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

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

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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 toupies 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 $F^{(4J)}_{h\ell\ell}$ 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obtain exact values for most $F$ coefficients and one must use numerical tables computed by Moret-Bailly [4], Dang Nhu (unpublished) and Krohn [5].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 $J$, $F^{(4J)}_{h\ell\ell}$ 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 $Q_A$, $Q_B$, ... on one side and $Q_Y$, $Q_Z$ 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

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

McDowell et al. could obtain these beautiful results for the $Q$ branch of $v_3$ 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 $F^{(4J)}_{h\ell\ell}$ coefficients were recently given by Harter and Patterson [10, 11].
but we prefer the previous results of Michelot and Moret-Bailly [12, 13] which may easily be made more explicit [14] as follows:

For a given value of \( J \), an \( F^{(AJ)}_{\alpha\beta\gamma} \) vector coupling coefficient depends on two parameters symbolized by \( \rho \) : 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

\[
J = T + S + U
\]

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:

- \( A_1 \) (resp. \( A_2 \)) \( \rightarrow U = 0 \):
- \( E \) \( \rightarrow U = 2 \) or \( 4 \)
- \( F_1 \) (resp. \( F_2 \)) \( \rightarrow U = 3, 4 \) or \( 5 \):
- \( F_2 \) (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:

\[
F^{(AJ)}_{\alpha\beta\gamma} = (-1)^{J} \frac{10}{3} \left[ \left( \frac{2J - 4}{2J + 5} \right)^{\frac{1}{2}} \right] P(J, x, U)
\]

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

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

\[
P(J, T, U) = -\frac{8}{5} J^4 + 4 J^3 T + \frac{24}{5} J^3 - 6 J^2 T(T + 3) - \frac{222}{5} J^2 + 8 J T^3 + (12 U + 6) J T^2 + (12 U^2 - 24 U + 146) J + \gamma J^2 - 2 T^4 - 4 U T^3 + (6 U^2 + 18 U - 95) T^2 + \delta T + \epsilon
\]

where \( \alpha, \beta, \gamma \) 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:

\[
Q(J, \rho) \approx m + vJ(J + 1) + wJ^2 (J + 1)^2 + \left[ -2g + uJ(J + 1) \right] \frac{5 \sqrt{21} P(J, x, U)}{18 J(J + 1)}.
\]

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:

\[
Q(J, \rho) \approx m + vJ^2 - \frac{5 \sqrt{21}}{9 J^2} P(J, x, U).
\]

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

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

\[
\frac{\partial Q}{\partial J} = 2 vJ + 2 k_1 J + k_2 x + k_3
\]
which is equal to 0 for the value of \( J \):
\[
j = - \frac{k_2 x + k_3}{2(v + k_1)}.
\]
(13)

This value may be introduced into (6); using only the less precise equation (7), we obtain:
\[
v = m - \frac{(k_2 x + k_3)^2}{4(v + k_1)}
\]
or, replacing the \( k \)'s by their values
\[
v_t = m - \frac{84 g^2}{9(9v + 8g \sqrt{21})} (5T + 6)^2 \quad (T \text{ small})
\]
(15)
\[
v_s = m - \frac{84 g^2}{27(3v - 4g \sqrt{21})} (10S + 9)^2 \quad (S \text{ small})
\]
(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 \( T = 0, 4, 8 \ldots \) we obtain the \( Q \) subbands called \( Q_Z, Q_Y, Q_X \ldots \) by McDowell et al. [8]; in the second case, for \( S = 0, 3, 6 \ldots \) the subbands \( Q_A, Q_B, Q_C \ldots \)

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 substituted in equation (4) and (6) then the agreement is very good (Table 1).

<table>
<thead>
<tr>
<th>( j, S )</th>
<th>( (C, n) )</th>
<th>( v_c ) (*)</th>
<th>( Q(J, p) ) (*)</th>
<th>( v_m ) (*)</th>
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<td>(3, 0)</td>
<td>F(_1), 0</td>
<td>947.979</td>
<td>947.979 2</td>
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<td>947.979 0</td>
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<td>947.955 9</td>
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<td>947.933 7</td>
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<td>947.933 7</td>
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<td>(31, 9)</td>
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<td>947.864 6</td>
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</tbody>
</table>

(*) Eq. (14). All frequencies are in cm\(^{-1}\).

(*) Eq. (6) is used with \( m = 947.979 5 \text{ cm}^{-1} \):
\[
v = -7.09 \times 10^{-5} \text{ cm}^{-1}; \quad w = 0;
\]
\[
g = -2.488 59 \times 10^{-5} \text{ cm}^{-1}.
\]

\( u = 0 \) (Ref. [8]) and with \( j \) as given by Eq. (13). For the values of \( n \) see Refs [4, 5].

(*) Approximate values deduced from figure 1 of Ref. [8].

References