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NORMAL COORDINATE ANALYSIS OF $\text{CF}_3\text{-CH}_3$,
 C_2F_6 AND C_2H_6 . VIBRATIONAL SPECTRA OF
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VIBRATIONAL SPECTRA OF $\text{CF}_2\text{Br-CH}_2\text{Br}$ AND $\text{CF}_2\text{Cl-CH}_2\text{Cl}$.

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HOMER PARK BUCKER, JR.

Norman, Oklahoma

1962

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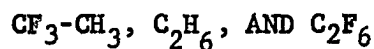
INTRODUCTION

A research project that deals with both the theoretical and experimental aspects of molecular structure would reasonably concern the same sets of molecules. However, the experimental and theoretical work reported in this thesis are for different molecules. Essentially of an experimental nature are the results reported for $\text{CF}_2\text{Br-CH}_2\text{Br}$ and $\text{CF}_2\text{Cl-CH}_2\text{Cl}$. This includes infrared and Raman spectra and assignment of fundamentals for both rotational isomers of each molecule. The low symmetry of these molecules and uncertainty in the assignment of some fundamentals make a theoretical treatment of the vibrational frequencies impractical. On the other hand, there were several reasons for undertaking the normal coordinate analysis of $\text{CF}_3\text{-CH}_3$. This molecule has rather high symmetry and the assignment of its fundamentals are probably correct. Further, use of the Urey-Bradley potential, which has previously been applied to more simple molecules, offers both a test of this potential and the opportunity for obtaining a set of force constants applicable to other fluorine substituted ethanes.

Accordingly, this thesis is divided into two parts. Part I is a normal coordinate analysis of $\text{CF}_3\text{-CH}_3$; part II gives experimental results concerning the vibrational frequencies of $\text{CF}_2\text{Br-CH}_2\text{Br}$ and $\text{CF}_2\text{Cl-CH}_2\text{Cl}$.

PART I

NORMAL COORDINATE ANALYSIS OF



CHAPTER I

INTRODUCTION

The radiation emitted by a molecule in the frequency range from 100 to 5000 cm^{-1} is usually due to changes in electric moments because of vibration of the atoms comprising the molecule. By considering the atoms to be point masses joined by various springs, which represent the electrical forces between atoms, a model is obtained which will vibrate at approximately the same frequencies as the molecule. The mathematical process of finding a correct set of springs, or force constants, is called normal coordinate analysis; it is the only direct method of calculating the interatomic forces of any but the most simple molecules. Alternatively, the problem can be reversed with force constants of similar molecules being utilized to predict the vibration frequencies of a molecule.

The choice of a set of force constants is equivalent to choosing a potential function. If the potential function is overly complicated the model can be made to vibrate at the proper frequencies, but the "springs" joining two atoms in one molecule will probably not be the same as those

necessary between the same atoms in a slightly different molecule. In other words, the force constants of a too general potential function are not transferable among similar molecules. Another defect of a general potential function is the lack of uniqueness in the calculated force constants, since there are more force constants than vibrational frequencies. The general quadratic function¹ which contains cross-terms between all of the vibrational coordinates is an example of a potential with an excess of force constants. Here there are $(3n-6)(3n-5)/2$ force constants for a molecule of n atoms but only $3n-6$ vibrational frequencies.

The central force potential² is an example of the other extreme; it is simple, but cannot be adjusted to fit the vibration frequencies of most molecules. The inadequacy of this potential is easily demonstrated for a linear molecule where central forces offer no resistance to out-of-line bending.

A more successful potential contains terms which represent forces that resist changes in bond lengths or variations in the angles between adjacent bonds. This so-called valence force potential is often used for rough calculations to check assignments of fundamentals. However, for moderately complicated molecules it is usually necessary to add additional terms to a valence force potential to obtain good agreement between theory and experiment.

The Urey-Bradley modification of the valence force potential has been

¹E. B. Wilson, J. C. Decius, and P. C. Cross, Molecular Vibrations, (New York: McGraw-Hill, 1955).

²G. Herzberg, Infrared and Raman Spectra, (New York, D. Van Nostrand Co. Inc., 1945).

used by several investigators^{3,4} with success. Shimanouchi⁵, in particular, has calculated the vibrational frequencies of more than twenty methyl halides and a few molecules of the type C_2X_6 . Overend and Scherfer⁶ have demonstrated the transferability of Urey-Bradley⁷ force constants for methyl and silyl halides, among others. The Urey-Bradley modification consists essentially of the addition of terms to account for the interaction, usually repulsion, of non-bonded atoms. For example, the terms $2F_{FF}^{'}dd_i + F_{FF}^{''}d_i^2$ would be added to the potential energy of CH_2F_2 to account for the fluorine-fluorine repulsion, where d is the equilibrium separation of the fluorine atoms and d_i is the variation in this distance as the molecule vibrates. The first two terms in the Taylor expansion of the repulsive force between the fluorine atoms can be calculated from the adjusted force constants F_{FF} and $F_{FF}^{'}.$

Since the valence potential has only quadratic terms, the introduction of repulsive terms contributes linear terms to the potential energy which must be removed. This is accomplished by adding other terms that are linear in the valence coordinates. The coefficients of these terms are chosen so as to make all sums of linear terms of the same kind equal to zero.

³D. F. Heath and J. W. Linnett, Trans. Faraday Soc. 44, 561 (1948).

⁴D. E. Mann, et. al., J. Chem. Phys. 27, 43 (1957).

⁵T. Shimanouchi, J. Chem. Phys. 17, 245, 734, 848 (1949); 20, 726 (1952).

⁶J. Overend and J. R. Scherer, J. Chem. Phys. 32, 1289, 1296, 1720 (1960); 33, 446, 1681 (1960); 34, 574 (1961).

⁷H. C. Urey and C. A. Bradley, Phys. Rev. 38, 1969 (1931).

Several years ago a normal coordinate analysis of the eclipsed form of $\text{CF}_3\text{-CH}_3$ based on a Urey-Bradley potential was made at this University.⁸ It has been found since then that the equilibrium configuration of such molecules is staggered rather than eclipsed.^{8a} For this reason, and because a better computer is now available, a normal coordinate analysis of the staggered form of $\text{CF}_3\text{-CH}_3$ has been made and a set of Urey-Bradley force constants have been determined for this molecule. As a test of the transferability of these constants, the vibrational frequencies of C_2H_6 and C_2F_6 have been calculated on the basis of the $\text{CF}_3\text{-CH}_3$ force constants, with some adjustment made in three of them.

Theory of Normal Vibrations

The vibrational motion of the atoms comprising a molecule can be described in terms of changes in bond lengths, bond angles, and other internal coordinates. In general only $3N-6$ of these coordinates are independent, as six coordinates are needed to specify the translation and rotation of the molecule. The exception to this rule occurs for linear molecules, in which case only two coordinates are necessary to define the rotational motion.

If the vibration of the molecule results in displacements of the nuclei which are small compared to the interatomic distances the kinetic and potential energies can be written as quadratic functions of the vibrational coordinates and their time derivatives.⁹

⁸Chi Yuan Pan and J. Rud Nielsen, J. Chem. Phys. 8, 1426 (1953).

^{8a}J. L. Brandt and R. L. Livingston, J. Am. Chem. Soc. 74, 3573 (1956).

⁹E. T. Whittaker, Analytical Dynamics (New York: Dover, 1944).

$$2T = \sum_{ij} (g^{-1})_{ij} \dot{r}_i \dot{r}_j.$$

$$2V = \sum_{ij} f_{ij} r_i r_j.$$

In matrix form the two expressions can be written as $2T = \dot{\mathbf{r}}^T \mathbf{g}^{-1} \dot{\mathbf{r}}$ and $2V = \mathbf{\tilde{r}}^T \mathbf{f} \mathbf{r}$ where $\mathbf{r}$ is a column matrix whose elements are the vibrational coordinates and $\mathbf{\tilde{r}}$ is its transpose. The elements of the matrix $\mathbf{f}$ are determined by the magnitude of the forces between atoms and are, therefore, called force constants. The elements of the kinetic energy matrix $\mathbf{g}^{-1}$ are determined by the masses of the atoms and the equilibrium configuration of the molecule.

It will be shown that linear combinations of the vibrational coordinates can be formed by a transformation matrix $\mathcal{L}$ so that $2T = \sum_j \dot{Q}_j^2$ and $2V = \sum_j \lambda_j Q_j^2$. These conditions require that $\mathcal{L} \mathbf{Q} = \mathbf{r}$, $\mathcal{\tilde{L}} \mathbf{f} \mathcal{L} = \mathbf{\Lambda}$, and $\mathcal{\tilde{L}} \mathbf{g}^{-1} \mathcal{L} = \mathbf{E}$, where $\mathbf{Q}$ is a column matrix whose elements Q_j are called normal coordinates, $\mathbf{\Lambda}$ is a diagonal matrix whose elements are λ_j , and $\mathbf{E}$ is a unit matrix. In the new coordinate basis the various Q 's are independent and their solutions are immediately obtained from Lagrange's equations to be $Q_n = A_n \exp. (i \sqrt{\lambda_n} t)$, $n = 1, 2, \dots, 3N-6$.¹⁰ The internal coordinates are related to the normal coordinates by the relations $r_j = \sum_n \mathcal{L}_{jn} Q_n$. Thus, although the motion of a single atom is quite complicated, it can be described as the sum of $3N-6$ simple harmonic motions called normal vibrations.

To determine the normal frequencies it is necessary to go back to the expressions for T and V in terms of the internal coordinates. Application

¹⁰ H. Goldstein, Classical Mechanics, (Reading, Mass: Adison-Wesley Publishing Co. Inc., 1959).

of Lagrange's equations yields the following equations of motion:

$$\sum_j (g_{ij}^{-1} \ddot{r}_j + f_{ij} r_j) = 0, \quad i = 1, 2, \dots, 3N-6.$$

Substitution of the solution $r_j = r_j^0 e^{i\omega t}$ reduces these relations to the set of algebraic equations

$$\sum_j (f_{ij} r_j^0 - \omega^2 g_{ij}^{-1} r_j^0) = 0,$$

which can also be written as the matrix equation

$$f \vec{r}^0 = \omega^2 g^{-1} \vec{r}^0.$$

Multiplication on the left by the matrix g results in the eigenvalue equation

$$g f \vec{r}^0 = \lambda \vec{r}^0, \quad \lambda = \omega^2.$$

Therefore, the normal frequencies multiplied by 2π are square roots of the eigenvalues of the gf matrix and the $\vec{r}^0$'s are eigenvectors of this matrix. Since both f and g^{-1} are symmetrix matrices with real elements and the quadratic forms representing the potential and kinetic energy are positive definite, the values of λ are real and positive.¹⁰ Calculation of the eigenvalues is accomplished by diagonalizing the gf matrix. This can be done by an interactive procedure described in Appendix I.

By constructing a diagonal matrix Λ , whose elements are the λ 's, and a second matrix R , formed by aligning the various $\vec{r}^0$ vectors in the same order as the λ 's, the equations $gf\vec{r}_n^0 = \lambda_n \vec{r}_n^0$, $n = 1, 2, \dots, 3N-6$, can be written in the compact form $gfR = R\Lambda$.

However, from the equations $\tilde{L} f L = \Lambda$ and $\tilde{L} g^{-1} L = E$, we can easily show that $gfL = L\Lambda$.

Thus, the column vectors that make up both the L and R matrices are eigenvectors of the same matrix. The matrix R can, therefore, be made identical to L by the condition $\tilde{R} g^{-1} R = E$.

The labor required in the diagonalization process can be greatly reduced by the use of group theory^{1,11} to find a set of coordinates in which the energy matrices have a reduced or block structure. These so-called symmetry coordinates can be formed from well known formulas as linear combinations of the internal coordinates. Let S be a column matrix whose elements are the symmetry coordinates and U an orthogonal transformation. If $r = US$, $2V = \tilde{r} f r = \tilde{S} \tilde{U} f U S = \tilde{S} F S$. Thus $F = \tilde{U} f U$ and from similar arguments $G^{-1} = \tilde{U} g^{-1} U$ and because U is orthogonal $G = \tilde{U} g U$. Since a similarity transformation does not change the eigenvalues of a matrix, the normal frequencies can be obtained by diagonalization of $U^{-1} g f U = U^{-1} g U U^{-1} f U = G F$. As the product matrix GF has the same block structure as F and G , each of the blocks of GF can be diagonalized separately.

At this point the calculations of this normal coordinate analysis can be outlined. The potential energy matrix was set up in the internal coordinate basis using force constants derived by Shimanouchi⁵ for similar molecules. Symmetry coordinates were then formed as linear combinations of the internal coordinates so as to reduce the energy matrices. The potential energy matrix in the symmetry basis was obtained by similarity transformation, while the inverse kinetic energy matrix was calculated directly by means of Wilson's method.¹² The product GF was then formed and diagonalized, thus giving a set of vibrational frequencies.

¹¹E. P. Wigner, Group Theory and its Applications to the Quantum Mechanics of Atomic Spectra (New York: Academic Press, 1959).

¹²E. B. Wilson, J. Chem. Phys. 8, 1047 (1939), 10, 76 (1941).

The force constants were then varied to obtain better agreement between the observed and calculated frequencies, and the process was repeated.

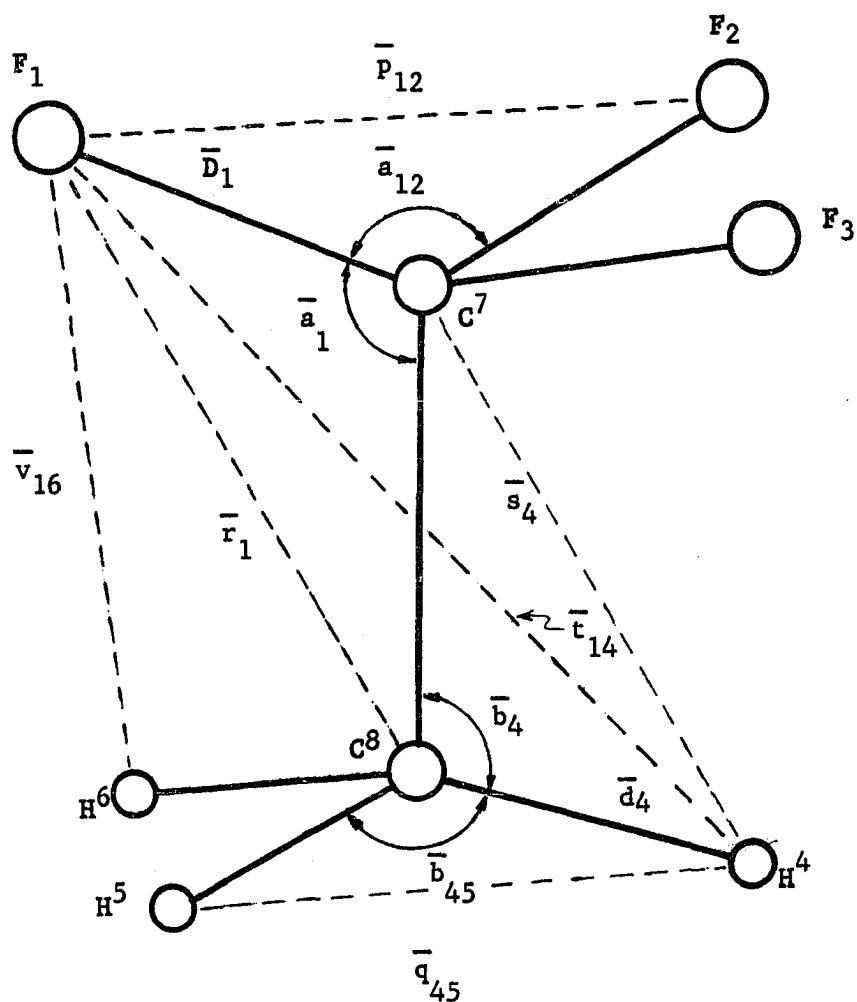
CHAPTER II

UREY-BRADLEY POTENTIAL ENERGY FUNCTION FOR $\text{CF}_3\text{-CH}_3$

f Matrix

As the atoms of a molecule are displaced slightly from their equilibrium positions the increase of potential energy can be written as $\sum_{ij} f_{ij} r_i r_j$ + higher order terms, where r_i is a change in the i th internal coordinate and the f_{ij} 's are force constants. As mentioned before, the general quadratic potential, which includes all possible second order terms, does not have the physical significance of the specialized potential adopted for this problem. In order to discuss this potential in detail reference is made to Fig. 2-1 and Table 1-I. In Fig. 2-1, for example, $\bar{p}_{12}$ is the distance between atoms F^1 and F^2 and is therefore the sum of the equilibrium distance p and the small variation in this value, p_{12} . Table 2-I is a list of typical internal coordinates and their equilibrium values.

The basic part of the Urey-Bradley potential is a valence force potential consisting of products of a force constants times the square of a change of bond distance or bond angle. Some typical terms of this kind are $K_{\text{CF}} D_1^2$ and $H_{\text{FCF}} a_{12}^2$, where K_{CF} and H_{FCF} are force constants, D_1 is the increment of the C^7F^1 bond length from its equilibrium value D and a_{12} is the change in the $\text{F}^1\text{C}^7\text{F}^2$ bond angle from its equilibrium value a .



F^1 , C^7 , C^8 , and H^4 are in the plane of the paper. F^2 and H^6 are behind the plane and F^3 and H^5 are in front of the plane of the paper.

Fig. 2-1. Molecular Constants for $\text{CF}_3\text{-CH}_3$

TABLE 2-1

INTERNAL AND VIBRATIONAL COORDINATES OF $\text{CF}_3\text{-CH}_3$

Internal Coordinate	Symbol	Equilibrium Value	Symbol for Equil. Value	Vibrational Coordinate
C^7F^1 bond length	$\bar{D}_1$	1.36 $\text{\AA}^\circ$	D	D_1^a
C^8H^4 bond length	$\bar{d}_4$	1.09	d	d_4
C^7C^8 bond length	$\bar{R}_1$	1.53	R	R_1
F^1F^2 separation	$\bar{P}_{12}$	2.22	P	P_{12}
F^1C^8 separation	$\bar{r}_1$	2.36	r	r_1
H^4H^5 separation	$\bar{q}_{45}$	1.78	q	q_{45}
H^4C^7 separation	$\bar{s}_4$	2.15	s	s_4
F^1H^4 separation	$\bar{t}_{14}$	3.29	t	t_{14}
F^1H^5 separation	$\bar{v}_{15}$	2.62	v	v_{15}
$\text{F}^1\text{C}^7\text{F}^2$ angle	$\bar{a}_{12}$	$109^\circ 28'$	a	a_{12}
$\text{H}^4\text{C}^8\text{F}^5$ angle	$\bar{b}_{45}$	$109^\circ 28'$	b	b_{45}
$\text{F}^1\text{C}^7\text{C}^8$ angle	$\bar{a}_1$	$109^\circ 28'$	a'	a_1
$\text{H}^4\text{C}^8\text{C}^7$ angle	$\bar{b}_4$	$109^\circ 28'$	b'	b_4

^a $\bar{D}_1 = D + D_1$, etc.

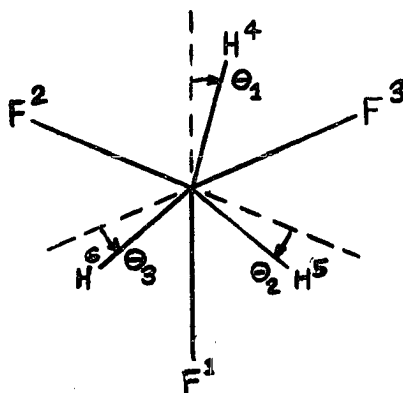
To the valence force potential are added terms that represent the effect of interaction of non-bonded atoms. Thus, the potential energy of interaction of F^1 and H^4 is given by $2F_{FH}' t_{14} + F_{FH} t_{14}^2$. From the sign of the constant F_{FH}' it will be shown that the force between an F and H atom in this molecule is repulsive.

Finally, terms like $K_{CF}' D D_1$ and $H_{FCF}' D^2 a_{12}$ are added. The force constants such as K_{CF}' and H_{FCF}' are chosen so that the linear terms in V will vanish.

The complete Urey-Bradley potential energy function for CF_3-CH_3 in terms of small variations of the internal coordinates is:

$$\begin{aligned}
 2V = & 2K_{CF}' D(D_1 + D_2 + D_3) + K_{CF}(D_1^2 + D_2^2 + D_3^2) \\
 & + 2K_{CH}' d(d_1 + d_2 + d_3) + K_{CH}(d_1^2 + d_2^2 + d_3^2) \\
 & + 2K_{CC}' R R_1 + K_{CC} R_1^2 \\
 & + 2H_{FCC}' R D(a_1 + a_2 + a_3) + H_{FCC} R D(a_1^2 + a_2^2 + a_3^2) \\
 & + 2H_{FCF}' D^2(a_{12} + a_{23} + a_{31}) + H_{FCF} D^2(a_{12}^2 + a_{23}^2 + a_{31}^2) \\
 & + 2H_{HCC}' R d(b_4 + b_5 + b_6) + H_{HCC} R d(b_4^2 + b_5^2 + b_6^2) \\
 & + 2H_{HCH}' d^2(b_{45} + b_{56} + b_{64}) + H_{HCH} d^2(b_{45}^2 + b_{56}^2 + b_{64}^2) \\
 & + 2F_{FF}' p(p_{12} + p_{23} + p_{31}) + F_{FF}(p_{12}^2 + p_{23}^2 + p_{31}^2) \\
 & + 2F_{FC}' r(r_1 + r_2 + r_3) + F_{FC}(r_1^2 + r_2^2 + r_3^2) \\
 & + 2F_{HH}' q(q_{45} + q_{56} + q_{64}) + F_{HH}(q_{45}^2 + q_{56}^2 + q_{64}^2) \\
 & + 2F_{HC}' s(s_4 + s_5 + s_6) + F_{HC}(s_4^2 + s_5^2 + s_6^2) \\
 & + 2F_{FH}' t(t_{14} + t_{25} + t_{36}) + F_{FH}(t_{14}^2 + t_{25}^2 + t_{36}^2) \\
 & + 2F_{FH}' v(v_{15} + v_{26} + v_{34} + v_{16} + v_{34} + v_{25}) \\
 & + F_{FH}(v_{15}^2 + v_{26}^2 + v_{34}^2 + v_{16}^2 + v_{34}^2 + v_{25}^2) \\
 & + \Omega \tau^2.
 \end{aligned}$$

The last term in the potential energy function is due to the torsional motion of the molecule defined as follows. Let the atoms lie in arbitrarily displaced positions. The smallest angle between the $F^1C^7C^8$ plane and the $H^4C^8C^7$ plane is defined as θ_1 , with θ_2 and θ_3 defined in a similar manner.



The internal coordinate describing the relative orientation between the end groups is then defined as $\tau = (\theta_1 + \theta_2 + \theta_3)/3$.

There are 41 internal coordinates in the equation for the potential energy, but only 18 are independent, since there are only $3N-6$ vibrational degrees of freedom.

The small displacements p_{ij} , q_{mn} , r_i , s_m , t_{im} and v_{in} can be expressed in terms of the other vibrational coordinates. These relations, correct to the second order, are as follows:

$$p_{ij} = (D_i + D_j)(1 - \cos a') D/p + a_{ij} (\sin a') D^2/p \\ + (D_i^2 + D_j^2) [1 - (1 - \cos a')^2 D^2/p^2]/2p + a_{ij}^2 [D^2 \cos a' - \sin^2 a' (D^4/p^2)]/2p + D_i D_j [-\cos a' - (1 - \cos a')^2 D^2/p^2]/p \\ + (D_i + D_j) a_{ij} [\sin a' - \sin a' (1 - \cos a') D^2/p^2] D/p.$$

$$q_{mn} = (d_m + d_n)(1 - \cos b') d/q + b_{mn} (\sin b') d^2/q$$

$$\begin{aligned}
& + (d_m^2 + d_n^2) \left[1 - (1 - \cos b')^2 d^2/q^2 \right] / 2q + b_{mn}^2 \left[d^2 \cos b' - \sin^2 b' (d^4/q^2) \right] / 2q + d_m d_n \left[-\cos b' - (1 - \cos b')^2 d^2/q^2 \right] / q \\
& + (d_m + d_n) b_{mn} \left[\sin b' - \sin b' (1 - \cos b') d^2/q^2 \right] d/q.
\end{aligned}$$

$$\begin{aligned}
r_i &= R_1 (R - D \cos a)/r + D_i (D - R \cos a)/r + a_i \sin a RD/r \\
&+ R_1^2 \left[1 - (R - D \cos a)^2/r^2 \right] / 2r + D_i^2 \left[1 - (D - R \cos a)^2/r^2 \right] / 2r \\
&+ a_i^2 (RD \cos a - \sin^2 a R^2 D^2/r^2) / 2r \\
&+ R_1 D_i \left[-\cos a - (R - D \cos a)(D - R \cos a)/r^2 \right] / r \\
&+ R_1 a_i \left[\sin a - \sin a (R - D \cos a)R/r^2 \right] D/r \\
&+ D_i a_i \left[\sin a - \sin a (D - R \cos a)D/r^2 \right] R/r.
\end{aligned}$$

$$\begin{aligned}
s_m &= R_1 (R - d \cos b)/s + d_m (d - R \cos b)/s + b_m \sin b Rd/s \\
&+ R_1^2 \left[1 - (R - d \cos b)^2/s^2 \right] / 2s + d_m^2 \left[1 - (d - R \cos b)^2/s^2 \right] / 2s \\
&+ a_m^2 \left[Rd \cos b - (\sin^2 b) R^2 d^2/s^2 \right] / 2s \\
&+ R_1 d_m \left[-\cos b - (R - d \cos b)(d - R \cos b)/s^2 \right] / s \\
&+ R_1 a_m \left[\sin b - \sin b (R - d \cos b) R/s^2 \right] d/s \\
&+ d_m a_m \left[\sin b - \sin b (d - R \cos b) d/s^2 \right] R/s.
\end{aligned}$$

$$\begin{aligned}
t_{im} &= D_i t_D + d_m t_d + R_1 t_R + a_i t_a + b_m t_b \\
&+ \{ D_i^2 (1 - t_D^2) + d_m^2 (1 - t_d^2) + R_1^2 (1 - t_R^2) \\
&+ a_i^2 [RD \cos a - Dd \cos (a-b) - t_b^2] \\
&+ b_m^2 [Rd \cos b - Dd \cos (b-a) - t_b^2] \\
&+ (a_{ki}^2 + a_{ij}^2 + b_{om}^2 + b_{mn}^2) (-dD/9) \\
&+ \tau^2 (-dD \sin a \sin b) \\
&+ D_i a_i^2 [R \sin a - d \sin (a-b) - t_D t_a] \\
&+ D_i b_m^2 [-d \sin (b-a) - t_D t_b] \\
&+ d_m a_i^2 [-D \sin (a-b) - t_d t_a] \\
&+ d_m b_m^2 [R \sin b - D \sin (b-a) - t_d t_b] \\
&+ d_m R_1^2 [-\cos b - t_d t_R + R_1 a_i^2 D \sin a - t_R t_a]
\end{aligned}$$

$$\begin{aligned}
& + R_1 b_m 2 [d \sin b - t_R t_b] + a_i b_m 2 [Dd \cos (a-b) - t_a t_b] \\
& + (a_{ki} a_{ij} + b_{om} b_{mn} + a_{ki} b_{om} + a_{ki} b_{mn} - a_{ij} b_{om} - a_{ij} b_{mn}) 2 (Dd/9) \} / 2t. \\
v_{in} = & D_i v_D + d_n v_d + R_1 v_R + a_i v_a + b_n v_b \\
& + (a_{ki} - a_{ij} - b_{mn} + b_{no}) (v_c^*/3) + \tau v_\tau^* \\
& + \{ D_i^2 (1 - v_D^2) + d_n^2 (1 - v_d^2) + R_1^2 (1 - v_R^2) \\
& + a_i^2 [RD \cos a - Dd \cos a \cos b + \frac{1}{2} Dd \sin a \sin b - v_a^2] \\
& + b_n^2 [Rd \cos b - Dd \cos a \cos b + \frac{1}{2} Dd \sin a \sin b - v_b^2] \\
& + (a_{ki}^2 + a_{ij}^2 + b_{mn}^2 + b_{no}^2) (-Dd/2 - v_c^{*2})/9 \\
& + \tau^2 [(Dd \sin a \sin b)/2 - v_\tau^{*2}] \\
& + D_i d_n 2 [\cos a \cos b - \frac{1}{2} \sin a \sin b - v_D v_d] \\
& + D_i R_1 2 [-\cos a - v_D v_R] \\
& + D_i a_i 2 [R \sin a - d \sin a \cos b - \frac{1}{2} d \sin b \cos a - v_D v_a] \\
& + D_i b_n 2 [-d \sin b \cos a - \frac{1}{2} d \sin a \cos b - v_D v_b] \\
& + d_n R_1 2 [-\cos b - v_d v_R] \\
& + d_n a_i 2 [-D \sin a \cos b - \frac{1}{2} D \sin b \cos a - v_d v_a] \\
& + d_n b_n 2 [R \sin b - D \sin b \cos a - \frac{1}{2} D \sin a \cos b - v_d v_b] \\
& + R_1 a_i 2 [D \sin a - v_R v_a + R_1 b_n 2 d \sin b - v_R v_a] \\
& + a_i b_n 2 [Dd \sin a \sin b - \frac{1}{2} Dd \cos a \cos b - v_a v_b] \\
& + (a_{ki} a_{ij} + b_{mn} b_{no} + a_{ki} b_{mn} + a_{ki} b_{no} - a_{ij} b_{mn} - a_{ij} b_{no}) \\
& [2 - (Dd)/2 + v_c^{*2}]/9 \} / 2v.
\end{aligned}$$

In these formulas $i, j, k = 1, 2, 3$; $m, n, o = 4, 5, 6$, with the restriction that if $i = 1$ then $m = 4$, if $i = 2$ then $m = 5$, and if $i = 3$ then $m = 6$. Also, the following abbreviations have been used:

$$t_D = [D + d \cos (a-b) - R \cos b]/t,$$

$$t_d = [d + D \cos (b-a) - R \cos a]/t,$$

$$t_R = [R - D \cos a - d \cos b]/t,$$

$$t_a = [RD \sin a - Dd \sin (a-b)] / t,$$

$$t_b = [Rd \sin b - Dd \sin (b-a)] t,$$

$$v_D = [D-R \cos a + d \cos a \cos b - \frac{1}{2} d \sin a \sin b] / v,$$

$$v_d = [d-R \cos b + D \cos a \cos b - \frac{1}{2} D \sin a \sin b] / v,$$

$$v_R = [R-D \cos a - d \cos b] / v$$

$$v_a = [RD \sin a - Dd \sin a \sin b - \frac{1}{2} Dd \sin a \sin b] / v,$$

$$v_b = [Rd \sin b - Dd \sin a \sin b - \frac{1}{2} Dd \sin a \sin b] / v,$$

$$v_c^* = [(\epsilon_{in} - 3 Dd \sin a \sin b) / 2] / v = v_c \epsilon_{in},$$

$$v_\tau^* = [(\epsilon_{in} - 3 Dd \sin a \sin b) / 2] / v = v_\tau \epsilon_{in}, \text{ and}$$

$$\epsilon_{in} = 1 \text{ for } in = 15, 26, \text{ or } 34 \text{ and } -1 \text{ for } in = 16, 24, \text{ or } 35.$$

Substitution of these terms into the potential energy function and collection of terms with the same internal coordinates results in the following form of the Urey-Bradley potential:

$$\begin{aligned} 2V = & I' \sum D_i + J' \sum d_m + S' R_1 + \bar{M} \sum a_i + \bar{O} \sum a_{ij} \\ & + \bar{P} \sum b_m + \bar{U} \sum b_{mn} + X \sum D_i^2 + B \sum d_m^2 + S R_1^2 \\ & + \bar{E}' \sum a_i^2 + \bar{E} \sum a_{ij}^2 + \bar{Y}' \sum b_m^2 + \bar{Y} \sum b_{mn}^2 + \Omega \tau^2 \\ & + 2 X' \sum D_i D_j + 2 W \sum D_i d_m + 2 W' \sum D_i d_n \\ & + 2 Z' \sum d_m R_1 + 2 N \sum D_i a_i + 2 Q \sum D_i a_{ij} \\ & + 2 A \sum D_i b_m + 2 A' \sum D_i b_n + 2 B' \sum d_m d_n \\ & + 2 Z' \sum d_m R_1 + 2 G \sum d_m a_i + 2 G' \sum d_m a_j \\ & + 2 Q' \sum d_m b_{mn} + 2 N' \sum d_m b_m + 2 T \sum R_1 a_i \\ & + 2 T' \sum R_1 b_m + 2 C \sum a_i b_m + 2 C' \sum a_i b_n \\ & + 2 \bar{F} (a_{12} a_{23} + a_{23} a_{31} + a_{31} a_{12}) + 2 \bar{H} (b_{45} b_{56} + b_{56} b_{64} + b_{64} b_{45}) \\ & + 2 L (a_{12} b_{45} + a_{23} b_{56} + a_{31} b_{64}) \\ & + 2 L' (a_{12} b_{56} + a_{23} b_{64} + a_{31} b_{45} + a_{12} b_{64} + a_{23} b_{45} + a_{31} b_{56}), \end{aligned}$$

where $i, j, k = 1, 2, 3$; $m, n, o = 4, 5, 6$, and

$$\sum D_i = (D_1 + D_2 + D_3), \sum d_m = (d_4 + d_5 + d_6),$$

$$\sum a_{ij} = (a_{12} + a_{23} + a_{31}), \sum b_{mn} = (b_{45} + b_{56} + b_{64}),$$

$$\sum D_i d_m = (D_1 d_4 + D_2 d_5 + D_3 d_6),$$

$$\sum D_i d_n = (D_1 d_5 + D_2 d_6 + D_3 d_4 + D_1 d_6 + D_2 d_4 + D_3 d_5),$$

$$\sum d_m a_j = (d_4 a_2 + d_5 a_3 + d_6 a_1 + d_4 a_3 + d_5 a_1 + d_6 a_2).$$

The two remaining restrictions on the coordinates are the redundancy conditions:⁵

$$H_1 = \sum a_i + \sum a_{ij} + \sqrt{2}/8 [3 a_i^2 + 3 a_{ij}^2 + 8 (\sum a_i a_j + 2 \sum a_i a_{ij} + a_{12} a_{23} + a_{23} a_{31} + a_{31} a_{12})] = 0 \text{ and}$$

$$H_2 = \sum b_m + \sum b_{mn} + \sqrt{2}/8 [3 b_m^2 + 3 b_{mn}^2 + 8 (\sum b_m b_n + 2 \sum b_m b_{mn} + b_{45} b_{56} + b_{56} b_{64} + b_{64} b_{45})] = 0.$$

Following Lagrange's method of indeterminate multipliers,¹³ a new potential energy function $2V + 2kH_1 + 2k'H_2$ is formed in which now all of the coordinates are independent. The new potential includes the additional terms:

$2\sqrt{2} k \sum a_i a_j + 2\sqrt{2} k' \sum b_m b_n + 2\sqrt{2} k \sum a_i b_{mn} + 2\sqrt{2} k' \sum b_m a_{ij}$, and the following modifications are made in the meanings of the constants.

$$\bar{M} \rightarrow \bar{M} + 2k = M, \bar{O} \rightarrow \bar{O} + 2k = 0,$$

$$\bar{P} \rightarrow \bar{P} + 2k' = P, \bar{U} \rightarrow \bar{U} + 2k' = U,$$

$$\bar{E} \rightarrow \bar{E} + (3\sqrt{2}/4) k = E, \bar{E}' \rightarrow \bar{E}' + (3\sqrt{2}/4) k = E',$$

$$\bar{Y} \rightarrow \bar{Y} + (3\sqrt{2}/4) k' = Y, \bar{Y}' \rightarrow \bar{Y}' + (3\sqrt{2}/4) k' = Y'$$

$$\bar{F} \rightarrow \bar{F} + 2\sqrt{2} k = F, \bar{H} \rightarrow \bar{H} + 2\sqrt{2} k' = H.$$

Since the potential energy of the molecule must increase for any

¹³R. Courant, Differential and Integral Calculus, Vol. II (New York: Interscience Publishers, 1934).

displacement from equilibrium, the linear terms must be zero. The coefficients of these terms are:

$$\begin{aligned}
 I' &= 2[K_{CF}' D + F_{FF}' D (1 - \cos a') + F_{FC}' (D - R \cos a) \\
 &\quad + F_{FH}' (2D + 2d \cos a \cos b - \frac{1}{2} Dd \sin a \sin b - 2R \cos a)] \\
 J' &= 2[K_{CH}' d + F_{HH}' d (1 - \cos b') + F_{HC}' (d - R \cos b) \\
 &\quad + 2 F_{FH}' (2d + 2D \cos a \cos b - \frac{1}{2} Dd \sin a \sin b - 2R \cos b)] \\
 S' &= 2[K_{CC}' R + 3 F_{FC}' (R - C \cos a) + 3 F_{HC}' (R - d \cos b) \\
 &\quad + 9 F_{FH}' (R - D \cos a - d \cos b)] \\
 M &= 2[H_{FCC}' RD + F_{FC}' RD \sin a + 3 F_{FH}' (RD \sin a - Dd \sin a \cos b) + k] \\
 O &= 2[H_{FCF}' D^2 + F_{FF}' D^2 \sin a' + k] \\
 P &= 2[H_{HCC}' Rd + F_{HC}' Rd \sin a + 3 F_{FH}' (Rd \sin b - Dd \sin b \cos a) + k] \\
 U &= 2[H_{HCH}' d^2 + F_{HH}' d^2 \sin b' + k]
 \end{aligned}$$

The K primes and H primes are chosen so that the above expressions are zero. The equilibrium conditions will then be satisfied.

The potential function can now be written in the matrix form $2V = \tilde{r} f r$, where r is a column matrix with the internal coordinates as elements and $\tilde{r}$ is its transpose. The coefficients of the internal coordinates form the symmetry matrix f given in condensed form in Table 1-II.

The complete algebraic expressions for the elements of the f matrix are:

$$\begin{aligned}
 X &= K_{CF}' + F_{FF}' 2[1 - (1 - \cos a')^2 D^2/p^2] + F_{FF}' 2(1 - \cos a')^2 D^2/p^2 \\
 &\quad + F_{FC}' [1 - (D - R \cos a)^2/r^2] + F_{FC}' (D - R \cos a)^2/r^2 \\
 &\quad + F_{FH}' (3 - t_D^2 - 2 v_D^2) + F_{FH}' (t_D^2 + 2 v_D^2) \\
 B &= K_{CH}' + F_{HH}' 2[1 - (1 - \cos b')^2 d^2/q^2] + F_{HH}' 2(1 - \cos b')^2 d^2/q^2 \\
 &\quad + F_{HC}' [1 - (d - R \cos b)^2/s^2] + F_{HC}' (d - R \cos b)^2/s^2 \\
 &\quad + F_{FH}' (3 - t_d^2 - 2 v_d^2) + F_{FH}' (t_d^2 + 2 v_d^2)
 \end{aligned}$$

TABLE I-II

F MATRIX

[illegible]

$$\begin{aligned}
S &= K_{CC} + F_{FC}' \cdot 3 \left[1 - (R-D \cos a)^2/r^2 \right] + F_{FC}' \cdot 3 (R-D \cos a)^2/r^2 \\
&+ F_{HC}' \cdot 3 \left[1 - (R-d \cos b)^2/s^2 \right] + F_{HC}' \cdot 3 (R-d \cos b)^2/s^2 \\
&+ F_{FH}' \cdot 3 (3-t_R^2 - 2 v_R^2) + F_{FH}' \cdot 3 (t_R^2 + 2 v_R^2). \\
E &= H_{FCF} D^2 + F_{FF}' (D^2 \cos a' - \sin^2 a' D^4/p^2) \\
&+ F_{FF}' \sin^2 a' D^4/p^2 - F_{FH}' \cdot 4 v_c^2/9 + F_{FH}' \cdot 4 v_c^2/9 + (3 \sqrt{2}/4) k. \\
E' &= H_{FCC} R D + F_{FC}' (R D \cos a - \sin^2 a R^2 D^2/r^2) \\
&+ F_{FC}' (\sin^2 a R^2 D^2/r^2) + F_{FH}' (3 R D \cos a - 3 D d \cos a \cos b - t_a^2 - 2 v_a^2) \\
&+ F_{FH}' (t_a^2 + 2 v_a^2) + (3 \sqrt{2}/4) k. \\
Y &= H_{HCH} d^2 + F_{HH}' (d^2 \cos b' - \sin^2 b' d^4/q^2) \\
&+ F_{HH}' \sin^2 b' d^4/q^2 - F_{FH}' \cdot 4 v_c^2/9 + F_{FH}' \cdot 4 v_c^2/9 + (3 \sqrt{2}/r) k'. \\
Y' &= H_{HCC} R d + F_{HC}' (R d \cos b - \sin^2 b R^2 d^2/s^2) \\
&+ F_{HC}' \sin^2 b R^2 d^2/s^2 + F_{FH}' (3 R d \cos b - 3 D d \cos a \cos b - t_b^2 - 2 v_b^2) \\
&+ F_{FH}' (t_b^2 + 2 v_b^2) + (3 \sqrt{2}/4) k'. \\
X' &= F_{FF}' [- \cos a' - (1-\cos a')^2 D^2/p^2] + F_{FF}' (1-\cos a')^2 D^2/p^2. \\
W &= F_{FH}' [\cos (a-b) - t_D t_d] + F_{FH}' (t_D t_d). \\
W' &= F_{FH}' [\cos a \cos b - \frac{1}{2} \sin a \sin b - v_D v_d] + F_{FH}' v_D v_d. \\
Z &= F_{FC}' [- \cos a - (R-D \cos a) (D-R \cos a)/r^2] + F_{FC}' (R-D \cos a) (D-R \cos a)/r^2 \\
&+ F_{FH}' (- 3 \cos a - t_D t_R - 2 v_D v_R) + F_{FH}' (t_D t_R + 2 v_D v_R). \\
Q &= F_{FF}' D \sin a' [1 - (1-\cos a') D^2/p^2] + F_{FF}' \sin a' (1-\cos a') D^3/p^2. \\
N &= F_{FC}' R \sin a [1 - (D-R \cos a) D/r^2] + F_{FC}' \sin a (D-R \cos a) R D/r^2 \\
&+ F_{FH}' (3 R \sin a - 3 d \sin a \cos b - t_D t_a - 2 v_D v_a) + F_{FH}' (t_D t_a + 2 v_D v_a). \\
A &= F_{FH}' [d \sin (a-b) - t_D t_b] + F_{FH}' t_D t_b. \\
A' &= F_{FH}' (-d \sin b \cos a - \frac{1}{2} d \sin a \cos b - v_D v_b) + F_{FH}' v_D v_b. \\
B' &= F_{HH}' [- \cos b' - (1-\cos b')^2 d^2/q^2] + F_{HH}' (1-\cos b')^2 d^2/q^2. \\
Z' &= F_{HC}' [- \cos b - (R-d \cos b) (d-R \cos b)/s^2] + F_{HC}' (R-D \cos b) (d-R \cos b)/s^2 \\
&+ F_{FH}' (- 3 \cos b - t_d t_R - 2 v_d v_R) + F_{FH}' (t_d t_R + 2 v_d v_R).
\end{aligned}$$

$$\begin{aligned}
G &= F_{FH}' [-D \sin(b-a) - t_d t_a] + F_{FH} t_d t_a. \\
G' &= F_{FH}' (-D \sin a \cos b - \frac{1}{2} D \sin b \cos a - v_d v_a) + F_{FH} v_d v_a. \\
Q' &= F_{HH}' d \sin b' [1 - (1 - \cos b') d^2/q^2] + F_{HH} \sin b' (1 - \cos b') d^3/q^2. \\
N' &= F_{HC}' R \sin b [1 - d(d - R \cos b) \sin b/s^2] + F_{HC} \sin b (d - R \cos b) Rd/s^2 \\
&\quad + F_{FH}' (3R \sin b - 3D \sin b \cos a - t_d t_b - 2v_d v_b) + F_{FH} (t_d t_b + 2v_d v_b). \\
T &= F_{FC}' D \sin a [1 - (R - D \cos a) R/r^2] + F_{FC} \sin a (R - D \cos a) RD/r^2 \\
&\quad + F_{FH}' (3D \sin a - t_R t_a - 2v_R v_a) + F_{FH} (t_R t_a + 2v_R v_a). \\
T' &= F_{HC}' d \sin b [1 - (R - d \cos b) R/s^2] + F_{HC} \sin b (R - d \cos b) Rd/s^2 \\
&\quad + F_{FH}' (3d \sin b - t_R t_b - 2v_R v_b) + F_{FH} t_a t_b. \\
C &= F_{FH}' [Dd \cos(a-b) - t_a t_b] + F_{FH} t_a t_b. \\
C' &= F_{FH}' (Dd \sin a \sin b - \frac{1}{2} Dd \cos a \cos b - v_a v_b). \\
F &= F_{FH}' 2 v_c^2/9 - F_{FH} 2 v_c^2/9 + 2 \sqrt{2} k. \\
H &= F_{FH}' 2 v_c^2/9 - F_{FH} 2 v_c^2/9 + 2 \sqrt{2} k'. \\
L' &= F_{FH}' (Dd/3 - 2 v_c^2/9) + F_{FH} 2 v_c^2/9. \\
L &= F_{FH}' (-Dd/6 + v_c^2/9) - F_{FH} v_c^2/9. \\
I &= \sqrt{2} k. \\
J &= \sqrt{2} k'.
\end{aligned}$$

Symmetry Coordinates

Any complete set of vibrational coordinates can be used for calculating the energy matrices. If the molecular vibration is described in terms of cartesian displacements of the atoms the kinetic energy matrix is diagonal; the use of internal coordinates usually simplifies the elements of the potential energy matrix and gives them more direct physical meanings. The most useful set of coordinates which can be obtained prior to the diagonalization process are called symmetry coordinates. The nature of these coordinates is determined by the symmetry of the undis-

torted molecule and in this coordinate system both energy matrices have block structure. The group theory that provides the background for discussion of these coordinates is not given here, since the theory, although somewhat involved, is well known and readily accessible.¹¹ Instead, only the results of the application of group theory and a list of symmetry coordinates are presented.

The undistorted $\text{CF}_3\text{-CH}_3$ molecule has the symmetry C_{3v} . Group-theoretical methods show that there are five non-degenerate normal vibrations of this molecule each of which belongs to the irreducible representation, or species, A_1 of the group C_{3v} . Also, there is one non-degenerate normal vibration belonging to species A_2 and six doubly-degenerate normal coordinates belonging to species E. By application of the formulas of Nielsen and Berryman¹⁴ five symmetry coordinates belonging to species A_1 and two sets of six coordinates of the species E can be formed as linear combinations of the internal coordinates. As there is only one normal coordinate belonging to A_2 , which corresponds to the torsional vibration of the molecule, it has been treated separately.

A simple set of symmetry coordinates for $\text{CF}_3\text{-CH}_3$, classified according to species, are:

$$\begin{aligned} A_1: \quad S_1 &= 1/\sqrt{3} (d_4 + d_5 + d_6) \\ S_2 &= 1/\sqrt{3} (D_1 + D_2 + D_3) \\ S_3 &= R_1 \\ S_4 &= 1/\sqrt{6} (b_4 + b_5 + b_6 - b_{45} - b_{56} - b_{64}) \\ S_5 &= 1/\sqrt{6} (a_1 + a_2 + a_3 - a_{12} - a_{23} - a_{31}) \end{aligned}$$

¹⁴J. Rud Nielsen and L. H. Berryman, J. Chem. Phys. 17, 659 (1949).

$$\begin{aligned}
E: \quad s_{1a} &= 1/\sqrt{6} (2d_4 - d_5 - d_6) \\
s_{2a} &= 1/\sqrt{6} (2D_1 - D_2 - D_3) \\
s_{3a} &= 1/\sqrt{6} (2b_4 - b_5 - b_6) \\
s_{4a} &= 1/\sqrt{6} (2a_1 - a_2 - a_3) \\
s_{5a} &= 1/\sqrt{6} (2b_{45} - b_{56} - b_{64}) \\
s_{6a} &= 1/\sqrt{6} (2a_{12} - a_{23} - a_{31}) \\
s_{1b} &= 1/\sqrt{2} (d_5 - d_6) \\
s_{2b} &= 1/\sqrt{2} (D_2 - D_3) \\
s_{3b} &= 1/\sqrt{2} (b_5 - b_6) \\
s_{4b} &= 1/\sqrt{2} (a_2 - a_3) \\
s_{5b} &= 1/\sqrt{2} (b_{56} - b_{64}) \\
s_{6b} &= 1/\sqrt{2} (a_{23} - a_{31})
\end{aligned}$$

The new form of the potential energy matrix that results from the transformation of internal coordinates into symmetry coordinates can be determined by means of a similarity transformation. Let S be a column matrix whose elements are the symmetry coordinates and U be the orthogonal transformation matrix from the internal to the symmetry basis. Then $r = US$ and $2V = \tilde{S} \tilde{U} f U S$. If F represents the potential energy matrix in the symmetry basis it must be related to f by the congruent transformation $F = \tilde{U} f U$. The F matrix has block structure as shown below.

$$F = \left[\begin{array}{ccc|c} \boxed{\begin{array}{c} A_1 \text{ block} \\ 5 \times 5 \end{array}} & & & \\ & \boxed{\begin{array}{c} \text{first} \\ E \text{ block} \\ 6 \times 6 \end{array}} & & \\ & & \boxed{\begin{array}{c} \text{second} \\ E \text{ block} \\ 6 \times 6 \end{array}} & \\ & & & \boxed{\Omega} \end{array} \right]$$

All matrix elements outside of the square blocks are zero. The use of Nielsen and Berryman's formulas¹⁴ to calculate the symmetry coordinates insures that the two E blocks are identical. The blocks of the F matrix are presented in Table 2-III.

TABLE 2-III
F MATRICES FOR $\text{CF}_3\text{-CH}_3$

Species A_1 :					
B + 2B'	W + 2W'	$\sqrt{3} z'$	$(N' - 2Q')/\sqrt{2}$	$(G + 2G')/\sqrt{2}$	
	X + 2X'	$\sqrt{3} z$	$(A + 2A')/\sqrt{2}$	$(N - 2Q)/\sqrt{2}$	
		S	$\sqrt{3} T'/\sqrt{2}$	$\sqrt{3} T/\sqrt{2}$	
			$\frac{Y+Y'}{2} + H-J$	$\frac{C+2C'+L+2L'}{2}$	
				$\frac{E+E'}{2} + F-I$	
Species E:					
B - B'	W - W'	N'	G - G'	Q'/2	0
	X - X'	A - A'	N	0	Q/2
		Y' - J	C - C'	J/2	0
			E' - I	0	I/2
				Y - H	L - L'
					E - F

CHAPTER III

KINETIC ENERGY MATRIX FOR $\text{CF}_3\text{-CH}_3$

The G matrix for the molecule $\text{CF}_3\text{-CH}_3$ was constructed by Wilson's Method.¹² In Wilson's formulas the elements of the inverse kinetic energy matrix in the symmetry coordinate basis are given by $G_{LL'} = \sum_a \sum_p \mu_p g_p \vec{s}_{La}^t \cdot \vec{s}_{L'a}^t / d$. Here $\sum_a$ represents a summation over degenerate sets of $\vec{s}$ vectors, $\sum_p$ represents a summation over sets of equivalent atoms, d is the degree of the degeneracy, g_p the number of equivalent atoms in the p th set, and μ is the reciprocal of the mass of one of these atoms. If the degeneracy of the set of $\vec{s}$ vectors is one the summation over a is omitted. Further, $\vec{s}_{La}^t = \sum_k U_{La,k} \vec{s}_{kt}$, where $\sum_k$ is a summation over the internal coordinates, and $U_{La,k}$ is an element of the matrix that transforms the internal coordinates into symmetry coordinates. Finally, $\vec{s}_{kt}$ has the direction in which a given displacement of atom t will produce the greatest increase in the k th internal coordinate and a magnitude equal to the increase of this coordinate produced by a unit displacement of the atom in the most effective direction.

A selected list of $\vec{s}$ vectors is given in Table 3-I. After substitution of numerical values for the sines and cosines in the expressions for the $\vec{s}$ vectors the results listed in Tables 3-II, III, IV are obtained. The blocks of the G matrix are presented in Table 3-V.

TABLE 3-I

 $\vec{s}_{kt}$ VECTORS FOR $\text{CF}_3\text{-CH}_3$

R_k	t	F^1	H^4	C^7	C^8
D_1		$\vec{r}_1$		$-\vec{r}_1$	
D_2				$-\vec{r}_2$	
D_3				$-\vec{r}_3$	
d_4			$\vec{r}_4$		$-\vec{r}_4$
d_5					$-\vec{r}_5$
d_6					$-\vec{r}_6$
R_1				$\vec{r}_8$	$\vec{r}_7$
a_1		$(\cos a' \vec{r}_1 - \vec{r}_7)/D \sin a$		$(w \vec{r}_1 + u \vec{r}_7)/RD \sin a$	$(\cos a' \vec{r}_7 - \vec{r}_1)/R \sin a$
a_2				$(w \vec{r}_2 + u \vec{r}_7)/RD \sin a$	$(\cos a' \vec{r}_7 - \vec{r}_2)/R \sin a$
a_3				$(w \vec{r}_3 + u \vec{r}_7)/RD \sin a$	$(\cos a' \vec{r}_7 - \vec{r}_3)/R \sin a$
b_4			$(\cos b' \vec{r}_4 - \vec{r}_8)/d \sin b$	$(\cos b' \vec{r}_8 - \vec{r}_4)/R \sin b$	$(c \vec{r}_4 + h \vec{r}_8)/Rd \sin b$
b_5				$(\cos b' \vec{r}_8 - \vec{r}_5)/R \sin b$	$(c \vec{r}_5 + h \vec{r}_8)/Rd \sin b$
b_6				$(\cos b' \vec{r}_8 - \vec{r}_6)/R \sin b$	$(c \vec{r}_6 + h \vec{r}_8)/Rd \sin b$
a_{12}		$(\cos a' \vec{r}_1 - \vec{r}_2)/D \sin a'$		$3(\vec{r}_1 + \vec{r}_2)/D \sin a'$	
a_{23}		$(\cos a' \vec{r}_1 - \vec{r}_3)/D \sin a'$		$3(\vec{r}_2 + \vec{r}_3)/D \sin a'$	
a_{31}			$(\cos b' \vec{r}_4 - \vec{r}_5)/d \sin b'$	$3(\vec{r}_3 + \vec{r}_1)/D \sin a'$	$x(\vec{r}_4 + \vec{r}_5)/d \sin b'$
b_{45}					$x(\vec{r}_5 + \vec{r}_6)/d \sin b'$
b_{56}			$(\cos b' \vec{r}_4 - \vec{r}_6)/d \sin b'$		$x(\vec{r}_6 + \vec{r}_4)/d \sin b'$
b_{64}					

 $\vec{r}_1$ is a unit vector along the C^7F^1 bond. $\vec{r}_4$ is a unit vector along the C^8H^4 bond. $\vec{r}_7$ is a unit vector along the C^7C^8 bond. $\vec{r}_8$ is a unit vector along the C^8C^7 bond. $w = (D-R \cos a)$, $u = (R-D \cos a)$, $z = (1-\cos a')$, $c = (d-R \cos b)$, $h = (R-d \cos b)$, $x = (1-\cos b')$.

TABLE 3-II

 $\vec{S}_L^t$ VECTORS OF SPECIES A_1

L^t	F^1	H^4	C^7	C^8
1	0	$\vec{r}_4/\sqrt{3}$	0	$\vec{r}_8/\sqrt{3}$
2	$\vec{r}_1/\sqrt{3}$	0	$\vec{r}_7/\sqrt{3}$	0
3	0	0	$\vec{r}_8$	$\vec{r}_7$
4	$-\sqrt{3}(\vec{r}_8 + \frac{\vec{r}_4}{3})/2D$	0	0	$4\vec{r}_8/(\sqrt{3} d)$
5	0	$-\sqrt{3}(\vec{r}_7 + \frac{\vec{r}_1}{3})/2d$	$4\vec{r}_8/\sqrt{3} D$	0

TABLE 3-III

 $\vec{S}_{La}^t$ VECTORS OF SPECIES E_a

L^t	F^1	H^4	C^7	C^8
1a	0	$2 \vec{r}_4/\sqrt{6}$	0	$(\vec{r}_7 - 3\vec{r}_1)/\sqrt{6}$
2a	$2 \vec{r}_1/\sqrt{6}$	0	$(\vec{r}_8 - 3\vec{r}_4)/\sqrt{6}$	0
3a	0	$-\sqrt{3}(\frac{\vec{r}_4}{3} + \vec{r}_1)/2D$	$\sqrt{3}(\vec{r}_7 - 3\vec{r}_4)/4R$	$\sqrt{3} c(3\vec{r}_4 + \vec{r}_8)/4 Rd$
4a	$-\sqrt{3}(\frac{\vec{r}_1}{3} + \vec{r}_4)/2D$	0	$\sqrt{3}w(3\vec{r}_1 + \vec{r}_7)/4RD$	$\sqrt{3}(\vec{r}_8 - 3\vec{r}_1)/4 R$
5a	0	$\sqrt{3}(\vec{r}_6 - \frac{\vec{r}_4}{3} - 2\vec{r}_3)/4d$	0	$\sqrt{3}x(\vec{r}_7 - 3\vec{r}_6)/4d$
6a	$\sqrt{3}(\vec{r}_3 - \frac{\vec{r}_1}{3} - 2\vec{r}_2)/4D$	0	$\sqrt{3}z(\vec{r}_8 - 3\vec{r}_3)/4D$	0

TABLE 3-IV

 $\vec{s}_{Lb}^t$ VECTORS OF SPECIES E_b

$L \backslash t$	F^1	H^4	C^7	C^8
1b	0	0	0	$(\vec{r}_6 - \vec{r}_5)/\sqrt{2}$
2b	0	0	$(\vec{r}_3 - \vec{r}_2)/\sqrt{2}$	0
3b	0	0	$3(\vec{r}_6 - \vec{r}_5)/4R$	$3c(\vec{r}_5 - \vec{r}_6)/4Rd$
4b	0	0	$3w(\vec{r}_2 - \vec{r}_3)/4RD$	$3(\vec{r}_3 - \vec{r}_2)/4R$
5b	0	$4(\frac{\vec{r}_4}{3} + \vec{r}_6)/3d$	0	$3(\vec{r}_5 - \vec{r}_4)/4d$
6b	$4(\frac{\vec{r}_1}{3} + \vec{r}_3)/3D$	0	$3(\vec{r}_2 - \vec{r}_1)/4D$	0

TABLE 3-V

G MATRICES OF $\text{CF}_3\text{-CH}_3$

Species A_1					
$W_H + W_C/3$	0	$-W_C/\sqrt{3}$	$4W_C/3d$	0	
	$W_F + W_C/3$	$-W_C/\sqrt{3}$	0	$4W_C/3D$	
		$2W_C$	$-4W_C/\sqrt{3}d$	$-4W_C/\sqrt{3}D$	
			$\frac{2}{d^2}(W_H + \frac{8W_C}{3})$	0	
				$\frac{2}{D^2}(W_F + \frac{8W_C}{3})$	
Species E					
$W_H + \frac{4W_C}{3}$	0	$-\sqrt{2} W_C M_d$	$\sqrt{2} W_C/R$	$-2\sqrt{2} W_C/3d$	0
	$W_F + \frac{4W_C}{3}$	$\sqrt{2} W_C/R$	$-\sqrt{2} W_C/M_D$	0	$-2\sqrt{2} W_C/3D$
		$\frac{W_H}{d^2} + W_C L_d$	$3W_C N/2$	$-\frac{W_H}{4d^2} + \frac{W_C M_d}{d}$	W_C/RD
			$\frac{W_F}{D^2} + W_C L_D$	W_C/Rd	$-\frac{W_F}{4D^2} + \frac{W_C M_D}{D}$
				$\frac{5W_H}{2d^2} + \frac{8W_C}{3d^2}$	0
					$\frac{5W_F}{2D^2} + \frac{8W_C}{3D^2}$

Where

$$M_d = \left(\frac{1}{R} + \frac{1}{3d} \right)$$

$$L_d = \left(\frac{1}{6d^2} + \frac{1}{Rd} + \frac{3}{R^2} \right)$$

$$N = \left(\frac{d}{R^2 D} + \frac{1}{3RD} + \frac{1}{3Rd} + \frac{D}{R^2 d} \right)$$

$$M_D = \left(\frac{1}{R} + \frac{1}{3D} \right)$$

$$L_D = \left(\frac{1}{6D^2} + \frac{1}{RD} + \frac{3}{R^2} \right)$$

CHAPTER IV

RESULTS FOR $\text{CF}_3\text{-CH}_3$ AND DISCUSSION

Vibrational assignments for $\text{CF}_3\text{-CH}_3$ have been made by Yost¹⁵, Thompson¹⁶, Nielsen¹⁷, and Herzberg.¹⁸ The assignments of Nielsen and Herzberg are essentially the same and are probably correct. Comparison between Nielsen's assignment and the calculated frequencies is made in Table 4-I. Also, the values calculated by Pan and Nielsen⁸ for the eclipsed configuration of this molecule are listed.

The initial set of force constants used in this calculation was taken from the work of Shimanouchi⁵ on CF_4 , C_2H_6 , and C_2F_6 and the calculations of Pan and Nielsen⁸ for $\text{CF}_3\text{-CH}_3$. These are listed in Table 4-II together with the final set of force constants. Some of the differences between the initial and final force constants are caused by the fact that Shimanouchi's constants were determined for a set of different molecules, while those of Pan and Nielsen were calculated for a different configuration of $\text{CF}_3\text{-CH}_3$. Some differences are also due to the inclusion of terms in the potential function resulting from changes in the distances between non-

¹⁵H. Russell, D.R.V. Golding and D. M. Yost, J. Am. Chem. Soc. 66, 16 (1944).

¹⁶H. W. Thompson and R. B. Temple, J. Am. Chem. Soc. 90, 1428 (1948).

¹⁷J. Rud Nielsen, H. H. Claassen and D. C. Smith, J. Chem. Phys. 18, 1471 (1950).

¹⁸R. D. Cowan, G. Herzberg and S. P. Sinha, J. Chem. Phys. 18, 1538 (1950).

bonded atoms with the variation of HCH and FCF angles, which were neglected by the previous workers.

The agreement between calculated and observed frequencies is about as good as can be expected for an eight-atom molecule. Although some improvement could be obtained by the finer adjustment of some of the force constants, this would hardly be meaningful, since better agreement should not be expected from this model, in which anharmonic terms are neglected, all angles are assumed to be tetrahedral, and the uncertainty in some of the bond lengths may be one percent or more.

Table 4-III is a listing of the matrix elements of L^{-1} , which is related to the symmetry and normal coordinates by the equation $Q = L^{-1} S$. Thus, the composition of each normal coordinate can be determined by reading across the appropriate row of this table.

The present normal coordinate analysis throws some new light upon the nature of the A_1 vibrations at 1280 and 831 cm^{-1} , which have formerly been characterized as C-F and C-C stretching, respectively. However, the present work shows that, while there is considerable mixing of these motions, the vibration with the higher frequency is predominantly C-C stretching. The final value, 3.6 $\text{md}/\text{\AA}^0$, for the force constant K_{CC} is considerably higher than the value, 2.8 $\text{md}/\text{\AA}^0$, of the corresponding force constant for ethane. This indicates a strengthening of the C-C bond with fluorine substitution. A similar effect occurs in ethylenes¹⁹, whose C=C stretching frequency increases with fluorine substitution.

Table 4-IV is a list of the changes in the calculated frequencies that result from an increase of 0.1 in particular force constants, all other variables being held constant.

¹⁹ J. Rud Nielsen, Monthly Research Report of the ONR, May, 1952.

TABLE 4-I
VALUES OF THE FORCE CONSTANTS FOR $\text{CF}_3\text{-CH}_3$

Symbol	Final Value	Initial Value	Transferred from
F_{FF}	1.1 md/A [°]	1.3 md/A [°]	CF_4
F_{FF}'	-0.2	-0.3 md/A [°]	CF_4
K_{CF}	4.4	3.75 md/A [°]	CF_4
H_{FCF}	0.1	0.15 md/A [°]	CF_4
H_{FCC}	0.3	0.15 md/A [°]	$\text{CF}_3\text{-CH}_3$
F_{FC}	0.4	0.23 md/A [°]	$\text{CF}_3\text{-CH}_3$
F_{FC}'	-0.04	-0.04 md/A [°]	$\text{CF}_3\text{-CH}_3$
k	0.35	0.56 md·A [°] /rad ²	$\text{CF}_3\text{-CH}_3$
F_{HH}	0.09	0.1 md/A [°]	$\text{CH}_4, \text{C}_2\text{H}_6$
F_{HH}'	0	0 md/A [°]	$\text{CH}_4, \text{C}_2\text{H}_6$
K_{CH}	4.6	4.8 md/A [°]	$\text{CH}_4, \text{C}_2\text{H}_6$
H_{HCH}	0.43	0.4 md/A [°]	$\text{CH}_4, \text{C}_2\text{H}_6$
H_{HCC}	0.14	0.15 md/A [°]	$\text{CH}_4, \text{C}_2\text{H}_6$
F_{HC}	0.4	0.4 md/A [°]	C_2H_6
F_{HC}'	-0.05	-0.05 md/A [°]	C_2H_6
k'	0.04 0.04	0.5 md·A [°] /rad ²	C_2H_6
K_{CC}	3.6	2.8 md/A [°]	C_2H_6
F_{FH}	0.06	0.12 md/A [°]	$\text{CF}_3\text{-CH}_3$
F_{FH}'	-0.01	- .045 md/A [°]	$\text{CF}_3\text{-CH}_3$

TABLE 4-II

VIBRATIONAL FREQUENCIES OF $\text{CF}_3\text{-CH}_3$ (in cm^{-1})

Species	Observed	Calculated	
		Present Work	Pan and Nielsen ⁸
A_1	2975	2970	
	1408	1447	1478
	1280	1287	1158
	830	857	831
	602	581	632
E	3035	3028	
	1443	1447	1366
	1233	1263	1242
	970	968	1046
	541	563	601
	365	373	320

TABLE 4-III

ELEMENTS OF THE TRANSFORMATION MATRIX L^{-1} ($\times 10^{12}$)Species A₁:

	S ₁	S ₂	S ₃	S ₄	S ₅
Q ₁ (2975)	1.276	.017	.122	.045	.013
Q ₂ (1408)	-.144	.187	- .390	.856	.105
Q ₃ (1280)	.024	-1.297	2.210	.353	- .470
Q ₄ (830)	.079	4.981	2.490	.214	- .154
Q ₅ (602)	.108	-1.888	3.080	.253	3.378

Species E:

	S ₁	S ₂	S ₃	S ₄	S ₅	S ₆
Q ₁ (3035)	1.230	.001	.048	- .014	- .005	- .004
Q ₂ (1443)	.069	.002	- .030	.039	.853	.013
Q ₃ (1233)	- .045	2.525	- .432	- .278	- .017	- .177
Q ₄ (970)	.105	1.880	1.361	.023	.103	.021
Q ₅ (541)	.082	2.091	- .245	1.509	- .054	2.825
Q ₆ (365)	.207	1.795	- .370	3.569	- .100	-1.260

TABLE 4-IV

CHANGES IN THE CALCULATED FREQUENCIES (cm^{-1}) DUE TO AN INCREASE
OF VARIOUS FORCE CONSTANTS BY 0.1 md/A

$\begin{matrix} \text{F} \\ \text{V} \end{matrix}$	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9	ν_{10}	ν_{11}
F_{FF}	0	0	0	6	3	0	0	4	1	6	1
F_{FF}'	0	-1	-17	0	-10	0	0	5	1	-25	-7
F_{FC}	0	1	1	13	7	0	0	0	1	0	14
F_{FC}'	0	1	3	0	7	0	0	15	0	0	24
F_{FH}	4	6	8	2	2	3	2	1	10	2	5
F_{FH}'	39	-28	-1	0	0	4	-2	-12	-27	-3	-7
H_{FCF}	0	1	11	2	13	0	0	3	1	38	10
H_{FCC}	0	0	14	0	15	0	0	13	0	4	37
K_{CF}	0	0	2	3	0	0	9	1	0	0	0
k	0	0	15	7	12	0	0	2	0	3	-25

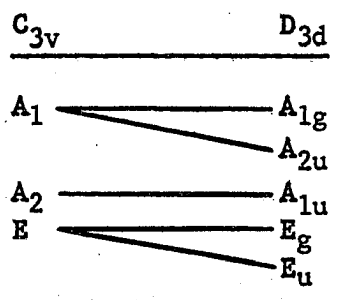
CHAPTER V

F AND G MATRICES FOR C_2H_6 AND C_2F_6

The validity of a set of force constants may be tested by using them to predict the vibration frequencies of molecules similar to the one for which they have been determined. In the present case the frequencies of C_2H_6 and C_2F_6 can be calculated with essentially the same constants as obtained for CF_3-CH_3 .

The following paragraphs describe the modification of the F and G matrices needed for the calculation of the vibrational frequencies of ethane. The corresponding matrices for C_2F_6 have the same form.

The ethane frequencies could be obtained from the previous matrices by the simple substitution of carbon-hydrogen bond lengths, force constants, and masses for the corresponding carbon-fluorine quantities. However, this would not take advantage of the additional factoring of the F and G matrices possible because of the higher symmetry, D_{3d} , of the ethane molecule. The correlation between the relevant irreducible representations of the C_{3v} and D_{3d} groups is indicated by the following diagram.¹



Symmetry coordinates of the three A_{1g} and two A_{2u} vibrations for ethane can be formed as linear combinations of the A_1 symmetry coordinates of CF_3CH_3 after modification required by the substitution of hydrogen for fluorine. Linear combinations of the six symmetry coordinates of the species E of CF_3-CH_3 can be combined into two sets of three symmetry coordinates for the E_g and E_u species of ethane. Thus, the symmetry coordinates for ethane in terms of the appropriately modified symmetry coordinates of CF_3-CH_3 are:

$$A_{1g} \quad S_1 = 1/\sqrt{2} (S_1^{A_1} + S_2^{A_1})$$

$$S_2 = 1/\sqrt{2} (S_4^{A_1} + S_5^{A_1})$$

$$S_3 = S_3^{A_1}$$

$$A_{2u}: \quad S_1 = 1/\sqrt{2} (-S_1^{A_1} + S_2^{A_1})$$

$$S_2 = 1/\sqrt{2} (-S_4^{A_1} + S_5^{A_1})$$

$$E_g: \quad S_1 = 1/\sqrt{2} (S_1^E + S_2^E)$$

$$S_2 = 1/\sqrt{2} (S_3^E + S_4^E)$$

$$S_3 = 1/\sqrt{2} (S_5^E + S_6^E)$$

$$E_u: \quad S_1 = 1/\sqrt{2} (-S_1^E + S_2^E)$$

$$S_2 = 1/\sqrt{2} (-S_3^E + S_4^E)$$

$$S_3 = 1/\sqrt{2} (-S_5^E + S_6^E).$$

Since the symmetry coordinates for both molecules are orthogonal, the F and G matrices for ethane can be obtained by similarity transformation. Thus, $F(C_2F_6) = UF(CF_3-CH_3)U^{-1}$, where U is the transformation matrix from the symmetry coordinates of CF_3-CH_3 to those of ethane. The blocks of the F and G matrices are listed in Tables 5-I and 5-II.

TABLE 5-I
F MATRICES FOR C_2H_6

Species A_{1g} :

$X + 2X' + W + 2W'$	$(N + A + 2A' - 2Q)/\sqrt{2}$	$\sqrt{6} z$
	$\frac{E+E'+C+L}{2} + F+C'+L'-I$	$\sqrt{3} T$
		S

Species A_{2u} :

$X + 2X' - W - 2W'$	$(N - A - 2A' - 2Q)/\sqrt{2}$
	$\frac{E+E'-C-L}{2} + F-C'-L'-I$

Species E_g :

$X - X' + W - W'$	$N + a - A'$	$Q/2$
	$E' - I + C - C'$	$I/2$
		$E - F + L - L'$

Species E_u :

$X - X' - W + W'$	$N - A + A'$	$Q/2$
	$E' - I - C + C'$	$I/2$
		$E' - F - L + L'$

TABLE 5-II

G MATRICES FOR C_2H_6 Species A_{1g} :

$W_H + W_C/3$	$4 W_C/3d$	$-2 W_C/\sqrt{6}$
	$W_H/d^2 + W_C/6d^2$	$-8 W_C/\sqrt{6} d$
		$2 W_C$

Species A_{2u} :

$W_H + W_C/3$	$4 W_C/3d$
	$W_H/d^2 + W_C/6d^2$

Species E_g :

$W_H + W_C/3$	$-\sqrt{2} W_C \left(\frac{1}{3d} + \frac{2}{R} \right)$	$-2\sqrt{2} W_C/3d$
	$\frac{W_H}{d^2} + W_C \left(\frac{1}{6d^2} + \frac{2}{Rd} + \frac{6}{R^2} \right)$	$W_C \left(\frac{2}{Rd} + \frac{1}{3d^2} \right) - \frac{W_H}{4d^2}$
		$\frac{5W_H}{2d^2} + \frac{8W_C}{3d^2}$

Species E_u :

$W_H + W_C/3$	$-\sqrt{2} W_C/3d$	$-2\sqrt{2} W_C/3d$
	$\frac{W_H}{d^2} + \frac{W_C}{6d^2}$	$\frac{W_C}{2d^2} - \frac{W_H}{3d^2}$
		$\frac{5W_H}{2d^2} + \frac{8W_C}{3d^2}$

CHAPTER VI

RESULTS FOR C_2H_6 AND C_2F_6 AND DISCUSSION

All but three force constants obtained for CF_3-CH_3 were used in the calculation of the vibrational frequencies of C_2H_6 and C_2F_6 . Since the interaction between two hydrogen or fluorine atoms at opposite ends of the molecule is not the same as between such atoms in the same end-group, the force constants F_{FH} and F_{FH}' are replaced by new constants F_{HH}^+ , F_{HH}' , F_{FF}^+ , and F_{FF}' . Also, in order to obtain satisfactory agreement between calculated and observed frequencies it was found necessary to use a separate constant K_{CC} for the two molecules. The values of these special force constants and other molecular constants for C_2H_6 and C_2F_6 are listed in Table 6-I.

The vibrational frequencies of C_2H_6 and C_2F_6 calculated in the present work and by Shimanouchi⁵ are listed in Table 6-II. The rather close agreement between the two sets of calculated frequencies is not surprising, since the final force constants obtained here for C_2H_6 differ little from those determined by Shimanouchi for CH_4 and C_2H_6 . The calculated frequencies agree well with those observed, except for the lowest frequency of the species E_g . It is possible that the experimental value of this frequency is in error, since, although it is Raman-active, it has never been observed directly but has been inferred from three infrared combina-

tion bands.²⁰

The calculated frequencies for C_2F_6 seem satisfactory, although tending to be slightly lower than the observed values. This may indicate that C-F forces are also strengthened by the increasing fluorination of ethane.

The calculated C-F stretching frequencies, of species E_g and E_u are separated by about 100 cm^{-1} , while the observed frequencies are approximately equal. Since in this case there seems to be little doubt about the assignment, this lack of agreement is either caused by a difference of force constants of CF_3-CH_3 and C_2F_6 or by an inadequacy of the potential function.

A strong mixing of C-C and C-F stretching occurs in vibrations of species A_{1g} , with the highest frequency, observed at 1417 cm^{-1} having largely the character of C-C stretching. The calculated C-C stretching force constant is higher in C_2F_6 than in CF_3-CH_3 , 4.0 as compared to 3.6 $\text{md/\AA}^0$, which is in accord with the empirical finding that fluorine substitution strengthens the C-C bond.

There has been considerable interest in this 1417 cm^{-1} Raman bond since it was reported by Rank and Pace²¹ in the spectrum of the liquid and by Nielsen and Gullikson²² for the gas. It is rather surprising to have a C-C or C-F stretching frequency above 1400 cm^{-1} when the highest frequency of CF_4 is at 1265 cm^{-1} . In a recent paper, Carney *et al.*²³

²⁰L. G. Smith, J. Chem. Phys. 17, 139 (1949).

²¹D. H. Rank and E. L. Pace, J. Chem. Phys. 15, 39 (1947).

²²J. Rud Nielsen and C. W. Gullikson, J. Chem. Phys. 21, 1416 (1953).

²³Rose A. Carney, E. A. Piotrowski, A. G. Meister, J. H. Braun, and F. F. Cleveland, J. Mol. Spect. 7, 209 (1961).

interpret the 1417 cm^{-1} band as the overtone of the A_{2u} fundamental at 714 cm^{-1} and ascribe to the highest A_{1g} fundamental the frequency 1228 cm^{-1} , chosen on the basis of infrared combination bands. While this is a possible interpretation, it seems less plausible than that adopted here.

For all three molecules the torsional vibration is in a species by itself and does not interact with the other vibrations. For C_2H_6 the torsional frequency is 278 cm^{-1} ,²⁴ which corresponds to a force constant of $0.036\text{ md A}^\circ/\text{rad}^2$. For CF_3-CH_3 the torsional frequency has been determined by a study of infrared combination bands to be 238 cm^{-1} ,¹⁷ corresponding to a force constant of $0.044\text{ md}\cdot\text{A}^\circ/\text{rad}^2$. This value is consistent with the microwave measurements of Minden and Dailey.²⁵ For both molecules the contribution to the potential function resulting from the intrinsic torsional stiffness of the C-C bond, as expressed by the force constant Ω , is about equal to the contributions arising from the forces between unbonded atoms.

²⁴J. Romanko, T. Feldman, and H. L. Welsh, Canadian J. Phys. 33, 588 (1955).

²⁵H. Minden and B. P. Dailey, Phys. Rev. 82, 338 A (1951).

TABLE 6-I

FORCE CONSTANTS AND MOLECULAR CONSTANTS FOR C_2H_6 AND C_2F_6

Description	Value for C_2H_6	Value for C_2F_6
F_{XX}^+ force constant	0.035 md/A $^\circ$	0.06 md/A $^\circ$
$F_{XX}^{' +}$ force constant	-0.01 md/A $^\circ$	-0.01 md/A $^\circ$
K_{CC} force constant	2.8 md/A $^\circ$	4.0 md/A $^\circ$
C-C bond length	1.54 A $^\circ$	1.52 A $^\circ$
C-X bond length	1.09 A $^\circ$	1.36 A $^\circ$
XCX bond angle	109 $^\circ$ 28'	109 $^\circ$ 28'
XCC bond angle	109 $^\circ$ 28'	109 $^\circ$ 28'

TABLE 6-II

VIBRATIONAL FREQUENCIES OF C_2H_6 AND C_2F_6 (in cm^{-1})

Species	C_2H_6			C_2F_6		
	Observed ^{20,24}	Present	Shimanouchi	Observed ^{17,22}	Present	Shimanouchi
A_{1g}	2954	2958	2916	1417	1395	1231
	1388	1401	1369	808	806	846
	994	1021	1005	348	343	391
A_{2u}	2915	2948	2938	1117	1050	1154
	1380	1409	1400	714	678	698
E_g	2955	3012	2973	1250	1289	1224
	1460	1440	1438	619	579	612
	1190	1004	997	372	367	376
E_u	2996	3018	2984	1251	1190	1159
	1472	1447	1457	523	537	531
	823	893	825	216	223	248

APPENDIX I

DIAGONALIZATION OF NON-SYMMETRIC MATRIX

Since many techniques are available for the calculation of the eigenvalues and eigenvectors of a matrix^{1,26}, only that used in this work is discussed here. Let L_i be a row vector composed of the elements in the i th row of the matrix L and let L_j be a column vector formed in a similar manner. Let the eigenvectors of a block of $GF=H$ be L_k , $k=1,2,\dots,N$, with eigen values λ_k so that $H L_k = \lambda_k L_k$. This set of equations can also be written as $H L = L \Lambda$, where Λ is a diagonal matrix with elements λ_k . The equivalent form of this equation, $L^{-1} H L = \Lambda$, shows that the eigenvalues of H can be determined by diagonalization of H by similarity transformation, and that the eigenvectors of H are represented by the columns of the transformation matrix L .

Excluding the case of accidental degeneracy, the eigenvalues of a block of the GF matrix are distinct and the corresponding eigenvectors are linearly independent by the following argument. Assume there is one and only one dependency relation among the N eigenvectors of a GF block. This can be written as: $L_1 = \sum_{k=2}^N a_k L_k$, where not all a_k 's are $= 0$. Then $H L_1 = \sum_{k=2}^N a_k \lambda_k L_k = \lambda_1 L_1 = \sum_{k=2}^N a_k \lambda_1 L_k$. And therefore, $\sum_{k=2}^N a_k (\lambda_k - \lambda_1) L_k = 0$. Since $\lambda_k \neq \lambda_1$, $k = 2,3,\dots,N$, the last equation is a second dependency relation among the eigenvectors, in contradiction to the initial assumptions. Thus, there cannot be a single dependency relation among the eigenvectors. In a similar manner it can

²⁶H. W. Turnbull and A. C. Aitken, An Introduction to the Theory of Canonical Matrices (London: Blackie and Son Ltd., 1932).

be shown that there can not be two, or three, or any other number of dependency relations. The space spanned by the eigenvectors is, therefore, N dimensional.

An arbitrary column matrix X , in the space spanned by the eigenvectors, can be written as a linear combination of the eigenvectors, $X = \sum_k a_k L_k$. The L_k 's form a linearly independent set of vectors, since the normal coordinates are independent. If the vector X is multiplied repeatedly by H the result is : $H^p X = \sum_k a_k \lambda_k^p L_k$. If $\lambda_1 > \lambda_2 > \lambda_3 \dots$, then for p sufficiently large and $a_1 \neq 0$ the term with $k = 1$ will dominate on the right hand side of this equation. As a result,

$$H^p X = H(H^{p-1} X) = \lambda_1^p a_1 L_1 = \lambda_1 (\lambda_1^{p-1} a_1 L_1) = \lambda_1 H^{p-1} X.$$

Thus, $H^{p-1} X$, denoted as V_1 , is an approximation to L_1 the eigenvector of H corresponding to the largest eigenvalue λ_1 . The eigenvalue λ_1 is approximately equal to the normalization constant of $H^p X$ divided by the normalization constant of $H^{p-1} X$.

The matrix H is then modified for the calculation of the next largest eigenvalue and corresponding vector by the deflation method of Aitken.²⁷ An approximate value of $(L^{-1})_1$, designated U_1 , is calculated by an iteration method similar to that above with V_1 chosen as the first approximation. It is now easy to verify that the matrix $H - \lambda_1 (V_1) (U_1) / \sum_k U_{1k} V_{k1}$ has the same eigenvectors as H and also the same eigenvalues, except for λ_1 which has been changed to zero. The above procedure is then repeated to calculate λ_2 , etc.

²⁷ A. C. Aitken, Proc. Roy. Soc. Edinburgh 57, 172 (1937).

PART II

VIBRATIONAL SPECTRA OF $\text{CF}_2\text{Br-CH}_2\text{Br}$ AND $\text{CF}_2\text{Cl-CH}_2\text{Cl}$

CHAPTER I

INTRODUCTION

Previous Work

The replacement of some hydrogen atoms by halogens in a hydrocarbon often results in a compound with useful physical properties. The fluorocarbons are particularly interesting in that they are in general highly volatile and have low surface tension, refractive index, and dielectric constant.²⁸ They are unusually stable, partly because the fluorine atoms form a protective shield about the carbon skeleton. Also contributing to the stability of these compounds is the strengthening of the C-C bond due to fluorine substitution, as noted in part I of this thesis.

The methyl halides and silyl halides have been thoroughly studied by Glockler and co-workers²⁹ and by Cleveland et al.³⁰ After satisfactory

²⁸J. H. Simons in Fluorine Chemistry, Volume I, page 403 (New York: Academic Press, 1950).

²⁹G. Glockler et al., J. Chem. Phys. 7, 278, 382, 553 (1939); 8, 125, 699, 897, (1940); 9, 224, 527 (1941); 10, 607 (1942).

³⁰F. F. Cleveland et al., J. Chem. Phys. 18, 346, 1073, 1076, 1081 (1950); 19, 119, 784, 1561 (1951); 20, 454, 1949 (1952); 22, 193 (1954); 23, 833 (1955); 25, 941 (1957).

force constants had been determined for these compounds much of the research effort in this field has turned to the more complicated ethylenes and ethanes. The molecular constants of these compounds can be determined by electron diffraction measurements, microwave spectroscopy, and by thermodynamic methods. The principal method of determining the interatomic forces for any but the most simple molecules is by study of the vibrational spectra, since the band frequencies are directly related to the strength of the chemical bonds.

At the University of Oklahoma Professor J. Rud Nielsen and co-workers have studied the vibrational spectra of a large number of these compounds with emphasis on fluorinated molecules. The infrared and Raman spectra of more than a dozen halogenated ethylenes have been reported³¹ with assignments and thermodynamical properties in most cases. More than twenty fluoroethanes and fluoro-haloethanes³² with symmetrical end groups have been examined in this laboratory. Complete assignments of the fundamentals and thermodynamic functions have been calculated for most of these compounds. More recently, Klaboe and Nielsen have extended this work to include eight compounds with no symmetrical end group.³³

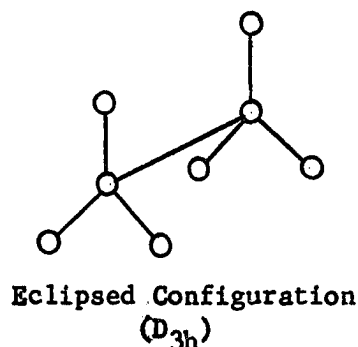
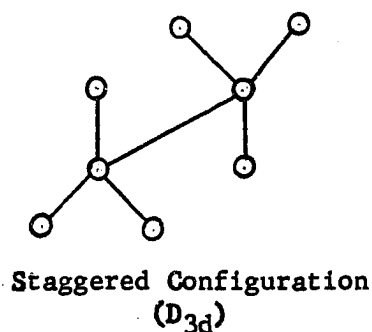
³¹J. Rud Nielsen *et al.*, J. Chem. Phys., 18, 326, 485, 812 (1950); 20, 1090, 1916 (1952); 23, 1944 (1955); 26, 1374 (1957); 27, 264 (1957); 30, 98, 103 (1959).

³²J. Rud Nielsen *et al.*, J. Chem. Phys., 16, 67 (1948); 18, 1471 (1950); 20, 473, 847 (1952); 21, 383, 1060, 1070 (1953); 23, 329 (1955); 27, 264, 887, 891 (1957).

³³Peter Klaboe and J. Rud Nielsen, J. Chem. Phys., 30, 1375 (1959); 32, 899 (1960); 34, 1819 (1961); J. Molecular Spectroscopy, 6, 379, 520 (1961).

Rotational Isomerism

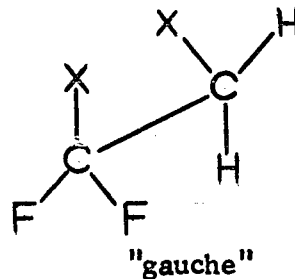
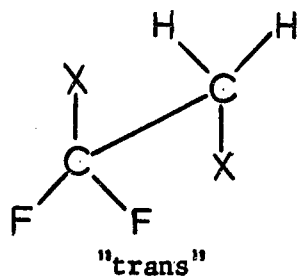
The relative orientation of the end groups of ethane and its halogenated derivatives has only recently been determined. For many years free rotation of the end groups about the C-C bond was assumed to occur, but this assumption was disproved by low temperature measurements of the heat capacity of C_2H_6 and C_2D_6 .³⁴ Since there is no free rotation, the equilibrium position must be either staggered or eclipsed with D_{3d} or D_{3h} symmetry, respectively.



As the selection rules for these two symmetries are quite similar the correct equilibrium configuration was not definitely known until Smith²⁰ resolved some of the rotational fine structure of C_2H_6 and C_2D_6 . Later Romanko, Feldman and Welsh²⁴ substantiated Smith's results with a high resolution study of the Raman bands of ethane, proving the staggered form to be the equilibrium configuration. The substituted ethanes are also believed to exist in this configuration.

If neither end group of a halogenated ethane is symmetrical there are two or three rotational isomers. For CF_2Br-CH_2Br and CF_2Cl-CH_2Cl the two rotational forms called "trans" and "gauche" are shown below.

³⁴G. Herzberg, Infrared and Raman Spectra of Polyatomic Molecules (New York: D. Van Nostrand Company, 1945).



In the work of Nielsen, Klaboe, and Lakshmi^{33,35} values of ΔH° , the enthalpy difference between the rotational isomers, varying from 0 to nearly 1200 cal/mole were determined for various molecules of this general type.

³⁵K. Lakshmi, "Vibrational Spectra of CFCl:CHBr , C_2H_2 , F Br and $\text{CF}_2\text{Br-CHBr}_2$," (Ph.D. Thesis, University of Oklahoma, 1959).

CHAPTER II

EXPERIMENTAL RESULTS

The samples of $\text{CF}_2\text{Br-CH}_2\text{Br}$ and $\text{CF}_2\text{Cl-CH}_2\text{Cl}$ used in the present work were prepared and purified by Dr. L. H. Beck in the laboratory of Professor A. L. Henne at Ohio State University. The spectra indicate that both samples are of high purity.

The infrared spectrum of liquid $\text{CF}_2\text{Br-CH}_2\text{Br}$ has previously been reported by the Naval Research Laboratory.³⁶ The infrared spectra of the gaseous and solid phases of $\text{CF}_2\text{Br-CH}_2\text{Br}$ and the gaseous, liquid and solid phases of $\text{CF}_2\text{Cl-CH}_2\text{Cl}$ were recorded in the region from 300 to 5000 cm^{-1} with the aid of a Perkin-Elmer double pass spectrometer equipped with CsBr, NaCl, and LiF prisms. Transmission curves plotted from these records are shown in Figs. 2-1, 2, ..., 11. The variation with temperature of the absorbances of the fundamentals, over the range from 25 to 110°C for $\text{CF}_2\text{Br-CH}_2\text{Br}$ and from 25 to 150°C for $\text{CF}_2\text{Cl-CH}_2\text{Cl}$, was determined.

The Raman spectrum of liquid $\text{CF}_2\text{Cl-CH}_2\text{Cl}$ was photographed with a 3-prism glass spectrograph of reciprocal linear dispersion $15\text{ A}^\circ/\text{mm}$ at 4358 A° , and polarization measurements were made. The Raman spectrum of

³⁶N. R. L. Report No. 3567. Spectroscopic Spectra of Fluorinated Hydrocarbons (Naval Research Laboratory, Washington D. C., 1952).

liquid $\text{CF}_2\text{Br-CH}_2\text{Br}$ was photographed by M. Z. El-Sabban³⁷ at this laboratory. In Table II-1 Raman data for $\text{CF}_2\text{Cl-CH}_2\text{Cl}$ are listed.

The frequencies of the stronger bands in the infrared and Raman spectra of liquid $\text{CF}_2\text{Br-CH}_2\text{Br}$ have been previously reported by R. E. Kagarise.³⁸ No previous vibrational spectra of $\text{CF}_2\text{Cl-CH}_2\text{Cl}$ have been published.

³⁷J. Rud Nielsen, Report to the A. E. C. Division of Research Under Contract AT-(40-1)-1074, June 15, 1954.

³⁸R. E. Kagarise, J. Chem. Phys. 24, 1264 (1956).

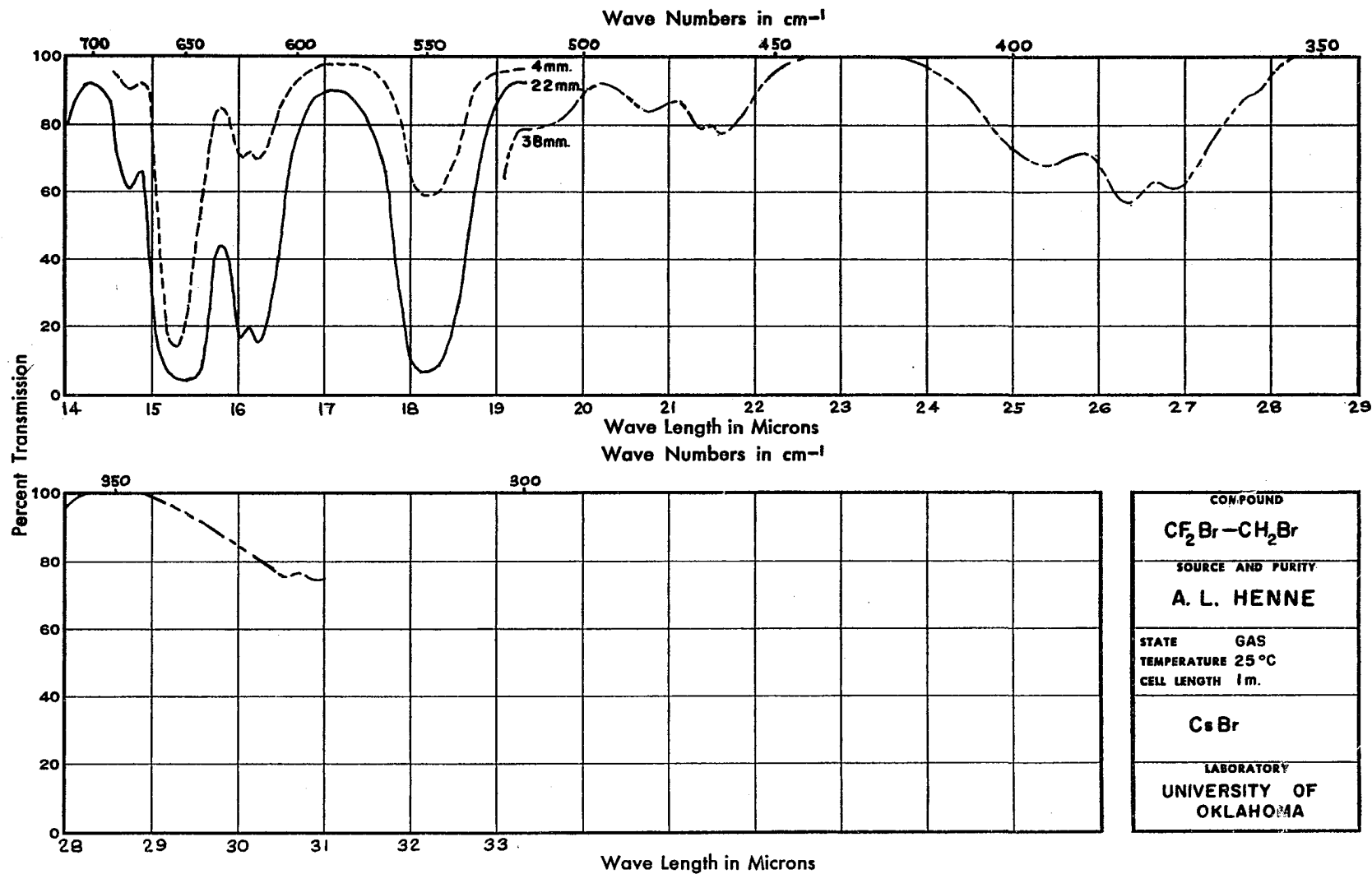


Fig. 2-1: Infrared Spectrum of Gaseous $\text{CF}_2\text{Br}-\text{CH}_2\text{Br}$ (Cs Br Region)

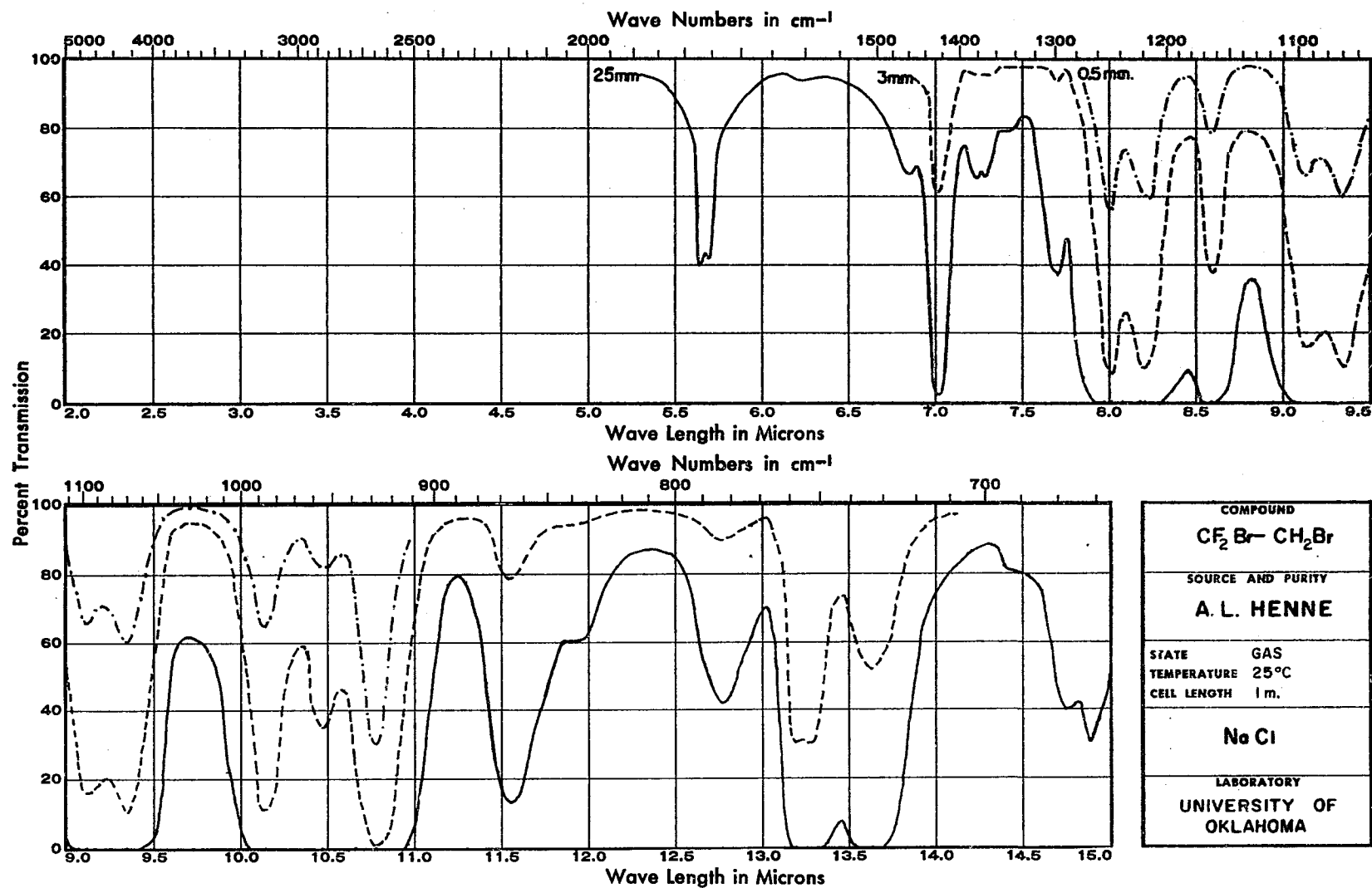


Fig. 2-2: Infrared Spectrum of Gaseous $\text{CF}_2\text{Br}-\text{CH}_2\text{Br}$ (Na Cl Region)

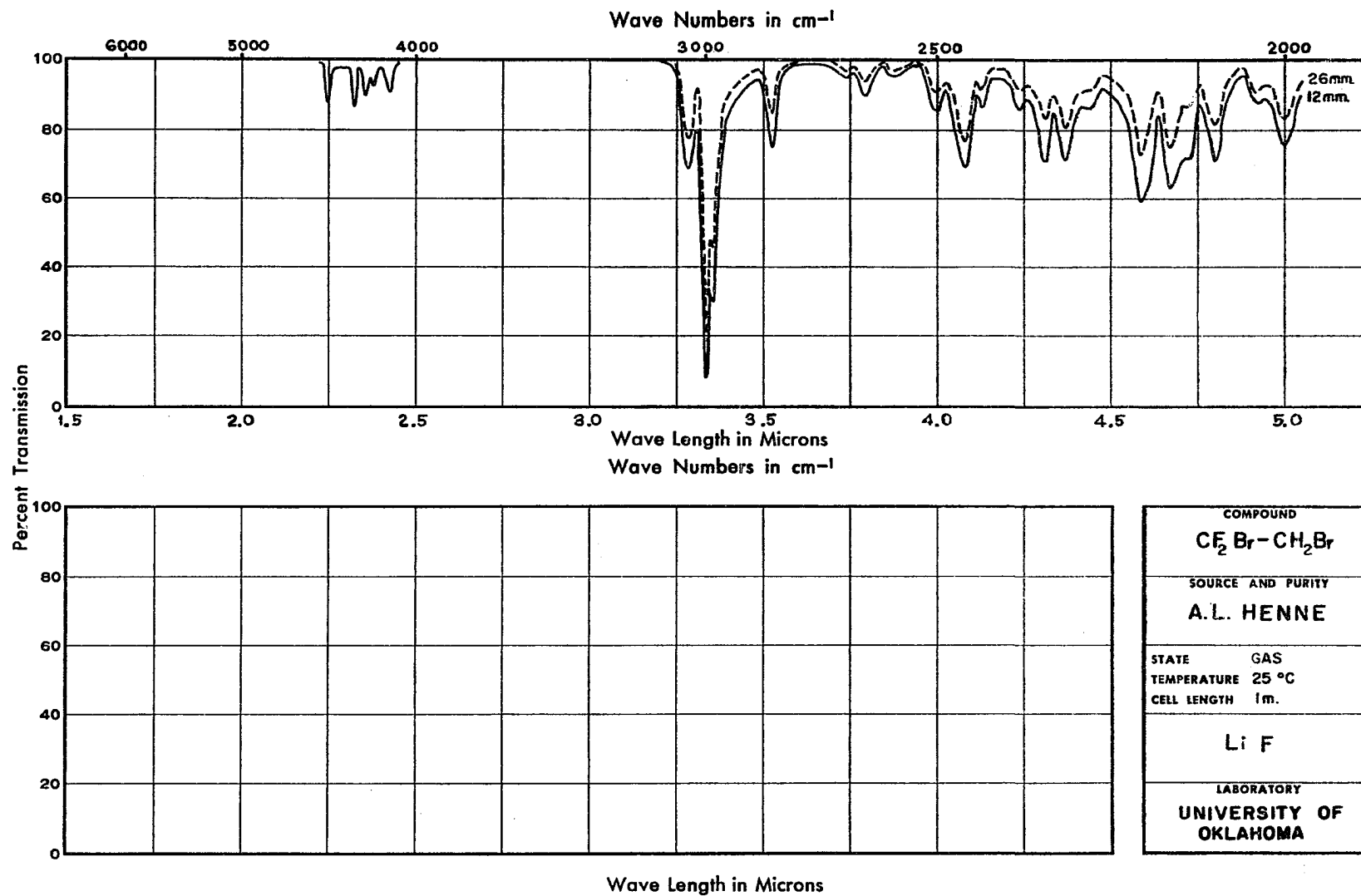


Fig. 2-3: Infrared Spectrum of Gaseous $\text{CF}_2\text{Br}-\text{CH}_2\text{Br}$ (Li F Region)

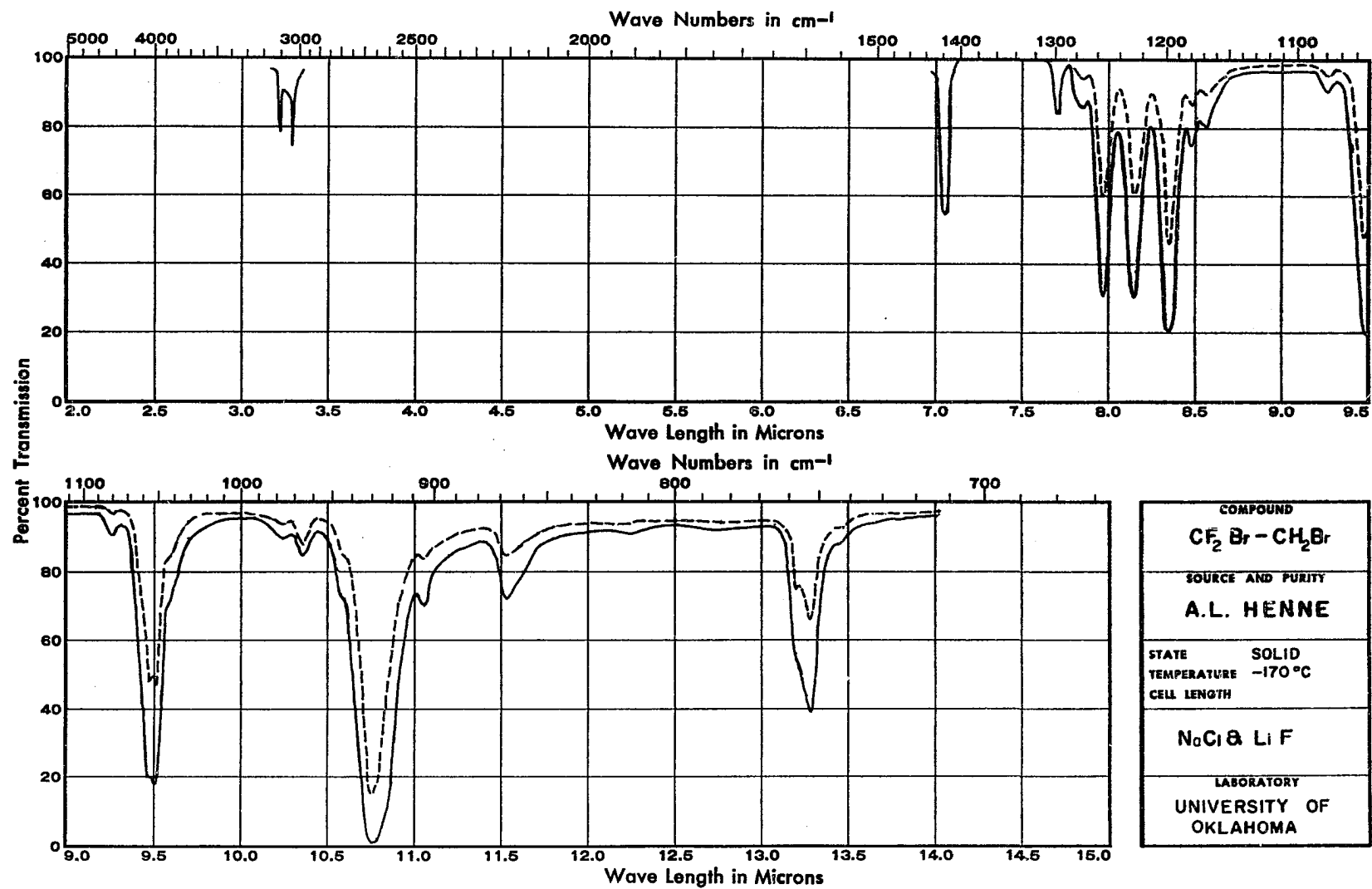


Fig. 2-4: Infrared Spectrum of Solid $\text{CF}_2\text{Br}-\text{CH}_2\text{Br}$ (NaCl and LiF Region)

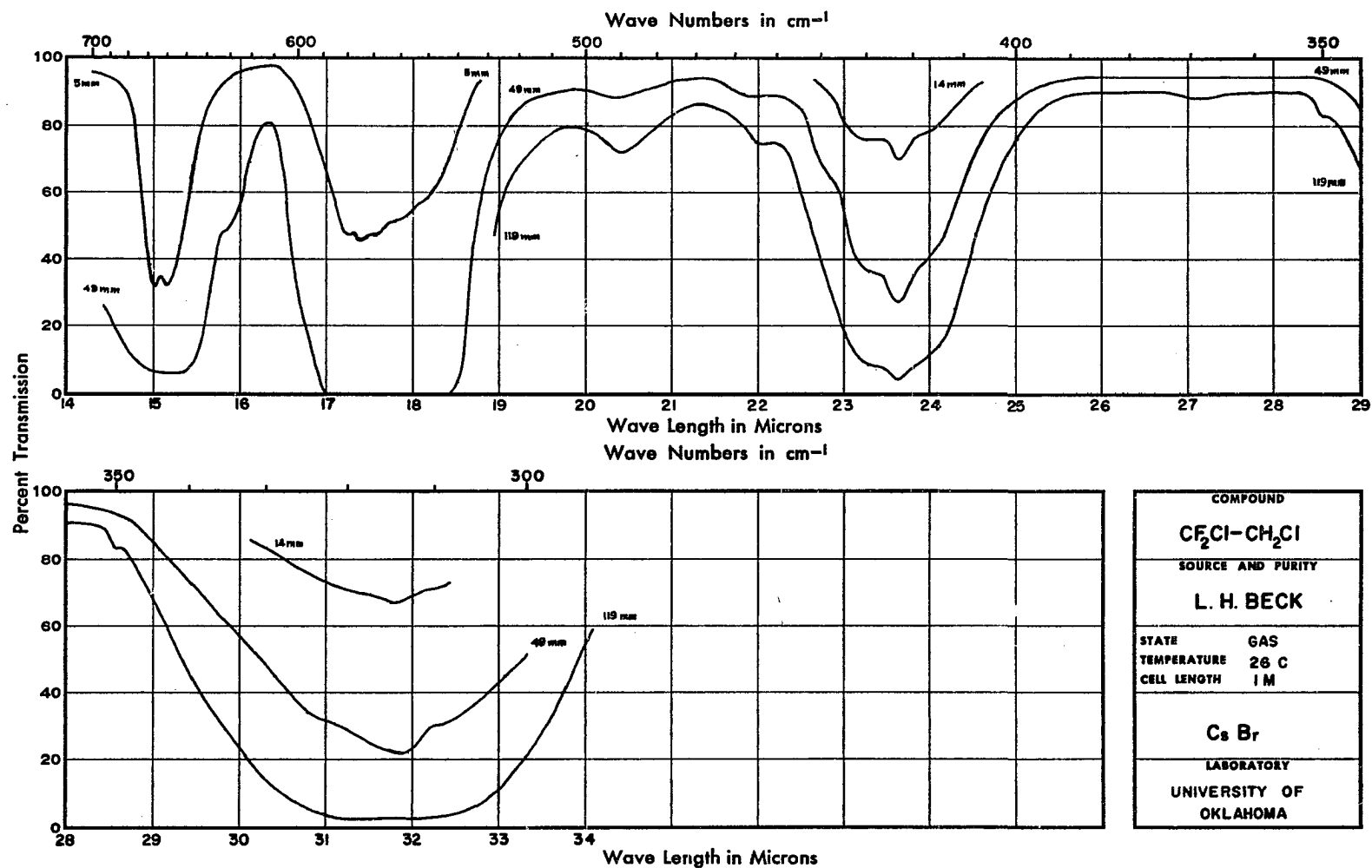


Fig. 2-5: Infrared Spectrum of Gaseous CF₂Cl-CH₂Cl (Cs Br Region)

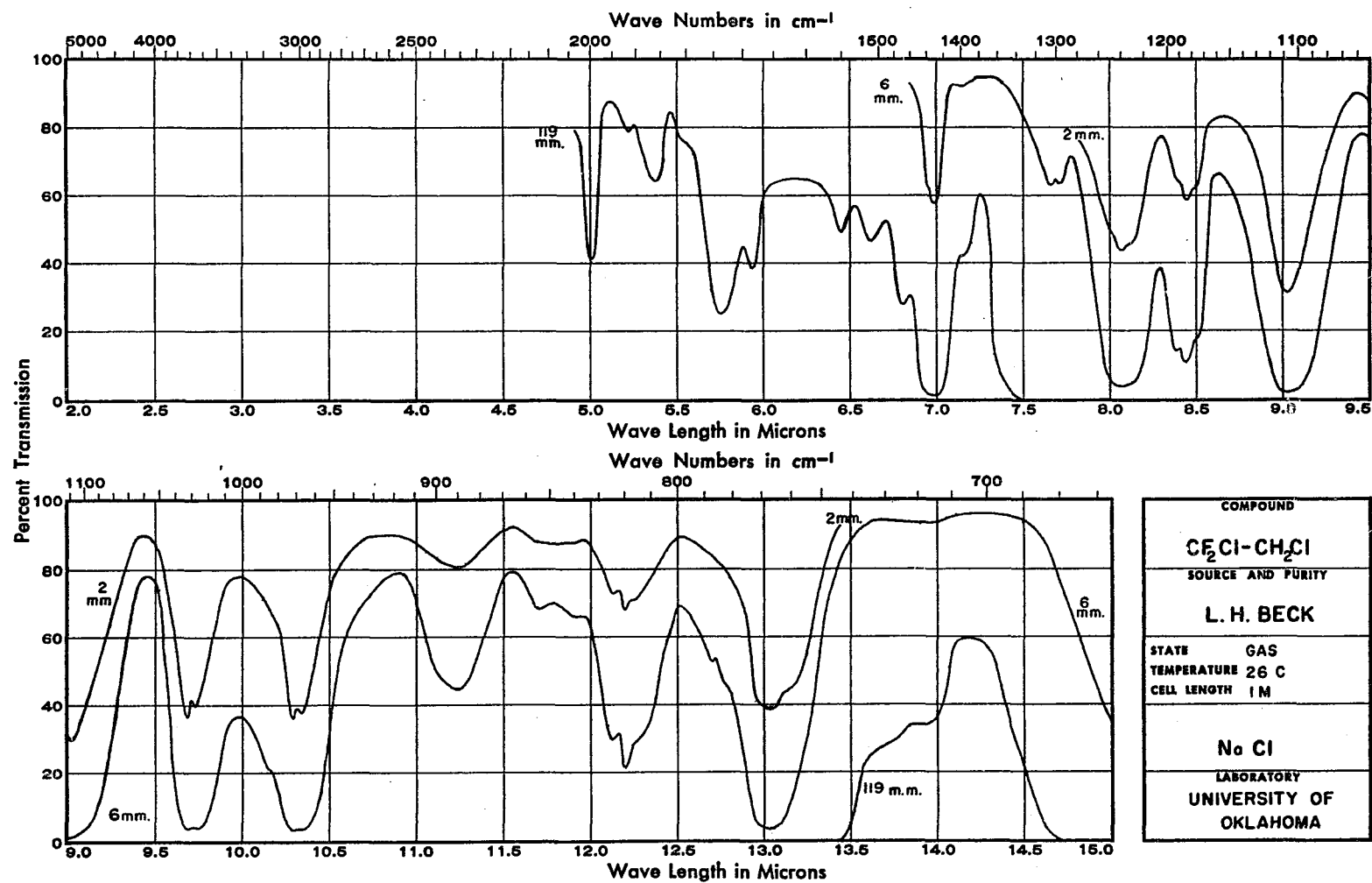
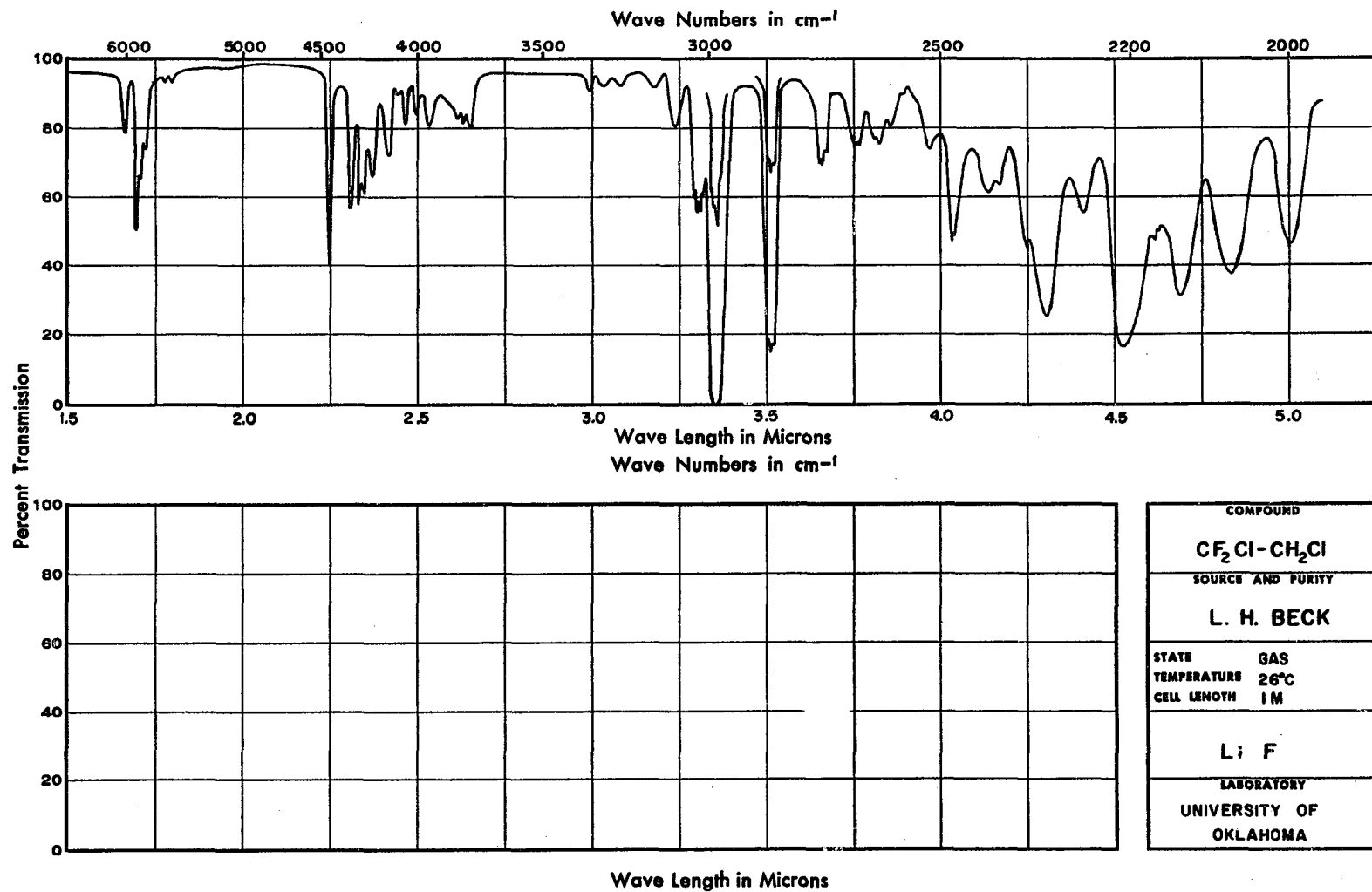


Fig. 2-6: Infrared Spectrum of Gaseous $\text{CF}_2\text{Cl}-\text{CH}_2\text{Cl}$ (Na Cl Region)



Fog. 2-7: Infrared Spectrum of Gaseous $\text{CF}_2\text{Cl}-\text{CH}_2\text{Cl}$ (Li F Region)

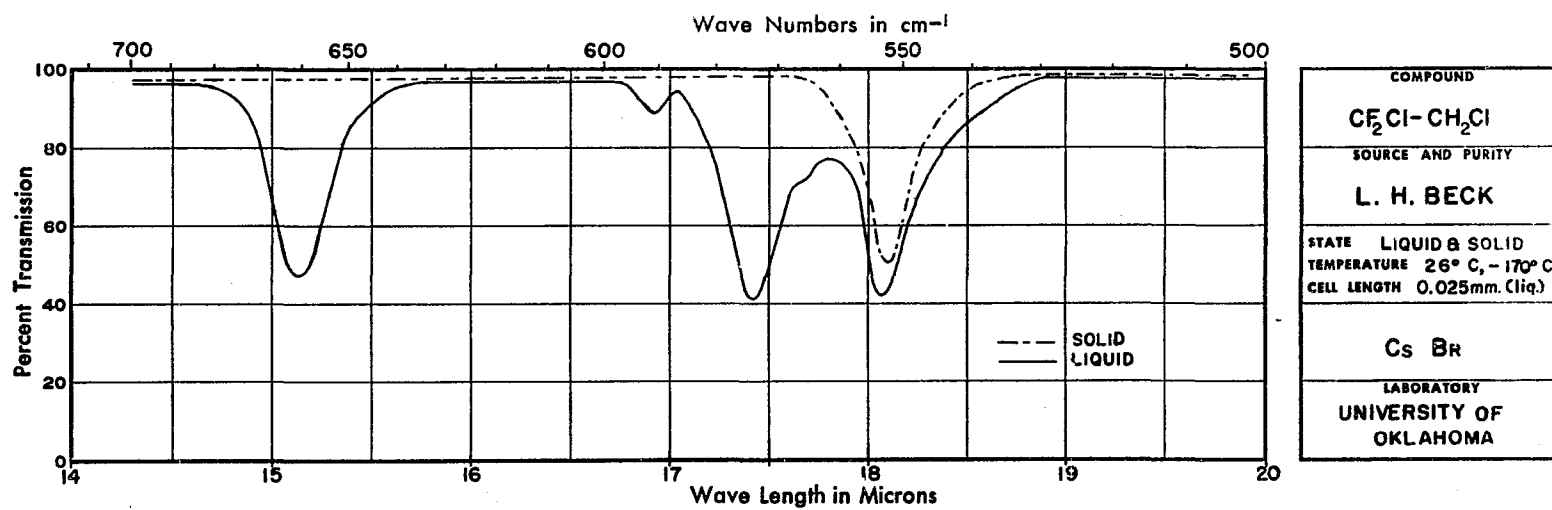


Fig. 2-8: Infrared Spectrum of Liquid and Solid $\text{CF}_2\text{Cl}-\text{CH}_2\text{Cl}$ (Cs Region)

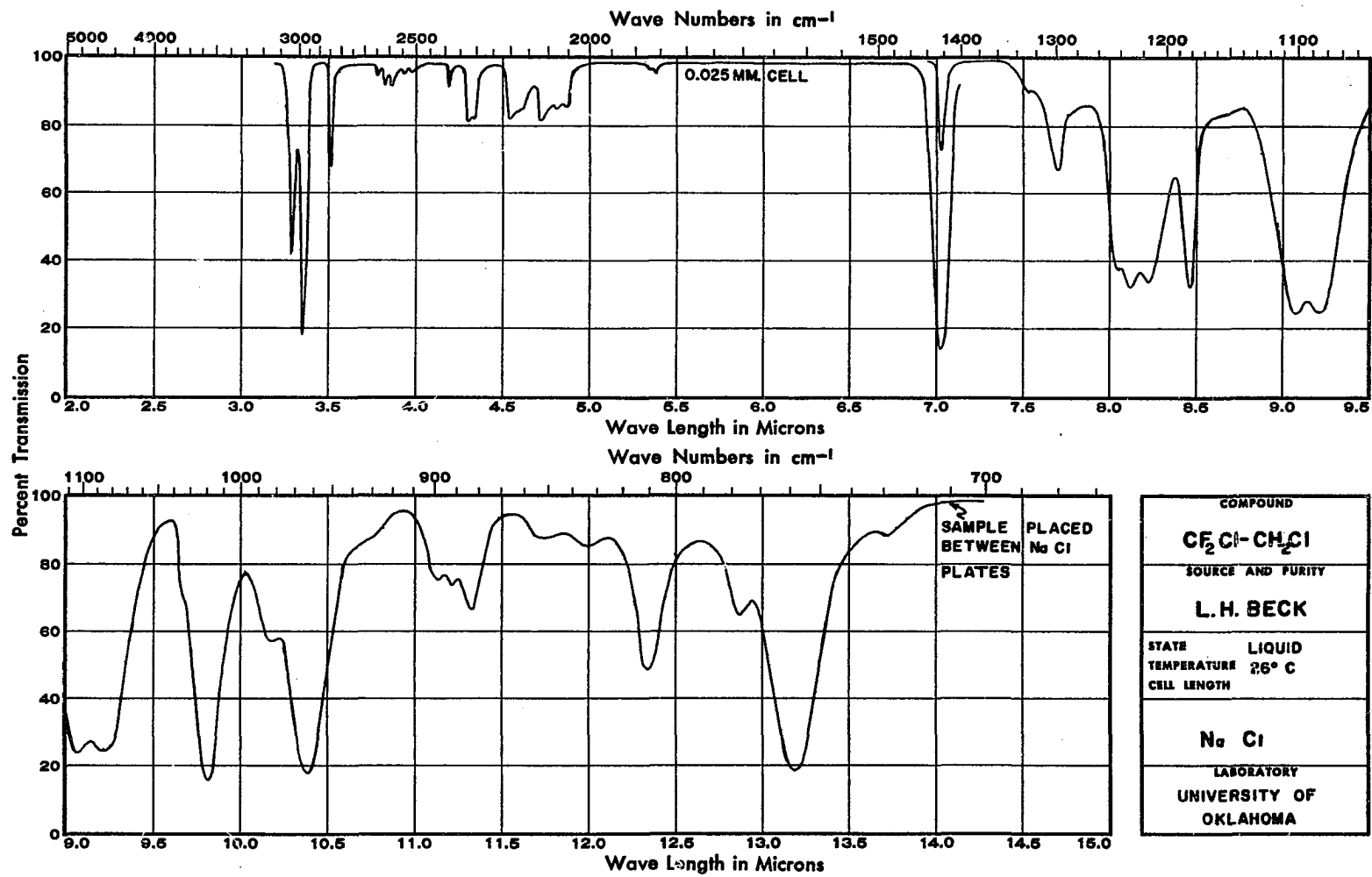


Fig. 2-9: Infrared Spectrum of Liquid $\text{CF}_2\text{Cl}-\text{CH}_2\text{Cl}$ (NaCl and LiF Region)

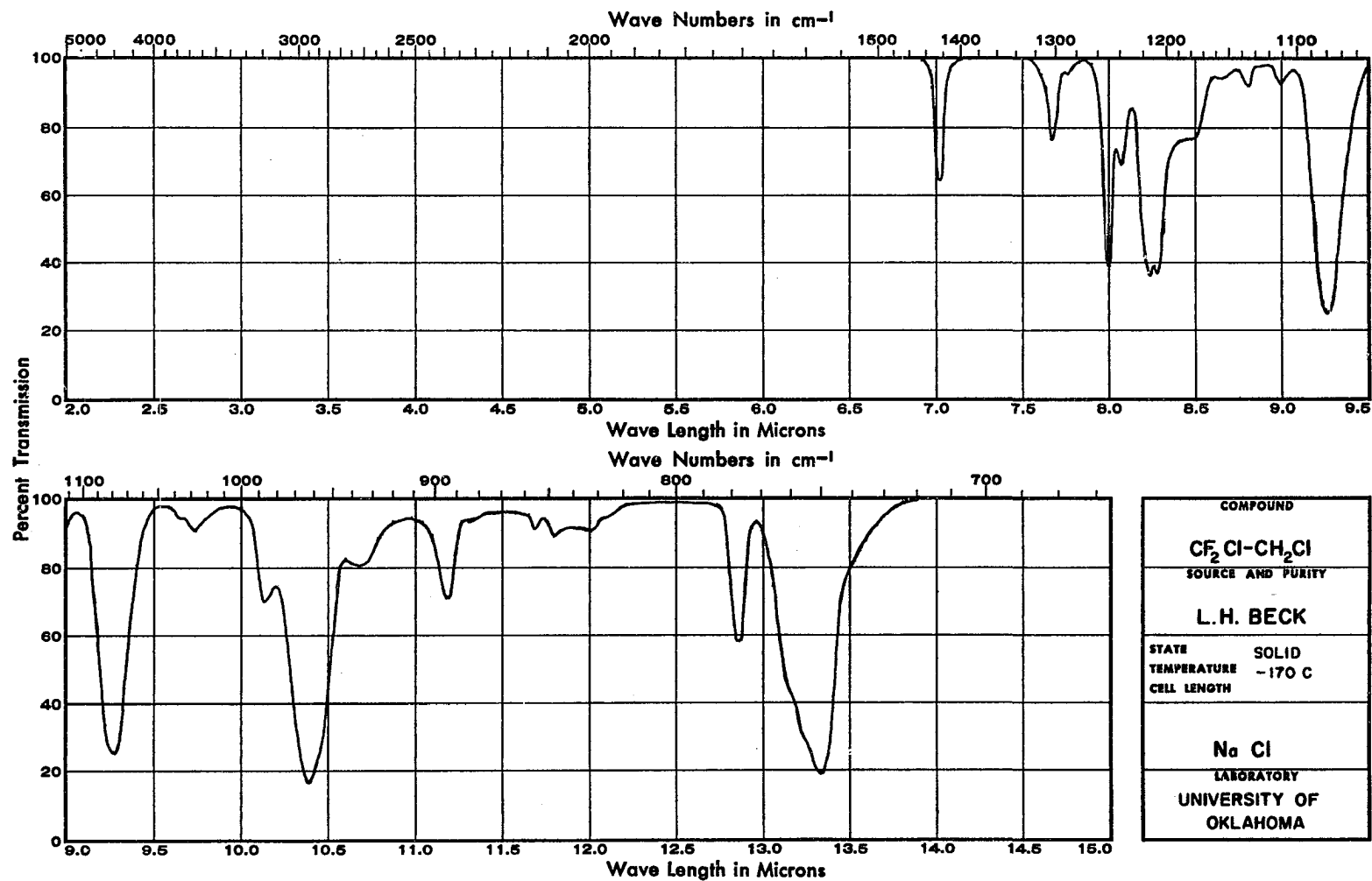


Fig. 2-10: Infrared Spectrum of Solid CF₂Cl-CH₂Cl (Na Cl Region)

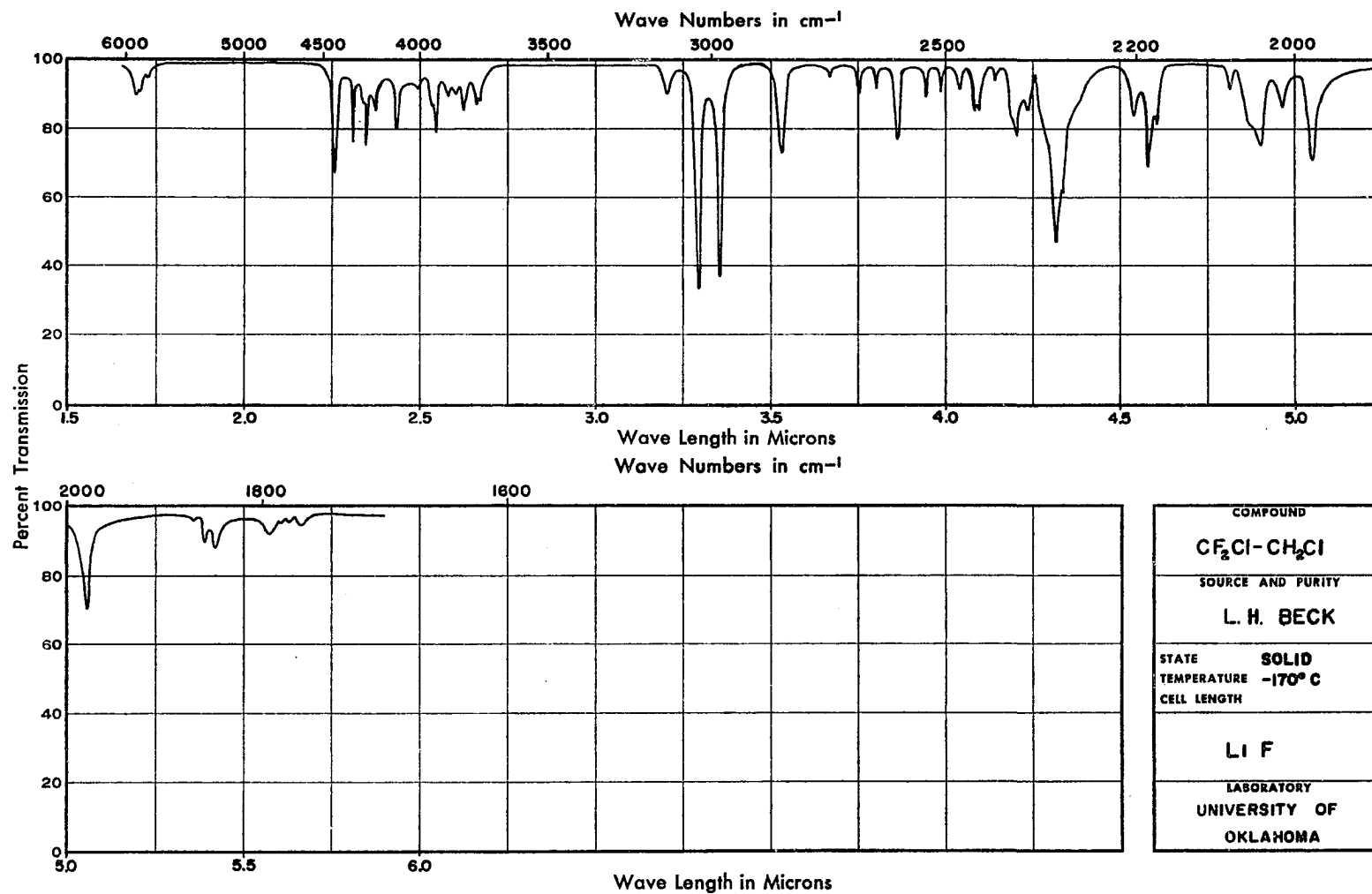


Fig. 2-11: Infrared Spectrum of Solid CF₂Cl-CH₂Cl (Li F Region)

TABLE 2-I

RAMAN SPECTRUM OF LIQUID $\text{CF}_2\text{Cl}-\text{CH}_2\text{Cl}$ AT ROOM TEMPERATURE

Wave Number	Description ^a	Depolarization	Interpretation ^b
126	vw		I, II
177	vw		I, II
195	vw		I, II
284	s, sh	0.60	I, II
~430	s, vd		I
433	vs, sh	0.59	II
556	w		I
577	vw		II
663	s, sh	0.33	II
~725	vw		177+556=733 (I)
761	w, d	dp	I, II
779	vs, sh	0.39	I
811	m	0.69	II
~835	vw		I
896	vw, vd		I, II
964	m, d	dp	I
984	vw, d		430+556=986 (I)
1022	vw	0.75	II
~1085	vw, vd		I
~1100	vw, vd		II
1185	vw		433+761=1194 (II)

TABLE 2-I (Continued)

Wave Number	Description ^a	Depolarization	Interpretation ^b
1219	vvw		I
1244	vvw		II
1251	vvw		284+964=1248 (I)
1303	w, sh	0.44	I, II
1430	m, sh	dp	I, II
2845	w	pol.	2x1430=2860 (I,II)
2973	vs		II
2983	vs	0.30	I
3036	m	0.84	I, II

^aThe following abbreviations have been used: s strong, m medium, w weak, v very, d diffuse, and sh sharp.

^bI designates the more stable isomer, and II the less stable isomer.

CHAPTER III

INTERPRETATION OF THE VIBRATIONAL FREQUENCIES OF $\text{CF}_2\text{Br-CH}_2\text{Br}$

The large number of strong infrared and Raman bands observed indicates that, like the previously investigated ethanes of this form, $\text{CF}_2\text{Br-CH}_2\text{Br}$ exists as a mixture of rotational isomers. These are undoubtedly a "trans" form of symmetry Cs and two enantiomorphous "gauche" forms having no symmetry. The normal vibrations of the "trans" form divide into 11 of species a' and 7 of species a'' . The former are polarized in the Raman effect and the latter depolarized. All 18 normal vibrations of the "gauche" form belong to the same species, and all fundamentals of either isomer are both infrared and Raman active.

Assuming the internuclear distances $\text{C-C} = 1.54$, $\text{C-H} = 1.093$, $\text{C-F} = 1.37$, and $\text{C-Br} = 1.98 \text{ \AA}$, and tetrahedral angles, one finds the principal moments of inertia to be 209.7, 1572 and $1599 \times 10^{-40} \text{ g cm}^2$ for the "trans" form. The axis of the largest moment of inertia is perpendicular to the symmetry plane, while the axis of intermediate moment lies in the symmetry plane making an angle of $38^\circ 42'$ with the C-C bond. Infrared bands of species a'' should therefore have type C contours, and bands of species a' should have contours that are hybrids between types A and B. However, it is not possible to make any reliable predictions of these contours on the basis of Badger and Zumwalt's³⁹ curves. On the

³⁹R. M. Badger and L. R. Zumwalt, J. Chem. Phys. 6, 711 (1938).

other hand, since the molecule is very nearly a symmetrical top, the curves of Gerhard and Dennison⁴⁰ can be applied. They show that a parallel band should have a PR separation of 6 cm^{-1} with a Q branch having an intensity of about 17 percent of the entire band. The perpendicular bands should have a single maximum. Vibrations of species a'' and a' should give rise to perpendicular and hybrid infrared bands respectively. Since the configuration of the "gauche" isomer is not accurately known, no predictions can be made about the contours of its infrared bands; however, they should be rather similar to those of the "trans" isomer. Actually, only eight bands show more than one absorption maximum. The observed PR separations vary from 5 to 10 cm^{-1} , the average being 7.1 cm^{-1} . For none of these bands is a Q branch observed.

When the temperature of gaseous $\text{CF}_2\text{Br}-\text{CH}_2\text{Br}$ was raised from 25° to 110°C six of the strong infrared bands were enhanced, while the intensities of ten strong bands decreased. The latter bands were assigned as fundamentals of the more stable rotational isomer, which will be designated I; the former bands were assumed to be fundamentals of the less stable isomer, II. A comparison of the intensities of Raman bands at 30° and -50°C provided a similar basis for ascribing a few additional bands to isomers I or II. Furthermore, it was found that all bands assigned to the less stable isomer are absent, or at least extremely weak, in the solid at -170°C .

Since a ^{rough} calculation showed that the dipole moments of the isomeric forms of $\text{CF}_2\text{Br}-\text{CH}_2\text{Br}$ should be equal to within less than 3 percent, no

⁴⁰S. L. Gerhard and D. M. Dennison, Phys. Rev. 43, 197 (1933).

attempt was made to differentiate between the spectra of the two isomers by observing the intensities of the infrared bands when the compound is dissolved in solvents of different polarity.

From the fundamentals assigned to other halogenated ethanes it is possible to predict roughly the frequencies of the present compound. This was used, in conjunction with the observed spectral data, as a criterion for the assignment of the fundamentals. To account for all the fundamentals of each rotational isomer it was necessary to assume that several fundamentals of I coincide or overlap with fundamentals of II. The choice of these is rather uncertain. The assigned fundamentals are listed in Tables 3-I and 3-II.

A test of these assignments is provided by the sum rule of Mizushima *et al.*⁴¹ One obtains $\sum_i \nu_i^2 = 27.80 \times 10^6$ and 27.68×10^6 for isomers I and II, respectively. The empirical sum rule of Bernstein and Pullin⁴² is also satisfied quite well, the sums being $\sum_i \nu_i = 16,469$ and $16,444$ for I and II, respectively.

Although consideration of steric hindrance would lead one to expect that the more stable isomer is the "trans" form, it was not possible to establish this on the basis of the present data.

In terms of the assigned fundamentals it has been possible to interpret satisfactorily practically all the observed infrared and Raman bands. Only the difficulties will be mentioned here. There is some uncertainty about the correlation of the Raman bands at 530 and 544 cm^{-1} , as well as

⁴¹S. I. Mizushima *et al.*, J. Chem. Phys. 21, 215 (1953).

⁴²H. J. Bernstein and A.D.A. Pullin, J. Chem. Phys. 21, 2188 (1953).

those at 639 and 648 cm^{-1} , with the corresponding infrared bands. This may be caused by Fermi coupling with the overtones of the fundamentals at 272 and 326 cm^{-1} . No explanation was found for the apparent splitting of the I fundamental at 756 cm^{-1} into two components at 753 and 758 cm^{-1} in the infrared spectrum of the solid. The similar splitting of the band at 1051 and 1056 cm^{-1} may be caused by Fermi coupling. The weak infrared band of the gas at 955 cm^{-1} , which appears to belong to II, can only be explained as a ternary combination band, or as an impurity band. It seems unrelated to the infrared bands in the solid at 943 and 965 cm^{-1} , which can be explained as binary combination bands of I, shifted somewhat due to their proximity to the fundamental at 928 cm^{-1} . A most peculiar feature in the spectrum of the solid is the strong band at 1227 cm^{-1} . While this can be explained as a binary combination band ($229 + 928 = 1227$), no plausible explanation has been found for its high intensity.

TABLE 3-I

FUNDAMENTAL VIBRATION FREQUENCIES OF THE MORE STABLE
 ROTATIONAL ISOMER (I) OF $\text{CF}_2\text{Br}-\text{CH}_2\text{Br}$ (in cm^{-1})

Infrared (gas) ^a	Infrared (liquid)	Infrared (solid)	Raman (liquid)
			80 m
			140 m
			170 m
			299 m
~320 vvw			326 vs
374 vvw			373 m
394 vvw			397 w
~540 w	542 m	540 m	530 m
651 s	641 vs	638 vs	639 } s 648 }
756 s	754 s	753 s	753 vs
866 m	864 m	867 m	865 w
928 vvs	923 vvs	929 vs	923 vs
1070 vs	1062 vs	1056 s	1065 w
1217 vs	1205 vs	1197 s	1206 m
1250 vs	1256 s	1254 s	1256 s
1423 s	1420 vs	1418 m	1420 m
2999 s	~2976 s	2989 s	2986 s
3047 w	3049 s	3052 s	

^aThe following abbreviations have been used: s strong, m medium, w weak, and y very.

TABLE 3-II

FUNDAMENTAL VIBRATION FREQUENCIES OF THE LESS STABLE
 ROTATIONAL ISOMER (II) OF $\text{CF}_2\text{Br}-\text{CH}_2\text{Br}$ (in cm^{-1})

Infrared (gas) ^a	Infrared (liquid)	Infrared (solid) ^b	Raman (liquid)
			80 m
			140 m
			187 vs
			272 m
~ 320 vw			326 vs
374 vw			373 m
394 vw			397 w
549 m	548 m	~ 547 vvw	544 m
618 m	613 s	~ 612 vvw	613 s
734 s	728 s		729 m
866 m	864 m	867 m	865 w
986 vs	978 vs	977 vvw	978 m
1097 vs	1086 vs	1079 w	1088 vw
1165 s	1167 s	1168 w	1166 vw
1247 s	1238 s		1241 vw
1423 s	1420 vs	1418 m	1420 m
2975 s	2976 s		2971 s
3047 w	3049 s	3052 s	

^aThe following abbreviations have been used: s strong, m medium, w weak, and y very.

^bThe bands listed in this column can all be interpreted as fundamentals or combination bands of isomer I.

CHAPTER IV

INTERPRETATION OF THE VIBRATIONAL FREQUENCIES OF $\text{CF}_2\text{Cl}-\text{CH}_2\text{Cl}$

The infrared spectrum of $\text{CF}_2\text{Cl}-\text{CH}_2\text{Cl}$ has fewer strong bands than observed for $\text{CF}_2\text{Br}-\text{CH}_2\text{Br}$, which indicates more overlapping of fundamentals. Otherwise, there are many similarities in the spectra, as might be expected. Both molecules have an isomer of symmetry C_s and the remarks made before concerning rotational isomerism, division of fundamentals according to symmetry species, and polarization of Raman bands apply also to $\text{CF}_2\text{Cl}-\text{CH}_2\text{Cl}$.

Assuming the internuclear distances $\text{C}-\text{C} = 1.54$, $\text{C}-\text{H} = 1.093$, $\text{C}-\text{F} = 1.37$, and $\text{C}-\text{Cl} = 1.77 \text{ \AA}$, and tetrahedral angles, one finds for the "trans" isomer the principal moments of inertia to be 191, 642, and 659 $\times 10^{-40} \text{ g cm}^2$. The axis of the largest moment of inertia is perpendicular to the symmetry plane, while the axis of the intermediate axis makes an angle of $42^\circ 18'$ with the $\text{C}-\text{C}$ bond. Since the molecule is very nearly a symmetrical top, the curves of Gerhard and Dennison⁴⁰ should be of some use in predicting the contours of infrared bands. They show that a parallel band should have a PR separation of 10 cm^{-1} and a Q branch with an intensity about 18 percent of that of the entire band. The perpendicular bands should have a single broad maximum. The a'' bands are perpendicular, while the a' bands are hybrids. The two bands at approximately 891 cm^{-1} , assigned as a'' fundamentals involving out-of-plane $\text{C}-\text{H}$ bending, have the broad single maxima expected of perpendicular

bands. On the other hand, the band at 819 cm^{-1} , which is ascribed to in-plane C-H bending and is associated with a change of dipole moment roughly along the axis of smallest moment of inertia, has the predicted PQR structure and a PR separation of 10 cm^{-1} . For the other bands the correlation between species and observed contours is less clear cut.

In the spectrum of the gas many fundamentals of the different isomers evidently overlap. In the spectrum of the liquid some of the overlapping bands are resolved because of the absence of rotational structure. Comparison of the spectrum of the liquid with that of the solid shows that many bands are almost totally absent in the solid phase. With this valuable aid for the separation of fundamentals of the isomers a reasonable assignment was achieved.

Measurement of the intensities of the infrared bands at temperatures up to 150°C confirmed the prevalence of overlapping bands. In the spectral region of the NaCl prism only the bands at 969 and 1032 cm^{-1} displayed a readily measurable temperature dependence. The former decreases in intensity with increasing temperature and must therefore be a fundamental of the more stable isomer, designated I. The band at 1032 exhibit the opposite temperature effect and is almost completely absent from the spectrum of the solid. It clearly belongs to the less stable isomer, II. The approximate vibrational motion giving rise to these bands is C-C stretching, which is strongly dependent on the relative orientation of the end groups.

The normal vibrations of $\text{CF}_2\text{Cl}-\text{CH}_2\text{Cl}$ can be conveniently divided into six which are essentially motions of the hydrogen atoms and twelve vibrations in which the heavier atoms participate strongly. There are

two C-H stretching modes near 3000 cm^{-1} and two C-H bending modes at 1431 and 1303 cm^{-1} . Two more C-H bending modes occur at approximately 890 and 840 cm^{-1} , with a small separation between frequencies of the two isomers.

The C-F and C-C stretching fundamentals are represented by strong infrared bands in the spectral range from 900 to 1300 cm^{-1} . Since the fluorine stretching modes are associated with only one end group, they should have about the same frequencies in both isomers. Because of strong combination bands in this region the assignment of these fundamentals is not certain, but they are reasonably chosen as 1235 and 1103 cm^{-1} for I and 1250 and 1109 cm^{-1} for II. The C-C stretching fundamentals undoubtedly lie at 968 and 1029 cm^{-1} for I and II, respectively. Of course, such a designation of a band as resulting from a simple motion of one or two atoms is at best a rough approximation, since any normal mode involves motion of all atoms.

The C-Cl stretching frequencies are identified with the bands at 785 and 761 cm^{-1} for the more stable isomer, I, and with those at 768 and 661 cm^{-1} for II. The separations of these bands offer some support for the natural assumption that isomer I has the "trans" form. Since the "gauche" isomer has no symmetry, interaction can occur between any two of its fundamentals. A larger separation may therefore be expected between its C-Cl frequencies than is observed for isomer I. The bands at 560 and 578 cm^{-1} are assigned as fundamentals involving a CF_2Cl deformation which is predominantly C-F bending. The bands at 423 and 430 cm^{-1} are interpreted as fundamentals associated with bending of the C-Cl bond of the CH_2Cl group, and the bands at 325 and 314 cm^{-1} are

ascribed to low frequency deformation of the CF_2Cl group. The bands observed in the Raman spectrum at 328, 284, 195 and 177 cm^{-1} are assumed to be common for both isomers and are assigned to rocking of the end groups. The torsional fundamental of either isomer is identified with the Raman band at 126 cm^{-1} . The assigned fundamentals are listed in Tables 4-II and 4-III. In terms of these fundamentals it is possible to interpret satisfactorily almost all of the observed bands.

A test of these assignments is provided by the sum rule of Mizushima et al.⁴¹ One obtains $\sum_i \nu_i^2 = 28.94 \times 10^6$ and 28.88×10^6 for isomers I and II, respectively. The empirical sum rule of Bernstein and Pullin⁴² is also satisfied reasonably well, the sums being $\sum_i \nu_i = 17,302$ for I and $\sum_i \nu_i = 17,359$ for II.

TABLE 4-I

FUNDAMENTAL VIBRATION FREQUENCIES OF THE MORE STABLE
 ROTATIONAL ISOMER (I) OF $\text{CF}_2\text{Cl}-\text{CH}_2\text{Cl}$ (in cm^{-1})

Infrared (gas) ^a	Infrared (liquid)	Infrared (solid)	Raman (liquid)
			126 vvw
			177 vw
			195 vw
			284 s
~325 s			328 m
423 s	~422 vw	~421 vw	430 s
560 s	553 m	553 m	556 w
761 w	758 s	754 s	761 w
785 w	777 w	777 w	779 s
~855 m	833 vvw	~835 vvw	~835 vvw
891 s	894 s	894 w	896 vw
968 s	964 s	962 s	964 m
1103 s	1086 s	1078 s	~1085 vw
~1235 m	1217 s	1212 m	1219 vvw
1303 w	1299 m	1303 w	1303 w
1431 s	1425 m	1422 m	1430 m
2989 s	2983 m	2982 s	2983 vs
3036 m	3037 m	3035 s	3036 m

^aThe following abbreviations have been used: s strong, m medium, w weak, and v very.

TABLE 4-II

FUNDAMENTAL VIBRATION FREQUENCIES OF THE LESS STABLE
ROTATIONAL ISOMER (II) OF $\text{CF}_2\text{Cl}-\text{CH}_2\text{Cl}$ (in cm^{-1})

Infrared (gas) ^a	Infrared (liquid)	Infrared (solid) ^b	Raman (liquid)
			126 vvw
			177 vw
			195 vw
			284 s
~314 s			328 m
430 s			433 vs
578 s	577 m		577 vw
661 s	661 s		663 s
768 s	758 s		761 w
819 s	811 s		811 m
891 s	883 s	882 vvw	896 vw
1029 s	1019 s	1017 vvw	1022 vw
1109 s	1101 s	1110 vvw	~1100 vw
~1250 m	1243 s	1239 vw	1244 vw
1303 w	1299 m	1303 w	1303 w
1431 s	1425 m	1422 m	1430 m
2979 s	2975 vw		2973 vs
3036 m	3037 m	3035 s	3036 m

^aThe following abbreviations have been used: s strong, m medium, w weak, and v very.

^bThe bands listed in this column can all be interpreted as fundamentals or combination bands of isomer I.

CHAPTER V

ENTHALPY DIFFERENCE BETWEEN ROTATIONAL ISOMERS

Although a potential barrier restricts the relative rotation of the end groups, it does not prohibit transition from one isomer to the other. A "trans" form is changed to one of the two enantiomorphic "gauche" forms by rotation of one of the end groups a certain angle, probably close to 120° . The standard enthalpy change in such a transition is related to the equilibrium constant K_p by the thermodynamic formula $\ln K_p = -\Delta H^\circ/(RT) + \text{const.}$ Since $K_p = (N \text{ "trans"}/N \text{ "gauche"})$, where N represents the number of molecules per unit volume, K_p is equal to $A_t/A_g \times \text{const.}$, where A_t is the integrated absorbance of a band belonging only to the "trans" isomer and A_g is the absorbance of a band of the "gauche" form. If these absorbances are measured at two different temperatures ΔH° can be calculated from the equation:⁴³

$$\Delta H^\circ = R \left[\ln(A_t/A_g)_{T_2} - \ln(A_t/A_g)_{T_1} \right] / (1/T_1 - 1/T_2).$$

Since the pressure and volume of the system remain constant during this isomeric transition, the value of ΔH° is also the change of internal energy of the molecules.

Measurement of the intensity variation with temperature of the bands

⁴³ H. J. Bernstein, J. Chem. Phys. 18, 987 (1950).

of $\text{CF}_2\text{Br-CH}_2\text{Br}$ at 928 and 986 cm^{-1} indicates a value of $\Delta H^\circ = 1030 \pm 100$ cal/mole (gas) for this molecule. Values of 710 ± 50 cal/mole for the gas and 1020 ± 50 cal/mole for the liquid have been reported by Kagarise³⁸, who based his calculations on the temperature-intensity variation of the 754 and 728 cm^{-1} bands. Since the dipole moments of the rotational isomers differ only slightly, being 1.92 D for the "trans" form and 2.01 D for the "gauche" isomer, the value of ΔH° should be about the same in the gaseous and liquid phases. It is possible that the value 710 cal/mole is low because of overlapping of the 754 and 728 cm^{-1} bands of the gas.

In the case of $\text{CF}_2\text{Cl-CH}_2\text{Cl}$, the temperature variation of the fundamentals at 969 and 1032 cm^{-1} indicates a value of $\Delta H^\circ = 430 \pm 100$ cal/mole (gas).

Most of the fundamentals of the two isomers of $\text{CF}_2\text{Br-CH}_2\text{Br}$ are fairly well separated, while many fundamentals of the rotational isomer of $\text{CF}_2\text{Cl-CH}_2\text{Cl}$ overlap. This is not unexpected, since the chemical bonds of the less stable isomer of either molecule are in a state of strain which is related to the magnitude of ΔH° .

Comparison of the values of ΔH° of the two molecules indicated that there is greater interaction between bromine atoms than between chlorine atoms at separations of from 2.5 to 5 $\text{\AA}$. This is probably due to the larger size of the bromine atoms, since ^{ider}conservation of the dipole moments of the C-Cl and C-Br bonds leads to the conclusion that the Cl-Cl repulsion should be somewhat larger.

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