

Morse Matrix Elements: An Asymptotic Expansion Treatment*

B. P. CHAKRABORTY

*Departamento de Físico-Química, Instituto de Química, Universidade Federal do Rio Grande do Sul,
90.000-Porto Alegre-RS, Brasil*

Abstract

An asymptotic expansion method has been used to calculate the Morse matrix elements for the vibration-rotation transition. A general expression has been derived for the quartic matrix elements, which can be reduced to the expressions for the cubic, quadratic, and linear matrix elements. The results agree extremely well with those given by the factorization method outlined by Badawi et al., and are similar to those given by Coquant et al., who used quite complicated and lengthy equations based on the Dunham potential. Earlier works to calculate the electronic transition probability parameters utilizing the above mentioned asymptotic expansion technique have also been extended and modified.

1. Introduction

Matrix elements needed in the calculation of intensity parameters for the vibration-rotation or electronic transition using the Morse [1] potential have been a major point of interest for over half a century. Recent [2, 3] interest in calculating position and momentum uncertainty of the coherent state have brought new perspectives in the study of the Morse molecule. Although the availability of high speed large core computers has somewhat undermined the importance of an analytic solution of Schrödinger equation, it has been shown previously [4] that for molecules in which the second anharmonicity constant $w_e y_e$ is vanishingly small, an asymptotic treatment to calculate the transition probability parameters for both the electronic [4] and vibration-rotation [5] transitions is simple and precise up to high vibrational quantum numbers. Besides, two very well-known programs to calculate the Franck-Condon factors and related quantities by Zare [6] and Jarman and McCallum [7] are formulated for large rather than small computers. For example, Jarman's program TRAPRB needs 8 min for completion of a sample work in a B-6700 computer. Just the first part of Zare's program to calculate the RKR potential curve requires over 3 min for completion of a sample work in the same computer. In this connection, several other works can be seen in the review works of Ortenberg and Antropov [8], Nicholls [9], Klemsdahl [10], Kuznetsova et al. [11], and Chakraborty and Pan [4d]. Expressions for the Morse vibration-rotation transition matrix elements are given by Badawi et al. [12] utilizing the factorization method, originally proposed by Schrödinger [13] and Infeld and Hull [14]. Heaps and Herzberg

* Part of the work was presented at the 33rd Annual Conference of the Brazilian Society for the Progress of Science, Salvador, Bahia, July 9-15, 1981.

[15], Herman and Rubin [16], and Garvin [17] also derived expressions for these matrix elements. Reference of other works can be seen in the works of Badawi et al.

In obtaining dipole moment function Rao and co-workers [18] also solved the radial Schrödinger equation numerically in order to calculate vibration-rotation matrix elements. However, they did not describe the procedure, and the values of the matrix elements are not given in their paper. Hence, comparison can not be made. Coquant et al. [19] in a series of papers (see references and cross references in Ref. 19) derived expressions for these matrix elements for up to eighth powers of displacement for the Dunham oscillator. In Ref. 19b authors calculated matrix elements for the CO ground state and compared with those obtained by a numerical RKR method. Again, details about the calculation of these matrix elements using RKR technique are not also found in their work. Meredith and Smith [20] introduced a computer code for the numerical integration of the radial Schrödinger equation for the computation of the electric dipole moment matrix elements. The effect of molecular rotation on these matrix elements has also been included. However, no numerical results are found in Ref. 20. Therefore, it is difficult to compare the results of this study with numerical methods. Under these circumstances, results obtained will be compared with those given by Badawi et al. [12] and Coquant et al. [19]. In this study, an asymptotic expansion technique introduced by Chang and Karplus [4a] has been extended, improved and developed. Wherever possible, comparison will be made with results given by other methods, to show the advantages and disadvantages.

2. Theory

We find that it is useful to present the eigenstates in terms of the Morse-Pekeris [21] oscillator, since the Morse oscillator can be treated as a special case of the Morse-Pekeris model. Within the model, the radial wave function for a rotating diatomic molecule is given approximately [22] by

$$\psi_{vj}(r) = N_{vj} e^{-z/2} z^{(K_2-2v-1)/2} L_{K_2-2v-1}^{K_2-2v-1}, \quad (1)$$

where v and j are the vibrational and rotational quantum numbers, respectively, and

$$z = K_1 \exp[-a(r - r_0)], \quad (2)$$

$$r_0 = r_e(1 + \alpha), \quad (3)$$

$$\alpha = 4AB_e/\omega_e^2 \quad (4)$$

$$A = B_e j(j+1), \quad (5)$$

$$K_1 = 2[(D_2 - C_2)/\omega_e x_e]^{1/2}, \quad (6)$$

$$K_2 = 2(2D_1 - C_1)/\omega_e x_e K_1, \quad (7)$$

$$D_1 = D_e \exp(-ar_e \alpha), \quad (8)$$

$$D_2 = D_e \exp(-2ar_e\alpha), \quad (9)$$

$$C_1 = [A/ar_0(1+\alpha)^2][4 - (6/ar_0)], \quad (10)$$

$$C_2 = [A/ar_0(1+\alpha)^2][1 - (3/ar_0)], \quad (11)$$

$$N_{vj} = [a(K_2 - 2v - 1)/v! \Gamma(K_2 - v)]^{1/2}, \quad (12)$$

$$L_{K_2-v-1}^{K_2-2v-1}(z) = \begin{cases} (-1)^v \sum_{n=0}^v (-1)^n \binom{v}{n} \frac{\Gamma(K_2 - v)}{\Gamma(K_2 - v - n)} z^{v-n}, \\ \sum_{n=0}^v (-1)^n \binom{v}{n} \frac{\Gamma(K_2 - v)}{\Gamma(K_2 - 2v - n)} z^n. \end{cases} \quad (13)$$

In the above expressions, ω_e , $\omega_e x_e$, B_e , and D_e are the usual spectroscopic constants, expressed in cm^{-1} ; r_e is the equilibrium internuclear separation, expressed in \AA ; and a is the Morse constant, expressed in \AA^{-1} . Symbols $!$, Γ , and $\binom{v}{n}$ represent factorials, gamma functions, and binomial coefficients, respectively. The above expressions also include a correction due to Shumaker [23]. Now, eigenstates can be written in any way one prefers, substituting Eqs. (2)–(13) in Eq. (1) and by further simplifications. For $j = 0$, Eqs. (1)–(13) are reduced to the Morse eigenstates and are given by

$$\psi_v(r) = N_v e^{-z/2} z^{(K-2v-1)/2} L_{K-v-1}^{K-2v-1}(z), \quad (14)$$

where

$$z = K \exp[-a(r - r_e)], \quad (15)$$

$$K = 1/x_e, \quad (16)$$

$$N_v = [a(K - 2v - 1)/v! \Gamma(K - v)], \quad (17)$$

$$L_{K-v-1}^{K-2v-1} = (-1)^v \sum_{n=0}^v (-1)^n \binom{v}{n} \frac{\Gamma(K - v)}{\Gamma(K - v - n)} z^{v-n}. \quad (18)$$

Clearly, in deriving Eqs. (14)–(18) from Eqs. (1)–(13) one accepts the following equalities:

$$r_0 = r_e, \quad K_1 = K_2 = K, \quad D_1 = D_2 = D_e,$$

$$\alpha = A = 0, \quad C_1 = C_2 = 0.$$

Birtwistle [24] claims that no normalization constant can be found for the Morse wave function. However, the normalization constant in the form of Eq. (12) or Eq. (17) was introduced by Pekeris [20]. In addition an expression for this constant has also been given by Wallace [25] in a different form. Recently, the normalization constant has been derived from the Coulomb integral in a general way, in Ref. 2, which can be reduced to Birtwistle's derivation. There exists also, some confusion regarding the proper value of K , given by Eq. (16). Two different ways of calculating K , are given by

$$K = \omega_e / \omega_e x_e \quad (16a)$$

or

$$K = 4D_e/\omega_e. \quad (16b)$$

Clearly, Eq. (16b) is reduced to Eq. (16a) if D_e is replaced by $\omega_e^2/4\omega_e x_e$. Equations (16a) and (16b) yield different values of K , depending on the closeness of the theoretical value of D_e , given by $\omega_e^2/4\omega_e x_e$, with experimental dissociation energy. Hence, calculated matrix elements differ depending on the value of K , used in the actual calculation. However, it has been shown [4, 5] that, in some cases, the ratios of the matrix elements with respect to band head (1-0 in the case of a vibration-rotation and 0-0 in the case of an electronic transition) are practically the same. One more point is that the Morse constant a should be calculated using the following expression:

$$a = (2\pi^2 c\mu/hN_a D_e)^{1/2} \times 10^{-8} \omega_e, \quad (20)$$

instead of

$$a = (8\pi^2 c\mu\omega_e x_e/hN_a)^{1/2} \times 10^{-8}, \quad (21)$$

where μ is the reduced mass; c , h , and N_a are, respectively, the velocity of light, Planck's constant, and Avogadro's number. Again, Eq. (21) becomes equal to Eq. (20) if D_e is replaced by $\omega_e^2/4\omega_e x_e$. Thus it appears that the experimental dissociation energy should be preferred to the calculated dissociation energy in calculating matrix elements. However, there is no doubt about the validity of Eq. (16a) in calculating K , and we find no justified preference in using Eq. (16b) instead of Eq. (16a).

A. Electronic Transition

In calculating transition probability parameters one encounters integrals of the following type:

$$I_{v'v''}^{j'j''} = \int_0^{+\infty} \psi_{v'j'} R_e(r) \psi_{v''j''} dr, \quad (22)$$

where $R_e(r)$ represents the transition moment. In the case of electronic transitions, the square of the above integral is known as the bandstrength. The band strength becomes equal to the Franck-Condon factor when $R_e(r) = 1$, i.e., when the effect of the transition moment is not known, or may be considered to be very small, $R_e(r)$ is taken outside of the integration and $|\int \psi_{v'} \psi_{v''} dr|^2$ is called the Franck-Condon factor (when molecular rotation is not considered). In order to evaluate the integral represented by Eq. (22) one needs to know the functional form of $R_e(r)$. The usual procedure has been to assume a polynomial of the type

$$R_e(r) = a_0 + a_1 r + a_2 r^2 + a_3 r^3 + \dots \quad (23)$$

However, several other functional forms exist. Each case has to be dealt with separately. A list of these transition moment functions as a function of r -centroids for various bands of diatomic molecules can be seen in the works of Klemsdahl

[10] and Kuznetsova et al. [11]. Now, substituting Eqs. (1)–(13) in Eq. (22), one gets

$$\begin{aligned}
 I_{v'v''}^{i'j''} &= (-1)^{v'+v''} \frac{N_{v'j'} N_{v''j''}}{a'} \xi^{(K_2''-1)/2} \\
 &\times \sum_{\lambda=0}^{v'} \sum_{\sigma=0}^{v''} (-1)^{\lambda+\sigma} \xi^{-\sigma} \xi^{(v')_{\lambda}} \xi^{(v'')_{\sigma}} \\
 &\times \frac{\Gamma(K_2' - v') \Gamma(K_2'' - v'')}{\Gamma(K_2' - v' - \lambda) \Gamma(K_2'' - v'' - \sigma)} I_{\sigma}^{\lambda}(\xi, \gamma, p),
 \end{aligned} \quad (24)$$

where

$$\gamma = a''/a', \quad (25)$$

$$\xi = K_1'' \exp(a''r_0'' - \gamma a'r_0')/(K_1')^{\gamma} \quad (26)$$

$$I_{\sigma}^{\lambda}(\xi, \gamma, p) = \int_0^{\infty} (z')^p \exp[-\tfrac{1}{2}(z' + z'^{\gamma})] R_e(z') dz', \quad (27)$$

$$p = \tfrac{1}{2}(K_2' + K_2'') - \tfrac{1}{2}(1 + \gamma) - \gamma - \gamma\sigma - 1. \quad (28)$$

The integral in the Eq. (27) above can be rewritten, transforming the variable $z' = pt$, as

$$I_{\sigma}^{\lambda}(\xi, \gamma, p) = p^{p+1} \int_0^{\infty} \exp[pg(t)] R_e(pt) dt, \quad (29)$$

where

$$g(t) = -\tfrac{1}{2}(t + \xi p^{\gamma-1} t^{\gamma}) + \ln t. \quad (30)$$

Now, the integral in Eq. (29) can be evaluated by the Laplace method of asymptotic expansion, since p is a large number. Considering up to p^{-2} terms, the integral is reduced to

$$I_{\sigma}^{\lambda}(\xi, \gamma, p) = p^{p+1/2} \left(\frac{\pi}{-b_2} \right)^{1/2} e^{pg_0} R_e(\rho_0) \left(1 + \frac{E_1}{p} + \frac{E_2}{p^2} \right), \quad (31)$$

where

$$\begin{aligned}
 E_1 &= \frac{3b_4 - 15b_3^2/4b_2}{4b_2^2} + \frac{3R_e^{(1)}(\rho_0)b_3/b_2 - R_e^{(2)}(\rho_0)}{4R_e(\rho_0)b_2}, \\
 E_2 &= 15 \left(\frac{7b_4^2}{4b_2} + \frac{7b_3b_5}{2b_2} + \frac{693b_3^4}{192b_2^3} - b_6 - \frac{189b_3^2b_4}{24b_2^2} \right) / 8b_2^3 \\
 &+ \left(\frac{R_e^{(4)}(\rho_0)}{4} + \frac{105R_e^{(2)}(\rho_0)b_3^2}{8b_2^2} + \frac{105R_e^{(1)}(\rho_0)b_3b_4}{2b_2^2} \right. \\
 &\quad \left. - \frac{5R_e^{(3)}(\rho_0)b_3}{2b_2} - \frac{15R_e^{(2)}(\rho_0)b_4}{2b_2} \right)
 \end{aligned} \quad (32)$$

$$-\frac{15R_e^{(1)}(\rho_0)b_5}{b_2} - \frac{945R_e^{(1)}(\rho_0)b_3^3}{24b_2^2} \Big) / 8R_e(\rho_0)b_2^2, \quad (33)$$

$$g_0 = g(t_0), \quad b_2 = \frac{1}{2}g^{(2)}(t_0), \quad b_3 = \frac{1}{6}g^{(3)}(t_0), \quad b_n = g^{(n)}(t_0)/n!, \quad (34)$$

$$\rho_0 = r'_0 + \ln(K'_1/pt_0)/a'. \quad (35)$$

For an electronic transition, $\gamma \neq 1$, hence, t_0 has to be calculated numerically from the expression of $g(t)$. Most of the time t_0 can be calculated by the Newton-Raphson technique. However, other methods have been found more helpful. One of these methods, utilized in the actual calculation of t_0 , will be shown explicitly. The first derivative of $g(t)$, when equated to zero, gives

$$t_0 = 2 - Xt_0, \quad (36)$$

where

$$X = \xi\gamma p^{\gamma-1}. \quad (37)$$

Now, starting from an initial value of t_1 , an iterative procedure is built for the calculation of t_0 , by

$$t_0 = \frac{1}{2}(S_1 + S_2), \quad (38)$$

where

$$S_1 = 2 - X[2 - X(2 - Xt_1^\gamma)^\gamma]^\gamma \quad (39)$$

and

$$S_2 = 2 - XS_1^\gamma, \quad (40)$$

until $g^{(1)}(t_0)$ is less than 10^{-20} or so. The above procedure has been found very suitable in all cases of electronic transitions studied. When $R_e(r)$ takes the form $R_e(r) = a_0 + a_1r + a_2r^2 + a_3r^3$, E_1 is given by

$$\begin{aligned} E_1 = & \frac{3b_4}{4b_2^2} - \frac{15b_3^2}{16b_2^3} - \left[a_1 \left(\frac{3b_3}{4b_2} + \frac{1}{4t_0} \right) \right. \\ & + a_2 \left(\frac{3b_3\rho_0}{2b_2} + \frac{\rho_0}{2t_0} + \frac{1}{2a't_0} \right) \\ & \left. + a_3 \left(\frac{9\rho_0^2b_3}{4b_2} + \frac{3\rho_0}{2a't_0} + \frac{3\rho_0^2}{4t_0} \right) \right] / a't_0b_2R_e(\rho_0), \end{aligned} \quad (41)$$

and E_2 is obtained by substituting

$$\begin{aligned} R_e^{(1)}(\rho_0) &= -(a_1 + 2a_2\rho_0 + 3a_3\rho_0^2)/a't_0, \\ R_e^{(2)}(\rho_0) &= (a_1 + 2a_2\rho_0 + 3a_3\rho_0^2)/a't_0^2 + (2a_2 + 6a_3\rho_0)/a'^2t_0^2, \\ R_e^{(3)}(\rho_0) &= -\frac{2(a_1 + 2a_2\rho_0 + 3a_3\rho_0^2)}{a'^3t_0^3} - \frac{6a_2 + 18a_3\rho_0}{a'^2t_0^3} - \frac{6a_3}{a'^3t_0^3}, \\ R_e^{(4)}(\rho_0) &= \frac{6(a_0 + 2a_2\rho_0 + 3a_3\rho_0^2)}{a'^4t_0^4} + \frac{22a_2 + 66a_3\rho_0}{a'^2t_0^4} + \frac{36a_3}{a'^3t_0^4} \end{aligned} \quad (42)$$

in Eq. (33). Of course, the procedure outlined above is cumbersome. However, for $R_e(r) = a_0 + a_1 r + a_2 r^2$, the equations are quite simple, and are reduced to those given in Ref. 4f, considering only p^{-1} terms. It is important to note that, up to this point very few authors [26] have suggested a transition moment with a third power r dependence. For every functional forms of $R_e(r)$ all the required derivatives of $R_e(r)$ have to be calculated after a variable substitution $z \rightarrow pt$, and must be substituted in Eqs. (32) and (33) in the evaluation of the integral represented by Eq. (24). When $R_e(r)$ has a simple exponential form of the type $R_e(r) = k_1 \exp(-k_2 r)$, we encounter an exception. An expansion of $R_e(r)$ in the form of a Taylor series is not needed for this particular case. $I_{v'v''}^{i'j''}$ and p , given by Eqs. (24) and (28), are changed and are given by

$$\begin{aligned}
 I_{v'v''}^{i'j''} &= (-1)^{v'+v''} f_c \frac{N_{v'f'} N_{v''j''}}{a'} \xi^{(K_2''-1)/2} \\
 &\times \sum_{\lambda=0}^{v'} \sum_{\sigma=0}^{v''} \binom{v'}{\lambda} \binom{v''}{\sigma} \xi^{-\sigma} \\
 &\times \frac{\Gamma(K_2' - v') \Gamma(K_2'' - v'')}{\Gamma(K_2' - v' - \lambda) \Gamma(K_2'' - v'' - \sigma)} I_{\sigma}^{\lambda}(\xi, \gamma, p), \quad (24a)
 \end{aligned}$$

$$p = \frac{1}{2}(K_2' + \gamma K_2'') - \frac{1}{2}(1 + \gamma) - \lambda - \gamma\sigma - 1 + k_2/a', \quad (28a)$$

where

$$f_c = (K_1')^{-k_2/a'} \exp(-k_2 r_0'). \quad (43)$$

It is important to note that, in this case, the terms $R_e^{(n)}(\rho_0)$ disappear from Eqs. (32) and (33). Equations (24a) and (28a) were used in Ref. 4b. The expectation values were also calculated using the general scheme outlined above, and the results did not change. In the calculation of the Franck-Condon factors, the procedure becomes even simpler. One substitutes $R_e(r) = 1$, i.e., $a_0 = 1$, $a_1 = a_2 = a_3 = 0$ in the evaluation of the integral given by Eq. (24). These can also be calculated considering $k_1 = 1$ and $k_2 = 0$ in the evaluation of Eqs. (24a) and (28a). Explicit equations are given in Refs. 4a and 4d. Another important factor r -centroids can be calculated using $a_1 = 1$ and $a_0 = a_2 = a_3 = 0$ in calculating the bandstrength factors. Next, these are divided by the Franck-Condon factors, and a square root of the quotient give the r -centroids. The method is quite general and one can calculate the expectation values of r^2 and r^3 , if needed.

We do not see the necessity of presenting the explicit equations for the r -centroids and expectation values of r^2 and r^3 ; r -centroids calculated by a similar manner have been reported in Ref. 4f for some band systems of ZrO and CuH. The obtained values were found to agree extremely well with those calculated by other methods.

B. Rotational Constant

Using the scheme outlined above, an expression for the rotational constant for a given electronic state can be given by

$$B_v = \frac{h}{8\pi^2 \mu c} \int_0^{+\infty} \psi_v^2 r^{-2} dr = \frac{16.8575}{\mu} \frac{N_v^2}{a} \Gamma^2(K-v) \times \sum_{\lambda=0}^v \sum_{\sigma=0}^v (-1)^{\lambda+\sigma} \frac{\binom{v}{\lambda}}{\Gamma(K-v-\lambda)} \frac{\binom{v}{\sigma}}{\Gamma(K-v-\sigma)} I(\lambda, \sigma), \quad (44)$$

where

$$I(\lambda, \sigma) = \int_0^\infty e^{-z} z^p \left(r_e + \frac{\ln(K/z)}{a} \right)^{-2} dz. \quad (45)$$

Now, applying an asymptotic expansion technique, the integral represented by Eq. (45), considering up to p^{-2} terms, is reduced to

$$I(\lambda, \sigma) = p^{p+1} e^{-p} \left(\frac{2\pi}{p} \right)^{1/2} \left(1 + \frac{e_1}{p} + \frac{e_2}{p^2} \right) / \rho_0^2, \quad (46)$$

where

$$e_1 = \frac{1}{12} + 1/a\rho_0 + 3/a^2\rho_0^2, \quad (47)$$

$$e_2 = \frac{1}{288} - \left(\frac{1}{12} - 1/2a\rho_0 + 2/a^2\rho_0^2 + 15/a^3\rho_0^3 \right) / a\rho_0, \quad (48)$$

$$\rho_0 = r_e + \frac{\ln(K/p)}{a}, \quad (49)$$

$$p = K - \lambda - \sigma - 2, \quad (50)$$

and where all other symbols have already been defined in the text. Clearly, Eqs. (44)–(50) are reduced to Eqs. (5) and (6) of Ref. 4g, where the p^{-2} term was not considered. Rotational constants calculated including p^{-2} term do not differ from those calculated excluding the p^{-2} term, reported earlier. It should also be noted here that the iterative procedure to calculate t_0 is not needed for this case.

C. Vibration–Rotation Transition

The linear and quadratic matrix elements were calculated using an asymptotic expansion and were reported in Ref. 5. We note the present efforts of Coquant et al. [19] to derive expressions for the said matrix elements up to the eighth power of displacement ($\langle |r - r_e|^8 \rangle$), using the Dunham potential. Special effort [19a] has been made to calculate the diagonal matrix elements as well. Under the circumstances, we feel that it is worthwhile to extend the work described in Ref. 5 to some extent. Here the previous work of Ref. 5 has been modified to calculate the Morse matrix elements up to the fourth power of displacement. A general

expression has been derived, which can be simplified and reduced to the equations given in Ref. 5. The task of calculating the Morse matrix elements is simple, since one considers only an electronic state. Needless to say, an iterative procedure to calculate t_0 is not needed here either. We feel it is important to repeat some of the equations given in Ref. 5 for the sake of completeness. The probability of transition between the two vibrational states (belonging to an electronic state) of a diatomic molecule by electric dipole radiation is proportional to the square of the matrix elements $M_{v'v''}$ of the dipole moment

$$M_{v'v''} = \int_0^{+\infty} \psi_{v'} M(r) \psi_{v''} dr \quad (51)$$

Substituting Eqs. (14)–(18) into eq. (51) one finds

$$M_{v'v''} = (-1)^{v'+v''} \frac{N_{v'} N_{v''}}{a} \sum_{\lambda=0}^{v'} \sum_{\sigma=0}^{v''} (-1)^{\lambda+\sigma} \binom{v'}{\lambda} \binom{v''}{\sigma} \\ \times \frac{\Gamma(K-v') \Gamma(K-v'')}{\Gamma(K-v'-\lambda) \Gamma(K-v''-\sigma)} I(\lambda, \sigma), \quad (52)$$

where

$$I(\lambda, \sigma) = \int_0^{\infty} e^{-z} z^p M[r(z)] dz, \quad (53)$$

and p is given by Eq. (50). If the variable z is substituted by pt , Eq. (53) can be reduced to

$$I(\lambda, \sigma) = p^{p+1} \int_0^{\infty} \exp[pg(t)] m(t) dt, \quad (54)$$

where

$$g(t) = -t + \ln t. \quad (55)$$

The function $m(t)$ in Eq. (54) is derived from Eq. (51) by proper variable substitutions of r by z , and, next, z by t . It is worthwhile mentioning that Eqs. (24)–(30) can very well be reduced to eqs. (52)–(55), considering

$$a' = a'', \quad \text{i.e., } \gamma = 1, \\ K'_1 = K''_1 = K'_2 = K''_2 = K, \\ r'_0 = r''_0 = r_e. \quad (56)$$

Now, applying an asymptotic expansion as described earlier, we have, considering up to a p^{-2} term,

$$I(\lambda, \sigma) = p^{p+1} e^{-p} M(\rho_0) (2\pi/p)^{1/2} (1 + \epsilon_1/p + \epsilon_2/p^2), \quad (57)$$

where

$$\varepsilon_1 = \frac{1}{12} + [M^{(1)}(\rho_0) + \frac{1}{2}M^{(2)}(\rho_0)]/M(\rho_0), \quad (58)$$

$$\varepsilon_2 = \frac{1}{288} + \left(\frac{M^{(1)}(\rho_0)}{12} + \frac{25M^{(2)}(\rho_0)}{24} + \frac{5M^{(3)}(\rho_0)}{6} + \frac{M^{(4)}(\rho_0)}{8} \right) / M(\rho_0), \quad (59)$$

and ρ_0 is given by Eq. (49). Now, the general expressions for ε_1 , ε_2 of Eq. (57) for the matrix elements, up to the fourth power of displacement, are given by

$$\varepsilon_1 = \frac{1}{12} - l/2a(r-r_e) + l(l-1)/2a^2(r-r_e)^2, \quad (60)$$

$$\begin{aligned} \varepsilon_2 = & \frac{1}{288} + \frac{l}{24a(r-r_e)} - \frac{l(l-1)}{12a^2(r-r_e)^2} \\ & - \frac{l(l-1)(l-2)}{12a^3(r-r_e)^3} + \frac{l(l-1)(l-2)(l-3)}{8a^4(r-r_e)^4}. \end{aligned} \quad (61)$$

Equation (60), without the $\frac{1}{12}$ term, is reduced to Eqs. (13) and (14) of Ref. 5 when l is equal to 1 and 2, respectively (for the linear and quadratic matrix elements). It should be noted that both Eqs. (60) and (61) are valid only for $l = 1$ to 4. In a similar manner expressions for ε_1 and ε_2 can be derived for any integer l . However, we do not find the calculations to be very interesting. They are lengthy but straightforward.

3. Results and Discussion

Some representative values for the OH ground state matrix elements calculated by the method outlined above for $l = 1$ to 4 are reported in Table I, along with those calculated by the factorization method described by Badawi et al. [12]. Equations given in Ref. 12 were utilized in a computer program* to verify the validity of the asymptotic expansion technique. No numerical values were reported by the authors of Ref. 12. In any case, it can be seen that linear, quadratic, and cubic matrix elements calculated including a p^{-2} term (first entries) are virtually identical to those calculated by the factorization technique (second entries). The quartic matrix elements also agree very well, but are not identical. The third entries are calculated by the same asymptotic expansion technique using only a p^{-1} term. The linear and quadratic matrix elements calculated using only a p^{-1} term agree quite well with those calculated by the factorization method and with those calculated including a p^{-2} term. However, the cubic and the quartic matrix elements do differ considerably for the 1-0 transition. We conclude that, in calculating higher order matrix elements a p^{-2} term must be included in the working equations.

In Table II are presented some matrix elements calculated including a p^{-2} term along with those given by Coquant et al. [19b], for the HBr and CO ground

* An Algol program written by the author utilizing equations given by Badawi et al. (Ref. 12b) has been sent to the Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN., for documentation (1980).

TABLE I. Some representative vibrational matrix elements $\langle |r - r_e/r_e|^l \rangle$ for OH ground state.

Transition	$\ell=1$	$\ell=2$	$\ell=3$	$\ell=4$
1-0	7.2015 (-2)	4.2035 (-3)	1.3507 (-3)	1.6270 (-4)
	7.2015 (-2)	4.2033 (-3)	1.3506 (-3)	1.6211 (-4)
	7.2008 (-2)	4.2087 (-3)	1.3669 (-3)	1.4560 (-4)
10-0	1.7707 (-6)	3.9384 (-6)	-4.9703 (-6)	4.1439 (-6)
	1.7707 (-6)	3.9384 (-6)	-4.9704 (-6)	4.1440 (-6)
	1.7699 (-6)	3.9366 (-6)	-4.9682 (-6)	4.1423 (-6)
4-2	-2.1446 (-2)	1.4779 (-2)	4.3332 (-3)	2.3776 (-3)
	-2.1446 (-2)	1.4780 (-2)	4.3331 (-3)	2.3769 (-3)
	-2.1446 (-2)	1.4779 (-2)	4.3427 (-3)	2.3862 (-3)
6-5	1.8902 (-1)	7.8368 (-2)	4.7198 (-2)	2.4442 (-2)
	1.8902 (-1)	7.8368 (-2)	4.7197 (-2)	2.4433 (-2)
	1.8898 (-1)	7.8379 (-2)	4.7338 (-2)	2.4464 (-2)
8-3	1.1073 (-3)	-1.6709 (-3)	9.9197 (-4)	-1.2299 (-4)
	1.1073 (-3)	-1.6709 (-3)	9.9199 (-4)	-1.2301 (-4)
	1.1070 (-3)	-1.6706 (-3)	9.9184 (-4)	-1.2289 (-4)

^a First entries are calculated including $1/p^2$ term, the second entries are calculated using equations given by Badawi et al., the third entries are calculated with only $1/p$ term.

states. Authors of Ref. 19b only presented elements for 0- v transitions. It is not really very clear whether or not their equations are applicable for all transitions. It may be that actual calculation using Eq. (8) of Ref. 19b becomes much more complicated than it appears. It is noted that the above mentioned equation (8) of Ref. 19b is apparently 16 lines long. However, the agreement is not unreasonable, except for the 0-5 transition for the CO molecule. It should be also noted that we used spectroscopic constants given by Herzberg [27] in the calculation. For the CO molecule the dissociation energy was approximated

TABLE II. Some representative vibrational matrix elements $\langle |r - r_e/r_e|^l \rangle$ for HBr and CO ground states.^a

Molecule	Transition	$\ell=1$	$\ell=2$	$\ell=3$	$\ell=4$
HBr	0-0	1.1182 (-2)	3.4054 (-2)	1.3630 (-4)	3.6488 (-5)
		1.180448 (-2)	3.415989 (-2)	.437206 (-4)	3.657561 (-5)
CO	0-0	3.5398 (-3)	9.1070 (-4)	1.1715 (-5)	2.5345 (-6)
		3.615532 (-3)	9.112249 (-4)	1.196259 (-5)	2.532034 (-6)
	0-2	-1.6767 (-3)	1.2422 (-3)	2.6751 (-5)	7.2877 (-6)
		-1.708929 (-3)	1.240891 (-3)	2.727926 (-5)	7.299134 (-6)
	0-5	2.6341 (-6)	-4.0749 (-6)	3.1214 (-6)	-1.2538 (-6)
		3.181115 (-6)	-4.504454 (-6)	3.262562 (-6)	-1.266197 (-6)
	3-7	-1.1314 (-4)	1.5044 (-4)	-8.4472 (-5)	1.5788 (-5)
	4-5	6.7759 (-2)	4.1267 (-3)	1.1408 (-3)	1.1678 (-4)

^a First entries are calculated using an asymptotic expansion technique including $1/p^2$ terms; the second entries are from Ref. 19b.

by $\omega_e^2/4\omega_e x_e$. For all other cases, experimental dissociation energies were used. The dissociation energy of HBr was taken from Rao et al. [18b]. Moreover, Coquant et al. [19b] used a Dunham potential, which invariably will give somewhat different results. Anyway, a glance at the Table II makes us quite confident about the application of an asymptotic expansion technique for the Morse molecule, when the spectroscopic constant $\omega_e y_e$ is negligibly small. The expressions given by Badawi et al. [12] for the vibration-rotation matrix elements are applicable only for $v' > v''$. An asymptotic expansion method enables one to calculate these matrix elements for all values of v' and v'' . The equations given in Appendix A can also be used for this purpose. It should be mentioned here that the method so described is so simple that it requires less than 3 min using a B-6700 computer to calculate the Morse matrix elements for an electronic transition, and does not need more than 1 min for a typical vibration-rotation transition. Matrix elements, for $l = 1$ to 4, were calculated for larger and full arrays, including and excluding the effect of a p^{-2} term, for the OH, CO, and HBr ground states. These can be obtained on request from the author.

Acknowledgments

A research grant obtained from Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Brasil, is gratefully acknowledged. The author thanks F. R. Volcato of the Centro de Processamento de Dados of this university for helping with the computations. The author is grateful to Dr. M. A. Moreira and Dr. P. J. Viccaro for reading the manuscript.

Appendix A: General Solution for the Morse Matrix Elements for the Vibration-Rotation Transition by the Mellin Transform

A general form for the matrix elements including the vibration-rotation interaction can be given by

$$M_{v'v''}^{j'j''} = \int_0^{+\infty} \psi_{v'j'}(r-r_e)^l \psi_{v''j''} dr. \quad (62)$$

Appropriate substitutions of Eqs. (1)–(13) of the text reduces Eq. (62) to

$$M_{v'v''}^{j'j''} = (-1)^{v'+v''} \frac{N_{v'j'} N_{v''j''}}{a^{l+1}} \sum_{\lambda=0}^{v'} \sum_{\sigma=0}^{v''} (-1)^{\lambda+\sigma+l} \binom{v'}{\lambda} \binom{v''}{\sigma} \\ \times \frac{\Gamma(K_2 - v') \Gamma(K_2 - v'')}{\Gamma(K_2 - v' - \lambda) \Gamma(K_2 - v'' - \sigma)} I, \quad (63)$$

where,

$$I = \int_0^{\infty} z^p e^{-z} [\ln(z/K_1)]^l dz, \quad (64)$$

and all other notation is given in the text. The integral appearing in Eq. (64) is directly solved after a variable transformation, $z = K_1 y$,

$$I = (K_1)^{p+1} \int_0^\infty y^p e^{-K_1 y} (\ln y)^l dy = \frac{d^l}{d(p+1)^l} [\Gamma(p+1)]. \quad (65)$$

Equation (65) is simply a Mellin transform [28]. Therefore, for all positive integer values of l , Eq. (62) can be written

$$\begin{aligned} M_{v'v''}^{j'j''} &= \langle |r - r_e|^l \rangle = (-1)^{v'+v''} \frac{N_{v'j'} N_{v''j''}}{a^{l+1}} \\ &\times \sum_{\lambda=0}^{v'} \sum_{\sigma=0}^{v''} (-1)^{\lambda+\sigma+l} \binom{v'}{\lambda} \binom{v''}{\sigma} \\ &\times \frac{\Gamma(K_2 - v') \Gamma(K_2 - v'')}{\Gamma(K_2 - v' - \lambda) \Gamma(K_2 - v'' - \sigma)} \frac{d^l}{d(p+1)^l} [\Gamma(p+1)]. \end{aligned} \quad (66)$$

A solution of the integral, represented in Eq. (65) for $l=1$, is given by Wallace [25]. Formulas for some other useful auxiliary integrals can also be found in Ref. 25. Some expressions for the successive derivatives of $\Gamma(p+1)$ are given in Ref. 12b. These are generally expressed in terms of psi functions (digamma) and successive derivatives of psi functions (trigamma, etc.). Gradshteyn and Ryzhik [29] also expressed these functions in the form of Riemann's zeta functions (numbers). These are expressed in various notation, however, the derivations are algebraic and simple. We will not make any attempt to derive those.

For the linear matrix elements, Eq. (66) is reduced to

$$\begin{aligned} \langle |r - r_e| \rangle &= (-1)^{v'+v''} \frac{N_{v'j'} N_{v''j''}}{a^2} \\ &\times \sum_{\lambda=0}^{v'} \sum_{\sigma=0}^{v''} (-1)^{\lambda+\sigma+1} \binom{v'}{\lambda} \binom{v''}{\sigma} \\ &\times \frac{\Gamma(K_2 - v') \Gamma(K_2 - v'')}{\Gamma(K_2 - v' - \lambda) \Gamma(K_2 - v'' - \sigma)} \Gamma(p+1) \\ &\times [\psi(p+1) - \ln K_1], \end{aligned} \quad (67)$$

where

$$\psi(p+1) \simeq \ln(p+1) - \frac{1}{2(p+1)} - \frac{1}{12(p+1)^2} + \frac{1}{120(p+1)^4}. \quad (68)$$

Next, considering only the first two terms of the series represented by Eq. (68), linear matrix elements are given by

$$\begin{aligned}
 \langle |r - r_e| \rangle &= (-1)^{v'+v''} \frac{N_{v'j'} N_{v''j''}}{a^2} \\
 &\times \sum_{\lambda=0}^{v'} \sum_{\sigma=0}^{v''} (-1)^{\lambda+\sigma+1} \binom{v'}{\lambda} \binom{v''}{\sigma} \\
 &\times \frac{\Gamma(K_2 - v') \Gamma(K_2 - v'')}{\Gamma(K_2 - v' - \lambda) \Gamma(K_2 - v'' - \sigma)} \Gamma(p+1) \\
 &\times \left[\left(\ln \frac{p+1}{K_1} - \frac{1}{2(p+1)} - \dots \right) \right]. \quad (69)
 \end{aligned}$$

An asymptotic expansion, utilizing Eqs. (51)–(60), considering only a p^{-1} term and the Stirling approximation, leads to

$$\begin{aligned}
 \langle |r - r_e| \rangle &= (-1)^{v'+v''} \frac{N_{v'j'} N_{v''j''}}{a} (-1)^{\lambda+\sigma} \binom{v'}{\lambda} \binom{v''}{\sigma} \frac{\Gamma(K_2 - v') \Gamma(K_2 - v'')}{\Gamma(K_2 - v' - \lambda) \Gamma(K_2 - v'' - \sigma)} \Gamma(p+1) \\
 &\times \left[\left(\ln \frac{K_1}{p} + \frac{\ln \frac{K_1}{p}}{12p} - \frac{1}{2p} \right) / a \right]. \quad (70)
 \end{aligned}$$

It is surprising that Eqs. (69) and (70) yield virtually identical results when molecular rotation is not considered (see Table I, second and third entries, column for $l = 1$). For $v' = v'' = 0$ and $j' = j'' = 0$, Eqs. (69) and (70) are reduced, respectively, to

$$M_{00}^{00} = (K-1) \frac{\ln [K/(K-1)] + 1/2(K-1)}{a} \quad (71)$$

and

$$M_{00}^{00} = (K-1) \left(\ln \frac{K}{K-2} + \frac{\ln [K/(K-2)]}{12(K-2)} - \frac{1}{2(K-2)} \right) / a. \quad (72)$$

For OH, using $K = 4D_e/\omega_e = 39.56940$ and $a = 2.30448$, Eqs. (71) and (72), respectively, yield 0.64538 and 0.64725. All the terms of Eq. (72) have been checked and none of these can be neglected. For the higher order matrix elements p^{-2} terms must be considered to obtain reliable results. We also note that the factorization method is basically a simplification of Eq. (66), which can be easily solved by a Mellin transform.

Appendix B

A general expression for the m th derivative of $(r - r_e)^l$ can be represented as

$$\frac{d^m}{dt^m}(r - r_e)^l = \frac{d^m}{dt^m} \left(\frac{\ln(K/pt)}{a} \right) = \frac{a^{-l}(-1)^m}{t^m} \\ \times \sum_{i=1}^m a_m(m-i-1) \frac{l!}{(l-m+i-1)!} \left(\ln \frac{K}{pt} \right)^{l-m+i-1} \quad \text{for } m \leq l. \quad (73)$$

The coefficients of $a_m(m-i+1)$, Stirling's numbers, are given in Table I or Ref. 12b.

Bibliography

- [1] P. M. Morse, Phys. Rev. **34**, 57 (1929).
- [2] M. M. Nieto and L. M. Simmons, Jr., Phys. Rev. A **19**, 438 (1979); Phys. Rev. Lett. **41**, 207 (1978).
- [3] R. B. Walker and R. K. Preston, J. Chem. Phys. **67**, 2017 (1977).
- [4] (a) T. Y. Chang and M. Karplus, J. Chem. Phys. **52**, 783 (1970); (b) B. P. Chakraborty, Y. K. Pan, and T. Y. Chang, *ibid.* **55**, 5147 (1971); (c) B. P. Chakraborty and Y. K. Pan, Theor. Chim. Acta **18**, 162 (1970); J. Chem. Phys. **56**, 3622 (1972); (d) B. P. Chakraborty and Y. K. Pan, Appl. Spectrosc. Rev. **7**, 283 (1973); (e) J. A. C. Gallas, H. P. Grieneisen, and B. P. Chakraborty, J. Chem. Phys. **69**, 612 (1978); (f) J. A. C. Gallas, R. E. Francke, H. P. Grieneisen, and B. P. Chakraborty, Astrophys. J. **229**, 851 (1979); (g) B. P. Chakraborty, H. P. Grieneisen, R. E. Francke, and J. A. C. Gallas, J. Chem. Phys. **70**, 3023 (1979).
- [5] J. A. C. Gallas and B. P. Chakraborty, J. Chem. Soc. Faraday Trans. II **77**, 67 (1981).
- [6] R. N. Zare, most recent version of RKR and FCF Program, Stanford University, Stanford, California, U.S.A. (1979).
- [7] W. R. Jarman and J. C. McCallum, TRAPRB, University of Western Ontario, London, Canada (1970).
- [8] F. S. Ortenberg and E. T. Antropov, Sov. Phys. Usp. **9**, 717 (1980).
- [9] R. W. Nicholls, Ann. Rev. Astron. Astrophys. **15**, 197 (1977).
- [10] H. Klemsdahl, J. Quantum Spectrosc. Radiat. Transfer **13**, 517 (1973).
- [11] L. A. Kuznetsova, N. E. Kuzmenko, Yu. Ya. Kuzyakov, and Yu. A. Plastinin, Sov. Phys. Usp. **17**, 405 (1974).
- [12] (a) M. Badawi, N. Besis and G. Besis, J. Phys. B **5**, 1470 (1972); **6**, 584 (1973); **5**, L157 (1972). (b) M. Badawi, N. Besis, and G. Besis, Can. J. Phys. **51**, 2075 (1973); (c) M. Badawi, N. Besis, G. Besis, and G. Hadinger, *ibid.* **52**, 110 (1974).
- [13] E. Schrödinger, Proc. R. Irish Acad. A **46**, 9 (1941); **46**, 183 (1941); **47**, 53 (1941).
- [14] L. Infeld and T. E. Hull, Rev. Mod. Phys. **23**, 21 (1951).
- [15] H. S. Heaps and G. Herzberg, Z. Phys. **133**, 48 (1952).
- [16] R. Herman and R. J. Rubin, Astrophys. J. **121**, 533 (1955).
- [17] D. Garvin, J. Am. Chem. Soc. **81**, 3173 (1959).
- [18] (a) B. S. Rao, J. Phys. B **4**, 791 (1971); (b) D. N. Urquhart, T. D. Clark, and B. S. Rao, Z. Naturforsch. A **27**, 1563 (1972); (c) Y. K. Chan and B. S. Rao, *ibid.* **32**, 897 (1977).
- [19] (a) C. Coquant, J. Quantum Spectrosc. Radiat. Transfer **23**, 451 (1980); (b) P. Niay, P. Bernage, and C. Coquant, Can. J. Phys. **57**, 572 (1979); (c) P. Niay, P. Bernage, C. Coquant, and A. Fayt, *ibid.* **55**, 1829 (1977).
- [20] R. E. Meredith and F. G. Smith, Willow Run Laboratories Report No. 84130-39-T(I), Institute of Science and Technology, University of Michigan, Ann Arbor, Mich., May (1971).
- [21] C. L. Pekeris, Phys. Rev. **45**, 98 (1934).

- [22] D. TerHaar, Phys. Rev. **70**, 222 (1946).
- [23] J. B. Shumaker, Jr., J. Quantum Spectrosc. Radiat. Transfer **9**, 153 (1969).
- [24] D. T. Birtwistle, Chem. Phys. Lett. **63**, 523 (1979).
- [25] R. Wallace, Chem. Phys. Lett. **37**, 115 (1976).
- [26] V. N. Egorov, L. N. Tunitskii, and E. M. Cherkasov, Zh. Prikl. Spectrosc. **8**, 479 (1968); L. L. Danylewych and R. W. Nicholls, Proc. R. Soc. London, Ser. A **360**, 557 (1978).
- [27] G. Herzberg, *Molecular Spectra and Molecular Structure, Vol. 1, Spectra of Diatomic Molecules*, 2nd ed. (Van Nostrand, New York, 1950).
- [28] *Tables of Integral Transforms, Vol. 1, Bateman Manuscript Project*, A. Erdelyi, Ed. (McGraw-Hill, New York, 1954).
- [29] I. S. Gradshteyn and I. M. Ryzhik, *Tables of Integrals, Series and Products*, 4th ed., A. Jeffrey Ed. (Academic, New York, 1966).

Received April 14, 1981

Accepted November 17, 1981