

A Critique of the Term Value Approach to Determining Molecular Constants from the Spectra of Diatomic Molecules

D. L. ALBRITTON, W. J. HARROP, AND A. L. SCHMELTEKOPF

*Aeronomy Laboratory, National Oceanic and Atmospheric Administration,
Boulder, Colorado 80302*

R. N. ZARE¹

Department of Chemistry, Columbia University, New York, New York 10027

AND

E. L. CROW

*Institute for Telecommunication Sciences, Office of Telecommunications,
Boulder, Colorado 80302*

Two alternative methods for the reduction of observed line positions to spectroscopic constants are compared. In the direct approach, the line positions are fit directly to expressions for the energy level differences in which the upper and lower state molecular constants enter as unknowns. In the traditional term value approach, a two-step procedure is followed where first a set of intermediate unknowns, the upper and lower state term values are calculated from the observed line positions and secondly these term values for each vibrational state, are fit separately to energy expressions in which the molecular constants of that state enter as unknowns. It is shown that there is correlation between the term values of all vibrational states included in the reduction. Thus, the separate fitting of term values to energy level expressions for each vibrational state does not retain this correlation and the molecular constants found in this manner cannot be the minimum-variance, linear, unbiased (MVLU) estimates and the accompanying standard deviations cannot be unbiased estimates. However, if the molecular constants of all the vibrational levels are determined simultaneously from all the term values in a *correlated* least-squares fit, then the molecular constants will be equal to those determined from the direct approach, i.e., the MVLU set. Furthermore, missing lines and the frequent occurrence of two independent sets of lines within a band both cause the molecular constants obtained from the traditional term value approach to differ even more from the MVLU set. Finally, the limitations of reducing groups of bands simultaneously are discussed. Certain singlet systems are given as examples of the above conclusions.

I. INTRODUCTION

There are basically two classes of problems in reducing spectroscopic line position measurements to molecular constants: (a) constructing the proper elements of the

¹ R. N. Z. gratefully acknowledges support from the National Science Foundation.

Hamiltonians for the electronic states involved and (b) fitting the measured line positions either directly or indirectly to the eigenvalues of these Hamiltonians using a sound statistical procedure. Our preceding paper (1) deals primarily with the first of these problems; the present paper considers the second.

The time-honored method of determining the rotational constants B_v and D_v is the use of combination differences, which permits the separation of the upper and lower vibrational states of the transition. The combination difference

$$\Delta_2 F_v''(J'') = R(J'' - 1) - P(J'' + 1) \quad (1)$$

is associated with the energy difference between the rotational levels $J'' - 1$ and $J'' + 1$ of the lower state, since the lines $R(J'' - 1)$ and $P(J'' + 1)$ *both* arise from the rotational level $J' = J''$ of the upper state. Furthermore, this combination difference is related, for the example of a singlet state, to the lower state rotational constants by

$$\Delta_2 F_v''(J'') = 4B_v''(J'' + \frac{1}{2}) - D_v''[(6 - 8\Lambda''^2)(J'' + \frac{1}{2}) + 8(J'' + \frac{1}{2})^2] \quad (2)$$

The evaluation of B_v'' and D_v'' using Eq. (2) and all such $\Delta_2 F_v''(J'')$ values from the lines of a band has usually been done graphically. The upper state rotational constants follow from a similar set of combination differences that are associated with energy differences between upper state rotational levels. The band origins $\nu_o(v', v'')$ have been determined either from the observed lines and the computed rotational constants, or, more commonly, from the lines alone using graphical techniques. Finally, where applicable, the spin-orbit, lambda-doubling, spin-spin, and spin-rotation constants have been determined separately either by appropriate differences between the observed lines or the above constants. Herzberg (2) describes all of these techniques extensively.

While combination differences are extremely useful to establish or check the assignment of rotational quantum numbers of observed lines, to search for common vibrational or electronic states among a set of band measurements, and to detect isolated faulty measurements, their use in graphically computing rotational constants suffers from several deficiencies. Combination differences can be graphically applied only to those rotational energy levels that can be represented by relatively simple algebraic expressions similar to Eq. (2). Thus, in many cases, only the lines from a fraction of the observed branches can be used in determining the rotational constants. Furthermore, for *each* line that must be omitted from the analysis due to blends, overlaps, rejection criteria, etc., *two* combination differences are usually lost. Graphical reduction of data is inherently subjective, and, even though a spectroscopist with sound intuition and an intimate knowledge of the data may use it to an advantage, it also often leads to unduly optimistic estimates of the experimental uncertainties of the resulting molecular constants. The deficiencies of using graphical analysis with combination differences to reduce the data for the $O_2 X^3\Sigma_g^-$ state are examined in a following paper (3).

Replacing the graphical analysis by the method of least squares should provide more realistic estimates of the uncertainties in the molecular constants, but it does not eliminate the deficiencies inherent in the method of combination differences itself. In addition to those given above, there are further, perhaps more subtle, reasons why the use of combination differences is less than optimum statistically. Identifying the combination difference $\Delta_2 F_v''(J'')$ in Eq. (1) as an energy that is characteristic of the lower state *alone* makes the implicit assumption that all of the measurement errors are as-

sociated with the lower state alone. This is, of course, not correct; the measurement errors are shared between the upper and lower states. Furthermore, determining the rotational constants B_v and D_v separately from the band origin and the spin-orbit, Λ -doubling, and other molecular constants is not a statistically sound procedure.

This paper considers the two commonly used alternatives to the use of combination differences to reduce line position measurements. Section II examines the details of fitting the observed line positions directly to expressions for the energy levels that contain the upper and lower state molecular constants as unknown parameters. Section III considers the two-step procedure that introduces a set of intermediate unknowns, the term values for the upper and lower state rotational levels. The closing section contrasts the term value approach to the direct approach and examines the relative strengths and weaknesses with the aid of examples of singlet systems.

II. DIRECT APPROACH

For the purpose of examining the details of the direct approach to obtaining molecular constants from observed line positions, we will consider one band of a singlet system in which Λ -doubling and the centrifugal distortion constants H_v and higher-order may be ignored. This simple example is sufficient to compare the direct and term value approaches and yet it does not require a complex notation. Furthermore, the results developed here can be easily extended to more complicated systems.

A set of equally weighted,² uncorrelated line position measurements $\nu_i, i = 1, 2, \dots, n$, for a singlet band may be represented by the n equations

$$\nu_i = \nu_o + B_v'[J_i'(J_i' + 1) - \Lambda'^2] - D_v'[J_i'(J_i' + 1) - \Lambda'^2]^2 - B_v''[J_i''(J_i'' + 1) - \Lambda''^2] + D_v''[J_i''(J_i'' + 1) - \Lambda''^2]^2 + \delta_i, \quad i = 1, 2, \dots, n, \quad (3)$$

where $\nu_o, B_v', D_v', B_v'',$ and D_v'' are the five unknown molecular constants; $J_i', \Lambda', J_i'',$ and Λ'' are the assumed-known quantum numbers; and δ_i are the unknown, uncorrelated measurement errors assumed to have zero mean and common unknown variance σ^2 . In matrix notation, Eq. (3) can be written quite succinctly as

$$\mathbf{v} = \mathbf{U}\boldsymbol{\beta} + \boldsymbol{\delta}, \quad (4)$$

where $\mathbf{v}, \boldsymbol{\beta},$ and $\boldsymbol{\delta}$ are the column vectors

$$\mathbf{v} = \begin{bmatrix} \nu_1 \\ \nu_2 \\ \cdot \\ \cdot \\ \nu_n \end{bmatrix}, \quad \boldsymbol{\beta} = \begin{bmatrix} \nu_o \\ B' \\ D' \\ B'' \\ D'' \end{bmatrix}, \quad \boldsymbol{\delta} = \begin{bmatrix} \delta_1 \\ \delta_2 \\ \cdot \\ \cdot \\ \delta_n \end{bmatrix}, \quad (5)$$

and \mathbf{U} is a $n \times 5$ matrix with elements given by 1,

$$[J_i'(J_i' + 1) - \Lambda'^2], \quad [J_i''(J_i'' + 1) - \Lambda''^2],$$

and the square of these latter two, all of which are known.

² The specification of equal weights is *only* for simplicity. There is no difficulty in generalizing to the situation of unequal weights (4), indeed, this is always desirable when practical.

Since n is usually much greater than five, the system is strongly overdetermined and the method of least squares may be applied to obtain $\hat{\beta}$, the minimum-variance, linear, unbiased (MVLU) estimate of β (4):

$$\hat{\beta} = (\mathbf{U}^t \mathbf{U})^{-1} \mathbf{U}^t \mathbf{v}, \quad (6)$$

where \mathbf{U}^t is the transpose of \mathbf{U} and $(\mathbf{U}^t \mathbf{U})^{-1}$ is the inverse of the matrix product $\mathbf{U}^t \mathbf{U}$. The associated unbiased estimate of the variance σ^2 is

$$\hat{\sigma}^2 = \frac{1}{n-5} (\mathbf{v} - \mathbf{U} \hat{\beta})^t (\mathbf{v} - \mathbf{U} \hat{\beta}). \quad (7)$$

The 5×5 symmetric matrix given by

$$\hat{\mathbf{V}} = \hat{\sigma}^2 (\mathbf{U}^t \mathbf{U})^{-1} \quad (8)$$

is the estimated variance-covariance matrix of $\hat{\beta}$. Specifically, the diagonal elements \hat{V}_{ii} are the estimated variances (i.e., the squares of the standard deviations) of the estimated values of the unknowns ν_0 , B_v' , D_v' , B_v'' , and D_v'' and the off-diagonal elements \hat{V}_{ij} ($i \neq j$) are their estimated covariances. The usefulness of the covariance between two quantities is best examined by normalizing $\hat{\mathbf{V}}$ to form the correlation matrix \mathbf{C} , the elements of which are given by

$$C_{ij} = \hat{V}_{ij} / (\hat{V}_{ii} \hat{V}_{jj})^{1/2}, \quad (9)$$

and lie in the range $-1 \leq C_{ij} \leq 1$. The C_{ij} are functions only of the known matrix \mathbf{U} , since the factor $\hat{\sigma}^2$ involving the measurements cancels in Eq. (9). Note that the correlation does not depend on the accuracy of the measurements, but rather on the extent of the measurements and the form of the equations (i.e., models) linking the measurements to the unknowns. If the correlation coefficient C_{ij} between the estimates of two molecular constants is very near $+1$ or -1 , it is relatively difficult to determine accurate values of the two constants simultaneously. On the other hand, if C_{ij} is near zero, the two constants are relatively independent of each other.

For a first example, this direct approach is applied to the high resolution data taken by Edvinsson, Selin, and Åslund (5) for the (0,0) band of the $G^1\Delta-H^1\Phi$ system of ThO^3 . The MVLU estimates given by Eq. (6) for the molecular constants are the first column of numbers in Table I. Also, in parentheses, are the estimates of the associated standard deviations $\hat{V}_{ii}^{1/2}$, given by Eqs. (7) and (8). The high quality of these data is demonstrated by the relatively low value of the estimate of σ , $\hat{\sigma} = 0.014 \text{ cm}^{-1}$. Table II lists the correlation coefficients C_{ij} given by Eq. (9) for the five molecular constants. Note that B_0' and B_0'' , as well as D_0' and D_0'' , are highly correlated. This merely expresses quantitatively a well-known spectroscopic fact; namely, $\Delta B \equiv B_0' - B_0''$ and $\Delta D \equiv D_0' - D_0''$ can be determined more accurately than B_0' and B_0'' or D_0' and D_0'' .

³ Edvinsson, Selin, and Åslund (5) interpreted one set of singlet bands as a $^1\Phi-^1\Delta$ system by analogy with the band spectra of TiO and ZrO . However, Edvinsson, Bornstedt, and Nylén (6) discovered that the $^1\Delta$ state is actually the upper state of this singlet system. Therefore the transition formerly called $H^1\Phi-G^1\Delta$ has now been given the new assignment $G^1\Delta-H^1\Phi$. Edvinsson, Bornstedt, and Nylén extended the (0,0) band, but, for the purposes of this example, we have used only the data of Edvinsson, Selin, and Åslund.

TABLE I
Molecular Constants Determined by Different Methods of Reduction from the $(0,0)$ Band of the $\text{ThO } G_{1\Delta} \text{ -- } H_{1\Phi}$ System^a

	Direct approach	Traditional term value approach	Improved term value approach	Δ_{2F}^b combination differences
$\nu_0(0,0)$	12 691.686(2)	12 691.685(10) ^b	12 691.686(2)	
F_0'	0.317586(20)	0.317571(3)	0.317586(21)	0.317552(25)
D_0'	$1.974(14) \times 10^{-7}$	$1.959(3) \times 10^{-7}$	$1.974(15) \times 10^{-7}$	$1.936(23) \times 10^{-7}$
F_0''	0.325827(20)	0.325811(3)	0.325827(21)	0.325789(27)
D_0''	$1.902(15) \times 10^{-7}$	$1.885(3) \times 10^{-7}$	$1.902(16) \times 10^{-7}$	$1.858(25) \times 10^{-7}$
degrees of freedom	293	79^c 107^d 106^e	79^c 214^f	77^g 77^h
$\hat{\sigma}$	0.014	0.011^c 0.038^d 0.037^e	0.011^c 0.015^f	0.020^g 0.021^h

^a The number(s) in parentheses are the uncertainty in the last digit(s) that corresponds to one standard deviation. All units are reciprocal centimeters.

^b $\nu_0(0,0)$ is the difference $F_0' - F_0''$, where $F_0' = 12\,690.698(7)$ and $F_0'' = -0.987(7)$.

^c Step one

^d Step two, upper state

^e Step two, lower state

^f Step two

^g Upper state

^h Lower state

TABLE II
Correlation Coefficients for the Molecular Constants of the (0,0)
Band of the $\text{ThO } G^1\Delta - H^1\Sigma$ System

	$v_0(0,0)$	B_0'	D_0'	B_0''	D_0''
$v_0(0,0)$	1				
B_0'	- 0.034	1			
D_0'	- 0.002	0.896	1		
B_0''	- 0.003	0.999	0.898	1	
D_0''	0.028	0.891	0.999	0.895	1

Table II also shows that the pairs (B', D') , (B'', D'') , (B', D'') , and (B'', D') are also strongly correlated but to a lesser extent. Finally, the band origin is relatively uncorrelated with the other constants.

For electronic states more complex than the simple states considered here, Eq. (3) is generally nonlinear. The use of nonlinear least-squares in the direct approach to reducing spectroscopic data is examined in a preceding paper (1).

With the increasing availability of large computers, more and more spectroscopists are using the approach outlined above, rather than the graphical application of combination differences, to obtain the molecular constants directly from the measured line positions for each band. Furthermore, with the interactive technology that is also becoming available in many computer centers, spectroscopists could effectively use the intuition gained by their detailed familiarity with their measurements directly in the reduction of the data.

While the illustration above has been for a single band, it is straightforward, at least conceptually, to extend this approach to include simultaneously all of the bands of a system, provided *all* of the measurement errors belong to the same distribution. Since the bands of an observed system will often have several vibrational states in common, the resulting single values for the molecular constants associated with these states will be the optimum values for these common states. Continuing in this vein, one could extend this approach to include all of the observed band systems of a molecule; i.e., a simultaneous reduction of all of the bands of all of the band systems. Again, the single values obtained for the electronic states that are common to more than one band system will be the optimum values. The column vector \mathbf{v} would then contain all of the lines measured for the molecule, and $\mathbf{\beta}$ would contain the unknown molecular constants for each of the appropriate vibrational levels of all of the electronic states. Since the matrix \mathbf{U} relates \mathbf{v} to $\mathbf{\beta}$, it may now be on the order of $10\,000 \times 1000$. Arrays of this size with elements that may differ in magnitude by 10^8 cannot be handled very effectively by most computers. Consequently, this is one of the major reasons why the direct approach has commonly been used in a band-by-band reduction of spectroscopic data, rather than in a simultaneous reduction of all bands.

III. TRADITIONAL TERM VALUE APPROACH

An alternative approach to reducing spectroscopic data has been developed by Åslund (7) and coworkers, who have applied it to the problem introduced above, namely a simultaneous determination of all possible molecular constants for a molecule from all observed lines for the molecule. The approach is to introduce intermediate unknowns, the term values $Y_i(J)$ of the rotational levels. The problem then divides into two parts: (1) the determination of the term values from the measured line positions, and (2) the determination of the molecular constants from the term values.

To illustrate this traditional term value approach the example of one singlet band without Λ -doubling is continued. The first step of the term value approach is to express the set of equally weighted,² uncorrelated line position measurements ν_i as differences between upper and lower state term values:

$$\nu_i = Y_i' - Y_i'' + \delta_i, \quad i = 1, 2, \dots, n. \quad (10)$$

In matrix notation, these n equations become

$$\mathbf{v} = \mathbf{W}\mathbf{Y} + \boldsymbol{\delta}, \quad (11)$$

where the column vector \mathbf{Y} ,

$$\mathbf{Y}^t = [Y_1', Y_2', \dots, Y_p', Y_1'', Y_2'', \dots, Y_q''], \quad (12)$$

contains the unknown Y_i' , $i = 1, 2, \dots, p$, and Y_i'' , $i = 1, 2, \dots, q$ term values; the column vector $\boldsymbol{\delta}$ contains the uncorrelated measurement errors δ_i with zero mean and common variance σ^2 ; and the $n \times (p + q)$ matrix \mathbf{W} (where $n > p + q$) contains the known coefficients.

On casual examination, this first step appears to be a backward step. For the (0,0) ThO $G^1\Delta-H^1\Phi$ band, 219 unknown term values must now be determined, rather than five unknown molecular constants. Furthermore, Eq. (11) is barely over-determined, 298 equations for 219 unknowns, compared to 298 equations for 5 unknowns for Eq. (4). However, these disadvantages are counteracted by the fact that most of the elements of the 298×219 \mathbf{W} matrix are zero and the few nonzero elements are +1 or -1. This means that the matrix multiplications in the expression for the MVLU estimates for the term values

$$\hat{\mathbf{Y}} = (\mathbf{W}'\mathbf{W})^{-1}\mathbf{W}'\mathbf{v} \quad (13)$$

are simple. Hence, the only technical difficulty associated with Eq. (13) is the large order of the matrices, particularly in taking the inverse of $\mathbf{W}'\mathbf{W}$. This problem, however, can be handled rather straightforwardly using the techniques developed by Tewarson (8) for such "sparse" matrices. Åslund (7) has used a technique to obtain the MVLU estimates of the term values that avoids the need for large storage, namely, the normal equations that lead to Eq. (13) are never explicitly formed; instead, the term values are obtained by a partitioning technique (7).

In the second step of the traditional term value approach, Åslund and coworkers assume that all of the term values are uncorrelated and have equal variance; hence, the upper and lower state molecular constants are determined separately from the \hat{Y}_i' and \hat{Y}_i'' values, respectively. In the upper state, for example, the term values are related

to the molecular constants by the matrix equation

$$\hat{\mathbf{Y}}' = \mathbf{Z}'\mathfrak{g}' + \boldsymbol{\varepsilon}', \quad (14)$$

where the column vector $\hat{\mathbf{Y}}'$ contains the upper state term values \hat{Y}'_i from the first step; \mathfrak{g}' contains the unknown rotational constants B'_0 and D'_0 and the unknown energy reference F'_0 ; and $\boldsymbol{\varepsilon}'$ contains the errors. The elements of the $p \times 3$ matrix \mathbf{Z}' (with $p > 3$) are 1, $[J'_i(J'_i + 1) - \Lambda'^2]$ and $[J'_i(J'_i + 1) - \Lambda'^2]^2$, all of which are known. The estimates of the molecular constants are given by

$$\hat{\mathfrak{g}}' = (\mathbf{Z}'^t\mathbf{Z}')^{-1}\mathbf{Z}'^t\hat{\mathbf{Y}}', \quad (15)$$

and the estimated variances of these values are given by the diagonal elements of the 3×3 matrix

$$\hat{\mathbf{V}}'_2 = \hat{\sigma}_2'^2(\mathbf{Z}'^t\mathbf{Z}')^{-1}, \quad (16)$$

where

$$\hat{\sigma}_2'^2 = [1/(p - 3)](\hat{\mathbf{Y}}' - \mathbf{Z}'\hat{\mathfrak{g}}')^t(\hat{\mathbf{Y}}' - \mathbf{Z}'\hat{\mathfrak{g}}'). \quad (17)$$

The molecular constants for the lower state are determined similarly, but separately. The band origin is the difference $F'_0 - F''_0$. When applied to the data for the (0,0) $H^1\Phi-G^1\Delta$ ThO band considered above, this traditional term value approach yields the results in the second column of numbers in Table I. For electronic states other than the singlet states considered here, the individual least-squares fits made in this second step become more complicated and perhaps nonlinear. In the first step, however, the single least-squares fit will always be linear.

The extension of the traditional term value approach to include all of the observed bands of a band system and then all of the observed band systems of a molecule in a simultaneous reduction is straightforward. The matrix \mathbf{W} in the first step (Eq. 11) becomes very large indeed, but most of its elements are still zero and the nonzero elements are regularly distributed values of -1 or $+1$. For the second step, this extension to all of the observed bands only increases the number of least-squares fits, rather than their complexity, since the term values of each vibrational level are fitted separately. Thus, Åslund (7) maintains that introducing the intermediate unknown term values and performing the reduction in two steps has circumvented the problem of handling a great bulk of numbers of widely different magnitudes encountered in the direct approach; namely, the first step is a fit that involves a large quantity of rather simple numbers, and the second step is a collection of individual and separate fits, each of which is relatively simple. It is further maintained that the traditional term value approach offers a gain in accuracy, often a decimal digit or more, over the combination difference method. Åslund and coworkers have reduced the data of several molecules using this method.³ For example, Edvinsson *et al.* (5) simultaneously reduced the data of all seven band systems of ThO, comprising a total of twenty bands, with a computer of only modest size.

³ Essentially all of the applications of the traditional term value approach have been published in the journal *Arkiv för Fysik* and its successor *Physica Scripta*.

IV. CRITIQUE

Variance-Covariance Matrix

Close comparison of the first two columns of numbers in Table I reveals that the values obtained for the molecular constants of the ThO (0,0) $G^1\Delta-H^1\Phi$ band by the direct approach and the traditional term value approach are, in this case, similar. Indeed, the standard deviations of the residuals between calculated and observed line positions using the two sets of molecular constants are essentially the same. In contrast, however, the standard deviations of the estimated molecular constants are very different. The traditional term value approach gives standard deviations that are, for the rotational constants, about a factor of six smaller than the comparable values given by the direct approach, and approximately the opposite is true for the uncertainties of the band origins. In terms of the standard deviations given by the direct approach, the differences between the values of the rotational constants is about one standard deviation. On the other hand, in terms of the standard deviations given by the traditional term value approach, these differences are about five standard deviations.

The cause of this inconsistency lies with the traditional term value approach. The two steps of this approach, as described above and as used in the literature (5,7), do not, in general, yield statistically optimum estimates for the molecular constants, and, particularly in the example above, for the standard deviations of these estimates. The difficulty arises because the second step, which determines the molecular constants from the upper and lower state term values separately, is based on the assumption that all of the calculated term values are uncorrelated and have equal variance, when actually they are correlated and have unequal variance, in general. Although this underlying assumption has been acknowledged (5,7) its consequences have never been pointed out.

Improved Term Value Approach

Since there is correlation between the term values of the upper and lower states, these two sets of term values cannot be fitted separately without losing the effect of this correlation on the estimates of molecular constants and their standard deviations. Instead, to be correct, the upper and lower state molecular constants must be determined from a correlated least-squares fit to both the \hat{Y}'_i and \hat{Y}''_i simultaneously. In such a fit, the calculated term values are related to the molecular constants by

$$\hat{\mathbf{Y}} = \mathbf{Z}\boldsymbol{\beta} + \boldsymbol{\varepsilon}, \quad (18)$$

where $\hat{\mathbf{Y}}$ is now the column vector that includes both \hat{Y}'_i and \hat{Y}''_i :

$$\hat{\mathbf{Y}}^t = [\hat{Y}'_1, \hat{Y}'_2, \dots, \hat{Y}''_p, \hat{Y}''_1, \hat{Y}''_2, \dots, \hat{Y}''_q]; \quad (19)$$

$\boldsymbol{\beta}$ is the column vector containing ν_o , B_v' , D_v' , B_v'' , and D_v'' ; and \mathbf{Z} is the known coefficient matrix. A correlated least-squares fit yields as the MVLU estimate of the unknowns (4)

$$\hat{\boldsymbol{\beta}} = (\mathbf{Z}^t \hat{\mathbf{V}}_1^{-1} \mathbf{Z})^{-1} \mathbf{Z}^t \hat{\mathbf{V}}_1^{-1} \hat{\mathbf{Y}}, \quad (20)$$

where

$$\hat{\mathbf{V}}_1 = \hat{\sigma}_1^2 (\mathbf{W}^t \mathbf{W})^{-1}, \quad (21)$$

with

$$\hat{\sigma}_1^2 = \frac{(\mathbf{v} - \mathbf{W}\hat{\mathbf{Y}})'(\mathbf{v} - \mathbf{W}\hat{\mathbf{Y}})}{n - (p + q)}, \quad (22)$$

is the estimated variance-covariance matrix of $\hat{\mathbf{Y}}$ from the first step. The estimated variances of $\hat{\mathfrak{B}}$ are given by the diagonal elements of

$$\hat{\mathbf{V}}_2 = \hat{\sigma}_2^2 (\mathbf{Z}'\mathbf{W}'\mathbf{W}\mathbf{Z})^{-1}, \quad (23)$$

where

$$\hat{\sigma}_2^2 = [(\hat{\mathbf{Y}} - \mathbf{Z}\hat{\mathfrak{B}})'(\mathbf{W}'\mathbf{W}(\hat{\mathbf{Y}} - \mathbf{Z}\hat{\mathfrak{B}}))]/(p + q - 5). \quad (24)$$

When this improved term value approach is applied to the (0,0) band of the ThO $G^1\Delta-H^1\Phi$ system, the results listed in the third column of numbers in Table I are obtained. Note that these values for the molecular constants are identical with those obtained from the direct approach. The standard deviations are slightly different. The reason for this difference is that $\hat{\sigma}^2$ in Eq. (7) is an estimate of the variance σ^2 of the original measurements ν_i based on $n - 5$ degrees of freedom, whereas $\hat{\sigma}_1^2$ and $\hat{\sigma}_2^2$ are estimates of σ^2 based on $n - (p + q)$ and $p + q - 5$ degrees of freedom, respectively. Here $n - 5 = 293$, $n - (p + q) = 79$, and $p + q - 5 = 214$. The estimates are made differently and need not be identical.

On the other hand, it is easy to show that $\hat{\mathfrak{B}}$ given by the improved term value approach must be identical to that given by the direct approach. The known coefficient matrix \mathbf{U} from the direct approach can always be related to the known coefficient matrices \mathbf{W} and \mathbf{Z} from the first and second step, respectively, of the improved term value approach by

$$\mathbf{U} = \mathbf{W}\mathbf{Z}. \quad (25)$$

When Eq. (13) for the term values from step one is substituted into Eq. (20) for $\hat{\mathfrak{B}}$ in the correlated-case second step, one obtains

$$\hat{\mathfrak{B}} = (\mathbf{Z}'\mathbf{W}'\mathbf{W}\mathbf{Z})^{-1}\mathbf{Z}'(\mathbf{W}'\mathbf{W})(\mathbf{W}'\mathbf{W})^{-1}\mathbf{W}'\mathbf{v}. \quad (26)$$

Substituting Eq. (25) into Eq. (26) yields

$$\hat{\mathfrak{B}} = (\mathbf{U}'\mathbf{U})^{-1}\mathbf{U}'\mathbf{v},$$

which is identical with Eq. (6) of the direct approach.

In matrix notation, the basic assumptions of the traditional term value approach, in which $\hat{\mathbf{Y}}'$ and $\hat{\mathbf{Y}}''$ are fitted separately to yield $\hat{\mathfrak{B}}'$ and $\hat{\mathfrak{B}}''$, can be expressed very simply; namely, the diagonal elements of the estimated variance-covariance matrix $\hat{\mathbf{V}}_1$ from the first step [Eq. (21)] are assumed to be equal and the off-diagonal elements are assumed to be zero, i.e., $\hat{\mathbf{V}}_1 = c\mathbf{I}$, where c is a constant and \mathbf{I} is the identity matrix. For illustration, if the variance-covariance matrix $\hat{\mathbf{V}}_1$ in Eqs. (20), (23), and (24) is replaced by $c\mathbf{I}$, the results obtained for the (0,0) ThO $G^1\Delta-H^1\Phi$ band are only very slightly different from those obtained from the traditional term value fit in Table I. The slight difference undoubtedly arises because F_o' and F_o'' must be separately fitted unknowns in one case and are combined into ν_o in the other. The neglect of the covariances appears to be more serious than the neglect of the unequal variances. If instead

of replacing \hat{V}_1 by $c\mathbf{I}$, it is replaced by another diagonal matrix \mathbf{D} , where the elements D_{ii} are the variances \hat{V}_{1ii} , the values obtained for the molecular constants and the associated standard deviations change only slightly from those obtained under the assumption $\hat{V}_1 = c\mathbf{I}$. Thus, in this example, the correlation between the upper and lower state term values contributes much more to the uncertainty of the molecular constants than does the inequality of the standard deviations of the term values.

It is clear from the foregoing (an additional example is also given below) that if the term value approach is to yield MVLU estimates for molecular constants and unbiased estimates of the associated standard deviations, then the variance-covariance matrix \hat{V}_1 must be carried from the first step into the second step; i.e., the improved rather than the traditional term value approach must be used. It must be noted that \hat{V}_1 is by no means a "sparse" matrix. Its number of elements is the square of the number of term values. Thus, in the simultaneous reduction of many bands, the term value approach, if it is to be done correctly, is encumbered with very nearly the same problem of large matrices that made the direct approach unwieldy in such cases.

This (0,0) ThO $G-H$ band also may be used to show the limitations of using combination differences to obtain estimates for the molecular constants. The fourth column of numbers in Table I lists the estimates of the rotational constants and the associated uncertainties obtained from the $\Delta_2 F(J)$ combination differences [Eq. (2)]. Note that these values differ substantially from the MVLU estimates. In fact, in this example, the traditional term value approach gives estimates that are in better agreement with the MVLU estimates than are the values from the combination difference approach. On the other hand, the standard deviations of the combination difference approach are more realistic than those of the traditional term value approach. Since combination differences are not used to estimate the band origin, no value for this constant has been listed in the fourth column.

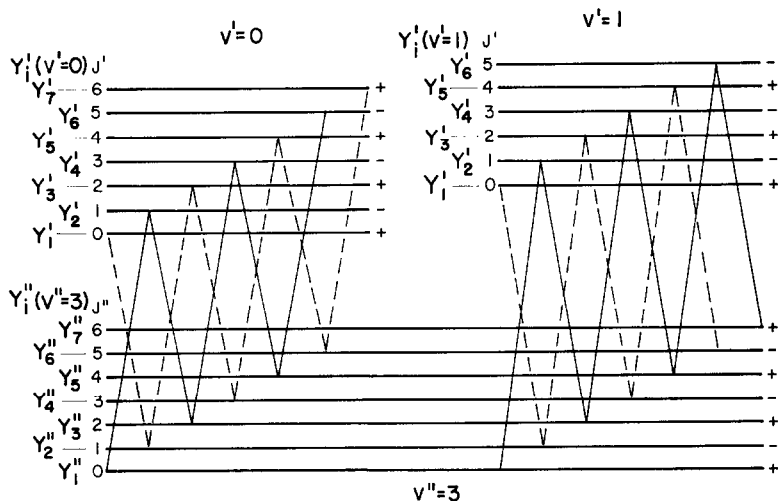


FIG. 1. Observed transitions and rotational energy levels of the (0, 3) and (1, 3) bands of the H_2 $B^1\Sigma_u^+ - X^1\Sigma_g^+$ Lyman system recorded by Herzberg and Howe (10).

TABLE III

Molecular Constants Determined by Different Methods of Reduction of the (0,3) and (1,3) Bands of the $H_2 B \ ^1\Sigma_u^+ - X \ ^1\Sigma_g^+$ System^a

	Simultaneously fit (0,3) and (1,3) bands		Individually fit (0,3) and (1,3) bands direct approach	
	Direct approach	Traditional term value approach ^b	(0,3)	(1,3)
$\nu_0(0,3)$	78 421.17(16)	78 421.55(37) ^c	78 421.00(4)	
$\nu_0(1,3)$	79 739.77(17)	79 739.97(37) ^c		79 739.80(18)
E_0'	19.463(26)	19.441(1)	19.437(6)	
D_0'	0.01546(56)	0.01482(3)	0.01474(13)	
E_1'	18.454(35)	18.477(11)		18.472(39)
D_1'	0.0117(11)	0.0129(4)		0.0123(11)
E_3''	50.662(22)	50.700(44)	50.584(8)	50.686(31)
D_3''	0.0410(5)	0.0421(10)	0.0383(2)	0.0417(6)
degrees of freedom	14	4 ^d 2 ^e 2 ^f 2 ^g	6	6
$\bar{\sigma}$	0.27	0.12 ^d 0.01 ^e 0.08 ^f 0.38 ^g	0.056	0.27

^a The number(s) in parentheses is the uncertainty in the last digit(s) that correspond to one standard deviation. All units are reciprocal centimeters.

^b $\nu_0(0,3)$ is the difference $F_0'(v'=0) - F_0''(v''=3)$, where $F_0'(v'=0) = 39\ 210.635(10)$ and $F_0''(v''=3) = -39\ 210.91(37)$. $\nu_0(1,3)$ is the difference $F_0'(v'=1) - F_0''(v''=3)$, where $F_0'(v'=1) = 40\ 529.06(6)$.

^c The values for X from the fits to the $v'' = 3$ and the $v' = 0$ and 1 levels are 39 210.27(16), 39 210.429(4), and 39 210.43(3), respectively.

^d Step one.

^e Step two, $v' = 1$.

^f Step two, $v' = 0$.

^g Step two, $v'' = 3$.

The importance of unbiased estimates⁴ of the standard deviations of the molecular constants should not be minimized. It is generally the relative magnitudes of an estimated molecular constant and its standard deviation that determine whether the interaction represented by that constant is statistically significant for the data (e.g., determining whether H_v is needed for a particular set of data). Furthermore, rotational constants from different investigations must often be combined in some logically weighted fashion to construct potential curves for an electronic state (θ). Realistic error estimates provide one basis for selecting relative weights. The fact that the biased

⁴ Unbiased estimates of variance do not yield unbiased estimates of standard deviation since taking the square root is a nonlinear operation. However, the bias is appreciable only for very small degrees of freedom.

TABLE IV

The Term Values and their Standard Deviations for $v' = 0$ and 1, B ${}^1\Sigma_u^+$ State, and $v'' = 3$, X ${}^1\Sigma_g^+$ State, of H_2

$v' = 0$, B ${}^1\Sigma_u^+$		$v' = 1$, B ${}^1\Sigma_u^+$		$v'' = 3$, X ${}^1\Sigma_g^+$	
term value	standard deviation	term value	standard deviation	term value	standard deviation
Y_0'	0	Y_0'	1 318.57 0.17	Y_0''	0
Y_1'	78 459.88 0.10	Y_1'	79 776.43 0.10	Y_1''	-78 319.93 0.12
Y_2'	116.33 0.16	Y_2'	1 429.10 0.16	Y_2''	302.26 0.12
Y_3'	78 652.23 0.16	Y_3'	79 959.31 0.16	Y_3''	-77 819.19 0.17
Y_4'	383.10 0.20	Y_4'	1 683.01 0.20	Y_4''	996.44 0.17
Y_5'	78 990.97 0.20	Y_5'	80 282.23 0.20	Y_5''	-76 937.74 0.20
Y_6'	790.59 0.24	Y_6'		Y_6''	2054.39 0.24

estimates of the standard deviations of the rotational constants given by the traditional term value approach in Table I are about a factor of five too small (and are even smaller in the second example below), strongly suggests that the claimed gain in accuracy of another decimal digit or so resulting from the traditional term value approach is not entirely due to fitting all of the data of a molecule simultaneously, but is due, to some extent, to the improper neglect of the variance-covariance matrix of the calculated term values.

Two Independent Sets of Term Values

There is an additional reason why the ThO $G^1\Delta-H^1\Phi$ band is a special case for the term value approach. If Λ -doubling had been observed in all of the rotational levels of the $G^1\Delta$ state, the observed lines of this band would then be divided into two independent sets, where each set is associated with one parity in each state. The independence of these two sets requires special consideration in the term value approach, but not in the direct approach. To examine this effect, a new example is introduced.

Figure 1 shows the lines and rotational energy levels of two ${}^1\Sigma^+ \rightarrow {}^1\Sigma^+$ bands that have a common lower vibrational state. In fact, this diagram depicts the 22 lines of the (0,3) and (1,3) bands of the H_2 B ${}^1\Sigma_u^+ - X^1\Sigma_g^+$ Lyman system recorded definitively by Herzberg and Howe (10). Note that the dashed set of lines never arise from or terminate on any of the lower or upper state levels joined by the solid set of lines. This is, of course, a consequence of the parity selection rule: $+\rightleftharpoons -$, $+\not\rightleftharpoons +$, $-\not\rightleftharpoons -$. The fact that the observed lines do divide into two completely independent sets causes no alteration in the direct approach. Equations (4-8) remain unchanged, and the first column of numbers in Table III contains the molecular constants obtained from the (0,3) and (1,3) bands simultaneously.⁵

On the other hand, the term value approach, either the improved or the traditional, requires consideration that there are two independent sets of lines. Since in the first

⁵ H_e' and H_e'' are not well determined for these bands and have been omitted from this example.

TABLE V

The Correlation Coefficients for the Herm Values of $v' = 0$ and 1 , $B \Sigma_u^+$ State, and $v'' = 3$, $X \Sigma_g^+$ State, of H_2

		$v' = 0, B \Sigma_u^+$						$v' = 1, B \Sigma_u^+$						$v'' = 3, X \Sigma_g^+$											
		Y_1'	Y_2'	Y_3'	Y_4'	Y_5'	Y_6'	Y_0'	Y_1'	Y_2'	Y_3'	Y_4'	Y_5'	Y_6'	Y_1''	Y_2''	Y_3''	Y_4''	Y_5''	Y_6''					
$+$	Σ_g^+	1																							
	Σ_g^+	0	1																						
	Σ_g^+	0.44	0	1																					
	Σ_g^+	0	0.68	0	1																				
	Σ_g^+	0.33	0	0.65	0	1																			
	Σ_g^+	0	0.57	0	0.75	0	1																		
	Σ_g^+	0	0.53	0	0.43	0	0.35	1																	
	Σ_g^+	0.33	0	0.44	0	0.33	0	0	1																
	Σ_g^+	0	0.71	0	0.68	0	0.57	0.53	0	1															
	Σ_g^+	0.44	0	0.71	0	0.65	0	0	0.44	0	1														
	Σ_g^+	0	0.68	0	0.82	0	0.75	0.43	0	0.68	0	1													
	Σ_g^+	0.33	0	0.65	0	0.67	0	0	0.33	0	0.65	0	1												
	Σ_g^+	0	0.76	0	0.60	0	0.50	0.71	0	0.76	0	0.60	0	1											
	Σ_g^+	0.58	0	0.76	0	0.58	0	0	0.58	0	0.76	0	0.58	0	1										
	Σ_g^+	0	0.80	0	0.85	0	0.71	0.50	0	0.80	0	0.85	0	0.71	0	1									
	Σ_g^+	0.41	0	0.80	0	0.82	0	0	0.41	0	0.80	0	0.82	0	0.71	0	1								
	Σ_g^+	0	0.65	0	0.87	0	0.87	0.41	0	0.65	0	0.87	0	0.58	0	0.82	0	1							
	Σ_g^+	0.29	0	0.57	0	0.58	0	0	0.29	0	0.57	0	0.87	0	0.50	0	0.71	0	1						

step of the term value approach, the term values are determined from the observed lines, there will also be two independent sets of term values: one set associated with the levels joined by the dashed lines in Fig. 1, and the other set associated with the levels joined by the solid lines. The zero energy reference point for each set can be arbitrarily established. For example, in Fig. 1, a simple choice would be to set $Y_1''(v'' = 3) = 0$ and $Y_1'(v' = 0) = 0$.

Since the size of this example is somewhat smaller than the preceding ThO example, it is practical and informative to tabulate the results of the first step of the term value approach. Table IV lists the term values and their standard deviations. The two independent sets are easily discerned since they have very different magnitudes. Note that the term values are not equally well determined; the variances differ by as much as a factor of about six. Table V lists the correlation coefficients of the term values. Note that the correlation is often strong, as high as 0.87, between the term values of different vibrational states. The correlations are indeed zero between the two independent sets. In the second step of either the improved or the traditional term value approach, the molecular constants must now be determined from a least-squares fit to a collection of term values consisting of members from both independent sets.

TABLE VI
Elements of the Matrix Z in Eq. (18) for the Term Values for $v' = 0$ and 1, $B^1\Sigma_u^+$ State, and $v'' = 0, X^1\Sigma_g^+$ State, of H_2

		$v_0(0,3)$	B_0'	D_0'	$v_0(1,3)$	B_1'	D_1'	B_3''	D_3''
$v' = 0$	Y_1'	1	2	-4	0	0	0	0	0
	Y_2'	0	6	-36	0	0	0	0	0
	Y_3'	1	12	-144	0	0	0	0	0
	Y_4'	0	20	-400	0	0	0	0	0
	Y_5'	1	30	-900	0	0	0	0	0
	Y_6'	0	42	-1764	0	0	0	0	0
$v' = 1$	Y_0'	-1	0	0	1	0	0	0	0
	Y_1'	0	0	0	1	2	-4	0	0
	Y_2'	-1	0	0	1	6	-36	0	0
	Y_3'	0	0	0	1	12	-144	0	0
	Y_4'	-1	0	0	1	20	-400	0	0
	Y_5'	0	0	0	1	30	-900	0	0
$v'' = 3$	Y_1''	-1	0	0	0	0	0	2	-4
	Y_2''	0	0	0	0	0	0	6	-36
	Y_3''	-1	0	0	0	0	0	12	-144
	Y_4''	0	0	0	0	0	0	20	-400
	Y_5''	-1	0	0	0	0	0	30	-900
	Y_6''	0	0	0	0	0	0	42	-1764

The improved term value approach handles this type of fit rather straightforwardly since the correlation requires that the molecular constants for the lower and upper states be determined simultaneously from all of the term values (Eqs. 18–24). The energy difference between the two zero reference points may always be expressed in terms of the known quantum numbers and the unknown molecular constants. In our example, this difference is simply $\nu_o(0,3)$. Therefore, in Eq. (18) the coefficient matrix \mathbf{Z} is written so that the unknown $\nu_o(0,3)$ is subtracted from each term value associated with the dashed lines, thereby effectively placing the zero of this set of term values at the zero of the set associated with the solid lines, $v'' = 3$, $J'' = 0$. The coefficient matrix \mathbf{Z} for this sample is given in Table VI. The values of the molecular constants obtained by applying the improved term value approach to this example are, as expected, identical with results listed in the first column of numbers in Table III obtained from the direct approach (and hence are not listed).

However, since the traditional term value approach ignores the correlation between the term values and least-squares fits are made separately to the term values of the $v' = 0$, $v' = 1$, and $v'' = 3$ vibrational states, then the problem of the two independent sets of term values with different zero energy reference points must be handled in a different way. Åslund (5,7) and coworkers solve this problem by introducing a new unknown constant, X , the value of which must be determined along with the molecular constants of each state. If $2X$ represents the unknown energy separation between the zero energy reference points of the two independent sets of term values, then the equations relating the term values of each vibrational state to the molecular constants of that state are

$$v' = 0: \quad \hat{Y}'_i = F'_o(0) + B'_0 J'_i (J'_i + 1) - D'_0 [J'_i (J'_i + 1)]^2 \\ - (-1)^{J'_i} X + \epsilon'_i(0); \quad (27)$$

$$v' = 1: \quad \hat{Y}'_i = F'_o(1) + B'_1 J'_i (J'_i + 1) - D'_1 [J'_i (J'_i + 1)]^2 \\ - (-1)^{J'_i} X + \epsilon'_i(1); \quad (28)$$

$$v'' = 3: \quad \hat{Y}''_i = F''_o(3) + B''_3 J''_i (J''_i + 1) - D''_3 [J''_i (J''_i + 1)]^2 \\ + (-1)^{J''_i} X + \epsilon''_i(3). \quad (29)$$

Three values of X are obtained from the three separate least-squares fits and these values should be the same, within experimental uncertainties. The term values \hat{Y}_i , which are based on two different zero energy references, can be converted into a new set of term values T_i that have a common zero energy reference by⁶

$$\hat{T}'_i = \hat{Y}'_i + (-1)^{J'_i} X \quad (30)$$

and

$$\hat{T}''_i = \hat{Y}''_i - (-1)^{J''_i} X. \quad (31)$$

It is the \hat{T}_i that are normally reported as “the term values,” although it should be

⁶ To facilitate comparison to Åslund (7), we have followed his practice of using Y_i to denote term values that have two independent zero energy reference points and T_i to denote term values that have one zero energy reference point. In the ThO $G^2\Delta^1-H^4\Phi$ example considered earlier, $T_i = Y_i$.

recognized that usually, as in the example above, the molecular constants are determined from the \hat{Y}_i ; rather than the \hat{T}_i .⁷

The second column of numbers in Table III contains the results from the three separate fits. The values for the molecular constants differ considerably from those in the first column given by the direct (or the equivalent improved term value) approach. If the values from the traditional term value approach are used to compute a set of calculated lines, the residuals between these and the observed line positions have a standard deviation of 0.37 cm^{-1} , compared to 0.27 cm^{-1} arising from the direct-approach values, the true MVLU estimates. Furthermore, the neglect of the variance-covariance matrix has once again caused the standard deviations to be unrealistic. For example, the standard deviation of B_0' is a factor of 26 too small.

The need of the traditional term value approach to introduce the new unknown X is particularly unfortunate in this example. In each of the separate fits the number of term values is six and the introduction of X raises the number of unknowns from three to four, making each fit much less overdetermined. Furthermore, the constant X is weakly correlated with F_o , B , and D and its presence in the fit will slightly influence the values obtained for these molecular constants. More importantly, in each state, $F_o(v)$ is rather highly correlated with B_v and D_v , much more so than $\nu_o(v',v'')$ is with any B_v and D_v in the direct (or the improved term value) approach. For example, $F_o'(v' = 0)$ is correlated with B_0' and D_0' by -0.83 and -0.70 , respectively. The $v' = 1$ and $v'' = 3$ states exhibit similar correlations. In contrast to these, $\nu_o(1,3)$ is correlated to B_1' by -0.56 and to D_0' by -0.07 . The other (ν_o, B) or (ν_o, D) correlation coefficients lie between these two values. This relatively larger correlation (up to a factor of ten larger) between $F_o(v)$ and the rotational constants may be the reason why, in Tables I and III, the standard deviations of $\nu_o = F_o' - F_o''$ from the traditional term value approach are higher than those of ν_o obtained from the direct approach.

In some applications of the traditional term value approach (δ, II), the molecular constants have been determined from the \hat{T}_i , rather than \hat{Y}_i as described above. An example of this application would be a ${}^2\Sigma\text{-}{}^2\Pi$ transition. Linear expressions for the energy levels of the ${}^2\Sigma$ state can be established rather unequivocally, whereas, for the ${}^2\Pi$ state, the expressions are generally nonlinear and complex. From a fit of the linear expressions to the \hat{Y}_i' values of the ${}^2\Sigma$ state, the molecular constants for that state and a value for \hat{X} is determined. This value of \hat{X} is then used to convert the \hat{Y}_i'' of the ${}^2\Pi$ state into \hat{T}_i'' values using Eq. (31). Various models can then be tried on the ${}^2\Pi$ state with particular attention paid to interactions like Λ -doubling and spin-orbit coupling. This procedure has also been applied to bands in which one state is perturbed (δ). It has been considered widely that the term values \hat{T}_i are independent of a model and that this is one of the virtues of the term value approach. This is, of course, not correct since the calculation of the \hat{T}_i require a value for \hat{X} that must be determined from some set of \hat{Y}_i using a model. While it is certainly true that \hat{X} often may be determined from a relatively simple state, this is by no means generally true. Consider the ${}^2\Pi_u\text{-}{}^2\Pi_g$ bands

⁷ The \hat{Y}_i , rather than the \hat{T}_i , would also be used to retrieve unidentified lines from among the identified lines on a plate, since the \hat{Y}_i do not require a determination of X . It should be noted, however, that this procedure can retrieve only those unidentified lines that arise from rotational levels whose term values have been established by identified lines. Only the molecular constants offer the possibility of extrapolating to new rotational levels.

of O_2^+ . The ${}^2\Pi_u$ state is near Hund's case (b) and the ${}^2\Pi_g$ state is near Hund's case (a) and no other band system includes either of these two states (12). Underlying all of this, of course, is also the fact that in treating the upper and lower state term values separately, all correlation between them has been lost and the molecular constants cannot be *MVLU* estimates and the standard deviations cannot be unbiased.

Systematic Errors

The main application of the traditional term value approach has been in the simultaneous reduction of all the bands of all of the band systems of a molecule and, indeed, this has been generally considered its forte. The consequences of the neglect of the (huge) variance-covariance matrix have been discussed above. However, even if the improved term value approach or the equivalent direct approach, is used, this simultaneous reduction is valid only if all of the measurement errors are members of the same distribution. The (0,3) and (1,3) Lyman bands serve as an example of this problem.

The third and fourth columns of numbers in Table III contain the molecular constants obtained by applying the direct approach to the (0,3) and (1,3) bands individually. The standard deviations imply that the (0,3) band is the better-measured band. It is instructive to compare the values obtained from these individual fits with those in the first column, which were obtained from a simultaneous reduction also using the direct approach. The differences between the values for $\nu_0(1,3)$, B_1' , and D_1' are each well within one of either of the standard deviations, which are themselves very similar. However, it is a different situation for $\nu_0(0,3)$, B_0' , and D_0' . The differences are comparable to about five standard deviations given by the separate fit. Apparently, the requirement that the better-measured (0,3) band be fitted simultaneously with the poorer-measured (1,3) band has degraded the values obtained for the $v' = 0$ state. This is not surprising in view of the correlation that exists between all of the rotational constants in the simultaneous fit. The separate fits yield two values for B_3'' and D_3'' . It can be shown by a modified Student *t* test (13), which is applicable to coefficients in a least-squares fit as well as to means, that the two values differ by more than can be expected on the basis of their estimated standard deviations.⁸ Thus, systematic errors occur in one or the other or both sets of data. Such errors are not totally unexpected, since the two bands occur at different wavelengths.

Since systematic errors are present, the direct approach to the combined data of the two bands does not give the best estimates of B_3'' and D_3'' and a few examples will be given of the possible ways of combining the values. A weighted average of the two values from the separate fits would be more realistic if it takes account of the systematic errors. For example, if the systematic error substantially exceeds the standard deviations of random error, as in this case, a simple unweighted average is a good combined estimate: $B_3'' = 50.635$ and $D_3'' = 0.0400$ cm^{-1} . Slightly better estimates can be obtained from

⁸ 95 percent confidence intervals for the differences between the two B_3'' values and the two D_3'' values, can be calculated to have the end points 0.102 ± 0.075 and 0.0034 ± 0.0016 cm^{-1} , respectively (where, for the degrees of freedom at hand, the half-lengths 0.075 and 0.0016 cm^{-1} are 2.4 times the respective standard deviations of the differences). Since neither of these intervals include zero, the differences between the two B_3'' values and the two D_3'' values are significant at the 5 percent level. (The differences between the two B_3'' values and the two D_3'' values cease to be significant at about the 2 and 0.5 percent levels, respectively.)

a more sophisticated statistical model that includes systematic error (from a common "superpopulation" of systematic errors) as well as differing standard deviations of random errors (14). These better estimates ("minimum-variance, linear, unbiased estimates") are $B_3'' = 50.629$ and $D_3'' = 0.0400 \text{ cm}^{-1}$, so that the estimates are the same to better than three significant figures. The estimated standard deviations (s.d.) of these estimates are negligibly smaller than those of the unweighted averages above: s.d. $B_3'' = 0.049$, s.d. $D_3'' = 0.0016 \text{ cm}^{-1}$, as compared with s.d. $B_3'' = 0.051$, s.d. $D_3'' = 0.0017 \text{ cm}^{-1}$. Each of the latter standard deviations is simply half the absolute difference of the two separately fitted values. Each of the former standard deviations is calculated from a more complicated formula that will not be given here (14). Note that the estimates of B_3'' and D_3'' are substantially different from those that would be obtained by a weighted average ignoring systematic error (i.e., using reciprocals of internal variances) and that the standard deviations are considerably larger.

It appears, therefore, that fitting many bands simultaneously may mask the existence of systematic errors. This strongly suggests that the improved term value approach be applied band-by-band where applicable.⁹ A band-by-band fit would, at least, indicate the severity of the problem of systematic errors. The common values could be combined in a judicious way and the bands with common levels refitted with these common values to determine the extent of variation in the other constants due to systematic errors. On the other hand, if all of the measurement errors essentially belong to the same distribution, then the value obtained by combining the values from common levels, as described above, will be identical to the value obtained from reducing the set of bands simultaneously.

Missing Lines

There are often lines or a group of lines that are missing in a set of measured line positions. These gaps arise because of poorly resolved lines near the band heads, overlapping lines from another band, statistically rejected lines, etc. These missing lines cause no problem for the direct approach. They simply mean one less equation in the set given in Eq. (3) for each line that must be omitted. However, for either the improved or traditional term value approaches, missing lines usually require special handling.

Figure 2 shows the lines that connect the lower rotational levels in a ${}^1\Sigma\text{--}{}^1\Sigma$ band. The $R(4)$ line has been deliberately omitted. Note that there are now *three* independent sets of lines—dashed, solid, and hatched—rather than two. The term values associated with each set are also independent and the zero energy of each independent set must be referenced independently. If there are other such missing lines, the number of independent groups of term values will increase.

Åslund (7) and coworkers keep the number of independent sets to two by interpolating approximate values for the missing lines or groups of lines if these missing lines would form new independent groups. The measured and interpolated lines then serve as the

⁹ We note that, for a band involving a ${}^1\Sigma$ state and another ${}^1\Sigma$ state or a singlet non-sigma state with A-doubling, term values would be determined from an exact fit, at best. This implies that the improved term value approach, in the present form, cannot be applied to systems with a band-by-band reduction. Although the traditional term value approach can be carried out, it still suffers the drawbacks described earlier. The direct approach, of course, can always be applied in such cases.

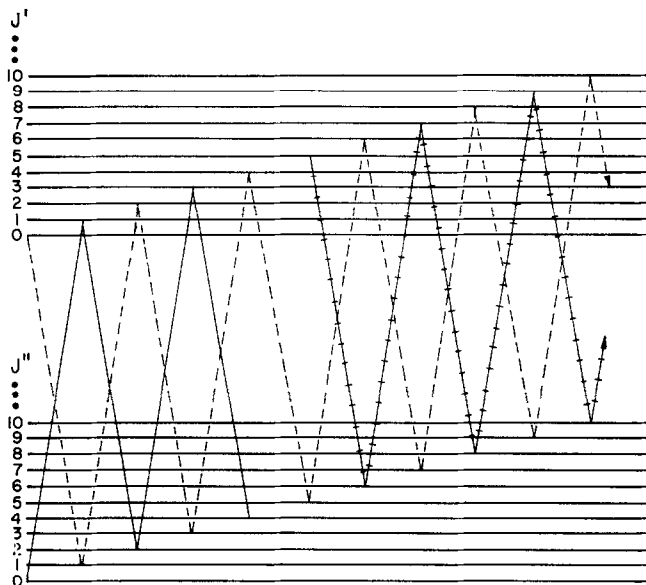


FIG. 2. Three independent groups of transitions in a $1\Sigma-1\Sigma$ band with the $R(4)$ transition missing.

input to the first step of the term value approach. Although this interpolation can sometimes be done very accurately, this is an unattractive requirement of the term value approach that increases the labor of applying the term value approach and decreases the statistical validity of the results.

V. SUMMARY AND CONCLUSIONS

It is clear that a spectroscopist faced with a fresh plate should use every method at his/her disposal to assign the quantum numbers to the observed lines. For this purpose, combination differences provide a powerful technique (2). However, it is equally clear that, to obtain final values of the molecular constants, a statistically sound technique should be employed. This warrants abandoning the combination difference approach for that purpose. We summarize in what follows two alternative approaches.

The term value approach to obtaining molecular constants from line positions consists of two steps. In the first step, intermediate unknowns—the term values for the rotational levels—are determined by a least-squares fit to the observed line positions. In the second step, the term value approach has two major variations depending on whether correlation and unequal variances are accounted for or ignored. The second step of the improved term value approach determines the molecular constants from a correlated least-squares fit to the term values using the variance-covariance matrix of the first step. The molecular constants determined from the improved term value approach are identical with those obtained from the direct approach, i.e., a determination of the molecular constants from a direct least-squares fit of the observed line positions. On the other hand, the second step of the traditional term value approach determines the molecular constants for each vibrational state separately by fitting the term values of that state alone. Thus, the traditional term value approach

ignores the correlations between the term values of different vibrational states. As it has been applied in the literature, this approach also ignores the correlation between the term values of the same state and ignores the fact that the variances of the term values are unequal. In short, the traditional term value approach assumes that the variance-covariance matrix is a constant times the identity matrix. Because of this generally erroneous assumption, this approach cannot, in general, yield minimum-variance, linear, unbiased (*MVLU*) estimates of the molecular constants and unbiased estimates of the standard deviations, as does the direct approach and the equivalent improved term value approach. The degree to which the molecular constants and their uncertainties determined from the traditional term value approach will differ from the *MVLU* estimates will depend on the particular application.

It is clear that the improved term value approach and the direct approach require the simultaneous specification of two model Hamiltonians in the reduction of one band to molecular constants. Thus, there is no way to correctly break the correlation between the upper and lower state constants without, of course, fixing the constants of one state to values obtained more accurately by another means.¹⁰

There are instances where one state of a system is so massively perturbed that a model Hamiltonian for that state cannot be specified. Then, neither the direct approach nor the improved term value approach can be applied. However, the traditional term value approach can still be applied to obtain molecular constants of the simpler state for which a model Hamiltonian can be specified. It should be recognized that these values will not be the *MVLU* estimates and the associated standard deviations are not unbiased. Because of the biased standard deviations, it may often be difficult to be certain of the statistical need of constants like D_v , H_v , γ_v , etc. that represent relatively small effects. Thus, if the traditional term value approach is to be applied to *one* state alone because of difficulties with the model of the other state in the transition, the advantages gained by avoiding the model of the more complex state must outweigh the disadvantages of obtaining non-*MVLU* estimates and biased standard deviations for the simpler state.

The separate fit to the term values of each vibrational state used in the traditional term value approach requires the determination of a molecular constant representing the reference energy $F_o(v)$. This constant may be rather strongly correlated to the other molecular constants of that state, much more so than $\nu_o(v', v'')$ is correlated to the other molecular constants in either the direct or the improved term value approaches.

In most bands, the parity selection rule divides the lines of a band, and hence the term values, into two independent sets. This causes no alteration in the direct approach and none of consequence in the improved term value approach. However, the traditional term value approach must introduce a new unknown X that is related to the independent and arbitrary zero energy reference of each set of term values. The value of this unknown must be determined along with the molecular constants in the second step. Furthermore, if the number of lines recorded in a band is small, the introduction of another unknown makes the second step of the traditional term value approach less over-determined. Finally the determination of \hat{X} requires a model for the rotational energy

¹⁰ It may be hoped that advances in microwave, Raman, and other related techniques will yield sufficiently accurate measurements of ground state energy levels that only one model Hamiltonian will be necessary in the reduction of optical spectra.

levels. Therefore, any term values that have been normalized to one zero energy reference using \bar{X} are also model dependent.

Missing lines may often cause the number of independent sets of lines in a band to be greater than two. To avoid more than two independent groups, the term value approach, as has been applied in the literature, used interpolated lines for those missing lines that would introduce new independent sets. Although such interpolation may often be done accurately, fitting to anything other than the measured line positions is, in general, less than ideal and introduces ambiguity in the statistical indicators of the fits.

There have been several cases in the literature where all of the bands of all of the band systems of a molecule have been reduced simultaneously. Indeed, this has been the main application of the traditional term value approach, since the neglect of the variance-covariance matrix makes such a reduction practicable. However, even the use of the direct approach or the improved term value approach would be valid *only* if all of the measurement errors have the same distribution. Systematic errors, such as wavelength-dependent errors, could be masked in such a simultaneous reduction. A band-by-band reduction gives much more information about these types of errors and hence a more realistic estimate of the absolute accuracies. The values of the molecular constants for common states obtained from a band-by-band reduction can be combined in a variety of ways, depending on the severity of the systematic errors, to yield the final single values for these constants.

RECEIVED: September 12, 1972

REFERENCES

1. D. L. ALBRITTON, W. J. HARROP, A. L. SCHMELTEKOPF, AND R. N. ZARE, *J. Mol. Spectrosc.* **46**, 37 (1973).
2. G. HERZBERG, "Spectra of Diatomic Molecules," pp. 168-192, D. Van Nostrand, New York, 1950.
3. D. L. ALBRITTON, W. J. HARROP, A. L. SCHMELTEKOPF, AND R. N. ZARE, *J. Mol. Spectrosc.* **46**, 103 (1973).
4. M. G. KENDALL AND A. STUART, "The Advanced Theory of Statistics," Vol. 2, 2nd ed., pp. 75-97. Hafner, New York, 1967. C. RADHAKRISHNA RAO, "Linear Statistical Inference and Its Applications," Ch. 4, John Wiley and Sons, Inc. New York, 1965.
5. G. EDVINSSON, L.-E. SELIN, AND N. ÅSLUND, *Ark. Fys.* **30**, 283 (1965).
6. G. EDVINSSON, A. V. BORNSTEDT, AND P. NYLÉN, *Ark. Fys.* **38**, 193 (1968).
7. N. ÅSLUND, *Ark. Fys.* **30**, 377 (1965).
8. R. P. TEWARSON, *SIAM Review* **12**, 527 (1970); R. P. TEWARSON, "Sparse Matrices," Academic Press, New York (forthcoming).
9. D. L. ALBRITTON, A. L. SCHMELTEKOPF AND R. N. ZARE, "Diatomic Intensity Factors," Wiley-Interscience, New York, N. Y. (in preparation).
10. G. HERZBERG AND L. L. HOWE, *Can. J. Phys.* **37**, 636 (1959).
11. E. A. MOORE AND W. G. RICHARDS, *Physica Scripta* **3**, 223 (1971).
12. D. L. ALBRITTON, W. J. HARROP, A. L. SCHMELTEKOPF, AND R. N. ZARE, *J. Mol. Spectrosc.* **46**, 89 (1973).
13. C. A. BENNETT AND N. L. FRANKLIN, "Statistical Analysis in Chemistry and the Chemical Industry," pp. 176-180, Wiley, New York (1954).
14. E. L. CROW (unpublished manuscript).