CODEN IEJMAT *Internet Electronic Journal of Molecular Design* **2006**, *5*, 296–305 ISSN 1538–6414
BioChem Press http://www.biochempress.com

Internet Electronic Journal of Molecular Design

May 2006, Volume 5, Number 5, Pages 296–305

Editor: Ovidiu Ivanciuc

Special issue dedicated to Professor Lemont B. Kier on the occasion of the 75th birthday

A New Formulation for the Herman–Wallis Coefficients for Infrared Transitions of A Diatomic Molecule

Mahmoud Korek and Claire Deeb

Faculty of Science, Beirut Arab University, P.O. Box 11–5020, Beirut, Lebanon

Received: May 24, 2005; Revised: December 2, 2005; Accepted: February 6, 2006; Published: May 31, 2006

Citation of the article:

M. Korek and C. Deeb, A New Formulation for the Herman–Wallis Coefficients for Infrared Transitions of A Diatomic Molecule, *Internet Electron. J. Mol. Des.* **2006**, *5*, 296–305, http://www.biochempress.com.

Inter*net* Electronic Journal of Molecular Design

BioChem Press
http://www.biochempress.com

A New Formulation for the Herman–Wallis Coefficients for Infrared Transitions of A Diatomic Molecule [#]

Mahmoud Korek * and Claire Deeb

Faculty of Science, Beirut Arab University, P.O. Box 11–5020, Beirut, Lebanon

Received: May 24, 2005; Revised: December 2, 2005; Accepted: February 6, 2006; Published: May 31, 2006

Internet Electron. J. Mol. Des. **2006**, *5* (5), 296–305

Abstract

Motivation. The problem of the radial matrix elements in the infrared transition $vJ\leftrightarrow v'J'$ of a diatomic molecule is considered. By using a new expansion in the perturbation theory of the eigenvalue and the eigenfunction of the two considered states in terms of the running number m we derived analytical expressions for the Herman–Wallis coefficients of the rotational factor in the rovibrational matrix elements. The numerical application to the ground states of the molecule HCl shows that the present formulation provides a simple and accurate method for the calculation of the Herman–Wallis coefficients, even for the high order coefficients, without any restriction on the potential function, the operator $f(r)$ and the vibrational levels v and v'.

Method. The most important methods used in this investigation are the Rayleigh–Schrödinger perturbation theory and the canonical functions approach.

Results. The main results reported in the paper are the determination of the Herman–Wallis coefficients.

Conclusions. The method used for the determination of the Herman–Wallis coefficients in this work allows the calculation of these coefficients for any type of potential function and to any order of correction in the perturbation theory.

Keywords. Herman–Wallis coefficients for infrared transitions.

Abbreviations and notations

CDC, centrifugal distortion constant

RSPT, Rayleigh –Schrödinger perturbation theory

1 INTRODUCTION

For the infrared transitions $vJ\leftrightarrow v'J'$ the radial matrix elements are defined by [1]

$$M_{vJ}^{v'J'} = \int_0^\infty \Psi_{vJ}(r) f(r) \Psi_{v'J'}(r) dr \tag{1}$$

where Ψ_{vJ} is the rovibrational wavefunction, r is the internuclear distance, v and v' and J and J' are respectively, the vibrational and rotational quantum numbers of the lower and upper state, and $f(r)$ is a given operator.

[#] Dedicated to Professor Lemont B. Kier on the occasion of the 75th birthday.

* Correspondence author; E–mail: fkorek@cyberia.net.lb.

Herman and Wallis [2] looked to simplify the problem of determination of the matrix elements (and then the line intensities) by defining the rotational factor in $M_{vJ}^{v'J'}$ as:

$$F_{vJ}^{v'J'} = (M_{vJ}^{v'J'} / M_{v0}^{v'0})^2 \tag{2}$$

where $M_{v0}^{v'0}$ is the pure vibrational matrix element and by approximating this factor by using the *m*–representation as:

$$F_{vm}^{v'm} = 1 + Cm + Dm^2 + ... \tag{3}$$

where the running number $m = ((J'(J'+1)–J(J+1))/2$ and C and D are the Herman Wallis coefficients [2]. In the conventional Rayleigh–Schrödinger perturbation theory (RSPT), the eigenvalue E_{vJ} and the eigenfunction Ψ_{vJ} of a rovibrational state *vJ* are expanded in terms of the integral number λ as:

$$E_{v\lambda} = E_v + B_v \lambda - D_v \lambda^2 + H_v \lambda^3 + L_v \lambda^4 + ... \tag{4}$$

nfunction Ψ_{vJ} of a rovibrational state *vJ* are expanded in terms of the integral number λ as:

where $\lambda = J(J+1)$, B_v is the rotational constant, D_v, H_v, L_v, … are the centrifugal distortion constants (CDC). In the literature [3], the authors used this approach to find analytical expressions for the coefficients *C* and *D*; their calculations were limited to the second order of correction in Eq. (3) and to the Dunham potential because of the complexity in their mathematical expressions by passing from λ–representation for E_{vJ} and Ψ_{vJ} [Eqs. (4)–(5)] to *m*–representation for $F_{vm}^{v'm}$ in the same perturbation theory, Eq. (2). This complexity may be removed by expanding the eigenvlue E_{vJ} and the eigenfunction Ψ_{vJ} in terms of the running number *m*. Recently [4] we presented respectively a *m*–representation for the eigenvalue and the eigenfunction for a given rovibrational state *vJ* as:

$$E_{vm} = \sum_{i=0} A_i m^i$$

$$\Psi_{vm} = \sum_{i=0} \phi_i m^i$$

where the coefficients A_i and ϕ_i are given by analytical expressions in the canonical functions approach [5]. The aim of this work is the use of this new approach in the perturbation theory to find analytical expressions for the Herman–Wallis coefficients, even for the high order coefficients, for any potential and any operator *f*(*r*).

2 THEORETICAL

Within the Born–Oppenheimer approximation [6], the vibrational–rotational motion of a diatomic molecule is governed by the radial Schrödinger equation [1]:

$$d^2\Psi_{vJ}(r)/dr^2+\{(2\mu/\hbar^2)[E_{vJ}-U(r)]-\lambda/r^2\}\Psi_{vJ}=0 \tag{6}$$

where $U(r)$ is the rotationless potential, r is the internuclear distance and $2\mu/\hbar^2$ is a known constant for the considered molecule. In the conventional perturbation theory E_{vJ} and Ψ_{vJ} are expanded in terms of the integral number λ [Eqs. (4) and (5)].

The eigenvalues and the eigenfuctions have been expanded [4] for the two considered states in infrared transitions in terms of the running number m as

$$E_{vm}=\sum_{i=0}A_i m^i \;;\; E_{v'm}=\sum_{i=0}A'_i m^i \tag{7}$$

$$\Psi_{vm}=\sum_{i=0}\phi_i m^i \;;\; \Psi_{v'm}=\sum_{i=0}\phi'_i m^i \tag{8}$$

where $J' = J+j$ with $j = -1$ for the branch P and $j = +1$ for the branch R. The coefficients A_n (n = 1, 2, 3, ...) for one state are given by the analytic expression:

$$A_n=(T_{n-2+}a_1T_{n-1}-\sum_{i=1}^{n-1}A_iI_{n-i})/I_0 \tag{9}$$

where $a_1 = -1$ for the lower state and $a_1 = +1$ for the upper state,

$$A_1=a_1T_{0/}I_0 \;,\; I_n=<\phi_0\phi_n>,\; T_n=<\phi_0|P|\phi_n> \;,\; P=\hbar^2/2\mu r \;,$$

ϕ_0 is the pure vibrational wavefunction and ϕ_n are solutions of a set of differential equations of the form [4]:

$$Z''(r)+(2\mu/\hbar^2)(A_0-U(r))Z(r)=S(R)$$

These functions are given, for the vJ state, by one analytical expression as

$$\phi_i=\sum_{n=0}^{1}b_n^{(i)}\alpha_n^{(i)}(r) \;;\; i\ge 0 \;\; (10\text{–}1) \tag{10}$$

where

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

$$b_0^{(i)}=-\lim_{\substack{r\to 0\\ r\to\infty}}\frac{\alpha_1^{(i)}(r)}{\alpha_0^{(i)}(r)}$$

and for the $v'J'$ state the entities ϕ_i, b_n^i and α_i^n should be replaced by their primed ϕ_i', b'^i_n and $\alpha'^{(i)}_n$ where the functions $\alpha_n^{(i)}$ and $\alpha'^{(i)}_n$ are given by analytic expressions [4].

The rovibrational matrix elements of the normalized wavefunctions Ψ_{vm} and $\Psi_{v'm}$ [Eq. (8)] are given by:

$$M_{vm}^{v'm} = <\Psi_{vm} \,|\, f(r) \,|\Psi_{v'm}> / <N_{vm} N_{v'm}>^{1/2} \tag{11}$$

where N_{vm} and $N_{v'm}$ are the normalization factors:

$$N_{vm} = <\Psi_{vm} \,|\Psi_{vm}> and\ N_{v'm} = <\Psi_{v'm} \,|\Psi_{v'm}> \tag{12}$$

By replacing Eq. (8) in the numerator of Eq. (11) we obtain:

$$<\Psi_{vm} \,|\, f(r) \,|\Psi_{v'm}> = <(\sum_{i=0} \Psi_{vm}) \,|\, f(r) \,|(\sum_{i=0} \Psi_{v'm})> \tag{13}$$

$$= H_{00} \sum_{i=0} \gamma_i m^i \tag{14}$$

With:

$$\gamma_o = 1$$

$$\gamma_i = \sum_{p=0}^{i} H_{p,i-p} / H_{00} \tag{15}$$

where

$$H_{jk} = <\phi_j \,|\, f(r) \,|\, \phi'_k>$$

By using Eq.(10) we obtain H_{jk} in terms of the canonical function $\alpha_n^{(i)}$ and $\alpha'^{(i)}_n$ as:

$$H_{jk} = \sum_{\ell=0}^{1} \sum_{h=0}^{1} < b_\ell^{(j)} \alpha_\ell^{(j)} \,|\, f(r) \,|\, b'^{(k)}_h \alpha'^{(k)}_h >$$

If we consider the orthogonality of the pure vibrational wavefunction $\Psi_v^{(0)}$ to the rotation harmonics [8] $\Psi_v^{(i)}$ ($i \geq 1$) [Eq. (5)], one can find [9] that the orthogonality of ϕ_0 to ϕ_i ($i \geq 1$). By replacing Eq. (8) in (12) and by using this property of orthogonality we obtain explicitly:

$$N_{vm} = <\phi_0 \,|\, \phi_0> [1 + \frac{<\phi_1|\phi_1>}{<\phi_0|\phi_0>} m^2 + 2\frac{<\phi_1|\phi_2>}{<\phi_0|\phi_0>} m^3 + (2\frac{<\phi_1|\phi_3>}{<\phi_0|\phi_0>} + \frac{<\phi_3|\phi_3>}{<\phi_0|\phi_0>}) m^4 + \ldots] \tag{16}$$

and for the *mv*' state the entities ϕ_i and N_{vm} should be replaced by their primed ϕ'_i and $N_{v'm}$.. Since the second, the third, the fourth and the fifth terms in Eq. (16) are small with respect to one, we can write:

$$(N_{vm})^{-1/2} = <\phi_0 \,|\, \phi_0>^{-1/2} [1 - \frac{<\phi_1|\phi_1>}{2<\phi_0|\phi_0>} m^2 - \frac{<\phi_1|\phi_2>}{<\phi_0|\phi_0>} m^3 - (\frac{<\phi_1|\phi_3>}{<\phi_0|\phi_0>} + \frac{<\phi_3|\phi_3>}{2<\phi_0|\phi_0>} + \frac{3}{8}(\frac{<\phi_1|\phi_1>}{<\phi_0|\phi_0>})^2) m^4 + \ldots] \tag{17}$$

By using these expressions, the normalization factors will be given in terms of the functions ϕ_i and ϕ'_i as:

$$(N_{vm} N_{v'm})^{-1/2} \cong (I_{00}\, I'_{00})^{-1/2} \sum_{i=0} \beta_i m^i \tag{18}$$

$$\beta_0 = 1 \tag{19–1}$$

$$\beta_1 = 0 \tag{19–2}$$

$$\beta_2 = -\frac{1}{2}\left(\frac{I_{11}}{I_{00}} + \frac{I'_{11}}{I'_{00}}\right) \tag{19–3}$$

$$\beta_3 = -\left(\frac{I_{12}}{I_{00}} + \frac{I'_{12}}{I'_{00}}\right) \tag{19–4}$$

$$\beta_4 = -\left(\frac{I_{13}}{I_{00}} + \frac{I'_{13}}{I'_{00}} + \frac{1}{2}\frac{I_{33}}{I_{00}} + \frac{1}{2}\frac{I'_{33}}{I'_{00}} - \frac{1}{4}\frac{I_{11}I'_{11}}{I_{00}I'_{00}}\right) \tag{19–5}$$

where

$$I_{jk} = <\phi_j \phi_k> \;\; ; \;\; I'_{jk} = <\phi'_j \phi'_k> \tag{20}$$

If we substitute Eqs. (10) in Eq. (20) we obtain the integrals I_{jk} and I'_{jk} in terms of the canonical functions α_i and α'_i as:

$$I_{jk} = \sum_{\ell=0}^{1}\sum_{h=0}^{1} < b_\ell^{(j)} \alpha_\ell^{(j)} b_h^{(k)} \alpha_h^{(k)} > \tag{21–1}$$

$$I'_{jk} = \sum_{\ell=0}^{1}\sum_{h=0}^{1} < b'^{(j)}_\ell \alpha'^{(j)}_\ell b'^{(k)}_h \alpha'^{(k)}_h > \tag{21–2}$$

If we replace Eqs. (14) and (18) in Eq. (11), we obtain:

$$M_{vm}^{v'm} = M_{v0}^{v'0} R_{vv'}(m) \tag{22}$$

where $M_{v0}^{v'0}$ is the pure vibrational matrix element:

$$M_{v0}^{v'0} = \frac{H_{00}}{(I_{00} I'_{00})^{1/2}} \tag{23}$$

and $R_{vv'}(m)$ is the rotational factor:

$$R_{vv'}(m) = \sum_{i=0} G_{vv'}^{(i)} m^i \tag{24}$$

with:

$$G_{vv'}^{(0)} = 1$$

$$G_{vv'}^{(i)} = \sum_{p=0}^{i} \beta_p \gamma_{i-p} \tag{25}$$

where β_p and γ_{i-p} are given respectively by Eqs. (15) and (19).

In the literature the rotational factor $R_{vv'}(m)$ is presented under two forms:(*i*) the Bouanich–Blumenfeld [10] representation; and (*ii*) the Herman–Wallis [2] representation. The Bouanich–Blumenfeld representation is defined as:

$$R_{vv'}(m) = 1 + C'm + D'm^2 + E'm^2 + H'm^4 . \tag{26}$$

In this work we used the Bouanich and Blumenfeld [10] representation; the comparison between Eqs.(26) and (24) gives

$$G_{vv'}^{(0)} = 1; \quad G_{vv'}^{(1)} = C'; \quad G_{vv'}^{(2)} = D'; \quad G_{vv'}^{(3)} = E'; \quad G_{vv'}^{(4)} = H' \tag{27}$$

The Herman–Wallis [2] representation, where the rotational factor is defined as:

$$F_{vJ}^{v'J'} = (M_{vJ}^{v'J'} / M_{v0}^{v'0}) = [R_{vv'}(m)]^2 \tag{28}$$

with:

$$F_{vJ}^{v'J'} = 1 + Cm + Dm^2 + Em^3 + Hm^4 + ... \tag{29}$$

and C, D, E,.. are the Herman–Wallis coefficients. The derivation of these coefficients from our formulation can be obtained by the identification of Eqs. (24) and (29), one obtains:

$$C = 2G_{vv'}^{(1)} \tag{30–1}$$

$$D = 2G_{vv'}^{(2)} + (G_{vv'}^{(1)})^2 \tag{30–2}$$

$$E = 2(G_{vv'}^{(3)} + G_{vv'}^{(1)}G_{vv'}^{(2)}) \tag{30–3}$$

$$H = 2G_{vv'}^{(4)} + 2G_{vv'}^{(3)}G_{vv'}^{(1)} + (G_{vv'}^{(2)})^2 \tag{30–4}$$

Thus, with the new m–representation of the eigenvalue E_{vm} and the eigenfunction Ψ_{vm} the Herman–Wallis coefficients are given by simple analytic expressions [Eq. (25)] in terms of the canonical functions α_i and α'_i ($i = 0,1$).

3 NUMERICAL APPLICATIONS

In the m–representation of the eigenvalue E_{vm} and the eigenfunction Ψ_{vm}, the determination of the Bouanich–Herman–Wallis coefficients $G_{vv'}^{(i)}$ [Eq. (24)] is reduced to that of calculating the coefficients β_i (Eqs.(19)) and γ_i [Eq. (15)]. These coefficients are given by analytical expressions in terms of the canonical functions α_i and α'_i for the two considered states where the determination of these functions, with high precision, is a solved problem [4]. In order to test the validity and the accuracy of the present formulation, we calculate the Bouanich–Herman–Wallis coefficients $G_{vv'}^{(i)}$ by using Eqs. (25) with a Dunham potential [11] of the molecule HCl for the transitions $1 \le v' - v \le 4$ and v = 0, 5, 10 (Table 1).

Table1. Values of the Bouanich–Herman–Wallis coefficients for several transitions ($v = 0, 5, 10$ and $v'-v \leq 4$) for the ground state of the molecule HCl

v	Δv	$G_{vv'}^{(1)}$	$G_{vv'}^{(2)}$	$G_{vv'}^{(3)}$	$G_{vv'}^{(4)}$
0	1	−1.28558(−2) [a]	4.30991(−5)	−8.66854(−7)	−2.28678(−8)
	2	−2.48105(−3)	1.74278(−4)	−5.45974(−7)	2.33123(−8)
	3	6.04177(−3)	2.47683(−4)	2.65309(−6)	4.42817(−8)
	4	1.36266(−2)	6.82356(−4)	1.48075(−5)	−1.09078(−7)
5	1	−1.78362(−2)	−9.29926(−5)	−1.13719(−6)	−4.69398(−8)
	2	−4.04660(−3)	2.16239(−4)	−1.48185(−6)	4.07718(−8)
	3	5.29612(−3)	2.32292(−4)	2.12458(−6)	2.01231(−7)
	4	9.04922(−3)	5.28196(−4)	4.13408(−6)	1.38309(−7)
10	1	−3.97154(−1)	−1.60597(−2)	−1.92539(−6)	−6.57557(−6)
	2	−6.47960(−3)	3.83621(−4)	−3.43933(−6)	4.78654(−8)
	3	5.76187(−3)	−1.46109(−4)	4.48213(−6)	2.81210(−8)
	4	4.55807(−3)	5.43568(−4)	−1.44991(−6)	−2.57616(−7)

[a] Number between parentheses stands for a multiplicative power of 10.

Table 2. Values of the rotational factor $R_{vv'}(m)$, (Eq.(24), for several values of v, Δv, and m for the R–branch of the ground state of the molecule HCl.

v	Δv	$m = -2$	$m = -4$	$m = -6$
0	1	1.02589 [a]	1.05217	1.07884
		1.02589 [b]	1.05217	1.07885
		1.02518 [c]	1.05261	1.07935
	2	1.00566	1.01275	1.02131
		1.00566	1.01275	1.02132
		1.00568	1.01272	1.14569
	3	0.98888	0.97962	0.97204
		0.98888	0.97961	0.97207
		0.98899	0.98004	1.00949
	4	0.97535	0.95544	0.93946
		0.97535	0.95598	0.93991
		0.97560	0.95708	0.94477
5	1	1.03531	1.06992	1.10385
		1.03531	1.06992	1.10385
	2	1.00897	1.01975	1.03244
		1.00897	1.01975	1.03247
	3	0.99032	0.98273	0.97634
		0.99032	0.98278	0.97635
	4	0.98398	0.97203	0.96401
		0.98398	0.97214	0.96468
10	1	1.72998	2.33010	2.79667
		1.72998	2.33008	2.79650
	2	1.01452	1.03229	1.05349
		1.01452	1.03231	1.05360
	3	0.98785	0.97434	0.95924
		0.98785	0.97436	0.95930
	4	0.99307	0.99062	0.99287
		0.99307	0.99068	0.99326

[a] First entry: The present work
[b] Second entry: Ref. [12]
[c] Third entry: Ref. [11]

The dipole moment function *f*(*r*), Eq. (1), is a polynomial in $(r - r_e)/r_e$ up to seventh order [11]. By using these coefficients we present in Table 2 (first entry) the values of the rotational factor $R_{vv'}(m)$ calculated from Eq. (24). The comparison of these values to those calculated by a numerical method [12] (second entry of Table 2) and those of Kobayashi and Suzuki [11] shows a good agreement for the considered levels except for $\Delta v = 4$ and $m = -6$. For $v = 10$ ($\Delta v = 4$ *and* $m = -6$) the agreement deteriorates.

This discrepancy for higher v and Δv may be explained by the limited region of validity of the Dunham potential around r_e, and the power series expansion of the dipole moment function f(r) which rapidly diverges outside the range of separation in which was determined. By using Eqs. (30) we calculate for the same molecule the Herman–Wallis coefficients, Eq. (29), for $\Delta v \leq 7$ and $v = 0$ (fifth column of Table 3).

Table 3. Values of the Herman–Wallis coefficients for the transitions $v = 0$ and $v' - v \leq 7$ for the ground state of the molecule HCl

v	Δv		Ref. [11]	Present Work
0	1	C	–2.6(–2)	–2.5712(–2)
		D	2.5(–4)	2.5147(–4)
		E	–	–2.8419(–6)
		H	–	–2.1590(–8)
	2	C	–5.0(3)	–4.9621(–3)
		D	3.5(–4)	3.5471(–4)
		E	–	–1.9567(–6)
		H	–	7.9707(–8)
	3	C	1.2(–2)	1.2083(–2)
		D	5.3(–4)	5.3187(–4)
		E	–	8.2991(–6)
		H	–	1.8197(–7)
	4	C	2.72(–2)	2.7253(–2)
		D	1.55(–3)	1.5504(–3)
		E	–	4.8211(–5)
		H	–	6.5101(–7)
	5	C	1.93(–2)	1.9312(–2)
		D	1.78(–4)	1.7738(–4)
		E	–	–2.3161(–5)
		H	–	–4.5408(–7)
	6	C	3.35(–2)	3.3488(–2)
		D	7.88(–4)	7.8173(–4)
		E	–	6.6285(–7)
		H	–	–3.2911(–8)
	7	C	4.31(–2)	4.2953(–2)
		D	1.08(–3)	1.1211(–3)
		E	–	1.3218(–5)
		H	–	1.2923(–7)

The comparison of these values to those calculated by Kobayashi and Suzuki [11] shows a very good agreement for all the considered transitions (fourth column of Table 3). No comparison with other results for the high order coefficients H because they are given here for the first time.

We calculate also of the rotational factor $R_{vv'}(m)$ of the molecule [8] CO for the transitions $0 \le \Delta v \le 4$, *v=0* and *m=–6* by using Eq. (24) and a numerical method [10] which are represented respectively by $R^{pw}_{vv'}(m)$ and $R^{num}_{vv'}(m)$ (not showed). The calculation of the ratio $\frac{\Delta R}{R} = (\sum_{\Delta v=1}^{4} \frac{|R^{pw}_{vv'}(m) - R^{num}_{vv'}(m)|}{R^{num}_{vv'}(m)})/4$ for the molecules CO and HCl gives:

$$(\frac{\Delta R}{R})_{CO} = 4.7x10^{-7} \text{ and } (\frac{\Delta R}{R})_{HCl} = 1.4x10^{-4}$$

To explain the high accuracy of this ratio for the molecule CO, we may notice that, in the perturbation theory the accuracy of calculation of the rotational factor $R_{vv'}(m)$ is inversely proportional to the ratio B_e / ω_e of the considered molecule ($(B_e / \omega_e)_{co} = 0.0008899$ and $(B_e / \omega_e)_{HCl} = 0.0035415$). Similar applications were completed for other potentials (Morse and RKR potentials) as well as for the operator exp(–*ar*). In all of these cases results similar to those presented here were obtained (not showed).

4 CONCLUSIONS

In a previous work [3] we expanded respectively the eigenvalue and the eigenfunction of a rovibrational state *vJ* in terms of the running number *m* as:

$$\mathbf{E}_{\mathbf{vm}} = \sum_{\mathbf{i}=0} \mathbf{A}_{\mathbf{i}} \mathbf{m}^{\mathbf{i}}, \qquad \Psi_{\mathbf{vm}} = \sum_{\mathbf{i}=0} \phi_{\mathbf{i}} \mathbf{m}^{\mathbf{i}}$$

where the coefficients A_i and ϕ_i are given by analytical expressions. By using this new formulation we showed that the Bouanich–Herman–Wallis coefficients are given by simple analytical expressions in terms of the canonical functions α_i and α'_i even for the high order coefficients with no restriction on the potential function, the operator *f*(*r*) and the vibrational level *v* (even for high vibrational levels). The numerical application showed the high accuracy of the present formulation with a simple algorithm and simple analysis tools.

5 REFERENCES

[1] G. Herzberg (Ed), *The Spectra of Diatomic Molecules*, Van Nostrand, Toronto, **1950**.

[2] R. C. Herman and R. F. Wallis, Influence of Vibration–Rotation Interaction of Line Intensities in Vibration–Rotation Band of Diatomic Molecule, *J.Chem.Phys*. **1955**, *23*, 637–646.

[3] R. A. Toth, R. H. Hunt, and E. K. Plyler, Line Strength, Line Widths and Dipole Moment Function, *J. Mol. Spectrosc*. **1970**, *35*, 110–126; R. H. Tipping and J. F. Ogilvie, Herman–Wallis Factors for Overtone Bands: Application to HCl, *J. Mol. Spectrosc*. **1982**, *96*, 442–450; J. P. Bouanich, Vibration–Rotational Matrix Elements for Infrared Transitions of Diatomic Molecules, *J. Quant. Spectrosc.Radiat Trans* **1987**, *37*, 17–21; H. Kobeissi and M. Korek, Diatomic Rovibrational Matrix Elements expression of the Rotational Factor of any Potential, *J. Phys. B: At. Mol. Opt.Phys*. **1994**, *27*, 3653–3658.

[4] M. Korek and B. Hamdoun, A New Perturbation–Approach to the Rovibronic Transition Matrix Elements of

Diatomics, *Internet Electron. J. Mol. Des.* **2004**, *3*, 271–287.

[5] M. Korek and H. Kobeissi, Diatomic Centrifugal Distortion Constants for Large Orders at any Level: Application to the XO_g^+–I_2, *Can. J. Chem.* **1993**, *71*, 313–317.

[6] M. Born and R. Oppenheimer, *Ann. Phys.* **1927**, *84*, 457.

[7] M. Korek and H. Kobeissi, New Analytical Expressions for the Herman–Wallis Coefficients for Infrared Transitions up to the Third Order, *J. Quant. Spectrosc. Radiat Trans.* **1994**, *52*, 631–638.

[8] J. M. Huston, Centrifugal Distortion Constants for Diatomic Molecules, *J. Phys. B: At. Mol. Opt.Phys.* **1981**, *14*, 851–857.

[9] P. W. Atkins and R. S. Friedman, *Molecular Quantum Mechanics*, 3^{thd} edition, Oxford University Press.

[10] J. P. Bouanich, and L. Blumenfeld, On the Vibration Rotational– Matrix Elements for Diatomic Molecules, *J Quant. Spectrosc. Radiat Trans* **1986**, *36*, 87–91.

[11] M. Kobayashi and I. Suzuki, Dipole Moment Function of Hydrogen Chloride, *J. Mol. Spectrosc.* **1986**, *116*, 422–434.

[12] H. Kobeissi, M. Dagher, M. Korek, and A. Chaalan, A New Treatment of the Vibration–Rotation Eigenvalue Problem for a Diatomic Molecule, *J. Comput. Chem.* **1983**, *4*, 218–225.

Biographies

Mahmoud Korek is professor of atomic and molecular physics at Beirut Arab University. After obtaining a Ph.D. degree in molecular Physics from the University of Claude Bernard Lyon I, France, Dr. Korek undertook postdoctoral at the American University of Beirut. More recently, Dr. Korek has collaborated on projects with University of Claude Bernard Lyon I, France. The major research projects are: new approach in the perturbation theory, determination of the electronic structure of diatomic molecules, and mixed clusters.

Claire Deeb is MSc student at Beirut Arab University.