JOURNAL
OF THE AMERICAN CHEMICAL SOCIETY

VOLUME 98, NUMBER 9 APRIL 28, 1976

Anharmonic Force Constants of Polyatomic Molecules. Test of the Procedure for Deducing a Force Field from the Vibration-Rotation Spectrum

Donald G. Truhlar,*[1a] Radley W. Olson,[1b]
Anthony C. Jeannotte II, and John Overend*

Contribution from Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. *Received July 28, 1975*

Abstract: The vibrational Hamiltonian of linear HCN, DCN, and TCN is solved by the finite-difference boundary value method and the eigenenergies and expectation values of the reciprocal of the moment of inertia are calculated for the seven lowest energy states. These values provide information equivalent to an observed vibration-rotation spectrum for each isotopic molecule but for a known potential energy surface. The "inversion" procedure by which a general quartic force field is obtained from experimental data is applied to this set of data. The anharmonic force constants thus obtained have errors in the cubic force constants less than 10% of the largest cubic force constant and errors in the quartic force constants less than 13% of the largest quartic force constant.

The least-squares determination of harmonic and anharmonic force constants of polyatomic molecules using spectroscopic data is usually accomplished using the general second-order perturbation theory formulas due to Nielson and others,[2,3] or when Fermi-Dennison resonance is important, by second-order perturbation theory and direct solution of the secular equation corresponding to a submatrix of the Hamiltonian. In such an approximate procedure there is always some question of the accuracy of the results obtained. To test this one requires a more accurate treatment for comparison. For diatomic molecules the vibrational eigenvalue problem is easily solved by many methods[4,5] and the exact solutions have been compared to perturbation theory results. The comparison shows that the perturbation theory approach is inaccurate unless the anharmonicity is very small.[6] However, the results of such comparisons cannot be used quantitatively for polyatomic molecules and it is the goal of this paper to provide a test of the perturbation theory treatments which is more directly applicable to the practical problems occurring in polyatomic molecules. In this article we test the usual perturbation theory treatment by solving for the exact vibrational wave functions and energies of a nonbending linear triatomic molecule for several assumed potential energy surfaces and comparing the results to the second-order perturbation theory treatment. In addition we calculate the rotational constants using these essentially exact vibrational wave functions for the linear model and we compare them to their perturbation theory values.

A technique for determining anharmonic force fields using the second-order perturbation theory treatment of spectroscopic data has been given by Pariseau et al.[7-9] and it is applied to some of the accurately calculated results in this article. Since the calculated results, unlike experimental data, correspond to a known potential energy surface, this provides a check on the accuracy of anharmonic force constants determined using second-order perturbation theory.

The example chosen for the test case is HCN and its isotopic analogues DCN and TCN. These molecules are particularly suitable for study because the isotope effect is rather large and the Fermi-Dennison resonance is weak.[10,11]

Finite-Difference Solution of the Vibrational Eigenvalue Problem and Numerical Calculation of the Rotational Constants

Method. Previously the multidimensional Schroedinger eigenvalue problem has been solved using an expansion in basis functions.[12] This method can involve difficult calculations, e.g., one attempt to use this method failed because the eigenvalues had not converged even for 128 basis functions[13] (note, however, that more than 128 basis functions were used successfully in some other cases and the basis function method may often be a convenient and useful method for solving this problem).

In this article we use the finite-difference boundary value method to solve the two-dimensional vibrational eigenvalue problem. This method has been applied previously to one-dimensional vibrational eigenvalue problems[5] and multidimensional eigenvalue problems occurring in the theory of electronic structure.[14]

We used the coordinates X, the H–C bond length, and Y, the distance from the center of mass of HC to N. The Schroedinger equation for the vibrational eigenfunction ψ_v for nonrotating, nonbending HCN in this coordinate system is

$$\left[-\frac{\hbar^2}{2}\left(\frac{1}{\mu_X}\frac{\partial^2}{\partial X^2}+\frac{1}{\mu_Y}\frac{\partial^2}{\partial Y^2}\right)+V(X,Y)-E_v\right]\psi_v(X,Y)=0 \tag{1}$$

where E_v is the vibrational eigenvalue, $V(X,Y)$ is the potential energy function, and

$$\mu_X = M_H M_C/(M_H + M_C) \tag{2a}$$

$$\mu_Y = (M_H + M_C)M_N/M \tag{2b}$$

$$M = M_H + M_C + M_N \tag{3}$$

We set up a grid of points with coordinates

$$X_i = X_0 + ig \qquad i = 0, 1, 2, \ldots, I+1 \tag{4}$$

and

$$Y_j = Y_0 + jfg \qquad j = 0, 1, 2, \ldots, J+1 \tag{5}$$

X_0, Y_0, f, and g are grid parameters to be chosen such that

$$\psi(X_0,Y) \simeq 0 \tag{6a}$$

$$\psi(X_{I+1},Y) \simeq 0 \tag{6b}$$

$$\psi(X,Y_0) \simeq 0 \tag{6c}$$

and

$$\psi(X,Y_{J+1}) \simeq 0 \tag{6d}$$

for all eigenfunctions of interest. Then the finite-difference approximation to (1) is

$$-\frac{\hbar^2}{2}\left[\frac{1}{\mu_X g}(\psi_{i-1,j,v} - 2\psi_{i,j,v} + \psi_{i+1,j,v}) + \frac{1}{\mu_Y fg}(\psi_{i,j-1,v} - 2\psi_{i,j,v} + \psi_{i,j+1,v})\right] + V_{ij}\psi_{i,j,v} = E_v\psi_{i,j,v} \tag{7}$$

where

$$\psi_{i,j,v} = \psi_v(X_i,Y_j) \tag{8}$$

and

$$V_{ij} = V(X_i,Y_j) \tag{9}$$

With the boundary conditions (6), eq 7 becomes a set of N homogenous linear equations in the N unknowns $\{\psi_{i,j,v}\}$, $i = 1, 2, \ldots, I$, $j = 1, 2, \ldots, J$ where $N = IJ$, and with the definition

$$\alpha = (j-1)I + i \tag{10}$$

this set of equations may be written in matrix form as

$$\mathbf{H}\psi_v = E\psi_v \tag{11}$$

where ψ_v is a vector of length N whose αth element $\psi_{\alpha,v}$ is $\psi_{i,j,v}$. Thus the problem is reduced, for a given f and g, to finding the several lowest energy eigenvalues of the matrix **H** and their associated eigenvectors. With X_0, Y_0, X_{I+1}, Y_{J+1}, and f fixed, calculations were performed for several values of g and the results extrapolated (as discussed below) to $g = 0$ to obtain solutions to eq 1.

The matrix **H** is real and symmetric with a bandwidth of $(2I + 1)$ but it has only three to five nonzero elements in a given row. The eigenvalues and eigenvectors are found by the method of optimal relaxations as described by Shavitt et al.,[15] using their root-shifting method for determination of higher eigenvalues. This method involves the minimization of the Rayleigh quotient $\phi^T\mathbf{H}\phi/(\phi^T\phi)$, where superscript T denotes a transpose, as follows. (i) An initial estimate of the kth eigenvector was orthogonalized, for $k > 1$, to the $(k-1)$ lower eigenvectors by Gram–Schmidt orthogonalization. From the resulting column vector ϕ (or the initial estimate for $k = 1$), the quantities $p = \phi^T\mathbf{H}\phi$, $q = \phi^T\phi$, and $\rho = p/q$ were calculated. Then ρ is the initial eigenvalue estimate. Next, for $k > 1$, eq 44 and 45 of ref 15 were used to calculate shift parameters to shift the previous $(k-1)$ eigenvalues to higher energy than the kth eigenvalue and **H** was modified so the kth eigenvalue became the lowest energy eigenvalue. (ii) Then, on an element-by-element basis, the approximate kth eigenvector was adjusted to satisfy more closely the eigenvalue equation. This was accomplished using (20), [(19), (39), (40)], [(22), (25)–(27)], [(21), (23)], (30), and (42) of ref 15, in order of the bracketed groups, to each element of the approximate eigenvector. This procedure also yields an improved estimate of the eigenvalue. Step (ii) was repeated until the eigenvector converged. Convergence was considered to have been attained when the maximum change in any eigenvector element for a given repetition of step (ii) was less than 10^{-6} times the norm of the eigenvector. Tests showed that the eigenvalue usually converged in about 10 iterations and the eigenvector converged in about 30–50 iterations.

To ensure orthogonality of the kth eigenvector to previous ones and to minimize round-off error in accumulated changes to p, q, ρ, and the shift factors, the approximate eigenvector was reorthogonalized to the previous $k-1$ eigenvectors and the quantities p, q, ρ, and the shift factors were recalculated about every 20 iterations. The extrapolation procedure of ref 15 was also applied every 20 iterations but it did not appear to speed convergence. Some special procedures are required[15] when some of the variables are essentially zero and these were applied when the variables were less than 10^{-12}.

Except as noted above, all constants in the program were the same as in ref 15 [s in their eq 45 was 1.3 and h in eq 62 was 20.0].

Initial guesses for the eigenvectors were obtained as follows. Grids were always run in order of increasing point density (decreasing g). For the least dense grid initial guesses were obtained using the procedure recommended in ref 15. Although this provides a very poor estimate of the eigenvector for the present problem, the number of iterations required for convergence using this procedure was not significantly larger than the number required using more accurate initial eigenvector estimates obtained by interpolation. For the more dense grids, the initial eigenvector estimate for each eigenvalue was obtained by two-dimensional four-point interpolation using the previous grid.

Converged eigenvectors were normalized such that

$$\sum_{\alpha=1}^{N} |\psi_{\alpha,v}|^2 = 1 \tag{12}$$

From the converged eigenvectors we wished to calculate the rotational constants defined by

$$B_v = \frac{\frac{\hbar^2}{2}\int \mathrm{d}X \int \mathrm{d}Y \frac{1}{I(X,Y)}|\psi_v(X,Y)|^2}{\int \mathrm{d}X \int \mathrm{d}Y |\psi_v(X,Y)|^2} \tag{13}$$

where I is the moment of inertia. Using the usual definition and letting HCN be located on the z axis,

$$I = \sum_{i=1}^{3} M_i(z_i{}'^0)^2 \tag{14}$$

where the M_i are atomic masses, and

$$z_i'^0 = z_i - z_{\text{com}} \tag{15a}$$

$$z_{\text{com}} = M^{-1} \sum_{i=1}^{3} M_i z_i \tag{15b}$$

where z_i are atomic coordinates. This may be rewritten as[16]

$$I = M_H X^2 + M_N W^2 - M^{-1}(M_H{}^2 X^2 + M_N{}^2 W^2 - 2M_H M_N XW) \tag{16}$$

where W is the C-N distance equal to

$$W = Y - M_H X/(M_H + M_C) \tag{17}$$

Using eq 16 and 17 and the normalization of eq 12, B_v may be calculated for a given grid as

$$B_v = \tfrac{1}{2}\hbar^2 \sum_{\alpha=1}^{N} I_\alpha{}^{-1} |\psi_{\alpha,v}|^2 \tag{18}$$

where I_α is $I(X_i, Y_j)$ [see eq 10].

The above procedures lead to E_v and B_v values corresponding to given values of X_0, Y_0, X_{I+1}, Y_{J+1}, f, and g. The first two of these parameters were chosen small enough and the next two large enough to ensure that along the edges of the grid the values of the eigenvectors of interest were always less than 10^{-12} times the maximum value of the eigenvector. Also additional runs with fixed f and g but smaller X_0 and Y_0 and larger X_{I+1} and Y_{J+1} showed that E_v values of interest were invariant with respect to such changes to ten significant figures and the B_v values of interest were unchanged to at least four significant figures and more often to six significant figures. Typical values used for the final calculations presented here were: $X_0 \simeq 0.5a_0$ (HCN), $0.7a_0$ (DCN), $0.8a_0$ (TCN); $X_{I+1} \simeq 4.4a_0$ (HCN), $3.9a_0$ (DCN), $3.8a_0$ (TCN); $Y_0 \simeq 1.5a_0$ (HCN), $1.6a_0$ *(DCN)*, $1.8a_0$ *(TCN)*; $Y_{J+1} \simeq 3.4a_0$ (HCN), $3.5a_0$ (DCN), and $3.6a_0$ (TCN).

Finally the E_v and B_v values for given values of X_0, Y_0, X_{I+1}, Y_{J+1}, and f and a sequence of values of g were extrapolated to $g = 0$ using the Richardson extrapolation method.[5,14,18] The extrapolation calculations were arranged in the form of a Neville table as described elsewhere.[5,14,19] In all cases we used $I = J$. For the results presented, we used five or six grid sizes with $30 \leq I \leq 70$ or $40 \leq I \leq 60$ although in some test cases we used I as large as 79. Then

$$g = (X_{I+1} - X_0)/(I + 1) \tag{19}$$

and since $I = J$

$$f = (Y_{J+1} - Y_0)/(X_{I+1} - X_0) \tag{20}$$

The Neville tables used in the extrapolation were also used to estimate the uncertainties in the extrapolated E_v and B_v values as discussed elsewhere.[5]

All the finite-difference calculations were performed in hartree atomic units and all conversion factors were computed from a recent NBS tabulation of physical constants.[20,21]

Results. We examined three isotopes[22] and four potential energy surfaces. All four potential energy surfaces have the form

$$V(R_1,R_2) = \sum_{i \leq j} K_{ij} R_i R_j + \sum_{i \leq j \leq k} K_{ijk} R_i R_j R_k + \sum_{i \leq j \leq k \leq l} K_{ijkl} R_i R_j R_k R_l \tag{21}$$

where

$$R_1 = X - X_e \tag{22}$$

$$R_2 = W - W_e \tag{23}$$

Table I. Parameters of the Potential Energy Surfaces Used for HCN, DCN, and TCN

		(i)[a]	(ii)[b]	(iii)	(iv)
K_{11},[c]	mdyn/Å	3.108	3.121	3.108	4.5
K_{12},	mdyn/Å	−0.242	−0.094	−0.242	−0.242
K_{22},	mdyn/Å	9.322	9.253	9.322	9.322
K_{111},	mdyn/Å^2	−5.39	−5.48	−5.39	−5.39
K_{112},	mdyn/Å^2	−0.13	−0.43	−0.13	−0.13
K_{122},	mdyn/Å^2	0.09	0.17	0.09	0.09
K_{222},	mdyn/Å^2	−20.98	−20.83	−20.98	−20.98
K_{1111},	mydn/Å^3	5.57	4.48	5.57	5.57
K_{1112},	mdyn/Å^3	0	−10.2	0	0
K_{1122},	mdyn/Å^3	0	12.9	0	0
K_{1222},	mdyn/Å^3	0	−10	0	0
K_{2222},	mdyn/Å^3	40	41	30	40
X_e,	Å	1.0659	1.0659	1.0659	1.0659
W_e,	Å	1.1531	1.1531	1.1531	1.1531

[a] Force constants taken from ref. 11, p 72, column (iv). [b] Force constants taken from ref 11, p 72, column (iii). [c] The subscript (1) refers to internal coordinate R_1 which is associated with the H–C stretch, while the subscript 2 refers to internal coordinate R_2, the C–N stretch

The constants appearing in these equations are given in Table I. The force constants in column (i) are those judged by Wang[11] to be the most accurate estimate of the general quartic force field based on an analysis of spectroscopic data. For our purposes they merely provide a realistic force field for our tests of second-order perturbation theory. The force constants in column (ii) are taken from the same study but include quartic stretch–stretch interaction force constants which were judged[11] to have unreasonably large dispersions. For our purposes they provide another test case so we can determine whether our conclusions using the force constants in column (i) are sensitive to the omission of quartic stretch–stretch force constants in that set. In column (iii) we arbitrarily decreased the largest quartic force constant to check whether this appreciably improved the perturbation theory treatment. In column (iv) we arbitrarily raised one of the quadratic force constants to simulate a Fermi-Dennison resonance-like situation in which[23] $\nu_1 \simeq 2\nu_1$. In this last case the convergence of the iterative calculations of the eigenvectors and eigenvalues was considerably slower than in the other cases and hence the calculation was considerably more expensive.

The results of the calculations are given in Table II (the numbers in parentheses below some of these results will be explained in the next section).

Tests of Perturbation Theory

Calculation of the Vibrational Energies and Rotational Constants. The perturbation-theory solution of the vibration-rotation Hamiltonian is well established. In the polyatomic case with no degenerate vibrations we may write the vibrational energies as an expansion in vibrational quantum numbers[25]

$$(E_v/hc) = E_0 + \sum_s \omega_s(v_s + \tfrac{1}{2}) + \sum_{s' \geq s} X_{ss'}(v_s + \tfrac{1}{2})(v_{s'} + \tfrac{1}{2}) + \ldots \tag{24}$$

and the effective rotational constant, B_v, for a linear molecule as

$$B_v = B_e - \sum_s \alpha_s{}^{xx}(v_s + \tfrac{1}{2}) + \ldots \tag{25}$$

where $\alpha_s{}^{xx}$ is the rotation-vibration interaction constant which is often denoted α_s or α_v. The harmonic frequencies, ω_s, are obtained by exact solution of the harmonic oscillator part of the Hamiltonian and the equilibrium rotational con-

Table II. Exact Values for the Zero-Point Energy and Exact and Approximate Values of Vibrational Excitation Energies and Rotational Constants[a]

Force field[b] isotope	(i) HCN	(i) DCN	(i) TCN	(ii) HCN	(iii) HCN	(iv) HCN
Zero-point energy	2767.1129 (1)[c]	2316.3698 (2)	2121.0391 (2)	2764.8444 (1)	2764.9354 (1)	3119.3471 (2)
υ_1	3345.188 (3)	2655.977 (6)	2483.283 (4)	3335.449 (4)	3344.246 (3)	4070.36 (3)
	(3330.47)[d]	(2650.30)	(2479.61)	(3330.77)	(3329.78)	(4064.59)
$2\upsilon_1$	6629.81 (2)	5285.42 (2)	4950.84 (2)	6601.45 (3)	6627.69 (2)	8125.4 (2)
	(6562.36)	(5263.03)	(4937.38)	(6566.61)	(6560.94)	(8100.55)
$\upsilon_1 + \upsilon_2$	5442.52 (1)	4561.49 (2)	4182.83 (2)	5407.93 (1)	5430.94 (1)	6190 (2)
	(5421.34)	(4545.10)	(4169.73)	(5422.86)	(5411.71)	(6176.36)
υ_2	2106.954 (2)	1924.482 (3)	1716.924 (2)	2102.611 (3)	2098.302 (2)	2127.930 (2)
	(2104.39)	(1921.87)	(1714.73)	(2103.86)	(2096.70)	(2125.69)
$2\upsilon_2$	4206.76 (2)	3841.54 (3)	3424.16 (1)	4196.18 (2)	4180.25 (2)	4252.18 (7)
	(4196.49)	(3833.46)	(3417.57)	(4194.44)	(4174.04)	(4242.79)
$3\upsilon_2$	6302.5 (1)	5752.3 (2)	5122.59 (7)	6283.3 (1)	6247.9 (1)	6373 (2)
B_{00}[e]	1.472451 (5)	1.20151 (1)	1.02659 (2)	1.47203 (3)	1.47209 (4)	1.47462 (13)
$(B_{00} - B_{10}) \times 10^3$	13.9 (2)	13.8 (0)	11.2 (1)	16.9 (0)	14.6 (1)	7.8 (1)
	(15.0)	(14.6)	(12.3)	(15.0)	(15.0)	(9.0)
$(B_{00} - B_{20}) \times 10^3$	27.8 (1)	27.2 (0)	22.6 (0)	35.8 (0)	27.8 (0)	26.3 (58)
	(30.0)	(29.2)	(24.6)	(30.0)	(30.0)	(18.1)
$(B_{00} - B_{11}) \times 10^3$	23.3 (0)	19.1 (0)	15.9 (0)	26.3 (0)	23.3 (1)	14.6 (15)
	(25.4)	(21.0)	(17.6)	(25.4)	(25.4)	(19.8)
$(B_{00} - B_{01}) \times 10^3$	9.6 (1)	5.7 (0)	4.9 (1)	9.9 (0)	8.6 (2)	6.3 (7)
	(10.4)	(6.4)	(5.3)	(10.4)	(10.4)	(10.8)
$(B_{00} - B_{02}) \times 10^3$	17.8 (1)	11.2 (0)	9.5 (1)	17.4 (3)	19.5 (1)	19.2 (3)
	(20.8)	(12.8)	(10.5)	(20.9)	(20.8)	(21.6)

[a] All values are in cm^{-1}. [b] Force fields are labeled as in Table I. [c] Estimated uncertainties in the last digits quoted are given in parentheses following the exact results. These estimates are based entirely on the Neville tables used for extrapolation to zero-step size. Other possible sources of error, e.g., those due to boundary placement, are not included (see text). [d] Perturbation-theory results are given in parentheses below the exact results. [e] The rotational constants B_υ are written with the subscript $\upsilon_1\upsilon_2$ to designate the state.

stants, B_e, by solution of the rigid-rotor part; all higher terms in the Hamiltonian, including the anharmonic potential-energy terms and the rotation-vibration interaction terms, are treated by second-order perturbation theory to give the coefficients $X_{ss'}$ and α_s. Note that the order parameter is defined such that cubic force constants are in the first-order perturbation and quartic force constants are in the second-order perturbation.

It is convenient to use the formalism developed by Nielsen[2] and to express the coefficients $X_{ss'}$ and α_s in terms of the normal-coordinate force constants, $k_{ss's''}$ and $k_{ss's''s'''}$. (Note that in the normal-coordinate space of Nielsen all force constants have units of inverse length.) In the case of a linear molecule with no degenerate vibrations these coefficients are given by[24]

$$X_{ss} = \frac{3}{2} k_{ssss} - \frac{15}{4}\frac{k_{sss}^2}{\omega_s} - \sum_{s' \neq s} \frac{k_{sss'}^2}{4\omega_{s'}}\left(\frac{8\omega_s^2 - 3\omega_{s'}^2}{4\omega_s^2 - \omega_{s'}^2}\right) \quad (26)$$

$$X_{ss'} = k_{sss's'} - 2k_{sss'}^2\left(\frac{\omega_s}{4\omega_s^2 - \omega_{s'}^2}\right) - 2k_{ss's'}^2\left(\frac{\omega_{s'}}{4\omega_{s'}^2 - \omega_s^2}\right) - 3\frac{k_{sss}k_{ss's'}}{\omega_s} - 3\frac{k_{sss'}k_{s's's'}}{\omega_{s'}} - \sum_{s'' \neq s,s'} \frac{k_{sss''}k_{s's's''}}{\omega_{s''}} - \sum_{s'' \neq s,s'} k_{ss's''}^2\omega_{s''}(\omega_{s''}^2 - \omega_s^2 - \omega_{s'}^2)D_{ss's''} \qquad s \neq s' \quad (27)$$

where

$$D_{ss's''}^{-1} = 2(\omega_s + \omega_{s'} + \omega_{s''})(\omega_s - \omega_{s'} - \omega_{s''}) \times (\omega_{s'} - \omega_s - \omega_{s''})(\omega_{s''} - \omega_s - \omega_{s'}) \quad (28)$$

and

$$\alpha_s^{xx} = (B_e^2/2\omega_s)[A_{ss}^{xx} - (a_s^{xx})^2/I_e] - 2\pi c[3k_{sss}a_s^{xx}I_e^{-1/2}\lambda_s^{-1/4} + \sum_{s' \neq s} k_{sss'}(a_{s'}^{xx})^2\lambda_s^{1/2}\lambda_{s'}^{-3/4}I_e^{-1/2}] \quad (29)$$

where

$$\lambda_s = (2\pi c\omega_s)^2 \quad (30)$$

$$A_{ss}^{xx} = \sum_i (l_{is}^z)^2 \quad (31)$$

$$a_s^{xx} = 2\sum_i M_i^{1/2} z_i'^0 l_{is}^z \quad (32)$$

M_i is still the mass of the ith atom, $z_i'^0$ is the center-of-mass Cartesian coordinate for the ith nucleus as defined in eq 15, the l_{is}^z are the coefficients of the matrix which transforms mass-weighted Cartesian coordinates to normal coordinates [see eq 23 of Pariseau et al.[7]], I_e is the equilibrium moment of inertia, and B_e is the equilibrium rotational constant given by

$$B_e = h/(4\pi cI_e) \quad (33)$$

The normal-coordinate force constants are obtained by transformation of the potential energy, expressed in internal coordinates, according to the algorithm given by Pariseau, Suzuki, and Overend.[7] The collinear problem was solved by eliminating all possible dependence of the stretching normal coordinate force constants on the bending internal coordinate force constant. This was effected by setting to zero the second and higher derivatives of the bending coordinate R_3 with respect to the Cartesian displacement coordinates (cf. ref 7). In the present problem it is found that the numerical values of the internal-coordinate force constants given in Table I yield the normal-coordinate force constants given in Table III. Note that all the coefficients of this transformation are known exactly and that, since the transformation is exact through the quartic terms, the normal-coordinate force constants are exactly equivalent to the internal-coordinate force constants.

The numerical results of Table III are then substituted into eq 26-29 to give the values of $X_{ss'}$ and α_s corresponding to a second-order perturbation treatment and these are then used with eq 24 and 25 to obtain the perturbation-theory estimates of the vibrational energies and the effective rotational constants. Table II shows the results of the second-

Table III. Normal-Coordinate Force Constants for HCN, DCN, and TCN (cm^{-1})

	Internal-coordinate force constants[a]					
	(i)	(i)	(i)	(ii)	(iii)	(iv)
Isotope	H	D	T	H	H	H
k_{11}[b]	3435.80	2701.40	2513.77	3431.57	3435.80	4100.16
k_{12}	0	0	0	0	0	0
k_{22}	2123.43	1945.68	1738.94	2123.04	2123.43	2124.03
k_{111}	−279.5	−87.3	−12.57	−285.0	−279.5	−221.0
k_{112}	−205.6	322.8	289.43	−197.9	−205.6	−106.8
k_{122}	58.66	5.22	55.0	59.4	58.66	63.09
k_{222}	−107.3	82.8	75.4	−107.8	−107.3	−111.3
k_{1111}	29.79	10.87	7.71	32.8	29.77	21.59
k_{1112}	23.30	−13.9	−1.37	−13.4	23.50	10.8
k_{1122}	12.47	35.8	32.9	12.28	11.22	5.19
k_{1222}	−10.12	4.8	5.0	−12.3	−7.33	−8.7
k_{2222}	9.32	5.29	4.31	9.12	7.00	9.98

[a] See Table I. [b] Note that the value of each of these force constants is independent of the order in which the subscripts are written.

order perturbation treatment compared with those of the more exact calculation described in the previous section.

It is immediately clear that there are significant deficiencies in the perturbation-theory estimates of the vibrational energies. E.g., for HCN with potential surface (i), the exact value of the CH stretching fundamental, ν_1, is 3345.19 cm^{-1} which differs by about 15 cm^{-1} from the perturbation-theory estimate. The formal reason for such a difference resides in the complete neglect of higher terms in the expansions given in eq 24 and 25. In fact the coefficients $X_{ss'}$ and α_s calculated from the set of force constants by eq 26, 27, and 29 are given exactly by second-order perturbation theory; they may be approximated by fitting the exact vibrational energies and rotational constants to eq 24 and 25. In Table IV we compare the exact and approximate values of $X_{ss'}$ and α_s for potential surface (i). They differ significantly and this implies again that the higher terms in the (v + ½) expansions of eq 24 and 25 are not negligible. One must be concerned whether the perturbation theory is breaking down because of resonance effects. If any of the normal-coordinate force constants is pathologically large with respect to the energy separation of the harmonic oscillator states it couples one must use degenerate perturbation theory. But Tables II and III show no resonance corrections should be required in the present case except possibly for potential surface (iv). We conclude that the failure of eq 24 and 25 to converge is an inherent problem in the perturbation theory approach to vibrational dynamics. As mentioned above, the discrepancies appear to be worse in the CH vibrational modes and could be a result of the relatively high amplitude of this vibration. It is interesting that Mills, using the experimental vibrational excitation energies, also found that the expansion in eq 24 was more slowly convergent for the HC normal mode in HCN than for the CN normal mode.[9] The perturbation theory calculation with no explicit correcting for Fermi–Dennison resonance works about as well for the transition frequencies on surface (iv) as for the transition frequencies on the other surfaces but it fails to adequately reproduce the somewhat anomalous rotational constants.

Since Table II shows that the accuracy (or lack of it) of pertubation theory is roughly comparable for potential surfaces (i), (ii), and (iii), we conclude that there is nothing too special about potential surface (i) and we examine the inversion problem only for this surface.

Table IV. Anharmonic Constants Calculated from (a) the "Observed" Data (Numerical Solution of Schroedinger Equation) of Table II and (b) Predicted from the Perturbation Treatment

	HCN		DCN		TCN	
	a	b	a	b	a	b
X_{11}	−30.28[a]	−49.29	−13.27	−18.78	−7.86	−10.92
X_{12}	−9.62	−13.51	−18.97	−27.06	−17.38	−24.62
X_{22}	−3.57	−6.14	−3.72	−5.14	−4.84	−5.95
$\alpha_1 \times 10^3$	−13.90	−15.01	−13.85	−14.57	−11.16	−12.32
$\alpha_2 \times 10^3$	−9.59	−10.38	−5.74	−6.41	−4.87	−5.26

[a] All values in this table are in cm^{-1} and are for potential energy surface (i) of Table I.

Recovery of the Force Constants from the Rotational–Vibrational Spectrum. Since we have available the exact vibrational energies and rotational constants calculated from a known set of anharmonic force constants we may usefully examine the problem of recovering the force constants from the spectroscopic data by least-squares adjustment. Admittedly the present case is only a two-dimensional problem[26] and, as such, has no analogue in a real polyatomic molecule but we do expect the results of such an examination to illuminate some of the difficulties usually encountered in this least-squares adjustment.

The least-squares adjustment procedure is most simply formulated in matrix notation.[27] We define an n-element vector of observables, $\mathbf{O}$, an m-element vector of explaining parameters, $\mathbf{X}$ (in this case the force constants), and a matrix, $\mathbf{J}(n \times m)$, the J_{ij} element of which is equal to $(\partial O_i/\partial X_j)$. Since in the present case the relationship between the explaining parameters and the observables is nonlinear, J_{ij} will depend on the values of the explaining parameters which we shall assume not to be known in advance. We further define a square weight matrix $\mathbf{P}(n \times n)$ which is formally the inverse of the variance-covariance matrix of the observables.[27] It is customary practice to assume that the spectroscopic observables are stochastically uncorrelated, in which case the weight matirx $\mathbf{P}$ assumes a diagonal form, the P_{ij} element of which is the square of the relative weight to be given to the ith observable.

In the case of a linear least-squares problem, i.e., one in which the $\mathbf{J}$ is independent of $\mathbf{X}$ and

$$\mathbf{O} = \mathbf{J}\mathbf{X} \tag{34}$$

the least-squares estimates of the explaining parameters, $\bar{\mathbf{X}}$, are given by

$$\bar{\mathbf{X}} = \mathbf{A}^{-1}\mathbf{J}^{\mathrm{T}}\mathbf{P}\mathbf{O} \tag{35}$$

where $\mathbf{J}^{\mathrm{T}}$ is the transpose of $\mathbf{J}$ and

$$\mathbf{A} = \mathbf{J}^{\mathrm{T}}\mathbf{P}\mathbf{J} \tag{36}$$

In the nonlinear case we assume an arbitrary starting set of explaining parameters and seek the corrections to these explaining parameters, $\Delta\bar{\mathbf{X}}$, which will minimize the weighted

Table V. Adjustment of Internal-Coordinate Force Constants to Observed Data[a]

	Exact	(i)	(ii)	(iii)	(iv)	(v)
K_{11}	3.108[b]	3.070 (3)	3.071 (2)	3.068 (7)	3.070 (7)	3.083 (1)
K_{12}	−0.242	−0.204 (6)	−0.228 (5)	−0.237 (6)	−0.24 (3)	−0.236 (2)
K_{22}	9.322	9.28 (1)	9.31 (1)	9.32 (4)	9.32 (5)	9.293 (4)
K_{111}	−5.39	−3.04 (3)	−5.3 (6)	−4.91 (6)	−4.95 (8)	−4.96 (4)
K_{112}	−0.13	−0.03 (2)	−0.43 (7)	−0.2 (1)	−0.07 (1)	−0.32 (4)
K_{122}	0.09	−3.3 (5)	−0.2 (2)	−0.09 (2)	−0.2 (2)	0.056 (8)
K_{222}	−20.98	−7.5 (7)	−19 (1)	−19.2 (2)	−19.2 (2)	−19.1 (1)
K_{1111}	5.57	0.0[c]	8 (2)	5.9 (3)	6.0 (3)	5.6 (2)
K_{1112}	0.0	0.0	0.0	0.0	−0.9 (9)	0.0
K_{1122}	0.0	0.0	0.0	0.0	−1 (2)	0.0
K_{1222}	0.0	0.0	0.0	0.0	0 (4)	0.0
K_{2222}	40	0.0	36 (5)	35 (4)	35 (4)	37.4 (6)
SUMD		14.4[d]	4.4	89.2	86.1	0.8
Z		10^{6}[e]	10^{15}	10^{6}	10^{10}	10^{11}

[a] The data bases for sets (i) and (ii) above were the vibrational transition energies only, the data base for sets (iii) and (iv) included the rotational constants (actually $B_V - B_{00}$) with P_{ii} for the vibrational part equal to 1 and for the rotational part equal to 10^6, and the data base for set (v) includes ν_2, $2\nu_2$, and α_2 for HCN and ν_1, $2\nu_1$, $\nu_1 + \nu_2$, ν_2, $2\nu_2$, α_1, and α_2 for DCN and TCN with P_{ii} for the ν values equal to 1 and P_{ii} for the α values equal to 10^6. [b] The units are the same as in Table I; dispersions in the last digits quoted are given in parentheses. [c] Values given as zero with no dispersion were constrained to be zero. [d] Units are $(\mathrm{cm}^{-1})^2$. [e] Unitless.

Table VI. Variation of Statistical Fit with the Relative Weight Assigned to the Rotational Constants ($B_V - B_{00}$)

	Exact	(i)	(ii)	(iii)	(iv)	(v)
K_{11}	3.108	3.03 (6)[a]	3.068 (7)	3.070 (2)	3.071 (2)	3.068 (3)
K_{12}	−0.242	−0.25 (5)	−0.238 (7)	−0.230 (5)	−0.229 (5)	−0.238 (9)
K_{22}	9.322	9.7 (3)	9.32 (4)	9.31 (1)	9.31 (1)	9.31 (2)
K_{111}	−5.39	−4.8 (2)	−4.91 (7)	−4.85 (8)	−5.1 (4)	−4 (3)
K_{112}	−0.13	−0.00 (2)	−0.2 (1)	−0.38 (6)	−0.42 (7)	0.3 (3)
K_{122}	0.09	−0.10 (2)	−0.09 (2)	−0.06 (2)	−0.09 (3)	−1.6 (8)
K_{222}	−20.98	−20.4 (10)	−19.2 (2)	−19.2 (3)	−18 (2)	−45 (20)
K_{1111}	5.57	7 (1)	5.9 (3)	5.6 (3)	6 (2)	3 (10)
K_{1112}	0.0	0.0[b]	0.0	0.0	0.0	0.0
K_{1122}	0.0	−3 (13)	−0.6 (14)	−0.3 (4)	−0.4 (6)	3 (11)
K_{1222}	0.0	0.0	0.0	0.0	0.0	0.0
K_{2222}	40	5 (28)	35 (4)	36 (2)	32 (8)	264 (239)
P_{ii} (rot)		10^{10}[c]	10^{8}	10^{6}	10^{4}	0.0
SUMD		7237[d]	88.6	5.5	5.5	3.6
Z		10^{7}[c]	10^{7}	10^{12}	10^{16}	10^{19}

[a] The units are the same as Table I; dispersions in the last digits quoted are given in parentheses. [b] Values given as zero were constrained to be zero. [c] Unitless. [d] Units are $(\mathrm{cm}^{-1})^2$.

sum SUMD of the squares of the differences between the true observables $\mathbf{O}$ and the values of the observables calculated from the explaining parameters $\mathbf{O}_c$. Thus SUMD is given by

$$\mathrm{SUMD} = \sum_i P_{ii}(\Delta \mathbf{O})_i^2 \tag{37}$$

and $\Delta\bar{\mathbf{X}}$ is given by

$$\Delta\bar{\mathbf{X}} = \mathbf{A}^{-1}\mathbf{J}^{\mathrm{T}}\mathbf{P}\Delta\mathbf{O} \tag{38}$$

where $\Delta\mathbf{O} = \mathbf{O} - \mathbf{O}_c$. The dependence of $\mathbf{J}$ on the values of the explaining parameters means that eq 38 must be solved iteratively until the corrections $\Delta\bar{\mathbf{X}}$ become arbitrarily small or until SUMD assumes a stationary value.

After eq 38 is solved in this way we calculate the variance (square of the dispersion σ_i) of the ith force constant as

$$\sigma_i^2 = \phi^{-1}\mathrm{SUMD}[(\mathbf{J}^{\mathrm{T}}\mathbf{P}\mathbf{J})]_{ii}^{-1} \tag{39}$$

where

$$\phi = n - m \tag{40}$$

We first considered a set of observables containing only ν_1, $2\nu_1$, $\nu_1 + \nu_2$, ν_2, and $2\nu_2$ for the three isotopes [see Table II, column (i)] and attempted, with all P_{ii} equal to 1, to fit all 12 force constants in the general quartic force field to these 15 observables. We found the solution to be very unstable and iteration on eq 38 diverged. The physical reason for this behavior lies in the fact that there are insufficient independent spectroscopic observables to fix all 12 force constants. Mathematically it is manifest in the matrix $\mathbf{A}$ being ill-conditioned for inversion. A useful measure of this ill-conditioning is obtained by taking the ratio Z defined by

$$Z = \prod_i A_{ii}/|\mathbf{A}| \tag{41}$$

which is infinite if $\mathbf{A}$ is singular and becomes very large as $\mathbf{A}$ becomes ill-conditioned for inversion. In this case Z was 1.1×10^{40}.

We then decided to constrain some of the explaining parameters at their starting values and to seek a solution to this least-squares problem which would converge in a stable way. We tried a number of constraints but none proved very satisfactory. In Table V we show in columns (i) and (ii) some typical results. In the first case we did not obtain values for quartic force constants but were modestly successful in recovering the seven cubic force constants. In the second case we obtained values for K_{1111} and K_{2222} but at the expense of considerably greater uncertainties in the other force constants.

From eq 29 it is clear that the coefficients α_s depend on the cubic normal-coordinate force constants but not on the quartic ones and our thought was that, by adding the observed α_v values to the set of observables (increasing n from 15 to 21 and ϕ from 3 to 9), we should be able to determine the cubic force constants more reliably and hence improve our recovery of the quartic force constants. We found this indeed to be so. In addition we found that inclusion of the α_v values in the calculation give a much lower value of Z, i.e., a better conditioned inversion. We show two typical results in Table V under columns (iii) and (iv). In the first set (iii) we constrained K_{1112}, K_{1122}, and K_{1222} to be zero and were able to determine the remaining force constants in a fairly satisfactory way. In the second set (iv) we adjusted all 12 force constants simultaneously and were able to obtain satisfactory values for all of them although the statistical dispersions were slightly larger than those in set (iii).

There was some question in our minds as to the correct relative weights to attribute to the vibrational energies and the rotational constants.[28] We are obviously willing to accept a set of force constants which give a vibrational energy differing by 1 cm^{-1} from the true one (cf. Table II) but it would be ridiculous to have a rotational constant in error by 1 cm^{-1}. For this reason we must weight the rotational constants more heavily in the least-squares calculation. We experimented with different relative weights (multiplying the rotational constants by a factor varying between 10^2 and 10^5). We found that the best results (cf. Table VI) were obtained with a multiplication factor of 10^3 which corresponds with a P_{ii} of 10^6 for the rotational constants and a P_{ii} of 1 for the vibrational energies.

The comparison of accurate and derived force constants shows there are significant errors associated with both the H–C stretch and the C–N stretch internal-coordinate force constants. In the test of perturbation theory for the vibrational transition frequencies and the α_v values, we noted that the $(v + \frac{1}{2})$ expansion is particularly slowly convergent for the H–C stretch normal mode. We thus repeated the culations of Table V, column (iii), but omitting the data which pertain to the H–C stretch and using only the data pertaining to D–C, T–C, and C–N stretches. The results are shown in Table V. The improvement in the accuracy of the recovered force constants is remarkable and the improvement in SUMD (two orders of magnitude) is even more marked. Clearly the accuracy of force constants recovered from experimental data by second-order perturbation theory can be improved by giving lower weight to the data associated with larger amplitude vibrational modes.

Summary of Conclusions

Second-order perturbation theory is in error by 1-15 cm^{-1} for fundamental frequencies and by larger amounts for overtones and combinations for realistic potential energy surfaces for linear HCN. The approximate theory is generally accurate within 0.001-0.002 cm^{-1} for the α_v values.

The errors[29] in the determination of a general quartic force field are larger for the anharmonic force constants than for the harmonic ones. The quadratic internal-coordinate force constants are determined to within about 1% or less. For the cubic force constants the errors are no larger than 1.8 mdyn/Å^2 and typically about 0.6 mdyn/Å^2 (while the largest cubic force constant is 21 mdyn/Å^2) and for the quartic force constants the errors are no larger than 5 mdyn/Å^3 (while the largest quartic force constant is 40 mdyn/Å^3).

Acknowledgment. This work was supported in part by the National Science Foundation and aided by computer-time subsidies from the University Computer Center of the University of Minnesota and the Ohio University Computer Center at Athens, Ohio.

References and Notes

(1) (a) Alfred P. Sloan Research Fellow, 1973–present; (b) Lando Summer Research Fellow, 1974 and 1975.

(2) H. H. Nielson, *Rev. Mod. Phys.*, **23**, 90 (1951); H. H. Nielson, "Handbuch der Physik", Vol. 37, S. Flügge, Ed., Springer-Verlag, Berlin, 1959, p 173.

(3) (a) Y. Morino, K. Kuchitsu, and S. Yamamoto, *Spectrochim. Acta, Part A*, **24,** 335 (1968); (b) K. T. Hecht, *J. Mol. Spectrosc.*, 5, 355 (1960).

(4) See, e.g., J. W. Cooley, *Math. Comp.*, **15**, 363 (1961); E. Davidson, *J. Chem. Phys.*, **34**, 1240 (1961); H. Harrison and R. B. Bernstein, *ibid.*, **38**, 2135 (1963), erratum; **47**, 1884 (1967); S. I. Chan and D. Stelman, *J. Mol. Spectrosc.*, **24**, 122 (1967); D. G. Rush, *Trans. Faraday Soc.*, **64**, 2013 (1968); J. T. Lewis and G. R. Mourdaunt, *J. Phys. B*, **1**, 768 (1968); F. M. Greenawalt and A. S. Dickinson, *J. Mol. Spectrosc.*, **30**, 427 (1969); J. N. Bass, *J. Comput. Phys.*, **9**, 555 (1972); and ref 5 for methods of solving the Schroedinger radial equation. A general diagonalization method for diatomics is given by I. Suzuki, *Bull. Chem. Soc. Jpn.* **44**, 3277 (1971).

(5) D. G. Truhlar, *J. Comput. Phys.*, **10**, 123 (1972).

(6) See, e.g., N. W. Bazley and D. W. Fox, *Phys. Rev.*, **124**, 483 (1961).

(7) M. A. Pariseau, I. Suzuki, and J. Overend, *J. Chem. Phys.*, **42**, 2335 (1965).

(8) General reviews of other techniques and of anharmonic force fields are in Y. Morino, *Pure Appl. Chem.*, **18**, 323 (1969); T. Shimanouchi, "Physical Chemistry: An Advanced Treatise", Vol. 4, H. Eyring, D. Henderson, and W. Jost, Ed., Academic Press, New York, N.Y., 1970, p 270; J. Overend, *Annu. Rev. Phys. Chem.*, **21**, 265 (1970); and ref 9.

(9) I. M. Mills, "Specialist Periodical Reports: Theoretical Chemistry", Vol. I, R. N. Dixon, Senior Reporter, the Chemical Society, London, 1974, p 110.

(10) I. Suzuki, M. A. Pariseau, and J. Overend, *J. Chem. Phys.*, **44**, 3561 (1966).

(11) V. K. Wang, Ph.D. Thesis, University of Minnesota, Minneapolis, 1973, unpublished.

(12) See, e.g., J. A. Ibers, *J. Chem. Phys.*, **41**, 25 (1964); R. G. Delaplane and J. A. Ibers, *ibid.*, **48**, 538 (1968); T. R. Singh and J. L. Wood, *ibid.*, **48**, 4567 (1968); S. Bell, R. Davidson, and P. A. Warsop, *J. Phys. B.*, **3**, 113 (1970); S. Bell, R. Davidson, and P. A. Warsop, *ibid.*, **3**, 123 (1970); M. G. Bucknell, N. C. Handy, and S. F. Boys, *Mol. Phys.*, **28**, 759 (1974); M. G. Bucknell and N. C. Handy, *ibid.*, **28**, 777 (1974); W. Eastes and R. A. Marcus, *J. Chem. Phys.*, **61**, 4301 (1974). Gribov and Khovrin and Foord et al. have recently applied the iterative least-squares adjustment procedure to determine anharmonic force fields for H_2O and OCS, respectively. Unlike previous such calculations, they did not use perturbation theory. Instead they used basis-set expansion techniques to obtain the energy levels from an assumed force field. See L. A. Gribov and G. V. Khovrin, *Opt. Spectrosc. (USSR)*, **36**, 475 (1974); A. Foord, J. G. Smith, and D. H. Whiffen, *Mol. Phys.*, **29**, 1685 (1975).

(13) R. G. Delaplane, J. A. Ibers, J. R. Ferraro, and J. J. Rush, *J. Chem. Phys.*, **50**, 1920 (1969).

(14) See, e.g., N. W. Winter, D. Diestler, and V. McKoy, *J. Chem. Phys.*, **48**, 1879 (1968), and other references given in ref 5 of the present article. The reader is referred to ref 5 and to these articles for an introduction to the finite-difference method for solving Schroedinger eigenvalue problems.

(15) I. Shavitt, C. F. Bender, A. Pipano, and R. P. Hosteny, *J. Comput. Phys.*, **11**, 90 (1973).

(16) P. R. Bartunek and E. F. Barker, *Phys. Rev.*, **48**, 516 (1935).

(17) $1a_0$ = 1 bohr = 1 atomic unit (au) of length = $0.529\,177\,21 \times 10^{-8}$ cm.

(18) L. F. Richardson, *Philos. Trans. R. Soc. London, Ser. A*, **226**, 299 (1927); Z. Kopal, "Numerical Analysis", Wiley, New York, N.Y., 1961, Section V-C.

(19) C. P. Miller, *Philos. Trans. R. Soc. London, Ser. A*, **263**, 525 (1968), and references therein.

(20) In hartree atomic units the unit of energy is the hartree. We used the conversion factors 1 hartree = $4.359\,827\,0 \times 10^{-11}$ ergs = $2.194\,745\,7 \times 10^5$ cm^{-1}.

(21) *Natl. Bur. Stand. (U.S.), Spec. Publ.*, **No. 344** (1971). The values of the constants used in this publication are taken from B. N. Taylor, W. H. Parker, and D. N. Langenberg, *Rev. Mod. Phys.*, **41**, 375 (1969). Conversion factors and physical constants are given in the present article to eight significant figures to adequately specify the values used in our calculations although they are not generally known to this accuracy.

(22) For masses we used: M_H = 1.007 825 amu = 1837.1085 au of mass; M_D = 2.0140 amu = 3671.2093 au of mass; M_T = 3.016 05 amu = 5497.7909 au of mass; M_C = 12.0 amu = 21 874.137 au of mass; M_N = 14.003 07 amu = 25 525.423 au of mass.

(23) We use the usual spectroscopic notation by which the wavenumbers of the fundamental frequencies are denoted ν_1 and ν_2 and overtones and combinations are designated using an algebraic formula involving ν_1 and ν_2 such that the band-origin frequencies would be given by the shorthand notation if anharmonicity constants were negligible. Further, we designate by ν_1 the fundamental frequency of the normal mode which is essentially an H–C stretch and by ν_2 the fundamental frequency of the normal mode which is essentially a C–N stretch. These are usually denoted ν_3 and ν_1, respectively.

(24) For the more general case, including degenerate modes, of a symmetric top, see ref 3a for X_{st}, X_{tt}, g_{tt}, and $g_{tt'}$. The expansion for α_s for degenerate modes is given in ref 2. Similar formulas for spherical tops are given in ref 3b.

(25) Note that $X_{ss'} = x_{ss'} + x_{s's}$ for $s \neq s'$ (and $X_{ss} = x_{ss}$) in Nielson's notation and that in ref 3a $x_{ss'}$ differs from Nielson's $x_{ss'}$ and equals our $X_{ss'}$.

(26) We refer to the two mathematical dimensions R_1 and R_2.

(27) H. Scheffe, "The Analysis of Variance", Wiley, New York, N.Y., 1959.

(28) The problem of statistical weights has also been considered by Y. Morino and T. Nakagawa, *J. Mol. Spectrosc.*, **26**, 496 (1968).

(29) These error estimates are obtained by using the three calculations given in Table V, columns (iii) and (iv), and Table VI, column (iii).