

The  $z$ -representation of Radial Functions of **Diatomic** Molecules

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From mostly spectroscopic data determined during the analysis of the frequencies and intensities of narrow spectral lines, the fundamental properties of diatomic molecules have been determined as functions of the internuclear distance expressed in terms of the variable  $z$  representing the reduced internuclear displacement from the equilibrium internuclear distance, within the Born-Oppenheimer procedure. Many instances of the determination of such radial functions are presented, all derived by means of the generally applicable  $Z_{k1}$  functions in terms of the potential-energy coefficients  $c_j$  and the additional coefficients  $h_j$  to take account of the various additional properties.

## 1. INTRODUCTION

Although implicitly practised by spectroscopists long before 1927, the procedure' by Born and Oppenheimer in which the separate treatment of the electronic and nuclear motions was justified according to pioneer quantum mechanics remains the most practical approach for the description of the properties of individual molecules. According to this procedure, the properties of the molecules either within a particular quantum state (denoted by a particular set of quantum numbers or indices) or in transitions between such states can be related to functions having an explicit dependence on the parameters describing the instantaneous molecular conformation (or geometric structure specified by the nuclear coordinates). For a diatomic molecule there is only one such parameter, the instantaneous internuclear separation  $R$ ; thus the properties of such a molecule in its quantum states may be related to the expectation values or matrix elements of the appropriate radial functions, applicable in general within a particular electronic state, although other functions are required to describe the properties encountered in transitions between different electronic states. The inherent nature of each such function necessitates a complicated representation,

because the function may in general conform to different limiting types of behaviour within different ranges of internuclear distance; for instance, in the long-range region, corresponding to the approach to the separate dissociation products, in some cases a behaviour proportional to  $R$  to some inverse power is applicable, whereas in the region near the equilibrium separation  $R_e$  possibly an exponential dependence on  $R$  obtains. Obviously a simple model to represent such complicated dependence throughout the entire range of molecular existence is in general unlikely to be accurate. Therefore a superior strategy is to adopt a form of representation with which work is relatively easy but which can be as flexible as required to describe the behaviour of all the types in the various regions of internuclear distance. Furthermore, to the maximum practicable extent, each radial function should be independent of the nuclidic masses of isotopic variants of the molecules comprising a particular chemical species, so that any theoretical calculation, almost of practical necessity based on the Born-Oppenheimer separation, may be directly related to the radial functions deduced from experimental observations.

To serve as the argument of such radial functions, a variable has been devised<sup>2</sup> that meets the requirement of good behaviour throughout the entire range of molecular existence, from the united atom ( $R = 0$ ) to the separate atoms ( $R \rightarrow \infty$ ), and that is employed in the simplest form of representation, namely a power series, for convenience of use. That variable is  $z$ , defined to be  $2(R - R_e)/(R + R_e)$ , so that its values at the limits corresponding to the united atom and separate atoms are respectively  $-2$  and  $+2$ . Then the general radial function has the form<sup>3</sup>

$$K(z) = \sum_j h_j z^j \quad (1)$$

with the power series starting and truncated as required by the limited amount of experimental data available to define the function in addition to any further terms derived as a result of the knowledge of the correct limiting behaviours<sup>4</sup>. One particular instance of the general form is sufficiently important to require a distinct notation; thus for the potential energy, we have the function\*

$$V(z) = V_0 + c_0 z^2 \left( 1 + \sum_{j=1} c_j z^j \right) \quad (2)$$

in which the value of  $V_0$ , serving to define the basis of the energy scale, is taken as zero for the ground electronic state, and  $c_0 = a$ , in the analogous function for potential energy used by Dunham<sup>5</sup>:

$$V(x) = a x^2 \left( 1 + \sum_{j=1} a_j x^j \right) \quad , \quad x \equiv (R - R_e)/R_e \quad (3)$$

Thus by means of these two basic functions  $V(z)$  and  $K(z)$  we are able to express, in terms of the numerical values of their respective coefficients  $c_j$  and  $h_j$ , the radial functions that can be related to essentially any property of the isolated molecules comprising a particular chemical species.

Two general approaches have been practised in relation to the determination of the radial functions of diatomic molecules. One approach has been purely numerical, such as the RKR method<sup>6</sup> for the determination of the potential energy; in this case the results are obtained directly as a table of values of the function at various values of the internuclear distance. The disadvantages of this approach are that a subsequent fitting operation may be required for the purpose of interpolation, that a separate type of numerical calculation, commonly involving quadrature, may be required for the function pertaining to each property, and that statistical measures either of the extent of propagation of error from the experimental data to the final values of the function, or of the sensitivity of those values to such error, may be difficult to determine (and are commonly though improperly ignored). In contrast, the analytic approach in the tradition of Kratzer<sup>7</sup> and Dunham<sup>8</sup> yields directly an algebraic function for which both analytic and numerical procedures to determine error propagation may be equally directly and readily applied. Moreover, there have been recently derived in a basically simple form general relations that permit the determination of the pertinent coefficients  $c_j$  and  $h_j$  according to a convenient and readily applicable procedure for any molecular property for which both a vibrational and a rotational dependence may be determined. In this paper we provide instances of these relations and of the results of their application to determine the radial functions corresponding to various properties of diatomic molecules.

## II. POTENTIAL ENERGY

The function for the potential energy of a diatomic molecule within a particular electronic state is of special importance because the relations required to determine many other radial functions involve not only their intrinsic coefficients  $h_j$  but also the potential-energy coefficients  $c_j$ .

We express the energies (conventionally expressed in wavenumber units) of the vibration-rotational states within a given electronic state of a particular isotopic variant of a diatomic molecule in the general form

$$E_{vJ}^i = \sum_{k=0} \sum_{\ell=0} (U_{k\ell} \mu_i^{-(k+2\ell)/2} + Z_{k\ell}) [v + 1/2]^k [J(J + 1)]^\ell \quad (4)$$

Here  $\mu_i$  is the reduced mass of the isotopic variant that may be considered to be composed from neutral atoms of types A and B having respectively masses  $M_a$  and  $M_b$ , although the molecule may possess a net electrical charge  $Z$  (a quantity having a sign) in units of the protonic charge; thus the reduced mass is given by

$$\mu_i = \frac{M_a M_b}{M_a + M_b + Zm_e} \quad (5)$$

in which  $m_e$  is the electronic (rest) mass (in the same units as  $M_a$  and  $M_b$ , commonly atomic mass units), and the numerator contains the product of the atomic masses whereas the denominator contains the total mass of the particular molecular species. Formally independent of mass, the coefficients  $U_{kl}$  are directly related to the potential-energy coefficients  $c_j$ , but also depend in general on the harmonic force coefficient  $k_e$  and the equilibrium internuclear separation  $R_e$ . The two special cases  $U_{01}$  and  $U_{10}$  each depend on only one of the latter two quantities; specifically,

$$U_{0,1} = h/(8\pi^2 c R_e^2) \approx B_e^i \mu_i \quad (6)$$

$$U_{1,0} = \sqrt{k_e}/(2\pi c) \approx \omega_e^i \sqrt{\mu_i} \quad (7)$$

In order to avoid the explicit presence in the expressions for the other coefficients  $U_k$  of the fundamental constants  $h$  and  $c$ , it is more convenient to express the latter in terms of  $U_{0,1}$  and  $U_{1,0}$  to various powers; for instance,

$$U_{1,1} = 6 U_{c,1}^2 c_1 / U_{1,0} \quad (8)$$

The expressions for the further coefficients  $U_{kl}$  with increasing values of the subscripts  $k$  and  $l$  become progressively more complicated, and eventually exceedingly extensive, functions of the coefficients  $c_j$ , although the functions remain of a nominally simple form. However the methods<sup>8,9</sup> of computer algebra have ensured that the expressions are correct, and have enabled the results to be produced<sup>10</sup> in machine-readable form (FORTRAN code); thereby the spectroscopist is readily able to use these results in the processing of the data from the measurements of the frequencies and wavenumbers of spectral lines. In the case of  $\text{HCl}^{11}$ , the resulting potential-energy function is

$$\begin{aligned} V(z)/m^{-1} = & (21113930 \pm 5600) z^2 [ 1, + (-1.36332725 \pm 0.0000352) z \\ & + (0.865517 \pm 0.000201) z^2 + (-0.47312 \pm 0.00138) z^3 \\ & + (0.08959 \pm 0.0105) z^4 + (0.15645 \pm 0.0440) z^5 \\ & + (-0.6061 \pm 0.171) z^6 + \dots ] \quad (9) \end{aligned}$$

Because of the use of the particular argument  $z$  in this function, further terms may be added by means of the application of the relevant long-range conditions, and the resulting curves" depicting the potential energy as a function of  $R$  approach smoothly the limiting dissociation energy with ultimately the correct dependence on  $R$ .

### III. OTHER RADIAL FUNCTIONS FROM FREQUENCY MEASUREMENTS

For the other radial functions there is a set of general relations between the quantities  $Z_{k\ell}$  in the equation for the energies of the quantum states and the coefficients  $c_j$  and  $h_j$  in the radial functions  $V(z)$  and  $K(z)$  respectively. We present here as samples of the larger collection of expressions already published<sup>3</sup> only the following that also include the quantity  $\gamma_i \equiv 2 B_e^1 / \omega_e^1$  of each particular isotopic species:

$$Z_{0,1} = \gamma_i^2 h, \quad (10)$$

$$Z_{1,0} = \gamma_i (h_1 + h_2 - 3c_1 h_1 / 2) \quad (11)$$

By means of the vibrational and rotational dependence of any particular molecular property to which these quantities  $Z_{k\ell}$  refer, the appropriate values of the coefficients  $h_j$  may be determined directly, either after the values of the potential-energy coefficients  $c_j$  have already been determined or in a concurrent fitting process.

Even in the absence of all contributions to the total molecular angular momentum other than that due to the molecular rotation about the centre of mass, there are always further contributions to the vibration-rotational energies  $E$ . These contributions arise from adiabatic effects (due to the finite mass of the nuclei) and nonadiabatic effects (considered to arise from interactions with other electronic states) both these constituting the partial breakdown of the Born-Oppenheimer approximation', as well as relativistic and radiative effects among possibly others. There are also some purely mechanical effects beyond those taken into account by means of the parameters  $U_{k\ell}$ , related<sup>5</sup> to the vibration and rotation of the nuclei and involving only the same parameters as in the  $U_{k\ell}$  coefficients, but including successively greater (negative) powers of the reduced mass, viz  $\mu_i^{-(k+2\ell+n)/2}$  with  $n = 2, 4, \dots$ . By means of the knowledge of the values of the coefficients  $c_j$  gained from the analysis of the  $U_{k\ell}$  coefficients, one can calculate" sufficiently accurately the latter mechanical contributions to the vibration-rotational energies. However, the adiabatic and nonadiabatic effects, and in practice any others having the same dependence on reduced mass, lead to the contributions that have conventionally been taken empirically into account by means of the parameters  $\Delta_{k\ell}^{a,b}$  in the equation<sup>12</sup>

$$E_{vJ}^i = \sum_{k=0} \sum_{\ell=0} U_{k\ell} \mu_i^{-(k+2\ell)/2} [v+1/2]^k [J(J+1)]^\ell [1 + m_e (\Delta_{k\ell}^a / M_a + \Delta_{k\ell}^b / M_b)] \quad (12)$$

If the diatomic molecule contains two nuclei with the same proton number, then the last term in the latter equation simplifies to  $[1 + m_e \Delta_{k\ell} / \mu_i]$ ; this form shows explicitly that the total power of the reduced mass that is the factor of  $A$ , is  $-(k+2\ell+2)/2$ , thus exactly equal to the power of the first term of the series of higher-order mechanical corrections (variously described<sup>13</sup> as second-order BKW corrections  $Y_{k\ell}^{(2)}$ ) to which reference is made above. For

the general diatomic molecule (with unlike nuclear charges), we define in this case the coefficients  $Z_{k\ell}$  to be the sum of contributions  $Z_{k\ell}^a$  and  $Z_{k\ell}^b$ . Then the relationship of the latter to the spectral parameters  $\Delta_{k\ell}^{a,b}$  is<sup>13</sup>

$$Z_{k\ell}^b = U_{k\ell} \mu_i^{-(k+21)/2} m_e \Delta_{k\ell}^b / M_b - Y_{k\ell}^{(2)} \Delta_{k\ell}^b / M_b / (\Delta_{k\ell}^a / M_a + \Delta_{k\ell}^b / M_b) \quad (13)$$

and analogously for  $Z_{k\ell}^a$  such that the contributions from the second-order mechanical effects  $Y_{k\ell}^{(2)}$  are apportioned between the two atomic types in the ratio of the terms  $\Delta_{k\ell}^a / M_a$  and  $\Delta_{k\ell}^b / M_b$ . The resulting functions that express collectively (and, at present, inextricably) for  $^1\text{H}^{35}\text{Cl}$  the adiabatic and nonadiabatic effects are<sup>13</sup>:

$$K^{\text{H}}(z)/B_e^i = (1.8614 \pm 0.0074) z + (-5.567 \pm 0.02) z^2 + (3.428 \pm 0.28) z^3 + (28.22 \pm 0.54) z^4 \quad (14)$$

$$K^{\text{Cl}}(z)/B_e^i = (-0.1016 \pm 0.0065) z + (0.304 \pm 0.020) z^2 \quad (15)$$

The absence of a constant term signifies that these effects are relative to those obtaining at  $R_e$  (at which  $z = 0$ ). Note also that in this case, unlike most other radial functions so far determined, the given equations (and  $B_e^i$ ) apply to a particular isotopic variant, specifically  $^1\text{H}^{35}\text{Cl}$ . The corresponding relations for the other isotopic variants may however be easily derived from the same experimental values of the parameters  $\Delta_{k\ell}^{\text{H,Cl}}$  through the appropriate atomic masses in the pertinent equations above. (The claim<sup>14</sup> by Hadinger et al to have determined the value of a further coefficient equivalent to  $h_5$  for  $K^{\text{H}}(z)$  of  $^1\text{H}^{35}\text{Cl}$  is entirely erroneous because no value of the required corresponding parameter  $\Delta_{2,1}^{\text{H}}, \Delta_{1,3}^{\text{H}}$  or  $\Delta_{0,5}^{\text{H}}$  has been determined" .)

For electronic states other than  $^1\Sigma$ , there may be contributions to the total angular momentum from the electronic orbital and intrinsic angular momenta, as well as from any intrinsic nuclear angular momenta. First we consider the electronic effects in order of increasing complexity, and then proceed cursorily to the nuclear effects.

For a  $^2\Sigma$  state there is a contribution  $h/2$  to the total angular momentum from the electronic spin. Such states conform to Hund's case b of the coupling of the various angular momenta; in this case the interaction is between the spin and the rotational angular momenta, of which the coefficient  $\gamma_s$  measures the extent of the coupling. The variation of  $\gamma_s$  with vibrational and rotational quantum provides the correspondence of this property with the general quantity  $Z_{k\ell}$ . The resulting radial function<sup>3</sup> for the CN free radical in the ground electronic state X  $^2\Sigma$  is

$$K^{\cdot}(z) = (0.003917 \pm 0.000010) + (-0.0113 \pm 0.019) z$$

$$\begin{aligned}
 &+ (0.028 \pm 0.0053) z^2 + (-0.303 \pm 0.13) z^3 \\
 &+ (0.40 \pm 0.46) z^4
 \end{aligned} \tag{16}$$

For a molecule with an electronic state denoted by  ${}^3\Sigma$ , there is again electronic spin angular momentum to couple with the rotational angular momentum, but there is a further interaction between the separate spins of the two unpaired electrons. The vibration-rotational energies thus contain the parameters  $\lambda$  and  $\gamma_s$  for the spin-spin and the spin-rotational interactions respectively. In the case of  $O_2$  in the ground electronic state  $X\ {}^3\Sigma_g^-$ , both vibrational and rotational dependences of these parameters have been determined<sup>15</sup>. By relating the resulting quantities to the general parameters  $Z_{kq}$ , we can readily determine the radial dependences of the corresponding interactions; specifically, for the spin-spin interaction,

$$\begin{aligned}
 K^\lambda(z)/m^{-1} &= (198.229 \pm 0.0027) + (55.56 \pm 0.06) z \\
 &+ (39.08 \pm 0.42) z^2 + (647.8 \pm 9.3) z^3 + (2526 \pm 1.0) z^4
 \end{aligned} \tag{17}$$

whereas for the spin-rotational interaction,

$$\begin{aligned}
 K^\gamma(z)/10^{-3} &= (-5.821377 \pm 0.00008) + (-1.67 \pm 0.35) z \\
 &+ (-0.970 \pm 0.090) z^2
 \end{aligned} \tag{18}$$

For the  $\Sigma$  electronic states of multiplicity greater than triplet, the corresponding radial dependences can be determined analogously.

Like the  ${}^2\Sigma$  state, the electronic state  ${}^1\Pi$  also belongs to Hund's case b, but in this instance there is one unit of net electronic orbital angular momentum instead of net electronic spin angular momentum. Few if any diatomic molecules have ground electronic states of this type, and the corresponding excited electronic states are commonly beset by strong perturbations arising from interactions with other nearby electronic states leading to the same dissociation products. However in the case of the  $A\ {}^1\Pi$  state of both  $CH'$  and  $CD^+$ , it has proved possible to determine the radial function<sup>17</sup> for the interaction of electronic orbital and rotational angular momenta. For  $CH'$  the resulting function is

$$\begin{aligned}
 K^q(z)/10^{-6} m &= (2.8649 \pm 0.0022) + (-6.8845 \pm 0.86) z \\
 &+ (11.47 \pm 3.5) z^2 + (-63.78 \pm 7.9) z^3 \\
 &+ (287 \pm 87) z^4 + (-492 \pm 300) z^5
 \end{aligned} \tag{19}$$

with a similar result for  $CD'$ . For singlet states of greater orbital angular momentum (such

as  $^1\Delta, ^1\Phi, \dots$ ), the splittings in the energies of the vibration-rotational states are relatively small by comparison with those for  $^1\Pi$  states; for this reason, to be able to determine the required rotational dependence of the parameters for the interaction of electronic orbital and rotational angular momenta seems unlikely in such cases until techniques imparting greatly improved spectral resolution and accuracy can be developed.

For the case of the  $^2\Pi$  electronic state, interactions between the spin and rotational, spin and orbital, and orbital and rotational angular momenta exist. Although there are well documented examples of the vibrational and rotational dependences of several parameters, the situation is complicated because the quantities pertaining to some nominally distinct physical properties are strongly correlated and thus physically indeterminate. For instance, two such parameters are the rotational dependence of the spin-orbital coupling parameter  $A$  and the vibrational dependence of the spin-rotational parameter  $\gamma_s$ . However by making the appropriate measurements for isotopically related species, one can in principle separate some effects. In the case of OH and OD in the ground electronic state  $X \ ^2\Pi_1$ , Amano has succeeded in distinguishing these effects<sup>18</sup>, but also found necessary the neglect of a hyper-fine doubling term of higher order. By this means, it was possible to determine the values of parameters corresponding to  $Z_{k\ell}$  for three different phenomena, namely the spin-orbital interaction and two separate A-doubling effects. The corresponding radial functions<sup>19</sup> are, for the spin-orbital interaction

$$K^A(z)/10^3 \text{ m}^{-1} = (-13.90637 \pm 0.00047) + (-0.398 \pm 0.14) z \\ + (-0.675 \pm 0.22) z^2 + (-3.7 \pm 2.25) z^3 + (-9.6 \pm 4.4) z^4 \quad (20)$$

and for the two A-doubling effects

$$K^P(z) = (0.0127180 \pm 7.7 \times 10^{-6}) + (-0.026745 \pm 0.0051) z \\ + (0.01781 \pm 0.0015) z^2 + (-0.024 \pm 0.04) z^3 + (0.349 \pm 0.36) z^4 \\ + (-1.06 \pm 0.22) z^5 + (-5.75 \pm 1.8) z^6 \quad (21)$$

$$K^Q(z)/10^{-6} \text{ m} = (-1.1062 \pm 0.0002) + (4.0663 \pm 0.063) z + (-6.93 \pm 0.18) z^2 \\ + (8.62 \pm 0.28) z^3 + (-7.46 \pm 0.54) z^4 + (8.47 \pm 2.5) z^5 \\ + (-28.6 \pm 16) z^6 \quad (22)$$

The claim by Bessis et al<sup>20</sup> to have discovered two different methods so as to determine a function equivalent to  $K^A(z)$  for the spin-orbital interaction from only the vibrational dependence of  $A$  (or  $Z_{k,0}^A$ ) has been demonstrated<sup>19</sup> to be fallacious.

From experiments based on electric resonance spectroscopy of molecular beams, both

the great spectral resolution and the great precision of measurements of frequency in the radio-frequency region have enabled the acquisition of accurate data related to the effects of angular momenta of atomic nuclei in molecules and their interactions with rotational angular momentum. One such interaction is that of the electric quadrupole moment of a nucleus having spin greater than  $h/2$  with the gradient of the electric field existing within a polar molecule. The radial function that has been determined<sup>3</sup> for the  $^{35}\text{Cl}$  nucleus in  $\text{H}^{35}\text{Cl}$  and  $\text{D}^{35}\text{Cl}$  is

$$\begin{aligned} K^{qQ}(z)/\text{m}^{-1} = & (-0.222839 \pm 1.3 \times 10^{-6}) + (-0.30687 \pm 0.0011) z \\ & + (0.1471 \pm 0.0035) z^2 + (-1.712 \pm 0.015) z^3 \\ & + (7.6208 \pm 0.084) z^4 \end{aligned} \quad (23)$$

Other possible hyperfine interactions include the intrinsic angular momentum of a nucleus with the molecular rotation, the spin of one nucleus with the spin of the other nucleus in both scalar and tensor forms, and even an interaction involving the electric octupolar moment of a nucleus. Radial functions for some of these interactions have been determined<sup>21</sup> for the  $\text{NaBr}$  molecule.

#### IV. RADIAL FUNCTIONS FROM INTENSITY MEASUREMENTS

In principle, data on which to base radial functions for the molecular electric dipole moment, magnetic dipole moment and electric quadrupole moment (all due to the distribution of electronic density about the atomic nuclei) may be obtained from measurements of frequencies of spectral lines under appropriate conditions. In fact, the frequency shifts due to the Stark effect constitute a useful source of data for the vibrational dependence of the electric dipole moment. However, the corresponding information about the rotational dependence has not generally been determined, partly because the effect is relatively small for linear molecules (for which the Stark effect is quadratic in the intensity of the applied electric field) and partly because of the inadequacy of the analyses of data from the most precise measurements. Therefore one must perforce have recourse to data from measurements of spectral intensities, which have commonly been orders of magnitude less precise than the corresponding frequency measurements. Nevertheless some useful knowledge of radial functions particularly for the electric dipole moment has been obtained, commonly from some combination of the precise data from the Stark effect and the less precise intensity data. For  $\text{HF}$  for instance, such data led to the following radial function<sup>22</sup> for the electric dipole moment of the ground electronic state  $X \ ^1\Sigma^+$ :

$$K^e(z)/10^{-30} \text{ C m} = (6.01344 \pm 0.00040) + (4.6970 \pm 0.0015) z$$

$$\begin{aligned}
 &+ (2.2537 \pm 0.0067) z^2 + (-1.7396 \pm 0.030) z^3 \\
 &+ (-5.302 \pm 0.095) z^4 + (-10.31 \pm 0.53) z^5 + (-7.15 \pm 7.0) z^6 \quad (24)
 \end{aligned}$$

Other electric dipole-moment functions have been determined up to the seventh power of  $z$  for HCl<sup>23</sup> and the eighth power for HBr<sup>24</sup>.

For diatomic molecules containing identical nuclei under conditions of no significant intermolecular perturbations, the intensity of the vibration-rotational spectrum in either absorption or emission must arise from other than the electric dipole moment which is entirely lacking. For <sup>14</sup>N<sub>2</sub> in its ground electronic state X <sup>1</sup>Σ<sub>g</sub><sup>+</sup>, a permanent magnetic dipole moment is also lacking. Thus the first moment that can give rise to the observed absorption spectrum<sup>25</sup> is the electric quadrupole moment. Because by virtue of a non-spherical electronic distribution all diatomic molecules must of necessity have a significant electric quadrupole moment, this mechanism for the origin of the intensity of the spectrum is acceptable. Although the available spectral data<sup>25</sup> permit one to deduce both the magnitude and the sign of  $h_1$ , the value of the constant term  $h_0$  is best taken from experimental measurements<sup>26</sup> of the optical birefringence that yield both the sign and the magnitude of this coefficient. According to the general method<sup>27</sup> for treating the available data, the resulting function for the electric quadrupole moment of N<sub>2</sub> is

$$K^Q(z)/10^{-40} \text{C m}^2 = (-5.07 \pm 0.3) + (8.68 \pm 0.36) z \quad (25)$$

For the vibration-rotational spectrum of <sup>16</sup>O<sub>2</sub>, the transitions may be due to magnetic dipole or electric quadrupole effects, but the fine structure proved conclusively that most observed intensity<sup>27</sup> arises from the electric quadrupole contribution. In this case, only the magnitude of  $h_1$  can be obtained, but the magnitude and sign of  $h_0$  are again derived from measurements of the optical birefringence<sup>26</sup>. The resulting radial function for the ground electronic state X <sup>3</sup>Σ<sub>g</sub><sup>-</sup> of 0, is

$$K^Q(z)/10^{-40} \text{C m}^2 = (-1.3 \pm 0.3) \pm (16.1 \pm 2.4) z \quad (26)$$

For the magnetic dipole moment, measurements of the expectation values in different vibration-rotational states by means of the Zeeman effect seem to be little practised. For the one known instance of this kind of function from experimental data, for O<sub>2</sub> in the ground electronic state X <sup>3</sup>Σ<sub>g</sub><sup>-</sup>, the constant term is derived from the knowledge of the number of unpaired electrons and the lack of orbital angular momentum implied by the fact of the Σ electronic state. From an estimate of the upper limit of the magnetic dipole contribution to the observed vibration-rotational absorption spectrum<sup>27</sup>, one can thus estimate the following radial function for the magnetic dipole moment:

$$K^m(z)/10^{-23} \text{J T}^{-1} = (1.85 \pm 0.03) \pm (\leq 9.13 \pm 1.6) \times 10^{-3} z \quad (27)$$

The relatively small magnitude of the (upper limit of the) coefficient  $h_1$  implies, in classical terms, that the molecular magnetic dipole moment is modulated to a very small extent by the molecular vibration.

## V. DISCUSSION AND CONCLUSIONS

In the above sections, radial functions of some dozen different types have been illustrated, all derived either in whole or in part from experimental measurements of spectral frequencies or intensities. Each given function is applicable to a particular electronic state, and within a particular range of internuclear distance to which the generating spectral data pertain; generally the range may be considered to lie between the classical turning points of the vibrational state having the largest value of the quantum number  $v$  in the applicable data set, and the specific range for each electronic state is invariably stated in the publications to which reference has been made. However the analytic nature of these functions has made practicable the designation of an appropriate error uncertainty attached to the value of each coefficient, and each such quantity has been included explicitly in the stated functions.

Within the Born-Oppenheimer treatment, these radial functions are true molecular properties; their calculation according to any *ab initio* procedure provides an excellent test of the accuracy and reliability of such a procedure. For the spectroscopist, these radial functions also represent the final objective of spectral analysis, because they constitute the most compact form of results—the ultimate achievement in data reduction and the ultimate test of self consistency of the analysis.

These radial functions have all been derived by fundamentally analytic methods, according to the expressions of  $U_{k\ell}$  and  $Z_{k\ell}$  of essentially simple form demonstrated in equations (6)-(8), (10) and (11). Because the radial functions are based on the well behaved variable  $z$ , so that asymptotic conditions may be applied at the approaches to the limits of the united atom and separate atoms, it is possible in principle to generate representations having at least qualitative significance throughout the entire range of molecular existence. At present, for some radial functions the limiting behaviours, depending on the nature of the united or separate atoms—or, more precisely, on the particular states of angular momentum of these atoms, have been incompletely investigated; the appropriate studies are in progress, but the methods to generate additional coefficients (by means of the application of these limiting behaviours) beyond those that may be derived from experimental measurements of frequencies and intensities have already been developed<sup>4</sup>

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## REFERENCES

1. M. Born and J. R. Oppenheimer, *Ann. Phys. Leipzig*, **84**, 457 (1927).
2. J. F. Ogilvie, *Proc. Roy. Soc. London*, **A378**, 287 (1981) and **A381**, 479 (1982).
3. J. F. Ogilvie, *J. Mol. Spectrosc.* **128**, 216 (1988).
4. J. F. Ogilvie, *J. Chem. Phys.* **88**, 2804 (1988).
5. J. L. Dunham, *Phys. Rev.* **41**, 713 (1932).
6. R. Rydberg, *Z. Phys.* **73**, 376 (1931) and **80**, 514 (1933); O. Klein, *Z. Phys.* **80**, 514 (1933); A. L. G. Rees, *Proc. Phys. Soc. London*, **59**, 998 (1948).
7. A. Kratzer, *Z. Phys.* **3**, 289 (1920).
8. J. F. Ogilvie and R. H. Tipping, *J. Symbol. Comput.*, 277 (1987).
9. J. F. Ogilvie, *Comput. Phys.* **3**, 66 (1989).
10. J. F. Ogilvie, *Comput. Phys. Commun.* **30**, 101 (1983).
11. J. A. Coxon and J. F. Ogilvie, *J. Chem. Soc. Faraday Trans. II* **78**, 1345 (1982).
12. A. H. M. Ross, R. S. Eng and H. Kildal, *Opt. Commun.* **12**, 433 (1974).
13. J. F. Ogilvie, *Chem. Phys. Lett.* **140**, 506 (1987); *Spectrosc. Lett.* **22** (in press, 1989).
14. G. Hadinger, Y. S. Tergiman and G. Hadinger, *J. Chem. Phys.* **88**, 4351 (1988).
15. M. Mizushima, *Jap. J. App. Phys.* **26**, 645 (1987).
16. J. F. Ogilvie, *Can. J. Spectrosc.* **33**, 72 (1988).
17. J. F. Ogilvie, *Aust. J. Chem.* **41**, 1501 (1988).
18. T. Amano, *J. Mol. Spectrosc.* **103**, 436 (1984).
19. J. F. Ogilvie, *Phys. Scripta* **38**, 802 (1988).
20. N. Bessis, G. Hadinger and Y. S. Tergiman, *J. Mol. Spectrosc.* **107**, 343 (1984).
21. J. F. Ogilvie, *J. Mol. Spectrosc.* **131**, 340 (1988).
22. J. F. Ogilvie, *J. Phys.* **B21**, 1663 (1988).
23. J. F. Ogilvie, to be published (1989).
24. C. B. Carlisle, H. Riris, L. G. Wang, G. R. Janik, T. F. Gallagher, A. Lopez Pineiro and R. H. Tipping, *J. Mol. Spectrosc.* **130**, 395 (1988).
25. D. Reuter, D. E. Jennings and J. W. Brault, *J. Mol. Spectrosc.* **115**, 294 (1986).
26. A. D. Buckingham, R. L. Disch and D. A. Dunmur, *J. Am. Chem. Soc.* **90**, 3104 (1968).
27. J. F. Ogilvie and R. H. Tipping, *Int. Rev. Phys. Chem.* **3**, 3 (1983).
28. J. Reid, R. L. Sinclair, A. M. Robinson and A. R. W. McKellar, *Phys. Rev.* **A24**, 1944 (1981).