

## A Direct Approach for the Reduction of Diatomic Spectra to Molecular Constants for the Construction of RKR Potentials

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A nonlinear fitting procedure is presented that employs all measured line positions and iteratively compares their values with those calculated from numerically diagonalized model Hamiltonians with adjustable molecular constants. Case (a) wavefunctions with definite parity are introduced as a convenient basis set, and the effects of spin-orbit, spin-spin, spin-rotation, and centrifugal distortion interactions neglected in the Born-Oppenheimer separation are included simultaneously using the Van Vleck transformation. The spectroscopic constants found by this procedure represent the minimum-variance, unbiased set and maintain, to a high degree of accuracy, the separate mechanical and magnetic meanings of the molecular constants. Arguments are presented that such spectroscopic constants with mechanical meaning allow the most accurate construction of potential energy functions using the Rydberg-Klein-Rees (RKR) procedure. Residual mechanical and magnetic ambiguities, such as engendered by  $\Lambda$ -type doubling, are discussed.

### I. INTRODUCTION

Diatomic molecular constants have held the interest of two groups, namely, positional spectroscopists who produce them, and "intensity spectroscopists" who use them. Unfortunately, the overlap integral between these two groups has not always been large. In positional spectroscopy, the molecular constants are often viewed as parameters that reproduce, interpolate, or extrapolate the measured line positions. On the other hand, in intensity spectroscopy, the molecular constants are viewed as parameters from which molecular intensity factors—Franck-Condon factors and rotational line strengths—can be calculated. As a consequence, positional spectroscopists sometimes have reported values for the molecular constants that fit the data but are not the most appropriate for calculating intensity factors, and in turn, intensity spectroscopists sometimes have used these constants without regard to their meaning. For example, a  $B_v$  value is often given for each multiplet of a  $\Pi$  state ( $S > 0$ ) and these effective  $B_v$  values have been used to construct a potential for each multiplet, from which intensity factors were deduced (see Sec. IV), despite the fact that these  $B_v$  values do not describe the moment of inertia of the molecule.

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In reducing line position measurements to molecular constants, ideally one formulates model Hamiltonians for the upper and lower electronic states of the band system and fits the measured line positions to the eigenvalues of these Hamiltonians using a sound statistical procedure. In practice, several impediments occur. Because of the inadequacy of the Born–Oppenheimer separation of the total molecular energy into electronic, vibrational, and rotational parts, a large number of molecular constants must be introduced to account for the energy level structure of the molecule. These constants appear in the expressions for the energy levels in an often complex and nonlinear manner so that their determination poses a burdensome problem, sometimes requiring the solution of transcendental equations. Moreover, additional difficulties may arise from the need to determine the molecular constants using proper statistics.

For closed-shell diatomics ( $^1\Sigma$  states), the energy levels may be represented by the simple expression  $E(v, J) = T_v + B_v J(J + 1) - D_v J^2(J + 1)^2 + H_v J^3(J + 1)^3 + \dots$ . For open-shell diatomics, the energy level expressions are the roots of a secular determinant calculated from the matrix elements of a model Hamiltonian.

Basically, these matrix elements have been available since the early work of Van Vleck (1). However, if the model requires many constants to represent the molecular energy levels, the application of these ponderous algebraic expressions to experimental data has encouraged truncation and simplification. In such simplified forms, the molecular constants no longer have exactly their original meanings because, as adjustable parameters in a least-squares fit, they have absorbed, to some extent, the effects of the missing constants. Consequently, the constants in these truncated or approximated forms often embody both mechanical and magnetic properties. This loss of the purely mechanical meaning attributed to the band origin and rotational constants, i.e., the vibrating rotator model (2), impairs the construction of a reliable potential (3) from these constants using the Rydberg–Klein–Rees (RKR) procedure. Of course, the accompanying loss of the purely magnetic meaning attributed to the other constants similarly impairs the direct comparison with *ab initio* calculations of the fine-structure splittings. In fact, this blurring of the mechanical and magnetic meanings of molecular constants and the concomitant uncertainty in the construction of RKR potentials was our original motivation (4) in examining the reduction of diatomic spectra.

In addition to the problem associated with the forms of the energy level expressions, there are problems of a purely statistical nature related to the fitting of the observed line positions to the theoretical energy level expressions. The time-honored method of determining rotational constants is the use of combination differences (5). Although combination differences are extremely useful in carrying out a preliminary analysis, their statistical shortcomings for producing final values of the molecular constants have been pointed out by Åslund (6) and are summarized in a following paper (7). It suffices here to note that combination differences do not use all the measured line positions and the method implicitly assumes that all measurement errors are associated with the state under analysis.

We present in this paper a practical procedure for reducing diatomic spectra to molecular constants that avoids the problems discussed above. Calculated line positions are iteratively compared to the measured line positions in a nonlinear least-squares fit. The calculated line positions are the appropriate differences between the eigenvalues of the upper and lower state Hamiltonians, in which the molecular constants appear as

adjustable parameters. Because this procedure is numerical, algebraic expressions for the roots of secular determinants are not explicitly required. Note that, in contrast to combination differences, this procedure utilizes the full body of measured line positions. Moreover, the resulting values of the molecular constants are the minimum-variance, unbiased estimates and their errors are statistically meaningful.

In the next section, we discuss the development of the model Hamiltonian and summarize the evaluation of its matrix elements in a Hund's case (a) basis set with well-defined parity. The matrix elements connecting different vibrational levels of the same electronic state (centrifugal distortion) and those connecting different electronic states ( $\Lambda$ -doubling and spin-splitting) are treated simultaneously in the same manner using the Van Vleck transformation. In Section III, we present the details of the nonlinear least-squares fitting procedure and in the final section we emphasize the problems associated with the loss of purely mechanical meaning in the molecular constants used to construct RKR potentials.

We feel that the more accurate reduction of data to molecular constants with sound statistical meaning and with a minimum loss of mechanical and magnetic significance warrants consideration of this direct approach. It is ironic that the approach of comparing measured line positions to those calculated from diagonalizing effective Hamiltonians with adjustable molecular constants is being increasingly applied to the analysis of polyatomic spectra ( $\delta$ ), while perhaps for historical reasons this approach has not yet won general favor for diatomics. We hope that some direct approach,<sup>2</sup> such as we present in what follows, will gain acceptance as a means of obtaining molecular constants from measured line positions.

## II. THEORY

### A. Molecular Hamiltonian

The problem of deriving a satisfactory, effective Hamiltonian for a freely vibrating, rotating diatomic molecule has been considered at length by several authors (9-10). In the absence of external fields we may write

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{rot}} + \mathcal{H}_{fs} + \mathcal{H}_{hfs}, \quad (1)$$

where  $\mathcal{H}_0$  represents the nonrelativistic Hamiltonian of the nonrotating molecule,  $\mathcal{H}_{\text{rot}}$  symbolizes the rotational motion of the nuclei,  $\mathcal{H}_{fs}$  contains magnetic terms that cause the fine structure, and  $\mathcal{H}_{hfs}$  includes all nuclear spin and nuclear moment terms that cause the hyperfine structure. Because hyperfine splittings are rarely resolved in optical spectra, we disregard  $\mathcal{H}_{hfs}$  in what follows.

According to the Born-Oppenheimer approximation, the energy associated with  $\mathcal{H}_0$  depends only on the electronic and vibrational quantum numbers  $n$  and  $v$ . Since we are concentrating our attention on the rotational analysis of diatomic spectra, the exact

<sup>2</sup> It is encouraging to note these techniques are under development at several laboratories, for example: L. Veseth J. Phys. **B 5**, 229 (1972); J. W. Johns (private communication); A. J. Merer (private communication); W. Klemperer, R. W. Field, T. H. Bergeman and co-workers (private communication); T. E. H. Walker (private communication).

form of  $\mathcal{H}_0$  is of little concern to us here, whereas the form of  $\mathcal{H}_{\text{rot}}$ , given by

$$\begin{aligned}\mathcal{H}_{\text{rot}} &= B(\boldsymbol{r})\mathbf{R}^2 \\ &= B(\boldsymbol{r})(\mathbf{J} - \mathbf{L} - \mathbf{S})^2,\end{aligned}\quad (2)$$

plays a major role in the subsequent analysis. In Eq. (2)

$$B(\boldsymbol{r}) = h/8\pi^2c\mu r^2 \quad (3)$$

is the radial part of the rotational energy operator, defined in terms of the internuclear distance  $r$  and the reduced mass  $\mu$ , and

$$\mathbf{R} = \mathbf{J} - \mathbf{L} - \mathbf{S} \quad (4)$$

is the rotational angular momentum operator of the nuclei, defined in terms of  $\mathbf{J}$ ,  $\mathbf{L}$ , and  $\mathbf{S}$ , the total, the electronic orbital, and the electronic spin angular momentum operators.

The fine structure Hamiltonian depends in a complex manner on the orbital and spin angular momenta,  $\mathbf{l}_i$  and  $\mathbf{s}_i$ , of the individual electrons  $i$ , the interelectronic distance  $r_{ij}$  between any two electrons, the distance between any electron and any nucleus  $r_{ki}$ , the charge  $Z_k$  on the nucleus  $k$ , and the internuclear distance  $r$ . We shall refer to this as the microscopic form of the fine structure Hamiltonian. However, it is traditional in spectroscopic work to replace the microscopic fine structure Hamiltonian by a phenomenological fine structure Hamiltonian that represents the major magnetic interactions by a limited set of adjustable parameters. In this procedure, all terms in  $\mathcal{H}_{f_s}$  are omitted that cause a uniform shift rather than a splitting of the fine structure components. The fine structure Hamiltonian is then regarded as a sum of three terms

$$\mathcal{H}_{f_s} = \mathcal{H}_{SO} + \mathcal{H}_{SS} + \mathcal{H}_{SR}, \quad (5)$$

where

$$\mathcal{H}_{SO} = A(\boldsymbol{r})\mathbf{L}\cdot\mathbf{S} \quad (6)$$

is the so-called spin-orbit interaction,

$$\mathcal{H}_{SS} = \epsilon(\boldsymbol{r})(3S_z^2 - S^2) \quad (7)$$

is the so-called spin-spin interaction, and

$$\mathcal{H}_{SR} = \gamma(\boldsymbol{r})\mathbf{N}\cdot\mathbf{S} \quad (8)$$

is the so-called spin-rotation interaction. In Eq. (7) the  $z$  axis is chosen to lie along the internuclear axis, and in Eq. (8)  $\mathbf{N} = \mathbf{J} - \mathbf{S} = \mathbf{R} + \mathbf{L}$  is the total orbital angular momentum operator. We note that some authors, e.g., Kovács (11) and Bennett (12), represent the phenomenological spin-rotation interaction by  $\gamma(\boldsymbol{r})\mathbf{R}\cdot\mathbf{S}$  rather than  $\gamma(\boldsymbol{r})\mathbf{N}\cdot\mathbf{S}$ . The difference between these two choices is a term  $\gamma(\boldsymbol{r})\mathbf{L}\cdot\mathbf{S}$  that mimics the phenomenological spin-orbit interaction  $A(\boldsymbol{r})\mathbf{L}\cdot\mathbf{S}$ . With the choice  $\gamma(\boldsymbol{r})\mathbf{R}\cdot\mathbf{S}$  Hund's case (b) coupling is given by the condition  $A = \gamma B$ . However, we wish to retain the more traditional identification of Hund's case (b) coupling with  $A = 0$ . Accordingly, we define the spin-rotation interaction as in Eq. (8).

There has been considerable attention given to the relation between the parameters of the phenomenological spin-orbit (1,13-15), spin-spin (16-20), and spin-rotation (21-23) interactions and the microscopic form of the fine structure Hamiltonian. It may

be shown that to good approximation the operator replacements given in Eqs. (6)–(8) may be used to calculate matrix elements diagonal in  $S$ . However, for matrix elements off-diagonal in  $S$ , the microscopic forms of these interactions must be employed for they connect states that according to Eqs. (6)–(8) would not otherwise be perturbed.

The energy levels of a diatomic molecule are given by the solutions to the time-independent Schrödinger equation

$$\mathcal{H}\psi = E\psi \quad (9)$$

for the molecular Hamiltonian  $\mathcal{H}$  shown in Eq. (1). In practice, one chooses a convenient finite basis set  $\varphi_i$  and expands the eigenfunctions  $\psi$  in terms of  $\varphi_i$

$$\psi = \sum_i a_i \varphi_i. \quad (10)$$

This then reduces the solution of Eq. (9) to finding the roots of the secular determinant

$$|\mathcal{H}_{ij} - E\delta_{ij}| = 0. \quad (11)$$

The choice of basis set is unquestionably arbitrary and any complete basis set would suffice provided the calculations are carried out to sufficient accuracy. However, by making a wise choice of the initial basis set,  $\mathcal{H}$  may be roughly partitioned into diagonal blocks (sub-matrices) that weakly interact with one another. The diagonal blocks refer to Born–Oppenheimer states.

We choose the wavefunctions appropriate to Hund's case (a) coupling as the basis set. These wavefunctions are simultaneously eigenfunctions of the operators  $J^2$ ,  $S^2$ ,  $J_z$ ,  $S_z$ , and  $L_z$  with eigenvalues  $J(J+1)$ ,  $S(S+1)$ ,  $\Omega$ ,  $\Sigma$ , and  $\Lambda$ , respectively, but the  $L^2$  operator is not diagonal in this representation. We choose the phase convention that

$$\langle J \Omega \pm 1 | J_{\mp} | J \Omega \rangle = [J(J+1) - \Omega(\Omega \pm 1)]^{\frac{1}{2}} \quad (12)$$

and

$$\langle S \Sigma \pm 1 | S_{\pm} | S \Sigma \rangle = -[S(S+1) - \Sigma(\Sigma \pm 1)]^{\frac{1}{2}}, \quad (13)$$

where  $J_{\pm} = J_x \pm iJ_y$  and  $S_{\pm} = S_x \pm iS_y$  and where we, follow Van Vleck's procedure of reversed angular momentum (1).

For a given electronic state  $n$ , vibrational level  $v$ , and rotational level  $J$ , there are  $2S+1$  possible spin projections  $-S, -S+1, \dots, S$ , and 2 possible orbital angular momentum projections  $-\Lambda$  and  $\Lambda$  for  $\Lambda \neq 0$ . Thus, the energy levels are found, to first approximation, by diagonalizing a  $(2S+1)(2-\delta_{\Lambda 0})$  by  $(2S+1)(2-\delta_{\Lambda 0})$  submatrix which we shall call the  $nvJSA$  block (Born–Oppenheimer state). Then the matrix elements that connect different  $nvJSA$  blocks must be considered. However, if their magnitude is small and the interacting blocks are well separated in energy, the effect of the off-diagonal matrix elements may be included simply by perturbation theory. In what follows we first consider the matrix elements within a single  $nvJSA$  block, and then the energy corrections caused by matrix elements that connect different blocks.

### B. Matrix Elements Within the Same $nvJSA$ Block

The calculation of case (a) matrix elements has been considered at length by various authors, most notably by Van Vleck (1), Hougen (24), Kovács (11), Freed (25), and

TABLE I  
CASE (a) MATRIX ELEMENTS WITHIN THE SAME  $nvJSA$  BLOCK

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$\langle \Lambda\Sigma   \mathcal{H}_0   \Lambda\Sigma \rangle$	$= T_v$
$\langle \Lambda\Sigma   \mathcal{H}_{\text{rot}}   \Lambda\Sigma \rangle$	$= B_v[J(J+1) - \Omega^2 + S(S+1) - \Sigma^2]$
$\langle \Lambda\Sigma   \mathcal{H}_{\text{rot}}   \Lambda, \Sigma \pm 1 \rangle$	$= B_v[J(J+1) - \Omega(\Omega \pm 1)]^\dagger[S(S+1) - \Sigma(\Sigma \pm 1)]^\dagger$
$\langle \Lambda\Sigma   \mathcal{H}_{SO}   \Lambda\Sigma \rangle$	$= A_v\Lambda\Sigma$
$\langle \Lambda\Sigma   \mathcal{H}_{SS}   \Lambda\Sigma \rangle$	$= \epsilon_v[3\Sigma^2 - S(S+1)]$
$\langle \Lambda\Sigma   \mathcal{H}_{SR}   \Lambda\Sigma \rangle$	$= \gamma_v[\Sigma\Omega - S(S+1)]$
$\langle \Lambda\Sigma   \mathcal{H}_{SR}   \Lambda, \Sigma \pm 1 \rangle$	$= -\frac{1}{2}\gamma_v[J(J+1) - \Omega(\Omega \pm 1)]^\dagger[S(S+1) - \Sigma(\Sigma \pm 1)]^\dagger$

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Miller, Levy, and Carrington (10). Consequently, we will not repeat these derivations but list instead in Table I the matrix elements that occur within the same  $nvJSA$  block. The parameter  $T_v$ ,  $B_v$ ,  $A_v$ ,  $\epsilon_v$ , and  $\gamma_v$  appearing in Table I are the familiar spectroscopic constants associated with each type of interaction for the state  $n, v$ . They represent the expectation values of the radial parts of their respective operators,<sup>3</sup> specifically

$$\begin{aligned}
 T_v &= \langle nv | \mathcal{H}_0 + B(\mathbf{r})(L_x^2 + L_y^2) | nv \rangle \\
 B_v &= \langle nv | B(\mathbf{r}) | nv \rangle \\
 A_v &= \langle nv | A(\mathbf{r}) | nv \rangle \\
 \epsilon_v &= \langle nv | \epsilon(\mathbf{r}) | n_v \rangle \\
 \gamma_v &= \langle nv | \gamma(\mathbf{r}) | nv \rangle.
 \end{aligned}
 \tag{14}$$

We follow the customary practice of incorporating into  $T_v$  the term  $\langle B(\mathbf{r})(L_x^2 + L_y^2) \rangle$  arising from the diagonal matrix elements of  $\mathcal{H}_{\text{rot}}$ . We note that this apparently unavoidable approximation introduces a rotational contribution into the band origin, which is normally regarded as having only vibrational significance.

Because of the radial dependence of these operators, the molecule, as it rotates, couples neighboring vibrational levels within the same electronic state. Furthermore, because of terms such as  $\mathbf{J} \cdot \mathbf{L}$  and  $\mathbf{L} \cdot \mathbf{S}$ , there are also nondiagonal matrix elements that couple different electronic states into the  $nvJSA$  block. The levels of the  $nvJSA$  block may be said to be perturbed by these other interactions. Occasionally, the perturbation can be ascribed to a pair or a small number of levels from neighboring blocks. Then the effect of the perturbation can be treated by diagonalizing the matrix of the interacting levels provided the locations and symmetry designations of the perturbing levels are known. This amounts to all orders of perturbation theory. For example, this technique has been applied with notable success to the low-lying valence states of CO (26); however, this requires the knowledge of energy locations (i.e.,  $T_v$ ,  $G_v$ ,  $B_v$ , and  $D_v$ ) and symmetry designation of all interacting levels. More generally, the perturbations are small in magnitude and large in number. Moreover, they involve many interacting levels from distant blocks whose energy positions are often poorly known. In this latter case, an exact treatment is impossible and resort must be made to some approximate pro-

<sup>3</sup> It is customary in microwave spectroscopy to call the diagonal spin-spin interaction constant  $\lambda_v$  where  $\lambda_v = \frac{2}{3}\epsilon_v$ .

cedure. Thus in order to construct a generally applicable procedure for obtaining molecular constants from the majority of diatomic spectra, we treat these interactions by incorporating their effects on the  $nvJSA$  block of interest. This is accomplished using an approximation, introduced by Van Vleck (1,27-29) which is similar to second-order perturbation theory. When this procedure is applicable, we need no longer diagonalize the supermatrix of interacting blocks.

### C. The Van Vleck Transformation

Let the Hamiltonian be written as

$$H = H_0 + \lambda H_1, \quad (15)$$

where  $\lambda$  denotes the order of the perturbation. We assume that the matrix elements of  $H_0$  lie entirely within diagonal blocks while the matrix elements of  $H_1$  may lie inside or outside diagonal blocks. A unitary transformation can be applied to  $H$  that removes, to first order in  $\lambda$ , the matrix elements of  $H_1$  that lie outside of the diagonal blocks. The remaining matrix elements of  $H_1$  that lie outside of the diagonal blocks are second order in  $\lambda$  and they contribute to the energy only in fourth order in  $\lambda$ . Thus through third order in  $\lambda$ , the transformed matrix of  $H$  consists of diagonal blocks. Let the matrix elements of the  $nvJSA$  block of interest be indexed by  $i, j, k$ , etc. and let  $\alpha, \beta, \gamma$ , etc. label levels of other blocks. Then the unitary transformation causes the matrix elements of  $H$  within the  $nvJSA$  block to have the form

$$H_{ij} = H_{ij}^{(0)} + \lambda H_{ij}^{(1)} + \lambda^2 H_{ij}^{(2)} + \lambda^3 H_{ij}^{(3)}, \quad (16)$$

where

$$H_{ij}^{(0)} = \langle i | H_0 | j \rangle = E_i \delta_{ij}, \quad (17)$$

$$H_{ij}^{(1)} = \langle i | H_1 | j \rangle, \quad (18)$$

$$H_{ij}^{(2)} = \sum_{\alpha} \frac{\frac{1}{2}(E_i + E_j) - E_{\alpha}}{(E_i - E_{\alpha})(E_j - E_{\alpha})} \langle i | H_1 | \alpha \rangle \langle \alpha | H_1 | j \rangle, \quad (19)$$

and

$$H_{ij}^{(3)} = \sum_{\alpha} \left[ \sum_{\beta} \frac{\langle i | H_1 | \alpha \rangle \langle \alpha | H_1 | \beta \rangle \langle \beta | H_1 | j \rangle}{(E_i - E_{\alpha})(E_j - E_{\beta})} - \frac{1}{2} \sum_k \frac{\langle i | H_1 | k \rangle \langle k | H_1 | \alpha \rangle \langle \alpha | H_1 | j \rangle}{(E_k - E_{\alpha})(E_j - E_{\alpha})} - \frac{1}{2} \sum_k \frac{\langle i | H_1 | \alpha \rangle \langle \alpha | H_1 | k \rangle \langle k | H_1 | j \rangle}{(E_k - E_{\alpha})(E_i - E_{\alpha})} \right]. \quad (20)$$

Equations (16)–(20) constitute the Van Vleck transformation. According to this procedure the corrections through third order in the perturbation  $H_1$  are found by diagonalizing the  $(2S + 1)(2 - \delta_{0\lambda})$  by  $(2S + 1)(2 - \delta_{0\lambda})$  block given by Eqs. (16)–(20). It suffices in most applications to retain only the second-order correction in the perturbation. A further simplification results if the energy separation between the interacting blocks is much larger than the energy separation between the fine structure components of the  $nvJSA$  block. Then to good approximation the correction matrix

$H_{ij}^{(2)}$  may be written

$$H_{ij}^{(2)} = \sum_{\alpha} \frac{\langle i | H_1 | \alpha \rangle \langle \alpha | H_1 | j \rangle}{E_{nvJ} - E_{n'v'J}}, \quad (21)$$

where  $E_{nvJ} - E_{n'v'J}$  is the energy difference between the centers of the unperturbed blocks  $nvJSA$  and  $n'v'JS'A'$ . Equation (21) closely resembles the form of second-order perturbation theory. We illustrate next the Van Vleck transformation by using it to correct for the effects of centrifugal distortion (24,30).

#### D. Matrix Elements Connecting Different Vibrational $nvJSA$ Blocks

The radial dependence of the interactions  $\mathcal{H}_{\text{rot}}$ ,  $\mathcal{H}_{SO}$ ,  $\mathcal{H}_{SS}$ , and  $\mathcal{H}_{SR}$  cause neighboring vibrational levels to be coupled together. Let us assume that the vibrational spacings are large compared to the fine structure splittings. Because  $\mathcal{H}_{\text{rot}}$  and  $\mathcal{H}_{SO}$  predominantly determine the rotational energy level structure, we ignore the radial dependence of  $\mathcal{H}_{SS}$  and  $\mathcal{H}_{SR}$  in what follows. First, let us concentrate our attention on  $\mathcal{H}_{\text{rot}}$ . According to Eq. (21) this may be treated through second order in this interaction by adding to  $H_{ij}^{(0)}$  and  $H_{ij}^{(1)}$  the correction matrix

$$H_{ij}^{(2)} = \sum_{v'\Omega'\Sigma'} \frac{\langle nvJ\Omega_i\Sigma_i | \mathcal{H}_{\text{rot}} | n'v'J\Omega'\Sigma' \rangle \langle n'v'J\Omega'\Sigma' | \mathcal{H}_{\text{rot}} | nvJ\Omega_j\Sigma_j \rangle}{E_{nv} - E_{n'v'}}. \quad (22)$$

We may separate Eq. (22) into a product of angular and radial factors

$$H_{ij}^{(2)} = \left[ \sum_{v'} \frac{\langle nv | B(r) | n'v' \rangle \langle n'v' | B(r) | nv \rangle}{E_{nv} - E_{n'v'}} \right] \times \left[ \sum_{\Omega'\Sigma'} \langle J\Omega_i\Sigma_i | \mathbf{R}^2 | J\Omega'\Sigma' \rangle \langle J\Omega'\Sigma' | \mathbf{R}^2 | J\Omega_j\Sigma_j \rangle \right] = -D_v \langle \Omega_i\Sigma_i | \mathbf{R}^4 | \Omega_j\Sigma_j \rangle, \quad (23)$$

where we have equated the radial factor to the centrifugal distortion constant  $-D_v$  (31), and where we have neglected the mixing of other electronic states caused by matrix elements of  $\mathbf{R}^2$  off-diagonal in  $\Lambda$ .

Similarly, if the perturbation  $\mathcal{H}_{\text{rot}}$  is treated through third order, we have the additional centrifugal distortion term of the form

$$H_{ij}^{(3)} = H_v \langle \Omega_i\Sigma_i | \mathbf{R}^6 | \Omega_j\Sigma_j \rangle. \quad (24)$$

The matrix elements of  $\mathbf{R}^4$  and  $\mathbf{R}^6$  within the same block may be evaluated by standard means (32), and the results are collected in Table II. From Eqs. (23) and (24) we see that centrifugal distortion may be treated as if  $\mathcal{H}_{\text{rot}}$  were replaced by an effective rotational Hamiltonian of the form

$$\mathcal{H}_{\text{rot}} = B_v \mathbf{R}^2 - D_v \mathbf{R}^4 + H_v \mathbf{R}^6. \quad (25)$$

The spin-orbit interaction may also couple together neighboring vibrational levels through the weak radial dependence of  $A(r)$  (33). If we consider the centrifugal distortion effects caused simultaneously by  $\mathcal{H}_{\text{rot}}$  and  $\mathcal{H}_{SO}$  we must introduce two additional



centrifugal distortion parameters

$$a_{Dv} = \sum_{v'} \frac{\langle nv | A(r) | nv' \rangle^2}{E_{nv} - E_{nv'}} \quad (26)$$

and

$$A_{Dv} = 2 \sum_{v'} \frac{\langle nv | A(r) | nv' \rangle \langle nv' | B(r) | nv \rangle}{E_{nv} - E_{nv'}}. \quad (27)$$

Table II also contains the additional matrix elements resulting from these centrifugal distortion corrections. We note that the matrix elements of  $a_{Dv}$  have no  $J$  dependence, and the  $\Sigma$  dependence is the same as the diagonal spin-spin interaction constant,  $\epsilon_v$ . Hence for  $\Lambda \neq 0$  states,  $a_{Dv}$  and  $\epsilon_v$  are inextricably mixed and in a least-squares fit to the data, *totally correlated*. Consequently, we omit further reference to  $a_{Dv}$ , but it must be recognized that the value for  $\epsilon_v$  will include the effects of  $a_{Dv}$ . The parameter  $A_{Dv}$  is often referred to as  $2A_J$  in the literature (33-34). Note that the matrix elements involving  $A_{Dv}$  are  $J$ -dependent.

Inspection of Tables I and II shows that there are no nonvanishing matrix elements between levels with different values of  $\Lambda$ . Thus, to this approximation, the  $nvJ\Sigma$  block separates into two identical, diagonal subblocks, one for  $+\Lambda$  and one for  $-\Lambda$ , provided  $\Lambda \neq 0$ . This corresponds to the twofold degeneracy of the  $\Lambda$  components. However, when we consider perturbations from neighboring electronic states, which are caused by terms we have so far neglected, then this degeneracy is removed.

TABLE II

CASE (a) CENTRIFUGAL DISTORTION MATRIX ELEMENTS OF THE ROTATIONAL AND OF THE SPIN-ORBIT HAMILTONIANS

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$$\begin{aligned} \langle \Lambda \Sigma | \mathcal{H}_{\text{rot}} + \mathcal{H}_{SO} | \Lambda \Sigma \rangle &= -D_v [f_1^2(\Omega \Sigma) + f_2(\Omega \Sigma) + f_3(\Omega \Sigma)] \\ &\quad + H_v f_1^3(\Omega \Sigma) + 2f_1(\Omega \Sigma) [f_2(\Omega \Sigma) + f_3(\Omega \Sigma)] \\ &\quad + f_1(\Omega + 1, \Sigma + 1) f_2(\Omega \Sigma) + f_1(\Omega - 1, \Sigma - 1) f_3(\Omega \Sigma) \\ &\quad + a_{Dv} \Lambda^2 \Sigma^2 + A_{Dv} \Lambda \Sigma f_1(\Omega \Sigma) \\ \langle \Lambda \Sigma | \mathcal{H}_{\text{rot}} + \mathcal{H}_{SO} | \Lambda, \Sigma \pm 1 \rangle &= -D_v f_4(\Omega \Sigma) [f_1(\Omega \Sigma) + f_1(\Omega \pm 1, \Sigma \pm 1)] \\ &\quad + H_v f_4(\Omega \Sigma) [f_1^2(\Omega \Sigma) + f_1(\Omega \Sigma) f_1(\Omega \pm 1, \Sigma \pm 1) \\ &\quad + f_1^2(\Omega \pm 1, \Sigma \pm 1) + f_4^2(\Omega \pm 1, \Sigma \pm 1) + f_4^2(\Omega \Sigma) \\ &\quad + f_4^2(\Omega \mp 1, \Sigma \mp 1)] - A_{Dv} \Lambda (\Sigma \pm \frac{1}{2}) f_4(\Omega \Sigma) \\ \langle \Lambda \Sigma | \mathcal{H}_{\text{rot}} + \mathcal{H}_{SO} | \Lambda, \Sigma \pm 2 \rangle &= -D_v f_4(\Omega \Sigma) f_4(\Omega \pm 1, \Sigma \pm 1) + H_v f_4(\Omega \Sigma) f_4(\Omega \pm 1, \Sigma \pm 1) \\ &\quad [f_1(\Omega \Sigma) + f_1(\Omega \pm 1, \Sigma \pm 1) + f_1(\Omega \pm 2, \Sigma \pm 2)] \\ \langle \Lambda \Sigma | \mathcal{H}_{\text{rot}} + \mathcal{H}_{SO} | \Lambda, \Sigma \pm 3 \rangle &= H_v f_4(\Omega \Sigma) f_4(\Omega \pm 1, \Sigma \pm 1) f_4(\Omega \pm 2, \Sigma \pm 2) \end{aligned}$$

where

$$\begin{aligned} f_1(\Omega \Sigma) &= J(J+1) - \Omega^2 + S(S+1) - \Sigma^2 \\ f_2(\Omega \Sigma) &= [J(J+1) - \Omega(\Omega+1)][S(S+1) - \Sigma(\Sigma+1)] \\ f_3(\Omega \Sigma) &= [J(J+1) - \Omega(\Omega-1)][S(S+1) - \Sigma(\Sigma-1)] \\ f_4(\Omega \Sigma) &= [J(J+1) - \Omega(\Omega \pm 1)]^2 [S(S+1) - \Sigma(\Sigma \pm 1)]^2 \end{aligned}$$


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TABLE III  
CASE (a) MATRIX ELEMENTS CONNECTING  $nvJSA$  BLOCKS WITH  
DIFFERENT VALUES OF  $\Lambda$  OR  $S$

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$$\begin{aligned} \langle nvJ\Omega SA\Sigma | \mathcal{H}_{\text{rot}} | n'v'J\Omega \pm 1, S \Lambda \pm 1, \Sigma \rangle &= \langle nvJ | 2B(r)(L_+ + L_-)/2 | n'v'J \rangle [J(J+1) - \Omega(\Omega \pm 1)]^\dagger \\ \langle nvJ\Omega SA\Sigma | \mathcal{H}_{\text{rot}} + \mathcal{H}_{SO} | n'v'J\Omega S \Lambda \pm 1, \Sigma \mp 1 \rangle &= \langle nvJ | [2B(r) + A(r)](L_+ + L_-)/2 | n'v'J \rangle [S(S+1) - \Sigma(\Sigma \mp 1)]^\dagger \\ \langle nvJ\Omega SA\Sigma | \mathcal{H}_{SO} | n'v'J\Omega S' \Lambda' \Sigma' \rangle &= (-1)^{\Lambda' - \Lambda} C(S'1S; \Sigma', \Lambda' - \Lambda, \Sigma) A_v^{\Lambda S; \Lambda' S'} \\ \langle nvJ\Omega SA\Sigma | \mathcal{H}_{SS} | nvJ\Omega S \Lambda \pm 2, \Sigma \mp 2 \rangle &= \frac{1}{2} \alpha_v [(S \mp \Sigma + 1)(S \pm \Sigma)(S \mp \Sigma + 2)(S \pm \Sigma - 1)]^\dagger \end{aligned}$$


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### E. Matrix Elements Connecting Different Electronic $nvJSA$ Blocks

Within the framework of the fine structure Hamiltonian given by Eqs. (5)–(8) there are only two types of terms that connect different electronic states. These are listed in Table III. The first type, which is of the form  $J_+L_- + J_-L_+$ , represents a Coriolis interaction arising from  $\mathcal{H}_{\text{rot}}$ . It connects electronic states differing by one unit in  $\Lambda$ . This interaction is  $J$ -dependent and its magnitude increases with increasing  $J$ . In the literature this is often referred to as  $L$ -uncoupling. Because this interaction may affect the  $\pm \Lambda$  components differently, it contributes to a  $J$ -dependent splitting of the  $\Lambda$  doublets. The second type of interaction, which is of the form  $L_+S_- + L_-S_+$ , arises from both  $\mathcal{H}_{\text{rot}}$  and  $\mathcal{H}_{SO}$ . It is independent of  $J$  and thus contributes primarily to  $J$ -independent shifts in the  $\Lambda$  doublets.

If the microscopic form of the fine structure Hamiltonian is considered, additional matrix elements are found that are diagonal in  $\Omega$  but with  $\Delta S = 0$ , or  $\pm 1$ . In particular, the microscopic form of the spin-orbit operator connects electronic states of different multiplicity for which  $\Delta \Lambda = 0$  and  $\pm 1$ . These are included in Table III where we introduce  $A_v^{\Lambda S; \Lambda' S'}$  as the intercombination analog of the spin-orbit parameter. Note that the matrix elements of the microscopic spin-orbit operator for  $\Delta S = \pm 1$  are in general different for different values of  $\Omega$  in the  $nvJSA$  block of interest, but they are related to each other through a factor  $(-1)^{\Lambda' - \Lambda} C(S'1S; \Sigma', \Lambda' - \Lambda, \Sigma)$  where  $C$  is a Clebsch-Gordan coefficient. The microscopic forms of the spin-spin and spin-rotation interaction have nonvanishing matrix elements for  $\Delta \Lambda = 0, \pm 1, \pm 2$  and  $\Delta S = 0, \pm 1$ , respectively (10,25). Other than the diagonal matrix elements shown in Table I, these matrix elements are usually neglected since these latter interactions are usually much smaller than the spin-orbit interaction. An exception occurs, however, for  $\Pi$  states of triplet and higher multiplicity. For such states the spin-spin interaction connects the  $\Lambda = +1$  and  $\Lambda = -1$  levels with the same value of  $\Omega$  (See Table III).

### F. Case (a) Wavefunctions with Parity

As pointed out by Kronig (35) and by Van Vleck (1), the task of calculating the molecular energy levels is significantly simplified if we transform to a basis set with well-defined parity. In such a basis set, each wavefunction may be classified as even or odd according to whether it remains unchanged or changes sign upon inversion through the origin of the spatial coordinates of all particles. Since the molecular Hamiltonian is invariant under inversion, only states of the same parity have nonvanishing matrix elements

connecting them. Consequently, the introduction of a parity basis set divides the secular determinant into two noninteracting blocks, one of even and one of odd parity. Thus the calculation of case (a) matrix elements between states of well-defined parity not only has the computational advantage of reducing the size of the secular equations we must solve, but also the conceptual advantage of allowing us to associate a definite parity with each calculated energy level.

The symmetry classification of diatomic molecules has been discussed by Wigner and Witmer (36), Hougen (37), and Bunker and Papoušek (38). Different parity conventions have been proposed by Freed (25), Hougen (24), Y.-N. Chiu (39), Pack and Hirschfelder (40), and Wofsy (41). Nevertheless, this topic has been a source of considerable confusion to us, and consequently, we present in Appendix A a development of the parity convention we adopt here. Let  $\mathbf{i}_{sp}$  denote the inversion of all spatial coordinates. In Appendix A, we show that when  $\mathbf{i}_{sp}$  acts on a case (a) wavefunction it transforms it as follows

$$\mathbf{i}_{sp}|nvJ\Omega S\Lambda\Sigma\rangle = (-1)^{J+S+\epsilon}|nvJ, -\Omega S, -\Lambda, -\Sigma\rangle, \quad (28)$$

where  $s = 1$  for  $\Sigma^-$  states and  $s = 0$  for  $\Sigma^+$  states; Appendix A shows that for all other states  $s$  may be set to zero.

Wavefunctions with well-defined parity  $p$  may then be constructed from case (a) wavefunctions in the following manner:

$$|n^{2S+1}\Lambda_{\Omega} vJp^{\pm}\rangle = \frac{1}{\sqrt{2}}[|nvJ\Omega S\Lambda\Sigma\rangle \pm |nvJ, -\Omega S, -\Lambda, -\Sigma\rangle], \quad (29)$$

(where in the molecular term symbol it is understood that  $\Lambda = |\Lambda|$ ) and for the special case  $\Lambda = 0, \Sigma = 0$ :

$$|n^{2S+1}\Sigma_0 vJp^{\pm}\rangle = |nvJ0S00\rangle. \quad (30)$$

In Eqs. (29) and (30) the parity  $p^{\pm}$  is given by

$$p^{\pm} = \pm (-1)^{J+S+\epsilon}, \quad (31)$$

where the plus sign refers to the state with the parity  $p^+$  and the minus sign to the state with the parity  $p^-$ .

For the matrix elements appearing in Table I and II it is readily shown that

$$\langle nvJ\Omega_i S\Sigma_i p^{\pm} | H | nvJ\Omega_j S\Sigma_j p^{\pm} \rangle = \langle nvJ\Omega_i S\Sigma_i | H | nvJ\Omega_j S\Sigma_j \rangle, \quad (32)$$

and the results listed in Tables I and II may be used directly. For the matrix elements appearing in Table III, however, the following two identities are required for their evaluation

$$\begin{aligned} &\langle nvJ\Omega S\Lambda\Sigma | H | n'v'J\Omega'S'\Lambda'\Sigma' \rangle \\ &= (-1)^{J+S+\epsilon+J'+S'+\epsilon'} \langle nvJ, -\Omega S, -\Lambda, -\Sigma | H | n'v'J, -\Omega'S', -\Lambda', -\Sigma' \rangle \end{aligned} \quad (33)$$

and

$$\begin{aligned} &\langle nvJ\Omega S\Lambda\Sigma | H | n'v'J, -\Omega'S', -\Lambda', -\Sigma' \rangle \\ &= (-1)^{J+S+\epsilon+J'+S'+\epsilon'} \langle nvJ, -\Omega S, -\Lambda, -\Sigma | H | n'v'J\Omega'S'\Lambda'\Sigma' \rangle. \end{aligned} \quad (34)$$

### G. Electronic Perturbation Parameters

The interaction between different electronic states may again be treated by means of the Van Vleck transformation. This causes additional adjustable parameters, often called  $\Lambda$ -doubling and spin-splitting constants, to appear in the  $2S + 1$  by  $2S + 1$  block of  $nvJ$  levels with the same parity. The second-order correction term has the general form

$$(y_v)_{ij} = \sum_{n'v'\Omega'\Sigma'} \frac{\langle n^{2S+1}\Lambda_{\Omega_i} vJp | H_a | n'^{2S'+1}\Lambda'_{\Omega'} v'Jp \rangle \langle n'^{2S'+1}\Lambda'_{\Omega'} v'Jp | H_b | n^{2S+1}\Lambda_{\Omega_j} vJp \rangle}{E_{nvJ} - E_{n'v'J}}, \quad (35)$$

where the matrix elements of  $H_a$  and  $H_b$  may be obtained from Table III with the help of the identities given in Eqs. (33) and (34).

The Franck-Condon principle primarily controls the magnitude of the contribution of each perturbing  $n'v'$  level to the numerator in Eq. (35). This may be seen by splitting off from Eq. (35) the factor  $\langle v | h_a(\mathbf{r}) | v' \rangle \langle v' | h_b(\mathbf{r}) | v \rangle$  where  $h_a(\mathbf{r})$  and  $h_b(\mathbf{r})$  are the radial parts of the perturbations  $H_a$  and  $H_b$ . We suppose  $h_a(\mathbf{r})$  and  $h_b(\mathbf{r})$  to vary slowly with  $\mathbf{r}$ . Then the radial factor is roughly equal to  $\langle v | v' \rangle^2$ , the square of the overlap integral of the two vibrational wavefunctions. Thus only those  $n'v'$  levels with appreciable Franck-Condon factors  $q_{v'v}$  connecting the levels  $nv$  and  $n'v'$  contribute to the value of  $y_v$ . Because the Franck-Condon factors are relatively insensitive to the rotational quantum number  $J$ , the numerator in Eq. (35) may be considered to be independent of  $J$  to first order.

The proximity of interacting levels controls the contribution of each perturbing  $n'v'$  level to the denominator in Eq. (35), which may be written approximately as

$$E_{nvJ} - E_{n'v'J} \simeq (E_{nv} - E_{n'v'}) + (B_v - B_{v'})J(J + 1). \quad (36)$$

When the separation between the two perturbing levels is much larger than  $(B_v - B_{v'}) \times J(J + 1)$ , then, to first order, the electronic perturbation parameter  $y_v$  is independent of  $J$ .

However, if data are available to high  $J$  values, centrifugal distortion corrections to  $y_v$  may be warranted. The  $J$ -dependence of the energy denominator may be expressed as a power series expansion in  $J(J + 1)$

$$(E_{nvJ} - E_{n'v'J})^{-1} = (E_{nv} - E_{n'v'})^{-1} \left[ 1 + \frac{B_v - B_{v'}}{E_{nv} - E_{n'v'}} J(J + 1) + \dots \right] \quad (37)$$

and the  $J$ -dependence of the radial matrix elements (31) as

$$\langle vJ | h(\mathbf{r}) | v'J \rangle = \langle v | h(\mathbf{r}) | v' \rangle + x_v J(J + 1). \quad (38)$$

Thus the effects of centrifugal distortion on  $y_v$  result in the replacement of  $y_v$  by  $y_v + y_{Dv}J(J + 1)$  everywhere  $y_v$  appears in the  $2S + 1$  by  $2S + 1$  parity block of interest. We note that  $y_{Dv}$  represents the collection of terms in  $J(J + 1)$  when Eqs. (37) and (38) are combined. Similar centrifugal distortion corrections have been developed previously by Veseth (34).

This discussion can be specialized to electronic perturbations arising from the form of

the rotational and fine structure Hamiltonians given by Eqs. (2) and (5-8). Within this framework only electronic states of the same multiplicity and with  $\Delta\Lambda = \pm 1$  may perturb each other, to first order. For  $\Sigma$  states, it may be shown that in general three additional electronic perturbation parameters appear in the rotational energy level expressions (1, 17, 42)

$$o_v^\Sigma = \sum_{n'v'} \frac{\langle n' {}^{2S+1}\Pi v' J | \frac{1}{2}A(r)L_+ | n {}^{2S+1}\Sigma^\pm v J \rangle^2}{E_{n'vJ} - E_{n'v'J}}, \quad (39)$$

$$p_v^\Sigma = 4 \sum_{n'v'} \frac{\langle n' {}^{2S+1}\Pi v' J | \frac{1}{2}A(r)L_+ | n {}^{2S+1}\Sigma^\pm v J \rangle \langle n' {}^{2S+1}\Pi v' J | B(r)L_+ | n {}^{2S+1}\Sigma^\pm v J \rangle}{E_{n'vJ} - E_{n'v'J}}, \quad (40)$$

and

$$q_v^\Sigma = 2 \sum_{n'v'} \frac{\langle n' {}^{2S+1}\Pi v' J | B(r)L_+ | n {}^{2S+1}\Sigma^\pm v J \rangle^2}{E_{n'vJ} - E_{n'v'J}}. \quad (41)$$

However, the presence of electronic perturbations in  $\Sigma$  states cannot be recognized from inspection of the spectroscopic data because the functional form of the energy level expressions for the rotational levels of a  $\Sigma$  state are unaltered (11, 42). This is illustrated for a  ${}^2\Sigma$  state in Appendix B, which also provides a concrete application of the preceding theory. Moreover, for  $\Sigma$  states, the adjustable molecular constants also absorb the effects of perturbations by any other state. Consequently, the perturbation of  $\Sigma$  states by other electronic states is an insidious problem since there is no simple way to ascertain whether the molecular constants determined in the rotational analysis, namely, the band origin  $\nu_0(v', v'')$ , the rotational constants  $B_v, D_v, H_v$ , etc., the spin-rotation constant  $\gamma_{v'}$  and the spin-spin constant  $\epsilon_v$  (for  $S \geq 1$ ), have the separate mechanical and magnetic meanings usually attributed to them.<sup>4,5</sup>

For non- $\Sigma$  states the presence of electronic perturbations may also go undetected, particularly for interactions between two electronic states with  $\Lambda \neq 0$ , e.g., a  $\Delta$  state interacting with a  $\Pi$  state. On the other hand, the perturbations caused by  $\Sigma^\pm$  states manifest themselves by splitting the rotational levels of the non- $\Sigma$  state into two  $\Lambda$  components ( $\Lambda$ -type doubling). In first order, only  $\Pi$  states interact with  $\Sigma$  states, and if we again restrict our attention to the commonly occurring situation of perturbations between states of the same multiplicity, then in general three  $\Lambda$ -doubling parameters must be introduced to describe the energy levels of such a  $\Pi$  state. In a manner similar

<sup>4</sup> Because of the presence of electronic perturbations the molecular constants of a  ${}^1\Sigma$  state, which is often regarded as the paragon of a molecular state that behaves as a vibrating rotator, do not describe the vibrational and rotational motions of nuclei in an effective radial potential. However, the departure of a  ${}^1\Sigma$  state from the vibrating rotator model may be detected by the following internal consistency test. First, the experimental  $G(v)$  and  $B_v$  values are used to construct the potential with the *RKR* procedure. Secondly, the wavefunctions and associated eigenvalues are obtained for this potential. Finally, a comparison is made between the observed and calculated  $G(v) + Y_{00}$  values and the observed and calculated rotational constants  $B_v, D_v, H_v$ , etc. (31). Deviations outside the experimental uncertainties signal undetected perturbations (or the unlikely failure of the *RKR* procedure).

<sup>5</sup> An additional indicator that a multiplet  $\Sigma$  state is perturbed is the magnitude of  $\gamma_v$  and  $\epsilon_v$  (for  $S \geq 1$ ), because often the values of these parameters include large (and for  $\gamma_v$ , dominant) contributions from the off-diagonal spin-orbit interaction. In particular,  $\gamma_v$  is usually well approximated by  $-\dot{p}_v^\Sigma$  (1, 43) (See Appendix C).

to Eqs. (39–41), these electronic perturbation parameters are conveniently defined as (42)

$$o_v^{\Pi} = \sum_{n'v'} \frac{\langle n^{2S+1}\Pi vJ | \frac{1}{2}A(r)L_+ | n'^{2S+1}\Sigma^{\pm} v'J \rangle^2}{E_{nvJ} - E_{n'v'J}}, \quad (42)$$

$$p_v^{\Pi} = 4 \sum_{n'v'} \frac{\langle n^{2S+1}\Pi vJ | \frac{1}{2}A(r)L_+ | n'^{2S+1}\Sigma^{\pm} v'J \rangle \langle n^{2S+1}\Pi vJ | B(r)L_+ | n'^{2S+1}\Sigma^{\pm} v'J \rangle}{E_{nvJ} - E_{n'v'J}}, \quad (43)$$

and

$$q_v^{\Pi} = 2 \sum_{n'v'} \frac{\langle n^{2S+1}\Pi vJ | B(r)L_+ | n'^{2S+1}\Sigma^{\pm} v'J \rangle^2}{E_{nvJ} - E_{n'v'J}}. \quad (44)$$

For  ${}^1\Pi$  states, only the  $\Lambda$ -doubling parameter  $q_v^{\Pi}$  occurs; for  $\Pi$  states of higher multiplicity, the energy level expressions depend on  $q_v^{\Pi}$ ,  $p_v^{\Pi}$ , and  $o_v^{\Pi}$ . However, the

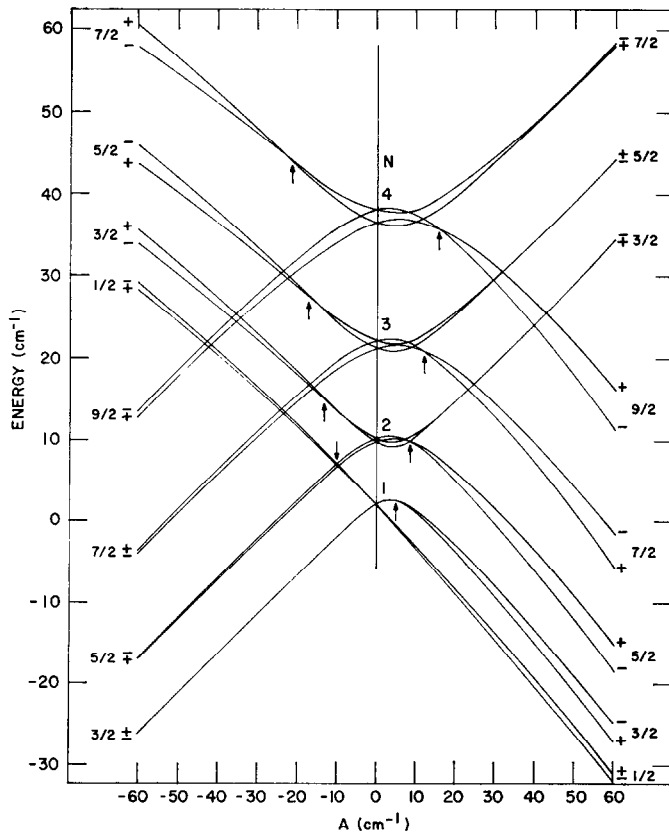


FIG. 1. Rotational energy level pattern of a  ${}^2\Pi$  state as a function of the spin-orbit parameter  $A_v^{\Pi}$ . The parities of the  $\Lambda$  components are indicated by  $\pm$  signs and the point at which the  $\Lambda$  components of the same  $F$  component but of opposite parity cross is marked by an arrow. The figure is constructed using the molecular constants  $B_v^{\Pi} = 2.0 \text{ cm}^{-1}$ ,  $q_v^{\Pi} = -0.08 \text{ cm}^{-1}$ , and  $p_v^{\Pi} = -0.016 A_v^{\Pi}$ . The figure refers to a  ${}^2\Pi$  state perturbed by a  ${}^2\Sigma^+$  state above. If the parities of the  $\Lambda$  components are reversed, then this figure refers to a  ${}^2\Pi$  state perturbed by a  ${}^2\Sigma^-$  state above.

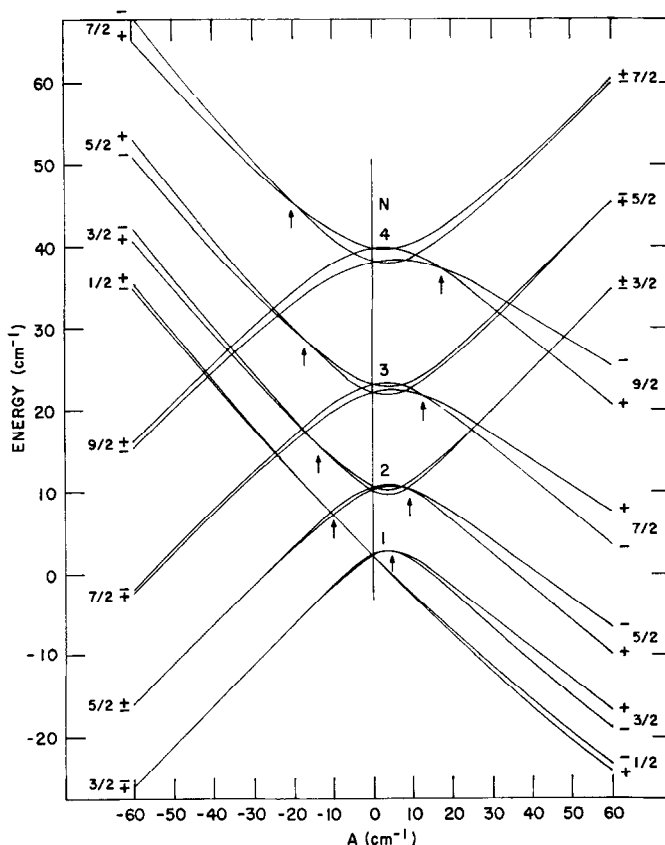


FIG. 2. Rotational energy level pattern of a  ${}^2\Pi$  state as a function of the spin-orbit parameter  $A_v^{\text{II}}$ . The parities of the  $\Lambda$  components are indicated by  $\pm$  signs and the point at which the  $\Lambda$  components of the same  $F$  component but of opposite parity cross is marked by an arrow. The figure is constructed using the molecular constants  $B_v = 2.0 \text{ cm}^{-1}$ ,  $q_v^{\text{II}} = 0.08 \text{ cm}^{-1}$ , and  $p_v^{\text{II}} = 0.016 A_v^{\text{II}}$ . The figure refers to a  ${}^2\Pi$  state perturbed by a  ${}^2\Sigma^+$  state below. If the parities of the  $\Lambda$  components are reversed, then this figure refers to a  ${}^2\Pi$  state perturbed by a  ${}^2\Sigma^-$  state below.

$\Lambda$ -doubling parameter  $o_v^{\text{II}}$  cannot be determined independently from experimental data because its effect can be totally absorbed into some of the other molecular constants already employed in the analysis.<sup>6</sup> Consequently, to help maintain the integrity of the other molecular constants we look for a means of estimating and fixing the value of  $o_v^{\text{II}}$ .

Often the contribution from one or a few  $\Sigma$  states outweighs those from all others in determining the values of the  $\Lambda$ -doubling parameters. When this situation occurs, then the  $\Lambda$ -doubling splittings are readily calculated using what we shall call the *unique*

<sup>6</sup> For  ${}^2\Pi$  states,  $T_v^{\text{II}}$ ,  $A_v^{\text{II}}$ , and  $o_v^{\text{II}}$  cannot be determined simultaneously, whereas any two of these three constants can. Of course, it is the first two, rather than the perturbation correction term, that should be retained. For  ${}^3\Pi$  states,  $T_v^{\text{II}}$ ,  $A_v^{\text{II}}$ ,  $\alpha_v^{\text{II}}$ ,  $\epsilon_v^{\text{II}}$ , and  $o_v^{\text{II}}$  cannot be determined simultaneously, whereas any four of these five constants can. Again, we regard  $o_v^{\text{II}}$  as the correction term and retain the first four. For  $\Pi$  states of higher even and odd multiplicity, it appears that  $o_v^{\text{II}}$  is involved in total correlations like those of the  ${}^2\Pi$  and  ${}^3\Pi$  states, respectively.

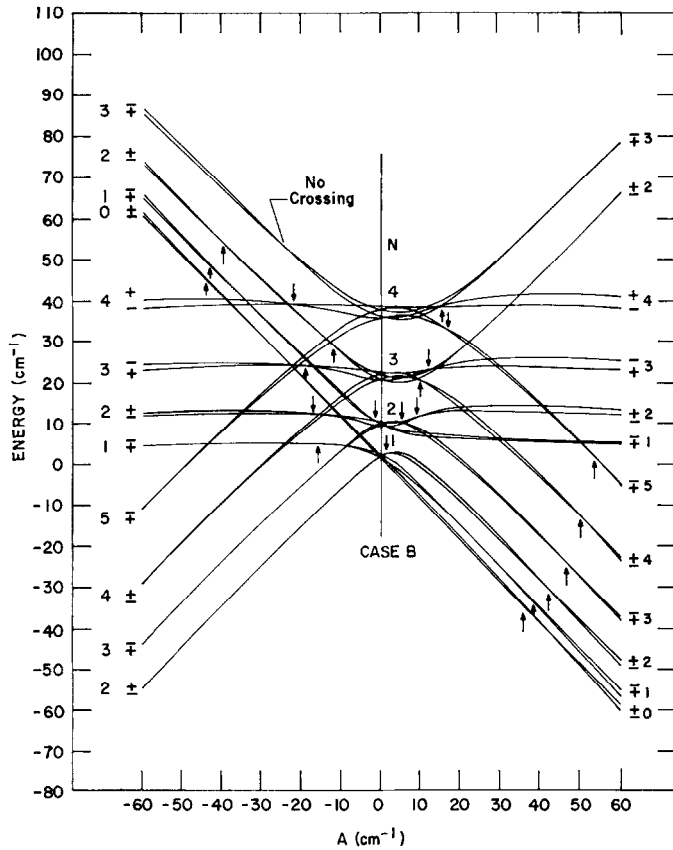


FIG. 3. Rotational energy level pattern of a  ${}^3\Pi$  state as a function of the spin-orbit parameter  $A_v^\Pi$ . The parities of the  $\Lambda$  components are indicated by  $\pm$  signs and the point at which  $\Lambda$  components of the same  $F$  component but of opposite parity cross is marked by an arrow. The figure is constructed using the molecular constants  $B_v^\Pi = 2.0 \text{ cm}^{-1}$ ,  $q_v^\Pi = -0.12 \text{ cm}^{-1}$ ,  $p_v^\Pi = -0.0024 A_v^\Pi$ , and  $\alpha_v^\Pi = 0.6 \text{ cm}^{-1}$ . The figure refers to a  ${}^3\Pi$  state perturbed by a  ${}^3\Sigma^+$  state above.

*perturber approximation* in which the effects of all perturbing electronic states are ascribed to the interaction with one real or effective (composite)  $\Sigma^+$  or  $\Sigma^-$  state whose position relative to the  $\Pi$  state (i.e., above or below) is known. We show in Appendix C that under a set of not very restrictive assumptions that  $p_v^\Pi$  is proportional to  $A_v^\Pi$  and that  $o_v^\Pi$  is proportional to  $(A_v^\Pi)^2$ . Moreover, when the unique perturber approximation is valid, Appendix C gives the development of the approximate relation,

$$o_v^\Pi = (1/8)(A_v^\Pi/B_v^\Pi)p_v^\Pi, \quad (45)$$

that permits  $o_v^\Pi$  to be calculated from the value of the  $\Lambda$ -doubling constant  $p_v^\Pi$  and the molecular constants  $A_v^\Pi$  and  $B_v^\Pi$  of the perturbed  $\Pi$  state. The use of Eq. (45) as a means of estimating  $o_v^\Pi$  has been suggested previously by Veseth (44).

To gain insight into the nature of  $\Lambda$  doubling in  $\Pi$  states, Figs. 1 and 2 show the lower rotational energy levels of a  ${}^2\Pi$  state perturbed by a  ${}^2\Sigma^+$  state as a function of  $A_v^\Pi$  under the above assumptions, where for simplicity we have set  $\gamma_v^\Pi$ ,  $D_v^\Pi$ ,  $H_v^\Pi$ , and  $A_{Dv}^\Pi$ ,



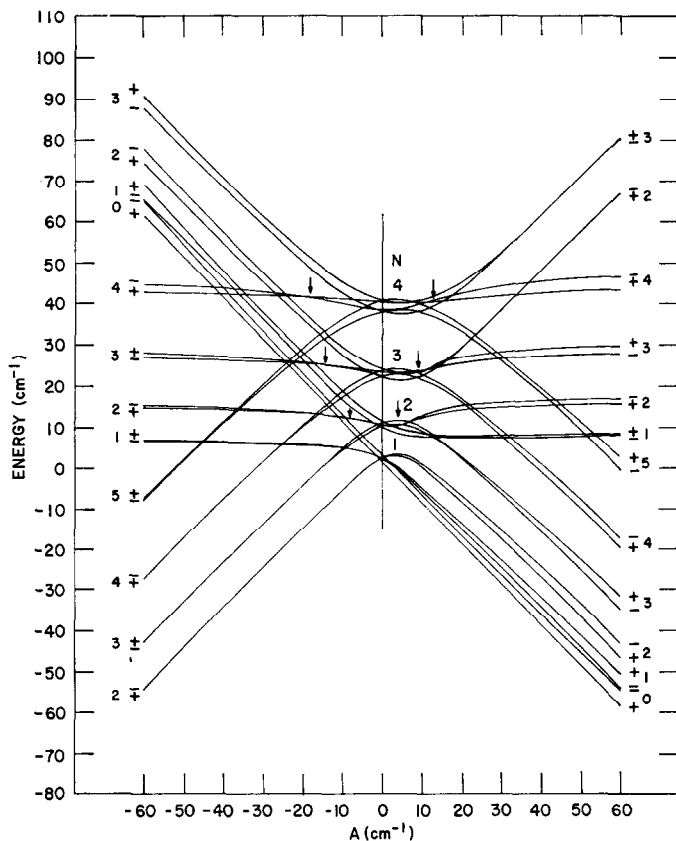


FIG. 4. Rotational energy level pattern of a  ${}^3\Pi$  state as a function of the spin-orbit parameter  $A_v^\Pi$ . The parities of the  $\Lambda$  components are indicated by  $\pm$  signs and the point at which  $\Lambda$  components of the same  $F$  component but of opposite parity cross is marked by an arrow. The figure is constructed using the molecular constants  $B_v^\Pi = 2.0 \text{ cm}^{-1}$ ,  $q_v^\Pi = 0.12 \text{ cm}^{-1}$ ,  $p_v^\Pi = 0.0024 A_v^\Pi$ , and  $\alpha_v^\Pi = 0.6 \text{ cm}^{-1}$ . The figure refers to a  ${}^3\Pi$  state perturbed by a  ${}^3\Sigma^+$  state below.

equal to zero. In this example, which cannot be assumed general, arrows mark the places where the two parity components for the same  $J$  and  $\Omega$  cross. Note that there occurs one and only one crossing for each  $(J, \Omega)$  pair. This means that for a given value of  $A_v^\Pi$  corresponding to the vibrational level of an actual molecule, the parity alternation of the upper  $\Lambda$ -component will change phase at some  $J$  value near the crossing. As a consequence, care must be taken in assigning the parity to the observed  $\Lambda$ -doublets, since these measured line positions are compared to calculated line positions of definite parity.

Figures 3 and 4 show the lower rotational energy levels of a  ${}^3\Pi$  state perturbed by a  ${}^3\Sigma^+$  as a function of  $A_v^\Pi$  in the same manner as  ${}^2\Pi$  levels shown in Figs. 1 and 2. In contrast to the  ${}^2\Pi$  states, a  ${}^3\Sigma^-$  above (below) is not identical to a  ${}^3\Sigma^+$  above (below) with the parities of the  $\Lambda$ -components reversed. However, the difference is a uniform shift of different magnitude for each multiplet. The crossing points, marked by arrows, have a distinctively different structure for Figs. 3 and 4. In Fig. 3 all the lower  $J$  levels

have two crossings each. However, for  $J = 3$  and above, the  $F_3$  components have no crossings. The minimum value of  $J$  for which  $F_3$  components do not cross, of course, depends on the particular choice of the molecular constants. In Fig. 4 only the  $F_2$  components above  $J = 1$  cross twice; otherwise there are no crossings. We note that a great deal of care must be taken in assigning the parity of the  $\Lambda$  components of a  $^3\Pi$  state. For  $\Pi$  states of higher multiplicity this problem is exacerbated, e.g., in  $^4\Pi$  states many levels have three crossings as a function of  $A$ . However, for homonuclear molecules whose nuclei have zero spin, only one parity exists and the above is not a problem. This is, of course, also no problem in transitions involving  $\Sigma$  states.<sup>7,8</sup>

### III. NUMERICAL PROCEDURE

A computer program has been written to calculate upper and lower state molecular constants from a direct, least-squares fit to the measured line positions of an individual band using the effective Hamiltonians described in the preceding section. The calculational procedure logically divides into three steps: (1) The matrix elements of the upper and lower state Hamiltonians are calculated for each  $J$  value using initial values of the adjustable molecular constants; (2) both Hamiltonians are numerically diagonalized and the resulting sets of eigenvalues are used to construct a set of calculated line positions; and (3) from a least-squares fit of the calculated to the observed line positions, an improved set of molecular constants is generated. This nonlinear least-squares procedure is repeated until a satisfactory set of molecular constants is obtained. As will be described, the speed of this program makes the band-by-band reduction of spectroscopic data with numerically diagonalized Hamiltonians a practical technique for obtaining molecular constants in which the separate mechanical and magnetic significance is largely retained.

At present, the scope of the computer program is as follows. All transitions between electronic states with  $\Lambda \leq 5$ ,  $S \leq 3$ , and  $|\Delta J| \leq 3$  are included. Any appropriate combination of the following molecular constants may be evaluated: the band origin  $\nu_0(v', v'')$  and, for the upper and lower states, the rotational constants  $B_v$ ,  $D_v$ , and  $H_v$ ; the spin-orbit constants  $A_v$ ,  $A_v^{\Lambda S; \Lambda' S'}$ , and  $A_{Dv}$ ; the spin-rotation constant  $\gamma_v$ ; the spin-spin constants  $\epsilon_v$  and  $\alpha_v$ ; and the  $\Lambda$ -doubling constants  $q_v$ , and  $p_v$  [ $o_v$  is fixed as in Eq. (45)] and their centrifugal distortion corrections  $q_{Dv}$  and  $p_{Dv}$ .  $\Lambda$ -doubling is considered only for  $\Pi$  states and only for a single perturbing state (unique perturber approximation) that differs from the perturbed  $\Pi$  state by  $\Delta S = 0, \pm 1$  and  $\Delta \Lambda = 0, \pm 1$ . This program has been designed so that it can be easily modified to include other interactions whose matrix elements are not given in Tables I-III.

For each band, the input data to this program are of two types: the identification and wavenumbers of the observed lines and the starting values of the requested molecular constants. Each measured line position is accompanied by the rotational quantum number  $J''$ , the branch designation  $J'-J''$ , the upper and lower  $F$ -levels, and the parities (when  $\Lambda$ -doubling is being considered). Numerous internal consistency tests may be

<sup>7</sup> It is customary to let  $c$  and  $d$  denote the upper and lower  $\Lambda$  components. However, Figs. 1-4 show that then  $c$  and  $d$  cannot generally represent the parity.

<sup>8</sup> In Figs. 1-4, case (b) coupling corresponds to  $A_v^{\Pi} = 0$  and the rotational levels are labeled by the quantum number  $N$ , as shown. It has often been considered that the assignment of  $N$  is ambiguous at low  $J$  levels. However, Figs. 1-4 shows that this assignment is, in fact, unambiguous.

made of these data. One of the most useful of these is a verification that the input quantities accompanying each line are compatible with the identification of the states involved since some published line positions do contain some physically impossible lines (45). Furthermore, unidentified blends are detected and flagged by testing whether two or more input lines have exactly the same wavenumber.

For each molecular constant that is to be included in the fit, there are three alternatives in the input to the program: (1) The value of the molecular constant is fixed to an assigned value; (2) the sign of the value of the molecular constant is fixed to be either positive or negative while its magnitude may be determined, (3) the sign and magnitude of the molecular constant is free to be found by the program. In the latter two options, trial values are required. If reasonable starting values ( $\pm 20$  percent) are not available from previous work, then the data are initially fit using only the major constants, i.e.,  $\nu_0(v', v'')$ ,  $A_v'$ ,  $A_v''$ ,  $B_v'$ , and  $B_v''$ . These estimates are then used as starting values for a detailed fit. Serious convergence and false-minima problems, which often occur in non-linear least-squares fitting, have not been encountered for reasonable, i.e., not unphysical, choices of the starting values of the molecular constants. In fact, the ease of convergence can be taken as some measure of the correctness of choices such as the location and the symmetry type of the perturbing state in  $\Lambda$ -doubling. In the discussion of Figs. 1-4, it was noted that the assignment of the parities to the observed  $\Lambda$  doublets may not be straightforward; in the application of this program, some of the parities may require iterative assignments. This often can be facilitated, for example, by initially analyzing a  $\Sigma$ - $\Pi$  transition that shares a common  $\Pi$  state with the  $\Pi$ - $\Pi$  transition of interest.

For the appropriate values of  $J'$  and  $J''$ , matrix elements for each  $(2S + 1) \times (2S + 1)$  parity block are constructed using Tables I-III and using first the starting values, and then the iteratively improved values of the requested molecular constants. The upper and lower state Hamiltonians are diagonalized to yield a set of eigenvalues (term values) for each  $J'$  and  $J''$ . From these eigenvalues, calculated line positions are determined for the appropriate branches. These are compared with the measured line positions and new estimates of the molecular constants are made that reduce the sum of the squares of the residuals. This least-squares procedure is based on the method of Marquardt (46) that combines the Gauss (Taylor series) method and the method of steepest descent. This numerical procedure was adapted to the computer by Meeter and Wolfe (47).

The molecular constants are iteratively improved until one of several specified convergence criteria are met. Upon completion, the program provides as output the values of the band origin and the molecular constants for the upper and lower states, as well as the associated standard deviations (based on a linear approximation to the model in the neighborhood of the constants). In addition to the standard deviation of each constant, the correlation coefficients between all pairs of constants (in the linear approximation) are also given. These correlation coefficients show quantitatively how the various constants are interrelated in the least-squares fit (7).

Although this nonlinear least-squares fitting procedure may appear, at first glance, to be complex, the time required to reduce the data of a typical band is sufficiently short to make this procedure practical. Of course, the running time depends on the number of requested constants, the number of lines in the band, etc., but particularly on the multi-

plicities of the states. For example, the reduction of a  ${}^2\Pi-{}^2\Pi$  band, with  $\Lambda$ -doubling in the lower state and about fifty lines in each of eight branches, requires less than two minutes on a CDC-3800 computer.

Documentation for distribution of this and related programs is now in preparation.

#### IV. DISCUSSION AND EXAMPLES

Detailed applications of the procedure discussed in the preceding two sections have been made to the  $O_2$   $b^1\Sigma_g^+-X^3\Sigma_g^-$  Red Atmospheric band system (48) and the  $O_2^+$   $A^2\Pi_u-X^2\Pi_g$  Second Negative band system (45). In this section, we present examples illustrating the problems that result from the lack of a proper separation of the mechanical and magnetic meanings of the molecular constants.

Since our main interest is in constructing reliable RKR potentials from which vibrational matrix elements such as Franck-Condon factors,  $r$ -centroids, centrifugal distortion constants, etc. may be calculated, the mechanical significance of experimentally obtained band origins and  $B_v$  values is of paramount importance to us. Because the Born-Oppenheimer separation is not exact, there is always some loss of the mechanical meaning of  $\nu_0$  and  $B_v$  values and in many cases, we know of no practical way to recoup this loss. However, some of the problems can be avoided and we give three examples.

One major problem is the use of "effective"  $B_v$  values that have absorbed some of the spin-orbit coupling constant  $A_v$ . The analysis of a  ${}^2\Pi$  state provides an example of this. Because of spin-orbit splitting the rotational term values of a  ${}^2\Pi$  state can be written for a given vibrational level  $v$  as

$$F_i(v, J) = B_v^{(i)}J(J+1) - D_v^{(i)}[J(J+1)]^2 + \dots \quad (46)$$

where  $\Lambda$ -doubling has been ignored. In Eq. (46)  $i = 1$  or  $2$ , corresponding to the lower or upper sub-bands, respectively. For moderate to large spin-orbit splittings, the empirical analysis of spectroscopic data for  ${}^2\Pi$  states yields, according to Eq. (46), two slightly different effective  $B_v$  values,  $B_v^{(1)}$  and  $B_v^{(2)}$ . If we only take into account the (diagonal) contribution to the  ${}^2\Pi$  energy of the spin-orbit interaction and ignore all other interactions, then Hill and Van Vleck (1) showed long ago that the rotational term values have the theoretical form

$$F_1(v, J) = B_v\{J(J+1) - \frac{3}{4} - \frac{1}{2}[(2J+1)^2 + Y_v(Y_v-4)]^{\frac{1}{2}}\} \quad (47)$$

and

$$F_2(v, J) = B_v\{J(J+1) - \frac{3}{4} + \frac{1}{2}[(2J+1)^2 + Y_v(Y_v-4)]^{\frac{1}{2}}\} \quad (48)$$

where  $Y_v = A_v/B_v$ . By rewriting the square root in Eqs. (47) and (48) as  $\mp \frac{1}{2}Y_v\{1 + [(2J+1)^2 - 4Y_v]/Y_v^2\}^{\frac{1}{2}}$ , making a power series expansion for

$$[(2J+1)^2 - 4Y_v]/Y_v^2 < 1,$$

and collecting terms in  $J(J+1)$ , we may equate

$$B_v^{(1)} = B_v[1 - Y_v^{-1} - \dots] \quad (49)$$

and

$$B_v^{(2)} = B_v[1 + Y_v^{-1} + \dots]. \quad (50)$$

Thus it can be seen that the effective  $B_v$  values have the spin-orbit interaction entangled with the mechanical  $B_v$  value appropriate to the  ${}^2\Pi$  potential, and potentials

TABLE IV  
FRANCK-CONDON FACTORS FOR THE  $ThO B^1\Pi - X^1\Sigma$  BAND SYSTEM

$v' \setminus v''$	0	1	2
0	9.134 (-1) <sup>a</sup>	0.828 (-1)	3.652 (-3)
	8.823 (-1)	1.113 (-1)	6.256 (-3)
1	0.825 (-1)	7.544 (-1)	1.523 (-1)
	1.096 (-1)	6.742 (-1)	1.979 (-1)
2	3.936 (-3)	1.510 (-1)	6.149 (-1)
	7.707 (-3)	1.917 (-1)	5.032 (-1)

<sup>a</sup> The upper entry is calculated using the  $B$  state  $RKR$  potential constructed from  $B_v^c$  values; the lower entry from  $B_v^d$  values. The number in parentheses is the power of 10, e.g., (-1) implies  $\times 10^{-1}$ .

constructed from the effective  $B_v$  values do not govern the mechanical motion of the nuclei.

Nevertheless, different  $RKR$  potentials have been constructed for  ${}^2\Pi_{1/2}$  and  ${}^2\Pi_{3/2}$  components using the  $B_v^{(1)}$  and  $B_v^{(2)}$  values (49-51). It is not surprising to find that, in the case of  $NO$   $\gamma$ -bands, the relative vibrational intensity measurements of Poland and Broida (52) disagree seriously with the predictions based on  $RKR$  potentials constructed from such effective  $B_v$  values (51), but agree fairly closely with the Franck-Condon factors calculated from a  $RKR$ -potential based on the mechanical  $B_v$  value (4).

Generally, the errors introduced into the  $\nu_o(v', v'')$  and  $B_v$  values by failing to maintain their mechanical significance are small compared to their magnitudes, provided of course, that  $A_v$  is not partially absorbed in  $B_v$  and  $\nu_o(v', v'')$ . However, an error of only a few parts per thousand in the  $B_v$  value can appreciably affect the values of calculated Franck-Condon factors; thus, maintaining the mechanical integrity even at this level often is required. This requires consideration of the mixing of electronic perturbation parameters into  $B_v$ .

The  $B^1\Pi-X^1\Sigma$  system of  $ThO$  illustrates this problem. In their analysis of this  $\Lambda$ -doubled system, Edvinsson, Selin, and Åslund (53) determined two  $B_v$  values,  $B_v^c$  and  $B_v^d$ , as is often done, where  $c$  and  $d$  refer to the upper and lower  $\Lambda$  components. For example, they found  $B_0^c = 0.324324 \text{ cm}^{-1}$  and  $B_0^d = 0.322988 \text{ cm}^{-1}$ , a difference of four parts per thousand. In Table IV we present the Franck-Condon factors for the  $ThO B^1\Pi-X^1\Sigma$  band system based on  $RKR$  potentials constructed from the two sets of  $B_v'$  values. For Franck-Condon factors on the order of  $10^{-1}$  the two sets differ by as much as 20%; for Franck-Condon factors on the order of  $10^{-3}$  the uncertainty is about a factor of two. Because the  $ThO A^1\Sigma$  state lies about  $500 \text{ cm}^{-1}$  below the  $B^1\Pi$  state it is reasonable to suppose it is responsible for the relatively large  $\Lambda$  doubling in the  $B^1\Pi$  state. If we further assume that the  $A^1\Sigma$  state is a  ${}^1\Sigma^+$  state (which is based on the assumption that the ground  ${}^1\Sigma$  state is a  ${}^1\Sigma^+$ ) then it is expected that the  $B_v^d$  values associated with the lower  $\Lambda$  component are the more mechanically meaningful. Unfortunately, there are no intensity measurements available for this band system so that a direct test of this hypothesis cannot be made.

It is traditional to take as the  $B_v$  value of the  ${}^1\Pi$  state the average of the  $B_v$  values for the two  $\Lambda$  components. In the absence of further information, there appears to be no simpler procedure for choosing a  $B_v$  value for the construction of an  $RKR$  potential. As the example of the  $ThO$   $B-X$  band system shows, when  $B_v^c$  and  $B_v^d$  differ substantially, the average  $B_v$  value has doubtful mechanical meaning. However, when the unique perturber approximation is valid, the values obtained for  $\nu_o(v', v'')$  and  $B_v$  refer more accurately to the mechanical motion of the nuclei (45).

Perhaps at the level of insignificant mixing of the meaning of molecular constants is the common replacement of  $[J(J+1) - \Omega^2 + S(S+1) - \Sigma^2]$  (see Table I) by simply  $J(J+1)$  in the expression for the energy levels. Note that this introduces  $\xi B_v$  into  $T_v$  (or, of more importance in the construction of  $RKR$  potentials,  $\xi \Delta B_v$  into  $\Delta G_{v+\frac{1}{2}}$ ) and  $\xi^2 D_v$  into  $B_v$ , where  $\xi = \Omega^2 - S(S+1) + \Sigma^2$ . These alterations in the  $T_v$  and  $B_v$  values are usually within the experimental uncertainty; even in those cases where the alterations are discernible, the impaired molecular constants lead to  $RKR$  potentials that are essentially indistinguishable for the calculation of various vibrational matrix elements.

#### V. ACKNOWLEDGMENTS

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#### APPENDIX A

The case (a) wavefunction  $|nvJ\Omega S\Lambda\Sigma M\rangle$  may be written as a product of two wavefunctions

$$|nvJ\Omega S\Lambda\Sigma M\rangle = |JM\Omega\rangle |nvS\Lambda\Sigma\rangle, \quad (A1)$$

where

$$|JM\Omega\rangle = [(2J+1)/8\pi^2]^{\frac{1}{2}} D^{J*}_{M\Omega}(\alpha\beta\gamma) \quad (A2)$$

is a rotational part and

$$|nvS\Lambda\Sigma\rangle = R_{n_v}(\mathbf{r})^{2S+1} \varphi_{\Lambda}(\mathbf{q}_i, \sigma_i; \mathbf{r}) \quad (A3)$$

is a vibronic part that pertains to the nonrotating molecule. In Eq. (A2)  $D^{J*}_{M\Omega}$  is a symmetric top wavefunction, given by

$$D^{J*}_{M\Omega}(\alpha\beta\gamma) = e^{iM\alpha} d^J_{M\Omega}(\beta) e^{i\Omega\gamma}, \quad (A4)$$

where  $d^J_{M\Omega}$  is a Jacobi polynomial and  $\alpha\beta\gamma$  are Euler angles that describe the orientation of the molecule-fixed frame with respect to the space-fixed frame (54). In Eq. (A3)  $R_{n_v}(\mathbf{r})$  is the vibrational wavefunction and  $^{2S+1}\varphi_{\Lambda}(\mathbf{q}_i, \sigma_i; \mathbf{r})$  is the electronic wavefunction. Here the internuclear distance is denoted by  $\mathbf{r}$ , the electronic coordinates by  $\mathbf{q}_i$ , and the electron spin coordinates by  $\sigma_i$ , where the  $\sigma_i$  are measured in the molecular frame. To determine the parity of the overall wavefunction  $|nvJ\Omega S\Lambda\Sigma M\rangle$  we consider the effect of the spatial inversion operation on  $|JM\Omega\rangle$  and  $|nvS\Lambda\Sigma\rangle$  separately.

In defining the molecular wavefunction  $|nvJ\Omega S\Lambda\Sigma M\rangle$  we use two coordinate systems, a frame  $XYZ$  fixed in space and a frame  $xyz$  that moves with the molecule. The origin of both frames coincide with the center of mass of the  $AB$  molecule. The  $xyz$  frame is defined to have its  $z$  axis along the internuclear axis pointing from nucleus  $A$  to nucleus  $B$ . Both frames are right-handed coordinate systems. The Euler angles  $\alpha\beta\gamma$  relate the

space-fixed frame  $XYZ$  to the molecule-fixed frame  $xyz$  where, by performing three successive rotations,  $XYZ$  may be made to coincide with  $xyz$ : (1) a positive rotation by  $0 \leq \alpha \leq 2\pi$  about the  $Z$  axis; (2) a positive rotation by  $0 \leq \beta \leq \pi$  about the line of nodes; and (3) a positive rotation by  $0 \leq \gamma \leq 2\pi$  about the  $z$  axis. The  $XYZ$  and  $xyz$  frames are then related by

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} c\alpha c\beta c\gamma - s\alpha s\gamma & -c\alpha c\beta s\gamma - s\alpha c\gamma & c\alpha s\beta \\ s\alpha c\beta c\gamma + c\alpha s\gamma & -s\alpha c\beta s\gamma + c\alpha c\gamma & s\alpha s\beta \\ -s\beta c\gamma & s\beta s\gamma & c\beta \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}, \quad (\text{A5})$$

where sine has been abbreviated by  $s$  and cosine by  $c$ . In Eq. (A5) the unitary transformation matrix is the transpose of the well-known direction cosine matrix.

Under spatial inversion,  $X \rightarrow -X$ ,  $Y \rightarrow -Y$ , and  $Z \rightarrow -Z$ . For Eq. (A5) to be an identity, we must determine how the Euler angles  $\alpha\beta\gamma$  and the molecule-fixed coordinates  $xyz$  transform under this symmetry operation. Note that spatial inversion may be regarded as an inversion of the positions of all particles (nuclei and electrons) in a fixed laboratory reference frame. It can be easily seen that the following transformation preserves Eq. (A5):

$$\begin{aligned} x &\rightarrow -x, \\ y &\rightarrow y, \\ z &\rightarrow z; \end{aligned} \quad (\text{A6})$$

and

$$\begin{aligned} \alpha &\rightarrow \pi + \alpha, \\ \beta &\rightarrow \pi - \beta, \\ \gamma &\rightarrow -\gamma. \end{aligned} \quad (\text{A7})$$

Physically, Eqs. (A6) and (A7) correspond to the symmetry operation  $\sigma_v^{yz}$  for the molecule-fixed coordinates and to the transformation  $C_2^z$  on the Euler angles.

We note that this choice is arbitrary. We could equally well have used the alternative transformation (24)  $\sigma_v^{xz}$  on the molecule-fixed coordinates ( $x \rightarrow x$ ,  $y \rightarrow -y$ ,  $z \rightarrow z$ ) and  $C_2^y$  on the Euler angles ( $\alpha \rightarrow \pi + \alpha$ ,  $\beta \rightarrow \pi - \beta$ ,  $\gamma \rightarrow \pi - \gamma$ ). The only difference in the Eulerian angle transformations is the behavior of the angle  $\gamma$  that measures rotation about the molecule-fixed  $z$  axis. However, a linear molecule has only two rotational degrees of freedom, and hence the angle  $\gamma$  is redundant. Thus the value of  $\gamma$  can be fixed arbitrarily. If one chooses to express the effect of spatial inversion on the molecular coordinates by Eqs. (A6) and (A7), then  $\gamma$  must be fixed equal to zero (the only number equal to its negative). If, however, the alternative transformation (24) is chosen, then  $\gamma$  must be fixed equal to  $\pi/2$ . As will be seen, we prefer choosing Eqs. (A6) and (A7) because the expressions for the resulting transformation properties are simpler.

The rotational wavefunction  $|JM\Omega\rangle$  may then be rewritten as

$$|JM\Omega\rangle = \left[ \frac{2J+1}{4\pi} \right]^{\frac{1}{2}} D^{J^*}_{M\Omega}(\alpha, \beta, 0), \quad (\text{A8})$$

where the normalization factor has been altered to reflect the fact that integration over the solid angle element no longer includes  $\gamma$ . The transformation properties of the rota-

tional wavefunction  $|JM\Omega\rangle$  may be derived with the help of the two identities (56)

$$d^j_{m',m}(\pi - \beta) = (-1)^{j-m'} d^j_{m,-m'}(\beta) \quad (\text{A9})$$

and

$$d^j_{m',m}(\beta) = d^j_{-m,-m'}(\beta). \quad (\text{A10})$$

We find that

$$\begin{aligned} \mathbf{i}_{sp} D^{J^*}_{M\Omega}(\alpha, \beta, 0) &= D^{J^*}_{M\Omega}(\pi + \alpha, \pi - \beta, 0) \\ &= (-1)^J D^{J^*}_{M,-\Omega}(\alpha, \beta, 0). \end{aligned} \quad (\text{A11})$$

Hence we conclude that

$$\mathbf{i}_{sp} |JM\Omega\rangle = (-1)^J |JM, -\Omega\rangle. \quad (\text{A12})$$

The vibrational wavefunction  $R_{nv}(\mathbf{r})$  depends solely on the internuclear distance  $\mathbf{r}$ , a quantity that is unchanged by the operation  $\mathbf{i}_{sp}$ . Thus the effect of  $\mathbf{i}_{sp}$  on  $|nvS\Lambda\Sigma\rangle$  may be determined from the behavior of the electronic function  ${}^{2S+1}\varphi_\Omega$  under spatial inversion. The electronic wavefunction  ${}^{2S+1}\varphi_\Omega$  may be regarded as an antisymmetrized linear combination of spin-orbitals of the form

$$\varphi_\Lambda(\mathbf{q}_i; \mathbf{r}) \chi_{S\Sigma}(\sigma_i) \quad (\text{A13})$$

where  $\varphi_\Lambda$  expresses the orbital part and  $\chi_{S\Sigma}$  the spin part, respectively. For the purposes of determining the behavior of the vibronic wavefunction  $|nvS\Lambda\Sigma\rangle$ , it suffices then to consider separately the behavior of  $\varphi_\Lambda$  and  $\chi_{S\Sigma}$ .

The dependence of the orbital part on  $\Lambda$  may be written explicitly as  $\varphi_\Lambda(\mathbf{q}_i; \mathbf{r}) e^{i\Lambda\gamma_e}$  where the electronic coordinates  $\mathbf{q}_i$  are conveniently represented in cylindrical coordinates,

$$\begin{aligned} x_i &= \rho_i \cos \gamma_i, \\ y_i &= \rho_i \sin \gamma_i, \\ z_i &= z_i, \end{aligned} \quad (\text{A14})$$

and the angle  $\gamma_e$  may be considered to be an electronic reference angle from which all other  $\gamma_i$  are measured (35). To preserve the transformation properties given in Eqs. (A6) and (A7),  $\sigma_v^{yz}$  must have the effect of transforming  $\rho_i \rightarrow \rho_i$  and  $\gamma_i \rightarrow \pi - \gamma_i$ .

In the special case of  $\Sigma$  states, corresponding to  $\Lambda = 0$ , we must distinguish between two types of  $\Sigma$  states,  $\Sigma^+$  and  $\Sigma^-$ , according to whether the state is unchanged or changes sign, respectively, under a reflection in the  $yz$  plane. Thus we have

$$\mathbf{i}_{sp} \varphi_0 = (-1)^s \varphi_0, \quad (\text{A15})$$

where  $s = 1$  for  $\Sigma^-$  states and  $s = 0$  for  $\Sigma^+$  states.

For non- $\Sigma$  states, we are at liberty to choose  $s = 0$ ; this choice<sup>9</sup> implies that

$$\varphi_\Lambda(\mathbf{q}_i; \mathbf{r}) = (i)^\Lambda \varphi_{|\Lambda|} e^{i\Lambda\gamma_e}. \quad (\text{A16})$$

Thus, for all states

$$\mathbf{i}_{sp} \varphi_\Lambda = (-1)^s \varphi_{-\Lambda}, \quad (\text{A17})$$

where  $s = 1$  for  $\Sigma^-$  states, and  $s = 0$  for all others.

<sup>9</sup> Note that sometimes it may be preferable, especially when  $L$  is at most a good quantum number, to let  $s$  be a function of  $L$  and possibly  $\Lambda$  (24, 40).



In Hund's case (a) coupling the spin coordinates  $\sigma_i$  are referred to the molecule-fixed frame so that the symmetry operation  $\mathbf{i}_{s,p}$  may alter the value of  $\sigma_i$ . We may make explicit the spatial dependence of the spin function  $\chi_{S\Sigma}$  by re-expressing  $\chi_{S\Sigma}$  in terms of Hund's case (b) spin functions  $\chi_{Sm_s}$ , where  $m_s$  is the projection of  $S$  on a space-fixed axis:

$$\chi_{S\Sigma} = \sum_{m_s} D_{m_s\Sigma}^S(\alpha, \beta, 0) \chi_{Sm_s}. \quad (\text{A18})$$

In Eq. (A18)  $\chi_{Sm_s}$  is unaffected by the symmetry operation  $\mathbf{i}_{s,p}$  while  $D_{m_s\Sigma}^S$  transforms under  $\mathbf{i}_{s,p}$  according to Eq. (A11). Thus

$$\mathbf{i}_{s,p} \chi_{S\Sigma} = (-1)^S \chi_{S, -\Sigma}. \quad (\text{A19})$$

Combining Eqs. (A12), (A17), and (A19) we conclude that

$$\mathbf{i}_{s,p} |nvJS\Lambda\Sigma\rangle = (-1)^{J+S+s} |nvJS, -\Lambda, -\Sigma\rangle, \quad (\text{A20})$$

where  $s = 1$  for  $\Sigma^-$  states and  $s = 0$  for all other states. In Eq. (A20) we have omitted  $M$  from the wavefunction since Eq. (A20) is independent of the value of  $M$ .

#### APPENDIX B

For a  ${}^2\Sigma$  state each  $J$  value is associated with two rotational levels, one of each parity. The case (a) basis set functions corresponding to the rotational level  $J$  with parity  $p^\pm = \pm (-1)^{J+S+s}$  may be written

$$\begin{aligned} |n {}^2\Sigma_{\frac{1}{2}}^\pm vJ p^\pm\rangle &= \frac{1}{\sqrt{2}} [ |n {}^2\Sigma^\pm vJS\Lambda\Sigma\rangle \pm |n {}^2\Sigma^\pm vJS, -\Lambda, -\Sigma\rangle ] \\ &= \frac{1}{\sqrt{2}} [ |n {}^2\Sigma_{\frac{1}{2}}^\pm vJ\rangle \pm |n {}^2\Sigma_{-\frac{1}{2}}^\pm vJ\rangle ], \end{aligned} \quad (\text{B1})$$

where we have abbreviated their form by introducing the signed value of  $\Lambda + \Sigma$  as a subscript on the term symbol. For a  ${}^2\Pi$  state each  $J$  value, except  $J = \frac{1}{2}$ , has four rotational levels associated with it, two of each parity. The  $2 \times 2$  blocks of parity  $p^\pm$  are constructed from the case (a) basis functions

$$|n {}^2\Pi_{\frac{1}{2}} vJ p^\pm\rangle = \frac{1}{\sqrt{2}} [ |n {}^2\Pi_{\frac{1}{2}} vJ\rangle \pm |n {}^2\Pi_{-\frac{1}{2}} vJ\rangle ] \quad (\text{B2})$$

and

$$|n {}^2\Pi_{\frac{3}{2}} vJ p^\pm\rangle = \frac{1}{\sqrt{2}} [ |n {}^2\Pi_{\frac{3}{2}} vJ\rangle \pm |n {}^2\Pi_{-\frac{3}{2}} vJ\rangle ]. \quad (\text{B3})$$

In the special case  $J = \frac{1}{2}$ , the  $\Omega = \frac{3}{2}$  basis functions are missing and there are only two rotational levels of opposite parity for this  $J$  value.

In the absence of perturbations, the  $p^+$  parity levels of a  ${}^2\Sigma$  state have the energy

$$\begin{aligned} H_{\frac{1}{2}}^{(0)}(p^+) + H_{\frac{1}{2}}^{(1)}(p^+) &= T_v{}^2 + B_v{}^2(J + \frac{1}{2})(J + \frac{3}{2}) - D_v{}^2[(J + \frac{1}{2})(J + \frac{3}{2})]^2 \\ &\quad + H_v{}^2[(J + \frac{1}{2})(J + \frac{3}{2})]^3 - \frac{1}{2}\gamma_v{}^2(J + \frac{3}{2}), \end{aligned} \quad (\text{B4})$$

while the  $p^-$  parity levels have the energy

$$H_{\frac{1}{2}}^{(0)}(p^-) + H_{\frac{1}{2}}^{(1)}(p^-) = T_v^{\Sigma} + B_v^{\Sigma}(J - \frac{1}{2})(J + \frac{1}{2}) - D_v^{\Sigma}[(J - \frac{1}{2})(J + \frac{1}{2})]^2 + H_v^{\Sigma}[(J - \frac{1}{2})(J + \frac{1}{2})]^3 + \frac{1}{2}\gamma_v^{\Sigma}(J - \frac{1}{2}). \quad (\text{B5})$$

Equations (B4) and (B5) show that even in the absence of perturbation the rotational levels of a  ${}^2\Sigma$  state are split by an amount

$$E(n^2\Sigma_{\frac{1}{2}}^{\pm} vJp^-) - E(n^2\Sigma_{\frac{1}{2}}^{\pm} v, J - 1, p^+) = \gamma_v^{\Sigma}J, \quad (\text{B6})$$

where the magnitude of the splitting increases linearly with  $J$  in the absence of centrifugal distortion corrections to  $\gamma_v^{\Sigma}$ . Thus each rotational level except the  $J = \frac{1}{2}$  level of  $p^-$  parity occurs in closely-spaced pairs. Equations (B4)–(B6) assume a more familiar form if  $J + \frac{1}{2}$  is replaced by the rotational quantum number  $N$ , which is a good quantum number in Hund's case (b) coupling.

Suppose  ${}^2\Pi$  states perturb the  ${}^2\Sigma$  state under study (42). Then, we may treat these perturbations according to the Van Vleck transformation by adding the correction term

$$H_{\frac{1}{2}}^{(2)}(+) = \sum_{n'v'} [E(n^2\Sigma_{\frac{1}{2}}^{\pm} vJ) - E(n'^2\Pi v'J)]^{-1} \times \{ [\langle n^2\Sigma_{\frac{1}{2}}^{\pm} vJ | H_1 | n'^2\Pi_{\frac{1}{2}} v'J \rangle + \langle n^2\Sigma_{\frac{1}{2}}^{\pm} vJ | H_1 | n'^2\Pi_{-\frac{1}{2}} v'J \rangle]^2 + [\langle n^2\Sigma_{\frac{1}{2}}^{\pm} vJ | H_1 | n'^2\Pi_{\frac{1}{2}} v'J \rangle + \langle n^2\Sigma_{\frac{1}{2}}^{\pm} vJ | H_1 | n'^2\Pi_{-\frac{1}{2}} v'J \rangle]^2 \} \quad (\text{B7})$$

to the unperturbed energy of the  $p^+$  levels of a  ${}^2\Sigma^+$  state or the  $p^-$  levels of a  ${}^2\Sigma^-$  state, and by adding the correction term

$$H_{\frac{1}{2}}^{(2)}(-) = \sum_{n'v'} [E(n^2\Sigma^{\pm} vJ) - E(n'^2\Pi v'J)]^{-1} \times \{ [\langle n^2\Sigma_{\frac{1}{2}}^{\pm} vJ | H_1 | n'^2\Pi_{\frac{1}{2}} v'J \rangle - \langle n^2\Sigma_{\frac{1}{2}}^{\pm} vJ | H_1 | n'^2\Pi_{-\frac{1}{2}} v'J \rangle]^2 + [\langle n^2\Sigma_{\frac{1}{2}}^{\pm} vJ | H_1 | n'^2\Pi_{\frac{1}{2}} v'J \rangle - \langle n^2\Sigma_{\frac{1}{2}}^{\pm} vJ | H_1 | n'^2\Pi_{-\frac{1}{2}} v'J \rangle]^2 \} \quad (\text{B8})$$

to the  $p^-$  levels of a  ${}^2\Sigma^+$  state or the  $p^+$  levels of a  ${}^2\Sigma^-$  state. Introducing the electronic perturbation parameters  $q_v^{\Sigma}$ ,  $p_v^{\Sigma}$ , and  $o_v^{\Sigma}$  defined in Eqs. (39–41), Eqs. (B7) and (B8) may be rewritten

$$H_{\frac{1}{2}}^{(2)}(+) = q_v^{\Sigma}(J + \frac{1}{2})(J + \frac{3}{2}) + \frac{1}{2}p_v^{\Sigma}(J + \frac{3}{2}) + o_v^{\Sigma} \quad (\text{B9})$$

and

$$H_{\frac{1}{2}}^{(2)}(-) = q_v^{\Sigma}(J - \frac{1}{2})(J + \frac{1}{2}) - \frac{1}{2}p_v^{\Sigma}(J - \frac{1}{2}) + o_v^{\Sigma}. \quad (\text{B10})$$

For  $J = \frac{1}{2}$ , the matrix elements involving the  ${}^2\Pi_{\frac{1}{2}}$  and  ${}^2\Pi_{-\frac{1}{2}}$  wavefunctions do not appear in Eqs. (B7) and (B8); however, Eqs. (B9) and (B10) are unaltered.

Comparison of Eqs. (B9) and (B10) with Eqs. (B4) and (B5) shows that  ${}^2\Pi$  perturbations contribute a term  $o_v^{\Sigma}$  to the effective band origin, a term  $-p_v^{\Sigma}$  to the effective spin-rotation constant  $\gamma_v$ , and a term  $q_v^{\Sigma}$  to the effective  $B_v$  value. If centrifugal distortion corrections to the parameters  $o_v^{\Sigma}$ ,  $p_v^{\Sigma}$ , and  $q_v^{\Sigma}$  are also introduced, the effective  $D_v$  and  $H_v$  values also differ from  $D_v^{\Sigma}$  and  $H_v^{\Sigma}$ . This illustrates how the presence of interacting  ${}^2\Pi$  states impairs the mechanical meaning of the rotational constants of a  ${}^2\Sigma$  state. Because both parity levels are affected equally, it is not possible to recover  $B_v^{\Sigma}$  from the experimental  $B_v$  value. In the unique perturber approximation we note

that  $B_v < B_v^2$  if the perturbing  ${}^2\Pi$  state lies above the  ${}^2\Sigma^\pm$  state, and  $B_v > B_v^2$  if the perturbing  ${}^2\Pi$  state lies below.

## APPENDIX C

There are in general three  $\Lambda$ -doubling parameters required to describe the shifts and splittings of the  $\Lambda$  components of a  $\Pi$  state caused by interactions with  $\Sigma^\pm$  states of the same multiplicity. These electronic perturbation parameters are conveniently defined as (42)

$$o_v^\Pi = \sum_{n'v'} \frac{\langle n^{2S+1}\Pi vJ | \frac{1}{2}A(\mathbf{r})L_+ | n'^{2S+1}\Sigma^\pm v'J \rangle^2}{E_{nvJ} - E_{n'v'J}}, \quad (C1)$$

$$p_v^\Pi = 4 \sum_{n'v'} \frac{\langle n^{2S+1}\Pi vJ | \frac{1}{2}A(\mathbf{r})L_+ | n'^{2S+1}\Sigma^\pm v'J \rangle \langle n^{2S+1}\Pi vJ | B(\mathbf{r})L_+ | n'^{2S+1}\Sigma^\pm v'J \rangle}{E_{nvJ} - E_{n'v'J}}, \quad (C2)$$

and

$$q_v^\Pi = 2 \sum_{n'v'} \frac{\langle n^{2S+1}\Pi vJ | B(\mathbf{r})L_+ | n'^{2S+1}\Sigma^\pm v'J \rangle^2}{E_{nvJ} - E_{n'v'J}}. \quad (C3)$$

It is possible to relate the  $\Lambda$ -doubling parameters to each other and to the constants  $A_v^\Pi$  and  $B_v^\Pi$  of the perturbed state. These approximate relations prove useful as a means of estimating or interpreting the sign and magnitude of the  $\Lambda$ -doubling constants. They also permit us to understand how the  $\Lambda$ -doubling structure of a  $\Pi$  state changes as a function of  $A_v^\Pi$  from Hund's case (a) coupling ( $A_v^\Pi \rightarrow \infty$ ), to Hund's case (b) coupling ( $A_v^\Pi = 0$ ), to inverted Hund's case (a) coupling ( $A_v^\Pi \rightarrow -\infty$ ) (See Figs. 1-4).

1. Born-Oppenheimer separation. Each vibronic matrix element appearing in Eqs. (C1)-(C3) are assumed to factor into the product of a vibrational and an electronic matrix element:

$$\langle n^{2S+1}\Pi vJ | \frac{1}{2}A(\mathbf{r})L_+ | n'^{2S+1}\Sigma^\pm v'J \rangle = \langle vJ | \frac{1}{2}A(\mathbf{r}) | v'J \rangle \langle n | L_+ | n' \rangle \quad (C4)$$

and

$$\langle n^{2S+1}\Pi vJ | B(\mathbf{r})L_+ | n'^{2S+1}\Sigma^\pm v'J \rangle = \langle vJ | B(\mathbf{r}) | v'J \rangle \langle n | L_+ | n' \rangle. \quad (C5)$$

2. Neglect of centrifugal distortion. The  $\Lambda$ -doubling parameters are assumed to be independent of  $J$ . Thus

$$\langle vJ | B(\mathbf{r}) | v'J \rangle = \langle v | B(\mathbf{r}) | v' \rangle, \quad (C6)$$

$$\langle vJ | \frac{1}{2}A(\mathbf{r}) | v'J \rangle = \langle v | \frac{1}{2}A(\mathbf{r}) | v' \rangle, \quad (C7)$$

and

$$E_{nvJ} - E_{n'v'J} = E_{nv} - E_{n'v'}. \quad (C8)$$

3. Variation of  $A(\mathbf{r})$  with  $\mathbf{r}$ . The spin-orbit parameter  $A$  is usually a slowly-varying function of internuclear distance (56). The reasons for this behavior are complex (15,57). In brief, the value of  $A$  is approximately the sum of the contributions  $\Sigma_i (Z_{ik})_{\text{eff}} \langle r_{ik}^{-3} \rangle$  for each nucleus  $k$ , where  $(Z_{ik})_{\text{eff}}$  is the effective (screened) nuclear charge seen by the unpaired electron  $i$  and  $\langle r_{ik}^{-3} \rangle$  is the average cubed inverse distance from the electron  $i$  to the nucleus  $k$ . As the internuclear distance changes by a small amount, the variation of the electronic wavefunction does not sensitively affect these essentially atomic con-

tributions. Therefore, we assume that

$$\langle v | \frac{1}{2}A(\mathbf{r}) | v' \rangle = \frac{1}{2}A_v^{\text{II}} \langle v | v' \rangle. \quad (\text{C9})$$

With the help of the foregoing approximations the  $\Lambda$ -doubling parameters may be rewritten

$$o_v^{\text{II}} = \frac{1}{4}(A_v^{\text{II}})^2 \sum_{n'} \langle n | L_+ | n' \rangle^2 \sum_{v'} \frac{\langle v | v' \rangle^2}{E_{n_v} - E_{n'_{v'}}}, \quad (\text{C10})$$

$$p_v^{\text{II}} = 2A_v^{\text{II}} \sum_{n'} \langle n | L_+ | n' \rangle^2 \sum_{v'} \frac{\langle v | B(\mathbf{r}) | v' \rangle \langle v' | v \rangle}{E_{n_v} - E_{n'_{v'}}}, \quad (\text{C11})$$

and

$$q_v^{\text{II}} = 2 \sum_{n'} \langle n | L_+ | n' \rangle^2 \sum_{v'} \frac{\langle v | B(\mathbf{r}) | v' \rangle \langle v' | B(\mathbf{r}) | v \rangle}{E_{n_v} - E_{n'_{v'}}}. \quad (\text{C12})$$

Equations (C10)–(C12) show that  $o_v^{\text{II}}$  is proportional to the square of  $A_v^{\text{II}}$ ,  $p_v^{\text{II}}$  is proportional to  $A_v^{\text{II}}$ , and  $q_v^{\text{II}}$  is independent of  $A_v^{\text{II}}$ .

4. Unique perturber approximation. We assume one  $\Sigma^+$  or one  $\Sigma^-$  state (real or composite) of the same multiplicity accounts for the  $\Lambda$  doubling. Then the summation over  $n'$  in Eqs. (C10)–(C12) may be omitted.

5. Effective energy denominator. Because of the Franck–Condon principle, only those vibrational levels  $v'$  of the  $n' {}^{2S+1}\Sigma^\pm$  state with appreciable Franck–Condon factors contribute to the vibrational sums shown in Eq. (C10)–(C12). Moreover, the vibrational spacings in the perturbing electronic state are usually small compared to the separation between the two electronic states  $n$  and  $n'$ . Accordingly, we assume that we can replace the energy denominators in Eqs. (C10)–(C12) by an effective value  $\Delta E(v)$  that is independent of  $v'$ . This permits us to carry out the summations over  $v'$  in Eqs. (C10)–(C12). The expressions for the  $\Lambda$ -doubling parameters reduce to

$$o_v^{\text{II}} = \frac{1}{4}(A_v^{\text{II}})^2 \langle n | L_+ | n' \rangle^2 / \Delta E(v), \quad (\text{C13})$$

$$p_v^{\text{II}} = 2A_v^{\text{II}} B_v^{\text{II}} \langle n | L_+ | n' \rangle^2 / \Delta E(v), \quad (\text{C14})$$

$$q_v^{\text{II}} = 2 \langle v | B^2(\mathbf{r}) | v \rangle \langle n | L_+ | n' \rangle^2 / \Delta E(v). \quad (\text{C15})$$

For calculational purposes<sup>10</sup>  $\Delta E(v)$  might be taken as

$$\Delta E(v) = \sum_{v'} q_{v'v} / (E_{n_v} - E_{n'_{v'}}), \quad (\text{C16})$$

where  $q_{v'v} = \langle v' | v \rangle^2$ .

Inspection of Eqs. (C13)–(15) shows that the sign of  $o_v^{\text{II}}$  is the same as  $q_v^{\text{II}}$ , i.e., the sign of  $\Delta E(v)$ , while the sign of  $p_v^{\text{II}}$  is the sign of  $o_v^{\text{II}}$  or  $q_v^{\text{II}}$  times the sign of  $A_v^{\text{II}}$ . Few exceptions are known to this rule and they have been traced to the failure of the unique perturber approximation (59). We also note that  $o_v^{\text{II}}$  and  $p_v^{\text{II}}$  may be related to each

<sup>10</sup> Often the evaluation of Eqs. (C13)–(C15) can be further simplified by assuming that the valence electrons have well-defined angular momenta  $l$  that make projections  $\lambda$  on the internuclear axis [Van Vleck's hypothesis of pure precession (42)]. This permits the matrix elements  $\langle n | L_+ | n' \rangle^2$  to be simply estimated. However, the pure precession hypothesis is not always satisfied (58) and, in any case, we need not make this assumption in what follows.

other by

$$o_v^\Pi = \frac{1}{8}(A_v^\Pi/B_v^\Pi)p_v^\Pi, \quad (\text{C17})$$

and  $p_v^\Pi$  and  $q_v^\Pi$  by

$$p_v^\Pi = \frac{8\pi^2c\mu}{h} \frac{\langle v|r^{-2}|v\rangle}{\langle v|r^{-4}|v\rangle} A_v^\Pi q_v^\Pi. \quad (\text{C18})$$

If we further approximate  $\langle v|r^{-4}|v\rangle$  as  $\langle v|r^{-2}|v\rangle^2$  then Eq. (C18) simplifies to

$$p_v^\Pi \approx (A_v^\Pi/B_v^\Pi)q_v^\Pi. \quad (\text{C19})$$

No study of the validity of Eqs. (C17) or (C18) appears to have been made to date; the validity of Eq. (C19) has been considered in the analysis of the  $O_2^+ A^2\Pi_u-X^2\Pi_g$  system (45).

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