The physical significance of energy coefficients of diatomic molecules

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Abstract—The importance of the nature of the reduction process for spectral data of diatomic molecules is discussed in relation to the physical significance of the resulting parameters. Spectral data for LiH and CO are examined to illustrate the determination of the applicable radial functions. It is recommended that appropriate constraints be routinely applied during the general fitting of pertinent spectral data of diatomic molecules.

After one has successfully contended with the metrological aspects of a new spectrum, the problem remains how to represent the data in the most compact and meaningful form. In the case of diatomic molecules, the relative simplicity of the carrier of the spectrum makes possible various approaches that have been practised over the years.

For the reduction of frequency or wavenumber data, NIAY *et al.* [1] have discussed that the term series for E_{eJ} , the energies of the vibration-rotational states within a particular ¹ Σ electronic state according to DUNHAM's [2] systematic representation,

$$E_{vJ} = \sum_{k=0} \sum_{l=0} Y_{kl} (v + 1/2)^k (J^2 + J)^l \qquad (1)$$

may be regarded as purely empirical, with the Y_{kl} coefficients serving merely as phenomenological fitting parameters [3]. DUNHAM [2] showed how the Y_{kl} coefficients could be related, assuming the Born-Oppenheimer separation of electronic and nuclear motions, to the coefficients a_j in his potential energy function

$$V(x) = a_0 x^2 (1 + \sum_{j=1}^{\infty} a_j x^j), \ x \equiv (R - R_e)/R_e$$
(2)

in which R and R_e denote respectively the instantaneous and equilibrium internuclear separations. Each coefficient Y_{kl} consists of a series of contributions

$$Y_{kl} = Y_{kl}^{(0)} + Y_{kl}^{(2)} + Y_{kl}^{(4)} + \cdots$$
(3)

of which the superscript indicates either the order of the integral according to the BKW theory that DUNHAM [4] used to derive the relations to the coefficients a_i or a different order of Rayleigh-Schrödinger perturbation theory that may also be applied [5] to produce identical analytic relations. In the DUNHAM theory [2], the parameter $\gamma \equiv 2 B_e/\omega_e$, commonly taking values in the range $[10^{-2}, 10^{-4}]$, plays an important role as the expansion parameter that determines the rapidity of convergence of the infinite series. Although each successive contribution $Y_{kl}^{(m)}$ decreases proportionally to a factor γ^2 , the sub-expression also contains four additional coefficients a_j ; for this reason it is impossible in principle to determine uniquely a set of values of these coefficients a_j applicable to a single electronic state from a finite set of spectral data.

If data for isotopic variants of a given molecular species are available, then one can fit simultaneously the wavenumbers of the vibration-rotational transitions of all variants to a more general form [6] of Eqn (1) for each variant i,

$$E_{vJ}^{i} = \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} U_{kl} \, \mu_{i}^{-(k+2l)/2} \, (v+1/2)^{k} \\ (J^{2} + J)^{l} [1 + m_{e} (\Delta_{kl}^{a} / M_{a} + \Delta_{kl}^{b} / M_{b})]$$
(4)

in which m_e is the rest mass of the electron and μ_i is the reduced mass of the molecule that dissociates into atoms of mass M_a and M_b . Of the new sets of coefficients in the latter equation, the parameters $\Delta_{kl}^{a,b}$ take into account not only the second-order energy coefficients $Y_{kl}^{(2)}$ but also adiabatic and nonadiabatic effects and in addition any other effects having the same dependence on atomic mass [7]. In contrast, the coefficients U_{kl} correspond exactly to the leading contributions $Y_{kl}^{(0)}$ of the term coefficients Y_{kl} of each isotopic variant, viz.

$$U_{kl} = Y_{kl}^{(0)} \,\mu_l^{(k+2l)/2}.\tag{5}$$

Because of the exact relationship of these leading contributions to each other, through the potential energy coefficients a_j of DUNHAM's function [2] (or equivalent), a finite set of spectral data of sufficient isotopic variants can in principle determine uniquely a corresponding potential energy function that is valid within a particular range of internuclear distance. Furthermore the latter has a sound theoretical significance in that it is in principle the Born-Oppenheimer potential energy that may be determined from conventional quantum computations of electronic properties or molecular structure in which the nuclear masses play no role.

In the determination of the potential energy function that embodies most of the significance of the

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wavenumber data from vibration-rotational spectra or energies, three principal approaches have been practised. The oldest method is through the band parameters $(G_v, B_v, D_v, H_v \text{ etc.})$ to the Y_{kl} coefficients and thence to the coefficients a_i by means of DUNHAM's relations [2], such as is described in Ref. [8]. A second approach is essentially to bypass the band parameters by fitting the spectral lines directly to the parameters U_{kl} (and $\Delta_{kl}^{a,b}$), from which the coefficients a_i may be generated in a succeeding series of merge procedures; in the case of HCl, the resulting values of the U_{kl} coefficients are internally consistent within two standard errors [9]. A third approach is to fit the wavenumbers of the spectral lines directly to the coefficients a_i [1], eliminating the determination of any intermediate parameters. The latter procedure, although somewhat more complicated computationally than the others, guarantees in principle the utmost physical significance of the results, because the potential energy function is then least arbitrarily related to the primary spectral data.

In their recent analysis of the spectra of four isotopic variants of lithium hydride, YAMADA and HIROTA [10] simply used the Y_{kl} , U_{kl} and Δ_{kl}^{a} b coefficients as empirical fitting parameters. Here we test the physical significance and consistency of their results through the analytic functions V(z) for potential energy [11] that has a greater range of validity than DUNHAM's function in Eqn (2) but is of the same form:

$$V(z) = c_0 z^2 \left(1 + \sum_{j=1}^{n} c_j z^j \right)$$
$$z \equiv 2(R - R_e)/(R + R_e)$$
(6)

and K(z) that is the corresponding radial function to describe collectively the adiabatic and nonadiabatic effects [7]:

$$K_{(z)}^{a,b} = \sum_{j=1}^{b} h_j^{a,b} z^j.$$
 (7)

Thus the physical significance becomes evident through the values of the coefficients c_j and $h_{j,1}^{I,I,H}$ respectively. The coefficients $U_{1,1}$, $U_{2,0}$, $U_{2,1}$ and $U_{3,0}$ lead [12] to the most accurate values $c_1 =$ -0.896675 ± 0.000041 , $c_2 = 0.350637 \pm 0.000010$, $c_3 =$ -0.116789 ± 0.00154 and $c_4 = -0.055094 \pm 0.00359$ respectively. The values of $U_{0,3}$, and $U_{1,2}$ or $U_{0,4}$ yield $c_1 = -0.8543 \pm 0.021$ and $c_2 = 0.33365 \pm 0.0016$ or 0.222 ± 0.056 respectively, in moderate consistency with the corresponding values above. A further relation, entirely independent of the nature of the potential energy function,

$$U_{0,2} = -4 \ U_{0,1}^3 / U_{1,0}^2 \tag{8}$$

yields $U_{0,2} = (-0.06682416 \pm 3.3 \times 10^{-7}) \text{ m}^{-1}$ differing from the freely fitted value [10] $(-0.066706 \pm 2.5 \times 10^{-5}) \text{ m}^{-1}$ by 4.7 experimental standard errors, thus very significantly. (Each indicated uncertainty corresponds to one standard error ultimately pro-

pagated from experimental error in wavenumber measurements.)

The coefficients $h_j^{\text{Li, H}}$ are directly related to the $\Delta_{kl}^{\text{Li, H}}$ parameters [7]. Thus the reported values [10] of $\Delta_{0,1}^{\rm H}, \Delta_{1,0}^{\rm H}, \Delta_{1,1}^{\rm H}$ and $\Delta_{2,0}^{\rm H}$ lead to $h_1^{\rm H}/B_e = -7.3863$ ± 0.0091 , $h_2^{\rm H}/B_e = 10.7216 \pm 0.011$, $h_3^{\rm H}/B_e = -18.503$ ± 0.41 and $h_4^{\rm H}/B_e = 45.665 \pm 0.22$ for ¹H respectively, and of $\Delta_{0,1}^{\text{Li}}$ and $\Delta_{1,0}^{\text{Li}}$ to $h_1^{\text{Li}}/B_e = -0.079649$ ± 0.000025 and $h_2^{\text{Li}}/B_e = 0.0295 \pm 0.048$ for ⁷Li, with B_e for ⁷Li¹H. These values have the same signs and roughly the same magnitudes as those estimated [7] earlier from less precise but more extensive spectral data [13]. A further value -13.65 ± 4.5 of $h_2^{\rm H}/B_{\rm e}$ of ¹H in ⁷Li¹H results from the reported value [10] of $\Delta_{0,2}^{H}$; this value disagrees markedly with the value +10.72given above. Correspondingly, with the known relation [7] between $\Delta_{0,2}^{\text{H. Li}}$ and the coefficients $h_1^{\text{H. Li}}$ and $h_2^{\rm H,Ll}$ through $Z_{0,2}$, one can estimate values $\Delta_{0,2}^{\rm H} =$ -3.72 ± 0.01 and $\Delta_{0,2}^{\text{Li}} = -0.13 \pm 0.08$; the former disagrees with the empirical value +1.85 by 5.4 experimental errors, but no value of the latter was determined [10]. These deviations are consistent with, and related to, the discrepancy described for $U_{0,2}$. As demonstrated for HCl [9], which like LiH has abundant and precise spectral data for isotopic sets of both nuclei, if the value of $U_{0,2}$ is constrained to that required by its relation to $U_{0,1}$ and $U_{1,0}$, then values of $\Delta_{0,2}^{a,b}$ may be determined with good numerical significance. If values of $U_{0,2}$ and $\Delta_{0,2}$ are both freely fitted, then their covariance coefficient (from the dispersion matrix in the statistical fitting process) has a relatively large magnitude, strongly indicating the lack of numerical significance; the application of at least one appropriate constraint serves to break this correlation.

Similar inconsistencies are found in the older, but not yet superseded, analysis of the spectra of CO [14] in which the U_{kl} coefficients were also used merely as independent fitting parameters. Thus for instance, the value of c_1 calculated from $U_{0,3}$ deviates by more than 10 standard errors from that calculated from $U_{0,1}$, and the value of $U_{0,2}$ calculated by means of Eqn (8) differs by more than 20 standard errors from the freely fitted value. The omission of the imposition of the constraint represented by Eqn (8) apparently precluded the significant determination of values of $\Delta_{0,2}^{C,O}$ as well as introducing model errors into the numerical values of other parameters. One can predict a value $\Delta_{0,2}^{0} = -5.98 \pm 0.05$, the accuracy of which is really limited by the model deficiencies in the wavenumber analysis [14]. Because the transition wavenumbers have never been published [14], a reanalysis of the CO data is not practicable; the vibration-rotational wavenumbers of LiH [10] will be combined with new measurements of the electronic spectrum for higher vibrational states, now in process, in order to obtain a global fit over a great range of the potential energy well.

Clearly, in order to ensure the physical significance of the values of spectral parameters, the applicable constraints must be brought into the fitting process. If the wavenumber data are fitted directly to the potential energy coefficients, as in the third approach described above, then the constraints are automatically applied. Alternatively, one can employ relations between the various U_{kl} parameters of which Eqn (8) is but one instance. Although the derivation of the published list [15] was based on the DUNHAM function for potential energy [V(x) in Eqn (1)], these relations are equally consistent with the superior function V(z) in Eqn (6), and could therefore be readily derived from the extensive collection of expressions for Y_{kl} or U_{kl} previously published [12]. By either method, the resulting values of parameters are much more useful for comparison with either theoretical or other experimental results. The application of constraints in the analyses of the spectra of LiH [10] and CO [14] should have produced not only better fits, according to the F-statistic [16], but also more physically consistent and meaningful values of the parameters.

As further proof of the validity of these constraints, consider three cases. The wavenumbers of $> 10^5$ transitions in the visible spectrum of I_2 were reproduced [17] satisfactorily by means of the values of only 46 parameters. Of these, seven are $Y_{k,0}$ and six $Y_{k,1}$ for the ground electronic state X up to vibrational state v'' = 19 and rotational states therein up to $J \sim 200$, whereas for the excited electronic state B sixteen values of each of $Y_{k,0}$ and $Y_{k,1}$ were required to fit vibration-rotational states up to v' = 80, the latter only 160 m^{-1} below the dissociation limit of the B state. Throughout this range, all other values of Y_{kl} , $2 \leq l \leq 6$, were fixed completely through their dependence on $Y_{k,0}$ and $Y_{k,1}$ and were thus not floating in the sense of empirical fitting parameters. The other parameter was considered [17] to reflect the neglect of even higher-order coefficients Y_{kl} , 1 > 5; however a more likely explanation is that the Y_{kl} parameters, in contradistinction to the U_{kl} parameters, are not quite independent because of slight interference from adiabatic and other effects taken into account through the $\Delta_{ki}^{a,b}$ coefficients in Eqn (4). Analogously, the analysis of the visible spectrum of Br₂ is equally impressive because the wavenumbers of 80 000 lines were well reproduced by means of only 38 parameters [18]. In this case for the ground electronic state X, five values of $Y_{k,0}$ and six of $Y_{k,1}$ were used for vibrational states up to v'' = 14, with J up to ~130; for the excited electronic state B, thirteen values of $Y_{k,0}$ and fourteen of $Y_{k,1}$ sufficed to represent states up to v' = 52, only 530 m⁻¹ below the dissociation limit of the B state. As for I₂, the values of the other coefficients Y_{kl} , $2 \le l \le 6$ were fixed relative to $Y_{k,0}$ and $Y_{k,1}$ and a further parameter was empirically employed to absorb other minor effects [18]. In both these cases, a fully numerical procedure was used to calculate [19] the centrifugal distortion coefficients based on the RKR potential energy rather than an analytic function. Undoubtedly the great success of these fits results at

least in part from the relatively small values of the expansion parameter γ for these electronic states, approximately 0.00035 and 0.00046 for the X and B states of I₂ respectively and 0.00050 and 0.00071 for the X and B states of Br₂; such values ensure, at least for small values of *l* a rapid convergence of the series for Y_{kl} in Eqn (3). However, even in the case of the ground electronic state of H₂, for which the value $\gamma = 0.0277$ is exceptionally large, apparently the centrifugal distortion coefficients D_v and H_v can still be accurately calculated [20] on the basis of an accurate potential energy function.

The method of these determinations [17, 18] for I_2 and Br₂ is equivalent to the third approach listed above, the RKR potential energy being implicit in the calculation of the values of the centrifugal distortion coefficients that are then imposed in the following iteration towards convergence of the Y_{kl} coefficients. The parameter additional to these Y_{kl} that was included in the method essentially took into account empirically the effects encompassed in the higher orders of the RKR procedure that were excluded from the first-order method used. The neglect of these higher orders may be alternatively avoided in the socalled inverted-perturbation approach [21], which is merely a fitting by least squares to experimental energies or energy differences to parameters of some function to correct some analytic or numerical (commonly first-order RKR) trial starting potential energy; this method is guantal insofar as the calculated energies are based on numerical solution of the Schrödinger equation, and the term "perturbation" implies that the partial derivatives used in the fitting were obtained by the Hellmann-Feynman theorem. It should be emphasized that this inverted-perturbation approach is neither more "exact" nor more "quantum-mechanical" than the DUNHAM or RKR procedures if the latter include the higher orders; the reason is that it has been proven analytically [5] that the Y_{kl} expressions are identically derived by either semi-classical or quantum-mechanical approaches, and the equivalence of RKR and DUNHAM methods has been equally demonstrated [22, 23]. Therefore, the V(z) potential energy function is proved to be the best representation available for diatomic molecules, and the tests of consistency implicit in its proper determination from experimental data are a necessary test of the completeness of a spectral analysis.

In conclusion, we recommend that for the vibration-rotational energies or transition wavenumbers of diatomic molecules the full physical basis of the vibration-rotational model, represented by the applicable constraints whether or not based on an explicit (analytic or numerical) potential energy function, should be incorporated during the fitting of the transition wavenumbers in the process of data reduction, in order that the resulting spectral parameters embody the maximum numerical and physical significance. By so doing, not only would the results render in a consistent manner the fundamental properties of the

molecular system as radial functions (within the Born-Oppenheimer framework), but also the maximum data compression may be obtained.

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