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Quantitative analysis of adiabatic and non-adiabatic effects in the vibration–rotational spectra of diatomic molecules

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Abstract. Expressions of the vibration–rotational, Z^v_{kl}, and additional rotational, Z^r_{kl}, coefficients in the vibration–rotational energies of a diatomic molecule to take quantitatively into account the separate vibrational adiabatic and non-adiabatic vibrational and rotational terms in the Hamiltonian for nuclear motion have been generated by methods of symbolic computation. All the radial functions have as argument $z=2(R-R_e)/(R+R_e)$. An algorithm to evaluate these coefficients from available spectral data was tested on simulated data and applied to HCl. The relative contributions of adiabatic and non-adiabatic effects to selected term coefficients and the need for experimental measurements of the Zeeman effect on rotational and vibration–rotational transitions are discussed.

1. Introduction

Since van Vleck's (1936) initial treatment of adiabatic and non-adiabatic effects that was strongly influenced by Dunham's (1932) analytic approach to the analysis of molecular spectra, there has been much progress in the understanding of the nature and extent of these effects. Adiabatic effects signify that the energy of a molecule within a particular electronic state depends not only on the internuclear distance but also on the relative nuclear momenta, hence on the nuclear masses. The non-adiabatic effects arise from the failure of the electrons to follow perfectly the nuclei during their vibrational and rotational motions, and are attributed formally to interactions between the electronic state of interest—typically the electronic ground state for purposes of vibration-rotational spectroscopy—and other electronic states. Non-adiabatic vibrational effects are associated with vibrational motion of the nuclei that is supposed to induce interactions between electronic states of the same electronic angular momentum, whereas rotational motion analogously gives rise to non-adiabatic rotational effects associated with interactions between electronic states of net electronic angular momenta differing by one unit (van Vleck 1936). All these effects arise from the approximate separation of electronic and nuclear motions according to which Born and Oppenheimer (1927) introduced the idea of molecular structure into quantum mechanics. If the energies of the rotational and vibrational states in the electronic state of interest are sufficiently distant from those in other electronic states, the interactions are sufficiently small to be considered weak and homogeneous perturbations; the dependence on internuclear distance of these effects may then be formally defined analogously to the potential energy that is the dominant factor governing the vibrational and rotational energies of the eigenstates belonging to the particular isolated electronic state. According to an

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analytic approach, we present a formalism by means of which one can for the first time separate purely from experimental data the various effects, and provide an instance of application to the particular molecular species HCl. Because of relentlessly increasing spectral resolution, the corresponding precise measurement of spectral lines reaches $\delta\nu/\nu \sim 10^{-9}$ in the best cases (for instance $\sim 2\times 10^{-9}$ for DCl; Klee and Ogilvie (1993)); available spectra of a particular molecular species may consist of thousands of assigned lines of isotopic variants that exhibit these mass effects. For these reasons spectral data of the present quality and quantity far surpass theoretical description within the confines of Dunham's theory. In the sense that we have during the course of the present work produced a quantitative description of these effects in terms of the applicable radial functions, we have been able to complete the task that van Vleck initiated. The radial functions on which we base our results provide simultaneously the most compact and most physically meaningful representation of the frequencies and wavenumbers of the corresponding spectral lines (Ogilvie 1990). In 1923 Randall recognised the importance both of the theoretical description of vibrational and rotational motions and of experimental information about HCl in particular that could serve as a test of any pertinent theory.

2. Analytic treatment

From the non-relativistic Hamiltonian of a dinuclear molecule in the electronic state of $^1\Sigma$ for which there is accordingly neither net orbital nor spin angular momentum of the set of N electrons and for which intrinsic nuclear angular momenta are neglected, we derived the following effective Hamiltonian for the motion of the nuclei (Fernandez and Ogilvie 1992 and references therein),

$$\mathcal{H}_{\mathrm{eff}} = \frac{-\hbar^2}{2\mu}\frac{\mathrm{d}}{\mathrm{d}R}[1+\beta(R)]\frac{\mathrm{d}}{\mathrm{d}R} + V_{\mathrm{eff}}(R) + \frac{\hbar^2}{2\mu R^2}[1+\alpha(R)]J(J+1). \tag{1}$$

Therein $V_{\mathrm{eff}}(R)$ comprises the effective internuclear potential energy of the non-rotating molecule,

$$V_{\mathrm{eff}}(R) = V^{\mathrm{BO}}(R) + V^{\mathrm{ad}}(R) + V^{\mathrm{na}}(R) \tag{2}$$

containing the contributions the potential energy $V^{\mathrm{BO}}(R)$ that is formally independent of nuclear mass, $V^{\mathrm{ad}}(R)$ that takes into account adiabatic effects and $V^{\mathrm{na}}(R)$ that takes partially into account vibrational non-adiabatic effects (Bunker and Moss 1977). In equation (1) the last term containing the quantum number J for the total angular momentum of the molecule represents the centrifugal effects; the function $\alpha(R)$ takes into account the rotational non-adiabatic effects, that the electrons fail to follow perfectly the nuclei as the latter rotate about the centre of molecular mass. In the term for nuclear kinetic energy $\beta(R)$ is an analogous function for vibrational inertia of the electrons.

Dunham's (1932) radial function for the internuclear potential energy, independent of nuclear mass, has the form of a series in the argument x to various powers,

$$V^{\mathrm{BO}}(x) = a_0 x^2 \left(1 + \sum_{j=1}^{\infty} a_j x^j\right) \tag{3}$$

in which the formally infinite series becomes truncated as governed by the finite quantity of experimental data. The reduced displacement x depends on the instantaneous internuclear distance R from its equilibrium length R_e; $x \equiv (R-R_e)/R_e$. Because this variable is poorly behaved as $R \to \infty$, we have introduced (Ogilvie 1981) the alternative variable $z \equiv 2(R-R_e)/(R+R_e)$ that places on an equivalent basis, $z=\pm 2$, the two limits of molecular existence, namely the separate atoms as $R \to \infty$ and the united atom at $R=0$. The function for potential energy

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

that remains formally independent of mass has the form of that due to Dunham; because of the everywhere well behaved nature of z one can in this case apply boundary conditions to make the energy approach properly the asymptotic limit $V^{\mathrm{BO}}(z) \to \boldsymbol{D}_e$, the equilibrium binding energy (relative to $V^{\mathrm{BO}}=0$ at $z=0$ or $R=R_e$) as $z \to 2$ (Ogilvie 1988); hence the number of coefficients c_j can be kept finite.

For a molecule that consists of two nuclei of distinct atomic numbers plus the associated electrons, there are in general two radial functions for each physical effect beyond the potential energy because the masses of nuclides of each atomic number influence separately the molecular energies. The effects that we must include are the adiabatic and rotational and vibrational non-adiabatic effects, corresponding to $V^{\mathrm{ad}}(R)$, $\alpha(R)$ and $\beta(R)$ respectively; the other function $V^{\mathrm{na}}(R)$ in equation (3) we ignore because its order in the expansion variable $\kappa \equiv (m_e/M_{\mathrm{at}})^{1/4}$ (Born and Oppenheimer 1927) makes it negligible relative to the retained terms (Fernandez and Ogilvie 1992); m_e is the electronic rest mass and M_{at} is the average atomic mass. To take into account these effects we introduce the following correspondences,

$$V^{\mathrm{ad}}(R) \to (m_e/M_a) \sum_{j=1} u_j^a z^j + (m_e/M_b) \sum_{j=1} u_j^b z^j \tag{5}$$

$$\alpha(R) \to (m_e/M_a) \sum_{j=0} t_j^a z^j + (m_e/M_b) \sum_{j=0} t_j^b z^j \tag{6}$$

$$\beta(R) \to (m_e/M_a) \sum_{j=0} s_j^a z^j + (m_e/M_b) \sum_{j=0} s_j^b z^j \tag{7}$$

that define the coefficients of the pertinent radial functions. The summations begin at $j=0$ for the latter two functions, but at $j=1$ for the adiabatic effects because any constant term therein contributes simply to the zero-point energy taken into account elsewhere. For a molecule containing two nuclei each having the same number of protons but not necessarily the same number of neutrons, each pair of related coefficients merges into a single coefficient having as quotient the reduced mass of the molecule instead of the individual atomic masses. We use in general atomic masses rather than nuclear masses because the latter are relatively inaccurately known and because the consequent error is much smaller than error propagated from currently available measurements of frequencies of transitions. According to these definitions the magnitudes of the coefficients c_j, $j>0$, and of all $t_j^{a,b}$ and $s_j^{a,b}$ are expected to be of order unity whereas the magnitudes of c_0 and of all coefficients $u_j^{a,b}$ are expected to be of order B_e/γ^2; γ is the ratio of the limiting separation $2B_e$ between adjacent rotational lines to the limiting separation ω_e between the centres of adjacent vibrational bands in a progression of an absorption spectrum; the range of values of $\gamma \equiv 2B_e/\omega_e$ is $[10^{-4}, 0.026]$ for known diatomic molecules in their electronic ground states. The expansion coefficient γ governs the rate of convergence of expressions consisting of a sequence of terms having as factor γ to successively increasing powers; magnitudes of γ within the stated range ensure that at most a few contributions suffice to define molecular energies with accuracy beyond that of the measurement of spectral lines.

Following Dunham (1932) and the subsequent extension (Herman and Short 1968), we express the vibration–rotational terms in the systematic form of a double summation,

$$\tilde{E}_{vJ}=\sum_{k=0}\sum_{l=0}(Y_{kl}+Z_{kl}^{v,a}+Z_{kl}^{v,b}+Z_{kl}^{r,a}+Z_{kl}^{r,b})(v+\tfrac{1}{2})^{k}[J(J+1)]^{l} \tag{8}$$

in which we take enough term coefficients to reproduce accurately the experimental data; we suppress the explicit isotopic dependence of $\tilde{E}_{vJ}$ and the term coefficients Y_{kl} and $Z_{kl}^{v,r}$. In this equation and elsewhere hereafter we assume that the units of all quantities $\tilde{E}_{vJ}$, Y_{kl}, Z_{kl}^{v}, Z_{kl}^{r}, the potential energy $V(z)$ and the coefficients c_0 and all $u_j^{a,b}$ are those of wavenumber; the remaining coefficients $c_j, j>0$, $t_j^{a,b}$ and $s_j^{a,b}$ are dimensionless. The term coefficients Y_{kl} depend on the molecular parameters the harmonic force coefficient k_e, the equilibrium separation R_e, the potential-energy coefficients c_j, $j>0$, and the atomic masses through the molecular reduced mass $\mu\equiv M_aM_b/(M_a+M_b-z_nm_e)$ in which z_n is the net electric charge of the molecular species in units of the protonic charge; $B_e\equiv h/(8\pi^2c\mu R_e^2)$, $\omega_e\equiv(k_e/\mu)^{1/2}/(2\pi c)$ and $c_0=\frac{1}{2}k_eR_e^2/(hc)$. Of these term coefficients Y_{kl} we have derived expressions containing c_j up to $j=24$, including all Y_{kl} such that $2k+l\leqslant 12$ and some important further terms up to $Y_{13,0}$, $Y_{12,1}$ etc. A few expressions appear in table 1 as examples; a collection containing c_j, $j\leqslant 10$, was published, with their derivatives with respect to the parameters, in machine-readable form (Ogilvie 1983) and further expressions will be similarly made available. These expressions Y_{kl} have the form

$$Y_{kl}=\sum_{m=0}Y_{kl}^{(2m)} \tag{9}$$

in which each successive contribution $Y_{kl}^{(2m)}$ contains a further factor γ^2; in practice for most combinations of the subscripts k and l only the leading term Y_{kl}^{0} provides sufficient accuracy, whereas even for the most important coefficients $Y_{1,0}$ and $Y_{0,1}$ only the first three contributions are required at most by comparison with experimental error of frequency measurements. These leading terms Y_{kl}^{0} are expressed also as the product $U_{kl}\mu^{-(\frac{1}{2}k+l)}$ of the reduced mass μ to the indicated power and the further term coefficients U_{kl} that in this way become formally independent of nuclear mass. The latter coefficients appear in an expression of vibration–rotational energies (Ross *et al* 1974),

$$\tilde{E}_{vJ}=\sum_{k=0}\sum_{l=0}U_{kl}\mu^{-(\frac{1}{2}k+1)}[1+m_e(\Delta_{kl}^{a}/M_a+\Delta_{kl}^{b}/M_b)](v+\tfrac{1}{2})^{k}[J(J+1)]^{l} \tag{10}$$

in which the additional empirical coefficients $\Delta_{kl}^{a,b}$ are supposed to take into account the deviations from the mass-scaling properties of the coefficients U_{kl} arising from the various adiabatic and non-adiabatic effects in inextricable combination. Although the expressions in table 1 are equivalent to those that Dunham (1932) reported in terms of his coefficients a_j, our expressions involving the coefficients c_j of z^j are more extensive and more practical for the reasons already stated.

The additional term coefficients of types Z_{kl}^{r} and Z_{kl}^{v} we assume to be experimentally distinguishable; this assumption we justify subsequently. According to our theoretical derivation, the total expressions Z_{kl} are directly partitioned on the basis of the terms in the Hamiltonian that lead to their various contributions (Fernandez and Ogilvie 1992). For instance, the coefficients $u_{kl}^{a,b}$ occur only in the corresponding $Z_{kl}^{v,a}$ and $Z_{kl}^{v,b}$

Table 1. Expressions of term coefficients Y_{kl} in terms of potential-energy coefficients c_j.

$$Y_{0,0}=0+B_e(-7c_1^2/32-c_1/8+3c_2/8+1/16)+\dots$$

$$Y_{0,1}=B_e+B_e^3/\omega_e^2(21c_1^3/4+27c_1^2/4-23c_1c_2/2+35c_1/8-8c_2+15c_3/2+2)+\dots$$

$$Y_{0,2}=-4B_e^3/\omega_e^2+B_e^5/\omega_e^4(-126c_1^4-495c_1^3/2+333c_1^2c_2-933c_1^2/4+434c_1c_2-205c_1c_3-147c_1-92c_2^2$$
$$+194c_2-200c_3+90c_4-535/8)$$

$$Y_{0,3}=16B_e^5/\omega_e^4(c_1+2)+\dots$$

$$Y_{0,4}=16B_e^7/\omega_e^6(-9c_1^2+4c_2-24c_1-22)+\dots$$

$$Y_{1,0}=\omega_e+B_e^2/\omega_e(-1155c_1^4/256-111c_1^3/32+459c_1^2c_2/32-33_1^2/64+61c_1c_2/8-95c_1c_3/8+3c_1/8-67c_2^2/16$$
$$-c_2/16-15c_3/4+25c_4/4-3/32)+\dots$$

$$Y_{1,1}=6B_e^2c_1/\omega_e+\dots$$

$$Y_{1,2}=6B_e^4/\omega_e^3(-9c_1^2-12c_1+8c_2-4)+\dots$$

$$Y_{2,0}=B_e(-15c_1^2/8+3c_1/2+3c_2/2-3/4)+\dots$$

$$Y_{2,1}=B_e^3/\omega_e^2(45c_1^3+27c_1^2-78c_1c_2+3c_1/2+30c_3)+\dots$$

$$Y_{2,2}=B_e^5/\omega_e^4(-1080c_1^4+2484c_1^2c_2-624c_2^2-1140c_1c_3+360c_4-1566c_1^3+1992c_1c_2-480c_3$$
$$-981c_1^2+264c_2-396c_1-87/2)+\dots$$

$$Y_{3,0}=B_e^2/\omega_e(-705c_1^4/64+15c_1^3/8+225c_1^2c_2/8+57c_1^2/16-17c_1c_2/2-35c_1c_3/2-2c_1$$
$$-17c_2^2/4-3c_2/4+5c_3+5c_4+1/2)$$

$$Y_{3,1}=B_e^4/\omega_e^3(19035c_1^5/32-7545c_1^3c_2/4+2175c_1^2c_3/2+2055c_1c_2^2/2-510c_1c_4-450c_2c_3+140c_5+450c_1^4$$
$$-780c_1^2c_2+300c_1c_3+345c_1^3/4+45c_1c_2-20c_3+15c_1^2)+\dots$$

$$Y_{4,0}=B_e^3/\omega_e^2(-115755c_1^6/1024+116325c_1^4c_2/256-9765c_1^3c_3/32-24945c_1^2c_2^2/64+2715c_1^2c_4/16$$
$$+2415c_1c_2c_3/8-315c_1c_5/4+375c_2^3/16-165c_2c_4/4-315c_3^2/8+35c_6/2-855c_1^5/256-1215c_1^3c_2/32$$
$$+615c_1^2c_3/16-165c_1c_4/4+1125c_1c_2^2/16-165c_2c_3/4+35c_5/2+18855c_1^4/512-5565c_1^2c_2/64+705c_1c_3/16$$
$$+195c_2^2/32-45c_4/8-45c_1^3/8+45c_1c_2/2-10c_3-135c_1^2/32-5c_2/8+15c_1/8-5/16)+\dots$$

and analogously the coefficients $t_{kl}^{a,b}$ only in $Z_{kl}^{r,a}$ and $Z_{kl}^{r,b}$, but the coefficients $s_{kl}^{a,b}$ occur in almost all $Z_{kl}^{r,a}$, $Z_{kl}^{r,b}$, $Z_{kl}^{v,a}$ and $Z_{kl}^{v,b}$, as tables 2 and 3 illustrate. These coefficients $Z_{kl}^{r,v}$ depend on the molecular parameters the harmonic force coefficient k_e, the equilibrium separation R_e, the potential-energy coefficients c_j, $j>0$, and the atomic masses through the reduced mass, in addition to the coefficients $u_j^{a,b}$, $t_j^{a,b}$ and $s_j^{a,b}$, all the latter in a linear manner. To produce these expressions, we used hypervirial perturbation theory (Fernandez and Ogilvie 1990) and suppressed terms of order beyond $(m_e/M_{at})^1$ relative to their context (Fernandez and Ogilvie 1992). Because direct expansion of the vibrational non-adiabatic function $\beta(R)$ in the effective Hamiltonian, equation (1), gives rise to unbound contributions of the form $(d/dx)x^j(d/dx)$, we assumed that $\beta(R)$ is a sufficiently well behaved function; we took $\beta(R)$ to be the local representation near $R=R_e$ of a function that possesses the correct asymptotic properties at $R=0$ and $R\to\infty$,

Table 2. Expressions of coefficients $Z_{kl}^{r,a}$ for non-adiabatic vibrational and rotational effects.

$$Z_{0,1}^{r,a}M_a/m_e = B_e t_0^a$$

$$Z_{0,2}^{r,a}M_a/m_e = B_e\gamma^2[-s_0^a - 2t_0^a + t_1^a]$$

$$Z_{0,3}^{r,a}M_a/m_e = B_e\gamma^4[s_0^a(3c_1/2+9/2-\tfrac{1}{2}s_1^a + t_0^a(3c_1+6) + t_1^a(-3c_1/2-4) + t_2^a]$$

$$\begin{aligned}Z_{0,4}^{r,a}M_a/m_e = B_e\gamma^6[&s_0^a(-9c_1^2/2+2c_2-33c_1/2-39/2+s_1^a(3c_1/2+19/6)-\tfrac{1}{3}s_2^a+t_0^a(-9c_1^2+4c_2-24c_1-22)\\&+t_1^a(9c_1^2/2-2c_2+15c_1+65/4)+t_2^a(-3c_1-6)+t_3^a]\end{aligned}$$

$$\begin{aligned}Z_{0,5}^{r,a}M_a/m_e = B_e\gamma^8[&s_0^a(135c_1^3/8-15c_1c_2+5c_3/2+585c_1^2/8-26c_2+993c_1/8+699/8)+s_1^a(-45c_1^2/8+2c_2\\&-69c_1/4-267/16)+s_2^a(3c_1/2+11/4)-\tfrac{1}{4}s_3^a+t_0^a(135c_1^3/4-30c_1c_2+5c_3+225c_1^2/2\\&-40c_2+615c_1/4+90)+t_1^a(-135c_1^3/8+15c_1c_2-5c_3/2-135c_1^2/2+24c_2-213c_1/2-70)\\&+t_2^a(45c_1^2/4-4c_2+33c_1+61/2)+t_3^a(-9c_1/2-8)+t_4^a]\end{aligned}$$

$$Z_{1,1}^{r,a}M_a/m_e = B_e\gamma[s_0^a(3c_1/2+3/2)-\tfrac{1}{2}s_1^a+3t_0^ac_1+t_1^a(-3c_1/2-1)+t_2^a]$$

$$\begin{aligned}Z_{1,2}^{r,a}M_a/m_e = B_e\gamma^3[&s_0^a(-27c_1^2/4+6c_2-63c_1/4-21/2)+s_1^a(9c_1/4+7/2)-s_2^a\\&+t_0^a(-27c_1^2/2+12c_2-18c_1-6)+t_1^a(27c_1^2/4-6c_2+27c_1/2+27/4)+t_2^a(-9c_1/2-6)+3t_3^a]\end{aligned}$$

$$\begin{aligned}Z_{1,3}^{r,a}M_a/m_e = B_e\gamma^5[&s_0^a(567c_1^3/16-99c_1c_2/2+15c_3+1755c_1^2/16-141c_2/2+261c_1/2+69)\\&+s_1^a(-189c_1^2/16+15c_2/2-27c_1-171/8)+s_2^a(9c_1/2+15/2)-3s_3^a/2+t_0^a(567c_1^3/8-99c_1c_2+30c_3\\&+297c_1^2/2-96c_2+126c_1+48)+t_1^a(-567c_1^3/16+99c_1c_2/2-15c_3-783c_1^2/8+63c_2\\&-819c_1/8-183/4)+t_2^a(189c_1^2/8-15c_2+99c_1/2+69/2)+t_3^a(-27c_1/2-21)+6t_4^a]\end{aligned}$$

$$\begin{aligned}Z_{2,1}^{r,a}M_a/m_e = B_e\gamma^2[&s_0^a(45c_1^3/8-39c_1c_2/4+15c_3/4+9c_1^2-9c_2/4+117c_1/16+3/16)\\&+s_1^a(-15c_1^2/8+3c_2/4-29c_1/8-13/32)+s_2^a(5c_1/4+5/8)-3s_3^a/8+t_0^a(45c_1^3/4-39c_1c_2/2\\&+15c_3/2+27c_1^2/4+3c_1/8)+t_1^a(-45c_1^3/8+39c_1c_2/4-15c_3/4-57c_1^2/8+3c_2/2-27c_1/8+3/8)\\&+t_2^a(15c_1^2/4-3c_2/2+6c_1)+t_3^a(-15c_1/4-3/2)+3t_4^a/2]\end{aligned}$$

and carried the function $\beta(R)$ through all the calculations until the final stage so as to avoid problems with the asymptotic behaviour of the polynomial form $\beta(x)$ or $\beta(z)$. Because the ratios $\kappa^4 \equiv m_e/M_{at}$ and $\gamma^2 \equiv (4B_e^2/\omega_e^2)$ have comparable magnitudes, to include in $Z_{kl}^{r,v}$ further contributions that contain successive factors γ^2 would be inconsistent without including terms proportional to $(m_e/M_{at})^2$; therefore only the leading contributions to $Z_{kl}^{r,v}$ appear in tables 2 and 3. A much larger collection of these expressions of $Z_{kl}^{r,v}$ and their derivatives with respect to the parameters will be published subsequently in machine-readable form.

All these expressions Y_{kl} and $Z_{kl}^{r,v}$ we have produced by methods of symbolic computation (Ogilvie 1989), first in the form containing the appropriate coefficients of x^j (Fernandez and Ogilvie 1992); we then converted the coefficients a_j, $\eta_j^{a,b}$, $\zeta_j^{a,b}$ and $\Xi_j^{a,b}$ of x^j into the present coefficients c_j, $u_j^{a,b}$, $t_j^{a,b}$, and $s_j^{a,b}$ of z^j respectively. For these analytic computations, we employed two separate processors Maple and Reduce to verify independently the accuracy of the results; the expressions and their partial derivatives with respect to the parameters were similarly converted into efficiently executable Fortran code for subsequent numeric application.

Table 3. Expressions of coefficients $Z^{v,a}_{kl}$ for adiabatic and non-adiabatic vibrational effects.

$$Z^{v,a}_{0,0}M_a/m_e = u_0^a$$

$$Z^{v,a}_{0,1}M_a/m_e = \gamma^2 u_1^a$$

$$Z^{v,a}_{0,2}M_a/m_e = B_\omega \gamma^2 s_0^a + \gamma^4[u_1^a(-3c_1/2-2)+u_2^a]$$

$$Z^{v,a}_{0,3}M_a/m_e = B_e\gamma^4[s_0^a(-3c_1/2-9/2)+\tfrac{1}{2}s_1^a] + \gamma^6[u_1^a(9c_1^2/2-2c_2+9c_1+25/4)+u_2^a(-3c_1-4)+u_3^a]$$

$$\begin{aligned} Z^{v,a}_{0,4}M_a/m_e = {} & B_e\gamma^6[s_0^a(9c_1^2/2-2c_2+33c_1/2+39/2)+s_1^a(-3c_1/2-19/6)+\tfrac{1}{3}s_2^a] \\ & +\gamma^8[u_1^a(-135c_1^3/8+15c_1c_2-5c_3/2-45c_1^2+16c_2-99c_1/2-47/2) \\ & +u_2^a(45c_1^2/4-4c_2+24c_1+33/2)+u_3^a(-9c_1/2-6)+u_4^a] \end{aligned}$$

$$Z^{v,a}_{1,0}M_a/m_e = \gamma^{-1}B_e s_0^a + \gamma[u_1^a(-3c_1/2+1)+u_2^a]$$

$$Z^{v,a}_{1,1}M_a/m_e = B_e\gamma[-3s_0^a/2+3s_1^a/2] + \gamma^3[u_1^a(27c_1^2/4-6c_2+9c_1/2+3/4)-9u_2^a c_1/2+3u_3^a]$$

$$\begin{aligned} Z^{v,a}_{1,2}M_a/m_e = {} & B_e\gamma^3[s_0^a(27c_1^2/8-3c_2+45c_1/4+9)+s_1^a(-9c_1/4-11/2)+2s_2^a] \\ & +\gamma^5[u_1^a(-567c_1^3/16+99c_1c_2/2-15c_3-405c_1^2/8+33c_2-243c_1/8-39/4)+u_2^a(189c_1^2/8 \\ & -15c_2+45c_1/2+9/2)+u_3^a(-27c_1/2-9)+6u_4^a] \end{aligned}$$

$$\begin{aligned} Z^{v,a}_{2,0}M_a/m_e = {} & B_e[s_0^a(-15c_1^2/8+3c_2/2+3c_1/2-3/4)+s_1^a(-3c_1/4+\tfrac{1}{2})+\tfrac{1}{2}s_2^a] \\ & +\gamma^2[u_1^a(-45c_1^3/8+39c_1c_2/4-15c_3/4+3c_1^2/8-3c_2/2+9c_1/8-3/8)+u_2^a(15c_1^2/4 \\ & -3c_2/2-3c_1/2)+u_3^a(-15c_1/4+3/2)+3u_4^a/2] \end{aligned}$$

$$\begin{aligned} Z^{v,a}_{2,1}M_a/m_e = {} & B_e\gamma^2[s_0^a(45c_1^3/8-39c_1c_2/4+15c_3/4-9c_1^2/4+9c_2/4-111c_1/16-3/16) \\ & +s_1^a(9c_1^2/4-9c_2/4+65c_1/8+1/32)+s_2^a(-11c_1/4-5/8)+15s_3^a/8]+\gamma^4[u_1^a(135c_1^4/2-621c_1^2c_2/4 \\ & +285c_1c_3/4+39c_2^2-45c_4/2+423c_1^3/8-66c_1c_2+15c_3+63c_1^2/4-15c_2/8+33c_1/8+3/32) \\ & +u_2^a(-45c_1^3+117c_1c_2/2-15c_3-81c_1^2/4-3c_1/4) \\ & +u_3^a(135c_1^2/4-39c_2/2+27c_1/2+3/8)-39u_4^a c_1/2+15u_5^a/2] \end{aligned}$$

3. Numerical treatment

The objective of this work is to enable in one stage the evaluation of parameters of the pertinent radial functions from the frequencies of the pure rotational and vibration–rotational spectral transitions. As spectral lines of a particular molecular species are in general much more numerous than the parameters of the radial functions of which one seeks to represent the frequencies of the lines in the most compact and physically meaningful form, we apply a statistically based process of reduction of the frequencies and wavenumbers of measured transitions. The wavenumbers of pure rotational or vibration–rotational transitions to which are assigned pairs of quantum numbers to specify the initial and final states of a particular isotopic variant are differences of spectral terms,

$$\tilde{\nu} = \tilde{E}_{v'J'} - \tilde{E}_{vJ}. \tag{11}$$

Because of the non-linear dependence on some ultimate parameters k_e, R_e, and c_j (even though $s_j^{a,b}$, $t_j^{a,b}$ and $u_j^{a,b}$ appear linearly), of these wavenumbers through the intermediate quantities—the vibration-rotational terms E_{vJ}, the coefficients Y_{kl} and various Z_{kl}—only indirect (iterative) methods of solution are possible.

For this purpose we use an algorithm that Newton originated and that Choleski, Hammarling, Levenberg, Marquardt, Morrison and others developed further (Osborne 1976, Bates and Watts 1988). To ensure the least biased and most precise values of resulting parameters (Albritton *et al* 1976), the criterion of best fit is the least sum of the squares of the residuals; the latter are the difference between the observables (the measured wavenumbers or frequencies converted to wavenumbers) and the values of the transition wavenumbers calculated by means of equations (8) and (11). Our calculation employs analytic expressions of the partial derivatives of the residuals with respect to the parameters. The process is therefore a fit of wavenumbers of transitions as the dependent variable; the atomic masses and the initial and final, vibrational and rotational quantum numbers are the independent regressors within simple but extensive functions, implicit in equation (8). The algorithm can be extended to apply to electronic states other than $^1\Sigma$; we made provision to include further appropriate indices as independent variables. The uncertainty assigned to each datum (the measured wavenumber) that reflects the absolute accuracy of its measurement, is converted into a weight as the inverse of its square; correlations between measurements are generally neglected. The criterion of convergence of the calculation is that in consecutive iterations the square root of the sum of the squares of the weighted residuals alters less than 0.1%; the actual tolerance in a particular fitting operation depends on both the precision of the data and the consistency of the various sets of data that are included in the collection of wavenumbers to be fitted. The analysis of data is conducted according to standard statistical methods; the results of the fit are values of parameters, selected according to the criterion of the F-statistic (Ogilvie 1982), in sets consisting of k_e, R_e and coefficients c_j, $u_j^{a,b}$, $t_j^{a,b}$ and $s_j^{a,b}$, accompanied by their estimated standard errors and the matrix of correlation coefficients of the parameters. The auxiliary quantities Y_{kl} and various Z_{kl}, $u_{kl}+\Delta_{kl}$ are evaluated directly from the primary parameters if required.

4. Tests of the algorithm and application to HCl

In order to demonstrate that this approach to the analysis of the frequencies and wavenumbers of spectral lines is practicable, we generated test data with assumed values of the parameters in finite sets. First only the parameters $U_{1,0}$, $U_{0,1}$ and c_j, $1 \leqslant j \leqslant 8$, of a single diatomic species specified by one mass of each nucleus were assigned finite values; thus only the quantities Y_{kl} were required. We selected 238 transitions in R and P branches within the range of states $0 \leqslant v \leqslant 7$ and $0 \leqslant J \leqslant 40$. The input wavenumbers were specified to a precision 0.0001 m^{-1} in the range/m^{-1} [2000, 2027000]; the initial values of all parameters were zero except for $U_{1,0}$, $U_{0,1}$ and c_1–c_3 which were given rounded values within about 30% of the set values used to generate the data. During the fit, the sum of the squares of the residuals decreased from 4.56×10^{11} m^{-2} to 1.0×10^{-5} m^{-2}, at which point the standard deviation of the residuals was 2.1×10^{-4} m^{-1} (or double the precision of the input data). The final estimates of the parameters agreed with the set values generally within two (small) estimated standards errors of the former;

in the correlation matrix, only four elements of the 45 independent values had magnitudes exceeding 0.95. The results of this test prove that to reproduce in one stage the potential-energy coefficients from the transition wavenumbers is practicable.

In the second test, also of a single isotopic species, the set of assumed parameters of the first test was augmented to include four coefficients t_j^a, $1 \leqslant j \leqslant 4$; the value of t_0^a was constained to zero during the fitting process. The same 238 transitions as in the first test but with correspondingly adjusted wavenumbers were selected. At convergence the standard deviation of the residuals was $2.2 \times 10^{-4}\ \mathrm{m}^{-1}$; the generated values of the parameters again agreed with the set values within about two estimated standard errors of the former, but only two elements of the enlarged correlation matrix had magnitudes exceeding 0.95. These results indicate that to reproduce both the potential-energy coefficients c_j and one set of coefficients reflecting the additional rotational effects is practicable.

In the third test, data were analogously simulated for a diatomic molecule like HCl having three supposed isotopic variants corresponding to $^1A^{35}B$, $^1A^{37}B$ and $^2A^{35}B$, with 187 transitions of each species within the ranges $0 \leqslant v \leqslant 8$ and $0 \leqslant J \leqslant 41$ in P and R branches. The parameters used to generate the transition wavenumbers numbered 24, comprising $U_{1,0}$, $U_{0,1}$, c_j, $1 \leqslant j \leqslant 8$, u_j^a, $1 \leqslant j \leqslant 4$, u_j^b, $1 \leqslant j \leqslant 2$, t_j^a, $0 \leqslant j \leqslant 4$, and t_j^b, $0 \leqslant j \leqslant 2$. During the fit to the same 24 parameters, the sum of the squares of the residuals decreased from $1.2 \times 10^{12}\ \mathrm{m}^{-2}$ to $2.1 \times 10^{-4}\ \mathrm{m}^{-2}$, at which point the standard deviation of the residuals was $1.9 \times 10^{-4}\ \mathrm{m}^{-1}$. As in the previous tests most deduced values of the parameters lay within about two standard errors of the set values; although several elements of the parameter correlation matrix had magnitudes near unity, especially those connecting $t_0^{a,b}$ with $U_{0,1}$, $t_1^{a,b}$ and a few other parameters, the quality of the fit indicated that the programme was capable of proper operation to reproduce the realistically set values of the parameters. Hence the results of this test demonstrate that to reproduce not only the potential-energy coefficients, namely t_j^a, t_j^b, u_j^a and u_j^b (in the neglect of s_j^a and s_j^b) related to the adiabatic and non-adiabatic effects apportioned to particular atomic centres, is practicable by means of this algorithm and its present implementation.

Following these tests of our programme we undertook the analysis of spectral data from pure rotational and vibration–rotational transitions of isotopic variants of several diatomic species. We present here results for HCl that not only provide a practical test of the programme but also are of intrinsic interest. The data set comprised 1329 lines of the variants $^1H^{35}Cl$ (619 lines), $^1H^{37}Cl$ (440 lines), $^2H^{35}Cl$ (136 lines), $^2H^{37}Cl$ (132 lines) and one pure rotational transition of each of $^3H^{35}Cl$ and $^3H^{37}Cl$. This set included the best or not superseded data from our previous global fit (Coxon and Ogilvie 1982), complemented by the following more recent data: pure rotational lines of $^1H^{35}Cl$ and $^1H^{37}Cl$ (Nolt *et al* 1987, Le Blanc *et al* 1993) and of $^2H^{35}Cl$ and $^2H^{37}Cl$ (Fusina *et al* 1992), the newly measured rotational and vibration–rotational bands of $^1H^{35}Cl$ and $^1H^{37}Cl$ (Rinsland *et al* 1993, Le Blanc *et al* 1993) and of $^2H^{35}Cl$ and $^2H^{37}Cl$ (Klee and Ogilvie 1993), and the emission lines in the sequence $\Delta v = 1$ of $^1H^{35}Cl$ and $^1H^{37}Cl$ (Clayton *et al* 1983). During the fit the values of t_0^{H} and t_0^{Cl} were constrained to what were deduced from the known value (de Leeuw and Dymanus 1973) of the rotational g factor according to the partitioning formulae (Tiemann *et al* 1975); all other parameters were constrained to null values. The results appear in table 4, in which the maximum range of validity of the radial functions is also specified. All 19 independent parameters were significantly evaluated; of only six of 171 correlation coefficients of the parameters the magnitudes exceeded 0.95, the largest being 0.9845, but there was neither systematic feature nor trend in the values.

Table 4. Coefficients of radial functions and other molecular properties of HCl X $^1\Sigma^+$, all independent of nuclear mass[a].

j	c_j	t_j^{Cl}	t_j^{H}	$u_j^{\mathrm{Cl}}/10^6\ \mathrm{m}^{-1}$	$u_j^{\mathrm{H}}/10^6\ \mathrm{m}^{-1}$
0	(21 114 007.91 $\pm$0.57) m^{-1}	0.099 66*	0.456 73*		
1	−1.363 4344 ±0.000 0067	−0.844 ±0.221	−0.5596 ±0.0098	−4.173 ±0.30	−6.1233 ±0.0026
2	0.865 804 ±0.000 035		−1.639 ±0.034	21.296 ±0.94	18.3836 ±0.0097
3	−0.473 56 ±0.000 42				−14.147 ±0.31
4	0.086 71 ±0.0023				15.995 ±1.37
5	0.207 01 ±0.0066				
6	−0.9506 ±0.039				
7	−0.1190 ±0.138				
8	8.857 ±0.31				

$U_{1,0} = (296031.780 \pm 0.037)\ \mathrm{m}^{-1}\ \mathrm{u}^{1/2}$
$U_{0,1} = (1037.63832 \pm 0.00023)\ \mathrm{m}^{-1}\ \mathrm{u}$
$k_e = (516.32982 \pm 0.00033)\ \mathrm{N\ m}^{-1}$
$R_e = (1.27460400 \pm 0.00000108) \times 10^{-10}\ \mathrm{m}$
range $0.98 \leqslant R/10^{-10}\ \mathrm{m} \leqslant 1.92$

[a] Each stated uncertainty represents one estimated standard error; the F-value of the fit of 1329 data with 19 independent unconstrained and two constrained* parameters (apart from those set to zero value) is 1.62×10^{15}, and the normalized standard deviation $\hat{\sigma}$ is 1.427.

5. Discussion

Examination of the expressions in tables 2 and 3 enables one to conclude that the parameters within a particular set of functions $Z_{kl}^{r,a}$ and $Z_{kl}^{v,a}$ (and similarly for the nucleus of other atomic number) number more than one can evaluate from available data. For instance, application of equation (10) to fit a similar set of 1066 data yielded *the significant estimation of* $U_{k,0}$ *with* $1 \leqslant k \leqslant 5$, $U_{k,1}$ *with* $0 \leqslant k \leqslant 4$, $\Delta_{1,0}^{\mathrm{H}}$, $\Delta_{2,0}^{\mathrm{H}}$, $\Delta_{0,1}^{\mathrm{H}}$, $\Delta_{1,1}^{\mathrm{H}}$, $\Delta_{0,2}^{\mathrm{H}}$, $\Delta_{0,3}^{\mathrm{H}}$, $\Delta_{1,0}^{\mathrm{Cl}}$ and $\Delta_{0,1}^{\mathrm{Cl}}$. The values of these $U_{1,0}$, $U_{0,1}$ and derived coefficients c_j are similar to the corresponding values given in table 4. The values of the parameters Δ_{kl}^{H} and $\Delta_{kl}^{\mathrm{Cl}}$ are proportional to the sums $Z_{kl}^{\mathrm{H}} = Z_{kl}^{r,\mathrm{H}} + Z_{kl}^{v,H}$ and $Z_{kl}^{\mathrm{Cl}} = Z_{kl}^{r,\mathrm{Cl}} + Z_{kl}^{v,\mathrm{Cl}}$, respectively, that result from the combination of the expressions in tables 2 and 3 or from expressions in a separate table that contain the corresponding coefficients of x^j (Fernandez and Ogilvie 1992). In either case only six values of the coefficients Δ_{kl}^{H} are available *to evaluate ten parameters comprising* u_j^{H} *with* $1 \leqslant j \leqslant 4$, t_j^{H} *with* $0 \leqslant j \leqslant 2$ *and* s_j^{H} *with* $0 \leqslant j \leqslant 2$; seven values of Z_{kl}^{H} are effectively available because we provided the value of t_0^{H} (and t_0^{Cl}) from supplementary experimental measurements. In these circumstances we constrained to zero all parameters s_j^{H} in order to derive the effective values of t_j^{H} and u_j^{H} presented in table 4. Hence only u_1^{H} and u_1^{Cl} represent purely the adiabatic effects (as the expression for $Z_{0,1}^{v,a}$ in table 3 makes clear), whereas the remaining values of $u_j^{\mathrm{H,Cl}}$ and $t_k^{\mathrm{H,Cl}}$ with $k \geqslant 0$ absorb to an unknown extent the values of the indeterminate parameters $s_j^{\mathrm{H,Cl}}$ with $0 \leqslant j \leqslant 2$ that pertain to the non-adiabatic vibrational effects. In order to estimate the latter parameters, one requires knowledge of the rotational and vibrational dependence of the rotational g factor; the rotational dependence of g_J would yield at least t_1^{H} (and t_1^{Cl}) and the vibrational dependence would in addition enable an estimate of t_2^{H} (and t_2^{Cl}). Experimental measurements of the rotational dependence of g_J (which is precisely the expectation value $\langle vJ|g(R)|vJ\rangle$) are rare, and only a few instances are known of molecular species for which even the vibrational dependence of g_J has been determined. If these data were known for HCl (for any specific isotopic variant), then to estimate s_j with $0 \leqslant j \leqslant 2$ would still require a value of $\Delta_{0,4}^{\mathrm{H}}$ acording to the use of equation (10); the latter value cannot be determined significantly from the present set of spectral transitions, but measurements of wavenumbers with increased accuracy might yield this value.

Can the term coefficients Z_{kl}^{r} be evaluated independently of Z_{kl}^{v}? The results of the second test with simulated spectral data appear to indicate an affirmative answer. To enable a definitive decision, we applied the fitting programme to only 482 spectral transitions of $^{1}\mathrm{H}^{35}\mathrm{Cl}$, for which isotopic variant the available data are most abundant. The set of fitting parameters included only the potential-energy coefficients c_j, $1 \leqslant j \leqslant 8$, $U_{0,1}$, $U_{1,0}$, t_1 and t_2 with t_0^{H} and t_0^{Cl} constrained and all others zero. Under these conditions in relation to equation (7), the proper mass coefficient of the composite quantities t_1 and t_2 is the reduced molecular mass μ, not M_{H}; we have accordingly adjusted the results of t_1^{H} and t_2^{H} produced by our programme. The values of $U_{0,1}$, $U_{1,0}$ and c_j with $1 \leqslant j \leqslant 8$ derived from this fit are similar to those in table 4, differing in each instance by several standard errors, as expected because in this fitting operation the potential-energy coefficients absorb the vibrational adiabatic and (to some extent) non-adiabatic effects. The remarkable results are that $t_1 = -0.5582 \pm 0.0090$ and $t_2 = -1.844 \pm 0.093$, to be compared with the values $t_1^{\mathrm{H}} = -0.5596 \pm 0.0098$ and $t_2^{\mathrm{H}} = -1.639 \pm 0.034$ in table 4. This satisfactory agreement demonstrates that one can distinguish experimentally the vibration–rotational Z_{kl}^{v} and the extra rotational Z_{kl}^{r} contributions to the vibration–rotational energies. As the contributions of the individual atomic nuclei cannot be derived from data of only one isotopic variant, this discovery fails to assist the evaluation of the parameters $s_j^{\mathrm{H,Cl}}$ related to the non-adiabatic vibrational effects.

By making use of the numerical values in table 4 and the expressions in tables 1–3, we identify the mechanical and extra-mechanical effects in the term coefficients Y_{kl} and Z_{kl} for a few principal values of k and l for the dominant isotopic species $^{1}\mathrm{H}^{35}\mathrm{Cl}$; for all values the units are m^{-1}. For $k=0$ and $l=1$, $Y_{0,1}^{(0)} = B_{\mathrm{e}} = 1059.255\,02 \pm 0.000\,23$, $Y_{0,1}^{(2)} = -0.021\,16$, $Y_{0,1}^{(4)} = -0.000\,047$. As expected, the magnitudes of the successive Dunham corrections $Y_{kl}^{(m)}$ decrease rapidly as the order m increases, such that, although $Y_{0,1}^{(2)}$ is larger than the experimental error, $Y_{0,1}^{(4)}$ is much smaller and hence negligible. According to table 2 the expression of the coefficient $Z_{0,1}^{\mathrm{r},a}$ contains only the non-adiabatic rotational contributions through the radial coefficient t_0^a, whereas in table 3 $Z_{0,1}^{\mathrm{v},a}$ consists entirely of an adiabatic contribution through the coefficient u_1^a. The term coefficients are then $Z_{0,1}^{\mathrm{r,H}} = 0.263\,34 \pm 0.000\,05$, $Z_{0,1}^{\mathrm{r,Cl}} = 0.001\,66 \pm 0.000\,05$, $Z_{0,1}^{\mathrm{v,H}} = -0.165\,550 \pm 0.000\,08$ and $Z_{0,1}^{\mathrm{v,Cl}} = -0.003\,26 \pm 0.000\,22$. Hence the magnitudes of the adiabatic and non-adiabatic rotational effects for each nucleus are comparable, and the actual values tend to cancel; the relative magnitudes of the adiabatic and non-adiabatic rotational effects are in the reverse order for the two nuclei, the adiabatic contribution having a larger magnitude for H but a smaller one for Cl. The magnitudes of these adiabatic and non-adiabatic contributions to the total coefficient of $[J(J+1)]$ of H are much larger than that of $Y_{0,1}^{(2)}$, although the corresponding contributions of Cl are much smaller. Although for the sums $Z_{0,l}^{\mathrm{r},a} + Z_{0,l}^{\mathrm{v},a}$ or $Z_{0,l}^{\mathrm{r},b} + Z_{0,l}^{\mathrm{v},b}$ there exists no net contribution due to the non-adiabatic vibrational effects through the coefficients s_j^a or s_j^b for any value of l, in actual expressions of the separate rotational $Z_{0,l}^{r,a}$ and vibrational $Z_{0,l}^{v,a}$ term coefficients these radial coefficients appear explicitly, except in the cases $Z_{0,1}^{r,a}$ and $Z_{0,1}^{v,a}$.

For the principal coefficient associated with centrifugal distortion, $Y_{0,2}^{(0)} = -D_e = -0.053\,131\,08 \pm 0.000\,0005$, $Y_{0,2}^{(2)} = -2.661\,51 \times 10^{-6}$ and $Y_{0,2}^{(4)} = 1.2 \times 10^{-7}$; $Z_{0,2}^{r,H} = (-4.261 \pm 0.08) \times 10^{-5}$ and $Z_{0,2}^{v,H} = (2.8693 \pm 0.0013) \times 10^{-5}$ have magnitudes larger than that of $Y_{0,2}^{(2)}$ and the latter values tend to cancel, whereas $Z_{0,2}^{r,Cl} = -9.0 \times 10^{-7}$ and $z_{0,2}^{v,Cl} = 8.3 \times 10^{-7}$ are much smaller. According to the expressions in tables 2 and 3, $t_1^H - s_0^H = -0.5596 \pm 0.0098$ and $u_2^H + s_0^H/\gamma^2 = (18.3841 \pm 0.0097) \times 10^6$; the values of t_1^H and u_2^H that appear in table 4 result from s_0^H being neglected in the lack of sufficient information to evaluate it. Similar conditions apply to the corresponding coefficients for Cl except that in this case both $Z_{0,2}^{r,Cl} = (-9.0 \pm 0.41) \times 10^{-7}$ and $Z_{0,2}^{v,Cl} = (8.3 \pm 0.33) \times 10^{-7}$ are much smaller than $Y_{0,2}^{(2)}$; again the values tend to cancel in their effects on the molecular energies.

For the principal vibrational coefficient, $Y_{1,0}^{(0)} = -\omega_e = 299\,099.4407 \pm 0.037$, $Y_{1,0}^{(2)} = -10.4727$ and $Y_{1,0}^{(4)} = 0.133$; $Z_{kl}^{r,H} = Z_{kl}^{r,Cl} = 0$ for all k with $l = 0$, but $Z_{1,0}^{v,H} = -0.7680 \pm 0.0004$ nearly cancels with $Z_{1,0}^{v,Cl} = 0.910 \pm 0.036$ in the sum for the total coefficient of $(v + \frac{1}{2})$. Although according to table 3 the expressions of both $Z_{1,0}^{v,a}$ and $Z_{0,2}^{r,a}$ contain the radial coefficients s_0^a and u_2^a in addition to u_1^a and c_1 that are separately defined, the former two parameters occur, apart from a factor γ to various powers, in the same linear combination $B_e s_0^a + \gamma^2 u_2^a$ that prevents their separate evaluation, and no other combination of the coefficients $Z_{kl}^{r,a}$ or $Z_{kl}^{v,a}$ allows their extrication, as described previously (Fernandez and Ogilvie 1992). For this reason, even if sufficient spectral data were available (such as sufficient values of Δ_{kl}^a according to the discussion above), the separate evaluation of the radial functions pertaining to the adiabatic and non-adiabatic rotational and vibrational effects from only data of wavenumbers of vibration–rotational transitions would still be impracticable; hence additional information from experiments on the Zeeman effect is essential for this purpose.

Comparison of the values in table 4 with published results is appropriate. The agreement with our previous results (Coxon and Ogilvie 1982) or their equivalent is reasonable when one takes into account the greatly increased precision of the pure rotational transitions and vibration–rotational bands used in the present work, which also employs more accurate values of the atomic masses (Wapstra and Audi 1985) and fundamental physical constants (Cohen and Taylor 1987). Comparison with the results of Coxon and Hajigeorgiou (1990) is problematic because, although they did not include the recent rotational and vibration–rotational data, their electronic spectra included extensive (although only moderately precise) data up to $v = 17$ for $^1H^{35}Cl$ and $v = 24$ for $^2H^{35}Cl$; for $V^{BO}(R)$ they employed exponential functions instead of our representation $V^{BO}(z)$. Coxon's (1992) comparison of z and exponential representations for the same data set of LiH demonstrated that the former was both more economical, 17 versus 19 unconstrained parameters, and more reliable, in that even with the extra parameters in the exponential case some were poorly defined; furthermore the fitting process appears unreliable because h_3^{Li} rather than c_6 of LiH was evaluated (Coxon 1992) whereas the reverse case provides a realistic description of the data (Ogilvie 1992b). Thus our representations in terms of the variable z are demonstrated to be superior to those in terms of the exponential functions (Coxon 1992), apart from the fact that these exponential functions possess quantitatively incorrect asymptotic behaviour in the approach to the dissociation limit. The radial functions (Coxon and Hajigeorgiou 1990, Coxon 1992) other than that for potential energy derived for both HCl and LiH have no particular physical significance, whereas in the present work we demonstrate that the use of the values of t_0^{H} and t_0^{Cl} deduced from the rotational g factor permits at least the values of $u_1^{\mathrm{H,Cl}}$ to be associated specifically with adiabatic (vibrational) effects. In a further analysis (Tiemann and Ogilvie 1994) of spectra of LiH according to two distinct numeric approaches based on analytic expressions for Y_{kl}, we derived a significant value of s_0^{H}; for LiH this achievement was practicable because of both the strongly electrically dipolar nature of this molecular species and the set of spectral data more internally consistent than those available for HCl analysed here. The two values (Coxon and Hajigeorgiou 1990) of R_e of HCl, of which the more precisely specified value differs by 43 standard errors from the other, suffer from systematic error because no account was taken of the non-zero value of g_J or $t_0^{\mathrm{H,Cl}}$; their associated standard errors take no account of the uncertainties of the physical constants h and N_A.

For spectra of another hydridic species AlH (Ogilvie 1992a), the application of our programme yielded a large magnitude for the coefficient t_0^{H} and hence the rotational g factor (not yet directly measured); because of the relationship between terms in the expressions for g_J and the molecular magnetic susceptibility (Gordy and Cook 1984), this result indicates that AlH in its electronic ground state X $^1\Sigma^+$ may be either net paramagnetic or much less diamagnetic than expected on the basis of an electronic configuration corresponding to a formally closed shell. In either case this experimental evidence is the first, although indirect, of a paramagnetic electronic ground state X $^1\Sigma^+$ predicted for the isovalent molecule BH (Stevens *et al* 1963).

The use of the analytic expressions in tables 1–3 enables one for the first time to distinguish purely from experimental data the effects attributed to adiabatic and non-adiabatic rotational and vibrational effects. These effects are not truly physical in origin because they arise from the approximations inherent in the separate treatment of electronic and nuclear motions (Born and Oppenheimer 1927). Knowledge of the operation of these effects is important so that one can ensure thereby the correct treatment of the effects of nuclear mass in the process of spectral reduction, even according to an essentially empirical relation such as equation (10). Although the expressions in tables 1–3 were produced by means of a wave-mechanical approach, i.e. through the explicit use of the Schrödinger equation, they are independent of that particular method of generation; we have produced some of them in identical form by means of both the JBKW method and perturbation theory in matrix mechanics, and expect also to apply Dirac's method of operators. The use of these expressions is simpler and computationally more efficient than fully numerical approaches, such as repeated solution of the Schrödinger equation at finite intervals (Coxon and Hajigeorgiou 1990), because mainly substitutions into these expressions and their analytic derivatives with respect to the parameters are involved in the fitting process. For these reasons the results derived according to this approach based on an analytic formalism may prove more reliable than those obtained by merely numerical methods.

6. Conclusions

The evaluation of separate radial functions for the potential energy, adiabatic and non-adiabatic vibrational and rotational effects by direct reduction of experimental spectral data is practicable provided that supplementary spectral data of the rotational g factor, and preferably also the rotational and vibrational dependence of g_J, are included in the analysis. Because the variation of the isotopic mass and the extra rotational dependence of the frequencies of vibration–rotational transitions provides for nuclei of each distinct atomic number information of only two kinds beyond the potential energy that is the dominant effect, whereas parameters pertaining to effects of three kinds—adiabatic, non-adiabatic vibrational and rotational—remain to be evaluated, these supplementary data from the vibrational and rotational dependence of the rotational g factor are essential to complete the analysis. As such data are sparse, measurements of the Zeeman effect on lines in radio-frequency transitions or in pure rotational and fundamental vibration-rotational bands of appropriate molecular species are warranted. Intensity measurements from the application of magnetic circular dichroism to vibration-rotational transitions are too inaccurate to provide useful data (Tam and Keiderling 1993). The large Dopplerian widths of vibration-rotational lines (for instance, $\sim 0.6\,\mathrm{m}^{-1}$ for the full width at half the maximum absorbance of lines in the fundamental vibration-rotational band of $^1H^{35}Cl$ at 300 K) demand correspondingly large magnetic flux densities ($B_0 \sim 51$ T for this band of HCl) to effect a splitting of magnitude similar to this Dopplerian width, unless one either employs a molecular beam or devises another method to avoid this width. Measurements of the Zeeman effect in radio-frequency or microwave spectra of molecules in rotationally and vibrationally excited states may thus enable one to derive these dependences more readily than from vibration-rotational spectra.

In the spirit of the work of Dunham (1932) and van Vleck (1936), the analytic expressions presented in tables 1–3 enable one to distinguish the pertinent phenomena from pure rotational and vibration-rotational transitions consisting of sufficiently numerous lines of multiple isotopic variants, in combination with essential supplementary data. Thereby one is able for the first time to derive accurately for diatomic molecular species these significant properties that are independent of nuclear mass.

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