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G. Amat

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Rotation-vibration energy levels of CO$_2$ using effective normal coordinates: definition of the spectroscopic constants

G. Amat

Laboratoire de Physique Moléculaire et Atmosphérique, Université Pierre et Marie Curie et CNRS, tour 13, 4 place Jussieu, 75252 Paris Cedex 05, France

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Résumé.-- Cet article traite du calcul des niveaux d'énergie de vibration-rotation de CO$_2$ par la méthode des "coordonnées normales effectives". La formule donnant les éléments de matrice diagonaux de l'hamiltonien transformé, en fonction des nombres quantiques et des constantes spectroscopiques, peut être écrite sous une forme plus simple que celle publiée précédemment, ce qui facilite la solution du problème inverse.

Abstract. -- This paper deals with the calculation of rotation-vibration energy levels of CO$_2$ using "effective normal coordinates". The formula giving the diagonal matrix elements of the transformed Hamiltonian in terms of quantum numbers and spectroscopic constants can be written in a form simpler than the one previously published and more convenient for the solution of the inverse problem.

As Bordé pointed out [1], the convergence of the perturbation calculation used to compute the rotation-vibration energy levels of CO$_2$ becomes less and less satisfactory when the value of the quantum number $v_3$ increases. This is due to the large value of $k_{133}$, coefficient of $q_1q_3^2$ in the cubic term $V_1$ of the potential function $V$.

$$V = V_0 + V_1 + V_2 + ...$$ (1)

expanded in a power series with respect to normal coordinates. In an attempt to improve the situation, we have proposed [2] to replace the standard normal coordinates $q_n$ by "effective normal coordinates" $\ast q_n$ according to the following scheme:

$$q_1 = a + b_1 \ast q_1 \quad p_1 = \frac{\ast p_1}{b_1}$$ (2)

$$q_m = b_m \ast q_m \quad p_m = \frac{\ast p_m}{b_m}$$

($m = 21, 22, 3$)

where $p_n$ and $\ast p_n$ are momenta conjugate to $q_n$ and $\ast q_n$ respectively ($n = 1, 21, 22, 3$) and where $a$, $b_1$, $b_2$ and $b_3$ are functions of $v_3$ defined by the relations

$$\left(\omega_1 + 3ak_{111} + 4a^2k_{1111}\right) a +$$

$$+ (k_{133} + 2ak_{1333}) b_3^2 \left(v_3 + \frac{1}{2}\right) \simeq 0$$ (3)

$$b_1^4 = \frac{\omega_1}{\omega_1 + 6ak_{111} + 12a^2k_{1111}}$$ (4a)

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Symbols $W_3, k_{33}, k_{333}, k'_{33}, (s = s' \text{ or } s \neq s')$ designate the coefficients appearing in $V_0, V_1$ and $V_2$ respectively. The effect of $a$ is to introduce in the first order Hamiltonian $H_1$ an operator proportional to $v_1$ whose matrix elements will approximately cancel out the troublesome matrix elements $(v_1 v_3 | k_{133} q_1 | v_1 \pm 1, v_3)$; the effect of $b_1, b_2$ and $b_3$ is to restore the harmonicity of $H_0$. In this formulation, the standard power series expansion (1) of the potential function $V$ is replaced by power series expansions with respect to the effective normal coordinates $q_n$:

$$V = \star V_0 + \star V_1 + \star V_2 \quad (5)$$

the coefficients $\star w_s, \star k_{s's'}, \star k_{s's's''}$ appearing in $\star V_0, \star V_1$ and $\star V_2$ respectively, depend upon the value of $v_3$; therefore we use the same potential $V$ throughout the calculation, but we have a different expansion (right hand side of Eq. (5)) for each value of $v_3$. The relations between the new coefficients and the standard coefficients appearing in equation (1) can be found in reference [3]. As an example

$$\star k_{133} = (k_{133} + 2ak_{1133}) b_1 b_3 \quad (6a)$$

As we have already said, $\star V_1$ contains, in addition to the cubic terms, a linear term $\star k_1 \star q_1$. Actually:

$$\star k_1 = (\omega_1 + 3ak_{1111} + 4a^2k_{1111}) ab_1 \quad (6b)$$

Grenier-Besson and Mahmoudi [3] have calculated, up to second order, the matrix elements of the rotation-vibration transformed $(1)$

$$x_{33} = \star x_{33} + \star x_{33}' \quad x_{13} = \star x_{13} + \star x_{13}' \quad x_{23} = \star x_{23} + \star x_{23}' \quad \star x_{33} = \frac{3}{2} \star x_{333} + \frac{k_{133} \omega_1}{4(\omega_1^2 - \omega_2^2)} \quad \star x_{33}' = -\frac{k_{133}}{2 \omega_1} \quad x_{23} = k_{2333} + B_e \frac{\omega_2^2 + \omega_3^2}{\omega_2 \omega_3}$$

Hamiltonian $H'$ using effective normal coordinates (ENC). The diagonal matrix elements of $H'$, expressed in cm$^{-1}$, can be written as the sum $(\star G + \star F)$ of a vibrational and a rotational spectral term:

$$\star G = \sum_{s=1}^{3} (\star w_s + \star x_s') \left( v_s + \frac{d_s}{2} \right) \times \sum_{s'=1}^{3} \sum_{s''} \star x_{ss's''} \left( v_{s'} + \frac{d_{s'}}{2} \right) + \star g_{22}' \ell^2 + \star C \quad (7a)$$

$$\ star F = \left[ B - \sum_{s=1}^{3} \star w_s \left( v_s + \frac{d_s}{2} \right) \right] \times \left[ J (J + 1) - \ell^2 \right] - \star D \left[ J (J + 1) - \ell^2 \right]^2 \quad (7b)$$

The expressions of the ENC spectroscopic constants appearing in equations (7a, 7b) can be found (2) in reference [3]:

$$\star w_s = \omega_s b_s^{-2} \quad \star x_1 = -\frac{3}{2} \frac{k_1 \star k_{1111}}{\omega_1} \quad \star x_m = -\frac{k_1 \star k_{1mm}}{\omega_1} \quad (m = 2, 3)$$

The ENC spectroscopic constants $\star x_{ss'}$ ($s = s'$ or $s \neq s'$) and $g_{22}'$ are given, in terms of $\omega_s, \star k_{s's'}, \star k_{s's's''}$, and $B_e$ by formulae identical (3) to those giving the corresponding standard spectroscopic constants in terms of $\omega_s, k_{s's'},$ $k_{s's's''}$, and $B_e$. For example:

$$\star x_{33} = \star x_{33}'' + \star x_{33}''' \quad \star x_{13} = \star x_{13}'' + \star x_{13}''' \quad \star x_{23} = \star x_{23}'' + \star x_{23}'''$$

$(1)$ $H'$ is obtained by performing a contact transformation $H' = T H T^{-1}$ on the rotation-vibration Hamiltonian $H$. $\star C$ is a function of $v_3$.
The calculation described above requires only that the quantity written on the left hand side of relation (3) is small. From now on, we shall assume that this quantity is exactly zero: simplifications can then be made in formulae (7a, 7b).

1) We can now write (compare relations (3), (6a) and (6b))

\[
\dot{k}_1 = -\dot{k}_{133} \left( v_3 + \frac{1}{2} \right)
\]  

(11)

As a consequence, the terms proportional to \( \frac{\dot{k}_{133}}{\omega_1} \) and \( \frac{\dot{k}_1}{\omega_1} \) will cancel out in \( \dot{x}_1 + \dot{x}_{13} (v_3 + \frac{1}{2}) \), in \( \dot{x}_2 + \dot{x}_{23} (v_3 + \frac{1}{2}) \), in \( \dot{C} + \dot{x}_3 (v_3 + \frac{1}{2}) + \dot{x}_{33} (v_3 + \frac{1}{2})^2 \). Therefore, in formula (7a), we can omit the coefficients \( \dot{x}_2 \), replace \( \dot{x}_{13} \) by \( \dot{x}_2 + \dot{x}_{23} \) \( \dot{x}_{33} \) by \( \dot{x}_{13} + \dot{x}_{23} + \dot{x}_{33} \) respectively and replace \( \dot{C} \) by \( \dot{C}' + \dot{C}'' \). In the same way, it can be shown that the terms proportional to \( \left( \frac{\dot{k}_{133}}{\omega_1} \right)^{1/2} \) in \( \dot{B} \) and in \( -\alpha_3 (v_3 + \frac{1}{2}) \) cancel out in formula (7b). After these simplifications, all terms involving \( \dot{k}_{133} \) have disappeared in the formulae giving the energy (4) (\( \omega_1 \) is the zeroth order energy difference between the states |v\rangle and |v - 1\rangle which are coupled by the operator \( \dot{k}_{133} \cdot q_1 \cdot q_3 \)).

2) By a redistribution of terms between \( \omega_1 \) and \( \omega_{13} \) \( (v_3 + \frac{1}{2}) \), between \( \omega_2 \) and \( \omega_{23} (v_3 + \frac{1}{2}) \), between \( C' \), \( \omega_3 (v_3 + \frac{1}{2}) \) and \( \omega_{33} (v_3 + \frac{1}{2}) \) and between \( \dot{B} \) and \( -\alpha_3 (v_3 + \frac{1}{2}) \), equations (7a, 7b) can be rewritten as follows:

\[
G = \omega_1 \left( v_1 + \frac{1}{2} \right) + \omega_2 (v_2 + 1) + \omega_3 (v_3 + \frac{1}{2}) + \dot{x}_{11} \left( v_1 + \frac{1}{2} \right)^2 + \dot{x}_{22} (v_2 + 1)^2 + \dot{x}_{33} \left( v_3 + \frac{1}{2} \right)^2 + \dot{x}_{12} \left( v_1 + \frac{1}{2} \right) (v_2 + 1) + \dot{x}_{13} \left( v_1 + \frac{1}{2} \right) (v_3 + \frac{1}{2}) + \dot{x}_{23} \left( v_2 + 1 \right) (v_3 + \frac{1}{2}) + \dot{g}_{22}^{\varepsilon\ell^2} + \dot{C}''
\]

(12a)

\[
F = \left[ B_0 - \gamma_1 (\alpha_1 + \frac{1}{2}) - \gamma_2 (\alpha_2 + 1) - \gamma_3 (\alpha_3 + \frac{1}{2}) \right] \times [J(J + 1) - \ell^2] - \gamma D [J(J + 1) - \ell^2]^2
\]

(12b)

with

(4) This situation can be compared with the one met in the case of Fermi resonance: there, the states |v_1 v_2\rangle and |v_1 - 1, v_2 + 2\rangle are coupled by the operator \( k_{122} q_1 (g_{21} + g_{22}) \); the energy difference between the two states is \( \omega_1 - 2\omega_2 \). The modification of the contact transformation performed on the Hamiltonian, as proposed by Nielsen [4] in the case of Fermi resonance, has the effect of removing from the diagonal part of the transformed Hamiltonian all terms involving \( \frac{\dot{k}_{133}}{\omega_1 - 2\omega_2} \).

(2) There are a few misprints on reference [3]: in \( \dot{\alpha}_2 \) the term proportional to \( \dot{k}_{122} \) within the brackets should be written with a + sign instead of the − sign; the expression (25) given for the \( \ell \)-type doubling constant \( q^0 \) should be multiplied by \( g_{31}^2 \).

(3) It is not so for the rotational spectroscopic constants \( B, \alpha, D \).
where \( C' \) is given by equation (10b) and

\[
\begin{align*}
\alpha_3^\dagger &= - \frac{2B_2}{\omega_3} \cdot \frac{\omega_3^2 + \omega_2^2}{\omega_3^2 - \omega_2^2} (1 - 2\varepsilon a)^2 + \\
&+ \frac{2B_2\varepsilon a}{(v_3 + \frac{1}{2})} \left( 1 - \frac{3}{2} \varepsilon a \right) \\
\epsilon &= \left( \frac{2B_2}{\omega_1} \right)^{1/2} 
\end{align*}
\]

(14a)

(14b)

In formulae (12a, 12b) the zeroth order spectroscopic constants \((\omega_1, \omega_2, \omega_3, B_2)\) are identical to the standard spectroscopic constants : they do not depend upon \(v_3\). The 11 second order spectroscopic constants \((\alpha, g_1, a, D)\) depend upon \(v_3\); when \(v_3 \rightarrow -\frac{1}{2}\), the limits of these "constants" are identical to the corresponding standard spectroscopic constants. The function \( C'' \) as defined by equation (10c) does not depend explicitly upon \(a\); when \(v_3 \rightarrow -\frac{1}{2}\), \(C'' \rightarrow C''\); this limit, \(C''\), is different from zero \((5)\).

About the two formulations obtained in paragraph 1) and in paragraph 2) above, we can make the following comments :

- when, in relation (3), the symbol \(\approx\) is replaced by a symbol \(\doteq\), it is clearly advantageous to make the simplifications described in paragraph 1);

- the formulations obtained in paragraphs 1) and 2) are strictly equivalent. In the direct problem, when energy levels are computed from the potential, it makes no difference to use one formulation or the other. In the inverse vibrational problem however, when one tries to determine the potential from the energy levels, formulation 2) should prove to be more convenient: the dependence of effective spectroscopic constants upon \(v_3\) has been concentrated in the second order constants \((\alpha, g_1, a, D)\) and in \(C''\); as a consequence, the zeroth order spectroscopic constants \((\omega, B_2)\) do not depend upon \(v_3\) and the limits of second order constants when \(v_3 \rightarrow -\frac{1}{2}\) are identical to the standard values of these constants.

References


\((5)\) The constant \(C''\) is given by a formula identical to the one giving \(C''\) (Eq. (10c)), but all the ENC coefficients (with *) must be replaced by the corresponding standard coefficients (without *). The constant \(C''\) is indeed present in the standard calculation (it comes from the matrix elements of operators of degree 4 with respect to the vibrational operators in the second order transformed Hamiltonian). \(C''\) is always omitted in the standard calculation because it disappears as the positions of lines are obtained from the difference of two spectral terms. \(C''\) cannot be omitted in the ENC calculation because it is a function of \(v_3\).