VIBRATIONAL ASSIGNMENTS OF TRIFLUOROACETIC ACID AND SOME OF ITS DERIVATIVES

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TABLE OF CONTENTS

		Page
ACKNOWLEDGMENT		ii
LIST OF TABLES		vi
LIST OF FIGURES		viii
I.	INTRODUCTION	1
	Properties of Fluorocarbons and Derivatives	1
	Application of Molecular Spectroscopy in the Study of Fluorocarbons and Derivatives	7
	Statement of the Problem	9
II.	THEORETICAL BACKGROUND	13
	Brief Review of Vibrational Theory	13
	Infrared Absorption Theory	17
	The Raman Effect	20
III.	PRESENT STATUS OF STRUCTURAL AND VIBRATIONAL PROBLEMS OF CARBOXYLIC ACIDS, AMIDES AND RELATED COMPOUNDS	26
	Structural Evidence and Bonding in:	
	Carboxylic Acids	26
	Acid Amides and Derivatives	28
	Interpretation of Vibrational Frequencies of:	
	Carboxylic Acids	31
	Acid Amides and Derivatives	33
IV.	STRUCTURE AND VIBRATIONAL FREQUENCIES ASSOCIATED WITH THE CF_3 GROUP	36
	Present Status of Structural and Vibrational Problems of Trifluoroacetic Acid and Derivatives	38
	Trifluoroacetic Acid (Methyl Trifluoroacetate, Trifluoroacetate Ion)	38
	Trifluoroacetamide	47
V.	EXPERIMENTAL PROCEDURES	48
	Preparation of Compounds	48
	Preparation of Samples for Obtaining Raman Spectra	48
	Gas Samples	50
	Solution Samples	50

TABLE OF CONTENTS (CONT'D)

	Page
Pure Liquid Samples	51
Pure Liquid Samples (Molten State)	51
Solution Studies of Hydrogen Bonded Compounds	54
Spectrographic Equipment	56
Infrared Spectrometer	56
Raman Spectrograph	56
VI. EXPERIMENTAL RESULTS AND THEIR INTERPRETATION	66
Trifluoroacetonitrile	66
Trifluoroacetic Acid	66
Trifluoroacetic Acid-d	77
The Trifluoroacetate Ion	83
Methyl Trifluoroacetate	91
Trifluoroacetamide	96
Trifluoroacetamide-d_2	108
N-Methyltrifluoroacetamide	114
N,N-Dimethyltrifluoroacetamide	123
Conclusions Drawn from the Spectra of Unsubstituted and Substituted Trifluoroacetamides	129
Trifluoroacetamidine	133
Trifluoroacetamidine-d_3	141
N-Methyl- and N,N-Dimethyltrifluoroacetamidine	143
Conclusions Based on the Spectra of Unsubstituted and Substituted Trifluoroacetamidines	155
Silver Salts of Trifluoroacetamide and Trifluoroacetamidine	159
SUMMARY	163
APPENDIX	165
Sources of Materials	165
Experimental	165
Magnesium Nitride	165
Deuterated Ammonia	166
Methylamine	166
Deuterated Trifluoroacetic Acid	167
Trifluoroacetamide	167
Trifluoroacetamide-d_2	169
N-Methyltrifluoroacetamide	169
N,N-Dimethyltrifluoroacetamide	170
Methyl Trifluoroacetate	170
Trifluoroacetonitrile	170

TABLE OF CONTENTS (CONT'D)

	Page
Trifluoroacetamidine	171
Trifluoroacetamidine-d_3	171
N-Methyl- and N,N-Dimethyltrifluoroacetamidine	172
Sodium Trifluoroacetate	172
Silver Salt of Trifluoroacetamide	172
Silver Salt of Trifluoroacetamidine	173
BIBLIOGRAPHY	174

LIST OF TABLES

Table		Page
I.	Melting Points and Boiling Points of Chloro- and Fluorocarbon Derivatives and Corresponding Non-halogenated Analogues	6
II.	Fundamental Frequencies of the CF_3 Group for Molecules of C_s Symmetry	37
III.	Infrared Frequencies and Assignments for CF_3COOH and CF_3COOD in the Vapor State	43
IV.	Vibrational Frequencies (in cm^{-1}) of CF_3CN	68
V.	Observed Raman Frequencies and Assignments for Liquid CF_3COOH	78
VI.	Observed Raman Frequencies and Assignments for Liquid CF_3COOD	84
VII.	Vibrational Frequencies (in cm^{-1}) and Intensities of CF_3COONa	90
VIII.	Observed Raman Frequencies and Assignments for CF_3COONa in Aqueous Solution	92
IX.	Observed Raman Frequencies and Assignments for Liquid CF_3COOCH_3	97
X.	Fundamental Vibrations of CF_3CONH_2	100
XI.	Vibrational Frequencies (in cm^{-1}) of Molten CF_3CONH_2	106
XII.	Observed Raman Frequencies and Assignments for Molten CF_3CONH_2	109
XIII.	Infrared Absorption Frequencies of Trifluoroacetamide in CCl_4: 3000 cm^{-1} to 3500 cm^{-1}	110
XIV.	Observed Raman Frequencies and Assignments for Molten CF_3COND_2	115
XV.	Infrared Absorption Frequencies of Trifluoro-acetamide-d_2 in CCl_4: 2000 cm^{-1} to 2800 cm^{-1}	116
XVI.	Observed Raman Frequencies and Assignments for Molten $CF_3CONH(CH_3)$	124

LIST OF TABLES (CONT'D)

Table		Page
XVII.	Observed Raman Frequencies and Assignments for Liquid $CF_3CON(CH_3)_2$	130
XVIII.	Observed Raman Frequencies and Assignments for Liquid $CF_3C(:NH)NH_2$	140
XIX.	Infrared Absorption Frequencies of Trifluoroacetamidine in CCl_4: 3000 cm^{-1} to 3500 cm^{-1}	141
XX.	Observed Raman Frequencies and Assignments for Liquid $CF_3C(:ND)ND_2$	144
XXI.	Observed Raman Frequencies and Assignments for Liquid $CF_3C(:NH)NH(CH_3)$	153
XXII.	Infrared Absorption Frequencies of N-Methyltrifluoroacetamidine in CCl_4: 3000 cm^{-1} to 3500 cm^{-1}	155
XXIII.	Observed Raman Frequencies and Assignments for Liquid $CF_3C(:NH)N(CH_3)_2$	156
XXIV.	The Vapor Pressure of Trifluoroacetamide as Determined by the Knudsen Method	168

LIST OF FIGURES

Figure		Page
1.	Vacuum Line Used in the Preparation of Raman Samples...	49
2.	Apparatus Used in the Preparation of Low Melting Solid Samples.....	53
3.	Raman Light Source Assembly.....	60
4.	Apparatus Used for Molten Samples.....	62
5.	Sample Tube Holder.....	63
6.	Raman Spectrum of $CF_3CN_{(g)}$.....	67
7.	Raman Spectrum of Saturated Aqueous Solution of CF_3CO_2Na.....	67
8.	Raman Spectra of Liquid CF_3COOH and CF_3COOD.....	71
9.	Polarized Raman Spectra of $CF_3COOH_{(l)}$.....	73
10.	Polarized Raman Spectra of $CF_3COOD_{(l)}$.....	79
11.	Polarized Raman Spectra of Saturated Aqueous Solution of CF_3CO_2Ag.....	86
12.	Raman Spectra of CF_3COOCH.....	94
13.	Raman Spectra of Molten CF_3CONH_2 and CF_3COND_2.....	101
14.	Polarized Raman Spectra of Molten CF_3CONH_2.....	103
15.	Infrared Absorption Spectra of Trifluoroacetamide.....	107
16.	Infrared Absorption Spectra of Trifluoroacetamide-d_2...	107
17.	Polarized Raman Spectra of Molten CF_3COND_2.....	113
18.	Raman Spectra of Molten $CF_3CONHCH_3$.....	118
19.	Infrared Absorption Spectra of N-Methyltrifluoro-acetamide.....	119
20.	Raman Spectrum of $CF_3CON(CH_3)_2$.....	119
21.	Polarized Raman Spectra of $CF_3CON(CH_3)_2$.....	128
22.	Raman Spectra of Liquid $CF_3C(:NH)NH_2$ and $CF_3C(:ND)ND_2$..	134

LIST OF FIGURES (CONT'D)

Figure		Page
23.	Infrared Absorption Spectrum of Trifluoroacetamidine in CCl_4	136
24.	Infrared Absorption Spectrum of N-Methyltrifluoroacetamidine	136
25.	Raman Spectra of $CF_3C(:NH)NHCH_3$	148
26.	Raman Spectra of $CF_3C(:NH)N(CH_3)_2$	149
27.	Infrared Absorption of $CF_3CONHAg$	162
28.	Infrared Absorption of $CF_3C(NH)NHAg$	162

CHAPTER I

INTRODUCTION

Properties of Fluorocarbons and Derivatives

In recent years, a new series of compounds has developed in which hydrogen attached to carbon has been replaced with fluorine. Attention has been focused on these compounds because of the unusual and often unexpected properties which the fluorine atom imparts to the molecule. The research that followed the discovery of fluorocarbons and their derivatives has shown that their properties are very useful in examining and extending theories of chemical and physical behavior.

An excellent example to demonstrate these effects is furnished by the comparison of fluorocarbons and hydrocarbons. Fluorocarbons can be produced by the direct reaction of carbon with fluorine whereas hydrocarbons are not easily made from the elements. Hydrocarbons, when heated to a sufficiently high temperature, will lose hydrogen and form cracked products, unsaturated compounds, or carbon. On the other hand, one of the most striking characteristics of fluorocarbons is their high degree of thermal stability. Removal of hydrogen atoms, either singly or in pairs, from the carbon skeleton is more readily accomplished than the removal of fluorine atoms; a much higher energy of activation is required to initiate reaction for fluorocarbons than for hydrocarbons.

It has been shown experimentally that unbranched hydrocarbons possess an almost negligibly small dipole moment. Further, replacement of a hydrogen on a straight chain by a hydrocarbon radical does not significantly increase the dipole moment and indicates that the electrical symmetry is not greatly disturbed in the absence of secondary effects.

Habgood[1] and LaRochelle[2] reported experimentally determined dipole moments of 0 ± 0.03 Debye for n-butane and 0.13 ± 0.01 Debye for both i-butane and i-pentane. In a similar fashion, substitution of a fluorocarbon radical for a fluorine atom in a fluorocarbon also does not produce a detectable dipole moment, although a dipole moment is observed when the fluorine atom is replaced by either hydrogen or a hydrocarbon radical. Gibbs and Smyth[3] were not able to detect any measurable decrease of polarization with rising temperature for either n-C_5F_{12} or i-C_5F_{12}, indicating an absence of a dipole moment in both molecules.

The above observations suggest that hydrocarbons can be considered as derivatives of methane whereas fluorocarbons are derivatives of tetrafluoromethane. Similarly, organic ethers may be considered derivatives of water, and the fluorocarbon oxides derivatives of OF_2, fluorocarbon nitrides may be considered as derivatives from nitrogen trifluoride rather than from ammonia, and so on.

Because of the variation in properties between the fluorocarbon and hydrocarbon systems reactions of fluorocarbon derivatives may not be identical to analogous organic reactions. Rather, the reactions may vary from modified organic reactions to reactions uncommon to organic chemistry. This variation in reactivity has led to the formation of many interesting compounds.

Of the various fluorocarbon derivatives, considerable attention has been given to the fluorocarboxylic acids. Their increasing role in chemical synthesis is clearly illustrated by numerous recent references. The physical properties of the fluorocarbon acids differ from the organic acids, the most notable difference being their high acid

strength which perhaps is to be expected in view of the high electronegativity of the fluorine atom. The boiling points of the acids show a maximum for a given carbon chain when the number of fluorine and hydrogen atoms is approximately equal. Completely fluorinated carboxylic acids are observed to boil at a substantially lower temperature than that of the corresponding organic acids.

Preparation of the acids has been accomplished by most of the methods analogous to those of hydrocarbon chemistry. Trifluoroacetic acid was first prepared by Swarts[4], in 1922, by the oxidation of an aromatic compound containing the trifluoromethyl group. Oxidation of olefines and hydrolysis of compounds such as 1,1,1-trifluoro-2,2,2-trichloroethane also have been used in the preparation of fluorocarbon acids.

In the associated state organic carboxylic acids exist generally as dimers, accounting for the abnormally high boiling points. Similarly, the results of electron diffraction measurements of trifluoroacetic acid in the vapor phase at room temperature and at elevated temperatures[5] indicate that the fluorocarboxylic acids may also be dimeric, the bridge of the dimer in acetic acid being essentially unchanged by the substitution of fluorine for the hydrogen atoms in the methyl group. The OH-O distance across the bridge also remains relatively constant in either acid. The C-C bond distance in the dimer, however, was found to be approximately 4 percent lower in trifluoroacetic acid than in acetic acid. This shortening effect on the C-C bond distance by the fluorine atom has been observed in other fluorocarbons as well. The bond distances and the FCF angle of the CF_3-group were found to agree with the corresponding values for CF_3H. The orientation of the CF_3-group with

respect to the rest of the molecule as interpreted from intensity curves will be discussed in a later section.

Additional information on the structure of trifluoroacetic acid in both gaseous and liquid phases has been obtained from dipole moment[3] and dielectric constant studies[6-8], although discordant results have been obtained in the latter case. The contribution of the data will be discussed in detail in Chapter IV.

One branch of fluorocarbon chemistry which shows great promise, but which has been investigated only to a limited extent is that of nitrogen-containing fluorocarbons - the nitriles, for example. The chemistry of the organic nitriles is dominated by their unsaturated character. With the addition of the strong electronegative effect of the fluorine atom, the unsaturated character of the C≡N-group should show increased reactivity to such an extent that many of the reactions and products should be quite different from those expected for simple organic nitriles. In many reactions of the normal compounds, an acid catalyst is required to initiate the reaction and, in some cases, the acid is required to stabilize the product. In the preparation of amidines, for example, the ammonolysis of the nitriles is generally carried out in the presence of amine hydrochlorides.

The reactive nitrile structure may be pictured as

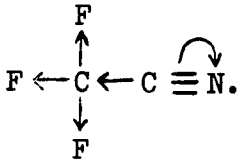
$$R\text{-}C\equiv N^{+\delta\ -\delta},$$

where δ represents a formal partial charge. In acid-catalyzed reactions presumably the proton combines with nitrogen, thereby enhancing the reactive carbon site to produce the following intermediate species:

$$R\text{-}C{=}NH^{\oplus}.$$

Oxley, Partridge, and Short[9] have shown that an equilibrium mixture is established from the reaction of amines and nitriles producing amidines. Amidines are generally more basic than either ammonia or the amines from which they are produced, and since they are carried out in the presence of an ammonium salt, the agent produced is an amidinium salt. The shift of the equilibrium is influenced by a number of factors, some of which act in opposition. If the temperature at which the reaction is carried out is lower than that at which the amidinium salt is dissociated, the equilibrium is disturbed and conversion of the nitrile into the amidine is promoted. Even though the presence of a stronger anionoid nitrogen base would facilitate addition to the nitrile, increase in strength of the base would decrease the amount of amidine which is converted into salt.

Fluorine-containing nitriles have the advantage that the cationoid properties of the unsaturated carbon of the cyano group become enhanced by the inductive effect of the fluorine atoms. The orientation in the addition reaction is indicated by the following tautomeric shift:



Thus, the molecule should be so reactive that in addition reactions, an acid catalyst is not necessary.

In agreement, Reilly and Brown[10] reported the preparation of trifluoroacetamidine by the addition of ammonia to trifluoroacetonitrile and found that an acid catalyst was not required. These authors

found the amidine unaffected by an equilibrium, because neither the base nor the amidine was competing for acid to stabilize itself, since there was no acid present.

One of the characteristic properties of simple organic nitriles is abnormally high boiling points. In the absence of the possibility of proton bonding, high boiling points may be ascribed to the large dipole moment of the molecule. The boiling points of acetonitrile and trichloroacetonitrile have been reported at 81.6° - 82.0°C and 85.7°C, respectively; however, the observed boiling point of trifluoroacetonitrile is -68.8°C. As a rule, trifluoromethyl compounds have a lower boiling point than the nonfluorinated analogues - trifluoroacetonitrile boiling 150° lower than acetonitrile is an extreme example.

A comparison of the melting points and boiling points of selected chloro- and fluorocarbon derivatives and their corresponding nonhalogenated analogues is shown in Table I.

TABLE I

MELTING POINTS AND BOILING POINTS OF CHLORO- AND FLUOROCARBON DERIVATIVES AND CORRESPONDING NONHALOGENATED ANALOGUES

Compound	M.p., °C	B.p., °C
CCl_3CN		85.7
CH_3CN		81.6 - 82.0
CF_3CN		-68.8
CCl_3COOH	58	195.5 (754 mm.)
CH_3COOH	16.7	118.1
CF_3COOH	-15.2	71.1 (746 mm.)
CCl_3CONH_2	141	238-9 (746 mm.)
CH_3CONH_2	81 (69.4)	222
CF_3CONH_2	74.9	162.5

Application of Molecular Spectroscopy in the Study of Fluorocarbons and Derivatives

The interpretation of the spectra of large molecules presents one of the basic problems in molecular spectroscopy. As a first approximation the molecule may often be treated as a composition of loosely connected units or groups, each forming an independent entity. Hence, many of the frequencies observed in the infrared and Raman spectra of polyatomic molecules may be correlated with vibrations localized in these units. Several of the unit frequencies are so constant that they may routinely be identified in molecules of unknown structure.

Unfortunately, while the spectroscopic technique may give very precise information on the polyatomic molecule, this method may not uniquely determine its structure. First of all, the complexity of the spectrum increases with the number of atoms present in the molecule causing the analysis of the spectrum to become unmanageable. Secondly, the high degree of symmetry usually associated with small molecules becomes practically nonexistent for large polyatomic molecules, thereby preventing the use of symmetry rules as aids in simplifying the structure determination.

The molecular structure and intramolecular forces in fluorine-containing molecules are of interest because of their bearing upon the theory of chemical binding. The analysis and characterization of these compounds by chemical methods have not been entirely satisfactory due to the relative inertness of the fluorocarbon group. Therefore, extensive use has been made of physical methods of identification, probably more so than in other fields of chemistry. The vibrational infrared and Raman spectra of simple fluorocarbons have been the subject of interest

in a number of investigations in recent years and work is rapidly being extended to include numerous fluorocarbon derivatives, as evidenced by increasing literature. Weiblen[11], for example, has compiled 150 infrared spectra of fluorocarbons and derivatives.

The vibrational assignments of various trifluoromethyl halides in both liquid and gas phases have been reported by a number of investigators.[12] The infrared and Raman spectra of a series of halogenated ethanes were obtained by Nielsen and coworkers[13], and the fundamental modes of vibration were assigned. Wait and Janz[14] investigated a series of halogenated methyl cyanides, CX_3CN, in which the X atom in the CX_3-group was progressively replaced by a more electronegative atom. A regular increase was observed in the C≡N stretching frequency through the series from CCl_3CN to CF_3CN.

The effect of the halogen atom on certain characteristic frequencies has also been observed in other molecules. Hartwell, Richards, and Thompson[15], as a result of their study of carbonyl stretching frequencies in a variety of compounds, reported a value of 1765 cm^{-1} for gaseous ethyl acetate. Fuson et al.[16] observed that in gaseous ethyl trifluoroacetate the inductive effect of α-fluoro-substitution raised the carbonyl stretching frequency to 1802 cm^{-1}. In saturated alkyl ketones, Thompson and Torkington[17] found the frequency of the stretching vibration of the carbonyl link lying close to 1710 cm^{-1}. However, the frequency of the same vibration for $(CF_3)_2CO$ lies nearly 100 cm^{-1} higher.

The above discussion represents a brief survey of the investigations of fluorocarbons and derivatives by spectroscopic methods

and of the effect of the highly electronegative fluorine atom on the spectrum of the molecule. A more detailed analysis of some representative spectra will be treated in later sections.

Statement of the Problem

Of the various fluorine-containing compounds that have been investigated spectroscopically, a general interest has been shown in simple molecules that contain a trifluoromethyl group. These studies have been limited, in general, to simple polyatomic molecules which have a fairly high degree of symmetry. The interpretation of the complex spectra of these particular molecules has been simplified considerably by means of group theory considerations. Further, any significant shifts in the "normal" characteristic frequencies of the simple system, with respect to its nonfluorinated analogue, may be attributed with considerable certainty to the perturbing influence of the electron attracting ability of the trifluoromethyl group. Examples of this effect were cited in the previous section.

Vibrational studies of molecules containing the C=O linkage have shown the importance of the characteristic carbonyl stretching frequency in structural analysis and theory of chemical binding. Extending these studies of the carbonyl group to include molecules such as trifluoroacetic acid and trifluoroacetamide might well provide additional data on acid and amide systems in addition to being valuable as further examples of trifluoromethyl group interaction on characteristic vibrations.

It is possible to investigate the vibrational spectra of the compounds by either infrared or Raman spectroscopy; the latter technique

was selected in the present case for several reasons. In particular, it allows the samples to be investigated in an all-glass system and eliminates the difficulties inherent in the use of rock salt or similar materials in sample cells. Furthermore, the Raman technique permits a wider spectral region of study which extends to quite low frequencies. Since several of the CF_3-group frequencies are expected in the 200-500 cm^{-1} region, the application of the Raman technique is a very convenient method of studying the region without requiring any change in the optical assembly.

Although the Raman spectrum of trifluoroacetic acid has been determined[16], polarization measurements of the bands were not reported. Analysis of the Raman bands in terms of polarization data might well permit some inference in regard to the symmetry of molecular association present in the liquid. Examination of the Raman spectra of gaseous trifluoroacetic acid both in monomeric and dimeric forms might also be valuable in indicating any significant change in association with change of state.

The early vibrational assignment of trifluoroacetamide by Fonteyne[18] now appears unsatisfactory, particularly in regard to the CF_3- and NH_2-group vibrations. In particular, the interpretation of recent association studies of amides by Richards and Thompson[19] is inconsistent with the assignments of the monomer and associated bands made by Fonteyne. These observations suggest that the Raman spectrum of trifluoroacetamide merits reinvestigation.

A logical extension of the investigation is to include the deuterated analogues of trifluoroacetic acid and trifluoroacetamide.

In addition, the N-methyl and N,N-dimethyl derivatives of trifluoroacetamide might be included in the plan of study particularly since no spectroscopic studies have been made on these derivatives. The proposed study of this series of closely related substances having the trifluoromethyl group in common, should prove valuable not only in establishing the general spectral characteristics of this type of compound but also in pointing out the more detailed effects resulting from coupling or chemical changes due to substitution.

Shortly after the preceding investigation was started, it became apparent that a further extension might be fruitful. This extension consisted of investigating a series of compounds in which the oxygen atom in the amide series was replaced by the isoelectronic NH-group, that is, the study of trifluoroacetamidine and the methyl derivatives. The spectroscopic study of the trifluoroacetamidine series was desirable for the following reasons:

a. The information provided by the spectra and by their comparison with the spectra of the isoelectronic amide series would serve as a cross check for the vibrational assignments of both the amide and amidine series.

b. The wider scope of the study would make it possible to compare the electron accepting effect of the trifluoromethyl group on the characteristic vibration of the C=NH group with the corresponding effect on the characteristic C=O frequency.

A complication to the interpretation of the spectral results is that hydrogen bonding is known to be present in the condensed phases

of several of the compounds. However, uncertainties in assigning the monomer and associated vibrations in other similar compounds have been resolved by studying the spectra in solution as a function of concentration. In this respect, infrared spectroscopy is particularly well adapted, especially in the study of very dilute solutions. The disadvantage of using the Raman effect is that prolonged exposure times are required for a satisfactory spectrum.

The observation of similar bands in the infrared spectra of sodium salts of carboxylic acids and acid amides led Lenormant[20] to conclude that these compounds had similar "resonating" structures. In view of the fact that the salts of trifluoroacetic acid, trifluoroacetamide, and trifluoroacetamidine are isoelectronic, it was thought that the spectra of these compounds would serve as additional supporting evidence for the common resonance structure.

CHAPTER II

THEORETICAL BACKGROUND

Brief Review of Vibrational Theory

Schrödinger's amplitude equation of a conservative system consisting of n particles (electrons and nuclei) and masses m_i is given by

$$\sum_{i=1}^{n} \frac{1}{m_i} \nabla_i^2 \Psi + \frac{8\pi^2}{h^2}(E - U)\Psi = 0,$$

where Ψ is the wave function; ∇_i^2 is the Laplace operator in terms of the coordinates of the ith particle; E, the total energy of the system; and U, the potential energy of the system. Theoretically, all molecular parameters may be derived from the above equation; however, solution of the wave equation has so far been possible for only the simplest molecules. Born and Oppenheimer[21], by making use of the fact that the mass of the nucleus far exceeds the mass of the electron, have shown that an approximate wave function for a molecule can be written as a product of the nuclear wave functions and the electronic wave functions. Thus, an approximate solution of the complete wave equation for a molecule is possible by considering the motions of the nuclei and electrons separately. The approximate wave equation in which only the vibrations of N nuclei are considered is

$$\sum_{i=1}^{N} \frac{1}{M_i} \nabla_i^2 \Psi_N + \frac{8\pi^2}{h^2}(E - V)\Psi_N = 0,$$

where M_i is the mass of the ith nucleus. In this equation V, the potential energy, is the characteristic electronic energy evaluated as a function of the nuclear coordinates. The theoretical calculation of

the electronic energy function requires the solution of the wave equation for the motion of the electrons, for which a satisfactory solution has been obtained for the simplest molecules only. Therefore, it is necessary to determine the electronic energy function empirically in order to obtain an approximate solution of the nuclear wave equation.

If the vibrations of the nuclei are restricted to small amplitudes, the potential energy may be expanded as a Taylor series in powers of the displacement coordinates q_i,

$$V(q_1 q_2 \cdots q_{3N}) = V_0 + \sum_i \left(\frac{\partial V}{\partial q_i}\right)_0 q_i + \frac{1}{2}\sum_{i,j}\left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_0 q_i q_j + \text{higher terms.}$$

For convenience the displacement coordinates are used since one is interested only in the internal energy of vibration. If the zero energy is chosen, such that V equals zero when q_1, q_2, and so forth are zero, then V_0 is zero. Likewise, the second term is zero because it is supposed, as a condition of equilibrium, that no forces are acting on the mass points when they are in their equilibrium positions. Neglecting higher terms, the final potential energy expression has only quadratic terms present, namely,

$$V(q_1 q_2 \cdots q_{3N}) = \frac{1}{2}\sum_{i,j}\left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_0 q_i q_j .$$

It is possible to eliminate the cross product terms by transforming the displacement coordinates q_i to normal coordinates Q_k ($k = 1, 2, \ldots, 3N$). The resulting potential energy expression contains only squares of Q's. Introducing the new potential energy expression into the nuclear wave equation results in the following:

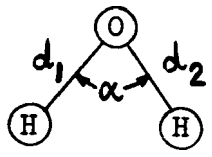
$$\sum_{k=1}^{3N} \frac{\partial^2 \psi_N}{\partial Q_k^2} + \frac{8\pi^2}{h^2}\left(E - \frac{1}{2}\sum \lambda_k Q_k^2\right)\psi_N = 0,$$

where $\Psi_N = \Psi_1(Q_1)\Psi_2(Q_2)\Psi_3(Q_3)\cdots\Psi_{3N}(Q_{3N})$. This equation can be separated into 3N one-dimensional equations, each of which is identical with the equation for the one-dimensional harmonic oscillator. Consequently, in this approximation the total energy of a molecule is the sum of the energies associated with each normal coordinate Q_k, where each normal coordinate is associated with a quantum number v_k and a normal frequency ν_k - the latter being the normal frequencies of vibration. However, six (five if the molecule is linear) of the 3N modes of vibration will have zero frequencies corresponding to translational and rotational motions of the molecule. Hence, the remaining 3N-6 (or 3N-5) normal coordinates describe the internal configuration of the molecule, without regard to its position in space. The normal coordinates can be represented by a linear equation involving changes in bond distances and interbond angles. Associated with the 3N-6 coordinates are 3N-6 normal frequencies of vibration. Each frequency represents the classical or fundamental value ν_k, obtained by a transition from the ground state to the state $v_k = 1$, where all other quantum numbers equal zero.

In order to simplify the calculation of the motions of a molecule very often symmetry coordinates, which are also linear combinations of the internal coordinates, are introduced. However, the choice of linear coordinates is not arbitrary, but is subject to certain restrictions if simplification is to be achieved.

For example, for the H_2O molecule, 3(3)-6, or three, symmetry coordinates are required. The internal coordinates are Δd_1 and Δd_2, the changes in the bond distances d_1 and d_2, respectively, and $\Delta\alpha$, the

change in the interbond angle α, as shown below:



A suitable set of symmetry coordinates would be:

$$R_1 = N_1(\Delta d_1 + \Delta d_2),$$

$$R_2 = N_2 \Delta \alpha,$$

$$R_3 = N_3(\Delta d_1 - \Delta d_2),$$

where N_i is a normalizing factor.

The molecule in its equilibrium position has a twofold axis of rotational symmetry and two mutually perpendicular planes of symmetry. By definition, the H_2O molecule belongs to the point group C_{2v}. There are two vibrations of the molecule that preserve all the elements of symmetry; these are classified as totally symmetric vibrations or type a_1. The third vibration places the molecule in a configuration that destroys two of the elements of symmetry and, therefore, is classified as an antisymmetric vibration or type b_2. In the above set of symmetry coordinates, R_1 and R_2 belong to type a_1; and R_3, to type b_2. For this particular symmetry group, the normal coordinates describing the fundamental vibrations are unique. Thus, the three vibrations are nondegenerate. In general, any nondegenerate normal mode of vibration will be either symmetric or antisymmetric with respect to any symmetry element of the molecule.

As a consequence of the presence of threefold or higher axes of symmetry in a molecule, two or more of the fundamental modes of vibration may be associated with the same frequency. This behavior, known

as degeneracy, is independent of the masses or force constants of the molecule. In addition to this type of degeneracy, there is encountered another type called "accidental degeneracy," which arises only when the masses and force constants have special values which cause two or more of the normal frequencies to become approximately equal. Furthermore, the latter effect may be observed in any molecule, regardless of symmetry. For a complete discussion of vibrational theory and the application of special techniques to the problems of molecular spectroscopy, several excellent texts are available.(22,23)

Infrared Absorption Theory

Infrared absorption bands arise as a result of transitions from some given vibration-rotation energy state to a higher vibration-rotation state. In most cases, the lower vibrational state is the ground state. Both the frequency and the intensity of an infrared band are of interest and particularly the conditions necessary for the interaction of the radiation field with the molecular field so that energy may be absorbed by the molecule. The interpretation of the gross features of the rotational spectra in terms of the rigid rotator is reasonably satisfactory. However, in order to explain the fine structure and irregular spacing of the rotational lines, one must take into account centrifugal distortion of the molecule with increased rotation and other higher order effects. The study of pure rotational spectra of polyatomic molecules is restricted because of experimental difficulties encountered. Since the possibility exists that a polyatomic molecule may have three different moments of inertia in the general case, the rotational structure may be quite complex. Furthermore, the spacing between the rotational lines

may be so small that complete resolution is nearly impossible experimentally.

The quantum mechanic treatment of vibrational transitions in terms of the harmonic oscillator model has been quite successful. This model accounts for fundamental vibrations which occur from the ground state to a state with one quantum of excited vibration. The appearance of overtone and combination frequencies, where the changes in vibrational quantum numbers are greater than one, must be explained by a more sophisticated concept. The restoring force in the simple harmonic oscillator model is proportional to the displacement and the potential function is proportional to the squares of the displacements. The inclusion of higher terms in the potential function, which introduces the so-called mechanical anharmonicity (third and higher powers of the displacements), results in the prediction of overtone and combination frequencies, as are observed.

In order to determine whether transitions may occur between vibrational energy states, it is necessary to calculate the transition probabilities. It can be shown by the methods of quantum mechanics that the vibrational transition probability is proportional to the square of the transition moments $[\underline{M}]^{nm}$, where the moments are defined theoretically by the following integral:

$$[\underline{M}]^{nm} = \int \Psi_n \, \underline{M} \, \Psi_m^* \, d\tau,$$

Ψ_n and Ψ_m^* are the vibrational eigenfunctions of the upper and lower states, respectively, and $\underline{M}$ is the dipole moment of the molecule. If the nuclei are not displaced too greatly from their equilibrium configuration, the dipole moment $\underline{M}$ may be expanded by a Taylor series in terms

of normal coordinates Q_i. The result is the following:

$$\underline{M} = \underline{M}^{o} + \sum_{k} \left(\frac{\partial \underline{M}}{\partial Q_k}\right)_o Q_k + \frac{1}{2} \sum_{k,l} \left(\frac{\partial^2 \underline{M}}{\partial Q_k \partial Q_l}\right)_o Q_k Q_l + \text{higher terms},$$

where $\underline{M}^{o}$ is the dipole moment in the equilibrium position. If the above terms are introduced into the integral defining the transition moments and the resulting expression analyzed term by term, the probable vibrational transitions involving the individual terms may be evaluated. The first term involving the permanent dipole moment $\underline{M}^{o}$ is zero because of the orthogonality relationship. The second term involving $(\partial \underline{M}/\partial Q_k)$ governs the appearance of fundamental frequencies. If the term is not zero, it follows that the dipole moment must change during vibration; otherwise the intensity is zero. If higher terms were neglected, then only the fundamental frequencies should be observed in the infrared spectra. The appearance of overtone and combination frequencies can be accounted for, however, by including the higher electrical anharmonicity terms.

The above discussion of infrared absorption spectra presents a brief outline of the parts of the theory considered relevant to the present investigation. In brief, the contributions of the rigid rotator and the harmonic oscillator to the appearance of the spectra have been discussed in terms of independent models, although the two concepts cannot be completely independent. Because the subject of rotation-vibration interaction is quite lengthy, it was excluded from consideration. The classical and quantum mechanical treatment of infrared theory as well as the topic of rotation-vibration interaction are discussed quite adequately by Herzberg.(22)

The Raman Effect

Smekal[24] predicted in 1923 that when light of any frequency ν_0 was scattered by matter, the scattered light should include radiation such as $\nu_0 \pm \nu$, where ν times Planck's constant would represent energy that was either absorbed or emitted by the molecule of the scattering material. In 1928, Raman[25] announced the discovery of this effect experimentally. Raman initially thought the effect was an optical analogue of the Compton effect.

It is unfortunate that there are terms that are used in common in describing both fluorescence and the Raman effect, since the two phenomena should be distinguished. Fluorescence represents the complete absorption of the incident light quantum by a molecular species. From the resulting excited state, the molecule decays by light emission to various lower states only after a certain mean lifetime. In general, the lines of this emitted spectrum are observed to be of lower frequency than the exciting radiation. Only wavelengths which are absorbed by the molecular species are effective in the production of fluorescence. In contrast to this, the Raman spectrum may be excited by light of any frequency which does not correspond to an energy transition of the molecule. In terms of the quantum mechanical approach, the Raman effect is observed when a photon of energy h ν_0 (ν_0 being the frequency of the incident light) strikes a molecule in a given stationary state. The incident photon can be scattered elastically, in which case its frequency remains unaltered, and the molecule remains in its initial ground state (Rayleigh scattering). Alternatively, the photon can be scattered inelastically, giving up part of its energy to the scattering system or taking energy

from it. In this latter case, the light scattered will differ in frequency from the Rayleigh scattering by the energy difference, $h(\nu_0 - \nu_r)$, between the initial and the final vibrational level. The energy of the incident photon is therefore decreased (or increased) by the amount $h\nu_r$ and the scattered photon has the frequency $\nu_0 \pm \nu_r$. The frequencies of light scattered with smaller energies than that of the exciting light give rise to Stokes Raman lines. In contrast, photons which appear with higher frequencies than the exciting light frequency yield anti-Stokes Raman lines. Since these latter lines involve molecules initially in vibrationally excited states, their intensity is always lower than that of the Stokes lines. Experimentally, one may observe a spectrum containing both Stokes and anti-Stokes lines and, in addition, the frequency of the incident light (Rayleigh scattering). The Raman lines generally show large differences in their intensity and in their width. The magnitude of the frequency shifts of the Raman lines is a measure of the resultant exchange of energy of the molecules by the scattered photons. Regardless of the light source, the displacements in terms of energy from the exciting line are the same for a given molecule; thus, the Raman displacements are characteristic of the scattering molecule.

It can be shown from quantum mechanical theory that the intensity of a Raman transition between states n and m is proportional to the square of the scattering moment. The moments are defined in terms of the tensor elements by the following integral:

$$P_{ij}^{mn} = \int \psi_m^* \alpha_{ij} \psi_n \, d\tau,$$

where α_{ij} is one of the six components of the polarizability tensor, Ψ_m^* is the complex conjugate of the wave function for the initial state m, and Ψ_n is the wave function for the final state n. The above integral, defining line intensity in the Raman spectrum, is analogous to the result derived for line intensity in infrared absorption. Because the polarizability components (and dipole moment components) are difficult to determine, the integral usually cannot be evaluated. However, whether the integral for a particular transition is identically zero or not may be determined from the symmetry properties of the integrand. Since the vibrational wave function can be written as a function of the normal coordinates, Q_k, the symmetry properties of the wave functions can be determined by examining the symmetry properties of the normal coordinates. In the case of nondegenerate vibrations, the wave functions are even and odd functions of the normal coordinates (the nondegenerate Q's always transform into $\pm$ Q). Because the integral of an odd function between symmetrical limits about zero is always zero, then at least one of the six integrands (each involving one of the six components of the polarizability tensor) must be totally symmetrical, that is, an even function, if the transition probability is to be finite. For fundamental vibrations, the initial state is the ground state and the final state represents any one of the normal vibrations raised to the first excited state. Since the ground state has a totally symmetric wave function (invariant to all symmetry operations) and since both the excited state and the normal coordinate describing the latter state have the same symmetry, then the only excited states to which transitions are permitted by the Raman effect are those which have the same transformation properties as the

components of α. The polarizability components are functions of the normal coordinates also and therefore will be transformed by the symmetry transformations permitted by the molecule. For each point group, the transformation properties of the polarizability components have been worked out and may be found in the literature. Herzberg[22] has compiled the species of the six tensor elements for all important symmetry groups and from these data the activity (active or inactive) of a particular fundamental vibration in the Raman effect may be readily determined for the given molecule. Similar considerations for dipole moment components lead to the prediction of the activity of fundamental vibrations in infrared absorption. An important point to note, however, is that even though a particular transition is allowed, for example, in the Raman spectrum, there is no assurance that the intensity will be of sufficient magnitude so as to permit the line to be observed in the vibrational spectrum. The selection rules for overtone and combination frequencies are developed in a similar fashion by examining the symmetry properties of the wave functions of other vibrational levels.

A measurable experimental quantity which is of considerable assistance in Raman spectroscopy is the state of polarization of the individual Raman lines. Theoretical considerations show that the degree of polarization of a Raman line is related to the symmetry of the molecular vibration from which the line originates. Classically, isotropic molecules such as methane should scatter completely polarized light in the plane normal to the incident beam, regardless of whether the incident light is polarized or unpolarized. Observing the scattered light of a sample of randomly oriented molecules with a beam of polarized light one finds, however, that the scattered radiation is not completely polarized.

The depolarization results from vibrations which destroy certain elements of symmetry in the molecule. Moreover, the degree of depolarization is found to depend on whether the incident beam is polarized or unpolarized. If the exciting beam is traveling in the -y direction and the scattered light is observed in the x direction, then, if the exciting radiation was polarized in the z direction, the degree of depolarization, ρ , is defined by the ratio of the observed intensity of light polarized in the y direction to that polarized in the z direction. For a non-polarized incident beam, the degree of depolarization ρ_n is given by $2\rho/(1+\rho)$, and ρ_n may assume any value between zero and 6/7 for Raman lines. Lines corresponding to totally symmetric vibrations of the molecule have depolarization ratios between zero and 6/7 and are classified as polarized Raman lines. Lines corresponding to non-totally symmetric or asymmetric vibrations have a ratio of exactly 6/7 and are said to be depolarized. The assignment of a particular vibration as a polarized or depolarized line is difficult when the depolarization ratio has a value very close to 6/7, since it is difficult to measure this ratio experimentally with high precision. For example, the techniques used ir the present work prevent convenient simultaneous observation of the intensity of the parallel and perpendicular components of the scattered light. Instead, the depolarization ratio is determined qualitatively from successive exposures using incident light with the electric vector polarized first parallel and then perpendicular to the observation direction. The theoretical ratios using this procedure are the same as above. If a comparison of the two exposures shows noticeable differences of intensity indicating a depolarization ratio of $\ll 6/7$, the line may be

assigned with reasonable certainty to a totally symmetric vibration. Although it is difficult to measure the depolarization ratio accurately, it has played an important part in simple molecules in the recognition of totally symmetric vibrations. The interpretation of characteristic vibrations such as C-H stretching bands, for example, is based ultimately on these measurements.

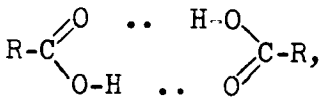
CHAPTER III

PRESENT STATUS OF STRUCTURAL AND VIBRATIONAL PROBLEMS OF CARBOXYLIC ACIDS, AMIDES, AND RELATED COMPOUNDS

Structural Evidence and Bonding in:

Carboxylic Acids

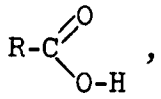
The boiling points of carboxylic acids are not far from those of alcohols of comparable molecular weight, but are much higher than those of alkanes of similar molecular size. The explanation of the abnormal boiling points of the acids is the same as that for the alcohols, namely association by proton bonds. However, the acids form double molecules, or dimers:



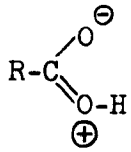
which are more stable than the associated complexes formed by the alcohols. The existence of dimers has been established by cryoscopic determinations in hydrocarbon solvents and by electron diffraction measurements on the vapor. Investigations of high molecular weight normal fatty acids have shown that dimers are also found in the solid.[26,27] However, the lower members of the series, formic and acetic acids, form hydrogen bonded chains rather than dimers in the solid.[28-29] It is of interest to note that Karle and Brockway[5] in their investigation of HCOOH and CH_3COOH found the two C-O distances in the unassociated molecules to be distinctly different as expected, the shorter distance being comparable to the C-O distance in ketones and the longer corresponding to that observed in ether linkages. In the dimer, the shorter C-O bond remained

unchanged, but the longer C-O bond became approximately 0.06 Å shorter than in the monomer. However, further conclusions from the dimer study indicated that the two hydrogen atoms were not located in the center position in the respective OH-O bonds, and that the OH-O distance across the bridge was substantially the same in the dimers of both compounds.

The only conventional structure that can be written for the carboxylic acids is the following:



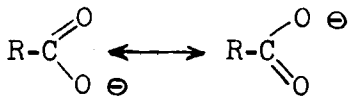
although a further structure may be involved in the resonance,



Any large contribution of the latter form to the ground state of the molecule ought not be very great because of the form's instability due to the wide separation of charge. This view appears to be confirmed by the findings of Bates and Hobbs.(30) The close agreement between the observed dipole moment and vector addition of accepted bond moments for the covalent structure of carboxylic acids led these authors to conclude that the contribution of the resonance form to the ground state of the molecule was of minor significance. Further, electron diffraction data show two carbon-oxygen distances in monomeric formic acid or acetic acid identical within experimental error with the single and double bond distances.

In contrast, when ionization of carboxylic acids occurs, giving the COO^- group, there is present neither a single nor a double bond in

the ion but a bond symmetrically encompassing all three atoms. The two CO bonds are identical as shown by x-ray diffraction. The observed CO distance is 1.27 Å in the formate anion[31], whereas the double bond distance between a carbon and oxygen atom in a normal carbonyl group is 1.24 Å, and the distance of a single bond between the two atoms is 1.43 Å. Further supporting evidence is obtained from spectroscopic data. Infrared and Raman data on a number of carboxylic acids indicate that salt formation results in the disappearance of the characteristic carbonyl frequency and its replacement by a band at lower frequency. These observations suggest that the $RCOO^-$ ion is a resonance hybrid composed of the two polar resonance forms



Thus, the resonance energy of the carboxylate ion is much greater than that of the undissociated carboxyl group. The source of the resonance energy arises from the ability of an electron to encompass three or more nuclei instead of two (delocalized mobile electrons).

Acid Amides and Derivatives

The recognition that certain biological reactions were closely related to molecular configurations of proteins has been the impetus for an intensive study of proteins. Investigations of related compounds such as amino acids and amides have been carried out in conjunction with the direct studies on proteins.

A knowledge of the detailed structure of amides is particularly desirable because of the role the amide group plays in compounds containing a peptide bond. Consequently, experimental methods employed in

investigations of unsubstituted and substituted amides have included the measurements of the dielectric constants, dipole moments, x-ray diffraction, Raman effect, infrared absorption, ultraviolet absorption, and nuclear magnetic resonance. Unfortunately, the interpretations of the results by the various investigators have not been in complete agreement.

From the results of the x-ray diffraction study of crystalline acetamide, Senti and Harker[32] concluded the following:

a. The skeleton of the acetamide molecule was planar.

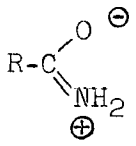
b. The molecule existed in the keto form.

c. The N-H bonds were in the plane of the molecule.

d. The formation of hydrogen bonds intramolecularly was unlikely.

The authors assumed the direction of the NH-O bridge was the direction of the bond from one of the terminal atoms in the bridge to hydrogen. Consequently, the hydrogen atoms were located indirectly.

The rather large value of the dipole moment for the amide group has usually been considered as arising from large contributions estimated between 30 and 40 percent, of the highly polar resonance form[33]



One important point about this ionic form is that the quadrivalent nature of the nitrogen atom demands that the $CONH_2$-group be planar. Evidence for the support of the resonance theory of amides has been cited by Mizushima et al.[34] From the comparison of the observed Raman and infrared frequencies, and from dipole moments results, these authors concluded that the contribution of double bond character to the C-N

linkage of N-methylacetamide was appreciable and that the stable configuration was most likely the trans form.

In addition, the NMR spectra of N,N-dimethylamides have been successfully interpreted in terms of restricted rotation about the C-N amide bond by Phillips.[35] A re-evaluation of the NMR spectra of several substituted amides led Gutowsky and Holm[36] to the conclusion that the presence of a significant amount of double bond character in the C-N bond was proved.

However, Bates and Hobbs[30] have stated that the structure of the amide group does not require significant contributions from the above polar resonance form and that vector addition of accepted bond moments for a planar covalent structure can account for almost all observed dipole moments. To support this contention, Worsham and Hobbs[37] measured the electric moments of several N-monosubstituted amides in dilute benzene solutions and observed that the results agreed with the results of a simple bond moment vector addition without having to consider the polar form. In order to explain the shortened C-N bond distance in amides as compared to the "normal" C-N single bond distance in amines, in the absence of the polar resonance form, increased overlap in the sp^2 orbitals over that for pure p orbitals was postulated. In addition, the data indicated that the amide group was planar and that the N-H bond of the amide group was trans to the carbonyl group. Further, since the electric moment of the associated species was observed to be larger than that of the monomer, it was concluded that the monosubstituted amides associated to form linear species. This view was in contrast to the rings or dimers suggested by Hobbs and Bates[38] for the case of

unsubstituted amides. The most that can be said at the present time regarding the polar resonance form is that this form probably contributes to the ground state of amides but the extent is not known with certainty.

Interpretation of Vibrational Frequencies of:

Carboxylic Acids

From the interpretation of the spectra of a considerable number of carboxylic acids, six major bands have been suggested as characteristic of the COOH-group. These are observed at approximately 3500, 3000, 1700, 1400, 1250, and 900 cm^{-1}. Assignments of two or three bands are still not yet entirely satisfactory. The assignment of the frequencies at 3500, 3000, and 1700 cm^{-1} is straightforward, the bands being assigned to the free OH stretching vibration, the associated OH stretching vibration, and the carbonyl C=O stretching vibration, respectively. It should be noted that the frequency of the associated OH stretching vibration has been observed to vary in a number of carboxylic acids. Thus, the 3000 cm^{-1} value assigned to this vibration is at best approximate.

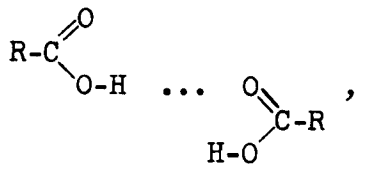
There has not been general agreement as to the detailed assignment of the strong band in the 1400 cm^{-1} region. From a study of association effects in several compounds, Davies(39) concluded that the 1400 cm^{-1} band was due to the deformation vibration δ(C-O). Hadzi and Sheppard(40), on the other hand, assigned the band to the deformation vibration δ(OH) in-plane, based on a study of several normal and deuterated carboxylic acids.

The detailed assignment of the 1250 cm^{-1} region band likewise has not been resolved satisfactorily. Davies assigned the frequency to the δ(OH) in-plane, whereas Hadzi and Sheppard assigned the stretching vibration ν(C-O) to a frequency at approximately 1300 cm^{-1}. On the basis of bands observed in acetic acid-d_4, Herman and Hofstadter[41] assigned the band at 1282 cm^{-1} to the C-O vibration.

Both Davies[39] and Hadzi and Sheppard[40] agreed that the band observed at approximately 930 cm^{-1} was due to the deformation vibration δ(OH) out-of-plane. The situation is complicated by the fact that in a mixture of monomer and associated molecules, two frequencies corresponding to the δ(OH) in- and out-of-plane vibrations for the monomer should be observed, as well as two frequencies corresponding to the associated deformation vibrations δ(OH) in- and out-of-plane.

In addition to the main bands just cited, many submaxima appear in the broad associated hydroxyl vibration band and various combination hypotheses have been proposed to explain the observed structure. Recently, an alternate hypothesis by Fuson and Josien[42] has been proposed in which they suggest that the proton may occupy different positions of equilibrium between the two oxygen atoms in the OH-O chain, each position corresponding to a different quantized ground state energy level of the dimeric molecule. Each absorption peak might then be correlated with a transition from a particular ground state to a first excited state. In view of the shortcomings of the combination band hypotheses as outlined by the above authors, the "multiple ground state energy level" hypothesis appears to adequately explain the series of equally spaced submaxima. However, this view fails to account for the many remaining submaxima observed in this region.

In still another hypothesis, Feneant[43] has proposed that the multiplicity of the submaxima in the spectrum of the associated band may be due simply to the existence of different kinds of polymers: ring dimers, chain dimers

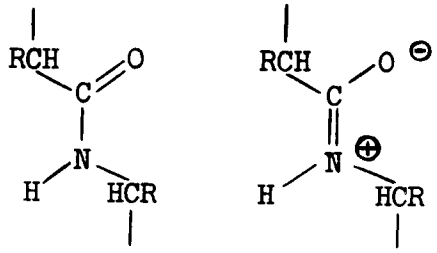


and chain polymers of different lengths. None of the suggestions appears completely satisfactory and the correct explanation is still uncertain.

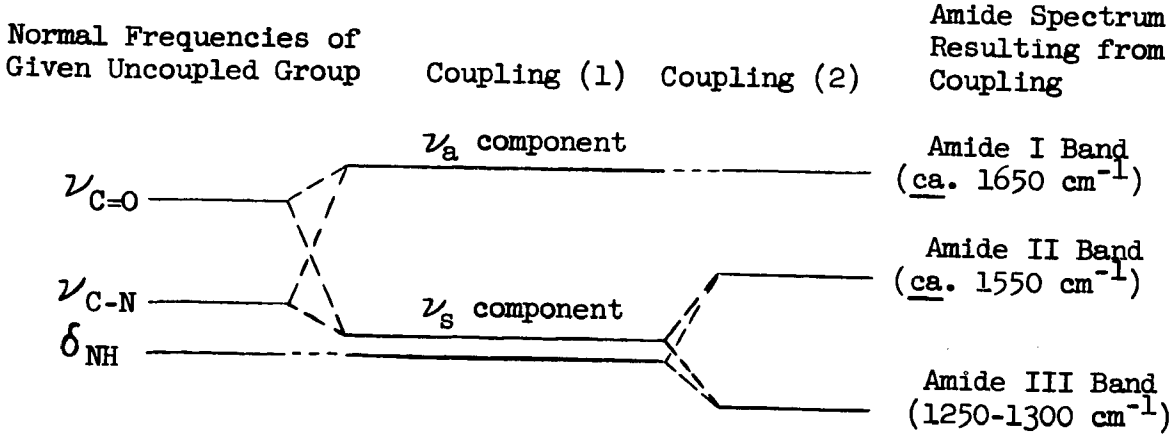
Acid Amides and Derivatives

The application of molecular spectroscopy to the study of amides has been of interest to many investigators. In particular, a large amount of work has been done on monosubstituted amides owing to their importance in the structure of proteins and in the ORSD penicillin program. Two characteristic bands at 1650 and 1550 cm^{-1} are observed in RCONHR' molecules in which R and R' are in the trans position with respect to each other. These bands are commonly designated as amide I and amide II bands, respectively.[44] Molecules in which R and R' are in the cis position show only one band at 1650 cm^{-1}. The assignment of the amide I band to the C=O stretching frequency has been generally accepted. However, the assignment of the amide II band of the trans form has given rise to much controversy. Randall et al.[44] and Letaw and Gropp[45] assigned the band to the C-N stretching vibration. On the basis of its absence in a study of N,N-disubstituted amides, Richards and Thompson[19] assigned the amide II band to the deformation of the

NH-group in the plane of the molecule. Subsequently, Fraser and Price[46] pointed out that considerable mechanical coupling would occur between the C=O and C-N bond vibrations in view of possible resonance between the two structures,



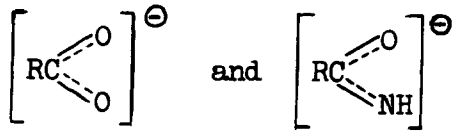
Two resultant modes of vibration involving the C, N, and O atoms were postulated. One mode, regarded as the out-of-phase component (principally C=O stretching mode), was assigned to the amide I band. The other mode, the in-phase component, had a calculated frequency very nearly equal to that of the NH bending vibration. Under these circumstances coupling between the two vibrations was considered to occur with the appearance of two new bands. One band was identified with the NH bending frequency observed near 1550 cm^{-1} (amide II band). The other band was confined to mainly carbon and nitrogen atoms and was tentatively assigned to the band observed at ca. 1270 cm^{-1} (amide III band). The overall interaction that occurs among the C=O, C-N, and NH band vibrations for monosubstituted amides is shown in the following schematic diagram:



In disubstituted amides, RCONR'R", the amide II band has not been observed. Miyazawa et al.[47] have suggested that it is probably due to the inability to identify the characteristic symmetrical stretching frequency of the OCN-group, ν_s. As cited above, there is considerable coupling between ν_s and δ(NH) so that the amide II band of monosubstituted amides is shifted to a higher frequency and can, therefore, be identified as a characteristic amide band. However, in the case of disubstituted amides, there is no N-H bond and, hence, no coupling. As a result, the ν_s band appears near the region of the C-H deformation frequencies and is not easily identified. The ν_s band has been identified, however, for $CH_3CON(CH_3)_2$ at 1497 cm^{-1} and for CH_3CONH_2 at 1406 cm^{-1}.

In order to explain why the amide II band has not been observed in monosubstituted amides in the <u>cis</u> form, it was suggested that little or no coupling takes place between ν_s and the deformation vibration δ(NH), so that the ν_s band remains undefined in the C-H deformation region.

A study of the infrared absorption spectra of the sodium derivatives of both the acid amides and the carboxylic acids by Lenormant[20] led to the conclusion that the two groups had similar "resonating" structures,



since in both cases the characteristic carbonyl band was not present and had been supplanted by a band at a lower frequency.

CHAPTER IV

STRUCTURE AND VIBRATIONAL FREQUENCIES ASSOCIATED WITH THE CF_3-GROUP

The normal modes of vibration of the trifluoromethyl group may be described in terms of internal modes and in terms of modes arising because the group is attached to the rest of the molecule. The isolated group has a pyramidal configuration with the carbon atom at the apex and the three fluorine atoms forming an equilateral triangular base, similar to the configuration of the ammonia molecule. Therefore, three stretching and three bending modes should be present. As a consequence of the symmetry of the molecule, not all six modes of vibration may be distinct. If the trifluoromethyl group shows a threefold axis of rotational symmetry then the group will have four degenerate vibrations (two degenerate pairs).

With respect to the rest of the molecule, the group may show rocking motions and a twisting or torsional motion. If the molecule possesses only a plane of symmetry, in which case the point group is C_s, the rocking motions should be distinct. That is, the rocking motion of the group may take place both in the plane and perpendicular to the symmetry plane of the molecule. Thus, the CF_3-group may contribute at most nine modes of vibration; however, whether all nine vibrations can be distinct will be determined by the symmetry of the molecule.

Examples of molecules containing a trifluoromethyl group and belonging to the point group C_s are shown in Table II. Vibrations that are symmetric and antisymmetric with respect to the plane of symmetry are labeled type a' and type a", respectively. The compiled frequencies

TABLE II

FUNDAMENTAL FREQUENCIES (IN cm^{-1}) OF THE CF_3-GROUP FOR MOLECULES OF C_s SYMMETRY

Compound	C-F Stretch			CF_3 Deformation			CF_3 Rock		CF_3 Torsion	Reference
	a''	a'	a''	a'	a'	a''	a'	a''		
CF_3CF_2Cl	1224	1349	1240	560	647	593	364	332	--	13b
CF_3CFCl_2	1247	1292	1218	505	588	559	312	331	--	13b
CF_3CH_2Cl	1152	1262	1285	537	639	455[a]	191[b], 358[b]	330[b]	109	13c
CF_3CHCl_2	1140	1270	1226	526	671	554	185[b], 263[b]	218[b]	141	13c
CF_3CH_2I	1098	1210	1252	513	626	537[a]	142[a]	355[a]	94	48
CF_3CHO	1145	1305	1200	708	837	528	266	320	184	49
CF_3COCl	1190	1279	1237	584	710[a]	--	202	400	68[c]	48
$CF_3NO(g)$[a]	1181	1250	1298	542	731	542	438	438	200[c]	50

[a] Results from infrared absorption spectrum.

[b] Assigned as rocking modes.

[c] Inferred.

for the most part were obtained from Raman spectra, except for the few indicated which were observed in the infrared absorption spectra. It is interesting to note that many of the C-F vibration bands varied from weak to medium intensity in the Raman spectra, while the corresponding bands in the infrared spectra were among the strongest observed.

One may generalize from the above data that the C-F stretching vibrations occur in the 1140-1300 cm^{-1} region and the deformation vibrations in the 500-700 cm^{-1} range. The rocking motion frequencies should be expected to lie in the region from approximately 200 to 450 cm^{-1} based on previous assignments (Table II). The range of the torsional vibration is difficult to determine since the intensity of this type of vibrational band is usually very weak in the Raman effect and very few data are available.(51)

Present Status of Structural and Vibrational Problems of Trifluoroacetic Acid and Derivatives

Trifluoroacetic Acid (methyl trifluoroacetate, trifluoroacetate ion)

Several of the physical properties of this acid have been investigated, in order to determine whether the inductive effect of the trifluoromethyl group appreciably alters the structure of the molecule from that normally found for carboxylic acids and particularly acetic acid. Electron diffraction studies(5) indicate that trifluoroacetic acid, like acetic acid, is associated in the vapor at room temperature and consists principally of dimers. The bridge structures of both trifluoroacetic acid and acetic acid dimers were found to be nearly identical. However, the value of the C-C bond distance in trifluoroacetic acid (1.48 ± 0.03 Å) was observed to be significantly shorter than in acetic

acid (1.54 ± 0.04 Å). The determined C-F bond distance of 1.36 ± 0.03 Å and FCF angle of 109 ± 2° were in agreement with the corresponding values for CF_3H, the FCF angle approximating the regular tetrahedral value.

The orientation of the CF_3-group was of some interest in the electron diffraction investigation. However, the intensity curve obtained for a 15° orientation of a C-F bond out of the plane of the carboxyl group was indistinguishable from one closely resembling a curve for free rotation. In addition, the electron diffraction results did not give any direct information concerning the carboxyl group because of the high scattering power of the CF_3-group, but it was possible to rule out an intramolecular hydrogen bond between oxygen and fluorine from the evidence that the CF_3-group was free to rotate or vibrate in arcs of large magnitude.

By assuming the hydroxyl hydrogen does not lie to any great extent in the plane of the rest of the carboxyl group, Gibbs and Smyth(3) by vector addition of group moments calculated a dipole moment of 2.50 Debyes which agreed with the experimentally determined value of 2.28 D. for the monomer. Their calculations indicated that the hydroxyl group could undergo a torsional oscillation or restricted rotation with the hydrogen moving out of the OCO plane.

The dielectric constant of liquid trifluoroacetic acid was initially determined by Simons and Lorentzen.(6) They reported relatively large values (39.0 at 20°C) and found the dielectric constant to increase with increasing temperature. The values were much larger than those reported by Smyth and Rogers(52) for acetic acid (6.13 at 20°C). Subsequently, Dannhauser and Cole(7) and later Harris and O'Konski(8) re-evaluated the dielectric constant of trifluoroacetic acid. Both groups

observed lower values (8.42 and 8.55, respectively, at 20°C) of the dielectric constant and a negative temperature coefficient. The results thus indicate that the liquid also consists largely of dimer molecules. Harris and O'Konski suggested that the high values obtained by Simons and Lorentzen were probably due to polarization effects which the latter investigators neglected to evaluate.

The application of infrared and Raman spectroscopy to the study of trifluoroacetic acid has been the subject of several recent papers. However, the interpretation of the vibrational spectrum has been sufficiently complicated by the association present that uncertainties in the assignments still exist. The maximum symmetry which the trifluoroacetic acid molecule can possess is a plane of symmetry. However, from the results of the electron diffraction and dipole moment studies cited previously it appears that the molecule may not even have this low order of symmetry. Consequently, the use of group theory methods as aids in assigning vibrations of the molecule do not appear to be as useful as for other molecules possessing higher orders of symmetry.

Fuson et al.[16] have reported the infrared and Raman spectra of light and heavy trifluoroacetic acids. They found the acids in the vapor state at room temperature to be composed of a mixture of monomer and associated molecules. The vibrations of the COOH- and COOD-groups were identified for both monomeric and associated molecules by a comparative study of the two acids as pure liquids, in the vapor state at various pressures, and in carbon tetrachloride solutions at various concentrations. They observed a sharp band in the infrared vapor spectrum of CF_3COOH at 3587 cm^{-1} and a broad band centered at approximately 3000 cm^{-1}, corresponding to the monomer and dimer O-H stretching vibrations,

respectively. The carbonyl stretching absorption band was resolved into two bands at 1826 and 1788 cm^{-1} in the gaseous trifluoroacetic acid spectrum at low pressure. In the liquid state, a very broad Raman band was observed centered about 1770 cm^{-1}.

The deformation vibration, δ(C-O), was assigned to the 1400 cm^{-1} band for both the normal and the deuterated acid for the following reasons:

a. The frequency remained largely unchanged in going from CF_3COOH to CF_3COOD.

b. In the deuterated compound, the band was resolved into two components. The higher frequency component increased in intensity at higher pressures and greater concentrations, which indicated the frequency was an associated vibration. Therefore, the authors concluded that the absorption was produced by a bending vibration rather than a stretching vibration.

The assignments of the OH and OD bending vibrations in the trifluoroacetic acids by Fuson et al. were based on variations of intensities of both monomer and associated bands with change of state (vapor and liquid) and with change of pressure of the vapor. A complete study of the hydroxyl band in the light acid was not possible because of strong neighboring absorption bands in the 1130 cm^{-1} region.

The stretching vibration, ν(C-O), of the monomer was assigned to a medium weak band at 1300 cm^{-1} in the vapor spectrum of the light acid. In the dimer, both the stretching vibration ν(C-O) and the deformation vibration δ(OH) in-plane were assigned to the very strong band at 1203 cm^{-1}.

The monomer and dimer O-D stretching vibrations were observed at 2648 cm^{-1} and at approximately 2370 cm^{-1}, respectively, in the vapor spectrum of CF_3COOD. At low pressure the carbonyl stretching absorption band was resolved into two bands at 1823 cm^{-1} and 1784 cm^{-1} in the infrared spectrum; the frequencies remaining almost unchanged with respect to the C=O frequencies observed in the spectrum of the normal acid. The corresponding Raman band of CF_3COOD was observed at 1760 cm^{-1} in the liquid state.

No distinct unassigned band was found at the position in the spectrum of CF_3COOD where the monomer ν(C-O) band was expected to appear. The associated ν(C-O) vibration was assigned by Fuson et al. at 1155 cm^{-1} in the vapor spectrum.

A reinvestigation of the infrared absorption spectrum of trifluoroacetic acid vapor was reported by Kagarise.(53) He concluded that the uncertainties due to hydrogen bonding in the acid could be resolved satisfactorily by studying the vapor at different temperatures; the investigation of the acid by Fuson et al. was carried out at a single temperature (25°C). Kagarise observed both monomer and dimer species in the vapor at room temperature, while at 100°C, the vapor was predominantly monomeric, in agreement with the results of the electron diffraction study. Partial vibrational assignments of the two species were then made on the basis of intensity variations of the bands with temperature. The previously reported spectrum of the heavy acid(16) was used as an aid in assigning the vibrations involving hydrogen motion.

The observed frequencies and assignments of the two studies are shown in Table III for comparison purposes. The numerous bands observed in the OH and OD stretching regions have not been included except

TABLE III

INFRARED FREQUENCIES AND ASSIGNMENTS FOR CF_3COOH AND CF_3COOD IN THE VAPOR STATE

CF_3COOH Frequency (cm^{-1}) (See Ref.53)	Assignment*	CF_3COOH Frequency (cm^{-1}) (See Ref.16)	CF_3COOD Frequency (cm^{-1}) (See Ref.16)
3587	m, OH stretching	3587	2648
3134	a, OH stretching	3144	2366
1830	m, C=O stretching	1826	1823
1792	a, C=O stretching	1788	1784
1466	a, C-O stretching	1203	1155
1415	m, C-O stretching	1300	1243
	a, C-O deformation	1465	1432
	m, C-O deformation	1465	1384
1350	m		
1297	a, OH deformation in-plane	1203	1039
1240	m,a, C-F stretching	1244	1243
1199	m,a, C-F stretching	1182	1187
1122	m, OH deformation in-plane	1130	993
903	a, OH deformation out-of-plane	1123	798
	m, OH deformation out-of-plane	904	667
823	a, C-C stretching	825	798
706	a, OCO deformation	708	667

TABLE III (CONT'D)

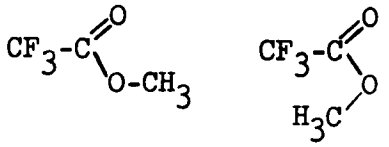
CF_3COOH Frequency (cm^{-1}) (See Ref.53)	Assignment*	CF_3COOH Frequency (cm^{-1}) (See Ref.16)	CF_3COOD Frequency (cm^{-1}) (See Ref.16)
673	m --		
665	m, OCO deformation		
661	m --		
596	a, CF_3 deformation		
580	m, CF_3 deformation		
521	a, CF_3 deformation		
507	m, CF_3 deformation		

* a = associated; m = monomer

for the fundamental modes of vibration. It is to be noted that the interpretation of several of the monomer-dimer bands by the two investigations are incompatible. Two additional bands at 1350 cm^{-1} and 1415 cm^{-1} were observed by Kagarise in the spectrum of trifluoroacetic acid which were not reported in the earlier study. The Raman spectra of trifluoroacetic acid and the deuterated acid in the liquid state were used to supplement the observed frequencies in the infrared absorption spectra. In addition, the Raman spectrum extended the region of study below 700 cm^{-1} which was inaccessible in the infrared work. A partial assignment was made by Fuson et al. of the Raman bands appearing in the region below 700 cm^{-1}. However, the assignment of the CF_3 twisting vibration to the strong Raman line at 260 cm^{-1} appears to be doubtful. In comparable compounds, as shown in Table II, the torsional vibration is usually found at lower frequencies and the intensity of the Raman band is generally quite weak. The asymmetric rocking vibration of the CF_3-group was tentatively assigned to one of three bands in the 400-450 cm^{-1} region by Fuson et al.

Although the Raman spectrum of methyl trifluoroacetate was determined by Hermann recently(54), neither the frequencies nor the vibrational assignments were reported. It has been noted that the stretching vibrational frequency of the carbonyl group in normal esters lies near 1765 cm^{-1} in the vapor state. However, in ethyl trichloroacetate the frequency is shifted upwards to 1786 cm^{-1}.(15) In the series: acetic acid, trichloroacetic acid, and trifluoroacetic acid, the carbonyl stretching frequency increases, as well as the acidity. This same trend in the carbonyl stretching frequency of the methyl ester series should be expected.

The methyl trifluoroacetate molecule presumably has a planar configuration involving the heavy atoms, and hence, the molecule has at most one plane of symmetry. Further, assuming hindered rotation around the C-O bond, there are two configurations possible for this molecule, cis (I) and trans (II).



(I) (II)

In the case of similar molecules such as methyl formate and methyl acetate, the cis configuration has been assumed on the basis of spectroscopic data[55], dipole moment measurements[56], and electron diffraction studies.[57]

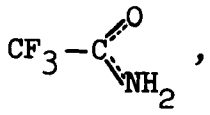
The early vibrational assignment of sodium trifluoroacetate by Fonteyne[58] led to the conclusion that the results were consistent with a resonance hybrid model. The vibrational assignment of the observed frequencies was based on the CF_3-group retaining a C_{3v} symmetry. Further, the configuration of the molecule which was considered most likely was the one in which the plane formed by a fluorine atom and the two carbon atoms bisected the OCO angle.

The potential barrier which the carboxyl group has to overcome by rotating around the C-C axis was considered by Fonteyne to be very high due to the repelling forces between the fluorine and oxygen atoms. He concluded that a relatively high frequency should be associated with this torsional vibration and, therefore, assigned the frequency of 1216 cm^{-1} to the vibration. With respect to recent vibrational analysis of

trifluoromethyl compounds several of the assigned vibrations of the trifluoroacetate ion proposed by Fonteyne appear unacceptable.

Trifluoroacetamide

An early attempt to resolve the concept of the polar resonance form for acid amides was carried out by Fonteyne[18] through the use of Raman spectroscopy. He considered the normal covalent structure and the polar resonance form of trifluoroacetamide to contribute equally to the ground state of the molecule. Fonteyne further concluded that the resonance structure of the amide could be represented as



on the basis of similar vibrational assignments observed in the study of the trifluoroacetate ion cited previously. The effect of dilution on the monomer-dimer equilibrium was investigated to a limited extent. It should be noted that several of the bands attributed to the CF_3-group vibrations and to both the monomeric and the dimeric NH_2-group vibrations are incompatible with assignments of recent vibrational studies.

CHAPTER V

EXPERIMENTAL PROCEDURES

Preparation of Compounds

With the exception of trifluoroacetic acid, which was available commercially, two different procedures were used in the preparation of the samples. One process involved the use of standard bench-top synthetic methods. The other was concerned with preparatory work conducted in a vacuum line. The use of the closed system permitted the condensation reaction producing the relatively nonvolatile amidines from the volatile materials to take place in situ. In addition, the deuterated compounds were prepared very conveniently in the system. The vacuum line shown in Figure 1 proved to be satisfactory in all respects. The left half of the manifold, labeled A, furnished the necessary apparatus for synthesizing the samples. The right half of the manifold, B, provided access to the fractionation train for purifying the samples.

Regardless of the procedure used, no difficulties were encountered in the preparations of the samples. At most, three-step syntheses were required, but the majority of the preparations were accomplished by one-step, standard organic reactions with few modifications. Fortunately, many of the preparation yields were in excess of 75 percent. The methods of preparation and analyses of the materials are listed in the Appendix.

Preparation of Samples for Obtaining Raman Spectra

In the initial phase of research, several problems were encountered in regard to the techniques used in preparing Raman samples.

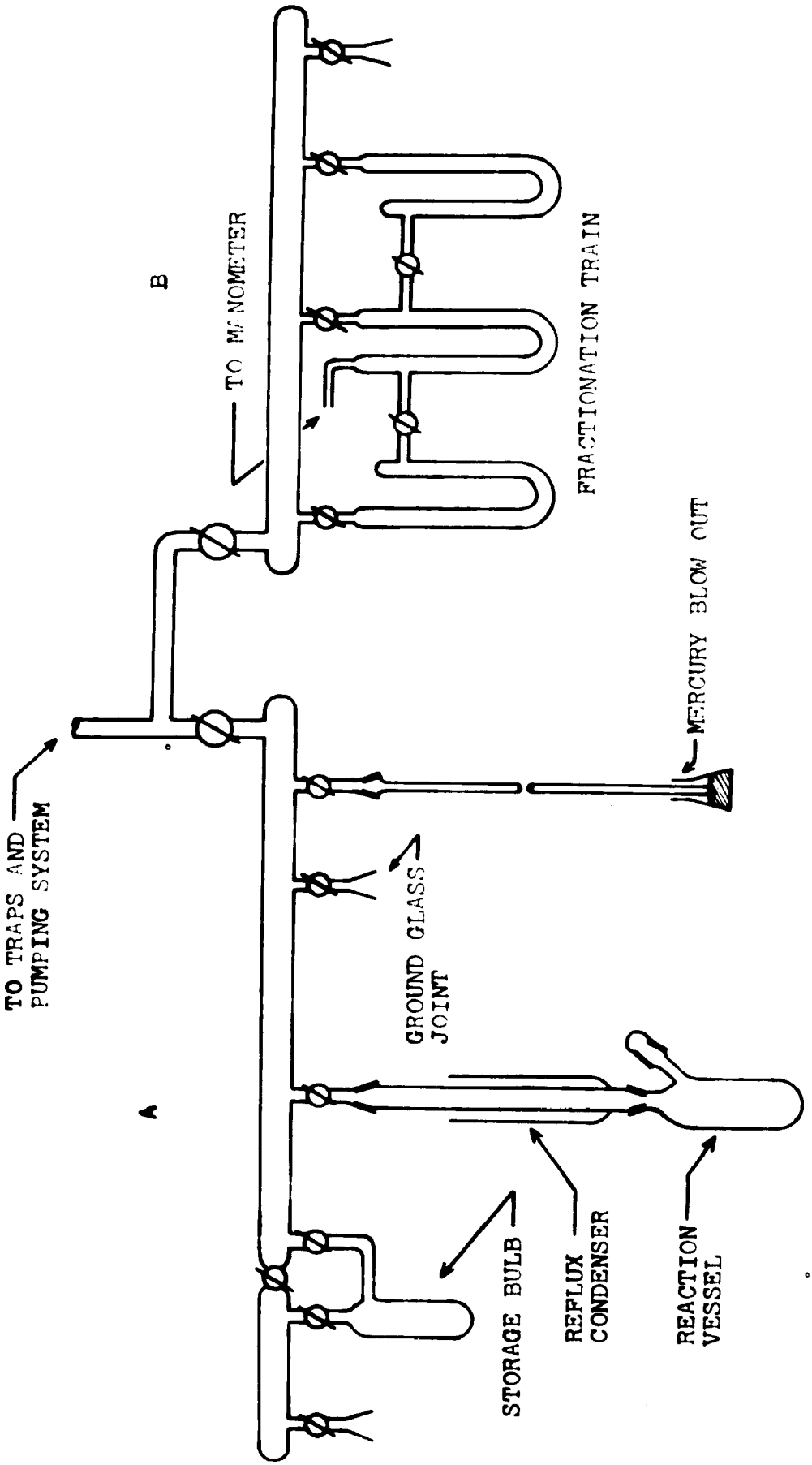


Figure 1

VACUUM LINE USED IN PREPARATION OF RAMAN SAMPLES

Rigorous exclusion of all dust particles and other foreign matter was required as a matter of course. In addition, trace quantities of stopcock grease in the sample were sufficient to produce strong fluorescence bands in the spectrum; in extreme cases, the entire region of study was obscured. The effects of Tyndall scattering and fluorescence were minimized by careful purification of the samples and thorough cleaning of the Raman tubes. The tubes were treated with hot chromic acid solution and rinsed with distilled water followed by steaming prior to using. The manner in which the Raman tubes were filled was also critical. Because the method varied with the state of the sample being investigated, the purpose of the present section is to discuss briefly the techniques in terms of these variations. It should be noted that suitable spectra were obtained by using a volume range of 1.5 to 15 milliliters.

Gas Samples

In the case of trifluoroacetonitrile, a Raman gas tube was attached to the vacuum line and the system evacuated. The tube was then cooled with liquid nitrogen, and the purified CF_3CN vacuum-transferred into the tube. After the tube was sealed off under vacuum, the frozen material was allowed to warm up. A sufficient quantity of trifluoroacetonitrile was used in order to develop approximately four atmospheres at room temperature when the material vaporized.

Solution Samples

The Raman spectra of the sodium and silver salts of trifluoroacetic acid could be obtained most conveniently as saturated aqueous solutions. A saturated solution of the recrystallized sodium salt in

triple distilled water was prepared, treated with Norite, and subsequently filtered through an ultrafine sintered glass filter directly into the Raman tube. The sample of the silver salt was prepared in a manner identical to that used for the sodium salt.

Pure Liquid Samples

This category included the following: trifluoroacetic acid, trifluoroacetic acid-d, methyl trifluoroacetate, N,N-dimethyltrifluoroacetamide, trifluoroacetamidine, trifluoroacetamidine-d_3, N-methyltrifluoroacetamidine, and N,N-dimethyltrifluoroacetamidine. The method of preparing the Raman sample consisted of fractional distilling the pure liquid directly into the Raman tube, collecting the middle fraction only. The distilling apparatus used a 15 cm vacuum jacketed column packed with glass helices. The first four compounds were distilled at atmospheric pressure, whereas the remaining were vacuum distilled.

It was necessary to exclude atmospheric moisture by suitable methods during the distillation of the deuterated compounds. After completing the distillation, the Raman tubes were quickly sealed.

Pure Liquid Samples (Molten State)

Since both the ordinary and the deutero trifluoroacetamide and N-methyltrifluoroacetamide were crystalline solids at room temperature, a different technique of preparing the Raman samples was required. The relatively low melting points of the amides made it experimentally possible to determine the Raman spectra of the compounds in the molten state. The sample preparation used was developed after several earlier methods had failed. The spectra obtained from the first few samples

of trifluoroacetamide made it apparent that purification of the compound was critical because of a fluorescent impurity which remained even after several recrystallizations of the amide from an ethyl ether-petroleum ether mixture. This complication was eliminated by the following sublimation procedure.

After recrystallizing twice from the ethyl ether-petroleum ether solution, approximately 10 g. of trifluoroacetamide was placed in a bulb and the latter attached to the vacuum line. In order to remove any residual solvent, the material was evacuated for one hour. The amide was then slowly vacuum sublimed into a trap cooled by a Dry Ice-isopropyl alcohol slush bath over a period of approximately five hours.

A small quantity of the initial and final phases of the sublimation was discarded. The trap-to-trap sublimation process was repeated several times to assure the removal of any impurities such as stopcock grease, dust, and so forth. After the final sublimation was completed, dry nitrogen gas was admitted into the evacuated system until the pressure was in slight excess of atmospheric. The bulb containing the purified trifluoroacetamide was removed from the vacuum line, quickly capped, and stored in a desiccator until the Raman sample was prepared.

The apparatus used in the preparation of the Raman samples is shown in Figure 2. The apparatus was attached to the vacuum line by means of the ground glass joint marked B. After the apparatus was thoroughly evacuated, dry nitrogen gas was admitted through the fine sintered glass frit into the apparatus. A drying tube containing barium oxide was attached to the side arm A, and the system flushed with dry nitrogen gas for approximately one hour after the stopcock in the side arm

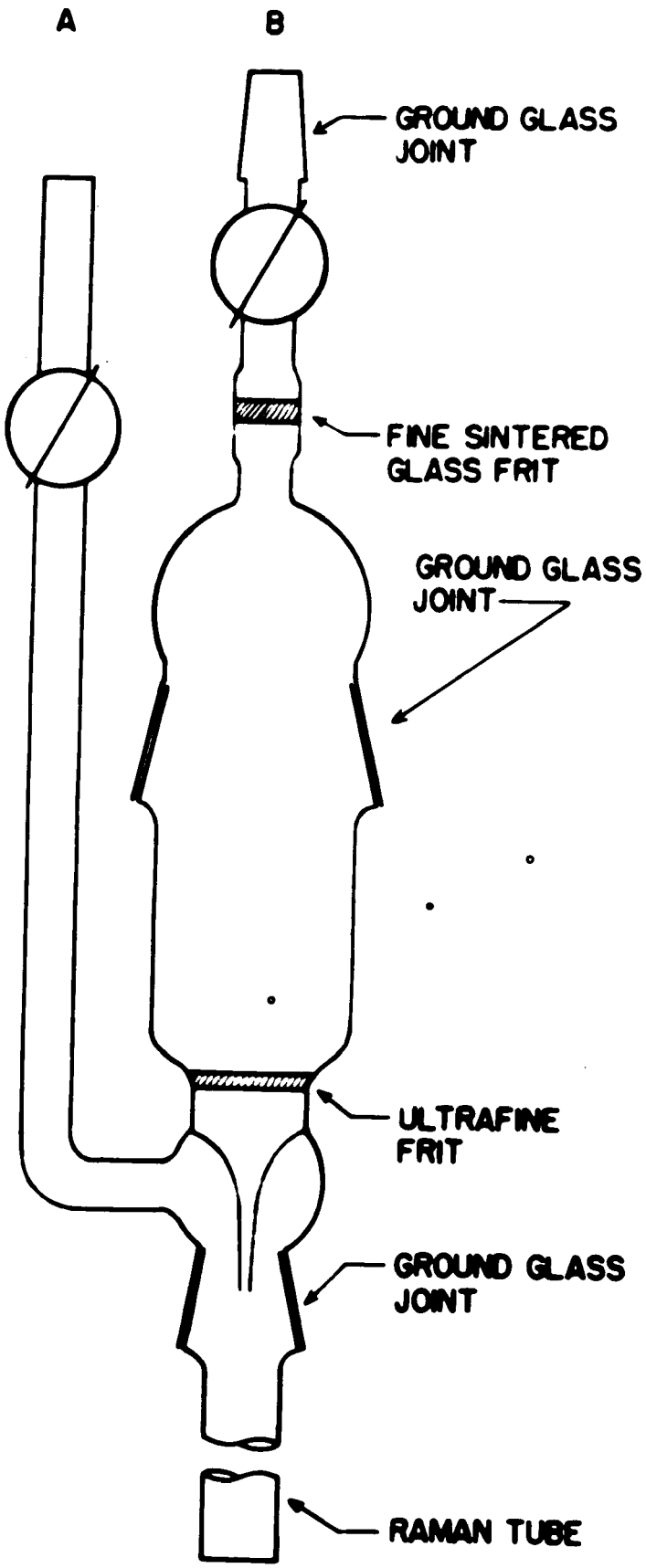


Figure 2
APPARATUS USED IN THE PREPARATION OF LOW MELTING SOLID SAMPLES

was opened. Both stopcocks were then closed, and the apparatus including the sample bulb containing the purified trifluoroacetamide was transferred to a dry box. Sufficient crystalline trifluoroacetamide to fill the Raman tube was transferred from the bulb to the chamber of the apparatus. The cap was greased lightly and was held in place by springs. A capillary tube was also filled for melting point determination. Upon removal from the dry box, the apparatus was attached to the vacuum line and the system evacuated. Dry nitrogen gas was readmitted through the joint B into the apparatus until the system was brought to atmospheric pressure. The entire apparatus was then warmed to approximately 80°C by bringing a quart Dewar flask filled with hot water up around it; the temperature being sufficient to melt the amide. The pressure of the dry nitrogen in the system was increased slowly and by regulating the pressure by means of the stopcock in the side arm of the apparatus, the molten material was forced through the ultra-fine sintered glass frit into the Raman sample tube. After the material filtered into the Raman tube, the Dewar was removed, the nitrogen gas pressure was reduced, and the sample was allowed to cool to room temperature. The Raman tube was then removed and quickly capped. Raman samples of deutero trifluoroacetamide and N-methyltrifluoroacetamide were prepared in an analogous manner. This procedure was successful in producing a sample sufficiently free from fluorescence to permit the observation of a satisfactory Raman spectrum.

Solution Studies of Hydrogen Bonded Compounds

Hydrogen bonding in several of the compounds was investigated by studying the effects of dilution in an inert solvent on the spectra.

Substances investigated in this way were: trifluoroacetamide, trifluoroacetamide-d_2, N-methyltrifluoroacetamide, trifluoroacetamidine, trifluoroacetamidine-d_3, N-methyltrifluoroacetamidine, and N,N-dimethyltrifluoroacetamidine.

Initially, the Raman spectrum of a 20 percent solution of trifluoroacetamide in purified dioxane was obtained. Further dilution proved impractical because of the prolonged exposure time required for a satisfactory Raman spectrum. Moreover, the selection of dioxane as a solvent appeared to be an unsatisfactory choice since the results of this preliminary study were found to be inconsistent with the findings of the amide dilution study reported by Richards and Thompson.(19) It appears likely that these anomalies may be due to complex formation between trifluoroacetamide and dioxane. The study of the solutions was repeated using carbon tetrachloride as the solvent. Because of the low solubility of the compounds in CCl_4, the investigation of the dilute solutions necessitated using infrared spectroscopy as the means of differentiating between the monomer and associated bands.

Saturated solutions of the compounds in this solvent, with the exception of N-methyltrifluoroacetamide and N,N-dimethyltrifluoroacetamidine, were prepared by weighing a suitable volume of CCl_4 and adding the particular compound until the undissolved material was visible. The solution was weighed and the approximate concentration of the saturated solution calculated. The concentrations were found to vary between 0.1 and 1.5 percent among individual saturated solutions. The N-methyltrifluoroacetamide was appreciably soluble in CCl_4 and a solution of approximately 4 percent was prepared. A solution of similar concentration of N,N-dimethyltrifluoroacetamidine in CCl_4 was prepared.

Because of the rapid exchange of the deuterated compounds in the presence of atmospheric moisture, it was necessary to prepare these solutions in the dry box. All dilutions were performed in apparatus that had been previously baked in the oven and transferred to desiccators to cool to room temperature.

Spectrographic Equipment

Infrared Spectrometer

The infrared spectrometer used in the investigation was a Perkin-Elmer Model 21 Double Beam Spectrometer employing NaCl optics. All work was done at room temperature, 20°C. In order to compensate for the solvent bands in the spectra of the solutions, a Perkin-Elmer variable thickness liquid absorption cell was used. The cell containing the solvent was placed in the reference beam and adjusted until the solvent absorption band just slightly over compensated the absorption of the solvent in the sample cell.

Sample cells having cell path lengths of 0.1 mm and 5 mm were used. The former cell was a standard Perkin-Elmer liquid cell. The latter cell, of similar construction, used a circular Teflon spacer of 5 mm thickness. Filling of the cells was done with a hypodermic syringe. After filling, the orifices were sealed with special Teflon plugs. The 0.1 mm sample cell was required for concentrated solutions with strong solute absorption bands. The Model 21 computed transmittance automatically and the spectrum was scanned linearly in frequency units (cm^{-1}).

Raman Spectrograph

An inherent disadvantage in the Raman effect is that the intensity of the scattered light is very weak. Consequently, special

techniques are required to study the effect. Radiation that enters the sample is scattered in all directions by the randomly oriented molecules, but only the part that is scattered perpendicular to the incident radiation is convenient to study spectroscopically. In this manner, any stray or direct radiation from the source is less likely to reach the detecting device. Unfortunately, the weak intensity of the scattered light is further reduced by observing only a fraction of the total scattered radiation. In order to obtain a satisfactory exposure, exposure time for spectrographic equipment may require several hours. Great strides have been made in the last few years in developing spectrophotometers with increased speed. Advantage of improved systems and components which give high light gathering power and freedom from the effects of scattered light have aided greatly in the improvement. Recording times as short as five minutes for a complete record have been reported.

The basic requirement in studying the effect is an intense source of monochromatic radiation. The mercury vapor arc has proved the most generally useful, although other vapor arcs have been used. The light source used in the present investigation was a Toronto type spiral mercury arc.(59) The helix consisted of 32 mm Pyrex tubing wound into three complete turns. The mercury reservoirs were water-cooled with cold fingers projecting well above the surface of the mercury. Whenever the arc was in operation, cold water was circulated through the cold fingers. The arc was operated at 220 volts direct current. By means of ballast resistors connected in series with the arc, various operating currents could be selected. In this investigation, a current of 24 amperes was normally used and gave satisfactory results.

In order to concentrate the light more effectively on the sample, a coat of bright platinum metal was deposited on the outer half of the coil. Although platinum is not as efficient a reflector as silver or chromium, the possibility of easily forming a reflecting layer on the arc itself resulted in a favorable gain in intensity as compared to a reflector of a more efficient metal located at some distance from the arc. The metal coating was easily prepared by painting a solution of an organo-platinum complex on the glass surface. The dried material was then flamed with a gas-air hand torch until only the platinum metal residue remained. The loss of scattered light was further minimized by partially enclosing the arc within a cylindrical reflector of chromium plated brass, the curved surface serving also as a light shield.

One of the great advantages of the mercury spectrum is the number of fairly widely separated intense lines. The most commonly used lines are the blue 4358 Å line, the violet 4047 Å line, and the green 5461 Å line, in that order. The mercury spectrum contains no lines of appreciable intensity between 4358 and 4916 Å, leaving a region of approximately 2600 cm^{-1} for investigation. Since any one of the mercury frequencies may give rise to a Raman shift, overlapping of the Raman lines from the various exciting frequencies may occur despite the relatively wide separation of the mercury frequencies. These complications are largely eliminated, however, by use of special filters which selectively absorb or reduce the intensity of undesirable exciting frequencies; thus, isolating the preferred mercury frequency. In addition, the background due to the continuous radiation of the source may be cleared up by the appropriate choice of filters. In this investigation the blue

4358 Å line was used exclusively. In order to reduce the intensity of the 4047 Å line, the light from the arc was passed through a cylindrical filter jacket containing a nearly saturated solution of sodium nitrite in water. The solution in the filter jacket was continuously circulated through a heat exchanger to dissipate the heat produced by the arc. The arrangement of the arc and filter jacket is shown as a cross section in Figure 3. The cylindrical inner filter jacket served as an additional means of reducing the intensity of undesirable exciting frequencies. Since this particular unit was self contained, interchange of various filter solutions was convenient. The filter solution most commonly used in the inner filter jacket was one of rhodamine 5GDN extra dye and p-nitrotoluene dissolved in isopropyl alcohol. This solution was useful in reducing the intensity of the mercury lines in the region 4600-5400 Å.

The glass Dewar flask shown in the inner filter jacket was designed primarily to serve as an insulating device for maintaining sample temperatures below room temperature. By means of a suitable arrangement, precooled dry air was passed into the air inlet located at the bottom of the flask. Temperatures as low as -130°C could be maintained. In the present research, the flask was used to maintain the samples at room temperature only since this study was not concerned with low temperature measurements. The light scattered from the sample in the downward direction passed through flat Pyrex plates at the bottom of the inner and outer walls. The light, in turn, was reflected by a mirror into the spectrograph.

During the investigation of the solid samples at temperatures above room temperature, it was necessary to replace the Dewar flask with

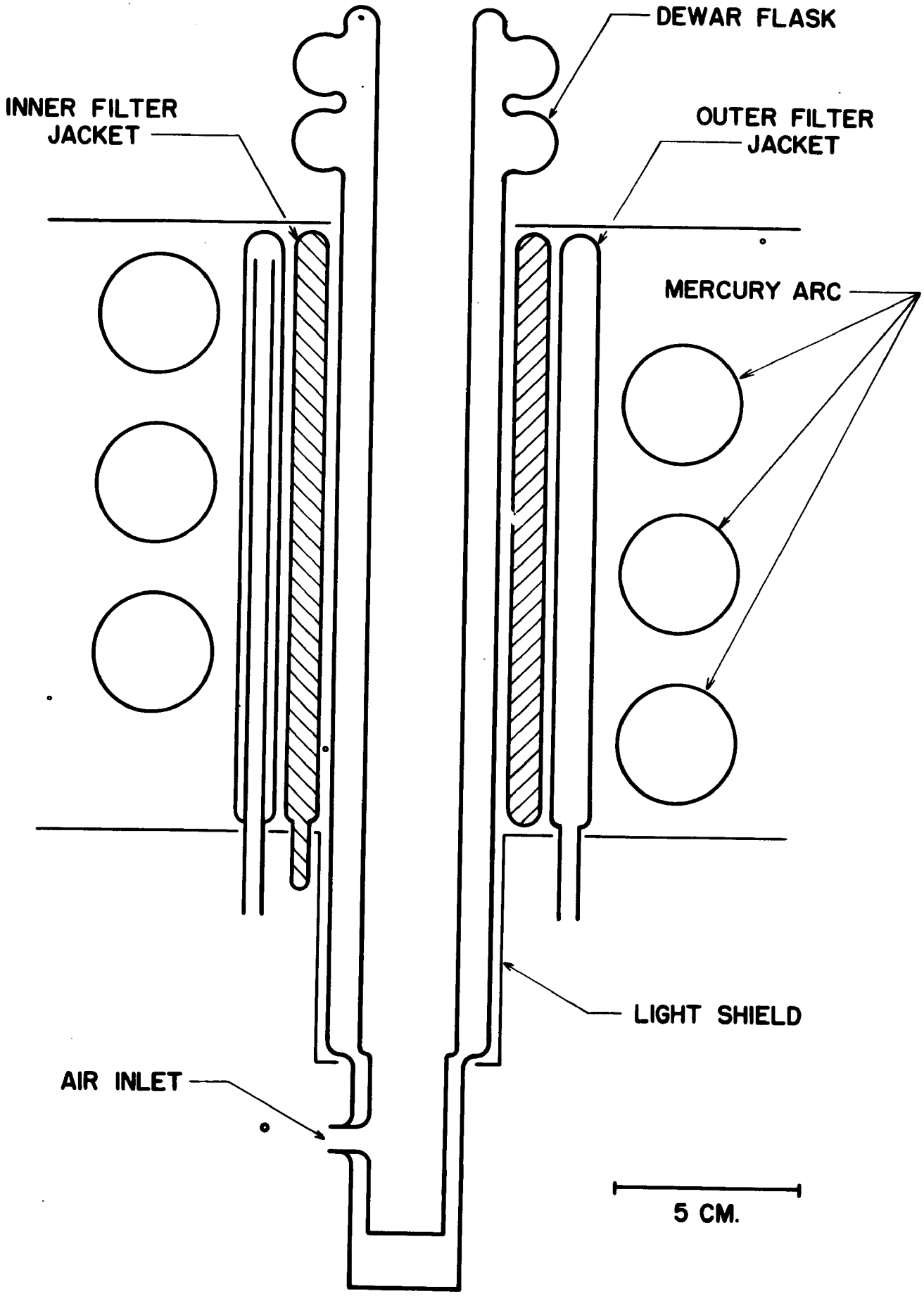


Figure 3
RAMAN LIGHT SOURCE ASSEMBLY

the apparatus shown in Figure 4. The glass apparatus was constructed to include a single flat Pyrex plate at the bottom of the wall. The compounds were melted by circulating warm air around the sample. This was accomplished by use of an electric heater which blew heated air into the apparatus through the side arm inlet. A thermocouple was placed inside the apparatus alongside the sample to measure the temperature, which did not exceed 85°C for any of the compounds. The temperature of the air stream was varied by adjusting the current of the heater, allowing temperature control within 1°C in a normal operation.

The Raman tubes containing the sample under investigation were supported and centered in a sample holder as shown in Figure 5. It was designed to fit snugly into either the Dewar flask or the high temperature apparatus. A set of interchangeable collars made it possible to use Raman tubes of various diameters.

The state of polarization of the individual Raman lines was determined qualitatively from two successive exposures of the sample using incident light with the electric vector polarized parallel and perpendicular, respectively, with the direction of observation. The technique involved placing a cylinder of Polaroid film around the supporting posts of the tube holder. The orientation of the film determined the polarization characteristics of the exciting light. Collimating baffles were used to assure the incident beam was perpendicular to the observed scattered beam. The limited space between the sample and the outer filter jacket prevented the simultaneous use of both the inner filter jacket and the baffles. Under these circumstances, a plastic film(60) incorporating both rhodamine and p-nitrotoluene was used as a substitute for the inner

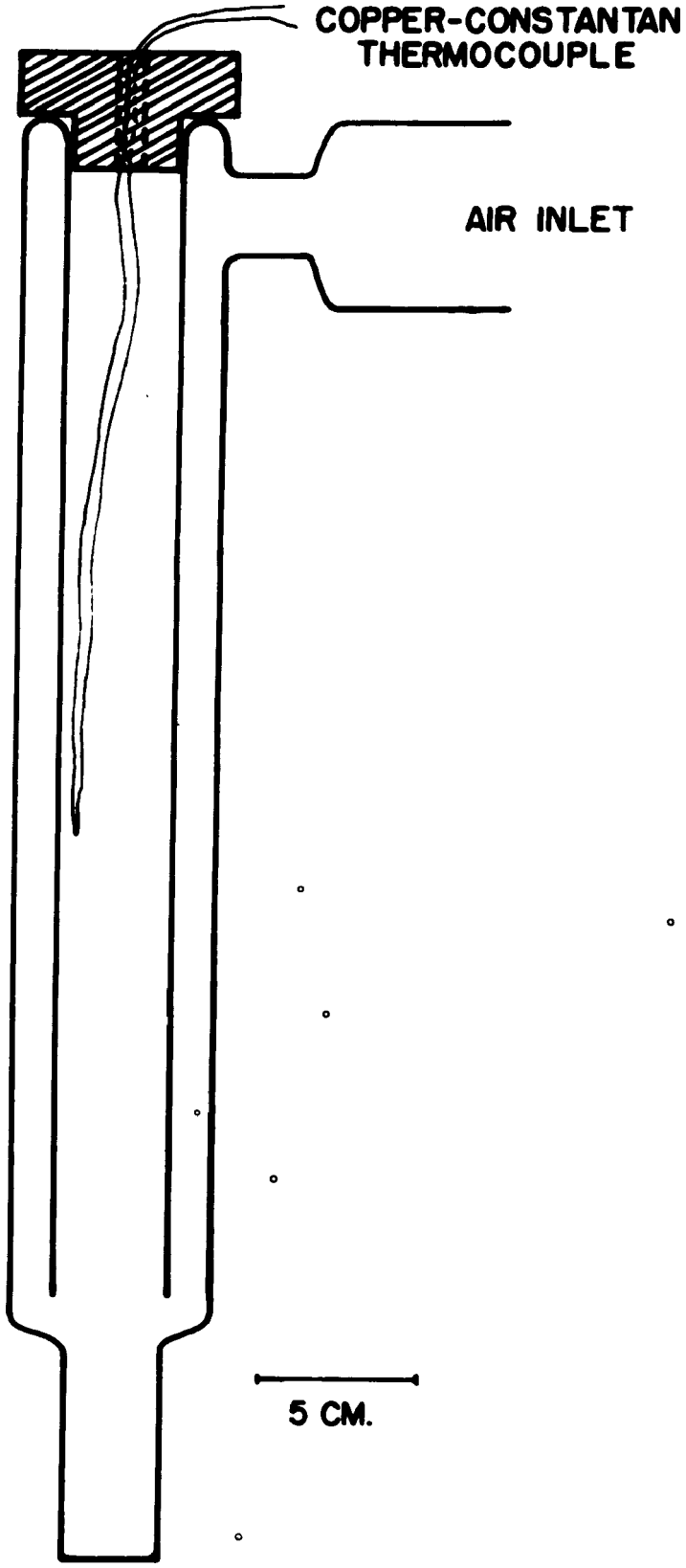


Figure 4
APPARATUS USED FOR MOLTEN SAMPLES

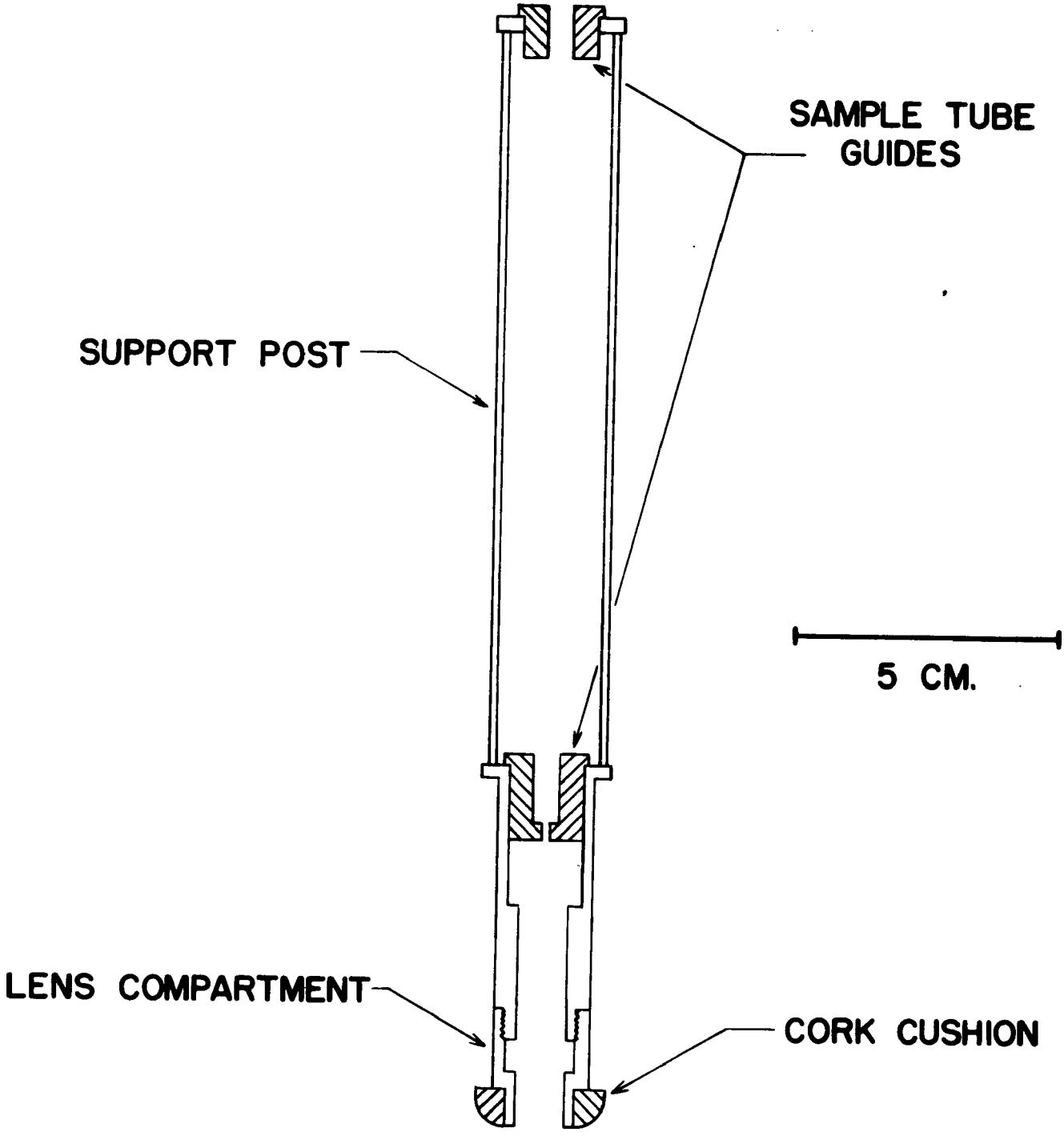


Figure 5
SAMPLE TUBE HOLDER

filter jacket. The film was prepared by spreading the plastic solution evenly on one side of the Polaroid sheet and allowing to dry. The concentration of the rhodamine was adjusted so that the transmission characteristics of the film were nearly identical to those for the filter jacket solution. In the temperature region 20-85°C, the film proved to be quite satisfactory. However, at temperatures above 85°C, the film deteriorated.

In order to determine the Raman spectrum of gaseous trifluoroacetic acid in the unassociated state, it was necessary to maintain the temperature of the material at approximately 140°C. This was accomplished by the use of an apparatus designed to accommodate the Raman tube within an electrically heated container. The heater was prepared by coiling a Nichrome heating element around a 25 mm section of Pyrex tubing. The operation of the heater was controlled automatically by a copper-Constantan thermocouple placed near the sample tube. The temperature of the sample was recorded by a Leeds and Northrup recording potentiometer. In a normal operation, the maximum fluctuation of the temperature was approximately 10°C. The dimensions of the apparatus were such that the use of the inner filter jacket was prevented during the study.

The spectrograph used in the investigation was a Gaertner two prism instrument with a dispersion of approximately 180 cm^{-1} per mm in the blue region of the spectrum. Eastman Kodak 103a-C and 103a-J spectrographic plates with antihalation backing were used to photograph the spectra because of their high sensitivity to the blue and green regions of the spectrum. After exposure, the plates were developed for three and one-half minutes in D-19 developer at 20°C. The image was fixed in

F-6 solution. The positions of the observed Raman lines were measured with a modified cathetometer from tracings of the spectrographic plates obtained with a Leeds and Northrup microphtometer. The frequencies were calculated with the aid of a dispersion curve based upon the spectrum of argon. Several of the exposures were remeasured directly on a comparator to provide a check on the values. For measurement of sharp bands this method is more accurate whereas for broad and diffuse bands, the former method is preferred.

CHAPTER VI

EXPERIMENTAL RESULTS AND THEIR INTERPRETATION

Trifluoroacetonitrile

The vibrational analysis of trifluoroacetonitrile has been carried out by several investigators[14,61,62] and the detailed assignments of the vibrational modes are reasonably well agreed upon. The spectrum was investigated in the present research primarily to provide a reference showing typical intensities and Raman shifts of the trifluoromethyl group vibrations. However, CF_3CN was used as starting material in several syntheses and the spectrum also served as a means of checking the purity of the compounds prepared.

The trifluoroacetonitrile molecule has one threefold axis of rotational symmetry and three vertical planes of symmetry. Accordingly, the molecule belongs to the point group C_{3v}. Selection rules for a molecule of this symmetry show that there should be four totally symmetric fundamentals (type a_1) and four doubly degenerate fundamentals (type e). A microphotometer tracing of one of the exposures of gaseous CF_3CN is shown in Figure 6. The measured Raman shifts are compared in Table IV with the results reported by earlier investigators.

Trifluoroacetic Acid

As cited previously, the maximum symmetry which the trifluoroacetic acid molecule can possess is a plane of symmetry; however, it has been suggested that on the basis of electron diffraction and dipole moment studies the molecule may not have even this low order of symmetry. In the liquid state, there are several possible configurations which the

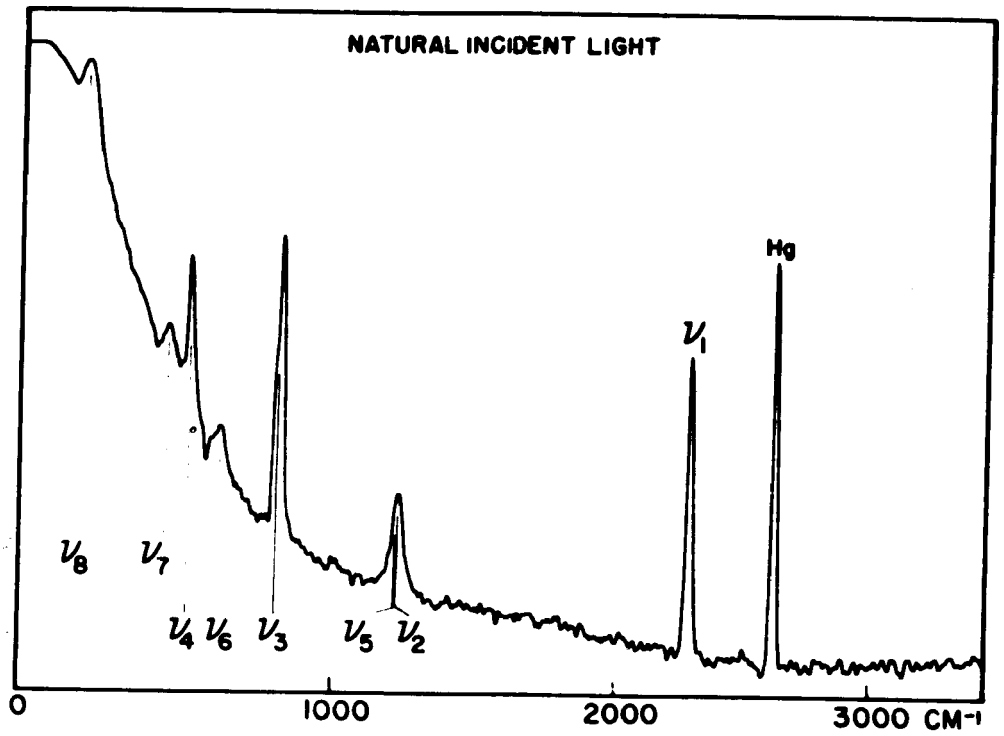


Figure 6

RAMAN SPECTRUM OF $CF_3CN_{(g)}$

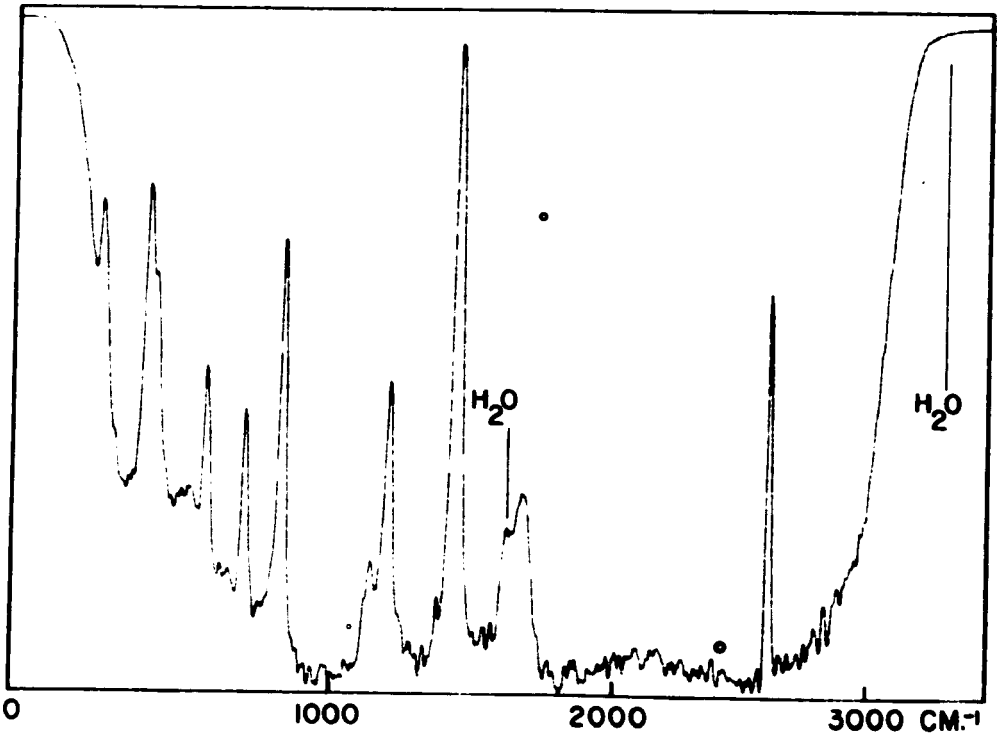


Figure 7

RAMAN SPECTRUM OF SATURATED AQ. SOLN.

OF CF_3CO_2Na

TABLE IV

VIBRATIONAL FREQUENCIES (IN cm^{-1}) OF CF_3CN

Liquid		Gas			Assignment(62)
Wait and Janz	Edgell and Potter	Gullikson and Nielsen	This Research	Assignment(62)	Symmetry
192	192	187	190	ν_8	e
462	463	460	459	ν_7	e
520	521	519.7	522	ν_4	a_1
620	620	620	621	ν_6	e
803	803[a]	799[b]	802		A_1
		809[b]			E
820	818[c]	818[b]	819	ν_3	a_1
1194	1192	1212	1210	ν_5	e
1220	1222	1226	1219	ν_2	a_1
2274	2274	2277	2273	ν_1	a_1

[a] Assigned as a_1.

[b] Interpreted as Fermi coupling.

[c] Interpreted as a combination band.

molecules may assume because of association. First of all, a cyclic dimer may be formed for which the point group would be C_i, C_2, or C_{2h} depending upon the relative positions of the CF_3-group and the hydrogens with respect to the plane of the ring formed by the two carbon and four oxygen atoms. If the trifluoromethyl group approximates a free rotator and the two hydroxyl hydrogens lie in the plane, then the selection rules are those of C_{2h} point group. Alternatively, the hydrogens may not lie in the plane, in which case there are two possible positions the hydrogens may assume with respect to each other. Both hydrogens may lie out of the plane but on the same side (C_2 point group), or one hydrogen may lie above the plane, the other below (C_i point group). Theoretically, the presence of a center of symmetry in a molecule can be identified by the application of the mutual exclusion rule, that is, the infrared active fundamentals are Raman inactive, and vice versa. In contrast, for the point group C_2 the selection rules predict that all fundamentals are both infrared and Raman active. However, the breadth of the infrared absorption bands of the acid in the liquid spectrum prevents a satisfactory interpretation in terms of either a center of symmetry or a point group C_2.

There also exists the possibility that the associated species may form chain dimers or longer polymeric species in the liquid state. For example, dielectric constant measurements of trifluoroacetic acid, while favoring the cyclic dimer configuration, do not definitely rule out the presence of noncyclic polar dimers or higher polymeric species.(8) In fact, the possibility of chain or polymeric species has been proposed to account for the numerous submaxima observed in the hydroxyl vibration

band in the infrared spectra of associated acids.[43] The spectroscopic point group for these configurations is most likely C_1. Thus, all modes of vibration are both infrared and Raman active and belong to the same species, namely, type A. Moreover, all fundamental vibrations of a molecule of this symmetry would have depolarization ratios of less than 6/7. It must be understood, however, that the polarization ratio of a polarized line may be close to 6/7 and therefore observing a ratio value of 6/7 for a particular band does not exclude necessarily the possibility that it is a symmetric vibration. It does preclude, however, any inference that the particular associated species belongs to C_1 point group unequivocally.

Due to the difficulty in determining the correct configuration of the associated species a detailed interpretation of the vibrational spectrum is unlikely. Nevertheless, observed frequencies may be associated with certain groups based on frequency shifts with deuterium substitution. Formation of the associated species would be expected to affect essentially the frequencies associated with the COOH-group while the frequencies associated with skeletal motions and the trifluoromethyl group should remain reasonably constant in both monomeric and associated forms.

Raman spectra of CF_3COOH and CF_3COOD in the liquid state were obtained at room temperature using natural (unpolarized) incident light, and representative tracings are presented in Figure 8. Interpretation of the observed spectrum of CF_3COOH will be discussed by considering various spectral regions in turn. Following this analysis, the frequencies of CF_3COOD will be considered in a similar fashion.

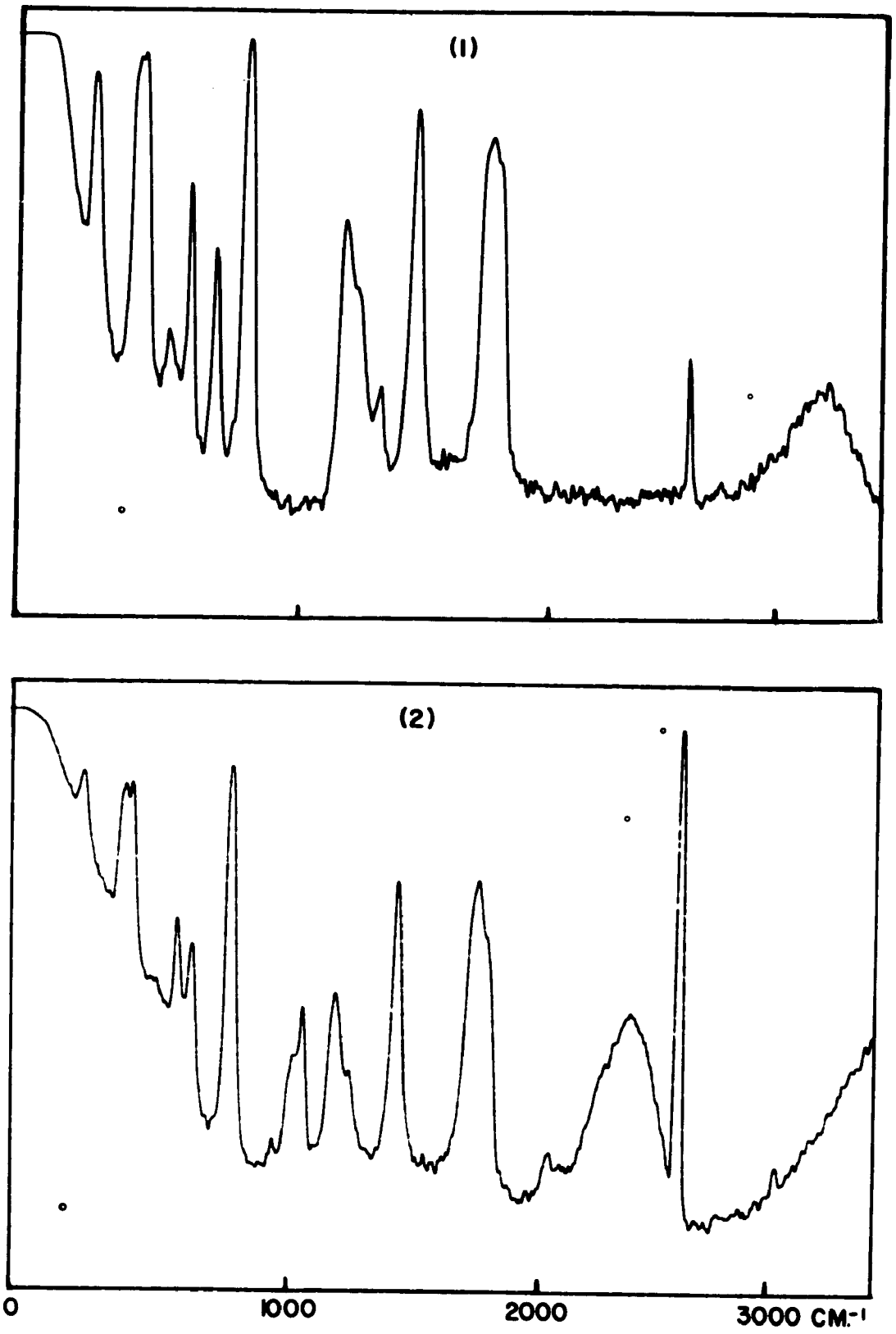


Figure 8

RAMAN SPECTRA OF LIQUID

(1) CF_3COOH, (2) CF_3COOD

Region from 3500 cm^{-1} to 1500 cm^{-1}

The very broad diffuse band centered at about 3200 cm^{-1} is the logical choice for the associated OH stretching vibration of the liquid. The band is observed to be polarized as shown in Figure 9. The corresponding infrared absorption band was reported by Fuson et al. at approximately 3140 cm^{-1} in the vapor spectrum.

The fundamental carbonyl stretching mode is expected in the 1750-1800 cm^{-1} region. The spectrum shows an intense band at 1753 cm^{-1} and a band of slightly less intensity at 1787 cm^{-1} appearing as a shoulder on the intense band. The coexistence of these two bands suggests the presence of more than one form of the molecule. Both bands are polarized and their positions remain almost unchanged in the Raman spectrum of the deuterated acid. The carbonyl band in the infrared spectrum of the vapor also was resolved into two bands at 1826 cm^{-1} and 1788 cm^{-1}.(16) Since association customarily lowers stretching frequencies, Fuson et al. assigned the higher frequency to the carbonyl stretching vibration of the monomer while the lower frequency was assigned to the stretching vibration of the dimer. Assuming that only monomeric and dimeric forms are present in the liquid, the assignment of the carbonyl bands in the Raman spectrum is made in a similar fashion: the band at 1787 cm^{-1} is assigned to the C=O stretching vibration of the monomer and the band at 1753 cm^{-1} is assigned to the corresponding vibration of the dimer. It has been observed that for carboxylic acids the difference between the infrared and Raman carbonyl stretching frequencies is about 60 cm^{-1}. For CF_3COOH the difference is approximately 39 cm^{-1} based on the monomer bands. It may be fortuitous that the difference between the two Raman carbonyl

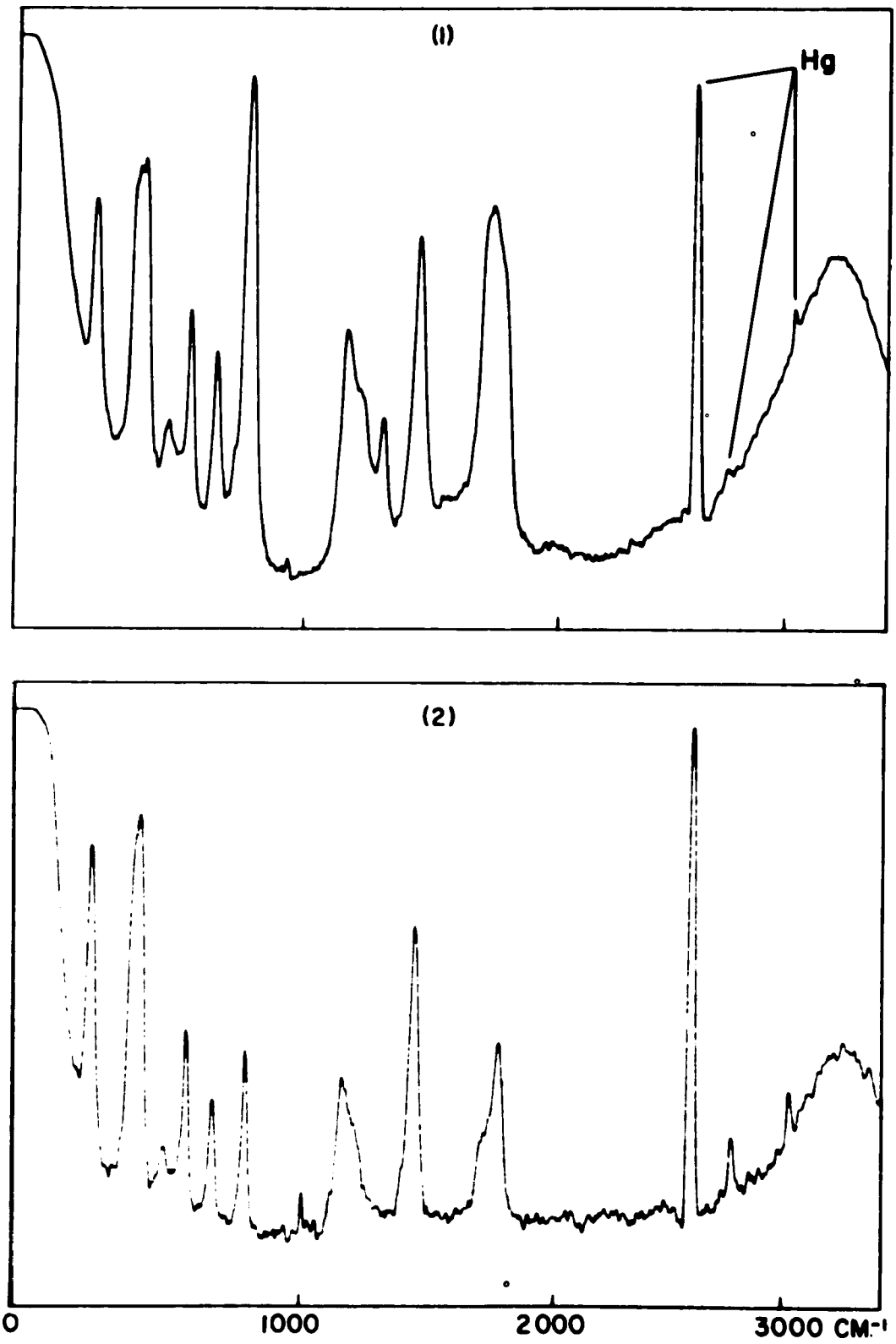


Figure 9

POLARIZED
RAMAN SPECTRA OF $CF_3COOH_{(l)}$

(1) $E_\perp$, (2) $E_\parallel$

stretching frequencies (34 cm^{-1}) is nearly identical to the difference observed between the two corresponding infrared frequencies (38 cm^{-1}) in the vapor spectrum.

There also exists the possibility that in the liquid only dimers and higher polymeric species are present. Thus, an alternate assignment of the carbonyl bands presents itself. The Raman band at 1787 cm^{-1} could be assigned to the carbonyl stretching vibration of the dimer. In turn, the Raman band at 1753 cm^{-1} would be the likely choice for the C=O stretching vibration of a higher polymeric species. Fuson et al. reported a single infrared absorption band at 1785 cm^{-1} for the acid in the liquid state.

Region from 1500 cm^{-1} to 800 cm^{-1}

The assignment of the strong band at 1451 cm^{-1} likewise is not completely satisfactory. The sharp profile suggests a stretching mode; however, the state of polarization of the band is not completely certain. The band is tentatively assigned to the stretching vibration ν(C-O), agreeing with the assignment proposed by Kagarise, although disagreeing with the assignment made by Fuson et al. The latter authors suggested that the observed band was due to the deformation vibration δ(C-O) but the frequency seems high for this type of motion.

Two bands due to the deformation vibration, δ(OH), of the simple molecule are expected in this region, one in-plane and one out-of-plane. In a mixture containing molecules in both monomeric and associated forms four bands should be expected, although they might not be distinguishable experimentally. Kagarise assigned a band at 1297 cm^{-1} in the infrared absorption spectrum to the associated vibration δ(OH)

in-plane while the same band was assigned to the stretching vibration ν(C-O) of the monomer by Fuson et al. The Raman spectrum in the present work shows a polarized band of weak intensity at 1315 cm^{-1} which is absent in the spectrum of the deuterated acid. These observations suggest that the band at 1315 cm^{-1} is due to the associated vibration δ(OH) in-plane. It is to be noted that the Raman frequencies reported by Fuson et al. for CF_3COOH did not include the band at 1315 cm^{-1} observed in the present investigation. The corresponding monomer band assigned to a band at 1122 cm^{-1} in the infrared absorption spectrum by Kagarise is not observed in the Raman spectrum. The band probably would be of rather low intensity in the liquid spectrum and failure to observe it is not unexpected. No distinct band was found in the spectrum where the associated vibration δ(OH) out-of-plane was expected to appear. Kagarise proposed a correlation of the infrared absorption band at 903 cm^{-1} with the deformation vibration δ(OH) out-of-plane of the dimer. However, Fuson et al. assigned this band to the deformation vibration of the monomer and placed the associated vibration somewhat higher at 1123 cm^{-1}. Unfortunately, neither band was observed in the Raman spectrum, the region between 812 and 1175 cm^{-1} being quite clear in all exposures, and it appears that the out-of-plane deformation frequency for the associated species is of negligible intensity in the Raman effect.

The spectrum of CF_3COOH in the 1175-1300 cm^{-1} region is complicated by the overlapping of several bands. In particular, three broad bands are observed at approximately 1175, 1197, and 1219 cm^{-1}. The first band is of medium intensity and not well defined, while the last two bands are less intense and partially obscured by the overlapping of the more intense band. Since the C-F stretching modes are expected in

this region, these bands appear to be the most likely candidates. Generally, the C-F stretching modes give rise to weak bands in the Raman effect; however, the above bands are observed to be of medium intensity. In the Raman spectrum of the liquid, Fuson et al. reported a weak band at 1241 cm^{-1}. In the present investigation, this band was not observed; however, the spectrum shows a weak, diffuse band at 1219 cm^{-1}.

The strong Raman band at 812 cm^{-1} is readily assigned to the C-C stretching mode. The fact that the band is polarized is evidence for a totally symmetrical vibration. The corresponding band in the infrared absorption spectrum was reported at 823 cm^{-1} by Kagarise and 825 cm^{-1} by Fuson et al.

Region Below 800 cm^{-1}

In this region one expects the various skeletal deformation modes to occur. Of these, the bending vibration, $\delta(OCO)$, is expected to have the highest frequency and is assigned to the weakly polarized band at 693 cm^{-1}. The deformation vibrations of the CF_3-group are expected in the 500-700 cm^{-1} region. The spectrum shows a weak band at 521 cm^{-1}, and a band of medium intensity at 599 cm^{-1}. A third C-F deformation mode is predicted but since no other band was observed, it must be concluded that either the band is coincident with one of the other two bands or is very weak. The state of polarization of the CF_3 deformation vibrations is not certain.

The four remaining Raman bands in the spectrum are observed at 263, 407, 419, and 434 cm^{-1}. Of the group, only the bands at 407 and 419 cm^{-1} appear to be polarized; none of the four bands are shifted appreciably in the spectrum of the deuterated acid. The rocking motions

of the CF_3-group have been observed to lie between 200 and 450 cm^{-1} for several trifluoromethyl compounds (see Table II). Consequently, the bands at 263 and 407 cm^{-1} are assigned to the antisymmetric and symmetric CF_3 rocking modes, respectively. The remaining two bands at 419 and 434 cm^{-1} are attributed to the CO_2H-group symmetric and antisymmetric rocking modes, respectively, by analogy with the assignment of acetic acid in the vapor phase.(63) The CF_3 torsional frequency normally would be a rather weak band and, moreover, would be expected at a rather low frequency, probably less than 200 cm^{-1}. Failure to observe the frequency may then be attributed to a combination of these factors.

The positions, intensities, and assignments for the bands observed for CF_3COOH are presented in Table V. The frequencies reported by Fuson et al. are shown for comparison purposes.

The investigation of the Raman spectrum of gaseous CF_3COOH at 140°C proved to be unsatisfactory. After several prolonged exposures at the elevated temperature, deposits of waxy residue were observed in the sample tube. Apparently, decomposition of the acid was taking place possibly due to photolysis brought about by radiation from the mercury arc.

Trifluoroacetic Acid-d

The polarization study of the deuterated acid in the liquid state shows that all the Raman lines in the spectrum are polarized with the possible exception of the low lying frequency at 261 cm^{-1} (Figure 10). If this band is polarized also then the results suggest that the vibrational modes all belong to the same species, in which case, the point group undoubtedly is C_1. One would expect to find this lack of symmetry

TABLE V

OBSERVED RAMAN FREQUENCIES AND ASSIGNMENTS FOR LIQUID CF_3COOH

Frequency (cm^{-1}) (See Ref.16)	This Research Frequency (cm^{-1})	Intensity[a]	State of Polarization	Assignment[b]
260	263	m	depol.	CF_3 rocking
401	407	m, sh	pol.	CF_3 rocking
419	419	m	pol.	COOH rocking
436	434	m	depol.	COOH rocking
525	521	w		CF_3 deformation
[illegible]	599	m-w	depol. ?	CF_3 deformation
[illegible]	693	m-w	pol.	OCO deformation
794				
[illegible]	812	s	pol.	C-C stretching
1174	1175	m	pol. ?	C-F stretching
	1197	m-w, sh	pol. ?	C-F stretching
1241	1219	m-w, sh	pol. ?	C-F stretching
	1315	w	pol.	OH deformation in-plane (associated)
1445	1451	s	pol.	C-O stretching
1770	1753	s, br	pol.	C=O stretching (associated)
	1787	s, sh	pol.	C=O stretching (monomer ?)
	3200[c]	m, vbr	pol.	O-H stretching (associated)

[a] w = weak; m = medium, s = strong; sh = shoulder; br = broad.

[b] The description of the fundamentals is for purposes of classification.

[c] Frequency represents a broad band for which the measurement must be considered to have a rather large uncertainty.

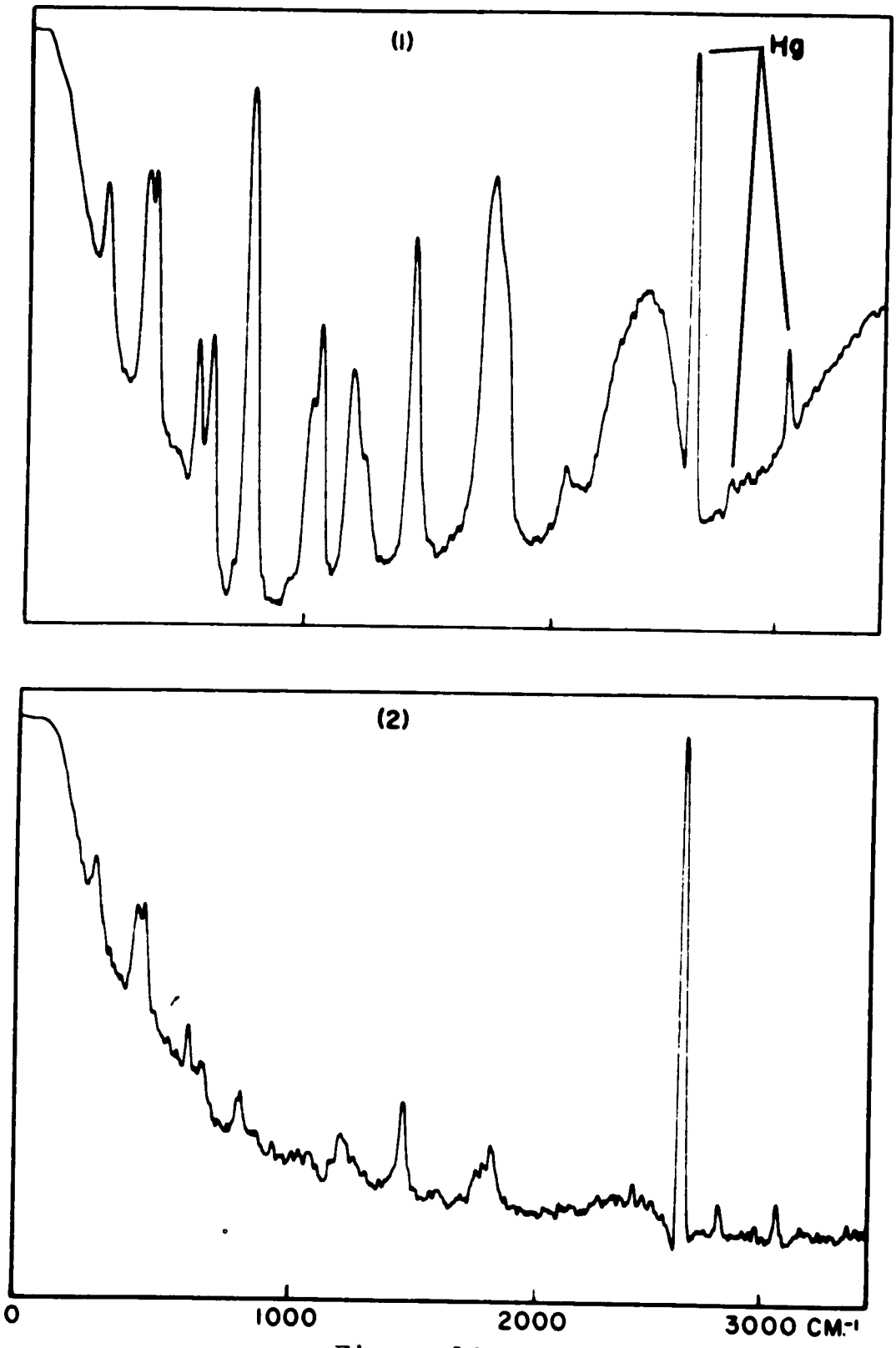


Figure 10

POLARIZED
RAMAN SPECTRA OF $CF_3COOD_{(l)}$
(l) $E_\perp$, (2) $E_\parallel$

present also in CF_3COOH in the liquid state, providing the associated forms present in both CF_3COOH and CF_3COOD are identical. This assumption appears to be valid since deuterium substitution should not affect the symmetry of the associated species present in this particular case. It is unfortunate that the polarization measurements for CF_3COOH (see Figure 9) are not sufficiently clear-cut to confirm the above evidence for the C_1 symmetry group.

Region from 2400 cm^{-1} to 1500 cm^{-1}

The broad band of the associated OH stretching vibration is observed to shift to approximately 2390 cm^{-1} in the Raman spectrum of the deuterated acid. The frequency ratio ν(OH) associated/ ν(OD) associated is about 1.34, which may be compared with the ratio reported by Fuson et al. based on the vapor spectra (1.33).

The strong carbonyl stretching band is resolved into two principal bands at 1739 and 1773 cm^{-1}. The latter band is less intense and appears as a shoulder on the more intense band. The bands are not well resolved and the presence of association is shown clearly by the breadth of the bands. Lack of sufficient data prevents a conclusive assignment of the bands in terms of more than one form, monomer and dimer or dimer and polymeric species, of the molecule.

Region from 1500 cm^{-1} to 700 cm^{-1}

The band observed at 1419 cm^{-1} is assigned to the associated stretching vibration ν(C-O) in view of the similar assignment made for the normal acid. The corresponding band in CF_3COOH was observed at 1451 cm^{-1}.

The region where the bands due to C-F stretching modes are to be expected is complicated by overlapping of several bands. It is interesting to note that the overall intensity of the bands is reduced in comparison with that observed for the corresponding region in CF_3COOH. Two bands are observed at 1179 and 1187 cm^{-1}. Because the bands are quite diffuse, the measurements are approximate only. The band at 1187 cm^{-1} is slightly less intense than the band at 1179 cm^{-1} and appears as a shoulder on the latter band. In addition, a weak band is observed at approximately 1234 cm^{-1}. A band appearing at 1241 cm^{-1} in the Raman spectrum of CF_3COOD was reported by Fuson et al. as a very strong band. This intensity description may be due to a typographical error.

Fuson et al. have assigned the deformation vibration $\delta(OD)$ in-plane of the dimer to a band at 1039 cm^{-1} and the corresponding monomer vibration to a band at 993 cm^{-1} in the vapor spectrum. The latter band is expected to be of negligible intensity in the liquid spectrum. In the infrared absorption spectrum of liquid CF_3COOD, a medium strong band at 1027 cm^{-1} was reported which presumably corresponds to the strong band observed at 1039 cm^{-1} in the vapor spectrum. Two moderately weak Raman bands observed at 1058 cm^{-1} and at approximately 1022 cm^{-1} are possible candidates for the $\delta(OD)$ in-plane associated vibration. Observing that the corresponding associated band in the Raman spectrum of CF_3COOH was relatively weak suggests that the band at 1022 cm^{-1} is the logical choice (frequency ratio is about 1.29), especially since the band at 1058 cm^{-1} can be assigned to a combination band. In view of the lack of sufficient evidence, however, an unequivocal assignment of these two bands does not seem possible. It is interesting to note that Fuson et

al. reported no Raman bands between 792 and 1170 cm^{-1} for the spectrum of CF_3COOD.

The C-C stretching frequency can be assigned with considerable certainty to the Raman band at 790 cm^{-1}. The corresponding frequency in CF_3COOH was observed at 812 cm^{-1}.

Region Below 700 cm^{-1}

The OCO deformation frequency occurring at 693 cm^{-1} in CF_3COOH should not be expected to shift appreciably in the deuterated acid. Accordingly, a medium weak line observed at 650 cm^{-1} in CF_3COOD is assigned to this motion.

Similarly, the CF_3 deformation frequencies are expected to remain relatively constant in both acids. A very weak band observed at approximately 513 cm^{-1} and a medium weak band at 599 cm^{-1} in CF_3COOD correspond to the bands at 521 and 599 cm^{-1} in the spectrum of CF_3COOH. The remaining CF_3 deformation mode is not readily identified, but presumably it is coincident with either of the other two vibrations or is too weak to be observed as in the case of the hydrogen compound.

The remaining four bands in the spectrum may be assigned, by arguing through the same reasons as in the case of CF_3COOH, to the rocking motions of the CF_3- and COOD- groups. The lines at 261 and 403 cm^{-1} are correlated with the CF_3 rocking vibrations while the bands at 413 and 434 cm^{-1} are assigned to the COOD-group rocking modes. The torsional motion of the CF_3-group is not observed but in view of its expected weak intensity and low lying frequency, failure to find the mode is not unexpected.

The positions, intensities, and assignments for the bands of CF_3COOD are shown in Table VI together with the values reported by Fuson et al.

The Trifluoroacetate Ion

Molecules of the type CX_3NO_2 (X = H,D,F,Cl, or Br) as well as $CH_3CO_2^-$ and $CD_3CO_2^-$ have been shown to have effectively the symmetry of the C_{2v} point group. Consequently, it is assumed that $CF_3CO_2^-$ also belongs to this symmetry group. The selection rules for this symmetry allow all fifteen fundamental modes in the Raman spectrum. Moreover, these modes are distributed among four symmetry classes a_1, a_2, b_1, and b_2. There are five modes of class a_1 which will give polarized Raman lines. Three of these are composed of symmetrical stretching and two, of symmetrical bending. The sole member of class a_2, the torsional mode, will be depolarized. The two remaining classes, b_1 and b_2, are composed of five and four asymmetric modes, respectively, and will be depolarized. Since the interaction between the CF_3- and the CO_2-groups may not be sufficient to split the frequencies corresponding to the degenerate CF_3 modes, all fifteen distinct fundamental frequencies will not necessarily be observed.

In the discussion of the frequencies of the ion, it will be convenient to analyze the spectrum in terms of bands arising from the CF_3-group alone, those from the CO_2-group, and finally, bands in terms of the ion, itself. The Raman spectra of both silver trifluoroacetate and sodium trifluoroacetate were studied and the small real differences observed between the two spectra were attributed to the differences in the polarizing effect of the cations. The Raman spectrum of a saturated

TABLE VI

OBSERVED RAMAN FREQUENCIES AND ASSIGNMENTS FOR LIQUID CF_3COOD

Frequency (cm^{-1}) (See Ref.16)	This Research Frequency (cm^{-1})	Intensity[a]	Assignment[b]
260	261	m	CF_3 rocking
399	403	m, sh	CF_3 rocking
417	413	m	COOD rocking
434	434	m	COOD rocking
	513	vvw	CF_3 deformation
596	599	m-w	CF_3 deformation
648	650	m-w	OCO deformation
792	790	s	C-C stretching
	1022	m-w, sh	OD deformation in-plane ? (associated)
	1058	m-w	(790 + 261) ? OD deformation in-plane ? (associated)
1170	1179	m-w	C-F stretching
	1187	m-w, sh	C-F stretching
1241	1234	w	C-F stretching
1427	1419	s	C-O stretching
	1739	s, br	C=O stretching (associated)
1760			
	1773	s, sh	C=O stretching (monomer ?)
	2047	vw	(261 + 1773)
	2390[c]	m, vbr	O-D stretching (associated)

[a] w = weak; m = medium; s = strong; sh = shoulder; br = broad.

[b] The description of the fundamentals is for classification purposes.

[c] Frequency represents a broad band for which the measurement must be considered to have a rather large uncertainty.

solution of sodium trifluoroacetate in water is shown in Figure 7. Qualitative polarization measurements were made by the two exposure method for both sodium and silver salts of trifluoroacetic acid, and the results for silver trifluoroacetate are shown in Figure 11.

In regard to the CO_2-group, the frequencies of the symmetric and asymmetric stretching modes have been given as 1413 and 1556 cm^{-1}, respectively, for sodium acetate.(64) The corresponding frequencies in the trifluoroacetate ion are expected to be shifted due to the perturbing effect of the fluorine atoms. Consequently, the very strong band at 1435 cm^{-1} is assigned to the CO symmetric stretching mode and the weak, depolarized band at approximately 1681 cm^{-1} must represent the asymmetric stretching vibration. The symmetric stretching band is observed to be weakly polarized. It is interesting to point out in the comparison of the Raman spectra of CF_3COOH (Figure 8) and the sodium salt of the acid (Figure 7) that the disappearance of the characteristic carbonyl stretching frequency as a result of salt formation is shown clearly. The OCO symmetric deformation frequency occurring at 650 cm^{-1} in the acetate ion also is expected to be shifted in the trifluoroacetate ion and the band should be polarized. The vibrational analysis of the isoelectronic molecule CF_3NO_2 serves as an additional aid in assigning this vibrational mode. The analogous vibration, ONO symmetric deformation, has been assigned to a band at 604 cm^{-1}.(65) Accordingly, the polarized band observed at 601 cm^{-1} in the spectrum of sodium trifluoroacetate is assigned to the OCO symmetric deformation. Fonteyne proposed the assignment of the C-F symmetric stretching for this band in the previous vibrational study of the trifluoroacetate ion.(58) Data which have been

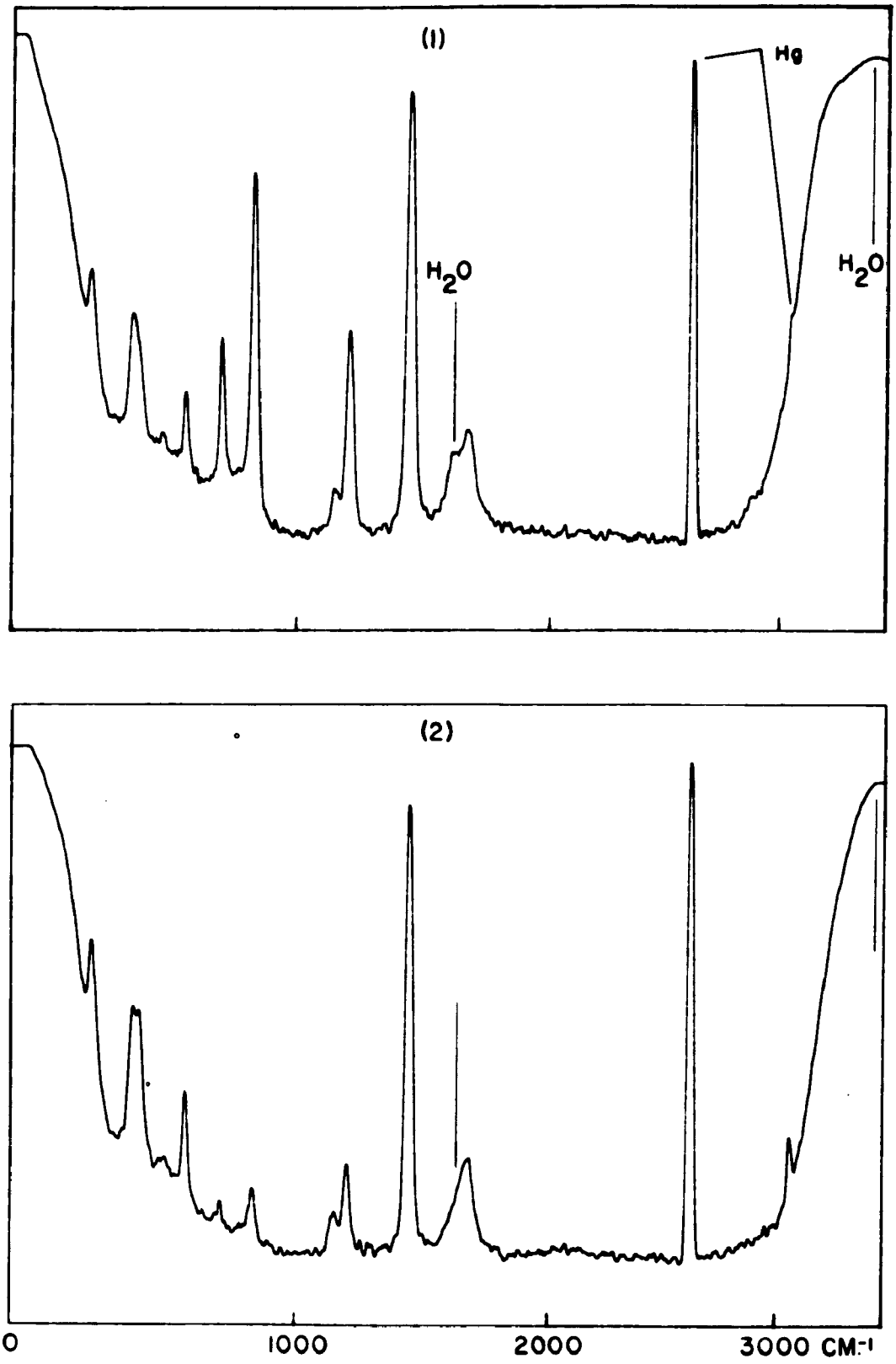


Figure 11

POLARIZED RAMAN SPECTRA OF SATURATED AQ. SOLN. OF CF_3CO_2Ag

(1) $E_\perp$, (2) $E_{||}$

accumulated for trifluoromethyl compounds since this assignment was published suggest that a C-F stretching mode occurring at such a low frequency as 601 cm^{-1} is unlikely.

In the CF_3 stretching region are found a very weak band at 1143 cm^{-1} with its state of polarization uncertain and a polarized band of medium intensity at 1202 cm^{-1}. The band at 1202 cm^{-1} is chosen as the asymmetric C-F stretching vibration despite the polarization evidence since the least symmetrical stretching vibration in CF_3 compounds usually has the higher frequency.(65) The 1143 cm^{-1} band is assigned to the symmetric C-F stretching motion. A possible explanation of the polarization results is that the first overtone of the OCO deformation mode (2x601) is accidentally degenerate with the asymmetric C-F stretching motion and the observed polarization of the 1202 cm^{-1} band results from the presence of the former mode. The remaining C-F stretching mode is not observed in the spectrum and is tentatively assigned also to the 1202 cm^{-1} band in view of the possibility that the frequencies of the degenerate CF_3 stretching vibration are not split sufficiently to be resolved. As mentioned previously, Fonteyne assigned the band at 1216 cm^{-1} (corresponding to the frequency at 1202 cm^{-1} observed in the present investigation) to the torsional vibration. However, this frequency is obviously far too high for such a motion when compared with values observed in other CF_3 compounds (see Table II). On the other hand, the assignment made by the present investigation is further supported by consideration of C-F stretching modes reported by various investigators.

The next group of fundamentals associated with the CF_3-group comprises the three CF_3 deformation modes which generally lie in the

500-700 cm^{-1} region. The spectrum shows three bands in this region. One of these has been assigned already to the OCO symmetric deformation, therefore, the very weak band at 521 cm^{-1} is assigned to the asymmetric CF_3 deformation mode and the medium intensity, polarized band at 729 cm^{-1} is assigned to the symmetric deformation vibration. In view of apparent degeneracy of the asymmetric modes, the remaining unresolved CF_3 deformation vibration may be tentatively assigned also to the band at 521 cm^{-1}. An alternative possibility, which was mentioned also in the case of trifluoroacetic acid molecule, is that the modes are split but that the intensity of only one band is sufficient to be observed. Fonteyne concluded that a band observed at 511 cm^{-1} was possibly degenerate; however, the band was assigned to both the OCO symmetric deformation mode and the asymmetric OCO rocking motion, the band at 728 cm^{-1} being assigned to the symmetric OCO rocking mode. The present assignment of these frequencies appears to be in closer agreement with values observed in other CF_3 compounds.

In addition to the frequencies described above, six new vibrations should be present resulting from the loss of the translational and rotational motions of the individual CF_3- and COO-groups. These modes may be described as the C-C stretching vibration, two rocking motions of the CF_3-group, two rocking motions of OCO, and finally, the torsional vibration of the CF_3-group about the C-C axis.

The assignment of 844 cm^{-1} to the C-C stretching mode is consistent with the assignment proposed by Fonteyne for the trifluoroacetate ion and is remarkably similar to the C-N stretching frequency of CF_3NO_2 (863 cm^{-1}). The band is one of the strongest observed in the spectrum and is strongly polarized.

Although there are four rocking modes predicted for the CF_3COO^- molecule, four distinct Raman bands may not be observed necessarily. For example, in the case of the fluoropicrin molecule, both rocking frequencies of the CF_3-group were tentatively assigned to the infrared absorption band at 450 cm^{-1} while the two NO_2 rocking modes were correlated with a band at 400 cm^{-1}. The latter band was not directly observed in the infrared spectrum but was postulated from combination bands and overtones. In the Raman spectrum of the trifluoroacetate ion, three bands are seen in the 250-450 cm^{-1} region: a weak band at 267 cm^{-1} and two overlapping bands of medium intensity at 410 and 437 cm^{-1}. The frequencies 267 and 437 cm^{-1} are assigned to CF_3 rocking. The remaining band at 410 cm^{-1} is then assigned to the rocking motion of the COO-group; assigning the frequencies 410 and 437 cm^{-1} to COO^- rocking is, however, equally reasonable. Fonteyne assumed that the CF_3-group retained its threefold symmetry and, consequently, assigned the band at 410 cm^{-1} to the CF_3 symmetric deformation vibration, the band at 265 cm^{-1} to the degenerate deformation vibration, and the band at 439 cm^{-1} to the degenerate stretching. However, more recent work (see Table II) shows that these frequencies are far too low. A satisfactory assignment of the rocking modes is further complicated by the fact that the band at 410 cm^{-1} appears to be polarized, whereas the bands due to the rocking modes should be depolarized according to the selection rules for the point group C_{2v}. An alternative interpretation of the symmetry of trifluoroacetate ion can be proposed (C_s point group) which would explain satisfactorily the polarized band at 410 cm^{-1} (symmetric rocking mode). However, this suggestion would require a potential barrier of sufficient magnitude to prevent free

rotation of the CF_3-group. Since the torsional vibration was not observed in the spectrum, an estimate of such a barrier is not possible. In view of the satisfactory interpretations of the vibrational spectra for similar molecules (CF_3NO_2, CH_3COO^-, CD_3COO^-) in terms of the point group C_{2v}, no definite decision can be made as to the orientation of the CF_3-group with respect to the COO-group.

The frequencies and intensities obtained for CF_3COONa are compared in Table VII with the results reported by Fonteyne.

TABLE VII

VIBRATIONAL FREQUENCIES (IN cm^{-1}) AND INTENSITIES OF CF_3COONa

Fonteyne		This Research	
	Intensity		Intensity
265	(3)	267	w
343	(0)		
410	(3)	410	m
439	(2)	437	m
511	(1b)	521	vw, diff.
601	(3)°	601	m
728	(2)	729	m
850	(5)	844	s
1031	(1/2)		
1115	(1)	1143	w, diff.
1216	(2b)	1202	m
1442	(10)	1435	vs
1621[a]	(1/2)	1608[a]	w, diff.
1703	(1)	1681	w, br

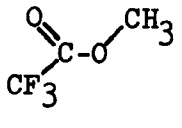
[a] Interpreted as H_2O band.

In Table VIII the assignments and qualitative polarization measurements for CF_3COO^- are shown. The assignments of CF_3NO_2 by Mason and Dunderdale[65] are given also to illustrate the great similarity between the trifluoroacetate ion and the fluoropicrin molecule.

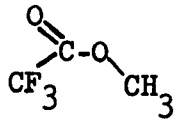
Methyl Trifluoroacetate

The only possible symmetry element of the CF_3COOCH_3 molecule is a plane containing the heavy atoms. The selection rules for this symmetry (point group C_s) allow all twenty-seven fundamental vibrations in the Raman spectrum. Of these, seventeen will be symmetric (a' species) and ten asymmetric (a" species) with respect to this plane. The modes of class a' will give polarized Raman lines while those of class a" will be depolarized.

There are two possible configurations for this molecule, the cis configuration (I) and the trans configuration (II).



(I)



(II)

In similar molecules, namely, methyl formate and methyl acetate, the stable configuration has been assumed to be cis and the vibrational assignments have been interpreted satisfactorily on this assumption.[55] In regard to the methyl trifluoroacetate molecule, no decision as to the correct configuration can be made. It should be noted that because of possible steric hindrance between the CF_3- and CH_3-groups the cis configuration might be favored. However, this question must be left open until further experimental data become available, particularly the interpretation of the band envelopes of the vapor spectrum.

TABLE VIII

OBSERVED RAMAN FREQUENCIES AND ASSIGNMENTS FOR CF_3COONa IN AQUEOUS SOLUTION

Symmetry Class		Vibrational Mode	State of Polarization	CF_3NO_2[a] (Gas) (See Ref.65)	CF_3COO^- (Aq. Soln.) This Research
a_1	ν_1	CO stretching	pol.	1315	1435
	ν_2	C-F stretching		1154	1143
	ν_3	C-C stretching	pol.	863	844
	ν_4	CF_3 deformation	pol.	751	729
	ν_5	OCO deformation	pol.	604	601
a_2	ν_6	Torsion		220[b,c]	--
b_1	ν_7	CO stretching	depol.	1620	1681
	ν_8	C-F stretching	pol.[b]	1288	1202
	ν_9	CF_3 deformation	depol.	529	521
	ν_{10}	COO rocking (in-plane)	pol. ?	400[c]	410 ?
	ν_{11}	CF_3 rocking	depol.	450	437 ?
b_2	ν_{12}	C-F stretching	pol.[b]	1277	1202 ?
	ν_{13}	CF_3 deformation	depol.	529	521 ?
	ν_{14}	COO rocking (out-of-plane)	depol.	400[c]	437[d] ?
	ν_{15}	CF_3 rocking	depol.	450	267

[a] Frequencies observed in infrared absorption spectrum.

[b] See the Trifluoroacetate Ion Section for a discussion of the nature of this vibration.

[c] Postulated from combination bands and overtones.

[d] The higher rocking mode was taken as the out-of-plane mode to be consistent with the analogous assignment for CH_3COO^- (see Reference 64).

The present investigation is concerned with the Raman analysis of methyl trifluoroacetate in the liquid state. Identification of all frequencies and a complete assignment does not appear feasible without the aid of the isotopically substituted molecule CF_3COOCD_3. Moreover, interpretation of the spectrum is complicated because of the superposition of bands in several regions of the spectrum. Microphotometer tracings of the liquid spectrum using natural and polarized light are shown in Figure 12.

The Raman bands centered around 3000 cm^{-1} are concerned with the methoxy group. In the region between 2870 and 3060 cm^{-1}, four resolved lines appear, three of which are relatively sharp. The difficulty in assigning these bands is due, at least in part, to the fact that the first overtones of the methyl group deformation frequencies fall in the middle of the C-H stretching region and give rise to Fermi resonance. One is tempted to assign the strong polarized band at 2970 cm^{-1} to the C-H symmetrical stretching mode on the basis of the corresponding assignment in methyl acetate (2966 cm^{-1}). The a' and a" C-H asymmetric stretching frequencies are not readily identified unless the overlapping bands at 3036 and 3056 cm^{-1} are considered as likely candidates.

The medium intensity band at 1790 cm^{-1} is assigned with certainty to the C=O stretching mode. It is interesting to note that in the series: CH_3COOCH_3, CCl_3COOCH_3, and CF_3COOCH_3, the respective carbonyl stretching frequencies are observed in the Raman spectra at 1738, 1768, and 1790 cm^{-1}. The striking influence of the CF_3-group on the carbonyl frequency persists in the ester as well as in the acid.

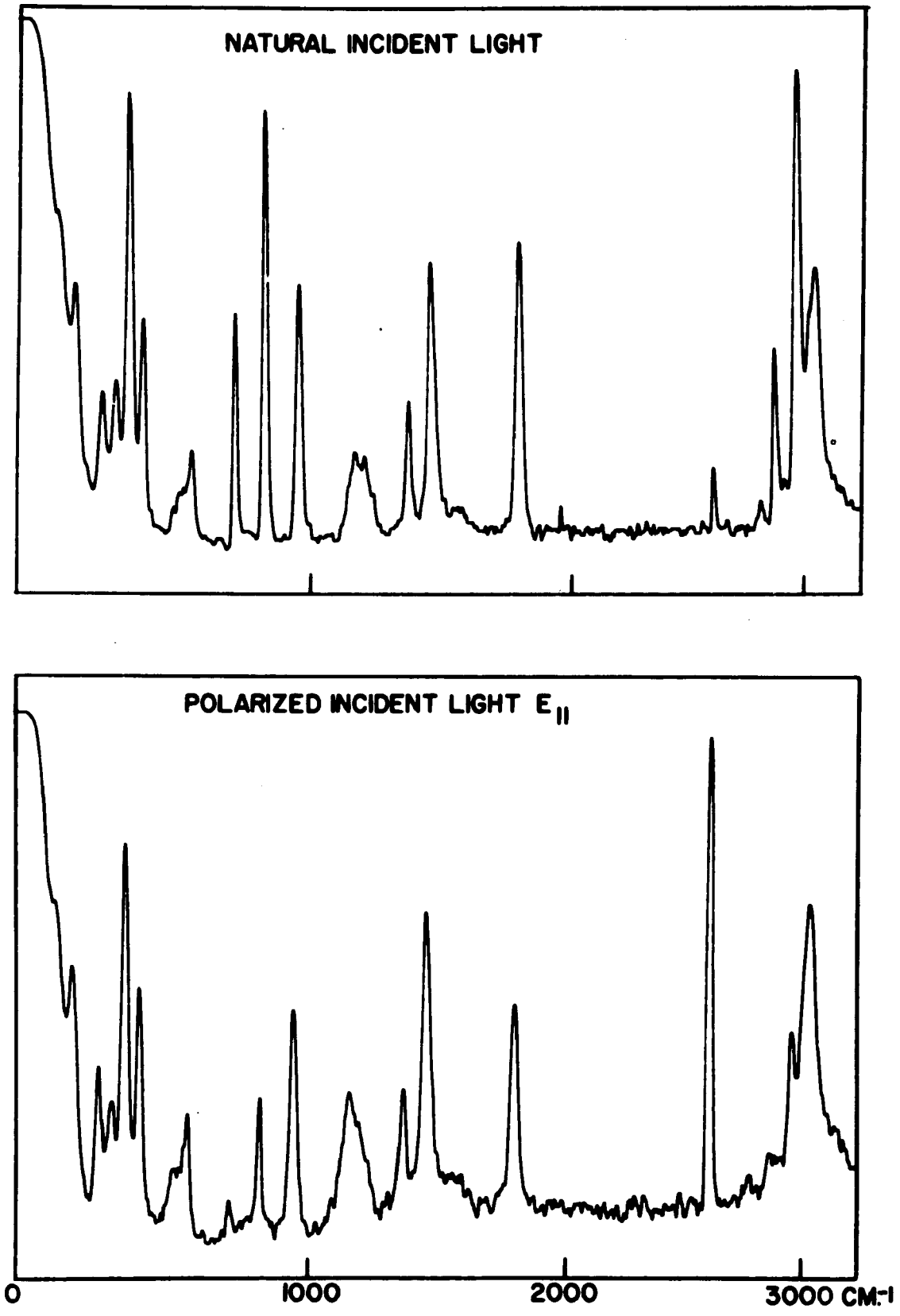


Figure 12
RAMAN SPECTRA OF CF_3COOCH_3

In the methoxy group deformation region around 1450 cm^{-1}, the medium intensity, depolarized band at 1448 cm^{-1} is assigned to the a" asymmetric CH_3 bending mode. The only other band that is observed in this region is the medium weak, polarized band at 1363 cm^{-1} and is assigned tentatively to the a' symmetric CH_3 bending.

Because the 1175 cm^{-1} region in the spectrum is crowded with bands, it seems pointless to attempt any detailed assignment. A total band width of about 125 cm^{-1} results from the overlapping of weak bands in which six vibrational modes are expected. These include three C-F stretching frequencies, two methoxy rocking motions, and the $C-OCH_3$ stretching mode. An examination of the region shows that there are no isolated bands whose assignments can be made with certainty.

The CH_3-O stretching frequency is associated with the medium, polarized 959 cm^{-1} band, while the C-C stretching mode is assigned to the very strong band at 839 cm^{-1}. The two corresponding modes in methyl acetate were reported at 1060 and 844 cm^{-1}, respectively.

The region around 550 cm^{-1} is also complicated by several superimposed bands. The strongest band at 586 cm^{-1} may be associated with either the OCO bending vibration or the CF_3 deformation mode. The remaining group of overlapping bands is too irregular to be measured accurately although these frequencies probably are due largely to the CF_3 deformation vibrations. The frequencies 421 and 370 cm^{-1} are logical choices for the planar $C-CO_2$ bending mode and CF_3 rocking mode, although it cannot be said with certainty which is which. One is tempted to assign the 421 cm^{-1} band to the $C-CO_2$ bending on the basis of the corresponding assignment for methyl acetate (429 cm^{-1}). The corresponding

asymmetric bending motion is expected at a higher frequency and may lie obscured in the CF_3 deformation region. The asymmetric CF_3 rocking mode is assigned to the 286 cm^{-1} band. The COC bending vibration for methyl acetate was reported at 303 cm^{-1}. The counterpart in methyl trifluoroacetate appears responsible for the medium weak band at 329 cm^{-1}.

The three remaining modes of interest are the torsional motions of the methyl and trifluoromethyl groups and the COC out-of-plane bending. These frequencies are expected to lie below 300 cm^{-1} and may be considered as possible candidates for the two weak bands observed at 139 and 195 cm^{-1}.

The observed frequencies, estimated relative intensities, qualitative polarization measurements, and assignments are given in Table IX.

Trifluoroacetamide

The trifluoroacetamide molecule in a rigid configuration has at most a plane of symmetry containing the C-CON grouping and a fluorine atom. For this symmetry, C_s point group, the selection rules predict that all twenty-one fundamental vibrations will be active in the Raman spectrum. If the amino hydrogen atoms are assumed to lie in this symmetry plane, in accord with the assertions cited previously that the acetamide molecule is completely planar, then of the twenty-one fundamental modes, fourteen will be symmetric (a' species) and seven will be asymmetric (a" species) with respect to this plane. Further, the vibrations of species a' will give polarized lines while those of species a" will

TABLE IX

OBSERVED RAMAN FREQUENCIES AND ASSIGNMENTS FOR LIQUID CF_3COOCH_3

Frequency (cm^{-1})	Intensity	State of Polarization	Assignment[a]
139	w	depol.	torsion
195	w	depol.	torsion
286	m-w	depol.	CF_3 rocking
329	m-w	pol.	COC bending
370	vs	pol.	CF_3 rocking or $C-CO_2$ bending
421	m	pol. ?	$C-CO_2$ bending or CF_3 rocking
(527)[b]	vvw		CF_3 deformation
(551)	vvw		CF_3 deformation
586	w		CF_3 deformation or OCO bending
733	m	pol.	CF_3 deformation
839	vs	pol.	C-C stretching
959	m	pol.	CH_3-O stretching
(1153)	w, diff.		C-F stretching (a',a',a"), CH_3 rocking (a',a"), and $C-OCH_3$ stretching (a').
1165	w		
(1192)	w, diff.		
1202	w		
(1238)	w, diff.		
1363	m-w	pol.	CH_3 deformation
1448	m	depol.	CH_3 deformation
1790	m	pol.	C=O stretching
2809	vw		1448 + 1363, c ?

TABLE IX (CONT'D)

Frequency (cm^{-1})	Intensity	State of Polarization	Assignment[a]
2871	m-w	pol.	c
2914	vw, diff.		c
2970	vs	pol.	C-H stretching
3036	m, sh	depol. ?	C-H stretching ?
3056	m	depol.	C-H stretching ?

[a] Description of the fundamentals is for formal classification. Owing to the closeness of several frequencies, considerable mixing must occur.

[b] Frequencies enclosed in parentheses represent broad and rather diffuse bands for which the measurements must be considered to have a rather large uncertainty.

[c] These bands may be the first overtone of the CH_3 deformation in strong Fermi resonance with the C-H stretching frequencies or the fundamentals of C-H stretching.

give polarized lines while those of species a" will be depolarized. An approximate description of the fundamental vibrations is given in Table X.

The reasonably low melting point of this amide (75°C) allowed the investigation to be carried out on the molten material. To aid in assigning the fundamental modes, the Raman spectrum of the deuterated amide also in the molten state was obtained. Microphotometer tracings of the Raman spectra are shown in Figure 13. The strong, broad band centered at about 3800 cm^{-1} is due primarily to fluorescent products. This fluorescence was observed to increase both in intensity and width during the time the materials were kept molten.

Interpretation of the observed spectrum of CF_3CONH_2 will be discussed by considering various spectral regions in turn. Because of the tendency toward hydrogen bond formation in the liquid state, line breadth, which is often a useful indication of symmetry species, is probably meaningless in the case of either CF_3CONH_2 or CF_3COND_2.

Region from 3500 cm^{-1} to 1400 cm^{-1}

The broad bands occurring in the 3200-3500 cm^{-1} region are concerned with the N-H stretching modes. Detailed assignment of these frequencies is complicated by overlapping bands due to associated molecules and possibly monomers as well. The bands observed at 3216 and 3327 cm^{-1} appear due to N-H bonds and may be assigned to the vibrations of an associated NH_2-group, on the basis of the corresponding assignments reported for acetamide in the solid state (3180 and 3350 cm^{-1}) by Richards and Thompson.(19) The presence of monomers in the molten amide may be responsible for the broad band at approximately 3408 cm^{-1} and the

TABLE X

FUNDAMENTAL VIBRATIONS OF CF_3CONH_2

Species	Approximate Description
a'	NH_2 asymmetric stretching
	NH_2 symmetric stretching
	C=O stretching
	NH_2 deformation
	C-N stretching
	C-F asymmetric stretching
	C-F symmetric stretching
	NH_2 rocking
	C-C stretching
	OCN deformation
	CF_3 asymmetric deformation
	CF_3 symmetric deformation
	CCO deformation
	CF_3 rocking
a''	C-F asymmetric stretching
	CF_3 asymmetric deformation
	NH_2 rocking
	C-CON out-of-plane bending
	CF_3 rocking
	CF_3-C torsion
	NH_2-C torsion

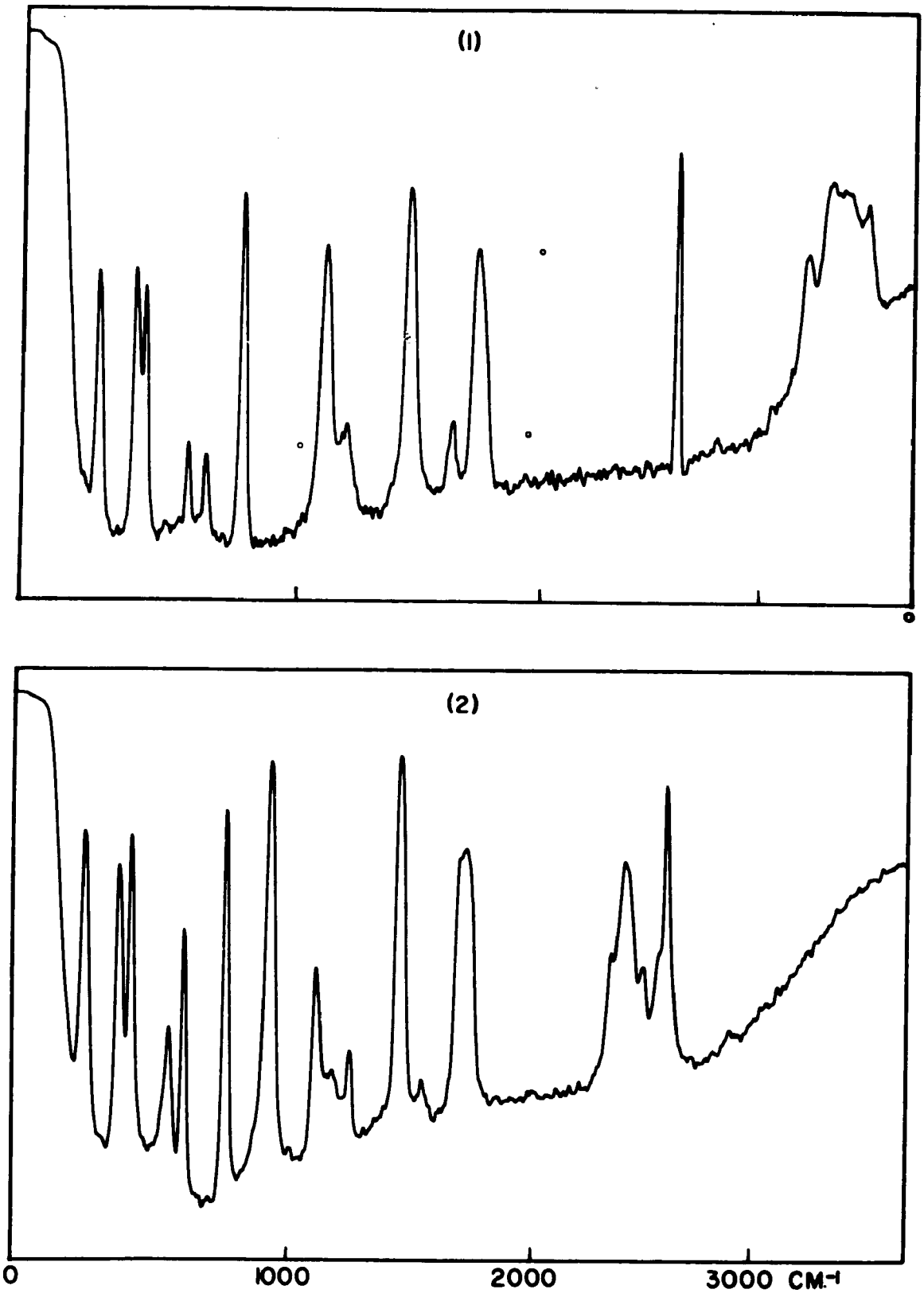


Figure 13

RAMAN SPECTRA OF MOLTEN

(1) CF_3CONH_2, (2) CF_3COND_2

3506 cm^{-1} band, although the concentration of such species in the liquid state is expected to be low.

The doublet structure of the band in the carbonyl region suggests complete association does not occur even in the liquid state. The two components are resolved into a strong band at 1721 cm^{-1} and a shoulder of less intensity at approximately 1735 cm^{-1}. The appearance of more than one C=O stretching component is confirmed by the previous study of CF_3CONH_2 by Fonteyne(18) and the assignments are made in a similar manner: 1721 cm^{-1} band is assigned to the associated species while the band at 1735 cm^{-1} is correlated with the monomer. Assigning these bands to a' species is confirmed by polarization measurements (Figure 14).

It is felt that the bands observed at 1619 and 1439 cm^{-1} can not be adequately described in terms of simple vibrations. Rather, each band most likely arises from a vibration containing components of NH_2 deformation and C-N stretching vibrations due to coupling between these modes. The main justification for this view is found in the behavior of these bands upon deuteration. In the spectrum of CF_3COND_2, the 1619 cm^{-1} band appears to be absent while new bands are observed at 1449 and 1250 cm^{-1}. The 1116 cm^{-1} band also observed in CF_3COND_2 may be new but it is difficult to say with certainty since this band may be attributed to the presence of undeuterated amide. The small but significant increase in frequency from 1439 to 1449 cm^{-1} observed in the two spectra suggests that the same vibration responsible for these bands is highly unlikely.(66) Therefore, it seems reasonable to assume that the 1619 cm^{-1} band in CF_3CONH_2, involving mixed NH_2 deformation and C-N stretching modes, shifts to 1449 cm^{-1} in CF_3COND_2 (frequency ratio of 1.12). Further, the

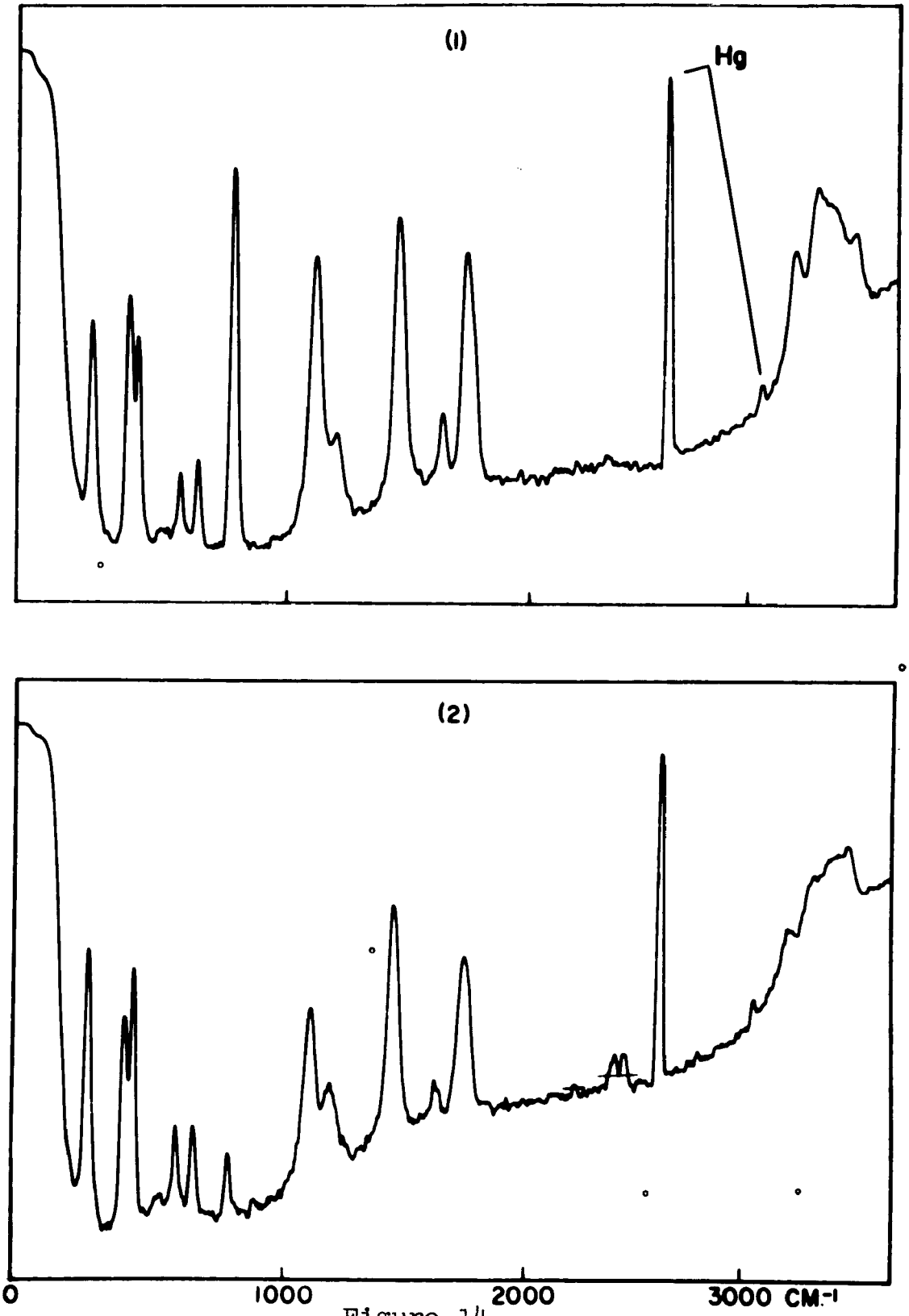


Figure 14

POLARIZED
RAMAN SPECTRA OF MOLTEN CF_3CONH_2

(1) $E_\perp$, (2) $E_\parallel$

1439 cm^{-1} band also containing both NH_2 deformation and C-N stretching characteristics is assumed to shift to either 1251 cm^{-1} (ratio of 1.15) or 1116 cm^{-1} (ratio of 1.29) upon deuteration. The choice involving the 1116 cm^{-1} band appears more reasonable since the 1251 cm^{-1} band can be attributed to a C-F stretching vibration. This latter assignment is not entirely satisfactory, however, because of the absence of a band near 1250 cm^{-1} in CF_3CONH_2. It is to be emphasized that the assignment of these vibrations is at best approximate since motions of other atoms of the molecule are also involved.

Region from 1400 cm^{-1} to 800 cm^{-1}

The three overlapping Raman frequencies observed at approximately 1197, 1178, and 1159 cm^{-1} must represent fundamentals involving largely C-F stretching. The strong, polarized band observed at 1108 cm^{-1} is assigned to the rocking NH_2 motion in-plane on the basis of its frequency shift in the deuterated amide. Miyazawa has assigned the analogous vibration to 1092 cm^{-1} in formamide.(67) No evidence for the asymmetric NH_2 rocking motion was observed in the Raman spectrum.

Region Below 800 cm^{-1}

The intense, strongly polarized Raman line at 791 cm^{-1} must represent an a' fundamental involving largely C-C stretching. The three bands observed at 656, 593, and 520 cm^{-1} are assigned by analogy with CF_3COOH. That is, the 656 cm^{-1} band is attributed to the OCN skeletal deformation mode while the bands at 593 and 520 cm^{-1} are assigned to CF_3 deformation vibrations. Interchange of the assignments of the 656 and 593 cm^{-1} bands is, however, equally reasonable. Although these last

three assignments are inconsistent with those suggested by Fonteyne, the present assignments appear to be supported by a consideration of other trifluoromethyl compounds.

The low lying frequencies at 263, 397, and 432 cm^{-1} represent, in part, fundamentals involving rocking motions. The bands at 263 and 432 cm^{-1} are assigned to asymmetric and symmetric CF_3 rocking, respectively, on the basis of the expected slight frequency shift in going from CF_3CONH_2 to CF_3COND_2. The polarized Raman band at 397 cm^{-1} is of medium intensity and the motion responsible for this band probably involves largely CCO deformation. Owing to the closeness of the 432 and 397 cm^{-1} frequencies, considerable mixing probably occurs. Fonteyne assigned these bands to C-F stretching and CF_3 deformation modes; however, these frequencies are obviously far too low, when compared with values observed in other CF_3 compounds.

The torsional motions identified with the CF_3- and NH_2- motions about the C-C axis were not observed in the Raman spectrum. This is not unexpected in view of the weak intensities associated with these modes.

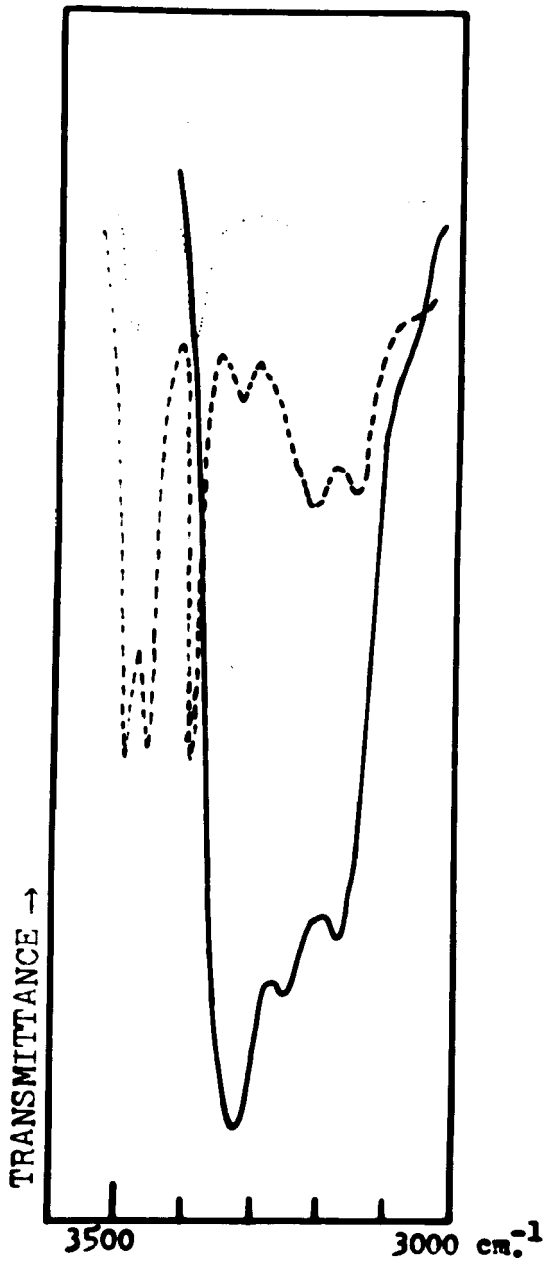
The frequencies and estimated relative intensities obtained for CF_3CONH_2 are compared in Table XI with results reported by Fonteyne.

In order to study the influence of molecular association on the N-H stretching frequencies in more detail, the infrared absorption spectrum of trifluoroacetamide was studied in the region from 3000 to 3600 cm^{-1} in CCl_4 at various concentrations. Figure 15 shows this region. The sharp peaks at 3395 and 3490 cm^{-1} are assigned to the symmetric and asymmetric NH_2 stretching frequencies, respectively, in the monomer molecule. Association of trifluoroacetamide leads to the appearance of

TABLE XI

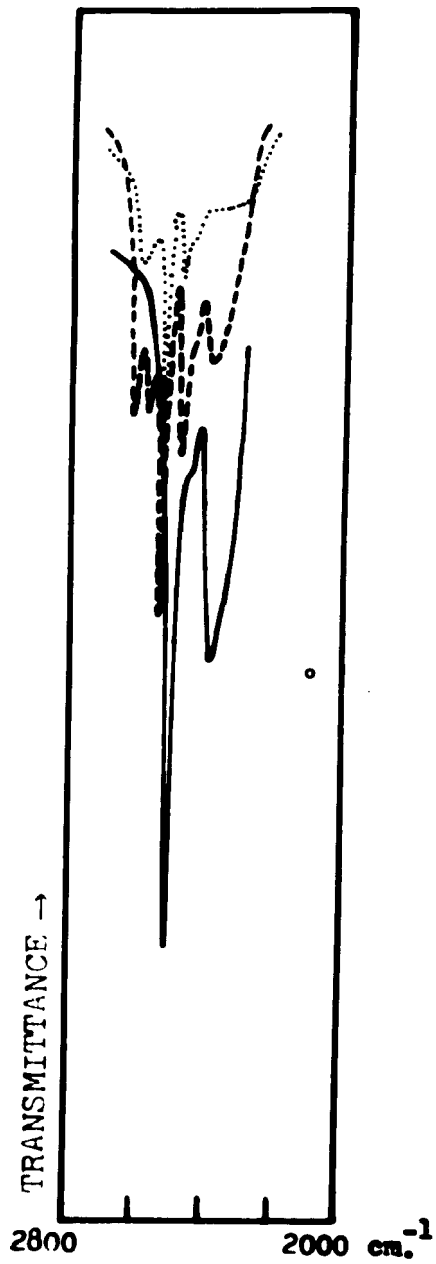
VIBRATIONAL FREQUENCIES (IN cm^{-1}) OF MOLTEN CF_3CONH_2

Fonteyne		This Research	
	Intensity		Intensity
202	(1/2)		
259	(4b)	263	s
394	(4b)	397	s
429	(5)	432	s
506	(1/2)	520	vw
587	(3)	593	w
651	(3)	656	w
740	(1)		
789	(7)	791	vs
1032	(1/2)		
1106	(3b)	1108	s
		1159	w
1189	(1b)	1178	w
		1197	w
1437	(7b)	1439	vs
1615	(1)	1619	w
1723 ± 7	(3b)	1721	s
1740 ± 10	(2b)	1735	s, sh
3190	(1b)	3216	w
3310	(1b)	3327	m-w
3365	(0)	3408	m-w, v br
3489	(1b)	3506	w



INFRARED ABSORPTION SPECTRA OF:
Trifluoroacetamide.
— solid,
--- 0.12% in CCl_4 (5 mm. cell),
••• 0.01% in CCl_4 (5 mm. cell).

Figure 15



Trifluoroacetamide-d_2.
— Nujol mull,
--- 0.06% in CCl_4 (5 mm. cell),
••• 0.02% in CCl_4 (5 mm. cell).

Figure 16

four new absorption centers at 3460, 3325, 3220, and 3155 cm^{-1} in the saturated solution. In the solid film, apparently only associated species are present but of a different nature than those present in solution because of the disappearance of the band at 3460 cm^{-1} and the simultaneous shift of relative intensities and frequencies in the 3150-3250 cm^{-1} region. The study of acetamide in chloroform solutions led Davies and Hallam[68] to conclude that the preferred form of associated molecules in this particular solvent was the trimer, whereas Senti and Harker[32] described the structure of acetamide in the solid as planar molecules arranged in rings of six adjacent molecules in the ring held together by hydrogen bonding. Data for the trifluoroacetamide case are lacking such that any statement would be purely hypothetical. The results for acetamide are suggestive, however. It is of interest to note that these submaxima observed in the associated NH stretching region of the amides are analogous to those observed in the associated OH stretching region of carboxylic acids.

The measured band positions, polarization characteristics of the bands, and assignments for the Raman spectrum of CF_3CONH_2 are given in Table XII. Table XIII summarizes the results of the infrared observations concerned with the NH stretching region.

Trifluoroacetamide-d_2

Region from 2700 cm^{-1} to 1400 cm^{-1}

Deutero trifluoroacetamide appears to be as highly associated as the normal amide. This is shown by the numerous bands observed in the N-D stretching region between 2400 and 2650 cm^{-1}. The strongest band appearing in this region at 2415 cm^{-1} is a likely candidate for the

TABLE XII

OBSERVED RAMAN FREQUENCIES AND ASSIGNMENTS FOR MOLTEN CF_3CONH_2

Frequency (cm^{-1})	State of Polarization	Approximate Assignment
263	depol.	CF_3 rocking
397	pol.	CCO deformation (CF_3 rocking)
432	depol. ?	CF_3 rocking (CCO deformation)
520		CF_3 deformation
593	depol. ?	CF_3 deformation
656	pol.	OCN deformation
791	pol.	C-C stretching
1108	pol.	NH_2 rocking
1159		C-F stretching
1178	depol.	C-F stretching
1197	pol.	C-F stretching
1439	pol.	Components of the accidental resonance of the NH_2 deformation and C-N stretching frequencies.
1619	pol.	
1721	pol.	C=O stretching (associated)
1735	pol.	C=O stretching (monomer)
3216	pol.	NH_2 stretching (associated)
3327	pol.	NH_2 stretching (associated)
3408	pol.	NH_2 symmetric stretching ? (monomer)
3506	depol. ?	NH_2 asymmetric stretching ? (monomer)

TABLE XIII

INFRARED ABSORPTION FREQUENCIES OF TRIFLUOROACETAMIDE IN CCl_4: 3000 cm^{-1} TO 3500 cm^{-1}

Frequency (cm^{-1})	Assignment
3490	NH_2 asymmetric stretching (monomer)
3460	NH_2 stretching (associated) ?
3395	NH_2 symmetric stretching (monomer)
3325	NH_2 stretching (associated)
3220	NH_2 stretching (associated)
3155	NH_2 stretching (associated) ?

associated ND_2 stretching mode. The less intense frequencies, 2358 and 2502 cm^{-1}, may be attributed to other associated stretching modes and to combination bands, although it cannot be said with certainty which is which. The remaining bands at 2571 and at approximately 2632 cm^{-1} (partially obscured by the 4916 Å mercury line) appear to be vibrations arising from monomer molecules.

Investigation of N-D stretching frequencies as a function of concentration in an inert solvent, CCl_4, was carried out in a manner similar to that discussed previously for the normal amide. Figure 16 shows the 2000-2800 cm^{-1} region containing these frequencies. The spectrum in solution shows that the intensities of the monomer absorption bands at 2550 and 2630 cm^{-1} attributed to monomer symmetric and asymmetric ND_2 stretching vibrations are increased by dilution with respect to the intensities of associated band maxima which gradually decrease. In the spectrum of the Nujol mull of CF_3COND_2, there is no evidence of monomer frequencies present. The ratios of corresponding frequencies in CF_3CONH_2 and CF_3COND_2, calculated for the monomer symmetric and asymmetric stretching modes, respectively, are both about 1.33. It does not seem worthwhile to discuss possible interpretations of the associated ND_2 stretching frequencies until additional studies on the nature of the associated structure become available.

The band associated with the C=O stretching frequency observed in the deuterated amide appears more complex than that in the normal compound. The Raman line shows two resolved, overlapping components at 1707 and 1725 cm^{-1}; however, the latter band corresponding to the monomeric stretching mode is slightly more intense than the former band which is assigned to the associated C=O stretching vibration. Both components

belong to species a' as shown in Figure 17. A possible explanation for the observed intensity pattern is that the intensity of the 1725 cm^{-1} band has been enhanced by a coincident combination band of a" species (617 + 1116).

The sharp, intense band at 1449 cm^{-1} corresponds to the motion involving both ND_2 deformation and C-N stretching vibrations. An analysis of this vibrational mode has been discussed in the previous section.

Region from 1400 cm^{-1} to 800 cm^{-1}

Assignment of the polarized, weak line at 1251 cm^{-1} and the medium intensity band at 1116 cm^{-1} has been discussed in the previous section. The C-F stretching frequencies of other molecules mentioned all lie in the region 1100-1300 cm^{-1}, and the assignment of the observed bands is consistent with this.

The intense, sharp band at 936 cm^{-1} is assigned to the rocking motion in-plane of the ND_2-group. A consideration of the effect of deuteration on this motion suggests a ratio of νNH_2 rocking/νND_2 rocking = 1.18, which may be compared with the value of 1.20 calculated for the corresponding motions of $HCONH_2$ and $HCOND_2$. The frequency associated with out-of-plane motion could not be identified in the spectrum.

Region Below 800 cm^{-1}

This region contains five vibrational bands. Of the three at 258, 380, and 425 cm^{-1}, which are sharp and intense, the 258 and 425 cm^{-1} bands are assigned to asymmetric and symmetric CF_3 rocking. The planar CCO bending mode which is considered to be more sensitive to isotopic substitution than the CF_3 rocking vibrations is, accordingly, assigned

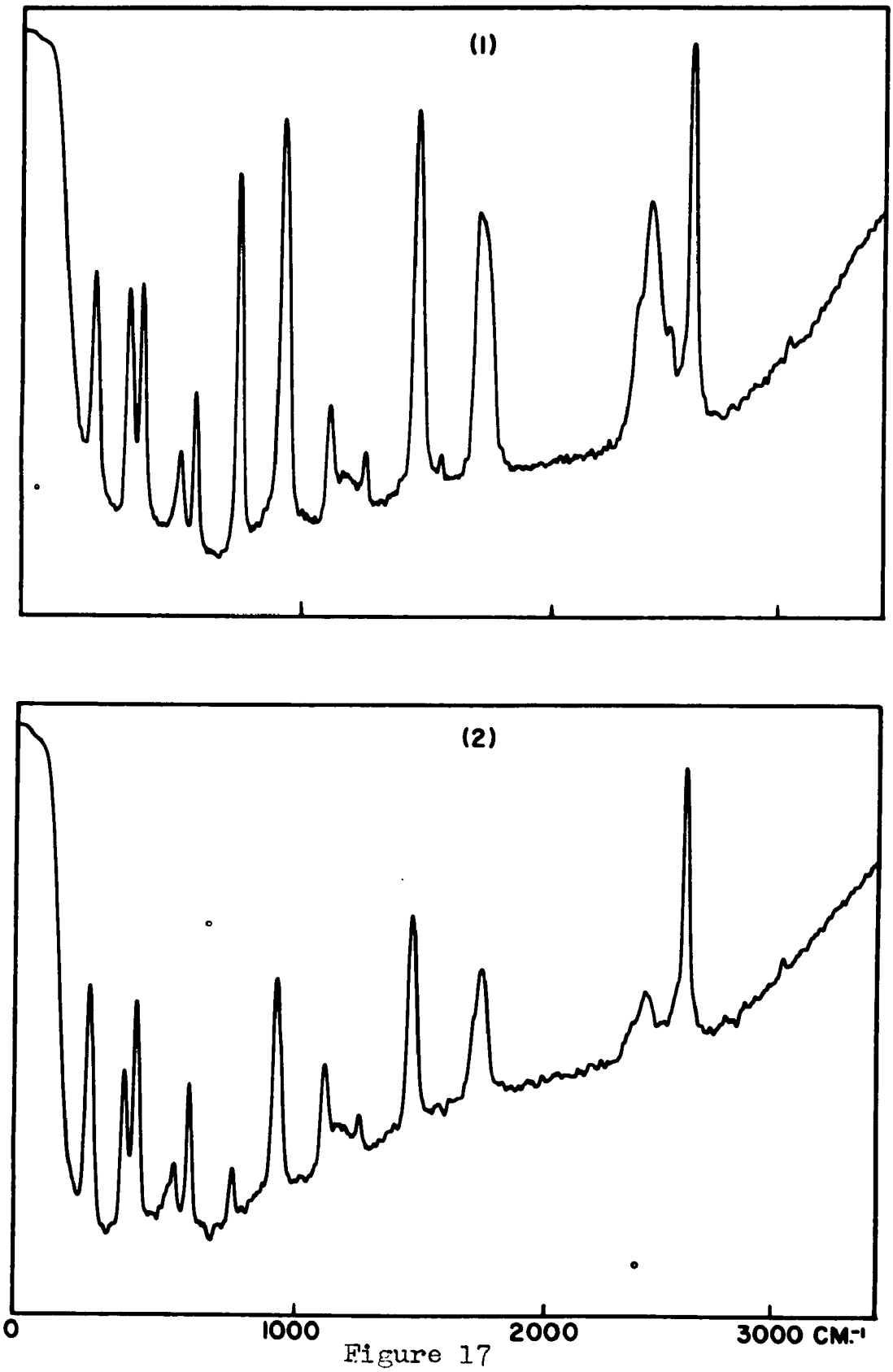


Figure 17

POLARIZED
RAMAN SPECTRA OF MOLTEN CF_3COND_2

(1)$E_\perp$, (2)$E_\parallel$

to 380 cm^{-1}. The descriptions of the 380 and 425 cm^{-1} modes again are approximate in view of mixing that probably occurs between the two. The remaining two bands, 563 and 617 cm^{-1}, must be associated with CF_3 deformations and the OCN deformation, but a clear-cut assignment of the latter band does not seem possible. The spectrum did not show any evidence of bands corresponding to torsional motions of either the CF_3- or the NH_2-group.

The frequencies, relative intensities, polarizations, and approximate descriptions of the vibrational bands of CF_3COND_2 are given in Table XIV. Table XV summarizes the results of the infrared observations concerned with the ND stretching region.

N-Methyltrifluoroacetamide

All elements of symmetry are eliminated by the probable configurations for the N-methyltrifluoroacetamide (NMT) molecule with the possible exception of a plane of symmetry containing the O, N, and three C atoms and also the amino-hydrogen atom. Two possible configurations are determined by the relative position of the hydrogen atom of the methylamine residue group with respect to the carbonyl bond: either cis or trans. The trans configuration proposed for N-methylacetamide by Mizushima et al. is assumed for NMT, although this configuration cannot be regarded as more than reasonably probable. Nevertheless, construction of the molecular model with this configuration shows less steric hindrance between the trifluoromethyl and methyl groups than with the alternative form. All thirty fundamental vibrations are expected to be active but not necessarily distinct in the Raman spectrum. In a first approximation, these can be classified as eleven bond stretching modes and nineteen deformations, three of which are torsional vibrations.

TABLE XIV

OBSERVED RAMAN FREQUENCIES AND ASSIGNMENTS FOR MOLTEN CF_3COND_2

Frequency (cm^{-1})	Intensity	State of Polarization	Approximate Description
258	s	depol.	CF_3 rocking
380	s	pol.	CCO deformation (CF_3 rocking)
425	s	depol. ?	CF_3 rocking (CCO deformation)
563	m-w, br	pol.	CF_3 deformation
617	m	depol. ?	CF_3 deformation or OCN deformation
773	s	pol.	C-C stretching
936	vs	pol.	ND_2 rocking
1116	m-w	depol. ?	Component of ND_2 deformation and C-N stretching interaction ? NH_2 rocking ?
1162	w		C-F stretching
1184	w		C-F stretching
1251	w	pol.	C-F stretching or component of ND_2 deformation and C-N stretching interaction.
1449	vs	pol.	Component of ND_2 deformation and C-N stretching interaction.
1544	vvw		936 + 617 ?
1707	s	pol.	C=O stretching (associated)
1725	s	pol.	C=O stretching (monomer)
2358	m	pol.	1725 + 617 ? ND_2 stretching (associated) ?
2415	s, br	pol.	ND_2 stretching (associated)
2502	m-w	pol.	1725 + 773 ? ND_2 stretching (associated)
2571	w	pol.	ND_2 symmetric stretching (monomer) ? 1449 + 1116 ?
2632	w, sh	depol. ?	ND_2 asymmetric stretching (monomer) ? 1707 + 936 ?

Examining first the vibrations which can be described as internal CF_3 modes, these will be the symmetric C-F stretching and two asymmetric stretching vibrations; the degeneracy of the asymmetric vibrations having been removed by the rest of the molecule. The physical representations of the asymmetric stretching modes are identical except for their orientation with respect to the plane of symmetry. It is therefore likely that these modes cannot be observed as two distinct spectral bands. In addition, a symmetric and two asymmetric CF_3 deformation modes are expected. It is reasonable to assume that the asymmetric deformations also will give rise to a single band as a result of accidental degeneracy. In addition to the CF_3 vibrations, six proper internal vibrations are predicted for the methyl group analogous to the motions described above.

TABLE XV

INFRARED ABSORPTION FREQUENCIES OF TRIFLUOROACETAMIDE-d_2 IN CCl_4: 2000 cm^{-1} TO 2800 cm^{-1}

Frequency (cm^{-1})	Assignment
2630	ND_2 asymmetric stretching (monomer)
2590	ND_2 stretching (associated) ?
2550	ND_2 symmetric stretching (monomer)
2500	ND_2 stretching (associated)
2400	ND_2 stretching (associated)

Considering the methyl and trifluoromethyl groups moving as rigid units, each group will show two rocking motions with respect to the symmetry plane: in-plane and out-of-plane. Further, each group

will exhibit a torsional motion. The amino-hydrogen will be involved in three vibrations: N-H stretching, NH rocking in the symmetry plane, and NH rocking perpendicular to this plane.

The remaining frequencies arise from the skeleton composed of the O, N, and three C atoms; four frequencies will be essentially of bond stretching character and five will be principally angular deformations. The skeletal stretching modes can be allocated one to each bond while the deformation modes consist of three bending vibration in the symmetry plane and two out of the plane. This description of the fundamental modes must be regarded as approximate only.

It was found convenient to obtain the Raman spectrum of NMT in the molten state in view of the relatively low melting point (56-57°C). Figure 18 shows densitometric tracings of the spectrum using natural and parallel polarized incident light. A discussion of the various regions of the spectrum follows.

Region from 3600 cm^{-1} to 3100 cm^{-1}

It is generally accepted that the 3300 cm^{-1} absorption band in the spectra of monosubstituted amides is the N-H stretching vibration reduced in frequency by hydrogen bonding. The Raman spectrum shows a very broad band at approximately 3340 cm^{-1} and is assigned, accordingly, to the associated N-H stretching. Assigning the weak Raman line at 3466 cm^{-1} to the monomer N-H stretching is based on the observation of the line's intensity as a function of dilution in the infrared absorption spectrum. In Figure 19, this band, absent in the Nujol mull of NMT, is shown to increase in intensity in dilute CCl_4 solutions with respect to the strong associated N-H stretching band. The latter decreases in intensity and subsequently disappears as dilution proceeds.

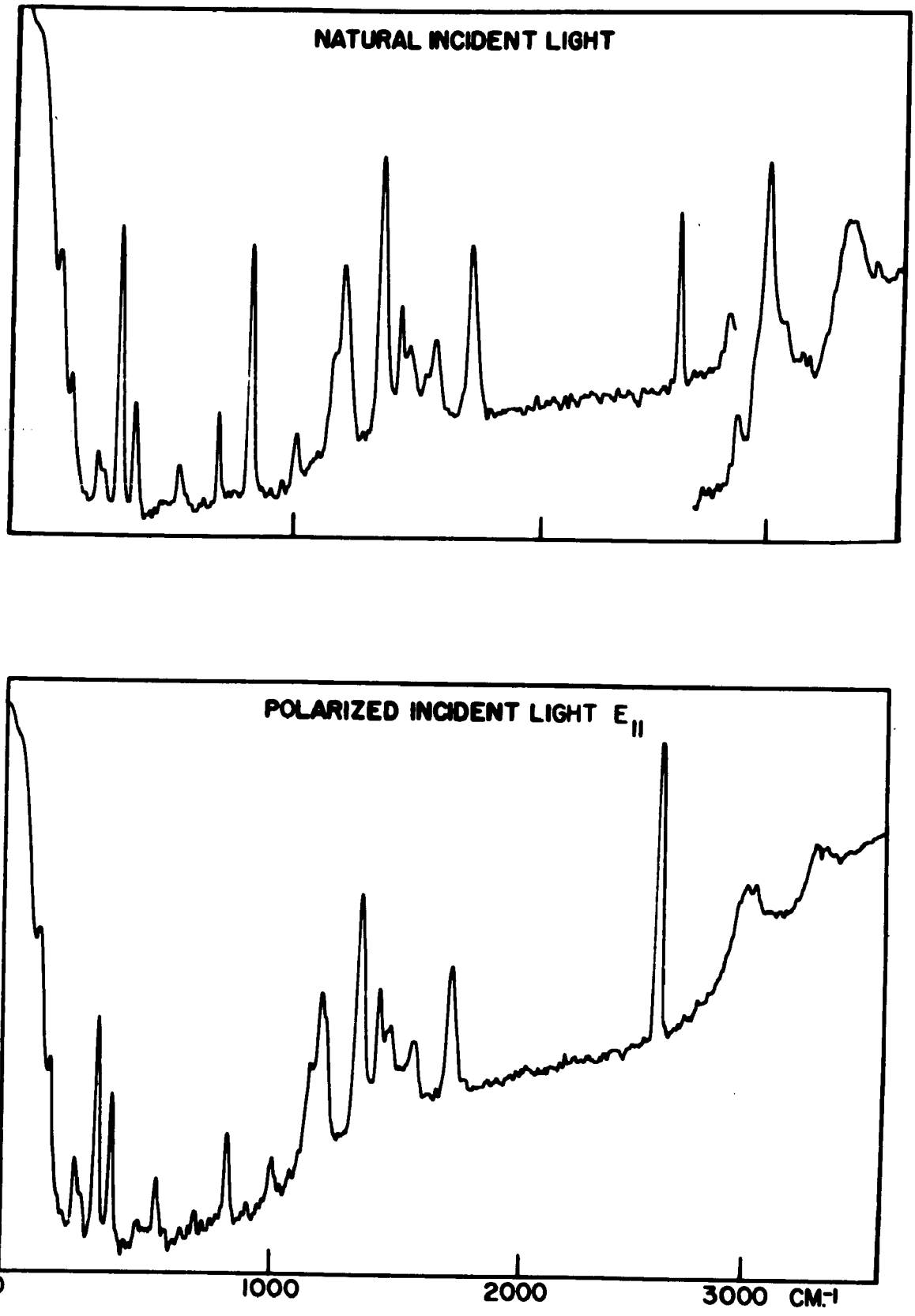


Figure 18
RAMAN SPECTRA OF MOLTEN $CF_3CONHCH_3$

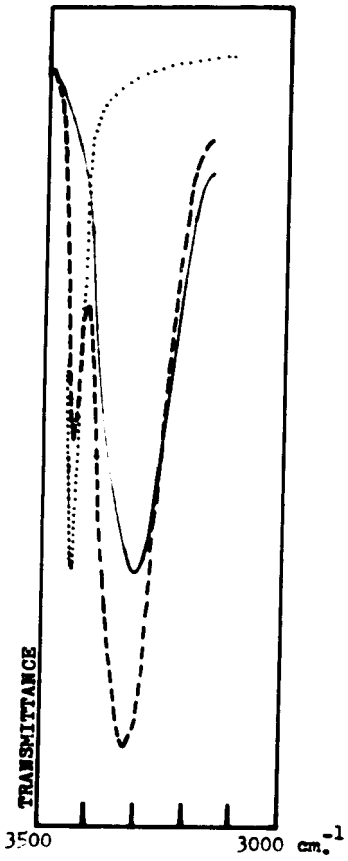


Figure 19

INFRARED ABSORPTION SPECTRA OF N-METHYLTRIFLUOROACETAMIDE.
— Nujol mull,
--- 4.0% in CCl_4 (0.1 mm. cell),
... 0.4% in CCl_4 (0.1 mm. cell).

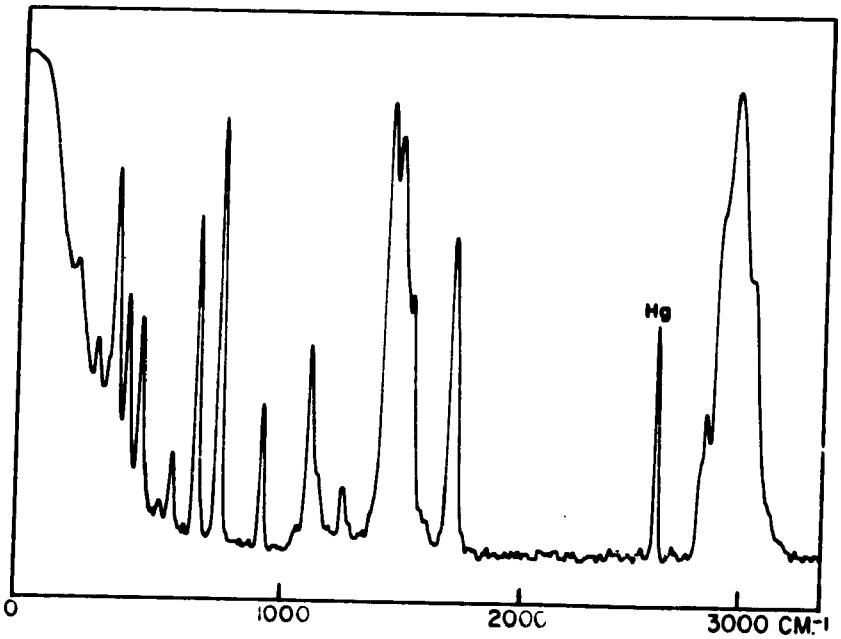


Figure 20

RAMAN SPECTRUM OF $CF_3CON(CH_3)_2$

Region from 3100 cm^{-1} to 1800 cm^{-1}

A consideration of established results for other molecules shows that the C-H stretching modes are expected to occur in the present region. Bellamy[69] suggests that the symmetrical and asymmetrical C-H stretching vibrations are found at 2872 cm^{-1} and 2962 cm^{-1}, respectively. The influence of other substituents has not yet been investigated sufficiently to permit any precise statements to be made in regard to shifts of these frequencies although the 2872 cm^{-1} frequency is expected to shift upward when the methyl group is attached to nitrogen. However, Nielsen et al. have observed the symmetric and asymmetric C-H stretching frequencies to occur as high as 2975 and 3035 cm^{-1}, respectively, in 1,1,1-trifluoroethane. The strongest band in this region of NMT appears at 2958 cm^{-1} with broad shoulders occurring at 2914 and 3002 cm^{-1} and an additional shoulder at 3034 cm^{-1}. The interpretation of these bands is complicated by the possibility of Fermi resonance occurring between the first overtones of CH_3 deformation modes and fundamental C-H stretching vibrations. A reasonable assignment of these Raman lines is to consider the symmetrical C-H stretching frequency responsible for the most intense and polarized Raman band at 2958 cm^{-1} and, in turn, assign the bands at 3002 and 3034 cm^{-1} to the asymmetric stretching modes. The remaining frequencies may be attributed to overtone and combination bands. It may be concluded that the localized force field of the methyl group is sufficiently perturbed by the inductive effect of the fluorine atoms to account for the shifts of the C-H stretching bands to higher frequencies even though the two groups are located at opposite ends of the molecule.

Region from 1800 cm^{-1} to 1300 cm^{-1}

A very large number of simple N-monosubstituted amides has been examined and many of the results show a strong absorption band near 1640 cm^{-1} which has been designated as the amide I band (principally carbonyl absorption). A second strong band in the 1500-1600 cm^{-1} region has been observed and is referred to generally as the amide II band, although the origin of this band is not with certainty established. However, the most generally favored explanation at present is that this frequency, in addition to a second frequency, arises from coupling of in-plane deformation mode of the N-H group with the pseudo-symmetric ν_s(OCN) vibration. The position of the second frequency has been suggested as about 1300 cm^{-1}. Since this latter frequency also appears to be characteristic of the amide grouping, it is referred to as the amide III band. The medium intensity, broad 1710 cm^{-1} band in the Raman spectrum of NMT is the logical choice for the amide I band. The C=O stretching frequency for NMT, thus, is significantly higher than that for N-methylacetamide and is due undoubtedly to the influence of the α-halogen substitution. This striking influence of the CF_3-group on the carbonyl group does not appreciably affect the amide II and amide III bands since their frequencies lie approximately at the expected positions, that is, 1564 and 1347 cm^{-1}, respectively. Since these bands correspond to vibrations of species a', it is seen in Figure 18 that the correct assignment has been made.

Deformation modes of the methyl group attached to a nitrogen atom can be expected to give bands at 1413 and 1445 cm^{-1} corresponding to symmetric and asymmetric frequencies. The assignment of 1422 and 1462 cm^{-1} to the CH_3 deformation modes observed in the Raman spectrum is consistent with this.

Region from 1300 cm^{-1} to 800 cm^{-1}

Some confusion arises in trying to assign the symmetric and asymmetric CH_3 rocking frequencies as there are five different frequencies in the same region. The other three frequencies arise from C-F stretching vibrations. At best one can perhaps assign 1155 and 1195 cm^{-1} to the respective asymmetric and symmetric rock and 1209 cm^{-1} to C-F stretch, the remaining C-F stretching modes being obscured by the overlapping bands; however, this choice is somewhat arbitrary.

As there is no reason to suppose that the bond order of the H_3C-N link of the methyl amine residue has been increased in NMT, assignment of this stretching vibration can be compared with those in simple amines. This assignment to the weak, polarized band at 1021 cm^{-1} appears consistent with the similar assignment in CH_3NH_2 (1044 cm^{-1}). The intense, strongly polarized band at 851 cm^{-1} must involve largely C-C stretching.

Region Below 800 cm^{-1}

In the trifluoromethyl group deformation region, there might be a question as to choice between 732 and 593 cm^{-1} for the OCN deformation frequency. However, the assignment is made by analogy with N-methylacetamide (627 cm^{-1}).

The a' and a" CF_3 rocking modes are assigned tentatively to the bands at 303 and 429 cm^{-1}, respectively, and the planar CCO bending mode to the intense, strong band at 375 cm^{-1}. Interchange of the last two assignments is, however, equally reasonable. It is possible that the rocking and bending modes interact strongly because of the closeness of the frequencies. The result is that the observed vibrational frequencies,

325 and 429 cm^{-1}, may be regarded as combinations of the corresponding characteristic frequencies. It should be noted that in the Raman spectrum of N-methylacetamide no bands between 300 and 400 cm^{-1} were observed but a medium intensity 440 cm^{-1} line was reported.(34) The weak intensity, polarized band at 325 cm^{-1} is assigned to the CNC bending mode by analogy with the COC bending assignment for methyl trifluoroacetate (329 cm^{-1}).

The remaining modes of interest are the torsional motions of the methyl and trifluoromethyl groups and the motion of the methylamine residue about the C-N link. The weak, depolarized Raman lines at 164 and 209 cm^{-1} are likely candidates for these motions and the depolarized 303 cm^{-1} line is also a possibility, although the last frequency has been assigned already to CF_3 rocking.

The measured band positions and approximate assignments of $CF_3CONH(CH_3)$ are given in Table XVI.

N,N-Dimethyltrifluoroacetamide

The plane containing the O, N, and four C atoms is assumed to be the only element of symmetry present in the N,N-dimethyltrifluoroacetamide(DMT) molecule. The thirty-nine fundamental vibrations predicted by the selection rules for a C_s symmetry are distributed between the two symmetry classes: 24 a' and 15 a". Frequencies belonging to both classes are Raman active but only the a' fundamentals give rise to polarized Raman bands. Of these fundamental vibrations, twenty-three degrees of vibrational freedom arise from the motions of the $H_3C\text{-}N\text{-}CH_3$ group which may be described as follows:

TABLE XVI

OBSERVED RAMAN FREQUENCIES AND ASSIGNMENTS FOR MOLTEN $CF_3CONH(CH_3)$

Frequency (cm^{-1})	Intensity	State of Polarization	Approximate Description[a]
164	w	depol.	torsion
209	w	depol.	torsion
303	w	depol.	CF_3 rocking, torsion ?
325	w, sh	pol.	CNC deformation
375	vs	pol.	CCO deformation or CF_3 rocking
429	m	pol. ?	CF_3 rocking or CCO deformation
531	vw		CF_3 deformation
551	vw		CF_3 deformation
593	w	pol. ?	OCN deformation
732	m-w	pol.	CF_3 deformation
851	vs	pol.	C-C stretching
1021	w	pol.	H_3C-N stretching
1155	m-w	depol. ?	CH_3 rocking (a',a") and C-F stretching (a',a',a")
1195	m-s, br	pol.	
1209	m, sh	pol. ?	
1347	s	pol.	amide III band
1422	m-w	pol.	CH_3 deformation
1462	w, br	depol.	CH_3 deformation
1564	w, br	pol.	amide II band
1710	m	pol.	amide I band

TABLE XVI (CONT'D)

Frequency (cm^{-1})	Intensity	State of Polarization	Approximate Description[a]
2825	w	pol.	b
2914	m-w, sh	pol.	1710 + 1209 ?, b
2958	m	pol.	C-H stretching
3002	w, sh	pol. ?	C-H stretching
3034	w, sh	depol.	C-H stretching ?
3340	w, vbr	pol.	N-H stretching (associated)
3466	vw	pol. ?	N-H stretching (monomer)

[a] Description of the fundamentals is for formal classification.

[b] These bands may be the first overtone of the CH_3 deformation in strong Fermi resonance with the C-H stretching frequencies or the fundamentals of C-H stretching.

a. Twelve of the vibrational frequencies may be attributed to motions of the hydrogen atoms. Six C-H stretching frequencies are expected to lie between 2800 and 3000 cm^{-1} while six deformation frequencies should occur in the 1300-1500 cm^{-1} region.

b. Bands due to rocking motions of the methyl groups occur around 1000-1200 cm^{-1}. It is unlikely that the four frequencies in the present case will be sufficiently split so as to allow all bands to be observed.

c. Two vibrational frequencies will arise from torsional motions of the methyl group. Such motions are very difficult to observe, particularly in the liquid state, since the intensity associated with these modes is usually very weak. The probable frequencies of these are expected to lie below 300 cm^{-1}.

d. Two of the vibrational degrees of freedom may be attributed to the rocking motion of the $-N(CH_3)_2$ group moving as a unit both in the symmetry plane and out of the plane.

e. The three remaining motions are due to the skeletal vibrations of the $H_3C-N-CH_3$-group. These may be described as the symmetric and asymmetric stretching of the H_3C-N bonds, and the deformation of the CNC angle. As a first approximation, these modes may be correlated with those found for dimethylamine.

The sixteen remaining fundamental vibrations for DMT are concerned with the CF_3CON-group. A description of these modes has been given in the previous section with regard to the vibrational assignment of NMT.

The Raman spectrum was obtained of DMT in the liquid state at room temperature and a tracing of the spectrum is shown in Figure 20.

Qualitative polarization data were obtained using Polaroid cylinders and the results are shown in Figure 21.

It seems pointless to attempt a detailed assignment for the C-H stretching region in view of the difficulties likely to be encountered (Fermi resonance); the assignment of such a large number of frequencies can only be tentative. Similarly, the CH_3 deformation region is complicated by several overlapping bands. Further, the characteristic frequency $\nu_s(OCN)$ now is expected in this region[47], since coupling between the latter vibration and the planar N-H deformation found in trifluoroacetamide and N-methyltrifluoroacetamide is eliminated by the removal of the amino-hydrogen. One is tempted to assign the medium intensity, polarized band at 1492 cm^{-1} to the characteristic frequency $\nu_s(OCN)$ on the basis of the similar assignment for N,N-dimethylacetamide (1497 cm^{-1}). Accordingly, the remaining bands in this region are attributed to CH_3 deformation modes.

The strong band at 1691 cm^{-1} is assigned to amide I (carbonyl stretching) with considerable certainty. It is interesting to note that the width of this band has been markedly reduced with the elimination of association in this disubstituted amide. The Raman band which was assigned to amide II of NMT is absent in the present spectrum.

The assignment of the methyl group rocking fundamentals from the observed Raman spectrum is by no means an easy task. The bands should be nearly the same frequencies as the corresponding bands of dimethylamine. Therefore, bands in the 1150-1250 cm^{-1} region are to be expected from these modes. It can be seen in the spectrum that there is an overlapping of CH_3 rocking and C-F stretching lines, and neither can be assigned with certainty.

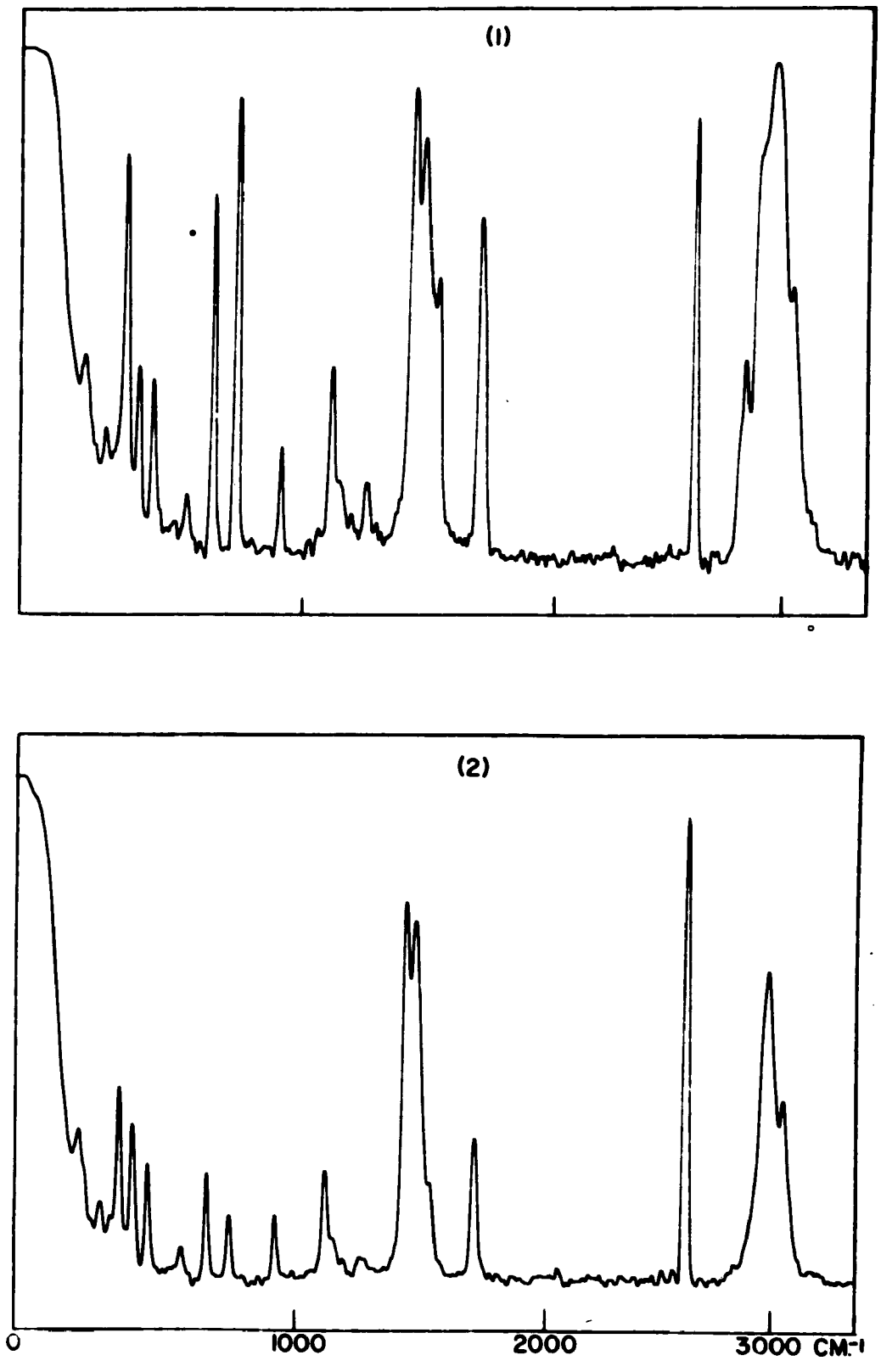


Figure 21

POLARIZED RAMAN SPECTRA OF $CF_3CON(CH_3)_2$

(1) $E_\perp$, (2) $E_{||}$

The medium weak 928 cm^{-1} line is assigned tentatively to the symmetric H_3C-N stretching frequency. The asymmetric skeletal motion is not readily identified unless it is responsible for the medium intensity band at 1111 cm^{-1}. The H_3C-N-CH_3 deformation frequency occurring at 397 cm^{-1} in dimethylamine is assigned to the polarized band at 464 cm^{-1}. The very intense, polarized line at 756 cm^{-1} must represent an a' fundamental involving largely C-C stretching.

Assignment of CF_3 deformation and OCN bending modes is consistent with previous assignments. Frequencies below 450 cm^{-1} are assigned on the basis of the probable regions appropriate to the different modes of vibration, and the Raman spectrum of N,N-dimethylacetamide has been helpful in this assignment. Rocking modes of the CF_3-group are assigned tentatively to the bands at 297 and 362 cm^{-1} and the planar CCO bending mode is attributed to the medium intensity band at 411 cm^{-1}. Identification of the two methyl torsional motions is particularly uncertain. It may be the pair of depolarized lines at 219 and 297 cm^{-1} although the latter band has been assigned already to CF_3 rocking. The remaining weak line at 336 cm^{-1} is a likely candidate for either $N(CH_3)_2$ rocking or C-N torsional vibration.

Table XVII contains the measured band positions and an approximate assignment for the Raman spectrum of DMT.

Conclusions Drawn from the Spectra of Unsubstituted and Substituted Trifluoroacetamides

The observed spectra in this investigation possessed the same gross features as the corresponding series of nonfluorinated acid amides reported by various investigators. In particular, the amide II band

TABLE XVII

OBSERVED RAMAN FREQUENCIES AND ASSIGNMENTS FOR LIQUID $CF_3CON(CH_3)_2$

Frequency (cm^{-1})	Intensity	State of Polarization	Approximate Assignment[a]
219	w	depol.	CH_3 torsion ?
297	w	depol.	CF_3 rocking or CH_3 torsion
336	w, sh	depol.	$N(CH_3)_2$ rocking or C-N torsion
362	m-s	pol.	CF_3 rocking
411	m	pol. ?	CCO deformation
464	m	pol.	CNC deformation
539	w		CF_3 deformation
585	m-w		OCN deformation
673	s	pol.	CF_3 deformation
756	vs	pol.	C-C stretching
928	m-w	pol.	H_3C-N symmetric stretching
1111	m	pol.	CH_3 rocking or H_3C-N asymmetric stretching
1148	w-m	depol.	CH_3 rocking or C-F stretching
1192	vw		CH_3 rocking or C-F stretching
1252	w-m	pol.	CH_3 rocking or C-F stretching
1420	vs	pol.	CH_3 deformation
1457	vs	depol. ?	CH_3 deformation
1492	m-s, sh	pol.	ν_s(OCN)
1518	m-s	pol.	CH_3 deformation
1691	m-s	pol.	amide I

TABLE XVII (CONT'D)

Frequency (cm^{-1})	Intensity	State of Polarization	Approximate Assignment[a]
2808	w	•	b
2830	m-w	pol. ?	b
2892	s, sh	pol.	b
2952	vs, br	pol.	C-H stretching
2970	vs, sh	depol. ?	C-H stretching
3026	s, sh	depol.	C-H stretching
3050	s, sh	depol.	C-H stretching ?

[a] The description of the fundamentals is for classification purposes.

[b] Bands may be the fundamentals of symmetric C-H stretching frequencies or the first overtone of the CH_3 deformation in Fermi resonance with the stretching frequencies.

observed when hydrogen was attached to the amide nitrogen disappeared upon complete methylation. It was felt that the lack of coupling in DMT adequately explained its absence and that the subsequent assignment of the pseudo-symmetric ν_s(OCN) vibration in the methyl deformation region of DMT is probably correct. The detailed findings of the present research indicate that the influence of the trifluoromethyl group on the C=O stretching frequency persists in the amides as well as in the acid and the ester. In the molecule $CF_3CONR_1R_2$, where R_1,R_2 = H, the C=O stretching frequency was observed to be the highest and in the case where both R's were methyl groups, this frequency was the lowest. This similar effect is noticed in the corresponding nonfluorinated amide series, $CH_3CONR_1R_2$. Furthermore, it was observed that the carbonyl stretching frequency of the fluorine-containing amide was always higher than the nonfluorinated analogue.

Unfortunately, the results of this study did not indicate what contribution the resonance structure makes to the actual electronic configuration of the amide. It was assumed in the discussion of the series that rotation about the C-N bond was restricted and that the molecule was planar or nearly planar. In regard to NMT, the <u>trans</u> form was assumed although the only basis for this assumption was the similar configuration suggested for N-methylacetamide.

Although a really complete justification of the above assignments of the various compounds cannot be given, the one presented probably is the best choice in a situation which is confused by the mixing of important fundamentals, association in the case of CF_3CONH_2, CF_3COND_2, and $CF_3CONHCH_3$, and the superposition of several bands. By comparing

corresponding bands particularly those of the CF_3-group in this closely related series, inconsistencies in assigning these spectral bands were partially eliminated; the weak intensities of several of the CF_3-group Raman bands prevented a conclusive assignment.

Trifluoroacetamidine

The problem of assigning the fundamental vibrations for trifluoroacetamidine may be conveniently attacked by using the spectrum of trifluoroacetamide as a starting point. Since the two molecules have nearly identical configurations and are isoelectronic, it may be concluded that the symmetry for trifluoroacetamidine cannot be of any higher order (but may be less) than that assumed for trifluoroacetamide. Therefore, the only possible symmetry element most likely to be present is a plane. If the amidine polar resonance form, analogous to that for amides, contributes to the actual electronic structure of amidines, then the double bond character of the C-N linkage restricts rotation about that bond and the molecule is planar or nearly planar.

The Raman spectrum of deutero trifluoroacetamidine was used as an aid in assigning the fundamental vibrations of the normal compound. In Figure 22, the spectra of the two molecules in the liquid state are shown. The spectra were observed to change during the several hours that elapsed between the first and the last exposures taken on a given sample. Furthermore, both the viscosity and index of refraction were found to increase throughout the period of investigation. It was concluded from these observations that the compounds were unstable and a good deal more complex than had been anticipated. The spectra were obtained immediately after preparation and exposure times were limited

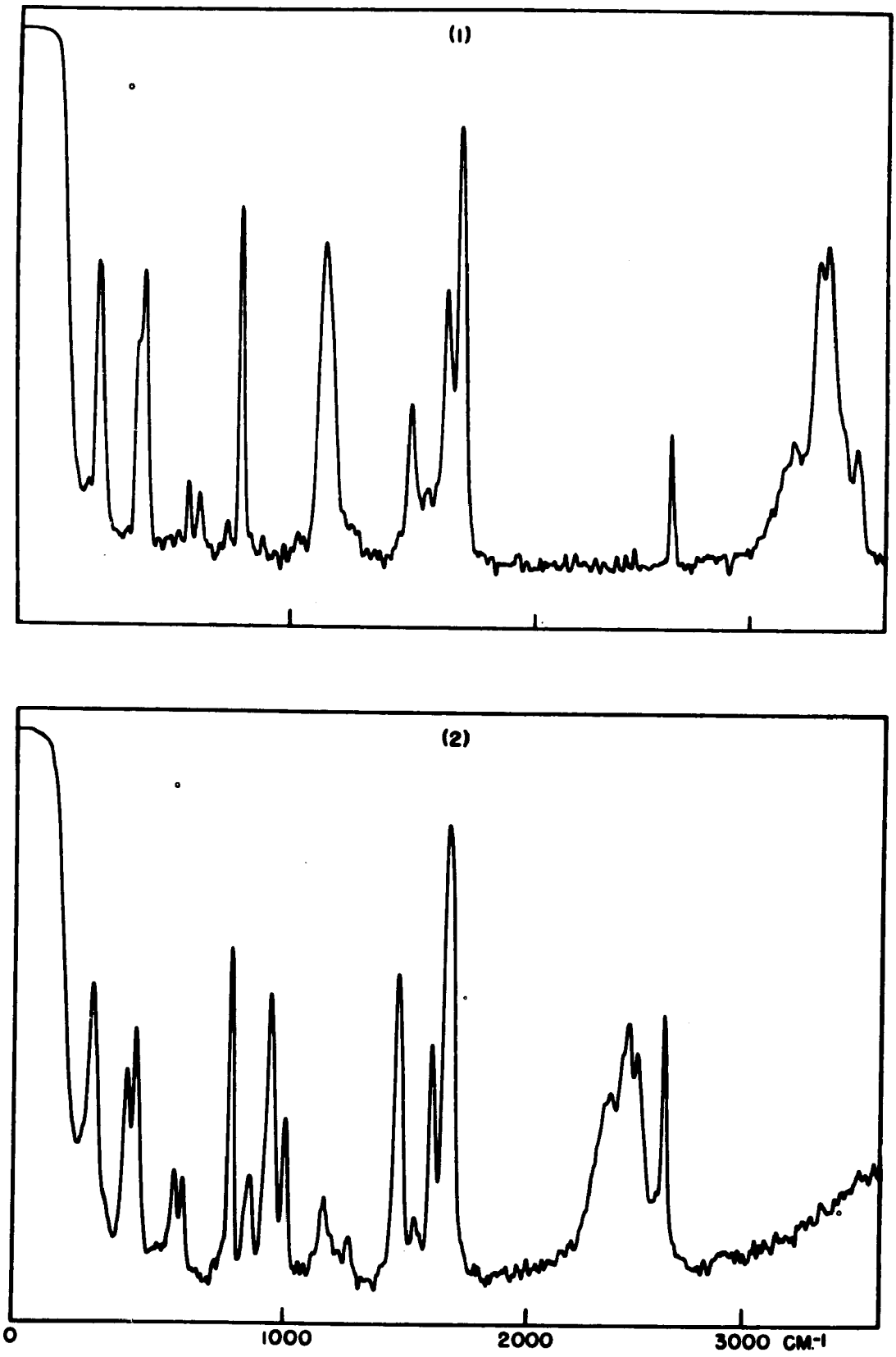


Figure 22

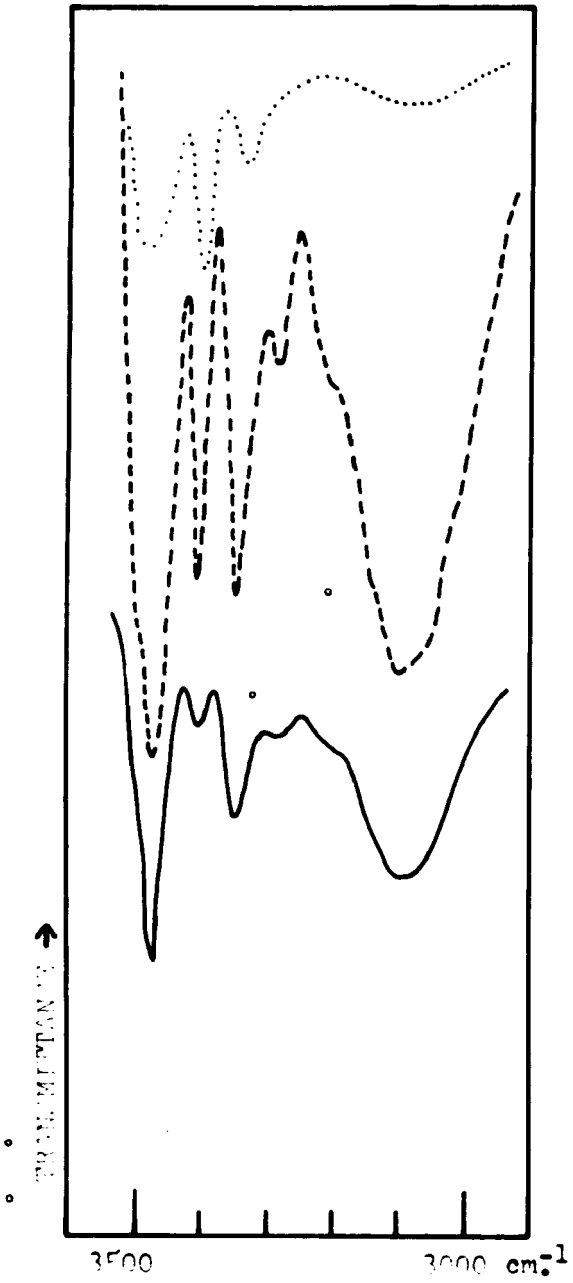
RAMAN SPECTRA OF LIQUID

(1) $CF_3C(=NNH_2)NH_2$, (2) $CF_3C(=ND)ND_2$

to several minutes in an attempt to record the spectrum of the desired compound before appreciable quantities of side products were formed. It was not possible to use polarization data in making assignments with as much effectiveness as in the case of stable compounds because of the limited exposure time.

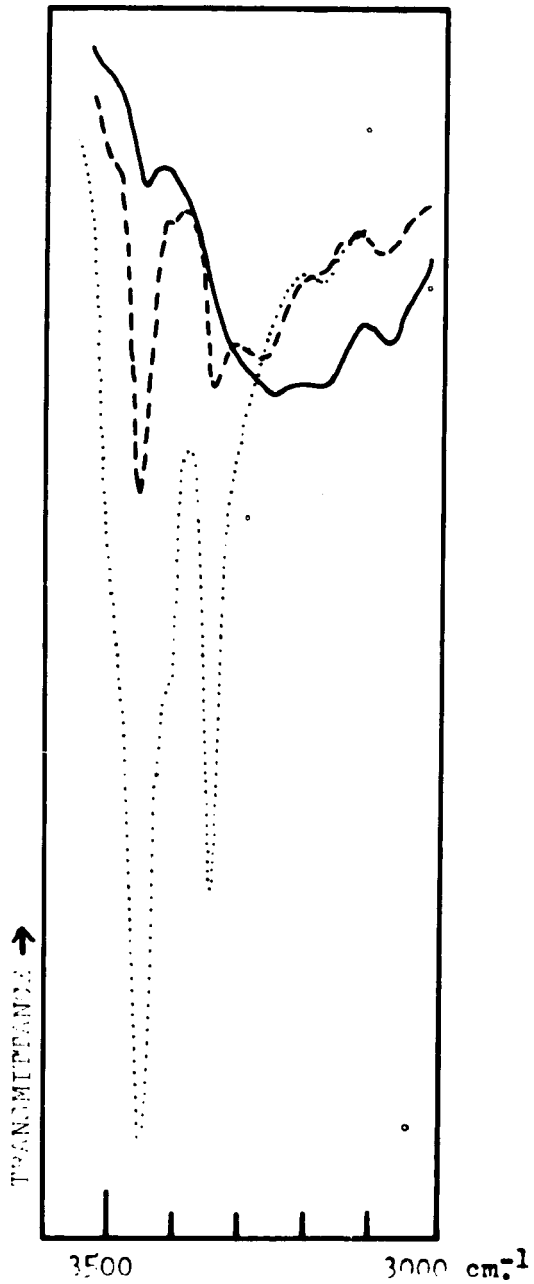
The similarity of the molecular configuration of trifluoroacetamidine to that of trifluoroacetamide is shown by the comparison of the two spectra (Figures 13 and 22). Theoretically, the amidine spectrum should show three additional bands due to the motions involving the imino-hydrogen atom: N-H stretch, N-H deformation in-plane, and N-H deformation out-of-plane. Since the fundamental vibrations common to both compounds are assigned under the same argument, repeating this discussion for the amidine derivative will not be necessary. Therefore, vibrational frequencies peculiar to this molecule will be treated. Although all twenty-four fundamental vibrations of trifluoroacetamidine are predicted to be active in the Raman spectrum, several of these frequencies were not observed.

One of the major differences which exists between the amide and amidine spectra occurs in the N-H stretching region. In addition to the NH_2 stretching vibrations, the imino-hydrogen stretch falls in this region. Three major bands appearing in the 3180-3350 cm^{-1} region are attributed to associated N-H stretching vibrations. In order to investigate the monomer N-H stretching region in detail, the infrared intensities of both monomers and associated molecules were studied as a function of dilution in CCl_4. The results of the investigation are shown in Figure 23.



INFRARED ABSORPTION SPECTRUM OF
Trifluoroacetamidine in CCl_4.
—— 0.49% soln. in 0.1 mm. cell,
--- 0.08% soln. in 5 mm. cell,
••• 0.01% soln. in 5 mm. cell.

Figure 23



INFRARED ABSORPTION SPECTRUM OF
N-Methyltrifluoroacetamidine.
—— liquid film,
--- 1.40% in CCl_4 (0.1 mm. cell),
••• 0.14% in CCl_4 (5 mm. cell).

Figure 24

In the saturated solution, both monomer and associated species are present while in the most dilute concentration shown, the solution is predominately monomeric. The absorption band at 3410 cm^{-1} is due undoubtedly to the monomeric form. Bands at 3350 and 3480 cm^{-1} are attributed also to monomer molecules although their assignment is not as clear-cut as that of the 3410 cm^{-1} band. The bands at 3410 and 3480 cm^{-1} are assigned to the respective symmetric and asymmetric NH_2 stretching vibrations. The infrared absorption band at 3350 cm^{-1} is assigned to the monomer imino-hydrogen stretching which agrees reasonably well with the corresponding assignment for N,N-dimethyltrifluoroacetamidine (3368 cm^{-1}, Raman value) which will be discussed later.

On the other hand, infrared spectra of dialkyl ketimines show a band in the 3205-3236 cm^{-1} region which the authors[70] apparently assign to the N-H stretching mode. The present assignment is considerably higher but in view of the possible contribution of the polar resonance form to the actual electronic configuration of the amidine molecule, one might expect the imino-hydrogen motion to be affected. Also, the lower frequency suggests that the imino-hydrogen is more strongly hydrogen bonded in ketimines.

The C=N stretching frequency for acetamidine is found at 1640 cm^{-1}[71] and, accordingly, the very strong band at 1673 cm^{-1} is assigned to this motion for the compound studied. The influence of the trifluoromethyl group on carbonyl frequencies thus appears paralleled by a similar effect on the imino group frequency. The assignment of the strong band at 1612 cm^{-1} presents a problem. The behavior of this band upon deuteration shows that it does not involve hydrogen motion (frequency ratio is

about 1.02). Previous investigations of associated molecules have resulted in assigning similar double bands (for example, carbonyl stretching frequency in CF_3COOH) to monomer and associated vibrations. In the present case, attributing bands at 1673 and 1612 cm^{-1} to monomer and associated imino stretching modes is not entirely satisfactory. The intensity of the associated frequency (1612 cm^{-1}) is observed to be less than that of the monomer (1673 cm^{-1}). One would expect the molecule to be highly associated in the liquid phase, in which case the observed intensities of the double bands should be reversed.

An alternative possibility is that both bands are due to associated species but not from the same associated form. In other words, both ring structures and linear polymers may be present in this highly associated liquid and the two components represent imino stretching frequencies in different configurations. It is not likely that the two bands arise from tautomerism involving the release of a proton (prototropy) since the tautomerides are identical. There does not appear to be a satisfactory explanation for these double bands other than to assume the imino group is responsible for these frequencies.

The NH_2 deformation frequency apparently is obscured by the broad overlapping C=N stretching bands in the present spectrum. The assignment of this vibration to the weak 1542 cm^{-1} line is not satisfactory in view of the latter's behavior on deuteration. The corresponding shift of about 12 cm^{-1} excludes the possibility that hydrogen motion is responsible for this band. It seems reasonable to assume that this band is due to a combination frequency or to an impurity band appearing from prolonged exposure.

The two bending modes of the imino-hydrogen group have not been completely characterized in compounds containing this group. One might take as a basis the comparison with the spectra of related molecules, namely, dimethylamine and methylhydrazine. The out-of-plane bending has been suggested as 724 cm^{-1} for dimethylamine.(72) The only likely candidate for this frequency in the spectrum is the weak 742 cm^{-1} band, although the relatively small shift of this band upon deuteration implies that assigning it to CF_3 deformation is more reasonable.

The planar NH bending frequency is also difficult to identify. Considering the assignment for methylhydrazine given by Axford et al.(73), one may suppose that it must occur near 1100 cm^{-1}, in which case, it probably appears superimposed on the NH_2 rocking frequency present also in this region, a reasonable explanation for the very broad band centered at about 1125 cm^{-1}. Accordingly, the strong, broad band at 1121 cm^{-1} is assigned to the planar NH_2 rocking and the shoulder appearing on the high frequency side of the above band at approximately 1133 cm^{-1} is attributed to the planar NH deformation.

In regard to the very weak, diffuse line at 878 cm^{-1}, there is no reasonable fundamental vibration that can be assigned to this band and it is assumed to be a combination frequency or due to an impurity. On deuteration this band apparently shifts to 848 cm^{-1} with increased intensity. The remaining spectral bands are assigned by analogy with trifluoroacetamide. No attempt was made to assign the torsion modes in the amidine spectrum. Band positions, relative intensities, and approximate assignments for $CF_3C(:NH)NH_2$ are collected in Table XVIII. Polarization data are not included because the limited exposure time

TABLE XVIII

OBSERVED RAMAN FREQUENCIES AND ASSIGNMENTS FOR LIQUID $CF_3C(:NH)NH_2$

Frequency (cm^{-1})	Intensity	Approximate Assignment
277	s	CF_3 rocking
413	m	CF_3 rocking or CC=N deformation
435	s	CF_3 rocking or CC=N deformation
522	vvw	CF_3 deformation
601	w	CF_3 deformation
640	w	NCN deformation
742	vw	CF_3 deformation or NH deformation out-of-plane (associated) ?
792	s	C-C stretching
878	vw	2 x 435? 1673-792? impurity?
1121	s, vbr	NH_2 rocking
1133	m, sh	NH planar deformation?
1196	vw, sh	C-F stretching
1243	vw	C-F stretching
1466	m	C=N stretching
1542	vw	1121 + 413? impurity?
1612	s	C=N stretching
1673	vs	C=N stretching
3183	w, br	N-H stretching (associated)
3310	s	N-H stretching (associated)
3347	s	N-H stretching (associated), (monomer) ?
3414	w, sh	N-H stretching (monomer)
3490	w	N-H stretching (monomer)

prevented satisfactory spectral measurements. The results of the dilution study of trifluoroacetamidine in CCl_4 are shown in Table XIX.

TABLE XIX

INFRARED ABSORPTION FREQUENCIES OF TRIFLUOROACETAMIDINE IN CCl_4: 3000 cm^{-1} TO 3500 cm^{-1}

Frequency (cm^{-1})	Assignment
3480	NH_2 asymmetric stretching (monomer)
3410	NH_2 symmetric stretching (monomer)
3350	Imino N-H stretching (monomer)
3300	N-H stretching (associated)
3100	N-H stretching (associated) ?

Trifluoroacetamidine-d_3

The N-H stretching frequencies in normal trifluoroacetamidine are observed to shift upon deuteration to the 2300-2600 cm^{-1} region. The strongest bands at 2347, 2438, and 2482 cm^{-1}, and a shoulder appearing on the low frequency side of the 2347 cm^{-1} band at 2417 cm^{-1} are likely candidates for the associated N-D stretching vibrations, using as a basis the observed spectrum of trifluoroacetamide-d_2. The low intensity bands at approximately 2540 and 2581 cm^{-1} are attributed, accordingly, to monomer N-D stretching. An attempt to study the effect of dilution on the intensities of the monomer and associated bands proved unsuccessful because of the rapid exchange of $CF_3C(:ND)ND_2$ with atmospheric moisture.

The double imino bands observed at 1673 and 1612 cm^{-1} for normal trifluoroacetamidine are shifted to 1642 and 1577 cm^{-1}, respectively, in the deuterated derivative. In both compounds, the higher frequency component appears as the more intense band. In addition, the weaker band in the deuterated compound (1577 cm^{-1}) has a diminishing intensity as dilution is increased (CCl_4 solvent) in the infrared spectrum whereas, in contrast, the band at 1642 cm^{-1} becomes more intense. This would imply that the latter band is due to monomeric species while the former has its origin in associated forms. The assignment of the weak 1531 cm^{-1} band to a combination frequency or to an impurity has been discussed in the previous section.

The very broad NH_2 rocking band at 1121 cm^{-1} is observed to shift on deuteration to 927 cm^{-1} (frequency ratio about 1.21). Similarly, the imino-hydrogen deformation appearing as a shoulder at 1133 cm^{-1} is shifted to 986 cm^{-1} (ratio about 1.15). Apparently isotopic substitution has affected these two frequencies by different amounts so that in the deuterated spectrum two frequencies can be clearly observed while in the normal spectrum, these frequencies are separated by about 12 cm^{-1}.

The remaining bands in the 1135-1250 cm^{-1} region are relatively weak. It is not certain whether the 1139 cm^{-1} band was present in the spectrum of trifluoroacetamidine since the strong 1121 cm^{-1} band could have easily obscured this band. The ND_2 deformation is expected in this region and is tentatively assigned to the 1139 cm^{-1} band. The other likely choice is the 1241 cm^{-1} band; however, since this band appears at nearly the same position in trifluoroacetamidine (1243 cm^{-1}), the assignment of the ND_2 bending to the 1139 cm^{-1} band appears more satisfactory.

Assigning the 1241 cm^{-1} band to C-F stretching is consistent with the previous assignment for the normal compound. It is entirely reasonable that the 1139 cm^{-1} frequency in the present spectrum corresponds to the band appearing as a shoulder at 1133 cm^{-1} in the spectrum of the normal compound, in which case the bands may be due to C-F stretching vibrations.

The only other band not readily identified in the spectrum and which does not appear in CF_3COND_2 is the medium weak band at 848 cm^{-1}. The origin of this band as discussed in the previous section apparently does not involve hydrogen motion and is assigned to a combination frequency.

The remaining observed spectral bands are assigned under the same argument used in assigning trifluoroacetamidine and trifluoroacetamide-d_2. The band positions, relative intensities, and approximate description of fundamentals for trifluoroacetamidine-d_3 are given in Table XX.

N-Methyl- and N,N-Dimethyltrifluoroacetamidine

These molecules are discussed together since it is convenient to analyze the spectral features from a comparison of their spectra. The respective isoelectronic molecules N-methyl- and N,N-dimethyltrifluoroacetamide have been discussed in detail and for a first approximation the spectra of the corresponding amidines should be similar. An inspection of the spectrum of N-methyltrifluoroacetamidine (NMT') indicated, however, that the molecule is more complex than had been anticipated. In contrast, the spectra of N,N-dimethyltrifluoroacetamidine (DMT') and N,N-dimethyltrifluoroacetamide are remarkably similar. In

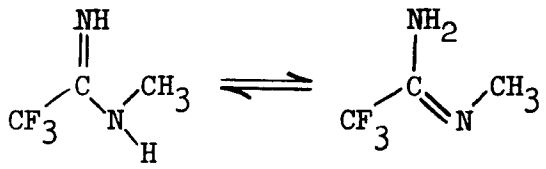
TABLE XX

OBSERVED RAMAN FREQUENCIES AND ASSIGNMENTS FOR LIQUID $CF_3C(:ND)ND_2$

Frequency (cm^{-1})	Intensity	Approximate Assignment
261	m	CF_3 rocking
385	m	CF_3 rocking or CC=N deformation
417	m	CC=N deformation or CF_3 rocking
505	vvw	CF_3 deformation
563	w	CF_3 deformation
596	w	NCN deformation
713	vw	CF_3 deformation
774	s	C-C stretching
848	m-w	2 x 417?, impurity?
927	s	ND_2 rocking
986	m	ND deformation
1139	w, diffuse	ND_2 deformation?
1191	w, diffuse	C-F stretching
1241	w, diffuse	C-F stretching
1437	s	C-N stretching
1531	w, diffuse	927 + 596?, impurity?
1577	m	C=N stretching (associated)
1642	vs	C=N stretching (monomer) ?
2347	m	N-D stretching (associated), 1577 + 774?
2417	m, sh	N-D stretching (associated), 1642 + 774?
2438	m	N-D stretching (associated)
2482	m	N-D stretching (associated)
2540	w, diffuse	N-D stretching (monomer)?
2581	w, diffuse	N-D stretching (monomer)?

order to explain the spectral differences for NMT', the phenomenon of tautomerism is suggested as a possibility.

In the case of NMT', the transfer of a proton results in the following tautomers:



(I) (II)

Assuming that appreciable quantities of both forms are present at equilibrium, in the absence of evidence that indicates one form predominates, the spectrum is expected to exhibit characteristic vibrations of both configurations. Considering that the polar resonance form contributes significantly to the electronic structure of amidines, one might conclude that both forms (I and II) are planar or nearly planar. In the case of I, two possible configurations are determined by the relative position of the hydrogen atom of the methylamine residue with respect to the imino bond must be considered. One is tempted to assume that the trans configuration is more likely on the basis of the similar configuration proposed for N-methylacetamide. Moreover, steric hindrance between methyl and trifluoromethyl groups might favor the trans form.

Regardless of the configuration, I or II, either molecule has thirty-three internal degrees of freedom. For the two forms (C_s point group) all the fundamentals are Raman active and there should be twenty-one fundamental modes of vibration symmetrical with respect to the plane

of symmetry (species a') and twelve antisymmetric with respect to the plane of symmetry (species a"). In addition to considering the spectral assignment on the basis of symmetry, comparison with the vibrational frequencies of other molecules, namely, N-methyltrifluoroacetamide, should aid in identifying the observed frequencies.

In order for tautomerism to take place in N,N-dimethyltrifluoroacetamidine (DMT'), a methyl transfer must be involved, which is not considered likely. Therefore, the spectrum should show evidence of only one form. DMT' has forty-two internal degrees of freedom. In view of this large number of expected lines, all active in the Raman effect, detailed assignment of these must be considered tentative. The assumption of a C_s symmetry for DMT' results in the distribution of 42 fundamental modes between two symmetry classes: 26 a' and 16 a". The a' modes should give polarized Raman lines while the a" modes should give depolarized lines. Most of the spectral bands were identified with possible group vibrations by comparison with the vibrational frequencies of N,N-dimethyltrifluoroacetamide. The DMT' molecule exhibits in addition to the 39 vibrational degrees of freedom described previously for N,N-dimethyltrifluoroacetamide three fundamental vibrations arising from the imino-hydrogen atom.

It was observed that the spectra of both mono- and dimethyl substituted trifluoroacetamidines did not change during the several days that elapsed between the initial and final exposures of the compounds. Furthermore, the viscosity and index of refraction remained constant throughout the investigation. These observations are certainly indicative of the stability of these compounds, so it is assumed that methyl

substitution of the parent compound, trifluoroacetamidine, enhances the stability of these compounds quite markedly.

As discussed above, these compounds were sufficiently stable to permit polarization measurements to be carried out. Microphotometer tracings of the Raman spectra using natural and parallel polarized light are shown in Figures 25 and 26 for the respective molecules.

Association which is expected to be present in NMT' is clearly shown by the associated N-H stretching bands occurring in the region extending from approximately 3100 cm^{-1} to about 3400 cm^{-1}. In contrast, the spectrum of DMT' shows an intense, polarized Raman band at 3368 cm^{-1} and a shoulder of less intensity at approximately 3328 cm^{-1}. The former band is immediately assigned to the =N-H stretching frequency whereas the latter is attributed to a combination frequency.

The uncertainties in the N-H stretching region of NMT' due to hydrogen bonding were partially resolved by studying the infrared spectrum of NMT' as a function of dilution in CCl_4. Spectra were obtained of the pure liquid and in CCl_4 solutions from 3000 to 3500 cm^{-1}. The results given in Figure 24 show that the ratio of the monomer to the dimer species is increased by dilution. The two strong bands appearing at 3350 and 3450 cm^{-1} are attributed to monomeric N-H stretching frequencies. The 3450 cm^{-1} band is tentatively assigned to the N-H stretching of the methylamine residue (form I) on the basis of the similar assignment for N-methyltrifluoroacetamide (3440 cm^{-1}). Accordingly, the band at 3350 cm^{-1} is attributed to the imino-hydrogen stretching which is consistent with the corresponding assignment for DMT' (3368 cm^{-1}, Raman value).

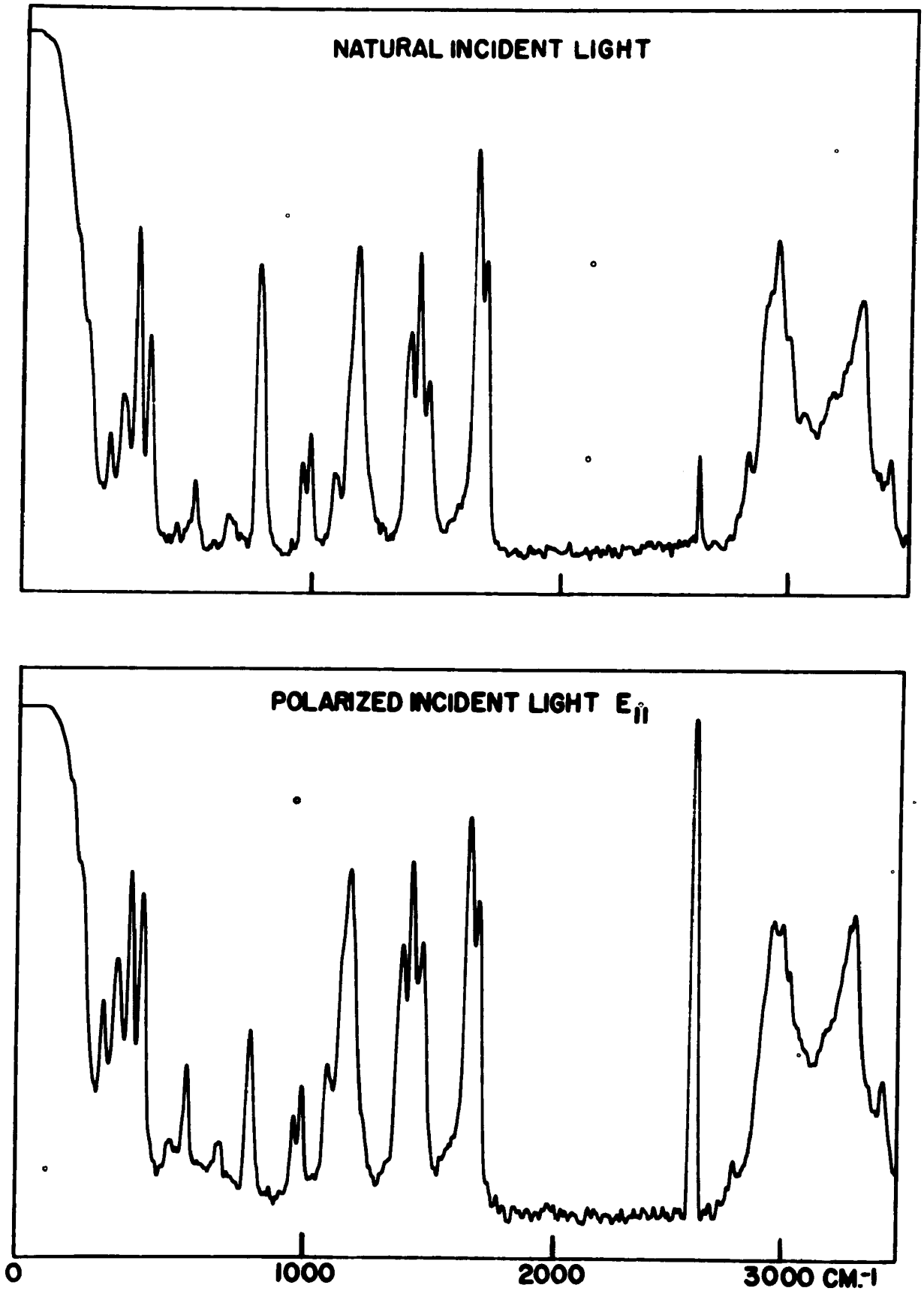


Figure 25
RAMAN SPECTRA OF $CF_3C(:NH)NHCH_3$

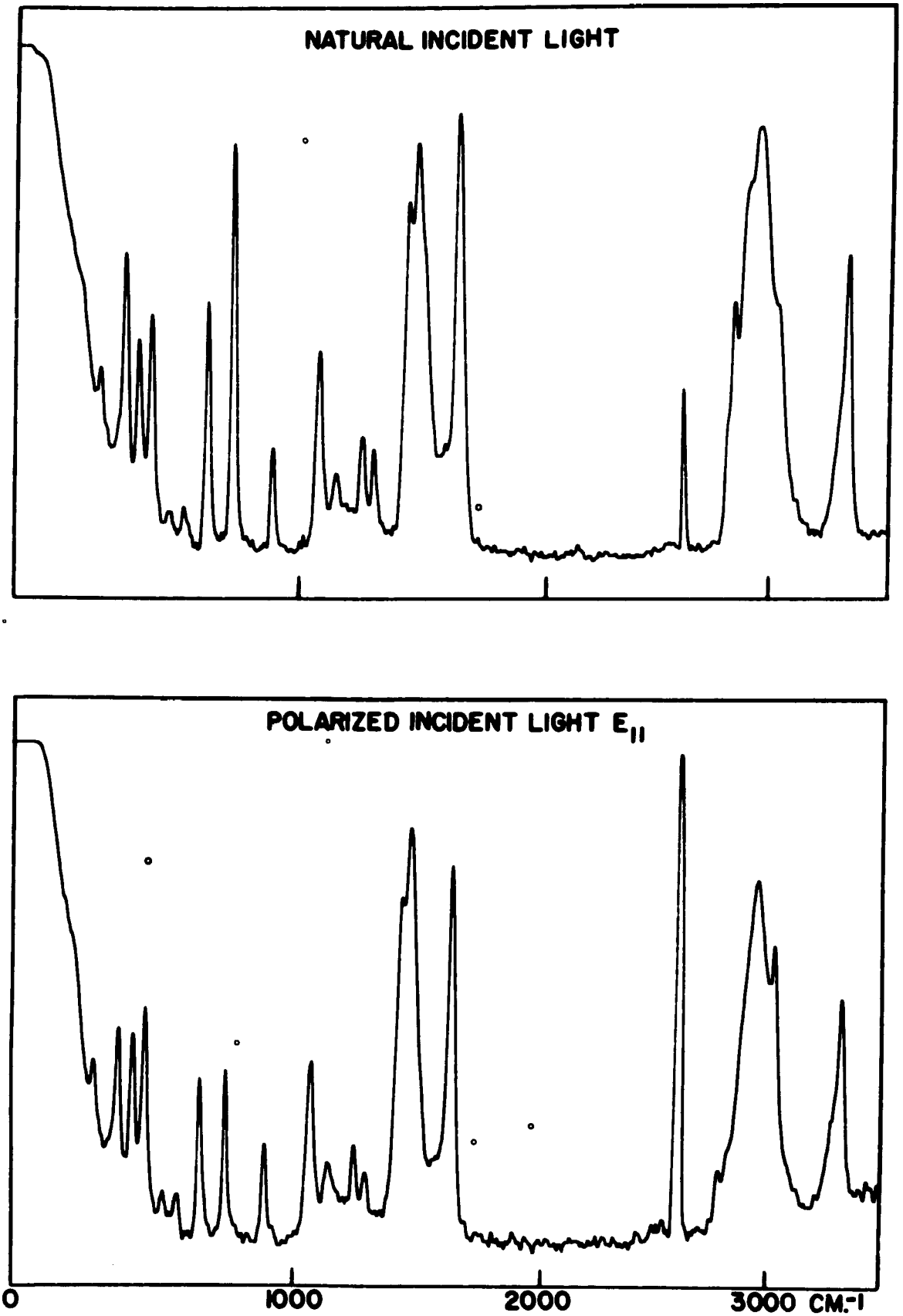


Figure 26
RAMAN SPECTRA OF $CF_3C(:NH)N(CH_3)_2$

This assignment suggests that at least in dilute CCl_4 solutions form I predominates. It does not seem possible at the present to make a definite assignment of these bands observed in the present spectrum. Investigation of the intensities of these bands as a function of temperature should indicate what role the equilibrium plays in regard to NMT'.

In the imino stretching region, DMT' shows a single intense, polarized Raman band at 1631 cm^{-1}, whereas two polarized bands at 1655 and 1690 cm^{-1} are observed for NMT'. Presumably these two bands arise from forms I and II for MNT'. The dilution studies indicated that in moderately dilute CCl_4 solutions both bands were present although the N-H stretching region was interpreted in terms of form I only. This is not unexpected since the bands attributed to C=N stretching are quite intense in the spectrum and presumably even in dilute solutions the imino stretching frequency corresponding to form II may be observed. An alternative explanation for the appearance of the 1690 cm^{-1} band is that it is due to a combination frequency. Since the remaining bands in the spectrum which are assigned to form II may also be attributed to combination frequencies or arising from Fermi resonance, it must be understood that the presence of forms I and II in the spectrum of NMT' due to tautomerism is still conjectural and by no means definitely established.

The results of the dilution study of both the imino-hydrogen and C=N stretching frequencies for DMT' led to the conclusion that this molecule is not appreciably hydrogen bonded. Those bands observed as intense lines in the Raman spectrum of the pure liquid at 3368 and 1631

cm^{-1}, respectively, remained unchanged in their positions in the infrared absorption spectrum throughout the range of dilution study (30.0 - 0.02 percent). These results are in agreement with the similar observation made from comparing the boiling point of DMT' (92°C) with that of N,N-dimethyltrifluoroacetamide (135°C) which exhibits no hydrogen bonding.

Neither the NH_2 deformation vibration of form II nor the planar NH deformations arising from the imino and amide groups of form I is identified for certain. In the case of form I, the degree of coupling in the C(:NH)NH-group may be different from that observed for the amide group. This is shown in the spectrum of NMT' by the absence of the amide II band which normally characterizes N-monosubstituted amides. However, the band at 1390 cm^{-1} might well correspond to the amide III band observed in N-methyltrifluoroacetamide (1347 cm^{-1}), in which case the 1390 cm^{-1} band ("amidine III") would most likely contain components involving C-N stretching and NH deformation vibrations. The assignment of the planar imino-hydrogen bending mode in trifluoroacetamidine to 1133 cm^{-1} presumably corresponds to the weak band at 1102 cm^{-1} in the present spectrum of NMT'. Identification of the corresponding mode in N,N-dimethyltrifluoroacetamidine is tentatively assigned to a polarized band at 1295 cm^{-1} on the basis of its absence in the spectrum of N,N-dimethyltrifluoroacetamide. This assignment is considerably higher than the corresponding assignments in trifluoroacetamidine and NMT' but in view of the absence of hydrogen bonding and the possibility of altered coupling in the amidine group of DMT', this assignment appears reasonable.

The assignment of the C-N stretching vibration contiguous to the imino bond for DMT' is consistent with the corresponding assignment

of the characteristic frequency $\nu_s(OCN)$ in N,N-dimethyltrifluoroacetamide. The remaining spectral bands for DMT' are assigned by analogy with N,N-dimethyltrifluoroacetamide.

Similarly, except for two regions which need discussion, the remaining frequencies in NMT' are assigned under the argument used in assigning the corresponding frequencies in N-methyltrifluoroacetamide. The C-C stretching mode and C-N stretching of the methylamine residue in N-methyltrifluoroacetamide occur at 851 and 1021 cm^{-1}, respectively. The two corresponding regions in the Raman spectrum of NMT' show two lines each, although one set is not completely resolved. In view of the two possible forms, I and II, one is tempted to assign these bands to both I and II. However, it is equally reasonable that the weaker of the two bands centered at about 1000 cm^{-1} is due to a combination frequency. Furthermore, in the C-C stretching region, the two bands observed at 818 and 831 cm^{-1} may be the result of Fermi coupling between a combination frequency (390 + 432) and the C-C stretching fundamental lying at about 825 cm^{-1}. The more intense band presumably is due to the C-C stretching fundamental mode. Without additional information about tautomerism occurring in this compound, an exact assignment of the observed bands is not possible.

The assigned fundamental vibrational frequencies for $CF_3C(:NH)NH(CH_3)$ are listed in Table XXI. Table XXII summarizes the results of the infrared observations concerned with the NH stretching region. The measured band positions and approximate assignments of $CF_3C(:NH)N(CH_3)_2$ are given in Table XXIII.

TABLE XXI

OBSERVED RAMAN FREQUENCIES AND ASSIGNMENTS FOR LIQUID $CF_3C(:NH)NH(CH_3)$

Frequency (cm^{-1})	Intensity	State of Polarization	Approximate Assignment[a]
183	vw	depol.	torsion
217	vw	depol.	torsion
296	w	depol.	CF_3 rocking, torsion?
343	w	pol.	CNC deformation
390	m-s	pol.	CF_3 rocking
432	m	pol. ?	CC=N deformation
524	vw		CF_3 deformation
592	w		NCN deformation
712	w, diffuse		CF_3 deformation
818	m-s	pol.	C-C stretching[b]
831	m, sh	pol.	390 + 432[b]
980	w	pol.	390 + 592? H_3C-N stretching?
1009	m-w	pol.	H_3C-N stretching
1102	w, br	pol.?	N-H deformation?
1160	m, sh	pol.	C-F stretching, CH_3 rocking
1185	m-s	pol.	C-F stretching, CH_3 rocking
1236	w, sh		C-F stretching
1390	m	pol.	"amidine III"
1425	m-s	pol.	CH_3 deformation
1465	m-w	depol.	CH_3 deformation
1619	w, sh		NH_2 deformation?, 1185 + 432?

TABLE XXI (CONT'D)

Frequency (cm^{-1})	Intensity	State of Polarization	Approximate Assignment[a]
1655	s	pol.	C=N stretching
1690	m-s	pol.	C=N stretching
2823	w	pol.	c
2907	m, sh	pol. ?	c
2920	m	pol.	C-H stretching
2954	m-s	pol.	C-H stretching
3005	m-w	depol.	C-H stretching
3078	w, diffuse		1655 + 1425 ?
3210	w, diffuse	pol. ?	N-H stretching (associated)
3334	m, sh	pol.	N-H stretching (associated)
3349	m	pol.	N-H stretching (associated), (monomer) ?
3489	w	pol.	N-H stretching (monomer)

[a] Description of the fundamentals is for formal classification.

[b] Interpreted as Fermi interaction.

[c] These bands may be fundamentals of C-H stretching or first overtones of the CH_3 deformation in strong Fermi interaction with the C-H stretching frequencies.

TABLE XXII

INFRARED ABSORPTION FREQUENCIES OF N-METHYLTRIFLUOROACETAMIDINE IN CCl_4: 3000 cm^{-1} TO 3500 cm^{-1}

Frequency (cm^{-1})	Assignment[a]
3450	NH stretching of the methylamine residue (monomer)
3350	Imino N-H stretching (monomer)
3250	NH stretching (associated)
3170	NH stretching (associated) ?
3070	NH stretching (associated) ?

[a] Description of the fundamentals for the monomer is based on form I, see N-Methyl- and N,N-Dimethyltrifluoroacetamidine Section for details.

Conclusions Based on the Spectra of Unsubstituted and Substituted Trifluoroacetamidines

This investigation was essentially concerned with the study of α-halogen substituted acetamidine and its methyl derivatives with the expectation of making a relatively complete vibrational assignment of these molecules. In addition to providing spectral data for these compounds, the results were of interest in order to determine what correlation, if any, exists between these compounds and the analogous amide series. Since the corresponding pairs are isoelectronic, one might expect similar vibrational spectra.

The detailed assignment of the amidine compounds was made difficult by hydrogen bonding and overlapping bands. Moreover, the spectra were complicated by bands not readily explained; the phenomenon

TABLE XXIII

OBSERVED RAMAN FREQUENCIES AND ASSIGNMENTS FOR LIQUID $CF_3C(:NH)N(CH_3)_2$

Frequency (cm^{-1})	Intensity	State of Polarization	Approximate Assignment[a]
227	vw		torsion
290	w		CF_3 rocking, torsion?
352	w, sh		$N(CH_3)_2$ rocking or C-N torsion
377	m	pol.	CF_3 rocking
427	m	pol.	CC=N deformation
469	m	pol. ?	CNC deformation
533	w		CF_3 deformation
587	w	pol. ?	NCN deformation
669	m	pol.	CF_3 deformation
761	vs	pol.	C-C stretching
910	m	pol. ?	H_3C-N symmetric stretching
1082	m	pol.	H_3C-N asymmetric stretching
1146	w	depol. ?	CH_3 rocking or C-F stretching
1179	vw, diffuse		C-F stretching
1209	vw, diffuse		C-F stretching
1251	w	pol.	CH_3 rocking or C-F stretching
1295	w	pol. ?	NH deformation?
1430	s	pol.	CH_3 deformation
1463	vs	depol.	CH_3 deformation
1491	m-s, sh	pol.	C-N stretching
1579	w, diffuse		669 + 710?

TABLE XXIII (CONT'D)

Frequency (cm^{-1})	Intensity	State of Polarization	Approximate Assignment[a]
1631	vs	pol.	C=N stretching
2810	m-w, sh	pol.	b
2833°	m	pol.	b
2907	s, sh	pol.	b
2954	vs, br	pol.	C-H stretching
3020	m, sh	depol. ?	C-H stretching
3038	m, sh	depol.	C-H stretching ?
3328	w, sh	pol.	2954 + 377 ?
3368	m-s	pol.	N-H stretching

[a] The description of the fundamentals is for formal classification.

[b] Bands may be the fundamentals of symmetric C-H stretching frequencies or the first overtone of the CH_3 deformation in Fermi resonance with the C-H stretching frequencies.

of tautomerism was suggested as a possible interpretation. Since several of the important characteristic frequencies of the amidine group were not identified with certainty (for example, the imino-hydrogen bending modes), any statements made concerning the relative coupling in the amide and amidine groups can only be conjectural. It is interesting to note, however, that the spectra of the two series are remarkably similar. Further, the observed decrease in the carbonyl stretching frequency with increasing methyl substitution in the amide series is similarly observed in the imino stretching frequency of the amidine series. In addition, as in the case of the carbonyl stretching frequency, the substitution of α-halogen results in the imino stretching bands shifting toward higher frequencies.

In regard to the disubstituted amide and amidine molecules, one is tempted to conclude that the C-N stretching frequency assigned for the latter compound (1491 cm^{-1}) is identified as the characteristic frequency ν_s(OCN) associated with the former. However, inferring that results of the amide studies are applicable to the amidine compounds may not be entirely valid, particularly since the amide II band observed in monosubstituted trifluoroacetamide is absent in the corresponding amidine derivative. Since the mechanical interactions in the amide and amidine group are not identical, the resultant modes should not agree necessarily. It would be of interest to investigate the mechanical coupling in the C(:NH)NH-group analogous to the calculations made for the CONH-group by Fraser and Price.

The results of the spectral data of the amidine and amide derivatives suggest that in the absence of hydrogen bonding the N-H

stretching frequency depends on the remaining groups attached to the nitrogen atom. For example, this frequency is observed at about 3466 cm^{-1} in the methyl amine residue group of N-methyltrifluoroacetamide whereas in N,N-dimethyltrifluoroacetamidine, the imino-hydrogen stretching frequency is observed at 3368 cm^{-1}.

Other than these few isolated examples discussed above many important questions regarding the structure of the halogen substituted amidines still remain unanswered. Further experimental studies are necessary before detailed conclusions can be drawn about these compounds.

Silver Salts of Trifluoroacetamide and Trifluoroacetamidine

The study of these compounds is the logical extension of the investigation of trifluoroacetamide and trifluoroacetamidine in view of the similar treatment carried out for trifluoroacetic acid and its ionized carboxyl salt. The silver salts of CF_3CONH_2 and $CF_3C(:NH)NH_2$ were readily prepared although there are doubts as to the possibility of forming the alkali metal salts.(10) The preparation of the potassium salt of trifluoroacetamide was attempted but the results were unsatisfactory; the material appeared to decompose slowly with the evolution of ammonia. The choice of solvent for the silver salts presented a problem since no common solvent could be found. Water was a suitable solvent for silver trifluoroacetate but decomposed silver trifluoroacetamide and, furthermore, would not dissolve silver trifluoroacetamidine. It was, therefore, decided to investigate the infrared absorption spectra of the last two compounds as mulls suspended in Nujol and hexachlorobutadiene-1,3. The latter mull technique is useful in investigating the 1450 cm^{-1} region in order to avoid the C-H absorption bands due to the mineral oil.

The present investigation was primarily interested in the 6μ (1667 cm^{-1}) and 7.5μ (1333 cm^{-1}) regions. When ionization occurs in carboxylic acids, the characteristic carbonyl absorption disappears and in replaced by two bands between 1550 and 1610 cm^{-1} and between 1300 and 1400 cm^{-1}, corresponding to the asymmetric and symmetric stretching modes of the COO^- group. If similar resonance hybrid structures occur for the silver salts of the fluorine-containing amide and amidine compounds, analogous spectral features should be observed.

In the case of trifluoroacetamide, the carboxyl frequency observed at about 1700 cm^{-1} in the Nujol mull spectrum disappears in the spectrum of the silver salt. Furthermore, the latter spectrum shows an intense absorption at approximately 1605 cm^{-1} which is immediately assigned to the asymmetric stretching of the CON group. The corresponding symmetric stretching frequency of the CON group is found in the spectrum of the hexachlorobutadiene-1,3 mull at 1450 cm^{-1}. It should also be noted that a single N-H stretching band at 3370 cm^{-1} is observed in the spectrum as expected. This suggests that only one hydrogen has been replaced by the silver atom which is consistent with earlier findings of amide studies.

The corresponding vibrational assignment for the silver salt of trifluoroacetamidine is not quite as clear-cut. The double bands attributed to the imino stretching frequencies for trifluoroacetamidine at 1612 and 1673 cm^{-1} (the latter being more intense) are absent in the Nujol mull spectrum of the silver salt with the subsequent appearance of a new band at about 1585 cm^{-1} in the spectrum of the latter. This band is tentatively assigned to the asymmetric stretching of the CNN

group. The asymmetric stretching vibration for acetamidine hydrochloride has been reported at 1568 cm^{-1}[71] and the present assignment is consistent with this. The identification of the symmetric stretching vibration is more difficult. The region between 1350 and 1550 cm^{-1} is free from any absorption bands. Shigorin[71] has suggested that the symmetric stretching vibration for amidine hydrochlorides probably occurs in the 1100-1350 cm^{-1} region. Accordingly, the medium intensity band observed at about 1310 cm^{-1} in the present spectrum is tentatively assigned to this mode. The N-H stretching region shows two partially resolved bands at about 3350 and 3380 cm^{-1} which might correspond to the two expected N-H stretching vibrations.

Infrared absorption spectra of the silver salts of trifluoroacetamide and trifluoroacetamidine are shown in Figures 27 and 28. The composite spectra represent the results from Nujol and hexachlorobutadiene-1,3 mull spectra. In view of the fact that the metal salts of trifluoroacetic acid, trifluoroacetamide, and trifluoroacetamidine are isoelectronic and that their vibrational spectra appear to be related one may conclude that these compounds have similar "resonating" structures. In regard to the silver salt of trifluoroacetamide, it is difficult to say to what extent each of the separate valence structures contributes to the resonance hybrid structure.

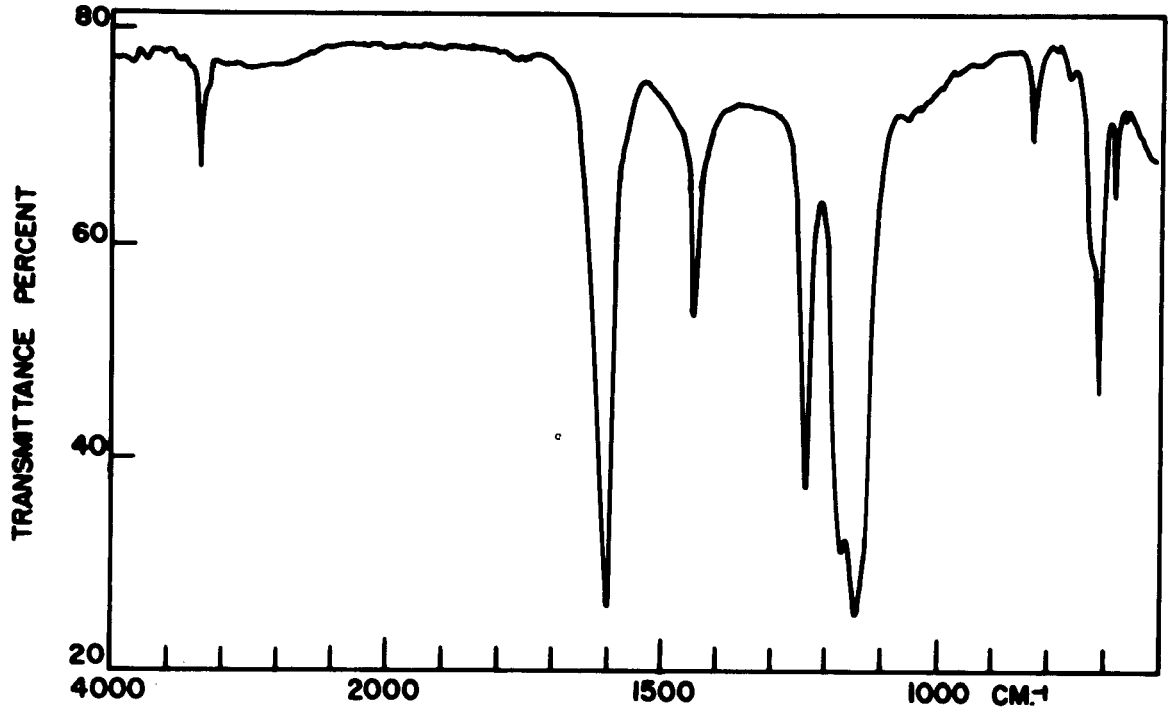


Figure 27
INFRARED ABSORPTION OF $CF_3CONHAg$

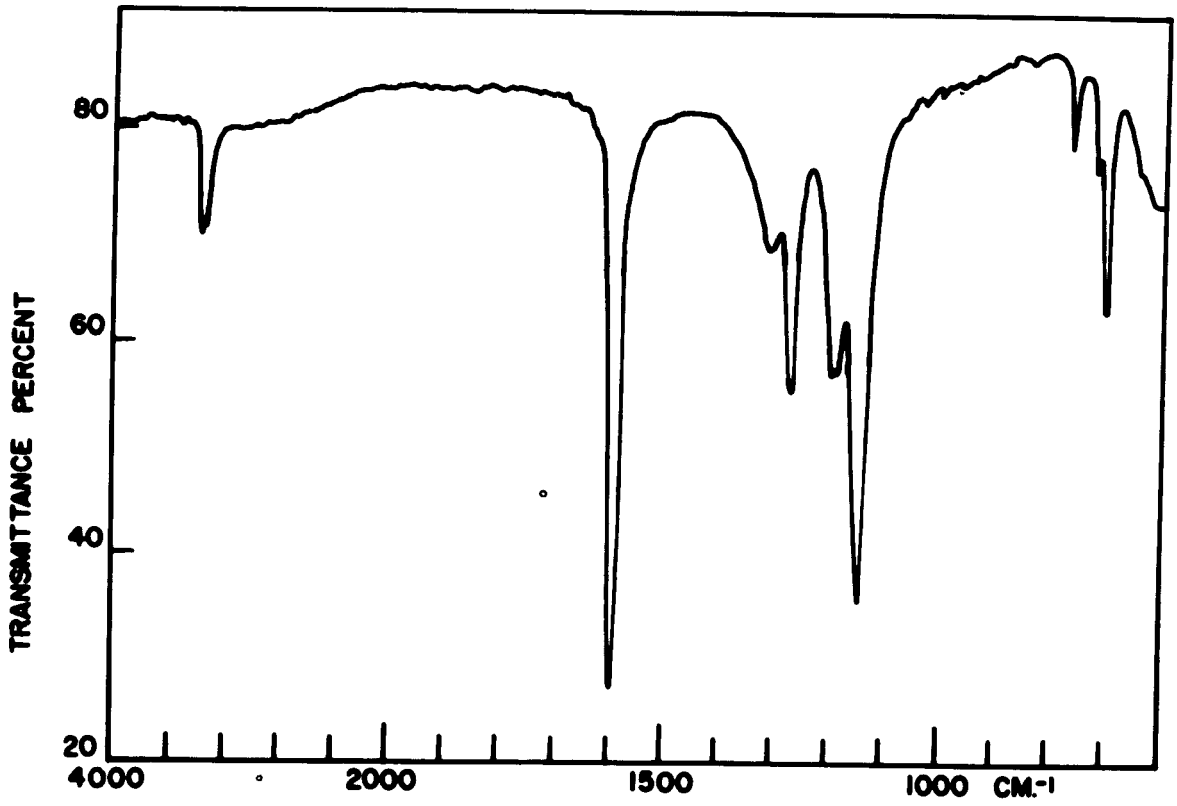


Figure 28
INFRARED ABSORPTION OF $CF_3C(NH)NHAg$

SUMMARY

The vibrational spectra of a series of compounds containing the trifluoromethyl group in common have been investigated, chiefly by means of the Raman effect. Vibrational assignments of CF_3COOH and CF_3COOD in the liquid phase are proposed using as a basis the previous investigations of these molecules in the vapor state. Polarization data for the deuterated compound in the liquid state are interpreted in terms of C_1 symmetry. Interpretation of similar data for CF_3COOH is more difficult in view of indefinite polarization characteristics of the latter's Raman bands. Raman spectra of CF_3CONH_2 and $CF_3C(:NH)NH_2$ have been also obtained as well as those of their deuterated compounds and, in addition, the following methyl derivatives: $CF_3CONH(CH_3)$, $CF_3CON(CH_3)_2$, $CF_3C(:NH)NH(CH_3)$, and $CF_3C(:NH)N(CH_3)_2$. Vibrational frequencies of this amide series are assigned using arguments similar to those used by Miyazawa et al. in assigning the corresponding nonfluorinated series. Treatment of the vibrational spectra of the unsubstituted and substituted trifluoroacetamidines in terms of the results obtained for the amides has been attempted.

Included in the present investigation were Raman spectra of methyl trifluoroacetate and sodium trifluoroacetate, and infrared absorption spectra of silver salts of trifluoroacetamide and trifluoroacetamidine. The analysis of the last three compounds led to the conclusion that all three molecules possessed similar "resonating" structures.

As part of future study of vibrational spectra of trifluoroacetic acid derivatives, infrared spectroscopic investigation of methyl trifluoroacetate in the vapor state would supplement the Raman study of

this molecule. The infrared vapor band contours of this spectrum might identify the correct configuration of the molecule (cis or trans).

It would be of interest to confirm the assignments of substituted trifluoroacetamide and trifluoroacetamidine compounds by extending the study to the corresponding deuterated compounds. It would also be useful to obtain Raman spectra of aldimines and ketimines, particularly $CF_3C(:NH)H$ and $(CF_3)_2C=NH$, so that a more complete analysis of the normal vibrations of the imino group could be made. Certain general conclusions regarding unsubstituted and substituted amidines may be drawn by an extensive study of their spectra, as in the case of amides. The investigations of N,N'-disubstituted amidines by Prevorsek(74) and others(75) have proceeded in this direction. Coupling in the above group has been suggested as an explanation of the observed bands. Presumably the spectra of disubstituted amidines would be less complex because of the presence of the single hydrogen atom and interpretation of the spectra would be less ambiguous.

Investigation of the amidine derivatives by other techniques especially nuclear magnetic resonance and dipole moment studies would be valuable in arriving at some definite conclusion regarding the correct configuration of these molecules. Furthermore, any significant change in the bond order of the C=N and C-N linkages in the amidine group arising from the contribution of the polar resonance form might be indirectly detected.

APPENDIX

Sources of Materials

Trifluoroacetic acid and trifluoroacetic anhydride were obtained from The Matheson Company, Inc., and were further purified by fractional distillation. Matheson commercial grade ammonia was recondensed into a steel gas cylinder containing sodium chips for storage until used. Eastman White Label dimethylamine was used without further purification. D_2O of 99.78 percent purity was obtained from Norsk Hydro-Electrisk Kvaelstofaktieselskat.

Experimental[a,b]

Magnesium Nitride

A very convenient method of preparing deuterated ammonia involves the use of Mg_3N_2. Magnesium nitride was produced by the direct combination of the elements in a stainless steel furnace at approximately 700°C. Magnesium metal turnings were placed in the furnace and nitrogen, from which water vapor and oxygen had been removed, was passed through the tube while the temperature was slowly raised. As soon as the reaction began, the flow rate of nitrogen was increased. When the reaction was finished, the furnace was allowed to cool to room temperature and the product was quickly removed to a flask in order to avoid hydrolysis with atmospheric moisture.

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[a] All melting and boiling points are uncorrected.

[b] Microanalyses are by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

Deuterated Ammonia

ND_3 was prepared by the reaction of Mg_3N_2 with D_2O according to the reaction:

$$Mg_3N_2 + 6D_2O \longrightarrow 3Mg(OD)_2 + 2ND_3$$

A two- to threefold excess of magnesium nitride was placed in a steel gas cylinder whose valve had been removed. The valve was replaced, the cylinder connected to the vacuum manifold, and the whole evacuated. Heavy water was condensed into the cylinder and after closing the valve the cylinder was allowed to warm up. The reaction was quite rapid and an immediate evolution of heat was noted. The cylinder was shaken repeatedly to insure complete contact between the reactants. The cylinder was then reattached to the vacuum line and the heavy ammonia was transferred to a small stainless steel storage cylinder containing a small piece of sodium. This method of preparing heavy ammonia proved to be quite satisfactory.

Methylamine

CH_3NH_2 was prepared by dropping an aqueous solution of recrystallized methylamine hydrochloride on KOH pellets in a three necked flask, fitted with a Friedrich's condenser. The gas was passed through a tube filled with soda lime and condensed in a trap surrounded with Dry Ice-isopropyl alcohol slush bath. The exit tube was immersed in mercury in order to observe the rate and completion of the reaction. The trap was then attached to the vacuum line, the contents frozen with liquid nitrogen, and the system evacuated. In order to remove any residual water the amine was transferred to a bulb containing small pieces of

sodium. This process was repeated until the solution took on the characteristic blue coloration in which case the sample was assumed to be dry.

Deuterated Trifluoroacetic Acid

Reagent grade trifluoroacetic anhydride was redistilled over P_2O_5 in a small column packed with glass helices. The middle fraction (b.p. 40°C) was used for the preparation of deuterated trifluoroacetic acid and for the Raman spectrum. The latter served as a check on the purity of CF_3COOD.

Trifluoroacetic anhydride, 11.3 g. (0.05 mole), was placed in a bulb and attached to the vacuum line. The contents were frozen out with liquid nitrogen and the system evacuated. D_2O, 1.0 g. (0.05 mole), was sublimed into the anhydride and the mixture was allowed to warm up to room temperature. After allowing for the reaction to near completion, the contents were transferred under vacuum to an apparatus for distilling the material. The heavy acid was purified by fractional distillation. The fraction boiling at 70-71°C was collected in a Raman tube and the contents sealed by means of an oxygen-gas hand torch. Spectroscopic investigation revealed no absorption bands in the 2700-3600 cm^{-1} region, evidence for the absence of undeuterated trifluoroacetic acid.

Trifluoroacetamide

The amide was prepared as described in the literature(76) with a slight modification in the procedure. Into a 500 cc. round bottom flask was placed 114 g. (1.0 mole) of trifluoroacetic acid. To this was added a cold mixture of 112 g. (2.4 moles) of absolute ethanol and 79 g. (0.8 mole) of concentrated sulfuric acid. After standing at room

temperature for approximately three hours, the crude ester was distilled off and washed with 100 cc. of cold 5 percent sodium carbonate solution. The ester was then dried with $CaCl_2$ at 0°C overnight.

The crude ester was redistilled through a vacuum jacketed column packed with glass helices. The fraction boiling between 60° and 62°C was collected and diluted with 100 cc. of ethyl ether. The solution was then cooled with an ice bath and saturated with gaseous ammonia. The solvent was removed by distillation at atmospheric pressure on a water bath at 60°-70°C. When no more distillate was collected, the pressure was reduced with an aspirator and distillation continued until the residue in the flask began to recrystallize. Upon cooling, the entire residue crystallized to a slightly wet cake. This was removed and subsequently recrystallized several times from petroleum ether-ethyl ether mixture to yield pure trifluoroacetamide (m.p. 75°C). The yield was 102 g., 90 percent yield based on the amount of acid used. The amide is rather volatile and will sublime very readily at room temperature.

The vapor pressure of trifluoroacetamide was determined(77) at three different temperatures by the Knudsen method (effusion of molecules through a small orifice into a large evacuated space) and the results are shown in Table XXIV.

TABLE XXIV

THE VAPOR PRESSURE OF TRIFLUOROACETAMIDE AS DETERMINED BY THE KNUDSEN METHOD

Temperature (°K)	Vapor Pressure (mm.Hg)
283.37	0.0854
290.65	0.2003
294.21	0.3072

Trifluoroacetamide-d_2

CF_3COND_2 was prepared in the vacuum line. A mixture of anhydrous ethyl trifluoroacetate and ethyl ether was placed in a bulb and the latter was attached to the vacuum manifold. The contents were frozen out with liquid nitrogen and the whole evacuated. Into this mixture was condensed an excess of ND_3. After bringing the mixture to room temperature, sufficient time was allowed for the reaction to take place.

The more volatile components were distilled off leaving CF_3COND_2. The product was then sublimed by a trap-to-trap distillation. Dry nitrogen was admitted into the vacuum manifold and the bulb containing CF_3COND_2 was removed and quickly capped, m.p. 80.5-81.0°C. Spectroscopic examination of the material revealed only weak absorption bands attributed to undeuterated amide.

N-Methyltrifluoroacetamide

A three necked 500 cc. round bottom flask containing 13.8 g. (0.1 mole) of ethyl trifluoroacetate and 20 g. of ethyl ether was fitted with a dropping funnel containing 4.2 g. (0.1 mole) of methylamine. The system was protected from atmospheric moisture by a drying tube. The reaction was conveniently carried out in a room cooled to -10°C. After the methylamine was added, the solution was stirred for approximately four hours. The mixture was then removed from the cold room and allowed to warm to room temperature. The solvent was removed by distillation using a water bath at 50-60°C. When no more distillate was collected, the pressure was reduced with an aspirator and distillation continued

until the residue began to crystallize. The residue was allowed to cool but the vacuum was maintained until crystallization was complete.

Crude $CF_3CONHCH_3$ was crystallized twice using ethyl ether-petroleum ether solution giving 6.5 g. of pure material (m.p. 56-57°C) and 51 percent yield.

Anal. Calcd. for $C_3H_4F_3NO$: C, 28.35; H, 3.17; N, 11.02.
Found : C, 28.46; H, 3.25; N, 10.91.

N,N-Dimethyltrifluoroacetamide

The disubstituted amide was prepared in the same manner described above for the monosubstituted compound except that dimethylamine was used in place of methylamine. In the present case, the disubstituted amide is liquid at room temperature, b.p. 135°C (atmospheric pressure); n_D^{25} 1.3613.

Anal. Calcd. for $C_4H_6F_3NO$: C, 34.05; H, 4.29; N, 9.93.
Found: C, 34.16; H, 4.47; N, 10.14.

Methyl Trifluoroacetate

The methyl ester was prepared by a similar procedure described above for the ethyl ester. The methyl ester was observed to boil at 43-44°C (atmospheric pressure).

Trifluoroacetonitrile

CF_3CN used in this research was prepared according to the method of Gilman and Jones(76) with only slight modifications in the procedure. In a 1 liter round bottom flask, 56.5 g. (0.5 mole) of CF_3CONH_2 was mixed with 150 g. (1.1 mole) of P_2O_5 and the intimate mixture heated with an electric mantle. Dry gaseous nitrogen was

passed through the system before heating but was discontinued when heating was begun as the amide sublimed. The vapors evolved were passed through two U-traps cooled by Dry Ice-isopropyl alcohol slush baths in series followed by a trap surrounded with liquid nitrogen. A barium oxide drying tube preceded the first trap and the exit tube was inserted in mercury.

At completion of the reaction the product was purified by several trap-to-trap distillations and subsequently transferred to a small steel pressure cylinder for storage. The yield of CF_3CN was 42 g. (88 percent based on the amount of amide used).

Trifluoroacetamidine

This compound was prepared by the addition of NH_3 to CF_3CN as described by Reilly and Brown.(10)

Into a small cylindrical reaction flask attached to the vacuum manifold and cooled with Dry Ice-isopropyl alcohol slush bath was condensed a large excess of ammonia. CF_3CN, 9.3 g. (0.1 mole), was added and the mixture allowed to reflux under a Dry Ice condenser (see Figure 1) for approximately one hour. Excess ammonia was distilled from the mixture and the product fractionated under reduced pressure in a small vacuum jacketed column packed with glass helices, b.p. 33-34°C (9 mm), n_D^{25} 1.3790 (immediately after preparation), n_D^{25} 1.3848 (24 hours after distillation).

Anal. Calcd. for $C_2H_3F_3N_2$: C, 21.43; H, 2.70; N, 25.01.
Found: C, 21.46; H, 2.59; N, 25.12.

Trifluoroacetamidine-d_3

$CF_3C(:ND)ND_2$ was prepared in the same manner described above

for the normal compound with the exception of replacing NH_3 with ND_3, b.p. 44-45°C (11 mm), n_D^{25} 1.3761 (immediately after preparation). Spectroscopic investigation of $CF_3C(:ND)ND_2$ revealed only a slight trace of undeuterated trifluoroacetamidine.

N-Methyl- and N,N-Dimethyltrifluoroacetamidine

These compounds were prepared using the technique described above for trifluoroacetamidine. In place of ammonia, methyl- and dimethylamine were used for the respective compounds. Both compounds exhibit aromatic odors (mint-like odor).

N-methyltrifluoroacetamidine: b.p. 42-43°C (15 mm), n_D^{25} 1.3897.

Anal. Calcd. for $C_3H_5F_3N_2$: C, 28.57; H, 4.00; N, 22.22.
Found: C, 28.71; H, 4.03; N, 21.97.

N,N-dimethyltrifluoroacetamidine: b.p. 92°C (atmospheric pressure), n_D^{25} 1.3803.

Sodium Trifluoroacetate

The sodium salt of trifluoroacetic acid was prepared by neutralization of the acid with an aqueous solution of sodium hydroxide. A small excess of acid was always present. The salt was then subjected to a number of evaporations and crystallizations. The silver salt was prepared in a similar manner using silver oxide in place of sodium hydroxide.

Silver Salt of Trifluoroacetamide

Silver oxide, 10 g. (0.04 mole), was added to 11.3 g. (0.10 mole) of molten trifluoroacetamide with vigorous stirring. The resultant

mixture was gray colored indicating unreacted silver oxide was present. The excess amide was removed by sublimation. Crude $CF_3CONHAg$ was purified by a number of crystallizations from hot benzene yielding a white silky product. The compound appeared to be light sensitive. For example, during filtration the material would darken in a few minutes. Melting point determination indicated the silver salt decomposed (black residue) at approximately 138°C.

Anal. Calcd. for C_2HF_3NOAg: N, 6.37; Ag, 49.05.
Found: N, 6.35; Ag, 48.88.

Silver Salt of Trifluoroacetamidine

Silver oxide, 4.6 g. (0.02 mole) was added to 5.0 g. (0.04 mole) of trifluoroacetamidine dissolved in 10 cc. of ethyl ether, while the mixture was stirred vigorously. It was necessary to warm the mixture initially to start the reaction. The white reaction mixture was filtered, washed with ethyl ether, and dried to give 8 g. (92 percent yield) of the silver salt. The salt decomposed on heating at 200°C.(10)

Anal. Calcd. for $C_2H_2F_3N_2Ag$: N, 12.84; Ag, 49.27.
Found: N, 12.58; Ag, 49.36.

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