I. A VIBRATIONAL STUDY OF THE CYANOETHYLENES

II. AN ALGORITHM FOR THE DETERMINATION OF THE SHAPE PARAMETERS OF INFRARED ABSORPTION BANDS

By

ARTHUR STANLEY ROSENBERG

Bachelor of Science
University of Vermont
Burlington, Vermont
1955

Master of Science
Massachusetts Institute of Technology
Cambridge, Massachusetts
1959

Submitted to the Faculty of the Graduate College
of the Oklahoma State University
in partial fulfillment of the requirements
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Thesis Approved:

J. Paul Devlin
Thesis Adviser

O.C. Dermer

Tom E. Moore

E.J. Eisenbraun

J. Lange

D. Durham
Dean of the Graduate College

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PART I

A VIBRATIONAL STUDY OF THE CYANOETHYLENES

CHAPTER I

INTRODUCTION

Vibrational Spectra

Infrared and Raman spectroscopy furnish one of the most powerful methods for investigating the internal forces of molecules. The vibrational frequencies, derived from spectroscopic studies, are functions of the kinetic and potential energies of the system. The kinetic energy is a function of molecular geometry and atomic masses and the potential energy is determined by the forces within the system. Therefore, if the geometry and mass distribution of a molecule are known, the vibrational frequencies of the molecule can be used to obtain information concerning the forces acting during the vibrational motions.

For a molecule containing N atoms, 3N coordinates are necessary to define the system at any point in time. Of these, 3 coordinates are necessary to define the center of mass of the molecule with respect to an external reference and, for a nonlinear molecule, 3 define rotational motions about the major axes of the molecule. The remaining 3N-6 coordinates are available to describe the motions of the component atoms with respect to the rotating coordinate system; that is, the molecular vibrations.

Each of the above-mentioned 3N-6 degrees of freedom corresponds to a normal mode of vibration of the molecule. In a normal mode, all nuclei move in phase and at the same frequency. Amplitudes of displacement from the equilibrium position may be different for each nucleus, but each must reach its maximum displacement at the same time and each atom must pass through its equilibrium position at the same time. The frequency associated with a normal mode is known as a normal, or fundamental, frequency.

In discussing kinetic and potential energy of a vibrating system it is convenient to introduce the concept of mass-weighted cartesian coordinates q_i. These are defined by the equations

$$q_i = \sqrt{M_j}\Delta X_i, \qquad \begin{matrix} i = 1,2, \ldots , 3N \\ j = 1,2, \ldots , N \end{matrix} \tag{1}$$

where M_j is the mass of the jth atom and ΔX_i is one of the three cartesian displacement coordinates for the jth atom. In terms of these coordinates, the kinetic energy is

$$2T = \sum_{i=1}^{3N} \dot{q}_i^{\,2} \tag{2}$$

where the dot implies differentiation with respect to time. For small displacements, the potential energy can be expressed as

$$2V = \sum_{i=1}^{3N} \sum_{j=1}^{3N} f_{ij}q_iq_j \tag{3}$$

where the f_{ij} are force constants given by

$$f_{ij} = \left(\frac{\partial^2 V}{\partial q_i \, \partial q_j}\right)_o \tag{4}$$

The zero subscript implies the equilibrium position, that is, $q_i = q_j = 0$.

Although it would be possible to describe the normal modes of vibration in terms of the 3N mass weighted cartesian coordinates, it is more advantageous to introduce a system of normal coordinates. These are defined as

$$Q_k = \sum_{i=1}^{3N} l_{ki} q_i, \; k = 1,2 \ldots , 3N \qquad (5)$$

in which the coefficients l_{ki} are chosen such that, in terms of the normal coordinates, the kinetic and potential energies have the forms

$$2T = \sum_{k=1}^{3N} \dot{Q}_k \qquad 2V = \sum_{k=1}^{3N} \lambda_k Q_k^{\,2} \qquad (6)$$

Thus the potential energy involves no cross products while the kinetic term retains the same form as in Equation 2. In normal coordinate space, then, each coordinate corresponds to one of the normal modes of the molecule. The λ_k of Equation 6 are related to the fundamental frequencis ν_k by

$$\lambda_k = 4\pi^2 \nu_k^{\,2} \qquad (7)$$

There is no problem in considering 3N, rather than 3N-6, normal coordinates since translation and rotation may be considered as normal modes with zero frequency.

The Potential Function

Virtually all studies of molecular force fields are based on the assumption that the vibrational motions are harmonic. This assumption would be expected to be true if the motions involved only infinitesimal displacements of the atoms from their equilibrium positions. Nevertheless, the success of quadratic potential energy functions in describing the force fields of many molecules confirms the validity of the harmonic approximation.

For the purpose of developing the potential function, the vibrational potential energy may be expressed in terms of 3N-6 internal displacement coordinates. These are most conveniently chosen as the instantaneous changes in the bond lengths and bond angles in the molecule. Under the assumption of harmonic motion, the potential energy in terms of the internal displacement coordinates is

$$2V = \sum_{i=1}^{3N-6} \sum_{j=1}^{3N-6} f_{ij} \Delta R_i \Delta R_j \qquad (8)$$

where ΔR is an internal displacement coordinate and f_{ij} is the force constant. This equation is entirely analogous to equation 3, the only difference being that a different coordinate set is used.

Equation 8 defines the general valence force field. This field includes not only the 3N-6 principal force constants ($i = j$), but also all interaction force constants ($i \neq j$). In the absence of symmetry considerations there are then (3N-5)(3N-6)/2 force constants to be evaluated to define this field. Since there are only 3N-6 vibrational degrees of freedom, the system is clearly underdetermined. In general, however, considerations of molecular symmetry reduce the number of unique force constants to be determined. Consider, for example, the planar vibrations of tetracyanoethylene. There are 17 degrees of freedom associated with the planar modes so that, if symmetry is neglected, 153 force constants would have to be evaluated to define the general valence force field. When molecular symmetry is taken into account, the number of unique force constants to be determined is reduced to 30. Even so, the problem is still underdetermined in that only 17 fundamental frequencies are available.

In addition to the above mentioned difficulties, the general valence force field does not present a clear picture of the nature of the interactions between nonbonded atoms. In order to decrease the number of force constants and to permit a clearer interpretation of the forces acting within a molecule, various assumptions concerning the nature of the force field have been made. These assumptions have led to the postulation of a number of special force fields.[1] Some of these are described below.

The Central Force Field

The central force field is based on the assumption that interactions exist in a molecule along the lines connecting pairs of atoms and that every atom exerts influence on every other atom, independent of whether the atoms are bonded to each other or not. The number of independent force constants required for this field is $N(N-1)/2$, a number quite small compared to the $(3N-5)(3N-6)/2$ required for the general valence force field. This model, however, has not given satisfactory results[2] and is now seldom used.

The Simple and Modified Valence Force Fields

The simple valence force field is similar to the central force field in its treatment of forces acting between bonded atoms, but does not include interactions between nonbonded atoms. Instead, it is assumed that a force constant is associated with the angle between bonds which opposes a change in the bond angle. This field can usually account for all molecular bending vibrations and in this respect is superior to the central force field. However, the lack of quantitative agreement between frequencies calculated on the basis of the simple valence force field and those actually observed indicate that this field is best regarded as only a rough approximation.

The modified valence force field consists of the simple valence force field with the addition of one or more judiciously chosen interaction terms. This generally leads to a set of force constants which can be evaluated in such a manner as to reproduce the observed frequencies well. It is not, however, always possible to predict just which of the interaction constants it is necessary to include. In fact, several different sets of force constants may adequately describe the frequencies of a given molecule. In addition to this lack of uniqueness, it is usually difficult to give a meaningful interpretation for the selected interaction constants.

The Urey-Bradley Force Field

The Urey-Bradley force field (UBFF)[3] may be considered as a simple valence force field modified to include central forces between nonbonded atoms. The potential energy can be expressed in terms of the basic UBFF as

$$2V = 2\sum_i K_i' r_i \Delta r_i + \sum_i K_i (\Delta r_i)^2 + 2\sum_j H_j' (\Delta\alpha_j) +$$

$$\sum_j H_j (\Delta\alpha_j)^2 + 2\sum_k F_k' q_k \Delta q_k + \sum_k F_k (\Delta q_k)^2 \qquad (9)$$

where r_i is an equilibrium bond distance, α_j a bond angle and q_k an equilibrium distance between nonbonded atoms. K and H are bond stretching and bending force constants respectively and F represents a force constant between nonbonded atoms. The linear terms in equation 9 are necessary because the set of internal coordinates used, which includes the q_k, is no longer linearly independent. The q_r, however, are related to the r_i and α_j by a simple geometric relationship. It is therefore possible to evaluate the H_j' and the K'_i in terms of the F'_k.

Based on the assumptions that, at nonbonded distances usually encountered, the principal force acting between nonbonded atoms is repulsive and that this repulsive force is proportional to $1/r^9$, it is common practice to reduce the number of necessary force constants further by setting F' equal to $-0.1F$. It has been pointed out that this practice is unwarranted in that the F_k may represent stabilizing as well as destabilizing forces.[4,5] The elimination of F' probably does little harm, however, since it is probably small compared to F.

The UBFF was first used extensively by Shimanouchi.[6] Since then it has been used successfully by many workers for a wide variety of molecular types.

Urey-Bradley force constants (UBFC's) are, to some extent, transferable; that is, force constants which have been evaluated for one molecule can often be used to calculate normal frequencies for similar molecules. This transferability has been studied extensively and Shimanouchi has published a compilation of UBFC's useful for many small molecules.[7] As a direct result of this transferability of force constants, it is possible to treat several molecular species in one normal coordinate calculation, evaluating force constants for similar groupings only once.[8] This technique, called an overlay calculation, makes it possible to determine UBFC's for a series of related molecules instead of attempting to determine a complete set for one molecule. The agreement between observed and calculated frequencies generally worsens as the number of molecules included in an overlay calculation is increased. This is because one is attempting to fit more data with the same number of parameters. The uncertainties in the calculated force constants decreases, however, and their possible physical significance increases.

Overend and co-workers have written a set of computer programs to perform an overlay normal coordinate analysis in which force constants are refined by an iterative least-squares method.[9] The algorithm used in the force constant calculations will not be discussed here as it is thoroughly described in a recent reference.[10] The above-mentioned computer program was modified slightly and used extensively throughout this investigation.

The Scope of the Present Investigation

The primary purpose of this investigation was to evaluate a consistent set of Urey-Bradley force constants for the planar modes of the series of cyanoethylenes: acrylonitrile, fumaronitrile, maleonitrile, 1,1-dicyanoethylene, tricyanoethylene and tetracyanoethylene.[11] These molecules were selected because they comprise a set of structurally similar molecules in which the degree of electron delocalization varies widely from one end of the series to the other. This provided an ideal situation to test the transferability of UBFC's under conditions of varying resonance. In addition, it was felt that confirmation of certain assignments in the spectrum of tetracyanoethylene could be accomplished by an overlay calculation involving all the cyanoethylenes.

The experimental phase of this study involved the preparation of 1,1-dicyanoethylene and the determination of its infrared spectrum. The infrared data, together with infrared and Raman data from the literature for the other cyanoethylenes, was used in a variety of overlay Urey-Bradley calculations.

The overlay calculations have resulted in a satisfactory assignment of the planar modes of 1,1-dicyanoethylene. In addition, the assignments for two of the tetracyanoethylene fundamentals have been changed.

CHAPTER II

SPECTROSCOPIC STUDIES OF THE CYANOETHYLENES

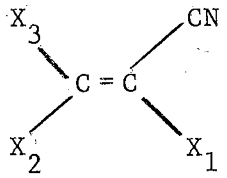
The cyanoethylenes (Table I) provide an interesting example of a series of structurally similar molecules in which the degree of π-electron delocalization varies smoothly throughout the series. Since these resonance effects should result in a weakening of the C≡N, C=C and perhaps the C—H bonds with a corresponding strengthening of the C—C bonds, the series provides an interesting ground for the transferability of UBFC's since deviations from transferability should have physical significance in terms of bonding differences. In addition, the possibility of modifying the UBFC of an open-chain molecule to include a resonance parameter is presented. The inclusion of such a parameter has been reported only for cyclic molecules.[12-16]

Halverson and co-workers[17] have reported a complete assignment for the infrared and Raman spectra of acrylonitrile. No vibrational analysis of the planar modes was attempted, but a 4-term modified valence force field was used to calculate approximate frequencies for the four out-of-plane modes.

Spectra and assingments have been reported for fumaronitrile,[18-20] maleonitrile,[19,20] tetracyanoethylene[19,20] and tricyanoethylene.[18] There are some differences between the spectra reported by Long and George[19] and those reported by Devlin, Overend and Crawford[18] and Miller, et al.[20] For those cases where differences occur, the

TABLE I

THE CYANOETHYLENES



Compound	X_1	X_2	X_3
Acrylonitrile	H	H	H
Fumaronitrile	H	CN	H
Maleonitrile	H	H	CN
1,1-Dicyanoethylene	CN	H	H
Tricyanoethylene	CN	CN	H
Tetracyanoethylene	CN	CN	CN

assignments proposed by Miller have been chosen for use in this investigation.

Devlin and co-workers[18] have performed an overlay UBFF vibrational analysis for acrylonitrile, fumaronitrile and tricyanoethylene. As a result of this calculation, a set of 16 force constants were determined from the 35 observed planar fundamental frequencies. As had been previously reported,[21] they found it necessary to include a quadratic cross term between trans-hydrogen bending coordinates in the potential function. This term was introduced to provide more accurate calculated values for the frequencies of in-plane rocking modes involving hydrogen. Examination of the potential energy distributions for acrylonitrile and fumaronitrile indicate that this force constant is involved mainly in C═C stretching and C—H rocking and deformation vibrations.

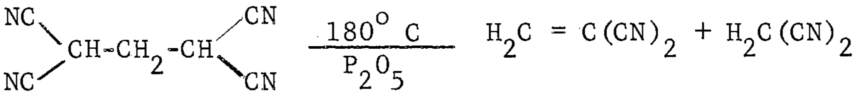
There are thus reasonably firm assignments for the planar modes of all but one of the cyanoethylenes. Vibrational spectra and assignments have more recently been published for 1,1-dicyanoethylene.[11] The remaining chapters of this work are concerned with the problem of the vibrational spectrum of this compound and with overlay normal coordinate analyses including all the cyanoethylenes.

CHAPTER III

EXPERIMENTAL

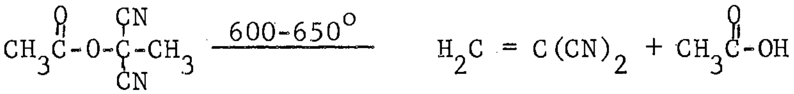
As was noted in the introduction, the experimental phase of this work consisted of the preparation of 1,1-dicyanoethylene and the determination of its infrared spectrum. Some experimental difficulty was encountered in the handling of this compound. It is easily polymerized in the presence of any source of labile protons. Many nucleophiles are also effective in initiating polymerization. As a result of this, extreme care was taken to exclude contaminants, particularly water vapor, during preparation and transfer of 1,1-dicyanoethylene.

The first synthesis of 1,1-dicyanoethylene was reported by Ardis and co-workers.[22] Two basic synthetic schemes were presented. These are outlined in equations 1 and 2. In this work, the synthesis involving



(1)

I III



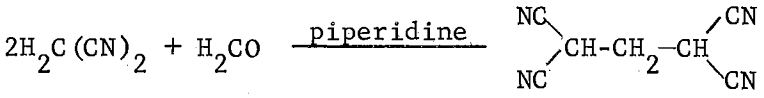
$$CH_3\overset{O}{\overset{\|}{C}}-O-\underset{CN}{\overset{CN}{C}}-CH_3 \xrightarrow{600-650^{\circ}} H_2C = C(CN)_2 + CH_3\overset{O}{\overset{\|}{C}}-OH$$

(2)

II III

the pyrolysis of 1,1,3,3-tetracyanopropane (I) was chosen.

The synthesis of I was accomplished by the method of Diels[23,24] as outlined in equation 3. Malononitrile (Eastman Practical Grade)



$$2H_2C(CN)_2 + H_2CO \xrightarrow{\text{piperidine}} (NC)_2CH\text{-}CH_2\text{-}CH(CN)_2 \qquad (3)$$

I

was purified by fractional distillation and condensed with formaldehyde (as formalin) in ethanol solution. The resultant solid material was washed with dilute sulfuric acid and with water and recrystallized from a 2:1 mixture of acetonitrile and benzene. The purified I thus prepared melted sharply at 137° C. Yields for this reaction were typically about 40% of theoretical, based on malononitrile as the limiting reagent.

In our early attempts to synthesize III, a closed system involving several ampule-to-ampule distillations was used for the pyrolysis of I. Yields using this apparatus were disappointingly low. We therefore reverted to a method similar to that used by Ardis.[22] Dried I and P_2O_5 were placed in a Claisen flask and covered with dry Pyrex wool. The side tube of the flask was connected to a receiver containing P_2O_5 and dry benzene. The receiver was cooled in a Dry Ice-acetone bath and the system was evacuated to about 10 torr. The flask was then heated to 180° C until pyrolysis was completed. The material in the receiver was melted and the benzene solution was fractionally distilled through a 20 cm vacuum-jacketed Vigreux column. The fraction boiling over the range 50.0 - 51.2° C at 10 torr was taken as 1,1-dicyanoethylene. The distilled material was stored in the cold over P_2O_5. No attempt was made to determine the yield in the pyrolysis.

Standard sampling cells, fitted with cesium iodide windows, were used in determining the infrared spectrum of III. All transfers were carried out in a dry box which was well purged with dry nitrogen. The cells were purged separately with dry nitrogen for one hour prior to use. For the determination of the spectrum of gaseous III, the samplong cell was placed in an electrically heated oven and maintained at a temperature in excess of 170° C during the spectral scan. Since it has been reported[25] that poly(1,1-dicyanoethylene) undergoes depolymerization at temperatures above 160° C, it was hoped that this would prevent deposition of the polymer in the gas sampling cell. Some polymer, however, was always formed during determination of the spectrum of gaseous III.

Much of the spectrum of 1,1-dicyanoethylene was recorded using a Perkin-Elmer Model 221 prism-grating spectrophotometer. More recent measurements were made with a Perkin-Elmer Model 521 dual-grating instrument. A Beckman IR-7 spectrophotometer with cesium iodide optics was used to determine spectra over the 200 - 250 cm^{-1} region. The parameters of the Perkin-Elmer instruments were set so that the spectral slit width was 1.2 cm^{-1} at 1000 cm^{-1}.

For the region above 500 cm^{-1}, well known absorption bands of polystyrene, atmospheric water vapor, atmospheric CO_2 and indene were used to calibrate the frequency scale of the spectrophotometer.[26] No attempt was made to calibrate below this point. It is estimated that spectral features are determined to within 2 cm^{-1} over the range 3500 - 500 cm^{-1} and to within 5 cm^{-1} below 500 cm^{-1}.

CHAPTER IV

INTERPRETATION OF THE SPECTRUM OF 1,1-DICYANOETHYLENE

If it is assumed that 1,1-dicyanoethylene is planar, then it must belong to the point group C_{2v}. Group theoretic considerations would lead one to expect that the 18 normal modes of vibration would be distributed among the symmetry classes as follows:

$$\Gamma_{vib} = 7A_1 + 2A_2 + 3B_1 + 6B_2$$

Of these, the modes belonging to classes A_1, B_1 and B_2 will exhibit infrared activity while all of the normal vibrations would be expected to be Raman-active. The planar vibrations belong to symmetry classes A_1 and B_2 and thus will all be infrared-active. As a consequence of the fact that 16 of the 18 normal vibrations are infrared-active, the infrared spectrum (Figure 1 and Table II) is quite rich in intense bands. However, with the aid of gas-phase band contours and a set of frequencies calculated for the planar modes from the overlay force constants used for acrylonitrile, fumaronitrile and tricyanoethylene,[18] it was possible to make a satisfactory assignment of the planar modes. As is the case for the other cyanoethylenes, the assignment of the out-of-plane modes is still unsatisfactory.

1,1-Dicyanoethylene is an asymmetric top, the moments of inertia about the three principal axes being

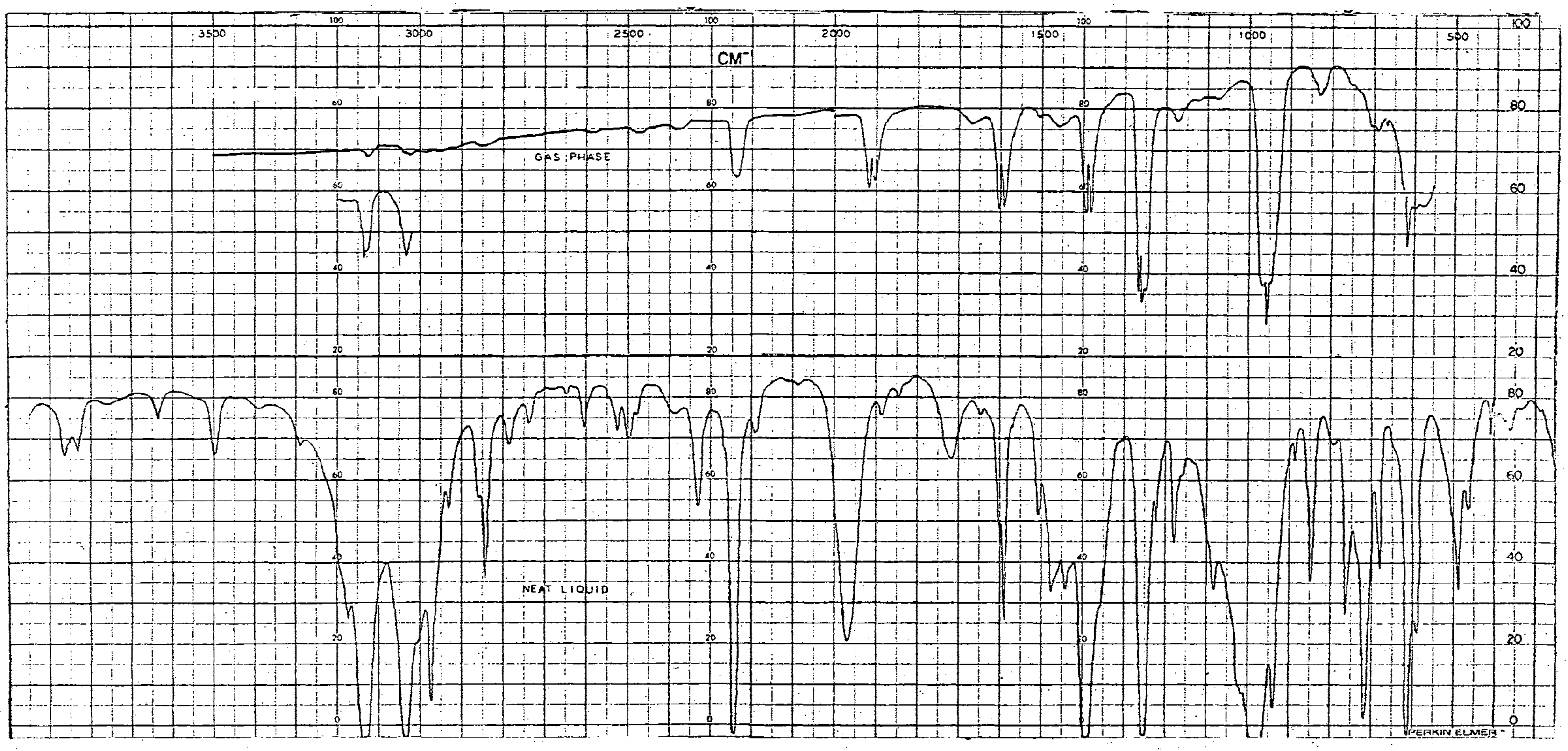


Figure 1. Infrared Spectrum of 1,1-Dicyanoethylene

TABLE II

INFRARED SPECTRUM OF 1,1-DICYANOETHYLENE

Liquid	Gas	Assignment
3964		3037 + 939 = 3976
3932		
3880		
3735		596 + 3140 = 3736
3498		2248 + 1262 = 3510
3390		
3288		
3175		
3135	3140	ν_{13}
3091		
3036	3037	ν_1
2966		720 + 2248 = 2968
2933		
2864		2255 + 620 = 2875
2846		1604 + 1262 = 2866
2791		2 x 1394 = 2788
2741		2248 + 494 = 2742
2653		1394 + 1262 = 2656
2610		
2531		1604 + 939 = 2543
2503		2 x 1394 = 2788
2482		2248 + 240 = 2488

TABLE II (Continued)

Liquid	Gas	Assignment
2334		1394 + 939 = 2333
2248	2255	ν_2
2245	2248	ν_{13}
2195		1262 + 939 = 2201
1974	1917	2 x 983 = 1966
1890		1394 + 494 = 1888
1722		
1605		983 + 620 = 1603
1594	1604	ν_3
1511		
1478		
1445		Polymer?
1395	1394	ν_4
1362		
1256	1262	ν_{15}
1227		2 x 620 = 1240
1182		Polymer
1088		
983	959	ν_{10}
939		ν_{16}
890		720 + 170 = 890
850		
762	758	596 + 170 = 766
720	709	ν_5 (?)

TABLE II (Continued)

Liquid	Gas	Assignment
685		Polymer?
620	620	ν_{11}
606		
596	587	ν_6
494		ν_{17}
469		Polymer?
415		170 + 240 = 410
383		
367		
339		2 x 170 = 340
240		ν_{18}(?)
170		ν_7

$$I_A \simeq 77.2 \times 10^{-40} \text{ g cm}^2$$

$$I_B \simeq 176.3$$

$$I_C \simeq 253.5$$

For this molecule, the A-axis lies in the molecular plane and corresponds to a line drawn through the center of mass perpendicular to the line of the C=C bond. The C-axis is perpendicular to the plane of the molecule.

The band contours to be expected for gas-phase spectra of planar asymmetric top molecules are well known.[27] For a molecule such as 1,1-dicyanoethylene, where $I_A/I_B \simeq 0.44$, we would expect that modes for which the change in dipole moment is along one of the major axes would exhibit A-, B- or C-type contours (corresponding to dipole change along the A-, B- or C-axis, respectively) as shown in Figure 2. Since 1,1-dicyanoethylene is of C_{2v} symmetry, it is to be expected that each normal mode will involve a net dipole change along one or the other of the major axes; i.e., there will be no mixing of contour types.

Of the more intense bands only the two at 959 and 620 cm^{-1} showed C-type structure. These were immediately assigned to the H-C-H and C-C-C out-of-plane wagging modes (υ_{10} and υ_{11}, respectively). The frequency of the third infrared active out-of-plane mode was apparently beyond the range of our spectrophotometer. No evidence of the infrared inactive out-of-plane modes has been found. By comparison with other cyanoethylenes the A-type bands at 3135 and 1262 cm^{-1} were assigned to the B_2 species stretch (υ_{13}) and CH_2 rock (υ_{15}). The B-type bands at 1604, 1395 and 709 cm^{-1} were similarly assigned to the C=C stretch (υ_3) and CH_2 deformation (υ_4) and the C-C stretch (υ_5) of the A_1 species.

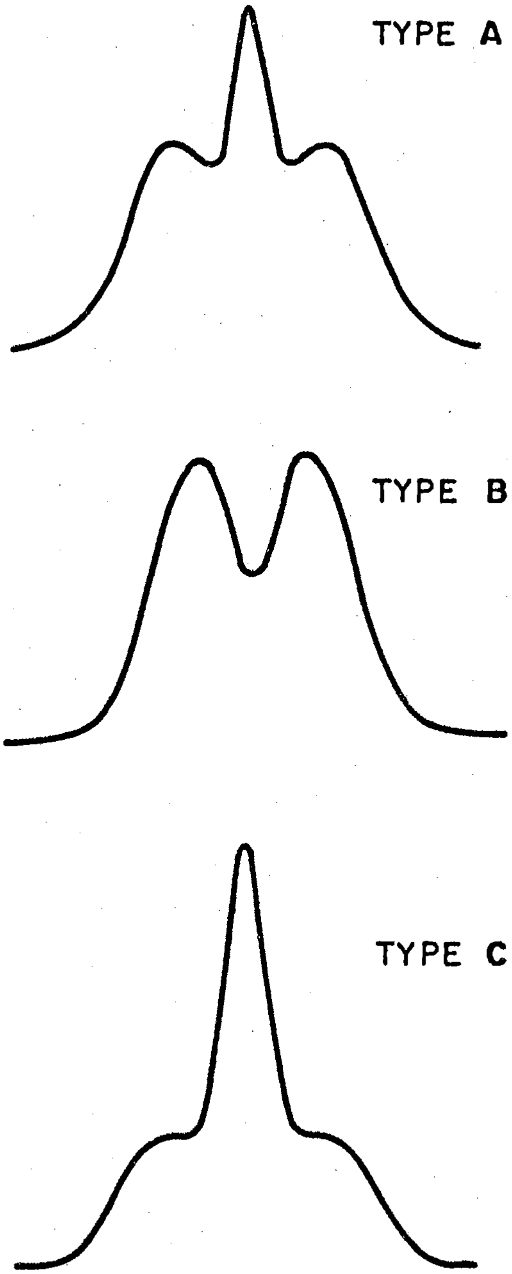


Figure 2. Gas-Phase Contours for a Planar Asymmetric Top with $I_A/I_B = 0.4$

Because of either weak gas-phase band intensities, lack of band structure or overlapping bands, the remaining fundamentals have been assigned primarily on the basis of frequencies calculated using the set of overlay Urey-Bradley force constants (UBFC) previously mentioned.[18] The observed and calculated frequencies, together with mode assignments, are shown in Table III. The calculated frequencies agree very closely with those assigned on the basis of band shapes and, except for three cases, permit immediate assignment of relatively intense bands to the remaining planar modes.

There was considerable hesitation in assigning the medium intensity band at 720 cm^{-1} as ν_5 since the calculated value of 762 cm^{-1} is assignable as $(\nu_6 + \nu_7)$, whereas no combination bands or overtones were found to explain the 720 cm^{-1} band. This, plus the greater intensity of the 720 cm^{-1} band, led to its assignment at ν_5. Unfortunately ν_7, used in the assignment of the 762 cm^{-1} band as $(\nu_6 + \nu_7)$, was not itself observed. However, the value 155 cm^{-1} calculated from the transferred UBFC was in fair agreement with the frequency of 170 cm^{-1} required to explain (by combination bands and overtones) the bands at 890, 762 and 339 cm^{-1}. Thus the assignment of ν_7 as 170 cm^{-1} is given. The third difficulty arose in the assignment of ν_{18} and has not been completely resolved. The original calculated value of 278 cm^{-1} for ν_{18} seemed to suggest that a band observed at 240 cm^{-1} should be assigned as ν_{18}. However, subsequent attempts to adjust the force constants so as to give an improved set for the entire molecular series invariably yielded a calculated frequency of about 275 cm^{-1} for ν_{18}, as can be seen in the next chapter. Nevertheless, the 240 cm^{-1} band is currently assigned as ν_{18} and only a normal coordinate treatment of the

TABLE III

RESULTS OF ZERO-ORDER CALCULATION FOR 1,1-DICYANO ETHYLENE

Symmetry Species	No.	$\nu_{obs.}$	$\nu_{calc.}$	Assignment[(a)]
A_1	1	3036	2999	C-H Stretch
	2	2248	2238	C≡N Stretch
	3	1594	1597	C=C Stretch
	4	1395	1412	HCH Bend
	5	720	765	C-C Stretch
	6	596	566	$C(CN)_2$ Scissor
	7	170	157	C-C≡N Bend
B_2	13	3135	3103	C-H Stretch
	14	2245	2237	C≡N Stretch
	15	1256	1304	HCH Bend
	16	939	956	C-C Stretch
	17	494	521	$C(CN)_2$ Rock
	18	240	278	C-C≡N Bend

(a) from the calculated potential energy distribution out-of-plane modes can help in confirming or disproving this assignment.

The assignments discussed herein appear in Table II. In addition, features have been assigned to combination, overtone or impurity bands where such an assignment was logically feasible.

CHAPTER V

FORCE CONSTANT CALCULATIONS

There are several prerequisites necessary before an overlay force constant analysis based on spectroscopic data can be attempted. First, a choice of a molecular force field must be made. As has been mentioned earlier, the Urey-Bradley force field has been selected for this investigation. Within the constraints of the force field a set of meaningful force constants must then be defined and initial values either estimated for them or transferred from similar molecules. The molecular geometry must be known, and finally, firm frequency assignments for at least most of the fundamental modes must be available.

For the planar vibrations of the cyanoethylenes a potential function involving 18 force constants was defined. A list of these constants is shown in Table IV. As before, K implies a bond stretching force constant, H a bending constant and F the interaction between nonbonded atoms. Here F is restricted to the interaction between atoms which are 1,3 with respect to each other, i.e., to the interaction between nonbonded atoms which are bonded to a common atom. The force constant C (for cis) is associated with nonbonded interactions between atoms which are 1,4 to each other and which have a cis relationship with respect to the 2,3 bond. There are, of course, three possible types of cis nonbonded interactions for the cyanoethylenes; H-H, H-C, and C-C. Throughout this investigation it was assumed that only the

TABLE IV

UREY-BRADLEY FORCE CONSTANTS FOR THE CYANOETHYLENES

Force Constant	Initial Value[(a)]
$K_{C=C}$	6.56
K_{CH}	4.83
K^*_{CH}	
K_{CN}	16.73
K_{CC}	5.17
$H_{C=CH}$	0.37
$H_{C=CC}$	0.52
H_{HCH}	0.40
H_{CCH}	0.32
H_{CCN}	0.30
H_{CCC}	0.237
$F_{C=CH}$	0.42
$F_{C=CC}$	0.76
F_{HCH}	0.00
F_{CCH}	0.18
F_{CCC}	0.64
$C_{CC=CC}$	-0.04
Tr	0.06

(a) The units of K, F and C are in mdyne/A and H is in 10^{-11} erg radian^{-2}.

last of these could be large enough to influence the calculated results. A pictorial representation of these selected force constants is shown in Figure 3 using acrylonitrile and tricyanoethylene as examples. The force constants are shown along the internal coordinates with which they are nominally associated. It should be noted that two CH stretching constants K_{CH} and K^*_{CH} are shown. During the course of this investigation it was found necessary to define one constant for the case where there are two hydrogens on a carbon (K_{CH}) and another for the case where there is only one (K^*_{CH}). The last entry in Table IV represents the interaction between trans-hydrogen bending coordinates previously mentioned.

Refined force constant values for acrylonitrile, fumaronitrile and tricyanoethylene by Devlin, Overend and Crawford[18] were used as a starting point in this work. The initial values used are listed in Table IV. Their value of 4.83 mdyne/A was used for both K_{CH} and K^*_{CH} since they used only one CH stretching constant for the 3 molecules.

Wilcox and co-workers, using microwave spectroscopy, have determined bond lengths and angles for acrylonitrile.[28,29] They concluded that the molecule is planar and thus belongs to symmetry groups C_S. The equilibrium bond distances and angles proposed are:

C-H bond	1.07A
C=C bond	1.34A
C-C bond	1.445A
C-N bond	1.159A
C=C-C angle	121.5^{o}
C=C-H angle	120^{o}

Other workers using electron diffraction[30,31] and microwave spectroscopy[31,32] have determined slightly different values for these parameters. Bond lengths for tetracyanoethylene have also been reported[33]

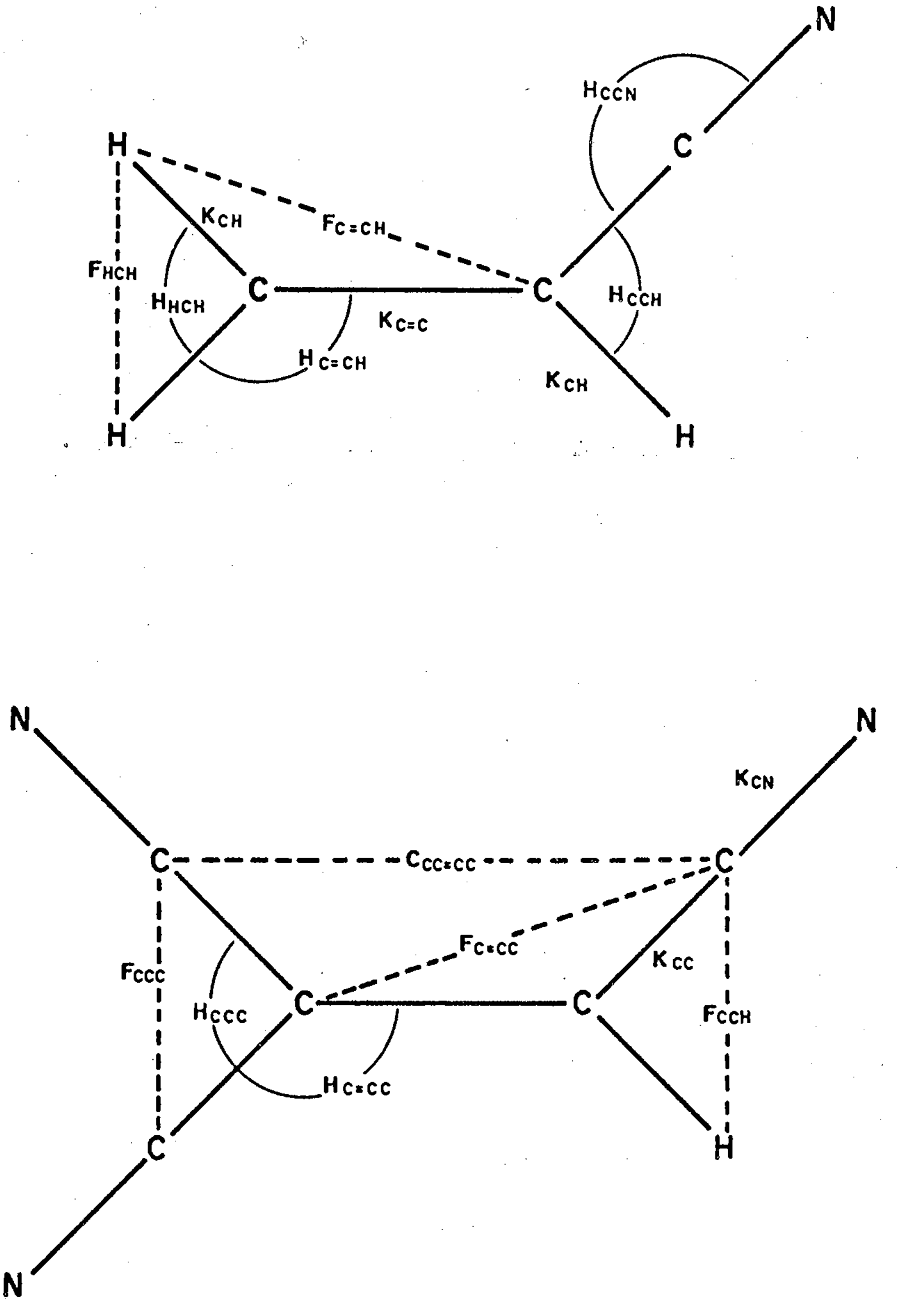


Figure 3. Urey-Bradley Force Constants for the Cyanoethylenes

which agree closely with those given by Wilcox. For the purpose of this investigation the bond lengths and bond angles given by Wilcox were employed. It was not felt that the small differences reported would affect our calculations noticeably. Moreover, the use of these values would make the present calculations more consistent with the earlier cyanoethylene work.

The calculations to be presented in the remainder of this chapter have been divided into two basic groups, calculations excluding tetracyanoethylene and calculations in which tetracyanoethylene is included. This partition is based on early evidence[20] that the bonding within tetracyanoethylene is not representative of the molecular series. Thus, force constants for the other five compounds were evaluated prior to consideration of tetracyanoethylene.

Calculations Excluding Tetracyanoethylene

Starting with the force constant values given in Table IV, overlay calculations involving the following sets of molecules have been performed: 1) fumaronitrile and maleonitrile, 2) fumaronitrile, maleonitrile and tricyanoethylene, 3) acrylonitrile, fumaronitrile, maleonitrile and tricyanoethylene and 4) all cyanoethylenes save tetracyanoethylene. The refined force constants resulting from these calculations are listed in Table V as $\Phi(1)$ through $\Phi(4)$. Calculated planar frequencies for each molecule appear in Tables VI-X. Although the percent errors in the frequencies and the stability of the force constants in sets (1), (2) and (4) are quite satisfying, these results were achieved only after extensive preliminary calculations. Set (3)

TABLE V

FORCE CONSTANTS AND DISPERSIONS OBTAINED FROM OVERLAY CALCULATIONS EXCLUDING TETRACYANOTHYLENE(a)

Force Constant	$\Phi(1)$	$\sigma_{\Phi(1)}$	$\Phi(2)$	$\sigma_{\Phi(2)}$	$\Phi(3)$	$\sigma_{\Phi(3)}$	$\Phi(4)$	$\sigma_{\Phi(4)}$
$K_{C=C}$	6.88	0.13	6.82	0.10	6.72	0.15	6.82	0.09
K_{CH}	____(d)	____	____	____	4.74(b)	0.06	4.94	0.03
K^*_{CH}	4.55	0.06	4.54	0.06			4.56	0.04
K_{CN}	16.99	0.11	16.94	0.10	16.85	0.15	16.94	0.08
K_{CC}	4.52	0.22	4.56	0.16	4.96	0.22	4.63	0.11
$H_{C=CH}$	0.29	0.09	0.29	0.08	0.29	0.06	0.35	0.03
$H_{C=CC}$	0.44	0.07	0.46	0.06	0.55	0.10	0.43	0.05
H_{HCH}	____	____	____	____	0.42	0.03	0.39	0.01
H_{CCH}	0.21	0.10	0.21	0.07	0.33	0.05	0.17	0.03
H_{CCN}	0.30	0.02	0.30	0.02	0.29	0.02	0.30	0.01
H_{CCC}	____	____	0.24	(c)	0.24	(c)	0.24	(c)
$F_{C=CH}$	0.51	0.11	0.49	0.10	0.50	0.09	0.43	0.04
$F_{C=CC}$	1.05	0.11	0.94	0.09	0.80	0.13	0.88	0.07
F_{HCH}	____	____	____	____	0.	(c)	0.	(c)

TABLE V (Continued)

Force Constant	$\Phi(1)$	$\sigma_{\Phi(1)}$	$\Phi(2)$	$\sigma_{\Phi(2)}$	$\Phi(3)$	$\sigma_{\Phi(3)}$	$\Phi(4)$	$\sigma_{\Phi(4)}$
F_{CCH}	0.52	0.14	0.53	0.10	0.26	0.07	0.57	0.06
F_{CCC}	——	——	0.80	0.10	0.75	0.16	0.86	0.07
$C_{CC=CC}$	0.08	0.05	0.04	0.05	0.05	0.07	0.04	(c)
Tr	0.06	(c)	0.06	(c)	0.06	(c)	0.06	(c)
Av. % Error in ν's	0.87		1.11		1.31		1.09	

(a) Force constants are in mdyne/A exept for the bending constants, which are in 10^{-11} erg/rad^2.

(b) Only one CH stretching constant was considered in this calculation.

(c) The value of the corresponding force constant was constrained.

(d) A line indicates that the calculation is independent of the indicated force constant.

TABLE VI

OBSERVED AND CALCULATED PLANAR FUNDAMENTAL FREQUENCIES FOR ACRYLONITRILE

ν_{obs}	$\nu(3)^{(a)}$	$\nu(4)$
3125	3090	3137
3078	3076	3064
3042	2987	3031
2239	2233	2236
1615	1604	1604
1416	1423	1407
1282	1280	1280
1096	1059	1090
869	862	868
570	574	569
242	250	251
Av. % Error	1.18	0.66

(a) The number in parentheses refers to the corresponding Φ in Table V.

TABLE VII

OBSERVED AND CALCULATED PLANAR FUNDAMENTAL FREQUENCIES FOR FUMARONITRILE

Symmetry	$\nu_{obs.}$	$\nu(1)^{(a)}$	$\nu(2)$	$\nu(3)$	$\nu(4)$
A_g	3049	3056	3052	3069	3057
	2232	2234	2231	2231	2234
	1611	1616	1610	1615	1613
	1297	1297	1294	1298	1292
	1002	1006	1008	994	1005
	545	530	520	518	514
	261	268	266	265	266
B_u	3067	3073	3068	3087	3069
	2240	2242	2237	2236	2239
	1260	1258	1259	1264	1260
	1001	992	990	982	996
	538	523	518	518	516
	155	154	153	153	152
Ave. % Error		0.86	1.11	1.32	1.24

(a) The number in parentheses refers to the corresponding Φ in Table V.

TABLE VIII

OBSERVED AND CALCULATED PLANAR FUNDAMENTAL FREQUENCIES FOR MALEONITRILE

Symmetry	$\nu_{obs.}$	$\nu(1)^{(a)}$	$\nu(2)$	$\nu(3)$	$\nu(4)$
A_1	3072	3063	3059	3077	3062
	2230	2238	2235	2234	2237
	1597	1592	1585	1588	1582
	1200	1202	1203	1183	1205
	877	884	880	886	883
	480	480	466	465	463
	126	122	119	119	117
B_2	3072	3067	3063	3080	3065
	2250	2237	2234	2233	2236
	1371	1371	1372	1393	1381
	1012	1010	1011	996	1009
	714	729	715	715	705
	269	279	278	277	279
Av. % error		0.88	1.22	1.49	1.57

(a) The number in parentheses refers to the corresponding Φ in Table V.

TABLE IX

OBSERVED AND CALCULATED PLANAR FUNDAMENTAL FREQUENCIES FOR 1,1-DICYANOETHYLENE

Symmetry	$\nu_{obs.}$	$\nu(4)^{(c)}$	$\nu(7)$
A_1	3036	3033	3036
	2248	2245	2246
	1594	1606	1598
	1395	1405	1391
	720	763 (a)	752
	596	589	592
	170	160 (a)	160 (a)
B_2	3135	3137	3136
	2245	2233	2235
	1256	1259	1262
	939	934	936
	494	519	481
	240	276 (a)	266
Av. % Error		0.91 (b)	1.63 (b)

(a) Not weighted in calculation.

(b) Calculated on basis of weighted frequencies only.

(c) The number in parentheses refers to the corresponding Φ in Table V or Table XV.

TABLE X

OBSERVED AND CALCULATED PLANAR FUNDAMENTAL FREQUENCIES FOR TRICYANOETHYLENE

$\nu_{obs.}$	$\nu(2)^{(a)}$	$\nu(3)$	$\nu(4)$	$\nu(6)$	$\nu(7)$
3043	3061	3079	3064	3043	3043
2249	2243	2244	2245	2246	2246
2234	2235	2238	2237	2235	2236
2210	2230	2233	2232	2229	2232
1594	1607	1606	1606	1581	1584
1327	1330	1353	1333	1329	1332
1171	1169	1189	1163	1181	1176
1000	998	990	1002	995	995
780	794	797	790	778	770
591	589	588	596	600	601
506	521	518	516	498	494
447	461	461	458	442	443
275	278	276	278	273	273
155	158	157	159	158	158
	119	119	117	111	111
Av. % Error	1.02	1.24	0.99	0.72	0.87

(a) The number in parentheses refers to the corresponding Φ in Table V or Table XV.

is from such a calculation and is included only to demonstrate the guidance obtained from preliminary results.

These calculations were originated with the constraints (a) force constants for similar internal coordinates are equal for all members of the series, (b) $C_{CC=CC} = -0.04$, (c) Tr = 0.06, (d) $H_{CCC} = 0.237$ and (e) $F_{HCH} = 0.0$. A comparison of the results of calculations (2) and (3) resulted in a modification of constraint (a). The molecules fumaronitrile, maleonitrile and tricyanoethylene considered in (2) contain only a single type of hydrogen, i.e., one alpha to a cyano group. An average error of 9 cm^{-1} was obtained for the C-H stretching frequencies. However, in calculation (3) acrylonitrile, which contains a (CH_2) group, was also considered and the average error in C-H stretching frequencies jumped to 23 cm^{-1} and K_{CH} increased from 4.54 to 4.74 mdyne/A. At this point it became clear that two C-H stretching force constants should be allowed, one for each type of CH bond. This was done in calculation (4). The average error in the ν_{CH} fell back to 9 cm^{-1}, even though 1,1-dicyanoethylene is also considered in this calculation. Further, two well determined K_{CH} force constants emerged: $K_{CH} = 4.56$ for hydrogen alpha to cyano and $K^*_{CH} = 4.94$ for hydrogen in a (CH_2) grouping.

Multiple values for the force constants associated with other internal coordinates would perhaps be warranted. There are, for example, large errors in the calculated frequencies for ν_6 and ν_{17} in fumaronitrile, for ν_6 in maleonitrile and for ν_{17} in 1,1-dicyanoethylene. The potential energy distributions, based on calculation (4), for these molecules are shown in Tables XI-XIII. It is clear that these modes are highly dependent on $F_{C=CC}$ and that there should perhaps be more than one force constant describing this interaction.

No attempt has been made to redetermine Tr in this investigation since no additional molecules containing trans hydrogen were considered. However, on the basis of potential energy distributions, constraint (b) was eliminated. In calculation (2), $C_{CC=CC}$ adopted a value of 0.04 mdyne/A during the least squares analysis and this value was used in subsequent calculations.

Calculations Including Tetracyanoethylene

A zero-order calculation for tetracyanoethylene using the UBFC's given in Table IV has already been reported.[20] Since the calculations described above seemed to yield a set of force constants more representative of the series, a new zero-order calculation was performed using $\Phi(4)$. The results of this calculation are given in Table XIV. Since the average error in frequency for the original zero-order calculation is 4.05%, there is only slight improvement on using the $\Phi(4)$. Nevertheless, on the basis of this calculation, ν_{17} and ν_{24}, originally assigned as 426 and 443 cm^{-1} respectively, were switched. This brings ν_{17} more in line with the calculated value of 451 cm^{-1}.

With this additional evidence that the bonding in tetracyanoethylene is not typical of the series, the approach to the vibrational analysis was altered. Rather than attempt to include this molecule in overlay calculations with other members of the series, a minimum number of force constants were transferred from overlay calculation (2) and the remaining constants were then adjusted in a least squares analysis involving only tetracyanoethylene. Thus $C_{CC=CC}$ was assigned the value of 0.04 mdyne/A and H_{CCC}, as for this entire study, was fixed

TABLE XI

DISTRIBUTION OF POTENTIAL ENERGY AMONG PLANAR INTERNAL COORDINATES OF FUMARONITRILE(a)

Force Constant	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_{13}	ν_{14}	ν_{15}	ν_{16}	ν_{17}	ν_{18}
$K_{C=C}$	0.4	0.2	59.2	19.7	0.9	2.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0
K_{CH}	89.0	0.1	0.0	0.1	0.4	0.0	0.0	88.3	0.1	0.0	0.2	0.2	0.3
K_{CN}	0.0	86.5	1.9	0.0	7.1	3.9	0.5	0.0	85.9	0.4	13.7	0.0	0.0
K_{CC}	0.1	11.4	10.9	0.7	37.9	21.2	2.8	0.1	11.5	4.6	65.8	1.1	0.8
$H_{C=CH}$	0.1	0.1	10.3	27.3	0.0	0.9	0.4	0.0	0.0	33.6	0.7	6.7	4.1
$H_{C=CC}$	0.2	0.0	0.0	3.6	14.7	11.4	6.9	0.0	0.0	0.3	0.0	18.2	18.3
H_{HCC}	0.0	0.0	5.4	6.0	6.4	2.1	1.4	0.0	0.0	19.2	0.4	0.8	1.6
H_{CCN}	0.0	0.0	0.4	0.4	2.1	22.3	74.8	0.0	0.0	0.4	0.0	49.3	50.3
$F_{C=CH}$	3.9	0.0	2.0	26.9	0.0	0.2	0.3	5.5	0.0	19.2	0.5	3.4	2.0
$F_{C=CC}$	0.1	0.8	3.3	2.1	7.1	34.4	11.4	0.0	1.7	1.8	9.3	19.7	20.2
F_{CCH}	6.3	0.8	4.8	8.6	23.4	1.1	1.3	6.1	0.9	26.4	9.6	1.8	3.1
Tr	0.0	0.0	1.8	4.7	0.0	0.2	0.1	0.0	0.0	-5.8	-0.1	-1.1	-0.7

(a) Based on the results of calculation (4).

TABLE XII

DISTRIBUTION OF POTENTIAL ENERGY AMONG PLANAR INTERNAL COORDINATES OF MALEONITRILE(a)

Force Constant	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_{13}	ν_{14}	ν_{15}	ν_{16}	ν_{17}	ν_{18}
$K_{C=C}$	0.4	0.2	70.1	6.0	5.2	0.7	0.1	0.0	0.0	0.0	0.0	0.0	0.0
K_{CH}	88.7	0.1	0.0	0.1	0.2	0.1	0.4	88.5	0.1	0.0	0.4	0.0	0.0
K_{CN}	0.0	86.2	1.4	1.0	11.1	0.2	0.0	0.0	86.3	1.8	7.6	4.1	0.2
K_{CC}	0.1	11.4	8.8	1.7	62.7	0.2	0.2	0.1	11.4	11.9	40.6	18.9	0.9
$H_{C=CH}$	0.0	0.0	4.9	28.8	1.7	2.8	3.2	0.1	0.1	37.0	0.2	4.0	0.4
$H_{C=CC}$	0.0	0.0	0.7	0.0	1.1	12.7	19.2	0.2	0.0	1.3	12.4	17.7	4.6
H_{HCC}	0.0	0.0	4.3	13.7	0.1	1.1	2.3	0.0	0.0	12.4	6.5	1.5	0.8
H_{CCN}	0.0	0.0	0.1	0.0	1.0	56.3	42.1	0.0	0.0	0.0	1.6	13.4	85.0
$F_{C=CH}$	4.6	0.0	2.5	22.4	2.4	1.0	1.7	4.8	0.0	21.1	0.2	2.4	0.2
$F_{C=CC}$	0.1	1.1	2.8	0.2	10.1	19.2	21.5	0.1	1.2	0.7	6.0	37.1	7.1
F_{CCH}	6.1	0.9	4.0	26.1	4.4	1.5	3.7	6.2	0.8	13.7	24.4	0.8	0.8
$C_{CC=CC}$	0.0	0.0	0.0	0.0	0.2	4.1	5.5	0.0	0.0	0.0	0.2	0.0	0.0

(a) Based on the results of calculation (4).

TABLE XIII

DISTRIBUTION OF POTENTIAL ENERGY AMONG PLANAR INTERNAL COORDINATES OF 1,1-DICYANOETHYLENE[a]

Force Constant	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_{13}	ν_{14}	ν_{15}	ν_{16}	ν_{17}	ν_{18}
$K_{C=C}$	0.0	0.2	58.1	17.0	6.0	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0
K_{CH}	93.8	0.0	0.5	1.1	0.0	0.0	0.0	95.1	0.0	0.0	0.2	0.2	0.1
K_{CN}	0.0	86.2	0.9	1.1	9.1	2.7	0.1	0.0	85.9	7.6	4.8	1.4	0.2
K_{CC}	0.0	10.1	4.6	4.8	44.3	9.6	0.0	0.0	12.8	42.3	32.8	4.4	0.0
$H_{C=CH}$	0.1	0.0	8.7	17.6	0.3	0.0	0.0	0.1	0.0	22.8	38.2	2.8	0.7
$H_{C=CC}$	0.0	0.0	0.6	0.7	2.2	7.9	5.3	0.1	0.1	9.9	0.4	25.0	11.3
H_{HCH}	0.2	0.0	19.3	39.2	0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H_{CCN}	0.0	0.0	0.5	0.6	3.7	27.7	67.5	0.0	0.0	0.8	0.2	26.1	72.8
H_{CCC}	0.0	0.0	0.7	0.7	2.5	8.6	5.8	0.0	0.0	0.0	0.0	0.0	0.0
$F_{C=CH}$	5.2	0.0	2.3	16.5	1.3	0.0	0.0	4.6	0.0	12.5	20.8	1.4	0.3
$F_{C=CC}$	0.1	1.1	3.1	0.2	25.5	5.6	6.1	0.1	1.2	4.5	2.7	38.7	14.5
F_{HCH}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
F_{CCC}	0.0	2.3	0.6	0.7	4.4	37.7	15.3	0.0	-0.1	-0.4	-0.3	0.0	0.0

(a) Based on the results of calculation (4).

TABLE XIV

OBSERVED AND CALCULATED PLANAR FUNDAMENTAL FREQUENCIES FOR TETRACYANOETHYLENE

Symmetry	$\nu_{obs.}$	$\nu(4)$	$\nu(5)$	$\nu(6)$	$\nu(7)$	$\nu(8)$
A_g	2235	2243	2248	2243	2246	2230
	1569	1622	1570	1582	1576	1570
	677	617	637	633	632	639
	535	529	515	518	514	516
	130	130	130	130	130	130
B_{1u}	2263	2248	2251	2247	2248	2268
	958	982	982	985	975	979
	579	594	604	599	601	603
	165	170	170	170	170	170
B_{2u}	2230	2236	2240	2237	2237	2241
	1155	1109	1150	1148	1142	1151
	443	451	435	437	437	436
	119	112	104	104	104	103
B_{3g}	2247	2231	2236	2232	2233	2236
	1282	1299	1282	1278	1283	1282
	490	509	481	485	482	481
	254	276	269	270	270	269
Av. % Error		2.88	2.74	2.69	2.76	2.66

at 0.237×10^{-11} erg/rad^2. This left 7 UBFC's to be determined by 17 frequencies.

The resulting force constants ($\Phi(5)$ in Table XV) do not differ greatly from the $\Phi(4)$. The differences which are present are easily explained. For example, the C=C and C≡N bonds are apparently significantly weaker and the C-C bond much stronger than in the other cyanoethylenes, as would be expected on the basis of increased electron delocalization. A comparison of the $\Phi(1)$ and $\Phi(2)$ indicates that this trend is detectable in tricyanoethylene before becoming critical in tetracyanoethylene. The agreement of the calculated with the observed frequencies for this calculation (Table XIV) is still not striking.

Force constants for overlay calculations involving tetracyanoethylene and tricyanoethylene [$\Phi(6)$] and tetracyanoethylene, tricyanoethylene and 1,1-dicyanoethylene [$\Phi(7)$] also appear in Table XV. Calculated frequencies corresponding to these Φ's are shown in Tables IX, X and XIV. These calculations were of no significant value in determining either the force constants or the vibrational assignment for tetracyanoethylene. Rather (7) is included because it is the only calculation in which F_{HCH} was allowed to vary. The refined value of 0.02 mdyne/A supports the choice of $F_{HCH} = 0.0$ as used in the other calculations. Calculation (6) is of some value in confirming that bonding in tricyanoethylene is intermediate to that of tetracyanoethylene and the other four molecules of the series. Furthermore, this calculation hints that the effect of an alpha cyano group on the C-H bond in tricyanoethylene is somehow attenuated, since the C-H stretching constant adopts a value midway between those found for K_{CH} and K^*_{CH} in calculation (4).

TABLE XV

FORCE CONSTANTS AND DISPERSIONS OBTAINED FROM CALCULATIONS INCLUDING TETRACYANOETHYLENE(a)

Force Constant	$\Phi(5)$	$\sigma_{\Phi(5)}$	$\Phi(6)$	$\sigma_{\Phi(6)}$	$\Phi(7)$	$\sigma_{\Phi(7)}$	$\Phi(8)$	$\sigma_{\Phi(8)}$
$K_{C=C}$	6.26	0.26	6.37	0.16	6.36	0.17	6.34	0.26
K_{CH}	____(c)	____	____	____	5.01	0.07	____	____
K^*_{CH}	____	____	4.62	0.10	4.71	0.11	____	____
K_{CN}	16.76	0.22	16.70	0.14	16.77	0.12	16.88	0.23
K_{CC}	5.22	0.26	5.17	0.19	5.12	0.17	5.19	0.25
$H_{C=CH}$	____	____	0.25	0.09	0.40	0.04	____	____
$H_{C=CC}$	0.31	0.08	0.30	0.06	0.34	0.06	0.31	0.08
H_{HCH}	____	____	____	____	0.42	0.04	____	____
H_{CCH}	____	____	0.40	0.17	0.34	0.09	____	____
H_{CCN}	0.31	0.04	0.31	0.02	0.31	0.02	0.31	0.04
H_{CCC}	0.24	(b)	0.24	(b)	0.24	(b)	0.24	(b)
$F_{C=CH}$	____	____	0.49	(b)	0.29	0.08	____	____
$F_{C=CC}$	0.67	0.19	0.73	0.11	0.65	0.09	0.66	0.18

TABLE XV (Continued)

Force Constant	$\Phi(5)$	$\sigma_{\Phi(5)}$	$\Phi(6)$	$\sigma_{\Phi(6)}$	$\Phi(7)$	$\sigma_{\Phi(7)}$	$\Phi(8)$	$\sigma_{\Phi(8)}$
F_{HCH}	——	——	——	——	0.02	0.06	——	——
F_{CCH}	——	——	0.27	0.16	0.32	0.16	——	——
F_{CCC}	0.97	0.13	0.93	0.08	0.94	0.07	0.96	0.13
$C_{CC=CC}$	0.04	(b)	0.04	(b)	0.04	(b)	0.04	(b)
Tr	——	——	——	——	——	——	——	——
ρ	——	——	——	——	——	——	0.06	0.05

(a) Force constants are in mdyne/A except for the bending constants, which are in 10^{-11} erg/rad^2.

(b) The value of the corresponding force constant was constrained.

(c) A line indicates that the calculation is independent of the indicated force constant.

Seemingly the UBFF cannot adequately encompass the effects which the resonance stabilization in tetracyanoethylene has on the vibrational energy. Scherer and Overend[13] have developed a method whereby the UBFF is modified to correct for resonance effects in aromatic rings. This method should be useful in considering electron delocalization effects in tetracyanoethylene, as will be developed below.

Several canonical forms for tetracyanoethylene are shown in Figure 4. Many more forms could be written on the basis of molecular symmetry. Considering Figure 4, stretching of the bond labeled (1) would tend to stabilize structures (b) and (c) and thus increase the energy necessary to stretch bonds (2), (3), (4) and (5). This can be expressed by the inclusion of cross terms $\rho\Delta R_1 \Delta R_2$, $\rho\Delta R_1\Delta R_3$, $\rho\Delta R_1\Delta R_4$, and $\rho\Delta R_1\Delta R_5$ in the potential energy function. Here ρ is the Kekule' constant to be adjusted in the least squares calculation and the ΔR are bond length internal displacement coordinates corresponding to the numbered bonds in Figure 4. Conversely, compression of bond (1) would stabilize structure (a), giving rise to cross terms $\rho(-\Delta R_1)\Delta R_6$, $\rho(-\Delta R_1)\Delta R_8$ and $\rho(-\Delta R_1)\Delta R_9$. These, together with similar terms which arise from consideration of the remaining bond stretching coordinates, comprise a set of cross terms which is added to the basic UBFF. The results of such a calculation appear as $\Phi(8)$ in Table XV and the calculated frequencies are shown in Table XIV. This calculation was performed exactly as was calculation (5) except that the Kekule' constant ρ was added to the set of force constants to be refined. Although there is some improvement in the agreement between calculated and observed frequencies for calculation (8) over calculation (5), the agreement is still not satisfactory. Better results might be had if more

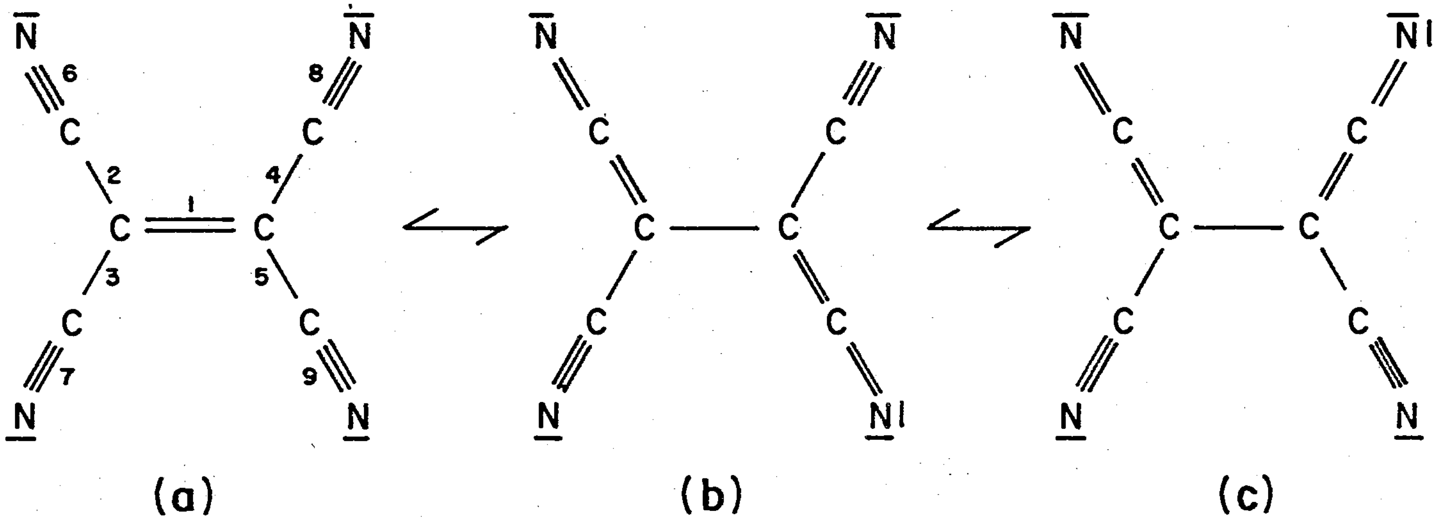


Figure 4. Some Canonical Forms for Tetracyanoethylene

than one Kekule' constant were used. This would remove the inherent assumption that all canonical forms contribute to the bond-bond interactions to the same extent. One calculation which included 3 Kekule' constants would not converge, possibly because, with 9 stretching modes primarily determined by 6 stretching force constants, the problem was too nearly exactly determined.

Nevertheless, the results of calculation (8) indicate that the modification is in the right direction. Compared to the $\Phi(5)$, $K_{C=C}$ and K_{CN} increase slightly while K_{CC} decreases slightly. As would be expected, the bending and nonbonded interaction constants show little or no change.

CHAPTER VI

DISCUSSION

As a result of the overlay calculations reported in the previous chapter, a set of force constants $\Phi(4)$ has been determined which adequately determines the planar fundamental modes of all cyanoethylenes with the exception of tetracyanoethylene. Satisfactory results for tetracyanoethylene were not derived, even when effects of electron delocalization were considered.

Considering the results of calculations (1), (2) and (4), it is surprising that the error in the calculated frequencies is nearly constant regardless of the number of molecules included in the overlay. The average percent errors in calculated frequencies for these three calculations are 0.87, 1.11 and 1.09 respectively. The only difference between calculations (1) and (2) lies in the fact that tricyanoethylene is included in (2) but not in (1). It thus appears again that the inclusion of tricyanoethylene does introduce some bonding features not common to the other four molecules. This effect is undoubtedly a result of increased conjugation.

The average percent error (1.09%) quoted for calculation (4) is somewhat misleading. During that calculation neither ν_5, ν_7 nor ν_{13} of 1,1-dicyanoethylene were weighted so that error in these modes was not included in the average. If the presently assigned values of 720, 170 and 240 cm^{-1} are used, the average percent error is increased to 1.49

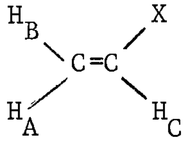
for the entire calculation. Also, it would seem that the results of calculation (4) confirms the assignment of ν_7 as 170 cm^{-1} while favoring the alternate assignment of ν_5 as 762 cm^{-1} and suggesting that ν_{13}, tentatively assigned as 240 cm^{-1}, has not as yet been observed.

Examination of stretching force constants calculated for other small molecules indicates that resonance effects are important even in lower cyanoethylenes. In calculation (4) a value of 6.82 mdyne/A was adopted by $K_{C=C}$. A similar calculation for ethylene yields a value of 7.46 mdyne/A.[21] Likewise, for a series of saturated nitriles K_{CN}= 18.2-18.5 and K_{CC}= 3.1-3.2 mdyne/A as opposed to 16.94 and 4.63 mdyne/A in this investigation.[7] It is clear that, for the cyanoethylenes, the C≡N and C=C bonds are weaker and the C-CN bond is stronger than would be expected in the absence of delocalization.

It is quite apparent that the C-H bond is significantly weakened by an alpha-cyano group. Consideration of the force constants for cis-, trans- and gem-difluoroethylenes shows the same phenomenon for an alpha-fluorine,[34] whereas an alpha-bromine has very little effect.[21] In fact the weakening of the C-H bond is definitely correlated with the magnitude of the F_{HX} interaction which has the values 1.10, 0.57 and 0.33 mdyne/A when X is F, CN and Br respectively. It is also known that the C-H bond is lengthened by an adjacent fluorine.[35] Further, the relative chemical shifts in the nuclear magnetic resonance spectra of a large number of vinyl compounds show that alpha electronegative groups have the effect on the electron density about hydrogen which is typical of hydrogen bonding.[36,37] These data, summarized in Table XVI, show that a strong correlation also exists between these electron densities and the magnitude of F_{HX}. These facts indicate the possible existence of an intramolecular hydrogen bond. If this is so, then the interaction force constant F_{HX} is a measure of the strength of this hydrogen bond, not a measure of the H-X repulsive force.

TABLE XVI

RELATIVE CHEMICAL SHIFTS FOR A SERIES OF VINYL COMPOUNDS



X	$\delta_B - \delta_C$(a)	$\delta_A - \delta_C$	F_{HX}(b)
F	77	89	1.10
Cl	32	37	0.57
CH_3	34	37	0.55
Br	25	19	0.33
OCH_3	91	99	——

(a) Units for chemical shifts are hertz.

(b) Units are mdyne/A.

The positive value adopted by $C_{CC=CC}$ may be indicative of a stabilizing interaction between cis carbon atoms. Thus one might expect ΔH for the cis-trans conversion to be greater than zero, as is the case for the 1,2-difluoroethylenes.[38] However, fumaronitrile is predominant at equilibrium, suggesting that ΔH is less than zero. This indicates that, for the cyanoethylenes, resonance stabilization, which favors the trans configuration, dominates over any stabilizing cis nonbonded interaction.

An alternative explanation for the magnitude of the nonbonded interaction constants is suggested by the work of Bruns et al.[39] The results of a semi-empirical molecular orbital calculation for OF_2 raise the possibility that many nonbonded interaction force constants are greatly inflated by electron delocalization. Thus F_{HX} may not be an accurate measure of a nonbonded interaction but may arise mainly from a (CH,CX) bond-bond interaction term. If this is true, then no conclusions concerning the nature of the nonbonded interaction can be drawn from considerations of the sign or magnitude of the force constant since its effect would be effectively masked by that of the bond-bond interaction.

PART II

AN ALGORITHM FOR THE DETERMINATION OF THE SHAPE PARAMETERS OF INFRARED ABSORPTION BANDS

CHAPTER I

INTRODUCTION

The Problem

There are basically two types of information which may be derived from an infrared spectrum, the positions of absorption bands and their intensities and shape factors. Band positions are indicative of the energy associated with the vibrational or vibrational-rotational transitions causing the absorption and, because of this, have been used for decades in studies of inter- and intramolecular forces. The work in Part I is but one example of the use of spectroscopic data for this purpose.

Intensity and shape information have not been used extensively as a tool for the interpretation of infrared spectra. Whereas primary frequency standards make it possible to exchange band position data between laboratories, no intensity standards have been developed for use with ordinary laboratory spectrophotometers. Also, observed intensity values are highly dependent on instrumental parameters. As a result, it is almost impossible to compare uncorrected data from different instruments. Finally, any given infrared absorption band, being of finite line width, is often overlapped with an adjacent band. This overlap adds to the difficulty in evaluating the intensity and shape factors for either band.

The purpose of this investigation was to develop a mathematical technique whereby accurate intensity and shape information could be derived from ordinary infrared spectra.

The Shape of Infrared Absorption Bands

Seshadri and Jones[40] have published a definitive review article concerning the shapes of infrared absorption bands. The discussion in this section is largely based on this review, with additional references as cited.

Consideration of absorption and emission spectra of materials in gas phase indicates that there are three factors which contribute to the line width of spectroscopic transitions. These are radiation damping, the Doppler effect and collision broadening.

According to classical theory,[41] radiation damping arises because a vibrating electric charge radiates, and thus constantly loses, energy. As a consequence the amplitude of vibration is diminished while the natural frequency ν_o of the oscillator is maintained. A damped vibration of this type is not monochromatic; its frequency distribution may be determined by a Fourier analysis of the electric moment as a function of time. This yields

$$I_\nu = \frac{\Delta\nu/2\pi}{(\nu-\nu_o)^2 + (\Delta\nu/2)^2} \qquad (1)$$

where I_ν is the intensity at frequency ν and $\Delta\nu$ is the line width at half-height in cm^{-1}. The line width is given by

$$\Delta\nu = \frac{4\pi e^2}{3mc^2} \; \nu_o^2 \qquad (2)$$

where m and e are the mass and charge, respectively, of the oscillator and c is the speed of light. In terms of wavelength the line width is

$$\Delta\lambda = \frac{4\pi e^2}{3mc^2} = 1.17 \times 10^{-4} \text{ Å} \tag{3}$$

According to quantum mechanics, the natural line width (equivalent to radiation damping in the classical treatment) arises because each of the two energy levels E_1 and E_2, between which a transition occurs, is not sharp but has a finite width ΔE_1 and ΔE_2 respectively. The expression for the half width of the transition is then made up of the term widths of the two states:

$$\Delta\nu = \Delta E_1/h + \Delta E_2/h \tag{4}$$

where h is the Planck constant. Applying the Heisenberg uncertainty principle:

$$\Delta E_1 \cdot \Delta t_1 \sim h/2\pi \tag{5a}$$

$$\Delta E_2 \cdot \Delta t_2 \sim h/2\pi \tag{5b}$$

where Δt_1 and Δt_2 are the average times that the molecule remains in energy states E_1 and E_2. Under the assumption that only infrared fundamental bands are to be considered; i.e., that all transitions are between the ground and first excited states, the band width can be expressed as

$$\Delta\nu = \frac{4\pi e^2}{mc^2} (\nu_{2,1}^2 \ f_{2,1}) \tag{6}$$

where $f_{2,1}$ is the oscillator strength of the transition whose frequency is $\nu_{2,1}$.

A comparison of equations 2 and 6 shows that the quantum mechanical treatment differs from the classical approach by a factor of $3f_{1,2}$. The oscillator strengths of infrared transitions are less than unity[40] so that the value derived from the classical model may be regarded as an upper limit to the true natural line width. Line widths calculated by this method are of the order of 10^{-6} cm^{-1} at 1000 cm^{-1}. Since observed band widths are of the order of 1-20 cm^{-1}, it may be concluded that radiation damping is relatively unimportant in the evaluation of infrared absorption band shapes.

Doppler broadening results from thermal motion of the molecules. Molecules having a velocity component, V, toward or away from the radiation source will absorb or emit at the frequency ν according to

$$\nu = \nu_o(1 \pm V/c) \tag{7}$$

where ν_o is the frequency which would be observed for the molecule at rest. The fraction of molecules within a velocity range ∂V is given by

$$\frac{dn}{n} = \left[\frac{M}{2\pi RT}\right]^{\frac{1}{2}} \exp\left[-(M/2RT)\nu^2\right] \quad d\nu \tag{8}$$

where M is the molecular weight of the gas, R is the gas constant and T is the absolute temperature. The total intensity at frequency ν is then

$$I_\nu = \left[\frac{Mc^2}{2\pi RT\nu_o^{\;2}}\right]^{\frac{1}{2}} \exp\left[-\left(\frac{Mc^2}{2RT\nu_o^{\;2}}\right)(\nu-\nu_o)^2\right] \tag{9}$$

The Doppler effect thus predicts a Gaussian band shape with a band width given by

$$\Delta\nu = 2(\ln 2)^{\frac{1}{2}} \left[\frac{2RT}{Mc^2}\right]^{\frac{1}{2}} \nu_o \qquad (10)$$

Using equation 10 with $\nu_o = 1000\ \text{cm}^{-1}$ and a molecular weight of 100 at 20^oC, $\Delta\nu$ is calculated to be $1.2 \times 10^{-3}\ \text{cm}^{-1}$. This is less than the limits of precision in infrared spectroscopy and it may then be concluded that Doppler broadening is too small to affect band shape measurements.

Collision broadening arises from a perturbation of the energy levels of an absorbing or emitting molecule caused by close approach of other molecules. The effect of such perturbations on a band profile was first derived by Lorentz[42] and later refined by Van Vleck and Weisskopf.[43] Classically, the equation of motion for an oscillator of natural frequency ω_o radians/sec., mass m and charge e with an electrical field $E \cos \omega t$ is

$$m \frac{d^2X}{dt^2} + \omega_o^2 X = eE \cos \omega t \qquad (11)$$

This differential equation has a solution of the form:

$$X = C_1 \exp(i\omega t) + C_2 \exp(i\omega_o t) + C_3 \exp(-i\omega_o t) \qquad (12)$$

where

$$C_1 = \frac{eE}{m(\omega_o^2 - \omega^2)} \qquad (13)$$

and C_2 and C_3 are determined by the nature of the collision. As the result of a collision, X and dX/dt have taken on values which determine the behavior of the oscillator until the occurrence of the next collision. In order to evaluate an average value of X over the varying time intervals from the last collision, equation 12 is multiplied by the probability that the molecule will collide again after a lapsed time θ. The probability is given by

$$n(t) = \frac{1}{V} \exp\left(-\frac{1}{V}\right) \partial\theta \tag{14}$$

where V is the mean time between collisions. The resulting equation for $\overline{X}$ (the average value) is a function containing real and imaginary parts and, for the imaginary part, it can be shown that the absorption coefficient α at frequency ω is

$$\alpha_{\omega} = \frac{2\pi n e^2}{mc} \cdot \frac{\omega}{\omega_o} \left[\frac{1/V}{(\omega-\omega_o)^2 + (1/V)^2} - \frac{1/V}{(\omega+\omega_o)^2 + (1/V)^2} \right] \tag{15}$$

where n is the number of molecules in the system. This equation defines a profile which will be referred to in succeeding portions of this work as a Lorentz profile. On modifying the expression so that it is more useful for the analysis of infrared absorption spectra, equation 15 becomes[40]

$$\alpha_{\nu} = \frac{K}{\pi} \frac{\Delta\nu/2}{(\nu-\nu_o)^2 + (\Delta\nu/2)^2} \tag{16}$$

where K is a function of the particular band. At $\nu = \nu_o$, equation 16 yields

$$\alpha_{\nu o} = \frac{2K}{\pi\Delta\nu} \tag{17}$$

or

$$\frac{K}{\pi} = \frac{\alpha_{\nu o}\,\Delta\nu}{2} \tag{18}$$

Making the appropriate substitution and designating $\alpha_{\nu o}$ as A_o, the peak absorbance of the absorbing species, and α_ν as A_ν, the absorbance at frequency ν, equation 16 may be written

$$A_\nu = \frac{A_o(\Delta\nu/2)^2}{(\nu-\nu_o)^2 + (\Delta\nu/2)^2} \qquad (19)$$

Finally, multiplying numerator and denominator by $(2/\Delta\nu)^2$ yields

$$A_\nu = \frac{A_o}{1 + (2/\Delta\nu)^2(\nu-\nu_o)^2} \qquad (20)$$

Although the above derivations arise from consideration of the behavior of gases, many workers have used the Lorentz function or modifications of it in studies involving condensed materials.

The Effect of Finite Slit Widths

When a spectrometer is set to transmit radiation of a given frequency a frequency band of finite width is actually transmitted. The energy distribution of this band is generally symmetrical about the nominal frequency and its width is a function of the mechanical slit settings, resolving power and optical aberrations of the spectrometer. The transmittance observed for a sample at any frequency ν' is thus not only dependent on the absorption coefficient at ν' but is also a function of the absorption coefficients across the detected frequency band. If the energy distribution over the detected frequencies is designated as $g(\nu,\nu')$, the apparent transmittance value, T_ν^a, is given by[44]

$$T^a_{\nu'} = \frac{\int T\nu g(\nu,\nu')d\nu}{\int g(v,\nu')d\nu} \qquad (21)$$

where the convolution is performed over the range of detected frequencies. It is apparent from this equation that the magnitude of error introduced by a symmetric slit function is dependent on $\partial^2 T_\nu/\partial\nu^2$. Where the slope of the observed spectrum is relatively constant, T_ν^a will approach T_ν. However, where the slope is changing rapidly, as is the case near the center of an absorption band, considerable error results. Moreover, the relative error varies for bands of different intensity[45,46] giving rise to the curvature often observed in Beer's law plots derived from data taken at large slit widths.

The function $g(\nu,\nu')$ may be visualized by considering the effect of scanning a spectrometer with a finite spectral slit width across a region of the spectrum containing an infinitely narrow absorption band. The signal observed under these conditions could be regarded as the locus of $g(\nu,\nu')$, where ν' is the position of the absorption. For very narrow slits $g(\nu,\nu')$ may be regarded as a diffraction function with a large maximum at ν'. If the slits are wide compared to the wavelength of the transmitted radiation, as is usually the case in infrared spectrometry, the secondary maxima of the diffraction function may be disregarded, and the distribution regarded as approximately triangular,[44] as shown in Figure 5. The triangular distribution actually applies only to the situation where the entrance and exit slits are of equal size, but this configuration is used in all commercial infrared spectrometers. The function depicted in Figure 5 may be described by the equation

$$g(\nu,\nu') = \begin{cases} S-|\nu'-\nu|, & |\nu'-\nu| \leq S \\ 0 & , |\nu'-\nu| \geq S \end{cases} \tag{22}$$

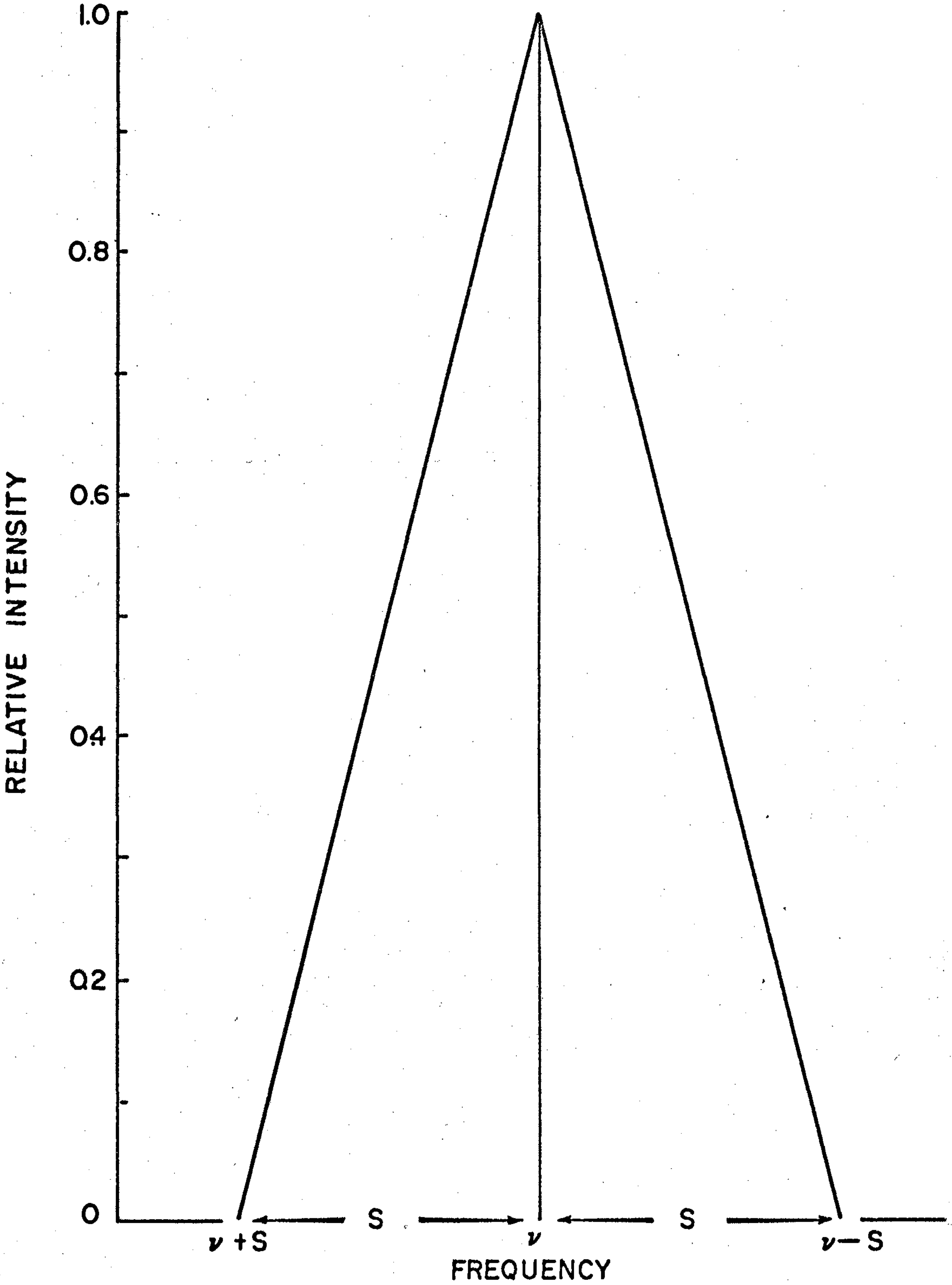


Figure 5. The Triangular Spectral Slit Function

where S, the spectral slit width, is defined as half the frequency interval subtended by the spectrometer when set to ν'.

Studies of Infrared Band Profiles

Most of the significant work in the study of the shapes of infrared absorption bands has been done by Jones and co-workers.[40,47-49] Their study has included the Lorentz and Gauss functions and the sum and product functions of these two. At present, Jones is using the Lorentz-Gauss sum function almost exclusively.[50] It should be pointed out that the primary object of this group is to reduce infrared data to a minimal number of numerical indices, not to extract true intensity data.

Abramowitz and Bauman[51] and Fraser and Suzuki[52] have also used Lorentz-Gauss sum and product functions, but the former have concluded that, at narrow slit widths, most absorption bands are almost purely Lorentzian. Early work in this laboratory indicates that this conclusion is correct. In a study of the hydrogen bonding of esters and alcohols, overlapped carbonyl stretching absorption bands were successfully resolved on the basis of a Lorentz band shape.[53,54] The same algorithm was used to resolve carbon-hydrogen stretching bands in the spectra of aliphatic molecules.[55]

The Scope of the Present Investigation

For the purposes of this investigation infrared absorption bands are regarded as Lorentz functions convolved by a triangular slit function. This mathematical model was chosen because (1) unlike the earlier models used in this laboratory and elsewhere, the effect of finite slits is included as a separable factor and (2) it is felt, in light of the above discussion of the factors influencing band shape, that the parameters derived from this model would have more physical significance than those calculated using more complex models such as the Lorentz-Gauss sum function.

A computer program was designed and written for the purpose of performing the calculations necessary for the analysis. Several spectra, containing varying amounts of noise, were synthesized and used in testing the convergence characteristics of the program.

The experimental phase of this study consisted of the acquisition of data from infrared spectra of several esters and simple aromatic compounds. The former were chosen because their carbonyl stretching bands are well isolated from other bands while the latter provided a system of relatively narrow out-of-plane hydrogen bending bands which are highly susceptible to slit broadening. In addition, the various aromatic compounds provided the opportunity to determine the effectiveness of the model in the separation of overlapping bands.

The infrared data was then fitted to the model described above. The results clearly show that the slit-convolved Lorentz function is quite adequate to fit the observed data. In addition, analysis of data taken at several different slit widths indicate that the mathematical analysis is reasonably effective in removing distortion from this cause.

CHAPTER II

DEVELOPMENT OF THE ALGORITHM

The Calculated Spectrum

An infrared absorption spectrum containing one or more bands may be regarded, in the absence of slit perturbations, as a summation of functions of the type given in equation 20. Under this assumption, the absorbance calculated for any frequency ν is then

$$A_\nu^o = \sum_{i=1}^{N} \frac{A_{0i}}{1 + (2/\Delta\nu_i)^2(\nu-\nu_{0i})^2} + \beta \tag{23}$$

where A_{0i}, $\Delta\nu_i$, and ν_{0i} are the peak absorbance, line width and band position, respectively, for the i-th band and N is the number of bands contributing to the spectrum. The zero superscript on the left hand side denotes that the absorbance has been calculated under the assumption of zero slit width. The constant β is included to absorb small baseline errors.

The basic physical quantity measured by most commercial spectrometers is transmittance. It is thus more meaningful to perform the band shape analysis in terms of this variable. Also, for reasons which will become clear later, it is more convenient to regard the spectrum not as a continuous function but as a vector composed of discrete samples taken at equal increments of the independent variable (frequency).

The transmittance calculated for the k-th data point of the calculated spectrum is thus

$$T_k^o = \exp\left[-\sum_{i=1}^{N} \frac{A'_{0i}}{1 + \rho_i(\nu_k - \nu_{0i})^2} - \beta'\right] \tag{24}$$

where $A'_{0i} = 2.303\ A_{0i}$, $\beta' = 2.303\ \beta$, $\rho_i = (2/\Delta\nu_i)^2$ and ν_k is the frequency corresponding to the k-th datum.

In terms of discrete samples, the expression for the slit function (equation 22) becomes

$$g(\nu,\nu_k) = \begin{cases} S - \left|\nu_k - \nu_{k+j}\right| = S - jx; & j = 0,1,2,\cdots,m \\ 0, & j \geq m \end{cases} \tag{25}$$

where m is the number of samples contained in S cm^{-1} and x is the sampling interval. The slit convolution can then be expressed as a summation

$$T_k^{calc} = a_o\ T_k^{\ o} + \sum_{j=1}^{m} a_j\ (T^o_{k+j} + T^o_{k-j}) \tag{26}$$

where T_k^{calc} is the value calculated for the k-th datum. The coefficients a_j are easily shown from equation 25 to be

$$a_j = \frac{S - jx}{F}\ ; \qquad j = 0,1,2,\cdots,m-1 \tag{27a}$$

$$a_m = \frac{S - mx}{2F} \tag{27b}$$

where F is the normalization factor given by

$$F = 2mS - m^2x \tag{28}$$

The factor of 2 is included in the numerator of equation 27b to make the numerical integration in equation 26 conform to the trapezoidal rule.

An alternative model for the slit convolution may be developed if it is assumed that any 2 S cm^{-1} region of the calculated spectrum is well approximated by a simple polynomial in S - $(\nu_k - \nu)$, such as

$$T_Z^o = \sum_{i=0}^{m} a_i Z^i \quad , \quad -S \leq Z \leq S \tag{29}$$

where Z = S - $(\nu_k - \nu)$ and M is the degree of the polynomial. The convolution is then

$$T_k^{calc} = \frac{\int_0^S T_z^o (S-z)\partial Z + \int_{-S}^0 T_Z^o (S+Z)\, \partial Z}{\int_0^S (S-Z)\partial Z + \int_{-S}^0 (S+Z)\, \partial Z} \tag{30}$$

Substituting the expression for T_z^o, the integrals are easily evaluated and the expression for T_k^{calc} becomes

$$T_k^{calc} = 2 \sum_{i=0}^{m} \delta_i \left(\frac{1}{i+1} - \frac{1}{i+2}\right) a_i\, S^i \tag{31}$$

where δ_i is unity for even i and zero for odd i. The a_i are readily determined from the T_k^o by use of the simplified least-squares procedure outlined by Savitsky.[56] The computer program developed in this investigation allows the use of either slit convolution model.

The Least-Squares Procedure

The object of this algorithm is to choose a set of 3N+1 band parameters A_{0i}, $\Delta\nu_i$, ν_{0i}, and β for a spectrum containing N bands such that the best fit is obtained between the observed and calculated transmittance values. According to the least-squares criterion, this is achieved when the sum of squares of the deviations is a minimum:

$$\sum_{k=1}^{P} (T_k^{obs} - T_k^{calc})^2 = \text{minimum} \tag{32}$$

where P is the number of elements in the vector of observed transmittance values. Since the T_k^{calc} are not linearly related to the band parameters, the Gauss-Newton nonlinear regression method was chosen for the analysis.[57]

For the sake of convenience, the various band parameters are now regarded as elements of a parameter vector whose elements are Q_i, where $i=1,2,\cdots,3N+1$. A set of initial parameter values, Q_i', are estimated and used to calculate a vector of the T_k^{calc}. If the initial estimate is reasonably close to the true value, the residual function may be linearized by using a first order Taylor's expansion

$$R_k' = (T_k^{obs} - T_k^{calc})' = \sum_{i=1}^{3N+1} \left(\frac{\partial T_k}{\partial Q_i}\right)' \Delta Q_i \tag{33}$$

where $\Delta Q_i = Q_i - Q_i'$ and the primes indicate that the indicated terms are to be evaluated for the approximate values of the parameters. This equation is linear and may be solved for the ΔQ_i by ordinary least-squares methods, viz.:

$$\overline{\Delta Q} = B^{-1}\bar{Z} \tag{34}$$

where $\overline{\Delta Q}$ is a vector of the ΔQ_i, B^{-1} is the inverse of a matrix B whose i,j-th element is

$$B_{ij} = \sum_{k=1}^{P} \left(\frac{\partial T_k^{\text{calc}'}}{\partial Q_i}\right) \left(\frac{\partial T_k^{\text{calc}'}}{\partial Q_j}\right) \tag{35}$$

and $\bar{Z}$ is a vector whose i-th component is

$$Zi = \sum_{k=1}^{P} \left(R_k \frac{\partial T_k^{\text{calc}'}}{\partial Q_i}\right) \tag{36}$$

The Q_i' are adjusted by the ΔQ_i and the process is repeated until minimum for equation 32 is obtained.

A computer program (BANDFIT) has been written to implement the algorithm outlined in this chapter. The digitized infrared spectrum together with a set of band parameter estimates and control information comprise the input data for this routine. From the parameters and the specified spectral slit function, a calculated spectrum is generated and the error sum of squares is evaluated. The partial derivative sums necessary for the construction of matrix B are calculated at this time. Matrix B is then inverted, the ΔQ's are evaluated and the original estimate set is updated. The problem is then recycled using the new parameter set. This process is repeated until either a minimum in the error sum of squares has been reached or the fractional improvement in the sum of squares for two successive cycles falls below the limit set by the user. A listing of program BANDFIT and instructions for its use may be found in the Appendix.

CHAPTER III

EXPERIMENTAL

General

All materials, with the exception of solvents, used in this investigation were purified by preparative gas chromatography before use. Solvents were used without further purification.

Infrared sampling cells were calibrated in the normal manner from their diffraction pattern. Standard deviations in these calibrations were determined to be less than 0.4 percent relative to the path length.

The true zero reading for the slit micrometer of the infrared spectrometer was determined by plotting the square root of single beam energy vs. the micrometer index. The intercept of this plot was taken as the zero offset error and was used to correct subsequent micrometer readings.

Data Acquisition

All spectra were determined using a Perkin-Elmer Model 621 double-beam infrared grating spectrometer. The spectrometer was equipped with an encoding device so that digitization of transmittance values could be commanded at equal frequency intervals. These intervals could be varied from 0.1 to 10.0 cm^{-1}. All data for this investigation were acquired at intervals of either 0.5 or 0.2 cm^{-1}. The transmittance data were recorded as 3-digit numbers on computer-compatible magnetic tape for processing at a later time.

The scanning rate for all spectra was kept below 1 cm^{-1}/sec. This was done to minimize servo errors which might become important at higher rates.

Solution and solvent spectra were determined separately. During computer processing each solution spectrum was divided by the appropriate solvent spectrum to yield the equivalent of a differential spectrum determined with perfectly matched cells. This was done to cancel out all effects arising from cell aberrations and differences between the refractive indices of the salt plates and the solution.

Evaluation of the Spectral Slit Width

The equation given by Seshadri and Jones[40] was used to determine spectral slit width values in this investigation. For a spectrometer set at frequency ν with a mechanical slit width w_s, S is given by

$$S = \frac{\nu^2 d}{NnF} \left[1 - \left(\frac{n}{2\nu d}\right)^2\right]^{\frac{1}{2}} \left\{w_s + \left[\left(\frac{F}{B\nu}\right)^2 + w_A^2\right]^{\frac{1}{2}}\right\} \qquad (37)$$

where d is the grating spacing, N is the number of grating passes, n is the order of the spectrum, F is the focal length of the monochromator, B is the limiting aperture of the spectrometer and w_A is the virtual mechanical slit width arising from aberrations. All terms save B and w_A were available from either the instrument settings or the manufacturer's literature. The effective aperture was determined from a measurement of the illuminated portion of the grating and w_A was assigned the value of 0.004 cm as recommended by Seshadri and Jones.

A constant physical slit width was employed for spectra taken in the region 1950-1550 cm^{-1} since this procedure gives more flexibility in choosing a spectral slit width than does the instrumental slit program and since $\partial S/\partial \nu$ for a constant w_s is small in this region. For spectra in the 800-650 cm^{-1}, however, use of the slit program was necessary because the size of the derivative precluded the use of fixed slits.

CHAPTER IV

RESULTS AND DISCUSSION

Synthetic Spectra

As was mentioned previously, synthetic spectra were used to evaluate the band shape analysis computer program. Before discussing the results of these analyses, it would be appropriate to describe the method used to generate the spectra. For each synthetic spectrum, a vector of transmittance values was generated using equations 24 and 26. A "noise" vector was also generated by indexing a table of random normal deviates with a pseudo-random number generator. This vector was then scaled to the desired signal-to-noise ratio (S/N) and combined with the transmittance vector to yield the synthetic spectrum. Before analysis, each datum was truncated to three decimal places so as to conform to the data format of the real spectrometer.

Three sets of synthetic spectra were analyzed using program BANDFIT. The first set was composed of 24 spectra, each containing a single band with $A_o = 1.0$, $\Delta\nu = 1.0$, $\Delta\nu = 10.0\ \text{cm}^{-1}$ and $\nu_o = 1000\ \text{cm}^{-1}$. Transmittance vectors spanned the range 1050-950 cm^{-1} with a sampling interval of 0.5 cm^{-1}. Results of the least-squares procedure appear in Table XVII, and a graph of the synthetic spectrum and that calculated on the basis of the refined parameters for the case where $S = 4.0\ \text{cm}^{-1}$ and $S/N = 200$ is shown in Figure 6. Refined values for ν_o and β do not

TABLE XVII

RESULTS FROM ANALYSES OF SYNTHETIC SPECTRA CONTAINING ONE BAND

Spectral Slit Width, cm^{-1}	S/N	Refined Parameters		Error Sum of Squares x 10^2	Least-Squares Cycles
		Ao	$\Delta\nu$, cm^{-1}		
0.	400	1.0012	9.98	0.105	3
	200	1.0034	9.95	0.410	3
	100	1.0069	9.90	1.615	3
	50	1.0142	9.80	6.397	3
1.	400	1.0018	9.97	0.099	5
	200	1.0035	9.95	0.407	4
	100	1.0080	9.89	1.621	4
	50	1.0160	9.78	6.420	4
2.	400	1.0019	9.97	0.102	7
	200	1.0044	9.94	0.401	6
	100	1.0081	9.89	1.603	6
	50	1.0159	9.78	6.352	5
4.	400	1.0016	9.98	0.103	10
	200	1.0042	9.95	0.394	9
	100	1.0080	9.90	1.563	8
	50	1.0162	9.79	6.231	7
7.	400	1.0012	9.98	0.092	12
	200	1.0018	9.97	0.361	11
	100	1.0043	9.94	1.435	10
	50	1.0082	9.88	5.698	9
10.	400	0.9994	10.00	0.081	15
	200	1.0009	9.98	0.320	14
	100	1.0007	9.97	1.286	13
	50	1.0010	9.93	5.075	12

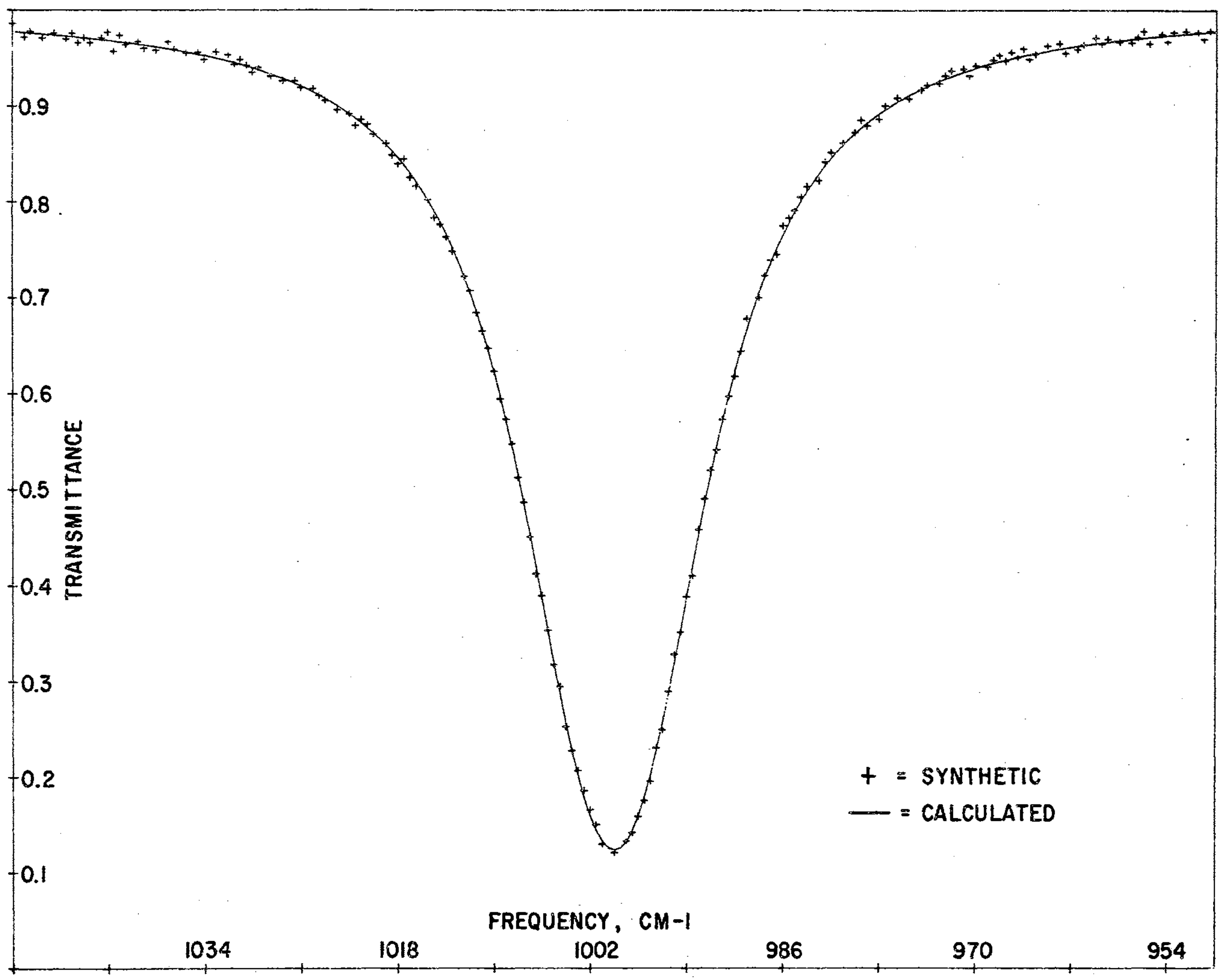


Figure 6. Single-Band Synthetic Spectrum with
4 cm^{-1} Spectral Slit

appear in the table since ν_o converged to the true value in all cases and β was constrained at zero. For the most part, the other two parameters converged to reasonably accurate values. There does, however, appear to be a relationship between S/N and the calculated values for A_o and $\Delta\nu$. The reason for this dependence is not completely understood, but it is believed to arise from a local bias in the noise vector. This is plausible since a single vector, scaled to give the various S/N values, was used for all spectra in the set. An examination of the noise pattern indicated some bias in the vicinity of the band center but it was not of sufficient magnitude to be responsible for the observed deviations. In any case, the effect is probably due to an artifact and is unimportant at moderate noise levels.

The relationship between the spectral slit width and the number of cycles taken in the analysis is a direct result of the fact that initial estimates of the parameter values were taken from the simulated spectrum. For wide spectral slits, therefore, the estimates are farther from the true values than for narrow slits and the least-squares procedure consequently requires more iterations to converge. Also, at smaller values of S/N, the error sum of squares levels off sooner because of the uncertainty introduced by the noise. This is the cause of the apparent relationship between S/N and the number of calculation cycles.

Five of the spectra referred to in Table XVII (those with S/N = 200) were re-analyzed under the assumption that S = 0; that is, that the spectra could be fitted by an unperturbed Lorentz function. Although the results of these calculations (Table XVIII) indicate that, for spectral slit width values of 4 cm^{-1} and below, the error sums of

TABLE XVIII

RESULTS OF ZERO-SLIT CALCULATIONS[a]

Spectral Slit Width, cm^{-1}	Refined Parameters			Error Sum of Squares x 10^2	Least-Squares Cycles
	Ao	$\Delta\nu$, cm^{-1}	β		
1.	0.9991	9.98	-0.0001	0.407	3
2.	0.9818	10.14	-0.0003	0.402	3
4.	0.9169	10.77	-0.0015	0.458	3
7.	0.7895	12.37	-0.0042	0.862	4
10.	0.6702	14.54	-0.0078	1.578	4

a) S/N = 200 for all spectra.

squares are comparable with those reported in Table XVII, it is apparent that A_o and $\Delta\nu$ have converged toward the apparent parameter values rather than the true values. Thus, a simple Lorentz function may be used to fit experimental data taken at narrow spectral slit widths but the calculated band parameters derived will not be independent of the instrument slit width.

The second set of 24 synthetic spectra considered each contain two bands with $A_{01} = 1.0$, $A_{02} = 0.5$, $\Delta\nu_1 = \Delta\nu_2 = 10.0$ cm^{-1}, $\nu_{01} = 1010$ cm^{-1} and $\nu_{02} = 990$ cm^{-1}. For these spectra the range was 1060-940 cm^{-1} with a sampling interval of 0.5 cm^{-1}. Results of the least-squares analyses for these spectra, shown in Table XIX, display the same types of trends and dependencies as were observed for the set of single band spectra. Again, the ν_o values are not listed since these parameters converged to the theoretical values in all cases. A plot of synthetic and calculated spectra for a representative member of the set appears in Figure 7.

A third set of synthetic spectra, each consisting of three bands, was also subjected to band shape analysis. The parameters used in the synthesis of the spectra are listed in Table XX. The results of the analyses for bands 1 and 2 are similar to those already discussed. The refined parameter values for the third band are noteworthy, however, and appear in Table XXI. Even though this band appears as an unresolved shoulder on the 1000 cm^{-1} band (see Figure 8) the least-squares analysis resulted in reasonably accurate parameter values in most cases. Exceptions are for those spectra generated with large spectral slit widths and/or high noise levels. Since the presence of band 3 was not obvious in plots of the 10 cm^{-1} spectral slit spectra, these

TABLE XIX

RESULTS FROM ANALYSES OF SYNTHETIC SPECTRA CONTAINING TWO BANDS

Spectral Slit Width, cm^{-1}	S/N	Refined Parameters				Error Sum of Squares x 10^2	Least-Squares Cycles
		A_{01}	$\Delta\nu_1$, cm^{-1}	A_{02}	$\Delta\nu_2$, cm^{-1}		
0.	400	1.0038	9.95	0.5002	10.04	0.107	4
	200	1.0071	9.90	0.5002	10.07	0.441	4
	100	1.0149	9.81	0.5005	10.14	1.784	4
	50	1.0304	9.61	0.5010	10.27	6.880	4
1.	400	1.0037	9.95	0.5002	10.03	0.114	8
	200	1.0065	9.92	0.5007	10.04	0.447	8
	100	1.0136	9.83	0.5010	10.10	1.761	7
	50	1.0271	9.66	0.5021	10.20	6.844	6
2.	400	1.0022	9.97	0.5005	10.01	0.113	10
	200	1.0055	9.93	0.5007	10.03	0.433	9
	100	1.0106	9.87	0.5015	10.06	1.738	8
	50	1.0214	9.74	0.5031	10.13	6.803	7
4.	400	1.0001	10.00	0.5006	9.99	0.107	11
	200	1.0008	9.99	0.5010	9.99	0.421	10
	100	1.0016	9.98	0.5023	9.97	1.685	9
	50	1.0037	9.96	0.5041	9.94	6.597	9
7.	400	0.9970	10.03	0.4998	9.99	0.097	13
	200	0.9941	10.07	0.4997	9.97	0.383	12
	100	0.9881	10.13	0.4999	9.93	1.537	11
	50	0.9768	10.26	0.5001	9.85	5.962	10

TABLE XIX (Continued)

Spectral Slit Width, cm^{-1}	S/N	Refined Parameters				Error Sum of Squares x 10^2	Least-Squares Cycles
		A_{01}	$\Delta\nu_1$, cm^{-1}	A_{02}	$\Delta\nu_2$, cm^{-1}		
10.	400	0.9966	10.02	0.4978	10.05	0.085	17
	200	0.9937	10.04	0.4963	10.09	0.332	15
	100	0.9876	10.07	0.4915	10.21	1.331	14
	50	0.9743	10.17	0.4850	10.37	5.293	13

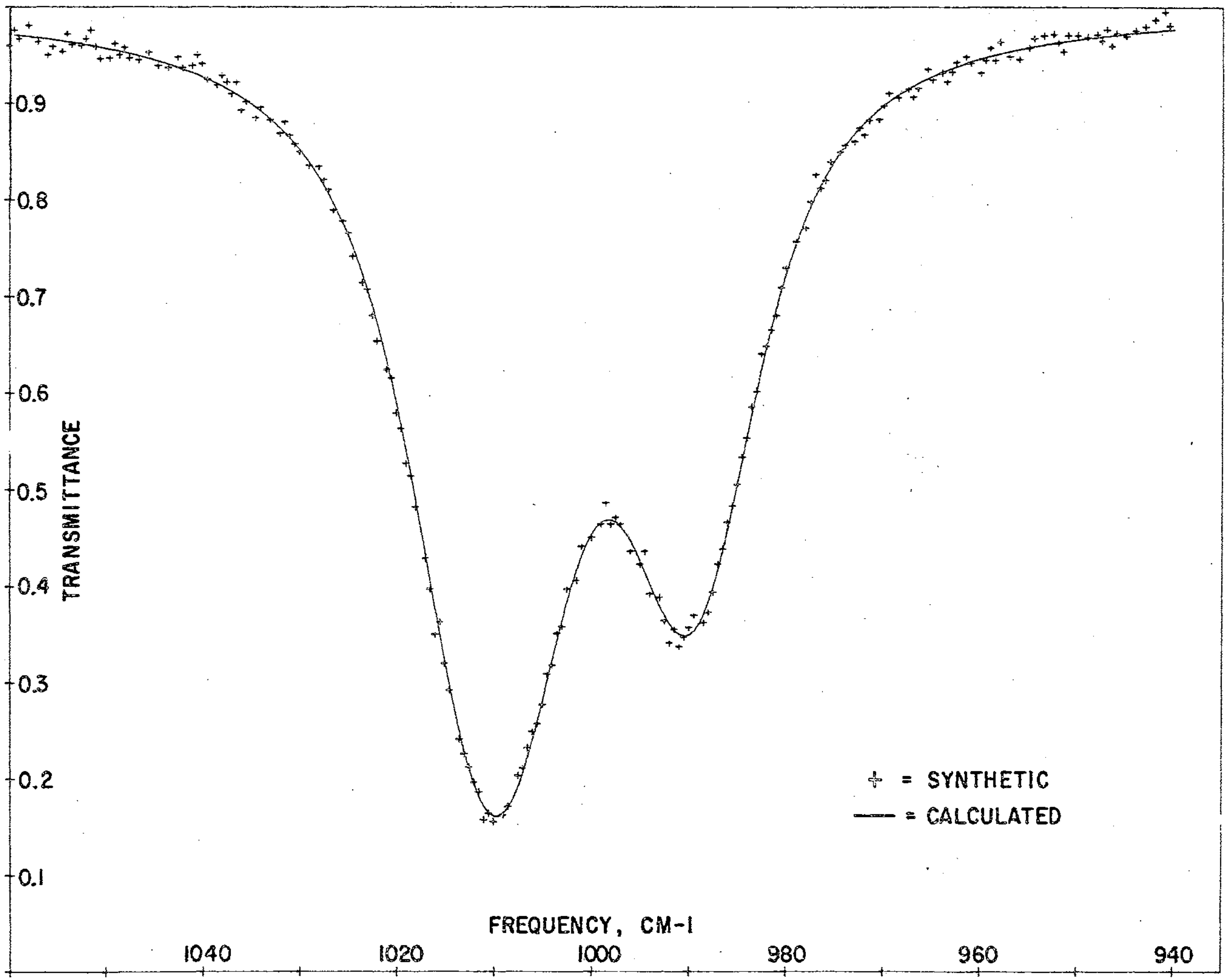


Figure 7. Two-Band Synthetic Spectrum with 7 cm^{-1} Spectral Slit and S/N = 100

TABLE XX

BAND PARAMETERS FOR SYNTHETIC SPECTRA CONTAINING THREE BANDS[a]

Band	A_0	$\Delta\nu$, cm^{-1}	ν_0, cm^{-1}
1	0.4	15.0	1020
2	1.0	10.0	1000
3	0.1	10.0	985

a) Spectra consist of 271 data points over the region 1070-935 cm^{-1}.

TABLE XXI

REFINED PARAMETERS FOR BAND 3 OF THE THREE-BAND SYNTHETIC SPECTRA

Spectral Slit Width, cm^{-1}	S/N	A_{03}	$\Delta\nu_3$, cm^{-1}	ν_{03}, cm^{-1}
0.	400	0.0991	10.06	985.0
	200	0.0979	10.13	984.9
	100	0.0960	10.19	984.8
	50	0.0919	10.39	984.7
1.	400	0.0993	10.11	985.0
	200	0.0982	10.25	985.0
	100	0.0964	10.53	985.0
	50	0.0929	11.11	985.0
2.	400	0.0993	10.19	985.0
	200	0.0987	10.35	985.1
	100	0.0976	10.71	985.1
	50	0.0951	11.49	985.2
4.	400	0.0999	10.18	985.1
	200	0.0999	10.42	985.1
	100	0.1001	10.82	985.3
	50	0.1008	11.81	985.6
7.	400	0.1007	10.26	985.1
	200	0.1013	10.47	985.2
	100	0.1030	10.91	985.3
	50	0.1072	11.89	985.7
10.	400	0.0972	9.29	984.6
	200	0.0961	9.11	984.5
	100	0.0916	7.67	984.0
	50	0.0922	5.88	983.5

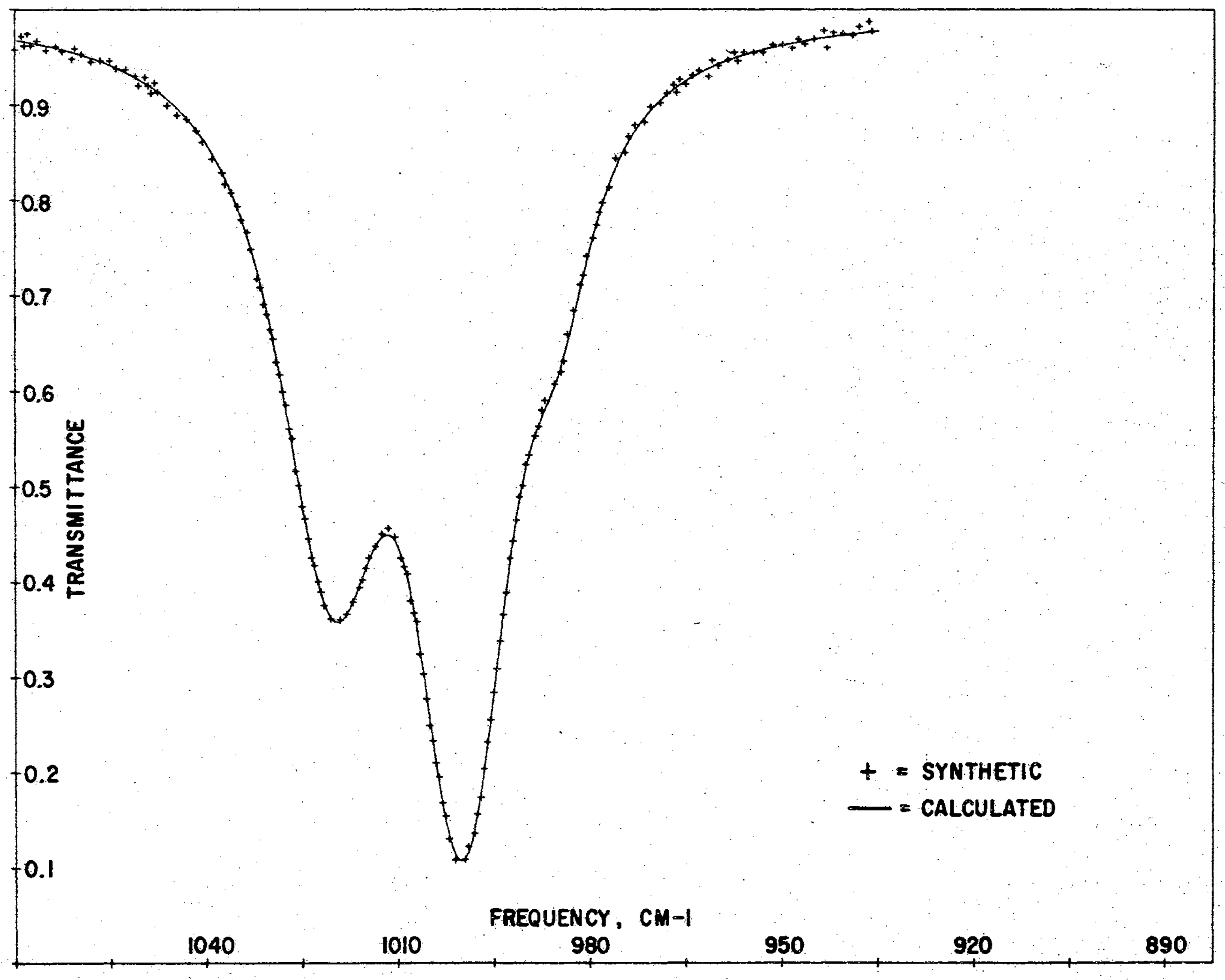


Figure 8. Three-Band Synthetic Spectrum with 4 cm^{-1} Spectral Slit and S/N = 200

spectra were analyzed again under the assumption that only two bands were present in the spectrum. The result of one such analysis is shown in Figure 9. The difference between the synthetic and calculated curves makes it apparent that an error of this type would not go undetected in an actual analysis.

The algorithm developed in this investigation has thus been proved capable of evaluating the true band parameters for a variety of synthetic spectra. It must be noted, however, that these spectra are ideal cases in that a Lorentzian band shape, triangular slit function and normally distributed noise are presumed. The following two sections of this chapter examine the applicability of the algorithm to the analysis of real spectra.

Carbonyl Stretching Bands of Aliphatic Esters

Four solutions of methyl oleate in n-tridecane were prepared and their infrared spectra determined at two different spectral slit widths over the 1800-1700 cm^{-1} region. Data from these spectra were analyzed in three phases. In the first phase, the data taken within 10 cm^{-1} of the carbonyl stretching band were fitted to a single band model. This was done to diminish the effect of any possible unresolved bands on the calculations. The refined parameters from these analyses were then used to calculate a spectrum over the entire 1800-1700 cm^{-1} range. Differences between the observed and calculated curves were examined to determine if further bands should be incorporated in the model. Finally, least-squares calculations based on the revised estimates were performed.

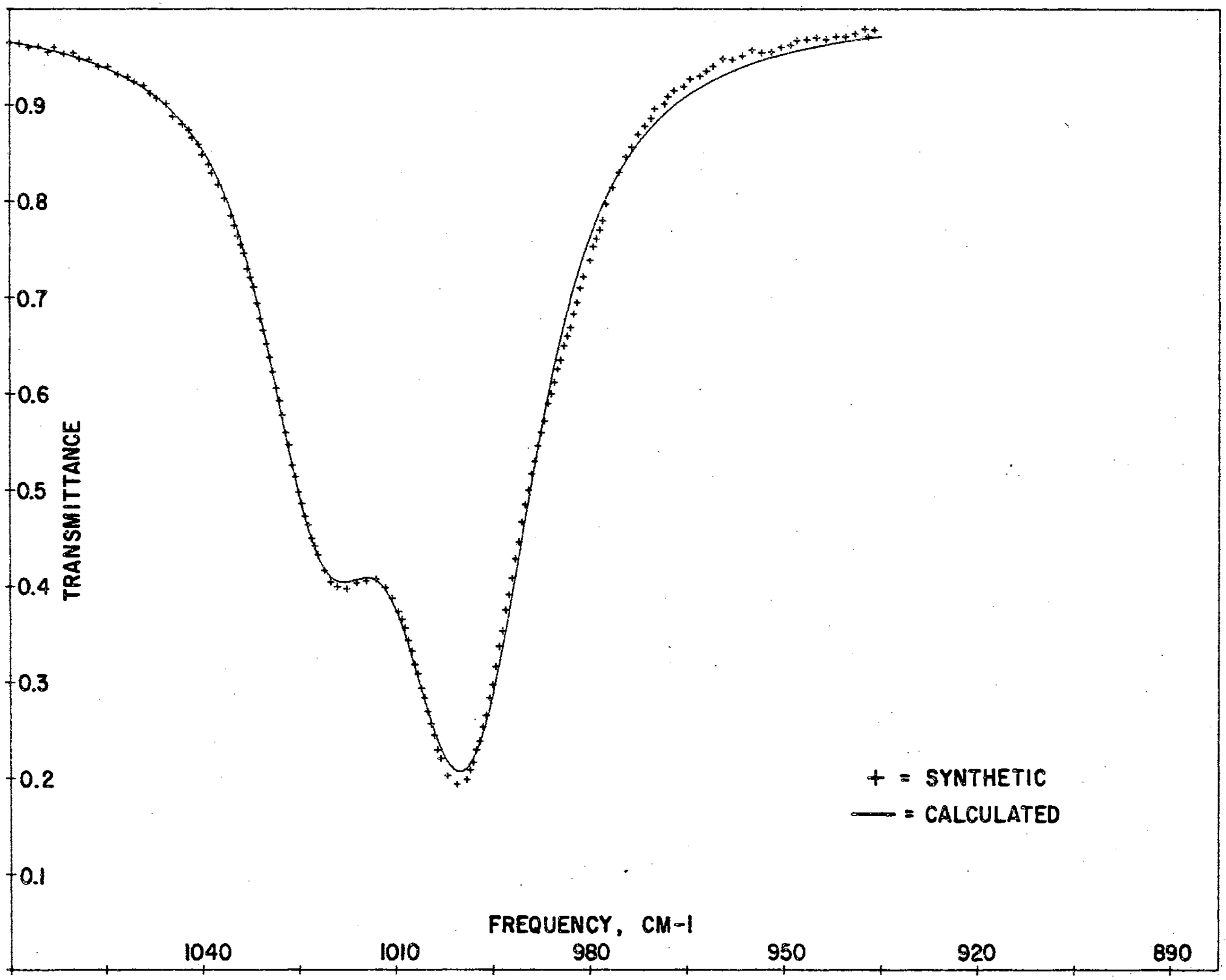


Figure 9. Result of Fitting a Two-Band Function to a Three-Band Synthetic Spectrum

Results for the analyses involving data in the vicinity of the methyl oleate carbonyl stretching band are shown in Table XXII. On the basis of the observed intensities, the molar absorptivity (ϵ) for the data at each slit value was calculated. Thus, with 1.5 cm^{-1} slits ϵ = (57.70 ± 0.36) $M^{-1}mm^{-1}$ while for the data taken at 3.2 cm^{-1}, ϵ = (55.99 ± 0.36) $M^{-1}mm^{-1}$. Using the refined intensities, however, the molar absorptivities are (59.87 ± 0.39) and 60.84 ± 0.68) $M^{-1}mm^{-1}$, respectively. Although no "true" value exists for comparison, the indications are that the molar absorptivities based on the refined parameters tend toward a single, and presumably correct, value. Also, there is a distinct improvement in the refined $\Delta\nu$ values over those observed. The mean values for the measured band widths are (11.66 ± 0.04) cm^{-1} and (12.17 ± 0.07) cm^{-1}, respectively, for the 1.5 cm^{-1} and 3.2 cm^{-1} data while the corresponding means for the refined parameters are (11.34 ± 0.06) and (11.28 ± 0.05) cm^{-1}.

Montigny[46] has published a table of coefficients whereby, for given values of apparent band intensity, apparent band width and spectral slit width, the ratio of apparent to true band width for a slit-broadened infrared absorption band may be evaluated. Using these coefficients, expected values for the refined $\Delta\nu$'s were calculated and appear as the rightmost column of Table XXII. The mean deviation between the refined and calculated band widths is 1.4 percent relative to the calculated value, certainly within acceptable limits for this parameter. Since Montigny's calculations were based on the assumption that an absorption band may be regarded as the convolution of a Lorentz function with a triangular slit function, the agreement observed here serves as justification for the choice of this model in the present

TABLE XXII

BAND-SHAPE PARAMETERS FOR THE CARBONYL STRETCHING BAND OF METHYL OLEATE[a]

Spectral Slit Width, cm^{-1}	Concentration M.	Observed Parameters			Refined Parameters			Calculated Values for $\Delta\nu$, cm^{-1}
		A_0	$\Delta\nu$, cm^{-1}	ν_0, cm^{-1}	A_0	$\Delta\nu$, cm^{-1}	ν_0, cm^{-1}	
1.5	0.00976	0.2786	11.73	1747.2	0.2846	11.42	1747.5	11.55
	0.01294	0.3642	11.66	1747.3	0.3750	11.39	1747.5	11.48
	0.01667	0.4694	11.68	1747.4	0.4843	11.32	1747.6	11.51
	0.01966	0.5513	11.58	1747.3	0.5675	11.25	1747.5	11.42
3.2	0.00976	0.2700	12.26	1747.0	0.2866	11.34	1747.3	11.51
	0.01294	0.3558	12.22	1747.1	0.3778	11.32	1747.4	11.48
	0.01667	0.4537	12.07	1747.2	0.4906	11.21	1747.4	11.37
	0.01966	0.5362	12.13	1747.0	0.5734	11.26	1747.3	11.45

a) Sample path for all spectra was 0.4788 mm.

investigation.

The differences between the observed and refined band position values are the result of a small amount of skew in the observed absorption bands. Because of this, the center of the band calculated by least squares does not correspond exactly to the position of zero slope.

Spectra calculated using the refined parameters from Table XXII were compared with the observed spectrum over the 1800-1700 cm^{-1} region. One such comparison is shown in Figure 10. Differences between the curves indicate that two more bands, one at 1726.5 cm^{-1} and one at 1706.5 cm^{-1}, should be included in the model. This was done and the calculations repeated. The results for the expanded model were less than satisfactory in that the parameters calculated for the additional bands varied markedly from spectrum to spectrum and the calculated band widths often assumed unrealistically large (50-100 cm^{-1}) values. As would be expected, however, inclusion of the additional bands did result in a better fit between observed and calculated spectra. The error sums of squares for the three-band model were lower by a factor of about 30 than equivalent calculations based on a single band. This behavior could indicate that another factor, such as spectrometer imbalance in a region of atmospheric absorbance, is instrumental in causing the deviations. The fact that all carbonyl stretching spectra examined in this investigation exhibited some structure in this region lends credence to this explanation.

Data from the carbonyl stretching region of spectra of ethyl acetate in <u>n</u>-tridecane were analyzed in a slightly different fashion. Preliminary calculations indicated the presence of a small band at 1729 cm^{-1} in addition to the carbonyl absorbance at 1748 cm^{-1}. The

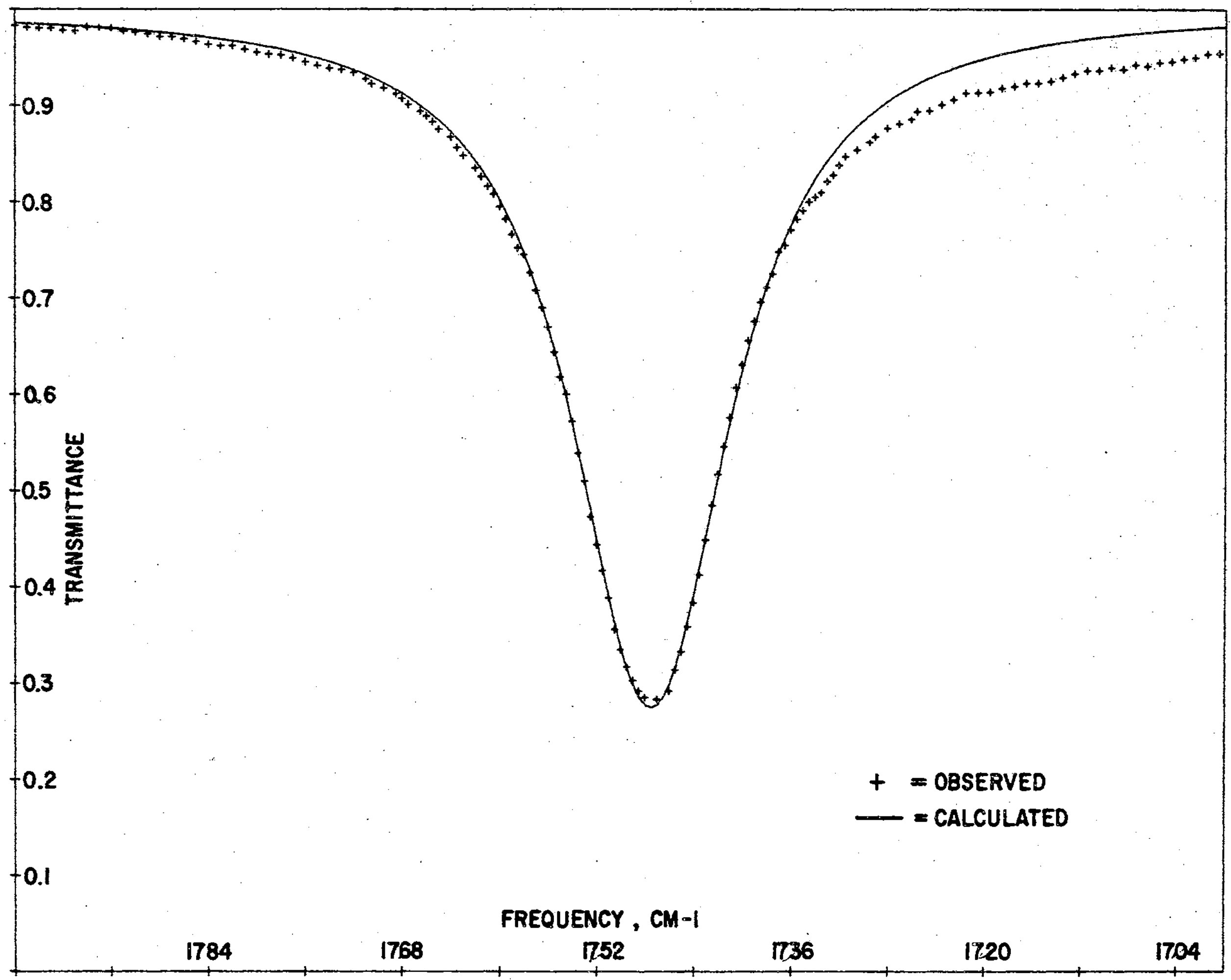


Figure 10. Observed and Calculated Carbonyl Stretching Bands for Methyl Oleate with 1.5 cm^{-1} Spectral Slit

band width for this minor feature was determined graphically as was an approximate value for the molar absorptivity. These values were then included in least-squares analyses of the 1800-1700 cm^{-1} region of the spectrum but were constrained to their original values so that only parameters for the carbonyl stretching band were refined. The results of these calculations appear in Table XXIII. A comparison of the observed and refined values for $\Delta\nu$ clearly demonstrates the power of the algorithm. Whereas the means of the observed values are 9.19, 10.45 and 12.48 cm^{-1} for spectra taken at spectral slit widths of 2.6, 5.0 and 7.5 cm^{-1} respectively, the mean for all 18 refined values is (8.66 ± 0.16) cm^{-1}. Also, the refined band widths agree reasonably well with the theoretical values shown in the last column. The behavior of the refined intensity parameters is shown in Table XXIV. Although there is a 26 percent difference between the observed molar absorptivities for the 2.6 and 7.5 cm^{-1} data, the refined intensities clearly define a single molar absorptivity.

Carbonyl stretching spectra for n-tridecane solutions of di-n-butyl oxalate were also studied. This compound exhibits strong bands at 1774 and 1748 cm^{-1} arising from out-of-phase and in-phase motions of the two carbonyl groups. In addition, there is a small unresolved band in the vicinity of 1720 cm^{-1}. Transmittance data were gathered over the 1825 to 1700 cm^{-1} region and analyzed on the basis of this three-band model. The refined parameters from these analyses are listed in Table XXV and the molar absorptivity values calculated from the refined intensities appear in Table XXVI. No observed parameters are listed since comparison of these with the refined values is meaningless in the presence of extensive overlap.

TABLE XXIII

BAND-SHAPE PARAMETERS FOR THE CARBONYL STRETCHING BAND OF ETHYL ACETATE

Spectral Slit Width, cm^{-1}	Concentration M	Observed Parameters			Refined Parameters			Calculated Values for $\Delta\nu$, cm^{-1}
		A_0	$\Delta\nu$, cm^{-1}	ν_0,cm^{-1}	A_0	$\Delta\nu$, cm^{-1}	ν_0, cm^{-1}	
2.6[a]	0.00324	0.1332	9.38	1747.8	0.1421	8.64	1747.9	8.64
	0.00648	0.2629	9.21	1748.2	0.2789	8.41	1748.3	8.53
	0.01027	0.4151	9.12	1747.8	0.4333	8.76	1748.0	8.49
	0.01381	0.5367	9.10	1748.0	0.5626	8.69	1748.1	8.51
	0.01717	0.6786	9.17	1747.8	0.7015	8.93	1748.0	8.61
	0.02054	0.8130	9.18	1747.8	0.8391	8.96	1748.1	8.66
5.0[a]	0.00324	0.1175	10.52	1747.3	0.1414	8.21	1747.6	8.13
	0.00648	0.2313	10.67	1747.6	0.2742	8.56	1747.7	8.42
	0.01027	0.3624	10.47	1747.6	0.4282	8.64	1747.7	8.29
	0.01381	0.4722	10.36	1747.6	0.5582	8.67	1747.8	8.26
	0.01717	0.6022	10.33	1747.6	0.7060	8.84	1747.8	8.34
	0.02054	0.7082	10.37	1747.6	0.8310	8.95	1747.8	8.57
7.5[b]	0.00324	0.1010	12.73	1747.2	0.1389	8.32	1747.6	8.14
	0.00648	0.1919	12.86	1747.5	0.2651	8.49	1747.7	8.49
	0.01027	0.3097	12.52	1747.6	0.4255	8.65	1747.8	8.24
	0.01381	0.4090	12.31	1747.6	0.5639	8.67	1747.8	8.10
	0.01717	0.4803	12.27	1747.6	0.6673	8.74	1747.8	8.15
	0.02054	0.5955	12.16	1747.5	0.8269	8.87	1747.7	8.16

a) Sample path was 0.4801 mm.

b) Sample path was 0.4789 mm.

TABLE XXIV

MOLAR ABSORPTIVITY FOR THE CARBONYL STRETCHING BAND OF ETHYL ACETATE

Spectral Slit Width, cm^{-1}	Molar Absorptivity, $M^{-1}mm^{-1}$	
	Observed Intensities	Refined Intensities
2.6	81.31 ± 0.91	83.26 ± 0.73
5.0	71.22 ± 0.83	83.12 ± 0.80
7.5	59.92 ± 0.74[a]	83.29 ± 0.69[a]

a) A_0 for the 0.01771M solution was not used in determination of this value.

TABLE XXV

REFINED BAND SHAPE PARAMETERS FOR THE CARBONYL STRETCHING REGION OF DI-N-BUTYL OXALATE SPECTRA[a]

Spectral Slit Width, cm^{-1}	Concentration M.	A_{01}	$\Delta\nu_1$, cm^{-1}	ν_{01}, cm^{-1}	A_{02}	$\Delta\nu_1$, cm^{-1}	ν_{02}, cm^{-1}	A_{03}	$\Delta\nu_3$, cm^{-1}	ν_{03}, cm^{-1}
3.0	0.00627	0.1077	13.01	1774.3	0.2230	10.91	1748.0	0.0184	36.11	1732.7
	0.01152	0.1975	13.75	1774.4	0.4230	10.75	1748.2	0.0103	25.24	1718.1
	0.01783	0.3027	13.80	1774.6	0.6451	10.78	1748.3	0.0175	25.36	1714.2
	0.02318	0.3924	13.91	1774.4	0.8279	10.82	1748.1	0.0228	23.67	1713.7
4.4	0.00627	0.1083	13.53	1773.9	0.2270	11.03	1747.8	0.0096	22.91	1720.7
	0.01152	0.1974	13.75	1774.2	0.4195	10.90	1748.1	0.0136	25.04	1717.5
	0.01783	0.3033	13.67	1774.1	0.6449	10.74	1747.9	0.0196	28.64	1714.0
	0.02318	0.3921	13.83	1774.2	0.8278	10.80	1747.9	0.0252	25.93	1713.2
6.0	0.00627	0.1084	13.01	1773.9	0.2293	10.02	1747.8	0.0227	30.89	1734.8
	0.01152	0.1982	13.65	1774.1	0.4268	10.55	1747.8	0.0127	21.80	1717.1
	0.01783	0.3042	13.74	1774.1	0.6606	10.45	1747.8	0.0175	25.66	1714.7
	0.02318	0.3947	13.74	1774.1	0.8506	10.48	1747.8	0.0239	23.53	1713.8
10.0	0.00627	0.1105	12.95	1773.7	0.2410	9.81	1747.7	0.0198	30.71	1731.9
	0.01152	0.2052	13.35	1774.0	0.4486	9.96	1747.8	0.0132	23.04	1718.8
	0.01783	0.3111	13.64	1774.0	0.7093	9.68	1747.8	0.0197	29.19	1714.6
	0.02318	0.4038	13.66	1774.0	0.9184	9.74	1747.7	0.0258	23.77	1713.8

a) Sample path for all spectra was 0.4780 mm.

TABLE XXVI

MOLAR ABSORPTIVITIES FOR THE CARBONYL STRETCHING REGION OF DI-N-BUTYL OXALATE SPECTRA[a]

Spectral Slit Width, cm^{-1}	ϵ_1	ϵ_2	ϵ_3[b]
3.0	35.18 ± 0.13	74.68 ± 1.24	2.25 ± 0.09
4.4	35.11 ± 0.11	74.37 ± 0.77	2.08 ± 0.06
6.0	35.39 ± 0.09	76.94 ± 0.66	2.00 ± 0.26
10.0	36.14 ± 0.35	84.13 ± 0.63	2.26 ± 0.07

a) The units for ϵ are $M^{-1}mm^{-1}$.

b) Data for the 0.00627M solution were not used in the calculation of these entries.

Examination of the table entries for the two major bands indicates that, for the data taken at spectral slit widths of 3.0 and 4.4 cm^{-1}, all parameters tend to converge to a common value. The uncertainty in the parameters for the small feature at about 1715 cm^{-1} was not unexpected, considering the small magnitude of the molar absorptivity and the fact that it appears on the wing of a much stronger band. They are more stable, however, than the small bands postulated for methyl oleate. It is therefore concluded that the band is real. A plot of observed and calculated spectra for this ester is given in Figure 11.

Intensity and band width parameters for the 1748 cm^{-1} band calculated using the 6.0 cm^{-1} slit data deviate somewhat from those calculated from the data taken with 3.0 and 4.4 cm^{-1} slits. For the spectra determined with $S = 10$ cm^{-1}, parameters for all but the 1715 cm^{-1} band have deviated significantly from the narrower slit width values. It thus appears that, for medium to strong absorption bands, shape parameters calculated using data taken at wide slit widths are unreliable. It should be noted, however, that slits of 6.0 and 10.0 cm^{-1} are far wider than those used in normal spectrometric work. One may conclude, therefore, that the least-squares algorithm has successfully described the carbonyl stretching region of the butyl oxalate spectrum.

Carbon-Hydrogen Bending Bands of Simple Aromatic Hydrocarbons

Aromatic compounds bearing ring hydrogen atoms generally exhibit one or more C-H bending bands in the 900-600 cm^{-1} region of the infrared spectrum. The final phase of this investigation involved a study of these bands for carbon disulfide solutions of toluene, _o_-xylene,

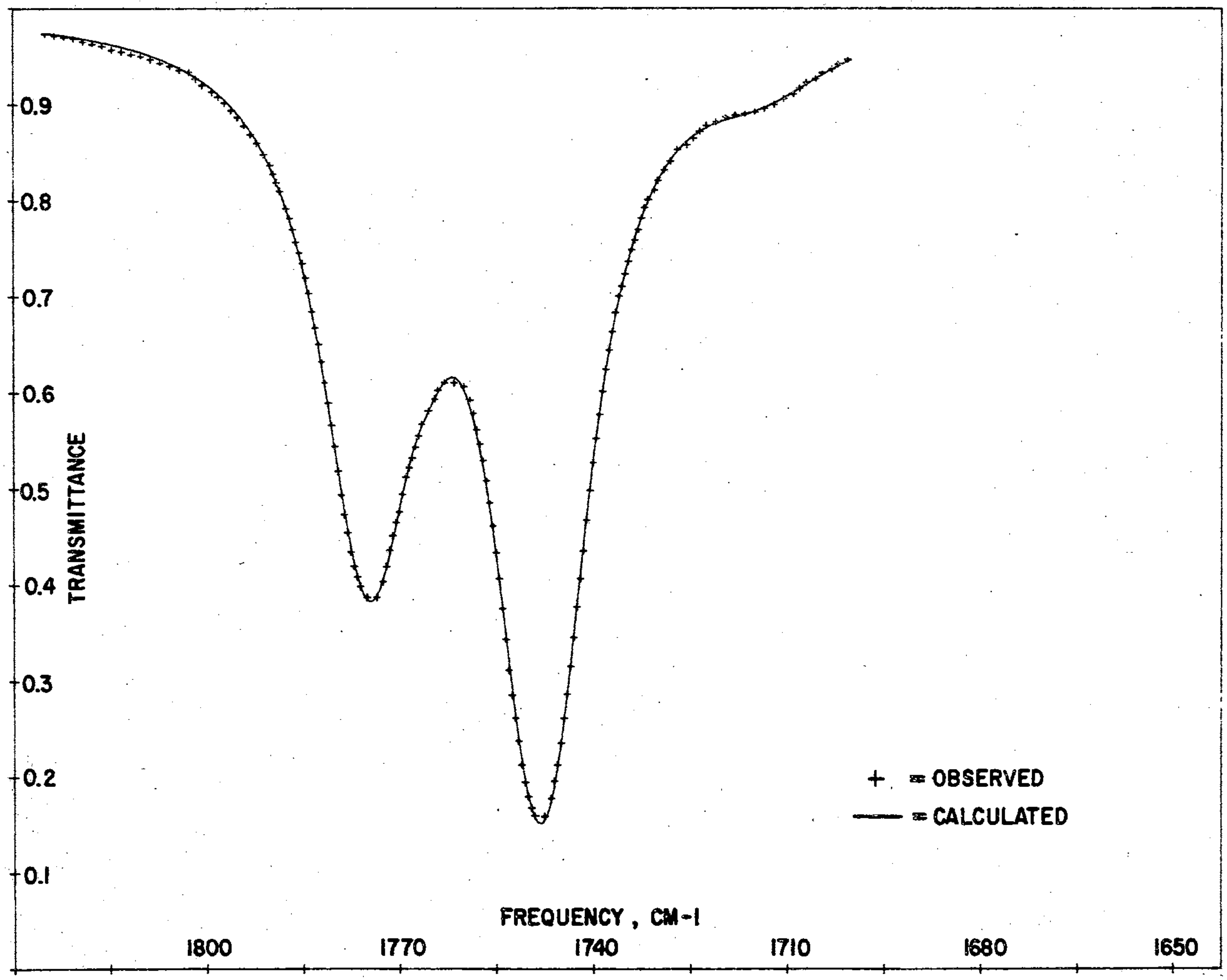


Figure 11. Observed and Calculated Carbonyl Stretching Bands for Di-n-Butyl Oxalate with 3 cm^{-1} Spectral Slit

m-xylene and t-butylbenzene. Spectra were determined over the region 800-650 cm^{-1} at frequency intervals of 0.2 cm^{-1}. Individual solute concentrations varied from 0.0306 to 0.1044 M and the spectral slit widths employed ranged from 1.0 to 2.2 cm^{-1}.

Several least-squares analyses were performed involving spectra of solutions containing a single solute. The results for 35 such calculations are summarized in Table XXVII. The refined parameters for the individual hydrocarbons were then used as initial estimates for analyses of the spectra of solutions containing two or more solutes.

As can be seen from Table XXVIII, most of the refined parameters for the spectra of mixtures fall within one or two standard deviations of the values derived from the spectra of single component solutions. Notable exceptions are those parameters for the 693.2 cm^{-1} toluene band and the 690.1 m-xylene band which were calculated from data acquired at a spectral slit width of 2.2 cm^{-1}. Although the observed data are apparently well described by the calculated model (see Figure 12), the molar absorptivity and band width values calculated for these absorbances do not agree with those listed in Table XXVII. It therefore seems that the algorithm cannot accurately resolve bands which are so extensively overlapped. Better values for these parameters are calculated from the data taken with 1.0 cm^{-1} slits. Here the apparent overlap is not so severe (see Figure 13) and the algorithm is more effective. It is also possible to calculate accurate parameters from the 2.2 cm^{-1} data if $\Delta\nu$ and ν_o for the overlapped bands are constrained to the initial values for 5 or 6 cycles. The success of this procedure, however, is somewhat predicated on the accuracy of the initial estimates. For the case of the mixture of o-xylene, m-xylene and t-butylbenzene,

TABLE XXVII

REFINED BAND SHAPE PARAMETERS FOR THE C-H BENDING BANDS OF AROMATIC HYDROCARBONS

Compound	ν_0, cm^{-1}	ϵ, M^{-1}mm^{-1}	$\Delta\nu$, cm^{-1}
Toluene[a]	727.9 ± 0.1 693.2 ± 0.1	52.52 ± 0.86 17.17 ± 0.43	4.15 ± 0.08 4.49 ± 0.09
o-Xylene[b]	741.5 ± 0.0	61.55 ± 0.38	3.87 ± 0.04
m-Xylene[a]	767.8 ± 0.0 690.1 ± 0.1	34.29 ± 0.65 17.22 ± 0.17	4.53 ± 0.09 3.86 ± 0.21
t-Butylbenzene[b]	761.7 ± 0.1 697.1 ± 0.1	27.34 ± 0.12 31.04 ± 0.67	3.92 ± 0.14 5.65 ± 0.18

a) Spectral slit width varies from 1.0 to 2.2 cm^{-1}.

b) Spectral slit width is 2.1 cm^{-1}.

TABLE XXVIII

REFINED CARBON-HYDROGEN BENDING BAND PARAMETERS FOR MIXTURES OF AROMATIC HYDROCARBONS

Components	Spectral Slit Width, cm^{-1}	ν_0, cm^{-1}	ϵ, $M^{-1}mm^{-1}$	$\Delta\nu$, cm^{-1}
Toluene + m-Xylene	2.2	767.8	34.72	4.42
		727.9	51.77	4.08
		694.0	12.23	1.99
		690.8	23.16	6.20
Toluene + m-Xylene	1.0	767.7	36.21	4.58
		727.8	53.21	4.31
		693.2	16.92	4.42
		690.1	17.97	3.59
o-Xylene, m-Xylene, t-Butylbenzene	2.1	767.7	33.79	4.35
		761.9	27.90	4.22
		741.5	61.16	3.88
		697.2	30.87	5.60
		689.9	15.16	3.76

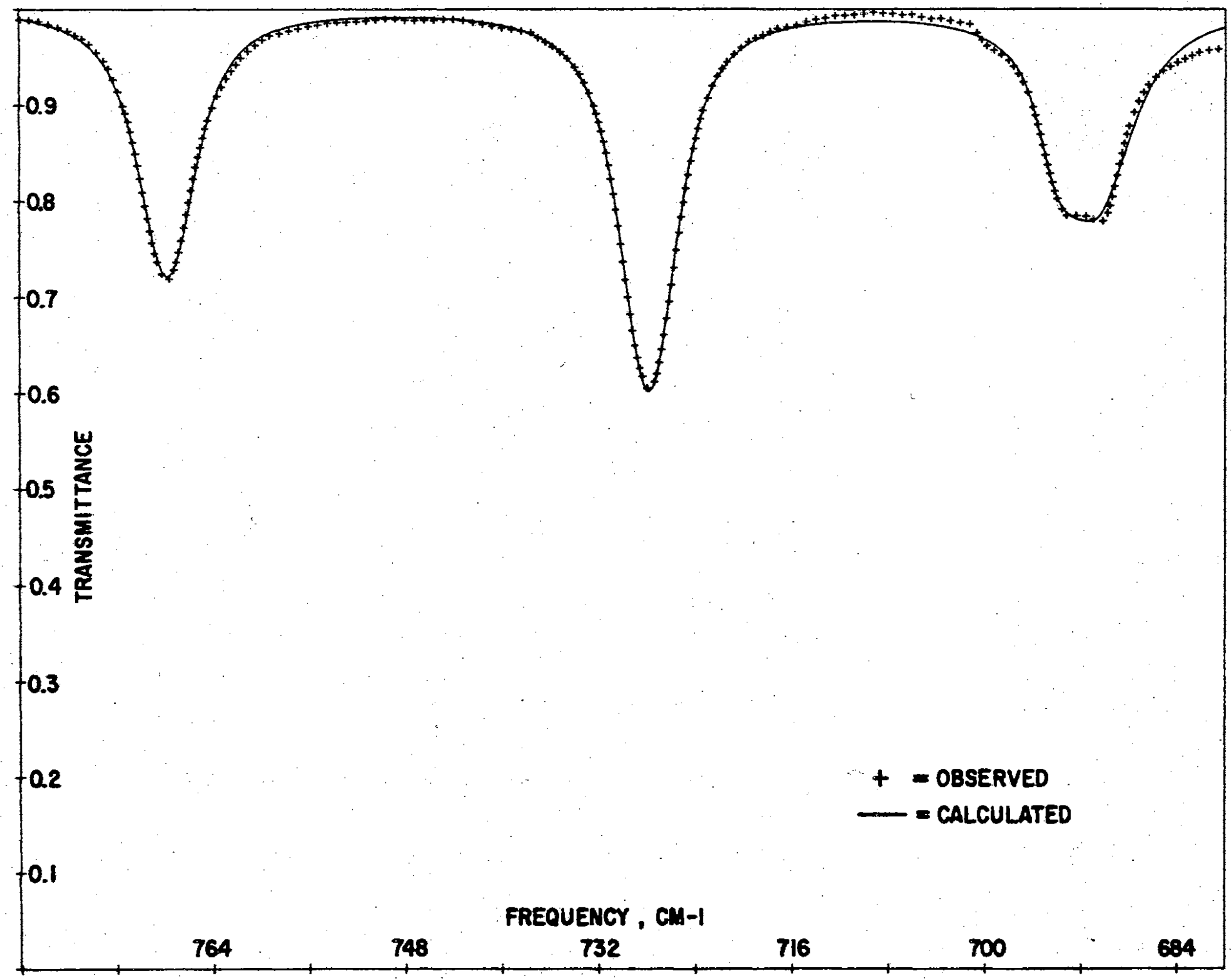


Figure 12. Observed and Calculated Carbon-Hydrogen Bending Bands for Toluene and m-Sylene with 2.2 cm^{-1} Spectral Slit

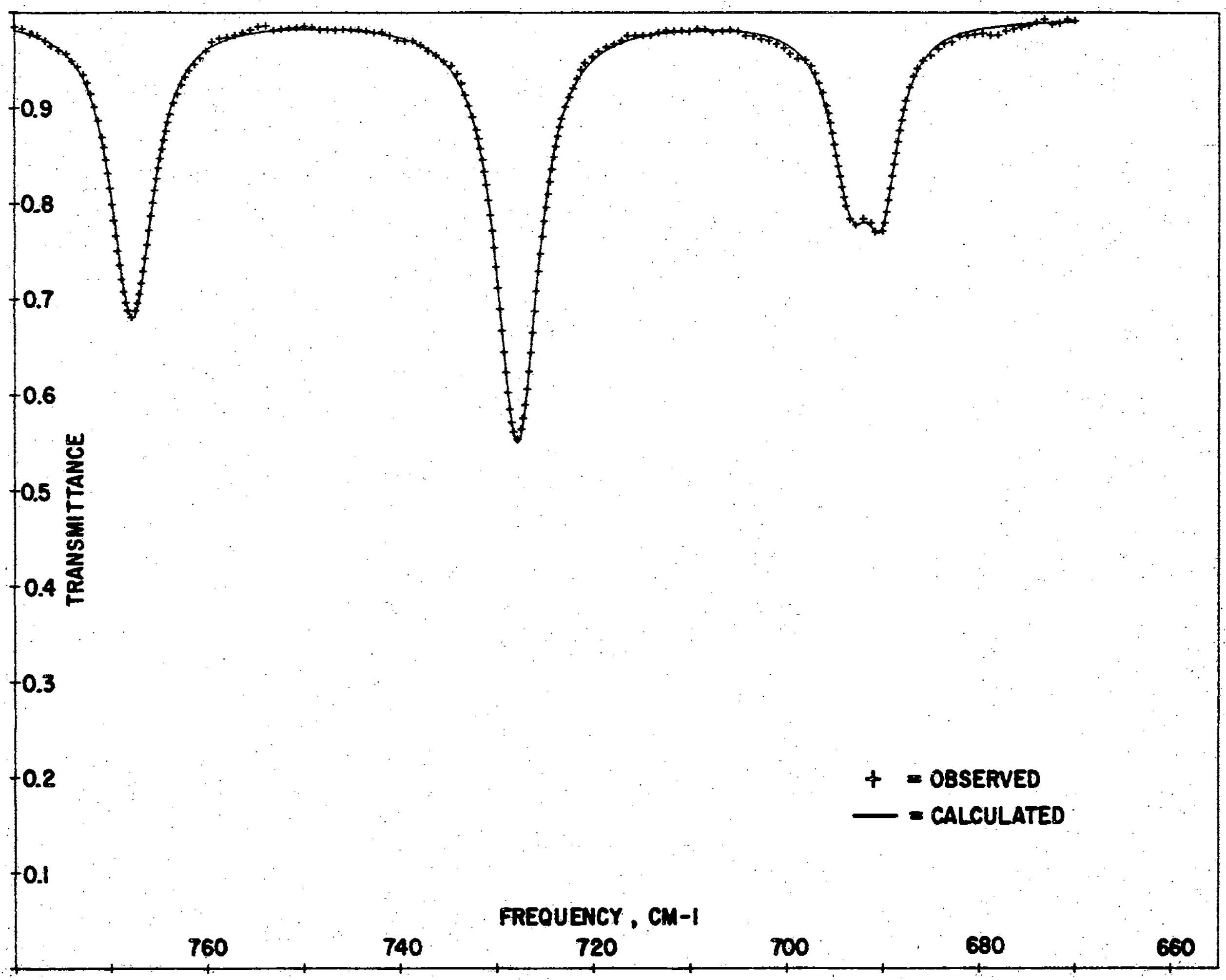


Figure 13. Observed and Calculated Carbon-Hydrogen Bending Bands for Toluene and m-Xylene with 1 cm^{-1} Spectral Slit

the value calculated for the width of the 690 cm^{-1} m-xylene band is only slightly lower than the single-component value. A plot of observed and calculated spectra for this mixture is shown as Figure 14.

Summary and Conclusions

The purpose of this invetigation was to develop an algorithm whereby reliable values for the shape parameters of infrared absorption bands could be calculated. In achieving this end, a mathematical model was devised wherein an infrared spectrum is represented by a set of one or more Lorentz functions convolved with a triangular spectral slit function. This model was implemented in the form of a digital computer program (BANDFIT) which serves to calculate the shape parameters for each component band of a spectrum.

The effectiveness of program BANDFIT was evaluated initially on the basis of calculations involving synthetic spectra. In the second phase of the study real data, taken from the infrared spectra of aliphatic esters and simple aromatic hydrocarbons, were subjected to analysis. The results of these calculations demonstrate that band shape parameters derived from these analyses may be used to generate spectra which closely approximate those determined experimentally. In addition, the calculated parameters are physically significant in that, for a given set of spectral features, they are essentially unaffected by changes in spectral slit width.

The algorithm is not entirely successful in the determination of shape parameters for systems of strongly overlapped bands. It appears that unrealistic band width and intensity values result if the features are approximately one band width apart and if the ratio of the spectral

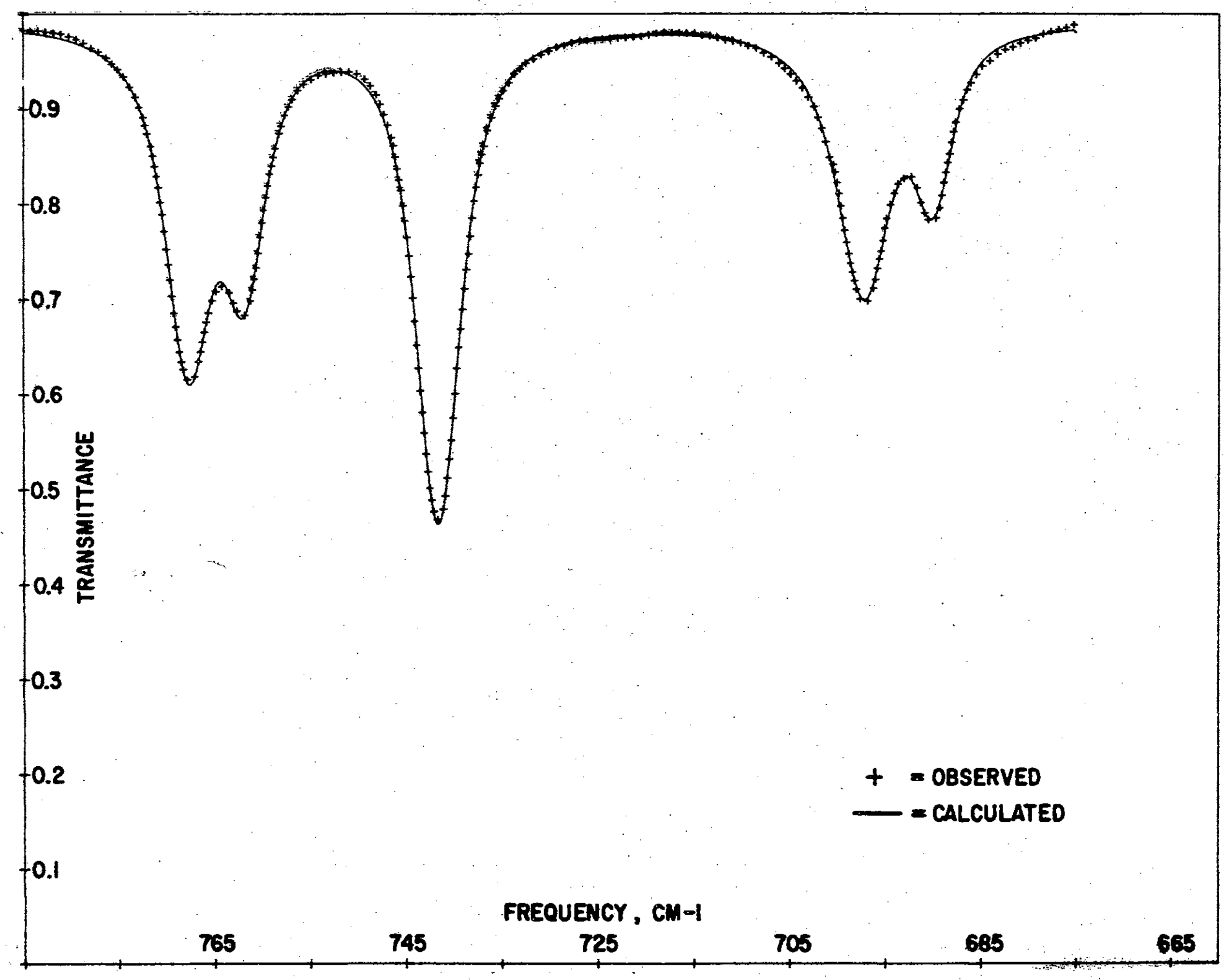


Figure 14. Observed and Calculated Carbon-Hydrogen Bending Bands for o-Xylene, m-Xylene and t-Butylbenzene with 2.1 cm^{-1} Spectral Slit

slit width to the apparent band width is greater than about 0.25. For greater frequency separation, however, accurate determination of shape parameters is easily accomplished, even for bands appearing as unresolved shoulders. This is evidenced by the calculations involving the three band synthetic spectrum and by the set of self-consistent parameters derived for the 1715 cm^{-1} band in di-n-butyl oxalate spectra.

It thus appears that infrared solution spectra are accurately described by the mathematical model devised and implemented during this investigation. Extraction of the shape parameters for a spectrum on the basis of this model is one step toward the removal of distortions introduced by the examining instrument. It is apparent, however, that there are other factors which influence the shapes and positions of infrared absorption bands. Perturbations of the detected signal by the electrical and mechanical systems of the spectrophotometer are probably instrumental in band broadening and in the skewing of peaks. As was previously mentioned, the effects of such distortions can possibly be eliminated by a deconvolution of the observed signal with the inverse of the instrument transfer function. Development of algorithms to evaluate the transfer function and to implement the deconvolution are the next logical steps in this field of research.

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APPENDIX

Instructions for Use of the Computer Program

Program BANDFIT was designed to implement the algorithm developed in this investigation. It is written in the Fortran IV programming language for execution on an IBM System 360/65 digital computer with full operating system. In its present configuration the program is limited to the analyses of spectra containing 10,000 or fewer digital values and which are composed of a maximum of 10 absorption bands.

The program consists of a main routine and seven subroutines; SPCTRM, SMTH1, SCAN, C0NMAT, L0RN3, PL0T1 and SCALAB. Also, a local subroutine (GDATE) is used to determine the date of the analysis. If this routine is not available the call to it and references to the variable DATE should be deleted. The functions of the other subroutines are briefly outlined below.

Subroutine SPCTRM is used to read ordinate values for the observed spectrum either from punched cards or from a user disk file. A call to entry point DISK of this subroutine serves to initialize the disk file. The program is written so that the method of reading the observed spectrum may be changed by simply modifying SPCTRM. Subroutine SMTH1 is used to digitally smooth the observed spectrum, SCAN generates the vector of coefficients employed in the slit convolution and C0NMAT is called to calculate the orthogonal polynomical coefficients required by both SMTH1 and SCAN. The calculated spectrum, error sum of squares and the sums of partial derivatives used in the least-squares calculation are evaluated in LØRN3. Finally, subroutines PLØT1 and SCALAB are used to generate graphs of the observed and calculated spectra and of the error function. In order to use PLØT1, the Calcomp (California Computer Products, Inc.) plotter subroutine package must be available. If it is not, calls to all entry points of subroutine PLØT1 should be eliminated from the main program.

Input requirements for program BANDFIT are detailed in TABLE XXIX. Although two types of spectrum header cards are described in the table, only one is required for a given problem. Also, it should be noted that band intensity estimates are input in terms of molar absorptivity rather than absorbance. This is done so that the same estimates may be used for the data from a series of solutions. The absorbance estimate is calculated in the program from the molar absorptivity, concentration and cell path values.

Printed output for a typical problem consists of the error sum of squares and parameter set for each calculation cycle and a list of the final refined parameter values together with estimates of their uncertainties. Listings of the observed and calculated spectra, punched and plotted output are optional as selected by control variables.

TABLE XXIX

INPUT REQUIREMENTS FOR PROGRAM BANDFIT

Card	Columns	Format	Variable Name and Function
Record	1-2	I2	KARD = 1 for the first and KARD = 2 for the second of the 2 record cards.
	5-80	19A4	ALPHA, any alphanumeric information desired to describe the problem.
Control	1-2	I2	KARD = 3
	3-8	I6	NØPRØB, the problem number.
	9-11	I3	If NPLT = 2, plots will be generated for the observed and calculated spectra and for the error function. If NPLT = 1, only the observed and calculated spectra will be plotted. If NPLT = 0, no plotting is done.
	12-14	I3	LTYPE = 1 if the observed spectrum is in transmittance units, LTYPE = 2 if it is in absorbance units.
	15-17	I3	NPEAK, the number of absorption bands in the spectrum.
	18-20	I3	IHØLD is nonzero if any of the parameter estimates are to be constrained. If IHØLD = -1, all parameters are constrained and a zero-order calculation is performed.
	21-23	I3	If MØDE = 1 the observed spectrum is to be input from cards, if MØDE = 2 it is accessed from the disk file.

TABLE XXIX (Continued)

Card	Columns	Format	Variable Name and Function
Control	24-26	I3	NGATE; if greater than zero the observed spectrum will be smoothed with an NGATE-point polynomial function of degree NPØLY (see below).
	27-29	I3	NPØLY
	30-32	I3	IFPNCH, if nonzero the final calculated spectrum will be punched on cards.
	33-35	I3	IFPRNT controls printing of the observed and calculated spectra. There are options for no listing (IFPRNT = 0), a single-spaced (IFPRNT = 1), or a double-spaced (IFPRNT = 2) listing.
	36-45	F10.5	TSTP; if the fractional improvement in the error sum of squares for two successive cycles falls below this value, the problem is terminated.
	46-55	F10.5	DX, the abcissa interval for the calculated spectrum. If DX is not input, the value for EDX (see below) is used.
	56-60	F5.2	FACTOR, used to scale the vector of corrections before the parameters are updated. If not input, a value of 1.0 is assumed.
Spectrum Header (MØDE = 1)[a]	1-5	I5	IDENT, the spectrum number.
	9-15	F7.0	XSTART, the starting frequency for the spectrum.
	16-20	F5.1	EDX, the abcissa sampling interval for the observed spectrum.

TABLE XXIX (Continued)

Card	Columns	Format	Variable Name and Function
Spectrum Header (MØDE = 1)[a]	21-25	I5	NIPTS, the number of data points in the observed spectrum.
	31-40	F10.5	BEGIN and END (see below) define the frequency range to be considered in the analysis. If not input, the range is determined from the spectrum.
	41-50	F10.5	END
Spectrum Header (MØDE = 2)[b]	1-5	I5	IDENT, the spectrum number.
	11-20	F10.5	BEGIN, see above.
	21-30	F10.5	END, see above.
Parameter[c]	1-2	I2	KARD = 4
	11-20	F10.5	EO, the initial molar absorptivity value in $M^{-1}mm^{-1}$.
	21-25	I5	IHEO, the number of cycles for which EO is to be constrained.
	31-40	F10.5	DELNU, the initial value for $\Delta\nu$ in cm^{-1}.
	41-45	I5	IHRHØ, the number of cycles for which DELNU is to be constrained.
	51-60	F10.5	XNU, the initial value for ν_o in cm^{-1}.
	61-65	I5	IHNU, the number of cycles for which XNU is to be constrained.

TABLE XXIX (Continued)

Card	Columns	Format	Variable Name and Function
Instrument	1-2	I2	KARD = 5
	11-20	F10.5	BETA, the initial value for the constant β.
	21-25	I5	IHBETA, the number of cycles for which BETA is to be constrained.
	26-30	I5	MPØLY, the degree of polynomial to be used for the slit integration. If MPØLY = 0, a trapezoidel rule integration is performed.
	31-40	F10.5	SLIT, the spectral slit width in cm^{-1}.
	41-50	F10.5	XL, the path of the sampling cell in mm.
Concentration	1-2	I2	KARD = 6
	11-80	10F7.4	C(1) through C(10), the concentration to be associated with each absorption band. NPEAK values must be entered.

---

a) This card must be followed by cards containing the observed spectrum punched in 20I4 format.

b) For this mode of input, the spectrum and header information are expected to be on a direct access disk file. Refer to the listing of subroutine SPCTRM for the required format.

c) There must be NPEAK parameter cards.

Program Listings

```
C.... PROGRAM BANDFIT
C
C.... REQUIRES SUBROUTINES SCAN, LORN3, PLOT1, SMTH1, CONMAT,
C....                       SCALAB, SPCTRM
C
      DEFINE FILE 7(2500,1288,L,KEY)
      DIMENSION  ALPHA(38),B(31,32),BSAVE(31),C(10),D(51),DATE(2),
     1           DELNU(10),E0(10),HOLDE0(10),HOLDRH(10),HOLDXN(10),
     2           IHE0(10),IHNU(10),IHRHO(10),NDX(32),NHOLD(31,2),
     3           VAR(31),WS(55),PLBL(9)
      DIMENSION  IR(5000),PLBL1(6)
      EQUIVALENCE  (IR(1),FREQ(1))
      COMMON  A(31,32),A0(10),CON(51),DELSQ,DX,ENU(5000),ETR(5000),
     1        FREQ(5000),FREQHI,NCOLS,NMAX,NPEAK,NROWS,NTPTS,NXPTS,
     2        PRTSUM(31),RHO(10),R(5000),T(5000),XNU(10),ISLIT,KEY,BETA
      REAL*8  A,B,WS
      DATA  PLBL/'CALC','D AN','D OB','SVD ','SPEC','TRA ','   P',
     1           'ROB ','    '/, BLANK,ZERO/' ','0'/
      DATA  PLBL1/'ERRO','R CU','RVE ','   P','ROB ','   .'/
C
C.... FORMAT STATEMENTS.
C
 5000 FORMAT(I2,2X,19A4)
 5001 FORMAT (I2,I6,9I3,2F10.5,F5.2)
 5003 FORMAT (I2,8X,F10.5,2I5,2F10.5)
 5005 FORMAT(I2,8X,10F7.4)
 5006 FORMAT(I2,8X,3(F10.5,I5,5X))
 6000 FORMAT(1H0,//,2X,15(1H*),13H CARD NUMBER I5,13H OUT OF ORDER,15(1H
     1*))
 6001 FORMAT(1H1,19A4///1X,19A4//)
 6002 FORMAT (I4)
 6003 FORMAT(1H0,5X,50HSPREAD TOO GREAT BETWEEN FHI AND FLO
     1    ,5X,9HTHEY ARE 2(2X,F10.5))
 6004 FORMAT (//'0',13X,'SLIT WIDTH',7X,'FREQLO',7X,'FREQHI',7X,
     1          'CELL PATH'/'0',15X,F5.2,8X,F8.2,5X,F8.2,8X,F7.4///
```

```
     2        '0',21X,'NUMBER OF EXPERIMENTAL POINTS =',I5///               BAND0360
     3        '0',20X,'PEAK      ABSORBANCE      CONCENTRATION')              BAND0370
 6005 FORMAT ('0',21X,I2,8X,F6.4,9X,F8.5)                                   BAND0380
 6006 FORMAT('0',22X,'***** PROBLEM NUMBER'I5,' *****'//20X,'NUMBER OF PBAND0390
     1EAKS = 'I2//15X,'THE INITIAL ESTIMATES OF THE PARAMETERS ARE ....'BAND0400
     2//3X,'PEAK',7X,'E0',7X,'HOLD'6X,'DELNU',5X,'HOLD'7X,'NU'7X,'HOLD')BAND0410
 6007 FORMAT ('0',15X,'.... IMPROVEMENT IN FIRST PHASE')                    BAND0420
 6008 FORMAT (/'0*** ENTERING 10THS CYCLE ON ITERATION',I3,' ***'/          BAND0430
     1        '0',5X,'PREVIOUS SUM SQ. = ',E14.7,5X,                        BAND0440
     2        'CURRENT SUM SQ. = ',E14.7)                                   BAND0450
 6009 FORMAT(1H0,15X,35H.... IMPROVEMENT FOUND ON PEAK NO. I4)              BAND0460
 6010 FORMAT(1H1)                                                           BAND0470
 6011 FORMAT (/'0',5X,'..... SUM OF SQUARES FOR ITERATION',I3,' = ',        BAND0480
     1        E13.6,' .....',19X,F11.6/'0',20X,'... PARAMETER SET ...'/     BAND0490
     2        '0',5X,'PEAK',8X,'E0',18X,'DELNU',17X,'NU')                   BAND0500
 6012 FORMAT(1H0,26H**** SINGULAR MATRIX, SET I3,14H ON ITERATION I3,4H*BAND0510
     1***)                                                                  BAND0520
 6013 FORMAT(1H0,15X,28H** HALTED AFTER 25 CYCLES **)                       BAND0530
 6014 FORMAT(1H0,///,10X,27HPROBLEM COMPLETED ON CYCLE I3)                  BAND0540
 6015 FORMAT(1H0,5X,36H... SUM OF SQUARES STATIONARY AFTER I3,2X, 9HCYCLBAND0550
     1ES...)                                                                BAND0560
 6016 FORMAT(1H1,20X,27H...RESULTS FOR PROBLEM NO. I6,4H ...///25X,17HSUBAND0570
     1M OF SQUARES = E13.6)                                                 BAND0580
 6017 FORMAT ('0',5X,'MOLAR',8X,'ABSORBANCE',11X,'LINE WIDTH',12X,          BAND0590
     1        'FREQUENCY'/'  ABSORPTIVITY  ',3('VALUE    STD DEV',6X))      BAND0600
 6018 FORMAT ('0',2X,2F9.4,1PE12.4,0PF9.2,1PE12.4,0PF10.1,1PE12.4)          BAND0610
 6019 FORMAT (////' ',23X,'ABSORBANCE',21X,'TRANSMITTANCE'///               BAND0620
     1        ' ',5X,'FREQUENCY',5X,'OBSERVED',5X,'CALCULATED',10X,         BAND0630
     2        'OBSERVED',5X,'CALCULATED')                                   BAND0640
 6020 FORMAT  (A1,I4,2X,F7.1,2(4X,F10.4),9X,F10.4,4X,F10.4,8X,2F10.4)       BAND0650
 6021 FORMAT(1H0,//,5X,29HSUM OF SQUARES FOR ABSORBANCE,10X,32HSUM OF SQBAND0660
     1UARES FOR TRANSMITTANCE//10X,E20.8,10X,E20.8)                         BAND0670
 6022 FORMAT('0',3X,I2,4X,3(F10.4,3X,'(',I2,')',3X))                        BAND0680
 6023 FORMAT (//'0 LARGEST ABSORBANCE ERROR AT',F7.1,' CM-1'/               BAND0690
     1        '  OBSERVED TRANS =',F7.4,5X,'CALCD TRANS =',F7.4)            BAND0700
```

```
6024 FORMAT (/'0 OBSERVED AND CALCD CURVES HAVE BEEN PLOTTED')          BAND0710
6025 FORMAT('0',5X,'** DATA SMOOTHED WITH ',I3,' POINT POLYNOMIAL OF DEBAND0720
    1GREE ',I3,' **')                                                   BAND0730
6026 FORMAT (1H0,5X,44HTHEORETICAL CURVE CALCULATED AT INTERVALS OFF5.2BAND0740
    1,5H CM-1)                                                          BAND0750
6027 FORMAT (//1H ,32X,2A4)                                             BAND0760
6028 FORMAT(' ',7X,I2,4X,3(F10.5,11X))                                  BAND0770
6029 FORMAT ('0',5X,'.... NO IMPROVEMENT IN 10THS CYCLE')               BAND0780
6030 FORMAT ('0 ERROR CURVE HAS BEEN PLOTTED')                          BAND0790
6031 FORMAT ('0',24X,'BETA =',F9.5,5X,'HOLD =',I3/                      BAND0800
    1        '0',29X,'DAMPING FACTOR =',F5.2//)                         BAND0810
6032 FORMAT ('0',4X,'BETA =',F9.5)                                      BAND0820
6033 FORMAT (//'0',18X,'BETA =',F8.4,5X,'STD DEV =',1PE11.4)            BAND0830
 801 FORMAT (I5,3X,F7.0,F5.1,I5)                                        BAND0840
 802 FORMAT (20I4)                                                      BAND0850
C                                                                       BAND0860
C                                                                       BAND0870
C.... INITIALIZE.                                                       BAND0880
C                                                                       BAND0890
      CALL GDATE (DATE)                                                 BAND0900
      CALL DISK                                                         BAND0910
      LIGHT = 1                                                         BAND0920
      IFLAG = 1                                                         BAND0930
C                                                                       BAND0940
C.... READ TWO ALPHANUMERIC INFORMATION CARDS, WRITE PAGE HEADING.      BAND0950
C                                                                       BAND0960
    1 READ (5,5000,END=43)  KARD,(ALPHA(I),I=1,19)                      BAND0970
      IF(KARD.EQ.1) GO TO 3                                             BAND0980
      IF (KARD.EQ.-9)  GO TO 43                                         BAND0990
    2 IF(LIGHT.EQ.1) WRITE (6,6000) KARD                                BAND1000
      LIGHT = 2                                                         BAND1010
      GO TO 1                                                           BAND1020
    3 READ (5,5000) KARD,(ALPHA(I),I = 20,38)                           BAND1030
      IF(KARD.NE.2) GO TO 2                                             BAND1040
      WRITE (6,6001) (ALPHA(I),I = 1,38)                                BAND1050
```

```
      WRITE (6,6027)  DATE
C
C.... READ PROBLEM CONTROL CARD.
C
      READ (5,5001)  KARD,NOPROB,NPLT,LPROB,NPEAK,IHOLD,MODE,NGATE,
     1               NPOLY,IFPNCH,IFPRNT,ISTP,DX,FACTOR
      IF(KARD.NE.3) GO TO 2
      IF (FACTOR.LE.0.0)  FACTOR = 1.0
C
C.... READ IN SPECTRAL DATA.
C
      CALL SPCTRM (LIGHT,MODE,EDX,&1)
      IF (DX.LE.0.0)  DX = EDX
      IF (NGATE.EQ.0)  GO TO 7
C
C.... SMOOTH THE DATA.
C
      CALL SMTH1 (NGATE,NPOLY,WS)
      CALL SMTH2 (NXPTS,ETR,ETR)
C
C.... INITIALIZE PLOT ROUTINE.
C
    7 IF (NPLT.EQ.0)  GO TO 31
      GO TO (20,31), IFLAG
   20 CALL PLOT1
      IFLAG = 2
C
C.... INITIALIZE MATRIX NHOLD.  NHOLD(I,1) IS A FLAG TO INDICATE IF
C.... A PARAMETER IS TO BE HELD CONSTANT.  NHOLD(I,2) CONTAINS
C.... THE NUMBER OF CYCLES FOR WHICH THE PARAMETER IS TO BE HELD
C.... CONSTANT.
C
   31 DO 30 I = 1,31
      NHOLD(I,1) = 1
      NHOLD(I,2) = 0
```

```
   30 CONTINUE
C
C.... READ PEAK PARAMETER CARDS.
C
      DO 4 I = 1,NPEAK
      READ(5,5006) KARD,EO(I),IHEO(I),DELNU(I),IHRHO(I),XNU(I),IHNU(I)
      RHO(I) = 4.0/(DELNU(I) * DELNU(I))
      IF (KARD.NE.4) GO TO 2
    4 CONTINUE
C
C.... READ ESTIMATE OF CONSTANT TERM, NUMBER OF ITERATIONS IT IS TO BE
C.... HELD CONSTANT, THE DEGREE OF POLYNOMIAL TO BE USED IN SLIT CON-
C.... VOLUTION, THE SPECTRAL SLIT WIDTH AND THE CELL THICKNESS.
C
      READ (5,5003)  KARD,BETA,IHBETA,MPOLY,SLIT,XL
      IF(KARD.NE.5) GO TO 2
C
C.... READ CONCENTRATION VALUES TO BE ASSOCIATED WITH EACH PEAK.
C
      READ(5,5005) KARD,(C(J),J = 1,10)
      IF(KARD.NE.6)  GO TO 2
C
C.... CALCULATE PEAK ABSORBANCE ESTIMATES.
C
      DO 5 J = 1,NPEAK
      AO(J) = EO(J) * XL * C(J)
    5 CONTINUE
      IF(SLIT.LE.0.0) GO TO 51
C
C.... BUILD VECTOR TO BE USED IN SLIT CONVOLUTION.
C
      CALL SCAN(SLIT,DX,MPOLY,NMAX,D,WS)
      NMP = NMAX + 1
      DO 50 NI = 1,NMP
      CON(NI) = D(NI)
```

```
   50 CONTINUE
      GO TO 6
   51 NMAX = 0
      CON(1) = 1.0
C
C.... WRITE PEAK PARAMETERS.
C
    6 WRITE(6,6006) NOPROB,NPEAK
      DO 60 I = 1,NPEAK
      WRITE(6,6022) I,EO(I),IHEO(I),DELNU(I),IHRHO(I),XNU(I),IHNU(I)
   60 CONTINUE
      WRITE (6,6031)  BETA,IHBETA,FACTOR
      WRITE (6,6026)  DX
      IF (NGATE.NE.0)  WRITE (6,6025) NGATE,NPOLY
C
C.... BUILD MATRIX NHOLD.
C
      NPK2 = 2 * NPEAK
      NDEL = 0
      IF(IHOLD.LE.0) GO TO 8
      DO 602 L = 1,NPEAK
      I = L + 1
      IF(IHEO(L).LE.0) GO TO 600
      NDEL = NDEL + 1
      NHOLD(I,1) = 2
        NHOLD(I,2) = IHEO(L)
  600 IF(IHRHO(L).LE.0) GO TO 601
      NDEL = NDEL + 1
      IS = I + NPEAK
      NHOLD(IS,1) = 2
      NHOLD(IS,2) = IHRHO(L)
  601 IF(IHNU(L).LE.0) GO TO 602
      NDEL = NDEL + 1
      IS = I + NPK2
      NHOLD(IS,1) = 2
```

```
      NHOLD(IS,2) = IHNU(L)                                             BAND2110
  602 CONTINUE                                                          BAND2120
      IF (IHBETA.LE.0)  GO TO 8                                         BAND2130
      NDEL = NDEL + 1                                                   BAND2140
      NHOLD(1,1) = 2                                                    BAND2150
      NHOLD(1,2) = IHBETA                                               BAND2160
C                                                                       BAND2170
C.... CALCULATE THE LIMITS OF THE FREQUENCY VECTOR ASSOCIATED WITH THE  BAND2180
C.... CALCULATED SPECTRUM.                                              BAND2190
C                                                                       BAND2200
    8 ISLIT = SLIT/DX + 0.001                                           BAND2210
      XSLIT = DX * ISLIT                                                BAND2220
      FREQLO = ENU(NXPTS) - XSLIT                                       BAND2230
      FREQHI = ENU(1) + XSLIT                                           BAND2240
      NTPTS    = (1.0/DX)*(FREQHI    - FREQLO    ) + 1.0                BAND2250
      IF(NTPTS .LT.5000) GO TO 12                                       BAND2260
      WRITE (6,6003)   FREQLO   ,FREQHI                                 BAND2270
      LIGHT = 2                                                         BAND2280
      GO TO 1                                                           BAND2290
   12 WRITE(6,6004) SLIT,FREQLO,FREQHI,XL,NXPTS                         BAND2300
      DO 13 J = 1,NPEAK                                                 BAND2310
      WRITE(6,6005) J,AO(J),C(J)                                        BAND2320
C                                                                       BAND2330
C.... SCALE CONCENTRATION VALUES AND PEAK ABSORBANCE ESTIMATES.         BAND2340
C                                                                       BAND2350
      C(J) = C(J) * XL                                                  BAND2360
      AO(J) = AO(J) * 2.302585                                          BAND2370
   13 CONTINUE                                                          BAND2380
      BETA = BETA * 2.302585                                            BAND2390
      IF(LPROB.EQ.1) GO TO 17                                           BAND2400
C                                                                       BAND2410
C.... IF THE INPUT SPECTRAL DATA IS IN TERMS OF ABSORBANCE, CONVERT     BAND2420
C.... TO TRANSMITTANCE.                                                 BAND2430
C                                                                       BAND2440
      DO 14 K = 1,NXPTS                                                 BAND2450
```

```
      EXPN = - 2.302585 * ETR(K)                                        BAND2460
      ETR(K) = EXP(EXPN)                                                BAND2470
   14 CONTINUE                                                          BAND2480
   17 IF (IHOLD.GE.0)   WRITE (6,6010)                                  BAND2490
C                                                                       BAND2500
C.... BUILD FREQUENCY VECTOR FOR THE CALCULATED SPECTRUM.               BAND2510
C                                                                       BAND2520
      DO 19  K=1,NTPTS                                                  BAND2530
      FREQ(K) = FREQHI - (K-1)*DX                                       BAND2540
   19 CONTINUE                                                          BAND2550
C                                                                       BAND2560
C.... INITIALIZE FOR FIRST CYCLE OF LEAST-SQUARES.                      BAND2570
C                                                                       BAND2580
      KGO = 1                                                           BAND2590
      ITER = 1                                                          BAND2600
      NROWS = 3 * NPEAK + 1                                             BAND2610
      NCOLS = NROWS + 1                                                 BAND2620
      NPK = 0                                                           BAND2630
      KBETA = 0                                                         BAND2640
      LAST = 1                                                          BAND2650
      IF (IHOLD.LT.0)  LAST = 2                                         BAND2660
      SUMSQ = 1.0 E 30                                                  BAND2670
      DO 200 I = 1,NROWS                                                BAND2680
      BSAVE(I) = 0.0                                                    BAND2690
  200 CONTINUE                                                          BAND2700
C                                                                       BAND2710
C.... BEGIN ITERATIVE LEAST-SQUARES LOOP.                               BAND2720
C.... CALCULATE DIMENSIONS OF COEFFICIENT MATRIX B FOR CURRENT CYCLE.   BAND2730
C                                                                       BAND2740
   21 NROWB = NROWS - NDEL                                              BAND2750
      NCOLB = NCOLS - NDEL                                              BAND2760
C                                                                       BAND2770
C.... INITIALIZE AND BUILD MATRIX A.                                    BAND2780
C                                                                       BAND2790
      DO 210 I = 1,NROWS                                                BAND2800
```

```
      DO 210 J = 1,NCOLS
      A(I,J) = 0.0
  210 CONTINUE
      DELSQ = 0.0
      CALL LORN3 (LAST)
C
C..... PROBLEM FINISHED?
C
      GO TO (212,40),LAST
C
C.....NO, CALCULATE PERCENT IMPROVEMENT.
C
  212 PERCNT = 1.0 -  DELSQ/SUMSQ
C
C.....TEST FOR DIVERGENCE OR CONVERGENCE.
C
      IF (PERCNT.LT.0.0)  GO TO (294,290,29), KGO
      IF (PERCNT.EQ.0.)  GO TO 28
      IF(PERCNT.LT.TSTP.AND.KGO.EQ.1)  GO TO 38
      GO TO (33,321,32), KGO
C
C.....BUILD A VECTOR CONTAINING THE INDECES OF THOSE ROWS OF MATRIX A
C.....WHICH WILL BE LOADED INTO MATRIX B.
C
   22 K = 0
      DO 221 I = 1,NCOLS
      IGO = NHOLD(I,1)
      GO TO (220,221),IGO
  220 K = K + 1
      NDX(K) = I
  221 CONTINUE
C
C.....BUILD MATRIX B.
C
      DO 223 I = 1,NROWB
```

```
      IS = NDX(I)
      DO 222 J = 1,NCOLB
      JS = NDX(J)
      B(I,J) = A(IS,JS)
  222 CONTINUE
  223 CONTINUE
C
C.....INVERT MATRIX B.
C
      DO 27 K = 1,NROWB
      IF(B(1,1).LT.0.000001) GO TO 36
      TEMP = 1.0/B(1,1)
      DO 23 J = 1,NROWB
      JP = J + 1
      WS(J) = TEMP * B(1,JP)
   23 CONTINUE
      WS(JP) = TEMP
      DO 25 J = 2,NROWB
      TEMP = B(J,1)
      JM = J - 1
      DO 24 L = 1,NROWB
      LP = L + 1
      B(JM,L) = B(J,LP) - TEMP * WS(L)
   24 CONTINUE
      B(JM,LP) = - TEMP * WS(LP)
   25 CONTINUE
      DO 26 J = 1,NCOLB
      B(NROWB,J) = WS(J)
   26 CONTINUE
   27 CONTINUE
C
C.... SCALE CORRECTIONS BY DAMPING FACTOR.
C
      DO 18  K=1,NROWB
      B(K,1) = FACTOR * B(K,1)
```

```
   18 CONTINUE                                                          BAND3510
      NP = NPEAK                                                        BAND3520
      JGO = 1                                                           BAND3530
      M = 0                                                             BAND3540
      IF (NHOLD(1,1).GT.1)  GO TO 269                                   BAND3550
      M = 1                                                             BAND3560
      BSAVE(1) = B(1,1)                                                 BAND3570
      BETA = BETA + BSAVE(1)                                            BAND3580
C                                                                       BAND3590
C.....SAVE CORRECTIONS FOR THOSE PARAMETERS NOT HELD CONSTANT.           BAND3600
C                                                                       BAND3610
  269 DO 276 L = 2,NROWS                                                BAND3620
      I = L - 1                                                         BAND3630
      IGO = NHOLD(L,1)                                                  BAND3640
      GO TO (270,275),IGO                                               BAND3650
C                                                                       BAND3660
C.....UPDATE ESTIMATES.                                                 BAND3670
C                                                                       BAND3680
  270 M = M + 1                                                         BAND3690
      BSAVE(L) = B(M,1)                                                 BAND3700
  271 IF(I.LE.NP) GO TO (272,273,274),JGO                               BAND3710
      NP = NP + NPEAK                                                   BAND3720
      JGO = JGO + 1                                                     BAND3730
      GO TO 271                                                         BAND3740
  272 AO(I) = AO(I) + B(M,1)                                            BAND3750
      GO TO 276                                                         BAND3760
  273 IM = I - NPEAK                                                    BAND3770
      TEMP = RHO(IM)                                                    BAND3780
      TEST = B(M,1)                                                     BAND3790
  277 IF ((TEMP+TEST).GT.0.0)  GO TO 278                                BAND3800
      TEST = 0.9 * TEST                                                 BAND3810
      GO TO 277                                                         BAND3820
  278 TEST1 = TEMP/4                                                    BAND3830
  279 TEST2 = TEMP + TEST                                               BAND3840
      IF (TEST2.GT.TEST1)  GO TO 280                                    BAND3850
```

```
      TEST = 0.9 * TEST                                                 BAND3860
      GO TO 279                                                         BAND3870
  280 B(M,1) = TEST                                                     BAND3880
      BSAVE(L) = TEST                                                   BAND3890
      RHO(IM) = RHO(IM) + B(M,1)                                        BAND3900
      GO TO 276                                                         BAND3910
  274 IM = I - NPK2                                                     BAND3920
      XNU(IM) = XNU(IM) + B(M,1)                                        BAND3930
      GO TO 276                                                         BAND3940
C                                                                       BAND3950
C.....TEST TO DETERMINE IF A PARAMETER BEING HELD CONSTANT SHOULD BE    BAND3960
C.....ALLOWED TO VARY.                                                  BAND3970
C                                                                       BAND3980
  275 IF(ITER.LE.NHOLD(L,2)) GO TO 276                                  BAND3990
      NHOLD(L,1) = 1                                                    BAND4000
      NHOLD(L,2) = 0                                                    BAND4010
      NDEL = NDEL - 1                                                   BAND4020
  276 CONTINUE                                                          BAND4030
      IF (NHOLD(1,1).LE.1)  GO TO 281                                   BAND4040
      IF (ITER.LE.IHBETA)  GO TO 281                                    BAND4050
      NHOLD(1,1) = 1                                                    BAND4060
      NHOLD(1,2) = 0                                                    BAND4070
      NDEL = NDEL - 1                                                   BAND4080
  281 IF(NDEL.LT.0) NDEL = 0                                            BAND4090
C                                                                       BAND4100
C.....RECYCLE.                                                          BAND4110
C                                                                       BAND4120
      GO TO 21                                                          BAND4130
C                                                                       BAND4140
C.....IF THE PROBLEM HAS DIVERGED, TRY 0.1 OF THE CALCULATED            BAND4150
C.....CORRECTIONS.                                                      BAND4160
C                                                                       BAND4170
  294 DO 293  I=1,NPEAK                                                 BAND4180
      IP = I + NPEAK + 1                                                BAND4190
      IPP = IP + NPEAK                                                  BAND4200
```

```
      AO(I) = HOLDEO(I) + 0.1*BSAVE(I+1)                                BAND4210
      RHO(I) = HOLDRH(I) + 0.1*BSAVE(IP)                                BAND4220
      XNU(I) = HOLDXN(I) + 0.1*BSAVE(IPP)                               BAND4230
  293 CONTINUE                                                          BAND4240
      BETA = HOLDBE + 0.1*BSAVE(1)                                      BAND4250
      KGO = 2                                                           BAND4260
      WRITE (6,6008)  ITER,SUMSQ,DELSQ                                  BAND4270
      GO TO 21                                                          BAND4280
C                                                                       BAND4290
C.....IF PROBLEM STILL DIVERGES, TRY 0.1 OF THE CALCULATED              BAND4300
C.....CORRECTIONS FOR EACH PEAK IN TURN.                                BAND4310
C                                                                       BAND4320
  290 DO 292  I=1,NPEAK                                                 BAND4330
      AO(I) = HOLDEO(I)                                                 BAND4340
      RHO(I) = HOLDRH(I)                                                BAND4350
      XNU(I) = HOLDXN(I)                                                BAND4360
  292 CONTINUE                                                          BAND4370
   29 IF ((NHOLD(1,1).GT.1).OR.(KBETA.GT.0))  GO TO 291                 BAND4380
      BETA = HOLDBE + 0.1*BSAVE(1)                                      BAND4390
      KBETA = 1                                                         BAND4400
      GO TO 35                                                          BAND4410
  291 NPK = NPK + 1                                                     BAND4420
      IF(NPK.GT.NPEAK) GO TO 39                                         BAND4430
      NPK1 = NPK + NPEAK                                                BAND4440
      NPK2 = NPK1 + NPEAK                                               BAND4450
      AO(NPK) = HOLDEO(NPK) + 0.1 * BSAVE(NPK + 1)                      BAND4460
      RHO(NPK) = HOLDRH(NPK) + 0.1 * BSAVE(NPK1 + 1)                    BAND4470
      XNU(NPK) = HOLDXN(NPK) + 0.1 * BSAVE(NPK2 + 1)                    BAND4480
      IF (NPK.GT.1)  GO TO 351                                          BAND4490
      BETA = HOLDBE                                                     BAND4500
      GO TO 35                                                          BAND4510
  351 IT = NPK - 1                                                      BAND4520
      AO(IT) = HOLDEO(IT)                                               BAND4530
      RHO(IT) = HOLDRH(IT)                                              BAND4540
      XNU(IT) = HOLDXN(IT)                                              BAND4550
```

```
   35 KGO = 3                                                           BAND4560
      GO TO 21                                                          BAND4570
C                                                                       BAND4580
C.....UPDATE ERROR SUM OF SQUARES, PRINT CURRENT ESTIMATES.             BAND4590
C                                                                       BAND4600
   32 WRITE (6,6009) NPK                                                BAND4610
      GO TO 33                                                          BAND4620
  321 WRITE (6,6007)                                                    BAND4630
   33 SUMSQ = DELSQ                                                     BAND4640
      WRITE (6,6011)  ITER,SUMSQ,PERCNT                                 BAND4650
      KGO = 1                                                           BAND4660
      ITER = ITER + 1                                                   BAND4670
      NPK = 0                                                           BAND4680
      KBETA = 0                                                         BAND4690
      DO 34 I1 = 1,NPEAK                                                BAND4700
      EOI1 = AO(I1) * 0.4342945/C(I1)                                   BAND4710
      DELX = 2.0/SQRT(RHO(I1))                                          BAND4720
      WRITE(6,6028) I1,EOI1   ,DELX    ,XNU(I1)                         BAND4730
C                                                                       BAND4740
C.....STORE RESULTS FROM CURRENT CYCLE.                                 BAND4750
C                                                                       BAND4760
      HOLDEO(I1)  = AO(I1)                                              BAND4770
      HOLDRH(I1)  = RHO(I1)                                             BAND4780
      HOLDXN(I1)  = XNU(I1)                                             BAND4790
   34 CONTINUE                                                          BAND4800
      BB = 0.434295 * BETA                                              BAND4810
      WRITE (6,6032)  BB                                                BAND4820
      HOLDBE = BETA                                                     BAND4830
      IF(ITER.GT.25) GO TO 37                                           BAND4840
C                                                                       BAND4850
C.....RECYCLE.                                                          BAND4860
C                                                                       BAND4870
      GO TO 22                                                          BAND4880
C                                                                       BAND4890
C.....SINGULAR MATRIX, DO FINAL CALCULATION ON PREVIOUS ESTIMATES.       BAND4900
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C                                                                          BAND4910
   36 WRITE (6,6012) K,ITER                                                BAND4920
      GO TO 390                                                            BAND4930
C                                                                          BAND4940
C.....PROBLEM EXCEEDED MAXIMUM NUMBER OF CYCLES.                           BAND4950
C                                                                          BAND4960
   37 WRITE (6,6013)                                                       BAND4970
      GO TO 40                                                             BAND4980
C                                                                          BAND4990
C.... NO CHANGE IN SUM OF SQUARES, TERMINATE.                               BAND5000
C                                                                          BAND5010
   28 WRITE (6,6015)  ITER                                                 BAND5020
      GO TO 40                                                             BAND5030
C                                                                          BAND5040
C.....PROBLEM COMPLETED.                                                   BAND5050
C                                                                          BAND5060
   38 WRITE (6,6014) ITER                                                  BAND5070
      GO TO 40                                                             BAND5080
C                                                                          BAND5090
C.....NO IMPROVEMENT ON TENTHS CYCLE, DO FINAL CALCULATION ON PREVIOUS     BAND5100
C.....ESTIMATES.                                                           BAND5110
C                                                                          BAND5120
   39 WRITE (6,6029)                                                       BAND5130
  390 LAST = 2                                                             BAND5140
      DO 391 I1 = 1,NPEAK                                                  BAND5150
      AO(I1) = HOLDEO(I1)                                                  BAND5160
      RHO(I1) =HOLDRH(I1)                                                  BAND5170
      XNU(I1) = HOLDXN(I1)                                                 BAND5180
  391 CONTINUE                                                             BAND5190
      BETA = HOLDBE                                                        BAND5200
      GO TO 21                                                             BAND5210
C                                                                          BAND5220
C.....PRINT FINAL RESULTS.                                                 BAND5230
C                                                                          BAND5240
   40 WRITE (6,6016) NOPROB,DELSQ                                          BAND5250
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      WRITE (6,6017)                                                    BAND5260
      NDF = NXPTS - NROWB                                               BAND5270
      M = 0                                                             BAND5280
      DO 45  J=1,NROWS                                                  BAND5290
      VAR(J) = 0.0                                                      BAND5300
      IF (IHOLD.LT.0)  GO TO 45                                         BAND5310
      JGO = NHOLD(J,1)                                                  BAND5320
      GO TO (44,45), JGO                                                BAND5330
   44 M = M + 1                                                         BAND5340
      VAR(J) = DELSQ*B(M,M+1)/NDF                                       BAND5350
   45 CONTINUE                                                          BAND5360
      DO 41 J = 1,NPEAK                                                 BAND5370
      JP = J + NPEAK                                                    BAND5380
      JPP = JP + NPEAK                                                  BAND5390
      AA = AO(J) * 0.4342945                                            BAND5400
      EOJ = AA/C(J)                                                     BAND5410
      DEL = 2.0/SQRT(RHO(J))                                            BAND5420
      SIGAO = 0.434295 * SQRT(VAR(J+1))                                 BAND5430
      TEMP = 1./(RHO(J)**3)                                             BAND5440
      SIGDEL = SQRT(TEMP*VAR(JP+1))                                     BAND5450
      SIGXNU = SQRT(VAR(JPP+1))                                         BAND5460
   41 WRITE (6,6018)  EOJ,AA,SIGAO,DEL,SIGDEL,XNU(J),SIGXNU             BAND5470
      BB = 0.434295 * BETA                                              BAND5480
      SIGBET = 0.434295 * SQRT(VAR(1))                                  BAND5490
      WRITE (6,6033)  BB,SIGBET                                         BAND5500
      CCHAR = BLANK                                                     BAND5510
      IF (IFPRNT.GT.1)  CCHAR = ZERO                                    BAND5520
      IF (IFPRNT.GT.0)  WRITE (6,6019)                                  BAND5530
      IBIG = 1                                                          BAND5540
      BIG = 0.0                                                         BAND5550
      SUMAB = 0.0                                                       BAND5560
      SUMTR = 0.0                                                       BAND5570
      DO 42 K = 1,NXPTS                                                 BAND5580
      ETRK = ETR(K)                                                     BAND5590
      RK = R(K)                                                         BAND5600
```

```
      XX = -ALOG10(ETRK)                                                BAND5610
      XY = - ALOG10(RK)                                                 BAND5620
      SUMTR = SUMTR + (ETRK - RK) * (ETRK - RK)                         BAND5630
      SUMAB = SUMAB + (XX - XY) * (XX - XY)                             BAND5640
      ERRA = XX - XY                                                    BAND5650
      ERRT = ETRK - RK                                                  BAND5660
      TEST = ABS(ERRA)                                                  BAND5670
      IF (TEST.LE.BIG)  GO TO 52                                        BAND5680
      IBIG = K                                                          BAND5690
      BIG = TEST                                                        BAND5700
   52 CONTINUE                                                          BAND5710
      IF (IFPRNT.EQ.0)  GO TO 42                                        BAND5720
      WRITE (6,6020)  CCHAR,K,ENU(K),XX,XY,ETRK,RK,ERRA,ERRT            BAND5730
   42 CONTINUE                                                          BAND5740
      WRITE (6,6021) SUMAB,SUMTR                                        BAND5750
      WRITE (6,6023)  ENU(IBIG),ETR(IBIG),R(IBIG)                       BAND5760
      KGO = 1                                                           BAND5770
      LIGHT = 1                                                         BAND5780
C                                                                       BAND5790
C.... PUNCH CALCULATED SPECTRUM.                                         BAND5800
C                                                                       BAND5810
      IF (IFPNCH.EQ.0)  GO TO 47                                        BAND5820
      WRITE (8,801)  NOPROB,ENU(1),EDX,NXPTS                            BAND5830
      DO 46  K=1,NXPTS                                                  BAND5840
   46 IR(K) = 1000*R(K) + 0.5                                           BAND5850
      WRITE (8,802)  (IR(K), K=1,NXPTS)                                 BAND5860
C                                                                       BAND5870
C.... PLOT RESULTS.                                                      BAND5880
C                                                                       BAND5890
   47 IF (NPLT.EQ.0)  GO TO 1                                           BAND5900
      XHI = ENU(1)                                                      BAND5910
      CALL STRING (C(1),4)                                              BAND5920
      WRITE (0,6002)  NOPROB                                            BAND5930
      PLBL(9) = C(1)                                                    BAND5940
      CALL PLOT2 (XHI,EDX,NXPTS,PLBL,36,1)                              BAND5950
```

```
      CALL PLOT3 (R,XHI,EDX,NXPTS)                                      BAND5960
      CALL PLOT4 (ETR,XHI,EDX,NXPTS,3)                                  BAND5970
      WRITE (6,6024)                                                    BAND5980
      IF (NPLT.LT.2)  GO TO 1                                           BAND5990
      DO 48  K=1,NXPTS                                                  BAND6000
      ETRK = ETR(K)                                                     BAND6010
      ETRK = ALOG10(R(K)/ETRK)                                          BAND6020
      IF (ETRK.LT.-0.2)  ETRK = -0.2                                    BAND6030
      IF (ETRK.GT.0.2)  ETRK = 0.2                                      BAND6040
   48 ETR(K) = ETRK                                                     BAND6050
      PLBL1(6) = C(1)                                                   BAND6060
      CALL PLOT2 (0.,0.,-1,PLBL1,24,2)                                  BAND6070
      CALL PLOT3 (ETR,XHI,EDX,NXPTS)                                    BAND6080
      WRITE (6,6030)                                                    BAND6090
C                                                                       BAND6100
C.....GET A NEW PROBLEM.                                                BAND6110
C                                                                       BAND6120
      GO TO 1                                                           BAND6130
C                                                                       BAND6140
C.....END OF JOB.                                                       BAND6150
C                                                                       BAND6160
   43 IF (IFLAG.GT.1)  CALL PLOT5                                       BAND6170
      STOP                                                              BAND6180
      END                                                               BAND6190


      SUBROUTINE SCAN (SLIT,DX,NPOLY,MPNT,SCNSET,X)                     SCAN0010
C     WRITTEN BY A S ROSENBERG          5 12 67                         SCAN0020
C     MODIFIED     5 7 69                                               SCAN0030
C                                                                       SCAN0040
C     CALCULATES A SET OF CONVOLVING NUMBERS, SCNSET (OF DIMENSION      SCAN0050
C     MPNT+1) TO BE USED IN SCANNING A DIGITIZED SPECTRUM WITH A TRIANG-SCAN0060
C     ULAR SPECTRAL SLIT FUNCTION.                                      SCAN0070
C                                                                       SCAN0080
C     SLIT = SPECTRAL SLIT WIDTH IN CM-1.                               SCAN0090
```

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C                                                                       SCAN0100
C     DX = ABCISSA INCREMENT, IN CM-1, FOR THE DIGITIZED SPECTRUM.      SCAN0110
C                                                                       SCAN0120
C     NPOLY = THE DEGREE OF POLYNOMIAL TO BE USED IN FITTING ORDINATE   SCAN0130
C     VALUES OVER A TWO SPECTRAL SLIT WIDTH INTERVAL OF THE SPECTRUM.   SCAN0140
C     IF NPOLY IS LESS THAN 2, THE SET OF CONVOLVING NUMBERS WILL BE    SCAN0150
C     CALCULATED ACCORDING TO THE TRAPEZOID RULE.                       SCAN0160
C                                                                       SCAN0170
C     X IS AN ARRAY (DOUBLE WORD) TO BE USED AS SCRATCH AREA FOR MATRIX SCAN0180
C     INVERSION.                                                        SCAN0190
C                                                                       SCAN0200
C     REQUIRES SUBROUTINE CONMAT.                                       SCAN0210
C                                                                       SCAN0220
      DIMENSION SCNSET(51)                                              SCAN0230
      REAL*8  A(4,55),X(55)                                             SCAN0240
C     INITIALIZATION                                                    SCAN0250
      TERM = SLIT/DX                                                    SCAN0260
      IF (NPOLY.LT.2)  GO TO 5                                          SCAN0270
      MPNT = TERM + 0.5                                                 SCAN0280
      IF (MPNT.GE.1)  GO TO 1                                           SCAN0290
    4 MPNT = 0                                                          SCAN0300
      SCNSET(1) = 1.                                                    SCAN0310
      RETURN                                                            SCAN0320
    1 IF (NPOLY.GT.6)    NPOLY = 6                                      SCAN0330
      IF (NPOLY.LT.2)    NPOLY = 2                                      SCAN0340
      IT = NPOLY/2                                                      SCAN0350
      IF (IT.GT.MPNT)    IT = MPNT                                      SCAN0360
C     CALCULATE A MATRIX.                                               SCAN0370
      NPOLY = 2*IT                                                      SCAN0380
      NROW = IT + 1                                                     SCAN0390
      IPAR = 0                                                          SCAN0400
      LPNT = MPNT + 1                                                   SCAN0410
      CALL CONMAT (NROW,LPNT,IPAR,A,X)                                  SCAN0420
C     SCALE A AND BUILD SCNSET.                                         SCAN0430
      TERM = TERM * TERM                                                SCAN0440
```

```
      TEMP = 1.                                                         SCAN0450
      IT = 1                                                            SCAN0460
      DO 2  I=1,LPNT                                                    SCAN0470
      SCNSET(I) = A(1,I)                                                SCAN0480
    2 CONTINUE                                                          SCAN0490
      DO 3  I=2,NROW                                                    SCAN0500
      IT = IT + 2                                                       SCAN0510
      TEMP = TEMP * TERM                                                SCAN0520
      FACTOR = IT*(IT + 1)                                              SCAN0530
      FACTOR = 2.*TEMP/FACTOR                                           SCAN0540
      DO 3  J=1,LPNT                                                    SCAN0550
      SCNSET(J) = SCNSET(J) + FACTOR*A(I,J)                             SCAN0560
    3 CONTINUE                                                          SCAN0570
      RETURN                                                            SCAN0580
    5 MPNT = TERM + 0.001                                               SCAN0590
      IF (MPNT.LT.1)  GO TO 4                                           SCAN0600
      LPNT = MPNT + 1                                                   SCAN0610
      TEMP = SLIT - MPNT*DX                                             SCAN0620
      SUM = TEMP/2                                                      SCAN0630
      SCNSET(1) = SUM                                                   SCAN0640
      DO 6  I=2,MPNT                                                    SCAN0650
      TEMP = TEMP + DX                                                  SCAN0660
      SCNSET(I) = TEMP                                                  SCAN0670
      SUM = SUM + TEMP                                                  SCAN0680
    6 CONTINUE                                                          SCAN0690
      SCNSET(LPNT) = SLIT                                               SCAN0700
      SUM = 2*SUM + SLIT                                                SCAN0710
      DO 7  I=1,LPNT                                                    SCAN0720
      SCNSET(I) = SCNSET(I)/SUM                                         SCAN0730
    7 CONTINUE                                                          SCAN0740
      RETURN                                                            SCAN0750
      END                                                               SCAN0760

      SUBROUTINE LORN3 (LAST)                                           LORN0010
```

```
      COMMON   A(31,32),A0(10),CON(51),DELSQ,DX,ENU(5000),ETR(5000),    LORN0020
     1         FREQ(5000),FREQHI,NCOLS,NMAX,NPEAK,NROWS,NTPTS,NXPTS,    LORN0030
     2         PRTSUM(31),RHO(10),R(5000),T(5000),XNU(10),ISLIT,KEY,BETA LORN0040
      REAL*8   A                                                        LORN0050
C                                                                       LORN0060
C.... BUILD VECTOR OF ABSORBANCE VALUES FOR CALCULATED SPECTRUM.        LORN0070
C                                                                       LORN0080
      NROWM = NROWS - 1                                                 LORN0090
      DO 100 J = 1,NTPTS                                                LORN0100
      T(J) = BETA                                                       LORN0110
  100 CONTINUE                                                          LORN0120
      DO 2 J = 1,NPEAK                                                  LORN0130
      RHOJ = RHO(J)                                                     LORN0140
      XNUJ = XNU(J)                                                     LORN0150
      DO 1 K = 1,NTPTS                                                  LORN0160
      FDIFF = XNUJ - FREQ(K)                                            LORN0170
      DENK   = 1.0 + RHOJ * FDIFF * FDIFF                               LORN0180
      T(K) = T(K) + A0(J)/DENK                                          LORN0190
    1 CONTINUE                                                          LORN0200
    2 CONTINUE                                                          LORN0210
C                                                                       LORN0220
C.... CONVERT TO TRANSMITTANCE.                                         LORN0230
C                                                                       LORN0240
      DO 4 K = 1,NTPTS                                                  LORN0250
      T(K) = EXP(-T(K))                                                 LORN0260
    4 CONTINUE                                                          LORN0270
C                                                                       LORN0280
C.... CONVOLVE CALCULATED SPECTRUM WITH SLIT FUNCTION, BUILD            LORN0290
C.... MATRIX A.                                                         LORN0300
C                                                                       LORN0310
      NMP = NMAX + 1                                                    LORN0320
      CONS = CON(NMP)                                                   LORN0330
      K = ISLIT                                                         LORN0340
      DO 14 J = 1,NXPTS                                                 LORN0350
      K = K + 1                                                         LORN0360
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```
      TK = T(K)                                                         LORNO370
      SUMTN = 0.0                                                       LORNO380
      JUMP = 1                                                          LORNO390
      DO 5 L = 1,NROWM                                                  LORNO400
      PRTSUM(L) = 0.0                                                   LORNO410
    5 CONTINUE                                                          LORNO420
      DO 11 I1= 1,NPEAK                                                 LORNO430
      I2 = I1 + NPEAK                                                   LORNO440
      I3 = I2 + NPEAK                                                   LORNO450
      IF(NMAX .NE.0) GO TO 3                                            LORNO460
      SUMTN = 0.0                                                       LORNO470
      GO TO 9                                                           LORNO480
    3 DO 8 N = 1,NMAX                                                   LORNO490
      NJ = NMP - N                                                      LORNO500
      CONIN = CON(NJ)                                                   LORNO510
      KPN = K + N                                                       LORNO520
      KMN = K - N                                                       LORNO530
      IF(KMN.EQ.0) KMN = 1                                              LORNO540
      TKPN = T(KPN)                                                     LORNO550
      TKMN = T(KMN)                                                     LORNO560
      GO TO (50,51),JUMP                                                LORNO570
   50 SUMTN = SUMTN + CONIN * (TKPN + TKMN)                             LORNO580
   51 GO TO (53,8),LAST                                                 LORNO590
   53 V3 = XNU(I1) - FREQ(KPN)                                          LORNO600
      V4 = XNU(I1) - FREQ(KMN)                                          LORNO610
      V1 = V3 * V3                                                      LORNO620
      V2 = V4 * V4                                                      LORNO630
      DENP = 1.0 + RHO(I1) * V1                                         LORNO640
      DENM = 1.0 + RHO(I1) * V2                                         LORNO650
      T1 = TKPN/(DENP * DENP)                                           LORNO660
      T2 = TKMN/(DENM * DENM)                                           LORNO670
    7 PRTSUM(I1) = PRTSUM(I1) + CONIN * (TKPN/DENP + TKMN/DENM)         LORNO680
      PRTSUM(I2) = PRTSUM(I2) + CONIN * (V1 * T1 + V2 * T2)             LORNO690
      PRTSUM(I3) = PRTSUM(I3) + CONIN * (V3 * T1 + V4 * T2)             LORNO700
    8 CONTINUE                                                          LORNO710
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    9 GO TO (90,10), JUMP                                               LORN0720
   90 JUMP = 2                                                          LORN0730
      R(J) = CONS * TK + SUMTN                                          LORN0740
      DELTA = ETR(J) - R(J)                                             LORN0750
      DELSQ = DELSQ + DELTA * DELTA                                     LORN0760
      GO TO (10,14),LAST                                                LORN0770
   10 DENKD = XNU(I1) - FREQ(K)                                         LORN0780
      DENKV = DENKD * DENKD                                             LORN0790
      DENK = 1.0 + RHO(I1) * DENKV                                      LORN0800
      DENS = DENK * DENK                                                LORN0810
      PRTSUM(I1) = -(TK/DENK + PRTSUM(I1))                              LORN0820
      PRTSUM(I2) = AO(I1) * ( TK * DENKV/DENS + PRTSUM(I2))             LORN0830
      PRTSUM(I3) = 2.0 * RHO(I1) * AO(I1) * ( TK * DENKD/DENS + PRTSUM(ILORN0840
     13))                                                               LORN0850
   11 CONTINUE                                                          LORN0860
      DO 13 I1 = 1,NROWM                                                LORN0870
      I1P = I1 + 1                                                      LORN0880
      DO 12 I2 = I1,NROWM                                               LORN0890
      I2P = I2 + 1                                                      LORN0900
      A(I1P,I2P) = A(I1P,I2P) + PRTSUM(I1)*PRTSUM(I2)                   LORN0910
   12 CONTINUE                                                          LORN0920
      A(I1P,NCOLS) = A(I1P,NCOLS) + PRTSUM(I1)*DELTA                    LORN0930
      A(1,I1P) = A(1,I1P) - PRTSUM(I1)*R(J)                             LORN0940
   13 CONTINUE                                                          LORN0950
      A(1,1) = A(1,1) + R(J)*R(J)                                       LORN0960
      A(1,NCOLS) = A(1,NCOLS) - R(J)*DELTA                              LORN0970
   14 CONTINUE                                                          LORN0980
      GO TO (140,16),LAST                                               LORN0990
C                                                                       LORN1000
C.... IF NOT THE LAST CYCLE, COMPLETE BUILDING OF MATRIX A.             LORN1010
C                                                                       LORN1020
  140 DO 15 K = 2,NROWS                                                 LORN1030
      KM = K - 1                                                        LORN1040
      DO 15 L = 1,KM                                                    LORN1050
      A(K,L) = A(L,K)                                                   LORN1060
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   15 CONTINUE                                                          LORN1070
   16 RETURN                                                            LORN1080
      END                                                               LORN1090


      SUBROUTINE PLOT1                                                  PLOT0010
      DIMENSION  BUFF(750),Y(500),PLABEL(20)                            PLOT0020
C.....INITIALIZE.                                                       PLOT0030
      CALL PLOTS (BUFF,3000)                                            PLOT0040
      CALL PLOT (0.,-31.,3)                                             PLOT0050
      CALL PLOT (0.,-29.,-3)                                            PLOT0060
      JOB = 0                                                           PLOT0070
      SIZE = 0.07                                                       PLOT0080
      TEST = SIZE + 0.01                                                PLOT0090
      TEST = TEST * TEST                                                PLOT0100
      RETURN                                                            PLOT0110
      ENTRY PLOT2 (XHI,DX,NPNT,PLABEL,NLABEL,ITYPE)                     PLOT0120
C.....START A NEW PAGE.                                                 PLOT0130
      JOB = JOB + 1                                                     PLOT0140
      IF (JOB.EQ.1)  GO TO 3                                            PLOT0150
      IT = MOD(JOB,2) + 1                                               PLOT0160
      GO TO (1,2),IT                                                    PLOT0170
    1 CALL PLOT (-1.0,10.5,-3)                                          PLOT0180
      GO TO 3                                                           PLOT0190
    2 CALL PLOT (13.0,-11.5,-3)                                         PLOT0200
    3 CALL PLOT (14.0,0.,2)                                             PLOT0210
      CALL PLOT (14.0,11.,2)                                            PLOT0220
      CALL PLOT (0.,11.,2)                                              PLOT0230
      CALL PLOT (0.,0.,2)                                               PLOT0240
      XJOB = JOB                                                        PLOT0250
      CALL SYMBOL (0.5,0.07,0.14,'PLOT ',0.,5)                          PLOT0260
      CALL NUMBER (1.1,0.07,0.14,XJOB,0.,-1)                            PLOT0270
      CALL PLOT (1.0,0.5,-3)                                            PLOT0280
C.....DRAW AXES.                                                        PLOT0290
      IF (NPNT.LT.0)  GO TO 7                                           PLOT0300
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      XLO = XHI - (NPNT-1)*DX                                           PLOT0310
      CALL SCALA8 (XHI,XLO,DX,12.5,XSTART,XINCR)                        PLOT0320
    7 GO TO (8,9), ITYPE                                                PLOT0330
    8 CALL AXIS (0.,0.,'TRANSMITTANCE',13,10.,90.,0.,0.1,10.)           PLOT0340
      GO TO 10                                                          PLOT0350
    9 CALL AXIS (0.,0.,'ABSORBANCE',10,10.,90.,-0.2,0.04,10.)           PLOT0360
   10 CALL AXIS (0.,0.,'FREQUENCY, CM-1',-15,12.5,0.,XSTART,XINCR,10.)  PLOT0370
      CALL PLOT (12.5,0.,3)                                             PLOT0380
      CALL PLOT (12.5,10.,2)                                            PLOT0390
      CALL PLOT (0.,10.,2)                                              PLOT0400
      CALL SYMBOL (0.5,10.18,0.14,PLABEL,0.,NLABEL)                     PLOT0410
      RETURN                                                            PLOT0420
      ENTRY PLOT3 (Y,XHI,DX,NPNT)                                       PLOT0430
C.....DRAW A LINE PLOT.                                                 PLOT0440
      FACTOR = 10.                                                      PLOT0450
      IF (ITYPE.EQ.1)  GO TO 11                                         PLOT0460
      DO 6  I=1,NPNT                                                    PLOT0470
    6 Y(I) = Y(I) + 0.2                                                 PLOT0480
      FACTOR = 25.                                                      PLOT0490
   11 YY = FACTOR * Y(1)                                                PLOT0500
      XX = (XHI - XSTART)/XINCR                                         PLOT0510
      DIF = DX/XINCR                                                    PLOT0520
      CALL PLOT (XX,YY,3)                                               PLOT0530
      DO 4  I=2,NPNT                                                    PLOT0540
      XX = XX - DIF                                                     PLOT0550
      YY = FACTOR * Y(I)                                                PLOT0560
      CALL PLOT (XX,YY,2)                                               PLOT0570
    4 CONTINUE                                                          PLOT0580
      RETURN                                                            PLOT0590
      ENTRY PLOT4 (Y,XHI,DX,NPNT,IBCD)                                  PLOT0600
C.....DRAW A POINT PLOT.                                                PLOT0610
      XOLD = -1.                                                        PLOT0620
      YOLD = -1.                                                        PLOT0630
      DIF = DX/XINCR                                                    PLOT0640
      XX = (XHI - XSTART)/XINCR + DIF                                   PLOT0650
```

```
      DO 5  I=1,NPNT                                                    PLOT0660
      XX = XX - DIF                                                     PLOT0670
      YY = 10 * Y(I)                                                    PLOT0680
      DIST2 = (XOLD-XX)*(XOLD-XX) + (YOLD-YY)*(YOLD-YY)                 PLOT0690
      IF (DIST2.LE.TEST)  GO TO 5                                       PLOT0700
      CALL SYMBOL (XX,YY,SIZE,IBCD,0.,-1)                               PLOT0710
      XOLD = XX                                                         PLOT0720
      YOLD = YY                                                         PLOT0730
    5 CONTINUE                                                          PLOT0740
      RETURN                                                            PLOT0750
      ENTRY PLOT5                                                       PLOT0760
C.....TERMINATE.                                                         PLOT0770
      CALL PLOT (18.0,0.,-3)                                            PLOT0780
      CALL PLOT (0.,0.,999)                                             PLOT0790
      RETURN                                                            PLOT0800
      END                                                               PLOT0810

      SUBROUTINE SMTH1 (NPNT,NPOLY,X)                                   SMTH0010
C     WRITTEN BY A S ROSENBERG          5 12 67                         SMTH0020
C     FIRST SECTION:                                                    SMTH0030
C     CALCULATES A MATRIX B TO BE USED IN A LEAST-SQUARES SMOOTHING OF  SMTH0040
C     DIGITAL DATA.                                                     SMTH0050
C     NPNT = NUMBER OF DATA POINTS IN SMOOTHING GATE.                   SMTH0060
C     NPOLY = DEGREE OF POLYNOMIAL TO BE USED TO FIT NPNT ORDINATE      SMTH0070
C             VALUES.                                                   SMTH0080
C     X IS A DOUBLE-WORD ARRAY USED FOR SCRATCH.                        SMTH0090
C     REQUIRES SUBROUTINE CONMAT.                                       SMTH0100
      DIMENSION  B(7,13)                                                SMTH0110
      REAL*8  A(4,17),X(25)                                             SMTH0120
C     INITIALIZE.                                                       SMTH0130
      KOUNT = 1                                                         SMTH0140
      IF (MOD(NPNT,2).NE.1)   NPNT = NPNT + 1                           SMTH0150
      IF (NPNT.GT.25)         NPNT = 25                                 SMTH0160
      IF (NPNT.LT.5)          NPNT = 5                                  SMTH0170
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      IF (NPOLY.GT.6)          NPOLY = 6                                 SMTH0180
      IF (NPOLY.LT.2)          NPOLY = 2                                 SMTH0190
      IF (NPOLY.GE.NPNT)       NPOLY = NPNT - 2                          SMTH0200
C     COMPUTE PARITY AND DIMENSIONS OF INTERMEDIATE MATRIX A.            SMTH0210
      IPAR = MOD(NPOLY,2)                                                SMTH0220
      NROW = NPOLY/2 + 1                                                 SMTH0230
      LPNT = (NPNT - 1)/2 + 1                                            SMTH0240
C     CALCULATE EVEN (OR ODD) ROWS OF B.                                 SMTH0250
    1 CALL CONMAT (NROW,LPNT,IPAR,A,X)                                   SMTH0260
      I = IPAR + 1                                                       SMTH0270
      DO 3  J=1,NROW                                                     SMTH0280
      DO 2  K=1,LPNT                                                     SMTH0290
      B(I,K) = A(J,K)                                                    SMTH0300
    2 CONTINUE                                                           SMTH0310
      I = I + 2                                                          SMTH0320
    3 CONTINUE                                                           SMTH0330
C     FINISHED WITH FIRST SECTION?                                       SMTH0340
      IF (KOUNT.GT.1)  RETURN                                            SMTH0350
C     NO.....CALCULATE ODD (OR EVEN) ROWS OF B.                          SMTH0360
      KOUNT = 2                                                          SMTH0370
      I = NPOLY - 1                                                      SMTH0380
      NROW = I/2 + 1                                                     SMTH0390
      IPAR = MOD(I,2)                                                    SMTH0400
      GO TO 1                                                            SMTH0410
C     SECOND SECTION:                                                    SMTH0420
      ENTRY SMTH2 (N,YIN,YOUT)                                           SMTH0430
C     OPERATES ON AN ARRAY OF DIGITIZED DATA YIN WITH MATRIX B. THE      SMTH0440
C     SMOOTHED DATA IS PLACED IN ARRAY YOUT. YIN AND YOUT MAY REFER TO   SMTH0450
C     THE SAME ARRAY IN THE CALLING PROGRAM.                             SMTH0460
C     N IS THE DIMENSION OF ARRAYS YIN AND YOUT.                         SMTH0470
      DIMENSION  YIN(1),YOUT(1)                                          SMTH0480
      DIMENSION  COEF(7)                                                 SMTH0490
C     STORE FIRST NPNT DATA POINTS IN TEMPORARY STORAGE.                 SMTH0500
      DO 4  I=1,NPNT                                                     SMTH0510
      X(I) = YIN(I)                                                      SMTH0520
```

```
    4 CONTINUE                                                          SMTH0530
      MPNT = LPNT - 1                                                   SMTH0540
C     CALCULATE SMOOTHED VALUES FOR FIRST LPNT DATA POINTS.             SMTH0550
      NROW = NPOLY + 1                                                  SMTH0560
      KOUNT = 1                                                         SMTH0570
    5 DO 8  K=1,NROW                                                    SMTH0580
      SUM1 = 0.0                                                        SMTH0590
      IPAR = MOD(K,2)                                                   SMTH0600
      DO 7  L=1,MPNT                                                    SMTH0610
      M = NPNT - L + 1                                                  SMTH0620
      IF (IPAR.EQ.0)  GO TO 6                                           SMTH0630
      SUM1 = SUM1 + (X(L) + X(M))*B(K,L)                                SMTH0640
      GO TO 7                                                           SMTH0650
    6 SUM1 = SUM1 + (X(L) - X(M))*B(K,L)                                SMTH0660
    7 CONTINUE                                                          SMTH0670
      COEF(K) = SUM1 + X(LPNT)*B(K,LPNT)                                SMTH0680
    8 CONTINUE                                                          SMTH0690
      IF (KOUNT.GT.1)  GO TO 14                                         SMTH0700
      DO 10  I=1,LPNT                                                   SMTH0710
      L = I - LPNT                                                      SMTH0720
      J = 1                                                             SMTH0730
      SUM1 = 0.0                                                        SMTH0740
      DO 9  K=1,NROW                                                    SMTH0750
      SUM1 = SUM1 + J*COEF(K)                                           SMTH0760
      J = J * L                                                         SMTH0770
    9 CONTINUE                                                          SMTH0780
      YOUT(I) = SUM1                                                    SMTH0790
   10 CONTINUE                                                          SMTH0800
C     SMOOTH MAIN BODY OF DATA.                                         SMTH0810
      M = N - 2*MPNT                                                    SMTH0820
      DO 13  I=2,M                                                      SMTH0830
      DO 11  J=2,NPNT                                                   SMTH0840
      K = J - 1                                                         SMTH0850
      X(K) = X(J)                                                       SMTH0860
   11 CONTINUE                                                          SMTH0870
```

```
      X(NPNT) = YIN(NPNT + I - 1)                                       SMTH0880
      SUM1 = 0.                                                         SMTH0890
      DO 12  J=1,MPNT                                                   SMTH0900
      K = NPNT - J + 1                                                  SMTH0910
      SUM1 = SUM1 + (X(J) + X(K))*B(1,J)                                SMTH0920
   12 CONTINUE                                                          SMTH0930
      YOUT(MPNT+I) = SUM1 + X(LPNT)*B(1,LPNT)                           SMTH0940
   13 CONTINUE                                                          SMTH0950
C     OPERATE ON LAST MPNT DATA POINTS.                                 SMTH0960
      KOUNT = 2                                                         SMTH0970
      GO TO 5                                                           SMTH0980
   14 DO 16  I=1,MPNT                                                   SMTH0990
      J = 1                                                             SMTH1000
      SUM1 = 0.0                                                        SMTH1010
      DO 15  K=1,NROW                                                   SMTH1020
      SUM1 = SUM1 + COEF(K)*J                                           SMTH1030
      J = I * J                                                         SMTH1040
   15 CONTINUE                                                          SMTH1050
      L = N - MPNT + I                                                  SMTH1060
      YOUT(L) = SUM1                                                    SMTH1070
   16 CONTINUE                                                          SMTH1080
      RETURN                                                            SMTH1090
      END                                                               SMTH1100

      SUBROUTINE CONMAT (NROW,LPNT,IPAR,A,X)                            CNMT0010
C     WRITTEN BY A S ROSENBERG      5 12 67                             CNMT0020
C     CORRECTED      7 10 67                                            CNMT0030
C     BUILDS AND INVERTS AN AUGMENTED MATRIX A USED IN CALCULATING A    CNMT0040
C     LEAST-SQUARES CONVOLVING SET.                                     CNMT0050
C     THE DIMENSIONS OF A ARE NROW BY (NROW + LPNT).                    CNMT0060
C     IF IPAR=0, AN EVEN SET OF POLYNOMIALS IS INVOLVED. IF IPAR=1, THE CNMT0070
C     SET IS ODD.                                                       CNMT0080
C     X IS A VECTOR USED AS WORKING STORAGE IN THE MATRIX INVERSION     CNMT0090
C     ROUTINE.                                                          CNMT0100
```

```
      REAL*8  A(4,55),X(55),SUM(7),TEMP                                 CNMT0110
C     INITIALIZE AND BUILD FIRST ROW OF AUGMENTING MATRIX.              CNMT0120
      IT = NROW + 1                                                     CNMT0130
      MPNT = LPNT - 1                                                   CNMT0140
      NCOL = NROW + LPNT                                                CNMT0150
      IF (IPAR.NE.0)  GO TO 2                                           CNMT0160
      DO 1  I=1,LPNT                                                    CNMT0170
      J = I + NROW                                                      CNMT0180
      A(1,J) = 1.                                                       CNMT0190
      X(I) = 1.                                                         CNMT0200
    1 CONTINUE                                                          CNMT0210
      GO TO 4                                                           CNMT0220
    2 DO 3  I=1,LPNT                                                    CNMT0230
      J = I - LPNT                                                      CNMT0240
      K = NROW + I                                                      CNMT0250
      A(1,K) = J                                                        CNMT0260
      X(I) = J*J                                                        CNMT0270
    3 CONTINUE                                                          CNMT0280
C     BUILD REMAINDER OF AUGMENTING MATRIX.                             CNMT0290
    4 IF (NROW.LE.1)  GO TO 13                                          CNMT0300
      DO 5  I=2,NROW                                                    CNMT0310
      DO 5  J=1,LPNT                                                    CNMT0320
      K = LPNT - J                                                      CNMT0330
      K = K*K                                                           CNMT0340
      L = NROW + J                                                      CNMT0350
      A(I,L) = K*A(I-1,L)                                               CNMT0360
    5 CONTINUE                                                          CNMT0370
C     CALCULATE SUMS                                                    CNMT0380
   13 SUM(1) = 0.0                                                      CNMT0390
      DO 6  I=1,MPNT                                                    CNMT0400
      SUM(1) = SUM(1) + 2.*X(I)                                         CNMT0410
    6 CONTINUE                                                          CNMT0420
      SUM(1) = SUM(1) + X(LPNT)                                         CNMT0430
      IF (NROW.LE.1)  GO TO 14                                          CNMT0440
      IT = 2*NROW - 1                                                   CNMT0450
```

```
      DO 7  K=2,IT                                                      CNMT0460
      SUM(K) = 0.0                                                      CNMT0470
      DO 7  I=1,MPNT                                                    CNMT0480
      J = I - LPNT                                                      CNMT0490
      J = J*J                                                           CNMT0500
      X(I) = J*X(I)                                                     CNMT0510
      SUM(K) = SUM(K) + 2.*X(I)                                         CNMT0520
    7 CONTINUE                                                          CNMT0530
C     BUILD LEFT-HAND SIDE OF MATRIX.                                   CNMT0540
   14 DO 8  I=1,NROW                                                    CNMT0550
      DO 8  J=1,NROW                                                    CNMT0560
      K = I + J - 1                                                     CNMT0570
      A(I,J) = SUM(K)                                                   CNMT0580
    8 CONTINUE                                                          CNMT0590
C     INVERT AUGMENTED MATRIX.                                          CNMT0600
      NCOLM = NCOL - 1                                                  CNMT0610
      DO 12  I=1,NROW                                                   CNMT0620
      TEMP = 1.0/A(1,1)                                                 CNMT0630
      DO 9  J=1,NCOLM                                                   CNMT0640
      JP = J + 1                                                        CNMT0650
      X(J) = TEMP * A(1,JP)                                             CNMT0660
    9 CONTINUE                                                          CNMT0670
      X(JP) = TEMP                                                      CNMT0680
      IF (NROW.LE.1)  GO TO 15                                          CNMT0690
      DO 11  J=2,NROW                                                   CNMT0700
      TEMP = A(J,1)                                                     CNMT0710
      JM = J - 1                                                        CNMT0720
      DO 10  L=1,NCOLM                                                  CNMT0730
      LP = L + 1                                                        CNMT0740
      A(JM,L) = A(J,LP) - TEMP*X(L)                                     CNMT0750
   10 CONTINUE                                                          CNMT0760
      A(JM,LP) = -TEMP*X(LP)                                            CNMT0770
   11 CONTINUE                                                          CNMT0780
   15 DO 12  J=1,NCOL                                                   CNMT0790
      A(NROW,J) = X(J)                                                  CNMT0800
```

```
   12 CONTINUE                                                          CNMT0810
      RETURN                                                            CNMT0820
      END                                                               CNMT0830

      SUBROUTINE SCALAB (XMAX,XMIN,XINCR,S,XSTART,DX)                   SCAL0010
C.....WRITTEN BY A S ROSENBERG     7 3 67                               SCAL0020
C.....ABCISSA SCALING ROUTINE FOR SUBROUTINE PLOT1.                     SCAL0030
C.....USED IN PLACE OF SUBROUTINE SCALE IN CALCOMP PLOTTER PACKAGE.     SCAL0040
      DX = (XMAX - XMIN)/S                                              SCAL0050
      IF (DX)  1,7,2                                                    SCAL0060
    7 DX = 1.0                                                          SCAL0070
      XSTART = XMAX + 0.5                                               SCAL0080
      RETURN                                                            SCAL0090
    1 TEMP = XMAX                                                       SCAL0100
      XMAX = XMIN                                                       SCAL0110
      XMIN = TEMP                                                       SCAL0120
      DX = -DX                                                          SCAL0130
    2 IDX = 0.4343 * ALOG(DX)                                           SCAL0140
      IXMX = XMAX * (10.0**(-IDX)) + 0.99                               SCAL0150
      XSTART = IXMX                                                     SCAL0160
      XSTART = XSTART * (10.0**IDX)                                     SCAL0170
      DX = ALOG10 ((XSTART - XMIN)/S)                                   SCAL0180
      IDX = DX                                                          SCAL0190
      TEMP = IDX                                                        SCAL0200
      DX = 10.0**(DX-TEMP)                                              SCAL0210
      TEMP = 1.0                                                        SCAL0220
    3 IF (DX - 1.0)  4,6,5                                              SCAL0230
    4 DX = DX * 10.0                                                    SCAL0240
      IDX = IDX - 1                                                     SCAL0250
      GO TO 3                                                           SCAL0260
    5 TEMP = 1.5                                                        SCAL0270
      IF (DX.LE.1.5)  GO TO 6                                           SCAL0280
      TEMP = 2.0                                                        SCAL0290
      IF (DX.LE.2.0)  GO TO 6                                           SCAL0300
```

```
      TEMP = 4.0                                                        SCAL0310
      IF (DX.LE.4.0)  GO TO 6                                           SCAL0320
      TEMP = 5.0                                                        SCAL0330
      IF (DX.LE.5.0)  GO TO 6                                           SCAL0340
      TEMP = 8.0                                                        SCAL0350
      IF (DX.LE.8.0)  GO TO 6                                           SCAL0360
      TEMP = 10.0                                                       SCAL0370
    6 DX = TEMP * (10.0**IDX)                                           SCAL0380
      DX = -DX                                                          SCAL0390
      RETURN                                                            SCAL0400
      END                                                               SCAL0410


      SUBROUTINE SPCTRM (LIGHT,MODE,EDX,*)                              SPCT0010
      DIMENSION  IT(20),IDNO(500),INDEX(500),XDATE(2),Y(10000)          SPCT0020
      COMMON  A(31,32),A0(10),CON(51),DELSQ,DX,ENU(5000),ETR(5000),     SPCT0030
     1        FREQ(5000),FREQHI,NCOLS,NMAX,NPEAK,NROWS,NTPTS,NXPTS,     SPCT0040
     2        PRTSUM(31),RHO(10),R(5000),T(5000),XNU(10),ISLIT,KEY,BETA SPCT0050
      EQUIVALENCE  (R(1),Y(1)),(T(1),Y(5001))                           SPCT0060
      REAL*8  A                                                         SPCT0070
      IF (MODE.EQ.2)  GO TO 6                                           SPCT0080
C.... READ SPECTRUM HEADER CARD.                                         SPCT0090
      READ (5,501)  IDENT,XSTART,EDX,NIPTS,BEGIN,END                    SPCT0100
  501 FORMAT (I5,3X,F7.0,F5.1,I5,5X,2F10.5)                             SPCT0110
C.... CALCULATE INDICES OF INITIAL AND FINAL POINTS TO BE INPUT.         SPCT0120
      JBRNCH = 1                                                        SPCT0130
   10 XEND = XSTART - (NIPTS-1)*EDX                                     SPCT0140
      IF (BEGIN.GT.XSTART.OR.BEGIN.LT.XEND)  BEGIN = XSTART             SPCT0150
      IF (END.GT.BEGIN.OR.END.LT.XEND)       END = XEND                 SPCT0160
      IBEGIN = (XSTART - BEGIN)/EDX + 1                                 SPCT0170
      IEND = (XSTART - END)/EDX + 1                                     SPCT0180
      NXPTS = IEND - IBEGIN + 1                                         SPCT0190
      IF (NXPTS.LE.5000)  GO TO (1,9), JBRNCH                           SPCT0200
C.... ERROR RETURN.                                                      SPCT0210
      WRITE (6,601)                                                     SPCT0220
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  601 FORMAT ('0',5X,'TOO MANY DATA POINTS, PROBLEM TERMINATED')        SPCT0230
      LIGHT = 2                                                         SPCT0240
      RETURN 1                                                          SPCT0250
C.... INPUT LOOP.                                                       SPCT0260
    1 IBRNCH = 1                                                        SPCT0270
      L = 1                                                             SPCT0280
      DO 5  I=1,NIPTS,20                                                SPCT0290
      IN = 20                                                           SPCT0300
      IP = I + 19                                                       SPCT0310
      IF (IP.GT.NIPTS)   IN = 20 + NIPTS - IP                           SPCT0320
C.... READ ONE DATA CARD.                                                SPCT0330
      READ (5,502)  (IT(J), J=1,IN)                                     SPCT0340
  502 FORMAT (20I4)                                                     SPCT0350
      GO TO (2,5), IBRNCH                                               SPCT0360
    2 DO 4  J=1,IN                                                      SPCT0370
      K = I + J - 1                                                     SPCT0380
C.... TEST TO SEE IF DATA POINT IS WITHIN PROPER SPECTRAL REGION.        SPCT0390
      IF (K.LT.IBEGIN)   GO TO 4                                        SPCT0400
      IF (K.LE.IEND)     GO TO 3                                        SPCT0410
      IBRNCH = 2                                                        SPCT0420
      GO TO 5                                                           SPCT0430
C.... TRANSFER VALUE TO TRANSMITTANCE VECTOR AND CALCULATE              SPCT0440
C.... CORRESPONDING ELEMENT OF FREQUENCY VECTOR.                         SPCT0450
    3 ETR(L) = IT(J)/1000.                                              SPCT0460
      ENU(L) = BEGIN - (L-1)*EDX                                        SPCT0470
      L = L + 1                                                         SPCT0480
    4 CONTINUE                                                          SPCT0490
    5 CONTINUE                                                          SPCT0500
      WRITE (6,603)  IDENT,BEGIN,END                                    SPCT0510
  603 FORMAT (/'0',9X,'SPECTRUM',I6,' READ FROM CARDS, RANGE =',        SPCT0520
     1       F7.1,' TO',F7.1)                                           SPCT0530
      RETURN                                                            SPCT0540
    6 READ (5,503)  IDENT,BEGIN,END                                     SPCT0550
  503 FORMAT (I5,5X,2F10.5)                                             SPCT0560
      DO 7  I=1,NSPEC                                                   SPCT0570
```

```
      IF (IDENT.NE.IDNO(I))  GO TO 7
      KEY = INDEX(I)
      GO TO 8
    7 CONTINUE
      WRITE (6,602)  IDENT
  602 FORMAT ('0',5X,'SPECTRUM',I6,' NOT ON DISK')
      LIGHT = 2
      RETURN 1
    8 READ (7'KEY)  IDENT,XSTART,EDX,NIPTS,INST,XDATE,(Y(I), I=1,315)
      JBRNCH = 2
      GO TO 10
    9 IF (IEND.LE.315)  GO TO 13
      DO 11  I=316,IEND,322
      IP = I + 321
      READ (7'KEY)  (Y(J), J=I,IP)
   11 CONTINUE
   13 DO 12  I=1,NXPTS
      IM = I - 1
      IP = IM + IBEGIN
      ETR(I) = Y(IP)
      ENU(I) = BEGIN - IM*EDX
   12 CONTINUE
      WRITE (6,604)  IDENT,BEGIN,END
  604 FORMAT (/'0',9X,'SPECTRUM',I6,' READ FROM DISK, RANGE =',
     1       F7.1,' TO',F7.1)
      RETURN
      ENTRY DISK
      KEY = 1
      READ (7'KEY)  NSPEC,NREC,IDNO,INDEX
      RETURN
      END
```

VITA

2

Arthur Stanley Rosenberg

Candidate for the Degree of

Doctor of Philosophy

Thesis: I. A VIBRATIONAL STUDY OF THE CYANOETHYLENES
II. AN ALGORITHM FOR THE DETERMINATION OF THE SHAPE PARAMETERS OF INFRARED ABSORPTION BANDS

Major Field: Chemistry

Biographical:

Personal Data: Born in New York City, New York, January 27, 1933, the son of Jack and Evelyn Rosenberg.

Education: Graduated from Teaneck High School, Teaneck, New Jersey in 1951; received the Bachelor of Science degree from the University of Vermont in 1954; received the Master of Science degree from the Massachusetts Institute of Technology in 1959; completed requirements for the Doctor of Philosophy degree at Oklahoma State University in May, 1970.

Professional Experience: Associate Research Scientist, Continental Oil Company, 1959-65; Research Scientist, Continental Oil Company, 1965-1969; Senior Research Scientist, Continental Oil Company, 1969 to present.

Membership in Professional Societies: American Chemical Society and The Chemical Society (London).