and ψ and consider that the coupling constant $k^*_{r\psi}$ vanishes because of this equivalence. Thus, for ethane, the non-vanishing of the coupling constant $k_{r\psi}$ indicates the non-equivalence of θ (H-C-H angle) and ψ (H-C-C angle).

Treating the hydrogen nucleus 4 of methane as formally analogous to the primed carbon nucleus (or the primed methyl group) of ethane, then the correlations between the two sets of force constants is established. Table XVII gives a listing of these correlations together with the numerical values of the force constants. The nine remote coupling constants of ethane have no analogues in the set of methane force constants and hence do not appear in this table.

Table XVII

Correlation of the valence force constants of ethane and methane

(force constants expressed in units of 10^5 dynes/cm.)

Nature of force constant	Ethane		Methane
C-H stretching	$k_r = 5.55$	--	$K_r = 5.394$
H-C-H bending	$k_\theta = 0.51$	--	$K_\psi = 0.420$
$C-H_i$ to $C-H_j$ coupling	$k_{rr'} = -0.04$	--	$K_{rr} = 0.037$
$C-H_i$ to H_k-C-H_l coupling	$k_{r\theta} = -0.20$	--	$K_4 = -0.276$

Formal Correlations

Ethane: Nature of force constant	Value		Value	Methane: Nature of force constant
C-C stretching	$k_R = 4.57$	--	$K_r = 5.394$	C-H stretching
H-C-C bending	$k_\psi = 0.63$	--	$K_\psi = 0.420$	H-C-H bending
C-H to C-C coupling	$k_{Rr} = 0.00$	--	$K_{rr} = 0.037$	$C-H_j$ to $C-H_i$ coupling
H_k-C-H_l to H_i-C-C coupling	$k_{\theta\psi} = -0.07$	--	$K_5 = -0.075$	H_k-C-H_{k+1} to $H_{i+2}-C-H_i$ coupling
$C-H_i$ to $H_{i-1}-C-C$ coupling	$k_r = -1.99$	--	$2K_4 = -0.552$	$C-H_i$ to $H_{i-1}-C-H_{i+1}$ coupling
$C-H_i$ to H_i-C-C coupling	$k_r = -0.07$	--	$k_{rr} = 0.000$	$C-H_i$ to H_i-C-H_{i+1} coupling
C-C to H_i-C-C coupling	$k_R = 0.60$	--	$-k_4 = 0.276$	$C-H_{i+2}$ to H_i-C-H_{i+2} coupling
H_i-C-C to $H_{i+1}-C-C$ coupling	$k_{\psi\psi} = 0.03$	--	$K_{\psi\psi} = 0.000$	H_i-C-H_{i+2} to $H_{i+1}-C-H_{i+2}$ coupling

CHAPTER IX

SUMMARY

The precision determination of the general potential function of ethane has been completed and presented both in terms of a symmetry coordinate system and a valence coordinate system. The fundamental frequencies and zeta values of ethane and heavy ethane, which have formed the basis for this calculation, have been reconsidered and best values selected. In the case of C_2H_6, analysis of the perturbed fine structure of the vibrational band ν_8 has led to reliable values for the fundamental frequencies of ν_8 and ν_{12+4} as well as for the unperturbed rotational spacing of this band. These results have permitted the more accurate determinations of (1) the small moment of inertia, (2) the zeta values for the perpendicular active vibrations, and (3) the "uncertain frequency", ν_{12}. (This new value for the "uncertain frequency" permits a more certain assignment of the critical combination band ν_{9+12} upon which the D_{3d} equilibrium configuration of ethane is based. The explanation of the fine structure of ν_8 has also required this configuration and hence constitutes an independent check.) From a consideration of the appropriate combination bands and the 3.3 μ Stokes lines, it has been shown that there is an appreciable interaction between the vibrations ν_{8+4} and ν_{10} and that this interaction can explain the apparent failure of the zeta sum rule for the perpendicular inactive vibrations. Also on the basis of the observed

combination bands, the value of the fundamental frequency ν_2 has been established at 1400 $cm.^{-1}$ as compared to be previously accepted value of 1375 $cm.^{-1}$

In the case of C_2D_6, high resolution observations of the infra-red spectrum were made. This work has given (1) more precise values for the fundamental frequencies of the parallel and perpendicular active vibrations, (2) the zeta values associated with the vibrations ν_8^* and ν_9^*, and (3) the value for the large moment of inertia of C_2D_6, and hence has completed the spectroscopic determination of the dimensions of ethane.

The anharmonic contributions to the fundamental frequencies were empirically subtracted out, using a method devised by Dennison, and the "corrected" or normal frequencies have been employed in the secular equations for the potential constants. The possibility of making higher order corrections to the zeta values also, was briefly investigated and it has been shown that under favorable conditions (i.e. in the absence of resonance interactions) these corrections may be estimated either through information on certain quartic potential terms or by measurements of the zeta values associated with simple combination bands. For the ethane molecule, the requisite data for these corrections was not available. However, the magnitude of these corrections was estimated to be of the order $\pm$ .01 and this uncertainty was taken into account in the weighting scheme for the least squares solution of the potential constants for the degenerate vibrations.

The expression of the potential energy function in terms

of valence coordinates has established a set of valence force constants which permits a comparison between ethane and other molecules for which similar force constants are known. "Uncertainty" values have been assigned to each of these force constants. These values give a measure of the precision with which the fundamental frequencies and zeta values have been determined and give a limit to the meaningful correlation of these results with similar results for other molecules. Due to the redundancy of the valence coordinate system, it has been shown that one can construct numerous equivalent sets of valence force constants and hence that an individual valence force constant may not have an intrinsic physical meaning. This redundancy makes it necessary to correlate sets of force constants rather than individual force constants, and as an illustration, the correlation table between the constants of ethane and methane has been given.

The single table of the valence force constants and their estimated uncertainties may be considered as containing the results and the evaluation of the results of this thesis. Because of the nature of their origin, the uncertainty values cannot be reduced by more precise measurements of already available spectroscopic data. In principle, a substantial reduction of these uncertainties may be secured only through observations and analyses of the several hundred simple combination bands of ethane and heavy ethane, and only then provided that there is a minimum of resonance interactions between these bands.

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