UCRL-16247

University of California

Ernest O. Lawrence Radiation Laboratory

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

THE NMR SPECTRUM OF 3-CHLOROTHIETANE, AN EXAMPLE OF COMPLETE NMR SPECTRAL ANALYSIS BY COMPUTER TECHNIQUES

Berkeley, California

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UCRL-16247

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

THE NMR SPECTRUM OF 3-CHLOROTHIETANE, AN EXAMPLE OF COMPLETE NMR SPECTRAL ANALYSIS BY COMPUTER TECHNIQUES

Warren D. Keller, T. R. Lusebrink, and C. H. Sederholm

July, 1965

The NMR Spectrum of 3-Chlorothietane, an Example of Complete NMR Spectral Analysis by Computer Techniques

Warren D. Keller, T. R. Lusebrink,* and C. H. Sederholm**

Inorganic Materials Research Division
of the Lawrence Radiation Laboratory, and
Department of Chemistry, University of California
Berkeley, California

Abstract

The NMR spectrum of 3-chlorothietane has been analysed by the use of three computer techniques. These are: 1) Spectral decomposition (DECOMP), 2) Spectral assignment (ASSIGN), and 3) Swalen and Reilly's iterative program (NMRIT). DECOMP determines to a large extent the frequencies and intensities of all lines which make up an unresolved multiplet. ASSIGN calculates all possible sets of energy levels which are consistent with the observed frequencies and intensities of the completely resolved spectrum. NMRIT calculates, for each set of energy levels, the corresponding coupling constants and chemical shifts if they are real. Only one set of coupling constants and chemical shifts is consistent with the NMR spectrum of 3-chlorothietane. The chemical shifts and vicinal coupling constants are quite normal. The geminal

coupling constant is -8.63 cps. There is a large long-range coupling constant across the ring of +3.12 cps. The other two long-range coupling constants are smaller and negative. The geminal and long-range coupling constants are compared with theoretical calculations.

Introduction

Four-membered ring compounds are of much interest in NMR. The molecular structures of these compounds are relatively well defined, having been determined exactly in several cases.[1-3] Thus, it should be possible to determine experimentally those factors of geometry and/or substitution which are important in influencing coupling constants and chemical shifts. In addition the simplicity of these molecules invites theoretical calculations[4-6] which can be compared with experimental results.

Further interest in these molecules, arising from the complexity of their spectra, involves possible large coupling across the ring between protons separated by four saturated chemical bonds. Such long-range coupling constants have been observed in both saturated and unsaturated systems.[7] Observed coupling through four saturated bonds has nearly always been less than two cps[7] although exceptions have been found in such highly strained systems as a tricyclo-[1.1.1.0]-pentane,[8] certain bicyclo-[2.1.1]-hexanes,[7,9,10] and some bicyclo-[2.2.1]-heptanes.[7,11] Although the equilibrium configuration of these strained molecules is often known, no detailed knowledge of the actual bond lengths and bond angles is available. Furthermore, the complexity of the NMR spectra rules out with few exceptions[12-18] the determinations of relative signs of the coupling constants. As a result any successful attempt to correlate long-range coupling constants with molecular structure or to make theoretical calculations appears distant. However,

if it is indeed found that four-membered ring compounds in general have measurable long-range coupling constants, this series of molecules will provide a simple system in which to investigate this phenomenon.

This history led to the present investigation of one member of this series, 3-chlorothietane. Unfortunately, its highly complicated non-first-order spectrum did not lend itself to easy analysis by conventional methods. The NMR parameters of many molecules having quite complex spectra have been determined through the use of iterative computer techniques, such as NMRIT developed by Swalen and Reilly;[19] however, in the case of four-membered ring compounds these methods have generally failed. Only a few highly substituted molecules have been analyzed[20-24] while such basic molecules as trimethylene oxide and trimethylene sulfide, despite much effort, have defied analysis.

This failure of NMRIT can be understood by a consideration of the information necessary for its success. Essentially it depends upon sufficient prior knowledge of the NMR parameters, unavailable in the case of four-membered ring compounds, so that individual experimental transitions can be assigned to theoretically expected transitions, thus determining the true energy levels of the molecule. In general these energy levels are greatly overdetermined by all of the transitions, so that some transitions need not be assigned or can be assigned incorrectly without causing failure of the technique. However, in the analysis of 3-chlorothietane as well as many other molecules, the spectra are so highly mixed that many of the individual lines cannot be resolved, even under optimum experimental conditions. Thus, there are two problems to be solved to insure the successful analysis of these molecules. 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 as dependent on prior knowledge of the approximate values of the NMR parameters.

In order to determine enough experimental lines to apply NMRIT successfully it is necessary to utilize more powerful methods than visual estimations of line positions and intensities. Mathematical methods for improving the resolution of overlapping spectral lines have been reported,[25-29] but do not appear to be widely used. DECOMP, a computer method of resolving overlapping NMR spectral peaks described below, was found extremely useful in this analysis and promises to be useful in the analysis of many similar spectra.

DECOMP solves the first of the above mentioned problems 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[28] has discussed a computer assignment technique and has applied it to a well resolved A_2B_2 spectrum. Although in theory this technique 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 technique described below, helps to overcome these problems and has been used successfully for 3-chlorothietane.

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 one may 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.

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.

One way of doing this 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 to 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 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, $G(\nu)$, then, is assumed to consist of a superposition of lines having the same form

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

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 equation 1.

$$F(I_1, \ldots I_n, \nu_1, \ldots \nu_n, \Delta\nu) = \sum_{i=1}^{m} [P_i - \sum_{j=1}^{n} I_j f(\Delta\nu, t_i - \nu_j^\circ)]^2 \tag{2}$$

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 equation (2). Mathematical details of the minimization program are available elsewhere.[29]

A Lorentzian shape function was originally used, since it is a good approximation to many slow passage NMR spectra. Unfortunately it is very difficult to establish and maintain spectrometer conditions such that perfect Lorentzian curves are obtained 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 been used. Considerable improvement in the fit to spectra consisting of skewed Lorentz-like peaks is thus obtained.

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. This data is fed into the 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 spectrum. 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. In all instances investigated so far, these cases have been easy to recognize.

An example of the method is shown in Figs. 1 and 2. The decomposition of a group of twelve peaks using the Lorentz approximation is shown in Fig. 1 while Fig. 2 shows the same group decomposed using a

standard digital peak taken from another part of the spectrum. 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.

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. In the following discussion of ASSIGN, the word "transition" will be used to denote an unknown transition between two energy levels, and the word "line" will be used to denote an experimentally determined transition. The purpose of ASSIGN, then, 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, hence, 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 (or B) transitions. Such information might also be obtained from order of magnitude guesses of the spectral parameters.

In addition, ASSIGN is completely general for any system of spins 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. This algorithm is easily constructed for any given system, e.g., ABC or A_2B_2X. Of course it is necessary to make up the algorithm only once for each type of system. 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[28,30] at the earliest possible time in the assignment procedure. Fig. 3 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 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, 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. 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 establishes 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. The 24 lines in an A_2B_2 system require between 1 and 3 minutes.

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 of 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, and 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 tickling experiments[31] 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.

Experimental

The 3-chlorothietane was synthesized according to the procedure of Dittmer and Christy.[32,33] The final distillation, carried out on a spinning band column, yielded several fractions. Only the middle constant boiling fractions were used to obtain the NMR spectra. The samples, containing a small amount of tetramethylsilane as an internal reference, were degassed under vacuum and the tubes were sealed.

Spectra were recorded on a Varian A-60 spectrometer which had been modified by replacing the 25 rpm sweep motor with a 2 rpm motor, allowing

very slow sweep rates. The X and the A_2B_2 parts of the 3-chlorothietane spectrum were taken separately with a sweep width of 50 cps and a sweep time of 1250 seconds. The spectra were filtered at 0.2 cps to reduce the noise and to facilitate the subsequent digitization.

Spectrum Analysis

The two best resolved spectra were used for the analysis. A Benson-Lehner "OSCAR" x-y analogue-to-digital reader, directly coupled to an IBM 026 card punch, was used to digitize the spectra.

The experimental spectrum of 3-chlorothietane in Fig. 4 was decomposed using the DECOMP program described above. A total of 64 lines were resolved and are shown in Fig. 5. In these figures, the experimental data points, as read by the "OSCAR" are shown as dots. The results of DECOMP are shown as vertical lines, and the calculated spectrum based on the frequencies and intensities resulting from the decomposition is shown as a solid curve. As can be seen, the agreement between the calculated curve and the data points is very good; however, use of the OSCAR introduces some noise which could be avoided by use of a direct coupled A/D converter. The line positions and their decomposed intensities are tabulated in Table 3.

These results were put into the ASSIGN program discussed above, along with reasonable limits on the frequencies for the various types of transitions. ASSIGN yielded three sets of energy levels consistent with the frequencies and intensities as determined by DECOMP. These energy levels are listed in Table 4. The various sets of energy levels

were put into NMRIT. Two of the sets of energy levels corresponded to complex parameters as was shown by the failure of NMRIT to converge. The other set of energy levels corresponds to a real set of parameters. These parameters are also listed in Table 4. The numbering system used for the protons is shown in Fig. 6.

As a check on this determination of the NMR parameters, the calculated spectrum based on these parameters is compared with the experimental spectrum and the decomposed lines in Fig. 7. In this figure, the top curve with its set of vertical lines corresponds to the theoretical spectrum based upon the NMR parameters listed in Table 4, and upon the experimentally determined line shape function. The bottom curve is the experimental spectrum and the bottom set of vertical lines corresponds to the line positions and intensities found by decomposition of the spectrum. As can be seen, the agreement is magnificent.

Discussion

The vicinal coupling constants in 3-chlorothietane are quite similar to those found in other 4-membered ring compounds[20,22,24] and are in agreement with the usual correlations with dihedral angles, substitution, and bond lengths. The geminal coupling constant, however, is smaller (more positive) than those found in other 4-membered ring molecules.[20-22,24] These previous results, ranging from -10 cps to -17 cps, are in all cases found in substituted cyclobutanes, whereas the constant reported here is in a substituted thietane. This result is to be expected in light of Pople's recent molecular orbital treatment of geminal proton coupling constants.[5] His theory predicts a positive shift in the geminal coupling constant for an electronegative sulfur atom α to the geminal hydrogens.

The long-range coupling constants are quite interesting. One is unusually large and is positive. The other two are not only smaller but also negative. Before discussing these long-range coupling constants further, some estimates of the geometry of the molecule are in order.

The exact structure of 3-chlorothietane has not been determined. However, for our purposes the structure can be surmised from that of chlorocyclobutane which has been determined exactly.[3] Chlorocyclobutane is puckered in its ground vibrational state. The equilibrium angle is 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 to pucker arising from the preferred staggered configuration of the hydrogen atoms or other substituted atoms on the adjacent ring carbon atoms. In chlorocyclobutane the puckering tendencies seem to be stronger and the ring is bent. In considering 3-chlorothietane we are subtracting from both of these forces. The ring sulfur atom decreases the ring strain and thus would allow for more puckering, but the loss of one methylene group decreases the tendency toward the staggered configuration. The relative sizes of these two effects would determine whether chlorothietane is more or less puckered than chlorocyclobutane. For the purposes of the following calculations we will assume the puckering is roughly the same in the two molecules.

From the NMR data alone it is not possible to determine whether the quasi-axial or the quasi-equitorial protons account for the large cross ring coupling. Empirical evidence indicates that in nearly all cases one specific configuration, that in which both protons and all of the connecting bonds are nearly coplanar, allows an observable long-range

coupling constant. On this basis, one would be tempted to say that the quasi-equitorial protons account for the large coupling, since they are more nearly in a staggered planar configuration. However, this is by no means conclusive, since there have been exceptions to this "planar zig-zag" rule.[7,34]

Some evidence as to which protons show the large long-range coupling constant can be obtained by applying Karplus' correlation between vicinal coupling constants and dihedral angles.[4] Using the available data on chlorocyclobutane, it is found that the dihedral angles between H_3 and the equitorial protons is 28°, while that between H_3 and the axial protons is 155°. Using Karplus' results, one would predict $J_{3equi} \cong 5\text{-}6$ cps and $J_{3ax} \cong 7$ cps. Therefore, this would indicate that protons 1 and 2, which are coupled by 3 cps, are indeed the equitorial protons.

Recently, Barfield[6] has made some theoretical calculations of long-range coupling constants using valence bond wave functions. These calculations indicate an angular dependence of the long-range coupling constants through four saturated bonds. In Table 5 are shown the contributions to the various long-range couplings by both paths around the ring. The appropriate angles were calculated for the chlorocylobutane molecule, and the contributions to the couplings were taken from Fig. 2 in Barfield's paper. It can be seen that J_{12} is predicted to be the largest and positive, J_{45} is predicted to be small and negative, and $J_{15} = J_{24}$ are predicted to be small and positive. Only the coupling between the equitorial and axial protons fails to agree qualitatively with Barfield's theory.

Of course, exact agreement between experimental coupling constants and the theoretical predictions would have been surprising. The application of Barfield's theory is based on many simplifying assumptions such as perfect SP^3 carbon hybrid orbitals, no hetero atoms in the coupling path, and bond lengths equal to those in ethane. Furthermore, Barfield's angular calculations are based only on the "indirect" (through bond) contribution to the coupling constants. Any "direct" (through space) contribution has been neglected. These approximations could easily account for the discrepancies found. As more of these four-membered rings are analysed, it should be possible to discover more quantitative relationships between molecular structure and the long-range coupling constants.

Acknowledgements

The authors wish to express their appreciation to Dr. Ernest Lustig and Mr. J. Ferretti for originally suggesting the study of 4-membered ring molecules. They would also like to thank Mr. Richard Millikan for his work in signal to noise ratio improvement. Finally, support is gratefully acknowledged from the United States Atomic Energy Commission through the Inorganic Materials Research Division of the Lawrence Radiation Laboratory.

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

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 3 (Continued)

Line	Frequency (cps)	Intensity
44	-206.457	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 4

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 4 (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 5

Theoretical Contributions to Long-Range Coupling Constants

Path	Dihedral Angle*		$^4J_{HH'}$ (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.

References

* Present address: Douglas Aircraft Company, Inc., Missiles and Space Systems Division, Santa Monica, California.

** Present address: International Business Machines Systems Research and Development, 2670 Hanover Street, Palo Alto, California.

1. J. D. Dunitz and V. Schomaker, J. Chem. Phys. 20, 1703 (1952).
2. S. I. Chan, J. Zinn, and W. D. Gwinn, J. Chem. Phys. 34, 1319 (1961).
3. H. Kim, "Studies of Cyclobutene, Chlorocyclobutane, and Formic Acid by Microwave Spectroscopy," Ph.D. thesis, University of California, Berkeley, (1964).
4. M. Karplus, J. Chem. Phys. 30, 11 (1959).
5. J. A. Pople and A. A. Bothner-By, J. Chem. Phys. 42, 1339 (1965).
6. M. Barfield, J. Chem. Phys. 41, 3825 (1964).
7. S. Sternhell, Rev. Pure and Appl. Chem. 14, 15 (1964).
8. S. Masamune, J. Am. Chem. Soc. 86, 735 (1964).
9. J. Meinwald and A. Lewis, J. Am. Chem. Soc. 83, 2769 (1961).
10. K. B. Wiberg, B. R. Lowry, and B. J. Nist, J. Am. Chem. Soc. 84, 1594 (1962).
11. J. Meinwald and Y. C. Meinwald, J. Am. Chem. Soc. 85, 2514 (1963).
12. C. A. Reilly and J. D. Swalen, J. Chem. Phys. 35, 1522 (1961).
13. H. Finegold, Proc. Chem. Soc. 1962, 213.
14. R. Freeman and K. G. R. Pachler, Mol. Phys. 5, 85 (1962).
15. A. A. Bothner-By and C. Naar-Colin, J. Am. Chem. Soc. 84, 743 (1962).
16. F. A. L. Anet, J. Am. Chem. Soc. 84, 747 (1962).

17. R. Freeman and N. S. Bhacca, J. Chem. Phys. 38, 1088 (1963).

18. D. D. Elleman, S. L. Manatt, and C. D. Pearce, J. Chem. Phys. 42, 650 (1965).

19. J. D. Swalen and C. A. Reilly, J. Chem. Phys. 37, 21 (1962).

20. E. Lustig, J. Chem. Phys. 37, 2725 (1962).

21. M. Takahashi, D. R. Davis, and J. D. Roberts, J. Am. Chem. Soc. 84, 2935 (1962).

22. K. L. Servis and J. D. Roberts, J. Phys. Chem. 67, 2885 (1963).

23. V. Georgian, L. Georgian, and A. V. Robertson, Tetrahedron 19 (8), 1219 (1963).

24. B. Braillon, J. Salaün, J. Gore, and J. Conia, Bull. Soc. Chim. France, 1964, 1981.

25. P. Medgyessy, Decomposition of Superpositions of Distribution Functions (Publishing House of the Hungarian Academy of Sciences, Budapest, 1961).

26. H. Stone, J. Opt. Soc. Am. 52, 998 (1962).

27. L. C. Allen, H. M. Gladney, and S. H. Glarum, J. Chem. Phys. 40, 3135 (1964).

28. D. R. Whitman, J. Chem. Phys. 36, 2085 (1962).

29. W. C. Davidson, Variable Metric Method for Minimization, Argonne National Laboratory Report ANL-5990 (Rev.), (1959).

30. G. Gioumousis and J. D. Swalen, J. Chem. Phys. 36, 2077 (1962).

31. R. Freeman and W. A. Anderson, J. Chem. Phys. 37, 2053 (1962).

32. D. C. Dittmer and M. E. Christy, J. Org. Chem. 26, 1324 (1961).

33. M. E. Christy, "The Synthesis and Reactions of Derivatives of Thietane and Thietene," Ph.D. Thesis, Univ. of Pennsylvania, (1961).

34. Y. Osawa and M. Neeman, J. Am. Chem. Soc. 85, 2856 (1963).

Figure Captions

Figure 1 Group of twelve peaks decomposed with Lorentz 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.

Figure 2 Group of twelve peaks decomposed with digital shape function.

Figure 3 Energy level diagram for ABC example.

Figure 4 Experimental spectrum of 3-chlorothietane: (a) X region, (b) A_2B_2 region.

Figure 5 a,b,c,d, e,f,g,h Decomposed groups of peaks from the spectrum of 3-chlorothietane using a digital shape function.

Figure 6 3-chlorothietane, structure and identification of protons.

Figure 7 Comparison of results from NMRIT and DECOMP of the spectrum of 3-chlorothietane. (a) X region, (b) A_2B_2 region. 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.

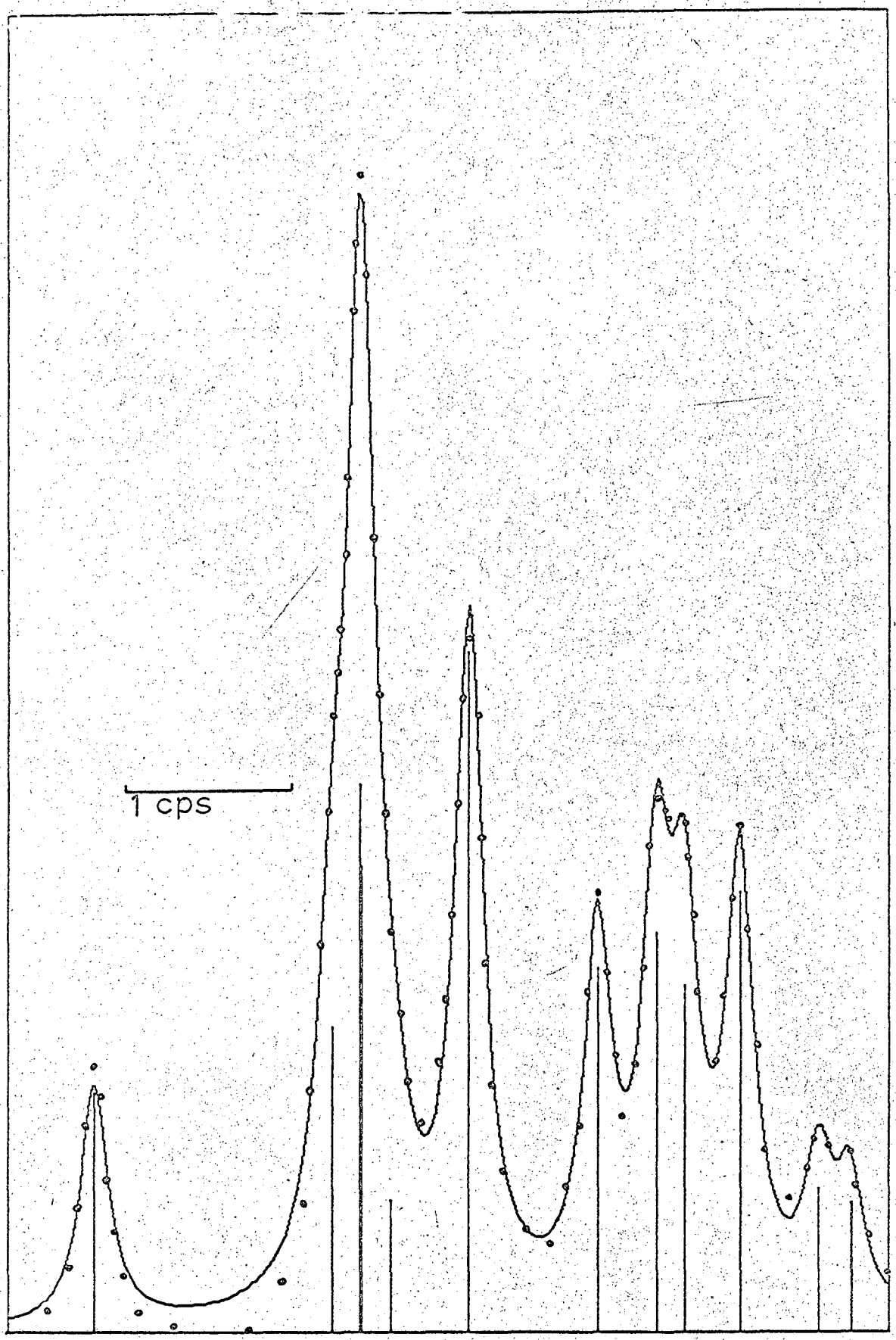

Figure 1

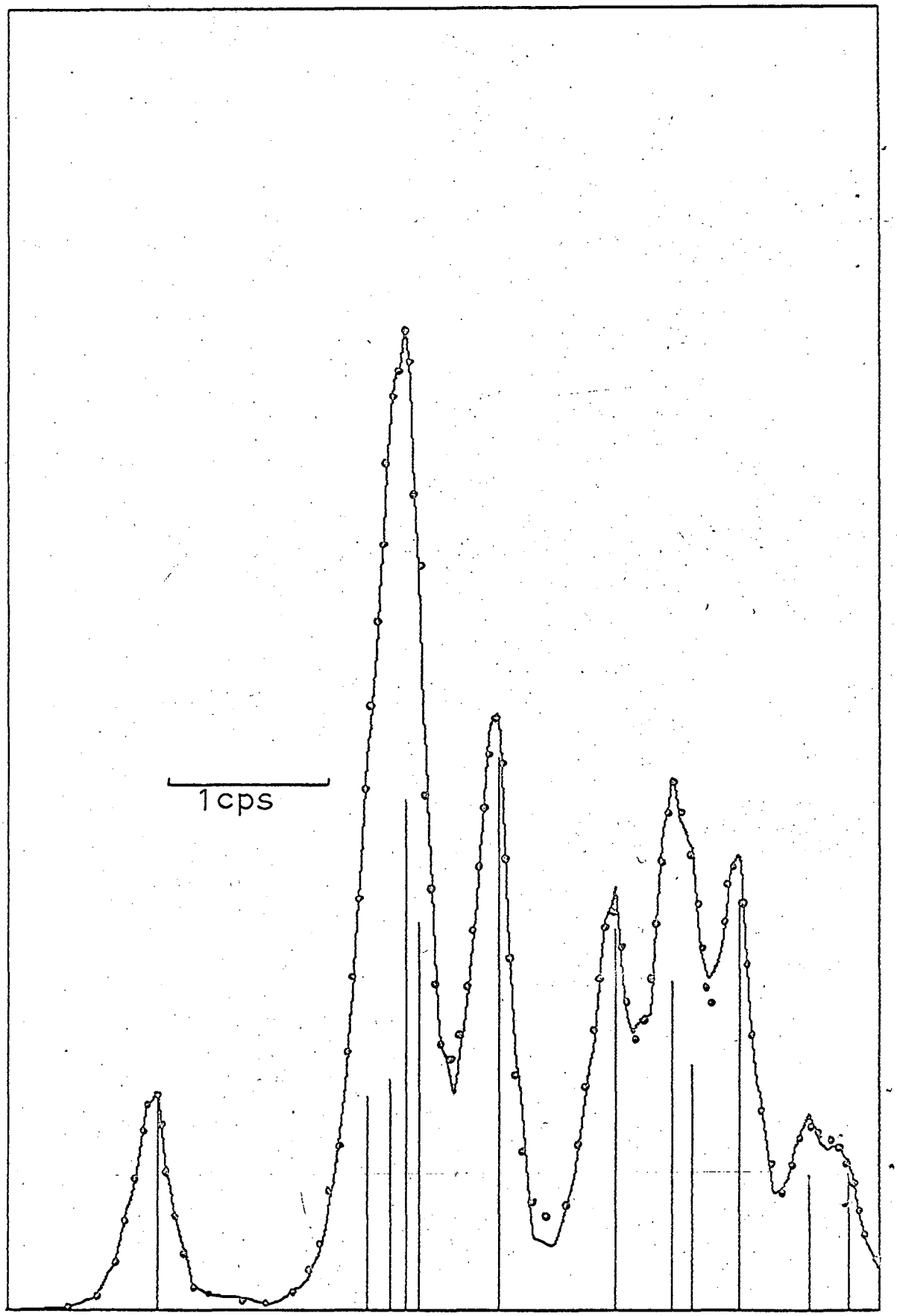

Figure 2

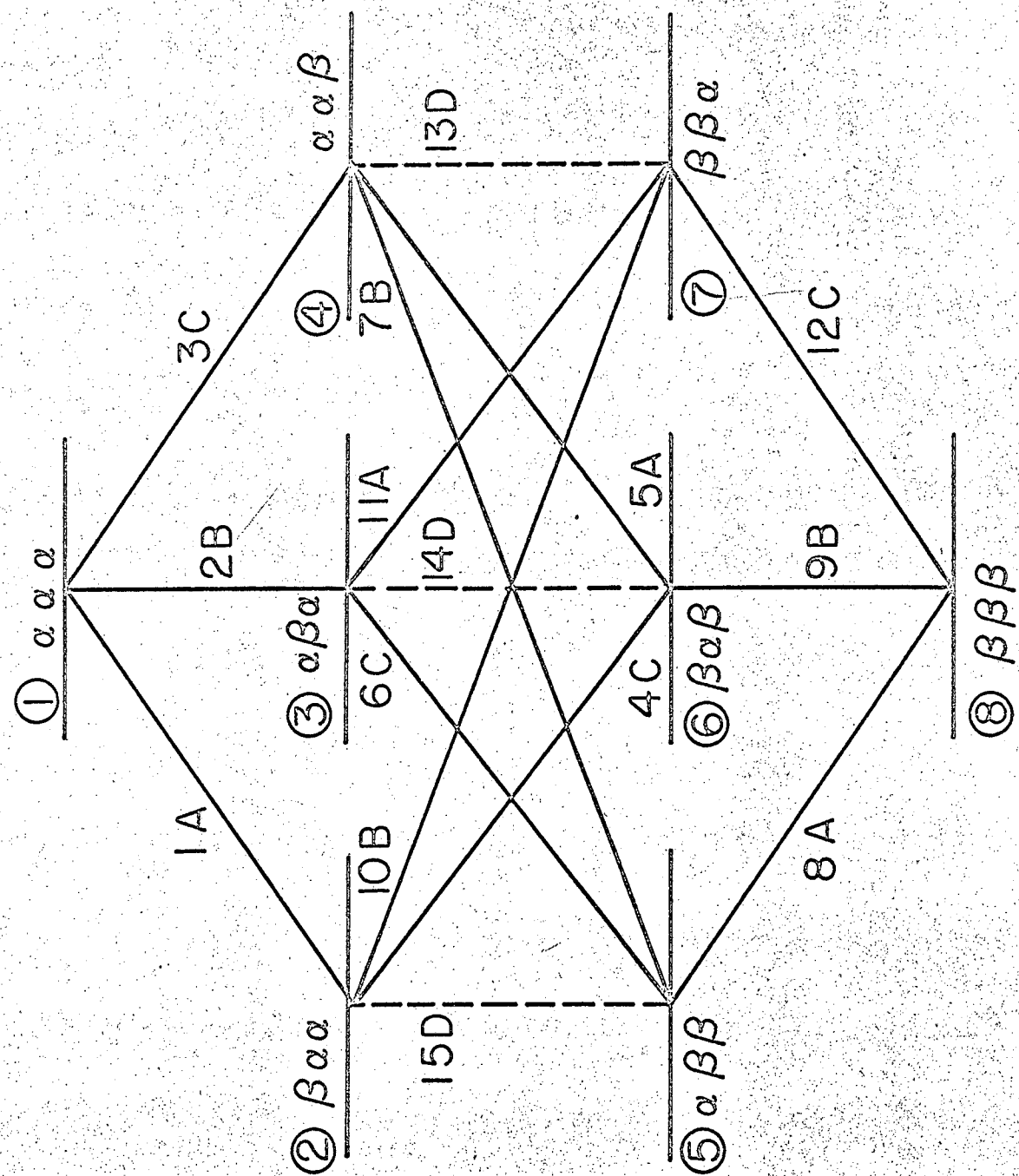
① α α α
② β α α
③ α β α
④ α α β
⑤ α β β
⑥ β α β
⑦ β β α
⑧ β β β
1A
2B
3C
4C
5A
6C
7B
8A
9B
10B
11A
12C
13D
14D
15D

Figure 3

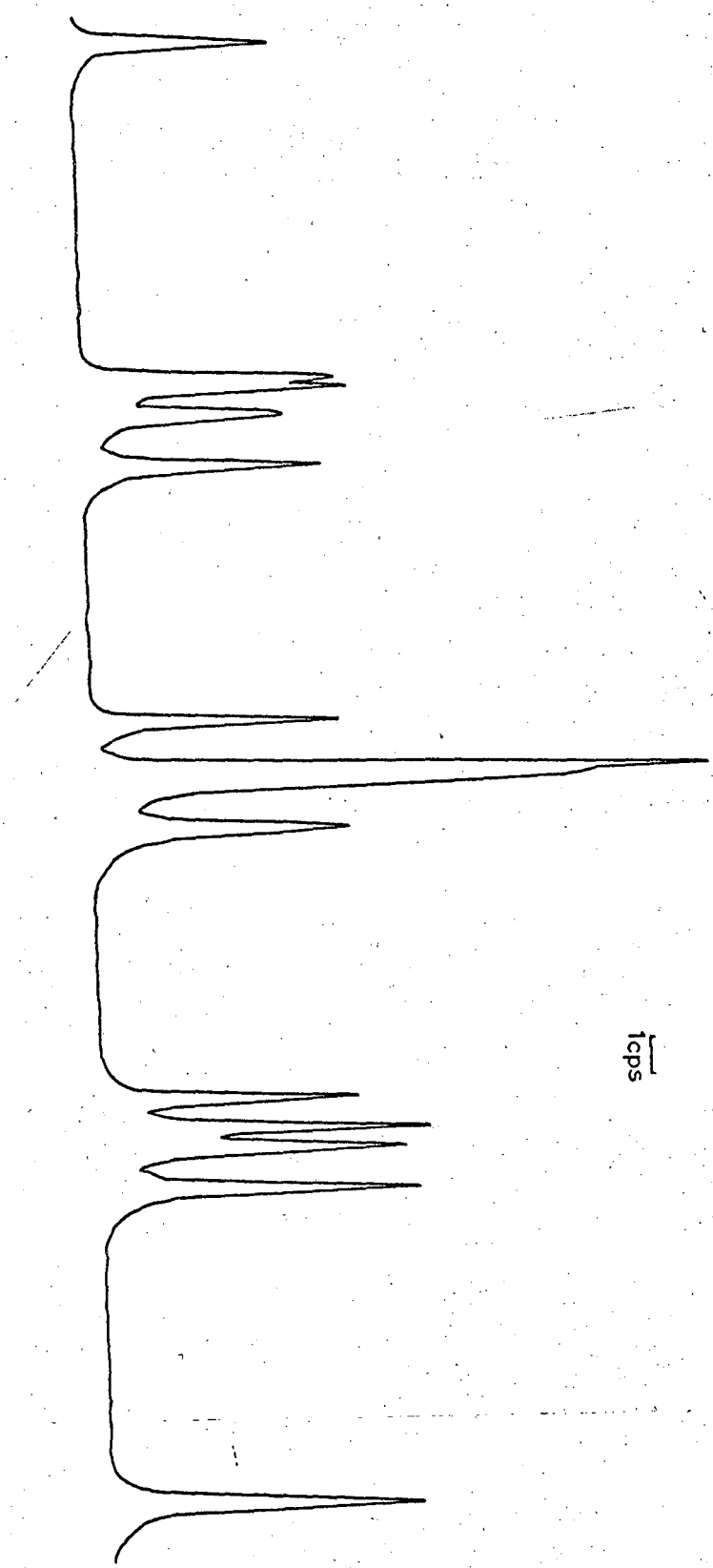

Figure 4 (a)

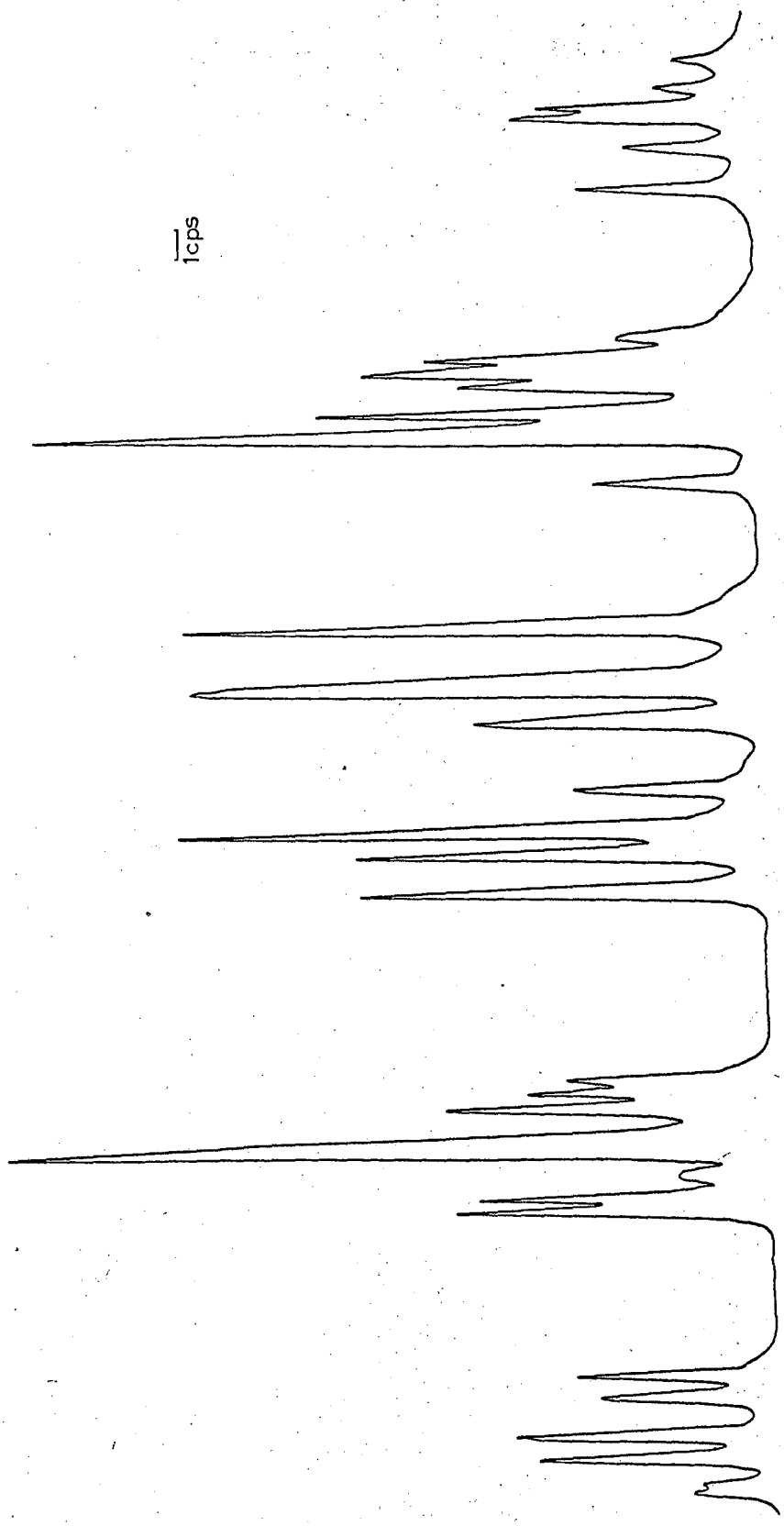

Figure 4 (b)

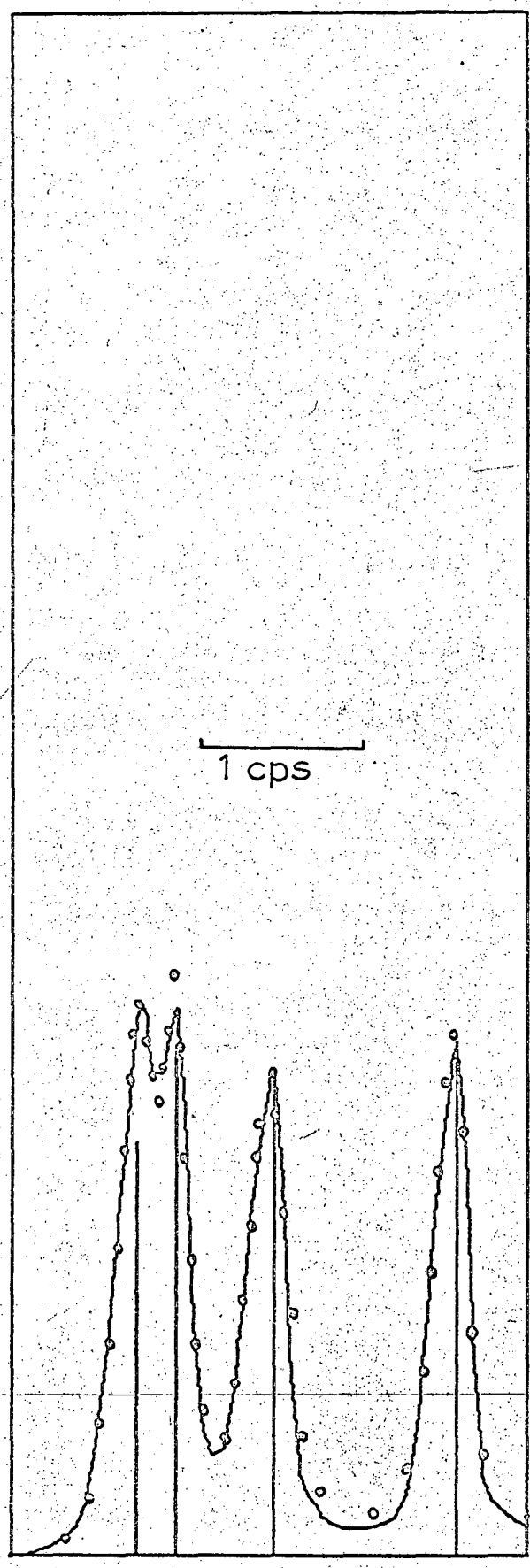

Figure 5 (a)

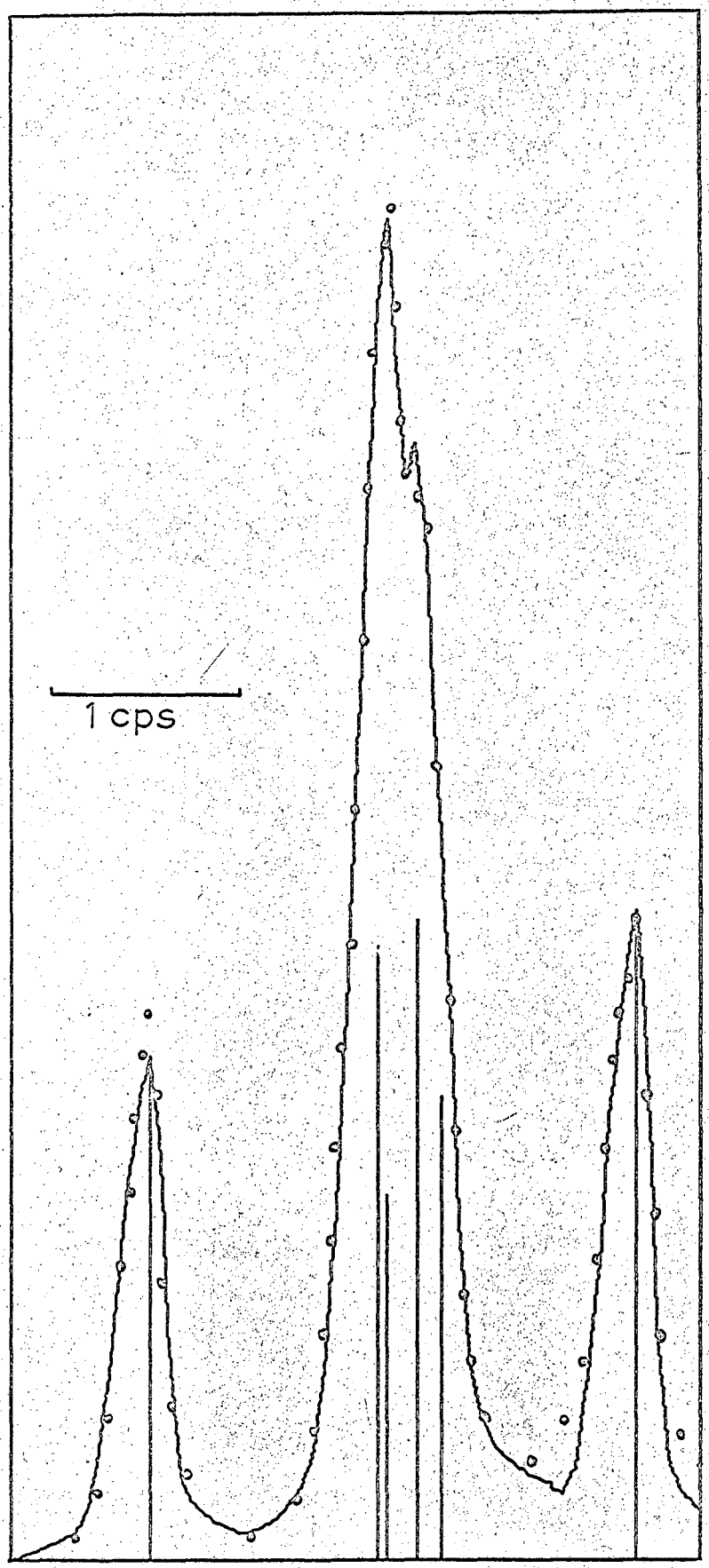

Figure 5 (b)

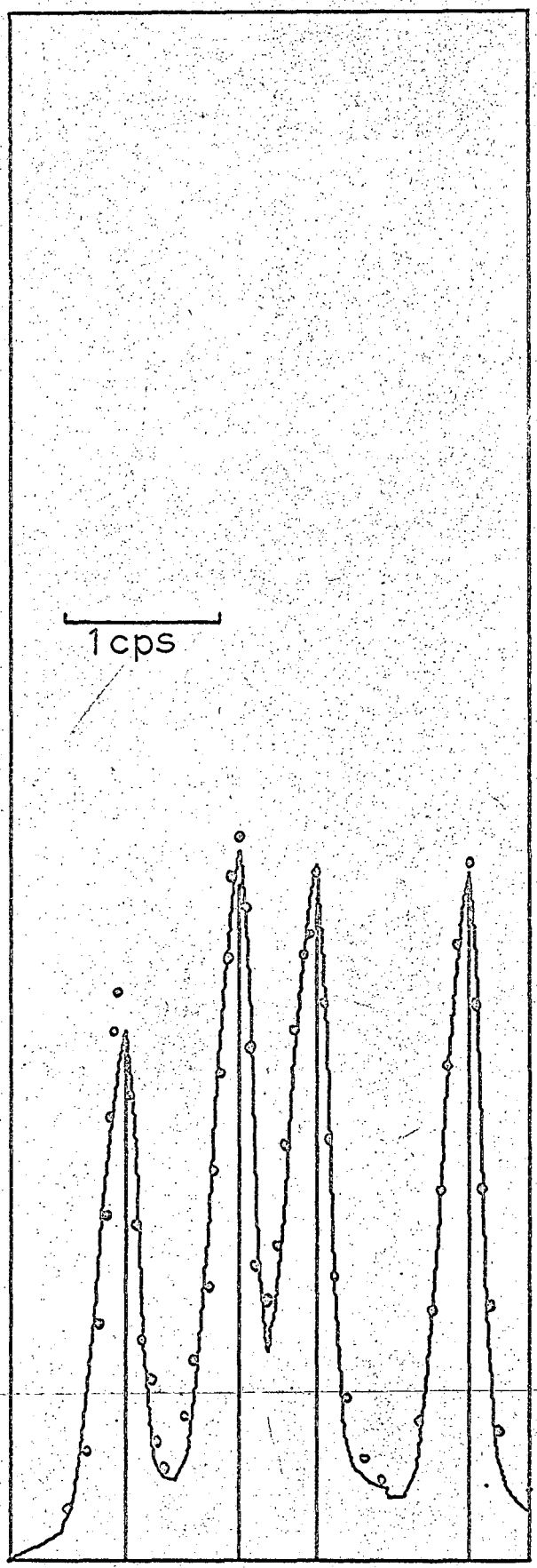

Figure 5 (c)

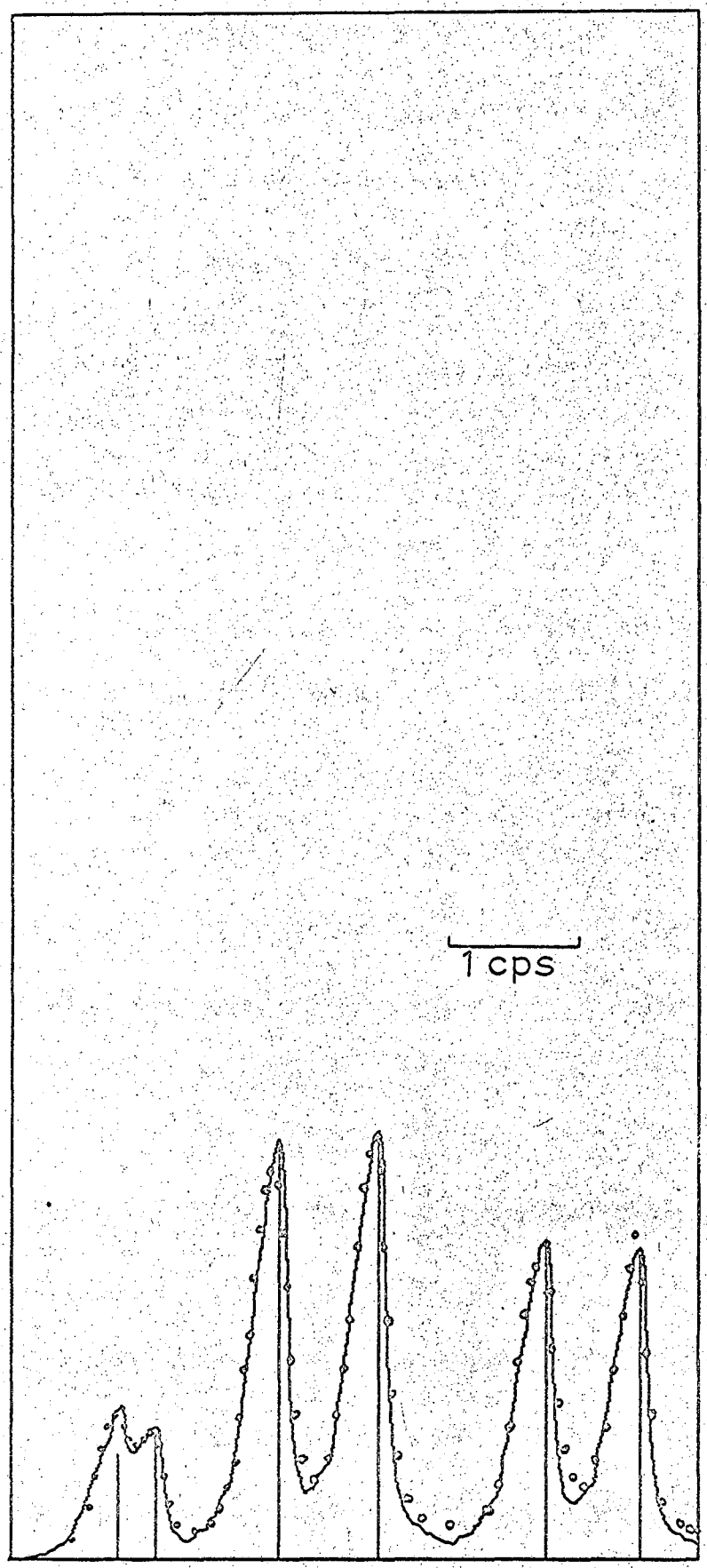

Figure 5 (d)

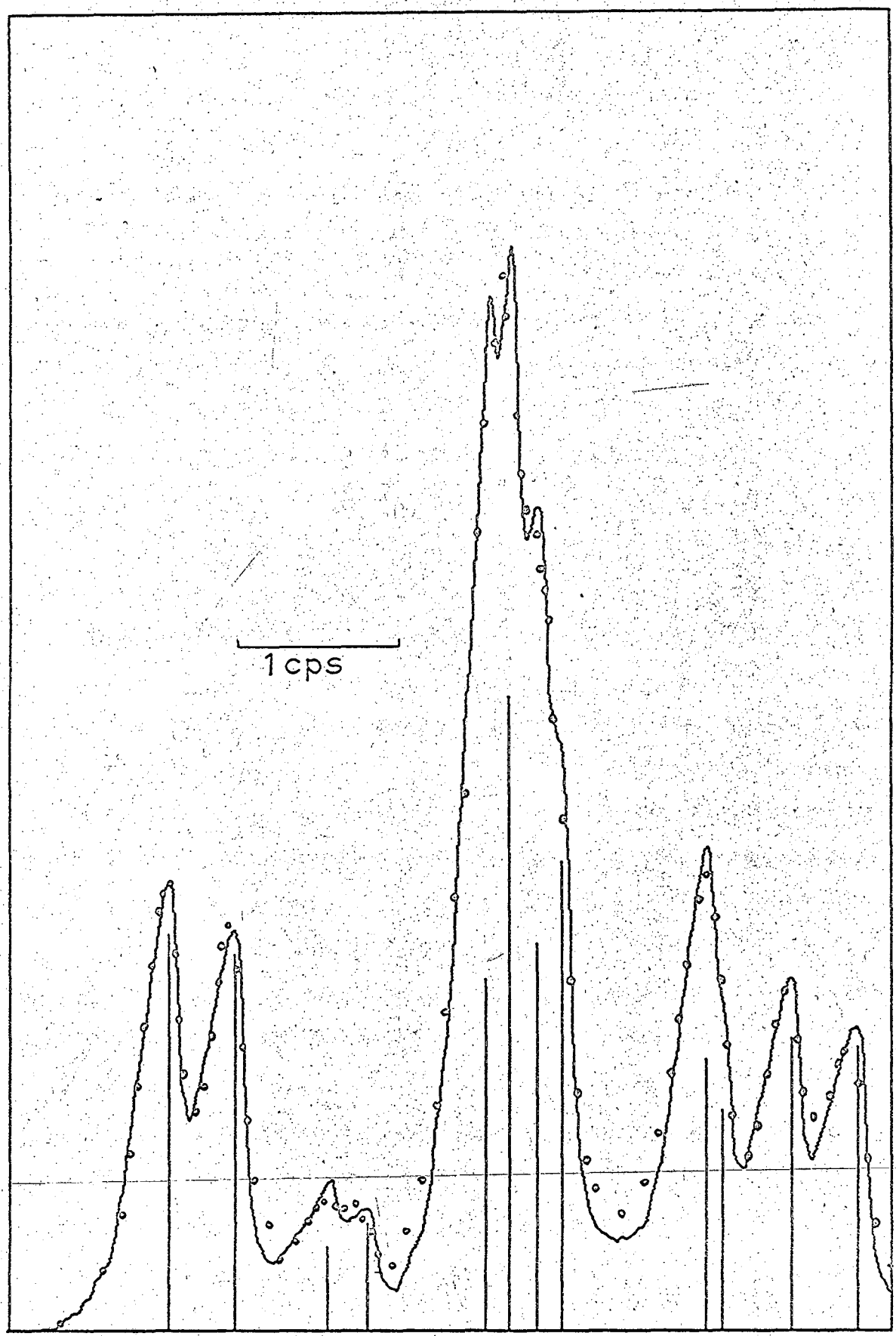

Figure 5 (e)

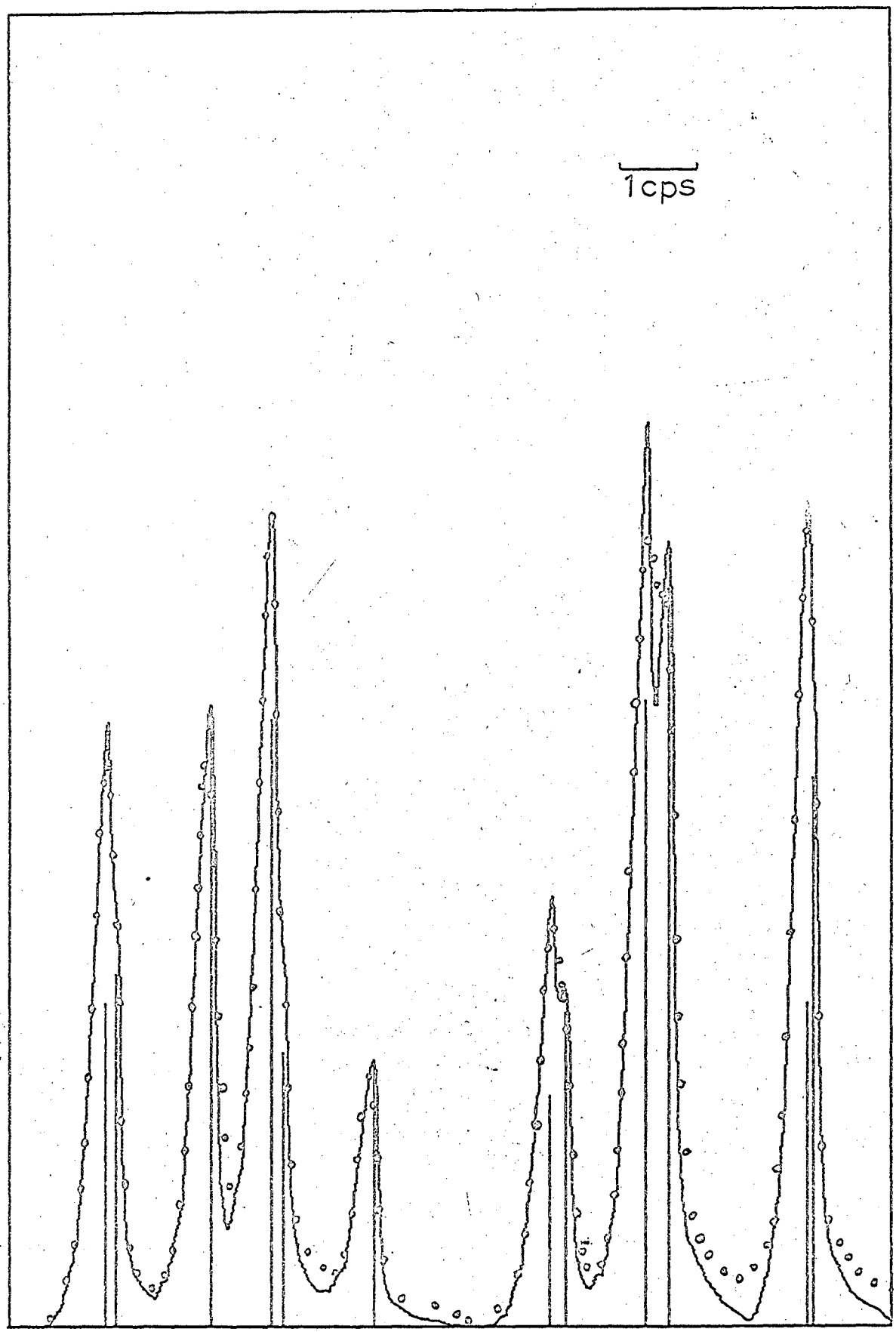

Figure 5 (f)

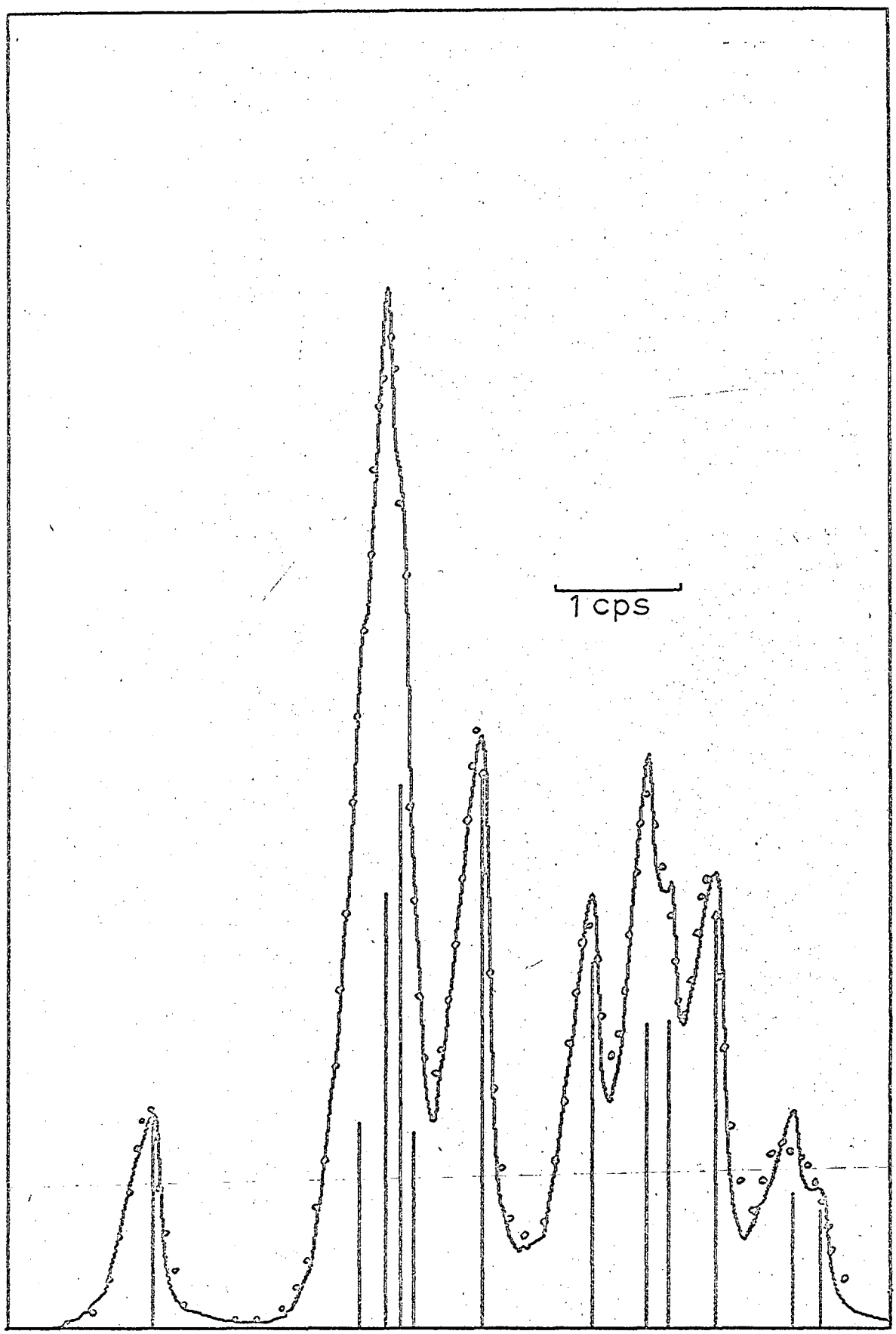

Figure 5 (g)

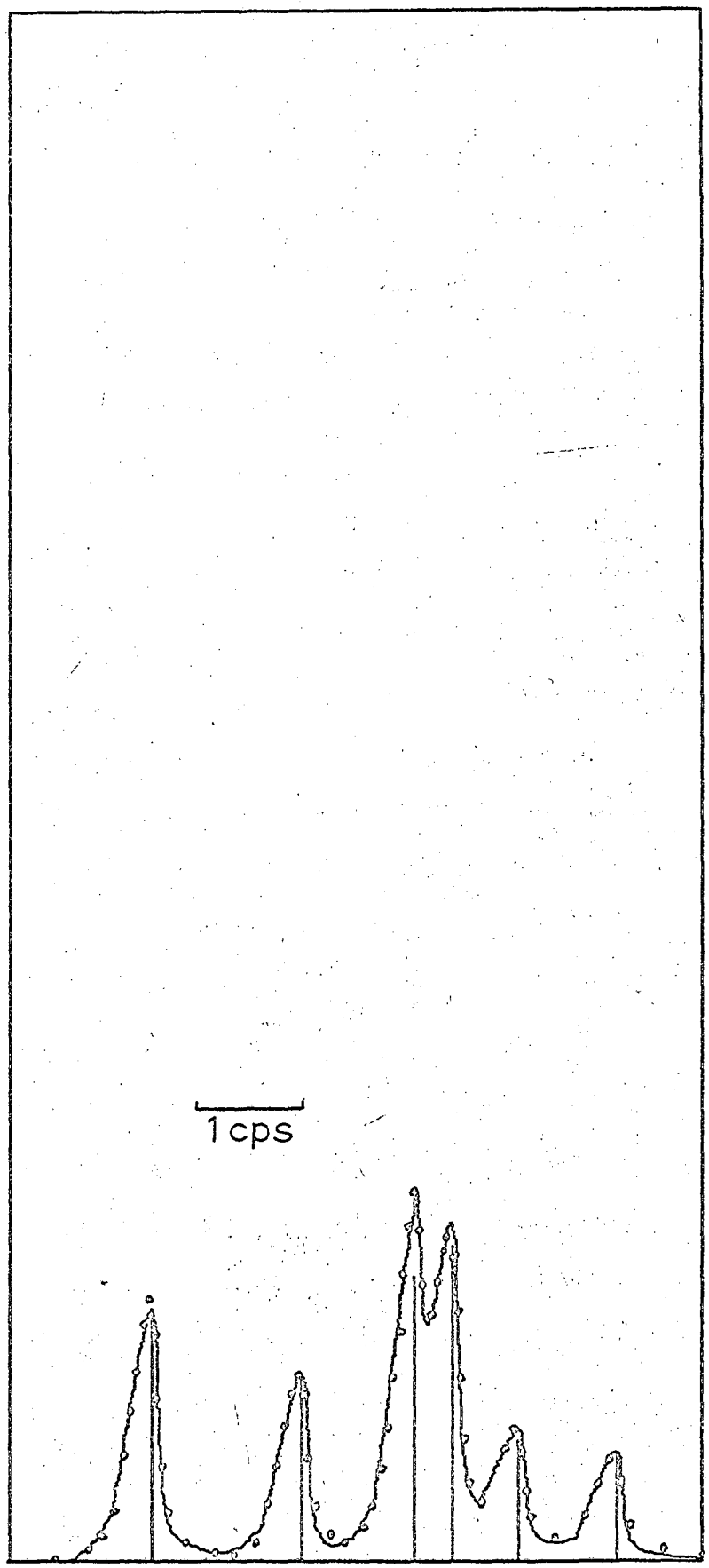

Figure 5 (h)

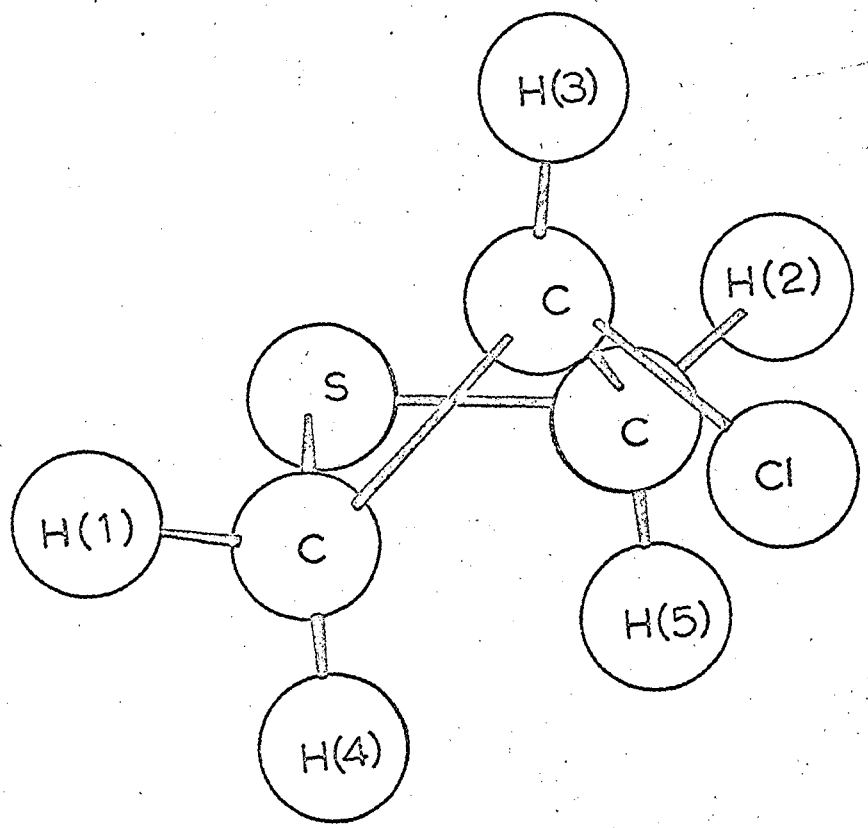

Figure 6

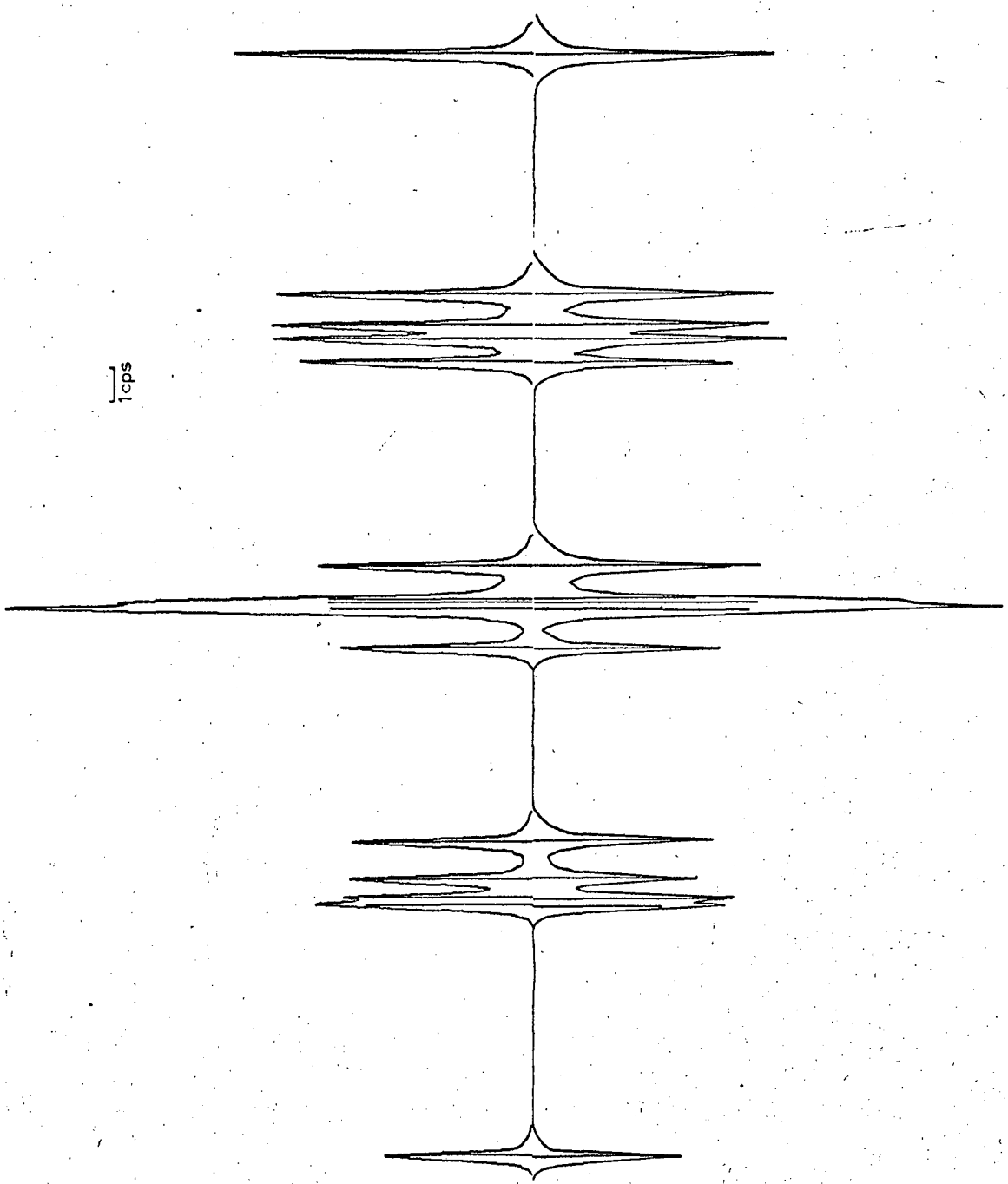

Figure 7 (a)

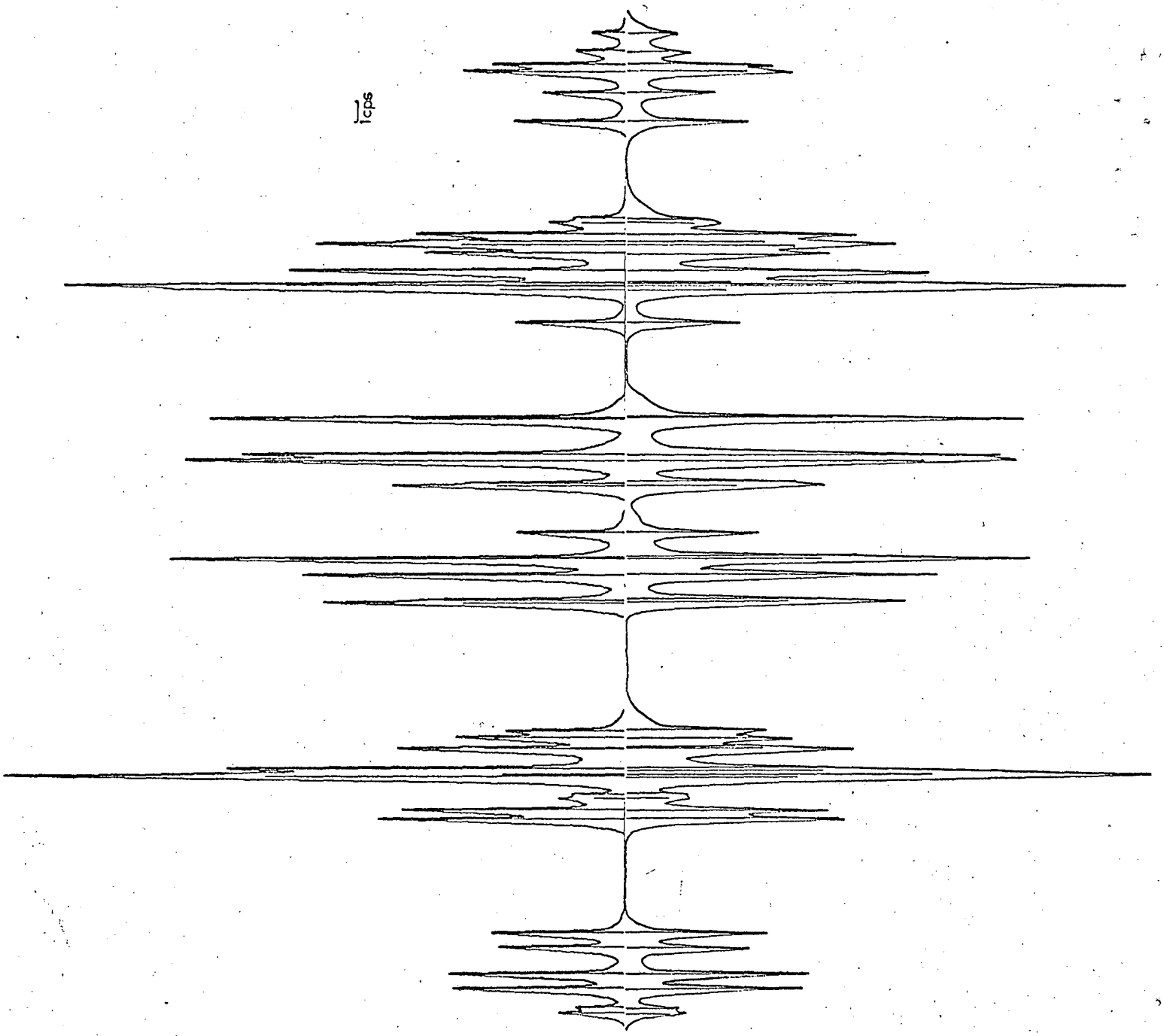

Figure 7 (b)

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.