The interpretation of infrared and raman spectra using pattern recognition

John Martin Comerford
New Jersey Institute of Technology
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Engineering, chemical

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THE INTERPRETATION OF INFRARED AND RAMAN SPECTRA USING PATTERN RECOGNITION

by

John Martin Comerford

A dissertation
presented in partial fulfillment of
the requirements for the degree
of
DOCTOR OF ENGINEERING SCIENCE IN CHEMICAL ENGINEERING
AT
NEWARK COLLEGE OF ENGINEERING

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Newark, New Jersey
1974
ABSTRACT

An automatic classification of chemical compounds by computer processing of digitized spectral data is presented. The classification system is based on a branch of artificial intelligence known as supervised learning, and used binary linear classifiers to identify compounds as alcohols, esters, ethers, ketones or compounds containing double bonds.

Each of the 1117 spectra in volume one of Sadtler's Standard Raman Spectra was coded using a scale from 0 to 9 in the range from 4000 to 200 cm⁻¹. One hundred and twelve readings were taken on each spectrum. These data were then examined using pattern recognition techniques, and several methods of combining infrared and Raman data from the same compound were tested.

The classification techniques were most successful when applied to concatenated infrared and Raman data. By taking the infrared data in the range from 500 to 1900 cm⁻¹ and concatenating them with Raman data from the same range, a vector representing each of the 400 compounds in the data set was obtained. The parallel polarized Raman was used in preference to the perpendicularly polarized spectrum when both were available, otherwise the nonpolarized spectrum was used. Using an iterative pattern recognition technique a
vector was then calculated which would recognize compounds as members of a class or not members based on the sign of the dot product of the calculated vector and the vector representing the compound.

When vectors were calculated using only half the data set, then tested for their ability to correctly classify the remaining compounds; it was found that they could correctly classify compounds more than 90% of the time.

Vectors which were trained using the entire data set were helpful in determining characteristic group frequencies and each class treated is discussed.

Several compounds for which observed frequencies have been assigned in the literature were tested to determine if the assignments could be supported by the trained vectors. In nearly every case supporting evidence for the assignment was available from the appropriate trained vector.
APPROVAL OF DISSERTATION

THE INTERPRETATION OF INFRARED AND RAMAN SPECTRA

USING

PATTERN RECOGNITION

BY

JOHN MARTIN COMERFORD

FOR

DEPARTMENT OF CHEMICAL ENGINEERING AND CHEMISTRY

NEWARK COLLEGE OF ENGINEERING

BY

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William H. Snyder

Newark, New Jersey
September, 1974
ACKNOWLEDGEMENT

The author wishes to express his sincere appreciation to Dr. Howard Kimmel for his guidance and support throughout the work and through the years of graduate study.

I also wish to thank Dr. William H. Snyder for the many useful discussions and particularly for his encouragement through my graduate work.

Dr. Edward C. Roche, Dr. Howard D. Perlmutter and Dr. Peter G. Anderson are each thanked for serving on the advisory committee and for helping to shape this work.

Finally, I find it difficult to pen an adequate expression of my love and appreciation for my wife, Marie, who typed the manuscript, took care of our four children and loved and encouraged when I needed it most.
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INTRODUCTION

1. Background

Artificial intelligence is the name given to the developing body of knowledge concerning computer techniques for handling large bodies of data or attacking very complex problems. The techniques are as varied as the problems and the body of knowledge is ill-defined. Generally the techniques are ad hoc to the problem at hand. One branch of artificial intelligence, however, which has been developing at a rapid pace and which does have universal application is the area known as pattern recognition. In Nagy's¹ review of the state of the art in pattern recognition (1968) he conceded at the outset that pattern recognition was hardly a discipline in its own right, and at best was a collection of highly varied problems. In his review, however, he managed to outline the skeleton of what he viewed as a highly amorphous structure. In 1972 in an effort to introduce pattern recognition to the chemical literature Kowalski and Bender² offered the functional breakdown of pattern recognition which has been reproduced in Figure 1.

A general statement of the problem which pattern recognition seeks to resolve is: "Given a set of objects and a list of measurements made on these objects, is it possible to find and/or predict a property of the object that is not directly measured but is related to the measurements via some unknown relationship?" In most of the early work in the field it is assumed that a statistically representative data set is available for designing or training the pattern recognition apparatus. This leads to parametric methods which recognize patterns based on the underlying probability distributions of the data. Thus far these techniques have not proven useful with chemical data and they are not discussed in this work.
Nonparametric techniques usually attempt to develop a **linear categorizer** which assigns objects to category one or two based upon the sign of the weighted sum of measurements made on the object. Let the set of measurements made on any one object be represented by the vector \( \mathbf{f} \), and let the linear categorizer be represented by the vector \( \mathbf{w} \). Both vectors have \( n \) members. Then:

\[
\mathbf{f} = (f(1), f(2), \ldots, f(n))
\]

and

\[
\mathbf{w} = (W(1), W(2), \ldots, W(n))
\]

The linear categorizer assigns an unknown vector to class one if \( \sum_{i=1}^{n} W(i) \cdot f(i) > 0 \), otherwise to class two.

From the beginning we will discuss only two-class problems. In principle, however, any multiclass problem can be treated as a number of two class problems involving the separation of each class from the remainder of the universe. A discussion of optimal assignments in multiclass problems can be found in the article by Braverman\(^3\) or the thesis by Kiessling\(^4\). Jurs et al\(^5\) also treated this topic.

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Preprocessing simply refers to the necessary manipulation of the data which must be done in certain cases to render the problem amenable to an orderly solution. It is referred to variously as preprocessing, filtering or prefiltering, feature or measurement extraction or dimensionality reduction. Some form of preprocessing is frequently needed when the data is taken from more than one source, for example when infrared and mass spectra were used to classify chemical compounds. Occasionally data from a single source, such as nuclear magnetic resonance spectral data must be preprocessed.

Learning and classification is supervised if a set of objects whose classes are known is used to develop the weight vector \( \mathbf{W} \). In unsupervised learning the data is clustered or classified into groups without prior knowledge as to what defines a group. For example the classification of archaeological artifacts by applying pattern recognition to trace element data was done using unsupervised learning. We will concern ourselves with supervised learning only.


2. Application of Pattern Recognition

Pattern recognition has application in computer assisted medical diagnosis and treatment, drug interaction studies, neurobiological signal processing, etc. Clinical data such as electrocardiograms and electroencephalograms have been analyzed using pattern recognition techniques. Manning studied teleseismic event classification in order to differentiate nuclear explosions from earthquakes on the basis of the characteristics of the wave which travels through the earth's mantle. Problems arising from satellite photography for weather, earth-resource and even the sensing for life on remote planets have been attacked using pattern-recognition. And these diverse applications only touch the surface of the hundreds of areas where pattern recognition is being used.


In the late sixties papers began appearing in the chemical literature, and now many types of chemical data have been explored using pattern recognition. Sybrandt and Perone\textsuperscript{16} evaluated a pattern recognition technique for qualitative analysis of mixtures by stationary electrode polarography. Molecular formula determination from low resolution mass spectrometry was investigated by Jurs, Kowalski and Isenhour\textsuperscript{17, 18} and Kowalski and Reilly\textsuperscript{7} considered nuclear magnetic resonance spectral interpretation by pattern recognition. Wangen and Isenhour\textsuperscript{19} applied pattern recognition methods to the semiquantitative determination of seventeen light elements by resolution of 14-Mev neutron induced gamma ray spectra. Infrared data were first treated by Kowalski, Jurs, Isenhour and Reilly\textsuperscript{20} in 1969 then again in 1973 by Liddell and Jurs\textsuperscript{21}. Melting and boiling point data\textsuperscript{6, 22} have also been investigated.

3. The Problem

In late 1972 the Sadler Research Laboratories announced the publication of a collection of infrared and Raman spectra. It was decided that the first volume of this collection would be used as the data base to investigate the use of pattern recognition in interpreting infrared and Raman spectra. While earlier work was done with infrared spectra\textsuperscript{20, 21}, no work has yet been reported in which Raman data were investigated using pattern recognition. In the first work done with infrared data\textsuperscript{20} the coding of the data was crude (a 0, 1, 2, or 3 was used to represent spectral peaks), and the thrust of the first attempt was simply to explore the feasibility of the approach. Using these data these first workers were able to achieve about 75\% recognition of various chemical classes (acids, esters, amides, etc.) and thus demonstrated the feasibility of using the approach. In general our recognition rate was slightly above 90\%.

Liddell and Jurs\textsuperscript{21} improved their coding system and by doing so were able to improve their recognition rate to approximately 87\%. The bulk of this second look at infrared data, however, concentrated on attempting by various empirical methods to improve the recognition rate and reduce the number of features (i.e. elements in each vector) used in the decision making process.
None of the earlier workers attempted to use the trained vectors as an aid in interpreting infrared spectra. The unique relationship between infrared and Raman makes these data particularly interesting for this purpose. Additionally, the study of Raman data with pattern recognition techniques provides an orderly approach to the development of spectra-structure correlations. The rapid advance of Raman spectroscopy since the development of the laser has outpaced the development of correlation tables; and workers frequently refer to infrared correlation tables, when Raman data are being analyzed since Raman correlation tables are not available. The differences between the selection rules of infrared and Raman point out the hazards of this practice.

With this background in mind the objectives of this investigation were: (1) to use the vectors trained with infrared and Raman data and combinations of those data to distinguish characteristic group frequencies, and (2) to investigate the predictive ability of the trained vectors.

4. The Data

Volume One of the Sadtler Standard Raman Spectra includes 400 organic compounds (including water) selected with the intention of providing simple compounds with representative functional groups at the beginning of the publication. When liquid compounds are presented both the
parallel polarized and the perpendicularly polarized Raman spectra are given. When solids are presented only the nonpolarized Raman is given. There are no gases in the collection. The infrared spectrum of each compound is given. Among the 400 compounds in Volume One there are 317 liquids and 83 solid compounds. Thus there are a total of 1117 spectra in the data bank for this work.

The Raman spectra in this volume were obtained using the Cary 83 instrument which utilizes the 4880 Å argon line. The laser power was a nominal 100 mW at the laser head and 30-60 mW at the sample. The source used in this volume of spectra was a Coherent Radiation model 59B Argon Ion laser and the detector was a bi-alkali cathode type photodetector. Sample scattering was always detected at right angles to the direction of the incident radiation.

**Coding Procedure**

1. A base line is drawn which connects the two points of least intensity in the spectrum and which runs along the base of the spectrum (the top of the IR prints; the bottom of the Raman prints).

2. The largest peak in the spectrum is assigned an intensity of 9.
3. The spectrum is divided into 112 bands. From 4000 cm$^{-1}$ to 2000 cm$^{-1}$ the band width is 50 cm$^{-1}$. From 2000 cm$^{-1}$ to 200 cm$^{-1}$ the band width is 25 cm$^{-1}$.

4. Within each band the intensity is measured on a scale from 0 to 9 depending on the relative intensity compared to the strongest peak in the spectrum.

5. When the intensity is measured within a band, the strongest intensity within the band is used as the position at which the measurement is made.

To aid in measuring intensities a system based on the one suggested by Durkin et al.\textsuperscript{23} was used. A template similar to the one shown in Figure 2 was drawn. Copies were xeroxed on Albanene tracing paper (Keuffel and Esser Co. #10 5351). By sliding the template across the strongest peak until the perpendicular distance from the base line of the spectrum to the top of the peak just spans the perpendicular distance on the template from the base to

the top line, one is able to quickly find a 0 to 9 scale appropriate for the spectrum being coded. It was convenient to draw a line on the template and then fold it on the line. The templates were discarded after a few uses. We found that this system was superior to the plexiglass type of arrangement suggested in the literature.

FIGURE 2

Template Used for Coding

When measuring the intensities it is important to measure the strongest intensity within each band (step 5), rather than to make the measurement precisely at a particular frequency. Several trials with different types of coding suggested that this system gives the most faithful reproduction of the actual spectrum when manually digitalizing the spectrum. Figure 3 shows the spectrum of a typical
compound, the digital code and a plot of the code vs wave number. It is clear that some detail is lost by the coding process, but most of the peak definition is retained.

FIGURE 3
Coding Illustration

\[

c_{\text{CH}_3-\text{O-CH}_2-\text{CH}-\text{CH}_2-\text{O-CH}_3}
\]

TRIACETIN
Table I shows the 17 classes of compounds in the data, and gives the number of compounds in each class. The classes which have been treated in this work are noted with an asterisk. There are two ortho-esters in the data, and they have been treated as ethers. Since there are only 4 tertiary alcohols in the data, these were not treated separately. The classes are not mutually exclusive, and there are 21 compounds which do not belong to any of the classes included in Table I. Appendix A gives the data bank and lists the classes to which each compound belongs.

**TABLE I**

Classes of Compounds in Data Set

<table>
<thead>
<tr>
<th>Description of Class</th>
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<tbody>
<tr>
<td>1. esters</td>
<td>94*</td>
</tr>
<tr>
<td>2. nitrogen containing compounds</td>
<td>64</td>
</tr>
<tr>
<td>3. primary alcohols</td>
<td>32*</td>
</tr>
<tr>
<td>4. secondary alcohols</td>
<td>12*</td>
</tr>
<tr>
<td>5. tertiary alcohols</td>
<td>4</td>
</tr>
<tr>
<td>6. ethers and ortho esters</td>
<td>49*</td>
</tr>
<tr>
<td>7. chlorine containing compounds</td>
<td>47</td>
</tr>
<tr>
<td>8. fluorine containing compounds</td>
<td>1</td>
</tr>
<tr>
<td>9. bromine containing compounds</td>
<td>29</td>
</tr>
<tr>
<td>10. iodine containing compounds</td>
<td>4</td>
</tr>
<tr>
<td>11. aromatic compounds (containing benzene ring)</td>
<td>157</td>
</tr>
<tr>
<td>12. compounds containing a saturated hexane ring</td>
<td>8</td>
</tr>
<tr>
<td>13. compounds containing C=C bond (not benzenes)</td>
<td>38*</td>
</tr>
<tr>
<td>14. compounds containing a triple bond</td>
<td>3</td>
</tr>
<tr>
<td>15. ketones</td>
<td>15*</td>
</tr>
<tr>
<td>16. compounds containing a phenol group</td>
<td>13</td>
</tr>
<tr>
<td>17. compounds containing sulfur</td>
<td>28</td>
</tr>
</tbody>
</table>

(* indicates those classes treated in this work)
1. Prologue to the Discussion

The purpose of this section is to briefly outline the differences between infrared and Raman spectra and to acquaint the uninitiated reader with the selection rules which govern vibrational spectra. The ideas presented here will not be developed, but rather will be stated in as concise a form as seems practicable. These concepts have been thoroughly discussed elsewhere, and for an extensive and authoritative treatment the reader should consult the classical works: *Infrared and Raman Spectra of Polyatomic Molecules* by Herzberg and *Molecular Vibrations* by Wilson, Decius and Cross. Supplementally the more recent works by Woodward and Steele both provide an excellent introduction to the topic.


2. Infrared and Raman - Different Techniques

Classical electrodynamics teaches that a system emits radiation by virtue of periodic changes in its electric dipole moment, the frequency of the emitted radiation being the same as that of the dipole oscillations. Absorption is the inverse of emission, and the system is able to absorb radiation of the same frequency as it is able to emit. Infrared spectroscopy is concerned with the absorption of radiation incident upon a sample and is thus a phenomenon which is dependent on the behavior of the vibrating dipole moment, \( \mu \), within a molecule. When monochromatic radiation passes through a homogenous material some of the radiation is scattered. Most of the scattered radiation is unaltered in frequency but a portion suffers a frequency shift. This shift results from transference of internal vibrational energy (and also rotational and electronic energy) from the beam to the sample material and vice versa. This effect is known as Raman scattering. It is a molecular light-scattering phenomenon in which a change of frequency occurs in a small portion of the incident radiation. It does not involve absorption at all, and the intrinsic dipole moment \( \mu \) of the molecular vibration is of no consequence. Unlike infrared the Raman effect is concerned with the induced dipole moment \( \vec{\mu} \) which is induced in the molecule by the electric field of the incident light. For field strengths of the magnitude ordinarily used in Raman
spectroscopy the relation between $\pi$ and $E$, the applied electric field, may be written

$$\pi = \kappa E$$

where $\kappa$ is the electric polarizability of the molecule.

Thus while infrared and Raman spectroscopy are techniques for investigating the vibrational characteristics of molecules, the underlying principles for each method are different. In principle, the observed frequencies in each technique (i.e. the observed shifts in the Raman and the observed absorption in the infrared) are the same provided they are allowed by both techniques. Vibrational transitions that are forbidden (not allowed) in infrared absorption may be permitted in the Raman effect, and vice versa. Frequently, however, the same frequencies are observed by both techniques. The two experimental methods are thus essentially complementary in character.

3. **Selection Rules**

The rules or guidelines by which one predicts that a vibration will or will not be allowed using either infrared or Raman spectroscopy are called selection rules. Because the mechanisms of the two techniques are different the selection rules are different. The development of these rules, however is similar in each case.
Three distinct approaches to deriving the selection rules exist. The first is through classical mechanics, the second is through quantum mechanics and the third is through symmetry properties and group theory. The first two methods lead to what are called restricted selection rules because they are restricted by the assumptions used in their derivation. The development based on group theory leads to the general selection rules. While it is outside of the scope of this work to review in detail these approaches, a few comments on each method may help the reader appreciate the meaning and limitations of these rules.

4. Classical Approach

The electric dipole \( \mu \) in a molecule is a vector, and therefore has three components \( \mu_x, \mu_y, \) and \( \mu_z \) in a Cartesian system. The molecule will only be able to absorb radiation of frequency \( \nu \) provided that \( \mu \) (i.e., at least one of its three components) can oscillate with this frequency. Now the dipole moment is a function of the nuclear configuration and so, when the molecule vibrates, the dipole varies correspondingly. In the simple harmonic approximation, all molecular vibrations can be regarded as superpositions of a limited number of fundamental modes, each with its own fundamental frequency \( \nu_k \). It follows that the electric dipole moment can only oscillate with these fundamental frequencies, and only radiation of these fre-
In general the magnitudes of the components of the molecular dipole moment will be functions of all the vibrational coordinates $Q$, and thus capable of expansion as a Taylor series:

$$
\begin{align*}
\mu_x &= (\mu_x)_0 + \sum_k \left\{ \left( \frac{\delta \mu_x}{\delta Q_k} \right)_0 Q_k \right\} + \text{higher terms} \\
\mu_y &= (\mu_y)_0 + \sum_k \left\{ \left( \frac{\delta \mu_y}{\delta Q_k} \right)_0 Q_k \right\} + \text{higher terms} \\
\mu_z &= (\mu_z)_0 + \sum_k \left\{ \left( \frac{\delta \mu_z}{\delta Q_k} \right)_0 Q_k \right\} + \text{higher terms}
\end{align*}
$$

The zero subscripts in the above equations indicate values at the equilibrium configuration of the molecule. We adopt the general convention whereby the three separate expressions for $\mu_x$, $\mu_y$, and $\mu_z$ are all implied by the single condensed form

$$
\mu = \mu_0 + \sum_k \left( \frac{\delta \mu}{\delta Q_k} \right)_0 Q_k
$$

The condition that the molecular dipole moment shall be able to oscillate with the frequency $\nu_k$, i.e. the condition that this normal frequency shall be capable of being absorbed is that $\left( \frac{\delta \mu}{\delta Q_k} \right)_0$ shall not be zero. This implies that

$$
\left( \frac{\delta \mu_i}{\delta Q_k} \right)_0 \neq 0
$$

for at least one of the components ($i = x, y, z$).
This is a statement of the restricted selection rule for infrared absorption. Its derivation is dependent upon two special approximate assumptions. The first is that the molecular vibrations are simple-harmonic, for otherwise the normal modes would not be separable and the meaning of the individual normal coordinates $Q_k$ would be lost. The second assumption is that in the Taylor expansion of the electric dipole moment all the higher terms are negligible.

Similarly, the corresponding selection rule for Raman scattering may be derived. Like the dipole moment the electric polarizability of a molecule $\alpha$ will in general be a function of all the normal vibrational coordinates. We may therefore expand $\alpha$ as a Taylor series with respect to these coordinates and neglect powers higher than the first. We thus obtain

$$\alpha = \alpha_0 + \sum \left\{ \left( \frac{\delta \alpha}{\delta Q_k} \right)_0 Q_k \right\}$$

where $\alpha_0$ is the polarizability in the equilibrium configuration of the molecule. Since, as we have seen, the induced dipole moment, $\mathbf{\Pi}$, is given by

$$\mathbf{\Pi} = \alpha E$$

we may write

$$\mathbf{\Pi} = \alpha_0 E + \sum_k \left\{ \left( \frac{\delta \alpha}{\delta Q_k} \right)_0 Q_k \right\} E$$
Consider the first term, $\mathcal{E}$, in the expression for $\Pi$. Since every component of $\mathcal{E}$ is simply a molecular constant and every component of $E$ oscillates with the incident light frequency $\nu_0$, it follows that the corresponding part of every component of $\Pi$ must oscillate with this same frequency. Thus light of the incident frequency $\nu_0$ will be emitted and will be observable in directions which differ from that of the incident light. This is the phenomenon known as classical or Rayleigh scattering. Since it is of no interest in this discussion we can ignore this term.

Considering the second term, let us fix attention on the contribution from the particular vibrational mode with the normal coordinate $Q_k$. Every component of $(\delta \mathcal{E} / \delta Q_k)_0$ is simply a constant. The time dependent factors are $Q_k$ which oscillates with the normal frequencies $\nu_k$, and all the components of $E$, which oscillate with $k$ the incident frequency $\nu_0$. These time dependences could be expressed by including the respective factors $\cos(2\Pi \nu_k t)$ and $\cos(2\Pi \nu_0 t)$. In view of the identity $\cos A \cos B = \frac{1}{2}(\cos(A+B) + \cos(A-B))$ we see that all the corresponding contributions to all the components of the induced dipole moment $\Pi$ are characterized by the two new frequencies $(\nu_0 + \nu_k)$ and $(\nu_0 - \nu_k)$. These frequencies are referred to as anti-Stokes and Stokes frequencies respectively, and they constitute the contribution of the $k$th
normal mode to the Raman spectrum of the scattering molecule.

The condition that a particular normal frequency \( \nu_k \) shall be active in Raman scattering is that the factor \( \frac{\delta \alpha}{\delta Q_k} \) shall be different from zero, i.e.,

\[
\left( \frac{\delta \alpha}{\delta Q_k} \right)_0 \neq 0
\]

for at least one of the components (i or j = x, y or z) of the polarizability. This statement is the restricted selection rule for Raman scattering and is similar to the selection rule for infrared. As was true with the infrared rule, the Raman rule is subject to the limitation that the vibrations are simple-harmonic and that in the Taylor expansion of the induced dipole moment all higher terms may be neglected.

5. Quantum Mechanical Approach

For the transition between the two states characterized by the wave functions \( \Psi^n \) and \( \Psi^m \) we denote the wave mechanical quantity known as the transition moment by \( \mu_{nm} \).

The transition moment is defined by the following equations:

\[
(\mu_x)_{nm} = \int \Psi^n \mu_x \Psi^m \, d\tau
\]

\[
(\mu_y)_{nm} = \int \Psi^n \mu_y \Psi^m \, d\tau
\]

\[
(\mu_z)_{nm} = \int \Psi^n \mu_z \Psi^m \, d\tau
\]
in which \( \mu_x, \mu_y, \) and \( \mu_z \) are the magnitudes of the components of \( \mu \), and \( d\tau \) is a volume element. As is generally done we condense the three expressions into the conventional equation

\[
\mu_{nm} = \int \Psi^n \mu \Psi^m d\tau
\]

The importance of the transition moment is that it determines the intensity of the absorption of radiation by the transition in question. In fact the relation of this intensity to the magnitude \( \mu_{nm} \) of the transition moment is similar to that of the intensity of classical absorption to the amplitude of oscillation of an ordinary dipole moment. Thus the total intensity is proportional to the square of \( \mu_{nm} \), or more precisely, the total intensity is proportional to the sum of the squares of \( (\mu_x)_{nm}, (\mu_y)_{nm} \) and \( (\mu_z)_{nm} \). Thus a very general statement of the selection rule is that a transition is forbidden in the infrared if \( \mu_{nm} = 0 \), i.e. if

\[
(\mu_x)_{nm} = (\mu_y)_{nm} = (\mu_z)_{nm} = 0.
\]

A more particular statement of the selection rule can be derived by substituting the Taylor expansion value of \( \mu \) into the equation for the transition moment. This gives

\[
\mu_{nm} = \mu_0 \int \Psi^n \Psi^m d\tau \sum_k \left\{ \frac{\partial \mu}{\partial Q_k} \right\}_0 \int \Psi^n q_k \Psi^m d\tau \right\}
\]
Because of the mutual orthogonality of the wave functions, the first integral of the right hand of the equation is zero unless $n=m$. This, however, corresponds to no transition, and may be neglected where absorption is concerned. Thus, as was seen in the classical development, one necessary condition for infrared absorption is that \( \left( \frac{\partial \alpha}{\partial Q_k} \right)_o \neq 0. \)

The quantum mechanical treatment of Raman scattering is similar to the treatment of absorption. The transition moment arising from the induced dipole moment $\mathcal{W}$ is given by

\[
\int \Psi^n \mathcal{W} \Psi^m d\tau = E \left( \int \Psi^n \alpha \Psi^m d\tau \right) = E \alpha_o \int \Psi^n \Psi^m d\tau + E \sum_k \left( \frac{\partial \alpha}{\partial Q_k} \right)_o \Psi^{m Q_k} \Psi^m d\tau \]

Because of the mutual orthogonality of the eigenfunctions, the integral in the first term on the right hand side vanishes unless $\Psi^n = \Psi^m$, in which case its value is unity. This term accounts for the Rayleigh scattering without change of frequency. When $n \neq m$ one necessary condition for Raman scattering is that $\left( \frac{\partial \alpha}{\partial Q_k} \right)_o \neq 0$. As occurs in the classical development of selection rules the quantum mechanical treatment relies on the restrictive assumptions that the molecular vibrations are simple-harmonic, and that in the Taylor expansion higher terms may be neglected.
6. **Group Theoretical Approach**

It is the molecular symmetry that determines whether or not \[ \frac{\delta}{\delta Q} \neq 0 \] or \[ \frac{\delta}{\delta Q} \neq 0 \] for a particular vibrational mode. This may be illustrated by the very simple example of a linear \( Y-X-Y \) molecule in which the two bonds are identical. Its two modes of vibration along the line of the masses are shown in Figure 4.

**FIGURE 4**

*Forms of the Normal Vibrational Modes Along the Molecular Axis*
*(Linear \( X-Y-X \) Molecule)*

(a) \( \leftarrow X \quad Y \quad X \rightarrow \)

(b) \( X \rightarrow \leftarrow Y \quad X \rightarrow \)

Remembering that the molecule is composed of positively charged nuclei and negatively charged electrons, we see that in its equilibrium configuration its structural symmetry will carry with it a corresponding electrical symmetry and will result in a zero molecular dipole. In the totally symmetric vibration (a in Figure 4) this symmetry is conserved throughout. The dipole moment therefore remains unchanged. This means that \( \left( \frac{\delta}{\delta Q} \right)_0 = 0 \).
i.e. that the mode must be forbidden in infrared absorption. In the antisymmetric mode (b), on the other hand, the molecule does not conserve its equilibrium symmetry. The structural asymmetry through which it passes in the course of a vibration causes a corresponding electrical asymmetry, i.e. produces a non-zero dipole moment which oscillates synchronously with the mechanical vibration, passing through values of equal magnitude but opposite sign at corresponding values of the normal coordinate $Q_b$. This is shown diagramatically in Figure 5, where the abscissa represents the normal coordinate and the ordinate represents the magnitude of the dipole moment.

FIGURE 5

Variation of Dipole Moment $\mu$ or Polarizability $\alpha$ with Vibration along the Normal Coordinate
In this simple case the moment is always directed along the line of the nuclei, which may be called the x direction. Thus we need consider the component \( \mu_x \) only, the other two (\( \mu_y \) and \( \mu_z \)) being always zero. From Figure 5 we see that \( (\delta \mu / \delta Q)_0 \neq 0 \). The mode is therefore active in infrared absorption.

Similarly it is molecular symmetry that determines whether or not \( (\delta \mu / \delta Q)_0 \neq 0 \), i.e. whether a normal vibrational mode shall be active in Raman scattering. Consider again the modes a and b of Figure 4 in the totally symmetric mode a, both are stretched in one phase of a vibrational cycle and both are compressed in the other. Although this leaves the molecular dipole unaltered, it is clear that the electrical polarizability will be different in the two phases. In general therefore \( (\delta \mu / \delta Q)_0 \) will differ from zero. In mode b, on the other hand, the structural situation is the same in both phases, in that one bond is stretched and the other is compressed. The end-for-end interchange caused a reversal in the sign of the non-zero electric dipole moment vector, but there is no such reversal for the components of the electrical polarizability.

Thus the value of is the same for \( +Q_b \) as for \( -Q_b \). This is shown diagrammatically in Figure 5. It is true that the value of any polarizability component at each extreme value of the normal coordinate may be different from its value at
\( Q_b = 0 \), but from Figure 5 it is clear that the slope at the equilibrium configuration, i.e. \( \left( \frac{\partial \alpha}{\partial Q_b} \right)_o \), is zero. Thus mode \( b \) is forbidden in Raman scattering. In this very simple example it happens that the mode which is forbidden in infrared is permitted in Raman and vice versa. This, however, is a special circumstance for in general many molecular vibrational modes are permitted in both kinds of spectra, and some are forbidden in both. The example illustrates the importance of symmetry in the context of the restricted selection rules. Generalization of the symmetry considerations in the form of group theory makes it possible to predict the spectroscopic consequences of the application of the rules to molecules containing any number of nuclei and belonging to any point group. In addition it should be recognized that symmetry theory is independent of the particular physical nature of the system to which it is applied. The relevant symmetry properties are independent of whether the intramolecular force field is simple harmonic or anharmonic and no special assumptions about Taylor expansions in terms of normal vibrational coordinates are needed.

While a development of the general selection rules based on group theory is well outside the intention of this section, we will simply conclude this section with
Woodward's formal statement of the general selection rules:

"A transition between the states characterized by the wave functions $\Psi_n$ and $\Psi_m$ is forbidden in the infrared absorption unless for at least one of the components $\mu_i$ of the molecular electric dipole moment ($i = x, y, \text{or } z$) the product $\Psi_n^{\mu_i} \Psi_m^{\mu_i}$ belongs to a representation whose structure contains the totally symmetric species.

"A transition between states characterized by the wave functions $\Psi_n^\alpha$ and $\Psi_m^\alpha$ is forbidden in Raman scattering unless for at least one of the components $\alpha_{ij}$ of the molecular polarizability tensor ($i$ or $j = x, y, \text{or } z$) the product $\Psi_n^{\alpha_{ij}} \Psi_m^{\alpha_{ij}}$ belongs to a representation whose structure contains the totally symmetric species."
PROOF OF CONVERGENCE

1. Terminology

In developing the proof of convergence for the algorithm used in the main computer program, we have availed ourselves of the symbolism common in texts on linear algebra. For a review of this topic and a further development of the principles involved, the reader is directed to the text by Curtis\textsuperscript{28}. Table II should suffice, however, for complete understanding of those symbols used in this work.

TABLE II

Notation Used in Proof

<table>
<thead>
<tr>
<th>Notation</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a \in B$</td>
<td>$a$ is a member of set $B$</td>
</tr>
<tr>
<td>$A \cap B$</td>
<td>denotes the intersection of set $A$ and set $B$</td>
</tr>
<tr>
<td>$\emptyset$</td>
<td>represents an empty set</td>
</tr>
<tr>
<td>$A \cap B = \emptyset$</td>
<td>$A$ and $B$ are disjoint sets; no member of $A$ is in set $B$ and no member of $B$ is in $A$.</td>
</tr>
<tr>
<td>$A \subseteq B$</td>
<td>implies set $A$ is a subset of set $B$</td>
</tr>
</tbody>
</table>

It is convenient to think of the data set as a set of vectors, $F$. Each vector in the set represents one vibrational spectrum and is denoted $\mathbf{f}$. The set $F$ is composed of two disjoint sets $F^+$ and $F^-; \text{i.e. } F^+ \cap F^- = \emptyset$, and $F^+, F^- \subseteq F$. Furthermore we denote the members of $F^+$ as $\mathbf{f}^+$ and the members $F^-$ as $\mathbf{f}^-.$

To express these ideas in more familiar terms we can consider the problem of developing a means for distinguishing the esters in our data bank from all other spectra. The spectrum of an ester can be represented by $\mathbf{f}^+$ and the entire set of esters makes up the set $F^+$. All other spectra can be represented by $\mathbf{f}^-$ and the set of spectra which are not esters is called $F^-$. Our entire data bank is called $F$.

The task at hand is to develop a rule which will correctly classify any member of $F$ so that all $\mathbf{f}^+$ are classified as $\mathbf{f}^+ \in F^+$ and all $\mathbf{f}^-$ as $\mathbf{f}^- \in F^-$. That is, we must develop a simple to use decision procedure (frequently called a predicate) by which we can select any spectrum and tell whether it is an ester or not an ester. A number of conventional classification methods which might be used to attack the problem are discussed in the literature. Nagy's review is comprehensive and a large
number of other works are available\textsuperscript{29, 30, 31, 32, 33}. These approaches, however, construct the predicate by a specific mathematical analysis of the entire data set $F$. Each approach is \textit{ad hoc} to each predicate and suffers from the need to work on the entire data set at once. Such approaches are prohibitive when using large data sets.

In this chapter we will describe such a simple decision procedure based upon the sign of the weighted sum of the components of $\vec{f}$, and an algorithm in which a set of coefficients, $\vec{W}$, can be found by a systematic and easily mechanized procedure. The procedure begins with the selection of an arbitrary set of coefficients. A vector $\vec{f}$ is selected from $F$ and the predicate $\vec{W}$ is tested to see if it works properly. If it does not, $\vec{f}$ is used to modify $\vec{W}$. If it does, $\vec{W}$ is left unchanged. A new $\vec{f}$ is then selected from $F$. The algorithm proceeds in this manner until $\vec{W}$ will correctly classify all $\vec{f}$ in $F$. Because $\vec{W}$ is modified every time it makes a mistake the procedure has been termed a "learning machine".

\begin{itemize}
\item[(32)] J. MacQueen, Proc. 5th Berkeley Symp. on Statistics and Probability, University of California Press, 281 (1967).
\end{itemize}
Before proceeding it might be helpful to the reader to define a few terms.

The magnitude of a vector \( \vec{W} \) is represented by \( |\vec{W}| \) where

\[
|\vec{W}| = \sqrt{\sum_{i} (W(i))^2}
\]

The dot product of 2 vectors \( \vec{W} \) and \( \vec{f} \) is given by

\[
\vec{W} \cdot \vec{f} = \sum_{i} W(i) \times f(i)
\]

Note that \( |\vec{W}|^2 = \vec{W} \cdot \vec{W} \), i.e. the magnitude squared of a vector is the vector dotted on itself.

A unit vector \( \vec{W}^* \) is the direction of \( \vec{W} \), i.e. it is the vector divided by its magnitude.

\[
\vec{W}^* = \frac{\vec{W}}{|\vec{W}|}
\]

Provided, of course, \( |\vec{W}| \neq 0 \).

Note that the magnitude of a unit vector is 1, and

\[
|\vec{W}^*|^2 = \vec{W}^* \cdot \vec{W}^* = 1
\]

2. The Learning Machine

We will show how to pick a \( \vec{W} \) which determines whether \( \vec{f} \in F^+ \) or \( F^- \) by \( \vec{W} \cdot \vec{f} > 0 \) if and only if \( \vec{f} \in F^+ \). Intuitively one might suggest the simplest type of feedback or correction of \( \vec{W} \) such as the following procedure.
START: Let \( \hat{W} \) be any vector

**TEST:** Choose the next \( \vec{F} \) from \( F \) (If \( F \) is exhausted without going to ADD or SUBTRACT, the procedure is done; else begin again with 1st \( \vec{F} \).)

- If \( \vec{F} \in F^+ \) and if \( \vec{W} \cdot \vec{F} > 0 \) Go to test
- If \( \vec{F} \in F^+ \) and if \( \vec{W} \cdot \vec{F} < 0 \) Go to add
- If \( \vec{F} \in F^- \) and if \( \vec{W} \cdot \vec{F} < 0 \) Go to test
- If \( \vec{F} \in F^- \) and if \( \vec{W} \cdot \vec{F} > 0 \) Go to subtract

**ADD** Replace \( \vec{W} \) by \( \vec{W} + R_{\vec{F}} \vec{F} \)
Go to TEST

**SUBTRACT:** Replace \( \vec{W} \) by \( \vec{W} - R_{\vec{F}} \vec{F} \)
Go to TEST

\( R_{\vec{F}} \) is a positive correction factor with an upper bound \( A \), i.e. \( 0 \leq R_{\vec{F}} < A \). (\( A \) is some number chosen in advance.)

A priori, any procedure of this sort runs the risk of oscillating wildly. An adjustment of \( \vec{W} \) for one vector \( \vec{F} \) might undo the previous adjustment for another \( \vec{F} \). As will be shown, however, this procedure will eventually converge to vector \( \vec{W} \) which will correctly classify all \( \vec{F} \) in \( F \) provided that \( F \) is linearly separable into \( F^+ \) and \( F^- \), i.e. provided a hyper-plane exists which will separate \( F^+ \) from \( F^- \). Remember \( F^+ \cap F^- = \emptyset \) does not imply that \( F^+ \) and \( F^- \) are linearly separable, i.e. it is not a sufficient condition to guarantee that a solution \( \vec{W} \) exists.

This simple feedback algorithm converges by the "perceptron convergence theorem.\(^{12}\) The theorem states that
whatever choice is made in \textbf{START} and whatever function is used in \textbf{TEST} the vector $\hat{W}$ will be changed only a finite number of times, provided that $F$ is linearly separable into $F^+$ and $F^-$. 

Before developing the proof of convergence one minor restriction must be placed on the members of any vector, $\hat{f}$. No element of $\hat{f}$ may be unbounded (i.e. $\pm \infty$). Thus for all $\hat{f} \in F$, $\hat{f}(i) \leq L$, where $L$ is some established upper bound. This restriction is necessary to the proof, but in practice poses no real limitation. In our data bank, for example, every element is in the range from 0 to 9.

Note that if a vector $\hat{W}$ separates $F^+$ from $F^-$ then any positive multiple of $\hat{W}$ will also separate $F^+$ from $F^-$ since 

\[(a \cdot \hat{W}) \cdot \hat{f} = a \cdot (\hat{W} \cdot \hat{f})\]

From this it follows that we can find a unit vector as the $\hat{W}$.

The proof of convergence which we present is adapted from Minsky and Papert\textsuperscript{29}. Minsky and Papert assumed that $|\hat{f}| = 1$ for all $\hat{f} \in F$, and $R_F = 1$. We make no such assumptions.

3. \textbf{Proof}

The program in the previous section is more complicated than is needed for the proof. Recognize that the following
is equivalent.

**START:**
Let $\mathbf{w}$ be any vector.

**TEST:**
Choose the next $\mathbf{f}$ from $F$ (Done when $F$ is exhausted without going through ADD)

If $\mathbf{f} \in F^+$ change the sign of $\mathbf{f}$ by multiplying $\mathbf{f}$ by -1

If $\mathbf{w} \cdot \mathbf{f} > 0$, go to TEST, otherwise go to ADD

**ADD:**
Replace $\mathbf{w}$ by $\mathbf{w} + R\mathbf{f}$, where $R$ is a positive weighting factor with an upper bound $A$

Go to TEST

**Proof:**

Define $G = \frac{\mathbf{w}^* \cdot \mathbf{w}}{|\mathbf{w}|}$

where $\mathbf{w}^*$ is a unit vector which is a solution, i.e.

$\mathbf{w}^* \cdot \mathbf{f} > 0 \rightarrow \mathbf{f} \in F^+$

and $\mathbf{w}^* \cdot \mathbf{f} \leq 0 \rightarrow \mathbf{f} \in F^-$

Because $|\mathbf{w}^*| = 1$, $|G| \leq 1$.

(It may help the reader to note that $G$ is the cosine of the angle between $\mathbf{w}^*$ and $\mathbf{w}$.)

Consider the behavior of $G$ on successive passes of the program through ADD. Considering first the numerator as each trial $t$ progresses,

$\mathbf{w}^* \cdot \mathbf{w}_{t+1} = \mathbf{w}^* \cdot (\mathbf{w}_t + R_t \mathbf{f}_t)$

$= \mathbf{w}^* \cdot \mathbf{w}_t + \mathbf{w}^* \cdot R_t \mathbf{f}_t$

$\geq \mathbf{w}^* \cdot \mathbf{w}_t + \delta$

where $\delta > 0$
This holds because since $\vec{W}^*$ is a solution
$$\vec{W}^* \cdot R \vec{f} \vec{t} > 0$$
(after the appropriate adjustment of the sign if $\vec{f} \in F'$)

Thus after the nth application of add we obtain
$$\vec{W}^* \cdot \vec{w}_n \geq n \delta$$

The numerator of $G$ increases with $n$, the number of changes of $\vec{W}$, that is the number of errors.

As for the denominator, since $\vec{W} \cdot R \vec{f} \vec{f}$ must be negative or zero or the program would not have gone through add

$$\left| \vec{w}_{t+1} \right|^2 = \vec{W}_{t+1} \cdot \vec{W}_{t+1}$$
$$= \left( \vec{W}_t + R \vec{f} \vec{f}_t \right) \cdot \left( \vec{W}_t + R \vec{f} \vec{f}_t \right)$$
$$\left| \vec{W}_{t+1} \right|^2 = \left| \vec{W}_t \right|^2 + 2 \vec{W}_t \cdot \left( R \vec{f} \vec{f}_t + R^2 \vec{f}^2 \vec{f}_t + \vec{f} \vec{f}_t \right) \cdot \left| \vec{f}_t \right|^2$$
$$\left| \vec{W}_t \right|^2 + L^2 K^2$$

after the nth application of add

$$\left| \vec{w}_n \right|^2 < n L^2 K^2$$
$$\left| \vec{w}_n \right| < n^{3/2} L K$$

combining the results

$$G = \frac{\vec{W}^* \cdot \vec{w}_n}{\vec{w}_n} > \frac{n \delta}{n^{3/2} L K}$$
but \( G \ll 1 \) so this can only be so if

\[
\frac{n \delta}{n^{1/3} L K} \ll 1
\]

That is

\[
n \ll \frac{L^2 K^2}{\delta^2}
\]

This completes the proof.

4. Variations

The proof presented in this work closely follows the computer program used in the body of this work. A number of minor variants in procedure are possible, however. For example \( R^2_\hat{f} \) may be defined as \( 1/|\hat{f}| \) so that a unit vector is added each time a correction is made to \( \hat{W} \). \( R^2_\hat{f} \) may, of course, be a constant, i.e., independent of \( \hat{f} \).

In the program we used, \( R^2_\hat{f} \) was defined in the way suggested by Agmon\(^{(34)}\):

\[
R^2_\hat{f} = -k \left[ \frac{\hat{W}_t \cdot \hat{f}}{|| \hat{f} ||^2} \right]
\]

where \( k \) is a positive constant. In this manner the magnitude of \( R^2_\hat{f} \) is dependent on how "badly" \( \hat{W}_t \) failed to

classify \( \hat{f} \). Following the suggestion of Jurs, Kowalski, Isenhour and Reilley we usually set \( k = 2 \), but a few experiments were done with other values.

It was pointed out earlier that if \( \vec{W} \) is a solution vector, \( \vec{W}' \) is also a solution vector where

\[
\vec{W}' = k \vec{W}
\]

\( k \) being a positive constant. Similarly it should be noted that if \( \vec{W} \) is a solution and \( \vec{W}' \) is a solution, then \( \vec{W}'' \) is also a solution where

\[
\vec{W}'' = \vec{W} + \vec{W}'
\]

Thus all solution vectors form a convex cone and the program will stop changing \( \vec{W} \) as soon as it penetrates the cone.

(Convex cone: a set \( S \) of vectors for which

1. \( A \in S \Rightarrow kA \in S \) for all \( k > 0 \), and
2. \( A \in S \) and \( B \in S \Rightarrow (A+B) \in S \).

Any solution defines a hyper-plane dividing the space in which we are operating. All \( \vec{f} \) in \( F^+ \) are on one side of the plane while all \( \vec{f} \) in \( F^- \) are on the other side.

Notice, however, that if we are dealing with \( n \) dimensional space (i.e., \( \vec{f} \) has \( n \) members) and our solution hyper-plane is limited to \( n \) members, the hyper-plane must pass through the origin of the space. If, however, we add one member to \( \vec{f} \) and make that member \( +1 \), the solution hyper-
plane is not constrained to pass through the origin. Thus, while we take 112 readings from each spectrum, the dimensionality of the space we are working in is 113. The resulting vector passes through the origin of the 113 dimensional space but not through the origin of the 112 dimensional space.
THE PROGRAMS

1. Program Names

Three programs were written in Fortran IV to analyze the spectral data. The first program, called TRAIN, trains vectors, the second program, SNOOP, is used for either of two jobs. SNOOP is used to average several trained vectors, or it is used to calculate the average spectrum of a class of compounds. Program TEST tests vectors which have been trained to determine how they perform with a new set of data. A listing of each program with a sample set of input and output for the program TRAIN is included in Appendix B. The comment cards in each program are intended to instruct the interested reader in the details necessary for use of each program.

2. TRAIN

Program TRAIN reads a set of options from a card file. It then reads the appropriate spectral data from a file. (The data have been previously stored in the file.) Figure 6 shows a simplified flow diagram for TRAIN and Table III lists the options which are currently available as a part of program TRAIN. In Figure 6 the weight vector being trained is labeled \( \vec{W} \) and a vector representing a spectrum is labeled \( \vec{f} \).
FIGURE 6

Program TRAIN•Flow Diagram

Read options to be used
Read spectral data from disk
Set initial value of $\vec{W}$

Begin
Iteration

NO
Present Next
Pattern($\vec{P}$)

YES— Have the
maximum #
of iterations
been reached?

Calculate
$S = \vec{W} \cdot \vec{f}$

Desire
Response?

YES

YES

$\vec{W} = \vec{W} + c \vec{f}$

Feedback correction

NO

$\vec{f}$

More Patterns?

NO

All Yes
Correct?

YES

Plot the vector
and write the vector
on the disk

END
### TABLE III

**OPTIONS IN PROGRAM TRAIN**

<table>
<thead>
<tr>
<th>Option Number</th>
<th>Portran Label</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NOPT1</td>
<td>Type of spectra to be considered. For complete details see Table III.</td>
</tr>
<tr>
<td>2</td>
<td>NCARD</td>
<td>Number of spectra in the data file stored on disk. For all of the work reported here NCARD = 1117.</td>
</tr>
<tr>
<td>3</td>
<td>NOPT2</td>
<td>Class of compounds being considered. For complete details see Table IV.</td>
</tr>
<tr>
<td>4</td>
<td>FIN</td>
<td>Initial value of all elements of ( \vec{W} ), the vector being trained. If FIN = 0 the program will read a starting vector from disk file. (see Option 12)</td>
</tr>
<tr>
<td>5</td>
<td>NSHUT</td>
<td>Specifies an upper limit to the number of iterations.</td>
</tr>
<tr>
<td>6</td>
<td>LEN</td>
<td>The vector ( \vec{W} ) will be printed every &quot;LEN' th&quot; iteration (and again at the end of the calculation).</td>
</tr>
<tr>
<td>7</td>
<td>NOPT3</td>
<td>The number of spectra not in class (Option #3) which are to be included in the training deck.</td>
</tr>
<tr>
<td>8</td>
<td>NOPT4</td>
<td>The number of spectra in the class (Option #3) which are to be included in the training set.</td>
</tr>
<tr>
<td>9</td>
<td>NOPT4</td>
<td>If NOPT6 = 1 every element in the trailing vectors will be used in the training process, else every &quot;NOPT6'th&quot; element is used until the vector ( \vec{W} ) is trained or until &quot;NSHUT&quot; iterations have been completed. Then ( \vec{W} ) is used as the initial vector for training with every element.</td>
</tr>
<tr>
<td>10</td>
<td>NOPT5</td>
<td>If NOPT5 ( \neq 0 ) another set of data is expected. The necessary disk files will be rewound.</td>
</tr>
<tr>
<td>11</td>
<td>FKOR</td>
<td>A constant used to weight the correction factor. (FKOR is the value of ( k ) in Fig.IV)</td>
</tr>
<tr>
<td>12</td>
<td>NFILE</td>
<td>The position in the disk file of the initial vector. If FIN ( \neq 0 ) NFILE should not be specified.</td>
</tr>
</tbody>
</table>
The value of LEN (Option 6) determines how often the vector is printed during the training process. In the early experiments it was useful to be able to watch the vector develop. In later work only the trained vector was needed; this was done by setting the value of LEN higher than NSHUT.

Options 8 and 9 are used to limit the number of compounds used to train the vector. In those experiments where all the available compounds were not used in the training process, the resulting vector was later used with program TEST to determine how well the vector classifies those compounds not used in the training set.

Table IV provides a detailed description of the type of spectra treated by TRAIN (option one).

**TABLE IV**

The Type of Spectra Considered
(Option One in Program TRAIN)

<table>
<thead>
<tr>
<th>Value of Option</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>*Infrared spectra only are used</td>
</tr>
<tr>
<td>2</td>
<td>*Raman nonpolarized spectra only are used</td>
</tr>
<tr>
<td>3</td>
<td>*Raman parallel polarized spectra only are used</td>
</tr>
<tr>
<td>4</td>
<td>*Raman perpendicular polarized spectra only are used</td>
</tr>
<tr>
<td>5</td>
<td>Infrared plus Raman nonpolarized spectra are averaged</td>
</tr>
<tr>
<td>6</td>
<td>Infrared plus Raman parallel plus Raman perpendicular polarized spectra are averaged</td>
</tr>
<tr>
<td>7</td>
<td>*Infrared plus all Raman data are averaged</td>
</tr>
<tr>
<td>8</td>
<td>*All Raman data are averaged</td>
</tr>
<tr>
<td>9</td>
<td>Raman parallel plus Raman perpendicular polarized spectra are averaged</td>
</tr>
</tbody>
</table>

(* indicates those types of spectra treated in this work)
Table V shows in detail the variations which are possible through option number 3. If the input value of option 3 is from 1 to 17 the program will use the class of compounds corresponding to the input value. (The 17 classes were given earlier in Table I.) As shown in Table V, however, 4 other values of option 3 are allowable. These values simply instruct the program to combine certain classes.

<table>
<thead>
<tr>
<th>Value of Option 1 through 17</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>All halogens (class 7 through 10)</td>
</tr>
<tr>
<td>19</td>
<td>Compounds containing F, Br and/or I (classes 8, 9 and 10)</td>
</tr>
<tr>
<td>20</td>
<td>All alcohols (classes 3, 4 and 5)</td>
</tr>
<tr>
<td>21</td>
<td>Compounds containing O-H (classes 3, 4, 5 and 16)</td>
</tr>
</tbody>
</table>
A separate program called TRAIN\textsuperscript{i} was used to combine spectra in a entirely different way. TRAIN\textsuperscript{i} uses the infrared spectrum of each compound and either the parallel polarized Raman spectrum or, in the case of solids, the nonpolarized Raman spectrum. For each compound the infrared data from 1875 cm\textsuperscript{-1} to 500 cm\textsuperscript{-1} is concatenated, i.e. linked in series with the Raman data from the same region to form a single vector. Thus 58 infrared readings and 56 Raman readings are joined to make a single vector representing the compound. TRAIN\textsuperscript{i} has all of the options that are in TRAIN except, of course, option one. When trained vectors are printed TRAIN\textsuperscript{i} separates the infrared portion of the vector from the Raman portion and plots them separately on the same scale as is used by TRAIN.

Clearly TRAIN\textsuperscript{i} could have been incorporated in TRAIN as yet another option, but a separate program was written to reduce the complexity of the programming effort.

3. TEST and SNOOP

Appendix B includes listings of both TEST and SNOOP. The use of TEST is self-explanatory and needs no discussion. When SNOOP was used to calculate the average representation of a class of compounds, two types of representations were generated. The average representation of each class was calculated and plotted, and the average of all compounds in the class minus the average of all compounds not in the
class was plotted. This second type of average representation was obtained by making a minor program change in SNOOP, and is not shown in Appendix B.
RESULTS AND DISCUSSION

1. Results from SNOOP

As mentioned earlier there are two types of "average" spectra which have been obtained. We have called the first type the Simple Average; and the second, the Muted Average. The Simple Average is obtained by adding all the spectra from a given class and specified type of spectrum and dividing the total by the number of spectra. Let $\tilde{f}_i$ represent the $i$th spectrum of the $n$ spectra in a particular class. Then the Simple Average representation of a class is given by:

$$\text{Simple Average} = \frac{1}{n} \sum_{i=1}^{i=n} \tilde{f}_i$$

If $\tilde{f}_j$ represents the $j$th spectrum of the $m$ spectra not in the class, the Muted Average representation of the class is given by:

$$\text{Muted Average} = \left[ \frac{1}{n} \sum_{i=1}^{i=n} \tilde{f}_i \right] - \left[ \frac{1}{m} \sum_{j=1}^{j=m} \tilde{f}_j \right]$$
When the Muted Average is calculated, negative intensities are encountered. For example, Figure 7 shows the Muted Average of Raman parallel polarized spectra of esters. Figure 8 shows the same spectrum, but only the positive intensities are printed. Since negative intensities do not give any direct information about the class of compounds being treated, we have adopted the convention of printing only the positive portion of the average spectra or the calculated vector under discussion. In this context it should be noted that a strong positive band does provide evidence that a compound in that class would be expected to have that vibrational frequency. Conversely, however, the presence of a strong negative band does not mean that a compound in the particular class is forbidden to vibrate with the frequency which appeared as a negative band. The only interpretation which can be given to negative bands is that compounds not in the class being treated have vibrational frequencies in that region. In general this information is not useful to the chemist interested in vibrational analysis.

The Simple Average representation has the advantage that it shows all of the bands characteristic of a chemical class, and tends to preserve their relative intensities. No bands are lost or muted simply because they happen to be common in compounds both in and out of the class. The Muted Average, of course, has the advantage that while some common bands
FIGURE 7

Muted Average

Raman Parallel Polarized Spectra

of

Esters

FIGURE 8

Muted Average

Raman Parallel Polarized Spectra

of

Esters

(Positive Portion Only)
may be reduced in intensity or lost, much of the noise is eliminated. Figures 9 and 10, for example, show the Simple Average and Muted Average spectra of the parallel polarized Raman spectra of ethers. Notice that the intensity scale for the two spectra differ. This must be considered when making comparisons. The Muted Average spectrum shows the peaks more sharply defined than does the Simple Average, but notice the relative intensity change when using the Muted Average. The C-H stretching bands around 3000 cm\(^{-1}\) are no longer the strongest peak in the spectrum. More importantly perhaps, the bands between 1600 and 1800 cm\(^{-1}\) have disappeared in the Muted Average. This is a clear example of how the Muted Average helps to remove noise. There are no ether vibrational bands above about 1550 cm\(^{-1}\). The bands appearing in the Simple Average spectrum in that region occur because 31 out of the 41 ethers used to calculate the average contain either a \(\text{C}_6\text{H}_6\), C=O, or C=O moiety.

Table VI lists the classes and the types of spectra for which Simple Average and Muted Average spectra have been calculated and gives the number of compounds used to calculate each average. Since there are so few nonpolarized Raman spectra in each class it is unlikely that their averages will be useful, and the combination spectra (all Raman or all IR plus Raman) do not have significance outside of the context of this work. Thus only the Muted and
FIGURE 9
Simple Average
Parallel Polarized Spectra
of
Ethers

Figure 10
Muted Average
Parallel Polarized Spectra
of
Ethers
<table>
<thead>
<tr>
<th>Type of Spectrum</th>
<th>IR</th>
<th>All Raman</th>
<th>Parallel Raman</th>
<th>Perpendicular Raman</th>
<th>Nonpolarized Raman</th>
<th>IR plus Raman</th>
</tr>
</thead>
<tbody>
<tr>
<td>CLASS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Esters</td>
<td>92</td>
<td>92</td>
<td>87</td>
<td>87</td>
<td>5</td>
<td>92</td>
</tr>
<tr>
<td>Alcohols</td>
<td>45</td>
<td>45</td>
<td>43</td>
<td>43</td>
<td>2</td>
<td>45</td>
</tr>
<tr>
<td>Ethers</td>
<td>48</td>
<td>48</td>
<td>41</td>
<td>41</td>
<td>7</td>
<td>48</td>
</tr>
<tr>
<td>C =C bonds</td>
<td>39</td>
<td>39</td>
<td>33</td>
<td>33</td>
<td>6</td>
<td>39</td>
</tr>
<tr>
<td>Ketones</td>
<td>15</td>
<td>15</td>
<td>14</td>
<td>14</td>
<td>1</td>
<td>15</td>
</tr>
<tr>
<td>1° Alcohols</td>
<td>32</td>
<td>32</td>
<td>30</td>
<td>30</td>
<td>2</td>
<td>32</td>
</tr>
<tr>
<td>2° Alcohols</td>
<td>12</td>
<td>12</td>
<td>11</td>
<td>11</td>
<td>1</td>
<td>12</td>
</tr>
</tbody>
</table>
Simple Averages of IR, the parallel Raman, and perpendicular Raman are included in Appendix C.

2. TRAIN and TEST

Table VII shows the number of iterations in one series of experiments needed for TRAIN to converge on a solution vector. In this set of experiments the initial value of the vector was set at -1. All of the available data were used in these tests. A plus (+) sign in Table VII indicates that TRAIN did not converge and was halted at the number of iterations shown.

The type of spectra labeled "all Raman" in Table VI were obtained by averaging all the Raman spectra for a particular compound. "IR plus Raman" indicates that the IR spectrum and all available Raman spectra were averaged to form a single spectrum for each compound. As was mentioned earlier, "concatenated IR plus Raman" spectra were formed by taking the infrared data from 1900 cm\(^{-1}\) to 500 cm\(^{-1}\) and combining them with Raman data from the same region. In the case of solids, nonpolarized Raman data were used. For liquid compounds parallel polarized Raman data were used.

The extremely low number of iterations in all cases where nonpolarized Raman spectra were tested is due to the very limited number of data available. (See Table VI.)
### TABLE VII

<table>
<thead>
<tr>
<th>Type of Spectrum</th>
<th>IR</th>
<th>All Raman</th>
<th>Para. Raman</th>
<th>Perp. Raman</th>
<th>Nonpol. Raman</th>
<th>IR plus Raman</th>
<th>IR plus Raman Concatenated</th>
</tr>
</thead>
<tbody>
<tr>
<td>CLASS Esters</td>
<td>40</td>
<td>500⁺</td>
<td>100⁺</td>
<td>100⁺</td>
<td>4</td>
<td>80</td>
<td>32</td>
</tr>
<tr>
<td>Alcohols</td>
<td>15</td>
<td>100⁺</td>
<td>94</td>
<td>100⁺</td>
<td>4</td>
<td>19</td>
<td>45</td>
</tr>
<tr>
<td>Ethers</td>
<td>54</td>
<td>100⁺</td>
<td>92</td>
<td>100⁺</td>
<td>7</td>
<td>100⁺</td>
<td>27</td>
</tr>
<tr>
<td>C = C</td>
<td>87</td>
<td>22</td>
<td>11</td>
<td>54</td>
<td>4</td>
<td>37</td>
<td>9</td>
</tr>
<tr>
<td>Ketones</td>
<td>22</td>
<td>49</td>
<td>24</td>
<td>66</td>
<td>2</td>
<td>40</td>
<td>16</td>
</tr>
<tr>
<td>1° Alc.</td>
<td>32</td>
<td>100⁺</td>
<td>100⁺</td>
<td>100⁺</td>
<td>4</td>
<td>52</td>
<td>53</td>
</tr>
<tr>
<td>2° Alc.</td>
<td>67</td>
<td>18</td>
<td>11</td>
<td>21</td>
<td>3</td>
<td>23</td>
<td>13</td>
</tr>
</tbody>
</table>

IR = Infrared  
Para. = Parallel Polarized  
Perp. = Perpendicular Polarized  
Nonpol. = Nonpolarized  
Alc. = Alcohol  
1° = primary  
2° = secondary
The only reason for running these tests was to determine whether these data were linearly separable from the rest of the data. In all cases they are.

When all the Raman spectra were combined and the esters were used as the class to be trained, TRAIN was permitted to go to 500 iterations. Prior to doing that test, TRAIN was modified so that all the variables in the iterative part of the program were double precision. The program was not able to train a vector which would correctly classify esters even after 500 iterations. Furthermore, the final vector after 500 iterations did not look significantly different from the vector after 100 iterations. After 500 iterations there were 448 compounds out of 4000 which could not be correctly classified by the vector, while after only 100 iterations there were only 46 compounds out of 4000 which the vector could not correctly classify. In addition, the compounds which could not be classified correctly after 500 iterations were substantially the same ones which could not be classified after 100 iterations.

After the 100 iteration run with the esters the coding and chemical structure of the most troublesome compounds were checked. Only one anomaly appeared significant. The tri-p-tolyl ester of phosphorous acid was not included in the ester class because it is not a carboxylic acid ester.
It failed to be correctly classified 100 times out of 100 iterations. When the 500 iteration run was made the ester of phosphorous acid was included in the ester category, but this did not make the data linearly separable. In all of the other runs with esters the phosphorous acid ester was not included in the ester class. This experience was typical of what was observed a number of other times during this work. On occasion a computer run was made, then on scrutinizing the data a compound was found in the training set which was not coded correctly. Each time this occurred it was found on rerunning the data that the change in one compound did not significantly alter the vector. Even when one compound in the training set was incorrectly identified as not in the class being treated, the error made little difference in the final vector. In a sense the pattern recognition technique is rather forgiving.

The notation 100+ in Table VII means that the program was halted at 100 iterations without converging. Failure to converge could be due to a failure to allow the program to go far enough or due to a lack of linear separability in the data.

With every class of compounds except alcohols we found that the concatenated data trains considerably faster than other types of spectra. It is not surprising that alcohols do not train as well with the concatenated
vector since these data do not include the very characteristic O-H stretch region in the infrared. We would expect similar results if amines or other N-H compounds were classified. Interestingly, however, the secondary alcohols are an exception to what might have been anticipated. The reason for this appears to be in the characteristic Raman of secondary alcohols, but further discussion will be deferred until the section on alcohols.

3. Program TEST

In pattern recognition the final criterion of success is the measure of how well the trained vector categorizes new patterns, i.e. patterns not used in the training. Program TEST reads trained vectors previously written on disk by program TRAIN and tests the appropriate set of spectra.

Tables VIII, IX, and X summarize the data obtained with TRAIN. The vector in each case reported in these tables was initiated at -1. In Table VIII the predictive ability of vectors trained with 50% of the available deck is reported. Tables IX and X show the predictive ability of vectors trained with 75% and 80% of the data, respectively. In every case the ratio of compounds in the class to compounds not in the class was maintained. For example, among the 400 compounds in the data there are 94 esters


TABLE VIII

Percentage of Compounds Correctly Classified

50% of Data Used in Training Set

<table>
<thead>
<tr>
<th>Type of Spectra</th>
<th>IR</th>
<th>All Raman</th>
<th>Paralled Polarized Raman</th>
<th>Perpendicular Polarized Raman</th>
<th>IR and Raman Averaged</th>
<th>IR and Raman Concatenated</th>
</tr>
</thead>
<tbody>
<tr>
<td>CLASS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ester</td>
<td>74</td>
<td>--</td>
<td>(86)</td>
<td>--</td>
<td>72</td>
<td>92</td>
</tr>
<tr>
<td>Alcohol</td>
<td>97</td>
<td>(82)</td>
<td>86</td>
<td>--</td>
<td>95</td>
<td>84</td>
</tr>
<tr>
<td>Ether</td>
<td>80</td>
<td>(68)</td>
<td>79</td>
<td>(70)</td>
<td>(69)</td>
<td>87</td>
</tr>
<tr>
<td>C = C</td>
<td>89</td>
<td>89</td>
<td>86</td>
<td>86</td>
<td>87</td>
<td>89</td>
</tr>
<tr>
<td>Ketones</td>
<td>89</td>
<td>91</td>
<td>89</td>
<td>85</td>
<td>89</td>
<td>91</td>
</tr>
</tbody>
</table>

-- indicates that the training set did not converge in 100 iterations.

( ) that larger training sets of the same type failed to converge.
TABLE IX

Percentage of Compounds Correctly Classified
75% of Data Used in Training Set

<table>
<thead>
<tr>
<th>Type of Spectra</th>
<th>IR</th>
<th>All Raman</th>
<th>Parallel Polarized Raman</th>
<th>Perpendicular Polarized Raman</th>
<th>IR and Raman Averaged</th>
<th>IR and Raman Concatenated</th>
</tr>
</thead>
<tbody>
<tr>
<td>CLASS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ester</td>
<td>82</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>83</td>
<td>95</td>
</tr>
<tr>
<td>Alcohols</td>
<td>98</td>
<td>--</td>
<td>72</td>
<td>--</td>
<td>96</td>
<td>87</td>
</tr>
<tr>
<td>Ethers</td>
<td>81</td>
<td>--</td>
<td>81</td>
<td>--</td>
<td>--</td>
<td>90</td>
</tr>
<tr>
<td>C = C</td>
<td>91</td>
<td>90</td>
<td>91</td>
<td>85</td>
<td>91</td>
<td>92</td>
</tr>
<tr>
<td>Ketones</td>
<td>97</td>
<td>93</td>
<td>89</td>
<td>85</td>
<td>94</td>
<td>97</td>
</tr>
</tbody>
</table>

-- indicates that the training set did not converge in 100 iterations.
### TABLE X

Percentage of Compounds Correctly Classified

80% of Data Used in Training Set

<table>
<thead>
<tr>
<th>Type of Spectra</th>
<th>IR</th>
<th>All Raman</th>
<th>Parallel Polarized Raman</th>
<th>Perpendicular Polarized Raman</th>
<th>IR and Raman Averaged</th>
<th>IR and Raman Concatenated</th>
</tr>
</thead>
<tbody>
<tr>
<td>CLASS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Esters</td>
<td>86</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>84</td>
<td>96</td>
</tr>
<tr>
<td>Alcohols</td>
<td>97</td>
<td>--</td>
<td>85</td>
<td>97</td>
<td>96</td>
<td>83</td>
</tr>
<tr>
<td>Ethers</td>
<td>84</td>
<td>--</td>
<td>81</td>
<td>--</td>
<td>--</td>
<td>93</td>
</tr>
<tr>
<td>C = C</td>
<td>90</td>
<td>91</td>
<td>90</td>
<td>87</td>
<td>93</td>
<td>97</td>
</tr>
<tr>
<td>Ketones</td>
<td>97</td>
<td>93</td>
<td>89</td>
<td>85</td>
<td>93</td>
<td>97</td>
</tr>
</tbody>
</table>

-- indicates that the training set did not converge in 100 iterations.
When IR spectra of esters were trained using 50% of the data deck, 47 esters and 153 compounds which were not esters were chosen as the training set. The data were not randomized before each run, and the first compounds in the deck were always included in the training set. Thus all the compounds included in the training set where 50% of the deck was used were also included in those sets where 75% and 80% of the deck was used.

In Table VIII the numbers in brackets signify that while the vector trained with 50% of the deck did converge, the particular experiment did not converge when a larger portion of the data was used. Where data are not presented, signified by a dashed line, the vector did not converge and no run of TEST was made.

With every class except alcohols the type of spectra which are concatenated IR and Raman data are at least as predictive as other types of data. The apparent exception of alcohols is no doubt due to the exclusion of the O-H stretching region in the concatenated data. Interestingly, with esters the Raman data alone did not converge, but the use of Raman data in the concatenated vector seems to significantly improve the predictive ability over what is achieved with IR data alone or Raman data alone. When IR and Raman are combined by simply averaging vectors, the
FIGURE 11
Predictive Ability of Concatenated Vectors
(Vectors Initiated at -1)

Legend:
- Ester
- Alcohol
- Ether
- Double bond
- Ketones

Percent Correctly Classified

Number of Compounds in Training Set
data suggests that the predictive ability is not as good as when the IR is used alone.

Figure 11 shows a plot of the percent correctly predicted versus the number of compounds used in the training set. All of the vectors referred to in Figure 11 were obtained from concatenated infrared and Raman data using -1 as the initial value of the starting vector. In general the data suggests that there is improvement in the predictive ability when more compounds are used in the training set and moving from 200 compounds in the training set to 320 compounds improves the predictive ability on the average by about 5%.

It seems that the initial values of the vector plays a relatively minor part in determining what the final vector will look like. In a series of tests using 50% of the deck we trained a number of classes of compounds by initiating the vector at +1, and -1. A third solution vector was then calculated by averaging the positively initiated vector and the negatively initiated vector. In each test in this series the type of spectra used were concatenated IR and Raman data. Table XI shows that the predictive ability of the vector obtained by averaging the two calculated vectors did not differ significantly from the predictive ability of the two calculated solutions, and in no case was the average solution poorer than either of the calculated solu-
tions. Remembering that the average of two solution vectors is itself a solution to the training set, and noting that the training set used for each class in Table XI was the same it is understandable that the solution arrived at by averaging is about as predictive as the others. In the two instances where the average solution appears to be more predictive than either calculated solution, we must, at this time, attribute that to scatter.

TABLE XI

Predictive Ability of Concatenated Vectors

50% of Data Used in Training Set

<table>
<thead>
<tr>
<th>CLASS</th>
<th>% Correctly Predicted</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Positively Initiated</td>
</tr>
<tr>
<td>Ester</td>
<td>97</td>
</tr>
<tr>
<td>Alcohols</td>
<td>93</td>
</tr>
<tr>
<td>Ethers</td>
<td>85</td>
</tr>
<tr>
<td>C = C</td>
<td>98</td>
</tr>
<tr>
<td>Ketones</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure 12 shows the Raman portion of vectors which were trained using concatenated data. In both cases the class treated was ketones, and the result of initiating the vector at +1 and at -1 is shown. Notice that the in-
FIGURE 12
TRAINED VECTORS OF KETONES
RAMAN PORTION OF CONCATENATED VECTOR

ALL ELEMENTS OF VECTOR INITIATED AT +1

ALL ELEMENTS OF VECTOR INITIATED AT -1
tensity scales in the two plots are different; this should be taken into account when making comparisons. In general, vectors which are trained with a particular class of compounds but using different starting values are remarkably similar. Usually there are only three or four bands which appear in one spectrum but not the other. In Figure 12 for example, the only major discrepancy between the two spectra is a band which appears at 500 cm$^{-1}$ in the vector initiated at $+1$. With the exception of some minor shifts and line broadening the spectra are about the same. There is no significant difference in the number of iterations to converge on a solution when the vector is initiated with either $+1$ or $-1$.

In view of the data presented we have concluded that the best way to combine infrared and Raman data is to concatenate the data from the two sources and treat the result as a single vector. The parallel polarized spectra or the nonpolarized spectra should be used to represent the Raman spectrum. Perpendicularly polarized data in general do not seem to be easily separated, but this may be due mainly to the quality of the starting spectra. They are frequently very low intensity spectra and manually coding them is difficult. The predictive ability of vectors trained with concatenated data seems to be superior to those trained with either infrared or Raman separately.
While averaging vectors which were initiated with different values does not significantly improve the predictive ability, it does seem to average out some of the scatter, without adversely affecting the predictive ability.

In the sections that follow emphasis will be placed on interpreting vectors which were obtained by averaging positively initiated and negatively initiated trained vectors. The trained vectors were obtained from concatenated data.
4. Esters

Figure 13 shows the average trained vector of esters. The vector was obtained by averaging two vectors, one trained by initiating all elements at +1, and a second trained by initiating all elements at -1. The intensity scale has been adjusted so that the strongest peak in either the infrared or the Raman is set at 10. All other
peaks in both spectra are scaled to the strongest peak.

The C=O stretch from 1800 to 1700 cm\(^{-1}\) appears in both the infrared and Raman and is perhaps the most well-known peak in the entire IR range. This band is generally expected to occur in the region from 1780 to 1600 cm\(^{-1}\), but we might note that carboxylic acid anhydrides, acid halides, acyl peroxides and ketones have fundamental modes between 1850 and 1750 cm\(^{-1}\), which might account for the relatively low cutoff of this band in the trained vector. Similarly the low end of the carbonyl stretching region is also the region where double bond stretching (1700 to 1500) occurs, and could easily account for the absence of strong bands in the region from 1700 to 1600 cm\(^{-1}\). C-O stretching and/or bending is reported from 1300 to 1000 and is generally seen in the IR but not in the Raman. Our vector has this characteristic.

The strongest peak in the vector is a narrow band

---


in the Raman at 825 cm\(^{-1}\) which does not seem to have a correspondingly strong band in the IR. Looking at the Simple Average and Muted Average representations of Esters (Appendix C) we see that there could well be a characteristic Raman ester band in the region from about 950 to 800 cm\(^{-1}\). The band seems greatly reduced in intensity in the Simple Average IR of esters and is totally absence in the Muted Average IR representation of esters. These data prompted us to look at the Raman spectra of all of the 94 esters in our data set. All except 5 of the compounds have a strong generally sharp Raman band in the region from about 950 to 800 cm\(^{-1}\). Table XII lists the exceptions and also shows the nearest band which might be assigned to the vibration.

**TABLE XII**

**Esters Without a Band in the Region from 950 to 800**

<table>
<thead>
<tr>
<th>Name of Compound</th>
<th>Nearest Assignable Band (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid, o-tolyl ester</td>
<td>1040 or 780</td>
</tr>
<tr>
<td>Resorcinol, diacetate</td>
<td>1000</td>
</tr>
<tr>
<td>Benzoylacetic acid, ethyl ester</td>
<td>1000</td>
</tr>
<tr>
<td>Cinnamic acid, ethyl ester</td>
<td>1000</td>
</tr>
<tr>
<td>Bromophenylacetic acid, methyl ester</td>
<td>1000 or 780</td>
</tr>
</tbody>
</table>
based on proximity, shape and intensity. It would appear that the proximity of the aromatic ring shifts the frequency to higher wave numbers, but further work would have to be done before an assignment could be made. For now we tentatively suggest that in general esters have a characteristic Raman band in the region from 950 to 800 cm\(^{-1}\), and that band is frequently weak or absent in the IR.

5. Ethers

The characteristic feature of the vibrational spectra of ethers is the broad strong asymmetric stretching band between 1000 and 1300 cm\(^{-1}\) in the infrared\(^{38}\), which is weak or absent in the Raman. In Figure 14 the trained vector of ethers shows that characteristic. The band at about 525 in the infrared or 575 in the Raman is interesting because it corresponds to a reported \(^{37,38}\) characteristic infrared vibration for ethers which is found in the region from 625 to 500 cm\(^{-1}\). In reviewing the 49 ethers included in the data we find only 4 which do not have a band in the IR and/or Raman in the region from 625 to 500 cm\(^{-1}\). Table XIII lists those four exceptions. The symmetry of the compounds

FIGURE 14
TRAINED VECTOR OF ETHERS
(AVERAGE OF TWO SOLUTIONS)

TABLE XIII

Ethers Without a 625 to 500 cm\(^{-1}\) Band

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isopentyl ether</td>
<td>C-C-C-C-O-C-C-C-C</td>
</tr>
<tr>
<td>Butyl ether</td>
<td>C-C-C-C-O-C-C-C-C</td>
</tr>
<tr>
<td>Isopropyl ether</td>
<td>C-O-C-C-C</td>
</tr>
<tr>
<td>Ethyl ether</td>
<td>C-O-C-C</td>
</tr>
</tbody>
</table>
might be responsible for the suppression of the band; and, indeed, we have found that the band is very weak with other totally symmetric ethers.

6. Ketones

There are only 15 ketones in the entire data set, and therefore any conclusions based on the trained vector must be made tentatively. Of course, this caveat applies to all of the trained vectors, but it applies a fortiori to such a small class. Some comments will be made on the appropriate size and composition of training sets in a following section.

Figure 15 shows the average of two trained vectors using ketones as the class of trained compounds. The $\text{C}=\text{O}$ stretch is clearly evident in both the IR and Raman at about 1700 cm$^{-1}$. The 15 ketones in our set are all aliphatic, we would therefore expect an IR band of medium intensity in the region from 1225 to 1075 cm$^{-1}$, but the trained vector does not show this band. The Simple Average (Appendix C) spectrum of ketones, however, does show the band. Undoubtedly, the reason for this is that the ethers have such a strong band in this area that they dominate.

In the training process, every time an ether fails to be correctly classified as not-a-ketone (none of the ketones in the set are also ethers), this band gets subtracted out. This points out the care that must be taken in interpretation of trained vectors. While the absence of a band in a particular region would suggest that the class of compounds being trained does not have a characteristic
band there, there are exceptions to this.

It is interesting to note that the strongest band in the Raman portion of the ketone vector is at 1250 cm⁻¹. This is precisely what we expect since the ether band in that region is usually not observable in the Raman spectrum.

We were prompted to train a vector using ketones in spite of the small number of compounds available, because of a desire to estimate the extent to which esters might be considered a combination of ketones and ethers. Figure 16 shows the trained vector of esters as was shown in Figure 13, but traced over the computer print is the outline of all those bands occurring in the trained vectors of ethers and ketones.

The carbonyl band in the ester at 1775 cm⁻¹ is shifted to higher wave numbers than is found in ketones, as expected. The band centered around 550 in the IR, which is characteristic of ethers, is absent in the IR of esters, but interestingly (and possibly fortuitously) the Raman of esters shows a band at 550. Many of the esters in the data have a distinct, sharp band around 500, but there are sufficient examples of esters without the band to leave in doubt the question of assignment.
The similarity between the vector of esters and the combination of ethers and ketones is remarkable, particularly in the infrared. Yet, there are apparent differences to permit the differentiation of an ester from a ketone or an ether. This tends to show the power of the pattern recognition technique.
7. **Double Bonds**

In the data set there are 38 compounds which have a double bond in their structure, excluding double bonds which are a part of a benzene ring. Figure 17 shows the trained vector which resulted from treating these compounds.
as a class. The vector is dominated by the band between 1700 and 1600 cm$^{-1}$ in the Raman, as might be expected. All 38 of the compounds included in this class have a strong band in the Raman between 1700 and 1600 cm$^{-1}$ and usually the Raman band is much stronger than the corresponding IR band. The infrared portion of the vector has a broad band between 1050 and 875 cm$^{-1}$ which probably corresponds to the bands generally assigned to vinyl substituted, trans substituted (not cis) or geminally substituted double bonds. All of the compounds in the data set which fit one of these categories, with one exception, have a strong IR band around 1000 cm$^{-1}$, and the corresponding Raman band is weak or absent. The exception to this is cinnamyl alcohol (O-C=O-C-OH) which has a very strong Raman band at 1000 cm$^{-1}$ with a corresponding IR band. Unfortunately the Sadtler index does not label the compound as cis or trans, which undoubtably means that it is a mixture.

8. Alcohols

Figure 18 shows the trained vector which resulted when all of the 45 alcohols were treated as a single class of compounds. The data were composed of 29 primary alcohols, 9 secondary alcohols, and 4 tertiary alcohols. Three compounds have both primary and secondary moieties.

In order to test the power of the pattern recognition
FIGURE 18
TRAINED VECTOR OF ALCOHOLS
(AVERAGE OF TWO SOLUTIONS)

Infrared technique, the primary alcohols and the secondary alcohols were tested as separate classes. When the primary class was treated those 3 compounds which have both primary and secondary groups were included as being primary alcohols. Similarly, when the secondary alcohols were trained the three compounds were treated as members of the class of
secondary alcohols. In both instances the program converged on a solution. Figure 19 shows the vectors which resulted from this treatment of alcohols.

Alcohols are characterized by the strong O-H band in the region from 3500 to 3100 cm$^{-1}$ in the IR$.^37,38,39$. This same band is absent in the Raman. Many other bands also exist in the fingerprint region of the spectrum, and it is these that are treated in this work.

In Figure 19 the band at 1725 cm$^{-1}$ in the IR portion of the secondary alcohol vector is the only band which clearly does not appear in the vector for all alcohols (Figure 18). In all likelihood this occurs because three of the secondary alcohols also contain carbonyl groups. Since the class was so small this should be considered an artifact of the data set.

Figure 19 suggests that secondary alcohols differ from primary alcohols in the Raman in that they do not have a band at 1500 cm$^{-1}$ as do the primary compounds. In reviewing the actual spectra it is difficult to justify such a statement, although some band shifting in that region is evidenced. In view of the small number of data we refrain from any conclusion.
FIGURE 19

TRAINED VECTORS OF PRIMARY AND SECONDARY ALCOHOLS

(EACH VECTOR IS AN AVERAGE OF TWO SOLUTIONS)

(VECTORs WERE TRAINED USING ONLY ALCOHOLS IN THE DATA SET.)
A band in the Raman around 500 cm\(^{-1}\) would appear to be characteristic of secondary alcohols and not primary, but again because of the small number of data we withhold further comment.

Pursuing the topic of primary vs secondary alcohols a little farther, we extracted from the data all compounds which were either primary, secondary or tertiary alcohols; but not combinations. In this manner we made a small data deck composed of alcohols only. We found that we could train vectors for either primary or secondary alcohols using IR data alone, using parallel polarized Raman alone, using perpendicularly polarized Raman alone or using linear combinations of these data. In every case the program converged in less than fifty iterations, offering a convincing demonstration of the power of the pattern recognition technique.
SPECTRAL INTERPRETATION

1. Method Used

In this section we have attempted to carry the results of the pattern recognition techniques as far as seems practical, i.e. we attempt to use the trained vectors as supportive evidence for the assignment of vibrational frequencies. The original assignments were made using more traditional types of evidence.

*Ab initio* frequency assignments using pattern recognition data alone are well outside the power of the technique at this stage, and it seems likely that such assignments will remain outside the scope of pattern recognition for some time to come. In view of the success that the method enjoys when classifying compounds not used in the training set, however, it seems appropriate to use trained vectors to support frequency assignments. *This is so particularly in view of the fact that spectroscopists frequently use the "reasonableness" of an assignment as supportive evidence, sighting similar assignments made for other molecules.*

In an earlier section when presenting the data on predictive ability, we showed an advantage to using concatenated IR and Raman data. When averaging positively initiated and negatively initiated trained vectors, however, there does not seem to be an increase in the predictive ability
(nor any decrease). The average vector, nevertheless, did give a single representation which could be used to look for characteristic group frequencies. In looking for support for frequency assignments, however, we choose to have the broadest representation we can. To this end we have combined positively and negatively initiated trained vectors which resulted for concatenated data by superimposing the two vectors on the same frequency scale. The two superimposed vectors were traced in such a way that the strongest intensity in either of the two vectors appeared on the trace. Thus when one intensity at a particular frequency is stronger than the other, the strongest appears on the trace; and when one vector shows a positive intensity and the other does not, the positive intensity is traced. We have referred to this type of trace as a "broad representation".

The effect of this type of treatment is to broaden slightly the frequency bands associated with each chemical group and to emphasize strong bands. For this reason the broad representations which follow are presented without frequency scales.

Figures 20 and 21 show the broad representation of the infrared of ethers and the broad representation of the Raman of ethers respectively. Similarly, Figures 22 and 23 show the broad representation of the IR of compounds containing C=C and the broad representation of the Raman
FIGURE 20

Broad Representation of Ethers

INFRARED

FIGURE 21

Broad Representation of Ethers

RAMAN
FIGURE 22

Broad Representation of Double Bonds

INFRARED
FIGURE 23

Broad Representation of Double Bonds

RAMAN
of compounds containing C=C. These representations were used to provide the supportive evidence for the frequency assignments made in the literature for 3 compounds, and to provide suggested assignments where possible. In each case, when an assignment was made in the literature the appropriate broad representations were checked to determine if the observed frequency appeared in one of the representations. If it did the frequency was labeled "supportable". If it did not appear in the proper broad representation, the observed frequency was labeled "no supporting evidence". When an observed frequency was not assigned, all four broad representations were scrutinized and a suggested assignment was made only if there was no conflicting evidence.

2. cis-1,2-dimethoxyethylene

Kimmel, Waldron and Snyder\(^{(40)}\) recently published a vibrational analysis of cis- and trans-1,2-dimethoxyethylenes. The observed frequencies for the cis molecule, the assignments made and the available evidence from pattern recognition are included in Table XIV. The IR data were taken from the reported data on liquids since most of the IR data in the Sadtler Spectra were taken from liquids.

TABLE XIV

Interpretation of cis-1,1-Dimethoxyethylene

<table>
<thead>
<tr>
<th>Observed Frequency (cm$^{-1}$)</th>
<th>Assignment</th>
<th>Evidence from Pattern Recognition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IR</td>
<td>Raman</td>
</tr>
<tr>
<td>1843 vw</td>
<td>----</td>
<td>G=C str.</td>
</tr>
<tr>
<td>1700 m</td>
<td>1720 ..s</td>
<td>G=C str.</td>
</tr>
<tr>
<td>1675 m</td>
<td>1690 vs</td>
<td>----</td>
</tr>
<tr>
<td>1562 w</td>
<td>----</td>
<td>CH$_3$ asym. def.,</td>
</tr>
<tr>
<td>1460 s</td>
<td>1470 w</td>
<td>CH$_3$ sym. def.,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>=$\text{C}^2\text{H}$ i.p. rock</td>
</tr>
<tr>
<td>1377 vs</td>
<td>----</td>
<td>o-CH$_3$ rock</td>
</tr>
<tr>
<td>1305 sh</td>
<td>1300 m</td>
<td></td>
</tr>
<tr>
<td>1292 m</td>
<td>----</td>
<td>o-CH$_3$ rock</td>
</tr>
<tr>
<td>1220 vs</td>
<td>1220 vw</td>
<td></td>
</tr>
<tr>
<td>1188 sh</td>
<td>1195 vs</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1165 vw</td>
</tr>
<tr>
<td>1155 vs</td>
<td>1120 vw</td>
<td>C-O-C asym. str.</td>
</tr>
<tr>
<td>1028 m</td>
<td>1030 vw</td>
<td></td>
</tr>
<tr>
<td>978 w</td>
<td>985 vw</td>
<td>C-O-C sym. str.</td>
</tr>
<tr>
<td>911 m</td>
<td>----</td>
<td>H-C=C-H twist</td>
</tr>
<tr>
<td>878 w</td>
<td>885 w</td>
<td>C-O-C sym. str.</td>
</tr>
<tr>
<td></td>
<td>860 w</td>
<td></td>
</tr>
<tr>
<td></td>
<td>790 vw</td>
<td></td>
</tr>
<tr>
<td></td>
<td>745 w</td>
<td>=$\text{C-H 0.0.P. wag}$</td>
</tr>
<tr>
<td>725 m</td>
<td>----</td>
<td>=$\text{C-H 0.0.P. wag}$</td>
</tr>
<tr>
<td>615 s</td>
<td>----</td>
<td>C-O-C i.p. bend</td>
</tr>
<tr>
<td></td>
<td>545 w</td>
<td>O.0.P skel. def.</td>
</tr>
</tbody>
</table>
Several frequency assignments have been made to carbon-hydrogen type vibrations or skeletal type deformations. Since we have no corresponding pattern recognition data to either support or contradict this type of assignment we have simply used the term "not apply" in the column: Evidence from Pattern Recognition.

There are two bands in cis dimethoxyethylene (Table XIV) which have been assigned by the authors for which there is no supporting evidence.

The frequencies around 1700 and 1675 cm\(^{-1}\) (IR data) are stronger in the Raman than in the IR, and this is in agreement with what is observed in the broad representations of the IR and Raman of compounds with double bonds. The 1120 Raman band is not seen in the Raman representation of ethers, but we expect this since it was observed as a very weak band. The 978 IR band is observed as a weak band and is weak in the IR representation of ethers, while the corresponding 985 Raman band is very weak in the observed spectrum and missing in the broad representation of ethers. The 885 Raman band is seen in the appropriate Raman representation, but the corresponding weak 878 band is not in the IR representation. Both the 725 and 615 IR bands are in the correct representations, but they are weaker in the representations than would be expected based on their observed intensities.
around 1125 cm\(^{-1}\) the IR in that region has a strong band. Thus we might have expected to have observed a corresponding IR band in the spectrum.

Conversely, the assigning of the 635 Raman band to an ether type vibration seems appropriate since the Raman of the broad representation of ethers has a weak band in that region and the representation of the C=C in the Raman has no band there. Additionally, the IR representation of ethers shows only a very weak band at 625 (compared to the corresponding Raman); so it is not unexpected that no 625 IR band was observed in the spectrum.

3. Divinyl Ether

Table XVII shows how the evidence from the broad representations of ethers and double bonds applies to divinyl ether. The spectral data were taken from Clague and Danti\(^{41}\) and solution IR data were used rather than the vapor data. Unfortunately no data from neat samples were reported in the IR.

No suggested assignment was made for the 1220 band, because both C=C and ethers vibrate in this region. It should be noted, however, that it is characteristic of ethers and not C=C to be strong in the IR and weak in the Raman near 1220 cm⁻¹. Similarly, the 1030-1028 band is in a region where double bonds are characterized by strong IR and weak Raman bands as observed; yet the interpretation is not clear due to overlapping ether bands. The very weak 790 Raman band corresponds to a band in the Raman of ethers and double bonds do not have a Raman band here, but the broad representation suggests that a strong band should appear. Since the observed band was very weak, no suggested assignment was made.

Table XV defines the abbreviations used in those Tables which describe frequency assignments.

4. trans-1,2-dimethoxyethylene

The data for trans-dimethoxyethylene were taken from the same source as the cis data⁴⁰ and are presented in Table XVI. Again the IR data used were the liquid data.

The evidence from pattern recognition pertaining to the trans molecule is similar to that pertaining to the cis-dimethoxyethylene. Again there are two assignments made by the authors for which there is no supporting
### TABLE XV

Abbreviations Used in Describing Frequency Assignments

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>vvw</td>
<td>very, very weak</td>
</tr>
<tr>
<td>vw</td>
<td>very weak</td>
</tr>
<tr>
<td>m</td>
<td>medium</td>
</tr>
<tr>
<td>s</td>
<td>strong</td>
</tr>
<tr>
<td>vs</td>
<td>very strong</td>
</tr>
<tr>
<td>sh</td>
<td>shoulder</td>
</tr>
<tr>
<td>str.</td>
<td>stretch</td>
</tr>
<tr>
<td>asym.</td>
<td>asymmetric</td>
</tr>
<tr>
<td>sym.</td>
<td>symmetric</td>
</tr>
<tr>
<td>def.</td>
<td>deformation</td>
</tr>
<tr>
<td>i.p.</td>
<td>inplane</td>
</tr>
<tr>
<td>o.o.p.</td>
<td>out of plane</td>
</tr>
</tbody>
</table>
TABLE XVI

Interpretation of trans-1,2-Dimethoxyethylene

<table>
<thead>
<tr>
<th>Observed (cm⁻¹)</th>
<th>Frequency</th>
<th>Assignment</th>
<th>Evidence from Pattern Recognition</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR</td>
<td>Raman</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1737 w</td>
<td>1688 m</td>
<td>C=C str.</td>
<td>C=C band, not ether</td>
</tr>
<tr>
<td>1670 m</td>
<td>1675 s</td>
<td>C=C str.</td>
<td>supportable</td>
</tr>
<tr>
<td>1467 m</td>
<td>1460 w</td>
<td>CH₃ asym. def.</td>
<td>supportable</td>
</tr>
<tr>
<td>1455 m</td>
<td></td>
<td>CH₃ sym. def.</td>
<td>not apply</td>
</tr>
<tr>
<td>1333 w</td>
<td>1330 w</td>
<td></td>
<td>ether band, not C=C</td>
</tr>
<tr>
<td>1310 m</td>
<td>1310 m</td>
<td>=C-H i.p. rock</td>
<td>supportable</td>
</tr>
<tr>
<td>1292 m</td>
<td></td>
<td>=C-H i.p. rock</td>
<td>no supporting evidence</td>
</tr>
<tr>
<td>1218 vs</td>
<td>1215 vw</td>
<td>C-O-C asym. str.</td>
<td>supportable</td>
</tr>
<tr>
<td>1182 m</td>
<td></td>
<td>O-CH₃ rock</td>
<td>no supporting evidence</td>
</tr>
<tr>
<td>1172 vs</td>
<td>1170 vw</td>
<td>C-O-C asym. str.</td>
<td>supportable</td>
</tr>
<tr>
<td>1135 vs</td>
<td>1155 vw</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1125 vw</td>
<td>1025 vw</td>
<td></td>
<td></td>
</tr>
<tr>
<td>995 m</td>
<td>995 w</td>
<td>C-O-C sym. str.</td>
<td>supportable</td>
</tr>
<tr>
<td>957 s</td>
<td></td>
<td>=C-H o.o.p. wag</td>
<td>supportable</td>
</tr>
<tr>
<td>945 m</td>
<td>945 w</td>
<td>=C-H o.o.p. wag</td>
<td>supportable</td>
</tr>
<tr>
<td>910 w</td>
<td></td>
<td>C-O-C sym. str.</td>
<td>supportable</td>
</tr>
<tr>
<td>900 s</td>
<td></td>
<td>H-C=C-H twist</td>
<td></td>
</tr>
<tr>
<td>785 w</td>
<td>785 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>735 vw</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>605 w</td>
<td>605 w</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

46
evidence from pattern recognition. This, of course, does not indicate that the assignments are wrong; and indeed, we do not think they are wrong. It simply indicates that we can not look to pattern recognition (as we have developed the data thus far) for support in making these assignments.

The 995 band is not seen in the Raman of the broad representation of double bonds, but this is in fairly good agreement with the observation that it is a medium strength band in the IR but weak in the Raman. The 945 Raman band is also not seen in the Raman representation, but it too is weak while its IR band has a medium intensity.

The weak 1737 band in the IR could be assigned to a C=C type vibration but not to an ether type vibration. We note, however, that in the broad representation of C=C in the IR, the band is not weak in the 1737 region. Similarly the 1333 (IR) band is seen in both the IR and Raman of the ether representations, but not in the IR or Raman of the double bond representations. The band strengths, however, do not correspond to the observed weak bands.

A band at 1125 is seen in the Raman representation of double bonds, and is not seen in the Raman representation of ethers. We refrained from suggesting an assignment, however, because the observed frequency is very weak, and because, although the representation in the Raman is weak we would have expected a strong corresponding IR band.
### TABLE XVII

**Interpretation of Divinyl Ether**

<table>
<thead>
<tr>
<th>Observed Frequency (cm⁻¹)</th>
<th>Assignment</th>
<th>Evidence from Pattern Recognition</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>IR</strong></td>
<td><strong>Raman</strong></td>
<td></td>
</tr>
<tr>
<td>1672 vw</td>
<td>1670 s</td>
<td>C=O str.</td>
</tr>
<tr>
<td>1641 s</td>
<td>1643 vs</td>
<td>supportable</td>
</tr>
<tr>
<td>1623 sh</td>
<td></td>
<td>C=O str.</td>
</tr>
<tr>
<td>1619 vs</td>
<td>1627 s</td>
<td>supportable</td>
</tr>
<tr>
<td>1546 vw</td>
<td>1545 VW</td>
<td></td>
</tr>
<tr>
<td>1445 w</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1392vw</td>
<td>1400 vw</td>
<td>CH₂ sym. def.</td>
</tr>
<tr>
<td>1378 m</td>
<td>1383 m</td>
<td>supportable</td>
</tr>
<tr>
<td>1330 m</td>
<td>1323 vs</td>
<td>C-H i.p. rock</td>
</tr>
<tr>
<td>1300 m</td>
<td>1299 vs</td>
<td>supportable</td>
</tr>
<tr>
<td>1260 vs</td>
<td>1205 m</td>
<td>C-O-C asym. str.</td>
</tr>
<tr>
<td>1169 vs</td>
<td>1186 m</td>
<td>supportable</td>
</tr>
<tr>
<td>1111 m</td>
<td>1116 w</td>
<td>CH₂ rock</td>
</tr>
<tr>
<td>1012 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>990 m</td>
<td>993 w</td>
<td>C-O-C sym. str.</td>
</tr>
<tr>
<td>961vw</td>
<td>985 vw</td>
<td>supportable</td>
</tr>
<tr>
<td>944 m</td>
<td>953 m</td>
<td></td>
</tr>
<tr>
<td>938 w</td>
<td>940 w</td>
<td></td>
</tr>
<tr>
<td>848 s</td>
<td>850 s</td>
<td>H₂C= torsion</td>
</tr>
<tr>
<td>838 sh</td>
<td></td>
<td>supportable</td>
</tr>
<tr>
<td>713sh</td>
<td></td>
<td></td>
</tr>
<tr>
<td>688 m</td>
<td>709 m</td>
<td>vinyl wag o.o.p.</td>
</tr>
<tr>
<td>582 vw</td>
<td>585 w</td>
<td>supportable</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C=O-C def.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>not apply</td>
</tr>
<tr>
<td><strong>---</strong></td>
<td><strong>---</strong></td>
<td></td>
</tr>
</tbody>
</table>
Two of the bands in the divinyl ether spectrum have been assigned to C=C=O deformations (585 and 510 in the Raman). Since they cannot be classed as ether or double bond type assignments, they simply have been labeled "not apply" in Table XVII. The assignment for the weak shoulder in the IR at 713 is the only assigned band for which we do not have some supporting evidence.

In the original paper the 1445 and 1546 IR bands were not labeled with a description of intensity. We assumed the intensities reported for the vapor data.

The 1330 band in the IR is not seen in the representation of double bonds, but judging from the Raman the band might be centered a little lower. Between 1300 and 1325 our representations do show an IR band and a corresponding much stronger Raman band. For both the 1200 and 1168 (IR) bands we see an IR band in the broad representation but we do not see a corresponding Raman. While this is not entirely in agreement with the spectral observation for this assignment, at least the relative intensities (IR stronger than Raman) are in the proper direction.

The only truly weak point in the support that pattern recognition data has to offer with regard to these assignments concerns the assignment of the 990 (IR) to the C-O-C symmetrical mode. We see a small Raman band in this region, but no IR band at all in the pattern recognition
data. Assigning this mode to the 1012 vibration would be in better agreement with our patterns. The author rejects this based on band shape considerations, but the point must still be considered unresolved.

5. **Broad Representation of Esters**

There are 45 alcohols in the data but alcohols as a class represent too broad a group to be useful in spectral assignments. If only primary alcohols are considered we are reduced to a class with only 29 members. This may be too few to be useful. We do have 92 esters, however, and the broad representations of esters may be of considerable use. Figure 24 shows these representations.

Considering only the infrared portion of Figure 24 we have recast the data presented to construct a table of characteristic frequencies for the ester moiety (Table XVIII). One might test the validity of such a table by examining the spectra of many molecules to determine how often the expected frequencies appear in molecules containing esters. More rigorously, however, it is desirable to compare the newly constructed table with frequency assignments which have been confirmed by normal coordinate analysis. Unfor-
FIGURE 24

Broad Representation of Esters
tunately, molecules containing C=0 groups\textsuperscript{42, 43, 44, 45} appear to present difficulties in all except the simplest cases. Matzke, Chacon and Andrade\textsuperscript{46}, however, completed the normal coordinate analysis of methyl formate, methyl acetate and dimethyl oxalate; and all of their assignments can be supported using either the IR or the Raman data from Figure 24. In Table XVIII the IR approximate descriptions which have been shown are taken from Matzke et al. For the 3 molecules considered, there are only 5 frequencies which do not correspond to a frequency range in Table XVIII. All 5, however, correspond to Raman frequencies (Figure 24) which are apparently characteristic of esters.


TABLE XVIII
Infrared Group Frequencies for Esters

<table>
<thead>
<tr>
<th>Range</th>
<th>Approximate Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1850 - 1725</td>
<td>C=O stretch ( a,b,c )</td>
</tr>
<tr>
<td>1700 - 1650</td>
<td></td>
</tr>
<tr>
<td>1625 - 1575</td>
<td></td>
</tr>
<tr>
<td>1550 - 1525</td>
<td></td>
</tr>
<tr>
<td>1450 - 1420</td>
<td>C=O stretch ( a,b,c )</td>
</tr>
<tr>
<td>1400 - 1375</td>
<td></td>
</tr>
<tr>
<td>1350 - 1175</td>
<td>O-R stretch ( a,b,c )</td>
</tr>
<tr>
<td>1150 - 1050</td>
<td></td>
</tr>
<tr>
<td>1025 - 975</td>
<td></td>
</tr>
<tr>
<td>875 - 800</td>
<td>O-R stretch, O-C=O bend, ( b,c )</td>
</tr>
<tr>
<td>750 - 725</td>
<td></td>
</tr>
<tr>
<td>700 - 675</td>
<td></td>
</tr>
<tr>
<td>550 - 500</td>
<td></td>
</tr>
</tbody>
</table>

\( a = \text{methyl formate} \)
\( b = \text{methyl acetate} \)
\( c = \text{dimethyl oxylate} \)

Critically reviewing Table XVIII, we see that if we were to join bands separated by only 25 cm\(^{-1}\) (the limit of the resolution used in coding the data) we could distinguish 5 band areas as shown by the dashed lines in the table. These may be considered areas where IR bands for esters, i.e. characteristic group frequencies, are likely to be found.
HEURISTICS

1. **Purpose**

The purpose of this section is to include in the work certain observations and impressions which are peripheral to the main theme; but which, nevertheless, might be useful to future workers in this area. In the course of this investigation over a hundred computer experiments were run which did not contribute directly to the body of data already presented, but rather directed us to abandon certain paths and follow others. What follows draws on that experience without attempting to document and quantify each observation. Indeed, many of the observations are not able to be proven; hence the title of the section, Heuristics.

2. **Starting Vector**

We made several computer runs in which we attempted to use the Muted Average representation of a class (both the positive and negative portion) as the starting vector. In general the program does converge slightly faster when the vector is initiated in this way, but the savings was only about 5 iterations. In a few instances it actually took more iterations to converge than when initiated at -1. In none of the 7 cases tried were we able to get a set of Raman data to converge within 100 iterations starting with the appropriate Muted Average, if that same set would not
converge starting with a vector initiated at -1.

One of the options in the program permits us to train a vector using every "n th" element in the data bank. This vector is then used as the starting vector and the entire data set (using every element) is trained. With the infrared spectra of esters as the class to be trained, we tried to train a vector using every 10th element. The vector would not train within 100 iterations. Nevertheless, the program takes the vector "as is" at 100 iterations and uses it as the initial vector to train the entire set. When it did this it trained the entire set of esters in 62 iterations. When this set of data is trained using a vector initialized at -1, it takes only 40 iterations to converge. Similar results were obtained when we tried every 5th element. We abandoned the idea without trying other cases.

Using the trained infrared vector as the starting vector for training the same class of compounds with Raman data did not improve the rate of convergence. Nor did it permit us to train Raman sets which would not converge when initiated at -1.

3. Weighting Factor

In the training process the vector being trained is corrected by adding or subtracting a weighted pattern which failed to be correctly classified. The program has an
option which permits the weight factor to be adjusted by a multiplier which is read into the program at the beginning of each run. (See Figure VI.) Jurs, Kowalski, Isenhour and Reilley, using data from mass spectrometry, reported that multipliers ranging from 1 to 3 seemed to minimize the number of iterations necessary to reach convergence. We did not repeat their work with our data, but simply used the value 2 throughout the reported runs. We did verify, however, that changing the multiplier does not alter the appearance of the final vector any more than does changing the initial value of the starting vector.

4. Transforms

Two additional data sets were formed by taking the log (base 10) and the anti-log (base 10) of the original data. All of the runs which were done on the original data set were repeated on the two transformed sets in an effort to get certain cases to converge (within 100 iterations). We used the reciprocal transform on the resulting vector and plotted the result in the usual way. With the class of ethers and using perpendicular polarized Raman data we could train a vector using the log set. These data would not train using the untransformed data. In every other case, however, data which would not train without transformation remained untrainable.
In those cases where data sets were trainable without transforms, they remained trainable using either transformed data set. The resulting vectors were substantially different from what resulted from untransformed data, however. We did not attempt to interpret these vectors and did not pursue this, because we found that in every class concatenated data converge very quickly without the need of transforms. There remains here an opportunity for further work.

5. Size of Data Set

A number of workers have suggested that data sets should be over determined by a factor of 10, i.e. there should be 10 times as many patterns in a training set as elements in a pattern. This is rarely done with chemical data, however, because of the scarcity of coded data. Liddell and Jurs, for example use as few as 22 patterns in a set with 131 elements, and report that the resulting vector is 90% predictive with patterns not in their training set.

Our experience suggests that the data should be over determined by at least a factor of one. In developing the reported vectors using concatenated data we were always over determined by a factor of 3.5 (400 patterns, 112 elements per pattern). In other trials we found that predictive ability deteriorates as the data set gets smaller (see Figure 11) and falls below 90% predictive when the data is over deter-
mined by a factor of only 1.75.

Ideally, the number of compounds in the class and the number not in the class being treated should both be over determined. In no case did we have enough compounds to do this and still use full spectra. Nagy suggests that the percentage of patterns in the training set which are members of the class being trained should be the same as the ratio in the real world, i.e. should reflect the universal population. Using spectral data such an approach seems impractical, however, since we have no way of estimating such a number nor attaching significance to its meaning.

We found that when the number of compounds in the class was extremely low compared to the number in the training set, the set would always train. Even when we had a set composed of two class members and 398 compounds not in the class, a vector could be trained. Such vectors are useless, however. Our experience suggests that at least 5% of the total set should be members of the class being trained.

6. Errors

In any situation where over 125,000 data points are observed and recorded manually there are bound to be errors. Every effort was made, however, to minimize the errors. All of the data keypunching was verified, for example. In order
to estimate the magnitude of the errors we recoded 200 spectra. The second coding was not done by the person who first coded the spectrum. In comparing the two codes of the same spectrum we considered a pair in error if they did not match in every element within 3. Using this criteria we found 6 errors in the original 200 spectra (and another 4 errors in the second coding of the 200). Thus we would estimate that in the 1117 coded spectra our error level is about 3%.

After making the original estimate of error level, we continued for some time to comb the data. The training program prints a list of the compounds used and the number of times each failed to be correctly classified during the training process. In the early runs we made it a practice to review the coding of the 10 compounds which failed most often. When errors were found they were corrected. We did not return to make a second estimate of the error level, however. When the final runs were made for inclusion in this work, they were all made using the same data set. No changes were permitted once it was decided to develop the results presented.
SUMMARY AND CONCLUSIONS

We have taken a segment of the Infrared and Raman data which are currently available and manually reduced each spectrum to a digital code. We then explored these data using pattern recognition techniques. We found that the most effective way of treating the data was to consider the infrared code and the Raman code of a compound as a single concatenated vector. In order to save computer space we used the spectral range from 500 to 1900 cm$^{-1}$ only, thus covering the most complicated portion of the vibrational spectrum.

The vectors which result from the training process can be used to categorize compounds not used in the training and they will correctly categorize approximately 93 percent of the time. This is superior to what can be achieved using either infrared or Raman alone, even though we did not use the full vibrational spectrum as we did when using IR or Raman alone.

The positive portion of the trained vector provides new insight into the characteristic frequencies of chemical groups. In every instance tried, all of the normally reported IR group frequencies appear as positive bands in the trained vector of the group. Other bands suggest the presence of characteristic group frequencies not previously
assigned. A band from 950 to 800 cm\(^{-1}\) in the Raman, for instance, seems to be characteristic of esters. Usually the corresponding IR band is weak or absent.

It is well known that ethers have a characteristic broad band around 1250 cm\(^{-1}\) in the IR which is greatly reduced or absent in the Raman. Our data suggests (based on the 15 ketones available) the ketones have a Raman band in that region, although it is not a strong band.

The IR band around 1050 to 875 cm\(^{-1}\) is usually assigned to double bonds (vinyl, trans or geminal), but the band is not easily picked out in a crowded spectrum. The knowledge that the band is generally weak or absent in the Raman is most helpful.

Three spectra not present in the coded data were selected from the literature, because they have been partially interpreted, and contain two groups for which we have trained vectors. It was shown that with nearly every assignment supportive evidence for the assignment could be found in the trained vectors. What is perhaps a greater contribution, however, is that using the trained vectors we were able, in a few instances, to suggest which group might be responsible for certain observed frequencies. Thus advancing the problem of making band assignments.
In short, what we have done here is to explore an orderly, computerized approach to the interpretation of IR and Raman. In a few years Raman spectroscopy will be as common as infrared, and much can be learned from this approach to those data. What is needed is a method for digitizing the spectra so that the data being explored is error free. What we hope we have contributed, is that we have made a beginning.
THE DATA

The digital codes of spectra are shown in the following pages. Each code uses the following format:

\[(I3, I2, 1x, 58I2/4x, 54I2)\]

The first integer \((I3)\) is the compound number, and corresponds to the compound number in the Sadtler Index. The second integer \((I2)\) is the spectrum type: 1 = IR, 2 = Raman parallel polarized, 3 = Raman perpendicularly polarized, 4 = Raman nonpolarized. The 112 readings from each spectrum are in I2 format.
The following 400 lines of data show the chemical classes to which each of the 400 compounds used belongs. Each line corresponds to a compound, and every 10th line has been numbered to facilitate reading.

The data are written in the format: (4i2). No compound belongs to more than 4 classes. The classes are described in the body of the text. (See Table 1)

In this listing class 15 includes all compounds with a carbonyl group. Compounds 160 through 174 inclusive are the ketones.
APPENDIX B
PROGRAM TRAIN
plus
SAMPLE OF INPUT AND OUTPUT
LEVEL 21.7 (JAN 73)  OS/360 FORTRAN H

COMPILED OPTIONS - NAME= MAIN,OPT=02,LIST=NO,SIZE=000K,
SOURCE=PROC,NOLIST=OCC,ECK=LOAD,NOEDIT=O,NOXFF

ISN 0007 COMMON FX(400),JC(113),TT(400),W(113),NRF(400), Terr(400)

DIMENSION FC(400),CN(400),SC(400),NECOM(400)

C PERFORMING THE MATRICES IS DONE HERE

DO 2 i=1,400
TT(i) = 0
FC(I+113) = 1
FX(I+114) = 0
DD(I,J) = 0
FX(I+1) = 0
W(I+13) = 0

L COUNTS THE # OF TIMES THE DATA SET IS TREATED (PASS).
NOC IS THE NUMBER OF THE DATA CARD (SHCFFRNUM) BEING WORKED ON
NCARD IS THE TOTAL NUMBER OF CARDS (SPECTRAL),
NSHUT LIMITS THE NUMBER OF PASSES ON THE DATA,
N equals the number of terms in the vector being trained,
I.E. IT IS THE DIMENSIONALITY OF THE SPACE WE ARE WORKING IN.

ISN 0013 N=113
ISN 0014 NTP=1

SUBROUTINE REDP READS THE OPTIONS DESIRED AND
SUBROUTINE PFI READS THE MAIN DATA DECK ACCORDING
C TO THE SPECIFIED OPTIONS. THE MAIN DATA DECK IS STORED
C ON THE DISK IN BINARY FORM, THE OPTIONS AVAILABLE
C ARE EXPLAINED IN THE SUBROUTINE REDP.

CALL RECP(NOPT),NCARD,NOPT2,PFI,NSHUT,LEN,NOPT3,NOPT4,NOPT5,
THE SUM OF SQUARES FOR EACH COMPOUND IN THE TRAINING SET IS CALCULATED

THE FOLLOWING SECTION INITIALIZES THE VECTOR(W) WHICH IS TO
BE TRAINED. EITHER THE INITIAL VECTOR IS READ FROM A DISK
FILE (FIN=*,0) OR IT IS INITIALIZED AS FIN.*

FXOR IS THE CONSTANT USED TO MULTIPLY THE CORRECTION FACTOR.
THIS SECTION CONTAINS THE MAIN TRAINING ROUTINE.

K IS THE ERROR CHECK TO SEE IF THE VECTOR W IS TRAINED. IF K IS C NO ERROR YET FOUND IN THE LTH READ OF THE DATA.

IF(NCONT-NDC) 49,40,32
IF(IFIT(NDC) = 5,0 ) 34,33,33
S=0
DO 35 1=1,NT
40
C=CM(FX(NDC+1))
S=S+ (WN) *FX(NDC+1))
IF (T(NDC)) 36,36,37
IF(S) 33,33,38
IF(S) 36,36,37
K = K+1
NDC=NDC+1
IFCOM(NDC) = NDC+1
TERM(K) = T(NDC)
C = (-1.0*K)/(FX(NDC))
CC=FX(NDC)
S1(K) = S
C1(K) = C
ON 39 1=1,NOPT6
W(1) = W(1) + (CC*FX(NDC+1))
W(N) = W(N) + (C * FX(NDC+1))
GO TO 33
IF(K) 100,100,41
FK = K
IFIFJON=LEN150,51,51

THE VALUE IF LEN DETERMINES HOW OFTEN THE UNTRAINED VECTOR WILL BE PRINTED. C.E.G. IF LEN = 10, THE UNTRAINED VECTOR WILL IF PRINTED EVERY 10TH ITERATION.

L=LEN1
LJNN,LJNN1
GO TO 30
LJNN1
FNDC = N*0
FPRE = (FXVFNDC)*100.0
WRITE(NDC,002)X,N,NO,FPRE
FORMAT(HL)"AFTER *15*
OUTS ARE *15, SPECTRA +-9.2* PERCENT ERRORS")
WRITE(NDC,4409)
FORMAT(H)"COMPOUND SIGN VALUE OF S VALUE OF C")
I+K
WRITE(NDC,4409)
THE FOLLOWING IS THE WRITE ROUTINE:

```fortran
WRITE(N06,909) L
FORMAT(H1, 'THE DATA HAVE BEEN READ', I6, ' TIMES')
WRITE(N06,907)
FORMAT(H1, 'THE FOLLOWING IS THE TRAINED VECTOR')
WRITE(N06,997) (W(I), I=1,N)
WRITE(N06,10F4.5) /11(I*10F4.5/11)/
GO TO 300
```

THE FOLLOWING SECTION IS ENTERED ONLY IF THE MAXIMUM NUMBER OF ALLOWED ITERATIONS (NSHUT) IS REACHED.

```fortran
WRITE(N06,699)NSHUT
L=I-1.
FORMAT(H1, 'ITERATION=', I6, ' OF=', I6)
WRITE(N06,4499)
DO 201 I=1,K
WRITE(N06,997) (W(I), I=1,N)
FORMAT(H1, 'THE FOLLOWING IS THE LAST VECTOR')
WRITE(N06,10F4.5) /11(I*10F4.5/11)/
WRITE(N06,10993)
WRITE(N06,10998)
FORMAT(H1, 'PROGRAM Halted', I6, ' PASSES MADE')
```

```fortran
GO TO 300
```
STATISTICS CONCERNING THE NUMBER OF COMPOUNDS USED AND THE PERCENT IN THE CLASS ARE CALCULATED AND PRINTED.

THE VECTOR IS PLOTTED.
ISN 0134  352  FORMAT (F5.1,F4.1,I3,I3))
ISN 0137  CALL UNPACK
ISN 0138  IF(NOPT6 .GE. 1) GO TO 500
ISN 0139  NTZ = NOTPA = 1
ISN 0141  DO 470 IM = 1, NTZ
ISN 0142  IF(II .GE. NT) GO TO 400
ISN 0143  II = I + J
ISN 0144  IF(I .GE. NT) GO TO 400
ISN 0146  W(II) = W(I)
ISN 0147  400  CONTINUE
ISN 0148  NOTPA = 1
ISN 0149  L=1
ISN 0150  GO TO 30
ISN 0151  500  CONTINUE
C  C  C  C  C  C  C  C  C  C  C  C
C  THE OPTIONS WHICH WERE USED DURING THE RUN ARE LISTED
C  C  C  C

ISN 0152  WRITE(*6,8099)
ISN 0153  WRITE(*8,8099)
ISN 0154  WRITE(*9,8099)
ISN 0155  WRITE(*6,8099)
ISN 0156  WRITE(*8,8099)
ISN 0157  WRITE(*9,8099)
ISN 0158  4500  FORMAT(*THE OPTIONS FOLLOWED WERE THE FOLLOWING*)
ISN 0159  WRITE(*6,4451)INOPT1
ISN 0160  WRITE(*8,4451)INOPT1
ISN 0161  WRITE(*9,4451)INOPT1
ISN 0162  4591  FORMAT(*OPTION 1 = *14)
ISN 0163  WRITE(*6,4452)INOPT2
ISN 0164  WRITE(*8,4452)INOPT2
ISN 0165  4592  FORMAT(*OPTION 2 = *14)
ISN 0166  WRITE(*6,4453)INOPT3
ISN 0167  WRITE(*8,4453)INOPT3
ISN 0168  4593  FORMAT(*OPTION 3 = *14)
ISN 0169  WRITE(*6,4454)INOPT4
ISN 0170  WRITE(*8,4454)INOPT4
ISN 0171  4594  FORMAT(*OPTION 4 = *14)
ISN 0172  WRITE(*6,4455)INOPT5
ISN 0173  WRITE(*8,4455)INOPT5
ISN 0174  4595  FORMAT(*OPTION 5 = *14)
ISN 0175  WRITE(*6,4456)INOPT6
ISN 0176  WRITE(*8,4456)INOPT6
ISN 0177  4596  FORMAT(*OPTION 6 = *14)
ISN 0178  WRITE(*6,4457)INOPT7
ISN 0179  WRITE(*8,4457)INOPT7
ISN 0180  4597  FORMAT(*THE UNTRAINED VECTOR WAS PRINTED EVERY 1ST ITERATION*)
ISN 0181  WRITE(*6,4505)INCARD
ISN 0182  WRITE(*8,4505)INCARD
ISN 0183  4595  FORMAT(*TOTAL NUMBER OF SPECTRA CONSIDERED (INCARD) = *14)
ISN 0184  WRITE(*6,4506)INSHUT
ISN 0185  WRITE(*8,4506)INSHUT
ISN 0186  4596  FORMAT(*MAXIMUM NUMBER OF ITERATIONS (INSHUT) = *14)
ISN 0187  WRITE(*6,4507)FIN
ISN 0188  WRITE(*8,4507)FIN
ISN 0189  4597  FORMAT(*THE INITIAL VALUE OF THE VECTOR WAS (FIN) *14, 1ST ITERATION*)
ISN 0190  4598  FORMAT(*FINISHING VALUE OF THE VECTOR WAS (FIN) *14)
ISN 0191  IF(NOPT6 .GE. 1000) GO TO 600
ISN 0192  401  GOTO 71
ISN 0193  601  GOTO 74
ISN 0170  AND  CONTINUE
ISN 0180  ENDFILE 72
ISN 0191  STOP
ISN 0182  END
LEVEL 21.7 (JAN 73)  05/360 FORTRAN II

COMPILER OPTIONS - NAME= MAIN,OPT=02,LINECNT=58,SIZE=0000K,
SOURCE,EBCDIC,NOLIST,NODECK,LOAD,MAP,NOEDIT,IDL,NOXREF

SUBROUTINE EC71(NOPT1,NCARD,NCONT,NOPT2,NOPT3,NOPT4,N30)
COMMUN FX(I400,114),JC(I12),T(I400),W(I113),HERR(I400),ERRR(I400)

THIS READ SECTION READS IR AND RAMAN DATA IN THE RANGE FROM
C 1900 TO 500 CM-1. IT CONSIDERS BOTH THE IR AND THE RAMAN AS A
C SINGLE VECTOR. WHERE THE PARALLEL AND PERPENDICULAR RAMAN DATA
C ARE AVAILABLE, THE PARALLEL SPECTRUM ONLY IS USED.
NCONT ≠ 0
DO 204 KON = 1,NCARD
READ(71)(NI,J=1,JC(J),I1,J1,JN54)
READ(71)(JC(I1),I=59,112)
IF(JP2.GT.1) GO TO 100
NCONT = NCONT + 1
DO 1 I=1,56
J=I+44
FX(NCONT,I) = JC(J)
FX(NCONT,114) = NI
GO TO 210
100 IF(N2.EQ.4) GO TO 200
J=45
GO TO 101
FX(NCONT,11) = JC(J)
CONTINUE

THE CLASS IS NOW READ AS PRESCRIBED BY OPTION 2 (NOPT2).
NOPT2 = 1 THRU 17: CLASS 1 THRU 17
NOPT2 = 18: CLASSES 7,8,9 AND 10 (ALL HALOGENS)
NOPT2 = 19: CLASSES 6,9, AND 10 (F,BR AND I)
NOPT2 = 20: CLASSES 3,4 AND 31(ALCOHOLS)
C. NPOT2 = 21 : CLASSES 3,4,5 AND 16 (ALCOHOLS AND PHENOLS)

ISN 0023  1000  IF (NPOT2 < EO 15) GO TO 1081
ISN 0025  DD 1060 JF1,400
ISN 0026  READ(1) (JCF(1)+F1,17)
ISN 0027  IF (NPOT2 = 19) 1001,1002,1003
ISN 0028  GO TO 1085
ISN 0029  1001  H = JCF(NPOT2)
ISN 0030  GO TO 1059
ISN 0031  1002  IF CJF(7) + JCF(8) + JCF(9) + JCF(10)
ISN 0032  GO TO 1059
ISN 0033  1003  IF CJF(20) 1004,1005,1006
ISN 0034  GO TO 1059
ISN 0035  1004  IF CJF(2) + JCF(9) + JCF(10)
ISN 0036  GO TO 1059
ISN 0037  1005  GO TO 1059
ISN 0038  1006  GO TO 1059
ISN 0039  1007  IF (NPOT3 < EO 0) GO TO 4000
ISN 0040  GO 3900 11,CONT
ISN 0041  IF(TI1) 3001,3002,3003
ISN 0042  3001  IF (NP1-NPOT3) 3100,3101,3102
ISN 0043  3100  N20=N19+1
ISN 0044  N20=N20+1
ISN 0045  GO TO 3900
ISN 0046  3101  TI1 = 9,0
ISN 0047  N30=N30+1
ISN 0048  GO TO 3900
ISN 0049  IF (NP3-NPOT4) 3200,3201,3202
ISN 0050  3200  N30=N30+1
ISN 0051  N30=N30+1
ISN 0052  3201  TI1 = 9,0
ISN 0053  N30=N30+1
ISN 0054  3202  CONTINUE
ISN 0055  4000  N30=CONT=N30
ISN 0056  RETURN
ISN 0057  END

THE FOLLOWING SECTION SETS T01(N) TO 9,0 IF THAT
C COMPOUND IS NOT TO BE USED IN THE TRAINING SET BECAUSE
C OPTION 3 OR 4 HAS ALREADY BEEN SATISFIED.
C.
C

ISN 0043  1062  N19=0
ISN 0044  N20=0
ISN 0045  N29=0
ISN 0046  IF (NP3 = EO) GO TO 4000
ISN 0047  DD 3900 11,CONT
ISN 0048  IF (TI1) 3001,3002,3003
ISN 0049  3001  IF (NP1-NPOT3) 3100,3101,3102
ISN 0050  3100  N20=N19+1
ISN 0051  N20=N20+1
ISN 0052  GO TO 3900
ISN 0053  3101  TI1 = 9,0
ISN 0054  N30=N30+1
ISN 0055  GO TO 3900
ISN 0056  3102  IF (NP3-NPOT4) 3200,3201,3202
ISN 0057  3200  N30=N30+1
ISN 0058  N30=N30+1
ISN 0059  3201  TI1 = 9,0
ISN 0060  N30=N30+1
ISN 0061  3202  CONTINUE
ISN 0062  4000  N30=CONT=N30
ISN 0063  RETURN
ISN 0064  END
LEVEL 21.7 (JAN 73)  

DS/360 FORTRAN H

COMPILER OPTIONS - NAME=MAIN,OPT=02,LINECNT=58,SIZE=0000K,
SOURCE=EDOIC,HOLIST,NODECK,LOAD,NAP,NOEDIT,NO,NREF

C C C C C

ISN 0607

SUBROUTINE PERROROPT, NCARD, NOPT2, FIN, NSHUT, LEN, NOPT3, NOPT4, NOPT5, NOPT6

ISN 0603

COMMON FR(100,114), J(112), T(100), W(113), ERR(100), TERR(100)

C C C

C NOPT1 = 1: IR DATA ONLY
C NOPT1 = 2: RAMAN NONPOLARIZED DATA ONLY
C NOPT1 = 3: RAMAN PARALLEL DATA ONLY
C NOPT1 = 4: RAMAN PERPENDICULAR DATA ONLY
C NOPT1 = 5: IR PLUS RAMAN NONPOLARIZED DATA
C NOPT1 = 6: IR PLUS RAMAN POLARIZED (PARALLEL AND PERPENDICULAR)
C NOPT1 = 7: IR PLUS ALL RAMAN DATA
C NOPT1 = 8: ALL RAMAN DATA
C NOPT1 = 9: RAMAN PARALLEL & PERPENDICULAR
C
C NCARD IS THE NUMBER OF SPECTRA IN THE DECK
C
C NOPT2 = 1 THRU 17: CLASS 1 THRU 17
C NOPT2 = 18: CLASSES 7,8,9, AND 10 (ALL HALOSENS)
C NOPT2 = 19: CLASSES 8,9, AND 10 (F, O, AND I)
C NOPT2 = 20: CLASSES 3,4, AND 5 (ALCOHOLS)
C NOPT2 = 21: CLASSES 3,4,5, AND 16
C
C FIN IS THE INITIAL VALUE OF THE VECTOR *W() WHICH IS TO BE TRAINED.
C IF FIN IS 0.0, THE PROGRAM WILL READ AN INITIAL
C VECTOR FROM FILE 73; NOTE THAT IF THE PROGRAM IS TO BE USED IN THIS
C MODE THE APPROPRIATE FILE CARD TO DEFINE FILE 73 (READ(73)) MUST
C NOT BE USED.
C
C NSHUT LIMITS THE NUMBER OF ITERATIONS
C
C LFN DETERMINES HOW OFTEN THE UNTRAINED VECTOR
C WILL BE PRINTED. IF LFN=10, THE UNTRAINED VECTOR WILL BE
C PRINTED EVERY 10TH ITERATION. IF LFN=1, THE UNTRAINED
C VECTOR WILL BE PRINTED AT EVERY ITERATION
C
C NOPT3 = THE NUMBER OF SPECTRA NOT IN THE CLASS WHICH ARE TO BE
C INCLUDED IN THE DECK FOR TRAINING.
C NOPT4 = THE NUMBER OF SPECTRA IN THE CLASS WHICH ARE TO BE
C Included in the deck.

C If NOPT3 = 00, the program will read the entire data deck
C and count the number of spectra in the class and the number
C of spectra not in the class.

C

C NOPT6 permits a part of the training vectors to
C be used for the training routine. If NOPT6 is 1, every element
C of the vectors will be used. If, however, NOPT6 equals N,
C every nth element will be used for the training routine.
C After the program trains with every nth element being used
C it writes the vector on the disk and places the trained elements
C in the N-1 positions of W(I) immediately to the right of the element used for
C training. The program then uses this new vector as the starting vector for
C the whole routine. In the event that NSHUT is reached before any vector
C is trained (either using every element or every nth element), the
C program stops training and continues with the partially trained vector.

C

C If NOPT5 = 0000, the program will end.
C If, however, NOPT5 = 1111, the program will zero all matrices and
C start over again. More data is expected.

C

ISN 0004 READ(15, 999) NOPT1, NCARD, NOPT2, PIN, NSHUT, LEN, NOPT3, NOPT4, INPUT6
ISN 0005 15 0006 999 FORMAT (14, 2X, IA, 14, 2X, IA, 14, 2X, IA, 14, 2X, IA, 14, 2X, IA, 14, 2X, IA, 14, 2X, IA, 14)
ISN 0007 998 FORMAT (14)
ISN 0008 RETURN
ISN 0009 END
CO M P I L E R O P T I O N S - N A M E  N A M E  O P T = O P T 2 . L I N E CNT = 5 0 , S I Z E = 4 0 0 0 K , 

IS N 0 0 1 2 . S U R R A N T H I F P L O T
IS N 0 0 2 3 . C O M M O N F X ( 4 0 0 , 1 1 4 ) , J C ( 4 0 0 , 1 1 2 ) , T ( 4 0 0 , 1 1 3 ) , N E R R ( 4 0 0 , 1 1 4 ) , T E R R ( 4 0 0 , 1 1 5 )
IS N 0 0 2 4 . D I M E N S I O N O U T ( 5 0 , 1 1 3 )
IS N 0 0 2 5 . D A T A A N F * * / , D A N F * * / , / , T P P = 0
IS N 0 0 2 6 . T O P = 0 , 0
IS N 0 0 2 7 . O N 1 0 1 = 1 , 1 1 3
IS N 0 0 0 9 . T O P = A N K ( W ( I ) , T O P )
IS N 0 0 1 0 . H O T = A N K ( W ( I ) , H O T )
IS N 0 0 1 1 . 1 0 C O N T I N U E
IS N 0 0 1 2 . T O P = T O P
IS N 0 0 1 3 . D I S T = T O P - H O T
IS N 0 0 1 4 . F I N = D I S T / 4 9
IS N 0 0 1 5 . 9 9 9 F O R M A T ( 1 A 1 )
IS N 0 0 1 6 . K = 0
IS N 0 0 1 7 . D O S 1 0 1 = 1 , 1 0 5
IS N 0 0 1 8 . I F ( K ) 9 5 = 9 4 , 9 5
IS N 0 0 1 9 . 9 1 I F ( T O P ) H O T , 9 4 , 9 5
IS N 0 0 2 0 . 9 4 K = 1
IS N 0 0 2 1 . 9 5 O N 1 0 4 I J = 1 , 1 1 3
IS N 0 0 2 2 . I F ( 1 ( I , J ) ) - T O P 2 4 , 2 5 , 2 5
IS N 0 0 2 3 . 2 5 N U T ( 1 , J ) = A N F
IS N 0 0 2 4 . 2 5 G O T O 1 9 4
IS N 0 0 2 5 . 2 4 N U T ( 1 , J ) = R A N F
IS N 0 0 2 6 . 1 0 4 C O N T I N U E
IS N 0 0 2 7 . 1 5 0 T O P = T O P - F I N

C T H E  F O L L O W I N G  I S  T H E  W R I T E  A L G O R I T H M

C
IS N 0 0 2 9 . W R I T E ( 6 , 9 4 9 ) T O P A . ( O U T ( I , J ) ) J = 1 , 1 1 3 )
IS N 0 0 3 0 . N . I O C = 1 0 2 , 4 9
IS N 0 0 3 1 . W R I T E ( 6 , 6 9 7 ) ( O U T ( I , J ) ) J = 1 , 1 1 3 )
IS N 0 0 3 2 . 2 0 2 W R I T E ( 6 , 8 7 8 )
IS N 0 0 3 3 . 3 0 5 C O N T I N U E
IS N 0 0 3 4 . W R I T E ( 6 , 8 9 3 ) I N T
IS N 0 0 3 5 . 2 6 5 W R I T E ( 6 , 8 9 4 )
IS N 0 0 3 6 . W R I T E ( 6 , 8 9 5 )

C
IS N 0 0 3 7 . 9 9 9 F O R M A T ( 1 H , 5 X , F 7 ) , 3 , 1 H * , 1 2 2 A 1 , 6 K , 1 A 1 )
IS N 0 0 3 8 . 8 9 9 F O R M A T ( 1 H , 7 X , 1 H * , 1 2 4 A 1 - 1 )
IS N 0 0 4 0 . 8 9 7 F O R M A T ( 1 H , 1 2 2 A 1 , 6 K , 1 A 1 )
IS N 0 0 4 1 . 8 9 5 F O R M A T ( 1 H a , 1 2 2 A 1 , 1 H , 2 0 1 , 1 H , 1 H * , 7 2 , 1 H , 3 1 9 , 1 H * , 3 1 9 , 1 H * , 1 1 1 , 1 H * , 7 2 , 1 H , 3 1 9 , 1 H * , 3 1 9 , 1 H * , 1 1 1 , 1 H * , 7 2 , 3 K M C O N S T )
IS N 0 0 4 3 . 8 9 4 F O R M A T ( 1 H a , 1 2 2 A 1 , 6 K , 1 H , 4 M 3 5 0 0 , 6 X , 4 M 3 5 0 0 , 6 X , 4 M 3 5 0 0 , 6 X , 4 M 3 5 0 0 , 6 X , 4 M 3 5 0 0 , 6 X , 4 M 3 5 0 0 , 6 X , 4 M 3 5 0 0 , 6 X , 4 M 3 5 0 0 , 6 X , 4 M 3 5 0 0 , 6 X , 4 M 3 5 0 0 , 6 X , 4 M 3 5 0 0 , 6 X , 4 M 3 5 0 0 , 6 X , 4 M 3 5 0 0 , 6 X , 4 M 3 5 0 0 , 6 X , 4 M 3 5 0 0 , 6 X , 4 M 3 5 0 0 , 6 X , 4 M 3 5 0 0 , 6 X , 4 M 3 5 0 0 , 6 X , 4 M 3 5 0 0 , 6 X , 4 M 3 5 0 0 , 6 X , 4 M 3 5 0 0 , 6 X , 4 M 3 5 0 0 , 6 X , 4 M 3 5 0 0 , 6 X , 4 M 3 5 0 0 , 6 X , 4 M 3 5 0 0 , 6 X , 4 M 3 5 0 0 , 6 X , 4 M 3 5 0 0 , 6 X , 4 M 3 5 0 0 , 6 X
IS N 0 0 4 4 . 4 5 1 F O R M A T ( 1 H a , 5 X , 1 2 2 A 1 , 1 H * )
IS N 0 0 4 5 . W R I T E ( 6 , 7 9 0 ) T O P A . O U T
IS N 0 0 4 6 . 7 9 9 F O R M A T ( 1 H a , T H E  R A N G E  I S F R O M * F 9 . 5 * T O * F 9 . 5 *
IS N 0 0 4 7 . W R I T E ( 6 , 7 9 0 ) F I N
IS N 0 0 4 8 . 7 9 4 F O R M A T ( 1 H a , E A C H  D I V I S I O N  O N  T H E  P L O T  I S * F 9 . 5 * U N I T S * )
IS N 0 0 4 9 . W R I T E ( 6 , 8 9 9 ) T O P A . ( O U T ( 1 , J ) ) J = 1 , 1 1 3 )
IS N 0 0 5 0 . D I 6 0 0 I = 0 , 4 9
IS N 0 0 5 1 . I F ( 1 - K ) 6 0 2 , 6 6 2 , 6 0 0
052 602 WRITE(6,807) (OUT(I,J),J=1,113)
053 600 CONTINUE
054 WRITE(6,808)
055 WRITE(6,796)
056 796 FORMAT(1H,12X,1H*,20(1X,1H*),19(3X,1H*))
057 WRITE(6,795)
058 WRITE(6,795)
059 FORMAT(1H,14X,1H*,7X,1H*,3(9X,1H*),3(19X,1H*),11X,1H*)
060 WRITE(6,794)
061 RETURN
062 FND
LEVEL 21.7 (JAN 73)

COMPILER OPTIONS - NAME = MAIN, OPT = 02, LINECNT = 56, SIZE = 00000k,
SOURCE = ERDNC, NOLIST, N3DECK, LOAD, MAP, NOEDIT, NOXREF.

ISN 0002 "RUNROUTINE UNPACK"
ISN 0003 COMMON FX(4001:414), JC(112), TF(4001), W(113), HFR(4001), TERR(4001)

ISN 0004 DIMENSION WAI(13)
ISN 0005 DO 1 I=1,113
ISN 0006 1 WAI(I) = W(I)
ISN 0007 DO 2 I=1,44
ISN 0008 2 W(I) = 0
ISN 0009 J=0
ISN 0010 DO 3 I=45,100
ISN 0011 J=J+1
ISN 0012 3 W(I) = WAI(J)
ISN 0013 DO 4 I=101,112
ISN 0014 4 W(I) = 0
ISN 0015 CALL PLOT
ISN 0016 J=6
ISN 0017 DO 5 I=65,100
ISN 0018 J=J+1
ISN 0019 5 W(I) = WAI(J)
ISN 0020 CALL PLOT
ISN 0021 DO 7 I=1,113
ISN 0022 7 W(I) = WAI(I)
ISN 0023 RETURN
ISN 0024 END
COMPILER OPTIONS - NAMES MAIN,OPT=02,LINCNT=59,SIZE=6000K,
SOURCE,NOEDIC,NOLIST,NODFCK,LOAD,MAP,NOEDIT,NO,NOREF

ISN 0002 SUBROUTINE CLASS15
ISN 0003 COMMON FX(400), JCT(112), T(400), W(113), NERR(400), TERR(400)
ISN 0004 D0 10 I=160,174
ISN 0005 10 T(I) = 1.0
ISN 0006 RETURN
ISN 0007 END
The output shown on the following pages was generated by program TRAIN from the three lines of input shown below. (Each space on the fortran card is shown by a dash.)

```
1 1117 20 +1.0000 100 200 177 22 1
0000
 2.0
```
The data have been read 10 times.

The following is the trained vector:

\[
\begin{align*}
0.44463 & -0.06072 -0.37861 -0.38255 -1.14696 -0.05685 0.25123 -0.69059 -1.27755 -0.40787 \\
-0.38603 & -0.27513 -0.53106 -0.01010 -0.75227 -2.35996 -0.02401 0.22525 0.30021 -1.40743 \\
-2.26163 & -2.07911 -0.52956 0.27117 -1.19552 -0.44860 0.00326 0.15155 -0.02795 -1.40902 \\
0.41236 & 0.84202 2.11065 2.44915 2.01166 1.23842 0.30444 -1.84465 -0.17165 -1.16293 \\
0.13072 & 0.55187 0.18116 -0.37255 -0.35937 0.14132 1.31463 -0.47219 -0.20140 1.34689 \\
0.77279 & 1.45959 0.86057 -0.13755 0.63046 1.01151 0.66423 0.20194 -0.15637 0.51862 \\
0.31229 & 1.36355 1.25963 0.48559 -0.20144 -0.43015 -0.94010 -1.03402 -1.43975 0.07042 \\
0.29623 & 0.93576 -1.15590 -0.49966 -0.50012 -0.95333 -1.32729 -0.19421 -0.62487 0.25418 \\
-2.21942 & -0.61043 0.24954 0.52647 -0.42905 -0.39708 -0.31255 -0.33021 -0.07330 0.07126 \\
0.02820 & -1.19361 -0.92905 -2.04557 -0.32950 -0.86659 1.76589 1.89221 1.92398 -1.13274 \\
0.05665 & -1.65610 0.75714 -0.64107 -0.59027 -1.22720 -1.02229 -0.37610 -0.53357 0.50579 \\
0.32441 & 0.4915 0.30108
\end{align*}
\]

The deck was composed of 177.01 98.94 percent) compounds not in the class, and 22.01 11.06 percent) in the class.
THE RANGE IS FROM 2·61166 TO -2·35986
EACH DIVISION ON THE PLOT IS 0·010166 UNITS
THE OPTICKS FOLLOWED WERE THE FOLLOWING:

OPTICK 1 = 1
OPTICK 2 = 2C
OPTICK 3 = 177
OPTICK 4 = 22
OPTICK 6 = 1

TOTAL NUMBER OF SPECTRA CONSIDERED (NCAOD) = 1177
MAXIMUM NUMBER OF ITERATIONS (NSHUT) = 100
THE UNTRAINED VECTOR WAS PRINTED EVERY 200TH ITERATION
THE INITIAL VALUE OF THE VECTOR WAS (FIN) 1.0000
PROGRAM TEST
COMMON FX(400,114), JC(112), T(400), W(113), NERR(400), TERR(400)
DIMENSION CI(400)

1
NOPT6 = 1
FNTJ = 0
FNT2 = 0
FNT4 = 0
K = 0
IF(NOPT6.EQ.1) GO TO 2
IF(NOPT6.EQ.0) GO TO 2
NA1 = 1
GO TO 3
2
DO 4000 I=1,400
F(I) = 0
DC NOPT J = 1,114
4000
IF(I.EQ.1) GO TO 2
IF(N4 .EQ. 1) GO TO 2
N6 = 1
GO TO 3
2
DO 8000 F(M) = 40000
T(I, 114) = 1
8000
CALL Redux(NOPT1, NCARD, OPT2, FIN, NSHUT, LLEN, OPT3, OPT4, OPT5, OPT6)

C C C

OPT7 IS EITHER 1 OR 2. 1 IF SUBROUTINE Redux IS TO BE USED; ELSE 2.
C OPTA GIVES THE POSITION ON THE FILE WHERE THE TEST VECTOR IS TO BE FOUND.
C OPTA GIVES THE FILE NUMBER WHICH IS TO BE READ.
C C C

CALL Redux(NOPT1, NCARD, OPT2, FIN, NSHUT, LLEN, OPT3, OPT4, OPT5, OPT6)
500
FOPVAT(14, 2X, 14, 2X, 14)
K = 1
OPT4
GO TO 7
4
CALL Redux(NOPT1, NCARD, OPT2, FIN, NSHUT, LLEN, OPT3, OPT4, OPT5)
GO TO 6
5
CALL Redux(NOPT1, NCARD, OPT2, OPT3, OPT4, OPT5, OPT7)
6
N4 = 2
3
CALL Redux(NOPT1, NOPT7)
7
PPAT(NOPT7)(W(1), I=1,113)
CP 100 = 1 + NCONT
FD 0 = 0
DO 10 J=1,114
10
F(I,J) = F(I,J) + F
FD *(I1) = 20, 20, 30
20
FD *(I1) = 21, 21, 25
21
FNT1 = FNT1 + 1
GO TO 100
25
FNT7 = FNT2 + 1
K = 1
NEEK(K) = F(I,J)
TREK(K) = T(I)
C1(K) = F
GO TO 100
30
IP = 31, 31, 35
31
FNT3 = FNT3 + 1
K = 1
NEEK(K) = F(I,J)
TREK(K) = T(I)
C1(K) = F
GO TO 100
35
FNT4 = FNT4 + 1
100 CONTINUE
F1 = FNT1
F2 = FNT1(1, FNT4 + FNT2)/100.0
F3 = FNT2
F4 = (FNT1 + FNT2)/100.0
1000 CONTINUE
      STOP
END
SUBROUTINE PET1(NOPT1,NCONT,NCARD,NOPT2,NOPT3,NOPT4,N30)
COMMON FX(400,114),JC(112),T(400),W(113),NERR(100),TPER(400)
C NOPT1 = 1 : IR DATS ONLY
C NOPT1 = 2 : RAMAN NONPOLARIZED DATA ONLY
C NOPT1 = 3 : RAMAN PARALLEL DATA ONLY
C NOPT1 = 4 : RAMAN PERPENDICULAR DATA ONLY
C NOPT1 = 5 : IR PLUS RAMAN NONPOLARIZED DATA
C NOPT1 = 6 : IR PLUS RAMAN POLARIZED (PARALLEL AND PERPENDICULAR)
C NOPT1 = 7 : IR PLUS ALL RAMAN DATA
C NOPT1 = 8 : ALL RAMAN DATA
C NOPT1 = 9 : RAMAN PARALLEL + PERPENDICULAR
NSkip = 0
NCNT = 0
GO TO (100,100,100,400,500,500,100,900),NOPT1
100 DC 109 Jw,NCARD
READ(Jw) N1,J2,JC(I),I=1,581
READ(Jw) JC(I),I=1,112
IF(2+NOPT1)109,101,101
101 NCNT = NCONT
DO 102 I=1,112
   102 FX(NCONT),I = JC(I)
FX(NCONT) = N1
 CONTINUE
GO TO 1000
500 DC 509 Jw,NCARD
READ(Jw) N1,J2,JC(I),I=1,581
READ(Jw) JC(I),I=1,112
IF(1+1) 501,502,501
501 NCNT = NCONT
DO 502 I=1,112
   502 FX(NCONT),I = JC(I)
   FX(NCONT) = N1
   NT = 599
510 GO TO (599,599,599,599,599,599,599,599),NOPT1
511 IF(N2+1) 500,502,500
500 NSkip = NSkip + 1
   IF(NSkip EQ. 1) GO TO 599
   NCNT = NCONT
   NSkip = 0
   GO TO 599
512 DO 513 I=1,112
   F1 = JC(I)
513 FX(NCONT),I = (FX(NCONT),I + F1)/2
   GO TO 599
520 IF(N2+1) 500,502,500
502 NSkip = NSkip + 1
   DO 521 I=1,112
      F2 = JC(I)
521 FX(NCONT),I = FX(NCONT),I + F2
   IF(NSkip EQ. 2) 522,523,523
522 ON = 1
   523 ON = 2
524 FX(NCONT),I = FX(NCONT),I / 3
   NSkip = 0
   GO TO 599
530 DO 531 I=1,112
      F3 = JC(I)
531 FX(NCONT),I = FX(NCONT),I + F3
   IF(N3+1) 333,333,333
532 DO 534 I=1,112
      F4 = FX(NCONT),I / 2
   GO TO 599
533 DO 535 I=1,112
      F5 = FX(NCONT),I / 3
CONTINUE
GO TO 1000

DO 999 I = 1,112

PRINT 1000, NCONT
END

1000 CONTINUE
GO TO 1050

C NOPT3 = 17 : CLASSES 1, 2, 3 AND 10 (HALOGENS) 17
C NOPT2 = 19 : CLASSES 4, 5 AND 16
C NOPT2 = 24 : CLASSES 3, 4, 5 AND 16
C NOPT3 = 21 : CLASSES 3, 4, 5 AND 16
GO TO 1050

C N = JCN(NOPT2)
GO TO 1050

1050 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1060 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1070 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1080 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1090 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1100 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1110 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1120 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1130 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1140 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1150 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1160 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1170 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1180 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1190 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1200 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1210 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1220 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1230 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1240 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1250 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1260 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1270 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1280 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1290 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1300 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1310 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1320 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1330 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1340 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1350 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1360 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1370 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1380 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1390 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1400 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1410 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1420 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1430 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1440 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1450 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1460 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
GO TO 1050

1470 CONTINUE
GO TO 1050

C C N = JCN(NOPT2)
RETURN
END
SUBROUTINE PNF1(NOPT1,NCARD,NOPT2,FN,NSHUT,LEN,NOPT3,NOPT4,NOPT5)
COMMON FX(400,114),JC(1121,400),W(1131),NER(400),TERR(400)
C
C  NOPT1 = 1 : IR DATA ONLY
C  NOPT1 = 2 : RAMAN NONPOLARIZED DATA ONLY
C  NOPT1 = 3 : RAMAN PARALLEL DATA ONLY
C  NOPT1 = 4 : RAMAN PERPENDICULAR DATA ONLY
C  NOPT1 = 5 : IR PLUS RAMAN NONPOLARIZED DATA
C  NOPT1 = 6 : IR PLUS RAMAN POLARIZED (PARALLEL AND PERPENDICULAR)
C  NOPT1 = 7 : IR PLUS ALL RAMAN DATA
C  NOPT1 = 9 : ALL RAMAN DATA
C  NOPT1 = 9 : RAMAN PARALLEL + PERPENDICULAR
C
C  NCARD IS THE NUMBER OF SPECTRA IN THE DECK
C
C  NOPT2 = 1 : THRU 17 : CLASS 1 THRU 17
C  NOPT2 = 19 : CLASS 8,9, AND 10 (ALL HALOGENS)
C  NOPT2 = 19 : CLASS 8,9, AND 10 (F,BR, AND I)
C  NOPT2 = 20 : CLASS 9,4 AND 5 (ALCOHOLs)
C  NOPT2 = 21 : CLASS 9,4,5 AND 16
C
C  FIN IS THE INITIAL VALUE OF THE VECTOR W(I) WHICH IS TO BE TRAINED
C  IF FIN IS 0.0, THE PROGRAM WILL READ AN INITIAL
C  VECTOR FROM FILE 73. NOTE THAT IF THE PROGRAM IS TO BE USED IN THIS
C  WORK THE APPROPRIATE FILE CARD TO DEFINE FILE 73 (DSET 73) MUST
C  BE USED
C
C  NNSHUT LIMITS THE NUMBER OF ITERATIONS
C
C  LFN DETERMINES HOW OFTEN THE UNTRAINED VECTOR WILL BE PRINTED. IF LENICL0 THE UNTRAINED VECTOR WILL BE
C  PRINTED EVERY 10TH ITERATION. IF LFN=1 THE UNTRAINED VECTOR WILL BE PRINTED AT EVERY ITERATION
C
C  NOPT1 = THE NUMBER OF SPECTRA NOT IN THE CLASS WHICH ARE TO BE
C  INCLUDED IN THE DECK FOR TRAINING.
C  NOPT4 = THE NUMBER OF SPECTRA IN THE CLASS WHICH ARE TO BE
C  INCLUDED IN THE DECK.
C  IF NOPT1 = 0, THE PROGRAM WILL READ THE ENTIRE DATA DECK
C  AND PRINT THE NUMBER OF SPECTRA IN THE CLASS AND THE NUMBER
C  OF SPECTRA NOT IN THE CLASS.
C  A REAL ERROR WILL OCCUR IF THE PROGRAM IS INSTRUCTED TO
C  READ MORE COMPOUNDS EITHER IN THE CLASS OR NOT IN THE CLASS THAN
C  ACTUALLY EXIST IN THE DECK
C
C  IF NOPT5#00000, THE PROGRAM WILL END
C  IF NOPT5#1111, THE PROGRAM WILL ZERO ALL MATRICES AND
C  START OVER AGAIN. MORE DATA IS EXPECTED.
C
READ(9,991)NOPT1,NCARD,NOPT2,FN,NSHUT,LEN,NOPT3,NOPT4
READ(5,995)NOPT5
990 FORMAT(14.2X,14.2X,14.2X,9.2X,4.2X,14.2X,14.2X,14.2X,14.2X,14.2X,14.2X)
995 FORMAT(14)
RETURN
END
SUBROUTINE PNF2(NOPT1,NCARD,NOPT2,NOPT3,NOPT4,NOPT5,NS3)
COMMON FX(400,114),JC(1121,400),W(1131),NER(400),TERR(400)
NCONT = 0
DO 200 KVC = 1,NCARD
READ(71) N1,N2,(JC(I),I=1,58)
READ(71) (JC(I),I=59,112)
IF(N2 .GT. 1) GO TO 100
NCONT = NCONT + 1
GO TO 1
J=1
1 PX(NCONT+1) = JC(J)
IF(NCONT+1) = N1
GO TO 200
100 IF(N2 .EQ. 1) GO TO 200
J=5
GO TO 101
101 N=JC(J)
CONTINUE
1050 CONTINUE
DO 1090 J=1,400
READ(71) (JC(I),I=1,17)
IF(NOPT2 = 15) 1001,1002,1003
1001 N = JC(NOPT2)
GO TO 1090
1002 N = JC(7) + JC(8) + JC(9) + JC(10)
GO TO 1090
1003 IF(NOPT2=20) 1004,1005,1006
1004 N = JC(8) + JC(9) + JC(10)
GO TO 1090
1005 N = JC(1) + JC(4) + JC(5)
GO TO 1090
1006 N = JC(7) + JC(4) + JC(5) + JC(16)
1009 IF(N) 1,50,1060,1061
1061 T(11) = 1
1060 CONTINUE
N30 = 0
RETURN
END
// THOR END
PROGRAM SNOOP

Subroutines RE71 and PLOT are not included in this listing. They were included in the listing of earlier programs.
COMMON FX(400,114),JC(112),TF(400),W(113)
DIMENSION W1(113)
C IF N1 = 1, THE PROGRAM AVERAGES VECTORS
C WHICH USED IN THIS MODE N2 EQUALS THE NUMBER OF VECTORS TO BE AVERAGED.
C N5 EQUALS 00 IF THE VECTOR CALCULATED (AVERAGED) IS NOT TO BE WRITTEN ON
C A DISK FILE.
C N3 AND N4 GIVE THE FILE NUMBER AND THE POSITION ON THE FILE TO BE READ.
C THERE SHOULD BE N2 CARDS SHOWING N3.nA DATA.
C
C IF N1 EQUALS 2 THE PROGRAM WILL CALCULATE THE AVERAGE REPRESENTATION
C (A VECTOR) FOR A PARTICULAR CLASS.
C IF THE PROGRAM IS USED IN THIS MODE, N2 IS 00. N5 AGAIN IS 00 IF IT IS NOT
C DESIRED TO WRITE THE CALCULATED VECTOR ON A DISK FILE.
C IF THE PROGRAM IS USED WITH N2 SET AT 2 THE SECOND CARD MUST GIVE
C N0PT1,N0PT2,N0PT3 AND N0PT4.
C
C IF N1 IS 3 OR GREATER THE PROGRAM WILL HALT.
C
C 1003 DO 1001 1=1,400
   T(I) = 0
   DC 1001 J=1,114
1004 FX(I,J) = 0
   DC 1007 I=1,112
   JC(I) = 0
   W(I) = 0
1002 W1(I) = 0
   W1(I) = 0
   W1(113) = 0
C
C ND5 = 5
   NDH = 6
   WRITE(996,9999) N1,ND,ND
9999 FORMAT(12,2X,14)
   WRITE(ND,9999) N2
9409 FORMAT(12,THE VALUE OF N1 IS*,1X,14)
   WRITE(NDH,9999) N2
9999 FORMAT(12,THE VALUE OF N2 IS*,1X,14)
   WRITE(N06,9996) N5
9997 FORMAT(12,IF N5 > 0. THE VECTOR WILL BE SAVPO. N5 =*,15)
   WRITE(N06,9995)
   WRITE(N06,9995)
   WRITE(N06,9995)
   WRITE(N06,9995)
9996 FORMAT(1)
   IF(N1 - 2) .EQ.100
9999 FORMAT(12,100,1000
C
C
C
C DO 4 I=1,N2
   READ(ND5,9999) N3,N4
9998 FORMAT(12,2X,14)
   WRITE(NDH,9995) N3,N4
9935 FORMAT('IH*FILE*14.*WAS READ. VECTOR*IS*WAS USED.*')
IF('IN*END.*') GO TO 17
DO 2 J=1,N4
2 READ(N3) (T(K),K=1,113)
GO TO 14
13 READ(N3) (T(K),K=1,113)
14 FORMAT(N3)
DO 3 K=1,113
3 W(K) = W(K) + T(K)
FN2 = FN2
DO 4 K=1,113
4 W(K) = W(K) / FN2
GO TO 200
C C C C
100 FORMAT('4*9944A) NOPT1,NOPT2,NOPT3,NOPT4')
9956 FORMAT(14.2X,14.2X,14.2X,14.2X*14)
9954 FORMAT(IH*OPTION 1 =*15)
9952 FORMAT(IH*OPTION 2 =*15)
9950 FORMAT(IH*OPTION 3 =*15)
9948 FORMAT(IH*OPTION 4 =*15)
NCARD = 117
CALL P571(NOPT1,NCARD,NCONT,NOPT2,NOPT3,NOPT4,N30)
51 FORMAT 111
K = 0
W(I) = 0
DO 101 I=1,NCONT
IF(T(I) .LT. 0.0) GO TO 103
IF(T(I) .GE. 0.0) GO TO 101
K = K + 1
DO 104 J=1,113
104 W(I,J) = W(I,J) + FX(I,J)
GO TO 101
101 FORMAT
CONTINUE
FK = K
FK1 = K1
DO 102 I=1,113
102 W(I) = W(I)/FK
501 FORMAT
 Респ. STOP
END
SIMPLE AVERAGE REPRESENTATIONS

and

MUTED AVERAGE REPRESENTATIONS
ESTERS
Simple Average Representation
Infrared

[Graph with data points and frequency scale]
ESTERS
Muted Average Representation
Infrared
KETONES
Simple Average Representation
Raman Parallel Polarized
KETONES
Simple Average Representation
Raman Perpendicularly Polarized
KETONES
Muted Average Representation
Raman Parallel Polarized
KETONES
Muted Average Representation
Raman Perpendicularly Polarized
DOUBLE BONDS
Simple Average Representation
Raman Parallel Polarized
DOUBLE BONDS
Simple Average Representation
Raman Perpendicularly Polarized
DOUBLE BONDS
Muted Average Representation
Infrared
DOUBLE BONDS
Muted Average Representation
Raman Parallel Polarized
DOUBLE BONDS
Muted Average Representation
Raman Perpendicularly Polarized
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UNIVERSITY MICROFILMS
ETHERS
Simple Average Representation
Raman Perpendicularly Polarized
ETHERS
Muted Average Representation
Infrared
ETHERS
Muted Average Representation
Raman Parallel Polarized
ALCOHOLS

Simple Average Representation

Raman Perpendicularly Polarized
ALCOHOLS

Muted Average Representation

Raman Parallel Polarized
ALCOHOLS
Muted Average Representation
Raman Perpendicular Polarized
PRIMARY ALCOHOLS

Simple Average Representation

Infrared
PRIMARY ALCOHOLS

Simple Average Representation

Raman Parallel Polarized
PRIMARY ALCOHOLS

Simple Average Representation

Raman Perpendicularly Polarized
SECONDARY ALCOHOLS

Simple Average Representation

Infrared
SECONDARY ALCOHOLS

Simple Average Representation

Raman Parallel Polarized
SECONDARY ALCOHOLS

Muted Average Representation

Infrared
VITA

The author was born in  
He graduated from Northeast Catholic High School, and received the Bachelor of Science degree in Chemistry from Niagara University, graduating Summa Cum Laude.

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