

A NEW APPROACH IN THE RAYLEIGH - SCHRÖDINGER PERTURBATION THEORY FOR THE ROVIBRATIONAL PROBLEM

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ABSTRACT

For a transition $vJ \leftrightarrow v'J'$ ($J'=J\pm 1$) the eigenvalues and the eigenfunctions of the two considered states can be expressed respectively in terms of one variable m (transition number), relating these two states, as

$$E_{vm} = \sum_{i=0} e_{v'}^{(i)} m^i,$$

and

$$\Psi_{vm} = \sum_{i=0} \phi_v^{(i)} m^i \quad \text{and} \quad E_{v'm} = \sum_{i=0} e_{v'}^{(i)} m^i, \quad \Psi_{v'm} = \sum_{i=0} \phi_{v'}^{(i)} m^i,$$

where

$$m = [J'(J'+1) - J(J+1)]/2,$$

and the coefficients $e_v^{(i)}$, $\phi_v^{(i)}$, $e_{v'}^{(i)}$ and $\phi_{v'}^{(i)}$ are given by analytical expressions. This new expansion in the perturbation theory permits a direct calculation of many factors in spectroscopy that are expanded in terms of m as the line intensities, the wave number of a transition, the Herman-Wallis coefficients, ... etc. The numerical application shows that the present unconventional approach in the perturbation theory provides a simple and accurate method for the calculation of the eigenvalues and the eigenfunctions for the two considered states of the molecule CO and for the calculation of the Herman-Wallis coefficients for the ground state of the molecule HCl.

Keywords: quantum mechanics, perturbation theory, infrared transition, Herman - Wallis coefficients

INTRODUCTION

In the conventional Rayleigh-Schrödinger perturbation theory (RSPT), the eigenvalue E_{vJ} and the eigenfunction Ψ_{vJ} of a rovibrational state (vJ) are given respectively by

$$E_{vJ} = E_v + B_v \lambda - D_v \lambda^2 + H_v \lambda^3 + L_v \lambda^4 + \dots \quad (1)$$

$$\Psi_{vJ} = \Psi_v^{(0)} + \Psi_v^{(1)} \lambda + \Psi_v^{(2)} \lambda^2 + \Psi_v^{(3)} \lambda^3 + \Psi_v^{(4)} \lambda^4 + \dots \quad (2)$$

where v and J are respectively the vibrational and rotational quantum numbers, $\lambda = J(J+1)$, B_v is the rotational constant, D_v, H_v, L_v, \dots are the centrifugal distortion constants (CDC), $\Psi_v^{(0)}$ is the pure vibrational wavefunction and $\Psi_v^{(i)}$ are the $\Psi_v^{(0)}$ -rotational corrections. In the transitions $vJ \leftrightarrow v'J'$ the eigenvalue and eigenfunction of the state ($v'J'$) are given respectively by

$$E_{v'J'} = E_{v'} + B_{v'} \lambda' - D_{v'} \lambda'^2 + H_{v'} \lambda'^3 + L_{v'} \lambda'^4 + \dots \quad (3)$$

$$\Psi_{v'J'} = \Psi_{v'}^{(0)} + \Psi_{v'}^{(1)} \lambda' + \Psi_{v'}^{(2)} \lambda'^2 + \Psi_{v'}^{(3)} \lambda'^3 + \Psi_{v'}^{(4)} \lambda'^4 + \dots \quad (4)$$

Where $\lambda' = J'(J'+1)$.

For the considered transitions, the wave number (Herzberg, 1950) and (Bailly, *et al.*, 1997) and many factors in spectroscopy are expressed in terms of the transition number $m = (\lambda' - \lambda)/2$, such as the Herman-Wallis rotational factor (Herman and Wallis, 1955)

$$F_v^{v'}(m) = 1 + C' m + D' m^2 + E' m^3 + H' m^4 \quad (5)$$

the line intensities (Bailly *et al.*, 1997)

$$\ln(I_{mes}) = \ln(N_{v,J}) - \frac{hc}{KT} B_v m(m+1) + \text{constant} \quad (6)$$

the Hönl-London factor, the Einstein coefficients, The use of the λ and λ' -expansions of E_{vJ}, Ψ_{vJ} and $E_{v'J'}, \Psi_{v'J'}$ (1), (2), (3), (4) for the calculation of these factors, that are expanded in terms of m , leads to a mathematical complexity if high accuracy is required.

This study presents a new expansion of the eigenfunction and the eigenvalue in the perturbation theory in terms of the transition number m as

$$\Psi_{vm} = \sum_{i=0} \phi_v^{(i)} m^i \tag{7}$$

$$E_{vm} = \sum_{i=0} e_v^{(i)} m^i \tag{8}$$

where the coefficients $\phi_v^{(i)}$ and $e_v^{(i)}$ are well expressed by analytical expressions. Using the present unconventional approach in the perturbation theory the calculation of the factors in spectroscopy, that are expanded in terms of m , can be calculated directly by using Ψ_{vm} and $\Psi_{v'm}$ (without passing by the intermediate calculation of Ψ_{vJ} and $\Psi_{v'J'}$) where the complexity in the mathematical calculation of these factors can be avoided and higher degree of precision can be reached. The numerical applications to the ground state of the molecules CO and HCl showed the validity and the high accuracy of the present formulation.

THE THEORY

In the Born-Oppenheimer approximation, a rovibrational state (v,J) of a diatomic molecule is characterized by the eigenvalue E_{vJ} and the eigenfunction Ψ_{vJ} of the radial Schrödinger equation

$$d^2 \Psi_{vJ}(r) / dr^2 + \{K[E_{vJ} - U(r)] - \lambda / r^2\} \Psi_{vJ} = 0 \tag{9}$$

where $U(r)$ is the rotationless potential, r is the internuclear distance, $\lambda=J(J+1)$ and $K=2\mu/\hbar^2$ is a known constant for the considered molecule.

For the infrared transitions $vJ \leftrightarrow v'J'$, the integral numbers λ and λ' are related to the transition number m as $m=(\lambda'-\lambda)/2$, thus λ and λ' are expressed in terms of m in the form (Korek and Kobeissi, 1994) and (Korek, 1997)

$$\lambda = \sum_{i=0} a_i m^i \tag{10}$$

where $J'=J\pm 1$, $a_0 = 0$, $a_2 = +1$ and $a_i=0$ for $i>2$ for the two considered states, $a_1 = -1$ for the lower state and $a_1 = +1$ for the upper state.

By using the boundary conditions of the wave function $\Psi_{vm}(r)$ (7)(for a given rovibrational state vJ), one can find (Kobeissi and Korek, 1982)

$$\phi_v^{(i)}(r) \xrightarrow[r \rightarrow \infty]{r \rightarrow 0} 0 \quad \text{for } i \geq 0 \quad (11)$$

For the unnormalized wave function Ψ_{vm} and at any arbitrary origin r_0 we take without any loss of the generality of the problem

$$\Psi_{vm}(r_0) = \phi_v^{(i)}(r_0) = 1 \quad \text{and} \quad \phi_v^{(i)}(r_0) = 0 \quad \text{for } i > 0 \quad (12)$$

Analytic expressions of the coefficients $e_v^{(i)}$

In order to pass from the conventional λ -expansion of Ψ_{vJ} and E_{vJ} ((1) and (2)), in the perturbation theory, to the m -expansion of these functions we replace (7), (8) and (10) in (9), we obtain

$$\sum_{i=0} \varphi_v^{(i)} m^i + \{K[\sum_{i=0} e_v^{(i)} m^i - u(r)] - \sum_{i=0} a_i m^i / r^2\} \sum_{i=0} \varphi_v^{(i)} m^i = 0 \quad (13)$$

since this equation is satisfied for any value of m , one can write

$$\frac{d^2 \varphi_v^{(i)}}{dr^2} + K \varepsilon_v \varphi_v^{(i)} = \sum_{n=0}^i \gamma_n \varphi_v^{(i-n)} \quad (14)$$

where

$$\varepsilon_v = e_v^{(0)} - U$$

$$\gamma_n = -K e_v^{(n)} + a_n / r^2 \quad \text{for } n \geq 1 \quad (15)$$

with

$$\gamma_0 = 0$$

For $i=0$ the conventional pure vibrational Schrödinger equation is given by

$$\frac{d^2 \varphi_v^{(0)}}{dr^2} + K \varepsilon_v \varphi_v^{(0)} = 0 \quad (16)$$

and for $i > 0$ we obtain from (14) a set of differential equations where the solutions give the coefficients $e_v^{(i)}$, $\phi_v^{(i)}$, $e_v^{(i)}$, and $\phi_v^{(i)}$ ((7) and (8)) for the two considered states according to the value of a_n (15) ($a_1 = -1$ for the lower state and $a_1 = +1$ for the upper state (10)).

If (14) is multiplied by $\phi_v^{(0)}$ and we integrated between an arbitrary origin r_0 and infinity, one obtains

$$\int_{r_0}^{\infty} \left(\frac{d^2 \phi_v^{(i)}}{dr^2} \phi_v^{(0)} - \frac{d^2 \phi_v^{(0)}}{dr^2} \phi_v^{(i)} \right) dr = \int_{r_0}^{\infty} \sum_{n=0}^i \gamma_n \phi_v^{(i-n)} \phi_v^{(0)} dr \quad (17)$$

by using (16) in (17), we can write

$$\frac{d\phi_v^{(i)}}{dr} = - \sum_{n=0}^i \int_{r=0}^{\infty} \gamma_n \phi_v^{(i-n)} \phi_v^{(0)} dr$$

if the integration of (17) is repeated between r_0 and zero and by using the continuity of $\phi_v^{(i-n)}$, one obtains

$$\begin{aligned} \sum_{n=0}^i \int_{r_0}^{\infty} \gamma_n \phi_v^{(i-n)} \phi_v^{(0)} dr &= \sum_{n=0}^i \int_{r_0}^0 \gamma_n \phi_v^{(i-n)} \phi_v^{(0)} dr \\ \sum_{n=0}^i \int_0^{\infty} \gamma_n \phi_v^{(i-n)} \phi_v^{(0)} dr &= \sum_{n=0}^i \langle \phi_v^{(0)} | \gamma | \phi_v^{(i-n)} \rangle = 0 \end{aligned} \quad (18)$$

By replacing (15) in (18), one can find for a given value of $i \geq 1$ that

$$\sum_{n=1}^i e_v^n \langle \phi_v^{(0)} | \phi_v^{(i-n)} \rangle = \sum_{n=1}^i \langle \phi_v^{(0)} | \frac{a_n}{Kr^2} | \phi_v^{(i-n)} \rangle \quad (19)$$

Thus, for a given rovibrational state vJ , analytic expressions are obtained for the new constants $e_v^{(i)}$ in terms of simple definite integrals of the forms $\langle \phi_v^{(0)} | \phi_v^{(i-n)} \rangle$ and $\langle \phi_v^{(0)} | \frac{a_n}{Kr^2} | \phi_v^{(i-n)} \rangle$.

Analytic expressions for the functions $\phi_v^{(i)}$

For the solution of the pure vibrational Schrödinger equation (16) the pure vibrational wave function can be expanded as

$$\varphi_v^{(0)} = \sum_{n=0}^1 b_n^{(0)} \alpha_n^{(0)}(x) \quad (20)$$

where $x=r-r_e$, and $\alpha_n^{(0)}$ ($n=0, 1$) are the pure vibrational canonical functions (Kobeissi and Korek, 1982). Using the boundary condition (11) one may write

$$b_0^{(0)} = - \lim_{\substack{x \rightarrow 0 \\ x \rightarrow \infty}} \frac{\alpha_1^{(0)}(x)}{\alpha_0^{(0)}(x)} \quad (21)$$

$$b_1^{(0)} = 1$$

To calculate the functions $\phi_v^{(i)}$ (14) is replaced by the Volterra integral equation (Piskunov, 1969)

$$\phi_v^{(i)}(r) = \phi_v^{(i)}(r_0) + (r - r_0) \phi_v^{\prime(i)}(r_0) + \int_{r_0}^r (r-t) \varepsilon_v(t) \phi_v^{(i)}(t) dt + \sum_{n=1}^i \int_{r_0}^r (r-t) \gamma_n \phi_v^{(i)}(t) dt \quad (22)$$

this equation is equivalent to (14) in the sense that any solution of (14) is solution of (22) and vice versa. Using the canonical functions approach, a rotation harmonics $\phi_v^{(i)}$ can be expanded (Courant and Hilbert, 1966) as

$$\phi_v^{(i)} = \sum_{n=0}^2 b_n^{(i)} \alpha_n^{(i)} \quad (23)$$

where the canonical functions $\alpha_n^{(i)}$, in this work, are given by

$$\alpha_0^{(i)} = \alpha_0^{(0)} \tag{24a}$$

$$\alpha_1^{(i)}(x) = \sum_{p=0}^i R_p^{(i)}(x) \tag{24b}$$

$$R_0^{(i)}(x) = \int_0^x (x-t) \left(\sum_{n=0}^i \gamma_n \phi_V^{(i-n)} \right) \phi_V^{(0)}(t) dt \tag{24c}$$

$$R_p^{(i)}(x) = \int_0^x (x-t) \left(\sum_{n=0}^i \gamma_n \phi_V^{(i-n)} \right) R_{p-1}^{(i)}(t) dt \tag{24d}$$

where γ_n is given in terms of $e_V^{(i)}$ and a_n and the coefficients b_n are given by

$$b_0^{(i)} = - \lim_{\substack{x \rightarrow 0 \\ x \rightarrow \infty}} \frac{\alpha_1^{(i)}(x)}{\alpha_0^{(i)}(x)} \tag{25a}$$

$$b_1^{(i)} = 1 \tag{25b}$$

$$b_2^{(i)} = \phi_V^{(i)}(r_0) = 0 \tag{25c}$$

Since $b_2^{(i)} = 0$, (23) can be written as

$$\phi_V^{(i)} = \sum_{n=0}^1 b_n^{(i)} \alpha_n^{(i)} \tag{26}$$

Thus, the functions $\phi_V^{(i)}$ in the new m-expansion are well expressed by analytical expressions.

APPLICATION TO THE CALCULATION OF MATRIX ELEMENTS

The rovibrational matrix elements for a transition $vJ \leftrightarrow v'J'$ are given by

$$M_{vm}^{v'm} = \langle \Psi_{vm} | f(r) | \Psi_{v'm} \rangle \quad (27)$$

By replacing (7) in (27) one obtains

$$\langle \Psi_{vm} | f(r) | \Psi_{v'm} \rangle = \langle \left(\sum_{i=0}^m \varphi_v^{(i)} m^i \right) | f(r) | \left(\sum_{i=0}^{m'} \varphi_{v'}^{(i)} m^i \right) \rangle \quad (28)$$

$$= H_{00} \sum_{i=0}^m \beta_i m^i \quad (29)$$

with

$$\beta_0 = 1$$

$$\beta_i = \sum_{p=0}^i H_{p,i-p} / H_{00} \quad (30)$$

where

$$H_{jk} = \langle \varphi_v^{(j)} | f(r) | \varphi_{v'}^{(k)} \rangle$$

By using (23) we obtain the expression of H_{jk} in terms of the canonical functions $\alpha_n^{(i)}$ and $\alpha'_n{}^{(i)}$ as

$$H_{jk} = \sum_{\ell=0}^j \sum_{h=0}^k \langle b_\ell^{(j)} \alpha_\ell^{(j)} | f(r) | b'_h{}^{(k)} \alpha'_h{}^{(k)} \rangle \quad (31)$$

NUMERICAL APPLICATION

To test the validity and the accuracy of the coefficients $e_v^{(i)}$ for the calculation of the eigenvalue E_{vm} of a given state vJ , (10) is replaced ($\lambda = a_1 m + m^2$) in (1) and by identification with (8), expressions of $e_v^{(i)}$ are obtained in terms of B_v , D_v , H_v , L_v , ... (2), derived in the conventional perturbation theory, as

$$e_v^{(0)} = E_v \tag{32a}$$

$$e_v^{(1)} = a_1 B_v \tag{32b}$$

$$e_v^{(2)} = B_v - D_v \tag{32c}$$

$$e_v^{(3)} = a_1(-2D_v + H_v) \tag{32d}$$

$$e_v^{(4)} = -D_v + 3H_v + L_v \tag{32e}$$

$$e_v^{(5)} = a_1(3H_v + 4L_v + M) \tag{32f}$$

$$e_v^{(6)} = H_v + 6L_v + 5M + N_v \tag{32g}$$

The present formulation is applied to the ground state of the molecule CO by using a Dunham potential (Farrenq *et al.*, 1991). We present in Table 1 the values of the pure vibrational energy, the conventional rotational constant B_v and the CDC (Korek and Kobeissi, 1993) for $0 \leq v \leq 30$. In Table 2 we give the coefficients $e_v^{(i)}$ ($1 \leq i \leq 6$) (the coefficients $e_v^{(0)} = E_v$ are given in column 1 of Table 1) calculated from (19) (first entry), compared to those calculated from (32) by taking $a_1 = +1$ and by using the values of Table 1 (second entry). An excellent agreement is noticed between these values of $e_v^{(i)}$ for $1 \leq i \leq 4$ for all the considered vibrational levels v . This agreement becomes moderate for $e_v^{(5)}$ and $e_v^{(6)}$; these coefficients are given in (32) in terms of the CDC H_v, L_v, M_v and N_v where M_v and N_v are relatively small ($M_v = 1 \times 10^{-22}$; $N_v = 1 \times 10^{-26}$). Since we used in this work a double precision PC-computer, the values of $e_v^{(5)}$ and $e_v^{(6)}$ given in the first entry (calculated from (19)) are more accurate than those calculated from (32) because they are within the computer precision.

To illustrate the present formulation for the calculation of the functions $\phi_v^{(i)}$ ($i > 1$) (26) by a numerical example, the same Dunham potential is used (Farrenq *et al.*, 1991) for the

ground state of the molecule CO. For a given vibrational level v (given E_v), the computation of $\phi_v^{(i)}$ can be done by the following steps:

- i) For a given value of v , the solution of the pure vibrational Schrödinger equation (16) (Kobeissi and Korek, 1982; 1985) gives $e_v^{(0)}$ and $\phi_v^{(0)}$
- ii) by using these values of $e_v^{(0)}$ and $\phi_v^{(0)}$ in (19) for $i=1$ and $a_i=\pm 1$ (according to the state needed with $n \neq 0$) one obtains $e_v^{(1)}$
- iii) the use of $e_v^{(1)}$ in (26) gives $\phi_v^{(1)}$.

This procedure will be repeated for calculating the other functions $\phi_v^{(i)}$ by using alternatively (19) and (26), i.e., the wave function Ψ_{vm} for a given rovibrational state will be determined. We present in Table 3 the wave function $\Psi_{vm}(x)$ by successive approximations as

$$S_0 = \phi_v^{(0)} \quad (33a)$$

$$S_1 = S_0 + \phi_v^{(1)} m \quad (33b)$$

$$S_2 = S_1 + \phi_v^{(2)} m^2 \quad (33c)$$

$$S_3 = S_2 + \phi_v^{(3)} m^3 \quad (33d)$$

$$S_4 = S_3 + \phi_v^{(4)} m^4 \quad (33e)$$

$$S_5 = S_4 + \phi_v^{(5)} m^5 \quad (33f)$$

for $m=-3$, $x=0.03 \text{ \AA}$; 0.06 \AA ; 0.09 \AA ($x=r-r_e$) for the different vibrational levels $v=0, 5, 10$ the wave function Ψ_{vm} calculated from $\sum_{i=0}^5 \phi_v^{(i)} m^i$ is compared to those calculated by a direct method (Kobeissi *et al.*, 1983). We notice the excellent agreement between these values up to seven significant figures, or more, for all the considered vibrational levels and for different values of x . In Table 4 the calculation of the same functions is repeated as in Table 3 for $x=0.06 \text{ \AA}$ and $m=-2, -4, -6$. We notice also the good agreement between

$\Psi_{vm} = \sum_{i=0} \varphi_v^{(i)} m^i$ and Ψ_{vm} calculated by a direct method (Kobeissi *et al.*, 1988), but this agreement decreases slightly with the increasing value of $|m|$; this is may be explained by the perturbative aspect of the present formulation. Using the laser induced fluorescence combined with Fourier transform spectroscopy, Fellows *et al.* (1991) calculated the eigenvalues $E_v^{(Fellows)}$ and the rotational constants $B_v^{(Fellows)}$ for the ground state $X^1\Sigma^+$ of the molecule RbCs up to $v=125$. From the present formulation $E_v^{(Fellows)}$ and $B_v^{(Korek)}$ have been calculated for the considered levels of the same state of RbCs (not showed). The comparison between these values shows an average value of the relative error $(E_v^{(Fellows)} - E_v^{(Korek)})/E_v^{(Fellows)}$ equal 0.176 % and $(B_v^{(Fellows)} - B_v^{(Korek)})/B_v^{(Fellows)}$ equal 0.428 %. This very good agreement between the experimental results and those calculated by the present formulation shows the high accuracy of the later.

Korek (1997) calculated the Herman-Wallis coefficients for the molecule CO, up to the fourth order, by using the m -representation of the wave functions (7) where the functions $\varphi_v^{(i)}$ are expressed in terms of the conventional coefficients $\Psi_v^{(i)}$ (2). By repeating the calculation of these Herman-Wallis coefficients using (28) for the same molecule CO, an excellent agreement between these coefficients is obtained up to eight significant figures or more for the considered transitions (not showed). As another test, and by using a Dunham potential (Kobayashi and Suzuki, 1986) of the molecule HCl, Table 5 presents the values of the Herman-Wallis coefficients calculated from (25) (Korek, 1997) (28) in this work. The comparison of these values to those calculated by (Kobayashi and Suzuki, 1986) shows a very good agreement for all the considered transitions. No comparison for the higher order coefficients E' and H' (5) with the other results, because they are given here for the first time.

Thus by using the present new expansions in terms of m for the wave function and the eigenfunction the calculation of the Herman-Wallis coefficients can be done easier and with high precision.

CONCLUSION

Within the frame of the perturbation theory we expand in this work the eigenvalue and the eigenfunction of a rovibrational state vJ (or v^3J') in terms of the transition number m as

$$E_{vm} = \sum_{i=0} e_v^{(i)} m^i$$

$$\Psi_{vm} = \sum_{i=0} \varphi_v^{(i)} m^i$$

where the coefficients $e_v^{(i)}$ and $\phi_v^{(i)}$ are given by analytical expressions (19) and (26). The numerical application to the ground state of the molecule CO showed the excellent accuracy of the present m -expansion for the eigenvalue and the eigenfunction. Thus, for a given potential function $U(r)$ (either empirical or of the RKR-type), this work presents a new alternative method for the calculation of the eigenvalue and the eigenfunction for a given state (vJ) of a diatomic molecule which is greatly helpful in the calculation of the dipole moment function by using the Herman-Wallis approach, the matrix elements and the other factors in spectroscopy that are expanded in terms of the transition number m .

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TABLE 1
Values of the pure vibrational energy E_v , the rotational constant B_v and the centrifugal distortion constants for several vibrational levels for a Dunham potential of the ground state of the molecule CO (Farrenq *et al.*, 1991) (all values are in unit of cm^{-1})

v	$e_v^{(0)} = E_v$	B_v	$-D_v$
0	1081.776 425 149	1.922 528 872 188 5	6.119 538 190 045 3 (-6)
2	5341.839 421 117	1.887 524 152 442 3	6.118 492 729 471 8 (-6)
4	9496.254 651 896	1.852 527 317 693 0	6.118 625 997 469 0 (-6)
6	13 545.614 391 794	1.817 548 789 489 7	6.119 100 032 983 7 (-6)
8	17 490.662 193 355	1.782 619 318 243 6	6.117 607 635 512 5 (-6)
10	21 332.476 441 784	1.747 813 812 259 5	6.108 954 281 206 0 (-6)
12	25 072.809 945 635	1.713 291 562 308 3	6.082 872 374 545 4 (-6)
14	28 714.660 095 203	1.679 357 473 301 9	6.021 221 166 526 3 (-6)
16	32 263.136 697 405	1.646 540 916 591 7	5.895 879 015 814 4 (-6)
18	35 726.609 774 290	1.601292 269 809 6	5.510 807 274 654 1 (-6)
20	39 117.886 429 463	1.587 834 402 414 7	5.315 610 506 552 7 (-6)
22	42 454.800 636 464	1.564 253 664 184 5	4.826 271 956 870 5 (-6)
24	45 759.423 853 031	1.545 858 940 077 5	4.245 076 776 607 3 (-6)
26	49 055.652 098 069	1.532 966 429 972 4	3.647 513 646 660 3 (-6)
28	52 366.072 795 007	1.525 198 870 831 1	3.105 097 132 329 6 (-6)
30	55 709.572 095 718	1.521 723 364 840 8	2.657 034 054 079 7 (-6)

TABLE 1: continued

v	H_v	L_v	M_v	N_v
0	5.800 826 482 783 3(-12)	-3.644 482 111 190 6(-17)	-4.870 538 983 846 3(-23)	-7.944 614 835 080 5(-28)
2	5.509 987 029 567 8(-12)	-3.784 813 538 110 1(-17)	-5.465 733 238 874 5(-23)	-7.561 723 477 388 0(-28)
4	5.227 203 611 960 6(-12)	-3.867 822 122 676 3(-17)	-3.669 433 879 183 0(-23)	-2.543 232 973 892 9(-29)
6	4.997 018 262 846 4(-12)	-3.718 435 517 686 1(-17)	5.486 630 585 738 6(-23)	2.507 958 969 819 8(-27)
8	4.929 844 121 005 2(-12)	-2.955 551 078 410 7(-17)	3.192 650 510 607 5(-22)	8.926 318 846 993 5(-27)
10	5.254 508 023 902 3(-12)	-8.580 734 289 834 4(-18)	9.262 306 247 271 2(-22)	2.213 965 749 794 4(-26)
12	6.387 468 146 299 3(-12)	3.741 060 410 486 3(-17)	2.126 031 582 083 1(-21)	-4.315 667 676 211 5(-25)
14	8.982 135 667 280 9(-12)	1.225 984 449 899 9(-16)	3.886 215 418 142 5(-21)	6.377 156 385 974 1(-26)
16	1.383 672 397 466 9(-11)	2.523 399 991 177 2(-16)	5.662 469 305 930 8(-21)	4.693 363 779 516 5(-26)
18	2.143 274 362 889 6(-11)	3.968 333 710 284 3(-16)	5.376 047 145 200 2(-21)	-6.250 626 754 447 2(-26)
20	3.101 641 389 828 7(-11)	4.686 233 323 160 0(-16)	5.007 758 059 407 1(-22)	-2.417 255 305 457 1(-25)
22	3.995 058 931 136 8(-11)	3.658 848 567 127 3(-16)	-7.892 181356 112 5(-21)	-2.942 738 207 510 9(-25)
24	4.480 274 749 103 4(-11)	9.188 069 419 016 4(-17)	-1.341 804 507 678 7(-20)	-8.804 582 297 530 4(-26)
26	4.391 459 943 028 2(-11)	-2.113 958 905 543 7(-16)	-1.162 830 922 610 0(-20)	1.675 576 682 769 6(-25)
28	3.851 092 910 175 2(-11)	-4.029 874 342 312 2(-16)	-5.445 924 322 140 0(-21)	2.409 968 423 797 1(-25)
30	3.117 701 294 880 0(-11)	-4.545 633 566 306 7(-16)	8.328 183 714 433 3(-23)	3.596 097 485 858 3(-26)

(*) Number between parentheses stands for a multiplication power of 10

TABLE 2
Values of the Coefficients $e_v^{(i)}$ calculated from (32) (first entry) compared to those
calculated from (19) by taking $a_1 = +1$ (second entry) for the Dunham potential of the
ground state of CO (Farrenq, 1991) (all values are in unit of cm^{-1})

v	$e_v^{(1)}$	$e_v^{(2)}$	$e_v^{(3)}$
0	1.922 528 872 188 5 5**	1.922 522 752 650 3 3	-1.223 907 057 926 5(-5)* 5
2	1.887 524 152 442 7 7	1.887 518 033 950 0 0	-1.223 697 994 895 7(-5) 7
4	1.852 527 317 693 0 0	1.852 521 199 067 0 0	-1.223 724 676 773 4(-5) 4
6	1.817 548 789 489 7 7	1.817 542 670 389 7 7	-1.223 819 506 894 3(-5) 5
8	1.782 619 318 243 6 6	1.782 613 200 635 9 9	-1.223 521 034 118 0(-5) 1
10	1.747 813 812 259 5 5	1.747 807 703 305 2 2	-1.221 790 330 789 9(-5) 9
12	1.713 291 562 308 3 3	1.713 285 479 435 9 9	-1.216 573 836 161 1(-5) 5 2
14	1.679 357 473 301 9 9	1.679 351 452 080 8 8	-1.204 243 335 092 6(-5) 5
16	1.646 540 916 591 7 7	1.646 535 020 712 7 7	-1.179 174 419 490 9(-5) 1 0
18	1.615 664 736 688 3 3	1.615 659 065 648 5 5	-1.134 205 831 659 5(-5) 5
20	1.587 834 402 414 7 7	1.587 829 086 804 2 2	-1.063 118 999 695 0(-5) 69 2
22	1.564 253 664 184 5 5	1.564 248 837 912 5 5	-9.652 503 963 149 8(-6) 51 7
24	1.545 858 940 077 6 6	1.545 854 695 000 8 8	-8.490 108 750 466 6(-6) 7 2
26	1.532 966 429 972 4 4	1.532 962 782 458 8 8	-7.294 983 378 731 1(-6) 21 2
28	1.525 198 870 831 1 1	1.525 195 765 734 0 0	-6.210 155 753 730 0(-6) 1
30	1.521 723 364 840 8 8	1.521 720 707 806 7 7	-5.314 036 931 168 1(-6) 46 4

TABLE 2: continued

v	$e_v^{(4)}$	$e_v^{(5)}$	$e_v^{(6)}$
0	-6.119 520 787 602 7(-6) 8	1.740 233 366 943 6(-11) 5	5.800 607 813762 0(-12) 22 5
2	-6.118 476 199 548 8(-6) 6	1.652 980 969 604 0(-11) 10 7	5.509 759 940 430 7(-12) 82 2
4	-6.118 610 315 8970(-6) 6 9	1.568 145 612 318 7(-11) 296 0	5.226 971 542 697 9(-12) 4 498 2
6	-6.119 085 041 962 6(-6) 39	1.499 090 607 323 6(-11) 5 117 3	4.996 795 166 811 0(-12) 56 989 7
8	-6.117 592 846 009 4(-6) 7	1.478 941 414 195 3(-11) 29 2	4.929 666 789 866 2(-12) 536 8
10	-6.108 938 517 688 1(-6) 3	1.576 348 974 918 9(-11) 69 6	5.254 456 543 786 3(-12) 4 127 7
12	-6.082 853 212 076 9(-6) 118 2	1.916 255 516 655 5(-11) 408 344 0	6.387 693 129 707 7(-12) 2 620 553 7
14	-6.021 194 220 001 6(-6) 0 1	2.694 689 739 864 0(-11) 950 9	8.982 871 276 996 3(-12) 7 382 0
16	-5.895 837 505 391 8(-6) 2 7	4.151 118 129 146 2(-11) 8 966 5	1.383 823 804 388 9(-11) 297 6
18	-5.670 975 576 041 4(-6) 6	6.429 981 822 333 9(-11) 554 7	2.143 512 465 422 3(-11) 600 2
20	-5.315 517 456 971 7(-6) 842 4	9.305 111 615 400 4(-11) 8 869 0	3.101 922 562 875 4(-11) 4 078 4
22	-4.826 152 104 734 8(-6) 6 7	1.198 532 314 330 9(-10) 08 9	3.995 278 456 561 5(-11) 946 1
24	-4.244 942 368 272 4(-6) 3 0	1.344 086 099 826 0(-10) 4 6	4.480 329 870 802 9(-11) 10 9
26	-3.647 381 903 083 3(-6) 73 4	1.317 429 526 681 5(-10) 956 5	4.391 330 972 581 4(-11) 3 099 679 7
28	-3.104 981 599 945 2(-6) 3	1.155 311 753 493 2(-10) 500 7	3.850 851 114 961 3(-11) 91 7
30	-2.656 940 523 516 4(-6) 495 4	9.352 922 183 126 1(-11) 059 305 8	3.117 428 609 217 1(-11) 556 907 7

(*) Number between parentheses stands for a multiplication power of 10

(**) Omitted figures are identical to those of the first entry

TABLE 3
Values of the successive approximations of the wave function $\Psi_{vm} = S_p$ (33) compared to Ψ_{vm} calculated from a direct method (Kobeissi *et al.*, 1983) for $m = -3$ and $v = 0, 5, 10$ at $x = 0.03 \text{ \AA}$, 0.06 \AA , 0.09 \AA .

m = -3				
$x (\text{ \AA})$	$S_i(x)$	v=0	v=5	v=10
0.03	S_0	0.853 748 790	-0.628 876 761	-0.746 397 606
	S_1	0.853 869 795	-0.626 165 343	-0.745 894 600
	S_2	0.854 232 819	-0.626 031 185	-0.744 385 267
	S_3	0.854 232 870	-0.626 031 753	-0.744 385 384
	S_4	0.854 232 945	-0.626 032 605	-0.744 380 557
	S_5	0.854 232 945	-0.626 032 601	-0.744 380 547
	$\Psi_{vm} = \sum_{i=0}^5 \phi_v^{(i)} m^{(i)}$	0.854 232 945	-0.626 032 601	-0.744 380 547
	$\hbar \Lambda \omega$	5*	1	38
0.06	S_0	0.503 445 962	-0.508 969 560	0.340 441 326
	S_1	0.503 588 429	-0.509 583 822	0.343 441 124
	S_2	0.504 015 851	-0.511 426 523	0.340 439 923
	S_3	0.504 015 970	-0.511 426 005	0.340 436 350
	S_4	0.504 016 150	-0.511 425 230	0.340 430 986
	S_5	0.504 016 150	-0.511 425 233	0.340 430 967
	$\Psi_{vm} = \sum_{i=0}^5 \phi_v^{(i)} m^{(i)}$	0.504 016 150	-0.511 425 233	0.340 430 967
	$\hbar \Lambda \omega$	0	4	48
0.09	S_0	0.210 315 859	1.071 321 96	0.237 068 293
	S_1	0.210 404 997	1.070 971 45	0.238 449 379
	S_2	0.210 672 429	1.069 919 97	0.242 593 436
	S_3	0.210 672 542	1.069 920 47	0.242 598 232
	S_4	0.210 672 711	1.069 921 21	0.242 605 433
	S_5	0.210 672 711	1.069 921 21	0.242 605 459
	$\Psi_{vm} = \sum_{i=0}^5 \phi_v^{(i)} m^{(i)}$	0.210 672 711	1.069 921 21	0.242 605 459
	Ψ_{vm}	1	1	85

(*) Omitted figures are identical to those of the first entry

TABLE 4
Values of the successive approximations of the wave function $\Psi_{vm} = S_p$ (33) compared to Ψ_{vm} calculated from a direct method (Kobeissi *et al.*, 1983) for $m = -2, -4, -6$ and $v = 0, 5, 10$ at $x = 0.06 \text{ \AA}$.

		$x=0.06 \text{ \AA}$		
m	$S_i(x)$	v=0	v=5	v=10
-2	s_0	0.503 445 962	-0.508 969 560	0.344 441 326
	s_1	0.503 540 940	-0.509 379 068	0.343 774 524
	s_2	0.503 730 905	-0.510 198 047	0.342 440 628
	s_3	0.503 730 940	-0.510 197 893	0.342 439 599
	s_4	0.503 730 976	-0.510 197 740	0.342 438 539
	s_5	0.503 730 976	-0.510 197 741	0.342 438 537
	$\Psi_{vm} = \sum_{i=0}^5 \phi_v^{(i)} m^{(i)}$	0.503 730 976	-0.510 197 741	0.342 438 537
	Ψ_{vm}	6*	1	5
-4	s_0	0.503 445 962	-0.508 969 560	0.344 441 326
	s_1	0.503 635 918	-0.509 788 577	0.343 107 723
	s_2	0.504 395 778	-0.513 064 489	0.337 772 255
	s_3	0.504 396 062	-0.513 063 262	0.337 763 786
	s_4	0.504 396 630	-0.513 060 811	0.337 746 832
	s_5	0.504 396 630	-0.513 060 825	0.337 746 753
	$\Psi_{vm} = \sum_{i=0}^5 \phi_v^{(i)} m^{(i)}$	0.504 396 630	-0.513 060 825	0.337 746 753
	Ψ_{vm}	1	44	647
-6	s_0	0.503 445 962	-0.508 969 560	0.344 441 326
	s_1	0.503 730 896	-0.510 198 085	0.342 440 922
	s_2	0.505 440 581	-0.517 568 888	0.330 436 118
	s_3	0.505 441 539	-0.517 564 747	0.330 407 536
	s_4	0.505 444 414	-0.517 552 338	0.330 321 707
	s_5	0.505 444 416	-0.517 552 446	0.330 321 106
	$\Psi_{vm} = \sum_{i=0}^5 \phi_v^{(i)} m^{(i)}$	0.505 444 416	-0.517 552 446	0.330 321 106
	$\hbar \Lambda \omega$	95	661	19 882

(*) Omitted figures are identical to those of the first entry

TABLE 5
Values of the Herman-Wallis coefficients (5) for the transitions $v=0$ and $V'-v \leq 7$ for the ground state of the molecule HCl

v	Δv		Kobayashi and Suzuki 1986	Present Work
0	1	C'	-2.6(-2)*	-2.571 2(-2)*
		D'	2.5(-4)	2.514 7(-4)
		E'	-----	-2.841 9(-6)
		H'	-----	-2.159 0(-8)
	2	C'	-5.0(3)	-4.962 1(-3)
		D'	3.5(-4)	3.547 1(-4)
		E'	-----	-1.956 7(-6)
		H'	-----	7.970 7(-8)
	3	C'	1.2(-2)	1.208 3(-2)
		D'	5.3(-4)	5.318 7(-4)
		E'	-----	8.299 1(-6)
		H'	-----	1.819 7(-7)
4	C'	2.72(-2)	2.725 3(-2)	
	D'	1.55(-3)	1.550 4(-3)	
	E'	-----	4.821 1(-5)	
	H'	-----	6.510 1(-7)	
5	C'	1.93(-2)	1.931 2(-2)	
	D'	1.78(-4)	1.773 8(-4)	
	E'	-----	-2.316 1(-5)	
	H'	-----	-4.540 8(-7)	
6	C'	3.35(-2)	3.348 8(-2)	
	D'	7.88(-4)	7.817 3(-4)	
	E'	-----	6.628 5(-7)	
	H'	-----	-3.291 1(-8)	
7	C'	4.31(-2)	4.295 3(-2)	
	D'	1.08(-3)	1.121 1(-3)	
	E'	-----	1.321 8(-5)	
	H'	-----	1.292 3(-7)	

(*) Number between parentheses stands for a multiplication power of 10

REFERENCES

- Bailly, D., Camy - Peyret, C. and Lanquiten, R. 1997. Temperature measurement in flames through CO₂ and C emission: New highly excited level of CO₂. *J. Mol.Spectrosc.*182, 10.
- Courant, R. and Hilbert, D. 1966 *Methods of Mathematical Physics* wiley, New York.
- Farrenq, R., Guelachili, G., Sauval, A. J., Grevesse, N., and Farmer, C. B. 1991. Improved Dunham coefficients for CO from infrared solar lines of high rotational excitation. *J. Mol. Spectrosc.*, 149: 375.
- Fellows, C., E., Gutterres, R., F., Campos, A., P., C., Vergès, J. and Amiot, C. 1991. The RbCs X1+ ground electronic satae: New spectroscopic study. *J. Mol Spectrosc.*, 197: 19.
- Herman, R., and Wallis, R., F. 1955. Influence of vibration-rotation interaction on line intensities in vibration-rotation band of diatomic molecules. *J. Chem. Phys.*, 23: 637.
- Herzberg, G. 1950. *Spectra of Diatomic Molecule*. Van Nostrand, Toronto.
- Kobayashi, M. and Suzuki, I. 1986. Dipole moment function of Hydrogen Chloride. *J. Mol. Spectrosc.*, 116: 422.
- Kobeissi, H. and Korek, M. 1982. Analytic expression of the rotation harmonics in the vibration-rotation wave function of a diatomic molecule. *Int. J. Quant. Chem.*, 22: 23.
- Kobeissi, H., Dagher, M., Korek, M., and Chaalan, A. 1983. A new treatment of the vibration-rotation eigenvalue problem for a diatomic molecule. *J. Comp. Chem.*, 4: 218.
- Kobeissi, H. and Korek, M. 1985. Eigenvalue functions associated with diatomic rotation and distortion constants. *J. Phys. B: At. Mol. & Opt. Phys.*, 18: 1155.
- Kobeissi, H., Kobeissi, M. and El-Hajj, A. 1988. On testing difference equations for diatomic eigenvalue problem. *J. Comput. Chem.*, 8: 844.
- Korek, M. and Kobeissi, H. 1993. Diatomic centrifugal distortion constants for large order at any level: Application to the XO⁺-I₂ state. *Can. J. Chem.*, 71: 313.
- Korek, M., and Kobeissi, H. 1994. New analytical expression for the Herman-Wallis coefficients of infrared transitions up to the third order. *J. Quant. Spectrosc.Rad. Trans.*, 52: 631.
- Korek, M. 1997. Analytical expression for the high-order Herman-Wallis coefficients of a diatomic molecule. *Can. J. Phys.*, 75: 795.
- Piskonov, N. 1969. *Calcul différentiel et integral*. Mir. Moscow.