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Vibrational Analysis of Substituted and Perturbed Molecules. III. Green's Function Determination of Force Constants for XY_3 Planar Molecules

By Thomas WOLFRAM, C. D. BASS, Roger E. DEWAMES and L. LYNDS
North American Aviation Science Center, Thousand Oaks, California, U. S. A.

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Using the Green's function formulae for isotopic frequencies of the XY_3 molecule together with the spectral theorem, explicit formulae for the molecular force constants directly in terms of the vibrational frequencies have been obtained. The relationship between the Wilson force constants and the cartesian force constants is discussed and leads to the above formulae. The procedure is applied to the BCl_3 and BBr_3 molecules and force constants are obtained. A simple procedure for calculating the variations in the force constants with variations in vibrational frequencies is suggested.

In previous papers[1,2] (hereafter referred to as VAI and VAII), it was shown that the vibrational frequencies of isotopically substituted molecules can be calculated using a Green's function procedure, thereby avoiding the construction of a force constant model. It was pointed out in VAI that a unique set of force constants for the molecule can be generated directly from the vibrational frequencies once the mixing parameters were known. This procedure leads to explicit expressions for the force constants in terms of the vibrational frequencies. These formulae are the inverted relationships between the force constants and frequencies. One customarily obtains by the FG procedure explicit expressions for the frequencies involving non-linear combinations of the force constants. For example, the procedure employed recently by Ladd, Orville-Thomas, and Cox[3] in the treatment of the boron trihalides involves the solution of two simultaneous non-linear equations with the three unknown force constants (for the two doubly degenerate frequencies). By assuming value for one force constant, the corresponding values of the other two are calculated. When the sets of values of the three are plotted graphically, the resulting figure is an ellipse. The isotopic frequencies yield another, intersecting ellipse. One of the intersection points corresponds to a physically acceptable set of force constants. In this paper we illustrate a quite different approach which makes use of the spectral theorem together with the Green's function isotopic formulae and leads to exact, explicit formulae for the force constants. The procedure is easily applied to the BX_3 molecules, however it is clear that the solution of the isotopic Green's function equations can become a sizable task for larger molecules with lower symmetry. Determination of the mixing parameters may approach in more complex cases the difficulty associated with a standard force constant analysis. On the other hand, once the mixing parameters are known the Green's function procedure is extremely convenient for the analysis of related or perturbed molecular systems as discussed in previous papers[1,2] and in the companion paper.

In section I the relationships between the cartesian coordinate force constants and the Wilson internal coordinate force constants are reviewed. The spectral theorem for the force constants in the Wilson FG representation is derived. Explicit formulae for force constants of XY_3 planar molecules are derived in terms of the vibrational frequencies and the mixing parameter. The discussion in section I is given in some detail because it serves as the theoretical foundation for the development of the Green's function procedure in the internal coordinate system which is presented in the companion paper. In section II the explicit formulae developed in I are used to calculate the force constants for $^{10}BCl_3$, $^{11}BCl_3$, $^{10}BBr_3$, and $^{11}BBr_3$. The mixing parameters necessary for these calculations were obtained by application of the Green's function isotopic formulae discussed in VAII. The results of the calculations are presented in section III. A simple procedure of calculating the variation of the force constants with variations in the input data (frequencies) is discussed.

I. Valence and Cartesian Molecular Force Constants

A. General Formalism.—Consider a molecule with n atoms numbered 1 through n and label

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[1] R. E. DeWames and T. Wolfram, *J. Chem. Phys.*, **40**, 853 (1964).

[2] C. D. Bass, L. Lynds, T. Wolfram and R. E. DeWames, ibid., **40**, 3611 (1964).

[3] J. A. Ladd, W. J. Orville-Thomas and B. C. Cox, *Spectrochem. Acta*, **19**, 1911 (1963).

the cartesian coordinates x_i $(i=1,2,\dots,3n)$ so that, for example, the three cartesian coordinates of atom 1 are x_1, x_2, x_3, and those of atom 2 are x_4, x_5, and x_6. The internal coordinates are designated by α_i $[i=1,2,\dots,(3n-6+r)]$ where r is the number of redundant coordinates. An arbitrary motion of the entire molecule may be represented by a supervector, $\boldsymbol{X}$ in the cartesian system

$$\boldsymbol{X}=\begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_{3n} \end{pmatrix} \tag{1}$$

The internal symmetry coordinates do not span the entire vector space, but excluding translation and rotation, a vibratory motion of the molecule can be represented by a supervector, $\boldsymbol{\alpha}$, in the internal coordinate system

$$\boldsymbol{\alpha}=\begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \vdots \\ \alpha_{3n-6+r} \end{pmatrix} \tag{2}$$

Because the cartesian coordinates span a larger vector space than the internal coordinates it is not possible to define transformation from the external to the internal coordinate system. In order to relate the two systems we must eliminate the redundant coordinates from the internal system and rotations and translations from the external system. This task is conveniently accomplished by transforming to symmetry coordinates. Let $\boldsymbol{X}_t$ $[t=(\Gamma,\ \nu_i)]$ be a supervector in the cartesian coordinate representation which transforms according to the νth row of the Γth irreducible representation of the group of the molecule.[4] (The subscript i on ν indexes different coordinates with identical transformation properties.) A new set of orthogonal symmetry coordinates, $\boldsymbol{S}_t$, may be constructed from the $\boldsymbol{X}_t$ as follows: The $\boldsymbol{X}_t$ corresponding to translations and rotations (about the center of mass) are mass weighted. The mass weighted vibrational type motions with identical transformation properties are then orthogonalized to the translation and rotation vectors and to each other. The symmetry coordinates, $\boldsymbol{S}_t$, then consist of orthogonalized mass weighted, translations, rotations and vibrational type motions which tranform according to the irreducible representations of the group of the molecule. The set of internal symmetry coordinates, $\boldsymbol{\sigma}_r$, which define the representation for the Wilson reduced $\boldsymbol{F}^W$ matrix do not contain translations or rotation and are not mass weighted. The $\boldsymbol{\sigma}_r$ coordinates are simply those linear combinations of the internal coordinates α_i which transform irreducibly according to the molecular group. The internal symmetry coordinates can be expressed uniquely in terms of the external coordinates (although the converse is not true) by the usual procedure[4] so that a rectangular matrix, $\boldsymbol{T}$ $(3n-6\times 3n)$, may be constructed which transforms the $\boldsymbol{\sigma}_r$ into the cartesian representation. Let us define the matrix $\boldsymbol{\sigma}$ to be a $(3n-6+r\times 3n-6)$ matrix whose columns are the non-redundant $\boldsymbol{\sigma}_r$ and let $\boldsymbol{f}$ be the matrix of (valence) force constants $(3n-6+r\times 3n-6+r)$ in the internal coordinate system, then the Wilson reduced force constant matrix, $\boldsymbol{F}^W$, $(3n-6\times 3n-6)$ in the internal symmetry coordinate system is given by

$$\boldsymbol{F}^W=\tilde{\boldsymbol{\sigma}}\boldsymbol{f}\boldsymbol{\sigma} \tag{3}$$

where $\tilde{\boldsymbol{\sigma}}$ $(3n-6\times 3n-6+r)$ is the transpose of the matrix $\boldsymbol{\sigma}$.

The cartesian coordinate matrix of force constants $\boldsymbol{F}^c$ $(3n\times 3n)$ is then given by

$$\tilde{\boldsymbol{F}}^c=\tilde{\boldsymbol{T}}\boldsymbol{F}^W\boldsymbol{T} \tag{4}$$

We may now transform the mass transformed interaction matrix[1] or dynamical matrix $\boldsymbol{D}=\boldsymbol{M}^{-1/2}\boldsymbol{F}^c\boldsymbol{M}^{-1/2}$ to the external symmetry coordinate system defined by the symmetry vectors $\boldsymbol{S}_t$ with result that

$$\boldsymbol{D}^s=\boldsymbol{S}^+\boldsymbol{D}\boldsymbol{S}=\boldsymbol{S}^+\boldsymbol{M}^{-1/2}\tilde{\boldsymbol{T}}\boldsymbol{F}^W\boldsymbol{T}\boldsymbol{M}^{-1/2}\boldsymbol{S} \tag{5}$$

where $\boldsymbol{S}^+$ is the Hermetian conjugate of $\boldsymbol{S}$, and $\boldsymbol{D}^s$ is the dynamical matrix in the cartesian or external symmetry coordinate system. $\boldsymbol{S}$, the unitary transformation from cartesian to cartesian symmetry coordinates and $\boldsymbol{M}$ the diagonal mass matrix, are discussed in Refs. 1 and 2.

A few properties of $\boldsymbol{D}^s$ should be noted; first, $\boldsymbol{D}^s$ is block diagonal in the different irreducible representations of the molecule. Furthermore, since the vibrational symmetry coordinates of $\boldsymbol{S}$ are orthogonalized to the rotation and translation eigenvectors there are no matrix elements joining the vectors to the remaining symmetry coordinates. Thus the rows and columns corresponding to rotations and translations have zero matrix elements. The matrix $\boldsymbol{D}^s$ is Hermitian and its eigenvalues are the frequencies squared. If we arrange the rotations and translations to correspond to the last 6 columns of $\boldsymbol{S}$ then a square matrix $\boldsymbol{B}$ can be defined[5]

$$\boldsymbol{B}=\{\boldsymbol{T}\boldsymbol{M}^{-1/2}\boldsymbol{S}\}_{\text{truncated}} \tag{6}$$

by removing the last 6 columns of $\boldsymbol{T}\boldsymbol{M}^{-1/2}\boldsymbol{S}$. Whereas the matrix $\boldsymbol{T}\boldsymbol{M}^{-1/2}\boldsymbol{S}$ is singular, the $\boldsymbol{B}$ matrix is non-singular, block diagonal, and its inverse can be constructed so that the Wilson $\boldsymbol{F}^W$ matrix elements can be given in terms of the symmetrized dynamical matrix.

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4) See for example, Wilson, Decius and Cross, "Molecular Vibrations," McGraw-Hill, New York (1955). The connection between internal and cartesian coordinates has been discusssed previously by D. E. Mann (*J. Chem. Phys.*, **22**, 764 (1954)) and also by T. Shimanouchi and M. Tsuboi (*J. Chem. Phys.*, **35**, 1597 (1961)).

5) E. B. Wilson, J. C. Decius and P. C. Cross, *J. Mol. Spectroscopy*, ibid., **12**, 61, 74 (1964).

$$\boldsymbol{F}^W = \tilde{\boldsymbol{B}}^{-1}\boldsymbol{D}^s\boldsymbol{B}^{-1} \qquad (7)$$

From Eq. 7 it follows that $\boldsymbol{B}\tilde{\boldsymbol{B}}$ is the Wilson $\boldsymbol{G}$ matrix for the molecule. The Wilson force constants can now of course be related directly to the cartesian force constants since $\boldsymbol{D}^s = \boldsymbol{S}^+\boldsymbol{D}\boldsymbol{S} = \boldsymbol{S}^+\boldsymbol{M}^{-1/2}\boldsymbol{F}^c\boldsymbol{M}^{-1/2}\boldsymbol{S}$. The relation between the internal force constants and the external cartesian force constants is given by

$$\boldsymbol{f} = \bar{\boldsymbol{\sigma}}\tilde{\boldsymbol{B}}^{-1}\boldsymbol{S}^+\boldsymbol{M}^{-1/2}\boldsymbol{F}^c\boldsymbol{M}^{-1/2}\boldsymbol{S}\boldsymbol{B}^{-1}\bar{\boldsymbol{\sigma}}^+ \qquad (8)$$

where $\bar{\boldsymbol{\sigma}}$ is the $(3n-6+r\times 3n-6+r)$ matrix of all the $\boldsymbol{\sigma}_r$ including the redundant symmetry coordinates and r rows and columns of zero have been added to $\boldsymbol{F}^W$ to match the dimensionality of $\bar{\boldsymbol{\sigma}}$. (It is important to note that this corresponds to an arbitrary *definition* of f since as pointed out by Crawford and Overend⁶⁾ there is a true indeterminacy in the matrix elements associated with the redundant or null coordinates. This difinition is the same as that used in almost all force constant calculations and in particular for previous calculations for BX_3 force constants and allows us to make direct comparison with these other results. Other difinitions are, however, possible.) The matrix elements of $\boldsymbol{F}^W$ can be given directly in terms of the vibrational frequencies by making use of the spectral theorem. The matrix $\boldsymbol{D}^s$ is block diagonal and may be diagonalized by a unitary matrix $\boldsymbol{A}$ (the matrix of mixing parameters) which has non-zero matrix element only between rows and columns which correspond to the same row of the same irreducible representation, and thus $\boldsymbol{A}$ is also block diagonal. We have that

$$\boldsymbol{A}^+\boldsymbol{D}^s\boldsymbol{A} = \Lambda$$

where

$$\Lambda = \begin{bmatrix} \lambda_1 & & & & \\ & \lambda_2 & & & \\ & & \lambda_3 & & \\ & & & \ddots & \\ & & & & \lambda_{3N} \end{bmatrix} \qquad (9)$$

is the diagonal matrix of eigenvalues. It should be noted that a knowledge of the mixing parameter matrix, $\boldsymbol{A}$, is equivalent to a knowledge of the $\boldsymbol{L}$ matrix discussed by Wilson, Decius, and Cross.⁵⁾ From Eq. 9 we can write

$$\boldsymbol{D}^s = \boldsymbol{A}\Lambda\boldsymbol{A}^+ \qquad (10)$$

so that

$$\boldsymbol{F}^W = \tilde{\boldsymbol{B}}^{-1}\boldsymbol{A}\Lambda\boldsymbol{A}^+\boldsymbol{B}^{-1} \qquad (11)$$

Since both $\boldsymbol{B}$ and $\boldsymbol{A}$ are block diagonal we can write an equation for the force constants corresponding to a particular symmetry type Γ_ν (the ν row of the Γth irreducible representation) involving only the mixing parameters for that block:

$$\{\boldsymbol{F}^W\}^{\Gamma\nu} = \{\tilde{\boldsymbol{B}}^{-1}\}^{\Gamma\nu}\{\boldsymbol{A}\}^{\Gamma\nu}\{\Lambda\}^{\Gamma\nu}\{\boldsymbol{A}^+\}^{\Gamma\nu}\{\boldsymbol{B}^{-1}\}^{\Gamma\nu} \qquad (12)$$

where $\{\ \}^{\Gamma\nu}$ means the block whose rows and columns correspond to the νth row of the Γth irreducible representation. The dimensionality of the matrix Eq. 12 is equal to the number of vibrational symmetry coordinates which transform according to Γ_ν.

In VAI and VAII formulae for obtaining the mixing parameters using the Green's function approach were given. The mixing parameters, of course, allow the construction of the matrix A and thus the calculation of $\boldsymbol{F}^W$ from Eq. 11 or 12.

B. Application to the XY_3 Planar Molecule.—In this section we apply the preceding formalism to the XY_3 molecule and obtain the relations between the external and internal force constants. In anticipation of a following paper which deals with the XY_2Z planar molecule we have generalized the diagrams and force constants to the case of the XY_2Z molecule. The internal and external coordinate systems for the XY_3 and XY_2Z molecule are shown in Fig. 1.

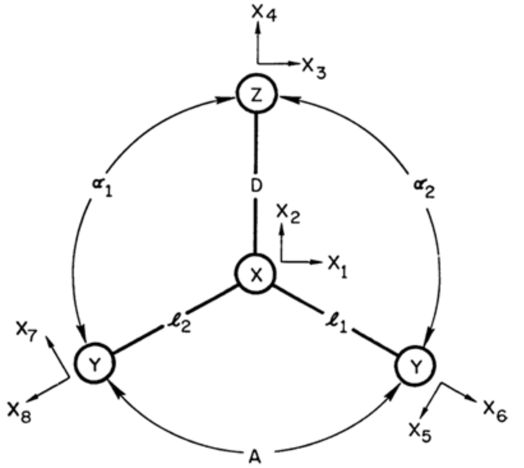

Fig. 1. Showing the internal and cartesian coordinate systems for the XY_2Z planer molecule.

In this section we shall be concerned with XY_3 molecules for which the bond lengths D, l_1 and l_2 are all of length l and the angles A, α_1 and α_2 are 120°, although no such restrictions need apply to the XY_2Z molecule. The external mass weighted symmetry coordinates for the XY_3 planar molecule given in VAII may be orthonormalized to give the unitary $\boldsymbol{S}$ matrix (13). where $r^2 = m_y/m_x$, $d_1{}^2 = 3r^2+1$, and $d_2{}^2 = 3r^2+2$. The first column of S corresponds to the A_1 symmetric stretch; the second column is a mass weighted E′ bending symmetry coordinate, and the third column is an E′ stretching symmetry coordinate which has been orthogonalized to column two. These three coordinates transform according to

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6) B. Crawford and J. Overend, ibid., **12**, 307 (1964).

$$\boldsymbol{S}=\begin{pmatrix} 0 & 0 & 0 & \frac{\sqrt{3}r}{d_2} & \frac{-\sqrt{3}r}{d_1d_2} & 0 & \frac{1}{d_1} & 0 \\ 0 & \frac{\sqrt{3}r}{d_2} & \frac{-\sqrt{3}r}{d_1d_2} & 0 & 0 & 0 & 0 & \frac{1}{d_1} \\ 0 & 0 & 0 & \frac{-2}{\sqrt{3}d_2} & \frac{-\sqrt{3}r^2}{d_1d_2} & \frac{1}{\sqrt{3}} & \frac{r}{d_1} & 0 \\ \frac{1}{\sqrt{3}} & 0 & \frac{d_2}{\sqrt{3}d_1} & 0 & 0 & 0 & 0 & \frac{r}{d_1} \\ 0 & \frac{1}{d_2} & \frac{3r^2}{2d_1d_2} & \frac{1}{\sqrt{3}d_2} & \frac{\sqrt{3}r^2}{2d_1d_2} & \frac{1}{\sqrt{3}} & \frac{-r}{2d_1} & \frac{-\sqrt{3}r}{2d_1} \\ \frac{1}{\sqrt{3}} & 0 & \frac{-d_2}{2\sqrt{3}d_1} & 0 & \frac{d_2}{2d_1} & 0 & \frac{\sqrt{3}r}{2d_1} & \frac{-r}{2d_1} \\ 0 & \frac{-1}{d_2} & \frac{-3r^2}{2d_1d_2} & \frac{1}{\sqrt{3}d_2} & \frac{\sqrt{3}r^2}{2d_1d_2} & \frac{1}{\sqrt{3}} & \frac{-r}{2d_1} & \frac{\sqrt{3}r}{2d_1} \\ \frac{1}{\sqrt{3}} & 0 & \frac{-d_2}{2\sqrt{3}d_1} & 0 & \frac{-d_2}{2d_1} & 0 & \frac{-\sqrt{3}r}{2d_1} & \frac{-r}{2d_1} \end{pmatrix} \qquad (13)$$

the A_1 irreducible representation for the group of the XY_2Z molecule. The fourth and fifth columns are E′ bending and stretching coordinates which correspond to B_1 type coordinates for the XY_2Z molecule. The remaining columns are the in-plane rotation and translation normal modes. The internal coordinates are taken to be ΔD, Δl_1, Δl_2, $l\Delta A$, $l\Delta\alpha_1$, and $l\Delta\alpha_2$. The internal symmetry coordinates for the XY_3 molecule define the $\bar{\boldsymbol{\sigma}}$ matrix given below:

$$\bar{\boldsymbol{\sigma}}=\begin{pmatrix} \frac{1}{\sqrt{3}} & \frac{2}{\sqrt{6}} & 0 & 0 & 0 & 0 \\ \frac{1}{\sqrt{3}} & \frac{-1}{\sqrt{6}} & 0 & \frac{1}{\sqrt{2}} & 0 & 0 \\ \frac{1}{\sqrt{3}} & \frac{-1}{\sqrt{6}} & 0 & \frac{-1}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & \frac{2}{\sqrt{6}} & 0 & 0 & \frac{1}{\sqrt{3}} \\ 0 & 0 & \frac{-1}{\sqrt{6}} & 0 & \frac{-1}{\sqrt{2}} & \frac{1}{\sqrt{3}} \\ 0 & 0 & \frac{-1}{\sqrt{6}} & 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{3}} \end{pmatrix} \qquad (14)$$

The first of $\bar{\boldsymbol{\sigma}}$ is the A_1 symmetric stretch, the second is the E′ stretching coordinate and the third is the E′ bending. These three coordinates transform like A_1 modes for the XY_2Z symmetry. The fourth and fifth columns are E′ stretching and bending coordinates which transform like B_1 modes for the XY_2Z molecule. The remaining column is the redundant symmetry coordinate and corresponds to a null vector in the cartesian coordinate system. The rectangular σ matrix is obtained from $\bar{\boldsymbol{\sigma}}$ by omitting the last column. The $\tilde{\boldsymbol{B}}$ and $\tilde{\boldsymbol{B}}^{-1}$ matrices for the XY_3 molecule are

$$\tilde{\boldsymbol{B}}=(m_y)^{-1/2}\begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & \frac{-3r^2}{\sqrt{2}d_2} & \frac{-3d_2}{\sqrt{6}} & 0 & 0 \\ 0 & \frac{\sqrt{2}d_1}{d_2} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{-3r^2}{\sqrt{2}d_2} & \frac{-3d_2}{\sqrt{6}} \\ 0 & 0 & 0 & \frac{\sqrt{2}d_1}{d_2} & 0 \end{pmatrix} \qquad (15)$$

and

$$\tilde{\boldsymbol{B}}^{-1}=(m_y)^{1/2}\begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{d_2}{\sqrt{2}d_1} & 0 & 0 \\ 0 & \frac{-\sqrt{6}}{3d_2} & \frac{-3r^2}{\sqrt{6}d_1d_2} & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{d_2}{\sqrt{2}d_1} \\ 0 & 0 & 0 & \frac{-\sqrt{6}}{3d_2} & \frac{-3r^2}{\sqrt{6}d_1d_2} \end{pmatrix} \qquad (16)$$

The internal force constant matrix $\boldsymbol{f}$ is

$$\boldsymbol{f}=\begin{pmatrix} f_D & f_{Dd} & f_{Dd} & f_{DA} & f_{D\alpha} & f_{D\alpha} \\ f_{Dd} & f_d & f_{dd} & f_{dA} & f_{d\alpha} & f'_{d\alpha} \\ f_{Dd} & f_{dd} & f_d & f_{dA} & f'_{d\alpha} & f_{d\alpha} \\ f_{DA} & f_{dA} & f_{dA} & f_A & f_{A\alpha} & f_{A\alpha} \\ f_{D\alpha} & f'_{d\alpha} & f'_{d\alpha} & f_{A\alpha} & f_\alpha & f_{\alpha\alpha} \\ f_{D\alpha} & f_{d\alpha} & f_{d\alpha} & f_{A\alpha} & f_{\alpha\alpha} & f_\alpha \end{pmatrix} \qquad (17)$$

in the case of the XY_3 planar molecule $f_D=f_d\equiv f_r$, $f_A=f_\alpha\equiv f_\alpha$, $f_{dA}=f_{d\alpha}\equiv f_{r\alpha}$, $f_{DA}=f'_{d\alpha}\equiv f'_{r\alpha}$, $f_{dd}=f_{Dd}\equiv f_{rr}$, and $f_{A\alpha}=f_{\alpha\alpha}\equiv f_{\alpha\alpha}$.

where, following Lindeman and Wilson,[7] we have distinguished the adjacent angle-bond force constant, $f_{d\alpha}$, from the opposite angle-bond interaction, $f'_{d\alpha}$.

The redundancy conditions reduce the number of independent internal force constants to 9 in the case of the XY_2Z molecule with the relations

$$\left.\begin{aligned} f_{D\alpha}&=-\frac{1}{2}f_{DA} \\ f'_{d\alpha}&=-(f_{dA}+f_{d\alpha}) \\ f_{A\alpha}&=-\frac{1}{2}f_{A} \\ f_{\alpha\alpha}&=\frac{1}{2}f_{A}-f_{\alpha} \end{aligned}\right\} \tag{18}$$

For XY_3 molecules, $f_D=f_d$, $f_{Dd}=f_{dd}$, $f_A=f_\alpha$, $f_{DA}=f'_{d\alpha}$, and $f_{dA}=f_{d\alpha}$, which leaves four independent force constants. The Wilson reduced $\boldsymbol{F}^W$ matrix in the internal symmetry coordinates for the XY_2Z molceule is

$$\boldsymbol{F}^W=\tilde{\boldsymbol{\sigma}}\boldsymbol{f}\boldsymbol{\sigma}=\begin{Bmatrix} \begin{pmatrix} F_{11} & F_{12} & F_{13} \\ F_{12} & F_{22} & F_{23} \\ F_{13} & F_{23} & F_{33} \end{pmatrix} & \begin{pmatrix} 0 & 0 \\ 0 & 0 \\ 0 & 0 \end{pmatrix} \\ \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} & \begin{pmatrix} F_{44} & F_{45} \\ F_{54} & F_{55} \end{pmatrix} \end{Bmatrix} \tag{19}$$

The F_{ij} have been given in terms of the f_{ij} by Lindeman and Wilson; however, because of a number of typographical errors in their paper the corrected relations are listed here.[7]

$$\left.\begin{aligned} F_{11}&=\frac{1}{3}(f_D+2f_d+4f_{Dd}+2f_{dd}) \\ F_{12}&=\frac{1}{3\sqrt{2}}(2f_D-2f_d+2f_{Dd}-2f_{dd}) \\ F_{13}&=\frac{1}{3\sqrt{2}}(2f_{DA}-2f'_{d\alpha}+4f_{dA} \\ &\quad -2f_{d\alpha}-2f_{d\alpha}) \\ &=\frac{1}{\sqrt{2}}(f_{DA}+2f_{dA}) \\ F_{22}&=\frac{1}{6}(4f_D+2f_d-8f_{Dd}+2f_{dd}) \\ F_{23}&=\frac{1}{6}(4f_{DA}+2f'_{d\alpha}-4f_{dA}-4f_{D\alpha} \\ &\quad +2f_{d\alpha})=f_{DA}-f_{dA} \\ F_{33}&=\frac{1}{6}(4f_A+2f_\alpha-8f_{A\alpha}+2f_{\alpha\alpha}) \\ &=\frac{3}{2}f_A \\ F_{44}&=f_d-f_{dd} \\ F_{45}&=f'_{d\alpha}-f_{d\alpha}=-(2f_{d\alpha}+f_{dA}) \\ F_{55}&=f_\alpha-f_{\alpha\alpha}=-\frac{1}{2}f_A+2f_\alpha \end{aligned}\right\} \tag{20}$$

In the case of the XY_3 molecule, $F_{12}=F_{13}=0$, $F_{22}=F_{44}$, $F_{33}=F_{55}$, and $F_{23}=F_{45}$. Using Eq. 7 one obtains the relations between the external symmetrized (mass weighted) force constants D_{ij}^s and the Wilson $\boldsymbol{F}^W$ force constants for the XY_3 molecule:

$$\left.\begin{aligned} F_{11}&=m_yD_{11}^s \\ F_{22}&=F_{44}=\frac{m_yd_2^2}{2d_1^2}D_{33}^s \\ F_{33}&=F_{55}=m_y\frac{2}{3d_2^2}D_{22}^s+\frac{2m_yr^2}{d_1d_2^2}D_{23}^s \\ &\quad +\frac{3}{2}m_y\frac{r^4}{d_1^2d_2^2}D_{33}^s \\ F_{23}&=-m_y\frac{1}{3d_1^2}\left\{d_1D_{23}^s+\frac{3}{2}r^2D_{33}^s\right\} \end{aligned}\right\} \tag{21}$$

Equation 7 may be inverted to give

$$\left.\begin{aligned} D_{11}^s&=F_{11}/m_y \\ D_{12}^s&=D_{13}^s=0 \\ D_{22}^s&=\frac{9}{2m_y}\left(\frac{r^4}{d_2^2}F_{22}+\frac{2r^2}{\sqrt{3}}F_{23}\right. \\ &\quad \left.+\frac{d_2^2}{3}F_{33}\right) \\ D_{23}^s&=\frac{-3d_1}{m_y}\left(\frac{r^2}{d_2^2}F_{22}+\frac{1}{\sqrt{3}}F_{23}\right) \\ D_{33}^s&=\frac{2}{m_y}\,\frac{d_1^2}{d_2^2}F_{22} \\ D_{44}^s&=D_{22}^s \\ D_{45}^s&=D_{23}^s \\ D_{55}^s&=D_{33}^s \end{aligned}\right\} \tag{22}$$

The mixing parameter matrix for the XY_3 molecule is (see VAII)

$$\boldsymbol{A}=\begin{pmatrix} 1 & & & & \\ & \frac{1}{A_0}\begin{pmatrix} a & 1 \\ 1 & -a \end{pmatrix} & & & & \\ & & \frac{1}{A_0}\begin{pmatrix} a & 1 \\ 1 & -a \end{pmatrix} & & & \\ & & & 1 & & \\ & & & & 1 & \\ & & & & & 1 \end{pmatrix} \tag{23}$$

where $A_0=(a^2+1)^{1/2}$.

Using Eq. 11 one obtains the Wilson force constants directly in terms of the frequencies of vibration and the mixing parameter a:

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[7] L. P. Lindeman and M. K. Wilson, *J. Chem. Phys.*, **24**, 242 (1956).

Table I. Frequency data (cm^{-1}) and molecular parameters for boron trihalides

Molecule		ν_1	ν_2	ν_3	Ref.	m_B	m_{halogen}
$^{10}BF_3$		888	1481.9	485.46	8	10.01	19.00
$^{11}BF_3$		888	1428.8	483.74	8		
$^{10}BCl_3$		471	993.7	243	9	10.01	35.456
$^{11}BCl_3$		471	954.2	243	9		
$^{10}BBr_3$	Set 1	278	856	150	10	10.01	79.916
$^{11}BBr_3$		278	820	150	10		
$^{10}BBr_3$	Set 2	282.5	856	155	8	10.01	79.916
$^{11}BBr_3$		282.5	819	155	8		

Table II. Force constants (mdyn./Å)

Molecule	Calculation	f_r	f_{rr}	f_α	$f_{\alpha\alpha}$	$f'_{r\alpha}$	$f_{r\alpha}$	$\omega_2^2+\omega_3^2$ (obs.) (cm$^{-2}\times 10^{-6}$)	$\omega_2^2+\omega_3^2$ (calcd.) (cm$^{-2}\times 10^{-6}$)
$^{10}BF_3$[a]	This work	7.14787	0.83787	0.35177	−0.17588	−0.21288	0.10644	14.321	14.324
$^{10}BF_3$	Ref. 1	7.14810	0.83819	0.35184	−0.17593	−0.21267	0.10633	14.321	14.326
$^{10}BCl_3$[b]	This work	3.78813	0.41925	0.15233	−0.07617	−0.13548	0.06774	6.1632	6.1638
$^{10}BCl_3$	Ref. 1	3.64622	0.49279	0.15818	−0.07909	−0.09206	0.04603	6.1632	6.1652
$^{10}BBr_3$[c] Set. 1	This work	3.5788	0.029105	0.12662	−0.06331	−0.30715	0.15357		
$^{10}BBr_3$[d]	This work	3.0669	0.34457	0.13587	−0.06794	−0.12279	0.06140	4.4569	4.4566
$^{10}BBr_3$	Ref. 1	2.95092	0.40233	0.14123	−0.07061	−0.09133	0.04566	4.4569	4.4586

a) Mixing parameter $a=-1.2765$
b) Mixing parameter $a=-1.7040$
c) Mixing parameter $a=-2.1889$
d) Mixing parameter $a=-2.6693$

$$\left.\begin{aligned}
F_{11}&=m_y\lambda_1\\
F_{22}&=F_{44}=\frac{m_y d_2^2(\lambda_2+a^2\lambda_3)}{2A_0^2 d_1^2}\\
F_{33}&=F_{55}=\frac{m_y}{2}\left\{\left(\frac{2ad_1+3r^2}{\sqrt{3}A_0 d_1 d_2}\right)^2\lambda_2\right.\\
&\qquad\left.+\left(\frac{2d_1-3ar^2}{\sqrt{3}A_0 d_1 d_2}\right)^2\lambda_3\right\}\\
F_{23}&=F_{45}=m_y\left\{\frac{-(2ad_1+3r^2)}{2\sqrt{3}A_0^2 d_1^2}\lambda_2\right.\\
&\qquad\left.+\frac{a(2d_1-3ar^2)}{2\sqrt{3}A_0^2 d_1^2}\lambda_3\right\}
\end{aligned}\right\}\tag{24}$$

where in Eq. 24 we have used the fact that $\lambda_2=\lambda_4$ and $\lambda_3=\lambda_5$. $\boldsymbol{F}^W$ can also be given directly in terms of $\boldsymbol{F}^c$ with the result that for the XY_3 molecule

$$\left.\begin{aligned}
F_{11}&=F_{44}^c+2F_{46}^c\\
F_{33}&=\frac{1}{2}F_{33}^c\\
F_{23}&=F_{36}^c\\
F_{22}&=F_{44}^c-F_{46}^c
\end{aligned}\right\}\tag{25}$$

II. Force Constants For BCl_3 and BBr_3

In this section we apply the equations given by 24 and calculate the Wilson force constants. In order to accomplish this we must first determine the mixing parameter a. The quadratic equation which determines a is (see VAII)

$$\begin{aligned}
&a^2\left\{\frac{\lambda_2+\lambda_3}{(1+\varepsilon)d_1^2}(d_1^2+\varepsilon)+\frac{3r^2\varepsilon}{(1+\varepsilon)d_1^2 d_2^2}(d_1^2\lambda_3+\lambda_2)\right.\\
&\quad\left.-(\lambda_2^{(i)}+\lambda_3^{(i)})^2\right\}+a\left(\frac{6r^2\varepsilon}{(1+\varepsilon)d_1 d_2}(\lambda_2-\lambda_3)\right)\\
&\quad+\left\{\frac{\lambda_2+\lambda_3}{(1+\varepsilon)d_1^2}(d_1^2+\varepsilon)+\frac{3r^2\varepsilon}{(1+\varepsilon)d_1^2 d_2^2}\right.\\
&\quad\left.\times(d_1^2\lambda_2+\lambda_3)-(\lambda_2^{(i)}+\lambda_3^{(i)})\right\}=0
\end{aligned}\tag{26}$$

where $\varepsilon=(m^{(i)}-m)/m$, λ_1 is the symmetric stretching frequency, λ_2 is the degenerate asymmetric stretching frequency, and λ_3 is the degenerate bending frequency. $\lambda_2^{(i)}$ and $\lambda_3^{(i)}$ are the corresponding frequencies for the isotopic molecule. If m is in atomic mass units, and $\lambda_i=5.8894\times10^{-2}\,\nu_i^2$ (ν_i is the observed frequency in cm^{-1}) then the F's are in units of dynes/cm. The λ's should be the zero order frequencies, and if these are available, then the equations constitute an exact determination of the molecular force constants.

The valence force constants are given by

$$\left.\begin{aligned}
f_r&=\frac{1}{3}(F_{11}+2F_{44}), &\quad f'_{r\alpha}-f_{r\alpha}&=F_{23}\\
f_{rr}&=\frac{1}{3}(F_{11}-F_{44}), &\quad f_\alpha-f_{\alpha\alpha}&=F_{55}
\end{aligned}\right\}\tag{27}$$

A number of sets of force constants available in the literature have recently been tabulated by Duncan[8] and consequently no summary of these calculations will be given in this paper. Various sets of observed frequencies are also available.[7,9,10] The frequencies used to compute the mixing parameters and force constants are listed in Table I. These sets were selected on the basis of reproducing results of other experiments on "perturbed systems" derived from the BX_3 molecules.[11] Selection of the mixing parameters from the two solutions of Eq. 26 was also made on this basis. Results for two sets of frequencies for the same molecule, BBr_3, are included to illustrate the effect of small changes in frequencies on the values of the force constants.

The results are shown in Table II. Calculations were made for $^{10}BY_3$ as the unperturbed molecule. Starting with the ^{11}B-species leads to slightly different values, due to anharmonicities. The force constants are quoted to five places only for comparison with those calculated in Ref. 3 for identical frequencies, which are also listed in Table I. The differences between our values and those of Ladd, Orville-Thomas, and Cox[3] are rather large. Small changes in F_{22} and F_{33} require a large change in F_{23}. This illustrates the inherent numeralogical difficulty of dealing with the non-linear equations. Inspection of the results for two different sets of input frequencies for BBr_3 emphasizes this point even more strongly. Thus, while it is possible, using the Green's function, to obtain a high degree of internal consistency, the force constants should in reality be considered known to, at most, two significant figures. The reason for the large variation in force constants with a small change in frequencies becomes apparent on inspection of Eq. 26: the mixing parameter is critically dependent on a small number, which is the difference between two large numbers.

Conclusions

Using the Green's function approach to analyze the dynamics of molecular systems, we have obtained explicit expressions for the force constants of XY_3 planar molecules. Application of these formulae is quite simple and extremely convenient. It is important to point out that the variation in the force constants with the frequencies can be studied quite simply from Eqs. 24 and 26. For example, if a range of values is specified for the XY_3 and $XY_3^{(i)}$ vibrational frequencies then the corresponding range in the mixing parameter can be determined from Eq. 26. This range in the mixing parameter then determines the range of values for the force constants by use of Eq. 24.

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8) J. L. Duncan, *J. Mol. Spectroscopy*, **13**, 338 (1964).

9) C. W. F. T. Pistorius, *J. Chem. Phys.*, **29**, 1174 (1958).

10) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York (1963), p. 90.

11) See VAII for results on BCl_3-$HBCl_2$. Also, we have carried out calculations on a series of mixed boron halides, and on $HBBr_2$ and HBF_2 which have subsequently been prepared and observed (L. Lynds). The results of these experiments and calculations will be reported at a later date.