# The Asymmetric Rotor

## III. Punched-Card Methods of Constructing Band Spectra

Gilbert W. King, *Arthur D. Little, Inc., Cambridge, Massachusetts,*
Paul C. Cross, *Brown University, Providence, Rhode Island,*

AND

George B. Thomas, *Massachusetts Institute of Technology, Cambridge, Massachusetts*
(Received October 10, 1945)

The stochastic method of analysis of band spectra of asymmetric rotors involves the calculation of line strengths and positions for successive estimates of six molecular constants, until the calculated intensities at all wave-lengths agree satisfactorily with the observed. This paper shows that these extensive calculations, as based on tables previously published, are well adapted to standard punched-card equipment. In addition to the above calculations, it is possible to construct the appearance of the rotational structure for various values of slit width. The procedure is carried through for $H_2S$ with some approximate constants. Very satisfactory representations of observed spectra are obtained for completely resolved spectra, as in the photographic region; for slit width 1 and 2 $cm^{-1}$, as in the near infra-red; for slit width 10 $cm^{-1}$, as in poorly resolved infra-red spectra.

## I. INTRODUCTION

BAND spectra still remain an important source of information about molecular structure and of precise values of the constants for calculating the thermodynamic properties of simple substances. The analysis of bands of polyatomic molecules is very difficult when the three moments of inertia are different, that is when the molecule is an asymmetric rotor. Figure 1 shows typical infra-red bands, in this case of $H_2S$.[1] Although these bands are not completely resolved into lines, one feels that there is enough information given by the position and intensities of the peaks to find out the dimensions of the molecule. However, only a very few of such bands have been analyzed. The difficulty arises partly because the positions of the peaks in the case of the asymmetric rotor are very irregular. It seems that the only approach to interpretation of these bands, whether more or less resolved than the ones shown, is a stochastic one. One assumes the dimensions of the molecule in the upper and lower states, calculates the position and intensity of the lines, and compares with the observed. This has been done success-

fully for only a few completely resolved bands of asymmetric rotors, namely, a number of bands of $H_2O$ and one band of $H_2S$, and even in these cases the comparison of intensities has been based on symmetric-rotor approximations.

The position of a line in a band is given by

$$\nu_{J'',\tau''; J',\tau'} = \nu_0 + E'(a', b', c')_{J',\tau'} - E''(a'', b'', c'')_{J'', \tau''}, \quad (1)$$

where $\nu_0$ is the band center, $E(a, b, c)_{J,\tau}$ being the rotational energy of the state defined by $J, \tau$; double primes indicate the lower state, single primes the upper state. In the case of the asymmetric rotor the rotational energies can be determined only by solving polynomials of various high degrees. In a previous paper[2] we believe we have simplified this part of the problem a great deal by tabulating a quantity $E(\kappa)$ in terms of which the rotational energy, a function of the three reciprocal moments $a \geqslant b \geqslant c$, can be expressed as

$$E(a, b, c)_{J, \tau} = \tfrac{1}{2}(a-c)E(\kappa)_{J,\tau} + \tfrac{1}{2}(a+c)J(J+1), \quad (2)$$

where $\kappa = (2b-a-c)/(a-c)$ is a parameter of asymmetry varying from $-1$ to $+1$, and $E(\kappa)_{J,\tau}$, called reduced energy levels, have been com-

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[1] H. H. Nielsen and E. F. Barker, Phys. Rev. **37**, 727 (1931). A reproduction of the completely resolved band of $H_2S$ at 10,100A was given by P. C. Cross, J. Chem. Phys. **5**, 370 (1937).

[2] G. W. King, R. M. Hainer, and P. C. Cross, J. Chem. Phys. **11**, 27–42 (1943), hereafter referred to as I.
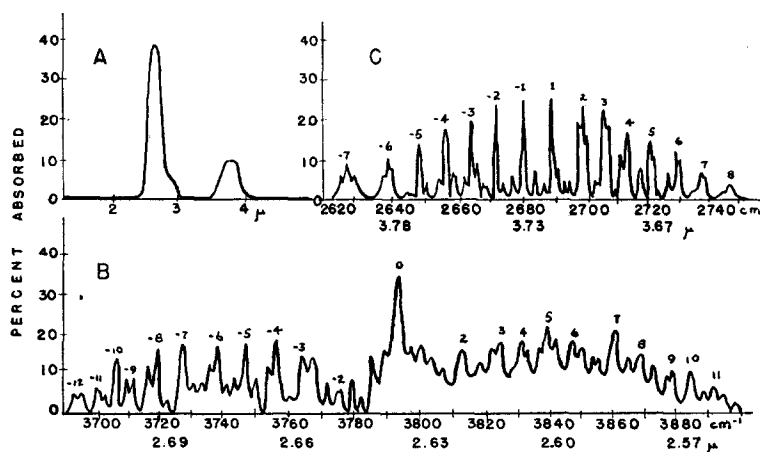
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FIG. 1. Absorption bands in hydrogen sulfide. *A*, Prism curve with low dispersion. *B*, Fine structure in the band at $2.6\mu$. *C*, Fine structure in the band at $3.7\mu$. (Copied from reference 1.)

puted[3] up to $J=12$ by solving continued fractions for all possible values of $\kappa$ in intervals of 0.1. Thus the energy levels for any molecule can be computed by (2) from the table of $E(\kappa)$ by simple multiplication and addition.

The intensity of a line in an absorption band as obtained[4] from II—(1) is

$$I_{J'',\tau'';\,J',\tau'} = \mathrm{const}\ \nu(1-e^{-\nu/kT})g_{J'',\tau''}$$

$$\times \exp -E''(a'', b'', c'')_{J'',\tau''}/kT$$

$$\sum_{F=X,Y,Z}\sum_{M''}\sum_{M'}|\Phi_{Fg}|^2_{J'',\tau'',M'';\,J',\tau',M'}, \quad (3)$$

where $\nu$ is the line position (1) in wave numbers, $k$ being the Boltzmann factor in $cm^{-1}\ deg^{-1}$, and $g_{J'',\tau''}$ is the nuclear-spin weight factor. The constant factor is given explicitly by II—(1) and II—(2). It includes the partition function and the absolute magnitude of the permanent and induced electric moment. The last term is the square of a matrix element of the direction cosine between the radiation field and molecular axes. The subscript $g$ refers to the direction of the permanent and induced components of the electric moment in fixed molecular coordinates. The triple sum is the strength of a line whose components are unresolved in an isotropic radiation field with no external field. In II we have computed the values of the line strengths for

five values of $\kappa(\pm 1, \pm 0.5, 0)$, which adequately cover the whole range of asymmetry possible.

Equations (1) and (3) are to be evaluated for all important lines of the spectrum. Even with the tables of energy levels and line strengths, the construction of a spectrum, which is composed even in the simplest cases of several hundred lines, is a considerable undertaking. The computational labor can be reduced by making use of certain calculating machines.

## II. ACCOUNTING-MACHINE METHODS

It is the purpose of this paper to illustrate the use of business accounting machines in carrying out certain types of quantum-mechanical calculations, in this case the construction of spectra by the evaluation of the above equations for line position and line intensity. Punched-card machines are probably the most suitable for this kind of work, for although they are only capable of adding, subtracting, and multiplying, they are well suited to the quantum-mechanical operations such as symmetry classifications, sorting according to parity or changes in quantum numbers, etc.

In the International Business Machines all the quantities used in the calculations are supplied on cards, the numbers or identification letters appearing as holes punched in certain locations. The machines read the information by brushes which make electrical contacts through the holes as the card runs through the machine.

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[3] Values of $E(\kappa)$, $\kappa = -1.0$ (0.1) 0.0, for $J=11$ and 12 will be published shortly.

[4] P. C. Cross, R. M. Hainer, and G. W. King, J. Chem. Phys. **12**, 210 (1944), hereafter referred to as II.

Several types of machines are available whose principal operations are briefly described below with special reference to the construction of band spectra.[5]

The ultimate object of this work is to represent a spectrum by a set of cards, each card corresponding to a line and bearing the line position, line intensity, the quantum numbers of the two states, and the symmetry classification. These cards can be prepared and handled by the following machines.

Key Punch—The original data can be punched onto cards by hand from printed tables. Since this step is subject to errors of the operator, the amount of material punched by hand should be kept to a minimum. It is necessary that the information on the cards be thoroughly checked. Various machine methods of testing the accuracy are described below.

Sorter—Fundamentally this machine separates a set of cards into ten groups depending on the value of a digit in any one column. It can be used to arrange the cards representing transitions in order of increasing wave number or to pick out the lines of intensity above any chosen value. It is also possible to classify the lines, for instance, into sub-branches, by sorting on the changes in quantum numbers.

In addition to the field in which digits are punched there are $X$ and $Y$ zones which can be used in combination with the digits to indicate letters, or used alone to indicate sign, parity, etc., or for control purposes. Thus lines can be sorted into symmetry classes determined by the parity of certain quantum numbers.

Collator—This machine is used to combine two sets of cards so that a card of the "primary" set defined say by a certain quantum number precedes all the cards in the "secondary" set with the same quantum number.

Reproducer—When two sets have been collated, the combined set can be put through this machine so that information is reproduced from the leading card (from the primary set) into all the cards with the same quantum numbers of the secondary set. This operation is called "gang punching."

Multiplier—This is the machine on which addition, subtraction, and multiplication can be done. The two numbers which are to be combined must appear on the same card, the answer being punched elsewhere on the card. Combined operations, such as $A \times B + C$, can be done simultaneously in this machine, the addition being called "cross-footing."

Group multiplying is the operation of multiplying all cards put through the machine by the same quantity which is inserted in the machine by a leading specially punched card. It is then not necessary to use up any columns of the detail card for the multiplier.

It is desirable in scientific work to have the Multiplier modified to take into account different signs of the terms in an equation such as (1); otherwise, the cards have to be sorted according to the signs and handled separately.

Summary Tabulator—At any stage in the operations the cards can be put through a Tabulator wired so that any or all of the information can be printed. Thus, the final results can be listed in any convenient form.

In addition, the Tabulator can sum the quantities on any part of the card and print either the grand total or subsidiary totals, the printing of which can be controlled by changes in identification columns, e.g., when a quantum number changes or when the tens digits change. Summation can also be controlled by $X$ zone punches.

## Operation

In conclusion, it should be pointed out that all the steps in the calculations can be set up in a standardized form, and the actual preparation and handling of the cards is done by specially trained operators at some computing center. All the spectroscopist has to do is to supply the necessary eight constants, namely, three reciprocal moments of inertia for both the upper and lower states, the absolute temperature, and the band center.

## Punched-Card Table of Reduced Energy Levels

It was not convenient to obtain the reduced energy levels $E(\kappa)$ by punched-card methods

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[5] A description of punched-card machines and of their application to astronomial calculations can be found in W. J. Eckert, *Punched-Card Methods in Scientific Computation* (Thomas J. Watson Astronomical Computing Bureau, Columbia University, New York, 1940).

since these were calculated by continued fractions, and punched-card machines are not adapted to frequent division. The table of reduced energy levels (I—Appendix) was set up on punched cards on the Key Punch. One card was made for each level for each value of $\kappa$ (running from $-1$ to $0$ in intervals of $0.1$), bearing the values of $J$, $K_{-1}$, $K_1$, and $E(\kappa)$.

The $\tau$-values of the levels were then obtained by finding the difference $\tau = K_{-1} - K_1$ on the Multiplier. The cards were sorted according to the parity of the $K$'s and the resulting four symmetry species identified by punching the characters $ee$, $eo$, $oe$, $oo$ (I—Sec. IV). Similarly by sorting on the last digit of $\tau$ and $X$ punching the odd numbers, the parity of $\tau$ was indicated on the cards for use in applying weight factors. The parity of $\gamma$ was obtained from that of $J + \tau$ for use in grouping into sub-branches.

The major source of error in punched-card operations is the copying of tabulated material onto punched cards, which is done by an operator. The punched cards representing the table had to be carefully checked. This was done very easily as follows: the cards were sorted on $J$ and the four symmetry classifications and then put through a tabulator which printed the sums of each set with the same $J$ and symmetry. These numbers are the traces of the sub-matrices whose values are known.[6]

## Calculation of Term Values

To obtain the actual energy levels of any molecule, the required information is copied from the master set described above. In general it is necessary to interpolate to find $E(\kappa)$ for intermediate values of $\kappa$. This can be done by machine methods since interpolation involves only multiplication and addition. It is sometimes more convenient, however, not to interpolate, but to carry through the calculation for line position $\nu$ for several values of $\kappa$, and interpolate the line position. In many cases it will be found that the variation of $\nu$ over the interval of $0.1$ in $\kappa$ is either negligible or of the order of the centrifugal-distortion correction. This method emphasizes the sensitivity of certain lines to the asymmetry parameter (which in $XY_2$ type triatomic molecules is a function of the valence angle only, not of the interatomic distances). The positions of these lines can be used to determine $\kappa$ accurately.

The original table of reduced energy levels (I—Appendix) covered only the range of negative $\kappa$. Values for positive $\kappa$ are obtained by means of the symmetry relation (I—12):

$$E(\kappa)_{J, K_{-1}, K_1; \tau} = -E(-\kappa)_{J, K_1, K_{-1}; -\tau}. \quad (4)$$

The inversion of $K_{-1}$ and $K_1$ and change of signs of $\tau$ can be done automatically on reproducing from the master set by interchanging appropriate wires.

The value of $\frac{1}{2}(a+c)J(J+1)$ is punched onto the appropriate cards by collating and gang punching, a process to be described in more detail in another connection. The pack of cards is put through the Multiplier, in which the factor $\frac{1}{2}(a-c)$ is introduced as a group multiplier. The cards run through the machine so that the product $\frac{1}{2}(a-c)E(\kappa)$ is obtained and simultaneously added to $\frac{1}{2}(a+c)J(J+1)$, so that (2) is evaluated at once and the answer $E(a, b, c)$ punched in other columns of the card.

This whole operation is repeated for the chosen constants of the upper state.

## Punched-Card Table of Line Strengths

Another master set of cards has been made, one card for each possible transition between rotational levels, $J < 13$, for all three components of the electric moment, bearing the quantum numbers, $J''$, $K''_{-1}$ and $K''_1$ of the lower state, and $J'$, $K'_{-1}$ and $K'_1$ of the upper state, together with the line strengths.

Since the line strengths were obtained by ordinary methods of calculation, they had to be key punched onto cards by a hand operation. This introduced numerous errors of identification which were fairly easily corrected by the application of sum rules (II—20 to 24). The cards were sorted by direction of moment, level identification[7] $J''$, $K''_{-1}$, $K''_1$ (or by $J'$, $K'_{-1}$, $K'_1$), and the sums of the line strengths obtained on the Tabulator. These sums being small whole

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[6] I—Table X.

[7] Since the double suffix $KK$-notation involves 4 integers ($J < 13$) and the $\tau$-notation involves 2 integers plus a sign, one sorting operation can be eliminated by the use of $J + \tau$ (running from 0 to $2J + 1$) as the index of the levels with the same $J$.

numbers, errors could be detected by visual inspection. The use of three different sum rules finally eliminated all errors except those due to rounding off.

## Punched-Card Table Representing a Band

A copy of this master set of line strengths was made for the chosen value of $\kappa$ and direction of the electric moment. Interpolation may be necessary, although, as in the case of $E(\kappa)$, it is sometimes of interest to carry through the calculations for the two neighboring values of $\kappa$, in order to follow the effect of changing asymmetry on intensities in the final construction of the spectrum.

This set is now sorted[7] on $J''$, $K''_{-1}$, $K''_1$ in the same order as the cards for the lower energy levels. The latter set is collated with the former. In this operation an energy-level card for a given value of $J''$, $K''_{-1}$, $K''_1$ is placed in front of the group of cards in the transition set having the same values for $J''$, $K''_{-1}$, and $K''_1$. The combined set is now put through a Reproducer which gang punches information from the energy-level cards onto the transition cards, namely $E''(a'', b'', c'')$ and other information to be described below. The transition set is now sorted on the quantum numbers of the upper state,[7] $J'$, $K'_{-1}$, $K'_1$, and collated with the set for the upper energy levels, from which $E'(a', b', c')$ is gang punched.

The next step is to gang punch[8] onto the whole set the value of the band center, $\nu_0$. The pack of cards is then put through the Multiplier, which carries out the addition and subtraction (1) to give the line position in one operation.

## Calculation of Line Intensity

In order to calculate the line intensity the Boltzmann factor has first to be determined. The set for the lower energy levels is group multiplied

by $1/kT$. The cards are arranged in order of increasing $E/kT$ on the sorter and collated with a set of cards representing the table of the exponential function, the latter being the primary set. The value of $\exp -E/kT$ is gang punched onto the energy-level cards.

The next step is to insert the appropriate weight factors $g_{J'', \tau''}$. These depend on the symmetry classification of the energy levels. For instance, in the case of $H_2O$ the levels with $\tau$ odd have a weight of three, and the levels with $\tau$ even have a weight of one. The cards can be put through the Sorter which separates the even and odd $\tau$'s. The Boltzmann factors for the $\tau$-odd set are multiplied by three; in the $\tau$-even set the Boltzmann factor is multiplied by unity in order that the combined factor appears in the same field on all cards. The whole set is now sorted[7] on $J''$, $K''_{-1}$, and $K''_1$ for the collation with the transition set described above. The Boltzmann factor is copied from this set at the same time as the energy levels.

For pure rotational spectra the quantity $\nu(1-e^{-\nu/kT})$ appearing in (3) is important. It can be calculated on the transition set by the following operations. First the exponential is evaluated by multiplying $\nu$ of (1) by $1/kT$, collating with the exponential table, gang punching $e^{-\nu/kT}$. Since the Multiplier can carry out the operation $C-AB$ in one run, the required quantity can be evaluated with $C=A=\nu$ and $B=e^{-\nu/kT}$, all of these factors having been punched on the cards.

The line intensity can now be obtained on the transition set by putting through the Multiplier, which evaluates (3). This computation can be verified by sorting on the quantum numbers of the lower state and summing the intensities of all lines arising from each lower level. The sums should be equal to

$$(2J+1)g_{J'', \tau''} \exp -E''(a'', b'', c'')/kT. \quad (5)$$

The product (5) is carried out on the lower-energy-level cards and listed.

The final result is a set of cards bearing the quantum numbers, line positions, and line intensities for each transition, constituting all the lines of the spectrum up to[9] $J<13$. These cards

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[8] At present there is no straightforward way to insert a quantity which is to be *added* to all cards directly into the machine to have the counterpart of group multiplying. If $\nu_0$ is not known beforehand, and only trial values are inserted in (1), we have found it convenient to avoid wasting columns for $\nu_0$ by assuming a center of 10,000 cm⁻¹. It is not necessary to punch this onto the cards, but merely to introduce unity into the fifth position of the summary counter by an impulse from the unit multiplier. The value of 10,000 rather than 0 was chosen to insure all calculated $\nu$'s are positive, whereby sorting is simplified.

[9] For molecules, such as $H_2O$ and $H_2S$, where one moment of inertia is small, the Boltzmann factor causes
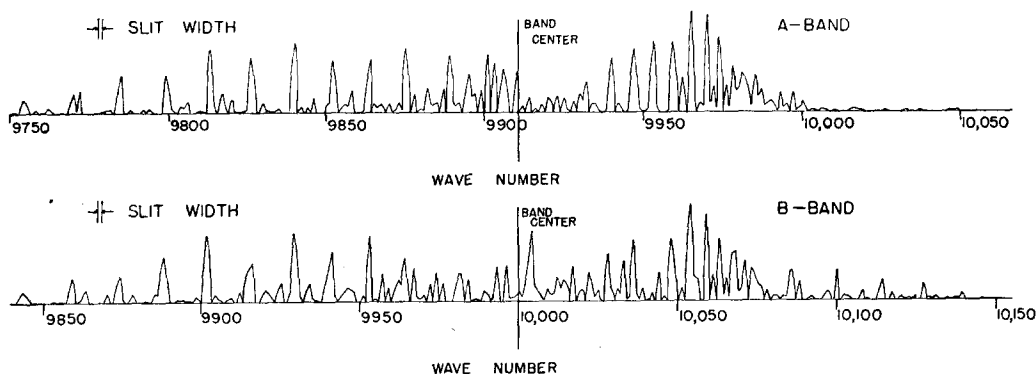
FIG. 2. The $a$-band represents the 10,100A band of $H_2S$ (with a slight change in the intermediate inertia as described in footnote 11) as it would appear with a slit width of 1 $cm^{-1}$ at infinite resolution. (Band center 9911 $cm^{-1}$.) The $b$-band respresents the appearance of a band under the same conditions arising from a transition between the same vibrational states if the moment were along the intermediate axis. (Band center arbitrarily taken as 10,000 $cm^{-1}$.) Note that in the asymmetric rotor there is not a very marked difference between the two types of bands when observed with a finite slit width.
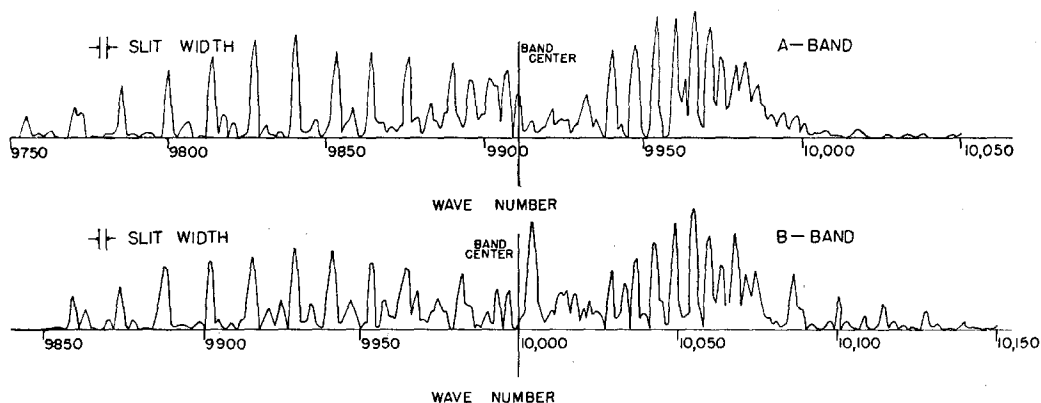


FIG. 3. Same bands as Fig. 2 with slit width 2 $cm^{-1}$.

can be sorted and the information listed in a variety of ways.

### III. SPECTRUM ANALYSIS

#### Completely Resolved Spectra

By sorting on $\Delta J$, $\Delta K_{-1}$, $\Delta K_1$, and $K_{-1}$ or $K_1$, the lines can be listed in branches, sub-branches, and wings (II—Appendix), by means of which the structure of a band is analyzed. Inspection of the rate of decay of intensity in the wings will indicate whether any strong lines occur above $J=12$, and the intensities of such lines can often be found by extrapolation.

all lines involving $J>12$ to be of negligible intensity. A satisfactory study of the bands of molecules with all moments large will require the extension of the tables of reduced energy levels and line strengths to higher $J$'s. We hope to do this by means of the Correspondence Principle.

The cards can also be sorted with the lines arranged in order of increasing or decreasing wave number; or the strong lines, say with intensity greater than some predetermined value, can be listed separately. These printed lists are extremely convenient in analyzing well-resolved spectra.

#### Unresolved Spectra

In the analysis of incompletely resolved spectra, punched-card methods can be used to further advantage. A set of cards bearing consecutive wave numbers in the region of interest is collated with the set of transition cards arranged in order of increasing wave number. The wave-number set has $X$ punches in various columns so that when the combined set is put through the Tabulator, successive totals can be
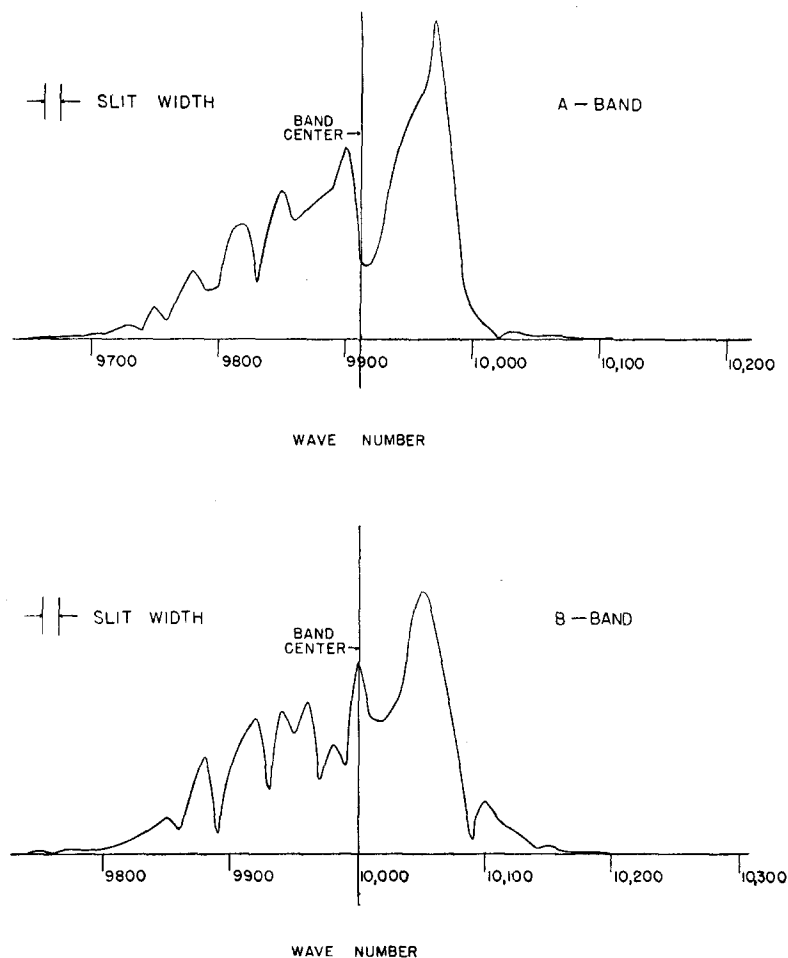
FIG. 4. Same bands as Fig. 2 with slit width 10 cm$^{-1}$.

listed, giving the sum of the intensities over any interval of wave numbers corresponding to a slit width. Additional $X$ punches are available to give the intensity at intermediate positions of the "slit." A plot of the results gives the appearance of the band at the resolution of the slit width equal to the interval chosen.

## IV. TYPICAL RESULTS

In order to test the punched-card procedure we have calculated the line positions and intensities $J<13$ for the 10,100A band of $H_2S$.[10] The

constants chosen[11] were those given by Cross for the greatest and least moments, but the intermediate moments were adjusted to make $\kappa''$ and $\kappa'$ exactly 0.5 and 0.4, respectively. Calculations for $\kappa'=0.5$ were done simultaneously. The plots in this paper refer to $\kappa'=0.4$ only.

A list of calculated positions and intensities, omitting all lines with intensities[12] $<1.0$, was

[10] P. C. Cross, Phys. Rev. 46, 536 (1934); 47, 7 (1935); J. Chem. Phys. 5, 370 (1937); P. C. Cross and B. L. Crawford, Jr., ibid. 5, 371 (1937); B. L. Crawford and P. C. Cross, ibid. 5, 621 (1937).

[11] The values chosen for computation were

$a''=10.393$ $a'=9.910$
$(b''=8.976)$ $(b'=8.278)$ and $(b'=8.550)$
$c''=4.723$ $c'=4.470$
$\kappa''=0.5$ $\kappa'=0.4$ and $\kappa'=0.5$.

Cross's value for $b''$ was 9.040, giving $\kappa''=0.523$; and for $b'$ was 8.379, giving $\kappa'=0.437$. The value of $T$ was 298°K. The band center was taken as 9911.03 cm$^{-1}$ for the calculations of the $a$-type band, and arbitrarily chosen as 10,000 cm$^{-1}$ for the $b$-type.

[12] Actually, relative intensities $I_{J'', \tau''; J', \tau'}/\text{const.}$ $\nu(1-e^{-\nu/kT})$ were used.

compared with the observed lines.[10] More than 90 percent of the observed lines were identified and accounted for. The exceptions were lines found in a subsidiary list of those with intensities lying between 0.5 and 1.0. A few lines whose calculated intensity is $\sim 3$ were not given in the original list of observed lines. The agreement in wave number was satisfactory considering the rigid-rotor approximation of the calculations.

The results of collating the wave-number set with progressive totals listed for successive unit wave-number intervals (slit width of 1 cm$^{-1}$) are plotted in Fig. 2. The curves for a resolution of 2 cm$^{-1}$ are given in Fig. 3. The synthetic spectra obtained by this method correspond very closely in character to the experimental curves. For example, the 2.63$\mu$ band of Fig. 1 (obtained with a slit width of 1.8 cm$^{-1}$) compares favorably with the $b$-band of Fig. 3, although the constants chosen in the latter are those for the 10,100A band.

One immediate result of importance is that the observed band seems to have the appearance of the type where the electric moment is parallel to the intermediate axis, contrary to predictions based on symmetric-rotor formulas.

By changing the control of the Summary Tabulator, sums were obtained for an interval of ten wave numbers. The results are plotted in Fig. 4. The appearance of the bands is characteristic of the envelopes observed experimentally at this resolution.

### V. CONCLUSIONS

The punched-card method of obtaining line position and intensity, and of listing the sums of the intensities within any arbitrary slit width, gives curves which correspond very closely in character to band envelopes observed experi-

mentally at all degrees of resolution. This method remains accurate when the slit width is of the order of the average line separation, so that the detail of irregularities characteristic of the asymmetric rotor is preserved.

The method also has the advantage over other procedures that the exact values of the position and intensity of the lines of the rigid rotor are used and are not averaged by replacing sums by integrals. This is particularly advantageous in parts of the spectrum involving levels of low $J$.

With the procedure for drawing up spectra mechanized, dimensions of the molecules in the upper and lower states can be obtained, with an accuracy dependent on the detail of the band, by successive approximations, that is, by a process similar to that used in interpreting electron-diffraction curves.

Even when the resolution is poor, band centers can be located quite accurately. This is of value in fixing the vibrational levels of the molecules, precise values of which are of importance in calculating thermodynamic quantities from the partition function.

The interpretation of the infra-red bands in terms of characteristic vibrations of the molecule is greatly dependent on the presence of certain branches or on the shape of the envelopes. With a judicious choice of constants even the first run is sufficient to identify the direction of the electric moment with certainty and to locate the center of the band accurately.