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UNIVERSITY OF SOUTHAMPTON

ASPECTS OF FREE RADICAL SPECTROSCOPY

by

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A dissertation submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Southampton.

August 1978.



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UNIVERSITY OF SOUTHAMPTON

ABSTRACT

FACULTY OF SCIENCE

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Aspects of Free Radical Spectroscopy

by Trevor John Sears.

Techniques for the computer solution to the eigenvalue problem for the effective Hamiltonian describing the rotational levels of asymmetric top free radicals in the presence of an external magnetic field are presented. They are used to perform the analysis of experimentally observed data for the HO<sub>2</sub> radical and derive refined values for the major parameters appearing in the effective Hamiltonian describing the ground state of the molecule.

The detailed form of the effective spin-rotation Hamiltonian including its centrifugal distortion correction for an asymmetric top free radical is derived and a form suitable for the empirical fitting of experimentally observed spectra is discussed. It is shown that for molecules of lower than orthorhombic symmetry there are fewer determinable quadratic spin-rotation parameters than have been used previously. Similar indeterminacies exist among the quartic terms and the case of a molecule of orthorhombic symmetry is discussed in detail. The results are applied to the available experimental data on the spin-rotation splittings of the HO<sub>2</sub>, NH<sub>2</sub> and NO<sub>2</sub> radicals in their ground vibronic states.

The observation of magnetic dipole transitions between the fine structure states of  $\tilde{X}^2 \Pi$  SeH by laser magnetic resonance spectroscopy is described. The spectra are analysed in terms of the effective Hamiltonian for a  $^2 \Pi$  electronic state and refined values for several of the major molecular parameters determined.

## CHAPTER 1.

### INTRODUCTION

Free radicals play an important role in our understanding of chemical reaction kinetics and mechanisms and their presence is frequently invoked in order to explain and predict the paths of reactions occurring in both gas and liquid phases. The understanding of the geometric shape and electronic structure of this class of molecule is therefore very important. By their very nature, free radicals are short-lived and highly reactive species and it is only really over the past twenty years that sufficiently sensitive experimental techniques have been developed and direct spectroscopic identification of such molecules become possible.

The study of short-lived paramagnetic molecules by gas phase magnetic resonance spectroscopy is now a well established technique. The early work (see, for example Refs. (1) to (5)) was performed at microwave frequencies. However there is a considerable increase in the sensitivity of the technique with increased operating frequency and the development of laser sources, especially in the far infra-red and sub-millimetre regions of the spectrum, has resulted in the observation of rotational spectra of molecular species whose E.P.R. spectra had proved elusive or which were at best poorly characterised. Prime examples are  $\text{HO}_2$  (6, 7, 8),  $\text{HCO}$  (9),  $\text{NH}_2$  (10) and  $\text{PH}_2$  (11). More recently still, vibrational magnetic resonance transitions in some of the better known free radicals have been detected using infra-red  $\text{CO}_2$  and  $\text{CO}$  gas discharge lasers (12, 13).

As more high resolution spectral information concerning short-lived free radicals has become available, our understanding of the interactions between the constituent electrons and nuclei has increased. Complete analyses of the observed spectra are now usually performed



using a large computer and the spectral line positions statistically related to parameters appearing in the effective Hamiltonian for the molecule in the state in question. Chapter 2 briefly reviews the current state of this type of analysis and presents some approaches towards the solution of the problems encountered in the analysis in terms of the effective Hamiltonian model. The techniques described are illustrated in the analysis of the available high resolution spectra of the HO<sub>2</sub> radical.

Chapter 3 deals specifically with the spin-rotation terms in the effective Hamiltonian and the form of the quadratic and quartic terms to be used in the analysis of asymmetric top spectra are derived. The results are applied to the analysis of the spectra of HO<sub>2</sub>, NH<sub>2</sub> and NO<sub>2</sub> in Chapter 4.

Departing from asymmetric top free radicals, Chapter 5 describes the observation and subsequent analysis of magnetic dipole transitions between the fine structure components of the ground ( $\tilde{X}^2\Pi$ ) state of the SeH radical. Refined values for several of the major constants appearing in the effective Hamiltonian for a  $^2\Pi$  molecule are derived and some comment on the theoretical significance of the numbers is included in terms of third order contributions to the effective Hamiltonian.

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CHAPTER 2.THE CALCULATION OF THE ROTATIONAL ENERGY LEVELS OF ASYMMETRIC  
TOP FREE RADICALS.2 (I) Introduction

With present day wide availability of very powerful computers such as the CDC 7600 or IBM 360/195, it is possible to attempt far more sophisticated analyses of experimentally observed spectra than would have been contemplated even five years ago. This chapter outlines two programs developed and tested over the past two years, which interpret the observed spectra in terms of an effective molecular Hamiltonian. The Hamiltonian, which is considered in more detail in the next section and in Chapter 3, contains a finite number of molecular constants to be determined from the experimental data. It is the aim of the analysis to determine these constants, or parameters, such that the eigenvalues of the Hamiltonian and the molecular energy levels, as defined by the observed spectra coincide.

The programs referred to above represent two different approaches to the analysis problem, and they are considered in detail in sections (IV) and (V) of this Chapter respectively. The results of their application to the analysis of the available high resolution spectra of the  $\text{HO}_2$  radical are presented in section (VI). We begin however, in section (II) by outlining the problem more fully and reviewing the standard least squares methods, used in the data reduction, which are common to both programs. Section (III) contains a discussion of general programming and efficiency aspects which are, in the main, again applicable to the approaches represented by both programs.

2 (II) Outline of the Problem.2 (II) a. Introduction

The position of the lines in a gas phase magnetic resonance spectrum of a free radical, contain, in principle, large amounts of information concerning the molecule's structure and its electronic states. The analysis of such a spectrum in terms of an effective molecular Hamiltonian aims to extract as much of this information as possible. In this type of analysis, the molecular energy levels, as inferred from the line positions, are identified with the eigenvalues of an effective Hamiltonian operator for the molecule in the (usually) vibronic state in question. The form of the Hamiltonian is derived making only physically acceptable assumptions regarding the molecule's geometry and the interactions between the individual particles from which it is constituted. The Hamiltonian then contains a number of empirical molecular constants which, when determined, will provide information concerning the detailed structure of the molecule.

The derivation of a suitable Hamiltonian is beyond the scope of this chapter, but the theory is well developed (1, 2, 3) and some aspects are considered in Chapter 3. The essential property of the effective Hamiltonian is that its eigenstates span a single vibronic state of the molecule, which, for most problems considered, is the lowest, i.e. ground, state. For the purposes of this chapter it will be adequate to consider the Hamiltonian as a sum of operator terms, each identified with a specific contribution to the energy of the molecule, thus we write:

$$H_{\text{eff}} = H_{\text{rot}} + H_{\text{cd}} + H_{\text{sr}} + H_{\text{srcd}} + H_{\text{hfs}} + H_Q + H_Z \quad (2.1)$$

when  $H_{\text{rot}}$  and  $H_{\text{cd}}$  describe the rotational energy and the centrifugal distortion correction to it and  $H_{\text{sr}}$  and  $H_{\text{srcd}}$  the spin rotation interaction and its centrifugal distortion correction.  $H_{\text{hfs}}$  and

$H_0$  account for the small corrections to the molecular energy levels necessary when one or more of the nuclei in the molecule have non-zero spin; the former represents the electron-nuclear spin-spin interactions and the latter the electric quadrupole interaction between a nucleus with spin greater than  $\frac{1}{2}$  and the electric field created by the other charged particles within the molecule.  $H_Z$  describes the interaction between the molecule and an external magnetic field which is an essential feature of magnetic resonance experiments. Each individual term in (2.1) is composed of a product of operators representing the different angular momenta possessed by the isolated molecule, and the appropriate molecular parameters.

We wish to calculate the eigenvalues and eigenvectors of this Hamiltonian and the problem may be written:

$$H_{\text{eff}} \psi = E \psi \quad (2.2)$$

in the usual notation. The standard method of solution, and the one to which this chapter is devoted, is numerical. The eigenfunctions are approximated by a linear combination of basis functions and the Hamiltonian matrix is constructed numerically in this basis then diagonalised using an electronic computer. The elements of the diagonalised matrix then represent the eigenvalues of the Hamiltonian and the transformation generating the diagonalised matrix yields the linear combinations of the basis vectors which constitute the eigenfunctions.

For the problems considered in this chapter, that is specifically asymmetric top molecules, the most convenient rotational basis functions are eigenfunctions of the total rotational angular operator  $N^2$  and its space- and molecule-fixed  $z$  components, the so-called symmetric top basis functions  $|N K M \rangle$ . The molecules of particular interest here possess an unpaired electron and we must take into account effects of spin angular momentum; this is represented by the spin angular momentum operator  $S$  and a convenient

basis set is one in which the electron spin angular momentum is coupled to the molecular rotational angular momentum to produce a resultant  $J$ . These basis functions are described by the ket  $|NKSJM_J\rangle$ . Similarly we must include nuclear spin angular momentum when the molecule possesses a nucleus with non-zero spin. The basis functions referred to most often in this chapter are the fully coupled  $|NKSJIFM_F\rangle$ , when the nuclear spin  $I$  is assumed to be coupled to the resultant of  $N$  and  $S$  to give a resultant  $F = J + I$ , and the  $I$ -decoupled basis set  $|NKSJM_JIM_I\rangle$ . The two are discussed in more detail in later sections and matrix elements of the Hamiltonian in both bases are quoted in the literature, (3, 18, 19, 20).

It is important to realise that the eigenvalues of the Hamiltonian do not depend on the basis set used in the calculation indeed in many ways the advent of high speed computers has eliminated the necessity for a careful choice of basis functions because the differences in time needed to diagonalise the Hamiltonian matrix set up in various different basis sets are minimal. In this case it is more efficient to choose a basis representation whose matrix elements are the simplest and easiest to set up.

The computer programs developed use an iterative procedure to find the 'best fit' molecular constants for the effective Hamiltonian. An initial set of molecular constants is employed and the matrix representation of the Hamiltonian is diagonalised giving eigenvalues, or calculated energy levels. From differences between the upper and lower state energy levels, calculated frequencies are obtained. Discrepancies between the observed and calculated frequencies, or in the case of magnetic resonance type experiments, fields, are inserted into a least squares fit to find corrections to the previous choice of molecular constants. With the new set of molecular constants, the Hamiltonian is rediagonalised. The iteration process continues to convergence, giving a set of constants for the particular model Hamiltonian which best reproduce the observed data.

2 (II) b Least squares procedure

The least squares method of analysis described in this chapter is based on techniques described elsewhere (4), (5) and only a brief outline is presented here. The 'best' values of the Hamiltonian parameters are those for which the observed and calculated spectra are most nearly identical. We can quantify this in the case of a magnetic resonance spectrum by requiring that the sum of the squared residuals in the observed fields, that is:

$$\sum_i (B_{\text{obs}}^{(i)} - B_{\text{calc}}^{(i)})^2$$

be minimum, implying

$$\begin{aligned} \frac{\partial}{\partial p_j} \left\{ \sum_{i=1}^n (B_{\text{obs}}^{(i)} - B_{\text{calc}}^{(i)})^2 \right\} = \\ - 2 \sum_{i=1}^n (B_{\text{obs}}^{(i)} - B_{\text{calc}}^{(i)}) \frac{\partial B_{\text{calc}}^{(i)}}{\partial p_j} = 0 \end{aligned} \quad (2.3)$$

Where  $n$  is the number of lines observed,  $p_j$  refers to the  $j^{\text{th}}$  Hamiltonian parameter and  $B_{\text{obs}}^{(i)}$  is the field at which the  $i^{\text{th}}$  observed line occurs. We assume that for small changes in the parameters,  $\Delta p_j$ , linear changes occur in the calculated transition fields,  $\Delta B_{\text{calc}}^{(i)}$ , so that we may write:

$$\Delta B_{\text{calc}}^{(i)} = \left( \frac{\partial B_{\text{calc}}^{(i)}}{\partial p_j} \right) \Delta p_j \quad (2.4)$$

We would like to find changes in the parameters such that the calculated and observed line positions are brought into coincidence.

The problem may be expressed in matrix form:

$$\underset{\sim}{D} \underset{\sim}{\Delta} = \underset{\sim}{X} \quad (2.5)$$

where  $\underset{\sim}{D}$  is a matrix of derivatives ( $\partial B_{\text{calc}}^{(i)} / \partial p_j$ ),  $\underset{\sim}{\Delta}$  is a vector of corrections to parameters and  $\underset{\sim}{X}$  a vector of residuals in the fields. Since we have many more independent transition fields than parameters to be fitted the set of equations is over determined. If  $\hat{\underset{\sim}{\Delta}}$  is the vector of corrections to the parameters which minimises the squared derivatives in the fields, it may be shown (4) to be given by:

$$\hat{\underset{\sim}{\Delta}} = (\underset{\sim}{D}^T \cdot \underset{\sim}{D})^{-1} \cdot \underset{\sim}{D}^T \cdot \underset{\sim}{X} \quad (2.6)$$

and the variance-co-variance matrix, related to the correlation matrix of the estimated parameters is given by:

$$\hat{\underset{\sim}{\sigma}}^2 = \hat{\sigma}^2 (\underset{\sim}{D}^T \cdot \underset{\sim}{D})^{-1} \quad (2.7)$$

where  $\hat{\sigma}$  is the estimated standard deviation of the variances in the field measurements, given by:

$$\hat{\sigma}^2 = \frac{1}{n - m} (\underset{\sim}{X} - \underset{\sim}{D} \hat{\underset{\sim}{\Delta}})^T (\underset{\sim}{X} - \underset{\sim}{D} \hat{\underset{\sim}{\Delta}}) \quad (2.8)$$

$m$  being the number of parameters to be fitted. The approximation, represented by Eq. (2.4), that small changes in the Hamiltonian parameters produce proportional changes in the calculated fields, is not strictly adhered to in practice, and the calculation proceeds by



repeating steps (2.6) to (2.8) with the corrected parameters until successive values of the estimated standard deviation  $\hat{\sigma}$  of the fit are identical to within the estimated accuracy of an individual measurement, or until successive changes to the parameters are smaller than their respective uncertainties.

The remaining problem in the analysis as outlined above is the efficient calculation of the (nxm) matrix of derivatives of the calculated fields with respect to the parameters (D). This may be performed by simply incrementing each parameter in turn by a 'small' amount and repeating the eigenvalue calculations for the levels involved in each transition with these new parameter values, then calculating the derivatives by subtraction and division. It is apparent that this would be a very tedious calculation and even on a fast computer, the time taken for this type of calculation becomes prohibitively long. A more efficient calculation of the derivatives may be performed using a modification of the method originally due to Castellano and Bothner-By (5). We first relate the derivatives of the calculated fields to the transition frequencies by the implicit function theorem

$$\frac{\partial B_i}{\partial p_j} = - \left( \frac{\partial v_i}{\partial p_j} \right)_{B_i} / \left( \frac{\partial v_i}{\partial B_i} \right)_{p_j} \quad (2.9)$$

$(\partial v_i / \partial B_i)_{p_j}$  is simply the rate at which the transition tunes in the magnetic field and may be calculated by linear interpolation between points a few gauss either side of the observed field.

The calculation of a tuning rate is required in any case to provide an estimate of the calculated field at which the transition occurs.

$(\partial v_i / \partial p_j)$  is related to the derivatives of the eigenvalues of the states involved in the transition ( $\lambda_{\alpha}^{(i)}$  and  $\lambda_{\beta}^{(i)}$  say) by:

$$\frac{\partial v_i}{\partial p_j} = \frac{\partial \lambda_{\alpha}^{(i)}}{\partial p_j} - \frac{\partial \lambda_{\beta}^{(i)}}{\partial p_j} \quad (2.10)$$

The derivatives of the eigenvalues with respect to the parameters can be estimated from the relationship (5):

$$\frac{\partial \lambda_{\alpha}^{(i)}}{\partial p_j} = \{ \underline{S}^T ( \frac{\partial H_{\alpha}^{(i)}}{\partial p_j} ) \underline{S} \}_{\alpha\alpha} \quad (2.11)$$

when  $\underline{S}$  is the matrix of the eigenvector coefficients, that is the transformation relating the eigenstate involved in the transition to a linear combination of the basis states, and  $(\partial H_{\alpha}^{(i)} / \partial p_j)$  is the derivative of the Hamiltonian matrix in the basis representation with respect to the  $j^{\text{th}}$  parameter which is straightforward to calculate. Evaluation of the derivatives matrix  $\underline{D}$  using Eqs. (2.9) to (2.11) is very much more efficient than a calculation based on incrementation of both parameters and fields. Analysis of spectra obtained at zero field is simpler since, in this case, there is no need to calculate the tuning rates  $(\partial v_i / \partial B_i)$  since we observe energy, ie. frequency, differences between molecular energy levels directly.

For a well constrained problem, it was usually found that the standard deviation of the fit  $\hat{\sigma}$  converged to within the estimated accuracy of the field measurements, usually better than one gauss, in two or three cycles. The final best fit parameters are then used to make a best fit spectrum prediction.

Slight modifications are necessary to Eqs. (2.6) to (2.8) when the data are known to be of unequal precision, these equations then

take the form : (4)

$$\hat{\underline{\Delta}} = (\underline{D}^T \cdot \underline{M}^{-1} \cdot \underline{D})^{-1} \underline{D}^T \cdot \underline{M}^{-1} \cdot \underline{X} \quad (2.6b)$$

$$\hat{\underline{\theta}} = \sigma^2 (\underline{D}^T \cdot \underline{M}^{-1} \cdot \underline{D})^{-1} \quad (2.7b)$$

$$\hat{\sigma}^2 = \frac{1}{n-m} (\underline{X} - \underline{D} \hat{\underline{\Delta}})^T \underline{M}^{-1} (\underline{X} - \underline{D} \hat{\underline{\Delta}}) \quad (2.8b)$$

where  $\underline{M}$  is a known diagonal weight matrix whose non-zero elements are ratios of variances  $\sigma_i^2 / \sigma_n^2$  of the measurements errors.

Both programs considered in detail in later sections make use of the weighted formulations (2.6b) - (2.8b) and hence data of unequal precision may be fitted simultaneously. The matrix inversions necessary in the solution of these equations are carried out using N.A.G. library routines available as a standard package on the computer systems used.

## 2 (III) Efficient solution of the eigenvalue problem.

### 2 (III) a Introduction

Advances in computer hardware have meant that efficiency considerations in programming do not assume the over-riding importance that they once held. However, in attempting to perform sophisticated analyses of large amounts of high resolution data, one can rapidly reach limitations imposed by computer time budgets; therefore it is still very worthwhile to attack the problem as efficiently as is reasonably possible.

In the last section, we touched on this subject while discussing the methods available for the calculation of the derivatives matrix

necessary in the least squares treatment of the data and calculation of the best fit molecular constants. This section is devoted to a general outline of the methods employed for setting up and obtaining solutions to the eigenvalue problem for the Hamiltonian (2.1) on an electronic computer in the most efficient way.

## 2 (III) b Rotational Basis Functions

The construction and diagonalisation of the Hamiltonian matrix are processes repeated many times during a full analysis calculation and are always the most time consuming parts of the calculation. Sections (IV) and (V) of this chapter discuss specific approaches to the problem; the discussion in this section is more general. Before reviewing the computational aspects, it is necessary that the model that we are to use is more precisely defined. An asymmetric top rotational energy level is specified by the quantum numbers  $N$ ,  $K_a$ , and  $K_c$  and usually symbolised  $N_{K_a K_c}$  (6). For each value of  $N$  there are  $2N+1$  distinct rotational energy levels which are uniquely identified in terms of the prolate top quantum number  $K_a$  and the oblate top quantum number  $K_c$ . The energy levels arranged in increasing energy for a particular value of  $N$  are:

$$(K_a, K_c) = (0, N), (1, N), (1, N-1), (2, N-1), (2, N-2), (3, N-2), \dots, \\ \dots, (N-1, 2), (N-1, 1), (N, 1), (N, 0).$$

We note that each value of  $K_a$  (or  $K_c$ ) except zero occurs twice in succession. Also  $K_a + K_c = N$  or  $N+1$ .

For reasons discussed later in this subsection, it is advantageous to work with functions which have a definite symmetry under the space-fixed inversion operation,  $E^*$ . Such functions are said to possess a parity which may be positive or negative depending on whether they are unchanged or change sign under the  $E^*$  operation. The functions  $N_{K_a K_c}$  are not in general eigenfunctions of  $E^*$  and do

not therefore possess a well defined parity; linear combinations of them do however, and we define the +- parity preserving combinations as:

$$|N K \pm \rangle = \frac{1}{\sqrt{2}} \{ |N K \rangle \pm (-)^{N-K} |N - K \rangle \} \quad (2.12a)$$

where  $|N K \rangle$  represents the symmetric top wavefunction  $N_{Ka}$ . A detailed discussion of the parity properties of the rotational levels of asymmetric top molecules has been given by Oka (7) using molecular symmetry group (8) arguments, and we will not debate the problems fully here. It is sufficient to realise that for all molecules belonging to groups containing the space-fixed inversion operation, the parity of a rotational level is well, and easily, defined. Planar asymmetric tops belong to this class of molecule and it turns out that the parity of a rotational level is given by the quantum number  $K_C$ ; odd  $K_C = -$  parity, even  $K_C = +$  parity. Complications arise when the molecule belongs to a group not containing the  $E^*$  operation. In some cases (groups containing permutation-inversion operations) the parity of a level is still well defined but must be discussed in conjunction with spin symmetry, whereas for all other cases the discussion of parity is irrelevant; the molecules possess stereoisomers.

Later in this chapter reference will be made to Wang combinations of the  $N_{Ka}$  functions. The Wang combination is defined as:

$$|N K (\pm) \rangle = \frac{1}{\sqrt{2}} \{ |N K \rangle \pm |N - K \rangle \}, \quad (2.12b)$$

and we will see that Wang ( $\pm$ ) and parity  $\pm$  descriptions coincide when  $N + K$  is even, but are opposite when  $N + K$  is odd. The comments made immediately below apply equally to the Wang combination.

Asymmetric top wavefunctions are linear combinations of the  $N_{Ka}$  functions and hence of the combinations (2.12a). The advantage of using a basis set composed of parity preserving combinations of the symmetric top functions is that the effective Hamiltonian (2.1) has non-zero matrix elements only between states of the same (+ or -) symmetry. Asymmetric top energy levels are thus represented by linear combinations of the + or - combinations, but the two sets are not mixed. For numerical calculations of the eigenvalues of the effective Hamiltonian the important result of the above discussion is that if we set up our asymmetric top Hamiltonian in a Wang or parity basis, it will be approximately half the size of that in a simple  $|N K\rangle$  representation, and thus require considerably less time to construct and diagonalise.

For asymmetric tops belonging to higher symmetry groups, that is orthorhombic symmetry groups, it is possible to further reduce the size of the Hamiltonian matrix representing a given rotational level. This arises because the irreducible representation to which a given + or - combination belongs depends upon whether the  $K$  is even or odd. It means that, for this type of molecule, the size of the Hamiltonian matrix can be made to be approximately one quarter the size that it would be if we were to use a crude symmetric top  $|N K\rangle$  basis representation and ignore symmetry division of the matrix.

For molecules belonging to lower than orthorhombic symmetry groups it is not strictly possible to effect this second reduction because levels of odd and even  $K$  in the combinations (2.12) transform according to the same irreducible representation of the molecular symmetry group and are hence connected by terms in the Hamiltonian. However, in practice, it happens that the terms in the Hamiltonian which connect these basis states have only very small effects on the eigenvalues and these are only rarely experimentally observable. The computer programs, described in the next two sections, make use of the symmetry properties of the Wang or parity combinations of the symmetric rotor basis functions to minimise the size of the

matrices representing the Hamiltonian. The inclusion of the effects of matrix elements between states of odd and even  $K$  is optional.

For near-symmetric top molecules a further reduction in diagonalisation time is possible, based not on symmetry but on order of magnitude considerations. In this type of molecule,  $K$  is very nearly a good quantum number and, assuming that one has chosen the correct representation, the eigenvectors have one principal component and only small contributions from other basis states. We can thus truncate the Hamiltonian matrix by including only basis states which make an experimentally observable contribution to the eigenvalues. This approach is carried further in one of the programs developed, section (IV), where perturbation theory is used to reduce the size of the Hamiltonian matrix still further. Fig. (1) shows, diagrammatically, the form of the matrix for various low  $N$  rotational levels in a parity basis for a molecule in a singlet electronic state in the absence of an external field.

## 2 (III) c Treatment of spin functions.

The Hamiltonian matrix becomes larger and more complicated when the molecule possesses unpaired electron spin, i.e. is a free radical. The appropriate basis set is one in which the electron spin angular momentum  $\underline{S}$  is coupled to the rotational angular momentum  $\underline{N}$  to give a resultant  $\underline{J}$ . The allowed values of  $J$  are  $N + S$ ,  $N + S - 1, \dots, |N - S|$ . There are hence  $2S + 1$  fine structure states associated with each rotational basis vector; they may be represented by the  $|N K (\pm) S J \rangle$  in the Wang representation, or  $|N K \pm S J \rangle$  in the parity representation. In the absence of external fields, the quantum number  $J$  is good, that is, the Hamiltonian contains no terms which mix states of different  $J$ , however there are terms present which mix states of different  $N$ , which is therefore no longer a good quantum number. The matrix in the Wang and parity representations for a molecule in a doublet state in the absence of external fields is shown for various low  $J$  values in Fig (2).

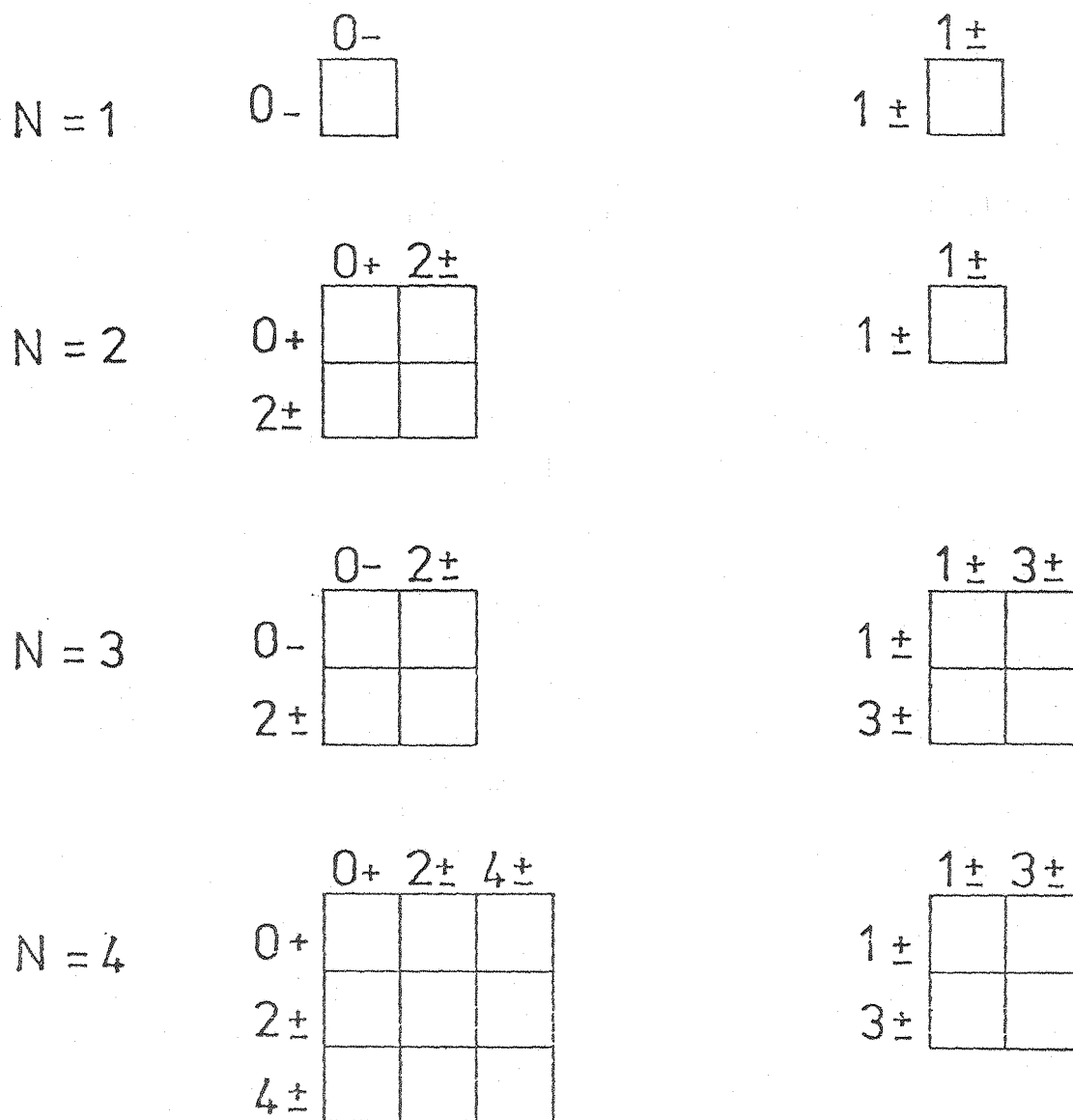


Figure 1. Hamiltonian matrices in a parity preserving basis for various low  $N$  values for a molecule in a singlet state. The rows and columns are labelled by the  $K$  values.



Figure 2. Hamiltonian matrix for the  $4_2^+$  levels of an ortho-rhombic molecule in a doublet state in (a) parity and (b) Wang representations in the absence of external fields.

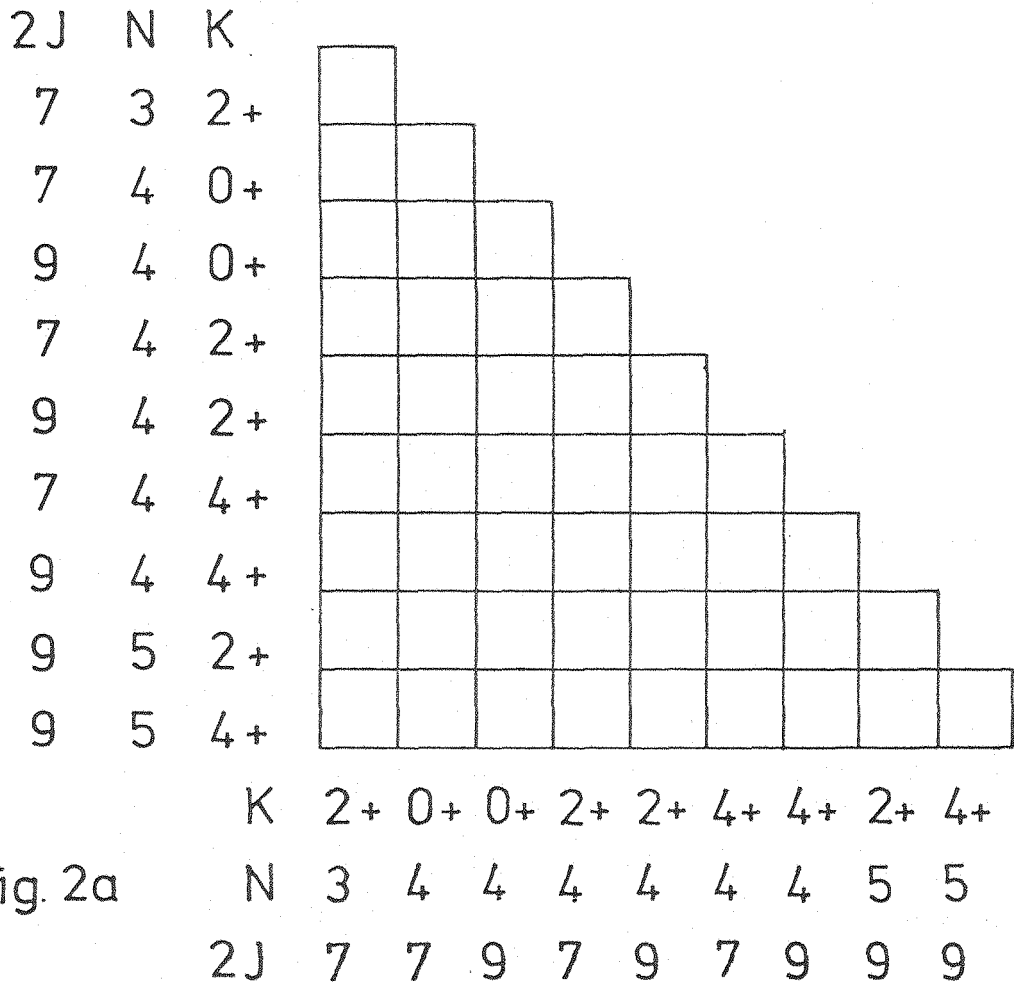


fig. 2a

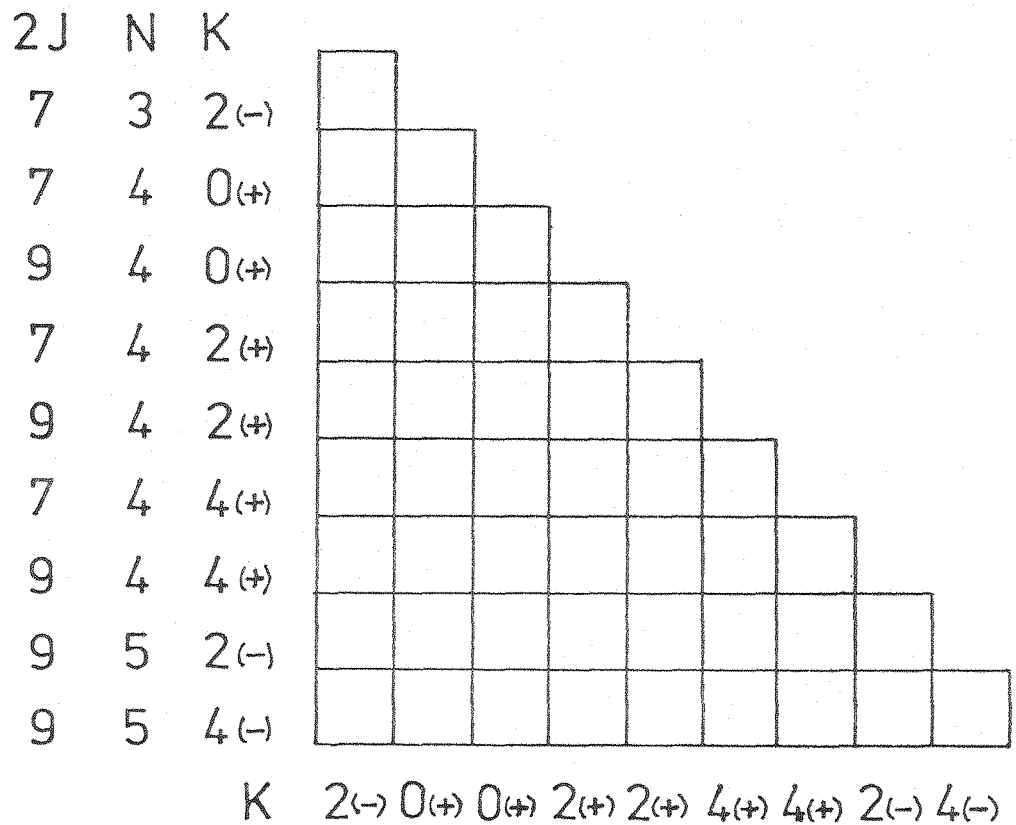


fig. 2b

The quantum number  $J$  is no longer a good one when the molecule is subjected to an external magnetic field. The direction of the field defines the space-fixed  $z$  axis direction and the projection of  $J$  on this axis is represented by  $M_J$ . There are  $2J + 1$  values of  $M_J$  for a given  $J$  and  $M_J$  is the only good quantum number in this case. The Hamiltonian matrix is now of infinite order and hence a complete solution to the eigenvalue problem cannot be achieved. To obtain eigenvalues it is therefore necessary to truncate the Hamiltonian matrix at a point where the inclusion of extra basis states makes experimentally undetectable changes to the required eigenvalue. Where and how this truncation is effected in practice is discussed in sections (IV) and (V). The Hamiltonian matrix for a molecule in a doublet state in an external magnetic field is shown diagrammatically in Fig. 3.

When the molecule contains one or more nucleus possessing non-zero spin each fine structure level is further divided into hyperfine levels associated, in zero field, with the allowed values of the quantum number  $F$ ,  $F = J + I$  where  $I$  is the total nuclear spin angular momentum of the state in question. Again, the Zeeman terms in the Hamiltonian will connect states of different  $F$  when the molecule is subjected to a magnetic field and the projection of  $F$  along the field direction ( $M_F$ ) is then the only good quantum number, i.e. the Hamiltonian matrix should strictly be constructed using an infinite basis set. Order of magnitude arguments are again used to decide where the necessarily finite matrix diagonalised by the computer is truncated.

In summary then, the exact calculation of a particular eigenvalue of the Hamiltonian may require the use of an infinitely large basis set, even when a symmetrised choice of basis functions is used. In this case, the matrix is truncated at points where the inclusion of more basis states makes a less than experimentally detectable change to the eigenvalue in question. For molecules possessing both unpaired electron and nuclear spins, the necessary basis may still be large. It is therefore important that the individual matrix elements are set up as efficiently as possible, so that

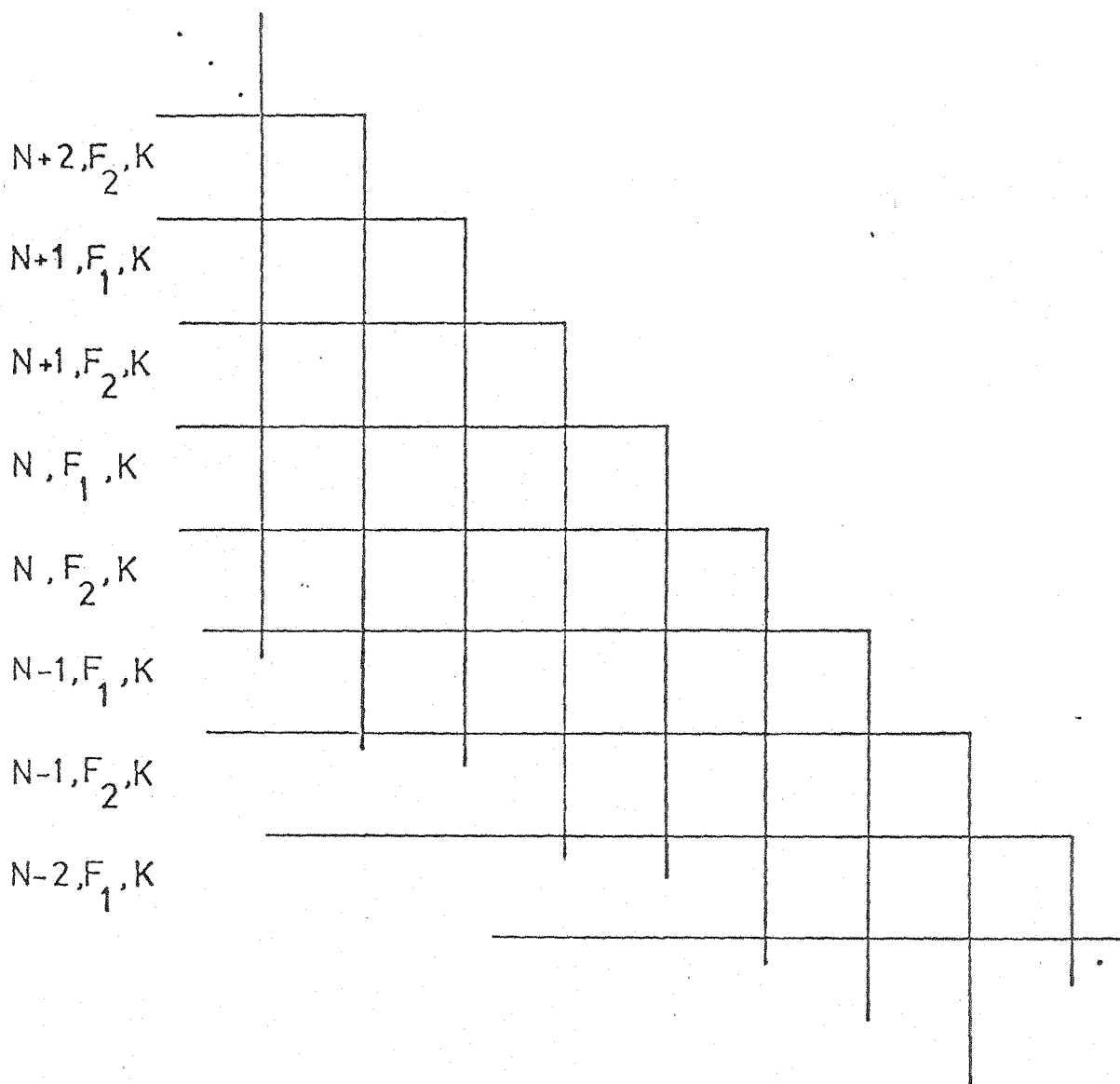


Figure 3. Diagrammatic representation of the lower half of the Hamiltonian matrix for a doublet state molecule in an external magnetic field. In the absence of nuclear spin hyperfine splittings, the quantum number  $M_J$  is good and the matrix contains all states  $J \geq |M_J|$ . Only one value of the quantum number  $K$  is shown in the basis for reasons of clarity, the matrix will contain contributions from states with all possible  $K$  associated with each included value of  $N$  (see Fig. 2).

execution time is kept to a minimum. In cases where the molecule possesses many different angular momenta, the calculation of matrix elements is facilitated by the use of the spherical tensor approach (9, 10, 11). The various operator terms in the Hamiltonian are expressed as components of spherical tensor operators and standard results from angular momentum theory are used to express the matrix in terms of 3, 6 and 9-j symbols. The spherical tensor approach is particularly well suited to computer solution and both programs make use of it.

In the next two sections we consider the approaches to solutions of the eigenvalue problem as represented by the two programs developed to perform complete spectrum analyses.

## 2 (IV) Program I.

### 2 (IV) a. Introduction.

This section describes a program developed with a view to the analysis of the spectra of near symmetric rotors in doublet states. Although it is restricted to this type of molecule alone, it is true to say that most known asymmetric top free radicals, e.g.  $\text{NO}_2$  (12, 13)  $\text{HCO}$  (14),  $\text{HO}_2$  (15, 16) fall into this category and the program has turned out to be a very useful one. We refer to it as program I. By restricting the molecular type, we are able to make various approximations and assumptions which dramatically reduce the computer time required to perform eigenvalue calculations. However the extremely fast execution time achieved by this program is at the expense of poor model accuracy in some cases, and a large computer storage requirement.

### 2 (IV) b Eigenvalue calculations: Program I.

The fast execution speed is achieved by the method used to construct the Hamiltonian matrix; the structure of the program

broadly follows that described in the previous sections. Use is made of the Wang factorisation of the matrix and small effects of matrix elements connecting states differing in  $K$  by one may be included by explicit 2<sup>0</sup> perturbation theory expressions which are added to the appropriate matrix elements, themselves coded explicitly in an  $J$ -decoupled basis representation. The matrix is truncated at elements with  $\Delta K = 0$ ,  $\Delta N = \pm 1$  and  $\Delta J = \pm 1$  and the inclusion of all elements with  $\Delta M_J = \Delta M_I = 0$ ,  $\pm 1$ ,  $\pm 2$  ..., i.e.  $\Delta M_F = 0$  is optional. The basic  $6 \times 6$  block is shown in Fig (4). This block is repeated for every allowed pair of  $M_I$ ,  $M_J$  values and hence the size of the Hamiltonian matrix depends on the value of the nuclear spin (the program assumes that the molecule contains only one nucleus with non-zero spin).

The effects of matrix elements off-diagonal in  $K$  have been included using perturbation theory. The treatment is complete to second order and dominant terms up to fourth order have been included.  $K$ -doubling effects in  $K = 3$  levels arise in third order and these have also been included. Fig. (5) shows how this process is achieved. There are small truncation errors associated with the neglect of matrix elements with  $\Delta N = \pm 2$  of the dipolar hyperfine and anisotropic Zeeman Hamiltonians, and other further off-diagonal elements of the latter operator. Comparison with a program which included these terms showed that these were almost never the dominant contributions to the program error. These arise due to the unreliability of the perturbation theory contributions in the treatment of the effects of matrix elements off-diagonal in  $K$ . It is these discrepancies which limit the program use to near-symmetric top rotors, because for more asymmetric top rotors, such as  $\text{NH}_2$ , the perturbation theory treatment is inadequate.

The extensive use of perturbation theory in the construction of the Hamiltonian matrix has several drawbacks, not the least being the amount of programming time and effort involved in deriving, coding and checking the complicated perturbation theory expressions. The main limitation is the inexact knowledge of the accuracy of the calculation being performed. For example, although the approach

$N+1, K$ $J=N+3/2$					
	$N+1, K$ $J=N+1/2$				
		$N, K$ $J=N+1/2$			
0			$N, K$ $J=N-1/2$		
0	0			$N-1, K$ $J=N-1/2$	
0	0	0			$N-1, K$ $J=N-3/2$

Figure 4. Diagram of the basic 6 x 6 building block for the treatment of the Hamiltonian matrix of program I. This block is repeated for each allowed value of  $M_I, M_J$ . The quantum number labels are shown in the diagonal elements.

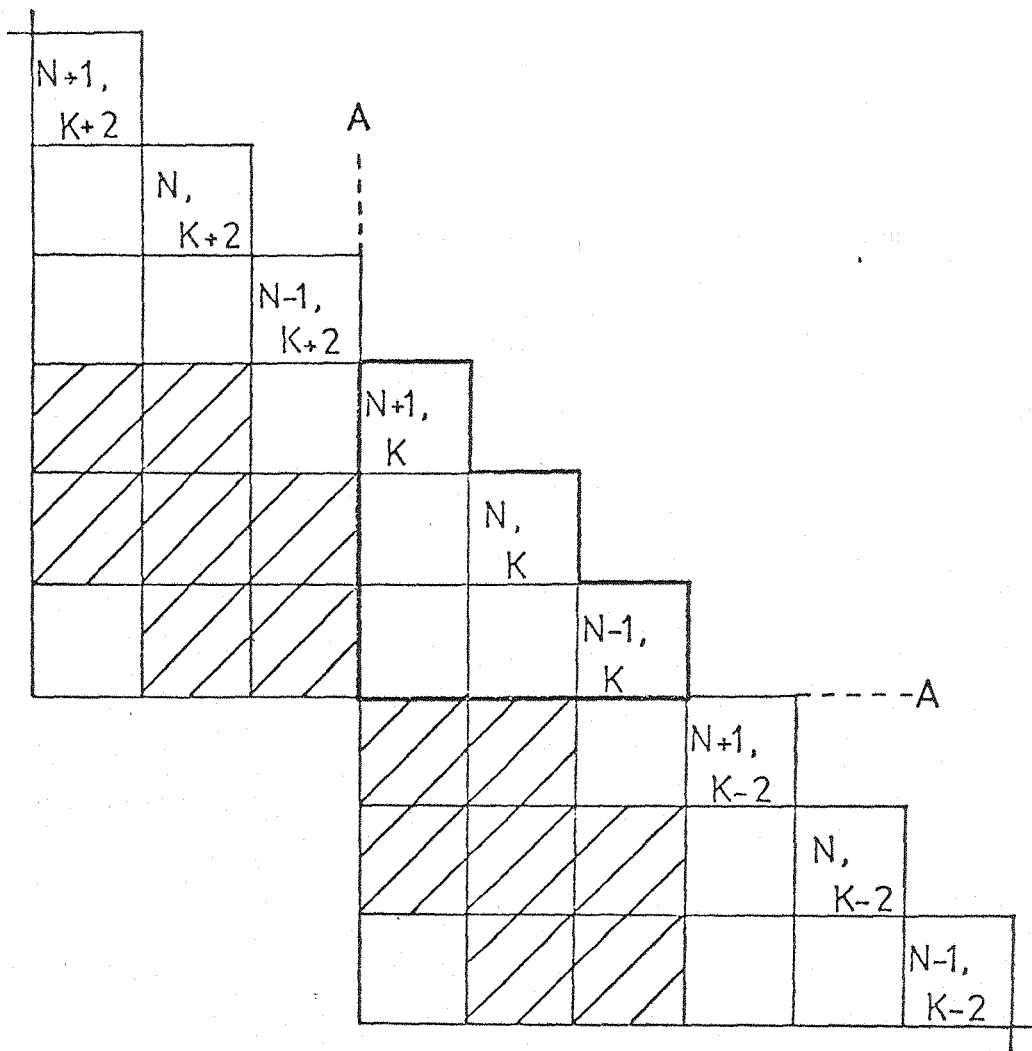


Figure 5. Treatment of matrix elements off-diagonal in the quantum number  $K$  in program I. The program sets up the matrix truncated at points  $A$  and the effects of the shaded matrix elements are collapsed into this central block using perturbation theory. The quantum number labels for the diagonal elements only are shown and fine structure states are not shown for reasons of clarity.



used is adequate for the molecules  $\text{NO}_2$  and  $\text{HCO}$ , the program did not reproduce more accurate calculations for  $\text{HO}_2$ , although this last molecule is no more asymmetric than the previous ones. The reason for the inaccuracy lies in the large spin rotation interaction in  $\text{HO}_2$ , a factor which had been overlooked during initial calculations; it causes breakdown of the third order treatment used in the program.

Diagonalisation of the Hamiltonian matrix is performed by a N.A.G. library routine F02ABF which returns the eigenvalues in order of ascending magnitude. It is necessary, therefore, to identify which of the eigenvalues is the one required. There are two general approaches to the problem. The first is to employ a counting method and include in the input data a number which identifies the state required by a simple countback from the end of the eigenvalue array. The second makes use of the eigenvector coefficient matrix which is computed by the library routine and used in the least squares and intensity calculations. Program I uses the latter approach which has the advantage that it is very general; countback methods run into difficulties when the calculations are being performed for very asymmetric top molecules (24) and the eigenvector analysis approach is more physically satisfying; however it is more difficult to program and slightly slower in terms of machine time.

The program has been used to analyse the available magnetic resonance and microwave data for  $\text{NO}_2$  in its ground electronic state and the results are discussed in Chapter (4). It was also used to perform preliminary analyses of the large body of magnetic resonance data recently obtained (15) from the spectrum of the  $\text{HO}_2$  radical. With large amounts of data available the high execution speed of this program is at a premium and although the final analysis was performed using program II (considered later) various different fits were attempted prior to this using program I.

2 (V) Program II.2 (V) a Introduction.

During the analysis of the microwave spectrum of  $\text{HO}_2$  (16) it became clear that the approximations in the calculation of the eigenvalues made by program I were not reliable, due mainly to the large spin-rotation interaction in this molecule. Rather than continue to program the higher orders of perturbation theory invoked to account for the discrepancies, it was decided to design a program in which the accuracy of the eigenvalue calculations performed was more easily defined and optionally variable, by choice of size of basis set, to suit the problem in hand. The program, referred to here as program II, assumes only one nucleus in the molecule, has non-zero spin, although this may be of any size, and will perform calculations for molecules in states of any multiplicity.

2 (V) b Eigenvalue Calculations: Program II.

The size of the basis set used in a particular calculation is chosen by the user. It is usual to choose the smallest required to reproduce larger basis set calculations to within the experimental accuracy, say 0.1 MHz for microwave data, slightly more for less accurate magnetic resonance data. The Hamiltonian matrix is set up in a fully-coupled, parity-conserving, basis set and optionally contains states with both odd and even  $K$  or assumes  $\Delta K = 1$  matrix elements make a negligible contribution to the energy and only includes either odd or even  $K$  basis vectors as appropriate. A calculation for a given rotational level can then be divided into four distinct steps, i.e:

1. Setting up the basis set appropriate to the calculation of the rotational level in question.
2. Setting up the Hamiltonian matrix in this basis.
3. Diagonalisation of the Hamiltonian matrix.

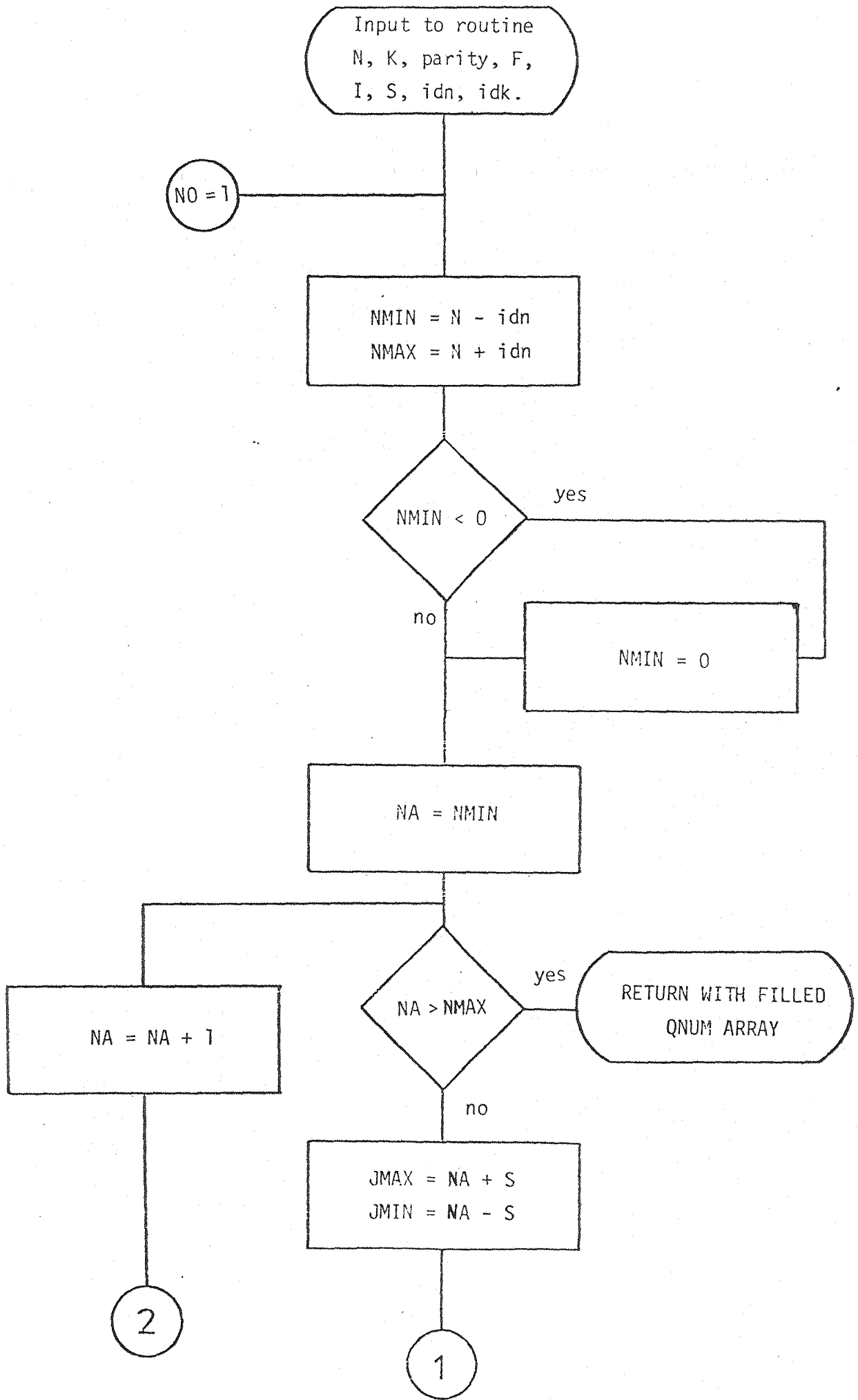
4. Selection of the correct eigenvalue from the set of eigenvalues of the Hamiltonian matrix.

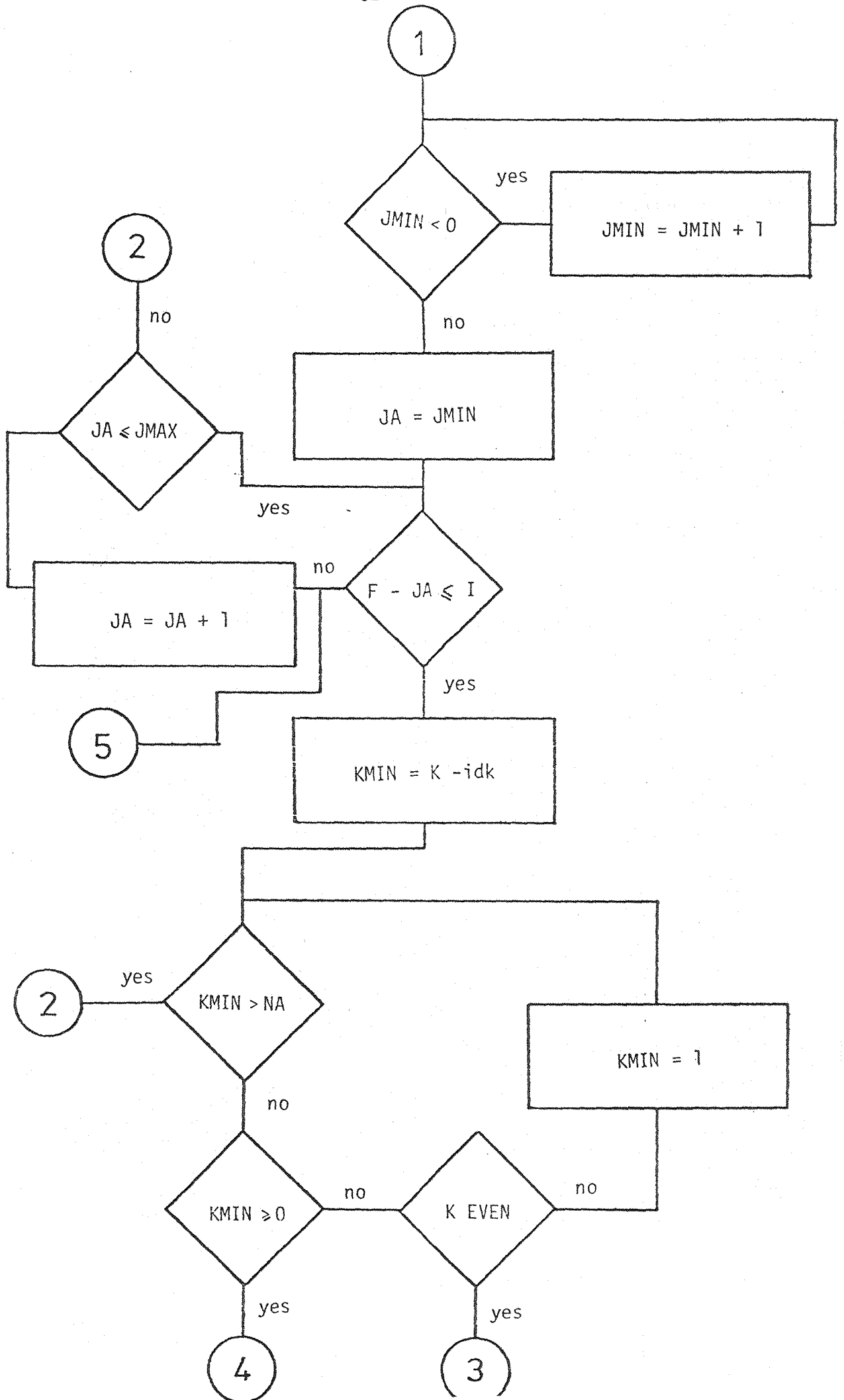
We will consider each of these points in turn and discuss the approach used in program II to solve the problems.

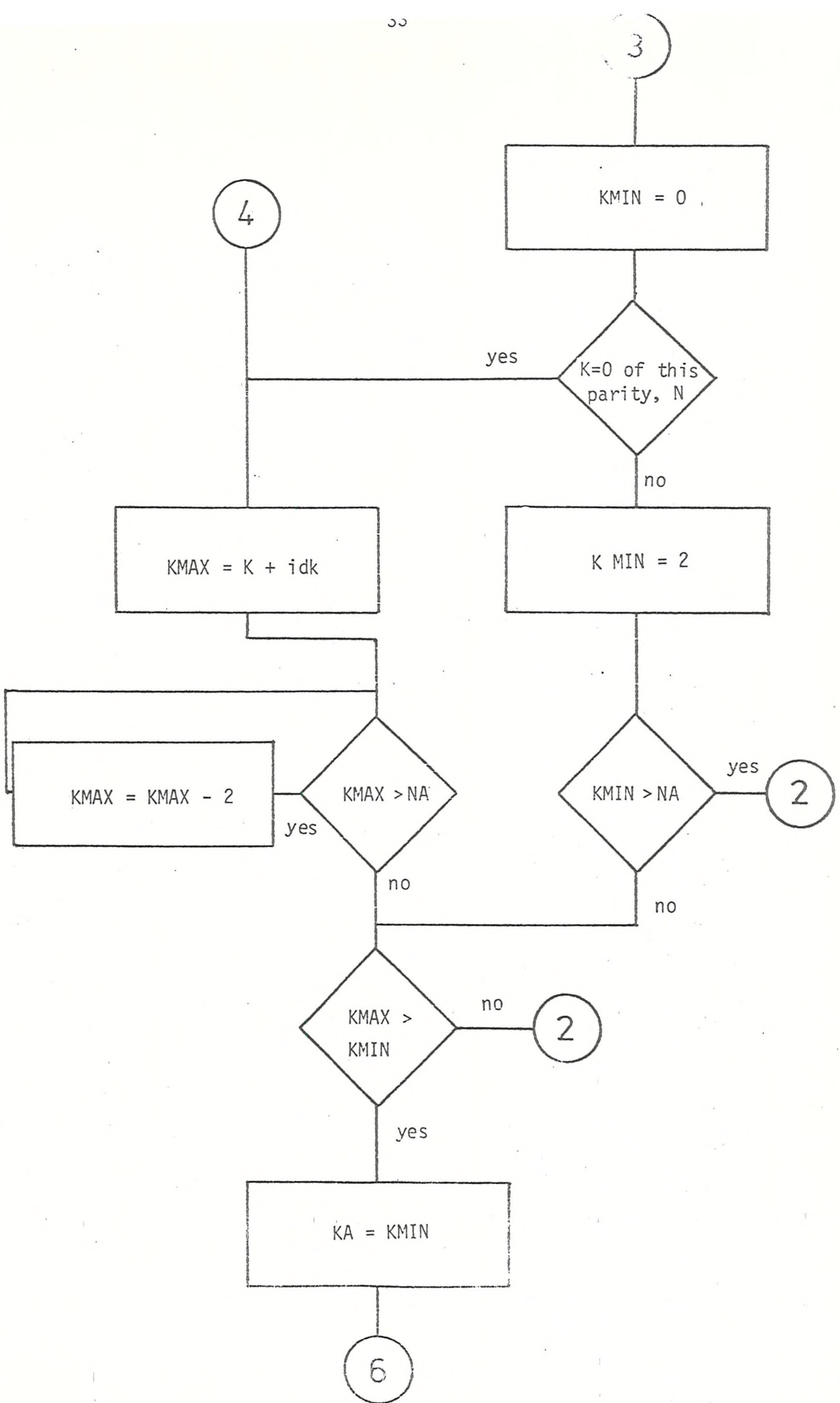
Firstly then, we must set up the basis set needed to calculate the energy of a particular rotational level reliably. Initially we discuss the zero field problem where  $F$  is a good quantum number and then outline the further complications when states of different  $F$  are to be included in the basis set. Given a set of quantum numbers  $N$ ,  $K$ , parity (plus or minus one), and  $F$ , the program sets up a basis set which contains adjacent rotational levels which are connected to the level in question by operator terms in the Hamiltonian, and which will therefore contribute to the energy of the level of interest. The number of these adjacent levels included is defined by the user as part of the program input as two parameters which define respectively, which states of different  $N$  and which of different  $K$  are to be included in the basis. For example, a calculation of the energy of the rotational level  $9_5^+$  with limits on  $N$  mixing (idn) set at one, and units on  $K$  mixing (idk) at two would include the levels  $8_3^+$ ,  $8_5^+$ ,  $8_7^+$ ,  $9_3^+$ ,  $9_5^+$ ,  $9_7^+$ ,  $10_3^+$ ,  $10_5^+$ ,  $10_7^+$  assuming that mixing of states of even  $K$  by terms in the Hamiltonian is not significant. This is a typical set of numbers and one would expect an adequate calculation of the energy of the  $9_5^+$  level of a near symmetric top molecule such as HCO or  $\text{NO}_2$  using this size of rotational level basis set. For more asymmetric rotors such as  $\text{NH}_2$ , it is usually necessary to include more levels of different  $K$  for a reliable calculation of the eigenvalue.

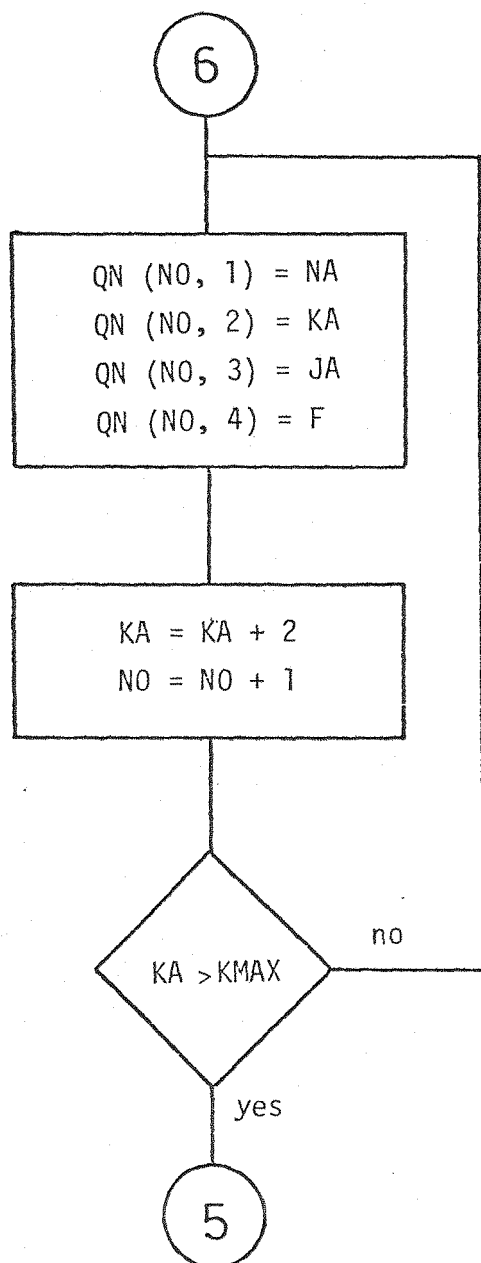
For these molecules, of course, we also have to tackle the problems of non-zero unpaired electron spin and nuclear spin. The way the program treats these problems is shown diagrammatically by the flow diagram, Fig (6), for the zero field case. When states of different  $F$  are to be included, i.e. the Zeeman Hamiltonian is to be included in the model, an extra loop over all possible  $F$  values for the given  $M_F$  is necessary. The quantum numbers of the  $n_0$  basis states to be

Figure 6. Flow diagram describing the logic used to load the required basis state quantum numbers in program II.









NOTES.

1. For simplicity this describes the route followed by the routine when it is required to set up a basis set for a zero field calculation, i.e. where  $F$  is a good quantum number.
2. The flow diagram assumes that only states having quantum number  $K$  differing by even numbers are connected by the Hamiltonian operator.



used in the calculation are loaded into an  $n_0 \times 4$  matrix and stored by the routine to be passed back to a second routine which sets up the Hamiltonian matrix using this basis set. The details of the quantum number storage are summarised by diagram (7).

The  $n_0$  basis states are then used to construct the Hamiltonian matrix and the matrix elements for all terms included in the model are given in the literature (3, 18, 19, 20). The matrix elements are coded directly in terms of 3, 6 and 9-j symbols which are computed as required by separate routines. This procedure minimises coding problems and eliminates the practice of coding the long and complicated algebraic formulae used by program I, and makes program checking a much easier task. Versions of the program exist employing both the A- and S- reduced forms of the rotational and spin-rotational Hamiltonians (see ref (18) and Chapter (3)). In the analysis of magnetic resonance data the matrix elements of the Zeeman Hamiltonian must be computed. This calculation is performed by a separate routine and the zero field and Zeeman matrices added immediately prior to diagonalisation. In this way the matrices may be used again in a subsequent calculation for the same rotational level at a different magnetic field simply by multiplying the Zeeman matrix by the appropriate field and repeating the addition and diagonalisation. It is important to minimise the number of times each matrix is set up in this way because re-calculation of the large numbers of 3, 6 and 9-j symbols is very time consuming. In the future it is possible that they will be stored as calculated, so making the process more efficient still.

The Hamiltonian matrix is diagonalised using N.A.G. library routine F02ABF which employs a Householder transformation to convert the symmetric matrix to symmetric tridiagonal form and the QL algorithm to perform the subsequent diagonalisation (21). The eigenvalues are returned in order of increasing magnitude with the eigenvectors, expressed as linear combinations of the basis vectors in a coefficient matrix, in the same order. The choice of

Fig. 7

I	J	1	2	3	4
1		$N_1$	$K_1$	$J_1$	$F_1$
2		$N_2$	$K_2$	$J_2$	$F_2$
3		$N_3$	$K_3$	$J_3$	$F_3$
4		$N_4$	$K_4$	$J_4$	$F_4$
.					
.					
.					
$n_0-1$		$N_{n_0-1}$	$K_{n_0-1}$	$J_{n_0-1}$	$F_{n_0-1}$
$n_0$		$N_{n_0}$	$K_{n_0}$	$J_{n_0}$	$F_{n_0}$

Figure 7. Basis state quantum number storage. For the zero field problem each basis state is labelled by five quantum numbers, one of which is the parity which is the same for all states in the basis set. The quantum numbers are stored such that each row of the array contains all necessary to identify a particular basis state.

the required eigenvalue presents some difficulty. Program I uses a method based entirely on a detailed analysis of the eigenvector coefficient matrix to pick out the eigenvector, and therefore eigenvalue, required. It was felt that the adoption of this method for program II would require an unjustified amount of programming effort and, for the very much larger matrices involved, prove inordinately inefficient. We have therefore opted for a counting method when a state is labelled by its quantum numbers,  $N, K, F$ , or  $N, K, M_F$  in the case of Zeeman calculations, and an index number which counts down from the highest energy level of this  $N$  and  $K$ . A unique level classification is thus provided by five numbers;  $N, K$ , parity,  $F$  (or  $M_F$ ) and  $i$ ; reverting to our original example  $9_5^+$ ,  $F = 9$ ,  $i = 2$  would specify the second highest level of  $F = 9$  in the  $9_5^+$  rotational level. The eigenvector coefficient matrix is used to pick out the rotational level,  $N$  always, and  $K$  almost always being reliable for this purpose.

The extra flexibility and markedly higher sophistication of program II is achieved at the expense of rather slower execution time when compared to program I. The gains lie in the precise knowledge of the accuracy of the calculation being performed and the ease with which the model, in the form of the basis set, can be varied. The coding of the program is simpler, there being no unwieldy algebraic perturbation theory expressions, implying that it is easier to check and occupies less storage area in the computer, a factor which had become a problem with program I. Program II has been used in the analysis of both MODR and magnetic resonance data pertaining to  $\text{NH}_2$ , a highly asymmetric top molecule; the spectra were not amenable to analysis using program I due to the inadequacy of the perturbation theory treatment. Spectra of the small free radicals  $\text{HCO}$ ,  $\text{HO}_2$  and  $\text{DO}_2$  have also been successfully analysed and some of the results are presented in the next section, whereas others are given in later chapters.

2 (VI) Application to the analysis of the microwave and magnetic resonance spectra of the HO<sub>2</sub> radical.

Considerable interest has been shown in the study of the HO<sub>2</sub> radical during the past five years. Prior to this, although widely invoked as a reaction intermediate, there had been no definite spectroscopic identification. However, observation of infra-red and ultra-violet spectra by Paukert and Johnston (22) and large numbers of lines in the L.M.R. spectrum at far infra-red wavelengths (15) provided good estimates for the main constants and subsequently microwave spectra resulting from both a- and b- type transitions were recorded by Saito (17) and Beers and Howard (23). E.P.R. transitions at around 9GHz have also been recorded (16). The large number of spectroscopic results supports the suggestion that HO<sub>2</sub> is an important species in chemical reactions. The programs have been used to fit all the available high resolution data and determine an improved set of parameters for the molecule in its ground vibronic state. In the process, some minor inconsistencies in the analysis of the microwave spectrum were removed and the quality of the fit of the L.M.R. data considerably improved (previously the latter were fitted to a very simple model).

The data were fitted to a model containing the symmetric (S-) reduced rotational Hamiltonian, however it was not sufficient to determine all the higher order constants and some were constrained to zero. In the process, it was confirmed that the S-reduced centrifugal distortion Hamiltonian gives a similar fit to that of the A-reduced form for the same number of parameters, but the parameters are less strongly correlated (18), (24). In order to obtain a satisfactory fit to the magnetic resonance data, it was found necessary to include the rotational Zeeman effect in the analysis and the values for the rotational g-factors were obtained.

The precision of the microwave data was estimated to be around 0.1 MHz, whereas that of the magnetic resonance data only approximately 5 MHz (assuming that, on average, a magnetic resonance line tunes at approximately one MHz/G). Due to this large disparity in precision,

it proved convenient to fit the two data sets separately since a larger basis set is needed to calculate the microwave frequencies to within the experimental accuracy. It was also necessary to include both odd and even  $K_a$  states in the calculation since these are significantly mixed by off-diagonal components of the spin-rotation tensor. None of the levels involved in the magnetic resonance data was significantly affected by this spin-rotation perturbation.

Analysis of the microwave data yielded values for the rotational constants, the quartic distortion constants  $D_N$ ,  $D_{NK}$  and  $d_1$ , the quadratic spin-rotation constants, the Fermi-contact parameter, and the diagonal components of the  $(I-S)$  dipolar hyperfine tensor. Subsequently, these parameters were constrained to their determined values in a fit of the magnetic resonance data which was used to determine the remaining quartic centrifugal distortion constants and some sextic ones, together with two quartic spin rotation parameters (the spin-rotation treatment used is discussed in detail in chapters (3) and (4)) and parameters describing the Zeeman interaction. The procedure of fitting first the zero field data and then the magnetic resonance data was repeated to ensure that convergence to the final set of parameters had been achieved.

The fit of the microwave data (17) is given in Table (I) and the constants obtained from the fit of this data in combination with the magnetic resonance data given in Table (II). The magnetic resonance data set included nine E.P.R. and one hundred and forty-one L.M.R. transitions, the latter chosen to be a representative sample of the very large data set listed by Hougan et al (15); approximately two lines of each polarisation were taken for each observed rotational transition. The Zeeman parameters determined are given in Table(III) and are found to agree well with the values predicted from theory, (16, 25).

TABLE I

FIT OF THE MICROWAVE SPECTRUM OF HO<sub>2</sub> IN THE  $\tilde{X}^2A'$  STATE

Transition	J' $\leftarrow$ J	F' $\leftarrow$ F	$\nu_{\text{obs}}$ /MHz	$\nu_{\text{calc}}$ /MHz	(obs-calc)/MHz
1 <sub>01</sub> $\leftarrow$ 0 <sub>00</sub>	1 $\frac{1}{2}$ $\leftarrow$ $\frac{1}{2}$	1 $\leftarrow$ 0	65070.85 <sup>1</sup>	65071.02 <sup>2</sup>	-0.17
		2 $\leftarrow$ 1	65081.82	65081.94	-0.12
		1 $\leftarrow$ 1	65098.44	65098.50	-0.06
	$\frac{1}{2}$ $\leftarrow$ $\frac{1}{2}$	1 $\leftarrow$ 0	65373.01	65372.93	0.08
		0 $\leftarrow$ 1	65396.15	65396.17	-0.02
		1 $\leftarrow$ 1	65400.63	65400.41	0.22
2 <sub>02</sub> $\leftarrow$ 1 <sub>01</sub>	2 $\frac{1}{2}$ $\leftarrow$ 1 $\frac{1}{2}$	2 $\leftarrow$ 1	130258.13	130257.92	0.21
		3 $\leftarrow$ 2	130260.07	130259.82	0.25
	1 $\frac{1}{2}$ $\leftarrow$ $\frac{1}{2}$	1 $\leftarrow$ 0	130463.68	130463.83	-0.15
		2 $\leftarrow$ 1	130467.41	130467.67	-0.26
2 <sub>12</sub> $\leftarrow$ 1 <sub>11</sub>	2 $\frac{1}{2}$ $\leftarrow$ 1 $\frac{1}{2}$	2 $\leftarrow$ 1	132959.56	132959.50	0.06
		3 $\leftarrow$ 2	132961.99	132962.03	-0.04
	1 $\frac{1}{2}$ $\leftarrow$ $\frac{1}{2}$	1 $\leftarrow$ 1	119137.04	119137.01	0.03
		2 $\leftarrow$ 1	119153.74	119153.69	0.05
		1 $\leftarrow$ 0	119159.19	119159.29	-0.10
2 <sub>11</sub> $\leftarrow$ 1 <sub>10</sub>	2 $\frac{1}{2}$ $\leftarrow$ 1 $\frac{1}{2}$	2 $\leftarrow$ 1	136492.09	136492.07	0.02
		3 $\leftarrow$ 2	136495.97	136495.98	-0.01
	1 $\frac{1}{2}$ $\leftarrow$ $\frac{1}{2}$	1 $\leftarrow$ 1	122856.61	122856.56	0.06
		1 $\leftarrow$ 0	122858.26	122858.16	0.10
		2 $\leftarrow$ 1	122858.92	122859.09	-0.17
6 <sub>16</sub> $\leftarrow$ 7 <sub>07</sub>	6 $\frac{1}{2}$ $\leftarrow$ 7 $\frac{1}{2}$	7 $\leftarrow$ 8	98117.82	98117.80	0.02
		6 $\leftarrow$ 7	98121.15	98121.11	0.04
	5 $\frac{1}{2}$ $\leftarrow$ 6 $\frac{1}{2}$	6 $\leftarrow$ 7	107640.22	107640.32	-0.10
7 <sub>17</sub> $\leftarrow$ 8 <sub>08</sub>	7 $\frac{1}{2}$ $\leftarrow$ 8 $\frac{1}{2}$	8 $\leftarrow$ 9	27474.24	27474.29	-0.05
		7 $\leftarrow$ 8	27477.69	27477.58	0.11
	6 $\frac{1}{2}$ $\leftarrow$ 7 $\frac{1}{2}$	7 $\leftarrow$ 8	35535.41	35535.37	0.04
		6 $\leftarrow$ 7	35530.88	35530.78	0.10
		5 $\leftarrow$ 6	107635.51	107635.55	-0.04
9 <sub>09</sub> $\leftarrow$ 8 <sub>18</sub>	9 $\frac{1}{2}$ $\leftarrow$ 8 $\frac{1}{2}$	10 $\leftarrow$ 9	44073.10	44072.89	0.21
		9 $\leftarrow$ 8	44069.56	44069.61	-0.05
	8 $\frac{1}{2}$ $\leftarrow$ 7 $\frac{1}{2}$	9 $\leftarrow$ 8	37138.59	37138.37	0.22
		8 $\leftarrow$ 7	37142.60	37142.81	-0.21
10 <sub>0</sub> , 10 $\leftarrow$ 9 <sub>19</sub>	10 $\frac{1}{2}$ $\leftarrow$ 9 $\frac{1}{2}$	11 $\leftarrow$ 10	116451.73	116451.71	0.02
		10 $\leftarrow$ 9	116448.40	116448.46	-0.06
	9 $\frac{1}{2}$ $\leftarrow$ 8 $\frac{1}{2}$	10 $\leftarrow$ 9	110472.20	110472.40	-0.20
		9 $\leftarrow$ 8	110476.90	110476.70	0.20

Table I (contd.)

<sup>1</sup> Data taken from ref. (17)

<sup>2</sup> Frequency calculated using the parameters given in Table II.  
Standard deviation of fit estimated as 0.17 MHz

TABLE II

MOLECULAR PARAMETERS OF HO<sub>2</sub> IN THE X<sup>2</sup>A<sup>1</sup> STATE IN MHz

Parameter	Present Work	Saito (5)
<i>A</i>	610274.31(72)	610257(14)
<i>B</i>	33513.838(34)	33511.95(24)
<i>C</i>	31671.662(37)	31673.46(24)
<i>D<sub>N</sub></i>	0.1151(13)	0.112(27)
<i>D<sub>NK</sub></i>	3.471(23)	3.47(19)
<i>D<sub>K</sub></i>	123.616(17) <sup>2</sup>	123 <sup>3</sup>
10 <sup>2</sup> <i>d<sub>1</sub></i>	-0.698(50)	-
10 <sup>3</sup> <i>d<sub>2</sub></i>	-0.811(12) <sup>2</sup>	-
10 <sup>3</sup> <i>H<sub>KN</sub></i>	2.095(94) <sup>2</sup>	-
10 <sup>2</sup> <i>H<sub>K</sub></i>	9.69(14) <sup>2</sup>	-
10 <sup>5</sup> <i>h<sub>1</sub></i>	4.50(29) <sup>2</sup>	-
<i>ε<sub>aa</sub></i>	-49569.89(58)	-49546.1(23)
<i>ε<sub>bb</sub></i>	-422.795(80)	-431.9(13) <sup>5</sup>
<i>ε<sub>cc</sub></i>	8.645(89)	17.6(13)
<i>ε<sub>ab</sub></i>	1891(11)	189(12) <sup>6</sup>
<i>ε<sub>ba</sub></i>	103.8 <sup>3,4</sup>	189 <sup>6</sup>
<i>D<sub>K</sub><sup>S</sup></i>	22.71(16) <sup>2</sup>	-
<i>D<sub>NK</sub><sup>S</sup> + D<sub>KN</sub><sup>S</sup></i>	0.1264(75) <sup>2</sup>	-
<i>a<sub>H</sub></i>	-27.48(15)	-27.6(6)
<i>T<sub>aa</sub></i>	-8.34(22)	-8.1(6)
<i>T<sub>bb</sub></i>	19.68(31)	19.5(6)

<sup>1</sup> The numbers in parentheses represent one standard deviation of the least-squares fit, in units of the last quoted place.

<sup>2</sup> Value determined from the fit of the EPR and LMR data. Parameter constrained at this value in the fit of the microwave data.

<sup>3</sup> Parameter constrained at this value.

<sup>4</sup> Value for *ε<sub>ba</sub>* determined from *ε<sub>ba</sub> = ε<sub>ab</sub> B/A*.

<sup>5</sup> Value for *ε<sub>bb</sub>* from *b*-type transitions determined as -417.9(6) MHz.

<sup>6</sup> Saito essentially assumed that *ε<sub>ba</sub> = ε<sub>ab</sub>*.



TABLE III.

ZEEMAN PARAMETERS FOR HO<sub>2</sub> IN THE  $\tilde{X}^2A''$  STATE

Parameter	Present Work	Solid State (26)	Theory
$g_s^{aa}$	2.04204(19) <sup>1</sup>	2.0353(5)	2.04293 <sup>2</sup>
$g_s^{bb}$	2.00790(24)	2.0086(5)	2.00863
$g_s^{cc}$	2.00152(24)	2.0042(5)	2.00219
10 <sup>3</sup> $g_r^{aa}$	-9.857(41)	-	-10.9 <sup>3</sup>
10 <sup>4</sup> ( $g_r^{bb} + g_r^{cc}$ )	-1.85(41)	-	-0.94

<sup>1</sup> The numbers in parentheses represent one standard deviation of the least-squares fit, in units of the last quoted decimal place.

<sup>2</sup> Calculated from Curl's relationship (25), using  $g_s = 2.00232$ .

<sup>3</sup> Electronic contribution only to the rotational  $g$ -factors (see text).

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## CHAPTER 3.

THE EFFECTIVE SPIN-ROTATION HAMILTONIAN FOR AN ASYMMETRIC TOP MOLECULE.3 (I) Introduction

The effective spin-rotation interaction is the coupling between the spin dipole moment and the magnetic field created by the charged particles (electrons and nuclei) in the molecule as they rotate. Information on this interaction is now available for several asymmetric top molecules in doublet states, derived from spectroscopic studies at a variety of wavelengths. Prime examples are  $\text{NO}_2$  (1) (2),  $\text{NH}_2$  (3) (4) (5),  $\text{PH}_2$  (6),  $\text{HCO}$  (7),  $\text{HNF}$  (8) and  $\text{HO}_2$  (9) (10). The principal components of the spin-rotation tensor  $\epsilon$ , have been determined for all these molecules; in addition, the splittings have been measured in a sufficient number of rotational levels that centrifugal distortion effects must be taken into account.

Van Vleck (11) has derived the form of the effective spin-rotation Hamiltonian from a consideration of the mixing of electronic states by the combined effects of spin-orbit coupling and the Coriolis term in the rotational Hamiltonian, viz.

$$H_{sr}^{(2)}/hc = \frac{1}{2} \sum_{\alpha, \beta} \epsilon_{\alpha\beta} (N_{\alpha} S_{\beta} + S_{\beta} N_{\alpha}) \quad (3.1)$$

where  $\alpha$  and  $\beta$  run separately over the molecule-fixed co-ordinates,  $x$ ,  $y$  and  $z$ . He has also shown that the second order (electronic) contribution to  $\epsilon_{\alpha\beta}$  usually predominates over the first order (nuclear) contribution. A similar conclusion was reached by Curl (12). Centrifugal distortion corrections to the spin rotation interaction were first discussed by Dixon and Duxbury (13) for symmetric top molecules. This work has recently been extended to asymmetric rotors by Cook, Hills and Curl (14), and by Brown and Sears (15) who cast the quartic spin rotation Hamiltonian in the form:

$$H_{sr}^{(4)}/hc = \frac{1}{2} \sum_{\alpha\beta\gamma\delta} \eta_{\alpha\beta\gamma\delta} (N_{\alpha} N_{\beta} N_{\gamma} S_{\delta} + S_{\delta} N_{\gamma} N_{\beta} N_{\alpha}). \quad (3.2)$$

To date, workers have contented themselves by adding two or three of the more important terms from (3.2) to the effective Hamiltonian used to fit their experimental data. In this chapter we derive the correct form for the reduced Hamiltonian to be used for this purpose, that is a Hamiltonian which contains only determinable combinations of parameters. The result is obtained by following the procedure formulated by Watson (16) in his classic paper on the centrifugal distortion of the rotational energy of a molecule. The Hamiltonian is subjected to a series of unitary transformations which eliminate the indeterminacies. These transformations, and their general implications are described in section III. The quadratic spin rotation terms are considered in section IV, where it is shown that there are indeterminacies which have not previously been detected for molecules belonging to non-orthorhombic groups. Section V deals with the specific reduction of the quartic spin-rotation Hamiltonian for an orthorhombic molecule. The results are applied to the well documented examples of  $\text{HO}_2$ ,  $\text{NH}_2$  and  $\text{NO}_2$  in the next chapter. We begin this chapter with a discussion of the origin of the quartic spin rotation terms and show how the  $\alpha\beta\gamma\delta$  parameters are related to other molecular properties.

### 3 (II) Derivation of the Effective Quartic Spin-Rotation Hamiltonian.

The derivation of the effective Hamiltonian (2.1) can be considered in two stages. First the removal of the effects of matrix elements which connect different electronic states, and secondly the corresponding process for the matrix elements off-diagonal in the vibrational state within the electronic state in question. The effects of such off-diagonal matrix elements are usually removed by some form of perturbation theory, taken to such an order that the resultant eigenvalues are more accurate than the experimental data. In the case of the construction of the effective vibration-rotation Hamiltonian (the first stage), it is usually sufficient to go to second order in perturbation theory. At this point in the calculation both the rotational and spin-rotational Hamiltonians are defined, although they are still functions of the nuclear (ie. vibrational) co-ordinates. The spin-rotation tensor

$\underline{\epsilon}$ , for example, has components which are identified as the coefficients of terms bilinear in rotational and electron spin angular momenta,  $\underline{N}$  and  $\underline{S}$  respectively (11).

The reduction of the vibration-rotation Hamiltonian to an effective Hamiltonian as given in (2.1) is the second stage in this process. It is most common to use a harmonic oscillator basis set to perform the perturbation calculation (17), since the contact transformation is then easy to formulate; it may however be most efficient in particular cases to use an anharmonic vibrational basis set (18). The centrifugal distortion terms  $H_{cd}$ , and the centrifugal distortion corrections to the spin-rotation interaction,  $H_{sr cd}$ , appear at this stage of the calculation. The quartic centrifugal distortion terms can be derived by a simple second order perturbation treatment (19). We now derive the corresponding corrections to the spin-rotation interaction by the same method. These corrections arise from the dependence of the inertial tensor and spin-rotation tensor on the vibrational coordinates  $Q_r$ :

$$H_{rot}/hc = \frac{\hbar^2}{2hc} \sum_{\alpha} \frac{N_{\alpha}^2}{I_{\alpha}^e} - \frac{\hbar^2}{2hc} \sum_{\alpha\beta} \frac{N_{\alpha} N_{\beta}}{I_{\alpha}^e I_{\beta}^e} \sum_r a_r^{(\alpha\beta)} Q_r + 0 (Q_r Q_s) \quad (3.3)$$

$$H_{sr}/hc = \frac{1}{2} \sum_{\alpha\beta} \epsilon_{\alpha\beta}^e (N_{\alpha} S_{\beta} + S_{\beta} N_{\alpha}) + \frac{1}{2} \sum_{\alpha\beta} (N_{\alpha} S_{\beta} + S_{\beta} N_{\alpha}) \sum_r b_r^{(\alpha\beta)} Q_r + 0 (Q_r Q_s) \quad (3.4)$$

where

$$a_r^{(\alpha\beta)} = \partial I_{\alpha\beta} / \partial Q_r$$

$$b_r^{(\alpha\beta)} = \partial \epsilon_{\alpha\beta} / \partial Q_r$$

and  $\alpha$  and  $\beta$  run over the molecule-fixed co-ordinates,  $x, y$ , and  $z$ . The first expansion is standard in vibration-rotation theory (20); the spin-rotation Hamiltonian has been expanded in a corresponding fashion. The term linear in  $Q_r$  in  $H_{rot}$  gives rise to the quartic centrifugal distortion terms in second order of perturbation theory:

$$H_{cd}/hc = \frac{\hbar^4}{4hc} \sum_{\alpha\beta} \sum_{\gamma\delta} \frac{N_\alpha N_\beta N_\gamma N_\delta}{I_{\alpha\alpha}^e I_{\beta\beta}^e I_{\gamma\gamma}^e I_{\delta\delta}^e} \sum_r a_r^{(\alpha\beta)} a_r^{(\gamma\delta)} \quad (3.5)$$

$$\times \sum_{v'}' \frac{\langle v | Q_r | v' \rangle^2}{(E_v - E_{v'})} \equiv \frac{1}{4} \sum_{\alpha\beta} \sum_{\gamma\delta} \tau_{\alpha\beta\gamma\delta} N_\alpha N_\beta N_\gamma N_\delta,$$

where  $\tau_{\alpha\beta\gamma\delta}$  are the parameters introduced by Wilson and Howard (21), multiplied by  $\hbar^4$ . If the perturbation calculation is performed using a simple harmonic oscillator basis set, then

$$\tau_{\alpha\beta\gamma\delta} = \frac{-\hbar^4}{hc} \sum_r \frac{1}{I_{\alpha\alpha}^e I_{\beta\beta}^e I_{\gamma\gamma}^e I_{\delta\delta}^e} \frac{a_r^{(\alpha\beta)} a_r^{(\gamma\delta)}}{8\pi^2 c^2 \omega_r^2}, \quad (3.6)$$

where  $\omega_r$  is a harmonic vibrational frequency in  $\text{cm}^{-1}$ . The centrifugal distortion corrections to the spin-rotation interaction arise in a similar fashion from the cross terms between  $H_{rot}$  and  $H_{sr}$  to give:

$$H_{srcd}/hc = \frac{1}{4} \sum_{\alpha\beta} \sum_{\gamma\delta} \eta_{\alpha\beta\gamma\delta} [N_\alpha N_\beta (N_\gamma S_\delta + S_\delta N_\gamma) + (N_\gamma S_\delta + S_\delta N_\gamma) N_\alpha N_\beta], \quad (3.7)$$

where

$$\eta_{\alpha\beta\gamma\delta} = \frac{\hbar^3}{4\pi hc^2} \sum_r \frac{a_r^{(\alpha\beta)} b_r^{(\gamma\delta)}}{I_{\alpha\alpha}^e I_{\beta\beta}^e \omega_r^2} \quad (3.8)$$

The components of both  $\tau$  and  $\eta$  tensors can be expressed more compactly in terms of the coupling parameters  $C_r^{\alpha\beta}$  introduced by Watson (22). Explicitly



$$\tau_{\alpha\beta\gamma\delta} = -2 \sum_r C_r^{(\alpha\beta)} C_r^{(\gamma\delta)} \omega_r$$

and

$$\eta_{\alpha\beta\gamma\delta} = \sum_r C_r^{(\alpha\beta)} \frac{\partial \epsilon_{\gamma\delta}}{\partial q_r}$$

in wavenumber units, when  $q_r$  is the dimensionless normal co-ordinate.

Equation (3.8) is an expression for the  $\eta$  parameters. It can be seen by comparison with (3.6) that there is not a rigorous relationship between  $\tau_{\alpha\beta\gamma\delta}$  and  $\eta_{\alpha\beta\gamma\delta}$  since  $a_r^{(\alpha\beta)}$  and  $b_r^{(\alpha\beta)}$  are independent quantities. However, an approximate relationship of the sort derived by Dixon and Duxbury (13) can be established by further investigation of the coefficient  $b_r^{(\alpha\beta)}$ . Using second order perturbation theory, Van Vleck (11) has shown that:

$$\epsilon_{\alpha\beta} = \frac{-4\pi^2}{2hc} \sum_{n \neq 0} \frac{\langle 0 | \zeta L_\beta | n \rangle \langle n | \sum_{\gamma} \mu_{\alpha\gamma} L_\gamma | 0 \rangle}{(E_0 - E_n)} \quad (3.9)$$

when  $\zeta$  is a spin-orbit coupling parameter and  $\mu_{\alpha\beta} = (I^{-1})_{\alpha\beta}$  is a component of the inverse inertial tensor (20). The molecule-fixed axis system is located so that it corresponds to the principal axes of the equilibrium inertial tensor:

$$\mu_{\alpha\beta} = (I_{\alpha\alpha}^e I_{\beta\beta}^e)^{-1} [I_{\alpha\beta}^e \delta_{\alpha\beta} - a_r^{(\alpha\beta)} Q_r + 0 (Q_r Q_s)] \quad (3.10)$$

The integration in the matrix elements in (3.9) is performed over electronic co-ordinates and 0 and  $n$  are the labels for the different electronic states. To determine  $b_r^{(\alpha\beta)}$  we need to know the vibrational dependence of all factors on the right hand side of (3.9). Since  $\mu_{\alpha\gamma}$  is a function of nuclear co-ordinates only, it can be taken as a factor outside the integral over electronic co-ordinates and the

derivative with respect to a vibrational co-ordinate involves

$$\frac{\partial}{\partial Q_r} \langle n | \mu_{\alpha\gamma} L_\gamma | 0 \rangle = \frac{-a_r^{(\alpha\gamma)}}{I_\alpha^e I_\gamma^e} \langle n | L_\gamma | 0 \rangle + \mu_{\alpha\gamma} \frac{\partial}{\partial Q_r} \langle n | L_\gamma | 0 \rangle. \quad (3.11)$$

The orbital angular momentum operator  $L_\gamma$  is independent of vibrational co-ordinates but the electronic wavefunctions in general are not. In consequence,  $\langle n | L_\gamma | 0 \rangle$  is a function of  $Q_r$ , as are  $\langle 0 | \zeta L_\beta | n \rangle$  and  $(E_0 - E_n)$ . If we make the approximation of a crude adiabatic basis set (that is, the electronic wavefunctions refer to fixed nuclei at some reference configuration, usually the equilibrium configuration) then

$$\begin{aligned} b_r^{(\alpha\beta)} &= \frac{4\hbar^2}{2hc} \sum_r \frac{a_r^{(\alpha\gamma)}}{I_\alpha^e I_\gamma^e} \sum_{n \neq 0} \frac{\langle 0 | \zeta L_\beta | n \rangle \langle n | L_\gamma | 0 \rangle}{(E_0 - E_n)} \\ &= - \sum_\gamma \epsilon_{\gamma\beta}^e a_r^{(\alpha\gamma)} / I_\alpha^e \end{aligned} \quad (3.12)$$

On substitution of this result in equation (3.8), we obtain

$$\eta_{\alpha\beta\gamma\delta} = \sum_s \frac{\tau_{\alpha\beta\gamma\delta} \epsilon_{s\delta}}{2B_s} \quad (3.13)$$

where  $B_s$  is the rotational constant associated with the principal inertial axis  $s$ . Strictly speaking, the quantities in (3.13) should be the equilibrium values of the parameters. However, in view of the approximations made in obtaining the expression for  $b_r^{(\alpha\beta)}$  in (3.12), the result is probably no less reliable if the values for a particular vibrational level are used. Some applications of equation (3.13) are considered in Chapter 4.

### 3 (III) General Considerations

#### 3 (III) a The standard form for the spin-rotation Hamiltonian

In the last section, the origin of terms in the effective Hamiltonian which describe centrifugal distortion corrections to the spin-rotation interaction was discussed. The form of the Hamiltonian considered up to now (3.2) is not well suited to the calculation of matrix elements and therefore fitting to experimental data. The remainder of this chapter is devoted to the transformation of the quartic spin-rotation Hamiltonian (3.2) to yield an operator form which is suitable for the empirical fitting of experimental data.

We start with the effective Hamiltonian as derived in Ref. (11) and the last section. This Hamiltonian is an operator function of the components of the rotational and spin angular momenta,  $N$  and  $S$ , and acts only within a single vibrational level of a given electronic state. The general form of the Hamiltonian contains products of  $N_\alpha$  and  $S_\beta$  with the individual factors in arbitrary order. By use of the commutation relations for molecule fixed components (11) :

$$[N_\alpha, N_\beta] = -ie_{\alpha\beta\gamma} N_\gamma \quad (3.14a)$$

$$[N_\alpha, S_\beta] = -ie_{\alpha\beta\gamma} S_\gamma \quad (3.14b)$$

$$[S_\alpha, S_\beta] = ie_{\alpha\beta\gamma} S_\gamma \quad (3.14c)$$

it is always possible to express the general term in the form :

$$\frac{1}{2} (N_x^p N_y^q N_z^r S_\alpha + S_\alpha N_z^r N_y^q N_x^p)$$

with  $\alpha = x, y$  or  $z$ , at the expense of introducing terms of lower

degree. The latter can then be re-arranged into the same form and the process repeated to yield a sum of terms of this type. In this way, the general spin-rotation Hamiltonian can be expressed in the standard form :

$$H_{sr}/hc = \frac{1}{2} \sum_{p,q,r} \sum_{\alpha} k_{pqr}^{(\alpha)} (N_x^p N_y^q N_z^r S_{\alpha} + S_{\alpha} N_z^r N_y^q N_x^p) \quad (3.15)$$

The coefficients  $k_{pqr}^{(\alpha)}$  which can be related to the components  $\epsilon_{\alpha\beta}$  and  $\eta_{\alpha\beta\gamma\delta}$  in equations (3.1) and (3.2) are in general complex. For application to physical systems, the Hamiltonian must be hermitian and invariant under the operation of time reversal, that is :

$$H_{sr} = H_{sr}^{\dagger} = T H_{sr} T^{-1} = (T H_{sr} T^{-1})^{\dagger} \quad (3.16)$$

The coefficients  $k_{pqr}^{(\alpha)}$  are transformed with their complex conjugates by either operation while the angular momentum components change sign under time reversal (T) but are invariant under the operation of hermitian conjugation (+). The combined effect of these operations requires that the coefficients  $k_{pqr}^{(\alpha)}$  be real and that the sum of the indices  $n, = p+q+r$ , be odd. The standard form of the spin-rotation is therefore given by the restricted sum :

$$H_{sr}/hc = \frac{1}{2} \sum_n \sum_{\alpha} k_{pqr}^{(\alpha)} (N_x^p N_y^q N_z^r S_{\alpha} + S_{\alpha} N_z^r N_y^q N_x^p) \quad (3.17)$$

with  $n$  odd and real coefficients  $k_{pqr}^{(\alpha)}$ . Terms with  $n = 1$  are identified with the quadratic spin rotation Hamiltonian,  $H_{sr}^{(2)}$  whereas those with  $n = 3$  represent the quartic spin-rotation terms, that is the centrifugal distortion of the spin-rotation interaction  $H_{sr}^{(4)}$ .

The total number of terms of degree  $n$  (odd) in the standard form of  $H_{sr}$  is  $\frac{3}{2} \times (n+1)(n+2)$  so that there are nine terms in general in  $H_{sr}^{(2)}$  and thirty in  $H_{sr}^{(4)}$ . However, if the molecule possesses symmetry elements other than the identity operation, there are fewer terms in the Hamiltonian because of the requirement that  $H_{sr}$  transforms according to the totally symmetric representation of the molecular symmetry group. Terms in  $H_{sr}$  of total degree  $(n+1)$  in angular momentum components transform under the molecular symmetry operations as the  $(n+1)^{\text{th}}$  direct product of the representations of the individual operators; the representations formed by the components of a molecule fixed rotation are listed in the character tables. Asymmetric top symmetry groups are sub-groups of  $D_{2h}$  and the numbers of terms in the quadratic and quartic Hamiltonians for this and all other orthorhombic groups are given in Table 1, together with the corresponding number of terms expected for molecules of the groups  $C_s$  and  $C_1$  (no symmetry elements other than the identity). It can be seen that there are three terms in  $H_{sr}^{(2)}$  and nine in  $H_{sr}^{(4)}$  for an orthorhombic molecule; when the molecule has only a plane of symmetry, the numbers are five and sixteen respectively.

Although symmetry arguments allow a certain number of independent terms in the Hamiltonian, it is still possible that the eigenvalues depend on particular combinations of these parameters only. In this case, an attempt to fit the Hamiltonian to observed molecular spectra and thereby determine its parameters will not succeed. It is therefore necessary to identify all possible indeterminacies and to remove them by reducing the number of parameters. The reduced Hamiltonian has the same eigenvalues as the original operator, but different parameters which are linear combinations of the previous ones and fewer in number. The simplest example of this effect is in the rigid rotor problem (23), where the molecule-fixed axes can always be re-oriented to bring the inertial tensor into diagonal form. The rotational eigenvalues thus depend on no more than three independent principal moments of inertia and these in turn are the most that can be determined from the rotational energy levels.

TABLE I

THE NUMBERS OF TERMS IN THE STANDARD AND REDUCED FORMS OF THE  
SPIN-ROTATION HAMILTONIAN

Number of terms	$C_1$	$C_s$	Orthorhombic
(a) Quadratic spin-rotation			
$H_{sr}^{(2)}$	9	5	3
$F_0$	3	1	0
$\tilde{H}_{sr}^{(2)}$	6	4	3
(b) Quartic spin-rotation			
$H_{sr}^{(4)}$	30	16	9
$F_2$	18	8	3
$\tilde{H}_{sr}^{(4)}$	12	8	6

3 (III) b Unitary Transformations

The standard form Hamiltonian, Eq (3.17) is to be subjected to a series of unitary transformations to yield the reduced Hamiltonian  $\tilde{H}$  which contains determinable parameters only. The transformed Hamiltonian is given by

$$\tilde{H} = U^{-1} H U \quad (3.18)$$

where  $U$  is some unitary operator ( $U^\dagger = U^{-1}$ ) Following Watson (16), we choose the convenient exponent form for the unitary operator :

$$U = \exp (iF) \quad (3.19)$$

where the unitary condition requires  $F$  to be hermitian. If the transformed Hamiltonian is to be both invariant under time reversal and hermitian, then so must  $U$  be also. This in turn implies that  $F$  change sign under time reversal. Using the arguments given in the previous section, it can be shown that, when  $F$  is expressed in a standard form similar to (3.15) it has real coefficients and contains terms of even  $p + q + r$  only.

The unitary transformations are assumed to be applied successively to the Hamiltonian, which is equivalent to expressing  $U$  as a product and considering each factor separately :

$$U = \exp (iF_0) \exp (iF_2) \exp (iF_4) \quad (3.20)$$

where  $F_n$  contains terms with  $n = p + q + r$  only:

$$F_n = \frac{1}{2} \sum_{p+q+r=n} \sum_{\alpha} f_{pqr}^{(\alpha)} (N_x^p N_y^q N_z^r S_{\alpha} + S_{\alpha} N_z^r N_y^q N_x^p) \quad (3.21)$$

and  $f_{pqr}^{(\alpha)}$  is real. From (3.20) it can be seen that :

$$U^\dagger = U^{-1} = \dots \exp(-iF_4) \exp(-iF_2) \exp(-iF_0) \quad (3.22)$$

so that the transformations of increasing  $n$  can be applied in order

$$\tilde{H} = (\dots \exp(-iF_4) \exp(iF_2) \exp(-iF_0) H \exp(iF_0) \exp(iF_2) \exp(iF_4) \dots) \quad (3.23)$$

The various stages in the transformation can thus be identified :

$$H_2 = \exp(-iF_0) H \exp(iF_0) \quad (3.24a)$$

$$H_4 = \exp(-iF_2) H \exp(iF_2) \quad (3.24b)$$

$$H_\infty = \tilde{H} \quad (3.24c)$$

One of the advantages of using the exponential form for the unitary transformation is that the process can be readily expanded in terms of commutators, for example:

$$H_2 = H + i [H, F_0] - \frac{1}{2} [[H, F_0], F_0] + \dots \quad (3.25)$$

so that the relations (3.14) can be invoked to give the transformation explicit form.

The transformation defined by equations (3.20) and (3.21) involves the components of spin angular momentum, and in this respect, it corresponds to a change in spin basis set. Because there is a mathematical connection between a matrix  $u$  of the special unitary group in two dimensions and a real orthogonal matrix of the rotation group (specifically,  $SU(2)$  is homomorphic with  $SO(3) = R_3$ ), there is always a certain rotation  $R$  which can be associated with this change of basis set. Abragam and Bleaney (23) refer to the rotation as fictitious to distinguish it from a real rotation of the co-ordinate system. As a result, the parameter  $\epsilon_{\alpha\beta}$  behaves like the component



of a double vector; the first subscript transforms under the operations of  $SO(3)$  whereas the second transforms under the operations of  $SU(2)$ . The consequence for the present work is that a unitary transformation involving  $S_\alpha$  is independent of the corresponding transformation involving  $N_\alpha$  and must be considered separately in the removal of indeterminacies in the spin-rotation Hamiltonian.

### 3 (III) c The reduced spin-rotation Hamiltonian.

We are concerned with the spin-rotational reduction of the molecular Hamiltonian to give an operator which contains determinable combinations of parameters only. Watson (16), (22) has discussed the analogous problem of the application of a rotational contact transformation to the rotational Hamiltonian by a succession of unitary transformations of the form (3.20) of odd degree in  $N_\alpha$ . There are extra complications in the present case in that the spin-rotational reduction of the rotational Hamiltonian and the rotational reduction of the spin-rotational Hamiltonian must also be considered. The commutation relationships (3.14b) and (3.14c) show that it is not possible to eliminate a dependence on  $S_\alpha$  by these transformations and hence terms are generated in the spin-rotation Hamiltonian. The simplest solution to this problem is to consider that the rotational contact transformation be applied first. This defines both the rotational and quartic and higher degree centrifugal distortion constants in the Hamiltonian. It also determines the co-ordinate system in which the standard form of the spin-rotation Hamiltonian Eq. (3.15) is expressed. In this discussion then, we only need consider the spin-rotational contact transformation, although it must be applied to both the rotational ( $H_{rot}$ ) and spin-rotational ( $H_{sr}$ ) Hamiltonians. The details of both the rotational and spin-rotational reductions must therefore be specified when quoting the results of a complete determination of parameters from experimental data. There is one more comment to be made before the implications of the spin-rotational reduction are considered. We are looking for terms in the Hamiltonian which are linear in  $S_\alpha$ . However the transformations themselves generate terms of higher

degree in  $S_\alpha$ , for example, terms of the form  $N^2S^2$ ,  $NS^3$  or  $S^4$ . For a molecule in a doublet state, these terms do not alter the form of the transformed Hamiltonian although the process of absorbing them does cause the values of the existing parameters to be altered. For molecules in triplet and higher multiplicity states, the extra terms contribute to the higher degree spin terms such as the spin-spin dipolar interactions. Such complications are not considered in this discussion which is restricted to doublet states.

It will become obvious in the next section that the first unitary transformation, Eq. (3.24a) is associated with the determination of parameters in the quadratic spin-rotation Hamiltonian, the second transformation in Eq. (3.24b) with the determinations of the quartic coefficients and so on. The number of determinable parameters in  $H_{sr}$  of given degree, therefore, is equal to the number of independent parameters in the standard form of the Hamiltonian Eq. (3.17), minus the number of non-zero parameters in the appropriate unitary transformation. The results of such an analysis for the quadratic and quartic Hamiltonians are given in Table 1. For orthorhombic molecules, there are three independent parameters in both the standard and reduced forms of  $H_{sr}^{(2)}$ . This is the expected result since there have been many successful determinations of the diagonal components of the spin-rotation tensor for this type of molecule. However for non-orthorhombic molecules with a plane of symmetry, the unitary transformation can be used to eliminate one of the five parameters in the standard form Hamiltonian, leaving four determinable parameters. In the general case (no symmetry elements) there are expected to be six determinable quadratic spin-rotation parameters. Table 1 also shows the numbers of determinable parameters in the quartic spin-rotation Hamiltonian are considerably fewer than suggested by the standard form Hamiltonians. There is a difference between the spin-rotation reduction discussed here and the analogous rotational reduction (16) which deserves emphasis. The number of determinable parameters in the spin-rotational Hamiltonian depends on the symmetry of the molecule concerned, whereas the rotational contact transformation leaves three determinable quadratic parameters, five quartic centrifugal distortion parameters and so on, irrespective of

the symmetry of the molecule. The details of the unitary transformations for the quadratic and quartic spin-rotation Hamiltonians are discussed in sections IV and V respectively.

### 3 (IV) The Quadratic Reduced Spin-Rotation Hamiltonian.

This section is devoted to the first unitary transformation, given in Eq. (3.24a) which defines the reduced form of the quadratic spin-rotation Hamiltonian. Three cases are discussed (i) a molecule belonging to an orthorhombic point group (ii) a molecule with a plane of symmetry ( $C_s$ ) and (iii) a molecule with no symmetry elements ( $C_1$ ). The first case is trivial since there are no independent parameters in the unitary transformation  $F_0$  and the standard and reduced forms of  $H_{sr}^{(2)}$  are identical; as shown in Table 1, both contain three parameters, usually taken as  $\epsilon_{aa}$ ,  $\epsilon_{bb}$  and  $\epsilon_{cc}$  (24) or equivalently  $A^S$ ,  $B^S$  and  $C^S$  (25).

The second case, that of a molecule with a plane of symmetry, is a common one and includes, for example, the non-symmetrical triatomic molecule. Table 1 indicates that the only one of the three possible terms in  $F_0$ , Eq (3.21) is allowed by symmetry, namely:

$$F_0 = f_{000}^{(x)} S_x \quad (3.26)$$

where  $x$  is assumed to be the out-of-plane axis of the molecule. The quadratic spin rotation Hamiltonian is defined by  $H_2$  in Eq. (3.24a) and we need only consider :

$$H = H_{rot}^{(2)} + H_{sr}^{(2)}$$

where

$$H_{rot}^{(2)} / hc = XN_x^2 + YN_y^2 + ZN_z^2 \quad (3.27)$$

and

$$H_{sr}^{(2)} / hc = k_{100}^{(x)} N_x S_x + k_{010}^{(y)} N_y S_y + k_{001}^{(z)} N_z S_z + \frac{1}{2} \{ k_{010}^{(z)} (N_y S_z + S_z N_y) + k_{001}^{(y)} (N_z S_y + S_y N_z) \} \quad (3.28)$$

We have used X, Y and Z as the principal rotational constants. The reduction of the Hamiltonian therefore involves the effect of the transformation  $\exp(iF_0)$  on the angular momentum components,  $N_\alpha$  and  $S_\alpha$ . Although the general transformation, Eq. (3.21) is equivalent to replacing these operators by an infinite power series in  $N_\alpha$  and  $S_\alpha$  the first transformation is exceptional in that it causes  $S_\alpha$  to be replaced simply by a linear combination of  $S_x$ ,  $S_y$  and  $S_z$  (16) (26):

$$\begin{aligned} \exp(-i\theta S_x) S_x \exp(i\theta S_x) &= S_x \\ \exp(-i\theta S_x) S_y \exp(i\theta S_x) &= \cos\theta S_y + \sin\theta S_z \\ \exp(-i\theta S_x) S_z \exp(i\theta S_x) &= -\sin\theta S_y + \cos\theta S_z \end{aligned} \quad (3.29)$$

where  $\theta$  is a dimensionless parameter, equal to  $f_{000}^{(x)}$  in the present application. The corresponding transformations of  $N_\alpha$  are given by:

$$\begin{aligned} \exp(-i\theta S_x) N_x \exp(i\theta S_x) &= N_x \\ \exp(-i\theta S_x) N_y \exp(i\theta S_x) &= N_y + (1-\cos\theta) S_y + \sin\theta S_z \\ \exp(-i\theta S_x) N_z \exp(i\theta S_x) &= N_z + \sin\theta S_y + (1-\cos\theta) S_z \end{aligned} \quad (3.30)$$

By use of these relationships, it is straightforward to obtain the transformed Hamiltonian  $H_2$ . When the resultant terms are collected together and cast in the standard form, it only remains to choose

the parameter  $f_{000}^{(x)}$  to eliminate one of the parameters. The most convenient choice would appear to be the elimination of the antisymmetric part of the spin-rotation tensor,  $\epsilon$ . The spin-rotation Hamiltonian in Eq. (3.28) is therefore rewritten:

$$\begin{aligned} H_{sr}^{(2)}/hc &= k_{100}^{(x)} N_x S_x + k_{010}^{(y)} N_y S_y + k_{001}^{(z)} N_z S_z \\ &+ \frac{1}{4} (k_{010}^{(z)} + k_{001}^{(y)}) (N_y S_z + S_z N_y + N_z S_y + S_y N_z) \\ &+ \frac{1}{4} (k_{010}^{(z)} - k_{001}^{(y)}) (N_y S_z + S_z N_y - N_z S_y - S_y N_z) \quad (3.31) \end{aligned}$$

After the transformation, the last term in (3.31) is eliminated if

$$\tan (f_{000}^{(x)}) = (k_{010}^{(z)} - k_{001}^{(y)}) / [2(Y + Z) - k_{010}^{(y)} - k_{001}^{(z)}] \quad (3.32)$$

When expressed in terms of the components of the  $\epsilon$  tensor, this condition becomes:

$$\tan (f_{000}^{(x)}) = (\epsilon_{yz} - \epsilon_{zy}) / [2(Y + Z) - (\epsilon_{yy} + \epsilon_{zz})] \quad (3.33)$$

The parameters in the reduced Hamiltonian  $\tilde{H}_{sr}^{(2)}$  in the form corresponding to Eq. (3.31) are

$$\begin{aligned} \tilde{\epsilon}_{xx} &= \epsilon_{xx} \\ \tilde{\epsilon}_{yy} &= \epsilon_{yy} \cos (f_{000}^{(x)}) - \epsilon_{yz} \sin (f_{000}^{(x)}) + 2Y [1 - \cos (f_{000}^{(x)})] \\ \tilde{\epsilon}_{zz} &= \epsilon_{zy} \sin (f_{000}^{(x)}) + \epsilon_{zz} \cos (f_{000}^{(z)}) + 2Z [1 - \cos (f_{000}^{(x)})] \\ \tilde{\epsilon}_{yz} + \tilde{\epsilon}_{zy} &= (\epsilon_{yz} + \epsilon_{zy}) \cos (f_{000}^{(x)}) + \\ &[\epsilon_{yz} - \epsilon_{zz} - 2(Y-Z)] \sin (f_{000}^{(x)}) \end{aligned}$$

$$\begin{aligned} \tilde{\epsilon}_{yz} - \tilde{\epsilon}_{zy} &= (\epsilon_{yz} - \epsilon_{zy}) \cos (f_{000}^{(x)}) + \\ [\epsilon_{yy} + \epsilon_{zz} - 2(Y + Z) \sin (f_{000}^{(x)})] &= 0 \end{aligned} \quad (3.34)$$

Reference to Eq. (3.33) shows that  $f_{000}^{(x)}$  is expected to be small in magnitude, in which case Eqs. (3.34) can be simplified by replacing  $\sin (f_{000}^{(x)})$  by  $f_{000}^{(x)}$  and  $\cos (f_{000}^{(x)})$  by unity. This approximation is equivalent to considering only the first commutator term in the expansion of Eq. (3.5) and it is found to be reliable in the application of the results in this section to  $\text{H}_2\text{O}$  (Chapter 4). The transformation also generates terms of degree 2 in  $S_\alpha$  but for a doublet state, these simply make a constant contribution to the energy levels. The rotational constants  $X$ ,  $Y$  and  $Z$  are not affected by the transformation.

The third case to be considered in this section is that of a molecule with no elements of symmetry. No data pertaining to this type of molecule has been found in the literature, but Table 1 shows that six determinable spin-rotation parameters are expected since there are three independent parameters in the transformation  $(f_{000}^{(x)}, f_{000}^{(y)}, f_{000}^{(z)})$ . The logical choice would appear to eliminate all three antisymmetric terms from the spin-rotation tensor in this case, so that the non-zero parameters are those in Eq. (3.34) plus  $(\tilde{\epsilon}_{xy} + \tilde{\epsilon}_{yx})$  and  $(\tilde{\epsilon}_{zx} + \tilde{\epsilon}_{xz})$ . The detailed form of the transformation can be derived by expanding the relations (3.34) in the appropriate manner.

### 3 (V) The Reduced Quartic Spin-Rotation Hamiltonian for an Orthorhombic Molecule.

#### 3 (V) a The quartic spin-rotation Hamiltonian in standard form.

It can be seen from Table 1 that there are nine independent terms in the standard form spin-rotation Hamiltonian for a molecule

of orthorhombic symmetry. We start by relating the parameters  $k_{pqr}^{(x)}$  in the Hamiltonian in Eq. (3.17) for this case to the parameters  $\eta_{\alpha\beta\gamma\delta}$  in the effective spin-rotation Hamiltonian  $H_{\text{srcd}}$  introduced in by Brown and Sears (15) and discussed in section II of this chapter (Eq.(3.7)). There are 21 non-zero parameters  $\eta_{\alpha\beta\gamma\delta}$  for an orthorhombic molecule, three of the form  $\eta_{\alpha\alpha\alpha\alpha}$  and six of each of the forms  $\eta_{\alpha\alpha\beta\beta}$ ,  $\eta_{\alpha\beta\alpha\beta}$  and  $\eta_{\alpha\beta\beta\alpha}$  with  $\alpha \neq \beta$ . However the last two sets are identical because of the equality

$$\eta_{\alpha\beta\gamma\delta} = \eta_{\beta\alpha\gamma\delta} \quad (3.35)$$

so that there are fifteen independent parameters in Eq. (3.7). The angular momentum commutation relationships are then used to cast the Hamiltonian into standard form and in the process  $\eta_{\alpha\alpha\beta\beta}$ ,  $\eta_{\alpha\beta\alpha\beta}$  and  $\eta_{\beta\alpha\alpha\beta}$  become coefficients of the same terms. Following Kivelson and Wilson (27) it is convenient to define the additional parameters

$$\eta'_{\alpha\alpha\beta\beta} = \eta_{\alpha\alpha\beta\beta} + 2\eta_{\alpha\beta\alpha\beta} \quad (3.36)$$

and the non-zero coefficients are:

$$\begin{aligned} k_{300}^{(x)} &= \eta_{xxxx} & k_{030}^{(y)} &= \eta_{yyyy} & k_{003}^{(z)} &= \eta_{zzzz} \\ k_{120}^{(x)} &= \eta'_{yyxx} & k_{102}^{(x)} &= \eta'_{zzxx} & k_{210}^{(y)} &= \eta'_{xxyy} \\ k_{012}^{(y)} &= \eta'_{zzyy} & k_{201}^{(z)} &= \eta'_{xxzz} & k_{021}^{(z)} &= \eta'_{yyzz} \end{aligned} \quad (3.37)$$

3 (V) b The transformation  $H_4 = e^{-iF_2} H_2 e^{iF_2}$

The parameters in the quartic spin-rotation Hamiltonian are determined by the transformation involving  $F_2$ , that is :

$$\tilde{H}_{sr}^{(4)} \approx \exp(-iF_2) \{H_{rot}^{(2)} + H_{sr}^{(2)} + H_{sr}^{(4)}\} \exp(iF_2) \quad (3.38)$$

For a molecule of orthorhombic symmetry, there are three independent terms in the function  $F_2$  and the number of independent terms in the quartic spin-rotation Hamiltonian can therefore be reduced to six by a suitable choice of the transformation parameters. The form of  $F_2$  is readily derived from the character table of any orthorhombic group:

$$F_2 = \frac{1}{2} \{ f_{011}^{(x)} (N_y N_z S_x + S_x N_z N_y) + f_{101}^{(y)} (N_x N_z S_y + S_y N_z N_x) + f_{110}^{(z)} (N_x N_y S_z + S_z N_y N_x) \} \quad (3.39)$$

The transformation in (3.28) is evaluated by rewriting it in terms of commutators :

$$\tilde{H}_{sr}^{(4)} = H_{sr}^{(4)} + i [H_{rot}^{(2)}, F_2] + i [H_{sr}^{(2)}, F_2] \quad (3.40)$$

The higher commutators in the expansion on the right hand side of Eq. (3.38) give rise to terms of higher degree in the transformed Hamiltonian which do not belong to the quartic spin-rotation Hamiltonian; this is the reason for the approximate equality in Eq. (3.38). The commutators in Eq. (3.40) are evaluated by some lengthy algebra and the result is cast into standard form by use of the commutation relations Eq. (3.14).



$$\begin{aligned}
H_{sr}^{(4)} / hc = & \frac{1}{2} \{ k_{300}^{(x)} (N_x^3 S_x + S_x N_x^3) + k_{030}^{(y)} (N_y^3 S_y + S_y N_y^3) \\
& + k_{003}^{(z)} (N_z^3 S_z + S_z N_z^3) \\
& + [k_{120}^{(x)} + 2(Y-X) f_{011}^{(x)} + (2Y-Y^S) f_{110}^{(z)}] (N_x N_y^2 S_x + S_x N_y^2 N_x) \\
& + [k_{102}^{(x)} + 2(X-Z) f_{011}^{(x)} - (2Z-Z^S) f_{101}^{(y)}] (N_x N_z^2 S_x + S_x N_z^2 N_x) \\
& + [k_{210}^{(y)} + 2(Y-X) f_{101}^{(y)} - (2X-X^S) f_{110}^{(z)}] (N_x^2 N_y S_y + S_y N_y N_x^2) \\
& + [k_{012}^{(y)} - 2(Y-Z) f_{101}^{(y)} + (2Z-Z^S) f_{011}^{(x)}] (N_y N_z^2 S_y + S_y N_z^2 N_y) \\
& + [k_{201}^{(z)} + 2(X-Z) f_{110}^{(z)} + (2X-X^S) f_{101}^{(y)}] (N_x^2 N_z S_z + S_z N_z N_x^2) \\
& + [k_{021}^{(z)} - 2(Y-Z) f_{110}^{(z)} - (2Y-Y^S) f_{011}^{(x)}] (N_y^2 N_z S_z + S_z N_z N_y^2) \} \quad (3.41)
\end{aligned}$$

The parameters  $X, Y, Z$  and  $X^S, Y^S, Z^S$  are the principal components of the rotational constant and spin-rotation tensors respectively. The coefficients in the standard form of  $H_{sr}^{(4)}$  can be referred to as  $\tilde{k}_{pqr}^{(\alpha)} = k_{pqr}^{(\alpha)} + g(f_{011}^{(x)}, f_{101}^{(y)}, f_{110}^{(z)})$ . The interesting result that the three parameters  $k_{300}^{(x)}, k_{030}^{(y)}, k_{003}^{(z)}$  are unaffected by the transformation should be noted. Both the transformation and the reduction to standard form generate terms which are either of higher degree in  $S_\alpha$  or lower degree in  $N_\alpha$ . As discussed in section IV, such terms make contributions to other parameters in the effective Hamiltonian (eg. the rotational constants). They have not been investigated further.

Three of the parameters in  $\tilde{H}_{sr}^{(4)}$ , Eq. (3.41) can be eliminated by suitable choices for  $f_{011}^{(x)}, f_{101}^{(y)}$  and  $f_{110}^{(z)}$ . However this form is not very convenient for the evaluation of matrix elements and so, before discussing specific reductions, we rewrite  $H_{sr}^{(4)}$  as:

$$\begin{aligned}
H_{sr}^{(4)} / hc = & a_1 N^2 (\underline{N} \cdot \underline{S}) + a_2 N^3 S_z + a_3 N^2 (\underline{N} \cdot \underline{S}) \\
& + \frac{1}{2} a_4 (N^2 N_z S_z + N_z S_z N^2) + a_5 (N_+^2 + N_-^2) (\underline{N} \cdot \underline{S}) \\
& + \frac{1}{2} a_6 \{ N^2 (N_{++} + N_{--}) + (N_{++} + N_{--}) N^2 \} \\
& + \frac{1}{2} a_7 \{ N_z^2 (N_{++} + N_{--}) + (N_{++} + N_{--}) N_z^2 \} \\
& + \frac{1}{2} a_8 \{ (N_+^2 + N_-^2) N_z S_z + N_z S_z (N_+^2 + N_-^2) \} \\
& + \frac{1}{2} a_9 \{ N_{++}^3 + S_{++}^3 + N_{--}^3 + S_{--}^3 \} \quad (3.42)
\end{aligned}$$

where  $N_{\pm} = N_x \pm iS_y$ ,  $S_{\pm} = S_x \pm iS_y$  and the parameters  $a_1$  to  $a_9$  are simple linear combinations of the  $k_{pqr}^{(\alpha)}$ :

$$a_1 = \frac{1}{8} (3k_{300}^{(x)} + 3k_{030}^{(y)} + k_{120}^{(x)} + k_{210}^{(y)}) \quad (3.43a)$$

$$a_2 = k_{003}^{(z)} - a_1 - a_3 - a_4 \quad (3.43b)$$

$$a_3 = \frac{1}{2} (k_{102}^{(x)} + k_{012}^{(y)}) - \frac{1}{8} (3k_{300}^{(x)} + 3k_{030}^{(y)} + k_{120}^{(x)} + k_{210}^{(y)}) \quad (3.43c)$$

$$a_4 = \frac{1}{2} (k_{201}^{(z)} + k_{021}^{(z)}) - \frac{1}{8} (3k_{300}^{(x)} + 3k_{030}^{(y)} + k_{120}^{(x)} + k_{210}^{(y)}) \quad (3.43d)$$

$$a_5 = \frac{1}{8} (k_{300}^{(x)} - k_{030}^{(y)} - k_{120}^{(x)} + k_{210}^{(y)}) \quad (3.43e)$$

$$a_6 = \frac{1}{8} (k_{300}^{(x)} - k_{030}^{(y)} + k_{120}^{(x)} - k_{210}^{(y)}) \quad (3.43f)$$

$$a_7 = \frac{1}{4} (k_{102}^{(x)} - k_{012}^{(y)}) - \frac{1}{8} (k_{300}^{(x)} - k_{030}^{(y)} + k_{120}^{(x)} - k_{210}^{(y)}) \quad (3.43g)$$

$$a_8 = \frac{1}{4} (k_{201}^{(z)} - k_{021}^{(z)}) - \frac{1}{8} (k_{300}^{(x)} - k_{030}^{(y)} - k_{120}^{(x)} + k_{210}^{(y)}) \quad (3.43h)$$

$$a_9 = \frac{1}{4} (k_{300}^{(x)} + k_{030}^{(y)} - k_{120}^{(x)} - k_{210}^{(y)}) \quad (3.43i)$$

The form for  $H_{sr}^{(4)}$  in Eq. (3.42) is much more convenient for the evaluation of matrix elements. The first four terms have elements

diagonal in the quantum number  $K$ , the next four terms have elements with  $\Delta K = \pm 2$  only and the final term has elements with  $\Delta K = \pm 4$ . The transformed Hamiltonian  $\tilde{H}_{sr}^{(4)}$  is given by the corresponding expression involving parameters  $\tilde{a}_r$  which are obtained by replacing the  $k_{pqr}^{(\alpha)}$  in Eqs. (3.43) by  $\tilde{k}_{pqr}^{(\alpha)}$  from Eq. (3.41)

It is evident that there are several possible ways in which parameters can be eliminated from Eq. (3.41). We discuss two such choices in the remainder of this section, referring to them as the S and A reductions. They are respectively analogous to the symmetric and asymmetric reductions of the rotational Hamiltonian discussed by Watson (22).

### 3 (V) c The S-reduced form of the quartic spin-rotation Hamiltonian.

The S-reduction corresponds to the elimination of the parameters  $\tilde{a}_6$ ,  $\tilde{a}_7$  and  $\tilde{a}_8$  from  $\tilde{H}_{sr}^{(4)}$  and the retention of the term involving  $\tilde{a}_9$ , the coefficient of the term that contains the shift operators  $N_{\pm}$  and  $S_{\pm}$  to the fourth power. The latter define the spin-rotation contribution to the K-splitting in levels with  $K = 2$  of an asymmetric top. The three parameters  $f_{011}^{(x)}$ ,  $f_{101}^{(y)}$  and  $f_{110}^{(z)}$  are therefore chosen so that :

$$\tilde{a}_6 = 0 = \tilde{k}_{300}^{(x)} - \tilde{k}_{030}^{(y)} + \tilde{k}_{120}^{(x)} - \tilde{k}_{210}^{(y)}$$

$$\tilde{a}_7 = 0 = \tilde{k}_{102}^{(x)} - \tilde{k}_{012}^{(y)} - \frac{1}{2} (\tilde{k}_{300}^{(x)} - \tilde{k}_{030}^{(y)} + \tilde{k}_{120}^{(x)} - \tilde{k}_{210}^{(y)})$$

$$\tilde{a}_8 = 0 = \tilde{k}_{201}^{(z)} - \tilde{k}_{021}^{(z)} - \frac{1}{2} (\tilde{k}_{300}^{(x)} - \tilde{k}_{030}^{(y)} - \tilde{k}_{120}^{(x)} + \tilde{k}_{210}^{(y)})$$

The result is obtained if :

$$\begin{aligned}
f_{011}^{(x)} &= (\text{Det})^{-1} \{-2[2(Y-Z) - (2Z-Z^S)] [(X-Z) + (Y-Z)] \\
&\quad (k_{300}^{(x)} - k_{030}^{(y)} + k_{120}^{(x)} - k_{210}^{(y)}) \\
&+ [4(X-Y)(X-Z+Y-Z) + (2X-X^S)(2X-X^S + 2Y-Y^S)](k_{102}^{(x)} - k_{012}^{(y)}) \\
&+ [2(Y-Z) - (2Z-Z^S)] [2X-X^S + 2Y-Y^S] (k_{201}^{(z)} - k_{021}^{(z)} - k_{300}^{(x)} + k_{030}^{(y)})\} \\
&\hspace{15em} (3.44a)
\end{aligned}$$

$$\begin{aligned}
f_{101}^{(y)} &= (\text{Det})^{-1} \{2[2(X-Z) - (2Z-Z^S)] [(X-Z) + (Y-Z)] \\
&\quad (k_{300}^{(x)} - k_{030}^{(y)} + k_{120}^{(x)} - k_{210}^{(y)}) \\
&+ [4(X-Y)(X-Z+Y-Z) + (2Y-Y^S)(2X-X^S+2Y-Y^S)] (k_{102}^{(x)} - k_{012}^{(y)}) \\
&- [2(X-Z) - (2Z-Z^S)] [2X-X^S + 2Y-Y^S] (k_{201}^{(z)} - k_{021}^{(z)} - k_{300}^{(x)} + k_{030}^{(y)})\} \\
&\hspace{15em} (3.44b)
\end{aligned}$$

and

$$\begin{aligned}
f_{110}^{(z)} &= (\text{Det})^{-1} \{- [(2X-X^S)\{2(X-Z) - (2Z-Z^S)\} - (2Y-Y^S)\{2(Y-Z) - (2Z-Z^S)\}] \\
&\quad (k_{300}^{(x)} - k_{030}^{(y)} + k_{120}^{(x)} - k_{210}^{(y)}) \\
&- 2(X-Y) [(2X-X^S) + (2Y-Y^S)] (k_{102}^{(x)} - k_{012}^{(y)}) \\
&+ 4(X-Y) [(X-Z) + (Y-Z) - (2Z-Z^S)] (k_{201}^{(z)} - k_{021}^{(z)} - k_{300}^{(x)} + k_{030}^{(y)})\} \\
&\hspace{15em} (3.44c)
\end{aligned}$$

where

$$\begin{aligned} \text{Det} = & (2X-X^S + 2Y - Y^S) \{ [2(X-Z) - (2Z-Z^S)] (2X-X^S) - \\ & [2(Y-Z)-(2Z-Z^S)] (2Y-Y^S) \} \\ & -8(X-Y)\{(X-Z) + (Y-Z)\}\{(Y-Z) + (X-Z) - (2Z-Z^S)\} \end{aligned} \quad (3.45)$$

The S-reduced quartic spin-rotation Hamiltonian for a molecule of orthorhombic symmetry can thus be written:

$$\begin{aligned} \tilde{H}_{sr}^{(4)} = & D_N^S N^2 (N.S) + \frac{1}{2} D_{NK}^S \{ N^2 N_Z S_Z + N_Z S_Z N^2 \} + D_{KN}^S N_Z (N.S) \\ & + D_K^S N_Z^2 N_Z S_Z + d_1^S (N_+^2 + N_-^2)(N.S) + d_2^S (N_+^3 S_+ + N_-^3 S_-) \end{aligned} \quad (3.46)$$

where the six parameters  $D_N^S$  to  $d_2^S$  have been introduced as the analogues of the quartic centrifugal distortion parameters in the S-reduced rotational Hamiltonian (22). The first and second subscripts in the parameters  $D_{NK}^S$  and  $D_{KN}^S$  indicate the quantum number dependence of the rotational and spin-rotational parts of the operator respectively. The non-zero matrix elements of the S-reduced quartic Hamiltonian in a case (b) basis set, using the phase conventions of Bowater, Brown and Carrington (28) are given by:

$$\begin{aligned} \langle NKSJ | \tilde{H}_{sr}^{(4)} | NKSJ \rangle = & \{ [J(J+1) - N(N+1) - S(S+1)] / 2N(N+1) \} \\ & \times \{ D_K^S K^4 + (D_{NK}^S + D_{KN}^S) K^2 N(N+1) + D_N^S N^2 (N+1)^2 \} \end{aligned} \quad (3.47)$$

$$\begin{aligned} \langle N-1, KSJ | \tilde{H}_{sr}^{(4)} | NKSJ \rangle = & -(K/2N) \{ D_K^S K^2 + D_{NK}^S N^2 \} \\ & \times [(N^2 - K^2)(N-J+S)(N+J+S+1)(S+J-N+1)(N+J-S) / (2N-1)(2N+1)]^{\frac{1}{2}} \end{aligned} \quad (3.48)$$

$$\langle N, K \pm 2S_J | \tilde{H}_{sr}^{(4)} | NKS_J \rangle = \frac{1}{2} d_1^S \{ J(J+1) - N(N+1) - S(S+1) \}$$

$$\times \left[ \{ N(N+1) - K(K \pm 1) \} \{ N(N+1) - (K \pm 1)(K \pm 2) \} \right]^{\frac{1}{2}} \quad (3.49)$$

$$\langle N, K \pm 4, S_J | \tilde{H}_{sr}^{(4)} | NKS_J \rangle = \frac{1}{2} d_2^S \{ [J(J+1) - N(N+1) - S(S+1)] / N(N+1) \}$$

$$\times \left[ \{ N(N+1) - K(K \pm 1) \} \{ N(N+1) - (K \pm 1)(K \pm 2) \} \{ N(N+1) - (K \pm 2)(K \pm 3) \} \right.$$

$$\left. \{ N(N+1) - (K \pm 3)(K \pm 4) \} \right]^{\frac{1}{2}} \quad (3.50)$$

$$\langle N-1, K \pm 4, S_J | \tilde{H}_{sr}^{(4)} | NKS_J \rangle = \mp d_2^S / N$$

$$\times \left[ (N-J+S)(N+J+S+1)(S+J-N+1)(N+J-S) / (2N-1)(2N+1) \right]^{\frac{1}{2}}$$

$$\times \left[ (N \mp K) \{ N^2 - (K \pm 1)^2 \} \{ N^2 - (K \pm 2)^2 \} \{ N^2 - (K \pm 3)^2 \} \{ N \mp K - 4 \} \right]^{\frac{1}{2}} \quad (3.51)$$

The matrix elements diagonal in  $K$  have the same form as in previous work (14, 15) although the parameters have different meanings because of the changes introduced by the transformation. In the present case, Eqs. (3.43) can be used to show that :

$$D_N^S = \frac{1}{8} (3k_{300}^{(x)} + 3k_{030}^{(y)} + \tilde{k}_{120}^{(x)} + \tilde{k}_{210}^{(y)})$$

$$D_{NK}^S = \frac{1}{2} (\tilde{k}_{201}^{(z)} + \tilde{k}_{021}^{(z)}) - D_N^S$$

$$D_{NK}^S = \frac{1}{2} (\tilde{k}_{102}^{(x)} + \tilde{k}_{012}^{(y)}) - D_N^S$$

$$D_K^S = k_{003}^{(z)} - D_N^S - D_{NK}^S - D_{KN}^S$$

$$\begin{aligned}
 d_1^S &= \frac{1}{2} (k_{300}^{(x)} - k_{030}^{(y)}) \\
 d_2^S &= \frac{1}{16} (k_{300}^{(x)} + k_{030}^{(y)} - \tilde{k}_{120}^{(x)} - \tilde{k}_{210}^{(y)})
 \end{aligned} \quad (3.52)$$

where the  $\tilde{k}_{pqr}^{(\alpha)}$  can be obtained from Eq.(3.41). From Eqs.(3.52) the six determinable combinations of parameters can be expressed in terms of the constants of the S-reduction :

$$\begin{aligned}
 \eta_{xxxx} &= k_{300}^{(x)} = D_N^S + 2d_1^S + 2d_2^S \\
 \eta_{yyyy} &= k_{030}^{(y)} = D_N^S - 2d_1^S + 2d_2^S \\
 \eta_{zzzz} &= k_{003}^{(z)} = D_N^S + D_{NK}^S + D_{KN}^S + D_K^S \\
 (\tilde{k}_{120}^{(x)} + \tilde{k}_{210}^{(y)}) &= 2D_N^S - 12d_2^S \\
 (\tilde{k}_{201}^{(z)} + \tilde{k}_{021}^{(z)}) &= 2D_{NK}^S + 2D_N^S \\
 (\tilde{k}_{102}^{(x)} + \tilde{k}_{012}^{(y)}) &= 2D_{KN}^S + 2D_N^S
 \end{aligned} \quad (3.53)$$

The results of this section are applied to the interpretation, of the spin-rotation splittings of  $\text{NH}_2$  in the  $\tilde{X}^2B_1$  state in Chapter 5.

### 3 (V) d The A-reduced form of the quartic spin-rotation Hamiltonian.

The essential characteristic of the A-reduced form of the spin-rotation Hamiltonian is that it has matrix elements with  $\Delta K=0, \pm 2$  only (22). The advantage of this reduction therefore is that it is easier to construct the Hamiltonian matrix and bring it to diagonal form by computer methods. Nevertheless, experience with the rotational problem shows that the S-reduced form is to be preferred since it is applicable to any molecule, irrespective of the value for the asymmetry parameter  $\kappa$ , and because it leads to a less strongly correlated set of parameters for a fit of the data than does the analysis using the A-reduced Hamiltonian (22, 29). Although it seems

likely that the same advantage will accrue to the S-reduced form of the quartic spin-rotation Hamiltonian, it is probably too early to dismiss the corresponding A-reduced form. We therefore consider the essential features of the Hamiltonian at this point.

The A-reduction is effected by the elimination of the parameters  $\tilde{a}_6$ ,  $\tilde{a}_7$  and  $\tilde{a}_9$  in  $\tilde{H}_{sr}^{(4)}$ , obtained from Eq. (3.42). It can be seen that two terms including the squares of the shift operator  $N_{\pm}$  and/or  $S_{\pm}$  are retained, namely those with coefficients  $\tilde{a}_5$  and  $\tilde{a}_8$ . The former defines the K-splitting effects on the spin-rotation coupling for levels with  $K = 1$  in first order while the latter produces the splitting of levels with  $K = 2$  in second order. The A-reduced quartic spin-rotation Hamiltonian for an orthorhombic molecule can then be written :

$$\begin{aligned} \tilde{H}_{sr}^{(4)} = & \Delta_N^S N_-^2 (N.S) + \frac{1}{2} \Delta_{NK}^S \{ N_-^2 N_Z S_Z + N_Z S_Z N_-^2 \} + \Delta_{KN}^S N_Z (N.S) \\ & + \Delta_K^S N_Z^3 S_Z + \delta_N^S (N_+^2 + N_-^2) (N.S) \\ & + \frac{1}{2} \delta_K^S \{ (N_+^2 + N_-^2) N_Z S_Z + N_Z S_Z (N_+^2 + N_-^2) \} \end{aligned} \quad (3.54)$$

where the parameters  $\Delta_N^S$ ,  $\Delta_{NK}^S$  etc. have been introduced by analogy with the corresponding quartic centrifugal distortion constants.

The matrix elements in a case (b) basis set are :

$$\begin{aligned} \langle NKSJ | \tilde{H}_{sr}^{(4)} | NKSJ \rangle = & \{ [J(J+1) - N(N+1) - S(S+1)] / 2N(N+1) \} \\ & \times \{ \Delta_K^S K^4 + (\Delta_{NK}^S + \Delta_{KN}^S) K^2 N(N+1) + \Delta_N^S N^2 (N+1)^2 \} \end{aligned} \quad (3.55)$$

$$\begin{aligned} \langle N-1, KSJ | \tilde{H}_{sr}^{(4)} | NKSJ \rangle = & -(K/2N) \{ \Delta_K^S K^2 + \Delta_{NK}^S N^2 \} \\ & \times [ (N^2 - K^2)(N-J+S)(N+J+S+1)(S+J-N+1)(N+J-S) / (2N-1)(2N+1) ]^{\frac{1}{2}} \end{aligned} \quad (3.56)$$



$$\begin{aligned}
\langle N, K \pm 2S_J | \tilde{H}_{sr}^{(4)} | NKS_J \rangle &= \{ [J(J+1) - N(N+1) - S(S+1)] / 2N(N+1) \} \\
&\times \{ [N(N+1) - K(K \pm 1)] \{ N(N+1) - (K \pm 1)(K \pm 2) \} \}^{\frac{1}{2}} \delta_N^S N(N+1) + \frac{1}{2} \delta_K^S [K^2 + (K \pm 2)^2] \} \\
\end{aligned} \tag{3.57}$$

$$\begin{aligned}
\langle N-1, K \pm 2 S_J | \tilde{H}_{sr}^{(4)} | NKS_J \rangle &= -\frac{1}{4} (\delta_K^S / N) \{ K(N \pm K) + (K \pm 2)(N \pm K + 2) \} \\
&\times \{ (N \mp K - 1)(N \pm K + 1)(N \mp K - 2)(N \mp K)(N - J + S)(N + J + S + 1)(S + J - N + 1)(N + J - S) / (2N - 1)(2N + 1) \}^{\frac{1}{2}} \\
\end{aligned} \tag{3.58}$$

The explicit expressions for the transformation parameters  $f_{pqr}^{(\alpha)}$  which effect the A-reduction have not been considered. If required they may be derived from the conditions:

$$\begin{aligned}
\tilde{a}_6 &= 0 = \tilde{k}_{300}^{(x)} - \tilde{k}_{030}^{(y)} + \tilde{k}_{120}^{(x)} - \tilde{k}_{210}^{(y)} \\
\tilde{a}_7 &= 0 = \tilde{k}_{102}^{(x)} - \tilde{k}_{012}^{(y)} - \frac{1}{2} (\tilde{k}_{300}^{(x)} - \tilde{k}_{030}^{(y)} + \tilde{k}_{120}^{(x)} - \tilde{k}_{210}^{(y)}) \\
\tilde{a}_9 &= 0 = \tilde{k}_{300}^{(x)} + \tilde{k}_{030}^{(y)} - \tilde{k}_{120}^{(x)} - \tilde{k}_{210}^{(y)}
\end{aligned}$$

with the values for  $\tilde{k}_{pqr}^{(\alpha)}$  taken from Eq. (3.41)

The A-reduced Hamiltonian has been applied by Cook, Hills and Curl (14) in their fit of the spin rotation splittings of  $NH_2$  in the ground state. They made the approximation that the effects of the matrix elements off-diagonal in  $N$ , Eqs (3.56) and (3.58) were negligible in their analysis. It can be seen from Eq. (3.55) that it is not then possible to separate  $\Delta_{NK}^S$  and  $\Delta_{KN}^S$  and only five parameters may be determined.

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## CHAPTER 4.

APPLICATIONS4(I) The determination of the quadratic spin-rotation parameters for  $\text{HO}_2$  in the  $\tilde{X}^2A''$  state.

The derivation of a reduced form of the quadratic spin-rotation Hamiltonian suitable for the empirical fitting of spectral data has been discussed in Chapter 3. For a molecule with a plane of symmetry only ( $C_s$ ) there are four determinable parameters, not five as suggested by the unreduced Hamiltonian. The implications of this result are explored in this section, using data that relate to the spin-rotation splittings of  $\text{HO}_2$  in the  $\tilde{X}^2A''$  state.

The microwave spectrum of  $\text{HO}_2$  has been observed and analysed by Saito (1). It involves both a- and b-type transitions between rotational levels with  $K_a = 0$  and 1. Saito found that he was not able to determine both the expected off-diagonal components,  $\epsilon_{ab}$  and  $\epsilon_{ba}$ , of the quadratic spin-rotation tensor and so he fitted the data with the assumption that  $\epsilon_{ab} = \epsilon_{ba}$ . In section V of Chapter 2 an outline is given of the more sophisticated analysis of all the published high resolution data for this molecule (1, 2, 3) as performed by Barnes, Brown, Carrington, Pinkstone, Sears and Thistlethwaite (2) but the same conclusion as Saito was reached with regard to the off-diagonal components of the spin-rotation tensor. A different constraint was imposed in the fit, namely:

$$\epsilon_{ba} = B \epsilon_{ab} / A \quad (4.1)$$

based on a simple theoretical model in which the spin-rotation interaction is attributed solely to spin-orbit coupling affects in the oxygen atoms. It can be seen from Chapter 3 that the indeterminacy revealed by these analyses is not caused by shortage of data, but rather is inherent in the form of the spin-rotation Hamiltonian. Under no circumstances is it possible to determine more than four spin-rotation parameters for this type of molecule.

The analysis outlined in Chapter 2 has been repeated using the reduced quadratic spin-rotation Hamiltonian,  $\tilde{H}_{sr}^{(2)}$ , described in Chapter 3. The computer program used was program II suitably modified to take account of the transformation of the spin-rotation Hamiltonian. The calculations were performed with a symmetric rotor basis set truncated at  $\Delta N = \pm 1$  and  $\Delta K = \pm 4$ , sufficient to reproduce "full" basis calculations to within the experimental accuracy (0.1 MHz for the microwave frequencies). In the least squares fit, all the parameters apart from the quadratic spin-rotation constants were fixed at the values obtained in the previous analysis; this included the quartic spin-rotation terms. The fit of the microwave data to the four parameters of  $\tilde{H}_{sr}^{(2)}$  Eq. (3.34), is identical in quality to that obtained previously when the relationship (4.1) was imposed. The values of the parameters determined in this way are given in Table I. For comparison, the values obtained in the other two analyses (1), (2), are also given.

The results are very satisfactory. The parameters  $\tilde{\epsilon}_{aa}$ ,  $\tilde{\epsilon}_{bb}$  and  $(\tilde{\epsilon}_{ab} + \tilde{\epsilon}_{ba})$  are modified in the revised fit, whereas  $\tilde{\epsilon}_{cc}$  is essentially unaltered, in accord with expectation. Columns 3 and 4 of Table I are the results for two different reduced forms of  $H_{sr}$ . In the earlier work, column 3, the constraint  $\tilde{\epsilon}_{ba} = B\tilde{\epsilon}_{ab}/A$  was imposed, corresponding to a transformation parameter.

$$f_1 = \tan^{-1}\{(A\epsilon_{ba} - B\epsilon_{ab})/[A(\epsilon_{bb} - 2B) - B(\epsilon_{aa} - 2A)]\} \quad (4.2)$$

when  $U = \exp(if_1 S_c)$ . In the present analysis, we have chosen to eliminate the antisymmetric part of the spin-rotation tensor so that  $\tilde{\epsilon}_{ab} = \tilde{\epsilon}_{ba}$ . This is achieved by the transformation parameter  $f_2$  where

$$f_2 = \tan^{-1}\{(\epsilon_{ba} - \epsilon_{ab})/[2(A + B) - (\epsilon_{aa} + \epsilon_{bb})]\} \quad (4.3)$$

The transformation of  $H_{sr}^{(2)}$  from the reduction of column 3 to that of column 4 is therefore achieved by  $U = \exp(i\{f_2 - f_1\}S_c)$  and the

TABLE I

QUADRATIC SPIN-ROTATION PARAMETERS OF HO<sub>2</sub> IN THE  $\tilde{X}^2A''$  STATE IN GHZ

Parameter	Saito (1)	Barnes <i>et al</i> (2)	This work	Predicted <sup>a</sup>
$\tilde{\epsilon}_{aa}$	-49.5688(23) <sup>b,c</sup>	-49.56989(58)	-49.57115(57)	-49.57242
$\tilde{\epsilon}_{bb}$	-0.4319(13) <sup>d</sup>	-0.422795(80)	-0.422573(80)	-0.422651
$\tilde{\epsilon}_{cc}$	0.0176(13)	0.008645(89)	0.008623(89)	0.008645
$ \epsilon_{ab} $	...	1.891(11) <sup>e</sup>	...	...
$\tilde{\epsilon}_{ab} + \tilde{\epsilon}_{ba}$	0.378(24)	...	0.3879(11)	0.3880

<sup>a</sup> Values predicted from Eq. (3.34)

<sup>b</sup> The numbers in parentheses represent one standard deviation of the least squares fit, in units of the last quoted decimal place.

<sup>c</sup> Value corrected for  $D_K^S = 0.02271$  GHz (2).

<sup>d</sup> This value determined from  $a$ -dipole transitions. Value for  $\epsilon_{bb}$  from  $b$ -type transitions determined as -0.4179(6) GHz.

<sup>e</sup> Value obtained from fit subject to the constraint  $\epsilon_{ba} = \epsilon_{ab} B/A = 0.1038$  GHz.

relationship between the two sets of parameters is given by Eqs. (3.33) and (3.34) on the understanding that the right hand sides of these equations refer to the first reduction rather than the unreduced form of the Hamiltonian. Eq. (3.34) can be used to predict the parameters to be obtained from reduction 2 and the results of such a calculation are given in the last column of Table I. The agreement with the parameters obtained in the least squares fit is highly satisfactory and is a pleasing confirmation of the present approach. However, it does not provide any independent support for the relationship given in Eq. (4.1) proposed by Barnes et al (2), since it is possible to go from one form of  $\tilde{H}_{sr}^{(2)}$  to the other by a unitary transformation. Finally we note that, in his analysis (1), Saito in effect used the same reduced form for  $\tilde{H}_{sr}^{(2)}$  as described here. His value for  $\tilde{\epsilon}_{ab} + \tilde{\epsilon}_{ba}$  is therefore in good agreement with that determined by the least squares fit.

#### 4.(I). The effective spin-rotation Hamiltonian for $\text{NH}_2$ in the $X^2 B_1$ state.

##### 4.(I).a . The determination of the spin-rotation parameters for $\text{NH}_2$ in the $X^2 B_1$ state.

The recent observation of microwave-optical double resonance transitions in the  $\text{NH}_2$  radical by Cook, Hills and Curl (4), (5), has produced a large amount of high quality data on the rotational levels of the molecule in the  $X^2 B_1$  state. In particular, the observation of magnetic dipole transitions between the two spin components of a given rotational state provides direct information about the size of the spin-rotation splittings in many of the lower rotational levels(5). The availability of this data makes  $\text{NH}_2$  an ideal candidate for treatment in terms of the theoretical description of the spin-rotation interaction previously outlined. Curl and his co-workers (6), (7) have interpreted these splittings in terms of three quadratic and five quartic spin-rotation parameters; their approach is essentially that of the A-reduced Hamiltonian discussed in section 3 V (d). By invoking planarity relationships and neglecting some parameters, they were able to determine values for



five  $\eta_{\alpha\beta\gamma\delta}$  parameters.

For the reasons given in section 3.V(d), the data have been analysed using the S-reduced Hamiltonians for both the centrifugal distortion (36) and for the quartic spin-rotation terms. This has been done in an attempt to establish whether the six parameters in Eq. (3.46) can be determined and, if so, how they can best be interpreted. The M.O.D.R. frequencies were taken from Ref (6) and they are reproduced in Table II. In a more recent paper (7), Hills, Lowe, Cook and Curl have measured the magnetic dipole transition frequencies between the states  $3_{31}$  and  $4_{13}$  and remeasured the spin-rotation splitting in the  $4_{13}$  level. Professor R.F. Curl (8), has kindly provided values for these frequencies, for inclusion in the analysis ( $3_{31}; J = 7/2 \leftarrow 4_{13}; J = 7/2, \nu = 5350.56$  MHz; see also Table II). The data were fitted using the program described in the previous subsection and Chapter 2, Section V. Since  $\text{NH}_2$  ( $\kappa = -.3846$ ) is a more asymmetric rotor than  $\text{HO}_2$  ( $\kappa = -.9936$ ), a larger basis set was necessary and the calculations were performed in a full basis set for the zero-field problem ( $\Delta N = \pm 1$ ).

Initially, the constants determined by Davies et al (9), in their fit of the far infra-red L.M.R. data were used, converted to the S-reduced form using the relationships given by Watson (36). However numerical tests on the A to S transformation showed that it was not sufficiently reliable for such a light molecule as  $\text{NH}_2$  (the equations given by Watson are simply the leading terms in a series expansion). Since the fit of the M.O.D.R. spin-rotation splittings is quite sensitive to the values of the rotational parameters (6), a representative sample of the L.M.R. data was refitted to the S-reduced Hamiltonian, taking approximately two Zeeman lines per polarisation for each rotational transition. Nuclear hyperfine effects were suppressed by taking the flux density for the centre of the hyperfine pattern; this was the procedure followed by Davies et al in their analysis (9). Additional information on the  $3_{31} - 4_{13}$  and  $5_{23} - 6_{16}$  separations has been provided by the measurement of magnetic (7), (8) and electric (4), (10) dipole transition frequencies respectively. The appropriate M.O.D.R. frequencies were therefore included in the least squares fit, weighted 100 times more heavily than the L.M.R. data. The

TABLE II

THE LEAST SQUARES FIT OF SPIN ROTATION SPLITTINGS OF  $\text{NH}_2$  IN THE  $\tilde{X}^2B_1$  STATE

$N_{K_a K_c}$	$\nu_{\text{obs}}/\text{MHz}$ (S)	$\nu_{\text{obs-calc}}/\text{MHz}^a$	$N_{K_a K_c}$	$\nu_{\text{obs}}/\text{MHz}$ (S)	$\nu_{\text{obs-calc}}/\text{MHz}$
3 <sub>03</sub>	2374.83	0.24	4 <sub>13</sub>	6334.92 <sup>b</sup>	-0.08
4 <sub>04</sub>	2843.99	-0.63	5 <sub>14</sub>	7383.43	-0.20
5 <sub>05</sub>	3114.88	-0.38	6 <sub>15</sub>	8198.18	-0.06
6 <sub>06</sub>	3255.77	-0.01	3 <sub>22</sub>	12307.36	0.03
7 <sub>07</sub>	3329.73	-0.15	4 <sub>23</sub>	10733.25	0.53
8 <sub>08</sub>	3371.81	0.06	5 <sub>24</sub>	10001.66	0.28
1 <sub>11</sub>	6931.97	-0.44	6 <sub>25</sub>	9696.00	-0.28
2 <sub>12</sub>	4418.62	-0.56	7 <sub>26</sub>	9614.17	-0.24
3 <sub>13</sub>	3680.93	0.43	4 <sub>22</sub>	10884.92	-0.02
4 <sub>14</sub>	3426.51	0.39	5 <sub>23</sub>	10561.24	-0.67
5 <sub>15</sub>	3352.07	0.10	6 <sub>24</sub>	10870.36	-0.65
6 <sub>16</sub>	3346.92	0.54	7 <sub>25</sub>	11556.36	0.87
7 <sub>17</sub>	3363.10	-0.07	2 <sub>21</sub>	~15842 <sup>c</sup>	0.94
1 <sub>10</sub>	7956.05	0.30	2 <sub>20</sub>	~15790 <sup>c</sup>	-10.4
2 <sub>11</sub>	6120.54	0.65	3 <sub>21</sub>	~12273 <sup>c</sup>	-3.7
3 <sub>12</sub>	6083.21	0.33			

<sup>a</sup> Calculated frequencies obtained using the parameters in Table III and a full basis set. Standard deviation of fit = 0.49 MHz.

<sup>b</sup> R. F. Curl, private communication (8).

<sup>c</sup> Approximate frequencies only. Included in the fit but with relative weight 0.01.

basis set was truncated at  $\Delta N = \pm 1$  and  $\Delta K = \pm 6$  in performing the calculation. The electron spin g-factors were constrained at the values calculated from Curl's relationship (11) which should be reliable for  $\text{NH}_2$ . As in the previous fit of the L.M.R. and E.P.R. data of  $\text{HO}_2$  (2; and chapter 2), the inclusion of terms that describe the rotational Zeeman effect produced a significant improvement in the least squares fit.

In the fit of the L.M.R. data, the nine quadratic and quartic spin-rotation parameters were fixed at the values obtained from the fit of the M.O.D.R. frequencies. The latter were then re-fitted using the improved rotational constants and the process repeated iteratively until it had converged. The final values of the parameters obtained are given in Table III, they have been obtained from a fit to a data set which included rotational levels up to  $N = 7$  and  $K = 4$  and can be used to calculate reliable term values within this range of quantum numbers. All the parameters listed are better determined than in previous work (12), (5) and in particular we note that all six quartic spin-rotation parameters are determined (i.e. it has proved possible to separate  $D_{NK}^S$  and  $D_{KN}^S$ ). Furthermore we have been able to determine all three components of the rotational g-tensor. The values obtained are consistent with the predictions of the simple formula for the electronic contribution to  $g_r^{\alpha\alpha}$  (2):

$$g_r^{\alpha\alpha} (e1) = -|\epsilon_{\alpha\alpha}|/\zeta \quad (4.4)$$

when  $\zeta$  is the atomic spin-orbit coupling parameter (suitably weighted if necessary). The appropriate value for  $\zeta$  in the present case is that for the N atom,  $76 \text{ cm}^{-1}$  (13) which leads to

$$g_r^{aa} (e1) = -4.07 \times 10^{-3}, \quad g_r^{bb} (e1) = -5.94 \times 10^{-4}$$

$$g_r^{cc} (e1) = -5 \times 10^{-6}$$

The nuclear contribution to the rotational g-factor is expected to be a positive quantity  $\sim 10^{-4}$  for a magnetic moment expressed in Bohr magnetons.

TABLE III

MOLECULAR PARAMETERS OF THE  $\text{NH}_2$  RADICAL IN THE GROUND STATE<sup>a</sup>

Fit of L.M.R. data <sup>b</sup>			Fit of M.O.D.R. data <sup>c</sup>		
	<i>A</i>	710.3024(10) <sup>d</sup>		$\epsilon_{aa}$	-9.26754(62)
	<i>B</i>	388.22258(61)		$\epsilon_{bb}$	-1.35262(20)
	<i>C</i>	245.0641(13)		$\epsilon_{cc}$	0.01099(10)
10 <sup>2</sup>	<i>D<sub>N</sub></i>	2.8917(23)	10 <sup>4</sup>	<i>D<sub>N</sub><sup>s</sup></i>	2.786(29)
	<i>D<sub>NK</sub></i>	-0.111148(78)	10 <sup>3</sup>	<i>D<sub>NK</sub><sup>s</sup></i>	-1.65(51)
	<i>D<sub>K</sub></i>	0.645469(97)	10 <sup>3</sup>	( <i>D<sub>NK</sub><sup>s</sup> + D<sub>KN</sub><sup>s</sup>)</i>	-3.195(56)
10 <sup>2</sup>	<i>d<sub>1</sub></i>	-1.25986(88)	10 <sup>2</sup>	<i>D<sub>K</sub><sup>s</sup></i>	3.295(27)
10 <sup>3</sup>	<i>d<sub>2</sub></i>	-1.286(11)	10 <sup>4</sup>	<i>d<sub>1</sub><sup>s</sup></i>	1.480(17)
			10 <sup>5</sup>	<i>d<sub>2</sub><sup>s</sup></i>	1.21(14)
10 <sup>4</sup>	<i>H<sub>NK</sub><sup>e</sup></i>	-1.368(30)			
10 <sup>4</sup>	<i>H<sub>KN</sub></i>	1.425(93)			
10 <sup>3</sup>	<i>H<sub>K</sub></i>	1.314(11)			
10 <sup>6</sup>	<i>h<sub>2</sub></i>	0.64(24)			
10 <sup>3</sup>	<i>g<sub>r</sub><sup>aa</sup></i>	-4.986(95)			
10 <sup>4</sup>	<i>g<sub>r</sub><sup>bb</sup></i>	-4.94(76)			
10 <sup>4</sup>	<i>g<sub>r</sub><sup>cc</sup></i>	2.50(76)			

<sup>a</sup> Values in GHz (where appropriate).

<sup>b</sup> From a fit of 60 L.M.R. data points (12) and three M.O.D.R. frequencies (8, 10). Standard deviation of fit = 6.8 MHz. Spin-rotation parameters constrained to values obtained from M.O.D.R. fit. Electron spin *g*-factors fixed at the values obtained from Curl's relationship (11), viz.  $g_s^{aa} = 2.00884$ ,  $g_s^{bb} = 2.00406$  and  $g_s^{cc} = 2.00230$ .

<sup>c</sup> From a fit of 31 M.O.D.R. spin-rotation splittings (6, 7). Rotational and centrifugal distortion constants constrained to values obtained from L.M.R. fit.

<sup>d</sup> The numbers in parentheses represent one standard deviation of the least-squares fit, in units of the last quoted decimal place.

<sup>e</sup> All other sextic centrifugal distortion constants ( $H_{ij}$ ,  $h_1$  and  $h_3$ ) constrained to zero.

4.(II) b The interpretation of the quartic spin-rotation parameters for NH<sub>2</sub> in the  $\tilde{X}^2B_1$  state.

The values for the quartic spin-rotation parameters for NH<sub>2</sub> can be used to determine six linear combinations of the  $\eta$  parameters in the effective Hamiltonian Eq. (3.7). The relations appropriate to the S-reduced Hamiltonian are given in Eq. (3.53), and the results of such a calculation are given in Table IV. Eqs. (3.53) show that it is possible to determine the three "diagonal" components,  $\eta_{\alpha\alpha\alpha\alpha}$  and it is interesting to compare these results with the predictions of the formula derived in section 3(II) which relates the quartic rotational and spin-rotational parameters:

$$\eta_{\alpha\beta\gamma\delta} = \sum_{\xi} \tau_{\alpha\beta\gamma\delta} \epsilon_{\xi\delta} / 2B_{\xi}, \quad (4.5)$$

where  $B_{\xi}$  is the rotational constant associated with the principal inertial axis  $\xi$ . This relationship is based on the assumption that the electronic wavefunctions and eigenvalues are independent of vibrational coordinates. The values for the three  $\eta_{\alpha\alpha\alpha\alpha}$  parameters calculated from Eq. (4.5) with the constants in Table III are also given in Table IV. It can be seen that, although the results are of the right order of magnitude, they underestimate the value in each case (by a factor of  $\sim 2$  for  $\eta_{aaaa}$  and  $\eta_{bbbb}$ ). Similar conclusions were reached in other applications of (4.5) (14, 15, section 4(III)), so that some measure of the reliability of the formula is now apparent. For NH<sub>2</sub>, the three parameters  $\eta_{\alpha\alpha\alpha\alpha}$  all depend on the variation of the spin-rotation interaction with the vibrational co-ordinates  $Q_1$  (symmetric stretch) and  $Q_2$  (bend). The parameter  $\epsilon_{aa}$  arises primarily from the admixture of the  $\tilde{A}^2A_1$  state (16), and the strong dependence of the separation between  $\tilde{A}$  and  $\tilde{X}$  states on the bending co-ordinate is well established (17, 18). For the case of  $\eta_{aaaa}$  then, the assumptions on which Eq. (4.5) is based are patently incorrect and its failure is not surprising.

Hills et al (7, 5) have determined five parameters of the A-reduced form of  $H_{sr}^{(4)}$  in their analysis. They were able to

TABLE IV

QUARTIC SPIN-ROTATION PARAMETERS FOR NH<sub>2</sub> IN THE  $\tilde{X}^2B_1$  STATE IN MHz

Parameter	This work	Hills et al ( 7)	Calculated <sup>a</sup>
$\eta_{aaaa}$	30.03(28)	30.7(2)	14.70
$\eta_{bbbb}$	0.5978(54)	0.624(5)	0.395
$\eta_{cccc}$	0.0070(54)	0.0 <sup>b</sup>	-0.0006
$(\tilde{k}_{120}^{(b)} + \tilde{k}_{210}^{(c)})$	0.413(19)	...	...
$(\tilde{k}_{201}^{(a)} + \tilde{k}_{210}^{(a)})$	-2.8(10)	...	...
$(\tilde{k}_{102}^{(b)} + \tilde{k}_{012}^{(c)})$	-2.5(10)	...	...
$\eta_{aabb}$	-2.3(10)	-3.9(5)	...
$\eta_{bbaa}$	-12.6(15)	-12.8(5)	...
$\eta_{abab}$	1.22(10)	1.5(3)	...
$\eta_{baba}$	4.57 <sup>c</sup>	5.0 <sup>c</sup>	...

<sup>a</sup> Calculated from Eq. (45) and the parameters in Table III.

<sup>b</sup> This value assumed to be zero.

<sup>c</sup>  $\eta_{baba}$  constrained to the value  $\eta_{abab}^{(B/A)}(\epsilon_{bb})$  in this determination.

relate these parameters to the  $\eta_{\alpha\beta\gamma\delta}$  of Eq. (3.7), by imposing the planarity relationships and assuming all  $\eta_{\alpha\beta CC}$  to be zero. The three planarity relationships which can be derived from the work of Oka and Morino (19) are:

$$\eta_{ccaa} = (C/A)^2 \eta_{aaaa} + (C/B)^2 \eta_{bbaa} \quad (4.6a)$$

$$\eta_{ccbb} = (C/A)^2 \eta_{aabb} + (C/B)^2 \eta_{bbbb} \quad (4.6b)$$

$$\eta_{cccc} = (C/A)^2 \eta_{aacc} + (C/B)^2 \eta_{bbcc} \quad (4.6c)$$

These equations refer strictly to the equilibrium values for the  $\eta$  parameters rather than to the values in a particular vibrational level. However experience with corresponding relationships for the rotational centrifugal distortion constants (20, 36) suggests that Eqs. (4.6) should be quite reliable. The assumption that the  $\eta_{\alpha\alpha CC}$  are negligible for  $\text{NH}_2$  is not so well-founded since it is based on Eq. (4.5) and the observation that  $\epsilon_{CC}$  is very small (Table III). We have already demonstrated that Eq. (4.5) does not hold well for this molecule but possibly its order-of-magnitude level of reliability is sufficient; it is certainly true that  $\eta_{cccc}$  is very small (Table IV). By making these assumptions, Hills et al (7) were able to determine 5 of a possible 11 non-zero parameters, namely,  $\eta_{aaaa}$ ,  $\eta_{bbbb}$ ,  $\eta_{aabb}$ ,  $\eta_{bbaa}$  and  $\frac{1}{2}(\eta_{abab} + \eta_{baba})$ . It was only possible to separate  $\eta_{abab}$  and  $\eta_{baba}$  by using the relationship

$$\eta_{abab}/\eta_{baba} = (A/B)(\epsilon_{bb}/\epsilon_{aa}) \quad (4.7)$$

derived from Eq. (4.5). Again the reliability of this relationship is questionable but since the  $\eta$  parameters involved depend on the variation of  $\epsilon_{bb}$  and  $\epsilon_{cc}$  with the antisymmetric stretching co-ordinate ( $Q_3$ ) only, it is possible that the results are better in this particular application. The values obtained by Hills et al are given in Table IV.

The analysis performed here shows that the 6 parameters of the S-reduction ( $D_N^S$ ,  $D_{NK}^S$ ,  $D_{KN}^S$ ,  $D_K^S$ ,  $d_1^S$ ,  $d_2^S$ ) can be used to determine

the 6 coefficients  $\eta_{aaaa}$ ,  $\eta_{bbbb}$ ,  $\eta_{cccc}$ ,  $(\tilde{k}_{120}^{(b)} + \tilde{k}_{210}^{(c)})$ ,  $(\tilde{k}_{201}^{(a)} + \tilde{k}_{021}^{(a)})$  and  $(\tilde{k}_{102}^{(b)} + \tilde{k}_{012}^{(c)})$ . The latter three parameters can be related to the three  $\eta_{\alpha\alpha\alpha\alpha}$ , which are known, and the six  $k_{pqr}^{(\alpha)}$  by use of Eqs. (3.41), (3.44) and (3.45). For a symmetric triatomic molecule, the  $k_{pqr}^{(\alpha)}$  are from Eqs. (3.37)

$$\begin{aligned}
 k_{120}^{(b)} &= \eta'_{ccbb} = \eta_{ccbb} \\
 k_{102}^{(b)} &= \eta'_{aabb} = \eta_{aabb} + 2\eta_{abab} \\
 k_{210}^{(c)} &= \eta'_{bbcc} = \eta_{bbcc} \\
 k_{012}^{(c)} &= \eta'_{aacc} = \eta_{aacc} \\
 k_{201}^{(a)} &= \eta'_{bbaa} = \eta_{bbaa} + 2\eta_{baba} \\
 k_{021}^{(a)} &= \eta'_{ccaa} = \eta_{ccaa}
 \end{aligned}$$

Even if  $\eta_{bbcc}$  and  $\eta_{aacc}$  are assumed to be zero, there are still four parameters ( $\eta'_{aabb}$ ,  $\eta'_{bbaa}$ ,  $\eta_{ccaa}$  and  $\eta_{ccbb}$ ) to be determined from three experimental quantities. The imposition of the two planarity conditions, Eqs. (4.6a) and (4.6b) does not help because two extra parameters ( $\eta_{abab}$  and  $\eta_{baba}$ ) are introduced in the process. We therefore follow Hills et al (7) and invoke the extra constraint of Eq. (4.7) in order to determine  $\eta_{aabb}$ ,  $\eta_{bbaa}$  and  $\eta_{baba}$  from the three combinations  $(\tilde{k}_{120}^{(b)} + \tilde{k}_{210}^{(c)})$ ,  $(\tilde{k}_{201}^{(a)} + \tilde{k}_{021}^{(a)})$  and  $(\tilde{k}_{102}^{(b)} + \tilde{k}_{012}^{(c)})$ . The results of this calculation are given in Table IV where it can be seen that there is good agreement with the earlier workers, particularly for the parameters  $\eta_{aaaa}$  and  $\eta_{bbbb}$  whose values are not dependent on the assumptions made in the calculation. The fact that the values for the other three parameters are close to those of Hills et al (7), may just be an indication that the same assumptions are involved in both treatments. Certainly the relationship analogous to Eq. (4.7) between  $\eta_{aabb}$  and  $\eta_{bbaa}$  :

$$\eta_{aabb} / \eta_{bbaa} = (A/B) (\epsilon_{bb} / \epsilon_{aa}) \quad (4.8)$$



is not well satisfied by our results ( $\eta_{aabb}/\eta_{bbaa} = 0.178$  compared with the value of 0.267 from Eq. (4.8))

In conclusion, the analysis of the quartic spin-rotation parameters with the aid of the planarity relationships, does not seem to be very fruitful. This observation is in contrast to that for the quartic centrifugal distortion constants, where successful determinations of the non-zero  $\tau$ 's have been made by invoking the planarity conditions (36). It seems likely that the interface between experiment and interpretation for the spin-rotation problem will be established at the level of the parameters  $D_N^S$  etc., in the effective Hamiltonian, Eq. (3.46). Model vibrational potential energy surfaces for  $\text{NH}_2$  are becoming available (21, 22) and it would be extremely interesting to estimate the quartic spin-rotation parameters from these potential surfaces.

4 (III) A determination of Zeeman parameters for  $\text{NO}_2$  in its ground state.

4 (III) a Introduction.

Nitrogen dioxide has long been used as a prototype for studying interactions characteristic of open-shell molecules, as can be judged from the size of its literature. It has been studied extensively in its ground  $^2A_1$  state by both microwave (23, 24) and infra-red techniques (25, 26) so that rotational, spin-rotational and  $^{14}\text{N}$  hyperfine constants are well determined. The E.S.R. spectrum has been recorded in a variety of solid state environments (27, 28). The gas phase E.P.R. spectrum is very much more complex (29), and only selected parts of it have been analysed to date (30). Finally some far infra-red L.M.R. spectra have been obtained (31); these data provide information on higher rotational levels. Curl (11), has derived an extremely useful relationship between the electron spin-rotation coupling constants  $\epsilon_{\alpha\beta}$  and the g-tensor components  $g_{\alpha\beta}$ :

$$g_{\alpha\beta} = g_s \delta_{\alpha\beta} - \frac{1}{\hbar^2} \sum_{\gamma} I_{\alpha\gamma} \epsilon_{\gamma\beta} \quad (4.9)$$

where  $g_s$  is the free spin g-factor,  $I_{\alpha\beta}$  is a component of the inertial tensor and  $\alpha$ ,  $\beta$  and  $\gamma$  run over the three cartesian components in a molecule-fixed axis system\*. This relationship is rather well satisfied by the spin-rotation constants, as determined from the microwave spectrum (23) and the g-tensor components from the solid state work (27) and this was used by Curl in support of his relationship. It was therefore disconcerting when the analysis of the L.M.R. spectrum suggested markedly different values for the g-tensor components (31), especially as the molecule was studied in the gas phase where results are free from solid state lattice effects.

In this section extended measurements and assignments of magnetic dipole transitions in the gas phase E.P.R. spectrum of  $\text{NO}_2$  are described. These data, in conjunction with the L.M.R. data, have been fitted to an effective Hamiltonian which includes a description of the centrifugal distortion of the spin-rotation interaction and improved values for the g-tensor components, which conform closely to the predictions of Curl's relationship, have been determined. It was the neglect of the quartic spin rotation terms which led to the apparent conflict with Curl's relationship in the earlier analysis.

#### 4(III) b Experimental Details.

The E.P.R. spectrum of nitrogen dioxide was recorded with a Decca X-3 spectrometer using Zeeman modulation at a frequency of 100 kHz. A rectangular  $\text{TE}_{102}$  cavity resonant at 9270 MHz was placed in the field of a Varian 12 in. magnet and a static sample of gas introduced in a quartz sample tube. Optimum gas pressure was found to be about 0.25 torr; above this pressure line broadening was observed.

Accurate field measurements were made with an AEG proton

\*contrary to Curl, the second subscript of  $g_{\alpha\beta}$  and  $\epsilon_{\alpha\beta}$  refers to the component of the spin angular momentum,  $S_\beta$ .

fluxmeter and were corrected for the field difference between the proton probe, which was mounted on the magnet pole-face, and the sample in the centre of the magnet gap. Each observed line position quoted in Table V, is the average of at least five scans through the line. The spectrometer operating frequency was monitored continuously by a Hewlett Packard 5245L counter with a 5255A frequency convertor, although it was very nearly constant under the conditions of the experiment.

The transitions observed were of the same type as those studied earlier by Burch et al (30), and are discussed in more detail in section 4.III (d). Under the experimental conditions the lines were several gauss wide and the signal to noise ratio less than 20:1, even with a 3 s time constant. The accuracy of an individual measurement was estimated to be about one gauss.

#### 4 (III) c Theoretical Background.

The effective Hamiltonian for the rotational energy levels of an asymmetric top in a doublet state has been discussed by Van Vleck (32), Lin (33) and Raynes (34) and takes the form:

$$H_{\text{eff}} = H_{\text{rot}} + H_{\text{cd}} + H_{\text{sr}} + H_{\text{srcd}} + H_{\text{hfs}} + H_Q + H_Z \quad (4.10)$$

Here,  $H_{\text{rot}}$  is the rigid rotor Hamiltonian and  $H_{\text{cd}}$  the quartic and sextic centrifugal distortion corrections to the rotational energy.  $H_{\text{sr}}$  and  $H_{\text{srcd}}$  are the quadratic and quartic spin-rotation Hamiltonians which have been discussed in detail in Chapter 3, while  $H_{\text{hfs}}$  represents the magnetic hyperfine interactions between the  $^{14}\text{N}$  nucleus and the unpaired electron spin and consists of the Fermi-contact and spin-spin dipolar contributions. The nuclear electric quadrupole interaction is represented by  $H_Q$  and the interaction of the molecule with the external magnetic field by  $H_Z$ . The explicit forms for the various terms are given in many places in the literature. As discussed in Chapter 2, it has been convenient to use the spherical tensor

formulations for the operators given by Bowater et al (35), and the quartic and sextic centrifugal distortion Hamiltonians as given by Watson (36). The spin-rotation Hamiltonian was taken in the form discussed in Chapter 3, as applicable to an orthorhombic molecule.

The reliable determination of the molecular Zeeman parameters depends critically upon the use of the correct zero-field Hamiltonian, as will be seen in the next sub-section. In particular, it is important to include a description of the centrifugal distortion of the spin-rotation interaction. Program I was used to analyse the data, the approximations inherent in its structure were checked against a more accurate program and the eigenvalues were found to be reliable to within 0.1 MHz for the problem in hand.

#### 4 (III) d Results and Analysis.

Magnetic dipole transitions within the  $F_1$  spin component of a given rotational level have been studied with an E.P.R. spectrometer at 9.3 GHz. A typical transition is shown in Figure 1; the nuclear hyperfine splitting has been suppressed for the sake of clarity. Although the  $F_1$  and  $F_2$  spin component labels are strictly only defined in the zero field limit (where  $J$  is a good quantum number), all the  $M_J$  levels which correlate with a particular spin component are characterised by the appropriate label. Hougan (37) has suggested a different way of labelling Zeeman levels, but the scheme adopted here has the advantages that it is independent of the size of the spin-rotation splitting and of the magnetic field. The transitions studied in this work are of the same type as those studied earlier by Burch et al (30), although the measurements reported here are more extensive than theirs. The complete data set is listed in Table V together with the quantum number assignments. A section of the observed spectrum is shown in Figure 2.

The far infra-red L.M.R. data together with the E.P.R. data reported here were fitted simultaneously to the effective Hamiltonian discussed previously using the unweighted least squares method described in Chapter 2. The success of this process depended on

Figure 1. The energy levels of the  $2_{20}$  rotational state of  $\text{NO}_2$  as a function of magnetic field. The labelling of the spin components is indicated together with the type of transition observed in the E.P.R. experiment. All the  $M_J$  levels which correlate with the upper spin component in the zero-field limit are labelled  $F_1$  and those which correlate with the lower are labelled  $F_2$  (see Table V). The  $^{14}\text{N}$  hyperfine structure has been suppressed.

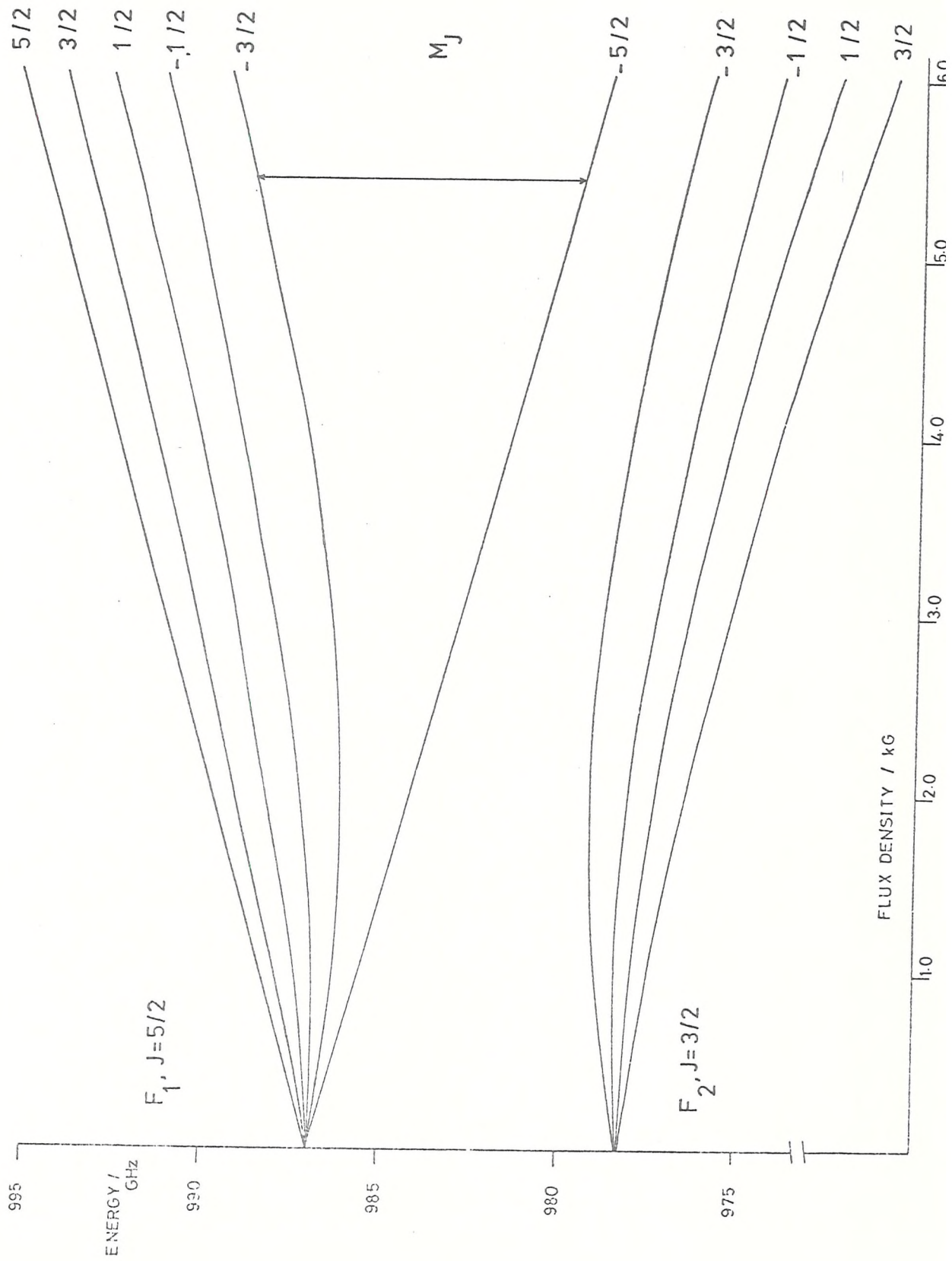


Figure 2. Section of the observed spectrum around 6170 G. The drawing shows the hyperfine triplets assigned to transitions occurring within the a)  $8_{44}$  and b)  $4_{31}$  rotational levels.

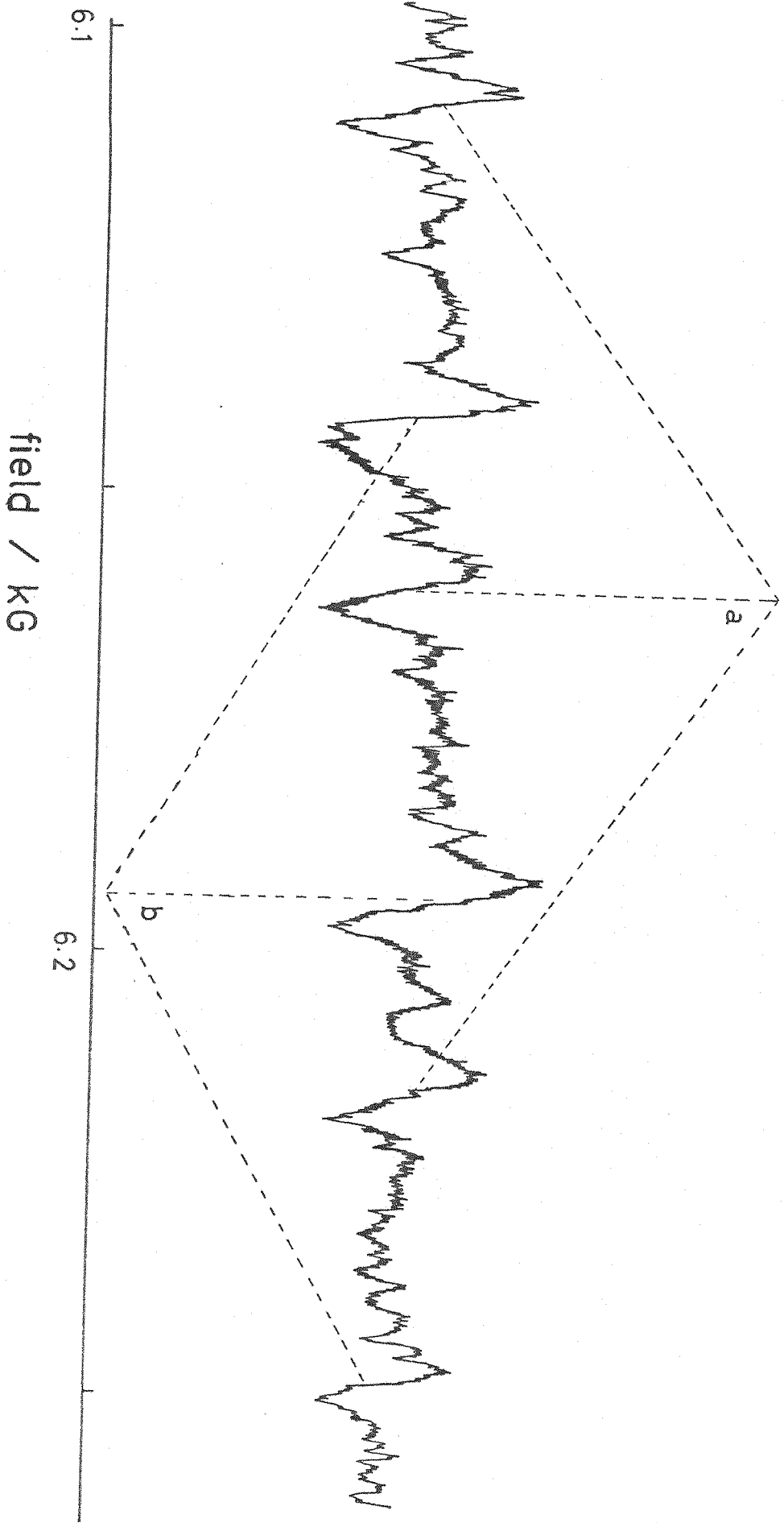




Table V Data and results of least-squares fits

TRANSITION								FLUX DENSITY/G	CALC/G	(O-C)/G	CALC/G	(O-C)/G
N'	K'	M <sub>J</sub> '	M <sub>I</sub> ' + N''	K''	M <sub>J</sub> ''	M <sub>I</sub> ''		Fit 1		Fit 2		
(a) LMR transitions of type F <sub>2</sub> + F <sub>1</sub> .												
8	2	-6½	1	7	1	-6½	1	1011.6 <sup>a</sup>	1011.77	-.17	1011.65	-.05
8	2	-6½	0	7	1	-6½	0	1058.8	1058.29	.51	1058.15	.65
8	2	-6½	-1	7	1	-6½	-1	1107.1	1107.21	-.10	1107.04	.06
8	2	-6½	-1	7	1	-5½	-1	1104.3	1104.42	-.12	1104.13	.17
8	2	-6½	1	7	1	-5½	1	1008.3	1008.41	-.11	1008.18	.12
8	2	-7½	-1	7	1	-6½	-1	1185.0	1185.02	-.02	1184.60	.40
9	2	1½	1	8	1	2½	0	1698.5	1698.84	-.34	1699.06	-.56
9	2	-6½	-1	8	1	-6½	-1	2115.3	2115.45	-.15	2115.57	-.27
9	2	7½	1	8	1	6½	1	1469.0	1468.81	.19	1469.38	-.38
9	2	-4½	1	8	1	-3½	1	1914.5	1914.77	-.26	1914.72	-.22
9	2	-8½	1	8	1	-7½	1	2091.4	2091.31	.09	2091.05	.35
9	2	-7½	0	8	1	-6½	0	2099.2	2099.62	-.42	2099.39	-.19
9	2	-6½	-1	8	1	-5½	-1	2105.0	2105.27	-.27	2105.02	-.02
9	2	-8½	-1	8	1	-7½	-1	2204.6	2204.48	.12	2204.16	.44
5	3	-1½	0	6	2	-2½	0	5394.4 <sup>b</sup>	5393.05	1.35	5394.69	-.28
5	3	-4½	0	6	2	-5½	0	6651.8 <sup>b</sup>	6652.27	-.47	6651.77	.03
6	3	2½	0	7	2	3½	0	2746.2 <sup>b,c</sup>	2745.07	1.13	2745.54	.65
6	3	-4½	0	7	2	-5½	0	4604.0 <sup>b,c</sup>	4601.70	2.30	4603.27	.73
(b) EPR transitions recorded at 9270.3 MHz and of type F <sub>1</sub> + F <sub>1</sub>												
2	2	-1½	1	2	2	-2½	1	5372.1	5372.40	-.30	5372.28	-.18
2	2	-1½	0	2	2	-2½	0	5424.5	5423.31	1.19	5423.20	1.30
2	2	-1½	-1	2	2	-2½	-1	5474.5	5474.71	-.21	5474.60	-.10
10	4	-9½	1	10	4	-10½	1	5558.6	5558.54	.06	5558.32	.28
10	4	-9½	0	10	4	-10½	0	5612.2	5612.65	-.15	5612.42	.08
10	4	-9½	-1	10	4	-10½	-1	5667.3	5667.24	.06	5667.01	.29
5	3	-4½	1	5	3	-5½	1	5684.3	5683.48	.82	5683.25	1.05
5	3	-4½	0	5	3	-5½	0	5735.7	5736.19	-.49	5735.96	-.26
5	3	-4½	-1	5	3	-5½	-1	5789.3	5789.37	-.07	5789.13	.17
9	4	-8½	1	9	4	-9½	1	5809.6	5809.58	.02	5809.38	.22
9	4	-8½	0	9	4	-9½	0	5863.3	5863.37	-.07	5863.17	.13
9	4	-8½	-1	9	4	-9½	-1	5917.1	5917.63	-.52	5917.42	-.32
8	4	-7½	1	8	4	-8½	1	6106.9	6108.21	-1.31	6108.05	-1.15
8	4	-7½	0	8	4	-8½	0	6160.2	6161.60	-1.40	6161.44	-1.24
8	4	-7½	-1	8	4	-8½	-1	6216.4	6215.42	.98	6215.25	1.15
4	3	-3½	1	4	3	-4½	1	6141.6	6143.07	-1.47	6142.93	-1.33
4	3	-3½	0	4	3	-4½	0	6194.2	6194.82	-.62	6194.68	-.48
4	3	-3½	-1	4	3	-4½	-1	6247.1	6247.00	.10	6246.85	.25

Table V (contd)

TRANSITION								FLUX DENSITY/G	CALC/G	(O-C)/G	CALC/G	(O-C)/G
N'	K'	M <sub>J</sub> '	M <sub>I</sub> ' + N''	K''	M <sub>J</sub> ''	M <sub>I</sub> ''		Fit 1		Fit 2		
12	5	-11½	1	12	5	-12½	1	6288.6	6288.88	-.28	6288.98	-.38
12	5	-11½	0	12	5	-12½	0	6343.4	6342.90	.51	6342.99	.41
12	5	-11½	-1	12	5	-12½	-1	6396.9	6397.33	-.43	6397.43	-.53
7	4	-6½	1	7	4	-7½	1	6468.5	6469.15	-.65	6469.05	-.55
7	4	-6½	0	7	4	-7½	0	6522.6	6522.01	.59	6521.90	.69
7	4	-6½	-1	7	4	-7½	-1	6575.0	6575.28	-.28	6575.17	-.17
11	5	-10½	1	11	5	-11½	1	6560.2	6560.03	.17	6560.15	.04
11	5	-10½	0	11	5	-11½	0	6615.3	6613.77	1.53	6613.89	1.41
11	5	-10½	-1	11	5	-11½	-1	6667.6	6667.91	-.31	6668.02	-.42
3	3	-2½	1	3	3	-3½	1	6752.8	6752.18	.62	6751.95	.85
3	3	-2½	0	3	3	-3½	0	6802.8	6802.61	.19	6802.38	.42
3	3	-2½	-1	3	3	-3½	-1	6852.9	6853.43	-.53	6853.20	-.30
10	5	-9½	1	10	5	-10½	1	6873.7	6873.33	.37	6873.49	.22
10	5	-9½	0	10	5	-10½	0	6926.6	6926.72	-.12	6926.87	-.27
10	5	-9½	-1	10	5	-10½	-1	6979.8	6980.49	-.69	6980.63	-.83
6	4	-5½	1	6	4	-6½	1	6913.4	6912.62	.78	6912.58	.82
6	4	-5½	0	6	4	-6½	0	6965.1	6964.79	.31	6964.75	.35
6	4	-5½	-1	6	4	-6½	-1	7016.0	7017.34	-1.34	7017.29	-1.29
9	5	-8½	1	9	5	-9½	1	7240.2	7239.25	.95	7239.44	.76
9	5	-8½	0	9	5	-9½	0	7292.4	7292.21	.19	7292.39	.01
9	5	-8½	-1	9	5	-9½	-1	7345.2	7345.53	-.33	7345.71	-.51
5	4	-4½	1	5	4	-5½	1	7465.3	7465.17	.13	7465.13	.17
5	4	-4½	0	5	4	-5½	0	7516.1	7516.43	-.33	7516.39	-.29
5	4	-4½	-1	5	4	-5½	-1	7567.4	7568.04	-.44	7568.00	-.60
8	5	-7½	1	8	5	-8½	1	7670.8	7671.44	-.64	7671.67	-.87
8	5	-7½	0	8	5	-8½	0	7724.8	7723.86	.94	7724.08	.72
8	5	-7½	-1	8	5	-8½	-1	7777.0	7776.61	.39	7776.84	.16
4	4	-3½	1	4	4	-4½	1	8154.0	8154.30	-.30	8153.93	.07
4	4	-3½	0	4	4	-4½	0	8203.1	8204.40	-1.30	8204.02	-.92
4	4	-3½	-1	4	4	-4½	-1	8254.6	8254.83	-.23	8254.45	.15
5	5	-4½	1	5	5	-5½	1	9552.0	9551.89	.11	9551.39	.61
5	5	-4½	0	5	5	-5½	0	9601.6	9601.74	-.14	9601.23	.37
5	5	-4½	-1	5	5	-5½	-1	9652.1	9651.89	.21	9651.37	.73

<sup>a</sup> LMR transitions observed at a frequency of 890760.7 MHz.

<sup>b</sup> LMR transitions observed at a frequency of 964313.4 MHz.

<sup>c</sup> These LMR transitions are of type  $F_1 + F_2$ .

Table VI: Zero Field Parameters for NO<sub>2</sub> in GHz

Parameter <sup>a</sup>		Parameter <sup>b</sup>	
A	239.90489	$\epsilon_{aa}$	5.40676(7) <sup>c,d</sup>
B	13.002238	$\epsilon_{bb}$	0.00765(2)
C	12.304844	$\epsilon_{cc}$	-0.09524(2)
$\Delta_N$	$9.01416 \times 10^{-6}$	$a_N$	0.14723(3)
$\Delta_{NK}$	$-5.8416 \times 10^{-4}$	$T_{aa}$	-0.02216(7)
$\Delta_K$	$8.05872 \times 10^{-2}$	$T_{bb}$	0.03985(5)
$\delta_N$	$9.5304 \times 10^{-7}$		
$\delta_K$	$1.23814 \times 10^{-4}$	$(aa)_Q$	0.00045(6)
		$(bb)_Q$	-0.00171(4)
$\phi_N^e$	$1.5889 \times 10^{-11}$		
$\phi_{NK}$	$-1.109 \times 10^{-8}$		
$\phi_{KN}$	$-5.9054 \times 10^{-7}$		
$\phi_K$	$8.83189 \times 10^{-5}$		
$\phi_N$	$6.5954 \times 10^{-12}$		
$\phi_{NK}$	-		
$\phi_K$	$-2.3384 \times 10^{-6}$		
$L_K$	$1.064 \times 10^{-7}$		

<sup>a</sup> From reference [26]

<sup>b</sup> From reference [23]

<sup>c</sup> Corrected from the value given in [23] by -5.0 MHz (see text).

<sup>d</sup> The numbers in parentheses represent one standard deviation, in units of the last quoted decimal place.

<sup>e</sup> Sextic distortion parameters defined in reference [26].

Table VII Parameters for NO<sub>2</sub> from fits of the Zeeman Data

Parameter	Solid state [27]	LMR [31]	This work, 1.	This work, 2.	Theory
$D_K^{(s)}$ /MHz	-	-	5.100(28) <sup>a</sup>	-5.069(27)	-3.628
$(D_{NK}^{(s)} + D_{KN}^{(s)})$ /MHz	-	-	$4.2(10) \times 10^{-2}$	$4.7(9) \times 10^{-2}$	$2.80 \times 10^{-2}$
$D_N^{(s)}$ /MHz	-	-	-	-	$-9.73 \times 10^{-6}$
$g_{aa}^{(s)}$	1.9910(5)	2.0030	1.99049(27)	1.98993(9)	1.99105 <sup>e</sup>
$g_{bb}^{(s)}$	2.0015(5)	2.0205	2.00256(190)	2.00204(276)	2.00203
$g_{cc}^{(s)}$	2.0057(5)	2.0155	2.00716(190)	2.00844(276)	2.00619
$\frac{1}{2}(g_{bb}^{(s)} + g_{cc}^{(s)})$	2.0036(5)	2.0180	2.00486(27)	2.00524(9)	2.00411
$T_0^0(g_r)^b$	-	c	-	-0.0113(24)	-
$T_0^2(g_r)$	-	c	-	-0.00081(18)	-
$T_2^2(g_r)$	-	c	-	d	-

<sup>a</sup> The numbers in parentheses represent one standard deviation of the least-squares fit, in units of the last quoted decimal place.

<sup>b</sup> For definition, see reference [35].

<sup>c</sup> Not determined within  $4 \times 10^{-4}$ .

<sup>d</sup> Not determined within  $10^{-4}$ .

<sup>e</sup> Calculated assuming  $g_s = 2.00232$ .

the availability of reliable zero field parameters, and on the inclusion of terms in the quartic spin-rotation Hamiltonian. Unfortunately the accurately measured microwave frequencies (23, 24) involve b-dipole transitions between levels with  $K_a = 0$  and 1 and it is not possible to determine separate values for  $\epsilon_{aa}$  and  $D_K^S$  from this data; the value quoted for  $\epsilon_{aa}$  in the fit of the microwave data (23) is actually the value for  $(\epsilon_{aa} + D_K^S)$ . The value for  $\epsilon_{aa}$  was therefore corrected using the value of  $D_K^S$  determined from preliminary fits of the magnetic resonance data (-5.0 MHz). The best available values for the zero field parameters are given in Table VI. The spin-rotation and  $^{14}\text{N}$  hyperfine parameters are taken from the work of Lees et al (23). The rotational and centrifugal distortion constants have been determined by Lafferty and Sams (26) from a simultaneous fit of microwave and infra-red data, appropriately weighted.

In the least squares fit of the magnetic resonance data, the values for the molecular Zeeman parameters and some of the quartic spin-rotation constants were allowed to vary. It did not prove possible to determine values for all the predicted quartic spin-rotation parameters; nitrogen dioxide is a less asymmetric top than  $\text{NH}_2$  and the available data are less extensive. However, values for the dominant parameters  $D_K^S$  and  $(D_{KN}^S + D_{NK}^S)$  were determined, the other expected quartic spin rotation parameters ( $D_{KN}^S - D_{NK}^S$ ,  $D_N^S$ ,  $d_1^S$  and  $d_2^S$ ) were constrained to zero.

The results of two fits are shown in Table V. In the first, the data were fitted to  $D_K^S$ ,  $D_{KN}^S + D_{NK}^S$  and the three principal components of the spin g-tensor. In the second fit, terms from the rotational Zeeman interaction were added and the two dominant rotational g-factors were determined in addition to the parameters varied in the first fit. Both fits are very satisfactory, since they are consistent with the experimental data to their quoted precision. The major difference between the two is that the inclusion of the rotational Zeeman terms reduces the slightly larger residuals associated with the laser magnetic resonance transitions  $6_{33} + 7_{26}$  and  $5_{33} + 6_{24}$ . The parameters determined in

this way are listed in Table VII, together with the results of previous determinations and some theoretical estimates based on equations (4.5) and (4.9).

#### 4 (III) e Discussion.

The aim of this study was to determine the three principal components of the electron spin  $g$ -tensor from a large body of magnetic resonance data for  $\text{NO}_2$  in the gas phase. The extent to which it has been achieved can be judged from Table VII. It can be seen that the components are reasonably well determined,  $g_{bb}$  and  $g_{cc}$  rather less so than  $g_{aa}$ . In fact the data determine  $g_{aa}$  and  $(g_{bb} + g_{cc})$  better as can be seen from Table VII. The difference between  $g_{bb}$  and  $g_{cc}$  primarily affects levels with  $K_a = 1$  and only a few transitions involving such levels are included in the data. Close scrutiny of Table VII reveals that, although the  $g$ -factors are not inconsistent with Curl's relationship, they do not provide really positive support for it. It proved much more difficult to determine reliable  $g$ -factors for a gas phase molecule than had been anticipated. This is partly because the data are relatively insensitive to these parameters (the quality of the fit of the data in Table V with the  $g$ -tensor components fixed at the values predicted by Curl's relationship is only slightly worse than that of the two fits shown) and partly because the data are more sensitive to certain zero field parameters. This sensitivity was exploited to determine two of the quartic spin-rotation parameters, but the reliability of the fit has depended critically upon the availability of good zero-field frequencies and particularly on the determination of centrifugal distortion constants from the analysis of the infra-red spectrum (26).

The satisfactory feature of the analysis is that the far infra-red L.M.R. data can be fitted with  $g$ -factors in essential agreement with the predictions of Curl's relationship; this conclusion holds irrespective of whether rotational Zeeman terms are included or not.

The g-factors from the gas phase study are also consistent with the values obtained from the solid state E.S.R. spectrum (27), as can be seen from Table VII. The difficulty experienced in determining the electron spin g-factors has made it doubly important to assess Curl's relationship. In the study of short-lived polyatomic free radicals in the gas phase by magnetic resonance techniques, it is rare that the data are sufficient to determine the molecular Zeeman parameters independently (see, for example (12) and (14)). In this case, it becomes vital to have an alternative way of estimating these g-factors. It would appear that Curl's relationship Eq. (4.8) is reliable for this purpose, at least for molecules containing elements in the first and second rows of the Periodic Table. Curl established his relationship in terms of second-order perturbation contributions to  $g_{\alpha\beta}$  and  $\epsilon_{\alpha\beta}$ , neglecting the first-order contribution in each case on the grounds that it was much smaller in magnitude. Watson (38) has recently shown that, even for these first-order contributions, Curl's relationship holds well, that is to the order of  $\alpha^2$  where  $\alpha$  is the fine structure constant. However, if heavier elements are involved, a breakdown in Curl's relationship is anticipated since third and higher-order perturbation contributions involving the spin-orbit interaction can become significant. There are some suggestions that this situation is reached when heavier elements are contained in the molecule; for example in  $S_2$  (39) and  $SeO$  (40).

The magnitude of the quartic spin-rotation parameters determined in the course of the analysis has been commented upon in section 4 (II) b. The approximate formula (4.5) appears to underestimate the size of these parameters in all cases; in the case of  $NO_2$  it is reliable to about 30 per cent. The size of the rotational g-factors can be compared with the values calculated from the appropriate relationship derived by Barnes et al (2) and quoted in section 4 (II) a, Eq. (4.4). The value for  $\zeta$  was taken to be an average of the values for the two oxygen and nitrogen atoms contained in the molecule whence:

$$T_0^0(g_r) = -.00083$$

$$T_2^2(g_r) = -0.15 \times 10^{-4}$$

$$T_0^2(g_r) = -.00117$$

These numbers do not agree well with those determined in the fit. This is probably due to the latter being used by the program to take up small discrepancies in the zero field frequencies, highlighting again the need for a good set of zero field parameters.



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## CHAPTER 5.

THE OBSERVATION OF MAGNETIC DIPOLE TRANSITIONS IN  $\tilde{X}^2\Pi$  SeH BY LASER MAGNETIC RESONANCE SPECTROSCOPY.

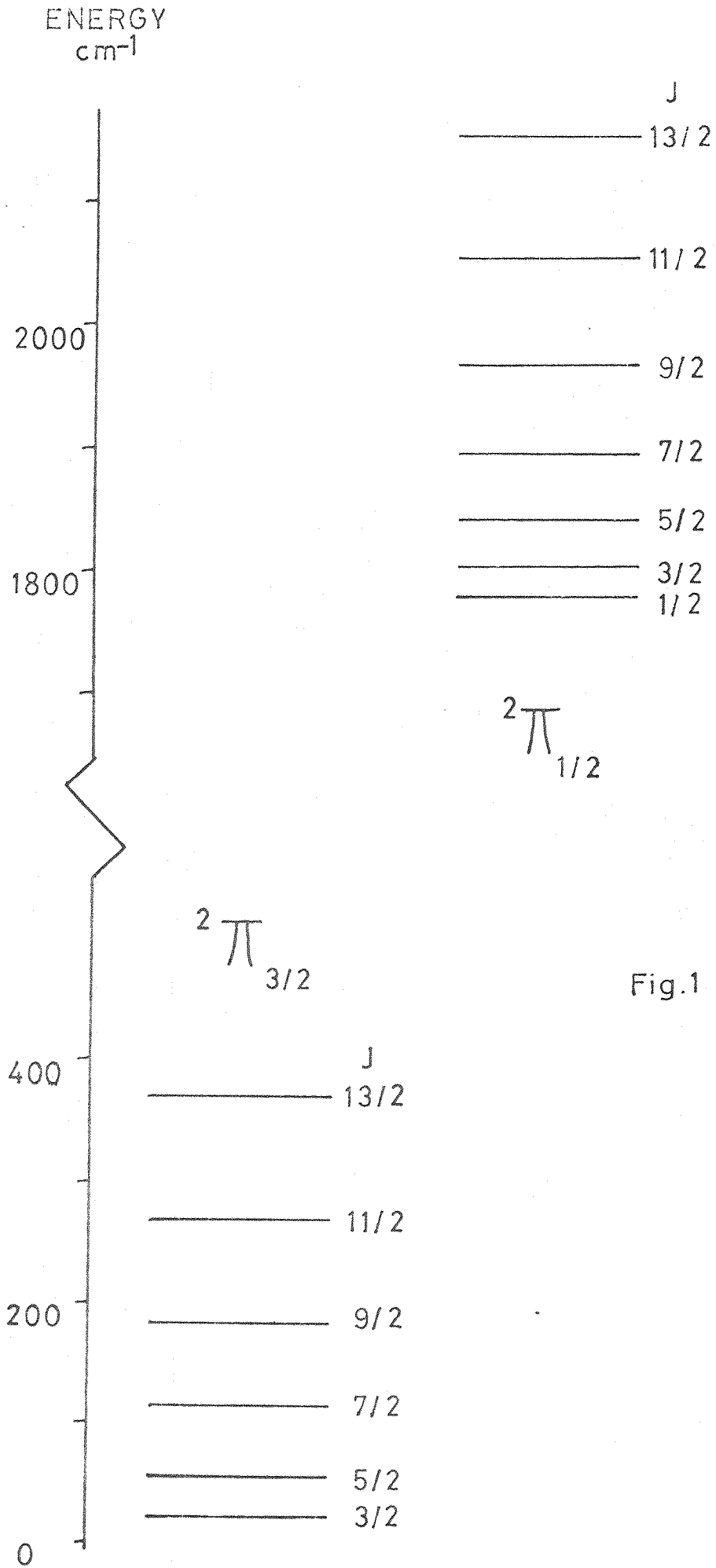
5 (I) Introduction

Selenium hydride has an inverted  $^2\Pi$  ground electronic state which is well described in terms of Hunds' case (a) functions (1). Under these circumstances, the projections of the electronic orbital ( $\Lambda$ ) and spin ( $\Sigma$ ) angular momenta and their sum ( $\Omega$ ) along the internuclear axis are all well defined. For a  $^2\Pi$  molecule, the possible values of  $|\Omega|$  are 3/2 and 1/2 and these are associated with the fine structure states  $^2\Pi_{3/2}$  and  $^2\Pi_{1/2}$ . The separation between these states is primarily determined by the spin orbit and rotational constants appearing in the effective Hamiltonian describing the ground electronic state of the molecule.

Recent analysis of the electronic emission spectrum ( $\tilde{B}^2\Sigma \rightarrow \tilde{X}^2\Pi$ ) of SeH (2, 3) has resulted in much improved values for the major molecular constants. Using these results it is possible to predict that in SeH the fine structure states are separated by approximately  $1780\text{ cm}^{-1}$ ; a frequency which lies within the operating range of a CO gas discharge laser. Fig (1) is a diagram showing the lower rotational levels associated with each fine structure state. This chapter describes the observation of transitions which occur between the rotational levels of the two fine structure states by the technique of laser magnetic resonance spectroscopy and the subsequent analysis of the spectrum in conjunction with previously reported E.P.R. data (4). Electric dipole transitions between the components of a  $^2\Pi$  electronic state are forbidden in a case (a) representation and the observation of the spectrum relied upon the interaction of the molecules' magnetic dipole moment with the laser radiation. Aspects of the intensity of electric and magnetic dipole transitions between the states in question are discussed in section 5 (III) b.

Figure 1. Relative energy level diagram showing the lower rotational levels associated with the two fine structure components of the  $\tilde{X}^2\Pi$  state of SeH. Lambda-doubling has been omitted for reasons of clarity.





This chapter is divided into three main sections; the experimental techniques are described immediately following this section and a summary of the theoretical background is presented in section III. The results are discussed in the last section of the chapter; as a result of the analysis of the L.M.R. and E.P.R. spectra it has proved possible to determine refined values for several of the major parameters appearing in the effective molecular Hamiltonian. High resolution spectroscopic studies of molecules containing heavy atoms such as selenium are of interest because the large spin orbit effects associated with them test the validity of some of the assumptions involved in the derivation of the effective Hamiltonian for the  $^2\Pi$  electronic state (5, 6, 7). Some discussion of this aspect of the analysis is included in sections 5 (III) and 5 (IV).

#### 5 (II) Experimental Details.

The spectra were recorded using the CO L.M.R. spectrometer described by Brown et al (8). The laser beam is directed through an absorption cell which is situated between the pole-faces of a Varian 15" magnet and focussed on to a gold-doped germanium detector which operates at liquid nitrogen temperatures. The laser is a modified Edinburgh Instruments PL3 instrument. The gain tube operating temperature may now be varied between  $0^{\circ}$  and  $-100^{\circ}$  centigrade; this greatly increases the number of accessible lines on which the laser may be made to oscillate and, generally, the lower operating temperatures provide greater gain and therefore larger output powers at a given frequency. There is a drawback to this low temperature operation in that the laser may oscillate at several, closely spaced frequencies, at one time. This process is known as multilining and the problem may be partially overcome by the use of a higher dispersion grating. However this is not a complete solution and the presence of several different laser frequencies can cause complication of the observed spectrum.

The magnetic field is modulated at a frequency of around 25 kHz by means of a pair of copper Helmholtz coils mounted between the pole faces of the electromagnet and the sides of the absorption cell and the molecular species of interest generated in a continuous flow system in the centre of the field gap. A spectrum is obtained by sweeping the magnetic field while operating at a fixed laser frequency and detecting the absorption lines by means of conventional lock-in amplification.

The absorption cell itself is constructed of glass with calcium fluoride windows to minimise unwanted absorption of the infra-red radiation. Two entry and one (pumped) exit ports allow various mixtures of reactants to be used to generate the transient species to be studied. Selenium hydride radicals were generated by the reaction of the products of a microwave discharge in water vapour with selenium metal powder which was glued to the sides of the absorption cell using a rubber based adhesive. Optimum water vapour pressure was about one torr and under these circumstances the metal sample lasted for about half a day. The spectra were also detected when fluorine atoms, from a microwave discharge in  $\text{CF}_4$ , were reacted with  $\text{H}_2\text{Se}$  in the absorption cell. The signal to noise ratio was not high, typically less than 25:1 even with a 3s output time constant.

In the normal configuration of the system, the electric vector of the laser radiation and the space-fixed z direction, as defined by the applied magnetic field, are perpendicular. For reasons discussed in section 5 (III), the observation of particular types of transition in the SeH radical requires the two to be parallel to one another. Rotation of the plane of polarisation of the laser radiation through  $90^\circ$  was achieved by the use of three Fresnel rhombs made of calcium fluoride and mounted back to back. The use of this optical device enabled the observation of both  $\Delta M = 0$  and  $\Delta M = \pm 1$  transitions. The advantage of the use of the rhombs over the more conventional mirror arrangement is that the rotation of the plane of polarisation is performed without moving the beam more than a few millimeters off axis so avoiding the re-aligning of both the absorption cell and the detector.



Under the conditions of the experiment, the spectral linewidth was determined by the Doppler spread in the velocities of the SeH radicals. At 300K and  $1780\text{cm}^{-1}$  the Doppler line width is estimated to be approximately 50 MHz. Individual lines may appear wider than others on the spectrum however, because different transitions tune at different rates in the magnetic field. Some discussion of these aspects of the experiment is included in section 5 (III) c. The magnetic fields were measured with an A.E.G. proton fluxmeter and are estimated to be accurate to within  $\pm 10\text{G}$ .

### 5 (III) Theoretical Background.

#### 5 (III) a The effective Hamiltonian for a $^2\Pi$ molecule.

The problems encountered in the derivation of a spectroscopically useful effective Hamiltonian for a  $^2\Pi$  molecule have been discussed at length by a number of authors (References 5 to 11) and in this short section, no attempt is made to justify either the form or content of the Hamiltonian operator in any detail. An effective Hamiltonian for the selenium hydride radical which is adequate to reproduce the experimental data is given by:

$$H_{\text{eff}} = H_{\text{so}} + H_{\text{rot}} + H_{\text{cd}} + H_{\text{sr}} + H_{\text{LD}} + H_{\text{cdLD}} + H_{\text{z}} \quad (5.1)$$

where  $H_{\text{so}}$  represents the spin orbit coupling energy and  $H_{\text{rot}}$  and  $H_{\text{cd}}$  the rotational energy and its centrifugal distortion correction respectively.  $H_{\text{sr}}$  is the electron spin-rotation interaction which, for the present application, makes a contribution to the molecular energy levels which is indistinguishable from that of the centrifugal distortion correction to the spin orbit coupling energy (12).  $H_{\text{LD}}$  and  $H_{\text{cdLD}}$  represent the lambda doubling energy correction and the corresponding centrifugal distortion term. Finally  $H_{\text{z}}$  represents the interaction of the molecule with an externally applied magnetic field. The operator forms for the various terms in (5.1) were taken

from Brown et al (9). The Hamiltonian makes no reference to hyperfine effects; they are not expected to be resolved since the hyperfine splitting in SeH is less than the experimental linewidth.

Discussion in this section is limited to the lambda doubling and Zeeman contributions to the effective Hamiltonian. These effect minor perturbations to the crude energy level diagram given in Fig. (1); the form of the diagram is determined by the spin orbit and rotational contributions to the Hamiltonian.

To a first approximation, the levels associated with each fine structure component in a  $^2\Pi$  electronic state are orbitally doubly degenerate. However spin orbit and rotational mixing of higher electronic states lifts this degeneracy with the result that each level in Fig. (1) should be shown as a closely spaced doublet. This phenomenon is known as lambda type doubling and is discussed by Mulliken and Christy (10) and Brown et al (9). In the case of SeH in its  $\tilde{X}^2\Pi$ , the major contaminating state is probably the  $\tilde{A}^2\Sigma$  state which lies approximately  $30900\text{ cm}^{-1}$  to higher energy (13). Mulliken and Christy derived expressions for the lambda doubling parameters appearing in the effective Hamiltonian by the use of second order perturbation theory on the assumption that contamination is by  $^2\Sigma$  states only; however the lambda doubling parameters determined in the fit include second and higher order contributions from all the excited electronic states of the molecule connected to the ground state by the spin orbit and rotational terms in the complete molecular Hamiltonian. The higher order contributions are expected to be significant in SeH where the spin orbit constant,  $A$ , is large. To obtain a satisfactory fit to the experimental data, it was found necessary to include the (two) terms in the Hamiltonian describing the centrifugal distortion correction to the lambda doubling energy. The origins of these terms has been discussed by Brown et al (9) and Mizushima (11) and will not be elaborated upon here. Although the inclusion of the parameters  $D_p$  and  $D_q$  describing this effect was required before an adequate fit to the data could be performed, the data were not sufficient to determine them unambiguously and they

were constrained to the values predicted by the formulae:

$$D_p = -2 \frac{D p}{B} \quad (5.2)$$

$$D_q = -4 \frac{D q}{B}$$

(where  $D$  is the quartic centrifugal distortion constant and  $B$  the rotational constant) as derived in Reference (14) on the assumption that the electronic wavefunctions are independent of the vibrational co-ordinates. The effective Zeeman Hamiltonian used to analyse the data was taken in the form derived by Carrington et al (15, 16) and quoted by Brown et al (9). There are six determinable parameters for a molecule in a  $^2\Pi$  state. Relationships between some of the  $g$ -factors can be derived by the use of second order perturbation theory on the assumption that the  $^2\Pi$  state is perturbed by  $^2\Sigma$  states only (9, 15, 16) and these relationships were found to be quite reliable for OH (9). Their reliability is questionable for SeH however, because of the large spin orbit effects associated with the heavy atom. It was found necessary to include some third order contributions to the Zeeman Hamiltonian, which have the effect of making corrections to terms already included in the model, during the data analysis. These are discussed in section IV.

The eigenvalues of the effective Hamiltonian were calculated using a program written by Drs. D.J. Milton and C.M.L. Kerr. The Hamiltonian matrix is constructed in a parity conserving case (a) basis:

$$|n \Lambda|; J M_J |\Omega|; \pm \rangle = \frac{1}{\sqrt{2}} \{ |n\Lambda; S\Sigma; J M_J \Omega \rangle \pm$$

$$(-)^{J-S+\Sigma} |n-\Lambda; S-\Sigma; J M_J -\Omega \rangle \}$$

in the usual rotation,  $s$  is only included in the case of  $\Sigma$  electronic states and is even or odd according to the symmetry ( $\Sigma^+$  or  $\Sigma^-$ ) of the state in question. The matrix for a particular value of  $J$  in the absence of a magnetic field is then of order  $2 \times 2$  with only the basis functions:

$$|n|\Lambda|; J M_J | \Omega = 3/2 | ; \pm \rangle \quad \text{and} \quad |n|\Lambda|; J M_J | \Omega = 1/2 | ; \pm \rangle$$

involved. As in the case of the eigenvalue problem for asymmetric top molecules (discussed in chapter 2) the matrix is strictly infinite when the Zeeman Hamiltonian is included in the model. However truncation of the matrix at  $\Delta J = \pm 2$  produced no significant errors in the calculation of the energy of the rotational levels included in the data.

### 5 (III) b. Transition intensity considerations.

In the introductory section of this chapter it was asserted that the observation of transitions between the fine structure states in  $\tilde{X}^2\Pi$  SeH is dependent upon magnetic dipole intensity. It is unusual in L.M.R. spectroscopy to detect magnetic dipole transitions since, in general, they are expected to be approximately  $10^4$  times weaker than the corresponding electric dipole transitions when the molecule has an electric dipole moment of the order of one Debye (7). In order to understand how, in this particular case, the magnetic dipole transitions between the fine structure states are actually more easily observed than the corresponding electric dipole ones, it is necessary to examine the matrix elements of both the electric and magnetic dipole moment operators between the molecular eigenstates in question.

The fine structure components  $^2\Pi_{1/2}$   $^2\Pi_{3/2}$  are represented by eigenfunctions of the effective molecular Hamiltonian (5.1) for the  $^2\Pi$  electronic state, which are in turn expressed as linear combinations of case (a) basis functions  $|n\Lambda; S\Sigma; JM_J\rangle$ . In the case of  $\tilde{X}^2\Pi$  SeH, the quantum number  $\Omega$  is very nearly good and to this approximation the intensity of the transition between the

$\Omega = 3/2$  and  $\Omega = 1/2$  components of the electronic state may be represented by the square of the matrix element of the magnetic or electric dipole moment operator between the pure case (a) functions. The molecular magnetic dipole moment is represented by  $\underline{\mu}_m$  with

$$\underline{\mu}_m = g_S \mu_B T^1(\underline{S}) + g_L \mu_B T^1(\underline{L}) \quad (5.3)$$

where  $\underline{S}$  and  $\underline{L}$  are the total electron spin and orbital angular momenta respectively,  $g_S$  and  $g_L$  the spin and orbital g-factors and  $\mu_B$  the Bohr magneton. We are interested in the probability of a transition between two case (a) states, i.e:

$$\begin{aligned} (\text{Intensity})_m &\propto \\ &|\langle n' \Lambda'; S' \Sigma'; J' \Omega' M_{J'}' | \underline{\mu}_m \cdot T^1(\underline{B}) | n \Lambda; S \Sigma; J \Omega M_J \rangle|^2 \end{aligned} \quad (5.4)$$

where  $\underline{B}$  is the magnetic field vector of the applied radiation. This expression may be evaluated using standard angular momentum results to give:

$$\begin{aligned} (\text{Intensity})_m^{\frac{1}{2}} &\propto \\ &\sum_P T_{-P}^1(B) (-)^{J' - M_{J'}'} \begin{bmatrix} J' & 1 & J \\ -M_{J'}' & P & M_J \end{bmatrix} \sum_Q (-)^{J' - \Omega'} [(2J' + 1)(2J + 1)]^{\frac{1}{2}} \\ &\times \begin{bmatrix} J' & 1 & J \\ -\Omega' & Q & \Omega \end{bmatrix} \{ \delta_{\Lambda \Lambda'} \delta_{\eta \eta'} \delta_{S S'} g_S \mu_B (-)^{S - \Sigma'} \begin{bmatrix} S & 1 & S \\ -\Sigma' & Q & \Sigma \end{bmatrix} [S(S+1)(2S+1)]^{\frac{1}{2}} \\ &+ \delta_{S S'} \delta_{\Sigma \Sigma'} g_L \mu_B \langle n' \Lambda' | T_Q^1(\underline{L}) | n \Lambda \rangle \} \end{aligned} \quad (5.5)$$

It is evident that magnetic dipole transitions between states differing in  $\Omega$  are fully allowed. This result must be compared with the analogous one for the electric dipole moment operator  $\underline{\mu}_e$ ,

$$\underline{\mu}_e = T^1(\underline{\mu}) \quad (5.6)$$

interacting with the electric vector of the applied radiation:

$$(\text{Intensity})_e \propto$$

$$|\langle n'\Lambda'; S'\Sigma'; J'\Omega'M_J' | \underline{\mu}_e \cdot T^1(\underline{E}) | n\Lambda; S\Sigma; J\Omega M_J \rangle|^2 \quad (5.7)$$

which may be evaluated to give:

$$(\text{Intensity})_e^{\frac{1}{2}} \propto$$

$$\delta_{n'n} \delta_{\Lambda'\Lambda} \delta_{S'S} \delta_{\Sigma'\Sigma} \sum_p (-)^{J-M_J'} \begin{bmatrix} J' & 1 & J \\ -M_J' & p & M_J \end{bmatrix} T_{-p}^1(E)$$

$$\times \sum_q [(2J'+1)(2J+1)]^{\frac{1}{2}} \begin{bmatrix} J' & 1 & J \\ -\Omega' & q & \Omega \end{bmatrix} \langle n' | T_q^1(\underline{\mu}) | n \rangle \quad (5.8)$$

Since the dipole moment ( $\underline{\mu}_e$ ) lies along the internuclear axis the only non-zero component of the first rank spherical tensor  $T^1(\underline{\mu})$  is  $T_0^1(\underline{\mu})$ ; consequently electric dipole transitions between states differing in  $\Omega$  are rigorously forbidden in a pure case (a) representation.

The above results hold so long as  $|\Omega|$  is a good quantum number, that is, while the eigenfunctions of the effective Hamiltonian are accurately represented by single case (a) functions. However, there are terms in the rotational Hamiltonian which connect the  $|\Omega| = \frac{1}{2}$  and  $3/2$  states for a given value of  $J$ ; the true eigenfunctions are thus linear combinations of case (a) basis functions of different  $\Omega$  and therefore electric dipole transitions between the two components of a  ${}^2\Pi$  state are not completely forbidden. The rotational mixing of states of different  $|\Omega|$  can also be expected to modify the magnetic dipole transition intensities slightly.

A computer program has been developed (17) to calculate the relative intensities of both magnetic and electric dipole transitions between the fine structure components in  $\tilde{X} {}^2\Pi$  SeH. Reference to the energy level diagram (Fig. 1) and Equations (5.5) and (5.8) suggests that we can expect transitions with  $\Delta J = -1, 0$  and  $+1$ ; these are labelled P, Q and R branches respectively. Table (1) shows the computed ratios of electric to magnetic dipole intensities for P and R branch lines in the  ${}^2\Pi_{\frac{1}{2}} - {}^2\Pi_{\frac{3}{2}}$  transition in SeH. The calculations neglect the effects of  $\Lambda$ -doubling and the rotational mixing is estimated from the values of the spin orbit and rotational constants for the molecule.

J	R-Branch	P-Branch
3/2	$5.44 \times 10^{-2}$	$5.45 \times 10^{-2}$
5/2	5.43	5.44
7/2	5.43	5.44
9/2	5.42	5.43
11/2	5.41	5.43
13/2	5.39	5.42
15/2	5.38	5.41
17/2	5.36	5.39
19/2	5.35	5.38
21/2	5.33	5.36
23/2	5.31	5.35

Table 1. Computed ratios of electric to magnetic dipole intensities for the low  $J$  lines in the  ${}^2\Pi_{\frac{1}{2}} - {}^2\Pi_{\frac{3}{2}}$  spectrum of SeH. The corresponding ratio for all Q-branch lines is  $5.45 \times 10^{-2}$  (see text)

The dipole moment of SeH was taken to be 0.49 Debye (18). It can be seen that in all cases, the magnetic dipole intensity is approximately twenty times the electric dipole intensity. The ratio of the electric to magnetic dipole intensity for Q branch lines is independent of the quantum number J. This result is discussed in Ref. (17), the ratio is equal to  $(\mu_e B / \mu_B A)^2$ .

The entries in Table 1 imply that the observed spectrum is of the magnetic dipole type. With the given signal-to-noise it is very unlikely that even the strongest electric dipole transitions could be observed. The transitions observed in the experiment described in this chapter are between individual ( $M_J$ ) components of a given rotational level, however the same ratio of electric to magnetic dipole intensity is to be expected.

### 5 (III) c Tuning rates and spectrum isotope structure.

The successful observation of a L.M.R. spectrum depends upon the tuning of the molecular transition into co-incidence with the fixed laser frequency by means of a variable magnetic field. The behaviour of the molecular energy levels in the presence of an external magnetic field is described by the Zeeman terms in the effective Hamiltonian (5.1) and the rate at which a transition frequency tunes with applied field is given by the difference in the rates at which the levels connected by the transition tune. The dominant terms in the Zeeman Hamiltonian for  $^2\Pi$  molecule derive from the interaction of the electronic spin and orbital angular momenta with the magnetic field. Explicitly these are :  
(see for example Ref. (9))

$$H_Z^{(1)} = g_S \mu_B T^1(\underline{S}) \cdot T^1(\underline{B}) + g_L \mu_B T^1(\underline{L}) \cdot T^1(\underline{B}) \quad (5.9)$$

where  $\underline{B}$  is the flux density. The diagonal matrix element in a case (a) representation is given by :



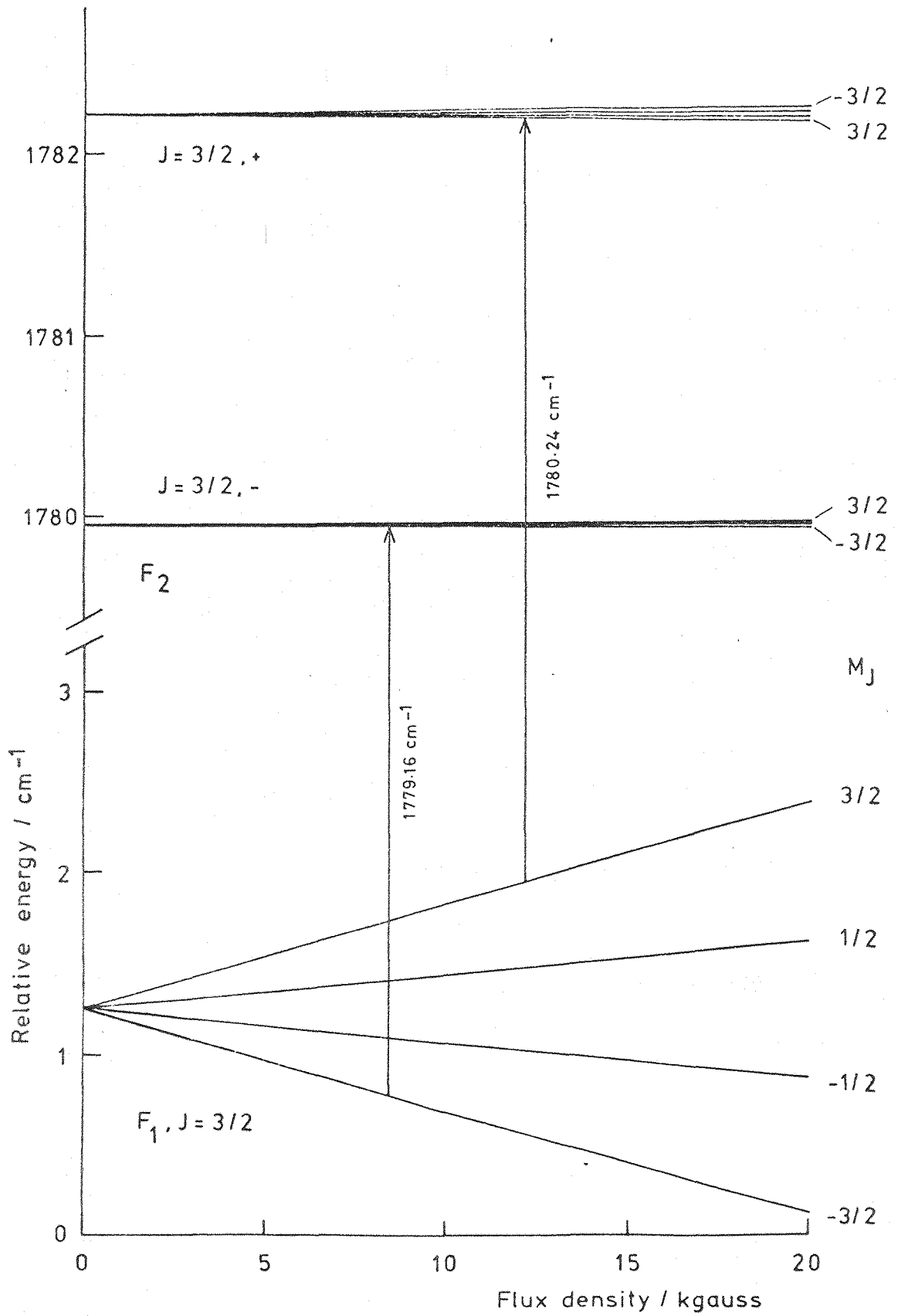
$$\frac{\mu_B B_0 M_J \Omega \{ g_S \Sigma + g_L \Lambda \}}{J(J+1)} \quad (5.10)$$

and this gives us the first order contribution to the energy of a rotational level associated with the case (a) quantum numbers discussed previously. If we assume that  $g_S = 2.0$  and  $g_L = 1.0$  then for the  ${}^2\Pi_{1/2}$  component, there is no contribution from the Zeeman Hamiltonian (5.9) to the energy of a rotational level because  $g_S \Sigma + g_L \Lambda = 0$ . There will of course be some contribution to the energy of these levels derived from the rotational mixing of  ${}^2\Pi_{3/2}$  character discussed in the previous sub-section and from other terms in the full effective Zeeman Hamiltonian for the  ${}^2\Pi$  state discussed by Brown et al (9). These however represent small perturbations to the molecular energy levels and the form of the observed spectrum can be readily understood in terms of the Zeeman effect in the  ${}^2\Pi_{3/2}$  manifold. Figure 2 shows the energy levels associated with the  $J = 3/2$  rotational level for the two fine structure components in SeH, and it is evident that nearly all tuning occurs in the  ${}^2\Pi_{3/2}$  manifold as predicted by Eq. (5.10). Using Eq. (5.10) we can construct a table of relative tuning rates for transitions from various  $M_J$  components of low rotational levels associated with the  $\Omega = 3/2$  component. This is shown in Table II. As might be predicted from (5.10) the fastest tuning transitions for a given  $J$  arise from the largest magnitude  $M_J$  components.

J	$ M_J $	1/2	3/2	5/2	7/2	9/2	11/2
3/2		0.56	1.68				
5/2		0.24	0.72	1.20			
7/2		0.13	0.40	0.67	0.93		
9/2		0.08	0.25	0.42	0.59	0.76	
11/2		0.06	0.18	0.32	0.45	0.57	0.70

Table II. Tuning rates (in MHz/G) for transitions from various  $M_J$  components of low rotational levels in the  ${}^2\Pi_{3/2}$  component. Calculated using Eq. (5.10) assuming no Zeeman shifts in the  ${}^2\Pi_{1/2}$  manifold and  $\mu_B = 1.3996$  MHz/G

Figure 2. The energy levels of the  $J = 3/2$  rotational state of SeH as a function of magnetic field. The lambda doubling in the  ${}^2\Pi_{3/2}$  ( $F_1$ ) component is too small to be shown on the diagram.



Selenium has four main naturally occurring isotopes viz.  $^{76}\text{Se}$  (9%),  $^{78}\text{Se}$  (24%),  $^{80}\text{Se}$  (50%) and  $^{82}\text{Se}$  (9%) and the observed spectrum is expected to show evidence of transitions occurring in molecules containing these different mass nuclei. The case of Q-branch ( $\Delta J = 0$ ) transitions is discussed in detail; similar but not identical results apply for the P- and R- branches of the spectrum. The Q-branch frequencies between the fine structure components in SeH may be approximated by the formula:

$$\nu_Q(J) = \frac{-(A-2B) - 2B^2\{(J + \frac{1}{2})^2 - 1\}}{A} \quad (5.12)$$

+ (small correction terms)

in zero field where A is the spin orbit coupling constant and B the rotational constant. For  $\tilde{X}^2\Pi$  SeH the spin orbit constant is much larger than the rotational constant and the second term in (5.12) represents only a minor J-dependant perturbation to the frequency  $-(A-2B)$ . In the present case, the spin orbit constant is negative and since, for the two most abundant isotopes,  $B^{(78)} > B^{(80)}$  the Q-branch spectrum is predicted to consist of closely spaced doublets the lower frequency component being approximately double the intensity of the other due to the relative isotope abundances. Calculation of the relative sizes of the rotational constants for  $^{78}\text{SeH}$  and  $^{80}\text{SeH}$  suggests a separation between the doublet components of approximately 150 MHz so that this isotope splitting is predicted to be an observable feature of the spectrum; the Doppler linewidth being approximately 1/3 of this value.

The situation in the case of a swept field - fixed frequency experiment is more complicated but in the end more revealing. The possible situations are summarised in Figure 3. Depending on whether the molecular frequency ( $\nu_m$ ) is above or below the laser frequency ( $\nu_l$ ), the line associated with the more abundant  $^{80}\text{Se}$  containing molecules lies to lower or higher magnetic field respectively. In frequency terms the separation between the lines

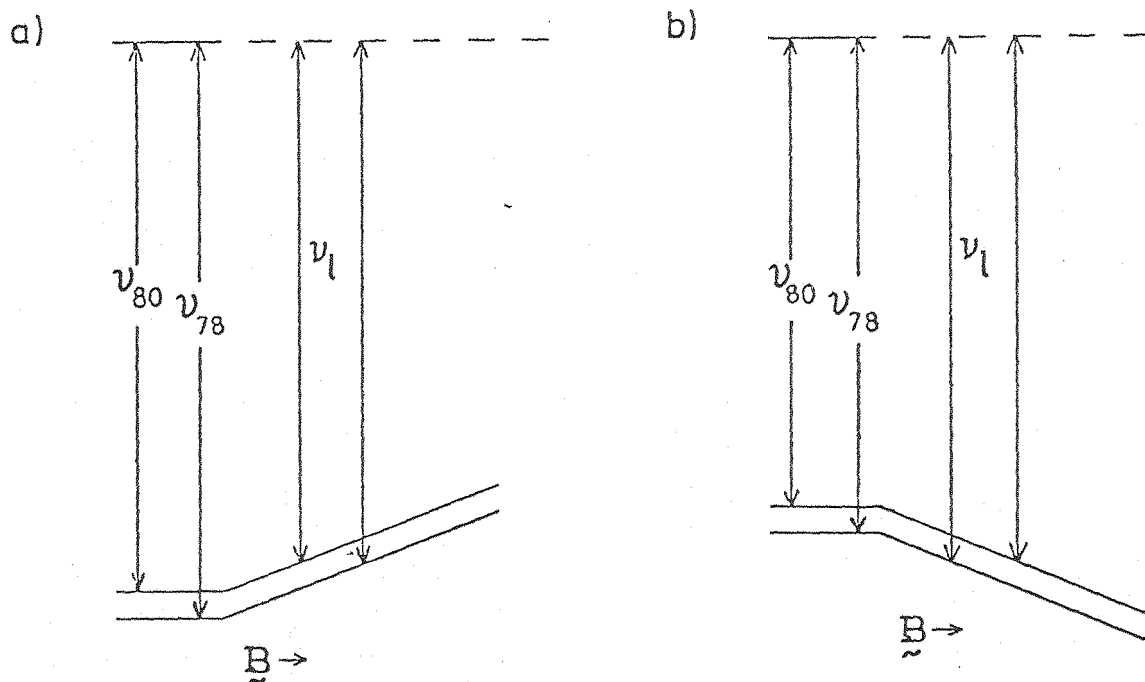


Figure 3. Spectrum isotope structure in a swept field - fixed frequency experiment. The possibilities are a)  $\nu_1 < \nu_m$  when the line associated with molecules containing the  $^{80}\text{Se}$  isotope is observed at lower magnetic field and b)  $\nu_1 > \nu_m$  where the lower field line is associated with those containing the  $^{78}\text{Se}$  isotope. The effects are exaggerated for clarity.

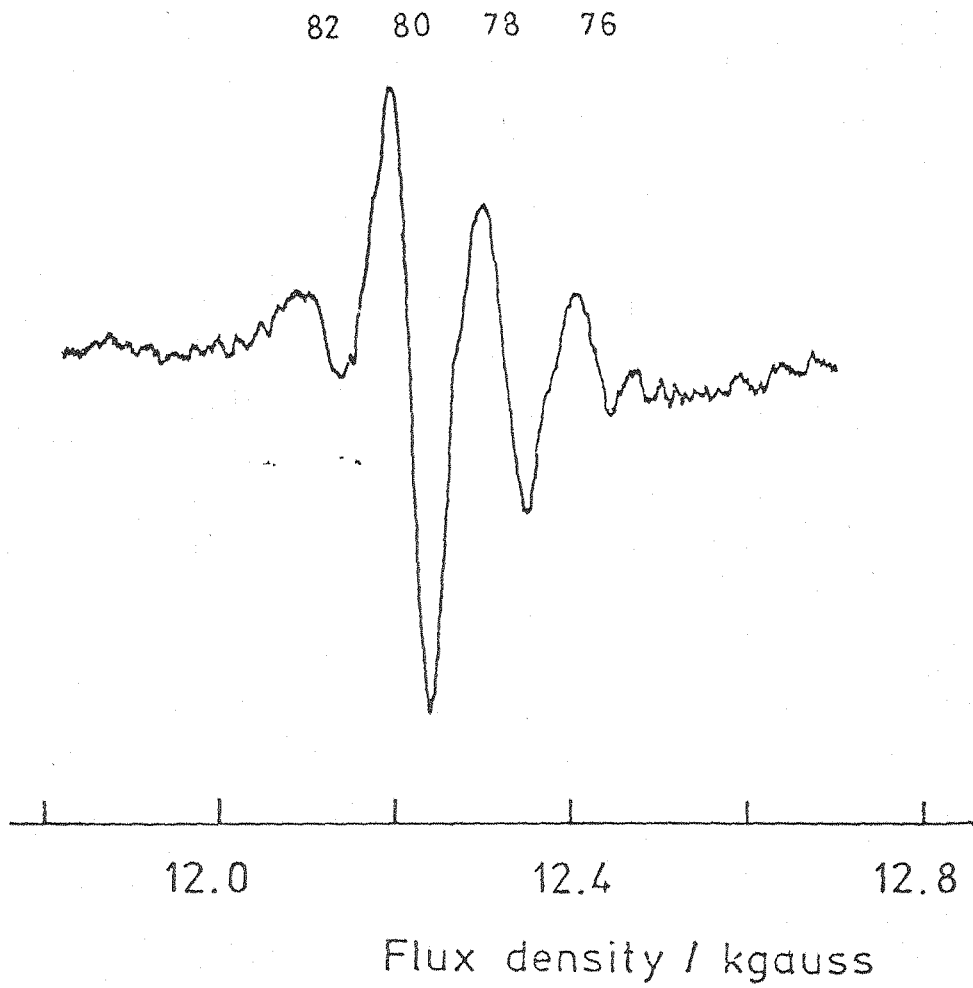


Figure 4. Parallel Q ( $3/2$ ) spectrum observed on the  $1780.24 \text{ cm}^{-1}$  laser line showing clearly the (labelled) isotope structure.

Table III Data and results of least squares fit

J'	M <sub>J</sub> '	parity'	J''	M <sub>J</sub> ''	parity''	field/G	freq/cm <sup>-1</sup>	o-c freq/cm <sup>-1</sup>
1½	1½	+	1½	1½	+	12177.0	1780.23963 <sup>(a)</sup>	-0.67x10 <sup>-3</sup> <sup>(b)</sup>
1½	-1½	-	1½	-1½	-	8484.6	1779.15798	0.17x10 <sup>-2</sup>
1½	-½	-	1½	-1½	-	8390.0	1779.15798	-0.14x10 <sup>-2</sup>
4½	-4½	-	4½	-4½	-	5368.3	1784.33618	-0.60x10 <sup>-3</sup>
4½	-3½	-	4½	-3½	-	6909.0	1784.33618	0.49x10 <sup>-3</sup>
4½	-2½	-	4½	-2½	-	9748.0	1784.33618	-0.70x10 <sup>-3</sup>
1½ <sup>(c)</sup>	1½	+	1½	½	-	7686.75	0.29117	0.17x10 <sup>-5</sup>
1½	½	+	1½	-½	-	7705.91	0.29117	-0.15x10 <sup>-5</sup>
1½	-½	+	1½	-1½	-	7725.02	0.29117	-0.54x10 <sup>-5</sup>
1½	1½	-	1½	½	+	7711.75	0.29117	-0.12x10 <sup>-4</sup>
1½	½	-	1½	-½	+	7731.52	0.29117	-0.89x10 <sup>-5</sup>
1½	-½	-	1½	-1½	+	7751.36	0.29117	-0.93x10 <sup>-5</sup>
2½	-1½	+	2½	-2½	-	17609.6	0.29117	0.55x10 <sup>-4</sup>
2½	-½	+	2½	-1½	-	17723.1	0.29117	-0.86x10 <sup>-5</sup>
2½	½	+	2½	-½	-	17841.3	0.29117	-0.48x10 <sup>-5</sup>
2½	1½	+	2½	½	-	17969.7	0.29117	-0.69x10 <sup>-5</sup>
2½	2½	+	2½	1½	-	18110.5	0.29117	-0.29x10 <sup>-4</sup>
2½	-1½	-	2½	-2½	+	17374.1	0.29117	-0.32x10 <sup>-6</sup>
2½	-½	-	2½	-1½	+	17487.0	0.29117	0.43x10 <sup>-5</sup>
2½	½	-	2½	-½	+	17609.6	0.29117	-0.14x10 <sup>-4</sup>
2½	1½	-	2½	½	+	17738.9	0.29117	0.12x10 <sup>-4</sup>
2½	2½	-	2½	1½	+	17880.1	0.29117	0.17x10 <sup>-4</sup>

(a) Laser frequencies calculated from the Dunham coefficients of Killal et al. [21].

(b) L.M.R. transition frequencies taken to be ten times less precise in the fit.

(c) E.P.R. measurements from Carrington et al. [16]. Note that Table 2 of this reference contains some misassignments of the M<sub>J</sub> quantum number.

Table IV. Molecular Constants for SeH in the  $X^2\Pi$  State<sup>(a)</sup>

	$\tilde{A}$	-1763.34763(41) <sup>(b)</sup>	$g_S$	2.00122 <sup>(e)</sup>
	B	7.791 <sup>(c)</sup>	$g_L'$	1.00072(24) <sup>(b)</sup>
$10^3$	D	0.342 <sup>(c)</sup>	$g_\lambda$	0.0349 <sup>(d)</sup>
	$p + 2q$	1.13526(25) <sup>(b)</sup>	$10^3 g_r$	-0.321(71) <sup>(b)</sup>
$10^2$	q	-0.600403(93) <sup>(b)</sup>	$g_\lambda'$	0.1075(28) <sup>(b)</sup>
$10^4$	$(p_D + 2q_D)$	-0.996 <sup>(d)</sup>	$10^3 g_r^{e_1}$	0.791 <sup>(d)</sup>
$10^5$	$q_D$	0.108 <sup>(d)</sup>		
	$\tilde{\gamma}$	-0.6733 <sup>(c)</sup>		

(a) Values in  $\text{cm}^{-1}$  (where appropriate)

(b) This work. The number in parenthesis is one standard deviation, expressed in units of the last quoted decimal place. The fit was performed with  $A_D$  constrained to zero.

(c) Value from the analysis of the 1500  $\text{\AA}$  band system of SeH [2]. The parameter was constrained to this value in the fit.

(d) Parameter value estimated from a theoretical relationship derived by second order perturbation theory [9,14] and constrained in the fit.

(e)  $g_S$  estimated from the free electron value with corrections for relativistic effects and for spin-orbit mixing of other electronic states by third order perturbation theory (see text).



associated with molecules containing the two more abundant selenium isotopes is always approximately 150 MHz. However in a swept field experiment their separation in gauss will depend on the tuning rate associated with the particular transition. In principle then, the isotope structure of a given line in the L.M.R. spectrum gives information on both the sign and magnitude of the tuning rate of the molecular transition, giving rise to the absorption. This information can then be compared with the entries in Table II and analysis of the spectrum is made considerably easier.

#### 5 (IV) Results and Discussion.

Magnetic dipole transitions between the fine structure components of the  $\tilde{X}^2\Pi$  state of SeH have been observed at a frequency of around  $1780\text{ cm}^{-1}$ . Typical transitions within the Q(3/2) branch are shown in Figure 2 and a portion of the observed spectrum showing clearly the isotope structure predicted in the previous section is reproduced in Figure 4. All lines observed were assigned to belong to the Q-branch of the spectrum and although low J P-branch transitions of  $\Delta M_J = \pm 1$  polarisation are predicted to be both equally intense and have favourable tuning rates, extensive searches failed to reveal any trace of them. This failure is probably due to the sparser nature of the P-branch region of the spectrum; however calculations suggested close coincidence between the P(5/2) spectrum and the  $1742\text{ cm}^{-1}$  laser frequencies and it is unfortunate that no spectra were observed in this region. The observed line positions are quoted in Table III together with their quantum number assignments. They were combined with the previously observed (4) E.P.R. data (also quoted in Table III) in a least squares fit to the parameters appearing in the effective Hamiltonian (5.1).

The complete data set listed in Table III was insufficient to determine all the parameters appearing in the effective Hamiltonian for a  $^2\Pi$  state, and some approximations were necessary in order to

extract the maximum number of parameters reliably. Although the rotational constant could be determined from the second order Zeeman shifts in the E.P.R. data both it and the quartic centrifugal distortion constant ( $D$ ) were better determined in the analysis of the electronic emission data performed by Bollmark et al (2) and were constrained at their values in the final analysis. Similarly, the value adopted for  $\gamma$ , the spin rotation coupling constant, was calculated from the value for  $A_D$  (the centrifugal distortion correction to  $A$ ) determined by the previous authors using the formula derived by Brown and Watson (12).

The fit of the data shown in Table III was obtained by allowing the values of  $A$ ,  $p+2q$ ,  $q$ ,  $g_L'$ ,  $g_R$  and  $g_I'$  to vary.  $D_{p+2q}$  and  $D_q$  and  $g_R^e$  and  $g_I$  were fixed at values predicted by the formulae derived by Veseth (14) and Brown et al (9) using second order perturbation theory suitably corrected to include the dominant third order contributions discussed below. It should be emphasised that fits of similar quality to the one shown could be obtained by allowing other combinations of  $g$ -factors to vary, however the value for the spin anisotropy  $g$ -factor,  $g_I$  was particularly poorly determined (ie. highly correlated with other parameters) by the data. The data was also sensitive to the sum of  $g_L'$  (the effective orbital  $g$ -factor) and  $g_S$  (the effective spin  $g$ -factor) only; consequently the two could not be separately determined in the fit.

For SeH the largest third order contributions to the effective Zeeman Hamiltonian arise from terms which include the spin-orbit operator twice that is of the form  $H_{SO} \times H_{SO} \times H_Z$ . These yield contributions to the values of  $g_L'$ ,  $g_S$  and  $g_I$  in the effective Hamiltonian which may be evaluated if we make the approximation that only the  $\tilde{A}^2\Sigma$  state significantly contaminates the ground state. They are :

$$g_L = g_L^{(1)} - \frac{\alpha^2}{2} (g_L - g_S) \quad (5.13)a$$

$$g_S = g_S^{(1)} + \alpha^2 (g_L - g_S) \quad (5.13)b$$

$$g_I = g_I^{(2)} + \alpha^2 \frac{(g_S - g_L)}{2} \quad (5.13)c$$

where

$$\alpha^2 = \left| \langle \tilde{X}_{\Pi}^2 \frac{1}{2} | H_{SO} | \tilde{A}_{\Sigma}^2 \frac{1}{2} \rangle \right|^2 / (\Delta E)^2$$

and  $\Delta E$  is the separation between the  $\tilde{X}_{\Pi}^2$  and  $\tilde{A}_{\Sigma}^2$  electronic states (a negative quantity).  $g_L^{(1)}$ ,  $g_S^{(1)}$  and  $g_I^{(2)}$  are the values of the g-factors before the third order contributions are taken into account. The correction to  $g_I$  is evidently very small however those to  $g_S$  and  $g_L$  are significant. In the fit the value of  $g_S$  was constrained at 2.00122 a figure arrived at after making relativistic corrections to the free spin g-value of 2.002319 and including the third order contribution above. The latter correction together with the  $\Delta g_L$  second order correction derived by Brown et al (19) predicts a value of 1.0079 for  $g_L'$  which is in accordance with that determined in the fit and to some extent vindicates the approximations made in the third order perturbation theory treatment.

The largest third order contributions to the other g-factors were also investigated. For  $g_R$  and  $g_r^{e'}$  (the rotational and 'off-diagonal' lambda doubling g-factors respectively) the largest third order terms are of the form  $H_{SO} \times H_{rot} \times H_Z$  while for  $g_I'$  (the second lambda doubling g-factor) terms of the form  $H_{SO} \times H_{SO} \times H_Z$  contribute. This last correction is significant, being of the order of 10% of the second order contributions and additive and this is in line with the experimental results; the value of  $g_I'$  determined is larger than the figure estimated by the second order relationships derived by Brown et al (9). The third order contributions to  $g_r^{e'}$  are very small suggesting that the second order relationships (9) should be reliable in this case, however those to  $g_R$  lead to extra terms in the effective Hamiltonian; these were not investigated further since the data were not adequate to determine all the terms already included.

The values determined for  $g_I'$  and  $g_R$  in the fit should not be regarded as definitive because they are sensitive to the value adopted for  $g_I$  which was estimated from the second order relationship

given by Brown et al (9), the third order contribution (5.13)c is negligible in this case. However the values for the parameters appearing in the zero field effective Hamiltonian, ie. A, p and q are comparatively insensitive to the values of the g-factors and can thus be accepted with some confidence. The observation of a P-branch transition would allow a better estimate of the rotational constant and the smaller g-factors, however the former should be available in the near future from analysis of the far infra-red L.M.R. spectrum recently obtained by Davies et al (20).

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