AN ANALYTIC REPRESENTATION OF THE RADIAL DEPENDENCE OF ADIABATIC AND NON-ADIABATIC CORRECTIONS FROM MOLECULAR SPECTRA OF DIATOMIC MOLECULES

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A method of determining the radial dependence of the adiabatic and non-adiabatic corrections contributing to the spectroscopic parameters $\Delta_{kl}^{a,b}$ of diatomic molecules according to an analytic representation is proposed. The method is applied to HCl and CO, and results for LiH are compared with published data.

1. Introduction

Although simple model potential-energy functions had already been developed, in 1932 Dunham [1] made a great advance in the treatment of molecular spectra by introducing a flexible general potential-energy function

$$V(x)=a_0x^2\left(1+\sum_{j=1} a_jx^j\right), \quad x\equiv(R-R_e)/R_e, \tag{1}$$

the parameters a_j of which he directly related to the term coefficients Y_{kl} in the series representation of the vibration–rotational energies (in wavenumber units) of a diatomic molecule in a $^1\Sigma$ electronic state:

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

Each coefficient Y_{kl}, a function of equilibrium internuclear separation R_e, the harmonic force coefficient k, the nuclear or atomic masses M_a and M_b or the reduced mass μ as well as the coefficients a_j, is the sum of contributions

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

of which the parenthesized superscript numeral indicates the order of the integral (according to the BKW theory [2–4]) from which the contribution originates. (The first-order integral is evaluated exactly, and leads to the addend $\frac{1}{2}$ of the vibrational quantum number v; other integrals of odd order vanish.) Successive contributions $Y_{kl}^{(n)}$ decrease by factors γ^2, in which γ is the dimensionless expansion parameter

$$\gamma=\frac{2B_e}{\omega_e}=\frac{\hbar(10^3N_A)^{1/2}}{(\mu k)^{1/2}R_e^2} \tag{4}$$

depending on the equilibrium rotational B_e and vibrational ω_e parameters or the other parameters already defined above (as well as the reduced Planck constant $\hbar$ and the Avogadro constant N_A); values of γ, lying within the range $10^{-4}\leqslant\gamma\leqslant0.026$ for known diatomic molecules, generally ensure a satisfactorily rapid convergence to within experimental uncertainties. (All atomic or nuclear masses and the reduced mass μ are assumed to be expressed in atomic mass units (amu)). By this method Dunham [1] expressed the purely vibrational coefficients $Y_{k,0}$, $k\geqslant0$, in terms of the potential-energy coefficients.

Furthermore, by including the centrifugal term (to take account of the rotation of the nuclei about the centre of molecular mass) in a effective potential-energy function

$$V_{\rm eff}(x)=a_0x^2\left(1+\sum_{j=1} a_jx^j\right)+\frac{B_eJ(J+1)}{(1+x)^2}\,. \tag{5}$$

Dunham [1] formed the J-dependent potential-energy parameters $a_j(J)$ and thus derived the vibration–rotational term coefficients Y_{kl}, $l>0$. (It should be noted that Dunham arbitrarily introduced the form $J(J+1)$ of the functional containing the rotational quantum number J into this treatment, and that therefore this form is not a necessary consequence of the theory.) Thus by fitting the measured spectra to these vibration–rotational energy terms E_{vJ}, one can readily, either directly or indirectly (through the intermediacy of the quantities Y_{kl}), determine the values of the coefficients a_j that define the potential-energy function of the molecule within a certain range of internuclear separation. Previously Dunham had demonstrated [5] how to extract the radial dependence of the molecular electric dipole moment from the intensities of vibration–rotational bands. These procedures and their applications have been reviewed [6].

With the increase in the precision and resolution of spectroscopic measurements, the use of isotopically labeled molecules led to the conclusion that the vibration–rotational energy terms E'_{vJ} pf a particular isotopic molecule were better represented by the empirical equation [7], later justified theoretically [8,9],

$$E'_{vJ}=\sum_{k=0}\sum_{l=0}U_{kl}\mu_i^{-(k+2l)/2}(v+\tfrac{1}{2})^k$$

$$\times[J(J+1)]^l[1+m_e(\Delta^{a}_{kl}/M_a+\Delta^{b}_{kl}/M_b)] \qquad (6)$$

in which the parameters U_{kl} and $\Delta^{a,b}_{kl}$ are formally independent of the nuclear masses M_a and M_b and thus of the reduced mass μ_i of a particular isotopic molecule in a specific electronic state; m_e is the rest mass of the electron. The coefficient U_{kl} is simply equal to $Y^{(0)}_{kl}\mu_i^{(k+2l)/2}$. However the terms $\Delta^{a,b}_{kl}$ include not only (formally) the second-order BKW terms $Y^{(2)}_{kl}$ but also the deviations arising from the (partial) breakdown of the Born–Oppenheimer approximation, the adiabatic and non-adiabatic effects, as well as (in practice) any relativistic, radiative and other effects that follow the appropriate mass dependence. In this paper we present a simple procedure that enables the determination of the combined radial dependence of these effects embodied in the values of the parameters $\Delta^{a,b}_{kl}$ that are now customarily determined in the processing of vibration–rotational spectroscopic data of diatomic molecules.

2. Method

A direct method to accomplish the stated objective is to add a further term $K(x)$ to the effective potential energy, in order to take account of any effects beyond the vibrational and rotational motions,

$$V_{\mathrm{eff}}(x)=a_0x^2\left(1+\sum_{j=1}a_jx^j\right)+\frac{B_eJ(J+1)}{(1+x)^2}$$

$$+\sum_{j=0}k_jx^j \qquad (7)$$

and then simply to follow a procedure analogous to Dunham's [1], outlined above. The additional terms (functions of γ, and the coefficients a_j and k_j) that arise in the coefficients of $(v+\frac{1}{2})^k[J(J+1)]^l$ are assigned to the quantities Z_{kl} [10]:

$$E_{vJ}=\sum_{k=0}\sum_{l=0}(Y_{kl}+Z_{kl})(v+\tfrac{1}{2})^k[J(J+1)]^l\,. \qquad (8)$$

By means of computer algebra [11], we have derived (and checked) the analytic expressions for Y_{kl}, including all contributions $Y^{(0)}_{kl}$, $Y^{(2)}_{kl}$, $Y^{(4)}_{kl}$, and $Y^{(6)}_{kl}$, $2k+l\leqslant 12$, containing terms in the potential-energy coefficients up to a_{10}, plus $Y_{6,1}$ (a_{11}) and $Y_{7,0}$ (a_{12}), and Z_{kl}, $2k+l\leqslant 9$, containing terms up to a_7 and k_9. (The expressions derived for Z_{kl} are really only the contributions $Z^{(0)}_{kl}$ obtained from the zero-order integral of the BKW procedure.)

The potential-energy function $V(x)$ in the Dundam treatment suffers from a finite region of convergence, $|x|\leqslant 1$ or $0\leqslant R\leqslant 2R_e$, because of the reduced displacement variable x. For this reason and because of other useful properties [12], the alternative series representation $V(z)$ 13],

$$V(z)=c_0z^2\left(1+\sum_{j=1}c_jz^j\right),$$

$$z\equiv 2(R-R_e)/(R+R_e)\,, \qquad (9)$$

is preferable because its range of convergence $|z|\leqslant 2$ spans the entire range of molecular existence $0\leqslant R<\infty$. The expressions for Y_{kl}, all orders and $2k+l\leqslant 12$ up to c_{10}, with their derivatives in terms of their parameters (useful for purposes of fitting spectra), have been published [14] in machine-readable form (FORTRAN code). Here we intro-

Table 1
Expressions for Z_{kl}

$$Z_{0,1}=\gamma^2 h_1$$
$$Z_{1,0}=\gamma(h_1+h_2-\tfrac{3}{2}c_1h_1)$$
$$Z_{0,2}=\gamma^4(h_2-2h_1-\tfrac{3}{2}c_1h_1)$$
$$Z_{1,1}=\gamma^3[(\tfrac{27}{4}c_1^2+\tfrac{9}{2}c_1-6c_2+\tfrac{3}{4})h_1-\tfrac{9}{2}c_1h_2+3h_3]$$
$$Z_{2,0}=\gamma^2[(\tfrac{9}{8}c_1+\tfrac{3}{8}c_1^2-\tfrac{45}{8}c_1^3+\tfrac{39}{4}c_1c_2-\tfrac{3}{2}c_2-\tfrac{15}{4}c_3-\tfrac{3}{8})h_1 + (\tfrac{15}{4}c_1^2-\tfrac{3}{2}c_1-\tfrac{3}{2}c_2)h_2+(\tfrac{3}{2}-\tfrac{15}{4}c_1)h_3+\tfrac{3}{2}h_4]$$

duce a further series representation $K(z)$ corresponding to $K(x)$,

$$K(z)=\sum_{j=0} h_j z^j\,, \tag{10}$$

and the expressions $Z_{kl}(\gamma, c_j, h_j)$ to be applied in this paper are listed in table 1.

3. Application to HCl and CO

Some moderately accurate values of $\Delta_{kl}^{a,b}$ are known for HCl [15] and CO [16]. These and other necessary input data, converted from the published data where necessary, are listed in table 2. The equations to generate the values of the new coefficients h_j are the following:

$$Z_{kl}=Z_{kl}^{a}+Z_{kl}^{b}\,, \tag{11}$$

$$Z_{kl}^{a}=U_{kl}\mu^{-(k+2l)/2}m_e\Delta_{kl}^{a}/M_a-\frac{Y_{kl}^{(2)}\Delta_{kl}^{a}/M_a}{\Delta_{kl}^{a}/M_a+\Delta_{kl}^{b}/M_b} \tag{12}$$

and analogously for Z_{kl}^{b}. Thus the two functions $K(z)$, one for each atomic type, are generated separately, and the contributions $Y_{kl}^{(2)}$ [14] from the second-order BKW integral are apportioned between the two atomic types in the ratio of the terms Δ_{kl}^{a}/M_a and Δ_{kl}^{b}/M_b. Because there are so few $\Delta_{kl}^{a,b}$ data available, for a given molecule the fitting process is done directly in a serial manner. The value of h_1 is derived from $\Delta_{0,1}$, then with that value h_2 is determined from $\Delta_{1,0}$, etc. The results are given in table 3. The ranges of validity, between R_- and R_+, of the polynomial representations $K(z)$ are also given in table 3.

Table 2
Data used in the analysis of adiabatic and non-adiabatic effects

	^{1}H ^{35}Cl	^{12}C ^{16}O	^{7}Li ^{1}H
B_e (m^{-1})	1059.349943	193.12831	751.96123
γ (10^{-3})	7.083589	1.7801366	10.696795
c_1	−1.33725	−1.69715	−0.89577
c_2	0.865517	1.21065	0.35160
c_3	−0.473118	−0.505215	−0.14284
c_4	0.089594	0.31739	0.001355
R_e^{BO} (10^{-10} m)	1.2746032	1.1282294	1.594983
a	^{1}H	^{12}C	^{1}H
b	^{35}Cl	^{16}O	^{7}Li
$\Delta_{0,1}^{a}$	0.1320 ±0.0007	−2.0466 ±0.0111	−1.25616±0.00043
$\Delta_{1,0}^{a}$	−0.06382±0.00088	0.700875±0.000957	−0.61039±0.00055
$\Delta_{0,2}^{a}$	0.74 ±0.04		
$\Delta_{1,1}^{a}$	0.462 ±0.019	−0.205 ±0.214	0.0116 ±0.0044
$\Delta_{2,0}^{a}$	−0.324 ±0.0174	0.4169 ±0.014	
$\Delta_{3,0}^{a}$		−13.975 ±0.438	
$\Delta_{0,1}^{b}$	−0.250 ±0.017	−2.1248 ±0.0138	−0.176 ±0.009
$\Delta_{1,0}^{b}$	0.1280 ±0.0158	−0.17222 ±0.00126	
$\Delta_{1,1}^{b}$		−1.617 ±0.258	
$\Delta_{2,0}^{b}$		−0.9804 ±0.0355	
$\Delta_{3,0}^{b}$		−4.48 ±2.37	

Table 3
Values of the coefficients h_j deduced from the given experimental data for the specified molecules, and the limits R_- and R_+ of the range of validity of $K(z)$

	^{1}H ^{35}Cl	^{12}C ^{16}O	^{7}Li ^{1}H
a	^{1}H	^{12}C	^{1}H
b	^{35}Cl	^{16}O	^{7}Li
h_1^a/B_e	1.8614 ± 0.0074	-29.32 ± 0.16	-5.8437 ± 0.002
h_2^a/B_e	-5.5673 ± 0.02	124.71 ± 0.65	8.4508 ± 0.005
h_3^a/B_e	3.428 ± 0.28	-261.0 ± 5.1	-14.411 ± 0.02
h_4^a/B_e	28.218 ± 0.54	513.2 ± 4.6	-0.1202 ± 0.006
h_1^b/B_e	-0.1016 ± 0.0065	-22.837 ± 0.15	
h_2^b/B_e	0.304 ± 0.02	77.150 ± 0.66	
h_3^b/B_e		-128.24 ± 4.7	
h_4^b/B_e		212.28 ± 4.5	
R_- (10^{-10} m)	1.0	0.98	1.15
R_+ (10^{-10} m)	1.7	1.35	2.30

4. Discussion

The series expansion $K(z)$ really represents the difference between the adiabatic and non-adiabatic corrections (and any other effects with the same dependence on mass), embodied in the values of the coefficients $\Delta_{kl}^{a,b}$, at any internuclear separation R and those at equilibrium R_e. Because of the relatively large experimental uncertainties associated with the experimentally determined quantities $\Delta_{kl}^{a,b}$, it is immaterial whether one uses atomic masses or nuclear masses, or correspondingly the adiabatic equilibrium internuclear separation (estimated from B_e) or the Born–Oppenheimer equilibrium internuclear separation defined through $U_{0,1}$; in this work atomic masses and the latter separation R_e^{BO} have been used. There are few experimental or theoretical data with which the present results for HCl and CO can be compared, but such a comparison is possible for LiH; for this reason the corresponding data and results for the latter molecule have been included in tables 2 and 3. For the purpose of this analysis, the vibration–rotational energy term coefficients of LiH [17] were converted to the form compatible with eq. (6); the only statistically significant values of $\Delta_{kl}^{Li,H}$ possible to derive are listed in table 2. Hadinger and Tergiman [18] used a different analytic approach for the same objective as in the present work, but did not use the commonly available $\Delta_{kl}^{a,b}$ parameters as the basis of their treatment. For comparison with their results, they fitted numerically the experimentally derived data of Vidal and Stwalley [17]. The function $K(x)$ for the hydrogen atom corresponding to the coefficients of $K(z)$ in table 3 is

$$K(x)/10^2\ \mathrm{m}^{-1}=(-43.943\pm0.015)x$$

$$+(85.47\pm0.04)x^2+(-182.81\pm0.15)x^3;$$

the values of the coefficients in this function are similar to those derived by Hadinger and Tergiman [18] (who fail to provide in their results any estimate of uncertainty propagated from the experimental data), but k_3 in particular lies much closer to the result -183 fitted from Vidal and Stwalley [17] than to the value -155.5 obtained in ref. [18]. The close agreement between the present and previous results [17], obtained by different methods, supports the correctness of the present approach.

Some comments about the new results for HCl and CO are necessary. For HCl, the availability of $\Delta_{0,2}^{H}$ makes possible an alternative estimate of h_2^H; the value obtained is -7.166 ± 0.44, in reasonable agreement with the value (derived from $\Delta_{1,0}^{H}$) given in table 3 if one considers the sensitivity of these small corrections $\Delta_{kl}^{a,b}$ to experimental error. Thus for instance, the magnitudes [16] of both $\Delta_{3,0}^{C}$ and $\Delta_{3,0}^{O}$ are much larger than expected [9], and are of doubtful physical significance; for this reason, and because of the absence of any value of $\Delta_{kl}^{C,O}$ that could lead to a value of h_5, no attempt was made to derive a value of h_6 from these values of $\Delta_{3,0}^{C,O}$. In the analysis [16] of the wavenumber data of CO, the U_{kl}

quantities were treated simply as fitting parameters; the consistency conditions that are applicable through the potential-energy function were omitted. Thus for instance, the values of $U_{0,2}$ obtained through independent fitting and from the relation $U_{0,2}=-4U^3_{0,1}/U^2_{1,0}$ differ by more than twenty standard errors. The omission of the imposition of this condition precluded the significant determination of values of $\Delta^{C,O}_{0,2}$, as well as introducing model errors into the numerical values of other parameters, as demonstrated during the analysis of the frequency data of HCl [15]. However the values of the coefficiens h_j derived for CO in this work probably retain some physical significance. Anyhow, by means of the values of h^O_1 and h^O_2 from table 3, the expression for $Z_{0,2}$ from table 1 and eq. (12), one can for instance predict a value $\Delta^O_{0,2}=-5.98\pm0.05$ of which the accuracy is really limited by the model deficiencies in the wavenumber analysis [16]. A fit to a fourth-order polynomial of the "u_H" data for HCl [19] yields the values of the coefficients $h^H_1/B_e=1.804\pm0.02$, $h^H_2/B_e=-5.36\pm0.26$, $h^H_3/B_e=3.47\pm1.05$ and $H^H_4/B_e=12.3\pm8.6$; the first three values agree well with those in table 3, but the last is statistically not well defined. In contrast, a fit of the "u_{Cl}" data for HCl [19] provides no agreement with the results in table 3; no indication of the statistical uncertainty of the "u_{Cl}" data was given [19], but the present results cast doubt on their significance.

According to Tiemann et al. [20], the adiabatic corrections are more important than the non-adiabatic corrections, and both are more important than the terms $Y^{(2)}_{kl}$ from the second-order BKW integral except for "light" molecules; in the case of the three molecules treated here at least the hydrides HCl and LiH are in the latter category, but the effect of $Y^{(2)}_{kl}$ is explicitly taken into account in the present work. If the $Y^{(2)}_{kl}$ correction is entirely omitted for CO, and for Δ^{Cl}_{kl} of HCl and $\Delta^{Li}_{0,1}$ of LiH, the values of all h^C_j, h^O_j, h^{Cl}_j and h^{Li}_1 in table 3 are altered only slightly.

The expressions in table 1 are related to those given earlier by Bessis et al. [21] who obtained their analytic results by unnecessarily complicated procedures. Also, the expressions in their paper contain many errors (for instance, in $\mathscr{y}_{3,1}$, $\mathscr{y}_{4,1}$ and $\mathscr{y}_{2,2}$). Their replacement of the powers of $v+\frac{1}{2}$ in eq. (2) by $v!$ also leads to inconsistencies in the calculation of vibrational energy differences due to the upper limit of the summation over k also being v. Their inclusion [21] of the factor B_e in the function $K(x)$ also imparts an incorrect mass dependence, adversely affecting calculations for isotopic molecules.

5. Concluding remarks

In the spirit of the theory of Dunham [1], a simple method has been developed to determine the radial dependence of the adiabatic and non-adiabatic corrections (in an unknown proportion), based on the experimentally determined spectroscopic parameters $\Delta^{a,b}_{kl}$. This method is generally applicable to any set of spectroscopic data consisting of the parameters U_{kl} and $\Delta^{a,b}_{kl}$, and can be extended to as many coefficients in the power series $K(z)$ as correspond to the set of independent values of the various $\Delta^{a,b}_{kl}$. Furthermore, a similar analysis could be applied to the volume coefficients V_{kl} [22]. Thus the recommended analysis of the vibration–rotational energies of diatomic molecules is by means of eq. (6), or better still directly to the potential-energy coefficients c_j by a non-linear fitting procedure using all the available data [14]. However, in recognition of the inter-relations between these $\Delta^{a,b}_{kl}$ quantities and of their physical significance, just as for the U_{kl} quantities, one must take care during the process of fitting the spectral frequencies so that the resulting information about the radial dependence of the adiabatic and non-adiabatic corrections has the maximum physical significance.

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