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IMPROVED TECHNIQUES FOR THE ANALYSIS OF NUCLEAR MAGNETIC RESONANCE SPECTROSCOPIC DATA: ANALYSIS OF FOUR-MEMBERED RING COMPOUNDS

Berkeley, California

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AEC Contract No. W-7405-eng-48

March 31, 1966

ERRATA

TO: All recipients of UCRL-16344

FROM: Technical Information Division

Subject: UCRL-16344, "Improved Techniques for the Analysis of Nuclear Magnetic Resonance Spectroscopic Data: Analysis of Four-Membered Ring Compounds," T. R. Lusebrink (Ph. D. Thesis), August 1965.

Please make the following corrections on subject report.

Page 15 4th line from bottom of page should be ...units of $\hbar$ ....

Page 77 Table 8 Values for transition No. 11 should be changed to Upper energy - 8, Lower energy level - 19, Frequency check - -0.

Page 128 In the second line of the Note: black should be blank.

Page 138 and 139 - are reversed

Page 147 Line 4, requiences should be frequencies.

Research and Development

UCRL-16344

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California

AEC Contract W-7405-eng-48

IMPROVED TECHNIQUES FOR THE ANALYSIS OF NUCLEAR MAGNETIC RESONANCE SPECTROSCOPIC DATA: ANALYSIS OF FOUR-MEMBERED RING COMPOUNDS

T. R. Lusebrink

(Ph.D. Thesis)

August 1965

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IMPROVED TECHNIQUES FOR THE ANALYSIS OF NUCLEAR MAGNETIC RESONANCE SPECTROSCOPIC DATA: ANALYSIS OF FOUR-MEMBERED RING COMPOUNDS

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ABSTRACT

August 1965

Two computer programs have been written which substantially aid the analysis of complex NMR spectra. One program, DECOMP, allows the decomposition of superimposed groups of peaks so that peak positions in an unresolved group can be determined nearly as accurately as resolved peaks. The second program, ASSIGN, calculates all possible sets of energy levels which are consistent with the observed frequencies and intensites of the completely resolved spectrum.

These two methods rectify the major limitations of the Swalen and Reilly iterative method by providing peak positions and intensities for essentially all the lines in a spectrum and by making it possible, in principle, to calculate the NMR parameters directly from a spectrum without any prior knowledge of these parameters. These programs, in conjunction with the Swalen and Reilly method, result in a more complete and objective analysis in less time than the present methods.

This system of programs has been utilized in the complete spectral analysis of two four-membered ring compounds; a class of compounds which have not previously been analyzed. The compounds are 3-chlorothietane and 3-thietanyl acetate, two highly mixed five-spin systems of the A_2B_2X type. The most interesting parameters resulting from these analyses are the

three long-range coupling constants across the ring. One of the cisoid coupling constants is unusually large for unstrained rings, 3.1 cps for the chloro compound and 2.6 cps for the acetate. The other two long-range coupling constants are small and negative. These values agree qualitatively with the semiempirical valence bond treatment of Barfield. The vicinal coupling constants agree with the trends predicted by Karplus' theory and the geminal constants with the theory of Pople and Bothner-By.

Details of the analyses and listings of the computer programs are given. Extension of the method to six nuclei A_2B_4 systems, occurring in four membered rings, is also indicated.

I. INTRODUCTION

Nuclear magnetic resonance spectra obtained under resolution sufficient to distinguish chemical shifts of nonequivalent nuclei in the same molecule are referred to as "high-resolution" nuclear magnetic resonance (NMR) spectra. In addition, present spectrometers have sufficient resolution to allow observation of the fine-structure splitting of these resonance signals due to nuclear spin-spin interaction. Such spectra are observed in liquids and gases where the rapid motion of the molecules averages the direct magnetic dipole interaction to zero.

The factors modifying the magnetic environments of the nuclei in a molecule which lead to the observation of chemical shifts and spin coupling are caused by the interactions of the electrons and nuclei.[1-3] The chemical shift is a result of the induced orbital motion of the electrons when the molecule is placed in an external field and is proportional to the applied field, H_o. The local field at the nucleus is given by $H = H_o (1 - \sigma)$, where σ is the screening constant. A complete theory for the chemical shift was first given by Ramsey.[4]

On the other hand, the fine structure due to nuclear spin-spin coupling is independent of the external field and arises from magnetic fields within the molecule itself. The first successful theory explaining these interactions was given by Ramsey and Purcell[5] and further expanded by Ramsey.[6]

High-resolution NMR spectra can be completely described by the chemical shift and spin-spin coupling parameters; however, in most spectra of interest these are related in such a complicated manner

that a complete analysis must be carried out in order to obtain these parameters from the spectrum.[7] During the past few years much effort has been directed toward extracting information regarding spin-spin coupling from the fine structure of high-resolution NMR spectra, particularly with regard to coupling between protons.

Several theoretical calculations, based on Ramsey's work, have been made to explain and predict spin coupling constants. McConnell[8] first developed a molecular-orbital method of calculating coupling constants which, however, predicted proton spin coupling constants to all be positive. An approach using valence-bond wave functions was used by Karplus, et al., in a series of papers[9-11] which showed good agreement with a number of experimental data, particularly with regard to vicinal coupling constants in substituted ethanes and ethylenes. For a period it appeared that the valence-bond approach might be a more satisfactory way to calculate the coupling constants in molecular systems while the molecular orbital method seem more appropriate for the conduction electrons in metals. Recently, however, Pople and Bothner-By[12] have presented a molecular orbital method for calculating nuclear spin coupling between geminal protons which gives quite satisfactory agreement with experimental data.

Since nuclear spin coupling is rapidly attenuated through saturated bonds, it has only been recently that coupling has been observed through as many as four saturated bonds.[13-17] The observed long-range coupling is always less than one to two cps, unless the system is highly strained and/or highly substituted. A recent calculation, using valence bond wave functions, has been made by Barfield[18] to calculate proton spin coupling across four bonds in both saturated and unsaturated compounds. A rigorous test of his calculations for saturated systems

has not been possible, since the experimental long-range coupling constants which have been reported are obtained in highly strained or substituted molecules for which the molecular configurations are not well enough known. Furthermore, the calculations were based on exchange integrals for unstrained and unsubstituted hydrocarbons and extrapolation to the strained or substituted systems should be made with circumspection.

Saturated four-membered ring compounds are excellent subjects for a study of spin coupling constants. They contain geminal, vicinal, and at least two types of long-range coupling constants in the same molecule, so a complete analysis will yield all the relative signs as well as magnitudes for these parameters. Furthermore, the molecular structures of these compounds are relatively well defined, having been determined exactly in several cases.[19 -21] These factors should allow rigorous tests of the various theories discussed above, when information from the analyses of these ring compounds becomes available. Due to the complexity of their spectra, no NMR analyses of simple saturated four-membered ring compounds have yet been reported.

Probably the most important advance in the analysis of complex NMR spectra has been the development of iterative computer techniques[22 - 25] such as NMRIT developed by Swalen and Reilly.[24] NMR parameters of many molecules having quite complex spectra have been determined through the use of these methods, however, in the case of the above mentioned four-membered ring compounds they have generally failed. The failure of attempts with NMRIT can be understood by a consideration of the information necessary for a successful analysis using the method. It depends upon sufficient prior knowledge of the NMR parameters so that individual experimental lines can be assigned to theoretically calculated transi-

tions, thus determining the true energy levels of the molecule. However, for highly mixed spectra, not enough of the experimental lines can be resolved to make such an assignment, even under optimum experimental conditions. Thus there are two problems to be solved to insure the successful application of the iterative method. First, as many as possible of the experimental lines must be known accurately to insure the determination of the energy levels and to check the agreement of the experimental spectrum with the calculated one. Second, the analysis must be carried out so that it is not so dependent on prior knowledge of the approximate values of the NMR parameters.

The increasing complexity of problems encountered makes the use of computer techniques essential. Spectrometers are usually operated at their limit and it is often possible to extract still more information from the existing data with the aid of a computer. Furthermore, computers operate in a completely different time domain than that of most experimental instruments and if the computer can be used, this is generally preferable to accomplishing the same end experimentally.

This dissertation will describe computer techniques which have been developed to extend the present methods of analysis of high-resolution NMR spectra by solving the two problems stated above. These techniques are then applied to some four-membered ring compounds to demonstrate the method and to obtain spin coupling constants of these systems for comparison with values predicted by theory.

In order to determine enough experimental lines to apply NMRIT successfully, it is necessary to utilize more powerful methods than the usual visual estimations of the line positions and intensities. DECOMP, a computer method of resolving over-lapping NMR spectral peaks described below, was found extremely useful in such analyses and promises to be

useful in the analysis of many similar spectra.

DECOMP solves the first problem in the analysis of complicated second-order NMR spectra. However, even with this technique, one is left with the problem of constructing an energy level diagram from the observed transitions. Whitman[26] has discussed a computer assignment technique and has applied it to a well resolved A_2B_2 spectrum. Although in theory this method could be applied to any system with well resolved lines, it has two drawbacks: It becomes prohibitively time consuming with larger systems and the program must be rewritten for each system of different symmetry. ASSIGN, a computer assignment program described below, helps to overcome these problems and has been used on complex four-membered ring systems with five spins; the extension to six spin systems is also indicated.

Once all possible sets of energy levels are known, the chemical shifts and the coupling constants can easily be found by NMRIT. Any set of starting parameters, consistent with the symmetry and equivalence requirements of the molecule, will quickly converge to the corresponding sets of parameters, if they are real. Thus, the second problem is solved, and in principle it is possible to proceed directly from the experimental spectrum to the NMR parameters in a systematic manner with little or no previous knowledge or estimates of those parameters.

II. THEORY

A. Nuclear Spin-Spin Coupling

The complexity of high-resolution NMR spectra is greatly increased due to nuclear spin-spin coupling. This phenomenon was discovered by Gutowsky and McCall and Hahn and Maxwell. The first successful theory, based on the complete Hamiltonian for electron-nuclear interactions in a magnetic field, was given by Ramsey and Purcell[5] and developed in detail by Ramsey.[6]

The complete Hamiltonian for a molecular system in a magnetic field consists of four terms:

$$\mathcal{H}_1 = \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_3 + \mathcal{H}_4 \tag{1}$$

where

$$\mathcal{H}_1 = \sum_k \left(\frac{1}{2m_k}\right)\left[\frac{\hbar}{i}\nabla_k + \frac{e}{c}\left(\sum_N \frac{\hbar\gamma_N \underline{I}_N \times \underline{r}_{kN}}{r_{kN}^3} + \frac{1}{2}\underline{H} \times \underline{r}_k\right)\right]^2$$

$$+ V + \mathcal{H}_{LL} + \mathcal{H}_{LS} + \mathcal{H}_{SS} + \mathcal{H}_{SH} \tag{2}$$

$$\mathcal{H}_2 = 2\beta\hbar \sum_{kN} \gamma_N \left\{\frac{3(\underline{S}_k \cdot \underline{r}_{kN})(\underline{I}_N \cdot \underline{r}_{kN})}{r_{kN}^5} - \frac{\underline{S}_k \cdot \underline{I}_N}{r_{kN}^3}\right\} \tag{3}$$

$$\mathcal{H}_3 = \left(\frac{16\pi\beta\hbar}{3}\right) \sum_{kN} \gamma_N \, \delta(\underline{r}_{kN}) \, \underline{S}_k \cdot \underline{I}_N \tag{4}$$

$$\mathcal{H}_4 = -\hbar^2 \sum_{NN'}{}' \gamma_N \gamma_{N'} \left\{\frac{3(\underline{I}_N \cdot \underline{r}_{NN'})(\underline{I}_{N'} \cdot \underline{r}_{NN'})}{r_{NN'}^5} - \frac{\underline{I}_N \cdot \underline{I}_{N'}}{r_{NN'}^3}\right\} \tag{5}$$

$\mathcal{H}_4$ can be eliminated immediately for our systems since it is the term for the dipole interaction and averages to zero under conditions of rapid molecular collisions. The squared term in $\mathcal{H}_1$ is the orbital term which was discussed by Ramsey[4] in the calculation of the chemical shift. The last terms in this Hamiltonian are, respectively; the electrostatic potential energy, electron orbital-orbital, spin-orbital, spin-spin and spin-external field interactions. None of these latter terms enter into this discussion since none of them involve the nuclear spin vectors, $\underline{I}_N$. The two terms, $\mathcal{H}_2$ and $\mathcal{H}_3$ are the terms for the magnetic interactions between the nuclear and electronic spins. $\mathcal{H}_2$ corresponds to the classical magnetic interaction energy of two magnetic moments. $\mathcal{H}_3$ is the hyperfine structure interaction or Fermi contact term.

The indirect nuclear coupling energies are found by treating the parts of the Hamiltonian which depend on $\underline{I}_N$, the nuclear spin vector, as a perturbation on the remainder. It is necessary to carry the perturbation calculation to second order since all first order terms vanish for molecules in singlet ground states (no resultant angular momentum).

In most cases the largest contribution comes from the contact term $\mathcal{H}_3$ since this corresponds to the electrons being closest to the nucleus. Letting $E^{(3)}_{NN'}$ represent the energy of interaction between nuclei N and N', the second order perturbation energy is:

$$\sum_{N \leq N'} E^{(3)}_{NN'} = - \sum \frac{\langle 0|\mathcal{H}_3|n\rangle\langle n|\mathcal{H}_3|0\rangle}{E_n - E_o} \qquad (6)$$

Substituting the value of $\mathcal{H}_3$, separating out the NN' terms and multiplying by a factor of 2 to account for the terms in which N occurs in the first matrix element and N' in the second and vice versa, we finally obtain:

$$E^{(3)}_{NN'} = -2\left(\frac{16\pi\beta\hbar}{3}\right)^2 \gamma_N \gamma_{N'} \sum_{nkj} \frac{\langle 0|\delta(\underline{r}_{kN})\underline{S}_k \cdot \underline{I}_N|n\rangle\langle n|\delta(\underline{r}_{jN'})\underline{S}_j \cdot \underline{I}_{N'}|0\rangle}{E_n - E_o} \quad (7)$$

Since the sum is not over the nuclei, the nuclear spin vectors can be taken outside the summation giving:

$$E^{(3)}_{NN'} = -2\left(\frac{16\pi\beta\hbar}{3}\right)^2 \gamma_N \gamma_{N'} \underline{I}_N \cdot \sum_{nkj} \frac{\langle 0|\delta(\underline{r}_{kN})\underline{S}_k|n\rangle\langle n|\delta(\underline{r}_{jN'})\underline{S}_j|0\rangle}{E_n - E_o} \cdot \underline{I}_{N'} \quad (8)$$

The numerator under the sum is a second rank tensor with principle axes in the molecule. In a liquid it can be replaced by its rotational average which gives

$$E^{(3)}_{NN'} = -\frac{2}{3h}\left(\frac{16\pi\beta\hbar}{3}\right)^2 \gamma_N \gamma_{N'} \sum_{nkj} \frac{\langle 0|\delta(\underline{r}_{kN})\underline{S}_n|n\rangle \cdot \langle n|\delta(\underline{r}_{jN'})\underline{S}_j|0\rangle}{E_n - E_o} \times \underline{I}_N \cdot \underline{I}_N \quad (9)$$

The above expression is the one which should be used for accurate calculations of the coupling constant $J_{NN'}$, however it requires a knowledge of the wave functions of the excited state. Therefore it is necessary to make the so called average energy or closure approximation in which the operator $\Sigma' \frac{|n\rangle\langle n|}{E_n - E_o}$ is replaced by the constant $\frac{1}{\Delta E}$, where ΔE has the meaning of an average excitation energy of the molecule. The closure approximation is correct if the contribution of one particular state to the above sum far exceeds that of all the other states, for instance if this state is abnormally close to the ground state. In the general case it is little more than a shorthand notation, used because of lack of knowledge or excited state wave functions. Using this approximation the equation for the coupling constant becomes

$$J^{3}_{NN'} = -\left(\frac{2}{3h}\right)\left(\frac{16\pi\beta\hbar}{3}\right) \gamma_N\gamma_{N'}\left(\frac{1}{\Delta E^{(3)}}\right)\left(0\left|\sum_{kj} \delta(\underline{\gamma_{kN}})\delta(\underline{r_{jN'}})\underline{S_k} \cdot \underline{S_j}\right|0\right) \quad (10)$$

and evaluation of the matrix element requires only a knowledge of the wave function for the ground electronic state.

The perturbation energy due to the direct magnetic dipole interaction between electronic and nuclear spins, $\mathcal{H}_2$, can be treated in an analogous manner. The contribution to the spin coupling constant is

$$J^{(2)}_{NN'} = -\left(\frac{2}{3h}\right)\left(2\beta\hbar\right)^2 \gamma_N\gamma_{N'} \sum_{\substack{n\neq 0\\ k,j}} \frac{1}{E_n-E_o}\left(0\left|\frac{3(\underline{S_k}\cdot\underline{r_{kN}})\underline{r_{kN}}}{r^5_{kN}} - \frac{\underline{S_k}}{r^3_{kN}}\right|n\right)\cdot$$

$$\left(n\left|\frac{3(\underline{S_j}\cdot\underline{r_{jN'}})\underline{r_{jN'}}}{r^5} - \frac{\underline{S_j}}{r^3_{jN'}}\right|0\right) \quad (11)$$

Again using the closure relation this reduces to a term containing $\frac{1}{\Delta E^{(2)}}$. It is also possible to obtain cross terms in $\mathcal{H}_2$ and $\mathcal{H}_3$ which are bilinear in the nuclear spin vectors, however Ramsey[6] showed these averaged to zero for liquids.

The remaining contributions to the total spin coupling constant $J_{NN'}$ arise from the interaction of the orbital electronic currents with the nuclear magnetic moments. This can be thought of in classical terms, for each nuclear magnetic moment will induce certain currents in the molecule, which in turn will set up a secondary magnetic field experienced by other nuclei. In general this contribution will not average to zero over rotations.

There are two terms in the expanded Hamiltonian, $\mathcal{H}_1$, which involve nuclear spins. These are

$$\mathcal{H}_1^{(a)} = \frac{e^2\hbar^2}{2mc^2} \sum_{N,N';k} \gamma_N\gamma_{N'} \left(\underline{I}_N \times \frac{\underline{r}_{kN}}{r_{kN}^3} \right) \cdot \left(\underline{I}_{N'} \times \frac{\underline{r}_{kN'}}{r_{kN'}^3} \right)$$

$$= \frac{e^2\hbar^2}{2mc^2} \sum_{N,N';k} \gamma_N\gamma_{N'} \frac{\left[\left(\underline{I}_N \cdot \underline{I}_{N'} \right)\left(\underline{r}_{kN} \cdot \underline{r}_{kN'} \right) - \left(\underline{I}_N \cdot \underline{r}_{kN'} \right)\left(\underline{I}_{N'} \cdot \underline{r}_{kN} \right) \right]}{r_{kN}^3 \quad r_{kN'}^3} \tag{12}$$

and

$$\mathcal{H}_1^{(b)} = \frac{e\hbar^2}{mci} \sum_{Nk} \gamma_N \frac{\left(\underline{I}_N \times \underline{r}_{kN} \right) \cdot \nabla_k}{r_{kN}^3}$$

$$= \frac{e\hbar^2}{mci} \sum_{Nk} \gamma_N \frac{\underline{I}_N \cdot \left(\underline{r}_{kN} \times \nabla_k \right)}{r_{kN}^3} \tag{13}$$

The term $\mathcal{H}_1^{(a)}$ is already bilinear in $\underline{I}$ and the corresponding nuclear coupling is simply $\langle \Psi_o | \mathcal{H}_1^{(a)} | \Psi_o \rangle$ where Ψ_o is the ground state wave function for the molecule. Although this is a first order term, it is very small. This is essentially due to the fact that it is a sum of one electron operators

$$\frac{\left(\underline{I}_N \times \underline{r}_{kN} \right) \cdot \left(\underline{I}_{N'} \times \underline{r}_{kN'} \right)}{r_{kN}^3 \quad r_{kN'}^3}$$

so that when the first factor is relatively large, the kth electron being near the nuclear moment I_N, the second term is necessarily small.

The other term, $\mathcal{H}_1^{(b)}$, is treated by second order perturbation theory in the same manner we treated $\mathcal{H}_2$ and $\mathcal{H}_3$. The contribution to $J_{NN'}$ from $\mathcal{H}_1$ are then

$$J_{NN'}^{(1a)} = \frac{4}{3h} \frac{e^2\hbar^2}{2mc^2} \gamma_N\gamma_{N'} \langle 0 | \sum_k \frac{\underline{r}_{kN} \cdot \underline{r}_{kN'}}{r_{kN}^3 \; r_{kN'}^3} | 0 \rangle \tag{14}$$

$$J_{NN'}^{(1b)} = -\frac{8}{3h}\beta^2\hbar^2\gamma_N\gamma_{N'}\frac{1}{\Delta E^{(1b)}}$$

$$\times \langle 0 \Big| \sum_{kj} \frac{\left(\underline{r}_{kN} \times \nabla_k\right)\cdot\left(\underline{r}_{jN'} \times \nabla_j\right)}{r_{kN}^3 \; r_{kN'}^3} \Big| 0 \rangle \qquad (15)$$

In order to evaluate the relative importance of the above contributions to the nuclear spin coupling constant, Ramsey[6] made a calculation of J_{HD}. Using the closure approximation and the James-Coolidge wave function for the hydrogen molecule, he obtained

$$J_{HD}^{(3)} = \frac{55.8}{\Delta E}$$

where ΔE is in Rydberg units. It is difficult to estimate a good value for ΔE, however based on available data he used $\Delta E = 1.4$ Ry as a reasonable value. This gives $J_{HO}^{(3)} = 40$ cps; the best experimental value is 43.5 cps indicating that the contact term accounts for the main contribution to J_{HD}. Ramsey also made estimates of the other contributions and concluded that J_{HD} was approximately 3 cps and that the orbital contributions were probably less than 0.5 cps. Based on these conclusions, later work has considered only the contact term when attempts were made to calculate coupling constants, as will be seen below.

It seems reasonable to assume that Fermi-type coupling contributes the major portion of the coupling constant between protons in other molecules where there is no direct bond. This is primarily because the electrons on a hydrogen atom are well represented by a 1s type orbital, whereas the other spin coupling terms of the Hamiltonian depend on the presence of angular dependent atomic orbitals. It should be possible, therefore, to interpret the observations on proton-proton couplings in

terms of the matrix element from Eq. (10) $\langle 0 \left| \sum_{kj} \delta(\underline{r}_{kN})\, \delta(\underline{r}_{jN'}) \underline{S}_k \cdot \underline{S}_j \right| 0 \rangle$ together with a value of the mean triplet excitation energy ΔE. However, to use Eq. (10) in the calculation of spin coupling constants, it is necessary to know the ground state electronic wave functions. Theories using both molecular-orbital and valence-bond wave functions have been advanced for this purpose.

The method of molecular orbitals was first used by McConnell[8] to calculate spin coupling constants. In principle, the method of molecular orbitals is an extension to molecules of the self-consistent field method for atoms. Instead of a central self-consistent field as in atoms, a self-consistent field is sought that has the symmetry of the molecule. In practice this is too difficult, and the usual procedure is to represent each molecular orbital as a linear combination of atomic orbitals (LCAO). In the ground state of a diamagnetic molecule is it assumed that p orthogonal orbitals, $\Psi_1, \ldots \Psi_p$, are available to contain 2p electrons. If we take the spin into account, a Slater determinant Ψ_o can be constructed from the 2p one-electron states.

Using the LCAO-MO's and assuming that the values of all atomic orbitals, except local 1s orbitals, were negligible at the protons, McConnell obtained the following formula for the coupling constant

$$J_{NN'} = \frac{16\beta^2\gamma^2 h}{9\Delta E} \left[\Phi(0)\right]^4 \eta_{NN'} \tag{16}$$

where

$$\eta_{NN'} = 2 \sum_s C_{SN}\, C_{SN'}$$

and $\Phi(0)$ is the value of a hydrogen 1s AO at its center and C_{SN} is the LCAO coefficient of the orbital centered on proton N. McConnell's calculations predicted coupling constants to be positive (neglecting

configuration interaction) whereas experimentally they have been found to have either sign.

Valence-bond wave functions were used by Karplus et al.[9-11] for the calculation of proton spin coupling constants. They also used only the Fermi interaction term of Ramsey's Hamiltonian, Eq. (10) and obtained the following expression for $J_{NN'}$

$$J_{NN'} = \frac{3\times10^{-46}}{\Delta E} [\Phi(0)]^4 \sum_{\ell m} \frac{C_\ell C_m}{2^{n-ij\ell}} [1+2f(\ell,m,P_{NN'})] \qquad (17)$$

In this equation the complete wave function is written

$$\Psi = \sum_\ell C_\ell \Psi_\ell$$

where Ψ_ℓ denotes the functions for the canonical valence-bond structures; n, $i(\ell,m)$ and $f(\ell,m,P_{NN'})$ are quantities occurring in the evaluation of matrix elements between the valence-bond functions Ψ_ℓ and Ψ_m.

This approach predicted a coupling constant of 10.4 cps for methane while the experimental value is now considered to be -12.4 cps. The theory has been more successful in accounting for the dependence of protons in vicinal groups of ethanes and ethylenes upon the azimuthal angle between the C-H bonds.[11]

Recently molecular orbital calculations for spin coupling between geminal hydrogen atoms have been published by Pople and Bothner-By.[12] For this calculation, electrons are treated independently and assigned to molecular orbitals, Ψ_i, with energies ϵ_i. The molecular orbitals are approximated by linear combinations of valence atomic orbitals (LCAO),

$$\Psi_i = \sum_\mu C_{i\mu} \Phi_\mu$$

The nuclear spin coupling constant is calculated, as usual, by consider-

ing only the contact interaction and using perturbation theory. For protons the spin coupling constant is given by

$$J_{HH'} = h(4\beta\gamma_H/3)^2 \, S_h^{\,4}(0) \, \Pi_{h,h'}$$

where

$$\Pi_{h,h'} = -4 \sum_i^{occ} \sum_j^{unocc} \frac{C_{ih} \, C_{ih'} \, C_{jh} \, C_{jh'}}{\epsilon_j - \epsilon_i}$$

and $s_h(0)$ is the magnitude of a hydrogen 1s orbital at the nucleus. The agreement with experimental values for geminal coupling constants is more satisfactory than previous treatments.

Barfield[18] has recently calculated long-range coupling constants over four bonds in both saturated and unsaturated systems. He used valence-bond wave functions after the manner of Karplus et al., and obtained reasonably good agreement with unsaturated molecules, where a considerable amount of data is available. The method essentially considers the long range system as two coupling vicinal systems treated in the manner of Karplus.[11] However, to improve the correlation with experimental data, Barfield used semiempirical exchange integrals derived from experimental data on the parent molecules, ethane and ethylene. Using this information, he then plotted the variation of the long-range coupling constant as a function of each of the dihedral angles of the C-H bonds with the skeletal C-C-C plane. As mentioned in the introduction, it was not possible for Barfield to compare his theory with data from saturated systems, because the only data available for such systems was for highly substituted and/or strained molecules.

B. Analysis of High-Resolution NMR Spectra

An NMR spectrum arises from rf radiation induced transitions between stationary state energy levels of the system under consideration. The calculation of the energy levels and the derivation of the spectroscopic selection rules are calculated from the Hamiltonian (18) which is based on Ramsey's Hamiltonian discussed above.

$$\mathcal{H} = \mathcal{H}_1^{o} + \mathcal{H}' \tag{18}$$

where

$$\mathcal{H}^{o} = \frac{1}{2\Pi} \sum_i \gamma_i H_i I_z(i) \tag{19}$$

and

$$\mathcal{H}' = \sum_{i<j} J_{ij} \underline{I}(i) \cdot \underline{I}(j) \tag{20}$$

The complete Hamiltonian $\mathcal{H}$ is the sum of the two terms $\mathcal{H}^{o}$ and $\mathcal{H}'$. The term $\mathcal{H}^{o}$ gives the sum of the magnetic interactions of all nuclei with the externally applied field, and $\mathcal{H}'$ gives the sum of the spin-spin interactions of all pairs of nuclei, which is the main topic of this discussion. In the above equations, γ_i is the gyromagnetic ratio of nucleus i, H_i is the stationary magnetic field acting at nucleus i, and $I_z(i)$ is the component of the spin angular momentum vector of i along the stationary field which is taken to be in the negative z direction. J_{ij} is the spin-spin coupling constant between nuclei i and j. The spin angular momentum vector of nucleus i is $\underline{I}(i)$. It is convention to express all energies in cps for convenience in comparison with experimental data. Thus in the above expression, all spins $\underline{I}(i)$ are in units of making the quantities $\underline{I}(i)$ and $I_z(i)$ dimensionless and the J_{ij} in cps.

The analysis of an NMR spectrum involves the calculation of the transition frequencies and intensities by diagonalizing the matrix of

this Hamiltonian in the manner shown below. The best available method of accomplishing the analysis of complex spectra with an iterative computer method, NMRIT, will then be described. Finally the methods which have been developed in this research, to extend the analysis to systems of higher complexity than has been feasible, will be discussed.

This discussion will consider only nuclei with spin 1/2. For a system containing p magnetic nuclei there is a total of 2^p possible states. The simplest set of functions which describes the system is the 2^p basis product spin functions, such as

$$\Psi_m = \alpha(1)\beta(2) \ldots \beta(p) \tag{21}$$

where α is the wave function for the state $I_z = \frac{1}{2}$ and β for the state $I_z = -\frac{1}{2}$. This product function will be written in the usual manner as $\alpha\beta\ldots\beta$, where the symbols are in special order, i.e. the ith symbol applies to the ith nucleus. If the nuclei were actually independent, these basic spin functions would themselves be stationary-state wave functions in the presence of the external magnetic field. However, the spin-interaction Hamiltonian $\mathcal{H}'$ may cause mixing between different basic functions, considerably complicating the calculation. In order to diagonalize the matrix of the complete Hamiltonian (18) we construct linear combinations of the orthogonal basic functions. The corresponding energies are obtained by solving the secular equation

$$\left|\mathcal{H}_{mn} - E\delta_{mn}\right| = 0 \tag{22}$$

This equation is of order 2^p but can be greatly simplified by factoring into a number of equations of lower order. This can always be done by classifying the basis functions according to the expectation value of

the total spin component in the z direction, $M_z = \sum_i I_z(i)$. It is possible to show[7] that there are no off-diagonal matrix elements of the Hamiltonian between basis functions corresponding to different values of M_z since the operator M_z commutes with the Hamiltonian.

Additional simplification occurs if more than one species of nuclei is involved. This is an approximation to the order that the coupling constant, J, is small (a few cps) compared to the difference in resonance frequencies, several megacps. This approximation is best when nuclei are different elements but it is also good if the chemical shift is large compared to J.

The matrix elements of the total Hamiltonian (18) can now be evaluated between basic product functions corresponding to the same value of M_z. Because each basic product function, Ψ_m, is an eigenfunction of each term in the external-field Hamiltonian (19), we have only diagonal elements which are easily evaluated by replacing $I_z(i)$ in (19) by $\pm \frac{1}{2}$ corresponding to its spin function α or β. Thus, for two nuclei, the diagonal element of (19) for the function $\alpha\beta$, is $\frac{1}{4\Pi} (\gamma_1 H_1 - \gamma_2 H_2)$.

The spin coupling Hamiltonian (20) has both on- and off-diagonal matrix elements. The diagonal element of a term such as $J_{12}\, \underline{I}(1)\cdot\underline{I}(2)$ depends only on whether the spin functions associated with nuclei 1 and 2 in Ψ_m are $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$, or $\beta\beta$ since integration over the remaining spins yields unity. Integration of the above term is carried out by writing the vector product in component form and using the appropriate components of the Pauli spin matrices (23)

$$I_x = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad I_y = \frac{1}{2}\begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix} \quad I_z = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{23}$$

Thus, for the example above

$$\langle \Psi_m | \mathcal{H}' | \Psi_m \rangle = \langle \alpha\beta | J_{12} \, \underline{I(1)} \cdot \underline{I(2)} | \alpha\beta \rangle$$

$$= J_{12} \, [\langle \alpha | I_x | \alpha \rangle \langle \beta | I_x | \beta \rangle + \langle \alpha | I_y | \alpha \rangle \langle \beta | I_y | \beta \rangle + \langle \alpha | I_z | \alpha \rangle \langle \beta | I_z | \beta \rangle$$

$$= - 1/4 \, J_{12} \tag{24}$$

The general expression for the diagonal element is given by

$$\langle \Psi_m | \mathcal{H}' | \Psi_m \rangle = \frac{1}{4} \sum_{i<j} J_{ij} \, T_{ij} \tag{25}$$

where T_{ij} is 1 or -1 depending on whether spins i and j are parallel or antiparallel in Ψ_m.

The off-diagonal elements are calculated in a similar manner. Again using the term $J_{12} \, \underline{I}(1) \cdot \underline{I}(2)$, the matrix element between two different basic product functions Ψ_m and Ψ_n will be zero unless the spin functions for all the nuclei except 1 and 2 are identical in both Ψ_m and Ψ_n. In addition, the only possibility to be considered is the interchange of $\alpha\beta$ for $\beta\alpha$, due to the restriction of considering only elements between functions with the same M_z. Hence, the off-diagonal matrix element is given by

$$\langle \Psi_m | \mathcal{H}' | \Psi_n \rangle = \langle \alpha\beta | J_{12} \underline{I}(1) \cdot \underline{I}(2) | \beta\alpha \rangle$$

$$= J_{12} [\langle \alpha | I_x | \beta \rangle \langle \beta | I_x | \alpha \rangle + \langle \alpha | I_y | \beta \rangle \langle \beta | I_y | \alpha \rangle + \langle \alpha | I_z | \beta \rangle \langle \beta | I_z | \alpha \rangle$$

$$= \frac{1}{2} J_{12} \tag{26}$$

The general expression for off-diagonal terms in (19) is

$$\langle \Psi_m | \mathcal{H}' | \Psi_n = \frac{1}{2} U J_{ij}, \; m \neq n \tag{27}$$

where U = 1 if Ψ_m differs from Ψ_n by one interchange of spins i and j and is zero otherwise.

We now have all the matrix elements of H_{mn} and can obtain the

eigenvalues by solution of (22). The corresponding stationary state wave functions can be found as linear combinations of the basic product functions

$$\Phi_q = \sum_m a_{qm} \Psi_m \qquad q = 1,2 \ldots 2^p \tag{28}$$

where the coefficients a_m satisfy the following set of equations which determine the relative values of a_{qm}.

$$\sum_n \mathcal{H}_{mn} a_{qn} = E_q a_{qm} \tag{29}$$

Since (28) should also be normalized the coefficients also must satisfy

$$\sum_m a^*_{qm} a_{qm} = 1 \tag{30}$$

The probability $P(m \to n)$ (in sec^{-1}) that a nuclear system undergoes the transition $m \to n$ (i.e., $\Phi_m \to \Phi_n$) is given by the relation

$$P(m \to n) = \frac{8\pi^3}{h^2} (M_x)^2_{mn} \rho_\nu \tag{31}$$

where

$$M_x = \hbar \sum_i \gamma_i I_x(i) \tag{32}$$

and

$$(M_x)_{mn} = \langle \Phi_m | M_x | \Phi_n \rangle \tag{33}$$

In (31), ρ_ν is the energy density per unit frequency range arising from the oscillatory rf field in the x-direction.

In Eq. (31) the operator $I_x(i)$ will have a matrix element only between two basic products which differ only in the spin of nucleus i. This means that the total matrix element in Eq. (31) will be non-vanishing only between states which have values of the total spin component M_z differing by ± 1. In addition, if several species of nuclei are involved,

both the states m and m' correspond to definite values of the separate spin components of each species $M_x(X)$, $M_z(Y)$, ... to a good approximation. Only the terms involving X nuclei in Eq. (31) will contribute to the intensity of an X transition in proportion to

$$\left|\langle q\left|\sum_i^x I_x(i)\right|q'\rangle\right|^2$$

where the sum is only over nuclei of type X.

If the molecule possesses elements of symmetry, further simplification is possible. This approach was first proposed by McConnell, McLean, and Reilly[24] and later discussed by Wilson.[25] It is often the case that unperturbed states which would otherwise interact are forbidden by symmetry conditions to do so. In symmetrical molecules some of the coupling constants, J, will be equal. The Hamiltonian must remain unaltered when a permutation of equivalent nuclei is carried out which is equivalent to one of the point group symmetry operations of the molecule. The wave functions must then conform to the group theory restrictions that each function or set of degenerate functions must transform in the same way as one of the symmetry species of the point group. States which belong to different symmetry species cannot interact with each other.

To determine the species which are represented by the unperturbed wave functions we consider separately each set, X, of symmetrically equivalent nuclei and each value of M_z for that set of nuclei. The spin product functions can be set up, and if necessary, can be further divided into equivalent sets, such that the product functions of one set are all obtainable by operating on any one member with the permutations of the molecule. Thus they will form the basis for a representation of the point group. This representation can be reduced to

irreducible representations using the character, χ_p, for the set of wave functions, ϕ, and each permutation operation, P. (Alternatively, the representations of the space group can be used for clearer pictorial value.) The character is the number of spin product functions of a given set which are not changed by P.

The simple case of two equivalent nuclei will be given here as an example; systems with more spins will be treated as they arise in Sec. IV. We can take the simple spin product functions as a set of basis functions for a group and classify them according to their total spin component, M_z. However, these basic product functions will not necessarily belong to the irreducible representations of the symmetry group. It is always possible, however, to construct a new set of basic functions which do belong to irreducible representations by taking linear combinations of the simple product functions. Such a set is called the basic symmetry functions. For the set of two nuclei the functions $\alpha\alpha$ and $\beta\beta$ are symmetrical under interchange. However, the pair $\alpha\beta$ and $\beta\alpha$ must be replaced by the normalized pair $2^{-1/2}(\alpha\beta + \beta\alpha)$ and $2^{-1/2}(\alpha\beta - \beta\alpha)$, which are now symmetrical and anti-symmetrical respectively. The basic symmetry functions for this case are shown below with their notation designated.

Spin Function	Spin Component M_z	Designation
$\alpha\alpha$	1	s_1
$2^{-1/2}(\alpha\beta + \beta\alpha)$	0	s_o
$2^{-1/2}(\alpha\beta - \beta\alpha)$	0	a_o
$\beta\beta$	-1	s_{-1}

The symbols s and a are used for symmetrical and antisymmetrical respectively with subscripts indicating the value of M_z.

Use of basic symmetry functions greatly reduces the order of the secular determinants to be solved and also results in additional selection rules for the transitions. This arises because there are no matrix elements of the Hamiltonian between functions belonging to different irreducible representations. This is because the Hamiltonian is totally symmetric with respect to permutations of equivalent nuclei. Thus the basic functions can be divided into classes according to their values of M_z and their symmetries.

In addition, M_x, the x-component of the nuclear moment, Eq. (32), is also a totally symmetric operator with respect to permutations, so that it will have no matrix elements between functions of different symmetry. As a result, transitions between states of different symmetry are forbidden, resulting in a very considerable reduction in the number of lines in a molecule where symmetry exists.

Only the simplest cases are solved by direct application of the above methods[7] because of the difficulty or impossibility of obtaining closed solutions for matrices of order higher than two. Castellano and Waugh[30] solved the general three spin case by use of a set of complicated algebraic equations which indicate that the method is unlikely to be used for systems with a greater number of spins. They were able to show that for the ABC case, there are four sets of parameters which are entirely consistent if only frequency sum rules are applied, and that it is necessary to resort to intensity information to decide which of these is the correct answer. Whitman[29] has also obtained some expressions for the direct analysis of certain special cases of up to four spins.

In general, however, it is necessary to resort to numerical methods[22-25] for systems of any complexity. One widely used method, which is used in this investigation is that of Swalen and Reilly[24] (S and R).

The S and R method utilizes two computer programs (NMRIT) and (NMREN) to analyze the spectrum in three steps. NMRIT is an iterative program and the number of iterations used will be designated in parentheses after the name, e.g. NMRIT(N).

The analysis is performed by first estimating a trial set of NMR parameters (chemical shifts and coupling constants) for the system. These values are used by NMRIT(0) to generate the matrix elements of the high-resolution Hamiltonian, Eq. (18), and then to diagonalize this Hamiltonian, using two by two rotations in the computer, to obtain the energy levels. The diagonalization can be written as

$$\underset{\sim}{S}^{-1} \underset{\sim}{\mathcal{H}} \underset{\sim}{S} = \underset{\sim}{\Lambda} \tag{34}$$

where $\underset{\sim}{S}$ is a transformation matrix, the columns of which represent the eigenvectors, and $\underset{\sim}{\Lambda}$ is a diagonal matrix of the eigenvalues. The diagonal elements of $\underset{\sim}{\Lambda}$ are the spin energy levels. NMRIT(0) then computes the spectrum which corresponds to these parameters, using all the selection rules, and prints out a listing of the transitions, frequencies and intensities of the calculated lines. The estimation of the parameters is, of course, a critical part of such an analysis. If it is not possible to make close estimates, perhaps based on moment calculations,[50] observations of separations in the spectrum, or from similar known systems, it is difficult to obtain a calculated spectrum which resembles the experimental one. Current procedure is to continue guessing at these parameters, using all possible intuition, until a reasonable fit to the

observed spectrum is made.

After a reasonable resemblance to the experimental spectrum is found, the second phase is begun. Here it is necessary to build up an energy level diagram based on the transitions calculated by NMRIT(O). The experimental lines are matched as well as possible to the frequencies calculated by NMRIT(O) and assigned to the corresponding transitions. If it is possible to identify enough of these transitions so all the energy levels are connected at least once, these assignments are used by NMREN to calculate the best least squares fit to all the energy levels. These calculated energy levels are now called the "experimental" energy levels.

The experimental energy levels, together with the original estimates of the parameters are then used as input to NMRIT(N). NMRIT(N) then calculates the energy levels corresponding to the estimated parameters and compares them to the experimental values. If the fit is not good it then changes the parameters and recalculates the energy levels corresponding to the new set. In this way it iterates the procedure until it converges on a best solution for the given set of experimental energy levels. One then compares the final calculated values for line positions with the experimental spectrum and if the match is not sufficiently good, the lines are reassigned, put back through the NMREN calculation and the procedure repeated until the calculated and experimental spectra match satisfactorily.. It may be seen that this method becomes difficult, especially for complicated systems where all the lines are not resolved.

It is also possible that more than one set of trial parameter estimates in NMRIT(O) may give a fit which is close enough to allow a tentative assignment. For example, in many systems, changing the relative signs of small coupling constants has a very subtle effect on

the spectrum. Small lines may merely be permuted within a group of partially resolved lines and/or intensities of small peaks may change slightly. It is necessary to either eliminate some of these possibilities or to carry all of them through NMREN and perhaps NMRIT(N). The usual procedure is to reject assignments which are significantly poorer than the best assignment, on the basis of frequency information alone. (It might be mentioned here that the S and R method does not utilize intensity information since this is not generally known nearly as well as frequencies.) If more than one assignment is good after the NMRIT(N) step, intensities of the peaks are used to make the choice of the best solution.

From the above discussion it is obvious that some severe limitations exist for the iterative method as currently practiced. The experimental spectrum must be well enough resolved so that a majority of the lines may be assigned to the calculated spectrum. Secondly, one must be able to estimate the parameters close enough so that the calculated spectrum at least resembles the experimental one. While a large amount of information is available on trends of these parameters with molecular structure, the unusual situations are precisely the ones of interest in many instances. A case in point is the simple four-membered ring compounds which have not been analyzed until the present time. Another possible difficulty is that the method may not converge to a unique solution to the problem. The tacit assumption has been made that the systems are so complex that if one finds a set of parameters which describe the experimental spectrum closely, one considers the problem solved.

Our interest in the hitherto unanalyzed class of four-membered ring compounds and the above limitations of the best available method of solving the problem has led us to develop more powerful methods to

assist in the analysis of NMR spectra. A better method than visual estimations of line positions and intensities was needed to enable the identification of more lines in these highly mixed spectra. Accordingly, DECOMP, a computer method of resolving overlapping NMR spectral lines, was developed and found extremely useful for these analyses and promises to be useful in the analysis of many similar spectra. This method will be described in the next section.

The use of DECOMP was successful enough in resolving spectral lines so that another computer program, ASSIGN, was written to find all possible sets of energy levels from the experimentally determined lines, using frequency and intensity sum rules. This program will be described in the section following DECOMP.

C. Spectral Decomposition

Generally, when an absorption spectrum consists of unresolved peaks, visual estimates of the total number of peaks and their positions and intensities are made using those maxima, minima and inflection points which are visually observable. Only a very small part of the information available in the recorded spectrum is utilized in this procedure. In fact, the intensity at all points on the abscissa provides information. By using all of this data far more information can be extracted from the spectrum than is possible by the usual visual procedure. Mathematical methods for improving the resolution of overlappling spectral lines have been reported[32-34] but do not appear to have been widely used.

One way of mathematically improving resolution is to consider an unresolved group as a superposition of peaks of the same general type, e.g., Lorentzian, and to minimize a least-squares fit of the experimental

spectrum with respect to the parameters: intensity, half-width and position required to describe the peaks. In the case of NMR, overlapping absorption lines are caused by similar nuclei having similar relaxation times, i.e., half-widths. In order to reduce the parameters required for n peaks from 3n to 2n + 1, the half-widths are assumed to be equal. This assumption is not necessary, of course, and if in fact the individual line shapes do turn out to be substantially different, a minor modification of the program would allow all 3n variables to be used.

The experimental spectrum, $G(\nu)$, is assumed to consist of a superposition of lines having the same form

$$G(\nu) = \sum_{i=1}^{n} I_i \, f(\Delta\nu_i, \nu-\nu_i^\circ) \tag{35}$$

where $f(\Delta\nu_i, \nu-\nu_i^\circ)$ is a shape function of half width $\Delta\nu_i$ and centered at $\nu = \nu_i^\circ$, I_i is the intensity of the ith peak, and n is the number of peaks in the multiplet. As stated above all of the half widths are assumed equal. Hence $\Delta\nu_i = \Delta\nu$.

The function to be minimized, F, is a least-squares difference function which is a measure of the fit of the experimental data with the curve calculated from Eq. (1).

$$F(I_i,\ldots I_n, \nu_i,\ldots \nu_n,\Delta\nu) = \sum_{i=1}^{m} [P_i - \sum_{j=1}^{n} I_j f(\Delta\nu, t_i-\nu_j^\circ)]^2 \tag{36}$$

where m is the number of data points taken over the multiplet, and P_i and t_i are the ordinant and abscissa of the ith data point.

The value of F after it has been minimized is a measure of the fit. For a given number of variables this minimum value will be referred to as the error function.

Numerous computer programs are available for the minimization of

a function of a large number of variables. One of these which appears to converge rapidly was chosen. This program was adapted to minimize the function given in Eq. (35). Mathematical details of the minimization program are available elsewhere.[35]

In actual spectra there exists an additional problem besides that of noise. Although under ideal experimental conditions it is possible to obtain a spectrum which consists of nearly perfect Lorentzian lines, it is very difficult to establish and maintain such conditions over long periods of time. It is relatively easy, however, to obtain high resolution curves which have a slightly skewed Lorentz-like shape. In many cases these peaks are sufficiently Lorentzian to be fit well assuming a Lorentzian shape function. In general a slight deviation from the ideal shape does not substantially change line positions but can have a serious influence on the intensities of the peaks. For this reason a "digital shape function", reflecting the actual spectrometer conditions at the time the spectrum is recorded, has also been used. Considerable improvement in the fit to spectra consisting of skewed Lorentz-like peaks is thus obtained.

DECOMP will fit spectra with either a Lorentz function or a standard digital function. If the Lorentz function is desired, T2, the spin relaxation time related to the half-width is read in as a parameter. To use a digital function T2 is set equal to zero and introduces the set of points which represent the standard digital shape function. (Details are explained in Appendix B). The data points for this standard peak are then treated as a "continuous" function by linear interpolation between points. The appropriate partial derivatives are calculated by TABLED so that the fit can be minimized in an exactly analogous manner to that using an

analytical expression. For the digital shape function, only two parameters, peak position and intensity, are needed for each peak in the superposition.

Since the use of DECOMP is greatly facilitated by visual comparison of the fit to the observed data points, a description and Fortran IV listing of a plotting program PLOT is given in Appendix C. PLOT provides the option of plotting peaks as Lorentzian or digital shaped peaks and can be used as a guide, although details will vary at different computer installations.

In practice, the spectra are decomposed in the following manner. A spectrum of an unresolved group with good signal-to-noise ratio is digitized by one of various means. A single peak in the spectrum is selected and digitized for use as the standard shape function. Points of the standard peak are taken such that a linear interpolation can be used between adjacent points to provide a "continuous" curve. Although this standard peak need not belong to the compound under investigation, better results have been obtained when such a peak was selected. Estimates are made of frequencies and intensities for those peaks which are at all visually discernible. These data are fed into a computer and the difference function is minimized. A theoretical spectrum is then calculated using the calculated frequencies and intensities, and this spectrum is plotted along with the experimental points. In the frequency regions where the fit is poor, estimated lines are added. The original results along with the additional estimates are then fed back into the computer for another minimization of the difference function, this time with more arbitrary parameters. This process is continued until a sufficiently good fit is obtained.

As one adds more and more peaks, the fit continues to improve

indefinitely, and it might appear difficult to determine the actual number of peaks in a group. In practice, this problem resolves itself very nicely. When DECOMP is allowed too many peaks to fit the observed spectrum, one of the following three types of spurious results occur. The additional peak can be used to fit noise; this manifests itself in a small intensity for the additional peak which is of the order of magnitude of the noise. Consequently the addition of this peak does not improve the resulting error function by a reasonable percentage. Alternatively, the additional peak can be used to correct a line which is too broad or too narrow. If the line is too broad, the additional line will appear, with comparable intensity, very close to an already existing line. If the line is narrower than the standard line the extra line will appear very close to an already existing line, but with negative intensity. Finally, the additional peak can be wasted by assigning two lines immediately on top of each other with the algebraic sum of their intensities equal to the true intensity.

An example of the method is shown in Figs. 1-4. The decomposition of the same group of twelve peaks from two different spectra using a digital shape function is shown in Figs. 1 and 2. The same two groups decomposed with a Lorentz function are shown in Figs. 3 and 4. In the figures, the dots are the original data points taken from the experimental spectrum, the vertical lines are the decomposed positions and intensities of the individual peaks, and the solid line is the calculated spectrum based on the decomposed frequencies and intensities. The agreement between the calculated and experimental spectra is excellent. Table 1 compares values of positions and intensities for the twelve lines among the digital and Lorentzian decompositions for

the same group of peaks taken from two different spectra obtained under different spectrometer operating conditions. Spectrum 2 contained lines which were quite skewed, and it may be seen that the agreement between the two groups decomposed with the digital function is good. However, the values for intensities derived from the Lorentzian shapes show a larger scatter. In fact it was not possible to fit twelve Lorentzian peaks to this spectrum. Several sets of starting parameters were tried, including the best values from the other spectra, but one peak with negative intensity was still obtained.

The ability to decompose an entire spectrum into its constituent peaks is complimentary to, and agreatly facilitates the use of Swalen and Reilly's NMRIT. For example, in the spectra to be discussed below, there are several groups containing twelve lines, several of which are not visible, even as shoulders on other peaks. These lines would be impossible to assign in the usual application of NMRIT(0). (This would not necessarily invalidate the method, however, since the energy levels involved might be connected by other transitions.) With DECOMP it is possible to obtain values for positions and intensities for almost all the lines in the group. Thus far more lines can be assigned than would be possible from a visual estimate, making the experimental energy levels more representative of the real spectrum. Even in the worst case only one or two of the lines in a group would not be identified. Conversely, NMRIT(0) can help in the decomposition of a spectrum by showing how many lines of appreciable intensity are to be expected in a given region of the spectrum, if the estimated parameters are close enough to the true values. The application of these methods will be discussed in more detail in the specific cases covered in Section IV.

D. Spectral Assignment

Once the frequencies and intensities of all lines in an NMR spectrum are known, there remains the problem of building consistent sets of spin energy levels which account for the experimental frequencies and intensities. As discussed above, when using the S and R method of analysis it is necessary to continue guessing parameters until the calculated spectrum is close enough to the experimental spectrum to allow the assignment of pairs of energy levels to observed transitions. Even though all the experimental lines were known from DECOMP, the use of this method requires estimation of the parameters close enough to the real values so all the line positions and intensities correspond close enough for identification.

A less subjective method is to assign these experimental lines according to frequency and intensity sum rules with the aid of a computer. A computer program, ASSIGN, has been written to accomplish this task for any system of spins by use of a computational algorithm which is part of the input data for the problem. In the following discussion of ASSIGN, upper and lower energy levels refer to the position of the energy level in the energy level diagrams, not to the actual value of the energy. The convention within ASSIGN is that $\Delta M_Z = -1$. Also the word "transition" will be used to denote an unknown transition between two energy levels, and the work "line" will be used to denote an experimentally determined transition. The purpose of ASSIGN is to assign the lines to the transitions.

In order to take advantage of any information which limits the frequency region in which a given transition occurs, ASSIGN, allows constraints to be placed on the ranges of lines searched for a particular type of transition. This considerably reduces the number of lines to be searched for each assignment, and reduces the computer time considerably. For example, in an A_2B_2X spectrum, only the lines in the X

region of the spectrum are searched for X transitions and all of the A_2B_2 lines need not be searched for A transitions. Even more specific restrictions might be applied with information obtained from order of magnitude guesses of the spectral papameters, for example from NMRIT (0).

In addition, ASSIGN is completely general for any system of spin of any symmetry. This generality arises from the use of a computational algorithm, part of the input to ASSIGN, which guides the manner of assigning the lines for a given system, e.g., ABC, A_2B_2X. Ideally it would be necessary to make up the algorithm only once for each type of system, but additional information about a specific case may merit a special algorithm.

The first step in the construction of the computational algorithm is to work out the symmetry basis functions for the system and to draw an energy level diagram for each symmetry group. Next, all transitions are put onto the diagram and the type of nucleus associated with each transition is determined. For some molecules it will be strongly suspected that some transitions will have vanishingly small intensities. If this is so, these transitions can be left out. The transitions are next numbered in the order in which it is desired to assign lines to them. This is done so as to allow the maximum number of checks against frequency and intensity sum rules[24,26,30,36] at the earliest possible time in the assignment procedure. Fig. 5 shows the energy level diagram for the ABC case with the energy levels numbered. The transitions are also numbered and labeled as to type.

An algorithm for the ABC case appears in Table 2. The second column specifies the type of transition, i.e., what range of lines should be tried as possible assignments for the transition. The next two columns give the upper and lower energy levels for each transition. Minus signs are attached to an energy level number after all transitions

to and from that energy level have appeared in the algorithm. This indicates that an intensity check for that energy level is to be made after a line is assigned to that particular transition. The frequency check column contains a 1 when the transition under consideration completes a frequency sum rule "loop", and a check of this loop is to be made.

In order to use the intensity sum rules it is necessary to normalize the total spectral intensity to $n \cdot 2^{n-1}$, where n is the number of protons. The sum of all transition intensities from a given energy level will then be 2m plus the sum of all transition intensities to that energy level, where m is the Z component of the spin angular momentum associated with that energy level. In Table 2 the sum of intensities column (SI) lists the value of 2m for each of the energy levels.

ASSIGN can best be explained by following it through the ABC case given in Table 2. The first energy level is set equal to zero. As the assignments are made the other energy levels are calculated, by adding the frequency of the assigned line to the upper energy level of the transition. ASSIGN initially assigns the first A line to transition 1, the first B line to transition 2 and the first C line to transition 3, thus temporarily establishing E_2,E_3, and E_4. The intensities of each of these lines are subtracted from the sum of intensity (SI) associated with E_1, i.e., 3.0, as they are assigned. The minus sign at the upper energy level for transition 3 causes a check to be made to see if the value of SI at E_1 is zero to within $\pm \Delta$, an input parameter. This criterion assures that the sum of the intensities of the three lines assigned is 3.0. If not, the program negates the last assignment and continues on through the range of the type C lines. If none of these fit, the program backs up one step to the B transition and tries the next line in the B range, and then goes back through the range of the C lines

again. This is repeated until three lines are found, one from each of the specified ranges, which have the total intensity required by the intensity sum rule.

Next, the fourth transition is assigned the first unused line from the C range, thus establishing E_6. Transition 5 is assigned the first unused A line. This last assignment established E_6 a second time and hence it is possible to make a frequency check around the loop of transitions 1,4,3, and 5. If E_6 is not the same by both paths to within δ, another input parameter, i.e., $1 + 4 - (3 + 5) > \delta$ then the next unused A line is assigned to transition 5. This is continued until the sum rule is satisfied or until the A range is exhausted. If no consistent assignment is found then the next C line is assigned to transition 4 and the search continued. If no two lines, when assigned to transitions 4 and 5 are consistent with the temporary values of E_2 and E_4, then the program must back up further yet and find another set of three lines which satisfy the intensity sum rule associated with E_1. The program continues in this manner until a complete set of lines is assigned. The assigned transitions and energy levels are printed out and the process is continued until all possible sets of transitions and energy levels are obtained.

All 15 lines in an ABC system can be assigned to all possible arrangements, consistent with the sum rules in 0.05 minutes by an IBM 7094.

There are several further aspects of ASSIGN which can be quite useful at certain points in a problem. It is quite possible that one or more first order lines in the algorithm do not appear in the spectrum due to lack or resolution or low intensity. If this occurs in the middle of the sequence, no assignment would be possible even though each of the

energy levels is established by several paths. There is no a priori way to know where such a line will occur so a provision is made to allow the inclusion of one or more "dummy" lines which can fit by assigning a frequency equal to the difference between the upper and lower energy levels for the last frequency assignment in the loop. This line would be assigned an intensity of zero. For example, if two combination lines in the ABC system discussed above were not seen, two dummy lines could be used which would eventually be assigned as two of the lines 13,14, or 15. The use of such lines greatly increases the time required since they have to be assigned through the entire scheme, if it is assumed that one has no idea where they might be needed. For the ABC case cited above, the computer time was increased from 0.05 minutes to 0.5 minutes. Clearly for systems with a large number of spins, it is desirable to know which transitions will have negligible intensities. This information can often be found by a computer calculation of the expected transitions for the molecule using order of magnitude guesses for the unknown parameters.

ASSIGN can be made to converge much more rapidly if the frequencies of some of the transitions are known exactly, or even within a small range. This type of information might be obtainable from double resonance experiments or from calculations based on order of magnitude guesses for the unknown parameters. It is then possible to designate that transition as a unique type in the algorithm and restrict the assignment to one of a few lines. If several such transitions are known and fixed in this manner, a considerable reduction in time is realized. In this way, any knowledge about the coupling constants or chemical shifts can be used to restrict the limits of search for given transitions.

In case a molecule has transitions of several different symmetry types, each symmetry type may be assigned separately. After one obtains all possible assignments for the first symmetry type, one uses the same data for the second symmetry class. However, on the second run, a vector is added which indicates the lines which have already been assigned in a previous assignment.

A simple example of a system which contains more than one symmetry class is an A_2B_2 system, such as o-dichlorobenzene. The proton system of this molecule contains a plane of symmetry. Thus there will be two sets of energy levels, one symmetric and the other antisymmetric with respect to reflection of the spins in this plane. The basic symmetry functions, given in Table 3, are easily constructed by multiplying the basic symmetry functions for A_2 and B_2 derived earlier. These basic functions are then used to make up symmetric and antisymmetric energy level diagrams, since no transitions are allowed between states of different symmetry. The energy levels, identified with the numbers of the corresponding basis functions in Table 3, are shown in the diagram of Fig.6. As a first approximation, it was assumed that the only lines to be seen in the spectrum would be those which occurred as a result of the change of spin of a single nucleus (first order transitions). Although it is known that combination lines, i.e., those occurring as a result of simultaneous change or spin of more than one nucleus, can have a non-zero intensity, this intensity is generally very low. The first order transitions which were used to build up the computational algorithm for ASSIGN are alos shown in the figure. In this case, where more than one symmetry group exists, each group can be considered as a separate problem. The algorithms for the A_2B_2 case are shown in Table 4.

Ordinarily the transitions are considered as going to successively lower M_z levels. When more than one energy level is in the highest M_z level, one of these is used as the zero point. When the energy levels in the next lower M_z level are established, two transitions back up to the undetermined energy level at higher M_z are designated by a minus sign before the type of transition. After this upper level is established, additional transitions can be designated in the usual manner. After all the anti-symmetric sets of energy levels have been determined, the assigned lines are given values of one in the input vector and the unused lines are used to find all the sets of symmetric energy levels for the particular anti-symmetric set.

The analysis of o-dichlorobenzene will not be discussed here since it has been reported in the literature.[26,27] It was used as a test for ASSIGN in the case of more than one symmetry group and as an example of construction of the algorithm for such cases. The time required to find the sets of energy levels for o-dichlorobenzene was between two and three minutes with the IBM 7094.

E. Additional Methods to Aid the Assignment of Spectral Lines

In the ideal case, to make an assignment with ASSIGN one needs to know a minimum of information, that is, only the general region of the spectrum for each type of nuclear transition and the line positions and intensities from DECOMP. Unfortunately there is enough uncertainty or noise in present spectrometers so that DECOMP cannot always locate all the lines in a complex spectrum precisely enough to allow ASSIGN to automatically make all assignments. If the uncertainty limits are set too narrow in ASSIGN, it is possible to miss the correct assignment due to a bad value for a line position or intensity, or to get no assignments

at all. If the limits are too wide too many assignments are obtained.

The two five spin systems which will be discussed in detail below, were difficult to assign for two reasons, both resulting from experimental limitations. The spectrum of one compound was decomposed quite satisfactorily, however many of the peaks which were close together also had very similar intensities. This meant that with reasonable uncertainty limits the number of possibilities was so large that the time required to make the assignments greatly increased. On the other hand, the spectrum of the second compound contained peaks with greater intensity differences, but a number of small peaks located between two or more large peaks made the decomposition more difficult. These situations may exist in any complex spectrum, of course, but it is felt that slight improvements in instruments and techniques will result in spectra which can be analyzed directly from the experimental data.

In such cases, the time required to assign lines can be greatly reduced by placing additional constraints on the system. This can be done by the use of estimates of parameters in NMRIT (0) and the use of double resonance experiments. The information obtained from these sources can be used separately or in conjunction with each other.

If the parameters can be estimated with any degree of accuracy, a convenient way to calculate approximate line positions and their transitions is by use of NMRIT (0), as discussed above. For the spectra discussed below, it was possible to estimate the large coupling constants fairly well. The problem was then to sort out the effect of changing the three small coupling constants, whose effect was mainly to change transitions of peaks within the larger groups of peaks. This meant that in a partially resolved group of twelve peaks the transitions were

known, but it was not known which lines in the group corresponded to each transition. Accordingly, each unresolved group of peaks was called a "type" and all of the transitions occurring in that region, as calculated by NMRIT (0), were assigned to that type. Thus the number of lines to be searched for a particular A transition, for example, was reduced from 36 to 12. This will be described in detail in connection with the particular analysis.

The second method of obtaining information regarding the locations of transitions is the use of a second rf field.[38-43] If the second irradiating field is strong, the irradiated nucleus is effectively decoupled from the rest of the system, simplifying the spectrum considerably. The method has been used for such purposes as the measurement of chemical shifts of hidden resonance lines and the determination of the relative signs of nuclear spin coupling constants.[44,45] For these applications the rf field strengths have usually been of the same order as, or greater than, the perturbed spin coupling constant J. Since, in general, the spectra of strongly coupled spin systems have transitions separated by frequencies much less than J, it is not possible to selectively irradiate single lines in these spectra with the strong rf field. Freeman and Anderson[43] have investigated the effect of using weak irradiating fields. They found that the use of a weak field made it possible to determine which transitions have energy levels in common, and furthermore to distinguish the two possible cases, i.e., where $\Delta M_z = 0$ and $\Delta M_z = 2$.

Freeman and Anderson consider three double irradiation experiments: 1) field sweep, where the main magnetic field, H_o is varied while ω_1 and ω_2 remain constant; 2) frequency sweep, in which H_o

and ω_2 remain constant while varying the observing frequency, ω_1; and 3) varying the perturbing frequency, ω_2, while H_o and ω_1 remain constant. Although the field sweep method is simpler and requires less equipment, they conclude that it has several disadvantages and the frequency sweep method is preferable.

They describe in detail frequency sweep(method 2) above in which one peak in the spectrum is irradiated with the weak field and the spectrum is recorded by sweeping the observing frequency, ω_1. The spectrum thus obtained has the usual appearence except for those transitions which have energy levels in common with the transition being perturbed with ω_2. If the transition shares an energy level with the irradiated peak and the change in M_z is 0, the peak will appear as a sharp doublet whereas if the change in M_z is two, the peak is broadened. The method requires a separate spectrum for each peak irradiated and the peaks must be reasonably resolved in the spectrum (at least visible as a shoulder) to observe the phenomenon. Those peaks for which changes can be observed may be used to build up at least part of an energy level diagram and may provide the additional amount of information required to solve a given problem.[46]

The third possibility, that of sweeping the perturbing frequency while observing a single line, was mentioned by Freeman and Anderson and is of most interest to us for use with ASSIGN. For this experiment the observing frequency is positioned on a peak miximum using a very stable oscillator. The perturbing frequency, ω_2, is then swept across the spectrum and as it traverses peaks which have an energy level in common with the observed peak, the height of the observed peak will change. In the above paper Freeman and Anderson stated that the peak

height would dip for both cases where the lines shared a common energy level. The dip would be sharp where $\Delta M_z = 0$ and broad for $\Delta M_z = 2$. Such information would be very useful for ASSIGN. Accordingly the program was modified to take advantage of such information. The method has the advantage over the first frequency sweep method in that the peaks which are perturbed do not have to be resolved. The location of a dip will indicate the perturbed peak within a small frequency range and all the peaks which have been found by DECOMP in that range can be used as a transition type. This will further reduce the location from, say twelve peaks to three or four. The advantage here is that the peaks do not have to be resolved in the original spectrum at all. (The other frequency sweep method would be of less interest here since it would be necessary to decompose each of the separate spectra to observe differences which occurred due to the perturbation.) It is necessary to observe a peak which is far enough from its nearest neighbors so it may be observed alone. If another peak is too close, the lines which have energy levels in common with both lines will be observed. For the limited number of experiments we performed this required separation appeared to be about one cps although this could probably be reduced by further improvements in the instrumentation. The recorder pen is swept with the perturbing frequency and will dip at the frequencies of lines which have common energy levels. Since these dips may cover a range of several lines all the lines within say ±0.5 cps will be included.

The input algorithm of ASSIGN was changed so this information could be incorporated in the following manner. The ranges of all the lines in the dips showing common energy levels are included in the algorithm opposite the corresponding observed line. Again this can per-

haps be best explained by returning to the ABC case of Fig.5. For simplicity, assume that all the lines are well enough resolved so that it has been possible to observe each of them as the spectrum has been swept by the perturbing field. The array of common energy levels (determined from the transitions of the correct assignment) is written as shown in Table 5. In an actual experiment, of course, these values would be obtained by doing the experiment. Each set of two numbers in the horizontal direction indicates the beginning and end of the range of lines which was indicated by the dip as having an energy level is common with the line indicated in column one. Now the restriction on the choice of lines for a given transition is very much more restricted than in the original ABC case where the range for A was 1 - 10, B was 1 - 15, C was 5 - 15 and that for D was 1 - 15. The double resonance restriction is invoked from the second line assignment, even before the sum rule checks come into play. Thus to assign line 2, ASSIGN checks the energy levels of previously assigned transitions to see if any of these energy levels are common with those of transition 2. Since energy level 1 is common to both transitions 1 and 2, the choice of lines for transition 2 is restricted to lines 3,5,6,8,9, or 15, rather than the whole range of 14 lines as was previously the case. The choice for transition 3 is now restricted, within its range of type C (lines 5 - 15), to a line which is in common with both transitions 1 and 2, as well as having to conform to the intensity sum rule check. After a few lines have been assigned, the possibilities are almost unique for this trivial case. As an example, one assignment for the first six transitions is the lines 2,4,9,13,6, and 12. To assign a line to transition 7 ASSIGN first notes that transitions 3,5, and 6 have energy levels in common

with transition 7 and have been assigned lines 9,6 and 12 respectively. The range of the type for transition 7 is 1 - 15 so no restriction operates here. ASSIGN then compares the ranges in the common energy level array for lines 9 and 6, and when it finds a line common to both these lines, it then checks the array at line 12 to see if the line is common to all three lines. In this case the only line common to all three previously assigned transitions is line 8 and it is then assigned, if it will meet the sum rule criteria. In a more complicated case the lines in the array would be replaced by small ranges but it can be seen by the above example that a considerable simplification is to be expected when such information is available.

To test the utility of these ideas, the double resonance frequency sweep experiment was tried with one of the five spin systems which is discussed in detail later. Instead of the dips predicted by Freeman and Anderson, it was observed that both dips and peaks occurred during the sweep of ω_2. Furthermore, the dips corresponded to the case where $\Delta M_z = 0$ and the peaks to $\Delta M_z = 2$. This information is far more useful than had been expected since it is much easier to distinguish peaks from dips than it is broad dips from narrow dips. One difficulty which occurs, is that at a few places in the spectrum the two types of transition occur rather close together. It was observed in one case that two such transitions canceled each other and could not be distinguished from noise. With present instrumentation, two such transitions have to be separated by about 0.5 cps or greater to be seen. After the above effect had been observed in these experiments, it was also found that the effect had previously been observed by Kaiser[47] who explained it qualitatively as a nuclear Overhauser effect.

III. EXPERIMENTAL

The 3-chlorothietane was synthesized by Mr. W. D. Keller[48] according to the method of Dittmer and Christy.[57,58] Purification was carried out in a spinning band column; a middle, constant boiling fraction was used to obtain the NMR spectra. The 3-thietanyl acetate was made in a similar way by Mr. R. Millikan; purification being carried by vacuum distillation. The samples, containing a small amount of tetramethylsilane as an internal reference, were degassed under vacuum and sealed.

Spectra for the 3-chlorothietane were recorded with a Varian A-60 spectrometer which had been modified by replacing the 25 rpm sweep motor with a 2 rpm motor, allowing slow passage sweep rates. The X and the A_2B_2 parts of the spectrum were taken separately with a sweep width of 50 cps and a sweep time of 1250 seconds (0.04 cps/sec). The spectra were also filtered at 0.2 cps to reduce noise and to facilitate the subsequent digitization.

All other spectra were taken with a Varian HR-60 spectrometer which had been modified by Mr. J. A. Ferretti with a field lock system for maintanence of a stable field and with auxiliary equipment to allow double resonance experiments to be performed.[43,46,59] The spectra taken with this instrument were directly digitized through an analog-to-digital converter connected to an SDS 910 computer. The spectra were recorded at a rate of 1800 seconds for a 50 cps range (0.028 cps/sec) and were smoothed in the computer using a nine point smoothing function, after the method of Savitzky and Golay.[56]

IV. RESULTS AND DISCUSSION

A. Systems with Five Spins

1. 3-chlorothietane

Two well resolved spectra were used for the analysis, one of which is shown in Fig. 7. The spectra were digitized using a Benson-Lehner "OSCAR" x-y analog-to-digital reader, directly coupled to an IBM 026 card punch. As can be seen from Fig. 7, the spectrum is divided into ten groups of peaks which show the fine structure due to nuclear spin-spin coupling. Each of these ten groups were decomposed using DECOMP in the manner described above. All 64 lines in the spectrum were resolved; results for each of the separate groups are shown in Figs. 9-16. Again, the experimental data points are shown as dots, the lines found by the decomposition are shown as vertical lines, and the calculated spectrum based on the sum of the vertical lines is shown as a solid curve. The agreement between the calculated curve and the data points is very good. The average difference between lines decomposed in the two spectra was 0.03 cps; the two largest disagreements out of the 64 pairs of lines was 0.1 cps. The line positions and normalized intensities of the average of the two spectra, used in the subsequent work, are listed in Table 6.

The set of basi symmetry functions, formed by multiplying the A_2B_2 symmetry functions in Table 3 by the spin functions α or β for the X nucleus is shown in Table 7. These functions were then used to make up the symmetric and antisymmetric energy level diagrams shown in Figs. 17 and 18. Using only single nucleus transitions, the algorithm in Table 8 was made. The transitions are not numbered in the figures but can easily be identified by their upper and lower energy level designations in the algorithm and diagrams. The order of making

assignments is arbitrary; paths are chosen to allow the maximum number of frequency and intensity checks as early in the scheme as possible.

The above algorithm will apply to any A_2B_2X system of spins for which the line positions and intensities are available. However, as discussed earlier, additional information is often available and can be used to further simplify the problem. Such information may be different for each system and the algorithms will then have to be constructed to fit the specific circumstances.

Using the direct approach of limiting transition types to the three types of nuclei, and setting reasonable limits for the uncertainty of the frequency and intensity, no assignments were made for the anti-symmetric energy levels of 3-chlorothietane in two hours by the IBM 7094. As mentioned above this was probably due to many of the peaks having similar frequencies and intensities. Accordingly, additional constraints were placed on the problem by using NMRIT (0) as discussed earlier.

Since one of the objects of this study was to simplify the analysis of complex spectra, the first approach was to use estimates of the parameters obtained from the spectrum in NMRIT (0) to calculate a spectrum which could be matched to the lines obtained from DECOMP. If this approach were not satisfactory, it would then be necessary to resort to more complicated procedures, perhaps double resonance experiments or the calculation of moments.[50]

For 3-chlorothietane the parameters were estimated as follows. The A and B parts of the spectrum each consist of 24 lines in groups of six, twelve, and six lines. The chemical shifts are approximately in the middle of the respective groups of twelve peaks and can thus be estimated as the positions of the second group of peaks from each end of the A_2B_2

spectrum. The chemical shift of X is given by the center of its spectrum.

The next important parameters are the larger coupling constants. These are the "cis" and "trans" vicinal coupling constants between protons on adjacent carbon atoms and the geminal coupling constant between protons on the same carbon atom. The vicinal constants can be calculated reasonably well, since their sum is given by half the width of the X spectrum and their difference is given by the splitting of the two doublets in the second and fourth peaks in the X spectrum. This can be estimated to within a few tenths of a cps from the values obtained by DECOMP, since the entire group is only two cps wide.

Estimation of the geminal coupling constant is less certain. It was estimated to be between -9 and -11cps on the basis of representative values in a recent review by Banwell and Sheppard.[49] Since it has been well established that geminal coupling constants are negative and opposite in sign to vicinal coupling constants, the latter were taken as positive.

All the long-range coupling constants across the ring were estimated as small and positive according to the best knowledge at the time of beginning this study.

After a few adjustments, these estimates resulted in a spectrum calculated by NMRIT (0) which resembled the experimental spectrum. As discussed under the section on spectral analysis, this estimate was good enough to localize the sets of transitions within the ten large groupings of peaks.

A second algorithm was constructed using energy level assignments from NMRIT (0) and classifying each of the ten groups of peaks in the spectrum as a "type of nucleus". Used in this manner, "type of nucleus"

has lost its original meaning and merely serves to indicate the general location of a line. This new algorithm and the ranges for the transitions are shown in Table 9. Using this algorithm, the time required to find the two antisymmetric sets of energy levels was reduced to 50 minutes with the IBM 7094. The lines remaining from each of these sets were then used to make symmetric assignments. No symmetric assignment was possible for one of the antisymmetric sets of energy levels, but three symmetric sets were possible with the other antisymmetric set of energy levels. The three complete sets of transitions corresponding to the sets of energy levels were then used in NMREN to get the best least squares fit of the energy levels and adjust the traces. These adjusted energy levels were then used in NMRIT(N) to calculate the corresponding chemical shifts and coupling constants. The two worst sets of energy levels correspond to complex parameters, as shown by the failure of NMRIT(N) to converge. A number of peaks in these sets are several tenths of a cps away from the experimental peaks, whereas only one peak calculated from the best set of parameters was as far away as 0.13 cps from the experimental peak.

The numbering system used for the protons in the molecule is shown in Fig. 18. The reasons for numbering the protons as shown will be given below, however, it must be pointed out that these experiments cannot determine whether the large long-range coupling constant is between protons 1 and 2 or protons 4 and 5. This information could be obtained, for example, by substituting one of the protons with deuterium.

The theoretical spectrum calculated by NMRIT from the best set of parameters is compared with the experimental spectrum and the lines found by DECOMP in Figs. 19 and 20. In these figures the upper vertical lines are the line positions and intensities calculated by NMRIT and the upper solid curve is the theoretical spectrum calculated from the sum of all these lines. The lower curve is the experimental spectrum and the

lower vertical lines represent the line positions and intensities obtained by decomposition of the experimental curve. The agreement between the line positions is excellent; the average frequency deviation is 0.031 cps and the largest single deviation in the 64 lines is 0.133 cps. The intensities do not agree as well; in some cases being off by 50 per cent of the calculated peak height. These worst cases, however, are for those peaks which cannot be seen at all visually; in the cases where the peaks can be at all distinguished, the agreement is quite satisfactory, being of the order of 5 - 10 percent.

After 3-chlorothietane was analyzed, additional instrumentation became available so that the double resonance experiments described above could be performed. Since the NMR parameters and transition frequencies of the chlorothietane were now known, it appeared to be a good test of the double resonance experiment in which the perturbing frequency was swept while a single line was observed. The X part of the spectrum has several lines which are separated by nearly one cps and it was possible to do the experiment while observing lines 1,4,5,6, 11,12,15 and 16 in the X spectrum and line 59 in the A_2B_2 spectrum.

A calibration spectrum was first taken of the entire chlorothietane spectrum on the modified HR-60 using a frequency sweep rate of 180 seconds for a 50 cps range. A very stable oscillator was then used to set the observing frequency right at the peak to be observed. The perturbing frequency was then swept at the same rate as the calibration spectrum was taken, with the recorder pen following this sweep. A fairly noisy base line was observed which showed the dips ($\Delta M_z = 0$) and peaks ($\Delta M_z = 2$) which were discussed above. Fig. 21b shows the calibration spectrum for the A_2B_2 part of the spectrum; 21a and 21c are the records obtained while observing lines 11 and 12 respectively

while sweeping across the same frequency range. Using values of line positions obtained from DECOMP, it is easy to determine the position of the line corresponding to the peak or dip, to within three or four lines. This information, shown in Table 11a, can then be put into the algorithm for ASSIGN, further restricting the choice of lines in a given type. A large beat frequency appears at the right of spectrum 21a and in this case does not correspond to a line with an energy level in common with line 11. In some of the experiments, a line did lie at the same place as a beat frequency and the only hint that the two were superimposed was that the beat pattern was slightly asymmetrical. Of course, this could not be relied upon in an unknown system and some information might be lost in this manner. Figure 21c shows the effect obtained when two transitions, which have an energy level in common with the observed line, are close together. As seen by the dip and peak, the first transition has $\Delta M_z = 0$ and the second $\Delta M_z = 2$. The separation of these two lines is 0.7 cps. A similar set of lines occurs at the position indicated by the arrow, but in this case the separation of the lines is only 0.007 cps and the peak and dip cancel and are not observed.

Because of limited access to the instrument it was not possible to exhaustively explore experimental variables in this system. The present set of experiments indicated that the observed peak had to be approximately one cps away from adjacent peaks to be sure of observing only one peak. Considerably more difficulty was encountered when the observed peak was between two peaks, even when separated by one cps, than when the observed peak was at the edge of a group. These limitations could undoubtedly be reduced by refining the technique more thoroughly.

The information from the double resonance experiments with the

nine lines was put into ASSIGN using only the three types of nucleus, A, B, or X, as constraints. The two antisymmetric assignments were calculated in 82 minutes by the IBM 7094 compared to no assignment being made in 120 minutes without the double resonance information. After the antisymmetric set of energy levels has been assigned in such a problem, assignment of the symmetric set takes even less time due to the considerable reduction in available lines. Since 3-chlorothietane had already been completely analyzed, the assignment of the symmetric lines was not attempted because it was felt that the computer time could be better utilized.

This experiment verifies our original premise that it is feasible to determine the energy levels of a complex system directly from the experimental spectrum without any assumptions regarding the NMR parameters. Double resonance information from even a few more lines would probably reduce the time appreciably, however, it cannot be assumed that more than nine or ten lines would be available in the general case. In fact, this approach would be less successful with the thietanyl acetate since the X part of that spectrum is considerably less well resolved than for the chlorothietane, with only the two outside single peaks resolved.

Due to the particular nature of the A_2B_2X spectrum, a great deal of information can be extracted from the use of a combination of all the techniques discussed above, in the following manner. The X spectrum of 3-chlorothietane has two single peaks at either end. It was observed from several NMRIT (0) calculations that these two lines, numbers 1 and 16, were always assigned to transitions 31-32 and 1-2 respectively. Additional NMRIT (0) calculations, using values

for the initial parameters far outside the ranges which would ever be used, showed that lines 1 and 16 were always given the same assignments. Referring to Fig. 17a, it can be seen that double resonance information on just these two lines can be extremely helpful in building an algorithm for the symmetrical energy levels. In the use of ASSIGN a large portion of the total time is used in establishing the first few energy levels. Using the information about ΔM_z from the two double resonance experiments, several levels can be established very rapidly.

Use of such specific information about a system requires a new algorithm, which is formed in the following way: Transitions 1 - 2 and 1 -5 are known to be lines 16 and 52 respectively, from NMRIT (0) and the double resonance data in Table 11b. Transition 1 - 4 is one of lines 27 - 32 but the intensity sum rule limits this choice to one of two lines. Thus the entire set of energy levels for the second M_z level are determined to within the choice of two lines for level 4. The transitions 2 - 7 and 2 - 9 are also given to within four lines and can be established quickly using frequency sum rules around loops from energy levels 4 and 5. We have thus established six energy levels to a fairly high degree of certainty. Even if one of these assignments were incorrect, there are very few lines left to choose from is ASSIGN were to back up to make a new assignment. This is a very great reduction over the usual arbitrary assignment of these lines when this information is not available. The same amount of information is also available at the bottom of the diagram so the algorithm is written to establish a skeleton fromework of two energy levels for each intermediate M_z level in order to connect the top and bottom of the diagram as directly as possible. This is done from energy levels 7 and 9 to levels 18 and 20, which can then be used to establish levels 27 and 30.

These intermediate energy levels are not known with as much certainty, since the transitions are only known to be within one of the usual large groups of lines. We are now in a position to start assigning the lines at the bottom of the diagram. More restrictive constraints are again operative, since these lines are known to lie within narrow limits, from the double resonance experiment. Assignments 27 - 32 and 30 - 32 will quickly determine whether the intermediate assignments were all consistent. If so, level 31 can be established using line 1 and the negative sign in front of the transition type as explained earlier. The balance of the double resonance information from line 1 can be used to establish energy levels 23 and 26. We have thus used double resonance information from only two lines plus information from an approximate NMRIT (0) calculation to establish 12 energy levels and 22 line assignments with a much higher degree of certainty than by use of an arbitrary algorithm. This information is shown in Fig. 22. The transitions and energy levels which are known quite well from the double resonance experiments are shown in bold lines and those known with less certainty are shown with light lines. Once this much of the energy level diagram is known, the remainder is assigned arbitrarily since no specific information is known about the rest of the lines. Furthermore, since the assignment of the symmetric energy levels is the largest part of the task, the remaining antisymmetric levels will almost fall into place and accordingly the entire system is made up in one algorithm and the problem done all at once. Using this approach with the same data and using the ten types of transitions, the time to calculate the entire assignment for the 3-chlorothietane molecule was reduced from 50 minutes to 20 minutes.

2. 3-Thietanyl acetate

The spectrum of 3-thietanyl acetate was also analyzed to see what effect another group had on the NMR parameters. The spectrum, shown in Figs. 23 and 24 was taken with the modified HR-60 and the data digitized directly with an analog-to-digital converter. The details of the spectrum have been considerably altered by changes in the chemical shifts, although of course the general features are similar. The X part of the spectrum has shifted downfield by 26 cps and is also nearly first order, making the decomposition of this portion more difficult. (Double resonance experiments would be considerably less effective for this analysis since only the two end lines are resolved.) The total width of the A_2B_2 part of the spectrum is 34 cps, a reduction of eight cps from the chlorothietane due primarily to a reduction in the chemical shift between A and B.

The A_2B_2 region of this spectrum was more difficult to decompose than the chloride because there were several small peaks between large peaks in two of the large groups of twelve. Slightly more noise was also evident in the spectrum. Accordingly, DECOMP was used in conjunction with NMRIT (0) for the entire analysis.

Since chlorothietane had already been analyzed, the easiest method for analysis would have been to use the same coupling constants with the new values for the chemical shifts. This was not done in order to again test and see whether estimates made entirely from the spectrum were satisfactory to use with DECOMP in a straightforward manner. Initial estimates were made in the same manner as described for 3-chlorothietane and the small coupling constants were again set to small values. Although the calculated and experimental spectra did not match quite as

well as in the case of the chlorothietane, the calculated spectrum could still be matched fairly well with the lines from DECOMP. Of the 64 lines in the spectrum, 59 were well resolved by DECOMP. The decompositions of each of the separate groups is shown in Figs. 25 - 32. Three of the unresolved lines were separated from adjoining peaks by only 0.03 cps and the other two were small and between two large peaks. The 59 well determined lines were assigned to the transitions calculated by NMRIT (0) and after three trials gave a very good fit to the spectrum. In Fig. 33 and 34 the experimental and calculated spectra are compared. The upper curves show the experimental spectra and the line positions and intensities found by DECOMP. The lower curves show the lines calculated by NMRIT (20) and the calculated spectrum which is the sum of all these lines. The average difference between the 59 calculated and decomposed lines was 0.05 cps and the largest difference was 0.18 cps for one line.

It will be recalled that this part of the S & R method calls for assigning the experimental lines to the calculated transitions and these are then put into NMREN for a least squares fit to all the energy levels in the symmetry type. These energy levels are then used in the iterative part of the calculation to fit the best set of parameters. The assignments from the initial assignment will not be correct and some will have to be changed on the basis of the values obtained from the iteration. These new assignments are then used again by NMREN to get a new set of energy levels, and so on. Having almost all of the line positions and intensities from DECOMP greatly facilitates these assignments, yielding an assignment which fits more lines than can usually be seen in the spectrum.

This is shown by comparison of the above analysis with an analysis made by the conventional visual estimation of line positions. Figs. 35 and 36 show the results of an analysis of 3-theitanyl acetate which gave a very good fit according to the criteria generally used in the S & R method,[61] however, it can be seen that the second and fourth peaks in the X region of the spectrum do not have the same shape as the experimental spectrum in Fig.33. Since the positions of the four lines cannot be seen, it would be necessary to adjust these lines until the calculated spectrum was a closer match to the experimental spectrum. Such a procedure would require several additional NMREN and NMRIT (N) calculations, whereas the positions are known directly from DECOMP. Intensities are not as satisfactory, but they are not used in NMRIT (N) and do not affect the analysis.

B. Six Spin A_2B_4 Systems

In principle, the use of DECOMP and ASSIGN can be extended to systems of any complexity, however, there will be practical limitations because of the large amounts of computer time required to solve the more complex problems. DECOMP is at present limited to a maximum of 20 peaks so that the program will have to be redimensioned for use with larger groups of lines. ASSIGN will be limited by the amount of time one is willing to spend finding all possibilities for a given number of lines. It therefore becomes necessary to use all auxiliary methods available, such as NMRIT (O) and double resonance.

A six spin system of interest here is thietane (trimethylene sulfide), the parent compound of the two molecules analyzed above. Thietane has two geminal coupling constants and two long-range coupling constants, the cisoid and transoid. The two cisoid long-range coupling constants

cannot be distinguished as in the case of the substituted compound because ring inversion of theitane is rapid at room temperature and only the average values of the NMR parameters will be observed. Thus for the purposes of NMR analysis, the system can be considered as an A_2B_4 system with C_{2v} symmetry. (The A_4X_2 system, which allows some of the transitions to be calculated explicitly, has been treated by Lynden-Bell.[60])

An analysis of thietane has recently been carried out, using NMRIT and extensive double resonance experiments in the conventional way, by Mr. J.A. Ferretti.[46] It would be interesting to compare the results obtained and time required for this analysis with an analysis carried out using the methods described in this dissertation.

The method for building up the basic functions and algorithms for the general A_2B_4 system will be indicated below. The four B protons have a rectangular configuration and have D_{2h} symmetry. The basic symmetry functions for both the A_2 and B_4 protons are given in Table 15. Combining these sets of symmetry functions in the usual manner, we obtain the states, spins and symmetries for the basic product functions, according to the C_{2v} symmetry for the molecule, tabulated in Table 16. The basic symmetry functions, separated according to their symmetry group, are given in Tables 17 to 20. The corresponding energy level diagrams are given in Figs. 37 to 40. Again, only single spin transition are considered for making up the algorithms shown in Tables 21 to 24.

To indicate the magnitude of the decomposition problem, the spectrum of thietane is shown in Fig. 41. The system is highly mixed, with all 120 - 130 lines lying in a range of about 60 cps. The number of first order transitions is predicted to be 136, however, all of these may not have high enough intensity to be seen in the experimental spectrum.

The algorithms were made up without assuming any supplementary information, but in view of the complexity of the six-spin problems, the use of all the various techniques discussed in this dissertation would facilitate the analysis of these systems.

V. CONCLUSIONS

A. Use of Computer Techniques for NMR Spectral Analysis

Two computer methods have been described which are believed to substantially aid in the analysis of complex NMR spectra. The first of these, DECOMP, determines the line positions of unresolved lines nearly as accurately as resolved lines have been located in the past. Due to instrumental limitations, the intensities of unresolved lines are not determined as accurately but are good enough to assist in making assignments of lines unresolved in the experimental spectrum. With modest improvements in instrumentation, it appears feasable to improve this situation so that all the experimental lines can be uniquely determined from the experimental spectrum.

In the cases where all the lines are known accurately, the second method, ASSIGN, will provide the ideal situation of finding all possible solutions to the problem directly from the experimental data without any prior knowledge about the parameters to be determined. This is probably feasable at the present time with almost all three and four spin systems. For the more complicated cases of five or more spins, the direct approach may still be possible if the spectrum has several peaks well enough resolved to permit the use of double resonance and the instrumentation is available.

The most practical method at present is to use DECOMP and ASSIGN in conjunction with NMRIT and NMREN if possible, because computer time is inexpensive compared to experimental time. The transitions for a five or six spin system can be calculated as less than 0.5 minutes so that a number of parameters can be tried at little cost. Having a fair approximation to the experimental spectrum, the lines obtained with

DECOMP can facilitate obtaining the correct energy levels for the iteration. With the greater number of lines from DECOMP the calculation of the energy levels is more constrained than in the usual case where a number of lines must be left out. Thus inconsistencies are shown up more readily and can be corrected earlier in the analysis. After a few refinements in the parameters the transitions may be well enough localized, in many cases, to allow the use of ASSIGN. This will allos the determination of all the sets of energy levels.

Although the additional methods add considerable complexity to the analysis, their use in the above cases demonstrates that time is saved and a more objective and complete analysis results from their use. Computers are continually becoming more available and less expensive to use while experimental apparatus becomes more complex. It therefore behooves one to continually consider ways to use computers to maximize the information obtained from these complex experiments.

B. Coupling Constants in Four-Membered Rings

The complete analysis of the above two substituted thietanes provides an opportunity to compare the effects of minor structural changes on the coupling constants. Unfortunately, the exact structure of 3-chlorothietane is not known and the discussion[48] will invoke extrapolation* from chlorocyclobutane whose structure has been determined exactly.[21] Chlorocyclobutane is puckered in its ground vibrational state within the equilibrium angle of about 20°. The amount of puckering in a ring can be considered to arise from two opposing forces. One is ring strain which tends to keep the ring planar. The other is a tendency

* This appears to be a valid assumption since it has been pointed out by Prof. W. D. Gwinn[62] that the equilibrium structure for cyclobutane[63] is very close to that recently obtained by Dr. D. O. Harris[64] for trimethylene sulfide.

to pucker arising from the preferred staggered configuration of the hydrogen atoms or other substituted atoms on the adjacent ring carbon atoms. In 3-chlorothietane both of these forces are less than in chlorocyclobutane. The ring sulfur atom decreases ring strain allowing more puckering, but the loss of one methylene group decreases the tendency toward the staggered configuration. Since we do not know the relative sizes of these effects we have assumed the puckering is roughly the same in the two molecules for the subsequent calculations.

It is impossible to say whether the quasi-axial or the quasi-equatorial protons account for the large cross ring coupling from the present analysis. With the present data it is only possible to compare the results with current theories.

The vicinal coupling constants (J_{13} and J_{23}) are similar to those found in other four-membered compounds[48-50] and are in agreement with the usual correlations with dihedral angles, substitution, and bond lengths. The geminal coupling constant, however, is more positive than those found in other four-membered ring molecules.[48 - 51] The previous values ranged from -10 to -17 cps and were found in substituted cyclobutanes. The present values were obtained for substituted thietanes and are in agreement with the trend predicted by the recent molecular orbital treatment by Pople and Bothner-By.[12]

Of greatest interest in these molecules are the long-range coupling constants across the ring. One of the cisoid coupling constants is especially unusual in that it is unexpectedly large and positive, 3.1 cps in the chloride and 2.5 cps in the acetate. The other cisoid and the transoid coupling constants, -0.48 and -0.75 cps respectively, are more nearly the usual sign and magnitude and nearly identical for the two molecules.

The bulk of empirical evidence indicates that the configuration in which both protons and all of the connecting bonds are nearly coplanar, allows an observable coupling constant across four saturated bonds. This would indicate that the quasi-equatorial protons account for the large coupling, however, exceptions to this rule have been reported.[13,52]

Perhaps the best correlations between theory and experimental date for vicinal coupling constants has been made by Karplus.[11] Again using the data for chlorocyclobutane, the dihedral angles between H_3 and the equitorial protons is 28° and the dihedral angle with the axial proton is 155°. Karplus' correlations between the dihedral angle and vicinal coupling constant, predice J_{equi} = 5-6 cps and J_{3ax} = 7 cps. This would indicate that protons 1 and 2, which are coupled by 3 cps, are the equitorial protons.

As discussed above, Barfield[18] has made some theoretical calculations of long range coupling constants across four saturated bonds. The calculations follow the method of Karplus, and Barfield has given a diagram of long-range coupling constants as a function of the angle of the C-H bond with the plane of the three C atoms. Again using the data for chlorocyclobutane, the appropriate angles were calculated and the contributions to the coupling due to these angles were taken from Fig.2 in Barfield's paper. These calculated contributions are shown in Table 14. The calculations predict J_{12} to be the largest and positive while J_{45} is predicted to be small and negative. The transoid constant, $J_{15} = J_{24}$, is predicted to be small and positive. Only the transoid coupling fails to agree qualitatively with Barfield's theory.

As Barfield pointed out in his paper, many simplifying assumptions are made in his calculations. For example, the closure approximation, perfect sp^3 carbon hybrid orbitals, no hetero atoms in the coupling path

and bond lengths equal to those in ethane. Furthermore, the angular calculations are based only on the "indirect" (through bond) contribution to the coupling constants. Any "direct" (through space) contribution has been neglected. Using all these approximations, it is notable that the above degree of agreement was achieved. This limited agreement with theory is encouraging and with the improved methods for analysis, a number of molecules in this and similar series can be easily analyzed, resulting either in verification or in modification of the theoretical approach.

ACKNOWLEDGEMENTS

I wish to express my gratitude to Professor C. H. Sederholm for his enthusiastic encouragement and suggestions during the course of this work. It has been a pleasure working with him.

I would also like to express my gratitude to my wife who made many valuable suggestions while helping with the manuscript.

The work on the 3-chlorothietane was done in collaboration with Mr. W. D. Keller and I wish to thank him for this work as well as for reading this manuscript.

The directly digitized spectra of the 3-thietanyl acetate and thietane were obtained with the aid of Mr. R. Millikan and I would like to express my appreciation for this work.

I would also like to thank Mr. J. Ferretti for operating the spectrometer during the double resonance experiments.

Finally, I would like to thank Mrs. Pat Cookson, Mrs. Judy Purcell, and Mrs. Charlotte Machen for their efficient work in preparing the final manuscript.

This work was performed under the auspices of the United States Atomic Energy Commission.

Table 1.

Frequencies and Intensities Obtained by Decomposition of a Superposition of Peaks from Two Spectra

Decomposition with Digital Standard Peak				Decomposition with Lorentz Shape Peak			
Spectrum 1		Spectrum 2		Spectrum 1		Spectrum 2	
Frequency(cps)	Intensity	Frequency(cps)	Intensity	Frequency(cps)	Intensity	Frequency(cps)	Intensity
10.063	0.904	10.063	0.925	10.063	0.920	10.063	0.921
8.712	0.860	8.724	0.913	8.673	1.176	8.685	1.334
8.529	1.830	8.578	0.983	8.508	2.096	8.734	-0.142
8.434	2.291	8.478	2.180	8.503	1.789	8.536	1.860
8.349	0.828	8.394	1.656	8.328	0.511	8.420	2.851
7.889	2.356	7.889	2.361	7.873	2.581	7.891	2.377
7.150	1.536	7.153	1.624	7.123	1.380	7.149	1.531
6.815	1.006	6.791	1.407	6.778	1.534	6.784	1.479
6.683	1.456	6.663	1.046	6.618	1.329	6.642	1.083
6.368	1.779	6.356	1.749	6.293	1.661	6.348	1.680
5.935	0.512	5.914	0.575	5.833	0.537	5.884	0.539
5.695	0.643	5.662	0.580	5.648	0.486	5.676	0.487

Table 2.

Algorithm for ABC Case

Transition	Type	Energy Level Upper	Energy Level Lower	Frequency Check
1	1 (A)	1	2	
2	2 (B)	1	3	
3	3 (C)	-1	4	
4	3 (C)	2	6	
5	1 (A)	4	6	1
6	3 (C)	3	5	
7	2 (B)	4	5	1
8	1 (A)	5	8	
9	2 (B)	6	8	1
10	2 (B)	2	7	
11	1 (A)	3	7	1
12	3 (C)	7	-8	1
13	4 (D)	-4	-7	1
14	4 (D)	-3	-6	1
15	4 (D)	-2	-5	1

Energy Level	Sum of Intensities
1	3.
2	1.
3	1.
4	1.
5	-1.
6	-1.
7	-1.
8	-3.

Table 3. Basic Symmetry Functions for Four Nuclei A_2B_2

Energy Level	Function	Basic Symmetry Function
1	S_2	$\alpha\alpha\alpha\alpha$
2	$1S_1$	$\frac{1}{\sqrt{2}}(\alpha\beta\alpha\alpha + \beta\alpha\alpha\alpha)$
4	$2S_1$	$\frac{1}{\sqrt{2}}(\alpha\alpha\alpha\beta + \alpha\alpha\beta\alpha)$
11	$1S_o$	$\beta\beta\alpha\alpha$
6	$2S_o$	$\alpha\alpha\beta\beta$
8	$3S_o$	$\frac{1}{2}(\alpha\beta\alpha\beta - \alpha\beta\beta\alpha - \beta\alpha\alpha\beta + \beta\alpha\beta\alpha)$
9	$4S_o$	$\frac{1}{2}(\alpha\beta\alpha\beta + \alpha\beta\beta\alpha + \beta\alpha\alpha\beta + \beta\alpha\beta\alpha)$
12	$1S_{-1}$	$\frac{1}{\sqrt{2}}(\alpha\beta\beta\beta + \beta\alpha\beta\beta)$
14	$2S_{-1}$	$\frac{1}{\sqrt{2}}(\beta\beta\alpha\beta + \beta\beta\beta\alpha)$
16	S_{-2}	$\beta\beta\beta\beta$
3	$1a_1$	$\frac{1}{\sqrt{2}}(\alpha\beta\alpha\alpha - \beta\alpha\alpha\alpha)$
5	$2a_1$	$\frac{1}{\sqrt{2}}(\alpha\alpha\beta\alpha - \alpha\alpha\beta\alpha)$
7	$1a_o$	$\frac{1}{2}(\alpha\beta\alpha\beta - \alpha\beta\beta\alpha + \beta\alpha\alpha\beta - \beta\alpha\beta\alpha)$
10	$2a_o$	$\frac{1}{2}(\alpha\beta\alpha\beta + \alpha\beta\beta\alpha - \beta\alpha\alpha\beta - \beta\alpha\beta\alpha)$
13	$1a_{-1}$	$\frac{1}{\sqrt{2}}(\alpha\beta\beta\beta - \beta\alpha\beta\beta)$
15	$2a_{-1}$	$\frac{1}{\sqrt{2}}(\beta\beta\alpha\beta - \beta\beta\beta\alpha)$

Table 4. Algorithm for Four Spins A_2B_2 Using Two Transition Types; 1(A) and 2(B).

Transition		Energy Level		Frequency Check
No.	Type	Upper	Lower	
1	1	3	7	
2	1	-3	10	
3	1	7	15	
4	1	10	-15	1
5	2	7	13	
6	2	10	-13	1
7	-2	5	-7	
8	-2	-5	-10	1
9*	2	1	2	
10	1	-1	4	
11	1	2	8	
12	2	4	8	1
13	1	2	9	
14	2	4	9	1
15	2	8	12	
16	2	9	12	1
17	1	-8	14	
18	1	-9	14	1
19	1	12	16	
20	2	14	-16	1
21	2	-2	6	
22	1	-6	-12	1
23	1	-4	11	
24	2	-11	-14	1

* The algorithm may be used in two parts; lines 1 - 8 are the anitsymmetric transitions, lines 9 - 24 are symmetric transistion. Symmetric transition numbers would then begin with 1 rather than 9.

Table 5. Input Data for Double Resonance Experiment with ABC Case Showing Ranges of Nuclei with Common Energy Levels.

Line No.	Obs.Freq.	Obs. Int.	Lines with Common Energy Levels											
1	-10.600	0.016	3	3	5	5	6	6	8	8	9	9	15	15
2	-0.	0.319	4	4	5	5	9	9	13	13	14	14	-0	-0
3	3.960	0.231	1	1	4	4	5	5	11	11	12	12	15	15
4	11.020	0.062	2	2	3	3	9	9	11	11	12	12	-0	-0
5	14.990	0.940	1	1	2	2	3	3	13	13	14	14	15	15
6	15.930	0.243	1	1	8	8	9	9	10	10	11	11	13	13
7	19.890	2.618	8	8	10	10	12	12	14	14	15	15	-0	-0
8	21.780	3.330	1	1	6	6	7	7	9	9	12	12	14	14
9	25.590	2.589	1	1	2	2	4	4	6	6	8	8	-0	-0
10	25.740	0.180	6	6	7	7	11	11	13	13	15	15	-0	-0
11	30.490	0.655	3	3	4	4	6	6	10	10	12	12	13	13
12	36.340	0.205	3	3	4	4	7	7	8	8	11	11	14	14
13	41.520	0.281	2	2	5	5	6	6	10	10	11	11	14	14
14	47.370	0.083	2	2	5	5	7	7	8	8	12	12	13	13
15	52.220	0.202	1	1	3	3	5	5	7	7	10	10	-0	-0

Line	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
LX(I)	-0	-0	-0	-0	-0	-0	-0	-0	-0	-0	-0	-0	-0	-0	-0

Table 5. (Continued)

The range of nucleus 1 is 1 - 10

The range of nucleus 2 is 1 - 15

The range of nucleus 3 is 5 - 15

The range of nucleus 4 is 1 - 15

Uncertainty in frequency = 0.100, in intensity = 0.500

Values for intensity sum rules

Energy Level	1	2	3	4	5	6	7	8
Sum of intensities	3.00	1.00	1.00	1.00	-1.00	-1.00	-1.00	-3.00

Table 6

3-Chlorothietane: Average DECOMP Values of Two Spectra

Line	Frequency (cps)	Intensity
1	-326.430	0.734
2	-318.750	0.757
3	-318.497	0.919
4	-317.880	0.843
5	-316.728	0.915
6	-310.856	0.951
7	-309.776	0.683
8	-309.619	1.213
9	-309.445	1.303
10	-309.317	0.605
11	-308.309	1.117
12	-302.091	1.031
13	-301.383	1.273
14	-300.909	1.141
15	-299.969	1.243
16	-292.650	1.272
17	-231.010	0.387
18	-230.754	0.405
19	-229.907	1.481
20	-229.225	1.530
21	-228.045	1.117
22	-227.411	1.089
23	-222.446	1.629
24	-222.065	1.585
25	-221.548	0.331
26	-221.342	0.437
27	-220.645	1.648
28	-220.532	1.906
29	-220.425	1.748
30	-220.255	2.237
31	-219.413	1.199
32	-219.357	0.752
33	-218.926	1.268
34	-218.545	1.210
35	-212.936	1.314
36	-212.813	1.485
37	-211.737	2.524
38	-211.042	1.684
39	-210.945	1.919
40	-209.837	1.038
41	-207.803	0.982
42	-207.643	1.209
43	-206.710	2.665

Table 6 (Continued)

Line	Frequency (cps)	Intensity
44	-205.457	2.961
45	-204.885	1.735
46	-204.804	1.929
47	-200.639	0.883
48	-199.225	0.936
49	-199.054	1.854
50	-198.974	2.102
51	-198.858	0.961
52	-198.370	2.377
53	-197.611	1.492
54	-197.252	1.431
55	-197.080	1.309
56	-196.740	1.632
57	-196.255	0.523
58	-196.073	0.537
59	-191.792	0.947
60	-190.532	0.642
61	-189.610	1.094
62	-189.305	1.080
63	-188.730	0.412
64	-187.952	0.384

Table 7. Basic Symmetry Functions for Five Nuclei A_2B_2X

Energy Level	Function	Basic Symmetry Function
1	$S_{5/2}$	$\alpha\alpha\alpha\alpha\alpha$
2	$1S_{3/2}$	$\alpha\alpha\alpha\alpha\beta$
4	$2S_{3/2}$	$\frac{1}{\sqrt{2}}(\alpha\beta\alpha\alpha\alpha + \beta\alpha\alpha\alpha\alpha)$
5	$3S_{3/2}$	$\frac{1}{\sqrt{2}}(\alpha\alpha\alpha\beta\alpha + \alpha\alpha\beta\alpha\alpha)$
7	$1S_{1/2}$	$\beta\beta\alpha\alpha\alpha$
9	$2S_{1/2}$	$\alpha\alpha\beta\beta\alpha$
11	$3S_{1/2}$	$1/2(\alpha\beta\alpha\beta\alpha - \alpha\beta\beta\alpha\alpha - \beta\alpha\alpha\beta\alpha + \beta\alpha\beta\alpha\alpha)$
12	$4S_{1/2}$	$1/2(\alpha\beta\alpha\beta\alpha + \alpha\beta\beta\alpha\alpha + \beta\alpha\alpha\beta\alpha + \beta\alpha\beta\alpha\alpha)$
14	$5S_{1/2}$	$\frac{1}{\sqrt{2}}(\alpha\beta\alpha\alpha\beta + \beta\alpha\alpha\alpha\beta)$
16	$6S_{1/2}$	$\frac{1}{\sqrt{2}}(\alpha\alpha\alpha\beta\beta + \alpha\alpha\beta\alpha\beta)$
17	$1S_{-1/2}$	$\beta\beta\alpha\alpha\beta$
18	$2S_{-1/2}$	$\alpha\alpha\beta\beta\beta$
21	$3S_{-1/2}$	$1/2(\alpha\beta\alpha\beta\beta - \alpha\beta\beta\alpha\beta - \beta\alpha\alpha\beta\beta + \beta\alpha\beta\alpha\beta)$
22	$4S_{-1/2}$	$1/2(\alpha\beta\alpha\beta\beta + \alpha\beta\beta\alpha\beta + \beta\alpha\alpha\beta\beta + \beta\alpha\beta\alpha\beta)$
23	$5S_{-1/2}$	$\frac{1}{\sqrt{2}}(\alpha\beta\beta\beta\alpha + \beta\alpha\beta\beta\alpha)$
26	$6S_{-1/2}$	$\frac{1}{\sqrt{2}}(\beta\beta\alpha\beta\alpha + \beta\beta\beta\alpha\alpha)$
27	$1S_{-3/2}$	$\beta\beta\beta\beta\alpha$

Table 7. (Continued)

Energy Level	Function	Basic Symmetry Function
29	$^{2}S_{-3/2}$	$\frac{1}{\sqrt{2}}(\alpha\beta\beta\beta\beta + \beta\alpha\beta\beta\beta)$
31	$^{3}S_{-3/2}$	$\frac{1}{\sqrt{2}}(\beta\beta\alpha\beta\beta + \beta\beta\beta\alpha\beta)$
32	$^{S}_{-5/2}$	$\beta\beta\beta\beta\beta$
3	$^{1a}_{3/2}$	$\frac{1}{\sqrt{2}}(\alpha\beta\alpha\alpha\alpha - \beta\alpha\alpha\alpha\alpha)$
6	$^{2a}_{3/2}$	$\frac{1}{\sqrt{2}}(\alpha\alpha\alpha\beta\alpha - \alpha\alpha\beta\alpha\alpha)$
8	$^{1a}_{1/2}$	$\frac{1}{\sqrt{2}}(\alpha\beta\alpha\alpha\beta - \beta\alpha\alpha\alpha\beta)$
10	$^{2a}_{1/2}$	$\frac{1}{\sqrt{2}}(\alpha\alpha\alpha\beta\beta - \alpha\alpha\beta\alpha\beta)$
13	$^{3a}_{1/2}$	$1/2(\alpha\beta\alpha\beta\alpha - \alpha\beta\beta\alpha\alpha + \beta\alpha\alpha\beta\alpha - \beta\alpha\beta\alpha\alpha)$
15	$^{4a}_{1/2}$	$1/2(\alpha\beta\alpha\beta\alpha + \alpha\beta\beta\alpha\alpha - \beta\alpha\alpha\beta\alpha - \beta\alpha\beta\alpha\alpha)$
19	$^{1a}_{-1/2}$	$1/2(\alpha\beta\alpha\beta\beta - \alpha\beta\beta\alpha\beta + \beta\alpha\alpha\beta\beta - \beta\alpha\beta\alpha\beta)$
20	$^{2a}_{-1/2}$	$1/2(\alpha\beta\alpha\beta\beta + \alpha\beta\beta\alpha\beta - \beta\alpha\alpha\beta\beta - \beta\alpha\beta\alpha\beta)$
24	$^{3a}_{-1/2}$	$\frac{1}{\sqrt{2}}(\alpha\beta\beta\beta\alpha - \beta\alpha\beta\beta\alpha)$
25	$^{4a}_{-1/2}$	$\frac{1}{\sqrt{2}}(\beta\beta\alpha\beta\alpha - \beta\beta\beta\alpha\alpha)$
28	$^{1a}_{-3/2}$	$\frac{1}{\sqrt{2}}(\alpha\beta\beta\beta\beta - \beta\alpha\beta\beta\beta)$
30	$^{2a}_{-3/2}$	$\frac{1}{\sqrt{2}}(\beta\beta\alpha\beta\beta - \beta\beta\beta\alpha\beta)$

Table 8. Algorithm for 3-Chlorothietane Using Three Types of Transitions

a) Symmetric Transitions

Transition No.	Type	Energy Level Upper	Lower	Frequency Check	Transition No.	Type	Energy Level Upper	Lower	Frequency Check
1	1	1	4	0	21	1	18	27	1
2	3	1	2	0	22	2	23	31	0
3	2	-1	5	0	23	1	26	31	1
4	3	4	7	0	24	2	20	30	0
5	1	2	7	1	25	2	18	30	1
6	2	-2	9	0	26	1	-7	17	0
7	3	5	9	1	27	2	17	27	1
8	2	4	12	0	28	2	-9	22	0
9	1	5	12	1	29	1	22	30	1
10	2	4	14	0	30	1	-4	11	0
11	1	5	14	1	31	2	11	23	1
12	1	12	23	0	32	2	-5	16	0
13	1	14	23	1	33	1	16	26	1
14	2	7	20	0	34	2	27	32	0
15	1	9	20	1	35	3	-31	32	1
16	2	7	18	0	36	1	30	-32	1
17	1	9	18	1	37	3	-23	-27	1
18	2	12	26	0	38	3	-26	-30	1
19	2	14	26	1	39	3	11	17	1
20	1	20	27	0	40	3	16	22	1

Table 8. Algorithm for 3-Chlorothietane Using Three Types of Transitions

b) Antisymmetric Transitions

Transition No.	Type	Energy Level Upper	Lower	Frequency Check	Transition No.	Type	Energy Level Upper	Lower	Frequency Check
1	2	6	13	-0	12	3	-13	19	1
2	2	6	15	-0	13	2	10	19	1
3	3	-6	10	-0	14	1	8	21	-0
4	2	13	24	-0	15	3	-15	21	1
5	2	15	24	1	16	2	-10	21	1
6	-1	3	13	-0	17	2	19	28	-0
7	-1	3	15	1	18	2	21	28	1
8	3	-3	8	-0	19	1	-19	29	-0
9	1	13	25	-0	20	1	-21	29	1
10	1	15	25	1	21	3	-24	-28	1
11	1	15	25	1	22	3	-25	-29	1

Table 9. Algorithm for 3-Chlorothietane Using Ten Types of Transitions

a) Symmetric Transitions

Transition No.	Type	Energy Level Upper	Energy Level Lower	Frequency Check	Transition No.	Type	Energy Level Upper	Energy Level Lower	Frequency Check
1	7	1	4	0	21	7	18	27	1
2	5	1	2	0	22	10	23	31	0
3	9	-1	5	0	23	8	26	31	1
4	4	4	7	0	24	8	20	30	0
5	6	2	7	1	25	9	18	30	1
6	8	-2	9	0	26	6	-7	17	0
7	4	5	9	1	27	9	17	27	1
8	10	4	12	0	28	8	-9	22	0
9	8	5	12	1	29	7	22	30	1
10	9	4	14	0	30	7	-4	11	0
11	7	5	14	1	31	10	11	23	1
12	7	12	23	0	32	9	05	16	0
13	8	14	23	1	33	8	16	26	1
14	9	7	20	0	34	9	27	32	0
15	7	9	20	1	35	1	-31	32	1
16	8	7	18	0	36	7	30	-32	1
17	6	9	18	1	37	2	-23	-27	1
18	10	12	26	0	38	2	-26	-30	1
19	9	14	26	1	39	3	11	17	1
20	6	20	27	0	40	3	16	22	1

Table 9. Algorithm for 3-Chlorothietane Using Ten Types of Transitions

b) Antisymmetric Transitions

Transition No.	Type	Energy Level Upper	Energy Level Lower	Frequency Check	Transition No.	Type	Energy Level Upper	Energy Level Lower	Frequency Check
1	7	6	13	-0	12	3	-13	19	1
2	8	6	15	-0	13	6	10	19	1
3	4	-6	10	-0	14	9	8	21	-0
4	8	13	24	-0	15	3	-15	21	1
5	7	15	24	1	16	7	-10	21	1
6	-9	3	13	-0	17	7	19	28	-0
7	-10	3	15	1	18	6	21	28	1
8	4	-3	8	-0	19	9	-19	29	-0
9	10	13	25	-0	20	8	-21	29	1
10	9	15	25	1	21	2	-24	-28	1
11	8	8	19	-0	22	2	-25	-29	1

Table 10

Energy Levels and Parameters of All Possible Assignments of 3-Chlorothietane

	Assignment 1	Assignment 2	Assignment 3
No.	Energy Level (cps)	Energy Level (cps)	Energy Level (cps)
1	-568.782	-569.932	-570.037
2	-276.137	-277.401	-277.672
3	-347.827	-346.567	-347.012
4	-348.242	-349.407	-349.039
5	-370.415	-371.411	-371.247
6	-372.639	-371.542	-371.857
7	-46.185	-45.162	-45.588
8	-46.485	-47.540	-46.899
9	-69.478	-70.764	-70.332
10	-72.665	-71.441	-71.867
11	-127.777	-128.890	-128.509
12	-151.029	-149.844	-150.286
13	-151.078	-150.116	-149.974
14	-159.472	-158.488	-158.290
15	-159.842	-158.619	-159.088
16	-171.443	-172.618	-172.050
17	183.055	181.797	182.405
18	158.632	159.601	159.172
19	158.350	159.702	159.392
20	149.873	151.337	151.623
21	149.780	150.975	150.572
22	136.898	135.738	136.371
23	61.896	60.761	61.041
24	58.733	59.960	59.514
25	40.779	41.985	41.540
26	39.566	38.329	38.757
27	380.656	379.349	379.793
28	377.232	378.456	378.030
29	357.555	358.715	358.289
30	357.494	356.362	356.729
31	251.267	250.095	250.232
32	577.728	576.581	576.284

Table 10 (Continued)

No.	Assignment 1 Chemical Shift (cps)*	Assignment 2 Chemical Shift (cps)*	Assignment 3 Chemical Shift (cps)*
1	-199.036	-199.040	-199.123
2	-199.036	-199.040	-199.123
3	-308.780	-308.777	-308.784
4	-219.822	-219.826	-219.753
5	-219.822	-219.826	-219.753

No.	Coupling Constant (cps)	Coupling Constant (cps)	Coupling Constant (cps)
12	3.116	0.606	1.119
13	7.670	7.728	7.613
14	-8.633	-8.633	-8.931
15	-0.751	-0.587	-1.051
23	7.670	7.728	7.613
24	-0.751	-0.587	-1.051
25	-8.633	-8.633	-8.931
34	9.343	9.341	9.350
35	9.343	9.341	9.350
45	-0.482	-3.006	-2.585
Sum of Squares of Residuals	.0096	.2023	1.5064

* Chemical shifts are measured at 60 mc relative to TMS.

Table 11. 3-Chlorothietane; Lines with Common Energy Levels, Obtained with Double Resonance Experiments.

Line	Lines with common energy levels					
1	27-30	(37-40)*	54-56	(61-64)		
4	27-30	(29-32)	37-37	(38-39)	41-44	(60-62)
5	41-42	(47-47)	59-59			
6	20-20	(27-30)	(53-55)	59-62		
11	(27-30)	38-39	43-44	(48-52)		
12	19-20	(20-22)	43-44	(45-46)	53-56	
15	(17-18)	(23-24)	(35-36)	52-55		
16	(17-22)	27-30	(42-46)	52-55		
59	(5-5)	(25-26)	40-40	47-48	(58-58)	
			b			
1	27-30	(37-40)	54-56	(61-64)		
16	(17-22)	27-30	(42-46)	52-52		

* Parentheses indicate a peak, i.e., $\Delta M_z = 2$.

Table 12. 3-Chlorothietane: Algorithm Used with Double Resonance Information From Lines 1 and 16.

Transition No.	Transition Type	Energy Level Upper	Energy Level Lower	Frequency Check	Transition No.	Transition Type	Energy Level Upper	Energy Level Lower	Frequency Check
1	5	1	2	-0	33	9	-17	-27	1
2	11	1	5	-0	34	3	12	-18	1
3	12	-1	4	-0	35	8	12	23	1
4	13	2	7	-0	36	10	-12	26	1
5	4	4	7	1	37	7	14	-23	1
6	14	-2	9	-0	38	3	14	-20	1
7	4	5	9	1	39	9	-14	-26	1
8	9	7	20	-0	40	3	-16	22	-0
9	7	9	20	1	41	8	-9	22	1
10	8	7	18	-0	42	7	-22	-30	1
11	6	9	18	1	43	4	3	8	-0
12	7	18	27	-0	44	10	3	15	-0
13	6	20	27	1	45	9	-3	13	-0
14	9	18	30	-0	46	3	15	21	-0
15	8	20	30	1	47	9	8	21	1
16	15	27	32	-0	48	8	-8	19	-0
17	16	30	32	1	49	3	13	19	1
18	-1	31	-32	-0	50	-7	6	13	-0
19	-17	23	31	-0	51	-8	6	15	1
20	-2	23	27	1	52	4	-6	10	-0
21	-18	26	31	-0	53	6	10	19	1
22	-2	26	30	1	54	7	-10	21	1
23	7	4	11	-0	55	7	19	28	-0
24	10	11	23	1	56	6	21	28	1
25	9	4	12	-0	57	-2	24	-28	-0
26	7	5	12	1	58	8	13	24	1
27	10	-4	14	-0	59	7	15	-24	1
28	8	5	14	1	60	10	-13	25	-0
29	9	-5	16	-0	61	9	-15	25	1
30	8	16	26	1	62	2	-25	29	-0
31	3	-11	17	-0	63	9	-19	29	1
32	6	-7	17	1	64	8	-21	-29	1

Table 13. 3-Thietanyl Acetate: Line Positions and Intensities Obtained by DECOMP

Line No.	Obs. Freq.	Obs. Int.	Line No.	Obs. Freq.	Obs. Int.
1	-350.690	0.903	31	-205.689	1.636
2	-343.028	1.333	32	-202.969	1.742
3	-342.877	0.991	33	-202.632	1.591
4	-342.720	0.519	34	-202.169	3.443
5	-342.345	0.908	35	-201.892	2.764
6	-335.059	1.058	36	-200.960	1.837
7	-335.057	0.896	37	-200.772	1.604
8	-335.037	1.460	38	-199.089	1.377
9	-334.967	0.744	39	-199.808	3.145
10	-334.955	1.035	40	-199.011	1.781
11	-334.849	0.976	41	-198.605	3.791
12	-327.372	1.078	42	-198.722	0.491
13	-327.274	0.499	43	-197.722	1.249
14	-327.066	1.644	44	-195.462	1.813
15	-326.563	1.035	45	-194.384	3.484
16	-319.170	0.737	46	-194.298	1.943
17	-217.090	0.487	47	-194.033	2.611
18	-216.600	0.712	48	-193.865	0.495
19	-215.752	0.951	49	-193.331	0.615
20	-215.394	0.386	50	-193.167	1.740
21	-214.505	0.531	51	-192.964	0.659
22	-208.981	0.385	52	-192.786	1.492
23	-208.699	0.368	53	-192.198	0.841
24	-208.505	0.725	54	-191.801	0.188
25	-208.303	1.954	55	-191.721	0.100
26	-207.860	2.053	56	-186.482	0.500
27	-206.962	2.671	57	-184.975	0.942
28	-206.827	1.223	58	-184.292	0.237
29	-206.657	3.133	59	-183.800	0.375
30	-206.199	1.677			

Table 14

Theoretical Contributions to Long-Range Coupling Constants

Path	Dihedral Angle*		$^4I_{J_{HH'}}$ (cps)
	ϕ_1'	ϕ_3'	
$H_1C_\alpha C_\beta C_\alpha' H_2$	140°	220°	+0.7
$H_1C_\alpha SC_\alpha' H_2$	230°	130°	+0.5
$H_4C_\alpha C_\beta C_\alpha' H_5$	285°	75°	-0.2
$H_4C_\alpha SC_\alpha' H_5$	100°	260°	-0.2
$H_1C_\alpha C_\beta C_\alpha' H_5$	140°	75°	+0.3
$H_1C_\alpha SC_\alpha' H_5$	230°	260°	+0.2
$H_4C_\alpha C_\beta C_\alpha' H_2$	285°	220°	+0.3
$H_4C_\alpha SC_\alpha' H_2$	100°	130°	+0.2

* ϕ_1' is the dihedral angle measured clockwise from the C_α-C_β-C_α' (C_α-S-C_α') plane to the C_α-H_1(H_4) bond. Similarly ϕ_3' is measured clockwise from the C_α-C_β-C_α' (C_α-S-C_α') plane to the C_α'-H_2(H_5) bond.

Table 15. Basic Functions for Six Nuclei A_2B_4

Spin	Symmetry	Function
		A_2
1	A_1	$\alpha\alpha$
0	A_1	$1/\sqrt{2}\ (\alpha\beta + \beta\alpha)$
	B_2	$1/\sqrt{2}\ (\alpha\beta - \beta\alpha)$
-1	A_1	$\beta\beta$
		B_4
2	A_1	$\alpha\alpha\alpha\alpha$
1	A_1	$\frac{1}{2}(\beta\alpha\alpha\alpha + \alpha\beta\alpha\alpha + \alpha\alpha\beta\alpha + \alpha\alpha\alpha\beta)$
	A_2	$\frac{1}{2}(\beta\alpha\alpha\alpha - \alpha\beta\alpha\alpha + \alpha\alpha\beta\alpha - \alpha\alpha\alpha\beta)$
	B_1	$\frac{1}{2}(\beta\alpha\alpha\alpha + \alpha\beta\alpha\alpha - \alpha\alpha\beta\alpha - \alpha\alpha\alpha\beta)$
	B_2	$\frac{1}{2}(\beta\alpha\alpha\alpha - \alpha\beta\alpha\alpha - \alpha\alpha\beta\alpha + \alpha\alpha\alpha\beta)$
0	A_1^1	$1/\sqrt{2}(\alpha\beta\beta\alpha + \beta\alpha\alpha\beta)$
	A_1^2	$1/\sqrt{2}(\beta\beta\alpha\alpha + \alpha\alpha\beta\beta)$
	A_1^3	$1/\sqrt{2}(\beta\alpha\beta\alpha + \alpha\beta\alpha\beta)$
	A_2	$1/\sqrt{2}(\beta\alpha\beta\alpha - \alpha\beta\alpha\beta)$
	B_1	$1/\sqrt{2}(\beta\beta\alpha\alpha - \alpha\alpha\beta\beta)$
	B_2	$1/\sqrt{2}(\alpha\beta\beta\alpha - \beta\alpha\alpha\beta)$
-1	A_1	$\frac{1}{2}(\alpha\beta\beta\beta + \beta\alpha\beta\beta + \beta\beta\alpha\beta + \beta\beta\beta\alpha)$
	A_2	$\frac{1}{2}(\alpha\beta\beta\beta - \beta\alpha\beta\beta + \beta\beta\alpha\beta - \beta\beta\beta\alpha)$
	B_1	$\frac{1}{2}(\alpha\beta\beta\beta + \beta\alpha\beta\beta - \beta\beta\alpha\beta - \beta\beta\beta\alpha)$
	B_2	$\frac{1}{2}(\alpha\beta\beta\beta - \beta\alpha\beta\beta\ \alpha\ \beta\beta\alpha\beta + \beta\beta\beta\alpha)$
-2	A_1	$\beta\beta\beta\beta$

Table 16. Symmetries and Spins of a System of Six Nuclei A_2B_4

Energy Level	Spin B, A	Symmetry B A	Energy Level	Spin B, A	Symmetry B A
1	1,2	$A_1 \times A_1 = A_1$	24		$A_1 \times A_2 = A_2$
2	1,1	$A_1 \times A_1 = A_1$	25		$A_1 \times B_1 = B_1$
3		$A_1 \times A_2 = A_2$	26		$A_1 \times B_2 = B_2$
4		$A_1 \times B_1 = B_1$	27	1,-1	$A_1 \times A_1 = A_1$
5		$A_1 \times B_2 = B_2$	28		$A_1 \times A_2 = A_2$
6	0,2	$A_1 \times A_1 = A_1$	29		$A_1 \times B_1 = B_1$
7		$B_2 \times A_1 = B_2$	30		$A_1 \times B_2 = B_2$
8	0,1	$A_1 \times A_1 = A_1$	31	0,0	$A_1 \times A_1^1 = A_1$
9		$B_2 \times B_2 = A_1$	32		$A_1 \times A_1^2 = A_1$
10		$A_1 \times A_2 = A_2$	33	0,0	$A_1 \times A_1^3 = A_1$
11		$B_2 \times B_1 = A_2$	34		$B_2 \times B_2 = A_1$
12		$A_1 \times B_1 = B_1$	35		$A_1 \times A_2 = A_2$
13		$B_2 \times A_2 = B_1$	36		$B_2 \times B_1 = A_2$
14		$A_2 \times B_2 = B_2$	37		$A_1 \times B_1 = B_1$
15		$B_2 \times A_1 = B_2$	38		$B_2 \times A_2 = B_1$
16	1,0	$A_1 \times A_1^1 = A_1$	39		$A_1 \times B_2 = B_2$
17		$A_1 \times A_1^2 = A_1$	40		$B_2 \times A_1^1 = B_2$
18		$A_1 \times A_1^3 = A_1$	41		$B_2 \times A_1^2 = B_2$
19		$A_1 \times A_2 = A_2$	42		$B_2 \times A_1^3 = B_2$
20		$A_1 \times B_1 = B_1$	43	0,-1	$A_1 \times A_1 = A_1$
21		$A_1 \times B_2 = B_2$	44		$B_2 \times B_2 = A_1$
22	-1,2	$A_1 \times A_1 = A_1$	45		$A_1 \times A_2 = A_2$
23	-1,1	$A_1 \times A_1 = A_1$	46		$B_2 \times B_1 = A_2$

Table 16. (Continued)

Energy Level	Spin B, A	Symmetry B A	Energy Level	Spin B, A	Symmetry B A
47		$A_1 \times B_1 = B_1$	56		$A_1 \times B_2 = B_2$
48		$B_2 \times A_2 = B_1$	57	1,-2	$A_1 \times A_1 = A_1$
49		$B_2 \times A_1 = B_2$	58	-1,-1	$A_1 \times A_1 = A_1$
50		$A_1 \times B_2 = B_2$	59		$A_1 \times A_2 = A_2$
51	-1,0	$A_1 \times A_1^1 = A_1$	60		$A_1 \times B_1 = B_1$
52		$A_1 \times A_1^2 = A_1$	61		$A_1 \times B_2 = B_2$
53		$A_1 \times A_1^3 = A_1$	62	0,-2	$A_1 \times A_1 = A_1$
54		$A_1 \times A_2 = A_2$	63		$B_2 \times A_1 = B_2$
55		$A_1 \times B_1 = B_1$	64	-1,-2	$A_1 \times A_1 = A_1$

Table 17. A_1 Basic Symmetry Functions for Six Nuclei A_2B_4

Energy Level	Spin A B	Basic Symmetry Function
1	1,2	$(\alpha\alpha\alpha\alpha\alpha\alpha)$
2	1,1	$\frac{1}{2}(\alpha\alpha\beta\alpha\alpha\alpha+\alpha\alpha\alpha\beta\alpha\alpha+\alpha\alpha\alpha\alpha\beta\alpha+\alpha\alpha\alpha\alpha\alpha\beta)$
6	0,2	$1/\sqrt{2}(\alpha\beta\alpha\alpha\alpha\alpha+\beta\alpha\alpha\alpha\alpha\alpha)$
8	0,1	$1/2\sqrt{2}(\alpha\beta\beta\alpha\alpha\alpha+\alpha\beta\alpha\beta\alpha\alpha+\alpha\beta\alpha\alpha\beta\alpha+\alpha\beta\alpha\alpha\alpha\beta+\beta\alpha\beta\alpha\alpha\alpha+\beta\alpha\alpha\beta\alpha\alpha\alpha+\beta\alpha\alpha\alpha\beta\alpha+\beta\alpha\alpha\alpha\alpha\beta)$
9	0,1	$1/2\sqrt{2}(\alpha\beta\beta\alpha\alpha\alpha-\alpha\beta\alpha\beta\alpha\alpha-\alpha\beta\alpha\alpha\beta\alpha+\alpha\beta\alpha\alpha\alpha\beta-\beta\alpha\beta\alpha\alpha\alpha+\beta\alpha\alpha\beta\alpha\alpha+\beta\alpha\alpha\alpha\beta\alpha-\beta\alpha\alpha\alpha\alpha\beta)$
16	1,0	$1/\sqrt{2}(\alpha\alpha\alpha\beta\beta\alpha+\alpha\alpha\beta\alpha\alpha\beta)$
17	1,0	$1/\sqrt{2}(\alpha\alpha\beta\beta\alpha\alpha+\alpha\alpha\alpha\alpha\beta\beta)$
18	1,0	$1/\sqrt{2}(\alpha\alpha\beta\alpha\beta\alpha+\alpha\alpha\alpha\beta\alpha\beta)$
22	-1,2	$(\beta\beta\alpha\alpha\alpha\alpha)$
23	-1,1	$\frac{1}{2}(\beta\beta\beta\alpha\alpha\alpha+\beta\beta\alpha\beta\alpha\alpha+\beta\beta\alpha\alpha\beta\alpha+\beta\beta\alpha\alpha\alpha\beta)$
27	1,-1	$\frac{1}{2}(\alpha\alpha\alpha\beta\beta\beta+\alpha\alpha\beta\alpha\beta\beta+\alpha\alpha\beta\beta\alpha\beta+\alpha\alpha\beta\beta\beta\beta)$
31	0,0	$\frac{1}{2}(\alpha\beta\alpha\beta\beta\alpha+\alpha\beta\beta\alpha\alpha\beta+\beta\alpha\alpha\beta\beta\alpha+\beta\alpha\beta\alpha\alpha\beta)$
32	0,0	$\frac{1}{2}(\alpha\beta\beta\beta\alpha\alpha+\alpha\beta\alpha\alpha\beta\beta+\beta\alpha\beta\beta\alpha\alpha+\beta\alpha\alpha\alpha\beta\beta)$
33	0,0	$\frac{1}{2}(\alpha\beta\beta\alpha\beta\alpha+\alpha\beta\alpha\beta\alpha\beta+\beta\alpha\beta\alpha\beta\alpha+\beta\alpha\alpha\beta\alpha\beta)$
34	0,0	$\frac{1}{2}(\alpha\beta\alpha\beta\beta\alpha-\alpha\beta\beta\alpha\alpha\beta-\beta\alpha\alpha\beta\beta\alpha+\beta\alpha\beta\alpha\alpha\beta)$
43	0,-1	$1/2\sqrt{2}(\alpha\beta\alpha\beta\beta\beta+\alpha\beta\beta\alpha\beta\beta+\alpha\beta\beta\beta\alpha\beta+\alpha\beta\beta\beta\beta\alpha+\beta\alpha\alpha\beta\beta\beta+\beta\alpha\beta\alpha\beta\beta+\beta\alpha\beta\beta\alpha\beta+\beta\alpha\beta\beta\beta\alpha)$
44	0,-1	$1/2\sqrt{2}(\alpha\beta\alpha\beta\beta\beta-\alpha\beta\beta\alpha\beta\beta-\alpha\beta\beta\beta\alpha\beta+\alpha\beta\beta\beta\beta\alpha-\beta\alpha\alpha\beta\beta\beta+\beta\alpha\beta\alpha\beta\beta+\beta\alpha\beta\beta\alpha\beta-\beta\alpha\beta\beta\beta\alpha)$
51	-1,0	$1/\sqrt{2}(\beta\beta\alpha\beta\beta\alpha+\beta\beta\beta\alpha\alpha\beta)$
52	-1,0	$1/\sqrt{2}(\beta\beta\beta\beta\alpha\alpha+\beta\beta\alpha\alpha\beta\beta)$
53	-1,0	$1/\sqrt{2}(\beta\beta\beta\alpha\beta\alpha+\beta\beta\alpha\beta\alpha\beta)$
57	1,-2	$(\alpha\alpha\beta\beta\beta\beta)$
58	-1,-1	$(\beta\beta\alpha\beta\beta\beta+\beta\beta\beta\alpha\beta\beta+\beta\beta\beta\beta\alpha\beta+\beta\beta\beta\beta\beta\alpha)$
62	0,-2	$1/\sqrt{2}(\alpha\beta\beta\beta\beta\beta+\beta\alpha\beta\beta\beta\beta)$
64	-1,-2	$(\beta\beta\beta\beta\beta\beta)$

Table 18. A_2 Basic Symmetry Functions for Six Nuclei A_2B_4

Energy Level	Spin A,B	Basic Symmetry Function
3	1,1	$\frac{1}{2}(\alpha\alpha\beta\alpha\alpha\alpha-\alpha\alpha\alpha\beta\alpha\alpha+\alpha\alpha\alpha\alpha\beta\alpha-\alpha\alpha\alpha\alpha\alpha\beta)$
10	0,1	$1/2\sqrt{2}(\alpha\beta\beta\alpha\alpha\alpha-\alpha\beta\alpha\beta\alpha\alpha+\alpha\beta\alpha\alpha\beta\alpha-\alpha\beta\alpha\alpha\alpha\beta+\beta\alpha\beta\alpha\alpha\alpha-\beta\alpha\alpha\beta\alpha\alpha+\beta\alpha\alpha\alpha\beta\alpha-\beta\alpha\alpha\alpha\alpha\beta)$
11	0,1	$1/2\sqrt{2}(\alpha\beta\beta\alpha\alpha\alpha+\alpha\beta\alpha\beta\alpha\alpha-\beta\alpha\beta\alpha\alpha\alpha+\beta\alpha\alpha\beta\alpha\alpha-\alpha\beta\alpha\alpha\beta\alpha-\alpha\beta\alpha\alpha\alpha\beta+\beta\alpha\alpha\alpha\beta\alpha+\beta\alpha\alpha\alpha\alpha\beta)$
19	1,0	$1/\sqrt{2}(\alpha\alpha\beta\alpha\beta\alpha-\alpha\alpha\alpha\beta\alpha\beta)$
24	-1,1	$\frac{1}{2}(\beta\beta\beta\alpha\alpha\alpha-\beta\beta\alpha\beta\alpha\alpha+\beta\beta\alpha\alpha\beta\alpha-\beta\beta\alpha\alpha\alpha\beta)$
28	1,-1	$\frac{1}{2}(\alpha\alpha\alpha\beta\beta\beta-\alpha\alpha\beta\alpha\beta\beta+\alpha\alpha\beta\beta\alpha\beta-\alpha\alpha\beta\beta\beta\alpha)$
35	0,0	$\frac{1}{2}(\alpha\beta\beta\alpha\beta\alpha-\alpha\beta\alpha\beta\alpha\beta+\beta\alpha\beta\alpha\beta\alpha+\beta\alpha\alpha\beta\alpha\beta)$
36	0,0	$\frac{1}{2}(\alpha\beta\beta\beta\alpha\alpha-\alpha\beta\alpha\alpha\beta\beta-\beta\alpha\beta\beta\alpha\alpha+\beta\alpha\alpha\alpha\beta\beta)$
45	0,-1	$1/2\sqrt{2}(\alpha\beta\alpha\beta\beta\beta-\alpha\beta\beta\alpha\beta\beta+\alpha\beta\beta\beta\alpha\beta-\alpha\beta\beta\beta\beta\alpha+\beta\alpha\alpha\beta\beta\beta-\beta\alpha\beta\alpha\beta\beta+\beta\alpha\beta\beta\alpha\beta-\beta\alpha\beta\beta\beta\alpha)$
46	0,-1	$1/2\sqrt{2}(\alpha\beta\alpha\beta\beta\beta+\alpha\beta\beta\alpha\beta\beta-\alpha\beta\beta\beta\alpha\beta-\alpha\beta\beta\beta\beta\alpha-\beta\alpha\alpha\beta\beta\beta-\beta\alpha\beta\alpha\beta\beta+\beta\alpha\beta\beta\alpha\beta+\beta\alpha\beta\beta\beta\alpha)$
54	-1,0	$1/\sqrt{2}(\beta\beta\beta\alpha\beta\alpha-\beta\beta\alpha\beta\alpha\beta)$
59	-1,-1	$\frac{1}{2}(\beta\beta\alpha\beta\beta\beta-\beta\beta\beta\alpha\beta\beta+\beta\beta\beta\beta\alpha\beta-\beta\beta\beta\beta\beta\alpha)$

Table 19. B_1 Basic Symmetry Functions for Six Nuclei A_2B_4

Energy Level	Spin A, B	Basic Symmetry Function
4	1,1	$\frac{1}{2}(\alpha\alpha\beta\alpha\alpha\alpha+\alpha\alpha\alpha\beta\alpha\alpha-\alpha\alpha\alpha\alpha\beta\alpha-\alpha\alpha\alpha\alpha\alpha\beta)$
12	0,1	$1/2\sqrt{2}(\alpha\beta\beta\alpha\alpha\alpha+\alpha\beta\alpha\beta\alpha\alpha-\alpha\beta\alpha\alpha\beta\alpha-\alpha\beta\alpha\alpha\alpha\beta+\beta\alpha\beta\alpha\alpha\alpha+\beta\alpha\alpha\beta\alpha\alpha-\beta\alpha\alpha\alpha\beta\alpha-\beta\alpha\alpha\alpha\alpha\beta)$
13	0,1	$1/2\sqrt{2}(\alpha\beta\beta\alpha\alpha\alpha-\alpha\beta\alpha\beta\alpha\alpha+\alpha\beta\alpha\alpha\beta\alpha-\alpha\beta\alpha\alpha\alpha\beta-\beta\alpha\beta\alpha\alpha\alpha+\beta\alpha\alpha\beta\alpha\alpha-\beta\alpha\alpha\alpha\beta\alpha+\beta\alpha\alpha\alpha\alpha\beta)$
20	1,0	$1/\sqrt{2}(\alpha\alpha\beta\beta\alpha\alpha-\alpha\alpha\alpha\alpha\beta\beta)$
25	-1,1	$\frac{1}{2}(\beta\beta\beta\alpha\alpha\alpha+\beta\beta\alpha\beta\alpha\alpha-\beta\beta\alpha\alpha\beta\alpha-\beta\beta\alpha\alpha\alpha\beta)$
29	1,-1	$\frac{1}{2}(\alpha\alpha\alpha\beta\beta\beta+\alpha\alpha\beta\alpha\beta\beta-\alpha\alpha\beta\beta\alpha\beta-\alpha\alpha\beta\beta\beta\alpha)$
37	0,0	$\frac{1}{2}(\alpha\beta\beta\beta\alpha\alpha-\alpha\beta\alpha\alpha\beta\beta+\beta\alpha\beta\beta\alpha\alpha-\beta\alpha\alpha\alpha\beta\beta)$
38	0,0	$\frac{1}{2}(\alpha\beta\beta\alpha\beta\alpha-\alpha\beta\alpha\beta\alpha\beta-\beta\alpha\beta\alpha\alpha\alpha+\beta\alpha\alpha\beta\alpha\beta)$
47	0,-1	$1/2\sqrt{2}(\alpha\beta\alpha\beta\beta\beta+\alpha\beta\beta\alpha\beta\beta-\alpha\beta\beta\beta\alpha\beta-\alpha\beta\beta\beta\beta\alpha+\beta\alpha\alpha\beta\beta\beta+\beta\alpha\beta\alpha\beta\beta-\beta\alpha\beta\beta\alpha\beta-\beta\alpha\beta\beta\beta\alpha)$
48	0,-1	$1/2\sqrt{2}(\alpha\beta\alpha\beta\beta\beta-\alpha\beta\beta\alpha\beta\beta+\alpha\beta\beta\beta\alpha\beta-\alpha\beta\beta\beta\beta\alpha-\beta\alpha\alpha\beta\beta\beta+\beta\alpha\beta\alpha\beta\beta-\beta\alpha\beta\beta\alpha\beta+\beta\alpha\beta\beta\beta\alpha)$
55	-1,0	$1/\sqrt{2}(\beta\beta\beta\beta\alpha\alpha-\beta\beta\alpha\alpha\beta\beta)$
60	-1,-1	$\frac{1}{2}(\beta\beta\alpha\beta\beta\beta+\beta\beta\beta\alpha\beta\beta-\beta\beta\beta\beta\alpha\beta-\beta\beta\beta\beta\beta\alpha)$

Table 20. B_2 Basic Symmetry Functions for Six Nuclei A_2B_4

Energy Level	Spin A, B	Basic Symmetry Function
5	1,1	$\frac{1}{2}(\alpha\alpha\beta\alpha\alpha\alpha-\alpha\alpha\alpha\beta\alpha\alpha-\alpha\alpha\alpha\alpha\beta\alpha+\alpha\alpha\alpha\alpha\alpha\beta)$
7	0,2	$1/\sqrt{2}(\alpha\beta\alpha\alpha\alpha\alpha-\beta\alpha\alpha\alpha\alpha\alpha)$
15	0,1	$1/2\sqrt{2}(\alpha\beta\beta\alpha\alpha\alpha+\alpha\beta\alpha\beta\alpha\alpha+\alpha\beta\alpha\alpha\beta\alpha+\alpha\beta\alpha\alpha\alpha\beta-\beta\alpha\beta\alpha\alpha\alpha-\beta\alpha\alpha\beta\alpha\alpha-\beta\alpha\alpha\alpha\beta\alpha-\beta\alpha\alpha\alpha\alpha\beta)$
14	0,1	$1/2\sqrt{2}(\alpha\beta\beta\alpha\alpha\alpha-\alpha\beta\alpha\beta\alpha\alpha-\alpha\beta\alpha\alpha\beta\alpha+\alpha\beta\alpha\alpha\alpha\beta+\beta\alpha\beta\alpha\alpha\alpha-\beta\alpha\alpha\beta\alpha\alpha-\beta\alpha\alpha\alpha\beta\alpha+\beta\alpha\alpha\alpha\alpha\beta)$
21	1,0	$1/\sqrt{2}(\alpha\alpha\alpha\beta\beta\alpha-\alpha\alpha\beta\alpha\alpha\beta)$
26	-1,1	$\frac{1}{2}(\beta\beta\beta\alpha\alpha\alpha-\beta\beta\alpha\beta\alpha\alpha-\beta\beta\alpha\alpha\beta\alpha+\beta\beta\alpha\alpha\alpha\beta)$
30	1,-1	$\frac{1}{2}(\alpha\alpha\alpha\beta\beta\beta-\alpha\alpha\beta\alpha\beta\beta-\alpha\alpha\beta\beta\alpha\beta+\alpha\alpha\beta\beta\beta\alpha)$
39	0,0	$\frac{1}{2}(\alpha\beta\alpha\beta\beta\alpha-\alpha\beta\beta\alpha\alpha\beta-\beta\alpha\alpha\beta\beta\alpha+\beta\alpha\beta\alpha\alpha\beta)$
40	0,0	$\frac{1}{2}(\alpha\beta\alpha\beta\beta\alpha+\alpha\beta\beta\alpha\alpha\beta-\beta\alpha\alpha\beta\beta\alpha-\beta\alpha\beta\alpha\alpha\beta)$
41	0,0	$\frac{1}{2}(\alpha\beta\beta\beta\alpha\alpha+\alpha\beta\alpha\alpha\beta\beta-\beta\alpha\beta\beta\alpha\alpha-\beta\alpha\alpha\alpha\beta\beta)$
42	0,0	$\frac{1}{2}(\alpha\beta\beta\alpha\beta\alpha+\alpha\beta\alpha\beta\alpha\beta-\beta\alpha\beta\alpha\beta\alpha-\beta\alpha\alpha\beta\alpha\beta)$
49	0,-1	$1/2\sqrt{2}(\alpha\beta\alpha\beta\beta\beta+\alpha\beta\beta\alpha\beta\beta+\alpha\beta\beta\beta\alpha\beta+\alpha\beta\beta\beta\beta\alpha-\beta\alpha\alpha\beta\beta\beta-\beta\alpha\beta\alpha\beta\beta-\beta\alpha\beta\beta\alpha\beta-\beta\alpha\beta\beta\beta\alpha)$
50	0,-1	$1/2\sqrt{2}(\alpha\beta\alpha\beta\beta\beta-\alpha\beta\beta\alpha\beta\beta-\alpha\beta\beta\beta\alpha\beta+\alpha\beta\beta\beta\beta\alpha+\beta\alpha\alpha\beta\beta\beta-\beta\alpha\beta\alpha\beta\beta-\beta\alpha\beta\beta\alpha\beta+\beta\alpha\beta\beta\beta\alpha)$
56	0,-1	$1/\sqrt{2}(\beta\beta\alpha\beta\beta\alpha-\beta\beta\beta\alpha\alpha\beta)$
61	-1,-1	$\frac{1}{2}(\beta\beta\alpha\beta\beta\beta-\beta\beta\beta\alpha\beta\beta-\beta\beta\beta\beta\alpha\beta+\beta\beta\beta\beta\beta\alpha)$
63	0,-2	$1/\sqrt{2}(\alpha\beta\beta\beta\beta\beta-\beta\alpha\beta\beta\beta\beta)$

Table 21. Algorithm for A_1 Basic Symmetry Functions for Six Nuclei A_2B_4

Transition No.	Type	Energy Upper	Level Lower	Frequency Check	Transition No.	Type	Energy Upper	Level Lower	Frequency Check
1	1	1	6		29	2	23	51	
2	2	-1	2		30	1	31	51	1
3	2	6	8		31	2	23	52	
4	1	2	8	1	32	1	32	52	1
5	2	6	9		33	2	-23	53	
6	1	2	9	1	34	1	33	53	1
7	1	8	23		35	2	-51	58	
8	1	9	23	1	36	2	-52	58	1
9	1	-6	22		37	2	-37	58	1
10	2	-22	23	1	38	2	31	43	
11	2	8	31		39	2	32	43	1
12	2	9	31	1	40	2	33	43	1
13	2	8	32		41	2	34	43	1
14	2	9	32	1	42	1	27	43	1
15	2	8	33		43	2	-31	44	
16	2	9	33	1	44	2	-32	44	1
17	2	-8	34		45	2	-33	44	1
18	2	-9	34	1	46	2	-34	44	1
19	2	2	16		47	1	-34	51	1
20	1	16	31	1	48	1	27	44	1
21	1	16	34	1	49	2	-43	62	
22	2	2	17		50	2	44	62	1
23	1	17	32	1	51	2	-27	57	
24	2	-2	18		52	1	-57	62	1
25	1	-18	33	1	53	1	-43	58	1
26	2	-16	27		54	1	-44	58	1
27	2	-17	27	1	55	2	-58	64	
28	2	-18	27	1	56	1	-62	-64	1

Table 22. Algorithm for A_2 basic symmetry functions for six nuclei A_2B_4

Transition		Energy level		Frequency check
No.	Type	Upper	Lower	
1	1	3	10	
2	1	3	11	
3	2	-3	19	
4	1	10	24	
5	1	11	24	1
6	2	10	35	
7	1	19	35	1
8	2	-24	54	
9	1	35	54	1
10	2	-10	36	
11	2	11	36	1
12	2	-11	35	1
13	2	-19	28	
14	2	35	45	
15	1	28	45	1
16	2	-35	46	
17	1	-28	46	1
18	2	36	45	1
19	2	-36	46	1
20	1	-45	59	
21	1	-46	59	1
22	2	-54	-59	1

Table 23. Algorithm for B_1 Basic Symmetry Function for Six Nuclei A_2B_4

Transition No.	Type	Energy Level Upper	Energy Level Lower	Frequency Check	Transition No.	Type	Energy Level Upper	Energy Level Lower	Frequency Check
1	1	4	12		12	2	-13	37	1
2	1	4	13		13	2	-20	29	
3	2	-4	20		14	2	37	47	
4	1	12	25		15	1	29	47	1
5	1	13	25	1	16	2	-37	48	
6	2	12	37		17	1	-29	48	1
7	1	20	37	1	18	2	38	47	1
8	2	-25	55		19	2	-38	48	1
9	1	37	55	1	20	1	-47	60	
10	2	-12	38		21	1	-48	60	1
11	2	13	38	1	22	2	-55	-60	1

Table 24. Algorithm for B_2 Basic Symmetry Functions for Six Nuclei A_2B_4

Transition No.	Type	Energy Level Upper	Lower	Frequency Check	Transition No.	Type	Energy Level Upper	Lower	Frequency Check
1	1	5	14		19	2	-14	42	
2	1	5	15		20	2	-15	42	1
3	2	-5	21		21	2	-21	30	
4	2	14	39		22	2	39	49	
5	2	15	39	1	23	1	30	49	1
6	-2	7	14		24	2	-24	50	
7	-2	-7	15	1	25	1	-25	50	1
8	1	21	39	1	26	2	-56	61	
9	1	14	26		27	1	-49	61	1
10	1	15	26	1	28	1	50	-61	1
11	2	-26	56		29	2	49	63	
12	1	39	56	1	30	2	50	-63	1
13	1	21	40		31	2	40	49	1
14	2	15	40	1	32	2	-40	50	1
15	1	40	56	1	33	2	41	49	1
16	2	14	40	1	34	2	-41	50	1
17	2	14	41		35	2	42	-49	1
18	2	15	41	1	36	2	-42	-50	1

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APPENDIX

A. Steps in Making an Analysis

In this appendix, the steps required to carry out an analysis will be outlined for two cases: 1) the situation in which noise level is fairly high and the decomposition is not perfectly clear cut so that ASSIGN cannot be used directly and 2) the case in which the noise level is low and a good decomposition is obtained, so that ASSIGN may be used directly to obtain all the sets of energy levels.

The original digital data is scaled to a form which is optimal for use in DECOMP (Appendix B) by using the base line adjustment program BLINE (Appendix E). The individual groups of peaks in the spectrum are then decomposed using DECOMP as discussed in Appendix B.

If the noise level of the spectrum is low enough and the nature of the peaks are such as to give an unambiguous decomposition, the peaks found by DECOMP can be used in ASSIGN (Appendix D). Before using ASSIGN it is necessary to normalize the intensities and it is also convenient to scale the frequencies so they correspond to those of the experimental spectrum. This can be done with SCALE (Appendix E).

The sets of transitions which are calculated by ASSIGN can be directly used in NMREN to get a least squares fit to the energy levels and to adjust the trace. (This function was not built into ASSIGN since it is readily available in NMREN.) An option in ASSIGN will cause these assignments to be punched on cards for direct insertion into NMREN. The adjusted sets of energy levels are then put into NMRIT(N) for calculation of the parameters. Any set of initial parameters can be used as long as they are consistent with the equivalence and symmetry properties of the molecule.

If the spectrum is such that ASSIGN cannot be used directly with the decomposed lines, it is very helpful to use NMRIT(0) as an aid. It will be necessary to estimate parameters until a reasonable resemblence to the experimental spectrum is obtained. When this has been accomplished, assign all of the lines which have been decomposed to transitions calculated by NMRIT(0), in the usual manner. Since a far larger number of lines are known from DECOMP than would have been known by visual estimation, the task should be easier and more efficient.

The analysis is then carried out in the usual manner for the S & R method. These assignments are used in NMREN and the calculated energy levels used in NMRIT(N) to obtain a set of parameters and transitions. These are then reassigned as necessary and the process repeated until a good set of parameters is obtained. After a reasonably good fit is obtained, the assignment should be close enough so that it can be used in the construction of an algorithm for ASSIGN. This will allow the possibility of picking out the correct assignment faster than the trial and error method, if the transitions can be localized to within a region as was done in the five-spin cases above. ASSIGN will not only save time but will provide all sets of assignments consistent with the constraints placed on the system.

All programs are written in FORTRAN IV for an IBM 7094 and are listed in the subsequent appendices, along with sample problems. Problems can be stacked in all programs and the last card in the entire data deck is blank, causing the program to call exit. It is assumed that input and output data formats will vary with the personal preference of the user and have only been mentioned in the descriptions.

B. DECOMP

A listing of DECOMP, a description of the information needed for input, and two sample problems are given below. After the spectrum has been obtained in an arbitrary digital form it is necessary to be certain it is scaled properly for use in DECOMP. This is necessary because the program changes the fitting parameters in proportion to the fit as well as the partial derivative of the function with respect to that particular parameter. Consequently all the parameters must be of the same order of magnitude. This is easily accomplished with the simple program, BLINE, in Appendix E which scales the x- and y-axes, adjusts the base line to zero and will find initial starting parameters if desired.

A convenient scale has been to set the x and y axes over a range of about 0-50. The final values for peak positions and intensities can then be normalized and shifted to any frequency range desired by using SCALE, also described in Appendix E.

The best procedure has been found to make the initial decomposition based on the peaks which can be visually distinguished, plus two or three additional estimates. The results from this decomposition can then be plotted (Appendix B) and subsequent problems done with peaks added where the fit is unsatisfactory. The present program will decompose a maximum of 19 peaks using a Lorentzian shape function of 20 peaks using a digital standard shape function.

CARD 1 Read M, IZ, IMOUT, IDATA (I4,3I3)

M is the number of data points. If M=0 program calls exit.

IZ is number of peaks which are to be fit to the data.

IMOUT is an option to select printout. If IMOUT = 1, values of F (fit), G (gradients), x (parameters) are printed at

every interaction and the entire error matrix is printed out with the final values. This option is only used for diagnostic purposes since most of this information is not ordinarily desired. IMOUT = 2 prints out only the initial and final values and is the usual option.

IDATA $\neq$ 0 if all the data points are to be printed out, IDATA = 0 if data points not printed.

CARD 2 T2 (20X,F10.3)

T2 is the reciprocal of the peak half-width at half-height when a Lorentz function is used for peak shapes. If T2 = 0 then the program assumes a digital standard function will be used. This is read in later. These two types of problems can be mixed.

DECK 3 TT_i, VV_i $i = 1,M$ (10F8.0)

These are the x_i, y_i values of the data points.

DECK 4 X_{ii}, X_i $i = 1, IZ$ (30X,2F10.3)

X_{ii} and X_i are the estimated frequencies and intensities of the ith peak, one set per card.

Note: If T2 = 0 the digital standard function must be read in after the frequencies and intensities.

CARD 5 Read MSTD, LST (2I3)

MSTD is the number of data points in the digital standard peak.

LST The program searches for the maximum in the digital standard peak, starting from the LST^{th} data point. This is necessary because there might be a local maximum in the noise at the beginning of the peak and this would be used as an erroneous peak position. LST is chosen as the just point

located on the digital standard peak which is high enough to be above the noise level but below the maximum.

DECK 6 $XSTD_{\ell}$, $YSTD_{\ell}$, $\ell = 1$, MSTD (10F8.0)

Data points for the digital standard peak.

```
$IBFTC MAIN
      DIMENSION H(40,40),X(40),G(40),S(40),XP(40),GP(40), T(40),GB(40)
      DIMENSION TITLE(12),XIN(40) ,TT(500,1 ),VV(500)
      DIMENSION V(3)
      COMMON  H       , X       , G       , S       , XP      , GP
      COMMON  T       , GB      , M       , N       , L       , LS
      COMMON  M1      , MS      , NS      , IT      , GS      , GSP
      COMMON  GTP     , GSS     , GTT     , GSB     , F       , FP
      COMMON  FB      , FO      , E       , K       , P       , TO
      COMMON  RS      , SL      , Z       , Q       , A       , EL
      COMMON  DELTA   , TITLE   , IMOUT   , IFOUT   , V       , IDH
      COMMON  LTEST
 1000 READ(2,1)M,IZ,IMOUT,IDATA
      IF(M .EQ.0)CALL EXIT
      E=.001
      P=0.
      K=0
      READ (2,20) T2
      IF(T2.NE.0.) X(1)=T2
      READ (2,15)(TITLE(I),I=1,12)
 151  IF(IDATA.NE.0) WRITE(3,16) TITLE
      READ (2,4) (TT(I,1),VV(I), I=1,M)
      IF(IDATA.EQ.0) GO TO 148
      DO 51 I=1, M
                        WRITE(3,155) TT(I,1),VV(I)
 51   CONTINUE
 148  M1=1
      DO 99 I=1,3
 99   V(I)=0.0
      IDH =0
      LTEST=0
      MS=0
      IF(T2.EQ.0.) GO TO 53
      N=2*IZ+1
      DO 777 I=1,IZ
      III=I+IZ+1
      READ (2,18) X(III),X(I+1)
      XIN(I+1)=X(I+1)
 777  XIN(III)=X(III)
      GO TO 52
 53   N=2*IZ
      DO 778 I=1,IZ
      II=I+IZ
      READ(2,18) X(II),X(I)
      XIN(II)=X(II)
 778  XIN(I)=X(I)
 52   DELTA =1.
      DO 175 I=1,N
      DO 175 J=1,N
 175  H(I,JJ=0.
      DO 180 I=1,N
 180  H(I,I)=1.
      CALL FCN(N,G,F,X,M1,IZ,TT,VV,T2)
      IZ=IZ
      WRITE (3,6)N,K,E,P,DELTA
      WRITE (3,7)
```

```
      WRITE (3,8)(X(I),I=1,N)
      WRITE (3,13)F
  120 L=1
  121  CALL READY(IZ,TT,VV,T2)
      IZ=IZ
  122 L=L
  123 GO TO (139,159,137,126),L
  124 L=2
  125 GO TO 121
  126 CALL AIM(IZ,TT,VV,T2)
      IZ=IZ
  127 L=L
  128 GO TO (129,135,137),L
  129 CALL FIRE(IZ,TT,VV,T2)
      IZ=IZ
  130 L=L
  131 GO TO (135,132,126),L
  132 L=1
  133 CALL DRESS
      GO TO 124
  135 L=2
      GO TO 133
  137 L=3
      GO TO 133
  159 L=4
      GO TO 133
  139 L=2
      MS=0
      GO TO (120,142),L
  142  WRITE (3,16) TITLE
      WRITE (3,14)F ,IT
      WRITE (3,10)
      WRITE (3,7)
      IF(T2.EQ.0.) GO TO 54
      IF(T2.NE.0.)WRITE(3,19)T2,X(1)
      WRITE(14,20) X(1)
      DO 57 I=1,IZ
      III=I+IZ+1
      WRITE(14,18) X(III),X(I+1)
   57 WRITE(3,5) XIN(III),XIN(I+1),X(III),X(I+1)
      GO TO 56
   54 DO55 I=1,IZ
      II=I+IZ
      WRITE (14,18) X(II),X(I)
   55 WRITE(3,5)XIN(II),XIN(I), X(II),X(I)
   56 IF(IMOUT.EQ.2) GO TO 700
      WRITE (3,12)
      WRITE (3,8) (G(I),I=1,N)
      WRITE (3,11)
      WRITE (3,8)((H(I,J),J=1,N),I=1,N)
  700 M1=3
      CALL FCN(N,G,F,X,M1,IZ,TT,VV,T2)
      IZ=IZ
  161 GO TO 1000
    1 FORMAT(I4,3I3 ,F7.2)
    2 FORMAT (2I3,I1,I4,F9.3,2F10.3)
```

```
3     FORMAT (8F10.5)
4     FORMAT (10F8.0)
5     FORMAT (1H 4F14.3)
    6 FORMAT (3HON=I2,4H  K=I2,4H  E=E14.5,4H  P=E14.5,8H  DELTA=E14.5)
7     FORMAT (1H0,15X,1HX/)
8      FORMAT (1H 8E14.5)
    9 FORMAT (1H0,55X,1HH/)
10    FORMAT (1H0,13X,14HINITIAL VALUES,12X,12HFINAL VALUES)
   11 FORMAT (1H0,13X,12HERROR MATRIX)
   12 FORMAT (1H0,55X,1HG/)
   13 FORMAT (3HOF=E14.5)
14    FORMAT (3HOF=F16.4,8H      IT=I3)
   15 FORMAT (12A6)
16     FORMAT (1H1//////  12A6)
18    FORMAT (30X,2F10.3)
19    FORMAT(1H F14.3,14X,F14.3)
20    FORMAT(20X,F10.3)
  105 FORMAT ( 13H  DATA POINTS//)
  155 FORMAT( 5(E20.5))
      END
```

```
$IBFTC FCN
      SUBROUTINE FCN(N,G,F,X,M1,IZ,TT,VV,T2)
      DIMENSION H(40,40),X(40),G(40),S(40),XP(40),GP(40), T(40),GB(40)
      DIMENSION V(3),PD(40),AA(10)
      DIMENSION TITLE(12),XIN(40) ,TT(500,1 ),VV(500)
      COMMON  H       , X       , G       , S       , XP      , GP
      COMMON  T       , GB      , M       , N       , L       , LS
      IF(M1-1) 60,40,60
40    KK=1
      MP=M
      WRITE(3,153)M1
      WRITE(3,150)N
      WRITE (3,151) M
   60 F=0.
      DO 4 I=1, N
      PD(I) =0.
      G(I)= 0.
    4 CONTINUE
      A= 0.
      DO5 IDAPT= 1, MP
      DO6 J= 1, KK
6     AA(J)=TT(IDAPT, J)
      IF(T2  .EQ.0.) GO TO 20
        CALL TABLEL(FIT,PD,X,AA,M1,IZ)
      GO TO 13
20      CALL TABLED(FIT,PD,X,AA,M1,IZ)
13    IF(M1.NE.1) GO TO 14
      M1=2
   14 F= F+          (FIT-VV(IDAPT))**2
      DO 7 J=1, N
      G(J)= G(J) +(FIT-VV(IDAPT))*PD(J)*2.
    7 CONTINUE
    5 CONTINUE
100    FORMAT (5(I10))
  105 FORMAT ( 13H  DATA POINTS//)
  150 FORMAT(36H  THE NUMBER OF FITTING PARAMETERS =I2)
  151 FORMAT(29H  THE NUMBER OF DATA POINTS =I3/)
  153 FORMAT(1H1,5H  M1=I2/)
  155 FORMAT( 5(E20.5))
   22 RETURN
      END
```

```
$IBFTC TABLED
      SUBROUTINE TABLED(FIT,PD,X,T,M1,IZ)
      DIMENSION X(40),PD(40),XSTD(100),YSTD(100),Y(20)
      IF (M1-1) 20,10,20
 10   READ (2,1) MSTD,LST,SCALE
      IF(SCALE.EQ.0.) SCALE =1.
      READ (2,2) (XSTD(L),YSTD(L), L=1,MSTD)
      DD= YSTD(1)
      EE = XSTD(1)
      DO 25 I=1,MSTD
      XSTD(I) = XSTD(I) - EE
 25   YSTD(I) = (YSTD(I) - DD)*SCALE
      DO40 J=LST,MSTD
      IF(YSTD(J+1)-YSTD(J)) 30,40,40
 30   RESSTD = XSTD(J)
      IM=J
      WIDEL= RESSTD-XSTD(1)
      WIDER = XSTD(MSTD) - RESSTD
      YRESTD = YSTD(J)
      GO TO 20
 40   CONTINUE
 20   FIT = 0.
      DO 55 I=1,IZ
      II = I+IZ
      SHIFT = X(II) - RESSTD
      IF(T-(X(II)-WIDEL))60,70,70
 60   Y(I) =0.
      PD(I) = .00001
      PD(II) =-.00001
      GO TO 50
 70   IF(T-(X(II)+WIDER))80,80,65
 65   Y(I) = 0.
      PD(I) = .00001
      PD(II)= .00001
      GO TO 50
 80   IF(X(II)-T) 90,100,110
 100  Y(I) = YRESTD*X(I)
      PD(I) = YRESTD
      PD(II) = 0.
      GO TO 50
 90   IA = IM
 95   IF(XSTD(IA) + SHIFT-T) 96,97,97
 96   IA =IA+1
      GO TO 95
 97   Y(I) = X(I)*(YSTD(IA)+((XSTD(IA)+SHIFT-T)*(YSTD(IA-1)-YSTD(IA)))/
     1 (XSTD(IA)-XSTD(IA-1)))
      PD(I) = Y(I)/X(I)
      IF (MSTD-IA  ) 98,98,99
 98   PD(II) = 0.00001
      GO TO 50
 99   PD(II) =-((YSTD(IA  )-YSTD(IA-1))*X(I))/(XSTD(IA  ) -XSTD(IA-1))
      GO TO 50
 110  IN = IM
 111  IF(XSTD(IN) + SHIFT-T) 120,120,115
 115  IN = IN-1
      GO TO 111
```

```
120 Y(I) = X(I)*(YSTD(IN+1)-((XSTD(IN+1)+SHIFT-T)*(YSTD(IN+1)-
   1 YSTD(IN)))/(XSTD(IN+1)-XSTD(IN)))
    PD(I) = Y(I)/X(I)
    IF(IN - ) 121,121,122
121 PD(II)=0.00001
    GO TO 50
122 PD(II) =-((YSTD(IN+1)-YSTD(IN  ))*X(I))/(XSTD(IN+1) -XSTD(IN  ))
    GO TO 50
50  FIT = FIT+Y(I)
55  CONTINUE
    RETURN
1   FORMAT(2I3,F7.3)
2   FORMAT (10F8.0)
3   FORMAT (5E14.5)
    END
```

```
$IBFTC TABLEL
C       DECOMPOSITION OF NORMALIZED LORENTZIAN SUM
         SUBROUTINE TABLEL(FIT,PD,X,T,M1,IZ)
         DIMENSION X(40),PD(40)
         IZ=IZ
         FIT=0.0
        PD(1)=0.0
         DO 10 I=1,IZ
         III=I+IZ+1
        Z=X(III)-T
        Y=X(1)*Z
        RECIP=1./(1.+Y*Y)
        FIT=FIT+2.*  X(1)*X(I+1)*RECIP
        PD(1)=PD(1)+2.*  X(I+1)*RECIP*(1.-2.*Y*Y*RECIP)
        PD(I+1)=2.*  X(1)*RECIP
 10     PD(III)=-4.* X(1)*X(1)*X(I+1)*Y*RECIP*RECIP
         RETURN
         END
```

```
$IBFTC READY
      SUBROUTINE READY(IZ,TT,VV,T2)
      DIMENSION H(40,40),X(40),G(40),S(40),XP(40),GP(40), T(40),GB(40)
      DIMENSION TITLE(12)          ,TT(500,1 ),VV(500)
      COMMON  H      , X      , G      , S      , XP     , GP
      COMMON  T      , GB     , M      , N      , L      , LS
      COMMON  M1     , MS     , NS     , IT     , GS     , GSP
      COMMON  GTP    , GSS    , GTT    , GSB    , F      , FP
      COMMON  FB     , FO     , E      , K      , P      , TO
      COMMON  RS     , SL     , Z      , Q      , A      , EL
      COMMON  DELTA  , TITLE  , IMOUT  , IFOUT
      IZ=IZ
      L=L
      GO TO (200,201),L
  200 IT=1
  201 CALL MATMPY(N,N,H,G,S)
      DO 203 I=1,N
  203 S(I)=-S(I)
      M=1
      CALL MATMPY(M,N,S,G,GS)
      IF(GS+E) 207,228,228
  207 EL=AMIN1(2.0,-(F/GS)-(F/GS))
      SL=-GS
  210 DO 211 I=1,N
  211 XP(I)=X(I)+EL*S(I)
      M1=2
      CALL FCN(N,GP,FP,XP,M1,IZ,TT,VV,T2)
      IZ=IZ
      CALL OVERFL(KOOOFX)
      GO TO(214,215),KOOOFX
 214  WRITE (3,2141)
 2141 FORMAT (1H0,5X,14HREADY OVERFLOW)
      EL=EL/2.0
      GO TO 210
  215 CALL MATMPY (M,N,S,GP,GSP)
  216 IF (GSP) 217,229,229
  217 IF(FP-F)218,229,229
 218  IF(IMOUT.EQ.1) WRITE(3,1)
      FB=FP
      DO 234 I=1,N
      GB(I)=GP(I)
  234 T(I)=XP(I)
      IF(EL-2.0)221,223,223
  221 L=3
      RETURN
  223 DELTA=DELTA+DELTA
      TO=1.0/SL
      L=2
      RETURN
  228 L=1
      RETURN
  229 L=4
      RETURN
    1 FORMAT (10HOUNDERSHOT)
      END
```

```
$IBFTC AIM
      SUBROUTINE AIM(IZ,TT,VV,T2)
      DIMENSION H(40,40),X(40),G(40),S(40),XP(40),GP(40), T(40),GB(40)
      DIMENSION TITLE(12)          ,TT(500,1 ),VV(500)
      COMMON  H       , X       , G       , S       , XP      , GP
      COMMON  T       , GB      , M       , N       , L       , LS
      COMMON  M1      , MS      , NS      , IT      , GS      , GSP
      COMMON  GTP     , GSS     , GTT     , GSB     , F       , FP
      COMMON  FB      , FO      , E       , K       , P       , TO
      COMMON  RS      , SL      , Z       , Q       , A       , EL
      COMMON  DELTA   , TITLE   , IMOUT   , IFOUT
      IZ=IZ
      M=M
      GO TO (301,313),M
  301 Z=GS+GSP+3.0*(F-FP)/EL
      TO=GS/Z
      TI=GSP/Z
      Q=ABS(Z*SQRT(1.0-TO*TI))
      A=(GSP+Q-Z)/(GSP-GS+Q+Q)
      TO=(EL*(GSP+Z+Q+Q)*A*A)/3.0
      FO=FP-TO
      CALL MATMPY(N,N,H,GP,T)
      TP1=GSP/SL
      DO 308 I=1,N
  308 T(I)=-T(I)+TP1*S(I)
      M=1
      CALL MATMPY(M,N,T,GP,GTP)
      TP1=F+GTP/2.0
      IF (FO-TP1) 312,312,317
  312 CALL OVERFL(K000FX)
       GO TO(340,313),K000FX
  340 WRITE (3,2)
      A=.5
  313 TP1=1.0-A
      DO 314 I=1,N
  314 T(I)=A*X(I)+TP1*XP(I)
      L=1
      RETURN
  317 IF (TP1) 312,318,318
  318 DO 319 I=1,N
  319 T(I)=T(I)+XP(I)
      M1=2
  321 CALL FCN(N,GB,FB,T,M1,IZ,TT,VV,T2)
      IZ=IZ
      CALL OVERFL(K000FX)
       GO TO(350,322),K000FX
  322 IF (FB-FO) 323,312,312
  323 IF(IMOUT.EQ.1) WRITE(3,1)
      DO 325 I=1,N
  325 S(I)=T(I)-XP(I)
      CALL MATMPY(M,N,S,GB,GTT)
      IF(GTT-GTP) 335,330,330
  330 GSS=GTT-GTP
      SL=-GTP
      EL=1.0
      L=2
```

```
      RETURN
  335 L=3
      RETURN
  350 WRITE (3,3)
      DO 352 I=1,N
  352 T(I)=(T(I)+XP(I))/2.0
      GO TO 321
    1 FORMAT (9H0RICOCHET)
  2   FORMAT (1H0,5X,15HAIM OVERFLOW--I)
  3   FORMAT (1H0,5X,16HAIM OVERFLOW--II)
      END
```

```
$IBFTC FIRE
      SUBROUTINE FIRE (IZ,TT,VV,T2)
      DIMENSION H(40,40),X(40),G(40),S(40),XP(40),GP(40), T(40),GB(40)
      DIMENSION TITLE(12)          ,TT(500,1 ),VV(500)
      COMMON  H      , X      , G      , S      , XP     , GP
      COMMON  T      , GB     , M      , N      , L      , LS
      COMMON  M1     , MS     , NS     , IT     , GS     , GSP
      COMMON  GTP    , GSS    , GTT    , GSB    , F      , FP
      COMMON  FB     , FO     , E      , K      , P      , TO
      COMMON  RS     , SL     , Z      , Q      , A      , EL
      COMMON  DELTA  , TITLE  , IMOUT  , IFOUT
      IZ=IZ
      M1=2
      CALL FCN(N,GB,FB,T,M1,IZ,TT,VV,T2)
      IZ=IZ
      CALL OVERFL(K000FX)
       GO TO(440,403),K000FX
  440 WRITE (3,4401)
 4401 FORMAT (1H0,5X,13HFIRE OVERFLOW)
      M=2
      A=(1.0+A)/2.0
      GO TO 426
  403 M=1
      CALL MATMPY(M,N,S,GB,GSB)
      TP1=AMIN1(F,FP)
      ABAR=1.0-A
      IF(TP1-FB+E) 418,406,406
  406 TP1=A/ABAR
      TP2=ABAR/A
      TO=GSB*(TP1-TP2)
      IF(ABS(TO)-Q) 413,410,410
  410 GSS=Q+Q
      L=1
       LOOPF=0
      RETURN
  413 GSS=TO+Q+Q
      DO 415 I=1,N
  415 G(I)=(GB(I)-G(I))*TP1+(GP(I)-GB(I))*TP2
       LOOPF=0
      L=2
      RETURN
418    CONTINUE
       LOOPF=LOOPF+1
       IF(LOOPF-60)382,383,383
383    CALL EXIT
382    CONTINUE
       IF(F-FP)419,428,428
  419 IF(IMOUT.EQ.1) WRITE(3,1)
      EL=ABAR*EL
      FP=FB
      GSP=GSB
      DO 425 I=1,N
      XP(I)=T(I)
  425 GP(I)=GB(I)
  426 L=3
      RETURN
```

```
428   IF(IMOUT.EQ.1) WRITE(3,2)
      EL=EL*A
      F=FB
      GS=GSB
      DO 434 I=1,N
      X(I)=T(I)
434   G(I)=GB(I)
      GO TO 426
    1 FORMAT (10HOMOVE LEFT)
    2 FORMAT (11HOMOVE RIGHT)
      END
```

```
$IBFTC DRESS
      SUBROUTINE DRESS
      DIMENSION H(40,40),X(40),G(40),S(40),XP(40),GP(40), T(40),GB(40)
      DIMENSION TITLE(12)
      DIMENSION V(3)
      COMMON  H      , X      , G      , S      , XP     , GP
      COMMON  T      , GB     , M      , N      , L      , LS
      COMMON  M1     , MS     , NS     , IT     , GS     , GSP
      COMMON  GTP    , GSS    , GTT    , GSB    , F      , FP
      COMMON  FB     , FO     , E      , K      , P      , TO
      COMMON  RS     , SL     , Z      , Q      , A      , EL
      COMMON  DELTA  , TITLE  , IMOUT  , IFOUT  , V      , IDH
      COMMON  LTEST
      IF(IMOUT.EQ.1) WRITE(3,13)L
      GO TO (500,525,529,510),L
  500 CALL MATMPY(N,N,H,G,X)
      M=1
      CALL MATMPY(M,N,X,G,TO)
      TP1=SL-GSS*GSS/TO
      IF(TP1) 505,524,504
  504 IF (TP1-E) 524,505,505
  505 DO 507 I=1,N
      DO 507 J=1,N
  507 H(I,J)=H(I,J)-X(I)*X(J)/TO
      DELTA=DELTA*(EL*GSS/TO)
      TO=EL/GSS
  510 DO 512 I=1,N
      DO 512 J=1,N
  512 H(I,J)=H(I,J)+TO*S(I)*S(J)
  529 CALL OVERFL(K000FX)
       GO TO(531,519),K000FX
  519 F=FB
      DO 522 I=1,N
      G(I)=GB(I)
  522 X(I)=T(I)
      J=IMOUT
      GO TO (515,517),J
  515 WRITE (3,1)IT,MS,F
      WRITE (3,2)
      WRITE (3,12)(X(I),I=1,N)
      WRITE (3,10)
      WRITE (3,12)(G(I),I=1,N)
      WRITE (3,3)DELTA
      WRITE (3,4)
  517 DO 518 I=1,3
      IF (V(I)-F) 523,518,523
  518 CONTINUE
      IF (LTEST) 550,560,550
  550 WRITE (3,16)
      GO TO 532
  560 LTEST=1
      WRITE (3,15)
      DO 562 I=1,N
      DO 562 J=1,N
      H(I,J)=0.0
  562 H(I,I)=1.0
```

```
      DELTA=1.0
      DO 563 I=1,3
563   V(I)=0.0
      IT=IT+1
      RETURN
523   V(3)=V(2)
      V(2)=V(1)
      V(1)=F
      IT=IT+1
      RETURN
524   WRITE (3,5)
      GO TO 530
525   TO=EL/GSS-1.0/SL
530   DELTA=DELTA*EL*SL/GSS
      GO TO 510
531   WRITE (3,6)
532   WRITE (3,7)
      WRITE (3,12)((H(I,J),J=1,N),I=1,N)
      WRITE (3,14)F
      WRITE (3,2)
      WRITE (3,12)(X(I),I=1,N)
      WRITE (3,10)
      WRITE (3,12)(G(I),I=1,N)
      J=2-IFOUT
      GO TO (539,543),J
539   WRITE ( 3,11)(X(I),I=1,N),((H(I,J),J=1,N),I=1,N),       DELTA
543   CALL EXIT
1     FORMAT (4H0IT I4,7H  STEP I4,4H  F=E16.8)
    2 FORMAT (1H0,55X,1HX/)
    3 FORMAT (7H0DELTA=E14.5)
    4 FORMAT (20H0- - - - - - - - - -  )
    5 FORMAT (9H0COLINEAR)
    6 FORMAT (9H0OVERFLOW)
    7 FORMAT (1H0,13X,12HERROR MATRIX)
    9 FORMAT (3H0F=E14.5)
   10 FORMAT (1H0,55X,1HG/)
   11 FORMAT (5E14.5)
   12 FORMAT (1H 8E14.5)
13    FORMAT (6H0DRESSI3)
14    FORMAT (3H0F=E16.8)
15    FORMAT (50H0    FOUR CONSECUTIVE VALUES FOR F ARE IDENTICAL    ///
     15X,30HPROGRAM ASSUMED TO BE IN LOOP
     25X,36HH IS SET TO IDENTITY FOR ANOTHER TRY              )
16    FORMAT (1H0,5X,24HSECOND LOOP---CALL EXIT          )
      RETURN
      END
```

```
$IBFTC MATMPY
      SUBROUTINE MATMPY(M,N,H,G,S)
      DIMENSION H(40,40),X(40),G(40),S(40),XP(40),GP(40), T(40),GB(40)
      COMMON  H      , X      , G      , S      , XP     , GP
      COMMON  T      , GB     , M      , N      , L      , LS
      COMMON  M1     , MS     , NS     , IT     , GS     , GSP
      COMMON  GTP    , GSS    , GTT    , GSB    , F      , FP
      COMMON  FB     , FO     , E      , K      , P      , TO
      COMMON  RS     , SL     , Z      , Q      , A      , EL
      COMMON  DELTA  , TITLE  , IMOUT  , IFOUT
      IF (M-1) 705,705,702
  702 DO 703 I=1,M
      S(I)=0.0
      DO 703 J=1,N
  703 S(I)=H(I,J)*G(J)+S(I)
      RETURN
  705 S(1)=0.0
      DO 706 I=1,N
  706 S(1)=H(I,1)*G(I)+S(1)
      RETURN
      END
                    *** 'END-OF-FILE' CARD ***
```

0170012002

600. 100. 3.3

DECOMPOSITION USING LORENTZ SHAPE FUNCTION

53.125	2.402	53.187	2.482	53.250	2.642	53.312	2.722	53.375	2.882
53.437	3.042	53.500	3.282	53.562	3.362	53.625	3.362	53.687	3.442
53.750	3.602	53.812	4.082	53.875	4.562	53.937	5.202	54.000	6.002
54.062	6.802	54.125	7.602	54.187	8.482	54.250	9.522	54.312	10.722
54.375	12.162	54.437	13.202	54.500	14.002	54.562	13.922	54.625	12.882
54.687	11.042	54.750	8.802	54.812	6.802	54.875	5.202	54.937	4.242
55.000	3.922	55.062	3.922	55.125	3.922	55.187	3.842	55.250	3.842
55.312	3.682	55.375	3.682	55.437	3.682	55.500	3.842	55.562	4.082
55.625	4.322	55.687	4.562	55.750	4.802	55.812	4.962	55.875	5.042
55.937	5.362	56.000	5.682	56.062	6.162	56.125	6.642	56.187	7.202
56.250	7.602	56.312	8.162	56.375	8.882	56.437	9.922	56.500	11.202
56.562	12.882	56.625	15.042	56.687	17.602	56.750	20.642	56.812	24.322
56.875	28.562	56.937	32.882	57.000	36.802	57.062	39.682	57.125	40.962
57.187	40.162	57.250	37.202	57.312	32.882	57.375	28.242	57.437	24.162
57.500	21.202	57.562	19.522	57.625	19.042	57.687	19.122	57.750	19.362
57.812	19.522	57.875	19.922	57.937	20.882	58.000	22.162	58.062	23.762
58.125	25.122	58.187	25.762	58.250	25.042	58.312	23.042	58.375	19.842
58.437	16.322	58.500	12.962	58.562	10.322	58.625	8.322	58.687	7.202
58.750	6.642	58.812	6.482	58.875	6.562	58.937	6.882	59.000	7.442
59.062	8.082	59.125	8.882	59.187	9.682	59.250	10.562	59.312	11.522
59.375	12.322	59.437	13.122	59.500	14.082	59.562	15.282	59.625	16.562
59.687	17.762	59.750	18.802	59.812	19.202	59.875	18.722	59.937	17.682
60.000	16.322	60.062	15.282	60.125	14.722	60.187	14.562	60.250	14.642
60.312	14.562	60.375	14.482	60.437	14.482	60.500	14.802	60.562	15.282
60.625	15.842	60.687	15.922	60.750	15.202	60.812	13.762	60.875	11.922
60.937	10.082	61.000	8.402	61.062	7.042	61.125	5.922	61.187	4.962
61.250	4.322	61.312	3.842	61.375	3.762	61.437	3.922	61.500	4.162
61.562	4.482	61.625	4.802	61.687	5.042	61.750	5.362	61.812	5.922
61.875	6.482	61.937	7.042	62.000	7.522	62.062	7.682	62.125	7.522
62.187	6.962	62.250	6.242	62.312	5.442	62.375	4.722	62.437	4.162
62.500	3.762	62.562	3.682	62.625	3.762	62.687	3.842	62.750	3.922
62.812	3.922	62.875	3.922	62.937	3.682	63.000	3.522	63.062	3.362
63.125	3.282	63.187	3.202	63.250	2.962	63.312	2.722	63.375	2.402
63.437	2.002	63.687	1.280	63.937	1.120	64.187	1.280	74.437	0.800

54.	2.
57.	4.
57.3	2.
57.8	.5
58.2	3.
59.4	.7
59.8	2.
60.2	.7
60.7	2.
62.	1.
62.5	.5
63.	.5

0170012002

600. 100.

DECOMPOSITION USING STANDARD DIGITAL FUNCTION

53.125	2.402	53.187	2.482	53.250	2.642	53.312	2.722	53.375	2.882
53.437	3.042	53.500	3.282	53.562	3.362	53.625	3.362	53.687	3.442
53.750	3.602	53.812	4.082	53.875	4.562	53.937	5.202	54.000	6.002
54.062	6.802	54.125	7.602	54.187	8.482	54.250	9.522	54.312	10.722
54.375	12.162	54.437	13.202	54.500	14.002	54.562	13.922	54.625	12.882
54.687	11.042	54.750	8.802	54.812	6.802	54.875	5.202	54.937	4.242
55.000	3.922	55.062	3.922	55.125	3.922	55.187	3.842	55.250	3.842
55.312	3.682	55.375	3.682	55.437	3.682	55.500	3.842	55.562	4.082
55.625	4.322	55.687	4.562	55.750	4.802	55.812	4.962	55.875	5.042
55.937	5.362	56.000	5.682	56.062	6.162	56.125	6.642	56.187	7.202
56.250	7.602	56.312	8.162	56.375	8.882	56.437	9.922	56.500	11.202
56.562	12.882	56.625	15.042	56.687	17.602	56.750	20.642	56.812	24.322
56.875	28.562	56.937	32.882	57.000	36.802	57.062	39.682	57.125	40.962
57.187	40.162	57.250	37.202	57.312	32.882	57.375	28.242	57.437	24.162
57.500	21.202	57.562	19.522	57.625	19.042	57.687	19.122	57.750	19.362
57.812	19.522	57.875	19.922	57.937	20.882	58.000	22.162	58.062	23.762
58.125	25.122	58.187	25.762	58.250	25.042	58.312	23.042	58.375	19.842
58.437	16.322	58.500	12.962	58.562	10.322	58.625	8.322	58.687	7.202
58.750	6.642	58.812	6.482	58.875	6.562	58.937	6.882	59.000	7.442
59.062	8.082	59.125	8.882	59.187	9.682	59.250	10.562	59.312	11.522
59.375	12.322	59.437	13.122	59.500	14.082	59.562	15.282	59.625	16.562
59.687	17.762	59.750	18.802	59.812	19.202	59.875	18.722	59.937	17.682
60.000	16.322	60.062	15.282	60.125	14.722	60.187	14.562	60.250	14.642
60.312	14.562	60.375	14.482	60.437	14.482	60.500	14.802	60.562	15.282
60.625	15.842	60.687	15.922	60.750	15.202	60.812	13.762	60.875	11.922

M1 = 1
THE NUMBER OF FITTING PARAMETERS = 25
THE NUMBER OF DATA POINTS = 170

N = 25 K = 0 E = 0.10000E-02 P = 0. DELTA = 0.10000E 01

0.33000E 01	0.20000E 01	0.40000E 01	0.20000E 01	0.50000E 00
0.30000E 01	0.70000E 00	0.20000E 01	0.70000E 00	0.20000E 01
0.10000E 01	0.50000E 00	0.50000E 00	0.54000E 02	0.57000E 02
0.57300E 02	0.57800E 02	0.58200E 02	0.59400E 02	0.59800E 02
0.60200E 02	0.60700E 02	0.62000E 02	0.62500E 02	0.63000E 02

F = 0.12083E 04

DECOMPOSITION USING LORENTZ SHAPE FUNCTION

F = 86.8509 IT = 83

INITIAL VALUES		FINAL VALUES	
3.300		3.107	
54.000	2.000	54.464	2.155
57.000	4.000	57.107	6.261
57.300	2.000	56.160	0.317
57.800	0.500	57.745	0.433
58.200	3.000	58.170	3.203
59.400	0.700	59.456	0.664
59.800	2.000	59.809	2.076
60.200	0.700	60.269	0.658
60.700	2.000	60.680	1.812
62.000	1.000	62.064	0.962
62.500	0.500	62.867	0.286
63.000	0.500	63.239	0.193

60.937	10.082	61.000	8.402	61.062	7.042	61.125	5.922	61.187	4.962
61.250	4.322	61.312	3.842	61.375	3.762	61.437	3.922	61.500	4.162
61.562	4.482	61.625	4.802	61.687	5.042	61.750	5.362	61.812	5.922
61.875	6.482	61.937	7.042	62.000	7.522	62.062	7.682	62.125	7.522
62.187	6.962	62.250	6.242	62.312	5.442	62.375	4.722	62.437	4.162
62.500	3.762	62.562	3.682	62.625	3.762	62.687	3.842	62.750	3.922
62.812	3.922	62.875	3.922	62.937	3.682	63.000	3.522	63.062	3.362
63.125	3.282	63.187	3.202	63.250	2.962	63.312	2.722	63.375	2.402
63.437	2.002	63.687	1.280.	63.937	1.120	64.187	1.280	74.437	0.800

54.	2.
57.	4.
57.3	2.
57.8	.5
58.2	3.
59.4	.7
59.8	2.
60.2	.7
60.7	2.
62.	1.
62.5	.5
63.	.5

020001

8.31		8.562	.25	8.812	.4	9.062	.64	9.312	.8
9.562	1.04	9.812	2.002	9.875	2.482	9.937	3.122	10.	3.922
10.062	4.722	10.125	5.202	10.187	5.282	10.25	4.802	10.312	3.842
10.37	2.722	10.625	.322	10.875	.24	13.4	.1	15.	

*** 'END-OF-FILE' CARD ***

M1 = 1
THE NUMBER OF FITTING PARAMETERS = 24
THE NUMBER OF DATA POINTS = 170

N = 24 K = 0 E = 0.10000E-02 P = 0. DELTA = 0.10000E 01

0.20000E 01	0.40000E 01	0.20000E 01	0.50000E 00	0.30000E 01
0.70000E 00	0.20000E 01	0.70000E 00	0.20000E 01	0.10000E 01
0.50000E 00	0.50000E 00	0.54000E 02	0.57000E 02	0.57300E 02
0.57800E 02	0.58200E 02	0.59400E 02	0.59800E 02	0.60200E 02
0.60700E 02	0.62000E 02	0.62500E 02	0.63000E 02	

F = 0.45956E 04

DECOMPOSITION USING STANDARD DIGITAL FUNCTION

F = 144.3512 IT = 52

INITIAL VALUES		FINAL VALUES	
54.000	2.000	54.539	3.128
57.000	4.000	57.223	5.159
57.300	2.000	56.981	2.778
57.800	0.500	57.746	2.040
58.200	3.000	58.233	4.365
59.400	0.700	59.446	0.855
59.800	2.000	59.849	2.427
60.200	0.700	60.339	1.549
60.700	2.000	60.766	2.260
62.000	1.000	62.087	1.138
62.500	0.500	62.734	0.425
63.000	0.500	63.209	0.395

END EXEC. 2036.66

796 LINES OUTPUT THIS JOB.

C. PLOT

It is highly desirable to plot the data obtained in an analysis in order to visualize how well the curves are decomposed, how well the values from DECOMP match those from NMRIT, etc. The types of data to be treated consist of the original data points, peak positions and intensities, and the curve which results from these peaks. PLOT can shift and scale any or all of these sets of data to any values desired and plot any combination of them for graphical comparison. PLOT has been written so that it is compatible with DECOMP, that is, the entire deck from DECOMP can be put directly into PLOT (after replacing the original estimates of peak positions and intensities with the results of the decomposition) and vice versa.

CARD 1 Read M, IZ (I4, I3)

M is the number of data points. The first and last data points define the length of the X-axis and at least two points must be used. When it is desired to plot only the peaks of the curve of the sum of the peaks M = 2 and the data points are 0,0 and X_2,0.

CARD 2 Read XLONG, LS, YMAX, T2, XINT, DP1, DD, DP (F8.3, I2, 7F10.3)

XLONG is the length of the X-axis in inches.

LS determines the option for the way the data is plotted. Any combination of points, peaks or curves can be chosen. The options are best described by the following array; 0 = not plotted, X = plotted.

PLOT Options

Value of LS	Data Points	Curve of the sum of peaks	Vertical lines
-1	O	O	X
1	O(end 2)*	X	O
0	X(not joined)	O	O(I=O)**
-3	X(joined)	O	O(I=O)
1	X(not joined)	X	O
-2	X(not joined)	O	X
-3	X(joined)	O	X
0	O(end 2)	X	X
0	X(not joined)	X	X

* Two points must be used to define X-axis.

** Read in one peak, IZ = 1, use arbitrary T2, and put in a blank card for the line. This gives a peak of zero intensity so no vertical lines are plotted.

YMAX is the maximum value for the Y-axis, used to scale plot in vertical direction.

T2 is the reciprocal of the half-width at half-height. If no value for T2 is given PLOT then plots the curve as a sum of the digital shape functions and this data must be read in. Again, this entire deck is identical to that from DECOMP. Problems can be mixed, since this option is exercised for each problem.

XINT scales the height of the peaks independently of the data points. This allows a direct comparison of the output from NMRIT(N) on the same plot with the experimental points. One peak is scaled with XINT so its height matches the data peak and the remaining peaks are scaled accordingly. The curve which is the sum of the peaks will then be superimposed on the data points.

DP1 is the value of the first peak in the digital data points. This value is used to shift the spectrum of lines (from NMRIT(N)) so the first line is at the first data peak.

DD is the difference between the first and n^{th} peaks in the data. DD and DP scale the line spectrum between the first and n^{th} peaks.

DP is the difference between the first and n^{th} peaks in the line spectrum.

Note: Only the desired values above are punched as input. Those values which are left black are set to zero or one so they have no effect on the plot.

CARD 3 Read TITLE (12A6)

DECK 4 X_i, Y_i, i 1,M

Data points read in format desired.

DECK 5 X_{ii}, X_i, i 1, IZ (30X,2F10.3)

Frequencies and intensities from DECOMP or NMRIT.

Last card in deck is blank and calls exit, problems can be stacked.

```
$ID    400510,PLOT,2,LUSEBRINK
$IBJOB          MAP
$IBFTC PLOT
C       PROGRAM TO PLOT EITHER SUM OF DIGITAL SHAPE OR LORENTZIAN SHAPES.
C       READ IN VALUE OF     T2 =(1/HW)    IF WANT LORENTZ, NOTHING OTHERWISE
C       HOWEVER SET OF DATA FOR DIGITAL SHAPE PEAK MUST BE PUT IN IF T2=0
C       WILL COVER RANGE OF 60 CPS
C
C
        DIMENSION X(300),TT(2200),VV(2200),T( 6000),FIT( 6000),F(150),
       1 XX(150),TITLE(12), XSTD(100), YSTD(100)
        COMMON/CCPOOL/XMIN,XMAX,YMIN,YMAX,CCXMIN,CCXMAX,CCYMIN,CCYMAX
        CALL CCBGN
 10     READ (2,7) M,IZ
        IF (M.EQ.0) CALL CCEND
        IF(M .EQ.0) CALL EXIT
        READ(2,3) XLONG,LS,YMAX,T2,XINT,DP1,DD,DP
        T2=T2*.01
        XLONG=XLONG*100.
        READ(2,4)(TITLE(I),I=1,12)
        WRITE (3,4) TITLE
        READ (2,2) (TT(I),VV(I),I=1,M)
        DO 15 I=1,M
 15     TT(I)=(TT(I)+SHFTX)*100.
        N = 2*IZ
        IF(DD)29,29,26
 29     FM=1.
        GO TO 32
 26     FM =DD/DP
 32     IF(XINT) 27,27,28
 27     XINT =1.
 28     DO 67 I=1,IZ
        II=I+IZ
        READ (2,5) X(II), X(I)
        X(I) = X(I)*XINT
 67     X(II) = X(II)*FM*100.
        III=1+IZ
        IF (DP1) 33,33,34
 34     SHFT=DP1-X(III)
        GO TO 35
 33     SHFT =0.
 35     DO 68 I=1,IZ
        II=I+IZ
        X(II)=(X(II)+SHFT)
 68     WRITE(3,6) X(II),X(I),TT(I)
        IF (T2) 16,16,17
 17     IF (LS.LT.0) GO TO 43
        T(1)=TT(1)
        I=TT(1)
        J=TT(M)
        L=((J-I)/5)+1
        DO 42 K=1,L
        FI =0.
        DO 31 I=1,IZ
        II =I+IZ
        Z=T(K)-X(II )
        Y = T2*Z
```

```
      RECIP = 1./(1.+Y*Y)
31    FI = FI+200.*T2*X(I   )*RECIP
      FIT(K)=FI
42    T(K+1)=T(K)+5.
      GO TO 43
16    READ (2,1) MSTD ,LST
      READ (2,2) (XSTD(I),YSTD(I), I=1,MSTD)
      DD= YSTD(1)
      EE = XSTD(1)
      DO 25 I=1,MSTD
      XSTD(I) =(XSTD(I) - EE)*100.
25    YSTD(I) =YSTD(I) - DD
      DO 40 J=LST,MSTD
      IF(YSTD(J+1)-YSTD(J)) 30,40,40
30    RESSTD = XSTD(J)
      IM=J
      WIDEL= RESSTD-XSTD(1)
      WIDER = XSTD(MSTD) - RESSTD
      YRESTD = YSTD(J)
      GO TO 20
40    CONTINUE
20    IF (LS.LT.0) GO TO 43
      T(1)=TT(1)
      I=TT(1)
      J=TT(M)
      L=((J-I)/2)+1
      DO 41 K=1,L
      FI = 0.
      DO 55 I=1,IZ
      II = I+IZ
      SHIFT = X(II) - RESSTD
      IF (T(K)-(X(II)-WIDEL))60,70,70
60    Y=0.
      GO TO 50
70    IF (T(K) -(X(II)+WIDER)) 80,80,65
65    Y=0.
      GO TO 50
80    IF(X(II)-T(K)) 90,100,110
100   Y     = YRESTD*X(I)
      GO TO 50
90    IA = IM
95    IF(XSTD(IA) + SHIFT-T(K)) 96,97,97
96    IA =IA+1
      GO TO 95
97    Y= X(I) *(YSTD(IA)+((XSTD(IA)+SHIFT-T(K))*(YSTD(IA-1)-YSTD(IA)))/
     1 (XSTD(IA)-XSTD(IA-1)))
      GO TO 50
110   IN = IM
111   IF(XSTD(IN) + SHIFT-T(K)) 120,120,115
115   IN = IN-1
      GO TO 111
120   Y= X(I) *(YSTD(IN+1)-((XSTD(IN+1)+SHIFT-T(K))* (YSTD(IN+1)-
     1 YSTD(IN)))/(XSTD(IN+1)-XSTD(IN)))
      GO TO 50
50    FI = FI + Y
55    CONTINUE
      T(K+1) = T(K) +2.
```

```
41    FIT(K)=FI
43    XMIN=TT(1)
      XMAX=TT(M)
      YMIN=0.
      CCXMIN=0.
      CCXMAX =XLONG/1024.
      CCYMIN =100./1024.
      CCYMAX=1000./1024.
      CALL CCGRID(1,6HNOLBLS,1)
      IF(LS+1) 178,77,178
178   IF(LS+2) 179,176,179
179   IF (LS+3) 180,177,180
180   CALL CCPLOT(T,FIT,L,4HJOIN,0,0)
176   CALL CCPLOT(TT,VV,M,6HNOJOIN,1,1)
      GO TO 181
177   CALL CCPLOT (TT,VV,M,4HJOIN,0,0)
181   IF(LS.GT.0) GO TO 66
77    IF(T2) 62,62,63
62    DO 61 I=1,IZ
      II = I+IZ
      F(1) =X(I)*YRESTD
      F(2)=YMIN
      XX(1)=X(II)
      XX(2)=X(II)
61    CALL CCPLOT(XX,F,2,4HJOIN,0,0)
      GO TO 66
63    DO 64 I=1,IZ
      II =I+IZ
      F(1) = 200. * T2* X(I)
      F(2)=YMIN
      XX(1)=X(II )
      XX(2)=X(II )
64    CALL CCPLOT(XX,F,2,4HJOIN,0,0)
66    CALL CCNEXT
      GO TO 10
1     FORMAT (10I3)
02    FORMAT (10F8.0)
3     FORMAT(F8.3,I2,7F10.3)
4      FORMAT(12A6)
5     FORMAT (30X,2F10.3)
6     FORMAT(8F15.3)
7     FORMAT (I4,I3)
      END
```

D. ASSIGN

The theory of ASSIGN was described in the text; the input details, a listing, and a sample problem will be given below. The dimensions have been set somewhat arbitrarily, a maximum of nine assignments is made, to prevent an excessive number of assignments if the limits are set too wide. Other limits in the present program are; 200 lines, 50 types of transitions, and 64 energy levels.

CARD 1 Read LIN, LINO, LEN, LEU, NU, IREAD, ICOUNT (10I3)

LIN is the number of lines to be assigned.

LINO is the number of experimental lines from spectrum.

LEN is the number of energy levels for the molecule.

LEU is the number of energy levels used in the assignment.

NU is the number of types of transitions.

IREAD chooses input format for lines;=0 for 8X,2F10.3, $\neq$ 0 for 30X,2F10.3.

ICOUNT is used as a diagnostic or for problems which may run overtime and thus not yield any information. ICOUNT = N prints out every N^{th} assignment and allows one to follow the progress of assignments. If N = 0, only the complete assignments are printed.

CARD 2 TITLE (12A6)

DECK 3 X,Y Frequencies and intensities, one set per card, according to format selected by IREAD above.

CARD 4 LXT_i, k = 1, LINO (80I1)

When information from double resonance experiment is available, punch 1 in columns corresponding to the lines observed, which have common energy levels to be read in.

If no double resonance information is put in, use a blank card.

DECK 5 Read IB_{ij}, IE_{ij}, j = 1,10; i = 1, LINO (25I3)

This deck contains the array of ranges for lines with energy levels in common with line i. IB is the number of the first line and IE is the last line in the range; for one line IB = IE. i is the number of the lines for which $LXT_i = 1$ and j is the number of ranges, arbitrarily limited to ten. If all $LXT_i = 0$, no cards are used in this deck.

CARD 6 Read LX_i, i = 1, LINO (80I1)

This card designates which lines have been assigned in a previous part of the problem, i.e. another symmetry group. LX = 1 for lines which have already been assigned and 0 for those lines available for assignment. If no lines have previously been assigned, insert a blank card. A card containing the LX_i for each assignment is punched for use in successive problems.

DECK 7 Read MIN_i, MAX_i i =1, NU (2I3)

MIN is the lowest number and MAX is the highest number of the lines in the range of transition type, i.

CARD 8 DX, DI (2F10.5)

DX is the frequency limit and DI the intensity limit to be used for fitting the sum rules. These values should be approximately the estimated experimental error.

DECK 9 Read SI_j, j = 1, LEN (8F10.5)

The SI_j are the values from the intensity sum rules ($2M_z$) to be used for each energy level.

CARD 10 Read LEV_j, j = 1, LEU (25I3)

The LEV_j are the numbers of the energy levels actually used in the algorithm. These levels are used for ordering and comparing assignments to avoid duplicate assignments.

CARD 11 Read JT_j, j = 1, LIN (25I3)

The JT_j are the types of transitions.

CARD 12 Read ICU_j, j = 1, LIN (25I3)

The ICU_j are the upper energy levels of a transition. If all the theoretical transitions to and from an energy level have been used in the algorithm, a minus sign in front of the last ICU in such a transition indicates that an intensity sum rule check is to be made for that energy level.

CARD 13 Read ICL_j, j = 1, LIN (25I3)

The ICL_j are the lower energy levels of the transition, j. An intensity sum rule check is made in the same manner as for ICU.

CARD 14 Read IFC_j, j = 1, LIN (80I1)

IFC_j 1 is a frequency check is to make for a closed frequency loop.

Problems can be stacked, last card in entire deck is blank to call exit.

```
$IBFTC ASSIGN
C
C
      DIMENSION TITLE(12),X(200),Y(200),MIN(50),MAX(50),EN(64),
     1ER(10,64 ),K(200),JT(200), IFC(200), ICU(200), ICL(200),
     2LEV(64),  SI( 64),MA(200,10),IB(200,10),IE(200,10),LXT(200),
     3 IAT(40),EMO(64), LX(200)
 20   READ(2,100)LIN,LINO,LEN,LEU,NU,IPUNCH,IREAD,ICOUNT
      IF(LIN.EQ.0) CALL EXIT
      READ (2,101) (TITLE (I),I=1,12)
      WRITE (3,111) TITLE
      WRITE  (3,112)
      DO 38 I=1,LINO
      IF(IREAD.EQ.0) READ(2,129) X(I),Y(I)
 38   IF(IREAD.NE.0) READ(2,125) X(I),Y(I)
      LINT=0
      READ(2,126) (LXT(I),I=1,LINO)
      DO 39 I=1,LINO
      IF (LXT(I).EQ.0) GO TO 37
      READ(2,103) (IB(I,J), IE(I,J),J=1,10)
      WRITE(3,113) I,X(I) , Y(I),(IB(I,J),IE(I,J),J=1,10)
      GO TO 39
 37   WRITE (3,113) I,X(I),Y(I)
      LINT=LINT+1
      IB(I,1)=0
 39   CONTINUE
      READ (2,126) (LX(I), I=1,LINO)
      WRITE (3,127) (I,I=1,LINO)
      WRITE (3,128) (LX(I), I=1,LINO)
      DO 19 I=1,NU
      READ (2,100) MIN(I),MAX(I)
 19   WRITE (3,117)  I, MIN(I),MAX(I)
      READ (2,102) DX,DI
      WRITE (3,118)  DX,DI
      READ (2,102) (SI(J),J=1,LEN)
      READ(2,103) (LEV(J),J=1,LEU)
      WRITE (3,119)
      WRITE (3,120) (I,I=1,LEN)
      WRITE (3,121) (SI(I), I=1,LEN)
      READ (2,103) (JT (J), J=1,LIN)
      READ (2,103) (ICU(J), J=1,LIN)
      READ (2,103) (ICL(J), J=1,LIN)
      READ (2,126) (IFC(J), J=1,LIN)
      WRITE (3,114)
      WRITE (3,115)
      DO 40 I=1,LIN
      DO 55 J=1, 10
 55   MA(I,J) =0.
 40   WRITE (3,116) I,JT(I), ICU(I),ICL(I),IFC(I)
      I4=1
      LD=1
      NOTR =1
      ICO=0
      NO = 0
      DO 32 I=1,LEN
 32   EN(I)=0.
```

```
C       300 SERIES STATEMENTS CAUSE SEARCH FOR LINES ONLY OVER THOSE
C       LINES WHICH HAVE COMMON ENERGY LEVELS AS DETERMINED BY DOUBLE
C       RESONANCE EXPTS.  IB=ARRAY FOR BEGINNING OF RANGE ABOUT
C       LINE PERTURBED, IE=END OF RANGE
        J = 1
        GO TO 309
 1      JA=J-1
        IF(J.EQ.1) GO TO 307
        IF(LINT.EQ.LINO) GO TO 310
        I1=1
        DO 302 IA=1,JA
        IF(IABS(ICU(J)).EQ.IABS(ICU(IA)).OR.IABS(ICU(J)).EQ.IABS
       1  (ICL(IA))) GO TO 308
        IF(IABS(ICL(J)).EQ.IABS(ICU(IA)).OR.IABS(ICL(J)).EQ.IABS
       1  (ICL(IA))) GO TO 308
        GO TO 302
 308    IAT(I1)=IA
        I1=I1+1
 302    CONTINUE
        I3=I1-1
 310    IF(JCN-J) 309,309,307
 309    KT = IABS(JT(J))
        I = MIN(KT)-1
 301    I=I+1
 307    IF(I.GT.MAX(KT)) GO TO 12
        IF(LX(I).EQ.1) GO TO 301
        IF(J.EQ.1) GO TO 9
        IF(LINT.EQ.LINO) GO TO 13
        DO 303 I2=1,I3
        KCD=IAT(I2)
        KC=K(KCD)
        DO 304 KA=1,10
        IX=IB(KC,KA)
        IF(IX.EQ.0) GO TO 303
        IY=IE(KC,KA)
        DO 306 KB=IX,IY
        IF(LX(KB).EQ.1)  GO TO 306
        IF(I-KB) 305,303,306
 306    CONTINUE
 304    CONTINUE
 305    I=KB
        GO TO 307
 303    CONTINUE
 13     IF (LX(I)) 9,9,14
 9      ME = IABS(ICU(J))
        LE = IABS(ICL(J))
        SI(ME) = SI(ME) - Y(I)
        SI(LE) = SI(LE)+Y(I)
        IF(IFC(J)) 3,3,2
 3      IF(ICU(J)) 4,5,5
 5      IF(ICL(J)) 10,6,6
 2      IF(ABS(X(I)+EN(ME)-EN(LE))-DX) 3,3,7
 4      IF (ABS(SI(ME))-DI) 5,5,7
 10     IF(ABS(SI(LE))-DI) 6,6,7
 6      K(J) = I
        LX(I) = 1
```

```
      MA(J,NO+1) = I
      IF(JT(J)) 52,52,53
52    EN(ME) = EN(LE)-X(I)
      GO TO 54
53    EN(LE) = EN(ME) + X(I)
54    J = J+1
      JCN=J-1
      IF(ICOUNT.EQ.0) GO TO 11
      ICO    =ICO    +1
      IF(ICO.LT.ICOUNT) GO TO 11
      WRITE(3,123)  (MA(IJ,NO+1),IJ=1,JCN)
      ICO=1
11    IF(LIN-J) 21,1,1
7     SI(ME) = SI(ME)+Y(I)
      SI(LE) = SI(LE) -Y(I)
14    I=I+1
15    IF(I-MAX(KT))  307,307,12
12    LDU =LINO+LD
      IF(LDU-LIN) 35,35,34
35    I=LDU
      X(I) = EN(LE)-EN(ME)
      Y(I) =0.
      LD=LD+1
      GO TO 6
34    J=J-1
      JCN=J+1
56    IF(J      ) 17,17,16
17    IF (NO) 45,45,31
45    WRITE (3,110) TITLE
46    GO TO 31
16    IF(K(J)-LINO) 43,43,41
41    LD = LD-1
      I = K(J)
      LX(I) = 0
      J=J-1
      JCN=J+1
      GO TO 16
43    I=K(J) +1
      LX(I-1) =0
      ME=IABS(ICU(J))
      LE=IABS(ICL(J))
      SI(ME)= SI(ME)+Y(I-1)
      SI(LE)= SI(LE)-Y(I-1)
      KT = IABS(JT(J))
      GO TO 1
21    IF(NO- 9 ) 50,31,31
50    NO = NO+1
C     200 SERIES STATEMENTS ORDER ENERGY LEVELS USED IN PROB AND
C     COMPARE THEM.  LEU=ENERGY LEVELS USED, LEV=NO OF LEU, ENO=ENERGY
C     LEVELS ORDERED
      DO215 IEN=1,LEU
      IG=LEV(IEN)
215   ENO(IEN)=EN(IG)
200   MN=0
      DO 201 IO=2,LEU
      IF(ENO(IO-1)-ENO(IO)) 202,201,201
```

```
108  FORMAT (15H0 ENERGY LEVELS)
109  FORMAT (1H I3,F10.4)
110  FORMAT (15H NO ASSIGNMENT 12A6)
111  FORMAT (1H1//////13H INPUT DATA--12A6)
112  FORMAT (92H0    LINE NO.    OBS. FREQ.    OBS. INT.
    1       LINES WITH COMMON ENERGY LEVELS)
113  FORMAT (1H 6X,I3,6X,F9.3,5X,F9.3,10X,20I4)
114  FORMAT(1H0//46H      TRANSITION      ENERGY LEVEL      FREQUENCY)
115  FORMAT (44H        NO.  TYPE       UPPER LOWER        CHECK)
116  FORMAT (1H 5X,I3,3X,I3,6X,I3,3X,I3,7X,I3)
117  FORMAT (23H0 THE RANGE OF NUCLEUS I3,4H IS I3,3H - I3)
118  FORMAT (29H0 UNCERTAINTY IN FREQUENCY = F5.3,17H, IN INTENSITY = F
    15.3)
119  FORMAT (32H0 VALUES FOR INTENSITY SUM RULES)
120  FORMAT (19H0ENERGY LEVEL       22(I4,1X))
121  FORMAT (19H SUM OF INTENSITIES22(F5.2))
123  FORMAT  (1H 44I3)
124  FORMAT (1H1//////20X,17HASSIGNMENTS FOR--12A6)
125  FORMAT (30X,2F10.3)
126  FORMAT (80I1)
127  FORMAT (6H0LINE 62I2)
128  FORMAT (6H LX(I)62I2)
129  FORMAT(8X,2F10.3)
130  FORMAT(2I4,2F10.3)
     END
```

```
202   AE=ENO(IO)
      ENO(IO)=ENO(IO-1)
      ENO(IO-1)=AE
      MN=1
201   CONTINUE
      IF(MN) 203,203,200
203   IF(NO.EQ.1) GO TO 206
      NOO=NO-1
      INV=1
209   DO 204 IC=1,NOO
      DO 205 ID=1,LEU
      IF(ER(IC,ID).NE.ENO(ID)) GO TO 204
205   CONTINUE
      GO TO 211
204   CONTINUE
      IF(INV.NE.1) GO TO 210
206   DO 207 IBT=1,LEU
207   ER(NO,IBT)= ENO(IBT)
      IF(NO.EQ.1) GO TO 210
      DO 208 IET =1,LEU
208   ENO(IET)= ENO(LEU)-ENO(IET)
      INV=-1
      GO TO 209
211   NO=NO-1
      GO TO 213
210   WRITE (3,105) TITLE
      WRITE (3,104) NO
      WRITE (3,106)
      WRITE(14,126)(LX(JZ),JZ=1,LINO)
      DO 22 L=1,LIN
      LL=K(L)
      ME = IABS(ICU(L))
      LE = IABS(ICL(L))
      IF(IPUNCH.NE.0) WRITE(14,130) ME,LE,X(LL),Y(LL)
22    WRITE (3,107) L,ME,     LE,      X(LL), Y(LL)
      WRITE (3,108)
      DO 23 IME = 1,LEN
23    WRITE (3,109) IME,EN(IME)
213   N = JT(1)
      IF (K(1)-MAX(N)) 33,33,31
33    LX(I) =0
      J=LIN
      GO TO 7
31    WRITE (3,124) TITLE
      DO 48 MC=1,NO
48    WRITE (3,123) MC,(MA(MB,MC), MB=1    ,LIN)
      GO TO 20
100   FORMAT (10I3)
101   FORMAT (12A6)
102   FORMAT (8F10.5)
103   FORMAT (25I3)
104   FORMAT(1H037X,15H ASSIGNMENT NO.I3)
105   FORMAT (1H1//////30X,12A6)
106   FORMAT (62H0   LINE    TRANSITION          FREQUENCY                IN
     1TENSITY)
107   FORMAT (3H    I4,I9,2H -I3,2F19.3)
```

```
015015008008004     1
 THREE NUCLEI ABC EXAMPLE PROBLEM
                                        -10.6        .016
                                         0.0         .319
                                        3.96         .231
                                        11.02        .062
                                        14.99        .94
                                        15.93        .243
                                        19.89        2.618
                                        21.78        3.33
                                        25.59        2.589
                                        25.74        .18
                                        30.49        .655
                                        36.34        .205
                                        41.52        .281
                                        47.37        .083
                                        52.22        .202

   1 10
   1 15
   5 15
   1 15
 .1          .1
3.          1.          1.          1.         -1.         -1.         -1.         -3.
   1  2  3  4  5  6  7  8
   1  2  3  3  1  3  2  1  2  2  1  3  4  4  4
   1  1 -1  2  4  3  4  5  6  2  3  7 -4 -3 -2
   2  3  4  6  6  5  5  8  8  7  7 -8  7 -6 -5
      1 1 1 11111
                          *** 'END-OF-FILE' CARD ***
```

```
015015008008004     1
 THREE NUCLEI ABC SIMULATED DOUBLE RESONANCE EXPT  EXAMPLE PROBLEM
                                        -10.6       .016
                                         0.0        .319
                                        3.96        .231
                                        11.02       .062
                                        14.99       .94
                                        15.93       .243
                                        19.89       2.618
                                        21.78       3.33
                                        25.59       2.589
                                        25.74       .18
                                        30.49       .655
                                        36.34       .205
                                        41.52       .281
                                        47.37       .083
                                        52.22       .202
111111111111111
  3  3  5  5  6  6  8  8  9  9 15 15
  4  4  5  5  9  9 13 13 14 14
  1  1  4  4  5  5 11 11 12 12 15 15
  2  2  3  3  9  9 11 11 12 12
  1  1  2  2  3  3 13 13 14 14 15 15
  1  1  8  8  9  9 10 10 11 11 13 13
  8  8 10 10 12 12 14 14 15 15
  1  1  6  6  7  7  9  9 12 12 14 14
  1  1  2  2  4  4  6  6  8  8
  6  6  7  7 11 11 13 13 15 15
  3  3  4  4  6  6 10 10 12 12 13 13
  3  3  4  4  7  7  8  8 11 11 14 14
  2  2  5  5  6  6 10 10 11 11 14 14
  2  2  5  5  7  7  8  8 12 12 13 13
  1  1  3  3  5  5  7  7 10 10

  1 10
  1 15
  5 15
  1 15
.1          .1
3.          1.          1.          1.          -1.         -1.         -1.         -3.
  1  2  3  4  5  6  7  8
  1  2  3  3  1  3  2  1  2  2  1  3  4  4  4
  1  1 -1  2  4  3  4  5  6  2  3  7 -4 -3 -2
  2  3  4  6  6  5  5  8  8  7  7 -8  7 -6 -5
     1 1 1 11111
```

INPUT DATA-- THREE NUCLEI ABC EXAMPLE PROBLEM

LINE NO.	OBS. FREQ.	OBS. INT.	LINES WITH CO
1	-10.600	0.016	
2	0.	0.319	
3	3.960	0.231	
4	11.020	0.062	
5	14.990	0.940	
6	15.930	0.243	
7	19.890	2.618	
8	21.780	3.330	
9	25.590	2.589	
10	25.740	0.180	
11	30.490	0.655	
12	36.340	0.205	
13	41.520	0.281	
14	47.370	0.083	
15	52.220	0.202	

LINE 1 2 3 4 5 6 7 8 9101112131415
LX(I)-0-0-0-0-0-0-0-0-0-0-0-0-0-0-0

THE RANGE OF NUCLEUS 1 IS 1 - 10

THE RANGE OF NUCLEUS 2 IS 1 - 15

THE RANGE OF NUCLEUS 3 IS 5 - 15

THE RANGE OF NUCLEUS 4 IS 1 - 15

UNCERTAINTY IN FREQUENCY = 0.050, IN INTENSITY = 0.100

VALUES FOR INTENSITY SUM RULES

ENERGY LEVEL	1	2	3	4	5	6	7	8
SUM OF INTENSITIES	3.00	1.00	1.00	1.00	-1.00	-1.00	-1.00	-3.00

TRANSITION NO.	TYPE	ENERGY LEVEL UPPER	LOWER	FREQUENCY CHECK
1	1	1	2	-0
2	2	1	3	-0
3	3	-1	4	-0
4	3	2	6	-0
5	1	4	6	1
6	3	3	5	-0
7	2	4	5	1
8	1	5	8	-0
9	2	6	8	1
10	2	2	7	-0
11	1	3	7	1
12	3	7	-8	1
13	4	-4	7	1
14	4	-3	-6	1
15	4	-2	-5	1

INPUT DATA-- THREE NUCLEI ABC SIMULATED DOUBLE RESONANCE EXPT EXAMPLE PROBLEM

LINE NO.	OBS. FREQ.	OBS. INT.	LINES WITH COMMON ENERGY LEVELS											
1	-10.600	0.016	3	3	5	5	6	6	8	8	9	9	15	15
2	0.	0.319	4	4	5	5	9	9	13	13	14	14	-0	-0
3	3.960	0.231	1	1	4	4	5	5	11	11	12	12	15	15
4	11.020	0.062	2	2	3	3	9	9	11	11	12	12	-0	-0
5	14.990	0.940	1	1	2	2	3	3	13	13	14	14	15	15
6	15.930	0.243	1	1	8	8	9	9	10	10	11	11	13	13
7	19.890	2.618	8	8	10	10	12	12	14	14	15	15	-0	-0
8	21.780	3.330	1	1	6	6	7	7	9	9	12	12	14	14
9	25.590	2.589	1	1	2	2	4	4	6	6	8	8	-0	-0
10	25.740	0.180	6	6	7	7	11	11	13	13	15	15	-0	-0
11	30.490	0.655	3	3	4	4	6	6	10	10	12	12	13	13
12	36.340	0.205	3	3	4	4	7	7	8	8	11	11	14	14
13	41.520	0.281	2	2	5	5	6	6	10	10	11	11	14	14
14	47.370	0.083	2	2	5	5	7	7	8	8	12	12	13	13
15	52.220	0.202	1	1	3	3	5	5	7	7	10	10	-0	-0

```
LINE  1 2 3 4 5 6 7 8 9101112131415
LX(I)-C-0-0-C-C-0-0-0-0-0-0-C-0-0-0
```

THE RANGE OF NUCLEUS 1 IS 1 - 10

THE RANGE OF NUCLEUS 2 IS 1 - 15

THE RANGE OF NUCLEUS 3 IS 5 - 15

THE RANGE OF NUCLEUS 4 IS 1 - 15

UNCERTAINTY IN FREQUENCY = 0.050, IN INTENSITY = 0.100

VALUES FOR INTENSITY SUM RULES

ENERGY LEVEL	1	2	3	4	5	6	7	8
SUM OF INTENSITIES	3.00	1.00	1.00	1.00	-1.00	-1.00	-1.00	-3.00

TRANSITION NO.	TYPE	ENERGY LEVEL UPPER	LOWER	FREQUENCY CHECK
1	1	1	2	-0
2	2	1	3	-0
3	3	-1	4	-0
4	3	2	6	-0
5	1	4	6	1
6	3	3	5	-0
7	2	4	5	1
8	1	5	8	-0
9	2	6	8	1
10	2	2	7	-0
11	1	3	7	1
12	3	7	-8	1
13	4	-4	7	1
14	4	-3	-6	1
15	4	-2	-5	1

THREE NUCLEI ABC EXAMPLE PROBLEM

ASSIGNMENT NO. 1

LINE	TRANSITION	FREQUENCY.	INTENSITY
1	1 - 2	0.	0.319
2	1 - 3	11.020	0.062
3	1 - 4	25.590	2.589
4	2 - 6	41.520	0.281
5	4 - 6	15.930	0.243
6	3 - 5	36.340	0.205
7	4 - 5	21.780	3.330
8	5 - 8	19.890	2.618
9	6 - 8	25.740	0.180
10	2 - 7	14.990	0.940
11	3 - 7	3.960	0.231
12	7 - 8	52.220	0.202
13	4 - 7	-10.600	0.016
14	3 - 6	30.490	0.655
15	2 - 5	47.370	0.083

ENERGY LEVELS

1	0.
2	0.
3	11.0200
4	25.5900
5	47.3700
6	41.5100
7	14.9900
8	67.2000

THREE NUCLEI ABC SIMULATED DOUBLE RESONANCE EXPT EXAMPLE PROBLEM

ASSIGNMENT NO. 1

LINE	TRANSITION	FREQUENCY	INTENSITY
1	1 - 2	0.	0.319
2	1 - 3	11.020	0.062
3	1 - 4	25.590	2.589
4	2 - 6	41.520	0.281
5	4 - 6	15.930	0.243
6	3 - 5	36.340	0.205
7	4 - 5	21.780	3.330
8	5 - 8	19.890	2.618
9	6 - 8	25.740	0.180
10	2 - 7	14.990	0.940
11	3 - 7	3.960	0.231
12	7 - 8	52.220	0.202
13	4 - 7	-10.600	0.016
14	3 - 6	30.490	0.655
15	2 - 5	47.370	0.083

ENERGY LEVELS

1	0.
2	0.
3	11.0200
4	25.5900
5	47.3700
6	41.5100
7	14.9900
8	67.2000

E. Miscellaneous Computer Programs

1. BLINE

As mentioned under DECOMP, it is convenient to have the ranges of requencies and intensities within ranges of 0 - 100 and 0 - 50 respectively. Since raw digital data is usually not suitable for direct introduction into DECOMP, a simple program, BLINE, was written to perform various manipulations upon the original data to make it more suitable for DECOMP and PLOT.

Input data cards:

CARD 1 Read M, MA, MC, IPUNCH (5I1)

$M \neq 0$ if problem follows

MA allows choice of two input data formats, MA = 1 for format 1, MA $\neq$ 1 for format 2. All output data is standard.

MC designates the number of points to be skipped below a level read in as BL. If no points are to be skipped, MC = 0, skip 1 point, MC = 1, etc.

IPUNCH equals 0 if data not to be punched on cards, unequal to 0 for data to be punched.

CARD 2 Read BL, SCALEX, SCALEY, T2 (10F8.3)

BL is the level below which MC points are skipped. If the points along the base line are too dense because sufficient density was desired near the peak maxima, this option will allow as many of the lower points to be discarded as desired. If the entire spectrum is too dense BL > the maximum peak will skip points all through the spectrum. N.B., the value of BL must correspond to the values of the

data points <u>after</u> the values of X_1, Y_1 have been subtracted.

SCALEX and SCALEY are the multiplicative factors to change the respective ranges of the raw data to the desired ranges. To invert data points for plotting SCALEX can be -. If the fields are left blank, SCALEX and SCALEY are set to 1.

T2 In order to use DECOMP, one must estimate peak positions and intensities from the spectrum for initial estimates as described under DECOMP. BLINE will search for all maxima and left shoulders and calculate the intensities, using the value of T2 which is obtained from the spectrum and would be used in the manual calculation. These values are printed out after the data points and punched on cards in the correct format for direct insertion into DECOMP. Small noise peaks are also given but these can be discarded. Right shoulders were not calculated because they cannot be distinguished from some minima, with the 3 point comparison used. The program is arbitrarily dimensioned to 200 peaks. If T2 = 0 this part of the program is skipped.

CARD 3 TITLE (12A6)

DATA DECK Data points are read in as X_i, Y_i using format convenient to user. Last card in data deck is blank so the program can detect end of data points, since the number of points is not read in. The number of data points in the final deck is printed out.

```
$IBFTC BLINE
C       PROGRAM TO SHIFT BASELINE TO 0 AND ADJUST INTENSITY.  CAN ALSO
C       ELIMINATE ANY NO OF DESIRED POINTS BELOW A GIVEN VALUE.  NO OF
C       NO OF DATA POINTS DOES NOT NEED TO BE READ IN BUT MUST BE GT 0
        DIMENSION TITLE(12),X(3000),Y(3000),XIN(200),YIN(200)
 1      READ (2,100) M,MA,MC,IPUNCH
        IF(M.EQ.0) CALL EXIT
        READ(2,109) BL,SCALEX,SCALEY,T2
        IF(SCALEX.EQ.0.)SCALEX =1.
        IF(SCALEY.EQ.0.)SCALEY =1.
        READ(2,101)(TITLE(I),I=1,12)
        WRITE (3,103) TITLE
        IF(MA.EQ.1) GO TO 8
        DO 10 J=1,3000,5
        K=J+4
        READ(2,102)(X(I),Y(I),I=J,K)
        IF (X(J+1).EQ.0.) GO TO 9
 10     CONTINUE
 8      DO 11 J=1,3000,8
        K=J+7
        READ(2,105)(X(I),Y(I),I=J,K)
        IF (X(J+1).EQ.0.) GO TO 9
 11     CONTINUE
 9      M=J-1
        YA=Y(1)
        XA=X(1)
        DO 2 I=1,M
        X(I)=(X(I)-XA)*SCALEX
 2      Y(I)=(Y(I)-YA)*SCALEY
        J=2
        I=2
 3      IF(Y(I).GT.BL) GO TO 4
        I=I+MC
 4      X(J)=X(I)
        Y(J)=Y(I)
        J=J+1
 5      I=I+1
        IF(I.GE.M) GO TO 6
        GO TO 3
 6      K=J-1
        WRITE(3,102)(X(I),Y(I),I=1,K)
        WRITE(3,104) K
        IF(IPUNCH.NE.0) WRITE(14,102) (X(I),Y(I),I=1,K)
        IF(T2.EQ.0.) GO TO 1
        KX=1
        MK=M-1
        DO 771I=2,MK
        IF( Y(I).GT.Y (I-1).AND.Y (I).GE.Y (I+1)) GO TO 773
        GO TO 771
 773    XIN(KX)=X(I)
        YIN(KX)=Y(I)/(2.*T2)
        KX=KX+1
 771    CONTINUE
        IZ=KX-1
        WRITE (3,106) (XIN(I),YIN(I),I=1,IZ)
        IF(IPUNCH.NE.0) WRITE(14,107) T2
        IF(IPUNCH.NE.0) WRITE(14,108) (XIN(I),YIN(I),I=1,IZ)
```

```
      GO TO 1
100   FORMAT(5I1)
101   FORMAT (12A6)
102   FORMAT (10F8.3)
103   FORMAT (1H1//////12A6)
104   FORMAT(16HONO. OF POINTS =I4)
105   FORMAT (16F5.3)
106   FORMAT (2F10.3)
107   FORMAT(20X,F10.3)
108   FORMAT (30X,2F10.3)
109   FORMAT (8F10.3)
      END
                    *** 'END-OF-FILE' CARD ***
```

2. SCALE

SCALE is a program which scales the frequencies from the arbitrary values obtained in DECOMP to the frequency values obtained with the spectrometer and normalizes the intensities to $n2^{n-1}$ so intensity sum rules can be applied. The program will linearly expand or contact the spectrum and shift it to any values desired. The scaled lines are then printed and punched on cards in one of two formats. Up to 10 spectra can be averaged if desired.

Input data cards:

CARD 1 Read JS, NS, NN, M, IOUT (9I3)

JS is the number of spectra to be read in and averaged. JS = 1 to 10.

NS is the total number of spins in the system used for normalization, i.e. $NS(2)^{NS-1}$.

NN is the number of spins in the part of the spectrum which is being scaled. If the X part of the A_2B_2X spectrum is being scaled; NN = 1, NS = 5.

M is the number of peaks to be scaled. If more than one set is to be averaged, M must be the same for all sets.

IOUT allows a choice of formats to be punched on cards. (see listing.)

Note: If more than one set of lines is to be averaged, only the following cards are to be repeated in the problem.

CARD 2 Read TITLE (12A6)

CARD 3 Read DCPS, SHIFT (2F10.3)

DCPS is the difference in values desired between the first and last peaks. All other peaks are scaled proportionally between.

SHIFT is the value desired for the first peak.

DECK 4 Read FREQ, PINT (30X,2F10.3)

This deck consists of the frequencies and intensities of the lines, one set per card, which are output from DECOMP.

```
$IBFTC SCALE
C       THIS PROGRAM SCALES DIGITAL DATA TO SPECTROMETER DATA BY ADJUSTING
C        FREQUENCIES TO UNITS OF CPS AND BY NORMALIZING INTENSITIES.  IT
C       THEN AVERAGES UP TO 10 DIFFERENT SPECTRA.
        DIMENSION FREQ(10,200),PINT(10,200),TITLE(12)
   60   READ(2,1) JS,NS,NN,M,IOUT
        IF(NS.EQ.0) CALL EXIT
        FJS = JS
        KI = NS*2**(NS-1)
        HI = NN*KI/NS
        DO 10 I=1,JS
        READ (2,2) (TITLE(J),J=1,12)
        READ (2,3) DCPS,SHIFT
        READ (2,4) (FREQ(I,J),PINT(I,J),J=1,M)
        SI=0.
        DO 20 J=1,M
   20   SI=PINT(I,J)+SI
        FM = DCPS/(FREQ(I,M)-FREQ(I,1))
        FRI = FREQ(I,1)
        DO 30 J=1,M
        FREQ(I,J) = (FREQ(I,J)-FRI)*FM+SHIFT
   30   PINT(I,J) = PINT(I,J)*HI/SI
        WRITE (3,5) (TITLE(J),J=1,12)
        IF(JS.GT.1) GO TO 10
        IF(IOUT.EQ.0) WRITE(14,9 ) (FREQ(I,J),PINT(I,J),J=1,M)
        IF(IOUT.NE.0) WRITE(14,4 ) (FREQ(I,J),PINT(I,J),J=1,M)
10      WRITE (3,6) (FREQ(I,J),PINT(I,J),J=1,M)
        IF (JS.EQ.1) GO TO 60
        DO 40 J=1,M
        DO 40 I=2,JS
        FREQ(1,J) = FREQ(1,J)+FREQ(I,J)
   40   PINT(1,J) = PINT(1,J) + PINT(I,J)
        WRITE (3,7)JS
        DO 50 J=1,M
        FREQ(1,J) = FREQ(1,J)/FJS
        PINT(1,J) = PINT(1,J)/FJS
50      WRITE (3,8) FREQ(1,J),PINT(1,J)
        IF(IOUT.EQ.0) WRITE(14,9 ) (FREQ(1,J),PINT(1,J),J=1,M)
        IF(IOUT.NE.0) WRITE(14,4 ) (FREQ(1,J),PINT(1,J),J=1,M)
        GO TO 60
    1   FORMAT (9I3)
    2   FORMAT (12A6)
    3   FORMAT (2F10.3)
    4   FORMAT (30X,2F10.3)
    5   FORMAT (1H112A6/1H )
    6   FORMAT (1H 2F10.3)
    7   FORMAT (19H1AVERAGE VALUES FORI3,8H SPECTRA/1H )
    8   FORMAT(1H 2F10.3)
9       FORMAT (8X,2F10.3)
        END
                        *** 'END-OF-FILE' CARD ***
```

FIGURE CAPTIONS

Fig. 1 Group of twelve peaks from spectrum 1 decomposed with digital shape function. Dots are experimental points; vertical lines show position and intensity of peaks found by DECOMP; the solid curve is calculated from the peaks represented by the vertical lines.

Fig. 2 Group of twelve peaks from spectrum 2 decomposed with digital shape function.

Fig. 3 Group of twelve peaks from spectrum 1 decomposed with Lorentz function.

Fig. 4 Group of twelve peaks from spectrum 2 decomposed with Lorentz function.

Fig. 5 Energy level diagram for ABC example.

Fig. 6 Energy level diagram for A_2B_2 example.

Fig. 7 Experimental spectrum of 3-chlorothietane, X region.

Fig. 8 Experimental spectrum of 3-chlorothietane, A_2B_2 region.

Fig. 9-16 Decomposed groups of peaks from the spectrum of 3-chlorothietane, digital shape function.

Fig. 17 Energy level diagrams for 3-chlorothietane: (a) symmetric, (b) antisymmetric.

Fig. 18 3-chlorothietane, structure and identification of protons.

Fig. 19 Comparison of results from NMRIT and DECOMP of the X region of the spectrum of 3-chlorothietane. Top curves are calculated using positions and intensities of vertical lines representing peaks obtained with NMRIT. Bottom curves are experimental spectra; the vertical lines show positions and intensities obtained by DECOMP.

Fig. 20 Comparison of results from NMRIT and DECOMP of the A_2B_2 region of 3-chlorothietane.

Fig. 21 Double resonance spectra for 3-chlorothietane: (a) frequency sweep spectrum obtained while observing line 11, (b) single resonance frequency sweep calibration spectrum, (c) frequency sweep spectrum obtained while observing line 12.

Fig. 22 Energy level diagram for double resonance experiment.

Fig. 23 Experimental spectrum of 3-thietanyl acetate, X region.

Fig. 24 Experimental spectrum of 3-thietanyl acetate, A_2B_2 region.

Fig. 25-32 Decomposed groups of peaks from the spectrum of 3-thietanyl acetate, Lorentz shape function.

Fig. 33 Comparison of results from NMRIT and DECOMP of the X region of the spectrum of 3-thietanyl acetate. The top curve is the experimental spectrum; the vertical lines show positions and intensities obtained by DECOMP. Bottom curve is calculated using positions and intensities of the vertical lines, representing peaks obtained with NMRIT.

Fig. 34 Comparison of results from NMRIT and DECOMP of the A_2B_2 region of 3-thietanyl acetate.

Fig. 35 Best spectrum using visual estimation of peaks with NMRIT, X region of 3-thietanyl acetate.

Fig. 36 Best spectrum using visual estimation of peaks with NMRIT, A_2B_2 region of 3-thietanyl acetate.

Fig. 37 Energy level diagram for A_1 symmetry; A_2B_4 example.

Fig. 38 Energy level diagram for A_2 symmetry; A_2B_4 example.

Fig. 39 Energy level diagram for B_1 symmetry; A_2B_4 example.

Fig. 40 Energy level diagram for B_2 symmetry; A_2B_4 example.

Fig. 41 Experimental spectrum of trimethylene sulfide, digital data.

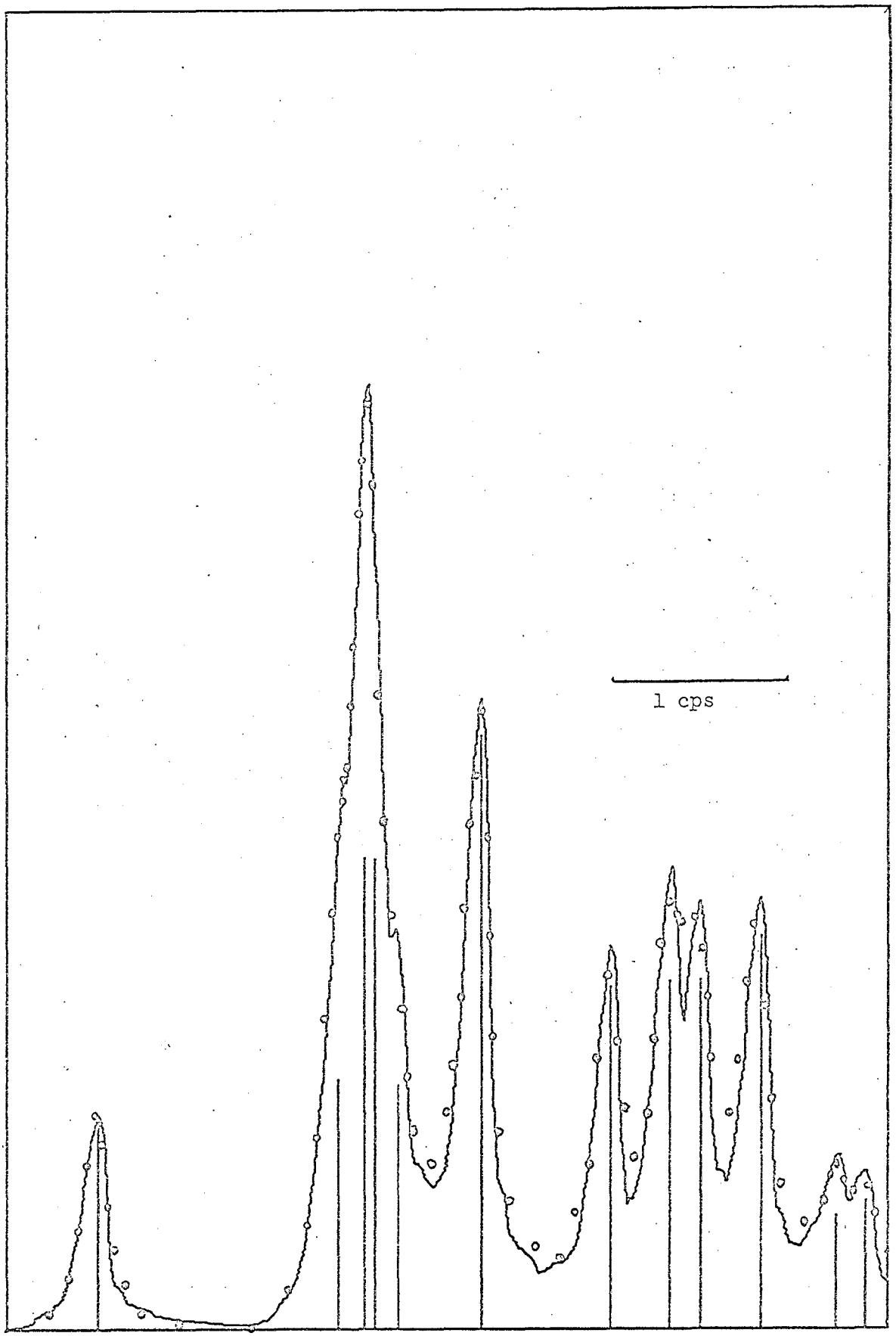
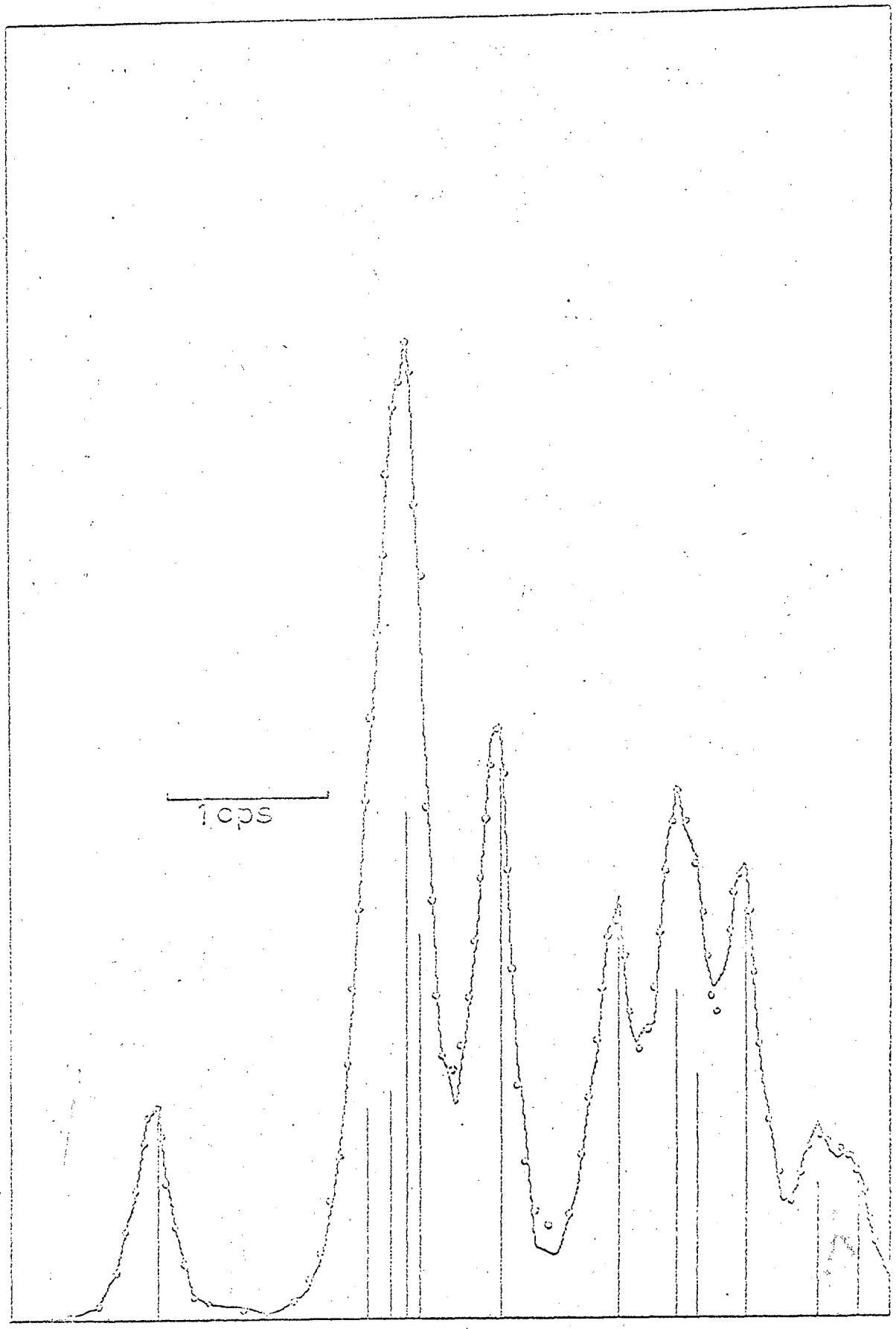


Fig. 1



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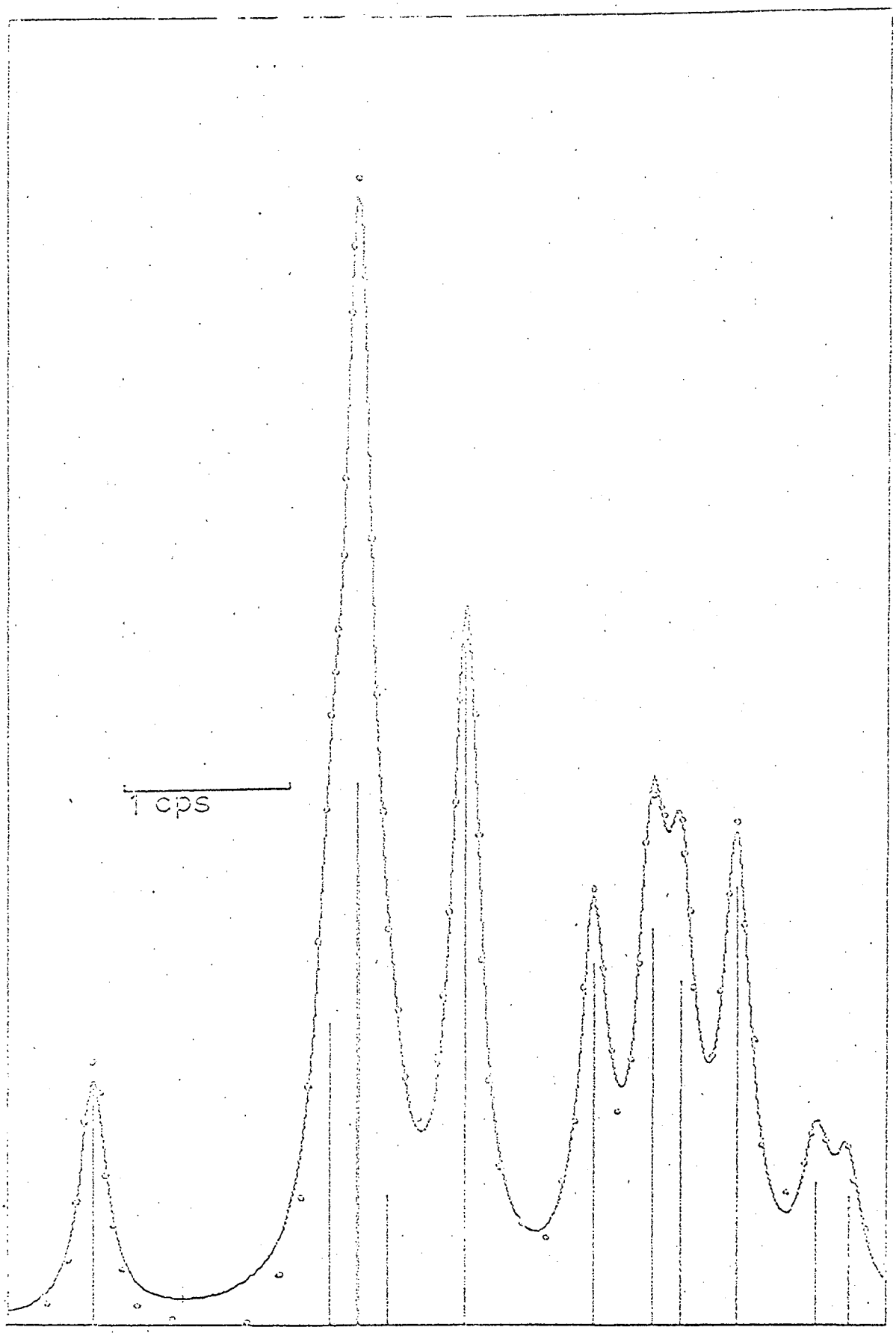


Fig. 3

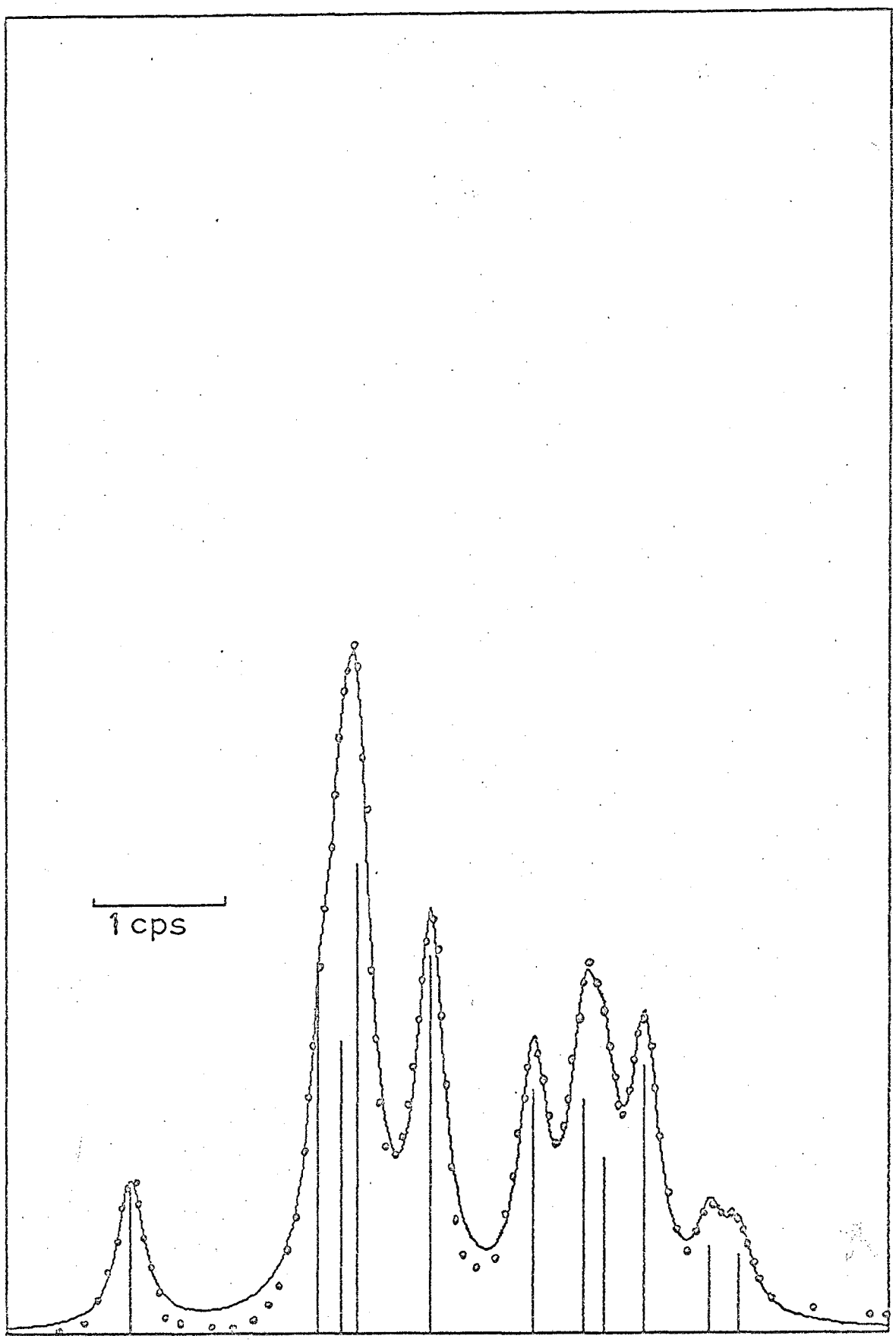


Fig. 4

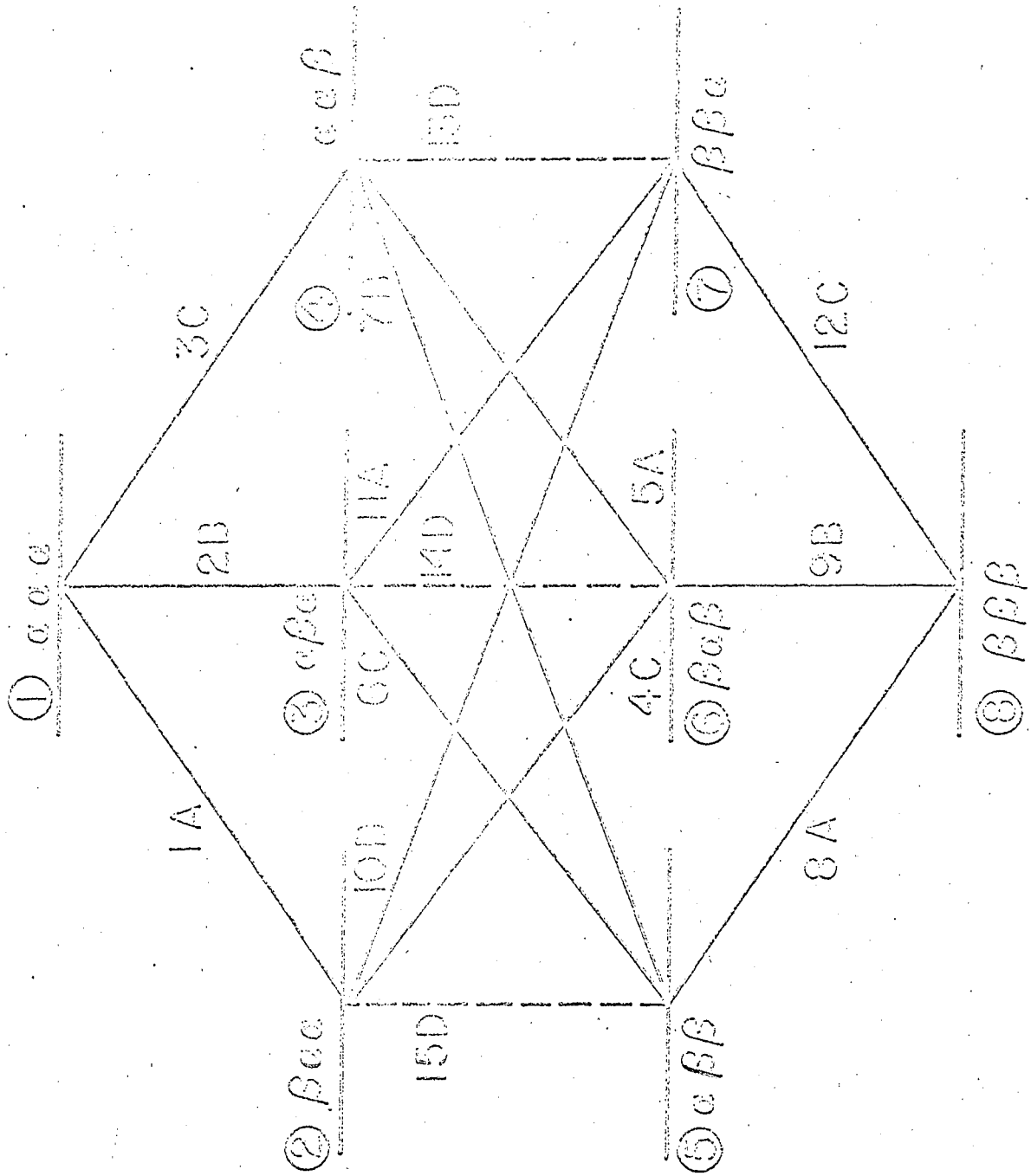

① ααα
② βαα
③ αβα
④ ββα
⑤ αββ
⑥ βαβ
⑦ ααβ
⑧ βββ
1A
2B
3C
4C
5A
6D
7D
8A
9B
10D
11A
12C
15D

Fig. 5

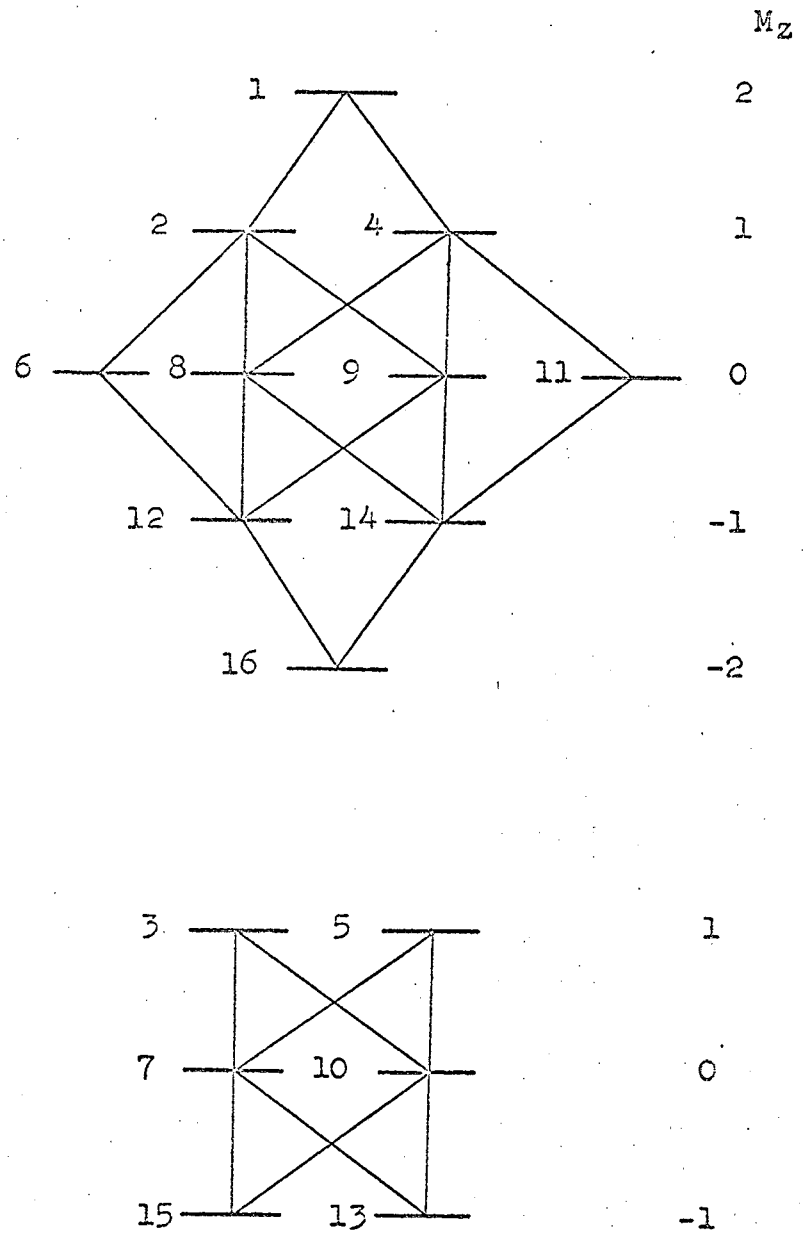


Fig. 6

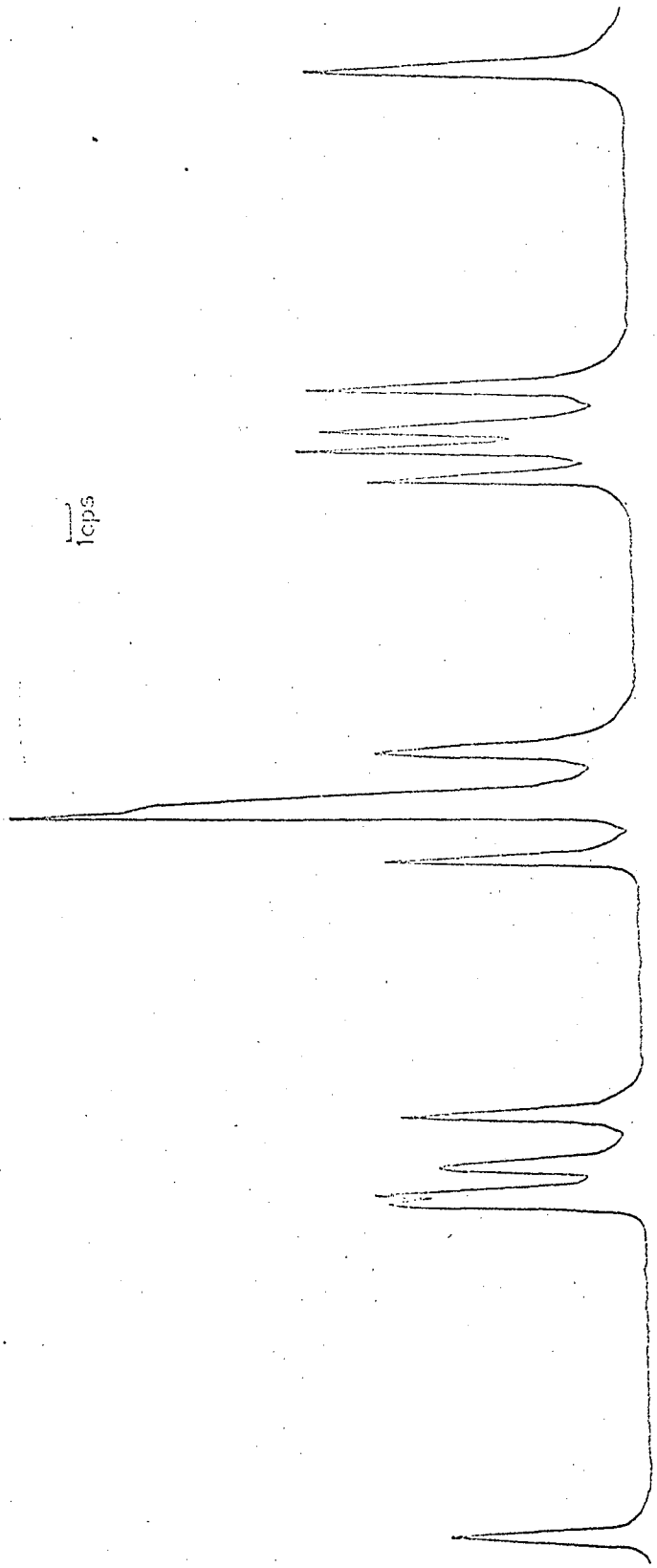


Fig. 7

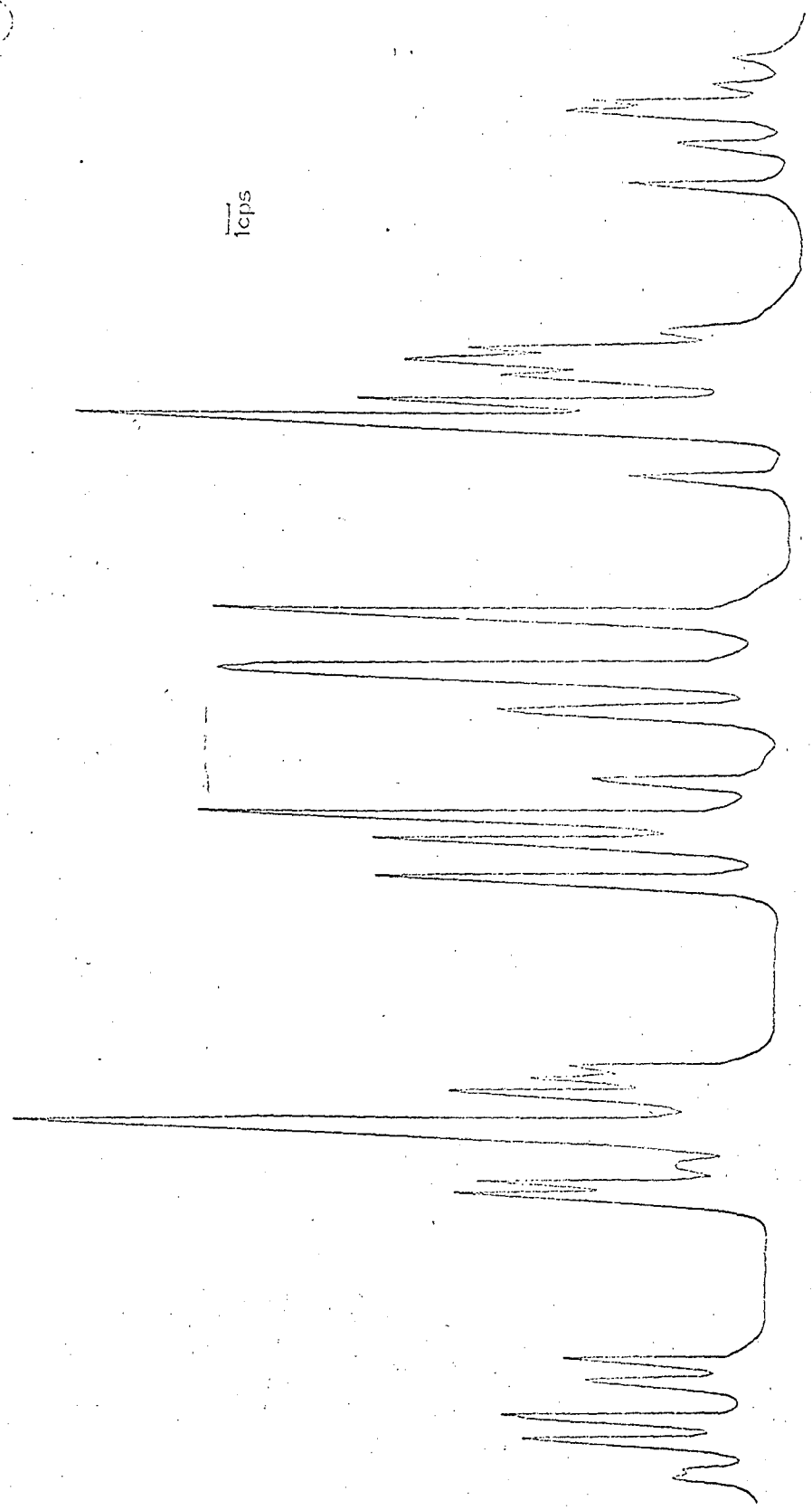


Fig. 8

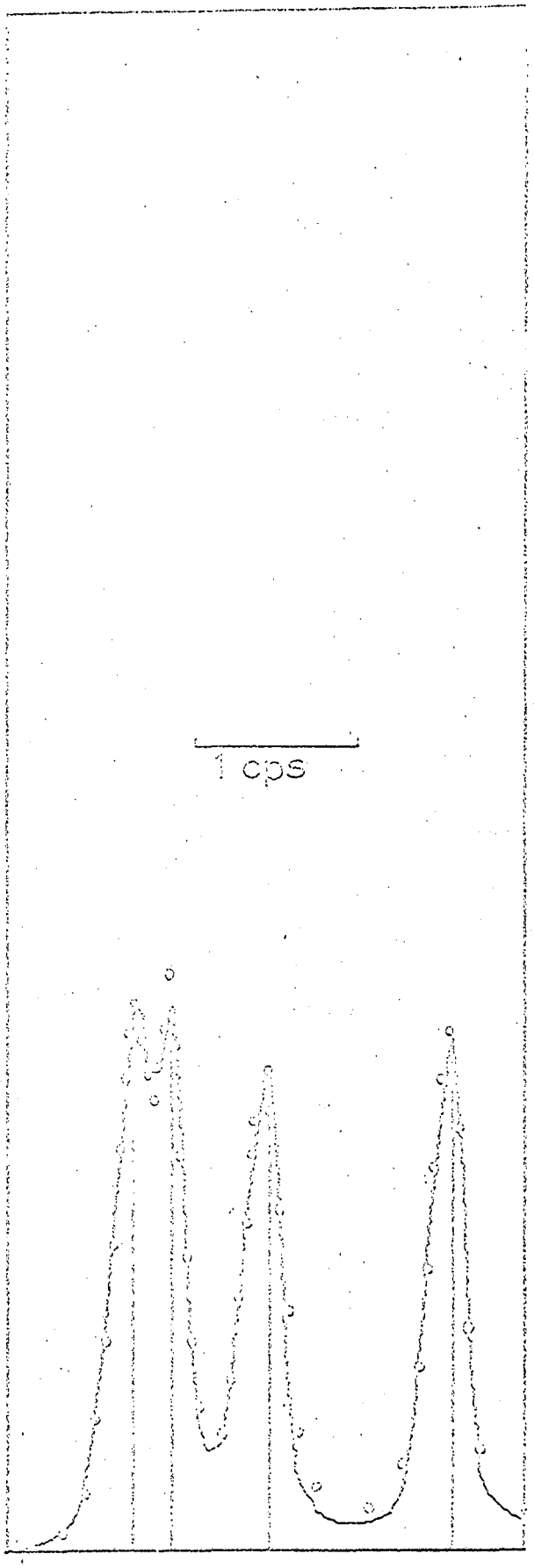


Fig. 9

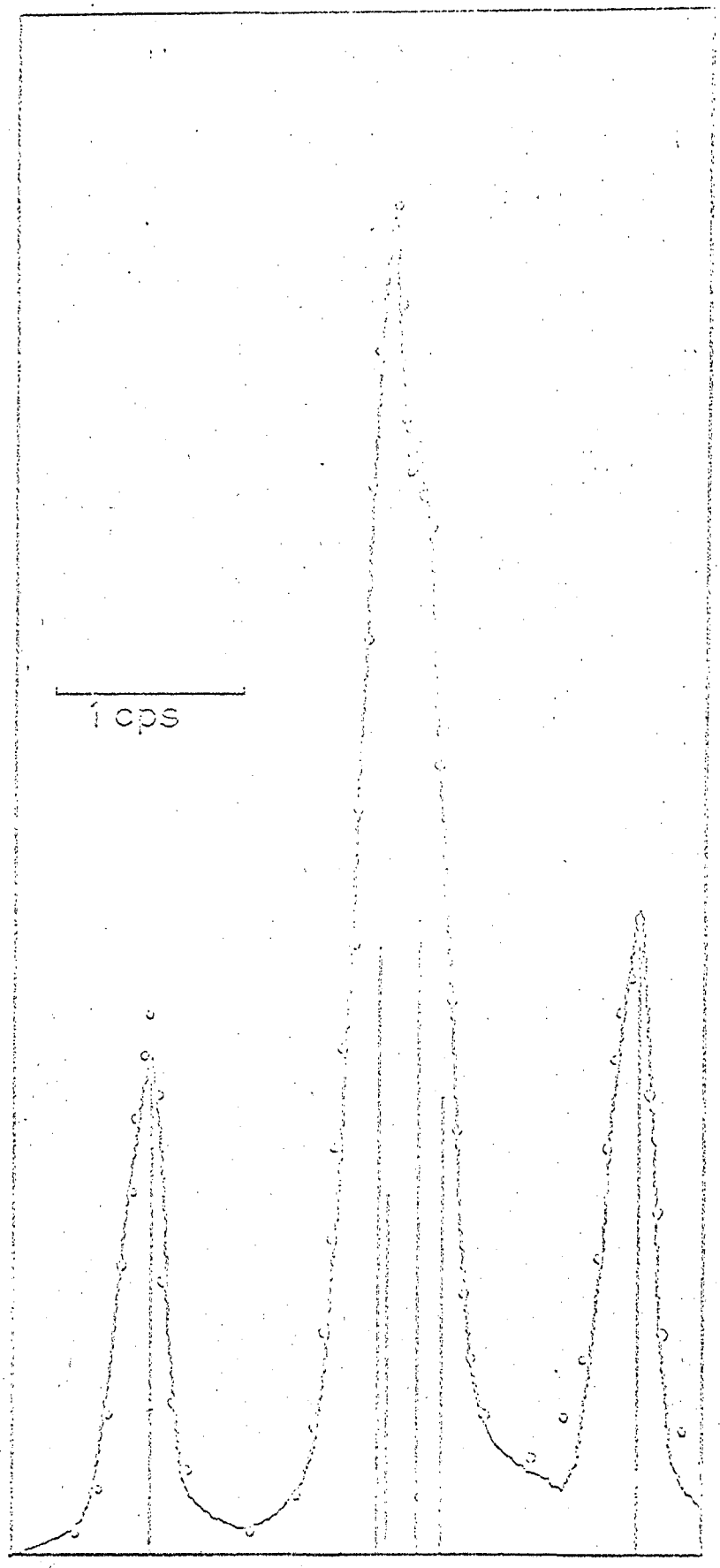


Fig. 10

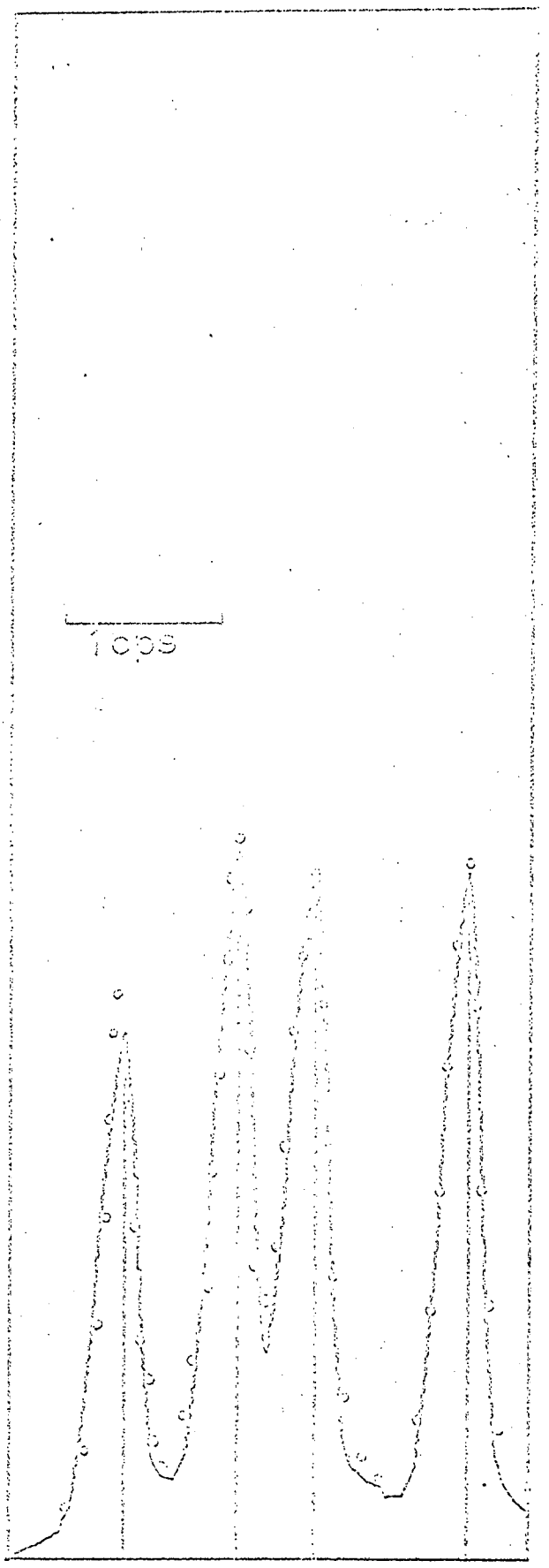


Fig. 11

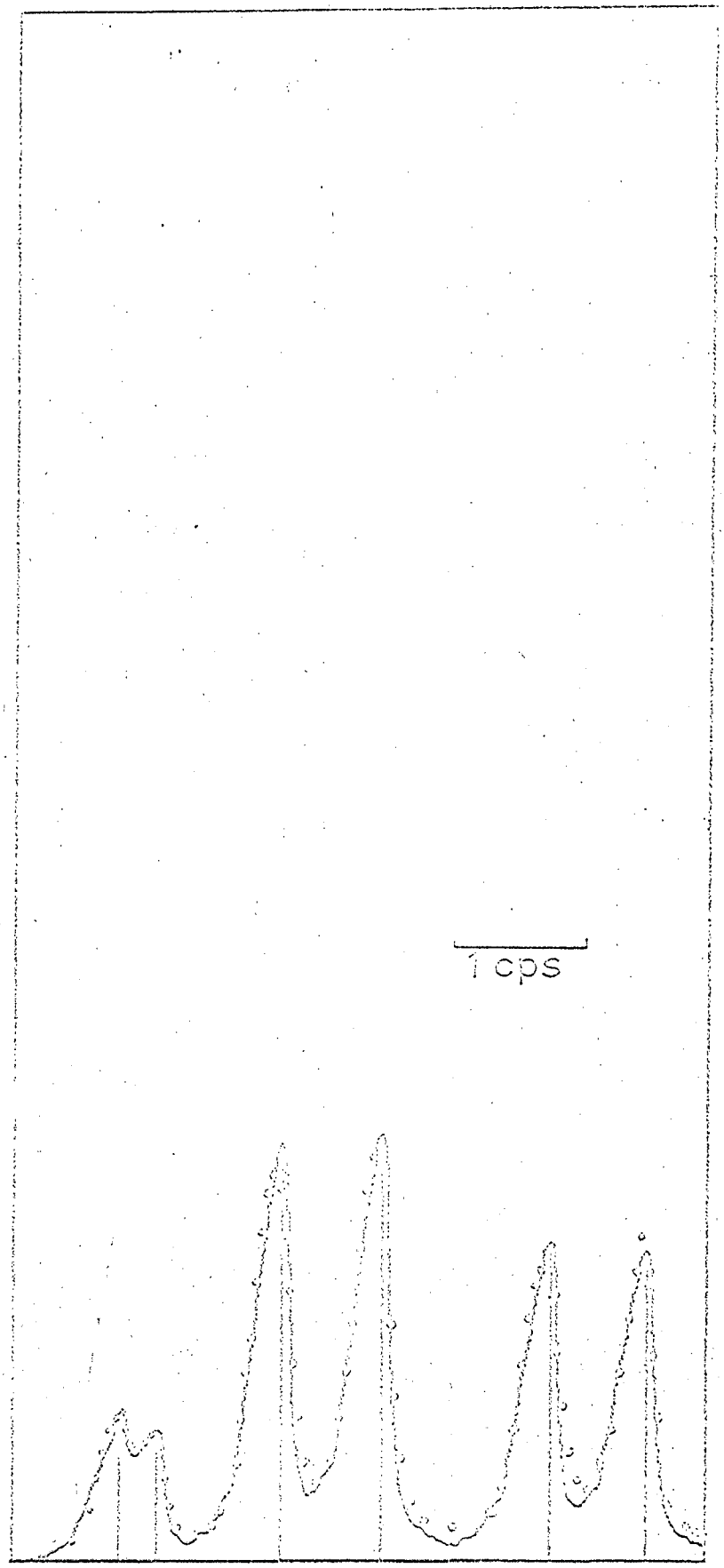


Fig. 12

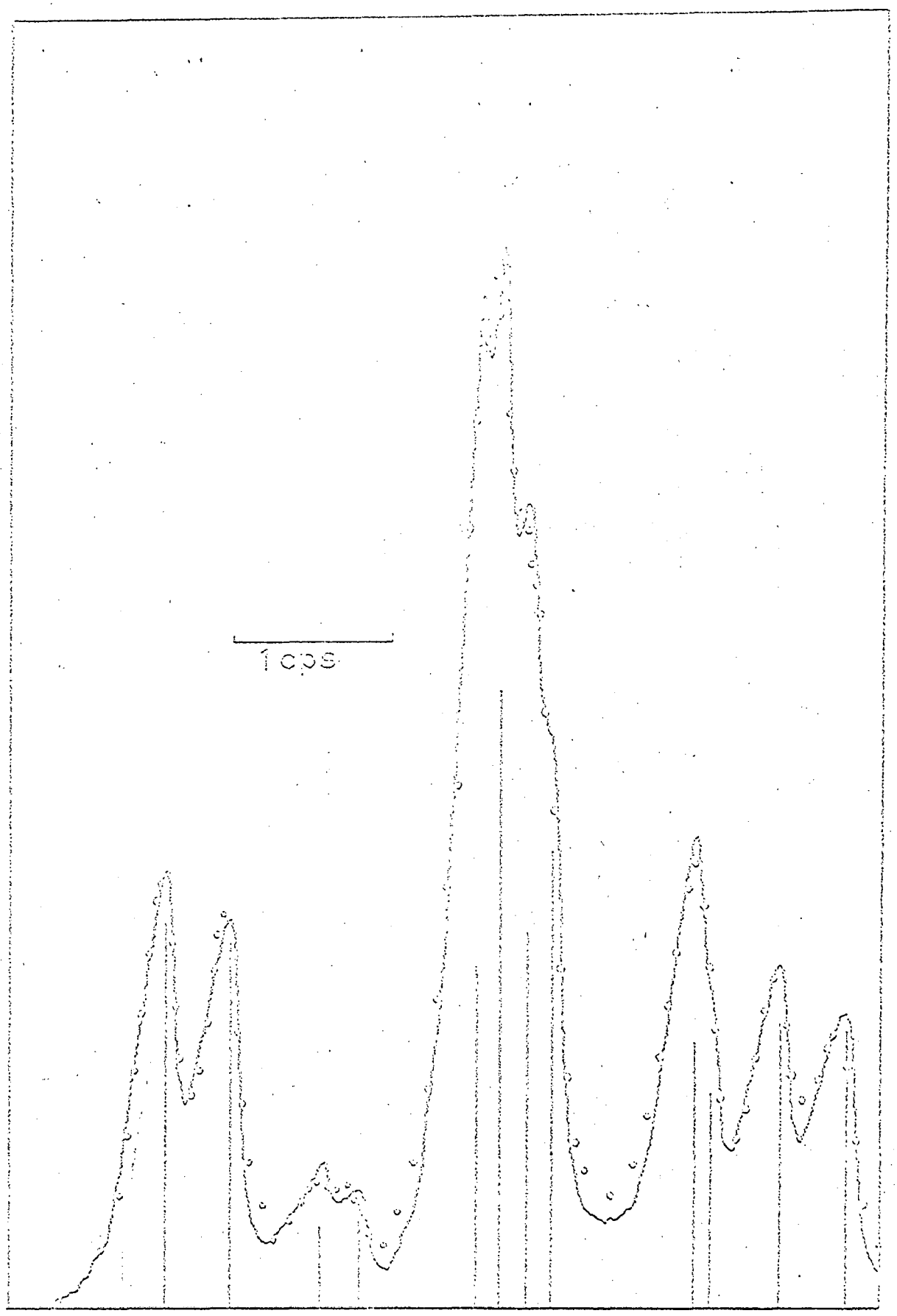


Fig. 13

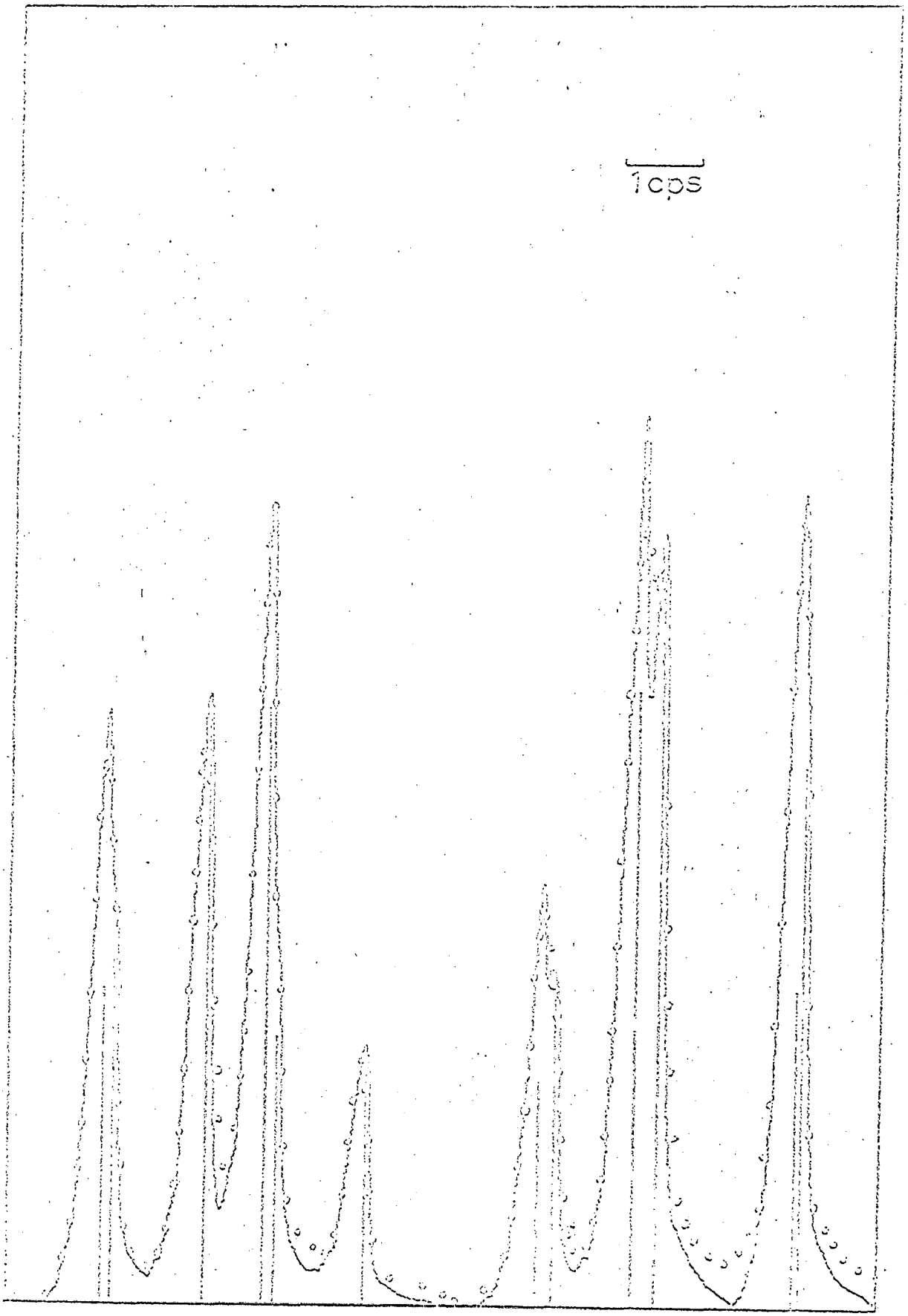


Fig. 14

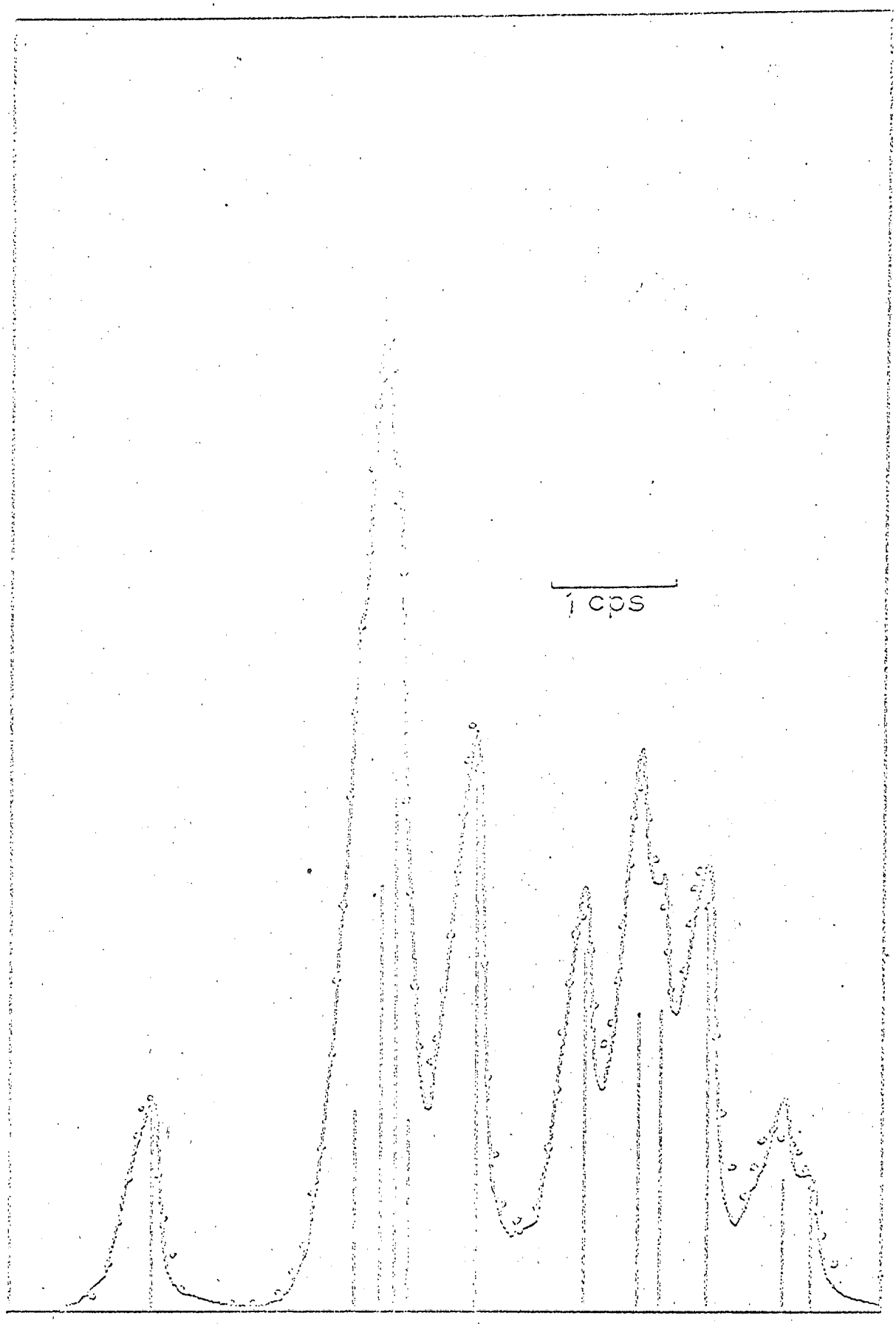


Fig. 15

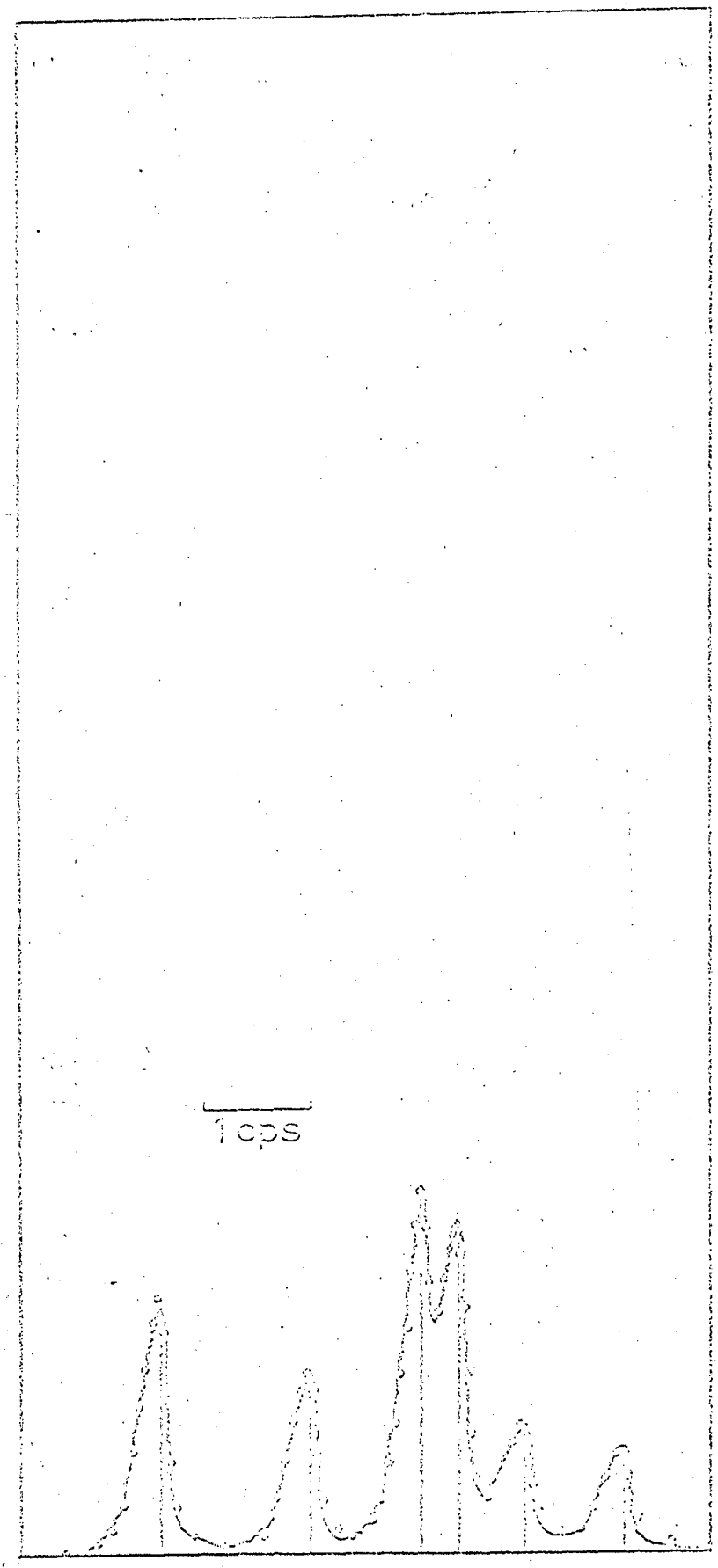
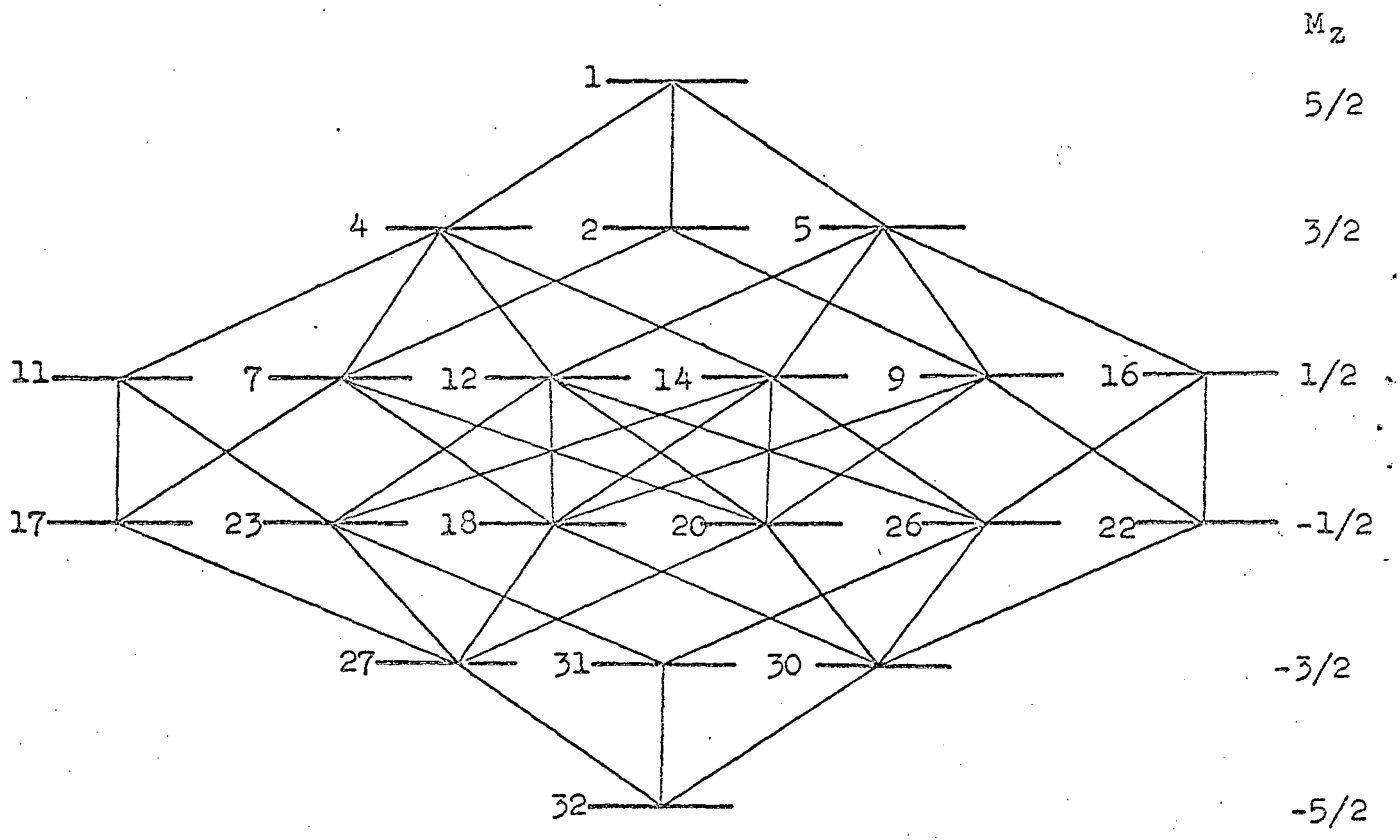


Fig. 16


M_z
1
5/2
4
2
5
3/2
11
7
12
14
9
16
1/2
17
23
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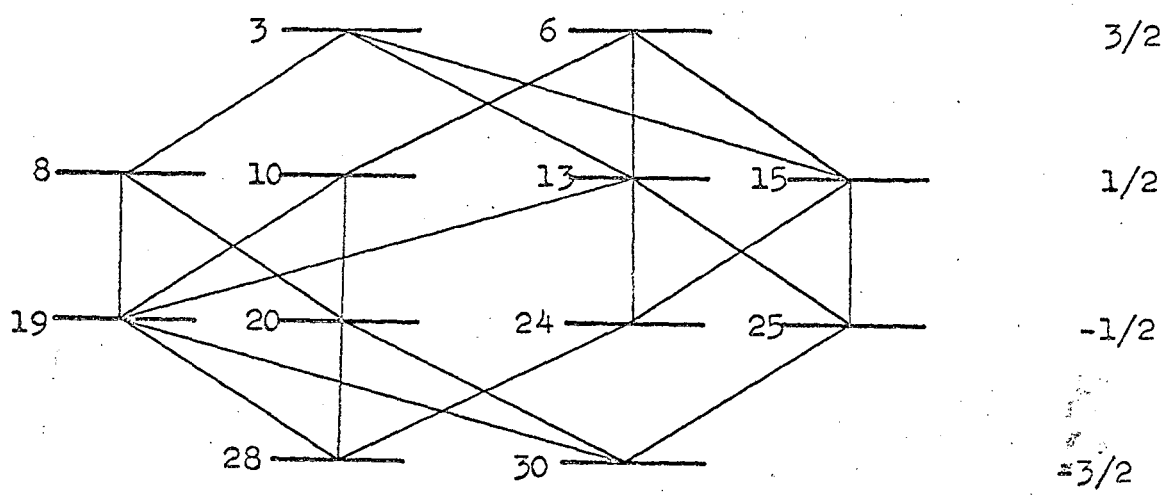
30
-3/2
32
-5/2


3
6
3/2
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25
-1/2
28
30
-3/2

Fig. 17

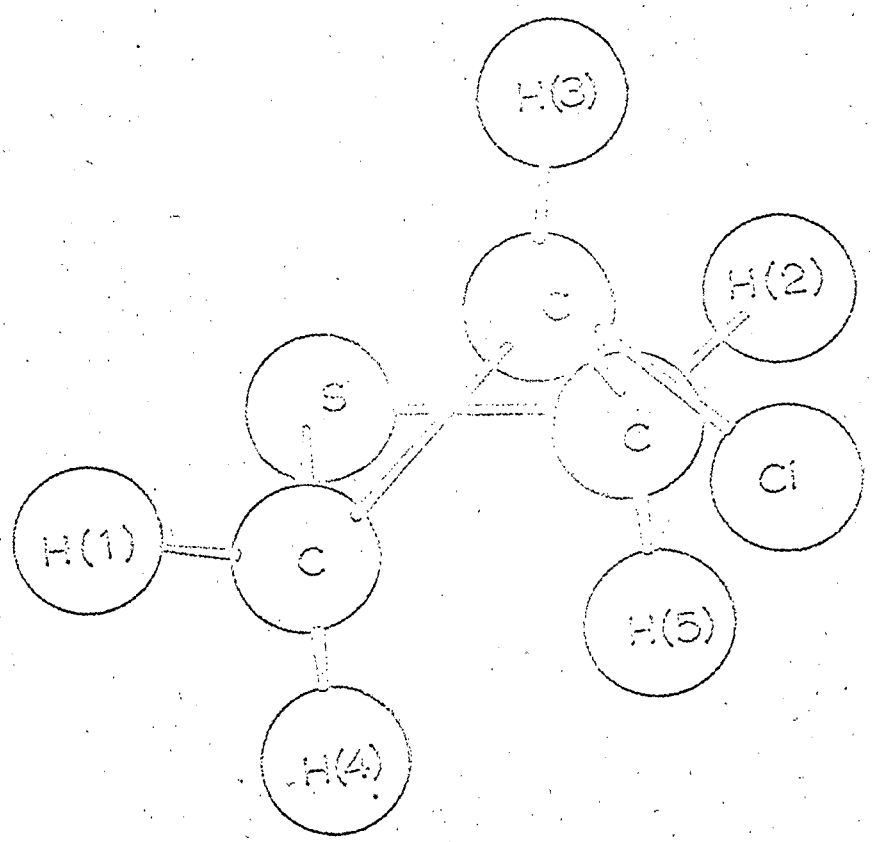
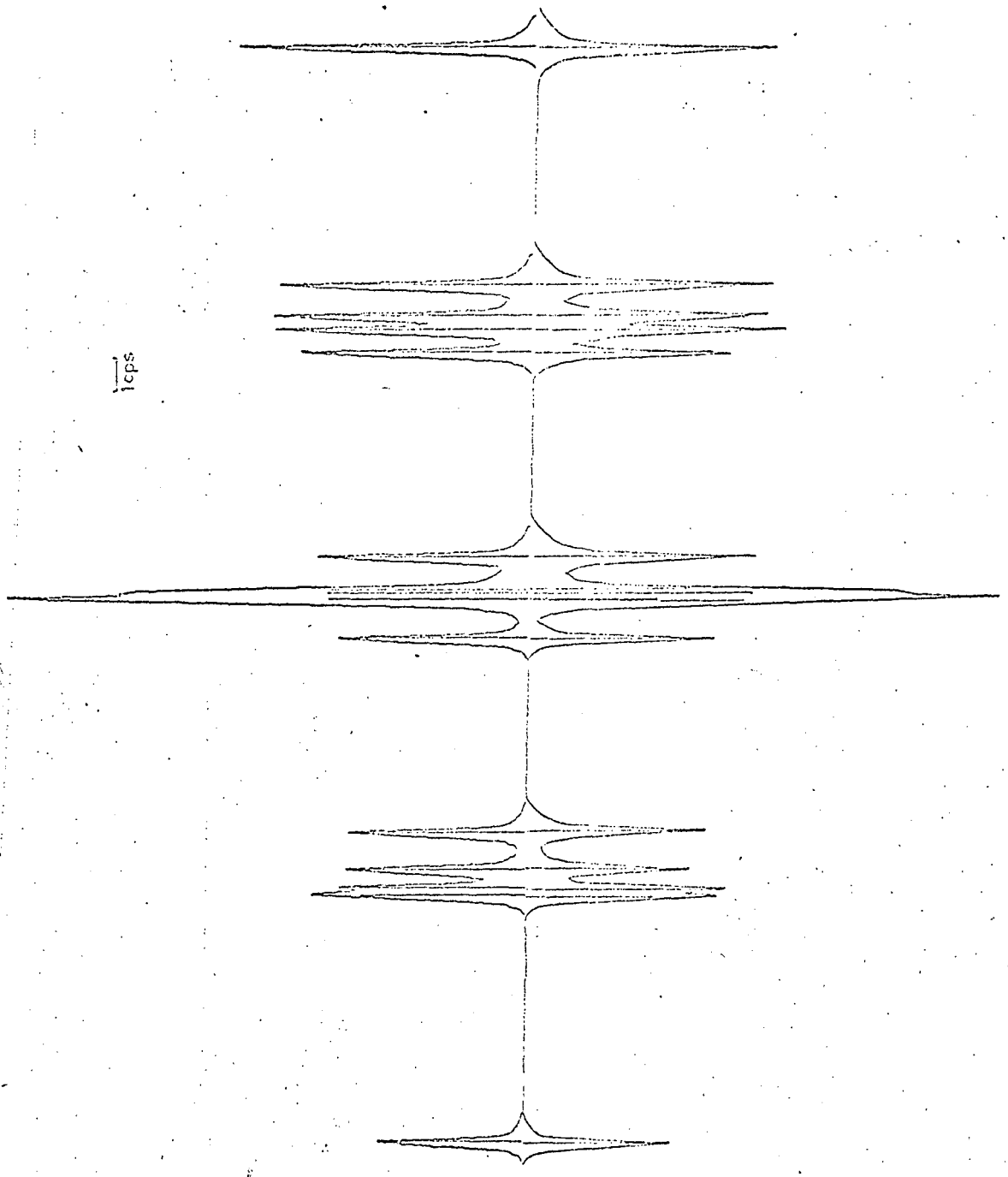


Fig. 18



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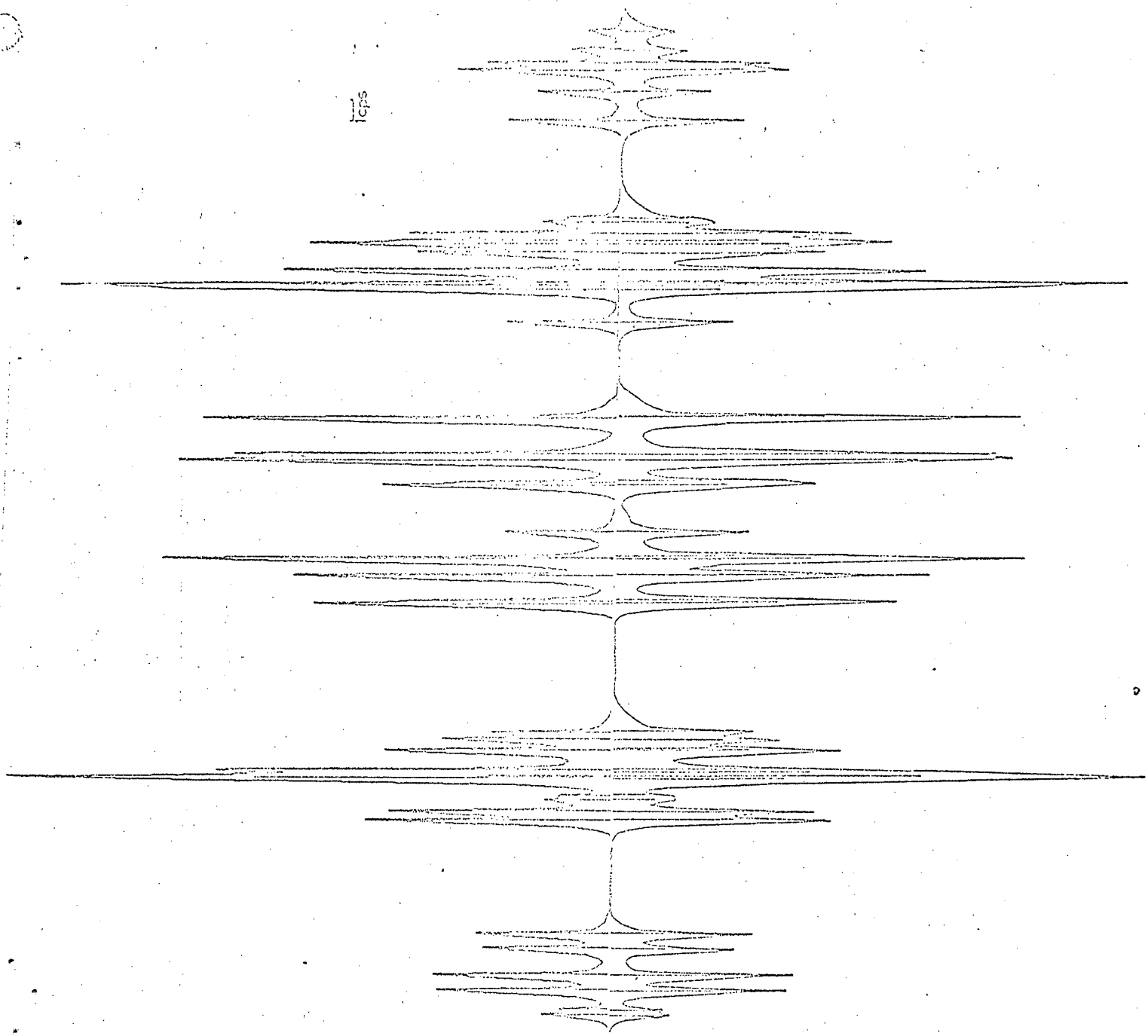

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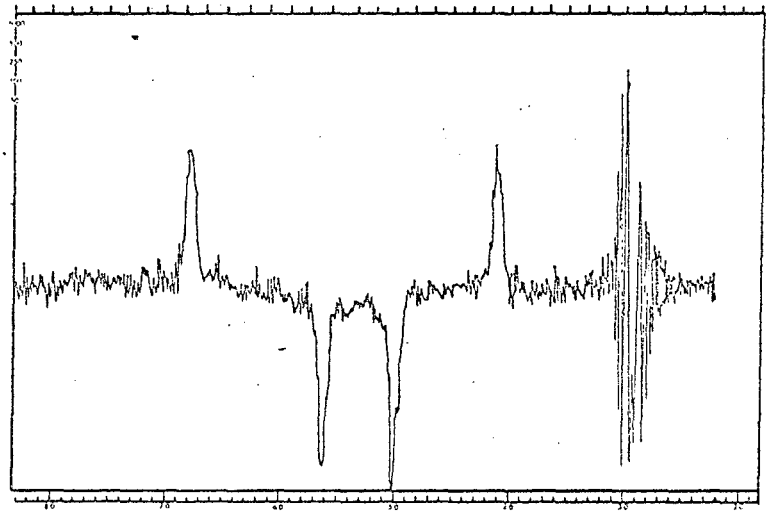
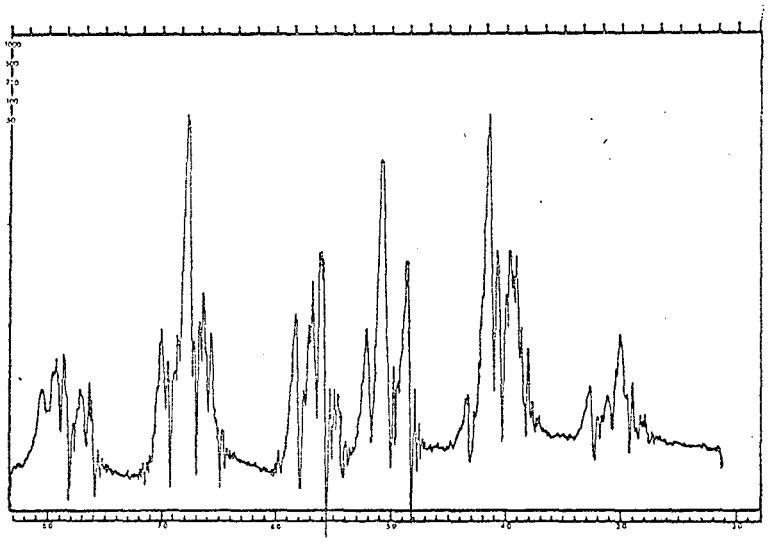
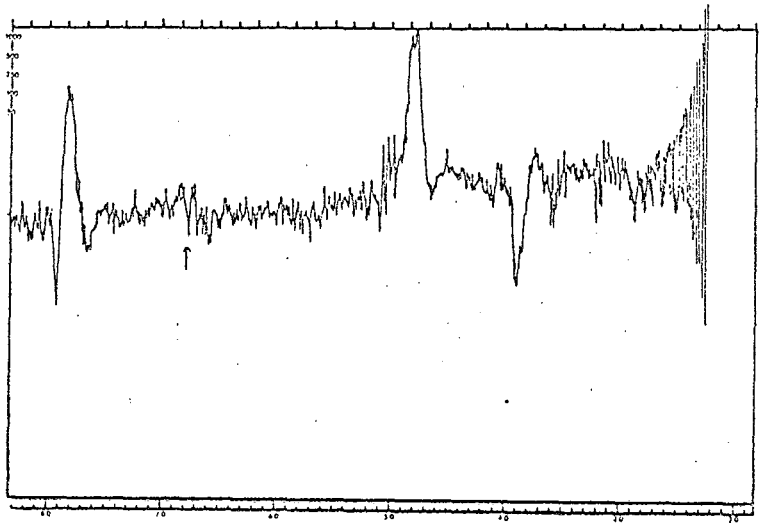


(a)



(b)



(c)

Fig. 21

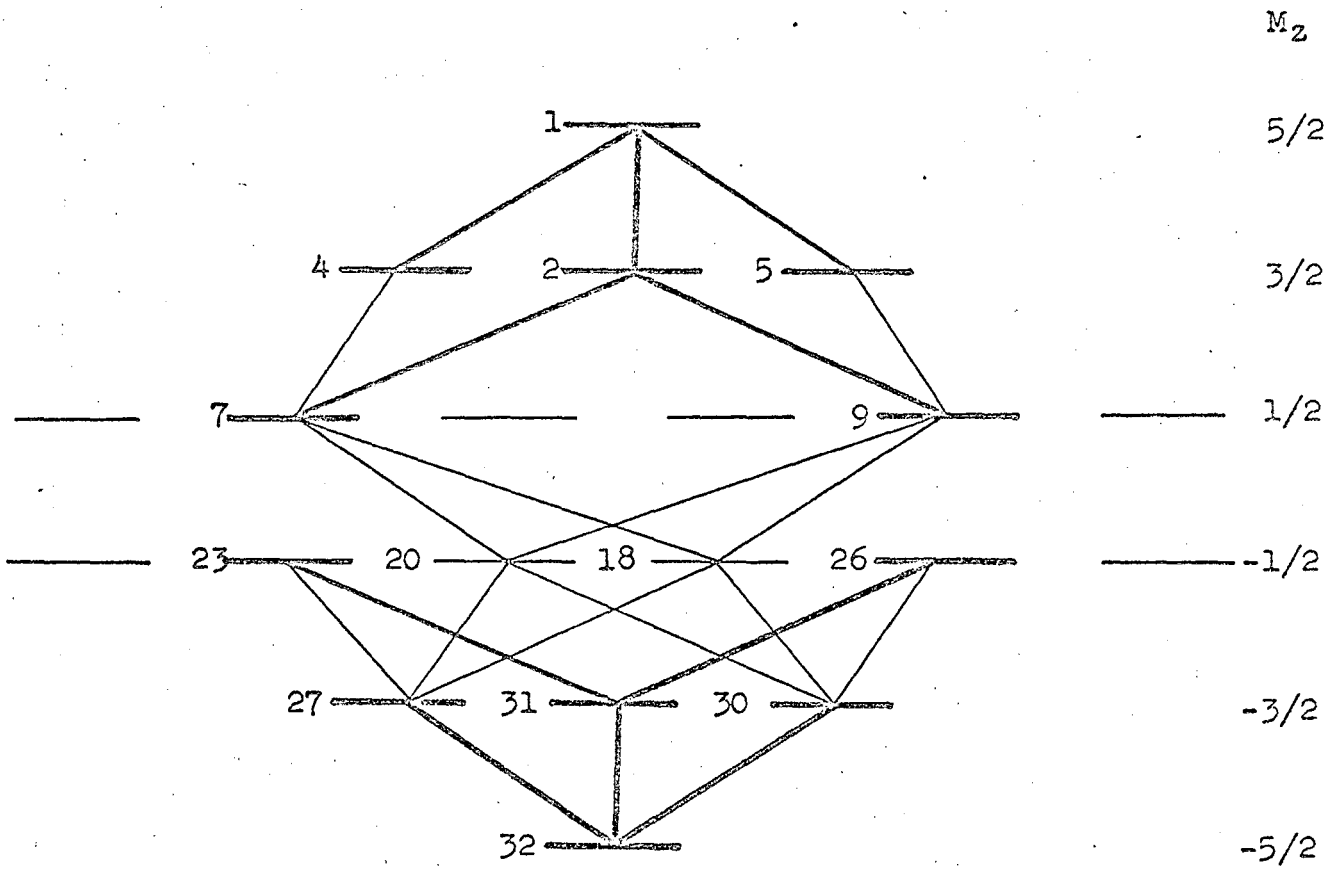


Fig. 22

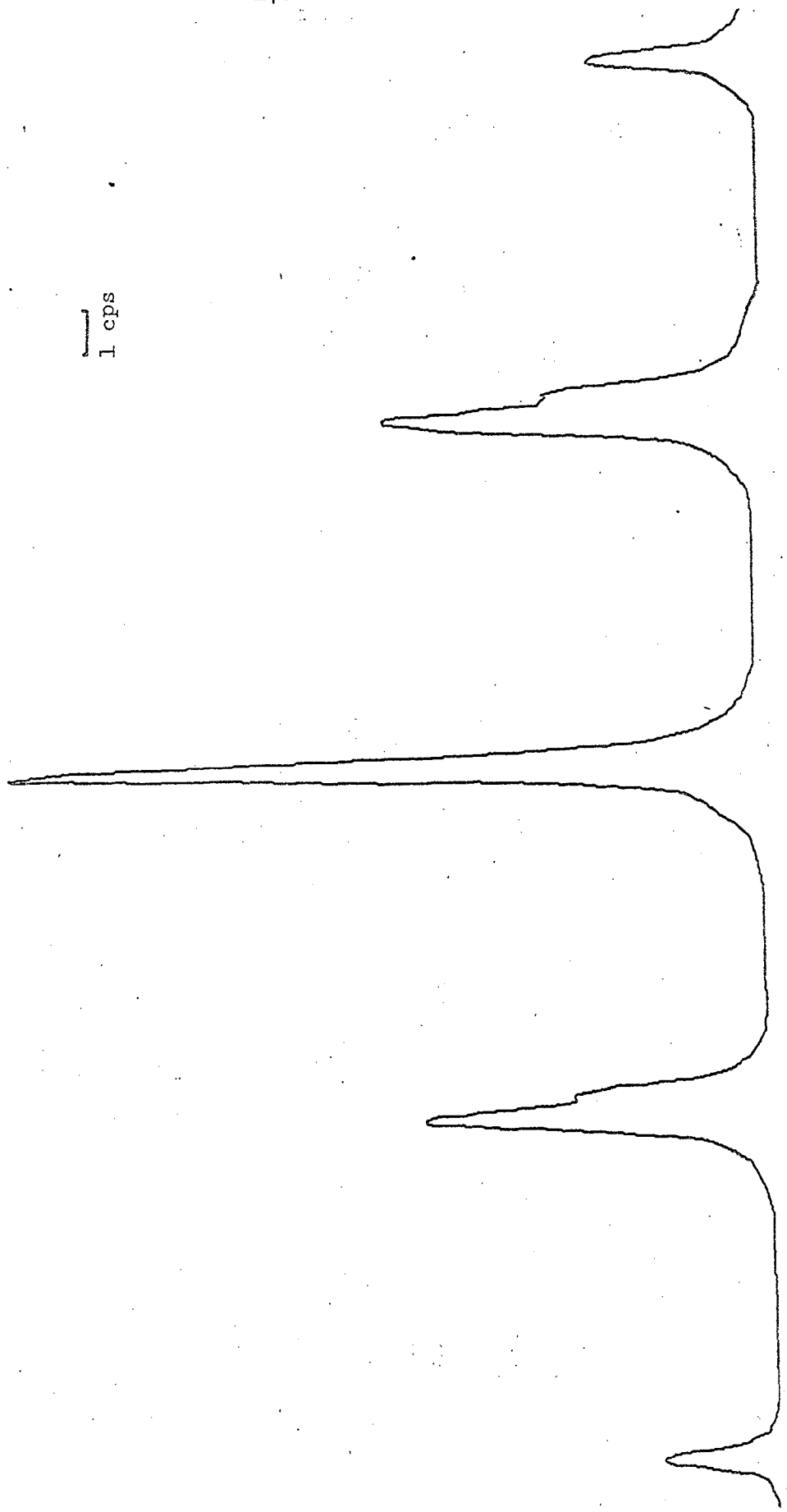


Fig. 23

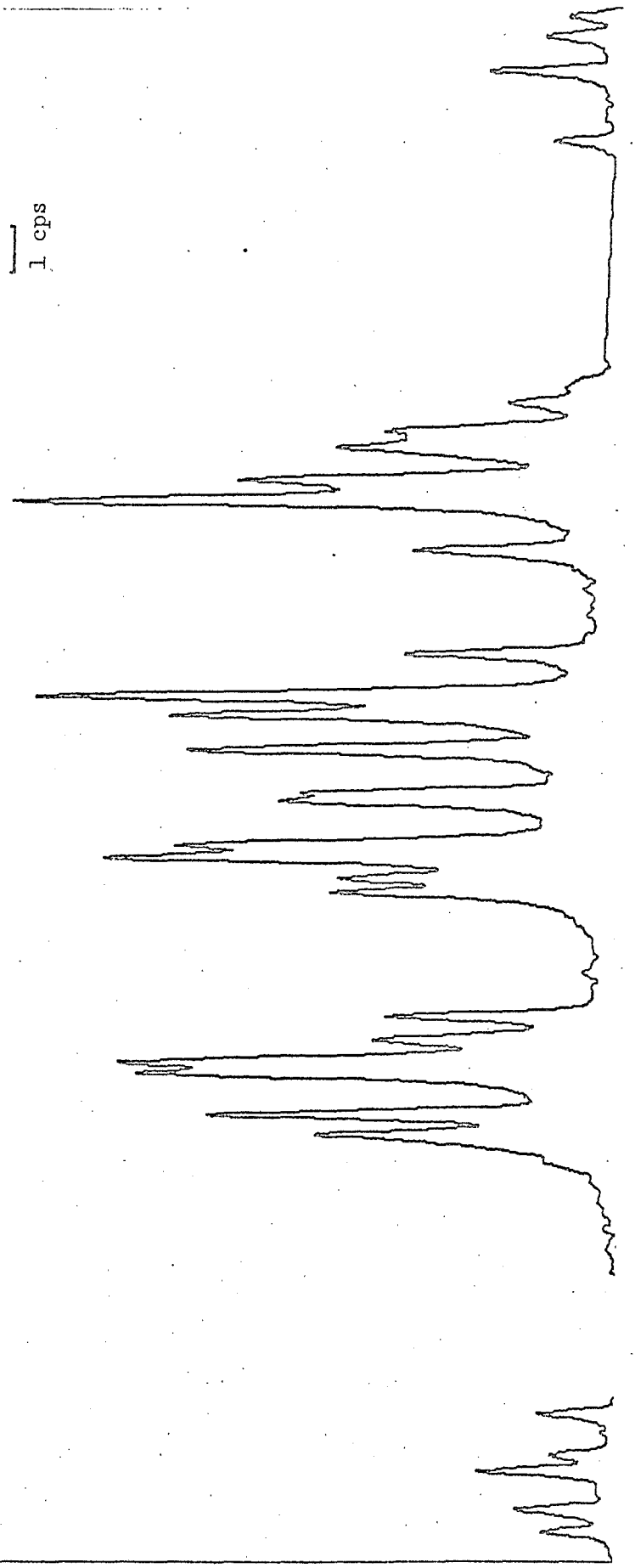


Fig. 24

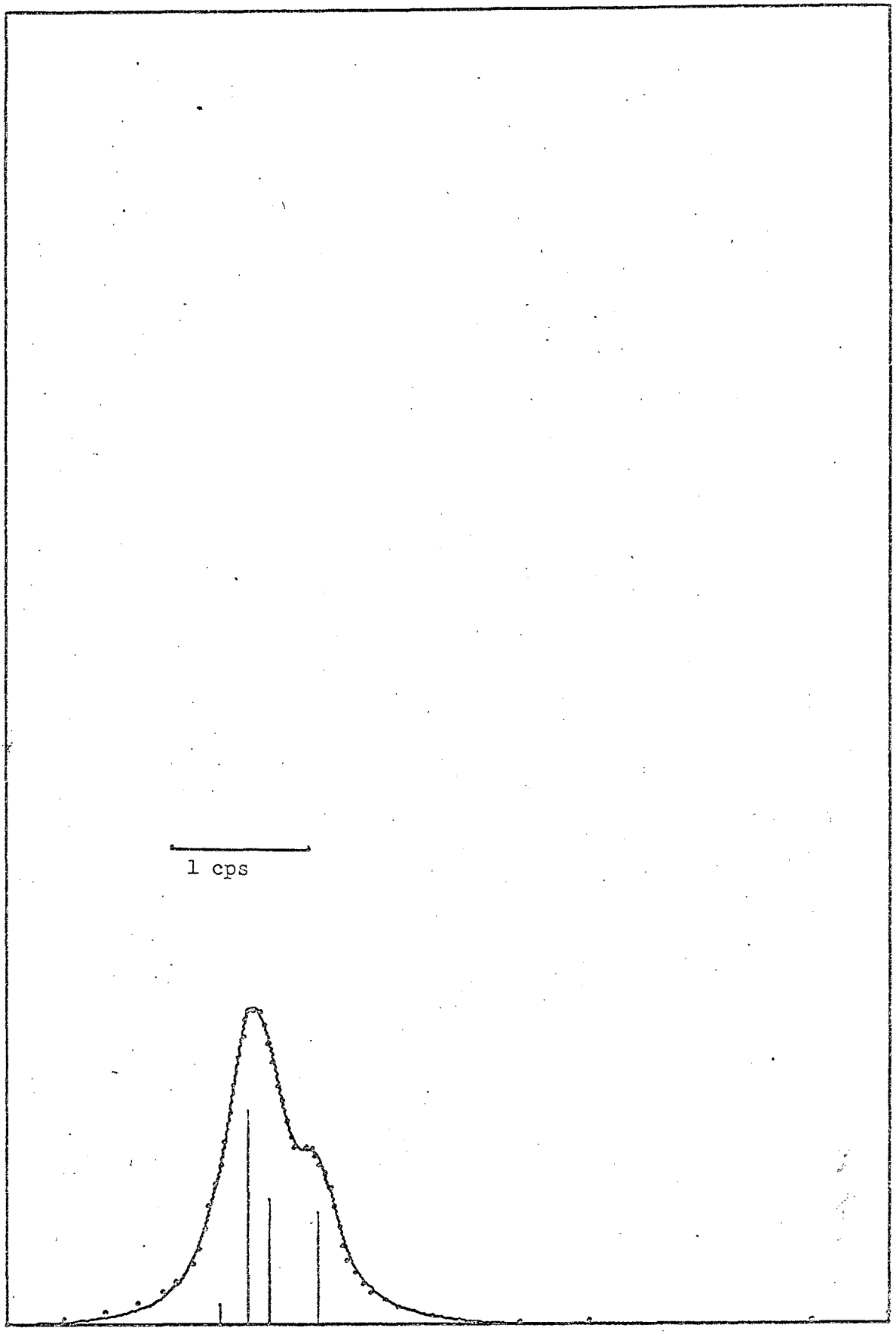


Fig. 25

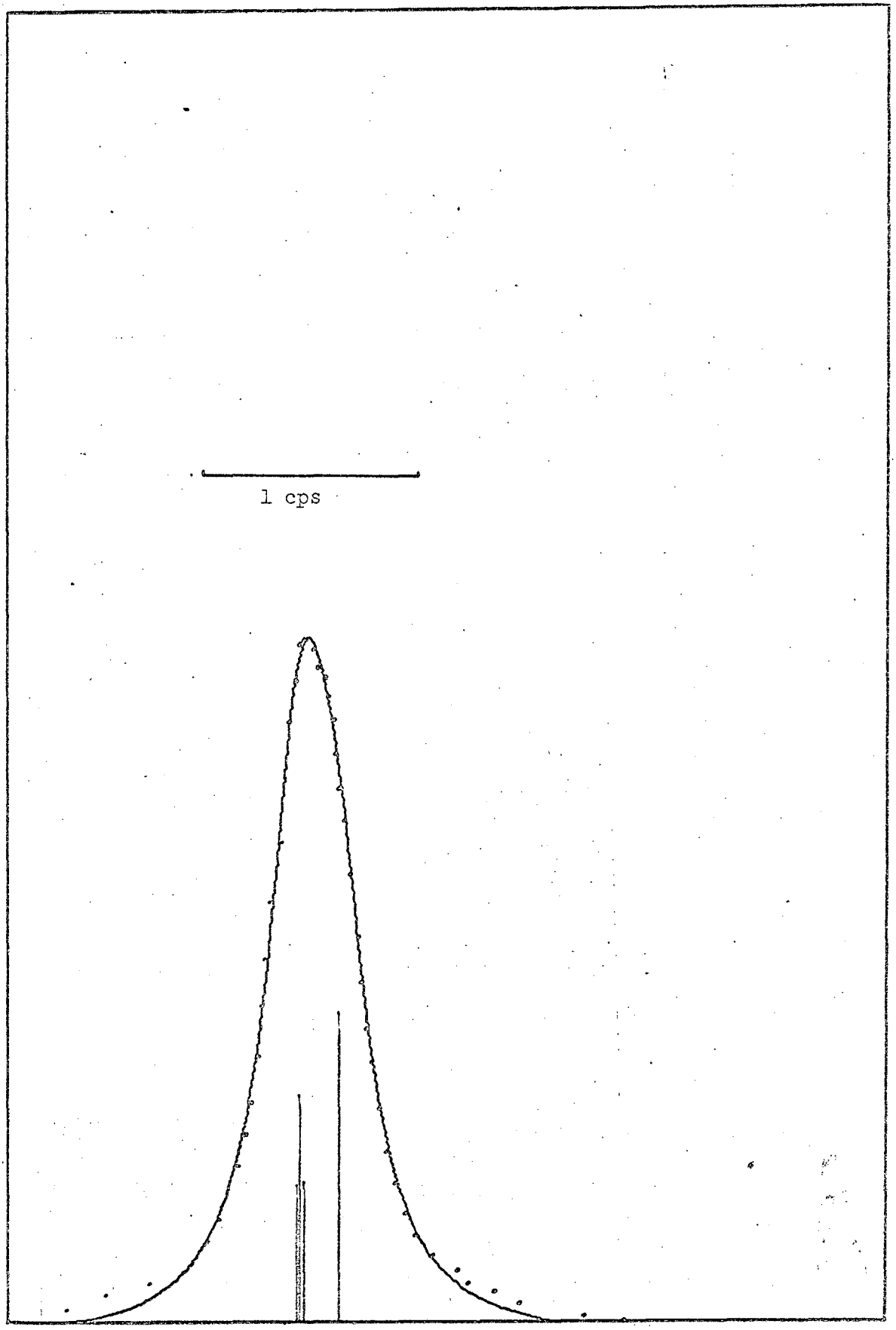


Fig. 26

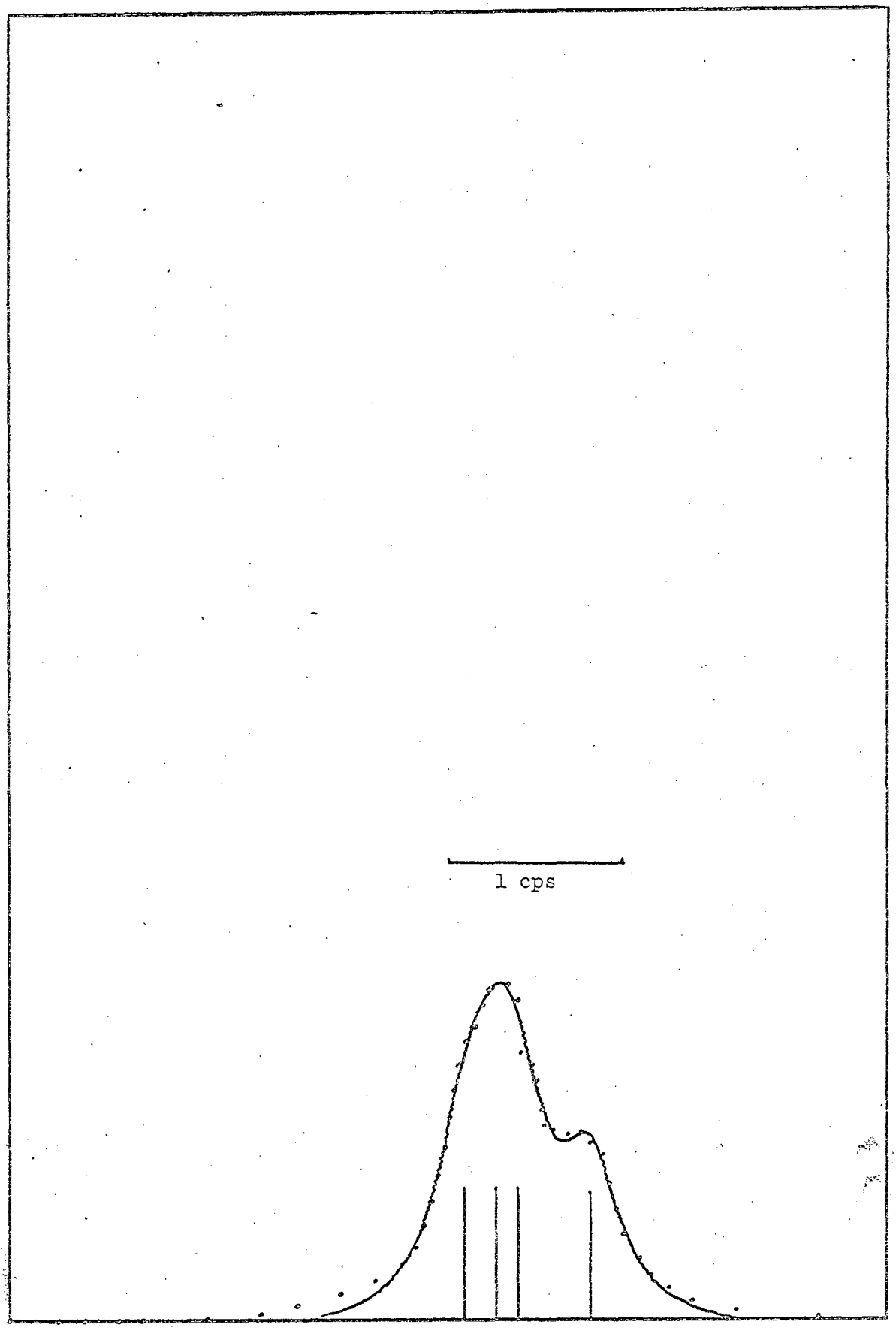


Fig. 27

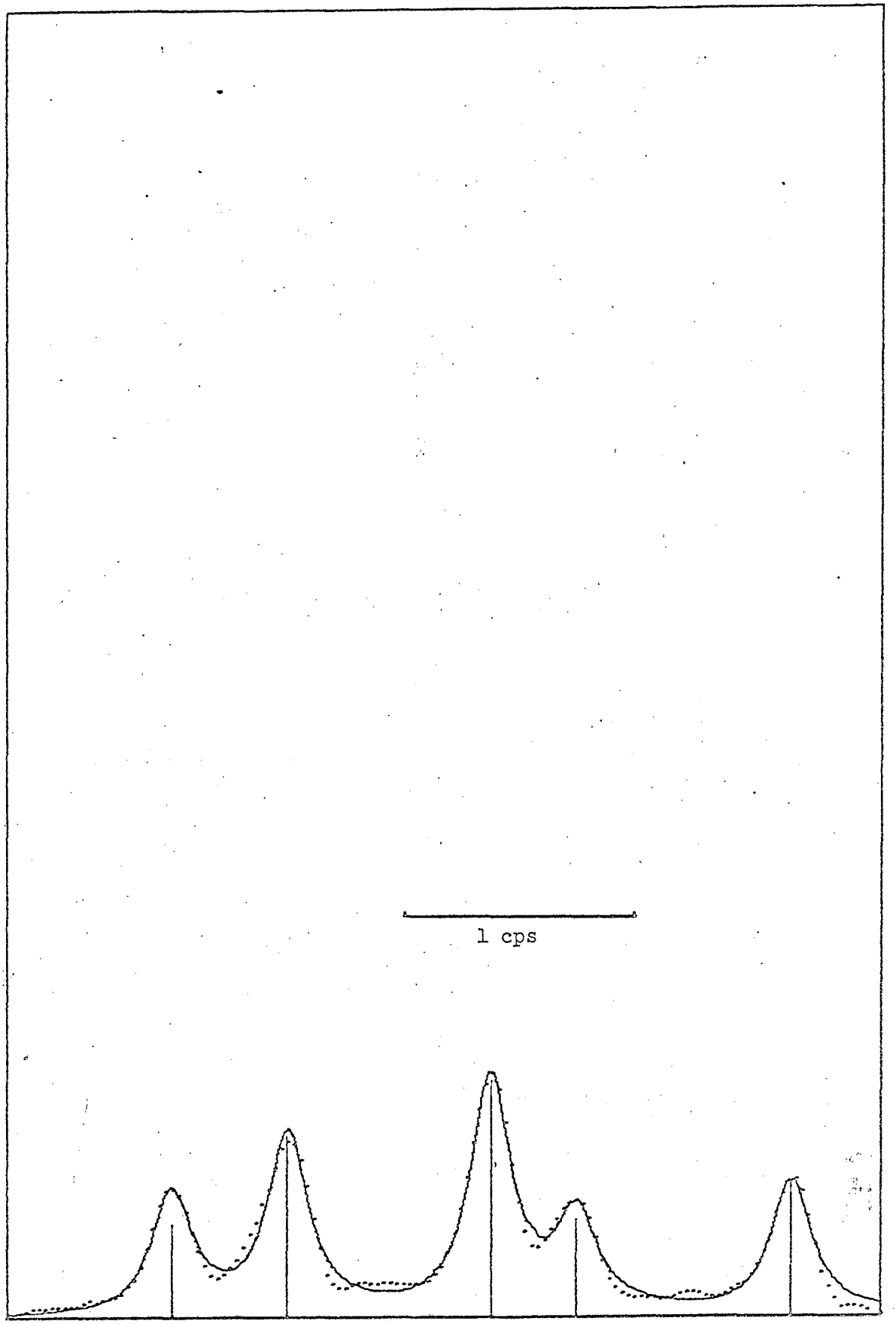


Fig. 28

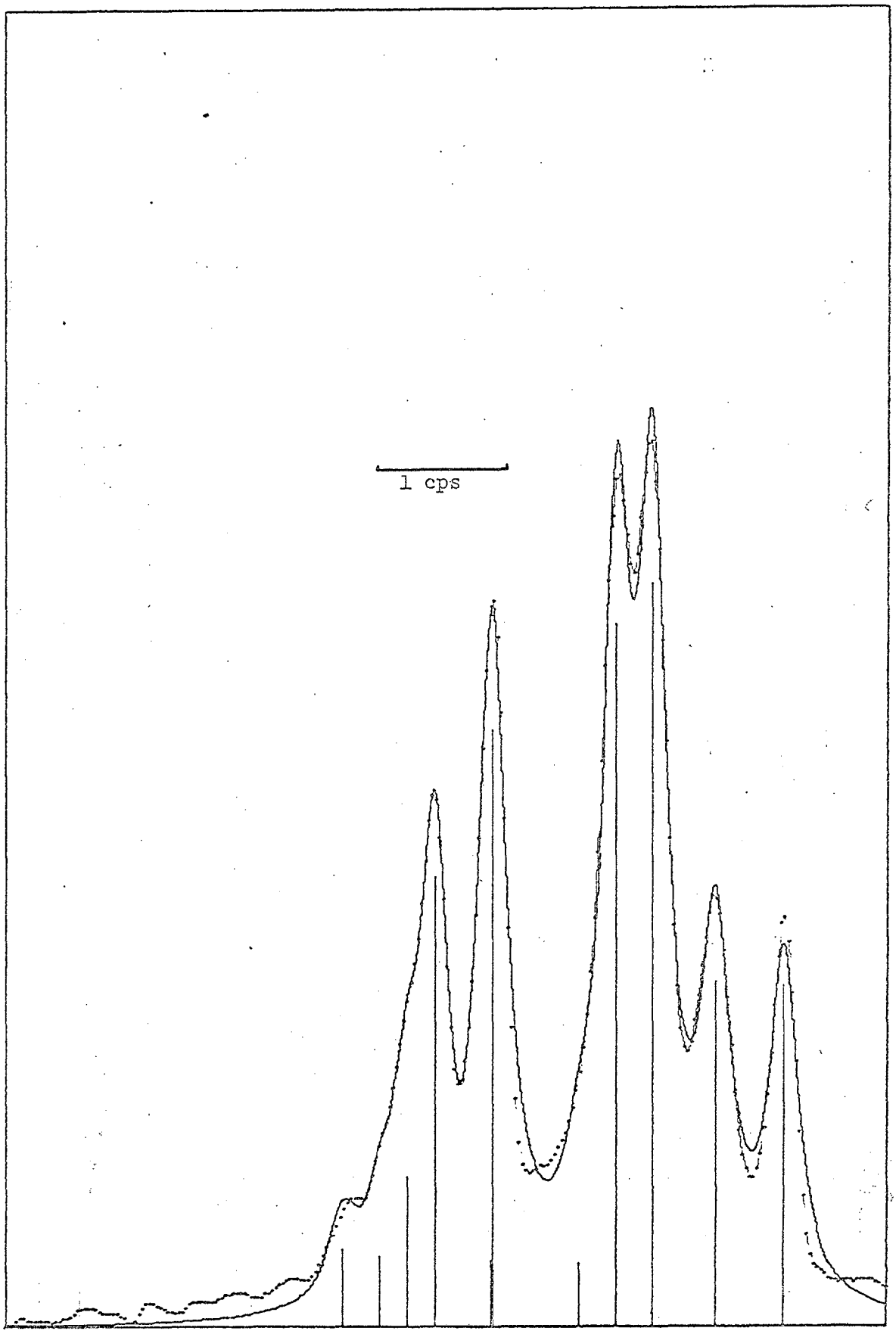


Fig. 29

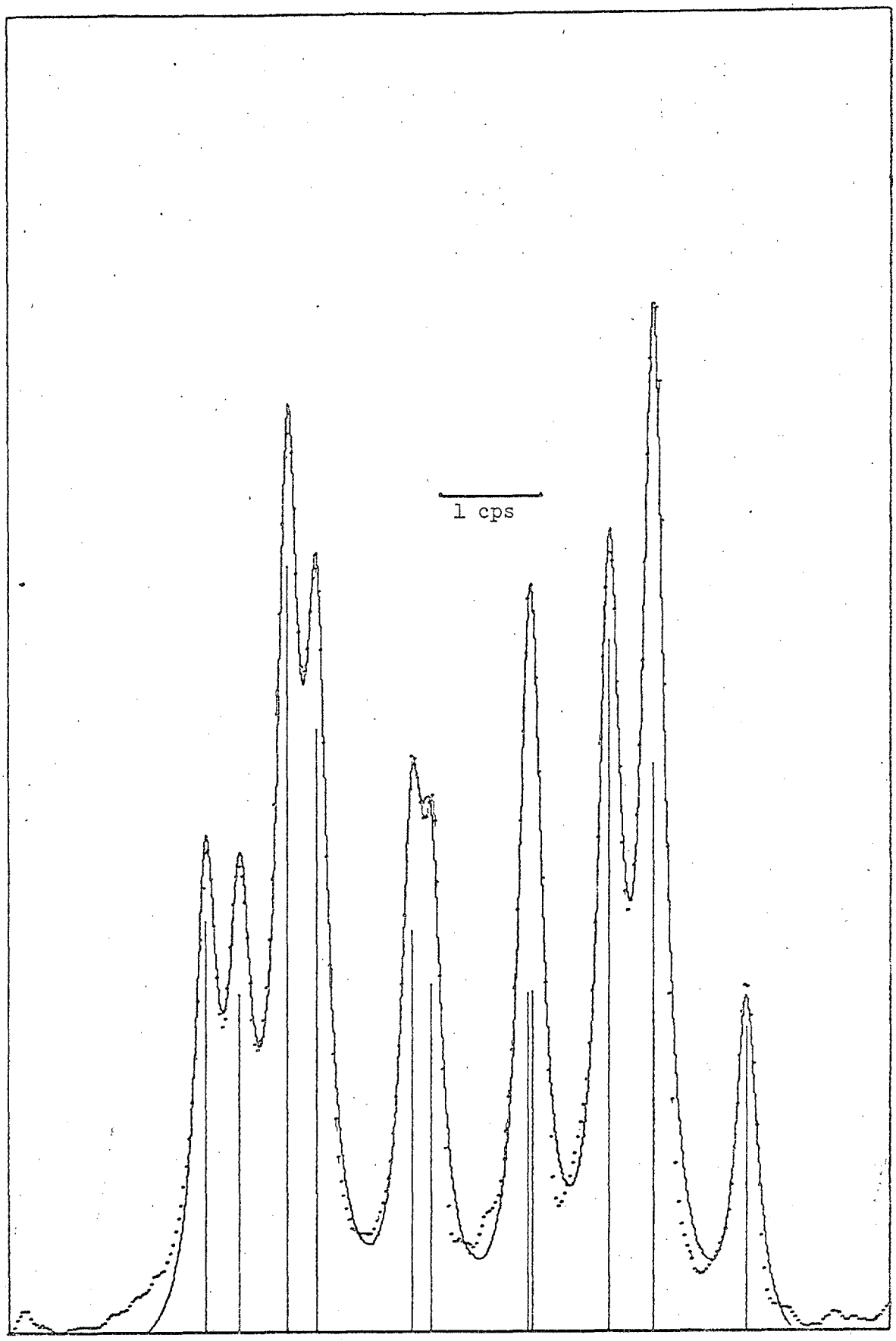


Fig. 30

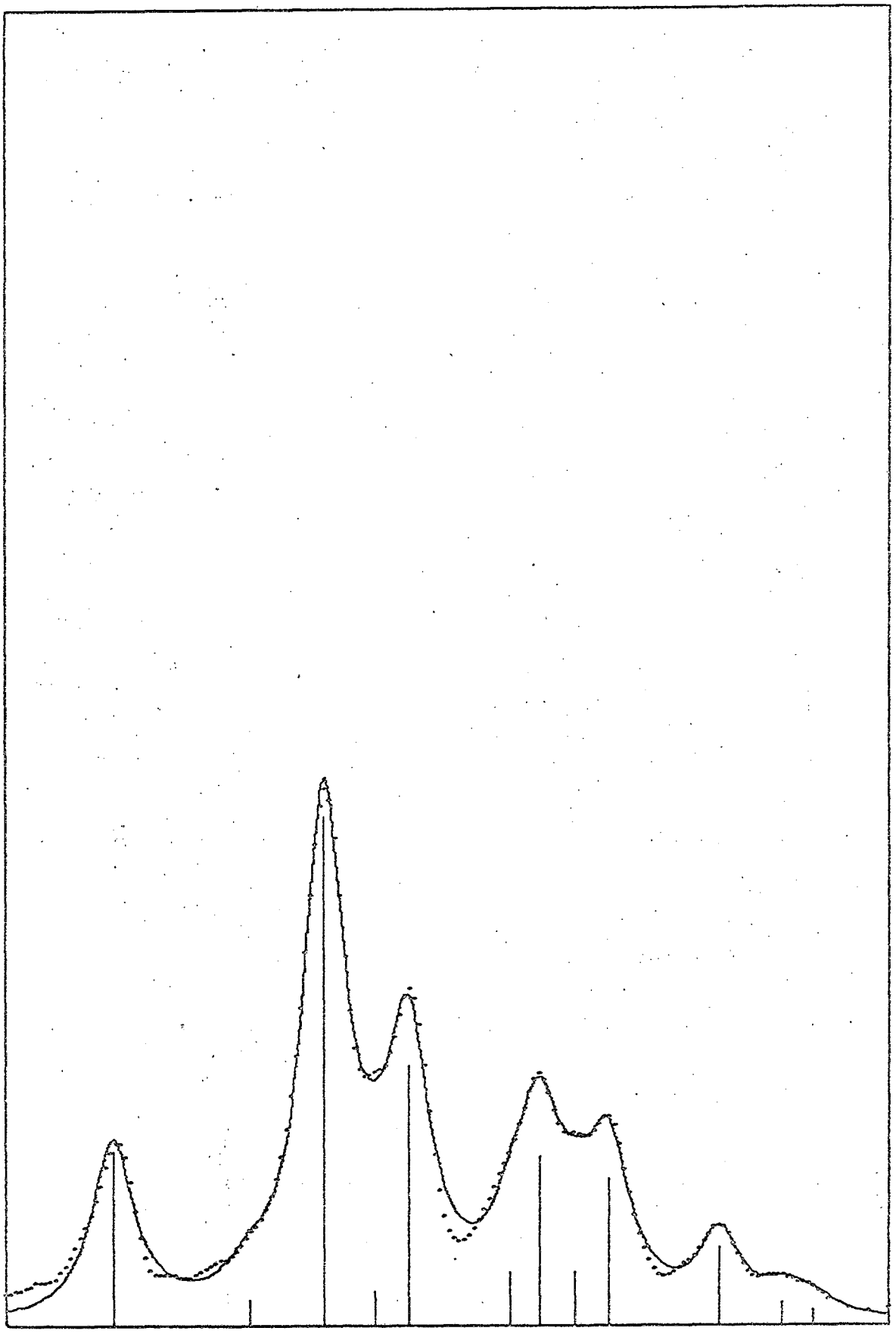


Fig. 31

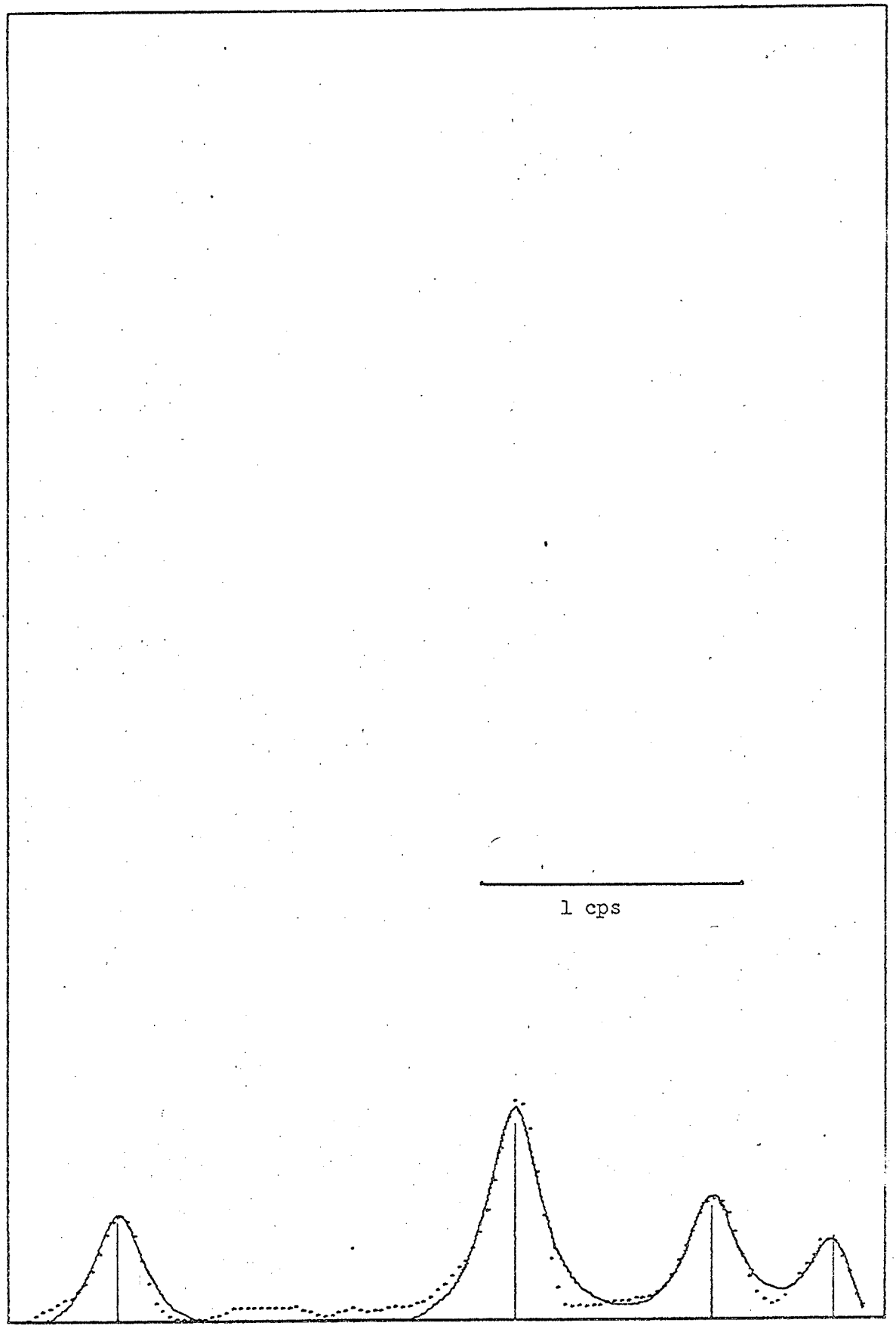


Fig. 32

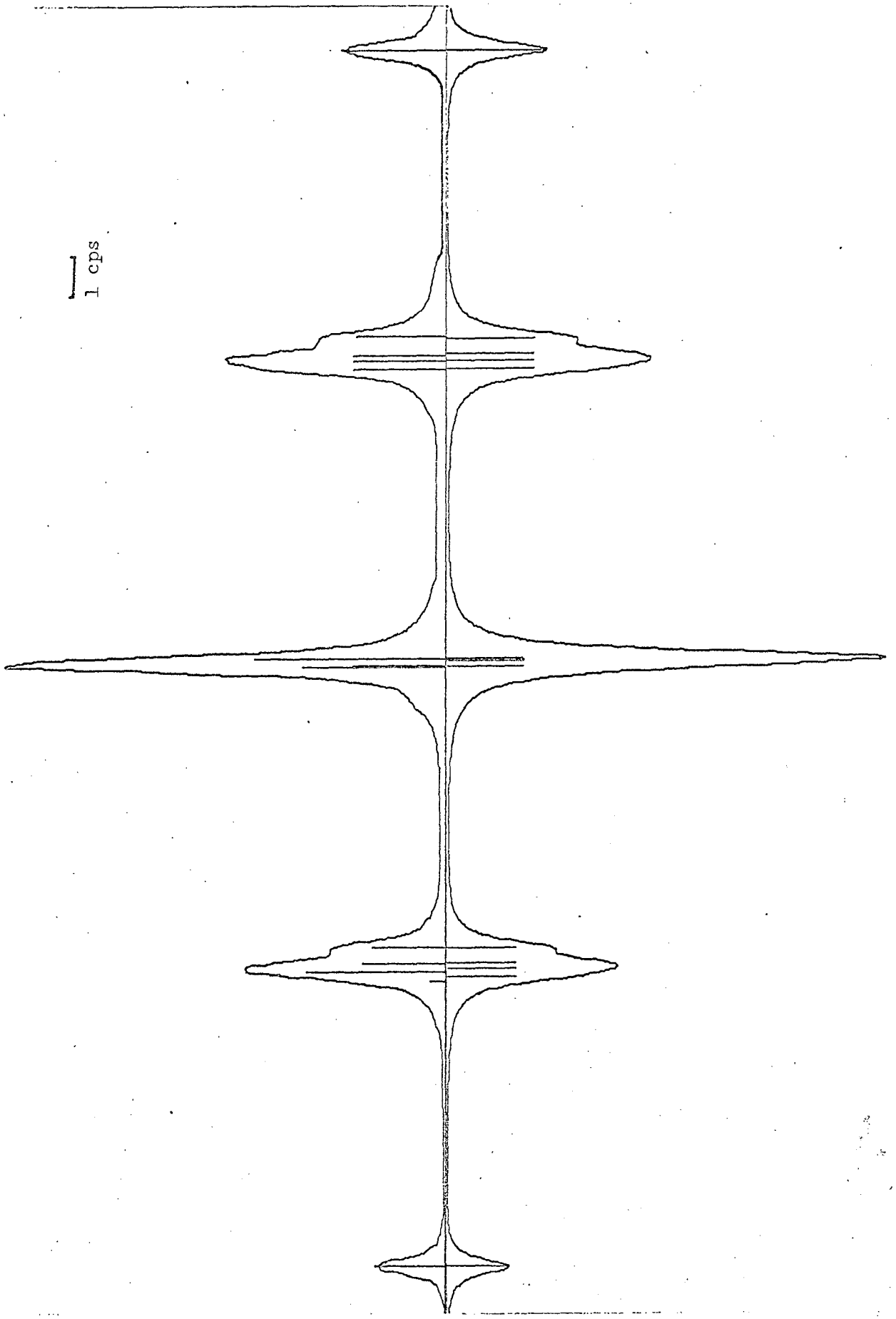


Fig. 33

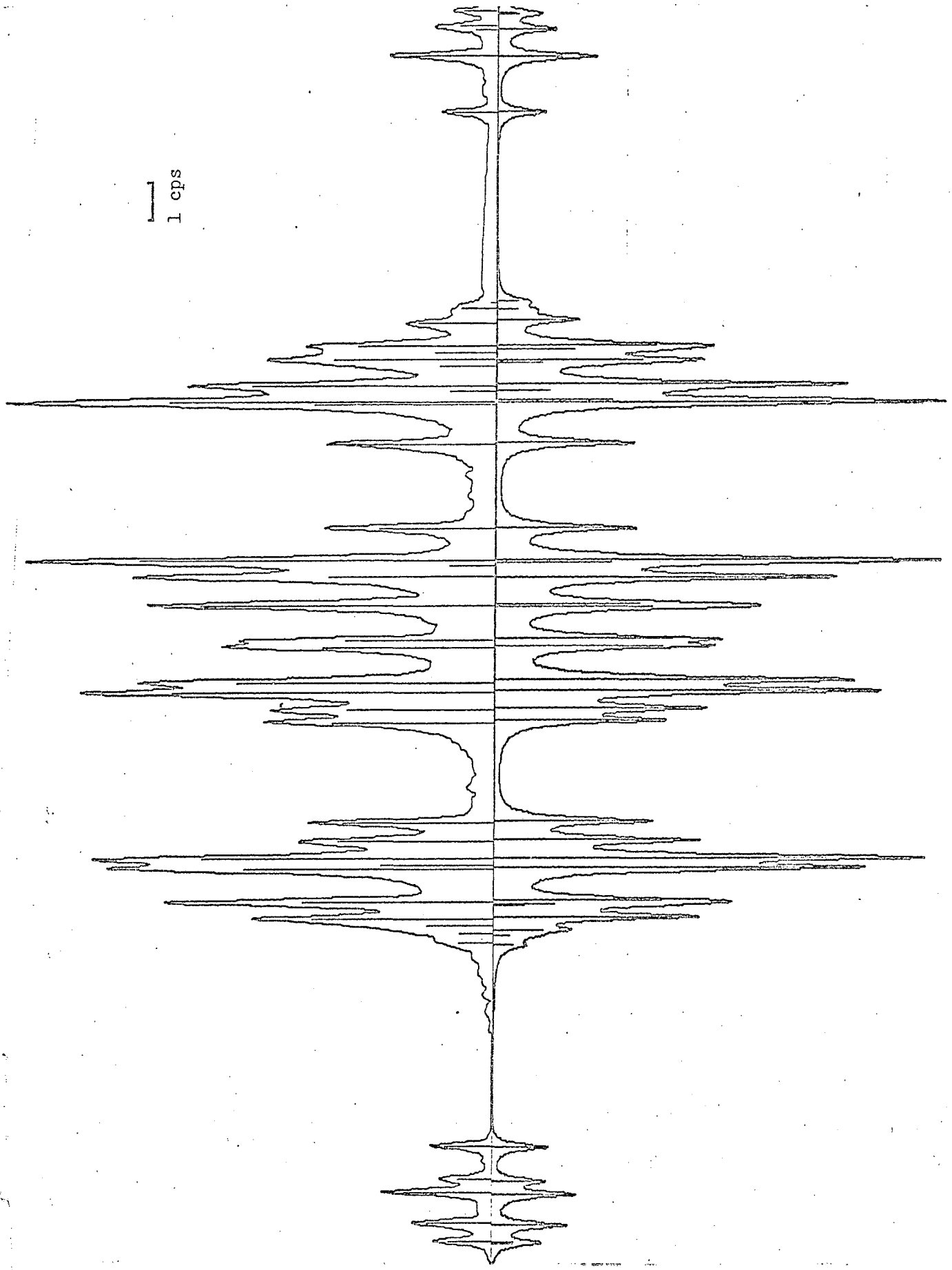


Fig. 34

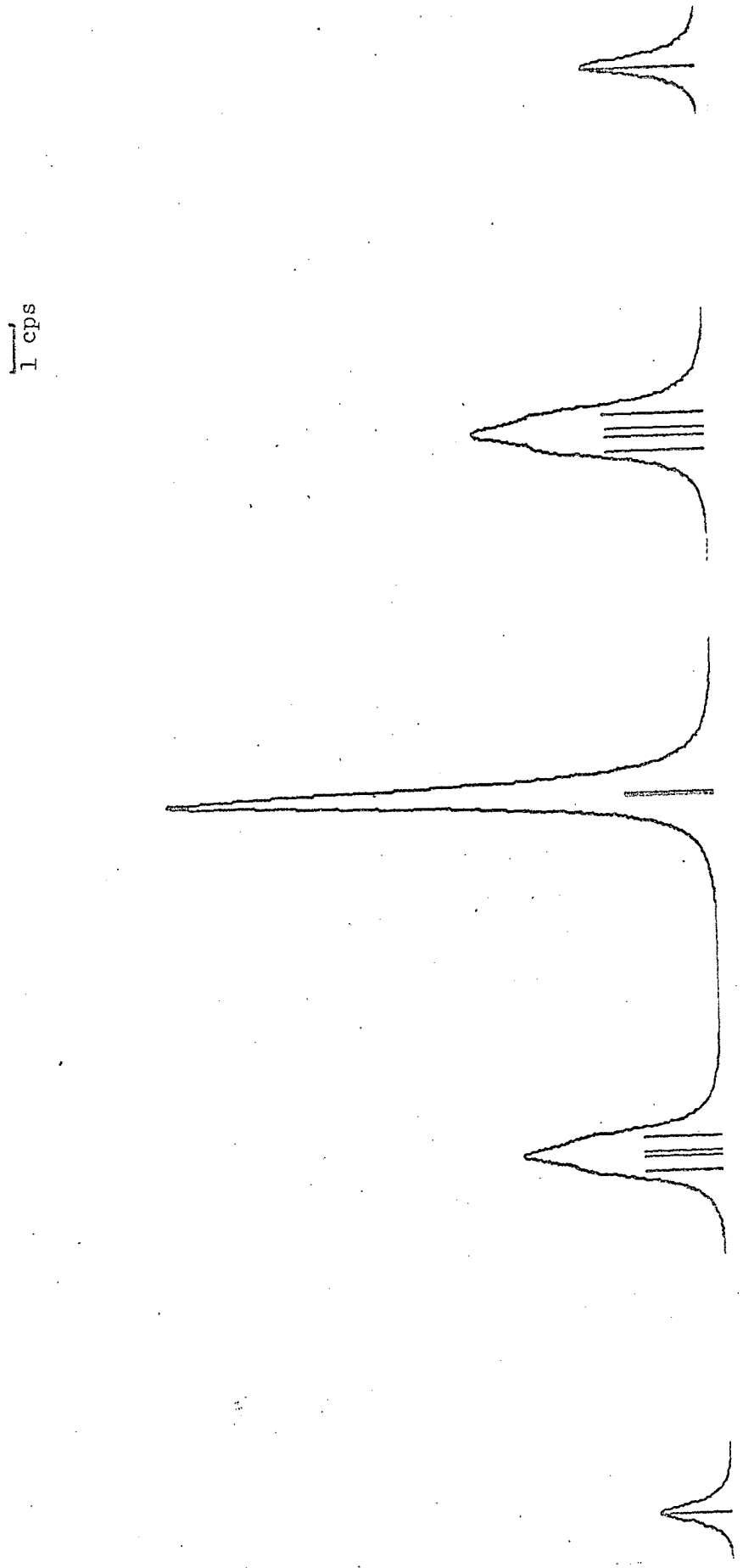


Fig. 35

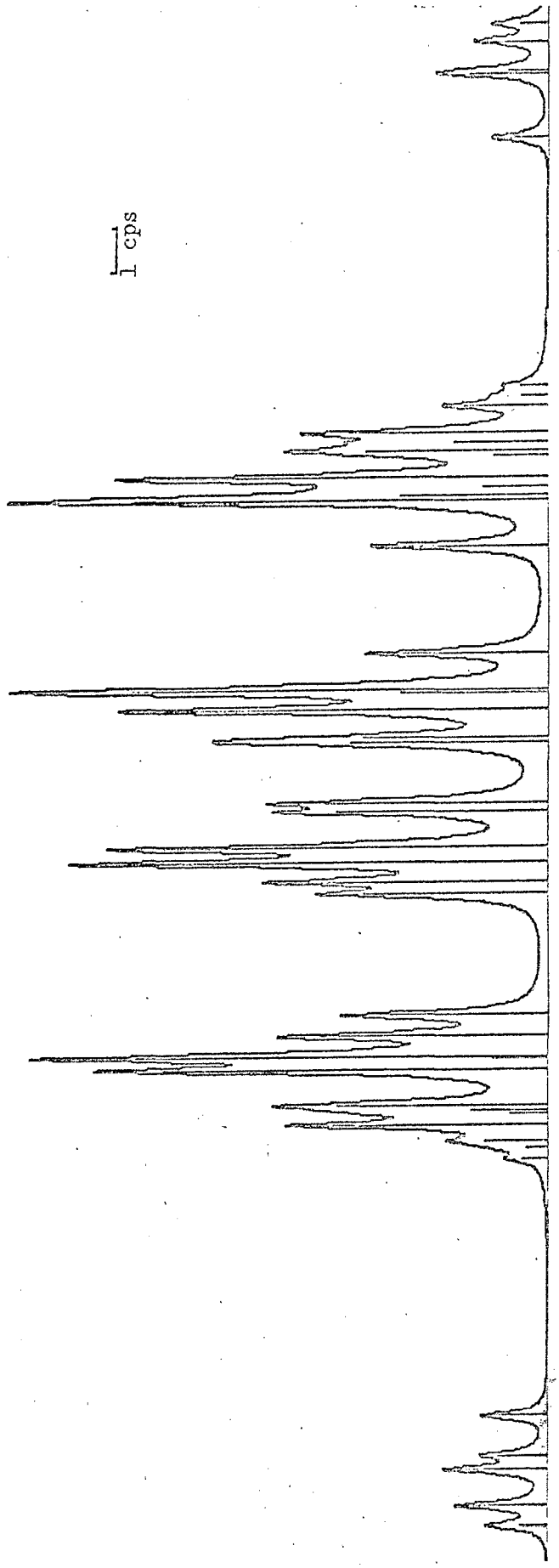


Fig. 36

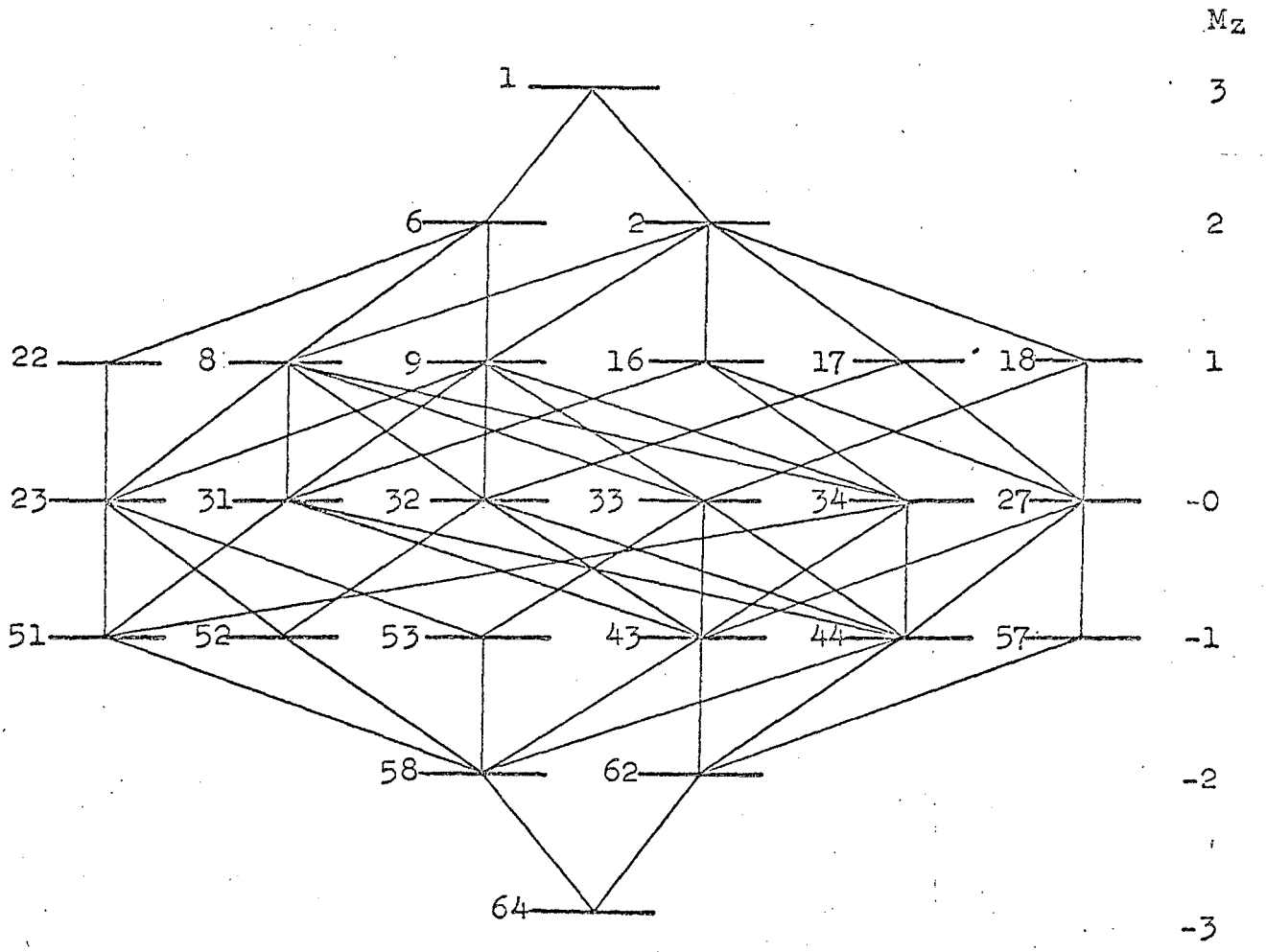

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Fig.37

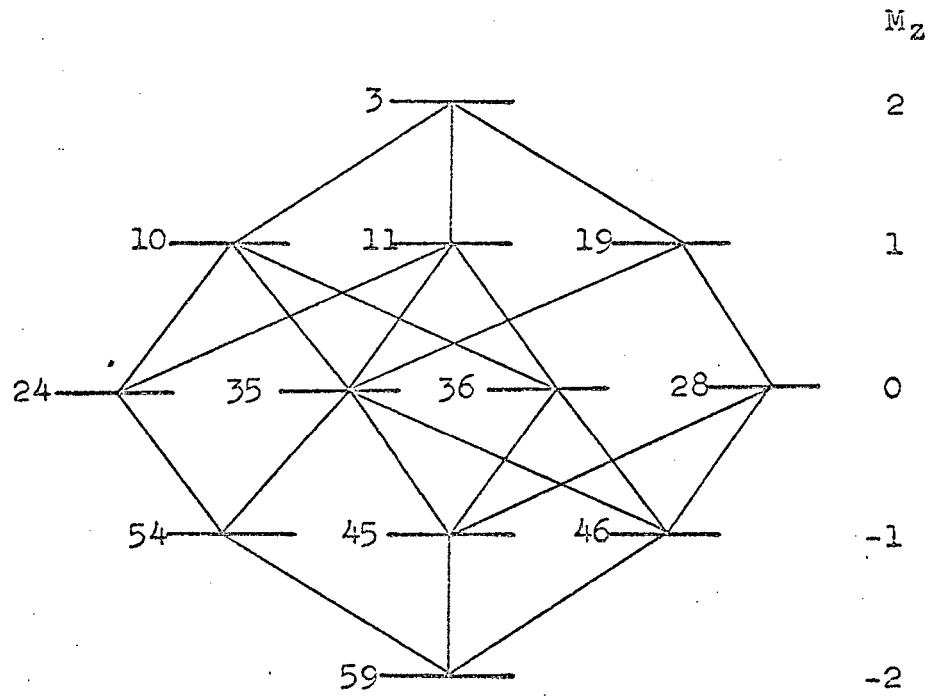

Fig. 38

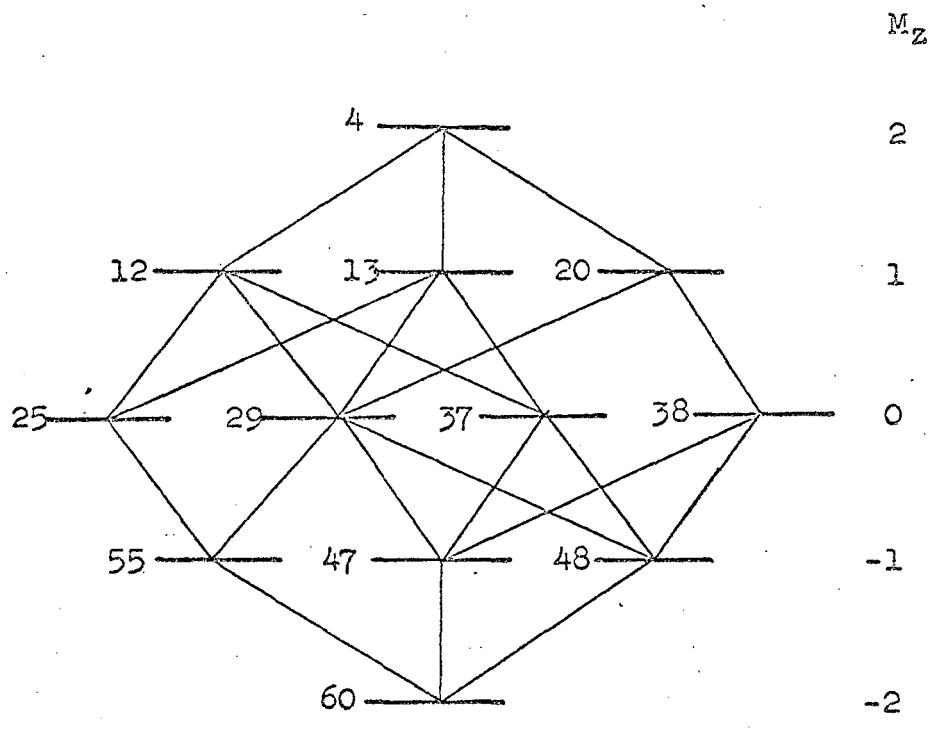

Fig. 39

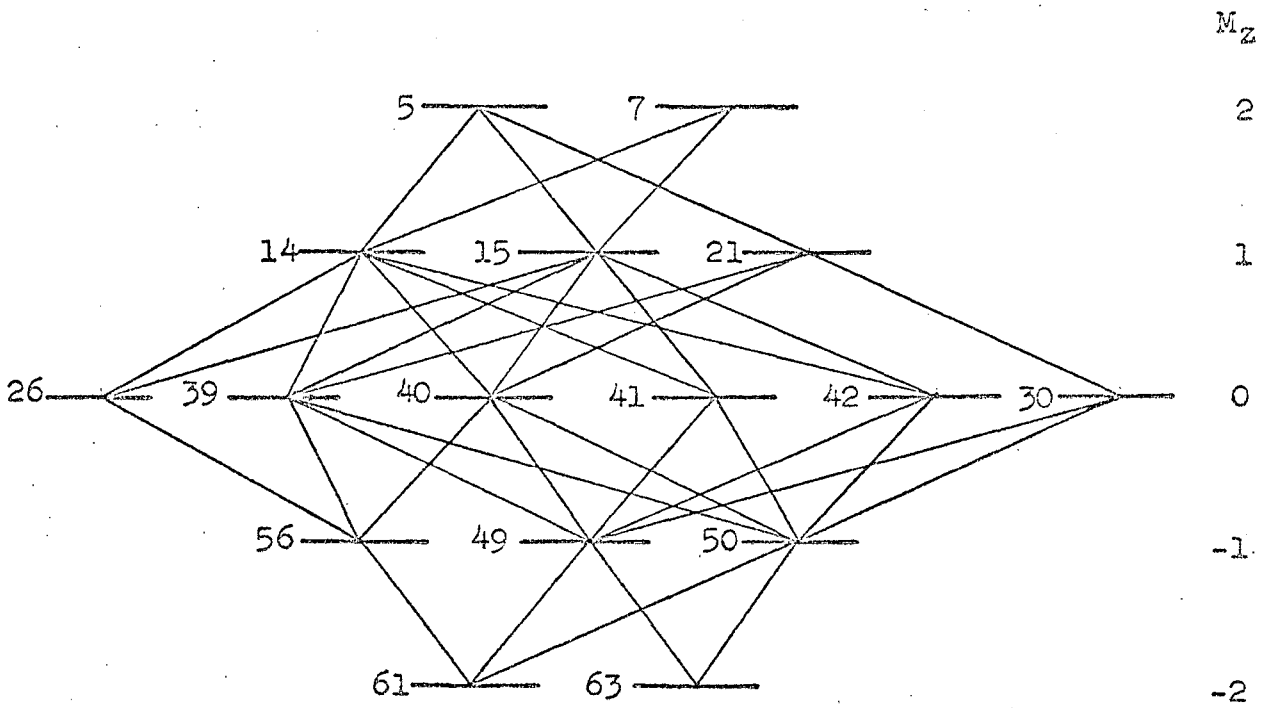

Fig. 40

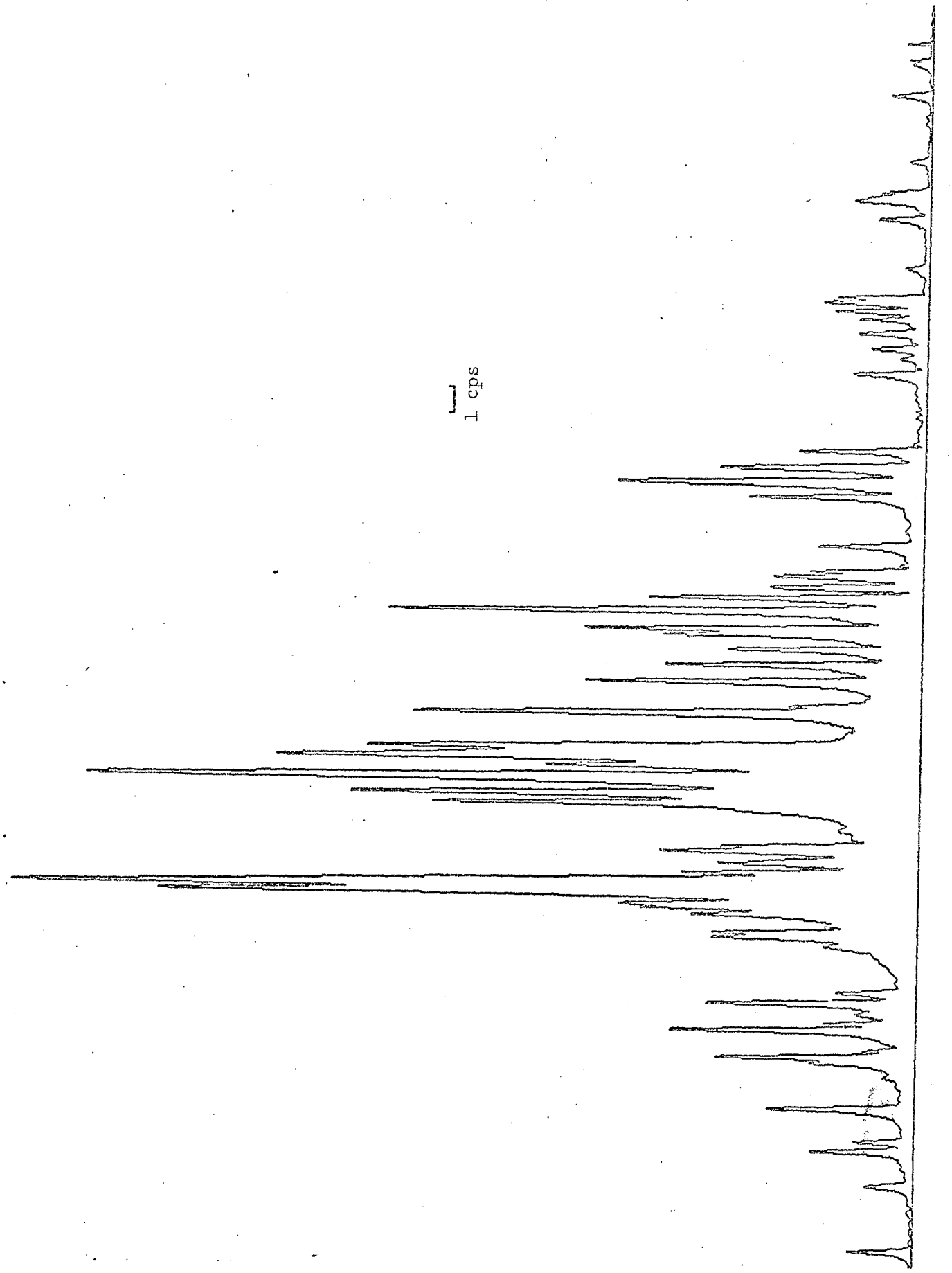

Fig. 41

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