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THE SIGNIFICANCE OF THE Δ_{kl} PARAMETERS IN THE VIBRATION-ROTATIONAL ENERGIES OF DIATOMIC MOLECULES

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J. F. Ogilvie

Academia Sinica
Institute of Atomic and Molecular Sciences
P. O. Box 23-166, Taipei 10764, Taiwan
Bitnet: cc7b0001 @ twnmoe10

ABSTRACT

We discuss the physical significance of the parameters Δ_{kl} that arise from mostly the adiabatic and nonadiabatic effects in the vibration-rotational energies of diatomic molecules for which data from isotopic variants are available. Examples are given of the use of these parameters to derive radial functions for HCl and LiH. Similar to those for the U_{kl} coefficients, relations among the Δ_{kl} coefficients have been developed, but caution is urged in their use.

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In fitting simultaneously the wavenumbers of spectral lines due to several isotopic variants of carbon oxide CO in vibration-rotational transitions, Ross, Eng and Kildal found[1] it necessary to include in the equation for the energies of the quantum states, beside a factor being the molecular reduced mass μ_i to various powers, a term having an inverse dependence on the mass M_a or M_b of each atomic centre. The empirical parameters $\Delta_{kl}^{a,b}$ then became the coefficients of these inverse masses, according to the following formula:

$$E_{vJ}^{i} = \sum_{k=0} \sum_{l=0} U_{kl}\, \mu_i^{-(k+2l)/2}\, (v+½)^k\, [J^2+J]^l$$
$$[1 + m_e(\Delta_{kl}^{a}/M_a + \Delta_{kl}^{b}/M_b)] \qquad (1)$$

In this relation for the vibration-rotational energies of a particular isotopic variant i of the diatomic molecule in a $^1\Sigma$ electronic state with quantum numbers v for vibration and J for the total angular momentum supposed to be due only to rotation of the nuclei and associated electrons about the molecular centre of mass, the coefficients U_{kl} and $\Delta_{kl}^{a,b}$ are supposed independent of mass; the reduced mass μ_i of the particular isotopic variant is defined in terms of the masses M_a and M_b of the separate neutral atoms, but there is allowance for the fact that the molecule may carry a net electric charge of Z units in terms of the protonic charge:

$$\mu_i = M_a\, M_b/(M_a + M_b + Z\, m_e) \qquad (2)$$

In the special case of two nuclei having the same number of protons and thus being of the same type, then equation (1) reduces to the simpler one considered earlier by Bunker[2] and Watson[3] in which the correction term also incorporates the reduced mass:

$$[1 + m_e \Delta_{kl}/\mu_i] \tag{3}$$

The physical interpretation of the parameters is possible in terms of the Born-Oppenheimer treatment separately of the motions of the electrons and nuclei. Accordingly, the coefficients U_{kl} may be related to parameters associated with the internuclear potential energy; in terms of the general flexible potential-energy function[4],

$$V(z) = c_0 z^2 (1 + \sum_{j=1} c_j z^j) \tag{4}$$

in which the reduced variable z for internuclear separation is related to the instantaneous R and equilibrium R_e distances according to $z \equiv 2(R-R_e)/(R+R_e)$, the coefficients U_{kl} are expressed in terms of R_e, the harmonic force coefficient k_e and the coefficients c_j. In practice, these coefficients U_{kl} also absorb any other effects with the same dependence on reduced mass. Likewise, although it is known that the $\Delta_{kl}^{a,b}$ parameters contain certain adiabatic and nonadiabatic effects, beside the second-order mechanical effects (arising from the vibration and rotation of the nuclei about the centre of mass), other effects such as relativistic or radiative may also be absorbed by the latter quantities if the effect follows the appropriate mass dependence.

However, Tiemann et al have argued[5] that the adiabatic effects are more important than the nonadiabatic effects, that are in turn more important than the second-order mechanical effects except for "light" molecules (i.e. those with reduced mass less than ~ 3 amu); the further effects are presumably negligible.

Recently there has been considerable interest in the accurate determination of the radial functions that, according to the Born-Oppenheimer procedure, are related to certain measurable effects in molecular spectra, such as the deviations of vibration-rotational energies from the law of simple scaling according to the reduced mass[6]. Dunham's equation for the vibration-rotational energies of a diatomic molecule in a $^1\Sigma$ electronic state

$$E_{vJ}^{i} = \sum_{k=0} \sum_{l=0} Y_{kl}^{i} \, (v + \tfrac{1}{2})^{k} [J^{2} + J]^{l} \qquad (5)$$

actually provides such a scaling law for each separate contribution $Y_{kl}^{(j)}$, corresponding to a particular order in perturbation theory for instance, to the total coefficient Y_{kl}^{i} for each isotopic species,

$$Y_{kl}^{i} = Y_{kl}^{(0)} + Y_{kl}^{(2)} + Y_{kl}^{(4)} + \ . \ . \ . \qquad (6)$$

but the total coefficient scales accurately only to the extent that the contributions beyond $Y_{kl}^{(0)}$ are negligible. According to this approach, the coefficients $U_{kl} \equiv Y_{kl}^{(0)} \mu_{i}^{(k+2l)/2}$ lead to the radial function for the internuclear potential energy; correspondingly each set of coefficients $\Delta_{kl}^{a,b}$ leads to a radial function expressing collectively, and at present inextricably, the combined effects of essentially the adiabatic and nonadiabatic effects for that atomic type a or b. (Although it may seem incongruous to consider the existence of a radial function for nonadiabatic effects, such models have in fact been previously discussed[7-9] in which even separate functions for the rotational and vibrational contributions were proposed--*vide infra*.)

In order to determine the radial functions pertaining to the adiabatic and nonadiabatic effects by means of the available values of the $\Delta_{kl}^{a,b}$ parameters, it is necessary to eliminate the effects of the second-order mechanical effects $Y_{kl}^{(2)}$. A general procedure embodying some analytic relations has already been described[10], according to which any measurable spectral quantity Z_{kl} that shows a dependence on both the rotational and the vibrational quantum numbers may be treated in order to yield the appropriate radial function. The problem is that for a diatomic molecule with nuclei belonging to different chemical elements there may exist two sets of parameters Δ_{kl}^{a} and Δ_{kl}^{b} between which the second-order mechanical effects must be partitioned before the two separate radial functions may be determined. Watson has proposed[9] one method of such partitioning, namely in proportion to the relative values of the inverse atomic masses. Thus for the set of coefficients Z^a_{kl}, one writes

$$Z^a_{kl} = U_{kl}\,\mu_i^{-(k+2l)/2}\,m_e\,\Delta^a_{kl}/M_a - Y^{(2)}_{kl}\mu_i/M_a \qquad (7)$$

and analogously for Z^b_{kl}. Applying this approach to the available[11] values of the parameters Δ^H_{kl} and Δ^{Cl}_{kl} of HCl, we obtain through the relations[10] for Z_{kl} in terms of the potential-energy coefficients c_j and the additional coefficients h_j in the radial function

$$K(z) = \sum_{j=1} h_j\, z^j \qquad (8)$$

the following results for ^1H and ^{35}Cl (B_e for $^1H^{35}Cl$):

$$K^H(z)/B_e = (1.8266\pm.0076)\ z + (-5.586\pm.019)\ z^2 + (3.49\pm0.28)\ z^3 + (28.0\pm1.2)\ z^4 \qquad (9)$$

$$K^{Cl}(z)/B_e = (-0.0668\pm.0050)\ z + (0.323\pm0.016)\ z^2 \qquad (10)$$

The numerical values of the coefficients differ only slightly from those in the previous treatment[12] in which the effects of $Y^{(2)}_{kl}$ were apportioned between the two functions $Z^{a,b}_{kl}$ in proportion to the relative values of the ratios Δ^a_{kl}/M_a and Δ^b_{kl}/M_b. One may as before estimate[10] from the value[11] of $\Delta^H_{0,2}$ an alternative, but much less accurate, value $h^H_2/B_e = -7.19 \pm0.43$, in only fair agreement with that -5.586 ± 0.019 above.

Since the publication[12] of the first analytic method for the determination of these radial functions for adiabatic and nonadiabatic effects, Hadinger et al[13] have proposed a different method, much more complicated; in this method it is unclear whether the corrections for the second-order mechanical contributions $Y_{kl}^{(2)}$ are taken into account. Although their numerical results for HCl according to a different form of radial function (but equivalent to that in equation 8) are roughly comparable (but lacking both the specification of the units (cm^{-1}) and any indication of accuracy propagated from experimental error[11]) to those in equations 9 and 10, these workers claim to have derived a value equivalent to h_5^H; because such a determination was based[14] upon a clearly nonexistent[11] value of $\Delta_{2,1}^H$, this result must be considered an artefact. (In fact there exists no other value of Δ_{kl}^H, such as $\Delta_{1,3}^H$ or $\Delta_{0,5}^H$, from which the value of h_5^H might be derived.)

Also since the earlier analysis[12] of the then available[15] spectral data for LiH, new and more precise data[16] but more limited in the extent of vibrational and rotational quantum numbers have become available, however including more numerous values of the parameters Δ_{kl}^H and Δ_{kl}^{Li}, in fact equivalent to the set determined[11] for HCl. We thus generate the following radial functions for ^1H and ^7Li (with B_e for $^7Li^1H$):

$$K^H(z)/B_e = (-7.3959\pm0.0090)\ z + (10.678\pm0.041)\ z^2 + (-19.17\pm0.39)\ z^3 + (59.6\pm1.3)\ z^4 \qquad (11)$$

$$K^{Li}(z)/B_e = (-0.0697\pm.0028)\ z + (0.0727\pm.035)\ z^2 \qquad (12)$$

The significant changes from the previous[12] values of the coefficients h_j^H/B_e merely reflect the more precise new values[16] of the parameters Δ^{H}_{kl}, and in addition it has become possible to define some values for the coefficients h^{Li}_{j}/B_e. From the available[16] value of $\Delta^{H}_{0,2}$ it is possible to obtain an alternative estimate of h^{H}_{2}/B_e, specifically -12.9±4.5. Although the standard error of the latter value is relatively large, this value is still more than five standard errors from the more accurate value, 10.68, obtained from $\Delta^{H}_{1,0}$. The source of at least the major part of the discrepancy is easily deduced: the value of $U_{0,2}$ was not constrained according to its relation[17] to $U_{1,0}$ and $U_{0,1}$, namely

$$U_{0,2} = -\,4\, U^{3}_{0,1} \,/\, U^{2}_{1,0} \qquad (13)$$

and the resulting discrepancy between the freely fitted value of $U_{0,2}$ and the value from the constraint corresponds to 4.7 nominal experimental standard errors, thus highly significant. An earlier fitting[11] of diverse and extensive spectral data of HCl demonstrated that the significant determination of a value of $\Delta^{H}_{0,2}$ required such a constraint as in equation 13.

In fact, the subsequent[12] development of the theory has permitted, through the coefficients h_j, the derivation of a relation analogous to equation 13 among $\Delta_{0,2}$, $\Delta_{0,1}$ and $\Delta_{1,0}$:

$$\begin{aligned}\Delta_{0,2} = 3\,\Delta_{0,1} - 2\,\Delta_{1,0} + [2\,Y^{(2)}_{1,0}\,\mu_i^{1/2}/U_{1,0}\\ - 3\,Y^{(2)}_{0,1}\,\mu_i/U_{0,1} + Y^{(2)}_{0,2}\,\mu_i^{2}/U_{0,2}]\,\mu_i/M_a \qquad (14)\end{aligned}$$

In the approximation that the second-order mechanical effects represented by $Y_{kl}^{(2)}$ are neglected, then equation 14 transforms to the simple relation:

$$\Delta_{0,2} \approx 3\,\Delta_{0,1} - 2\,\Delta_{1,0} \qquad (15)$$

Of course both equations 14 and 15 apply with equal validity for $\Delta_{0,2}^{a}$ and $\Delta_{0,2}^{b}$. Moreover each expression is but one of each kind of two general sets of relations of Δ_{kl}, $l>1$, in terms of the more prominent parameters $\Delta_{k,0}$ and $\Delta_{k,1}$ that correspond exactly to those published[17] previously for U_{kl}, $l>1$, in terms of $U_{k,0}$ and $U_{k,1}$. At present, the relations in equations 14 and 15 are practically the most useful ones of their types.

It should be emphasized that, to the extent that the coefficients U_{kl} represent only the mechanical effects (there has been neither direct experimental evidence nor the theoretical proposal of an experimentally significant contribution from other effects), then the relations of the type represented by equation 13 are exact and must be adhered to in any acceptable analysis of spectral wavenmumbers to which the series representation in equation 1 is applied. In contrast, because the various nonadiabatic effects may contribute in a somewhat different form to the full hamiltonian of the rotating vibrator, perhaps the relations of the types of equation 14 and 15 ought not to be routinely imposed as constraints in spectral analyses. Then the latter relations may provide a significant test whether such effects can be distinguished. Specifically, there exists a rotational gyromagnetic function $g_1(R)$, of which the physical interpretation relates to the extent to which electrons slip with respect to the rotating nuclei, and the analogous function $g_2(R)$ characterising the vibrational inertia of the electrons[8]. Although the Zeeman effect on rotational transitions has been used to obtain expectation values of the former function, no direct experimental method to determine expectation values of $g_2(R)$ has yet been devised. The possibility arises in the future to obtain some information about the latter indirectly from the combination of the knowledge about $g_1(R)$ and that derived from the analysis of the Δ_{kl} parameters.

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