PINSA, **67, A,** No. 4 & 5, July & September 2001, pp. 479-491.
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SYMMETRIC TOP MOLECULES: PRACTICE AND PRECEPTS*

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(Received 19 April 1999; Accepted 7 July 1999)

The practical aspects of the application of the theory of vibration–rotation spectroscopy to the analysis of the high resolution spectra of symmetric top molecules are briefly reviewed in this article. The vibration-rotation Hamiltonian and the expressions for the non-degenerate and degenerate energy levels of symmetric top molecules are presented. The various diagonal and off-diagonal perturbation terms in the vibration-rotation Hamiltonian are reviewed. The nomenclature commonly employed in reporting molecular constants and perturbation parameters is discussed with illustrative examples. Attention is also drawn to the problem of correlation between molecular parameters frequently encountered in fitting high resolution vibration-rotation data.

Key Words: Vibration-Rotation Energy Levels; Molecular Parameters; Symmetric Top Molecules

Introduction

Rapid technological advances in the field of high resolution molecular spectroscopy based on the use of Fourier transform methods in the microwave, millimeter and infrared regions together with sophisticated laser based techniques, have generated vast data banks of high quality vibration rotation spectroscopic measurements. Ultra high resolution techniques such as side band laser spectroscopy and Sub-Doppler spectroscopic measurements make it possible to resolve very closely spaced rotation/ rotation-vibration lines (A_1-A_2 splittings, nuclear quadrupole splittings etc). Development of ultra high sensitive detection systems such as optothermal and optoacoustic detectors permit the detection of very weak signals such as 'forbidden transitions'. Theoretical advances have had to keep pace with the progress in the availability of precise experimental measurements where even subtle perturbations become discernible and fitting the data within the limits of the experimental accuracy poses a challenging problem.

Recognition of this need has led to the refinement and development of advanced theoretical models with "correlation free" reduced forms of the Hamiltonians in order to obtain precise molecular parameters which are physically meaningful[1]. Accurate spectroscopic data and precise molecular parameters obtained from these studies form the basis of the wide range of applications of molecular spectroscopy in the realm of chemical physics.

Most spectroscopic applications in various fields such as astrophysics and astrochemistry (interpretation of terrestrial, stellar and planetary data), pollution monitoring or laser development programmes rely on the availability of molecular parameters in a readily usable form. This has led to the concept of reduced effective rotational or rotational vibrational Hamiltonians which is based on the fact that the contact transformation of the Hamiltonian keeps the eigen values invariant. However since there are infinite number of such transformations they lead to an infinite number of unitary equivalent Hamiltonians. It is this ambiguity which is the root cause of correlation between some of the fitted parameters and the resulting problem of comparison of results obtained from different sources or multiple fits.

J K G Watson[2] was one of the first spectroscopists to address this vexing problem and found a solution, which led to his classical paper on the reduction of rotational Hamiltonians for orthorhombic molecules (Watson's Hamiltonian)[2]. Extension of this approach for the treatment of degenerate vibrational states of symmetric top molecules, and vibration-rotation Hamiltonians for interacting vibrational states in

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general has been carried out almost exclusively by Tyuterev and co-workers[3]. The theory of reduction of the effective rotational and vibration-rotational Hamiltonian developed for molecules with C_{3V} symmetry with a view to provide proper understanding of the relations between molecular parameters from unitary equivalent sets, has been elegantly reviewed by Sarka *et al.*[1]

One of the problems frequently encountered in the analysis of experimental data is the correlation between the fitted molecular parameters mentioned earlier. The reduced Hamiltonian provides a means of recognising such correlations and helps in selecting proper constraints when the correlations are severe and in checking the internal consistency of parameters obtained from "multiple fits".

The fitting of the measured vibration-rotational transitions between the energy levels, to obtain spectroscopic constants (which are related to the structural parameters of the molecule) is essentially the well known "Inverse" eigen value problem. One needs to set up the Hamiltonian operator for the system

$$H = F(\mathbf{J}^2, \mathbf{J}_z, \mathbf{J}_\pm, L_v^\pm, X)$$

which depends on the rotational operators $\mathbf{J}^2$, $\mathbf{J}_z$, $\mathbf{J}_\pm$ and the vibrational operators $L_v^\pm = q_v \pm i\rho_v$ and a set of spectroscopic constants $X = (\omega_v, x_{vv'}, B, \zeta, D, H .....)$ such as the vibrational frequency ω_v, the rotational and distortion constants B, D etc. The Hamiltonian matrix is usually set up in the rigid rotor Harmonic oscillator approximation. The diagonalisation of the Hamiltonian matrix gives the eigen values (energies of the levels). The differences between the energy levels correspond to the transition wave numbers. The problem reduces to determining the set of parameters X which minimise the weighted sum of the squares of the errors (observed-calculated values of data) by using standard least squares procedures. The difficulties frequently encountered in such a fitting procedure lie with the inadequacy of the experimental data (eg. in determining higher order parameters) or data that are not representative of the parameters to be determined (eg. spectroscopically 'forbidden constants' such as A or C, D_K , H_{KKK} for symmetric tops which cannot be determined solely from allowed transitions). Even when these difficulties are sorted out there remains the problem of the correlation among the parameters to be determined. Correlations arise when two or more fitted parameters have the same dependence on the variables. Methods to identify such correlations even when they are not obvious, and introduce appropriate constraints have been discussed in detail in the recent review by Sarka *et al.*[1] with several illustrative examples.

Another vexing problem frequently encountered in the practical use of molecular constants is the difference in the nomenclature of the fitted parameters reported by different groups which may lead to a certain degree of confusion. The problem is not as acute with symmetric top molecules as in the case of linear molecules.

In the following section, the vibration-rotation Hamiltonians for the nondegenerate and degenerate vibrational levels of symmetric top molecules are briefly reviewed with particular reference to axially symmetric molecules of C_{3V} symmetry which constitute one of the most widely studied class of compounds. The nomenclature commonly followed in reporting the molecular parameters is discussed with several illustrative examples. Attention has been drawn to the problem of correlation frequently encountered, in reporting molecular parameters obtained from unitary equivalent Hamiltonians.

Vibrational Energy Levels

The vibrating-rotating symmetric top is described by Watson's Hamiltonian[4] specialized for the case of two equal moments of inertia, $I_x = I_y$. In the harmonic oscillator/rigid rotor representation, perturbation calculation yields a vibrational term diagonal in the quantum numbers v_i and l_t of the same form as for a linear molecule:

$$\begin{aligned} G(v, l) = {} & \sum_s \omega_s (v_s + {}^1/_2) + \sum_t \omega_t (v_t + 1) \\ & + \sum_{s \le s'} x_{ss'} (v_s + {}^1/_2)(v_{s'} + {}^1/_2) \\ & + \sum_{s,t} x_{st} (v_s + {}^1/_2)(v_t + 1) \\ & + \sum_{t \le t'} x_{tt'} (v_t + 1)(v_{t'} + 1) + \sum_{t \le t'} g_{tt'} l_t l_{t'} \qquad \ldots(1) \end{aligned}$$

where s and t denote nondegenerate and doubly degenerate normal modes of vibration respectively, the x_{ij}'s are the anharmonic constants and the $g'_{tt'} l_t l'_t$ terms represent the contributions to the vibrational energy from the vibrational angular momenta, associated with degenerate modes. It is possible to express these constants in terms of the molecular parameters such as the harmonic vibrational frequencies (ω_i) and the cubic and higher order force constants[5-7].

In the absence of accidental anharmonic resonances, eq. (1) can be used to determine the vibrational energy of levels pertaining to the excitation of nondegenerate vibrational modes. However, when degenerate modes are excited, it represents only the diagonal contributions to the vibrational energy matrix and off-diagonal elements in l_t exist in general (the matrix is diagonal in the vibrational quantum number v_i in the absence of accidental resonances). The situation is then analogous to the vibrational l-type doubling and l-type resonances as in linear molecules, except that off-diagonal matrix elements of the form

$\langle v_t, l_t; v_{t'}, l_t |H_2'| v_t, l_t \pm 2; v_t', l_t' \pm 2 \rangle$ and $\langle v_t, l_t |H_2'| v_t, l_t \pm 4 \rangle$

also occur for some symmetric top molecules[5,8].

Expressions for the various coefficients appearing in these matrix elements have been derived by Grenier-Besson[9].

Rotational Hamiltonian for Nondegenerate States

The general form of the rotational Hamiltonian for the symmetric top molecule through sixth degree, for a nondegenerate state may be written in the form[10]

$$\mathbf{H}_{rot} = B_x \mathbf{J}^2 + (B_z - B_x) \mathbf{J}_z^2 - D_J(\mathbf{J}^2)^2 - D_{JK} \mathbf{J}^2 \mathbf{J}_z^2 - D_K \mathbf{J}_z^4 + H_J(\mathbf{J}^2)^3 + H_{JK}(\mathbf{J}^2)^2 \mathbf{J}_Z^2 + H_{KJ} \mathbf{J}^2 \mathbf{J}_Z^4 + H_K \mathbf{J}_Z^6 + \mathbf{H}_{split}, \quad ...(2)$$

where the form of H_{split} depends on the point group and is given by[5,11-13]

$$\mathbf{H}_{split}(C_{3v}, D_3) = (\varepsilon + \varepsilon_J \mathbf{J}^2 + \varepsilon_K \mathbf{J}_z^2) \times [\mathbf{J}_z, (\mathbf{J}_+^3 + \mathbf{J}_-^3)]_+ + h_3' (\mathbf{J}_+^6 + \mathbf{J}_-^6) \quad ....(3a)$$

$$\mathbf{H}_{split}(D_{3h}, C_{6v}, D_6, D_{6h}) = h_3 (\mathbf{J}_+^6 + \mathbf{J}_-^6), \quad ...(3b)$$

$$\mathbf{H}_{split}(D_{2d}, C_{4v}, D_4, D_{4h}) = (d_2 + h_2 \mathbf{J}^2)(\mathbf{J}_+^4 + \mathbf{J}_-^4) + \eta(\mathbf{J}_+^2 \mathbf{J}_Z^2 \mathbf{J}_+^2 + \mathbf{J}_-^2 \mathbf{J}_Z^2 \mathbf{J}_-^2) \quad ...(3c)$$

with $\mathbf{J}_\pm = \mathbf{J}_+ \pm i \mathbf{J}_y$ and $\mathbf{J}^2 = \mathbf{J}_x^2 + \mathbf{J}_y^2 + \mathbf{J}_z^2$

The splitting constants h_3, h_3' and ε contribute in the first order to splitting of the degeneracy for the K=3 levels, and d_2 and h_2 to splitting of the K=2 levels for the respective point groups shown above. However there is a strong correlation between the terms with h_3' and ε, and d_2 and h_2 and they cannot be determined independently. The terms involving these constants can be eliminated by a suitable transformation[10] and the reduced Hamiltonian for the symmetric top may be written in the generalized form

$$\mathbf{H}_{rot} = B_x \mathbf{J}^2 + (B_z - B_x) \mathbf{J}_z^2 - D_J(\mathbf{J}^2)^2 - D_{JK} \mathbf{J}^2 \mathbf{J}_z^2 - D_K \mathbf{J}_z^4 + H_J(\mathbf{J}^2)^3 + H_{JK}(\mathbf{J}^2)^2 \mathbf{J}_z^2 + H_{KJ} \mathbf{J}^2 \mathbf{J}_z^4 + H_K \mathbf{J}_z^6 + h_3 (\mathbf{J}_+^6 + \mathbf{J}_-^6) + (d_2 + h_2 \mathbf{J}^2)(\mathbf{J}_+^4 + \mathbf{J}_-^4) \quad ...(4)$$

For molecules with three- or six-fold axes of symmetry $d_2 = h_2 = 0$, for molecules with D_{2d} symmetry and those with four-fold axes of symmetry $h_3 = 0$, while for all other cases $d_2 = h_2 = h_3 = 0$. The other terms in the reduced Hamiltonian retain a form similar to those in the original Hamiltonian, and the relationship between the coefficients before and after the reduction may be found in the original review by Watson[10].

The well-known formula for the rotational energy levels of the nondegenerate vibrational state of an oblate symmetric top ($B_z = C$), up to sextic order, based on the above Hamiltonian is given by

$$E(J, K) = G_v + BJ(J+1) + (C - B) K^2 - D_J\{J(J+1)\}^2 - D_{JK} J(J+1)K^2 - D_K K^4 + H_J\{J(J+1)\}^3 + H_{JK}\{J(J+1)\}^2 K^2 + H_{KJ} J(J+1) K^4 + H_K K^6 + E_{-K, K} \quad ...(5)$$

where G_v accounts for the pure vibrational contributions to the energy and the magnitudes of the splittings are given by[5]

$$E_{-3,3} = h_3 J(J+1)[J(J+1) - 2][J(J+1) - 6]$$

for molecular groups D_{3h}, C_{6v}, D_6 and D_{6h} ...(6)

$$E_{-2,2} = \pm[d_2 + h_2 J(J+1)] J(J+1)[J(J+1) - 2]$$

for molecular groups D_{2d}, C_{4v}, D_4 and D_{4h} ...(7)

In molecules such as NH_3, PH_3, etc. having trigonal symmetry, the K=3 levels are split into A_1 and A_2 levels, while in molecules with C_{4v} symmetry like BrF_5, SF_5Cl, etc. the K=2 levels are split into B_1 and B_2 levels[5]. Experimental studies have provided confirmation of the J dependence of the splittings expressed by eqs. (6) and (7).

For lighter symmetric top molecules such as NH_3, at higher J values of the rotational quantum number, octic and higher order distortion constants become necessary to fit the data and the energy level expres-

sion including the splitting for the K=3 levels may be written in the form[14]

$$E(J,K) = G_v + BJ(J+1) + (C-B)K^2 - D_J J^2 (J+1)^2 - D_{JK} J(J+1)K^2 - D_K K^4 + H_{JJJ} J^3 (J+1)^3 + H_{JJK} J^2 (J+1)^2 K^2 - H_{JKK} J(J+1)K^4 + H_{KKK} K^6 + G_{JJJJ} J^4(J+1)^4 + G_{JJJK} J^3(J+1)^3 K^2 + G_{JJKK} J^2(J+1)^2 K^4 + G_{JKKK} J(J+1)K^6 + G_{KKKK} K^8 \pm h_3(-1)^J [(J+3)!/(J-3)!] \delta_{K,3} \quad ...(8)$$

where h_3 is the parameter representing the splitting of the K=3 levels. The upper and lower signs before the last term refer to the inversion components with s and a parity (as in NH_3) respectively and $\delta_{K,3}$ is the Kronecker symbol. It may be verified that the coefficients of h_3 in eqs. (6) and (8) are identical[a]. The standard polynomial expression for the nondegenerate energy levels of an oblate symmetric rotor can also be expressed more compactly in the form[15]

$$E^0(J,K) = G_v + BJ(J+1) + (C-B)K^2 - \sum_{p=2}^{n} \sum_{m=2}^{n} (-1)^p D_{pm} [J(J+1)]^m K^{2(p-m)} \quad ...(9)$$

where p is the order of the term and m is the power of $J(J+1)$. When expressed in this fashion, the sextic distortion constants, for example, are D_{33}, D_{32}, D_{31} and D_{30} corresponding to H_{JJJ}, H_{JJK}, H_{JKK}, and H_{KKK} respectively. When the energy levels are expressed in this form, the signs alternate for successive higher order centrifugal distortion terms — for e.g., the octic centrifugal distortion terms (G's) in the above equation would have signs opposite to those in eq. (8). This can sometimes lead to confusion in comparing results from different sources (see Ref. [16]) and it is therefore always useful to state the explicit form of the Hamiltonian employed in fitting the experimental data. The octic centrifugal distortion constants are frequently also represented by L's with the appropriate subscripts[17]. (The labelling of the octic and decadic centrifugal distortion constants has been rather arbitrary with G's and L's used interchangeably in the literature.)

Transitions between two nondegenerate states subject to the selection rules

$\Delta J = 0, \pm 1$ with $\Delta K = 0$, give rise to "parallel" bands. Spectroscopic constants obtained for the ν_3 parallel vibrational band of methyl chloride[18] are shown in Table I. Since methyl chloride is a prolate symmetric top, the rotational constant C appearing in the above equation is replaced by A.

Table I

Molecular Constants for ν_3=1 Vibrational State of $^{13}CH_3{}^{35}Cl$ and $^{13}CH_3{}^{37}Cl$ (in cm^{-1})

Constants	$^{13}CH_3{}^{35}Cl$		$^{13}CH_3{}^{37}Cl$	
ν_0	714.9111	(2)	708.9874	(3)
$(A_3-A_0)\times 10^3$	8.43	(1)	8.300	(4)
B_3	0.4232029	(6)	0.4164078	(2)
$D_3^J \times 10^7$	5.666	(3)	5.483	(*)
$D_3^{JK} \times 10^6$	6.303	(*)	6.140	(*)
$(D_0^K - D_3^K) \times 10^6$	1.0	(2)	0	
H_3^{JJ}	0	(*)	0	(*)
H_3^{JK}	0	(*)	0	(*)
$H_3^{KJ} \times 10^{10}$	2.5	(*)	4	(*)

*Constrained to the ground state value.

A point to note here, is that the selection rule $\Delta K = 0$ for the "allowed transitions," does not permit the determination of purely K-dependent coefficients namely A(or C), D_K, H_{KKK}, etc., in the energy level expression for symmetric tops. These coefficients can, however, be determined from "forbidden transitions", which violate the $\Delta K = 0$ selection rule[14,19,20].

Vibration-Rotation-Inversion Levels

Due to the large inversion splitting in Ammonia and its consequent repercussions on the vibration rotation energy levels, it has been the subject of numerous theoretical investigations and merits special mention. For molecules with trigonal symmetry, the general fourth order theory of the interactions due to matrix elements of the type $< J, k \ |H| \ J, k \pm 3n >$, which cause K-type splittings of the $k = \pm 3n$ rotational levels, has been discussed by Aliev and Watson[13]. For the inversion-rotation levels of NH_3, the theory has been suitably modified to account for the inversion motion and has been successfully applied to the treatment of precise data on the ground state and ν_2 band transitions. The operators which describe the $\Delta k = \pm 3n$ interactions in the ground and ν_2 states have been explicitly defined[21] and to fit the data to the available accuracy it was found necessary to

[a] The splitting parameter for the K=3 levels is sometimes denoted by η_3 in literature, in place of h_3. Using the symbol h_3, however, appears more appropriate since the symbol η is also commonly employed in denoting the centrifugal distortion effects of the Coriolis coupling interaction along the z axis, for degenerate vibrational levels.

Table II

Ground state and v2 state molecular parameters of 14NH3 (in cm-1)[a]

Parameter	Ground State	v_2 State	Parameter	Ground State	v_2 State
(s) g^o	0.[b]	932.4338787(98)	ΔB^o	0.79340312(95)	35.6881062(32)
$(s)_B$	9.94664268(75)	10.07017463(94)	ΔB	$-5.053222(68) \times 10^{-3}$	-0.18015883(52)
$(s)_{C-}$ $(s)_B$	-3.7191374(17)	-3.9818658(18)	$\Delta(C-B)$	$7.053516(99) \times 10^{-3}$	0.25167574(91)
$(s)_{D_J}$	$8.49460(41) \times 10^{-4}$	$1.130565(26) \times 10^{-3}$	ΔD_J	$-1.67810(20) \times 10^{-5}$	$-4.34232(21) \times 10^{-4}$
$(s)_{D_{JK}}$	$-15.78093(98) \times 10^{-4}$	$-2.422446(82) \times 10^{-3}$	ΔD_{JK}	$4.63532(50) \times 10^{-5}$	$11.89134(68) \times 10^{-4}$
$(s)_{D_K}$	$9.1383(11) \times 10^{-4}$	$1.52044(11) \times 10^{-3}$	ΔD_K	$-3.17569(41) \times 10^{-5}$	$-8.06754(57) \times 10^{-4}$
$(s)_{H_{JJJ}}$	$2.5914(51) \times 10^{-7}$	$0.55533(40) \times 10^{-6}$	ΔH_{JJJ}	$-3.8549(24) \times 10^{-8}$	$-0.61772(38) \times 10^{-6}$
$(s)_{H_{JJK}}$	$-9.056(19) \times 10^{-7}$	$-2.2281(16) \times 10^{-6}$	ΔH_{JJK}	$15.8387(73) \times 10^{-8}$	$2.4660(14) \times 10^{-6}$
$(s)_{H_{JKK}}$	$10.796(26) \times 10^{-7}$	$2.9346(29) \times 10^{-6}$	ΔH_{JKK}	$-21.4917(82) \times 10^{-8}$	$-3.2402(21) \times 10^{-6}$
$(s)_{H_{KKK}}$	$-4.151(20) \times 10^{-7}$	$-1.2455(21) \times 10^{-6}$	ΔH_{KKK}	$9.6701(49) \times 10^{-8}$	$1.40103(92) \times 10^{-6}$
$(s)_{G_{4J}}$	$-1.536(32) \times 10^{-10}$	$-0.2284(22) \times 10^{-9}$	ΔG_{4J}	$0.6236(10) \times 10^{-10}$	$0.4884(22) \times 10^{-9}$
$(s)_{G_{3JK}}$	$7.91(17) \times 10^{-10}$	$1.646(29) \times 10^{-9}$	ΔG_{3JK}	$-3.4223(44) \times 10^{-10}$	$-2.572(13) \times 10^{-9}$
$(s)_{G_{2J2K}}$	$-15.33(40) \times 10^{-10}$	$-4.151(29) \times 10^{-9}$	ΔG_{2J2K}	$6.9474(71) \times 10^{-10}$	$4.815(31) \times 10^{-9}$
$(s)_{G_{J3K}}$	$13.14(36) \times 10^{-10}$	$4.198(23) \times 10^{-9}$	ΔG_{J3K}	$-6.2095(57) \times 10^{-10}$	$-3.830(27) \times 10^{-9}$
$(s)_{G_{4K}}$	$-4.29(15) \times 10^{-10}$	$-1.460(61) \times 10^{-9}$	ΔG_{4K}	$2.0523(24) \times 10^{-10}$	$1.089(12) \times 10^{-9}$
$(s)_{L_{5J}}$	$0.888(62) \times 10^{-13}$	$-0.525(42) \times 10^{-13}$	ΔL_{5J}	$-05337(17) \times 10^{-13}$	$-1.314(42) \times 10^{-13}$
$(s)_{L_{4JK}}$	$-5.16(39) \times 10^{-13}$	$2.20(31) \times 10^{-13}$	ΔL_{4JK}	$3.7087(81) \times 10^{-13}$	$8.23(31) \times 10^{-13}$
$(s)_{L_{3J2K}}$	$13.2(12) \times 10^{-13}$	$-20.46(94) \times 10^{-13}$	ΔL_{3J2K}	$-10.123(16) \times 10^{-13}$	$-13.51(92) \times 10^{-13}$
$(s)_{L_{2J3K}}$	$-17.4(18) \times 10^{-13}$	$72.2(14) \times 10^{-13}$	ΔL_{2J3K}	$13.664(18) \times 10^{-13}$	$1.58(92) \times 10^{-13}$
$(s)_{L_{J4K}}$	$11.3(13) \times 10^{-13}$	$-90.3(86) \times 10^{-13}$	ΔL_{J4K}	$-9.153(12) \times 10^{-13}$	$12.0(11) \times 10^{-13}$
$(s)_{L_{5K}}$	$-2.78(40) \times 10^{-13}$	$37.0(30) \times 10^{-13}$	ΔL_{5K}	$2.4619(61) \times 10^{-13}$	$-7.06(36) \times 10^{-13}$
$(s)_{\eta^o_3}$	$3.011(88) \times 10^{-9}$	$2.845(45) \times 10^{-9}$	$\Delta\eta^o_3$	$1.11(18) \times 10^{-11}$	$-2.12(16) \times 10^{-10}$
$(s)_{\eta^J_3}{}^C$	$-6.090(39) \times 10^{-12}$	$-8.63(48) \times 10^{-12}$	a^o	$1.05(43) \times 10^{-4}$	$1.3266(11) \times 10^{-4}$
$(s)_{\eta_3}{}^{JC}$	$2.96(10) \times 10^{-15}$	$1.10(12) \times 10^{-14}$	a^J	0.[c]	$-3.758(82) \times 10^{-4}$
$(s)_{\eta_6}{}^C$	$3.72(20) \times 10^{-20}$	$3.14(96) \times 10^{-19}$	a^K	0.[c]	$-16.46(98) \times 10^{-4}$

[a]Values in parentheses are standard deviations of parameters, given in units of the last digit quoted.
[b]Constrained value.
[c]The difference between the constants for the symmetric and the antisymmetric states was constrained to zero.

include matrix elements of the operator involving $\Delta k = \pm 3n$ interactions with $n = 4$, and the details may be found in refs. [14, 21]. Results obtained by fitting extensive data on the ground and v_2 states of NH_3 are summarized in Table II. η_3 and η_6 in Table II stand for the $\Delta k = \pm 6$ and $\Delta k = \pm 12$ interactions which contribute to the diagonal terms for the special case, when $K = 3$ and $K = 6$ respectively, while α represents the off-diagonal $\Delta k = \pm 3$ interaction parameter. η^J_t, η^{JJ}_t, α^J etc., represent the J, K dependence of these parameters. The purely K dependent constants (C, D_k, H_{kkk} etc.) reported in the table were obtained from ground state combination differences derived from an extensive set of allowed and "forbidden transitions" to the v_4 state of NH_3[14]. In Table II the octic constants have been represented by G's while the next higher order constants by L's.

Rotational Energy Levels for Degenerate Vibrational States

The energy levels in a degenerate vibrational state for an oblate symmetric top are represented by the polynomial expression for the diagonal matrix elements in the form

$$E_v(J, k, l) = G_v + B_v[(J(J+1) - k^2] + C_v k^2 - 2(C\zeta)_v k l - D^V_J J^2(J+1)^2 - D^V_{JK} J (J+1)k^2 - D^V_K k^4 + \eta_{vJ} J(J+1)k l + \eta_{vK} k^3 l + H^V_J J^3 (J+1)^3 + H^V_{JK} J^2(J+1)^2 k^2 + H^V_{KJ} J(J+1)k^4 + H^V_K k^6 + \tau_{vJ} J^2(J+1)^2 k l + \tau_{vJK} J (J+1)k^3 l + \tau_{vK} k^5 l + \tau^*_{vK} k^3 l^3 \quad \ldots(10)$$

The above energy level expression is equally good for nondegenerate vibrational states ($l = 0$), in which case all the l-dependent terms would vanish. G_v, as before, stands for the pure vibrational contribution to the energy given by eq. (1), and the coefficients of terms in $k\ l$ represent the contribution of the z axis Coriolis coupling to the energy in the first order. τ and η's represent higher order centrifugal distortion corrections and ζ is the z axis Coriolis coupling

constant. The superscript v is to denote the vibrational dependence of the rotational and centrifugal distortion constants. (Note that some authors as in Table I denote the J k dependence of the coefficients by superscripts and vibrational dependence by subscripts).

In the absence of significant perturbations of the degenerate levels, the vibration-rotation transitions subject to the selection rules $\Delta J = 0, \pm 1$ with $\Delta k = \pm 1$ and $\Delta l = \pm 1$ (perpendicular band) may be fitted to the term value expressions derived from eq. (10). Again, it should be pointed out that the purely K-dependent terms (constants A or C, D_K, H_{KKK}) cannot be determined from an analysis of a single perpendicular band. Methods allowing such determinations involve, for example the use of combination differences obtained from three different perpendicular transitions[22], (Such as ν_t, $\nu_t + \nu_{t'}$ and $\nu_t + \nu_{t'} - \nu_t$) or from transitions to a degenerate state measured by infrared (absorption) and Raman (scattering) spectroscopy which have different selection rules[23] or from "forbidden transitions", as in the case of $^{14}NH_3$ and $^{15}NH_3$ molecules[14].

The determinable parameters are given in Table III for the case of the ν_4 band of CF_3I[24]. Centrifugal distortion constants up to quartic order only have been included in this analysis, and transitions involving the $k = 0$ and $k = 1$ levels were excluded from the fit.

Table III

Spectroscopic Parameters for the ν_4 Band of $^{12}CF_3I$ and $^{13}CF_3I$[a]

Molecule	$^{12}CF_3I$	$^{13}CF_3I$
$\bar{\nu}_4$	1187.62799(8)	1154.46889(14)
$\Delta(A-B) \times 10^4$	-7.7182 (22)	-7.1376 (39)
$[A_4(1-\zeta_4)-B_4]\times10^3$	-7.3047 (50)	-5.7941 (67)
B_4	0.05080267 (12)	0.05056786 (39)
B_0	0.05081124 (*)	0.0507696 (*)
$D_4^J\times10^8$	0.4568(11)	0.244 (23)
$D_0^J\times10^8$	0.549113(*)	0.54571(*)
$D_4^{JK}\times10^8$	3.317(31)	3.819(43)
$D_0^{JK}\times10^8$	3.311(*)	3.2956(*)
$D_4^K\times10^8$	0.797(33)	0.183(37)
$D_0^K\times10^8$	0.570(*)	0.570(*)
$\eta_4^J\times10^7$	-0.642(69)	-0.172(71)
$\eta_4^J\times10^7$	5.038(85)	2.208 (80)
Std. dev. (fit) $\times 10^4$	9.85	10.91
No. Lines assigned	1124	1257
No Lines Fitted	845	1100

All parameters are in cm^{-1}. The standard deviations given in parentheses are in units of the last digit quoted.

* denotes constrained constants.

$\bar{\nu}_4 = \nu_4 + (A\zeta)_4$

Off-Diagonal Matrix Elements in Quantum Numbers l and k

In most of the symmetric top molecules it is seldom possible to obtain a satisfactory fit to the rotation-vibration data involving excited degenerate states using the conventional power series expansion, due to perturbations arising from interactions between the energy levels. These interactions give rise to off-diagonal matrix elements connecting states with different k and l values which are no longer good quantum numbers, while k-l is still a good quantum number.

Three types of rotational matrix elements off-diagonal in l and k occur for symmetric top molecules[5]

$\langle v_t, l_t, k \,|H_2'|\, v_t, l_t \pm 2, k \pm 2\rangle$ ...type (A)

$\langle v_t, l_t, k \,|H_2'|\, v_t, l_t \pm 2, k \mp 1\rangle$ ...type (B)

$\langle v_t, l_t, k \,|H_2'|\, v_t, l_t \pm 2, k \mp 2\rangle$ ...type (C)

Type (A) referred to as l type doubling occurs for all symmetric tops, type (B) known as the "2, -1" interaction occurs for those having symmetry axes C_n with $n = 3, 5 \ldots$ and type (C) for $n = 4, 6, \ldots$ These matrix elements give rise to rotational l-type doublings and resonances, which can have profound influence on the observed spectra. It is the "2, -1" interaction term which is responsible for the numerous forbidden transitions to the degenerate ν_4 state of NH_3 reported in ref. [14].

Table IV lists spectroscopic constants for two perpendicular bands ν_{10} and ν_{11} of cyclopropane which are strongly affected by rotational l-type resonance (type A)[25,26]. The l-type interaction parameter is q and h_{42} is the coefficient of a fourth-order off-diagonal element:

$\langle v_t, l_t, k \,|H_4'|\, v_t, l_t \pm 2, k \mp 4\rangle$.

Vibration-Rotational Perturbations

The vibration-rotation levels of most symmetric top molecules are severely perturbed due to coupling of the rotational levels belonging to different vibrational states. Several off-diagonal matrix elements coupling levels with different k and l values subject to the condition $\Delta(k - l) = 0$ for all symmetric tops, and $\Delta(k - l) = \pm 3, \pm 6 \ldots$ for molecules with 3-fold axes of symmetry often need to be introduced in the analysis

Table IV
Spectroscopic constants of the ν_{11} and ν_{10} bands of Cyclopropane (in cm^{-1})

Parameter	ν_{11}	ν_{10}
ν_0	868.3549±0.0011	1028.3682±0.0011*
$(B' - B_0)\times10^{-3}$	-1.6742±0.0020	+0.0573±0.0015
$(C' - C_0)\times10^{-3}$	-1.8378±0.0020	-1.4053±0.0018
$q\times10^{-3}$	+5.8036±0.0021	+2.4731±0.0012
$(C\zeta)$	-0.40549±0.00002	-0.03479±0.00002
$\eta_J\times10^6$	-2.924±0.063	+0.237±0.043
$\eta_k\times10^6$	+0.050±0.069	-2.597±0.051
$(D_J'-D_J'')\times10^6$	+0.0495±0.0021	+0.0029±0.0014
$(D_{JK}'-D_{JK}'')\times10^6$	-0.1193±0.0042	-0.0124±0.0032
$(D_K'-D_K'')\times10^6$	+0.0694±0.0039	+0.0032±0.0031
$[h_{42}]\times10^8$	1.221±0.229	0.655±0.094
Standard deviation	0.0009	0.0008

*The error limits shown are 90% confidence intervals

of perturbations in the high resolution spectra of this class of molecules. The lowest lying vibrational-inversion-rotational levels of NH_3 for example, form a complicated system of interacting levels[27] with a strong Coriolis resonance between the ν_2 (nondegenerate) and ν_4 (degenerate) fundamental levels. A similar situation exists for the ν_1, ν_3 and $2\nu_4$ levels of NH_3 which are in resonance with the $2\nu_2 + \nu_4$ and $4\nu_2$ combination levels[28]. In all such situations it becomes mandatory to set up the secular determinant which includes the various off-diagonal matrix elements coupling the levels, and solve for the eigen values.

In most of the reported studies the authors explicitly mention the matrix elements and symbols used in describing the interaction parameters. Various authors choose to use different notations and it is not possible to give a generalised list of symbols for the various types of perturbation parameters. In the following section some attempt is made in drawing attention to the commonly used symbols, and some typical examples cited from literature. For more specific details one needs to refer to the original publications.

x-y Coriolis Coupling

Coriolis coupling between a degenerate (ν_t) and a nondegenerate (ν_s) vibrational level through rotation about the x, y axes is given by

$$\langle v_t,\ l_t = \pm1;\ J,\ k \pm 1\ |H|\ v_s,\ J,\ k\rangle$$
$$= \pm 2\zeta^{xy}\ [(\omega_t/\omega_s)^{1/2} + (\omega_s/\omega_t)^{1/2}]\ [J(J+1) - k(k\pm1)]^{1/2}$$

ζ^{xy} = the x-y Coriolis coupling constant

ω_t, ω_s = the vibrational frequencies of the fundamentals

The "**k-type doubling**" term coupling rotational levels of a degenerate and non-degenerate fundamental is given by

$$\langle v_t,\ l_t = \pm1;\ J,\ k \pm 2\ |H|\ v_s,\ J,\ k\rangle$$
$$= \sqrt{2}\ D\ [\{J(J+1) - k(k\pm1)\}\{J(J+1) - (k\pm1)(k\pm2)\}]^{1/2}$$

In literature ζ^{xy} is often represented by the notation C_{11} to indicate that the levels that are coupled differ in their k and l values by ±1 each i.e. $\Delta k = \pm1$; $\Delta l = \pm1$;

$(\Delta(k - l) = 0)$.

Similarly C_{21} would indicate the coefficient of the coupling term between rotational levels of the vibrational states satisfying the condition $\Delta k = \pm2$; $\Delta l = \mp1$; $(\Delta(k - l) = \pm3)$ for molecules with C_{3v} symmetry.

One of the earliest attempts to include the various perturbations in the analysis of the ν_1, ν_3 fundamentals of AsH_3 were by Olson *et al.* [29]. The matrix elements for the various off-diagonal perturbations used in the analysis of the data have been discussed in detail by the authors. The notations used in reporting the parameters are different from those commonly being used in the more recent literature and are therefore not reproduced here.

Fusina *et al.*[30] have applied the generalized Hamiltonian including the various perturbation terms outlined above, to the analyses of the ν_2 and ν_4 band systems in AsH_3 [30] and ND_3 [31]. The notations adopted by them are similar to those introduced in the original work of Amat *et al.*[8]

In the notation H_{mn} used for the various terms in the expansion of the vibration-rotation Hamiltonian given in Table V of ref. [30], the first subscript indicates the degree in the vibrational operators (q and/or p) and the second subscript the degree in the components of the total angular momentum J[5,30]. The nomenclature of the coefficients is similar to that used by Tarrago *et al.*[32,33]. The subscripts of the constants are suggestive of the Δk and Δl values of the vibration-rotational levels coupled by the corresponding interaction term (e.g., C_{11} denotes the Coriolis interaction constant coupling rovibration levels which differ in their k and l values by ±1 each), C_{21} represents the k type

doubling which couples levels with $\Delta k = \pm 2$ and $\Delta l = \mp 1$ of the two interacting states.

The comparison of the matrix elements given by Olson *et al.*[26] with those given in Table V is straight forward if one recognizes that $[J(J+1) - k(k+1)]$ has been replaced by $F(J, k)$ for brevity. In setting up the matrix elements in Table V the authors have assumed the phase convention of Di Lauro and Mills[34] for the vibration-rotation basis functions. The parameters obtained from the fit to the vibration-rotation data on the ν_2 and ν_4 bands of AsH_3 as taken from ref. [30] are given in Table VI.

Table V

Off-Diagonal Matrix Elements of the vibration-Rotation Hamiltonian
(The basis functions used are $|v_2 v_4^l Jk\rangle = |1\ 0^0\ Jk\rangle$ *and* $|0\ 1^{\pm 1}\ Jk\rangle$*)*

$\|v_2 v_4^l Jk\rangle = \|1\ 0^0\ Jk\rangle$ and $\|0\ 1^{\pm 1}\ Jk\rangle$
$\langle 0\ 1^{+1} Jk+1 \| H_{21}+H_{23} \| 1\ 0^0 Jk\rangle = \sqrt{2}\{c_{11}^1 + c_{11}^{3a} J(J+1) + c_{11}^{3b}[k^2+(k+1)^2]\} F(J, k)$
$\langle 1\ 0^0 Jk+1 \| H_{21}+H_{23} \| 0\ 1^{-1} Jk\rangle = -\sqrt{2}\{c_{11}^1 + c_{11}^{3a} J(J+1) + c_{11}^{3b}[k^2+(k+1)^2]\} F(J, k)$
$\langle 0\ 1^{+1} Jk+1 \| H_{22} \| 1\ 0^0 Jk\rangle = \langle 1\ 0^0 Jk+1 \| H_{22} \| 0\ 1^{-1} Jk\rangle = \sqrt{2} c_{11}^2 (2k+1) F(J, k)$
$\langle 0\ 1^{-1} Jk+1 \| H_{22}+H_{24} \| 0\ 1^{+1} Jk\rangle = 2\{[q_{12}^4 + f_{12}^{4,J} J(J+1)](2k+1) + f_{12}^{4,k}[k^3+(k+1)^3]\} F(J, k)$
$\langle 1\ 0^0 Jk+2 \| H_{22}+H_{24} \| 0\ 1^{+1} Jk\rangle = \sqrt{2}\{c_{21}^2 + c_{21}^{4a} J(J+1) + c_{21}^{4b}[k^2+(k+2)^2]\} F(J, k) F(J, k+1)$
$\langle 0\ 1^{-1} Jk+2 \| H_{22}+H_{24} \| 1\ 0^0 Jk\rangle = \sqrt{2}\{c_{21}^2 + c_{21}^{4a} J(J+1) + c_{21}^{4b}[k^2+(k+2)^2]\} F(J, k) F(J, k+1)$
$\langle 1\ 0^0 Jk+2 \| H_{23} \| 0\ 1^{+1} Jk\rangle = -\sqrt{2}\{c_{21}^3 (2k+2) F(J, k) F(J, k+1)$
$\langle 0\ 1^{-1} Jk+2 \| H_{23} \| 1\ 0^0 Jk\rangle = -\sqrt{2} c_{21}^3 (2k+2) F(J, k) F(J, k+1)$
$\langle 0\ 1^{+1} Jk+2 \| H_{22}+H_{24} \| 0\ 1^{-1} Jk\rangle = 2\{[q_{22}^4 + f_{22}^{4,J} J(J+1) + f_{21}^{4,k}[k^2+(k+2)^2]\} F(J, k) F(J, k+1)$
$\langle 1\ 0^0 Jk+3 \| H_{24}+H_{26} \| 1\ 0^0 Jk\rangle = \{[\varepsilon^2 + \varepsilon_J^2 J(J+1)](2k+3) + \varepsilon_k^2[k^3+(k+3)^3]\} F(J, k) F(J, k+1) F(J, k+$
$\langle 0\ 1^{\pm 1} Jk+3 \| H_{24}+H_{26} \| 0\ 1^{\pm 1} Jk\rangle = \{[\varepsilon^2 + \varepsilon_J^2 J(J+1)](2k+3) + \varepsilon_k^2[k^3+(k+3)^3]\} F(J, k) F(J, k+1) F(J, k-$
$\langle 0\ 1^{-1} Jk+4 \| H_{24} \| 0\ 1^{+1} Jk\rangle = 2 f_{42}^4 F(J, k) F(J, k+1) F(J, k+2) F(J, k+3)$
$F(J, k) = \langle J\ k+1 \| Jx - iJy \| Jk\rangle = [J(J+1) - k(k+1)]^{1/2}$

Table VI

Spectroscopic constants for the ν_2=1 and ν_4=1 vibrational states of AsH_3[a]

Constant	Value		Unit	Constant	Value		Unit
ν_2	906.7518314	(702)	cm^{-1}	τ_{4j}	2.00277	(4469)	10^{-7} cm^{-1}
B_2	3.73876124	(2519)	cm^{-1}	τ_{4JK}	-1.70683	(4532)	10^{-7} cm^{-1}
C_2	3.52617467	(1055)	cm^{-1}	τ_{4K}	0.0[b]		
D_J^2	9.898050	(4925)	10^{-5} cm^{-1}	c_{11}^1	1.9314506	(1494)	cm^{-1}
D_{JK}^2	-1.312698	(1653)	10^{-4} cm^{-1}	c_{11}^2	5.87050	(3150)	10^{-3} cm^{-1}
D_K^2	1.232106	(1730)	10^{-4} cm^{-1}	c_{11}^{3a}	-1.624538	(5220)	10^{-4} cm^{-1}
H_J^2	6.71589	(7236)	10^{-9} cm^{-1}	c_{11}^{3b}	4.0411	(1407)	10^{-5} cm^{-1}
H_{JK}^2	-1.41758	(2850)	10^{-8} cm^{-1}	c_{21}^2	1.425386	(9375)	10^{-2} cm^{-1}
H_{KJ}^2	9.5015	(4866)	10^{-9} cm^{-1}	c_{21}^3	-3.70871	(8060)	10^{-5} cm^{-1}
H_K^2	5.8943	(2483)	10^{-9} cm^{-1}	c_{21}^{4a}	8.3835	(6673)	10^{-7} cm^{-1}
ν_4	999.2245023	(589)	cm^{-1}	c_{21}^{4b}	3.51605	(6545)	10^{-6} cm^{-1}
B_4	3.76607139	(1330)	cm^{-1}	q_{22}^4	-1.546718	(6325)	10^{-3} cm^{-1}
C_4	3.48044359	(1033)	cm^{-1}	$f_{22}^{4,J}$	0.0[b]		
D_J^4	1.0194343	(3198)	10^{-4} cm^{-1}	f_{22}^{4K}	0.0[b]		
D_{JK}^4	-1.3021101	(9730)	10^{-4} cm^{-1}	q_{12}^4	-1.456125	(7345)	10^{-2} cm^{-1}
D_K^4	1.1382049	(9174)	10^{-4} cm^{-1}	$f_{12}^{4,J}$	4.04594	(5788)	10^{-6} cm^{-1}
H_J^4	7.45981	(4432)	10^{-9} cm^{-1}	$f_{12}^{4,K}$	0.0[b]		
H_{JK}^4	-1.30882	(1695)	10^{-8} cm^{-1}	f_{42}^4	-1.2303	(1234)	10^{-7} cm^{-1}
H_{KJ}^4	5.1734	(2983)	10^{-9} cm^{-1}	ε^2	2.372830	(7712)	10^{-5} cm^{-1}
H_K^4	7.3823	(1654)	10^{-9} cm^{-1}	ε^4	2.056183	(9168)	10^{-5} cm^{-1}
$(c\zeta)_4$	-1.583546905	(9233)	cm^{-1}	$\varepsilon_J^2 - \varepsilon_J^4$	-3.96726[b]		10^{-9} cm^{-1}
η_{4J}	-2.320723	(1915)	10^{-4} cm^{-1}	$\varepsilon_K^2 - \varepsilon_K^4$	2.55109[b]		10^{-9} cm^{-1}
η_{4K}	0.0[b]						

[a]Standard deviations in parentheses refer to the least significant digits.
[b]Fixed at the ground state value or zero.

At this juncture it seems appropriate to point out the importance of the phase factor of the wave functions in the evaluation of the off-diagonal matrix elements of the secular determinant. While the choice of phase has no effect on the diagonal matrix elements, it can lead to changes in the relative signs of the off-diagonal matrix elements. This phase dependence often leads to confusion regarding the signs of some of the parameters in the molecular Hamiltonian, associated with the off-diagonal matrix elements such as the l-type doubling constant for linear and symmetric top molecules. When several vibration-rotation interactions need to be considered as in the treatment of high resolution data on AsH_3, PH_3 etc., outlined here, it is important to be consistent in the choice of the phase convention employed in evaluating the various matrix elements. Moreover, in any treatment, the phase choice adopted for the vibration-rotation basis functions needs to be explicitly stated to enable a more meaningful comparison of results from different sources. A detailed and useful discussion on the effect of phase choices of vibration-rotational wave functions on the labelling of K and l-type doubling of molecular energy levels has been presented by Yamada[35].

With the advent of high speed computers setting up the secular determinant with various off-diagonal interaction terms and simultaneous analysis of the data of the various perturbing levels is becoming increasingly popular, although results reported so far are limited to just a handful of molecules. On the other hand, for several symmetric top molecules, the secular determinant involving the $\Delta l = \pm 2$ interaction terms (l-type doubling and l-type resonance) and the x-y Coriolis interaction have been set up and solved with a reasonable degree of success[36,37].

It should be noted at this point that there are strong correlations between off-diagonal matrix elements, as well as between certain diagonal and off-diagonal matrix elements[38,39]. These correlations lead to strongly effective values of parameters and therefore a comparison between different studies when a correct reduction has not been performed is usually not possible. Methods to identify these correlations and effective means of dealing with them have been elegantly described by Sarka *et al.*[1] in a recent publication. The results are briefly outlined in the following section.

Correlation-Free Reduced Forms of Hamiltonians

A problem frequently encountered in fitting the molecular constants to experimental data is the strong correlation that exists between the fitted parameters. The cause for the indeterminacy of some of the fitted parameters could be of experimental origin. The solution to this type of problems would be to use adequate data (e.g. high J, K transitions to determine higher order distortion constants) or appropriate data (e.g. forbidden transitions to determine purely K dependent parameters A or C, D_k, H_{kkk} etc.) representative of the parameters to be determined.

A more serious problem of correlations between the parameters arises from the inherent properties of the Hamiltonian and the solution lies in arriving at correlation free "reduced" forms of the Hamiltonian. The procedure of predicting the correlations, finding the proper constraints and determining how the constraints transform the values of the non constrained parameters is called reduction. In a recent review Sarka *et al.*[1] have discussed methods to identify and remove such correlations by selecting appropriate constraints. The use of "multiple fitting" schemes in testing the internal consistency of the theory, data and analysis have been illustrated with several examples for molecules with C_{3V} symmetry.

To illustrate the application of the above procedures typical results reported for the first excited $v_{10} = 1$ isolated degenerate vibrational state of CF_3CCH are reproduced in Table VII. The off-diagonal matrix elements in quantum numbers l and k included in the description of the degenerate vibrational state of a molecule with C_{3V} symmetry are reproduced below in order to explain the notations of the parameters reported in the Table

(i) The "2, 2" l-Type Interaction

$$< l^{+1},\ J,\ k+2\ \ (H_{22} + H_{24} + H_{26}) l^{-1};\ J,\ k>$$
$$= 2\{\ q_{22} + f^{J}_{22}\ J(J+1) + f^{JJ}_{22}\ J^2(J+1)^2$$
$$+ [f^{K}_{22} + f^{JK}_{22} J(J+1)$$
$$+ f^{KK}_{22}\ k(k+2)]\ k(k+2)\}\ F(J,k)\ F(J,k+1)$$

where $F(J,k) = [J(J+1) - k(k+1)]^{1/2}$,

q_{22} = the "2 , 2" l type interaction coefficient,

f^{J}_{22}, f^{K}_{22}, f^{JK}_{22} = are the J & K dependent higher order coefficients of the l-type interaction term.

(The "2, 2" interaction term couples levels with $\Delta k = \pm 2$ and $\Delta l = \pm 2$)

i.e. $\Delta(k - l) = 0$.

Table VII

Parameters of the v_{10}=1 Vibrational State of CF3C ≡ CH (in units of MHz)[a]

Parameter	Set A	Set B
B	2883.461090(112)	2883.461306(108)
A	5718.8562(74)	5718.84367(71)
$(A\zeta)^{z}_{10}$	3293.5662(73)	3293.5541(71)
$D_J/10^{-3}$	0.275890(35)	0.275891(33)
$D_{JK}10^{-3}$	6.23932(48)	6.23928(46)
D_K10^{-3}	-5.23[b]	-5.23[b]
$H_J/10^{-9}$	0.0349(34)	0.0348(33)
$H_{JK}/10^{-9}$	17.824(45)	17.824(43)
$H_{KJ}/10^{-9}$	-12.13(69)	-12.19(66)
H_K	0.[b]	0.[b]
$\eta_J/10^{-3}$	25.06569(91)	25.50129(89)
$\eta_K/10^{-3}$	-18.7562(44)	-19.1916(42)
$\tau_J/10^{-6}$	-0.084651(94)	-0.086360(93)
q_{22}	-0.90515827(18)	-0.90515835(18)
$f^{J}_{22}/10^{-6}$	1.095439(90)	1.074585(86)
f^{JJ}_{22}/10-12	-2.3707(104)	-2.3379(99)
q_{12}	0.[b]	0.716329(159)
$f^{J}_{12}/10^{-6}$	0.[b]	-2.668(24)
$d/10^{-3}$	0.275247(64)	0.[b]
$d_J/10^{-9}$	-0.4555(94)	0.[b]
$f_{42}/10^{-9}$	2.159(110)	-18.5313(117)
σ[c]/kHz	4.34	4.17
Number of data	633	

[a])Values in parentheses are one standard deviation in units of the last digit quoted.
[b]) Constrained value
[c]) Standard deviation of the fit

(ii) *The "2, –1" l-Type Interaction*

$$< l^{1}; J, k+1 \,|(H_{22} + H_{24})|\, l^{+1}; J, k> = 2\{[q_{42} + f^{J}_{12} J(J+1)](2k+1) + f^{K}_{12}[k^3 + (k+1)^3]\} F(J,k)$$

q_{12} = the "2, -1" *l*-type interaction coefficient, f^{J}_{12}, f^{K}_{12} = the *J* and *K* dependent higher order coefficients of the "2, -1" interaction term

(The "2, -1" interaction term couples levels with $\Delta l = \pm 2$ and $\Delta k = \mp 1$ i.e. $\Delta(k - l) = \mp 3$)

(iii) *The "2 , -4" l-Type Interaction Term*

$$< l^{1}; J, k+4 \,|(H_{24} + H_{26})|\, l^{+1}; J, k> = 2\{[f_{42} + f^{J}_{42} J(J+1) + f^{K}_{42} k(k+4)] \times \prod_{i=0}^{i=3} F(J, k+i)$$

f_{42} = the "2, - 4" interaction coefficient, f^{J}_{42}, f^{K}_{42} = the *J* and *K* dependent higher order coefficients of the "2, - 4" interaction term. (The "2, - 4" interaction term couples levels with $\Delta k = \pm 4$ and $\Delta l = \mp 2$)

i.e.($\Delta(k - l) = \pm 6$).

(iv) *The "0 , ±3" Interaction Term*

$$< l^{1}; J, k+3 \,|(H_{22} + H_{25})|\, l^{1}; J, k> = l\{d_t + d^{J}_{t} J(J+1) + d^{K}_{t}[k^2 + (k+3)^2]\} \times F(J,k)\, F(J, k+1)\, F(J, k+2)$$

where $l = \pm 1$,

d_t is the $\Delta k = \pm 3$ interaction coefficient, d^{J}_{t}, d^{K}_{t} are the *J* and *K* dependent corrections to the $\Delta k = \pm 3$ interaction term.

The "0 , ±3" interaction is defined by di Lonardo *et al.*[29] by the matrix element

$$< l^{\pm 1}; J, k+3 \,|(H_{24} + H_{26})|\, l^{\pm 1}; J, k> = \{[\varepsilon + \varepsilon_j J(J+1)](2k+3) + \varepsilon_k[k^3 + (k+3)^3]\} \times F(J,K)\, F(J, k+1)\, F(J, k+2)$$

The relation between the two interactions has been discussed by Sarka[40] and the coefficient d_t is shown to be actually a coefficient in a transformed effective rotational Hamiltonian which has the following relation to the "original" coefficient $d^{(1)}_{t}$ and the coefficient ε

$$d_t = d^{(1)}_{t} - 6\varepsilon(A\zeta^{z}_{t}) / (A_0 - B_0) \qquad ...(11)$$

The parameters of the "2, -1" interaction term, q_{12}, f^{J}_{12} are found to be correlated with the coefficients d_t, d^{J}_{t} of the $\Delta k = \pm 3$ interaction term. The parameters obtained from the two fits with q_{12}, f^{J}_{12} constrained to zero (Q Reduction) and d_t, d^{J}_{t} fixed to zero (*D* reduction) are compared in Table VII for the $v_{10} = 1$ vibrational state of $CF_3C \equiv CH$ [41].

The non-constrained parameters from the two fits are found to be in very good agreement. The relationships between the constrained parameters are given by

$$q^{B}_{12} = q_{12} + F\, d_t = F\, d^{A}_{t} \qquad ...(12)$$

$$\text{and } n^{B}_{J} - n^{A}_{J} = -(n^{B}_{K} - n^{A}_{K}) = -4q_{12}\, q^{B}_{12}/(q_{22} F) \qquad ...(13)$$

$$\text{where } F = -(2\,(A\delta)^{Z}_{t} + A_0 - B_0)/(4q_{22}) \qquad ...(14)$$

The parameter *F* is fully determined by either of the two fits. The superscripts *A* and *B* refer to the *D* and *Q* reductions respectively. From the results

of the two fits (D and Q reductions) as well as the above expressions one can calculate the "true" coefficients q_{12} and d_t. The true values for η_J and η_K can also be calculated using the equations

$$\eta_J = \eta_J^B + 4d_t\, q_{12}/(q_{22}) \quad ...(15)$$

$$\eta_K = \eta_K^B + 4d_t\, q_{12}/(q_{22}) \quad ...(16)$$

In the absence of the constraints used, the non-correlated parameters would be expected to assume widely differing values due to the ill conditioning of the normal matrix.

Table VIII

Demonstration of the unitary equivalence of the two sets of parameters (MHz) the v_{10}=1 Vibrational State of $CF_3C \equiv CH$

Parameter	Value
$\eta_J^B - \eta_K^A$	0.00043560(126)
$\eta_J^B - \eta_J^A$	-0.0004354(61)
q_{12}^B (*see*[a])	0.71633(16)
q_{12}^B (*see*[b])	0.71632(17)
Derived "True" parameters[c]	
q_{12}	0.3581(12)
$d_t/10^{-4}$	1.376(5)
$\eta_J/10^{-3}$	25.2835(14)
$\eta_K/10^{-3}$	-18.9738(42)

[a]) Fitted value
[b]) Calculated by using eq. (12)
[c]) Calculated with eqs. (12,15,16)

The excellent agreement between the fitted values of the parameters (Table VII) and the values calculated from the above relationships (shown in Table VIII) for the v_{10} = 1 vibrational state of $CF_3C \equiv CH$ illustrates the internal consistency of the theory, data and analysis employed in these studies. Failure to recognise these correlations on the contrary could lead to widely varying values of the fitted parameters making intercomparison of results from different sources or "multiple fits" meaningless.

Appendix

List of Symbols for Symmetric Top Molecules

The Vibrational Energy Term (Diagonal in Quantum Nos. v and l)

$$G(v, l) = \sum \omega_s(v_s + {}^1/_2) + \sum \omega_s(v_t + 1) + \sum x_{ss'} (v_s + {}^1/_2)(v_{s'} + {}^1/_2) + \sum^{s} x_{st} (v_s + {}^1/_2)(v_t + 1) + \sum_{t \geq t'} x_{tt'} (v_t + 1)(v_{t'} + 1) + \sum_{t \geq t'} g_{tt'}\, l_t\, l_{t'}$$

$G(v, l)$ = vibrational term value

ω_s = the harmonic frequency of the s^{th} non-degenerate normal mode

ω_t = the harmonic frequency of the t^{th} degenerate normal mode

$x_{ss'}$, $x_{tt'}$, x_{st} = the anharmonic constants (2nd order)

$g_{tt'}$ = contribution of vibrational angular momenta l_t, $l_{t'}$, to the vibrational energy (t and t' designate degenerate bending modes)

The Rotational Energy of the Nondegenerate Vibrational State of a Symmetric Top molecule (upto Sextic Order)

$$E(J, K) = G_v + B_X J(J+1) + (B_Z - B_X) K^2 - D_J \{J(J+1)\}^2 - D_{JK} J(J+1)K^2 - D_K K^4 + H_J \{J(J+1)\}^3 + H_{JK}\{J(J+1)\}^2$$

Conclusion

The vibration-rotation Hamiltonians used in the interpretation of high resolution molecular spectra of symmetric top molecules have been briefly reviewed. The various off-diagonal matrix elements required to take into account the different types of vibration-rotation perturbations of the energy levels of molecules with C_{3v} symmetry have been discussed, along with the symbols commonly used in reporting the molecular parameters. The importance of using correlation free "reduced" Hamiltonians to eliminate ambiguities in the reported parameters has also been discussed. Typical examples have been presented to illustrate the symbolism or nomenclature used in reporting molecular constants and perturbation parameters obtained from the analysis of high resolution molecular spectra.

For convenience the expressions for the energy levels and the off-diagonal matrix elements for the various types of perturbations in symmetric top molecules are summarised in the Appendix, along with the definitions of the molecular constants and perturbation parameters.

With the high sensitivity, high resolution capability, and wide spectral coverage provided by Fourier transform instruments in the infrared region, "global fit" of the spectral data including several interacting bands is becoming increasingly common, and becomes mandatory in several cases, if the data have to be fitted within the limits of the experimental accuracy. With the availability of high speed computers, the problem no longer appears formidable.

Acknowledgement

Thanks are due to Dr M N Deo for help in preparing the manuscript.

$K^2 + H_{KJ}\ J\ (J+1)\ K^4 + H_K\ K^6 + E_{-K,\ K}$

G_v = Pure vibrational contribution to the energy

B_X = effective rotational constant along x axis

$^*B_Z$ = effective rotational constant along z axis (chosen as unique axis)

D_J, D_{JK}, D_K = quartic centrifugal distortion constants

H_J, H_{JK}, H_{KJ}, H_K = sextic centrifugal distortion constants

$E_{-3,3}$ = $\pm\ h_3\ J\ (J+1)\ [J\ (J+1) - 2]\ [J\ (J+1) - 6]$ (for molecules with 3 or 6 fold axes of symmetry)

$E_{-2,2}$ = $\pm\ [d_2 + h_2\ J\ (J+1)]\ J\ (J+1)\ [J\ (J+1) - 2]$ (for molecules of point group symmetry D_{2d}, C_{4v}, D_4, D_{4h} . . . . .)

** h_3; d_2, h_2 = splitting constants for K=3 and K=2 levels respectively (d_2 and h_2 are correlated and cannot be determined independently)

$^*B_Z$ = A for prolate sym. tops. ($A < B = C$)

= C for oblate sym. tops. ($A = B < C$)

** splitting of the K=3 and K=6 levels have sometimes been denoted in literature by η_3 and η_6.

The Rotational Energy of the Degenerate Vibrational State of a Symmetric Top Molecule (upto Sextic Order)*

The matrix element of the effective Hamiltonian for the doubly degenerate vibrational state of a symmetric top molecule which is diagonal in all the quantum Nos. v, k and l:

$$E_v\ (J, K, l) = G_v + B_X\ J\ (J+1) + (B_Z - B_X)k^2 - 2\ (C\zeta)_l^z\ k\ l + \eta_J\ J(J+1)\ k\ l + \eta_k\ k^3\ l + \tau_J\ J^2\ (J+1)^2\ k\ l + \tau_{JK}\ J\ (J+1)k^3\ l + \tau_K\ k^5\ l + D_J\ J^2\ (J+1)^2 - D_{JK}\ J\ (J+1)\ k^2 - D_k\ k^4 + H_J\ J^3\ (J+1)^3 + H_{JK}\ J^2\ (J+1)^2\ k^2 + H_{KJ}\ J\ (J+1)\ k^4 + H_k\ k^6 + \ldots\ldots$$

G_v = The vibrational contribution to the energy

ζ_l^z = the z axis Coriolis coupling constant usually reported as $C\zeta$ for oblate or $A\zeta$ for prolate symmetric tops

η_J, η_K = quartic centrifugal distortion correction coefficients of the Coriolis coupling term

τ_J, τ_{JK}, τ_K = sextic centrifugal distortion correction coefficients of the Coriolis coupling term

* when $l = 0$, the expression reduces to that for a nondegenerate state

The Off-Diagonal Matrix Elements in Quantum Numbers l and k

For the doubly degenerate vibrational level (E) of a symmetric top molecule with C_{3v} symmetry there are two essential resonances that need to be considered.

(A) The "2, 2" l - Type Interaction

$$\langle l^{l+1};\ J,\ k+2\ |(H_{22} + H_{24} + H_{26})|\ l^{l-1};\ J,\ k\rangle$$

$$= 2\{q_{22} + f_{22}^J\ J\ (J+1) + f_{22}^{JJ}\ J^2\ (J+1)^2 + [f_{22}^K + f_{22}^{JK}\ J\ (J+1) + f_{22}^{KK}\ k\ (k+2)]\ k\ (k+2)\}\ F\ (J,\ k)\ F\ (J,\ k+1)$$

where $F\ (J,\ k) = [J\ (J+1) - k\ (k+1)]^{1/2}$,

q_{22} = the "2 , 2" l type interaction coefficient,

f_{22}^J, f_{22}^K, f_{22}^{JK} = are the J & K dependent higher order coefficients of the l-type interaction term.

(The "2 , 2" interaction term couples levels with $\Delta k = \pm 2$ and $\Delta l = \pm 2$) i.e. $\Delta(k - l) = 0$.

(B) The "2, –1" l - Type Interaction

$$\langle l^{l-1};\ J,\ k+1\ |(H_{22} + H_{24})|\ l^{l+1};\ J,\ k\rangle$$

$$= 2\{[q_{12} + f_{12}^J\ J\ (J+1)]\ (2k+1) + f_{12}^K\ [k^3 + (k+1)^3]\}\ F(J,\ k)$$

q_{12} = the "2, -1" l-type interaction coefficient,

f_{12}^J, f_{12}^K = the J and k dependent higher order coefficients of the "2, -1" interaction term. (The "2, -1" interaction term couples levels with $\Delta l = \pm 2$ and $\Delta k = \mp 1$ i.e. $\Delta(k - l) = \mp 3$).

(C) The "2 , - 4" l Type Interaction Term

$$\langle l^{l-1};\ J,\ k+4\ |(H_{24} + H_{26})|\ l^{l+1};\ J,\ k\rangle$$

$$= 2\ [f_{42} + f_{42}^J\ J\ (J+1) + f_{42}^K\ k(k+4)]\ \times \prod_{i=0}^{i=3} F\ (J,\ k+i)$$

f_{42} = the "2, -4" interaction coefficient,

f_{42}^J, f_{42}^K = the J and K dependent higher order coefficients of the "2, - 4" interaction term . (The "2, - 4" interaction term couples levels with $\Delta k = 4$ and $\Delta l = \mp 2$) i.e. $(\Delta(k - l) = 6)$.

(D) The "0 , ± 3" Interaction Term

$$\langle l^{l};\ J,\ k+3\ |(H_{22} + H_{25})|\ l^{l};\ J\ ,\ k\rangle$$

$$= l\{d_t + d_t^J\ J\ (J+1) + d_t^K\ [k^2 + (k+3)^2]\}\ F(J,\ k)\ F\ (J,\ k+1)\ F\ (J,\ k+2)$$

where $l = \pm 1$

d_t = the $\Delta k = \pm 3$ interaction coefficient, d_t^J, d_t^K = the J and K dependent corrections to the $\Delta k = \pm 3$ interaction term.

x-y Coriolis Coupling

Coriolis coupling between a degenerate (v_t) and a nondegenerate (v_s) vibrational level through rotation about the x, y axes is given by

$$\langle v_t,\ l_t = \pm 1;\ J,\ k \pm 1\ |H|\ v_s,\ J,\ k\rangle$$

$$= 2\zeta^{xy}\ [(\omega_t/\omega_s)^{1/2} + (\omega_s/\omega_t)^{1/2}]\ [J\ (J+1) - k(k \pm 1)]^{1/2}$$

ζ^{xy} = the x-y Coriolis coupling constant

ω_t, ω_s = the vibrational frequencies of the fundamentals

In literature ζ^{xy} is often represented by the notation C_{11} to indicate that the levels that are coupled differ in their k and l values by ±1 each i.e. $\Delta k = \pm 1$; $\Delta l = \pm 1$; $(\Delta(k - l) = 0)$. Similarly C_{21} would indicate the coefficient of the coupling term between rotational levels of the vibrational states satisfying the condition $\Delta k = \pm 2$; $\Delta l = \mp 1$; $(\Delta(k - l) = \pm 3)$ for molecules with C_{3v} symmetry.

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