One-Photon Spectroscopy of Vibration-Rotational States of Diatomic

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ONE-PHOTON SPECTROSCOPY OF VIBRATION–ROTATIONAL STATES OF DIATOMIC MOLECULES

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ABSTRACT

In this review (containing 185 references) we discuss the vibration–rotational spectroscopy arising from one-photon electric-dipole moment transitions of diatomic molecules in the $^1\Sigma$ state. After a brief survey of the physical effects underlying the interaction of two atoms, we invoke the customary Born–Oppenheimer separation of electronic and nuclear motions in the molecule and introduce the concept of the potential-energy function. We discuss several model functions for the potential energy and their relationship to a general power-series representation, first treated by Dunham, that provides the framework for the analysis of accurate experimental data on transition frequencies. The WKB method of obtaining the term values of energy as functions of the Dunham potential-energy coefficients is described in detail and new results generated by computer algebra are presented. An analytic algorithm for obtaining the wavefunctions corresponding to the Dunham potential-energy function is reviewed and extended. One can use these wavefunctions to derive expressions for expectation values and matrix elements of powers of the reduced displacement from equilibrium; we also discuss several alternative methods, not involving the wavefunctions directly. The use of these matrix elements in the extraction of the dipole-moment function from experimental data on spectral intensities is illustrated by explicit calculations for HCl. In the final section we consider deviations from the Born–Oppenheimer approximation for both the potential-energy and dipole-moment functions, as well as other limitations of the Dunham formalism. Finally we mention briefly some recent trends and developments that we expect to become increasingly important as experimental sophistication advances.

INTRODUCTION

The infrared spectra of a gas containing diatomic molecules can yield much information about the mechanical and electrical properties of the individual molecules.

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The mechanical properties are conventionally discussed in terms of a potential-energy function, whereas the electrical properties may be analogously described quantitatively by means of a dipole-moment function. Our objective in this review is to indicate how a spectroscopic analysis leads to determination of these molecular properties, as well as to suggest some trends in the progress of this kind of investigation. Many of the basic applications and implications of this information in chemistry and physics have been outlined by Herzberg (1950, Chapter 8); the increase of the knowledge of these properties since publication of that monograph has permitted an extension of both the qualitative (i.e., detection and characterization) and quantitative analysis of such molecules occurring in planetary atmospheres (including the terrestrial one), interstellar clouds, etc., as a result of either natural processes or human activities (such as industrial pollution).

In this review, we consider the interaction of polar molecules with electromagnetic radiation; specifically, we restrict our attention to molecules consisting of only two nuclei and the associated electrons interacting with a single photon. We omit discussion of processes involving multiple photons (Grunwald *et al.*, 1978; Halpern *et al.*, 1980), absorption induced by electric fields (Condon, 1932; Brannon *et al.*, 1968), or scattering of light (e.g., Raman spectroscopy) that can be formally regarded as a two-photon process (Weber, 1979). Some of our results may, however, be applicable in the analysis of these phenomena. Our discussions apply strictly only to free molecules; thus we do not treat collision-induced absorption (Poll, 1980), effects of collisional interference (Tipping *et al.*, 1978; Herman *et al.*, 1979), or pressure effects such as collisional broadening and shifting of spectral lines (De Pristo and Rabitz, 1980; Breene, 1981). Instead we assume that each molecule exists for a sufficient interval of time in discrete quantum states that we can specify by rotational, vibrational and electronic quantum numbers. Furthermore, we restrict our discussion to transitions in which the electronic quantum numbers do not change; thus we consider only pure rotational and vibration–rotational transitions. Although one can obtain vibration–rotational spectra of transitions within excited electronic states, almost all experimental data (Herzberg, 1950; Huber and Herzberg, 1979) pertain to the ground state. Furthermore, as most stable molecules have $^1\Sigma$ ground states (two important exceptions being NO and O_2), our results apply specifically to this electronic state; the extension to other electronic states can, however, be made, usually by straightforward generalizations (Gordy and Cook, 1970). Finally, although we recognize that each nucleus may possess intrinsic angular momentum, specified by a quantum number for nuclear spin, we consider only transitions induced by the electric-dipole component of the electromagnetic field; thus we exclude nuclear magnetic resonance effects (Jackman and Cotton, 1975; Slichter, 1980), magnetic dipole transitions (Garstang, 1962; Mizushima, 1975), and electric multipolar transitions of higher order (Buckingham, 1981; Camy-Peyret *et al.*, 1981; Reid *et al.*, 1981). Again, some of our results, such as matrix elements, are useful in these other fields.

Although these circumscriptions defining the scope of our review may seem restrictive, there nevertheless exist abundant data from the vibration–rotational spectra of diatomic molecules in their $^1\Sigma$ states (Barrow *et al.*, 1979; Huber and Herzberg, 1979). The experimental data consist primarily of transition frequencies and intensities, and our purpose is to relate these data to the internuclear potential-energy function and to the electric dipole-moment function of the molecule. As limitations of space preclude a detailed description of the importance and utility of this kind of spectral information, we refer the interested reader to other sources for discussion of these topics (Penner, 1959; Rao and Mathews, 1972; Rao, 1976; Barnes and Orville-Thomas, 1977).

We have organized the review as follows. In the next section, we discuss the potential-energy function. Although many model functions have been proposed, most precise measurements have been interpreted according to the formalism developed by Dunham (1932b); hence we discuss this theory in detail. In the third section, we review the WKB method (Fröman and Fröman, 1965) for obtaining the energies of discrete vibration–rotational states for the Dunham form of the potential energy; we present extensive new results, obtained by methods of computer algebra (Bryukhanov et al., 1980, Howard, 1980; Ogilvie, 1982), that one can use in order to interpret data from recent high-resolution experiments (Dale et al., 1979; Gelfand et al., 1981; Guelachvili et al., 1981). In the fourth section we discuss briefly the wavefunctions (Herman et al., 1970) corresponding to the vibration–rotational states; these functions may be used in obtaining analytic expectation values and matrix elements of various powers of the displacement from equilibrium. The latter integrals, discussed in the fifth section, enable one to analyse measurements of intensities of spectral lines and bands, and to relate these quantities to parameters of the potential-energy and electric dipole-moment functions. Again we present some new results; a more comprehensive compilation will be published separately (Tipping and Ogilvie, 1983). These results are used in the sixth section in an analysis of extensive data for intensities of a specific molecule, HCl. This analysis demonstrates not only the accuracy of the results presented in preceding sections but also some of their limitations. In the final section we discuss some fundamental limitations of the Dunham formalism, such as the Born–Oppenheimer (1927) approximation, the radius of convergence of the Dunham function for potential energy, etc. We indicate briefly some recent refinements in these topics that will become increasingly important as experimental techniques improve. Some speculation concerning future developments, both theoretical and experimental, concludes this review.

POTENTIAL-ENERGY FUNCTIONS

By means of neutron-diffraction experiments, it is possible to locate (within the unit cells of suitable crystalline samples) the time-averaged positions of individual nuclei, with an uncertainty small compared with typical equilibrium internuclear separations. Other diffraction experiments demonstrate that these positions practically coincide, except possibly for hydrides (Coulson and Thomas, 1971), with local maxima of electronic density, but it has not been possible to locate individual electrons in the same way, because of the relatively small mass of these particles. The theoretical formulation of this observation is the Born–Oppenheimer (1927) separation of electronic and nuclear motions (Born and Huang, 1954; Herman and Asgharian, 1966), according to which the total energy of the molecule, with the positions of nuclei fixed in space, becomes to a good approximation a potential energy for the vibrational motion of these nuclei. Although this general concept of molecular structure has been criticized (Woolley, 1976), a defence of it rapidly ensued, from both the theoretical (Essen, 1977) and empirical (Wilson, 1979) points of view. In any case the applicability to diatomic molecules was not doubted (Woolley and Sutcliffe, 1977). Further discussion of the implications of the Born–Oppenheimer approximation appears in the final section of this review.

The potential energy in which the nuclei move is called the potential-energy function $V(R)$, which for diatomic molecules depends parametrically on the internuclear separation R. The form of this potential-energy function, excluding any effects of molecular rotation, is illustrated in *Figure 1* for the molecule CO (Ogilvie, 1981). There
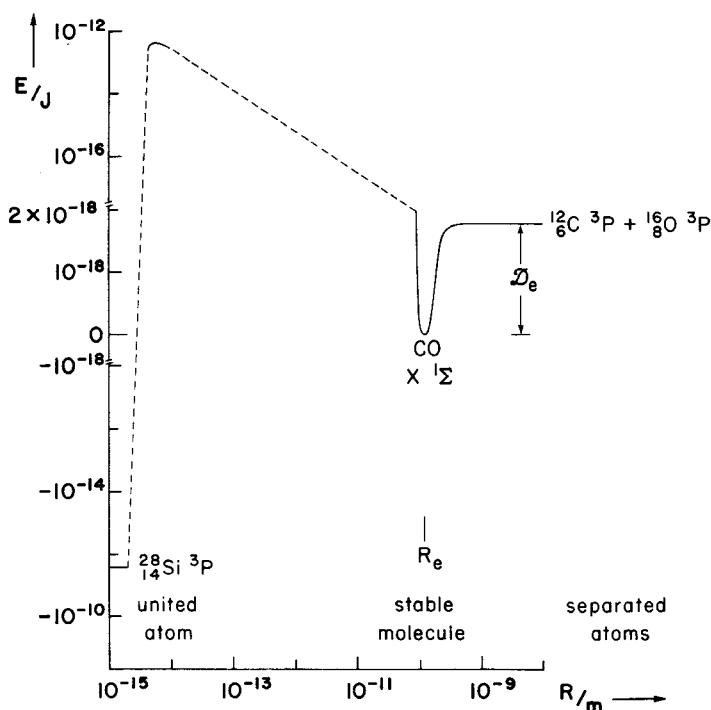
FIG. 1. Qualitative representation of the potential energy of CO as a function of internuclear separation between the limits of united atom and separated atoms. Note that the ordinate scale is discontinuous.

are evident three distinct regions in the figure:

1. The limit for separated atoms at large R.
2. The united atom at small R.
3. The intermediate region about the secondary energy minimum (at R_e) corresponding to a stable molecule.

For all electrically neutral diatomic molecules, or pairs of neutral atoms in the dissociation limit, the potential-energy function has a similar form, except that in some cases (such as $^1H_2$) the nucleus of the united atom may be unstable, implying an energy maximum as $R \to 0$. We hereafter neglect that portion of the potential-energy function at separations much less than R_e where the energy is not accessible by conventional molecular spectroscopy. However, information about the steeply repulsive curve at $R \lesssim R_e$ from atomic scattering experiments or spectroscopic continua may be incorporated into the potential-energy function.

As two neutral atoms approach each other, one can envisage several physical effects (Hirschfelder, 1967a; Margenau and Kestner, 1971) that contribute to the potential-energy function. At large separations $R \gg R_e$, but not so large that retardation effects are important, dispersion forces produce a net attraction proportional to $-R^{-6}$; this is a quantum mechanical effect that may crudely be attributed to an interaction between an instantaneous dipole in one atom and the dipole induced in the other atom. There are also higher multipolar interactions (Hirschfelder *et al.*, 1964), for instance due to the

quadrupole, that have a dependence on $-R^{-8}$, $-R^{-10}$, etc. There are also small contributions proportional to $-R^{-3}$ and $-R^{-4}$ at $R > R_e$, attributed to quantum electrodynamic effects (Hirschfelder, 1967b). Further discussion of long-range interactions is given by Le Roy (1973).

A more important effect for strongly polar molecules, those with dipole moments greater than about 6×10^{-30} C m*, may be interpreted in terms of a partial transfer of charge; from Coulomb's law the potential energy thus varies as $-R^{-1}$ in a region $R_e < R < R_x$, approaching the limit of ionic products of dissociation. Because this limit is of greater energy (for all known diatomic molecules in the ground electronic state) than the limit corresponding to dissociation into neutral atoms, the curve of actual potential energy may be considered to undergo an avoided crossing near some point R_x. The separation R_c at the intersection of the curve for the ionic state with the asymptote of the curve for the dissociation into neutral products may be estimated according to the relation (in SI units):

$$R_c/\text{metre} = 2.3 \times 10^{-28}/[(E_I - E_A)/\text{joule}]; \qquad (1)$$

E_A and E_I are respectively the first ionization energies of the anion and the other atom (Hildenbrand, 1967). This relation for R_c underestimates the actual distance R_x of the avoided crossing by about 15 per cent in the case of some alkali hydride molecules (Yang and Stwalley, 1982).

Apart from these classical electrostatic interactions, there are quantum-mechanical exchange effects that produce an attraction, varying as $-e^{-aR}$; the corresponding term in the so-called 'Coulomb integral' leads to repulsion, varying as $+e^{-2aR}$, in the treatment of H_2^+ or H_2 by Heitler and London (Pauling and Wilson, 1935). In more complicated molecules there are also combinations of such exponential functions and their products with polynomials in R.

In the case of some pairs of neutral atoms, each with ${}^1S$ ground states (like Be_2 or NeAr), the binding energy $\mathcal{D}_e$ may be relatively small, and the corresponding equilibrium separation relatively large, by comparison with those values for CO in *Figure 1*. It remains true, however, that dispersion forces invariably cause a net attraction between the neutral atoms at large distances. If, however, both of the separated atoms carry a net charge of the same sign, then a Coulomb repulsion operates at all meaningful separations, and an energy maximum may occur in the region $R > R_e$. Similar complications may be applicable if one separated atom (or both) is in an excited electronic state; then phenomena such as double minima of the potential-energy function can result at intermediate separations.

It is evident that any attempt to represent such varied behaviour by a potential-energy function of relatively simple analytic form must prove unsuccessful. Nevertheless, many empirical model functions have been proposed (Varshni, 1957; Steele *et al.*, 1962; Torrens, 1972; Goodisman, 1973) in order to interpret results in molecular spectroscopy and various other investigations of molecular structure and interactions. Most of these functions have been of the types of inverse powers, R^{-n}, or exponential functions, e^{-R}, or some combination thereof. One early function still in use is that due to Lennard-Jones (1924, 1925).

$$V(R) = \mathcal{D}_e[(R_e/R)^{12} - 2(R_e/R)^6] \qquad (2)$$

We can conveniently express this function in terms of a reduced variable x for internuclear separation, $x \equiv (R - R_e)/R_e$; furthermore, if we choose the zero of the

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* 3.33564×10^{-30} C m $= 1$ Debye.

energy scale to correspond to the minimum at $R = R_e$, we obtain

$$V(x) = \mathscr{D}_e[1 - 1/(1+x)^6]^2. \tag{3}$$

This form can be made more general by replacement of the power 6 by a parameter n, in order that one can generate a series of functions having attractive $(-R^{-n})$ and repulsive $(+R^{-2n})$ contributions. The special case $n = 1$, known as the Kratzer (1920) potential-energy function, was one of the first to be solved according to wave mechanics (Fues, 1926). Another function admitting an exact solution of the Schrödinger equation is of the exponential type, due to Morse (1929):

$$V(x) = \mathscr{D}_e(1 - e^{-a_M x})^2 \tag{4}$$

More complicated functions, containing more free parameters, are being continually proposed (e.g., Thakkar, 1975; Huffaker, 1976).

All these specified functions are anharmonic in the sense that classically the frequency of oscillation depends on the amplitude, and another common property is that the dissociation energy $(x \to \infty)$ is finite. Furthermore the quantum-mechanical eigen-energies merge, as the energy increases towards the dissociation limit. In contrast, for a classical harmonic oscillator, the frequency is independent of the amplitude, or quantum-mechanically the energy difference between adjacent eigenstates is constant, inconsistent with a finite energy of dissociation. In general the number of harmonic potential -energy functions is uncountable (Nieto, 1981), but one of these, the canonical harmonic oscillator, has a particularly simple form, $V(x) = a_0 x^2$. Although this parabolic dependence is obviously a poor approximation to the potential-energy function of a real molecule, such as CO in *Figure 1*, this form may be taken as a limiting case for infinitesimal vibrations about $x = 0$. Anharmonic terms can be incorporated within an expansion as a power series. The function due to Dunham (1932b) has this form:

$$V(x) = a_0 x^2 (1 + \sum_{j=1} a_j x^j) \tag{5}$$

Because of the variable number of coefficients a_j available as parameters to be fitted for a particular molecule, this function is quite flexible, and can thus represent the actual potential-energy function accurately within some limited range of internuclear separation about $R = R_e$ or $x = 0$; this is just the range in which the Born–Oppenheimer approximation is most valid (Longuet-Higgins, 1961).

The general inverse-power function and the Morse function are useful approximations for real molecules, if experimental data are sparse, because they display qualitatively correct behaviour over the entire range of internuclear separation and have the correct dissociation limit. One can convert these functions into the Dunham form by finding algebraic relations of the potential-energy coefficients a_j to the parameters of the other functions (Tipping and Ogilvie, 1976). For the general inverse-power function.

$$V(x) = \mathscr{D}_e[1 - 1/(1+x)^n]^2 \tag{6}$$

the coefficients are:

$$a_0 = n^2 \mathscr{D}_e;$$
$$a_j = \frac{2(-1)^j}{n(j+2)!} \left[\frac{(2n+j+1)!}{(2n)!} - \frac{(n+j+1)!}{n!} \right], j > 0. \tag{7}$$

Some particular cases are, for $j > 0$,

$$n = 1: a_j = (-1)^j (j+1)$$

$$n = 3: a_j = (-1)^j (j+1)(j+3)(j+4)(j^2 + 17j + 90)/1080 \qquad (8)$$

$$n = 6: a_j = (-1)^j (j+1)(j+3)(j+4)(j+5)(j+6)(j+7)(j+20)$$

$$(j^4 + 42j^3 + 743j^2 + 6342j + 28512)/3(12!)$$

For the Morse function, we have similarly: $a_0 = a_M^2 D_e$;

$$a_j = (2^{j+2} - 2)(-a_M)^j/(j+2)!, j > 0 \qquad (9)$$

One can also convert into the Dunham form any other analytic and continuous function $V(R)$ for the potential energy of an electronic state having a minimum of energy at $R = R_e$ by finding derivatives of the function at $R = R_e$:

$$a_0 = \tfrac{1}{2} R_e^2 [d^2 V(R)/dR^2]_{R=R_e};$$

$$a_j = (2R_e^j)[d^{j+2} V(R)/dR^{j+2}]_{R=R_e}/(j+2)! [d^2 V(R)/dR^2]_{R=R_e}, j > 0 \qquad (10)$$

As we show in the following section, one can determine the eigen-energies for the function in equation (5) in terms of the potential-energy coefficients a_j. Thus by transforming another function into the Dunham form, one can find the approximate eigen-energies of other potential-energy functions.

There are several procedures by which one can determine the potential-energy function from an experimental spectrum of any particular molecule. A typical spectrum generally consists of several different bands (denoted by vibrational quantum numbers of initial and final states) each of which is composed of numerous lines (similarly denoted by rotational quantum numbers). Additional information may be available from spectra of isotopic species of the same substance. For instance, the spectra of gaseous hydrogen chloride commonly consist of lines due to $^1H^{35}Cl$ and $^1H^{37}Cl$; less common isotopic molecules such as $^2H^{35}Cl$, $^2H^{37}Cl$, $^3H^{35}Cl$, etc. can be detected after suitable chemical preparation. For HCl, about 1200 lines in total have been measured with at least moderate precision for the pure rotational and the vibration–rotational transitions of all these isotopic variants. If, for each vibration–rotational band, we fit the line wavenumbers to a set of band parameters, in particular the band origin v_0, the rotational (B'_v, B''_v) and centrifugal distortion (D'_v, D''_v, etc.) parameters of the upper and lower vibrational states (Herzberg, 1950), then we generate values of ~ 260 parameters; these may include redundant values of the same rotational parameters B_v, D_v obtained from different vibrational transitions having one state in common. We can further reduce these band parameters for $^1\Sigma$ states according to the term values $E(v, J)$ for each isotopic species i by using a double summation over vibrational v and rotational (angular momentum) J quantum numbers:

$$E^i(v, J) = \sum_{k=0} \sum_{l=0} Y_{kl}^i (v + \tfrac{1}{2})^k [J(J+1)]^l, \qquad (11)$$

in which the energy coefficients Y_{kl}^i may at this stage be regarded as fitting parameters. By this means we can decrease the number of parameters from ~ 260 to ~ 50. As is discussed in the last section, the energy coefficients Y_{kl}^i are dependent on the various masses, according to (Ross et al., 1974):

$$Y_{kl}^i = \mu_i^{-(k+2l)/2} U_{kl}[1 + m_e(\Delta_{kl}^a/M_a + \Delta_{kl}^b/M_b)]; \qquad (12)$$

in this equation the U_{kl} quantities and $\Delta_{kl}^{a,b}$ parameters are isotopically invariant; the

mass of the electron is m_e, and the reduced mass μ_i of each isotopic molecule i is related to the atomic masses M_a and M_b according to

$$\mu_i = M_a M_b / (M_a + M_b). \tag{13}$$

By this means one can decrease the total number of parameters from ~ 50 to ~ 25 (Coxon and Ogilvie, 1982): the quantities U_{kl} and $\Delta_{kl}^{a,b}$ (because only a few of the possible $\Delta_{kl}^{a,b}$ values can be determined with statistical significance).

The term-value equation (11) may be transformed to

$$E^i(v, J) = \sum_{k=0} \sum_{l=0} U_{kl}^i [\mu^{-1/2}(v + \tfrac{1}{2})]^k [\mu^{-1}(J^2 + J)]^l \tag{14}$$

in which the U_{kl}^i quantities still contain a small mass dependence:

$$U_{kl}^i = U_{kl}[1 + m_e(\Delta_{kl}^a / M_a + \Delta_k^b / M_b)] \tag{15}$$

however, almost all the mass dependence has been incorporated into the quantities $\mu^{-1/2}(v + \tfrac{1}{2})$ and $\mu^{-1}[J(J+1)]$ that can be regarded as mass-reduced quantum numbers (Stwalley, 1975).

So far, the analysis of the wavenumbers of the spectral lines has proceeded entirely empirically, without recourse to any physical model, but merely dependent on ascribing quantum numbers to discrete states and assuming a convergent representation of the term values (Niay et al., 1977). This fitting procedure is useful and rapidly convergent provided that the states involved are neither perturbed nor near the dissociation limit.

Using the concept of a suitable potential-energy function, one can then find relationships between the parameters of this function and the energy coefficients U_{kl} or Y_{kl} such that the number of parameters required to reproduce accurately the wavenumbers of measured spectral lines can be still further decreased. Consequently one is able to ascribe some physical meaning to the U_{kl} or Y_{kl} quantities expressed in terms of the potential-energy coefficients and R_e. Furthermore one can test the internal consistency of the over-determined set of U_{kl} or Y_{kl}. One also achieves a predictive capacity both for further (undetermined) Y_{kl} of the same isotopic molecule and for wavenumbers of lines corresponding to unobserved transitions of a different isotopic variant; such predicted transitions, to have an accuracy commensurate with that of measured transitions, should lie within the range of energy for which the potential-energy function has been experimentally defined. These results have been realized in the case of HCl, for which 17 molecular parameters suffice to reproduce the wavenumbers of 1200 lines of the various isotopic species within the range of energy up to 0.52 of the dissociation limit (Coxon and Ogilvie, 1982); the values are presented in *Table 1*.

Three slightly different approaches have been applied for determining an analytic potential-energy function from experimental data (wavenumbers of transitions), with full monitoring of statistical significance:

1. Through the band parameters (B_v, D_v, etc.) to the Y_{kl} and thence to the coefficients a_j (Ogilvie and Koo, 1976).
2. Through the U_{kl} without direct use of the band parameters (by means of a merge procedure; Coxon and Ogilvie, 1982).
3. Directly from the line wavenumbers to the coefficients a_j (Niay et al., 1977).

All three approaches should yield equivalent results if carried out with proper statistical techniques.

Before completing this section on potential-energy functions, we mention an

TABLE 1. Molecular parameters of HCl
(Coxon and Ogilvie, 1982)

$$R_e = 1.2746084 \times 10^{-10} \pm 1.5 \times 10^{-16} \; m$$
$$a_0 = 2.111393 \times 10^7 \pm 56 \; m^{-1}$$
$$a_1 = -2.3633725 \pm 3.5 \times 10^{-5}$$
$$a_2 = 3.6605756 \pm 1.9 \times 10^{-4}$$
$$a_3 = -4.74921 \pm 0.0013$$
$$a_4 = 5.4529 \pm 0.0099$$
$$a_5 = -5.516 \pm 0.032$$
$$a_6 = 4.284 \pm 0.13$$
$$a_7 = -1.726 \pm 0.42$$
$$a_8 = -0.0267 \pm 0.39$$
$$\Delta_{10}^H = -0.06382 \pm 0.00088$$
$$\Delta_{10}^{Cl} = 0.1280 \pm 0.016$$
$$\Delta_{20}^H = -0.3824 \pm 0.017$$
$$\Delta_{01}^H = 0.1320 \pm 0.0007$$
$$\Delta_{01}^{Cl} = -0.250 \pm 0.017$$
$$\Delta_{11}^H = 0.462 \pm 0.019$$
$$\Delta_{02}^H = 0.74 \pm 0.04$$

alternative, purely numerical method for constructing potential-energy curves from experimental data. This procedure, due to Rydberg (1931, 1933), Klein (1932) and Rees (1947) and referred to as the RKR method, uses the spectral data $E(v, J = 0)$ and B_v and two auxiliary integrals in order to compute the inner and outer turning points of the nuclear motion. These points can then be fitted by a suitable interpolation scheme, for instance a spline function, in order to generate a potential-energy curve. This procedure is in principle no more accurate than the analytic Dunham treatment (Jarmain, 1960; Hurley, 1962; Davies and Vanderslice, 1966a,b), and is not considered explicitly in this review.

THE WKB METHOD AND DISCRETE ENERGIES

For diatomic molecules in $^1\Sigma$ states, we can factor the wavefunction $\Psi(\vec{R})$ describing the nuclear motion (within the Born–Oppenheimer approximation) into a radial part $\Phi(R)$ and an angular part:

$$\Psi(R, \theta, \phi) = \Phi(R) Y_{JM_J}(\theta, \phi) \tag{16}$$

in which Y_{JM_J} is the usual spherical harmonic function (Rose, 1957). Making the traditional substitutions,

$$x = (R - R_e)/R_e \tag{17}$$

and

$$\psi(x) = R\Phi(R), \tag{18}$$

we find that the function $\psi(x)$ satisfies the radial Schrödinger equation

$$\frac{d^2 \psi_{vJ}(x)}{dx^2} + \frac{2\mu_N R_e^2}{\hbar^2} \left[E(v, J) - V(x) - \frac{\hbar^2 J(J+1)}{2\mu_N R_e^2 (1+x)^2} \right] \psi_{vJ}(x) = 0 \tag{19}$$

in which μ_N is the reduced nuclear mass. We first consider the case of no rotation $(J = 0)$; later we generalize our results to include the rotational effects.

One can determine the discrete energies, $E_v \equiv E(v, J = 0)$, for the vibrational problem

$$\frac{d^2\psi_v(x)}{dx^2} + \frac{1}{B_e}[E_v - V(x)]\psi_v(x) = 0 \tag{20}$$

(in which E_v, $V(x)$ and $B_e \equiv h/8\pi^2\mu_N cR_e^2$ are all expressed in wavenumber units), via the WKB* (or quasi-classical or semi-classical) method without solving explicitly for the eigenfunctions. Briefly, in this method we assume a solution of the form

$$\psi_v(x) = \exp(i/\hbar \int_0^x y(x', E, \hbar)dx') \tag{21}$$

in which $y(x', E, \hbar)$ is represented by its asymptotic series

$$y(x', E, \hbar) = \sum_{s=0}^{\infty} (\hbar/i)^s y_s(x', E) \tag{22}$$

and substituted into equation (20); hereafter we ignore the formal distinction between x' and x. Equating powers of $\hbar$, we find

$$y_0 = \pm\hbar[(E - V(x))/B_e]^{1/2} \tag{23}$$

and the recursion formula for the y coefficients:

$$dy_{s-1}/dx = -\sum_{m=0}^{s} y_{s-m}y_m, \quad s = 1, 2, \ldots \tag{24}$$

These are expressed in terms of $V(x)$ and its derivatives with respect to x. We then determine the eigen-energies from the quantization condition

$$\oint y_0(x, E_v)\, dx + \sum_{s=2} (\hbar/i)^s \oint y_s(x, E_v)\, dx = 2\pi\hbar(v + \tfrac{1}{2}) \tag{25}$$

in which the domain of x is the complex plane cut along the real axis between the classical turning points; the integration is along a contour, not crossing the cut, and contains only the singularities at the turning points. Kesarwani and Varshni (1980a, b, 1982) have given explicit results for the first six non-vanishing integrals; although further integrals could easily be derived, these are not warranted for the spectroscopic applications in which we are interested, because of the limited accuracy of the experimental data, the approximate nature of the Born–Oppenheimer separation and the neglect of relativistic effects (Tipping and Herman, 1966). Using equation (25), one can determine the vibrational energies implicitly through the formula,

$$\oint(E_v - V(x))^{1/2}\, dx - B_e\oint V'^2(E_v - V(x))^{-5/2}\, dx/2^5 - B_e^2\oint[49V'^4$$

$$- 16V'V'''(E_v - V(x))^2](E_v - V(x))^{-11/2}\, dx/2^{11} - B_e^3\oint[1675V'^6$$

$$(E_v - V(x))^{-17/2} + 4020V'^4V''(E_v - V(x))^{-15/2} + 48(20V'^3V'''$$

$$+ 49V'^2V''^2)(E_v - V(x))^{-13/2} + 64(18V'V''V''' - V''^3)(E_v - V(x))^{-11/2}$$

$$+ 128V'''^2(E_v - V(x))^{-9/2}]\, dx/2^{16} = 2\pi B_e^{1/2}(v + \tfrac{1}{2}) \tag{26}$$

* There is considerable controversy regarding the nomenclature of this method; some authors prefer WKBJ (Kesarwani and Varshni, 1980a,b), JWKB (Fröman and Fröman, 1965) or WBK (Beckel, 1964). In conformity with Dunham's (1932a) pioneering work, we use the notation WKB.

in which $V' \equiv dV(x)/dx$, etc. Following Dunham (1932b), we rewrite the potential energy of equation (5) in the form

$$V(x) = \gamma^{-2} B_e x^2 (1 + \sum_{j=1} a_j x^j) \qquad (27)$$

in which $a_0 = B_e/\gamma^2$, and $\gamma \equiv 2B_e/\omega_e$ plays the role of a dimensionless expansion parameter, having values typically within the range 10^{-2}–10^{-3}. The contour integrations can be carried out by a direct but tedious evaluation of the residues.

To simplify this procedure and to avoid the possibility of errors, we have used programs in computer algebra to carry out the operations analytically (Ogilvie, 1982). Expressing the results in the Dunham form

$$E_v = \sum_{k=0} Y_{k,0}(v + \tfrac{1}{2})^k, \qquad (28)$$

we have determined all contributions to the $Y_{k,0}$ expressions up to, and including, terms of order a_1^{10} ($a_1 a_9$, a_2^5, a_{10}, etc.). For most applications, only results up to a_1^6 are required, and these have been published. The set of $Y_{k,0}$ with $k \leqslant 4$ was first given by Dunham (1932b), with the exception of the a_1^6 contribution to $Y_{0,0}$ given implicitly by Sandeman (1940) and explicitly by Bouanich (1978a). The extended set of $Y_{k,0}$ coefficients will be published elsewhere (Tipping and Ogilvie, 1983).

These results can easily be compared with results from other common potential-energy functions, such as that of Morse, equation (4). By substituting the results in equation (9) into the expressions for $Y_{k,0}$ we find:

$$Y_{1,0} = \omega_e \quad \text{and} \quad Y_{2,0} = -B_e a_M^2; \qquad (29)$$

all the other $Y_{k,0}$ vanish in agreement with the known result (Morse, 1929; ter Haar, 1946). This substitution procedure is a convenient algorithm for checking the expressions and for guarding against transcription errors.

Returning to the solution of equation (19), we incorporate the rotational effects in a formal way following the method outlined by Dunham (1932b). First we expand the rotational term in the potential-energy function, with $[J(J+1)]$ denoted by β:

$$\begin{aligned}
V(x, \beta)/B_e &= \gamma^{-2} x^2 (1 + \sum_{j=1} a_j x^j) + \beta/(1+x)^2 \\
&= \beta - 2\beta x + (\gamma^{-2} + 3\beta)x^2 + (\gamma^{-2} a_1 - 4\beta)x^3 + \cdots \\
&\quad + (\gamma^{-2} a_n + (-1)^n (n+3)\beta)x^{n+2} + \cdots
\end{aligned} \qquad (30)$$

Then we eliminate the linear term $(-2\beta x)$ by a coordinate translation:

$$x = x_J + \varepsilon(\beta), \qquad (31)$$

in which the new β-dependent variable x_J represents the reduced displacement from the minimum of the effective potential energy: i.e.,

$$\left. \frac{\partial V(x, \beta)}{\partial x} \right|_{x=\varepsilon(\beta)} = 0. \qquad (32)$$

By reverting the series obtained from equation (32) one can write

$$\varepsilon(\beta) = \sum_{j=1} h_j (\gamma^2 \beta)^j; \qquad (33)$$

the coefficients h_i through terms in a_1^6 are listed in *Table 2*.* Using equations (31) and (33), we then rewrite the effective potential-energy function, apart from a constant term, in the Dunham form:

$$V(x, \beta) = \gamma^{-2} B_e f_0(\beta) + \gamma^{-2}(\beta) B_e x_J^2 (1 + \sum_{j=1} a_j(\beta) x_J^j) \qquad (34)$$

for which the leading terms of the β-dependent coefficients are presented in Table 3. Finally, the vibration–rotational eigen-energies $E(v, J)$ are given by

$$E(v, J) = E_v(\beta) + \gamma^{-2} B_e f_0(\beta) = \sum_{k=0} \sum_{l=0} Y_{kl}(v+\tfrac{1}{2})^k [J(J+1)]^l; \qquad (35)$$

the expressions for $Y_{0,l}$ are obtained from $f_0(\beta)$, and the other Y_{kl} ($l > 0$) from the corresponding $Y_{k,0}$ on substitution of $\gamma(\beta)$ and $a_j(\beta)$. The new results with terms up to a_1^6 are presented in *Table 4*. We note that the other Y_{kl} not given in *Table 4* agree with the previously published expressions (Dunham, 1932b; Sandeman, 1940; Woolley, 1962, 1972; Bouanich, 1978a) except for that of $Y_{3,2}$ given by Woolley (1962) which was incorrect. The complete set of results including terms up to order a_1^{10} will be published elsewhere.

As an independent check on these results for Y_{kl}, one can consider the analogous results for a simpler potential-energy function (including rotation) that can be solved exactly, namely the Fues (1926) function:

$$V(x) = \mathcal{D}_e [1 - 1/(1+x)]^2 + B_e \beta /(1+x)^2 \qquad (36)$$

The vibration–rotational energies associated with this function are (Fues, 1926):

$$E(v, J) = B_e \gamma^{-2} \{1 - 1/[1 + 2\gamma(v+\tfrac{1}{2})(1 + \gamma^2 (J+\tfrac{1}{2})^2)^{1/2} + \gamma^2((v+\tfrac{1}{2})^2 + (J+\tfrac{1}{2})^2)]\} \qquad (37)$$

Expanding this result for low vibrational and rotational levels ($\gamma^2(v+\tfrac{1}{2})^2$ and $\gamma^2(J+\tfrac{1}{2})^2 < 1$), we obtain simple expressions for the Y_{kl} coefficients, listed in Table 5 as an extension of Sandeman's (1940) results. We obtained identical results by substituting the relations for the a_j coefficients in equation (8) into our Y_{kl} formulae. Again this procedure provides a convenient test of the more general Dunham results in

TABLE 5. Values of Y_{kl} for the potential-energy function of Fues

$Y_{0,0} = \gamma \omega_e /8$	$Y_{1,0} = \omega_e - 3\gamma^2 \omega_e /8$
$Y_{0,1} = \gamma \omega_e /2 - \gamma^3 \omega_e /4$	$Y_{1,1} = -3\gamma^2 \omega_e /2 + 15\gamma^4 \omega_e /16$
$Y_{0,2} = -\gamma^3 \omega_e /2 + 3\gamma^5 \omega_e /8$	$Y_{1,2} = 15\gamma^4 \omega_e /8 - 105\gamma^6 \omega_e /64$
$Y_{0,3} = \gamma^5 \omega_e /2 - \gamma^7 \omega_e /2$	$Y_{1,3} = -35\gamma^6 \omega_e /16$
$Y_{0,4} = -\gamma^7 \omega_e /2 + 5\gamma^9 \omega_e /8$	$Y_{1,4} = 315\gamma^8 \omega_e /128$
$Y_{0,5} = \gamma^9 \omega_e /2$	$Y_{1,5} = -693\gamma^{10}\omega_e /256$
$Y_{0,6} = -\gamma^{11}\omega_e /2$	$Y_{1,6} = 3003\gamma^{12}\omega_e /1024$
$Y_{0,7} = \gamma^{13}\omega_e /2$	$Y_{2,0} = -3\gamma \omega_e /2 + 3\gamma^3 \omega_e /4$
$Y_{0,8} = -\gamma^{15}\omega_e /2$	$Y_{2,1} = 3\gamma^3 \omega_e$
	$Y_{2,2} = -9\gamma^5 \omega_e /2$
	$Y_{2,3} = 6\gamma^7 \omega_e$
	$Y_{2,4} = -15\gamma^9 \omega_e /2$
	$Y_{3,0} = 2\gamma^2 \omega_e$
	$Y_{3,1} = -5\gamma^4 \omega_e$
	$Y_{3,2} = 35\gamma^6 \omega_e /4$
	$Y_{4,0} = -5\gamma^3 \omega_e /2$

* Because of their length, Tables 2, 3, 4, 6, 8 and 9 are in the Appendix at the end of the review.

which the a_j are assumed both to be independent and to be determined through fitting an experimental spectrum.

VIBRATION–ROTATIONAL WAVEFUNCTIONS

One can obtain the vibrational wavefunctions $\psi_v(x)$, or more generally the vibration–rotational wavefunctions $\psi_{vJ}(x)$ corresponding to the potential-energy function in equation (30), by following the method proposed by Herman *et al.* (1970) and extended by Tipping and Ogilvie (1976). Although we outline briefly this method for completeness, there are powerful alternative methods for deriving the physically meaningful matrix elements of x directly (obviating the need for explicit wavefunctions) that are discussed in the following section. Even though the algebra becomes tedious quite rapidly with the addition of higher-order terms in the Dunham potential-energy function, the algorithm is quite simple and amenable to algebraic programming (Ogilvie, 1982). For this reason we outline only the essential steps here.

In parallel with our discussion of the energy states in the preceding section, we first consider only the vibrational case, afterwards generalizing our results using the β-dependent potential-energy parameters. The first step of the method consists of a WKB-like transformation of the wavefunctions

$$\psi_0(x) = \exp(-\tfrac{1}{2} \int_0^x y(x')\, dx') \tag{38}$$

and

$$\psi_v(x) = g_v(x)\psi_0(x), \tag{39}$$

resulting in a pair of coupled non-linear differential equations:

$$y^2(x) - 2dy(x)/dx - 4[V(x) - E_0]/B_e = 0 \tag{40}$$

and

$$d^2g_v(x)/dx^2 - y(x)\,dg_v(x)/dx + [(E_v - E_0)/B_e]g_v(x) = 0, \tag{41}$$

that are equivalent to the vibrational Schrödinger equation (20).

We seek solutions in power series of the form

$$y(x) = \sum_{j=0}^{\infty} b_j x^j \tag{42}$$

and

$$g_v(x) = \sum_{j=0}^{\infty} c_{vj} x^j \tag{43}$$

for a given vibrational state labelled by v, in the following way. First we obtain the exact solution for the harmonic oscillator ($V(x) = \gamma^{-2} B_e x^2$ and $E_v = 2\gamma^{-1} B_e(v + \tfrac{1}{2})$), for which $y(x) = 2x/\gamma$ and the $g_v(x)$ functions are proportional to the Hermite polynomials (Pauling and Wilson, 1935). Then in the first iteration we include one additional term in the potential energy, $\sim a_1 x^3$, while terms of order higher than a_1 (such as a_1^2, a_2 etc.) appearing in the (known) energies E_v are neglected. We concurrently truncate the series, equations (42) and (43) according to

$$b_j = 0, j \geqslant 3 \tag{44}$$

and

$$c_{vj} = 0, \, j \geqslant v + 2; \tag{45}$$

then we determine the coefficients b_j and c_{vj} using the results of the previous iteration. We can continue this procedure, keeping one additional term in $y(x)$ and $g(x)$ each iteration, and thus generate accurate vibrational wavefunctions for the Dunham potential-energy function. Results for $y(x)$ and $g_v(x)$ up to terms of order a_1^5 inclusive for $0 \leqslant v \leqslant 4$ (Tipping and Ogilvie*, 1976), and up to a_1^3 for $0 \leqslant v \leqslant 10$ (Herman *et al.*,† 1970), have already been published. By means of methods of computer algebra, we have extended these results to include terms up to a_1^6 for $y(x)$ and $g_v(x)$, $0 \leqslant v \leqslant 7$.

One can thus express vibrational matrix elements in terms of ground-state expectation values and the functions $g_v(x)$ (Herman *et al.*, 1970)

$$\int_0^\infty \psi_v(x) x^l \psi_{v'}(x) \, dx \equiv \langle v | x^l | v' \rangle$$

$$= \frac{\langle 0 | g_v(x) x^l g_{v'}(x) | 0 \rangle}{\langle 0 | g_v^2(x) | 0 \rangle^{1/2} \langle 0 | g_{v'}^2(x) | 0 \rangle^{1/2}} \tag{46}$$

the denominator of which contains the normalization factors.

One can easily extend this procedure to include rotational effects. The generalization of equation (46) is

$$\langle vJ | x^l | v'J \rangle = \frac{\langle 0J | g_v(x_J) [x_J + \varepsilon(\beta)]^l g_{v'}(x_J) | 0J \rangle}{\langle 0J | g_v^2(x_J) | 0J \rangle^{1/2} \langle 0J | g_{v'}^2(x_J) | 0J \rangle^{1/2}} \tag{47}$$

in which $g_v(x_J)$ is obtained by substituting the β-dependent potential-energy parameters $\gamma(\beta)$ and $a_j(\beta)$ from *Table 3* into the expression for $g_v(x)$; the expectation values of x_J^l are obtained from those of x^l by the same substitution.

Finally, in order to express matrix elements off-diagonal in J in terms of ground-state expectation values, we define a normalized rotational function $g_J(x)$ according to

$$\psi_{0,J}(x_J) = g_J(x) \psi_{0,0}(x) \tag{48}$$

This function, correct through terms of orders a_1^6 and $\gamma^2 \beta^2$, is given in *Table 6*. The general vibration–rotational matrix element can then be written

$$\langle vJ | x^l | v'J' \rangle = \frac{\langle 00 | g_v(x - \varepsilon(\beta)) g_J(x) x^l g_{v'}(x - \varepsilon(\beta')) g_{J'}(x) | 00 \rangle}{\langle 0J | g_v^2(x_J) | 0J \rangle^{1/2} \langle 0J' | g_{v'}^2(x_{J'}) | 0J' \rangle^{1/2}} \tag{49}$$

Explicit results and discussion of other methods of deriving matrix elements that do not involve wavefunctions are presented in the following section.

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* There are errors in the Table 2 of Tipping and Ogilvie (1976) that we here correct. The coefficient of $a_1^3 a_2$ in the x^0 term of g_3 should read $+1038165/128$ instead of $26495613/256$, and the coefficient of $a_2 a_3$ should be $+7833/8$ instead of $7917/8$; also, in the coefficient of x^2 in g_3, the multiplicative factor of the a_1^5 terms should be $3\gamma^3/2$ instead of $3\gamma^2/2$, and the coefficient of $a_2 a_3$ should read $3387/4$ instead of $3429/4$. In g_4 there are several corrections: in the coefficient of x, $93291/2$ should be replaced by $+55368$, $-831239/64 \to -584279/24$, $5617 \to +5467$, and $849 \to +9633/2$; in the coefficient of x^3, $+492913/8 \to +328273/8$, $-38079/4 \to -36879/4$, $-225 \to -8160$; in the coefficient of x^5, $-33789/8 \to -17325/8$, $-1803/5 \to -4329/10$; in the coefficient of x^7, $-299/2 \to -201/2$.

† Corrections to g_9 have been published by Tipping and Ogilvie (1976), in which there are still errors. In the coefficients of a_1^3, the following changes apply: $43093833/16 \to 43072393/16$, $-21023159/16 \to -21012439/16$, $40767533/16 \to 40746093/16$, $-4902361/16 \to -4899681/16$, and $1167253/16 \to 1166583/16$.

EXPECTATION VALUES AND MATRIX ELEMENTS FOR THE DUNHAM POTENTIAL–ENERGY FUNCTION

For the comparison between theoretical and experimentally determined molecular properties (for instance rotational parameters B_v, shielding factors (Kaiser, 1970), line intensities (Ogilvie *et al.*, 1980, etc.), one requires accurate vibration–rotational expectation values (diagonal in v and J) and matrix elements (off-diagonal in either, or both, v and J). In this section we review published procedures for determining these quantities directly (obviating the need for explicit wavefunctions) and present new results accurate through terms of order a_1^6. As with the Y_{kl} discussed previously, more extensive results generated through use of computer algebra will be published elsewhere (Tipping and Ogilvie, 1983).

We first consider vibrational expectation values of powers of the reduced displacement from equilibrium. One can directly generalize these results to vibration–rotational expectation values of x_J via the β-dependent potential-energy parameters. We next consider matrix elements of x^l, viz. $\langle v|x^l|v'\rangle$, that one can likewise generalize easily to include rotational effects. The latter matrix elements, $\langle vJ|x_J^l|v'J\rangle$, would be required for interpreting, for instance, the intensities of Q-branches in electric quadrupole transitions, or in vibrational Raman spectra (Hamaguchi *et al.*, 1981) if the isotropic polarizability were represented by an expansion:

$$\alpha(x) = \sum_{j=0} \alpha_j x^j. \tag{50}$$

Finally we consider the most general matrix elements, off-diagonal in J, that are applied in the following section to an analysis of vibration–rotational spectral intensities of HCl.

Because of the iterative nature of the generating algorithm, one can in principle extend the results to arbitrary accuracy (within the Born–Oppenheimer approximation); in practice, however, one needs only a few iterations in order to derive results the accuracy of which is limited only by that of the input data (spectroscopic parameters γ and a_j).

Expectation values

Various methods have been proposed for the derivation of expectation values, for instance by Schlier (1961), Bonham and Su (1966), Herman and Short (1968, 1970) and Swenson and Danforth (1972). One can determine the vibration–rotational expectation values directly in terms of the eigen-energies E_{vJ} by use of the Hellmann–Feynman theorem (Bonham and Su, 1966) or equivalently by a novel perturbational method (Herman and Short, 1968, 1970). By differentiating the energy expression for the Dunham potential energy,

$$E_{vJ} = \langle vJ| - B_e d^2/dx^2 + \gamma^{-2} B_e x^2 (1 + \sum_{j=1} a_j x^j) + B_e \beta (1+x)^{-2} |vJ\rangle \tag{51}$$

with respect to the parameters a_j and γ, one finds respectively

$$\langle vJ|x^{j+2}|vJ\rangle = \gamma^2 B_e^{-1} \, \partial E_{vJ}/\partial a_j, j = 1, 2 \ldots \tag{52}$$

and

$$\langle vJ|x^2|vJ\rangle = -\tfrac{1}{2}\gamma^3 B_e^{-1} \, \partial E_{vJ}/\partial \gamma - \gamma^2 B_e^{-1} \sum_{j=1} a_j \, \partial E_{vJ}/\partial a_j \tag{53}$$

One can obtain the expectation value of x in two ways: either the perturbational

method of Herman and Short (1968)

$$\langle vJ|x|vJ\rangle = \gamma^2 B_e^{-1}\{-\tfrac{3}{4}a_1\omega_e\, \partial/\partial\omega_e + B_e\, \partial/\partial B_e - [\tfrac{1}{2}a_1 - \tfrac{3}{2}a_1^2 + 2a_2]\, \partial/\partial a_1 - \cdots$$
$$-[\tfrac{1}{2}na_n - \tfrac{3}{2}a_1a_n + (n+3)a_{n+1}/2]\, \partial/\partial a_n\}E_{vJ} \tag{54}$$

or from the known Dunham result (Tipping and Ogilvie, 1976)

$$\langle vJ|(1+x)^{-2}|vJ\rangle = B_e^{-1}\sum_{k=0} Y_{k,1}(v+\tfrac{1}{2})^k, \tag{55}$$

after expanding $(1+x)^{-2}$ and using the results in equations (52) and (53) above.

An iterative scheme for generating expectation values of powers of x has been discussed previously (Herman *et al.*, 1970; Tipping, 1973a; Tipping and Ogilvie, 1976; Coquant, 1980). Essentially, one can deduce an exact recursion relation between different powers of x by using the commutator result (Tipping, 1973a)

$$\langle v|[x^{l-1}\,d/dx, \mathscr{H}]|v\rangle = 0 \tag{56}$$

in which $\mathscr{H}$ is the hamiltonian operator in equation (51). For the Dunham potential-energy function, equation (27), one obtains the expression

$$[2(l-1)E_v\gamma^2/B_e]\langle v|x^{l-2}|v\rangle + \tfrac{1}{2}[(l-1)(l-2)(l-3)]\gamma^2\langle v|x^{l-4}|v\rangle$$
$$= \langle v|x^l\{2l + (2l+1)a_1x + (2l+2)a_2x^2 + \cdots\}|v\rangle \tag{57}$$

that one can iteratively solve in a manner similar to that used in determining $y(x)$ or $g_v(x)$. The results can be expressed as a recursion relation

$$\langle v|x^l|v\rangle = f_{-1}\langle v|x^{l-1}|v\rangle + f_{-2}\langle v|x^{l-2}|v\rangle + f_{-3}\langle v|x^{l-3}|v\rangle + f_{-4}\langle v|x^{l-4}|v\rangle, \tag{58}$$

in which the functions f_{-n} depend on l, v, γ and a_j. Explicit results correct through terms of order a_1^6 have been published (Niay *et al.*, 1979; Coquant, 1980). One can obtain the vibration–rotational expectation values $\langle vJ|x_J^l|vJ\rangle$ directly from these results by substituting the β-dependent potential-energy parameters.

Before concluding this discussion of expectation values, we wish to state two additional points. First, for $v=0$, one can obtain a simpler two-term recursion relation (Herman *et al.*, 1970) in lieu of equation (58). In order to make equation (23) of Tipping and Ogilvie (1976) correct to terms of order a_1^6, one has only to add the following expression:

$$+\gamma^4\{a_1^6(601/8192\ l^4 + 18817/16384\ l^3 + 22427/4096\ l^2 + 97155/16384\ l$$
$$-103441/8192) + a_1^4a_2(-343/1024\ l^4 - 20977/4096\ l^3 - 48955/2048\ l^2 - 104683/4096\ l$$
$$+112471/2048) + a_1^3a_3(117/512\ l^4 + 1779/512\ l^3 + 8359/512\ l^2 + 9571/512\ l - 9913/256)$$
$$+a_1^2a_4(-19/128\ l^4 - 573/256\ l^3 - 335/32\ l^2 - 3187/256\ l + 3239/128) + a_1^2a_2^2(189/512\ l^4$$
$$+5599/1024\ l^3 + 3159/128\ l^2 + 25733/1024\ l - 28491/512) + a_1a_2a_3(-39/128\ l^4$$
$$-573/128\ l^3 - 2599/128\ l^2 - 2827/128\ l + 3019/64) + a_1a_5(5/64\ l^4 + 19/16\ l^3 + 45/8\ l^2$$
$$+467/64\ l - 227/16) + a_2^3(-1/16\ l^4 - 223/256\ l^3 - 463/128\ l^2 - 749/256\ l + 957/128)$$
$$+a_2a_4(3/32\ l^4 + 85/64\ l^3 + 185/32\ l^2 + 365/64\ l - 413/32) + a_3^2(5/128\ l^4 + 73/128\ l^3$$
$$+83/32\ l^2 + 49/16\ l - 401/64) + a_6(-1/32\ l^4 - 15/32\ l^3 - 35/16\ l^2 - 45/16\ l$$
$$+11/2)\}\langle 0|x^{l-2}|0\rangle \tag{59}$$

Second, for computing numerical values, one can treat equation (57) for $l = 1, 2, \ldots N$ as a set of N linearly independent algebraic equations for the N unknown quantities $\langle v | x^l | v \rangle$. Because of the rapidly decreasing magnitude of the elements as l increases, one can truncate each equation by setting $\langle v | x^l | v \rangle = 0$ for $l > N$ and solving the resulting set of equations by, for instance, Cramer's rule. Results for $v = 0$ for the first few expectation values of HCl as a function of N are listed in *Table 7* along with the results obtained from equation (59) for comparison. The property of rapid convergence makes it possible to obtain moderate accuracy with a minimal effort, even with a hand calculator.

TABLE 7. Expectation values of x^l for HCl in $v = 0$ from application of equations (57) and (59)

N	$\langle 0 \vert x^1 \vert 0 \rangle / 10^{-2}$	$\langle 0 \vert x^2 \vert 0 \rangle / 10^{-3}$	$\langle 0 \vert x^3 \vert 0 \rangle / 10^{-4}$	$\langle 0 \vert x^4 \vert 0 \rangle / 10^{-5}$
2	1.2456	3.5136		
3	1.26427	3.6886	0.59229	
4	1.26859	3.79221	1.66413	3.87999
5	1.26871	3.79389	1.70665	4.33905
6	1.26869	3.79424	1.71328	4.51315
Equation (59)	1.26881	3.79462	1.71374	4.51952

Matrix elements off-diagonal in v

For such matrix elements, one can derive a recursion relation analogous to equation (58) by considering the double commutation relation (Tipping, 1973b):

$$\langle v | [\mathscr{H}, [\mathscr{H}, x^l]] | v' \rangle = (E_v - E_{v'})^2 B_e^{-2} \langle v | x^l | v' \rangle$$

$$= -2l(l-1)(E_{v'} + E_v)/B_e \langle v | x^{l-2} | v' \rangle + 4l(l-1)/B_e \langle v | V(x) x^{l-2} | v' \rangle$$

$$+ 2l/B_e \langle v | x^{l-1} \, dV(x)/dx | v' \rangle - l(l-1)(l-2)(l-3) \langle v | x^{l-4} | v' \rangle \qquad (60)$$

which, after substitution of the Dunham potential-energy function, yields the exact recursion result:

$$\langle v | x^l \{ [l^2 - (E_{v'} - E_v)^2 \gamma^2 / 4B_e^2] + l(2l+1) a_1 x/2 + l(l+1) a_2 x^2 + \cdots \} | v' \rangle$$

$$= l(l-1)(E_{v'} + E_v) \gamma^2 \langle v | x^{l-2} | v' \rangle / 2B_e + l(l-1)(l-2)(l-3) \gamma^2 \langle v | x^{l-4} | v' \rangle / 4 \qquad (61)$$

One can solve this equation iteratively, finding again a four-term recursion relation:

$$\langle v | x^l | v' \rangle = F_{-1} \langle v | x^{l-1} | v' \rangle + \cdots + F_{-4} \langle v | x^{l-4} | v' \rangle \qquad (62)$$

in which the coefficients F_{-n} depend on l, v, v', γ and a_j; explicit results have also been published (Tipping, 1973b; Niay *et al.*, 1979). Inspection of the form of equation (62) reveals that, in contradistinction to equation (58), one needs to know some matrix elements of small powers of x (depending on $v' - v$) in order to generate elements of larger powers through equation (62). One can derive these 'initial elements' by several methods, such as use of the g_v functions (Herman *et al.*, 1970), through sum rules (Tipping, 1973b) or by perturbation methods (Bouanich and Brodbeck, 1974, 1975, 1976; Bouanich, 1976). Results from all these methods have been published (Tipping and Ogilvie, 1976; Bouanich, 1977, 1978a,b; Niay *et al.*, 1979). Again, all these results can be generalized to the elements $\langle vJ | x_J^l | v'J \rangle$ by substitution of the β-dependent

parameters. More accurate and extensive results will be published separately (Tipping and Ogilvie, 1983).

Matrix elements off-diagonal in J

The most general matrix elements $\langle vJ|x^l|v'J'\rangle$ can be derived by a method analogous to, but more complicated than, those discussed above.

In particular, by considering the matrix relation (Tipping, 1973b)

$$\langle vJ|\mathscr{H}^2 x^l - 2\mathscr{H}x^l\mathscr{H}' + x^l\mathscr{H}'^2|v'J'\rangle = (E_{v'J'} - E_{vJ})^2\langle vJ|x^l|v'J'\rangle/B_e^2$$

$$= -2l(l-1)(E_{v'J'} + E_{vJ})\langle vJ|x^{l-2}|v'J'\rangle/B_e + 4l(l-1)\langle vJ|V(x)x^{l-2}|v'J'\rangle/B_e$$

$$+ 2l\langle vJ|x^{l-1}dV(x)/dx|v'J'\rangle/B_e - l(l-1)(l-2)(l-3)$$

$$\langle vJ|x^{l-4}|v'J'\rangle + 2l(\beta+\beta')\langle vJ|(l-1)x^{l-2}(1+x)^{-2} - x^{l-1}(1+x)^{-3}|v'J'\rangle$$

$$\cdot (\beta'-\beta)(E_{v'J'} - E_{vJ})\langle vJ|x^l(1+x)^{-2} + lg(x)|v'J'\rangle/B_e$$

$$- l(\beta'-\beta)^2\langle vJ|g(x)(1+x)^{-2}|v'J'\rangle \tag{63}$$

in which $\mathscr{H}$ and $\mathscr{H}'$ denote the hamiltonians containing the β- and β'-dependent potential-energy functions respectively, and

$$g(x') = \int_0^{x'} x^{l-1}(1+x)^{-2}\,dx \tag{64}$$

one can solve iteratively by treating the (small) rotational effects approximately (Tipping, 1973b; Niay, 1980). Alternatively, one can use the g_v and g_J functions discussed in the previous section in order to rewrite the matrix elements in terms of expectation values, as in equation (49). For analysis of vibration-rotational intensities, we can conveniently express these results in the form

$$\langle vJ|x^l|v'J'\rangle = \langle v0|x^l|v'0\rangle + G_l(v, v', m) \tag{65}$$

in which $m \equiv \frac{1}{2}(\beta' - \beta)$. The rotational contributions are therefore given by

$$G_l(v, v', m) = \langle 00|N_{v\beta}g_v(x - \varepsilon(\beta))g_J x^l N_{v'\beta'}g_{v'}(x - \varepsilon(\beta'))g_{J'}(x)$$

$$- N_{v0}g_v(x)N_{v'0}g_{v'}(x)x^l|00\rangle \tag{66}$$

in which the normalization factor $N_{v\beta}$ is defined to be

$$N_{v\beta} = \langle 00|\{g_J(x)g_v(x - \varepsilon(\beta))\}^2|00\rangle^{-1/2}. \tag{67}$$

Representing the dipole-moment function (to be discussed in detail in the following section) as a power series:

$$M(x) = \sum_l M_l x^l, \tag{68}$$

one can express the factors $F_v^{v'}(m)$ (Herman and Wallis, 1955) in the form:

$$[F_v^{v'}(m)]^{1/2} \equiv \langle vJ|M(x)|v'J'\rangle/\langle v0|M(x)|v'0\rangle$$

$$= \sum_{l=0} M_l\{\langle v0|x^l|v'0\rangle + G_l(v, v', m)\}/\langle v0|M(x)|v'0\rangle$$

$$= 1 + \sum_{l=0} M_l G_l(v, v', m)/\langle v0|M(x)|v'0\rangle \tag{69}$$

Squaring this expression and keeping only the terms linear and quadratic in m (the

accuracy of present experiments warrants no terms of higher order such as m^3, etc.), one can write

$$F_v^{v'}(m) = 1 + C_v^{v'} m + D_v^{v'} m^2. \tag{70}$$

In order both to check the results published by Toth *et al.* (1969a,b, 1970), Tipping and Herman (1970), Tipping and Forbes (1971), Tipping (1976), Bouanich (1977) and Ogilvie *et al.* (1980) and to derive new results for overtones higher than the 5←0 band, we have carried out the derivations of $C_0^{v'}$ and $D_0^{v'}$ correct to terms of order a_1^6. The new results* appear in *Tables 8* and *9*, in which we have employed the following notation:

$$\varepsilon_j = \gamma^{5/2} \sqrt{15 M_j / 2} \langle 0 | M(x) | 5 \rangle$$
$$\delta_j = 3\gamma^3 \sqrt{5 M_j / 2} \langle 0 | M(x) | 6 \rangle \tag{71}$$

The utility of these theoretical expressions for matrix elements and Herman–Wallis coefficients in an analysis of vibration–rotational line intensities is illustrated in the following section.

DIPOLE-MOMENT FUNCTIONS

In this section we discuss the nature of the dipole-moment function, the experimental and theoretical approaches to its determination, forms for its representation, and the principal method of its derivation from spectral intensities (in some detail); in conclusion we present some results for HCl (Tipping and Ogilvie, 1982).

Just as we can, within the Born–Oppenheimer approximation of the separation of electronic and nuclear motions, define a function for potential energy that expresses the manner in which the total energy of the molecule depends on the distance between the stationary nuclei, so we can also define a function for the dipole moment that expresses the manner in which the electric-dipole moment of the molecule, in a particular electronic state, depends on the instantaneous internuclear separation. In each case we assume that the distribution of electronic density is in equilibrium about the nuclei at that distance. The observed internuclear separation of a macroscopic collection of molecules in thermal equilibrium, as measured in a diffraction experiment for instance, depends on a Boltzmann average of the mean separation in each quantum state; analogously, the apparent electric-dipole moment, as obtained from (macroscopic) permittivity measurements, depends on a similar average over the occupied quantum states. On the microscopic level of an individual molecule, the electric-dipole moment has some 'effective' or expectation value in a particular quantum state, or alternatively a matrix element between two states. The derivation of a dipole-moment function therefore relies on an indirect extraction of the dependence on the separation from either experimental measurements or theoretical computations (or both).

With regard to *ab initio* computations, the procedure is relatively direct, because the electric-dipole moment is a one-electron operator (Diercksen *et al.*, 1981). Thus the calculation of the molecular electronic wavefunction at a particular internuclear separation directly yields an electronic charge-density matrix from which the electronic contribution to the dipole moment is readily obtained. For molecular ions, because of experimental difficulties, this theoretical approach is an important method. As in

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* We note the following misprints and mistakes that have appeared in the literature:

1. The coefficient of $\gamma^2 \phi_0 a_1 a_2$ in equation (12) of Toth *et al.* (1970) should read 129/8, not 127/8.
2. The coefficients of $\gamma^2 \rho_0 a_1^5$, $\gamma^2 \rho_0 a_1 a_4$ and $\gamma^2 \rho_1 a_4$ in Table 3 of Tipping (1976) should read $-63/32$, 3/5 and -6 respectively, not $+63/32$, 1/10 and $-45/8$.

experimental methods, there are sources of error in theoretical computations also. These sources may be summarized (Green, 1974; Ogilvie *et al.*, 1980) as due to coupling of electronic and nuclear motions, relativistic effects including spin-orbit coupling, incompleteness of the basis set, and electron correlation; in general each of these effects has an intrinsic dependence on internuclear separation, so that the resulting error is thus dependent on R.

The equation of Clausius, Mossotti and Debye (Chelkowski, 1980) for molar polarization P_M connects the measured relative permittivity ε_r as a function of temperature T with the mean molecular polarizability $\bar{\alpha}$ and electric-dipole moment $\bar{\mu}$:

$$P_M = \left(\frac{\varepsilon_r - 1}{\varepsilon_r + 2} \right) V_M = \frac{N_A}{3\varepsilon_0} \left(\bar{\alpha} + \frac{\bar{\mu}^2}{3k_B T} \right), \tag{72}$$

in which V_M is the molar volume, k_B the Boltzmann constant, N_A the Avogadro number, and ε_0 the permittivity of free space. Any attempt to deduce a temperature dependence of $\bar{\mu}^2$ that can be related to an occupancy of molecular quantum states, and hence to a dependence on internuclear separation, meets with difficulties (Scher *et al.*, 1982) not only because of the relatively large experimental inaccuracy associated with a measurement of the electric susceptibility ($\varepsilon_r - 1$), but also because of the unknown, but not negligible, dependence of polarizability upon temperature. Therefore spectroscopic methods of measurement of dipole-moment quantities are essential if one seeks results of an accuracy approaching that of the potential-energy function.

In order to discuss these spectroscopic methods, and by analogy with the Dunham function for potential energy, we use the customary representation of molecular electric-dipole moment $M(x)$ as a function of reduced internuclear separation:

$$M(x) = \sum_{j=0} M_j x^j \tag{68}$$

The value of $M(x)$ at $x = 0$ or $R = R_e$, namely M_0, is called the permanent electric-dipole moment of the molecule. Because of the limited extent of experimental data, the power series has to be truncated at moderate values of j in practice. Hence the problem of determining the dipole-moment function is reduced to one of finding values of some coefficients M_j that correctly represent the behaviour within some finite range of x.

Among the physical quantities most precisely measurable are frequencies of electromagnetic radiation. Use of the Stark effect, the shift of the frequency of light absorbed or emitted by a molecule in an applied electric field $\tilde{\varepsilon}$, permits us to relate these frequency shifts to some dipole-moment coefficients M_j. The frequency shift associated with the second-order Stark effect (proportional to ε^2) involves both expectation values of the dipole-moment function and the principal components of polarizability: $\alpha_{\parallel}$ and $\alpha_{\perp}$ denote the components parallel and perpendicular, respectively, to the internuclear axis, and are related to the mean polarizability by $\bar{\alpha} = (\alpha_{\parallel} + 2\alpha_{\perp})/3$. If the energy terms are approximated by those for an harmonic oscillator and a non-rigid rotor, viz. $E(v, J, M_J) = \omega_e(v + \frac{1}{2}) + B_v J(J+1) - D_v[J(J+1)]^2$, in which M_J is the quantum number denoting the component of rotational angular momentum about a space-fixed axis (parallel to $\tilde{\varepsilon}$), then the expression for the Stark displacement (in energy units) of the energy levels in second-order, $W^{(2)}_{\text{Stark}}(v, J, M_J)$, consists of six terms (Charifi *et al.*, 1978):

$$W^{(2)}_{\text{Stark}}(v, J, M_J) = \frac{\varepsilon^2}{hc} \left\{ \frac{\mu_v^2}{B_v} \frac{J^2 + J - 3M_J^2}{2J(J+1)(2J-1)(2J+3)} - \frac{D_v \mu_v^2}{B_v^2} \frac{J^2 + J + M_J^2 - 1}{(2J-1)(2J+3)} \right.$$

$$-\frac{D_v}{B_v^2}\,\mu_v\mu\,\frac{J^2+J+M_J^2-1}{(2J-1)(2J+3)}-\frac{1}{B_v}\left(\frac{B_e}{\omega_e}\right)^2\mu^2\,\frac{2(J^2+J-M_J^2)-1}{(2J-1)(2J+3)}\Bigg\}$$

$$+\varepsilon^2\Bigg\{-\frac{(\alpha_{\parallel}-\alpha_{\perp})_v}{2}\,\frac{2(J^2+J-M_J^2)-1}{(2J-1)(2J+3)}-\frac{(\alpha_{\perp})_v}{2}\Bigg\} \tag{73}$$

(Stark effects of higher orders give rise to additional terms; Meerts *et al.*, 1979.) The molecular coefficients in each term of equation (73) indicate their physical meaning; these are respectively the Stark effect of a rigid rotor interpreted as a polarization of the molecular rotation, the influence of centrifugal distortion on the rotational energy, an interference between the Stark effect of the rigid rotor and the centrifugal extension of the dipole, a polarization of the molecular vibration, and (the last two together) a polarization of the electronic motion. These coefficients of each term, in the same order, have approximate magnitudes (in units $F\,m^2$) for HCl, as follows:

$$\mu_v^2/hcB_v\approx6.32\times10^{-38},$$

$$\mu_v^2D_v/hcB_v^2\approx3.17\times10^{-42},$$

$$\mu_v\mu D_v/hcB_v^2\approx3.50\times10^{-42},$$

$$\mu^2D_e/4hcB_v^2\sim\mu^2(B_e/\omega_e)^2/hcB_v\approx9.65\times10^{-43},$$

$$\tfrac{1}{2}(\alpha_{\parallel}-\alpha_{\perp})_v\approx1.73\times10^{-41},$$

and

$$(\tfrac{1}{2}\alpha_{\perp})_v\approx1.39\times10^{-40}.$$

For these estimates, we have used the approximations: $\mu_v\equiv\langle v|M(x)|v\rangle\sim M_0$, $\mu=M_1$, $D_v\sim D_e\sim-Y_{0,2}$, and $B_v\sim B_e$. The most important term is clearly the first, μ_v^2/hcB_v; even the two polarizability terms are of greater magnitude than the remaining terms that involve the deviation from the rigid rotor model. Other coefficients $M_j,\,j>1$, in higher orders of approximation would enter this equation as factors of $(B_e/\omega_e)^{j+1}$, and would thus lead to even smaller corrections than those considered. Because the equation (73) may be rewritten (Charifi *et al.*, 1978)

$$W^{(2)}_{Stark}(v,J,M_J)=\frac{\varepsilon^2\mu_v^2}{hcB_v}\,\frac{(J^2+J-3M_J^2)}{)2J(J+1)(2J-1)(2J+3)}$$

$$-\frac{\varepsilon^2}{3}\,(\gamma_{\parallel}-\gamma_{\perp})+\frac{(J^2+J-3M_J^2)}{(2J-1)(2J+3)}-\varepsilon^2(2\gamma_{\perp}+\gamma_{\parallel})_v/6, \tag{74}$$

in which the definitions of the 'effective polarizabilities' are

$$\gamma_{\parallel}=\alpha_{\parallel}+2\mu^2(B_e/\omega_e)^2/hcB_v$$

and

$$\gamma_{\perp}=\alpha_{\perp}+(\mu_v^2+\mu_v\mu)D_v/hcB_v^2, \tag{75}$$

clearly one cannot determine independently the different parameters $\alpha_{\parallel}$, $\alpha_{\perp}$, μ and μ_v simply by such measurements using the Stark effect. If, however, one can determine the component of polarizability by means of other measurements, such as the Rayleigh and Raman intensities, or the refractive index and the depolarization ratio (Bridge and Buckingham, 1966), then some estimate of $\mu\,(=M_1)$ might be obtained. Kaiser (1970) observed no rotational dependence of μ_v in the case of HCl, but with improvement of techniques, such effects may be observable (Dyke and Muenter, 1973; Freund *et al.*, 1974; Tanaka and Tanaka, 1978).

For measurements on hyperfine transitions (for molecules with non-zero nuclear-quadrupole moments) through the Stark effect, the frequency shifts are directly proportional to the square of expectation values $\langle vJ|M(x)|vJ\rangle$ (Kaiser, 1970). In the vibration–rotational transitions, the frequency displacements due to the Stark effect are proportional to the differences of these same expectation values $\langle vJ|M(x)|vJ\rangle$ for the different states of v (Gough *et al.*, 1981). Even though all such frequency measurements can be made with relatively greater precision than intensities, because the coefficients $M_j, j > 1$, contribute only small corrections to these expectation values, the determination of these M_j becomes progressively more uncertain.

Measurement of the radiative lifetime is another method of determination of the coefficients $M_j, j > 0$. The first such determination, by Bedding and Moran (1973), was for LiF in an experiment on a molecular beam in an electric-resonance spectrometer. To analyse the lifetime $\tau_{1,0}$ of the transition $v = 1 \rightarrow v = 0$, these workers used the expression

$$\tau_{1,0}^{-1} \equiv A_{1,0} \propto M_1^2 \tag{76}$$

in which $A_{1,0}$ is the Einstein coefficient for spontaneous emission; the latter quantity was assumed proportional to the square of the dipole-moment coefficient M_1. Little detailed information from overtones that would enable one to extract values of other coefficients M_j from such experiments is at present available.

The principal, and currently the only feasible, experimental methods of determining $M_j, j > 1$ are from measurements of spectral intensities of pure rotational (Sanderson *et al.*, 1971), vibrational, and vibration–rotational transitions. The measurement of the intensity of a particular transition (Pugh and Rao, 1976) yields a line strength S, the total (integrated) absorption of the line, that is proportional to the squared vibration–rotational matrix element $|\langle vJ|M(x)v'J'\rangle|^2$; this is the electric-dipole matrix element connecting the two vibration–rotational states, specified by quantum numbers vJ and $v'J'$ respectively, involved in the transition ($v = v'$ for the pure rotational case). The band strength, the sum of line strengths of all the rotational lines in the band, is proportional to the squared rotationless transition moment $|\langle v0|M(x)|v'0\rangle|^2$. Because of this squared dependence one cannot determine uniquely the signs of the coefficients M_j from only the rotationless matrix elements. If one however considers vibration–rotational interaction (i.e., individual line strengths), then one finds that the Herman–Wallis coefficients, $C_v^{v'}$ and $D_v^{v'}$ in equation (70), depend linearly on the coefficients M_j; this additional information enables one to make a specific choice of signs of $M_j, j > 0$, relative to M_0. One can otherwise determine the absolute sign of M_0 from measurements of the isotopic dependence of the rotational gyromagnetic ratio by means of the Zeeman effect (Townes *et al.*, 1955). Measurements of the intensity of absorption of the lines in either the pure rotational spectrum or the fundamental vibration–rotational band ($v' = 1 \leftarrow v = 0$) lead to determination of the sign of M_1/M_0, for instance, through D_0^0 or C_0^1 respectively; similar measurements in the overtone bands ($v > 1 \leftarrow v = 0$) provide the signs of $M_j/M_0, j > 1$. Thus one can determine entirely from intensity measurements the coefficients M_j of the dipole-moment function $M(x)$ up to M_k of which k is the value of Δv, the largest change in vibrational quantum number of a transition for which intensity data are available. Because such intensity measurements do not have a particularly great relative accuracy, and because of effects of partial cancellation between terms, the higher coefficients M_{k-1}, M_k, etc. in such a series are known with progressively less precision. In summary, it has therefore proved possible to determine the first few dipole-moment coefficients $M_j, 0 \leqslant j \leqslant 5$, for several molecules (Bernage and Niay, 1977) through use of not only the   k effect but also, primarily, through intensities of vibration–rotational lines.

Although the representation of the dipole-moment function as a truncated polynomial, according to equation (68), is a convenient, flexible and economical model (in that about eight coefficients $M_j, j < 8$, can reproduce the intensities of some hundreds of lines in various bands of HCl, for instance), it possesses the familiar defect of such a representation, namely rapid divergence outside the particular range of x in which it is defined (from experimental data). Unlike the potential-energy function, the dipole-moment function has well defined values at both the limits of the united atom and the separated atoms; the limits are specifically zero if, as is the case for all known neutral diatomic molecules in their ground electronic states, the molecule dissociates into neutral atoms. The behaviour of the dipole-moment function near these limits is known as well (Goodisman, 1963). For molecules that dissociate either into atoms both of which are in S states, or into atoms both of which have total angular momentum less than $\hbar$, then for sufficiently large separations the dipole moment should decrease in magnitude as R^{-7}; for all other cases, the corresponding dependence is R^{-4}. As $R \to 0$, there is a dependence on R^3 for a united atom in an S- or P-state, but R^5 for a D- or F-state. Between these two limits there must exist at least one extremum if the dipole moment has somewhere a non-zero magnitude, but there may exist more than a single extremum. In the latter case, if the molecule changes polarity, there must exist one (or more) internuclear distance, $0 < R < \infty$, at which the dipole moment is zero. Clearly any general functional form that can incorporate all such features and still represent accurately the behaviour derived from experiment must be complicated.

Because of the nature of these asymptotic behaviours and the known experimental derivatives of $M(x)$ at $x = 0$, a natural form to model the function would appear to be a ratio of truncated polynomials, a Padé approximant (King and Queen, 1979). These Padé functions have already been used for dipole-moment applications in a few cases (Herbelin and Emanual, 1974; Kirschner et al., 1977; Tipping and Chackerian, 1981; Ogilvie et al., 1980; Ogilvie and Hasan, 1981), but only in the latter two have both limiting conditions been imposed on its construction. The conversion of a function from a power series into a Padé form is straightforward (Kirschner et al., 1977), provided that the number of parameters in the latter exceeds the number of coefficients in the former. There still remains the task of finding the appropriate parameter to ensure an accurate asymptotic behaviour at $R \gg R_e$. Because only limited information about the dipole-moment function for this region is currently available from experiment (Zemke and Stwalley, 1980), recourse has been made to data from quantum computations (Ogilvie et al., 1980; Tipping and Chackerian, 1981). Such ab initio results are however subject to error, as discussed above, and as confirmed by the lack of agreement between data derived from both theory and experiment in regions in which comparison is possible. Furthermore the method of combining the data from the two disparate sources tends to be arbitrary, so that, even if the data fitted at $R \gg R_e$ were as accurate as those from experiment about $R \sim R_e$, the resulting function could have only qualitative accuracy in the intervening region. Such a model is, however, more physically realistic than extrapolation of the obviously divergent polynomial function outside the range in which the latter has been determined. In the region $0 < R \lesssim 2R_e/3$, the accuracy of the dipole-moment function in Padé form is largely immaterial because such internuclear distances are accessible only at energies much greater than that of the dissociation limit; even the concept of a specific electronic state in this region is suspect. In summary, the Padé approximant for dipole moment should ideally meet the following criteria:

1. $M(R) = 0$ at $R = 0$ and as $R \to \infty$.
2. $M(R) \to 0$ as R^m for $R \to 0$, m depending on angular momentum state of united atom.

3. $M(R) \to 0$ as R^{-n} for $R \to \infty$, n depending on the angular momentum states of the separated atoms in the dissociation limit.
4. If $M(R)$ changes sign, then $M(R) = 0$ at the point $x = x_0$; otherwise $x_0 = -1$.
5. The function must fit adequately the data from experiment, and must have no additional roots or poles cn the real axis.

Ogilvie and Hasan (1981) found that a function of the form

$$M(x) = M_0(x+1)^{m-1}(x-x_0) / \left(-x_0 + \sum_{j=1}^{m+n} e_j x^j \right) \qquad (77)$$

satisfied all these criteria in the cases tested so far.

In order to illustrate our discussion of the extraction of the coefficients M_j from the experimental intensity data, we have performed a reanalysis of the data for HCl, using the improved potential-energy parameters given in *Table 1*, $\gamma = 7.083694 \times 10^{-3}$, and the recently published results from the measurements of intensity of the higher overtones by Gelfand *et al.* (1981). The rotationless matrix elements $\langle 0|M(x)|v \rangle$ are listed in *Table 10*; the relative signs of the first five matrix elements have been determined from the Herman–Wallis factors of the fundamental and lower overtone bands, as described above (Ogilvie *et al.*, 1980). We wish to determine the sign of $\langle 0|M(x)|6 \rangle$ and to find the corresponding coefficients M_j, $0 \leqslant j \leqslant 6$, in the series expansion, equation (68). In order to accomplish this, we write the system of equations

$$\sum_{j=0} M_j \langle 0|x^j|v \rangle = \pm \langle 0|M(x)|v \rangle, \quad 0 \leqslant v \leqslant 6, \qquad (78)$$

and, using the known vibrational matrix elements of x^j, solve for the two sets of M_j (denoted $(+)$ and $(-)$), corresponding to the two choices of the sign of $\langle 0|M(x)|6 \rangle$. We list these sets also in *Table 10*. One can then use these sets of coefficients and the theoretical expressions in *Table 8* and *9* to evaluate the $C_0^v(m)$ and $D_0^v(m)$ coefficients. The latter results are presented in *Table 11* together with the experimental results. As one can conclude from this table, the set of coefficients labelled $(+)$ yields the better agreement with the experimental data and is therefore preferred. Finally, one could use these coefficients M_j in order to construct a Padé approximant for the dipole-moment function that would embody the correct asymptotic behaviour and limits as discussed

TABLE 10. Numerical values of rotationless matrix elements* and the corresponding coefficients M_j of the dipole-moment function for HCl given in both traditional (Debye) and SI (C m) units

v	Experimental $\langle 0|M(x)|v \rangle$		$M_j(+)$		$M_j(-)$	
	$/10^{-30}$C m	/Debye	$/10^{-30}$ C m	/Debye	$/10^{-30}$ C m	Debye
0	3.69746	1.10847	3.64696	1.09333	3.64693	1.09333
1	0.2375	7.12×10^{-2}	4.02071	1.20538	4.02238	1.20588
2	-0.02585	-7.75×10^{-3}	0.12816	0.03842	0.13556	0.04064
3	1.718×10^{-3}	5.15×10^{-4}	-4.96417	-1.48822	-5.36288	-1.60775
4	-1.022×10^{-4}	-3.063×10^{-5}	-3.29608	-0.98814	-2.80164	-0.83991
5	-2.81×10^{-5}	-8.42×10^{-6}	-2.16026	-0.64763	12.6031	3.77831
6	$\pm 2.205 \times 10^{-5}$	$\pm 6.61 \times 10^{-6}$	-3.12143	-0.93578	46.3994	-13.9102

* The sources of the experimental data for $v < 4$ are given in Ogilvie *et al.* (1980); otherwise the data are from Gelfand *et al.* (1981).

TABLE 11. Experimental* and theoretical Herman–Wallis
coefficients for HCl

	Experimental	Theory (+)	Theory (−)
C_0^0	—	0	0
D_0^0	—	1.1×10^{-4}	1.1×10^{-4}
C_0^1	-2.60×10^{-2}	-2.66×10^{-2}	-2.66×10^{-2}
D_0^1	4.5×10^{-4}	2.8×10^{-4}	2.8×10^{-4}
C_0^2	-8.60×10^{-3}	-5.67×10^{-3}	-5.69×10^{-3}
D_0^2	4.1×10^{-4}	3.1×10^{-4}	3.3×10^{-4}
C_0^3	1.70×10^{-2}	1.07×10^{-2}	1.09×10^{-2}
D_0^3	—	3.7×10^{-4}	4.8×10^{-4}
C_0^4	2.77×10^{-2}	1.20×10^{-2}	1.78×10^{-2}
D_0^4	1.42×10^{-3}	7.9×10^{-4}	-3.3×10^{-3}
C_0^5	1.74×10^{-2}	3.21×10^{-2}	3.99×10^{-2}
D_0^5	4.61×10^{-4}	1.4×10^{-3}	1.8×10^{-2}
C_0^6	3.35×10^{-2}	4.99×10^{-2}	-4.27×10^{-2}
D_0^6	7.99×10^{-4}	1.3×10^{-3}	-1.1×10^{-2}

— Not determined.
* Sources of the experimental data are indicated in the footnote of *Table 10*.

above. This form of the dipole-moment function would consequently allow one to compute dipole matrix elements for any bound state with a much greater reliability than if one attempted to use the (divergent) series expansion. We will publish elsewhere the details of this analysis, also incorporating the results of the band $v = 7 \leftarrow v = 0$.

CONCLUSION

Deviations from the Born–Oppenheimer approximation

The theoretical discussions in the preceding sections are based, for the most part, on the Born–Oppenheimer separation of electronic and nuclear motions. For all but the most precise work, this approximation suffices, and one can directly relate the theoretical and experimental quantities, for instance R_e. In addition, both the functions for potential energy and dipole moment are isotopically invariant within this approximation. However, as already noted, small but systematic deviations have been observed for HCl (Kaiser, 1970; Bunker, 1973; Watson, 1973; Coxon and Ogilvie, 1982) and also for other molecules (Tipping and Herman, 1966; Bunker, 1968, 1970, 1972; Tiemann *et al.*, 1982). In order to account for these effects, Herman and Asgharian (1966) derived an 'effective' radial Schrödinger equation that accounts for all deviations leading to changes in the energy levels of order m_e/M_p times the Born–Oppenheimer values:

$$\left\{ \frac{-\hbar^2}{2M_A} \left[1 + \frac{m_e}{M_P} g_2(R_e) \right] \frac{d^2}{dR^2} + \frac{\hbar^2}{2M_A R^2} \left[1 + \frac{m_e}{M_P} (g_1(R) - g_2(R) + g_2(R_e)) \right] J(J+1) \right.$$

$$\left. + \left[1 - \frac{m_e}{M_P} (g_2(R) - g_2(R_e)) \right] V(R) + \frac{m_e}{M_P} [g_2(R) - g_2(R_e)] E_{vJ}^{BO} \right\} \Phi_{vJ}(R)$$

$$= E_{vJ} \Phi_{vJ}(R) \tag{79}$$

in which m_e and M_P are respectively the masses of the electron and proton, and M_A is the

reduced atomic mass of the molecule. The quantity $g_1(R)$ is the rotational gyromagnetic function for the molecule, whereas $g_2(R)$ is an analogous function arising from vibrational electronic inertia. The potential-energy function $V(R)$ is related to the Born–Oppenheimer quantity $V^{BO}(R)$ through

$$V(R) = V^{BO}(R) - \hbar^2(\langle \nabla_a^2 \rangle / M_a + \langle \nabla_b^2 \rangle / M_b)/2 + E_{\mathrm{rel}}(R) \tag{80}$$

in which the expectation values (over the ground electronic state) of the kinetic-energy operators of nuclei a and b constitute the 'adiabatic' correction (Kołos and Wolneiwicz, 1964a,b); the relativistic contribution to the potential-energy function is denoted $E_{\mathrm{rel}}(R)$. (Bunker and Moss, 1977, later derived a similar 'effective' Schrödinger equation.)

In principle one can solve these effective Schrödinger equations by means of the usual WKB method to obtain the energy values E_{vJ} correct to terms of order m_e/M_P times the Born–Oppenheimer result E_{vJ}^{BO}. Tipping and Herman (1966) carried out explicitly this procedure for the rotational parameter B_e for H_2 and its isotopic variants, and expressed their result in the form

$$B_e^{th} = h\left(1 + \frac{m_e}{M_P} g_1(R_e)\right) / (8\pi^2 M_A c R_e^2) \tag{81}$$

with

$$R_e = R_e^{BO}\left\{ 1 + \frac{1}{2a_0 R_e^{BO}} \frac{d}{dR} \left[\frac{\hbar^2}{2M_a} \langle \nabla_a^2 \rangle + \frac{\hbar^2}{2M_b} \langle \nabla_b^2 \rangle + E_{\mathrm{rel}}(R) \right] R_e^{BO} \right\} \tag{82}$$

The term proportional to $g_1(R_e)$ arises from the non-adiabatic corrections (admixture of excited electronic states) while the adiabatic (diagonal in the electronic state) and relativistic effects are contained within R_e (equation 82). This value of B_e is the proper one to compare with the experimental result

$$B_e^{\mathrm{exp}} = Y_{0,1} - \Delta Y_{0,1}^D \tag{83}$$

in which the Dunham (1932b) corrections (arising from the higher-order WKB integrals) are denoted $\Delta Y_{0,1}^D$. Similar analyses have been carried out for other spectroscopic parameters by Herman and Asgharian (1966) and Bunker (1970).

By neglecting the (small) relativistic effects and all but the lowest-order Dunham corrections, and by noting that the remaining corrections are all of order m_e/M_i times the Born–Oppenheimer value, one can write the approximate expression (Ross *et al.*, 1974; Bunker, 1977) in equation (12); this equation was in fact used for the analysis of wavenumber data of HCl (Coxon and Ogilvie, 1982). Watson (1980) introduced a formula slightly different from the latter, in which he replaced μ_i by a 'charge-modified' reduced mass μ_c, defined by

$$\mu_c = M_a M_b / (M_a + M_b - c m_e) \tag{84}$$

in which c is the charge number of the molecular ion; because $c = 0$ for a neutral molecule, this formula reduces to equation (13) in that case.

From the above discussion one can deduce that the parameters Δ_{kl} incorporate corrections to the Born–Oppenheimer energy coefficients Y_{kl} arising both from adiabatic and non-adiabatic terms in the complete Schrödinger equation, and from higher-order WKB integrals (Dunham corrections). Except in the case of H_2 and its isotopic species (Tipping and Herman, 1966; Bunker, 1968), these corrections have been determined only empirically from the fitting of experimental data (frequencies of spectral lines). As the accuracy of frequency measurements continues to improve, to

include these corrections will become increasingly more important and the parameters more accurately determined (Guelachvili *et al.*, 1981; Coxon and Ogilvie, 1982; Lefloch and Rostas, 1982; Tiemann *et al.*, 1982).

Limitations of the standard Dunham formalism

There are two interrelated problems concerning the validity of the Dunham formalism that have received considerable attention in the past: the applicability of the WKB method to the radial problem, and the significance of the pole arising from the nuclear Coulombic repulsion at $R=0$. We consider these topics only briefly and refer the interested reader to more extensive discussions elsewhere.

Although the WKB method was initially developed to treat one-dimensional problems (of range $-\infty < R < \infty$), Dunham (1932a,b) applied it to solve the radial Schrödinger equation (range $0 \leqslant R < \infty$). Kramers (1926) found, however, that the first-order WKB solutions have the wrong nature at $R=0$; the correct behaviour could be obtained only if one replaced $J(J+1)$ in the effective potential energy by $(J+\frac{1}{2})^2$. The subsequent work of Langer (1937) and Kemble (1937) supported this conclusion. However, Beckel and co-workers (Beckel and Nakhleh, 1963; Beckel *et al.*, 1964; Engelke and Beckel, 1970) showed that the problems encountered at the origin ($R=0$) in the first WKB approximation disappeared when one included higher-order WKB integrals. Two final points on this topic are worth stating.

1. Kilpatrick (1959) demonstrated that perturbation theory applied to the potential-energy function of the anharmonic oscillator, equation (5), yielded precisely the same results as the WKB method.
2. Hurley (1962) proved that the standard first-order numerical technique (RKR) for obtaining potential-energy functions from experimental data was entirely equivalent to the WKB method.

Davies and Vanderslice (1966a,b) later proved that the turning points obtained with the higher approximations in the RKR method were identical to those derived by reverting the Dunham series for potential energy. These papers have assuaged any lingering doubts concerning the applicability of the WKB method to radial problems.

Some concern has been voiced, however, regarding the range of applicability of the Dunham expansion, equation (5), and by implication the entire formalism. Because of the existence of the pole at $R=0$, the formal range of convergence is $0 < R < 2R_e$ (Beckel and Engelke, 1968). Several authors (Simons *et al.*, 1973; Thakkar, 1975; Beckel, 1976; Nalewajski and Parr, 1977; Mattera *et al.*, 1980; Ogilvie, 1981) have proposed to alter the range of convergence by considering series in terms of variables other than x; Engelke (1978, 1979) has reviewed the merits and disadvantages of many of these alternatives, so repetition here of such discussion is unnecessary. Suffice it to say that none offers much improvement or convenience for representing the potential energy in the range accessible by conventional vibration–rotational spectroscopy. Some representations do, of course, lend themselves to more physically realistic extrapolations (Jordan *et al.*, 1974; Jordan, 1975; Engelke, 1978; Hashemi-Attar and Beckel, 1979; Beckel and Findley, 1980), especially to energies near the dissociation limit. However, in this region other methods are perhaps more valid (Le Roy, 1973).

Limitations for determinations of dipole moments

The limitations discussed above apply specifically to the Dunham potential-energy function and its corresponding spectroscopic term values. We would like to describe

some similar limitations and caveats concerning the dipole-moment function and spectral intensities. Like the corrections discussed previously, these refinements will become increasingly important as both experimental techniques and accuracy improve. Although there have appeared relatively numerous papers on the implications of the breakdown of the Born–Oppenheimer approximation *vis-à-vis* the observation of dipole transitions in HD (see for instance Nelson and Tabisz (1982), Bishop and Cheung (1980) and references therein), few have been published on the analogous effects in heavier or polar molecules (Bunker, 1977). Kaiser (1970) attributed an isotopic effect for M_0 in HCl to the breakdown of the Born–Oppenheimer approximation. In order to determine the magnitude of this small deviation, one has to employ other data, for instance from the potential-energy function and spectral intensities for vibrational transitions, because the measured quantity is an expectation value of the dipole-moment function within a particular vibration–rotational state, not the permanent moment itself. For only a few molecules is sufficiently accurate information available for this type of analysis at present.

Several other experimental factors may complicate the interpretation of spectral intensities. For instance, at sufficiently large densities, collision-induced absorption (Poll, 1980; Piollet-Mariel *et al.*, 1981) or interference effects (Tipping *et al.*, 1978; Herman *et al.*, 1979) may be important and have to be taken into account before theoretical and experimental values can be compared.

If the rate of publication of intensity data within the past few years indicates a general trend, then in the next few years one will witness a renaissance of accurate data on dipole-moment functions and other electronic properties of diatomic molecules.

Before concluding this review, we wish to indicate briefly some recent innovations and trends in the spectroscopy of diatomic molecules. One should not construe this list as being exhaustive, but rather as being indicative of progress being made in a few directions.

The first area of activity is in the production and measurements of free radicals; within recent years numerous experimental results on both frequencies and intensities have been reported (Herzberg, 1971; Huber and Herzberg, 1979). Because most of these radicals have electronic ground states other than $^1\Sigma$, concomitant progress in the theoretical description of the structure of these states has also been achieved.

With the advent of the laser, state-selective excitation is now routinely practised (Jortner *et al.*, 1981). Radiative lifetimes and luminescence measurements will thus become an increasingly important source of information for both potential-energy and dipole-moment functions (Hirota, 1980). With these techniques, one is furthermore able to probe the states near the dissociation limit (Zemke and Stwalley, 1980; Carrington and Buttenshaw, 1981), in order to obtain information complementary to that derived from conventional absorption spectroscopy.

The laser has also been used in conjunction with other standard experimental techniques, for instance, laser Stark spectroscopy (Allegrini *et al.*, 1980) or laser magnetic resonance spectroscopy (Evenson *et al.*, 1980), in order to increase both the sensitivity and the resolution.

Another sphere of activity is the spectroscopy of simple diatomic ions (Wing *et al.*, 1976; Carrington and Buttenshaw, 1981; Bernath and Amano, 1982). These measurements provide data that are not only of fundamental importance but also of interest in the realm of astrophysics (Mallia, 1974).

The final topic that we wish to mention is that of spectral line shapes. With the improvements in spectral resolution and the accuracy of frequency determinations now available, one is able to measure precisely changes in width, shift, and shape of individual spectral lines as a function of density, temperature and the nature of the

perturbing molecule (Guelachvili and Smith, 1978; Pine, 1980). The interpretation of these data that contain implicitly all the complications of intermolecular interactions will be a challenge to the theoretician.

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APPENDIX

This appendix contains Tables 2, 3, 4, 6, 8 and 9.

TABLE 2. Coefficients for the rotational dependence of the reduced displacement

$h_1 = 1$

$h_2 = -3/2a_1 - 3$

$h_3 = 9/2a_1^2 + 27/2a_1 - 2a_2 + 15$

$h_4 = -135/8a_1^3 - 135/2a_1^2 + 15a_1a_2 - 117a_1 + 24a_2 - 5/2a_3 - 91$

$h_5 = 567/8a_1^4 + 2835/8a_1^3 - 189/2a_1^2a_2 + 810a_1^2 - 270a_1a_2 + 45/2a_1a_3 + 1020a_1 + 12a_2^2 - 240a_2 + 75/2a_3 - 3a_4$
$\quad + 612$

$h_6 = -5103/16a_1^5 - 15309/8a_1^4 + 567a_1^3a_2 - 10773/2a_1^3 + 2268a_1^2a_2 - 315/2a_1^2a_3 - 17955/2a_1^2 - 168a_1a_2^2$
$\quad + 3591a_1a_2 - 945/2a_1a_3 + 63/2a_1a_4 - 17955/2a_1 - 252a_2^2 + 35a_2a_3 + 2280a_2 - 855/2a_3 + 54a_4 - 7/2a_5$
$\quad - 4389$

$h_7 = 24057/16a_1^6 + 168399/16a_1^5 - 13365/4a_1^4a_2 + 280665/8a_1^4 - 17010a_1^3a_2 + 2025/2a_1^3a_3 + 143451/2a_1^3$
$\quad + 1620a_1^2a_2^2 - 37422a_1^2a_2 + 8505/2a_1^2a_3 - 243a_1^2a_4 + 95634a_1^2 + 4536a_1a_2^2 - 540a_1a_2a_3 - 42504a_1a_2$
$\quad + 6930a_1a_3 - 756a_1a_4 + 42a_1a_5 + 79695a_1 - 96a_2^3 + 3696a_2^2$
$\quad - 840a_2a_3 + 48a_2a_4 - 21252a_2 + 25a_3^2 + 8855/2a_3 - 693a_4 + 147/2a_5 - 4a_6 + 32890$

TABLE 3. Rotational dependence of potential-energy parameters

$f_0(\beta) = (1 - \gamma^2\beta + \gamma^4\beta^2(a_1 + 3) + \gamma^6\beta^3(-9/4a_1^2 - 9a_1 + a_2 - 13))\gamma^2\beta$

$\gamma(\beta) = \gamma - 3/2\gamma^3\beta(a_1 + 1) + 3/8\gamma^5\beta^2(15a_1^2 + 30a_1 - 8a_2 + 25) + 1/16\gamma^7\beta^3(-405a_1^3 - 1215a_1^2 + 408a_1a_2$
$\quad - 1665a_1 + 504a_2 - 80a_3 - 1095)$

$a_1(\beta) = a_1 + \gamma^2\beta(-3a_1^2 - 3a_1 + 4a_2 - 4) + \gamma^4\beta^2(27/2a_1^3 + 27a_1^2 - 24a_1a_2 + 33a_1 - 24a_2 + 10a_3 + 32)$
$\quad + \gamma^6\beta^3(-135/2a_1^4 - 405/2a_1^3 + 150a_1^2a_2 - 324a_1^2 + 288a_1a_2 - 70a_1a_3 - 363a_1 - 32a_2^2 + 204a_2 - 90a_3$
$\quad + 20a_4 - 264)$

$a_2(\beta) = a_2 + \gamma^2\beta(-3a_1a_2 - 3a_2 + 5a_3 + 5) + 3\gamma^4\beta^2(9/2a_1^2a_2 + 9a_1a_2 - 15/2a_1a_3 - 5a_1 - 2a_2^2 + 7a_2 - 10a_3 + 5a_4$
$\quad - 15) + \gamma^6\beta^3(-135/2a_1^3a_2 - 405/2a_1^2a_2 + 225/2a_1^2a_3 + 135/2a_1^2 + 60a_1a_2^2 - 270a_1a_2 + 270a_1a_3$
$\quad - 90a_1a_4 + 270a_1 + 72a_2^2 - 50a_2a_3 - 195a_2 + 225a_3 - 135a_4 + 35a_5 + 390)$

$a_3(\beta) = a_3 + 3\gamma^2\beta(-a_1a_3 - a_3 + 2a_4 - 2) + 3\gamma^4\beta^2(9/2a_1^2a_3 + 9a_1a_3 - 9a_1a_4 + 6a_1 - 2a_2a_3 + 7a_3 - 12a_4 + 7a_5$
$\quad + 20) + \gamma^6\beta^3(-135/2a_1^3a_3 - 405/2a_1^2a_3 + 135a_1^2a_4 - 81a_1^2 + 60a_1a_2a_3 - 270a_1a_3 + 324a_1a_4 - 126a_1a_5$
$\quad - 351a_1 + 72a_2a_3 - 48a_2a_4 + 36a_2 - 10a_3^2 - 115a_3 + 270a_4 - 189a_5 + 56a_6 - 546)$

$a_4(\beta) = a_4 + \gamma^2\beta(-3a_1a_4 - 3a_4 + 7a_5 + 7) + \gamma^4\beta^2(27/2a_1^2a_4 + 27a_1a_4 - 63/2a_1a_5 - 21a_1 - 6a_2a_4 + 21a_4 - 42a_5$
$\quad + 28a_6 - 77) + \gamma^6\beta^3(-135/2a_1^3a_4 - 405/2a_1^2a_4 + 315/2a_1^2a_5 + 189/2a_1^2 + 60a_1a_2a_4 - 270a_1a_4$
$\quad + 378a_1a_5 - 168a_1a_6 + 441a_1 + 72a_2a_4 - 56a_2a_5 - 42a_2 - 20a_3a_4 - 165a_4 + 315a_5 - 252a_6 + 84a_7$
$\quad + 735)$

$a_5(\beta) = a_5 + \gamma^2\beta(-3a_1a_5 - 3a_5 + 8a_6 - 8) + 3\gamma^4\beta^2(9/2a_1^2a_5 + 9a_1a_5 - 12a_1a_6 + 8a_1 - 2a_2a_5 + 7a_5 - 16a_6$
$\quad + 12a_7 + 32) + \gamma^6\beta^3(-135/2a_1^3a_5 - 405/2a_1^2a_5 + 180a_1^2a_6 - 108a_1^2 + 60a_1a_2a_5 - 270a_1a_5 + 432a_1a_6$
$\quad - 216a_1a_7 - 540a_1 + 72a_2a_5 - 64a_2a_6 + 48a_2 - 10a_3a_5 - 165a_5 + 360a_6 - 324a_7 + 120a_8 - 960)$

$a_6(\beta) = a_6 + 3\gamma^2\beta(-a_1a_6 - a_6 + 3a_7 + 3) + 3\gamma^4\beta^2(9/2a_1^2a_6 + 9a_1a_6 - 27/2a_1a_7 - 9a_1 - 2a_2a_6 + 7a_6 - 18a_7$
$\quad + 15a_8 - 39) + \gamma^6\beta^3(-135/2a_1^3a_6 - 405/2a_1^2a_6 + 405/2a_1^2a_7 + 243/2a_1^2 + 60a_1a_2a_6 - 270a_1a_6$
$\quad + 486a_1a_7 - 270a_1a_8 + 648a_1 + 72a_2a_6 - 72a_2a_7 - 54a_2 - 10a_3a_6 + 155a_9 - 155a_6 + 405a_7 - 405a_8$
$\quad + 1224)$

TABLE 4. Energy coefficients Y_{kl} previously unpublished

$$Y_{0,7} = 512B_e^{13}/\omega_e^{12}(729a_1^5 + 5103a_1^4 - 1296a_1^3a_2 + 16632a_1^3 - 6048a_1^2a_2 + 360a_1^2a_3 + 31878a_1^2 + 384a_1a_2^2$$
$$- 11088a_1a_2 + 1260a_1a_3 - 72a_1a_4 + 36432a_1 + 672a_2^2 - 80a_2a_3 - 8096a_2 + 1320a_3 - 144a_4 + 8a_5$$
$$+ 20240)$$

$$Y_{0,8} = 256B_e^{15}/\omega_e^{14}(-24057a_1^6 - 192456a_1^5 + 53460a_1^4a_2 - 729000a_1^4 + 311040a_1^3a_2 - 16200a_1^3a_3 - 1684800a_1^3$$
$$- 25920a_1^2a_2^2 + 777600a_1^2a_2 - 77760a_1^2a_3 + 3888a_1^2a_4 - 2527200a_1^2 - 82944a_1a_2^2 + 8640a_1a_2a_3$$
$$+ 998400a_1a_2 - 144000a_1a_3 + 13824a_1a_4 - 672a_1a_5 - 2358720a_1 + 1536a_2^3 - 76800a_2^2 + 15360a_2a_3$$
$$- 768a_2a_4 + 561600a_2 - 400a_3^2 - 104000a_3 + 14400a_4 - 1344a_5 + 64a_6 - 1085760)$$

$$Y_{1,6} = 4B_e^{12}/\omega_e^{11}(-1066527a_1^6 - 6399162a_1^5 + 2973672a_1^4a_2 - 18804555a_1^4 + 13351392a_1^3a_2 - 1213920a_1^3a_3$$
$$- 35175060a_1^3 - 1816128a_1^2a_2^2 + 26753328a_1^2a_2 - 4665600a_1^2a_3 + 409536a_1^2a_4 - 45050985a_1^2$$
$$- 4613760a_1a_2^2 + 817920a_1a_2a_3 + 28838880a_1a_2 - 7218720a_1a_3 + 1213056a_1a_4 - 102144a_1a_5$$
$$- 38366298a_1 + 136704a_2^3 - 3538368a_2^2 + 1198080a_2a_3 - 102912a_2a_4 + 14421960a_2 - 51200a_3^2$$
$$- 4584000a_3 + 1104192a_4 - 177408a_5 + 14336a_6 - 17457693)$$

TABLE 6. Pre-exponential factor g_J of rotational wavefunction

$$g_J = 1 + \gamma\beta[x - (a_1+3)x^2/4 + (a_1^2/8 + a_1/4 - a_2/6 + 2/3)x^3 + (-5a_1^3/64 - 9a_1^2/64 + 3a_1a_2/16 - a_1/4 + 3a_2/16$$
$$- a_3/8 - 5/8)x^4 + (7a_1^4/128 + 3a_1^3/32 - 3a_1^2a_2/16 + 3a_1^2/20 - 9a_1a_2/40 + 3a_1a_3/20 + a_1/4 + 3a_2^2/40 - a_2/5$$
$$+ 3a_3/20 - a_4/10 + 3/5)x^5 + (-21a_1^5/512 - 35a_1^4/512 + 35a_1^3a_2/192 - 5a_1^3/48 + 15a_1^2a_2/64 - 5a_1^2a_3/32$$
$$- 5a_1^2/32 - 5a_1a_2^2/32 + a_1a_2/4 - 3a_1a_3/16 + a_1a_4/8 - a_1/4 - 3a_2^2/32 + a_2a_3/8 + 5a_2/24 - a_3/6 + a_4/8$$
$$- a_5/12 - 7/12)x^6 + (33a_1^6/1024 + 27a_1^5/512 - 45a_1^4a_2/256 + 5a_1^4/64 - 15a_1^3a_2/64 + 5a_1^3a_3/32 + 25a_1^3/224$$
$$+ 15a_1^2a_2^2/64 - 15a_1^2a_2/56 + 45a_1^2a_3/224 - 15a_1^2a_4/112 + 9a_1^2/56 + 45a_1a_2^2/224 - 15a_1a_2a_3/56 - 15a_1a_2/56$$
$$+ 3a_1a_3/14 - 9a_1a_4/56 + 3a_1a_5/28 + a_1/4 - 5a_2^3/112 + 3a_2^2/128 - 9a_2a_3/156 + 3a_2a_4/28 - 3a_2/14 + 3a_3^2/56$$
$$+ 5a_3/28 - a_4/7 + 3a_5/28 - a_6/14 + 4/7)x^7] + \gamma^2\beta[(7a_1+3)/8 + (17a_1^2/16 + 3a_1/2 - 5a_2/4 + 2)x$$
$$+ (-29a_1^3/32 - 21a_1^2/16 + 7a_1a_2/4 - 7a_1/4 + 9a_2/8 - 7a_3/8 - 15/8)x^2 + (213a_1^4/256 + 39a_1^3/32$$
$$- 77a_1^2a_2/32 + 13a_1^2/8 - 9a_1a_2/4 + 3a_1a_3/2 + 15a_1/8 + 13a_2^2/16 - 3a_2/2 + a_3 - 3a_4/4 + 2)x^3$$
$$+ (-403a_1^5/512 - 297a_1^4/256 + 391a_1^3a_2/128 - 99a_1^3/64 + 423a_1^2a_2/128 - 279a_1^2a_3/128 - 235a_1^2/128$$
$$- 9a_1a_2^2/4 + 47a_1a_2/16 - 33a_1a_3/16 + 11a_1a_4/8 - 33a_1/16 - 33a_2^2/32 + 47a_2a_3/32 + 55a_2/32 - 11a_3/8$$
$$+ 15a_4/16 - 11a_5/16 - 35/16)x^4 + (1549a_1^6/2048 + 573a_1^5/512 - 1889a_1^4a/512 + 191a_1^4/128 - 69a_1^3a_2/16$$
$$+ 91a_1^3a_3/32 + 115a_1^3/64 + 555a_1^2a_2^2/128 - 69a_1^2a_2/16 + 99a_1^2a_3/32 - 327a_1^2a_4/160 + 33a_1^2/16 + 99a_1a_2^2/32$$
$$- 21a_1a_2a_3/5 - 55a_1a_2/16 + 11a_1a_3/4 - 39a_1a_4/20 + 13a_1a_5/10 + 91a_1/40 - 23a_2^3/32 + 11a_2^2/8$$
$$- 39a_2a_3/20 + 11a_2a_4/8 - 39a_2/20 + 11a_3^2/16 + 13a_3/8 - 13a_4/10 + 9a_5/10 - 13a_6/20 + 12/5)x^5]$$
$$+ \gamma^2\beta^2[x^2/2 - (a_1+3)x^3/4 + (5a_1^2/32 + 7a_1/16 - a_2/6 + 91/96)x^4 + (-7a_1^3/64 - 19a_1^2/64 + 11a_1a_2/48$$
$$- 29a_1/48 + 5a_2/16 - a_3/8 - 9/8)x^5 + (21a_1^4/256 + 7a_1^3/32 - 49a_1^2a_2/192 + 1661a_1^2/3840 - 109a_1a_2/240$$
$$+ 29a_1a_3/160 + 73a_1/96 + 4a_2^2/45 - 1301a_2/2880 + 39a_3/160 - a_4/10 + 1859/1440)x^6 + (-33a_1^5/512$$
$$- 87a_1^4/512 + 17a_1^3a_2/64 - 423a_1^3/1280 + 21a_1^2a_2/40 - 67a_1^2a_3/320 - 181a_1^2/320 - 33a_1a_2^2/160$$
$$+ 131a_1a_2/192 - 59a_1a_3/160 + 3a_1a_4/20 - 437a_1/480 - 290a_2^2/160 + 7a_2a_3/48 + 47a_2/80 - 29a_3/80 + a_4/5$$
$$- a_5/12 - 29/20)x^7 + (429a_1^6/8192 + 561a_1^5/4096 - 275a_1^4a_2/1024 + 10793a_1^4/40960 - 1437a_1^3a_2/2560$$
$$+ 573a_1^3a_3/2560 + 7957a_1^3/17920 + 849a_1^2a_2^2/2560 - 29053a_1^2a_2/35840 + 7863a_1^2a_3/17920 - 199a_1^2a_4/1120$$
$$+ 12491a_1^2/17920 + 3897a_1a_2^2/8960 - 1557a_1a_2a_3/4480 - 4091a_1a_2/4480 + 3799a_1a_3/6720 - 87a_1a_4/280$$
$$+ 43a_1a_5/336 + 169a_1/160 - 2a_2^3/35 + 2993a_2^2/10752 - 1357a_2a_3/4480 + 13a_2a_4/105 - 9691a_2/13440$$
$$+ 55a_3^2/896 + 1079a_3/2240 - 1019a_4/3360 + 19a_5/112 - a_6/14 + 7187/4480)x^8]$$

TABLE 8. Theoretical expressions for the Herman–Wallis coefficients C_0^5 (correction term)* and C_0^6 (leading contribution), previously unpublished

$$C_0^5 = \gamma\{\ldots\} + \gamma^2\{\varepsilon_0(-1935a_1^6/2048 + 585a_1^5/32 - 2271a_1^4a_2/512 - 297a_1^4/4 + 9a_1^3a_2/16 - 337a_1^3a_3/64 + 285a_1^3/4$$
$$+ 891a_1^2a_2^2/128 + 441a_1^2a_2/4 + 57a_1^2a_3/16 + 3a_1^2a_4/160 + 117a_1^2/4 - 171a_1a_2^2/4 + 629a_1a_2a_3/80 - 165a_1a_2$$
$$- 69a_1a_3/4 + 27a_1a_4/40 + 3a_1a_5/10 - 63a_1/5 + 51a_2^3/32 + 27a_2^2 + 3a_2a_3/10 + 9a_2a_4/8 + 99a_2/5 - 23a_3^2/12$$
$$+ 46a_3 - 153a_4/10 + 27a_5/5 - 7a_6/5 - 168/5) + \varepsilon_1(-7857a_1^5/256 + 22143a_1^4/256 - 277a_1^3a_2/32$$
$$- 6119a_1^3/80 - 21873a_1^2a_2/160 - 171a_1^2a_3/20 - 951a_1^2/32 + 6343a_1a_2^2/80 + 3503a_1a_2/20 + 2137a_1a_3/160$$
$$+ 111a_1a_4/80 + 54a_1/5 - 549a_2^2/16 + 65a_2a_3/24 - 145a_2/8 - 160a_3/3 + 285a_4/16 - 10a_5 + 35)$$
$$+ \varepsilon_2(-4389a_1^4/32 + 2361a_1^3/32 + 373a_1^2a_2/2 + 131a_1^2/5 - 8967a_1a_2/40 - 997a_1a_3/40 - 27a_1/4$$
$$+ 551a_2/10 + 62a_2/5 + 537a_3/10 - 531a_4/20 - 186/5) + \varepsilon_3(-4575a_1^3/32 - 2475a_1^2/32 + 2361a_1a_2/8$$
$$- 15a_1/2 - 279a_2/8 - 295a_3/4 + 165/4) + \varepsilon_4(135a_1^2/4 - 60a_1 + 49a_2 - 52) + \varepsilon_5(75a_1/2 + 45/2) - 30\varepsilon_6\}$$

$$C_0^6 = \gamma\{\delta_0(-a_1^5/256 + 35a_1^4/256 - 5a_1^3a_1/96 - 7a_1^3/6 + 21a_1^2a_2/32 - a_1^2a_3/8 + 15a_1^2/4 - a_1a_2^2/16 - 2a_1a_2$$
$$+ 5a_1a_3/8 - 3a_1a_4/20 - 5a_1 + 3a_2^2/16 - a_2a_3/15 + 5a_2/3 - 2a_3/3 + a_4/4 - a_5/15 + 7/3) + \delta_1(-15a_1^4/64$$
$$+ 45a_1^3/32 - 5a_1^2a_2/4 - 41a_1^2/10 + 101a_1a_2/40 - 27a_1a_3/20 + 21a_1/4 - 23a_2^2/60 - 28a_2/15 + 9a_3/10$$
$$- 3a_4/5 - 12/5) + \delta_2(-35a_1^3/16 + 77a_1^2/16 - 49a_1a_2/12 - 17a_1/3 + 9a_2/4 - 3a_3/2 + 5/2) + \delta_3(-7a_1^2$$
$$+ 13a_1/2 - 10a_2/3 - 8/3) + \delta_4(-9a_1 + 3) - 4\delta_5\}$$

* The leading contribution to C_0^5, with a factor of γ, has been given by Ogilvie *et al.* (1980).

TABLE 9. Theoretical expression for the Herman–Wallis coefficient D_0^6

$$D_0^6 = \{C_0^6/2\}^2 + \gamma^2\{\delta_0(5a_1^4/64 - 25a_1^3/16 + 5a_1^2a_2/12 + 4051a_1^2/480 - 173a_1a_2/60 + 9a_1a_3/20 - 197a_1/12$$
$$+ 23a_2^2/180 + 1429a_2/360 - 21a_3/20 + a_4/5 + 1859/180) + \delta_1(-117[a_1^6 + a_1^5]/512 - 75a_1^4a_2/32 - 15a_1^4/64$$
$$- 165a_1^3a_2/64 - 137a_1^3a_3/32 + 65a_1^3/32 - 21a_1^2a_2^2/32 - 15a_1^2a_2/8 - 81a_1^2a_3/16 - 99a_1^2a_4/40 - 75a_1^2/8$$
$$- 81a_1a_2^2/32 + 111a_1a_2a_3/40 + 35a_1a_2/8 - 3a_1a_3 - 189a_1a_4/40 + 33a_1a_5/20 + 691a_1/40 + 3a_2^3/4 - 3a_2^2/4$$
$$- 21a_2a_3/10 + 3a_2a_4 - 47a_2/10 + a_3^2 + 2a_3 - 9a_4/5 - 3a_5/2 + 8a_6/5 - 53/5) + \delta_2(-1149a_1^5/256$$
$$- 1155a_1^4/256 - 417a_1^3a_2/32 - 35a_1^3/8 - 567a_1^2a_2/32 - 93a_1^2a_3/16 + 189a_1^2/16 + 111a_1a_2^2/16 - 21a_1a_2/2$$
$$- 105a_1a_3/8 + 93a_1a_4/20 - 19a_1 - 63a_2^2/16 + 183a_2a_3/20 + 77a_2/12 - 5a_3 - 15a_4/4 + 39a_5/10 + 133/12)$$
$$+ \delta_3(-2919a_1^4/128 - 189a_1^3/8 - 105a_1^2a_2/16 - 21a_1^2 - 63a_1a_2/2 + 45a_1a_3/4 + 23a_1 + 105a_2^2/8 - 12a_2$$
$$- 15[a_3 - a_4]/2 - 12) + \delta_4(-161a_1^3/4 - 189a_1^2/4 + 33a_1a_2 - 36a_1 - 15a_2 + 14a_3 + 14) + \delta_5(-15a_1^2$$
$$- 75a_1/2 + 30a_2 - 20) + \delta_6(21a_1 - 9) + 14\delta_7\}$$