Vibrational Analysis of Substituted and Perturbed Molecules. Direct Determination of Force Constants from the Coriolis Interaction

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Molecular spectroscopists generally acknowledge the importance of obtaining the molecular force constants since there is much potential information contained in them if they can be determined accurately enough. For example, these force constants may be related to the chemical bonding and the electronic structure; they are useful to the spectroscopist for predicting the molecular frequencies beyond the range of his instruments and in interpreting the combination and overtone bands he observes. Also, determining accurate values of the anharmonic forces goes hand in hand with determing the harmonic forces. The analysis required to obtain molecular force constants using the ***F*-*G*** matrix techniques rapidly becomes very complex as the molecular size increases and must proceed in a backward manner.

A great deal of the computational difficulties of the ***F*-*G*** matrix procedure has been obviated by means of the molecular Green's function.(1)

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1) a) R. E. DeWames and T. Wolfram, *J. Chem. Phys.*, **40**, 853 (1964); b) C. D. Bass, L. Lynds, T. Wolfram and R. E. DeWames, ibid., **40**, 3611 (1964); c) T. Wolfram, C. D. Bass, R. E. DeWames and L. Lynds, This Bulletin, **39**, 201 (1966); d) L. Lynds, T. Wolfram and C. D. Bass, *J. Chem. Phys.*, **43**, 3775 (1965).

For XY_3 planar molecules, the Green's function method allows direct computation of the mixing parameter connecting two modes of the same symmetry type using only the observed frequencies as input data. The force constants can then be calculated directly from the mixing parameter. It is not necessary to make mathematical approximations in order to solve the equations and so computational errors are negligible. However, the number of molecular frequencies available to the computation are usually not more than just sufficient to determine the force constants, and since the off-diagonal components2) of the force constant matrix are very sensitive to small variations of the frequencies there will remain large uncertainties in the values of these numbers. It is important to find measurable quantities which determine the force in a less sensitive way. One such quantity is the Coriolis coefficient. Mills,3) Meal and Polo,4) Kristiansen and Cyvin,5) Boyd and Longuet-Higgins6) have shown how to relate the Coriolis coefficient to force constants.

Calculations

The Coriolis coefficient, ζ_r, can be measured directly from the splitting of the degenerate frequencies of a molecular vibration. Following the procedure of Boyd and Lonquet-Higgins6) we denote the two real normal coordinates of a degenerate vibration P_r, Q_r; these are written in a basis of mass adjusted cartesian coordinate u_k, v_k, w_k:

$$u_k=\sqrt{m_k}x_k;\quad v_k=\sqrt{m_k}y_k;\quad w_k=\sqrt{m_k}z_k.$$

$$P_r=\sum_j \alpha_{rj}S_j;\quad Q_r=\sum_j \alpha_{rj}S_j. \tag{1}$$

As an example of this we apply the method to the calculations of the mixing parameter for a molecule of type XY_3-planar. The normal coordinates for this molecule have been tabulated in Ref. 1b.

This leads to the following expression for the Coriolis coefficient ζ_3:

$$\zeta_3=\sum_k \begin{vmatrix} \dfrac{\partial P_r}{\partial u_k} & \dfrac{\partial P_r}{\partial v_k} \\ \dfrac{\partial Q_r}{\partial u_k} & \dfrac{\partial Q_r}{\partial v_k} \end{vmatrix}$$

$$=\frac{1}{A^2 d_1{}^2 d_2{}^2}[3r^2(a^2 d_1{}^2-2ad_1+1)-d_2{}^2(2ad_1+3r^2)]. \tag{2}$$

This may be rewritten as an equation with a as the unknown:

$$d_1{}^2(3r^2-d_2{}^2\zeta_3)a^2-4d_1{}^3a-d_1{}^2(3r^2+d_2{}^2\zeta_3)=0. \tag{3}$$

As a specific illustration we shall consider the case of BF_3. From the potential constants $F_{33}=6.303\times10^5$, $F_{34}/d=-0.259\times10^5$, and $F_{44}/d^2=0.528\times10^5$ (all force constants are millidynes/Angstrom), Meal and Polo4) calculated $\zeta_3=0.83$ for BF_3. Substitution of this value for ζ_3 into Eq. 3 gives a value -1.2761 for a, which compares with $a=-1.2765$ calculated from Eq. 12, Ref. 1b. The force field, calculated from the equations in 1c is: $F_{33}=6.310\times10^5$, $F_{34}/d=-0.3198\times10^5$, $F_{44}/d^2=0.528\times10^5$. The frequencies used to obtain the latter results appear in a publication of Ladd et al.7) Aside from F_{34}/d, which is the potential constant most sensitive to observed frequencies, the results are in substantial agreement.

However, a different set of data, (Ref. 5) results in a quite different force field, as calculated by the Wilson method: $F_{33}=7.4068\times10^5$, $F_{34}/d=-0.6398\times10^5$, $F_{44}/d^2=0.50013\times10^5$. The value of ζ_3 calculated in Ref. 5 is 0.717. Abramowitz has recently measured ζ_3 and found a value 0.70.8) Equation 2 gives $a=-1.0385$ for $\zeta_3=0.70$, and, using the frequencies of Ref. 5 with the equations of 1c: $F_{33}=7.5807\times10^5$, $F_{34}/d=0.7934\times10^5$, $F_{44}/d^2=0.5060\times10^5$. Equation 12, Ib gives $a=-1.1261$. There is substantial agreement within this last set of data, the largest discerpancy again appearing in F_{34}/d.

The new result of Abramowitz indicates that the BF_3 vibrational data of Kristiansen and Cyvin5) is more reliable that other reported data. Utilizing the simple formalism of this paper, and our previous results (1a—1b) we have performed the calculations with much less effort than earlier investigators.

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2) We are speaking of off-diagonal in the sense of a matrix constructed in a basis of internal coordinates. However, the Green's function analysis is most conveniently carried out in a basis of external cartesian coordinates which form an ortho-normal set. The advantage is that we deal with unitary matrices.

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5) L. Kristiansen and S. J. Cyvin, *J. Mol. Spect.,* **11**, 185 (1963).

6) D. J. R. Boyd and H. C. Longuet-Higgins, *Proc. Royal Soc.,* **A213**, 55 (1952).

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8) S. Abramowitz, Private Communication, *J. Chem. Phys.,* **43**, 4213 (1965).