The Derivation of the $\mathbf{r_s}$ Structure by the Use of a Nondiagonal Weight Matrix for Rotational Constants

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The use of a nondiagonal weight matrix in a least-squares analysis of the quantities which themselves are derived from another least-squares analysis is discussed in relation to the analysis of rotational constants in determining molecular geometry. The method is applied to the calculation of the r_s structure of ethylene oxide, and the result is compared with those obtained by Kraitchman's formula and by a least-squares fit by the use of a diagonal weight matrix.

Least-squares procedure are commonly used in microwave spectroscopy in two ways: (1) for deriving rotational constants and centrifugal distortion constants from observed transition frequencies, and (2) for deriving structural parameters and/or force constants from rotational or centrifugal distortion constants. In these procedures, however, not all the parameters to be determined are always linearly independent. Lees[1] described a procedure to diagonalize a matrix of the normal equation in order to decouple the equations which correlate the parameters. When the limits of uncertainties in the parameters can be estimated, a *diagonostic least-squares* described by Curl[2] can replace the estimated limits for those calculated by means of a least-squares fit.

As Kirchhoff[3] has pointed out, there is another difficulty in the correlated data. The values derived from a least-squares fit or from a linear combination of directly-observed values (*i.e.*, indirect or secondary observations) are, in general, correlated with one another. Since rotational constants are derived from transition frequencies, correlations among them should be accounted for in a calculation of structural parameters. Similar circumstances are encountered in a structure analysis of gas-electron diffraction,[4–6] where correlations are dealt with by the use of a nondiagonal weight matrix. The present paper will describe the use of a nondiagonal weight matrix in the least-squares fit of rotational constants for determining molecular geometry. The derivation of an r_s structure from the rotational constants for various isotopic species is considered. Following the definition of the r_s structure,[7] no explicit account of the systematic errors due to the neglect of zero-point vibrations is made. Though such systematic errors are usually much larger than the uncertainties originating from errors in the measurement, the correction requires knowledge of the force field; such an undertaking is beyond the range of the present statistical treatment. In the absence of a complete force field, as in the case of ethylene oxide, effective structures, such as r_0 and r_s, are the best one can derive from spectroscopic measurements.

Below, the r_s structure obtained by using a nondiagonal weight matrix will be compared with those derived by neglecting the correlations among rotational constants. The r_s structure calculated by Kraitchman's method is also examined: the formulation for the error analysis in this case is described in the Appendix.

Weight Matrix for Indirect Observations

As Morino *et al.* have pointed out,[4] when a set of observations, $\boldsymbol{\mu}$, which are linear combinations of direct observations, $\mathbf{y}$, is used as the data in the least-squares fit, the weight matrix is expressed by:

$$\mathbf{W} = (\mathbf{G}\mathbf{P}^{-1}\tilde{\mathbf{G}})^{-1} \tag{1}$$

where $\mathbf{G}$ is the matrix which relates $\mathbf{y}$ to $\boldsymbol{\mu}$ as:

$$\boldsymbol{\mu} = \mathbf{G}\mathbf{y}\,, \tag{2}$$

and where $\tilde{\mathbf{G}}$ is the transpose of $\mathbf{G}$. $\mathbf{P}$ is a weight matrix for the direct observations, $\mathbf{y}$, and is diagonal provided each direct observation is measured independently.

This idea can readily be applied to the case where a set of indirect observations, $\boldsymbol{\mu}$ (rotational constants, for example), are derived from a set of direct observations, $\mathbf{y}$ (transition frequencies), by way of a least-squares fit. In that case, the matrix, $\mathbf{G}$, to be used is expressed as:

$$\mathbf{G} = \mathbf{B}^{-1}\tilde{\mathbf{J}}\mathbf{P}\,, \tag{3}$$

where:

$$\mathbf{B} = \tilde{\mathbf{J}}\mathbf{P}\mathbf{J}\,. \tag{4}$$

$\mathbf{J}$ is the Jacobian matrix used in deriving $\boldsymbol{\mu}$ from $\mathbf{y}$, and matrix element, J_{ik}, is the first derivatives of the i-th observation, y_i, with respect to the k-th parameter, μ_k, at the point of convergence, that is, $J_{ik} = (\partial y_i/\partial \mu_k)_0$. Since the $\mathbf{P}$ and $\mathbf{B}$ matrices are symmetric, the substitution of Eq. 3 into Eq. 1 gives:

$$\mathbf{W} = (\mathbf{B}^{-1}\tilde{\mathbf{J}}\mathbf{P}\mathbf{P}^{-1}\mathbf{P}\mathbf{J}\mathbf{B}^{-1})^{-1} = \mathbf{B}\,. \tag{5}$$

Furthermore, when a set of indirect observations, γ, is a linear combination of the $\boldsymbol{\mu}$ set like isotopic changes of rotational constants:

$$\boldsymbol{\gamma} = \mathbf{F}\boldsymbol{\mu}\,, \tag{6}$$

the weight matrix to be used for the $\boldsymbol{\gamma}$ set is given by:

$$\mathbf{W} = (\mathbf{F}\mathbf{G}\mathbf{P}^{-1}\tilde{\mathbf{G}}\tilde{\mathbf{F}})^{-1} = (\mathbf{F}\mathbf{B}^{-1}\tilde{\mathbf{F}})^{-1}\,. \tag{7}$$

In this scheme, the diagonal elements of the matrix $\mathbf{W}$ expressed in Eqs. 1, 5 and 7 account for the propagation of errors, and the off-diagonal terms represent correlations among the indirect observations.[4–6] When a set of indirect observations are composed of subsets, each obtained independently, such as the rotational constants for each isotopic species, the $\mathbf{W}$

matrix splits into submatrices.

Calculation of Structural Parameters

The r_0 structure of a molecule is the one which makes a best fit to the rotational constants in its ground state. In this case, the J_{ik} element of $\mathbf{J}$ is $(\partial\nu_i/\partial A_k)_0$, where ν_i and A_k are the i-th transition frequency and the k-th rotational constant (*i.e.*, A, B, or C) respectively. The i-th element, P_{ii}, of a diagonal matrix, $\mathbf{P}$, is inversely proportional to the square of the measurement error for the i-th frequency. Since an independent analysis is made for each isotopic species, the weight matrix is calculated by the use of Eqs. 4 and 5:

$$\mathbf{W}(r_0)=\begin{bmatrix} \mathbf{B}^{(1)} & & 0 \\ & \mathbf{B}^{(2)} & \\ & \cdots\cdots & \\ 0 & & \mathbf{B}^{(n)} \end{bmatrix}^{-1}, \tag{8}$$

where $\mathbf{B}^{(s)}=\mathbf{J}_s\mathbf{P}_s\mathbf{J}_s$ $(s=1,2,\cdots,n)$ is a 3×3 submatrix for the s-th isotopic species and where n is the number of isotopic species for which the rotational constants are obtained.

The r_s structure is defined as a set of parameters derived from isotopic changes in the rotational constants:

$$\Delta A_\alpha^{(s)}=A_\alpha^{(\mathrm{ref})}-A_\alpha^{(s)}, \tag{9}$$

where $A_\alpha^{(s)}$ is the rotational constants along the principal axis, α, for the s-th isotopic species. The value for the reference species (normal ethylene oxide in the present study) is denoted as $A_\alpha^{(\mathrm{ref})}$. The matrix, $\mathbf{F}$ (Eq. 6), consists of $3(n-1)$ rows and $3n$ columns:

$$\mathbf{F}=\begin{bmatrix} \mathbf{E} & -\mathbf{E} & \mathbf{0} & \mathbf{0} & \cdots\cdots & \mathbf{0} \\ \mathbf{E} & \mathbf{0} & -\mathbf{E} & \mathbf{0} & \cdots\cdots & \mathbf{0} \\ & & \cdots\cdots & & & \\ \mathbf{E} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \cdots\cdots & -\mathbf{E} \end{bmatrix}, \tag{10}$$

where $\mathbf{E}$ is a three-dimensional unit matrix. From Eq. 7, the following weight matrix of rank $3(n-1)$ is obtained:

$$\mathbf{W}(r_s)=\begin{bmatrix} \mathbf{B}^{(\mathrm{ref})}+\mathbf{B}^{(1)} & \mathbf{B}^{(\mathrm{ref})} & \cdots\cdots & \mathbf{B}^{(\mathrm{ref})} \\ \mathbf{B}^{(\mathrm{ref})} & \mathbf{B}^{(\mathrm{ref})}+\mathbf{B}^{(2)} & \cdots\cdots & \mathbf{B}^{(\mathrm{ref})} \\ \cdots\cdots & \cdots\cdots & \cdots\cdots & \cdots\cdots \\ \mathbf{B}^{(\mathrm{ref})} & \mathbf{B}^{(\mathrm{ref})} & \cdots\cdots & \mathbf{B}^{(\mathrm{ref})}+\mathbf{B}^{(n-1)} \end{bmatrix}^{-1}. \tag{11}$$

This matrix represents the correlation among the ΔA_α values used for the r_s structure.

The r_s Structure of Ethylene Oxide. As an ap-

TABLE 1. ROTATIONAL CONSTANTS AND THEIR VARIANCES OF ETHYLENE OXIDES (in MHz)[a)]

	A	σ(A)	B	σ(B)	C	σ(C)
Normal	25483.96	0.070	22120.77	0.072	14097.81	0.069
^{13}C	25291.89	0.055	21597.77	0.058	13825.75	0.056
^{18}O	23992.83	0.112	22121.58	0.117	13628.56	0.126
D_1	24252.47	0.058	19905.34	0.057	13327.40	0.056
t-D_2	22943.19	0.030	18198.47	0.032	12585.27	0.030
t-D_2-^{13}C	22786.84	0.061	17852.32	0.072	12377.50	0.060
t-D_2-^{18}O	21646.74	0.092	18202.46	0.099	12186.66	0.093
c-D_2	22700.41	0.050	18318.39	0.054	12650.08	0.051
c-D_2-^{13}C	22555.61	0.037	17963.42	0.040	12438.85	0.038
c-D_2-^{18}O	21424.03	0.042	18317.20	0.050	12243.45	0.048

a) Identifications of the substances indicated in the first column are; *Normal* = $^{12}C_2H_4{}^{16}O$, ^{13}C = $^{12}C^{13}CH_4{}^{16}O$, ^{18}O = $^{12}C_2H_4{}^{18}O$, *t*-D_2 = *trans*-$^{12}C_2H_2D_2{}^{16}O$, *t*-D_2-^{13}C = *trans*-$^{12}C^{13}CH_2D_2{}^{16}O$, *t*-$D_2$-$^{18}O$ = *trans*-$^{12}C_2H_2D_2{}^{18}O$, *c*-D_2 = *cis*-$^{12}C_2H_2D_2{}^{16}O$, *c*-D_2-^{13}C = *cis*-$^{12}C^{13}CH_2D_2{}^{16}O$, *c*-$D_2$-$^{18}O$ = *cis*-$^{12}C_2H_2D_2{}^{18}O$, and D_1 = $^{12}C_2H_3D^{16}O$.
Variances derived from a least-squares fit of the observed frequencies are listed. As for the details of the analysis see Ref. 7.

TABLE 2. ELEMENTS OF WEIGHT MATRIX USED IN THE CALCULATION OF r_s STRUCTURE OF ETHYLENE OXIDE[a)]

	A, A	A, B	A, C	B, B	B, C	C, C
$\mathbf{B}^{\mathrm{ref}}$ [b)]	0.1394	0.1354	0.1102	0.1460	0.1108	0.1382
$\mathbf{B}^{\mathrm{ref}}+\mathbf{B}^1$	0.2850	0.2469	0.2473	0.3117	0.2159	0.2898
$\mathbf{B}^{\mathrm{ref}}+\mathbf{B}^2$	0.2771	0.2653	0.2383	0.2955	0.2067	0.3113
$\mathbf{B}^{\mathrm{ref}}+\mathbf{B}^3$	0.2749	0.2641	0.2322	0.2998	0.2253	0.2764
$\mathbf{B}^{\mathrm{ref}}+\mathbf{B}^4$	0.2833	0.2462	0.2326	0.3418	0.2233	0.2772
$\mathbf{B}^{\mathrm{ref}}+\mathbf{B}^5$	0.4024	0.3930	0.3511	0.4480	0.3454	0.4069
$\mathbf{B}^{\mathrm{ref}}+\mathbf{B}^6$	0.2747	0.2641	0.2327	0.3046	0.2219	0.2772
$\mathbf{B}^{\mathrm{ref}}+\mathbf{B}^7$	0.2755	0.2652	0.2308	0.3028	0.2262	0.2797
$\mathbf{B}^{\mathrm{ref}}+\mathbf{B}^8$	0.2776	0.2671	0.2283	0.3034	0.2189	0.2822
$\mathbf{B}^{\mathrm{ref}}+\mathbf{B}^9$	0.2883	0.2568	0.2365	0.2897	0.2244	0.2745

a) See Eqs. (4), (5) and (11). b) ref: normal ethylene oxide, which is the reference species, 1: ^{13}C-ethylene oxide, 2: ^{18}O-ethylene oxide, 3: *trans*-D_2-ethylene oxide, 4: *trans*-D_2-^{13}C-ethylene oxide, 5: *trans*-D_2-^{18}O-ethylene oxide, 6: *cis*-D_2-ethylene oxide, 7: *cis*-D_2-^{13}C-ethylene oxide, 8: *cis*-D_2-^{18}O-ethylene oxide, and 9: monodeutero-ethylene oxide.

Table 3. r_s Structures of ethylene oxide[a]

	L. S. 1[b]	L. S. 2[c]	K. M. 1[d]	K. M. 2[e]
r(CO)	1.4309(10)	1.4303(13)	1.4313(31)	1.4294(24)
r(CC)	1.4663(18)	1.4657(28)	1.4648(16)	1.4630(23)
r(CH)	1.0854(10)	1.0858(10)	1.0859(18)	1.0824(34)
∠HCH	116.61(10)	116.57(13)	116.50(40)	——
θ[f]	21.99(15)	22.01(10)	21.95(28)	——

a) Bond lengths are in Å and the angles are in degrees. C_{2v} symmetry is assumed for the normal ethylene oxide. Uncertainties given in parentheses are 2.5 times the standard errors attached to the last digit. b) Derived from the least-squares analysis using the nondiagonal weight matrix given in Eq. (11). c) Derived from the least-squares analysis using a diagonal weight matrix following the law of propagation of errors. d) Derived from Kraitchman's method by combination of *normal*, ^{13}C-, ^{18}O-, and monodeutero ethylene oxide. e) Derived from Kraitchman's method by combination of *trans*-D_2-, *trans*-D_2-^{13}C-, *trans*-D_2-^{18}O-, and monodeutero ethylene oxide. f) θ is the dihedral angle of the C–C bond to the H_2C plane.

plication of the present method, the r_s structure of ethylene oxide was calculated by the use of the rotational constants of ten isotopic species.[8] The observed rotational constants and the elements of $\mathbf{B}^{(s)}$ are shown in Tables 1 and 2 respectively.*

Calculation of the r_s structure were made with a nondiagonal weight matrix and with a diagonal matrix set up by leaving out the diagonal elements of the former. The molecule is assumed to have C_{2v} symmetry. Table 3 lists the derived values of the r_s parameters.

The converged values based on the two weight matrices are not significantly different, but the correlation factors based on the nondiagonal matrix are somewhat smaller than those based on the diagonal matrix. On the other hand, similar calculations based on nondiagonal weight matrices gave larger correlation factors in the r_0 and r_m structures.[9]

For the sake of comparison, the parameter values obtained by Kraitchman's formula[10] are also shown in Table 3. The reliability intervals of these values were estimated by way of the propagation of errors; the procedure is shown in the Appendix.

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Appendix

Error Estimation of the r_s Structure Obtained by Kraitchman's Method. Kraitchman's formula is given in a matrix form as:

$$\mathbf{a} = \mathbf{A}\mathbf{x}\,, \tag{A1}$$

where

$$a_\alpha = (P_\alpha'-P_\alpha)(P_\alpha'-P_\beta)(P_\alpha'-P_\gamma) = p_{\alpha\alpha}p_{\alpha\beta}p_{\alpha\gamma}\,, \tag{A2}$$

$$A_{\alpha\alpha} = \mu(P_\alpha'-P_\beta)(P_\alpha'-P_\gamma) \equiv \mu p_{\alpha\beta}p_{\alpha\gamma}\,, \tag{A3a}$$

$$A_{\alpha\beta} = \mu(P_\alpha'-P_\alpha)(P_\alpha'-P_\gamma) \equiv \mu p_{\alpha\alpha}p_{\alpha\gamma}\,, \tag{A3b}$$

and

$$x_\alpha = \alpha_s^2 \tag{A4}$$

$(\alpha, \beta, \gamma = \mathrm{a, b}$ or c with $\alpha, \beta \neq \gamma$ and $\beta \neq \alpha$, and

$p_{\alpha\beta} \equiv P_\alpha' - P_\beta)$.

In the above equations, P_α and P_α', are derived from the moments of inertia, I_α and I_α' for the reference and substituted species, respectively, as:

$$P_\alpha = (-I_\alpha+I_\beta+I_\gamma)/2\,, \tag{A5}$$

$$P_\alpha' = (-I_\alpha'+I_\beta'+I_\gamma')/2\,, \tag{A6}$$

μ is the reduced mass difined as $M\Delta m/(M+\Delta m)$, where M is the molecular weight of the reference molecule and Δm is the difference in molecular weight caused by the isotopic substitution, and α_s is the coordinate of the substituted atom referred to the principal axis α of the reference species. One gets from (Al) that

$$\mathbf{x} = \mathbf{A}^{-1}\mathbf{a}\ . \tag{A7}$$

If the moments of inertial, I_α and I_α' (α=a,b or c), contain error limits of ΔI_α and $\Delta I_\alpha'$ which are positive and independent of one another, error limits of P_α and P_α' can be estimated as:

$$\Delta P_\alpha = (\Delta I_\alpha+\Delta I_\beta+\Delta I_\gamma)/2 = \Delta\,, \tag{A8}$$

$$\Delta P_\alpha' = (\Delta I_\alpha'+\Delta I_\beta'+\Delta I_\gamma')/2 = \Delta'\ . \tag{A9}$$

Thus the error in $p_{\alpha\beta}$ is given by

$$\Delta p_{\alpha\beta} = \Delta + \Delta'\ . \tag{A10}$$

The error limits of a_α and $A_{\alpha\beta}$ are obtained by substituting (A10) into A(2) and A(3) to be:

$$\begin{aligned}\Delta a_\alpha &= \Delta p_{\alpha\alpha}|p_{\alpha\beta}^0 p_{\alpha\gamma}^0| + \Delta p_{\alpha\beta}|p_{\alpha\alpha}^0 p_{\alpha\gamma}^0| + \Delta p_{\alpha\gamma}|p_{\alpha\alpha}^0 p_{\alpha\beta}^0| \\ &= (\Delta+\Delta')(|A_{\alpha\alpha}^0| + |A_{\alpha\beta}^0| + |A_{\alpha\gamma}^0|)/|\mu| \end{aligned} \tag{A11}$$

$$\Delta A_{\alpha\alpha} = |\mu|(\Delta+\Delta')(|p_{\alpha\beta}^0| + |p_{\alpha\gamma}^0|) \tag{A12a}$$

$$\Delta A_{\alpha\beta} = |\mu|(\Delta+\Delta')(|p_{\alpha\alpha}^0| + |p_{\alpha\gamma}^0|)\ . \tag{A12b}$$

When some of the $P_{\alpha\alpha}$'s are set to zero from a consideration of symmetry, $\Delta_\alpha'' = |P_{\alpha\alpha}^0|$ should be added to Δ and Δ', where $p_{\alpha\alpha}^0$ is the observed value which is set equal to zero. The errors are modified as:

$$\Delta a_\alpha' = \Delta a_\alpha + \Delta_\alpha''|A_{\alpha\alpha}^0|/|\mu| \tag{A11a}$$

and the corresponding modification on $\Delta A_{\alpha\beta}$. When $\mathbf{A}^0$ and $\mathbf{x}^0$ are given prior to the error analysis, the error limit $\Delta\mathbf{x}$ can be derived by use of the above equations.*

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* The correlation factor between A and B, for instance, is given by $c_{AB} = B_{AB}^{-1}/(B_{AA}^{-1} \cdot B_{BB}^{-1})^{1/2}$. The value of c_{AB} for normal ethylene oxide, 0.9299, indicates that A and B in Table 1 are considerably correlated. The $0 \leqq |c_{AB}| \leqq 1$ relation holds, and the upper limit is realized when A and B are in exact linear dependence.

* Since the propagation of errors is dealt with in a matrix representation, the formula $\boldsymbol{\Delta}\mathbf{x} = (\mathbf{A}^0)^{-1}(\boldsymbol{\Delta}\mathbf{a} + \boldsymbol{\Delta}\mathbf{A}\cdot\mathbf{x}^0)$ does not apply here when it is solved algebraically, but correct solutions are given as follows:

Referring to (A4), the error limits of the coordinates are derived following the law of propagation of errors as:

$$\varDelta\alpha_s = \varDelta x_\alpha/2(x_\alpha{}^0)^{1/2} \quad (\text{when } x_\alpha{}^0 \neq 0)\ , \tag{A13a}$$

or

$$\varDelta\alpha_s = 0 \quad (\text{when } x_\alpha{}^0 = 0 \text{ by symmetry})\ . \tag{A13b}$$

The error limits $\varDelta r_{ij}$ of the distance between the *i*-th and the *j*-th atoms is given by,

$$\begin{aligned}\varDelta r_{ij} = [&|a_i{}^0-a_j{}^0|(\varDelta a_i+\varDelta a_j)+|b_i{}^0-b_j{}^0|(\varDelta b_i+\varDelta b_j)\\&+|c_i{}^0-c_j{}^0|(\varDelta c_i+\varDelta c_j)]/r_{ij}{}^0\ ,\end{aligned} \tag{A14}$$

where

$$r_{ij}{}^0 = [(a_i{}^0-a_j{}^0)^2+(b_i{}^0-b_j{}^0)^2+(c_i{}^0-c_j{}^0)^2]^{1/2}\ . \tag{A15}$$

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(footnote continued)

$$\begin{aligned}\varDelta x_a = (&b_1(|A_{22}{}^0A_{33}{}^0|+|A_{23}{}^0A_{32}{}^0|)\\&+b_2(|A_{32}{}^0A_{13}{}^0|+|A_{12}{}^0A_{33}{}^0|)\\&+b_3(|A_{13}{}^0A_{22}{}^0|+|A_{12}{}^0A_{23}{}^0|))/|A^0|^*\ ,\\ \varDelta x_b = (&b_1(|A_{23}{}^0A_{31}{}^0|+|A_{21}{}^0A_{33}{}^0|)\\&+b_2(|A_{11}{}^0A_{33}{}^0|+|A_{31}{}^0A_{13}{}^0|)\\&+b_3(|A_{23}{}^0A_{11}{}^0|+|A_{21}{}^0A_{13}{}^0|))/|A^0|^*\ ,\\ \varDelta x_c = (&b_1(|A_{31}{}^0A_{22}{}^0|+|A_{21}{}^0A_{32}{}^0|)\\&+b_2(|A_{31}{}^0A_{12}{}^0|+|A_{11}{}^0A_{320}|)\\&+b_3(|A_{11}{}^0A_{22}{}^0|+|A_{12}{}^0A_{21}{}^0|))/|A^0|^*\ ,\end{aligned}$$

where,

$$\mathbf{b} = \varDelta\mathbf{A}\cdot\mathbf{x}^0 + \varDelta\mathbf{a}\ ,$$

and $|A^0|^*$ denotes the absolute value of the determinant of the matrix $\mathbf{A}^0$.