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PERTURBED-MORSE-OSCILLATOR WAVEFUNCTIONS AND THEIR APPLICATION TO CALCULATION OF FRANCK-CONDON FACTORS

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PERTURBED-MORSE-OSCILLATOR WAVEFUNCTIONS AND THEIR APPLICATION TO CALCULATION OF FRANCK-CONDON FACTORS

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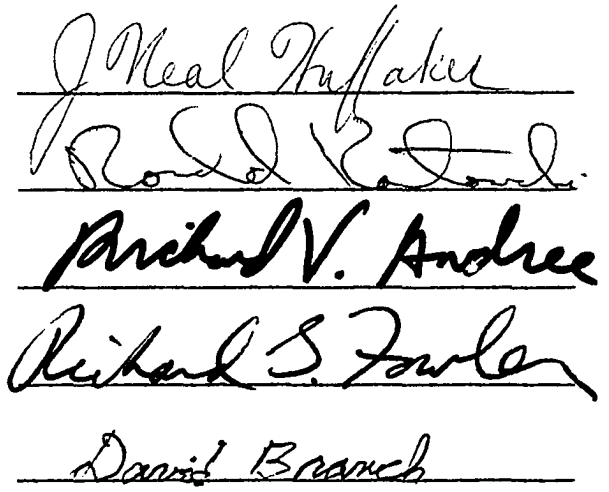

DISSERTATION COMMITTEE

DEDICATION

This dissertation is dedicated to my parents, Dr. Shanker Hari Dwivedi and Uma Sundri Dwivedi.

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CHAPTER I

INTRODUCTION

The calculation of rotational and vibrational motions of diatomic molecules is usually based on the rotating-oscillator model,[1] in which to a good approximation the wavefunction for the molecular state is the product of electronic and nuclear wave functions. The radial Schrödinger equation for the rotating oscillator is given by

$$\left[\frac{-\hbar^2}{2\mu}\frac{d^2}{dr^2} + V(r) + \frac{\hbar^2 J(J+1)}{2\mu r^2}\right]\psi_{vJ}(r) = E_{vJ}\psi_{vJ}(r) \ , \qquad (1.1)$$

where r is internuclear distance, μ reduced mass, and v and J are vibrational and rotational quantum numbers, respectively.

There are at present three standard approaches for treating the vibrational motion of a diatomic molecule. First is the Dunham[2] method, in which the vibrational potential energy V(r) is expressed as a power series:

$$V(\xi) = hc\,a_o\xi^2(1 + a_1\xi + a_2\xi^2 + \ldots) \ , \qquad (1.2)$$

where

$$\xi = \frac{u}{r_e} = \frac{r-r_e}{r_e} \ ,$$

and where r_e is the equilibrium separation. The energy eigenvalues and rotation-vibration parameters for this potential have been calculated[2] via the W.K.B. approximation and can be matched with empirical values to determine the coefficients a_n of the series. The drawbacks of this method are that a power-series potential has poor convergence properties and that it does not produce analytic wavefunctions.

The second approach, called the RKR[3] method, is a computer calculation in two steps: first producing V(r) from the observed vibrational spectra via the classical turning points and the WKB approximation, then obtaining eigenfunctions.

The third approach involves the use of a "realistic potential" with analytic solutions, such as the Morse potential[4] given by

$$V(r) = V_e[\exp(-2au) - 2\exp(-au)] , \tag{1.3}$$

where $u = r-r_e$, involving the three parameters V_e (well depth), r_e and a. For convenience, we describe the Morse oscillator by the three parameters ρ, σ, and τ defined by

$$\rho = ar_e , \tag{1.4a}$$

$$\sigma = \frac{[2\mu V_e]^{\frac{1}{2}}}{a\hbar} , \tag{1.4b}$$

$$\tau = \frac{V_e}{hc} . \tag{1.4c}$$

The parameter σ is approximately the number of bound states of the Morse oscillator, roughly $\omega_e/2\omega_e x_e$. While the Morse potential has analytic solutions and is probably the best three-parameter model

for actual molecules, it fails to describe finer spectroscopic details.

Huffaker and Dwivedi[5] showed that perturbation methods may be applied to the Morse oscillator to any order. The perturbed Morse oscillator (hereinafter abbreviated as PMO) with potential

$$V(u) = V_e\left[(1 - \exp(-au))^2 + \sum_{n=4}^{8} b_n(1 - \exp(-au))^n\right] , \qquad (1.5)$$

where $u = r-r_e$, has been shown to be a useful model[6] for rotational-vibrational motion of diatomic molecules. This potential converges for all r (except for a singularity at r=0), and its parameters are related to the dissociation energy D_e by

$$D_e + E_{v=0,J=0} = V_e(1 + b_4 + b_5 + b_6 + \ldots) . \qquad (1.6)$$

Huffaker[6] used perturbation theory to calculate formulas for perturbed energy levels. From these formulas one can derive values of the Morse parameters ρ, σ, and τ and the perturbation parameters b_4, b_5, b_6, b_7 and b_8 from spectroscopic data. The parameters for the unperturbed Morse oscillator which best represents the actual potential for small values of u are determined from experimental values of ω_e, B_e and α_e, at least to a first approximation, as follows:

$$\rho = (\alpha_e\omega_e + 6B_e^2)/6B_e^2 ; \qquad (1.7a)$$

$$\tau = \frac{\omega_e^2}{4B_e\rho^2} ; \qquad (1.7b)$$

$$\sigma = \frac{2\tau}{\omega_e} . \qquad (1.7c)$$

One can also determine the first five perturbation parameters from $\omega_e x_e$, γ_e, $\omega_e y_e$, δ_e, and $\omega_e z_e$. Formulas for the first three are

$$b_4 = \frac{2}{3}\left[1 - (\sigma^2 \omega_e x_e/\tau)\right] , \tag{1.8a}$$

$$b_5 = (5\rho^3)^{-1}\left[(2\sigma^4\rho^6\gamma_e/3\tau) + 7\rho^3/6 - 23\rho^2/4 + 10\rho - 5 - 3\rho^2 b_4(\rho-1)\right] , \tag{1.8b}$$

$$b_6 = \frac{1}{5}\left[2\sigma^3\omega_e x_e/\tau + b_4 - 5b_5 + 17b_4^2/4\right] . \tag{1.8c}$$

In a similar fashion, formulas for b_7 and b_8 may be written in terms of δ_e and $\omega_e z_e$.

In a subsequent paper, Huffaker used the WKB method to extend the PMO analysis up through b_{12}.[7] In more accurate analyses, Eqs (1.7) and (1.8) provide first approximations to be used in an iterative calculation. The higher-order corrections are most important for molecular states having few vibrational levels, and, consequently, small values of σ.

There are several advantages to the PMO approach. First, since the Morse potential is a good approximation to that of actual molecules, the perturbations are small and the convergence properties of the perturbation series are very good. Second, the formulas for the energy levels are much simpler than those of Dunham. Huffaker[6,7] applied the PMO approach to the ground state of CO and found excellent agreement with RKR results. Finally, as we will show in the next chapter, an additional advantage of the PMO is that one can obtain analytic wave functions which are linear combinations of Morse eigenfunctions.

In chapter II we use fifth-order time-independent perturbation

theory of discrete, nondegenerate states to calculate PMO wavefunctions. Our perturbation consists of the potential of Eq. (1.5) plus rotational energy $\hbar^2 J(J+1)/2\mu r^2$.

An important application of vibrational wavefunctions concerns the calculation of relative intensities of different vibrational bands in electronic spectra of diatomic molecules. For a transition between electronic states n' and n", we must use a different PMO potential for each state. In the rotating-oscillator model, the wavefunction for a diatomic molecule in electronic state n', vibrational state v', and rotational state J' is the product of an electronic, a vibrational, and a rotational factor:

$$\Psi_{n'v'J'} = \Psi_{n'}^{(e\ell)} \Psi_{n'v'J'}^{(vib)}(r) \Psi_{J'}^{(rot)}(\theta,\phi) \quad , \tag{1.9}$$

The probability of an electronic transition between states N' = (n',v',J') and N" = (n",v",J") is proportional to the absolute value squared of the matrix element $R_{N'N"}$ of the dipole moment M:

$$|R_{N'N"}|^2 = |\int \Psi_{N'}^{*} M \Psi_{N"} d\tau|^2 \quad . \tag{1.10}$$

The integration over rotational eigenfunctions may be carried out independently, and produces a factor $S_{J'J"}$, called the Hönl-London factor. Since the electronic functions involve the internuclear distance r parametrically, the integration over these functions produces a quantity $R_{n'n"}^{(e\ell)}(r)$ which also depends on r:[8]

$$R_{n'n"}^{(e\ell)}(r) = \int \Psi_{n'}^{*(e\ell)} M^{(e\ell)} \Psi_{n"}^{(e\ell)} d\tau^{(e\ell)} \quad . \tag{1.11}$$

This function should then be included in the integral over dr, so that

$$|R_{N'N''}|^2 = S_{N'N''} \left| \int \psi_{v'}^{*(vib)} R_{n'n''}^{(e\ell)} \psi_{v''}^{(vib)} \, dr \right|^2 . \qquad (1.12)$$

In practice, it is usually assumed that $R_{n'n''}^{(e\ell)}$ depends only very slightly on r, and that it may be replaced with an average value $\bar{R}_{n'n''}^{(e\ell)}$. In this case, we may write

$$|R|^2 = S_{J'J''} \left| \bar{R}_{n'n''}^{(e\ell)} \right|^2 q_{v'v''} , \qquad (1.13)$$

where the quantity $q_{v'v''}$, called the Franck-Condon factor (FCF)[9] because of its obvious association with the Franck-Condon principle, is the absolute value squared of the overlap integral of vibrational eigenfunctions:

$$q_{v'v''} = \left| \int \psi_{v'}^{(vib)} \psi_{v''}^{(vib)} \, dr \right|^2 . \qquad (1.14)$$

The set of values of $q_{v'v''}$ (for fixed n', n'', J', and J'') is called a FCF array. FCF arrays should thus be related to the intensity distribution between different v'→v'' bands across an electronic band system.

The set of functions $\psi_{n'v'J'}^{(vib)}$ for varying v' (and likewise $\psi_{n''v''J''}^{(vib)}$ for varying v'') form an orthonormal set of functions. Since the number of such bound states is finite, this cannot be a complete set of functions; nevertheless, it behaves much like a complete set when used to expand other functions with similar boundary conditions at r = 0 and r = ∞. In particular, we may use the set $\psi_{n'v'J'}^{(vib)}$ to expand the function $\psi_{n''v''J''}^{(vib)}$ and vice versa. To the extent that these behave like complete sets of orthonormal functions, we would expect the FCF arrays to obey the following sum rules:

$$\sum_{v'} q_{v'v''} = \sum_{v''} q_{v'v''} = 1 \ . \qquad (1.15)$$

Of previous calculations of FCF arrays, the most popular choices for vibrational eigenfunction have been RKR functions and Morse functions (for $J=0$) and Morse-Pekeris[10] functions (for $J\neq 0$.) In Chapter III, we use perturbed-Morse wavefunctions for both upper and lower electronic states to calculate FCF arrays for several electronic transitions in N_2, Na_2 and TiO and compare our results with those of pure Morse and RKR calculations. We also investigate the degree to which the sum rule is obeyed.

The distributions of relative rotational and vibrational intensities in diatomic band spectra are used for measurements of effective temperature in flames and stellar spectra.[11] Before 1958 it was a general tendency to neglect the vibrational-rotational interaction in computing FCF overlap integrals. Learner and Gaydon[12,13] first pointed out the need to include rotational effects since the potential functions of which $\psi^{(vib)}_{n'}$ and $\psi^{(vib)}_{n''}$ are eigenfunctions contain centrifugal terms $\frac{\hbar^2 J(J+1)}{2\mu r^2}$ involving the internuclear distance r and the rotational quantum number J. Therefore the eigenfunctions, the FCF, and the vibrational transition probabilities should also depend to some extent upon J. To express this dependence on J we use the following notation for the FCF appropriate to the transition $v'J' \rightarrow v''J''$:

$$q_{v'J',v''J''} = \left| \int \psi^{(vib)}_{v'J'}(r)\, \psi^{(vib)}_{v''J''}(r) dR \right|^2 , \qquad (1.16)$$

where $\Psi^{(vib)}_{v'J'}$ and $\Psi^{(vib)}_{v''J''}$ are the eigenfunctions of the nuclear motion for upper and lower electronic states respectively.

Since the PMO wavefunctions in Table II contains the J-dependence, we can use them to calculate $q_{v'J',v''J''}$. This is done in Chapter IV, where we calculate the effect of the vibration-rotation interaction on FCF for the Ca_2 molecule and compare our results with an RKR calculation.

Chapter V contains a discussion of the accuracy and usefulness of our PMO wavefunctions.

Appendix A describes the perturbation formalism through fifth order. Matrix elements of powers of [exp(au) - 1] are given in Appendix B.

CHAPTER II

PERTURBED MORSE WAVE FUNCTIONS

The radial Schrodinger equation for the Morse oscillator [see Eqs. (1.1) and (1.3)] is given by

$$\frac{d^2\psi}{du^2} + \frac{2\mu}{\hbar^2}\left[E - V_e\{\exp(-2au) - 2\exp(-au)\}\right]\psi = 0 \ , \tag{2.1}$$

where $u = r - r_e$, and the energy eigenvalues can be written as

$$E_v + V_e = \sigma t\ (v + \tfrac{1}{2}) - \frac{t}{2}(v + \tfrac{1}{2})^2 \ , \tag{2.2A}$$

where

$$t = \frac{(\hbar a)^2}{\mu} \ , \tag{2.2B}$$

and where σ is defined in Eq. (1.4). The eigenfunction for the ground state (v=0), is

$$\psi_{v=0}(r) = [2\sigma]^{(\sigma-\frac{1}{2})}\left[\frac{a}{\Gamma(2\sigma-1)}\right]^{\frac{1}{2}} \exp[-(\sigma-\tfrac{1}{2})au - \sigma\exp(-au)] \ . \tag{2.3}$$

To calculate the eigenfunctions for other vibrational states, we use the recursion relation given by Huffaker and Dwivedi:[5]

$$(e^{au} - 1)\psi_v = A_{v+1}\psi_{v+1} + A_v\psi_{v-1} + C_v\psi_v \ , \tag{2.4}$$

where A_v and C_v are given by

$$A_v = \frac{\sigma}{2(\sigma-v)}\left[\frac{v(2\sigma-v)}{(\sigma-v-\frac{1}{2})(\sigma-v+\frac{1}{2})}\right]^{\frac{1}{2}} \ , \tag{2.5}$$

$$C_v = \frac{2\sigma(v+\frac{1}{2}) - v(v+1)}{(\sigma-v)(\sigma-v-1)} \ . \tag{2.6}$$

Then by Eq. (2.4) the eigenfunctions for vibrational levels v = 1,2,... can easily be calculated by

$$\Psi_1 = [\exp(au) - 1 - C_o]\frac{\Psi_o}{A_1} , \tag{2.7a}$$

$$\Psi_2 = \left[\{\exp(au) - 1 - C_1\}\Psi_1 - A_1\Psi_o\right]\frac{1}{A_2} , \tag{2.7b}$$

$$\Psi_3 = [\{\exp(au) - 1 - C_2\}\Psi_2 - A_2\Psi_1]\frac{1}{A_3} , \tag{2.7c}$$

$$\vdots$$

$$\Psi_V = \frac{1}{A_V}\left[\{\exp(au) - 1 - C_{V-1}\}\Psi_{V-1} - A_{V-1}\Psi_{V-2}\right] . \tag{2.7d}$$

The wavefunctions given by Eqs. (2.3) and (2.7) are normalized.

As shown in the introduction, the internuclear potential can be expressed as that of a PMO given in Eq. (1.5). For small values of b_n, the true potential can be well approximated by

$$V(u) = hc\tau\left[(1 - e^{-au})^2 + \sum_{n=4}^{7} b_n(1 - e^{-au})^n\right] . \tag{2.8}$$

If the molecule has rotational quantum number $J \neq 0$ we must add the rotational kinetic energy, given by

$$E_R = \frac{\hbar^2}{2\mu r^2} J(J+1) . \tag{2.9}$$

This nonrigid rotational energy can be expressed in the form,

$$\frac{\hbar^2 J(J+1)}{2hc\mu r^2} \cong K \sum_{\ell} P_\ell(\rho)\ (e^{au} - 1)^\ell \cong A_{rot}(e^{au} - 1) + B_{rot}(e^{au} - 1)^2$$

$$+ C_{rot}(e^{au} - 1)^3 + D_{rot}(e^{au} - 1)^4 + E_{rot}(e^{au} - 1)^5$$

$$+ F_{rot}(e^{au} - 1)^6 + \quad , \tag{2.10}$$

where

$$K = \frac{\tau J(J+1)}{\sigma^2 \rho^2} \tag{2.11}$$

and the polynomials $P_\ell(\rho)$ are given by Huffaker.[6] Formulas for A_{rot} , ..., F_{rot} are as follows

$$\frac{A_{rot}}{hc} = \frac{-2K}{\rho} \; ; \tag{2.12a}$$

$$\frac{B_{rot}}{hc} = \frac{K}{\rho^2} (\rho+3) \; ; \tag{2.12b}$$

$$\frac{C_{rot}}{hc} = \frac{-K}{\rho^3} (\frac{2}{3} \rho^2 + 3\rho + 4) \; ; \tag{2.12c}$$

$$\frac{D_{rot}}{hc} = \frac{K}{\rho^4} (\frac{\rho^3}{2} + \frac{11}{4} \rho^2 + 6\rho + 5) \; ; \tag{2.12d}$$

$$\frac{E_{rot}}{hc} = \frac{-K}{\rho^5} (\frac{2}{5} \rho^4 + \frac{5}{2} \rho^3 + 7\rho^2 + 10\rho + 6) \; ; \tag{2.12e}$$

$$\frac{F_{rot}}{hc} = \frac{K}{\rho^6} (\frac{\rho^5}{3} + \frac{137}{60} \rho^4 + \frac{15}{2} \rho^3 + \frac{85}{6} \rho^2 + 15\rho + 7) \; . \tag{2.12f}$$

Following is the formalism we use for first, second, third,[14] fourth and fifth order time-independent perturbation theory of discrete non-degenerate states. The unperturbed Hamiltonion H^0 has eigenfunctions and eigenvalues E_m^0 related by

$$H_0 \; \psi_m^0 = E_m^0 \; \psi_m^0 \; , \tag{2.13}$$

where ψ_m^0 and E_m^0 are given by Eqs. (2.7) and (2.2a) respectively.

The perturbed Hamiltonion H is the sum of H^0 and the perturbation $\lambda H'$:

$$H = H_0 + \lambda H'$$

$$\lambda H' = H_{per} + H_{rot}$$

where H_{rot} is the rotational energy of Eq. (2.10) and H_{per} is given by

$$H_{per} = hc\tau \sum_{n=4}^{7} b_n(1-e^{-au})^n = hc\tau \sum_{n=4}^{7} C_n(e^{au}-1)^n \qquad (2.14)$$

where, as shown by Huffaker,[6] the coefficients C_n are related to b_n by

$$C_4 = b_4 \ , \qquad (2.15a)$$

$$C_5 = b_5 - 4b_4 \ , \qquad (2.15b)$$

$$C_6 = b_6 - 5b_5 + 10b_4 \ , \qquad (2.15c)$$

$$C_7 = b_7 - 6b_6 + 15b_5 - 20b_4 \ . \qquad (2.15d)$$

Thus our total $\lambda H'$ can be written as

$$\lambda H' = A[\exp(au) - 1] + B[\exp(au) - 1]^2 + C[\exp(au) - 1]^3 + D[\exp(au) - 1]^4 + E[\exp(au) - 1]^5 + F[\exp(au) - 1]^6 + G[\exp(au) - 1]^7 \ , \qquad (2.16)$$

where

$$\begin{aligned} A &= A_{rot} \ , \\ B &= B_{rot} \ , \\ C &= C_{rot} \ , \\ D &= D_{rot} + C_4 \ , \\ E &= E_{rot} + C_5 \ , \\ F &= F_{rot} + C_6 \ , \\ G &= C_7 \ . \end{aligned} \qquad (2.17)$$

Using the binomial expansion, we expand the various quantities needed in the perturbation calculations in the form,

$$A_v = \left|\frac{n-\frac{1}{2}}{2\sigma}\right|^{\frac{1}{2}} \left\{1 + \frac{\frac{7}{4}(n-\frac{1}{2})}{\sigma} + \frac{\frac{79}{32}(n-\frac{1}{2})^2 + \frac{1}{8}}{\sigma^2} + \ldots\right\}, \qquad (2.18)$$

$$C_v = \frac{2n}{\sigma} + \frac{3n^2 + \frac{1}{4}}{\sigma^2} + \frac{4n^3 + n}{\sigma^3} + \ldots, \qquad (2.19)$$

$$[E_v - E_{v+i}]^{-1} = -\left(\frac{\sigma}{2iV_e}\right)\left[1 + \frac{u}{\sigma} + \left(\frac{u}{\sigma}\right)^2 + \ldots\right], \qquad (2.20)$$

where

$$u = n + \frac{i}{2} \quad \text{and} \quad n = v + \tfrac{1}{2}.$$

An analysis of perturbation equations gives us the rule that the lowest-order term of $\int \Psi_{v\pm m}(e^{au} - 1)^n \Psi_v dr$ is of order $\sigma^{-n/2}$ for m=n, n-2, n-4, ... , and is of order $\sigma^{-(n+1)/2}$ for m=n-1, n=3, n-5, ... , while the lowest-order term of the energy denominator $(E_v - E_{v+n})^{-1}$ is of order σ. Consequently the term in Eq. (2.17) involving C_4 is of order 1, C_5 is of order 3/2, C_6 is of order 2, and C_7 is of order 5/2. The extension of the concept of order to rotational effects is not as straightforward, since rotational perturbation includes powers of K, which is proportional to σ, as well as power of $\sigma^{-\frac{1}{2}}$ arising from the perturbation equations themselves. We arbitrarily define the quantity

$$J(J+1)/(\sigma\rho^3) = \sigma K/\rho$$

to be of order zero (order-of-magnitude unity), so A is of order ½, B of order 1, ... , etc. The order of a perturbation term is the sum of the orders of its factors. Thus A^3B is of order 5/2. We choose to include all terms of order 5/2 or less. If the order of a given term

is 3/2 or smaller, we need more terms of the expansions for A_n, C_n, etc. Since these are expansions in powers of σ^{-1}, each additional term increases the order by unity. (Thus we need three terms in the perturbation in A, etc.)

Our perturbation formalism is described in Appendix A. The matrix elements of powers of exp(au)-1 may conveniently be calculated from the formulas of Appendix B, which contains all terms which contribute to wave-function corrections of order 5/2 or less.

The results of the perturbation calculation for v±1, v±2, v±3, v±4, ... , v±9, are given in Table I, grouped by the order of perturbation and then alphabetically.

TABLE I

Perturbation terms contributing to coefficients $X^{\ell}_{\pm mjk}$ with $m \leq 9$, $j \leq 4$, $k \leq 4$, and with $\ell \leq 5$ for odd m and $\ell \leq 4$ for even m. Parameters A, B, ... , G are defined by Eq. (2.17) and σ by Eq. (1.4b), while $n = v + \frac{1}{2}$.

(V±1) State

First-order Correction

$$\frac{P_{\mp 1}}{2V_e\sigma^{5/2}}\left\{A[\pm\sigma^3 + \sigma^2(\pm\frac{11}{4}n - \frac{11}{8}) + \sigma(\pm\frac{167}{32}n^2 - \frac{167}{32}n \pm \frac{183}{128})]\right.$$

$$+ B[\sigma^2(\pm 4n - 2) + \sigma(\pm 17n^2 - 17n \pm \frac{25}{4})]$$

$$+ C[\sigma^2(\pm\frac{3}{2}n - \frac{3}{4}) + \sigma(\pm\frac{171}{8}n^2 - \frac{171}{8}n \pm \frac{315}{32})]$$

$$+ D[\sigma(\pm 12n^2 - 12n \pm 7) + (\pm 125n^3 - \frac{375}{2}n^2 \pm \frac{771}{4}n - \frac{521}{8})]$$

$$+ E[\sigma(\pm\frac{5}{2}n^2 - \frac{5}{2}n \pm \frac{15}{8}) + (\pm\frac{675}{8}n^3 - \frac{2025}{16}n^2 \pm \frac{5015}{32}n - \frac{3665}{64})]$$

$$+ F[\pm 30n^3 - 45n^2 \pm \frac{135}{2}n - \frac{105}{4}]$$

$$\left.+ G[\pm\frac{35}{8}n^3 - \frac{105}{16}n^2 \pm \frac{385}{32}n - \frac{315}{64}]\right\}$$

Second-order Correction

$$\frac{P_{\pm 1}}{4V_e^2\sigma^{5/2}}\left\{A^2[\sigma^3(\pm 2) + \sigma^2(\pm\frac{27}{2}n + \frac{27}{4})]\right.$$

$$+ AB[\sigma^3(-\frac{n}{4} \pm \frac{13}{8}) + \sigma^2(-\frac{29}{16}n^2 \pm \frac{269}{8}n + \frac{1025}{64})]$$

$$+ AC[\sigma^2(-\frac{3}{2}n^2 \pm \frac{81}{4}n + \frac{39}{4})]$$

$$+ AD[\sigma^2(-\frac{n^2}{2} \pm \frac{19}{4}n + \frac{9}{4}) + \sigma(-\frac{91}{8}n^3 \pm 191n^2 + \frac{5795}{32}n \pm 100)]$$

TABLE I (continued)

$$+ AE[\sigma(-5n^3 \pm \frac{145}{2} n^2 + \frac{135}{2} n \pm \frac{185}{4})]$$

$$+ AF[\sigma(-\frac{15}{16} n^3 \pm \frac{375}{32} n^2 + \frac{675}{64} n \pm \frac{1125}{128})]$$

$$+ B^2[\sigma^2(-n^2 \pm 9n + \frac{15}{4})] + BC[\sigma^2(-\frac{5}{12} n^2 \pm \frac{95}{24} n + \frac{13}{8})]$$

$$+ BD[\sigma(-\frac{16}{3} n^3 \pm \frac{194}{3} n^2 + 53n \pm 32)]$$

$$+ BE[\sigma(-\frac{35}{48} n^3 \pm \frac{875}{96} n^2 + \frac{445}{64} n \pm \frac{795}{128})]$$

$$+ CD[\sigma(-\frac{27}{32} n^3 \pm \frac{715}{64} n^2 + \frac{1235}{128} n \pm \frac{1213}{256})]$$

$$+ D^2[-\frac{27}{4} n^4 \pm \frac{217}{2} n^3 + \frac{1077}{8} n^2 \pm \frac{1311}{8} n + \frac{3537}{64}]$$

$$+ DE[-\frac{119}{80} n^4 \pm \frac{4019}{160} n^3 + \frac{9811}{320} n^2 \pm \frac{27789}{640} n + \frac{981}{64}]\Big\}$$

Third-order Correction

$$\frac{P_{\mp 1}}{8V_e^3\sigma^{5/2}} \Big\{A^3[\sigma^4(\pm \frac{n}{4} + \frac{1}{8}) + \sigma^3(\pm \frac{33}{16} n^2 + \frac{5}{4} n \pm \frac{391}{64})]$$

$$+ A^2B[\sigma^3(\pm 3n^2 + 3n \pm \frac{43}{4})] + A^2C[\sigma^3(\pm \frac{7}{6} n^2 + \frac{23}{24} n \pm \frac{31}{16})]$$

$$+ A^2D[\sigma^2(\pm \frac{28}{3} n^3 + \frac{35}{3} n \pm 67n - \frac{105}{4})] + AB^2[\sigma^3(\frac{3}{4} n \pm \frac{23}{8})]$$

$$+ ABD[\sigma^2(\pm \frac{n^3}{64} + \frac{1555}{384} n^2 \pm \frac{16789}{768} n - \frac{4585}{512})]$$

$$+ AD^2[\sigma(\pm \frac{n^4}{32} + \frac{339}{64} n^3 \pm \frac{4873}{128} n^2 - \frac{7867}{256} n \pm \frac{3943}{256})]$$

$$+ A^2E[\sigma^2(\pm \frac{95}{48} n^3 + \frac{215}{96} n^2 \pm \frac{695}{64} n - \frac{465}{128})]\Big\}$$

Fourth-order Correction

$$\frac{P_{\pm 1}}{16V_e^4\sigma^{5/2}} \Big\{A^4[\sigma^4(\pm \frac{3}{2} n - \frac{3}{4})] + A^3D[\sigma^3(-\frac{11}{64} n^3 \pm \frac{1489}{384} n^2 - \frac{1735}{768} n \pm \frac{1053}{512})]\Big\}$$

TABLE I (continued)

Fifth-order Correction

$$\frac{P_{\mp 1}}{32V_e^5\sigma^{5/2}}\left\{A^5[\sigma^5(\pm\frac{n^2}{12}+\frac{n}{24})]\right\}$$

(V±2) State

First-order Correction

$$\frac{P_{\mp 2}}{2V_e\sigma^2}\left\{B[\sigma^2(\pm\tfrac{1}{2})+\sigma(\pm\frac{9}{4}n-\frac{9}{4})]+C[\sigma(\pm 3n-3)]\right.$$

$$+D[\sigma(\pm n-1)+(\pm 20n^2-40n\pm\frac{211}{8})]$$

$$\left.+E[\pm 10n^2-20n\pm 15]+F[\pm\frac{15}{8}n^2-\frac{15}{4}n\pm\frac{105}{32}]\right\}$$

Second-order Correction

$$\frac{P_{\pm 2}}{4V_e^2\sigma^2}\left\{A^2[\sigma^3(\tfrac{1}{2})+\sigma^2(\frac{11}{4}n\pm\frac{5}{2})]+AB[\sigma^2(4n\pm 5)]\right.$$

$$+AC[\sigma^2(\frac{4}{3}n\pm\frac{11}{6})]+B^2[\sigma^2(\pm\tfrac{1}{2})]+AD[\sigma(\frac{32}{3}n^2\pm\frac{86}{3}n+24)]$$

$$+AE[\sigma(\frac{25}{12}n^2\pm\frac{35}{6}n+\frac{85}{16})]+BD[\sigma(-\frac{n^2}{32}\pm\frac{45}{16}n+\frac{349}{128})]$$

$$\left.+D^2[-\frac{n^3}{16}\pm\frac{63}{16}n^2+\frac{469}{64}n\pm\frac{303}{64}]\right\}$$

Third-order Correction

$$\frac{P_{\mp 2}}{8V_e^3\sigma^2}\left\{A^3[\sigma^3(-2)+A^2B[\sigma^3(-\frac{3}{2})]+A^2D[\sigma^2(\pm\frac{n^2}{32}-\frac{217}{48}n\pm\frac{1385}{384})]\right\}$$

Fourth-order Correction

$$\frac{P_{\pm 2}}{16V_e^4\sigma^2}\left\{A^4[\sigma^4(\frac{n}{6}\mp\frac{1}{12})]\right\}$$

TABLE I (continued)

$V_{\mp 3}$ State

First-order Correction

$$\frac{P_{\mp 3}}{2V_e\sigma^{5/2}}\left\{C\left[\sigma^2\left(\pm\frac{1}{3}\right)+\sigma\left(\pm\frac{25}{12}n-\frac{25}{8}\right)\right]\right.$$

$$+D\left[\sigma\left(\pm\frac{8}{3}n-4\right)+\left(\pm\frac{62}{3}n^2-62n\pm\frac{311}{6}\right)\right]$$

$$+E\left[\sigma\left(\pm\frac{5}{6}n-\frac{5}{4}\right)+\left(\pm\frac{515}{24}n^2-\frac{515}{8}n\pm\frac{5515}{96}\right)\right]$$

$$\left.+F\left[\pm 10n^2-30n\pm\frac{175}{6}\right]+G\left[\pm\frac{7}{4}n^2-\frac{21}{4}n\pm\frac{91}{16}\right]\right\}$$

Second-order Correction

$$\frac{P_{\pm 3}}{4V_e^2\sigma^{5/2}}\left\{AB\left[\sigma^3\left(\tfrac{1}{2}\right)+\sigma^2\left(\frac{29}{8}n\pm\frac{241}{48}\right)\right]+AC\left[\sigma^2\left(3n\pm\frac{17}{3}\right)\right]\right.$$

$$+AD\left[\sigma^2\left(\frac{7}{8}n\pm\frac{91}{48}\right)+\sigma\left(\frac{685}{32}n^2\pm\frac{7813}{96}n+\frac{10437}{128}\right)\right]$$

$$+B^2\left[\sigma^2\left(2n\pm\frac{7}{3}\right)\right]+BC\left[\sigma^2\left(\frac{3}{4}n\pm\frac{29}{24}\right)\right]$$

$$+AE\left[\sigma\left(\frac{35}{4}n^2\pm\frac{875}{24}n+\frac{165}{4}\right)\right]+AF\left[\sigma\left(\frac{3}{2}n^2\pm\frac{107}{16}n+\frac{261}{32}\right)\right]$$

$$+BD\left[\sigma\left(\frac{57}{6}n^2\pm\frac{179}{6}n+\frac{657}{24}\right)\right]+BE\left[\sigma\left(\frac{49}{40}n^2\pm\frac{119}{30}n+\frac{787}{160}\right)\right]$$

$$+CD\left[\sigma\left(\frac{21}{16}n^2\pm\frac{95}{16}n+\frac{285}{64}\right)\right]$$

$$+D^2\left[\frac{21}{2}n^3\pm\frac{257}{4}n^2+\frac{859}{8}n\pm\frac{3661}{48}\right]$$

$$\left.+DE\left[\frac{171}{80}n^3\pm\frac{2379}{160}n^2+\frac{8511}{320}n\pm\frac{13259}{640}\right]\right\}$$

Third-order correction

$$\frac{P_{\mp 3}}{8V_e^3\sigma^{5/2}}\left\{A^3\left[\sigma^4\left(\pm\frac{1}{6}\right)+\sigma^3\left(\pm\frac{33}{24}n-\frac{29}{16}\right)\right]+A^2B\left[\sigma^3\left(\pm 2n-5\right)\right]\right.$$

$$+A^2C\left[\sigma^3\left(\pm\frac{3}{4}n-\frac{11}{8}\right)\right]+A^2D\left[\sigma^2\left(\pm 6n^2-\frac{49}{2}n\pm\frac{371}{12}\right)\right]$$

TABLE I (continued)

$$+ AB^2\left[\sigma^3\left(\pm\frac{1}{16}n - \frac{41}{32}\right)\right] + ABD\left[\sigma^2\left(\mp\frac{9}{32}n^2 - \frac{97}{16}n \mp \frac{1173}{128}\right)\right]$$
$$+ A^2E\left[\sigma^2\left(\pm\frac{51}{40}n^2 - \frac{183}{40}n \pm \frac{2689}{480}\right)\right]$$
$$+ AD^2\left[\sigma\left(\mp\frac{5}{16}n^3 - \frac{111}{16}n^2 \mp \frac{1585}{64}n - \frac{1107}{64}\right)\right]\Bigg\}$$

Fourth-order Correction

$$\frac{P_{\pm 3}}{16V_e^4\sigma^{5/2}}\left\{A^4\left[\sigma^4(\pm 1)\right] + A^3D\left[\sigma^3\left(\frac{7}{32}n^2 \pm \frac{21}{8}n + \frac{289}{128}\right)\right]\right\}$$

Fifth-order Correction

$$\frac{P_{\mp 3}}{32V_e^5\sigma^{5/2}}\left\{A^5\left[\sigma^5\left(\pm\frac{n}{16} + \frac{1}{32}\right)\right]\right\}$$

(V±4) State

First-order Correction

$$\frac{P_{\mp 4}}{2V_e\sigma^2}\left\{D\left[\sigma\left(\pm\tfrac{1}{4}\right) + (\pm 2n-4)\right] + E\left[\pm\frac{5}{2}n - 5\right] + F\left[\pm\frac{3}{4}n - \frac{3}{2}\right]\right\}$$

Second-order Correction

$$\frac{P_{\pm 4}}{4V_e^2\sigma^2}\left\{AC\left[\sigma^2\left(\frac{1}{3}\right) + \sigma^2\left(\frac{8}{3}n \pm \frac{59}{12}\right)\right] + AD\left[\sigma\left(\frac{8}{3}n \pm \frac{13}{2}\right)\right] + AE\left[\sigma\left(\frac{11}{15}n \pm \frac{41}{20}\right)\right]\right.$$
$$+ B^2\left[\sigma^2\left(\frac{1}{8}\right) + \sigma\left(n \pm \frac{15}{8}\right)\right] + BD\left[\sigma\left(\frac{n}{2} \pm \frac{5}{4}\right)\right] + CD\left[11n^2 \pm 39n + \frac{115}{3}\right]$$
$$\left.+ D^2\left[\frac{n^2}{2} \pm \frac{11}{4}n + 3\right]\right\}$$

TABLE I (continued)

Third-order Correction

$$\frac{P_{\mp 4}}{8V_e^3\sigma^2}\left\{A^2B[\sigma^3(\pm\tfrac{1}{4})] + A^2D[\sigma^2(\pm\tfrac{n}{2} - \tfrac{4}{3})]\right\}$$

Fourth-order Correction

$$\frac{P_{\pm 4}}{16V_e^4\sigma^2}\left\{A^4[\sigma^4(\tfrac{1}{24})]\right\}$$

(V±5) State

First-order Correction

$$\frac{P_{\mp 5}}{2V_e\sigma^{5/2}}\left\{E[\sigma(\pm\tfrac{1}{5}) + (\pm\tfrac{39}{20}n - \tfrac{39}{8})] + F[\pm\tfrac{12}{5}n - 6] + G[\pm\tfrac{7}{10}n - \tfrac{7}{4}]\right\}$$

Second-order Correction

$$\frac{P_{\pm 5}}{4V_e^2\sigma^{5/2}}\left\{AD[\sigma^2(\tfrac{1}{4}) + \sigma(\tfrac{43}{16}n \pm \tfrac{1007}{160})] + AE[\sigma(\tfrac{5}{2}n \pm \tfrac{37}{5})]\right.$$
$$+ AF[\sigma(\tfrac{2}{3}n \pm \tfrac{269}{120})] + BC[\sigma^2(\tfrac{1}{6})] + BD[\sigma(\tfrac{7}{3}n \pm \tfrac{49}{10})]$$
$$+ BE[\sigma(\tfrac{5}{12}n \pm \tfrac{53}{40})] + CD[\sigma(\tfrac{17}{24}n \pm \tfrac{293}{240})]$$
$$\left.+ D^2[\tfrac{17}{3}n^2 \pm \tfrac{313}{15}n + \tfrac{103}{4}] + DE[\tfrac{35}{24}n^2 \pm \tfrac{757}{120}n + \tfrac{263}{32}]\right\}$$

Third-order Correction

$$\frac{P_{\mp 5}}{8V_e^3\sigma^{5/2}}\left\{A^2C[\sigma^3(\pm\tfrac{1}{6})] + A^2D[\sigma^2(\pm\tfrac{4}{3}n - 5)] + A^2E[\sigma^2(\pm\tfrac{5}{12}n - \tfrac{11}{8})]\right.$$
$$+ AB^2[\sigma^3(\pm\tfrac{1}{8})] + ABD[\sigma^2(\pm\tfrac{7}{16}n - \tfrac{199}{96})]$$
$$\left.+ AD^2[\sigma(\pm\tfrac{3}{8}n^2 - \tfrac{221}{48}n \pm \tfrac{3014}{480})]\right\}$$

TABLE I (continued)

Fourth-order Correction

$$\frac{P_{\pm 5}}{16V_e^4\sigma^{5/2}}\left\{A^3D[\sigma^3(\frac{11}{48}\,n \pm \frac{47}{96})]\right\}$$

Fifth-order Correction

$$\frac{P_{\mp 5}}{32V_e^5\sigma^{5/2}}\left\{\sigma^5(\pm\frac{1}{120})\right\}$$

(V±6) State

First-order Correction

$$\frac{P_{\mp 6}}{2V_e\sigma^2}\left\{F[\pm\frac{1}{6}]\right\}$$

Second-order Correction

$$\frac{P_{\pm 6}}{4V_e\sigma^2}\left\{AE[\sigma(\frac{1}{5})] + BD[\sigma(\frac{1}{8})] + D^2[\frac{n}{4} \pm \frac{7}{12}]\right\}$$

Third-order Correction

$$\frac{P_{\mp 6}}{8V_e^3\sigma^2}\left\{A^2D[\pm\frac{1}{8}]\right\}$$

(V±7) State

First-order Correction

$$\frac{P_{\mp 7}}{2V_e\sigma^{5/2}}\left\{G[\pm\frac{1}{7}]\right\}$$

Second-order Correction

$$\frac{P_{\pm 7}}{4V_e^2\sigma^{5/2}}\left\{AF[\sigma(\frac{1}{6})] + BE[\sigma(\frac{1}{10})] + CD[\sigma(\frac{1}{12})] + D^2[\frac{2}{3}\,n \pm \frac{15}{7}]\right.$$

TABLE I (continued)

$$+ DE\left[\frac{49}{120} n \pm \frac{647}{560}\right]\Bigg\}$$

Third-order Correction

$$\frac{P_{\mp 7}}{8V_e^3\sigma^{5/2}}\left\{A^2E\left[\sigma^2\left(\pm\frac{1}{10}\right)\right] + ABD\left[\sigma^2\left(\pm\frac{1}{8}\right)\right] + AD^2\left[\sigma\left(\pm\frac{105}{448} n - \frac{2149}{2688}\right)\right]\right\}$$

Fourth-order Correction

$$\frac{P_{\pm 7}}{16V_e^4}\left\{A^3D\left[\sigma^3\left(\frac{1}{24}\right)\right]\right\}$$

(V±8) State

Second-order Correction

$$\frac{P_{\pm 8}}{4V_e^2\sigma^2}\left\{D^2\left[\frac{1}{32}\right]\right\}$$

(V±9) State

Second-order Correction

$$\frac{P_{\pm 9}}{4V_e^2\sigma^{5/2}}\left\{DE\left[\frac{1}{20}\right]\right\}$$

Third-order Correction

$$\frac{P_{\mp 9}}{8V_e^3\sigma^{5/2}}\left\{AD^2\left[\sigma\left(\pm\frac{1}{32}\right)\right]\right\}$$

By using Eq. (2.12), (2.15), and (2.17), we can rewrite the wavefunction correction in terms of PMO parameters. We express PMO wavefunctions including rotation in the form

$$\Psi_v = \Psi_v^0 + \sum_m A(v,J,m)\Psi_{v+m}^0 + \sum_m B(v,J,m)\Psi_{v-m} , \tag{2.21}$$

where $A(v,J,m)$ and $B(v,J,m)$ are expressed as follows in terms of σ, ρ, J and coefficients X_{mjk}^{ℓ} :

$$A(v,J,m) = P_m \sum_{j=0} \sum_{k=0} n^j (\sigma\rho^3)^{-k} [J(J+1)]^k \sum_{\ell=0} \sigma^{-\ell/2} X_{mjk}^{\ell} ; \tag{2.22}$$

$$B(v,J,m) = P_{-m} \sum_{j=0} n^j (\sigma\rho^3)^{-k} [J(J+1)]^k \sum_{\ell=0} \sigma^{-\ell/2} X_{-mjk}^{\ell} \tag{2.23}$$

where

$$P_{\pm m} = \left[\frac{(n\pm\tfrac{1}{2})(n\pm 3/2) \ldots (n+m\mp\tfrac{1}{2})}{2^{|m|}}\right]^{\frac{1}{2}} \tag{2.24}$$

and

$$n = v + \tfrac{1}{2} . \tag{2.25}$$

The coefficients $X_{\pm mjk}^{\ell}$ with $m \leq 9$, $j \leq 4$, and $k \leq 5$ are given in Table II in terms of b_4, b_5, b_6, b_7, and ρ, σ and τ. Note that X_{-mjk}^{ℓ} and X_{+mjk}^{ℓ} are related by $X_{-mjk}^{\ell} = \pm X_{mjk}^{\ell}$. Which sign to use is indicated in Table II by whether (+) or (-) precedes X_{mjk} .

The perturbed wavefunctions given by Eq. (2.21) are unnormalized. The correctly normalized wavefunction may be calculated after substitution of values of the quantities X_{mjk}^{ℓ} for different vibrational levels: the correctly normalized perturbed Morse wavefunction is given by

$$\Psi_v = \frac{\Psi_v^0 + \sum_{\ell=1} [B_\ell(v,J)\Psi_{v-\ell}^0 + A_\ell(v,J)\Psi_{v+\ell}^0]}{\sqrt{1 + \sum_\ell [B_\ell(v,J)^2 + A_\ell(v,J)^2]}} . \tag{2.26}$$

TABLE II

Coefficients for rotational-vibrational wavefuncitons of a perturbed Morse oscillator. Wave functions are given by Eq. (2.21) and various parameters are defined by Eqs. (2.17) and (1.4).

$$X^3_{\pm 100} = \pm\left[\frac{b_4}{4} - \frac{15}{16} b_5\right]$$

$$X^5_{\pm 100} = \left[-\frac{b_4}{16} + \frac{5}{64} b_5 + \frac{105}{64} b_6 - \frac{315}{128} b_7 - \frac{387}{256} b_4^2 + \frac{981}{256} b_4 b_5\right]$$

$$X^3_{\pm 110} = \left[-b_4 - \frac{5}{4} b_5\right]$$

$$X^5_{\pm 110} = \pm\left[-\frac{b_4}{8} + \frac{5}{32} b_5 + \frac{75}{32} b_6 - \frac{385}{64} b_7 - \frac{1569}{640} b_4^2 + \frac{27789}{2560} b_4 b_5\right]$$

$$X^3_{\pm 120} = \pm\left[-b_4 - \frac{5}{4} b_5\right]$$

$$X^5_{\pm 120} = \left[-\frac{45}{16} b_6 - \frac{105}{32} b_7 + \frac{959}{320} b_4^2 + \frac{9811}{1280} b_4 b_5\right]$$

$$X^5_{\pm 130} = \pm\left[-\frac{15}{8} b_6 - \frac{35}{16} b_7 + \frac{321}{160} b_4^2 + \frac{4019}{640} b_4 b_5\right]$$

$$X^5_{\pm 140} = \left[-\frac{b_4^2}{5} - \frac{119}{320} b_4 b_5\right]$$

$$X^1_{\pm 101} = \pm[1]$$

$$X^3_{\pm 101} = \frac{1}{\rho^2}\left[\left(\frac{5}{8}\rho^2 - \frac{15}{8}\rho + \frac{3}{2}\right) - \frac{9}{8}\rho^2 b_4\right]$$

$$X^5_{\pm 101} = \frac{\pm 1}{\rho^4}\left[\left(\frac{27}{128}\rho^4 - \frac{121}{64}\rho^3 + \frac{21}{4}\rho^2 - \frac{65}{8}\rho + \frac{45}{8}\right)\right.$$
$$+ b_4\rho^2\left(-\frac{685}{1536}\rho^2 + \frac{1857}{1024}\rho - \frac{1213}{256}\right) + b_5\rho^3\left(\frac{205}{512}\rho + \frac{2385}{512}\right)$$
$$\left. - b_6\rho^4\left(\frac{1125}{256}\right) + b_4^2\rho^4\left(\frac{3943}{1024}\right)\right]$$

$$X^3_{\pm 111} = \frac{\pm 1}{\rho^2}\left[\left(\frac{5}{4}\rho^2 - \frac{15}{4}\rho + 3\right) - \frac{19}{8} b_4\rho^2\right]$$

$$X^5_{\pm 111} = \frac{1}{\rho^4}\left[\left(\frac{43}{32}\rho^4 - \frac{109}{16}\rho^3 + \frac{31}{2}\rho^2 - \frac{35}{2}\rho + \frac{15}{2}\right)\right.$$

TABLE II (continued)

$$+ b_4\rho^2\left(-\frac{2759}{768}\rho^2 + \frac{5967}{512}\rho - \frac{1235}{128}\right) + b_5\rho^3\left(-\frac{1445}{256}\rho + \frac{1335}{256}\right)$$

$$- b_6\rho^4\left(\frac{675}{128}\right) + \frac{7867}{1024}b_4^2\rho^4\Big]$$

$$X^5_{\pm 121} = \frac{\pm 1}{\rho^4}\left[\left(\frac{43}{32}\rho^4 - \frac{109}{16}\rho^3 + \frac{31}{32}\rho^2 - \frac{35}{2}\rho + \frac{15}{2}\right)\right.$$

$$+ b_4\rho^2\left(-\frac{1499}{384}\rho^2 + \frac{3271}{256}\rho - \frac{715}{64}\right) + b_5\rho^3\left(-\frac{1795}{384}\rho + \frac{875}{128}\right)$$

$$- b_6\rho^4\left(\frac{375}{64}\right) + \frac{4873}{512}b_4^2\rho^4\Big]$$

$$X^5_{\pm 131} = \frac{1}{\rho^2}\left[b_4\left(-\frac{17}{192}\rho^2 - \frac{151}{128}\rho + \frac{27}{32}\right) + b_5\rho\left(-\frac{5}{192}\rho - \frac{35}{64}\right)\right.$$

$$+ \frac{15}{32}b_6\rho^2 - b_4^2\rho^2\left(\frac{339}{256}\right)\Big]$$

$$X^5_{\pm 141} = \pm\left[\frac{b_4^2}{128}\right]$$

$$X^3_{\pm 102} = \frac{\pm 1}{\rho}\left[\frac{19}{16}\rho - \frac{39}{16}\right]$$

$$X^5_{\pm 102} = \frac{1}{\rho^3}\left[\left(\frac{805}{384}\rho^3 - \frac{1139}{128}\rho^2 + \frac{509}{32}\rho - \frac{21}{2}\right) - b_4\rho^2\left(\frac{7415}{2048}\rho - \frac{13755}{2048}\right)\right.$$

$$- \frac{465}{256}b_5\rho^3\Big]$$

$$X^3_{\pm 112} = \frac{1}{\rho}\left[\left(\frac{2\rho+6}{16}\right)\right]$$

$$X^5_{\pm 112} = \frac{\pm 1}{\rho^3}\left[\left(\frac{553}{144}\rho^3 - \frac{433}{24}\rho^2 + \frac{3229}{96}\rho - \frac{95}{4}\right)\right.$$

$$- b_4\rho^2\left(\frac{19403}{3072}\rho - \frac{16789}{1024}\right) - \frac{695}{128}b_5\rho^3\Big]$$

$$X^5_{\pm 122} = \frac{1}{\rho^3}\left[\left(\frac{101}{288}\rho^3 + \frac{17}{96}\rho^2 - \frac{115}{48}\rho + \frac{5}{2}\right)\right.$$

$$+ b_4\rho^2\left(\frac{525}{1536}\rho - \frac{1555}{512}\right) + \frac{215}{192}b_5\rho^3\Big]$$

TABLE II (continued)

$$X^3_{\pm 103} = \left[-\frac{1}{8}\right]$$

$$X^5_{\pm 103} = \frac{\pm 1}{\rho^2}\left[\left(\frac{403}{192}\rho^2 - \frac{285}{32}\rho + \frac{331}{32}\right) - \frac{1053}{1024}b_4\rho^2\right]$$

$$X^3_{\pm 113} = \pm 1\left[\tfrac{1}{4}\right]$$

$$X^5_{\pm 113} = \frac{1}{\rho^2}\left[\left(-\frac{11}{192}\rho^2 + \frac{363}{128}\rho - \frac{77}{32}\right) + \frac{1735}{1536}b_4\rho^2\right]$$

$$X^5_{\pm 123} = \frac{\pm 1}{\rho^2}\left[\left(\frac{137}{144}\rho^2 - \frac{11}{4}\rho + \frac{7}{3}\right) - \frac{1489}{768}b_4\rho^2\right]$$

$$X^5_{\pm 133} = \left[\frac{11}{128}b_4\right]$$

$$X^5_{\pm 104} = \left[-\frac{3}{4}\right]$$

$$X^5_{\pm 114} = \pm\left[\frac{3}{2}\right]$$

$$X^5_{\pm 115} = \left[-\frac{1}{24}\right]$$

$$X^5_{\pm 125} = \pm\left[\frac{1}{12}\right]$$

$$X^2_{\pm 200} = \left[-\frac{b_4}{2}\right]$$

$$X^4_{\pm 200} = \pm\left[\frac{13}{32}b_4 + \frac{45}{64}b_5 - \frac{105}{64}b_6 + \frac{303}{256}b_4^2\right]$$

$$X^2_{\pm 210} = \pm\left[-\frac{b_4}{2}\right]$$

$$X^4_{\pm 210} = \left[\frac{5}{4}b_4 - \frac{5}{8}b_5 - \frac{15}{8}b_6 + \frac{469}{256}b_4^2\right]$$

$$X^4_{\pm 220} = \pm\left[\frac{5}{8}b_4 - \frac{5}{16}b_5 - \frac{15}{16}b_6 + \frac{63}{64}b_4^2\right]$$

$$X^4_{\pm 230} = \left[-\frac{b_4^2}{64}\right]$$

TABLE II (continued)

$$X^4_{\pm 201} = \frac{1}{\rho^3}\left[\left(-\frac{3}{8}\rho^3 - \frac{1}{4}\rho^2 + 3\rho - \frac{5}{2}\right) + b_4\rho^2\left(-\frac{355}{512}\rho + \frac{1047}{512}\right) - b_5\rho^3\,\frac{85}{32}\right]$$

$$X^4_{\pm 211} = \frac{\pm 1}{\rho^3}\left[\left(-\frac{3}{8}\rho^3 - \frac{\rho^2}{4} + 3\rho - \frac{5}{2}\right) - b_4\rho^2\left(\frac{377}{192}\rho - \frac{135}{64}\right) - \frac{35}{12}\,b_5\rho^3\right]$$

$$X^4_{\pm 221} = \frac{1}{\rho}\left[b_4\left(-\frac{451}{384}\rho - \frac{3}{128}\right) - \frac{25}{24}\,b_5\rho\right]$$

$$X^2_{\pm 202} = \left[\tfrac{1}{2}\right]$$

$$X^4_{\pm 202} = \frac{\pm 1}{\rho^2}\left[\left(\frac{53}{72}\rho^2 - 4\rho + \frac{115}{24}\right) - \frac{1385}{768}\,b_4\rho^2\right]$$

$$X^4_{\pm 212} = \frac{1}{\rho^2}\left[\left(\frac{43}{36}\rho^2 - 4\rho + \frac{8}{3}\right) - \frac{217}{96}\,b_4\rho^2\right]$$

$$X^4_{\pm 222} = \pm\left[-\frac{b_4}{64}\right]$$

$$X^4_{\pm 203} = \frac{1}{\rho}\left[\frac{5}{4}\rho - \frac{9}{4}\right]$$

$$X^4_{\pm 204} = \pm\left[\frac{-1}{12}\right]$$

$$X^4_{\pm 214} = \left[\frac{1}{6}\right]$$

$$X^3_{\pm 300} = \left[\frac{b_4}{2} - \frac{5}{8}\,b_5\right]$$

$$X^5_{\pm 300} = \pm\left[\frac{b_4}{48} + \frac{295}{192}\,b_5 + \frac{119}{48}\,b_6 - \frac{91}{32}\,b_7 - \frac{3167}{1920}\,b_4^2 + \frac{13259}{2560}\,b_4b_5\right]$$

$$X^3_{\pm 310} = \pm\left[\frac{b_4}{3} - \frac{5}{12}\,b_5\right]$$

$$X^5_{\pm 310} = \left[\frac{b_4}{4} + \frac{55}{16}\,b_5 + \frac{3}{4}\,b_6 - \frac{21}{8}\,b_7 + \frac{79}{320}\,b_4^2 + \frac{8511}{1280}\,b_4b_5\right]$$

$$X^5_{\pm 320} = \pm\left[\frac{b_4}{12} + \frac{55}{48}\,b_5 + \frac{b_6}{4} - \frac{7}{8}\,b_7 + \frac{191}{160}\,b_4^2 + \frac{2379}{640}\,b_4b_5\right]$$

$$X^5_{\pm 330} = \left[\frac{39}{80}\,b_4^2 + \frac{171}{320}\,b_4b_5\right]$$

$$X^3_{\pm 301} = \frac{\pm 1}{\rho^2}\left[\left(\frac{\rho^2}{9} + \frac{\rho}{2} + \frac{2}{3}\right) - \frac{91}{96}\,b_4\rho^2\right]$$

TABLE II (continued)

$$X^5_{\pm 301} = \frac{1}{\rho^4}\left[\left(\frac{7}{24}\rho^4 + \frac{3}{4}\rho^3 - \frac{11}{8}\rho^2 - \frac{15}{4}\rho + \frac{15}{4}\right) + b_4\rho^2\left(\frac{2729}{1280}\rho^2 + \frac{3117}{1280}\rho - \frac{285}{64}\right) + b_5\rho^3\left(\frac{637}{640}\rho + \frac{2361}{640}\right) + \rho^4\left(\frac{1107}{256}b_4^2 - \frac{261}{64}b_6\right)\right]$$

$$X^5_{\pm 311} = \frac{\pm 1}{\rho^4}\left[\left(\frac{7}{36}\rho^4 + \frac{\rho^3}{2} - \frac{11}{12}\rho^2 - \frac{5}{2}\rho + \frac{5}{2}\right) + b_4\rho^2\left(\frac{1237}{960}\rho^2 + \frac{1927}{320}\rho - \frac{95}{16}\right) + b_5\rho^3\left(-\frac{83}{160}\rho + \frac{357}{120}\right) - b_6\rho^4\left(\frac{107}{32}\right) + \frac{1585}{256}b_4^2\rho^4\right]$$

$$X^5_{\pm 321} = \frac{1}{\rho^2}\left[b_4\left(\frac{73}{320}\rho^2 + \frac{789}{320}\rho - \frac{21}{16}\right) + b_5\rho\left(\frac{-51}{160}\rho + \frac{147}{160}\right) - \frac{3}{4}b_6\rho^2 + \frac{111}{64}b_4^2\rho^2\right]$$

$$X^5_{\pm 331} = \pm\left[-\frac{5}{64}b_4^2\right]$$

$$X^3_{\pm 302} = \frac{1}{\rho}\left[-\left(\frac{\rho}{4} + \frac{3}{4}\right)\right]$$

$$X^5_{\pm 302} = \frac{\pm 1}{\rho^3}\left[\left(-\frac{137}{192}\rho^3 + \frac{135}{384}\rho^2 + \frac{223}{32}\rho - \frac{803}{96}\right) - b_4\rho^2\left(-\frac{15077}{7680}\rho - \frac{3519}{512}\right) - \frac{2689}{960}b_5\rho^3\right]$$

$$X^5_{\pm 312} = \frac{1}{\rho^3}\left[\left(-\frac{21}{32}\rho^3 - \frac{5}{64}\rho^2 + \frac{87}{16}\rho - \frac{71}{16}\right) - b_4\rho^2\left(\frac{507}{320}\rho - \frac{291}{64}\right) - \frac{183}{80}b_5\rho^3\right]$$

$$X^5_{\pm 322} = \frac{\pm 1}{\rho}\left[-b_4\left(\frac{333}{640}\rho + \frac{27}{128}\right) - \frac{51}{80}b_5\rho\right]$$

$$X^3_{\pm 303} = \pm\left[\frac{1}{6}\right]$$

$$X^5_{\pm 303} = \frac{1}{\rho^2}\left[\left(\frac{33}{128}\rho^2 - \frac{161}{64}\rho + \frac{913}{128}\right) - \frac{289}{256}b_4\rho^2\right]$$

TABLE II (continued)

$$X^5_{\pm 323} = [-\frac{7}{64} b_4]$$

$$X^5_{\pm 304} = \pm[1]$$

$$X^5_{305} = [\frac{-1}{32}]$$

$$X^5_{\pm 315} = \pm[\frac{1}{16}]$$

$$X^2_{\pm 400} = \pm[-\frac{b_4}{8}]$$

$$X^4_{\pm 400} = [\frac{b_4}{2} + \frac{5}{4} b_5 - \frac{3}{4} b_6 + \frac{3}{4} b_4^2]$$

$$X^4_{\pm 410} = \pm[\frac{b_4}{4} + \frac{5}{8} b_5 - \frac{3}{8} b_6 + \frac{11}{16} b_4^2]$$

$$X^4_{\pm 420} = [\frac{b_4^2}{8}]$$

$$X^4_{\pm 401} = \frac{\pm 1}{\rho^3} [-\frac{1}{8}(\frac{\rho^3}{2} + \frac{11}{4}\rho^2 + 6\rho + 5) + b_4\rho^2(\frac{93}{80}\rho + \frac{15}{16}) + \frac{41}{40} b_5\rho^3]$$

$$X^4_{\pm 411} = \frac{1}{\rho} [b_4(\frac{31}{120}\rho + \frac{3}{8}) - \frac{11}{30} b_5\rho]$$

$$X^4_{\pm 402} = \frac{1}{\rho^2}[(\frac{41}{288}\rho^2 + \frac{11}{16}\rho + \frac{91}{96}) - \frac{2}{3} b_4\rho^2]$$

$$X^4_{\pm 412} = \pm[-\frac{b_4}{4}]$$

$$X^4_{\pm 403} = \frac{\pm 1}{\rho}[-(\frac{4\rho+12}{32})]$$

$$X^4_{\pm 404} = [\frac{1}{24}]$$

$$X^3_{\pm 500} = \pm[-\frac{b_5}{10} + \frac{2b_4}{5}]$$

$$X^5_{\pm 500} = [-\frac{11}{4} b_4 - \frac{9}{16} b_5 + \frac{9}{4} b_6 - \frac{7}{8} b_7 - \frac{57}{32} b_4^2 + \frac{263}{128} b_4 b_5]$$

TABLE II (continued)

$$X^5_{\pm 520} = \left[-\frac{b_4^2}{24} + \frac{35}{96} b_4 b_5\right]$$

$$X^3_{\pm 501} = \left[-\frac{b_4}{8}\right]$$

$$X^5_{\pm 505} = \pm\left[\frac{1}{120}\right]$$

$$X^5_{\pm 501} = \frac{\pm 1}{\rho^4}\left[\left(\frac{\rho^4}{25} + \frac{\rho^3}{4} + \frac{7}{10}\rho^2 + \rho + \frac{3}{5}\right) + b_4\rho^2\left(\frac{407}{2880}\rho^2 - \frac{389}{320}\rho - \frac{293}{240}\right)\right.$$
$$\left. + b_5\rho^3\left(\frac{1073}{480}\rho + \frac{159}{160}\right) - \frac{269}{240} b_6\rho^4 + \frac{1507}{960} b_4^2\rho^4\right]$$

$$X^5_{\pm 511} = \frac{1}{\rho^2}\left[b_4\left(\frac{107}{288}\rho^2 - \frac{\rho}{32} - \frac{17}{24}\right) + b_5\rho\left(\frac{25}{48}\rho + \frac{5}{16}\right) - \frac{b_6\rho^2}{3} + \frac{221}{192} b_4^2\rho^2\right]$$

$$X^5_{\pm 521} = \pm\left[\frac{3}{32} b_4^2\right]$$

$$X^5_{\pm 502} = \frac{1}{\rho^3}\left[\left(-\frac{13}{144}\rho^3 - \frac{53}{96}\rho^2 - \frac{31}{24}\rho - \frac{9}{8}\right) - b_4\rho^2\left(-\frac{481}{640}\rho - \frac{963}{640}\right)\right.$$
$$\left. - \frac{11}{16} b_5\rho^3\right]$$

$$X^5_{\pm 512} = \frac{\pm 1}{\rho}\left[b_4\left(\frac{297}{960}\rho + \frac{137}{320}\right) - \frac{5}{24} b_5\rho\right]$$

$$X^5_{\pm 503} = \frac{\pm 1}{\rho^2}\left[\left(\frac{25}{288}\rho^2 + \frac{7}{16}\rho + \frac{57}{96}\right) - \frac{47}{192} b_4\rho^2\right]$$

$$X^5_{\pm 513} = \left[-\frac{11}{96} b_4\right]$$

$$X^4_{\pm 600} = \pm\left[-\frac{b_6}{12} + \frac{5}{12} b_5 - \frac{5}{6} b_4 + \frac{7}{48} b_4^2\right]$$

$$X^4_{\pm 610} = \left[\frac{b_4^2}{16}\right]$$

$$X^4_{\pm 601} = \frac{1}{\rho}\left[b_4\left(\frac{69}{160}\rho + \frac{3}{32}\right) - \frac{b_5\rho}{10}\right]$$

$$X^4_{\pm 602} = \pm\left[-\frac{b_4}{16}\right]$$

TABLE II (continued)

$$X^5_{\pm 710} = \left[-\frac{29}{120} b_4^2 + \frac{49}{480} b_4 b_5\right]$$

$$X^5_{\pm 701} = \frac{1}{\rho^2}\left[-b_4\left(\frac{341}{360}\rho^2 + \frac{29}{80}\rho + \frac{1}{12}\right) + b_5\rho\left(\frac{53}{120}\rho + \frac{3}{40}\right) - \frac{b_6\rho^2}{12} + b_4^2\rho^2\left(\frac{2149}{384\times 28}\right)\right]$$

$$X^5_{\pm 711} = \pm\left[\frac{105}{256\times 7} b_4^2\right]$$

$$X^5_{\pm 702} = \frac{\pm 1}{\rho}\left[b_4\left(\frac{37}{160}\rho + \frac{3}{32}\right) - \frac{b_5\rho}{20}\right]$$

$$X^5_{\pm 703} = \left[-\frac{b_4}{48}\right]$$

$$X^4_{\pm 800} = \left[\frac{b_4^2}{128}\right]$$

$$X^5_{\pm 900} = \left[-\frac{b_4^2}{20} + \frac{b_4 b_5}{80}\right]$$

$$X^5_{\pm 901} = \pm\left[\frac{b_4^2}{128}\right]$$

$$X^3_{\pm 121} = \frac{b_4}{4}$$

$$X^5_{\pm 132} = \frac{\pm 1}{\rho}\left[b_4\left(-\frac{541}{768}\rho + \frac{3}{256}\right) - b_5\rho\left(\frac{95}{96}\right)\right]$$

$$X^2_{\pm 201} = \frac{\pm 1}{\rho}\left[-\frac{(\rho+3)}{4}\right]$$

$$X^3_{\pm 311} = \left[-\frac{7}{16} b_4\right]$$

$$X^5_{\pm 313} = \frac{\pm 1}{\rho^2}\left[\left(\frac{383}{576}\rho^2 - \frac{157}{96}\rho + \frac{119}{64}\right) - \frac{21}{16} b_4\rho^2\right]$$

$$X^5_{\pm 510} = \pm\left[-\frac{11}{10} b_4 - \frac{9}{40} b_5 + \frac{9}{10} b_6 - \frac{7}{20} b_7 - \frac{131}{120} b_4^2 + \frac{757}{480} b_4 b_5\right]$$

$$X^5_{\pm 700} = \pm\left[-\frac{b_7}{14} + \frac{3b_6}{7} - \frac{15b_5}{14} + \frac{10b_4}{7} - \frac{347}{560} b_4^2 + \frac{647}{2240} b_4 b_5\right]$$

CHAPTER III

CALCULATION OF FRANCK-CONDON FACTORS FOR N_2, TiO AND Na_2

As discussed in the introduction, the perturbed-Morse-oscillator potential given by Eq. (1.5) is a good approximation for the true internuclear potential. Since the perturbed-Morse wavefunctions described in the previous chapter are suitable for both ground and upper electronic states of an electronic transition, we can use them to calculate arrays of Franck-Condon factors (FCF arrays). In this chapter we present calculations of FCF arrays for various transitions in N_2, TiO, and Na_2,comparing our results for the rotationless case to published results obtained by using Morse and RKR eigenfunctions. In this chapter we consider only the case J=0; we will discuss rotational effects in the next chapter.

We used numerical methods to evaluate the FCF overlap integrals,proceeding in two steps. First we used the basic spectroscopic data ω_e, $\omega_e x_e$, $\omega_e y_e$, $\omega_e z_e$, B_e, α_e, γ_e, δ_e,and μ as input for Huffaker's[6] computer program to calculate the best fitted Morse parameters σ, ρ, τ and perturbation coefficients b_4, b_5, b_6, b_7. These parameters were then used as input for a new computer program which produced the following quantities:

(a) Coefficients X^L_{mjk} for upper and lower electronic states;

(b) A(v,J) and B(v,J) for upper and lower electronic states;

(c) Vibrational wavefunctions $\Psi_{v'}(r)$ and $\Psi_{v''}(r)$ corresponding to upper and lower electronic states respectively;

(d) Normalization of the wavefunctions for lower and upper electronic states;

(e) Orthonormality properties of the wavefunctions;

(f) 20 x 20 FCF arrays;

(g) Sums of columns and rows of the FCF arrays, used to check the sum rule.

All numerical integrations were performed by the trapezoidal rule. The uniform step size for the numerical integration was taken to be .0025Å and values of r ranged from r=0 to $r = r_{max}$, where r_{max} is different for different electronic transitions. We used double precision in our calculations, providing accuracy up to 18 significant digits.

Accuracy of the Calculation

As a check of the FCF computational procedure, we first tested the orthonormality properties of the wavefunctions. For each state of each molecule, we first obtained Morse eigenfunctions, using Eqs. (2.3) - (2.7), and calculated the 20 x 20 matrix consisting of the overlap integrals of the first twenty vibrational eigenfunctions. Theoretically, these eigenfunctions should be orthonormal, that is

$$\int \Psi_v^* \Psi_n \, d\tau = \delta_{vn} ,$$

and we should obtain a 20 x 20 unit matrix. It was found that the

diagonal elements of the matrices differed from unity by less than 10^{-12}, and that the off-diagonal elements differed from zero by less than 10^{-15}. Thus, the combined error due to our calculation of Morse eigenfunctions and our integration would only introduce errors smaller than 10^{-14} into the calculation of FCF matrices.

Perturbed Morse wavefunctions Ψ_v can be written in matrix form as

$$\begin{pmatrix} \Psi_0 \\ \Psi_1 \\ \cdot \\ \cdot \\ \cdot \\ \Psi_L \end{pmatrix} = \begin{pmatrix} M_{00}, M_{01}, M_{02} \cdots M_{0L} \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ M_{L0} \cdots \cdots M_{LL} \end{pmatrix} \begin{pmatrix} Q_0 \\ Q_1 \\ \cdot \\ \cdot \\ \cdot \\ Q_L \end{pmatrix}$$

where Q_v is a pure Morse eigenfunction and L is equal to the number of bound states. Matrix elements M_{ij} can easily be calculated from Eq. (2.26). Theoretically the matrix T, given by

$$T = M^{+}M = I$$

should be the unit matrix. To check this we performed another calculation for the $A^3\Sigma_u^+$ state of N_2, which has approximately 52 bound vibrational states, and calculated T_{ij} where both i and j range from 1 to 51. We can summarize the value of T_{ij} for different vibrational levels, as

$$i \leq 5,\ j \leq 5,\ |T_{ij}| < 8.8 \times 10^{-6}$$

$$i \leq 10,\ j \leq 10,\ |T_{ij}| < 2.8 \times 10^{-4}$$

$$i \leq 15,\ j \leq 15,\ |T_{ij}| < 2.3 \times 10^{-3}$$

$$i \leq 20,\ j \leq 20,\ |T_{ij}| < 9.9 \times 10^{-3}$$

$$i \leq 25,\ j \leq 25,\ |T_{ij}| < 3.02 \times 10^{-2}$$

$$i \leq 30,\ j \leq 30,\ |T_{ij}| < 7.11 \times 10^{-2}$$

$$i \leq 35,\ j \leq 35,\ |T_{ij}| < .1369$$

$$i \leq 40,\ j \leq 40,\ |T_{ij}| < .222$$

$$i \leq 45,\ j \leq 45,\ |T_{ij}| < .3039$$

$$i \leq 50,\ j \leq 50,\ |T_{ij}| < .3129$$

From the above values of T_{ij} we can see that for low vibrational levels ($v \leq 20$) the orthonormality of the PMO wavefunctions is good, but for vibrational levels near to the bound state limit our orthonormality is very poor. This can be explained from the fact that our perturbation expansions are in terms of v/σ so as v approaches σ the convergence of the various power series becomes very poor.

FCF for N_2, TiO and Na_2

We chose to study N_2 and TiO not only because of their great astrophysical interest but also because they are among the few molecules for which very accurate term values are available for several electronic states. The spectroscopic data[15,16,17,18] and perturbed Morse coefficients ρ, σ, τ, b_4, b_5, b_6 and b_7 for several electronic states of N_2, TiO and Na_2 are given in Table III. We chose the following electronic transition of N_2, and TiO for which to calculate FCF arrays:

$B^3\Pi_g - A^3\Sigma_u^+$ (N_2), listed in Table IV

$A^3\Sigma_u^+ - X^1\Sigma_g^+$ (N_2), listed in Table V

$a^1\Pi_g - X^1\Sigma_g^+$ (N_2), listed in Table VI

$C^3\Delta - X^3\Delta$ (TiO), listed in Table VII

$A^3\phi - X^3\Delta$ (TiO), listed in Table VIII

For each transition of N_2 and TiO we compared our results, using the rotationless perturbed Morse oscillator, with RKR results obtained for N_2 by Benesch and Vanderslice[19,20] and for TiO by Collins and Fay.[21] As may be seen from these tables, our results agree very well with those of the RKR analysis. We also made additional calculations for the other six transitions of N_2 and several transitions of CN and NO (which we have not listed here) and compared our FCF values to the RKR values and found excellent agreement between these two methods up to sufficiently high values of v' and v".

Most published FCF calculations have been done by using pure Morse-oscillator eigenfunctions. As described by Nicholls,[22] the parameters a, τ, r_e (in our formalism ρ, σ,τ) are calculated from the following relations:

$$a = 0.243534(\mu_A \omega_e x_e)^{\frac{1}{2}} , \tag{3.2}$$

$$\tau = \omega_e^2/4\omega_e x_e , \tag{3.3}$$

$$\sigma = \frac{\omega_e}{2\omega_e x_e} . \tag{3.4}$$

Demtröder, McClintock, and Zare[17] used the RKR method to compute the FCF arrays for the ($B^1\Pi_u - X^1\Sigma_g^+$) transition in Na_2. We compare FCF values calculated from our PMO method to pure Morse

and RKR values. This is done in Table IX, where it may be seen that our PMO results agree very well with those of the RKR analysis and differ from the results obtained with pure Morse eigenfunctions.

A similar comparison of FCF values for the ($C^3\Pi_u$ - $B^3\Pi_g$) transition in N_2 is made in Table X, where FCF values calculated from RKR and pure Morse potentials are obtained from references 19 and 20. For v'=0, 1, and 2, our results are in very good agreement with RKR results, but for higher values of v' our results differ significantly from RKR. This could be explained as due to the fact that the perturbation parameters for the $C^3\Pi_u$ states in N_2 are large and increasing in magnitude, so that perhaps higher-order perturbation parameters are significant.

In order to illustrate the significance of the various parameters b_n of the perturbed Morse oscillator, we performed an additional calculation for the $X^1\Sigma_g^+$ - $B^1\Pi_u$ transition in Na_2.[17] We calculated FCF arrays for a truncated PMO using the potential V_n given by

$$V_N(R) = V_e[(1 - e^{-au})^2 + \sum_{n=4}^{N} b_n(1 - e^{-au})^n \qquad (3.5)$$

where N ranged from 3 (pure Morse oscillator) to 7 (full perturbed Morse oscillator to order 5/2). Results are listed in Table XI for the (v'=7,8,9 to v''=0,1...5) bands and again compared with previous pure Morse and RKR calculation. The comparison illustrates several important points: First, our N=3 results are much closer to the RKR results than the previous pure Morse results; this shows that our way of choosing the unperturbed Morse oscillator so as to agree

with the actual potential in the neighborhood of $r=r_e$ is more appropriate than the old method by using Eqs. (3.2), (3.3) and (3.4). Second, as N increases from 3 to 7, our FCFs steadily approach the RKR results, showing the relative significance of the various parameters.

TABLE III

Spectroscopic data and perturbed Morse coefficients used in Franck-Condon factor calculations.

Molecule	N_2[a]	N_2[a]	N_2[a]	N_2[a]
State	$X^1\Sigma_g^+$	$A^3\Sigma_u^+$	$B^3\Pi_g$	$C^3\Pi_u$
ω_e (cm^{-1})	2358.027	1460.518	1733.391	2047.178
$\omega_e x_e$ (cm^{-1})	14.1351	13.8313	14.1221	28.4450
$\omega_e y_e$ (cm^{-1})	-1.7510×10^{-2}	5.999×10^{-3}	-5.688×10^{-2}	2.08833
$\omega_e z_e$ (cm^{-1})	1.144×10^{-4}	-1.853×10^{-3}	3.612×10^{-3}	-5.350×10^{-1}
B_e (cm^{-1})	1.9980	1.45455	1.6374	1.82473
α_e (cm^{-1})	1.772×10^{-2}	1.8009×10^{-2}	1.791×10^{-2}	1.8683×10^{-2}
γ_e (cm^{-1})		-8.214×10^{-5}	-7.647×10^{-5}	-2.275×10^{-3}
δ_e (cm^{-1})			7.33×10^{-4}	7.33×10^{-4}
r_e (Å)	1.0977	1.2866	1.2126	1.1487
ρ	2.7447748	3.0714722	2.9303503	2.9651880
σ	78.327835	53.215698	61.642242	63.632156
τ (cm^{-1})	92350.938	38860.148	53426.070	64977.457
b_4	0.40703017×10^{-1}	-0.50519295×10^{-2}	-0.33512115×10^{-2}	-0.37622130
b_5	0.15942525×10^{-1}	-0.27038269×10^{-1}	-0.33950776×10^{-1}	-1.8111362
b_6	-0.42839903×10^{-1}	0.35355348×10^{-1}	-0.66457272×10^{-1}	5.1684713
b_7	0.34381751×10^{-1}	-0.17442126×10^{-1}	0.2228301×10^{-1}	16.915421
μ_A	7.00377	7.00377	7.00377	7.00377

TABLE III (continued)

Molecule	Na_2[b]	Na_2[b]	TiO[c]	TiO[c]
State	$X^1\Sigma_g^+$	$B^1\Pi_u$	$X^3\Delta$	$A^3\phi$
$\omega_e(cm^{-1})$	159.1268	124.0656	1009.0208	867.7799
$\omega_e x_e(cm^{-1})$	0.7262	0.6863	4.4978	3.9422
$\omega_e y_e(cm^{-1})$	-9.154×10^{-4}	-5.441×10^{-3}	-0.0107	
$\omega_e z_e(cm^{-1})$	-5.02×10^{-5}	-1.15×10^{-4}		
$B_e(cm^{-1})$	0.154853	0.125829	0.535412	0.507390
$\alpha_e(cm^{-1})$	8.5637×10^{-4}	8.6754×10^{-4}	0.003011	0.003145
$\gamma_e(cm^{-1})$	$-7.646.10^{-6}$	-1.535×10^{-5}	-0.000011	-0.000010
$\delta_e(cm^{-1})$				
$r_e(\AA)$	3.07745	3.41398	1.6201	1.6642
ρ	1.9470310	2.1329203	2.7665014	2.7666464
σ	135.53203	108.36212	123.11803	111.71835
$\tau(cm^{-1})$	10783.246	6721.9023	62114.570	48472.938
b_4	-0.15785468	-0.13214874	-0.65027237×10^{-1}	-0.1006698×10^{-1}
b_5	-0.15460426	-0.33452040	-0.58225088×10^{-1}	-0.55146657×10^{-1}
b_6	0.59676655×10^{-1}	-0.8904773×10^{-1}	-0.79778314×10^{-1}	0.53219385×10^{-1}
b_7	-0.20388709×10^{-2}	0.29489435×10^{-1}	0.27459331×10^{-1}	-0.36311213×10^{-1}
μ_A	11.49822	11.49822	11.9979	11.9979

TABLE III (continued)

Molecule	TiO[c]	N_2[a]	N_2[a]	N_2[a]
State	$C^3\Delta$	$B'^3\Sigma_u^-$	$a'^1\Sigma_u^-$	$a^1\Pi_g$
$\omega_e(cm^{-1})$	838.2567	1516.883	1530.254	1694.208
$\omega_e x_e(cm^{-1})$	4.7592	12.1810	12.0747	13.9491
$\omega_e y_e(cm^{-1})$	0.0468	4.1858×10^{-2}	4.1292×10^{-2}	7.9346×10^{-3}
$\omega_e z_e(cm^{-1})$		-7.323×10^{-4}	-2.896×10^{-4}	2.911×10^{-4}
$B_e(cm^{-1})$	0.489888	1.47359	1.47988	1.61688
$\alpha_e(cm^{-1})$	0.003062	1.6861×10^{-2}	1.6574×10^{-2}	1.7933×10^{-2}
$\gamma_e(cm^{-1})$	-0.000030	3.619×10^{-5}	2.408×10^{-5}	-2.929×10^{-5}
$\delta_e(cm^{-1})$		-9.464×10^{-7}		
$r_e(\AA)$	1.6937	1.2782	1.2755	1.2203
ρ	2.7806702	2.9629002	2.9299965	2.9369402
σ	110.63786	58.629196	60.224380	60.739182
τ	46366.570	44466.926	46079.109	51452.402
b_4	-0.17135870	0.38914956×10^{-1}	0.3305164×10^{-1}	-0.1494089×10^{-3}
b_5	-0.18016392	0.52458003×10^{-1}	0.4404665×10^{-1}	0.80510192×10^{-2}
b_6	0.71762991	0.3249489×10^{-1}	0.4178801×10^{-1}	0.5741585×10^{-2}
b_7	-0.25137603	0.11556738×10^{-3}	0.1256874×10^{-1}	0.74309856×10^{-2}
μ_A	11.9979	7.00377	7.00377	7.00377

TABLE III (continued)

Molecule	$^{40}Ca_2$ [d]	^{40}Ca [d]
State	$X^1\Sigma_g^+$	$A^1\Sigma_u^+$
$\omega_e(cm^{-1})$	64.928	136.66
$\omega_e x_e(cm^{-1})$	1.0651	0.71656
$\omega_e y_e(cm^{-1})$	0.25902×10^{-2}	-0.37351×10^{-2}
$\omega_e z_e(cm^{-1})$		-0.80088×10^{-4}
$B_e(cm^{-1})$	0.46113×10^{-1}	0.58247×10^{-1}
$\alpha_e(cm^{-1})$	0.70277×10^{-3}	0.31040×10^{-3}
$\gamma_e(cm^{-1})$	-0.73486×10^{-5}	-0.21496×10^{-5}
$\delta_e(cm^{-1})$		-0.96654×10^{-7}
$r_e(\AA)$	4.2774	3.8059
ρ	4.5751905	3.0835543
σ	33.630524	123.37915
$\tau(cm^{-1})$	1091.7085	8430.6328
b_4	-0.689767×10^{-1}	-0.19600677
b_5	-0.1052871×10^{-3}	-0.1148839
b_6	0.3687582×10^{-1}	-0.22426313
b_7	-0.1707783×10^{-2}	-0.39838874
μ_A	19.98129	19.98129

[a] Spectroscopic constants from Ref. (15).

[b] Spectroscopic constants from Ref. (17).

[c] Spectroscopic constants from Ref. (16).

[d] Spectroscopic constants from Ref. (18).

Table IV. A comparison of FCF calculated from RKR and PMO potentials for the $B^3\Pi_g - A^3\Sigma_u^+$ system in N_2. For each set of values of v' and v", the two numbers are FCF's calculated from RKR[a] and PMO potentials respectively.[b]

v' \ v" =	0	1	2	3	4
0	.4011-0	.3309-0	.1661-0	.6692-1	.2384-1
	.4009-0	.3303-0	.1661-0	.6691-1	.2392-1
1	.3976-0	.2907-2	.1595-0	.1973-0	.1306-0
	.3992-0	.2873-2	.1593-0	.1964-0	.1301-0
2	.1617-0	.2744-0	.6877-1	.2208-1	.1246-0
	.1613-0	.2748-0	.6898-1	.2199-1	.1244-0
3	.3423-1	.2757-0	.9557-1	.1516-0	.5122-2
	.3417-1	.2770-0	.9568-1	.1519-0	.5241-2
4	.4063-2	.9739-1	.2976-0	.7468-2	.1509-0
	.4088-2	.9713-1	.2974-0	.7545-2	.1510-0
5	.2680-3	.1640-1	.1690-0	.2425-0	.1046-1
	.2757-3	.1637-1	.1690-0	.2434-0	.1040-1
6	.1338-4	.1408-2	.3929-1	.2311-0	.1564-0
	.9861-5	.1408-2	.3897-1	.2299-0	.1572-0
7	.4460-6	.6177-4	.4318-2	.7188-1	.2657-0
	.1707-6	.6112-4	.4253-2	.7155-1	.2664-0
8	.2788-6	.8721-6	.2221-3	.9946-2	.1118-0
	.2356-8	.1171-5	.2155-3	.9647-2	.1116-0
9	.1086-6	.2812-7	.6736-5	.6234-3	.1917-1
	.3490-9	.1647-7	.4450-5	.5681-3	.1845-1

TABLE IV (continued)

v' \ v'' =	5	6	7	8	9
0	.7992-2	.2570-2	.8211-3	.2605-3	.8249-4
	.8009-2	.2593-2	.8295-3	.2658-3	.8624-4
1	.6578-1	.2833-1	.1133-1	.4274-2	.1566-2
	.6550-1	.2840-1	.1135-1	.4332-2	.1616-2
2	.1431-0	.1006-0	.5608-1	.2724-1	.1213-1
	.1430-0	.1008-0	.5619-1	.2739-1	.1234-1
3	.4236-1	.1073-0	.1120-0	.8058-1	.4750-1
	.4194-1	.1072-0	.1110-0	.7999-1	.4742-1
4	.5125-1	.2223-2	.5492-1	.9428-1	.8989-1
	.5156-1	.2055-2	.5402-1	.9310-1	.8905-1
5	.9517-1	.9428-1	.8782-2	.1409-1	.5993-1
	.9523-1	.9509-1	.9198-2	.1331-1	.5804-1
6	.5839-1	.3521-1	.1041-0	.3932-1	.2021-5
	.5780-1	.3528-1	.1043-0	.4040-1	.1156-4
7	.7415-1	.1057-0	.3002-2	.8127-1	.6737-1
	.7568-1	.1051-0	.3055-2	.8107-1	.6876-1
8	.2695-0	.1991-1	.1278-0	.4815-2	.4441-1
	.2732-0	.2110-1	.1275-0	.4682-2	.4397-1
9	.1564-0	.2493-0	.1676-3	.1198-0	.2937-1
	.1550-0	.2526-0	.3766-3	.1198-0	.2891-1

(a) References (19,20).

(b) Negative digit refers to power of 10, for example, entry .13990-1 is equal to $.1399 \times 10^{-1}$.

TABLE V. A comparison of FCF calculated from RKR and PMO potentials for the ($A^3\Sigma_u^+ - X^1\Sigma_g^+$) system in N_2. For each set of values of v' and v'', the two numbers are FCF's calculated from RKR[a] and PMO potentials respectively.[b]

v'	v'' = 0	1	2	3	4
0	.9777-3	.8180-2	.3230-1	.8019-1	.1408-0
	.9723-3	.8140-2	.3212-1	.8003-1	.1405-0
1	.5214-2	.3235-1	.8754-1	.1313-0	.1106-0
	.5184-2	.3220-1	.8730-1	.1313-0	.1105-0
2	.1482-1	.6638-1	.1142-0	.8242-1	.1089-1
	.1476-1	.6620-1	.1142-0	.8264-1	.1097-1
3	.3008-1	.9377-1	.9019-1	.1458-1	.1590-1
	.2999-1	.9342-1	.9014-1	.1468-1	.1580-1
4	.4863-1	.1004-0	.4117-1	.3107-2	.5954-1
	.4842-1	.1003-0	.4136-1	.3054-2	.5949-1
5	.6722-1	.8565-1	.6276-2	.3331-1	.5285-1
	.6680-1	.8556-1	.6391-2	.3314-1	.5291-1
6	.8175-1	.5756-1	.1661-2	.5481-1	.1567-1
	.8142-1	.5804-1	.1578-2	.5504-1	.1595-1
7	.9145-1	.2935-1	.1851-1	.4713-1	.6088-4
	.9037-1	.2976-1	.1813-1	.4741-1	.4040-4
8	.9457-1	.9065-2	.3852-1	.2280-1	.1446-1
	.9307-1	.9510-2	.3798-1	.2331-1	.1406-1
9	.9180-1	.4141-3	.4839-1	.3831-2	.3413-1
	.9022-1	.5870-3	.4816-1	.4226-2	.3378-1

TABLE V (continued)

	v'' = 5	6	7	8	9
0	.1854-0	.1910-0	.1569-0	.1056-0	.5806-1
	.1853-0	.1906-0	.1569-0	.1053-0	.5822-1
1	.3966-1	.6520-5	.3739-1	.1108-0	.1500-0
	.3988-1	.1069-4	.3709-1	.1098-0	.1497-0
2	.1548-1	.7836-1	.8100-1	.2127-1	.4015-2
	.1544-1	.7838-1	.8138-1	.2143-1	.3885-2
3	.7253-1	.4484-1	.5276-5	.4362-1	.8094-1
	.7249-1	.4482-1	.5486-5	.4359-1	.8139-1
4	.4067-1	.4966-3	.4965-1	.5280-1	.2044-2
	.4083-1	.4843-3	.4972-1	.5276-1	.2046-2
5	.7711-3	.3902-1	.4424-1	.4647-4	.4169-1
	.8035-3	.3883-1	.4424-1	.4968-4	.4172-1
6	.1740-1	.4785-1	.1615-2	.3413-1	.3939-1
	.1733-1	.4809-1	.1663-2	.3399-1	.3967-1
7	.4370-1	.1379-1	.1697-1	.4203-1	.2843-3
	.4368-1	.1401-1	.1678-1	.4183-1	.3027-3
8	.3727-1	.6938-3	.4078-1	.7146-2	.2311-1
	.3767-1	.6058-3	.4081-1	.7309-2	.2289-1
9	.1261-1	.1951-1	.2646-1	.4735-2	.3778-1
	.1321-1	.1911-1	.2709-1	.4493-2	.3812-1

(a) References (19,20).

(b) Negative digits refer to power of 10, for example, entry .3966-1 is equal to $.3966 \times 10^{-1}$.

TABLE VI. A comparison of FCF calculated from RKR and PMO potentials for the ($a^1\Pi_g$ - $X^1\Sigma_g^+$) system in N_2. For each set of values of v' and v'', the two numbers are FCF's calculated from RKR[a] and PMO potentials respectively.[b]

v'	v'' = 0	1	2	3	4
0	.4308-1	.1526-0	.2495-0	.2502-0	.1728-0
	.4295-1	.1522-0	.2492-0	.2503-0	.1728-0
1	.1155-0	.1931-0	.7983-1	.5680-3	.9050-1
	.1156-0	.1935-0	.8034-1	.5247-3	.8996-1
2	.1707-0	.9710-1	.3407-2	.1084-0	.8488-1
	.1705-0	.9712-1	.3365-2	.1085-0	.8510-1
3	.1832-0	.1232-1	.7583-1	.6864-1	.4177-2
	.1829-0	.1236-1	.7565-1	.6879-1	.4141-2
4	.1600-0	.6199-2	.9643-1	.4799-3	.7834-1
	.1601-0	.6148-2	.9650-1	.5052-3	.7828-1
5	.1217-0	.4655-1	.4658-1	.3444-1	.5591-1
	.1217-0	.4639-1	.4670-1	.3423-1	.5592-1
6	.8296-1	.8456-1	.4521-2	.7273-1	.2471-2
	.8333-1	.8472-1	.4599-2	.7283-1	.2524-2
7	.5262-1	.9919-1	.5751-2	.5616-1	.1783-1
	.5275-1	.9930-1	.5690-2	.5629-1	.1768-1
8	.3153-1	.9235-1	.3372-1	.1805-1	.5400-1
	.3145-1	.9208-1	.3347-1	.1805-1	.5366-1
9	.1784-1	.7332-1	.6077-1	.1087-3	.5440-1
	.1788-1	.7358-1	.6079-1	.1154-3	.5450-1

TABLE VI (continued)

v'	v'' = 5	6	7	8	9
0	.8679-1	.3306-1	.9684-2	.2210-2	.3933-3
	.8697-1	.3305-1	.9699-2	.2230-2	.4085-3
1	.1882-0	.1755-0	.1014-0	.4104-1	.1201-1
	.1877-0	.1750-0	.1012-0	.4073-1	.1204-1
2	.4928-3	.6907-1	.1681-0	.1612-0	.9090-1
	.5267-3	.6852-1	.1676-0	.1606-0	.9101-1
3	.9685-1	.6357-1	.5541-3	.8533-1	.1668-0
	.9701-1	.6376-1	.5128-3	.8430-1	.1665-0
4	.3555-1	.1909-1	.9785-1	.3279-1	.1244-1
	.3576-1	.1901-1	.9808-1	.3289-1	.1221-1
5	.9399-2	.7899-1	.6290-2	.5127-1	.8354-1
	.9300-2	.7883-1	.6324-2	.5105-1	.8399-1
6	.6401-1	.1323-1	.4320-1	.5269-1	.3557-2
	.6415-1	.1341-1	.4295-1	.5234-1	.3545-2
7	.4583-1	.1418-1	.5590-1	.1899-2	.6886-1
	.4597-1	.1405-1	.5600-1	.1842-2	.6853-1
8	.3650-2	.5550-1	.3734-2	.5251-1	.1475-1
	.3736-2	.5501-1	.3781-2	.5197-1	.1484-1
9	.1001-1	.3844-1	.1759-1	.3658-1	.1433-1
	.9880-1	.3859-1	.1743-1	.3675-1	.1401-1

(a) References (19,20).

(b) Negative digits refer to power of 10, for example, entry .8679-1 is equal to $.8679 \times 10^{-1}$.

TABLE VII. A comparison of FCF calculated from RKR and PMO potentials for the ($C^3\Delta$ - $X^3\Delta$) system in TiO. For each set of values of v' and v'', the two numbers are FCF's calculated from RKR[a] and PMO potentials respectively.

v'	v'' = 0	1	2	3	4
0	.4097-0	.3753-0	.1624-0	.4345-1	.7956-2
	.4097-0	.3753-0	.1624-0	.4345-1	.7952-2
1	.3524-0	.4464-2	.2398-0	.2553-0	.1130-0
	.3523-0	.4447-2	.2401-0	.2552-0	.1130-0
2	.1643-0	.2002-0	.6335-1	.7084-1	.2439-0
	.1642-0	.1999-0	.6357-1	.7113-1	.2439-0
3	.5490-1	.2278-0	.4445-1	.1481-0	.1797-2
	.5490-1	.2275-0	.4406-1	.1487-0	.1867-2
4	.1464-1	.1259-0	.1823-0	.1719-3	.1519-0
	.1469-1	.1258-0	.1813-0	.2227-3	.1530-0
5	.3295-2	.4778-1	.1691-0	.9482-1	.3409-1
	.3346-2	.4789-1	.1684-0	.9343-1	.3516-1
6	.6443-3	.1416-1	.8993-1	.1666-0	.2547-1
	.6768-3	.1437-1	.8993-1	.1648-0	.2413-1
7	.1114-3	.3488-2	.3453-1	.1256-0	.1265-0
	.1260-3	.3662-2	.3495-1	.2148-0	.1233-0
8	.1721-4	.7399-3	.1055-1	.6208-1	.1415-0
	.2243-4	.8347-3	.1103-1	.6246-1	.1390-0
9	.2394-5	.1380-3	.2707-2	.2332-1	.9057-1
	.3974-5	.1782-3	.3035-2	.2423-1	.9020-1

TABLE VII (continued)

	v'' = 5	6	7	8	9
0	.1048-2	.1020-3	.7449-5	.4103-6	.1683-7
	.1043-2	.1001-3	.7122-5	.3835-6	.1784-7
1	.2929-1	.5030-2	.6069-3	.5304-4	.3405-5
	.2927-1	.5001-2	.5934-3	.5014-4	.3092-5
2	.1775-0	.6365-1	.1396-1	.2053-2	.2120-3
	.1774-0	.6359-1	.1386-1	.1999-2	.1978-3
3	.1687-0	.2136-0	.1055-0	.2924-1	.5183-2
	.1691-0	.2136-0	.1054-0	.2899-1	.5018-2
4	.1981-1	.8227-1	.2128-0	.1466-0	.5107-1
	.1956-1	.8310-1	.2132-0	.1465-0	.5055-1
5	.9829-1	.7142-1	.2138-1	.1797-0	.1784-0
	.9937-1	.7106-1	.2215-1	.1809-0	.1785-0
6	.8444-1	.3739-1	.1117-0	.5470-4	.1275-0
	.8673-1	.3812-1	.1117-0	.1278-3	.1299-0
7	.1041-3	.1100-0	.3430-2	.1198-0	.1345-1
	.1393-3	.1131-0	.3621-2	.1208-0	.1233-1
8	.7140-1	.1435-1	.1001-0	.4781-2	.9740-1
	.6751-1	.1654-1	.1034-0	.4680-2	.9967-1
9	.1323-0	.2489-1	.4724-1	.6633-1	.3046-1
	.1275-0	.2154-1	.5217-1	.6899-1	.3081-1

(a) Reference (21).

TABLE VIII. A comparison of FCF calculated from RKR and PMO potentials for the ($A^3\phi$ - $X^3\Delta$) system in TiO. For each set of values of v' and v'', the two numbers are FCF's calculated from RKR[a] and PMO potentials respectively.

v'	v'' = 0	1	2	3	4
0	.7195-0	.2362-0	.3976-1	.4223-2	.3043-3
	.7206-0	.2354-0	.3947-1	.4176-2	.2998-3
1	.2360-0	.3195-0	.3314-0	.9690-1	.1478-1
	.2353-0	.3216-0	.3308-0	.9629-1	.1463-1
2	.3983-1	.3294-0	.1044-0	.3350-0	.1552-0
	.3948-1	.3291-0	.1061-0	.3350-0	.1544-0
3	.4401-2	.9728-1	.3294-0	.1459-1	.2863-0
	.4327-2	.9659-1	.3299-0	.1530-1	.2871-0
4	.3310-3	.1584-1	.1549-0	.2763-0	.1897-2
	.3220-3	.1559-1	.1541-0	.2776-0	.1644-2
5	.1516-4	.1640-2	.3500-1	.2004-0	.2011-0
	.14409-4	.1600-2	.3452-1	.1998-0	.2020-0
6	.2242-6	.1037-3	.4783-2	.6077-1	.2270-0
	.1835-6	.9939-3	.4677-2	.6004-1	.2269-0
7	.7676-8	.2700-5	.4005-3	.1065-1	.9057-1
	.1231-7	.2349-5	.3861-3	.1043-1	.8964-1
8	.6778-8	.9133-8	.1601-4	.1145-2	.1994-1
	.9198-8	.2574-7	.1445-4	.1108-2	.1957-1
9	.9145-9	.4234-7	.1210-7	.6477-4	.2688-2
	.1583-8	.6016-7	.2935-9	.5986-4	.2613-2

TABLE VIII (continued)

	v'' = 5	6	7	8	9
0	.1513-4	.5103-6	.1151-7	.1371-9	.5595-19
	.1470-4	.4550-6	.6036-7	.2937-11	.1051-10
1	.1391-2	.8536-4	.3400-5	.8541-7	.1124-8
	.1373-2	.8313-4	.3070-5	.4808-7	.1799-10
2	.3212-1	.3801-2	.2797-3	.1289-4	.3612-6
	.31809-1	.3755-2	.2732-3	.1178-4	.2138-6
3	.2039-0	.5540-1	.8039-2	.6956-3	.3653-4
	.2031-0	.5490-1	.7949-2	.6811-3	.3375-4
4	.2148-0	.2370-0	.8298-1	.1451-1	.1455-2
	.2161-0	.2364-0	.8228-1	.1435-1	.1427-2
5	.2957-1	.1411-0	.2521-0	.7127-0	.2345-1
	.2861-1	.1427-0	.2518-0	.1118-0	.2321-1
6	.1258-0	.7127-1	.7827-1	.2498-0	.1423-0
	.1278-0	.7002-1	.7968-1	.2500-0	.1413-0
7	.2324-0	.6412-1	.1099-0	.3306-1	.2326-0
	.2329-0	.6573-1	.1087-0	.3409-1	.2334-0
8	.1209-0	.2183-0	.2267-1	.1358-0	.7456-2
	.1199-0	.2195-0	.2371-1	.1351-0	.7971-2
9	.3299-1	.1481-0	.1889-0	.2691-2	.1456-0
	.3243-1	.1471-0	.1906-0	.3058-2	.1454-0

(a) Reference (21).

TABLE IX. A comparison of FCF calculated from Morse, RKR and PMO potentials for the $B^1\Pi_u - X^1\Sigma_g^+$ system in Na_2. For each set of values of v' and v'', the three numbers are FCF's calculated from pure Morse, RKR[a] and PMO potentials respectively.

v' \ v'' =	0	1	2	3	4	5
0	.653-1	.157-1	.207-0	.196-0	.151-0	.999-1
	.655-1	.161-1	.213-0	.200-1	.151-0	.977-1
	.655-1	.161-1	.213-0	.200-1	.151-0	.975-1
1	.197-0	.193-0	.568-1	.381-4	.396-1	.951-1
	.193-0	.192-0	.533-1	.247-3	.452-1	.103-0
	.193-0	.192-0	.553-1	.240-3	.450-1	.102-0
2	.275-0	.389-1	.323-1	.114-0	.758-1	.105-1
	.269-0	.405-1	.319-1	.115-0	.740-1	.832-2
	.269-0	.404-1	.319-1	.115-0	.742-1	.843-2
3	.236-0	.199-1	.132-0	.265-1	.163-1	.799-1
	.235-0	.167-1	.130-0	.268-1	.169-1	.817-1
	.235-0	.167-1	.130-0	.269-1	.169-1	.819-1
4	.139-0	.146-0	.405-1	.418-1	.921-1	.143-1
	.143-0	.136-0	.439-1	.384-1	.915-1	.141-1
	.143-0	.135-0	.438-1	.383-1	.916-1	.141-1
5	.605-1	.201-0	.138-1	.109-0	.191-2	.570-1
	.644-1	.196-0	.962-2	.108-0	.286-2	.545-1
	.644-1	.196-0	.962-2	.108-0	.289-2	.546-1
6	.197-1	.145-0	.129-0	.178-1	.721-1	.506-1
	.222-1	.149-0	.116-0	.224-1	.654-1	.529-1
	.222-1	.148-0	.116-0	.224-1	.651-1	.531-1
7	.501-2	.685-1	.181-0	.312-1	.798-1	.102-1
	.595-2	.741-1	.177-0	.228-1	.828-1	.665-2
	.593-2	.740-1	.176-0	.226-1	.827-1	.653-2
8	.993-3	.229-1	.127-0	.143-0	.588-3	.947-1
	.126-2	.263-1	.133-0	.131-0	.255-2	.892-1
	.124-2	.263-1	.133-0	.130-0	.259-2	.888-1
9	.155-3	.569-2	.570-1	.165-0	.691-1	.351-1
	.209-3	.696-2	.634-1	.165-0	.553-1	.426-1
	.202-3	.692-2	.633-1	.164-0	.546-1	.427-1

(a) Reference (17).

TABLE X. A comparison of FCF calculated from Morse, RKR and PMO potentials for the ($C^3\Pi_u$ - $B^3\Pi_g$) system in N_2. For each set of values of v' and v'', the three numbers are FCF's calculated from pure Morse,[a] RKR[a] and PMO potentials respectively.

v''	v' = 0	1	2	3	4
0	.4884-0	.3487-0	.1161-0	.1306-1	.1450-3
	.4527-0	.3949-0	.1330-0	.2038-1	.8858-3
	.44972-0	.38713-0	.13567-0	.24799-1	.25197-2
1	.3240-0	.4131-1	.3785-0	.2329-0	.4393-1
	.3291-0	.2157-1	.3413-0	.2536-0	.5445-1
	.330266-0	.18446-1	.31634-0	.25104-0	.7296-1
2	.1304-0	.2280-0	.8970-2	.2704-0	.3244-0
	.1462-0	.2033-0	.2384-1	.2117-0	.3364-0
	.14664-0	.20636-0	.3421-1	.15463-0	.2983-0
3	.4064-1	.2067-0	.9143-1	.6135-1	.1664-0
	.5172-1	.1989-0	.6344-1	.8817-1	.1260-0
	.51469-1	.20243-0	.6013-1	.121-0	.404-1
4	.1105-1	.1108-0	.1676-0	.2293-1	.1015-0
	.1588-1	.1097-0	.1605-0	.4806-2	.1075-0
	.158118-1	.1124-0	.1644-0	.163-2	.1585-0
5	.3367-2	.4547-1	.1303-0	.1195-0	.9777-3
	.4540-2	.4663-1	.1393-0	.9423-1	.3920-2
	.4473-2	.4768-1	.144-0	.9054-1	.1565-1
6	.1324-2	.1409-1	.6543-1	.1213-0	.7079-1
	.1224-2	.1686-1	.7913-1	.1291-0	.4239-1
	.1200-2	.1730-1	.8319-1	.1375-0	.2923-1

(a) References (19,20).

TABLE XI. A comparison of FCF calculated from pure Morse, PMO (given by Eq. (2.8) with N=3 to N=7) and RKR potentials for the $B^1\Pi_u$ - $X^1\Sigma_g^+$ system in Na_2. For each set of values of v' and v'', the seven numbers are FCF's calculated from pure Morse, PMO with N=3 to N=7 and RKR[a] respectively.

	v' = 0	1	2	3	4	5
	.5008-2	.6847-1	.1811-0	.3118-1	.7980-1	.1023-1
	.6700-2	.7725-1	.1706-0	.1731-1	.8577-1	.5328-2
	.6139-2	.7496-1	.1745-0	.2139-1	.8240-1	.6877-2
v'=7	.5912-2	.7398-1	.1767-0	.2290-1	.8252-1	.6626-2
	.5934-2	.7406-1	.1764-0	.2264-1	.8265-1	.6520-2
	.5934-2	.7406-1	.1765-0	.2265-1	.8264-1	.6534-2
	.595-2	.741-1	.177-0	.228-1	.828-1	.665-2
	.9932-3	.2291-1	.1276-0	.1435-0	.5884-3	.9474-1
	.1542-2	.2920-1	.1344-0	.1178-0	.5041-2	.8706-1
	.1317-2	.2713-1	.1331-0	.1266-0	.2910-2	.8819-1
v'=8	.1231-2	.2619-1	.1327-0	.1308-0	.2485-2	.8899-1
	.1241-2	.2629-1	.1327-0	.1301-0	.2598-2	.8880-1
	.1242-2	.2629-1	.1327-0	.1301-0	.2591-2	.8881-1
	.126-2	.263-1	.133-0	.131-0	.255-2	.892-1
	.1555-3	.5696-2	.5701-1	.1651-0	.6913-1	.3515-1
	.2907-3	.8463-2	.6856-1	.1590-0	.4278-1	.4906-1
	.2226-3	.7348-2	.6490-1	.1625-0	.5171-1	.4289-1
v'=9	.1992-3	.6859-2	.6311-1	.1646-0	.5540-1	.4235-1
	.2026-3	.6921-2	.63329-1	.1643-0	.5463-1	.4277-1
	.2026-3	.6930-2	.6333-1	.1642-0	.5467-1	.4272-1
	.209-3	.696-2	.634-1	.165-0	.553-1	.426-1

(a) Reference (17).

CHAPTER IV

ROTATIONAL EFFECTS ON FRANCK-CONDON FACTORS

The perturbed Morse wavefunctions given by Eq. (2.26) and Table II include the rotational parameter K as well as the perturbation parameters b_n. In the previous chapter we considered eigenfunctions of a nonrotating PMO obtained by simply substituting J=0 in Eq. (2.26). In this chapter we present FCF including molecular rotation, using the same method of calculation as described in the previous chapter.

Recently Balfour and Whitlock[18] used the RKR method to compute the rotational dependence of FCF array for the $A^1\Sigma_u^+ - X^1\Sigma_g^+$ transition in Ca_2. We calculated the same array, and compared our results with theirs in Tables XII and XIII. We also calculated rotational effects on FCF arrays for CN and NO (which we have not listed here) and found good agreement with RKR results.

There is one disadvantage to our present PMO approach. This method works very well for moderate values of the rotational quantum number J; however, for high values of J such as those encountered in N_2, TiO, and CN (where J can go as high as 100) our present approach does not work very well. This is evidenced by poor orthonormality

properties of the perturbed wavefunctions, as shown in Table XIII. We can understand this difficulty as follows: The rotational energy, which we treat as a perturbation, is roughly equal to $\frac{\tau}{\sigma^2\rho^2} J(J+1)$. For high values of J this term becomes very large, so that the perturbation series fails to converge.

This difficulty could be removed if one could include the major part of the rotational energy in the original Hamiltonian and then treat the remaining part as a perturbation, or if one could include the rotational energy in the PMO model, so that the PMO coefficients ρ, σ, τ and b_4 . . . b_7 would be functions of J. We will pursue this topic in further research.

TABLE XII. A comparison of rotational effect on FCF calculated from RKR and PMO potentials for the $A^1\Sigma_u^+ - X^1\Sigma_g^+$ system in Ca_2. For each set of values of (v',1) and (v",0), the two numbers are FCF's calculated from RKR[a] and PMO potentials respectively.

J"=0

J'	v'	v"=0	1	2	3	4	5
1	0	.0017	.0085	.0228	.0433	.0656	.0847
		.0017	.0085	.0227	.0431	.0652	.0840
	1	.0103	.0386	.0744	.0969	.0945	.0711
		.0103	.0386	.0743	.0969	.0945	.0711
	2	.0323	.0845	.1048	.0760	.0294	.0022
		.0323	.0845	.1048	.0760	.0295	.0023
	3	.0685	.1144	.0730	.0131	.0027	.0295
		.0685	.1143	.0730	.0132	.0026	.0294
	4	.1105	.1008	.0163	.0074	.0455	.0504
		.1104	.1007	.0163	.0073	.0454	.0505
	5	.1441	.0528	.0025	.0503	.0488	.0092
		.1438	.0527	.0025	.0502	.0489	.0094
	6	.1574	.0091	.0394	.0578	.0077	.0092
		.1569	.0091	.0390	.0578	.0079	.0090
	7	.1476	.0029	.0223	.0192	.0085	.0435
		.1470	.0028	.0717	.0194	.0082	.0434
	8	.1209	.0354	.0603	.0006	.0450	.0295
		.1203	.0345	.0602	.0005	.0443	.0302
	9	.0875	.0812	.0209	.0300	.0444	.0005
		.0871	.0793	.0215	.0288	.0447	.0006

(a) Reference (18).

TABLE XIII. A comparison of rotational effect on FCF calculated from RKR and PMO potentials for the $A^1\Sigma_u^+ - X^1\Sigma_g^+$ system in CA_2. For each set of values of (v',51) and (v",50), the two numbers are FCF's calculated from RKR[a] and PMO potentials respectively.

J' = 51 v' =	J" = 50 v" = 0	1	2
0	.0012	.0065	.0178
	.0012	.0065	.0179
1	.0080	.0313	.0635
	.0080	.0313	.0636
2	.0262	.0734	.0997
	.0262	.0734	.0996
3	.0582	.1077	.0817
	.0581	.1075	.0813
4	.0982	.1054	.0224
	.0980	.1050	.0271
5	.1331	.0653	.0000
	.1332	.0650	.0000
6	.1530	.0183	.0256
	.1520	.0184	.0252
7	.1501	.0001	.0646
	.1500	.00005	.0637
8	.1287	.0216	.0679
	.1275	.0206	.0673
9	.0974	.0653	.0340
	.0965	.0626	.0346

(a) Reference (18).

TABLE XIV.

Orthonormality of the perturbed Morse wavefunctions for the $A^1\Sigma_u^+$ states of Ca_2 for the different values of J.

J	$\int \Psi_0\Psi_1 d\tau$
1	1.9×10^{-8}
50	9.5×10^{-4}
80	1.4×10^{-2}
100	4.5×10^{-2}
120	.10339
140	.178359

CHAPTER V

CONCLUSION

Franck-Condon-factor arrays are very important quantities in spectroscopy, molecular physics and astrophysics. The accuracy with which one can calculate a given Franck-Condon factor depends upon the accuracy of the vibrational wavefunctions. This in turn, depends upon the extent to which the internuclear potential used in the Schrödinger equation truly represents the potential of the molecule and also upon the method used in solving the Schrödinger equation.

Most of the published FCF were calculated from either a Morse potential or an RKR potential. There is no doubt that use of the RKR method will result in reliable values of the FCF, but RKR calculations are very complicated. Since the Morse potential is a good approximation to that of actual molecules for small vibrational levels, and since it has analytic eigenfunctions, it is much more convenient to use. The author of Ref. (23) showed that for most diatomic molecules the differences between FCF values calculated from RKR and pure Morse potentials are not more than 10% for small vibrational transitions.

The PMO potnetial is a good approximation to the true internuclear potential for most diatomic molecules. We believe that FCF

calculated from PMO wavefunctions are nearly as good as FCF calculated by using RKR analysis for low-lying states. In Tables III-VIII we compared FCF calculated from PMO and RKR potential; the tables show that our PMO values are in good agreement with RKR results.

In contrast to the RKR method, our PMO calculation is very easy, being no more difficult than a Morse calculation. Our method of generating the Morse function by using recursion relation (2.7) is simpler and more efficient in numberical calculations than the old method using confluent hypergeometric functions.

PMO calculations are very accurate and give much better results than the pure Morse method for moderate values of v. But it is less accurate for the electronic states for which PMO coefficients b_n's are large and increasing with n. It fails to produce the correct results for the higher vibrational levels (near the bound limit) because the perturbation expansion converges poorly for these levels, actually diverging at the dissociation limit.

APPENDIX A

PERTURBATION FORMALISM

For a perturbation $H' = \lambda V$, the approximate eigenfunctions correct to fifth order in the parameter λ are given by

$$\Psi_v = \psi_v^0 + \lambda \sum_{k\neq v} a_{vk}\, \psi_k^0 + \lambda^2 \sum_{k\neq v} b_{vk}\, \psi_k^0 + \lambda^3 \sum_{k\neq v} C_{vk}\, \psi_k^0$$

$$+ \lambda^4 \sum_{k\neq v} d_{vk}\, \psi_k^0 + \lambda^5 \sum_{k\neq v} e_{vk}\, \psi_k^0 \,, \tag{A1}$$

where the coefficients a_{vk}, b_{vk}, c_{vk}, and d_{vk} are given by

$$a_{vk} = \frac{H_{vk}}{E_v - E_k} \qquad k \neq v \,, \tag{A2}$$

$$b_{vk} = \frac{1}{E_v - E_k}\left[\sum_{n\neq v} a_{nv}\, H_{kn} - a_{vk}\, H_{vv}\right] , \tag{A3}$$

$$c_{vk} = \frac{1}{E_v - E_k}\left[\sum_n \sum_m \left(\frac{H_{kn} H_{nm} a_{mv}}{E_v - E_n}\right) + \frac{a_{vk} H_{vv}^2}{(E_v - E_k)}\right.$$

$$\left. - H_{vv} \sum_n \left\{\frac{a_{vn} H_{kn}}{E_v - E_n} + \frac{H_{kn} a_{nv}}{E_v - E_k}\right\} - \sum_n a_{vk}\, a_{vn} H_{nv}\right], \tag{A4}$$

$$d_{vk} = \frac{1}{E_v - E_k}\left[\sum_n \sum_m \sum_\ell \frac{H_{km}\, H_{mn}\, H_{n\ell}\, a_{\ell v}}{(E_v - E_m)(E_v - E_n)}\right.$$

$$- \sum_n \sum_m H_{vv} H_{km} H_{mn} a_{nv} \left\{\frac{1}{(E_v - E_k)(E_v - E_m)} + \frac{1}{(E_v - E_m)^2} + \frac{1}{(E_v - E_m)(E_v - E_n)}\right\}$$

$$\left. - \sum_n \sum_m H_{vn} a_{nv} H_{km} a_{mv} \left\{\frac{1}{(E_v - E_k)} + \frac{1}{(E_v - E_m)}\right\}\right.$$

$$- \sum_n \sum_m a_{vk}\, a_{mv}\, a_{nv}\, H_{mn}$$

$$+ \sum_m H_{vv}^2\, a_{mv}\, H_{km} \left\{ \frac{1}{(E_v - E_k)^2} + \frac{1}{(E_v - E_k)(E_v - E_m)} + \frac{1}{(E_v - E_m)^2} \right\}$$

$$+ \sum_m 2H_{vv}\, a_{kv}\, a_{mv}\, H_{mv} \left\{ \frac{1}{E_v - E_k} \right\} + \sum_m H_{vv}\, a_{kv}\, a_{vm}\, a_{vm}$$

$$- \frac{H_{vv}^3\, a_{kv}}{(E_v - E_k)^2} \Bigg] , \tag{A5}$$

where the matrix elements H_{nm} are defined by

$$H_{nm} = \int \psi_m^0\, H'\, \psi_n^0\, dx \ . \tag{A6}$$

The general expression for the fifth order perturbation is very complicated. Since the only fifth-order perturbation we require is the lowest-order term of A^5, and since $H_{vv} = 0$ for this case, we can use the following abbreviated form for e_{vk}:

$$e_{vk} = \frac{}{E_v - E_k} \Bigg[\sum_{n \neq v} \sum_{m \neq v} \sum_{\ell \neq v} \sum_{j \neq v} \frac{H_{kn} H_{nm} H_m H_{\ell j} a_{jv}}{(E_v - E_n)(E_v - E_m)(E_v - E_\ell)}$$

$$- \sum_{n \neq v} \sum_{m \neq v} \sum_{\ell \neq v} \frac{H_{vn} H_{nm} H_{m\ell} H_{\ell v} a_{kv}}{(E_v - E_n)(E_v - E_m)(E_v - E_\ell)}$$

$$- \left(\sum_{n \neq v} \frac{|H_{vn}|^2}{E_v - E_n} \right) \sum_{m \neq v} \sum_{\ell \neq v} \frac{H_{km} H_{m\ell} a_{\ell v}}{(E_v - E_m)} \left(\frac{1}{E_v - E_m} + \frac{1}{E_v - E_\ell} + \frac{1}{E_v - E_k} \right)$$

$$+ \left(\sum_{n \neq v} \frac{(H_{vn})^2}{E_v - E_n} \right) \sum_{m \neq v} \frac{(H_{vm})^2}{E_v - E_m} \left(\frac{1}{E_v - E_m} + \frac{1}{E_v - E_k} \right) a_{kv} \Bigg] . \tag{A7}$$

APPENDIX B

EXPANSIONS OF $[\mathrm{EXP}(au)-1]^n$ NEEDED FOR PERTURBATION CALCULATIONS

Here are the basic equations which we used to calculate the coefficients a_{nk}, b_{nk}, c_{nk}, d_{nk}, and e_{nk}. In each equation, terms like $P_{\pm1}\Psi_{v\pm1}$, etc. appear; these stand for $P_{+1}\Psi_{v+1} + P_{-1}\Psi_{v-1}$, etc.

$$[\exp(au)-1]\Psi_v = \left[\frac{2n}{\sigma} + \frac{3n^2+\frac{1}{4}}{\sigma^2} + \frac{4n^3+n}{\sigma^3}\right]\Psi_v$$

$$+ P_{\pm1}\left[1 + \frac{7/4(n\pm\frac{1}{2})}{\sigma} + \frac{79/32(n\pm\frac{1}{2})^2+1/8}{\sigma^2} + \right.$$

$$\left. + \frac{407/128(n\pm\frac{1}{2})^3 + 15/32(n\pm\frac{1}{2})}{\sigma^3}\right] \quad \Psi_{v\pm\frac{1}{2}} \qquad \text{(B1)}$$

$$[\exp(au)-1]^2\Psi_v = \left[\frac{n}{\sigma} + \frac{15/2n^2+7/8}{\sigma^2} + \frac{20n^3 + 29/4n}{\sigma^3}\right]\Psi_v$$

$$+ P_{\pm1}\left[\frac{4(n\pm\frac{1}{2})}{\sigma} + \frac{13(n\pm\frac{1}{2})^2+2}{\sigma^2} + \frac{227/8(n\pm\frac{1}{2})^3+12(n\pm\frac{1}{2})}{\sigma^3}\right]\Psi_{v\pm1}$$

$$+ P_{\pm2}\left[1 + \frac{7/2(n\pm1)}{\sigma} + \frac{8(n\pm1)^2+23/32}{\sigma^2}\right]\Psi_{v\pm2} \; ; \qquad \text{(B2)}$$

$$[\exp(au)-1]^3\Psi_v = \left[\frac{6n^2+1}{\sigma^2} + \frac{38n^3+19n}{\sigma^3}\right]\Psi_v$$

$$+ P_{\pm1}\left[\frac{3/2(n\pm\frac{1}{2})}{\sigma} + \frac{159/8(n\pm\frac{1}{2})^2+9/2}{\sigma^2} + \frac{5241/64(n\pm\frac{1}{2})^3+807/16(n\pm\frac{1}{2})}{\sigma^3}\right]\Psi_{v\pm1}$$

$$+ P_{\pm2}\left[\frac{6(n\pm1)}{\sigma} + \frac{30(n\pm1)+27/4}{\sigma^2} + \frac{183(n\pm1)^3+879/16(n\pm1)}{\sigma^3}\right]\Psi_{v\pm2}$$

$$+ P_{\pm3}\left[1 + \frac{21/4(n\pm3/2)}{\sigma} + \frac{531/32(n\pm3/2)^2+9/4}{\sigma^2}\right]\Psi_{v\pm3} \; ; \qquad \text{(B3)}$$

$$[\exp(au)-1]^4\Psi_v = \left[\frac{3/2n^2+3/8}{\sigma^2} + \frac{69/2n^3+187/8n}{\sigma^3} + \frac{1715/8n^4+4505/16n^2}{\sigma^4}\right]\Psi_v$$

$$+ P_{\pm1}\left[\frac{12(n\pm\frac{1}{2})^2+4}{\sigma^2} + \frac{113(n\pm\frac{1}{2})^3+95(n\pm\frac{1}{2})}{\sigma^3}\right]\Psi_{v\pm1}$$

$$+ P_{\pm2}\left[\frac{2(n\pm1)}{\sigma} + \frac{38(n\pm1)^2+51/4}{\sigma^2}\right]\Psi_{v\pm2}$$

$$+ P_{\pm3}\left[\frac{8(n\pm3/2)}{\sigma} + \frac{54(n\pm3/2)^2+16}{\sigma^2}\right]\Psi_{v\pm3}$$

$$+ P_{\pm4}\left[1 + \frac{7(n\pm2)}{\sigma}\right]\Psi_{v\pm4} \; ; \qquad \text{(B4)}$$

$$[\exp(au)-1]^5\Psi_v = \left[\frac{15n^3+55/4n}{\sigma^3} + \frac{415/2n^4+1405/4n^2}{\sigma^4}\right]\Psi_v$$

$$+ P_{\pm1}\left[\frac{5/2(n\pm\frac{1}{2})^2+5/4}{\sigma^2} + \frac{655/8(n\pm\frac{1}{2})^3+1475/16(n\pm\frac{1}{2})}{\sigma^3}\right]\Psi_{v\pm1}$$

$$+ P_{\pm2}\left[\frac{20(n\pm1)^2 + 10}{\sigma^2}\right]\Psi_{v\pm2}$$

$$+ P_{\pm3}\left[\frac{5/2(n\pm3/2)}{\sigma} + \frac{395/8(n\pm3/2)^2+ 9/4}{\sigma^2}\right]\Psi_{v\pm3}$$

$$+ P_{\pm4}\left[\frac{10(n\pm2)}{\sigma}\right]\Psi_{v\pm4}$$

$$+ P_{\pm5}\left[1 + \frac{35/4(n\pm5/2)}{\sigma}\right]\Psi_{v\pm5} \; ; \qquad \text{(B5)}$$

$$[\exp(au)-1]^6\Psi_v = \left[\frac{5/2n^3+25/8n}{\sigma^3} + \frac{465/4n^4+1005/4n^2}{\sigma^4}\right]\Psi_v$$

$$+ P_{\pm1}\left[\frac{30(n\pm\frac{1}{2})^3+45(n\pm\frac{1}{2})}{\sigma^3}\right]\Psi_{v\pm1} + P_{\pm2}\left[\frac{15/4(n\pm1)^2+15/16}{\sigma^2}\right]\Psi_{v\pm2}$$

$$+ P_{\pm3}\left[\frac{30(n\pm3/2)^2+20}{\sigma^2}\right]\Psi_{v\pm3} + P_{\pm4}\left[\frac{3(n\pm2)}{\sigma}\right]\Psi_{v\pm4}$$

$$+ P_{\pm5}\left[\frac{12(n\pm5/2)}{\sigma}\right]\Psi_{v\pm5} + P_{\pm6}\Psi_{v\pm6} \; ; \qquad \text{(B6)}$$

$$[\exp(au)-1]^7\Psi_v = \left[\frac{35n^4+385/4n^2}{\sigma^4}\right]\Psi_v + P_{\pm1}\left[\frac{35/8(n\pm\frac{1}{2})^3+35/4(n\pm\frac{1}{2})}{\sigma^3}\right]\Psi_{v\pm1}$$

$$+ P_{\pm2}\left[\frac{105(n\pm1)^3+875/8(n\pm1)}{\sigma^3}\right]\Psi_{v\pm2}$$

$$+ P_{\pm 3}\left[\frac{21/4(n\pm 3/2)^2+21/4}{\sigma^2}\right]\Psi_{v\pm 3} + P_{\pm 4}\left[\frac{42(n\pm 2)^2+35}{\sigma^2}\right]\Psi_{v\pm 4}$$

$$+ P_{\pm 5}\left[\frac{7/2(n\pm 5/2)}{\sigma}\right]\Psi_{v\pm 5} + P_{\pm 6}\left[\frac{14(n\pm 3)}{\sigma}\right]\Psi_{v\pm 6}$$

$$+ P_{\pm 7}\Psi_{v\pm 7} \cdot \qquad \text{(B7)}$$

Here $P_{\pm m}$ is given by

$$P_{\pm m} = \left[\frac{(n\pm\tfrac{1}{2})(n\pm 3/2) \ . \ . \ . \ (n+m\mp\tfrac{1}{2})}{2^{|m|}\ \sigma}\right]^{\frac{1}{2}} , \qquad \text{(B8)}$$

and terms for both $\pm m$ are to be included.

REFERENCES

(1) M. Born and R. Oppenheimer, Ann. Physik 84, 457 (1927).

(2) J. L. Dunham, Phys. Rev. 41, 721 (1932).

(3) R. Rydberg, Z. Phys. 73, 376 (1931); O. Klien, Z. Phys. 76, 226 (1932); J. T. Vanderslice et al, J. Mol. Spect. 3, 17 (1959).

(4) P. M. Morse, Phys. Rev. 34, 57 (1929).

(5) J. N. Huffaker and P. H. Dwivedi, J. Math. Phys. 16, 862 (1975).

(6) J. N. Huffaker, J. Chem. Phys. 64, No. 8, 3175 (1976).

(7) J. N. Huffaker, J. Chem. Phys. 64, No. 15, 4564 (1976).

(8) G. Herzberg, Spectra of Diatomic Molecules (Van Nostrand, New York, 1950), 2nd ed.

(9) D. R. Bates, Proc. Roy. Soc. A196, 217 (1949).

(10) C. L. Pekeris, Phys. Rev. 45, 98 (1934).

(11) A. G. Gayden, The Spectroscopy of Flames (Chapman and Hall), 1958.

(12) R. C. M. Learner and A. G. Gayden, Nature 183, 242 (1959).

(13) R. C. M. Learner, Proc. Roy. Soc. (London) A269, 311 (1962).

(14) L. Schiff, Quantum Mechanics (McGraw-Hill, New York, 1968), 3rd ed.

(15) W. Benesch, J. T. Vanderslice, S. G. Tilford and P. G. Wilkinson, Ap. J. 142, 1227 (1965).

(16) J. G. Phillips, Ap. J. Suppl. 26, 313 (1973).

(17) W. Demtröder, M. McClintocke and R. N. Zare, J. Chem. Phys. 51, 5495 (1969).

(18) W. J. Balfour and R. E. Whitlock, Can. J. Phys. 53, 472 (1975).

(19) W. Benesch, J. T. Vanderslice, S. G. Tilford and P. G. Wilkinson, Ap. J. 143, 236 (1966).

(20) W. Benesch, J. T. Vanderslice, S. G. Tilford and P. G. Wilkinson, Ap. J. 144, 408 (1966).

(21) J. G. Collins and T. D. Fay, J.Q.S.R.T. 14, 1259 (1974).

(22) R. W. Nichols, J. N.B.S. 65A, 451 (1961).

(23) L. A. Kuznetsova et al, Sov. Phys. Usp. 17, No. 3, 405 (1974).