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Internal Coordinate Green's Function Analysis of Molecular Vibrations with Application to XY_2Z Planar Molecules

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The Green's function formalism for the analysis of molecular vibrations has been formulated for the internal or valence coordinate system. A general procedure for calculating isotopic frequencies and changes in force constants associated with the characterization of a perturbed molecule in terms of the unperturbed molecule is developed. It is shown that the internal molecular Green's function can be constructed from the vibrational frequencies of the unperturbed molecule. Application is made to the XY_2Z planar molecule. Exact formulae for the $XY_2Y^{(i)}$ molecule are obtained. The shifts in the frequencies of an XY_2Z planar molecule due to mass and bond length changes are obtained. It is shown that the A_1 modes are unaffected by a change in the X–Z bond length while the B_1 modes move to higher frequencies as the bond distance decreases. An explicit expression for the change in the valence bond bending force constant, f_α, is obtained as an example of how force constant changes can be studied by means of the Green's function procedure. Qualitative results for $HBCl_2$ and $HBBr_2$ are obtained which indicate that f_α decreases in going from $BCl_3 \rightarrow HBCl_2$.

The purpose of this paper is to develop a well defined and exact procedure for relating the vibrational properties of similar molecules. The use of the Green's function procedure to obtain frequencies of isotopic molecules and approximate frequencies for $HBCl_2$ has been described in previous papers;[1-3] (hereafter referred to as VAI–III).

In these previous papers the Green's function procedure was developed for use in the cartesian coordinate system. The cartesian coordinate representation is reasonably convenient for treating the isotope problem but completely unsuited for introducing geometry changes. The Wilson FG representation appears to be the most convenient representation for formulating the general problem of relating the dynamics of similar molecules. For example, since the $\boldsymbol{G}$ matrix contains the geometry and masses of the molecule, changes in these parameters are conveniently handled by introducing a change in the $\boldsymbol{G}$ matrix, $\Delta\boldsymbol{G}$. It is also desirable to be able to separate the effects of force constant changes from these other effects. The essential idea of the approach may be illustrated as follows. Consider the problem of determining the force field of $HBCl_2$. One has at one's disposal the observed fundamental frequencies of $HBCl_2$ as well as those of BCl_3 and its isotopes. Using the Green's function formulae for isotopic substitution $XY_3 \rightarrow X^{(i)}Y_3$ one can determine the Green's function for BCl_3 as was demonstrated in a previous paper.[2] The first step in the analysis of $HBCl_2$ is to treat this molecule as if it possessed the same force field as BCl_3 and differed from BCl_3 only in that the hydrogen mass has replaced the chlorine mass and that the B–H bond length may be different from the B–Cl bond. The frequencies of this fictitious molecule, the mass-geometry shifted frequenceis, may be easily calculated using the Green's function procedure. These fictitious frequencies may be compared with the actual observed frequencies and the differences attributed entirely to changes in the Wilson $\boldsymbol{F}$ matrix. The point here is that two different molecules with identical $\boldsymbol{F}$ matrices will have different vibrational frequencies because of mass and geometry differences. The fictitious frequencies are corrected for these effects and comparison of these frequencies with the observed frequencies gives immediately a qualitative measure of the changes in the force constants. The last step in the analysis is to obtain by use of the Green's function method the change in force constants directly from the observed frequencies. This step-by-step analysis allows one to make maximum use of the similarity between the two systems. It should be pointed out here that the idea of using knowledge about one molecule to calculate the properties of another is not new. Previous techniques[4] which have been suggested, however, are perturbation schemes and depend upon the smallness of the off diagonal matrix elements. The Green's function procedure, on the other hand, is formally exact and imposes no such restrictions. A similar procedure has also been developed by the Uppsala Quantum Chemistry Group[5] for the study of molecular wave functions. In this paper we develop the Green's function approach for the internal or valence coordinate system. One advantage of this system is, of course, that one avoids the necessity of constructing the rotation and translation eigenvectors. Furthermore, correlation of molecules with different geometries appears to be most conveniently treated in the internal coordinate system because the geometry is contained explicitly in the Wilson $\boldsymbol{G}$ matrix.

In section I, the Green's function formalism is developed in the internal coordinate system for both the GF and FG representation. The analysis is oriented towards either calculating the frequencies of isotopic molecules or the force constants changes which characterize a new species.

By making extensive use of the spectral theorem for the dynamical matrix, and the transformation between internal and cartesian coordinates, it is shown in section II that the Green's function for the internal coordinates can be constructed directly from the "unperturbed" vibrational frequencies without a knowledge of the molecular force constants.

In section III the procedure is applied to the XY_2Z planar molecule. The frequencies of this molecule differ from those of the XY_3 molecule because of changes in mass, geometry and force constants. Explicit formulas for the mass and geometry corrected frequencies of an XY_2Z molecule whose X–Z bond length differs from the X–Y bond length of the XY_3 molecule are obtained. It is shown that this bond length change affects only the B_1 type vibrational modes and that the resulting frequency shifts can be quite large when the mass of the Z atom is much less than that of the Y atom. An explicit expression for studying the change in the valence bond-bending force constants, f_α, which includes the effects of changes in mass and X–Y bond length is derived. Using an X–Z bond length of 1.20 Å for $HBCl_2$ one arrives at the qualitative result that the bond bending force constant, f_α, is decreased on the order of 20% on going from BCl_3 to $HBCl_2$.

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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] T. Wolfram, C. D. Bass, R. E. DeWames and L. Lynds, This Bulletin, **39**, 201 (1966).

[4] W. H. Edgell and T. R. Riethof, *J. Phys. Chem.*, **56**, 326 (1952).

[5] See for example, J. E. Harriman, Scientific Report No. 19. Quantum Chemistry Group, University of Uppsala Uppsala Sweden. Also see, P. O. Löwdin, *J. Math. Phys.*, **3**, 969 (1961).

I. Internal Coordinate Green's Functions

In this section the Green's function formalism is developed in the internal or valence coordinate system from which the vibrational frequencies of a "perturbed" molecule can be obtained exactly in terms of the vibrational frequencies of the "unperturbed" molecule. The "perturbed" and "unperturbed" molecules are any two molecules whose internal coordinates can be set in a one to one correspondence. The utility of the approach is greatly enhanced when the two molecules whose vibrational properties are to be correlated are, in addition, physically similar. For example, if $^{10}B^{35}Cl_3$ is considered to be the "unperturbed" molecule, then the isotopes $^{11}B^{35}Cl_3$ and $^{10}B^{35}Cl_2{}^{37}Cl$ or the new species $H^{10}B^{35}Cl_2$ and $D^{10}B^{35}Cl_2$ may be selected as "perturbed" molecules.

The unperturbed molecule's vibrational frequencies are (in the internal symmetry coordinate system) determined, according to the Wilson procedure, by the secular matrix equation

$$(\boldsymbol{G}_0\boldsymbol{F}_0-\lambda)\boldsymbol{R}=0 \tag{1}$$

or

$$(\boldsymbol{F}_0\boldsymbol{G}_0-\lambda)\boldsymbol{G}_0{}^{-1}\boldsymbol{R}=0 \tag{2}$$

where $\boldsymbol{G}_0$ and $\boldsymbol{F}_0$ are the reduced Wilson $\boldsymbol{G}$ and $\boldsymbol{F}$ matrices for the unperturbed molecule. (The redundant coordinates are omitted) λ is the square of the angular frequency, $\boldsymbol{\omega}$ and $\boldsymbol{R}$ symbolize the internal symmetry coordinate vectors. Equation 2, of course, can be obtained from Eq. 1 by a similarity transformation with the matrix $\boldsymbol{G}_0$. The secular equation for the perturbed molecule is

$$\{(\boldsymbol{G}_0+\Delta\boldsymbol{G})(\boldsymbol{F}_0+\Delta\boldsymbol{F})-\lambda\}\boldsymbol{R}=0 \tag{3}$$

or

$$\{(\boldsymbol{F}_0+\Delta\boldsymbol{F})(\boldsymbol{G}_0+\Delta\boldsymbol{G})-\lambda\}\boldsymbol{G}_0{}^{-1}\boldsymbol{R}=0 \tag{4}$$

where $\boldsymbol{G}_p=\boldsymbol{G}_0+\Delta\boldsymbol{G}$ is the $\boldsymbol{G}$ matrix for the perturbed molecule. The $\Delta\boldsymbol{G}$ matrix accounts for changes in mass and geometry in going from the unperturbed to the perturbed system and $\Delta\boldsymbol{F}$ accounts for the force constant differences.

1. Isotope Case, $\Delta\boldsymbol{F}=0$.—When the perturbed molecule is an isotope of the initial molecule so that $\Delta\boldsymbol{F}=0$ we have for Eqs. 3 and 4

$$(\boldsymbol{G}_0\boldsymbol{F}_0-\lambda+\Delta\boldsymbol{G}\boldsymbol{F}_0)\boldsymbol{R}=0 \tag{5}$$

or

$$(\boldsymbol{F}_0\boldsymbol{G}_0-\lambda+\boldsymbol{F}_0\Delta\boldsymbol{G})\boldsymbol{G}_p{}^{-1}\boldsymbol{R}=0 \tag{6}$$

The eigenvalues are obtained by requiring the determinant to vanish. By factoring out $(\lambda-\boldsymbol{G}_0\boldsymbol{F}_0)$ from Eq. 5 we obtain the secular equations

$$|\boldsymbol{I}-\boldsymbol{J}_0(\lambda)\Delta\boldsymbol{G}\boldsymbol{F}_0|=0 \tag{7}$$

and

$$|\boldsymbol{J}_0{}^{-1}(\lambda)|=0 \tag{8}$$

where

$$\boldsymbol{J}_0(\lambda)=(\lambda-\boldsymbol{G}_0\boldsymbol{F}_0)^{-1}$$

is the Green's function for the unperturbed molecule and $\boldsymbol{I}$ is a unit matrix. Equation 8 gives the frequencies for the unperturbed molecule and Eq. 7 determines the isotopically shifted frequencies. Similarly we obtain from Eq. 6 the secular determinants

$$|\boldsymbol{I}-\boldsymbol{L}_0(\lambda)\boldsymbol{F}_0\Delta\boldsymbol{G}|=0 \tag{9}$$

$$|\boldsymbol{L}_0(\lambda)^{-1}|=0 \tag{10}$$

where

$$\boldsymbol{L}_0(\lambda)=(\lambda-\boldsymbol{F}_0\boldsymbol{G}_0)^{-1}=\boldsymbol{G}_0{}^{-1}\boldsymbol{J}_0(\lambda)\boldsymbol{G}_0 \tag{11}$$

Equation 9 is preferred to Eq. 7 when the $\Delta\boldsymbol{G}$ matrix is dimensionally smaller than $\boldsymbol{F}_0$ since Eq. 9 is truncated to the size of $\Delta\boldsymbol{G}$. Both Eqs. 7 and 9 can also be applied to the case in which geometry changes are considered. The utility of these equations obviously depends upon the elimination of the matrix $\boldsymbol{F}_0$. We shall show in the next section that the $\boldsymbol{F}_0$ matrix can, by making use of the spectral theorem, be replaced by a matrix involving the unperturbed vibrational frequencies.

All of the matrices involved are block diagonal according to the irreducible representation of the unperturbed molecule except for $\Delta\boldsymbol{G}$ which is block diagonalized according to the perturbed symmetry. Consequently, Eqs. 7 and 9 hold for each perturbed symmetry type, Γ,

$$|\boldsymbol{I}-\boldsymbol{J}_0{}^{\Gamma}(\lambda)\Delta\boldsymbol{G}^{\Gamma}\boldsymbol{F}_0{}^{\Gamma}|=0 \tag{7a}$$

or

$$|\boldsymbol{I}-\boldsymbol{L}_0{}^{\Gamma}(\lambda)\boldsymbol{F}_0{}^{\Gamma}\Delta\boldsymbol{G}^{\Gamma}|=0 \tag{9a}$$

where the superscript Γ refers to the Γ-type block of the matrices. $\boldsymbol{F}_0{}^{\Gamma}$, for example, contains those symmetry blocks of $\boldsymbol{F}_0$ which are coupled by $\Delta\boldsymbol{G}^{\Gamma}$ and gives rise to the Γ block of the perturbed symmetry. In subsequent equations it is to be assumed that an equivalent equation holds for each perturbed symmetry type.

2. General Case.—In the most general case both $\Delta\boldsymbol{F}$ and $\Delta\boldsymbol{G}$ are non-vanishing. One then obtains the determinantal equations

$$|\boldsymbol{I}-\boldsymbol{J}_p(\lambda)\boldsymbol{G}_p\Delta\boldsymbol{F}|=0 \tag{12}$$

$$|\boldsymbol{J}_p{}^{-1}(\lambda)|=0 \tag{13}$$

where

$$\boldsymbol{J}_p(\lambda)=(\lambda-\boldsymbol{G}_p\boldsymbol{F}_0)^{-1} \tag{14}$$

The matrix $\boldsymbol{J}_p(\lambda)$ is evidently the Green's function for a fictitious molecule having the geometry and mass of the perturbed molecule and the force constants of the unperturbed molecule. The eigenvalues of Eq. 12 are the vibrational frequencies of the perturbed molecule which are affected by $\Delta\boldsymbol{F}$ as well as $\Delta\boldsymbol{G}$. In the circumstance that a frequency is unaffected by $\Delta\boldsymbol{F}$ but shifted by $\Delta\boldsymbol{G}$ then this eigenvalue will be determined by Eq. 13.

(In section II we show that $\boldsymbol{J}_p(\lambda)$ can be obtained from $\boldsymbol{J}_0(\lambda)$. We can also obtain from Eq. 2

$$\boldsymbol{K}_p(\lambda)^{-1}[\boldsymbol{I}-\boldsymbol{K}_p(\lambda)(\boldsymbol{F}_0+\Delta\boldsymbol{F})\Delta\boldsymbol{G}]=0 \qquad (15)$$

where

$$\boldsymbol{K}_p(\lambda)=[\lambda-(\boldsymbol{F}_0+\Delta\boldsymbol{F})\boldsymbol{G}_0]^{-1} \qquad (16)$$

which leads to the determinants

$$|\boldsymbol{I}-\boldsymbol{K}_p(\lambda)(\boldsymbol{F}_0+\Delta\boldsymbol{F})\Delta\boldsymbol{G}|=0 \qquad (17)$$

and

$$|\boldsymbol{K}_p(\lambda)^{-1}|=0 \qquad (18)$$

Equation 18 gives the eigenvalues of a fictitious molecule with the perturbed molecule force constants and the geometry and mass of the unperturbed molecule, and Eq. 17 gives the perturbed molecular frequencies. This form of the secular equation is convenient when $\Delta\boldsymbol{G}$ truncates the matrix to a small dimension, or in the case that one makes a power series expansion of $\boldsymbol{K}_p(\lambda)$ for small $\Delta\boldsymbol{F}$.

A calculation of the force constant changes, $\Delta\boldsymbol{F}$, associated with the characterization of the new species XY_2Z may be made by using either Eq. 12 or 17. The matrix elements of $\Delta\boldsymbol{F}$ appear as parameters in the equations and if the perturbed frequencies are known then $\Delta\boldsymbol{F}$ may be determined. The frequencies of any isotope of the perturbed XY_2Z molecule can be utilized to give additiona equations for the $\Delta\boldsymbol{F}$ matrix elements. In Eq. 17 one simply substitutes $\Delta\boldsymbol{G}+\Delta\boldsymbol{G}_p$(isotope) for $\Delta\boldsymbol{G}$ where

$$\Delta\boldsymbol{G}_p(\text{isotope})=\boldsymbol{G}_p(\text{isotope})-\boldsymbol{G}_p \qquad (19)$$

In Eq. 12 one must use the new Green's function

$$\begin{aligned}\boldsymbol{J}_p(\lambda)(\text{isotope})&=(\lambda-\boldsymbol{G}_p(\text{isotope})\boldsymbol{F}_0)^{-1}\\&=(\boldsymbol{I}-\boldsymbol{J}_p(\lambda)\Delta\boldsymbol{G}_p(\text{isotope})\boldsymbol{F}_0)^{-1}\boldsymbol{J}_p(\lambda)\end{aligned} \qquad (20)$$

II. Construction of Green's Functions

In this section we show how the Green's functions $\boldsymbol{J}_0(\lambda)$, $\boldsymbol{J}_p(\lambda)$, $\boldsymbol{L}_0(\lambda)$, and $\boldsymbol{K}_p(\lambda)$ can be constructed starting from the spectral representation. It was shown in VAIII³⁾ that the vibrational part of the dynamical matrix in the cartesian symmetry representation, $\boldsymbol{D}^s$, was related to the Wilson reduced force constant matrix $\boldsymbol{F}$ by the congruent transformation

$$\tilde{\boldsymbol{B}}\boldsymbol{F}\boldsymbol{B}=\boldsymbol{D}^s \qquad (21)$$

and that

$$\boldsymbol{B}\tilde{\boldsymbol{B}}=\boldsymbol{G} \qquad (22)$$

where

$$\boldsymbol{B}=\boldsymbol{T}\boldsymbol{M}^{-1/2}\boldsymbol{S} \qquad (23)$$

and $\tilde{\boldsymbol{B}}$ is the transpose of $\boldsymbol{B}$. $\boldsymbol{T}$ is the transformation from the internal symmetry coordinates to the cartesian coordinates, $\boldsymbol{M}$ is the diagonal mass matrix and $\boldsymbol{S}$ is the transformation from the cartesian coordinates to the orthonormal mass weighted cartesian vibrational symmetry coordinates.

The matrix $\boldsymbol{D}^s$ has the square of the angular vibrational frequencies, λ_i, for its eigenvalues and is diagonalized by the unitary matrix $\boldsymbol{A}$

$$\boldsymbol{A}^+\boldsymbol{D}^s\boldsymbol{A}=\Lambda \qquad (24)$$

$$\Lambda_{ij}=0 \quad i\neq j \qquad (25)$$

$$\Lambda_{ii}=\lambda_i \qquad (26)$$

where $\boldsymbol{A}^+$ is the Hermetian conjugate of $\boldsymbol{A}$. The matrix $\boldsymbol{A}$ is the matrix of mixing parameters discussed in previous papers,¹⁻³⁾ where it was shown that $\boldsymbol{A}$ can be determined directly from isotope data on the XY_3 molecule. Making use of the above equations one finds that

$$\boldsymbol{F}_0=\tilde{\boldsymbol{H}}^{-1}\Lambda\boldsymbol{H}^{-1} \qquad (27)$$

$$\boldsymbol{G}_0\boldsymbol{F}_0=\boldsymbol{H}\Lambda\boldsymbol{H}^{-1} \qquad (28)$$

and

$$\boldsymbol{F}_0\boldsymbol{G}_0=\tilde{\boldsymbol{H}}^{-1}\Lambda\tilde{\boldsymbol{H}} \qquad (29)$$

where

$$\boldsymbol{H}=\boldsymbol{B}\boldsymbol{A} \qquad (30)$$

Thus,

$$\boldsymbol{J}_0(\lambda)=\boldsymbol{H}(\lambda-\Lambda)^{-1}\boldsymbol{H}^{-1} \qquad (31)$$

and

$$\boldsymbol{L}_0(\lambda)=\tilde{\boldsymbol{H}}^{-1}(\lambda-\Lambda)^{-1}\tilde{\boldsymbol{H}}=\tilde{\boldsymbol{J}}_0(\lambda) \qquad (32)$$

Thus we see that $\boldsymbol{J}_0$ and $\boldsymbol{L}_0$ can be constructed from the unperturbed vibrational frequencies and the mixing parameters. The mixing parameters can be obtained from isotope data as discussed in VAI¹⁾ and II²⁾ or from Coriolis and centrifugal distortion constants.⁶⁾ From Fq. 31 it is clear that $\boldsymbol{J}_0(\lambda)$ is just the internal coordinate representation of the vibrational part of the cartesian symmetry coordinate Green's function $\boldsymbol{D}^s$ discussed in VAIII.³⁾

It should be pointed out again that all of the above equations hold for each of the symmetry types, Γ.

The matrix $\boldsymbol{J}_p(\lambda)$ can be constructed directly with the result that

$$\boldsymbol{J}_p(\lambda)=\boldsymbol{H}(\lambda-(\boldsymbol{I}+\Delta\boldsymbol{G}_t)\Lambda)^{-1}\boldsymbol{H}^{-1} \qquad (33)$$

where $\Delta\boldsymbol{G}_t$ is the transformed $\Delta\boldsymbol{G}$ matrix

$$\Delta\boldsymbol{G}_t=\boldsymbol{H}^{-1}\Delta\boldsymbol{G}\tilde{\boldsymbol{H}}^{-1} \qquad (34)$$

We may also construct $\boldsymbol{J}_p(\lambda)$ from $\boldsymbol{J}_0(\lambda)$ since

$$\boldsymbol{J}_p(\lambda)=[\boldsymbol{I}-\boldsymbol{J}_0(\lambda)\Delta\boldsymbol{G}\tilde{\boldsymbol{H}}^{-1}\Lambda\boldsymbol{H}^{-1}]^{-1}\boldsymbol{J}_0(\lambda) \qquad (35)$$

Similarly for $\boldsymbol{K}_p(\lambda)$ we obtain,

$$\boldsymbol{K}_p(\lambda)=\tilde{\boldsymbol{H}}^{-1}(\lambda-\Lambda-\Delta\boldsymbol{F}_t)^{-1}\tilde{\boldsymbol{H}} \qquad (36)$$

where $\Delta\boldsymbol{F}_t$ is the transformed $\Delta\boldsymbol{F}$ matrix

$$\Delta\boldsymbol{F}_t=\tilde{\boldsymbol{H}}\Delta\boldsymbol{F}\boldsymbol{H} \qquad (37)$$

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6) J. S. Margolis and C. D. Bass, *J. Chem. Phys.*, **40**, 1590 (1964).

$\boldsymbol{K}_p$ may also be written in terms of $\boldsymbol{L}_0$,

$$\boldsymbol{K}_p(\lambda)=[\boldsymbol{I}-\boldsymbol{L}_0(\lambda)\varDelta\boldsymbol{F}\boldsymbol{G}_0]^{-1}\boldsymbol{L}_0(\lambda) \tag{38}$$

It is important to realize that in all cases the $\boldsymbol{H}$ matrix refers to the unperturbed molecule and one never needs the $\boldsymbol{H}$ matrix for the perturbed molecule.

III. Application to XY_2Z Planar Molecules

In this section, as an example, we apply the Green's function formalism developed in the preceding sections to the problem of the in-plane vibrational frequencies of the XY_2Z planar molecule. In determining the force constant changes, $\varDelta\boldsymbol{F}$, associated with the characterization of the XY_3Z molecule in terms of the corresponding XY_3 molecule it is important to first calculate the frequency shifts due to changes in mass and geometry. These mass-geometry corrected frequencies can then be compared with the observed XY_2Z frequencies and the differences attributed to pure force constant changes. We consider in this section the problem of obtaining the mass-geometry corrected frequencies of XY_2Z planar molecules whose X–Z bond length differs from the X–Y bond length of the unperturbed XY_3 molecule. This situation arises in connection with the analysis of the dihaloboranes in terms of the parent boron trihalide. For example, $HBCl_2$ has the same 120° bond angles as BCl_3 but the H–B bond length is believed to be smaller than the B–Cl bond length.7) The same circumstance obtains in the case of $HBBr_2$.

The internal coordinates and $\boldsymbol{G}$ matrix for an XY_2Z planar molecule with 120° bond angles has been discussed by Lindeman and Wilson.8) The internal coordinates used in VAIII3) are the same as those discussed by Lindeman and Wilson except that the angular coordinates are multiplied by the X–Y bond distance. Following this convention the $\varDelta\boldsymbol{G}$ matrix elements associated with the characterization of the XY_2Z planar molecule are given by

$$\varDelta G_{11}=\frac{1}{3}\varDelta\mu$$

$$\varDelta G_{12}=\frac{\sqrt{2}}{3}\varDelta\mu$$

$$\varDelta G_{22}=\frac{2}{3}\varDelta\mu$$

$$\varDelta G_{45}=\sqrt{3}\,\varDelta l\mu_x$$

$$\varDelta G_{55}=2\varDelta\mu+2\varDelta l[\mu_z(\varDelta l+2)+\mu_x(\varDelta l+3)]$$

$$\varDelta\mu=\mu_z-\mu_y$$

$$\varDelta l=(l-l')/l'$$

where μ_α is the reciprocal of the αth atom's mass, l is the X–Y bond length and l' is the Z–X bond length. All other $\varDelta\boldsymbol{G}$ matrix elements vanish. It is evident that the A_1 modes are independent of the geometry change since the A_1 part of $\varDelta\boldsymbol{G}$ (the upper 3×3) involves only mass changes. The $\varDelta G_{45}$ matrix elements involve only pure geometry effects while $\varDelta G_{55}$ contains both mass and geometry effects.

1. A_1 Modes.—In order to calculate the A_1 vibrational frequencies we solve the secular determinant given by Eq. 9

$$|\boldsymbol{I}-\boldsymbol{Z}|=0 \tag{40}$$

where

$$\boldsymbol{Z}=[\boldsymbol{L}_0(\lambda)\boldsymbol{F}_0\varDelta\boldsymbol{G}]_{A_1} \tag{41}$$

The subscript refers to the A_1 block; the upper 3×3 matrix. It is convenient to transform Eq. 40 to a representation in which $\varDelta G$ is diagonal

$$|\boldsymbol{I}-\boldsymbol{U}^{+}\boldsymbol{Z}\boldsymbol{U}|=0 \tag{40a}$$

where

$$\boldsymbol{U}=\frac{1}{\sqrt{3}}\begin{pmatrix} 1 & \sqrt{2} & 0 \\ \sqrt{2} & -1 & 0 \\ 0 & 0 & \sqrt{3} \end{pmatrix} \tag{42}$$

In this representation $\varDelta\boldsymbol{G}$ assumes the simple form

$$\boldsymbol{U}^{+}\varDelta\boldsymbol{G}\boldsymbol{U}=\begin{pmatrix} \varDelta\mu & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{43}$$

so that Eq. 40a reduces to a 1×1 transcendental determinant

$$1-\{\boldsymbol{U}^{+}\boldsymbol{L}_0(\lambda)\boldsymbol{F}_0\boldsymbol{U}\}_{11}\varDelta\mu=0 \tag{44}$$

where $\{\ \}_{11}$ is the $1-1$ matrix element. Thus we need only a single matrix element to determine the A_1 isotope frequencies. Using Eqs. 27 and 32 we find that

$$\begin{aligned}\{\boldsymbol{U}^{+}\boldsymbol{L}_0(\lambda)\boldsymbol{F}_0\boldsymbol{U}\}_{11} &= \{\boldsymbol{U}^{+}\tilde{\boldsymbol{H}}^{-1}[\varLambda(\lambda-\varLambda)^{-1}]\boldsymbol{H}^{-1}\boldsymbol{U}\}_{11} \\ &= \{\boldsymbol{U}^{+}{}_1,\tilde{\boldsymbol{H}}^{-1}[\varLambda(\lambda-\varLambda)^{-1}]\boldsymbol{H}^{-1}\boldsymbol{U}_1\}\end{aligned} \tag{45}$$

One need only calculate the inner product given by Eq. 45 where $\boldsymbol{U}_1$ is the first column of $\boldsymbol{U}$ and $\boldsymbol{U}^{+}{}_1$ is the first row of $\boldsymbol{U}^{+}$. The matrices $\boldsymbol{A}$ and $\boldsymbol{B}$ are given in VAIII3) and their product, $\boldsymbol{H}$, is

$$\boldsymbol{H}=\boldsymbol{B}\boldsymbol{A}=\begin{pmatrix} (BA)_{A_1} & 0 \\ 0 & (BA)_{B_1} \end{pmatrix} \tag{46}$$

where

$$(BA)_{B_1}=\frac{\mu_y{}^{1/2}}{\sqrt{2}A_0d_2}\begin{pmatrix} (2d_1-3r^2a) & -(3r^2+2ad_1) \\ -\sqrt{3}\,d_2{}^2a & -\sqrt{3}\,d_2{}^2 \end{pmatrix} \tag{47}$$

and

$$(BA)_{A_1}=\begin{pmatrix} \mu_y{}^{+1/2} & 0 \\ 0 & (BA)_{B_1} \end{pmatrix} \tag{48}$$

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7) L. Lynds and C. D. Bass, ibid., **40,** 1590 (1964).

8) P. Lindeman and M. K. Wilson, ibid., **24,** 242 (1956).

where

$$\left.\begin{aligned} d_1^2&=1+3r^2\\ d_2^2&=2+3r^2\\ r^2&=m_y/m_x\\ A_0^2&=1+a^2 \end{aligned}\right\} \tag{49}$$

$$a=\text{mixing parameter}$$

Equation 45 leads to the following equations for mass shifted A_1 frequencies of the XY_2Z molecule,

$$\lambda_1{}^p\lambda_2{}^p\lambda_3{}^p=\lambda_1\lambda_2\lambda_3\left\{1+\frac{\Delta\mu}{3\mu}\left(1+\frac{d_2^2}{d_1^2}\right)\right\}, \tag{50}$$

$$\begin{aligned}\lambda_1{}^p\lambda_2{}^p+\lambda_1{}^p\lambda_3{}^p+\lambda_2{}^p\lambda_3{}^p&=\lambda_1\lambda_2+\lambda_1\lambda_3+\lambda_2\lambda_3\\ &+\frac{\Delta\mu}{3\mu_y}\left\{\lambda_1(\lambda_2+\lambda_3)+\frac{d_2^2\lambda_1}{d_1^2A_0^2}(\lambda_2+a^2\lambda_3)\right.\\ &\left.+\frac{d_2^2}{d_1^2}\lambda_2\lambda_3\right\}\end{aligned} \tag{51}$$

$$\begin{aligned}\lambda_1{}^p+\lambda_2{}^p+\lambda_3{}^p&=\lambda_1+\lambda_2+\lambda_3\\ &+\frac{\Delta\mu}{3\mu_y}\left\{\lambda_1+\frac{d_2^2}{d_1^2A_0^2}(\lambda_2+a^2\lambda_3)\right\}\end{aligned} \tag{52}$$

where the λ^p are the square of the XY_2Z A_1 angular frequencies. λ_1 refers to the A_1 totally symmetric mode of the XY_3 molecule and λ_2 and λ_3 refer to the E′ modes of the XY_3 molecule. Equations 50—52 were derived in VAII[2)] using the cartesian coordinate Green's function and are exact for the isotopic case $Z \rightarrow Y^{(i)}$.

2. B_1 Modes.—The mass and geometry corrected B_1 modes may be easily calculated from Eq. 7 which takes the form

$$|\boldsymbol{I}-\boldsymbol{Z}|=0 \tag{53}$$

$$\boldsymbol{Z}=[\boldsymbol{J}_0(\lambda)\Delta\boldsymbol{G}\boldsymbol{F}_0]_{B1} \tag{54}$$

It is convenient to proceed from the relation (for a 2×2 matrix)

$$|\boldsymbol{I}-\boldsymbol{Z}|=1+|\boldsymbol{Z}|-\mathrm{Tr}\boldsymbol{Z} \tag{55}$$

since the determinant of Z can be written down by inspection,

$$\begin{aligned}|\boldsymbol{Z}|&=\frac{|\boldsymbol{J}_0(\lambda)||\boldsymbol{G}_0\boldsymbol{F}_0||\Delta\boldsymbol{G}|}{|\boldsymbol{G}_0|}\\ &=\left[\frac{1}{(\lambda-\lambda_4)(\lambda-\lambda_5)}\right]\frac{(\lambda_4\lambda_5)(-3\Delta l\mu_x{}^2)}{3\mu_y(\mu_y+3\mu_x)}\end{aligned} \tag{56}$$

The trace of Z is given by

$$\begin{aligned}\mathrm{Tr}\boldsymbol{Z}&=\mathrm{Tr}(\boldsymbol{J}_0(\lambda)\Delta\boldsymbol{G}\boldsymbol{F}_0)=\mathrm{Tr}(\boldsymbol{F}_0\boldsymbol{J}_0(\lambda)\Delta\boldsymbol{G})\\ &=\frac{\lambda_4}{\lambda-\lambda_4}(\Delta\boldsymbol{G}_t)_{44}+\frac{\lambda_5}{\lambda-\lambda_5}(\Delta\boldsymbol{G}_t)_{55}\end{aligned} \tag{57}$$

where $\Delta\boldsymbol{G}_t$ is given by Eq. 34.

Equation 55 gives rise to the following set of equations for the mass-geometry corrected B_1 frequencies of the XY_2Z molecule,

$$\begin{aligned}\lambda_4{}^p\lambda_5{}^p=\lambda_4\lambda_5\Biggl\{1&-\frac{3\Delta l\mu_x}{\mu_yd_1^2}\left(\frac{\Delta l\mu_x}{3\mu_y}+r^2\right)\\ &+\frac{(\beta+2\Delta\mu)}{6\mu_yd_1^2}d_2^2\Biggr\}\end{aligned} \tag{58}$$

$$\begin{aligned}\lambda_4{}^p+\lambda_5{}^p&=(\lambda_4+\lambda_5)\\ &+\frac{\lambda_4}{\mu_yA_0^2}\left[\frac{-\sqrt{2}\,\alpha d_2}{d_1}+(\beta+2\Delta\mu)\right.\\ &\left.\times\left(\frac{\sqrt{6}\,a}{3d_2}+\frac{3r^2}{\sqrt{6}\,d_1d_2}\right)\right]\left[\frac{\sqrt{6}\,a}{3d_2}+\frac{3r^2}{\sqrt{6}\,d_1d_2}\right]\\ &+\frac{\lambda_5}{\mu_yA_0^2}\left[-\frac{\sqrt{2}\,\alpha d_2}{d_1}+(\beta+2\Delta\mu)\right.\\ &\left.\times\left(\frac{-\sqrt{6}}{3d_2}+\frac{3r^2a}{\sqrt{6}\,d_1d_2}\right)\right]\left[\frac{-\sqrt{6}}{3d_2}+\frac{3r^2a}{\sqrt{6}\,d_1d_2}\right]\end{aligned} \tag{59}$$

where

$$\alpha=\sqrt{3}\,\Delta l\mu_x \tag{60}$$

and

$$\beta=2\Delta l[\mu_z(\Delta l+2)+\mu_x(\Delta l+3)] \tag{61}$$

In the above equations $\lambda_4{}^p$ and $\lambda_5{}^p$ are the mass-geometry corrected B_1 eigenvalues of the XY_2Z molecule while λ_4 and λ_5 ($\lambda_4=\lambda_2$, $\lambda_5=\lambda_3$) are the E′ eigenvalues of the XY_3 molecule.

When $\Delta l=0$ Eqs. 58 and 59 reduce to the exact isotopic equations given in VAII[2)] for $XY_2Y^{(i)}$. Positive (negative) Δl has an effect similar to decreasing (increasing) the molecular mass so that the geometry shift is towards higher (lower) frequencies. Furthermore, if μ_z is much larger than either μ_x or μ_y then the term with β will dominate the geometry dependent terms. In the case of the dihaloboranes this effect is comparable to the pure isotope or mass shift and explicit results will be published in a subsequent paper.

3. Example of Force Constant, Mass and Geometry Change.—As an example of how the force constant changes can be studied by means of the Green's function procedure let us consider the XY_2Z planar molecule treated in the preceding section in which the valence force constant f_α differs from that of the XY_3 unperturbed molecule. Knowing the XY_3 and XY_2Z vibrational frequencies we wish to calculate *directly* the change in f_α. We use Eq. 12 for this calculation. The bond bending constant f_α affects only the B_1 modes and ΔF is given by

$$\left.\begin{aligned}(\Delta F)_{44}&=0\\ (\Delta F)_{45}&=0\\ (\Delta F)_{55}&=2\Delta f_\alpha\end{aligned}\right. \tag{62}$$

and Eq. 12 can be rewritten in the simple form

$$\Delta f_\alpha=\frac{1}{2\{\boldsymbol{J}_p(\lambda)\boldsymbol{G}\}_{55}} \tag{63}$$

The quantity $\{\boldsymbol{J}_p(\lambda)\boldsymbol{G}_p\}_{55}$ is the 5–5 matrix element of the matrix product of the B_1 block. A little manipulation shows that

$$\{\boldsymbol{J}_p(\lambda)\boldsymbol{G}_p\}_{55}=|\boldsymbol{J}_p(\lambda)|\{\lambda(\boldsymbol{G}_p)_{55}-|\boldsymbol{G}_p|F_{44}\} \tag{64}$$

where F_{44} is the 4—4 element of the force constant matrix for the XY_3 unperturbed molecule and may be expressed directly in terms of the vibrational frequencies by application of Eq. 27 which (see VAIII) gives

$$F_{44}=\frac{m_y d_2^2(\lambda_2+a^2\lambda_3)}{2A_0^2 d_1^2} \tag{65}$$

Next we make use of the fact that

$$|\boldsymbol{J}_p(\lambda)|=\frac{1}{(\lambda-\lambda^*_4)(\lambda-\lambda^*_5)}=\frac{1}{\mu(\lambda-\lambda^*)} \tag{66}$$

where $\lambda^*_{4,5}$ are the mass-geometry corrected frequencies calculated in section I.2. Thus we obtain the final result that

$$\Delta f_\alpha=\frac{\pi(\lambda-\lambda^*)}{2\{\lambda(\boldsymbol{G}_p)_{55}-|\boldsymbol{G}_p|F_{44}\}} \tag{67}$$

In this example Δf_α is overdetermined. Evaluating Eq. 67 by substitution of an XY_2Z B_1 frequency $\lambda_4{}^p$ or $\lambda_5{}^p$ for λ yields two values of Δf_α. If the fundamental (anharmonically corrected) frequencies were available and if only changes in f_α were involved the two values of Δf_α would coincide.

4. $HBCl_2$ Force Field.—The infrared spectrum of $HBCl_2$ was discussed in VAII. In this work an assignment of the vibrational bands was made on the basis of an "isotope" calculation in which $HBCl_2$ was treated as if the hydrogen was an isotope of chlorine. The observed in-plane frequencies for $H^{11}BCl_2$ were $\nu_1=740(729)$, $\nu_2=2617(2607)$, $\nu_4=1089(1000)$ and $\nu_5=892(851)\ \mathrm{cm}^{-1}$. (The isotopically calculated frequencies are in parenthesis.) ν_3 was calculated to be at $287\ \mathrm{cm}^{-1}$ and was outside the range of the instrument. The A_1 frequencies (ν_1, ν_2, and ν_3) are so close to the calculated values that corrections for force constant changes would be meaningless. Anharmonic corrections can be greater than these differences.

The apparent agreement of the calculated B_1 frequencies with the observed values is somewhat fortuitous. In the above calculation no correction was made for the change in bond length. When Eqs. 58 and 59 are used to obtain the mass-geometry corrected frequencies one gets the results $\nu_4=1363$ and $\nu_5=912$ for a B–H bond length of 1.20Å. The A_1 modes are not affected by the bond length change. If we assume that the force constants involved in the A_1 modes are essentially unchanged as suggested by the fact that the calculated frequencies are so close, then we must have changes in the force field which affect only the B_1 modes. There are two such constants, f_α and $f_{d\alpha}$ (see VAIII). Application of Eq. 67 (the frequencies and mixing parameter are given in VAII) using $\lambda_4{}^p(\lambda_4{}^p=\nu_4{}^2/4\pi^2)$ gives a value of $\Delta f_\alpha=-0.038$ mdynes/Å or 25% decrease in f_α in going from BCl_3 $\rightarrow HBCl_2$. With this single force constant change the calculated frequencies are $\nu_5=1089$, $\nu_5=912$. ν_5 is about 20 wave numbers higher than the value estimated from the band center in VAII indicating that some other small force constant changes may be involved. A similar calculation for $DBCl_2$ indicates about a 15% decrease in f_α and predicts frequencies $\nu_4=1005$ and $\nu_5=793$. ν_4 agrees exactly with the observed $DBCl_2$ frequency but ν_5 was not observed. The change in f_α is therefore qualitatively the same for both $HBCl_2$ and $DBCl_2$. This calculation is of course not intended to constitute an accurate determination of the force field. In fact, it is not possible to obtain accurate force constants without having the anharmonically corrected frequencies. For example, in VAIII one finds that two sets of BBr_3 data which differ by less than 5 wave numbers gives values of f_α which differ by 10%. Nevertheless, the preceding analysis gives a fairly quantitative picture of the $HBCl_2$ force field; it is nearly identical to the BCl_3 force field with a 15 to 25% decrease in the bending force constant f_α. A calculation for the molecules $HBBr_2$ and $DBBr_2$ in terms of BBr_3 yields almost identical results. A more detailed account of these results along with the infrared spectra will be published at a later date.

A more accurate determination of the force constants does not seem to be meaningful until the anharmonic corrections are known. It should also be noted that the change in f_α becomes smaller as one increases the B–H bond length and in fact goes to zero at about 1.56Å.

Discussion and Conclusions

In the preceding sections we have developed the Green's function procedure for molecular analysis in the internal coordinate system.

By making use of the spectral representation of the cartesian dynamical matrix and the transformation between internal and cartesian symmetry coordinates we have shown how to construct the internal molecular Green's function directly from observed vibrational frequencies of the unperturbed molecule. It was shown that the changes in force constants associated with the characterization of a perturbed molecule can be calculated without reference to the unperturbed force constants. This procedure circumvents to a large degree the difficulties encountered in a direct procedure in which the unperturbed molecular force constants vary wildly with small changes in the unperturbed molecular frequencies. It was shown that all of the internal Green's functions can be constructed from a knowledge of the transformation matrix $\boldsymbol{B}$ and the mixing parameters.

In section III we obtained explicit formulae for the mass and geometry frequency shifts in going from an XY_3 to an XY_2Z planar molecule with a different bond length. It was shown that the A_1 modes are unaffected by the change in bond length and that the B_1 modes were shifted to higher (lower) frequencies whenever $\Delta l>0$ ($\Delta l<0$).

As an example of force constant changes, an explicit formula was obtained for the change in f_α directly in terms of the perturbed and unperturbed frequencies.

The Green's function formalism in the internal coordinate system appears to be a particularly simple and appealing procedure for correlating the vibrational properties of families of related molecular species.

A qualitative analysis of the $HBCl_2$ and $DBCl_2$ was given which shows that these molecules have a force field almost identical with the BCl_3 force field except that the bending force constant f_α is decreased by about 20%.

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