

THE **FG** MATRIX TREATMENT OF NORMAL VIBRATIONS IN ETHYLENE-LIKE AND NITROMETHANE-LIKE MOLECULES WITH FREE INTERNAL ROTATION

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The symmetry groups, transformation to symmetry coordinates, factorization of the **FG** matrices, and the form of the eigenvectors of the vibrational secular equation were discussed for the ethylene-like and nitromethane-like molecules with free internal rotation. An attempt was made at least squares refinement calculation of the quadratic force constants from the fundamental frequencies of vibrations of CH_3NO_2 and CD_3NO_2 .

The treatment of normal vibrations of nonrigid molecules with free internal rotation differs from that of rigid molecules. Hougen¹⁻³ and Bunker⁴ have recently developed the theory of the vibrational-rotational motions of nonrigid molecules with the use of the Longuet-Higgins' concept of symmetry groups⁵, and discussed the **FG** matrix treatment of normal vibrations in dimethylacetylene-like and silylmethylacetylene-like molecules. Since the theory differs for individual types of molecules (compare Hougen's discussion of dimethylacetylene² and silylmethylacetylene³), an extension of these methods to other types of molecules with free internal rotation is certainly desirable.

In this paper, we will discuss the **FG** matrix treatment of the normal vibrations in ethylene-like and nitromethane-like molecules with free internal rotation. Among the ethylene-like molecules those which have a low barrier to internal rotation are *e.g.* the diboron tetrafluoride⁶, mercury diphenyl, or the ethylene molecule in the excited electronic state⁷. The nitromethane-like molecules where the nearly free internal rotation was proved by microwave spectroscopy⁸⁻¹⁰ are *e.g.* the nitromethane, methyl difluoroborane, toluene *etc.* Problems which will be discussed in this paper are the double-valued representations of the symmetry groups of these molecules, their symmetry coordinates of vibrations, kinematic matrices, factorization of the **FG** matrices, and the form of the eigenvectors of the vibrational secular equation for ethylene-like molecules. In case of nitromethane, an attempt was made at a refinement calculation of the quadratic force constants from the fundamental frequencies of CH_3NO_2 and CD_2NO_2 .

During our work on this problem, a paper of Fleming and Banwell¹¹ appeared in which the problem of the symmetry coordinates and the **FG** matrix factorization was discussed for the nitromethane molecule. Although our results agree basically with those of Fleming and Banwell, we include them into this paper since certain corrections are needed to the symmetry coordinates and the **G** matrix elements of Fleming and Banwell.

Ethylene-Like Molecules

Born-Oppenheimer coordinates. We can divide the ethylene-like molecule X_2Y_4 into two equal parts XY_2 , called the "top" and "frame" parts of the molecule (Fig. 1). The system of the "top" and "frame" -fixed coordinates will be defined and the reference configuration of the atomic nuclei will be chosen in the same way as was described by Hougen for dimethylacetylene¹. The Born-Oppenheimer variables will be the Euler angles Θ , Φ , χ_t , χ_f which specify the orientation of the top and frame system of axes with respect to the space-fixed axes X , Y , Z , and the $3N-7$ symmetry coordinates Q_s describing the vibrations of the molecule. Instead of Θ , Φ , χ_t , χ_f we can use Θ , Φ , $\chi = \frac{1}{2}(\chi_t + \chi_f)$, $\gamma = \frac{1}{2}(\chi_t - \chi_f)$, where Θ , Φ , χ specify the orientation of the molecule-fixed axis system with respect to the X , Y , Z axis system, and γ is the angle of internal rotation relating the orientation of the top half to the orientation of the frame half of the molecule.

The top and frame axis systems are exactly defined by the center-of-mass, Eckart, and Sayvetz conditions (*cf.* Eqs (3) in ref.¹), which define 7 nongenuine vibrational coordinates T_x , T_y , T_z (center-of-mass conditions), R_x , R_y , R_z (Eckart conditions), and τ (Sayvetz condition) as linear combinations of the Cartesian displacement vectors \mathbf{d}_i with coefficients which in general are functions of γ . The remaining $3N-7$ genuine vibrational coordinates $Q_1, Q_2, \dots, Q_{3N-7}$ are defined as

$$Q_s = \sum_{i=1}^N \mathbf{f}_i^s(\gamma) \cdot \mathbf{d}_i. \quad (1)$$

Since Q_s are orthogonal to the nongenuine normal coordinates, at least some of the coefficients \mathbf{f}_i^s in Eq. (1) must be functions of γ .

In terms of these coordinates, the simplified vibrational-rotational Hamiltonian (corresponding to that used by Bunker for dimethylacetylene⁴) can be written as

$$\mathbf{H} = \left\{ \sum_{\alpha=x,y,z} \frac{(\mathbf{P}_\alpha - \mathbf{p}_\alpha)^2}{2I_{\alpha\alpha}} + \frac{(\mathbf{P}_\gamma - \mathbf{p}_\gamma)^2}{2I_{\gamma\gamma}} \right\} + \left\{ \frac{1}{2} \sum_s \mathbf{p}_s^2 + V(Q_s, \gamma) \right\}, \quad (2)$$

In correspondence to this equation, $P_\alpha = \partial T / \partial \omega_\alpha$ ($\alpha = x, y, z$) are the components of the total angular momentum, $P_\gamma = \partial T / \partial \gamma$ is the angular momentum of internal rotation, P_x and P_y are related to $P_{\chi_t} = \partial T / \partial \chi_t$ and $P_{\chi_f} = \partial T / \partial \chi_f$ as

$$P_x = P_{\chi_t} + P_{\chi_f} \quad \text{and} \quad P_y = P_{\chi_t} - P_{\chi_f}. \quad (3)$$

The p'_α 's ($\alpha = x, y, z$) are the components of the vibrational angular momentum, p_γ is the torsional vibrational angular momentum. The p'_s are the linear vibrational momenta conjugate to Q_s , V is the potential energy which can be written in the harmonic approximation as

$$V = V_0(\gamma) + \frac{1}{2} \sum_s F_s(\gamma) Q_s^2, \quad (4)$$

where $V_0(\gamma)$ is the potential energy of internal rotation in the vibrationless state (a function of γ with a period 2γ) and the $F_s(\gamma)$'s are the quadratic potential constants which will in general be the functions of γ . The rotational-torsional wavefunctions in which the first term on the right side of Eq. (2) is diagonal are in general linear combinations of the functions

$$\psi_{r,t} = S_{J,k,M}(\Theta, \Phi) \exp(ik_t\chi_t) \exp(ik_t\chi_t) = S_{J,k,M}(\Theta, \Phi) \exp(ik\chi) \exp(ik_t\gamma), \quad (5)$$

where $k = k_t + k_f$ is the rotational quantum number and $k_t = k_t - k_f$ is the torsional quantum number.

The Symmetry Group. The generators of the Longuet-Higgins' group⁵ considered as the set of feasible symmetry operations for ethylene-like molecules with nearly free internal rotation, are the operations

$$A = (12), B = (34), E^*, D = (ab)(14)(23),$$

where for example (12) means the permutation of the positions and spins of the identical atomic nuclei 1 and 2 (Fig. 1) etc., and E^* is the operation of inversion of the positions of all particles (electrons and atomic nuclei) in the center-of-mass. The effect of these operations on the Euler angles Θ, Φ, χ and the torsional angle γ is given in Table I. We can see from the effect of say A on χ or γ that the order of A is rather 4 than 2, since e.g. $A^2 \exp(ik_t\gamma) = -\exp(ik_t\gamma)$ and we arrive at the double-valued representation G_{16}^+ of the Longuet-Higgins' groups of ethylene-like molecules*. The irreducible representations and characters of this group are given in Table II. It is obvious that this table has a different structure from that described by Hougen for the double-group of dimethylacetylene¹ or silylmethylacetylene³. The Longuet-Higgins' group of ethylene-like molecules, G_{16} , is isomorphic with the D_{4h} point group⁵, however, G_{16} is contained only once in the double-valued representation G_{16}^+ and all the double-valued representations in G_{16}^+ have dimension 2.

* Dr Watson informed us that he arrived also at the double-group of these properties¹².

The FG Matrix Problem

We now can derive the symmetry species of the genuine and nongenuine normal coordinates of vibrations. The species of T_x , T_y is E_{1d} , of T_z is B_1^+ , of R_x , R_y is E_{2d} , of R_z is B_1^- , and of τ is A_1^- . The nongenuine vibrational coordinates T_z , R_z , and τ

TABLE I

Transformation of the Euler Angles Θ , Φ , χ and of the Torsional Angle γ by the Operations of the Symmetry Group of Ethylene-Like Molecules

	E	A	B	D	E^*	A^2
Θ	Θ	Θ	Θ	$\pi - \Theta$	$\pi - \Theta$	Θ
Φ	Φ	Φ	Φ	$\Phi + \pi$	$\Phi + \pi$	Φ
χ	$\chi + \frac{1}{2}\pi$	$\chi + \frac{1}{2}\pi$	$\chi + \frac{1}{2}\pi$	$\pi - \chi$	$-\chi$	$\chi + \pi$
γ	$\gamma + \frac{1}{2}\pi$	$\gamma + \frac{1}{2}\pi$	$\gamma - \frac{1}{2}\pi$	γ	$-\gamma$	$\gamma + \pi$

TABLE II

The Representations and Characters of the Molecular Symmetry Group for the Born-Oppenheimer Variables of the Ethylene-Like Molecules^a

	$1E$	$2A^3$ $2A$	$2D$	$2A^2BD$ $2BD$	$1AB$	$1A^2E^*$ $1E^*$	$2A^3E^*$ $2AE^*$	$2D^*$	$2A^2BD$ $2BD^*$	$1A^3B^*$ $1AB^*$	$1A^2$	$2A^2D$	$1A^3B$	$2A^2D^*$
A_1^+	1	1	1	1	1	1	1	1	1	1	1	1	1	1
A_2^+	1	-1	-1	1	1	1	-1	-1	1	1	1	-1	1	-1
B_1^+	1	1	-1	-1	1	1	1	-1	-1	1	1	-1	1	-1
B_2^+	1	-1	1	-1	1	1	-1	1	-1	1	1	1	1	1
E_s^+	2	0	0	0	-2	2	0	0	0	-2	2	0	-2	0
A_1^-	1	1	1	1	1	-1	-1	-1	-1	-1	1	1	1	-1
A_2^-	1	-1	-1	1	1	-1	1	1	-1	-1	1	-1	1	1
B_1^-	1	1	-1	-1	1	-1	-1	1	1	-1	1	-1	1	1
B_2^-	1	-1	1	-1	1	-1	1	-1	1	-1	1	1	1	-1
E_s^-	2	0	0	0	-2	-2	0	0	0	2	2	0	-2	0
E_{1d}	2	0	0	0	-2	0	0	2	0	0	-2	0	2	-2
E_{2d}	2	0	0	0	-2	0	0	-2	0	0	-2	0	2	2
E_{3d}	2	0	-2	0	2	0	0	0	0	0	-2	2	-2	0
E_{4d}	2	0	2	0	2	0	0	0	0	0	-2	-2	-2	0

^a $B^* = E^*B$, $D^* = E^*D$.

TABLE III

Transformation of the Valence and Angle-Deformation Coordinates of the X_2Y_4 Molecule

	<i>E</i>	<i>A</i>	<i>B</i>	<i>D</i>	<i>E*</i>
r_1	r_2	r_1	r_4	r_1	r_1
r_2	r_1	r_2	r_3	r_2	r_2
r_3	r_3	r_4	r_2	r_3	r_3
r_4	r_4	r_3	r_1	r_4	r_4
r_{ab}	r_{ab}	r_{ab}	r_{ab}	r_{ab}	r_{ab}
φ_1	φ_2	φ_1	φ_4	φ_1	φ_1
φ_2	φ_1	φ_2	φ_3	φ_2	φ_2
φ_3	φ_3	φ_4	φ_2	φ_3	φ_3
φ_4	φ_4	φ_3	φ_1	φ_4	φ_4
α_{12}	α_{12}	α_{12}	α_{34}	α_{12}	α_{12}
α_{34}	α_{34}	α_{34}	α_{12}	α_{34}	α_{34}
q_a^a	$-q_a$	q_a	q_b	$-q_a$	$-q_a$
q_b^a	q_b	$-q_b$	q_a	$-q_b$	$-q_b$

^a q_a and q_b are the out-of-plane coordinates defined by the equations $\sin q_a = (\mathbf{e}_{a1} \times \mathbf{e}_{a2}) \cdot \mathbf{e}_{ab} / \sin \alpha_{12}$ and $\sin q_b = (\mathbf{e}_{b4} \times \mathbf{e}_{b3}) \cdot \mathbf{e}_{ba} / \sin \alpha_{34}$.

are obtained by an orthogonal transformation of the \mathbf{d}_i 's with coefficients independent of γ , the coordinates T_x, T_y and R_x, R_y with coefficients which are functions of $\cos \gamma, \sin \gamma$. We now want to find the species of the genuine vibrational coordinates Q_s ($s = 1, 2, \dots, 3N - 7$) which are orthogonal to all the nongenuine vibrational coordinates and transform according to the irreducible species of the symmetry group G_{16}^+ . It is obvious that coordinates which have this property can be constructed from the valence and angle-deformation coordinates (Fig. 1). Their transformation properties are given in Table III and we find by standard group-theoretical methods that the internal symmetry coordinates of the X_2Y_4 molecule form the basis of the completely reduced representation whose structure in terms of the direct sums of the irreducible representations of the G_{16}^+ group is

$$3A_1^+ + 2B_1^+ + 2E_s^+ + E_s^-$$

(cf. Table IV).

Consider now the kinematic matrix \mathbf{G} for the symmetry coordinates in Table IV. The elements of \mathbf{G} can be calculated by standard methods¹³ and it is immediately obvious that the \mathbf{G} matrix does not factor completely according to the irreducible species of the symmetry coordinates in Table IV, namely, there are interaction terms among the coordinates of the species E_s^+ and E_s^- of the type $G_{ij}(\gamma) \cdot S_{ia} S_{jb}$ where the

TABLE IV
The Internal Vibrational Symmetry Coordinates of the X_2Y_4 Molecule

Species A_1^+

$$S_1 = \frac{1}{2}(r_1 + r_2 + r_3 + r_4)$$

$$S_2 = r_{ab}$$

$$S_3 = \frac{1}{2 \times 3^{1/2}}(\varphi_1 + \varphi_2 + \varphi_3 + \varphi_4 - 2\alpha_{12} - 2\alpha_{34})$$

$$S_{r_1} = \frac{1}{6^{1/2}}(\varphi_1 + \varphi_2 + \varphi_3 + \varphi_4 + \alpha_{12} + \alpha_{34})$$

Species B_1^+

$$S_4 = \frac{1}{2}(r_1 + r_2 - r_3 - r_4)$$

$$S_5 = \frac{1}{2 \times 3^{1/2}}(\varphi_1 + \varphi_2 - \varphi_3 - \varphi_4 - \alpha_{12} + \alpha_{34})$$

$$S_{r_2} = \frac{1}{6^{1/2}}(\varphi_1 + \varphi_2 - \varphi_3 - \varphi_4 + \alpha_{12} - \alpha_{34})$$

Species E_s^+

$$S_{6a} = \frac{1}{2^{1/2}}(r_1 - r_2)$$

$$S_{6b} = \frac{1}{2^{1/2}}(r_3 - r_4)$$

$$S_{7a} = \frac{1}{2^{1/2}}(\varphi_1 - \varphi_2)$$

$$S_{7b} = \frac{1}{2^{1/2}}(\varphi_3 - \varphi_4)$$

Species E_s^-

$$S_{8a} = q_a$$

$$S_{8b} = q_b$$

G_{ij} 's are the functions of $\cos 2\gamma$, $\sin 2\gamma$. This is in agreement with the group theory since the species in the G_{16}^+ group of $\cos 2\gamma$, $\sin 2\gamma$ are B_2^+ and B_2^- , respectively, and the species B_2^+ or B_2^- is contained in the direct products $E_s^+ \times E_s^+$, $E_s^- \times E_s^-$ and $E_s^+ \times E_s^-$. Hence, the direct product of the species of G_{ij} , S_i , and S_j contains A_1^+ , which is the only condition which

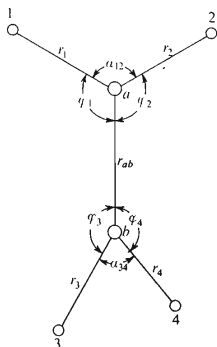


FIG. 1

The Numbering Convention for Atoms and the Designation of the Valence and Angle Deformation Coordinates in the X_2Y_4 Molecule (the $1a_2$ and $3b_4$ planes subtend angle 2γ)

A_1^+	S_1					
	S_2	A_1^+				
	S_3					
B_1^+	S_4					
	S_5	A_1^+				
E_s^+	S_{6a}		A_1^+	B_2^+	A_1^-	B_2^-
	S_{7a}					
	S_{6b}		B_2^+	A_1^+	B_2^-	A_1^-
	S_{7b}					
E_s^-	S_{8a}		A_1^-	B_2^-	A_1^+	B_2^+
	S_{8b}		B_2^-	A_1^-	B_2^+	A_1^+

FIG. 2

Factorization of the F and FG Matrices for the X_2Y_4 Molecule

must be satisfied for $G_{ij}S_iS_j$ may be nonvanishing. The symmetry coordinates which are given in Table IV are of course not the only ones which can be found for this molecule. We could form new symmetry coordinates from those in Table IV by orthogonal transformations with coefficients which are the functions of $\cos(n\gamma)$, $\sin(n\gamma)$ where n is integer. This would change the species of the symmetry coordinates and in general also the factorization of the **G** matrix, however, it can be found from the direct products of the species of the corresponding factors that such transformations cannot remove the γ -dependent terms from the **G** matrix. The physical interpretation of this results is simple: The $\mathbf{s}_{i\alpha,i}$ vectors relating the \mathbf{d}_i 's to the degenerate symmetry coordinates $S_{i\alpha}$ (cf.¹³) follow the rotation of the top half of the molecule while the $\mathbf{s}_{i\beta,i}$ vectors follow the rotation of the frame half of the molecule. This is obvious from Fig. 1 and Table IV. Hence, it is impossible to find an orthogonal transformation of the $S_{i\alpha}, S_{i\beta}$ pair of coordinates to new coordinates $S'_{i\alpha}, S'_{i\beta}$ such that the angles between the new vectors $\mathbf{s}'_{i\alpha,i}$ and $\mathbf{s}'_{i\beta,i}$ become independent of γ .

We shall now discuss the factorization of the force constant matrix **F** in terms of the symmetry coordinates of Table IV. Using arguments similar to those of Hougen^{1,2}, we shall find that the **F** matrix factors in blocks as illustrated by Fig. 2, *i.e.*, there are cross-terms between the coordinates of the species E_s^+ and E_s^- which are functions of γ (the species of $\sin 2\gamma$, $\cos 2\gamma$ is B_2^- and B_2^+ , respectively, the species of $\sin 4\gamma$, $\cos 4\gamma$ is A_1^- and A_1^+ , respectively). The factorization of the **G** matrix is described by Fig. 2 if we consider zeros in places of elements of blocks of the species A_1^- ; the **FG** matrix factorizes therefore like the **F** matrix (Fig. 2).

We shall now discuss the normal modes corresponding to the matrix **FG** in Fig. 2. Consider the eigenvectors and normal modes of the two 3×3 and 2×2 submatrices of $(\mathbf{GF})_{rs}$ which involve the symmetry coordinates of the species A_1^+ and B_1^+ , respectively. Arguments similar to those in Hougen's paper² lead to the result that each element of the corresponding column matrices of these vectors has the symmetry A_1^+ and the corresponding normal modes are also of the symmetry species A_1^+ and B_1^+ , respectively.

Consider now the eigenvectors and normal modes of the submatrix of $(\mathbf{GF})_{rs}$ involving the E_s^+ and E_s^- coordinates. It is obvious from Fig. 2 that the column matrix of the elements of these eigenvectors can be partitioned as follows

$$\mathbf{L} \equiv \begin{bmatrix} I_1 \\ \dots \\ I_2 \\ \dots \\ I_3 \\ \dots \\ I_4 \end{bmatrix}, \quad (6)$$

where I_1, I_2 are the 2×1 submatrices, and I_3, I_4 are the 1×1 submatrices.

The transformation properties of the elements of the individual blocks in the 6×6 submatrix in Fig. 2 can be written symbolically as follows

$$\begin{array}{ccccc}
 [A_1^+] & & [A_1^+] & & [A_1^+] \\
 [A_1^-] & \xleftarrow{A, B} & [A_1^-] & \xrightarrow{E^*} & -[A_1^-] \\
 -[B_2^+] & & [B_2^+] & & [B_2^+] \\
 -[B_2^-] & & [B_2^-] & & -[B_2^-]
 \end{array} \quad (7)$$

and therefore (cf. ref.²).

$$\begin{bmatrix} I_1 \\ \dots \\ I_2 \\ \dots \\ I_3 \\ \dots \\ I_4 \end{bmatrix} \xrightarrow{E^*} \pm \begin{bmatrix} I_1 \\ \dots \\ I_2 \\ \dots \\ -I_3 \\ \dots \\ -I_4 \end{bmatrix}, \quad (8a)$$

$$\begin{bmatrix} I_1 \\ \dots \\ I_2 \\ \dots \\ I_3 \\ \dots \\ I_4 \end{bmatrix} \xrightarrow{A, B} \pm \begin{bmatrix} I_1 \\ \dots \\ -I_2 \\ \dots \\ I_3 \\ \dots \\ -I_4 \end{bmatrix}. \quad (8b)$$

The operation D leaves all the blocks of the submatrix unchanged ($D\gamma = +\gamma$) and the eigenvectors are therefore invariant with respect to D . We must now decide the signs in relations (8). When $\gamma = 0$ the blocks A_1^- and B_2^- vanish and the eigenvectors must be either

$$\mathbf{L}_1 = \begin{bmatrix} I_1 \\ \dots \\ I_2 \\ \dots \\ 0 \\ \dots \\ 0 \end{bmatrix} \quad \text{or} \quad \mathbf{L}_2 = \begin{bmatrix} 0 \\ \dots \\ 0 \\ \dots \\ I_3 \\ \dots \\ I_4 \end{bmatrix}. \quad (9)$$

Since the transformation $\gamma \rightarrow -\gamma$ is the identity when $\gamma = 0$, we conclude (*cf.* ref.²) that the upper signs in relations (8a) must be chosen for the vectors of the type L_1 and the lower signs in relation (8a) for the vectors of the type L_2 .

When $\gamma = -\pi/4$ the blocks A_1^- and B_2^+ vanish and the eigenvectors must be therefore either

$$L_3 = \begin{bmatrix} I_1 \\ \dots \\ 0 \\ \dots \\ 0 \\ \dots \\ I_4 \end{bmatrix} \quad \text{or} \quad L_4 = \begin{bmatrix} 0 \\ \dots \\ I_2 \\ \dots \\ I_3 \\ \dots \\ 0 \end{bmatrix}. \quad (10)$$

According to Eq. (8), these vectors transform by the operation A as follows

$$L_3 \xrightarrow{A} \pm \begin{bmatrix} I_1 \\ \dots \\ 0 \\ \dots \\ 0 \\ \dots \\ -I_4 \end{bmatrix}, \quad L_4 \xrightarrow{A} \pm \begin{bmatrix} 0 \\ \dots \\ -I_2 \\ \dots \\ +I_3 \\ \dots \\ 0 \end{bmatrix}. \quad (11)$$

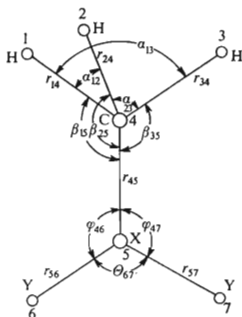


FIG. 3

The Numbering Convention for Atoms and the Designation of the Valence and Angle Deformation Coordinates in Nitromethane

The effect of applying operation A at $\gamma = -\pi/4$, however, must be the same as that obtained after applying operation E^* (note that $A\gamma (= \gamma + \pi/2) = E^*\gamma$ for $\gamma = -\pi/4$). Let the eigenvector \mathbf{L}_{ij} ($i = 1, 2; j = 3, 4$) be the eigenvector of the type \mathbf{L}_i at $\gamma = 0$ and of the type \mathbf{L}_j at $\gamma = -\pi/4$. Now, the transformation properties of the eigenvectors \mathbf{L}_{ij} in (11) with respect to the operation A must be the same as the above determined transformation properties of \mathbf{L}_i with respect to the operation E^* . Consequently, we must choose the upper signs for the eigenvectors \mathbf{L}_{13} and \mathbf{L}_{24} in Eq. (11), and the lower signs for the eigenvectors \mathbf{L}_{23} and \mathbf{L}_{14} . Following Hougen's arguments² we find again that the upper sign in Eq. (8b) is the proper one for the eigenvectors \mathbf{L}_{13} and \mathbf{L}_{24} and the lower sign in Eq. (8b) is the proper one for the eigenvectors \mathbf{L}_{14} and \mathbf{L}_{23} . The sign choice for the eigenvectors \mathbf{L}_{1j} and \mathbf{L}_{2j} in Eq. (8a) is obviously identical with the above determined sign choice for \mathbf{L}_1 and \mathbf{L}_2 , respectively.

Having determined the sign choice in Eqs (8) we can symbolically write the four possible types of eigenvectors of the submatrix of the \mathbf{FG} matrix corresponding to the E_s^+ and E_s^- symmetry coordinates:

$$\mathbf{L}_{13} = \begin{bmatrix} A_1^+ \\ \dots \\ B_2^+ \\ \dots \\ A_1^- \\ \dots \\ B_2^- \end{bmatrix} \quad \mathbf{L}_{14} = \begin{bmatrix} B_2^+ \\ \dots \\ A_1^+ \\ \dots \\ B_2^- \\ \dots \\ A_1^- \end{bmatrix} \quad \mathbf{L}_{23} = \begin{bmatrix} B_2^- \\ \dots \\ A_1^- \\ \dots \\ B_2^+ \\ \dots \\ A_1^+ \end{bmatrix} \quad \mathbf{L}_{24} = \begin{bmatrix} A_1^- \\ \dots \\ B_2^- \\ \dots \\ A_1^+ \\ \dots \\ B_2^+ \end{bmatrix} \quad (12)$$

The species of the associated normal coordinates are:

$$\mathbf{L}_{13} \sim E_s^+, \quad \mathbf{L}_{14} \sim E_s^+, \quad \mathbf{L}_{23} \sim E_s^-, \quad \mathbf{L}_{24} \sim E_s^-.$$

It is obvious from these results that only the single-valued representations are needed for the classification of the normal modes and vibrational states of ethylene-like molecules. However, the single-valued as well as the double-valued representations appear in the classification of the functions $\exp(iny)$, $\exp(-iny)$ and $\exp(ix)$, $\exp(-ix)$ as is obvious from Table V.

Nitromethane-Like Molecules

Symmetry Group and the \mathbf{FG} Matrix Problem. The generators of the symmetry group of nitromethane-like molecules are the operations $A = (123)$, $B = (12)^*$, and $C = (45)$ (the numbering of atoms is obvious from Fig. 3). If the torsional angle α is defined as $\alpha = \chi_1 - \chi$, where χ_1 is the Euler angle of the top-fixed system of axes (fixed say to the CH_3 group) and χ is the Euler angle of the system of axes fixed in the

NO_2 group, the rotational-torsional wave function will be linear combination of the functions

$$\psi_{rt} = S_{JKM}(\Theta, \Phi) \exp(ik\chi) \exp(ip\alpha), \quad (13)$$

where the quantum numbers k and p are defined by $P_z \psi_{rt} = k \psi_{rt}$ and $P_\alpha \psi_{rt} = p \psi_{rt}$. Since A^3 transforms α to $\alpha + 2\pi$, we arrive at the single-valued representation of the symmetry group G_{12} of the nitromethane-like molecule which is isomorphic with the D_{3h} group⁵.

TABLE V

Species of the Functions e^{iny} , e^{-iny} and e^{inx} , e^{-inx}

Function ^a	Species	Function ^a	Species
e^{iy} , e^{-iy}	E_{4d}	e^{ix} , e^{-ix}	E_{2d}
e^{i2y} , e^{-i2y}	$B_2^+ + B_2^-$	e^{i2x} , e^{-i2x}	$A_2^- + B_2^+$
e^{i3y} , e^{-i3y}	E_{4d}	e^{i3x} , e^{-i3x}	E_{2d}
e^{i4y} , e^{-i4y}	$A_1^+ + A_1^-$	e^{i4x} , e^{-i4x}	$A_1^+ + B_1^-$

^a Mod 4.

TABLE VI

The Representations and Characters of the Molecular Symmetry Group G_{12}^+ for the Born-Oppenheimer Coordinates of the Nitromethane-Like Molecules

Species	E	$2A$	$3BC^2$ $3B$	C^3 C	$2AC$	$3BC^3$ $3BC$	C^2	$2AC^2$	$2AC^4$
A_1'	1	1	1	1	1	1	1	1	1
A_2'	1	1	-1	1	1	-1	1	1	1
E_2'	2	-1	0	2	-1	0	2	-1	-1
A_1''	1	1	1	-1	-1	-1	1	1	-1
A_2''	1	1	-1	-1	-1	1	1	1	-1
E_3''	2	-1	0	-2	1	0	2	-1	1
E_{1d}	2	1	0	0	$3^{1/2}$	0	-2	-1	$-3^{1/2}$
E_{2d}	2	1	0	0	$-3^{1/2}$	0	-2	-1	$3^{1/2}$
E_{3d}	2	-2	0	0	0	0	-2	2	0

We could also introduce the double-valued group for nitromethane by defining the top-fixed and frame-fixed system of coordinates as in ethylene-like molecules. Then factors will appear in the wave function of the type

$$\exp(ik_t\chi_t)\exp(ik_f\chi_f) = \exp[i\frac{1}{2}(k_t + k_f)(\chi_t + \chi_f)]\exp[i\frac{1}{2}(k_t - k_f)(\chi_t - \chi_f)] \quad (14)$$

and for example the effect of operation A^3 on $\gamma = \frac{1}{2}(\chi_t - \chi_f)$ is $A^3\gamma = \gamma + \pi$; the order of A is then 6 rather than 3 (and similarly the order of C is rather 4 than 2) and we arrive at the double-group G_{12}^+ whose characters are given in Table VI. The structure of the character table of this group is similar to that of ethylene-like molecules, *i.e.* all the double-valued representations are of dimension 2. However, it can easily be shown that we need not introduce functions of the type described by Eq. (14) for nitromethane-like molecules. Suppose we neglect the asymmetry of these molecules; then the approximate rotorsional energy levels E_{rt} are

$$E_{rt} = \{Ak^2 + B[J(J+1) - k^2]\} + \{A_t k_t^2 + A_f k_f^2 - A(k_t + k_f)^2\}. \quad (15)$$

TABLE VII

The Internal Vibrational Symmetry Coordinates of the Nitromethane Molecule^a

Species A'_1		
S_1	$= 3^{-1/2}(r_{14} + r_{24} + r_{34})$	
S_2	$= r_{45}$	
S_3	$= 2^{-1/2}(r_{56} + r_{57})$	
S_4	$= 6^{-1/2}(\varphi_{46} + \varphi_{47} - 2\varphi_{67})$	
S_5	$= 6^{-1/2}(\alpha_{12} + \alpha_{13} + \alpha_{23} - \beta_{15} - \beta_{25} - \beta_{35})$	
S_{r_1}	$= 3^{-1/2}(\varphi_{46} + \varphi_{47} + \varphi_{67})$	
S_{r_2}	$= 6^{-1/2}(\alpha_{12} + \alpha_{13} + \alpha_{23} + \beta_{15} + \beta_{25} + \beta_{35})$	
Species A''_1		
S_6	$= 2^{-1/2}(r_{56} - r_{57})$	
S_7	$= 2^{-1/2}(\varphi_{46} - \varphi_{47})$	
Species A''_2		
S_8	$= q$ (out-of-plane)	
Species E'_g		
S'_{9a}	$= 6^{-1/2}(2r_{14} - r_{34} - r_{24}),$	$S'_{9b} = 2^{-1/2}(r_{34} - r_{24})$
S'_{10a}	$= 6^{-1/2}(2\alpha_{23} - \alpha_{12} - \alpha_{13}),$	$S'_{10b} = 2^{-1/2}(\alpha_{12} - \alpha_{13})$
S'_{11a}	$= 6^{-1/2}(2\beta_{15} - \beta_{25} - \beta_{35}),$	$S'_{11b} = 2^{-1/2}(\beta_{35} - \beta_{25})$

^a The redundant symmetry coordinates are S_{r_1} and S_{r_2} .

Consider for example states ($k_t = +1, k_f = 0$), ($k_t = -1, k_f = 0$), ($k_t = 0, k_f = 1$), ($k_t = 0, k_f = -1$). The first two states belong to the energy level E_{rt} , the latter two states to E'_{rt} , however, $E_{rt} = E'_{rt}$ only when $A_t = A_f$. The species of the $\exp(i\gamma)$, $\exp(-i\gamma)$ pair in G_{12}^+ is E_{1d} , that of $\exp(i\chi)$, $\exp(-i\chi)$ is E_{2d} ; then the species of the rotorsional function is $A'_1 + A'_2 + E'_s$. The group theory tells us merely that there is a splitting of these levels due to different values of A_t, A_f , which is not of great practical importance.

Furthermore, consider the internal symmetry coordinates of nitromethane constructed from the valence and angle-deformation coordinates (*cf.* Fig. 3), as indicated in Table VII. These coordinates form the basis of the completely reduced representation whose structure is

$$5A'_1 + 2A''_1 + A''_2 + 3E'_s.$$

The **G** matrix does not factorize completely according to the irreducible species of the symmetry coordinates in Table VII, since cross terms of the type $G_{ij}(\gamma) S_i^{(E'_s)} S_j$ appear where the species of S_j is either A''_1 or A''_2 , and G_{ij} are functions of $\sin 2\gamma$, $\cos 2\gamma$, of the species E''_s (note that $E''_s \times E'_s = A''_1 + A''_2 + E''_s$). However, we can introduce new symmetry coordinates by an orthogonal transformation of the coordinates S'_{ka}, S'_{kb} in Table VII ($k = 9, 10, 11$)

TABLE VIII
Fundamental Frequencies of CH_3NO_2 and CD_3NO_2 (in cm^{-1})

ν_i^a	Symmetry species in D_{3h}	CH_3NO_2^b	CD_3NO_2^c	Assignment
ν_1	A'_1	2 964.3	2 260	CH_3 sym. stretch
ν_2	A'_1	1 397	1 389	NO_2 sym. stretch
ν_3	A'_1	1 378.8	1 076	CH_3 sym. bend
ν_4	A'_1	917.1	891	CN stretch
ν_5	A'_1	656	636	NO_2 bend
ν_6, ν_{11}	A''_1, A''_2	3 080.4	2 340	CH_3 asym. stretch
ν_7	A''_1	1 583.3	1 554	NO_2 asym. stretch
ν_8, ν_{12}	A''_1, A''_2	1 438.0	1 051	CH_3 asym. bend
ν_9, ν_{13}	A''_1, A''_2	$\begin{cases} 1\ 146 \\ 1\ 091 \end{cases}$	876	CH_3 rock
ν_{10}	A''_1	478	430	NO_2 rock
ν_{14}	A''_2	605	543	N out-of-plane

^a The numbering of frequencies respects the factorization of the **FG** matrix of nitromethane.

^b Ref.¹⁴. ^c B. Jordanov: Unpublished results.

$$S_{ka}^{(A_1'')} = \cos 2\gamma \cdot S_{ka}'^{(E_s')} - \sin 2\gamma \cdot S_{kb}'^{(E_s')}, \quad (16a)$$

$$S_{kb}^{(A_2'')} = \sin 2\gamma \cdot S_{ka}'^{(E_s')} + \cos 2\gamma \cdot S_{kb}'^{(E_s')}. \quad (16b)$$

In terms of these coordinates, the \mathbf{G} matrix is γ -independent and factorized into a 5×5 block corresponding to the coordinates of the species A_1' , a 5×5 block corresponding to A_1'' , and a 4×4 block corresponding to A_2'' . The physical interpretation of this transformation is simple: the $s'_{ka,i}$ and $s'_{kb,i}$ ($k = 9, 10, 11$) vectors pertaining to S'_{ka} , S'_{kb} follow the rotation of the top half of the molecule and it is therefore possible to find an orthogonal transformation such that the new vectors $s_{ka,i}$, $s_{kb,i}$ pertaining to $S_{ka}^{(A_1'')}$, $S_{kb}^{(A_2'')}$ ignore this rotation and subtend angles with all other s -vectors which are γ -independent.

These results agree basically with those of Fleming and Banwell¹¹ except that their symmetry coordinate S_4 is not orthogonal to the redundant symmetry coordinate of the species A_1' (the co-

TABLE IX
Force Constants of Nitromethane (in mdyn/Å)

Constant	Set I ^a	Set II ^b	Set III ^c	Set IV ^d	Set V ^e
$F(r_{CH}^2)$	4.55	4.58	4.58	4.61	4.45
$F(r_{CH}r'_{CH})$	-0.14	-0.12	-0.13	-0.13	-0.13
$F(r_{CH}r_{CN})$	-0.61	-0.70	-0.70	-0.73	-0.49
$F(r_{CH}\alpha)$	-0.54	-0.51	-0.51	-0.49	-0.64
$F(r_{CH}\beta)$	-0.07	-0.11	-0.11	-0.10	-0.13
$F(r_{CN}^2)$	4.62	4.72	4.72	4.76	4.42
$F(r_{CN}r_{NO})$	0.72	0.64	0.64	0.63	0.83
$F'f$	0.62	0.62	0.62	0.61	0.62
$F''f$	0.18	0.16	0.16	0.16	0.20
$F(r_{NO}\varphi)$	0.31	1.22	0.99	1.53	0.20
$F(r_{NO}\theta)$	-0.11	-1.06	-0.82	-1.32	-1.72
$F(\varphi^2)$	0.99	1.28	1.15	1.49	1.84
$F(\alpha^2)$	0.60	0.59	0.59	0.59	0.56
$F(\beta^2)$	0.86	0.80	0.80	0.78	1.01
$F(\theta^2)$	1.47	1.31	1.37	1.21	1.08
$F(r_{NO}\theta)$	0.55	0.57	0.57	0.59	0.49
$F(r_{NO}^2)$	10.3	11.6	11.3	11.9	12.3
$F(r_{NO}r'_{NO})$	2.58	1.26	1.54	0.95	0.64
$F(q^2)$	0.35	0.35	0.35	0.36	0.35

^a Calculated for $\nu_9 = 1091 \text{ cm}^{-1}$, $\nu_{13} = 1146 \text{ cm}^{-1}$. ^b for $\nu_9 = \nu_{13} = 1096 \text{ cm}^{-1}$. ^c for $\nu_9 = 1087 \text{ cm}^{-1}$, $\nu_{13} = 1100 \text{ cm}^{-1}$. ^d for $\nu_9 = \nu_{13} = 1091 \text{ cm}^{-1}$. ^e for $\nu_9 = \nu_{13} = 1146 \text{ cm}^{-1}$. ^f $F' = (2/3)^{1/2}[F(r_{CN}\varphi) - F(r_{CN}\theta)]$, $F'' = 3/6^{1/2}[F(r_{CN}\alpha) - F(r_{CN}\beta)]$.

ordinate S_{r_1} in Table VII) and consequently, the corresponding \mathbf{G} matrix elements should be changed (there are also obvious typographical errors in the elements G_{11} and G_{66} in ref.¹¹). The form of the eigenvectors of the \mathbf{FG} matrix of nitromethane was discussed by Fleming and Banwell¹¹ and will not be therefore discussed here.

Refinement Calculation of the Force Constants of CH_3NO_2 . We tried a least squares iterational calculation^{15,16} of the quadratic force constants of nitromethane, neglecting the γ -dependent terms in the \mathbf{F} matrix (cf. ref.⁴), and using the fundamental frequencies of CH_3NO_2 and CD_3NO_2 listed in Table VIII. We assumed the tetrahedral symmetry for the CH_3 group, and used the values $r_{\text{CH}} = 1.09 \text{ \AA}$, $r_{\text{CN}} = 1.49 \text{ \AA}$, $r_{\text{NO}} = 1.22 \text{ \AA}$, $\angle \text{ONO} 127^\circ$. We tried to adjust several sets of force constants among which the set described in the first column of Table IX provided physically acceptable solutions which reproduced experimental frequencies within few wavenumbers for most frequencies, except ν_5 , ν_{14} and the nearly degenerate pair ν_8 , ν_{12} where differences up to 17 cm^{-1} remained between the experimental and calculated frequencies. Slightly poorer agreement between calculated and experimental frequencies was observed for CD_3NO_2 where the experimental data were not analyzed in detail. There remains of course uncertainty in the converged values of some force constants in Table IX due to the uncertain values of ν_8 , ν_{12} (Table VIII) and it is obvious that a further high resolution infrared study of CH_3NO_2 and its isotopic species is necessary for a better determination of the force constants of nitromethane.

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