Interpretation of low-resolution spectra of Q branches of triply degenerate vibration-rotation fundamental bands of spherical top molecules

F. Michelot, J. Moret-Bailly

► To cite this version:

F. Michelot, J. Moret-Bailly. Interpretation of low-resolution spectra of Q branches of triply degenerate vibration-rotation fundamental bands of spherical top molecules. *Journal de Physique Lettres*, 1978, 39 (16), pp.275-277. 10.1051/jphyslet:019780039016027500 . jpa-00231496

HAL Id: jpa-00231496

<https://hal.science/jpa-00231496>

Submitted on 1 Jan 1978

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

LE JOURNAL DE PHYSIQUE-LETTRES

Classification
Physics Abstracts
33.10 — 33.20E — 33.70

INTERPRETATION OF LOW-RESOLUTION SPECTRA OF Q BRANCHES OF TRIPLY DEGENERATE VIBRATION-ROTATION FUNDAMENTAL BANDS OF SPHERICAL TOP MOLECULES

F. MICHELOT and J. MORET-BAILLY

Laboratoire de spectrométrie moléculaire (*)
Université de Dijon, 6, Bd Gabriel, 21000 Dijon, France

(Reçu le 5 mai 1978, accepté le 29 juin 1978)

Résumé. — L'emploi de valeurs explicites approchées de coefficients de Clebsch-Gordan adaptés à la symétrie cubique permet d'obtenir les fréquences des bandes de vibration-rotation triplement dégénérées des molécules *touties sphériques* sous une forme analytique valable dans les *amas* et hors des *amas*. Si une branche Q n'est pas résolue, ses pics d'absorption sont donnés par une formule explicite simple.

Abstract. — Approximate explicit values of vector coupling coefficients adapted to cubic symmetry enable analytic formulas to be obtained for the frequencies of the fundamental bands of spherical top molecules. The frequencies of the absorption peaks of unresolved Q branches are given by explicit formulas.

The use of vector coupling coefficients adapted to cubic symmetry $F_{A_1pp}^{(4JJ)}$ introduced by Moret-Bailly [1] enables the frequencies of triply degenerate vibration-rotation fundamental bands of spherical top molecules, tetrahydrides and, more recently, hexafluorides [2, 3] to be computed. Unfortunately, it is not possible to obtain exact values for most F coefficients and one must use numerical tables computed by Moret-Bailly [4], Dang Nhu (unpublished) and Krohn [5].

For a given value of J , $F_{A_1pp}^{(4JJ)}$ coefficients display a typical *tetrahedral structure* quite apparent in simple spectra : so, the assignment of lines is easy and initial computations can be made, allowing in a later step a very precise computer calculation of frequencies.

In hexafluorides, the rotational quantum number J may be very large, so that the number of lines in a Q branch is correspondingly large : a complete resolution of the spectra implies the use of Doppler free spectroscopy [6] available only for a small number of lines. Diode laser spectroscopy [2, 7] gives spectra, whose study is very difficult for Q branches [8].

McDowell *et al.* [8] drew a graph of Q branch line frequencies *versus* J ; for a given value of J , it is almost a graph of the F_4 coefficients, in which the highest and lowest values are grouped into the clusters noticed for the first time by Dorney and Watson [9]. McDowell *et al.* [8] observed that interpolation between the points which correspond to the clusters leads to regular curves for which they introduced the names $Q_A, Q_B, \dots$ on one side ... Q_Y, Q_Z on the other side (Fig. 1). They show that the maximum intensity (bandheads) of the unresolved structure of a Q branch occurs as shown by the arrows, at frequencies for which

$$\frac{\partial Q(J, p)}{\partial J} = 0 \quad (1)$$

McDowell *et al.* could obtain these beautiful results for the Q branch of ν_3 of SF_6 because SF_6 is the easiest hexafluoride to study, so that its spectrum was quite good ; we propose a method still applicable for spectra with a lower resolution.

McDowell *et al.* did not write equation (1) because the derivation implies analytical values of $Q(J, p)$, i.e. of the vector coupling coefficients.

Approximate formulas for the $F_{A_1pp}^{(4JJ)}$ coefficients were recently given by Harter and Patterson [10, 11],

(*) Equipe de recherche associée au CNRS.

FIG. 1. — Frequencies of the clusters versus J , and spectrum (See ref. [8].)

but we prefer the previous results of Michelot and Moret-Bailly [12, 13] which may easily be made more explicit [14] as follows :

$$P(J, S, U) = \frac{12}{5} J^4 - 8 J^3 S - \frac{36}{5} J^3 + 6 J^2 S(S+1) + \frac{33}{5} J^2 + 6 JS^2 + 44 JS + \frac{306}{5} J - 2 S^4 - 4 US^3 - 6 U^2 S(S-3) - 95 S^2 + \alpha S + \beta \quad (4)$$

$$P(J, T, U) = -\frac{8}{5} J^4 + 4 J^3 T + \frac{24}{5} J^3 - 6 J^2 T(T+3) - \frac{222}{5} J^2 + 8 JT^3 + (12 U + 6) JT^2 + (12 U^2 - 24 U + 146) JT + \gamma \frac{J}{5} - 2 T^4 - 4 UT^3 + (-6 U^2 + 18 U - 95) T^2 + \delta T + \varepsilon \quad (5)$$

$\alpha, \beta, \gamma, \delta, \varepsilon$ are constants which depend on C [14] and will be neglected here. Using the parameters introduced by McDowell *et al.* [2] to shorten equation (195) of reference [1], the frequencies of a Q branch are :

$$Q(J, p) \simeq m + vJ(J+1) + wJ^2(J+1)^2 + [-2g + uJ(J+1)] \frac{5\sqrt{21} P(J, x, U)}{18 J(J+1)}. \quad (6)$$

This formula may be used to solve equation (1) for J ; but we prefer here a rough approximation which leads to an extremely simple and apparently sufficiently precise result :

$$Q(J, p) \simeq m + vJ^2 - \frac{5g\sqrt{21}}{9J^2} P(J, x, U). \quad (7)$$

For large J , (5) and (4) may be simplified

$$P(J, T, U) \simeq -\frac{8}{5} J^4 + 4 J^3 T + \frac{24}{5} J^3 \quad (T \text{ small}) \quad (8)$$

For a given value of J , an $F_{A_1 pp}^{(4JJ)}$ vector coupling coefficient depends on two parameters symbolized by p : the first, C , is the symbol for an irreducible representation of $T_d(A_1, A_2, E, F_1, F_2)$, the second is a numerical integer index n ; C and n are connected to the solutions of the equation

$$J = T + S + U \quad (2)$$

where $T/4$ and $S/3$ are zero or positive integers, and U is deduced from the symmetry C , for J even (resp. J odd) by :

$$A_1 \text{ (resp. } A_2) \rightarrow U = 0; \quad A_2 \text{ (resp. } A_1) \rightarrow U = 6; \\ E \rightarrow U = 2 \text{ or } 4$$

$$F_1 \text{ (resp. } F_2) \rightarrow U = 3, 4 \text{ or } 5;$$

$$F_2 \text{ (resp. } F_1) \rightarrow U = 1, 2, 3;$$

n takes increasing values, starting at 0 as, for a given symmetry, T (resp. S) increases. We have :

$$F_{A_1 pp}^{(4JJ)} = (-1)^J \frac{10}{3} \sqrt{\frac{7}{3}} \left[\frac{(2J-4)!}{(2J+5)!} \right]^{1/2} P(J, x, U) \quad (3)$$

where $P(J, x, U)$, with $x = S$ or T as related by equation (2), is either of the equal polynomials :

$$P(J, S, U) \simeq \frac{12}{5} J^4 - 8 J^3 S - \frac{36}{5} J^3 \quad (S \text{ small}). \quad (9)$$

Setting

$$k_1 = -8g \frac{\sqrt{21}}{9}, \quad k_2 = -20g \frac{\sqrt{21}}{9}, \\ k_3 = -8g \frac{\sqrt{21}}{3} \quad (x = T) \quad (10)$$

or

$$k_1 = -12g \frac{\sqrt{21}}{9}, \quad k_2 = 40g \frac{\sqrt{21}}{9}, \\ k_3 = 4g \sqrt{21} \quad (x = S) \quad (11)$$

we obtain a single expression :

$$\frac{\partial Q}{\partial J} = 2vJ + 2k_1 J + k_2 x + k_3 \quad (12)$$

which is equal to 0 for the value of J :

$$j = -\frac{k_2 x + k_3}{2(v + k_1)} \quad (13)$$

This value may be introduced into (6); using only the less precise equation (7), we obtain:

$$v = m - \frac{(k_2 x + k_3)^2}{4(v + k_1)} \quad (14)$$

or, replacing the k 's by their values

$$v_T = m - \frac{84g^2}{9(9v + 8g\sqrt{21})} \quad (5T + 6)^2 \quad (T \text{ small}) \quad (15)$$

$$v_S = m - \frac{84g^2}{27(3v - 4g\sqrt{21})} \quad (10S + 9)^2 \quad (S \text{ small}) \quad (16)$$

The two possible sets of k coefficients (equations (10) and (11)) give j values (eq. (13)) which have generally opposite signs : as j must be positive, equation (15) or equation (16) is generally significant : in the first case, for $T = 0, 4, 8, \dots$ we obtain the Q subbands called $Q_Z, Q_Y, Q_X, \dots$ by McDowell *et al.* [8] ; in the second case, for $S = 0, 3, 6, \dots$ the subbands $Q_A, Q_B, Q_C, \dots$

We tested our approximate formulation using the data and results of reference [8]. The precision of the value of j given by formula (13) is of the order of one unit. Approximate values for the frequencies are obtained through equation (14) ; but if the value

of j given by equation (13) is substituted in equation (4) and (6) then the agreement is very good (Table I).

TABLE I				
Frequencies of the Q subbranches of v_3 of SF_6				
(j, S)	(C, n)	$v_c^{(a)}$	$Q(J, p)^{(b)}$	$v_m^{(c)}$
(3, 0)	F ₁ , 0	947.979	947.979 2	947.976
	F ₂ , 0		947.978 4	
(12, 3)	F ₂ , 2	947.967	947.972 0	947.968
	F ₁ , 1		947.970 9	
(22, 6)	A ₁ , 1	947.942	947.956 8	947.953
	F ₁ , 3		947.956 0	
	E, 2		947.955 9	
(31, 9)	E, 1	947.902	947.933 7	947.930
	F ₁ , 2		947.933 7	
	A ₁ , 0		947.932 3	
(40, 12)	A ₁ , 2	947.848	947.903 8	947.902
	F ₁ , 6		947.902 4	
	E, 4		947.902 4	
(50, 15)	F ₂ , 8	947.780	947.864 6	947.860
	F ₁ , 8		947.864 6	

(^a) Eq. (14). All frequencies are in cm^{-1} .
 (^b) Eq. (6) is used with $m = 947.979\,5\,\text{cm}^{-1}$;
 $v = -7.09 \times 10^{-5}\,\text{cm}^{-1}$; $w = 0$;
 $g = -2.488\,59 \times 10^{-5}\,\text{cm}^{-1}$.

$u = 0$ (Ref. [8]) and with j as given by Eq. (13). For the values of n see Refs [4, 5].
 (^c) Approximate values deduced from figure 1 of Ref. [8].

References

[1] MORET-BAILLY, J., *Cah. Phys.* **15** (1961) 237-314.

[2] ALDRIDGE, J. P., FILIP, H., FLICKER, H., HOLLAND, R. F., McDOWELL, R. S., NERESON, N. G. and FOX, K., *J. Mol. Spectrosc.* **58** (1975) 165-168.

[3] McDOWELL, R. S., GALBRAITH, H. W., KROHN, B. J., CANTRELL, C. D. and HINKLEY, E. D., *Opt. Commun.* **17** (1976) 178-183.

[4] MORET-BAILLY, J., GAUTIER, L. and MONTAGUTELLI, J., *J. Mol. Spectrosc.* **15** (1965) 355-377.

[5] KROHN, B. J., Los Alamos Scientific Report LA-6554 MS (1976).

[6] LOETE, M., CLAIRON, A., FRICHET, A., McDOWELL, R. S., GALBRAITH, H. W., HILICO, J. C., MORET-BAILLY, J. et HENRY, L., *C. R. Acad. Sci. Paris* **285B** (1977) 175-178.

[7] HINKLEY, E. D. and KELLEY, P. L., *Science* **171** (1971) 635.

[8] McDOWELL, R. S., GALBRAITH, H. W., CANTRELL, C. D. and NERESON, N. G., *J. Mol. Spectrosc.* **68** (1977) 288-298.

[9] DORNEY, A. J. and WATSON, J. K. G., *J. Mol. Spectrosc.* **42** (1972) 135-148.

[10] HARTE, W. G. and PATTERSON, C. W., *J. Chem. Phys.* **66** (1977) 4872-4885.

[11] PATTERSON, C. W. and HARTE, W. G., *J. Chem. Phys.* **66** (1977) 4886-4892.

[12] MICHELOT, F. and MORET-BAILLY, J., *J. Physique* **36** (1975) 451-460.

[13] MICHELOT, F., *J. Physique* **37** (1976) 209-212.

[14] MORET-BAILLY, J. and MICHELOT, F. (to be published).