Closed form formulas for the Rosen-Morse and Manning-Rosen rotation-vibration intensities from ladder operator considerations

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It is shown that the *accelerated* ladder operator method, leads to closed form expressions of the Rosen-Morse and Manning-Rosen rotation vibration dipole moment matrix elements. These closed form formulas, which are valid for any degree t of the dipole moment Taylor's expansion, allows the calculation of the rotation vibration intensities for any $\Omega v J \rightarrow \Omega' v' J'$ transition. Explicit expressions of the rotation vibration energy levels in terms of the quantum numbers and of the specific parameters of each potential are also given.

1. Introduction

In previous papers, it has been shown how the introduction of *multi-step* or *accelerated* ladder operators, within the Schrödinger Infeld-Hull factorization method (Schrödinger 1940, 1941; Infeld & Hull 1951), enables a straightforward determination of closed form expressions of radial as well as angular matrix elements. Particularly, this method has proved to be very efficient to obtain hydrogenic r^k radial off-diagonal matrix elements (Badawi *et al* 1973; Bessis *et al* 1973; Hadinger *et al* 1973) and, also, closed form formulas for the Morse-Pekeris rotation vibration intensities of diatomics (Badawi *et al* 1973; Badawi *et al* 1974). In fact, these two problems are closely related. As it has been shown elsewhere (Badawi *et al* 1972), for several other types of diatomic potential functions, the nuclear radial equation is still factorizable if an adequate expansion technique is used to include the rotation-vibration coupling; moreover the Morse-Pekeris, Rosen-Morse (1932) and Manning-Rosen (1933) potentials can be considered as three particular cases of the same general expression.

In the present paper, the determination of the Rosen-Morse and Manning-Rosen rotation-vibration intensities is investigated. From a theoretical point of view, the last investigation differs from the previous ones : indeed, since the application of our former procedure would result in intricate *accelerated* ladder operators, a new canonical expression of these operators is introduced. This new aspect of the ladder operator method has been thoroughly considered elsewhere (Hadinger *et al* 1974). General results of this last reference are largely

used hereafter to obtain closed form formulas for the Rosen-Morse and Manning-Rosen rotation-vibration intensities and, also, the energy levels. Such expressions, which to our knowledge have not been yet given, could enable a comparative interpretation of experimental results where using Morse-Pekeris, Rosen-Morse or Manning-Rosen potentials. This last point will be investigated in a forthcoming paper.

2. THEORY

Within the Born-Oppenheimer approximation, the expression of the intensity of a line associated with the transition $\Omega v J \to \Omega' v' J'$ in a rotation-vibration band of a diatomic molecules is well known to be (Herzberg 1950; Landau & Lifshitz 1971)

$$I_{\substack{\Omega v J \\ \Omega' v' J'}} = \frac{4\pi^2 N_{\Omega v J}(2J'+1)}{3\hbar c[2-\delta(\Omega, \Omega')]} \begin{pmatrix} J & 1 & J' \\ -\Omega & \Omega-\Omega' & \Omega' \end{pmatrix}^2 \omega_{\substack{\Omega v J \\ \Omega' v' J'}} |M|^2_{\substack{\Omega v J \\ \Omega' v' J'}}, \qquad \dots (1)$$

where $N_{\Omega v J}$ is the number of molecules in the initial state, $\omega_{\substack{\Omega v J \\ \Omega' v' J'}}$ the vibrational frequency (in cm^{-1}), M the dipole moment matrix element, J and Ω the total angular quantum numbers for the rotational state under consideration (Hund's coupling case (a)) and $\begin{pmatrix} J & 1 & J' \\ -\Omega & \Omega-\Omega' & \Omega' \end{pmatrix}$ a Wigner $3j$ coefficient (Edmonds 1957)

The expression (1) can be easily extended to n-pole moments, and, of course, for singlet states ($S = 0$) is identical with the Höln & London formulas (Höln & London 1925).

When a Taylor expansion near the equilibrium distance r_e is introduced for the dipole moment i.e.,

$$M(r) = \sum_t \bar{M}_t (r-r_e)^t \qquad \dots (2)$$

the dipole moment matrix element can be written

$$M_{\substack{\Omega v J \\ \Omega' v' J'}} = cc' \sum_t \bar{M}_t M^{(t)}_{\substack{\Omega v J \\ \Omega' v' J'}}, \qquad \dots (3)$$

where

$$M^{(t)}_{\substack{\Omega v J \\ \Omega' v' J'}} = \int_0^\infty R_{\Omega v J}(r)(r-r_e)^t R_{\Omega' v' J'}(r) r^2 dr \qquad \dots (4)$$

c and c' are the normalization constants of the nuclear radial wavefunctions $R_{\Omega v J}(r)$. In view of further simplifications occuring in the calculation, we have not introduced the normalization constants within the matrix element (4).

The nuclear rotation-vibration wavefunctions $R_{\Omega v J}(r)$ are solutions of the well known equation

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left[\frac{\Omega^2 - J(J+1)}{r^2} + \frac{2\mu}{\hbar^2} (E - E_{el} - Q(r)) \right] R = 0, \qquad \dots (5)$$

where μ, E, E_{el}, $Q(r)$ are respectively the reduced mass, the total energy, the electronic energy and the potential function. Ω, J and v are the usual quantum numbers characterizing the rotation-vibration state $(\Omega J v)$.

When setting $U(r) = rR(r)$, eq. (5) becomes

$$\frac{d^2U}{dr^2}+\frac{2\mu}{\hbar^2}\left[W-Q(r)-A_e\left(\frac{r_e}{r}\right)^2\right] U = 0, \qquad \ldots \text{ (6)}$$

where r_e is the equilibrium distance of the nuclei and

$$W = E-E_{el},$$

$$A_e = B_e[J(J+1)-\Omega^2], \qquad \ldots \text{ (7)}$$

$$B_e = \frac{\hbar^2}{2\mu r_e^2}.$$

The Rosen-Morse potential function is

$$Q(r) = B\tanh(r/d-k)-C\operatorname{sech}^2(r/d-k), \qquad \ldots \text{ (8)}$$

where k is assumed to be positive (see also Appendix A).
The Manning-Rosen potential function is :

$$Q(r) = \frac{1}{K\rho^2}\left[\frac{\beta(\beta-1)\exp(-2r/\rho)}{[1-\exp(-r/\rho)]^2}-\frac{A\exp(-r/\rho)}{[1-\exp(-r/\rho)]}\right]. \qquad \ldots \text{ (9)}$$

In the expressions (8) and (9), the authors's original symbols B, d, C, k, and K, ρ, A and β are used.

As it has been pointed out elsewhere (Badawi et al 1972), the potential functions (eqs. (8) and (9)), as well as the Morse-Pekeris potential already investigated (Badawi et al 1974), are particular cases of the general expression

$$Q(r) = M\left(\frac{\exp(-\gamma r)}{1+\tau\exp(-\gamma r)}\right)^2+N\left(\frac{\exp(-\gamma r)}{1+\tau\exp(-\gamma r)}\right)+L. \qquad \ldots \text{ (10)}$$

For the Rosen-Morse potential

$$\tau = \exp(2k),$$
$$\gamma = 2/d,$$
$$M = 4C\exp(4k),$$
$$N = -(2B+4C)\exp(2k), \qquad \ldots \text{ (11)}$$
$$L = B.$$

For the Manning-Rosen potential

$$\tau = -1,$$

$$\gamma = \frac{1}{\rho},$$

$$M = \frac{\beta(\beta-1)}{K\rho^2}, \qquad \qquad \cdots \quad (12)$$

$$N = -\frac{A}{K\rho^2},$$

$$L = 0.$$

Eq. (6) is factorizable if an adequate expansion technique is used to include the rotation-vibration coupling term $A_0(r_e/r)^2$ i.e., by equating this term to an expression homogeneous to eq. (10)

$$\left(\frac{r_e}{r}\right)^2 = C_2\left(\frac{\exp(-\gamma r)}{1+\tau\exp(-\gamma r)}\right)^2 + C_1\left(\frac{\exp(-\gamma r)}{1+\tau\exp(-\gamma r)}\right) + C_0, \qquad \cdots \quad (13)$$

where the C_i are functions of the specific parameters τ and γ of each potential (Badawi *et al* 1972).

$$C_0 = \left\{1 - \frac{4}{\gamma r_e}(1+\tau\exp(-\gamma r_e)) + \left(\frac{3}{\gamma^2 r_e^2} + \frac{1}{\gamma r_e}\right)(1+\tau\exp(-\gamma r))^2\right\},$$

$$C_1 = \frac{1}{\tau}2\exp(\gamma r_e)\left\{\frac{3}{\gamma r_e}(1+\tau\exp(-\gamma r_e))^2 - \left(\frac{3}{\gamma^2 r_e^2} + \frac{1}{\gamma r_e}\right)(1+\tau\exp(-\gamma r_e))^3\right\},$$

$$\cdots \quad (14)$$

$$C_2 = \frac{1}{\tau^2}\exp(2\gamma r_e)\left\{-\frac{2}{\gamma r_e}(1+\tau\exp(-\gamma r_e))^3 + \left(\frac{3}{\gamma^2 r_e^2} + \frac{1}{\gamma r_e}\right)(1+\tau\exp(-\gamma r_e))^4\right\}.$$

Then, the nuclear rotation-vibration eq. (6) becomes

$$\left\{\frac{d^2}{dr^2} - \frac{2\mu}{\hbar^2}\left[(M+A_eC_2)\left(\frac{\exp(-\gamma r)}{1+\tau\exp(-\gamma r)}\right)^2 + (N+A_eC_1)\left(\frac{\exp(-\gamma r)}{1+\tau\exp(-\gamma r)}\right)\right.\right.$$

$$\left.\left. + (L+A_eC_0) - W\right]\right\}U(r) = 0 \qquad \cdots \quad (15)$$

When setting

$$x = \frac{\gamma r}{2} - \tfrac{1}{2}\ln|\tau| \qquad \cdots \quad (16)$$

and expressing exp $(-\gamma r)$ in terms of trigonometric functions, it is easily shown that the eq. (15) can be written.

$$\left\{\frac{d^2}{dx^2} - \frac{S(S+1)}{\left[\frac{1}{a}\sin a(x+p)\right]^2} - 2aq\cot a(x+p) + \lambda\right\}U(x) = 0 \qquad \cdots \quad (17)$$

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with

$$a = i \,,$$

$$p = i\frac{\pi}{4}(1+\epsilon) \,,$$

$$S = \tfrac{1}{2}\left[1+\frac{8\mu}{\hbar^2\gamma^2}\left(\frac{M}{r^2}+A_\epsilon C_2\right)\right]^{\frac{1}{2}}-1/2 \,,$$

$$q = -\frac{2\mu}{\hbar^2\gamma^2}\left[\frac{M}{r^2}+\frac{N}{r}+A_\epsilon(C_1+C_2)\right], \qquad \ldots (18)$$

$$\lambda = 2q+\frac{8\mu}{\hbar^2\gamma^2}(W-L-C_0) \,,$$

$\epsilon = +1$, for the Rosen-Morse potential,

$\epsilon = -1$, for the Manning-Rosen potential.

Eq. (17) appears to be a Infeld-Hull's type E factorizable equation already investigated in a previous paper (Hadinger *et al* 1974). Within the Infeld-Hull's factorization scheme, the factorizable eq. (17) can be replaced by each of the two following differential equations

$$H_S{}^+ H_S{}^- U_S{}^m = [\lambda - L(S)]U_S{}^m$$
$$H^-{}_{S+1} H^+{}_{S+1} U_S{}^m = [\lambda - L(S+1)]U_S{}^m, \qquad \ldots (19)$$

where S and m are quantum numbers characterizing the state under consideration and $L(S)$ is a function independent of x. For a type E factorizable case.

$$L(S) = a^2 S^2 - q^2/S^2. \qquad \ldots (20)$$

The *one step* up/down ladder operators are

$$H_S{}^\pm = Sa \cot a(x+p) + \frac{q}{S} \mp \frac{d}{dx}. \qquad \ldots (21)$$

The necessary condition for the existence of quadratically integrable solutions is

$$|m-S| = v = \text{integer}. \qquad \ldots (22)$$

Each eigenfunction $U_S{}^m(S = m\pm v)$ of the whole discrete spectrum is completely characterized by the integer value of v which fixes its rank starting from the key function $U_S{}^S(v=0)$.

From *accelerated* ladder operator considerations, it has been shown that a general expression of $U_S{}^m(x)$ is [1]

$$U_S{}^m(x) = U_S{}^m(x)[\sin a(x+p)]^v \, P_v{}^{(\alpha_1-v,\ \alpha_2-v)}[\coth ia(x+p)], \qquad \ldots (23)$$

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[1] Hereafter, purposely, the normalization constants of the eigenfunction $U_S{}^m(x)$ and also of the wavefunction $R_v(r)$ are not explicited. They are calculated further (eqs. (41) and (60)) from the explicit expression of the particular ($t = 0$) dipole moment integral $M(t)$ [eq. (4)].

where $P_v^{(\alpha_1 - v, \; \alpha_2 - v)}$ is a Jacobi polynomial whose parameters α_1 and α_2 will be specified further for each of the two potentials under consideration.

The key function $(v = 0)$ is

$$U_S^S(x) = [\sin a(x+p)]^{-\left(\frac{\alpha_1 + \alpha_2}{2}\right)} \exp\left[-i\left(\frac{\alpha_1 - \alpha_2}{2}\right)a(x+p)\right]. \quad \dots \quad (24)$$

Hence, the Rosen-Morse wavefunctions as well as the Manning-Rosen wavefunctions can be derived from these general results. At this stage it is better to consider each case separately.

3, ROSEN-MORSE ROTATION-VIBRATION INTENSITIES

The specific parameters of the Rosen-Morse potential are assumed to verify the Varshni's (1957) conditions which will be given at the end of the present section. Nevertheless the mathematical treatment is independant of these conditions.

A. *Wave functions*

When specifying in (23) the parameters a and p (with $\epsilon = +1$) [see eq. (18)] one obtains the expression of the Rosen-Morse U_S^m function[1]

$$U_S^m(x) = U_S^S(x)[\text{ch}(x)]^v P_v^{(\alpha_1 - v, \; \alpha_2 - v)}(-\text{th } x) \quad \dots \quad (25)$$

with the following expression of the key function

$$U_S^S(x) = [\text{ch}(x)]^{-\left(\frac{\alpha_1 + \alpha_2}{2}\right)} \exp\left[\tfrac{1}{2}(\alpha_1 - \alpha_2)x\right] \quad \dots \quad (26)$$

and [see eq. (16)]

$$x = \frac{r}{d} - k; \quad (-k \leqslant x \leqslant +\infty). \quad \dots \quad (27)$$

The eigenfunction U_S^m must satisfy the boundary conditions

$$U_S^m(-k) = U_S^m(+\infty) = 0 \quad \dots \quad (28)$$

It is sufficient, and of course necessary, that these conditions be fulfilled by the key function U_S^S (Infeld & Hull 1951).

In fact, as for the Morse-Pekeris functions (ter Haar 1946), it can be shown (see Appendix A) that, when the Rosen-Morse parameter k is large enough, the boundary conditions (28) can be replaced, to a fair approximation, by the following ones

$$U_S^m(-\infty) = U_S^m(+\infty) = 0. \quad \dots \quad (29)$$

Then, the eigenfunctions satisfying the conditions (29) turn to be, within the factorization scheme, class II $(v = S - m)$ solution of eq. (17).

Finally, when specifying in (25) the values of the parameters α_1 and α_2 of the Jacobi polynomial, one obtains the closed form expression, of the Rosen-Morse rotation-vibration wave function[1]

$$R_{\Omega v J}(r) = \frac{1}{r}\left[\text{ch}\left(\frac{r}{d}-k\right)\right]^{-m} \exp\left[-\frac{q}{m}\left(\frac{r}{d}-k\right)\right] P_v^{\left(m-\frac{q}{m}, m+\frac{q}{m}\right)}$$

$$\left[-\text{th}\left(\frac{r}{d}-k\right)\right], \qquad \qquad \dots \ (30)$$

where from eqs. (18) and (11)

$$m = S-v = \tfrac{1}{2}\left[1+\frac{2\mu}{\hbar^2}d^2(4C+A_eC_2)\right]^{\frac{1}{2}}-(v+\tfrac{1}{2}) \qquad \dots \ (31)$$

$$q = -\frac{\mu}{2\hbar^2}d^2[-2B+A_e(C_1+C_2)]$$

provided that $m^4 > q^2$ (class II eigenfunctions).

B. *Energy levels*

The eigenvalue λ in eq. (17) is $\lambda_m = L(m)$. From the expression (20) with $a = i$, one gets :

$$\dots \qquad \qquad \lambda_m = -m^2-q^2/m^2. \qquad \qquad \dots \ (32)$$

By equating the expressions (32) and (18) of λ, and taking into account the quantification condition $v = S-m$ one obtains the energy levels expressed in terms of the quantum numbers v, J and Ω, and of the potential parameters

$$E = E_{el}-\frac{\hbar^2}{8\mu d^2}-C+A_e(C_0+\tfrac{1}{2}C_1+\tfrac{1}{4}C_2)-\frac{\hbar^2}{2\mu d^2}(v+\tfrac{1}{2})^2$$

$$+\frac{\hbar^2}{2\mu d^2}(v+\tfrac{1}{2})S_J-\frac{\mu d^2}{2\hbar^2}\left[\frac{A_e(C_1+C_2)-2B}{2(v+\tfrac{1}{2})-S_J}\right]^2, \qquad \dots \ (33)$$

where C_0, C_1, C_2 are given by (14) and

$$S_J = \left[1+\frac{2\mu}{\hbar^2}d^2(4C+A_eC_2)\right]^{\frac{1}{2}}$$

$$A_e = B_e[J(J+1)-\Omega^2]. \qquad \qquad \dots \ (34)$$

The expressions (11) have been used to express the coefficients M, N and L of $Q(r)$ (eq. (10)) in terms of the Rosen-Morse parameters.

C. *Dipole moment matrix elements*

The current matrix element [eq.(4)] to be calculated can be rewritten

$$M^{(t)}_{\substack{\Omega v J \\ \Omega' v' J'}}(s, s') = \int_{-\infty}^{+\infty} U_S{}^{m*}(x)(xd+k-r_e)^t\ U_S{}'^{m'}(x)dx, \qquad \dots \ (35)$$

where the integration bounds $(-k, +\infty)$ have been replaced by $(-\infty, +\infty)$. This can be justified to a fair approximation provided that k is large enough (see Appendix A). This condition is compatible with the Varshni's conditions.

When introducing the classical expression of the Jacobi polynomial (Gradshteyn & Ryzhik 1965), ond obtains an alternative expression of the Rosen-Morse function (25)

$$U_S{}^m(x) \simeq \sum_{j=0}^{v} A_j (\operatorname{ch} x)^{-m-j} \exp\left[\left(-\frac{q}{m}+j\right)x\right] \qquad \dots (36)$$

where[2]

$$A_j = \binom{v}{j} \frac{\Gamma(S+m+j+1)}{2^j \Gamma(m-q/m+j+1)}. \qquad \dots (37)$$

Hence, ono obtains[3].

$$M^{(t)}_{\substack{\Omega v J \\ \Omega' v' J'}} (s, s') = \sum_{j=0}^{v} \sum_{l=0}^{v'} A_j A'_l \mathcal{J}_{jl}{}^{(t)} \qquad \dots (38)$$

where

$$\mathcal{J}_{jl}{}^{(t)} = \int_{-\infty}^{+\infty} (\operatorname{ch} x)^{-m-m'-j-l} \exp\left[\left(-\frac{q}{m}-\frac{q'}{m'}+j+l\right)x\right](xd+k-r_e)^t dx. \quad \dots (39)$$

For $t = 0$, the determination of the integral (39) is straight forward and, from tables (Gradshteyn & Ryzhik 1965), one gets :

$$\mathcal{J}_{jl}{}^{(0)} = 2^{m+m'+j+l-1} \frac{\Gamma\left(\frac{m+m'}{2}-\frac{q}{2m}-\frac{q'}{2m'}+j+l\right)\Gamma\left(\frac{m+m'}{2}+\frac{q}{2m}+\frac{q'}{2m'}\right)}{\Gamma(m+m'+j+l)} \qquad \dots (40)$$

It should be noted that the normalization constant c of the wavefunction is

$$c = [M^{(0)}_{\substack{\Omega v J \\ \Omega' v' J'}} (s, s')]^{-\frac{1}{2}}.$$

Hence, from eq. (40), one gets

$$c = \left\{ \sum_{j=0}^{v} \sum_{l=0}^{v} A_j A_l \frac{2^{2m+j+l-1}\Gamma(m-q/m+j+l)\Gamma(m+q/m)}{\Gamma(2m+j+l)} \right\}^{-\frac{1}{2}} \qquad \dots (41)$$

For $t \neq 0$, the $\mathcal{J}_{jl}{}^{(0)}$ integral [eq (39)] is obtainable by use of formal derivation (see Appendix B)

$$\mathcal{J}_{jl}{}^{(t)} = \sum_{s=0}^{t-1} \binom{t-1}{s} \mathcal{J}_{jl}{}^{(t-1-s)}\left(\frac{\partial}{\partial\sigma}\right)^s [g(\sigma)d^{s+1}+k-r_e] \qquad \dots (42)$$

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[2]In the expression of $U_s{}^m$, a multiplicative factor, independent of j, has been deleted since it cancels out, in the final result, when the expression (35) with $t = 0$ is used to calculate the normalization constants of the wavefunctions.

[3]Primed notation corresponds to quantum numbers S', m' and v'.

where

$$\sigma = -q/m - q'/m' + j + l$$

$$g(\sigma) = \tfrac{1}{2} \left[\psi\left(\frac{\sigma}{2} + \frac{m+m'+j+l}{2}\right) - \psi\left(-\frac{\sigma}{2} + \frac{m+m'+j+l}{2}\right) \right] \qquad \dots \quad (43)$$

$$\left(\frac{\partial}{\partial\sigma}\right)^s g(\sigma) = (\tfrac{1}{2})^{(s+1)} \left\{ \psi^{(s)}\left(\frac{\sigma}{2} + \frac{m+m'+j+l}{2}\right) + (-)^{(s+1)}\psi^{(s)}\left(-\frac{\sigma}{2} + \frac{m+m'+j+l}{2}\right) \right.$$

ψ is the Euler function and $\psi^{(s)}$ stands for the s-th derivative with respect to σ which can be obtained by the following relationships.

$$\psi(z) = -\frac{1}{z} - C - \sum_{n=1}^{\infty}\left(\frac{1}{z+n} - \frac{1}{n}\right)$$

$$\psi^{(s)}(z) = (-)^{s+1}s! \sum_{n=0}^{\infty}\frac{1}{(z+n)^{s+1}}$$

(44)

where $C = -0.577215665$ is the Euler-Mascheroni constant. For large values of z, asymptotic expansions of these functions are available elsewhere (see for instance Badawi *et al* 1974).

D.   *Rosen-Morse potential parameters*

Following Varshni (1957), the necessary conditions to be fulfilled by the potential energy curve are

1. This curve should have at least a minimum located at $r = r_e$ i.e., the potential parameters must verify

$$-1 \leqslant \frac{B}{2C} \leqslant 1$$

and

$$kd > r_e \quad \text{if} \quad B > 0$$

$$kd < r_e \quad \text{if} \quad B < 0.$$

As pointed out before, k is chosen positive although it is not a necessary condition to be fulfilled by the potential energy curve (see Appendix A).

2. This curve should come asymptotically to a finite value as $r \to +\infty$ i.e. the potential parameters must verify

$$\frac{1}{4C}(B+2C)^2 = D_e = Q(+\infty) - Q(\overline{r_e}).$$

4.   MANNING-ROSEN ROTATION-VIBRATION INTENSITIES

The treatment of the Manning-Rosen potential is analogous to that of the Rosen-Morse potential.

A. *Wave functions*

From eqs. (18), (12) and (23), one obtains the expression of the Manning-Rosen $U_S{}^m$ function

$$U_S{}^m(x) = U_S{}^S(x).(\text{sh } x)^v P_v{}^{(\alpha_1-v,\ \alpha_2-v)}(-\coth x) \qquad \dots (45)$$

with the following expression of the key function

$$U_S{}^S(x) = (\text{sh } x)^{-\left(\frac{\alpha_1+\alpha_2}{2}\right)} \exp[\tfrac{1}{2}(\alpha_1-\alpha_2)x]. \qquad \dots (46)$$

and [see eq. (16)]

$$x = \frac{r}{2\rho} \; ; (0 \leqslant x \leqslant +\infty) \qquad \dots (47)$$

Within the factorization scheme, the class I $(v = m-S)$ solutions of eq. (17) will satisfy the necessary boundary conditions

$$U_S{}^m(0) = U_S{}^m(+\infty) = 0. \qquad \dots (48)$$

Hence, one obtains the closed form expression of the Manning-Rosen rotation vibration-wavefunction [1]

$$R_{0vJ}(r) = \frac{1}{r} \left[\text{sh}\left(\frac{r}{2\rho}\right) \right]^{m+1} \exp\left[\frac{qr}{2\rho(m+1)}\right]$$

$$P_v{\left(-m-1+\frac{q}{m+1},\ -m-1-\frac{q}{m+1}\right)}\left(-\coth\frac{r}{2\rho}\right), \quad \dots (49)$$

where from eqs. (18) and (12)

$$m+1 = S+v+1 = (v+\tfrac{1}{2})+\tfrac{1}{2}\left[1+\frac{8\mu\rho^2}{\hbar^2}\left(\frac{\beta(\beta-1)}{K\rho^2}+A_eC_2\right)\right]^{\frac{1}{2}}$$

$$q = -\frac{2\mu\rho^2}{\hbar^2}\left[\frac{\beta(\beta-1)}{K\rho^2}+\frac{A}{K\rho^3}+A_e(C_1+C_2)\right] \qquad \dots (50)$$

provided that $q < 0$ and $(m+1)^2 < -q$; (Class I eigenfunctions)

B. *Energy levels*

The eigenvalue λ in the eq. (17) is $\lambda_m = L(m+1)$. From the expression (20) with $a = i$, one gets

$$\lambda_m = -(m+1)^2-q^2/(m+1)^2. \qquad \dots (51)$$

Then, by equating the expressions (51) and (18) of λ and taking into account the quantification condition $v = m - S$, one obtains the energy levels in terms of the quantum numbers v, J, and Ω and of the potential parameters.

$$E = E_{el} - \frac{\hbar^2}{32\mu\rho^2} + \frac{1}{4K\rho^2}[\beta(\beta-1)+2A] + A_e[C_0 + \tfrac{1}{2}C_1 + 1/4\ C_2] -$$

$$- \frac{\hbar^2}{8\mu\rho^2}(v+\tfrac{1}{2})^2 - \frac{\hbar^2}{8\mu\rho^2}(v+\tfrac{1}{2})\mathcal{S}_J \qquad \qquad \dots (52)$$

$$- \frac{2\mu\rho^2}{\hbar^2}\left[\frac{A_e(C_1+C_2)+[\beta(\beta-1)+A]/K\rho^2}{2(v+\tfrac{1}{2})+\mathcal{S}_J}\right]^2,$$

where C_0. C_1, C_2 are given by (14) and

$$\mathcal{S}_J = \left\{1 + \frac{8\mu\rho^2}{\hbar^2}\left[\frac{\beta(\beta-1)}{K\rho^2} + A_e C_2\right]\right\}^{\frac{1}{2}}$$

$$A_e = B_e[J(J+1)-\Omega^2]. \qquad\qquad \dots (53)$$

C. *Dipole moment matrix element*

The current matrix element eq. (4) to be calculated is

$$M^{(t)}_{\substack{\Omega v J \\ \Omega' v' J'}}(S, S') = \int_0^\infty U_S{}^{m*}(x)(2\rho x - r_e)^t U_{S'}{}^{m'}(x)dx, \qquad \dots (54)$$

where the $U_S{}^m$ and $U_S{}'^{m'}$ functions are given by eqs. (45) and (46).

An alternative expression of the Manning-Rosen $U^m{}_S$ function is

$$U^m{}_S \simeq \sum_{j=0}^{v} A_j(\text{sh } x)^{m+1-j} \exp\left[\left(\frac{q}{m+1}+j\right)x\right] \qquad \dots (55)$$

where[2]

$$A_j = (-)^j \binom{v}{j} \frac{\Gamma(-m-S-1+j)}{2^j\Gamma\left(-m+\dfrac{q}{m+1}+j\right)}. \qquad \dots (56)$$

Hence, one obtains[3]

$$M^{(t)}_{\substack{\Omega v J \\ \Omega' v' J'}}(S, S') = \sum_{j=0}^{v} \sum_{l=0}^{v'} A_j A'_l \, \mathcal{J}_{jl}{}^{(t)}, \qquad \dots (57)$$

where

$$\mathcal{J}_{jl}{}^{(t)} = \int_0^\infty (\text{sh } x)^{2+m+m'-j-l} \exp\left[\left(\frac{q}{m+1}+\frac{q'}{m'+1}+j+l\right)x\right](2\rho x - r_e)^t dx. \ \dots (58)$$

For $t = 0$, one gets (Gradshteyn & Ryzhik 1965)

$$J_{jl}^{(0)} = 2^{j+l-3-m-m'} \frac{\Gamma\left(-\frac{m+m'}{2} - \frac{q}{2(m+1)} - \frac{q'}{2(m'+1)} - 1\right)\Gamma(m+m'+3-j-l)}{\Gamma\left(\frac{m+m'}{2} - \frac{q}{2(m+1)} - \frac{q'}{2(m'+1)} + 2 - j - l\right)} \quad \dots \quad (59)$$

and, consequently, the following expression of the normalization constant of the wavefunction.

$$c = \left\{ \sum_{j=0}^{v} \sum_{l=0}^{v} A_j A_l \frac{2^{j+l-3-2m}\Gamma\left(-m-\frac{q}{(m+1)}-1\right)\Gamma(2m+3-j-l)}{\Gamma\left(m-\frac{q}{(m+1)}+2-j-l\right)} \right\}^{-1/2} \quad \dots \quad (60)$$

For $t \neq 0$, the $J_{jl}^{(t)}$ integral [eq (58)] is obtainable by use of formal derivation (see Appendix B).

$$J_{jl}^{(t)} = \sum_{s=0}^{t-1}\binom{t-1}{s} J_{jl}^{(t-1-s)} \left(\frac{\partial}{\partial\sigma}\right)^s [\eta(\sigma)(2\rho)^{s+1}-r_e], \quad \dots \quad (61)$$

where

$$\sigma = q/(m+1)+q'/(m'+1)+j+l$$

$$g(\sigma) = \tfrac{1}{2}\left\{\psi\left(-\frac{\sigma}{2}+2+\frac{m+m'-j-l}{2}\right)-\psi^{(s)}\left(-\frac{\sigma}{2}-1-\frac{m+m'-j-l}{2}\right)\right\} \quad (62)$$

$$\left(\frac{\partial}{\partial\sigma}\right)^s g(\sigma) = \tfrac{1}{2}^{(S+1)}(-)^s\left\{\psi^{(s)}\left(-\frac{\sigma}{2}+2+\frac{m+m'-j-l}{2}\right)\right.$$

$$\left. -\psi^{(s)}\left(-\frac{\sigma}{2}-1-\frac{m+m'-j-l}{2}\right)\right\}$$

is the Euler ψ function and $\psi^{(s)}$ stands for the s-th derivative with respect to σ (see eq. (44)).

D. *Manning-Rosen potential parameters.*

1. For the existence of a minimum of the potential energy curve at $r = r_e$, the necessary condition to be fulfilled by the potential parameters is

$$A = 2\beta(\beta-1)[\exp(r_e/\rho)-1]^{-1}$$

2. The potential curve should come asymptotically to a finite value as $r \rightarrow +\infty$ i.e., the potential parameters must verify

$$\frac{A^2}{4K\rho^2\beta(\beta-1)} = D_e = Q(\infty)-Q(r_e).$$

with $K > 0$ and $\rho > 0$.

5. Conclusion

Finally, our ladder operator procedure enables the determination of closed form expressions of the Rosen-Morse and Manning-Rosen dipole moment matrix elements of a diatomic molecule, which is valid for any degree t of the dipole moment Taylor's expansion, hence, the calculation of the rotation-vibration intensities for any transition $\Omega v J \to \Omega' v' J'$. Of course, from a physical point of view, the limitations of the usefulness come from the knowledge of reliable Taylor coefficients $\overline{M}_t$ [eq. (2)] and also from the availability of good parameters for these potentials which are likely to be more flexible than the Morse-Pekeris potential. Explicit expressions of the rotation-vibration energy levels in terms of the quantum numbers $\Omega v J$ and the potential parameters have been given. Since such formulas have been previously obtained for the Morse-Pekeris potential (Herman & Rubin 1955; Badawi et al 1974), it is now possible, and should be interesting, to study the comparative merits of the three potentials. It should be noted that the calculation of the Morse-Pekeris, Rosen-Morse and Manning-Rosen potentials rotation-vibration dipole moment is also possible by use of four terms recursion formulas (Badawi 1973); nevertheless, from a computational point of view, the use of the closed form expression is, by far, more advantageous.

Appendix A

Extension of the Boundary Conditions for the Rosen-Morse Wave Functions

I. *Wave functions*

As pointed out in Section (3A), the Rosen-Morse function $U_S{}^m$ must satisfy the boundary conditions

$$U_S{}^m(-k) = U_S{}^m(+\infty) = 0 \qquad \ldots \text{(A1)}$$

Our purpose is to show that, to a fair approximation, these conditions can be replaced by the following ones

$$U_S{}^m(-\infty) = U_S{}^m(+\infty) = 0 \qquad \ldots \text{(A2)}$$

Since the application of the ladder operators preserves the boundary conditions (Infeld & Hull 1951), it is necessary and sufficient that the approximative equivalence of condition (A1) and (A2) be fulfilled by the key function $U_S{}^S$.

$$U_S{}^S(x) = [\text{ch } x]^{-S} \exp(-qx/m) \qquad \ldots \text{(A3)}$$

with $S^4 \geqslant m^4 > q^2$.

We need to demonstrate that it is possible to choose $k > 0$ in order to arbitrarily lessen the ratio $U_S{}^S(-k)/U_S{}^S(x_0)$, $U(x_0)$ being the maximum value of the

function. Since $U_S{}^S(x_0) \geqslant U_S{}^S(0) = 1$, it is sufficient to prove that, by a suitable choice of k, one can get $U_S{}^S(-k) < \epsilon U_S{}^S(0)$, ϵ being arbitrary small i.e.;

$$(\mathrm{ch}\ k)^{-S}\ \exp(qk/m) < \epsilon$$

After a few manipulations, one obtains the required condition

$$k > \ln\frac{1}{\epsilon}.$$

II. *Dipole moment matrix element*

Correspondingly, when calculating the current dipole matrix element (eq. (35)), one can replace the integration bounds $(-k, +\infty)$ by $(-\infty, +\infty)$ From eq. (38), since the A_j coefficients do not depend on k, and from the recurrence formulas (42), it is easily seen that it is sufficient to prove the validity of the extension of the integration bounds for $J_{jl}{}^{(0)}$ i.e., that, by a suitable choice of k, one can get

$$\int_{-\infty}^{-k}(\mathrm{ch}\ x)^{-2S}\ \exp(-2qx/m)dx < \epsilon, \ \epsilon\ \text{arbitrary small}.$$

One obtains, in terms of the incomplete-Beta function, or the hypergeometric function (Gradshteyn & Ryzhik 1965)

$$B\left(\frac{1}{1+e^k}\right)^{(S-q/m,\ S+q/m)}$$

$$-\frac{F(S-q/m,\ 1-S-q/m;\ S-q/m+1;\ (1+e^k)^{-1})}{(S-q/m)(1+e^k)^{S-q/m}} < \epsilon$$

For k large enough, one can retain only the first term of the hypergeometric serie and obtain the required condition

$$k > \ln 1/\epsilon$$

From analogous considerations, such an extension of the bounds is usually made for the Morse potential. It has been justified for the wavefunction by Ter Haar (1946).

APPENDIX B

Recurrence formulas for the Rosen-Morse and Manning Rosen $J_{jl}{}^{(t)}$ integral

The Rosen-Morse $\zeta_{jl}{}^{(t)}$ integral is (eq. (39))

$$J_{jl}{}^{(t)} = d^t \int_{-\infty}^{+\infty}(\mathrm{ch}\ x)^{-m-m'-j-l}\ \exp[\sigma x](x+b)^t dx \qquad \dots \text{(B1)}$$

where

$$\sigma = -q/m - q'/m' + j + l$$
$$b = (k-r_e)/d. \qquad \dots \text{(B2)}$$

By formal derivation with respect to the σ parameter it is easy to find the following relationships

$$J^{(t+1)}(\sigma) = d \left(\frac{\partial}{\partial \sigma} + b \right) J^{(t)}(\sigma) \qquad \ldots \text{(B3a)}$$

$$\frac{\partial}{\partial \sigma} [J_{(\sigma)}{}^{(0)}] = g(\sigma) J^{(0)}(\sigma), \qquad \ldots \text{(B3b)}$$

where $g(\sigma)$ is defined by the expression (43).

The Manning-Rosen $J_{fl}{}^{(t)}$ integral is (eq (58))

$$J_{fl}{}^{(t)} = (2\rho)^t \int_0^{+\infty} (\text{sh } x)^{m+m'+\tilde{2}-j-l} \exp [\sigma x](x+b)^t dx, \qquad \ldots \text{(B4)}$$

where

$$\sigma = q/(m+1) + q'/(m'+1) + j + l$$

$$b = -\frac{r_e}{2\rho} \qquad\qquad \ldots \text{B5)}$$

By formal derivation with respect to the σ parameter it is easy to find the following relationships

$$J^{(t+1)}(\sigma) = 2\rho \left(\frac{\partial}{\partial \sigma} + b \right) J^{(t)}(\sigma \qquad \ldots \text{(B6a)}$$

$$\frac{\partial}{\partial \sigma} [J^{(0)}(\sigma)] = g(\sigma) J^{(0)}(\sigma) \qquad \ldots \text{(B6b)}$$

where $g(\sigma)$ is given by the expression (62)

Consequently, both Rosen-Morse and Manning $\hbar$ Rosen integrals verify the same function relationships (see eq (B3) and (B6).

From (B3a), $\left(\frac{\partial}{\partial \sigma} + b \right)$ can be considered as a one-step up ladder operator, Consequently,

$$J^{(t)}(\sigma) = d^t \left[\frac{\partial}{\partial \sigma} + b \right]^t J^{(0)}(\sigma). \qquad \ldots \text{(B7)}$$

On the other hand, from (B3, b) and (B7)

$$\frac{\partial}{\partial \sigma} [J^{(t)}(\sigma)] = d^t \left(\frac{\partial}{\partial \sigma} + b \right)^s [g(\sigma) J^{(0)}(\sigma)].$$

Hence, using Leibnitz's rule, one obtains

$$J^{(t+1)}(\sigma) = \sum_{s=0}^{t} \binom{t}{s} \left(\frac{\partial}{\partial \sigma} \right)^s [g(\sigma) d^{s+1} + bd].$$

This formula holds both for the Rosen-Morse and the Manning-Rosen inte-
For the Rosen-Morse case, b and σ are given by (B2) and $g(\sigma)$ is defined by eq. (43). For the Manning-Rosen case, b and σ are given by (B5), $g(\sigma)$ by (62), and d has to be replaced by 2ρ.

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