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THE INFLUENCE OF THE POTENTIAL FUNCTION ON VIBRATION—ROTATION WAVEFUNCTIONS AND MATRIX ELEMENTS OF DIATOMIC MOLECULES*

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ABSTRACT

The influence of the form of the internuclear potential function on the resulting $^1\Sigma$-state diatomic vibrational wavefunctions is discussed with specific reference to the Morse, Lennard-Jones, and Dunham potentials for HCl. In an investigation of the effects on the corresponding matrix elements, the recent iterative methods for the derivation of analytic matrix elements for the Dunham oscillator are reviewed and extended. The resulting vibrational matrix elements are then computed for HCl and compared with the corresponding numerical results for the Dunham, Morse and R.K.R. potentials. Explicit rotational corrections to the various Dunham vibrational elements are derived for the first few vibrational levels, and applied in the final section to a detailed analysis of the experimental spectral intensity data for the hydrogen halides. The corresponding dipole-moment functions are obtained and their systematic trends discussed.

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I. INTRODUCTION

Our present experimental knowledge of diatomic molecules is quite sophisticated in both its scope and its precision. For instance, numerous unstable radicals [1] and exotic species known only to spectroscopists have remarkably well-determined molecular parameters [2], while recent microwave measurements on the hydrogen halides have led to the determination of the equilibrium internuclear separation with uncertainties of the order of nuclear dimensions [3]. On the theoretical side, ab initio calculations are now possible which, for smaller molecules, notably hydrogen [4—6], permit calculation of dissociation energies, equilibrium internuclear separations, etc., to an accuracy [7] of one part in 10^5. Furthermore, extremely small effects such as differences in the potential energy within the Born—Oppenheimer, adiabatic and non-adiabatic frameworks, relativistic corrections etc., [4—6], can be computed with considerable accuracy and enable a direct comparison between theory and experiment. However, despite these spectacular successes, further work is necessary especially in the area of spectral line intensities, where sophisticated techniques have recently improved the accuracy of the experimental data available [8—10].

In the present paper we are concerned primarily with the influence of the internuclear potential on the calculation of accurate matrix elements necessary for analysis of vibration—rotation (or pure rotation) line intensities. After a brief discussion of some of the more widely used potentials and associated wavefunctions, we derive matrix elements appropriate to a generalized (Dunham) potential. These are the most accurate analytic results to date and are computed in detail for HCl to enable comparison with the numerical results of previous workers [10, 11], and to illustrate the accuracy attained. Finally, we indicate how these matrix elements may be used to make vibration—rotation corrections to molecular parameters, and to deduce the dipole-moment function from experimental spectral intensities. In the latter regard, we analyze the available experimental data for the hydrogen halides and calculate the corresponding dipole-moment functions.

II. POTENTIALS AND WAVEFUNCTIONS

A. Potential energy functions

The prototype of all potential functions for bound states of diatomic molecules is the harmonic oscillator potential

$$V(x)/\mathrm{hc} = \frac{k_e R_e^2}{2} x^2 = a_0 x^2 \tag{1}$$

where x is the reduced displacement from equilibrium, $x = (R - R_e)/R_e$ and a_0 is related to the curvature of the potential at the minimum. In terms of the standard spectroscopic vibrational and rotational constants [2] (in units of cm^{-1}), $a_0 = \omega_e^2/4B_e$. Although this potential implies an infinite dissociation energy, the simplicity of the resulting wavefunctions and matrix elements has led to its widespread adoption for approximate theoretical calculations. However, for more refined work, a more flexible potential is obviously required.

Numerous alternative potentials have been proposed, differing both in their number of adjustable parameters and in their complexity. In the following, we discuss briefly the three most commonly used, namely the Dunham [12], the Morse [13] and the Lennard-Jones [14]. For a more complete discussion of internuclear functions, the reader is referred to the excellent review articles [15] and to two recent books [16].

Dunham, in a systematic generalization of the harmonic oscillator results (including rotational effects), considered a potential of the form

$$V(x)/\mathrm{hc} = a_0 x^2 \,(1 + \sum_{i=1} a_i x^i) + B_e J(J+1)/(1+x)^2 \tag{2}$$

Employing the W.K.B. technique, he obtained the vibration—rotation energy levels

$$E_{vJ} = \sum_{l,j=0} Y_{lj}\,(v+\tfrac{1}{2})^l\,[J(J+1)]^j, \tag{3}$$

where the Y_{lj} are functions of ω_e, B_e and the potential constants, a_i, without explicitly solving for wavefunctions. This theory is used almost exclusively for the analysis of high-resolution frequency spectra from which one can deduce the a_i and thereby extract information about the potential. (If sufficient accuracy is warranted, one can take account of deviations resulting from the breakdown of the Born—Oppenheimer approximation assumed in the Dunham theory while retaining the form of eqn. (3) [17].) Recently, analytic wavefunctions appropriate to the potential in eqn. (2) have been derived [18]; their derivation and use in calculating vibration—rotation matrix elements are discussed in subsequent sections. Since the flexible Dunham potential is obtained directly from experimental frequency data, it can evidently be quite accurate in a limited region around the minimum. When truncated, however, this potential ultimately diverges for large x (positively or negatively, depending on the sign of the coefficient of the highest power term) and wavefunctions deduced from it are hence not valid for describing high vibrational states. It has been pointed out, however, that turning points obtained by inverting Dunham's series are applicable to the dissociation limit [19]. In an attempt to circumvent the drawback of this divergence, many model potentials having the correct asymptotic behaviour have been proposed.

One of the earliest and most widely used model potentials is due to Morse [13]

$$V(x)/\mathrm{hc} = \mathscr{D}_e\,[1 - e^{-ax}]^2 \tag{4}$$

Here, $\mathscr{D}_e$ (cm^{-1}) corresponds to the depth of the potential well (approximately the dissociation energy) and the (vibrational) energy levels are given by

$$E_v \simeq \omega_e\,(v+\tfrac{1}{2}) - \omega_e x_e\,(v+\tfrac{1}{2})^2 \tag{5}$$

where $\omega_e = a/\pi R_e\,(\mathscr{D}_e h/2Mc)^{\frac{1}{2}}$, $\omega_e x_e = \omega_e^2/4\,\mathscr{D}_e$, and M is the reduced mass of the molecule; a is thus related to the anharmonicity parameter $\omega_e x_e$ by the equation

$$a = (\omega_e x_e/B_e)^{\frac{1}{2}}$$

(Equation (5) is also valid for other potential functions, so that the goodness of fit of the measured energy levels does not in itself constitute a proof of the applicability of the Morse potential.)

For the rotationless problem, the Schrödinger equation can be solved exactly for the Morse potential, and the resulting wavefunctions expressed in closed form; these are discussed briefly in the following section. Unfortunately, the inclusion of rotational effects and the calculation of matrix elements both lead to expressions which are intractable for convenient application [20].

In order to facilitate comparison, eqn. (4) can be written in the Dunham form

$$V(x)/\mathrm{hc} = a_0 x^2\,(1 + \sum_{i=1} a_i x^i)$$

where $a_0 = \mathscr{D}_e a^2$, and

$$a_i = \frac{2^{i+2} - 2}{(i+2)!}\, \mathrm{a}^i\,(-1)^i, \quad i = 1, 2, 3 \ldots . \tag{6}$$

For HCl this comparison is presented in Table 1 and the corresponding potential illustrated in Fig. 1. As can be seen, the truncation of the Dunham potential, in contradistinction to the recursion relation (eqn. (6)), does not alter the potential drastically in the vicinity of the minimum; however, for large x ($x \geqslant 1$), this distinction is crucial and accounts for the better representation of the actual potential by the Morse form.

Another popular model potential due to Lennard-Jones [14] can be written

$$V(x)/\mathrm{hc} = \mathscr{D}_e\,[1 - 1/(1 + x)^n]^2 \tag{7}$$

where $n = 6$ in the usual (6—12) formulation. It is interesting to note that for $n = 1$, eqn. (7) is sometimes referred to as the Kratzer potential and was one of the first potentials for which the exact solution of the radial Schrödinger equation was carried out [22]. For $n \neq 1$, however, this is not possible although several approximate schemes have been proposed [23].

Again, to enable direct comparison with the previous potentials, eqn. (7) can be written in the Dunham form where

$$a_0 = n^2 \mathscr{D}_e$$

$$a_i = \frac{2(-1)^i}{n(i+2)!}\left[\frac{(2n+i+1)!}{(2n)!} - \frac{(n+i+1)!}{n!}\right], \quad i = 1, 2, 3 \ldots . \tag{8}$$

This can be simplified for a given value of n and the results for $n = 1$, 3 and

TABLE 1

Potential constants of HCl: $V(x)/\mathrm{hc} = a_0x^2\,(1 + \sum_{i=1} a_ix^i)$

	Dunham[a]	Morse[b]	Lennard-Jones[c] $n = 3$	Lennard-Jones[c] $n = 6$
a_0 (cm^{-1})	211129	209950	338040	1352160
a_1	−2.364257	−2.364257	−4	−7
a_2	3.66290	3.26067	10.6667	30.91667
a_3	−4.7063	−3.3039	−23.333	−107.333
a_4	5.215	2.691	45.111	318.111
a_5	−5.522	−1.847	−80	−840
a_6	8.364	1.100	133	2028

[a] Derived from data in ref. 21.

[b] Calculated assuming $\mathscr{D}_e = 37560\ \mathrm{cm}^{-1}$ and $a = |a_1|$ Dunham. The values of 'a' corresponding to the 'spectroscopic' or 'dissociation energy' bases are 2.23351 or 2.37084 respectively (cf. section III C).

[c] Calculated assuming $\mathscr{D}_e = 37560\ \mathrm{cm}^{-1}$.

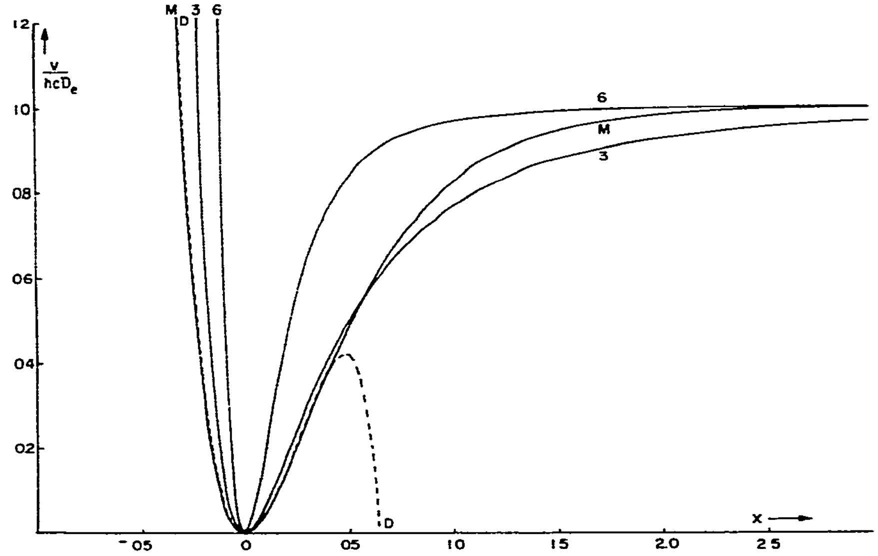

Fig. 1. Potential energy functions for HCl. M = Morse function (based on experimental dissociation energy); 3,6 are Lennard-Jones type functions with the specified exponent, and the broken line is the Dunham function including terms up to a_5.

6 are as follows:

$n = 1 \quad a_0 = \mathscr{D}_e$

$$a_i = (-1)^i\,(i+1)$$

$n = 3 \quad a_0 = 9\,\mathscr{D}_e$

$$a_i = \frac{(-1)^i\,(i+1)\,(i+3)\,(i+4)\,(i^2+17i+90)}{1080}$$

$$n = 6 \quad a_0 = 36\,\mathscr{D}_{\mathrm{e}}$$

$$a_i = [\![(-1)^i (i+1)(i+3)(i+4)(i+5)(i+6)(i+7)(i+20) (i^4 + 42i^3 + 743i^2 + 6342i + 28512)]\!] [3(12!)]^{-1}$$

Specific results are also displayed in Table 1 and Fig. 1 for two values of the exponent n.

Perhaps a brief discussion of the physical basis for the internuclear potential is useful at this point. The Lennard-Jones model originated from calculations on uncharged atoms at large separations. Dispersion forces produce a net attraction with a potential energy proportional to R^{-6}. Corresponding to this induced dipole—induced dipole contribution, there are also induced dipole—induced quadrupole, induced quadrupole—induced quadrupole, etc., terms varying as R^{-8}, R^{-10}, etc., the effects of which combined with more complicated repulsive overlap forces can be conveniently approximated by a repulsive R^{-12} term. For actual molecules, however, the 6—12 form may not provide the best fit to experimental data and indeed many other choices for the exponents along with more drastic modifications have been employed [15, 16]. On the other hand, the form of the Morse potential is qualitatively plausible if one considers the Heitler—London treatment of simple molecular systems (e.g. H_2). Exchange effects give rise to attractive long-range contributions to the potential which vary as e^{-R/a_0} (a_0 being the Bohr radius), while coulombic contributions are shorter-range ($\sim e^{-2R/a_0}$) and repulsive. Although it represents gross over-simplifications of the highly complex (and not completely understood) intramolecular forces, it is somewhat remarkable that a Morse potential is applicable even for some states for which no (substantial) minimum exists. For instance, Mg_2, having a nominal bond order of zero and thus being appropriately described as a van der Waals molecule, has a ground-state potential curve fitted quite well by the Morse function [24]

$$V(x) = 424\,(1 - e^{-4\cdot 10x})^2$$

For Ar_2, a potential function derived from non-spectroscopic data [25] resembles a Lennard-Jones function (with $n = 6$). Meager spectroscopic data [26] available for this molecule ($\mathscr{D}_{\mathrm{e}}$, ω_{e}, $\omega_{\mathrm{e}}x_{\mathrm{e}}$ and estimated B_{e}) indicate both a form of potential, and the presence of only six vibrational levels ($v = 0$—5), consistent with a Morse function (with $a = 6$, 6.0 ± 0.4 levels are predicted). Both a Lennard-Jones potential and detailed consideration of the influence of long-range forces lead to the prediction of 9—10 vibrational levels [27], with the last three very near the dissociation limit and thus difficult to detect experimentally. The true potential function seems to be intermediate between the Lennard-Jones and Morse curves on the attractive side, but more repulsive than either of these on the small separation side (J. F. Ogilvie, unpublished results).

In any case, the Dunham potential (eqn. (2)) is, in principle, capable of representing all analytic potentials to any desired accuracy (over the range in which it converges) by including sufficient terms in the infinite series. In subsequent sections, we show explicitly how the higher terms in the potential (a_i, $i > 0$) affect both the wavefunctions and the corresponding matrix elements. Furthermore, some generalizations about the magnitudes of the a_i have been discovered. For many molecules, Calder and Ruedenberg [28] have shown that $a_1 = -3.22 \pm 0.09$ and $a_2 = 6.49 \pm 0.75$. For hydrides, these coefficients are somewhat smaller. The magnitudes increase systematically for the hydrogen halides from $a_1 = 2.25$ to -2.53 and $a_2 = 3.49$—3.96 for HF through HI [29], while weakly bound molecules (ground-state well depths from 100—1000 cm^{-1}) have markedly larger magnitudes for a_1 (~ -5 to -7) and probably for the higher a_i as well.

Before concluding this section, it should be emphasized that even if several potentials are in good agreement over a specified region and, furthermore, that if they reproduce the vibration—rotation energy levels accurately, they may still lead to significantly different wavefunctions and, consequently, different matrix elements [30]. Precisely for this reason, matrix elements can provide a sensitive gauge for judging the accuracy of wavefunctions. This point will be discussed in more detail in Section III where matrix elements of HCl are computed utilizing different potentials.

B. Wavefunctions

In this section, we outline the derivation of analytic wavefunctions for the Dunham oscillator. Because the procedure is iterative, the results can theoretically be made as accurate as desired; in practice, however, the algebra becomes quite tedious after five iterations for low vibrational states ($v = 1$—5) and sooner for the higher v states.

Here we discuss only vibrational wavefunctions as rotational effects can be incorporated in a straightforward formal way [18]. The method consists of a W.K.B.-like transformation of the radial Schrödinger equation

$$\psi_0(x) = \exp\left(-\frac{1}{2}\int_0^x y(x')\mathrm{d}x'\right) \tag{9}$$

and

$$\psi_v(x) = g_v(x)\psi_0(x) \tag{10}$$

to a pair of coupled, nonlinear differential equations

$$y(x)^2 - \frac{2\mathrm{d}y(x)}{\mathrm{d}x} - \frac{4}{B_e}\left[\mathrm{V}(x) - E_0\right] = 0 \tag{11}$$

and

$$\frac{\mathrm{d}^2 g_v(x)}{\mathrm{d}x^2} - y(x)\frac{\mathrm{d}g_v(x)}{\mathrm{d}x} + \frac{E_v - E_0}{B_e}g_v(x) = 0 \tag{12}$$

where E_v are the (known) Dunham energy levels (eqn. (3)). This set of equations may be solved by the power series

$$y(x) = \sum_{i=0}^{\infty} b_i x^i \tag{13}$$

$$g_v(x) = \sum_{i=0}^{\infty} c_{v_i} x^i \tag{14}$$

in the following manner. First the exact solution for the harmonic oscillator ($V(x)/\mathrm{hc}B_e = \gamma^{-2}x^2$; $E_v/B_e = 2\gamma^{-1}(v + \frac{1}{2})$ where $\gamma \equiv 2B_e/\omega_e$) is obtained; then, in the first iteration, one additional term is added to the potential ($V(x)/\mathrm{hc}B_e = \gamma^{-2}x^2\,(1 + a_1x)$) while terms higher than a_1 appearing in the Dunham energies are neglected; at the same time, the series of eqns. (13) and (14) are truncated according to

$$\begin{aligned} b_i &= 0, \quad i \geqslant 3 \\ c_{v_i} &= 0, \quad i \geqslant v + 2 \end{aligned} \tag{15}$$

Continuing this procedure, for the n^{th} iteration we obtain the wavefunction for the potential

$$V(x)/\mathrm{hc}B_e = \gamma^{-2}x^2\,(1 + a_1x + a_2x^2 + \ \ldots + a_nx^n) \tag{16}$$

expressed in terms of the polynomial series truncated according to

$$\begin{aligned} b_i &= 0, \quad i \geqslant n + 2 \\ c_{v_i} &= 0, \quad i \geqslant n + v + 1 \end{aligned} \tag{17}$$

The results for the first four vibrational wavefunctions correct through five iterations are listed in Table 2. Additional results up to $v = 10$ correct through three iterations have been tabulated elsewhere [18]*.

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*The expression for g_9 is in error in ref. 18; the small corrections to the even powers of x should read

$$\begin{aligned} &\frac{\gamma^6}{16}\left[\frac{43093833}{16}\,a_1^3 - \frac{2683233}{4}\,a_1a_2 + 91539\,a_3\right] \\ &+ \frac{9}{8}\gamma^5\left[-\frac{21023159}{16}\,a_1^3 + \frac{1243809}{4}\,a_1a_2 - 45717\,a_3\right]x^2 \\ &+ \frac{21}{32}\gamma^4\left[\frac{40767533}{16}\,a_1^3 - \frac{2249793}{4}\,a_1a_2 + 91329\,a_3\right]x^4 \\ &+ \frac{7}{4}\gamma^3\left[-\frac{4902361}{16}\,a_1^3 + \frac{243153}{4}\,a_1a_2 - 11415\,a_3\right]x^6 \\ &+ \frac{3}{4}\gamma^2\left[\frac{1167253}{16}\,a_1^3 - \frac{45915}{4}\,a_1a_2 + 2859\,a_3\right]x^8 \\ &+ 9\gamma\left[-\frac{1995}{16}\,a_1^3 - \frac{17}{4}\,a_1a_2 - 5a_3\right]x^{10} \\ &+ \frac{3}{2}\left[-\frac{253}{16}\,a_1^3 + \frac{33}{4}\,a_1a_2 - a_3\right]x^{12} \end{aligned}$$

TABLE 2

UNNORMALIZED $g_v(x)$ AND $y(x)$ FUNCTIONS

$$
\begin{aligned}
y(x) = {} & \left[a_1 + \gamma \left(\frac{5}{4} a_1^3 - 3a_1a_2 + 2a_3 \right) + \frac{\gamma^2}{4} \left(\frac{681}{32} a_1^5 - \frac{339}{4} a_1^3a_2 + \frac{131}{2} a_1^2a_3 \right.\right. \\
& \left.\left. + \frac{125}{2} a_1a_2^2 - 46a_1a_4 - 42a_2a_3 + 24a_5 \right) \right] \\
& + \left[\frac{2}{\gamma} + \frac{1}{2} \left(- \frac{7}{4} a_1^2 + 3a_2 \right) + \frac{\gamma}{4} \left(- \frac{305}{32} a_1^4 + \frac{123}{4} a_1^2a_2 \right.\right. \\
& \left.\left. - \frac{49}{2} a_1a_3 - \frac{21}{2} a_2^2 + 15a_4 \right) \right] x \\
& + \left[\frac{a_1}{\gamma} + \left(\frac{13}{16} a_1^3 - \frac{9}{4} a_1a_2 + 2a_3 \right) + \frac{\gamma}{4} \left(\frac{917}{64} a_1^5 - \frac{483}{8} a_1^3a_2 + \frac{199}{4} a_1^2a_3 \right.\right. \\
& \left.\left. + \frac{193}{4} a_1a_2^2 - \frac{77}{2} a_1a_4 - 36a_2a_3 + 24a_5 \right) \right] x^2 \\
& + \left[\frac{1}{\gamma} \left(- \frac{a_1^2}{4} + a_2 \right) + \frac{1}{2} \left(- \frac{99}{64} a_1^4 + \frac{47}{8} a_1^2a_2 - \frac{11}{2} a_1a_3 - \frac{11}{4} a_2^2 + 5a_4 \right) \right] x^3 \\
& + \left[\frac{1}{\gamma} \left(\frac{a_1^3}{8} - \frac{a_1a_2}{2} + a_3 \right) + \frac{1}{4} \left(\frac{191}{64} a_1^5 - \frac{115}{8} a_1^3a_2 + \frac{55}{4} a_1^2a_3 \right.\right. \\
& \left.\left. + \frac{55}{4} a_1a_2^2 - 13a_1a_4 - 13a_2a_3 + 12a_5 \right) \right] x^4 \\
& + \left[\frac{1}{4\gamma} \left(- \frac{5}{16} a_1^4 + \frac{3}{2} a_1^2a_2 - 2a_1a_3 - a_2^2 + 4a_4 \right) \right] x^5 \\
& + \left[\frac{1}{\gamma} \left(\frac{7}{128} a_1^5 - \frac{5}{16} a_1^3a_2 + \frac{3}{8} a_1^2a_3 + \frac{3}{8} a_1a_2^2 \right.\right. \\
& \left.\left. - \frac{a_1a_4}{2} - \frac{a_2a_3}{2} + a_5 \right) \right] x^6
\end{aligned}
$$

$$
g_1 = \left[a_1\gamma + \gamma^2 \left(\frac{67}{16} a_1^3 - \frac{27}{4} a_1a_2 + 3a_3 \right) + \gamma^3 \left(\frac{8973}{256} a_1^5 - \frac{3507}{32} a_1^3a_2 \right.\right.
$$

TABLE 2 CONTINUED

$$+ \frac{1083}{16} a_1^2 a_3 + \frac{937}{16} a_1 a_2^2 - \frac{269}{8} a_1 a_4 - 30 a_2 a_3 + 12 a_5 \Big) \Bigg]$$

$$+ x + \Bigg[- \frac{a_1}{2} + \frac{\gamma}{2} \left(- \frac{27}{8} a_1^3 + \frac{15}{2} a_1 a_2 - 4 a_3 \right) + \frac{\gamma^2}{2} \Big(- \frac{1851}{64} a_1^5$$

$$+ \frac{429}{4} a_1^3 a_2 - \frac{587}{8} a_1^2 a_3 - \frac{289}{4} a_1 a_2^2 + \frac{89}{2} a_1 a_4 + \frac{81}{2} a_2 a_3 - 18 a_5 \Big) \Bigg] x^2$$

$$+ \left[\frac{1}{4} \left(\frac{5}{4} a_1^2 - a_2 \right) + \frac{\gamma}{4} \left(\frac{561}{64} a_1^4 - \frac{185}{8} a_1^2 a_2 + \frac{89}{6} a_1 a_3 + \frac{17}{4} a_2^2 - 5 a_4 \right) \right] x^3$$

$$+ \Bigg[\frac{1}{2} \left(- \frac{7}{16} a_1^3 + \frac{3}{4} a_1 a_2 - \frac{a_3}{3} \right) + \frac{\gamma}{2} \Big(- \frac{1223}{256} a_1^5 + \frac{519}{32} a_1^3 a_2 - \frac{21}{2} a_1^2 a_3$$

$$- \frac{151}{16} a_1 a_2^2 + \frac{11}{2} a_1 a_4 + 5 a_2 a_3 - 2 a_5 \Big) \Bigg] x^4$$

$$+ \left[\frac{1}{8} \left(\frac{21}{16} a_1^4 - \frac{7}{2} a_1^2 a_2 + \frac{13}{6} a_1 a_3 + a_2^2 - a_4 \right) \right] x^5$$

$$+ \Bigg[\frac{1}{2} \Big(- \frac{33}{128} a_1^5 + \frac{15}{16} a_1^3 a_2 - \frac{2}{3} a_1^2 a_3 - \frac{5}{8} a_1 a_2^2$$

$$+ \frac{17}{40} a_1 a_4 + \frac{23}{60} a_2 a_3 - \frac{a_5}{5} \Big) \Bigg] x^6$$

$$g_2 = \Bigg[- \frac{\gamma}{2} + \frac{\gamma^2}{8} \left(- \frac{13}{4} a_1^2 + 9 a_2 \right) + \frac{\gamma^3}{8} \Big(- \frac{1731}{128} a_1^4$$

$$+ \frac{2415}{16} a_1^2 a_2 - \frac{191}{2} a_1 a_3 - \frac{459}{8} a_2^2 + 45 a_4 \Big) \Bigg]$$

$$+ \Bigg[4 a_1 \gamma + \gamma^2 \left(\frac{151}{4} a_1^3 - 45 a_1 a_2 + 18 a_3 \right) + \frac{\gamma^3}{2} \Big(\frac{18429}{16} a_1^5 - 2916 a_1^3 a_2$$

$$- \frac{3221}{2} a_1^2 a_3 + 1187 a_1 a_2^2 - 623 a_1 a_4 - 552 a_2 a_3 + 192\, a_5 \Big) \Bigg] x$$

$$+ x^2 + \Bigg[- a_1 + \gamma \left(- \frac{21}{4} a_1^3 + 9 a_1 a_2 - \frac{16}{3} a_3 \right) + \frac{\gamma^2}{2} \Big(- \frac{8523}{64} a_1^5$$

TABLE 2 CONTINUED

$$+ \frac{3267}{8} a_1^3 a_2 - \frac{1651}{6} a_1^2 a_3 - \frac{907}{4} a_1 a_2^2 + 145 a_1 a_4 + 132 a_2 a_3 - 60 a_5 \Bigg) \Bigg] x^3$$

$$+ \Bigg[\frac{1}{2} \left(\frac{7}{4} a_1^2 - a_2 \right) + \frac{\gamma}{4} \Bigg(\frac{4549}{128} a_1^4 - \frac{1253}{16} a_1^2 a_2 + \frac{557}{12} a_1 a_3$$

$$+ \frac{85}{8} a_2^2 - \frac{25}{2} a_4 \Bigg) \Bigg] x^4$$

$$+ \Bigg[\left(- \frac{3}{4} a_1^3 + a_1 a_2 - \frac{a_3}{3} \right) + \frac{\gamma}{2} \Bigg(- \frac{2901}{128} a_1^5 + \frac{1053}{16} a_1^3 a_2 - \frac{155}{4} a_1^2 a_3$$

$$- \frac{245}{8} a_1 a_2^2 + \frac{157}{10} a_1 a_4 + \frac{76}{5} a_2 a_3 - \frac{24}{5} a_5 \Bigg) \Bigg] x^5$$

$$+ \Bigg[\frac{1}{8} \left(\frac{165}{32} a_1^4 - \frac{45}{4} a_1^2 a_2 + \frac{17}{3} a_1 a_3 + \frac{5}{2} a_2^2 - 2 a_4 \right) \Bigg] x^6$$

$$+ \Bigg[- \frac{143}{256} a_1^5 + \frac{55}{32} a_1^3 a_2 - \frac{25}{24} a_1^2 a_3 - \frac{15}{16} a_1 a_2^2 + \frac{11}{20} a_1 a_4 + \frac{7}{15} a_2 a_3 - \frac{a_5}{5} \Bigg] x^7$$

$$g_3 = \Bigg[- \frac{7}{2} a_1 \gamma^2 + \frac{\gamma^3}{2} \left(- \frac{4893}{32} a_1^3 + \frac{1041}{8} a_1 a_2 - 41 a_3 \right) + \frac{\gamma^4}{2} \Bigg(- \frac{4276013}{1024} a_1^5$$

$$+ \frac{26495613}{256} a_1^3 a_2 - \frac{124273}{32} a_1^2 a_3 - \frac{157037}{64} a_1 a_2^2 + \frac{4451}{4} a_1 a_4$$

$$+ \frac{7917}{8} a_2 a_3 - 276 a_5 \Bigg) \Bigg]$$

$$+ \Bigg[- \frac{3}{2} \gamma + \frac{9}{16} \gamma^2 \left(- \frac{23}{4} a_1^2 + 11 a_2 \right) + \frac{3\gamma^3}{16} \Bigg(- \frac{5201}{128} a_1^4 + \frac{15669}{16} a_1^2 a_2$$

$$- \frac{1119}{2} a_1 a_3 - \frac{2601}{8} a_2^2 + 225 a_4 \Bigg) \Bigg] x$$

$$+ \Bigg[\frac{39}{4} a_1 \gamma + \frac{3}{2} \gamma^2 \left(\frac{7997}{64} a_1^3 - \frac{1689}{16} a_1 a_2 + 40 a_3 \right) + \frac{3\gamma^2}{2} \Bigg(\frac{6785537}{2048} a_1^5$$

$$- \frac{1628133}{256} a_1^3 a_2 + \frac{103273}{32} a_1^2 a_3 + \frac{245\,209}{128} a_1 a_2^2$$

TABLE 2 CONTINUED

$$- \frac{15317}{16} a_1a_4 - \frac{3429}{4} a_2a_3 + 273a_5\Big)\Big] x^2 + x^3$$

$$+ \Big[- \frac{3}{2} a_1 + \frac{3\gamma}{4} \Big(- \frac{77}{4} a_1^3 + 19a_1a_2 - 13a_3\Big) + \frac{3\gamma^2}{2} \Big(- \frac{415}{2} a_1^5 + \frac{12829}{32} a_1^3a_2$$

$$- \frac{17125}{64} a_1^2a_3 - \frac{1121}{8} a_1a_2^2 + \frac{815}{8} a_1a_4 + \frac{1453}{16} a_2a_3 - 45a_5\Big)\Big] x^4$$

$$+ \Big[\frac{3}{4} \Big(\frac{9}{4} a_1^2 - a_2\Big) + \frac{3\gamma}{8} \Big(75a_1^4 - \frac{477}{4} a_1^2a_2 + \frac{259}{4} a_1a_3 + 13a_2^2 - \frac{29}{2} a_4\Big)\Big] x^5$$

$$+ \Big[\frac{1}{2} \Big(- \frac{55}{16} a_1^3 + \frac{15}{4} a_1a_2 - a_3\Big) + \frac{3\gamma}{2} \Big(- \frac{3397}{128} a_1^5 + \frac{1959}{32} a_1^3a_2 - \frac{1035}{32} a_1^2a_3$$

$$- \frac{89}{4} a_1a_2^2 + \frac{809}{80} a_1a_4 + \frac{54}{5} a_2a_3 - \frac{27}{10} a_5\Big)\Big] x^6$$

$$+ \Big[\frac{3}{8} \Big(\frac{143}{32} a_1^4 - \frac{33}{4} a_1^2a_2 + \frac{7}{2} a_1a_3 + \frac{3}{2} a_2^2 - a_4\Big)\Big] x^7$$

$$+ \Big[\frac{3}{2} \Big(- \frac{273}{256} a_1^5 + \frac{91}{32} a_1^3a_2 - \frac{3}{2} a_1^2a_3 - \frac{21}{16} a_1a_2^2$$

$$+ \frac{27}{40} a_1a_4 + \frac{11}{20} a_2a_3 - \frac{a_5}{5}\Big)\Big] x^8$$

$$g_4 = \Big[\frac{3}{4} \gamma^2 + \frac{\gamma^3}{8} \Big(\frac{173}{4} a_1^2 - 63a_2\Big) + \frac{\gamma^4}{8} \Big(\frac{40403}{256} a_1^4 - \frac{95343}{32} a_1^2a_2$$

$$+ \frac{11621}{8} a_1a_3 + \frac{15291}{16} a_2^2 - \frac{2115}{4} a_4\Big)\Big]$$

$$+ \Big[- 20a_1\gamma^2 + 3\gamma^3 \Big(- \frac{547}{2} a_1^3 + 172a_1a_2 - 50a_3\Big) + \gamma^4 \Big(- \frac{2445197}{64} a_1^5$$

$$+ \frac{93291}{2} a_1^3a_2 - \frac{831239}{48} a_1^2a_3 - \frac{51571}{4} a_1a_2^2 + 5617 a_1a_4$$

$$+ 849a_2a_3 - 1248a_5\Big)\Big] x$$

TABLE 2 CONTINUED

$$\begin{aligned}
&+ \biggl[- 3\gamma + \frac{\gamma^2}{4}\biggl(- \frac{281}{4} a_1^2 + 81a_2\biggr) + \frac{\gamma^3}{4}\biggl(- \frac{53493}{64} a_1^4 + \frac{33867}{8} a_1^2a_2 \\
&- \frac{8221}{4} a_1a_3 - \frac{4545}{4} a_2^2 + \frac{1395}{2} a_4\biggr)\biggr] x^2 \\
&+ \biggl[19a_1\gamma + \gamma^2\biggl(\frac{11061}{16} a_1^3 - \frac{1645}{4} a_1a_2 + 148a_3\biggr) + \frac{\gamma^3}{2}\biggl(\frac{8044187}{128} a_1^5 \\
&- \frac{1394729}{16} a_1^3a_2 + \frac{492913}{8} a_1^2a_3 - \frac{38079}{4} a_1a_4 \\
&+ \frac{154359}{8} a_1a_2^2 - 225a_2a_3 + 2484a_5\biggr)\biggr] x^3 + x^4 \\
&+ \biggl[- 2a_1 + 3\gamma\biggl(- \frac{25}{2} a_1^3 + 6a_1a_2 - 5a_3\biggr) + \frac{\gamma^2}{2}\biggl(- \frac{47045}{16} a_1^5 + \frac{6401}{2} a_1^3a_2 \\
&- \frac{33789}{8} a_1^2a_3 - 525a_1a_2^2 + \frac{2592}{5} a_1a_4 - \frac{1803}{5} a_2a_3 - \frac{1248}{5} a_5\biggr)\biggr] x^5 \\
&+ \biggl[\biggl(\frac{11}{4} a_1^2 - a_2\biggr) + \frac{\gamma}{4}\biggl(\frac{1297}{4} a_1^4 - 343a^2_1a_2 + \frac{502}{3} a_1a_3 + 32a_2^2 - 32a_4\biggr)\biggr] x^6 \\
&+ \biggl[\biggl(- \frac{13}{4} a_1^3 + 3a_1a_2 - \frac{2}{3} a_3\biggr) + \gamma\biggl(- \frac{3983}{32} a_1^5 + \frac{435}{2} a_1^3a_2 - \frac{299}{2} a_1^2a_3 \\
&- \frac{121}{2} a_1a_2^2 + \frac{121}{5} a_1a_4 + \frac{146}{5} a_2a_3 - \frac{29}{5} a_5\biggr)\biggr] x^7 \\
&+ \biggl[\frac{1}{8}\biggl(\frac{455}{16} a_1^4 - \frac{91}{2} a_1^2a_2 + \frac{50}{3} a_1a_3 + 7a_2^2 - 4a_4\biggr)\biggr] x^8 \\
&+ \biggl[- \frac{119}{32} a_1^5 + \frac{35}{4} a_1^3a_2 - \frac{49}{12} a_1^2a_3 - \frac{7}{2} a_1a_2^2 + \frac{8}{5} a_1a_4 \\
&+ \frac{19}{15} a_2a_3 - \frac{2}{5} a_5\biggr] x^9
\end{aligned}$$

The role of the g_v-polynomials in the calculation of analytic matrix elements is developed in detail in the following section. As discussed previously [18], the accuracy of the wavefunctions after three iterations is at least as great as that associated with the standard numerical R.K.R. procedure. The results listed in Table 2 are consequently even more accurate and, indeed reproduce the (experimental) energy levels to the accuracy of the Born—Oppenheimer approximation.

The first five vibrational wavefunctions are plotted for HCl in figures 2—6 along with the harmonic oscillator and Morse wavefunctions. The harmonic oscillator wavefunctions may of course be considered to be special cases of

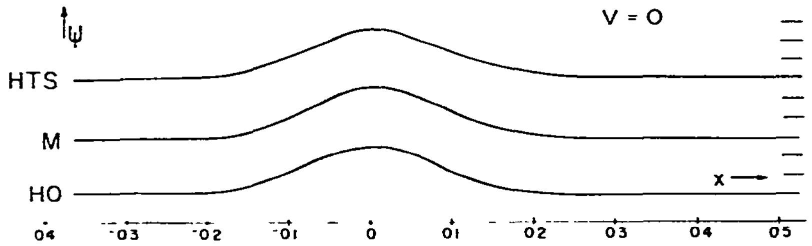

Fig. 2. Normalised vibrational wavefunctions for v = 0. H.O. = harmonic oscillator, M = Morse, and H.T.S. = anharmonic oscillator wavefunctions based on Dunham potential function including terms up to a_5.

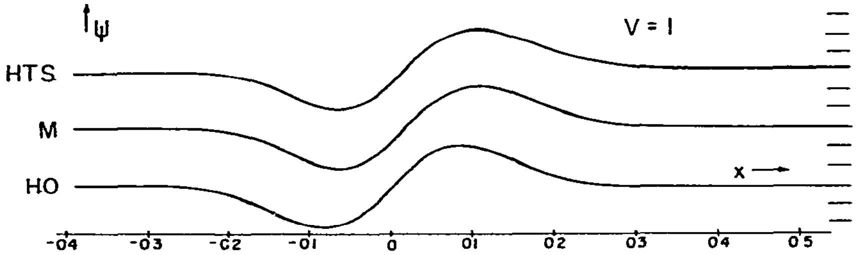

Fig. 3. Normalised vibrational wavefunctions for v = 1. H.O. = harmonic oscillator, M = Morse, and H.T.S. = anharmonic oscillator wavefunction based on Dunham potential function including terms up to a_5.

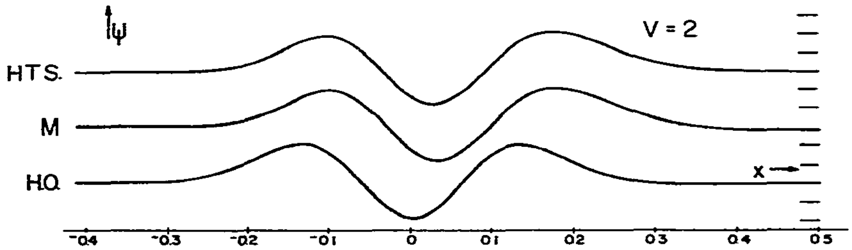

Fig. 4. Normal vibrational wavefunctions for v = 2. H.O. = harmonic oscillator, M = Morse, and H.T.S. = anharmonic oscillator wavefunction based on Dunham potential function including terms up to a_5.

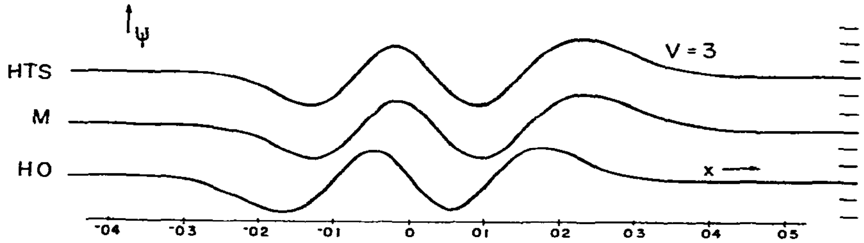

Fig. 5. Normalised vibrational wavefunctions for $v = 3$. H.O. = harmonic oscillator, M = Morse, and H.T.S. = anharmonic oscillator wavefunction based on Dunham potential function including terms up to a_5.

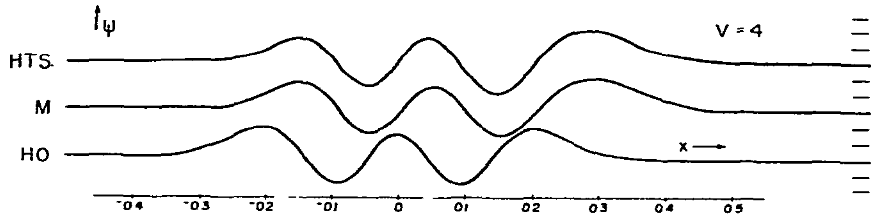

Fig. 6. Normalised vibrational wavefunctions for $v = 4$. H.O. harmonic oscillator, M = Morse, and H.T.S. = anharmonic oscillator wavefunction based on Dunham potential function including terms up to a_5.

the solutions of eqns. (11) and (12) in which $a_i = 0$ for $i > 0$. As mentioned previously, the Morse functions can be expressed in closed form [11]

$$\psi_v(x) = N_v e^{-y/2} y^{(k-2v-1)/2} L_{kv}(y) \tag{18}$$

where

$$y = ke^{-ax},\ k = \frac{\omega_e}{\omega_e x_e} \text{ or } \frac{4\mathscr{D}_e}{\omega_e},$$

$$L_{kv}(y) = \sum_{j=0}^{v} \frac{(-1)^j v!\,\Gamma(k-v)\, y^{v-j}}{(v-j)!\,\Gamma(k-v-j)\, j!},$$

$$N_v = \left[\frac{a(k-2v-1)}{v!\,\Gamma(k-v)}\right]^{\frac{1}{2}} (-1)^v, \tag{19}$$

such that $\int \psi_{v'}(x)\, \psi_v(x) \mathrm{d}x = \delta_{vv'}$.

We note that approximate Morse wavefunctions (and matrix elements) may be obtained from the accurate Dunham results through the use of the recursion relation (eqn. (6)). The effects of the slight differences in wavefunctions on the calculation of matrix elements will be considered in detail in the next section.

III. MATRIX ELEMENTS

A. *Introduction*

For many problems in molecular physics (e.g. vibration—rotation line intensities, Franck—Condon factors, molecular beam studies, rotational dependence of molecular parameters, deviation from Born—Oppenheimer behaviour, electron diffraction studies, etc.), explicit expressions for radial matrix elements of various analytic operators are desirable. If very great accuracy is not required, simple harmonic oscillator wavefunctions or anharmonic (cubic potential) wavefunctions may be used to calculate matrix elements. These, in general, give reasonable results for $\Delta v = 1$ elements; however, they fail noticeably for $\Delta v = 2$ or higher. To determine these overtone matrix elements or if higher accuracy is required, one must employ wavefunctions deduced from a more representative intramolecular potential. Heretofore, one had three main options: firstly to use electronic computers and to calculate required matrix elements numerically [10, 11, 30]; secondly to use the Morse potential (or some similar solvable model potential) and the resulting closed-form Morse wavefunctions to deduce matrix elements [20]; thirdly to use harmonic-oscillator wavefunctions and to treat the corrections introduced by mechanical anharmonicities via perturbation theory [9, 31]. While the first method leads to accurate results, these are of limited applicability since matrix elements must be determined individually for each operator and for each molecular system. Furthermore, matrix elements calculated with Morse wavefunctions prove to be too cumbersome for practical use. Even in a simplified approximate form, these have never gained widespread acceptance. The perturbation approach has been carried out through fourth-order (keeping the a_4 term in the potential) for the fundamental and first three overtone bands [9, 31]. To obtain results of comparable accuracy for other matrix elements, or more accurate expressions for these elements, fifth and/or higher-order perturbation theory with its concomitant complexities is mandatory.

In an attempt to circumvent the above shortcomings, alternative methods have recently been developed whereby matrix elements can be determined in a relatively straightforward manner to the accuracy of the Dunham theory (ultimately to the accuracy of the Born—Oppenheimer approximation). These methods have been described elsewhere [18, 32] so we confine ourselves here merely to a cursory review and a complete listing of the most accurate results obtained to date. In the following, we first consider expectation values, then matrix elements off-diagonal in v but diagonal in J, and finally, the most general case of matrix elements off-diagonal in both v and J.

B. *Expectation values*

Two different approaches have been formulated for the calculation of expectation values within the Dunham framework [18, 32]. Assuming a potential of the form

$$\frac{V(x,J)}{\mathrm{hc}B_e} = \gamma^{-2}x^2\,(1 + a_1x + a_2x^2 + \ldots) + \frac{J(J+1)}{(1+x)^2} \tag{20}$$

$$= \gamma^{-2}x^2\,(1 + a_1x + a_2x^2 + \ldots) + J(J+1)\,(1 - 2x + 3x^2 \ldots)$$

$$\equiv \gamma^{-2}(J)x_J{}^2\,(1 + a_1(J)x_J + a_2(J)x_J{}^2 \ldots)$$

$$+ \text{ constant } (J),$$

where the J-dependent parameters are listed in Table 3, one can use the defining equations for the g_v functions (see eqn. (10)) in order to reduce the problem of finding expectation values to one of calculating ground-state expectation values of powers of x. That is,

$$\langle vJ|\mathcal{O}(x)|vJ\rangle = \frac{\langle 0J|[g_{0J}^{vJ}(x_J)]^2\,\mathcal{O}\,(x_J + \gamma^2\beta[1 - 3\gamma^2\beta(1 + a_1/2)]\,|0J\rangle}{\langle 0J|[g_{0J}^{vJ}(x_J)]^2|0J\rangle} \tag{21}$$

where $\beta = J(J+1)$. The function $\mathcal{O}(x)$ is assumed to be an algebraic operator, and the normalization factor for the g_V function has been explicitly included. The β-dependent terms in the argument of $\mathcal{O}(x)$ arise from the fact that the integral is taken about an equilibrium position of x_J shifted from that of the non-rotating case; i.e. $x_J = x - \gamma^2\beta[1 - 3\gamma^2\beta(1 + a_1/2)]$. The $g_{0J}^{vJ}(x_J)$ functions are identical to $g_v(x)$ except that the J-dependent potential constants listed in Table 3 are used.

Ground-state expectation values have been worked out previously by Herman and Short [33] using a novel perturbation approach. However, as discussed in ref. 18, one can obtain ground-state expectation values of x_J^l in terms of those for x_J^{l-1} and x_J^{l-2} via a recursive technique. Utilizing the identity

$$\langle 0J|x_J^{l-1}\,y(x_J)|\,0J\rangle = (n-1)\langle 0J|x_J^{l-2}|0J\rangle \tag{22}$$

with the accurate expression for $y(x_J)$ (Table 2), one can consistently (with respect to powers of γ) reduce powers of x_J higher than x_J^l. The following expression accurate through a_1^5 (a_1a_4, $a_1^2a_3$, . . ., a_5) is thus obtained

$$\langle 0J|x_J^l|0J\rangle = \Big\{ -\frac{\gamma a_1}{4}(2+l) - \frac{\gamma^2}{8}\Big[(l^2 + 6l + 8)a_3$$

$$+ \left(\frac{2l^2 + 14l + 17}{2}\right)a_1^3 - (2l^2 + 13l + 16)a_1a_2\Big]$$

$$-\frac{\gamma^3}{16}\Big[(l^3 + 12l^2 + 44l + 48)a_5 - \left(\frac{5l^3 + 59l^2 + 206l + 200}{2}\right)a_2a_3$$

$$+ \left(\frac{35l^3 + 425l^2 + 1514l + 1392}{8}\right)a_1a_2^2 - \left(\frac{5l^3 + 61l^2 + 229l + 230}{2}\right)a_1a_4$$

TABLE 3

J-DEPENDENT POTENTIAL CONSTANTS

$$x_J = x - \gamma^2\beta \left[1 - 3\gamma^2\beta \left(1 + \frac{a_1}{2}\right)\right]$$

$$\begin{aligned}\gamma(J) = \gamma \Bigg[1 - \frac{3}{2}\gamma^2\beta \ (1 + a_1) \\ + 3\gamma^4\beta^2 \left(\frac{15}{8} a_1^2 - a_2 + \frac{15}{4} a_1 + \frac{25}{8}\right)\Bigg]\end{aligned}$$

$$\begin{aligned}a_1(J) = a_1 + \gamma^2\beta\left[4 \ (a_2 - 1) - 3a_1 \ (1 + a_1)\right] \\ + \gamma^4\beta^2 \left(\frac{27}{2} a_1^3 - 24a_1a_2 + 10a_3 + 27a_1^2 - 24a_2 + 33a_1 + 32\right)\end{aligned}$$

$$\begin{aligned}a_2(J) = a_2 + \gamma^2\beta \left[5 \ (a_3 + 1) - 3a_2 \ (1 + a_1)\right] \\ + 3\gamma^4\beta^2 \left(\frac{9}{2} a_1^2a_2 - \frac{15}{2} a_1a_3 - 2a_2^2 + 5a_4 + 9a_1a_2 - 10a_3 + 7a_2 - 10\right)\end{aligned}$$

$$\begin{aligned}a_3(J) = a_3 + \gamma^2\beta \left[6 \ (a_4 - 1) - 3a_3 \ (1 + a_1)\right] \\ + 3\gamma^4\beta^2 \left(\frac{9}{2} a_1^2a_3 - 9a_1a_4 - 2a_2a_3 + 7a_5 + 9a_1a_3 - 12a_4 + 7a_3 + 14\right)\end{aligned}$$

$$\begin{aligned}a_4(J) = a_4 + \gamma^2\beta \left[7 \ (a_5 + 1) - 3a_4 \ (1 + a_1)\right] \\ + \gamma^4\beta^2 \left(\frac{27}{2} a_1^2a_4 - \frac{63}{2} a_1a_5 - 6a_2a_4 + 28a_6 + 27a_1a_4 - 42a_5 + 21a_4\right)\end{aligned}$$

$$a_5(J) = a_5 + \gamma^2\beta \left[8 \ (a_6 - 1) - 3a_5 \ (1 + a_1)\right]$$

TABLE 3 CONTINUED

$$+ 3\gamma^4\beta^2 \left(\frac{9}{2} a_1^2 a_5 - 12a_1a_6 - 2a_2a_5 + 12a_7 + 9a_1a_5 - 16a_6 + 7a_5 + 24\right)$$

$$a_n(J) = a_n + \gamma^2\beta \left[(n + 3)(a_{n+1} + (-1)^n) - 3a_n (1 + a_1)\right]$$

$$+ \text{Order } \gamma^4\beta^2$$

TABLE 4

GROUND STATE EXPECTATION VALUES*

$$< 0J \mid x_J^0 \mid 0J > = 1$$

$$< 0J \mid x_J^1 \mid 0J > = -\frac{3}{4} a_1 \gamma - \frac{\gamma^2}{8} \Big[\frac{33}{2} a_1^3 - 31 a_1 a_2 + 15 a_3\Big]$$

$$+ \frac{\gamma^3}{16} \Big[- \frac{12555}{64} a_1^5 + \frac{5451}{8} a_1^3 a_2 - \frac{915}{2} a_1^2 a_3 - \frac{1683}{4} a_1 a_2^2$$

$$+ \frac{525}{2} a_1 a_4 + 235 a_2 a_3 - 105 a_5\Big]$$

$$< 0J \mid x_J^2 \mid 0J > = \frac{\gamma}{2} + \frac{\gamma^2}{4} \Big[\frac{11}{2} a_1^2 - 3 a_2\Big] + \frac{\gamma^3}{16} \Big[\frac{4185}{32} a_1^4$$

$$- \frac{1197}{4} a_1^2 a_2 + \frac{325}{2} a_1 a_3 + \frac{105}{2} a_2^2 - 45 a_4\Big]$$

$$< 0J \mid x_J^3 \mid 0J > = - \frac{11}{8} a_1 \gamma^2 - \frac{\gamma^3}{16} \Big[\frac{465}{4} a_1^3 - 171 a_1 a_2 + 65 a_3\Big]$$

$$+ \frac{\gamma^4}{64} \Big[- \frac{119127}{32} a_1^5 + \frac{45507}{4} a_1^3 a_2 - \frac{13551}{2} a_1^2 a_3$$

$$- \frac{11827}{2} a_1 a_2^2 + 3230 a_1 a_4 + 2844 a_2 a_3 - 1050 a_5\Big]$$

$$< 0J \mid x_J^4 \mid 0J > = \frac{3}{4} \gamma^2 + \frac{3\gamma^3}{8} \Big[\frac{57}{4} a_1^2 - 7 a_2\Big]$$

$$+ \frac{\gamma^4}{16} \Big[\frac{45507}{64} a_1^4 - \frac{11827}{8} a_1^2 a_2 + 711 a_1 a_3$$

$$+ \frac{999}{4} a_2^2 - 180 a_4\Big]$$

$$< 0J \mid x_J^5 \mid 0J > = - \frac{65}{16} a_1 \gamma^3 + \frac{\gamma^4}{16} \Big[- \frac{4517}{8} a_1^3 + 711 a_1 a_2 - \frac{449}{2} a_3\Big]$$

TABLE 4 CONTINUED

$$- \frac{30865}{8} a_1 a_2^2 + \frac{30107}{16} a_1 a_4 + 1647\, a_2 a_3 - \frac{4179}{8} a_5 \Big)$$

$$< 0J \mid x_J^6 \mid 0J > = \frac{15}{8} \gamma^3 + \frac{5\gamma^4}{4} \left(\frac{323}{16} a_1^2 - 9a_2 \right)$$

$$+ \frac{\gamma^5}{32} \Big(\frac{146121}{16} a_1^4 - \frac{69741}{4} a_1^2 a_2 + \frac{30107}{4} a_1 a_3$$

$$+ 2805 a_2^2 - \frac{3495}{2} a_4 \Big)$$

---

* J-dependent potential constants

Table 5

VIBRATION-ROTATION EXPECTATION VALUES

$$< vJ \mid x^0 \mid vJ > = 1$$

$$< vJ \mid x^1 \mid vJ > = -\frac{3}{2}a_1\gamma\left(v + \frac{1}{2}\right) + \frac{\gamma^2}{4}\biggl[4J(J + 1) + \biggl(-\frac{21}{8}a_1^3$$

$$+ \frac{23}{4}a_1a_2 - \frac{15}{4}a_3\biggr) + \biggl(-\frac{45}{2}a_1^3 + 39a_1a_2 - 15a_3\biggr)\left(v + \frac{1}{2}\right)^2\biggr]$$

$$+ \frac{\gamma^3}{8}\biggl[(54a_1^2 - 48a_2 + 54a_1 + 48)\left(v + \frac{1}{2}\right) J(J + 1)$$

$$+ \biggl(-\frac{31185}{256}a_1^5 + \frac{14259}{32}a_1^3a_2 - \frac{5145}{16}a_1^2a_3 - \frac{4677}{16}a_1a_2^2$$

$$+ \frac{795}{4}a_1a_4 + \frac{715}{4}a_2a_3 - \frac{175}{2}a_5\biggr)\left(v + \frac{1}{2}\right)$$

$$+ \biggl(-\frac{19035}{64}a_1^5 + \frac{7545}{8}a_1^3a_2 - \frac{2175}{4}a_1^2a_3 - \frac{2055}{4}a_1a_2^2$$

$$+ 255a_1a_4 + 225a_2a_3 - 70a_5\biggr)\left(v + \frac{1}{2}\right)^3\biggr]$$

$$< vJ \mid x^2 \mid vJ > = \gamma\left(v + \frac{1}{2}\right) + \frac{\gamma^2}{4}\biggl[\biggl(\frac{7}{4}a_1^2 - \frac{3}{2}a_2\biggr) + (15a_1^2 - 6a_2)\left(v + \frac{1}{2}\right)^2\biggr]$$

$$+ \frac{\gamma^3}{8}\biggl[(-36a_1 - 12)\left(v + \frac{1}{2}\right) J(J + 1) + \biggl(\frac{10395}{128}a_1^4$$

$$- \frac{3213}{16}a_1^2a_2 + \frac{475}{4}a_1a_3 + \frac{335}{8}a_2^2 - \frac{75}{2}a_4\biggr)\left(v + \frac{1}{2}\right)$$

$$+ \biggl(\frac{6345}{32}a_1^4 - \frac{1575}{4}a_1^2a_2 + 175a_1a_3 + \frac{85}{2}a_2^2 - 30a_4\biggr)\left(v + \frac{1}{2}\right)^3\biggr]$$

$$< vJ \mid x^3 \mid vJ > = \frac{\gamma^2}{4}\biggl[-\frac{7}{4}a_1 - 15a_1\left(v + \frac{1}{2}\right)^2\biggr] + \frac{\gamma^3}{8}\biggl[24\left(v + \frac{1}{2}\right) J(J + 1)$$

TABLE 5 CONTINUED

$$+ \Bigl(- \frac{1155}{16} a_1^3 + \frac{459}{4} a_1 a_2 - \frac{95}{2} a_3\Bigr)\Bigl(v + \frac{1}{2}\Bigr)$$

$$+ \Bigl(- \frac{705}{4} a_1^3 + 225 a_1 a_2 - 70 a_3\Bigr)\Bigl(v + \frac{1}{2}\Bigr)^3 \Biggr]$$

$$+ \frac{\gamma^4}{16} \Biggl[\frac{1}{16} \Bigl(- \frac{304437}{128} a_1^5 + \frac{131817}{16} a_1^3 a_2 - \frac{44331}{8} a_1^2 a_3$$

$$- \frac{40261}{8} a_1 a_2^2 + \frac{6055}{2} a_1 a_4 + \frac{5667}{2} a_2 a_3 - 1155 a_5\Bigr)$$

$$+ \frac{1}{2} \Bigl(- \frac{627165}{128} a_1^5 + \frac{239985}{16} a_1^3 a_2 - \frac{71595}{8} a_1^2 a_3$$

$$- \frac{62013}{8} a_1 a_2^2 + \frac{8535}{2} a_1 a_4 + \frac{7335}{2} a_2 a_3 - 1365 a_5\Bigr)\Bigl(v + \frac{1}{2}\Bigr)^2$$

$$+ 5\Bigl(- \frac{69453}{128} a_1^5 + \frac{23265}{16} a_1^3 a_2 - \frac{5859}{8} a_1^2 a_3$$

$$- \frac{4989}{8} a_1 a_2^2 + \frac{543}{2} a_1 a_4 + \frac{483}{2} a_2 a_3 - 63 a_5\Bigr)\Bigl(v + \frac{1}{2}\Bigr)^4$$

$$+ (63 a_1^2 - 46 a_2 + 42 a_1 + 28)\ J(J + 1)$$

$$+ 12(45 a_1^2 - 26 a_2 + 30 a_1 + 20)\Bigl(v + \frac{1}{2}\Bigr)^2\ J(J + 1)\Biggr]$$

$$< vJ \mid x^4 \mid vJ > = \frac{\gamma^2}{4} \Biggl[\frac{3}{2} + 6\Bigl(v + \frac{1}{2}\Bigr)^2\Biggr]$$

$$+ \frac{\gamma^3}{8} \Biggl[\Bigl(\frac{459}{8} a_1^2 - \frac{67}{2} a_2\Bigr)\Bigl(v + \frac{1}{2}\Bigr) + \Bigl(\frac{225}{2} a_1^2 - 34 a_2\Bigr)\Bigl(v + \frac{1}{2}\Bigr)^3\Biggr]$$

$$+ \gamma^4 \Biggl[- \frac{1}{8} (23 a_1 + 9)\ J(J + 1) - \frac{3}{2} (13 a_1 + 3)\Bigl(v + \frac{1}{2}\Bigr)^2\ J(J + 1)$$

$$+ \frac{1}{256} \Bigl(\frac{131817}{64} a_1^4 - \frac{40261}{8} a_1^2 a_2 + \frac{5667}{2} a_1 a_3$$

TABLE 5 CONTINUED

$$+ \frac{4617}{4} a_2^2 - 945a_4\Big) + \frac{3}{32} \Big(\frac{79995}{64} a_1^4 - \frac{20671}{8} a_1^2 a_2$$

$$+ \frac{2445}{2} a_1 a_3 + \frac{1707}{4} a_2^2 - 295a_4\Big)\Big(v + \frac{1}{2}\Big)^2$$

$$+ \frac{15}{16} \Big(\frac{7755}{64} a_1^4 - \frac{1663}{8} a_1^2 a_2 + \frac{161}{2} a_1 a_3 + \frac{75}{4} a_2^2$$

$$- 11a_4\Big)\Big(v + \frac{1}{2}\Big)^4\Bigg]$$

$$< vJ \mid x^5 \mid vJ > = \frac{\gamma^3}{8} \Bigg[- \frac{95}{2} a_1 \Big(v + \frac{1}{2}\Big) - 70a_1 \Big(v + \frac{1}{2}\Big)^3\Bigg]$$

$$+ \gamma^4 \Bigg[\frac{1}{256} \Big(- \frac{14777}{8} a_1^3 + \frac{5667}{2} a_1 a_2 - 1107a_3\Big)$$

$$+ \frac{1}{32} \Big(- \frac{23865}{8} a_1^3 + \frac{7335}{2} a_1 a_2 - 1085a_3\Big)\Big(v + \frac{1}{2}\Big)^2$$

$$+ \frac{1}{16} \Big(- \frac{9765}{8} a_1^3 + \frac{2415}{2} a_1 a_2 - 315a_3\Big)\Big(v + \frac{1}{2}\Big)^4$$

$$+ \frac{15}{8} J(J + 1) + \frac{15}{2} \Big(v + \frac{1}{2}\Big)^2 J(J + 1)\Bigg]$$

$$+ \gamma^5 \Bigg[\frac{5}{8} \Big(\frac{1029}{8} a_1^2 - \frac{143}{2} a_2 + \frac{285}{4} a_1 + 38\Big)\Big(v + \frac{1}{2}\Big) J(J + 1)$$

$$+ \frac{5}{2} \Big(\frac{435}{8} a_1^2 - \frac{45}{2} a_2 + \frac{105}{4} a_1 + 14\Big)\Big(v + \frac{1}{2}\Big)^3 J(J + 1)$$

$$+ \frac{1}{256} \Big(- \frac{11535783}{128} a_1^5 + \frac{4354275}{16} a_1^3 a_2 - 158085\, a_1^2 a_3 - \frac{1119415}{8} a_1 a$$

$$+ \frac{145417}{2} a_1 a_4 + 64731a_2 a_3 - 22029a_5\Big)\Big(v + \frac{1}{2}\Big) + \frac{5}{16} \Big(- \frac{1125489}{256} a_1^5$$

$$+ \frac{370485}{32} a_1^3 a_2 - 5845a_1^2 a_3 - \frac{78465}{16} a_1 a_2^2 + \frac{8853}{4} a_1 a_4 + \frac{3759}{2} a_2 a_3$$

TABLE 5 CONTINUED

$$- \frac{1071}{2} a_5 \Big) \Big(v + \frac{1}{2} \Big)^3$$

$$+ \frac{3}{16} \Big(- \frac{468069}{128} a_1^5 + \frac{136185}{16} a_1^3 a_2 - 3815 a_1^2 a_3 - \frac{23765}{8} a_1 a_2^2$$

$$+ \frac{2303}{2} a_1 a_4 + 1029 a_2 a_3 - 231 a_5 \Big) \Big(v + \frac{1}{2} \Big)^5 \Bigg]$$

$$< vJ \mid x^6 \mid vJ > = \frac{\gamma^3}{8} \Bigg[25 \Big(v + \frac{1}{2} \Big) + 20 \Big(v + \frac{1}{2} \Big)^3 \Bigg]$$

$$+ \frac{\gamma^4}{16} \Bigg[\frac{1}{16} \Big(\frac{6055}{4} a_1^2 - 945 a_2 \Big) + \frac{1}{2} \Big(\frac{8535}{4} a_1^2 - 885 a_2 \Big) \Big(v + \frac{1}{2} \Big)^2$$

$$+ \Big(\frac{2715}{4} a_1^2 - 165 a_2 \Big) \Big(v + \frac{1}{2} \Big)^4 \Bigg]$$

$$+ \frac{\gamma^5}{16} \Bigg[\frac{1}{16} \Big(\frac{4785249}{64} a_1^4 - \frac{1246797}{8} a_1^2 a_2 + \frac{145417}{2} a_1 a_3$$

$$+ \frac{117281}{4} a_2^2 - 19277 a_4 \Big) \Big(v + \frac{1}{2} \Big)$$

$$+ \frac{5}{2} \Big(\frac{413463}{64} a_1^4 - \frac{90459}{8} a_1^2 a_2 + \frac{8853}{2} a_1 a_3$$

$$+ \frac{5911}{4} a_2^2 - 829 a_4 \Big) \Big(v + \frac{1}{2} \Big)^3$$

$$+ 3 \Big(\frac{143955}{64} a_1^4 - \frac{26775}{8} a_1^2 a_2 + \frac{2303}{2} a_1 a_3$$

$$+ \frac{1043}{4} a_2^2 - 131 a_4 \Big) \Big(v + \frac{1}{2} \Big)^5$$

$$- 15 (53 a_1 + 15) \Big(v + \frac{1}{2} \Big) J(J + 1)$$

$$- 60 (17 a_1 + 3) \Big(v + \frac{1}{2} \Big)^3 J(J + 1) \Bigg]$$

TABLE 6.

OFF-DIAGONAL VIBRATIONAL MATRIX ELEMENTS*

$$< 0J \mid x_J^1 \mid 1J> \; = \Big(\frac{\gamma}{2}\Big)^{\frac{1}{2}} \Big[1 + \frac{\gamma}{4}\Big(\frac{11}{4}\,a_1^2 - 3a_2\Big) + \frac{\gamma^2}{32}\Big(\frac{2989}{32}\,a_1^4$$

$$+ 195a_1a_3 - \frac{1149}{4}\,a_1^2a_2 + \frac{189}{2}\,a_2^2 - 90a_4\Big)\Big]$$

$$< 0J \mid x_J^2 \mid 1J> \; = \Big(\frac{\gamma}{2}\Big)^{\frac{1}{2}} \Big[- \frac{5}{2}\,a_1\gamma + \frac{\gamma^2}{4}\;\Big(- \frac{205}{4}\,a_1^3 + 88a_1a_2 - 35a_3\Big)\Big]$$

$$< 0J \mid x_J^3 \mid 1J> \; = \Big(\frac{\gamma}{2}\Big)^{\frac{1}{2}} \Big[\frac{3}{2}\gamma + \frac{9\gamma^2}{2}\;\Big(\frac{17}{8}\,a_1^2 - a_2\Big)\;\Big]$$

$$< 0J \mid x_J^4 \mid 1J> \; = \Big(\frac{\gamma}{2}\Big)^{\frac{1}{2}} \Big[-\frac{17}{2}\,a_1\gamma^2 + \frac{\gamma^3}{4}\Big(- \frac{2491}{8}a_1^3 + \frac{819}{2}\,a_1a_2 - 133a_3\Big)\Big]$$

$$< 0J \mid x_J^5 \mid 1J> \; = \Big(\frac{\gamma}{2}\Big)^{\frac{1}{2}} \Big[\frac{15}{4}\,\gamma^2 + \frac{5\gamma^3}{16}\;\Big(\frac{689}{4}\,a_1^2 - 69a_2\Big)\Big]$$

$$< 0J \mid x_J^6 \mid 1J> \; = \Big(\frac{\gamma}{2}\Big)^{\frac{1}{2}} \Big[-\frac{285}{8}\,a_1\gamma^3 + \frac{3\gamma^4}{8}\;\Big(- \frac{10857}{8}\,a_1^3 + 1506a_1a_2 - \frac{829}{2}\,a_3\Big)\Big]$$

$$< 0J \mid x_J^1 \mid 2J> \; = \frac{\gamma}{\sqrt{2}}\Big[\frac{a_1}{2} + \frac{\gamma}{2}\Big(\frac{243}{32}\,a_1^3 - \frac{111}{8}\,a_1a_2 + 5a_3\Big) + \frac{\gamma^2}{8}\;\Big(\frac{189097}{512}\,a_1^5$$

$$- \frac{80277}{64}\,a_1^3a_2 + 742a_1^2a_3 + \frac{23953}{32}\,a_1a_2^2 - \frac{1475}{4}\,a_1a_4 - \frac{663}{2}\,a_2a_3 + 105a_5\Big)\Big]$$

$$< 0J \mid x_J^2 \mid 2J> \; = \frac{\gamma}{\sqrt{2}}\Big[1 + \frac{3\gamma}{8}\Big(\frac{a_1^2}{4} - 5a_2\Big) + \frac{\gamma^2}{16}\Big(- \frac{28663}{128}\,a_1^4 + \frac{3611}{16}\,a_1^2a_2$$

$$+ \frac{61}{2}\,a_1a_3 + \frac{1233}{8}\,a_2^2 - 135a_4\Big)\Big]$$

$$< 0J \mid x_J^3 \mid 2J> \; = \frac{\gamma}{\sqrt{2}}\Big[- \frac{9}{2}\,a_1\gamma + \frac{3\gamma^2}{8}\;\Big(- \frac{641}{8}\,a_1^3 + \frac{305}{2}\,a_1a_2 - 57a_3\Big)\Big]$$

TABLE 6 CONTINUED

$$< 0J \mid x_J^4 \mid 2J> = \frac{\gamma}{\sqrt{2}} \left[3\gamma + \frac{\gamma^2}{8} \left(\frac{917}{4} a_1^2 - 117 a_2 \right) \right]$$

$$< 0J \mid x_J^5 \mid 2J> = \frac{\gamma}{\sqrt{2}} \left[- \frac{215}{8} a_1 \gamma^2 + \frac{15\gamma^3}{4} \left(- \frac{5943}{64} a_1^3 + \frac{1947}{16} a_1 a_2 - 37 a_3 \right) \right]$$

$$< 0J \mid x_J^6 \mid 2J> = \frac{\gamma}{\sqrt{2}} \left[\frac{45}{4} \gamma^2 + \frac{45\gamma^3}{32} \left(\frac{703}{4} a_1^2 - 67 a_2 \right) \right]$$

$$< 0J \mid x_J^1 \mid 3J> = \frac{\gamma^{3/2}\sqrt{3}}{2} \left[\frac{1}{4} \left(\frac{3a_1^2}{4} + a_2 \right) + \frac{3\gamma}{8} \left(\frac{303}{32} a_1^4 \right. \right.$$

$$\left. \left. - \frac{41}{4} a_1^2 a_2 - \frac{3}{2} a_1 a_3 - \frac{13}{2} a_2^2 + 5 a_4 \right) \right]$$

$$< 0J \mid x_J^2 \mid 3J> = \frac{\gamma^{3/2}\sqrt{3}}{2} \left[a_1 + \frac{7}{2} \gamma \left(3a_1^3 - 6 a_1 a_2 + 2 a_3 \right) \right]$$

$$< 0J \mid x_J^3 \mid 3J> = \frac{\gamma^{3/2}\sqrt{3}}{2} \left[1 - 3\gamma \left(a_1^2 + a_2 \right) \right]$$

$$< 0J \mid x_J^4 \mid 3J> = \frac{\gamma^{3/2}\sqrt{3}}{2} \left[- 6 a_1 \gamma + \frac{\gamma^2}{8} \left(- \frac{993}{4} a_1^3 + 725 a_1 a_2 - 276 a_3 \right) \right]$$

$$< 0J \mid x_J^5 \mid 3J> = \frac{\gamma^{3/2}\sqrt{3}}{2} \left[5\gamma + \frac{15}{16} \gamma^2 \left(\frac{233}{4} a_1^2 - 37 a_2 \right) \right]$$

$$< 0J \mid x_J^6 \mid 3J> = \frac{\gamma^{3/2}\sqrt{3}}{2} \left[- \frac{245}{4} a_1 \gamma^2 + \frac{5\gamma^3}{2} \left(- \frac{12201}{32} a_1^3 + \frac{4269}{8} a_1 a_2 - 157 a_3 \right) \right]$$

$$< 0J \mid x_J^1 \mid 4J> = \frac{\gamma^2\sqrt{6}}{2} \left[\frac{1}{4} \left(\frac{a_1^3}{4} + a_1 a_2 + \frac{2a_3}{3} \right) + \frac{\gamma}{4} \left(\frac{555}{64} a_1^5 + \frac{35}{4} a_1^3 a_2 \right. \right.$$

$$\left. \left. + \frac{35}{24} a_1^2 a_3 - 3 a_1 a_4 - \frac{135}{4} a_1 a_2^2 - \frac{a_2 a_3}{2} + 7 a_5 \right) \right]$$

TABLE 6 CONTINUED

$$< 0J \mid x_J^2 \mid 4J> = \frac{\gamma^2\sqrt{6}}{2}\left[\frac{1}{2}\left(\frac{5}{4}a_1^2 + a_2\right) + \frac{5\gamma}{4}\left(\frac{395}{32}a_1^4 - 18a_1^2a_2 + \frac{5}{3}a_1a_3 - \frac{11}{2}a_2^2 + 4a_4\right)\right]$$

$$< 0J \mid x_J^3 \mid 4J> = \frac{\gamma^2\sqrt{6}}{2}\left[\frac{3}{2}a_1 + \frac{5}{4}\gamma\left(\frac{117}{8}a_1^3 - \frac{69}{2}a_1a_2 + 11a_3\right)\right]$$

$$< 0J \mid x_J^4 \mid 4J> = \frac{\gamma^2\sqrt{6}}{2}\left[1 - \frac{5}{4}\gamma\left(\frac{29}{4}a_1^2 + 3a_2\right)\right]$$

$$< 0J \mid x_J^5 \mid 4J> = \frac{\gamma^2\sqrt{6}}{6}\left[-\frac{25}{4}a_1\gamma + \frac{5}{4}\gamma^2\left(20a_1^3 + 61a_1a_2 - 29a_3\right)\right]$$

$$< 0J \mid x_J^6 \mid 4J> = \frac{\gamma^2\sqrt{6}}{2}\left[\frac{15}{2}\gamma + \frac{15\gamma^2}{4}\left(19a_1^2 - 18a_2\right)\right]$$

$$< 0J \mid x_J^1 \mid 5J> = \frac{\gamma^{5/2}\sqrt{15}}{2}\left[\frac{1}{8}\left(\frac{5}{32}a_1^4 + \frac{5}{4}a_1^2a_2 + \frac{11}{6}a_1a_3 + \frac{a_2^2}{2} + a_4\right)\right]$$

$$< 0J \mid x_J^2 \mid 5J> = \frac{\gamma^{5/2}\sqrt{15}}{2}\left(\frac{5}{16}a_1^3 + \frac{3}{4}a_1a_2 + \frac{a_3}{3}\right)$$

$$< 0J \mid x_J^3 \mid 5J> = \frac{\gamma^{5/2}\sqrt{15}}{2}\left[\frac{3}{4}\left(\frac{7}{4}a_1^2 + a_2\right)\right]$$

$$< 0J \mid x_J^4 \mid 5J> = \frac{\gamma^{5/2}\sqrt{15}}{2}\left(2a_1\right)$$

$$< 0J \mid x_J^5 \mid 5J> = \frac{\gamma^{5/2}\sqrt{15}}{2}\left(1\right)$$

$$< 0J \mid x_J^6 \mid 5J> = \frac{\gamma^{5/2}\sqrt{15}}{2}\left(-\frac{9}{2}a_1\gamma\right)$$

$$< 1J \mid x_J^1 \mid 2J> = \sqrt{\gamma}\left[1 + \frac{\gamma}{2}\left(\frac{11}{4}a_1^2 - 3a_2\right) + \frac{\gamma^2}{16}\left(\frac{24911}{128}a_1^4 + \frac{665}{2}a_1a_3 - \frac{8691}{16}a_1^2a_2 + \frac{1287}{8}a_2^2 - 135a_4\right)\right]$$

TABLE 6 CONTINUED

$$< 1J \mid x_J^2 \mid 2J> \; = \sqrt{\gamma}\left[-5a_1\gamma + \frac{\gamma^2}{4}\left(-\frac{2815}{16}a_1^3 + \frac{1159}{4}a_1a_2 - 105a_3\right)\right]$$

$$< 1J \mid x_J^3 \mid 2J> \; = \sqrt{\gamma}\left[3\gamma + \frac{9\gamma^2}{16}\left(\frac{241}{4}a_1^2 - 25a_2\right)\right]$$

$$< 1J \mid x_J^4 \mid 2J> \; = \sqrt{\gamma}\left[-\frac{59}{2}a_1\gamma^2 + \gamma^3\left(-\frac{14057}{32}a_1^3 + \frac{4293}{8}a_1a_2 - 161a_3\right)\right]$$

$$< 1J \mid x_J^5 \mid 2J> \; = \sqrt{\gamma}\left[\frac{45}{4}\gamma^2 + \frac{5}{16}\gamma^3\left(\frac{3691}{4}a_1^2 - 303a_2\right)\right]$$

$$< 1J \mid x_J^6 \mid 2J> \; = \sqrt{\gamma}\left[-\frac{345}{2}a_1\gamma^3 + \frac{3\gamma^4}{16}\left(-\frac{336363}{16}a_1^3 + \frac{83643}{4}a_1a_2 - 23599a_3\right)\right]$$

$$< 1J \mid x_J^1 \mid 3J> = \frac{\gamma\sqrt{6}}{2}\left[\frac{a_1}{2} + \frac{5\gamma}{6}\left(\frac{243}{32}a_1^3 - \frac{111}{8}a_1a_2 + 5a_3\right)\right]$$

$$< 1J \mid x_J^2 \mid 3J >= \frac{\gamma\sqrt{6}}{2}\left[1 + \frac{5\gamma}{8}\left(\frac{a_1^2}{4} - 5a_2\right)\right]$$

$$< 1J \mid x_J^3 \mid 3J> = \frac{\gamma\sqrt{6}}{2}\left[-\frac{15}{2}a_1\gamma + \frac{\gamma^2}{8}\left(-\frac{4635}{8}a_1^3 + \frac{2139}{2}a_1a_2 - 367a_3\right)\right]$$

$$< 1J \mid x_J^4 \mid 3J> = \frac{\gamma\sqrt{6}}{2}\left[5\gamma + \frac{\gamma^2}{8}\left(\frac{2413}{4}a_1^2 - 285a_2\right)\right]$$

$$< 1J \mid x_J^5 \mid 3J> = \frac{\gamma\sqrt{6}}{2}\left[-\frac{555}{8}a_1\gamma^2 + \frac{25}{4}\gamma^3\left(-\frac{13491}{64}a_1^3 + \frac{4135}{16}a_1a_2 - 73a_3\right)\right]$$

$$< 1J \mid x_J^6 \mid 3J> = \frac{\gamma\sqrt{6}}{2}\left[\frac{105}{4}\gamma^2 + \frac{105}{32}\gamma^3\left(\frac{1121}{4}a_1^2 - 93a_2\right)\right]$$

$$\begin{aligned}< 1J \mid x_J^1 \mid 4J> = \gamma^{3/2}\sqrt{3}\Bigg[&\frac{1}{4}\left(\frac{3}{4}a_1^2 + a_2\right) + \frac{9}{16}\gamma\Bigg(\frac{303}{32}a_1^4 \\ &- \frac{41}{4}a_1^2a_2 - \frac{3}{2}a_1a_3 - \frac{13}{2}a_2^2 + 5a_4\Bigg)\Bigg]\end{aligned}$$

$$< 1J \mid x_J^2 \mid 4J> = \gamma^{3/2}\sqrt{3}\left[a_1 + \frac{21}{4}\gamma\left(3a_1^3 - 6a_1a_2 + 2a_3\right)\right]$$

TABLE 6 CONTINUED

$$< 1J \mid x_J^3 \mid 4J> \; = \gamma^{3/2}\sqrt{3}\left[1 - \frac{9}{2}\gamma \left(a_1^2 + a_2\right)\right]$$

$$< 1J \mid x_J^4 \mid 4J> \; = \gamma^{3/2}\sqrt{3}\left[-9a_1\gamma + \gamma^2 \left(- \frac{1713}{32} a_1^3 + \frac{1325}{8} a_1a_2 - 57a_3\right)\right]$$

$$< 1J \mid x_J^5 \mid 4J> \; = \gamma^{3/2}\sqrt{3}\left[\frac{15}{2}\gamma + \frac{15\gamma^2}{16} \left(\frac{513}{4} a_1^2 - 77a_2\right)\right]$$

$$< 1J \mid x_J^6 \mid 4J> \; = \gamma^{3/2}\sqrt{3}\left[- \frac{265}{2} a_1\gamma^2 + 15\gamma^3 \left(- \frac{2995}{16} a_1^3 + 246a_1a_2 - \frac{267}{4} a_3\right)\right]$$

$$\begin{aligned} < 1J \mid x_J^1 \mid 5J> \; = {} & \gamma^2 \frac{\sqrt{30}}{2}\Bigg[\frac{1}{4}\left(\frac{a_1{}^3}{4} + a_1a_2 + \frac{2a_3}{3}\right) + \frac{7\gamma}{20}\Bigg(\frac{555}{64} a_1^5 \\ & + \frac{35}{4} a_1^3a_2 + \frac{35}{24} a_1^2a_3 - 3a_1a_4 - \frac{135}{4} a_1a_2^2 - \frac{1}{2} a_2a_3 + 7a_5 \Bigg)\Bigg] \end{aligned}$$

$$\begin{aligned} < 1J \mid x_J^2 \mid 5J> \; = {} & \gamma^2 \frac{\sqrt{30}}{2}\Bigg[\frac{1}{2}\left(\frac{5}{4} a_1^2 + a_2\right) + \frac{7\gamma}{4}\Bigg(\frac{395}{32} a_1^4 \\ & - 18 a_1^2a_2 + \frac{5}{3} a_1a_3 - \frac{11}{2} a_2^2 + 4 a_4\Bigg)\Bigg] \end{aligned}$$

$$< 1J \mid x_J^3 \mid 5J> \; = \gamma^2 \frac{\sqrt{30}}{2}\left[\frac{3}{2} a_1 + \frac{7\gamma}{4}\left(\frac{117}{8} a_1^3 - \frac{69}{2} a_1a_2 + 11a_3\right)\right]$$

$$< 1J \mid x_J^4 \mid 5J> \; = \gamma^2 \frac{\sqrt{30}}{2}\left[1 - \frac{7\gamma}{4}\left(\frac{29}{4} a_1^2 + 3a_2\right)\right]$$

$$< 1J \mid x_J^5 \mid 5J> \; = \gamma^2 \frac{\sqrt{30}}{2}\left(- \frac{35}{4} a_1\gamma\right)$$

$$< 1J \mid x_J^6 \mid 5J> \; = \gamma^2 \frac{\sqrt{30}}{2}\left(\frac{21}{2}\gamma\right)$$

$$< 2J \mid x_J^1 \mid 3J> \; = \frac{\sqrt{6\gamma}}{2}\left[1 + \frac{3}{4}\gamma\left(\frac{11}{4} a_1^2 - 3a_2\right)\right]$$

TABLE 6 CONTINUED

$$< 2J \mid x_J^2 \mid 3J> \; = \; \frac{\sqrt{6}\gamma}{2}\left[-\frac{15}{2}a_1\gamma + \frac{\gamma^2}{2}\left(-\frac{1535}{8}a_1^3 + 313a_1a_2 - \frac{665}{6}a_3\right)\right]$$

$$< 2J \mid x_J^3 \mid 3J> \; = \; \frac{\sqrt{6}\gamma}{2}\left[\frac{9}{2}\gamma + 3\gamma^2\left(\frac{397}{16}a_1^2 - 10a_2\right)\right]$$

$$< 2J \mid x_J^4 \mid 3J> \; = \; \frac{\sqrt{6}\gamma}{2}\left[-\frac{129}{2}a_1\gamma^2 + \frac{3\gamma^3}{4}\left(-\frac{14591}{8}a_1^3 + \frac{4359}{2}a_1a_2 - 637a_3\right)\right]$$

$$< 2J \mid x_J^5 \mid 3J> \; = \; \frac{\sqrt{6}\gamma}{2}\left[\frac{95}{4}\gamma^2 + \frac{15}{16}\gamma^3\left(\frac{3773}{4}a_1^2 - 289a_2\right)\right]$$

$$< 2J \mid x_J^6 \mid 3J> \; = \; \frac{\sqrt{6}\gamma}{2}\left[-\frac{4095}{8}a_1\gamma^3 + \frac{3\gamma^4}{2}\left(-\frac{350077}{32}a_1^3\right.\right.$$

$$\left.\left. + \; 10439a_1a_2 - \frac{20749}{8}a_3\right)\right]$$

$$< 2J \mid x_J^1 \mid 4J> \; = \; \gamma\sqrt{3}\left[\frac{a_1}{2} + \frac{7}{3}\gamma\left(\frac{243}{64}a_1^3 - \frac{111}{16}a_1a_2 + \frac{5}{2}a_3\right)\right]$$

$$< 2J \mid x_J^2 \mid 4J> \; = \; \gamma\sqrt{3}\left[1 + \frac{7}{8}\gamma\left(\frac{a_1^2}{4} - 5a_2\right)\right]$$

$$< 2J \mid x_J^3 \mid 4J> \; = \; \gamma\sqrt{3}\left[-\frac{21}{2}a_1\gamma + \frac{\gamma^2}{8}\left(-\frac{8703}{8}a_1^3 + \frac{3975}{2}a_1a_2 - 661a_3\right)\right]$$

$$< 2J \mid x_J^4 \mid 4J> \; = \; \gamma\sqrt{3}\left[7\gamma + \frac{\gamma^2}{8}\left(\frac{4657}{4}a_1^2 - 537a_2\right)\right]$$

$$< 2J \mid x_J^5 \mid 4J> \; = \; \gamma\sqrt{3}\left[-\frac{1065}{8}a_1\gamma^2 + \frac{35\gamma^3}{4}\left(-\frac{24813}{64}a_1^3 + \frac{7417}{16}a_1a_2 - 127a_3\right)\right]$$

$$< 2J \mid x_J^6 \mid 4J> \; = \; \gamma\sqrt{3}\left[\frac{195}{4}\gamma^2 + \frac{105}{32}\gamma^3\left(\frac{2869}{4}a_1^2 - 225a_2\right)\right]$$

TABLE 6 CONTINUED

$$< 2J \mid x_J^1 \mid 5J> = \frac{\gamma^{3/2}\sqrt{30}}{2}\left[\frac{1}{4}\left(\frac{3a_1^2}{4} + a_2\right) + \frac{3\gamma}{4}\left(\frac{303}{32}a_1^4 - \frac{41}{4}a_1^2a_2 - \frac{3}{2}a_1a_3 - \frac{13}{2}a_2^2 + 5\,a_4\right)\right]$$

$$< 2J \mid x_J^2 \mid 5J> = \frac{\gamma^{3/2}\sqrt{30}}{2}\left[a_1 + 7\gamma\left(3a_1^3 - 6a_1a_2 + 2a_3\right)\right]$$

$$< 2J \mid x_J^3 \mid 5J> = \frac{\gamma^{3/2}\sqrt{30}}{2}\left[1 - 6\gamma\left(a_1^2 + a_2\right)\right]$$

$$< 2J \mid x_J^4 \mid 5J> = \frac{\gamma^{3/2}\sqrt{30}}{2}\left(- 12a_1\gamma\right)$$

$$< 2J \mid x_J^5 \mid 5J> = \frac{\gamma^{3/2}\sqrt{30}}{2}\left(10\,\gamma\right)$$

$$< 2J \mid x_J^6 \mid 5J> = \frac{\gamma^{3/2}\sqrt{30}}{2}\left(- \frac{929}{4}a_1\gamma^2\right)$$

TABLE 6 CONTINUED

$$< 3J \mid x_J^1 \mid 4J> = \sqrt{2}\gamma \left[1 + \gamma\left(\frac{11}{4} a_1^2 - 3a_2\right)\right]$$

$$< 3J \mid x_J^2 \mid 4J> = \sqrt{2}\gamma \left[-10a_1\gamma + \frac{\gamma^2}{4} \left(- \frac{10795}{16} a_1^3 + \frac{4387}{4} a_1a_2 - 385a_3\right)\right]$$

$$< 3J \mid x_J^3 \mid 4J> = \sqrt{2}\gamma \left[6\gamma + \frac{27}{16} \gamma^2 \left(\frac{311}{4} a_1^2 - 31a_2\right)\right]$$

$$< 3J \mid x_J^4 \mid 4J> = \sqrt{2}\gamma \left[- \frac{227}{2} a_1\gamma^2 + \gamma^3 \left(- \frac{50357}{16} a_1^3 + \frac{14913}{4} a_1a_2 - 1078a_3\right)\right]$$

$$< 3J \mid x_J^5 \mid 4J> = \sqrt{2}\gamma \left[\frac{165}{4} \gamma^2 + \frac{5}{16} \gamma^3 \left(\frac{12943}{2} a_1^2 - 1845a_2\right)\right]$$

$$< 3J \mid x_J^6 \mid 4J> = \sqrt{2}\gamma \left[- 1155a_1\gamma^3 + \frac{3\gamma^4}{64} \left(- \frac{4097593}{4} a_1^3\right.\right.$$

$$\left.\left. + 959883a_1a_2 - \frac{930967}{4} a_3\right)\right]$$

$$< 3J \mid x_J^1 \mid 5J> = \gamma\sqrt{5}\left[\frac{a_1}{2} + \frac{3\gamma}{2} \left(\frac{243}{32} a_1^3 - \frac{111}{8} a_1a_2 + 5a_3\right)\right]$$

$$< 3J \mid x_J^2 \mid 5J> = \gamma\sqrt{5}\left[1 + \frac{9\gamma}{8} \left(\frac{1}{4} a_1^2 - 5a_2\right)\right]$$

$$< 3J \mid x_J^3 \mid 5J> = \gamma\sqrt{5} \left(- \frac{27}{2} a_1\gamma\right)$$

$$< 3J \mid x_J^4 \mid 5J> = \gamma\sqrt{5} \left(9 \gamma\right)$$

$$< 3J \mid x_J^5 \mid 5J> = \gamma\sqrt{5} \left(- \frac{1745}{8} a_1\gamma^2\right)$$

$$< 3J \mid x_J^6 \mid 5J> = \gamma\sqrt{5} \left(\frac{315}{4} \gamma^2\right)$$

TABLE 6 CONTINUED

$$< 4J \mid x_J^1 \mid 5J> \; = \frac{\sqrt{10}\gamma}{2} \left[1 + \frac{5\gamma}{4} \left(\frac{11}{4} a_1^2 - 3a_2\right)\right]$$

$$< 4J \mid x_J^2 \mid 5J> \; = \frac{\sqrt{10}\gamma}{2} \left(- \frac{25}{2} a_1 \gamma\right)$$

$$< 4J \mid x_J^3 \mid 5J> \; = \frac{\sqrt{10}\gamma}{2} \left(\frac{15}{2} \gamma\right)$$

$$< 4J \mid x_J^4 \mid 5J> \; = \frac{\sqrt{10}\gamma}{2} \left(- \frac{353}{2} a_1 \gamma^2\right)$$

$$< 4J \mid x_J^5 \mid 5J> \; = \frac{\sqrt{10}\gamma}{2} \left(\frac{255}{4} \gamma^2\right)$$

$$< 4J \mid x_J^6 \mid 5J> \; = \frac{\sqrt{10}\gamma}{2} \left(- \frac{17625}{8} a_1 \gamma^3\right)$$

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* J-dependent potential constants

TABLE 7

NUMERICAL COMPARISON OF VIBRATIONAL MATRIX ELEMENTS $\langle v|x^n|v'\rangle$ FOR HCℓ

vnv'	Exponent	Dunham HTS Formula[a]	Dunham HTS Num. Int.[b]	Morse Spec.[c]	Morse Diss.En.[d]	RKR Num. Int.[e]	H.O. Expansion[f]	H.O.
000	0	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
010	-2	1.2687	1.2692	1.2020	1.2780	1.2764	1.2723	0.0000
020	-3	3.7948	3.7952	3.7826	3.8140	3.7957	3.7967	3.5417
030	-4	1.718	1.715	1.625	1.737	1.723	1.718	0.000
040	-5	4.519	4.521	4.478	4.574	4.657		3.763
050	-6	3.81	3.81	3.61	3.89			0.00
060	-7	9.40	9.42	9.25	9.62			6.66
001	-5	0.0000	1.9931	0.0000	0.0000	0.0000	0.0000	0.0000
011	-2	5.9975	5.9976	6.0036	6.0101	6.0096	5.9982	5.9513
021	-3	2.5514	2.5540	2.4279	2.5874	2.5993	2.5583	0.0000
031	-4	7.427	7.474	7.410	7.556	7.564	7.479	6.323
041	-5	6.633	6.672	6.333	6.818			0.000
051	-5	1.59	1.64	1.60	1.67			1.12
061	-6	2.17	2.21	2.09	2.28			0.00
002	-3	0.0000	-1.3237	0.0000	0.0000	0.0000	0.0000	0.0000
012	-3	-5.9919	-5.9287	-5.7422	-6.1152	-6.1440	-5.9953	0.0000
022	-3	4.7731	4.7714	4.8137	4.7862	4.7821	4.7731	5.0088
032	-4	3.781	3.785	3.617	3.845	3.861	3.783	0.0000
042	-4	1.332	1.342	1.330	1.365			1.064
052	-5	1.83	1.85	1.76	1.90			0.00
062	-6	4.67	4.93	4.80	5.10			2.83
003	-3	0.0000	-2.2509	0.0000	0.0000	0.0000	0.0000	0.0000
013	-3	1.0251	-0.4665	0.9048	1.0262	1.0361	1.0271	0.0000
023	-3	-1.1835	-1.1018	-1.1482	-1.2173	-1.2223	-1.1820	0.0000
033	-4	4.148	4.105	4.231	4.103	4.090	4.123	5.163
043	-5	4.638	4.802	4.449	4.650			0.000
053	-5	2.29	2.28	2.26	2.31			1.83
063	-6	4.28	4.33	4.12	4.45			0.00

TABLE 7 CONTINUED

		Dunham HTS	Dunham HTS	Morse	Morse	RKR Num.	H.O.	
vnv'	Exponent	Formula[a]	Num. Int.[b]	Spec.[c]	Diss.En.[d]	Int.[e]	Expansion[f]	H.O.
004	-2	0.0000	-2.3689	0.0000	0.0000	0.0000	0.0000	0.0000
014	-4	-2.3473	-28.6261	-1.8688	-2.2598	-2.2930		0.0000
024	-4	3.1785	-5.6591	2.8969	3.2739	3.3039		0.0000
034	-4	-1.887	-1.928	-1.860	-1.943	-1.948		0.000
044	-5	3.342	2.757	3.652	3.333			6.145
054	-6	3.90	4.97	3.78	3.67			0.00
064	-6	3.73	3.56	3.52	3.51			3.26
101	0	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
111	-2	3.8566	3.8625	3.6774	3.9201		3.8664	0.0000
121	-2	1.2507	1.2514	1.2403	1.2644		1.2519	1.0625
131	-3	1.180	1.180	1.121	1.209		1.182	0.000
141	-4	2.865	2.875	2.808	2.943			1.882
151	-5	4.12	4.13	3.91	4.28			0.00
161	-6	9.59	9.70	9.34	10.08			4.66
102	-3	0.0000	1.3462	0.0000	0.0000	0.0000	0.0000	0.0000
112	-2	8.5500	8.5484	8.5676	8.5871		8.5515	8.4163
122	-3	7.3749	7.4087	7.0704	7.5643		7.4026	0.0000
132	-3	2.371	2.418	2.383	2.467		2.419	1.789
142	-4	3.518	3.582	3.405	3.710			0.000
152	-5	8.53	9.26	8.97	9.62			4.75
162	-5	2.05	1.80	1.70	1.89			0.00
103	-2	0.0000	-2.1376	0.0000	0.0000	0.0000	0.0000	0.0000
113	-2	-1.0447	-0.8801	-1.0129	-1.0813			0.0000
123	-3	8.0257	7.9692	8.0855	7.9982			8.6755
133	-3	1.096	1.130	1.054	1.122			0.000
143	-4	4.339	4.442	4.366	4.545			3.073
153	-5	8.86	9.11	8.65	9.48			0.00
163	-5	2.38	2.68	2.59	2.82			1.14

TABLE 7 CONTINUED

vnv'	Exponent	Dunham HTS Formula[a]	Dunham HTS Num. Int.[b]	Morse Spec.[c]	Morse Diss.En.[d]	RKR Num. Int.[e]	H.O. Expansion[f]	H.O.
104	-2	0.0000	5.1298	0.0000	0.0000	0.0000	0.0000	0.0000
114	-3	2.0614	-11.2768	1.8603	2.1176			0.0000
124	-3	-2.3299	-2.2736	-2.2875	-2.4221			0.0000
134	-4	7.281	6.314	7.442	7.034			10.326
144	-4	1.319	1.510	1.258	1.299			0.000
154	-5	7.60	7.66	7.42	7.64			5.49
164	-5	1.98	2.09	1.92	2.10			0.00
202	0	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
212	-2	6.5202	6.5557	6.2629	6.6958		6.5409	0.0000
222	-2	2.2969	2.2999	2.2734	2.3446		2.3015	1.7709
232	-3	3.399	3.406	3.247	3.535		4.002	0.000
242	-4	9.243	9.329	9.057	9.709			4.892
252	-4	1.86	1.88	1.78	1.98			0.00
262	-5	4.78	4.94	4.71	5.25			1.67
203	-2	0.0000	3.0468	0.0000	0.0000	0.0000	0.0000	0.0000
213	-1	1.0548	1.0590	1.0590	1.0628		1.0561	1.0308
223	-2	1.3844	1.4265	1.3393	1.4389		1.3934	0.0000
233	-3	4.869	5.066	4.979	5.230		5.067	3.286
243	-3	1.015	1.052	1.004	1.108			0.000
253	-4	2.68	3.08	2.99	3.29			1.23
263	-5	7.02	7.70	7.35	8.37			0.00
204	-2	0.0000	9.4326	0.0000	0.0000	0.0000	0.0000	0.0000
214	-2	-1.4882	-0.6087	-1.4594	-1.5618			0.0000
224	-2	1.0983	1.0782	1.1039	1.0847			1.2269
234	-3	2.179	2.479	2.106	2.241			0.000
244	-4	9.578	10.156	9.776	10.309			6.083
254	-4	2.59	2.78	2.59	2.87			0.00
264	-5	7.56	9.11	8.83	9.87			3.00

TABLE 7 CONTINUED

vnv'	Exponent	Dunham HTS Formula[a]	Dunham HTS Num. Int.[b]	Morse Spec.[c]	Morse Diss.En.[d]	RKR Num. Int.[e]	H.O. Expansion[f]	H.O.
303	0	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
313	-2	9.2596	9.5446	8.9677	9.6182			0.000
323	-2	3.5313	3.5043	3.4989	3.6500			2.4792
333	-3	7.079	7.026	6.813	7.496			0.000
343	-3	2.163	2.160	2.140	2.343			0.941
353	-4	5.57	5.50	5.38	6.12			0.00
363	-4	1.61	1.65	1.63	1.87			0.42
304	-1	0.0000	1.6207	0.0000	0.0000	0.0000	0.0000	0.0000
314	-1	1.2272	1.2630	1.2344	1.2403			1.1903
324	-2	2.1771	2.4158	2.1285	2.2971			0.0000
334	-3	8.294	8.749	8.691	9.526			5.059
344	-3	2.211	2.309	2.252	2.518			0.000
354	-4	6.35	7.51	7.61	8.57			2.46
364	-4	2.04	2.25	2.29	2.66			0.00
404	0	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
414	-1	1.2075	1.3588	1.1802	1.2702			0.000
424	-2	4.9670	4.7498	4.9415	5.2140			3.1876
434	-2	1.250	1.190	1.215	1.352			0.000
444	-3	4.243	3.933	4.274	4.776			1.543
454	-3	1.32	1.19	1.30	1.51			0.00
464	-4	4.22	3.95	4.48	5.29			0.86

a. matrix elements in Table 6 with potential constants from Table 1.

b. Dunham wavefunctions from Table 2, potential data from Table 1, and numerical integration.

c. assuming ω_e and $\omega_e x_e$ from ref. 21.

d. assuming ω_e and $\mathcal{D}_e$ (experimental) = 37560 cm^{-1} from ref. 35.

e. ref. 10.

f. ref. 36.

$$+\left(\frac{35l^3 + 433l^2 + 1628l + 1564}{8}\right) a_1^2 a_3 + \left(\frac{231l^3 + 2997l^2 + 11450l + 10432}{128}\right.$$

$$-\left(\frac{105l^3 + 1323l^2 + 4938l + 4536}{16}\right) a_1^3 a_2 \Big]\Big\} \langle 0J|x_J^{l-1}|0J\rangle$$

$$+\frac{\gamma}{2}(l-1)\left\{1 + \frac{\gamma}{4}\left[\left(\frac{3l+14}{4}\right) a_1^2 - (4+l)a_2\right]\right.$$

$$+\frac{\gamma^2}{8}\left[-(l^2 + 9l + 23)\, a_4 + \left(\frac{4l^2 + 38l + 101}{2}\right) a_1 a_3\right.$$

$$+\left(\frac{5l^2 + 45l + 100}{4}\right) a_2^2 + \left(\frac{73l^2 + 745l + 1932}{64}\right) a_1^4$$

$$-\left(\frac{27l^2 + 263l + 664}{8}\right) a_1^2 a_2 \Big]\Big\} \langle 0J|x_J^{l-2}|0J\rangle \qquad (23$$

where γ and a_i are the J-dependent potential constants listed in Table 3. Explicit results for the first few powers of $\langle 0J|x_J^l|0J\rangle$ are listed in Table 4 accurate through terms a_1^5. With these, the g_v functions, and the J-dependent parameters, one can easily obtain the expectation values $\langle vJ|x^l|vJ\rangle$.

Alternatively, one can derive expectation values of x_J^l directly (without first finding the g_v functions) by employing the hypervirial theorem [32]. Starting with the well-known commutator result

$$\langle vJ|[\mathscr{H},A]|vJ\rangle = 0 \qquad (24$$

where $\mathscr{H}$ is the Hamiltonian for nuclear motion and choosing $A = x_J^{l-1}\mathrm{d}/\mathrm{d}x_J$ one obtains [32] the general relation

$$[2(l-1)\,E_v\gamma^2/B_e]\langle vJ|x_J^{l-2}|vJ\rangle + \tfrac{1}{2}\,[(l-1)(l-2)(l-3)\,\gamma^2]\langle vJ|x_J^{l-4}|vJ\rangle$$
$$= \langle vJ|x_J^l[2l + (2l+1)a_1(J)x_J + (2l+2)a_2(J)x_J^2 + \ \ldots\ ]|vJ\rangle \qquad (25$$

The eigenenergies are known through the Dunham expression, $E_v = \sum_{l=0} Y_{l0}\,(v+1/2)^l$, in which the J-dependent potential parameters are assumed. Equation (25) can be solved by an iterative scheme analogous to that used in deriving the g_v functions [32]. The results can be put in the form

$$\langle vJ|x_J^l|vJ\rangle = C_{l-1}\,\langle vJ|x_J^{l-1}|vJ\rangle + C_{l-2}\langle vJ|x_J^{l-2}|vJ\rangle + C_{l-3}\langle vJ|x_J^{l-3}|vJ\rangle \qquad (26$$
$$+\ C_{l-4}\langle vJ|x_J^{l-4}|vJ\rangle$$

where the explicit dependence of C_i on l, v and a_i (correct through a_5) are given in ref. 32. Results for l up to 6 are listed in Table 5. For the special case $v = 0$, eqn. (26) can be shown to reduce to the previously obtained three-term recursion relation, eqn. (21). It is worthwhile to emphasize that all the above results can be extended without theoretical complications however, the algebra becomes quite tedious.

For certain problems, diagonal matrix elements of powers of the internuclear separation itself, R^n, are required (for example: $n = -2$ and -3 for treatment of rotational corrections to the rotational constant B_e, and the spin—spin interaction parameter (cf. section IV)). These are obtainable directly from Table 5 with the use of the binomial expansion

$$\langle vJ|R^n|vJ\rangle = R_e^n \langle vJ|(1+x)^n|vJ\rangle = R_e^n \Big(1 + n\langle vJ|x|vJ\rangle + \frac{n(n-1)}{2!}\langle vJ|x^2|vJ\rangle + \frac{n(n-1)(n-2)}{3!}\langle vJ|x^3|vJ\rangle + \ldots\Big), \quad |x|<1, \tag{27}$$

where sufficient terms in this expression must be retained to assure consistency in powers of γ.

C. Matrix elements off-diagonal in v

Matrix elements of the form $\langle vJ|x_J^l|v'J\rangle$ can readily be obtained by generalizing the previous arguments. For example, to avoid the tedium of lengthy algebraic manipulations necessary for the calculation of the matrix elements for higher powers of x_J, one can derive a recursion relation analogous to eqn. (26) by considering the commutator

$$\langle vJ|[\mathscr{H},[\mathscr{H},x_J^l]]|v'J\rangle.$$

One obtains [32]

$$\langle vJ|x_J^l\Big([l^2 - \frac{(E_v - E_{v'})^2}{4B_e^{\,2}}\gamma^2] + \frac{l(2l+1)}{2}a_1(J)x_J + \frac{l(2l+2)}{2}a_2(J)x_J^2 + \ldots\Big)|v'J\rangle$$
$$= \frac{l(l-1)(E_v + E_{v'})}{2B_e}\gamma^2\langle vJ|x_J^{l-2}|v'J\rangle + \frac{l(l-1)(l-2)(l-3)}{4}\gamma^2\langle vJ|x_J^{l-4}|v'J\rangle \tag{28}$$

This recursion equation can be iterated in the manner described before to provide all matrix elements for $l > |v' - v|$ in terms of those for which $l \leqslant |v' - v|$. The latter elements, however, must be found by a different method. Two alternative ways have been proposed. For instance, one method [18] would be to use the g_v functions, i.e.

$$\langle vJ|x_J^l|v'J\rangle = \frac{\langle 0J|g_{0J}^{vJ}(x_J)[x_J + \gamma^2\beta(1 - 3\gamma^2\beta(1 + a_1/2))]^l g_{0J}^{v'J}(x_J)|0J\rangle}{\langle 0J|[g_{0J}^{vJ}(x_J)]^2|0J\rangle^{\frac{1}{2}}\,\langle 0J|[g_{0J}^{v'J}(xJ)]^2|0J\rangle^{\frac{1}{2}}} \tag{29}$$

while another method has been proposed which bypasses the wavefunctions by considering quantum mechanical sum rules [34]. These sum rules relate the unknown off-diagonal matrix elements to the known diagonal ones and the known (Dunham) energy eigenvalues. Of course, one could always resort to straightforward perturbation theory [31].

In any event, the most accurate results derived to date for $v \leqslant 5$ and $l \leqslant 6$ are listed in Table 6 in terms of the J-dependent parameters. Again, extension of this table is straightforward albeit algebraically tedious.

In order to gauge the accuracy of the above results, matrix elements listed in Tables 5 and 6 to $v = 4$ were computed using the data of Table 1 and are tabulated in Table 7 along with numerical results obtained through a direct integration of the Dunham wavefunctions, numerical Morse results with $\mathcal{D}_e = \omega_e^2/4\omega_e x_e$ (denoted Morse spectroscopic, 'Morse spec'), Morse results with $\mathcal{D}_e$ equal to the experimental dissociation energy (denoted 'Morse diss. en.'), R.K.R. results from previous investigations [10, 11], and finally, harmonic oscillator results (both perturbation expansions and single-term results). It should be noted that the Morse results depend somewhat on the choice of $\mathcal{D}_e$ while the present matrix elements usually fall between*. As can be seen from Table 7, the analytic matrix elements, generally speaking, become progressively less accurate as n increases and as Δv increase. For example, consider the $\Delta v = 2, l = 1$ sequence: aside from the normalization factors, the leading term (i.e. $a_1/2$) is the same for all elements while the first correction term goes as $(v' + v + 1)/(|v' - v| + 1)$. Since for HCl this correction term has the opposite sign from the leading term, the matrix elements will eventually change sign; indeed, the $\langle 3|x|5\rangle$ element will be positive. Cashion's conjecture [11], on the basis of his results, that the first few elements of any sequence have the same sign, is corroborated in the present study for those sequences in which the correction term to a given element has the same sign as the leading term, and for other sequences only if the correction term and both v and v' are small.

In general, the analytic matrix elements are in good agreement with those obtained by the other methods, and, on the whole, are probably more accurate. The only anomalous values in Table 7 are those obtained through the numerical integration of the analytic Dunham wavefunctions for the orthogonality integral and the matrix elements of low powers of x for the higher v levels. These spurious results occur because the analytic wavefunctions are orthogonal only through terms like a_1^5, while in the numerical results contributions corresponding to $a_1^6, \ldots a_1^{10}$ etc. are included and lead to unrealistic results. This result demonstrates the necessity of keeping all terms consistent to a particular power of γ because of large cancellations among the various contributions.

D. Matrix elements off-diagonal in v *and* J

By analogy to eqn. (10), we can write

$$\psi_{v'J'}(x_{J'}) = g_{0J}^{v'J'}(x_J)\,\psi_{0J}(x_J) \tag{30}$$

By defining $g_{0J}^{0J'}(x_J)$ through the equation

$$g_{0J}^{v'J'}(x_J) = g_{0J'}^{v'J'}(x_J + \gamma^2(\beta - \beta') - 3\gamma^4(1 + a_1/2)(\beta^2 - \beta'^2))\,g_{0J}^{0J'}(x_J) \tag{31}$$

the general vibration—rotation matrix elements can be written

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*In the case of HCl, the best estimate of $\mathcal{D}_e$, from thermochemical data [35] with the appropriate zero-point energy correction, is 37560 ± 40 cm^{-1}, whereas the term $\omega_e^2/4\omega_e x_e$ has the value 42342 cm^{-1}.

$$\langle vJ|\mathcal{O}(x)|v'J'\rangle = [\![\langle 0J|g_{0J}^{vJ}(x_J)\ \mathcal{O}\ (x_J + \gamma^2\beta - 3\gamma^4(1 + a_1/2)\beta^2)g_{0J}^{0J'}\ (x_J)$$

$$g_{0J}^{v'J'}\ (x_{J'})|0J\rangle]\!]\ [\![\langle 0J|[g_{0J}^{vJ}(x_J)]^2|0J\rangle^{\frac{1}{2}}\ \langle 0J|[g_{0J'}^{v'J'}\ (x_{J'})]^2|0J\rangle^{\frac{1}{2}}]\!]^{-1} \qquad (32)$$

where the β'-dependent parameters in Table 3 are to be used in $g_{0J'}^{v'J'}\ (x_{J'})$ and the β-dependent parameters everywhere else. In order to use eqn. (32), one need only find the function $g_{0J}^{0J'}\ (x_J)$. As described previously [18], this can be found directly on taking the ratio of $\psi_{0J'}(x_{J'})$ to $\psi_{0J}(x_J)$ using $y(x_J)$ and the J-dependent potential constants. The (normalized) result, accurate enough for most purposes, is presented in Table 8.

If we choose $v = 0$, eqn. (32) simplifies to

$$\langle 0J|\ \mathcal{O}(x)|v'J'\rangle = \langle 0J|\mathcal{O}(x_J + \gamma^2\beta - 3\gamma^4(1 + a_1/2)\ \beta^2)\ g_{0J}^{0J'}\ (x_J)|v'J\rangle \qquad (33)$$

Using this result, the matrix elements listed in Table 6, and the β-dependent parameters, one can derive the two lowest-order rotational corrections to the pure rotational, fundamental and overtone bands. Explicit results for the case of dipole selection rules, viz $J' = J \pm 1$, have already been published elsewhere [29, 37] for $v' = 0$ to 4, but for completeness, these are collected in Table 9. The leading contributions (i.e., γm and $\gamma^2 m^2$) arise essentially from a shift of one wavefunction ($0J$) with respect to the other ($v'J'$) resulting in a breakdown of the orthogonality of the vibration—rotation states. As discussed elsewhere [37], the leading terms remain unchanged for hot-band transitions (i.e., $v,J \rightarrow v + v',\ J \pm 1$) while the second-order corrections (i.e. $\gamma^2 m$) are multiplied by the factor $(v + v' + 1)/(|v - v'| + 1)$.

The vibration—rotation matrix elements for the dipole selection rule will be applied in the following section to an analysis of hydrogen halide spectral line intensities. However, before concluding this section, we wish to point out that, using the results presented above, one can easily derive the vibration—rotation matrix elements corresponding to higher multipole selection rules (i.e., $\Delta J = 2, 3$ etc.).

IV. APPLICATIONS

In this section, we illustrate possible applications of the analytic vibration—rotation matrix elements derived above by two examples; the calculation of the vibration—rotation dependence of molecular parameters, and the analysis of spectrometric intensity data.

A. Spin—spin interaction

First, consider the vibration—rotation average which arises from spin—spin interaction [10]

$$S_{12} \sim \langle vJ|R^{-3}|vJ\rangle = R_e^{-3}\langle vJ|\ (1 + x)^{-3}\ |vJ\rangle$$

$$= R_e^{-3}\ \left\{1 + 6\gamma\left(\frac{3}{4}a_1 + 1\right)\ \left(v + 1/2\right)\right.$$

$$\begin{aligned}
&+ 3\gamma^2 \Bigg[-\beta + \frac{1}{8} \Bigg(\frac{21}{4} a_1^3 - \frac{23}{2} a_1 a_2 + \frac{15}{2} a_3 + 7a_1^2 - 6a_2 + \frac{35}{3} a_1 + 15 \Bigg) \\
&+ \frac{3}{2} \Bigg(\frac{15}{4} a_1^3 - \frac{13}{2} a_1 a_2 + \frac{5}{2} a_3 + 5a_1^2 - 2a_2 + \frac{25}{3} a_1 + 5 \Bigg) \Bigg(v + 1/2 \Bigg)^2 \Bigg] \\
&+ \gamma^3 \Bigg[-\frac{9}{4} \Bigg(9a_1^2 - 8a_2 + 21a_1 + \frac{76}{3} \Bigg) \Bigg(v + 1/2 \Bigg) \beta \\
&+ \frac{3}{8} \Bigg(\frac{31185}{256} a_1^5 - \frac{14259}{32} a_1^3 a_2 + \frac{5145}{16} a_1^2 a_3 + \frac{4677}{16} a_1 a_2^2 - \frac{795}{4} a_1 a_4 \\
&- \frac{715}{4} a_2 a_3 + \frac{175}{2} a_5 + \frac{10395}{64} a_1^4 - \frac{3213}{8} a_1^2 a_2 + \frac{475}{2} a_1 a_3 + \frac{335}{4} a_2^2 - 75a_4 \\
&+ \frac{1925}{8} a_1^3 - \frac{765}{2} a_1 a_2 + \frac{475}{3} a_3 + \frac{2295}{8} a_1^2 - \frac{335}{2} a_2 + \frac{665}{2} a_1 + \frac{700}{3} \Bigg) (v + 1/2) \\
&+ \frac{3}{8} \Bigg(\frac{19035}{64} a_1^5 - \frac{7545}{8} a_1^3 a_2 + \frac{2175}{4} a_1^2 a_3 + \frac{2055}{4} a_1 a_2^2 - 255a_1 a_4 - 225a_2 a_3 \\
&+ 70a_5 + \frac{6345}{16} a_1^4 - \frac{1575}{2} a_1^2 a_2 + 350a_1 a_3 + 85a_2^2 - 60a_4 + \frac{1175}{2} a_1^3 \\
&- 750a_1 a_2 + \frac{700}{3} a_3 + \frac{1125}{2} a_1^2 - 170a_2 + 490a_1 + \frac{560}{3} \Bigg) \Bigg(v + 1/2 \Bigg)^3 \Bigg] \Bigg\} \qquad (34)
\end{aligned}$$

Unfortunately, the experimental data [10] for HCl are not accurate enough to warrant the accuracy represented by eqn. (34). [For H_2, however, the situation is different, and the above results are in excellent accord with both the ab initio results and experiment [32].] We note in passing, that the present results reproduce the Dunham rotational result

$$B_e \langle v0|(1 + x)^{-2}|\ v0\rangle \equiv B_v = \sum_{l=0}^{3} Y_{l1} (v + \tfrac{1}{2})^l \qquad (35)$$

through terms of order γ^3.

B. Dipole-moment functions of hydrogen halides

As a second more extensive application, we analyze the available spectral intensity data (including molecular beam, pure rotation and vibration—rotation measurements) for the hydrogen halides, and deduce the first few coefficients in the power series expansion of the dipole-moment function:

$$M(x) = \sum_{i=0} M_i x^i \qquad (36)$$

It is well known that the intensity of a given vibration—rotational band depends on the square of the corresponding rotationless dipole-moment matrix element, and that this introduces some ambiguity in the set of coefficients, M_i. However, this uncertainty can be removed by considering the effect of vibration—rotation interaction (Herman—Wallis factor) on the individual line intensities, since these vary linearly [9, 37] with the M_i.

TABLE 8

J-DEPENDENT PRE-EXPONENTIAL POLYNOMIAL

$$g_{0J}^{0J'}(x_J) = 1 + \left(\frac{\beta-\beta'}{2}\right)\left\{\left[-\frac{\gamma^2}{4}(3 + 7a_1)\right]\right.$$

$$+ \left[-2\gamma + \gamma^2 \left(-\frac{17}{8}a_1^2 + \frac{5}{2}a_2 - 3a_1 - 4\right)\right] x_J$$

$$+ \left[\frac{\gamma}{2}(a_1 + 3) + \frac{\gamma^2}{2}\left(\frac{29}{8}a_1^3 - 7a_1a_2 + \frac{7}{2}a_3 + \frac{21}{4}a_1^2 - \frac{9}{2}a_2 + 7a_1 + \frac{15}{2}\right)\right] x_J^2$$

$$+ \left[\gamma\left(\frac{a_2}{3} - \frac{a_1^2}{4} - \frac{a_1}{2} - \frac{4}{3}\right) + \gamma^2 \left(-\frac{213}{128}a_1^4 + \frac{77}{16}a_1^2a_2 - 3a_1a_3\right.\right.$$

$$\left.\left. - \frac{13}{8}a_2^2 + \frac{3}{2}a_4 + \frac{9}{2}a_1a_2 - \frac{39}{16}a_1^3 - 2a_3 - \frac{13}{4}a_1^2 + 3a_2 - \frac{15}{4}a_1 - 4\right)\right] x_J^3$$

$$+ \left[\frac{\gamma}{2}\left(\frac{5}{16}a_1^3 - \frac{3}{4}a_1a_2 + \frac{a_3}{2} + \frac{9}{16}a_1^2 - \frac{3}{4}a_2 + a_1 + \frac{5}{2}\right)\right.$$

$$+ \frac{\gamma^2}{4}\left(\frac{403}{64}a_1^5 - \frac{391}{16}a_1^3a_2 + \frac{279}{16}a_1^2a_3 + 18a_1a_2^2 - 11a_1a_4\right.$$

$$- \frac{47}{4}a_2a_3 + \frac{11}{2}a_5 + \frac{297}{32}a_1^4 - \frac{423}{16}a_1^2a_2 + \frac{33}{2}a_1a_3$$

$$+ \frac{33}{4}a_2^2 - \frac{15}{2}a_4 + \frac{99}{8}a_1^3 - \frac{47}{2}a_1a_2 + 11a_3$$

TABLE 8 CONTINUED

$$+ \frac{235}{16} a_1^2 - \frac{55}{4} a_2 + \frac{33}{2} a_1 + \frac{35}{2} \Big) \Big] \; x_J^4$$

$$+ \Big[\gamma \Big(- \frac{7}{64} a_1^4 + \frac{3}{8} a_1^2 a_2 - \frac{3}{10} a_1 a_3 - \frac{3}{20} a_2^2 + \frac{a_4}{5}$$

$$- \frac{3}{16} a_1^3 + \frac{9}{20} a_1 a_2 - \frac{3}{10} a_3 - \frac{3}{10} a_1^2 + \frac{2}{5} a_2 - \frac{a_1}{2} - \frac{6}{5} \Big) \Big] \, x_J^5$$

$$+ \Big[\gamma \Big(\frac{21}{256} a_1^5 - \frac{35}{96} a_1^3 a_2 + \frac{5}{16} a_1^2 a_3 + \frac{5}{16} a_1 a_2^2$$

$$- \frac{a_1 a_4}{4} - \frac{a_2 a_3}{4} + \frac{a_5}{6} + \frac{35}{256} a_1^4 - \frac{15}{32} a_1^2 a_2 + \frac{3}{8} a_1 a_3$$

$$+ \frac{3}{16} a_2^2 - \frac{a_4}{4} + \frac{5}{24} a_1^3 - \frac{a_1 a_2}{2} + \frac{a_3}{3} + \frac{5}{16} a_1^2$$

$$- \frac{5}{16} a_2 + \frac{a_1}{2} + \frac{7}{6} \Big) \Big] \; x_J^6 \Big\}$$

$$+ \left(\frac{\beta - \beta'}{2} \right)^2 \Big\{ 2\gamma^2 \, x_J^2 + (a_1 - 3)\gamma^2 \, x_J^3$$

$$+ \frac{\gamma^2}{4} \left(\frac{5}{2} a_1^2 - \frac{8}{3} a_2 + 7a_1 + \frac{91}{6} \right) \; x_J^4$$

$$+ \frac{\gamma^2}{2} \left(- \frac{7}{8} a_1^3 + \frac{11}{6} a_1 a_2 - a_3 - \frac{19}{8} a_1^2 + \frac{5}{2} a_2 - \frac{29}{6} a_1 - 9 \right) \; x_J^5 \Big\}$$

TABLE 9

ROTATIONAL CORRECTIONS TO VIBRATION-ROTATIONAL MATRIX ELEMENTS

$$< 0J \mid x^1 \mid 0J + 1> \; = \; m^2\gamma^2$$

$$< 0J \mid x^0 \mid 1J \pm 1> \; = \; \left(\frac{\gamma}{2}\right)^{\frac{1}{2}}\left[- 2m\gamma + m\gamma^2 \left(- \frac{15}{4} a_1^2 + 3a_2 - \frac{15}{2} a_1 - 6 \right)\right]$$

$$< 0J \mid x^1 \mid 1J \pm 1> \; = \; \left(\frac{\gamma}{2}\right)^{\frac{1}{2}}\left[\frac{m\gamma^2}{4} (13a_1+3) - \frac{3m^2\gamma^2}{4} (a_1+1)\right]$$

$$< 0J \mid x^2 \mid 1J \pm 1> \; = \left(\frac{\gamma}{2}\right)^{\frac{1}{2}} \left(- m\gamma^2 + 2m^2\gamma^2\right)$$

$$< 0J \mid x^0 \mid 2J \pm 1> \; = \; \frac{\gamma}{\sqrt{2}} \left[\frac{m\gamma}{2} (-a_1 + 3)\right.$$

$$\left. + \frac{m\gamma^2}{2} \left(- \frac{333}{32} a_1^3 + \frac{129}{8} a_1a_2 - 5a_3 + \frac{279}{32} a_1^2 - \frac{99}{8} a_2 + 18a_1 + 15\right) + 2m^2\gamma^2\right]$$

$$< 0J \mid x^1 \mid 2J \pm 1> \; = \; \frac{\gamma}{\sqrt{2}} \left[-2m\gamma\right.$$

$$\left. + m\gamma^2 \left(- \frac{135}{16} a_1^2 + \frac{37}{4} a_2 - \frac{111}{8} a_1 - 10\right) + \frac{m^2\gamma^2}{4} \left(-9a_1^2 + 8a_2 - 9a_1 - 8\right)\right]$$

$$< 0J \mid x^2 \mid 2J + 1> \; = \; \frac{\gamma}{\sqrt{2}} \left[\frac{m\gamma^2}{4} (33a_1 + 9) - \frac{m^2\gamma^2}{2} (a_1 + 3)\right]$$

TABLE 9 CONTINUED

$$< 0J \mid x^3 \mid 2J \pm 1> \; = \frac{\gamma}{\sqrt{2}} \left(-3m\gamma^2 + 3m^2\gamma^2\right)$$

$$< 0J \mid x^0 \mid 3J \pm 1> \; = \frac{\gamma^{3/2}\sqrt{3}}{2} \Bigg[m\gamma \left(- \frac{a_1^2}{8} - \frac{a_2}{6} + a_1 - \frac{4}{3}\right)$$

$$+ m\gamma^2 \Big(- \frac{363}{128} a_1^4 + \frac{37}{16} a_1^2 a_2 + \frac{3}{8} a_1 a_3 + \frac{17}{8} a_2^2 - \frac{5}{4} a_4 + \frac{57}{4} a_1^3$$

$$- 24a_1a_2 + 7a_3 - a_1^2 + 8a_2 - 10a_1 - 10\Big) + m^2\gamma^2 \; (a_1 - 3) \Bigg]$$

$$< 0J \mid x^1 \mid 3J \pm 1> \; = \frac{\gamma^{3/2}\sqrt{3}}{2} \Bigg[\frac{3m\gamma}{2} \; (1 - a_1)$$

$$+ \frac{m\gamma^2}{4} \left(- \frac{717}{8} a_1^3 + \frac{283}{2} a_1a_2 - 39a_3 - \frac{69}{8} a_1^2 - \frac{81}{2} a_2 + 34a_1 + 45\right)$$

$$+ \frac{m^2\gamma^2}{4} \left(- \frac{99}{16} a_1^3 + \frac{3}{4} a_1a_2 + 5a_3 - \frac{99}{16} a_1^2 - \frac{21}{4} a_2 - 6a_1 + 13\right) \Bigg]$$

$$< 0J \mid x^2 \mid 3J \pm 1> \; = \frac{\gamma^{3/2}\sqrt{3}}{2} \Bigg[-2 \, m \, \gamma$$

$$+ \; m\gamma^2 \left(-7a_1^2 + \frac{44}{3} a_2 - 21a_1 - \frac{44}{3}\right) + m^2\gamma^2 \left(- \frac{39}{8} a_1^2 + \frac{9}{2} a_2 - \frac{21}{4} a_1 - 4\right) \Bigg]$$

TABLE 9 CONTINUED

$$< 0J \mid x^3 \mid 3J \pm 1> \; = \frac{\gamma^{3/2}\sqrt{3}}{2} \Big[\frac{m\gamma^2}{2} \; (27a_1 + 9) + \frac{m^2\gamma^2}{4} \; (3a_1 - 9) \Big]$$

$$< 0J \mid x^4 \mid 3J \pm 1> \; = \frac{\gamma^{3/2}\sqrt{3}}{2} \Big(- 6m\gamma^2 + 4m^2\gamma^2 \Big)$$

$$< 0J \mid x^0 \mid 4J \pm 1> \; = \frac{\gamma^2\sqrt{6}}{2} \Big[m\gamma \Big(- \frac{a_1^3}{32} - \frac{a_1a_2}{8} - \frac{a_3}{12} + \frac{5}{32} a_1^2 + \frac{3}{8} a_2 - \frac{3}{2} a_1 + \frac{5}{4} \Big)$$

$$+ m\gamma^2 \; \Big(\frac{315}{256} a_1^5 - \frac{25}{16} a_1^3a_2 - \frac{55}{96} a_1^2a_3 + \frac{a_1a_4}{16} + \frac{75}{16} a_1a_2^2 + \frac{3}{8} a_2a_3 - \frac{7}{8} a_5$$

$$+ \frac{3525}{256} a_1^4 - \frac{135}{8} a_1^2a_2 + \frac{25}{16} a_1a_3 - \frac{105}{16} a_2^2 + \frac{15}{4} a_4 - \frac{405}{16} a_1^3 + \frac{195}{4} a_1a_2$$

$$- \frac{165}{12} a_3 - \frac{175}{32} a_1^2 - \frac{75}{8} a_2 + \frac{75}{8} a_1 + \frac{105}{8} \Big) + m^2\gamma^2 \; \Big(\frac{3}{8} a_1^2 + \frac{a_2}{3} - \frac{11}{4} a_1 + \frac{91}{24} \Big) \Big]$$

$$< 0J \mid x^1 \mid 4J \pm 1> \; = \frac{\gamma^2\sqrt{6}}{2} \Big[m\gamma \; \Big(- \frac{3}{4} a_1^2 - \frac{2}{3} a_2 + \frac{7}{4} a_1 - \frac{4}{3} \Big)$$

$$+ m\gamma^2 \; \Big(- \frac{2865}{128} a_1^4 + \frac{2365}{96} a_1^2a_2 - \frac{73}{48} a_1a_3 + 12a_2^2 - \frac{45}{8} a_4 + \frac{3535}{128} a_1^3 - \frac{1917}{32} a_1a_2$$

$$+ \frac{61}{4} a_3 + \frac{131}{24} a_1^2 + 8a_2 - \frac{135}{16} a_1 - 14 \Big) + m^2\gamma^2 \; \Big(- \frac{3}{4} a_1^4 - \frac{3}{2} a_1^2a_2$$

TABLE 9 CONTINUED

$$+ \frac{a_3}{4} + a_2^2 + a_4 - \frac{3}{4} a_1^3 - \frac{9}{4} a_1 a_2 - a_3 - \frac{3}{4} a_1^2 - a_2 + \frac{13}{4} a_1 - 4 \Big) \Big]$$

$$< 0J \mid x^2 \mid 4J \pm 1> \; = \frac{\gamma^2\sqrt{6}}{2} \Big[m\gamma \; \Big(- \frac{5}{2} a_1 + \frac{3}{2} \Big)$$

$$+ \; m\gamma^2 \; \Big(- \frac{2965}{64} a_1^3 + \frac{3905}{48} a_1 a_2 - \frac{505}{24} a_3 - \frac{1045}{64} a_1^2 - \frac{225}{16} a_2 + \frac{55}{12} a_1 + \frac{125}{8} \Big)$$

$$+ \; m^2\gamma^2 \; \Big(- \frac{11}{2} a_1^3 + \frac{5}{2} a_1 a_2 + \frac{17}{6} a_3 - \frac{45}{8} a_1^2 - 3a_2 - 5a_1 + \frac{9}{2} \Big) \Big]$$

$$< 0J \mid x^3 \mid 4J \pm 1> \; = \frac{\gamma^2\sqrt{6}}{2} \Big[-2m\gamma + m\gamma^2 \; \Big(\frac{5}{4} a_1^2 + 20a_2 - \frac{105}{4} a_1 - 20 \Big)$$

$$+ \; m^2\gamma^2 \; \Big(- \frac{57}{8} a_1^2 + \frac{15}{2} a_2 - 9a_1 - 6 \Big) \Big]$$

$$< 0J \mid x^4 \mid 4J \pm 1> \; = \frac{\gamma^2\sqrt{6}}{2} \Big[\frac{m\gamma^2}{2} \; (35a_1 + 15) \; + 3m^2\gamma^2 \; (a_1 - 1) \Big]$$

$$< 0J \mid x^5 \mid 4J \pm 1> \; = \frac{\gamma^2\sqrt{6}}{2} \Big(- 10 \, m\gamma^2 + 5 \, m^2\gamma^2 \Big)$$

The potential constants utilized in the current study are listed in Table 10. These have been calculated from the experimental Y_{lj} by an iterative solution of the coupled, non-linear Dunham relations. It is important to allow ω_e, B_e and the a_i to vary independently in each iterative step, and to iterate until convergence is reached (typically six steps). This has not always been done consistently in the past [41], and would result in slightly different parameters.

The experimental rotationless transition moments (proportional to the square root of the integrated band intensities),

$$M_0{}^n(0) = \sum_i M_i \langle n0|x^i|00\rangle, \tag{37}$$

which were fitted in deriving the dipole moment coefficients, M_i, are collected in Table 11, and the resulting coefficients in Table 12.

To gauge the accuracy of these dipole-moment functions, we have also calculated the corresponding Herman—Wallis coefficients, C_n and D_n, defined by

$$F_v^{v+n}(m) \equiv \left[\frac{\sum_{i=0} M_i \langle v+n \;\; J \pm 1|x^i|vJ\rangle}{M_v^{v+n}(0)} \right]^2 \simeq 1 + C_n(v)m + D_n m^2 \tag{38}$$

The comparisons with experiment are displayed in Table 13. Since these results do not depend on any additional input parameters, they reflect essentially the internal consistency of the experimental data. Consequently, they are indicative of the accuracy of the derived dipole-moment functions.

The most extensive and accurate experimental data are those for HF and HCl. The resulting dipole-moment functions are very similar in form having large positive M_1, small M_2 and large negative M_3 coefficients. This suggests that the equilibrium separation in these molecules coincides approximately with the inflection point (defined as the point where $M_2 = 0$) on the increasing portion of the dipole-moment function.

On the other hand, the experimental data for HBr are, at present, somewhat controversial [37]. The more recent high-resolution measurements have

TABLE 10

Parameters of the Dunham potential functions for the hydrogen halides

Parameter	HF[a]	HCl[b]	HBr[c]	HI[d]
a_1	−2.25380	−2.36426	−2.43728	−2.53260
a_2	3.4881	3.6629	3.8458	3.9587
a_3	−4.4983	−4.7063	−5.0447	−5.4927
a_4	4.703	5.215	5.445	5.300
a_5	−2.909	−5.522	−4.634	−4.310
γ	1.01267×10^{-2}	7.08350×10^{-3}	6.39028×10^{-3}	5.64032×10^{-3}

[a] ref. 38. [b] ref. 21. [c] ref. 39. [d] ref. 40: a_1, a_2, a_3 are generated from experimental Y_{lj} while a_4 and a_5 are generated from eqn. (6) consistent with a_3 (Dunham) = a_3 (Morse).

TABLE 11

Experimental dipole-moment matrix elements for the hydrogen halides (in Debye units)

Band	HF	HCl	HBr	HI
0—0	1.826526[a]	1.10847[f]	0.82657[i]	0.445[k]
0—1	9.850×10^{-2}[b]	7.12×10^{-2}[g]	3.7036×10^{-2}[j]	-4.016×10^{-3}[l]
0—2	-1.253×10^{-2}[c]	-7.75×10^{-3}[g]	-2.87×10^{-3}[j]	1.80×10^{-3}[m]
0—3	1.628×10^{-3}[d]	5.15×10^{-4}[h]		-1.12×10^{-3}[m]
0—4	-3.48×10^{-4}[e]			
0—5	8.79×10^{-5}[e]			

[a] ref. 42. [b] ref. 43. [c] ref. 44. [d] ref. 45. [e] ref. 46. [f] ref. 10. [g] ref. 47. [h] ref. 9. [i] ref. 48. [j] ref. 49. [k] ref. 50; value deduced from measured DI moment. [l] ref. 51. [m] ref. 52.

TABLE 12

Coefficients of the dipole-moment function for the hydrogen halides (in Debye units)

Coefficient	HF	HCl	HBr	HI
M_0	1.80285	1.09323	0.81835	0.445
M_1	1.3935	1.2069	0.6435	−0.0744
M_2	−0.0583	0.02386	0.168	0.504
M_3	−0.884	−1.673		−1.95
M_4	−0.66	1.6[a]		
M_5	−0.68			

[a] Chosen to give best fit for the molecular beam data, $\langle 11|M|11\rangle$ and $\langle 21|M|21\rangle$.

resulted in intensities approximately one-half those of previous lower resolution work for the fundamental band and three-quarters those of the 2←0 band. However, the self-consistency of the latter measurements as judged by the comparison of experimental and theoretical Herman—Wallis factors is less satisfactory than the earlier work. In any event, using either set of data, one obtains positive first and second derivatives for the dipole-moment function [37]. This would imply that R_e is to the left of the inflection point in HBr. More experimental confirmation is needed to clarify the existing intensity discrepancies and to verify the above conclusion

The situation in HI is even more confusing. There is very strong vibration—rotation interaction in the fundamental band indicating unequivocally that M_0 and M_1 have opposite signs [51]. While the two independent measuremen for $M_0^2(0)$ differ [29] by 10 %, they both show little vibration—rotation interaction. As a consequence of the above, the relative signs of the first three coefficients of the dipole-moment function are (+ — +) and this can be interpreted in two ways; M_0 is positive, thus implying that R_e is beyond both the outer inflection point and the maximum of the dipole-moment function; this situation would be somewhat unexpected in the light of the

TABLE 13

Comparison between theoretical and experimental Herman–Wallis coefficients

Herman–Wallis coefficients	HF		HCl		HBr		HI	
	Exp.	Th.	Exp.	Th.	Exp.	Th.	Exp.	Th.
C_1	-4.96×10^{-2}	-5.38×10^{-2}	-2.60×10^{-2}	-2.66×10^{-2}	-3.12×10^{-2}	-3.26×10^{-2}	1.22×10^{-1}	1.37×10^{-1}
D_1	1.31×10^{-3}	8.63×10^{-4}	4.5×10^{-4}	2.71×10^{-4}	1.30×10^{-3}	3.95×10^{-4}	6.70×10^{-4}	3.51×10^{-4}
C_2	-1.93×10^{-2}	-2.38×10^{-2}	-8.6×10^{-3}	-5.9×10^{-3}	-2.63×10^{-2}	-1.93×10^{-2}	2.54×10^{-2}	3.20×10^{-2}
D_2	8.68×10^{-4}	2.67×10^{-4}	4.1×10^{-4}	4.3×10^{-5}	9.95×10^{-4}	7.07×10^{-5}	1.46×10^{-3}	-3.49×10^{-4}
C_3	-2.1×10^{-2}	-1.71×10^{-2}	1.7×10^{-2}	5.6×10^{-3}			1.58×10^{-2}	1.24×10^{-2}
D_3	1.45×10^{-3}	-1.15×10^{-4}	—	2.37×10^{-3}			—	-1.53×10^{-5}

results for the other hydrogen halides. Another interpretation which is in better agreement with the trend in the other halides but conflicts with physical intuition is that the sign of M_0 is negative (H^-I^+) for small values of R and that the polarity changes near the equilibrium separation. This type of behaviour has been established for the covalently bound molecule CO where the absolute sign of M_0 has been determined by the isotopic variation of the gyromagnetic ratio [53]. To the best of our knowledge, these ratios for HI and its isotopes have not been determined experimentally, but would allow one to discriminate between the above two interpretations. Alternatively, ab initio computations (e.g. self-consistent field all-electron bases) similar to those already carried out for HF [54] could be useful in resolving the above dilemma.

In conclusion, these illustrations indicate how the analytic matrix elements can be used to extract a unique dipole-moment function from vibration—rotation intensity measurements. This function can in turn be used to predict intensities for 'hot' bands and for isotopic molecules. However, great caution must be exercised in extrapolation of the results for the prediction of higher overtone intensities as the power series expansion for $M(x)$ may not converge to the true dipole-moment function. Furthermore, the coefficients of the higher-order powers of x have large error limits associated with them due to accumulated experimental uncertainties. Nevertheless, the accuracy of the present theoretical results suggests that future improvements depend primarily on the availability of improved intensity data.

NOTE ADDED IN PROOF

Since submission of this paper, further results on hydrogen halide intensities have become available. Stocker and Goldman [55], reanalysing previously published frequency and intensity data of HBr, have deduced a third-order dipole-moment function in reasonable agreement with that in Table 12. (Note that the sign of M_3 was omitted in ref. 55; thus M_3 should read —3.01.) P. Bernage and P. Niay (private communication) have recently obtained new frequency and intensity data for lines of the 0—2, 0—3, 0—4 and 0—5 bands of HBr, and have deduced coefficients through M_5 in the dipole-moment expansion; their first three coefficients are again in good agreement with ours. Sileo and Cool [56] have measured emission intensities of HF and DF laser lines, and have obtained ratios of rotationless dipole-moment matrix elements for many overtone transitions. They analysed their data in terms of sixth-order dipole-moment functions for HF and DF separately; the first four coefficients are similar to those listed in Table 12 for HF, but their values of M_4 and M_5 differ significantly from ours. Their M_i values lead to $C_4 > 0$, whereas ours lead to $C_4 < 0$ in agreement with experiment [46]. Also their values of M_4—M_6 for HF differ from those for DF more than would be expected because of failure of the Born—Oppenheimer approximation.

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