SPECTROSCOPY LETTERS, 20(9), 725-734 (1987)

THE REPRESENTATION OF THE VIBRATION-ROTATIONAL ENERGIES OF DIATOMIC MOLECULES

Key words: diatomic molecules, vibration-rotational energies, representation in power series

J. F. Ogilvie

Department of Chemistry,
National Tsing Hua University,
Hsinchu, Taiwan 30043

ABSTRACT

The forms of the dependences on the vibrational and rotational quantum numbers in the series representation of the vibration-rotational energies of diatomic molecules are discussed. It is concluded that the most convenient forms for diatomic molecules in $^1\Sigma$ electronic states are $(v+1/2)$ and $(J+1/2)^2$ respectively.

– – – – – –

Recently Bessis et al [1] proposed a representation of the vibration-rotational terms of diatomic molecules,

$$E_{vJ} = \sum_{k=0}^{v} \sum_{\ell=0} \frac{(-1)^k}{k!} (\mathcal{Y}_{k\ell} + \mathcal{Z}_{k\ell}) \frac{v!}{(v-k)!} X(J)^{\ell} \tag{1}$$

that differs from the conventional representation following Dunham [2], correspondingly expressed as

$$E_{vJ} = \sum_{k=0} \sum_{\ell=0} (Y_{k\ell} + Z_{k\ell}) \, (v+1/2)^{k} \, X(J)^{\ell} \qquad (2)$$

For molecules in $^{1}\Sigma$ electronic states, Dunham took the function X(J) as simply J(J+1), and the additional set of coefficients $Z_{k\ell}$ introduced later [3] may be unnecessary; however for molecules not in $^{1}\Sigma$ states X(J) takes a more complicated form depending on the quantum numbers for the various angular momenta, and then the $Z_{k\ell}$ coefficients take into account the additional branches of lines in each vibration-rotational band resulting from spin-orbit and spin-rotation coupling and other effects. For many years practising spectroscopists have commonly used relations equivalent to equation (2) for the purpose of data reduction: their voluminous frequently data have thus been represented compactly, but adequently to reproduce the experimental data, by means of a relatively small set of coefficents $Y_{k\ell}$.

The notable variation by Bessis et al from the Dunham treatment is the replacement of the powers of (v+1/2) by the factorial quantity v!. Because the quantum number v also appears as the upper limit of the summation over the subscript k, there must be an inconsistency in the use of this formula for vibrational energies. For instance, the energy of a $^1\Sigma$ molecule in the state defined by the quantum numbers v=1 and J=0 is precisely $\nu_{0,0} - \nu_{1,0}$ as if no further coefficients $\nu_{k\ell}$ had been determined; then the difference of energy $E_{2,0} - E_{1,0}$ is $Y_{1,0} + 2Y_{2,0}$ from equation (1) above and their [1] equation (10) that gives the correspondences between $\nu_{k\ell}$ and $Y_{k\ell}$, specifically,

$$\nu_{k\ell} = (-1)^k \; k! \; Y_{k\ell} \tag{3}$$

in contrast, according to equation (2) with terms up to $(v+1/2)^2$ the corresponding difference $E_{2,0} - E_{1,0}$ is $Y_{1,0} + 4Y_{2,0}$. For similar reasons equation (1) implies that for some elevated values of the vibrational quantum number v the calculation of the energy of that state requires that $\nu_{v,0}$ be known; thus for the vibrational energy of the state of CO with v=41, which can be accurately calculated [4] with $Y_{k,0}$ up to k=9, all the coefficients $\nu_{k,0}$ up to k=41 would be required, thus implying terms in the potential-energy function [1] containing up to h_{82} (equivalent to a_{80} in the Dunham [2] potential-energy function)! Apart from the absolutely intractable complexity of those analytic expressions, clearly one achieves no net data reduction whatsoever of vibrational energies through the use of equation (1); rather than resorting to this cumbersome, complicated and inconsistent formulation [1], one would do better simply to use directly the vibrational energies $G(v)$. Also, according to the formulation of Bessis et al, the coefficient $\mathcal{Y}_{0,0}$ (omitted from their [1] compilation of results) must accept all the zero-point energy implied by the inclusion of the addend 1/2 in the power series of the argument $(v+1/2)$:

$$\mathcal{Y}_{0,0} \approx \sum_{k=0}^{v} Y_{k,0}\,(1/2)^{k} \qquad (4)$$

$$\approx Y_{0,0} + 1/2\;Y_{1,0} + 1/4\;Y_{2,0} + \cdots$$

Furthermore the list of correspondences in equation (B2) of Bessis et al [1] is misleading because there are also omitted the higher contributions resulting from the factors of $(1/2)^{k}$ in $\mathcal{Y}_{k\ell}$, $\ell > 0$; for instance,

$$\mathcal{Y}_{0,1} \approx B_e + 1/2\;\alpha_e + \cdots \qquad (5)$$

A set of expressions for all $Y_{k\ell}$, $0 \leq k \leq 6$ and $0 \leq \ell \leq (12-2k)$, directly in terms of B_e, ω_e and the coefficients a_j in the potential-energy function due to Dunham [2],

$$V(x) = \frac{\omega_e^2}{4B_e}\,x^2\,(1 + \sum_{j=1} a_j x^j) \quad , \quad x \equiv (R-R_e)/R_e \qquad (6)$$

including all terms containing contributions up to a_{10}, plus $Y_{6,1}$ (of order a_{11}) and $Y_{7,0}$ (a_{12}), has been derived [5] and checked algebraically [6]; similarly all terms in $Y_{k\ell}$ up to c_{10} in the potential-energy function [7] that, unlike the Dunham function, suffers from no convergence problem in the range $0<R<\infty$ and has also other useful properties [8],

$$V(z) = \frac{\omega_e^2}{4B_e}\,z^2\,(1 + \sum_{j=1} c_j z^j) \quad , \quad z \equiv 2(R-R_e)/(R+R_e) \qquad (7)$$

have been obtained, checked and published [9] in machine-readable form (FORTRAN code). Expressions for $Z_{k\ell}$, $0 \leq k \leq 0$ and $0 \leq \ell (9-2k)$, have also been derived [5] (and checked) in terms of the coefficients a_j and k_j; the latter are the parameters in the power-series expansion

$$K(x) = \Sigma\, k_j x^j, \tag{8}$$

that may be used for diatomic molecules to represent various radial functions, such as the spin-orbit coupling function A(x).

A further question concerns the form of X(J) for diatomic molecules in $^1\Sigma$ states. By means of experimental measurements through pumping of states within pure rotational manifolds, one can certainly prove that the differences of rotational energy between successive rotational states (in the v=0 vibrational state, for instance), starting from the purely vibrational term, are to a sufficient approximation $2B_0$, $6B_0$, $12B_0$, $20B_0$ etc.; the effects of centrifugal distortion can be easily taken into account without affecting the argument to follow. Such a series of energy differences is consistent with the representation of rotational energies as $B_0(J^2+J+\text{constant})$. The two values of the constant that have used in the past are 0 and 1/4. The value 0 is consistent with the form of the function X(J) = J(J+1) used by Dunham [2]; however, it should be noted that Dunham introduced ad hoc this form into his formulation rather than obtaining it as a necessary consequence of his theory. $J(J+1)$ having thus been introduced in this way, naturally the resulting vibration-rotational energies (equation 2) are expressed in terms of powers of the same quantity. The alternative introduction of $(J+1/2)^2$ has the effect of altering slightly the numerical values of the coefficients $Y_{k\ell}$ in any spectroscopic application without changing the nature of the physical meaning, although small terms of higher order (of magnitudes comparable to similar terms already existing in the Dunham [2] theory) are generated in the analytic expressions of $Y_{k\ell}$. The form $(J+1/2)^2$ was in fact used for rotational energies in early investigations of molecular spectra [10], and of the two forms $J(J+1)$ and $(J+1/2)^2$ "it seems to be more or less a matter of convenience which form one would like to choose" [11]. The term $Y_{0,0}$, the coefficient of zero powers of both v and J,

$$Y_{0,0} \approx B_e/4 + \alpha_e\omega_e/(12B_e) + \alpha_e^2\omega_e^2/(144B_e^3) - \omega_e x_e/4 \quad (9)$$

according to the Dunham theory [2] contains precisely the rotational contribution $B_e/4$ [12] that is the difference $B_e(J+1/2)^2 - B_eJ(J+1)$. Thus the assertion [13] that the inclusion within $(J+1/2)^2$ of the addend 1/4 has the effect of raising the eigenvalues is incorrect, because this term (as $B_e/4$) is in any case present in the vibrational energies and can simply be transferred from $Y_{0,0}$. The removal of $B_e/4$ from $Y_{0,0}$ in fact leaves the remaining terms tending to cancel one another (at least for a molecule in its ground electronic state). Moreover it should be noted that the contribution $Y_{0,0}$ to the energy arises in the Dunham theory from the purely vibrational motion, before the centrifugal term is introduced into the procedure. Many years ago, Kemble [14,15] and Langer [16] each demonstrated that $(J+1/2)^2$ is in fact the proper form to use in the centrifugal term in the effective potential energy, whence the same form will appear in the vibration-rotational energy terms within X(J). Because the forms of the solutions of the coefficients $Y_{k\ell}$ in terms of the potential-energy parameters a_j are independent of the method of solution (whether semiclassical according to the JWKB procedure [2], quantum-mechanical according to Rayleigh-Schrodinger perturbation theory [17], or classical according to Fourier analysis [18]), the applicability of the form $(J+1/2)^2$ should not be an artifact of the JWKB approach.

With the vibrational and rotational quantum numbers both entering the Dunham [2] energy equation (2) in a similar form, viz. (v+1/2) and (J+1/2), it may be germane to consider these numbers in a different way: at least for $^1\Sigma$ states, instead of being integers starting at zero and having the addend 1/2, they may be more conveniently considered to be simply half the odd positive integers, i.e. $\hat{v}$ = 1/2, 3/2, 5/2 ··· ; $\hat{J}$ = 1/2, 3/2, ···. Analogously the mass-reduced quantum numbers [19] can be generated simply by dividing each of $\hat{v}$ and $\hat{J}$ by $\mu^{1/2}$.

In conclusion, it is clear that the form v! is not a useful alternative to represent the vibrational dependence of vibration-rotational energies, but that $(J+1/2)^2$ is a convenient form of X(J) in equation (2) for $^1\Sigma$ diatomic molecules.

REFERENCES

1. Bessis N., Hadinger G., Tergiman Y.S. Analytic Radial Dependence of Diatomic Electronic Structural Parameters in Terms of the Vibration-rotational Spectroscopic Data. J. Mol. Spectrosc. 1984; <u>107</u>: 343-372.

   Apart from the unnecessarily complicated formalism in this paper, there are errors in the expressions given for $\mathcal{Y}_{3,1}$, $\mathcal{Y}_{4,1}$ and $\mathcal{Z}_{2,2}$.

2. Dunham J.L. The Energy Levels of a Vibrating Rotator. Phys. Rev. 1932; 41: 721-731.

3. Herman R.M., Short S. A New Theoretical Method for the Accurate Calculation of Expectation Values of Internuclear Separation in Diatomic Molecules in $^1\Sigma$ States. J. Chem. Phys. 1968; 48: 1266-1272 and (erratum) 1969; 50: 572.

4. Guelachvili G., deVilleneuve D., Farrenq R., Urban W., Verges J. Dunham Term-value Coefficients for Seven Isotopic Species of CO. J. Mol. Spectrosc. 1983; 98: 64-79.

5. Ogilvie J.F., Tipping R.H. The Vibration-rotational Spectroscopy of Diatomic Molecules (to be published).

6. Ogilvie J.F., Applications of Computer Algebra in Physical Chemistry. Comput. Chem. 1982; 6: 169-172.

7. Ogilvie J.F. A General Potential-energy Function for Diatomic Molecules. Proc. R. Soc. London, 1982; A378: 287-300 and (erratum) 1982; A381: 479.

8. Engelke R. Vibrational Potential-energy Functions of Diatomic Molecules; II. New Representations. J. Chem. Phys. 1979; 70: 3745-3757.

9. Ogilvie J.F. Spectroscopic Energy Coefficients for Vibration-rotational States of Diatomic Molecules. Comput. Phys. Commun. 1985; 30: 101-105.

10. Herzberg G. Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules, 2nd ed. Princeton, U.S.A.: Van Nostrand, 1950.

11. Herzberg G. personal communication, 1987.

12. Ogilvie J.F. The Semiexperimental Determination of a Repulsive Potential-energy Function of HI. Trans. Faraday Soc. 1971; 67: 2205-2215.

13. Kirschner S.M., Le Roy R.J. On the Application, Breakdown and Near-dissociation Behaviour of the Higher-order JWKB Quantization Condition. J. Chem. Phys. 1978; 68: 3139-3148.

14. Kemble E.C. A Contribution to the Theory of the BWK Method. Phys. Rev. 1935; 48: 549-561.

15. Kemble E.C. The Fundamental Principles of Quantum Mechanics. New York: McGraw-Hill, 1937.

16. Langer R.E. The Connection Formulae and the Solutions of the Wave Equation. Phys. Rev. 1937; 51: 669-676.

17. Bouanich J.P. Higher-order Contributions to the Dunham Energy Coefficients; Application to the Ground State of CO. J. Quant. Spectrosc. Radiat. Transfer 1978; 19: 381-386.

18. Tipping R.H. A Semiclassical Treatment of Vibration-rotational Intensities of Diatomic Molecules. J. Mol. Spectrosc. 1972; 43: 31-35.

19. Stwalley W.C. Mass-reduced Quantum Numbers; Application to the Isotopic Mercury Hydrides. J. Chem. Phys. 1975; 63: 3062-3080.

Date Received: 06/26/87
Date Accepted: 07/31/87